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HEURISTIC MODELING OF THERMOPHYSICAL PROPERTIES OF PURE FLUIDS AND MIXTURES THROUGH INNOVATIVE METHODS

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NOMENCLATURE

Symbols

A	Molar or specific Helmholtz free energy (J mol ⁻¹ or J kg ⁻¹)
	Limiting value of the scaling interval for the inputs and outputs of the neural network
	Area
A_0	Parameter of BWR type equation
a	Vector of parameters
a	Attractive coefficient in cubic equations of state (J m ³ mol ⁻² or J m ³ kg ⁻²)
	Reduced Helmholtz free energy, $a = A/(RT)$
	Parameter of BWR type equation
	Adjustable parameter in DEoSs with optimized functional form
a_{20}	Parameter of the Bender equation
В	Second virial coefficient ($m^3 mol^{-1} or m^3 kg^{-1}$)
	Parameter of the Bender equation
\widetilde{B}	Second virial coefficient ($m^3 mol^{-1} or m^3 kg^{-1}$)
B_0	Parameter of BWR type equation
B^*_η	Reduced second viscosity virial coefficient
Bias1, Bias2	Neural network biases
b	Covolume in cubic equations of state $(m^3 mol^{-1} or m^3 kg^{-1})$
	Parameter of BWR type equation
	Adjustable parameter in DEoSs with optimized functional form
С	Number of species in mixture
	Third virial coefficient ($m^6 mol^{-2} or m^6 kg^{-2}$)
	Molar or specific heat capacity (J mol ⁻¹ K^{-1} or J kg ⁻¹ K^{-1})
	Parameter of the Bender equation
\tilde{C}	Third virial coefficient (m ⁶ mol ⁻² or m ⁶ kg ⁻²)
C_0	Parameter of BWR type equation
С	Peneloux volume translation in cubic equations of state (m ³ mol ⁻¹ or m ³ kg ⁻¹)
	Reduced isochoric heat capacity, $c = C/R$
	Molar concentration
	Parameter of BWR type equation

	Adjustable parameter in DEoSs with optimized functional form
C_{ψ}	Coefficient of the viscosity equation in ECS form
c _x	Coefficient of the thermal conductivity equation in ECS form
D	Fourth virial coefficient (m ⁹ mol ⁻³ or m ⁹ kg ⁻³)
	Diffusion coefficient
	Parameter of the Bender equation
\widetilde{D}	Fourth virial coefficient (m ⁹ mol ⁻³ or m ⁹ kg ⁻³)
D_0	Parameter of BWR type equation
D_T	Thermal diffusivity $(m^2 s^{-1})$
d	Deviation function
	Parameter of BWR type equation
	Adjustable parameter in the non-analytical term of DEoSs with optimized functional
	form
	Reduced density exponent in DEoSs with optimized functional form
d	Derivative
∂	Partial derivative
Ε	Energy
	Parameter of the Bender equation
E_0	Parameter of BWR type equation
е	Adjustable parameter in DEoSs with optimized functional form
F	Derivative of the temperature scale factor f
	Degrees of freedom
	Force
	Parameter of the Bender equation
f	Fugacity
	Neural network transfer function
	Temperature scale factor
	Function
	Adjustable parameter in DEoSs with optimized functional form
$f_{\rm int}$	Factor accounting for the energy conversion between internal and translational
	modes
G	Molar or specific Gibbs free energy (J mol ⁻¹ or J kg ⁻¹)
	input to a neuron of the hidden layer of the neural network

	Parameter of the Bender equation
g	Reduced Gibbs free energy, $g = G/(RT)$
	Gravitational acceleration $(m \cdot s^{-2})$
	Mass reducing ratio
Н	Molar or specific enthalpy (J·mol ⁻¹ or J·kg ⁻¹)
	Output of the hidden layer of the neural network
	Derivative of the density scale factor h
	Parameter of the Bender equation
ΔH^{vap}	Vaporization enthalpy
h	Density scale factor
	Reduced enthalpy, $h = H/(RT)$
Ι	Number of neurons in the input layer of the neural network
	Number of terms in equations with optimized functional form
J	Number of neurons in the hidden layer of the neural network
J	Flux vector of the generic transported quantity
	Molar flux
j	One-dimensional molar flux
Κ	Number of neurons in the output layer of the neural network
	Number of independent variables
k	Enthalpy scaling parameter
k _B	Boltzmann constant, $k_B = 1.3806503 \text{ J K}^{-1}$
k_{ij}	Binary-interaction parameter
$k_{T,ij}$	Binary-interaction parameter
$k_{v,ij}$	Binary-interaction parameter
L	Likelihood function
l_{ij}	Binary-interaction parameter
М	Molar mass (kg mol ⁻¹)
	Generic thermophysical property
	Number of points
\overline{M}_i	Generic partial molar thermodynamic property of species i in mixture
m	Mass of one molecule
N_A	Avogadro constant, $N_A = 6.0221353 \times 10^{-23} \text{ mol}^{-1}$

n	Vector of parameters
n	Number of moles (mol)
	Parameter in DEoSs with optimized functional form
Р	Pressure (Pa)
p	Partial pressure (Pa)
Q	Heat
Ż	Heat flow
ġ	Heat flux
\dot{q}	One-dimensional heat flux
q	Relative molecular surface area
R	Molar or specific gas constant (J mol ⁻¹ K^{-1} or J kg ⁻¹ K^{-1})
	input to a neuron of the output layer of the neural network
R_m	Molar gas constant, $R_m = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$
r	Relative molecular volume
	Distance between molecular centers
S	Molar or specific entropy (J mol ⁻¹ K^{-1} or J kg ⁻¹ K^{-1})
	Scaled output of the neural network
S	Reduced entropy, $s = S/R$
	Scaling value of a dependent physical variable W of the neural network
	Experimental uncertainties
Т	Temperature (K)
T^{*}	Reduced temperature, $T^* = k_B T / \varepsilon$
t	Time
	Inverse reduced temperature exponent in DEoSs with optimized functional form
U	Molar or specific internal energy (J mol ⁻¹ or J kg ⁻¹)
	Scaled input of the neural network
и	Reduced internal energy, $u = U/(RT)$
	Scaling value of an independent physical variable V of the neural network
	Parameter for the UNIQUAC equation
	Velocity $(m \cdot s^{-1})$
V	Physical input of the neural network
	Volume (m ³)
	Velocity

ν	Molar or specific volume ($m^3 mol^{-1} or m^3 kg^{-1}$)
W	Physical output of the neural network
	Work
w	Vector of weighting factors for the neural network
W	Speed of sound (m s ⁻¹)
	Weighting factor for the neural network
X	Vector of the true values of the independent variables (not affected by experimental
	error)
X	Generic transport property
x	Molar composition vector, generic or in liquid phase
	Independent variable vector
x	Molar composition of a specie in mixture
	Independent variable
	Direction
Y	Generic quantity (velocity, temperature, mass concentration of species A in solution
	of A and B)
	True value of the dependent variable (not affected by experimental error)
У	Dependent variable
	Molar composition in vapor phase
	Direction
у	Molar composition vector in vapor phase
Ζ	Compressibility factor, $Z = Pv/(RT)$
z^{R}	Residual compressibility factor, $z^{R} = Z - 1$

Greek Letters

α	Multiplying parameter of the neural network transfer function
	Parameter of BWR type equation
β	Multiplying parameter of the neural network transfer function
	Adjustable parameter in DEoSs with optimized functional form
Г	Integration constant
Г	Potential energy between two molecules
γ	Activity coefficient
	Multiplying parameter of the neural network transfer function

	Parameter of BWR type equation
	Adjustable parameter in DEoSs with optimized functional form
Δ	Error deviation
	Difference
Δ_{C}	Critical enhancement term
$\Delta_{\scriptscriptstyle E}$	Excess term
Δ_h	Higher-density term
δ	Reduced density, $\delta = \rho / \rho_c$
Е	Energy scaling parameter (K)
	Parameters of the cubic equation of state expressed in general form
	Adjustable parameter in DEoSs with optimized functional form
${\cal E}_{ij}$	Binary interaction coefficient
ζ	Approximated physical dependence between dependent and independent variables
H_{c}	Viscosity reducing parameter (Pa s)
η	Viscosity (Pa s)
	Adjustable parameter in DEoSs with optimized functional form
$\eta_{_{ij}}$	Binary interaction coefficient
$\eta^{\scriptscriptstyle (1)}$	Initial density dependence
θ	Temperature shape function
К	Scaling parameter for thermal conductivity
Λ_{c}	Thermal conductivity reducing parameter from dimensional analysis $(W \cdot m^{-1} \cdot K^{-1})$
$\widetilde{\Lambda}_{c}$	Thermal conductivity reducing parameter from an experimental point $(W \cdot m^{-1} \cdot K^{-1})$
λ	Thermal conductivity (W $m^{-1} K^{-1}$)
λ^{*}	Reducing parameter for thermal conductivity (W m ⁻¹ K ⁻¹)
μ	Joule-Thomson coefficient (K Pa ⁻¹)
μ_i	Chemical potential of a species in mixture (J mol ⁻¹)
μ_{ij}	Binary interaction parameter
ξ	Correlation length (m)
	True physical dependence between dependent and independent variables
	Weight of each property in the objective function
	Scalar parameter for viscosity

π	Ludolph number, $\pi = 3.1415926535$	
	Number of phases	
ρ	Molar or mass density (mol m^{-3} or kg m^{-3})	
ς^*	Reduced effective cross section	
σ	Length scaling parameter (m)	
	Standard deviation	
	Entropy scaling parameter	
τ	Momentum flux	
τ	Inverse reduced temperature, $\tau = T_c/T$	
	Temperature dependent parameter for the UNIQUAC equation	
	Shear stress	
ϕ	Density shape function	
	Mole ratio (moles of one phase / moles of the system)	
φ	Fugacity coefficient	
χ^{2}	Chi-square, weighted sum of squares of residua	
ψ	Function of a generic property	
\varOmega	Collision integral	
ω	Acentric factor	
$\tilde{\omega}$	Scaling parameter	
$arnothing_{ij}$	Binary interaction parameter	

Superscripts

bub	Bubble
С	Combinatorial
E	Excess
ev	Evaporation
id	Ideal mixture
L	Liquid
0	Ideal-gas
р	Reduced density exponent in the exponential function of DEoSs with optimized
	functional form
R	Residual
S	At saturation condition

sl	Saturated liquid
SV	Saturated vapor
t	Total
V	Vapor
/	First derivative of a function
<i>…</i>	Second derivative of a function
<i></i>	Third derivative of a function
^	In mixture
_	Partial molar property

Subscripts

0	Reference
Α	Species
В	Species
bubble	At bubble point
С	Critical enhancement term
С	Critical value
calc	Calculated value
се	Critical enhancement
cub	Cubic equation of state
dew	At dew point
DEoS	Calculated through the DEoS
dg	Dilute-gas
Ε	Excess term
EoS	Calculated through the EoS
exp	Experimental value
	Pseudo-experimental value
	Exponential term
GBS	Gaussian bell shaped
$G^{E} - EoS$	Calculated through the G^E -EoS model
Н	At constant enthalpy
H^{E}	For excess enthalpy
Ι	I^{-th} neuron of the input layer of the neural network
i	Neuron of the input layer of the neural network

	Dummy index	
int	Internal	
J	J^{-th} neuron of the hidden layer of the neural network	
j	Neuron of the hidden layer of the neural network	
	Dummy index	
	Target	
K	Kinetic	
k	Neuron of the output layer of the neural network	
l	Liquid	
М	Mixture	
т	Molar value	
	Dummy index	
max	Maximum value	
min	Minimum value	
n	Dummy index	
	Partial derivative with respect to number of moles	
	At constant number of moles	
NA	Non-analytical	
ob	Objective	
overall	Overall	
Р	Potential	
р	Isobaric	
	Dummy index	
pol	Polynomial term	
R1,R2	Reference fluids	
r	Reduced value	
rev	Reversible transformation	
S	Shaft	
SC	Supercritical region	
sl	Saturated liquid	
SV	Saturated vapor	
S	At constant entropy	
Т	Partial derivative with respect to temperature	
	At constant temperature	

t	Triple point
trans	Translational
v	Vapor
	Isochoric
x	At constant molar composition
	Direction
У	Direction
Z.	For volumetric properties
zd	Zero-density
α	Phase α
β	Phase β
δ	Partial derivative with respect to reduced density
η	For viscosity
λ	For thermal conductivity
ρ	Partial derivative with respect to density
	At constant density
τ	Partial derivative with respect to inverse reduced temperature
φ	For saturation properties

Acronyms

AAD	Average absolute deviation
ANN	Artificial neural network
CS	Corresponding states
DEoS	Dedicated equation of state
ECS	Extended corresponding states
EoS	Equation of state
FPMC	Forced Path Mechanical Calibration
LLE	Liquid-liquid equilibrium
MAD	Maximum absolute deviation
MLFN	Multilayer feed-forward neural network
NN	Neural network
NPT	Number of points
PR	Peng-Robinson cubic equation of state
RK	Redlich-Kwong cubic equation of state

SRK	Soave-Redlich-Kwong cubic equation of state
STD	Standard deviation
vdW	van der Waals cubic equation of state
VLE	Vapor-liquid equilibrium
VLLE	Vapor-liquid-liquid equilibrium
VTD	Vibrating tube densimeter

Introduction

This thesis work concerns to the development and set up of an innovative modeling technique for the representation of the thermophysical properties of fluids.

The thermophysical properties are usually subdivided into thermodynamic properties, as for instance phase equilibrium, density, enthalpy, entropy, heat capacities, speed of sound, etc., and transport properties, as for instance viscosity, thermal conductivity, diffusivity, etc.

The thermophysical properties of every substance depend directly on the nature of the molecules of the substance. A complete understanding of molecular behavior leads to a complete knowledge of the thermophysical properties of fluids. At present such an understanding is not yet available and the molecular theories developed up to now do not allow to predictively yield thermophysical property values with an accuracy sufficient to satisfy the requirements of technical applications.

On the other hand the value of some thermophysical properties can be measured through suitably designed apparatuses, but it is expensive and time consuming to obtain each time the desired properties taking new experimental measurements for the considered fluid, exactly at the given conditions of interest.

For scientific and technological applications the thermophysical property values are supplied in the format of equations correlating values produced by experiments or molecular theories. This allows to readily obtain the values of the thermophysical properties of interest as a function of the operative variables, usually temperature, pressure (or density) and composition.

Furthermore, thermodynamics supplies relations among different thermodynamic properties and then it permits to reduce the experimental efforts, since the knowledge of some properties allows the calculation of other ones.

The models used for the representation of thermophysical properties differentiate themselves for the amount of experimental information required as input; with respect to this aspect, two main groups of models can be roughly identified.

The first group includes predictive and semi-predictive models that move mainly from a theoretical basis which undergoes approximations or simplifications. The theory can yield a directly usable equation, or it can allow to transfer the knowledge about one property to other related properties for which measurements are not available, or to extend the information on pure fluids to mixtures of the same fluids. Otherwise, the theory may yield equations containing a set of parameters that have to be fitted on few experimental data for the fluid of interest. Different levels of prediction capability are encountered in this group of models, i.e. the number of required experimental data can be more or less large. The theoretical basis provides generality to the model

and it allows a quite safe extrapolation outside the range of the data given as input. On the other hand, also depending on the foundation of the assumed simplifications, such models are often not accurate enough or are reliable only in a limited interval of conditions.

The second group of models is constituted by empirical and semi-empirical methods, mainly based on correlations of experimental data. Even if they can have a simplified physical theory as a background, also in this case a relevant number of measurements is required to correct the deviation of the tentative model from the real behavior through empirical formulations. Other models simply assume an empirical equation that is fitted on experimental data. The precision of these models is higher with respect to the first group, but extrapolation has always to be attempted with care. This second group includes also the *heuristic* models considered in the present Ph.D. thesis.

The purpose of a heuristic model is to get the functional representation of a physical dependence directly from a properly organized data base; the most effective heuristic techniques are fundamentally based on mathematical models with the characteristic of *universal function approximators*.

The usual correlative techniques adopt semi-empirical analytical relations that have been previously established and that undergo subsequent modification steps in order to adapt the functional form to the physical evidence reported by experimental data, in a sort of trial-and-error procedure. On the contrary, a heuristic technique allows to infer the analytical relation between dependent and independent variables directly from a sufficiently detailed experimental representation of the studied phenomenon. Therefore no approximated physical model or tentative equation is initially assumed, but the analytical form of the model is set up through the mathematical optimization procedure strictly related to the universal function approximator itself.

This heuristic approach, though it does not claim to investigate in detail the physical bases of the studied phenomena, allows to get very precise, even if quite simple, equations for the representation of the quantities required in many scientific and technical fields.

Precise analytical expressions of the thermophysical properties of fluids are needed to design, simulate, and analyze operations of the process engineering in general and of the chemical engineering in particular. In modern technology there is a constant demand for increasing both the representation accuracy and the thermodynamic consistency, which is necessary to assure stability during process simulation.

The two described groups of models, predictive and semi-predictive from the one hand, empirical and semi-empirical from the other hand, find different applications in the study of a process. The study of the 2-propanol dehydration process, i.e., the extraction of 2-propanol from a liquid homogeneous mixture 2-propanol + water, is treated in this thesis work as an exemplification

case. 2-Propanol and water form an azeotropic mixture that cannot be separated by means of a conventional distillation process. To overcome this problem a third component can be added as solvent to allow the separation. How to chose a suitable solvent for the extraction process? Literature provide only fragmentary information about ternary systems. Predictive and semi-predictive models can be used to carry out a preliminary investigation of some key properties, especially phase equilibria, useful to find out a suitable solvent for the separation, to investigate the feasibility of the extraction process and to design it from a qualitative point of view.

Once the preliminary steps have been carried out and both the system (ternary mixture) and the process are defined, the necessity of a very precise representation of the thermophysical properties of the system arises in order to investigate the best operative conditions in which to carry out the process to optimize its energy consumption. These analysis needs a very precise knowledge of the thermophysical properties of the system, not only the phase equilibria, but also densities, enthalpies and entropies.

Usually predictive and semi-predictive models are not suitable to provide the aforementioned properties with the necessary accuracy; therefore the system of interest need to be deeply investigated from an experimental point of view in order to provide the basis of data to develop a very precise model of the system. The aim of the present Ph.D. thesis is the development of a modern *modus operandi* joining together powerful heuristic techniques and the most advanced experimental tools to obtain a very precise representation of the thermophysical properties of the system of interest with a reduced experimental effort.

In Chapter I the definitions of the thermophysical properties are provided; in Chapter II the regression techniques used in this thesis are presented.

Section One, comprising Chapters III-VIII, is about thermodynamic properties, Section Two, comprising Chapters IX and X, is about transport properties.

In Chapter III a review of the state-of-the-art thermodynamic modeling is given; in Chapter IV an original heuristic modeling technique to develop dedicated equations of state for pure fluids and mixtures is presented; in Chapter V and VI this modeling technique is applied to obtain dedicated equations of state for sulfur hexafluoride and 2-propanol respectively. For the fluid sulfur hexafluoride the entire set of experimental data is from the literature, while for 2-propanol the literature data have been integrated with ad hoc measured values (see Chapter VIII). In order to apply the EEoS-NN modeling technique to a case of industrial interest, in Chapter VII the system propylene + 2-propanol + water has been studied with semi-predictive methods, pointing out the need of new data. In Chapter VIII new measurements have been presented for the phase behavior and densities of the propylene + 2-propanol + water mixture, and the composing binary mixtures.

The thermodynamic properties of such a complex mixture need to be further investigated, in particular the phase equilibria and the caloric properties. At present this experimental work is still in progress and the development of a dedicated equation of state for the propylene + 2-propanol + water mixture will constitute the further development of this thesis work.

In Chapter IX the models for transport properties calculation are described. In Chapter X an original heuristic modeling technique to develop dedicated thermal conductivity equations of state for pure fluids is presented and thermal conductivity equations are obtained from experimental data for the fluids R152a and CO_2 .

Finally, the equations necessary for the application of the proposed models are collected in Appendix.

In this thesis work, treating the regression of equations for the representation of thermophysical properties directly from experimental data, some concepts and definitions recur very often. In the analysis of the performance of the obtained models with respect to the experimental data, the deviation of the values calculated through the model with respect to the data used to regress the model coefficients is defined as *residual error*, while the capability of the equation to represent the data not included in the regression process of the coefficients is defined as *prediction accuracy*. A *dedicated equation of state* is defined as a model with a functional form that is substance-specific. Dealing with thermodynamic properties, an equation of state is defined to be in a *fundamental form* when from it all the thermodynamic properties can be calculated only through differentiation with respect to the independent variables.

I. Definition and role of thermophysical properties

1.1. Introduction

Accurate thermophysical properties of fluids, that are gases and liquids, are essential to design and operation in the chemical process industries.

In the following the attention is focused on the *thermophysical* properties, that determine how the state of a fluid changes as response to external stimuli while the properties related to changes of the molecular entities of the fluid through chemical reactions, i.e. the *thermochemical* properties, are not considered. In the group of thermophysical properties a further subdivision can be drawn between *thermodynamic* properties and *transport* properties.

A *thermodynamic system* is said to be in *thermodynamic equilibrium* when it is in *thermal equilibrium*, temperature gradients are absent, in *mechanical equilibrium*, all the forces are in exact balance, and in *chemical equilibrium*, there is not net change upon time in chemical activities or concentrations of the system components. Therefore, a system in the thermodynamic equilibrium condition is a uniform system characterized by the absence of any tendency for a change of state on a macroscopic scale.

The *thermodynamic* properties are connected to differences between two states of *thermodynamic equilibrium*. It is fundamental to stress that these properties are *state functions*: these thermodynamic functions depend neither on the past history of the system nor on the means by which it has reached a given state, but they depend only on the present conditions, however reached. Moreover, in equilibrium condition the thermodynamic properties are not independent each other, being all linked through thermodynamic relations; this constitutes a relevant characteristic, because properties that are difficult or impossible to measure, but nonetheless are required for technical applications, can be obtained from the experimentally accessible properties related to them. This aspect will become clearer along the present Ph.D. thesis.

The *transport* properties are conversely concerned with a system which is in a non-uniform state and then it is affected by transport phenomena. A gradient in velocity, temperature or concentration of species inside the fluid causes a flux of momentum, energy or mass, respectively, that is opposite to the gradient itself and has an intensity proportional to it; the proportionality coefficient is the corresponding transport properties. Indicating with J the flux vector of the generic transported quantity, with ∇Y the imposed gradient and with X the transport property, it can be written [1,2]:

$$\boldsymbol{J} = -\boldsymbol{X} \, \nabla \boldsymbol{Y} \tag{1.1}$$

The corresponding quantities are reported in Table 1.1. The application of Eq. (1.1) to velocity gives Newton's law of viscosity, the application to temperature is Fourier's law of heat conduction, the application to molar concentration of species A in the mixture of species A and B represents Fick's law of diffusion in the case of constant molar concentration of the mixture [1]. All the transport properties depend on temperature, pressure and, if the considered system is a mixture of fluids, molar composition.

The knowledge of the thermophysical properties of pure fluids and mixtures is an absolutely crucial need for the design and the optimization of any equipment, particularly in the process industry but not limited only to this. For instance, thermodynamics is involved each time that quantities as density, heat capacity, enthalpy difference, vapor pressure, phase compositions at vapor-liquid equilibrium condition are required; examples of application cases are equipment design, process control, energetic optimization of unit operations, study of technical feasibility of processes, search for the best operating conditions, safety analysis, and many others.

J	Y	X
x -Momentum flux:	Velocity in x -direction:	Viscosity:
$\boldsymbol{\tau}_{x}$ (N m ⁻²)	$u_x \text{ (m s}^{-1}\text{)}$	η (N s m ⁻²)
Heat flux:	Temperature:	Thermal conductivity:
\dot{q} (W m ⁻²)	T (K)	$\lambda ~(W m^{-1} K^{-1})$
Molar flux of species A	Molar concentration of species A	Diffusion coefficient of species A
in solution of A and B:	in solution of A and B:	in solution of A and B:
$J_A \pmod{m^{-2} s^{-1}}$	$c_A \pmod{\text{m}^{-3}}$	$D_{AB} \text{ (m}^2 \text{ s}^{-1})$

Table 1.1: Variables and units for transport property equations, Eq. (1.1).

The transport properties are fundamental as well. As few examples, the heat exchange process between two fluid streams is conducted in a heat exchanger whose design requires the knowledge of the values of viscosity and thermal conductivity for the involved fluids; the calculation of pressure drop of fluids flowing inside pipes, and then the dimensioning of pumps and the selection of the pipe diameters, is possible only if viscosity is known; the design of separation equipments or of chemical reactors, especially if making use of porous solid catalysts, depends on diffusion coefficients, viscosity and thermal conductivity.

Moreover, the thermophysical properties have to be known in dependence on the controlling variables with a precision as high as possible: errors in the values of the required properties can

propagate throughout the entire calculation with amplification effects, yielding wrong design and driving away from the optimal operating conditions.

In the following paragraphs the most commonly used thermophysical properties are briefly presented.

1.2. Thermodynamic properties

In this paragraph a summary of thermodynamics for pure fluids and mixtures is given with the purpose to recall to the Reader both the definitions of the thermodynamic properties used in the present Ph.D. thesis and the fundamentals of the thermodynamic relations among such properties. For detailed explanations of all these subjects, several specialized texts can be consulted, as for instance Refs. 3 and 4.

The hypothetical system here considered is always a *non-reacting* one and then its chemical composition is not modified by any chemical reaction taking place in it.

1.2.1. The first law of thermodynamics and basic concepts

The general principle of conservation of energy was established at about the half of the 19th century as a generalization of the law of conservation of mechanical energy; no exception to it has been observed in ordinary processes and then it is now regarded as a law of nature. One of the several possible formulations of the first law of thermodynamics is the following [3]:

Although energy assumes many forms, the total quantity of energy is constant, and when energy disappears in one form it appears simultaneously in other forms.

The application of the first law of thermodynamics to a *closed* system, i.e. a system that cannot exchange matter with its surroundings, undergoing a process gives:

$$\Delta U^{t} + \Delta E_{K} + \Delta E_{P} = Q + W \tag{1.2}$$

where ΔU^{t} , ΔE_{K} and ΔE_{P} are the variations of total internal energy, of total kinetic energy and of total potential energy, respectively, of the system, while Q represents the heat transferred to the system and W the work done on the system.

If the variations of kinetic and potential energy are negligible, Eq. (1.2) reads:

$$\Delta U^t = Q + W \tag{1.3}$$

or in differential form:

$$\mathrm{d}U^t = \mathrm{d}Q + \mathrm{d}W \tag{1.4}$$

It is very important to keep in mind that internal energy, as the other thermodynamic properties, is a state function and depends only on the system conditions; this is not true for heat and work, that represent merely amounts exchanged between the system and its surroundings and then they depend on the process path.

The total internal energy U^t is an *extensive* property, since depends on the quantity of involved material, while on the contrary properties as temperature T and pressure P are *intensive*. The ratio of the extensive quantity U^t to the total number of moles (or to the total mass) of the system gives the corresponding *intensive* molar (or specific) property U.

The number of *degrees of freedom* F, i.e. the number of independent variables that is necessary to arbitrarily fix in order to exactly define the intensive state of a system, is given by the *phase rule* of Gibbs:

$$F = 2 + C - \pi \tag{1.5}$$

where *C* is the number of components in the system and π the number of phases. For example, a system constituted by a pure fluid has two degrees of freedom in liquid or vapor states, but at vaporliquid equilibrium there is only one independent variable and at the triple point none; a mixture of two components has three independent variables in liquid or vapor states, while it has only two independent variables in a two-phases equilibrium state.

In the following the reported thermodynamic properties are considered as intensive (molar or specific), unless the contrary is expressly indicated.

A widely used thermodynamic property related to internal energy is *enthalpy*, defined as:

$$H \equiv U + Pv \tag{1.6}$$

where P is the pressure and v is the molar (specific) volume. This property is particularly useful when studying *steady-state steady-flow* processes, for which the conditions and the flow rates at all points along the flow path are constant with time; an example of such a process is schematically represented in Fig. 1.1.



Figure 1.1: An example of steady-state steady-flow process.

A unit mass of fluid enters section 1 (placed at level z_1) with velocity u_1 , undergoes heat and work exchanges, and goes out from section 2 (placed at level z_2) with velocity u_2 ; such a unit mass can be regarded as a closed system, to which Eq. (1.2) is applied:

$$U_2 - U_1 + \frac{u_2^2 - u_1^2}{2} + g(z_2 - z_1) = Q + W$$
(1.7)

where the kinetic-energy change of the unit mass of fluid between sections 1 and 2 is $\Delta E_{K} = E_{K,2} - E_{K,1} = (u_{2}^{2} - u_{1}^{2})/2$ and the corresponding potential-energy change is $\Delta E_{P} = E_{P,2} - E_{P,1} = g(z_{2} - z_{1}).$

The work W is composed of two parts: the shaft work W_s and the work exchanged with the fluid surrounding the considered system.

The second contribution is made *on* the system at the entrance in section 1:

$$W_1 = P_1 A_1 \frac{V_1}{A_1} = P_1 V_1 \tag{1.8}$$

and by the system at the exit from section 2:

$$W_2 = -P_2 A_2 \frac{V_2}{A_2} = -P_2 V_2 \tag{1.9}$$

In these equations A denotes the cross-sectional area and V/A is the length of the considered system in the pipe, being V_1 and V_2 the volumes of the system in section 1 and 2 respectively; it has to be remembered that work is defined as the product of a force by a displacement in the same direction of force. Substitution into Eq. (1.7) reads:

$$U_2 - U_1 + \frac{u_2^2 - u_1^2}{2} + g(z_2 - z_1) = Q + W_s + P_1 v_1 - P_2 v_2$$
(1.10)

and finally, from Eq. (1.6):

$$H_2 - H_1 + \frac{u_2^2 - u_1^2}{2} + g(z_2 - z_1) = Q + W_s$$
(1.11)

If the variations of kinetic and potential energy are negligible, it comes out the simplified equation for a steady-state steady-flow process:

$$\Delta H = Q + W_s \tag{1.12}$$

The derivatives with respect to temperature of internal energy at constant volume and of enthalpy at constant pressure are the isochoric and isobaric heat capacity, respectively:

$$C_{v} \equiv \left(\frac{\partial U}{\partial T}\right)_{v} \qquad \qquad C_{p} \equiv \left(\frac{\partial H}{\partial T}\right)_{p} \qquad (1.13, 1.14)$$

1.2.2. The second law of thermodynamics

While the first law of thermodynamics states the conservation of energy, putting all the different forms of energy on a same level, the second law shows that they are not equivalent and imposes a restriction on the process direction. A common statement of such law is the following:

No apparatus can operate in such a way that its only effect, in system and in surroundings, is to convert heat absorbed by a system completely into work done by the system.

The concept of *reversible transformation* is also introduced, but for its precise definition reference is made to thermodynamics texts, as for instance Ref. 3.

From the developments related to the second law of thermodynamics the definition of the state function *entropy* comes out:

$$dS = \frac{dQ_{rev}}{T}$$
(1.15)

In Eq. (1.15) dQ_{rev} is the differential quantity of heat given to a unit mass of the system in an infinitesimal step of a reversible transformation. Being a state function, the entropy change of the system depends only on starting and final points, independently from the followed transformation path; in the case of an irreversible transformation between two state conditions *A* and *B*, Eq. (1.15) cannot be applied with the simple substitution of the heat effectively exchanged for dQ_{rev} , but a reversible path connecting *A* and *B* has to be found out along which the integration of Eq. (1.15) is performed.

It can be demonstrated that for any process the overall entropy value, comprising both the system and its surroundings, never decreases:

$$\Delta S_{total} \ge 0 \tag{1.16}$$

and equals zero only for reversible processes.

. .

1.2.3. Other property definitions and Maxwell's relations

The application of the first law of thermodynamics to a unit mass of a closed system gives:

$$\mathrm{d}U = \mathrm{d}W + \mathrm{d}Q \tag{1.17}$$

If the considered process is reversible, remembering also Eq. (1.15) it results that:

$$\mathrm{d}U = -P\mathrm{d}v + T\mathrm{d}S \tag{1.18}$$

being the work for a mechanically reversible, non-flow process given by dW = -Pdv [3]. In Eq. (1.18) all the *primary* thermodynamic properties P, v, T, S and U are included. For enthalpy, differentiating Eq. (1.6) and substituting dU from Eq. (1.18), it is:

$$dH = dU + d(Pv) = vdP + TdS$$
(1.19)

Other properties can be defined for convenience: the Helmholtz free energy A and the Gibbs free energy G; also their differentials are easily calculated:

$$A = U - TS \qquad \qquad dA = -Pdv - SdT \qquad (1.20, 1.21)$$

$$G = H - TS \qquad \qquad dG = vdP - SdT \qquad (1.22, 1.23)$$

The equations (1.18), (1.19), (1.21) and (1.23) are the *fundamental property relations* for a fluid. For an exact function f(x, y) the equality of the mixed second derivatives is valid:

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_{x}\right]_{y} = \left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_{y}\right]_{x}$$
(1.24)

When Eq. (1.24) is applied to the fundamental property relations, *Maxwell's equations* are obtained:

$$\left(\frac{\partial T}{\partial \nu}\right)_{S} = -\left(\frac{\partial P}{\partial S}\right)_{\nu} \qquad \qquad \left(\frac{\partial T}{\partial P}\right)_{S} = \left(\frac{\partial \nu}{\partial S}\right)_{P} \qquad (1.25, 1.26)$$

$$\left(\frac{\partial S}{\partial v}\right)_{T} = \left(\frac{\partial P}{\partial T}\right)_{v} \qquad \qquad \left(\frac{\partial S}{\partial P}\right)_{T} = -\left(\frac{\partial v}{\partial T}\right)_{P} \qquad (1.27, 1.28)$$

From the division of Eq. (1.19) by dT at constant P, remembering also Eq. (1.14), it results that:

$$\left(\frac{\partial H}{\partial T}\right)_{P} = T \left(\frac{\partial S}{\partial T}\right)_{P} = C_{P}$$
(1.29)

The division of Eq. (1.19) by dP at constant T gives:

$$\left(\frac{\partial H}{\partial P}\right)_T = v + T \left(\frac{\partial S}{\partial P}\right)_T \tag{1.30}$$

Therefore, from the differentiation of H and from Eqs. (1.28-1.30) it follows:

$$dH = \left(\frac{\partial H}{\partial T}\right)_{P} dT + \left(\frac{\partial H}{\partial P}\right)_{T} dP = C_{P} dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_{P}\right] dP$$
(1.31)

$$dS = \left(\frac{\partial S}{\partial T}\right)_{P} dT + \left(\frac{\partial S}{\partial P}\right)_{T} dP = \frac{C_{P}}{T} dT - \left(\frac{\partial v}{\partial T}\right)_{P} dP$$
(1.32)

The application of a similar procedure to U gives:

$$dU = \left(\frac{\partial U}{\partial T}\right)_{v} dT + \left(\frac{\partial U}{\partial v}\right)_{T} dv = C_{v} dT + \left[T\left(\frac{\partial P}{\partial T}\right)_{v} - P\right] dv$$
(1.33)

$$dS = \left(\frac{\partial S}{\partial T}\right)_{v} dT + \left(\frac{\partial S}{\partial v}\right)_{T} dv = \frac{C_{v}}{T} dT + \left(\frac{\partial P}{\partial T}\right)_{v} dv$$
(1.34)

Other interesting relations are obtained from:

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT} dG - \frac{G}{RT^2} dT$$
(1.35)

where R is the gas constant. The substitution of Eqs. (1.22) and (1.23) into Eq. (1.35) gives:

$$d\left(\frac{G}{RT}\right) = \frac{v}{RT} dP - \frac{H}{RT^2} dT$$
(1.36)

It is easy to obtain:

$$\frac{v}{RT} = \left[\frac{\partial(G/RT)}{\partial P}\right]_{T} \qquad \qquad \frac{H}{RT} = -T\left[\frac{\partial(G/RT)}{\partial T}\right]_{P} \qquad (1.37, 1.38)$$

and from Eqs. (1.6) and (1.22):

$$\frac{S}{R} = \frac{H}{RT} - \frac{G}{RT} \qquad \qquad \frac{U}{RT} = \frac{H}{RT} - \frac{Pv}{RT}$$
(1.39, 1.40)

An analogous procedure can be conveniently applied also to Helmholtz free energy:

$$d\left(\frac{A}{RT}\right) = -\frac{P}{RT}dv - \frac{U}{RT^2}dT$$
(1.41)

$$\frac{P}{RT} = -\left[\frac{\partial(A/RT)}{\partial v}\right]_{T} \qquad \qquad \frac{U}{RT} = -T\left[\frac{\partial(A/RT)}{\partial T}\right]_{v} \qquad (1.42, 1.43)$$

$$\frac{S}{R} = \frac{U}{RT} - \frac{A}{RT} \qquad \qquad \frac{H}{RT} = \frac{U}{RT} + \frac{Pv}{RT}$$
(1.44, 1.45)

It has been demonstrated that, if the state function G or A for the system is known on all the thermodynamic surface, all the other properties can be calculated simply for differentiation: Gibbs energy and Helmholtz energy are generating functions for the other thermodynamic properties and represent complete property information. Therefore, an analytical expression for one of these state functions is a *fundamental equation of state*. Unfortunately, these quantities are not experimentally accessible and then an equation for them cannot be directly regressed on experimental data of Gibbs

or Helmholtz energy; other methods have been developed to solve this problem and such a subject constitutes a part of the present Ph.D. thesis.

All the relations up to now presented can be written also using molar (or mass) density ρ instead of molar (specific) volume, being the two properties related through:

$$\rho = \frac{1}{\nu} \tag{1.46}$$

Other thermodynamic properties interesting from both a scientific and a technical point of view are the speed of sound:

$$w \equiv \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_{S}} \tag{1.47}$$

and the Joule-Thomson coefficient:

$$\mu = \left(\frac{\partial T}{\partial P}\right)_{H} \tag{1.48}$$

1.2.4. Ideal-gas properties

The *ideal-gas* condition represents the behavior of a hypothetical gas in which no intermolecular forces exist; in such a condition of absence of intermolecular interactions the internal energy depends only on temperature. The ideal-gas state can also be regarded as a limit condition for a real gas with pressure approaching zero.

The macroscopic behavior of an ideal gas, in the following denoted by superscript o, is completely described by:

- the equation of state $Pv^o = RT$; (1.49)
- an equation for internal energy, or alternatively for isochoric heat capacity C^o_v, that is a function of temperature only.

Given an equation for $C_v^o = C_v^o(T)$, from Eqs. (1.6), (1.13), (1.14) and (1.49) it comes out:

$$C_{p}^{o}(T) = C_{v}^{o}(T) + R \tag{1.50}$$

The C_{ν}^{o} and C_{p}^{o} equations are *fluid specific* and depend on the molecular structure. It is possible to theoretically derive them with satisfactory results for simple monatomic gases, but for molecules of higher complexity empirical expressions are often used.
All the ideal-gas thermodynamic properties are obtained from Eqs. (1.49) and (1.50) using the basic relations previously presented. Supposing to dispose of a C_p^o equation for the system constituted by a pure fluid and fixing arbitrary values H_0^o and S_0^o for enthalpy and entropy at the condition (T_0, P_0, v_0^o) , the followings equations are got:

$$H^{o}(T,P) = H^{o}(T) = H^{o}_{0} + \int_{T_{0}}^{T} C^{o}_{p} dT \qquad \qquad U^{o}(T,P) = U^{o}(T) = H^{o}(T) + RT \qquad (1.51, 1.52)$$

$$S^{o}(T,P) = S_{0}^{o} + \int_{T_{0}}^{T} \frac{C_{p}^{o}}{T} dT - R \ln\left(\frac{P}{P_{0}}\right) = S_{0}^{o} + \int_{T_{0}}^{T} \frac{\left(C_{p}^{o} - R\right)}{T} dT + R \ln\left(\frac{v^{o}}{v_{0}^{o}}\right)$$
(1.53)

$$A^{o}(T,P) = H_{0}^{o} - RT + \int_{T_{0}}^{T} C_{p}^{o} dT - TS_{0}^{o} - T \int_{T_{0}}^{T} \frac{C_{p}^{o}}{T} dT + RT \ln\left(\frac{P}{P_{0}}\right) =$$

= $H_{0}^{o} - RT + \int_{T_{0}}^{T} C_{p}^{o} dT - TS_{0}^{o} - T \int_{T_{0}}^{T} \frac{\left(C_{p}^{o} - R\right)}{T} dT - RT \ln\left(\frac{v^{o}}{v_{0}^{o}}\right)$ (1.54)

$$G^{o}(T,P) = H_{0}^{o} + \int_{T_{0}}^{T} C_{p}^{o} dT - TS_{0}^{o} - T \int_{T_{0}}^{T} \frac{C_{p}^{o}}{T} dT + RT \ln\left(\frac{P}{P_{0}}\right) =$$

$$= H_{0}^{o} + \int_{T_{0}}^{T} C_{p}^{o} dT - TS_{0}^{o} - T \int_{T_{0}}^{T} \frac{\left(C_{p}^{o} - R\right)}{T} dT - RT \ln\left(\frac{v^{o}}{v_{0}^{o}}\right)$$
(1.55)

1.2.5. Residual properties and fugacity for pure fluids

The deviation of real fluids from the ideal-gas behavior is quantitatively expressed through *residual* functions. The residual part of a generic thermodynamic property M is defined as the difference between the property value of real fluid and the corresponding value for ideal gas at the same temperature and pressure:

$$M^{R}(T,P) \equiv M(T,P) - M^{o}(T,P)$$
(1.56)

where superscript R stands for 'residual property'. For instance, the residual volume is:

$$v^{R} \equiv v - v^{o} = v - \frac{RT}{P} = \frac{RT}{P} (Z - 1)$$
(1.57)

where the *compressibility factor* Z is defined as:

$$Z = \frac{Pv}{RT}$$
(1.58)

All the preceding equations, Eqs. (1.18-1.45), are still valid when applied to residual properties.

Considering a transformation of a pure ideal gas along an isotherm starting from a pressure P_0 , from Eqs. (1.23) and (1.49) the final Gibbs energy value is:

$$G^{o}(T,P) = G_{0}^{o}(T,P_{0}) + \left(\int_{P_{0}}^{P} \frac{RT}{P} dP\right)_{T} = G_{0}^{o}(T,P_{0}) + RT \ln \frac{P}{P_{0}}$$
(1.59)

If the same process is applied to a real fluid, under the hypothesis that the starting pressure is so small that the fluid at the starting condition can be considered as an ideal gas, considering Eq. (1.58) it gives:

$$G(T,P) = G_0(T,P_0) + \left(\int_{P_0}^{P} Z \frac{RT}{P} dP\right)_T = G_0^o(T,P_0) + RT \left(\int_{P_0}^{P} \frac{Z}{P} dP\right)_T$$
(1.60)

The *fugacity* of the pure real fluid at T, P conditions is defined as that value f making:

$$\ln\frac{f}{P_0} = \left(\int_{P_0}^{P} \frac{Z}{P} dP\right)_T$$
(1.61)

Subtracting Eq. (1.59) from Eq. (1.60) and considering Eqs. (1.56) and (1.61), it results:

$$G^{R}(T,P) = RT \ln \frac{f}{P}$$
(1.62)

from which it is evident that fugacity is a state function. The ratio of fugacity to pressure is the fugacity coefficient φ :

$$\varphi \equiv \frac{f}{P} \qquad \qquad G^{R}(T,P) = RT \ln \varphi \qquad (1.63, 1.64)$$

The fugacity coefficient has a unit value for ideal gas; otherwise it can be calculated from:

$$\ln \varphi = \int_{0}^{P} \frac{(Z-1)}{P} dP$$
(1.65)

1.2.6. Mixtures

The relations up to now developed are referred to a unit quantity of material and they are valid both for pure fluids and for mixtures. Referring to n moles, the differential of total Gibbs energy nG for a closed system can be written as:

$$d(nG) = (nv)dP - (nS)dT$$
(1.66)

where:

$$nv = \left[\frac{\partial(nG)}{\partial P}\right]_{T,n} = n\left(\frac{\partial G}{\partial P}\right)_{T,n} \qquad nS = -\left[\frac{\partial(nG)}{\partial T}\right]_{P,n} = -n\left(\frac{\partial G}{\partial T}\right)_{P,n} \qquad (1.67, 1.68)$$

In these equations the *molar* values of the thermodynamic properties are considered. If an *open* system, that can exchange matter with its surroundings, is now taken into account, assuming it as composed of *C* different chemical species, the same differential is:

$$d(nG) = \left[\frac{\partial(nG)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial(nG)}{\partial P}\right]_{P,n} dT + \sum_{i=1}^{C} \left[\frac{\partial(nG)}{\partial n_i}\right]_{T,P,n_{j\neq i}} dn_i = (nv)dP - (nS)dT + \sum_{i=1}^{C} \left[\frac{\partial(nG)}{\partial n_i}\right]_{T,P,n_{j\neq i}} dn_i$$
(1.69)

The derivative of nG with respect to the number of moles of component *i* is the *chemical potential* of species *i* in mixture:

$$\mu_{i} = \left[\frac{\partial(nG)}{\partial n_{i}}\right]_{T,P,n_{j\neq i}}$$
(1.70)

Given a generic property M, the *partial molar* property \overline{M}_i of component *i* in mixture is defined as:

$$\overline{M}_{i} = \left[\frac{\partial (nM)}{\partial n_{i}}\right]_{T,P,n_{j\neq i}}$$
(1.71)

and it represents the rate of variation of the total property nM caused by the addition of differential amounts of species i to the system. A remarkable aspect of partial molar properties is that:

$$nM = \sum_{i=1}^{C} n_i \overline{M}_i$$
(1.72)

Other characteristics of partial molar properties are here not reported (see Ref. 3), but it is interesting to notice that the chemical potential represents the partial molar Gibbs energy.

1.2.7. Ideal-gas mixtures

The thermodynamic properties of a mixture of ideal gases are directly related to the properties of pure components; in particular, defined the partial pressure of the species i present in mixture with a molar fraction x_i as:

$$p_i = x_i P \tag{1.73}$$

Gibbs's theorem states that the partial molar property of a component in an ideal-gas mixture is equivalent to its corresponding molar property as a pure ideal gas at the same temperature and at pressure equal to its partial pressure in mixture.

Therefore, Eq. (1.49) is still valid and it is easy to obtain the following equations:

$$U^{o}(\boldsymbol{T},\boldsymbol{x}) = \sum_{i=1}^{C} x_{i} U_{i}^{o}(\boldsymbol{T})$$
(1.74)

$$H^{o}(T, \boldsymbol{x}) = \sum_{i=1}^{C} x_{i} H^{o}_{i}(T)$$
(1.75)

$$S^{o}(T, P, \mathbf{x}) = \sum_{i=1}^{C} x_{i} S_{i}^{o}(T, P) - R \sum_{i=1}^{C} x_{i} \ln x_{i}$$
(1.76)

$$A^{o}(T, P, \mathbf{x}) = \sum_{i=1}^{C} x_{i} A_{i}^{o}(T, P) + RT \sum_{i=1}^{C} x_{i} \ln x_{i}$$
(1.77)

$$G^{o}(T, P, \mathbf{x}) = \sum_{i=1}^{C} x_{i} G_{i}^{o}(T, P) + RT \sum_{i=1}^{C} x_{i} \ln x_{i}$$
(1.78)

The last term in Eqs. (1.76-1.78) is the property change of mixing of ideal gases; it has a positive value for entropy, while it is negative for Helmholtz and Gibbs free energies.

The chemical potential for a species i in a mixture of ideal gases, i.e. its partial molar Gibbs energy, can also be expressed as:

$$\mu_{i}^{o}(T, P, \mathbf{x}) = G_{i}^{o}(T, P) + RT \ln x_{i} = \Gamma_{i}(T) + RT \ln(x_{i}P)$$
(1.79)

where $\Gamma_i(T)$ depends only on temperature and on the chosen reference values, see Eq. (1.55).

1.2.8. Mixture residual properties and fugacity for species in solution

The residual properties for a real mixture are calculated similarly as for pure fluids:

$$M^{R}(T, P, \boldsymbol{x}) \equiv M(T, P, \boldsymbol{x}) - M^{o}(T, P, \boldsymbol{x})$$
(1.80)

The fugacity of species *i* in mixture, \hat{f}_i , is defined as that value that, in analogy with Eq. (1.79), satisfies:

$$\mu_i \left(T, P, \mathbf{x} \right) = \Gamma_i \left(T \right) + RT \ln \hat{f}_i \tag{1.81}$$

Applying the residual concept to partial molar Gibbs energy, it comes out:

$$\overline{G}_{i}^{R} = \overline{G}_{i} - \overline{G}_{i}^{o} = \mu_{i} - \mu_{i}^{o} = \Gamma_{i}(T) + RT \ln \hat{f}_{i} - \Gamma_{i}(T) - RT \ln (x_{i}P) = RT \ln \left(\frac{\hat{f}_{i}}{x_{i}P}\right)$$
(1.82)

from which the fugacity coefficient of species *i* in mixture, $\hat{\varphi}_i$, is defined as:

$$\hat{\varphi}_i \equiv \frac{\hat{f}_i}{x_i P} \qquad \qquad \overline{G}_i^R = RT \ln \hat{\varphi}_i \qquad (1.83, 1.84)$$

1.2.9. The ideal solution

The ideal gas is a useful model of the behavior of gases, and serves as a standard to which realgas behavior can be compared. This is formalized by the introduction of the residual properties. Another useful model is the *ideal solution*, which serves as a standard to which real-solution behavior can be compared. This is formalized by introduction of the excess properties. Eq (1.85) characterizes the behavior of a constituent species in an ideal gas mixture:

$$\overline{G}_{i}^{o}(T, P, \mathbf{x}) = G_{i}^{o}(T, P) + RT \ln x_{i}$$
(1.85)

Replacing the Gibbs energy of the pure species i in the ideal-gas state, G_i^o , by the Gibbs energy of the pure species i, G_i , as it actually exists at the mixture T and P and in the same physical state (real gas, liquid or solid) as the mixture, we obtain the definition of an ideal solution, Eq (1.86):

$$\overline{G}_{i}^{id}\left(T,P,\boldsymbol{x}\right) = G_{i}\left(T,P\right) + RT\ln x_{i}$$
(1.86)

where superscript *id* denotes an ideal-solution property.

All the other thermodynamic properties for an ideal solution follow differentiating equation (1.86) with respect to the independent variables:

$$\overline{S}_{i}^{id}(T, P, \mathbf{x}) = S_{i}(T, P) - R \ln x_{i}$$
(1.87)

$$(1.88)$$

$$\overline{H}_{i}^{id}\left(T,P,\boldsymbol{x}\right) = H_{i}\left(T,P\right) \tag{1.89}$$

The generic property M^{id} for an ideal solution is calculated as:

$$M^{id}\left(T,P,\boldsymbol{x}\right) = \sum_{i=1}^{C} x_{i} \overline{M}_{i}^{id}\left(T,P\right)$$
(1.90)

Application to Eqs. (1.86) through (1.89) yields:

$$G^{id}(T, P, \mathbf{x}) = \sum_{i=1}^{C} x_i G_i(T, P) + RT \sum_{i=1}^{C} x_i \ln x_i$$
(1.91)

$$S^{id}(T, P, \mathbf{x}) = \sum_{i=1}^{C} x_i S_i(T, P) - R \sum_{i=1}^{C} x_i \ln x_i$$
(1.92)

$$V^{id}\left(T,P,\boldsymbol{x}\right) = \sum_{i=1}^{C} x_i V_i \left(T,P\right)$$
(1.93)

$$H^{id}\left(T,P,\boldsymbol{x}\right) = \sum_{i=1}^{C} x_{i}H_{i}\left(T,P\right)$$
(1.94)

From Eq. (1.86) the fugacity of a species in the ideal solution follows:

$$\mu_i \left(T, P, \mathbf{x} \right) = \overline{G}_i^{id} \left(T, P, \mathbf{x} \right) = \Gamma_i \left(T \right) + RT \ln \hat{f}_i^{id}$$
(1.95)

Combining Eq. (1.95) with Eq. (1.86) and considering that $G_i(T, P) = \Gamma_i(T) + RT \ln f_i$ it follows:

$$\hat{f}_i^{id} = x_i f_i \tag{1.96}$$

known as the Lewis/Randall rule.

Considering:

$$\hat{\varphi}_i^{id} = \frac{\hat{f}_i^{id}}{x_i P} \tag{1.97}$$

an alternative form of Eq. (1.96) is:

$$\hat{\varphi}_i^{id} = \varphi_i \tag{1.98}$$

1.2.10. Excess properties

Liquid solutions are often deal with through properties that measure their derivation from idealsolution behavior. If M represents the molar (or unit-mass) value of any extensive thermodynamic property (e.g., V, U, H, S, G, etc.), then an *excess property* M^E is defined as the difference between the actual property value of a solution and the value it would have as an ideal solution at the same temperature, pressure and composition. Thus:

$$M^E \equiv M - M^{id} \tag{1.99}$$

and for the partial-property relation:

$$\overline{M}_{i}^{E} \equiv \overline{M}_{i} - \overline{M}_{i}^{id} \tag{1.100}$$

where \overline{M}_{i}^{E} is a partial excess property.

Eq. (1.81) may be written:

$$\overline{G}_{i}\left(T,P,\boldsymbol{x}\right) = \Gamma_{i}\left(T\right) + RT\ln\hat{f}_{i}$$
(1.101)

and, according to Eq. (1.96), this becomes:

$$\overline{G}_{i}^{id}(T, P, \mathbf{x}) = \Gamma_{i}(T) + RT \ln x_{i} f_{i}$$
(1.102)

By difference between Eq. (1.101) and Eq. (1.102) is the partial excess Gibbs energy:

$$\overline{G}_{i}(T,P,\boldsymbol{x}) - \overline{G}_{i}^{id}(T,P,\boldsymbol{x}) = \overline{G}_{i}^{E}(T,P,\boldsymbol{x}) = RT \ln \frac{\hat{f}_{i}}{x_{i}f_{i}}$$
(1.103)

where the dimensionless ratio $\hat{f}_i / x_i f_i$ appearing on the right is called the activity coefficient of species *i* in solution, and is given the symbol γ_i . Thus, by definition:

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i} \tag{1.104}$$

and

$$\overline{G}_{i}^{E}(T, P, \mathbf{x}) = RT \ln \gamma_{i}$$
(1.105)

or

$$\ln \gamma_i = \left[\frac{\partial \left(nG^E/RT\right)}{\partial n_i}\right]_{T,P,n_{j\neq i}}$$
(1.106)

The last relation demonstrates that $\ln \gamma_i$ is a partial property with respect to G^E/RT .

1.2.11. Phase equilibria

Considering a closed system constituted by two phases in equilibrium, Eq. (1.66) is still valid for it; each phase represents an open system that can exchange matter with the other phase and then Eq. (1.69) is applied to both, denoting the two phases with α and β :

$$d(nG)^{\alpha} = (nv)^{\alpha} dP - (nS)^{\alpha} dT + \sum_{i=1}^{C} \mu_{i}^{\alpha} dn_{i}^{\alpha}$$
(1.107)

$$d(nG)^{\beta} = (nv)^{\beta} dP - (nS)^{\beta} dT + \sum_{i=1}^{C} \mu_{i}^{\beta} dn_{i}^{\beta}$$
(1.108)

Their summation gives the overall system:

$$d(nG) = (nv)dP - (nS)dT + \sum_{i=1}^{C} \mu_i^{\alpha} dn_i^{\alpha} + \sum_{i=1}^{C} \mu_i^{\beta} dn_i^{\beta}$$
(1.109)

and Eq. (1.109) has to be equal to Eq. (1.66); this condition is verified only if:

$$\sum_{i=1}^{C} \mu_i^{\alpha} dn_i^{\alpha} + \sum_{i=1}^{C} \mu_i^{\beta} dn_i^{\beta} = 0$$
(1.110)

and then, being $dn_i^{\alpha} = -dn_i^{\beta}$ as it results from mass conservation of the molecules transferred between the phases:

$$\sum_{i=1}^{C} \left(\mu_{i}^{\alpha} - \mu_{i}^{\beta} \right) dn_{i}^{\alpha} = 0$$
(1.111)

Since the differential dn_i^{α} are independent each other, the fulfillment of this condition requires that:

$$\mu_i^{\alpha} = \mu_i^{\beta} \qquad \qquad \text{for each } i \ (1 \le i \le C) \qquad (1.112)$$

Therefore it has been demonstrated that the equality of chemical potential of each component in the coexisting phases is a necessary condition for equilibrium. The same reasoning can be extended to a system composed of several coexisting phases, showing that in all of them the chemical potential of each component must be the same.

In the case of a pure fluid, the chemical potential of the unique component coincides with its molar Gibbs energy, as it can be easily verified; therefore:

$$\left[G\left(T,P^{s}\right)\right]^{\alpha} = \left[G\left(T,P^{s}\right)\right]^{\beta} \Longrightarrow \left[G^{o}\left(T,P^{s}\right) + G^{R}\left(T,P^{s}\right)\right]^{\alpha} = \left[G^{o}\left(T,P^{s}\right) + G^{R}\left(T,P^{s}\right)\right]^{\beta}$$
(1.113)

and, since the ideal-gas contribution is equal for both the phases, from Eq. (1.113) and Eq. (1.62) it is:

$$\left[G^{R}\left(T,P^{s}\right)\right]^{\alpha} = \left[G^{R}\left(T,P^{s}\right)\right]^{\beta} \implies f^{\alpha} = f^{\beta} \implies \varphi^{\alpha} = \varphi^{\beta}$$

$$(1.114)$$

In a pure fluid, the equilibrium condition is equivalent to the iso-fugacity condition, that corresponds to the equality of the fugacity coefficients.

In the case of a multi-component system, considering Eq. (1.81):

$$\mu_i^{\alpha} = \mu_i^{\beta} \implies \left(\Gamma_i \left(T \right) + RT \ln \hat{f}_i \right)^{\alpha} = \left(\Gamma_i \left(T \right) + RT \ln \hat{f}_i \right)^{\beta}$$
(1.115)

and, since $\Gamma_i(T)$ depends only on temperature, it results that:

$$\hat{f}_{i}^{\alpha} = \hat{f}_{i}^{\beta} \implies x_{i}^{\alpha} \hat{\varphi}_{i}^{\alpha} = x_{i}^{\beta} \hat{\varphi}_{i}^{\beta}$$
(1.116)

This condition must be verified for all the components in the mixture.

In the case of a vapor-liquid equilibrium Eq. (1.116) becomes:

$$\hat{f}_i^V(T, P, y_i) = \hat{f}_i^L(T, P, x_i) \implies y_i \hat{\varphi}_i^V = x_i \hat{\varphi}_i^L \qquad \text{for each } i \ (1 \le i \le C) \qquad (1.117)$$

where \hat{f}_i^L and $\hat{\varphi}_i^L$ are the fugacity and the fugacity coefficient of the component *i* in the liquid phase, \hat{f}_i^V and $\hat{\varphi}_i^V$ are the fugacity and the fugacity coefficient of the component *i* in the vapor phase, x_i is the mole fraction of component *i* in the liquid phase and y_i is the mole fraction of component *i* in the vapor phase.

In the case of a liquid-liquid equilibrium Eq. (1.116) becomes:

$$\hat{f}_{i}^{L_{1}}(T, P, x_{i}^{L_{1}}) = \hat{f}_{i}^{L_{2}}(T, P, x_{i}^{L_{2}}) \implies x_{i}^{L_{1}}\hat{\varphi}_{i}^{L_{1}} = x_{i}^{L_{2}}\hat{\varphi}_{i}^{L_{2}} \qquad \text{for each } i \ (1 \le i \le C)$$
(1.118)

where $\hat{f}_i^{L_1}$ and $\hat{\varphi}_i^{L_1}$ are the fugacity and the fugacity coefficient of the component *i* in the first liquid phase, $\hat{f}_i^{L_2}$ and $\hat{\varphi}_i^{L_2}$ are the fugacity and the fugacity coefficient of the component *i* in the second liquid phase, $x_i^{L_1}$ is the mole fraction of component *i* in the first liquid phase and $x_i^{L_2}$ is the mole fraction of component *i* in the second liquid phase.

In the case of a vapor-liquid-liquid equilibrium Eq. (1.116) becomes:

$$\begin{cases} \hat{f}_{i}^{V}(T,P,y_{i}) = \hat{f}_{i}^{L}(T,P,x_{i}^{L_{1}}) \\ \hat{f}_{i}^{V}(T,P,y_{i}) = \hat{f}_{i}^{L}(T,P,x_{i}^{L_{2}}) \end{cases} \Rightarrow \begin{cases} y_{i}\hat{\varphi}_{i}^{V} = x_{i}^{L_{1}}\hat{\varphi}_{i}^{L_{1}} \\ y_{i}\hat{\varphi}_{i}^{V} = x_{i}^{L_{2}}\hat{\varphi}_{i}^{L_{2}} \end{cases} \text{ for each } i \ (1 \le i \le C) \end{cases}$$
(1.119)

Given an equation of state explicit in the Helmholtz free energy as a function of temperature and pressure for a pure fluid, or as function of temperature, pressure and composition for a mixture, the fugacity coefficients for the vapor and liquid phases can be calculated from the exact thermodynamic relationships:

$$\ln \hat{\varphi}_{i}^{V} = \frac{1}{RT} \int_{v^{V}}^{\infty} \left[\left(\frac{\partial P}{\partial n_{i}} \right)_{T,V,n_{i\neq j}} - \frac{RT}{V} \right] dv - \ln \left(\frac{Pv^{V}}{RT} \right) \qquad \text{for each } i \ (1 \le i \le C)$$
(1.120)

$$\ln \hat{\varphi}_{i}^{L} = \frac{1}{RT} \int_{v^{L}}^{\infty} \left[\left(\frac{\partial P}{\partial n_{i}} \right)_{T,V,n_{i\neq j}} - \frac{RT}{V} \right] dv - \ln \left(\frac{Pv^{L}}{RT} \right) \qquad \text{for each } i \ (1 \le i \le C) \tag{1.121}$$

$$\ln \hat{\varphi}_{i}^{L_{i}} = \frac{1}{RT} \int_{v^{L_{i}}}^{\infty} \left[\left(\frac{\partial P}{\partial n_{i}} \right)_{T,V,n_{i\neq j}} - \frac{RT}{V} \right] dv - \ln \left(\frac{Pv^{L_{i}}}{RT} \right) \qquad \text{for each } i \ (1 \le i \le C) \tag{1.122}$$

$$\ln \hat{\varphi}_{i}^{L_{2}} = \frac{1}{RT} \int_{v^{L_{2}}}^{\infty} \left[\left(\frac{\partial P}{\partial n_{i}} \right)_{T,V,n_{i\neq j}} - \frac{RT}{V} \right] dv - \ln \left(\frac{Pv^{L_{2}}}{RT} \right) \qquad \text{for each } i \ (1 \le i \le C)$$
(1.123)

where *R* is the gas constant, v^{V} is the molar volume of the vapor phase, v^{L} is the molar volume of the liquid phase, $v^{L_{1}}$ and $v^{L_{2}}$ are the molar volumes of the coexisting liquid phases 1 and 2, and n_{i} and n_{i} are the moles of components *i* and *j* respectively.

In this thesis work the analytical form $(\partial P/\partial n_i)_{T,V,n_{i\neq j}}$ for calculating the fugacity coefficients has been always determined using a unique equation of state for all the coexisting phases.

Given an equation of state explicit in the Helmholtz free energy as a function of temperature and density for a pure fluid, or as function of temperature, density and composition for a mixture, the fugacity coefficients for the vapor and liquid phases can be calculated by Eqs. (A2.26) and (A2.27) respectively, see Appendix A.2.

1.3. Transport properties

1.3.1. Viscosity

The definition of viscosity is given with the help of Fig. 1.2. Let us consider two very large parallel plates of area A and separated by a small distance Y, with a fluid contained between them. Initially the system is at rest, but at time t = 0 the lower plate is set in motion at a constant velocity V in the direction of x. As time proceeds, the fluid gains progressively momentum: initially it has an unsteady velocity profile, but after a sufficiently large time the steady-state is achieved.



Figure 1.2: Buildup to steady laminar velocity profile for a fluid contained between two plates.

In the final condition a constant force F has to be applied to the lower plate to maintain it in motion; this force can be expressed as:

$$\frac{F}{A} = \eta \frac{V}{Y} \tag{1.124}$$

The force per unit of area is proportional to the slope of the fluid velocity profile in the y direction and the constant of proportionality is the viscosity η of the fluid. This reasoning is valid under the hypothesis that the flow is laminar: imagining to 'section' the fluid into infinitesimal layers each one at constant y value, there is no mixing between adjacent layers.

The preceding equation can be rewritten in a more convenient form. It is indicated with τ_{yx} the shear stress exerted in the *x*-direction on a fluid layer at constant *y* by the portion of fluid at lower *y*, moving with a velocity having an *x*-component equal to u_x . With these definitions, from Eq. (1.124) it comes:

$$\tau_{yx} = -\eta \frac{\mathrm{d}u_x}{\mathrm{d}y} \tag{1.125}$$

A common interpretation of Eq. (1.125) is given. The layer of fluid adjacent to the lower plate acquires a certain amount of momentum in the *x*-direction and it transmits part of its momentum to the upper layer, causing it to move in the same direction; therefore τ_{yx} represents the viscous flux of *x*-momentum in the *y*-direction.

Eq. (1.125) expresses *Newton's law of viscosity*. The fluids for which such a law is valid are termed as *Newtonians fluids*; this category includes all the gases and the homogeneous non-polymeric liquids. For some substances, as slurries and high polymers, the proportionality between shear stress and velocity gradient is not verified and these are termed as non-Newtonian fluids [1].

It has been experimentally verified that the viscosity of Newtonian fluids depends on temperature and pressure, and also on composition in the case of mixtures.

1.3.2. Thermal conductivity

As in the previous case of viscosity, two large parallel plates of area A at small distance Y, see Fig. 1.3, contain a fluid at a uniform temperature T_0 . At time t = 0 the lower plate is suddenly brought to a slightly higher temperature T_1 and maintained at this temperature, while the upper plate is maintained at temperature T_0 .

The temperature profile in the fluid changes with time, until a steady-state is attained. If the difference between the two temperatures is sufficiently small and there is neither convection, i.e. mixing between iso-y layers in the fluid, nor radiation, the final temperature profile is linear and it can be written as:

$$\frac{\dot{Q}}{A} = \lambda \frac{T_1 - T_0}{Y} \tag{1.126}$$

where \hat{Q} is the heat flow required to maintain that temperature difference. The same equation, expressed in the limit of Y approaching zero, reads:

$$\dot{q}_{y} = -\lambda \frac{\mathrm{d}T}{\mathrm{d}y} \tag{1.127}$$

in which \dot{q}_{y} represents the local heat flow per unit area in the positive y-direction.



Figure 1.3: Buildup to steady-state temperature profile for a fluid between two plates.

In an isotropic medium, for which the thermal conductivity value is the same in all the directions as it is for most of fluids, *Fourier's law of heat conduction* is expressed as:

$$\dot{\boldsymbol{q}} = -\lambda \,\,\nabla T \tag{1.128}$$

The controlling variables of thermal conductivity are temperature and pressure. If the considered system is a mixture, the dependence on composition is added.

In addition to thermal conductivity, the *thermal diffusivity* D_T is widely used in the heat transfer literature; it is related to thermal conductivity by:

$$D_T = \frac{\lambda}{\rho C_p} \tag{1.129}$$

1.3.3. Diffusion

The driving forces for *mass transfer* in a fluid, i.e., the transport of one or more components of a mixture within a phase or over the phase boundary, are concentration, temperature or pressure gradients. Here only the mass transfer due to a concentration gradient within a phase is discussed.

The macroscopic relative movement of a single substance in a phase is known as *diffusion*. There are two different forms of diffusion: *molecular diffusion*, which occurs in quiescent fluids or in laminar flow, and *turbulent diffusion*, which occurs in turbulent flow.

Here only molecular diffusion is treated. In a mixture of two components A and B, the diffusion flux of component A is proportional to the gradient of the molar concentration $c_A = n_A/V$, where n_A is the number of moles of component A, while V is the volume of the considered phase. If the diffusion only takes place along one coordinate axis, for example the y-axis, the diffusional flux can be described by an empirical statement corresponding to the aforementioned Fourier's law of heat conduction:

$$j_A = -D_{AB} \frac{dc_A}{dy} \tag{1.30}$$

which was formulated by A. Fick and is called *Fick's law*. The proportionality factor D_{AB} (SI units m^2/s) is the *diffusion coefficient* in a mixture of two components A and B. Eq. (1.30) is valid when it is assumed that the molar concentration of the mixture c = n/V, where n is the total number of moles in the mixture, is constant. This condition is fulfilled in constant pressure, isothermal mixtures of ideal gases due to $c = n/V = P/R_mT$. Disregarding the condition of constant c, the general equation for mixtures of two substances is:

$$j_A = -cD_{AB}\frac{dx_A}{dy} \tag{1.30}$$

where x_A is the mole fraction of component A in the mixture. A more detailed discussion about diffusion can be find in Ref 1 and 5.

1.4. References

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II. Advanced regression methods

2.1. The bases of data reduction

The general background of every fitting procedure is the fact that the *true* physical relation describing the studied phenomenon is not known; therefore, an empirical formulation which approximates the true relation has to be developed starting from the experimental evidence.

In general the experimental procedure gives a set of M points $(x, y)_m$ (m=1,2,...,M), where x is a vector of K independent variables x_k (k=1,2,...,K) and y stands for the dependent variable. Because these data are affected by the inevitable experimental errors, they have to be regarded as estimates of the true values X and Y of the searched physical dependence $\xi(X,Y) = 0$.

The goal of the procedure is to determine, on the basis of experimental data, a functional relationship $\zeta(x, y, n)$ that approximates the unknown physical relation ξ between variables X and Y:

$$\xi(\boldsymbol{X},\boldsymbol{Y}) = 0 \approx \zeta(\boldsymbol{x},\boldsymbol{y},\boldsymbol{n})$$
(2.1)

where *n* denotes the vector of the *I* adjustable parameters n_i (*i*=1,2,...,*I*) of the functional form considered for the representation of the data. The deviation of $\zeta(\mathbf{x}, y, \mathbf{n})$ from zero is called *residuum*. The goal of the fitting procedure is then to find the numerical values *n* yielding the best approximation of $\zeta(\mathbf{x}, y, \mathbf{n}) = 0$.

The usual choosing criterion is to select the set of n_i with the highest statistical probability; this is the basic idea of the *maximum-likelihood* method [1] which aims at maximizing the likelihood function L(n).

Under the hypotheses that:

- the data are distributed according to the Gaussian distribution, which means that the experimental errors are normally distributed with a mean value equal to zero, both for the independent and the dependent variables;
- the experimental errors are independent from each other;
- the experimental uncertainties are known for all data points and the values for the corresponding variances can be given;
- the systematic error of the approximation of $\xi(\mathbf{X}, \mathbf{Y}) = 0$ using the relation $\zeta(\mathbf{x}, y, \mathbf{n}) = 0$ is negligible when compared to the uncertainty of the experimental data,

the likelihood function can be written as:

$$L(\boldsymbol{n}) = \prod_{m=1}^{M} \frac{1}{\sqrt{2\pi\sigma_m^2}} \exp\left[-\frac{\zeta^2(\boldsymbol{x}_m, \boldsymbol{y}_m, \boldsymbol{n})}{2\sigma_m^2}\right]$$
(2.2)

where σ_m^2 is the total variance which considers the uncertainties both of the independent and dependent variables.

The maximization of the quantity in Eq. (2.2) corresponds to the minimization of the *chi-square* function, i.e. the weighted sum of squares of residua:

$$\chi^{2}(\boldsymbol{n}) = \sum_{m=1}^{M} \left[\frac{\zeta(\boldsymbol{x}_{m}, \boldsymbol{y}_{m}, \boldsymbol{n})}{\sigma_{m}} \right]^{2}$$
(2.3)

The procedure of minimization of the chi-square is known as *weighted least squares fit* and it follows the theory first developed by Gauß [2]. Even if the four above-mentioned simplifying conditions are not always actually verified, the method is extensively applied.

When the implicit relation $\zeta(\mathbf{x}, y, \mathbf{n}) = 0$ is made explicit in the dependent variable as:

$$y = y(\boldsymbol{x}, \boldsymbol{n}) \tag{2.4}$$

then Eq. (2.3) can be rewritten as:

$$\chi^{2}(\boldsymbol{n}) = \sum_{m=1}^{M} \left[\frac{y_{m} - y(\boldsymbol{x}_{m}, \boldsymbol{n})}{\sigma_{m}} \right]^{2}$$
(2.5)

Given the experimental data set, both Eqs. (2.3) and (2.5) can be regarded as continuous functions of the parameters n_i , whose optimal values that minimize χ^2 are found simultaneously solving the *I* equations:

$$\left(\frac{\partial \chi^2}{\partial n_i}\right)_{n_{j\neq i}} = 0 \qquad 1 \le i \le I$$
(2.6)

The solution of the set of equations constituted by Eq. (2.6) in order to find the coefficients n_i is not trivial and its difficulty level depends both on the analytic form of the selected fitting equation and on the number I of free parameters; as a typical case, the set could be constituted by tens of non-linear equations, whose solution yields a large number of local minima. To overcome these difficulties several numerical methods have been developed, see for instance Ref. 3; nevertheless, a unique 'optimum' method does not exist but it has to be chosen according to the characteristics of the problem under investigation. In the works presented in this thesis very powerful and versatile regression tools were assumed for data modeling: they are mainly the artificial neural networks.

2.2. Neural networks

2.2.1. Introduction

Artificial neural networks (ANN) represent an extremely simplified model of the basic structure of brain; they are constituted by a certain number of elementary units variously interconnected, that simulate the essential behavior of biological neurons. Analogously to real neurons, the ANN neurons receive an input signal from some other neurons, on the base of which they reach a certain activation level and transmit a new signal to other neurons. The synaptic connections between different neurons are characterized by different strength, which is mathematically expressed through multiplicative factors called weights. Although this model neglects many properties of brain and of real neurons, ANNs have met an increasing success in many fields.

The history of artificial neural networks took its first steps in the '40s of the 20th century, when McCulloch and Pitts [4] proved that simple binary neurons could calculate some logical functions. In that format the weights were fixed and therefore the ANN could not be trained but it has to be specifically designed for the problem.

Several improvement attempts were made in the following decades and in the late '50s Rosenblatt [5] presented the first actual model of neural network, the *perceptron*. For some years research went on with changing fortunes; a subsequent milestone was the work of Rumelhart and McClelland [6,7]. They showed how to get over the perceptron shortcomings and above all they introduced a training method to set the weighting factors between the neurons.

In the last two decades ANNs have had a tumultuous growth, favored by the fast increase of the computational speed of modern computers, and they have been consequently applied to a wide range of problems pertaining to several disciplines.

Due to their classification and recognition capabilities, the ANNs are often employed in the recognition of images, written texts, speeches, sounds and signals in general. Moreover, they are a powerful tool for the study of processes or phenomena for which the analytical relation binding the interest variables to the controlling parameters is not known. Therefore ANNs can be applied to a lot of scientific and technical problems, as for instance the data regression and the process control.

2.2.2. Multilayer feed-forward neural networks

The multilayer feed-forward neural networks (MLFN) are the most used ANNs in scientific and engineering applications. They play a particularly important role because they are very powerful universal function approximators, i.e. they can represent any continuous function in a compact domain; for this reason MLFNs are used for data modeling.

As any other neural network, MLFNs are formed by a set of artificial neurons linked each other with weighted interconnections, in a way that will be made clearer in the following. The neural model is constituted by the assumed network structure and by the weighting factors, whose numerical values are the result of the *training* process, see Paragraph 2.2.3 for details.

Among the various ANNs typologies, MLFNs are characterized by their architecture: the neurons are organized in successive layers (*multilayer*) and then the single units work differently according to their position. The neurons are arranged on three or more layers, in such a way that each unit collects signals from all the units of the preceding level and it transmits its output to each unit in the following layer.

The first level, *input layer*, receives the inputs from the outside. The neurons in this layer do not perform any mathematical operation, but the signals coming in equal those going out. The last level, *output layer*, transmits to the outside the answers of the neural network to the input stimulation. The intermediate levels, *hidden layers*, are not directly accessible from the outside: the task of their neurons is the elaboration of information through non-linear transformations.

Another particular feature of MLFNs is that the information goes only in one direction, forward from the first to the last layer (*feed-forward*), when calculating the network outputs at given inputs.

It is demonstrated that MLFNs are universal function approximator [8,10] and in particular a MLFN with a single hidden layer is able to approximate any continuous function in a compact domain, as shown in the literature [9]. For these reasons only this last architecture will be considered in the following. The general architecture of a three-layer MLFN is shown in Fig. 2.1.

The input layer is composed by I neurons: the first I-1 ones receive the U_i inputs from outside and therefore their number equals the number of the independent variables of the considered problem. A constant value, *Bias1*, is associated to the last neuron I. All these signals are passed without transformation to the following level.

In the hidden layer J + 1 neurons are present: each of the first J ones gets signals from the input layer neurons, calculates a weighted summation of the received inputs, applies a transfer function f to the sum and transmits the result H_j to the output layer; the last neuron J + 1 assumes a constant value *Bias2*. The layer functioning is summed up as:

$$H_{j} = f\left(\sum_{i=1}^{I} w_{ij}U_{i}\right) \qquad 1 \le j \le J$$

$$H_{J+1} = Bias2$$
(2.7)

The neurons number K in the output layer equals the number of the output signals, i.e. the dependent variables of the problem. In this level the neurons operate similarly to the hidden layer units, with the only difference that the results S_k are passed to the outside and not to a subsequent layer:

$$S_{k} = f\left(\sum_{j=1}^{J+1} w_{jk} H_{j}\right) \qquad 1 \le k \le K$$
(2.8)



Figure 2.1: General topology of a three-layer feed-forward neural network.

The functional dependence relating input to output variables is contained into the two weighting factors matrixes $w_{ij} \in w_{jk}$ of dimensions $I \times J$ and $(J+1) \times K$, respectively. The weighting factors

are the mathematical equivalent of the strength of the synaptic connections between biological neurons.

The *Bias1* and *Bias2* neurons are not strictly necessary but they are useful to make easier the convergence during the training procedure.

The transfer function f can be regarded as a rough but effective simplification of the elaboration processes that occur in the single brain cell: it is responsible for the non-linear transformation that, applied to the input of a neuron, determines its output. The function numerical output has to be restricted to a range usually set as [0,1], where 0 corresponds to a turned-off neuron and 1 to total activation. Different analytical forms for the transfer function have been proposed in the literature, considering that it should be continuous, differentiable, with positive derivative and with restricted output.

The original format of the perceptron [5] assumed the step function:

$$f(x) = \begin{cases} 1 & \text{for } x > 0 \\ 0 & \text{for } x < 0 \end{cases}$$
(2.9)

This form is evidently not continuous and therefore many others are employed, as for instance the logistic function:

$$f(x) = \frac{1}{1 + e^{-\alpha x}} \tag{2.10}$$

the normalized scaled hyperbolic tangent:

$$f(x) = \frac{1}{2} \left(1 + \frac{e^{\beta x} - e^{-\beta x}}{e^{\beta x} + e^{-\beta x}} \right)$$
(2.11)

the normalized scaled arctangent:

$$f(x) = \frac{1}{\pi} \arctan(\gamma x) + \frac{1}{2}$$
(2.12)

The plots of these equations (2.9-2.12) are reported in Fig. 2.2.



Figure 2.2: Representation of some transfer functions.

Minimum and maximum values of the transfer function should be avoided because they correspond to the saturation of the signal, for which the output sensitivity to input variations is annihilated; the reaching of this condition at varying x can be tuned adjusting the multiplying parameter in the transfer function, as for example α in Eq. (2.10), β in Eq. (2.11), γ in Eq. (2.12). The choice of the transfer function and of its parameter value depends on the studied problem and it can influence the effectiveness of the regression algorithm. It should be noticed that in general the transfer functions for the hidden and the output layers, Eqs. (2.7) and (2.8), could be different each other; nevertheless, in the present works the same function was always assumed for both the layers.

The inputs of the neural network are the independent variables of the studied problem and then the ranges of their numerical values could be largely different one from the other; for example if the input variables would be temperature and density of a fluid, such ranges could be 200-400 K for the first one and 0-1500 kg/m³ for the second. Since the orders of magnitude of the two inputs are very different, some difficulties may arise in the training procedure; moreover, the outputs of the neural network are necessarily limited in the range [0,1], as resulting from the characteristics of the transfer function in the output layer, but the dependent variables ranges are probably very different from this. To solve these problems, both the independent and the dependent variables are scaled in a conventional interval, usually assumed as [0.05, 0.95], giving generality to the neural network and facilitating the training process. If V_i is an independent physical variable, a linear scaling is performed in this way:

$$u_i = \frac{A_{\max} - A_{\min}}{V_{i,\max} - V_{i,\min}}$$
(2.13)

$$U_i = u_i \left(V_i - V_{i,\min} \right) + A_{\min}$$
(2.14)

where A_{\min} and A_{\max} are the limits of the scaling interval, conventionally set to 0.05 and 0.95 respectively, while $V_{i,\min}$ and $V_{i,\max}$ are the prefixed limits of the independent variable. U_i is a general neural network independent input, see Fig. 2.1.

The network outputs S_k are converted into the corresponding dependent physical variables W_k in a similar manner:

$$s_k = \frac{A_{\max} - A_{\min}}{W_{k,\max} - W_{k,\min}}$$
(2.15)

$$W_{k} = \frac{S_{k} - A_{\min}}{s_{k}} + W_{k,\min}$$
(2.16)

where $W_{k,\min}$ and $W_{k,\max}$ are the allowed limits for the dependent variable W_k .

The path followed by information through the different steps of the global neural model is synthetically shown in Fig. 2.3.

A summary of the mathematical expressions useful for the application of the here exposed MLFN models is reported in Appendix A.1.



Figure 2.3: Path of information in the neural model.

2.2.3. MLFN application to data reduction

The possibility to use ANNs for data reduction is ensured by some theorems which prove that a MLFN, even with only one hidden layer, can approximate any continuous function in a compact domain [8-10]. Given a data set, the neural network model is able to identify the functional relationship between the dependent and the independent variables. When adopting a heuristic approach, ANNs recognize patterns in sparse data sets and they generalize these patterns through a continuous mathematical function.

One of the main advantages of using ANNs is that the mathematical structure is general and not depending on the specific problem. No assumption about the physics of the system is required: this is particularly helpful when studying very complex problems.

The matrixes of weighting factors contain all the information about the functional dependence; therefore the essence of a neural model developing is the training, i.e. the process that searches for the optimal values of the w_{ij} and w_{jk} coefficients with the aim at reproducing the given data set at best.

An objective function defined similarly to Eq. (2.5), in which the coefficients n are obviously represented by the weighting factors, is calculated from the training data set. The training procedure minimizes this function by applying numerical methods suitable to get satisfactory results with fast convergence and to avoid the local minima of the χ^2 function.

Once a set of weights has been obtained, a validation procedure of the resulting equation should be developed on a larger data set in order to test the prediction capability and to individuate the possible presence of incorrect trends. As for every heuristic model, it may happen that the equation performs very well on the training data, while it gets poor results with respect to the validation data. This could be due to *overfitting* problems: instead of inferring the function trends from data, the model follows the details of the single training points, being misled by both experimental noise and uneven distribution; as a consequence the model prediction capability on data not belonging to the training set is very poor. These problems arise particularly when the functional form has too many free parameters with respect to the number of training data.

As a general rule, the data on which neural network is trained have to be regularly distributed in the whole interest range of independent variables; additional data are required in regions where the dependent quantities present strong gradients. Moreover, experimental data have to be as precise as possible. The lack of fulfillment of these conditions can seriously hinder the training process; particular attention must be paid to check these aspects during the training process. The network architecture has to be specifically set up for each studied case. The number of neurons in input and output layers is strictly connected with the number of independent and dependent variables respectively, as resulting from a physical or conceptual model of the problem; ANNs can be useful in identifying the controlling variables in the case that data are provided in a sufficiently detailed form, since the analysis of the obtained neural equations allows to establish how much each independent variable influences the dependent ones.

It is evident that the output variables can be more than one, so the neural network model is able to represent at once different functions, provided they depend on the same independent variables.

The number of neurons in the hidden layer is not *a priori* known, but it has to be found with a trial-and-error procedure, searching at the same time for satisfactory performance on data and lower neurons number. If too small, the network is not sufficiently flexible to adequately represent the complexity of the functional dependence; if too large, the number of free parameters to regress is high and overfitting problems and incorrect trends may arise.

ANNs have been successfully applied in several typologies of problems; as examples limited to the field of chemical engineering, they have been used for prediction of thermodynamic properties of fluids [11-13], for prediction of viscosity of fluids [14-16], for studies of heat transfer [17-19] and mass transfer [20,21].

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PART ONE

Thermodynamic Properties

III. Models for thermodynamic properties

3.1. Introduction

This chapter deals with the models that are used to calculate the thermodynamic properties of pure fluids and mixtures. In particular, the attention is focused on the *equations of state* (EoS), i.e. relations among the thermodynamic variables that describe the behavior of the considered system as varying the controlling variables. Examples of EoSs are the relations in the forms $P = P(T, \rho)$ and $A = A(T, \rho)$, that are expressed in terms of pressure or Helmholtz free energy, respectively.

An important classification among the EoSs is evidenced. The equations in terms of Helmholtz free energy are *fundamental equations of state*: if an analytical formulation for $A(T, \rho)$ is known for a fluid, all its thermodynamic properties can be obtained simply through combination of derivatives of A with respect to T and ρ , as shown in Paragraph 1.2.3; no integral calculation is required. The equations in the form of pressure $P = P(T, \rho)$ or of compressibility factor $Z = Z(T, \rho) = P/(\rho RT)$ are *not* fundamental equations of state, because they have to be integrated to calculate the caloric properties, as for instance enthalpy, entropy, isobaric and isochoric heat capacities. The relations between the Helmholtz free energy and the main thermodynamic properties are reported for convenience in Appendix A.2.

In the following sections a brief history of the equations of state and a sufficiently detailed description of the background of the thermodynamic models used in the present Ph.D. thesis are given. This chapter does not claim to be exhaustive with respect to all the models published in the literature, but it is intended to give the Reader the bases for dealing with the next chapters.

3.2. Historical overview

The first and also the most well-known EoS is certainly the equation of *ideal gases*, inferred from the experiments of Boyle and Gay-Lussac in the period between the 17th and the first 19th century:

$$Pv = RT \tag{3.1}$$

This equation is extensively used still nowadays, favored by its extremely simplicity and by the representation of the low-pressure gases behavior with an approximation level acceptable for many applications. The ideal-gas equation constituted the starting point for all the subsequent equations developments.

The first equation able to represent the whole PvT surface of a fluid, in vapor, liquid and supercritical region, appeared only in 1873, when van der Waals published his famous equation [1] obtained from theoretical analysis:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \tag{3.2}$$

where a and b are positive parameters: a accounts for the intermolecular attraction forces, b is also known as *covolume* and it is related to the dimension of the molecules of the considered fluid. It is worth noticing that when both a and b are set to zero the ideal-gas equation is recovered. Adopting suitable mixing rules for the parameters, the equation can represent also mixtures of fluids. Van der Waals won the Nobel Prize in 1910 for his works on equations of state.

The van der Waals equation can be regarded as the 'founder' of the *cubic equation of state* family, whose name comes from the possibility to rewrite the equations of this family as third-order volume-implicit relations. In the case of Eq. (3.2), such procedure gives:

$$Pv^{3} - (bP + RT)v^{2} + av - ab = 0$$
(3.3)

Many cubic equations have been published after the work of van der Waals; in this class, the Redlich-Kwong [2], the Soave-Redlich-Kwong [3] and the Peng-Robinson [4] equations are the most significant ones. The various types of cubic equations are still widely used in many fields where high precisions are not required, since they are simple models valid in a wide range of fluid conditions and they allow the calculation of all the thermodynamic properties in a predictive mode often with acceptable performances. The cubic equations are discussed in more details in Paragraph 3.3.

Another family of equations is constituted by the *virial equations of state*, that are basically power series expansions of Z, in molar volume or in pressure, along an isotherm:

$$Z = \frac{Pv}{RT} = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \frac{D(T)}{v^3} + \dots$$
(3.4)

$$Z = \frac{P_V}{RT} = 1 + \widetilde{B}(T)P + \widetilde{C}(T)P^2 + \widetilde{D}(T)P^3 + \dots$$
(3.5)

where the temperature-depending coefficients B, C, and D are the second, the third, and the fourth virial coefficient, respectively; the symbols \tilde{B} , \tilde{C} , and \tilde{D} have similar meanings. Between the two, the preferred virial equation is often Eq. (3.4), that was introduced by Kamerlingh Onnes [5] in 1901; this is usually truncated after the third virial coefficient and it is employed to describe

gaseous states, with a greater accuracy with respect to cubic EoSs. Some more details about virial equations are given in Paragraph 3.5.

A further step ahead was proposed in 1940 by Benedict et al. [6], that introduced an exponential function into a truncated virial expansion:

$$P = RT\rho + \left(B_0RT - A_0 - \frac{C_0}{T^2}\right)\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + \frac{c\rho^3(1 + \gamma\rho^2)e^{-\gamma\rho^2}}{T^2}$$
(3.6)

This equation, also known as Benedict-Webb-Rubin (BWR), has eight adjustable parameters $(a,b,c,\alpha,\gamma,A_0,B_0,C_0)$ and it can describe the thermodynamic properties in the whole range of fluid states in a qualitatively correct way and with an accuracy superior to cubic EoSs.

Nevertheless, the BWR equation suffered of some disadvantages, considering also the computing powers of that period: the parameters of the equation for each compound had to be determined separately by reduction of plentiful $P\rho T$ data; its analytical complexity resulted in a relatively long computing time and the large number of adjustable parameters made it difficult to extend to mixtures.

In the meantime the principle of the corresponding states, see Paragraph 3.6.1, that had been first enunciated by van der Waals, found a justification on the basis of statistical mechanics for pure fluids with simple spherically-symmetric molecules [7,8,9]. During the decades the corresponding states principle underwent various modifications with the purpose to adapt it to the representation of less simple fluids.

A wide success was met by the three-parameter corresponding states technique. A first version was given by Pitzer et al. [10] in 1955, but considerable improvements were brought in mainly by the works of Lee and Kesler [11] and Teja et al. [12,13]. In Paragraph 3.6.2 the basic concepts of this method are reported.

Another promising modification of the original corresponding states principle was the extended corresponding states theory [9,14-17], that is applied still nowadays with successively improvements both for thermodynamics and for transport properties. A presentation of this method is given in Paragraph 3.6.3.

In the first '70s the technological advancement made reasonable computing powers available to scientists. This allowed the introduction of EoSs with a greater number of coefficients to be regressed on experimental data, that could be included in the fitting procedure in larger amounts when available. Also from users' point of view, the computing times required by more complicated equations could finally be borne.

In 1973 a modification of the BWR equation, Eq. (3.6), was published by Starling [18]:

$$P = RT\rho + \left(B_0RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4}\right)\rho^2 + \left(bRT - a - \frac{d}{T}\right)\rho^3 + \alpha\left(a + \frac{d}{T}\right)\rho^6 + \frac{c\rho^3\left(1 + \gamma\rho^2\right)e^{-\gamma\rho^2}}{T^2}$$
(3.7)

This EoS was mainly proposed for applications in the chemical and petrochemical industry, for which the possibility of representing many pure fluids and mixtures is fundamental. Therefore mixing rules and generalized forms were important features of equations of this type. Starling equation of state is still frequently used in technical applications.

Other more or less sophisticated modifications of Eq. (3.6) were developed by different research groups; in particular, it is worth remembering that of Bender [19] in 1970:

$$P = T\rho \left\{ R + B(T)\rho + C(T)\rho^{2} + D(T)\rho^{3} + E(T)\rho^{4} + F(T)\rho^{5} + \left[G(T) + H(T)\rho^{2}\right]\rho^{2}e^{-a_{20}\rho^{2}} \right\}$$
(3.8)

and that of Jacobsen and Stewart [20], known as MBWR, in 1973:

$$P = \sum_{i=1}^{9} a_i (T) \rho^i + e^{-(\rho/\rho_c)^2} \sum_{i=10}^{15} a_i (T) \rho^{2i-17}$$
(3.9)

In both these equations the coefficients are polynomial functions of temperature, whose analytical forms are here not reported. The Bender and the MBWR equations include 19 and 32 parameters, respectively; these huge sets of parameters have obviously to be regressed on experimental data. During the same period algorithms to fit the coefficients simultaneously on $P\rho T$ and phase equilibrium data were developed, allowing in this way to improve the performances of the obtained EoS both in the homogeneous regions and at vapor-liquid equilibrium conditions.

