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TESI DI DOTTORATO

**Hybrid Lattice Boltzmann Simulations
of Liquid Crystal Emulsions under Shear**

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Sommario

Al fine di studiare le caratteristiche all'equilibrio e le proprietà reologiche di emulsioni binarie di cristalli liquidi, in questo lavoro di tesi sono stati studiati, mediante un algoritmo di simulazione *Lattice Boltzmann* ibrido, la configurazione all'equilibrio e gli effetti di uno sforzo di taglio su una goccia di un cristallo liquido calamitico liotropico in fase isotropa, a coesistenza con la corrispondente fase nematica. All'equilibrio, sotto esame è sia la forma della goccia, in corrispondenza di diversi valori dei parametri fisici che governano il sistema, sia il profilo dell'orientazione e del grado di ordine del solvente nematico. Sia per un sistema bidimensionale che per un sistema tridimensionale, i risultati hanno evidenziato che la forma della goccia è essenzialmente determinata dai “rapporti di forza” tra la tensione superficiale, la forza di ancoraggio del nematico in corrispondenza dell'interfaccia, e le forze elastiche che si oppongono alle distorsioni del nematico stesso. Tutte le gocce simulate sono state in seguito sottoposte ad uno sforzo di taglio, esaminandone le deformazioni: si sono osservati diversi fenomeni non presenti in emulsioni di fluidi newtoniani o viscoelastici, spesso legati alla presenza di difetti topologici.

Abstract

In order to study the equilibrium and the rheological properties of binary emulsions of liquid crystals, in this thesis the equilibrium configuration and the effect of a shear flow on a calamitic, lyotropic liquid crystal droplet in the isotropic phase at coexistence with its corresponding nematic phase have been investigated through a hybrid Lattice Boltzmann algorithm. At equilibrium, both the shape of the droplet, corresponding to different values of the physical parameters which govern the system, and the orientation, as well as the order degree of the nematic solvent, have been investigated. Both for a two-dimensional and for a three-dimensional system, the results of the simulations have shown that the shape of the droplet is determined, essentially, by the relative values of the surface tension, the nematic anchoring strength at the interface, and the elastic forces opposing distortions inside the nematic phase. To all the simulated droplets a shear stress have been imposed, then, and the deformations have been examined: several features which are absent in emulsions of Newtonian or viscoelastic fluids have been observed, and are often related to the presence of topological defects.

Introduction

0.1 Aim of the thesis

The aim of this thesis is to investigate, by numerical simulations, the behaviour of a very diluted two-dimensional and three-dimensional nematic emulsion of liquid crystals, both at rest and under a shear stress.

More precisely, the system which I studied consists of a single droplet of isotropic phase in suspension with its corresponding nematic phase, at coexistence; and the whole system, if shear stress is applied, is sandwiched between two parallel walls, as in the twisted nematic cells of liquid crystal displays. Periodic boundary conditions along the walls simulate an infinitely extended system.

I started from the droplet at rest: I studied its shape and the structure of the surrounding nematic: in particular, the topological defects (see Sec. 1.6 for details) induced by its presence.

Then, I turned the shear stress on (i. e. the motion, in opposite direction, of the two walls confining the system), and I studied how the droplet deforms: to what extent it maintains its original shape (elliptical, for two-dimensional systems; ellipsoidal, in the three-dimensional case), if it breaks up when the shear rate increases, how the topological defects influence the deformation.

0.2 Drop deformation in simple and complex fluids

The first experiments about the deformation (and breakup) of an immiscible droplet inside a matrix fluid, due to a shear flow, date back to the 1930s (G. I. Taylor, [1, 2]). The problem is interesting for a better understanding of the rheological properties of multi-phase liquids and has a lot of science and engineering applications, as well. Immiscible polymer blend processing is one of these applications: Cristini and Renardy [6] performed numerical computations to explain the experimental fact that the application of a shear to

an emulsion with a broad distribution of droplet sizes carries out a monodisperse emulsion [7], and fabrication of monodisperse emulsion is crucial for droplet-based microfluidics [8]. In another branch of related science, it has been observed that one of the causes of hemolysis in people with cardiovascular prostheses is shear stress [9, 10], and the ability of red blood cells to deform influences the effective blood flow in the cardiovascular system [11].