The equations in the format of Eqs. (3.8) and (3.9) have been regressed for a large number of fluids and their functional forms have been used in thermodynamic modeling for at least twenty years.

The Bender-type equations were applied also to mixtures and today they can be considered as the most sophisticated *technical equations of state*. Instead, the MBWR-type equations represent the first example of *reference equations of state*: they were able to describe the available data within the experimental uncertainties achievable at that time. For instance, the EoS for nitrogen, developed by Angus at al. [21] in the MBWR format, was assumed as a reference for the thermodynamic properties of that fluid in several scientific and technical applications.

A new abrupt jump ahead was done in 1985, when Schmidt and Wagner published a new EoS for oxygen [22]. They proposed an equation of state in the form:

$$a^{R}(T,\rho) = \frac{A^{R}(T,\rho)}{RT} = \sum_{i=1}^{13} n_{i}\tau^{t_{i}}\delta^{d_{i}} + \sum_{i=14}^{24} n_{i}\tau^{t_{i}}\delta^{d_{i}}e^{-\delta^{2}} + \sum_{i=25}^{32} n_{i}\tau^{t_{i}}\delta^{d_{i}}e^{-\delta^{4}}$$
(3.10)

where a^R is the reduced residual Helmholtz energy, $\tau = T_c/T$ is the inverse reduced temperature, $\delta = \rho/\rho_c$ is the reduced density; *c* stands for a critical value. This equation is formulated in terms of Helmholtz free energy, contrarily to the preceding equations that are in terms of compressibility factor $Z(T,\rho)$ or of pressure $P(T,\rho)$. Therefore it is a fundamental EoS, from which all the thermodynamic properties can be calculated simply by combining its derivatives with respect to *T* and ρ . Although this property of fundamental EoSs was well known, only from that time this format has become a standard for the EoS development.

Anyway, the greatest novelty of the Schmidt-Wagner technique was the regression algorithm. In fact, up to that point only the coefficients of the EoS could be determined, whereas the functional form had to be established in a trial-and-error process based also on experience. On the contrary, Schmidt and Wagner used an original algorithm [23] that allowed also the *optimization* of the equation: not all the terms in Eq. (3.10) were included in the proposed oxygen EoS, but only those more suitable to represent the searched functional dependence, as established by the regression algorithm on the basis of statistical analyses.

Moreover, both the Helmholtz energy form of the EoS and the intrinsic characteristics of the regression algorithm made easier to consider experimental data of different thermodynamic properties in the fitting of the equation, performing a *multiproperty fitting*.

In the subsequent years the regression algorithm was further on improved by Setzmann and Wagner [24] and followers [25]; this technique is the present standard for the development of EoSs for pure fluids. The equation (3.10) itself has undergone successive modifications and other summations have been added to it in order to improve the capability of optimized multiparameter EoSs in representing the region in the vicinity of the critical point [25].

For details about the optimization algorithm, reference is made to the cited literature, in particular to Ref. 25. The optimized multiparameter EoSs are presented in Paragraph 3.7.

3.3. Cubic equations of state

3.3.1. Pure fluids

The pressure-explicit equation:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \tag{3.11}$$

synthetically indicated as vdW, was obtained by van der Waals [1] from a modification of the idealgas equation and it was the first EoS that could represent at the same time the thermodynamic properties in vapor, liquid and supercritical region of both pure fluids and mixtures. The constant parameters a and b in Eq. (3.11) are related to the attraction intermolecular forces and to the molecular volume, respectively.

After the publication of the van der Waals work, a lot of other cubic equations were developed, mainly proposing to substitute various expressions for the attractive term a/v^2 . Among all those works, the most remarkable and successful ones were probably the Redlich-Kwong (RK) equation [2]:

$$P = \frac{RT}{v-b} - \frac{a_{RK}(T_r)}{v(v+b)} \qquad a_{RK}(T_r) = \frac{a_{c,RK}}{\sqrt{T_r}}$$
(3.12, 3.13)

Soave's modification [3] of the Redlich-Kwong equation (SRK):

$$P = \frac{RT}{v-b} - \frac{a_{SRK}(T_r)}{v(v+b)} \qquad a_{SRK}(T_r) = a_{c,SRK} \left[1 + k_{SRK}(\omega) \left(1 - \sqrt{T_r} \right) \right]^2 \qquad (3.14, 3.15)$$

and the Peng-Robinson (PR) equation [4]:

$$P = \frac{RT}{v-b} - \frac{a_{PR}(T_r)}{v(v+b)+b(v-b)} \qquad a_{PR}(T_r) = a_{c,PR} \left[1 + k_{PR}(\omega) (1 - \sqrt{T_r}) \right]^2 \qquad (3.16, 3.17)$$

The parameters a_{RK} , a_{SRK} , and a_{PR} are functions of reduced temperature $T_r = T/T_c$, while the k functions depend on the fluid specific *acentric factor*, known also as Pitzer's parameter [10], defined from the reduced vapor pressure $P_r = P/P_c$ at $T_r = 0.7$ as:

$$\omega = -1 - \log_{10} \left(P_r^{s} \right)_{T_r = 0.7}$$
(3.18)

Common characteristic of all these equations is that they can be rewritten as a third-order polynomial form in volume, see Eq. (3.3) the case of vdW equation, from which the attribute 'cubic' given to this class of EoSs derives.

The parameters a, $a_{c,RK}$, $a_{c,RK}$, $a_{c,PR}$ and b are traditionally found by solving the equations system obtained from the imposition of the critical point constraints:
$$\begin{cases} \left(\frac{\partial P}{\partial v}\right)_{\substack{T=T_c\\v=v_c}} = 0\\ \left(\frac{\partial^2 P}{\partial v^2}\right)_{\substack{T=T_c\\v=v_c}} = 0 \end{cases}$$
(3.19)

It comes out that these parameters are fluid specific and they depend only on critical temperature and on critical pressure, see Table 3.1. Therefore, given the critical constants for the interest fluid and an experimental value of saturation pressure at $T_r = 0.7$ in order to calculate ω , the cubic EoS works as a predictive model.

The dependence of the *a* parameter on temperature was introduced by Redlich and Kwong [2] with the purpose of improving the performances of their equation with respect to the experimental data; the simple functional dependence in Eq. (3.13) was chosen. About a quarter of century later, Soave [3] empirically modified their original function searching for a better representation of the vapor-liquid equilibrium conditions: the equation was forced to represent experimental vapor pressures for various pure hydrocarbons through the fulfillment of the iso-fugacity condition; the so-obtained *a* values were correlated with Eq. (3.15), depending on both the reduced temperature and the acentric factor ω through the $k(\omega)$ function, for which a simple polynomial form was assumed:

$$k(\omega) = d_0 + d_1\omega + d_2\omega^2 \tag{3.20}$$

Some years later Peng and Robinson [4] developed their cubic equation following a similar procedure: the same expressions for $a(T_r)$ and for $k(\omega)$ were maintained, but starting from a different functional form of the equation of state.

The coefficients of Eq. (3.20) for both the cases are reported in Table 3.1. Since they were obtained from fitting on hydrocarbons data, these values should be valid only for fluids pertaining to such a family; notwithstanding this, they have been widely used for any fluid.

Another equation for the *a* function was proposed by Mathias and Copeman [26]:

$$a(T_r) = a_c \left[1 + d_1 \left(1 - \sqrt{T_r} \right) + d_2 \left(1 - \sqrt{T_r} \right)^2 + d_3 \left(1 - \sqrt{T_r} \right)^3 \right]^2$$
(3.21)

where the coefficients d_1 , d_2 and d_3 have to be fitted on experimental vapor pressures of the considered fluid, once selected the cubic EoS to use.

All the equations (3.11), (3.12), (3.14) and (3.16) are particular cases of:

$$P = \frac{RT}{v-b} - \frac{a}{(v+\varepsilon_1 b)(v+\varepsilon_2 b)}$$
(3.22)

with the individual coefficients ε_1 and ε_2 reported in Table 3.1.

Table 3.1: Parameters for the four cubic equations of state here considered.

Cubic	G	G	bP_c	aP_c	$k(\omega)$, Eq. (3.20)		
EoS	ε ₁	8 ₂	RT_{c}	$(RT_c)^2$	d_0	$d_{_1}$	d_2
vdW	0	0	0.125	0.421875	-	-	-
RK	1	0	0.08664	$0.42748 / \sqrt{T_r}$	-	-	-
SRK	1	0	0.08664	$0.42748 \left[1 + k \left(\omega \right) \left(1 - \sqrt{T_r} \right) \right]^2$	0.48	1.574	-0.176
PR	$1 + \sqrt{2}$	$1 - \sqrt{2}$	0.07780	$0.45724 \left[1 + k\left(\omega\right)\left(1 - \sqrt{T_r}\right)\right]^2$	0.37464	1.54226	-0.26992

The cubic equations, being expressed in terms of pressure, are not fundamental equations of state; nevertheless, they can be converted into an $A^{R}(T,v)$ fundamental form through the thermodynamic relation:

$$A^{R}(T,v) = \int_{v=\infty}^{v} \left[\frac{RT}{v} - P(T,v) \right]_{T} dv$$
(3.23)

that when applied to Eq. (3.22) gives:

$$A^{R}(T,v) = RT \ln\left(\frac{v}{v-b}\right) - \frac{a}{v}$$
(3.24)

for the vdW EoS and:

$$A^{R}(T,v) = RT \ln\left(\frac{v}{v-b}\right) - \frac{a}{(\varepsilon_{2} - \varepsilon_{1})b} \ln\left(\frac{v + \varepsilon_{2}b}{v + \varepsilon_{1}b}\right)$$
(3.25)

for the other three cubic EoSs.

The analytical representation of the ideal part $A^o(T,v)$ of the Helmholtz energy is obtained through integration of an equation for the ideal-gas isobaric heat capacity $C_p^o(T)$ for the interest fluid, that has to be given separately:

$$A^{o}(T,v) = U_{0}^{o} - TS_{0}^{o} + \int_{T_{0}}^{T} \left(C_{p}^{o} - R\right) dT - T \int_{T_{0}}^{T} \frac{\left(C_{p}^{o} - R\right)}{T} dT - RT \ln\left(\frac{v}{v_{0}}\right)$$
(3.26)

where U_0^o and S_0^o are the chosen values for internal energy and entropy, respectively, of ideal gas at a reference condition (T_0, v_0) . From Eqs. (3.24) or (3.25), in conjunction with Eq. (3.26), all the thermodynamic properties can be easily calculated.

Although cubic EoSs show quite correct trends of the thermodynamic properties, their quantitative representation is not accurate. In the vapor phase the precision can be rather acceptable, even if depending on the selected fluid and on the desired property; also the representation of vapor pressure for halocarbons is quite good thanks to the set up of the a functional form on this property. However, cubic equations fail in the liquid region representation [27,28], where the errors on density can be far beyond 10 %, with consequently high errors for the other thermodynamic properties.

Considering this fact, an attempt to improve the cubic equations performances in the liquid region was proposed by Peneloux et al. [29] in 1982. They suggested to obtain the molar volume of the fluid of interest by shifting the value calculated from the cubic EoS of a constant quantity c:

$$v = v_{cubic} - c \tag{3.27}$$

The parameter c assumes a fluid specific value that can be calculated either from the critical constants or from an experimental datum of saturated liquid density, with the second possibility giving better results. Introducing this modification, Eq. (3.22) becomes:

$$P = \frac{RT}{v+c-b} - \frac{a}{\left(v+c+\varepsilon_1 b\right)\left(v+c+\varepsilon_2 b\right)}$$
(3.28)

The transformation of Eq. (3.28) in an $A^{R}(T,v)$ fundamental form is reported in Appendix A.3, together with the derivatives required for the main thermodynamic properties calculation.

The presence of the Peneloux parameter improves the cubic EoSs behavior in the liquid region, but anyway the accuracy of such equations is far from being satisfactory when moving away from the saturation conditions. The validation of the SRK EoS with the Peneloux translation coefficient for a number of fluids is given in Paragraph 4.2.3.

3.3.2. Mixtures

The cubic EoSs can be applied to mixtures adopting a *one-fluid model* (OFM) approach, i.e. the mixture behavior at a fixed composition is regarded as equivalent to that of a pseudo-pure fluid whose parameters are obtained from the combination of the pure components parameters through empirical mixing rules. This also means that the critical properties are replaced by the pseudo-

critical properties, depending also on composition, of a hypothetical equivalent substance. Van der Waals mixing rules are usually assumed [28].

Considering a mixture of C components with molar composition vector \mathbf{x} , a quadratic mixing rule is adopted for the parameter a_M :

$$a_{M} = \sum_{i=1}^{C} \sum_{j=1}^{C} x_{i} x_{j} a_{ij}$$
(3.29)

where:

$$a_{ij} = \left(1 - k_{ij}\right) \sqrt{a_i a_j} \tag{3.30}$$

A linear mixing rule is instead used for both b_M and c_M :

$$b_M = \sum_{i=1}^{C} x_i b_i$$
 $c_M = \sum_{i=1}^{C} x_i c_i$ (3.31, 3.32)

The parameter k_{ij} in Eq. (3.30) is the *binary-interaction* parameter between components *i* and *j*; for i = j it is $k_{ij} = 0$. The interaction parameters are set to zero when the EoS for the mixture is used in predictive mode; otherwise, they are usually regressed on the available phase equilibrium data for the corresponding binary system to improve the equation representation of the saturation conditions.

The mathematical expressions necessary to apply a cubic EoS to mixtures are summarized in Appendix A.3.

3.3.3. G^E -EoSs for mixtures

Cubic EoS with mixing rules including a single interaction parameter for each binary pair, such as those given by Eqs. (3.30-3.32), have been very successful in correlating equilibrium properties of mixtures of non-polar components, in particular hydrocarbons. Their accuracy is much less satisfactory for mixtures consisting of polar components (e.g. acetone + water) and for mixtures containing both polar and non-polar components, such as alcohol + hydrocarbon mixtures.

One way to improve the cubic EoSs capability to represent the phase equilibria in the cited cases is integrating a flexible excess Gibbs energy model in suitable mixing rules. Among these, only Wong and Sandler [30] (WS) mixing rules have been used in this thesis work; these mixing rules are defined by the following equations:

$$b_M = \frac{1}{D} \sum_i \sum_j x_i x_j E_{ij}$$
(3.33)

$$E_{ij} = \frac{1}{2} \left(b_i - \frac{a_i}{RT} + b_j - \frac{a_j}{RT} \right) \left(1 - k_{ij} \right)$$
(3.34)

$$D = 1 + \frac{G^E}{0.62323 RT} - \sum_i x_i \frac{a_i}{b_i RT}$$
(3.35)

$$a_M = b_M RT (1 - D) \tag{3.36}$$

where k_{ij} is the conventional binary interaction parameter to regress from experimental data, and a_i , a_j , b_i and b_j are the pure component parameters of the cubic EoS. The G^E term in Eq. (3.35) is obtained from a G^E model, see paragraph 3.4. In the following of this thesis work we will refer to equations of state integrating G^E models as $G^E - EoSs$.

3.4. Models for the excess Gibbs energy

In general the dimensionless ratio G^{E}/RT is a function of T, P, and composition, but for liquids at low to moderate pressure it is a very weak function of P. Therefore the pressure dependence of the activity coefficients is usually neglected, and at constant T it is:

$$\frac{G^E}{RT} = g\left(x_1, x_2, \dots, x_C\right) \qquad (T = const)$$
(3.37)

For binary systems the G^{E} function is often represented as a truncation of the two power series in $(x_1 - x_2)$:

$$\frac{G^{E}}{x_{1}x_{2}RT} = B + C(x_{1} - x_{2}) + D(x_{1} - x_{2})^{2} + \dots \qquad (T = const)$$
(3.38)

and

$$\frac{x_1 x_2 RT}{G^E} = B' + C'(x_1 - x_2) + D'(x_1 - x_2)^2 + \dots \qquad (T = const)$$
(3.39)

Since $x_2 = 1 - x_1$ for a binary system of species 1 and 2, x_1 can be taken as the single independent variable in Eqs. (3.38) and (3.39).

Eq. (3.38) is known as Redlich/Kister [31] expansion.

Truncating the Eq. (3.38) after the second term, i.e., D = ... = 0, and by the substitutions $B + C = A_{21}$ and $B - C = A_{12}$ the Margules model is obtained.

Truncating the Eq. (3.39) after the second term, i.e., D' = ... = 0, and by the substitutions $B' + C' = 1/A'_{21}$ and $B' - C' = 1/A'_{12}$ the van Laar model is obtained.

 A_{12} , A_{21} , A'_{12} and A'_{21} are binary interaction parameters which have to be regressed on experimental data.

The Redlich/Kister expansion, the Margules equations, and the van Laar equations are all special cases of a general treatment based on rational functions, i.e., on equations for G^E given by ratios of polynomials. They provide great flexibility in the fitting of VLE data for binary systems, but they have scant theoretical foundation and they cannot be extended to multicomponent systems.

Modern theoretical developments in the molecular thermodynamics of liquid solution behavior are based on the concept of *local composition*. Within a liquid solution, local compositions, different from the overall mixture composition, are presumed to account for the short-range order and non-random molecular orientations that result from differences in molecular size and intermolecular forces. The concept was introduced by G. M. Wilson in 1964 with the publication of a model of solution behavior since known as the Wilson equation [32]. The success of this equation in correlation of VLE data prompted the development of alternative local composition models. Most notably the NRTL (Non-Random-Two-Liquid) equation of Renon and Prausnitz [33] and the UNIQUAC (UNIversal QUAsi-Chemical) equation of Abrams and Prausnitz [34]. A further significant development, based on the UNIQUAC equation, is the UNIFAC method [35], in which activity coefficients are calculated from contributions of various groups making up the molecules of a solution. Among these equations, in this thesis work only the UNIQUAC one has been used, and its functional form is reported in appendix A.4.

3.5. Virial equations of state

3.5.1. Pure fluids

The virial equations of state are simple equations obtained from the power series expansion of the compressibility factor in density along an isotherm:

$$Z = \frac{P}{\rho RT} = 1 + B(T)\rho + C(T)\rho^{2} + D(T)\rho^{3} + \dots$$
(3.40)

where the functions:

$$B(T) = \lim_{\rho \to 0} \left(\frac{\partial Z}{\partial \rho} \right)_T \quad C(T) = \frac{1}{2!} \lim_{\rho \to 0} \left(\frac{\partial^2 Z}{\partial \rho^2} \right)_T \quad D(T) = \frac{1}{3!} \lim_{\rho \to 0} \left(\frac{\partial^3 Z}{\partial \rho^3} \right)_T \quad \dots \tag{3.41}$$

are the second, third, fourth, ... virial coefficient, respectively.

The same power series expansion can be done also in pressure:

$$Z = 1 + \tilde{B}(T)P + \tilde{C}(T)P^{2} + \tilde{D}(T)P^{3} + \dots$$
(3.42)

with similar meanings of the functions \tilde{B} , \tilde{C} , \tilde{D} , that are connected to the other ones through analytical relations here not reported.

Though virial equations have been initially introduced as purely empirical formulations [5], a physical meaning has been afterwards attributed to the coefficients: B represents the interactions between pairs of molecules, C among triplets of molecules and so on. Therefore, the relations between virial coefficients and intermolecular potential functions can be derived from statistical mechanics [36,37]; for instance the second virial coefficient for a fluid with spherically symmetric intermolecular force field is:

$$B = 2\pi N_A \int_0^\infty \left[1 - e^{-\Gamma(r)/(k_B T)} \right] dr$$
(3.43)

where $\Gamma(r)$ is the potential energy between two molecules and r is the distance between molecular centers. For superior order virial coefficients and for non-spherical molecules the expressions are much more complicated, so it is practically impossible to calculate the virial coefficients in this way.

The virial coefficients are functions of temperature only and, obviously, are fluid specific. As a general rule inferred from practice, B is negative except at high temperatures, while C and higher coefficients are positive except at very low temperatures [28]. Theoretically, the power series expansion, Eq. (3.40), could be used to describe the fluid properties in the whole range of fluid states, but this would require at least eight virial coefficients; for this reason the equation is usually truncated to the third virial coefficient C and its validity is limited to the vapor phase up to pressures of few tens of bar. If the expansions are truncated to the term including the second coefficient, B and \tilde{B} , the two equations (3.40) and (3.42) show an equivalent behavior with respect to experimental data, but if also the third coefficient C and \tilde{C} are considered the first equation is much more accurate with respect to the second.

The virial coefficients can be calculated from generalized correlations based on multi-fluid regression, even if much less is known about third virial coefficient than about second virial coefficient. One of the first generalized correlations for B(T) is given in Ref. 38, where the second virial coefficient is written in a non-dimensional form and it is expressed as a function of the reduced temperature T_r and of the acentric factor ω :

$$\frac{BP_c}{RT_c} = \frac{B^{(0)}P_c}{RT_c} + \omega \frac{B^{(1)}P_c}{RT_c}$$
(3.44)

Following the common approach, the functions $B^{(0)}$ and $B^{(1)}$ in Eq. (3.44) depend only on reduced temperature and various equations have been published for them in literature, as for instance by Pitzer and Curl [38] or by Van Ness and Abbott [39]; in the second case the equations are simpler but valid only for normal fluids:

$$\frac{B^{(0)}P_c}{RT_c} = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad \qquad \frac{B^{(1)}P_c}{RT_c} = 0.139 - \frac{0.172}{T_r^{4.2}}$$
(3.45)

More complicated functional forms were also assumed instead of Eq. (3.44); Tsonopoulos [40,41] proposed an equation with two further parameters a and b, that can be either constants or functions of the dipole moment of the molecule:

$$\frac{BP_c}{RT_c} = f^{(0)} + \omega f^{(i)} + a f^{(i)} + b f^{(i)}$$
(3.46)

where the $f^{(i)}$ functions depend only on reduced temperature; their analytical relations are given in the cited works.

Similar generalized approaches are followed also for the representation of the third virial coefficient C, though less precise experimental data are available for it; as an example, Orbey and Vera [42] proposed the following equation, valid for non-polar substances:

$$C\left(\frac{P_c}{RT_c}\right)^2 = C^{(0)}\left(\frac{P_c}{RT_c}\right)^2 + \omega C^{(1)}\left(\frac{P_c}{RT_c}\right)^2$$
(3.47)

with:

$$C^{(0)} \left(\frac{P_c}{RT_c}\right)^2 = 0.01407 + \frac{0.02432}{T_r^{2.8}} - \frac{0.00313}{T_r^{10.5}}$$

$$C^{(1)} \left(\frac{P_c}{RT_c}\right)^2 = -0.02676 + \frac{0.01770}{T_r^{2.8}} + \frac{0.04}{T_r^3} - \frac{0.003}{T_r^6} - \frac{0.00228}{T_r^{10.5}}$$
(3.48)

Besides these predictive techniques, virial coefficients can be directly fitted on experimental density data of the fluid of interest, when density measurements in low-density region are available. It is also possible to assume equations for virial coefficients from simplified models of statistical mechanics and to fit the coefficients of such functional forms on experimental speed of sound data for the fluid [43,44]; this procedure is advantageous because the speed of sound can be measured in vapor phase with very high precision using modern instruments as for instance the spherical resonator.

As previously shown for cubic equations, also a virial equation can be converted into a fundamental EoS form through integration according to Eq. (3.23), giving:

$$A^{R}(T,\rho) = RT\left[B(T)\rho + \frac{C(T)\rho^{2}}{2} + \frac{D(T)\rho^{3}}{3} + ...\right]$$
(3.49)

from which all the thermodynamic properties can be calculated. Obviously, the validity range of the obtained fundamental equation is the same of the starting virial equation, i.e. it is limited to vapor phase at a maximum pressure of few tens of bar.

3.5.2. Mixtures

A one-fluid model approach is adopted for the extension of the virial equations from pure fluids to mixtures, similarly to what was previously explained for cubic EoSs.

The exact composition dependence of the virial coefficients is given by statistical mechanics without the need of any arbitrary assumption [36,37]. For the second and the third coefficients it reads:

$$B_M = \sum_{i=1}^{C} \sum_{j=1}^{C} x_i x_j B_{ij}$$
(3.50)

$$C_{M} = \sum_{i=1}^{C} \sum_{j=1}^{C} \sum_{k=1}^{C} x_{i} x_{j} x_{k} C_{ijk}$$
(3.51)

where the coefficient B_{ij} characterizes a bimolecular interaction between molecule *i* and molecule *j* and then $B_{ij} = B_{ji}$, while the coefficient C_{ijk} takes into account interactions among three molecules *i*, *j* and *k*. The cross coefficients coincide with the respective coefficients for pure fluids if i = j = k, otherwise they can be calculated from the same relations valid for pure fluids using parameters calculated from suitable mixing rules [37]. For the cross second coefficient B_{ij} , Eqs. (3.44) or (3.46) can still be used adopting the following mixing rules:

$$T_{c,ij} = (1 - k_{ij}) \sqrt{T_{c,i} T_{c,j}} \qquad P_{c,ij} = \frac{Z_{c,ij} R T_{c,ij}}{v_{c,ij}} \qquad Z_{c,ij} = \frac{Z_{c,i} + Z_{c,j}}{2}$$

$$v_{c,ij} = \left(\frac{v_{c,i}^{1/3} + v_{c,j}^{1/3}}{2}\right)^3 \qquad \omega_{ij} = \frac{\omega_i + \omega_j}{2} \qquad a_{ij} = \frac{a_i + a_j}{2} \qquad b_{ij} = \frac{b_i + b_j}{2}$$
(3.52)

The cross third virial coefficient C_{ijk} is calculated as:

$$C_{ijk} = \left(C_{ij}C_{jk}C_{ik}\right)^{1/3}$$
(3.53)

with each binary cross coefficient C_{ij} obtained for instance from Eq. (3.47) with the same mixing rules in Eq. (3.52).

In Eq. (3.52) $Z_{c,i}$ is the compressibility factor at the critical point for the component *i* and k_{ij} is an empirical interaction parameter specific for the *i* - *j* molecular pair; k_{ij} equals zero for *i* = *j* and for chemically similar species, otherwise it is regressed from fitting on experimental data, when available.

3.6. Corresponding states models

3.6.1. Two parameter corresponding states

The principle of *two-parameter corresponding states* was first stated by van der Waals: after a rearrangement, his cubic EoS, Eq. (3.11), can be expressed in reduced variables as:

$$P_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2}$$
(3.54)

where:

$$T_r = \frac{T}{T_c} \qquad P_r = \frac{P}{P_c} \qquad v_r = \frac{v}{v_c} \qquad (3.55)$$

Therefore, from Eq. (3.54) it comes out that all fluids when compared at the same reduced temperature and reduced pressure have the same reduced density (or the same compressibility factor Z) and all deviate from the ideal-gas behavior to about the same degree. This is the basic concept of the corresponding states principle: the existence of a unique function relating the reduced physical variables:

$$\Phi(T_r, P_r, v_r) = 0 \tag{3.56}$$

valid for all the substances, i.e. a generalized equation of state. The former equation, Eq. (3.56), can be made explicit for instance in reduced pressure as:

$$P_r = \Psi(T_r, v_r) \tag{3.57}$$

Operatively, this means that if a precise equation of state is available for a fluid, called *reference* fluid and denoted with subscript 0, the thermodynamic properties of any other *target* fluid *j* can be calculated in a predictive way through the application of the corresponding states principle; for example, the compressibility factor reads:

$$Z_{j}(T_{j}, P_{j}) = Z_{0}\left(T_{j}\frac{T_{c,0}}{T_{c,j}}, P_{j}\frac{P_{c,0}}{P_{c,j}}\right)$$
(3.58)

The *two parameters* are those necessary to calculate the reduced values of the independent variables. A plot of compressibility factor as a function of reduced pressure, at fixed values of reduced temperature, is shown in Fig. 3.1 for various fluids. The lines have been generated from the most precise equations of state at present available for the selected fluids. It is evident that the corresponding states principle is quite verified in the vapor region at low pressure, but it fails at higher pressures, in the supercritical region and in all the liquid region.

The corresponding states principle was demonstrated by means of statistical mechanics [7-9] under the hypothesis of the same reduced intermolecular force law for different fluids; the fluids that share such a condition are said to be *conformal*. In practice, only the family of noble gases, constituted by spherical and non-polar monatomic molecules, rigorously fulfills the conformality requirement. In the case of fluids pertaining to that family the physical theory states the equality of the reduced residual Helmholtz free energy for different compounds when evaluated at the same reduced temperature and density:

$$a_{j}^{R}(T_{r},\rho_{r}) = a_{0}^{R}(T_{r},\rho_{r})$$
(3.59)

It is worth noticing that all the other thermodynamic properties can be derived from Eq. (3.59) if an EoS for the reference fluid 0 is available.



Figure 3.1: Compressibility factor for different fluids in reduced variables.

For all the other fluids, whose molecules are polyatomic and in many cases even polar, the conformality condition is not verified and the application to them of the two-parameter corresponding states principle often leads to large deviations. Nevertheless, also if the curves are not perfectly superimposed, a certain degree of conformality is anyway attained. Therefore, modifications and extensions of this principle have been proposed, though maintaining a similar framework.

In any case, even if the representation of all the fluids at once with the van der Waals EoS is not precise and then Eq. (3.54) has to be regarded as an approximation, the use of variables reduced through their critical values in order to exploit the similitude in the behaviors of different fluids was surely not only an interesting intuition, but a real milestone in thermodynamic modeling.

3.6.2. Three parameter corresponding states

A way to extend the applicability of the corresponding states principle beyond the simple spherical fluids, i.e. noble gases and few other simple substances, was found with the introduction

of a third parameter that accounts for the deviation of the target fluid from the spherical fluid behavior. This technique has been successively improved during the last decades.

PITZER MODEL

In Fig. 3.2 the logarithm of the reduced vapor pressure versus the inverse reduced temperature is plotted for a group of fluids; the curves were produced with the most precise EoSs at present available for the fluids. It is evident that the plots are almost straight line for each fluid, i.e. they has a constant slope:

$$\frac{\mathrm{d}\log_{10}P_r^s}{\mathrm{d}\left(1/T_r\right)} \approx const$$
(3.60)

Moreover, the lines for argon, krypton, xenon and methane are substantially superimposed, while the remaining fluids deviate from that lines of an amount that increases with the molecule complexity.



Figure 3.2: Vapor pressure in reduced variables for different fluids.

From the figure it can be inferred that the two-parameter corresponding states principle is valid for the noble gases and for methane, that has a roughly spherical molecule, whereas it fails for the other substances.

Pitzer et al. [10] noticed that for noble gases it is:

$$\log_{10} \left(P_r^s \right)_{T_r=0.7} = -1.0 \tag{3.61}$$

and then they proposed to use the reduced vapor pressure at $T_r = 0.7$ as an index of the deviation of the fluid of interest from the simple fluids behavior, so defining the *acentric factor*:

$$\omega \equiv -\log_{10} \left(P_r^s \right)_{T_r = 0.7} - 1.0 \tag{3.62}$$

This quantity, calculated from an experimental vapor pressure, is the *third* parameter of the models developed by Pitzer et al. [10]. They considered the compressibility factor for a target fluid j as a function of reduced temperature, reduced pressure and acentric factor:

$$Z_j = Z_j \left(T_r, P_r, \omega_j \right) \tag{3.63}$$

The expansion as power series in acentric factor gives:

$$Z_{j}(T_{r}, P_{r}, \omega_{j}) = Z^{(0)}(T_{r}, P_{r}) + \omega_{j} \left[\left(\frac{\partial Z}{\partial \omega} \right)_{T_{r}, P_{r}} \right]_{\omega = 0} + \dots$$
(3.64)

Pitzer's assumption was that ω would describe deviations from the monatomic gases in a linear fashion, implying the corrections would be small. For example, the compressibility factor was given as:

$$Z_{j}(T_{r}, P_{r}) = Z^{(0)}(T_{r}, P_{r}) + \omega_{j}Z^{(1)}(T_{r}, P_{r})$$
(3.65)

where $Z^{(0)}$ and $Z^{(1)}$ are generalized functions of reduced temperature and pressure with $Z^{(0)}$ obtained from the monatomic species and $Z^{(1)}$ by averaging $(Z - Z^{(0)})/\omega$ for different substances. The same formulation was used for the other thermodynamic properties, for example the vapor pressure of a target fluid *j* is calculated as:

$$\log_{10} P_{r,j}^{s} (T_{r}) = \left(\log_{10} P_{r}^{s} \right)_{T_{r}}^{(0)} + \omega_{j} \left(\frac{\partial \log_{10} P_{r}^{s}}{\partial \omega} \right)_{T_{r},\omega=0}$$
(3.66)

Pitzer et al. [10] reported in their work also tabulations of the $Z^{(0)}$ and $Z^{(1)}$ values as functions of reduced temperature and pressure, and of the $(\log_{10} P_r^s)_{T_r}^{(0)}$ and $[\partial (\log_{10} P_r^s)/\partial \omega]_{T_r,\omega=0}$ values as functions of reduced temperature.

LEE-KESLER MODEL

Twenty years later, in 1975, Lee and Kesler [11] proposed a modification of the Pitzer et al. model [10] that avoided the necessity to calculate the derivatives of thermodynamic functions with respect to acentric factor.

They considered two reference fluids for which quite reliable EoSs were available. The first reference fluid, denoted with 0, is a simple spherical fluid, while the other one, denoted with R1, is a heavy compounds; argon and n-octane, respectively, were mainly used.

In the Lee-Kesler model the acentric factor of the target fluid j is the scaling parameter for the interpolation between the properties of the two reference fluids, that are known from their EoSs. In the case of compressibility factor the model reads:

$$Z_{j}(T_{r},P_{r}) = Z_{0}(T_{r},P_{r}) + \frac{\omega_{j}}{\omega_{RI}} \left[Z_{RI}(T_{r},P_{r}) - Z_{0}(T_{r},P_{r}) \right]$$
(3.67)

The same technique can be applied to the residual part of all the other reduced thermodynamic properties, always maintaining the acentric factor as scaling parameter. For instance, in the case of enthalpy it is:

$$\frac{H_{j}^{R}(T_{r},P_{r})}{RT_{c,j}} = \frac{H_{0}^{R}(T_{r},P_{r})}{RT_{c,0}} + \frac{\omega_{j}}{\omega_{RI}} \left[\frac{H_{RI}^{R}(T_{r},P_{r})}{RT_{c,RI}} - \frac{H_{0}^{R}(T_{r},P_{r})}{RT_{c,0}} \right]$$
(3.68)

This model is suitable for non-polar or slightly polar substances; when applied to highly polar compounds larger errors can be expected.

TEJA MODEL

A further improvement of the original Pitzer model was proposed in 1981 by Teja et al. [12,13]. The new model no longer retains a simple fluid as one of the references, but it assumes two reference fluids, denoted with R1 and R2, which are chosen among substances similar to the fluid of interest. Therefore a better conformality of the target fluid to the two references can be pursued suitably selecting the reference fluids themselves, with consequently better performances of the model.

As in the case of the Lee-Kesler technique [11], a precise EoS has to be available for each reference fluid, allowing to calculate its thermodynamic properties.

The Teja et al. model for compressibility factor is written as:

$$Z_{j}(T_{r},P_{r}) = Z_{RI}(T_{r},P_{r}) + \frac{\omega_{j} - \omega_{RI}}{\omega_{R2} - \omega_{RI}} \left[Z_{R2}(T_{r},P_{r}) - Z_{RI}(T_{r},P_{r}) \right]$$
(3.69)

and the other properties are similarly calculated applying the model only to the reduced residual part, as in the Lee-Kesler method, and using the acentric factor as scaling parameter in the same way of Eq. (3.69).

The extension to mixtures is based on the one-fluid model technique; the critical properties used to make the variables non-dimensional are substituted by pseudo-critical values calculated from the mixing rules:

$$T_{c,M}v_{c,M} = \sum_{i=1}^{C} \sum_{j=1}^{C} x_i x_j T_{c,ij} v_{c,ij} \qquad v_{c,M} = \sum_{i=1}^{C} \sum_{j=1}^{C} x_i x_j v_{c,ij} Z_{c,M} = \sum_{i=1}^{C} x_i Z_{c,i} \qquad \omega_M = \sum_{i=1}^{C} x_i \omega_i$$
(3.70)

where it is:

$$T_{c,ij}v_{c,ij} = (1 - \varepsilon_{ij}) \left(T_{c,i}v_{c,i}T_{c,j}v_{c,j} \right)^{/2} \qquad v_{c,ij} = (1 - \eta_{ij}) \frac{\left(v_{c,i}^{1/3} v_{c,j}^{1/3} \right)^3}{8}$$
(3.71)

The adjustable binary interaction coefficients ε_{ij} and η_{ij} equal zero for i = j, while for $i \neq j$ they can be regressed on available experimental data or, if this is not possible, set to zero. From the obtained values of $T_{c,M}$, $v_{c,M}$ and $Z_{c,M}$ it is possible to calculate the pseudo-critical pressure $P_{c,M}$ required to reduce the pressure variable.

SCALABRIN MODEL

In recent times Scalabrin et al. [45-48] developed a further improvement of the three-parameter corresponding states model, obtaining very accurate results. The idea from Teja et al. [12,13] of choosing two reference fluids as conformal as possible with the target fluids was maintained, but the novelty was constituted by the introduction of a property-specific quantity as scaling parameter instead of the acentric factor.

The basic concept is that different thermodynamic properties of a chosen group of fluids do not behave exactly in the same way when operating in reduced variables, but on the contrary the relative deviation between fluids can be very different from one property to the other. Therefore the extension of the acentric factor, that is no more than a scaling parameter for vapor pressure, to represent all the properties is a rough approximation that often leads to poor results.

Moving from these remarks, Scalabrin et al. proposed to substitute the acentric factor with a new parameter that is not only fluid-specific but also property-specific; the parameter has to be calculated from very few experimental data, typically one measurement at saturation condition, then maintaining the predictive character of the model. The set up of the most suitable scaling parameter has moved from a conformality analysis specific for the considered property.

As for the Teja et al. model [12,13], the target fluid is denoted with j, while R1 and R2 are the reference fluids, that have to dispose of reliable EoSs.

The new three-parameter model can be written in a general form, indicated with ψ and $\tilde{\omega}$ respectively a function of a generic property and the new scaling parameter:

$$\psi_{j}(T_{r},P_{r}) = \psi_{RI}(T_{r},P_{r}) + \frac{\widetilde{\omega}_{j} - \widetilde{\omega}_{RI}}{\widetilde{\omega}_{R2} - \widetilde{\omega}_{RI}} [\psi_{R2}(T_{r},P_{r}) - \psi_{RI}(T_{r},P_{r})]$$
(3.72)

The model has been developed for density [47], with:

$$\psi = \log_{10}\left(\frac{\rho RT_c}{P_c}\right) \qquad \qquad \tilde{\omega} = \delta \equiv -\log_{10}\left(\frac{\rho RT_c/P_c}{\rho_{RI}RT_{c,RI}/P_{c,RI}}\right)_{sl,T_r=0.8} \qquad (3.73, 3.74)$$

for residual enthalpy [48]:

$$\psi = \frac{H^{R}}{RT_{c}} \qquad \qquad \widetilde{\omega} = k \equiv \left[\frac{\Delta H^{ev}/(RT_{c})}{\Delta H^{ev}_{RI}/(RT_{c,RI})}\right]_{T_{r}=0.8} \qquad (3.75, 3.76)$$

and for residual entropy [48]:

$$\psi = \frac{S^{R}}{R} \qquad \qquad \widetilde{\omega} = \sigma \equiv \left(\frac{\Delta S^{ev}/R}{\Delta S^{ev}_{RI}/R}\right)_{T_{r}=0.8} = \left[\frac{\Delta H^{ev}/(RT_{c})}{\Delta H^{ev}_{RI}/(RT_{c,RI})}\right]_{T_{r}=0.8} \qquad (3.77, 3.78)$$

As it can be seen, the scaling parameter is calculated at a fixed reduced temperature, here chosen as $T_r = 0.8$, from a point of saturated liquid density in Eq. (3.74) and from enthalpy of vaporization in Eqs. (3.76) and (3.78); both the required input are experimentally accessible measurements. The corresponding values for the reference fluids are calculated from their necessarily available EoSs.

The representation of mixtures follows a one-fluid model approach applying suitable mixing rules, that in these cases have been derived from a modification of the Wong et al. [49] ones:

$$T_{c,M} / P_{c,M} = \sum_{i=1}^{C} \sum_{j=1}^{C} x_i x_j T_{c,ij} / P_{c,ij} \qquad T_{c,M}^2 / P_{c,M} = \sum_{i=1}^{C} \sum_{j=1}^{C} x_i x_j T_{c,ij}^2 / P_{c,ij}$$

$$T_{c,ij} = (1 - \varepsilon_{ij}) \sqrt{T_{c,i} T_{c,j}} \qquad P_{c,ij} = 8T_{c,ij} / \{(1 - \eta_{ij}) [(T_{c,i} / P_{c,i})^{1/3} + (T_{c,j} / P_{c,j})^{1/3}]\} \qquad (3.79)$$

$$\widetilde{\omega}_M (T_{c,M} / P_{c,M})^{2/3} = \sum_{i=1}^{C} \sum_{j=1}^{C} x_i x_j \widetilde{\omega}_{ij} (T_{c,ij} / P_{c,ij})^{2/3} \qquad \widetilde{\omega}_{ij} = (\widetilde{\omega}_i + \widetilde{\omega}_j)/2$$

and transforming Eq. (3.72) into:

$$\psi_{M}\left(T_{r},P_{r},\boldsymbol{x}\right) = \psi_{RI}\left(T_{r},P_{r}\right) + \frac{\widetilde{\omega}_{M}-\widetilde{\omega}_{RI}}{\widetilde{\omega}_{R2}-\widetilde{\omega}_{RI}}\left[\psi_{R2}\left(T_{r},P_{r}\right)-\psi_{RI}\left(T_{r},P_{r}\right)\right]$$
(3.80)

As usual, the adjustable binary interaction coefficients ε_{ij} and η_{ij} are null when i = j, while for $i \neq j$ they are regressed on available experimental data to improve the model accuracy, otherwise set to zero.

These models have been applied to halogenated alkanes [47,48] and to hydrofluoroethers [47] with very satisfying results.

3.6.3. Extended corresponding states

Another formulation moving from the corresponding states principle with the aim at extending its application also to non-spherical fluids is known as extended corresponding states (ECS) method [9,14-17]. In this approach the equality between the reduced residual Helmholtz free energies of reference and target fluids, as from the original two-parameter corresponding states model, is maintained:

$$a_{j}^{R}(T_{j},\rho_{j}) = a_{0}^{R}(T_{0},\rho_{0})$$
(3.81)

but the independent variables of reference and target fluids are related each other by the equations:

$$T_0 = T_j / f_j$$
 $\rho_0 = \rho_j h_j$ (3.82, 3.83)

where f_j and h_j are the so-called *scale factors*. In the case that the condition of the same reduced intermolecular force law for the two fluids is verified, the scale factors simply coincide with the ratios of the critical constants:

$$f_{j} = \frac{T_{c,j}}{T_{c,0}} \qquad \qquad h_{j} = \frac{\rho_{c,0}}{\rho_{c,j}} \qquad (3.84, 3.85)$$

and the basic two-parameter corresponding principle, Eq. (3.59), is recovered. If the condition is not fulfilled, two corrective factors, called *shape functions*, are introduced in order to account for the departure from perfect similarity:

$$f_{j} = \frac{T_{c,j}}{T_{c,0}} \; \theta_{j} \left(T_{j}, \rho_{j} \right) \qquad \qquad h_{j} = \frac{\rho_{c,0}}{\rho_{c,j}} \phi_{j} \left(T_{j}, \rho_{j} \right) \tag{3.86, 3.87}$$

The shape functions ϕ_j and θ_j , and then also the scale factors, are fluid-specific functions in the independent variables temperature and density of the interest fluid; they allow to represent the thermodynamic behavior of a target fluid with respect to a reference one, for which an EoS must be available. Once such functions have been determined for the considered fluid, all the other thermodynamic properties can be obtained through differentiation of the fundamental equation, Eq. (3.81). For instance, considering only the first derivatives, it is:

$$\left(\frac{\partial a_j^R}{\partial \rho_j}\right)_{T_j} = \frac{z_j^R}{\rho_j} = \frac{u_0^R F_\rho + z_0^R \left(1 + H_\rho\right)}{\rho_j} \qquad \Rightarrow \qquad z_j^R = u_0^R F_\rho + z_0^R \left(1 + H_\rho\right) \tag{3.88, 3.89}$$

$$\left(\frac{\partial a_{j}^{R}}{\partial T_{j}}\right)_{\rho_{j}} = -\frac{u_{j}^{R}}{T_{j}} = -\frac{u_{0}^{R}(1-F_{T})-z_{0}^{R}H_{T}}{T_{j}} \qquad \Rightarrow \qquad u_{j}^{R} = u_{0}^{R}(1-F_{T})-z_{0}^{R}H_{T} \qquad (3.90, 3.91)$$

where:

$$F_{\rho} = \frac{\rho_j}{f_j} \left(\frac{\partial f_j}{\partial \rho_j}\right)_{T_j} \qquad \qquad H_{\rho} = \frac{\rho_j}{h_j} \left(\frac{\partial h_j}{\partial \rho_j}\right)_{T_j} \qquad (3.92, 3.93)$$

$$F_{T} = \frac{T_{j}}{f_{j}} \left(\frac{\partial f_{j}}{\partial T_{j}}\right)_{\rho_{j}} \qquad \qquad H_{T} = \frac{T_{j}}{h_{j}} \left(\frac{\partial h_{j}}{\partial T_{j}}\right)_{\rho_{j}} \qquad (3.94, 3.95)$$

From Eqs. (3.88-3.95) the residual compressibility factor $z^R = Z - 1$ and the reduced residual internal energy $u^R = U^R / (RT)$ are calculated for the target fluid.

In the case of mixtures, Eqs. (3.81-3.85) are still valid with the substitution of target mixture M for pure fluid *j*:

$$a_M^R \left(T_M, \rho_M, \mathbf{x} \right) = a_0^R \left(T_0, \rho_0 \right) \tag{3.96}$$

$$T_0 = T_M / f_M \qquad \qquad \rho_0 = \rho_M h_M \qquad (3.97, 3.98)$$

where the mixture scale factors are usually obtained from van der Waals mixing rules [50]:

$$f_M h_M = \sum_{i=1}^C \sum_{j=1}^C x_i x_j f_{ij} h_{ij} \qquad \qquad h_M = \sum_{i=1}^C \sum_{j=1}^C x_i x_j h_{ij} \qquad (3.99, 3.100)$$

$$f_{ij} = (f_i f_j)^{1/2} (1 - k_{ij}) \qquad h_{ij} = (h_i^{1/3} + h_j^{1/3})^3 (1 - l_{ij})/8 \qquad (3.101, 3.102)$$

Also in this case the binary interaction parameters k_{ij} and l_{ij} are non-zero when $i \neq j$ and can be regressed on experimental data when available.

The pure fluid scale factors in Eqs. (3.101) and (3.102) are calculated in condition of conformality among the mixture, the pure components and the reference fluid, i.e. the following equations system has to be verified:

$$\begin{cases} T_0 = T_M / f_M \\ \rho_0 = \rho_M h_M \\ T_0 = T_j / f_j & 1 \le j \le C \\ \rho_0 = \rho_j h_j & 1 \le j \le C \end{cases}$$

$$(3.103)$$

At this point the heart of the problem is how to get the scale or the shape functions. Different procedures have been proposed in the literature aiming at such a goal: the two scale functions and all their derivatives can be determined through an analytical procedure, the *local solution*, without the definition of their functional form [50,51], or alternatively through a correlative procedure, the *continuous solution*, which requires the assumption of a functional form for them [52,54]. In the first case the shape functions are locally determined, whereas in the second one they are determined in a continuum space. Another approach only recently emerged in literature [55-57] is the optimization procedure, through which the analytical dependences of the scale factors are directly and simultaneously obtained for regression of the available experimental data. In the following sections these methods are presented and their effectiveness with respect to the ECS modeling technique is discussed.

LOCAL SOLUTION

Making available an EoS for both the target and the reference fluid, the mathematical problem presents two variables, f_j and h_j , and only one identity which is the 'mother' equation of the ECS method, Eq. (3.81). This gives rise to an undefined system of equations and a further relation is therefore required to determine the unknowns f_j and h_j . Once another equation posing a constraint between the variables would be found, the subsequent problem is to derive any other

thermodynamic function of the fluid of interest, as for instance Eqs. (3.89) and (3.91); in order to calculate them, all the local values of the derivatives of the scale factors are also needed, see Eqs. (3.92-3.95). Further equations are then to be found for determining the required scale factors derivatives.

Considering the Eqs. (3.81), (3.88), (3.90), in the case of local solution one could try to solve a system composed of such equations in order to get both the two scale factors and their four first derivatives values at a given point (T_j, ρ_j) [50]. From a check of the equations it appears that the first, Eq. (3.81), is the 'mother' one, the second, Eq. (3.88), is the first derivative of Eq. (3.81) with respect to density, the third, Eq. (3.90), is the first derivative of Eq. (3.81) with respect to temperature, while the remaining equations are linear combinations of the former three ones according to thermodynamic function definitions. The system of the mentioned equations is evidently undetermined and the same reasoning is furthermore convenient to show that also any general system involving all the derivatives, the first order ones and those of superior order, would be undetermined as well.

As always in presence of an undefined system, the chance to overcome the impasse is represented by the introduction of a number of arbitrary conditions sufficient to cover the gap between unknown variables and available equations. In this case the required arbitrary condition is a single analytical relation linking the scale functions one another and then saturating the remaining degree of freedom.

Limiting the interest to the representation of only those thermodynamic functions not involving higher order derivatives of the scale factors, another possibility is to choose a derived function m and to impose its transformation into the most essential relation reading:

$$m_j^R(T_j,\rho_j) = m_0^R(T_j/f_j,\rho_jh_j)$$
(3.104)

This leads to a particular function relating the scale factor derivatives. At this stage the thermodynamic model is composed of the primary equation (3.81) and the mentioned relation, Eq. (3.104). Supplying local values of the quantities a_j^R and m_j^R the system of equations can now be regularly solved for the local values of the scale factors f_j and h_j . Anyway, the scale factors first order derivatives are furthermore required to represent the remaining thermodynamic functions and these must be obtained from further thermodynamic relations, as for example those reported in Ref. 50.

Applying for instance Eq. (3.104) to z^{R} , the introduction of the condition from Ref. 50:

$$z_0^R H_\rho + u_0^R F_\rho = 0 aga{3.105}$$

leads to:

$$z_j^R = z_0^R \tag{3.106}$$

and to a simplification of the other relations for the thermodynamic functions.

This choice gets the advantage that the target fluid density is directly represented from the equations system itself, composed of Eqs. (3.81) and (3.106). An equivalent equations system under the same arbitrary condition, Eq. (3.105), could be composed of Eq. (3.81) and:

$$g_{j}^{R} = g_{0}^{R}$$
(3.107)

Instead of applying Eq. (3.104) to z^{R} , it could be for instance applied to u^{R} , Eq. (3.91), deriving a new condition for the scale factors derivatives reading:

$$z_0^R H_T + u_0^R F_T = 0 aga{3.108}$$

From this new condition another set of equations for the remaining thermodynamic properties is then obtained and it composes an alternative version of the ECS model.

A subsequent mathematical version of the ECS technique has been proposed [51,58]: the system of equations (3.81) and (3.106) is still used, the second being evidently derived from the assumption of the same arbitrary condition, Eq. (3.105), but in these works the functional dependence of the scale factors on density was omitted and the condition of Eq. (3.105) becomes:

$$H_{\rho} = F_{\rho} = 0 \tag{3.109}$$

In conclusion this modeling condition, applied in Refs. 51 and 58, represents only a simplification of the above mentioned model assuming Eq. (3.105). In this version the Authors modified the original ECS model and they did not generate 'exact' scale functions according to the technique discussed in the preceding, which requires the EoS also for the interest fluid, but two individual functions, one for vapor pressure and the other for saturated liquid density, were used instead of an EoS. These two equations together represent, from another point of view, the target fluid EoS limited to only the saturated liquid line.

The shape functions values were generated forcing the ECS model, Eqs. (3.81) and (3.106), to represent the thermodynamic surfaces of the fluid from these two individual equations along the saturated liquid line and consequently they are only temperature dependent. These generated values were then correlated through empirical fitting equations. The shape functions density dependence in the regions of the superheated vapor and of the compressed liquid was then omitted and the shape

functions values calculated at a local temperature were assumed to be valid at any density along that isotherm, arbitrarily extrapolating them to any other region, i.e. compressed liquid, saturated and superheated vapor, and the supercritical domain. This position is expected to introduce some sensible error deviations in those regions where the sensitivity of density to pressure is higher, as is the case of the superheated vapor region.

Looking at the arbitrary condition effectively applied, Eq. (3.105), it is evident that the scale functions density derivatives are linked together through the reference fluid functions $u_0^R(T,\rho)$ and $z_0^R(T,\rho)$. Going back to the arbitrary condition proposed in Refs. 51 and 58, Eq. (3.109), this has to be considered as a rough approximation, because it is contradicted by theory and practice [9,59].

Up to this stage the conversion of the original undefined system of equations into a defined one can be performed, but once an arbitrary condition is set up the various thermodynamic properties have furthermore to be analytically calculated as an 'exact solution'. The shape functions first derivatives F_{ρ} , H_{ρ} , F_T , H_T appearing in the preceding relations, Eqs. (3.88) and (3.90), after the introduction of the arbitrary condition have also to be locally calculated, as well as second and cross derivatives for the further thermodynamic functions.

Some considerations can be drawn from the preceding discussion:

- through the analytical local procedure any thermodynamic function of a pure fluid can be exactly obtained, but at the unavoidable condition that an EoS is available for each interest fluid, in addition to the necessary EoS for the reference fluid. For an interest fluid no practical advantage is coming from the application of this analytical local procedure. An EoS is in fact always required for it and no benefit is derived from its reproduction according to an ECS format. Consequently, the prospects of this procedure are only addressed to mixtures modeling for thermodynamics and to pure fluids and mixtures modeling for transport properties [60-65]. In any case the extension to mixtures requires the introduction of suitable mixing rules for both the scale factors and the pseudo-critical parameters as currently reported in the literature;
- being infinite the arbitrary conditions which it is possible to assume to make the equations system determined, then infinite are the scale factors local values of the resulting ECS EoS for the same interest fluid in the same condition. This is a misleading aspect, because it eludes the uniqueness of an analytical thermodynamic model;
- through this procedure the functional forms of the scale factors and their derivatives are not defined but only their local values are got;
- given the 'mother' equation, Eq. (3.81), and an arbitrary condition, the scale factors can be calculated and any other thermodynamic function can be derived through classical

thermodynamics. Consequently, the theoretically correct form of the so-obtained thermodynamic system must be always composed of the 'mother' equation, Eq. (3.81), and of the arbitrary condition.

In the case of assuming the first of the two formerly proposed arbitrary conditions, Eq. (3.105), the correct form of the system is:

$$\begin{cases} a_{j}^{R} (T_{j}, \rho_{j}) = a_{0}^{R} (T_{j} / f_{j}, \rho_{j} h_{j}) \\ z_{0}^{R} H_{\rho} + u_{0}^{R} F_{\rho} = 0 \end{cases}$$
(3.110)

but in such a system the scale factors density derivatives H_{ρ} and F_{ρ} are also present as unknowns preventing a mathematical solution for the scale factors. It is then more convenient to consider also Eq. (3.106) turning the system to be read:

$$\begin{cases} a_j^R \langle T_j, \rho_j \rangle = a_0^R \langle T_j / f_j, \rho_j h_j \rangle \\ z_j^R \langle T_j, \rho_j \rangle = z_0^R \langle T_j / f_j, \rho_j h_j \rangle \end{cases}$$
(3.111)

In this form the system takes into account only the scale factors as unknowns and it does not include any derivative of them, making this system the more essential that it is possible to get for a plain solution. This form is also currently assumed through all the literature as the true analytical representation of the conventional ECS model [50-54,58,59].

CONTINUOUS SOLUTION

The preceding study shows that after the assumption of an arbitrary condition linking the two scale functions the mathematical problem is not completely solved, because the analytical forms of the scale functions have to be furthermore found.

Aiming at an analytical solution of the scale functions a possibility is given. For the fluid of interest local values of the scale functions can be generated on a regular grid of the independent variables T_j , ρ_j , assuming an arbitrary condition and analytically solving the consequent equations system; the calculated points are then correlated with fitting equations, one for each scale function. The individual local values have to be fitted with some empirical correlations to proceed to the representation of any thermodynamic function; such fitting equations should be suitable for all the fluids of interest and possibly for different forms of the arbitrary condition, so flexible function approximators are required [52,53].

An evident advantage comes from the continuous solution mode with respect to the local solution mode. Once the scale factors have been locally generated all over the target fluid $P\rho T$

surface and the two $f_j(T_j, \rho_j)$ and $h_j(T_j, \rho_j)$ functions have been regressed on the generated values, the first, second and cross derivatives of the scale factors can be directly and more easily obtained from these functions, then avoiding the tiresome local generation procedure at each (T_i, ρ_i) point.

Even if the more recent models [52,53] in this framework omitted the original requirement of the target fluid EoS [50] and proposed to locally generate the individual scale factors from density data ordered along isotherms covering the range of interest, anyway such a regression procedure does not allow to fit either on different kind of data or on a multi-property data set, as it is generally required for an equilibrated and general dedicated EoS; for instance coexistence data of vapor pressure and saturated liquid and vapor densities should be required for any EoS development. Moreover, the procedure cannot avoid the imposition of an arbitrary condition [50,52,53], as for instance Eq. (3.105), to generate local values of the scale factors.

Besides, this second traditional approach presents at least two important drawbacks: the determination of the local values of the scale factors is very cumbersome and their successive separate correlation leads to incoherencies, as it is recognized by the Authors themselves [52-54]. Furthermore, the functional forms for the scale factors are arbitrarily chosen, with a trial-and-error approach and not with an objective optimization procedure.

As a conclusion, in both the former modes (local and continuous solutions) the ECS method remains undefined: in fact for each of the infinite possible arbitrary conditions, infinite forms of the ECS model are possible to represent the same fluid.

OPTIMIZATION PROCEDURE

The basic idea of the ECS model consists in the distortion of the independent variables of the EoS of the reference fluid to transform it into the EoS of the interest fluid. If the simple twoparameter corresponding states principle should work exactly, no tuning distortion would be necessary; since this is not the case, two tuning functions θ and ϕ , indicated as shape functions, are then individually required to exactly match the ECS model with a known thermodynamic surface of the interest fluid. Furthermore a general aim of the method would be to match the ECS model with a thermodynamic surface known through a certain amount of experimental data of the interest fluid.

For the two traditional approaches, the *local solution* and the *continuous solution*, the solving of the equations system, Eq. (3.111), is unavoidable and then either an EoS in the Helmholtz energy form [50,51,58,59] or properly organized density data [52,53] are always required to get the $a_i^R(T_i, \rho_i)$ local values.

If a flexible and robust function approximator, suitable to generally represent typical surface forms of the shape functions, could be introduced into the ECS model, the problem would be transformed into a general fitting procedure in which a mathematical form of the a^{R} surface has to be 'spread' on known values of it and of its derivatives. The new problem becomes in this case the minimization of an objective function composed of suitable forms of error deviations between predicted and known values of different thermodynamic properties. The result of this typical multiparameter minimization problem is a fundamental multiparameter ECS EoS through which any other thermodynamic property can be calculated.

This procedure is quite different from the local solution and from the continuous solution, because it avoids any local analytical solving of systems of equations and it requires neither an EoS for the interest fluid nor an arbitrary condition, from which the difficulties discussed in the preceding sections derive.

Moreover the new procedure yields at once the mathematical formulations of the two individual shape functions, which allow to move to any other thermodynamic function through the classical analytical transformations.

The general difficulty of any thermodynamic ECS model, due to its basic mathematical indeterminacy, is still present in the procedure, because the method is always based on a single equation, Eq. (3.81), with two unknowns, i.e. the local values of the shape functions, but this difficulty is overcome by the optimization procedure which allows to get the most effective solution.

The possibility to directly fit the shape functional forms on the experimental data has been only recently pointed out in the literature [55-57]; in paragraph 3.6.4. this approach will be exploited using a neural network to describe the functional dependence of the shape functions, both for pure fluids and for mixtures.

3.6.4. ECS-NN

The Extended Corresponding States Neural Network (ECS-NN) modeling technique is here treated in detail because it represents the basis for the development of the Extended Equation of State Neural Network (EEoS-NN) modeling technique, see Chap. IV, that represents the main subject of the part of this thesis regarding the thermodynamic properties representation. In the ECS-NN method the basic framework of the ECS is still maintained, but the novelty is represented by the application of a powerful heuristic technique to determine the scale factors as continuous functions of the target fluid thermodynamic variables. Starting from experimental data of the considered fluid, the regression procedure yields an equation of state in the fundamental Helmholtz energy form for

the fluid itself able to satisfactorily describe vapor, liquid and supercritical regions. The same technique can be applied also to mixtures. Therefore such a method pertains to the optimization procedure; the scale factors functional forms are represented by a multilayer feed-forward neural network, from which the acronym 'ECS-NN' given to this technique.

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The basic equation of the corresponding states theory, Eq. (3.81), expresses the equality of the reduced residual Helmholtz energy when evaluated in condition of conformality between the target fluid, denoted with *j*, and the reference fluid, denoted with 0.

The ECS technique relates the independent variables of target and reference fluids through Eqs. (3.82, 3.83, 3.86, 3.87). Once analytical equations are available for the shape functions, all the thermodynamic properties of the target fluid can be calculated from the necessary equation of state of the reference fluid. An example is given in Eqs. (3.89) and (3.91), which involve the scale factors derivatives, Eqs. (3.92-3.95).

The problem is how to get the equations for the scale or the shape functions.

The present innovative purpose is to express the shape functions through a multilayer feedforward neural network with one hidden layer. With reference to Paragraph 2.2 and in particular to Figs. 2.1 and 2.3, it is:

$$I = 3 V_1 = T_{r,j} = \frac{1}{\tau_j} = \frac{T_j}{T_{c,j}} V_2 = \delta_j = \frac{\rho_j}{\rho_{c,j}} (3.112, 3.113, 3.114)$$

 $K = 2 W_1 = \theta_j (T_{r,j}, \delta_j) W_2 = \phi_j (T_{r,j}, \delta_j) (3.115, 3.116, 3.117)$

For convenience the chosen independent variables of the shape functions are $T_{r,j}$ and δ_j , therefore, considering Eqs. (3.86, 3.87) and (3.112-3.117), the scale functions derivatives in Eqs. (3.92-3.95) are calculated as:

$$\left(\frac{\partial f_j}{\partial \rho_j}\right)_{T_j} = \left(\frac{\partial f_j}{\partial \delta_j}\right)_{T_{r,j}} \cdot \frac{\partial \delta_j}{\partial \rho_j} = \frac{T_{c,j}}{T_{c,0}} \frac{\partial W_1}{\partial V_2} \frac{1}{\rho_{c,j}}$$
(3.118)

$$\left(\frac{\partial h_j}{\partial \rho_j}\right)_{T_j} = \left(\frac{\partial h_j}{\partial \delta_j}\right)_{\delta_j} \cdot \frac{\partial \delta_j}{\partial \rho_j} = \frac{\rho_{c,0}}{\rho_{c,j}} \frac{\partial W_2}{\partial V_2} \frac{1}{\rho_{c,j}}$$
(3.119)

$$\left(\frac{\partial f_j}{\partial T_j}\right)_{T_i} = \left(\frac{\partial f_j}{\partial T_j}\right)_{T_{r,j}} \cdot \frac{\partial T_{r,j}}{\partial T_j} = \frac{T_{c,j}}{T_{c,0}} \frac{\partial W_1}{\partial V_1} \frac{1}{T_{c,j}}$$
(3.120)

$$\left(\frac{\partial h_{j}}{\partial T_{j}}\right)_{\rho_{j}} = \left(\frac{\partial f_{j}}{\partial T_{r,j}}\right)_{\delta_{j}} \cdot \frac{\partial T_{r,j}}{\partial T_{j}} = \frac{\rho_{c,0}}{\rho_{c,j}} \frac{\partial W_{2}}{\partial V_{1}} \frac{1}{T_{c,j}}$$
(3.121)

where terms $\partial W_k / \partial V_m$ ($1 \le m \le I - 1$, $1 \le k \le K$) are calculated by Eq. A1.14 in Appendix A.1.

The number of neurons in the hidden layer J has to be found by trial-and-error, searching for the best compromise between computational speed and accuracy of the resulting equation; it must not be too large, because if there are too many free parameters with respect to the number of experimental points overfitting problems may arise.

Moreover, the values $V_{i,\min}$ and $V_{i,\max}$ required for the linear scaling of the input variables are fluid-specific and they depend on the considered ranges of the independent variables T_j, ρ_j . The parameters $W_{k,\min}$ and $W_{k,\max}$ for the output variables scaling are fluid-specific as well and they are related to the deviation from conformality between the target and the reference fluid.

The weighting factors have then to be regressed for each fluid. Such values are obtained with a fitting procedure, the *training*, which aims at the minimization of an objective function calculated from the given thermodynamic properties data. Once the training has been completed, the shape functions and all their derivatives are obtained in continuous form from the equations given in Appendix A.1.

The a^{R} data are not experimentally accessible and then the neural shape functions have to be determined using other thermodynamic quantities. Density is the most favored one, because it can be quite easily measured in both vapor and liquid regions with high accuracy and, moreover, it is an independent variable, together with temperature, of fundamental Helmholtz energy equations of state. Also the accurate representation of the vapor-liquid saturation condition is a basic requirement for an EoS, therefore information about this locus has to be supplied during the training procedure.

The ECS-NN EoS can be trained on a derived quantity as density without any substantial loss of accuracy on the fundamental surface $a_j^R(T_j, \rho_j)$.

An inversion of variables is always needed for practical uses, since T,P are the controlling variables for experimentation and for technical applications, while T,ρ are the independent variables of the model. Such different choice of variables requires an iterative procedure to find a solution for $\rho(T,P)$.

As an example of the shape functions behavior, the $\theta_j = \theta_j(\tau_j, \delta_j)$ and $\phi_j = \phi_j(\tau_j, \delta_j)$ surfaces for the fluid R152a, using R134a as reference fluid, are shown in Figs. 3.3 and 3.4, respectively, using the dedicated EoS of Tillner-Roth and Baehr [66] as reference fluid EoS. τ_j and δ_j represent the inverse reduced temperature and the reduced density, as from Eqs. (3.113) and (3.114). Both the shape function surfaces are very smooth, with values centered around 1, corresponding to a null distortion of the variables, and with very small variations limited in few parts percent. This also confirms that the two-parameter corresponding states principle alone works well enough for these fluids and that the ECS technique, with the non-linear distortion of the independent variables, is very sensitive and effective.



Figure 3.3: Shape function $\theta_j = \theta_j(\tau_j, \delta_j)$ for the interest fluid R152a with the ECS-NN model trained on density and coexistence data.



Figure 3.4: Shape function $\phi_j = \phi_j(\tau_j, \delta_j)$ for the interest fluid R152a with the ECS-NN model trained on density and coexistence data.

A question is now posed about the possibility to extend the proposed model to fluids which are supposed not to share a condition of conformality with the reference fluid, at least according to the traditional theory which bases the conformality on the molecular potentials similitude. In order to verify such a possibility, water and ammonia have been selected as target fluids, since they are known as strongly polar and deviating fluids; the haloalkane R134a has been maintained as reference fluid. For both these two target fluids the conformality with the reference fluid is supposed to be rather poor.

In Fig. 3.5 and 3.6 the $\theta_j = \theta_j(\tau_j, \delta_j)$ and $\phi_j = \phi_j(\tau_j, \delta_j)$ surfaces are respectively shown for water. Similar plots are obtained also for ammonia.



Figure 3.5: Shape function $\theta_j = \theta_j(\tau_j, \delta_j)$ for water with the ECS-NN model trained on density data.



Figure 3.6: Shape function $\phi_j = \phi_j(\tau_j, \delta_j)$ for water with the ECS-NN model trained on density data.

The results are very satisfactory for both these strongly polar fluids and they demonstrate that the heuristic model can quite well correct the behavior discrepancies between reference and target fluids, allowing to go well beyond the traditional limit of conformality for the application of a corresponding states modeling technique.

MIXTURES

In Ref. 57 the same heuristic ECS-NN model developed for pure fluids has been applied also to mixtures using Eq. (3.96) with the relations:

$$T_{0} = \frac{T_{M}}{f_{M}(T_{M}, \rho_{M}, \mathbf{x})} \qquad \qquad \rho_{0} = \rho_{M}h_{M}(T_{M}, \rho_{M}, \mathbf{x}) \qquad (3.122, 3.123)$$

where x is the vector of molar compositions.

For mixtures it is more convenient to represent the scale factors instead of the shape functions, because in this way the definition of mixture pseudo-critical parameters is skipped.

Once the scale functions have been obtained all the thermodynamic properties can be calculated applying the same equations used for the pure fluids, substituting the mixture scaling factors to the pure fluid ones. For instance, in Eqs (3.89) and (3.91), the derivatives of the scale functions in the case of a mixture are:

$$F_{\rho} = \frac{\rho_M}{f_M} \left(\frac{\partial f_M}{\partial \rho_M}\right)_{T_M, x} \qquad \qquad H_{\rho} = \frac{\rho_M}{h_M} \left(\frac{\partial h_M}{\partial \rho_M}\right)_{T_M, x} \qquad (3.124, 3.125)$$

$$F_{T} = \frac{T_{M}}{f_{M}} \left(\frac{\partial f_{M}}{\partial T_{M}}\right)_{\rho_{M},x} \qquad \qquad H_{T} = \frac{T_{M}}{h_{M}} \left(\frac{\partial h_{M}}{\partial T_{M}}\right)_{\rho_{M},x} \qquad (3.126, 3.127)$$

The only novelty is the partial molar fugacity coefficient $\hat{\varphi}_{M,j}$ for the mixture component j, which includes also the differentiation of the scale factors with respect to the number of moles of the component j itself:

$$\ln \hat{\varphi}_{M,j} = -\ln \left[1 + u_0^R F_\rho + z_0^R \left(1 + H_\rho \right) \right] + a_0^R + u_0^R \left(F_{n_j} + F_\rho \right) + z_0^R \left(1 + H_{n_j} + H_\rho \right)$$
(3.128)

where:

$$F_{n_j} = \frac{n}{f_M} \left(\frac{\partial f_M}{\partial n_j} \right)_{T_M, \rho_M, n_{i\neq j}} = \frac{1}{f_M} \left\{ \left(\frac{\partial f_M}{\partial x_j} \right)_{T_M, \rho_M, x_{i\neq j}} - \sum_{k=1}^C \left[x_k \left(\frac{\partial f_M}{\partial x_k} \right)_{T_M, \rho_M, x_{i\neq k}} \right] \right\}$$
(3.129)

$$H_{n_{j}} = \frac{n}{h_{M}} \left(\frac{\partial h_{M}}{\partial n_{j}} \right)_{T_{M}, \rho_{M}, n_{i\neq j}} = \frac{1}{h_{M}} \left\{ \left(\frac{\partial h_{M}}{\partial x_{j}} \right)_{T_{M}, \rho_{M}, x_{i\neq j}} - \sum_{k=1}^{C} \left[x_{k} \left(\frac{\partial h_{M}}{\partial x_{k}} \right)_{T_{M}, \rho_{M}, x_{i\neq k}} \right] \right\}$$
(3.130)

The haloalkane R134a is taken as reference fluid, with the corresponding DEoS from Tillner-Roth and Baehr [66].

Also in this case the analytical form of the scale factors is expressed through a MLFN with a single hidden layer. The input variables are temperature and density of the mixture plus C-1 molar compositions, while the output variables are the scale factors. Therefore, it is:

$$I = C + 2 V_1 = T_M V_2 = \rho_M V_3 = x_1 \dots V_i = x_{i-2} \dots V_{I-1} = x_{C-1} (3.131)$$

$$K = 2 W_1 = f_M(T_M, \rho_M, \mathbf{x}) W_2 = h_M(T_M, \rho_M, \mathbf{x}) (3.132)$$

Considering Eqs. (3.131) and (3.132), the scale function derivatives in Eqs. (3.124-3.127, 3.129, 3.130) are calculated by Eq. A1.14 in Appendix A.1.

The training of the ECS-NN model aims at determining the individual scale functions over the entire (ρ, T, \mathbf{x}) domain of the mixture of interest through an optimization procedure. As in the case of pure fluids, the present inputs are density data (T, P, ρ, \mathbf{x}) covering the vapor, liquid, and supercritical regions, together with vapor-liquid equilibrium (VLE) data in the forms $(T, P^s, \mathbf{x}^s, \mathbf{y}^s)$, $(T, P^s, \rho^{st}, \mathbf{x}^s)$ and $(T, P^s, \rho^{sv}, \mathbf{y}^s)$. These VLE data are indispensable to locate the bubble and dew surfaces of the mixture.

It is worth noticing that the functional dependence of the mixture model from composition arises directly from the generation of the scale factors functions, because the reference pure fluid DEoS has obviously no composition dependence. The mathematical formulation of the composition dependence of the model is learnt by the MLFN during the training step.

In general the accuracies reached by the proposed modeling method can be regarded as quite close to those obtained by the corresponding DEoSs developed according to the method of Tillner-Roth [67-70], see also paragraph 3.7.

From the procedure presented in the preceding, for a mixture M of C components in the independent variables T_M , ρ_M and $\mathbf{x} (= x_1, ..., x_{C-1})$ the continuous scale factor functions $f_M(T_M, \rho_M, \mathbf{x})$ and $h_M(T_M, \rho_M, \mathbf{x})$ are obtained. Their composition dependence can be studied generating sections of these surfaces for constant values of some of the variables.

As an example, in Fig. 3.7 sections of f_M and h_M for the binary mixture R32/R125 are shown as a function of composition x_{R32} for given values of the variables T_M , ρ_M . It is worth noticing that the values of f_M and h_M at the composition bounds represent the scale factors values of the pure components R32 and R125, with respect to the reference fluid R134a, at the present temperature and density. Very regular curves result for this mixture, indicating that the surfaces of both the scale factors are very smooth. A similar behavior was verified for all the other mixtures studied in Ref. 57.



Figure 3.7: Plots of the ECS-NN scale factors f_M and h_M for the mixture R32/R125 for selected values of T_M and ρ_M .

It has been demonstrated that the shape functions regressed according to this technique on volumetric and saturation data are able to reproduce the other thermodynamic functions, as for instance Helmholtz energy and internal energy: this is a proof of the internal consistence of the proposed ECS-NN model. The uncertainties reached in the representation of the thermodynamic properties are at a level similar to group-two DEoSs for pure fluids (see Paragraph 3.7) and to the most advanced correlative techniques for mixtures. Therefore, the incorporation of a MLFN into a mathematically coherent corresponding states framework makes the ECS method suitable to reach a level of accuracy comparable to that of the DEoSs with optimized functional forms on multi-property data sets.

After these preliminary studies the ECS-NN modeling technique has been applied to a real case in order to obtain a DEoS using experimental data instead of generated data. In Ref. 71 the binary mixture composed by the refrigerant R134a and the lubricant Triethylene Glycol Dimethyl Ether (TriEGDME) has been studied as a representative system of the working fluids encountered in refrigeration plants.

Two dedicated equations of state in ECS-NN format has been developed, basing them on the available experimental data for the chosen system. The first one was obtained from data specifically measured for this modeling work and it covers the composition range that is usual for a refrigeration plant. The second equation was regressed from a larger data base, including also other available literature data, and it has a wider validity range. Both the equations reproduce the available experimental data within their experimental uncertainties.

The obtained results show the potentiality and the accuracy of the proposed modeling technique. The application of this method can be effectively extended to asymmetric systems, even where one of the components is practically unknown from the thermodynamic point of view.

3.7. Optimized multiparameter equations of state

The equations of state in optimized functional form were developed starting from 1985, when Schmidt and Wagner published an EoS for oxygen [22] in this format. In the following years this approach has been so widely applied and improved that at present it constitutes the standard procedure to develop high quality equations of state for pure fluids and mixtures valid in a wide range of fluid conditions. Such technique belongs to the group of the heuristic correlative methods and then it requires a large amount of experimental data of different thermodynamic properties for the fluid of interest. The result is a *dedicated* equation of state (DEoS), i.e. the equation is specific for the interest fluid.

The performances achievable with this method are excellent; in fact the equations of state obtained with this technique usually represent the available experimental data in the vapor, liquid and supercritical regions well within their experimental uncertainties.

The regression procedure is mainly based on the algorithm proposed in 1989 by Setzmann and Wagner [24]: a general functional form for the reduced residual Helmholtz energy is given and the procedure is aimed at optimizing this functional form searching for the best representation of the experimental data with the lower number of terms in the final equation. A *multi-property fitting*, including at the same time data of different thermodynamic properties, is performed in order to obtain a satisfactory description of all the thermodynamic surfaces.

For a detailed and exhaustive treatment of optimized multiparameter equations of state and of their regression techniques, reference is made to Ref. 25. In the following sections the mathematical structure of these thermodynamic models is presented both for pure fluids and for mixtures, together with the list of the at present available dedicated equations of state developed with the optimization technique.

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The equations of state belonging to this class are focused on directly representing the reduced residual Helmholtz free energy a^{R} of the fluid of interest. The general forms of a^{R} have been empirically set up and they are at present well established from experience [25]. The simplest version of such forms can be written as a sum of *polynomial* terms and *exponential* terms depending on inverse reduced temperature and on reduced density:

$$a^{R}(\tau,\delta) = a_{pol}^{R} + a_{exp}^{R} = \sum_{i=1}^{I_{pol}} n_{i}\tau^{t_{i}}\delta^{d_{i}} + \sum_{i=I_{pol}+1}^{I_{pol}+I_{exp}} n_{i}\tau^{t_{i}}\delta^{d_{i}}e^{-\delta^{p_{i}}}$$
(3.133)

where:

$$\tau = T_c / T \qquad \qquad \delta = \rho / \rho_c \qquad (3.134, 3.135)$$

The exponents t_i , d_i and p_i are set to values whose ranges are chosen by experience. It is common practice to give small positive integer values to the d_i and p_i parameters, while for t_i fractional values are also assumed.

All the thermodynamic properties are calculated from Eq. (3.133) and its derivatives with respect to the independent variables.

The terms to include in the final equation and the values of the coefficients n are obtained through the optimization algorithm on the basis of the available experimental data of several thermodynamic properties, that have to be as precise as possible.

The optimized multiparameter equations of state that include only polynomial and exponential terms are able to describe the whole fluid region with the highest accuracy, except in the critical region. In order to further improve the representation of thermodynamic properties also in the critical region, the bank of terms, Eq. (3.133), has been extended with *modified Gaussian bell shaped* terms:
$$a^{R}(\tau,\delta) = a_{pol}^{R} + a_{exp}^{R} + a_{GBS}^{R} = \sum_{i=1}^{I_{pol}} n_{i} \tau^{t_{i}} \delta^{d_{i}} + \sum_{i=I_{pol}+1}^{I_{pol}+I_{exp}} n_{i} \tau^{t_{i}} \delta^{d_{i}} e^{-\delta^{p_{i}}} + \frac{I_{pol}+I_{exp}+I_{GBS}}{\sum_{i=I_{pol}+I_{exp}+1}^{I_{pol}+I_{exp}+I_{GBS}} n_{i} \tau^{t_{i}} \delta^{d_{i}} e^{-\eta_{i} (\delta-\varepsilon_{i})^{2} - \beta_{i} (\tau-\gamma_{i})^{2}}$$
(3.136)

in which the internal parameters η_i , β_i , ε_i and γ_i are in general different among the terms, even if usually it is $\varepsilon_i = 1$.

Equations with these new terms can well represent the most accurate experimental data for thermodynamic properties in the critical region, but they fail for heat capacities and speeds of sound very close to the critical point. A further type of terms, namely *non-analytical* terms, was introduced into the bank of terms to correct even these discrepancies, so the most general expression for a^{R} reads:

$$a^{R}(\tau,\delta) = a_{pol}^{R} + a_{exp}^{R} + a_{GBS}^{R} + a_{NA}^{R} = \sum_{i=1}^{I_{pol}} n_{i} \tau^{t_{i}} \delta^{d_{i}} + \sum_{i=I_{pol}+1}^{I_{pol}+I_{exp}} n_{i} \tau^{t_{i}} \delta^{d_{i}} e^{-\delta^{p_{i}}} + \sum_{i=I_{pol}+I_{exp}+1}^{I_{pol}+I_{exp}+I_{GBS}} n_{i} \tau^{t_{i}} \delta^{d_{i}} e^{-\eta_{i}(\delta-\varepsilon_{i})^{2} - \beta_{i}(\tau-\gamma_{i})^{2}} + \sum_{i=I_{pol}+I_{exp}+I_{GBS}+1}^{I_{pol}+I_{exp}+I_{GBS}+I_{NA}} n_{i} \delta \Delta^{b_{i}} e^{-e_{i}(\delta-1)^{2} - f_{i}(\tau-1)^{2}}$$

$$(3.137)$$

where:

$$\Delta = \left\{ \left(1 - \tau\right) + c_i \left[\left(\delta - 1\right)^2 \right]^{1/(2\beta_i)} \right\}^2 + d_i \left[\left(\delta - 1\right)^2 \right]^{a_i}$$
(3.138)

The values of the internal parameters a_i , b_i , c_i , d_i , e_i , f_i and β_i are term-specific and they are chosen observing some important requirements [25].

The most complex form of the bank of terms, Eq. (3.137), is used only for reference equations dedicated to substances for which both the critical region is regarded as very important and very accurate experimental data in that region are available; otherwise the higher analytical complication and the numerical expense are not justified.

The *reference* EoSs are able to represent the experimental data for the thermodynamic properties of the corresponding fluid within their experimental uncertainties and can be used both as scientific and technical standards. Considering the regression technique and the available experimental data from which the equations were obtained, they are divided into two categories:

 group-one reference equations are highly accurate EoSs with excellent representation of also the critical region and with reasonable extrapolation behavior. Such equations describe the thermodynamic properties of the fluid with an accuracy corresponding to the accuracy that can be reached using state-of-the-art experimental techniques. Their development requires a huge number of measurements of exceptionally high quality and then they are made available only for few substances. Group-one EoSs can be used both for technical and for advanced scientific applications, as for instance calibration of instruments and test of physical models. In Table 3.2 the group-one optimized multiparameter equations of state developed up to date are listed.

group-two reference equations are high quality EoSs, but they do not satisfy the requirements of group-one equations because of limitations in distribution and/or in quality of the available experimental data, or due to the adopted regression technique. The equations in this group do not include terms for the description of the critical region; they are less accurate of group-one equations, but anyway they are accurate enough for most technical applications and for various scientific applications. Nevertheless, care is necessary when very high accuracies are required. A consistent number of group-two equations has been developed so far. Some of them are in a MBWR format [20] and then they do not belong to the family of optimized multiparameter EoSs.

		Range of v	validity	
Fluid	Literature reference	Т	$P_{\rm max}$	Type of terms ^a
		(K)	(MPa)	
	Group-one reference equa	ations of state		
Argon	Tegeler et al., 1999 [72]	83–700	1000	pol, exp, GBS
Nitrogen	Span et al., 1998 [73]	63–1000	2200	pol, exp, GBS
Carbon dioxide	Span and Wagner, 1996 [74]	216–1100	800	pol, exp, GBS, NA
Water	Wagner and Pruß, 2002 [75]	273–1273	1000	pol, exp, GBS, NA
Methane	Setzmann and Wagner, 1991 [76]	90–625	1000	pol, exp, GBS
Ethylene	Smukula et al., 2000 [77]	104–450	300	pol, exp, GBS

Table 3.2: Recent reference equations of state for pure fluids.

pol=polynomial terms; exp=exponential terms; GBS=Gaussian bell shaped terms; NA=non-analytical terms.

Apart from the reference equations, *technical* equations of state are available for many fluids. These are simple multiparameter equations, like BWR [6], Starling [18] or Bender [19] equations, that are often used in technical applications even if their accuracy is questionable. Moreover, Span and Wagner have recently developed technical EoSs [78] for both non-polar [79] and polar fluids [80]; such equations are much more accurate than the other technical ones and their performances are comparable with group-two EoSs. Recently Lemmon and Span [81] used the same functional

forms regressed in the aforementioned works for non-polar and polar fluids to develop fundamental equations for other fluids of industrial interest.

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As for pure fluids, all the thermodynamic properties of a mixture can be calculated from an analytical expression for the Helmholtz free energy, that in this case depends also on molar composition. The same equations reported in Appendix A.2 are still valid, with the further addition of the partial molar fugacity coefficients of the components.

The procedure adopted for developing a mixture equation of state requires the availability of the equations of state for all the involved pure components. In fact the mixture EoS is obtained 'mixing' the equations of the pure fluids and adding a departure function [70], composing a *multi-fluid* model.

The mixture reduced molar Helmholtz free energy reads:

$$a_{M}\left(T,\rho_{m},\boldsymbol{x}\right) = \frac{A_{m,M}}{R_{m}T} = a_{M}^{o}\left(T,\rho_{m},\boldsymbol{x}\right) + a_{M}^{R}\left(\tau,\delta,\boldsymbol{x}\right)$$
(3.139)

According to classical thermodynamics, the ideal part is obtained as a linear combination of the ideal parts of the pure components, plus the Helmholtz energy change for mixing of ideal gases:

$$a_{M}^{o}(T,\rho_{m},\boldsymbol{x}) = \sum_{i=1}^{C} x_{i} a_{i}^{o}(T,\rho_{m}) + \sum_{i=1}^{C} x_{i} \ln x_{i}$$
(3.140)

The residual part is usually described with the form:

$$a_{M}^{R}(\tau,\delta,\mathbf{x}) = \sum_{i=1}^{C} x_{i} a_{i}^{R}(\tau,\delta) + \Delta a_{M}^{R}(\tau,\delta,\mathbf{x})$$
(3.141)

in which the *departure function* Δa_M^R is expressed by:

$$\Delta a_M^R(\tau,\delta,\mathbf{x}) = \sum_{i=1}^{C-1} \sum_{j=i+1}^C f(x_i, x_j) \Delta a_{ij}^R(\tau,\delta)$$
(3.142)

The function f usually assumes the simple form [67,82-84]:

$$f(x_i, x_j) = x_i x_j \tag{3.143}$$

but in other cases [68,69] dealing with binary mixtures an adjustable parameter γ is also introduced to allow asymmetric influences of the departure function:

$$f(x_i, x_j) = f(x) = x(1 - x^{\gamma})$$
(3.144)

The binary departure functions can be written in a general form [67] as:

,

$$\Delta a_{ij}^{R}(\tau,\delta) = \sum_{k=1}^{K_{pol}} n_{k} \tau^{t_{k}} \delta^{d_{k}} + \sum_{k=K_{pol}+1}^{K_{pol}+K_{exp}} n_{k} \tau^{t_{k}} \delta^{d_{k}} e^{-\delta^{p_{k}}}$$
(3.145)

and the reduced variables τ and δ are obtained from the physical variables T and ρ_m using pseudo-critical parameters as reducing factors:

$$\tau = \frac{T_{c,M}(\mathbf{x})}{T} \qquad \qquad \delta = \frac{\rho_m}{\rho_{m,c,M}(\mathbf{x})} \qquad (3.146, 3.147)$$

Different suitable mixing rules [67-70,82-84] have been proposed to calculate the pseudo-critical parameters. For instance, in Ref. 67 they are:

$$T_{c,M}(\mathbf{x}) = \sum_{i=1}^{C} \sum_{j=1}^{C} x_i x_j \frac{A_{ij}(x_i + x_j) + 1}{A_{ij} + 1} T_{c,ij}$$
(3.148)

$$\frac{1}{\rho_{m,c,M}(\mathbf{x})} = v_{m,c,M}(\mathbf{x}) = \sum_{i=1}^{C} \sum_{j=1}^{C} x_i x_j \frac{B_{ij}(x_i + x_j) + 1}{B_{ij} + 1} v_{m,c,ij}$$
(3.149)

$$T_{c,ij} = \frac{k_{T,ij}}{2} \left(T_{c,i} + T_{c,j} \right) \qquad v_{m,c,ij} = \frac{k_{v,ij}}{2} \left(\frac{1}{\rho_{m,c,i}} + \frac{1}{\rho_{m,c,j}} \right) \qquad (3.150, 3.151)$$

where $T_{c,i}$ and $\rho_{m,c,i}$ are the critical temperature and the critical molar density of the component *i*, while A_{ij} , B_{ij} , $k_{T,ij}$ and $k_{v,ij}$ are interaction parameters regressed on data; A_{ij} and B_{ij} influence the equation of state only for non-binary mixtures and they are set to values different from zero when it is strictly necessary to improve the equation performances.

The development of an equation of state for a mixture requires experimental data of different thermodynamic properties evenly distributed also in the composition variable. Moreover, the availability of an equation of state in terms of Helmholtz energy for each pure fluid composing the mixture is a necessary prerequisite.

The goal of the fitting procedure is to find the suitable functional form for the departure function and to get the numerical values of the coefficients and of the adjustable parameters. This can be performed with an optimization procedure of the functional form similar to that applied to pure fluid EoSs development [67-69,84], even if this case presents some more complications and it is less straightforward. A simple equation with a limited number of free parameters can also be assumed for the departure function, in this way reducing the fitting procedure to the regression of the coefficients without optimization of the functional form [82,83]. The second procedure is easier, but at the same time it is less flexible.

In any case, the development of equations of state for mixtures with these techniques is not so well established as for pure fluids and it was applied to a quite limited number of binary and ternary systems, also due to the scarcity of experimental data available for mixtures; in fact an extensive data base covering the interest ranges of the independent variables is required for the target mixture. A list of the most precise multiparameter equations of state at present available for mixtures is reported in Table 3.3.

		Range of v	f validity	
Mixture	Literature reference	Т	$P_{\rm max}$	
		(K)	(MPa)	
Water / ammonia	Tillner-Roth and Friend, 1998 [69]	b	40	
Dronone / a butere	Miyamoto and Watanabe, 2003	000 500	<u> </u>	
Propane / n-outane	[84]	228-589	69	
Duanana / isahutana	Miyamoto and Watanabe, 2003	000 570	25	
Propane / isobutane	[84]	203-573	35	
N hutere / inchutere	Miyamoto and Watanabe, 2003	070 570	25	
N-butane / isobutane	[84]	213-513	30	
Decements (a bastance (is a bastance	Miyamoto and Watanabe, 2003	070 570	05	
Propane / n-butane / isobutane	[84]	273-573	35	
R32 / R125	Tillner-Roth et al., 1998 [67]	200–440	35	
R32 / R134a	Tillner-Roth et al., 1998 [67]	200–440	35	
R125 / R134a	Tillner-Roth et al., 1998 [67]	200–413	35	
R125 / R143a	Tillner-Roth et al., 1998 [67]	200–413	35	
R143 / R134a	Tillner-Roth et al., 1998 [67]	243–413	17	
R32 / R125 / R134a	Tillner-Roth et al., 1998 [67]	243–440	17	
R125 / R143a / R134a	Tillner-Roth et al., 1998 [67]	243–413	17	
R134a / R152a	Tillner-Roth, 1993 [68]	243-433	17	

Table 3.3: Recent equations of state for mixtures.

^b valid from the freezing line to the critical locus.

Lemmon and Jacobsen have also proposed a generalized mixture model [82] that has been applied to several binary mixtures between alkanes, nitrogen, carbon dioxide, argon and air.

3.8. References

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IV. An extended equation of state modeling technique

4.1. Introduction

In the former Paragraph 3.6.4 it has been discussed how to turn the ECS model into a powerful heuristic technique for the development of high accuracy equations of state. The basic requirements are anyway the fulfillment of a conformality condition between the reference and the target fluid, and the availability of an accurate equation of state in terms of Helmholtz energy for the reference fluid; even if it has been demonstrated that also fluids not pertaining to the same family of the reference one can be satisfactorily described through the ECS-NN technique, a large lack of conformality can in principle prevent from obtaining a reliable equation for the target fluid.

In the case that either the conformality condition is not verified among the fluids of a same family or no component of the family, whose fluids are supposed to share a conformality condition, disposes of a DEoS, the discussed ECS method cannot in general be effectually applied. Where the corresponding states conformality fails, the similitude connection among the fluids of the family is no longer sustainable and the method is supposed to become ineffective. On the other hand the unavailability of a reference DEoS practically prevents the application of the method, with an equivalent final result of failure of the modeling technique.

In these conditions one could wonder whether the 'correction' through the variables distortion could be profitably performed on a simple EoS representing, even if roughly, the target fluid itself. In other words the question is posed whether a simple EoS for the same target fluid could be a suitable starting point for the development of a DEoS through the variables distortion, avoiding in this way any problem about the conformality condition fulfillment. It would be then no more necessary to dispose of a 'reference fluid', following the classical interpretation of the ECS theory, but rather of only a 'reference equation', whose precision is enhanced, or 'extended', through the application of the shape functions. Hence the name of *extended equation of state* (EEoS) chosen to indicate this new modeling method.

Moreover, a basic requirement for the present technique is to obtain for the fluid of interest a DEoS in the default fundamental form $a(T, \rho)$ which allows to calculate any thermodynamic quantity through mathematical derivations only.

The simplest, but at the meantime sound, EoS that it is possible to choose for the present purpose is the cubic EoS in one of its more recurrent versions, see Paragraph 3.3. In this chapter an SRK cubic EoS with the Peneloux volume translation is assumed, due to its general applicability to practically any fluid since only the critical parameters and few saturation data are individually required. Anyway, the proposed method is not bound to the choice of a cubic EoS, but any fundamental EoS can be suitably assumed independently from its functional form, provided that the independent variables are T, ρ to which to apply the shape functions distortion. Furthermore, this allows to get a fundamental DEoS for the target fluid.

As in the case of ECS-NN model, the shape functions $\theta(T, \rho)$ and $\phi(T, \rho)$ have to be regressed forcing the model to represent known values of experimentally accessible thermodynamic quantities; their functional formulation is heuristically obtained applying a multilayer feed-forward neural network as universal function approximator. In this chapter the purpose is to set up the method and to test its potentialities; therefore data generated from a DEoS for each target fluid are used instead of experimental data, so that the model performances are not hindered by error noise and uneven data distribution. The application to experimental data is treated in Chapters V and VI for the fluids sulfur hexafluoride and 2-propanol respectively.

The proposed modeling technique comes from the combination of the EEoS method with the neural networks and then it can be concisely indicated as *EEoS-NN* model.

4.2. Pure fluids

4.2.1. Mathematical formulation

The mathematical structure of the EEoS-NN model is the same of the ECS-NN format exposed in Paragraph 3.6.4. The only difference resides in the calculation of the reference fluid properties: whereas in that case an EoS for the reference fluid was required, in the present one the reference properties are simply calculated from the SRK cubic EoS for the target fluid itself through the expressions given in Appendix A.3.

The set up of the SRK EoS requires only the critical parameters, the acentric factor, i.e. a value of saturation pressure, and a value of saturated liquid density to determine the Peneloux volume translation coefficient.

The mathematical structure of the EEoS-NN model for pure fluids is described by Eqs. (3.81-3.83); since in this framework the target and the reference fluid coincide, their critical parameters are the same and then the scale factors are identical to the respective shape functions:

$$f_{j}\left(T_{j},\rho_{j}\right) = \frac{T_{c,j}}{T_{c,0}}\theta_{j}\left(T_{j},\rho_{j}\right) = \theta_{j}\left(T_{j},\rho_{j}\right)$$

$$(4.1)$$

$$h_{j}\left(T_{j},\rho_{j}\right) = \frac{\rho_{c,0}}{\rho_{c,j}}\phi_{j}\left(T_{j},\rho_{j}\right) = \phi_{j}\left(T_{j},\rho_{j}\right)$$

$$(4.2)$$

With reference to Paragraph 2.2 and in particular to Figs. 2.1 and 2.3, it is:

$$I = 3$$
 $V_1 = T_j$ $V_2 = \rho_j$ (4.3, 4.4, 4.5)

$$K = 2 W_1 = \theta_j (T_j, \rho_j) W_2 = \phi_j (T_j, \rho_j) (4.6, 4.7, 4.8)$$

In the EEoS-NN case the independent variables of the shape functions are T_j and ρ_j , therefore the shape function derivatives included in the expressions for the calculation of the other thermodynamic properties, as for instance Eqs. (3.89) and (3.91), are directly calculated by Eq. A1.14 in Appendix A.1.

The transfer function assumed for the present case is the normalized scaled arctangent:

$$f(x) = \frac{1}{\pi}\arctan(\gamma x) + \frac{1}{2}$$
(4.9)

with $\gamma = 0.1$. In the following Paragraphs 4.2.2 and 4.2.3, the number of neurons in the hidden layer has been chosen as J = 9.

4.2.2. Training of the EEoS-NN model

Since the main aims of the present paragraph and the following Paragraph 4.2.3 are to test the proposed modeling technique and to verify its performances for a group of pure fluids, it was decided to use generated data of thermodynamic properties instead of experimental data. In this way the results of the analysis are not affected by the drawbacks related to experimental data. In fact these are in general affected by a significant experimental error noise, with a different accuracy for each thermodynamic quantity, and they are irregularly distributed in the (T, P) range of interest.

These aspects hinder the evaluation of the quality of a heuristic model. Thus, it was preferred not to assume experimental values for the model training and validation, but rather to use pseudoexperimental values generated on a regular grid of the independent variables from the DEoSs of the studied fluids. The surfaces represented by these equations are considered as 'true', as they are the best representation of the available experimental data base, and then the proposed method is evaluated in the most favorable conditions. The use of experimental data for obtaining a dedicated EoS for pure fluids in the EEoS-NN format will be the matter of Chapters V and VI.

Since the constraint of conformality between the target and the reference fluid affecting the ECS methods is in this work overcome, the considered fluids can belong to different chemical families. The chosen fluids, listed in Table 4.1, are divided into a group of non-polar fluids (three alkanes), a

group of polar fluids (four haloalkanes), and a group of strongly polar fluids (ammonia and water). The difficulties in accurately describing the properties of the selected fluids increase in this order.

For each of the considered substances, the fluid-specific Peneloux coefficient c, that is required for the chosen reference equation, has been determined from a saturated liquid density value generated with the DEoS of the target fluid at $T_r = 0.7$. For the considered fluids the critical constants, the acentric factor ω , and the parameter c, together with the literature references for the DEoSs from which the saturated liquid densities have been calculated, are reported in the same Table 4.1.

Fluid	<i>T_c</i> (K)	P_c (MPa)	ω	$\frac{c}{(1 \text{ mol}^{-1})}$	Ref.
C_2H_6	305.33	4.8718	0.0993	2.86496×10 ⁻³	[1]
C_3H_8	369.85	4.24766	0.15242	5.20115×10 ⁻³	[2]
$n-C_4H_{10}$	425.16	3.796	0.19959	7.85903×10 ⁻³	[2]
R32	351.255	5.782	0.2768	1.29133×10 ⁻²	[3]
R125	339.33	3.629	0.30349	7.79698×10 ⁻³	[4]
R134a	374.18	4.05629	0.32689	1.13412×10 ⁻²	[5]
R143a	346.04	3.7756	0.26113	1.34996×10 ⁻²	[6]
NH_3	405.4	11.333	0.25601	7.23145×10 ⁻³	[7]
H_2O	647.096	22.064	0.344	7.59369×10 ⁻³	[8]

Table 4.1: Physical constants for the nine pure fluids here considered.

The training of the neural network is performed minimizing an objective function, expressed in terms of mean squared error, which can include properties of different nature as in a multi-property fitting framework.

In a first step the EEoS-NN model is heuristically developed from density and coexistence properties assuming an objective function that includes both volumetric and saturation data, being composed of two parts. The one for volumetric data reads:

$$f_{ob,z} = \frac{1}{n_z} \sum_{i=1}^{n_z} \left(\frac{z_{j,DEoS}^R - z_{j,calc}^R}{z_{j,DEoS}^R} \right)_i^2$$
(4.10)

while that for saturation properties reads:

$$f_{ob,\varphi} = \frac{1}{n_{\varphi}} \sum_{i=1}^{n_{\varphi}} \left\{ \ln \varphi_{j,calc} \left[T, \rho_{DEoS}^{sl} \left(T \right) \right] - \ln \varphi_{j,calc} \left[T, \rho_{DEoS}^{sv} \left(T \right) \right] \right\}_{i}^{2}$$

$$(4.11)$$

where n_z and n_{φ} are the number of points composing the volumetric and the saturation properties training set, respectively.

The two objective functions, Eqs. (4.10) and (4.11), are composed together to form the overall objective function:

$$f_{ob, overall} = 0.8 f_{ob, z} + 0.2 f_{ob, \varphi}$$
(4.12)

in which the two functions $f_{ob,z}$ and $f_{ob,\varphi}$ are differently weighted.

In a second step of the study the EEoS-NN model is regressed assuming an objective function which includes also caloric quantities, together with the unavoidable volumetric and saturation properties. The considered caloric properties are isochoric heat capacity, isobaric heat capacity and speed of sound. In the objective function represented by Eq. (4.12) the term $f_{ob,z}$ is substituted by:

$$f_{ob,1} = \frac{1}{P n_1} \sum_{p=1}^{P} \xi_p \sum_{i=1}^{n_1} \left[\left(\frac{M_{j,DEoS}^R - M_{j,calc}^R}{M_{j,DEoS}^R} \right)_i \right]_p^2$$
(4.13)

where the $p^{-\text{th}}$ property M represents alternatively the compressibility factor Z, the isochoric heat capacity C_v , the isobaric heat capacity C_p , and the speed of sound w; in this case it is P = 4. Each of the four mentioned properties is composed of the same number of values n_1 and its contribution is weighted in the summation according to the individual factor ξ_p .

The part $f_{ob,\phi}$ is still represented by the former Eq. (4.11); the two contributions are combined together according to Eq. (4.12) again.

For each fluid considered in the present study, the DEoSs listed in Tab. 4.1 have been used to generate sets of values of several thermodynamic properties in the temperature and pressure ranges indicated in Table 4.2, taking care of having them distributed on a regular grid. The steps of the grid are fluid-specific, because they depend on the validity ranges of the corresponding DEoS aiming at obtaining the same number of points for each fluid; they are here not reported for brevity. The thermodynamic surface was divided into three regions: the liquid phase (denoted by 'l') for $T < T_c$ and $P > P^{sat}$, the supercritical condition (denoted by 'sc') for $T > T_c$ and $P > P_c$, and the vapor phase (denoted by 'v') for the remaining domain.

Besides density and saturation properties, the reduced residual functions of Helmholtz energy a^{R} , internal energy u^{R} , entropy s^{R} , enthalpy h^{R} , and Gibbs energy g^{R} have been considered.

These last functions are also indicated as 'first order' thermodynamic properties because they are analytically obtained from a^{R} through first order derivatives.

It has been furthermore considered the group of thermodynamic properties involving higher order derivatives of a^R , e.g. reduced residual isochoric heat capacity c_v^R , reduced residual isobaric heat capacity c_v^R , and speed of sound w; they are termed as 'second order' properties.

For each fluid and each property, both of the first and of the second order group of quantities, 5329 points were generated on the cited grid. Moreover, a certain number of points at saturation in the form $(T, P^s, \rho^{sl}, \rho^{sv})$ were generated as well.

For each of the two training steps above described, two data sets have been composed: one for training itself and the other for validation. For the first training process the distribution of the two data sets can be seen from Table 4.2. The training subset for this case has been obtained regularly extracting density values from the generated data on the original grid. For the validation set the remaining values of the grid have been taken. For the second training step, the training set for each of the four thermodynamic quantities included in the objective function has been as well regularly extracted from the same original grid, but with a larger interval. Also in this case the validation set has been composed of the remaining values of generated data. The distribution of these two data sets in the different thermodynamic regions is reported in Table 4.3.

Both the steps of the regression procedure have been applied to each considered fluid.

	T range	P range	Training NPT						Validation NPT					
Fluid	(K)	(MPa)		Ρ, μ	<i>э</i> , <i>Т</i>		$P, \rho, T \Big _{\text{VLE}}$	Each	of nine	e prope	rties ^a	$P, \rho, T \Big _{\text{VLE}}$		
			sc	1	v	total		sc	1	v	total			
C_2H_6	200-400	0.08-10	156	269	200	625	13	1174	2032	1498	4704	24		
C_3H_8	200-400	0.08-10	56	462	107	625	21	406	3553	745	4704	40		
$n-C_4H_{10}$	200-450	0.08-10	48	501	76	625	22	320	3856	528	4704	42		
R32	200-400	0.08-10	67	396	162	625	18	492	3017	1195	4704	36		
R125	200-400	0.08-10	128	380	117	625	17	906	2973	825	4704	33		
R134a	200-400	0.08-10	60	476	89	625	21	380	3693	631	4704	41		
R143a	200-400	0.08-10	112	401	112	625	18	808	3082	814	4704	34		
NH_3	200-450	0.08-14	25	411	189	625	20	157	3151	1396	4704	39		
H_2O	300-700	0.08-25	12	434	179	625	21	78	3335	1291	4704	41		

Table 4.2: Characteristics of pseudo-experimental data generated from the DEoSs for the nine pure fluids here considered. Case of regression on density and coexistence data.

^a properties: Z, a^R , u^R , s^R , h^R , g^R , c_v , c_p , w.

			Tra N	uining IPT		Validation NPT							
Fluid	Eacl	n of fou	r prop	erties ^b	$P, \rho, T \Big _{\text{VLE}}$	Ea	ach of nir	ne proper	ties ^c	$P, \rho, T \Big _{\text{VLE}}$			
	sc	1	v	overall		sc	1	v	overall				
C_2H_6	28	52	37	117	13	1302	2249	1661	5212	24			
C_3H_8	14	80	23	117	21	448	3935	829	5212	40			
$n-C_4H_{10}$	8	92	17	117	22	360	4265	587	5212	42			
R32	13	73	31	117	18	546	3340	1326	5212	36			
R125	24	69	24	117	17	1010	3284	918	5212	33			
R134a	16	83	18	117	21	424	4086	702	5212	41			
R143a	24	70	23	117	18	896	3413	903	5212	34			
NH_3	6	75	36	117	20	176	3487	1549	5212	39			
H ₂ O	4	115	50	169	21	86	3654	1420	5160	41			

Table 4.3: Dimensions of training and validation sets for the nine pure fluids. Multi-property case.

^b properties: Z, c_v , c_p , w.

^c properties: Z, a^R , u^R , s^R , h^R , g^R , c_v , c_p , w.

4.2.3. Validation

In the present section the validation of the obtained models is reported using the statistical indexes defined in Appendix A.6.

SRK CUBIC EOS WITH VOLUME TRANSLATION

As a first step, it is interesting to evaluate the prediction capability of the equation assumed as reference for the EEoS-NN technique, that is the SRK with the Peneloux volume translation.

The validation sets from Table 4.2 are used. The results for the first order properties are presented in detail for each fluid in Table 4.4. The following conclusions can be drawn from these results:

- notwithstanding the Peneloux volume translation, the prediction accuracy of the SRK equation for density is still far from being comparable to that of a DEoS, particularly for polar fluids. This can be argued looking at the results for Z and z^R in particular for R32, R143a, ammonia, and water. Even for simple alkanes the prediction accuracy is not homogeneous for different regions of the $P\rho T$ surface;
- increased errors are observed for properties involving the a^R derivatives with respect to temperature, such as u^R , h^R , and s^R . For them it was verified that the deviations are sometimes higher than 20% in the vapor region of the $P\rho T$ surface;

 for polar fluids the prediction accuracy is usually worse than that for non-polar ones, see for instance the alkanes.

Table 4.4: Accuracy of the SRK equation in terms of AAD for first order properties in the three main thermodynamic regions.

				A	AAD (%)				
		z^{R}			u^{R}			h^{R}	
Fluid	sc	1	v	sc	1	v	sc	1	v
C_2H_6	3.79	0.75	1.37	3.44	1.44	5.44	2.59	1.32	4.05
C_3H_8	4.68	0.73	1.72	3.05	1.18	6.87	3.35	1.10	5.12
$n-C_4H_{10}$	4.83	0.77	2.27	3.59	1.26	9.53	3.77	1.18	6.97
R32	5.99	0.77	7.06	7.87	2.83	19.67	7.44	2.59	16.30
R125	5.76	0.81	2.83	3.81	1.07	11.38	3.04	0.98	7.84
R134a	5.67	0.77	3.28	4.95	1.41	14.38	5.03	1.32	11.34
R143a	6.70	0.91	4.86	3.31	1.99	12.14	3.88	1.84	10.09
NH_3	3.51	0.54	5.49	9.60	2.85	21.16	8.13	2.60	16.95
H_2O	2.24	0.70	6.76	11.67	4.51	19.16	9.24	4.17	14.22
Mean	5.16	0.75	4.23	4.39	2.06	13.94	4.04	1.90	10.86
		a^{R}			g^{R}			s^{R}	
Fluid	sc	1	v	sc	1	v	sc	1	v
C_2H_6	3.24	1.83	1.73	3.47	1.49	1.49	4.96	2.53	9.31
C_3H_8	6.23	1.44	1.85	5.66	1.21	1.73	1.78	2.13	12.04
$n-C_4H_{10}$	6.60	1.37	2.45	5.96	1.17	2.29	2.44	2.17	16.87
R32	9.05	2.91	7.58	7.87	2.33	7.33	7.02	5.31	27.07
R125	7.11	1.64	3.42	6.58	1.37	3.14	8.25	2.15	21.25
R134a	8.17	1.79	3.09	7.26	1.49	3.17	3.32	2.46	21.44
R143a	8.80	2.28	5.10	8.03	1.88	4.99	2.70	4.01	17.04
NH_3	4.40	2.40	5.32	4.08	1.92	5.39	12.93	5.02	30.78
H_2O	5.67	3.12	8.03	3.84	2.59	7.29	18.96	31.19	7.29
Mean	6.50	2.07	4.60	5.99	1.71	4.38	5.34	6.44	18.10

The second order properties are considered in Table 4.5, where the heat capacities are examined both as residual and as overall quantities. Deviations for these properties are larger than the ones for properties involving only first derivatives. For some fluids the AADs for the residual heat capacities are very high and in particular for c_v^R they increase to average values above 40%. The error is obviously reduced when the ideal part is considered as well. Nonetheless it is clear that the SRK EoS is not at all effective for the residual part of this group of properties. The accuracy of calculated speeds of sound in the liquid and supercritical regions ranges from 5 to 25% for all the fluids, while the accuracy in the vapor phase is significantly better. The results are very similar for non-polar and polar fluids.

Results for the representation of saturation properties are reported in Table 4.5. The saturation densities are predicted with rather high deviations and with an evident difference between the liquid

and the vapor phase. For the saturated liquid the deviations for all the fluids are several percent showing that, notwithstanding the density correction at the temperature of $T_r = 0.7$ due to the volume translation, the basic trend of a cubic EoS for the dense phase is substantially wrong. The behavior for the saturated vapor density is far better, but this is probably due to the modest contribution of the residual density function in the vapor region, where the ideal part is prevailing.

The vapor pressure P^s is rather well represented without a relevant systematic error. This behavior is coherent with the specialization of the cubic EoS in representing this property because of the *ad hoc* function $\alpha(T_r)$.

It can be concluded that the representation of thermodynamic properties by the SRK cubic EoS is not satisfying, in particular when second order properties are considered.

							_			
					AAD (%)				
		C_v^R			c_p^R				w	
Fluid	sc	1	v	sc	1	v		sc	1	V
C ₂ H ₆	34.44	57.36	53.95	7.20	13.99	13.66	-	5.21	22.13	0.41
C_3H_8	30.22	63.19	70.30	10.16	8.01	25.82		7.88	23.44	0.36
$n-C_4H_{10}$	26.94	65.74	72.73	11.23	8.12	30.20		9.65	22.83	0.39
R32	52.17	28.11	75.42	16.04	19.28	16.04		12.75	22.36	1.73
R125	34.35	58.55	68.05	10.13	7.56	23.78		7.17	26.34	0.73
R134a	27.30	40.07	74.44	13.00	10.22	36.84		8.87	24.38	0.55
R143a	36.07	50.77	71.26	11.87	11.64	32.01		8.31	25.15	0.91
NH_3	70.46	12.07	80.49	18.85	19.22	45.05		16.18	14.43	2.34
H_2O	76.14	22.18	81.53	25.64	33.69	48.56		20.18	13.45	2.29
Mean	36.99	44.26	71.78	11.17	14.48	30.18		8.34	21.61	1.24
		C_{v}			C_p			Satu	ration Prop	perties
Fluid	sc	1	v	sc	1	v		P^{s}	$ ho^{\scriptscriptstyle sl}$	$ ho^{\scriptscriptstyle sv}$
C ₂ H ₆	3.85	9.66	2.81	4.17	6.80	2.42	-	0.88	5.31	0.55
C_3H_8	3.16	8.72	3.15	5.54	3.26	3.53		1.01	4.59	0.92
$n-C_4H_{10}$	2.34	7.63	2.48	5.00	2.66	3.18		1.49	4.09	1.41
R32	14.33	9.96	10.32	11.30	11.04	10.28		1.83	6.86	3.41
R125	4.31	9.33	3.66	5.08	3.25	3.27		0.85	5.12	0.80
R134a	4.58	8.16	4.99	7.46	4.49	5.85		1.22	4.91	1.51
R143a	5.32	9.30	4.42	6.31	5.04	4.85		1.38	5.69	1.83
NH_3	25.64	5.30	14.74	13.79	11.37	13.62		2.35	6.00	4.33
H_2O	36.23	12.58	18.81	20.18	19.81	17.02		5.37	8.67	5.47
Mean	6.44	8.90	8.39	6.48	7.41	8.02	-	1.90	5.71	2.35

Table 4.5: Accuracy of the SRK equation in terms of AAD for second order properties in the three main thermodynamic regions and for saturation properties.

EEOS-NN MODEL TRAINED ON DENSITY AND COEXISTENCE DATA

In a first step the EEoS-NN model was trained for each of the fluids listed in Table 4.1 solely on volumetric and saturation data, following the regression procedure presented in Paragraph 4.4.2. Nine fluid-specific EoSs in this format were obtained.

The training procedure yields the MLFN equations for the shape functions $\theta_j(T_j, \rho_j)$ and $\phi_j(T_j, \rho_j)$ for the target fluid. In Figs. 4.1 and 4.2 the two functions are plotted for the fluid R32 as an example, showing a quite regular trend for both of them. The method is very effective in reproducing the shape of the thermodynamic surface with limited distortions of the independent variables.



Figure 4.1: Shape function $\theta_j = \theta(T_j, \rho_j)$ for the target fluid R32.



Figure 4.2: Shape Function $\phi_j = \phi(T_j, \rho_j)$ for the Target Fluid R32.

The deviations of the EEoS-NN models with respect to the data of the validation sets are summarized in Table 4.6 for first order properties, separately for the three main thermodynamic regions. The representation of these quantities can be considered excellent for all properties and the deviations are quite similar for all fluids without any noteworthy decrease of accuracy.

The three thermodynamic regions are represented with small differences: while the liquid phase is always described with an excellent accuracy, for the vapor phase some fluctuations of accuracy were found but without an apparent regularity in dependence on the fluid. In the supercritical region the model behaves quite similarly as in the vapor. Properties involving the temperature derivative of a^{R} are represented with a lower accuracy. This can be explained by the fact that the model was not trained on quantities involving temperature derivatives; except for the coexistence curve, only a volumetric property was given as input and this one solely involves the density derivative of a^{R} , see Eq. (3.89).

				1	AAD(%)				
		z^{R}			u^{R}			h^{R}	
Fluid	sc	1	v	sc	1	v	sc	1	v
C_2H_6	0.030	0.001	0.040	0.118	0.078	0.250	0.094	0.067	0.181
C_3H_8	0.100	0.001	0.089	0.258	0.072	0.265	0.219	0.063	0.199
$n-C_4H_{10}$	0.048	0.001	0.056	0.387	0.052	0.320	0.316	0.046	0.234
R32	0.045	0.001	0.047	0.169	0.063	0.242	0.137	0.055	0.184
R125	0.056	0.002	0.119	0.302	0.051	0.917	0.240	0.045	0.644
R134a	0.047	0.001	0.058	0.222	0.039	0.279	0.187	0.036	0.216
R143a	0.031	0.001	0.031	0.279	0.059	0.277	0.218	0.053	0.204
NH ₃	0.137	0.002	0.085	0.331	0.069	0.528	0.279	0.061	0.403
H_2O	0.271	0.002	0.065	0.392	0.050	0.275	0.347	0.045	0.216
Mean	0.053	0.001	0.064	0.236	0.058	0.368	0.191	0.051	0.273
		a^{R}			g^{R}			s^{R}	
Fluid	sc	1	v	sc	1	v	sc	1	v
C_2H_6	0.030	0.018	0.034	0.030	0.013	0.035	0.191	0.151	0.447
C_3H_8	0.119	0.016	0.094	0.112	0.012	0.091	0.377	0.132	0.426
$n-C_4H_{10}$	0.083	0.011	0.042	0.068	0.009	0.047	0.605	0.095	0.542
R32	0.058	0.017	0.034	0.053	0.014	0.038	0.261	0.116	0.381
R125	0.080	0.011	0.170	0.065	0.008	0.130	0.484	0.089	1.716
R134a	0.073	0.012	0.036	0.062	0.009	0.044	0.315	0.071	0.435
R143a	0.043	0.018	0.029	0.037	0.014	0.029	0.459	0.106	0.460
NH_3	0.186	0.016	0.063	0.167	0.012	0.070	0.448	0.132	0.836
H_2O	0.385	0.013	0.056	0.339	0.010	0.057	0.443	0.094	0.405
Mean	0.070	0.014	0.059	0.062	0.011	0.058	0.367	0.107	0.614

Table 4.6: Accuracy of the EEoS-NN models in terms of AAD for first order properties in the three main thermodynamic regions.

The EEoS-NN models were also compared to the accuracy in predicting the second order properties; the results are presented in Table 4.7. The residual heat capacities are both represented with an accuracy which is worse by one or two orders of magnitude with respect to those of the first order properties. Moreover, deviations for the residual isochoric heat capacity are roughly three times worse than deviations for the residual isobaric heat capacity.

Fortunately these thermodynamic properties are used in practice only as overall quantities. For the overall heat capacities the deviations are significantly reduced and become comparable with current experimental uncertainties. This is evidently due to a 'dilution' of the residual function error in the summation of ideal and residual parts. In general deviations increase from the vapor to the liquid and to the supercritical region. The heat capacity functions in the vapor phase are often represented very well, whereas for the other regions their precision can be considered acceptable. The speed of sound is well represented for the vapor phase, but for the other regions the performance is worse, though it is anyway comparable with that of a multiparameter DEoS. The comparison for saturation densities and vapor pressures, reported in Table 4.7, shows a satisfactory performance in particular for the liquid density and the vapor pressure.

Table 4.7: Accuracy of the EEoS-NN models in terms of AAD for second order properties in the three main thermodynamic regions and for saturation properties.

					А	AD (%)				
		c_v^R				c_p^R			W	
Fluid	sc	1	v	_	sc	1	v	sc	1	V
C_2H_6	5.004	8.860	6.285	_	0.663	1.888	1.665	0.335	0.410	0.029
C_3H_8	13.436	5.797	2.392		2.200	1.384	1.090	0.872	0.352	0.061
$n-C_4H_{10}$	16.540	3.921	4.900		2.764	0.959	1.383	0.535	0.189	0.037
R32	7.286	3.453	4.601		1.360	1.236	1.805	0.832	0.305	0.095
R125	10.200	3.827	7.442		1.565	0.800	2.903	0.487	0.383	0.026
R134a	8.568	2.809	4.788		1.875	1.003	2.063	0.728	0.176	0.030
R143a	9.398	6.037	4.637		1.392	1.864	1.432	0.401	0.279	0.030
NH_3	7.360	2.851	6.411		3.569	1.375	2.739	0.734	0.566	0.182
H_2O	3.208	1.665	1.864		4.558	1.300	1.128	1.123	0.935	0.057
Mean	8.834	4.149	4.883	-	1.567	1.278	1.831	0.545	0.393	0.069
		C_{v}				C_p		Satu	ration Proj	perties
Fluid	sc	1	v		sc	1	v	P^{s}	$ ho^{\scriptscriptstyle sl}$	$ ho^{\scriptscriptstyle sv}$
C_2H_6	0.569	1.555	0.297	-	0.367	0.850	0.304	0.061	0.010	0.073
C_3H_8	1.199	0.801	0.137		1.333	0.532	0.343	0.066	0.089	0.211
$n-C_4H_{10}$	1.250	0.425	0.233		1.312	0.306	0.259	0.068	0.047	0.165
R32	1.871	1.206	0.612		0.928	0.679	0.499	0.064	0.064	0.172
R125	1.160	0.590	0.346		0.800	0.328	0.347	0.059	0.102	0.206
R134a	1.304	0.651	0.401		1.132	0.439	0.492	0.050	0.009	0.069
R143a	1.298	1.220	0.250		0.741	0.783	0.209	0.066	0.015	0.068
NH ₃	2.650	1.227	1.173		2.857	0.789	0.964	0.073	0.025	0.137
H_2O	1.817	0.962	0.393		4.275	0.746	0.432	0.047	0.048	0.153
Mean	1.192	0.916	0.481	_	0.929	0.587	0.461	0.061	0.046	0.142

As a conclusion the proposed model can produce quite reliable results also for the prediction of those thermodynamic quantities involving higher order derivatives of a^{R} , notwithstanding that no input was given for them during the training procedure. In fact the EEoS-NN model trained only on density and coexistence data can satisfactorily predict second order properties.

EEOS-NN MODEL TRAINED ON MULTI-PROPERTY DATA

A similar validation procedure has been performed for the models for the same fluids of Table 4.1 trained on values of the four thermodynamic quantities Z, C_v , C_p , w plus the coexistence ones, as discussed in Paragraph 4.2.2.

Comparing the results for the training on density and coexistence data, which were presented in Table 4.6, with the results of the multiproperty training reported in Table 4.8, it can be seen that the prediction of first order properties becomes globally worse more or less for all the properties, but in general the difference is not significant.

Table 4.8: Accuracy of the EEoS-NN models in multiproperty case in terms of AAD for first order properties in the three main thermodynamic regions.

					AA	D (%)					
		z^{R}				u^{R}			h^{R}		
Fluid	sc	1	v	sc		1	v	sc	1		v
C_2H_6	0.063	0.003	0.063	0.111	(0.016	0.226	 0.095	0.01	4	0.163
C_3H_8	0.128	0.002	0.164	0.220	(0.039	0.384	0.197	0.03	4	0.312
$n-C_4H_{10}$	0.092	0.002	0.122	0.190	(0.010	0.334	0.166	0.00	9	0.250
R32	0.197	0.002	0.112	0.325	(0.041	0.519	0.287	0.03	6	0.379
R125	0.094	0.002	0.283	0.091	(0.031	0.459	0.088	0.02	7	0.255
R134a	0.102	0.002	0.136	0.242	(0.016	0.410	0.196	0.01	4	0.314
R143a	0.136	0.002	0.232	0.159	().049	0.889	0.148	0.04	4	0.637
NH_3	0.615	0.009	0.417	0.905	().036	1.162	0.731	0.03	3	0.910
H_2O	0.744	0.002	0.095	1.267	().098	0.323	1.142	0.08	8	0.255
Mean	0.136	0.003	0.183	0.208	().037	0.541	0.183	0.03	3	0.402
		a^{R}				g^{R}			s^{R}		
Fluid	sc	1	v	sc		1	v	sc	1		v
C_2H_6	0.076	0.006	0.061	 0.069	(0.005	0.060	0.154	0.02	7	0.420
C_3H_8	0.147	0.024	0.123	0.139	(0.019	0.137	0.293	0.06	0	0.647
$n-C_4H_{10}$	0.150	0.021	0.092	0.124	(0.016	0.102	0.227	0.01	7	0.542
R32	0.199	0.013	0.121	0.201	(0.011	0.109	0.459	0.06	5	0.853
R125	0.095	0.014	0.451	0.080	(0.010	0.343	0.121	0.05	8	1.176
R134a	0.132	0.006	0.110	0.120	(0.005	0.119	0.348	0.02	7	0.632
R143a	0.117	0.027	0.227	0.123	(0.022	0.227	0.221	0.06	6	1.466
NH_3	0.719	0.037	0.391	0.673	(0.030	0.395	1.193	0.04	3	1.691
H_2O	1.099	0.028	0.077	0.953	(0.021	0.082	1.411	0.19	7	0.477
Mean	0.153	0.020	0.185	 0.143	().016	0.177	 0.279	0.06	3	0.892

For the second order properties, Table 4.9 shows that there is an evident improvement of performance for isochoric heat capacity in all the regions and for isobaric heat capacity in the liquid phase, both as residual and as overall values. For some fluids this improvement is larger, especially for isochoric heat capacity. The performance for the speed of sound remains at the same level as before with some small variations depending on the specific fluid.

The comparisons for the coexistence locus, reported in Table 4.9, are also very promising. The obtained accuracy is similar to the accuracy resulting from the training to first order properties, see Table 4.7.

The inclusion of data for second order quantities into the training set improves the EEoS-NN model for such properties, obtaining a more satisfactory performance also for them. In fact, in this case information about higher order derivatives of a^{R} is supplied to the model.

Table 4.9: Accuracy of the EEoS-NN models in multiproperty case in terms of AAD for second order properties in the three main thermodynamic regions and for saturation properties.

					AAD (%	%)			
		C_v^R			c_p^R			W	
Fluid	sc	1	v	sc	1	v	sc	1	v
C_2H_6	2.695	1.367	3.464	0.832	0.355	1.227	0.288	0.194	0.019
C_3H_8	1.929	1.292	1.399	2.154	0.318	1.042	0.323	0.408	0.046
$n-C_4H_{10}$	1.989	0.711	1.768	1.760	0.170	0.927	0.581	0.184	0.038
R32	2.778	0.706	2.710	2.250	0.388	1.162	0.931	0.291	0.059
R125	3.493	0.469	2.615	0.626	0.173	1.040	0.262	0.180	0.047
R134a	3.672	0.870	3.045	1.496	0.185	1.692	0.445	0.290	0.100
R143a	1.822	0.948	2.469	0.713	0.123	1.061	0.302	0.256	0.051
NH_3	5.725	0.939	3.258	6.613	0.363	1.652	1.713	0.617	0.197
H_2O	3.750	1.329	1.862	6.658	1.214	1.289	1.532	0.666	0.076
Mean	2.792	0.946	2.628	1.493	0.363	1.261	0.456	0.348	0.075
		C_v			C_p		Satu	ration Prop	perties
Fluid	sc	1	v	sc	1	v	P^{s}	$ ho^{\scriptscriptstyle sl}$	$ ho^{\scriptscriptstyle sv}$
C ₂ H ₆	0.387	0.224	0.250	0.554	0.182	0.307	 0.011	0.038	0.224
C_3H_8	0.211	0.187	0.082	1.478	0.130	0.320	0.085	0.065	0.192
$n-C_4H_{10}$	0.174	0.077	0.071	1.203	0.059	0.163	0.098	0.061	0.209
R32	0.856	0.243	0.477	1.767	0.229	0.406	0.041	0.075	0.151
R125	0.418	0.073	0.107	0.312	0.078	0.141	0.019	0.053	0.103
R134a	0.635	0.171	0.319	1.045	0.086	0.452	0.061	0.044	0.141
R143a	0.272	0.174	0.195	0.428	0.055	0.227	0.087	0.016	0.158
NH_3	2.221	0.399	0.709	5.613	0.213	0.727	0.140	0.136	0.596
H ₂ O	2.055	0.752	0.396	6.092	0.712	0.530	0.191	0.110	0.344
Mean	0.501	0.254	0.335	1.036	0.192	0.398	0.087	0.069	0.240

The validation procedure has demonstrated that the proposed EEoS-NN method is a promising and innovative modeling technique for the heuristic development of a multiparameter DEoS from multi-property data, also as an alternative to the at present available most advanced methods.

4.2.4. Choosing the number of points of the training set: the case of ethane

The technique here presented is particularly suited to heuristically draw a pure fluid fundamental DEoS from few available data. The question is now posed about how much it is possible to reduce the number of points composing the training set without compromising the final result, i.e. how limited the required experimental effort for the development of a DEoS in this format can be.

Using generated data as before, a theoretical test has been performed in order to determine the minimum number of data points sufficient to guarantee a good performance of the EEoS-NN model. Ethane has been chosen as test fluid for the analysis.

In this particular study reference is made to the training case in which only density and coexistence data were used as input for regression; the details of the corresponding training process have been described in Paragraph 4.2.2. In that occasion 625 $P\rho T$ points have been included in the set together with a limited number of coexistence data. Now six training cases are considered, in which the number of density points of the training set is each time halved starting from the original number of 625 data. The obtained models have been validated with respect to the values of the remaining points of the original grid of generation composed of 5329 points, Table 4.2.

The performances of such models are evaluated in terms of overall deviation $d_{overall}$, which is a linear combination of the volumetric deviation:

$$d_{z} = \frac{1}{n_{z}} \sum_{i=1}^{n_{z}} \left| \frac{z_{j,DEoS}^{R} - z_{j,calc}^{R}}{z_{j,DEoS}^{R}} \right|_{i}$$
(4.14)

and of the vapor-liquid coexistence condition:

$$d_{\varphi} = \frac{1}{n_{\varphi}} \sum_{i=1}^{n_{\varphi}} \left| \ln \varphi_{j,calc} \left[T, \rho_{DEoS}^{sl} \left(T \right) \right] - \ln \varphi_{j,calc} \left[T, \rho_{DEoS}^{sv} \left(T \right) \right] \right|_{i}$$

$$(4.15)$$

reading:

$$d_{overall} = 0.8 d_z + 0.2 d_{\varphi} \tag{4.16}$$

The weights of the two components of the overall deviation, i.e. 0.8 for the volumetric deviation and 0.2 for the coexistence condition, are the same of those assumed in the definition of the objective function, Eq. (4.12), that was used for the training of the previously exposed models.

The values reached by the objective function $f_{ob,overall}$ and by the error deviation function $d_{overall}$ for each of the six cases are plotted in Fig. 4.3 for both the training and the validation step as functions of the number of points in the training set.

It can be noted that the $f_{ob,overall}$ and $d_{overall}$ functions for the training set progressively reach better values as the number of training data gets smaller; correspondingly, there is a deterioration in the prediction accuracy with respect to the validation set, particularly when the number of points decreases under 100. The last two cases represent extreme extrapolations, since the number of conditions given to the model through the input data is lower than the number of the EEoS-NN model free parameters to regress: in these circumstances the regression produces an unacceptable overfitting. Anyway, when disposing of more than 100 $P\rho T$ points, the prediction accuracy of the model is satisfying and the overfitting is avoided.



Figure 4.3: Objective function $f_{ob, overall}$ and deviation function $d_{overall}$ in dependence on the number of points of the training set. Case of ethane.

4.3. Mixtures

4.3.1. Mathematical formulation

The proposed EEoS-NN technique has been applied also to the case of mixtures. A framework similar to that of the ECS-NN model in Paragraph 3.6.4 is maintained, though with a significant difference: in this case the reference is not a pure fluid, but a simple equation for the target mixture evaluated at the same mixture composition and at temperature and density corrected through the shape functions. The model is then written as:

$$a_M^R(T_M,\rho_M,\mathbf{x}) = a_0^R(T_0,\rho_0,\mathbf{x})$$

$$(4.17)$$

In order to fulfill Eq. (4.17), the independent variables T_0 and ρ_0 of the mixture basic EoS have to be 'distorted' through the scale factor functions f_M and h_M , which are individually determined for the mixture of interest:

$$T_0 = \frac{T_M}{f_M(T_M, \rho_M, \boldsymbol{x})}$$
(4.18)

$$\rho_0 = \rho_M h_M \left(T_M, \rho_M, \mathbf{x} \right) \tag{4.19}$$

The mixture shape functions θ_M and ϕ_M can be introduced to describe f_M and h_M :

$$f_{M} = \frac{T_{c,M}}{T_{c,0}} \; \theta_{M} \left(T_{M}, \rho_{M}, \boldsymbol{x} \right) \tag{4.20}$$

$$h_{M} = \frac{\rho_{c,0}}{\rho_{c,M}} \phi_{M} \left(T_{M}, \rho_{M}, \boldsymbol{x} \right)$$

$$(4.21)$$

but, as the target and the reference system are the same, the ratios of their pseudo-critical temperatures and densities are equal to 1 and consequently the scale factors and the shape functions coincide:

$$f_{M} = f_{M}\left(T_{M}, \rho_{M}, \boldsymbol{x}\right) = \theta_{M}\left(T_{M}, \rho_{M}, \boldsymbol{x}\right)$$

$$(4.22)$$

$$h_{M} = h_{M}\left(T_{M}, \rho_{M}, \boldsymbol{x}\right) = \phi_{M}\left(T_{M}, \rho_{M}, \boldsymbol{x}\right)$$

$$(4.23)$$

In Eq. (4.17) a_0^R is obtained from the mixture equation selected as reference. In this work the SRK cubic EoS with Peneloux volume translation, previously used for pure fluids, has been

assumed with the van der Waals mixing rules reported in Paragraph 3.3.2; the thermodynamic relations for this equation are given in Appendix A.3.

Differently from the ECS model for mixtures, the composition dependence is here already present in the reference equation and therefore it is simply refined through the shape functions depending also on composition. It is important to stress again that the reference equation is evaluated at the same composition x of the real system and no tuning function is applied to the molar fraction variables. Incidentally, this makes equivalent the scale and the shape functions, since the pseudo-critical parameters $T_{c,M}$ and $\rho_{c,M}$ for the system and for the reference equation are the same.

The mathematical relations for the calculation of thermodynamic properties, given in Appendix A.5, are the same as those for the ECS-NN model, see Paragraph 3.6.4, but in the present case the equation for the reference fluid is substituted by the basic equation for the mixture itself.

The only significant formal difference with the ECS-NN framework is the partial molar fugacity coefficient $\hat{\varphi}_{M,k}$ for the mixture component k , obtained from:

$$\ln \hat{\varphi}_{M,k} = \ln \hat{\varphi}_{0,k} - \ln \left(\frac{Z_M}{Z_0} \right) + u_0^R \left(F_{n_k} + F_\rho \right) + z_0^R \left(H_{n_k} + H_\rho \right)$$
(4.24)

where $\hat{\varphi}_{0,k}$ is the partial molar fugacity coefficient for the mixture component k calculated by the reference equation; the other thermodynamic properties are obtained similarly to the previous ECS-NN model.

The shape functions are expressed through the neural network assuming Eq. (4.9) as transfer function.

4.3.2. Training of the EEoS-NN model on generated density and coexistence values

The training of an EEoS-NN model aims at the determination of the mixture scale factor functions f_M and h_M over the whole (T, ρ, \mathbf{x}) range of interest through an optimization procedure that uses the available data of the experimentally accessible thermodynamic quantity as input.

The main goal of the Paragraph 4.3 is to verify the effectiveness of the proposed modeling technique and its capability in representing the thermodynamic surfaces of mixtures. Therefore, similarly to what was done for pure fluids in Paragraph 4.2, it was chosen to assume generated values of thermodynamic properties instead of experimental data.

Five binary and two ternary mixtures of haloalkanes were considered and for all of them the DEoSs used for data generation were taken from Ref. 9. The critical constants and the SRK

parameters for the pure fluids relevant as components of the selected mixtures are reported in the previous Table 4.1 together with their literature references.

In a first step, only density data (T, P, ρ, \mathbf{x}) covering the vapor, liquid, and supercritical regions, together with vapor-liquid equilibrium (VLE) data in the forms $(T, P^s, \mathbf{x}^s, \mathbf{y}^s)$, $(T, P^s, \rho^{sl}, \mathbf{x}^s)$ and $(T, P^s, \rho^{sv}, \mathbf{y}^s)$, were used as inputs for the regression. These VLE data are indispensable to locate the bubble and dew surfaces of the mixture. When considering saturation condition, \mathbf{y} denotes the vapor phase composition vector, while \mathbf{x} is the liquid one.

A grid in the independent variables T_M , P_M , x has been generated with a constant step for each variable inside the respective range. The generated data set is subdivided into a training set and a validation set, with the first one obtained regularly extracting a subset of values from the original set and the second composed of the remaining values.

The data of the training set were assumed for the regression of the mixture-specific equations, while the validation data were used to check the performances of the obtained models. Following similar criteria, sets of training and validation VLE data were produced for the whole coexistence locus in the considered temperature range. Moreover, values of several thermodynamic properties were generated for each point of the validation set, in order to verify the behavior of the equations also with respect to such quantities.

The number of data and their range for each considered mixture are reported in Table 4.10. The data are distributed in three main thermodynamic regions, that are the liquid phase (denoted by l), the vapor phase (denoted by v), and the supercritical region (denoted by sc). In this work the supercritical region is conventionally identified as the thermodynamic region at temperatures higher than the pseudocritical temperature and pressures higher than the pseudocritical pressure, calculated by the mixing rules of Tillner-Roth et al. [9].

For the training step an objective function f_{ob} accounting for the deviations between the model and the data has to be defined for each of the thermodynamic quantities to which the equation is regressed. The variables of the f_{ob} function are the parameters w_{ij} and w_{jk} , whose values are to be found through a minimization procedure of the f_{ob} function.

In the first step it was chosen to train the MLFN only on density values in the vapor, liquid, and supercritical regions, and on the liquid-vapor coexistence surface.

Mixture		T Rang (K)	je		Range (IPa)	z_1	Range		z ₂ Rang	e	
R32/R125		250-40	0	0.3	3-8.0	0.0	01-0.98		_		
R32/R134a		250-40	0	0.3	3-8.0	0.0	01-0.98	_			
R125/R134a		250-40	0	0.3	3-8.0	0.0	01-0.98		_		
R125/R143a		250-40	0	0.3	3-8.0	0.0	01-0.98		_		
R143a/R134a		250-40	0	0.3	3-8.0	0.0	01-0.98	_			
R32/R125/R134a		250-40	0	0.3	3-8.0	0.0	01-0.98		0.01-0.9	8	
R125/R143a/R134a		250-40	0	0.3	3-8.0	0.0	01-0.98	0.01-0.98			
			Training	r S				Validati	on		
			NPT					NPT			
-		Ρ, ρ	,T,Z		VLE	Ea	ch of nir	e proper	ties ^a	VLE	
	sc	1	v	overall		sc	1	v	overall		
R32/R125	137	388	253	778	44	834	2305	1448	4587	115	
R32/R134a	80	473	218	771	53	456	2822	1239	4517	140	
R125/R134a	126	471	185	782	51	677	2815	1030	4522	133	
R125/R143a	168	394	203	765	42	927	2391	1107	4425	113	
R143a/R134a	114	489	183	786	53	612	2893	1020	4525	136	
R32/R125/R134a	101	311	187	599	64	902	3382	1834	6118	354	
R125/R143a/R134a	111	321	170	602	64	1101	3491	1479	6071	344	

Table 4.10: Characteristics of the generated data for the considered mixtures.

^a properties: Z^{R} , a^{R} , u^{R} , h^{R} , g^{R} , s^{R} , c_{v}^{R} , c_{p}^{R} , w.

Considering a mixture of *C* components for which a set of n_z density data and a set of n_{φ} VLE data are available, the objective function $f_{ob,z}$ for the residual compressibility factor is defined as in Eq. (4.10), while the objective function $f_{ob,\varphi}$ for the coexistence is defined as:

$$f_{ob,\varphi} = \frac{1}{n_{\varphi}} \sum_{i=1}^{n_{\varphi}} \sum_{k=1}^{C} \left[\left(\ln x_{k}^{s} + \ln \hat{\varphi}_{k,calc}^{sl} \right)_{j} - \left(\ln y_{k}^{s} + \ln \hat{\varphi}_{k,calc}^{sv} \right)_{j} \right]_{i}^{2}$$
(4.25)

In Eq. (4.25) x_k^s and y_k^s are experimental values, while $\hat{\varphi}_k^{sl}$ and $\hat{\varphi}_k^{sv}$ are calculated through the EEoS-NN model at the experimental conditions (T, ρ^{sl}, x^s) and (T, ρ^{sv}, y^s) . Since in the present study only generated values were considered instead of real experimental data, the term 'experimental value' refers to values generated from the corresponding DEoS in Ref. 9.

The two objective functions, Eqs. (4.10) and (4.25), are composed together to form the overall objective function $f_{ob, overall}$, Eq. (4.12), in which the two functions $f_{ob, z}$ and $f_{ob, \varphi}$ are differently weighted.

The application of the training procedure to the generated data gave a mixture-specific equation in EEoS-NN format for each of the target mixtures reported in Table 4.10.

In a second step of the study the EEoS-NN model was regressed assuming an objective function which includes, besides the unavoidable density and VLE data, also some caloric quantities such as the isochoric heat capacity C_v , the isobaric heat capacity C_p , and the speed of sound w. As in the case of pure fluids, the overall objective function $f_{ob, overall}$ for this multiproperty fitting is again calculated as the sum of two contributions, but the first one now reads as in Eq. (4.13).

The part $f_{ob,\phi}$ is still represented by the former Eq. (4.25); the two contributions are combined together according to Eq. (4.12) again.

The main purposes of the present study are the test and the analysis of capability and performances of the proposed modeling method. Therefore the numerical details, i.e. the parameters w_{ij} and w_{jk} , of the functional forms obtained for the studied systems are not reported herein. In fact they have a limited interest for practical applications since DEoSs already exist for all the considered mixtures [9].

4.3.3. Validation

SRK CUBIC EOS WITH VOLUME TRANSLATION

First of all, the SRK cubic EoS with the van der Waals mixing rules and the Peneloux volume translation parameters reported in Table 4.1 was validated with respect to the generated data in the validation sets for properties involving only first order derivatives of a_M^R with respect to temperature or density. The physical constants and the coefficients reported in Table 4.1 were used for the components, whereas the binary interaction parameters k_{ij} were set to zero. The SRK performances represent the 'starting point' of the proposed modeling technique; in fact the discrepancies between the data and the predictions of this equation are corrected through the application of the scale factors.

Results for the SRK equation with $k_{ij} = 0$ are reported in Table 4.11 for the considered binary and ternary mixtures. The performances are rather homogeneous for all the systems, but the prediction errors for the properties depending on first derivatives of the residual Helmholtz energy range to several per cent. The worse performances are found for properties involving only temperature derivatives like u_M^R and s_M^R , in particular in vapor region where the AADs can largely exceed 10%.

Mixture	AAD (%)								
	SC	1	v	overall	SC	1	v	overall	
	z_M^R				s_M^R				
R32+R125	3.64	0.86	3.28	2.13	3.89	2.11	17.65	7.34	
R32+R134a	4.81	0.82	4.43	2.21	5.00	3.34	22.35	8.72	
R125+R134a	5.11	0.78	2.08	1.72	2.66	2.09	13.74	4.83	
R125+R143a	6.35	0.90	3.09	2.59	2.99	2.07	12.96	4.99	
R143a+R134a	6.29	0.82	4.08	2.29	3.25	3.08	18.07	6.48	
Mean	5.26	0.83	3.42	2.19	3.45	2.57	17.14	6.48	
R32+R125+R134a	4.12	0.80	3.56	2.12	3.57	2.55	19.24	7.70	
R125+R143a+R134a	5.93	0.80	2.83	2.22	2.88	2.12	14.25	5.21	
Mean	5.11	0.80	3.23	2.17	3.19	2.33	17.01	6.46	
		u	ι_M^R			a_M^R			
R32+R125	3.51	1.43	11.93	5.12	4.00	2.98	3.53	3.34	
R32+R134a	5.64	1.82	15.58	5.98	6.66	2.98	4.55	3.78	
R125+R134a	3.24	1.19	8.99	3.27	5.67	2.24	2.07	2.71	
R125+R143a	3.82	1.28	8.91	3.72	7.15	3.38	3.01	4.08	
R143a+R134a	5.16	1.57	12.63	4.55	8.46	2.81	4.09	3.86	
Mean	4.10	1.47	11.74	4.53	6.28	2.86	3.49	3.55	
R32+R125+R134a	3.72	1.51	13.18	5.33	4.74	2.73	3.70	3.32	
R125+R143a+R134a	3.59	1.21	9.66	3.70	6.60	2.72	2.72	3.42	
Mean	3.65	1.36	11.61	4.52	5.76	2.72	3.26	3.37	
		k	n_M^R		g_M^R				
R32+R125	3.23	1.32	9.44	4.23	3.83	2.38	3.41	2.97	
R32+R134a	5.44	1.66	12.58	5.04	5.94	2.37	4.49	3.31	
R125+R134a	3.36	1.10	7.01	2.79	5.49	1.82	2.04	2.42	
R125+R143a	4.15	1.20	7.22	3.32	6.87	2.70	3.04	3.65	
R143a+R134a	5.38	1.44	10.29	3.97	7.63	2.25	4.08	3.39	
Mean	4.16	1.35	9.41	3.87	5.89	2.29	3.44	3.15	
R32+R125+R134a	3.62	1.39	10.51	4.45	4.50	2.19	3.63	2.96	
R125+R143a+R134a	3.85	1.13	7.70	3.23	6.37	2.18	2.76	3.08	
Mean	3.75	1.26	9.26	3.84	5.53	2.18	3.24	3.02	

Table 4.11: Accuracy of the SRK equation for thermodynamic quantities depending on first derivatives of residual Helmholtz energy in the three main thermodynamic regions.

Table 4.12 shows the accuracy of the SRK model for the thermodynamic properties depending on second and cross derivatives of a_M^R . The results for isochoric and isobaric heat capacities, and for speed of sound are similar for binary and ternary mixtures, but are worse than those obtained for first order properties, see Table 4.11. In particular the residual heat capacities shows very high deviations, that are considerably reduced when also the ideal part of the properties is considered. The errors are rather homogeneous in all the regions for the heat capacities, but for speed of sound the good results in the vapor phase are in contrast with the poor performances in the liquid phase, where a mean deviation of about 25% is obtained. This is due to the ideal-gas contribution for speed of sound that is by far prevailing in the vapor phase.

Mixture	AAD (%)									
	sc	1	V	overall		sc	1	v	overall	
	$c^R_{v,M}$					$\overline{C_{v,M}}$				
R32+R125	48.88	30.22	69.97	46.16		8.33	6.26	6.08	6.58	
R32+R134a	52.39	31.08	73.71	44.93		11.01	7.16	7.00	7.50	
R125+R134a	39.29	41.35	67.51	47.00		5.33	6.74	3.90	5.88	
R125+R143a	40.36	41.95	65.45	47.50		4.94	6.54	3.60	5.47	
R143a+R134a	40.69	39.21	71.14	46.61		6.11	6.83	4.67	6.25	
Mean	43.80	36.86	69.68	46.43		6.82	6.73	5.17	6.34	
R32+R125+R134a	49.85	30.82	71.20	45.73		8.84	6.69	5.73	6.72	
R125+R143a+R134a	40.21	41.39	66.68	47.34		5.12	6.79	3.32	5.64	
Mean	44.55	36.19	69.18	46.53		6.80	6.74	4.65	6.18	
		C	R p,M			$C_{p,M}$				
R32+R125	11.01	15.84	31.87	20.02		6.25	8.03	6.15	7.11	
R32+R134a	12.54	17.29	36.45	22.07		8.19	8.71	7.31	8.28	
R125+R134a	10.23	10.61	28.71	14.67		5.67	4.63	4.26	4.70	
R125+R143a	12.14	14.18	27.58	17.11		6.29	6.12	4.02	5.63	
R143a+R134a	12.23	14.46	33.21	18.38		7.11	6.29	5.39	6.20	
Mean	11.57	14.43	31.71	18.46		6.55	6.73	5.53	6.39	
R32+R125+R134a	11.15	14.71	33.80	19.91		6.54	7.34	5.86	6.78	
R125+R143a+R134a	11.39	11.66	29.15	15.87		5.95	5.07	3.67	4.89	
Mean	11.28	13.16	31.72	17.90		6.22	6.19	4.88	5.84	
		V	V _M							
R32+R125	7.94	23.18	0.57	13.27		-	-	-	-	
R32+R134a	10.64	23.73	0.89	16.15		-	-	-	-	
R125+R134a	7.49	24.81	0.41	16.66		-	-	-	-	
R125+R143a	7.14	25.17	0.61	15.25		-	-	-	-	
R143a+R134a	8.46	24.39	0.76	16.91		-	-	-	-	
Mean	8.08	24.27	0.65	15.64		-	-	-	-	
R32+R125+R134a	8.77	23.67	0.61	14.56		-	-	-	-	
R125+R143a+R134a	7.16	25.02	0.47	15.80		-	-	-	-	
Mean	7.89	24.36	0.55	15.18		-	-	-	-	

Table 4.12: Accuracy of the SRK equation for thermodynamic quantities depending on second derivatives of residual Helmholtz energy in the three main thermodynamic regions.

Table 4.13 shows the SRK model performances for the prediction of the properties at equilibrium conditions for binary and ternary mixtures. The pressure of bubble and dew point and the phase compositions are predicted with acceptable accuracies, whereas the deviations for the densities at saturation are higher, with worse values for the saturated liquid density.

Considering the reported results, it can be concluded that from an overall point of view the accuracy of the SRK cubic EoS, using mixing rules set with $k_{ij} = 0$, cannot be regarded as satisfactory.

		AAD (%)		AAD		
Mixture	P^{s}_{bubble}	P_{dew}^{s}	$ ho^{\scriptscriptstyle sl}$	$ ho^{\scriptscriptstyle sv}$	$oldsymbol{x}^{s}_{dew}$	$oldsymbol{y}^{s}_{bubble}$	
R32+R125	0.86	0.82	7.79	2.28	0.0023	0.0023	
R32+R134a	1.03	0.79	7.37	2.18	0.0034	0.0034	
R125+R134a	0.84	0.72	6.26	1.25	0.0020	0.0020	
R125+R143a	2.99	3.02	7.53	1.44	0.0048	0.0047	
R143a+R134a	1.62	1.40	6.61	1.06	0.0029	0.0029	
Mean	1.43	1.31	7.08	1.63	0.0031	0.0030	
R32+R125+R134a	0.86	0.61	6.98	2.20	0.0027	0.0021	
R125+R143a+R134a	2.16	1.75	6.35	0.99	0.0036	0.0033	
Mean	1.50	1.17	6.67	1.60	0.0031	0.0027	

Table 4.13: Accuracy of the SRK equation for VLE conditions at bubble and dew point.

EEOS-NN MODEL TRAINED ON DENSITY AND COEXISTENCE DATA

The corresponding results for the EEoS-NN models regressed on density and coexistence data only are reported in Tables 4.14-4.16. The performance improvement achieved by the correction through the scale factors is very high; in most cases the deviations are reduced by two orders of magnitude compared to the SRK EoS.

Table 4.14 shows the performances of the EEoS-NN models with respect to properties depending on first derivatives of the residual Helmholtz energy; these results have to be compared with Table 4.11 for the SRK EoS. The values for the residual compressibility factor z_M^R in liquid phase are particularly impressive, since this property is described with very low deviations. The deviations for the other residual properties are absolutely satisfactory, also considering that no information for them was supplied to the regression procedure. Although maintaining an excellent overall performance, it can be observed that the poor performances of the SRK model on the properties u_M^R and s_M^R , involving only temperature derivatives of the a_M^R function, have consequences also on the representation of the same properties obtained by the EEoS-NN model. In general a limited worsening is found when ternary mixtures are considered.

Mixture	AAD (%)									
	sc	1	v	overall		sc	1	v	overall	
	$\overline{z_M^R}$					S_M^R				
R32+R125	0.122	0.003	0.134	0.066	0.	455	0.357	0.839	0.527	
R32+R134a	0.143	0.001	0.070	0.033	0.	466	0.170	0.356	0.742	
R125+R134a	0.057	0.001	0.055	0.022	0.	264	0.112	0.356	0.191	
R125+R143a	0.036	0.001	0.045	0.019	0.	131	0.081	0.377	0.166	
R143a+R134a	0.045	0.001	0.055	0.019	0.	266	0.177	0.569	0.278	
Mean	0.076	0.001	0.076	0.032	0.	301	0.176	0.517	0.382	
R32+R125+R134a	0.541	0.009	0.467	0.225	1.	372	0.612	1.577	1.013	
R125+R143a+R134a	0.308	0.006	0.277	0.127	1.	260	0.475	1.506	0.868	
Mean	0.413	0.007	0.382	0.176	1.	310	0.542	1.545	0.941	
		L	ι_M^R			a_M^R				
R32+R125	0.308	0.208	0.537	0.330	0.	139	0.038	0.117	0.081	
R32+R134a	0.313	0.097	0.470	0.221	0.	143	0.019	0.058	0.042	
R125+R134a	0.178	0.067	0.226	0.120	0.	061	0.023	0.042	0.033	
R125+R143a	0.090	0.059	0.235	0.109	0.	037	0.026	0.032	0.030	
R143a+R134a	0.173	0.102	0.354	0.168	0.	057	0.022	0.041	0.031	
Mean	0.202	0.104	0.379	0.190	0.	083	0.025	0.062	0.044	
R32+R125+R134a	0.944	0.343	1.010	0.632	0.	661	0.096	0.472	0.292	
R125+R143a+R134a	0.895	0.266	0.944	0.545	0.	351	0.085	0.245	0.172	
Mean	0.917	0.304	0.981	0.589	0.	491	0.090	0.371	0.232	
		ŀ	n_M^R			g_M^R				
R32+R125	0.252	0.184	0.410	0.268	0.	130	0.028	0.121	0.076	
R32+R134a	0.258	0.086	0.358	0.178	0.	136	0.015	0.060	0.039	
R125+R134a	0.144	0.059	0.172	0.097	0.	059	0.017	0.044	0.029	
R125+R143a	0.075	0.051	0.179	0.088	0.	036	0.020	0.035	0.027	
R143a+R134a	0.139	0.091	0.268	0.137	0.	052	0.017	0.045	0.028	
Mean	0.165	0.092	0.288	0.154	0.	079	0.019	0.065	0.040	
R32+R125+R134a	0.787	0.306	0.804	0.526	0.	604	0.072	0.461	0.267	
R125+R143a+R134a	0.757	0.237	0.722	0.449	0.	331	0.062	0.242	0.155	
Mean	0.771	0.271	0.767	0.488	0.	454	0.067	0.363	0.211	

Table 4.14: Accuracy of the EEoS-NN models for thermodynamic quantities depending on first derivatives of residual Helmholtz energy. Training on density and coexistence data.

Table 4.15 shows mean deviations of the proposed models with respect to $c_{v,M}^{R}$, $c_{p,M}^{R}$, $C_{v,M}$, $C_{p,M}$, and w_{M} for binary and ternary mixture. The description of these second order properties by the EEoS-NN models has to be regarded as predictive and consequently the obtained results are rather satisfactory. The residual caloric properties $c_{v,M}^{R}$ and $c_{p,M}^{R}$ are homogenously represented with an acceptable accuracy in the three thermodynamic regions; for $C_{v,M}$, $C_{p,M}$, and w_{M} the best results are found in the vapor region, where the ideal part of each of these properties gives the prevailing contribution to the overall value, allowing for a 'dilution' of the deviation for the residual
part. In the liquid phase the heat capacities are predicted worse, but in any case they are comparable with the experimental uncertainties for these properties.

Table 4.15:	Accuracy	of the	EEoS-NN	models	for	thermodynamic	quantities	depending	on
second deriv	atives of re	sidual l	Helmholtz e	energy. T	rain	ing on density ar	nd coexister	nce data.	

Mixture	AAD (%)										
	sc	1	v	overall	sc	1	v	overall			
		$c_{v,M}^R$					$C_{v,M}$				
R32+R125	9.157	7.582	7.213	7.752	1.469	1.568	0.656	1.262			
R32+R134a	8.406	4.292	7.153	5.492	1.715	1.050	0.684	1.017			
R125+R134a	4.905	2.599	4.029	3.270	0.624	0.422	0.307	0.426			
R125+R143a	2.823	1.083	5.074	2.446	0.362	0.170	0.253	0.231			
R143a+R134a	5.316	8.548	5.686	7.466	0.735	1.658	0.405	1.250			
Mean	5.893	4.856	5.967	5.305	0.917	0.981	0.480	0.841			
R32+R125+R134a	7.146	17.563	7.173	12.913	1.254	3.827	0.693	2.508			
R125+R143a+R134a	11.503	9.045	9.178	9.523	1.498	1.373	0.567	1.199			
Mean	9.541	13.236	8.068	11.225	1.388	2.581	0.637	1.856			
		$C_{p,M}^R$					$C_{p,M}$				
R32+R125	1.806	1.864	2.955	2.198	0.990	0.870	0.674	0.830			
R32+R134a	2.063	1.053	2.670	1.598	1.286	0.517	0.600	0.618			
R125+R134a	0.881	0.659	1.571	0.900	0.495	0.271	0.337	0.320			
R125+R143a	0.629	0.190	2.025	0.741	0.314	0.078	0.272	0.176			
R143a+R134a	0.846	2.671	2.094	2.294	0.489	1.086	0.412	0.853			
Mean	1.182	1.308	2.324	1.552	0.667	0.571	0.477	0.562			
R32+R125+R134a	3.706	4.486	3.533	4.085	2.530	2.027	0.756	1.720			
R125+R143a+R134a	2.503	1.510	4.050	2.309	1.402	0.632	0.715	0.792			
Mean	3.045	2.974	3.764	3.200	1.910	1.318	0.738	1.258			
		W _M									
R32+R125	0.749	0.885	0.055	0.598	-	-	-	-			
R32+R134a	0.808	0.625	0.066	0.490	-	-	-	-			
R125+R134a	0.342	0.181	0.024	0.169	-	-	-	-			
R125+R143a	0.176	0.139	0.013	0.116	-	-	-	-			
R143a+R134a	0.364	0.323	0.027	0.262	-	-	-	-			
Mean	0.459	0.422	0.039	0.329		-	-	-			
R32+R125+R134a	1.038	1.988	0.085	1.277	-	-	-	-			
R125+R143a+R134a	1.132	0.950	0.066	0.768	-	-	-	-			
Mean	1.090	1.461	0.077	1.023	-	-	-	-			

VLE data are reproduced in an excellent way as well, as shown in Table 4.16. The saturated liquid density is represented with a higher accuracy than the saturated vapor density. This is coherent with the results for z_M^R in compressed liquid and superheated vapor regions reported in Table 4.14.

		AAD (9	%)		AAD			
Mixture	P^{s}_{bubble}	P_{dew}^{s}	$ ho^{\scriptscriptstyle sl}$	$ ho^{\scriptscriptstyle sv}$	$oldsymbol{x}^{s}_{dew}$	$oldsymbol{y}^{s}_{bubble}$		
R32+R125	0.120	0.121	0.042	0.224	0.0001	0.0001		
R32+R134a	0.064	0.068	0.025	0.107	0.0001	0.0001		
R125+R134a	0.077	0.078	0.022	0.110	0.0000	0.0000		
R125+R143a	0.088	0.088	0.020	0.051	0.0000	0.0000		
R143a+R134a	0.080	0.083	0.021	0.072	0.0000	0.0000		
Mean	0.084	0.086	0.026	0.111	0.0000	0.0000		
R32+R125+R134a	0.264	0.321	0.181	0.710	0.0006	0.0005		
R125+R143a+R134a	0.177	0.189	0.072	0.668	0.0002	0.0003		
Mean	0.221	0.256	0.127	0.689	0.0004	0.0004		

Table 4.16: Accuracy of the EEoS-NN models for VLE conditions at bubble and dew point.Training on density and coexistence data.

Summarizing, a large improvement of performances was attained moving from the simple SRK equation to the EEoS-NN model. Even though the regression of the scale factor functions was based only on density and VLE data, the obtained equations show good predictions also for thermodynamic properties not involved in the training process.

VALIDATION OF THE EEOS-NN MODELS TRAINED ON MULTIPROPERTY DATA

The validation procedure was repeated for the model trained on generated values of the four thermodynamic quantities z_M^R , $c_{v,M}^R$, $c_{p,M}^R$, w_M plus the VLE data. For sake of brevity the study was carried out for only one mixture, i.e., for the system R32 + R134a.

Comparing the present results reported in Table 4.17 with those obtained for the model trained on density and VLE data, Tables 4.14 and 4.15, it can be noted that the performance in the representation of first order properties is decreased more or less for all properties, but in general not significantly. On the contrary, for the heat capacities an evident improvement is attained, in particular for the isochoric heat capacity. The representation of the speed of sound is improved as well, but to a lower extent than for the other properties. Therefore, the inclusion of second order quantities in the training set improves the accuracy of the EEoS-NN model for the same quantities, because information about higher order derivatives of a_M^R is supplied to the model.

The validation results for the vapor-liquid coexistence locus, reported in Table 4.18, are good and show a level of accuracy rather similar to the one obtained for the model trained on density and coexistence data only, Table 4.16.

Table 4.17: Accuracy of the EEoS-NN model for the mixture R32+R134a for thermodynamic quantities depending on first and second derivatives of residual Helmholtz energy. Multiproperty training cases.

Training	Phase			AAD	(%)		
		z_M^R	a_M^R	u_M^R	S_M^R	h_M^R	g_M^R
$z^R c^R c^R $ w	sc	0.263	0.300	0.384	0.689	0.301	0.271
\mathcal{L}_{M} , $\mathcal{C}_{v,M}$, $\mathcal{C}_{p,M}$, \mathcal{W}_{M}	1	0.010	0.029	0.112	0.175	0.099	0.025
+	ν	0.342	0.347	1.007	1.566	0.743	0.335
VLE	overall	0.127	0.144	0.385	0.609	0.296	0.135
	sc	0.349	0.380	0.526	0.676	0.482	0.368
σ^R \downarrow \downarrow VIF	1	0.005	0.037	0.159	0.288	0.140	0.027
$z_M, W_M + v LE$	v	0.193	0.167	0.675	1.068	0.512	0.171
	overall	0.091	0.107	0.338	0.541	0.276	0.101
		$c_{v,M}^R$	$c_{p,M}^R$	$C_{v,M}$	$C_{p,M}$	W_M	-
$z^R c^R c^R $ w	sc	1.954	1.295	0.446	0.963	0.404	-
\mathcal{L}_{M} , $\mathcal{C}_{v,M}$, $\mathcal{C}_{p,M}$, \mathcal{W}_{M}	1	0.402	0.258	0.091	0.126	0.393	-
+	v	1.218	0.805	0.130	0.172	0.115	-
VLE	overall	0.783	0.513	0.138	0.223	0.318	-
	sc	5.612	3.095	1.117	2.318	0.511	-
σ^R $\lambda \lambda = \lambda \Lambda \Gamma \Gamma$	1	8.781	3.060	2.051	1.410	0.138	-
Z_M , W_M + v LE	v	6.394	2.440	0.564	0.496	0.069	-
	overall	7.807	2.893	1.549	1.251	0.157	-

Table 4.18: Accuracy of the EEoS-NN model for the mixture R32+R134a for VLE conditions at bubble and dew point. Multiproperty training cases.

Training		AAD	AAD			
	P^s_{bubble}	P_{dew}^{s}	$ ho^{\scriptscriptstyle sl}$	$ ho^{sv}$	$oldsymbol{x}^{s}_{dew}$	$oldsymbol{y}^{s}_{bubble}$
z_M^R , $c_{v,M}^R$, $c_{p,M}^R$, w_M + VLE	0.142	0.155	0.124	0.257	0.0004	0.0004
$z_M^R, w_M + \text{VLE}$	0.171	0.186	0.089	0.412	0.0003	0.0003

A further training case, which involves density, VLE, and speed of sound data in the regression process, was considered. This set of data corresponds to the thermodynamic properties involving first order derivatives of the residual Helmholtz energy function and the speed of sound, which can be measured with great accuracy. The validation results reported in Tables 4.17 and 4.18 show an improvement for the performance on speed of sound compared to the former case, though slightly sacrificing accuracy on heat capacities. The other properties are reproduced approximately at the same level as before.

4.4. Conclusions

The new modeling technique here presented recovers the basic framework of extended corresponding states theory, but a reference equation is assumed instead of a reference fluid. This allows to get rid of the conformality requirement and of the necessity of the reference fluid EoS, because an equation for the target fluid itself is assumed as reference. It has been demonstrated that a simple equation, as the SRK cubic EoS, is sufficient for such a purpose.

Moving from generated data, the capability of the proposed method has been verified both for pure fluids and for mixtures. A group of pure alkanes, haloalkanes, and strongly polar substances has been considered; the results obtained for these fluids are very promising. The same is valid for the five binary mixtures and two ternary mixtures of haloalkanes here studied.

In the case of pure fluids it has been also verified that slightly more than 100 density points evenly distributed in the $P\rho T$ plane and with low experimental error can be a sufficient input for the model development, allowing to reduce the experimental efforts.

Having verified such promising performances for the proposed model basing it on generated data, it is then possible to reliably develop DEoSs in the EEoS-NN format directly from experimental data. This will be the matter of the following chapters of Part One of this thesis.

4.5 References

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V. A fundamental equation of state for sulfur hexafluoride (SF₆) in EEoS-NN format

5.1. Introduction

The EEoS-NN technique, preliminary studied in Chapter IV, is here applied to draw a DEoS for the pure fluid sulfur hexafluoride (SF₆) directly from the available data sets of the target fluid. In fact, one of the main purposes of the present chapter is the testing of the EEoS-NN modeling technique for a fluid in a real case, i.e., using experimental data instead of generated data as in the preliminary tests treated in Chapter IV.

Sulfur hexafluoride (SF₆) is a highly stable, non-toxic, non-polar, symmetrically-shaped chemical compound which is widely used in several industrial applications. The critical point of sulfur hexafluoride is at $T_c = 318.7232$ K and $P_c = 3.754983$ MPa.

Span and Wagner [1] published the most recent and precise equation for SF_6 . It is a fundamental equation with an optimized functional form obtained through the Setzmann and Wagner [2] method, and then it is expressed as a summation of polynomial and exponential terms depending on temperature and density. After the publication of the Span and Wagner [1] DEoS several and valuable data sets have been made available in the literature and this suggests to undertake the development of a new DEoS for this fluid, adopting the innovative EEoS-NN modeling method.

In particular, the works of Hurly et al. [3], Ihmels and Gmehling [4], and Claus et al. [5], which were not available when the Span and Wagner [1] DEoS was developed, have provided a large number of very precise density data in the vapor, liquid, and supercritical regions. Moreover, these data largely improved the experimental knowledge for the regions at temperatures greater than 375 K, which formerly were not sufficiently documented; in fact, thanks to the data of Ihmels and Gmehling [4], the upper temperature limit of the equation was heightened of about 100 K with respect to the Span and Wagner [1] DEoS. In addition, also the speed of sound data in the vapor phase measured by Hurly et al. [3] were assumed in the present work; in particular, these can be used to assess the reliability of the adopted ideal-gas isobaric heat capacity function.

Therefore, the DEoS for sulfur hexafluoride proposed in the present chapter should supersede the Span and Wagner [1] DEoS.

5.2. Training of the equation of state in EEoS-NN format

The mathematical formulation for the EEoS-NN model is given in Paragraph 4.2.1.

As it will be discussed in Paragraph 5.5.1, the equation for the ideal-gas isobaric heat capacity of sulfur hexafluoride used throughout this work was developed by Cole and de Reuck [7].

The main work in the development of an equation of state in EEoS-NN format is due to the regression of the residual contribution of Helmholtz energy. The free parameters in the regression procedure are the weighting factors w_{ij} and w_{jk} , which, with the present number of neurons in the hidden layer J = 9, constitute a set of 47 coefficients. Since the thermodynamic properties in EEoS-NN format are non-linearly dependent on the weighting factors, the regression method is necessarily non-linear. The technique here adopted is a combination of a stochastic method with a deterministic method, i.e., a *quasi-Newton* one. The so-obtained technique keeps the ability of the stochastic method in finding the minimum of the objective function when many local minima are present, but the introduction of the deterministic method allows the limitation of the required time for the regression and the improvement of the precision of the minimum determination.

The objective function that has to be minimized in the regression procedure is composed by sums of squares of the deviations between experimental data and calculated values.

For density data, the objective function is calculated as

$$f_{ob,\rho} = \frac{1}{n_{\rho}} \sum_{i=1}^{n_{\rho}} \left[\frac{z_{exp}^{R}}{\rho_{exp}} - \left(\frac{\partial a^{R}}{\partial \rho} \right)_{T} \right]_{i}^{2} / \sigma_{\rho,i}^{2}$$
(5.1)

where the subscript exp denotes the experimental value, n_{ρ} is the number of experimental density data, $\sigma_{\rho,i}^2$ is the variance of each point estimated from the Gaussian error propagation formula. The objective function for vapor pressure data is

$$f_{ob,\varphi} = \frac{1}{n_{\varphi}} \sum_{i=1}^{n_{\varphi}} \left\{ \frac{P^{s}}{RT} \left(\frac{1}{\rho^{sl}} - \frac{1}{\rho^{sv}} \right) + \ln \left(\frac{\rho^{sl}}{\rho^{sv}} \right) - \left[a^{R} \left(T, \rho^{sv} \right) - a^{R} \left(T, \rho^{sl} \right) \right]_{i}^{2} \right\}_{i}^{2} / \sigma_{\varphi,i}^{2}$$

$$(5.2)$$

in which n_{φ} is the number of vapor pressure data, $\sigma_{\varphi,i}^2$ is the variance of each point, P^s is the experimental vapor pressure, ρ^{sl} and ρ^{sv} are the densities of saturated liquid and vapor, respectively. The quantities a^R and $(\partial a^R/\partial \rho)_T$ are calculated at each step from the model using the current values of the free parameters w_{ij} and w_{jk} . Eq. (5.2) is obtained from Eq. (4.11) and (A2.26) dividing the i^{th} term by $\sigma_{\varphi,i}^2$.

During the development process of the equation of state, a first regression run is done considering only density data and assuming equation (5.1) as objective function; in this preliminary step $\sigma_{\rho,i}^2$ is set equal to 1 for each experimental point.

The obtained equation is then used for the calculation of ρ^{sl} and ρ^{sv} at given (T, P^s) conditions and for the evaluation of the variances of the data. A new regression is done on density and vapor pressure data, searching for the minimum of an objective function which is a combination of the former two:

$$f_{ob,overall} = f_{ob,\rho} + f_{ob,\varphi}$$
(5.3)

Successive regression steps are performed until the reaching of a satisfactory equation with good performances with respect to different thermodynamic properties; the saturated densities and the variances are recalculated at each step using the equation obtained in the previous step.

In the case of a multiproperty fitting, other objective functions for further properties are considered. For a generic property M the objective function can be written as

$$f_{ob,m} = \frac{1}{n_M} \sum_{i=1}^{n_M} \left(\frac{M_{exp} - M_{calc}}{M_{exp}} \right)_i^2 / \sigma_{M,i}^2$$
(5.4)

where the subscript *calc* denotes a property value calculated from the model with the current values of the free parameters; the other symbols have a meaning similar to the previous cases.

In the present work a multiproperty fitting was done considering also data of isobaric heat capacity C_p , speed of sound w, and Joule-Thomson coefficient μ_{JT} . The objective function to be minimized in such a regression case is

$$f_{ob,overall} = f_{ob,\rho} + f_{ob,\varphi} + f_{ob,C_p} + f_{ob,w} + f_{ob,\mu_{JT}}$$
(5.5)

In general, the available experimental data cannot be considered in the regression as a whole; in fact some of them are affected by systematic errors or show a lower precision with respect to other data sets. Therefore, the experimental sources have to be subdivided into two groups: the *primary* data, i.e., the most precise ones that are used for the regression, and the *secondary* data, that are used only for comparison in order to check the performances of the obtained DEoS.

The choice of primary data can be initially based on the analysis of their stated accuracy and of the adopted experimental techniques. Anyway, during the regression process some data sources can be moved from primary to secondary data and vice versa taking into account their deviations from the obtained equations and the consistency with other experimental sources.

5.3. Phase equilibria of sulfur hexafluoride

Since in many cases the user of an equation of state is interested only in phase equilibria representation, auxiliary equations for the calculation of vapor pressure and saturation densities have been developed and reported in the present section. Using these equations, such properties can be easily and precisely evaluated avoiding the whole implementation of the equation of state.

The units adopted through this work are K for temperature, MPa for pressure, and $mol \cdot m^{-3}$ for density, notwithstanding in the tables and figures the density is reported in kg·m⁻³ for reader's convenience. Since the correlation equations and all temperature values in this work are relative to the International Temperature Scale 1990 (ITS-90) [7], the temperature values of the available data were converted to ITS-90 when based on an older temperature scale.

In this section, each experimental data set was subdivided into three subsets depending on temperature: the *ordinary* region, with reduced temperature lower than 0.99, the *extended critical* region, with $0.99 \le T_r \le 0.998$, and the *critical* region, with $T_r \ge 0.998$. The number of experimental points and the validation results are separately given for these regions, which are respectively indicated by "Ord.", "Ext. Crit.", and "Crit." in the following tables.

In the following, the error deviation (Δ), the average absolute deviation (AAD) and the bias (Bias), are defined as in Appendix A.6.

5.3.1. Triple point and critical point

For sulfur hexafluoride, the triple-point temperature and the corresponding vapor pressure were recently measured by Funke et al. [8], who reported the values $T_t = 223.555$ K and $P_t = 0.23143$ MPa. The densities of liquid and vapor phases at the triple point have been calculated by means of the auxiliary equations developed in the following sections, Eqs. (5.7) and (5.8), yielding $\rho_t^{sl} = 1844.77$ kg·m⁻³ and $\rho_t^{sv} = 19.5603$ kg·m⁻³.

A high accuracy measurement of the critical temperature of sulfur hexafluoride was done by Kurzeja et al. [9]. This value and the other critical values assumed in this work are taken from the same source and are reported in Table 5.1.

5.3.2. Vapor pressure

Several sources of vapor pressure data for sulfur hexafluoride are available in the literature. These data were obtained through different techniques and consequently they have different accuracy levels.

		Ref.
M (kg·mol ⁻¹)	146.055×10 ⁻³	31
$T_{ m t}$ (K)	223.555	8
P_t (MPa)	0.23143	8
$T_{\rm c}$ (K)	318.7232	9
P_c (MPa)	3.754983	9
$\rho_{\rm c} ~({\rm mol} \cdot {\rm m}^{-3})$	5.0813×10 ³	9
ω	0.218	_
$c_{\text{SRK}} (\text{m}^3 \cdot \text{mol}^{-1})$	4.2833705×10 ⁻⁶	_

Table 5.1: Substance-specific parameters for SF₆.

The data sets selected as primary data for the regression of the auxiliary equation for vapor pressure are those measured by Funke et al.[8] and Gilgen et al. [10]; the first source is the most recent one among the available data, while the second one is from the same research group. Both sets were measured through a "Two-Sinker-Method", i.e., using an apparatus that was specifically developed for taking accurate measurements of vapor pressure, saturated liquid density, and saturated vapor density along the whole coexistence curve. These data are very precise and cover the whole range from the triple-point temperature to the critical temperature.

Other rather accurate data are available, as the sets of Hurly et al. [3], Blanke et al. [11], and Biswas and Ten Seldam [12], but they were not considered for the regression because the cited data of Funke et al. [8] and Gilgen et al. [10]. have a higher accuracy level and a population sufficient for the description of the whole vapor-liquid coexistence curve. Additional vapor pressure data for the present fluid were found in the literature, but they were considered only for comparison, due to their lower precision.

The data sources considered in the present work are reported in Table 5.2. The temperature range, the uncertainty claimed by the experimenters, and the number of points falling inside each of the identified three regions are reported for each data set. The primary data used for the regression are denoted by "I" in the column "Class", while the secondary data for the validation are denoted by "II". Moreover, the available data are graphically shown in Fig. 5.1.

The following auxiliary equation for the calculation of the vapor pressure of sulfur hexafluoride was obtained by fitting the selected primary data:

$$\ln\left(\frac{P^{s}}{P_{c}}\right) = \frac{T_{c}}{T} \left(N_{1}\tau + N_{2}\tau^{1.5} + N_{3}\tau^{2} + N_{4}\tau^{4}\right)$$
(5.6)

where $N_1 = -7.1238938$, $N_2 = 2.030119$, $N_3 = -1.5436745$, $N_4 = -2.6403455$, and $\tau = (1 - T/T_c)$. The values of the critical parameters are given in Table 5.1. The equation holds from the triple-point temperature up to the critical temperature.

The validation results of Eq. (5.6) with respect to the experimental data of vapor pressure are reported in Table 5.3. The equation excellently reproduces the primary data, showing very low deviations and a virtually null value for bias. The more recent secondary data sets are satisfactorily represented, in particular those of Hurly et al. [3], Blanke et al. [11], Biswas and Ten Seldam [12], and Biswas et al. [13].

Figure 5.2 shows the deviations between the primary and secondary experimental data and the values generated from Eq. (5.6); a comparison of this equation with the Funke et al. [8] auxiliary equation is also presented. The bias values in Table 5.3 and the deviations in Fig. 5.2 show that the majority of the secondary data is under-predicted by the equation, but this can be ascribed to the experimental quality of the data themselves.

Pof	First Author	Voor	T range		NPT for ea	ch regio	n	Uncertainty ^a	Class
Kel.	First Aution	I Cal	(K)	Ord.	Ext. Crit.	Crit.	Overall	(%)	
				Pı	rimary data				
8	Funke	2002	224-319	24	4	5	33	±0.01	Ι
10	Gilgen	1992	288-315	9	-	-	9	± 0.01 to ± 0.015	Ι
	Total pr	imary		33	4	5	42		
3	Hurly	2000	278-313	10	-	-	10	n.a.	II
11	Blanke ^b	1993	224-319	53	1	2	57	±0.01	II
32	Berg	1990	293-319	7	4	12	23	n.a.	II
12	Biswas	1989	303-319	6	4	4	14	±0.01	II
29,30	Jany	1986	284-319	19	13	17	49	n.a.	II
13	Biswas	1984	313-319	8	19	26	53	±0.01	II
33	Totskii ^b	1984	224-318	19	5	-	25	±0.35	II
14	Watanabe	1977	273-318	16	-	1	17	±0.03	II
17	Ulybin	1970	233-318	8	-	1	9	n.a.	II
15	Mears	1969	230-318	6	-	1	7	±0.2	II
34	Otto	1960	279-319	10	2	1	13	±0.1	II
35	Clegg	1955	273-319	8	1	-	9	n.a.	II
	Over	all		205	53	70	328		

Table 5.2: Summary of the available data sets for the vapor pressure of SF₆.

^a n.a. = not available.

^b The experimental points with temperature lower than the triple-point temperature assumed in this work are not considered for the validation.



Figure 5.1: Available experimental data for the vapor pressure of SF₆.

Table 5.3: Comparison between vapor pressure experimental data and values calculated with Eq. (5.6).

Ref.	First Author	Year	T range		AA (%	AD %)		Bias (%)	Class	
			(K)	Ord.	Ext. Crit.	Crit.	Overall	Overall		
	Primary data									
8	Funke	2002	224-319	0.001	0.002	0.001	0.001	-0.001	Ι	
10	Gilgen	1992	288-315	0.003	-	-	0.003	0.002	Ι	
	Total pr	imary		0.002	0.002	0.001	0.001	0.000		
Secondary data										
3	Hurly	2000	278-313	0.046	-	-	0.046	0.025	II	
11	Blanke	1993	224-319	0.058	0.016	0.018	0.056	0.053	II	
32	Berg	1990	293-319	0.653	0.897	0.724	0.733	0.732	II	
12	Biswas	1989	303-319	0.009	0.010	0.022	0.013	-0.006	II	
29,30	Jany	1986	284-319	0.506	0.258	0.355	0.388	0.022	II	
13	Biswas	1984	313-319	0.007	0.017	0.011	0.013	-0.011	II	
33	Totskii	1984	224-318	0.427	0.080	-	0.357	0.288	II	
14	Watanabe	1977	273-318	0.479	-	0.075	0.455	0.455	II	
17	Ulybin	1970	233-318	0.909	-	0.088	0.818	0.818	II	
15	Mears	1969	230-318	0.360	-	0.188	0.336	0.312	II	
34	Otto	1960	279-319	0.259	0.228	0.002	0.235	-0.071	II	
35	Clegg	1955	273-319	0.529	0.045	-	0.475	0.475	II	
	Over	all		0.246	0.155	0.221	0.226	0.147		



Figure 5.2: Deviations of the auxiliary equation for vapor pressure, Eq. (5.6), from the experimental data and from the auxiliary equation of Funke *et al.* [8].

5.3.3. Densities at saturation

Some researchers measured the densities of saturated liquid and saturated vapor together with the vapor pressure. The available data are reported in Table 5.4 and their distribution in the T, ρ plane is shown in Fig. 5.3, from which it is evident that the data cover the whole range of interest.

Table 5.4: Summary of the available data sets for the saturated liquid density and the saturated vapor density of SF_{6} .

Dof	First Author	Voor	T range		NPT for each	ch regio	on	Uncertainty ^a	Class
Kel.	First Aution	I Cal	(K)	Ord.	Ext. Crit.	Crit.	Overall	(%)	Class
				Satur	ated liquid c	lensity			
					Primary dat	a			
8	Funke	2002	224-319	24	4	3	31	±0.015	Ι
10	Gilgen	1992	288-315	13	-	-	13	±0.015	Ι
	Total pri	mary		37	4	3	44		
				S	Secondary da	ita			
12	Biswas	1989	305-319	2	3	3	8	±0.02 to ±2	II
29,30	Jany	1986	284-319	19	13	12	44	n.a.	II
14	Watanabe	1977	271-313	6	-	-	6	n.a.	II
15	Mears	1969	232-313	9	-	-	9	±0.1	II
34	Otto	1960	273-316	15	1	-	16	±0.1	II
35	Clegg	1955	294-317	6	1	-	7	n.a.	II
	Overa	ıll		94	22	18	134		
				Satur	rated vapor c	lensity			
					Primary dat	a			
8	Funke	2002	224-319	24	4	4	32	±0.016	Ι
10	Gilgen	1992	288-315	5	-	-	5	± 0.015 to ± 0.035	Ι
	Total pri	mary		29	4	4	37		
				S	Secondary da	ita			
12	Biswas	1989	303-318	4	1	1	6	±0.04 to ±0.36	II
29,30	Jany	1986	284-319	19	13	16	48	n.a.	
14	4 Watanabe 1977 306		1	-	-	1	n.a.	II	
35 Clegg 1955 294-317		6	1	-	7	n.a.	II		
	Overa	ıll		59	19	21	99		

^a n.a.= not available.



Figure 5.3: Available experimental data for the liquid and vapor saturation densities of SF₆.

Following the former discussion for vapor pressure data, also in this case the data of Funke et al. [8] and Gilgen et al. [10] were selected as primary data, whereas the other sources were included in the secondary data sets. New auxiliary equations for saturated liquid density and for saturated vapor density were regressed from the primary data.

The saturated liquid density ρ^{sl} is represented by the equation

$$\ln\left(\frac{\rho^{sl}}{\rho_c}\right) = N_1 \tau^{1.00 \times 10^{-8}} + N_2 \tau^{0.277} + N_3 \tau^{1.75} + N_4 \tau^{3.65} + N_5 \tau^{5.00}$$
(5.7)

where $N_1 = -0.036794807$, $N_2 = 1.3450165$, $N_3 = -0.23201563$, $N_4 = 2.0159862$, and $N_5 = -4.8275834$. The equation for the saturated vapor density ρ^{sv} is

$$\ln\left(\frac{\rho^{sv}}{\rho_c}\right) = \left(\frac{T_c}{T}\right) \cdot \left(N_1 \tau^{0.140} + N_2 \tau^{0.167} + N_3 \tau^{0.687} + N_4 \tau^{2.59} + N_5 \tau^{5.13}\right)$$
(5.8)

where $N_1 = 2.5558795$, $N_2 = -3.5771609$, $N_3 = -3.9125821$, $N_4 = -1.6069578$, and $N_5 = -4.6089451$. The critical parameters for temperature and density are reported in Table 5.1; both equations are valid from the triple-point temperature up to the critical temperature.

The validation results are given in Table 5.5. Figure 5.4 shows the deviations of the primary and secondary experimental data with respect to Eqs. (5.7) and (5.8), together with comparisons with the corresponding equations of Funke et al. [8]. For the primary data very good precisions are reached by both Eqs. (5.7) and (5.8); the errors are roughly lower than $\pm 0.01\%$ except approaching the critical temperature. The deviations from secondary data are greater due to their higher experimental errors. For the saturated liquid the data of Watanabe et al. [14] and Mears et al. [15] show a good agreement with Eq. (5.7).

Table 5.5: Comparison between saturated densities experimental data and values calculated with Eqs. (5.7) and (5.8).

D (* 7	T range		AA	AD		Bias	a
Ref.	First Author	Year	(K)		(%	6)		(%)	Class
			()	Ord	Ext. Crit.	Crit.	Overall	Overall	
			Sa	aturated lic	quid density				
8	Funke	2002	224-319	0.004	0.021	0.029	0.009	0.000	Ι
10	Gilgen	1992	288-315	0.006	-	-	0.006	0.003	Ι
	Total prin	nary		0.005	0.021	0.029	0.008	0.001	
				Seconda	ary data				
12	Biswas	1989	305-319	0.184	0.545	6.007	2.503	-1.605	II
29,30	Jany	1986	284-319	0.793	0.736	0.851	0.792	-0.792	II
14	Watanabe	1977	271-313	0.058	-	-	0.058	0.048	II
15	Mears	1969	232-313	0.079	-	-	0.079	-0.029	II
34	Otto	1960	273-316	0.110	0.418	-	0.130	-0.062	II
35	Clegg	1955	294-317	1.141	0.716	-	1.080	-1.080	II
	Overal	1		0.268	0.564	1.574	0.492	-0.419	
			Sa	aturated va	apor density				
				Primar	y data				
8	Funke	2002	224-319	0.003	0.006	0.010	0.004	-0.002	Ι
10	Gilgen	1992	288-315	0.020	-	-	0.020	0.013	Ι
	Total prin	nary		0.006	0.006	0.010	0.006	0.000	
	^								
12	Biswas	1989	303-318	0.186	0.342	0.816	0.317	-0.276	II
29,30	Jany	1986	284-319	1.837	0.472	0.239	0.949	-0.045	II
14 Watanabe 1977 306				0.301	-	-	0.301	0.301	II
35	Clegg	1955	294-317	0.218	0.600	-	0.273	0.028	II
	Overal	1		0.646	0.377	0.222	0.504	-0.034	



Figure 5.4: Deviations of the auxiliary equations for saturation densities, Eqs. (5.7) and (5.8), from the experimental data and from the auxiliary equations of Funke *et al.* [8].

5.4. Experimental basis of the new equation of state

The choice of primary data for phase equilibria exposed in Paragraph 5.3 was kept also for the development of the Helmholtz energy equation of state. In addition, the experimental data sources for other thermodynamic properties in the single phase regions are discussed in this section. The number of points, the ranges of temperature and pressure, and the uncertainty estimated by the authors are given for each data set; the classification of the data in primary and secondary sets is also discussed.

The data were subdivided into five regions of the P,T plane, see Fig. 5.5: the *vapor* region, for pressures lower than the vapor pressure or, for supercritical temperatures, for pressures lower than the critical pressure; the *liquid* region, for temperatures lower than the critical temperature and pressures higher than the vapor pressure; the *supercritical* region, for temperatures and pressures higher than the respective critical values; the *critical* region; the *extended critical* region.

The critical region is delimited by $0.998 \le T_r \le 1.01$ and $0.75 \le \rho_r \le 1.25$; the extended critical region covers the range $0.99 \le T_r \le 1.10$ and $0.7 \le \rho_r \le 1.3$, with the exclusion of the area pertaining to the critical region. The critical and the extended critical regions are superimposed to the other regions defined above, but, due to their particular characteristics, they are separately considered. Therefore the experimental points falling in the critical or in the extended critical region are computed as belonging to them and then such points are not included into the number of points of the vapor, liquid, or supercritical region.



Figure 5.5: Subdivision of *P*,*T* plane in five thermodynamic regions.

5.4.1. Density

Several sources of density data for sulfur hexafluoride were published in the literature and the most significant ones are listed in Table 5.6, while their distribution in the P,T plane is shown in Fig. 5.6. Some data sets [3-5,16] are recent and contain a large amount of points with very high

precision; even if they were measured through different experimental techniques, they show a good reciprocal consistency and consequently were selected as primary data for the equation development.

Claus et al. [5] measured the density with an accurate single-sinker densimeter. These data cover wide ranges both in temperature and in pressure, mainly investigating the supercritical region, even if some points in liquid and in vapor phase are also given.

The data of Funke et al. [16] were obtained using a two-sinker densimeter, which assures a very high experimental precision. This very large data set has narrower temperature and pressure ranges than Claus et al. [5], but its minimum pressure is the atmospheric one and the minimum temperature is near the triple-point temperature; therefore, this source gives valuable experimental information for both the vapor and the liquid region.

Ihmels and Gmehling [4] adopted a vibrating tube densimeter and performed their measurements in a very wide temperature range, reaching 623 K as maximum temperature. Their density data are mainly located in the supercritical region, where they are superimposed to both the data sets of Claus et al. [5] and Funke et al. [16].

A Burnett apparatus was used by Hurly et al. [3] to obtain data mainly in the vapor and in the supercritical region; also these data are claimed to have a very low experimental uncertainty.

In addition to the data sets discussed above, other sources [10,17,18,19] were considered as primary in order to improve the data distribution and to extend the validity range of the equation.

Gilgen et al. [10] used the same two-sinker densimeter of Funke et al. [16], even if with an equipment that was state-of-the-art about 10 years before. These measurements, which have then a precision level similar to Funke et al. [16], were included into primary data also considering that they are particularly focused on a narrow temperature range above the critical temperature.

The single isotherm at 298 K measured by Hoinkis [18] was assumed in order to increase the experimental information about the behavior of the fluid near the room temperature; even if the uncertainty of the measurements is not given in the reference, these data are consistent with the other measurements.

The data of Mollerup [19], obtained through a Burnett apparatus, are located in the vapor phase from 260 to 340 K and at pressures up to 2.5 MPa. Part of these points covers the region where the data of Funke et al. [16] and Hurly et al. [3] are also available; moreover, some data were measured at pressures lower than the atmospheric value and then they give additional and valuable experimental information in that region.

Also the data measured by Ulybin and Zherdev [17] in the liquid and supercritical regions were considered as primary. Since these measurements span the temperature interval from 233 to 473 K

and reach a pressure of 55 MPa, they were included to extend the pressure validity range of the obtained equation of state. In fact the maximum pressure of the other primary data is only 30 MPa and then the upper pressure limit of the model would be by far limited if the Ulybin and Zherdev [17] data would have not been considered in the regression. Even if these data were measured almost forty years ago and have a lower claimed accuracy, they are in rather good agreement with the other sources.

The final distribution of the primary density data for the regression of the EEoS-NN equation is shown in Fig. 5.7. The remaining experimental sources were included in the secondary data and they were used only for the validation of the obtained equation. Some of them, as for instance the data of Biswas et al. [13] and of Watanabe et al. [14], have a low claimed experimental uncertainty, but it was chosen not to considered them for the regression because in any case they cannot give any additional and significant improvement of the quantity and distribution of the primary data.

Pof	First Author	Voor	T range	P range			NPT for ea	ch region			Uncertainty ^a	Class
Kel.	First Aution	Tear	(K)	(MPa)	Vap.	Liq.	Supercrit.	Ext. Crit.	Crit.	Overall	(%)	Class
						Prir	nary data					
5	Claus	2003	240-490	1.1-30.0	24	53	138	5	-	220	±0.02 to ±0.03	Ι
16	Funke	2002	225-340	0.1-12.1	197	183	103	55	71	609	±0.015 to ±0.023	Ι
											Liq.: ±0.075 to ±0.02	
4	Ihmala	2002	272 622	20200		76	264	2		442	Supercrit.: ±0.3	т
4	mmens	2002	275-025	5.0-50.0	-	/0	304	2	-	442	Supercrit. near $P_{\rm c}$: ± 0.5	1
											Supercrit. near $T_c, P_c: \pm 2$	
3	Hurly	2000	283-393	0.3-9.0	64	-	17	2	-	83	± 0.02	Ι
10	Gilgen	1992	321-333	0.2-8.0	40	-	49	62	19	170	± 0.015 to ± 0.025	Ι
18	Hoinkis	1989	298	0.2-2.0	18	-	-	-	-	18	n.a.	Ι
19	Mollerup	1985	260-340	0.0-2.5	130	-	-	-	-	130	± 0.1	Ι
17	Ulybin	1970	233-473	0.7-55.0	1	37	37	-	-	75	±0.15 to ±0.25	Ι
	г -	Fotal prin	nary		474	349	708	126	90	1747		
						Seco	ndary data					
11	Blanke	1993	225-453	2.5-30.2	-	133	90	-	-	223	± 0.1	II
36	Kamimura	1989	320-380	3.8-7.0	-	-	30	4	1	35	±0.3	II
37	Blanke	1988	293-340	1.6-6.0	17	-	24	24	10	75	± 0.2	II
38	Freyhof	1986	333-423	0.2-57.0	41	-	32	10	-	83	n.a.	II
29,30	Jany	1986	315-322	1.5-11.7	57	34	26	8	46	171	n.a.	II
13	Biswas	1984	308-333	0.1-10.5	91	5	49	78	48	271	±0.02 to ±0.1	II
39	Likhatskii	1982	373	0.2-15.0	8	-	4	-	-	12	± 0.2	II
14	Watanabe	1977	273-363	2.0-19.6	7	31	44	3	-	85	±0.03	II
40	Keramati	1976	273-323	1.3-17.7	1	207	20	3	3	234	± 0.1	II
15	Mears	1969	298-523	1.1-7.9	13	1	14	6	-	34	± 0.1	II
34	Otto	1960	279-343	2.8-18.6	-	19	13	4	-	36	± 0.1	II
35	Clegg	1955	307-404	2.4-11.0	15	-	54	9	-	78	n.a.	II
	Overall					779	1108	275	198	3084		

Table 5.6: Summary of the available data sets for the density of SF₆.

^a n.a. = not available.



Figure 5.6: Available experimental data for the density of SF₆.



Figure 5.7: Primary experimental density data.

5.4.2. Isobaric heat capacity

Apart from density and vapor pressure data, few measurements of other thermodynamic properties have been published in the literature for sulfur hexafluoride. This is evidently a limiting aspect, because the performances of the obtained DEoS cannot be extensively verified with respect to experimental results. Anyway, the available data allow a basic evaluation of the equation behavior.

Two data sets of isobaric heat capacity of sulfur hexafluoride are present in the literature; they are reported in Table 5.7 and graphically shown in a P,T plot in Fig. 5.8.

Bier et al. [20] measured this property in the vapor phase in the temperature range from 298 to 473 K and at pressure up to 1.5 MPa. Their claimed uncertainty is very low, but it seems rather questionable. The data of Bier et al. [20] are shown in Fig. 5.9 together with the correlations for ideal-gas isobaric heat capacity C_p^o from Cole and de Reuck [6] and Hurly et al. [3]. Even if the two equations were obtained from different types of data, they agree each other. On the contrary, the Bier et al. [20] data at zero pressure show a deviation from the equations that becomes larger as the temperature increases, reaching at higher temperature a value that is far beyond the claimed uncertainty. In the temperature and pressure ranges of these data the ideal part gives a predominant

contribution to the isobaric heat capacity value, therefore it is expected that the error level verified for the data at zero pressure is maintained also at the higher pressures.

The data of Sirota et al. [21] were measured through a flow-type calorimeter and these points cover the liquid, critical, extended critical, and supercritical regions for pressures up to 20 MPa. The data in the liquid phase indicated by the authors as "close to the saturation line" are separately considered in the tables and in the figures of the present work.

Both the data sets were used as primary data in the regression of the EEoS-NN equation in the multiproperty case, see Paragraph. 5.5.2, while they were considered only for validation in the case of training on density and vapor pressure data.

Table 5.7: Summary of the available data sets for the isobaric heat capacity of SF₆.

	First		T range (K)	P range			NPT for ea	ch regio	n		Uncertainty
Ref.	Author	Year		(MPa)	Vap.	Liq.	Supercrit.	Ext. Crit.	Crit.	Overall	(%)
20	Bier	1980	298-473	0.0-1.5	42	-	-	-	-	42	±0.2
21	Sirota	1979	298-425	3.8-20.0	-	45	184	179	92	500	±0.3
21	Sirota ^c	1979	298-316	2.4-4.0	-	44	-	-	-	44	±0.3
Overall					42	89	184	179	92	586	

^c Data close to the saturation line.



Figure 5.8: Available experimental data for the isobaric heat capacity of SF₆.



Figure 5.9: Isobaric heat capacity data of Bier et al. [20] together with curves generated from two equations for ideal-gas isobaric heat capacity.

5.4.3. Speed of sound

Speed of sound is a particularly interesting property for thermodynamic modeling. In fact its analytical expression involves second order derivatives of the Helmholtz energy with respect to density and temperature and this makes it to be related to other properties depending on second order derivatives too. Moreover, adopting modern experimental techniques it can be measured with a high accuracy both in vapor and liquid phase. The availability of precise data for this property allows a valuable test for the quality of an equation of state. Unfortunately few data sets for sulfur hexafluoride have been published in the literature, see Table 5.8 and Fig. 5.10.

Hurly et al. [3] measured vapor-phase speed of sound data using a cylindrical acoustical resonator. This apparatus achieves a high measurement accuracy, that is estimated to be about 0.01%. The temperature range of the data is rather wide and the points are uniformly distributed also in pressure.

The speed of sound in liquid phase along isotherms at temperatures from 230 to 333 K and at pressures from near the saturation up to 60 MPa was measured by Vacek and Zollweg [22]. The

measurement apparatus was based on a pulse-echo-overlap technique; an uncertainty of 0.15% was estimated from the deviations given by the authors.

Also for this property the two data sets were included in the regression procedure for the development of the EEoS-NN equation in the multiproperty case.

Table 5.8: Summary of the available data sets for the speed of sound of SF₆.

Pof	First	Voor	Trange Prange			NPT for each region							
Kei.	Author	I Cal	(K)	(MPa)	Vap.	Liq.	Supercrit.	Ext.Crit.	Crit.	Overall	(%)		
3	Hurly	2000	230-460	0.0-1.5	285	-	-	-	-	285	±0.01		
22	Vacek	1993	231-333	2.1-59.0	-	118	20	-	-	138	±0.15		
Overall						118	20	-	-	423			



Figure 5.10: Available experimental data for the speed of sound of SF₆.

5.4.4. Joule-Thomson coefficient

Bier et al. [20], besides isobaric heat capacity data, measured also some experimental points of Joule-Thomson coefficient. The claimed uncertainty of these data is 0.5% and they cover the same temperature and pressure ranges in the vapor phase as for the heat capacity data. The characteristics of this data set are given in Table 5.9 and the distribution of the points is shown in Fig. 5.11. The data were used for the regression in the case of the multiproperty fitting.

Ref.	First	Voor	T range	P range		Uncertainty					
	Author	Tear	(K)	(MPa)	Vap.	Liq.	Supercrit.	Ext. Crit.	Crit.	Overall	(%)
20	Bier	1980	298-473	0.0-1.5	42	-	-	-	-	42	±0.5
Overall						-	-	-	-	42	

Table 5.9: Summary of the available data sets for the Joule-Thomson coefficient of SF₆.



Figure 5.11: Available experimental data for the Joule-Thomson coefficient of SF₆.

5.5. The new equation of state for sulfur hexafluoride

As discussed in previous sections, the new equation of state proposed for sulfur hexafluoride is a fundamental equation explicit in the reduced Helmholtz energy:

$$\frac{A(T,\rho)}{RT} = a(T,\rho) = a^{o}(T,\rho) + a^{R}(T,\rho)$$
(5.9)

The equation of state is split into two terms: the ideal-gas contribution a° and the residual contribution a^{R} . The first one is modeled following a classical procedure, if an equation for the isobaric heat capacity of the ideal gas $C_{p}^{\circ}(T)$ is known; the second one is developed in the EEoS-NN format as explained in Chap. IV. Both contributions are separately considered in this section. Since the Helmholtz energy as a function of temperature and density is one of the four fundamental

forms of an equation of state, all thermodynamic properties of a pure substance can be obtained by combining derivatives of Eq. (5.9). The mathematical expressions for calculating the most important thermodynamic properties from Eq. (5.9) are given in Appendix A.2.

5.5.1. Ideal-gas contribution

The ideal-gas contribution of the Helmholtz energy is given in dimensionless form by Eq. (A2.5) in Appendix A.2. Since the choice of the ideal values for enthalpy and entropy at the reference state (T_o, ρ_o) is arbitrary, H_o^o and S_o^o were selected so that the enthalpy and entropy of the saturated liquid state at 273.15 K assume the values of 200 kJ·kg⁻¹ and 1 kJ·kg⁻¹·K⁻¹, respectively. The value assumed for the molar gas constant is R=8.314472 J·mol⁻¹·K⁻¹ and it is taken from the work of Mohr and Taylor [23].

From Eq. (A2.5) it is evident that only the ideal-gas heat capacity function $C_p^o(T)$ is required for the calculation of the ideal-gas properties of the fluid. The equation for the ideal-gas isobaric heat capacity of sulfur hexafluoride used throughout this work was developed by Cole and de Reuck [6] by fitting the data of Glushko et al. [24]; such an equation is given by

$$\frac{C_p^o}{R} = f_1 + \sum_{i=2}^6 f_i \frac{(g_i/T)^2 \exp(g_i/T)}{[\exp(g_i/T) - 1]^2}$$
(5.10)

The values of f_i and g_i are given in Table 5.10. The ideal-gas Helmholtz energy equation, derived from Eqs. (A2.5) and (5.10), is

$$a^{o}(T,\rho) = \ln(\rho/\rho_{0}) + a_{1} + \frac{a_{2}}{T} - (f_{1}-1)\ln(T) - \sum_{i=2}^{6} \frac{f_{i}g_{i}}{T} + \sum_{i=2}^{6} f_{i}\ln[\exp(g_{i}/T) - 1]$$
(5.11)

where $a_1 = 1.8009691417$ and $a_2 = 3447.8990761$ K, while the other coefficients are given in Table 5.10.

i	f_i	g_i (K)
1	3.9837756784	-
2	2.2181851010	1114.38
3	-10.921337374	925.64
4	3.3102497939	499.26
5	17.5189671483	884.90
6	2.8903523803	1363.93

Table 5.10: Coefficients of Eqs. (5.10) and (5.11).

5.5.2. Residual part contribution

The residual part a^{R} of Helmholtz energy accounts for the deviations of the thermodynamic behavior of the real fluid from its ideal-gas condition. This contribution is then the most significant one when dealing with liquid states or with vapor conditions at pressures higher than few bars.

The most precise equations of state are obtained by regression of this part on experimental data for the fluid of interest. In the present work the residual contribution was developed assuming the EEoS-NN format presented in Chap. IV. The regression procedure explained in Paragraph 5.2 was applied to the experimental data discussed in Paragraph 5.4. In particular, three training cases were considered:

- training on density and vapor pressure data, assuming the SRK cubic EoS as basic equation;
- training on a multiproperty data set including data of density, vapor pressure, isobaric heat capacity, speed of sound, and Joule-Thomson coefficient; also in this case the SRK cubic EoS was assumed as basic equation;
- training on density and vapor pressure data, assuming the DEoS for sulfur hexafluoride developed by Span and Wagner [1] as basic equation.

A comparison between the first and the second case allows the quantification of the improvement of the equation performances attained when caloric data are included in the regression. The third case was considered in order to verify whether the EEoS-NN model is significantly affected by the precision of the EoS assumed as basic equation. In fact the SRK EoS roughly represents the chosen fluid, while the Span and Wagner [1] DEoS is at present the most precise equation available in the literature for sulfur hexafluoride.

Considering the equation performances, the required experimental effort, and the general applicability of the development procedure, it can be concluded that the most promising training case is the first one, i.e., the regression on data of density and vapor pressure with the SRK EoS as basic equation. Therefore, even if all the developed equations will be considered in the following, the validation tables and figures reported in Paragraph 5.6 are referred to said equation. The corresponding coefficients of the neural network for the representation of the shape functions are given in Table 5.11. The three-dimensional shape of such functions is shown in Figs. 5.12 and 5.13.

The proposed equation of state is valid from the triple point to the temperature of 625 K and for pressures up to 60 MPa. Anyway, it is not capable of reproducing the correct trends of isochoric heat capacity, isobaric heat capacity, and speed of sound in the vicinity of the critical point. In fact a suitable functional form dedicated to this region should be developed and included in the regression [25]. Consequently, the proposed equation is not recommended for the accurate calculation of such

properties in the critical region, i.e., within the temperature range 318–322 K and the density range $555-930 \text{ kg} \cdot \text{m}^{-3}$.

Table 5.11 : Parameters of the neural network for	the representation	of the shape functions.
--	--------------------	-------------------------

		ß =	- 1.5					
			= 3					
		1 - 1 -	= 9					
		J - K	-) -)					
		A = 0.05	- <u>-</u> <u>A</u> - 0.95					
		$\mathbf{n}_{\min} = 0.00$			$\mathbf{D}_{\text{max}} = 0 \cdot 1 \cdot 0$			
		B1as1 = 1.0			B1as2 = 1.0			
		$V_{\min,1} = I_{r,\min} = 0.65$			$V_{\max,1} = T_{r,\max} = 2.5$			
		$V_{\min,2} = \rho_{\rm r,min} = 0.0$		I	$V_{\max,2} = \rho_{r,\max} = 3.5$			
		$W_{\min,1} = \theta_{\min} = 0.7$			$W_{\max,1} = \Theta_{\max} = 1.3$			
		$W_{\min,2} = \phi_{\min} = 0.7$,	$W_{\max,2} = \phi_{\max} = 1.3$			
			1					
i	j	W _{ij}	j	k	w _{ik}			
1	1	3.54503	1	1	0.316204			
1	2	2.02829	1	2	2.48282			
1	3	-0.118765	2	1	0.0202340			
1	4	-1.23481	2	2	-3.31399			
1	5	-2.17567	3	1	-0.168394			
1	6	-3.34951	3	2	6.38428			
1	7	0.0203401	4	1	0.550613			
l	8	-4.44493	4	2	-0.722307			
1	9	-1.50009	5	1	6.26323			
2	1	2.77446	5	2	1.18885			
2	2	-1.09295	6	1	1.44977			
2	3	3.45563	6	2	0.368587			
2	4	1.59915	7	1	-0.464054			
2	5	-3.32511	7	2	-3.76838			
2	6	2.30443	8	1	-1.08736			
2	7	-2.05724	8	2	0.370607			
2	8	-0.605450	9	1	0.188264			
2	9	-3.05939	9	2	13.1372			
3	1	-1.72900	10	1	-5.48739			
3	2	-0.140518	10	2	-8.54672			
3	3	-1.05319						
3	4	0.240768						
3	5	3.72312						
3	6	-2.22128						
3	7	1.14563						
3	8	0.587702						
3	9	1.32096						



Figure 5.12: Shape function $\theta_j = \theta_j(T_r, \rho_r)$.



Figure 5.13: Shape function $\phi_j = \phi_j(T_r, \rho_r)$.

5.6. Comparison of the new equation of state with experimental data and other equations of state

The comparisons of the obtained equations with respect to the available experimental data are given in this section. Four models were considered: the SRK cubic EoS [26,27] with Peneloux volume translation [28], the DEoS for sulfur hexafluoride proposed by Span and Wagner [1], the EEoS-NN equation developed on density and vapor pressure data, and the EEoS-NN equation developed on the multiproperty data base.

For these equations the validation results are given as overall values for the primary data and for the overall data base, whereas the details for the single data sets are not given; the validation is separately done for each of the identified thermodynamic regions. The results for the primary data are written in italics.

A more detailed validation, reporting also the deviations of each data set, is given only for the EEoS-NN equation regressed on data of density and vapor pressure and for the Span and Wagner [1] DEoS.

The performances of the developed EEoS-NN models in the critical region are not fully reliable for all the thermodynamic properties, because their functional form is not specialized for such a region. Consequently, the validation results for the considered equations in the critical region were not included in the calculation of the overall deviation values, even if they are reported in the following tables for sake of completeness.

5.6.1 Vapor-liquid phase boundary

The validation results for vapor pressure, saturated liquid density, and saturated vapor density are shown in Table 5.12. In this table the results with respect to both the primary and the overall data are reported for comparison maintaining the same subdivision of the experimental points into ordinary, extended critical, and critical region reported in Table 5.3.

The best performance for the EEoS-NN models is obtained from the density and vapor pressure data regression; this result was to be expected because a multiproperty regression implies a wider compromise in the representation of a greater number of thermodynamic quantities. Anyway, for the first of the two EEoS-NN cases the accuracy is very good, even if it is significantly lower than that reported for the auxiliary equations, Eqs. (5.6-5.8), which present error deviations much lower than the experimental uncertainties and a practically null shifting. The result of said EEoS-NN equation is however better than the corresponding one for the Span and Wagner [1] DEoS. The cubic EoS performance is far worse and it testifies the improvement brought in by the variables distortion through the EEoS-NN method.

FoS ty	ne		AA	Bias	Class		
Los ty	рс -		(%)		(%)	Cluss
		Ord.	Ext. Crit.	Crit.	Overall	Overall	
		Vapor pres	ssure				
SRK cubic equa	tion [26-28]	0.590	0.255	0.489	0.554	-0.554	Ι
Span and Wa	agner [1]	0.109	0.007	0.013	0.098	-0.013	Ι
EEoS-NN with SRK	Density and vapor pressure	0.041	0.010	0.026	0.038	-0.004	Ι
Uase	Multiproperty	0.102	0.019	0.044	0.093	-0.091	Ι
SRK cubic equa	tion [26-28]	0.633	0.252	0.329	0.554	-0.436	I+II
Span and Wa	agner [1]	0.295	0.156	0.225	0.266	0.128	I+II
EEoS-NN with SRK	Density and vapor pressure	0.249	0.157	0.234	0.230	0.127	I+II
base	Multiproperty	0.243	0.159	0.250	0.225	0.052	I+II
	Satu	rated liqui	d density				
SRK cubic equa	9.043	19.844	12.321	10.097	9.918	Ι	
Span and Wa	0.143	0.446	1.230	0.173	-0.116	Ι	
EEoS-NN with SRK	Density and vapor pressure	0.028	0.283	2.628	0.053	-0.051	Ι
base	Multiproperty	0.068	0.381	8.034	0.098	-0.086	Ι
SRK cubic equa	tion [26-28]	10.319	19.710	12.472	12.211	12.141	I+II
Span and Wa	agner [1]	0.401	0.875	1.456	0.491	-0.451	I+II
EEoS-NN with SRK	Density and vapor pressure	0.292	0.742	3.529	0.377	-0.345	I+II
Dase	Multiproperty	0.335	0.761	7.186	0.416	-0.387	I+II
	Satu	rated vapo	or density				
SRK cubic equa	tion [26-28]	0.532	9.637	14.310	1.636	-0.667	Ι
Span and Wa	igner [1]	0.152	0.632	1.575	0.211	0.029	Ι
EEoS-NN with SRK	Density and vapor pressure	0.050	1.412	7.650	0.215	0.214	Ι
base	Multiproperty	0.089	0.970	8.943	0.196	0.064	Ι
SRK cubic equa	tion [26-28]	1.057	5.766	18.021	2.204	-0.318	I+II
Span and Wa	igner [1]	0.711	0.557	1.348	0.673	0.082	I+II
EEoS-NN with SRK	Density and vapor pressure	0.687	1.352	6.051	0.849	0.346	I+II
Dase	Multiproperty	0.669	0.930	6.535	0.733	0.134	I+II

 Table 5.12: Comparison between experimental data at saturation and values calculated with different EoS models.

In Table 5.13 a detailed validation of the EEoS-NN equation from density and vapor pressure data is exposed for each data source of the primary and secondary data sets. The percentage deviations of the present equation from the primary data are shown in Fig. 5.14 and the deviations from the secondary data are plotted in Fig. 5.15; the lines correspond to values calculated from the Span and Wagner [1] DEoS.

For the vapor pressure, the accuracy of the present EEoS-NN equation is roughly within $\pm 0.05\%$ between about 250 K and the critical temperature, while the equation presents higher deviations below 240 K. The accuracy of the Span and Wagner [1] DEoS for the more precise data sources is approximately two times the EEoS-NN one. The majority of the secondary vapor pressure data shows large positive deviations from the values predicted by both the equations.

For the saturated liquid density a better performance is obtained with respect to vapor density by the EEoS-NN models, as shown in Table 5.12. The Span and Wagner [1] DEoS has a similar behavior for the two phases, whereas the accuracy of the SRK EoS is always worse and it is particularly bad for the saturated liquid density, as it is in general expected for a cubic EoS. The good behavior of the EEoS-NN equation is confirmed also looking at the local performance reported in Fig. 5.14; the plot for the secondary data in Fig. 5.15 is less significant due to the higher experimental errors of such data sets. Both the saturation densities are precisely represented with deviations well within $\pm 0.1\%$ up to about 310 K, whereas the deviations increase approaching the critical temperature; this is also shown in Table 5.13 for the critical and the extended critical region. Apart from these regions, the prediction accuracy of the present EEoS-NN equation is comparable with the respective experimental uncertainties of the two quantities. With respect to this equation the performance of the Span and Wagner [1] DEoS is worse in the ordinary region, where it also seems to be less stable with temperature; moreover, as well as for the EEoS-NN equation, it is possible to notice a worsening when the critical temperature is approached.

							Average Abso	lute Deviation	n AAD (%)			
Ref	First	Vear	T range	Ordina	ry region.	Ext. crit	ical region	Critica	l region	Ove	erall	Class
Kel.	Author	i cai	(K)	FEOS NN	Span and	FEOS NN	Span and	FEOS NN	Span and	FEOS NN	Span and	
				EE05-ININ	Wagner [1]	EE05-ININ	Wagner [1]	EE05-ININ	Wagner [1]	EE05-ININ	Wagner [1]	
						Vapor	pressure					
8	Funke	2002	224-319	0.044	0.126	0.010	0.007	0.026	0.013	0.039	0.109	Ι
10	Gilgen	1992	288-315	0.032	0.062	-	-	-	-	0.032	0.062	Ι
	Total p	rimary		0.041	0.109	0.010	0.007	0.026	0.013	0.038	0.098	
3	Hurly	2000	278-313	0.065	0.108	-	-	-	-	0.065	0.108	II
11	Blanke	1993	224-319	0.047	0.147	0.013	0.012	0.002	0.009	0.046	0.144	II
32	Berg	1990	293-319	0.678	0.712	0.901	0.902	0.747	0.735	0.759	0.781	II
12	Biswas	1989	303-319	0.028	0.045	0.012	0.005	0.003	0.011	0.022	0.029	II
29,30	Jany	1986	284-319	0.479	0.460	0.260	0.263	0.378	0.366	0.390	0.380	II
13	Biswas	1984	313-319	0.017	0.012	0.015	0.014	0.015	0.006	0.016	0.014	II
33	Totskii	1984	224-318	0.370	0.388	0.084	0.079	-	-	0.310	0.324	II
14	Watanabe	1977	273-318	0.512	0.557	-	-	0.089	0.082	0.512	0.557	II
17	Ulybin	1970	233-318	0.905	0.908	-	-	0.102	0.094	0.905	0.908	Π
15	Mears	1969	224-319	0.358	0.342	-	-	0.204	0.195	0.358	0.342	Π
34	Otto	1960	279-319	0.286	0.305	0.228	0.223	0.034	0.019	0.276	0.292	Π
35	Clegg	1955	273-319	0.553	0.595	0.046	0.049	-	-	0.496	0.534	Π
	Ove	rall		0.249	0.295	0.157	0.156	0.234	0.225	0.230	0.266	
						Saturated li	quid density					
8	Funke	2002	224-319	0.023	0.132	0.283	0.446	2.628	1.230	0.060	0.177	Ι
10	Gilgen	1992	288-315	0.039	0.165	-	-	-	-	0.039	0.165	Ι
	Total p	rimary		0.028	0.143	0.283	0.446	2.628	1.230	0.053	0.173	
12	Biswas	1989	305-319	0.105	0.097	0.309	0.256	8.556	6.209	0.227	0.193	II
29,30	Jany	1986	284-319	0.847	0.983	1.007	1.186	2.497	0.324	0.912	1.065	II
14	Watanabe	1977	271-313	0.038	0.103	-	-	-	-	0.038	0.103	II
15	Mears	1969	232-313	0.099	0.194	-	-	-	-	0.099	0.194	II
34	Otto	1960	273-316	0.113	0.205	0.248	0.045	-	-	0.121	0.195	Π
35	Clegg	1955	294-317	1.209	1.352	0.916	1.229	-	-	1.167	1.335	II

Table 5.13: Comparison of each source of saturation data with the selected EEoS-NN model and the Span and Wagner [1] DEoS.

		Year		Average Absolute Deviation AAD (%)								
Ref.	First		T range	Ordinary region.		Ext. critical region		Critical region		Ove	erall	Class
	Author		(K)	EEoS-NN	Span and Wagner [1]	EEoS-NN	Span and Wagner [1]	EEoS-NN	Span and Wagner [1]	EEoS-NN	Span and Wagner [1]	
Saturated liquid density (continuation)												
	Ove	rall		0.292	0.401	0.742	0.875	3.529	1.456	0.377	0.491	
Saturated vapor density												
8	Funke	2002	224-319	0.037	0.160	1.412	0.632	7.650	1.575	0.234	0.227	Ι
10	Gilgen	1992	288-315	0.112	0.118	-	-	-	-	0.112	0.118	Ι
	Total p	rimary		0.050	0.152	1.412	0.632	7.650	1.575	0.215	0.211	
12	Biswas	1989	303-318	0.147	0.167	1.150	0.351	2.871	0.248	0.347	0.204	II
29,30	Jany	1986	284-319	1.941	1.884	1.408	0.595	5.849	1.359	1.725	1.361	II
14	Watanabe	1977	306	0.324	0.184	-	-	-	-	0.324	0.184	II
35	Clegg	1955	294-317	0.216	0.146	0.633	0.017	-	-	0.275	0.128	Π
Overall				0.687	0.711	1.352	0.557	6.051	1.384	0.849	0.673	



Figure 5.14: Comparison of saturation values calculated from the EEoS-NN equation to the primary experimental data and to the Span and Wagner [1] DEoS.


Figure 5.15: Comparison of saturation values calculated from the EEoS-NN equation to the secondary experimental data and to the Span and Wagner [1] DEoS.

5.6.2. Single phase region

DENSITY

The results of the validation of the EEoS-NN models, together with the Span and Wagner [1] DEoS and the SRK equation, are reported in Table 5.14. The EEoS-NN equation regressed on density and vapor pressure data presents deviation values of the same order of the experimental uncertainties in all the regions. The practically null bias value demonstrates that the equation is well centered on the experimental data. The EEoS-NN equation regressed on multiproperty data is moderately less accurate, but anyway it has a precision level slightly better than that of the Span and Wagner [1] DEoS. The SRK cubic equation has a very poor performance leading to AAD values higher than 3%, except for the vapor region where the accuracy is better.

A detailed analysis of the validation results for the chosen EEoS-NN model and for the Span and Wagner [1] DEoS are reported for each data set in Table 5.15. Pressure deviations are given instead of density deviations in the critical and extended critical regions. In fact, where the slopes of the isotherms on (P, ρ) coordinates are almost flat, the deviations in pressure are more meaningful because the uncertainty in this variable becomes the dominant contribution to the overall experimental uncertainty in density.

The EEoS-NN model presents satisfactory results for all the considered regions and a better performance for the liquid one. The primary data are represented with similar AAD values for all the data sets. The deviations of the primary data from the equation are shown in detail in Fig. 5.16, in which the size of the symbols is related to the magnitude of the deviation of each point. This figure confirms the validation results given in Table 5.15 and in particular the very good performance in the liquid phase is evidenced. A slight decrease of the accuracy is verified for the higher temperatures; a similar trend seems to be found at the higher pressures, but this is probably due to the lower accuracy of the Ulybin and Zherdev data [17] rather than to a worse behavior of the equation. In the critical and extended critical regions of Fig. 5.16 density deviations are presented instead of pressure deviations, leading to an apparent inconsistency with Table 5.15. In any case density deviations higher than 0.5% are verified only very close to the critical point.

EoS ty	ре		AAD (%)							
		Vap.	Liq.	Supercrit.	Ext. Crit. ^e	Crit. ^e	Overall	Overall		
SRK cubic equa	tion [26-28]	0.332	4.270	3.462	4.929	3.015	2.849	1.132	Ι	
Span and Wa	igner [1]	0.087	0.077	0.134	0.065	0.042	0.103	-0.001	Ι	
EEoS-NN with SRK base	Density and vapor pressure	0.038	0.013	0.039	0.038	0.035	0.033	-0.001	Ι	
-	Multiproperty	0.089	0.016	0.077	0.110	0.054	0.070	0.036	Ι	
SRK cubic equat	tion [26-28]	2.765	4.240	3.702	4.697	2.434	3.706	1.949	I+II	
Span and Wa	igner [1]	0.118	0.107	0.163	0.127	0.050	0.134	-0.016	I+II	
EEoS-NN with SRK base	Density and vapor pressure	0.079	0.062	0.087	0.106	0.051	0.080	-0.014	I+II	
	Multiproperty	0.121	0.065	0.123	0.178	0.061	0.112	0.022	I+II	

Table 5.14: Comparison between density experimental data and values calculated with different EoS models.^d

^d The data set of Jany and Straub [29,30] was excluded from the present validation, due to the much higher deviations of such data.

^e In the extended critical region and in the critical region, pressure deviations are given instead of density deviations.

								А	verage A	bsolute I	Deviation	AAD (%)				_
			-		Va	ap.	L	iq.	Supe	rcrit.	Ext.	Crit. ^e	Cı	rit. ^e	Ove	erall	
Ref.	First	Year	T range	<i>P</i> range		Span		Span		Span		Span		Span		Span	Class
	Author		(K)	(MPa)	EEoS-	and	EEoS-	and	EEoS-	and	EEoS-	and	EEoS-	and	EEoS-	and	
					NN	Wagner	NN	Wagner	NN	Wagner	NN	Wagner	NN	Wagner	NN	Wagner	
						[1]		[1]		[1]		[1]		[1]		[1]	
5	Claus	2003	240-490	1.1-30.0	0.014	0.061	0.009	0.077	0.037	0.119	0.067	0.188	-	-	0.028	0.104	Ι
16	Funke	2002	225-340	0.1-12.1	0.042	0.125	0.012	0.062	0.030	0.094	0.042	0.060	0.036	0.034	0.029	0.091	Ι
4	Ihmels	2002	273-623	3.0-30.0	-	-	0.015	0.095	0.034	0.145	0.025	0.049	-	-	0.030	0.136	Ι
3	Hurly	2000	283-393	0.3-9.0	0.068	0.085	-	-	0.158	0.297	0.072	0.077	-	-	0.087	0.128	Ι
10	Gilgen	1992	321-333	0.2-8.0	0.032	0.111	-	-	0.047	0.105	0.031	0.059	0.033	0.072	0.036	0.088	Ι
18	Hoinkis	1989	298	0.2-2.0	0.014	0.046	-	-	-	-	-	-	-	-	0.014	0.046	Ι
19	Mollerup	1985	260-340	0.0-2.5	0.025	0.033	-	-	-	-	-	-	-	-	0.025	0.033	Ι
17	Ulybin	1970	233-473	0.7-55.0	0.251	0.395	0.022	0.119-	0.057	0.150	-	-	-	-	0.043	0.138	Ι
	T	otal prin	nary		0.038	0.087	0.013	0.077	0.039	0.134	0.038	0.065	0.035	0.042	0.033	0.103	
11	Blanke	1993	225-453	2.5-30.2	-	-	0.039	0.059	0.034	0.067	-	-	-	-	0.037	0.063	Π
36	Kamimura	1989	320-380	3.8-7.0	-	-	-	-	0.292	0.475	0.133	0.132	0.153	0.211	0.273	0.434	Π
37	Blanke	1988	293-340	1.6-6.0	0.154	0.230	-	-	0.082	0.153	0.049	0.077	0.046	0.047	0.089	0.145	Π
38	Freyhof	1986	333-423	0.2-57.0	0.062	0.055	-	-	0.390	0.388	0.671	0.697	-	-	0.262	0.261	Π
13	Biswas	1984	308-333	0.1-10.5	0.122	0.103	0.162	0.140	0.142	0.134	0.058	0.068	0.049	0.034	0.105	0.100	Π
39	Likhatskii	1982	373	0.2-15.0	0.012	0.018	-	-	0.045	0.135	-	-	-	-	0.023	0.057	II
14	Watanabe	1977	273-363	2.0-19.6	0.450	0.639	0.042	0.082	0.044	0.102	0.066	0.087	-	-	0.078	0.138	II
40	Keramati	1976	273-323	1.3-17.7	3.266	3.126	0.151	0.183	0.428	0.369	0.223	0.233	0.530	0.493	0.189	0.213	II
15	Mears	1969	298-523	1.1-7.9	0.306	0.283	0.009	0.155	0.140	0.133	0.166	0.176	-	-	0.204	0.198	II
34	Otto	1960	279-343	2.8-18.6	-	-	0.157	0.183	0.237	0.169	0.463	0.556	-	-	0.220	0.219	II
35	Clegg	1955	307-404	2.4-11.0	0.541	0.703	-	-	0.337	0.413	0.761	0.755	-	-	0.425	0.508	II
		Overal	11		0.079	0.118	0.062	0.107	0.087	0.163	0.106	0.127	0.051	0.050	0.080	0.134	

Table 5.15: Comparison of each source of density data with the selected EEoS-NN model and the Span and Wagner [1] DEoS.^d

^d The data set of Jany and Straub [29,30] was excluded from the present validation table, due to the much higher deviations of such data.

^e In the extended critical region and in the critical region, pressure deviations are given instead of density deviations.



Figure 5.16: Deviations between the density data in the primary sets and the EEoS-NN equation.

Figure 5.17 gives the comparison between the primary density data sets and values calculated from the present EEoS-NN equation for several intervals of temperature; deviations between the Span and Wagner [1] equation and the EEoS-NN one are also plotted for the mean temperature of each interval. The considered pressure and temperature ranges correspond to the validity range of the proposed equation. An analogous representation for the secondary data is shown in Fig. 5.18.



Figure 5.17: Comparison of density values calculated from the EEoS-NN equation to the primary experimental data and the to Span and Wagner [1] DEoS.



Figure 5.18: Comparison of density values calculated from the EEoS-NN equation to the secondary experimental data and to the Span and Wagner [1] DEoS.

For the primary data very low deviations are verified below the critical temperature, whereas a worsening in the density deviations is evidenced approaching the critical point. For higher temperatures the performance is satisfactory, even if the deviation values are slightly larger. A similar trend is roughly verified for the secondary data, but in this case the magnitude of the deviations is larger due to the lower quality of the data. Pressure deviations for each primary and secondary data set are presented in Figs. 5.19 and 5.20, respectively, in a wide range of temperature and density around the extended critical region. The pressure deviations with respect to the primary data are within $\pm 0.15\%$ and have a rather uniform distribution also in the critical region, where the high deviations shown in Fig. 5.17 are no more present. Figure 5.20 for secondary data shows a similar behavior even if the deviation values are generally higher.

The error deviations of the secondary data of Jany and Straub [29,30], obtained from refractive index measurements, resulted to be not consistent with those of the other sets of this data group and it was decided to exclude them from the statistical results of Tables 5.14 and 5.15. In fact the overall AAD values of these data with respect to both the present EEoS-NN model and the Span and Wagner [1] DEoS are above 1.8%.

Table 5.15 proves that the Span and Wagner [1] DEoS has a slightly lower performance than the EEoS-NN equation through the different regions. The curves for the Span and Wagner [1] DEoS in Figs. 5.17-5.20 present a decrease of the accuracy for pressures higher than roughly 1 MPa and show oscillating deviations, whose magnitude increases with temperature, between calculated and experimental values.



Figure 5.19: Comparison of pressure values calculated from the EEoS-NN equation in the extended critical region to the primary experimental data and to the Span and Wagner [1] DEoS.



Figure 5.20: Comparison of pressure values calculated from the EEoS-NN equation in the extended critical region to the secondary experimental data and to the Span and Wagner [1] DEoS.

ISOBARIC HEAT CAPACITY

Table 5.16 reports the results of the validation of the EEoS-NN models, of the Span and Wagner [1] DEoS, and of the SRK equation for the available experimental data of caloric properties, i.e., the isobaric heat capacity, the speed of sound, and the Joule-Thomson coefficient. The isobaric heat capacity is considered in this section, whereas the other two properties are discussed in the following ones.

Looking at the two versions of the EEoS-NN model, the equation regressed on moltiproperty data improves the representation accuracy of the isobaric heat capacity data with respect to that regressed only on density and coexistence data. This result is not surprising because in the multiproperty case the isobaric heat capacity data were used for the regression, whereas in the other case such an information was not given during the equation development and the isobaric heat capacity is then predicted. The improvement is particularly evident in the liquid region and in the extended critical region; also the balancing of the equation is improved with a better bias value calculated for the overall data. Anyway, the two equations have a quite similar behavior in the vapor, liquid, and supercritical region, i.e., in the part of the P, T plane with common engineering interest. Therefore the equation regressed on density and vapor pressure data is preferred due to the lower experimental effort required for its development.

The Span and Wagner [1] DEoS has a performance comparable with that of the multiproperty EEoS-NN model, except in the extended critical region where it is worse with respect to both the EEoS-NN models. The results for the SRK EoS show a poor accuracy in the representation of the isobaric heat capacity data for all the regions, in particular for the liquid and extended critical ones.

A detailed analysis of the validation results for the chosen EEoS-NN model and for the Span and Wagner [1] DEoS is reported for each data set in Table 5.17. Comparable deviation values are shown in each region and the most evident difference is for the extended critical region, where the EEoS-NN model seems to perform better results.

EoS	type		AAD (%)								
	Vap.	Liq.	Supercrit.	Ext. Crit.	Crit.	Overall	Overall				
Isobaric heat capacity											
SRK cubic eq	uation [26-28]	1.538	14.207	3.093	22.059	33.807	12.264	6.322			
Span and V	Wagner [1]	0.783	0.888	1.050	3.966	27.333	2.055	1.270			
EEoS-NN with	Density and vapor pressure	0.797	1.014	1.141	2.983	29.156	1.760	0.808			
SKK Dase	Multiproperty	0.762	0.894	1.188	1.852	19.667	1.340	0.392			
Speed of sound											
SRK cubic eq	uation [26-28]	0.106	25.165	18.946	-	-	7.987	7.937			
Span and V	Wagner [1]	0.041	1.218	.218 1.594 -		-	0.443	0.383			
EEoS-NN with	Density and vapor pressure	0.026	0.388	1.101	-	-	0.178	0.098			
SKK base	Multiproperty	0.047	0.332	1.052	-	-	0.174	0.079			
		Jou	ile-Thomso	on coefficier	nt						
SRK cubic equation [26-28]		7.205	-	-	-	-	7.205	-7.067			
Span and Wagner [1]		1.924	-	-	-	-	1.924	-1.924			
EEoS-NN with SRK base	Density and vapor pressure	2.303	-	-	-	-	2.303	-2.303			
	Multiproperty	0.363	-	-	-	-	0.363	-0.172			

									Average	e Absolute	Deviatio	on AAD (%)			
	First		Trance	nranga	I	∕ap.]	Liq.	Sup	percrit.	Ex	t. Crit.	(Crit.	0	verall
Ref.	Author	Year	(K)	(MPa)	EEoS- NN	Span and Wagner [1]										
							Iso	baric heat o	capacity							
20	Bier	1980	298-473	0.0-1.5	0.797	0.783	-	-	-	-	-	-	-	-	0.797	0.783
21	Sirota	1979	298-425	3.8-20.0	-	-	0.416	0.441	1.141	1.050	2.983	3.966	29.256	27.333	1.874	2.262
21	Sirota ^c	1979	298-316	2.4-4.0	-	-	1.626	1.345	-	-	-	-	-	-	1.626	1.345
		Overa	11		0.797	0.783	1.014	0.888	1.141	1.050	2.983	3.966	29.256	27.333	1.760	2.055
								Speed of se	ound							
3	Hurly	2000	230-460	0.0-1.5	0.026	0.041	-	-	-	-	-	-	-	-	0.026	0.041
22	Vacek	1993	231-333	2.1-59.0	-	-	0.388	1.218	1.101	1.594	-	-	-	-	0.491	1.273
		Overa	11		0.026	0.041	0.388	1.218	1.101	1.594	-	-	-	-	0.178	0.443
							Joule	-Thomson	coefficie	ent						
20	Bier	1980	298-473	0.0- 1.5	2.303	1.924	-	-	-	-	-	-	-	-	2.303	1.924
		Overa	11		2.303	1.924	-	-	-	-	-	-	-	-	2.303	1.924

Table 5.17: Comparison of each source of caloric property data with the selected EEoS-NN model and the Span and Wagner [1] DEoS.

^c Data close to the saturation line.

Figure 5.21 shows the distribution in (P, T) coordinates of the prediction accuracy for the chosen EEoS-NN equation with respect to the available isobaric heat capacity data. The good performance of the model in the vapor and liquid regions is evident, with a worsening when approaching the saturation line and at the higher temperatures; this behavior is partly due to the decrease of the accuracy of the Bier et al. [20] data with increasing temperature, as discussed in Paragraph 5.4.2.



Figure 5.21: Deviations between the isobaric heat capacity data and the EEoS-NN equation.

Figure 5.22 gives the comparison between the isobaric heat capacity data sets and values calculated from the present EEoS-NN equation for several intervals of temperature; deviations between the Span and Wagner equation [1] and the EEoS-NN one are also plotted for the mean temperature of each interval. The data of Bier et al. [20] for the vapor region are accurately represented for low temperature values, while the prediction accuracy of the EEoS-NN equation

seems to be lower at higher temperatures, but this is probably due to the aforementioned drawbacks of these experimental data. Larger values of the deviations pertain to the data of Sirota et al. [21] in the liquid region. In any case, as also discussed in Paragraph 5.4.2, for both the data sets the very low claimed uncertainty seems rather questionable. In particular, as it is possible to notice in Fig. 5.22, there is a certain shifting between both the considered equations and the data at the higher temperatures.



Figure 5.22: Comparison of isobaric heat capacity values calculated from the EEoS-NN equation to the experimental data and to the Span and Wagner [1] DEoS.

In order to verify in more detail the EEoS-NN performance for the isobaric heat capacity in the extended critical and supercritical regions, plots of isobars for temperature and pressure around the critical point and up to 330 K and 20 MPa are reported in Fig. 5.23 together with the corresponding data by Sirota et al. [21] The figure shows that the trend of the isobaric heat capacity data is correctly represented and that there is only a slight shifting in temperature whose magnitude increases while pressure approaches the critical value. In particular the isobar at 3.8 MPa shows the largest shifting with also a basically different trend from the data; in fact it should be noted that the data at this pressure are in the critical region, where the use of the equation is not recommended for the calculation of the isobaric heat capacity.



Figure 5.23: Isobaric heat capacity from the EEoS-NN equation and from the experimental data.

SPEED OF SOUND

The accuracy of the representation of the speed of sound data is comparable in all the regions for the two EEoS-NN equations, see Table 5.16. This seems to show that the inclusion of this quantity in the regression data set may not lead to an increase of the corresponding accuracy, probably due to

the required compromise in the simultaneous representation of several properties in the objective function for the minimization procedure.

The Span and Wagner [1] DEoS gets worse results, in particular in the liquid and supercritical regions. The SRK equation has a reliable trend only in the vapor region, while very high deviation values from the experimental data are found elsewhere and particularly in the liquid region, so confirming the general limits of the model for the dense phase region.

From Table 5.17 it is evident that in the vapor region the speed of sound is represented by the chosen EEoS-NN equation with an accuracy comparable with the experimental uncertainty, whereas in the liquid region the deviations are higher. The distribution in (P, T) coordinates of the deviations from the available experimental data is also shown in Fig. 5.24, while Fig. 5.25 presents, for several temperature intervals, the deviations of the single points of each data set with respect to the EEoS-NN equation. A comparison between this equation and the Span and Wagner [1] DEoS is also plotted for the average temperature of each interval. Figure 5.25 evidences a scattering of the experimental points in the liquid region together with relevant deviations from both the considered equations, suggesting that the claimed uncertainty of the data for the dense phase region could be questionable.

The performance of the Span and Wagner [1] DEoS is satisfactory for the vapor region, whereas, just crossing the phase boundary, the equation does not correctly represent the data in the liquid region particularly at lower temperatures.

Moreover, it should be noted that the very good performance of the EEoS-NN equation with respect to the speed of sound data of Hurly et al. [3] at the lower pressures, as shown in Table 5.17 and in Figs. 5.24 and 5.25, is a proof of the reliability of the chosen ideal-gas heat capacity function, see Paragraph 5.5.1, notwithstanding it was regressed on data obtained nearly thirty years ago [24]. In fact, approaching the ideal-gas condition the speed of sound depends only on ideal-gas heat capacity; therefore, a satisfactory representation of precise speed of sound data near the ideal-gas condition is an index of the accuracy of the adopted ideal-gas heat capacity function.

The same conclusion could also be drawn looking at Fig. 5.9, where said ideal-gas heat capacity function, taken from the work of Cole and de Reuck [6], and the ideal-gas heat capacity function derived from the experimental speed of sound data of Hurly et al. [3] are compared showing a very good mutual agreement. In the present work it was chosen to adopt the equation from Cole and de Reuck [6], even if it is older, because it has a wider validity range.



Figure 5.24: Deviations between the speed of sound data and the EEoS-NN equation.



Figure 5.25: Comparison of speeds of sound values calculated from the EEoS-NN equation to the experimental data and to the Span and Wagner [1] DEoS.

JOULE-THOMSON COEFFICIENT

As Table 5.16 shows, the few data available for the Joule-Thomson coefficient in the vapor region are well represented by the EEoS-NN equation regressed on multiproperty data, for which the attained accuracy is within the claimed experimental uncertainty. The predictive representation of this quantity by the other version of the EEoS-NN model is less reliable, since the AAD value is much higher than the claimed uncertainty and all the data are overestimated by the equation, as the bias value shows. The error distribution for the EEoS-NN equation regressed on density and vapor pressure data is shown in Fig. 5.26.

The Span and Wagner [1] DEoS has a comparably poor performance, while the SRK equation is totally unreliable for this quantity.



Figure 5.26: Deviations between the Joule-Thomson coefficient data and the EEoS-NN equation.

5.6.3. Representation of the thermodynamic surfaces

The selected EEoS-NN equation, i.e., that developed from density and vapor pressure data, was used to produce the plot of pressure versus density shown in Fig. 5.27. The whole validity range of the equation is considered and the step of the plotted isotherms is 10 K. A magnification of the vapor region for pressures lower than 2 MPa and densities below 100 kg·m⁻³ is also shown.

The shape of the curves is reasonable for all the thermodynamic regions in the range of validity. This evidences that possible overfitting and inconsistent behaviors, also due to uneven data distribution, were avoided in the training procedure.

A similar plot is shown in Fig. 5.28, in which the pressure range was extended to 100 MPa and the temperature up to 800 K. Also in this case the isotherms have a qualitatively correct behavior. Therefore, the proposed equation of state can be reasonably extrapolated beyond the stated validity limits, but in any case the use of the equation at temperatures higher than 800 K is not recommended, because the limits of the independent variables given in Table 5.11 should not be exceeded.

The representation of the isothermal lines in a P, H plane covering the whole validity range of the equation is shown in Fig. 5.29. Also in this diagram the correct trend of the curves confirms the high quality of the equation.



Figure 5.27: Isothermal lines calculated by the EEoS-NN equation and plotted in a P, ρ plane.



Figure 5.28: Isothermal lines calculated by the EEoS-NN equation also outside its validity limits.



Figure 5.29: Isothermal lines calculated by the EEoS-NN equation and plotted in a P, H plane.

5.6.4. Uncertainty of the new equation of state

The new equation of state allows the calculation of vapor pressure with an estimated uncertainty below 0.1%. The calculated saturation densities have an uncertainty of 0.05% for the ordinary region, while in the extended critical region the uncertainty values can be cautiously estimated at 0.3% for saturated liquid and 1% for saturated vapor.

The estimated uncertainty for density calculation is 0.02% for the liquid phase, 0.04% for the vapor phase, and 0.05% for the supercritical region; in the extended critical region and in the critical region the uncertainty in pressure is 0.05%.

The uncertainty of the calculated values of isobaric heat capacity is 0.5% for the vapor phase and ranges from 1% to 1.5% for the liquid phase and the supercritical region; in the extended critical region the uncertainty is about 3%, while the equation should not be used for this property in the critical region.

The estimated uncertainty for speed of sound calculation in the vapor phase is 0.05%; in the liquid phase it is 0.5%, while a value of 1% can be ascribed to the supercritical region. In the extended critical region the accuracy can be cautiously estimated to be 2%, even if experimental data are not available there for comparison. As for isobaric heat capacity, also for speed of sound the calculation is not reliable in the vicinity of the critical point.

5.6.5. Validation of the EEoS-NN model with a DEoS as basic equation

As exposed in Paragraph 5.5.2, the EEoS-NN training procedure was also applied assuming the DEoS of Span and Wagner [1] for sulfur hexafluoride as basic equation. In this case the mathematical formalism given in Chapter IV was maintained, but the cited DEoS was assumed instead of the SRK cubic EoS for the calculation of the thermodynamic properties to which the variables distortion through the shape functions is applied.

Since the representation of the sulfur hexafluoride thermodynamic properties by the Span and Wagner [1] DEoS is good, as shown in Tables 5.12-5.17, the required correction through the neural shape functions to minimize the objective function Eq. (5.3) is much more limited than in the case of the SRK EoS assumed as basic equation. The present goal is then to verify whether the accuracy of the obtained EEoS-NN equation can be improved by basing it on an EoS closer to the experimental behavior of the chosen fluid. If this would be true, the drawback could be ascribed to a limited flexibility of the assumed mathematical expression of the shape functions in neural network form.

The results are presented in Tables 5.18, 5.19, and 5.20 for saturation properties, density, and caloric properties, respectively. The comparison between two equations, both regressed on the same

data base, i.e., the primary data of density and vapor pressure, but with different basic equations, is shown. For sake of brevity, the validation results are reported as overall values for the primary data and for the whole data base instead of deviations given for each data set. Also in this case, as it was done in Tables 5.14 and 5.15, the single phase density data of Jany and Straub [29,30] have been omitted from the statistical evaluation for the same aforementioned reasons.

The performances of the two equations with respect to data are very similar for all the properties and for all the regions, showing that the choice of the basic equation is not a limiting element for the equation development procedure. This is a very interesting and promising result for the proposed modeling technique, because it proves that a quite rough but substantially predictive model can be assumed as basic equation without affecting the accuracy of the obtained equation. This assures a wider applicability of the proposed method.

	EoS type		AA (%	D 5)		Bias (%)	Class
		Ord.	Ext. Crit.	Crit.	Overall	Overall	
		Vapor pr	essure				
Training	EEoS-NN with SRK base	0.041	0.010	0.026	0.038	-0.004	Ι
on density	EEoS-NN with DEoS [1] base	0.025	0.038	0.088	0.027	0.025	Ι
and vapor	EEoS-NN with SRK base	0.249	0.157	0.234	0.230	0.127	I+II
pressure	EEoS-NN with DEoS [1] base	0.257	0.178	0.292	0.240	0.150	I+II
	Sat	urated liq	uid density				
Training	EEoS-NN with SRK base	0.028	0.283	2.628	0.053	-0.051	Ι
on density	EEoS-NN with DEoS [1] base	0.024	0.049	1.844	0.026	-0.025	Ι
and vapor	EEoS-NN with SRK base	0.292	0.742	3.529	0.377	-0.345	I+II
pressure	EEoS-NN with DEoS [1] base	0.289	0.577	2.809	0.343	-0.298	I+II
	Sat	urated vap	oor density				
Training	EEoS-NN with SRK base	0.050	1.412	7.650	0.215	0.214	Ι
on density	EEoS-NN with DEoS [1] base	0.158	2.689	9.381	0.465	0.463	Ι
and vapor	EEoS-NN with SRK base	0.687	1.352	6.051	0.849	0.346	I+II
pressure	EEoS-NN with DEoS [1] base	0.843	2.652	7.764	1.284	0.779	I+II

Table 5.18: Comparison between experimental data at saturation and values calculated with two

 EEoS-NN models with different basic equations.

E			Bias (%)	Class					
		Vap.	Liq.	Supercrit.	Ext. Crit. ^e	Crit. ^e	Overall	Overall	
	EEoS-NN with SRK base	0.038	0.013	0.038	0.039	0.035	0.033	-0.001	Ι
Training on density	EEoS-NN with DEoS [1] base	0.067	0.016	0.042	0.047	0.044	0.044	0.006	Ι
and vapor pressure	EEoS-NN with SRK base	0.079	0.062	0.087	0.106	0.051	0.080	-0.014	I+II
	EEoS-NN with DEoS [1] base	0.098	0.063	0.094	0.113	0.068	0.088	-0.009	I+II

Table 5.19: Comparison between density experimental data and values calculated with two EEoS-NN models with different basic equations.^d

^d The data set of Jany and Straub [29,30] was excluded from the present validation table, due to the much higher deviations of such data.

^e In the extended critical region and in the critical region, pressure deviations are given instead of density deviations.

Table 5.20: Comparison between caloric property experimental data and values calculated with two EEoS-NN models with different basic equations.

Ec	S type		AAD (%)							
		Vap.	Liq.	Supercrit.	Ext. Crit.	Crit.	Overall	Overall		
			Isobari	c heat capaci	ty					
Training on	EEoS-NN with	0 707	1.014	1 1 / 1	2 0.92	20.256	1 760	0 808		
density and	SRK base	0.797	1.014	1.141	2.965	29.230	1.700	0.808		
vapor	EEoS-NN with	0.796	1.062	1 172	2 078	22 070	1 01/	0.061		
pressure	DEoS [1] base	0.780	1.005	1.172	5.078	23.070	1.014	0.901		
			Spe	ed of sound						
Training on	EEoS-NN with	0.026	0.200	1 101			0 179	0.008		
density and	SRK base	0.020	0.388	1.101	-	-	0.170	0.098		
vapor	EEoS-NN with	0.026	0.205	0.853			0.140	0.064		
pressure	DEoS [1] base	0.020	0.293	0.855	-	-	0.140	0.004		
		J	oule-Th	omson coeffi	cient					
Training on	EEoS-NN with	2 202					2 202	2 202		
density and	SRK base	2.303	-	-	-	-	2.303	-2.303		
vapor	EEoS-NN with	1 620					1 620	1 620		
pressure	DEoS [1] base	1.050	-	-	-	-	1.030	-1.030		

5.7. Conclusions

A new equation of state in Helmholtz energy form was obtained for sulfur hexafluoride by applying an innovative regression technique. The format of the equation is called "EEoS-NN" and it is constituted by a basic equation (in the present case a SRK cubic equation) whose functional form

is distorted through the application of shape functions, expressed as a neural network, to the independent variables. The coefficients of the neural network are obtained through regression from experimental data. The accuracies of the available sources of experimental data were discussed and only the more precise data sets were adopted for the training procedure of the neural network.

The validity ranges of the equation are from the triple-point temperature at about 223.6 K up to 625 K and for pressures up to 60 MPa, with the exclusion of a region close to the critical point in case of caloric property calculation; a moderate extrapolation outside these limits is reliably possible.

It was verified that the equation can be regressed on only density and vapor pressure data, though maintaining a good prediction accuracy for other thermodynamic properties as for instance isobaric heat capacity and speed of sound. This characteristic is advantageous when the proposed modeling technique is applied to a fluid for which a limited data base is available, because the required experimental effort can be reduced.

The representation of the available experimental data is satisfactory for all the considered properties; in fact the deviations of the equation from the data are comparable with the ascribed uncertainties of the experimental sources.

The performances of the basic SRK cubic EoS are by far improved through the application of the shape functions, as shown in the validation tables. Moreover, the comparison of the proposed equation with the most advanced EoS previously published in the literature shows that the two equations have a similar accuracy level, but the present one reaches better prediction results for many data sets.

In conclusion, the EEoS-NN modeling technique is a valuable and effective tool for the development of fundamental equations of state dedicated to pure fluids, since it provides an equation in Helmholtz energy form that is capable to reproduce the thermodynamic properties with high accuracy. Above all this result was an important goal for the present work and further enhancements of the EEoS-NN technique can be pursued in the future starting from the present result.

The obtained equation is at the same level of the "group-two dedicated equations of state" [25] developed in recent years through the so-called functional form optimization procedure [2]. In particular it can be applied with satisfactory results also when only density and vapor pressure data are available.

The present equation of state for sulfur hexafluoride could be enhanced when new density experimental data would be made available for the regions where they are lacking, in particular for temperatures from 350 K to 625 K and pressures up to 1 MPa and for pressures higher than 40 MPa in the whole temperature range.

5.8. References

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VI. A fundamental equation of state for 2-propanol (i-C₃H₈O) in extended equation of state format

6.1. Introduction

The EEoS-NN technique, preliminary studied in Chapter IV and applied to draw a DEoS for the pure fluid sulfur hexafluoride (SF₆) in Chapter V, has been employed in the present chapter to obtain a DEoS for the pure fluid 2-propanol (i-C3H8O). The available literature data together with the ad hoc measured density data, presented in Paragraph 8.6 of this thesis, have been used to regress the coefficient of the DEoS.

One of the advantages of the EEoS-NN method, as it has been shown for the fluid sulfur hexafluoride (SF₆) in Chapter V, is that the data set on which to base the regression procedure can include only density and coexistence values, getting in the meantime a satisfactory performance also for the other properties. On the other hand, when a multiproperty data set is assumed as input, i.e., also "second order" properties as for instance heat capacities and speeds of sound are considered, together with the necessary density and coexistence data, the model performance is improved for the prediction of the "second order" properties. The level of the obtained accuracy is evidently dependent on the choice of the inputs for the regression, but the new method allows to tune the required experimental effort on the prediction accuracy expected for the thermodynamic quantities of interest and this can be considered as an innovative "value added".

The new EEoS-NN method is here applied to draw a DEoS for 2-propanol (C_3H_8O) directly from the available data sets of the fluid. The literature is not reporting a DEoS for this fluid and this has been an important suggestion to undertake the development of a new DEoS for it.

The sulfur hexafluoride is a chemically inert, non-polar, symmetrically-shaped chemical compound presenting a regular thermodynamic behavior with a quite low deviation from ideality. For it a large base of good quality experimental data of several properties in homogeneous states and of properties at phase equilibrium were available with a rather even distribution inside the range of interest. For this fluid, considering the favorable conditions of the data base, the EEoS-NN method was applied using only density and coexistence data for the regression with the aim of verifying its "value added" mentioned in the preceding.

On the contrary, 2-propanol is a polar and associating compound able to create hydrogen bonds, i.e. strong molecular interactions making it to strongly deviate from ideality. Moreover, a completely different and less suitable experimental data base is available for the fluid because of a rather uneven distribution of the data, of some occasional inconsistencies among different

experimental sources and, in several cases, of the questionable uncertainty of the data. All this makes the fluid more difficult to represent with a high accuracy DEoS with respect to the former case of sulfur hexafluoride.

From preliminary tests it was verified that in this case, due in particular to the unfavorable situation of the data, it was necessary to include all the available type of data into the training set for the development of the residual contribution of the Helmholtz energy function in order to get the expected accuracy.

The main goal of the present chapter is then to show the effectiveness of the mentioned EEoS-NN modeling method³ in a not favorable condition asking for a challenge of increased difficulty. On the other hand very few DEoSs are available for this kind of fluids and among the remainder fluids 2-propanol present the wider and more regular data base.

The 2-propanol is widely used in several industrial applications: it is cheaply available, it dissolves a wide range of non-polar compounds and it is then often used as a solvent and as a cleaning fluid, in particular for electronic devices. As a cosolvent it is also added to the solvent carbon dioxide in supercritical extractions. In this case it changes the solvent density and critical properties producing strong interactions, i.e., hydrogen bonds, with solutes to be selectively extracted.

6.2. Training of an equation of state in EEoS-NN format

The mathematical formulation for the EEoS-NN model is given in Paragraph 4.2.1.

As previously explained in Chapter IV, in the framework of the EEoS model the reference fluid and the target fluid coincide and an equation is assumed as basic model to which the variables distortion through the scale factors is applied. In the present work the Peng-Robinson [1] (PR) cubic EoS, see also Paragraph 3.3, was chosen.

As it will be discussed in Sec. 6.6.1, the ideal-gas contribution of the Helmholtz energy of a pure fluid is directly obtained from an equation for the ideal-gas isobaric heat capacity of the fluid itself; the reference values of ideal enthalpy and entropy for a chosen thermodynamic condition have also to be arbitrarily selected. Values of ideal isobaric heat capacity can be derived from low-pressure experimental heat capacity data, from low-pressure experimental speed of sound data, or from statistical methods using fundamental frequencies. Accurate equations for this property are usually found in the literature or can be easily derived from the available data, since ideal isobaric heat capacity depends only on temperature with a rather smooth functional form.

The main work in the development of an equation of state in EEoS-NN format is due to the regression of the residual contribution of Helmholtz energy. Since Helmholtz energy is not an

experimentally-accessible property, its functional form has to be regressed on experimental data of other quantities, exploiting the relations linking Helmholtz energy to any other thermodynamic property, see Appendix A.2.

The most important properties to be included in the regression are density and vapor pressure. The first one, apart from its technical interest, is also an independent variable of Helmholtz energy expressed in fundamental form, Eq. (3.81), and then it must be known with high accuracy; this is easily reached with modern experimental apparatuses. The second one is often the main property that is required in technical applications and consequently its precise representation is a basic requirement for a DEoS.

In Chapter IV it was verified that an equation of state in EEoS-NN format regressed on density and vapor pressure data is able to satisfactorily represent also other properties as internal energy, entropy, speed of sound, and heat capacities. Anyway, if the accuracy on these properties should need to be improved, the available experimental data for them can be included in the regression, so performing a multiproperty fitting. Both such regression possibilities were exploited in the present work.

The free parameters in the regression procedure are the weighting factors w_{ij} and w_{jk} , which, with the present number of neurons in the hidden layer J = 7, constitute a set of 37 coefficients. Since the thermodynamic properties in EEoS-NN format are non-linearly dependent on the weighting factors, the regression method is necessarily non-linear. The technique here adopted is a combination of a stochastic method with a deterministic method, i.e., a *quasi-Newton* one. The so-obtained technique keeps the ability of the stochastic method in finding the minimum of the objective function when many local minima are present, but the introduction of the deterministic method allows the limitation of the required time for the regression and the improvement of the precision of the minimum determination.

The objective function that has to be minimized in the regression procedure is composed by sums of squares of the deviations between experimental data and calculated values.

For density and vapor pressure data, the objective function is the analogous of equations (5.1) and (5.2), respectively.

During the development process of the equation of state, a first regression run is done considering only density data and assuming equation (5.1) as objective function; in this preliminary step the variance $\sigma_{a,i}^2$ is set equal to 1 for each experimental point.

The obtained equation is then used for the calculation of ρ^{sl} and ρ^{sv} at given (T, P^s) conditions and for the evaluation of the variances of the data. A new regression is done on density and vapor pressure data, searching for the minimum of the objective function given by equation (5.3), combining equations (5.1) and (5.2).

Successive regression steps are performed until the reaching of a satisfactory equation with good performances with respect to different thermodynamic properties; the saturated densities and the variances are recalculated at each step using the equation obtained in the previous step.

In the case of a multiproperty fitting, other objective functions for further properties are considered. For a generic property M the objective function can be written as equation (5.4).

In the present work a multiproperty fitting was done considering also data of isobaric heat capacity C_p , isochoric heat capacity C_v , and speed of sound w. The objective function to be minimized in such a regression case is

$$f_{ob,overall} = f_{ob,\rho} + f_{ob,\varphi} + f_{ob,C_p} + f_{ob,C_y} + f_{ob,w}$$
(6.1)

In general, the available experimental data cannot be considered in the regression as a whole; in fact some of them are affected by systematic errors or show a lower precision with respect to other data sets. Therefore, the experimental sources have to be subdivided into two groups: the *primary* data, i.e., the most precise ones that are used for the regression, and the *secondary* data, that are used only for comparison in order to check the performances of the obtained DEoS.

The choice of primary data can be initially based on the analysis of their stated accuracy and of the adopted experimental techniques. Anyway, during the regression process some data sources can be moved from primary to secondary data and vice versa taking into account their deviations from the obtained equations and the consistency with other experimental sources.

6.3. Basic data of the fluid

In the present work the recommended values given in Gude and Teja [2] for the molar mass M, the critical temperature T_c , the critical pressure P_c , and the critical density ρ_c have been assumed, see Table 6.1. The triple point temperature, T_t , is taken from Kelley [3]. The value of ω was calculated from the auxiliary equation for vapor pressure, see Eq. (6.4). All the cited values are reported in Table 6.1 together with the corresponding literature sources.

The units adopted through this work are K for temperature, MPa for pressure, and mol·l⁻¹ for density.

Since the correlation equations and all temperature values in this work are relative to the International Temperature Scale 1990 (ITS-90) [4], the temperature values of the available data were converted to ITS-90 when based on an older temperature scale.

In the following, the error deviation (Δ), the average absolute deviation (AAD), the bias (Bias) and the maximum absolute deviation (MAD) are defined as in Appendix A.6.

		Ref.
Formula	C_3H_8O	
CAS Registry Number	67-63-0	
M (kg·mol ⁻¹)	60.096	2
$T_{\rm t}$ (K)	184.67	3
$T_{\rm c}$ (K)	508.3	2
P_c (MPa)	4.764	2
$ ho_{\rm c}~({\rm kg}{\cdot}{ m m}^{-3})$	271	2
ω	0.667714	Eq. (6.4)

 Table 6.1: Substance-specific parameters for 2-propanol.

6.4. Survey of experimental property data

A total of 2586 thermodynamic values for 2-propanol were collected from literature. These include the following properties: isobaric heat capacities for the ideal gas state, saturation pressures, saturation densities for liquid and vapor phase, isobaric heat capacities at saturation, speed of sound at saturation, enthalpies of vaporization, single phase densities, single phase isobaric heat capacities, single phase isochoric heat capacities, and single phase speed of sound.

The collected data cover a range from 50 to 1500 K for the ideal gas condition, from the triple point temperature T_t to 597 K and up to 174.1 MPa for the real fluid condition.

The available thermodynamic experimental data for the 2-propanol were not formerly summarized in the literature and a complete overview of them is therefore presented in the following sections.

The experimental data in the single phase were subdivided into three regions of the P,T surface: the *vapor/gas* region, for pressures lower than the vapor pressure or, for supercritical temperatures, for pressures lower than the critical pressure; the *liquid* region, for temperatures lower than the critical temperature and pressures higher than the vapor pressure; the *supercritical* region, for temperatures and pressures higher than the respective critical values.

In the present work the temperature values of all experimental data were converted to ITS-90 [4] if not yet presented in such scale.

6.4.1. Ideal-gas data

The isobaric heat capacity data for ideal gas conditions C_p^o available from the literature are presented in Tab. 6.2 and shown graphically in Fig. 6.1.

Chao et al. [5] and Chao and Hall [6] reported in total 48 values of C_p^o in the range from 50 to 1500 K. These data were chosen as *primary data* for their low uncertainty value and their wide temperature range.

Regarding the data sets considered as *secondary*, Berman et al. [7] reported 5 values of C_p^o in the range from 371 to 451 K, Chermin [8] reported 9 values of C_p^o in the range from 298 to 1000 K, Green [9] reported 6 values of C_p^o in the range from 359 to 473 K., Hales et al. [10] reported 6 values of C_p^o in the range from 359 to 473 K, Parks and Shomate [11] reported 3 values of C_p^o in the range from 428 to 480 K.

Table 6.2: Summary of the available data sets for the isobaric heat capacity in the ideal gas condition of 2-propanol.

Ref.	Authors	Year	T range (K)	NPT	Uncertainty ^a
		Primary data			
5	Chao et al.	1986	100.0-1500.0	18	0.15 %
6	Chao and Hall	1986	50.0-1500.0	30	n.a.
	Overall		50.0-1500.0	48	
		Secondary dat	a		
7	Berman et al.	1964	371.1-451.1	5	n.a.
8	Chermin	1961	298.1-1000.0	9	n.a.
9	Green	1963	358.7-473.1	6	n.a.
10	Hales et al.	1963	358.7-473.1	6	n.a.
11	Parks and Shomate	1940	427.9-480.3	3	n.a.
	Overall		50.0-1500.0	77	

^a n.a. = not available.



Figure 6.1: Literature data for the isobaric heat capacity of 2-propanol in the ideal gas condition.

6.4.2. Properties at saturation

VAPOR PRESSURE DATA

The available vapor pressure P^s data for 2-propanol are presented in Tab. 6.3 and shown in Fig. 6.2. The whole experimental data set includes a total amount of 301 points covering a temperature range from 273 K to close to the critical temperature T_c . It is therefore possible to notice a lack of experimental information from the triple point temperature T_t to 273 K.

Ref.	Authors	Year	T range (K)	NPT	Uncertainty ^a
12	Ambrose and Townsend	1963	395.1-508.2	25	n.a.
13	Biddiscombe et al.	1963	329.9-362.4	17	±0.133 kPa
14	Dejos et al.	1996	300.4-354.9	30	±0.1 K for T; ±0.01 kPa (±0.1 for 20 < P <100 kPa) for P
15	Garriga et al.	1996	278.1-323.1	10	n.a.
16	Gonzalez et al.	1999	339.0-367.5	65	0.02% for T; ±0.02 kPa for P
17	Hong et al.	2002	333.1-373.1	4	0.1%
18	Marzal et al.	1996	327.9-354.9	3	n.a.
19	Moreland et al.	1967	373.1-473.1	5	0.1%
20	Nasirzadeh et al.	2004	298.1-353.1	12	0.003 K for T; 0.01% for P
21	Nikiforova et al.	1985	313.1-355.6	6	n.a.
22	Ortega and Susial	1993	347.6-361.1	3	n.a.
23	Parks and Barton	1928	273.1-363.1	19	0.0263 kPa
24	Pereiro et al.	2005	345.5-385.4	38	0.01 K for T; ±0.001 kPa for P
25	Pokki et al.	2003	333.7-355.4	12	±0.15 kPa
26	Rao et al.	1998	323.1-355.4	8	0.1 K for T; ±0.133 kPa
27	Segura et al.	2002	321.7-355.4	15	±0.03 kPa
28	Weclawski	1983	298.1-348.1	7	n.a.
29	Wilson and Simons	1952	311.2-420.8	22	n.a.
	Overall		273.1-508.2	301	

Table 6.3: Summary of the available data sets for the vapor pressure of 2-propanol.

^a n.a. = not available.



Figure 6.2: Literature data for the vapor pressure of 2-propanol.
DENSITY DATA

The available saturation density data of 2-propanol for the liquid and the vapor phase are presented in Tab. 6.4 and shown in Fig. 6.3.

The whole experimental data set for the liquid saturated density ρ^{sl} includes a total amount of 44 points, covering a temperature range from 275 K to the critical temperature T_c . The whole experimental data set for the vapor saturated density ρ^{sv} comprises a total amount of 30 points, covering a temperature range from 275 K to the critical temperature T_c .

Looking at the saturated density data it is possible to notice a lack of experimental information from the triple point temperature T_t to 275 K for the liquid phase. Saturated density data in the vapor phase seem to be not consistent each other, see Paragraph 6.5; therefore reliable measurements in the whole temperature range from the triple point to the critical point for the saturated vapor density are needed in the future to improve the knowledge of the thermodynamic properties for 2-propanol.

Ref.	Authors	Year	T range (K)	NPT	Uncertainty ^a
	S				
12	Ambrose and Townsend	1963	407.3-506.7	16	n.a.
30	Ambrose et al.	1978	275.0-508.3	11	n.a.
31	Golubev et al.	1979	292.7-503.9	8	n.a.
32	Hales and Ellender	1976	298.1-430.0	9	$\pm 0.0025 \;(\text{mol} \cdot l^{-1})$
	Overall		275.0-508.3	44	
	S	aturated vap	or density		
12	Ambrose and Townsend	1963	407.3-506.7	16	n.a.
30	Ambrose et al.	1978	275.0-508.3	11	n.a.
19	Moreland et al.		1967 423.1-473.1		n.a.
	Overall		275.0-508.3	30	

Table 6.4: Literature data of saturated liquid density and saturated vapor density for 2-propanol.

^a n.a.= not available.



Figure 6.3: Saturated density data for 2-propanol.

VAPORIZATION ENTHALPY DATA

The available vaporization enthalpy ΔH^{vap} data for 2-propanol are presented in Tab. 6.5 and they are shown in Fig. 6.4.

The whole ΔH^{vap} data available from the literature cover a range from 298 to 477 K, showing a lack from the triple point temperature T_t to 298 K and from 477 K to the critical point T_c .

These data were considered for the validation of the present EoS.

Ref.	Authors	Year	T range (K)	NPT	Uncertainty ^a
33	Bennewitz and Rossner	1938	354.9	1	n.a.
7	Berman et al.	1964	330.2-362.7	4	± 8.4 (j·mol ⁻¹) for T=330 K; ± 40.2 (j·mol ⁻¹) for the other temperatures
13	Biddiscombe et al.	1963	355.4	1	n.a.
34	Brown	1903	356.0	1	n.a.
10	Hales et al.	1963	324.6-355.4	3	n.a.
35	Mathews	1926	354.4	1	$\pm 10.1 \ (j \cdot mol^{-1})$
36	Newsham and Mendez- Lecanda	1982	354.3	1	n.a.
37	Parks and Nelson	1928	355.4	1	n.a.
38	Polak and Benson	1971	298.1-333.1	4	$\pm 0.05\%$
39	Radosz and Lydersen	1980	402.1-477.3	10	n.a.
40	Shah and Donnelly	1967	355.3	1	n.a.
41	Vesely et al.	1988	359.6-433.9	5	n.a.
42	Wadso	1966	298.1	1	n.a.
43	Williamson and Harrison	1957	324.3-353.3	3	n.a.
	Overall		298.1-477.3	37	

 Table 6.5: Literature data for the vaporization enthalpy of 2-propanol.

^a n.a.= not available.



Figure 6.4: Vaporization enthalpy data for 2-propanol.

ISOBARIC HEAT CAPACITY AND SPEED OF SOUND DATA

The available data for saturated isobaric heat capacity and saturated speed of sound for 2propanol are presented in Tab. 6.6 and they are shown in Fig. 6.5.

For the saturated isobaric heat capacity, experimental data are available only in the liquid phase. The 12 values of C_p^{sl} measured by Ginnings and Corruccini [44] in the range from 273 to 473 K were used in the regression of the coefficients of the presented DEoS, whereas the 12 values of C_p^{sl} measured by Hoffman et al. [45] in the range from 353 to 463 K were used only for the EoS validation. The two sources of C_p^{sl} are not in a good agreement each other, but the data of Ginnings and Corruccini [44] seem to be more consistent with the other sources of isobaric heat capacity in the liquid phase.

The experimental data of isobaric heat capacity at saturation cover a narrow temperature range for the liquid phase and are totally lacking for the vapor phase.

The 19 experimental data of speed of sound measured by Otpushchennikov et al. [46] are available in the saturated liquid from 293 to 473 K and they were used in the regression of the coefficients of the presented EoS. The saturated speed of sound experimental data cover a quite narrow temperature range for the liquid phase and are totally lacking for the vapor phase.

Authors	Year	T range (K)	NPT	Uncertainty ^a
S	Saturated i	sobaric heat cap	acity	
Ginnings and Corruccini	1948	273.2-473.2	12	$\pm1\%$ for T>55°C; less than $\pm1\%$ for T<55°C
Hoffman et al.	1977	353.2-463.2	12	n.a.
Overall		273.2-473.2	24	
	Saturate	ed speed of soun	ıd	
Otpushchennikov et al.	1974	293.2-473.2	19	1-2 m/sec
Overall		293.2-473.2	19	
	Authors Ginnings and Corruccini Hoffman et al. Overall Otpushchennikov et al. Overall	AuthorsYearSaturated iGinnings and Corruccini1948Hoffman et al.1977OverallSaturated iOtpushchennikov et al.1974Overall1974	AuthorsYearTrange (K)YearTrange (K)Saturated isobaric heat capGinnings and Corruccini1948273.2-473.2Hoffman et al.1977353.2-463.2Overall273.2-473.2Saturated speed of sourOtpushchennikov et al.1974293.2-473.2Overall1974293.2-473.2	AuthorsYearT range (K)NPTSaturated isobaric heat capacityGinnings and Corruccini1948273.2-473.212Hoffman et al.1977353.2-463.212Overall273.2-473.224Saturated speed of soundOtpushchennikov et al.1974293.2-473.219Overall1974293.2-473.219

Table 6.6: Literature data of saturated isobaric heat capacity and saturated speed of sound for 2-propanol.

n.a.= not available.



Figure 6.5: Data for saturated isobaric heat capacity and for saturated speed of sound of 2-propanol.

6.4.3. Properties in the single phase region

DENSITY DATA

All the available density data in single-phase regions for 2-propanol are presented in Tab. 6.7. The whole experimental data set comprises a total amount of 1516 points, covering a range from 275 K to 594 K in temperature and up to 174 MPa in pressure.

On the base of the claimed accuracy, temperature range, pressure range and number of points the whole of the measurements was divided into a primary data set and into a secondary data set.

The following data sets were used as primary to regress the coefficients of the present EoS: 362 values measured by Ambrose et al. [30] in the range from 386 to 573 K and from 0.4 to 13.4 MPa, covering the vapor region, the liquid region and the supercritical region; 7 values measured by Foz et al. [47] at 350 K and up to 0.1 MPa, in the vapor region; 167 values measured by Golubev et al. [31] in the range from 293 to 594 K and from 1.1 to 49.1 MPa, covering the vapor region, the liquid region and the supercritical region; 98 values measured by Moreland et al. [19] in the range from 373 to 473 K and up to 2.5 MPa, covering the vapor region; 150 values measured by Stringari et al. [48] in the range from 280 to 393 K and from 0.1 to 9.8 MPa, covering the liquid region. The whole primary data set includes 784 values covering the range from 280 to 594 K and up to 49.1 MPa. The data chosen as primary are well-distributed in the vapor, liquid and supercritical region, and they give a satisfactory description of the fluid behavior also in the region close to the critical point.

The remainder data sets were classified as secondary and they were used to validate the obtained EoS. These sets are reported in the corresponding section of Tab. 6.7 where the main characteristics of each one are indicated.

The whole secondary data set includes 732 values covering the liquid region and the supercritical region in the range from 275 to 573 K and from 0.1 to 174.1 MPa. Some of these data sets show a good accuracy, but they were included in the secondary data set in order to get reliable points for the validation of the model, most of all to check and prevent any overfitting by the DEoS surface.

Some points of the primary and secondary sources were excluded and they do not appear in the number of points of the data sets in Tab. 6.7: the values from Golubev et al. [49] at 570 K were discarded because were considered not consistent with the data reported by Ambrose et al. [30], Golubev and Vagina [50] and Tseng and Stiel [51] close to the same temperature, see Fig. 6.6.

In Tseng and Stiel [51] the values at 513.15 K and 52.40 MPa, 513.15 K and 55.16 MPa and 573.15 K and 55.16 MPa were discarded because they show a physically inconsistent behavior due to density values decreasing with increasing pressure, see Fig. 6.7.

The whole density data set is shown in (P,T) coordinates in Fig. 6.8, while the density data classified as primary are shown in Fig. 6.9. From Fig. 6.9 one can see that the density points used for the regression present an even distribution in the range of interest.



Figure 6.6: Comparison of the (P, ρ, T) data of Ambrose et al. [30], Golubev and Vagina [50], Golubev et al. [49] and Tseng and Stiel [51] at about 570 K.



Figure 6.7: (P, ρ, T) data of Tseng and Stiel [51] at 513 and 573 K.

Def	Anotherm	Veen	T range	P range		NPT fo	or each region		
Kel.	Autions	rear	(K)	(MPa)	Vap.	Liq.	Supercr.	Overall	- Uncertainty
			Pri	nary data	-		-		
30	Ambrose et al.	1978	386-573	0.4-13.4	172	109	81	362	n.a.
47	Foz et al.	1954	350	0.0-0.1	7	-	-	7	n.a.
31	Golubev et al.	1979	293-594	1.1-49.1	3	87	77	167	n.a.
19	Moreland et al.	1967	373-473	0.1-2.5	98	-	-	98	n.a.
48	Stringari et al.	2008	280-393	0.1-9.8	-	150	-	150	$\pm 0.05\%$
	Total primary		280-594	0.0-49.1	280	346	158	784	
	· · ·		Seco	ndary data					
52	Aminabhavi and Aralaguppi	1993	298-318	0.1	-	5	-	5	n.a.
53	Aminabhavi et al.	1993	298-308	0.1	-	3	-	3	n.a.
54	Aminabhavi and Gopalakrishna	1995	298-313	0.1	-	4	-	4	n.a.
55	Boned et al.	2000	303-343	0.1-65.0	-	42	-	42	n.a.
56	Contreras	2001	298-313	0.1	-	4	-	4	n.a.
57	Egorov	2004	275-338	0.1	-	8	-	8	$\pm 0.166 \cdot 10^{-3} \text{ (mol·l^{-1})}$
50	Golubev and Vagina	1963	292-504	0.1-51.0	-	135	-	135	n.a.
49	Golubev et al.	1980	300-560	1.0-50.0	-	52	27	79	n.a.
58	Islam and Quadri	1987	298-323	0.1	-	6	-	6	n.a.
59	Khimenko et al.	1973	288-323	0.1	-	7	-	7	n.a.
60	Khimenko et al.	1982	288-328	0.1	-	9	-	9	n.a.
61	Krestov et al.	1980	288-328	0.1	-	4	-	4	n.a.
62	Ku and Tu	1998	293-323	0.1	-	4	-	4	n.a.
63	Kubota et al.	1987	283-348	0.1-174.1	-	44	-	44	$\pm 0.09\%$
64	Lee and Lin	1995	303-323	0.1	-	3	-	3	n.a.
65	Mato and Coca	1969	298	0.1	-	1	-	1	n.a.
66	Moha-Ouchane et al.	1998	303-343	0.1-60.0	-	12	-	12	n.a.
67	Nagata et al.	1973	298	0.1	-	1	-	1	n.a.
68	Nikam et al.	1998	298-313	0.1	-	4	-	4	$\pm 0.000832 \text{ (mol·l^{-1})}$
69	Oswal and Putta	2001	303-318	0.1	-	3	-	3	n.a.
70	Paez and Contreras	1989	293-323	0.1	-	5	-	5	n.a.
71	Sakurai	1988	278-318	0.1	-	5	-	5	n.a.

Table 6.7: Summary of the available data sets for the density of 2-propanol.

6.4. Survey of experimental property data

Pof	Authors	Voor	T range	P range		NPT fo	r each region		- Uncertainty ^a
Kei.	Autions	i cai	(K)	(MPa)	Vap.	Liq.	Supercr.	Overall	Oncertainty
	Secondary data (continuation)								
72	Sovilj	1995	278-308	0.1	-	3	-	3	n.a.
73	Tashima and Arai	1981	293-343	0.1	-	7	-	7	n.a.
51	Tseng and Stiel	1971	473-573	6.9-55.2	-	58	104	154	n.a.
74	Tu et al.	2001	293-313	0.1	-	4	-	4	n.a.
75	Wei and Rowley	1984	298	0.1	-	1	-	1	$\pm 0.166 \cdot 10^{-2} \text{ (mol·l^{-1})}$
76	Yaginuma et al.	1997	313	1.0-9.8	-	11	-	11	$\pm 0.0011 \text{ (mol·l^{-1})}$
77	Zuniga-Moreno and Galicia-Luna	2002	313-363	0.5-25.1	-	156	-	156	$\pm 0.05\%$
	Overall		275-594	0.0-174.1	280	947	289	1516	

^a n.a.= not available.



Figure 6.8: Single phase $P\rho T$ data.



Figure 6.9: Single phase $P\rho T$ primary data.

CALORIC DATA AND SPEED OF SOUND DATA

The available data of isobaric heat capacity in single-phase regions for 2-propanol are presented in Tab. 6.8. The whole experimental data set comprises a total amount of 355 points, covering a range from about the triple point temperature, $T_{\rm t}$, to 597 K and up to 50 MPa.

On the base of the claimed uncertainty and distribution in the p,T plane the following values were selected as primary data: the 60 measurements of Andon et al. [78] covering the liquid region in the range from 188 to 327 K at atmospheric pressure; the 57 measurements of Dreher [79] covering the liquid region and the supercritical region in the range from 323 to 573 K and from 4.8 to 30.0 MPa; the 19 measurements of Hales et al. [10] covering the vapor region from 329 to 473 K and up to 0.1 MPa. The whole primary data set has 136 experimental points in the range from 188 to 573 K and up to 30 MPa. The remainder data sets were classified as secondary and were used for the validation of the present EoS as the Tab. 6.8 indicates for each set.

The whole secondary data set includes 219 values covering the vapor, the liquid and the supercritical regions in the range from 188 to 597 K and up to 50.0 MPa.

The whole isobaric heat capacity data set is shown in (P,T) coordinates Fig. 6.10, while the isobaric heat capacity data classified as primary are shown in Fig. 6.11. A lack in the experimental information is evidenced for the vapor phase from about the atmospheric pressure up to the critical one P_c .



Figure 6.10: Single phase C_p data.

Pof	Authors	Voor	T range	P range		NPT fo	or each region		Uncortainty ^{a,b}
KCI.	Authors	I Cal	(K)	(MPa)	Vap.	Liq.	Supercr.	Overall	- Oncertainty
				Primary	data		2		
78	Andon et al.	1963	188-327	0.1	-	60	-	60	n.a.
79	Dreher	1979	323-573	4.8-30.0	-	27	30	57	$\pm 0.4\%$
10	Hales et al.	1963	329-473	0.0-0.1	19	-	-	19	n.a.
	Total primary		188-573	0.0-30.0	19	87	30	136	
				Secondary	y data				
33	Bennewitz and Rossner	1938	410	0.1	1	-	-	1	0.6%
7	Berman et al.	1964	371-451	0.1	18	-	-	18	n.a.
80	Grigor'ev et al.	1979	311-452	0.1-2.0	-	8	-	8	$\pm 0.9\%$
45	Hoffman et al.	1977	353-463	1.0-4.0	-	65	-	65	n.a.
81	Katayama	1962	283-343	0.1	-	8	-	8	n.a.
3	Kelley	1929	188-293	0.1	-	12	-	12	n.a.
82	Naziev et al.	1993	302-521	0.1-50	-	57	5	62	n.a.
83	Parks and Kelley	1925	195-293	0.1	-	9	-	9	n.a.
84	Shah and Donnelly	1967	300-349	0.1	-	8	-	8	n.a.
									$\pm 4.2 (j \cdot mol^{-1} \cdot K^{-1})$ for
85	Sinka and DaVrias	1053	350 437	0.1	0			0	b.p. <t<(b.p.+20 k);="" td="" ±0.8<=""></t<(b.p.+20>
85	Slike and Deviles	1955	557-457	0.1	9	-	-	7	$(j \cdot mol^{-1} \cdot K^{-1})$ for
									T>(b.p.+20) K.
86	Strömsöe et al.	1970	366-597	0.1	14	-	-	14	$\pm 0.3\%$
87	Williams and Daniels	1924	303	0.1	-	1	-	1	n.a.
88	Zhdanov	1945	280-320	0.1	-	4	-	4	n.a.
	Overall		188-597	0.0-50.0	61	259	35	355	

Table 6.8: Summary of the available data sets for the isobaric heat capacity of 2-propanol.

^a n.a.= not available.

^b b.p.= bubble point.



Figure 6.11: Single phase C_p data classified as primary.

Amirkhanov et al. [89] measured 159 values of isochoric heat capacity C_{ν} in the liquid phase from 324 to 533 K and from 7.5 to 12.6 mol·l⁻¹. The data are presented in Tab. 6.9 and their distribution in (ρ, T) coordinates is shown in Fig. 6.12. These data were used in the regression of the coefficients of the present EoS.

Table 6.9: Summary of the available data sets for the isochoric heat capacity of 2-propanol.

Ref	Authors	Vear	T range	nge p range		NPT fo	Uncertainty ^a		
Kei.	Autions	1 Cai	(K)	$(\text{mol} \cdot \mathbf{l}^{-1})$	Vap.	Liq.	Supercr.	Overall	Oncertainty
89	Amirkhanov et al.	1985	324-533	7.5-12.6	-	159	-	159	n.a.
	Overall		324-533	7.5-12.6	-	159	-	159	

^a n.a.= not available.



Figure 6.12: Single phase C_{v} data.

Speed of sound data w for the 2-propanol are available from the literature in the liquid region at atmospheric pressure. The data are presented in Tab. 6.10 and their distribution in (ρ, T) coordinates is shown in Fig. 6.13.

The 5 values measured by Sakurai et al. [90] in the range from 278 to 318 K were classified as primary and used to regress the coefficients of the present EoS.

The values in the following data sets were classified as secondary and used to validate the present EoS: Bruun et al. [91], Krestov et al. [61], Lara and Desnoyers [92] and Marks [93].

Table 6.10: Summary of the available data sets for the speed of sound of 2-propanol.

Ref	Authors	Vear	T range	P range		NPT for	r each regio	on	Uncertainty ^a
Ker.	Autions	i cai	(K)	(MPa)	Vap.	Liq.	Supercr.	Overall	Oncertainty
				Primary d	lata				
90	Sakurai et al.	1994	278-318	0.1	-	5	-	5	n.a.
	Total primary		278-318	0.1	-	5	-	5	
				Secondary	data				
91	Bruun and Hvidt	1977	293-298	0.1	-	2	-	2	n.a.
61	Krestov et al.	1980	283-328	0.1	-	4	-	4	n.a.
92	Lara and Desnoyers	1981	298	0.1	-	1	-	1	±0.05 m/s
93	Marks	1967	273-293	0.1	-	2	-	2	n.a.
	Overall		273-328	0.1	-	14	-	14	

^a n.a.= not available.



Figure 6.13: Single phase w data.

6.5. Phase equilibria correlations

The quantity and the quality of data available in the literature for the saturation region of 2propanol are not homogeneous for all the properties. In particular, several sources of vapor pressure data, 301 points, are available in the range from 273.1 to 508.2 K, but only few points are available for saturated density. For the saturated liquid density 44 points are available in the range from 275.0 to 508.3 K, while for saturated vapor density only 30 points are available and they are not consistent each other. This hinder the possibility to develop a realistic ancillary equation for the saturated vapor density. In order to obtain an ancillary equation for the saturated vapor density consistent with the other properties the 37 vaporization enthalpy data in the range from 298.1 to 477.3 K available in the literature, see Paragraph 6.4.2, were included in the regression of the coefficients of the ancillary equations for the saturation properties.

In fact, vapor pressure P^s , saturated liquid density ρ^{sl} , saturated vapor density ρ^{sv} and vaporization enthalpy ΔH^{vap} are related each other by the Clapeyron-Clausius equation:

$$\frac{dP^{s}}{dT} = \frac{\Delta H^{vap}}{T\left(\frac{1}{\rho^{sv}} - \frac{1}{\rho^{sl}}\right)}$$
(6.2)

The parameters of the four ancillary equations (6.4-6.7) have been regressed simultaneously minimizing an objective function composed of terms for vapor pressure, saturated liquid density, saturated vapor density, vaporization enthalpy and the Clapeyron-Clausius equation relating these same properties, Eq (6.3):

$$f_{ob} = \frac{1}{n_{P^{s}}} \sum_{i=1}^{n_{P^{s}}} \frac{1}{\sigma_{i}^{2}} \left(\frac{P_{calc}^{s} - P_{exp}^{s}}{P_{exp}^{s}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sl}}} \sum_{i=1}^{n_{\rho^{sl}}} \frac{1}{\sigma_{i}^{2}} \left(\frac{\rho_{calc}^{sl} - \rho_{exp}^{sl}}{\rho_{exp}^{sl}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\sigma_{i}^{2}} \left(\frac{\rho_{calc}^{sv} - \rho_{exp}^{sv}}{\rho_{exp}^{sv}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\sigma_{i}^{2}} \left(\frac{\rho_{exp}^{sv} - \rho_{exp}^{sv}}{\rho_{exp}^{sv}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\sigma_{i}^{2}} \left(\frac{\rho_{exp}^{sv} - \rho_{exp}^{sv}}{\rho_{exp}^{sv}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\sigma_{i}^{2}} \left(\frac{\rho_{exp}^{sv} - \rho_{exp}^{sv}}{\rho_{exp}^{sv}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\rho_{exp}^{sv}} \left(\frac{1}{\rho_{exlc}^{sv}} - \frac{1}{\rho_{exlc}^{sl}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\rho_{exlc}^{sv}} \left(\frac{1}{\rho_{exlc}^{sv}} - \frac{1}{\rho_{exlc}^{sl}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\rho_{exlc}^{sv}} \left(\frac{1}{\rho_{exlc}^{sv}} - \frac{1}{\rho_{exlc}^{sl}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\rho_{exlc}^{sv}} \left(\frac{1}{\rho_{exlc}^{sv}} - \frac{1}{\rho_{exlc}^{sl}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\rho_{exlc}^{sv}} \left(\frac{1}{\rho_{exlc}^{sv}} - \frac{1}{\rho_{exlc}^{sv}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\rho_{exlc}^{sv}} \left(\frac{1}{\rho_{exlc}^{sv}} - \frac{1}{\rho_{exlc}^{sv}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\rho_{exlc}^{sv}} \left(\frac{1}{\rho_{exlc}^{sv}} - \frac{1}{\rho_{exlc}^{sv}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\rho_{exlc}^{sv}} \left(\frac{1}{\rho_{exlc}^{sv}} - \frac{1}{\rho_{exlc}^{sv}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\rho_{exlc}^{sv}} \left(\frac{1}{\rho_{exlc}^{sv}} - \frac{1}{\rho_{exlc}^{sv}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\rho_{exlc}^{sv}} \left(\frac{1}{\rho_{exlc}^{sv}} - \frac{1}{\rho_{exlc}^{sv}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\rho_{exlc}^{sv}} \left(\frac{1}{\rho_{exlc}^{sv}} - \frac{1}{\rho_{exlc}^{sv}} \right)_{i}^{2} + \frac{1}{n_{\rho^{sv}}} \sum_{i=1}^{n_{\rho^{sv}}} \frac{1}{\rho_{exlc}^{sv}} \left(\frac{1}{\rho_{ex}$$

where n_{p^s} , $n_{\rho^{st}}$, $n_{\rho^{sv}}$ and $n_{\Delta H^{vap}}$ are the number of experimental points for vapor pressure, saturated liquid density, saturated vapor density and vaporization enthalpy, while *n* is the sum of the experimental points for the four properties. P_{calc}^s , ρ_{calc}^{sl} , ρ_{calc}^{sv} and ΔH_{calc}^{vap} are the properties calculated by the following Eqs. (6.4-6.7) respectively.

$$\ln\left(\frac{P^{sat}}{P_c}\right) = \frac{\alpha_1 \tau^{1.10} + \alpha_2 \tau^{1.27} + \alpha_3 \tau^{2.89} + \alpha_4 \tau^{4.51} + \alpha_5 \tau^{7.34}}{T_r}$$
(6.4)

$$\ln\left(\frac{\rho^{sl}}{\rho_c}\right) = \alpha_1 \tau^{0.003} + \alpha_2 \tau^{0.26} + \alpha_3 \tau^{0.27} + \alpha_4 \tau^{2.03}$$
(6.5)

$$\ln\left(\frac{\rho^{sv}}{\rho_c}\right) = \left(T_c / T\right) \left(\alpha_1 \tau^{0.588} + \alpha_2 \tau^{0.603} + \alpha_3 \tau^{0.606} + \alpha_4 \tau^{2.16}\right)$$
(6.6)

$$\Delta H^{vap} = \alpha_1 \tau^{0.461} + \alpha_2 \tau^{3.62} + \alpha_3 \tau^{5.38} + \alpha_4 \tau^{9.45}$$
(6.7)

with $\tau = 1 - T/T_c$.

The parameters for the equations (6.4) to (6.7) are presented in Tab. 6.11, while the values for the critical parameters involved in the equations were presented in the previous Tab. 6.1.

Eq.	$lpha_{_1}$	$lpha_2$	$\alpha_{_3}$	$lpha_4$	$lpha_{5}$
(6.4)	$-1.89913 \cdot 10^{1}$	$1.28986 \cdot 10^{1}$	$-1.67499 \cdot 10^{1}$	$2.04326 \cdot 10^{1}$	$-1.53832 \cdot 10^{1}$
(6.5)	$-3.5760 \cdot 10^{-2}$	$-2.955 \cdot 10^{-3}$	1.44586	$-2.54731 \cdot 10^{-1}$	
(6.6)	$-5.12147 \cdot 10^{1}$	$8.83036 \cdot 10^{1}$	$-4.20013 \cdot 10^{1}$	-8.17898	
(6.7)	$6.72317 \cdot 10^4$	$5.81558 \cdot 10^5$	$-4.23393 \cdot 10^{6}$	$6.73891 \cdot 10^7$	

Table 6.11: Parameters for the ancillary equations.

The Eq (6.4) represents the 301 vapor pressure data with an AAD less than 0.5 %, with a Bias of about -0.1 %, as shown in Tab. 6.12. The percentage deviations of Eq (6.4) with respect to the literature data are shown graphically in Fig. 6.14.

Table 6.12: Comparison between vapor pressure data and Eq. (6.4).

Ref	Authors	Year	T range	NPT	AAD	Bias	MAD
Rei.	7 tuniors	1 Cui	(K)	111 1	(%)	(%)	(%)
12	Ambrose and Townsend	1963	395.1-508.2	25	0.2919	-0.2587	0.7489
13	Biddiscombe et al.	1963	329.9-362.4	17	0.1346	-0.1346	0.1985
14	Dejos et al.	1996	300.4-354.9	30	0.6965	-0.5941	1.0578
15	Garriga et al.	1996	278.1-323.1	10	0.4649	0.2633	1.4957
16	Gonzalez et al.	1999	339.0-367.5	65	0.3238	-0.3238	0.4672
17	Hong et al.	2002	333.1-373.1	4	0.5822	-0.3177	0.8629
18	Marzal et al.	1996	327.9-354.9	3	0.8106	-0.8106	0.9582
19	Moreland et al.	1967	373.1-473.1	5	0.3966	-0.3966	1.2605
20	Nasirzadeh et al.	2004	298.1-353.1	12	0.2161	-0.1239	0.4031
21	Nikiforova et al.	1985	313.1-355.6	6	0.9010	0.9010	1.2477
22	Ortega and Susial	1993	347.6-361.1	3	1.0509	-1.0509	1.4495
23	Parks and Barton	1928	273.1-363.1	19	1.7522	0.0850	8.7190
24	Pereiro et al.	2005	345.5-385.4	38	0.6022	0.5074	1.0314
25	Pokki et al.	2003	333.7-355.4	12	0.1459	0.1338	0.2597
26	Rao et al.	1998	323.1-355.4	8	0.1208	-0.0320	0.2724
27	Segura et al.	2002	321.7-355.4	15	0.1697	-0.1697	0.2767
28	Weclawski	1983	298.1-348.1	7	0.4119	0.2059	1.2059
29	Wilson and Simons	1952	311.2-420.8	22	0.3263	-0.2436	1.4264
	Overall		273.1-508.2	301	0.4836	-0.1134	8.7190



Figure 6.14: Comparison between vapor pressure data and Eq. (6.4).

The Eq (6.5) represents the 44 saturated liquid density data with an AAD less than 0.2 %, with a Bias of about -0.01 %; the Eq. (6.6) represents the 30 saturated vapor density data with an AAD of about 2.6 %, with a Bias of about -1.3 %. In Tab. 6.13 the analysis for the single data sets of both the quantities are reported, while in Fig. 6.15 the corresponding error deviations are plotted for the points.

Table 6.13: Comparison between saturated liquid and vapor densities data and Eqs. (6.5) and (6.6).

Ref.	Authors	Year	T range (K)	NPT	AAD (%)	Bias (%)	MAD (%)
		Saturat	ed liquid density				
12	Ambrose and Townsend	1963	407.3-506.7	16	0.2611	0.1494	1.6739
30	Ambrose et al.	1978	275.0-508.3	11	0.2283	-0.1292	1.0804
31	Golubev et al.	1979	292.7-503.9	8	0.2024	-0.2024	0.4945
32	Hales and Ellender	1976	298.1-430.0	9	0.0198	0.0095	0.0490
	Overall		275.0-508.3	44	0.1929	-0.0128	1.6739
		Saturat	ed vapor density				
12	Ambrose and Townsend	1963	407.3-506.7	16	4.5024	-2.7994	18.1948
30	Ambrose et al.	1978	275.0-508.3	11	0.5666	0.4334	1.6248
19	Moreland et al.	1967	423.1-473.1	3	0.3409	0.1710	0.6224
	Overall		275.0-508.3	30	2.6431	-1.3170	18.1948



Figure 6.15: Comparison between saturated density data and Eqs. (6.5) and (6.6): a) saturated liquid density; b) saturated vapor density.

The Eq (6.7) represents the 37 vaporization enthalpy data with an AAD less than 1.0 %, with a Bias of about 0.8 %, as shown in Tab. 6.14. The percentage deviations of Eq (6.7) with respect to the literature data are shown graphically in Fig. 6.16.

Ref	Authors	Year	T range	NPT	AAD	Bias	MAD
11011		i oui	(K)	1.1.1	(%)	(%)	(%)
33	Bennewitz and Rossner	1938	354.9	1	0.3332	-0.3332	0.3332
7	Berman et al.	1964	330.2-362.7	4	0.9766	0.9766	1.4500
13	Biddiscombe et al.	1963	355.4	1	0.0752	-0.0752	0.0752
34	Brown	1903	356.0	1	0.5670	-0.5670	0.5670
10	Hales et al.	1963	324.6-355.4	3	0.8205	0.8205	1.3035
35	Mathews	1926	354.4	1	0.9748	0.9748	0.9748
36	Newsham and Mendez- Lecanda	1982	354.3	1	1.6124	1.6124	1.6124
37	Parks and Nelson	1928	355.4	1	0.7584	-0.7584	0.7584
38	Polak and Benson	1971	298.1-333.1	4	2.1793	2.1793	5.7209
39	Radosz and Lydersen	1980	402.1-477.3	10	0.2179	0.1799	0.6237
40	Shah and Donnelly	1967	355.3	1	1.3218	1.3218	1.3218
41	Vesely et al.	1988	359.6-433.9	5	0.6972	0.5285	0.9066
42	Wadso	1966	298.1	1	5.9803	5.9803	5.9803
43	Williamson and Harrison	1957	324.3-353.3	3	0.4730	0.4730	0.7449
	Overall		298.1-477.3	37	0.9133	0.7865	5.9803

Table 6.14: Comparison between vaporization enthalpy data and Eq. (6.7).



Figure 6.16: Comparison between vaporization enthalpy data of 2-propanol and Eq. (6.7).

6.6. The new equation of state for 2-propanol

As discussed in previous sections, the new equation of state proposed for 2-propanol is a fundamental equation explicit in the reduced Helmholtz energy:

$$\frac{A(T,\rho)}{RT} = a(T,\rho) = a^{\circ}(T,\rho) + a^{R}(T,\rho)$$
(6.8)

The equation of state is split into two terms: the ideal-gas contribution a° and the residual contribution a^{R} . The first one is modeled following a classical procedure, if an equation for the isobaric heat capacity of the ideal gas $C_{p}^{\circ}(T)$ is known; the second one is developed in the EEoS-NN format as explained in Paragraph 6.2. Both contributions are separately considered in this section. Since the Helmholtz energy as a function of temperature and density is one of the four fundamental forms of an equation of state, all thermodynamic properties of a pure substance can be obtained by combining derivatives of Eq. (6.8). The mathematical expressions for calculating the most important thermodynamic properties from Eq. (6.8) are given in the Appendix A.2.

6.6.1. Ideal-gas contribution

The ideal-gas contribution of the Helmholtz energy is given in dimensionless form by Eq. (A2.5) in Appendix A.2. Since the choice of the reference state point is arbitrary, H_0^o and S_0^o were selected so that the enthalpy and entropy of the saturated liquid state at 273.15 K assume the values of 200 kJ·kg⁻¹ and 1 kJ·kg⁻¹·K⁻¹, respectively. The value assumed for the molar gas constant is *R*=8.314472 J·mol⁻¹·K⁻¹ and it is taken from the work of Mohr and Taylor [94].

From Eq. (A2.5) it is evident that only the ideal-gas heat capacity function $C_p^o(T)$ is required for the calculation of the ideal-gas properties of the fluid.

The equation for the ideal-gas isobaric heat capacity of 2-propanol used throughout this work was developed by fitting the literature data of ideal gas heat capacity. The experimental sets for C_p^o have been deviled into primary and secondary as reported in Paragraph 6.4.1 and they are presented in Tab. 6.2.

The data have been fitted through the equation:

$$\frac{C_p^{ig}}{R} = f_1 + \sum_{i=2}^5 f_i \, \frac{(g_i/T)^2 \exp(g_i/T)}{[\exp(g_i/T) - 1]^2} \tag{6.9}$$

in which the values of f_i and g_i are given in Table 6.15.

Table 6.15 :	Ancillary	equation	parameters	for the	e isobaric	heat	capacity	in th	ne ideal	gas	state,	Eq.
(6.9).												

i	f_i	g_i
1	4.15473	-
2	$1.28915 \cdot 10^{1}$	$1.73544 \cdot 10^3$
3	4.54092	$4.02984 \cdot 10^2$
4	2.90755	$9.26287 \cdot 10^2$
5	6.54520	$4.46676 \cdot 10^3$

The validity range of the ideal gas equation (6.9) is from 50 to 1500 K. The results of the validation of the former Eq. (6.9) are reported in Tab. 6.16 and graphically shown in Fig. 6.17. It can be seen a high accuracy of the representation of the primary data; among the secondary data the sets of Berman et al. [7], Green [9], and Hales et al. [10] demonstrate to be consistent with the primary data whereas the remainder sets are of a far lower quality with high scattering and systematic deviation with respect to the other ones.

From Eqs. (A2.5) and (6.9) the form of the ideal-gas Helmholtz energy equation reads:

$$a^{o}(T,\rho) = \ln(\rho/\rho_{0}) + a_{1} + \frac{a_{2}}{T} - (f_{1}-1)\ln(T) - \sum_{i=2}^{5} \frac{f_{i}g_{i}}{T} + \sum_{i=2}^{5} f_{i}\ln[\exp(g_{i}/T) - 1]$$
(6.10)

where $a_1 = 6.9666736935$ and $a_2 = 5291.4775994$ K, while the other coefficients are given in Table 6.15.

Table 6.16: Comparison between isobaric heat capacity data in the ideal gas state and Eq. (6.9).

Ref.	Authors	Year	T range (K)	NPT	AAD (%)	Bias (%)	MAD (%)
			Primary data				
5	Chao et al.	1986	100.0- 1500.0	18	0.0008	0.0000	0.0022
6	Chao and Hall	1986	50.0-1500.0	30	0.0015	0.0000	0.0060
	Overall		50.0-1500.0	48	0.0012	0.0000	0.0060
			Secondary data				
7	Berman et al.	1964	371.1-451.1	5	0.0743	-0.0095	0.1315
8	Chermin	1961	298.1-1000.0	9	1.3350	-1.3350	2.4721
9	Green	1963	358.7-473.1	6	0.0579	-0.0439	0.0966
10	Hales et al.	1963	358.7-473.1	6	0.0244	0.0189	0.0903
11	Parks and Shomate	1940	427.9-480.3	3	2.9425	-2.9425	5.3278
	Overall		50.0-1500.0	77	0.2827	-0.2732	5.3278



Figure 6.17: Comparison between isobaric heat capacity data in the ideal gas state and Eq. (6.9).

6.6.2. Residual part contribution

The residual part a^{R} of Helmholtz energy accounts for the deviations of the thermodynamic behavior of the real fluid from its ideal-gas condition. This contribution is then the most significant one when dealing with liquid states or with vapor conditions at pressures higher than few bars.

The most precise equations of state are obtained by regression of this part on experimental data for the fluid of interest. In the present work the residual contribution was developed assuming the EEoS-NN format presented in Chap. IV. The regression procedure explained in Paragraph 6.2 was applied to the experimental data presented in Paragraph 6.4. The corresponding coefficients of the neural network for the representation of the shape functions are given in Table 6.17.

		β	= 0.01		
			I = 3		
			J = 7		
			K = 2		
		$A_{\min} = 0.05$			$A_{\rm max} = 0.95$
		Bias1 = 1.0			$Bias^2 = 1.0$
	,	V = T = 184.67		V	T = T = 1000
		W OO		' ma	
		$V_{\min,2} = \rho_{\min} = 0.0$		$V_{\rm max}$	$\rho_{r,max} = \rho_{r,max} = 16.0$
		$W_{\min,1} = \theta_{\min} = 0.7$		$W_{_{1}}$	$_{\max,1} = \theta_{\max} = 1.3$
		$W_{\min,2} = \phi_{\min} = 0.7$		$W_{ m r}$	$_{\max,2} = \phi_{\max} = 1.3$
i	j	W_{ij}	j	k	${\cal W}_{jk}$
1	1	$-3.8637901 \cdot 10^4$	1	1	1.1428544
1	2	$-2.5020396 \cdot 10^2$	1	2	$2.6297001 \cdot 10^4$
1	3	$-2.4944556 \cdot 10^2$	2	1	$-6.8098574 \cdot 10^{3}$
1	4	$3.5098474 \cdot 10^2$	2	2	$1.2440510 \cdot 10^3$
1	5	$-1.2492607 \cdot 10^3$	3	1	$5.0337434 \cdot 10^3$
1	6	$-7.4828584 \cdot 10^{2}$	3	2	$2.0046389 \cdot 10^2$
1	7	$3.1451497 \cdot 10^2$	4	1	$-1.8357513 \cdot 10^3$
2	1	$-1.2974242 \cdot 10^4$	4	2	$-9.2114177 \cdot 10^2$
2	2	$-1.4376269 \cdot 10^2$	5	1	$-2.2821420 \cdot 10^3$
2	3	$-1.6541755 \cdot 10^2$	5	2	$4.1913229 \cdot 10^3$
2	4	$4.4106993 \cdot 10^{1}$	6	1	$6.7630984 \cdot 10^2$
2	5	$-4.1265840 \cdot 10^2$	6	2	$-1.4279916 \cdot 10^4$
2	6	$-7.3512844 \cdot 10^{1}$	7	1	$7.0514476 \cdot 10^3$
2	7	$-6.2072798 \cdot 10^2$	7	2	$-7.1034481 \cdot 10^3$
3	1	$8.6907251 \cdot 10^3$	8	1	$-2.5460679 \cdot 10^3$
3	2	$1.1801736 \cdot 10^2$	8	2	$3.8584896 \cdot 10^3$
3	3	$1.2340248 \cdot 10^2$			
3	4	$-7.9568092 \cdot 10^{1}$			
3	5	$4.5591762 \cdot 10^3$			
3	6	$-5.8022350 \cdot 10^{1}$			
3	7	$9.3381448 \cdot 10^2$			

Table 6.17: Parameters of the neural network for the representation of the shape functions.

The proposed equation of state is valid from 280 to 600 K and up to 50 MPa. The few data available in the near critical region hinder the possibility to develop, through a heuristic method as the present one, a reliable representation of the correct trends of isochoric heat capacity, isobaric heat capacity, and speed of sound in the vicinity of the critical point. In fact a suitable functional form dedicated to this region should be developed and included in the regression [95]. Consequently, the proposed equation is not recommended for the accurate calculation of such properties in the critical region.

The critical point calculated through the EoS is at $T = T_{c,EoS} = 508.52$ K, $P = P_{c,EoS} = 4.746$ MPa and $\rho = \rho_{c,EoS} = 3.838$ mol·l⁻¹ = 230.65 kg·m⁻³.

The EoS coefficients were regressed on the saturated pressure values generated by Eq. (6.4), saturated liquid density values generated by Eq. (6.5), saturated vapor density values generated by Eq. (6.6), saturated liquid isobaric heat capacity values classified as primary in Tab. 6.6, saturated liquid speed of sound values in Tab. 6.6, density values classified as primary in Tab. 6.7, isobaric heat capacity values classified as primary in Tab. 6.9 and speed of sound data classified as primary in Tab. 6.10.

The obtained EoS has been validated for pressures up to 174 MPa.

6.7. Comparison of the new equation of state with experimental data

The comparisons of the obtained equations with respect to the available experimental data are given in this Paragraph. In the following the validation is separately done for each of the identified thermodynamic regions.

The performances of the developed EEoS-NN models in the region very close to the critical point cannot be verified, because very few data are available and the functional form is not specialized for such a region. Notwithstanding, the validation results for the considered equations in the critical region were included in the calculation of the overall deviation values.

6.7.1. Vapor-liquid phase boundary

The present section summarize the validation results of the developed EEoS-NN model with respect to all the available properties in the coexistence region.

The chosen strategy of simultaneously regressing the four ancillary equations (6.4) to (6.7) representing the saturation properties, vapor pressure, saturated liquid and vapor densities, and vaporization enthalpy, together with the Clapeyron-Clausius relation, exposed in section 4. gets a higher consistency for the representation of these properties. This is particularly necessary due to the lack of experimental values in certain parts of the validity range of the mentioned properties. In order both to overcome the mentioned lack of data in certain segments of the range, see the corresponding discussion at Paragraph 6.4.2, and to maintain a same whole consistency with all the saturation data it was decided to regress the DEoS using only data at saturation generated from the cited ancillary equations instead of directly using the experimental points.

The validation results for vapor pressure are shown in Tab. 6.18. In the regression procedure the 232 values generated through the Eq. (6.4) are here considered as primary while the overall validation was performed on a set composed by the 232 points generated from the ancillary Eq.

(6.4) and 299 experimental points considered as secondary data. The error deviation of the present EEoS-NN equation with respect to the generated points, represented by the dotted line, and to the mentioned 299 experimental points is shown in Fig. 6.18. The overall AAD is about 0.35 % and the value of the Bias quite close to a null value demonstrate the DEoS gets a good representation of the saturation condition, even if the available data sets are rather incoherent each other as it is evident from the plot of Fig. 6.18 which shows the points with an evident scattering, particularly for temperature lower than about 400 K. In particular the DEoS represents very well the sets of Biddiscombe et al. [13] and of Segura et al. [27] and the set of Ambrose and Townsend [12] are well represented too, particularly looking at the fact that they are practically the only values for temperature over about 400 K.

Table 6.18 : Comparison between vapor pressure data and the EEoS-NN model.	

Pof	Authors	Voor	T range	NPT	AAD	Bias	MAD
Kel.	Autiors	I Cal	(K)	INF I	(%)	(%)	(%)
			Primary data				
This	Values concepted by Eq. (6.4)		275 0 506 0	222	0.0051	-0.1068	0.0794
work	values generated by Eq. (6.4)	-	275.0-506.0	232	0.2251		0.9784
			Secondary data				
12	Ambrose and Townsend	1963	395.1-500.2	24	0.2726	-0.1078	0.8211
13	Biddiscombe et al.	1963	329.9-362.4	17	0.0976	0.0776	0.1541
14	Dejos et al.	1996	300.4-354.9	30	0.6067	0.5329	1.0580
15	Garriga et al.	1996	278.1-323.1	10	0.7158	0.1942	1.5555
16	Gonzalez et al.	1999	339.0-367.5	65	0.3300	0.3300	0.4545
17	Hong et al.	2002	333.1-373.1	4	0.5573	0.2851	0.6381
18	Marzal et al.	1996	327.9-354.9	3	0.7141	0.7141	0.9611
19	Moreland et al.	1967	373.1-473.1	5	0.5311	0.0459	1.3761
20	Nasirzadeh et al.	2004	298.1-353.1	12	0.1469	0.0069	0.4571
21	Nikiforova et al.	1985	313.1-355.6	6	0.9692	-0.9692	1.4538
22	Ortega and Susial	1993	347.6-361.1	3	1.0642	1.0642	1.4390
23	Parks and Barton	1928	278.1-363.1	18	1.5029	-0.4344	5.1402
24	Pereiro et al.	2005	345.5-385.4	38	0.5743	-0.4341	0.9598
25	Pokki et al.	2003	333.7-355.4	12	0.2093	-0.2093	0.2680
26	Rao et al.	1998	323.1-355.4	8	0.1474	-0.0637	0.3371
27	Segura et al.	2002	321.7-355.4	15	0.0961	0.0770	0.2519
28	Weclawski J.	1983	298.1-348.1	7	0.2317	-0.1686	0.8190
29	Wilson and Simons	1952	311.2-420.8	22	0.3275	0.2539	1.5707
	Overall		275.0-506.0	531	0.3538	-0.0141	5.1402



Figure 6.18: Comparison of each source of saturation pressure data with the EEoS-NN model.

The validation results for saturated liquid and vapor densities are shown in Tab. 6.19. In the regression procedure the 232 values generated for each of the two properties through the Eqs. (6.5) and (6.6) are here considered as primary and the overall validation was performed on a set composed by the generated and experimental points. The error deviation of the present EEoS-NN equation with respect to the generated points, represented by the dotted line, and to the experimental points is shown in Fig. 6.19. The overall AAD is largely different for the two densities being about 0.19 % and 2.77 % for the liquid and vapor, respectively. Taking advantage from the consistency of the chosen regression method mentioned above one can see from both Tab. 6.19 and Fig. 6.19 that

the data of both quantities are substantially incoherent among them and that the developed DEoS looses accuracy approaching the critical point.

Ref.	Authors	Year $T \text{ range}$ (K)		NPT	AAD (%)	Bias (%)	MAD (%)
		Satura	ted liquid densit	V	(70)	(70)	(70)
		Satura		y			
1		ł	Primary data				
This	$V_{\rm s}$ have constant d have $\Gamma_{\rm s}$ (6.5)		275 0 506 0	222	0.1766	0.0725	2 1 1 0 4
work	values generated by Eq. (6.5)		275.0-506.0	232	0.1/66	-0.0735	3.1194
		Se	econdary data				
12	Ambrose and Townsend	1963	407.3-504.2	15	0.3929	-0.3178	1.3632
30	Ambrose et al.	1978	275.0-500.0	10	0.2183	-0.0494	0.7734
31	Golubev et al.	1979	292.7-503.9	8	0.2612	0.0921	0.6406
32	Hales and Ellender	1976	298.1-430.0	9	0.0592	0.0193	0.1109
	Overall		275.0-506.0	274	0.1886	-0.0781	3.1194
		Satura	ted vapor densit	v			
		F	Primary data	<i>.</i>			
This		-	initial y batta				
1 1115	Values generated by Eq. (6.6)		275.0-506.0	232	2.4531	2.2823	14.2310
work							
		Se	econdary data				
12	Ambrose and Townsend	1963	407.3-504.2	15	8.0511	8.0511	19.7430
30	Ambrose et al.	1978	275.0-500.0	10	2.4385	1.8614	10.4955
19	Moreland et al.	1967	423.1-473.1	3	2.3406	2.3406	3.0349
	Overall		275.0-506.0	260	2.7742	2.5996	19.7430

Table 6.19: Comparison of each source of saturation density data with the EEoS-NN model.



Figure 6.19: Comparison between experimental data of saturated liquid and vapor density and values calculated with the EEoS-NN model.

The vaporization enthalpy data were not included in the regression procedure of the DEoS and the validation results of the developed DEoS with respect to the 37 experimental points is presented in Tab. 6.20 and shown graphically in Fig. 6.20.

The overall AAD is about 0.53 % and the value of the Bias is about -0.19%, demonstrating that the DEoS gets a good representation of these data despite a certain scattering appearing from the plot of Fig. 6.20. From the Tab. 6.20 a certain homogeneity of both the quality of the data sets and of the prediction accuracy by the DEoS can be outlined.

Ref.	Authors	Year	T range (K)	NPT	AAD (%)	Bias (%)	MAD (%)
33	Bennewitz and Rossner	1938	354.9	1	1.0134	1.0134	1.0134
7	Berman et al.	1964	330.2-362.7	4	0.4526	-0.4526	0.5783
13	Biddiscombe et al.	1963	355.4	1	0.7714	0.7714	0.7714
34	Brown	1903	356.0	1	1.2754	1.2754	1.2754
10	Hales et al.	1963	324.6-355.4	3	0.4532	-0.4532	0.5977
35	Mathews	1926	354.4	1	0.2978	-0.2978	0.2978
36	Newsham and Mendez- Lecanda	1982	354.3	1	0.9330	-0.9330	0.9330
37	Parks and Nelson	1928	355.4	1	1.4487	1.4487	1.4487
38	Polak and Benson	1971	298.1-333.1	4	0.1602	-0.1602	0.2866
39	Radosz and Lydersen	1980	402.1-477.3	10	0.7753	-0.5704	2.5481
40	Shah and Donnelly	1967	355.3	1	0.6185	-0.6185	0.6185
41	Vesely et al.	1988	359.6-433.9	5	0.1697	0.1347	0.3925
42	Wadso	1966	298.1	1	0.5327	-0.5327	0.5327
43	Williamson and Harrison	1957	324.3-353.3	3	0.1268	-0.0877	0.2230
	Overall		298.1-477.3	37	0.5320	-0.1886	2.5481

Table 6.20: Comparison between vaporization enthalpy data and the EEoS-NN model.



Figure 6.20: Comparison between vaporization enthalpy data and values calculated with the EEoS-NN model.

The validation results for saturated liquid isobaric heat capacity and speed of sound data are shown in Tab. 6.21 and the error deviations of both the quantities are plotted in Fig. 6.21. For the development of the DEoS the data sets of Ginnings and Corruccini [44] for the saturated liquid isobaric heat capacity and those of Otpushchennikov et al. [46] for the saturated liquid speed of sound were chosen as discussed in Paragraph 6.4.2. The Fig. 6.21 shows also the validation results for the data from Hoffman et al [45].

Both the Tab. 6.21 and the Fig. 6.21 evidence that the data quality of both quantities is rather questionable also considering the few sources and the limited number of available points.

Table 6.21: Comparison between saturated isobaric heat capacity data and saturated speed of sound data and the EEoS-NN model.

Ref.	Authors	Year	T range	NPT	AAD	Bias	MAD			
			(K)		(%)	(%)	(%)			
		Saturat	ed isobaric he	eat capacit	y					
			Primary da	ita						
44	Ginnings and Corruccini	1948	273-473	12	1.3086	-1.1026	6.4931			
	Total primary									
			Secondary d	lata						
45	Hoffman et al.	1977	353-463	12	3.9437	3.9437	5.2171			
	Overall		273-473	24	2.6261	1.4205	6.4931			
		Satu	urated speed of	of sound						
	Primary data									
46	Otpushchennikov et al.	1974	293-473	19	1.8418	1.3261	3.4208			
	Overall		293-473	19	1.8418	1.3261	3.4208			



Figure 6.21: Comparison between the EEoS-NN model and: a) saturated heat capacity data; b) saturated speed of sound data.

6.7.2. Single phase region

DENSITY

The results of the validation of the EEoS-NN equation are reported in Table 6.22. For the vapor region the error deviation was evaluated in terms of pressure while for all the other regions the deviation was evaluated in terms of density.

In the vapor region all the available data sets have been included into the primary data because the region is substantially lacking of experimental data so that the vapor data subset is composed mainly by the set from Moreland et al. [19] and the seven points from Foz et al. [47] under the atmospheric pressure. Many points from Ambrose et al. [30] are also present for pressure approaching the critical point. Furthermore, the subset does not present superposition of the data sets ranges. Consequently, in order to conveniently document the vapor region all the sets have been necessarily included into the regression procedure apart from their quality. Looking at Tab. 6.22 one can see that the accuracy of the equation with respect the mentioned data is not comparable with the usual experimental uncertainty for $P\rho T$ data in the vapor region indicating that the sets have a modest coherence among them and a relatively high scattering. This situation of the data suggests the necessity to better study the $P\rho T$ behavior in the region through a further experimental effort. The Fig. 6.22 reports the error deviation of the DEoS in this region and shows that approaching the coexistence condition a trend of increasing error is evidenced.

In the liquid region the number of available points is much higher as the Fig. 6.8 shows but the quality of the data for liquid is not better than for vapor. The expected experimental uncertainty in this region is usually better of at least one order of magnitude, but for this fluid the situation is unluckily comparable with that of the vapor region. The choice of the sets composing the liquid data subset also in this case was necessarily the result of a compromise: the set of Ambrose et al. [30] covers a region around the critical point, while the data of Golubev et al. [31] cover a range from 1 up to 50 MPa in a wide range of temperature. Recently have been available the data from Stringari et al. [48] covering a pressure range from atmospheric pressure up to 10 MPa and temperatures from 280 to 393 K. These three sets were selected to compose the primary data subset in the liquid region. A fourth set from Zuniga-Moreno and Galicia-Luna [77] is also available in the lower part of the temperature range and these data are of good quality too, but, due to the scarcity of reliable data, it was chosen to move them into the secondary data subset to have at least a reliable set in the liquid region for the validation procedure of the DEoS. The statistical analysis of the residual error presented in Tab. 6.22 documents a better result for this region with an AAD value which is about 38 % lower with respect to that of the vapor region, but a strong incoherence is

evidenced between the set from Ambrose et al. and the other two. Notwithstanding it is necessary to include the set of Ambrose et al. because its points regularly cover a rather large region extending toward the critical point. Alternatively, the data from Golubev et al. are not suitable to entirely describe this same region due to a more sparse distribution of its points. In Fig. 6.23 it is evidenced a systematic deviation of the points from Ambrose et al. in the temperature range from 360 to 480 K while approaching the critical temperature all the available data increase their scattering but the points of this set have a behavior quite similar to that of the points from Golubev et al. The Tab. 6.22 also shows that in this region the data from the more reliable sets of Zuniga-Moreno and Galicia-Luna and Yaginuma et al. [76] are basically consistent with the primary sets in their same range. For all the data close to the atmospheric pressure the DEoS presents a good quality as well as for the set of Golubev et al. [49] covering a rather wide range.

Among the sets reporting the higher number of points the DEoS shows for the sets of Tseng and Stiel [51] and of Golubev and Vagina [50] a low accuracy with a high AAD value. The data from Kubota et al. [63] are distributed at pressures up to 174 MPa, which is mostly outside the validity region of the DEoS but they allow a validation in extrapolation showing a consistent behavior of the equation also in a high pressure range where it was not regressed.

The validation with respect to the secondary data is plotted in Fig. 6.24; in the liquid region the prediction accuracy with respect to the secondary data looks to be consistent with that of the primary data and without significative deviations. The extrapolation behavior of the DEoS at low temperatures outside the validity range gives satisfactory results as it is documented by the points in the range from 200 to 280 K.

In the supercritical region the primary sets are of Ambrose et al. [30] and Golubev et al. [31]; the first covers a range much close to the critical point while the second extends to higher temperatures and pressures, i.e., up to 594 K and 49.1 MPa. From Tab. 6.22 the performance of the DEoS for these sets is shown to be very similar with close AAD values, even if of a modest quality. This modest result can be analyzed looking at the Fig. 6.23 where the points present a high scattering but well centered around the density surface of the DEoS.

For the secondary data subset the values from Tseng and Stiel [51] and Golubev et al. [49] have an AAD lower with respect to that of the primary data particularly because they are less close to the critical point, see Fig. 6.24, where the isotherms are not so affected by the flex at the critical point.

Dof	Author	Voor	NDT	T range	P range	Averag	ge Absolute	Deviation AA	AD (%)	Bias (%)	MAD (%)
Kel.	Aution	I Cal	INF I	(K)	(MPa)	Vap.	Liq.	Supercr	Overall	Overall	Overall
-					Primary data	ı					
30	Ambrose et al.	1978	362	386-573	0.4-13.4	0.5828	0.7876	0.8705	0.7153	0.0275	7.8563
47	Foz et al.	1954	7	350	0.0-0.1	0.1002	-	-	0.1002	-0.0318	0.1687
31	Golubev et al.	1979	167	293-594	1.1-49.1	0.6801	0.2007	0.8763	0.5208	-0.3404	4.7396
19	Moreland et al.	1967	98	373-473	0.1-2.5	0.5176	-	-	0.5176	-0.3165	3.0822
48	Stringari et al.	2008	150	280-393	0.1-9.8	-	0.0884	-	0.0884	0.0100	0.2333
	Total primary		784	280-594	0.0-49.1	0.5490	0.3369	0.8733	0.5207	-0.0862	7.8563
				S	econdary da	ta					
52	Aminabhavi and Aralaguppi	1993	5	298-318	0.1	-	0.0300	-	0.0300	-0.0209	0.0382
53	Aminabhavi et al.	1993	3	298-308	0.1	-	0.0334	-	0.0334	-0.0334	0.0510
54	Aminabhavi and Gopalakrishna	1995	4	298-313	0.1	-	0.0900	-	0.0900	-0.0900	0.0920
55	Boned et al.	2000	42	303-343	0.1-65.0	-	0.2196	-	0.2196	-0.2187	0.4331
56	Contreras	2001	4	298-313	0.1	-	0.0450	-	0.0450	-0.0436	0.0841
57	Egorov et al.	2004	8	275-338	0.1	-	0.0860	-	0.0860	-0.0700	0.1260
50	Golubev and Vagina	1963	135	292-504	0.1-51.0	-	0.4874	-	0.4874	-0.3767	1.4789
49	Golubev et al.	1980	79	300-560	1.0-50.0	-	0.1103	0.4469	0.2253	-0.0848	1.9890
58	Islam and Quadri	1987	6	298-323	0.1	-	0.1508	-	0.1508	0.1508	0.3478
59	Khimenko et al.	1973	7	288-323	0.1	-	0.0464	-	0.0464	-0.0261	0.0858
60	Khimenko et al.	1982	9	288-328	0.1	-	0.0745	-	0.0745	-0.0745	0.1315
61	Krestov et al.	1980	4	288-328	0.1	-	0.1826	-	0.1826	0.0363	0.3998
62	Ku and Tu	1998	4	293-323	0.1	-	0.0439	-	0.0439	-0.0274	0.0789
63	Kubota et al.	1987	44	283-348	0.1-174.1	-	0.2495	-	0.2495	-0.2325	0.5723
64	Lee and Lin	1995	3	303-323	0.1	-	0.0498	-	0.0498	0.0071	0.0853
65	Mato and Coca	1969	1	298	0.1	-	0.0767	-	0.0767	-0.0767	0.0767
66	Moha-Ouchane et al.	1998	12	303-343	0.1-60.0	-	0.2074	-	0.2074	-0.2047	0.4231
67	Nagata et al.	1973	1	298	0.1	-	0.1026	-	0.1026	-0.1026	0.1026
68	Nikam et al.	1998	4	298-313	0.1	-	0.0311	-	0.0311	-0.0311	0.0472
69	Oswal and Putta	2001	3	303-318	0.1	-	0.0406	-	0.0406	0.0278	0.0645
70	Paez and Contreras	1989	5	293-323	0.1	-	0.0712	-	0.0712	-0.0476	0.1046
71	Sakurai	1988	5	278-318	0.1	-	0.0909	-	0.0909	-0.0909	0.1395

 Table 6.22: Comparison of each source of density data with the EEoS-NN model.
Pof	Author	Voor	NDT	T range	P range	Averag	ge Absolute	Deviation A	AD (%)	Bias (%)	MAD (%)
Kel.	Author	i cai		(K)	(MPa)	Vap.	Liq.	Supercr	Overall	Overall	Overall
				Seconda	ry data (cont	inuation)					
72	Sovilj	1995	3	278-308	0.1	-	0.0257	-	0.0257	0.0181	0.0527
73	Tashima and Arai	1981	7	293-343	0.1	-	0.0760	-	0.0760	-0.0404	0.1174
51	Tseng and Stiel	1971	154	473-573	6.9-55.2	-	0.4312	0.3319	0.3675	0.2538	3.5303
74	Tu et al.	2001	4	293-313	0.1	-	0.0679	-	0.0679	-0.0679	0.1046
75	Wei and Rowley	1984	1	298	0.1	-	0.1535	-	0.1535	-0.1535	0.1535
76	Yaginuma et al.	1997	11	313	1.0-9.8	-	0.0641	-	0.0641	-0.0641	0.0806
77	Zuniga-Moreno and Galicia-Luna	2002	156	313-363	0.5-25.1	-	0.1558	-	0.1558	0.1557	0.3637
	Overall		1516	275-594	0.0-174.1	0.5490	0.4004	0.6386	0.3996	-0.0561	7.8563



Figure 6.22: Comparison of each primary source of density data with the EEoS-NN model in the vapor phase.



Figure 6.23: Comparison of each primary source of density data with the EEoS-NN model.



Figure 6.24: Comparison of each secondary source of density data with the EEoS-NN model.

HEAT CAPACITIES

The developed DEoS represents the isobaric heat capacity as shown in Tab. 6.23. The three data sets of Andon et al. [78], Hales et al. [10], and Dreher [79] have been chosen for the primary data subset, the first for the liquid region at atmospheric pressure and the second for the vapor region at low pressure. The third one covers the liquid and supercritical regions at pressure ranging from 4.8 up to 30 MPa, assuring also an enough detailed documentation in a region approaching the critical point as the Fig. 6.11 shows. The representation of the points of the Hales et al. set is unluckily modest also due to a systematic deviation as the value of Bias in Tab. 6.23 indicates. From the Fig. 6.25 it can be seen how the error deviation is distributed: at temperatures higher than 380 K the DEoS surface is close to the points whereas at lower temperatures the equation accumulates important deviations. The DEoS behavior for the other two sets is similar even if the points of Andon et al. have a negative shift and those of Dreher a positive shift, as the corresponding Bias values indicate. The data of Andon et al. range at temperatures much more lower than the validity of the equation and as much as they decrease in temperature there is an increase of the residual error. The points from Dreher present a shifting in the liquid region while they are well centered approaching the critical temperature and exceeding the critical temperature, see Fig. 6.25.

Looking at Tab. 6.23 it can be seen that the residual error of the DEoS with respect to the primary data subset and its prediction accuracy with respect to the overall data set, inclusive of the primary data, are rather close in values. Considering each singular region for the vapor the behavior for the secondary data is modest as it was for the primary data; in the liquid the situation is better with a more uniform performance, except few worse sets. For the supercritical region the single set of Naziev et al. [82] is available and for it a low accuracy is obtained as it is more evident looking at the Fig. 6.26, where the corresponding points present a systematic positive shifting with respect to the equation surface. Furthermore, the Tab. 6.23 indicates that the available isobaric heat capacity sets have a poor coherence each other presenting evident systematic shifting with consistent positive and negative values of the Bias.

This situation, particularly critical for this fluid with a not favorable condition of the experimental sources, has forced the choice of the primary sources of each property included into the training set looking primarily to the best overall compromise for the representation of all the properties; including some data sets of a property into the training subset infers an evident decrease in the representation capability of other properties.

Ref.	Authors	Year	T range	P range	NPT		AA	D (%)		Bias (%)	MAD (%)
			(K)	(MPa)		Vap.	Liq.	Supercr.	Overall	Overall	Overall
					Prima	ry data	_				
78	Andon et al.	1963	188-327	0.1	60	-	1.4591	-	1.4591	-0.5447	6.0134
10	Hales et al.	1963	329-473	0.0-0.1	19	4.4182	-	-	4.4182	4.1902	22.4061
79	Dreher	1979	323-573	4.8-30.0	57	-	1.5681	1.5913	1.5803	0.6447	5.5777
	Total primary		188-573	0.0-30.0	136	4.4182	1.5122	1.5913	1.9233	0.6153	22.4061
					Second	ary data					
33	Bennewitz and Rossner	1938	410	0.1	1	6.2231	-	-	6.2231	-6.2231	6.2231
7	Berman et al.	1964	371-451	0.0-0.1	18	1.1944	-	-	1.1944	0.8034	8.1713
80	Grigor'ev et al.	1979	311-452	0.1-2.0	8	-	0.7550	-	0.7550	-0.3084	1.7513
45	Hoffman et al.	1977	353-463	1.0-4.0	65	-	2.0653	-	2.0653	2.0530	4.2659
81	Katayama	1962	283-343	0.1	8	-	2.9138	-	2.9138	2.9138	5.3209
3	Kelley	1929	188-293	0.1	12	-	2.3299	-	2.3299	-2.1031	7.1963
82	Naziev et al.	1993	302-521	0.1-50	62	-	2.4524	5.4192	2.6917	2.3223	9.0394
83	Parks and Kelley	1925	195-293	0.1	9	-	1.2702	-	1.2702	-0.6785	2.8868
84	Shah and Donnelly	1967	300-349	0.1	8	-	4.1476	-	4.1476	3.7427	5.5763
85	Sinke and DeVries	1953	359-437	0.1	9	5.4619	-	-	5.4619	5.3011	23.1517
86	Strömsöe et al.	1970	366-597	0.1	14	2.3309	-	-	2.3309	0.7761	12.5491
87	Williams and Daniels	1924	303	0.1	1	-	5.0611	-	5.0611	5.0611	5.0611
88	Zhdanov	1945	280-320	0.1	4	-	1.8807	-	1.8807	1.8807	3.0767
	Overall		188-597	0.0-50.0	355	3.1714	1.9499	5.4192	2.2161	1.2956	23.1517

 Table 6.23: Comparison of each source of isobaric heat capacity data with the EEoS-NN model.



Figure 6.25: Comparison of each primary source of isobaric heat capacity data with the EEoS-NN model.



Figure 6.26: Comparison of each secondary source of isobaric heat capacity data with the EEoS-NN model.

The single source of Amirkhanov et al. [89] of 158 points in the liquid region is available for the isochoric heat capacity and it has been included in the primary set for the regression of the DEoS coefficients. The residual error of the DEoS with respect to this data set in term of AAD, reported in Tab. 6.24, is 0.73 % while the Bias is 0.22 %; it can be said that the performance of the equation is comparable with the usual experimental uncertainty of this property. Also looking at the upper part of the Fig. 6.27 it can be seen that the points are rather well centered with respect to the equation surface except in the range 400 to 450 K.



Figure 6.27: Comparison of each source of isochoric heat capacity data and of speed of sound data with the EEoS-NN model.

Ref.	Authors	Year	ear $T \text{ range } \rho \text{ range } \text{NPT} $ AAD (%)		Bias (%)	MAD (%)					
			(K)	(1101/1)		Vap.	Liq.	Supercrit.	Overall	Overall	Overall
89	Amirkhanov et al.	1985	324-533	7.5-12.6	158	-	0.725 6	-	0.7256	0.2194	5.3667
	Overall		324-533	7.5-12.6	158	-	0.725 6	-	0.7256	0.2194	5.3667

 Table 6.24: Comparison of each source of isochoric heat capacity data with the EEoS-NN model.

SPEED OF SOUND

The speed of sound region is scarcely documented because the points are very few and they lay only in the liquid region at atmospheric pressure in a narrow temperature range. The set of Sakurai et al. [90] has been taken as primary and the DEoS performance for its five points is modest, see Tab. 6.25, but its points are sufficiently centered with a low value of Bias. The validation with respect to the secondary data is consistent with the results for the primary data. For this quantity, for which 14 points are available, a precise analysis cannot be developed due to reduced number of data laying in a limited range. The lower part of the Fig. 6.27 presents the error deviation of the DEoS and shows that the points are substantially centered around the equation surface but that the evident and ambiguous trend has to be considered questionable. Anyway, the very limited number of available points is evidently not sufficient to condition the shape of the speed of sound surface as represented by the DEoS. On the other hand the general representation of the speed of sound surface by the DEoS, as plotted in Fig. 6.33, can be qualitatively considered regular and coherent with an expected behavior.

Pof	Authors	Voor	T range	P range	NDT		AA	AD (%)		Bias (%)	MAD (%)
KCI.	Autions	I Cal	(K)	(MPa)	INFI	Vap.	Liq.	Supercr.	Overall	Overall	
				Prim	nary data						
90	Sakurai et al.	1994	278-318	0.1	5	-	1.0229	-	1.0229	-0.0587	1.7479
	Total primary		278-318	0.1	5	-	1.0229	-	1.0229	-0.0587	1.7479
				Secon	dary data						
91	Bruun and Hvidt	1977	293-298	0.1	2	-	0.2675	-	0.2675	-0.2675	0.4953
61	Krestov et al.	1980	283-328	0.1	4	-	1.3057	-	1.3057	0.7954	2.5011
92	Lara and Desnoyers	1981	298	0.1	1	-	0.3774	-	0.3774	-0.3774	0.3774
93	Marks	1967	273-293	0.1	2	-	1.1289	-	1.1289	-1.1289	1.9657
	Overall		273-328	0.1	14		0.9648	-	0.9648	-0.0201	2.5011

 Table 6.25: Comparison of each source of speed of sound data with the EEoS-NN model.

6.8. Representation of the thermodynamic surfaces

The EEoS-NN equation developed from the whole training data set is valid from 280 to 600 K and up to 50 MPa. In Fig. 6.28 the pressure versus density behavior of the equation has been represented for temperatures from 280 to 1000 K and pressures up to 500 MPa.

The isotherms shape is reasonable and coherent with an expected behavior for all the thermodynamic regions. This evidences that possible overfitting and inconsistent behaviors, also due to uneven data distribution, were avoided in the training procedure.

The pressure versus enthalpy isothermal lines are plotted in Fig. 6.29, in which the temperature is inside the validity range of the DEoS and the pressure is extended up to 500 MPa. Also in this case the isotherms have a qualitatively correct behavior.

The representation of the isobaric lines in a C_p , T plane covering the temperature validity range of the equation and pressure extended to 200 MPa is shown in Fig. 6.30. Also in this diagram the correct trend of the curves confirms the reliable quality of the equation.

A region of the C_p , T plane close to the critical point, within 500 to 550 K and 4.7 to 20 MPa, is plotted in Fig. 6.31 together with all the available experimental points falling inside this range. An accurate representation of the data is evidenced in the figure.

In Fig. 6.32 the isobaric lines in a C_{ν} , *T* plane inside a window covering the whole validity range of the DEoS are plotted; this representation too demonstrates the correct trend of the curves confirming the good reliability of the equation.

The speed of sound versus temperature isobaric lines are plotted in Fig. 6.33 inside the validity range of the DEoS. In spite of the fact that the speed of sound data were available only at atmospheric pressure the behavior of the w surface in the whole validity range, as represented by the equation, presents a qualitatively correct trend.

At last, the proposed equation of state can be reasonably extrapolated beyond the stated validity limits, but in any case the use of the equation outside the range from triple point temperature to 1000 K and densities beyond 961.5 kg·m⁻³ is not recommended, because the limits of the independent variables given in Table 6.17 should not be exceeded.



Figure 6.28: Isothermal lines on a P vs. ρ diagram calculated by the EEoS-NN equation also outside the validity limits.



Figure 6.29: Isothermal lines on a P vs. H diagram calculated by the EEoS-NN equation also outside its validity limits.



Figure 6.30: Calculated isobaric heat capacity values along isobars using the EEoS-NN equation.



Figure 6.31: Isobaric heat capacity values along isobars near the critical point calculated using the EEoS-NN equation.



Figure 6.32: Calculated isochoric heat capacity values along isobars using the EEoS-NN equation.



Figure 6.33: Calculated speed of sound values along isobars using the EEoS-NN equation.

6.9. Conclusions

A new equation of state in Helmholtz energy form was obtained for 2-propanol by applying an innovative regression technique. The format of the equation is called "EEoS-NN" and it is constituted by a basic equation (in the present case a PR cubic equation) whose functional form is distorted through the application of shape functions, expressed as a neural network, to the independent variables. The coefficients of the neural network are obtained through nonlinear regression from experimental data. The accuracies of present equation with respect to the available sources of experimental data have been discussed and the composition of the training data subset has resulted from a necessary compromise due to the unfavorable conditions for the development of a DEoS, because in general the distribution of the data were irregular, the data sets were often inconsistent each other, a pronounced scattering of the experimental points was present, and for the isochoric heat capacity and the speed of sound the available data were insufficient.

The validity ranges of the developed equation are from 280 up to 600 K and for pressures up to 50 MPa. Due to the substantial lack of data in the near critical region and the non-specialization of this DEoS in representing such region very close to the critical point the present equation is not suggested to be used within a region very close to the critical point.

Notwithstanding, the qualitative behavior of several thermodynamic property surfaces is shown to be quite reasonable; it is then questionable only the quantitative behavior of the equation but not the qualitative one in the mentioned region. Anyway, a moderate extrapolation outside the equation limits is considered to be reliably possible.

The representation of the available experimental data is satisfactory for all the considered properties; in fact the deviations of the equation from the data are comparable with the realistic uncertainties of the experimental sources for this fluid.

In conclusion, the EEoS-NN modeling technique is a valuable and effective tool for the development of fundamental equations of state dedicated to pure fluids, since it provides an equation in Helmholtz energy form that is capable to reproduce the thermodynamic properties with high accuracy.

In the former application of this modeling technique for the development of the DEoS of sulfur hexafluoride, see Chapter V, the experimental situation was very favorable from the point of view of kind, quantity, quality and distribution of the available data and the obtained equation was of high accuracy, comparable with the "group-two dedicated equations of state" [95] developed in recent years through the so-called functional form optimization procedure [96].

In the present case the same EEoS-NN modeling technique has been deliberately applied to the unfavorable situation of the fluid 2-propanol with the express will to verify the effectiveness of the

method in much more difficult conditions. Beyond the mentioned situation of the base of data the 2propanol is well known as a strongly polar and self-associating fluid with a pronounced deviating behavior.

The obtained results instead demonstrate that the EEoS-NN modeling method is completely reliable for the purpose and that, compatibly with the experimental data situation for the fluid, highly effective DEoS can be anyway developed. This aspect is particularly favorable in the case a DEoS is required for engineering applications where the economy of the experimental effort and the representation accuracy have to be met through a suitable compromise.

The present equation of state for the fluid 2-propanol could be enhanced when new and coherent density experimental data would be made available for all the regions and in particular for the near critical one. Vapor pressure data from about 380 K to the critical point and saturated vapor densities in all the temperature range are needed. Coexistence data under 273 K are totally lacking. The data subset for the isobaric heat capacity has to be improved, while for the remainder caloric properties new experimental campaigns with rather wide ranges are evidently necessary.

6.10. References

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VII. VLLE and excess enthalpy for the propylene + 2-propanol + water mixture

7.1. Introduction

The EEoS-NN technique has been successfully applied in Chapters V and VI to develop DEoSs for the pure fluids sulfur hexafluoride and 2-propanol, respectively, starting from their experimental data. The precise knowledge of the thermophysical properties of a system is a basic requirement to optimize from an energetic point of view the process in which the system is involved, finding out the more suitable operative conditions for the unit operations. The EEoS-NN technique allows to obtain a precise DEoS, either for a pure fluid or a mixtures, drawing it through an heuristic procedure directly from a set of experimental data of selected properties. As a consequence the experimental effort is reduced both in the number of properties that have to be investigated and in the number of measurements that have to be carried out for each property, as it has been shown from the preliminary studies in Chapter IV. These features make the EEoS-NN technique a useful tool for the process analysis and optimization.

To investigate the potential of the EEoS-NN technique as a tool to study real processes typical of the chemical industry a propaedeutical system has to be chosen and studied as an exemplification case. This thesis work focuses on the study of the system propylene + 2-propanol + water encountered in the *extraction* process of 2-propanol from aqueous solutions using propylene as solvent. 2-Propanol and water form an azeotropic binary mixture that cannot be separated by means of a conventional distillation process. To overcome this problem a third component, propylene in this case, is added to allow the separation. This system was selected after a screening of the literature data which is rather lacking of detailed documentation, because it seems to present favorable conditions for an extraction operation.

Ranging from the liquid-liquid extraction to the supercritical extraction an accurate knowledge of the thermodynamics of the mixture in a wide range of temperature, pressure and composition is necessary to evaluate the conditions at which the process has to be driven for a minimum consumption of energy.

The propylene + 2-propanol + water system is thermodynamically strongly deviating from ideal behavior due to several causes as the strong polarity of the components, their association behavior, etc., which increases a lot the difficulties of a complete and accurate thermodynamic representation. Moreover, the literature is quite lacking of thermodynamic experimental data so that the study of the system has necessarily to start from an experimental activity.

In the present chapter the available literature data for the mixture propylene + 2-propanol + water are collected, and new measurements, carried out in order to improve the knowledge of the thermodynamic properties of such mixture, are presented.

The available experimental data are concerning phase equilibria and in particular they refer to the works of Zabaloy et al. [1] and Rojas et al. [2] for VLE and LLE, respectively. Solubility data are also available from Wu et al. [3].

In the context of the present research work VLLE and H^E data have been measured for the ternary mixture and for the binary 2-propanol + water system. The new data are presented in the present chapter, where also a semi-predictive model for the ternary mixture has been regressed to get a qualitative representation of the thermodynamic behavior of the system. In order to develop a precise DEoS for the propylene + 2-propanol + water mixture further measurements have to be carried out, in particular densities, and this will be the matter of the next Chapter VIII.

7.2. Chemicals

Water (H₂O, $M = 18.0153 \text{ kg} \cdot \text{kmol}^{-1}$, CAS-RN 7732-18-5) was distilled twice. The 2-propanol (CH₃CH(OH)CH₃, molar mass $M = 60.0959 \text{ kg} \cdot \text{kmol}^{-1}$, CAS-RN 67-63-0) was obtained from Carl Roth. Its final purity after drying over molecular sieve, degassing, and distillation was 99.95 mass % (checked by gas chromatography). The propylene (CH₃CH=CH₂, $M = 42.0806 \text{ kg} \cdot \text{kmol}^{-1}$, CAS-RN 115-07-1) was obtained from Messer Griesheim with a purity of 99.5 mass % (checked by gas chromatography) and used without further purification. For the H^E measurements the 2-propanol and the water were used without degassing.

7.3. Apparatus and experimental procedure for VLLE measurements

A static VLE apparatus, consisting of an isothermal total pressure cell, has been employed for measuring the VLLE of the selected ternary mixture. It is schematically shown in Fig. 7.1. This setup was developed by the LTP GmbH and can be applied for the experimental determination of phase equilibrium data as V(L)LE or gas solubility data using the static method at temperatures of about 270 to 470 K and pressures up to 10 MPa. The cylindrical pressure cell with a capacity of about 80 cm³ is made of Hastelloy C-276 and fitted with a magnet coupled stirrer.

The thermoregulation of the cell is performed with a metal jacket heated electrically or with an external liquid thermostat enabling the temperature to be constant within \pm 0.05 K. The temperature of the cell is measured with a nominally PRT-100 (Model 1502 A, Hart Scientific) calibrated on ITS-90 as indicator an AC resistance bridge ASL model F250 resolving 1 mK in the reading of temperature and estimating an overall uncertainty of 50 mK. The pressure inside the cell is

monitored with a Digiquartz pressure sensor (Model PA 25 HTC, Keller) which is calibrated using dead weight pressure balances.

After equilibration and phase settling samples can be taken from the phases and analyzed by gas chromatography. Therefore, small amounts of the substances are directly injected into the carrier gas stream of a gas chromatograph using a pneumatically driven micro sampler (ROLSI: rapid online sampler-injector). The complete cell can be turned so that the cusp of sampling capillary is immersed in the desired phase. For this purpose, the cell is equipped with borosilicate glass or sapphire windows which are sealed with PTFE. Because of the very small sample size (about 0.1 to 1 μ l) the equilibrium inside the cell is not disturbed. In order to avoid condensation and adsorption of high boiling components, the micro sampler and the lines for the gas stream of the gas chromatograph are superheated. In order to enable the sampling, the pressure inside the cell has to be larger than the pressure of the carrier gas stream of the gas chromatograph. For this purpose, at low system pressures an inert component (e.g. helium) can be added to the cell. To calculate the composition the chromatograph is calibrated directly with known amount of gaseous or liquid substance.

Besides the sampler port, the cell is provided of further three ports connected to the injection lines by microvalves.



Figure 7.1: Schematic diagram of the equilibrium cell with windows.

The sample injectors were three 100 cm³ positive displacement pumps (Ruska, mod. 2200-801) with a resolution of 0.01 cm³ and an estimated total uncertainty of ± 0.03 cm³. These allowed the injection of known volumes of the pure components, previously degassed, into the cell. For each component, the mass injected was determined accurately from the volumetric differences read between two stop-points, corresponding to the opening and closing conditions controlling that the starting and final pressure in the pumps reaches the same value. The volumetric to mass conversion is obtained knowing the temperature of the injectors and the compound densities.

Specifically dealing with the ternary mixture measurements procedure, after evacuating the cell and obtaining the thermal equilibrium in the bath at the set temperature of 331,15 K, the cell was filled with a starting binary propylene-water mixture having the following overall molar fraction composition: 0.1188 (propylene) - 0.8812 (water). At the selected temperature and composition two liquid phases, the organic and aqueous, besides the vapor one were observed.

The third component, the 2-propanol, was added to the cell moving then along a dilution line in the ternary diagram. Stirring the cell was a very important step for helping establishing a rapid thermodynamic equilibrium between fluid phases. Taking several constant pressure readings after stopping the stirrer, the micro sampler was positioned in contact with each single phase by turning the cell and the corresponding composition was measured by a gas chromatograph. A number of 8 dilution runs were done by adding corresponding amount of 2-propanol up to the following overall composition: 0.0933/0.2142/0.6925 for propylene/2-propanol/water.

7.4. Apparatus and experimental procedure for H^E measurements

For the determination of the heat of mixing a commercial isothermal flow calorimeter (Model 7501, Hart Scientific) was used. The principle of measurements is to compensate the heat effects of mixing of two thermostated liquid flows and to measure the required power. Two calibrated syringe pumps (ISCO, Model LC-2600, 260 cm³) provide the liquid flows whose temperatures and that of the thermostat are monitored with a Hart Scientific platinum resistance thermometer (model 1006 Micro-Therm) with an accuracy of 0.005 K. The selection of different flows for each pump allows to obtain a constant flow mixture of defined composition in the mixing tube section.

The corresponding heat of mixing effects are detected by a pulsed heater and a Peltier cooler. The Peltier cooler is working at constant power producing a constant heat loss from the calorimeter cell, which is compensated by the pulsed heater. The required frequency of the heater is influenced by endothermic or exothermic heat effects so that the heats of mixing can be determined from the observed frequency change between the base line and the actual measurement. Depending on the H^{E} values and the flow rate for the different systems, the power per pulse can be varied between 0.05 and 20 J.

The flow cell, the calibration and the pulsed heater, the Peltier cooler and the mixing tube wound around a copper cylinder are located in a stainless cylinder immersed in a thermostated calorimeter cell. Usually silicon oil is used as thermostating liquid so that the apparatus can work in the temperature range 273-453 K. A back-pressure regulator serves to keep the pressure at a level at which evaporation and degassing effects can be prevented and can be kept constant at up to 14 MPa. The experimental uncertainties of this device are as follows : s(T) = 0.03 K, $s(H^E) = 2$ J mol⁻¹ ± 0.01 (H^E , J mol⁻¹), $s(x_i) = 0.0001$.

One of the two pumps was filled with the water + 2-propanol binary system of known composition while the other one was filled with propylene. The heat of mixing measurements refer then to a mixing process of the binary water + 2-propanol mixture considered as the first flow and the pure propylene considered as the second one. Once the two pumps were filled, a stable base line was at first obtained for various propylene flow rate by selecting a suitable frequency for the pulsed heater. The measurements procedure required the selection of different flow rates for each pumps in order to cover the whole molar fraction range and maintaining a constant value for the total mixed flow rate that in this case was 80 cm³ hr⁻¹. For each value of the selected flow rates, the frequency of the pulsed heater was recorded for approximately 2000 s.

The apparatus is completely automated so that the changes of the flow rate of the pumps are under computer control together with the recording procedure of the frequency changes of the pulsed heater. Knowing the molar mass of the two fluid flows, their densities at 298.15 K and the recorded flow rates and frequency of the pulsed heater, the molar heat of mixing were determined from the calibration constant value of energy evolved per pulse obtained during the calibration procedure. A detailed description of the flow calorimeter was published previously [4], while for further details on operating procedure reference is made to [5]. Excess enthalpy measurements carried out with the same apparatus have been recently published [6,7].

7.5. Experimental results

7.5.1. Equilibrium results

The VLLE measurements have been carried out at 313.15 K for eight pressures from 1.381 to 1.690 MPa and they are presented in Table 7.1. The composition of the vapor phase has been measured only in four cases, see vapor phase columns in the table, even if the vapor phase presence was optically detected for all the cases. The compositions are reported as molar fractions.

	T = 313.15 K												
Pressure	Aqueou	is phase	Organi	c phase	Vapor Phase								
(MPa)	x_1	x_2	x_1	x_2	x_1	x_2							
1.690	0.00083	0.0	0.99173	0.0	-	-							
1.590	0.00193	0.05342	0.80471	0.16276	0.98502	0.00689							
1.516	0.00344	0.08007	0.38460	0.39898	0.99152	0.00848							
1.488	0.00409	0.08937	0.30792	0.40536	0.98380	0.00831							
1.473	0.00464	0.09706	0.28360	0.40399	-	-							
1.424	0.00632	0.10308	0.20483	0.39524	0.98247	0.00887							
1.403	0.00803	0.11363	0.17100	0.38760	-	-							
1.381	0.00971	0.11878	0.14373	0.36780	-	-							

Table 7.1: Experimental VLLE data for the propylene (1) + 2-propanol (2) + water (3) mixture.

7.5.2. Excess enthalpy results

Measurements of excess enthalpy for the pseudo-binary mixture propylene + (2-propanol + water) have been produced for four temperatures in the range from 313.15 to 353.15 K and pressures from 1.997 to 5.89 MPa. The measurements were done starting from three molar compositions of the binary mixture 2-propanol + water (pseudo-pure component), i.e., 0.25, 0.50, 0.75 in 2-propanol, adding to them increasing amounts of the solvent propylene, see for instance the ternary diagram in Fig. 7.7. The measured H^E data are presented in Table 7.2 where the compositions are reported as molar fractions.

Because for the binary mixture 2-propanol + water H^{E} data were only available at atmospheric pressure, H^{E} values have been measured for it in the temperature range 313.15-353.15 K and pressures up to 4.19 MPa. The measured data for such mixture are presented in Table 7.3.

7.6. Modeling methods

The experimental data were correlated with the Peng-Robinson [8] (PR) cubic EoS presented in detail in Paragraph 3.3. The mixture parameters a_M and b_M are calculated using the Wong-Sandler [9] (WS) mixing rules, Eqs (3.33-3.36), where k_{ij} is the conventional binary interaction parameter to regress from experimental data and the parameters a_i and a_j are expressed through the Mathias-Copeman [10] functional form:

$$a_{i}(T_{r}) = 0.45724 \left[1 + d_{1,i} \left(1 - \sqrt{T_{r}} \right) + d_{2,i} \left(1 - \sqrt{T_{r}} \right)^{2} + d_{3,i} \left(1 - \sqrt{T_{r}} \right)^{3} \right]^{2}$$
(7.1)

where: $T_r = T/T_c$ is the reduced temperature and $d_{1,i}$, $d_{2,i}$, $d_{3,i}$ are pure fluid parameters.

х.	H^{E} ,	х.	H^{E} ,	х.	H^{E} ,
	$(J \cdot mol^{-1})$]	$(J \cdot mol^{-1})$	1	$(J \cdot mol^{-1})$
		T = 313.15 K, I	P = 2.169 MPa		
		x_{water}/x_{2-pt}	$r_{opanol} = 3.3103$		
0.0503	153.1	0.8011	410.0	0.3015	342.0
0.9503	222.5	0.2011	284.9	0.4017	387.4
0.1006	224.6	0.7015	438.7	0.6017	443.4
0.9006	331.5	0.2513	315.0	0.5018	419.1
0.1509	254.5	0.6516	442.0	-	-
		T = 313.15 K, T	P = 1.997 MPa		
		x_{water}/x_{2-p}	$_{ropanol}$ =1.0121		
0.0503	131.7	0.8010	514.7	0.3013	429.8
0.9503	320.1	0.2010	365.1	0.6015	524.8
0.1006	234.7	0.7013	531.6	0.4015	470.7
0.9006	417.3	0.2512	404.3	0.5016	501.8
0.1508	310.4	0.6514	529.8	-	-
		T = 313.15 K, I	P = 3.897 MPa		
		x_{water}/x_{2-p}	ropanol =1.0121		
0.0509	129.7	0.8014	512.4	0.3019	443.2
0.9504	304.4	0.2014	369.2	0.6021	546.6
0.1008	232.3	0.7019	548.3	0.4021	480.3
0.9008	410.3	0.2517	411.4	0.5022	513.0
0.1511	310.3	0.6520	550.6	-	-
		T = 323.15 K, I	P = 3.980 MPa		
		x_{water}/x_{2-p}	ropanol =1.0040		
0.0509	146.9	0.8029	571.9	0.3038	496.0
0.9509	315.0	0.2029	409.2	0.6044	601.6
0.1016	260.7	0.7038	604.6	0.4044	541.1
0.9016	448.3	0.2534	461.5	0.5065	576.9
0.1523	346.5	0.6541	609.2	-	-
		T = 333.15 K, T	P = 3.975 MPa		
		x_{water}/x_{2-p}	ropanol =1.0040		
0.0507	157.7	0.8023	671.3	0.3031	547.2
0.9507	387.4	0.2023	454.8	0.6035	684.2
0.1013	287.9	0.7527	693.7	0.3533	576.6
0.9013	536.6	0.2527	510.8	0.5036	651.4
0.1519	384.0	0.703	698.2	0.4035	603.6
		T = 333.15 K, I	P = 3.980 MPa		
		x_{water}/x_{2-p}	ropanol =3.3290		
0.9010	379.0	0.5528	526.9	0.3526	424.3
0.8018	513.3	0.5029	507.3	0.3024	392.2
0.7024	550.1	0.4528	483.3	0.2018	316.4
0.6526	549.0	0.4027	454.5	0.1010	225.9
0.6027	541.2	0.3526	426.2	-	-

Table 7.2: Experimental H^{E} data for the pseudo-binary mixture propylene (1) + (2-propanol + water) (2).

<i>x</i> ₁	H^{E} $(\mathbf{J} \cdot \mathbf{mol}^{-1})$	x_1	H^{E} (J·mol ⁻¹)	<i>x</i> ₁	H^{E} (J·mol ⁻¹)
	· /	T = 333.15 K,	P = 3.980 MPa		
		$x_{water} / x_{2-\mu}$	propanol =0.3298		
0.0506	126.9	0.7026	882.7	0.3026	620.0
0.9011	649.5	0.2020	457.1	0.5031	828.9
0.1011	251.4	0.6030	874.1	0.3528	687.7
0.8020	838.4	0.2523	542.3	0.4531	791.5
0.1516	358.3	0.5531	855.1	0.4030	743.0
		T = 333.15 K, L	P = 5.890 MPa		
		$x_{water}/x_{2-\mu}$	oropanol =3.3290		
0.1015	245.7	0.6537	585.4	0.0406	160.7
0.9014	387.2	0.3537	467.5	0.0711	207.9
0.2026	348.4	0.6039	579.8	0.9409	283.6
0.8026	535.1	0.4540	525.8	0.1521	294.7
0.7034	581.6	0.5540	565.9	0.8521	464.3
0.3034	433.0	0.0508	183.7	0.2531	385.0
0.5041	551.0	0.4039	497.0	0.7530	553.7
		T = 353.15 K,	P = 4.190 MPa		
		x_{water}/x_{2-p}	_{ropanol} =1.0040		
0.0510	170.1	0.8033	725.9	0.3044	607.3
0.9510	433.2	0.2034	503.0	0.6050	743.4
0.1019	311.1	0.7044	762.0	0.4051	656.7
0.9019	591.7	0.2540	565.4	0.5053	703.4
0.1527	420.8	0.6548	756.4	-	-

Table 7.3: Experimental H^{E} data for the binary mixture 2-propanol (1) + water (2).

<i>x</i> ₁	H^{E}	x_1	H^{E}	X_1	H^{E}
	(5.1101-)	T = 313.15 K, T	P = 3.865 MPa		(J-11101)
0.0102	-97.3	0.8031	293.0	0.3041	-121.8
0.9509	96.1	0.1018	-448.1	0.6046	290.4
0.0306	-271.9	0.7040	325.9	0.4047	49.0
0.9017	178.1	0.2031	-302.6	0.5548	246.8
0.0611	-423.0	0.6544	315.7	0.5048	191.6
		T = 333.15 K, T	P = 3.800 MPa		
0.0713	-216.0	0.1018	-199.7	0.7040	442.5
0.0102	-62.8	0.9017	228.2	0.4047	272.7
0.0407	-189.9	0.2013	-43.5	0.6046	448.2
0.0611	-216.8	0.8031	374.1	0.5048	387.3
0.9509	100.4	0.3041	124.4	0.5548	425.8
		T = 353.15 K, T	P = 4.190 MPa		
0.0102	-27.0	0.8031	492.4	0.3041	404.8
0.9509	161.4	0.1018	0.9	0.6046	663.9
0.0306	-74.2	0.7040	630.6	0.4047	524.7
0.9017	279.7	0.2031	216.5	0.5548	637.5
0.0611	-76.3	0.6544	666.8	0.5048	598.8

The G^E term in the WS mixing rules is obtained from a modified UNIQUAC G^E model [11,12]. The mathematical formalism is presented in Appendix A.4, with the only exception for the residual term:

$$\left(\frac{G^E}{RT}\right)^R = -\sum_i q'_i x_i \ln \sum_j x_j F'_j \tau_{ji}$$
(7.2)

where

$$F_{i}' = \frac{q_{i}'}{\sum_{j} q_{j}' x_{j}}$$
(7.3)

In the modified UNIQUAC G^E model r_i and q_i in the *combinatorial term* reflect the sizes and the outer surface areas for the pure fluid molecules, while q'_i in the residual term are empirical modifications of the UNIQUAC model [13] to improve the representation of mixtures containing alcohols. A quadratic dependence from the temperature has been assumed for the Δu_{ij} binary interaction parameters:

$$\Delta u_{ij} = A_{ij} + B_{ij}T + C_{ij}T^2$$
(7.4)

with $A_{ii} = A_{jj} = 0$; $B_{ii} = B_{jj} = 0$; $C_{ii} = C_{jj} = 0$.

The values of the pure component parameters r_i and q_i have been assumed as in Ref. 12. On the other hand, due to the particular difficulty in the representation of the present mixture in a wide pressure range, the individual q'_i parameters were not assumed from the literature [11] but they have been regressed on the same data sets used for the binary interaction parameters regression, see next paragraph. The individual parameters of the present mixture components are listed in Table 7.4.

The binary interaction parameters A_{ij} , B_{ij} , C_{ij} , and k_{ij} of the model have regressed minimizing the objective function f_{ob} of Eq. (7.5), which is composed of the phase equilibria term $f_{ob,\phi}$ and the excess enthalpy term f_{ob,H^E} . Because for this case liquid-vapor (LV), liquid-liquid (LL), and liquidliquid-vapor (LLV) equilibria can be present in the chosen P,T range, the corresponding $f_{ob,\phi}$ objective functions in Eq. (7.6) have to consider together all the three cases and they have been assumed in form analogous to Eq. (7.7), which refers to the LV equilibrium only:

$$f_{ob} = f_{ob,\varphi} + f_{ob,H^E}$$
(7.5)

$$f_{ob,\varphi} = \left(f_{ob,\varphi}\right)_{LV} + \left(f_{ob,\varphi}\right)_{LL} + \left(f_{ob,\varphi}\right)_{LLV}$$
(7.6)

$$\begin{pmatrix} f_{ob,\varphi} \end{pmatrix}_{LV} = \frac{1}{n_{12}^{\varphi}} \sum_{i=1}^{n_{12}^{\varphi}} \sum_{j=1}^{2} \left[\left(\frac{y_{j} \hat{\varphi}_{j}^{v}}{x_{j} \hat{\varphi}_{j}^{l}} - 1 \right)_{i} \right]^{2} + \frac{1}{n_{13}^{\varphi}} \sum_{i=1}^{n_{13}^{\varphi}} \sum_{j=1}^{2} \left[\left(\frac{y_{j} \hat{\varphi}_{j}^{v}}{x_{j} \hat{\varphi}_{j}^{l}} - 1 \right)_{i} \right]^{2} + \frac{1}{n_{23}^{\varphi}} \sum_{i=1}^{2} \sum_{j=1}^{2} \left[\left(\frac{y_{j} \hat{\varphi}_{j}^{v}}{x_{j} \hat{\varphi}_{j}^{l}} - 1 \right)_{i} \right]^{2} + \frac{1}{n_{23}^{\varphi}} \sum_{i=1}^{2} \sum_{j=1}^{3} \left[\left(\frac{y_{j} \hat{\varphi}_{j}^{v}}{x_{j} \hat{\varphi}_{j}^{l}} - 1 \right)_{i} \right]^{2} + \frac{1}{n_{23}^{\varphi}} \sum_{i=1}^{2} \sum_{j=1}^{3} \left[\left(\frac{y_{j} \hat{\varphi}_{j}^{v}}{x_{j} \hat{\varphi}_{j}^{l}} - 1 \right)_{i} \right]^{2}$$

$$(7.7)$$

$$f_{ob,H^{E}} = \frac{1}{n_{12}^{H^{E}}} \sum_{i=1}^{n_{12}^{H^{E}}} \left[\left(\frac{\left(H_{12}^{E}\right)_{exp} - \left(H_{12}^{E}\right)_{calc}}{\left(H_{12}^{E}\right)_{exp}} \right)_{i} \right]^{2} + \frac{1}{n_{23}^{H^{E}}} \sum_{i=1}^{n_{23}^{H^{E}}} \left[\left(\frac{\left(H_{23}^{E}\right)_{exp} - \left(H_{23}^{E}\right)_{calc}}{\left(H_{23}^{E}\right)_{exp}} \right)_{i} \right]^{2} + \frac{1}{n_{1(23)}^{H^{E}}} \sum_{i=1}^{n_{23}^{H^{E}}} \left[\left(\frac{\left(H_{23}^{E}\right)_{exp} - \left(H_{23}^{E}\right)_{calc}}{\left(H_{23}^{E}\right)_{exp}} \right)_{i} \right]^{2} + \frac{1}{n_{1(23)}^{H^{E}}} \sum_{i=1}^{n_{23}^{H^{E}}} \left[\left(\frac{\left(H_{23}^{E}\right)_{exp} - \left(H_{23}^{E}\right)_{exp}}{\left(H_{23}^{E}\right)_{exp}} \right)_{i} \right]^{2} \right]^{2}$$

$$(7.8)$$

where in Eq. (7.7) the n^{φ} represent the number of VLE experimental points for each one of the mixtures. In Eq. (7.8) n^{H^E} is the number of H^E experimental points and the excess enthalpy values H_{12}^E , H_{23}^E , and $H_{1(23)}^E$ have been obtained through the data reduction procedure exposed in the following paragraph.

 Table 7.4: Pure component parameters for the considered mixture.

	Propylene	2-Propanol	Water
T_{c} (K)	365.57	508.3	647.13
P_c (MPa)	4.665	4.762	22.055
$\rho_c \pmod{1^{-1}}$	5.3079	4.5455	17.889
ω	0.139817	0.667714	0.344861
$d_{_1}$	0.569139	1.11495	0.919263
d_2	0.0953845	1.70548	-0.332035
d_{3}	0.0269034	-3.47044	0.317204
r_i	2.2465	2.7791	0.92
${q}_i$	2.024	2.508	1.4
q_i'	0.6063	1.2012	0.6942

7.6.1. Reduction of the experimental H^E pseudo-binary data

Considering the present ternary mixture as propylene (1) + (2-propanol (2) + water (3)), i.e., as a pseudo-binary mixture, the aforementioned H^E measurements have to be reduced in order to get the mole ratios ϕ^j of each j^{-th} phase present at equilibrium, their compositions x_i^j , with *i* as the component, the excess enthalpy H^E and the composition of the starting binary mixture (2-propanol (2) + water (3)) at the same (T, P) conditions of the pseudo-binary mixture. The pseudo-binary H^E experimental values can be expressed as a function $H^E_{1(23)}(T, P, x_1, x_2, x_3)|_{exp}$ where (x_1, x_2, x_3) are the local overall compositions. At the same time such value can be predicted through the proposed $G^E - EoS$ model reading:

$$H_{1(23)}^{E}(T, P, x_{1}, x_{2}, x_{3})_{G^{E}-EoS} = \sum_{j=1}^{\pi^{123}} \phi_{123}^{j} H_{123}^{j}(T, P, x_{1}^{j}, x_{2}^{j}, x_{3}^{j})_{G^{E}-EoS} - \sum_{i=1}^{3} x_{i} H_{i}(T, P)_{EoS} + (1-x_{1}) H_{23}^{E}(T, P, x_{2}^{*}, x_{3}^{*})_{G^{E}-EoS}$$

$$(7.9)$$

where $H_{23}^{E}(T, P, x_{2}^{*}, x_{3}^{*})|_{G^{E}-EoS}$ is:

$$H_{23}^{E}\left(T,P,x_{2}^{*},x_{3}^{*}\right)_{G^{E}-EoS} = \sum_{j=1}^{\pi^{23}} \phi_{23}^{j} H_{23}^{j}\left(T,P,x_{2}^{*,j},x_{3}^{*,j}\right)_{G^{E}-EoS} - \sum_{i=1}^{2} x_{i} H_{i}\left(T,P\right)_{EoS}$$
(7.10)

with:

$$\begin{cases} x_2^* = \frac{1}{1 + x_3/x_2} \\ x_3^* = 1 - x_2^* \end{cases}$$
(7.11)

and π is the number of equilibrium phases in the mixture at specified (T, P).

In Eq. (7.9) the terms ϕ^{j} , H_{123}^{j} , x_{i}^{j} (with i = 1,2,3), and H_{23}^{E} are predicted from the model while for consistency $H_{i}(T, P)|_{EoS}$ has to be calculated through the same EoS assumed in the G^{E} – EoS model.

Each experimental $H_{1(23)}^{E}(T, P, x_{1}, x_{2}, x_{3})\Big|_{exp}$ value is compared with the corresponding calculated value $H_{1(23)}^{E}(T, P, x_{1}, x_{2}, x_{3})\Big|_{G^{E}-EoS}$ in order to regress the binary interaction parameters k_{ij} , A_{ij} , B_{ij} , and C_{ij} appearing in the model. The deviations between the two H^{E} values are included in the third addend of the $f_{ob,H^{E}}$ objective function, Eq. (7.8).

7.6.2. Regression of the model

The values of the binary interaction parameters k_{ij} , A_{ij} , B_{ij} , and C_{ij} of the proposed model have been regressed on data of both phase equilibrium and H^E . For both the thermodynamic quantities the regression of the former interaction parameters was developed using both the present experimental data and those from the literature [1,2,14-17]. The whole data base for the phase equilibrium and the H^E used in this case is presented in Tables 7.5 and 7.6, respectively. For the ternary mixture all the available data have been used for the regression of the model, whereas for the three binary mixtures the available data have been selected sharing temperature and pressure ranges close to those of the ternary mixture, excluding the values falling outside such ranges.

Table 7.5: Experimental phase equilibrium data sets used for the regression of the G^{E} – EoS model.

			Experimenta	l phase equili	ibrium data						
Measurements range Model regression range											
			Mea	surements ra	nge	Model regression range					
Mixture	Type	Ref.	Т	Р	NDTa	Т	Р	NDTa			
			(K)	(MPa)	INF I	(K)	(MPa)	INF I			
propylene + 2-propanol	VLE	15	333-370	0.5-4.1	18	333-370	0.5-4.1	18			
monulona	VLE	16	311-411	0.3-33.0	46	311-411	0.3-9.1	33			
propytene +	LLE	16	311-344	3.2-33.0	10	314-344	3.2-7.5	3			
water	VLLE	16	311-364	1.6-4.6	6	311-364	1.6-4.6	6			
2-propanol + water	VLE	17	423-573	0.5-12.3	77	423-473	0.5-2.8	37			
Dronvlana	VLE	2	333-353	2.6-3.7	7	333-353	2.6-3.7	7			
Propylene +	LLE	3	313-363	1.6-6.0	22	313-363	1.6-6.0	22			
water	VLLE	present data	313	1.4-1.7	8	313	1.4-1.7	8			

^a NPT = number of points

Table 7.6: Excess enthalpy experimental data sets used for the regression of the G^E – EoS model.

		Excess	s enthalpy				
		Meas	surements r	ange	Model regression range		
Mixture	Ref.	Т	Р	NPT	Т	Р	NPT
		(K)	(MPa)		(K)	(MPa)	
Propylene + 2-propanol	17	333	3.1	21	333	3.1	21
2-propanol + water	present data	313-353	3.8-4.2	45	313-353	3.8-4.2	45
Propylene + 2-propanol + water	present data	313-353	2.0-5.9	135	313-353	2.0-5.9	135

Fig. 7.2 represents on the (P,T) plane the distribution of all the available data, whereas those used for the model regression are falling inside the hatched region, which also indicates the validity range of the model. The last one is from 300 to 475 K and up to 10 MPa and is consequently much more narrow than the maximum range of the existing data.



Figure 7.2: Distribution of the available data on the (P,T) plane; the hatched region includes those used for the regression of the G^{E} – EoS model and also indicates its validity limits.

The results of the regression for the binary interaction parameters of the model of the target mixture are presented in Table 7.7; these are then used in the present calculations.

Table 7.7: Binary interaction parameters values for the present mixture.

Component 1	Component 2	i	i	A_{ij}	B _{ij}	C_{ij}	k_{ij}
component i	component 2	v	5	$J \cdot mol^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-2}$	
nronulano	2 propagal	1	2	-5433.0	20.550	-2.1885×10 ⁻³	0 2270
propylette	2-propanor	2	1	6762.9	-43.166	6.3507×10 ⁻²	0.5570
		1	2	435.55	-4.9572	3.5838×10 ⁻³	0.2100
propylene	water	2	1	39.445	-2.7879	1.7755×10 ⁻⁴	0.3122
21		1	2	950.75	-5.4938	4.0634×10 ⁻³	0 4652
2-propanoi	water	2	1	715.94	-7.5048	1.5192×10 ⁻²	0.4055

The validity range of the G^{E} – EoS model for temperature is 300 to 475 K and for pressure is up to 10 MPa and it is the same of the experimental data used for the regression.

7.7. Discussion

The behavior of the G^{E} – EoS model with respect to the experimental data falling inside the validity range of the present model has been studied and a statistical analysis of the data representation is reported in the following. In such context the deviation in the composition of the coexisting phases is calculated as:

$$\Delta_{i,j} = \left(z_{j,exp} - z_{j,calc} \right)_i \tag{7.12}$$

where z_j represents the mole fraction of the j^{-th} component in the liquid or vapor phases (indicated either as x_j or as y_j respectively) for the i^{-th} point. The average absolute deviation (AAD) for the j^{-th} phase is evaluated as:

$$AAD_{z_{j}} = 100 \frac{1}{NPT} \sum_{i=1}^{NPT} \left| \Delta_{i,j} \right|$$
(7.13)

When dealing with H^E the deviation Δ_i for the i^{-th} point is evaluated as:

$$\Delta_{i} = \frac{\left(H^{E}\right)_{i,\exp} - \left(H^{E}\right)_{i,calc}}{\left(H^{E}\right)_{i,\exp}}$$
(7.14)

In this case the AAD is evaluated from Eq. (A6.3) with Δ_i as in Eq. (7.14), see Appendix A.6.

The statistical results of the validation for the equilibria of the three binary and the ternary mixture in terms of AAD_{z_j} , Eq. (7.13), are reported in Table 7.8 for each component in each of the coexisting phases. The considered data sets are the same of those presented in the former Table 7.5.

Some of the validation results are reported in the following figures. In the upper part of Fig. 7.3 the calculated vapor-liquid phase equilibrium of the binary system propylene + 2-propanol is shown in comparison with the data from Ref. 14. The vapor-liquid equilibrium is rather well represented at each of the three temperatures.

Mixture	Туре	Ref.	Vapor phase			Organic liquid phase			Aqueous liquid phase		
			AAD_{y_1}	AAD_{y_2}	AAD_{y_3}	AAD_{x_1}	AAD_{x_2}	AAD_{x_3}	AAD_{x_1}	AAD_{x_2}	AAD_{x_3}
propylene + 2- propanol	VLE	15	0.0054	0.0054	-	0.0394	0.0394	-	-	-	-
propylene + water	VLE	16	0.0040	0.0040	-	0.0000	0.0000	-	-	-	-
	LLE	16	-	-	-	0.0000	0.0000	-	0.0000	0.0000	-
	VLLE	16	0.0022^{a}	0.0022^{a}	-	0.0004^{a}	0.0004^{a}	-	0.0000^{a}	0.0000^{a}	-
2-propanol + water	VLE	17	0.0043 ^b	0.0043 ^b	-	0.0115 ^b	0.0115 ^b	-	-	-	-
propylene + 2-	VLE	2	0.0079	0.0093	0.0020	0.0179	0.0183	0.0014	-	-	-
propanol +	LLE	3	-	-	-	0.0117	0.0186	0.0211	0.0019	0.0169	0.0186
water	VLLE	present data	0.0059°	0.0024 ^c	0.0008°	0.1903	0.1197	0.1048	0.0023	0.0347	0.0369

Table 7.8: Validation of the G^{E} – EoS model for phase equilibrium.

^a VLLE has been calculated at the pressures of the experimental measurements; the AAD of the calculated equilibrium temperature with respect to the experimental temperature is 0.51%.

^b results obtained considering only the experimental VLE data at pressures below the azeotropic pressure calculated by the $G^{E} - EoS$ model at the given temperature (17 points).

^c results obtained considering the four experimental VLLE data for which the composition has been measured.



Figure 7.3: Calculated and experimental VLE and H^{E} data for the system propylene (1) + 2-propanol (2).

Table 7.8 shows some excellent results for the system propylene + water in each of the three considered equilibrium cases. The validation of the VLE data for the this system is also shown in Fig. 7.4. Due to the immiscibility of the two components and in order to better show the variation of
the bubble pressures very close to the pure water, a scale break is applied between 0.003 and 0.8 of molar fraction of propylene. In this case the bubble pressure is very well represented.



Figure 7.4: Calculated and experimental VLE data for the system propylene (1) + water (2).

For the binary mixture 2-propanol + water the AAD for VLE data were obtained considering only the experimental values at pressures below the azeotropic pressure calculated by the G^{E} – EoS model for the two temperatures (17 points). A discrepancy is here verified between the calculated and experimental azeotropic pressures as it is shown in particular in the upper part of Fig. 7.5.



Figure 7.5: Calculated and experimental VLE and H^E data for the system 2-propanol (1) + water (2).

For the ternary mixture the Table 7.8 reports satisfactory results for both the VLE and LLE predictions. For the VLLE the AAD in the vapor phase has been calculated on only the four measured values, while in the liquid phases all the eight measured values have been used. For the organic phase of the ternary mixture VLLE data a high deviation is verified and this has likely to be attributed particularly to the high error deviation with respect to the two points at the higher pressure, i.e., 15.9 and 16.9 MPa. The Fig. 7.6 evidences such deviating behavior of the model once one compares the upper and the lower ternary plots. In the lower plot it is evident the trend of the

model to group together the calculated compositions for the organic phase independently form the pressure values.

Evidently in the VLLE representation the pressure sensitivity of the G^E – EoS model is too weak and for this system it is not at all coherent with the experimental evidence.



Figure 7.6: Calculated and experimental VLLE data for the ternary system propylene + 2propanol + water.

In Table 7.9 the validation results for the excess enthalpy for two binary and the pseudo-binary mixture are reported for the same systems presented in the former Table 7.6.

Mixture	Ref.	AAD_{H^E} %
propylene + 2-propanol	17	6.78
2-propanol + water	present data	10.55
Propylene + 2-propanol + water	present data	10.11

Table 7.9: Validation of the G^E – EoS model for excess enthalpy.

The AAD_{H^E} of the three cases are comparably predicted with a better result for the propylene + 2-propanol system. For such system in the lower part of the former Fig 7.3 the calculated H^E values are plotted against the experimental data from Ref. 17. A limited negative deviation in correspondence of the central part of the composition range is evidenced in this case.

For the system 2-propanol + water the lower part of the former Fig. 7.5 shows the great sensitivity to the temperature of the experimental data, even if in the presence of a limited variation of the pressure. To overcome this aspect and considering also the large temperature range required to the G^E – EoS model a quadratic temperature dependence has been applied for the Δu_{ij} binary interaction parameters, notwithstanding the model clearly shows a difficulty to follow the temperature dependence of the H^E function.

For the pseudo-binary system propylene + (2-propanol + water) in Fig. 7.7 the model behavior is plotted for one of the three considered compositions of the starting 2-propanol + water mixture, i.e., that of 0.75. The upper part of the figure represents the predicted compositions of the two coexisting liquid phases (LLE) (open squares), for each H^E measured point at 333.15 K and 3.98 MPa (solid circles). The binodal curve is predicted by the model. The calculated compositions have been used to calculate, through Eqs. (7.9-7.11), the H^E curve reported against the H^E experimental data in the lower part of the figure.



Figure 7.7: Calculated and experimental LLE and H^{E} data for the pseudo-binary system propylene (1) + (2-propanol + water) (2).

Notwithstanding in this work H^E values of the ternary mixture were not directly measured it is also possible to built the trend of the ternary H^E surface applying the basic relation:

$$H_{123}^{E} = (1 - x_{1}) H_{23}^{E} \Big|_{G^{E} - EoS} + x_{1} H_{1(23)}^{E} \Big|_{\exp}$$
(7.15)

where $H_{1(23)}^{E}\Big|_{exp}$ is the present experimental value for the pseudo-binary system propylene + (2propanol + water) and $H_{23}^{E}\Big|_{G^{E}-EoS}$ is the value for the binary mixture 2-propanol + water calculated from the former G^{E} – EoS model. In this way the trend is more reliable with respect to a representation totally based on the model in which also the $H_{1(23)}^{E}$ term would be calculated from the model, adding in this way a further approximation. Because the sections are obtained at constant 2-propanol + water ratios it can be noted that for $x_{propylene} = 0$ the H^{E} values read from the plots correspond to the 2-propanol + water mixture H^{E} values.

The represented sections show a quite regular and smooth behavior of the ternary H^{E} surface varying propylene composition.



Figure 7.8: Sections of the ternary H^E surface as obtained from the former model including the pseudo-binary experimental H^E data.

7.8. Conclusions and description of the mixture behavior

VLLE values for the propylene + 2-propanol + water system have been measured at 313.15 K in the pressure range from 1.381 to 1.690 MPa and H^E measurements for the pseudo-binary mixture propylene + (2-propanol + water) have been obtained in the temperature range from 313.15 to 353.15 K and pressures from 1.997 to 5.89 MPa.

The ternary mixture was studied starting from the 2-propanol + water system at the three molar compositions of 0.25, 0.50, 0.75 in 2-propanol. Furthermore, for the binary system propylene + 2-propanol H^E values have been obtained in the temperature range from 313.15 to 353.15 K and pressures up to 4.19 MPa. A total of 180 experimental points has been obtained using an isothermal flow calorimeter.

Both the VLLE and the H^E data, included VLE, LLE and H^E literature data sets, have been correlated for the ternary mixture, including the binary ones, using a $G^E - EoS$ model composed of a PR cubic EoS and a UNIQUAC G^E model combined by the WS mixing rules. For the phase equilibrium representation the deviations of the model from the experimental points are in general satisfactory with the exception of the VLLE for the ternary mixture, where the limited number of the available points has hindered the accuracy. On the other hand the H^E data, of both the binary and the ternary mixtures, are satisfactorily represented by the model.

The phase equilibrium behavior of the mixture propylene + 2-propanol + water has been qualitatively studied with the obtained $G^E - EoS$ model. In the ternary system propylene (1) + 2-propanol (2) + water (3) different kinds of phase equilibria are possible at varying temperatures and pressures. The ternary mixture phase equilibrium behavior at a given temperature strongly depends on the closeness between the ternary mixture pressure and the vapor-liquid-liquid equilibrium pressure of the propylene + water binary mixture. Fig. 7.9 shows the phase equilibria of the propylene + water mixture at T = 313.15 K.



Figure 7.9: Phase equilibria of the propylene-water mixture at T = 313.15 K.

Propylene and water are almost completely immiscible components, so that two different vaporliquid regions are present. A VLLE exists for a pressure very close to the pure propylene saturation pressure and consequently at a fixed temperature the pure propylene saturation pressure and the VLLE pressure of the propylene + 2-propanol mixture are in practice the same. At higher pressures there is the liquid-liquid equilibrium (LLE) region.

According to the phase rule the propylene + water mixture has only a single degree of freedom when the vapor-liquid-liquid equilibrium condition is present. Therefore, for each temperature there is only a single pressure at which the VLLE exists. Adding the 2-propanol the degrees of freedom become two and therefore at each temperature there is a range of pressure for which the VLLE exists. Such a L_1L_2V range extends from a lower critical endpoint ($L_1 = L_2$)V to an upper critical endpoint $L_1(L_2 = V)$. This leads to the isothermal pressure dependence of the phase equilibrium envelope of the ternary mixture shown qualitatively for T = 313.15 K in Figs. 7.10-7.14. At pressures below the saturation pressures of the pure propylene, part a of Fig. 7.10, a vapor-liquid equilibrium (VLE) exists for both the propylene + 2-propanol and propylene + water binary mixtures, as it is possible to observe in Fig. 7.10 part b for a pressure of 1.0 MPa.



Figure 7.10: Phase equilibria of the ternary system at T = 313.15 K and P = 1.0 MPa.

The VLE tie-line at 1.0 MPa in the propylene + 2-propanol binary mixture graph is reported in the ternary mixture graph, Fig. 7.10 part c (in red). Adding water at the propylene + 2-propanol binary mixture, the vapor-liquid tie-lines have a clockwise rotation going toward the vapor-liquid tie-line of the propylene + water binary mixture.

When the saturation pressure of the propylene is approached, the change in the equilibrium behavior of the system is shown in Fig. 7.11 at 1.43 MPa.



Figure 7.11: Phase equilibria of the ternary system at T = 313.15 K and P = 1.43 MPa.

At these conditions a VLLE appears. Initially the two liquid phases have almost the same composition, that is a composition approaching the pure water. Rising the pressure the composition of the light liquid phase moves along the projection of the phase envelope toward the propylene + 2-propanol binary mixture side, as it is possible to see in Fig. 7.12 for 1.60 MPa.



Figure 7.12: Phase equilibria of the ternary system at T = 313.15 K and P = 1.60 MPa.

Increasing the pressure above the upper critical endpoint, a LLE exists, see Fig. 7.13 for 2.00 MPa.



Figure 7.13: Phase equilibria of the ternary system at T = 313.15 K and P = 2.0 MPa.

The tie-line slopes in the LLE region show a distribution coefficient of the 2-propanol between the organic phase and the aqueous phase suitable for an extraction operation. This has been in fact the main problem for the choice of a suitable system to be studied for the extraction operation.

The effect of the pressure on the LLE envelope could be seen comparing Fig. 7.13 at 2.00 MPa with Fig. 7.14 at 30.00 MPa: increasing the pressure the LLE envelope moves toward the propylene + water mixture side of the triangle.



Figure 7.14: Phase equilibria of the ternary system at T = 313.15 K and P = 30.0 MPa.

The effect of the temperature on the LLE envelope could be seen comparing Fig 7.13 for a pressure slightly above the propylene saturation pressure at 313.15 K with Fig. 7.15 for a pressure slightly above the propylene saturation pressure at 350.00 K: increasing the temperature the LLE envelope moves toward the propylene + water mixture side of the triangle.



Figure 7.15: Phase equilibria of the ternary system at T = 350.0 K and P = 4.0 MPa.

Representations of the phase equilibria prisms in the pressure range from 0.1 to 10 MPa at 300 and 380 K are shown in Figs. 7.16 and 7.17, respectively. These two temperatures represent roughly the upper and the lower limit of the possible range of interest for the extraction process.

The modeling effort has reconfirmed the difficulty of a conventional $G^E - EoS$ model to correctly represent the thermodynamics of a strongly polar and deviating ternary mixture as the present one in a wide temperature and pressure range, even if limiting the representation to phase equilibrium and excess enthalpy. Because this category of models is presently the most advanced tool to represent the thermodynamics of these kinds of ternary systems, new modeling methods are expected to allow the study of the unit operations involving strongly deviating multicomponent systems.



Figure 7.16: Phase envelopes of the ternary system at T = 300.0 K.



Figure 7.17: Phase envelopes of the ternary system at T = 380.0 K.

7.9. References

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VIII. Density and phase equilibrium via a vibrating tube densimeter

8.1. Introduction

The study of the propylene + 2-propanol + water mixture in the previous Chapter VII pointed out the need for further experimental measurements and new modeling methods to achieve a satisfactory representation of the thermodynamic properties of the mixture in order to study the 2propanol extraction process from an energetic point of view.

In Paragraph 4.3 it is demonstrated that the extended equation of state neural network (EEoS-NN) modeling method is a suitable tool to obtain a precise representation of the thermodynamic properties of a mixture in the (T, P, x) range of interest starting from density and coexistence data only. The EEoS-NN method requires precise, well-distributed data in the whole range of temperature T, pressure P and composition x.

It has been chosen to study the 2-propanol extraction from aqueous solution using propylene as solvent for operative conditions ranging from 300 to 350 K and up to 10 MPa; the composition range of interest extends up to the pure fluids. While very precise equations of state exist for propylene [1] and water [2], 2-propanol presents only experimental data, and they are not in good agreement each other.

In order to create a data base of density data suitable to regress a dedicated equation of state (DEoS) in the aforementioned range of interest, new density data have been produced using a vibrating tube densimeter (VTD) for the pure 2-propanol, for the propylene + 2-propanol mixture, for the 2-propanol + water mixture and for the propylene + 2-propanol + water mixture. Bubble pressure data were also determined using the VTD for the propylene + 2-propanol mixture and for the propylene + 2-propanol mixture and for the propylene + 2-propanol mixture.

8.2. Chemicals

The propylene (molar mass = 42.08 kg/kmol, CAS Number 115-07-1) is from Air Liquide with a certified purity higher than 99.99 vol %. The 2-propanol (molar mass=60.096 kg/kmol, CAS Number 67-63-0) is from Sigma-Aldrich with a GC certified purity higher than 99.8%. Ultra pure water is produced with a Direct-Q model from Millipore. Both 2-propanol and water were carefully degassed before use.

8.3. Apparatus

A detailed description of the apparatus is given in Ref. 3 and its schematic layout is presented in Fig. 8.1. The apparatus employs a vibrating tube made of stainless steel (Anton Paar, model DMA 512). The period of vibration τ is recorded by means of a data acquisition unit (Hewlett Packard, model 53131A).



Figure 8.1: Flow diagram of the equipment: 1, loading cell; 1a-1e, shut-off valves; 2a and 2b, regulating and shut-off inlet valves; 2c and 2d, regulating and shut-off outlet valves; 3, densimeter; 4, heat exchanger; 4a, bursting disk; 5a, 5b and 6a, 6b, double valves; 7, inlet and outlet for the VTD temperature regulation; 8a and 8b, mixers; 9a and 9b, Pt100 probes; 10, pressure transducers maintained at constant temperature; 11, data acquisition unit; 12, data acquisition unit; 13, data acquisition supervising; 14, temperature regulator of the pressure transducers; 15, temperature regulator of the thermostated tube (20); 16, temperature regulator of the liquid bath (18); 17, temperature regulator of the main liquid bath; 18, liquid bath; 19, nitrogen bomb; 20, thermostated tube.

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The temperature of the vibrating tube is controlled by a regulated liquid bath (Lauda, model RE206) with stability within $\pm 0.01 K$. The temperature of the remaining parts of the circuit is regulated by a liquid bath (Bioblock, model Variosat P1C50P as cooling source, electric resistor managed by a PID regulator West model 6100 as heating source). Temperatures are measured with two *Pt*100 probes connected to a data acquisition unit (Hewlett Packard, model 34970A). The probes have been calibrated in the 288–433 K range against a 25 Ω reference thermometer (Tinsley Precision Instrument) certified by Laboratoire National d'Essais (Paris, France). Pressure is measured using two pressure transducers (Druck, model PTX611) of two complementary ranges: 0 - 0.5 MPa and 0.5 - 8.0 MPa. These sensors were calibrated against a dead weight pressure balance (Desgranges & Huot, model 5202S) in the 0.3 to 10.6 MPa range. Vacuum was achieved by means of a vacuum pump (AEG, model LN38066008). Real time (τ , T, P) data are recorder every 3 seconds by a computer linked to both the HP units. Synthetic mixtures have been prepared gravimetrically under vacuum according to the procedures presented in Ref. 4. An analytical balance (Sartorius AG, Göttingen, model CC3000) was used to get accurate mass values. Viton 70 Shore O-rings have been used as seals for the piston in the loading cell.

8.4. Experimental procedure

The description of the experimental procedure refers to the schematic layout of the equipment presented in Fig. 8.1. The synthetic mixture is gravimetrically prepared in the loading cell (1) under vacuum, according to the procedure discussed in Ref. 4. The loading cell is connected to the circuit by means of the valve 1c and to a high-pressure nitrogen bomb by the valves 1a, 1b. Before starting the measurement the VTD liquid bath (18) is programmed at the measurement temperature, while the main bath is programmed at a temperature slightly higher $(0.5 \div 1 \text{ K})$ to obtain the first vaporization inside the VTD instead of in the other parts of the circuit; for details see Ref. 3. The whole circuit was evacuated connecting the vacuum pump to the valve 5a, while valves from 2a to 2d and 5b are open and valves 1c, 6a and 6b are closed. The period of vibration at the lowest accessible pressure, obtained with the vacuum pump, and at the measurement temperature is measured. To carry out density measurements in the liquid phase the pressure in the loading cell is increased to values higher than the bubble pressure of the mixture to assure the homogenization inside the cell. After the measurement of the vibration period at vacuum conditions the vacuum pump is disconnected closing the valve 5a and the fluid is loaded from the loading cell to the apparatus through the valve 1c. The movement of the piston inside the cell ensures the homogeneity of the mixture in the apparatus maintaining the mixture pressure constant during the loading of the circuit. If the loading pressure is higher than 0.5 MPa the valve 1e has to be closed during this

procedure to avoid a damage of the low-pressure transducer. The circuit is partially purged opening the valve 6a or 6b, and new mixture is introduced in the circuit from the loading cell. It is assumed that the liquid inside the VTD is representative of the fluid inside the loading cell when measured period of vibration remains constant and is not dependent on further purging. The pressure in the circuit is increased opening the valve 1a up to the highest measurement pressure (about 10 MPa in this work). A suitable opening of the valve 2d is then selected in order to assure that the pressure inside the circuit decreases continuously with a controlled rate not higher than 0.005 MPa·s⁻¹. Under these conditions the fluid inside the apparatus is assumed in mechanical equilibrium. The liquid phase is studied from the chosen upper pressure down to the bubble point, which is determined through the drastic change in the $P \div \tau$ behavior going from the single phase to the coexistence region as described in Ref. 3. During this process the pressure, the temperature inside the VTD and the period of vibration are recorded every 3 seconds. The period of vibration is converted into density using the Forced Path Mechanical Calibration (FPMC) [5]. The first reference for the calibration is the period of vibration measured at vacuum conditions while the second reference is the period of vibration of the refrigerant R134a, for witch measurements have been carried out at the same temperature and in the same pressure range of the target mixture, see Ref. 5.

8.5. Experimental uncertainties

The experimental uncertainties have been calculated taking into account the expanded uncertainties and coverage factor as described in Ref. 6. The global uncertainty on density data in the liquid phase is estimated to be within 0.05%. The uncertainty on vibrating period values is $\pm 10^{-8}$ s. Global temperature uncertainties are estimated to be about ± 0.02 K with a confidence level of approximately 68%. Global uncertainties on pressure measurement are ± 0.0001 MPa (for $0 < P \le 0.6$ MPa) and ± 0.0006 MPa (for $0.6 < P \le 10.6$ MPa) with a confidence level of approximately 68%. Uncertainties in mixture composition are within $2 \cdot 10^{-4}$ in molar fraction.

8.6. Experimental results for the 2-propanol system

8.6.1. Introduction

2-propanol has important industrial applications as raw material in paint and ink products and as solvent in electronics and it is also used in medicine.



Figure 8.2: Liquid density data distribution of 2-propanol in the range from 273 to 400 K and from atmospheric pressures up to 12 MPa.

The critical point of 2-propanol is at $T_c = 508.3 K$, $P_c = 4.764 MPa$ and $\rho_c = 271 kg \cdot m^{-3}$. The literature presents a number of experimental works about the $P\rho T$ properties of 2-propanol and the most extensive sources of $P\rho T$ data are listed in the following. Ambrose et al. [7] measured densities in the vapor, liquid and supercritical regions in the temperature range from 386 to 573 K and for pressures from 0.4 to 13 MPa. Boned et al. [8] and Moha-Ouchane et al. [9] measured the liquid density for the liquid phase from 303 to 343 K and from atmospheric pressure up to 65 MPa. Golubev and Vagina [10], Golubev et al. [11], and Golubev et al. [12] measured the densities in the

liquid and supercritical regions from 292 to 594 K and from atmospheric pressure up to 50 MPa. Kubota et al. [13] measured the liquid densities in the liquid region from 283 to 348 K and from the atmospheric pressure up to 174 MPa. Tseng and Stiel [14] measured the densities in the vapor and supercritical region from 473 to 573 K and from 7 to 55 MPa. Yaginuma et al. [15] measured the liquid density for 313 K from atmospheric pressure up to 10 MPa. Zuniga-Moreno and Galicia-Luna [16] measured the liquid density from 313 to 363 K and from 0.5 to 25 MPa.

A great number of authors reported experimental density data at atmospheric pressure: Aminabhavi et al. [17], Aminabhavi and Aralaguppi [18], Aminabhavi and Gopalakrishna [19], Contreras [20], Costello and Bowden [21], Egorov et al. [22], Islam and Quadri [23], Khimenko et al. [24], Khimenko et al. [25], Krestov et al. [26], Ku and Tu [27], Lee and Lin [28], Mato and Coca [29], Nagata et al. [30], Nikam et al. [31], Oswal and Putta [32], Paez and Contreras [33], Sakurai [34], Sovilj [35], Tashima and Arai [36], Tu et al. [37], Wei and Rowley [38].

In this work density measurements in the liquid region from 280 to 393 K and from atmospheric pressure up to 10 MPa have been carried out using a "synthetic open circuit method" [39] taking advantage of a vibrating tube densimeter (VTD).

The measured density data together with the available literature data in the range from 273 to 400 K and up to 12 MPa are shown in Fig. 8.2 in (P,T) coordinates.

8.6.2. Experimental results

The liquid density measurements for 2-propanol have been carried out at 280, 300, 325, 350, 375 and 393 K from 10 MPa down to near the atmospheric pressure. The measured (P, ρ, T) values are reported in Tab. 8.1.

8.6.3. Modeling methods

A modification of the BWR equation of state, published by Starling [40], has been used to correlate the measured liquid density values:

$$P = RT\rho + \left(B_0RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4}\right)\rho^2 + \left(bRT - a - \frac{d}{T}\right)\rho^3 + \alpha\left(a + \frac{d}{T}\right)\rho^6 + \frac{c\rho^3\left(1 + \gamma\rho^2\right)}{T^2}\exp\left(-\gamma\rho^2\right)$$
(8.1)

where *R* is the fluid specific gas constant and *P*, *T*, ρ are the temperature, the pressure and the density, respectively, while the other terms are the equation parameters to individually regress for a target fluid.

Р	ρ	Р	ρ	Р	ρ
(MPa)	$(\text{kg} \cdot \text{m}^{-3})$	(MPa)	$(\text{kg} \cdot \text{m}^{-3})$	(MPa)	$(kg \cdot m^{-3})$
T = 28	0.21 K	T = 30	0.09 K	T = 32	5.12 K
0.1179	797.61	0.1867	780.22	0.2027	757.05
0.4396	797.89	0.6105	780.62	0.6094	757.49
0.9387	798.29	0.9534	780.94	0.9600	757.87
1.3284	798.62	1.3395	781.31	1.2539	758.21
1.6566	798.89	1.7221	781.66	1.6388	758.63
1 9449	799 14	2.0448	781.96	2.0210	759.06
2.4406	799.56	2.4464	782.34	2.3288	759.39
2.8506	799.88	2.8346	782.70	2.6558	759 75
3,1980	800.17	3.2249	783.06	3.0149	760.15
3.6791	800.56	3.6711	783.47	3.3214	760.48
4.0711	800.90	4.0741	783.84	3.6594	760.85
4.4377	801.19	4.3625	784.11	4.0041	761.22
4 8326	801.50	4 7718	784 48	4 3992	761.65
5.1821	801.80	5.2265	784.89	4.6912	761.97
5 5591	802.10	5 5792	785.21	5 0107	762.32
5.9100	802.39	6.0016	785.59	5.3834	762.71
6 3349	802.73	6 4272	785.98	5 7305	763.08
6 7509	803.06	6 7803	786.29	6 1436	763.52
7 1665	803.39	7 2147	786.68	6 5256	763.91
7 5920	803.74	7 6299	787.05	6 9032	764 31
7.9990	804.07	8 0203	787.40	7 2938	764.72
8 3290	804 33	8 4175	787.75	7.6619	765.11
8 8170	804 70	8 8057	788.10	7.9186	765 38
9 3506	805.11	9 2129	788.45	8 2544	765.30
9.6585	805 38	9.6215	788.81	8 7555	766.24
T - 350	0.14 K	$\frac{7.0215}{T-37}$	5 01 K	$\frac{0.7555}{T-39}$	2 57 K
0.0004	721.02	1 - 575.01 K		0.4076	2.37 K
0.2204	731.92	0.3495	702.23	0.4076	6/9.26
0.0034	732.49	0.7033	702.82	0.8887	680.18
1.0/12	755.05	1.0408	703.38	1.1/14	680.72
1.4126	733.49	1.43/5	704.01	1.5266	681.39
1.8447	/34.07	1./916	704.58	1.8974	682.08
2.2267	/34.58	2.1017	/05.16	2.2723	682.77
2.0447	735.11	2.5457	705.76	2.0191	083.41
2.8427	/35.41	2.9099	706.34	3.0504	684.20
5.2009	733.99	3.3041	707.04	3.4112	004.00
5.0507	/ 30.45	3.0770	707.55	3.8330	085.03
4.0122	/ 30.94	4.0852	708.10	4.0957	080.12
4.3946	/3/.43	4.5157	708.82	4.5249	080.89
4.7576	737.91	4.8535	709.33	4.9028	687.57
5.1979	/ 38.48	5.2802	709.98	5.2855	088.24
5.5779	738.90	5.0409	710.55	5.7759	089.09
5.9595	739.42	0.1381	/11.20	0.0390	089.55
0.5215	/ 39.89	0.44/1	/11./3	0.4/00	090.30
0./309	/40.41	0.8809	/12.5/	0.889/	091.UI
1.119/	/40.89 741 45	1.2098	/12.94	7.3480	091./8
/.3044	/41.45	1.1124	/15.08	1.1280	092.42
/.9885 0.4725	/41.9/ 742.55	8.1192	/14.18	8.1/2/	093.17
8.4725	142.55	8.5572	/14.81	8.3983	093.88
8.9238	143.13	8.98/3	/15.42	9.0185	094.37
9.2808	/43.36 744.05	9.4238	/10.04	9.4050	095.20
7.0/01	(44.0.)	7.0477	/10.04	7.01/7	07.1.07

 Table 8.1: Experimental liquid density data for 2-propanol.

The following objective function f_{ob} has been minimized to regress the parameters of the BWR equation of state:

$$f_{ob} = \frac{1}{NPT} \sum_{i=1}^{N} \left(\frac{\rho_i^{calc} - \rho_i^{exp}}{\rho_i^{exp}} \right)^2$$
(8.2)

where *NPT* is the number of experimental density data. The obtained values of the parameters for the BWR equation of state are presented in Table 8.2.

Table 8.2: BWR EoS parameters for 2-propanol in the liquid region from 273 to 400 K and from atmospheric pressure up to 12 MPa.

Parameter	Value ^a	Parameter	Value ^a
R	$1.383532 \cdot 10^{-4}$	a	$1.783066 \cdot 10^{-8}$
A_0	$1.083884 \cdot 10^{-3}$	b	$5.789487 \cdot 10^{-6}$
B_0	9.886964·10 ⁻³	С	3.449836·10 ⁻²
C_{0}	$-1.138183 \cdot 10^{1}$	d	$2.042090 \cdot 10^{-6}$
D_0	$-3.464959 \cdot 10^3$	α	2.679133·10 ⁻⁸
E_0	$6.169326 \cdot 10^5$	γ	$5.469844 \cdot 10^{-7}$

^a The units used for the adjustment of parameters are MPa, K, and kg·m⁻³.

8.6.4. Discussion

The measured values of liquid density for 2-propanol have been represented with the BWR equation of state described in previous Paragraph 8.6.3 and a statistical analysis of the data representation is reported in the following.

In such a context the error deviation $\Delta \rho_i$ of the i^{-th} density point, the percentage average absolute deviation AAD %, the Bias %, and the percentage maximum absolute deviation MAD % with respect to a data base of NPT values are evaluated as in Appendix A.6.

The parameters of the BWR equation of state were regressed on the measured liquid density data. The values predicted by the same equation of state were compared with the corresponding ones of the available literature data in the range from 273 to 400 K and from atmospheric pressures up to 12 MPa. The residual errors against the measured data and the prediction accuracy with respect to the literature data are presented in Tab. 8.3 and shown graphically in Fig. 8.3. The AAD with respect to the 150 measured density data is 0.025 %, and it is well within the experimental uncertainty of the experimental data. The AAD with respect to the 428 points including the

measured and the literature data is about 0.1 %. A Bias value lower than 0.02 % shows a good balance of the present measurements with respect to all the available data for 2-propanol in the investigated range of temperature and pressure.

Table 8.3: Accuracy of the BWR	equation in the	representation	of the li	iquid den	sity data	for 2-
propanol.						

Ref.	NPT ^a	T Range	<i>P</i> Range	AAD	Bias	MAD
	D	(K)	(MPa)	(%)	(%)	(%)
this mont	150 P.		0109	0.025	0.000	0.059
	130	280.2-392.0	0.1-9.8	0.023	0.000	0.038
Ambrass et al [7]	12		0 4 10 7	0 (11	0 (11	0.690
Amorose et al. [/]	12	383.7 209.2.219.2	0.4-10.7	0.011	-0.011	0.080
Aminabnavi et al. [17]	2	298.2-318.2	0.1	0.040	0.040	0.004
Aminabnavi and Araiaguppi [18]	3	298.2-308.2	0.1	0.057	0.057	0.077
Aminabnavi and Gopalakrishna [19]	4	298.2-313.2	0.1	0.114	0.114	0.118
Boned et al. [8]	9	303.2-343.2	0.1-10.0	0.122	0.122	0.204
Contreras [20]	4	298.2-313.2	0.1	0.068	0.068	0.110
Costello and Bowden [21]	7	273.2-393.2	0.1	0.270	-0.234	0.767
Egorov et al. [22]	8	275.2-338.2	0.1	0.143	0.143	0.269
Golubev and Vagina [10]	38	292.2-377.7	0.1-10.5	0.276	0.263	0.497
Golubev et al. [11]	15	292.7-370.7	1.1-9.9	0.142	-0.058	0.315
Golubev et al. [12]	15	300.0-400.0	1.0-10.0	0.221	-0.168	0.481
Islam and Quadri [23]	6	298.2-323.2	0.1	0.128	-0.124	0.311
Khimenko et al. [24]	7	288.2-323.2	0.1	0.062	0.059	0.139
Khimenko et al. [25]	9	288.2-328.2	0.1	0.107	0.107	0.184
Krestov et al. [26]	4	283.2-328.2	0.1	0.192	0.007	0.357
Ku and Tu [27]	4	293.2-323.2	0.1	0.058	0.058	0.114
Kubota et al. [13]	4	283.2-348.2	0.1	0.124	-0.002	0.244
Lee and Lin [28]	3	303.2-323.2	0.1	0.053	0.021	0.072
Mato and Coca [29]	1	298.2	0.1	0.102	0.102	0.102
Moha-Ouchane et al. [9]	3	303.2-343.2	0.1	0.083	0.083	0.123
Nagata et al. [30]	1	298.2	0.1	0.128	0.128	0.128
Nikam et al. [31]	4	298.2-313.2	0.1	0.055	0.055	0.073
Oswal and Putta [32]	3	303.2-318.2	0.1	0.029	-0.002	0.041
Paez and Contreras [33]	5	293.2-323.2	0.1	0.085	0.077	0.140
Sakurai [34]	5	278.2-318.2	0.1	0.141	0.141	0.258
Sovili [35]	3	298.2-308.2	0.1	0.025	0.005	0.033
Tashima and Arai [36]	7	293.2-343.2	0.1	0.084	0.077	0.153
The tal $[37]$	4	293 2-313 2	0.1	0.095	0.095	0.140
Wei and Rowley [38]	1	298.2	0.1	0.179	0.179	0.179
Yaginuma et al [15]	11	313.2	1 0-9 8	0.111	0 1 1 1	0 149
Zuniga-Moreno and Galicia-Luna [16]	73	313.2-362.8	0.5-12.0	0.181	-0.180	0.310
	428	273.2-400.0	0.1-12.0	0.126	-0.017	0.767

^a NPT: number of experimental points.



Figure 8.3: Percentage error of the BWR equation of state in the representation of the liquid density data of 2-propanol.

8.7. Experimental results for the propylene + 2-propanol system

8.7.1. Introduction

The literature presents a number of experimental works about the propylene + 2-propanol mixture which in particular are: vapor-liquid equilibria at constant temperature in a range from 333 to 373 K in Zabaloy et al. [41]; vapor pressure for diluted 2-propanol mixtures from 293 to 333 K in Guzechak et al. [42]; bubble pressures at 298 K and excess enthalpies at 333 K and 3.1 MPa in Horstmann et al. [43].

The VTD was used to get density and bubble pressure measurements; the obtained liquid density and bubble pressure values have been correlated using two multilayer feedforward neural network (MLFN) functions.

8.7.2. Experimental results: liquid densities

The liquid density measurements for the propylene (1) + 2-propanol (2) mixture have been carried out at 300, 325 and 350 K from 10 MPa down to bubble pressures for the $x_1 = 0.20, 0.52$ and 0.65 molar fractions. The measured (P, ρ, T) values are reported in Tab. 8.4.

Р	ρ	Р	ρ	Р	ρ
(MPa)	$(kg \cdot m^{-3})$	(MPa)	$(kg \cdot m^{-3})$	(MPa)	$(kg \cdot m^{-3})$
		$x_1 = 0$	0.2011		
T = 30	00.14 K	T = 32	5.09 K	<i>T</i> = 35	0.18 <i>K</i>
0.5294	731.63	0.8109	703.07	1.6395	677.13
1.0513	732.17	1.2189	703.59	2.0700	677.93
1.4836	732.72	1.6087	704.14	2.4462	678.64
1.9544	733.24	2.0018	704.70	2.9243	679.50
2.3840	733.72	2.3837	705.30	3.2714	680.17
2.7986	734.18	2.8276	705.86	3.6753	680.86
3.2731	734.68	3.1592	706.38	4.0584	681.60
3.7402	735.18	3.7079	707.07	4.4468	682.32
4.1863	735.68	4.1236	707.68	4.7913	682.93
4.7286	736.23	4.5285	708.19	5.1719	683.60
5.2356	736.78	4.9253	708.73	5.5574	684.26
5.7673	737.30	5.3707	709.32	6.0020	684.96
6.2747	737.83	5.8835	709.98	6.4302	685.69
6.8325	738.41	6.3362	710.58	7.0712	686.73
7.2915	738.89	6.7884	711.17	7.5705	687.62
7.8118	739.42	7.3466	711.90	7.9441	688.25
8.2966	739.90	7.8793	712.57	8.3868	688.92
8.8103	740.41	8.3925	713.18	8.8268	689.60
9.3377	740.91	8.9852	713.89	9.2790	690.38
9.8864	741.45	9.5877	714.65	9.7796	691.08

Table 8.4: Experimental liquid density data for the propylene (1) + 2-propanol (2) mixture.

р	ρ	р	ρ	Р	ρ	
(MPa)	$(kg \cdot m^{-3})$	(MPa)	$(kg \cdot m^{-3})$	(MPa)	$(kg \cdot m^{-3})$	
(1011 u)	(15 11)	r -($\frac{(k_{\rm g}{\rm m})}{15201}$	(1011 u)	(kg m)	
	0 11 77	$x_1 = 0$	5.5201	T 25	0 1 0 K	
T = 30	0.11 K	T = 32	5.05 K	T = 350	0.12 K	
0.9667	644.49	1.6131	613.41	2.3323	576.59	
1.3733	645.21	1.9777	614.26	2.7314	577.92	
1.8356	645.98	2.3590	615.15	2.9924	578.85	
2.3409	646.83	2.7172	615.98	3.2180	579.68	
2.8124	647.62	3.1678	616.93	3.5061	580.58	
3.3301	648.49	3.5061	617.74	3.7656	581.46	
3.8175	649.27	3.8888	618.59	4.2255	582.95	
4.3861	650.18	4.3216	619.52	4.5506	583.87	
4.8737	650.95	4.6767	620.29	4.8244	584.73	
5.3752	651.72	5.0614	621.12	5.1037	585.64	
5.8888	652.52	5.4718	621.94	5.3993	586.54	
6.4420	653.35	5.8801	622.78	5.7155	587.44	
6.9428	654.09	6.2936	623.65	5.9995	588.29	
7.4982	654.90	6.7043	624.42	6.3039	589.18	
8.1047	655.77	7.1717	625.34	6.6328	590.10	
8.6718	656.58	7.5974	626.18	6.9755	591.05	
9.2267	657.35	8.0375	627.02	7.2800	591.94	
9.7870	658.16	8.5565	628.02	7.6413	592.87	
		9.0781	628.97	7.9635	593.76	
		9.6313	629.98	8.3120	594.68	
				8.7624	595.82	
				9.2110	596.88	
				9.6229	597.92	
		$x_{1} = 0$).6478			
T = 30	0 12 K	T = 32	5 12 K	T = 350.18 K		
1.0685	608.06	1 7475	573.20	2 6800	531.01	
1.0005	608.00	2 1518	574.52	2.0070	533.02	
1.4805	600.48	2.1318	575.84	3.1203	535.62	
1.7400	610 10	2.0075	577.00	3.0802	526 74	
2.1238	611.17	3.0221	578.16	3.9143	527.07	
2.0200	011.17	3.4227	570.22	4.2052	520.15	
2.9808	011.92	3.8203	579.25	4.4840	539.15	
3.4933	012.83	4.2890	501.40	4.7383	540.50	
5.8290	614.26	4.0823	J01.40 592.52	5.0254	541.05	
4.1933	614.20	5.0940	582.55	5.5212	542.00	
4.5428	014.93	5.5248	583.59	5.0140	545.95	
4.9054	615.01	5.9722	584.68	5.9389	545.10	
5.2037	616.27	6.4310	585.75	6.2684	540.55	
5.6341	616.94	6.9233	586.94	6.6221	547.76	
6.0113	61/.61	7.4335	588.03	6.9/86	548.98	
6.3953	618.28	7.9350	589.22	7.3620	550.27	
6./886	618.96	8.4599	590.39	1.1365	551.56	
/.1654	619.61	9.0240	591.62	8.1262	552.91	
7.5581	620.28	9.5585	592.78	8.5255	554.11	
7.9601	620.96			8.9798	555.58	
8.3772	621.66			9.4880	557.04	
8.7855	622.34			9.9898	558.59	
9.2342	623.05					
9.6821	623.79					

In Fig. 8.4 the measured data are shown together with liquid density values of the pure propylene and 2-propanol at the same temperatures of the mixture measurements and for pressures from the pure fluids bubble points up to 10 MPa. Values for propylene were generated by the DEoS in Ref. 1 and those for 2-propanol were generated by the BWR equation presented in the former Paragraph 8.6.3.

Temperature dependence at constant composition of the propylene (1) + 2-propanol (2) mixture is shown in Fig. 8.5a, while composition dependence at constant temperature is shown in Fig. 8.5b.



Figure 8.4: Liquid density measurements for the propylene (1) + 2-propanol (2) mixture.



Figure 8.5: Propylene (1) + 2-propanol (2) mixture: a) Temperature dependence of the liquid density at constant composition ($x_1 = 0.20$); b) Composition dependence of the liquid density at constant temperature (T = 300 K).

8.7.3. Experimental results: phase equilibrium

The VTD allows to obtain density measurements and furthermore, through a data reduction of such values, bubble pressures can be also evaluated as discussed in Ref. 3. In this way bubble pressures for the propylene (1) + 2-propanol (2) mixture have been obtained at 300, 325 and 350 K for $x_1 = 0.20$, 0.52 and 0.65 molar fractions. The values are reported in Tab. 8.5 while the Fig. 8.6 shows the obtained values in comparison to the available literature data in the same temperature range [41-43].

Table 8.5: Comparison of pressures and densities at bubble point conditions between those determined by the VTD (P and ρ) and those by the intersection of the compressed liquid density MLFN model and the bubble pressure MLFN model (P' and ρ').

Т (К)	<i>x</i> ₁	P (MPa)	P' (MPa)	ΔP %	ho (kg·m ⁻³)	ho' (kg·m ⁻³)	Δho %
300.14	0.2011	0.5224	0.4956	-5.125	731.63	731.23	-0.055
300.11	0.5201	0.9192	0.9199	0.076	644.42	644.63	0.032
300.12	0.6478	1.0297	1.0021	-2.677	607.97	607.84	-0.022
325.09	0.2011	0.7850	0.8604	9.606	703.01	703.25	0.034
325.05	0.5201	1.5583	1.5658	0.481	613.29	613.39	0.017
325.13	0.6478	1.7095	1.7394	1.748	573.24	573.50	0.045
350.18	0.2011	1.2620	1.2840	1.743	676.38	676.63	0.037
350.12	0.5201	2.1521	2.3275	8.149	575.99	576.57	0.102
350.18	0.6478	2.6200	2.6342	0.542	530.66	530.79	0.025



Figure 8.6: Bubble pressure data for the propylene (1) + 2-propanol (2) mixture.

8.7.4. Discussion

Multilayer feedforward neural network (MLFN) functional forms (see Paragraph 2.2.2) have been used to correlate liquid density and bubble pressure experimental values for the propylene (1) + 2-propanol mixture. An arctangent function normalized in the range [0,1] is assumed as the transfer function. A statistical analysis of the data representation is reported in the following.

The measured liquid density values, together with the liquid density values generated for the propylene and for the 2-propanol, at the same temperatures of the mixture measurements and for pressures ranging from the pure fluid bubble points up to 10 MPa, were correlated with a MLFN. The parameters used for the correlation of the liquid density data are presented in Tab. 8.6.

Table 8.6: Parameters of the feedforward neural network used for the correlation of the liquid density data for the mixture propylene (1) + 2-propanol (2).

$\beta = 0.5$				$V_{\min,1} = T_{\min} = 250$			$V_{\max,1} = T_{\max} = 400$			
I = 4				V	$_{\min,2} = P_{\min} = 0$		$V_{\rm max 2} = P_{\rm max} = 12$			
		J = 12		V_{\cdot}	$x_{\min 2} = x_{\min} = 0$		<i>V</i>	$x_{2} = x_{max} = 1$		
		V 1		1 117	250		1112			
		$\mathbf{V} = \mathbf{I}$		W _{mi}	$_{n,1} = \rho_{\min} = 350$		$W_{\rm max,}$	$_{1} = \rho_{\text{max}} = 800$		
i	j	W_{ij}	i	j	W_{ij}	j	k	W_{jk}		
1	1	$9.010170 \cdot 10^1$	3	1	$1.119710 \cdot 10^2$	1	1	$-4.617640 \cdot 10^{1}$		
1	2	-7.888430	3	2	-9.451570	2	1	$1.045780 \cdot 10^2$		
1	3	4.093740	3	3	$4.741180 \cdot 10^{1}$	3	1	$2.705210 \cdot 10^{1}$		
1	4	$3.175850 \cdot 10^{1}$	3	4	$3.745950 \cdot 10^{1}$	4	1	$-3.218450 \cdot 10^{1}$		
1	5	5.408060	3	5	4.226020	5	1	$4.131650 \cdot 10^{1}$		
1	6	$1.160290 \cdot 10^{1}$	3	6	$6.257430 \cdot 10^{1}$	6	1	1.148660		
1	7	-1.719460	3	7	$-6.859890 \cdot 10^{1}$	7	1	$7.869950 \cdot 10^{1}$		
1	8	$2.384800 \cdot 10^{1}$	3	8	$3.126750 \cdot 10^{1}$	8	1	$7.177710 \cdot 10^{1}$		
1	9	$-1.635840 \cdot 10^2$	3	9	$-5.275310 \cdot 10^{1}$	9	1	$-1.563460 \cdot 10^2$		
1	10	$7.722330 \cdot 10^2$	3	10	$2.476070 \cdot 10^2$	10	1	$-7.446350 \cdot 10^2$		
1	11	9.913330	3	11	8.709160	11	1	$-8.324710 \cdot 10^{1}$		
1	12	$2.627740 \cdot 10^{-1}$	3	12	$-9.278200 \cdot 10^{1}$	12	1	$-7.044190 \cdot 10^{1}$		
2	1	$-3.232040 \cdot 10^{1}$	4	1	$-1.615050 \cdot 10^2$	13	1	$3.140790 \cdot 10^{1}$		
2	2	$-6.101320 \cdot 10^{-2}$	4	2	$2.656600 \cdot 10^{1}$					
2	3	9.660710·10 ⁻⁴	4	3	$1.236170 \cdot 10^2$					
2	4	$-4.646080 \cdot 10^{1}$	4	4	$6.156810 \cdot 10^{1}$					
2	5	$-5.914600 \cdot 10^{-1}$	4	5	$-4.362300 \cdot 10^{-1}$					
2	6	-7.413220	4	6	$-6.507460 \cdot 10^{1}$					
2	7	1.424330	4	7	-1.663850					
2	8	$2.367740 \cdot 10^{1}$	4	8	$3.043150 \cdot 10^{1}$					
2	9	$9.005100 \cdot 10^{1}$	4	9	$1.339450 \cdot 10^2$					
2	10	$-4.175130 \cdot 10^2$	4	10	$-6.333350 \cdot 10^2$					
2	11	$-7.045390 \cdot 10^{-1}$	4	11	-9.259080·10 ⁻¹					
2	12	1.699010	4	12	-2.553360					

Residual errors are presented in Tab. 8.7 and shown graphically in Fig. 8.7. The simultaneous representation of mixture and pure fluid data shows a good coherence among the measured liquid density values for the mixture and independent density values for the pure fluids.

Table 8.7: Accuracy of the feedforward neural network model in the representation of the liquid density data of the propylene (1) + 2-propanol (2) mixture.

System	Ref.	NPT ^a	T Range (K)	P Range (MPa)	x ₁ Range	AAD (%)	Bias (%)	MAD (%)
binary mixture	this work	186	300.0-350.2	0.0-10.1	0.20-0.65	0.017	0.006	0.063
2-propanol	this work ^b	123	300.0-350.0	0.0-10.0	0.00	0.019	0.008	0.035
propylene	Angus <i>et al</i> . [1]	98	300.0-350.0	1.2-10.1	1.00	0.028	0.014	0.099
		407	300.0-350.2	0.0-10.1	0.00-1.00	0.020	0.009	0.099

^a NPT: number of experimental points.

^b values generated by the BWR equation presented in the former paragraph 8.6.3.



Figure 8.7: Percentage error of the feedforward neural network model in the representation of the liquid density data of the propylene (1) + 2-propanol (2) mixture; C3 = propylene, IPA = 2-propanol.

Using the obtained MLFN function excess molar volumes have been calculated and their composition dependence has been shown, varying pressure at constant temperature, in Fig. 8.8a, and, varying temperature at constant pressure, in Fig. 8.8b. In the same figures also the excess molar volumes calculated with the Peng-Robinson EoS including the Wong-Sandler mixing rules as obtained for this system in Paragraph 7.6 have been shown for comparison. A very good agreement between experimental excess volume values and values predicted by the MLFN can be noted in Fig. 8.8. This result comes from the very low residual error (AAD% = 0.0201) in the representation of the pure fluids and mixture density values with the MLFN. On the other hand the Peng-Robinson EoS represents the excess molar volumes only in a qualitative way, confirming that such EoS is not enough precise in the representation of compressed liquid densities, especially for systems involving associating fluids.



Figure 8.8: Excess molar volumes for the propylene (1) + 2-propanol (2) mixture: a) pressure dependence at constant temperature; b) temperature dependence at constant pressure.
The coefficients of a second MLFN have been regressed on the literature bubble pressure values [41,43] and on the saturation pressure of the pure propylene [1] and pure 2-propanol [44]. The parameters used for the correlation of the bubble pressure data are presented in Tab. 8.8. The percentage errors of the obtained MLFN with respect to the measured bubble pressures are presented in Tab. 8.9 together with the errors with respect to the literature data available in the same range of temperature. The AAD % with respect to the measured values is greater than the AAD % with respect to the literature data on which the weighting factors of the MLFN have been regressed. The AAD of the measured bubble pressures is about 3.35% while a value significantly lower is found for the literature data of Refs. 41 and 43. At the same time it can be noted that literature data [42] are not consistent with all the other bubble pressure data. A comparison between the MLFN predictions and the measured bubble pressures is shown in Fig. 8.6. In the same figure the bubble pressure predicted by the MLFN are compared with the Peng-Robinson EoS using Wong-Sandler mixing rules, which parameters were presented in Paragraph 7.6.

Table 8.8: Parameters of the feedforward neural network used for the correlation of the bubble pressure data for the mixture propylene (1) + 2-propanol (2).

		$\beta = 0.5$		$V_{\min,1} = T_{\min} = 250$			$V_{\max,1} = T_{\max} = 400$		
		<i>I</i> = 3		$V_{\min,3} = x_{\min} = 0$			$V_{\max,3} = x_{\max} = 1$		
		J = 10		$W_{\min 1} = P_{\min}^{bub} = 0$			$W_{\text{max},1} = P_{\text{max}}^{bub} = 12$		
<i>K</i> = 1					,			,	
i	j	W_{ij}	i	j	W_{ij}	j	k	W_{jk}	
1	1	-2.984260	2	6	-8.020910	1	1	$-4.286830 \cdot 10^{1}$	
1	2	-2.368580	2	7	$-1.477240 \cdot 10^{1}$	2	1	$1.003870 \cdot 10^{1}$	
1	3	$-5.797060 \cdot 10^{-2}$	2	8	1.219770	3	1	$-1.594220 \cdot 10^{1}$	
1	4	-7.176010	2	9	$6.848890 \cdot 10^{1}$	4	1	$1.780930 \cdot 10^{1}$	
1	5	8.495830	2	10	2.736060	5	1	$-3.840020 \cdot 10^{1}$	
1	6	5.252270	3	1	2.109340	6	1	6.209550	
1	7	-6.099100	3	2	5.568850	7	1	$-3.350460 \cdot 10^{1}$	
1	8	-1.445960	3	3	$9.371590 \cdot 10^{-1}$	8	1	$5.234110 \cdot 10^{1}$	
1	9	$-3.605730 \cdot 10^{1}$	3	4	4.846480	9	1	$5.640040 \cdot 10^{-1}$	
1	10	9.521860	3	5	-4.758900	10	1	$2.152770 \cdot 10^{1}$	
2	1	$-1.685540 \cdot 10^{-1}$	3	6	-4.523590	11	1	5.090110	
2	2	-5.177630	3	7	4.351610				
2	3	$-3.103680 \cdot 10^{1}$	3	8	$5.681530 \cdot 10^{-2}$				
2	4	-4.547720	3	9	$-5.409480 \cdot 10^{1}$				
2	5	$1.348860 \cdot 10^{1}$	3	10	-4.652040				

Ref	NPT	T Range	P Range	r. Range	AAD	Bias	MAD
101.	111 1	(K)	(MPa)	M ₁ Runge	(%)	(%)	(%)
this work	9	300.1-350.2	0.5-2.6	0.20-0.65	3.350	1.616	9.606
Horstmann et al. [43]	17	298.1	0.2-1.1	0.08-1.00	0.506	0.191	2.594
Zabaloy et al. [41]	17	333.1-353.1	0.6-3.4	0.08-0.94	0.794	-0.037	2.223
Guzechak et al. [42]	12	293.2-333.2	0.2-0.7	0.02-0.15	50.999	-50.999	59.794
	55	300.1-353.1	0.2-3.4	0.02-1.00	12.077	-10.815	59.794

Table 8.9: Accuracy of the feedforward neural network model in the representation of the bubble pressure data of the propylene (1) + 2-propanol (2) mixture.

From the intersection of the MLFN function regressed on single phase liquid densities and the MLFN function regressed on bubble pressures it is possible to obtain an accurate representation of the saturated liquid density surface of the mixture as a function of temperature and composition. The Fig. 8.9 shows several isothermal sections of such surface pointing out the regular trends in the saturated liquid density representation by the developed model.





Using the same approach the saturated liquid densities at the present experimental temperature and composition values have been calculated and the results are reported in Tab. 8.5 as ρ' . In the same Table the bubble pressures calculated by the MLFN model P' are also reported for comparison. The percentage relative deviation among the two evaluation methods of the saturated liquid density is quite close to the experimental uncertainty of the density measurements. The percentage deviations among the bubble pressures determined from the experimental data through the graphical procedure and the corresponding ones generated by the MLFN model are also reported in the Table. Reference is also made to former Tab. 8.9 and its relative comments.

8.8. Experimental results for the 2-propanol + water system

8.8.1. Introduction

The literature reports a number of experimental works about measurements of the liquid density and vapor liquid equilibria of the 2-propanol + water mixture with which the original data presented in the following will be compared. In particular, the sources in the range of interest for the density are: Grigiante et al. [45], which reports density values from 298 to 308 K at atmospheric pressure from $x_1 = 0.25$ to $x_1 = 0.74$; Egorov *et al.* [22], which reports density values from 275 to 338 K at atmospheric pressure in the whole composition range; Hynčica et al. [46], which reports density values from 298 to 573 K and from 0.4 to 30.3 MPa for dilute aqueous solutions; Origlia-Luster and Woolley [47], which reports density values from 278 to 368 K at 0.4 MPa for dilute aqueous solutions; Arce et al. [48], which reports density values at 298 K and atmospheric pressure from $x_1 = 0.07$ to $x_1 = 0.95$; Boned *et al.* [8], which reports density values from 303 to 343 K and from 0.1 to 65.0 MPa in the whole composition range; Schulte et al. [49], which reports density values from 301 to 521 K and from 0.1 to 28.0 MPa for dilute aqueous solutions; Rauf et al. [50], which reports density values from 298 to 308 K at atmospheric pressure from $x_1 = 0.03$ to $x_1 = 0.85$; Sakurai [34], which reports density values from 278 to 318 K at atmospheric pressure in the whole composition range; Kubota et al. [13], which reports density values from 283 to 348 K, from 0.1 to 190.9 MPa from $x_1 = 0.06$ to $x_1 = 0.75$; Høiland [51], which reports density values from 278 to 298 K at atmospheric pressure for dilute aqueous solutions; Roux et al. [52], which reports density values at 283 and 298 K at atmospheric pressure from $x_1 = 0.01$ to $x_1 = 0.91$; Friedman and Scheraga [53], which reports density values from 274 to 323 K at atmospheric pressure for dilute aqueous solutions.

For the bubble pressure the sources in the range of interest are: Arce *et al.* [54], which reports bubble pressure values from 353 to 372 K; Khalfaoui *et al.* [55], which reports bubble pressure

values from 352 to 373 K; Marzal *et al.* [56], which reports bubble pressure values from 325 to 373 K; Tsuji *et al.* [57], which reports bubble pressure values at 298 K; Gironi and Lamberti [58], which reports bubble pressure values from 353 to 373 K; Wu *et al.* [59], which reports bubble pressure values at 353 K; Sada and Morisue [60], which reports bubble pressure values from 308 to 359 K; Kato *et al.* [61], which reports bubble pressure values from 353 to 374 K; Wilson and Simons [63], which reports bubble pressure values from 309 to 418 K; Brunjes and Bogart [64], which reports bubble pressure values from 353 to 372 K.

The VTD was used to obtain liquid density values. The obtained values have been correlated using a multilayer feedforward neural network (MLFN) function. The produced model has been used to study the composition dependence of the excess volumes at constant temperature and pressure.

A bubble pressure model combining a MLFN and saturated pressure equations for the pure fluids was obtained correlating the literature bubble pressures for the 2-propanol (1) + water (2) mixture in the 298 to 374 K temperature range.

The saturated liquid density surface in the whole composition range and for temperatures ranging from 287 to 350 K has been obtained as intersection of the model regressed on single-phase liquid densities and the model regressed on bubble pressures.

8.8.2. Experimental results

The liquid density measurements for the 2-propanol (1) + water (2) mixture have been carried out at 300, 325 and 350 K from 10 MPa down to about atmospheric pressure for the $x_1 = 0.25$, 0.49 and 0.73 molar fractions. The measured (*P*, ρ , *T*, *x*) values are reported in Tab. 8.10. In Fig. 8.10 the measured data are shown together with liquid density values of the pure water and 2-propanol at the same temperatures of the mixture measurements and for pressures from the pure fluids bubble points up to 10 MPa. Values for water were generated by the DEoS in Ref. 2 and those for 2propanol were generated by the BWR equation presented in the former Paragraph 8.6.3.

The temperature dependence at constant composition of the 2-propanol (1) + water (2) mixture is shown in Fig. 8.11a, while the composition dependence at constant temperature is shown in Fig. 8.11b. In the Figs. 8.10 and 8.11 the dotted lines represent saturated liquid densities ρ^{sl} obtained through the models presented in the following Paragraph 8.8.3.

P	ρ	Р	ρ	Р	ρ
(MPa)	$(kg \cdot m^{-3})$	(MPa)	$(\text{kg}\cdot\text{m}^{-3})$	(MPa)	$(kg \cdot m^{-3})$
	(6)	,	$x_{1} = 0.2483$		
T = 30	00 08 K	T = 32	25 10 K	T –	350 18 K
$\frac{I - 30}{0.1462}$	005 50	$\frac{1-32}{0.0726}$	074.12	<u> </u>	• JJU.10 K
0.1462	895.50	0.0726	874.13	0.2200	850.53
0.3813	895.67	0.4103	8/4.3/	0.5110	850.54
0.7649	895.89	0.9621	8/4./1	0.9388	850.91
1.1011	896.11	1.3430	875.01	1.3697	851.29
1.5568	896.32	1.8595	875.37	2.0669	851.75
1.9219	896.56	2.3326	875.60	2.3810	852.09
2.1815	896.86	2.8264	875.91	2.7181	852.39
2.6101	897.09	3.3194	876.24	3.1077	852.73
3.0805	897.32	3.7763	876.52	3.4648	853.04
3.5223	897.58	4.2367	876.83	3.9576	853.37
4.0826	897.87	4.5987	877.08	4.3460	853.71
4.6633	898.17	5.0893	877.36	4.7811	854.06
5.1513	898.42	5.5642	877.68	5.2678	854.49
5.5625	898.65	5.9542	877.93	5.7438	854.83
5.9805	898.85	6.3943	878.21	6.1964	855.20
6.4143	899.11	6.8085	878.48	6.7342	855.63
6.7548	899.33	7.2880	878.80	7.3749	856.07
7.2468	899.56	7.7827	879.08	7.9990	856.54
7.6367	899.78	8.0791	879.34	8.6303	857.02
8.1316	900.04	8.4389	879.63	9.2983	857.54
8.6628	900.28	8.8285	879.87		
9.0873	900.54	9.3589	880.18		
9.5623	900.79				
		,	$x_1 = 0.4939$		
T = 30	00.10 K	T = 32	25.09 К	T =	350.15 K
0.2334	838.18	0.0654	814.96	0.1617	789.80
0.5030	838.33	0.3030	815.20	0.3878	790.10
0.9466	838.71	0.6453	815.47	0.6952	790.45
1.5453	839.06	1.0048	815.80	1.0208	790.78
1.9022	839.36	1.3919	816.13	1.4001	791.25
2.3035	839.65	1.7881	816.48	1.7958	791.61
2.7246	839.96	2.2420	816.83	2.1471	791.96
3.1365	840.26	2.8811	817.33	2.4979	792.31
3.5679	840.56	3.9046	818.19	2.8927	792.74
3.9958	840.87	4.2421	818.51	3.2779	793.12
4.4362	841.18	4.7844	818.94	3.6115	793.50
4.8355	841.48	5.1168	819.26	4.0873	794.01
5.2620	841.77	5.5073	819.61	4.6067	794.49
5.6998	842.07	5.9122	819.93	4.9552	794.83
6.1610	842.39	6.3221	820.28	5.3760	795.26
6.5884	842.68	6.7730	820.60	5.8376	795.69
7.0530	843.00	7.2145	820.97	6.2964	796.18
7,4379	843.28	7.6133	821.31	6.8866	796.77
7.8620	843.57	8.0805	821.70	7.4008	797.28
8.2485	843.86	8.6031	822.11	7.9356	797.73
8.7044	844.15	9.1973	822.51	8.4003	798.24
9.2606	844.49	9.5614	822.86	9.0006	798.68
0.0000	845 04			9 5212	799.18

Table 8.10: Experimental liquid density data for the 2-propanol (1) + water (2) mixture.

Р	ρ	Р	ρ	Р	ρ		
(MPa)	$(\text{kg} \cdot \text{m}^{-3})$	(MPa)	$(kg \cdot m^{-3})$	(MPa)	$(kg \cdot m^{-3})$		
		,	$x_1 = 0.7258$				
T = 30	00.08 K	T = 32	25.13 K	T = 2	<i>T</i> = 351.14 K		
0.0882	805.57	0.0830	782.69	0.2415	757.15		
0.3030	805.78	0.2681	782.93	0.4445	757.34		
0.5651	806.00	0.5283	783.18	0.8224	757.80		
1.1262	806.42	0.8737	783.50	1.2716	758.33		
1.7025	806.92	1.2986	783.92	1.6739	758.75		
2.2398	807.33	1.7092	784.33	2.0705	759.26		
2.7227	807.73	2.2007	784.79	2.4611	759.66		
3.1960	808.11	2.6521	785.22	2.8634	760.12		
3.7156	808.53	3.1017	785.67	3.2809	760.61		
4.2315	808.93	3.5506	786.11	4.2525	761.65		
4.5871	809.31	4.0683	786.61	4.6264	762.11		
5.3146	809.85	4.5794	787.07	5.0759	762.61		
5.7932	810.24	5.0217	787.49	5.5585	763.09		
6.3012	810.63	5.4961	787.93	5.9762	763.59		
6.7839	811.02	5.9723	788.38	6.4398	764.08		
7.2976	811.43	6.4508	788.82	6.8822	764.57		
7.8044	811.81	6.9030	789.24	7.3486	765.10		
8.3422	812.23	7.3920	789.70	7.8093	765.60		
8.8180	812.60	7.8611	790.11	8.2540	766.09		
9.3301	813.00	8.3228	790.52	8.7202	766.63		
9.9189	813.45	8.8139	790.98	9.2213	767.15		
		9.2874	791.41	9.7148	767.73		
		9.8297	791.93	10.2395	768.31		



Figure 8.10: Liquid density measurements for the 2-propanol (1) + water (2) mixture.



Figure 8.11: Liquid density measurements for the 2-propanol (1) + water (2) mixture. a) temperature dependence at constant composition; b) composition dependence at constant temperature.

8.8.3. Discussion

Multilayer feedforward neural network (MLFN) functional forms have been used to correlate experimental values for the compressed liquid density and literature values for the bubble pressure. The general architecture of a MLFN was illustrated in Paragraph 2.2.2.

Compressed liquid density as function of temperature, pressure and composition has been represented using a simple MLFN model with a logistic function as transfer function:

$$\rho\left(T, P, x_{1}\right) = W_{1} \tag{8.3}$$

 W_1 represents the density, while V_i , for i = 1, 2, 3, are temperature, pressure and 2-propanol molar fraction x_1 , respectively.

Bubble pressure, P^{bub} , as function of temperature and composition has been represented as:

$$P^{bub}\left(T,x_{1}\right) = x_{1}P_{1}^{s} + (1-x_{1})P_{2}^{s} + x_{1}(1-x_{1})\cdot W_{1}$$

$$(8.4)$$

where P_1^s and P_2^s are the 2-propanol and water saturated pressure as function of temperature calculated by the saturated pressure equations in Ref. 44 and in Ref. 2, respectively. In Eq. (8.4) W_1 is the denormalized output of a simple MLFN model in which V_i , for i = 1, 2, are temperature and composition x_1 , respectively. An arctangent function normalized in the range [0,1] is assumed as the transfer function.

The measured liquid density values, together with the liquid density values generated for the pure 2-propanol and for the pure water, at the same temperatures of the mixture measurements and for pressures ranging from the pure fluid bubble points up to 10 MPa, were used as training data to regress the parameters of a MLFN density model, Eq. (8.3). These parameters are presented in Tab. 8.11.

The obtained density model has been validated against literature data in the same range of temperature and pressure.

Tab. 8.12 presents the accuracy of the density model with respect to the training data and the validation data. The Fig. 8.12 shows graphically the errors presented in Tab. 8.12. A very good representation is achieved for the 443 points used as training data (AAD % = 0.009; Bias % = 0.004). The density model regressed on the training data represents the whole available density data (1137 points) in the considered range ($x_1 = 0.00 - 1.00$; T = 288 - 350 K; $P \le 10.24$ MPa) with an error (AAD % < 0.05) inside the experimental uncertainty of the density measurements.

Using the obtained density model, the excess molar volumes have been calculated and their composition dependence has been shown in Fig. 8.13a, varying pressure at constant temperature, and in Fig. 8.13b, varying temperature at constant pressure. A very good agreement between experimental excess volume values and values predicted by the MLFN can be noted in Fig. 8.13. This result comes from the very low residual error (AAD % = 0.009) in the representation of the pure fluids and of the measured mixture density values with the MLFN model. The Fig. 8.13 shows also a comparison with the excess volumes measured by Sakurai [34], Egorov et al. [22], and Boned et al. [8]; a good agreement between the excess molar volumes predicted by the MLFN density model and the cited experimental data can be noted.

		$\beta = 0.5$		$V_{\min,1} = T_{\min} = 250$			$V_{\max,1} = T_{\max} = 600$		
		I = 4		V_{m}	$_{nin,2} = P_{min} = 0$		$V_{\max,2} = P_{\max} = 200$		
	J = 6			$V_{\min,3} = x_{\min} = 0$			$V_{ m max}$	$x_{,3} = x_{\max} = 1$	
K = 1				$W_{ m mi}$	$_{n,1} = \rho_{\min} = 650$		$W_{\rm max,1}$	$= \rho_{\rm max} = 1050$	
i	j	W _{ij}	i	j	W_{ij}	j	k	W _{jk}	
1	1	-9.31363·10 ⁻¹	3	1	-7.46161·10 ⁻¹	1	1	$1.40240 \cdot 10^{1}$	
1	2	1.90004	3	2	8.78966	2	1	$-1.04466 \cdot 10^{1}$	
1	3	-2.65487	3	3	5.07904	3	1	-3.93483	
1	4	-7.11414	3	4	-1.29070	4	1	8.77578	
1	5	$4.42480 \cdot 10^{-1}$	3	5	2.27958	5	1	2.06857	
1	6	$-1.37567 \cdot 10^{1}$	3	6	$-1.41375 \cdot 10^{1}$	6	1	$-1.23929 \cdot 10^{1}$	
2	1	$2.02051 \cdot 10^{-1}$	4	1	$-3.92838 \cdot 10^{-1}$	7	1	$9.84349 \cdot 10^{-1}$	
2	2	-1.45314	4	2	1.95147				
2	3	2.17204	4	3	2.13417				
2	4	5.91087	4	4	6.00562				
2	5	$9.04961 \cdot 10^{-1}$	4	5	-2.26466				
2	6	-3.85432	4	6	-1.12442				

Table 8.11: Parameters of the feedforward neural network used in Eq. (8.3) for the correlation of the liquid density data of the 2-propanol (1) + water (2) mixture.

Table 8.12: Accuracy of the feedforward neural network model, Eq. (8.3), in the representation of the liquid density data of the 2-propanol (1) + water (2) mixture.

System	Ref.	NPT ^a	T Range	P Range	x ₁ Range	AAD	Bias	MAD
			(K) Training data	(MPa)	_	(%)	(%)	(%)
			Training data					
binary mixture	this work	200	300-350	0.07-10.24	0.25-0.73	0.003	0.000	0.012
2-propanol	this work ^b	123	300-350	0.01-10.00	1.00	0.016	0.004	0.030
water	Wagner and Pruß [2]	120	300-350	0.00-9.75	0.00	0.011	0.009	0.035
		443	300-350	0.00-10.24	0.00-1.00	0.009	0.004	0.035
			Validation data					
binary mixture	Grigiante et al. [45]	15	288-308	0.10	0.25-0.74	0.011	-0.006	0.026
binary mixture	Egorov et al. [22]	70	288-338	0.10	0.00-1.00	0.066	0.010	0.283
binary mixture	Hynčica et al. [46]	55	298-338	0.39-0.50	0.00-0.01	0.058	-0.058	0.150
binary mixture	Origlia-Luster and Woolley [47]	72	288-358	0.35	0.00-0.02	0.052	-0.048	0.208
binary mixture	Arce <i>et al.</i> [48]	19	298	0.10	0.07-0.95	0.035	0.017	0.120
binary mixture	Boned et al. [8]	81	303-343	0.10-10.00	0.10-0.90	0.071	-0.060	0.219
binary mixture	Schulte et al. [49]	9	302	0.10	0.00-0.02	0.086	-0.086	0.159
binary mixture	Rauf <i>et al.</i> [50]	27	298-308	0.10	0.03-0.85	0.279	0.242	0.687
binary mixture	Sakurai [34]	292	288-318	0.10	0.00-1.00	0.063	-0.028	0.274
binary mixture	Kubota <i>et al</i> . [13]	11	298-348	0.10	0.06-0.75	0.050	0.010	0.173
binary mixture	Høiland [51]	14	293-298	0.10	0.00-0.01	0.050	-0.033	0.115
binary mixture	Roux <i>et al</i> . [52]	14	298	0.10	0.01-0.76	0.156	0.027	0.691
binary mixture	Friedman and Scheraga [53]	15	293-323	0.10	0.00-0.01	0.028	-0.026	0.058
		1137	288-350	0.00-10.24	0.00-1.00	0.046	-0.010	0.691

^a NPT: number of experimental points.

^b values generated by the BWR equation presented in the former paragraph 8.6.3.



Figure 8.12: Percentage deviation of the feedforward neural network model, Eq. (8.3), in the representation of the liquid density data of the 2-propanol (1) + water (2) mixture. a) training data; b) validation data.



Figure 8.13: Excess molar volumes for the 2-propanol (1) + water (2) mixture. a) pressure dependence at constant temperature; b) temperature dependence at constant pressure.

The coefficients of the MLFN involved in the bubble pressure model as function of temperature and composition, Eq. (8.4), have been regressed on the literature bubble pressure values and on the saturated pressure of the pure 2-propanol [44] and pure water [2]. The parameters used for the correlation of the bubble pressure data are presented in Tab. 8.13. The percentage errors of the bubble pressure model, Eq. (8.4), with respect to the bubble pressure data available from the literature in the temperature range from 298 to 374 K are presented in Tab. 8.14. The bubble pressure model represents the considered 421 points of the literature with AAD % < 1.3. The AAD % value is quite homogeneous for all the data sets involved in the regression of the MLFN coefficients, and the Bias % value of 0.058 shows that the model is well centered with respect to the whole data set. A comparison between the bubble pressure model and the literature data presented in Tab. 8.14 is shown in Fig. 8.14. In Fig. 8.14a the model of Eq. (8.4) has been compared with bubble temperature data. In such a figure lines were obtained inverting Eq. (8.4) to calculate the

bubble temperature as function of pressure and composition. In Fig. 8.14b the model of Eq. (8.4) has been compared with bubble pressure data.

Table 8.13: Parameters of the feedforward neural network involved in the bubble pressure model, Eq. (8.4), for the mixture 2-propanol (1) + water (2).

		$\beta = 0.5$		$V_{\min,1} = T_{\min} = 260$			$V_{\max,1} = T_{\max} = 400$		
		I = 3		$V_{\min,2} = x_{\min} = 0$			$V_{ m ma}$	$x_{x,2} = x_{max} = 1$	
	J = 8			$W_{\min,1} = P_{\min}^{bub} = 0$			$W_{\max 1} = P_{\max}^{bub} = 10$		
K = 1					, ,			, 	
i	j	W_{ij}	i	j	W_{ij}	j	k	W _{jk}	
1	1	2.07887	2	5	2.49586	1	1	-2.73155	
1	2	-9.89624	2	6	1.82237	2	1	-6.95864	
1	3	-9.00570	2	7	7.67651	3	1	$-1.10463 \cdot 10^{1}$	
1	4	7.02491	2	8	4.55245	4	1	3.38399	
1	5	6.07017	3	1	$-8.25943 \cdot 10^{-1}$	5	1	5.52538	
1	6	3.19986	3	2	4.18945	6	1	-3.98819	
1	7	-4.60675	3	3	4.13969	7	1	5.93730	
1	8	$-8.25220 \cdot 10^{-1}$	3	4	-2.98387	8	1	2.53652	
2	1	1.67302	3	5	-6.41113	9	1	$-4.43300 \cdot 10^{-1}$	
2	2	6.71506	3	6	-2.03992				
2	3	$1.71764 \cdot 10^{1}$	3	7	$7.19708 \cdot 10^{-1}$				
2	4	-1.40865	3	8	-2.38406				

Table 8.14: Accuracy of the feedforward neural network model, Eq. (8.4), in the representation of the bubble pressure data of the 2-propanol (1) + water (2) mixture.

Ref	NDT	T Range	P Range	r Dongo	AAD	Bias	MAD
Kel.	NPI	(K)	(MPa)	x_1 Kange	(%)	(%)	(%)
Arce <i>et al</i> . [54]	27	353-372	0.10	0.00-0.98	0.914	-0.883	3.735
Khalfaoui et al. [55]	12	352-373	0.10	0.00-1.00	2.476	1.792	7.381
Marzal <i>et al</i> . [56]	78	325-373	0.03-0.10	0.00-1.00	1.494	0.465	6.231
Tsuji <i>et al</i> . [57]	10	298	0.01	0.07-0.90	0.554	0.177	2.571
Gironi and Lamberti [58]	32	353-373	0.10	0.00-1.00	1.229	0.041	6.102
Wu et al. [59]	21	353	0.05-0.10	0.00-1.00	0.844	-0.426	2.640
Sada and Morisue [60]	48	308-359	0.01-0.10	0.05-0.86	1.462	-1.031	3.017
Kato <i>et al</i> . [61]	17	353-370	0.10	0.01-1.00	1.646	-1.630	5.096
Ramalho and Drolet [62]	50	335-374	0.04-0.17	0.02-1.00	1.359	0.971	16.068
Wilson and Simmons [63]	99	309-373	0.01-0.10	0.00-1.00	0.974	-0.156	5.151
Brunjes and Bogart [64]	27	353-372	0.10	0.00-0.93	1.524	1.498	8.237
	421	298-374	0.01-0.17	0.00-1.00	1.276	0.058	16.068



Figure 8.14: Representation of the bubble point model in comparison with the saturated data for the 2-propanol (1) + water (2) mixture: a) bubble temperatures; b) bubble pressures.

Saturated liquid density values can be obtained through the intersection of Eq. (8.3) for the compressed liquid density and Eq. (8.4) for the bubble pressure. In Tab. 8.15 the saturated liquid density values obtained with this procedure for the temperatures and compositions corresponding to the density measurements presented in this work are reported. The Fig. 8.15 shows the saturated liquid densities obtained with this procedure in the whole composition range and for temperatures from 287 to 350 K. The figure shows several isothermal sections pointing out the regular trends in the saturated liquid density representation by the developed model.

Т ρ Р x_1 $(kg \cdot m^{-3})$ (K) (MPa) 300.08 0.2483 0.0070 895.51 325.10 874.07 0.2483 0.0273 350.18 0.2483 0.0844 850.19 0.4939 837.98 300.10 0.0072 325.09 0.4939 0.0286 814.94 350.15 0.4939 0.0880 789.82 300.08 805.50 0.7258 0.0073 325.13 0.7258 0.0292 782.68 351.14 0.7258 0.0932 756.90

Table 8.15: Saturated liquid densities for the 2-propanol (1) + water (2) mixture.





8.9. Experimental results for the propylene + 2-propanol+ water system

8.9.1. Introduction

The experimental data available in the literature for the propylene + 2-propanol + water mixture are: VLE data at 333 and 353 K, from 2.6 to 3.7 MPa and high propylene concentration from Zabaloy *et al.* [65]; LLE data from 313 to 363 K and from 1.6 to 6.0 MPa from Rojas *et al.* [66], solubility data from Wu *et al.* [67].

8.9.2. Experimental results

The VTD was used to measure liquid density for the propylene (1) + 2-propanol (2) + water (3) mixture at about 300, 325 and 350 K from 10 MPa down to about atmospheric pressure and for the following molar fractions: $(x_1 = 0.09; x_2 = 0.37)$, $(x_1 = 0.18; x_2 = 0.38)$, $(x_1 = 0.30; x_2 = 0.50)$, $(x_1 = 0.3906; x_2 = 0.4236)$ and $(x_1 = 0.61; x_2 = 0.30)$. The measured (P, ρ, T, x) values are reported in Tab. 8.16.

Table 8.16: Experimental liquid density data for the propylene (1) + 2-propanol (2) + water (3) mixture.

Р	ρ	Р	ρ	Р	ρ	
(MPa)	$(kg \cdot m^{-3})$	(MPa)	$(kg \cdot m^{-3})$	(MPa)	$(kg \cdot m^{-3})$	
		$x_1 = 0.0904$	$x_2 = 0.3697$			
T = 30	05.05 K	T = 32	5.13 K	T = 350.16 K		
0.4810	805.22	1.0965	787.78	1.9794	760.95	
0.7999	805.53	1.3765	788.08	2.2506	761.47	
1.1189	805.81	1.7884	788.50	2.6532	762.19	
1.5873	806.21	2.2055	788.92	2.7894	762.47	
1.9738	806.57	2.5256	789.26	3.1725	763.00	
2.3437	806.88	2.9169	789.68	3.4877	763.47	
2.8616	807.33	3.3853	790.18	3.8192	763.99	
3.0889	807.54	3.7252	790.51	4.1715	764.47	
3.6201	807.99	4.1353	790.90	4.5587	764.96	
3.9484	808.27	4.5483	791.31	4.9036	765.44	
4.3454	808.61	4.9428	791.70	5.2727	765.96	
4.7510	808.95	5.3524	792.10	5.6052	766.43	
5.1507	809.29	5.8171	792.53	5.9927	766.93	
5.5576	809.63	6.1588	792.87	6.3886	767.42	
5.9644	809.96	6.5713	793.27	6.7535	767.93	
6.3666	810.30	6.9706	793.68	7.1751	768.45	
6.7866	810.64	7.3611	794.07	7.5340	768.95	
7.2071	810.99	7.7525	794.47	7.8862	769.36	
7.6091	811.32	8.1263	794.84	8.2903	769.86	
8.0286	811.65	8.5563	795.24	8.7023	770.37	
8.4590	812.01	8.9514	795.67	8.9884	770.84	

Р	ρ	Р	ρ	Р	ρ
(MPa)	$(kg \cdot m^{-3})$	(MPa)	$(kg \cdot m^{-3})$	(MPa)	$(kg \cdot m^{-3})$
	x	$x_1 = 0.0904; x_2 = 0$.3697 (continuatio	on)	-
T = 30	5.05 K	T = 32	5.13 K	T = 35	0.16 <i>K</i>
8.8724	812.34	9.3597	796.03	9.3719	771.35
9.2723	812.66	9.7832	796.45	9.6929	771.80
9.6791	812.99	10.1933	796.86	10.0187	772.34
10.0684	813.35				
		$x_1 = 0.1828$	$x_2 = 0.3828$		
T = 30	0.10 K	T = 32	25.11 K	T = 34	5.10 <i>K</i>
1 0199	758 54	1 8728	738 13	2 2984	718.81
1 3355	758.91	2 2723	738.62	2 3475	718.97
1.5555	759 33	2.5648	739.03	2.7307	719.58
2.0684	759.75	2.8425	739.43	2,9939	720.06
2.5068	760.25	3 1636	740.00	3 2842	720.53
2.8233	760.61	3.4603	740.41	3.5454	720.93
3.2665	761.10	3.8021	740.80	3.9537	721.63
3.5650	761.44	4.2055	741.30	4.1125	721.93
3.9100	761.82	4.5705	741.79	4.4260	722.46
4.3613	762.31	4.9121	742.16	4.7064	722.89
4.6798	762.67	5.3304	742.65	5.0009	723.31
5.0641	763.09	5.7023	743.08	5.2821	723.84
5.4541	763.51	6.0691	743.56	5.5902	724.30
5.8503	763.93	6.4030	743.98	5.9446	724.83
6.3272	764.42	6.7761	744.45	6.1833	725.19
6 6228	764 75	7 0992	744 86	6 4859	725.68
6 9543	765.10	7 4957	745 33	6 7904	726.18
7.4566	765.62	7.8402	745.77	7.0883	726.63
7 8439	766.01	8 2173	746.22	7 3961	727.11
8 2379	766.41	8 5721	746.68	7 6975	727 55
8 6408	766.82	8 9346	747 14	8 0104	728.03
9.0641	767.26	9 2711	747.56	8 3245	728.51
9 4705	767.50	9 6208	747.98	8 6350	728.98
9 8583	768.09	10 0454	748 47	8 9472	729.42
2.00000	100109	1010101	, 10.17	9.2760	729.90
		$x_1 = 0.3031$	$x_2 = 0.5024$		
T = 30	0.10 K	T = 32	5.13 K	T = 35	0.13 <i>K</i>
0.9309	707.92	1.1870	678.16	2.4368	653.52
1.1970	708.29	1.4432	678.62	2.6048	653.96
1.5561	708.78	1.7278	679.11	2.9301	654.68
1.9481	709.29	2.1436	679.80	3.2025	655.27
2.4588	709.93	2.4797	680.35	3.7344	656.44
2.7801	710.37	2.8914	681.10	3.8724	656.79
3.1645	710.88	3.1544	681.59	4.1369	657.40
3.5128	711.35	3.5318	682.22	4.4889	658.17
4.0090	711.99	3.8344	682.74	4.8105	658.86
4.3604	712.44	4.1041	683.18	5.1260	659.50
4.7663	712.95	4.5529	683.87	5.4452	660.17
5.1546	713.45	4.9137	684.44	5.7662	660.85
5.5805	713.98	5.2916	685.03	6.0928	661.51
5.9734	714.47	5.6730	685.61	6.4190	662.19
6.4374	715.04	6.0311	686.15	6.7620	662.87
6.8139	715.51	6.4017	686.72	7.0907	663.50
7.2457	716.02	6.7892	687.28	7.4234	664.19

Р	ρ	Р	ρ	Р	ρ
(MPa)	$(\text{kg}\cdot\text{m}^{-3})$	(MPa)	$(kg \cdot m^{-3})$	(MPa)	$(\text{kg} \cdot \text{m}^{-3})$
	(8) X1	$= 0.3031; x_2 = 0$	0.5024 (continuation	on)	(
T = 30	$\frac{1}{0.10 \ K}$	$\frac{1}{T} = 32$	25.13 K	T = 35	0.13 <i>K</i>
7 6762	716 54	7 1736	687 86	7 7731	664 87
8.0953	717.04	7.5690	688.43	8.1258	665.54
8.5271	717.54	7.9652	689.02	8.4760	666.19
9.0259	718.13	8.3550	689.57	8.8295	666.84
9.4290	718.61	8.7637	690.16	9.1905	667.56
9.7855	719.09	9.1707	690.73	9.5447	668.20
10.2138	719.60	9.5748	691.28	9.9024	668.83
		9.9694	691.84		
		$x_1 = 0.3906$	$x_2 = 0.4236$		
T = 30	0.10 K	T = 32	25.11 <i>K</i>	T = 35	0.11 <i>K</i>
1 0187	680.98	1 9518	650.66	2 6205	618 74
1 1998	681.27	2 3561	651 45	3.0072	619.87
1.6209	681.88	2.5960	651.95	3 1830	620.39
1.0209	682 39	2.9341	652.61	3 5281	621.38
2 3279	682.91	3 2077	653 19	3 7312	621.90
2 7039	683.48	3 4938	653 75	4 0884	622.82
3 0296	683.95	3 8787	654 46	4 3645	623.62
3 3633	684 43	4 2234	655.08	4 6536	624 39
3 7581	685.00	4 5679	655 73	4 9512	625.19
4 0323	685.37	4.8926	656 32	5 2582	625.98
4.0323	686.01	5 2235	656.91	5 5968	626.78
4.4072	686 51	5 5586	657 52	5 9458	627.64
5 2112	687.02	5 9273	658.17	6 2382	628.34
5 5919	687.54	6 2780	658 79	6 5680	629.17
5 9575	688.05	6 6596	659.45	6 8828	629.92
6 3307	688 56	7.0051	660.05	7 2018	630.66
6 7084	689.06	7 3645	660.65	7.5611	631.49
7 0811	689 56	7.3043	661.26	7.9087	632.29
7.0011	690.07	8 1192	661.90	8 2357	633.07
7.4645	690.59	8 4743	662 48	8 5847	633.86
8 2519	691.10	8 8572	663 10	8 9126	634 62
8 6313	691.60	9 2336	663 72	9 2911	635 35
9.0140	692.09	9.6192	664 33	9.6659	636.22
9.0140	692.60	9.0172	664.93	9.0037	636.95
9.8324	693.12	2.2714	004.95	2.2074	050.75
		$x_1 = 0.6123$	$x_2 = 0.3039$		
T = 30	0.10 K	T = 32	25.12 K	T = 35	0.10 K
1.0854	614.94	1.8941	580.11	2.8501	540.02
1.5314	615.81	2.2073	580.96	3.0168	540.87
1.8707	616.53	2.5281	581.84	3.2315	541.94
2.3726	617.48	2.8474	582.67	3.5057	543.11
2.5272	617.84	3.2008	583.61	3.7827	544.27
2.9221	618.61	3.4991	584.39	3.9965	545.27
3.2262	619.19	3.7780	585.12	4.3281	546.57
3.5794	619.86	3.8175	586.14	4.6211	547.80
4.0682	620.74	4.2142	587.19	4.8667	548.79
4.2817	621.17	4.5221	587.93	5.1693	550.07
4.7290	622.00	4.8663	588.81	5.4573	551.09
5.1095	622.68	5.2102	589.63	5.7592	552.24
5.4945	623.39	5.5629	590.47	6.0943	553.32

<i>P</i>	ρ	Р	ρ	Р	ρ
(MPa)	$(kg \cdot m^{-3})$	(MPa)	$(kg \cdot m^{-3})$	(MPa)	$(kg \cdot m^{-3})$
	<i>x</i> ₁	$= 0.6123; x_2 = 0$).3039 (continuation	on)	
T = 30	0.10 K	T = 32	25.12 <i>K</i>	T = 35	0.10 K
5.8751	624.07	5.9303	591.32	6.4191	554.43
6.2521	624.73	6.3212	592.20	6.7321	555.54
6.6365	625.40	6.6863	593.02	7.0480	556.69
7.0329	626.07	7.0575	593.82	7.3729	557.82
7.4534	626.76	7.4688	594.69	7.7030	558.93
7.8662	627.47	7.8762	595.54	8.0598	559.96
8.2557	628.11	8.2536	596.34	8.4385	561.12
8.6619	628.75	8.6532	597.15	8.8208	562.37
9.0796	629.46	9.0784	597.99	9.1877	563.44
9.4742	630.08	9.5001	598.83	9.5755	564.54
9.8967	630.79	9.9155	599.65	9.9391	565.57

For each composition at each measurement temperature also the bubble pressure was determined and the corresponding values are reported in Tab. 8.17.

Table 8.17: Bubble pressures and saturated liquid densities for the propylene (1) + 2-propanol(2) + water (3) mixture.

Т			Р	ρ
(K)	X_1	x_2	(MPa)	$(kg \cdot m^{-3})$
305.05	0.0904	0.3697	0.4685	805.23
325.13	0.0904	0.3697	1.0136	787.71
350.16	0.0904	0.3697	1.6943	760.66
300.10	0.1828	0.3828	0.9366	758.45
325.11	0.1828	0.3828	1.5933	737.81
345.10	0.1828	0.3828	2.1873	718.66
300.10	0.3031	0.5024	0.9081	707.89
325.13	0.3031	0.5024	-	-
350.13	0.3031	0.5024	2.1351	652.85
300.10	0.3906	0.4236	0.9897	680.94
325.11	0.3906	0.4236	1.6609	650.10
350.11	0.3906	0.4236	2.4621	618.33
300.10	0.6123	0.3039	1.0583	614.87
325.12	0.6123	0.3039	1.7863	581.18
350.10	0.6123	0.3039	2.7101	539.52

8.9.3. Discussion

The measured liquid density values for the propylene + 2-propanol + water mixture, together with the liquid density values measured in this thesis for the propylene + 2-propanol mixture (Paragraph 8.7) and for the 2-propanol + water mixture (Paragraph 8.8), and liquid density values

generated for the pure fluids propylene, 2-propanol and water in the same range of temperature and pressure were correlated with a MLFN model (see Paragraph 2.2.2):

$$\rho\left(T, P, x_1, x_2\right) = W_1 \tag{8.5}$$

An arctangent function normalized in the range [0,1] is assumed as transfer function. W_1 represents the density, while V_i , for i=1, 2, 3, are temperature, pressure and composition respectively.

The parameters used for the correlation of the liquid density data are presented in Tab. 8.18. Residual errors are presented in Tab. 8.19 and shown graphically in Fig. 8.16. The simultaneous representation of the ternary mixture, the binary mixtures and pure fluid data shows a good coherence among the measured liquid density values for the mixtures and the generated liquid density values for the pure fluids. The overall AAD % (0.035) is less than the experimental uncertainty of the presented density measurements. The Bias % value (0.001) shows that the MLFN model is very well centered with respect to the experimental data.



Figure 8.16: Percentage error of the feedforward neural network model in the representation of the liquid density data of the propylene (1) + 2-Propanol (2) +water (3) mixture.

The MLFN model of Eq. (8.5) was used to generate the liquid density surfaces from 300 to 350 K in the whole composition range, Fig. 8.17. In the same figure, dash dot lines represent LLE boundaries generated with the $G^{E} - EoS$ model presented in Paragraph 7.6.

Table 8.18: Parameters of the feedforward neural network used for the correlation of the liquiddensity data for the mixture propylene (1) + 2-propanol (2) + water (3).

$\beta = 0.5$			$V_{\min,1} = T_{\min} = 250$			$V_{\max,1} = T_{\max} = 400$				
I = 5			$V_{\min,2} = P_{\min} = 0$			$V_{\text{max},2} = P_{\text{max}} = 12$				
I = 12			V = r = 0			$V_{\alpha} = x_{\alpha} = 1$				
		5 – 12		$V_{\min,3} = \lambda_{1,\min} = 0$			$v_{\max,3} = v_{1,\max} = 1$			
		K = 1		$V_{\min,4} = x_{2,\min} = 0$			$V_{\max,4} = x_{2,\max} = 1$			
			$W_{\min,1} = \rho_{\min} = 250$			$W_{\rm max,1} = \rho_{\rm max} = 1050$				
i	j	W _{ij}	i	j	W _{ij}	i	j	W _{ij}		
1	1	$-2.92762 \cdot 10^{1}$	3	1	$-1.99930 \cdot 10^{1}$	1	1	$-1.75403 \cdot 10^{1}$		
1	2	4.21347	3	2	-6.66933	2	1	$5.40361 \cdot 10^{-3}$		
1	3	2.47330	3	3	-1.49965	3	1	-1.24796		
1	4	-4.47885	3	4	-3.35238	4	1	$-1.27458 \cdot 10^{-1}$		
1	5	2.72143	3	5	-6.83433·10 ⁻¹	5	1	-1.53151		
1	6	-5.43393	3	6	1.71319	6	1	$1.24410 \cdot 10^{1}$		
1	7	3.52922	3	7	$3.09508 \cdot 10^{1}$	7	1	-3.00794		
1	8	$-2.15646 \cdot 10^{1}$	3	8	$-1.71309 \cdot 10^{1}$	8	1	$2.86986 \cdot 10^{1}$		
1	9	4.42482	3	9	-7.10556	9	1	$7.95524 \cdot 10^{-2}$		
1	10	$-2.08228 \cdot 10^{1}$	3	10	$-1.78988 \cdot 10^{1}$	10	1	$2.93360 \cdot 10^{1}$		
1	11	$-1.61511 \cdot 10^2$	3	11	$-5.20945 \cdot 10^{1}$	11	1	$1.30889 \cdot 10^2$		
1	12	5.47497	3	12	$1.55951 \cdot 10^{1}$	12	1	-2.90082		
2	1	1.88455	4	1	$-1.43946 \cdot 10^{1}$	j	k	W _{ik}		
2	2	$-1.88623 \cdot 10^{-1}$	4	2	-2.33862	1	1	$4.58186 \cdot 10^{1}$		
2	3	$-2.37482 \cdot 10^{-1}$	4	3	-2.14679	2	1	$-3.38637 \cdot 10^{1}$		
2	4	$2.08989 \cdot 10^{-1}$	4	4	2.63885	3	1	$2.68326 \cdot 10^{1}$		
2	5	$-2.83151 \cdot 10^{-1}$	4	5	-2.55880	4	1	1.27324		
2	6	2.97414	4	6	$3.26107 \cdot 10^{1}$	5	1	$-2.25387 \cdot 10^{1}$		
2	7	$-5.42178 \cdot 10^{-2}$	4	7	$2.03028 \cdot 10^{1}$	6	1	$-1.75728 \cdot 10^{1}$		
2	8	$1.10477 \cdot 10^{1}$	4	8	-1.37383	7	1	$-2.98598 \cdot 10^{1}$		
2	9	$-1.82864 \cdot 10^{-1}$	4	9	-2.46377	8	1	$-2.39993 \cdot 10^{1}$		
2	10	9.85172	4	10	-2.11137	9	1	$3.02683 \cdot 10^{1}$		
2	11	$9.06796 \cdot 10^{1}$	4	11	$4.02489 \cdot 10^{1}$	10	1	$2.75980 \cdot 10^{1}$		
2	12	$5.21938 \cdot 10^{-2}$		12	$2.33143 \cdot 10^{1}$	11	1	6.70185		
						12	1	$1.95301 \cdot 10^{1}$		
						13	1	$1.61961 \cdot 10^{1}$		

Table 8.19: Accuracy of the feedforward neural network model, Eq. (8.5), in the representation of the liquid density data of the propylene (1) + 2-propanol (2) + water (3) mixture.

System	Ref.	NPT ^a	T Range (K)	P Range (MPa)	x ₁ Range	x ₂ Range	AAD (%)	Bias (%)	MAD (%)
propylene (1) + 2-propanol (2) + water (3)	this work	378	300-350	0.47-10.21	0.09-0.61	0.30-0.50	0.052	-0.005	0.184
propylene (1) + 2-propanol (2)	this work (paragraph 8.7)	186	300-350	0.52-9.99	0.20-0.65	0.35-0.80	0.038	0.020	0.122
2-propanol (1) + water (2)	this work (paragraph 8.8)	200	300-351	0.07-10.24	0.00	0.25-0.73	0.035	-0.004	0.104
propylene	Angus et al. [1]	98	300-350	1.21-10.10	1.00	0.00	0.025	0.004	0.173
2-propanol	this work ^b	123	300-350	0.01-10.00	0.00	1.00	0.009	0.004	0.026
water	Wagner and Pruß [2]	120	300-350	0.00-9.75	0.00	0.00	0.013	-0.002	0.036
		1105	300-351	0.00-10.24	0.00-1.00	0.00-1.00	0.035	0.001	0.184

^a NPT: number of experimental points.

^b values generated by the BWR equation presented in the former paragraph 8.6.3.



Figure 8.17: Liquid density surfaces for the propylene (1) + 2-propanol (2) + water (3) mixture obtained with the regressed feedforward neural network model.

8.10. Conclusions

Density measurements have been carried out:

- for 2-propanol in the range from 273 to 400 K and up to 12 MPa;
- for the propylene (1) + 2-propanol (2) mixture at 300, 325 and 350 K from 10 MPa down to bubble pressures for x₁ = 0.20, 0.52 and 0.65;
- for the 2-propanol (1) + water (2) mixture at 300, 325 and 350 K from 10 MPa down to about atmospheric pressure for x₁ = 0.25, 0.49 and 0.73;
- for the propylene (1) + 2-propanol (2) + water (3) mixture at about 300, 325 and 350 K from 10 MPa down to about atmospheric pressure and for the following molar fractions: (x₁ = 0.09; x₂ = 0.37), (x₁ = 0.18; x₂ = 0.38), (x₁ = 0.30; x₂ = 0.50), (x₁ = 0.39; x₂ = 0.42) and (x₁ = 0.61; x₂ = 0.30).

Bubble pressures have been determined:

- for the propylene (1) + 2-propanol (2) mixture at 300, 325 and 350 K for x₁ = 0.20, 0.52 and 0.65;
- for the propylene (1) + 2-propanol (2) + water (3) mixture at about 300, 325 and 350 K for the following molar fractions: (x₁ = 0.09; x₂ = 0.37), (x₁ = 0.18; x₂ = 0.38), (x₁ = 0.30; x₂ = 0.50), (x₁ = 0.39; x₂ = 0.42) and (x₁ = 0.61; x₂ = 0.30)

The measurements have been correlated and compared with the available literature data showing a good agreement with them.

The obtained density database is suitable for the regression of a DEoS for the system propylene + 2-propanol + water in EEoS-NN format in the range of interest. In order to develop a thermodynamic model of the ternary mixture other experimental properties need to be measured, in particular VLE, LLE and VLLE data for the ternary mixture in the whole range of interest. Experimental isobaric heat capacity measurements in the range of interest are also important to validate the prediction accuracy of the model with respect to the caloric properties. This experimental work constitute the basis for the regression (density and coexistence data) and for the validation (isobaric heat capacity data) of a dedicated equation of state in EEoS-NN format for the propylene + 2-propanol + water system. Once a precise model for the ternary mixture is set up the 2-propanol extraction process can be studied in order to find the better operative conditions to optimize the process from an energetic point of view. The cited developments represent the prosecution of the present thesis work.

8.11. References

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PART TWO

Transport Properties

IX. Models for transport properties

9.1. General overview

If a complete and rigorous statistical mechanics theory, able to calculate the properties of a macroscopic ensemble of molecules of a fluid from the knowledge of molecular properties and of forces between the molecules, would be available, then the transport properties could be evaluated for each system in a completely predictive way. Unfortunately, at the present stage of scientific knowledge in these subjects this is far from being possible, except for approximate theoretical models in the dilute-gas state and asymptotically close to the critical point.

For example the kinetic theory of gases, as for instance the Chapman-Enskog theory [1,2], can be used for the dilute-gas region of monatomic gases, where the transport properties are almost independent of the existence of internal degrees of freedom and unaffected by inelastic collisions. In Ref. 3 the following equations are given for the viscosity η and the thermal conductivity λ of monatomic gases in dilute-gas region:

$$\eta^{o}(T) = \frac{1}{4} (\pi m k_{B} T)^{1/2} \frac{1}{\pi \sigma^{2} \varsigma_{\eta}^{*}}$$
(9.1)

$$\lambda^{o}\left(T\right) = \frac{5}{8} \left(\frac{\pi k_{B}^{3} T}{m}\right)^{1/2} \frac{1}{\pi \sigma^{2} \varsigma_{\lambda}^{*}}$$
(9.2)

where superscript o indicates a dilute-gas condition, k_B is Boltzmann's constant, m the mass of one molecule, σ a length scaling parameter, ζ_{η}^* and ζ_{λ}^* the *reduced effective cross section* for viscosity and thermal conductivity, respectively. The two ζ^* functions depend only on the reduced temperature $T^* = k_B T / \varepsilon$; several 'universal' correlations for the reduced effective cross sections are given, mainly obtained from fitting of experimental data although moving from some theoretical basis [3]. The fluid-specific parameters σ and ε are usually determined from experimental data; alternatively they can be estimated applying the corresponding states principle [4], but accepting higher inaccuracies.

For the viscosity of pure fluids constituted by polyatomic molecules the same equation (9.1) is usually maintained [5-17], also when the fluid of interest is characterized by quite complex molecules, as for instance halogenated alkanes or isobutane. Often equation (9.1) is written in the form:

$$\eta^{o}(T) = \frac{5}{16} \sqrt{\frac{Mk_{B}T}{\pi N_{A}}} \frac{1}{\sigma^{2} \Omega_{\eta}(T^{*})}$$

$$\tag{9.3}$$

where *M* is the molar mass, N_A the Avogadro constant and Ω_{η} the *collision integral* for which 'universal' correlations are given.

Experimental viscosity data for the target fluid are anyway required, because the coefficients of the Ω_{η} function, far from being universal, are often regressed directly on viscosity data [5-7,10,12,13,17]. Moreover, the parameters σ and ε are obtained by fitting on experimental data of the fluid of interest aiming at getting better performances.

On the contrary, equation (9.2) is no more valid for thermal conductivity of fluids with polyatomic molecules; in fact in this case the energy transfer mechanism is due both to the translational motion of the molecules and to internal degrees of freedom, indicated with subscripts *trans* and *int*, respectively [18]:

$$\lambda^{o}\left(T\right) = \lambda^{o}_{trans}\left(T\right) + \lambda^{o}_{int}\left(T\right)$$
(9.4)

The two terms can be expressed as:

$$\lambda_{trans}^{o}\left(T\right) = \frac{15R_{m}\eta^{o}\left(T\right)}{4M}$$
(9.5)

$$\lambda_{int}^{o}\left(T\right) = \frac{f_{int}\eta^{o}\left(T\right)}{M} \left[C_{p,m}^{o}\left(T\right) - \frac{5}{2}R_{m}\right]$$
(9.6)

where R_m is the molar gas constant, $C_{p,m}^o$ is the molar ideal-gas isobaric heat capacity, and the factor f_{int} accounts for the energy conversion between internal and translational modes, for which different interpretations are given [19].

For thermal conductivity in the dilute-gas limit Eq. (9.4) is sometimes assumed [5,6,9,20], but completely empirical formulations are preferred for most fluids [7,14-16,21-25]. In this second case, thermal conductivity experimental data are needed in order to fit the equation parameters.

These models for the dilute-gas region are extended to represent also mixtures of fluids adopting suitable mixing rules [19]. Moreover, they can be used at moderate pressures of few bars with acceptable results, but they become unreliable at higher pressures.

Both viscosity and thermal conductivity of pure fluids diverge to infinite when approaching the critical point [26]; this behavior is described by the mode-coupling theory for the dynamics of critical fluctuations, from which calculation models can be obtained [26-28]. These theoretical

models can be regarded as semi-predictive because they contain only few fluid-specific parameters to be regressed on data, but they are very complex and require both suitable equations of state and the knowledge of the *background* transport properties, see Paragraph 9.2 for more details.

For liquid phase, only few simple theories have been developed for transport properties, so there are practically no theoretical models able to calculate them with sufficient accuracy.

As an alternative, semi-theoretical methods are available; among this class, the most effective are those based on the corresponding states principle for transport properties, briefly outlined in Paragraph 9.3. In particular the three-parameter corresponding states models seem to be very promising: they are able to reproduce viscosity [29,30] and thermal conductivity [31,32] both for pure fluids and for mixtures with satisfactory accuracy, requiring as input only few experimental data.

Anyway, the most precise models for calculating the transport properties are the correlative ones. These have a limited or absent theoretical background and they are fluid-specific equations obtained from correlation of transport properties experimental data using different techniques. In their most advanced versions these correlative models are able to reproduce the experimental data of pure fluids in a wide range of conditions and with an accuracy comparable with the claimed experimental precision of data themselves.

It is common practice that the independent variables in these models are temperature and density, i.e. they are in the form $\eta(T, \rho)$ or $\lambda(T, \rho)$; this is justified on the basis of theoretical and practical considerations [33]. Therefore, since the controlling variables in the experimentation and in technical applications are usually temperature and pressure, a high accuracy equation of state is necessary to convert the T, P variables into T, ρ . The extension of these models to mixture is not yet been consolidated. The present standard technique for the development of transport properties equations is exposed in Paragraph 9.2; an innovative heuristic modeling technique based on the Setzmann and Wagner optimization algorithm [34] developed for both viscosity and for thermal conductivity is presented in Paragraph 9.4. Besides these, a new modeling technique that integrates the extended corresponding states with neural networks has provided satisfactory results for viscosity [35,36] and it is here applied to thermal conductivity in Chapter X.

More detailed reviews of theoretical, semi-theoretical and empirical models for calculating transport properties can be found in the literature, as for instance Refs. 19 and 37 for viscosity, and Ref. 19 for thermal conductivity.

9.2. Conventional dedicated equations

The present standard procedure for the development of transport property equations specific for the target fluid, in the following referred to as 'conventional technique', found its first applications in the late '80s of the last century [5,9,23]. According to this approach, the general structure of a transport property equation is written as:

$$X(T,\rho) = X^{o}(T) + \Delta_{E}X(T,\rho) + \Delta_{C}X(T,\rho)$$
(9.7)

where X denotes either viscosity or thermal conductivity, $X^{\circ}(T)$ is the *dilute-gas* term, $\Delta_E X(T, \rho)$ is the *excess* term and $\Delta_C X(T, \rho)$ is the *critical enhancement* term. The summation:

$$\overline{X}(T,\rho) = X^{o}(T) + \Delta_{E}X(T,\rho)$$
(9.8)

is also called *background* term.

The conventional technique separately determines each term through fitting of theoretical or empirical functional forms on the available experimental data.

9.2.1. Dilute-gas term

The dilute-gas term $X^{\circ}(T)$ represents the behavior of the considered transport property in the zero-density limit; it could be regarded as the equivalent of the ideal part in thermodynamic equations of state. It obviously depends only on temperature and it can be used with acceptable performances in the vapor phase at pressure limited to few bars.

Looking at some of the available transport property conventional equations [3,5-18,20-25], it can be seen that for the dilute-gas viscosity an equation similar to Eq. (9.3) is normally used, in which σ and ε are usually regressed from the available experimental data, while the coefficients of the Ω_n equation are either assumed from a generalized correlation or fitted on data too.

An expression of theoretical derivation can be used also for the dilute-gas thermal conductivity, Eqs. (9.4-9.6), but an empirical polynomial equation is often preferred, particularly when dealing with medium-sized polyatomic molecules. In the first case the equations for dilute-gas viscosity and for ideal-gas isobaric heat capacity are required, in the second case experimental data are needed in order to determine the equation coefficients.

9.2.2. Excess term

The contribution to the transport property value at non-zero density of effects like many-body collisions, molecular-velocity correlations and collisional transfer is taken into account by the excess term $\Delta_E X(T, \rho)$. For this term no theoretical guidance exists and then it has to be necessarily established from fitting of an empirical equation on experimental data. More or less complex polynomial forms are usually assumed, in some cases depending on both temperature and density, in other cases depending on density only.

In particular, some Authors [10,12,13,17] have divided the excess term of viscosity into two contributions:

$$\Delta_{E}\eta(T,\rho) = \eta^{(1)}(T)\rho + \Delta_{h}\eta(T,\rho)$$
(9.9)

that are the initial density-dependence $\eta^{(1)}(T)$ and the higher-density term $\Delta_h \eta(T, \rho)$.

The first term, that accounts for the portion of excess term linear with density and then it is particularly relevant in the low-density region, can be calculated from:

$$\eta^{(1)}(T) = \eta^{o}(T) N_{A} \sigma^{3} B_{\eta}^{*}(T^{*})$$
(9.10)

where $B_{\eta}^{*}(T^{*})$ is the reduced second viscosity virial coefficient, for which an universal correlation is given [12].

The term $\Delta_h \eta(T, \rho)$ is described with an empirical equation that is regressed on experimental data.

9.2.3. Critical enhancement term

As previously stated, the viscosity and the thermal conductivity of pure fluids diverge to infinite at the critical point [26], where long wave-length fluctuations become predominant inducing anomalies in the thermodynamic as well as in the transport properties; consequently the transport properties in the critical region show a marked increase as plotted in Fig. 9.1 for the thermal conductivity of carbon dioxide, calculated from Ref. 9.

The plot evidences that the effect of critical fluctuations on thermal conductivity is strong and it is observed in a large range of temperature and density around the critical point. On the contrary, for viscosity the effect is much weaker and restricted to a very small region around the critical point: the viscosity plot for carbon dioxide from Ref. 8 is reported in Fig. 9.2 for the same isotherms considered in Fig. 9.1.



Figure 9.1: Thermal conductivity of carbon dioxide for some isotherms in the critical region [9].



Figure 9.2: Viscosity of carbon dioxide for some isotherms in the critical region [8].
Some theories describing the behavior of fluids in the critical region have been developed, both for thermodynamic and for transport properties. For the second ones, the *crossover* equations from Olchowy and Sengers [38,39] are usually adopted. These models incorporate the singular behavior of transport properties asymptotically close to the critical point, but they reduce themselves to background values far away from the critical point.

According to Olchowy and Sengers, the critical enhancement terms are calculated from:

$$\Delta_C \eta = \overline{\eta} \left(e^{zH} - 1 \right) \tag{9.11}$$

$$\Delta_{C}\lambda = \rho C_{p} \frac{R_{0}k_{B}T}{6\pi\eta\xi} \left(\Omega - \Omega_{0}\right)$$
(9.12)

where H, Ω and Ω_0 are functions of density and temperature, R_0 and z are universal parameters, ξ is the correlation length of the density fluctuations. The analytical expressions of the three functions H, Ω and Ω_0 are very complex and therefore they are here not reported; for details see Refs. 27 and 28. The main aspect of the matter is that the calculation of these functions requires the knowledge of:

- thermodynamic properties like isothermal compressibility, isobaric and isochoric heat capacity;
- the background values of both viscosity and thermal conductivity;
- the values of some system-dependent parameters.

An equation of state suitable to accurately represent the asymptotic behavior of the thermodynamic properties in the critical region is needed; therefore, a *scaled* fundamental equation of state should be used in that region, see for instance Ref. 40. When this condition is not fulfilled, the numerical values calculated from Eqs. (9.11) and (9.12) could be unreliable. Moreover, transport properties experimental data in the critical region are required to obtain the system-dependent parameters by a fitting procedure; the number of free parameters is quite limited thanks to the theoretical foundation and this is a sure advantage.

Some simplifications are sometimes introduced for the critical enhancement term during the transport property equation development: for viscosity the term is often set to zero, because of its weak and limited influence; for thermal conductivity simpler functional forms with respect to the original ones can be assumed for Ω and Ω_0 , as for instance in Ref. 9.

9.2.4. General remarks

According to the conventional procedure, the value of each transport property at assigned temperature and density is calculated as a summation of three terms; for two of them, namely the dilute-gas and critical enhancement terms, theoretically founded equations are available, whereas the excess term has a completely empirical formulation. The use of expressions derived from physical theories is advantageous both for the limited number of free parameters to determine and for the extrapolation capability of the model, but experimental data are anyway needed in the whole interest ranges of the independent variables to regress the equation coefficients, particularly for the empirical excess term. Being substantially correlative models, the conventional equations representation of experimental data is satisfactory.

The procedure to develop an equation with this technique is not straightforward and it is a bit cumbersome, because each experimental value has to be decomposed into the three contributions (dilute-gas, excess and critical part) and each term of the equation has to be separately fitted. Therefore, data in vapor have to be extrapolated to zero-density limit with some procedure, in order to get the values on which the dilute-gas term coefficients are regressed. The extrapolation to zero-density limit can be a difficult task if the data are not suitably distributed in low-pressure region: for example data are often measured at atmospheric pressure or higher and therefore the extrapolation could either be impossible or introduce sensible errors. The parameters of the critical enhancement term have to be initially set up by tentative, so the experimental excess part can be calculated from the data as:

$$\Delta_{E} X \left(T_{exp}, \rho_{exp} \right) = X_{exp} - X^{o} \left(T_{exp} \right) - \Delta_{C} X \left(T_{exp}, \rho_{exp} \right)$$
(9.13)

and the excess term can be regressed.

At this stage, it is now possible to calculate the background properties and then the critical enhancement term can be more precisely set up. Therefore Eq. (9.13) is recalculated for each point and a new excess term fitting has to be performed, and so on in an iterative process.

It should be also noted from Eq. (9.12) that a thermal conductivity equation with a reliable behavior in the critical region could not be safely developed if a precise viscosity equation is not yet available.

Moreover, the functional forms of the excess term for viscosity and thermal conductivity seem to be not well established: in the literature many different equations for this part are assumed and it is not clear which choice criterion has to be used. This shortcoming increases the difficulties of the exposed regression process. A certain amount of precise and evenly distributed experimental data for the fluid of interest is always required to develop a transport property equation with this technique, but the results are far superior to the other types of models for transport properties.

Since quite few substances have been sufficiently investigated from the experimental point of view, the conventional technique has been so far applied to a limited number of pure fluids; the equations published in the literature up to this time are listed in Table 9.1.

Fluid	Viscosity	Thermal Conductivity
Argon	Lemmon and Jacobsen, 2004 [7]	Lemmon and Jacobsen, 2004 [7]
Carbon dioxide	Fenghour et al., 1998 [8]	Vesovic et al., 1990 [9]
Nitrogen	Lemmon and Jacobsen, 2004 [7]	Lemmon and Jacobsen, 2004 [7]
Oxygen	Lemmon and Jacobsen, 2004 [7]	Lemmon and Jacobsen, 2004 [7]
Air ^a	Lemmon and Jacobsen, 2004 [7]	Lemmon and Jacobsen, 2004 [7]
Ammonia	Fenghour et al., 1995 [10]	Yata et al., 2001 [21]
Water	Nagashima and Dymond, 1996 [22]	Nagashima and Dymond, 1996 [22]
Methane	_	Friend and Roder, 1987 [23]
Ethane	Hendl et al., 1994 [11]	Vesovic et al., 1994 [20]
Propane	Vogel et al., 1998 [12]	Ramires et al., 2000 [24]
Isobutane	Vogel et al., 2000 [13]	Yata et al., 2001 [21]
R23	Shan et al., 2000 [14]	Shan et al., 2000 [14]
R123	Tanaka and Sotani, 1996 [25]	Tanaka and Sotani, 1996 [25]
R134a	Krauss et al., 1993 [15]	Krauss et al., 1993 [15]
R152a	Krauss et al., 1996 [16]	Krauss et al., 1996 [16]

Table 9.1: Available transport property dedicated equations in conventional format.

^a in the Lemmon and Jacobsen work [7], air is treated as a pseudo-pure fluid; in fact it is considered as a ternary mixture of nitrogen, oxygen and argon at fixed composition.

9.3. Corresponding states principle

According to the principle of corresponding states, the reduced value of a selected property for a substance (*target* fluid) is equal to that for another substance (*reference* fluid) if both are evaluated at the same reduced conditions, see Paragraph 3.6.1. In the case of the here considered transport properties, the critical values cannot be used to calculate the reduced properties, since they diverge to infinite at the critical point [26]; values calculated either from dimensional analysis or from kinetic theory are assumed as an alternative.

A basic condition for the principle application is that the fluids are *conformal*, i.e. they obey the same intermolecular force laws at the same reduced conditions; for instance, fluids pertaining to a same family, like alkanes or haloalkanes, are supposed to share a condition of conformality. Besides this, the chosen reference fluid has to dispose of a precise equation for the considered property valid over a large range of conditions.

The application of the corresponding states principle to pure fluid viscosity reads [37]:

$$\eta_{j}\left(T_{r,j},\rho_{r,j}\right) = \eta_{0}\left(T_{r,0},\rho_{r,0}\right) \left(\frac{M_{j}}{M_{0}}\right)^{1/2} \left(\frac{T_{c,j}}{T_{c,0}}\right)^{1/2} \left(\frac{\rho_{c,j}}{\rho_{c,0}}\right)^{2/3}$$
(9.14)

where $T_r = T/T_c$ and $\rho_r = \rho/\rho_c$ are the reduced temperature and density respectively, and *M* is the molar mass. Moreover, subscript *c* denotes a critical value, while subscripts *j* and 0 indicate the target and the reference fluid, respectively. If a viscosity equation for the reference fluid is available, the viscosity of the target fluid can be readily calculated on the whole surface.

A similar technique can be applied also to the translational contribution of thermal conductivity [18], but the results are worse due to the greater complexity of the controlling physical phenomena.

In any case, the model of Eq. (9.14) and the equivalent one for thermal conductivity give reasonable results only at low density, whereas the performances are poor as density increases. Therefore, different alternative approaches have been developed, but sharing the corresponding states basic framework.

9.3.1. Extended corresponding states

PURE FLUIDS

The extended corresponding states (ECS) method previously exposed for thermodynamics in Paragraph 3.6.3 has been applied also to transport properties since the early '80s [18,41]. Different approaches are found in the literature, so the published models vary from predictive methods to correlative ones, though maintaining a similar format.

Following Ref. 42, the viscosity of a target pure fluid *j* is decomposed as:

$$\eta_j(T,\rho) = \eta_j^o(T) + \Delta_E \eta_j(T,\rho)$$
(9.15)

in which the first term, i.e. the dilute-gas viscosity η_j^o , is calculated from Eq. (9.3) or from an equivalent expression derived from kinetic theory of gases, while the ECS model is applied to the second term, i.e. the excess viscosity $\Delta_E \eta_i$:

$$\Delta_{E}\eta_{j}(T,\rho) = \Delta_{E}\eta_{0}(T/f_{j},\rho h_{j})F_{\eta}$$
(9.16)

where:

$$f_{j} = \frac{T_{c,j}}{T_{c,0}} \theta_{j} \qquad h_{j} = \frac{\rho_{c,0}}{\rho_{c,j}} \phi_{j} \qquad F_{\eta} = f_{j}^{1/2} h_{j}^{-2/3} \left(\frac{M_{j}}{M_{0}}\right)^{1/2}$$
(9.17, 9.18, 9.19)

In the preceding equations, f_j and h_j are the equivalent substance reducing ratios or scale factors, θ_j and ϕ_j are the shape factors, the multiplier F_{η} is derived from a theoretical analysis based on kinetic theory. From a comparison between Eqs. (9.7) and (9.16) it is evident that the critical enhancement part is neglected, due to its weak contribution for viscosity.

The case of thermal conductivity is analogous, though more complicated [43,44]. Moving from the splitting of thermal conductivity into two parts as:

$$\lambda_{j}(T,\rho) = \lambda_{j,int}^{o}(T) + \lambda_{j,trans}(T,\rho)$$
(9.20)

the translational contribution $\lambda_{i,trans}$ can be divided into three further terms:

$$\lambda_{j,trans}(T,\rho) = \lambda_{j,trans}^{o}(T) + \Delta_{E}\lambda_{j}(T,\rho) + \Delta_{C}\lambda_{j}(T,\rho)$$
(9.21)

that are the translational dilute-gas contribution $\lambda_{j,trans}^{o}$, the excess part $\Delta_{E}\lambda_{j}$ and the critical enhancement $\Delta_{C}\lambda_{j}$. The terms $\lambda_{j,trans}^{o}(T)$ and $\lambda_{j,int}^{o}(T)$ can be calculated from Eqs. (9.5) and (9.6) respectively, while the remaining two terms are obtained from the ECS technique:

$$\Delta_E \lambda_j (T, \rho) = \Delta_E \lambda_0 (T/f_j, \rho h_j) F_\lambda$$
(9.22)

$$\Delta_{c}\lambda_{j}(T,\rho) = \Delta_{c}\lambda_{0}(T/f_{C,j},\rho h_{C,j})F_{C,\lambda}$$
(9.23)

where the reducing ratios have the same meanings of Eqs. (9.17) and (9.18), while the multiplier F_{λ} is calculated by:

$$F_{\lambda} = f_{j}^{1/2} h_{j}^{-2/3} \left(\frac{M_{0}}{M_{j}} \right)^{1/2}$$
(9.24)

For the critical enhancement term, it is usually assumed $F_{C,\lambda} = F_{\lambda}$. Moreover, in some versions [43] it is:

 $f_{C,j} = f_j$ $h_{C,j} = h_j$ (9.25, 9.26)

while in other ones [44]:

$$f_{C,j} = \frac{T_{c,j}}{T_{c,0}} \qquad h_{C,j} = \frac{\rho_{c,0}}{\rho_{c,j}}$$
(9.27, 9.28)

but both the approaches present some drawbacks. Therefore, in the most recent works [17] the term $\Delta_c \lambda_j$ is not calculated from the ECS method but from Eq. (9.12) using simplified forms of the functions Ω and Ω_0 .

The basic problem of the ECS modeling technique is *how* to determine the scale factors, or equivalently the shape factors. A first possibility is to assume the same scale factors used for thermodynamic properties; for these, different correlations can be found in the literature, but the frequently adopted way is to obtain them locally solving the equations system [45]:

$$\begin{cases} a_j^R(T,\rho) = a_0^R(T/f_i,\rho h_i) \\ z_j^R(T,\rho) = z_0^R(T/f_i,\rho h_i) \end{cases}$$
(9.29)

as explained in Paragraph 3.6.3. The equations of state for both the target and the reference fluid are required. In this way the method is predictive for transport properties, because it does not require any viscosity or thermal conductivity data; nevertheless, the postulated equivalence between the scale factors for thermodynamic properties and those for transport properties is not verified and this assumption can lead to deviating results depending on the chosen target fluid, as shown in Ref. 42.

To overcome these shortcomings, the scale factors values have to be found from experimental data of the considered transport property for the target fluid. For example, it has been proposed [17,42,44] to introduce a third shape factor, ψ_j for viscosity and χ_j for thermal conductivity, that modifies the reference density, turning Eqs. (9.16) and (9.22) to be respectively:

$$\Delta_E \eta_j(T,\rho) = \Delta_E \eta_0 \left[T / f_j, \rho h_j \psi_j \right] F_\eta$$
(9.30)

$$\Delta_E \lambda_j (T, \rho) = \Delta_E \lambda_0 (T/f_j, \rho h_j \chi_j) F_\lambda$$
(9.31)

where f_j and h_j are still calculated solving Eq. (9.29). For such new shape factors general polynomial forms depending only on density are assumed:

$$\psi_{j}(\rho) = \sum_{k=1}^{n_{\psi}} c_{\psi,k} \left(\frac{\rho}{\rho_{c,j}}\right)^{k} \qquad \chi_{j}(\rho) = \sum_{k=1}^{n_{\chi}} c_{\chi,k} \left(\frac{\rho}{\rho_{c,j}}\right)^{k}$$
(9.32, 9.33)

and the coefficients c_{ψ} and c_{χ} are fitted respectively on viscosity or thermal conductivity experimental data for the target fluid. The application of the ECS method in this form gets acceptable results [17], but it is evidently no more predictive, though maintaining a quite complex formulation. In particular, the solution of the equations system (9.29) is 'straightforward, in principle, but somewhat complicated in practice' [42]. A completely correlative technique, based mainly on experimental evidence rather than on theoretical formulations, has been also presented for viscosity [35,36]. This method integrates the ECS framework with a powerful function approximator in the form of a neural network. It was shown that a single shape factor is sufficient and its analytical expression is obtained as a continuous function, depending on both the variables T and ρ , by regression of the available experimental data.

In this format the reduced viscosity is calculated as:

$$\eta_r = \frac{\eta}{H_c} \tag{9.34}$$

where the reducing parameter is obtained from an equation derived from the dimensional analysis:

$$H_{c} = \frac{M^{1/2} P_{c}^{2/3}}{R_{m}^{1/6} N_{A}^{1/3} T_{c}^{1/6}}$$
(9.35)

The ECS technique is applied to the whole reduced viscosity instead of to the excess part only:

$$\eta_{r,j}(T,\rho) = \eta_{r,0}\left(T\frac{T_{c,0}}{T_{c,j}}\theta_j, \rho\frac{\rho_{c,0}}{\rho_{c,j}}\theta_j\right)$$
(9.36)

For the shape θ_j a functional dependence expressed through a neural network is selected and the application of a regression method on the available viscosity experimental data for the target fluid allows to determine the coefficients and then to dispose of the function $\theta_j = \theta_j(T, \rho)$. The achieved performances are comparable, or even better, with those of the conventional viscosity equations [36]. A similar approach will be applied to thermal conductivity modeling in Chapter X.

MIXTURES

As for pure fluids, the extension of the ECS model to mixtures provides to apply the technique to the excess part of the transport property, while the dilute-gas term is separately calculated; the same Eqs. (9.15), (9.16), (9.20-9.23) are considered. A *one-fluid model* approach is followed, i.e. the equations are applied using mixture scaling factors that are calculated for example from the van der Waals one-fluid mixing rules. For a mixture of *C* pure components, with \mathbf{x} denoting the vector of the molar compositions, it is:

$$h_{M} = \sum_{i=1}^{C} \sum_{j=1}^{C} x_{i} x_{j} h_{ij}$$

$$f_{M} h_{M} = \sum_{i=1}^{C} \sum_{j=1}^{C} x_{i} x_{j} f_{ij} h_{ij}$$
(9.37, 9.38)

with:

$$h_{ij} = \left(\frac{h_i^{1/3} + h_j^{1/3}}{2}\right)^3 \left(1 - l_{ij}\right) \qquad f_{ij} = \sqrt{f_i f_j} \left(1 - k_{ij}\right) \qquad (9.39, 9.40)$$

The pure fluid scaling factors have to be evaluated in condition of conformality with the reference fluid [44]. In Eqs. (9.39) and (9.40) l_{ij} and k_{ij} are adjustable parameters that are either set to zero when the model is used in predictive mode or regressed on experimental data in correlative mode. As an alternative, if a reliable equation of state for the considered mixture would be available the mixture scaling factors could be calculated by solving the equations system:

$$\begin{cases} a_M^R \left(T, \rho, \mathbf{x} \right) = a_0^R \left(T / f_M, \rho h_M \right) \\ z_M^R \left(T, \rho, \mathbf{x} \right) = z_0^R \left(T / f_M, \rho h_M \right) \end{cases}$$
(9.41)

The multipliers F_{η} and F_{λ} in the model equations are substituted by:

$$F_{\eta,M} = f_M^{1/2} h_M^{-2/3} g_{\eta,M}^{1/2} \qquad F_{\lambda,M} = f_M^{1/2} h_M^{-2/3} g_{\lambda,M}^{1/2}$$
(9.42, 9.43)

where $g_{\eta,M}$ and $g_{\lambda,M}$ are the mass reducing ratios, for which several expressions are provided, see for instance Refs. 42 and 44.

Moreover, the mixture viscosity dilute-gas term $\eta_M^o(T, \mathbf{x})$ is required and it can be calculated from kinetic theory [1]; an additional term $\Delta_M \eta(\rho, \mathbf{x})$ is also suggested [46] in order to consider the effects of size and mass differences in the mixture.

For thermal conductivity, the theoretical expressions of the mixture dilute-gas term are very complicated, so empirical mixing rules are used. For instance, in Ref. 44 a quite simple equation for $\lambda_{M,int}^{o}(T, \mathbf{x}) + \lambda_{M,trans}^{o}(T, \mathbf{x})$, based on the Mason and Saxena mixing rules [47], is given. The critical enhancement term is treated in the same way as for pure fluids, also if some shortcomings are introduced [44].

9.3.2. Three-parameter corresponding states

The models based on a three-parameter corresponding states structure, already developed for thermodynamic properties, see for instance Paragraph 3.6.2, have been applied to transport properties too. They work in corresponding states format with a sort of interpolation scheme between two reference fluids through a suitable scaling parameter. Apart from the critical values of temperature and pressure, only one additional parameter is needed for a target pure fluid. Moreover, accurate transport property equations for the reference fluids are required. In the following, the two reference pure fluids are denoted with subscript R1 and R2, while the target pure fluid is indicated with j and the target mixture with M.

The model proposed by Teja and Rice [48] for viscosity uses the acentric factor as scaling parameter and it reads:

$$\ln(\eta_{j}\varepsilon_{j})_{T_{r}} = \ln(\eta_{RI}\varepsilon_{RI})_{T_{r}} + \frac{\omega_{j} - \omega_{RI}}{\omega_{R2} - \omega_{RI}} \left[\ln(\eta_{R2}\varepsilon_{R2})_{T_{r}} - \ln(\eta_{RI}\varepsilon_{RI})_{T_{r}}\right]$$
(9.44)

where:

$$\varepsilon = \frac{v_c^{2/3}}{(T_c M)^{1/2}}$$
(9.45)

The viscosities of the reference fluids are evaluated at the same reduced temperature. The model can be applied also to mixtures using suitable mixing rules for computing the pseudo-critical parameters and the mixture acentric factor.

For thermal conductivity the application of the model is limited to liquid phase [49,50] and its structure is similar:

$$\left(\lambda_{j}\right)_{T_{r}}\phi_{j} = \left(\lambda_{RI}\right)_{T_{r}}\phi_{RI} + \frac{\omega_{j} - \omega_{RI}}{\omega_{R2} - \omega_{RI}}\left[\left(\lambda_{R2}\right)_{T_{r}}\phi_{R2} - \left(\lambda_{RI}\right)_{T_{r}}\phi_{RI}\right]$$
(9.46)

where:

$$\phi = \frac{v_c^{2/3} M^{1/2}}{T_c^{1/2}} \tag{9.47}$$

A modification of these models has been proposed [29-32], in which the scaling parameter is calculated from very few experimental data of the considered transport property for the fluid of interest. Such an approach is similar to that adopted for thermodynamic properties, as explained in Paragraph 3.6.2 (Section: Scalabrin model).

In the viscosity model for pure fluids [29] the reduced viscosity is calculated from Eq. (9.34) with the reducing parameter in Eq. (9.35); the viscosity scaling factor ξ_j is obtained from an experimental point for the target fluid *j* in the condition of saturated liquid at a fixed value of the reduced temperature:

$$\xi_{j} = \left(\log_{10} \eta_{r,j} - \log_{10} \eta_{r,Rf} \right)_{sl,T_{r}=const.}$$
(9.48)

in which subscript *sl* stands for saturated liquid condition and $\eta_{r,Rf}$ denotes the reduced viscosity of the reference fluid *Rf*, calculated from its viscosity equation; the fluid *Rf* can coincide with *R1* or *R2*, but this is not strictly required.

Once the scalar ξ_i has been set up, the viscosity three-parameter model reads:

$$\eta_{r,j}(T_r, P_r) = \eta_{r,RI}(T_r, P_r) + \frac{\xi_j - \xi_{RI}}{\xi_{R2} - \xi_{RI}} [\eta_{r,R2}(T_r, P_r) - \eta_{r,RI}(T_r, P_r)]$$

$$\eta_j(T, P) = H_{c,j} \eta_{r,j}(T_r, P_r)$$
(9.49)

where ξ_{RI} and ξ_{R2} are calculated from Eq. (9.48) for the two reference fluids with the corresponding viscosity equations.

It should be noticed that the model independent variables are the reduced temperature and the reduced pressure; therefore the calculation of the density of the target fluid is avoided when using this model.

For pure fluid thermal conductivity [31] the reduced quantity is calculated from:

$$\lambda_r = \frac{\lambda}{\Lambda_c} \tag{9.50}$$

with the reducing parameter Λ_c derived from the dimensional analysis:

$$\Lambda_c = \frac{R_m^{5/6} P_c^{2/3}}{T_c^{1/6} M^{1/2} N_A^{1/3}}$$
(9.51)

Differently from viscosity, the thermal conductivity model is applied only to the residual part of the reduced property, defined as:

$$\Delta_{R}\lambda_{r}(T_{r},P_{r}) = \frac{\lambda(T,P) - \lambda^{o}(T)}{\Lambda_{c}}$$
(9.52)

An equation for the dilute-gas thermal conductivity of the target fluid is therefore needed and it can be regressed from experimental data in low-density vapor or derived from Eqs. (9.4-9.6). Also in this case the scaling parameter is calculated at saturated liquid condition from an experimental thermal conductivity value. Adopting the same formalism introduced for viscosity, the parameter κ_i is defined as:

$$\kappa_{j} = \left(\Delta_{R}\lambda_{r,j} - \Delta_{R}\lambda_{r,Rf}\right)_{sl,T_{r}=const.}$$
(9.53)

and the model reads:

$$\Delta_{R}\lambda_{r,j}(T_{r},P_{r}) = \Delta_{R}\lambda_{r,RI}(T_{r},P_{r}) + \frac{\kappa_{j} - \kappa_{RI}}{\kappa_{R2} - \kappa_{RI}} \left[\Delta_{R}\lambda_{r,R2}(T_{r},P_{r}) - \Delta_{R}\lambda_{r,RI}(T_{r},P_{r}) \right]$$

$$\lambda_{j}(T,P) = \Lambda_{c,j} \Delta_{R}\lambda_{r,j}(T_{r},P_{r}) + \lambda_{j}^{o}(T_{r})$$

$$(9.54)$$

The thermal conductivity equations for the two reference fluids have to be available, from which also the dilute-gas contributions can be calculated.

The extension of the three-parameter corresponding states models to a mixture of *C* components [30,32] is possible through a rearrangement of the mixing rules of Wong et al. [51], following a *one-fluid model* technique:

$$T_{c,M} / P_{c,M} = \sum_{i=1}^{C} \sum_{j=1}^{C} x_i x_j T_{c,ij} / P_{c,ij}$$

$$T_{c,M}^2 / P_{c,M} = \sum_{i=1}^{C} \sum_{j=1}^{C} x_i x_j T_{c,ij}^2 / P_{c,ij}$$

$$T_{c,ij} = (1 - \varepsilon_{ij}) \sqrt{T_{c,i} T_{c,j}}$$

$$P_{c,ij} = 8T_{c,ij} / \{(1 - \mu_{ij}) [(T_{c,i} / P_{c,i})^{1/3} + (T_{c,j} / P_{c,j})^{1/3}]\}$$

$$\xi_M = \sum_{i=1}^{C} x_i \xi_i \qquad \kappa_M = \sum_{i=1}^{C} x_i \kappa_i$$
(9.55)

The pseudo-critical parameters $T_{c,M}$ and $P_{c,M}$, together with the mixture molar mass:

$$M_{M} = \sum_{i=1}^{C} x_{i} M_{i}$$
(9.56)

enter into Eqs. (9.35) or (9.51) to calculate the reducing parameter of viscosity or thermal conductivity respectively and, moreover, they are used to calculate T_r and P_r . The mixture scaling factors ξ_M and κ_M work as those of pure fluids, for viscosity:

$$\eta_{r,M}(T_{r}, P_{r}, \mathbf{x}) = \eta_{r,RI}(T_{r}, P_{r}) + \frac{\xi_{M} - \xi_{RI}}{\xi_{R2} - \xi_{RI}} [\eta_{r,R2}(T_{r}, P_{r}) - \eta_{r,RI}(T_{r}, P_{r})]$$

$$\eta_{M}(T, P, \mathbf{x}) = H_{c,M} \eta_{r,M}(T_{r}, P_{r}, \mathbf{x})$$
(9.57)

and for thermal conductivity:

$$\Delta_{R}\lambda_{r,M}\left(T_{r},P_{r},\boldsymbol{x}\right) = \Delta_{R}\lambda_{r,RI}\left(T_{r},P_{r}\right) + \frac{\kappa_{M}-\kappa_{RI}}{\kappa_{R2}-\kappa_{RI}}\left[\Delta_{R}\lambda_{r,R2}\left(T_{r},P_{r}\right) - \Delta_{R}\lambda_{r,RI}\left(T_{r},P_{r}\right)\right]$$

$$\lambda_{M}\left(T,P,\boldsymbol{x}\right) = \Lambda_{c,M} \Delta_{R}\lambda_{r,M}\left(T_{r},P_{r},\boldsymbol{x}\right) + \lambda_{M}^{o}\left(T,\boldsymbol{x}\right)$$
(9.58)

For thermal conductivity it is also necessary to separately calculate the dilute-gas term for mixture; the model of Mason et Saxena [47], based on a previous work of Wassiljewa [52], is adopted:

$$\lambda_{M}^{o}\left(T,\boldsymbol{x}\right) = \sum_{i=1}^{C} \frac{x_{i} \lambda_{i}^{o}}{\sum_{j=1}^{C} y_{j} \boldsymbol{\Phi}_{ij}}$$
(9.59)

with:

$$\Phi_{ij} = \frac{\left(1 - \omega_{ij}\right) \left[1 + \left(\lambda_i^o / \lambda_j^o\right)^{1/2} \left(M_i / M_j\right)^{1/4}\right]^2}{\left[8 \left(1 + M_i / M_j\right)\right]^{1/2}}$$
(9.60)

In Eqs. (9.55) and (9.60) the adjustable coefficients ε_{ij} , μ_{ij} and ω_{ij} are set to zero if the method is used in predictive mode; when experimental data are available for the mixture, the coefficients can be regressed on data in order to improve the model performance.

These three-parameter corresponding states models have been applied with satisfactory results to the alkane and haloalkane families.

9.4. Dedicated equations in optimized multiparameter functional form

The Setzmann and Wagner [34] optimization algorithm, that is currently applied for thermodynamic modeling with excellent performances (see Paragraph 3.7), has been used to obtain dedicated transport property equations [53-58] through a completely heuristic technique, setting aside any limiting theoretical formulation and basing the equation functional form directly on the available experimental data.

9.4.1. Bank of terms

The Setzmann and Wagner [34] optimization technique first of all requires a bank of terms from which the elementary functional forms suitable to describe the searched functional dependence are taken out.

In the case of viscosity the effectually adopted bank of terms, composed of a total of 267 terms, can be written as:

$$\eta_r = \sum_{i=0}^{10} \sum_{j=0}^{20} n_{ij} T_r^i \rho_r^j + \sum_{k=0}^{5} \sum_{l=0}^{5} n_{kl} T_r^k \rho_r^l e^{-E\rho_r^2}$$
(9.61)

The value of the exponent E can be set equal to 1 or it can be found with a trial-and-error procedure searching for a further improvement of the obtained equation. The reduced variables in Eq. (9.61) are defined as:

$$T_r = \frac{T}{T_c}$$
 $\rho_r = \frac{\rho}{\rho_c}$ $\eta_r = \ln\left(\frac{\eta}{H_c} + 1\right)$ (9.62, 9.63, 9.64)

Moreover, since viscosity values can span several orders of magnitude from vapor condition to liquid at low temperature and high pressure, the logarithm function is applied to reduced viscosity in order to contain its variation and to facilitate the work of the regression algorithm. Once the functional form has been defined choosing the values of the exponents i, j, k, and l more suitable to represent the searched functional dependence and discarding the not-suitable ones, the coefficients n_{ij} and n_{kl} must be regressed on the experimental data.

In the case of thermal conductivity the modeling problem is greatly complicated by the strong influence of the critical enhancement contribution over a large region around the critical point, see Paragraph 9.2.3; therefore the bank of terms was adapted to the present case with the introduction of a single term specifically studied for the critical enhancement representation.

For the optimization of the functional form a bank of terms composed of a total of 285 terms is used. According to this choice, the most general form of the thermal conductivity equation is written as:

$$\lambda_{r} = \sum_{i=0}^{12} \sum_{j=0}^{10} n_{ij} T_{r}^{i/2} \rho_{r}^{j} + e^{-E\rho_{r}^{2}} \sum_{k=0}^{12} \sum_{l=0}^{10} n_{kl} T_{r}^{k/2} \rho_{r}^{l} + n_{c} \lambda_{r,ce} (T_{r}, \rho_{r}, \boldsymbol{a})$$
(9.65)

with $j \neq 0$ when i = 0, and $l \neq 0$ when k = 0. The term $\lambda_{r,ce}$ is responsible for the critical enhancement contribution and it depends on the set of parameters *a*.

The reduced variables in Eq. (9.65) are the reduced temperature T_r , Eq. (9.62), the reduced density ρ_r , Eq. (9.63) and the reduced thermal conductivity λ_r defined as:

$$\lambda_r = \frac{\lambda}{\Lambda_c} \tag{9.66}$$

For temperature, Eq. (9.62), and density, Eq. (9.63), the corresponding critical values are used as reducing parameters, but the same is not possible for viscosity, Eq. (9.64), and thermal conductivity, Eq. (9.66), since these properties become infinite at the critical point. Therefore, the reducing parameters H_c and Λ_c derived from the dimensional analysis, Eqs (9.35) and (9.51), are considered for viscosity and thermal conductivity respectively.

The representation of the thermal conductivity enhancement in the near-critical region relies on the critical term $\lambda_{r,ce}$, that is expressed as:

$$\lambda_{r,ce}(T_r,\rho_r,\boldsymbol{a}) = \frac{\rho_r e^{-\frac{\rho_r^{a_i}}{a_1} - [a_2(T_r-1)]^2 - [a_3(\rho_r-1)]^2}}{\left\{ \left\{ \left[\left(1 - \frac{1}{T_r}\right) + a_4\left((\rho_r - 1)^2\right)^{\frac{1}{2a_5}}\right]^2 \right\}^{a_6} + \left\{ \left[a_7\left(\rho_r - \alpha\right)\right]^2 \right\}^{a_8} \right\}^{a_9}}$$
(9.67)

in which it is:

$$\alpha = \alpha (T_r) = 1 - a_{10} \operatorname{arccosh} \left(1 + a_{11} \left[(T_r - 1)^2 \right]^{a_{12}} \right)$$
(9.68)

The functional form in Eq. (9.67) has been empirically obtained with a trial-and-error procedure on generated data of the thermal conductivity critical enhancement contribution for different fluids and it was verified that such a form is sufficiently flexible to follow the data trends. Obviously, the parameters a and the multiplying coefficient n_c in Eq. (9.65) have to be regressed on data for the target fluid.

From Eqs. (9.67) and (9.68) it is evident that the term diverges to infinite at the critical point, it is identically null at zero-density conditions and its numerical value decreases with a rate depending on the parameters a as moving away from the critical point.

The purpose of the function α is to allow the term $\lambda_{r,ce}$ to assume, for supercritical isotherms, the maximum value at density different from the critical density, following the trend shown by the experimental data; it is then a sort of 'unsymmetrizing' function with respect to density. The coefficients a_4 and a_5 , similarly with the corresponding parameters of the non-analytical terms for the EoS development [59], should be fitted to data of saturated densities of both vapor and liquid in the vicinity of the critical point.

9.4.2. Fitting procedure and screening of experimental data

Once the bank of terms has been defined, the objective function to minimize can be calculated from the available experimental data of viscosity or thermal conductivity for the target fluid as a function of the equation parameters, representing the vector of the fluid-specific coefficients that have to be fitted in the optimization procedure:

$$\chi^{2} = \sum_{i=1}^{\text{NPT}} \left[\frac{M_{calc} - M_{exp}}{M_{exp}} \right]_{i}^{2}$$
(9.69)

where *M* represents viscosity η or thermal conductivity λ , NPT is the total number of experimental points selected for the regression and the subscripts *calc* and *exp* stand for calculated and experimental values, respectively. In the case of viscosity it is $M_{calc} = \eta_{calc}(\mathbf{n})$ and therefore $\chi^2 = \chi^2(\mathbf{n})$, in the case of thermal conductivity it is $M_{calc} = \lambda_{calc}(\mathbf{n}, \mathbf{a})$ and therefore $\chi^2 = \chi^2(\mathbf{n}, \mathbf{a})$.

The applied minimization technique is the algorithm developed by Setzmann and Wagner [34]: given the bank of terms, the algorithm determines the functional form which yields the best representation of the selected experimental data with the shortest analytical formulation.

Since the data sets have different uncertainty levels and systematic errors could be present, a screening procedure is required in order to identify the *primary* data sources from which the final equation is drawn. The heuristic fitting technique is suitable for this purpose: the screening and the fitting procedure are performed during the development procedure, considering the statistical indexes from Appendix A.6 as a guide.

In the case of viscosity the general form of the obtained equations is expressed as:

$$\eta_r(T_r,\rho_r) = \sum_{i=1}^{I_{pol}} n_i T_r^{t_i} \rho_r^{d_i} + e^{-E\rho_r^2} \sum_{i=I_{pol}+1}^{I_{pol}+I_{exp}} n_i T_r^{t_i} \rho_r^{d_i}$$
(9.70)

In the case of thermal conductivity the general form of the obtained equations can be written as:

$$\lambda_{r}(T_{r},\rho_{r}) = \sum_{i=1}^{I_{pol}} n_{i} T_{r}^{t_{i}} \rho_{r}^{d_{i}} + e^{-E\rho_{r}^{2}} \sum_{i=I_{pol}+1}^{I_{pol}+I_{exp}} n_{i} T_{r}^{t_{i}} \rho_{r}^{d_{i}} + n_{c} \lambda_{r,ce} (T_{r},\rho_{r})$$
(9.71)

The variables in Eqs. (9.70) and (9.71) are defined in Eqs. (9.62-9.64) and (9.66). t_i and d_i are the reduced temperature and reduced density exponents, respectively; they correspond to the

exponents *i*, *j*, *k*, and *l* chosen during the optimization process of the functional form. I_{pol} and I_{exp} represent the number of polynomial and exponential terms, respectively.

Following this approach, dedicated viscosity equations have been developed for R134 [53], propane [54] and R152a [55]; dedicated thermal conductivity equations have been developed for carbon dioxide [56], R134a [57] and R152 [58].

9.5. References

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X. Heuristic thermal conductivity equations in extended corresponding states framework

10.1. Introduction

As discussed in Paragraph 9.3, the simple two-parameter corresponding states principle is not strictly followed when it is applied to transport properties, leading to unacceptable deviations. In order to improve its prediction accuracy, the extended corresponding states model has been introduced also for these properties, distorting the independent variables of a reference fluid equation by means of fluid-specific scale factors.

According to the traditional approach, the scale factors values are obtained from the dedicated equations of state of the target and reference fluids through the application of the local solution procedure in the thermodynamic ECS framework; the same values valid for thermodynamic properties are then assumed for transport properties as well. However, this assumption leads to shortcomings and consequently, trying to correct these further discrepancies, it was proposed to introduce a third shape factor whose functional form has to be regressed on the transport property experimental data.

Since it is not sufficient just to import the thermodynamic scale factors and then experimental data of the considered transport property for the target fluid are unavoidable to acceptably represent the surface, the possibility to apply a completely heuristic modeling technique was also investigated for viscosity representation [1]. A neural network was adopted to heuristically determine the functional form of the viscosity shape factors that carry out the distortion of the variables of the dedicated viscosity equation for the reference fluid. In this way the thermodynamic shape factors were no more required and the viscosity shape factors were directly obtained from viscosity data.

Such a modeling technique, indicated as ECS-NN, has been successfully applied to the representation of the viscosity surfaces of a number of fluids [2]. A single shape function, simultaneously distorting at the same degree the two independent variables, was found to be sufficient in the case of that transport property.

The high quality of the obtained results for viscosity suggests to attempt the application of a similar technique to thermal conductivity. Due to the characteristic behavior of the surface of this property, particularly in the near-critical region, each independent variable has to be distorted with an individual shape function in order to increase the model flexibility in terms of deformation of the thermal conductivity dedicated equation of the reference fluid, allowing the spreading of the equation on the target fluid experimental data.

10.2. Mathematical formulation

Generally speaking, the ECS model is focused on representing the residual part of the considered property, whereas the ideal part has to be separately given; this approach has been maintained also for thermal conductivity:

$$\lambda(T,\rho) = \lambda^{o}(T) + \lambda^{R}(T,\rho)$$
(10.1)

where λ^{o} is the dilute-gas thermal conductivity and λ^{R} is the residual part.

The corresponding states principle requires to operate in reduced variables: for temperature and density the respective critical values are used as reducing parameters, but this is not possible for thermal conductivity since it diverges to infinite at the critical point, see Paragraph 9.2.3. A suitable parameter λ^* , that will be afterwards defined, is assumed for this purpose. Denoting the target fluid with subscript *j* and the reference one with subscript 0, the ECS model for thermal conductivity reads:

$$\frac{\lambda_j^R(T_j,\rho_j)}{\lambda_j^*} = \frac{\lambda_0^R(T_0,\rho_0)}{\lambda_0^*}$$
(10.2)

with the usual ECS relations:

$$T_{0} = T_{j} \frac{T_{c,0}}{T_{c,j}\theta_{j}(T_{j},\rho_{j})} \qquad \rho_{0} = \rho_{j} \frac{\rho_{c,0}}{\rho_{c,j}} \phi_{j}(T_{j},\rho_{j}) \qquad (10.3, 10.4)$$

Given the dedicated thermal conductivity equation for the reference fluid, an expression for the dilute-gas thermal conductivity of the target fluid and the equations for the shape functions θ_j and ϕ_j , the thermal conductivity of the target fluid can be calculated as a function of the independent variables T_j and ρ_j .

In the present work the shape functions are expressed through a multilayer feed-forward neural network, that constitutes a powerful function approximator, see Paragraph 2.2.2. The network coefficients are regressed on thermal conductivity data for the target fluid analogously to the ECS-NN and EEoS-NN models presented in Paragraph 3.6.4 and in Chapter IV, respectively.

In order to make easier the work of the adopted mathematical regression method, the output variables of the neural network do not directly represent the shape functions, but two auxiliary quantities $\tilde{\theta}_j$ and $\tilde{\phi}_j$ related to the shape functions through:

$$\theta_{j}(T_{j},\rho_{j}) = \left[\tilde{\theta}_{j}(T_{j},\rho_{j})\right]^{a} \qquad \phi_{j}(T_{j},\rho_{j}) = \left[\tilde{\phi}_{j}(T_{j},\rho_{j})\right]^{b} \qquad (10.5, 10.6)$$

The exponents *a* and *b* have to be found with a trial-and-error procedure; it was verified that the values a = 2 and b = 3 are suitable for all the fluids here considered.

Recovering the mathematical formalism of neural networks given in Paragraph 2.2.2 and in Appendix A.1, the network structure is defined as:

$$I = 3 V_1 = T_{r,j} = \frac{T_j}{T_{c,j}} V_2 = \rho_{r,j} = \frac{\rho_j}{\rho_{c,j}} (10.7, 10.8, 10.9)$$

$$K = 2$$
 $W_1 = \tilde{\theta}_j$ $W_2 = \tilde{\phi}_j$ (10.10, 10.11, 10.12)

$$Bias1 = 1.0$$
 $Bias2 = 1.0$ (10.13, 10.14)

The number of neurons in the hidden layer J has been here chosen equal to 8, but this is an indicative value that can be varied according to the difficulties posed by the specific problem; the lowest and the highest values of the input and output physical variables, that are required for the linear scaling of the neural network variables, depend both on the target fluid and on the selected validity ranges.

A transfer function in the form of normalized scaled arctangent, Eq. (2.12), was assumed for the present work with $\gamma = 1$. The observance of the theoretical behavior at the critical point for the target fluid equation has been obtained by imposing to the regression algorithm the constraints:

$$\theta_i \left(T_{c,i}, \rho_{c,i} \right) = 1 \tag{10.15}$$

$$\phi_j(T_{c,j}, \rho_{c,j}) = 1 \tag{10.16}$$

With these constraints the critical points of target and reference fluids correspond each other, see Eqs. (10.3) and (10.4), and consequently also the obtained target fluid equation correctly represents the divergence at the critical point, provided that the reference equation supports such a behavior for the reference fluid.

For the thermal conductivity reducing parameter λ^* the same value from dimensional analysis used in the previous chapter, Eq. (9.51), was initially assumed, but it was verified that the residual thermal conductivity functions of the fluids considered in this work, when reduced by the Λ_c values, are far from satisfying the corresponding states principle, making less favourable the modeling technique application. Therefore, a new reducing factor $\tilde{\Lambda}_c$ obtained from a single experimental value at arbitrary conditions is proposed; in this work the parameter was evaluated for all the fluids at $T_r = 1.1$ and $\rho_r = 1.6$ as:

$$\lambda^* = \widetilde{\Lambda}_c = \left[\frac{\lambda^R(T_r, \rho_r)}{20}\right]_{\substack{T_r = 1.1\\\rho_r = 1.6}}$$
(10.17)

Moreover, it was here calculated for each fluid from its previously available dedicated thermal conductivity equation in order to avoid the experimental error effect, but in principle it can be obtained from an experimental point of the target fluid even at conditions different from those suggested; the corresponding value for the reference fluid is evaluated from its thermal conductivity equation, that is anyway required. The division by 20 of the residual thermal conductivity value in Eq. (10.17) has the only purpose to give a $\tilde{\Lambda}_c$ parameter with the same magnitude order of the former Λ_c . A certain degree of conformality is in this way attained, as shown in Fig. 10.1 where an isothermal line is plotted for different fluids at the same reduced temperature; the lines are calculated from the respective dedicated thermal conductivity equations [3-8].



Figure 10.1: Deviation from the corresponding states principle for a group of fluids at the same reduced temperature.

It is worth noticing that, since an equation representing the thermal conductivity of a pure fluid is required to simultaneously represent both the vapor and the liquid region and the thermal conductivity has a low sensitivity to pressure in the liquid phase, so a thermal conductivity equation is usually written in terms of T, ρ variables. The actual variables of the thermal conductivity experimental data are T, P, then a DEoS for the target fluid is needed for the conversion to T, ρ dependence; the following equation system is then set up:

$$\begin{cases} \lambda = \lambda(T, P) \\ P = P(T, \rho) \end{cases}$$
 (10.18)

from which the $\lambda = \lambda(T, \rho)$ format is obtained.

10.3. Application to generated data

In a first step the model capability has been tested assuming data generated from the dedicated thermal conductivity equations of the studied fluids, with the purpose to evaluate the performance of the proposed method in an 'aseptic' condition. The generated data have been considered as pseudo-experimental data; in this way the results are independent from any experimental uncertainty and uneven distribution in the range of interest.

The fluid R134a has been selected as reference, while R152a, carbon dioxide, ammonia, ethane and oxygen have been considered as target fluids. Conventional dedicated equations from the literature have been assumed for ammonia [6], ethane [7] and oxygen [8]; dedicated equations in optimized functional form, see Paragraph 9.4, have been adopted for R134a [9], R152a [10] and carbon dioxide [11].

Table 10.1 reports the critical values of the selected fluids and the λ^* coefficients obtained from Eq. (10.17) using the dedicated equations to calculate the required quantity.

Table 10.1: Reducing parameters for the considered fluids.

Fluid	<i>T</i> _c (K)	$ ho_c$ (kg m ⁻³)	λ^* , Eq. (10.17) (mW m ⁻¹ K ⁻¹)
R134a	374.274	515.25	1.6305
R152a	386.411	368.0	2.1552
CO_2	304.1282	467.6	3.1707
NH_3	405.4	225.0	9.1763
C_2H_6	305.33	206.584	2.5313
O_2	154.581	436.1436	2.5110

A wide set of thermal conductivity points has been generated for each fluid on a regular grid covering the whole validity range of its dedicated equation; the training data points have been regularly extracted from this grid.

The regression of the shape functions $\theta_j(T_r, \rho_r)$ and $\phi_j(T_r, \rho_r)$ is carried out minimizing the objective function:

$$f_{ob}\left(\boldsymbol{w}\right) = \frac{1}{\text{NPT}} \sum_{i=1}^{\text{NPT}} \left[\frac{\lambda_{j,calc}^{R}\left(T_{r}, \rho_{r}, \boldsymbol{w}\right) - \lambda_{j,exp}^{R}}{\lambda_{j,exp}} \right]_{i}^{2}$$
(10.19)

where the subscripts *calc* and *exp* stand for values calculated from the ECS-NN model and generated from the dedicated equation, respectively; w is the set of neural network parameters that have to be regressed.

The results of the regressions are given in Table 10.2 in terms of the statistical indexes defined in Appendix A.6. For all the fluids, the AAD of the residual error for the training set is quite similar to that of the prediction error for the whole data set; these values are very good, being limited to few parts per thousand, and they are lower than the estimated experimental uncertainty for thermal conductivity measurements. The Bias values, being close to zero, assure the absence of a systematic shifting of the obtained surfaces. The highest errors are localized in the near-critical area, where the sensitivity to the independent variables is by far increased, due to the particular trend of the thermal conductivity in that region.

Table 10.2: Training and validation results of the thermal conductivity ECS-NN models for R152a, CO_2 , NH₃, C_2H_6 and O_2 .

		Traini	ng set			Whole data set			
Fluid	NPT	AAD	Bias	MAD	NPT	AAD	Bias	MAD	
		%	%	%		%	%	%	
R152a	540	0.27	-0.01	2.12	12207	0.32	0.01	9.87	
CO_2	781	0.26	0.04	2.56	10349	0.30	0.04	14.61	
NH ₃	525	0.29	0.03	2.64	13867	0.32	0.05	18.75	
C_2H_6	538	0.32	-0.01	2.65	13149	0.33	-0.03	13.15	
O_2	673	0.16	0.01	2.05	15459	0.18	0.00	18.60	



Figure 10.2: Representation of the surface of the shape function θ for the ECS-NN thermal conductivity model for R152a.



Figure 10.3: Representation of the surface of the shape function ϕ for the ECS-NN thermal conductivity model for R152a.

The surfaces of the shape functions θ and ϕ produced through the neural network technique are very smooth and regular, with limited deviations from 1 as it is shown for R152a in Figs. 10.2 and 10.3. All these features demonstrate the potential of the present modeling technique for dedicated thermal conductivity equation development.

The question of the possible reduction of the number of points in the training data set has been also investigated. This aspect is of great importance in order to determine the lowest number of experimental measurements required for developing a dedicated thermal conductivity equation with high accuracy. Carbon dioxide has been assumed as test fluid. The number of points in the training set has been progressively reduced, each time regressing a new equation; the validation has been done on the whole generated data set, with the results reported in Table 10.3 and Fig. 10.4.

It appears that the prediction accuracy of the equation with respect to the whole data set is not compromised at about two hundred data points. This test suggests that a similar amount of accurate and regularly distributed points on the whole T, ρ domain could be a sufficient input for training the neural shape functions $\theta(T, \rho)$ and $\phi(T, \rho)$, obtaining in this way a dedicated thermal conductivity equation. Therefore the present ECS-NN technique allows the limitation of the experimental effort, while achieving at the same time high accuracies.

Table 10.3: Variation of the accuracy of the thermal conductivity ECS-NN model for carbon dioxide as varying the number of points in the training set.

	Train	ing set			Whole data set					
NPT	AAD	Bias	MAD	NPT	AAD	Bias	MAD			
	%	%	%		%	%	%			
781	0.26	0.04	2.56	10349	0.29	0.04	14.61			
451	0.20	0.01	2.84	10349	0.24	0.00	15.25			
319	0.17	0.01	1.28	10349	0.21	0.03	13.61			
253	0.14	0.00	0.87	10349	0.21	0.06	28.77			
192	0.12	0.01	1.04	10349	0.23	0.08	33.83			



Figure 10.4: AAD for training and validation set for carbon dioxide as varying the number of points in the training set.

10.4. Application to experimental data

The very promising results obtained in the previous Paragraph 10.3 suggest to move from generated to experimental data correlation to develop dedicated thermal conductivity equations. The present procedure was then applied to R152a and CO₂, assuming R134a as the reference fluid. The dedicated thermal conductivity equation selected for the reference fluid [9] is completely heuristic and it has an optimized multiparameter functional form as presented in Paragraph 9.4. Dedicated equations of state (DEoS) for the interest fluids are also needed for the conversion of the independent variables of the experimental data from T, P into T, ρ . On the other hand an equation of state is not required for the reference fluid.

The proposed technique is addressed to model the residual thermal conductivity of a target fluid, whereas the dilute-gas term has to be separately given. Such part was obtained for each considered fluid from former works dealing with non-conventional thermal conductivity equations [9,10,11]. A general form for the adopted dilute-gas equations is:

$$\lambda^{o}(T) = \Lambda_{c} \sum_{i=1}^{N_{terms}} n_{i} \left(\frac{T}{T_{c}}\right)^{t_{i}}$$
(10.20)

where N_{terms} is the number of terms of the summation. The individual coefficients are given in Table 10.4. The residual part for the reference fluid R134a has been calculated in the present work as the difference between the thermal conductivity equation in Ref. 9 and the dilute-gas part from Eq. (10.20).

Table 10.4: Parameters of the individual dilute-gas equations, Eq. (10.20), for the considered fluids.

	R13-	4a	R152a					CO ₂				
	T_c (K)	374.274		T_c (K)		386.411		T_c (K)			304.128	32
Λ_c	$(mW m^{-1} k$	(x^{-1}) 2.0547	Λ_c (1	$mW m^{-1}$	K^{-1})	2.72640	Λ	, (mW	m ⁻¹	K ⁻¹)	4.81384	4
	N_{terms}	3		N_{terms}		2		N_{t}	erms		3	
i	t_i	n _i	i	t _i		n _i	i		t_i		n_i	
1	1	6.544680	1	1.5	2.	110725	1		1.5	3	.715549	
2	5.5	13.07277	2	2	6.	016495	2		3.5	-().365989	
3	6	-10.06224					3		4	0	.131464	

Since the ECS-NN model relies on experimental data, the ranges covered by them directly give the ranges of validity of the individual thermal conductivity equation obtained through the technique; these ones are reported for both the target fluids in Table 10.5 together with the molar mass and the reducing parameters for the fluids themselves.

Table 10.5: Parameters and validity ranges of the individual ECS-NN models for thermal conductivity for the studied fluids.

Fluid	М	Т	Р	0	2^* Eq. (10.17)	Validity ranges		
Tiulu	171	1 c	1 c	P_c	λ , Eq. (10.17)	T	Р	
	(kg kmol ⁻¹)	(K)	(MPa)	(kg m^{-3})	$(mW m^{-1} K^{-1})$	(K)	(MPa)	
R152a	66.051	386.411	4.5200	368.0	2.155178	220-460	≤50	
CO_2	44.098	304.1282	7.3773	467.6	3.170663	186-1300	≤209.7	

All the available data for each fluid were collected from the literature and they were at first tested against the corresponding conventional thermal conductivity equation, i.e., the equation from Krauss et al. [4] for R152a and the one from Vesovic et al. [5] for CO_2 . Only the data sets with

overall deviations lower than 5 % were retained after this check. The data screened in this way were considered as *primitive* and a first version of the shape functions neural network was regressed from these data. This led to the first ECS-NN model which was tested against the primitive data.

Excluding the data sets with deviations higher than $2\div3$ %, especially if falling in a T, ρ region where more precise data are also available, a finer screening was iteratively done to identify the *primary* data subset, on which the final model was fitted. The data sets not adopted for the regression are considered as *secondary* sources and they have been used only for validation. Even if the separation of the single points of each data source into primary and secondary classes would be also possible using the present correlative technique, it was decided not to screen inside the individual data sources but to treat each of them as a whole.

Anyway, particularly for CO₂ some data sets with few points and in T, ρ regions already covered by other primary data were put into the secondary group even if they showed a precision comparable with the primary group of data; this allows to include some precise data for validation.

In the following the validations of the obtained equations with respect to experimental data are presented with the statistical indexes given in Appendix A.6.

Moreover, it is worth noting that all over the represented λ , ρ , T surface of a target fluid, including also the near-critical region, the present ECS-NN model expresses the thermal conductivity as an explicit function of the independent variables and this allows a very plain calculation without any of the cumbersome and misleading iterations characterizing the conventional critical enhancement models [3-5]. This is furthermore consistent considering that also for the thermal conductivity dedicated equation of the reference fluid an explicit function all over the λ , ρ , T surface is assumed [9].

10.4.1. R152a

As discussed before, a DEoS is needed for each target fluid for the conversion from T, P to T, ρ of the variables of the experimental measurements. For this goal in the case of the fluid R152a a fundamental DEoS [12] is used. That equation is effective all over the P, ρ, T domain but not in the near-critical region; therefore, a crossover model [13], based on the Sengers and coworkers theory, is combined with the DEoS to describe the thermodynamic behavior in such region. A similar model was also applied for the case of the conventional thermal conductivity equation [4]. It is stressed again that a DEoS is not necessary for the reference fluid R134a.

The MLFN parameters of the shape functions $\theta(T_r, \rho_r)$ and $\phi(T_r, \rho_r)$ for R152a are reported in Table 10.6 and the results obtained from the proposed model are shown in Table 10.7 for data in the liquid, vapor and supercritical regions.

R152a										
i	j	$\overline{w_{ij}}$	j	k	W _{jk}					
1	1	7.7676440	1	1	-1.6295664					
2	1	-6.3957480	2	1	1.2090802					
3	1	1.6864250	3	1	2.5624223					
1	2	1.2921719	4	1	2.4191014					
2	2	-1.8568936	5	1	-2.2880217					
3	2	1.1571883	6	1	2.8436492					
1	3	-4.2683402	7	1	-2.6995633					
2	3	16.222314	8	1	-1.1956900					
3	3	-6.9110329	9	1	-0.69523445					
1	4	-1.9353485	1	2	1.9184381					
2	4	-17.295467	2	2	1.9393159					
3	4	8.1299694	3	2	-0.096957909					
1	5	0.27037786	4	2	-0.57203386					
2	5	10.736104	5	2	-5.9905895					
3	5	0.89373767	6	2	-3.2926137					
1	6	3.4845624	7	2	1.5416576					
2	6	5.3064461	8	2	5.1852922					
3	6	-0.75659577	9	2	2.3020135					
1	7	0.54875912								
2	7	2.5866205								
3	7	-1.5484573								
1	8	-4.0566160								
2	8	3.1769069								
3	8	-0.02.1280748								
		$V_{\min,1} \equiv T_r^{\min}$			0.5					
		$V_{\max,1} \equiv T_r^{\max}$			5.0					
		$V_{\min,2} \equiv \rho_r^{\min}$			0.0					
		$V_{\max,2} \equiv \rho_r^{\max}$			3.0					
		$W_{min,1} \equiv \theta^{min}$			0.7					
		$W_{max,1} \equiv \theta^{max}$			1.3					
		$W_{min,2} \equiv \phi^{min}$			0.7					
		$W_{max,2} \equiv \phi^{max}$			1.3					
		J			8					

Table 10.6: Parameters of the ECS–NN thermal conductivity equation for R152a.

The results of the screening procedure, i.e. the final classification of the data sources as primary or secondary, are also indicated. The last column of the table gives the values of uncertainty of the primary data sets that were reported by the experimenters and that have been adopted for the weighting of data in the objective function, Eq. (10.21).

$$f_{ob}\left(\boldsymbol{w}\right) = \frac{1}{NPT} \sum_{i=1}^{NPT} \left[\frac{100}{u_{\%}} \frac{\lambda_{j,calc}^{R}\left(\boldsymbol{T}_{r},\boldsymbol{\rho}_{r},\boldsymbol{w}\right) - \lambda_{j,exp}^{R}}{\lambda_{j,exp}} \right]_{i}^{2}$$
(10.21)

where $u_{\%}$ is the uncertainty of the point in percent.

Table 10.7: Deviations of the thermal conductivity ECS-NN equation for R152a with respect to primary, secondary and overall data in liquid, vapor and supercritical regions.

Pof	First Author	Dhase ^a	NDT	T range	P range	AAD	Bias	MAD	u
Kel.	Thist Author	1 mase	111 1	(K)	(MPa)	%	%	%	%
			Li	iquid region					
15	Assael	1	37	253-333	0.5 - 22.4	0.51	0.02	1.05	0.5
16	Geller	1	108	306-382	1.1–6.9	1.26	-0.79	7.55	2.0
17	Gross	1	44	253-363	0.2-6.2	2.50	-2.50	4.89	1.6
18	Gurova	1	31	224-294	0.8 - 18.0	1.75	1.75	3.11	0.5
19	Kim	1	25	223-323	2.1 - 20.1	0.59	0.03	1.08	2.0
20	Tsvetkov	1	8	221-300	7.7-8.6	2.21	-2.21	3.39	2.0
21	Vargaftik	1	33	305-380	1.1 - 4.0	1.35	-1.29	3.70	-
22	Le Neindre	1	238	307-378	1.0 - 50.0	0.68	-0.57	1.93	1.5
15	Assael	sl	5	253-333	0.1 - 1.5	0.63	0.08	1.09	0.5
18	Gurova	sl	4	224-294	0.0-0.5	1.52	1.52	2.38	0.5
19	Kim	sl	5	223-323	0.0-1.2	0.60	-0.37	1.58	2.0
	Primary data		538			1.06	-0.62	_	-
23	Grebenkov	1	72	294-381	0.8-20.0	4.74	4.74	10.30	_
24	Kruppa	1	27	367-386	3.5-11.4	7.70	4.85	18.50	_
25	Yata	1	20	266-343	1.4-30.6	3.42	1.59	7.64	_
26	Gross	sl	24	253-313	0.1-0.9	4.12	-4.12	6.60	_
24	Kruppa	sl	49	293-386	0.5-4.5	12.02	-9.39	58.92	_
27	Kraft	sl	16	279-386	0.3–4.5	6.18	-0.86	32.76	_
	Total data		746			2.65	-0.54	_	-
			V	apor region					
28	Afshar	v	10	280-460	0.1	2.22	-0.66	3.81	3.0
16	Geller	v	19	305-433	0.1	0.88	-0.23	4.07	2.0
17	Gross	v	40	254-354	0.1-2.3	1.72	-1.40	4.73	2.0
24	Kruppa	v	46	367-425	2.2-4.5	3.27	0.25	10.09	5.0
29	Taxis-Reischl	v	54	277-400	0.0 - 2.4	1.45	-0.91	5.20	1.0
21	Vargaftik	V	10	280-460	0.2	2.36	2.36	4.82	-

Pof	First Author	Dhase ^a	NPT	T range	P range	AAD	Bias	MAD	u	
Kel.	First Aution	Fliase	INF I	(K)	(MPa)	%	%	%	%	
Vapor region (continuation)										
22	Le Neindre	v	48	298-456	0.1–4.5	1.96	0.07	8.91	1.5	
	Primary data		227			2.00	-0.34	_		
30	Hammerschmidt	v	4	303-423	0.1	4.62	-3.72	8.33	_	
31	Yin	v	14	279-349	0.1	6.98	6.98	8.58	_	
24	Kruppa	sv	30	348-386	2.1 - 4.5	11.07	7.99	44.46	_	
27	Kraft	SV	6	360-386	2.7 - 4.5	7.24	-7.24	32.41	_	
	Total data		281			3.37	0.72	_	_	
			Supe	rcritical regi	on					
24	Kruppa	SC	103	387-426	4.5-10.9	2.40	1.33	9.05	5.0	
22	Le Neindre	SC	108	391–455	5.0-41.0	1.36	-0.43	6.53	1.5	
	Primary data		211			1.87	0.43	_		
23	Grebenkov	SC	6	398–399	10.0-20.0	7.69	7.69	9.03	_	
	Total data		217			2.03	0.63	_	_	
				Overall						
	Overall primary		976			1.45	-0.33	_	-	
	Overall		1244			2.70	-0.05	_	_	

^a *Phase*: l = liquid, sc = supercritical region, sl = saturated liquid, sv = saturated vapor, v = vapor, zd = vapor at zero-density limit.

It can be noted that the most precise data sources are classified as primary, whereas the secondary sets show considerable inconsistencies with the other data sets, as it is shown by their large AAD and Bias values. The data from Kruppa and Straub [24] for vapor and supercritical regions have been included into the primary sources in spite of their high uncertainty level. In fact that source is the only one reporting a certain number of data in the near-critical region and then it cannot be set aside.

The overall AAD value for primary data is 1.31 %, whereas the corresponding value for the training set of generated data was 0.27 %, see Tab. 10.2. As a consequence of the procedure followed in this work, according to which the model was at first applied to generated data for testing purposes and then to primary experimental data for drawing the thermal conductivity equation, it is possible to claim that the lower performance in this second case is essentially due to the intrinsic quality of the experimental data and in particular to their error noise.

The bias values are very close to zero for the vapor and supercritical regions, whereas they are a little worse for the liquid region showing that here the thermal conductivity surface results in a slight shifting with respect to the data. This can be due to a certain lack of coherence among those data sets superimposing in this region as it can be verified looking at the Fig. 10.5.



Figure 10.5: Representation of the primary data points of R152a on the T, P plane.

A choice has necessarily to be done weighting the data sets for the regression according to the claimed experimental uncertainty of the sources involved. The Table 10.7 indicates that in particular the sets of Refs. 15 and 19 are represented with a better accuracy, whereas the data from Ref. 18, even if claimed with a low value of uncertainty, are represented in a slightly worse way, see also Fig. 10.6. On the other hand similar trends can be verified for the conventional equation [4] with respect to the same sets as shown in Table 10.8. The range of validity considered in such table is that of the conventional model, that is the narrower one between the two models, in order to allow a rigorous comparison of the results. Because of the smaller base of data, the results for the ECS-NN model are different from those of Table 10.7.



Figure 10.6: Deviations of primary experimental data in the liquid region from the thermal conductivity ECS-NN model for R152a.

In the vapor region the data set from Ref. 29 is composed of points distributed on the most part of the vapor region and the source claims furthermore a lower uncertainty with respect to the other sets. These data are then the main guide for the ECS-NN surface in this region, in fact they are well represented by the present equation; similar results are obtained by the conventional equation. At the lower pressure four data sets are superimposing and with a rather low level of relative consistency as it is also shown in Fig. 10.7.

			E	S NN mo	dal	Conventional eq.			
Ref	First Author	NPT	EV	S-ININ IIIO	uei	Krauss et al. [4]			
Kel.	Thist Author	111 1	AAD	Bias	MAD	AAD	Bias	MAD	
			%	%	%	%	%	%	
			Primary	y liquid reg	gion				
15	Assael	33	0.51	0.02	1.05	0.72	-0.71	1.46	
16	Geller	108	1.26	-0.79	7.55	3.58	-3.58	11.21	
17	Gross	44	2.50	-2.50	4.89	3.37	-3.37	4.86	
18	Gurova	23	1.82	1.82	3.11	1.50	1.48	3.05	
19	Kim	16	0.50	0.22	1.08	0.57	-0.35	2.03	
20	Tsvetkov	6	1.90	-1.90	2.59	2.17	-2.17	2.68	
21	Vargaftik	33	1.35	-1.29	3.70	2.62	-2.62	6.84	
22	Le Neindre	96	0.88	-0.75	1.93	2.05	-2.05	6.61	
15	Assael	5	0.63	0.08	1.09	0.64	-0.64	1.07	
18	Gurova	3	1.56	1.56	2.38	1.09	1.09	1.84	
19	Kim	4	0.55	-0.26	1.58	1.05	-0.85	2.55	
	Overall	371	1.25	-0.73	_	2.45	-2.24	_	
			Primar	v vapor reg	tion				
28	Afshar	9	2.04	-1.16	3.03	1.13	0.50	2.39	
16	Geller	19	0.88	-0.23	4.07	3.31	2.36	4.23	
17	Gross	40	1.72	-1.40	4.73	2.62	-0.90	8.89	
24	Kruppa	46	3.27	0.25	10.09	3.66	-0.18	11.83	
29	Taxis-Reischl	54	1.45	-0.91	5.20	1.26	-0.10	6.34	
21	Vargaftik	9	2.16	2.16	4.82	3.53	3.53	4.95	
22	Le Neindre	37	2.28	-0.10	8.91	2.80	0.71	11.64	
	Overall	214	2.04	-0.43	_	2.57	0.27	_	
]	Primary su	percritical	region				
24	Kruppa	103	2.40	1.33	9.05	2.89	0.65	8.71	
22	Le Neindre	31	1.60	-0.56	4.93	3.47	-3.11	6.47	
	Overall	134	2.22	0.89	_	3.02	-0.22	_	
			Over	all primar	V				
	Overall	719	1.66	-0.34	_	2.59	-1.12	_	
		r	Fotal prima	ary and sec	condary				
	Liquid	569	3.22	-0.63	_	3.22	-1.32	_	
	Vapor	268	3.46	0.69	_	4.35	2.15	_	
S	upercritical	140	2.45	1.18	_	3.12	0.01	_	
~~	Total	977	3.18	0.00	_	3.52	-0.18	_	

Table 10.8: Performance comparison among the present ECS-NN model and the conventionalmodel [4] for the fluid R152a.

In Fig. 10.8 the error deviations in the supercritical region are exposed. Here the data sets of Ref. 22 are very well spread on the domain almost without the coexistence of other sources, Fig. 10.5. Even if these data are claimed with a modest uncertainty the thermal conductivity surface has necessarily to be based on these points. The near-critical region requires a very accurate representation due to the strong variation of the thermal conductivity gradients and here the points from Ref. 24 are the only source available as shown in Fig. 10.9. The present model shows a trend which is basically in agreement with that of the conventional equation but the ECS-NN equation shows a better performance for the single points.



Figure 10.7: Deviations of primary experimental data in the vapor region from the thermal conductivity ECS-NN model for R152a.


Figure 10.8: Deviations of primary experimental data in the supercritical region from the thermal conductivity ECS-NN model for R152a.



Figure 10.9: Isotherms in the near-critical region of R152a generated from the ECS-NN model and from the conventional equation [4]; data from Kruppa et al. [24].

10.4.2. Carbon dioxide

For carbon dioxide the variables conversion from T, P to T, ρ for the experimental data was performed using the multiparameter equation of state from Ref. 14.

The first choice of primary data for this fluid was done considering the same data sets used in the development of the conventional equation of Vesovic et al. [5]: the data of Michels et al. [33], Le Neindre et al. [34,35,36], Dickins [48], Johnston and Grilly [49], Lenoir and Comings [50], Snel et al. [53], Clifford et al. [54], Scott et al. [55], Millat et al. [56], Keyes [57], Johns et al. [58], Franck [66]. The same values of experimental uncertainty adopted by Vesovic et al. were assumed. Since no relevant experimental source has been published after the development of the conventional equation, the analysis of the data sources done by Vesovic et al was exploited here as well.

After the first application of the regression algorithm the deviations of the experimental data from the obtained equation were calculated. It was evidenced that the data of Franck [66] have a lower accuracy compared to the other sources and this set was then moved to secondary data.

Moreover, the data of Le Neindre et al. [34,35,36] in the vapor phase showed inconsistencies and systematic shifting with respect to the other data sets. It was therefore decided to consider as primary data for the vapor phase only the points of Le Neindre et al. [35] for temperatures greater than 450 K, i.e., for the region scarcely cover by other experimental sources.

After a new regression on the modified set of primary data it was found that some secondary data sets in regions with few primary experimental data show deviations from the equation with an acceptable level. These are the data in the liquid region from Sellschopp [32] and from Salmanov and Tarzimanov [37], the vapor phase data from Bakulin et al. [51,52], and the data from Tarzimanov and Arslanov [38] for the liquid and supercritical regions. These data sets were included in the set of the primary sources assuming an uncertainty of 5 %.

It was also found that the vapor phase data from Michels et al. [33], indicated as 'near the coexistence line' in the original paper, have a lower quality compared to the others from the same source and these data have consequently been excluded from the set of primary data.

The distribution of the primary data points is shown in Fig. 10.10 where it can be seen that in the near-critical region there is a high concentration of values.



Figure 10.10: Representation of the primary data points of carbon dioxide on the T, P plane.

The coefficients of the neural functions $\theta(T_r, \rho_r)$ and $\phi(T_r, \rho_r)$ obtained from regression on the final selection of primary data are given in Table 10.9, while Table 10.10 reports the results of such ECS-NN model with respect to data in the liquid, vapor and supercritical regions. The final classification of the data sources as primary or secondary is also shown and in the last column the ascribed uncertainties of the primary sets are indicated.

Table 10.9: Parameters of the ECS-NN thermal conductivity equation for CO₂.

	CO_2							
i	j	W_{ij}	j	k	${\cal W}_{jk}$			
1	1	0.15500147	1	1	692.36842			
2	1	0.32909076	2	1	-3.6838585			
3	1	-4.6763011	3	1	-48.693328			
1	2	13.321343	4	1	22.364102			
2	2	2.4948783	5	1	-3.0464260			
3	2	-3.0369459	6	1	2.0145230			
1	3	-8.7841547	7	1	-1.9261433			
2	3	5.5795451	1	2	11.679066			
3	3	4.4938050	2	2	5.9962107			
1	4	24.765439	3	2	-13.776280			
2	4	5.7162171	4	2	-1.3555306			
3	4	-15.653981	5	2	-7.8192196			
1	5	2.1303984	6	2	-8.8522691			
2	5	-6.0650493	7	2	15.437907			
3	5	-0.68672137						
1	6	12.378067						
2	6	2.3068601						
3	6	-2.4562782						
		$V_{min,1} \equiv T_r^{min}$			0.5			
		$V_{max,1} \equiv T_r^{max}$			5.0			
		$V_{min,2} \equiv \rho_r^{min}$			0.0			
		$V_{max,2} \equiv \rho_r^{max}$			3.0			
		$W_{min,1} \equiv \theta^{min}$			0.7			
		$W_{max,1} \equiv \theta^{max}$			1.3			
		$W_{min,2} \equiv \phi^{min}$			0.7			
		$W_{max,2} \equiv \phi^{max}$			1.3			
		J			6			

Ref.	First Author	Phase ^a	NPT	T range	P range	AAD	Bias	MAD	u
				(K)	(MPa)	%	%	%	%
	Liquid region								
32	Sellschopp	l	22	285-304	5.7–9.0	2.05	-1.67	3.32	5.0
33	Michels	l	14	298-303	6.4–134.4	0.52	0.02	1.25	2.0
34	Le Neindre	l	13	295-304	10.7–104.1	1.21	1.21	2.11	5.0
35	Le Neindre	l	6	296-304	21.1-81.1	0.62	0.21	1.00	5.0
36	Le Neindre	1	10	298	10.0-110.0	0.41	-0.10	0.94	5.0
37	Salmanov	1	19	222–282	2.0 - 9.0	0.88	0.33	2.56	5.0
38	Tarzimanov	1	11	297-304	29.4–196.0	0.90	0.49	1.52	5.0
P	rimary data		95			1.08	-0.08	_	_
39	Borosvik	1	9	283-303	5.1–9.1	3.79	-3.79	7.26	_
40	Keyes	1	1	274	5.8	3.05	-3.05	3.05	_
41	Guildner	1	4	277-299	4.5-7.7	1.13	1.13	2.21	_
42	Paul	1	5	298	6.6-30.7	1.32	1.32	2.27	_
43	Becker	1	19	298	6.6-40.1	2.02	0.78	6.24	_
44	Koch	1	18	283-303	5.1-9.1	2.17	-2.17	4.32	_
45	Tarzimanov	1	4	299–299	10.1-81.0	0.87	-0.87	1.32	_
46	Shingarev	1	17	231-303	5.8-20.3	3.78	-2.01	12.95	_
47	Amirkhanov	sl	90	293-303	5.7-7.2	8.92	-7.20	42.30	_
44	Koch	sl	8	283-303	4.5-7.2	5.82	-5.5	28.71	_
	Total data 270					4.24	-2.92	_	_
				Vapor reg	gion				
48	Dickins	zd	1	285	0.0	0.24	-0.24	0.24	1.0
49	Johnston	zd	14	186-379	0.0	0.94	0.94	3.33	1.0
50	Lenoir	v	12	314-340	0.1-6.8	1.84	1.84	5.01	1.0
33	Michels	v	71	298-348	0.1 - 7.4	1.34	0.44	5.11	2.0
35	Le Neindre	v	70	456–961	0.1 - 7.1	2.32	-2.11	6.09	5.0
51	Bakulin	v	28	225-316	0.1 - 2.0	1.17	0.29	5.09	5.0
52	Bakulin	v	10	400-900	0.1	0.94	-0.03	2.10	5.0
53	Snel	v	133	298-323	0.0 - 5.5	1.06	-0.96	2.33	1.5
54	Clifford	v	22	301-304	0.6-5.9	0.60	0.20	1.50	0.5
55	Scott	v	42	301-350	0.3-6.8	0.67	-0.46	2.07	0.5
56	Millat	v	91	305-426	0.4-6.7	0.79	0.36	3.33	0.5
57	Keyes	zd	5	274-631	0.0	1.59	0.96	4.24	5.0
58	Johns	v	14	381-474	1.8-7.2	0.51	0.49	2.67	0.5
P	rimary data		513			1.18	-0.34	_	_
59	Trautz	zd	1	273	0.0	3.25	-3.25	3.25	_
32	Sellschopp	v	18	285-314	0.1-6.7	8.44	-8.44	16.9	_
60	Archer	zd	11	285-592	0.0	7.12	-7.12	11.14	_
61	Sherratt	zd	10	339-566	0.0	1.75	1.48	4.47	_
62	Eucken	zd	6	195-598	0.0	6.54	-4.72	9.38	_
44	Koch	 V	32	283-313	0.1-7 1	6.71	-6.71	33.59	_
63	Kannuluik	V	26	197-375	0.0-0.1	2.83	-0.54	8.67	_

Table 10.10: Deviations of the thermal conductivity ECS-NN equation for CO_2 with respect to primary, secondary and overall data in liquid, vapor and supercritical regions.

Ref.	First Author	Phase ^a	NPT	T range	P range	AAD	Bias	MAD	u
				(K)	(MPa)	%	%	%	%
vapor region (continuation)									
64 20	Stops	zd	6	577-1308	0.0	2.90	-2.04	8.49	-
39	Borosvik	V	1	293-313	5.1-7.1	10.81	-10.81	40.75	_
40	Keyes	V	14	274-298	0.1-6.1	6.47	6.47	17.95	_
65	Stolyarov	V	12	280-475	0.1–3.0	4.67	2.54	13.03	_
66	Franck	zd	1	197–598	0.0	5.63	-5.12	8.54	_
67	Salceanu	zd	1	303	0.0	6.02	-6.02	6.02	_
68	Vines	V	4	543-1173	0.1	3.79	3.79	5.64	—
69	Geier	V	12	2/3-13/3	0.1	2.39	-1.33	8.57	_
33	Michels	V	33	298-303	6.4-7.2	16.20	16.20	59.59	—
43	Becker	V	27	298-308	4.1–7.4	7.11	-6.75	16.50	_
38	Tarzimanov	v	12	290-654	0.1-6.1	2.93	2.15	7.07	_
70	Chen	v	19	304-316	1.4–7.4	20.61	14.76	37.42	_
71	Dohrn	v	7	300-420	0.1	4.14	4.14	5.48	_
72	Heinemann	V	3	323-420	0.1	4.39	4.39	5.39	_
73	Weber	zd	1	273	0.0	1.57	-1.57	1.57	_
74	Kannuluik	zd	1	273	0.0	1.60	-1.60	1.60	-
75	Kannuluik	V	9	275	0.0 - 0.1	2.15	-2.15	3.61	-
76	Keyes	V	9	274–423	0.1-6.1	1.51	0.80	3.68	-
77	Thomas	zd	4	314-337	0.0	1.34	-1.34	1.50	_
78	Rothman	V	25	631–1045	0.1	3.69	-2.06	7.49	_
79	Guildner	V	4	304-305	0.2-7.3	1.93	-1.31	2.55	-
41	Guildner	v	12	277-347	0.2 - 5.8	1.90	-1.75	3.17	-
80	Westenberg	zd	3	300-500	0.0	1.57	-1.57	2.03	_
81	Mukhopadhyay	v	7	258-473	0.1	1.86	-0.90	4.81	_
82	Barua	zd	5	273-473	0.0	2.62	-2.10	4.96	_
34	Le Neindre	v	11	294-309	0.1 - 5.7	1.43	-1.32	3.54	_
83	Christensen	zd	3	308-388	0.0	1.54	-1.54	1.72	_
84	Van Dael	v	1	297	0.1	1.15	-1.15	1.15	_
35	Le Neindre	v	105	327-802	0.1-7.1	2.32	-1.99	6.09	_
85	Rosenbaum	v	8	336–434	3.3-7.1	1.01	-0.11	2.00	_
86	Gupta	v	98	373-1348	0.0-0.1	3.19	-2.89	8.70	_
87	Murthy	v	2	305-308	0.2	0.59	0.26	0.85	_
45	Tarzimanov	v	8	299-581	0.1-6.5	2.53	-2.53	3.92	_
36	Le Neindre	v	37	298-951	0.1	2.53	-1.70	5.01	_
88	Haarman	zd	8	328-468	0.0	0.48	-0.48	0.63	_
42	Paul	v	12	298-313	0.7-6.9	1.85	-0.30	5.94	_
89	Shashkov	zd	9	315-403	0.0	1.21	-0.88	3.06	_
46	Shingarev	v	2	299-307	1.0	2.62	-2.62	3.25	_
44	Koch	SV	9	279-303	4.1-7.2	22.35	-22.35	78.48	_
	Total data		1174			3.27	-0.76	_	_
				Supercritical	region	-	-		
33	Michels	SC	94	304-348	7.4–209.7	1.11	-0.65	3.97	2.0
34	Le Neindre	SC	7	305-306	13.1-68.8	1.15	1.15	2.06	5.0
35	Le Neindre	SC	405	304-961	7.6–127.8	0.98	-0.40	6.20	5.0
36	Le Neindre	sc	145	327-951	10.0-120.0	0.94	-0.24	5.47	5.0
		~ -		, ,			·· ·		

Ref	First Author	Phase ^a	NPT	T range	P range	AAD	Bias	MAD	u		
Kci.	Thist Aution	1 hase	111 1	(K)	(MPa)	%	%	%	%		
	Supercritical region (continuation)										
38	Tarzimanov	sc	70	305-678	9.8–196.0	1.62	0.74	5.21	5.0		
55	Scott	sc	50	315-348	7.4–24.6	1.66	0.81	8.25	0.5		
58	Johns	sc	33	381–473	7.4–30.6	1.38	1.17	3.37	5.0		
Р	rimary data		804			1.10	-0.14	—	—		
32	Sellschopp	sc	10	304-323	7.5–9.1	14.26	10.06	30.13	_		
44	Koch	sc	4	308-313	8.1-9.1	39.80	-39.80	100.30	_		
39	Borosvik	sc	2	313	8.1-9.1	27.06	-27.06	30.41	_		
65	Stolyarov	sc	23	326-473	10.1-30.4	7.45	2.66	20.55	_		
50	Lenoir	sc	20	314-340	8.0 - 20.8	4.77	4.68	9.83	_		
79	Guildner	sc	18	305-348	7.5-30.4	12.38	11.53	52.84	_		
41	Guildner	sc	1	304	7.9	3.64	3.64	3.64	_		
85	Rosenbaum	sc	42	336-434	10.0-69.0	3.34	0.56	13.64	_		
90	Murthy	sc	53	305-310	7.5-8.3	17.89	15.32	41.27	_		
43	Becker	sc	170	304-308	7.4-48.8	12.22	-3.98	79.10	_		
70	Chen	sc	47	304-316	7.4–13.1	27.64	24.36	64.83	_		
91	Murthy	sc	65	305-310	7.5-8.3	14.85	12.75	41.27	_		
87	Murthy	sc	1	308	8.3	1.43	1.43	1.43	_		
45	Tarzimanov	sc	53	379–678	10.1-101.3	2.21	-2.20	4.11	_		
42	Paul	sc	4	313	9.1-27.6	0.84	0.43	1.51	_		
46	Shingarev	sc	4	310-326	19.9–20	8.89	-8.89	17.89	_		
	Total data		1321			5.54	1.61	_	_		
				Overal	1						
	Overall primary	,	1412			1.13	-0.21	_	_		
	Overall		2765			4.45	0.16	_	_		

^a *Phase*: l = liquid, sc = supercritical region, sl = saturated liquid, sv = saturated vapor, v = vapor, zd = vapor at zero-density limit.

Also for this fluid the performance of the obtained thermal conductivity model is obviously lower with respect to that of the corresponding one developed from generated data. In fact here the AAD for primary data is 1.13 % whereas in that case the corresponding value for the training set was about 0.26 %, see Tab. 10.2. Also in the case of carbon dioxide the decrease of performance has to be ascribed to the quality of the experimental data which primarily limits the attainable accuracy of the modeling method.

It has been verified that in general the single primary data sets are rather coherent each others and this is confirmed by the present bias values which are quite close to zero assuring that systematic shifting of the sets is in practice limited. Rather similar behaviors are shown for the single regions by the ECS-NN equation.

In Figs. 10.11 to 10.14 the error deviation distributions of the proposed model for carbon dioxide are shown with respect to the primary experimental points in the liquid, vapor and supercritical

regions, respectively. The small values of the deviations in all the regions and their balance with respect to the zero line are evident.

In the vapor region three data sets are prevailing for the number of points and for a low uncertainty, Refs. 53, 55 and 56, which are then the data sets better represented by the present equation. A similar behavior is also shown by the conventional equation from Ref. 5, Table 10.11. The validity range considered for the comparison of Table 10.11 is that of the conventional equation because it is the narrower one.

In the supercritical region three data sets have the higher number of points, i.e., the Refs. 33, 35 and 36, but they are rather coherent each others as it is also demonstrated by the AAD and Bias values obtained by the equation.

	First Author		FC	S-NN mo	أمل	Conventional eq.			
Ref.		NPT			uei	Vesovic et al. [5]			
	Thist Author		AAD	Bias	MAD	AAD	Bias	MAD	
			%	%	%	%	%	%	
		Р	rimary liqu	id region					
32	Sellschopp	22	2.05	-1.67	3.32	1.55	-0.97	4.74	
33	Michels	13	0.47	0.20	1.25	0.94	-0.27	2.24	
34	Le Neindre	12	1.24	1.24	2.11	1.03	0.99	2.06	
35	Le Neindre	6	0.62	0.21	1.00	0.35	-0.03	0.95	
36	Le Neindre	9	0.35	-0.22	0.70	0.70	-0.19	1.30	
37	Salmanov	19	0.88	0.33	2.56	1.51	1.51	2.42	
38	Tarzimanov	6	0.98	0.98	1.52	0.69	0.69	1.59	
	Overall	87	1.10	-0.09	_	1.15	0.21	_	
		Р	rimary vap	or region					
48	Dickins	1	0.24	-0.24	0.24	0.52	-0.52	0.52	
49	Johnston	12	0.64	0.64	1.81	0.26	-0.14	0.47	
50	Lenoir	12	1.84	1.84	5.01	0.87	0.66	2.98	
57	Keyes	5	1.59	0.96	4.24	1.72	0.08	3.50	
33	Michels	71	1.34	0.44	5.11	0.81	-0.31	2.36	
51	Bakulin	28	1.17	0.29	5.09	1.24	0.65	5.26	
52	Bakulin	7	0.66	-0.13	1.36	2.04	-2.04	3.21	
53	Snel	133	1.06	-0.96	2.33	1.15	-1.15	2.43	
54	Clifford	22	0.60	0.20	1.50	0.17	0.11	0.77	
55	Scott	42	0.67	-0.46	2.07	1.04	-1.04	2.50	
56	Millat	91	0.79	0.36	3.33	0.65	-0.54	4.19	
35	Le Neindre	70	2.32	-2.12	6.09	2.72	-2.51	5.98	
58	Johns	14	0.51	0.49	2.67	0.56	-0.40	4.85	
	Overall	508	1.17	-0.35	_	1.16	-0.87	_	

Table	10.11 :	Performance	comparison	among	the	present	ECS-NN	model,	the	conventional
model	[5] for	the fluid CO ₂ .								

			EC	S-NN mo	del	Conventional eq.			
Ref.	First Author	NPT		Diag	MAD		Dieg	. [J] 	
							D1as		
		Duina	70	70	70	70	70	70	
		Pfilli	lary superc	ritical reg	1011	1			
33	Michels	89	1.14	-0.65	3.97	1.23	0.47	8.81	
34	Le Neindre	7	1.15	1.15	2.06	0.74	0.58	2.12	
35	Le Neindre	367	0.99	-0.44	6.20	1.46	-1.14	6.84	
36	Le Neindre	134	0.96	-0.26	5.47	1.20	-0.77	4.19	
38	Tarzimanov	33	1.59	0.94	5.21	1.10	-0.06	3.39	
55	Scott	50	1.66	0.81	8.25	2.43	1.73	10.82	
58	Johns	33	1.38	1.17	3.37	0.56	-0.40	4.85	
	Overall	713	1.10	-0.19	_	1.39	-0.57	_	
			Overall p	rimary					
	Overall	1308	1.13	-0.25	_	1.28	-0.63	_	
Total primary and secondary									
Liquid		262	4.34	-3.01	_	4.47	-3.06	_	
Vapor		1054	3.38	-0.65	_	3.57	-1.47	_	
	Supercritical	1225	5.88	1.72	_	5.39	2.50	_	
	Total	2541	4.69	0.25	_	4.54	0.28	_	



Figure 10.11: Deviations of primary experimental data in the liquid region from the thermal conductivity ECS-NN model for CO_2 .



Figure 10.12: Deviations of primary experimental data in the vapor region from the thermal conductivity ECS-NN model for CO_2 regressed on generated data, Paragraph 10.3. The zero-density data are from Refs. 48, 49 and 57, Tab. 10.10.



Figure 10.13: Deviations of primary experimental data in the vapor region from the thermal conductivity ECS-NN model for CO_2 regressed on experimental data, Tab. 10.9.



Figure 10.14: Deviations of primary experimental data in the supercritical region from the thermal conductivity ECS-NN model for CO₂.

Similarly to what was done for R152a, sections at constant temperature of the thermal conductivity surface in the near-critical region of carbon dioxide are plotted in Fig. 10.15 for both the present ECS-NN model and the conventional model [5]. Also for carbon dioxide it is possible to observe a coherent trend and a significative improvement in the representation of the experimental data in this very crucial zone using the ECS-NN model.



Figure 10.15: Isotherms in the near-critical region of CO_2 generated from the ECS-NN model and from the conventional equation [5]; data from Michels et al. [33].

10.5. Conclusions

The potentiality of ECS modeling for thermal conductivity, when a heuristic technique is adopted, has been shown with application to both data generated from existing models and experimental data. The shape functions are got in a continuous analytical form expressed by a universal function approximator, i.e. a neural network, through regression of thermal conductivity data. The obtained results are very encouraging; in fact the proposed technique yields thermal conductivity equations that represent the experimental data within their experimental accuracy; moreover, the method is able to satisfactorily model the strong critical enhancement of thermal conductivity in the near-critical region.

Assuming R134a as reference fluid, two dedicated thermal conductivity equations have been regressed for carbon dioxide and R152a with the proposed technique, using the available

experimental data. The second fluid is supposed to share a conformality condition with the reference fluid, whereas this is not true for the first one. The performances of the equations are in both cases comparable with those of the corresponding models obtained with the at present most advanced heuristic method, i.e., the dedicated equations in optimized multiparameter functional form, as from Paragraph 9.4. A slight decrease of accuracy is counterbalanced by the lower number of experimental points required as input for the regression. In fact, it has been shown that about two hundred data points, regularly distributed on the $\lambda T \rho$ surface of the target fluid, are sufficient to draw a very precise equation, with evident saving of experimental efforts.

10.6. References

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CONCLUSIONS

In this Ph.D. thesis innovative modeling techniques for the representation of the thermophysical properties have been set up and applied to obtain substance-specific equations. The presented modeling techniques share a heuristic nature, allowing to infer the analytical relation between dependent and independent variables directly from a sufficiently detailed experimental representation of the studied phenomenon. Therefore no approximated physical model or tentative equation is initially assumed, but the analytical form of the model is set up through the mathematical optimization procedure strictly related to the universal function approximator itself.

An artificial neural network (NN), in a multilayer feedforward framework (MLFN), has been involved in the developed model as universal function approximator.

The Part One of the thesis work deals with the thermodynamic properties. An original modeling technique, concisely named EEoS-NN is presented. The EEoS-NN technique recovers the basic framework of the extended corresponding states (ECS) method, but it introduces the following improvement: the reference fluid coincides with the interest fluid itself and it is represented by an existing EoS for the fluid. Thus, there is actually no more a "reference fluid" with its own EoS, as in the classical ECS theory, but rather only a "reference equation" for the reference fluid itself. A powerful heuristic technique, the MLFN, is applied to determine the scale factors as continuous functions of the target fluid thermodynamic variables. Starting from experimental data of the considered fluid, the regression procedure yields an equation of state in the fundamental Helmholtz energy form for the fluid itself able to satisfactorily describe vapor, liquid and supercritical regions.

The format of the EEoS-NN model is constituted by a basic equation whose functional form is distorted through the application of shape functions, expressed as a neural network, to the independent variables. In the present thesis work different basic equations has been used, depending on the specific case. The more used basic EoS is the cubic equation of state, that requires only the critical parameters, the acentric factor, i.e. a value of saturation pressure, and a value of saturated liquid density to determine the Peneloux volume translation coefficient; but also a DEoS in optimized functional form has been used as basic equation from which the EEoS-NN model has been developed.

The EEoS-NN method allows to develop dedicated equations of state in a fundamental form from which all the thermodynamic properties can be calculated only through differentiation with respect to the independent variables temperature, density and composition.

The EEoS-NN model has been preliminary tested on generated data to set up the method and to test its potentialities; for this purpose data generated from a dedicated equation of state (DEoS) for

each target fluid are used instead of experimental data, so that the model performances are not hindered by error noise and uneven data distribution.

Moving from generated data, the capability of the proposed method has been verified both for pure fluids and for mixtures. A group of pure alkanes, haloalkanes, and strongly polar substances has been considered; the results obtained for these fluids are very promising. The same is valid for the five binary mixtures and two ternary mixtures of haloalkanes here studied.

In the case of pure fluids it has been also verified that slightly more than 100 density points evenly distributed in the $P\rho T$ plane and with low experimental error can be a sufficient input for the model development, allowing to reduce the experimental efforts.

The promising performances for the proposed model based on generated data leads to the possibility to reliably develop DEoSs in the EEoS-NN format directly from experimental data.

An equation of state in Helmholtz energy form was obtained for sulfur hexafluoride by applying the EEoS-NN technique using a Soave-Redlich-Kwong (SRK) cubic equation whose functional form is distorted through the application of shape functions, expressed as a neural network, to the independent variables. The coefficients of the neural network are obtained through regression from experimental data. The accuracies of the available sources of experimental data were discussed and only the more precise data sets were adopted for the training procedure of the neural network.

The validity ranges of the equation are from the triple-point temperature at about 223.6 K up to 625 K and for pressures up to 60 MPa, with the exclusion of a region close to the critical point in case of caloric property calculation; a moderate extrapolation outside these limits is reliably possible.

It was verified that the equation can be regressed on only density and vapor pressure data, though maintaining a good prediction accuracy for other thermodynamic properties as for instance isobaric heat capacity and speed of sound. This characteristic is advantageous when the proposed modeling technique is applied to a fluid for which a limited data base is available, because the required experimental effort can be reduced.

The representation of the available experimental data is satisfactory for all the considered properties; in fact the deviations of the equation from the data are comparable with the ascribed uncertainties of the experimental sources.

The performances of the basic SRK cubic EoS are by far improved through the application of the shape functions. Moreover, the comparison of the proposed equation with the most advanced EoS previously published in the literature shows that the two equations have a similar accuracy level, but the present one reaches better prediction results for many data sets.

The obtained equation is at the same level of the "group-two dedicated equations of state" developed in recent years through the so-called functional form optimization procedure. In particular it can be applied with satisfactory results also when only density and vapor pressure data are available.

The sulfur hexafluoride is a chemically inert, non-polar, symmetrically-shaped chemical compound presenting a regular thermodynamic behavior with a quite low deviation from ideality. For it a large base of good quality experimental data of several properties in homogeneous states and of properties at phase equilibrium were available with a rather even distribution inside the range of interest. For this fluid, considering the favorable conditions of the data base, the EEoS-NN method was applied using only density and coexistence data for the regression with the aim of verifying its "value added" mentioned in the preceding.

On the contrary, 2-propanol is a polar and associating compound able to create hydrogen bonds, i.e. strong molecular interactions making it to strongly deviate from ideality. Moreover, a completely different and less suitable experimental data base is available for the fluid because of a rather uneven distribution of the data, of some occasional inconsistencies among different experimental sources and, in several cases, of the questionable uncertainty of the data. All this makes the fluid more difficult to represent with a high accuracy DEoS with respect to the former case of sulfur hexafluoride.

The EEoS-NN modeling technique has been deliberately applied to the unfavorable situation of the fluid 2-propanol with the express will to verify the effectiveness of the method in much more difficult conditions.

The new fundamental equation of state was obtained for 2-propanol by applying the EEoS-NN technique using a PR cubic equation as basic EoS. The validity ranges of the developed equation are from 280 up to 600 K and for pressures up to 50 MPa. Due to the substantial lack of data in the near critical region and the non-specialization of this DEoS in representing such region very close to the critical point the present equation is not suggested to be used within a region very close to the critical point.

The representation of the available experimental data is satisfactory for all the considered properties; in fact the deviations of the equation from the data are comparable with the realistic uncertainties of the experimental sources for this fluid.

The results obtained for the fluid 2-propanol demonstrate that the EEoS-NN modeling method is completely reliable to develop highly effective DEoSs even if the experimental data situation for the fluid is not completely favorable. This aspect is particularly valuable in the case a DEoS is required for engineering applications where the economy of the experimental effort and the representation accuracy have to be met through a suitable compromise.

In conclusion, the EEoS-NN modeling technique is a valuable and effective tool for the development of fundamental equations of state dedicated to pure fluids, since it provides an equation in Helmholtz energy form that is capable to reproduce the thermodynamic properties with high accuracy. Above all, this result was an important goal for the present work and further enhancements of the EEoS-NN technique can be pursued in the future starting from the present result.

In particular, the developed EEoS-NN technique is a promising tool for the representation of the thermodynamic properties of fluids involved in many unit operations of process engineering; an accurate knowledge of such properties plays a crucial role in design and optimization.

To show the potential of such technique a propaedeutical system has to be chosen and studied as an exemplification case. This thesis work focuses on an extraction process to be studied from the energetic point of view.

The selected process is the dehydration of 2-propanol, i.e., the extraction of 2-propanol from a liquid homogeneous mixture 2-propanol + water using a light solvent which in this case is propylene. 2-Propanol and water form an azeotropic binary mixture that cannot be separated by means of a conventional distillation process. To overcome this problem a third component, propylene in this case, is added to allow the separation. This system was selected after a screening of the literature data which is rather lacking of detailed documentation, because it seems to present favorable conditions for an extraction operation. Equilibrium and excess enthalpy data have been correlated using a semi-predictive $G^{E} - EoS$ model composed of a Peng-Robinson (PR) cubic EoS with Wong-Sandler (WS) mixing rules and the G^{E} function represented through a modified UNIQUAC model. The complex phase equilibrium behavior of the system has been then studied in this thesis through the developed $G^{E} - EoS$ model, verifying that the system is suitable to study the extraction operation. Once the preliminary steps have been carried out and the system (ternary mixture) and the process are defined, the necessity of a very precise representation of the thermophysical properties of the system arises in order to investigate the best operative conditions in which to carry out the process to optimize its energy consumption. In order to provide a suitable data basis on which developing a DEoS for the system in EEoS-NN format new experimental measurements have been carried out in this thesis work. In particular, a vibrating tube densimeter has been used to carry out density measurements and to determine bubble pressures for the ternary mixture and for the composing binaries. The carried out experimental work provided a suitable basis of density data for the development of the EEoS-NN model, but a campaign of phase

equilibrium measurements are further necessary at this purpose. As it has been previously demonstrated the EEoS-NN model regressed on density and coexistence data is able to provide a reliable representation also for the caloric properties; nevertheless some isobaric heat capacity measurements in the range of interest for the extraction process are required for the model validation. At present this experimental work is still in progress and the development of a dedicated equation of state for the propylene + 2-propanol + water mixture will constitute the further development of this thesis work. Once a thermodynamic model in EEoS-NN format will be obtained, it will be possible to link it with a process simulator, studying the better operative conditions for the 2-propanol extraction process.

The Part Two of the thesis work deals with the transport properties. An original modeling technique, concisely named ECS-NN is presented. The ECS framework is maintained, but the shape functions are expressed through a multilayer feed-forward neural network, that constitutes a powerful function approximator.

The potentiality of the ECS-NN modeling technique for thermal conductivity, when a heuristic technique is adopted, has been shown with application to both data generated from existing models and experimental data. The shape functions are got in a continuous analytical form expressed by a universal function approximator, i.e. a neural network, through regression of thermal conductivity data. The obtained results are very encouraging; in fact the proposed technique yields thermal conductivity equations that represent the experimental data within their experimental accuracy; moreover, the method is able to satisfactorily model the strong critical enhancement of thermal conductivity in the near-critical region.

Assuming R134a as reference fluid, two dedicated thermal conductivity equations have been regressed for carbon dioxide and R152a with the proposed technique, using the available experimental data. The second fluid is supposed to share a conformality condition with the reference fluid, whereas this is not true for the first one. The performances of the equations are in both cases comparable with those of the corresponding models obtained with the at present most advanced heuristic method, i.e., the dedicated equations in optimized multiparameter functional form. A slight decrease of accuracy is counterbalanced by the lower number of experimental points required as input for the regression. In fact, it has been shown that about two hundred data points, regularly distributed on the $\lambda T \rho$ surface of the target fluid, are sufficient to draw a very precise equation, with evident saving of experimental efforts.

Summarizing, the present Ph.D. thesis has shown the effectiveness of the application of heuristic techniques to both thermodynamic and transport property modeling, as a valid alternative to the

techniques that are at present adopted. The proposed methods are robust and they yield equations representing the data well within their experimental uncertainties.

As for any correlative method, a sufficient number of experimental data is absolutely necessary and then a certain amount of experimental work is unavoidable for the development of a model with a heuristic technique. Anyway, the availability of accurate experimental facilities, the possibility to plan measurements covering a regular grid in the independent variables, and the selection of the most effective properties to measure allow to limit the experimental work to a minimum, keeping at the meantime the model accuracy as high as possible.

APPENDIX

A.1. MLFN model equations

The mathematical expressions involved in the use of multilayer feed-forward neural networks are here collected. The same definitions introduced in Paragraph 2.2.2 are maintained, then reference is made to that section. In addition, G_j and R_k , i.e. the input to neuron j of the hidden layer and the input to neuron k of the output layer respectively, and the derivatives of outputs with respect to inputs are defined.

SCALING RATIOS

$$u_i = \frac{A_{\max} - A_{\min}}{V_{i,\max} - V_{i,\min}} \qquad 1 \le i \le I - 1 \tag{A1.1}$$

$$s_k = \frac{A_{\max} - A_{\min}}{W_{k,\max} - W_{k,\min}} \qquad 1 \le k \le K$$
(A1.2)

NEURAL NETWORK INPUTS

,

$$U_{i} = u_{i} \left(V_{i} - V_{i,\min} \right) + A_{\min} \qquad 1 \le i \le I - 1$$
(A1.3)

$$U_I = Bias1 \tag{A1.4}$$

HIDDEN LAYER INPUTS AND OUTPUTS

$$G_j = \sum_{i=1}^{I} w_{ij} U_i \qquad 1 \le j \le J$$
(A1.5)

$$H_{j} = f\left(G_{j}\right) \qquad 1 \le j \le J \tag{A1.6}$$

 $H_{J+1} = Bias2$ (A1.7)

OUTPUT LAYER INPUTS AND OUTPUTS

$$R_{k} = \sum_{j=1}^{J+1} w_{jk} H_{j} \qquad 1 \le k \le K$$
(A1.8)

$$S_k = f\left(R_k\right) \qquad 1 \le k \le K \tag{A1.9}$$

PHYSICAL VARIABLE OUTPUTS

$$W_k = \frac{S_k - A_{\min}}{s_k} + W_{k,\min} \qquad 1 \le k \le K$$
(A1.10)

OUTPUT DERIVATIVES

$$\frac{\partial S_k}{\partial U_m} = f'(R_k) \sum_{j=1}^J w_{mj} w_{jk} f'(G_j) \qquad 1 \le m \le I - 1 , \ 1 \le k \le K$$
(A1.11)

$$\frac{\partial^2 S_k}{\partial U_m \partial U_n} = f''(R_k) \left[\sum_{j=1}^J w_{mj} w_{jk} f'(G_j) \right] \left[\sum_{j=1}^J w_{nj} w_{jk} f'(G_j) \right] + f'(R_k) \left[\sum_{j=1}^J w_{mj} w_{nj} w_{jk} f''(G_j) \right] \qquad 1 \le m, n \le I - 1 \ , \ 1 \le k \le K$$
(A1.12)

$$\frac{\partial^{3}S_{k}}{\partial U_{m}\partial U_{n}\partial U_{p}} = f'''(R_{k})\left[\sum_{j=1}^{J}w_{mj}w_{jk}f'(G_{j})\right]\left[\sum_{j=1}^{J}w_{nj}w_{jk}f'(G_{j})\right]\left[\sum_{j=1}^{J}w_{pj}w_{jk}f'(G_{j})\right]\left[\sum_{j=1}^{J}w_{pj}w_{jk}f'(G_{j})\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{mj}w_{pj}w_{jk}f''(G_{j})\right]\left[\sum_{j=1}^{J}w_{nj}w_{jk}f'(G_{j})\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{nj}w_{pj}w_{jk}f''(G_{j})\right]\left[\sum_{j=1}^{J}w_{mj}w_{jk}f'(G_{j})\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{nj}w_{pj}w_{jk}f''(G_{j})\right]\left[\sum_{j=1}^{J}w_{mj}w_{jk}f'(G_{j})\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{nj}w_{pj}w_{jk}f''(G_{j})\right]\left[\sum_{j=1}^{J}w_{mj}w_{jk}f'(G_{j})\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{nj}w_{pj}w_{jk}f''(G_{j})\right]\left[\sum_{j=1}^{J}w_{mj}w_{jk}f'(G_{j})\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{mj}w_{pj}w_{jk}f''(G_{j})\right]\left[\sum_{j=1}^{J}w_{mj}w_{jk}f'(G_{j})\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{mj}w_{pj}w_{jk}f''(G_{j})\right]\left[\sum_{j=1}^{J}w_{mj}w_{jk}f'(G_{j})\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{mj}w_{pj}w_{jk}f''(G_{j})\right]\left[\sum_{j=1}^{J}w_{mj}w_{jk}f'(G_{j})\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{mj}w_{pj}w_{jk}f''(G_{j})\right]\left[\sum_{j=1}^{J}w_{mj}w_{jk}f'(G_{j})\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{mj}w_{pj}w_{jk}f''(G_{j})\right]\left[\sum_{j=1}^{J}w_{mj}w_{jk}f'(G_{j})\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{mj}w_{pj}w_{jk}f''(G_{j})\right]\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{mj}w_{pj}w_{jk}f''(G_{j})\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{mj}w_{pj}w_{jk}f''(G_{j})\right]\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{mj}w_{pj}w_{pj}w_{jk}f''(G_{j})\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{mj}w_{pj}w_{pj}w_{jk}f''(G_{j})\right]\right] + f''(R_{k})\left[\sum_{j=1}^{J}w_{mj}w_{pj$$

$$\frac{\partial W_k}{\partial V_m} = \frac{u_m}{s_k} \frac{\partial S_k}{\partial U_m} \qquad 1 \le m \le I - 1 \quad , \ 1 \le k \le K$$
(A1.14)

$$\frac{\partial^2 W_k}{\partial V_m \partial V_n} = \frac{u_m u_n}{s_k} \frac{\partial^2 S_k}{\partial U_m \partial U_n} \qquad 1 \le m, n \le I - 1 \ , \ 1 \le k \le K$$
(A1.15)

$$\frac{\partial^{3} W_{k}}{\partial V_{m} \partial V_{n} \partial V_{p}} = \frac{u_{m} u_{n} u_{p}}{s_{k}} \frac{\partial^{3} S_{k}}{\partial U_{m} \partial U_{n} \partial U_{p}} \qquad 1 \le m, n, p \le I - 1 \quad , \ 1 \le k \le K$$
(A1.16)

where:

$$f'(x) = \frac{\mathrm{d}f(x)}{\mathrm{d}x} \tag{A1.17}$$

$$f''(x) = \frac{d^2 f(x)}{dx^2}$$
(A1.18)

$$f'''(x) = \frac{d^3 f(x)}{dx^3}$$
(A1.19)

are the derivatives of the selected transfer function.

A.2. Thermodynamic properties from equations of state in terms of Helmholtz free energy

The equations of state in terms of Helmholtz free energy are fundamental equations of state, i.e. once the equation has been set up all the thermodynamic properties can be calculated as combinations of derivatives without any integral calculation.

The reduced Helmholtz free energy can be expressed as a summation of ideal part and residual part ⁽¹⁾:

$$a(T,\rho) = \frac{A(T,\rho)}{RT} = a^{\circ}(T,\rho) + a^{R}(T,\rho)$$
(A2.1)

The ideal part a° is obtained from an equation for the ideal-gas isobaric heat capacity C_{p}° as a function of temperature; the residual part a^{R} is given as a function of temperature and density. Moreover, the reference values for enthalpy H_{0}° and entropy S_{0}° of ideal gas in the chosen reference condition (T_{0}, ρ_{0}) have to be set.

The equations for the calculation of the main thermodynamic properties are reported in the following. The quantities can be equivalently expressed either in molar units or in mass units, provided that consistency is maintained among the units of R, ρ , ρ_c , A and all the obtained properties. Particular attention has to be paid for speed of sound.

For mixtures the same equations for pure fluids are still valid, obviously with a° and a^{R} depending also on molar compositions; molar units should be used in this case. Moreover, the partial molar fugacity coefficient of component *i* in mixture is calculated from Eq. (A2.27). In the case of a mixture of *C* components, the ideal-gas Helmholtz energy is obtained from the linear combination of the ideal-gas Helmholtz energy of pure components plus the term representing the change of mixing of ideal gases:

$$a_{M}^{o}(T,\rho_{m},\boldsymbol{x}) = \sum_{i=1}^{C} x_{i} a_{i}^{o}(T,\rho_{m}) + \sum_{i=1}^{C} x_{i} \ln x_{i}$$
(A2.2)

$$a^{o}\Big|_{\text{Eq.(1.56)}} = a^{o}\Big|_{\text{Eq.(A2.1)}} + \ln Z$$
 $a^{R}\Big|_{\text{Eq.(1.56)}} = a^{R}\Big|_{\text{Eq.(A2.1)}} - \ln Z$

¹ The ideal and residual parts in Eq. (A2.1) are different from the corresponding terms in Eq. (1.56); in fact in Eq. (A2.1) they are calculated at the same *temperature* and *density* of the system, whereas in Eq. (1.56) they are at the same *temperature* and *pressure*. The two definitions are both valid, but when evaluated at the same fluid conditions the ideal and the residual parts according to the two definitions are related by:

DEFINITIONS

$$\tau = \frac{T_c}{T} \qquad \qquad \delta = \frac{\rho}{\rho_c} \qquad (A2.3, A2.4)$$

IDEAL PART

$$a^{o} = \frac{H_{0}^{o}\tau}{RT_{c}} - \frac{S_{0}^{o}}{R} - 1 + \ln\frac{\delta\tau_{0}}{\delta_{0}\tau} - \frac{\tau}{R} \int_{\tau_{0}}^{\tau} \frac{C_{p}^{o}}{\tau^{2}} d\tau + \frac{1}{R} \int_{\tau_{0}}^{\tau} \frac{C_{p}^{o}}{\tau} d\tau$$
(A2.5)

$$a_{\delta}^{o} = \left(\frac{\partial a^{o}}{\partial \delta}\right)_{\tau} = \frac{1}{\delta}$$
(A2.6)

$$a_{\tau}^{o} = \left(\frac{\partial a^{o}}{\partial \tau}\right)_{\delta} = \frac{H_{0}^{o}}{RT_{c}} - \frac{1}{\tau} - \frac{1}{R} \int_{\tau_{0}}^{\tau} \frac{C_{p}^{o}}{\tau^{2}} \mathrm{d}\tau$$
(A2.7)

$$a_{\delta\delta}^{o} = \left(\frac{\partial^2 a^{o}}{\partial \delta^2}\right)_{\tau} = -\frac{1}{\delta^2}$$
(A2.8)

$$a_{\tau\tau}^{o} = \left(\frac{\partial^{2} a^{o}}{\partial \tau^{2}}\right)_{\delta} = \frac{1}{\tau^{2}} \left(1 - \frac{C_{p}^{o}}{R}\right)$$
(A2.9)

$$a_{\delta\tau}^{o} = \left(\frac{\partial^2 a^{o}}{\partial \delta \partial \tau}\right) = 0 \tag{A2.10}$$

RESIDUAL PART

$$a_{\delta}^{R} = \left(\frac{\partial a^{R}}{\partial \delta}\right)_{\tau}$$
(A2.11)

$$a_{\tau}^{R} = \left(\frac{\partial a^{R}}{\partial \tau}\right)_{\delta}$$
(A2.12)

$$a_{\delta\delta}^{R} = \left(\frac{\partial^{2} a^{R}}{\partial \delta^{2}}\right)_{\tau}$$
(A2.13)

$$a_{\tau\tau}^{R} = \left(\frac{\partial^{2} a^{R}}{\partial \tau^{2}}\right)_{\delta}$$
(A2.14)

$$a_{\delta\tau}^{R} = \left(\frac{\partial^{2} a^{R}}{\partial \delta \partial \tau}\right) \tag{A2.15}$$

$$a_{\delta\delta\delta}^{R} = \left(\frac{\partial^{3} a^{R}}{\partial \delta^{3}}\right)_{\tau}$$
(A2.16)

PROPERTIES CALCULATION

Property	Relation	
Compressibility factor	$Z = \frac{P}{\rho RT} = 1 + \delta a_{\delta}^{R}$	(A2.17)
Internal energy	$u = \frac{U}{RT} = \tau \left(a_{\tau}^{o} + a_{\tau}^{R} \right)$	(A2.18)
Enthalpy	$h = \frac{H}{RT} = 1 + \tau \left(a_{\tau}^{o} + a_{\tau}^{R} \right) + \delta a_{\delta}^{R}$	(A2.19)
Gibbs energy	$g = \frac{G}{RT} = 1 + a^{\circ} + a^{R} + \delta a_{\delta}^{R}$	(A2.20)
Helmholtz energy	$a = \frac{A}{RT} = a^{\circ} + a^{R}$	(A2.21)
Entropy	$s = \frac{S}{R} = \tau \left(a_{\tau}^{o} + a_{\tau}^{R} \right) - a^{o} - a^{R}$	(A2.22)
Isochoric heat capacity	$c_{v} = \frac{C_{v}}{R} = -\tau^{2} \left(a_{\tau\tau}^{o} + a_{\tau\tau}^{R} \right)$	(A2.23)
Isobaric heat capacity	$c_{p} = \frac{C_{p}}{R} = \frac{C_{v}}{R} + \frac{\left(1 + \delta a_{\delta}^{R} - \delta \tau a_{\delta \tau}^{R}\right)^{2}}{1 + 2\delta a_{\delta}^{R} + \delta^{2} a_{\delta \delta}^{R}}$	(A2.24)
Speed of sound $(^2)$	$\frac{w^2}{RT} = \frac{C_p}{C_v} \left(1 + 2\delta a_{\delta}^R + \delta^2 a_{\delta\delta}^R \right)$	(A2.25)
Fugacity coefficient	$\ln \varphi = Z - 1 - \ln Z + a^R$	(A2.26)
Partial molar fugacity coefficient of component i in mixture (³)	$\ln \hat{\varphi}_i = a^R - \ln Z + n \left(\frac{\partial a^R}{\partial n_i}\right)_{T, nv, n_{j \neq i}}$	(A2.27)
2nd Virial coefficient	$B = \frac{1}{\rho_c} \lim_{\delta \to 0} \left(a_{\delta}^R \right)$	(A2.28)
3rd Virial coefficient	$C = \frac{1}{\rho_c^2} \lim_{\delta \to 0} \left(a_{\delta \delta}^R \right)$	(A2.29)
1st pressure derivative with respect to density	$\left(\frac{\partial P}{\partial \rho}\right)_{T} = RT\left(1 + 2\delta a_{\delta}^{R} + \delta^{2}a_{\delta\delta}^{R}\right)$	(A2.30)

² Eq. (A2.25) is valid when *R* is expressed in J kg⁻¹ K⁻¹. If *R* is in J mol⁻¹ K⁻¹, then the left-hand side of the equation is substituted by $w^2 M/(RT)$, where *M* is the molar mass in kg mol⁻¹.

³ The total number of moles is denoted with *n*, while the number of moles of component *i* is indicated with n_i .

A.3. Cubic equation of state transformed into fundamental Helmholtz free energy form

Limiting the present study to the cubic equations of state of van der Waals (vdW), Redlich-Kwong (RK), Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR), and considering also the Peneloux volume translation, a general form comprising all these equations reads:

$$P = \frac{RT}{v+c-b} - \frac{a_{cub}}{(v+c+\varepsilon_1 b)(v+c+\varepsilon_2 b)}$$
(A3.1)

with the parameters reported in Table 3.1. The parameter a of the cubic equation is here denoted by the subscript *cub* in order to avoid any misunderstanding with the reduced Helmholtz energy. From the relation:

$$a^{R}(T,v) = \frac{1}{RT} \int_{v=\infty}^{v} \left[\frac{RT}{v} - P(T,v) \right]_{T} dv$$
(A3.2)

one gets:

$$a^{R}(T,v) = \ln\left(\frac{v}{v+c-b}\right) - \frac{a_{cub}}{RTb(\varepsilon_{2}-\varepsilon_{1})}\ln\left(\frac{v+c+\varepsilon_{2}b}{v+c+\varepsilon_{1}b}\right)$$
(A3.3)

and substituting $\rho = 1/v$:

$$a^{R}(T,\rho) = -\ln[1+(c-b)\rho] - \frac{a_{cub}}{RTb(\varepsilon_{2}-\varepsilon_{1})}\ln\left[\frac{1+(c+\varepsilon_{2}b)\rho}{1+(c+\varepsilon_{1}b)\rho}\right]$$
(A3.4)

The derivatives of a^{R} with respect to the independent variables are here reported:

$$a_{\rho}^{R} = \left(\frac{\partial a^{R}}{\partial \rho}\right)_{T} = -\frac{c-b}{1+(c-b)\rho} - \frac{a_{cub}}{RTb(\varepsilon_{2}-\varepsilon_{1})} \left[\frac{c+\varepsilon_{2}b}{1+(c+\varepsilon_{2}b)\rho} - \frac{c+\varepsilon_{1}b}{1+(c+\varepsilon_{1}b)\rho}\right]$$
(A3.5)

$$a_T^R = \left(\frac{\partial a^R}{\partial T}\right)_{\rho} = -\frac{1}{RTb\left(\varepsilon_2 - \varepsilon_1\right)} \left(\frac{\partial a_{cub}}{\partial T} - \frac{a_{cub}}{T}\right) \ln\left[\frac{1 + \left(c + \varepsilon_2 b\right)\rho}{1 + \left(c + \varepsilon_1 b\right)\rho}\right]$$
(A3.6)

$$a_{\rho\rho}^{R} = \left(\frac{\partial^{2}a^{R}}{\partial\rho^{2}}\right)_{T} = \left[\frac{c-b}{1+(c-b)\rho}\right]^{2} - \frac{a_{cub}}{RTb(\varepsilon_{2}-\varepsilon_{1})} \left\{-\left[\frac{c+\varepsilon_{2}b}{1+(c+\varepsilon_{2}b)\rho}\right]^{2} + \left[\frac{c+\varepsilon_{1}b}{1+(c+\varepsilon_{1}b)\rho}\right]^{2}\right\}$$
(A3.7)

$$a_{TT}^{R} = \left(\frac{\partial^{2} a^{R}}{\partial T^{2}}\right)_{\rho} = -\frac{1}{RTb\left(\varepsilon_{2} - \varepsilon_{1}\right)} \left(\frac{\partial^{2} a_{cub}}{\partial T^{2}} - \frac{2}{T}\frac{\partial a_{cub}}{\partial T} + \frac{2a_{cub}}{T^{2}}\right) \ln\left[\frac{1 + \left(c + \varepsilon_{2}b\right)\rho}{1 + \left(c + \varepsilon_{1}b\right)\rho}\right]$$
(A3.8)

$$a_{\rho T}^{R} = \left(\frac{\partial^{2} a^{R}}{\partial \rho \partial T}\right) = -\frac{1}{RTb\left(\varepsilon_{2} - \varepsilon_{1}\right)} \left(\frac{\partial a_{cub}}{\partial T} - \frac{a_{cub}}{T}\right) \left[\frac{c + \varepsilon_{2}b}{1 + \left(c + \varepsilon_{2}b\right)\rho} - \frac{c + \varepsilon_{1}b}{1 + \left(c + \varepsilon_{1}b\right)\rho}\right]$$
(A3.9)

$$a_{\rho\rho\rho}^{R} = \left(\frac{\partial^{3}a^{R}}{\partial\rho^{3}}\right)_{T} = -2\left[\frac{c-b}{1+(c-b)\rho}\right]^{3} - \frac{2a_{cub}}{RTb(\varepsilon_{2}-\varepsilon_{1})}\left\{\left[\frac{c+\varepsilon_{2}b}{1+(c+\varepsilon_{2}b)\rho}\right]^{3} + \left[\frac{c+\varepsilon_{1}b}{1+(c+\varepsilon_{1}b)\rho}\right]^{3}\right\}$$
(A3.10)

$$a_{TTT}^{R} = \left(\frac{\partial^{3} a^{R}}{\partial T^{3}}\right)_{\rho} = -\frac{1}{RTb\left(\varepsilon_{2} - \varepsilon_{1}\right)} \left(\frac{\partial^{3} a_{cub}}{\partial T^{3}} - \frac{3}{T}\frac{\partial^{2} a_{cub}}{\partial T^{2}} + \frac{6}{T^{2}}\frac{\partial a_{cub}}{\partial T} - \frac{6a_{cub}}{T^{3}}\right) \ln\left[\frac{1 + \left(c + \varepsilon_{2}b\right)\rho}{1 + \left(c + \varepsilon_{1}b\right)\rho}\right]$$
(A3.11)

$$a_{\rho\rho T}^{R} = \left(\frac{\partial^{3} a^{R}}{\partial \rho^{2} \partial T}\right) = -\frac{1}{RTb\left(\varepsilon_{2} - \varepsilon_{1}\right)} \left(\frac{\partial a_{cub}}{\partial T} - \frac{a_{cub}}{T}\right) \left\{-\left[\frac{c + \varepsilon_{2}b}{1 + \left(c + \varepsilon_{2}b\right)\rho}\right]^{2} + \left[\frac{c + \varepsilon_{1}b}{1 + \left(c + \varepsilon_{1}b\right)\rho}\right]^{2}\right\}$$
(A3.12)

$$a_{\rho TT}^{R} = \left(\frac{\partial^{3} a^{R}}{\partial \rho \partial T^{2}}\right) = -\frac{1}{RTb\left(\varepsilon_{2} - \varepsilon_{1}\right)} \left(\frac{\partial^{2} a_{cub}}{\partial T^{2}} - \frac{2}{T} \frac{\partial a_{cub}}{\partial T} + \frac{2a_{cub}}{T^{2}}\right) \left[\frac{c + \varepsilon_{2}b}{1 + \left(c + \varepsilon_{2}b\right)\rho} + \frac{c + \varepsilon_{1}b}{1 + \left(c + \varepsilon_{1}b\right)\rho}\right]$$
(A3.13)

in which the derivatives $\partial a_{cub}/\partial T$, $\partial^2 a_{cub}/\partial T^2$ and $\partial^3 a_{cub}/\partial T^3$ are calculated from the suitable equation for a_{cub} in Table 3.1.

Moreover, for a mixture of C components, indicating with n the total number of moles in the system and with n_i the number of moles of component i, it is:

$$n\left(\frac{\partial a^{R}}{\partial n_{i}}\right)_{T,nv,n_{j\neq i}} = -\frac{\left(\overline{c}_{i}-\overline{b}_{i}\right)\rho}{1+\left(c_{M}-b_{M}\right)\rho} - \frac{a_{M,cub}}{RTb_{M}\left(\varepsilon_{2}-\varepsilon_{1}\right)}\left(\frac{\overline{a}_{cub,i}}{a_{M,cub}} - \frac{\overline{b}_{i}}{b_{M}}\right)\ln\left[\frac{1+\left(c_{M}+\varepsilon_{2}b_{M}\right)\rho}{1+\left(c_{M}+\varepsilon_{1}b_{M}\right)\rho}\right] + \frac{a_{M,cub}\rho}{RTb_{M}\left(\varepsilon_{2}-\varepsilon_{1}\right)}\left[\frac{\overline{c}_{i}+\varepsilon_{2}\overline{b}_{i}}{1+\left(c_{M}+\varepsilon_{2}b_{M}\right)\rho} - \frac{\overline{c}_{i}+\varepsilon_{1}\overline{b}_{i}}{1+\left(c_{M}+\varepsilon_{1}b_{M}\right)\rho}\right]$$
(A3.14)

where:

$$\overline{a}_{cub,i} \equiv \left[\frac{\partial \left(na_{M,cub}\right)}{\partial n_{i}}\right]_{T,nv,n_{j\neq i}} \qquad \overline{b}_{i} \equiv \left[\frac{\partial \left(nb_{M}\right)}{\partial n_{i}}\right]_{T,nv,n_{j\neq i}} \qquad \overline{c}_{i} \equiv \left[\frac{\partial \left(nc_{M}\right)}{\partial n_{i}}\right]_{T,nv,n_{j\neq i}} \tag{A3.15}$$

Assuming the mixing rules in Eqs. (3.29-3.32), it results:

$$\overline{a}_{cub,i} = 2\sum_{j=1}^{C} x_j \sqrt{a_i a_j} \left(1 - k_{ij} \right) - a_{M,cub} \qquad \overline{b}_i = b_i \qquad \overline{c}_i = c_i$$
(A3.16)

Since it is:

$$\begin{aligned} \delta a_{\delta}^{R} &= \rho a_{\rho}^{R} & \tau a_{\tau}^{R} &= -T a_{T}^{R} \\ \delta^{2} a_{\delta\delta}^{R} &= \rho^{2} a_{\rho\rho}^{R} & \tau^{2} a_{\tau\tau}^{R} &= T^{2} a_{TT}^{R} + 2T a_{T}^{R} \\ \delta \tau a_{\delta\tau}^{R} &= -\rho T a_{\rho T}^{R} & \delta^{3} a_{\delta\delta\delta}^{R} &= \rho^{3} a_{\rho\rho\rho}^{R} \end{aligned}$$
(A3.17)

all the thermodynamic properties can be calculated for the selected cubic equation ⁽⁴⁾ from the relations in Appendix A.2.

⁴ For the van der Waals cubic EoS the substitution of $\varepsilon_1=0$ and $\varepsilon_2=0$ into Eqs. (A3.3-A3.14) leads to indeterminate forms. The right procedure for that cubic equation is to set $\varepsilon_2=0$ and to calculate the limits of Eqs. (A3.3-A3.14) for $\varepsilon_1 \rightarrow 0$.

A.4. UNIQUAC equation

The UNIQUAC equation treats $g \equiv G^E/RT$ as comprised of two additive parts, a *combinatorial* term g^C to account for molecular size and shape differences, and a *residual* term g^R to account for molecular interactions:

$$g \equiv g^C + g^R \tag{A4.1}$$

Function g^{C} contains pure-species parameters only, whereas function g^{R} incorporates two binary parameters for each pair of molecules. For a system of *C* components:

$$g^{C} = \sum_{i=1}^{C} x_{i} \ln \frac{\Phi_{i}}{x_{i}} + 5 \sum_{i=1}^{C} q_{i} x_{i} \ln \frac{\theta_{i}}{\Phi_{i}}$$
(A4.2)

and

$$g^{R} = -\sum_{i=1}^{C} q_{i} x_{i} \ln \left(\sum_{j=1}^{C} \theta_{j} \tau_{ji} \right)$$
(A4.3)

where

$$\Phi_i \equiv \frac{x_i r_i}{\sum_{j=1}^C x_j r_j} \qquad \qquad \theta_i \equiv \frac{x_i q_i}{\sum_{j=1}^C x_j q_j} \qquad (A4.4, A4.5)$$

Subscript *i* identifies species, and *j* is a dummy index. It is $\tau_{ji} \neq \tau_{ij}$, and $\tau_{ii} = \tau_{jj} = 1$. In these equations r_i (a relative molecular volume) and q_i (a relative molecular surface area) are purespecies parameters. The influence of temperature on *g* enters through the interaction parameters τ_{ji} of Eq. (A4.3), which are temperature dependent:

$$\tau_{ji} = \exp\frac{-\left(\mu_{ji} - u_{ii}\right)}{RT}$$
(A4.6)

Parameters for the UNIQUAC equation are therefore values of $\Delta u_{ji} = (u_{ji} - u_{ii})/R$, which have to be found by regression on binary VLE data.

An expression for $\ln \gamma_i$ is found by application of equation (1.103) to the UNIQUAC equation for *g*, Eqs. (A4.1-A4.3).

A.5. EEoS-NN model equations

Denoted with subscript j the target fluid and with subscript 0 the reference fluid, the basic equation of the extended corresponding states model is:

$$a_{j}^{R}(T_{j},\rho_{j}) = a_{0}^{R}(T_{0},\rho_{0})$$
(A5.1)

where:

$$T_0 = T_j / f_j \qquad \qquad \rho_0 = \rho_j h_j \qquad (A5.2)$$

Since in the EEoS-NN framework the target and the reference fluid coincide, the scale factors f_j and h_j are identical to the respective shape functions θ_j and ϕ_j :

$$f_j = \theta_j (T_j, \rho_j) \qquad \qquad h_j = \phi_j (T_j, \rho_j) \qquad (A5.3)$$

LOGARITHMICAL DERIVATIVES OF THE SCALE FACTORS

$$F_{\rho} \equiv \frac{\rho_j}{f_j} \left(\frac{\partial f_j}{\partial \rho_j} \right)_{T_j} \qquad \qquad H_{\rho} \equiv \frac{\rho_j}{h_j} \left(\frac{\partial h_j}{\partial \rho_j} \right)_{T_j} \qquad (A5.4, A5.5)$$

$$F_{T} = \frac{T_{j}}{f_{j}} \left(\frac{\partial f_{j}}{\partial T_{j}} \right)_{\rho_{j}} \qquad \qquad H_{T} = \frac{T_{j}}{h_{j}} \left(\frac{\partial h_{j}}{\partial T_{j}} \right)_{\rho_{j}} \qquad (A5.6, A5.7)$$

$$F_{\rho\rho} \equiv \frac{\rho_j^2}{f_j} \left(\frac{\partial^2 f_j}{\partial \rho_j^2} \right)_{T_j} \qquad \qquad H_{\rho\rho} \equiv \frac{\rho_j^2}{h_j} \left(\frac{\partial^2 h_j}{\partial \rho_j^2} \right)_{T_j} \qquad (A5.8, A5.9)$$

$$F_{TT} \equiv \frac{T_j^2}{f_j} \left(\frac{\partial^2 f_j}{\partial T_j^2} \right)_{\rho_j} \qquad \qquad H_{TT} \equiv \frac{T_j^2}{h_j} \left(\frac{\partial^2 h_j}{\partial T_j^2} \right)_{\rho_j} \qquad (A5.10, A5.11)$$

$$F_{\rho T} \equiv \frac{\rho_j T_j}{f_j} \left(\frac{\partial^2 f_j}{\partial \rho_j \partial T_j} \right) \qquad \qquad H_{\rho T} \equiv \frac{\rho_j T_j}{h_j} \left(\frac{\partial^2 h_j}{\partial \rho_j \partial T_j} \right) \qquad (A5.12, A5.13)$$

$$F_{\rho\rho\rho} \equiv \frac{\rho_j^3}{f_j} \left(\frac{\partial^3 f_j}{\partial \rho_j^3} \right)_{T_j} \qquad \qquad H_{\rho\rho\rho} \equiv \frac{\rho_j^3}{h_j} \left(\frac{\partial^3 h_j}{\partial \rho_j^3} \right)_{T_j} \qquad (A5.14, A5.15)$$

The logarithmical derivatives of the shape functions with respect to temperature and/or density equal the respective derivatives of the scale factors.

DERIVATIVES OF THE HELMHOLTZ ENERGY

$$\rho_{j}a_{j,\rho}^{R} \equiv \rho_{j} \left(\frac{\partial a_{j}^{R}}{\partial \rho_{j}}\right)_{T_{j}} = \rho_{0}a_{0,\rho}^{R} \left(1 + H_{\rho}\right) - T_{0}a_{0,T}^{R}F_{\rho}$$
(A5.16)

$$T_{j}a_{j,T}^{R} \equiv T_{j} \left(\frac{\partial a_{j}^{R}}{\partial T_{j}}\right)_{\rho_{j}} = \rho_{0}a_{0,\rho}^{R}H_{T} + T_{0}a_{0,T}^{R}\left(1 - F_{T}\right)$$
(A5.17)

$$\rho_{j}^{2} a_{j,\rho\rho}^{R} \equiv \rho_{j}^{2} \left(\frac{\partial^{2} a_{j}^{R}}{\partial \rho_{j}^{2}} \right)_{T_{j}} = \rho_{0}^{2} a_{0,\rho\rho}^{R} \left(\mathbf{l} + H_{\rho} \right)^{2} + \rho_{0} a_{0,\rho}^{R} \left(2H_{\rho} + H_{\rho\rho} \right) + - 2\rho_{0} T_{0} a_{0,\rhoT}^{R} F_{\rho} \left(\mathbf{l} + H_{\rho} \right) + T_{0} a_{0,T}^{R} \left(2F_{\rho}^{2} - F_{\rho\rho} \right) + T_{0}^{2} a_{0,TT}^{R} F_{\rho}^{2}$$
(A5.18)

$$T_{j}^{2} a_{j,TT}^{R} \equiv T_{j}^{2} \left(\frac{\partial^{2} a_{j}^{R}}{\partial T_{j}^{2}} \right)_{\rho_{j}} = \rho_{0}^{2} a_{0,\rho\rho}^{R} H_{T}^{2} + \rho_{0} a_{0,\rho}^{R} H_{TT} + 2\rho_{0} T_{0} a_{0,\rhoT}^{R} H_{T} \left(1 - F_{T} \right) + T_{0} a_{0,T}^{R} \left(2F_{T}^{2} - 2F_{T} - F_{TT} \right) + T_{0}^{2} a_{0,TT}^{R} \left(1 - F_{T} \right)^{2}$$
(A5.19)

$$\rho_{j}T_{j}a_{j,\rho T}^{R} \equiv \rho_{j}T_{j}\left(\frac{\partial^{2}a_{j}^{R}}{\partial\rho_{j}\partial T_{j}}\right) = \rho_{0}^{2}a_{0,\rho\rho}^{R}H_{T}\left(1+H_{\rho}\right) + \rho_{0}a_{0,\rho}^{R}\left(H_{T}+H_{\rho T}\right) + \rho_{0}T_{0}a_{0,\rho T}^{R}\left[\left(1+H_{\rho}\right)\left(1-F_{T}\right)-F_{\rho}H_{T}\right] + T_{0}a_{0,T}^{R}\left(2F_{T}F_{\rho}-F_{\rho}-F_{\rho T}\right) + T_{0}^{2}a_{0,TT}^{R}F_{\rho}\left(F_{T}-1\right)$$
(A5.20)

$$\rho_{j}^{3}a_{j,\rho\rho\rho}^{R} \equiv \rho_{j}^{3} \left(\frac{\partial^{3}a_{j}^{R}}{\partial\rho_{j}^{3}} \right)_{T_{j}} = \rho_{0}^{3}a_{0,\rho\rho\rho}^{R} \left(1 + H_{\rho} \right)^{3} + 3\rho_{0}^{2}a_{0,\rho\rho}^{R} \left(1 + H_{\rho} \right) \left(2H_{\rho} + H_{\rho\rho} \right) + \rho_{0}a_{0,\rho}^{R} \left(3H_{\rho\rho} + H_{\rho\rho\rho} \right) - 3\rho_{0}^{2}T_{0}a_{0,\rho\rhoT}^{R}F_{\rho} \left(1 + H_{\rho} \right)^{2} + 3\rho_{0}T_{0}a_{0,\rhoT}^{R} \left[\left(1 + H_{\rho} \right) \left(2F_{\rho}^{2} - F_{\rho\rho} \right) - F_{\rho} \left(2H_{\rho} + H_{\rho\rho} \right) \right] + 3\rho_{0}T_{0}^{2}a_{0,\rhoTT}^{R}F_{\rho}^{2} \left(1 + H_{\rho} \right) + T_{0}a_{0,T}^{R} \left(6F_{\rho\rho}F_{\rho} - F_{\rho\rho\rho} - 6F_{\rho}^{3} \right) + 3T_{0}^{2}a_{0,TT}^{R}F_{\rho} \left(2F_{\rho}^{2} - F_{\rho\rho} \right) - T_{0}^{3}a_{0,TTT}^{R}F_{\rho}^{3}$$
(A5.21)

Remembering Eqs. (A3.17) all the thermodynamic properties can be calculated for the EEoS-NN model from the equations in Appendix A.2. Since in the EEoS-NN model the "reference" is a simple equation of the target fluid itself; if a cubic equation of state is chosen as reference the expressions for a_0^R and its derivatives included in Eqs. (A5.16-A5.21) are calculated through the Eqs. (A3.4-A3.13) in Appendix A3. Some properties are reported in the following for convenience.

EXAMPLES OF THERMODYNAMIC PROPERTIES CALCULATED FROM THE ECS MODEL:

 $z_{i}^{R} = (1 + H_{\rho}) z_{0}^{R} + F_{\rho} u_{0}^{R}$ Residual compressibility factor $z^{R} = Z - 1$: (A5.22) $u_j^R = \left(1 - F_T\right)u_0^R - H_T z_0^R$ Reduced residual internal energy $u^{R} = \frac{U^{R}}{PT}$: (A5.23) $h_{j}^{R} = h_{0}^{R} + (F_{\rho} - F_{T})u_{0}^{R} + (H_{\rho} - H_{T})z_{0}^{R}$ Reduced residual enthalpy $h^{R} = \frac{H^{R}}{PT}$: (A5.24) $a_j^R = a_0^R$ Reduced residual Helmholtz energy $a^{R} = \frac{A^{R}}{RT}$: (A5.25) Reduced residual Gibbs energy $g^{R} = \frac{G^{R}}{RT}$: $g_{j}^{R} = g_{0}^{R} + F_{\rho} u_{0}^{R} + H_{\rho} z_{0}^{R}$ (A5.26) $s_j^R = s_0^R - F_T u_0^R - H_T z_0^R$ Reduced residual entropy $s^R = \frac{S^R}{P}$: (A5.27)

MIXTURES

In the case of mixtures the preceding equations are still valid, substituting the mixture scaling factors for the pure fluid ones. The only novelty is given by the partial molar fugacity coefficient of component *i* in mixture, $\ln \hat{\varphi}_i$.

If the reference is a <u>pure fluid</u>, it is calculated as:

$$\ln \hat{\varphi}_{M,i} = \ln \varphi_0 - \ln \left(Z_M / Z_0 \right) + u_0^R \left(F_{n_i} + F_\rho \right) + z_0^R \left(H_{n_i} + H_\rho \right)$$
(A5.28)

where:

$$F_{n_i} = \frac{n}{f_M} \left(\frac{\partial f_M}{\partial n_i} \right)_{T_M, \rho_M, n_{j \neq i}} = \frac{1}{f_M} \left\{ \left(\frac{\partial f_M}{\partial x_i} \right)_{T_M, \rho_M, x_{j \neq i}} - \sum_{k=1}^C \left[x_k \left(\frac{\partial f_M}{\partial x_k} \right)_{T_M, \rho_M, x_{j \neq k}} \right] \right\}$$
(A5.29)

$$H_{n_{i}} = \frac{n}{h_{M}} \left(\frac{\partial h_{M}}{\partial n_{i}} \right)_{T_{M},\rho_{M},n_{j\neq i}} = \frac{1}{h_{M}} \left\{ \left(\frac{\partial h_{M}}{\partial x_{i}} \right)_{T_{M},\rho_{M},x_{j\neq i}} - \sum_{k=1}^{C} \left[x_{k} \left(\frac{\partial h_{M}}{\partial x_{k}} \right)_{T_{M},\rho_{M},x_{j\neq k}} \right] \right\}$$
(A5.30)

If the reference is a <u>mixture</u> with the same number of components and evaluated at the same molar composition of the system, it is calculated as:

$$\ln \hat{\varphi}_{M,i} = \ln \hat{\varphi}_{0,i} - \ln \left(Z_M / Z_0 \right) + u_0^R \left(F_{n_i} + F_\rho \right) + z_0^R \left(H_{n_i} + H_\rho \right)$$
(A5.31)

A.6. Statistical indexes definition

The statistical indexes used in the present thesis to evaluate the performances of the proposed models are here defined. The generic property is indicated with M, while NPT denotes the number of points in the considered data set, i is a generic point of the data set, *calc* and *exp* stand for calculated and experimental values, respectively. Sometimes, when indicated, *exp* can denote also pseudo-experimental values, generated with a thermodynamic model and assumed as substitutive for the experimental points.

ERROR DEVIATION OF THE i^{-th} POINT:

$$\Delta_{i} = \left(\frac{M_{calc} - M_{exp}}{M_{exp}}\right)_{i}$$
(A6.1)

AVERAGE ABSOLUTE DEVIATION:

$$AAD\% = 100 \frac{1}{NPT} \sum_{i=1}^{NPT} \left| \Delta_i \right|$$
(A6.2)

BIAS:

Bias % =
$$100 \frac{1}{\text{NPT}} \sum_{i=1}^{\text{NPT}} \Delta_i$$
 (A6.3)

MAXIMUM ABSOLUTE DEVIATION:

$$MAD\% = 100 \max_{i=1,NPT} \left| \Delta_i \right|$$
(A6.4)

STANDARD DEVIATION:

STD % = 100
$$\sqrt{\frac{1}{\text{NPT} - 1} \sum_{i=1}^{\text{NPT}} \left(\frac{M_{calc} - M_{exp}}{M_{calc}} \right)_{i}^{2}}$$
 (A6.5)
SYNTHETIC EXPOSITION

The subject of the present Ph.D. thesis is constituted by the development and application of innovative modeling techniques for the representation of the *thermophysical properties* of fluids.

The thermophysical properties are divided into *thermodynamic properties*, related to states of thermodynamic equilibrium and to transformation processes between two equilibrium conditions, and *transport properties*, concerning systems in a non-uniform state and then affected by transport phenomena; among these, thermal conductivity has been here considered.

The knowledge of the thermophysical properties of pure fluids and mixtures is an absolutely crucial need for the design and the optimization of any equipment in the process industry. The thermophysical properties have to be known in dependence on the controlling variables with a precision as high as possible: errors in the values of the required properties can propagate throughout the entire calculation with amplification effects, yielding wrong design and driving away from the optimal operating conditions.

The purpose of this thesis work is to set up modeling techniques able to represent the thermophysical properties with a precision comparable with the experimental uncertainty of the experimental measurements of the properties themselves reducing at the same time the required experimental effort. The proposed modeling techniques are based on a heuristic approach, that get the functional representation of a physical dependence directly from a properly organized data base; the effectiveness of the developed heuristic techniques is fundamentally based on the use of the *artificial neural network*, which have the characteristic of *universal function approximators*.

The development and application of a heuristic modeling technique to produce equations of state (EoS) in the *fundamental form* for the representation of thermodynamic properties of pure fluids and mixture are presented in the first part of this thesis work. The modeling technique here proposed for the representation of the thermodynamic properties is based on the extended corresponding states (ECS) principle. The basic idea of the ECS model consists in the distortion of the independent variables of the EoS of the reference fluid to transform it into the EoS of the interest fluid. If the simple two-parameter corresponding states principle should work exactly, no tuning distortion would be necessary; since this is not the case, two tuning functions θ and ϕ , indicated as shape functions, are then individually required to exactly match the ECS model with a known thermodynamic surface of the interest fluid.

The basic requirements of the ECS technique are the fulfillment of a *conformality* condition between the reference and the target fluid, and the availability of an accurate equation of state in terms of Helmholtz energy for the reference fluid. In the case that either the conformality condition is not verified among the fluids of a same family or no component of the family, whose fluids are supposed to share a conformality condition, disposes of a DEoS, the discussed ECS method cannot in general be effectually applied.

In the model proposed in this thesis the 'correction' through the variables distortion is performed on a simple EoS representing, even if roughly, the target fluid itself. In other words a simple EoS for the same target fluid is the starting point for the development of a DEoS through the variables distortion, avoiding in this way any problem about the conformality condition fulfillment. It would be then no more necessary to dispose of a 'reference fluid', following the classical interpretation of the ECS theory, but rather of only a 'reference equation', whose precision is enhanced, or 'extended', through the application of the shape functions. Hence the name of *extended equation of state* (EEoS) chosen to indicate this new modeling method.

The shape functions $\theta(T,\rho)$ and $\phi(T,\rho)$ have to be regressed forcing the model to represent known values of experimentally accessible thermodynamic quantities; in the present model their functional formulation is heuristically obtained applying a *multilayer feed-forward neural network* (MLFN) as universal function approximator. The new approach is constituted by a general fitting procedure in which a mathematical form of the a^R surface has to be 'spread' on known values of it and of its derivatives, overcoming the problems presented by the two traditional ECS approaches, i.e., the *local solution* and the *continuous solution*.

The proposed modeling technique comes from the combination of the EEoS method with the neural networks and then it can be concisely indicated as *EEoS-NN* model.

The EEoS-NN model allows to obtain for the fluid of interest a DEoS in the default fundamental form $a(T, \rho)$ which allows to calculate any thermodynamic quantity through mathematical derivations only.

In order to set up the method and to test its potentialities, data generated from a DEoS for each target fluid are used instead of experimental data, so that the model performances are not hindered by error noise and uneven data distribution. Moving from generated data, the capability of the proposed method has been verified both for pure fluids and for mixtures. A group of pure alkanes, haloalkanes, and strongly polar substances has been considered; the results obtained for these fluids are very promising. The same is valid for the five binary mixtures and two ternary mixtures of haloalkanes here studied.

In the case of pure fluids it has been also verified that slightly more than 100 density points evenly distributed in the $P\rho T$ plane and with low experimental error can be a sufficient input for the model development, allowing to reduce the experimental efforts.

The promising performances for the proposed model based on generated data leads to the possibility to reliably develop DEoSs in the EEoS-NN format directly from experimental data.

The EEoS-NN technique was then applied to draw DEoSs for the pure fluids sulfur hexafluoride (SF_6) and 2-propanol (iC₃H₈O) directly from the available data sets of the target fluids.

The DEoS for SF_6 is valid for the liquid, vapor and supercritical region in the ranges from the triple-point temperature at about 223.6 K up to 625 K and for pressures up to 60 MPa, with the exclusion of a region close to the critical point in case of caloric property calculation. The representation of the available experimental data is satisfactory for all the considered properties; in fact the deviations of the equation from the data are comparable with the ascribed uncertainties of the experimental sources. One of the advantages of the EEoS-NN method, shown for the fluid sulfur hexafluoride, is that the data set on which to base the regression procedure can include only density and coexistence values, getting in the meantime a satisfactory performance also for the other properties.

The DEoS for iC_3H_8O is valid for the liquid, vapor and supercritical region for temperatures from 280 up to 600 K and for pressures up to 50 MPa. Due to the substantial lack of data in the near critical region and the non-specialization of this DEoS in representing such region very close to the critical point the present equation is not suggested to be used within a region very close to the critical point. The representation of the available experimental data is satisfactory for all the considered properties; in fact the deviations of the equation from the data are comparable with the realistic uncertainties of the experimental sources for this fluid. The results obtained for the fluid 2propanol demonstrate that the EEoS-NN modeling method is completely reliable to develop highly effective DEoSs even if the experimental data situation for the fluid is not completely favorable. This aspect is particularly valuable in the case a DEoS is required for engineering applications where the economy of the experimental effort and the representation accuracy have to be met through a suitable compromise.

The pointed out features make the EEoS-NN technique a useful tool for the process analysis and optimization. To prove the potential of the cited technique as a tool to study real processes typical of the chemical industry the system propylene + 2-propanol + water has been chosen as an exemplification case. The objective is therefore to investigate the possibility to use the EEoS-NN technique to study the energetic optimization of the *extraction* process of 2-propanol from aqueous solutions using propylene as solvent. This system has been chosen after a screening of the literature data because it seems to present a favorable phase equilibrium behavior for an extraction operation. Furthermore, the propylene + 2-propanol + water system is thermodynamically strongly deviating from ideal behavior due to several causes as the strong polarity of the components, their association behavior, etc., which increases a lot the difficulties of a complete and accurate thermodynamic representation. For such a reason the set up of a DEoS for this system is an interesting challenge

from a scientific point of view, being the first case in which a dedicated equation of state is developed for a strongly deviating ternary mixture.

The experimental data available from the literature for the ternary mixture are vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE). In order to set up a semi-predictive thermodynamic model of the ternary mixture to study its phase behavior, vapor-liquid-liquid equilibrium (VLLE) measurements have been performed. Excess enthalpy measurements have also been carried out for the ternary mixture and for the 2-propanol + water binary mixture in order to obtain a good temperature dependence in the semi-predictive model, constituted of a Peng-Robinson cubic EoS with Wong-Sandler mixing rules and a modified UNIQUAC model to represent the excess Gibbs energy. This model has been used to investigate the phase equilibrium behavior of the ternary mixture from a qualitative point of view. This is a necessary preliminary step to efficiently plan an experimental campaign of measurements suitable to set up a DEoS of the ternary mixture in the EEoS-NN format. The chosen range of interest for the extraction operation is from about 300 to 350 K in temperature, up to 10 MPa in pressure and it extends up to the pure fluids in composition. The properties to be measured in the selected range in order to set up the DEoS are density and phase equilibria. Some isobaric heat capacity measurements are also required to validate the model capability to correctly predict the caloric properties in the range of interest.

Density data have been produced using a vibrating tube densimeter (VTD) for the pure 2propanol, for the propylene + 2-propanol mixture, for the 2-propanol + water mixture and for the propylene + 2-propanol + water mixture. Bubble pressure data were also determined using the VTD for the propylene + 2-propanol mixture and for the propylene + 2-propanol + water mixture.

At present the experimental work is still in progress and phase equilibrium and isobaric heat capacity data have to be carried out. This experimental work, together with the development of a DEoS for the propylene + 2-propanol + water mixture, will constitute the extension of this thesis work. Once a thermodynamic model in EEoS-NN format will be obtained, it will be possible to link it with a process simulator, studying the better operative conditions for the 2-propanol extraction process.

The development and application of a heuristic modeling technique to produce dedicated equations for the representation of the thermal conductivity of pure fluids is presented in the second part of this thesis work.

The proposed model is based on the ECS principle, but the shape functions are got in a continuous analytical form expressed by a universal function approximator, i.e. a neural network, through regression of thermal conductivity data. This innovative approach, named *ECS-NN*, allows to overcome the problems in obtaining the scale factors presented by the two traditional ECS

approaches for transport properties, i.e., the local solution and the continuous solution. The potentiality of the ECS-NN modeling technique for thermal conductivity has been shown with application to both values generated from existing models and experimental values. Assuming R134a as reference fluid, two dedicated thermal conductivity equations have been regressed for carbon dioxide and R152a from the available experimental data. The obtained results are very encouraging; in fact the proposed technique yields thermal conductivity equations that represent the experimental values in the liquid, vapor and supercritical regions within their experimental accuracy; moreover, the method is able to satisfactorily model the strong critical enhancement of thermal conductivity in the near-critical region.

The performance change of the model has been studied varying the number of experimental data in the training procedure, showing that about two hundred data points, regularly distributed on the $\lambda T \rho$ surface of the target fluid, are sufficient to draw a very precise equation, with evident saving of experimental efforts.

Summarizing, the present Ph.D. thesis has shown the effectiveness of the application of heuristic techniques to both thermodynamic and transport property modeling, as a valid alternative to the techniques that are at present adopted. The proposed methods, exploiting the prediction capability of the neural networks, allow to reduce the experimental effort, yielding at the same time equations representing the data within their experimental uncertainties. This feature makes the developed methods suitable tools for the design and optimization of unit operations of the industrial processes.

ESPOSIZIONE RIASSUNTIVA

L'argomento di questa tesi di Dottorato è lo sviluppo e l'applicazione di tecniche modellistiche innovative per la rappresentazione di *proprietà termofisiche* di fluidi.

Le proprietà termofisiche sono divise in *proprietà termodinamiche*, riguardanti stati di equilibrio termodinamico e processi di trasformazione tra due condizioni di equilibrio, e *proprietà di trasporto*, riguardanti sistemi in stato non uniforme e quindi caratterizzate da fenomeni di trasporto; tra queste è stata qui trattata la conduttività termica.

La conoscenza delle proprietà termofisiche di fluidi puri e miscele è un requisito assolutamente fondamentale nella progettazione ed ottimizzazione di qualsiasi apparecchiatura nell'industria di processo. Le proprietà termofisiche devono essere conosciute in dipendenza delle variabili controllanti con una precisione il più elevata possibile: errori nel valore delle proprietà richieste possono propagarsi attraverso l'intero calcolo amplificandosi, dando luogo ad una progettazione scorretta ed allontanando dalle condizioni operative ottimali.

Lo scopo di questa tesi è lo sviluppo di tecniche modellistiche capaci di rappresentare le proprietà termofisiche con un'accuratezza comparabile con l'incertezza sperimentale delle misure stesse, riducendo allo stesso tempo il lavoro sperimentale. Le tecniche modellistiche proposte sono basate su un approccio euristico, che deriva la rappresentazione funzionale di una dipendenza fisica direttamente da una appropriata base di dati; l'efficacia delle tecniche euristiche sviluppate è basata sull'utilizzo delle *reti neurali artificiali*, che hanno la caratteristica di essere *approssimatori universali di funzione*.

Lo sviluppo e l'applicazione di tecniche modellistiche di natura euristica atte a produrre equazioni di stato (EoS) in *forma fondamentale* per la rappresentazione delle proprietà termodinamiche di fluidi puri e miscele sono trattati nella prima parte di questa tesi. La tecnica modellistica qui proposta per la rappresentazione delle proprietà termodinamiche è basata sul principio degli stati corrispondenti estesi (ECS). L'idea alla base del modello ECS consiste nella distorsione delle variabili indipendenti della EoS del fluido di riferimento trasformandola nella EoS del fluido di interesse. Se il principio degli stati corrispondenti a due parametri fosse esatto non sarebbero necessari aggiustamenti delle variabili indipendenti, ma poiché questo non è verificato sono richieste due funzioni distorcenti $\theta \in \phi$, chiamate shape function, per far corrispondere il modello ECS con una superficie termodinamica nota del fluido d'interesse.

Per l'applicazione della tecnica ECS deve essere verificata la condizione di *conformality* tra il fluido di riferimento ed il fluido target, e l'esistenza di un'accurata equazione di stato espressa in forma di energia libera di Helmholtz per il fluido di riferimento. Nel caso in cui la condizione di conformality tra i fluidi non sia verificata, o nessun fluido della famiglia che si suppone presenti

una condizione di conformality con il fluido di interesse disponga di una DEoS, il metodo ECS non può essere applicato efficacemente.

Nel modello presentato in questa tesi la 'correzione' ottenuta attraverso la distorsione delle variabili è applicata ad un'equazione semplice che rappresenta, anche se approssimativamente, lo stesso fluido target. In altre parole, una EoS semplice per il fluido target stesso è il punto di partenza per lo sviluppo di una DEoS per mezzo della distorsione delle variabili, evitando in questo modo il vincolo costituito dalla necessità di soddisfare la condizione di conformality. Non è più quindi necessario disporre di un 'fluido di riferimento', come nell'interpretazione classica della teoria ECS, ma piuttosto solo di una 'equazione di riferimento', la cui precisione è aumentata, o 'estesa', per mezzo dell'applicazione delle shape function. Di qui deriva il nome di *extended equation of state* (EEoS) scelto per indicare questa nuova tecnica modellistica.

Le shape function $\theta(T,\rho) \in \phi(T,\rho)$ devono essere regredite forzando il modello a rappresentare valori noti delle grandezze termodinamiche sperimentalmente accessibili; nel modello proposto la loro forma funzionale è ottenuta in modo euristico utilizzando una *multilayer feed-forward neural network* (MLFN) come approssimatore universale di funzione. La nuova tecnica è costituita da una procedura di fitting in cui la forma matematica della superficie di a^R deve essere 'spalmata' su valori noti della stessa e delle sue derivate, superando i problemi che derivano dai due approcci ECS convenzionali, cioè la *local solution* e la *continuous solution*.

La tecnica modellistica proposta deriva dalla combinazione del metodo EEoS con le reti neurali ed è quindi brevemente indicata come *EEoS-NN*.

Il modello EEoS-NN permette di ottenere per il fluido di interesse una DEoS in forma fondamentale $a(T,\rho)$ che consente di calcolare ogni proprietà termodinamica attraverso il solo utilizzo di operazioni di derivazione.

Allo scopo di mettere a punto il metodo e di testare le sue potenzialità, sono stati scelti alcuni fluidi target per i quali sono stati utilizzati valori generati da una DEoS preesistente al posto dei dati sperimentali, in modo tale che la performance del modello non sia compromessa dall'error noise e dalla distribuzione irregolare dei dati. Utilizzando dati generati la performance del modello è stata verificata per fluidi puri e per miscele. E' stato considerato un gruppo di fluidi puri comprendenti alcani, aloalcani, e sostanze fortemente polari; in ogni caso i risultati ottenuti sono molto promettenti. La stessa considerazione può essere fatta per le cinque miscele binarie e le due miscele ternarie di aloalcani studiate.

Nel caso di fluidi puri è stato anche verificato che un numero poco superiore a 100 punti di densità regolarmente distribuiti sul piano $P\rho T$ e caratterizzati da un basso errore sperimentale

possono essere un input sufficiente per lo sviluppo del modello, permettendo di ridurre il lavoro sperimentale usualmente necessario per l'ottenimento di una DEoS.

Le promettenti prestazioni ottenute della tecnica modellistica applicata ai dati generati conducono alla possibilità di mettere a punto delle DEoS in forma EEoS-NN utilizzando direttamente dati sperimentali.

La tecnica EEoS-NN è stata quindi utilizzata per produrre la DEoS per i fluidi puri esafluoruro di zolfo (SF₆) e 2-propanolo (i C_3H_8O) direttamente dai dati sperimentali dei due fluidi.

La DEoS per il fluido SF₆ è valida nel liquido, vapore e supercritico dalla temperatura del punto triplo, a circa 223.6 K, fino a 625 K e per pressioni fino a 60 MPa, con l'esclusione della regione prossima al punto critico nel caso delle proprietà caloriche. La precisione con cui il modello rappresenta i dati è da considerarsi soddisfacente per tutte le proprietà termodinamiche, infatti le deviazioni dell'equazione dai dati sono confrontabili con l'incertezza attribuita alle fonti sperimentali. Uno dei vantaggi del metodo EEoS-NN, evidenziato nell'applicazione al fluido esafluoruro di zolfo, è che la procedura di regressione della DEoS può essere basata su una base dati comprendente solo valori di densità e coesistenza, ottenendo allo stesso tempo una rappresentazione accurata anche delle altre proprietà.

La DEoS per il fluido i C_3H_8O è valida nel liquido, vapore e supercritico per temperature da 280 a 600 K e per pressioni fino a 50 MPa. A causa della mancanza di dati nella regione prossima al punto critico e della non-specializzazione della forma funzionale di questa DEoS nella rappresentazione delle proprietà termodinamiche nelle immediate vicinanze del punto critico l'utilizzo della presente equazione è sconsigliato nella suddetta regione. La rappresentazione delle proprietà termodinamiche è soddisfacente per tutte le proprietà considerate, infatti le deviazioni dell'equazione dai dati sono confrontabili con i valori realisticamente attribuibili alle fonti sperimentali. I risultati ottenuti per il fluido 2-propanolo dimostrano che il metodo modellistico EEoS-NN è completamente affidabile per lo sviluppo di equazioni di stato dedicate anche nella condizione non favorevole in cui i dati sperimentali presentano una scarsa qualità. Questo aspetto è particolarmente importante nel caso in cui una DEoS sia necessaria per applicazioni ingegneristiche, dove deve essere raggiunto un compromesso tra l'economia del lavoro sperimentale e l'accuratezza della rappresentazione delle proprietà termodinamiche.

Le caratteristiche evidenziate fanno della tecnica EEoS-NN uno strumento utile per la progettazione e l'ottimizzazione dei processi. Il sistema propilene + 2-propanolo + acqua è stato scelto come caso esemplificativo per provare le potenzialità della tecnica EEoS-NN per l'analisi di processi reali tipici dell'industria chimica. L'obiettivo è perciò indagare la possibilità di utilizzare la tecnica EEoS-NN per studiare l'ottimizzare dal punto di vista energetico del processo di *estrazione*

del fluido 2-propanolo da soluzioni acquose utilizzando il propilene come solvente. Questo sistema è stato scelto dopo uno screening dei dati disponibili in letteratura poiché sembra presentare un andamento degli equilibri di fase adatto per un'operazione di estrazione. Inoltre il sistema propilene + 2-propanolo + acqua presenta un comportamento termodinamico fortemente deviante dall'idealità a causa della forte polarità dei componenti e del loro comportamento associante, aumentando le difficoltà per l'ottenimento di un modello che rappresenti accuratamente le proprietà termodinamiche. Per questo motivo la realizzazione di una DEoS per questo sistema è una sfida interessante dal punto di vista scientifico, infatti esso è il primo caso in cui viene realizzata un'equazione di stato dedicata per una miscela ternaria fortemente deviante.

I dati sperimentali disponibili in letteratura per la miscela ternaria sono di equilibrio vaporeliquido (VLE) e di equilibrio liquido-liquido vapore (LLE). Allo scopo di ottenere un modello termodinamico semi-predittivo per la miscela ternaria per studiarne l'equilibrio di fase, sono state effettuate anche misure di equilibrio vapore-liquido-liquido (VLLE). Inoltre, sono state misurate le entalpie di eccesso per la miscela ternaria e per la miscela binaria 2-propanolo + acqua al fine di ottenere una buona rappresentazione della dipendenza dalla temperatura nel modello semipredittivo, costituito da una EoS cubica di tipo Peng-Robinson, con regole di miscela di tipo Wong-Sandler e un modello UNIQUAC modificato per la rappresentazione della energia libera di Gibbs. Questo modello è stato utilizzato per investigare l'equilibrio di fase della miscela ternaria da un punto di vista qualitativo, step preliminare necessario per pianificare efficientemente una campagna di misure sperimentali adatte ad ottenere una DEoS nel formato EEoS-NN per la miscela. Il range di interesse scelto per il processo di estrazione è circa da 300 a 350 K in temperatura, fino a 10 MPa in pressione e si estende fino ai fluidi puri in composizione. Le proprietà che devono essere misurate in questo range al fine di regredire una DEoS sono densità ed equilibri di fase. Sono inoltre richieste alcune misure di calore specifico a pressione costante per valicare la capacità del modello di rappresentare in modo predittivo le proprietà caloriche nel range di interesse. Il range di interesse per la composizione si estende fino ai fluidi puri.

Utilizzando un densimetro a tubo vibrante (VTD) sono state effettuate misure di densità per il fluido puro 2-propanolo, per la miscela propilene + 2-propanolo, per la miscela 2-propanolo + acqua e per la miscela propilene + 2-propanolo + acqua. Ad oggi l'attività sperimentale è ancora in corso, e devono essere effettuate misure di equilibrio di fase e di calore specifico a pressione costante. Questo lavoro sperimentale, insieme alla regressione di una DEoS per la miscela propilene + 2-propanolo + acqua, costituirà il proseguimento di questo lavoro di tesi. Una volta che un modello termodinamico in forma EEoS-NN sarà stato ottenuto, sarà possibile integrarlo in un

simulatore di processo, permettendo quindi lo studio delle condizioni operative migliori per il processo di estrazione del fluido 2-propanolo.

Lo sviluppo e l'applicazione di tecniche modellistiche di natura euristica atte a produrre equazioni dedicate per la rappresentazione della conduttività termica di fluidi puri sono trattati nella seconda parte di questa tesi.

Il modello proposto è basato sul principio ECS, ma le shape functions sono prodotte in una forma analitica continua espressa attraverso un approssimatore universale di funzione, anche in questo caso una rete neurale, attraverso la regressione di dati di conduttività termica. Questo approccio innovativo, denominato *ECS-NN*, permette di superare i problemi che derivano dai due approcci ECS convenzionali, cioè la local solution e la continuous solution. Le potenzialità della tecnica modellistica ECS-NN per la conduttività termica sono state dimostrate con l'applicazione sia a dati generati da modelli preesistenti, sia a dati sperimentali. Assumendo R134a come fluido di riferimento, sono state ottenute equazioni dedicate di conduttività termica per l'anidride carbonica e per il fluido R152a basate sulle misure sperimentali disponibili in letteratura. I risultati ottenuti sono incoraggianti, infatti la tecnica proposta permette di ottenere equazioni dedicate di conduttività termica che rappresentano i valori sperimentali nelle regioni del liquido, vapore e supercritico con un'accuratezza confrontabile con la loro l'incertezza sperimentale dei dati stessi; inoltre il metodo è adatto alla rappresentazione dell'elevato critical enhancement della superficie di conduttività termica nella regione prossima al punto critico.

La variazione della performance del modello è stata studiata variando il numero di dati sperimentali nella procedura di training, mostrando che circa duecento punti, regolarmente distribuiti sulla superficie $\lambda T \rho$ del fluido target, sono sufficienti a ricavare un'equazione molto precisa, con notevole riduzione del lavoro sperimentale.

Riassumendo, questa tesi di Dottorato ha mostrato l'efficacia dell'applicazione di tecniche euristiche come valida alternativa alle tecniche attualmente utilizzate per la rappresentazione sia delle proprietà termodinamiche sia delle proprietà di trasporto. I metodo proposti, sfruttando la capacità predittiva delle reti neurali, permettono di ridurre il lavoro sperimentale, producendo allo stesso tempo equazioni in grado di rappresentare i dati con un'accuratezza all'interno della loro incertezza sperimentale. Questa caratteristica fa si che le tecniche sviluppate possano essere considerate strumenti adatti per la progettazione e l'ottimizzazione di operazioni unitarie di processi industriali.

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