Important reviews about shear-induced deformation of neutrally buoyant drops in viscous fluids are due to A. Acrivos [3], J. M. Rallison [4] and H. A. Stone [5]. These studies, and the studies related to them [12, 112], deal only with Newtonian emulsions, i. e. emulsions of two viscous fluids where the stress (force per unit area) is proportional to the shear rate, with the viscosity being the proportionality constant. Such systems are fully described in terms of three dimensionless numbers: the Reynolds number (inertial forces vs. viscosity), the capillary number (viscous forces vs. surface tension) and the ratio between the viscosities of the drop and the matrix fluid. Among the recent works, the papers of Farokhirad *et al.* [13] and Komrakova *et al.* [14] are worth to be mentioned, since the authors used the same simulation algorithm that I used. In the former, the effect of the confinement is investigated, as well.

Going beyond the relative simplicity of Newtonian fluids, an extensive literature [18, 15, 16, 19, 20] is dedicated to viscoelastic fluids: namely, fluids in which the current value of stress depends on its strain history. These fluids are somehow halfway between an ordinary liquid and an elastic solid. Not all non-Newtonian fluids are viscoelastic and, in order to distinguish between viscous and elastic effects, the above mentioned works focused on Boger fluids, i. e. elastic fluids where the viscosity is constant. Viscoelastic and Newtonian fluids can be mixed together, and experiments and calculations have been carried out, for instance, for Newtonian drops in a viscoelastic matrix, viscoelastic drops in a Newtonian matrix, viscoelastic drops in a viscoelastic matrix. Viscoelasticity is often modeled with Oldroyd-B equations [21], and a measure of the viscoelasticity is the dimensionless Deborah number [22], i. e. the ratio between the relaxation time of the fluid and the time of observation, the latter being, in this particular case, the reciprocal of the shear rate.

When studies of drop deformations under shear are carried out for emulsions of viscoelastic fluids the Deborah number is a further characteristic of the system that must be taken into account in addition to the three numbers mentioned above for emulsions of Newtonian fluids under shear.

0.3 Peculiarities of liquid crystals

When the emulsion is made by a mixture of liquid crystal phases the problem of equilibrium shape and shape deformation under stress is further enriched by the possible orientational order that the system may acquire locally. This is essentially due to the anisotropic character of the elementary constituents of the liquid crystal (molecules).

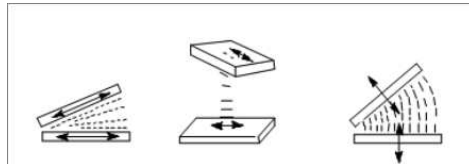


Figure 1: The three basic types of deformations occurring in nematic, obtained by imposing proper anchoring at the walls (see Sec. 1.5.3): from left to right, splay ($\nabla \cdot \hat{\mathbf{n}} \neq 0$), twist ($\nabla \wedge \hat{\mathbf{n}} \perp \hat{\mathbf{n}}$), and bend ($\nabla \wedge \hat{\mathbf{n}} \parallel \hat{\mathbf{n}}$). For the definitions, refer to Secs. 1.3 and 1.5.1.

Indeed the molecules of a liquid crystal often display a rod-like anisotropy and tend, under given conditions, to orient themselves on average along a common direction (local director) forming orientationally ordered phases, such as the nematic phase or the cholesteric phase. Local deviations from the common alignment produces distortions such as splay, bend and twist, each with an energetic cost to pay. These distortions couple with the velocity field of the system giving rise to the so-called backflow effect that, in turn, affects importantly the rheological properties of the system.

In nematic emulsions, in addition to the usual interface energy, one has to take into account anchoring strength and orientation of the director at the interface [24]: these two effects, together with the energetic cost of director distortions, can compete in determining the optimal shape of the droplet. Finally, and most importantly, a liquid crystal, being an ordered medium, may display topological defects, i. e. points, lines or surfaces of the systems where the order parameter changes abruptly [28]. Defects are the result of a frustration of the local orientation that needs to satisfy conflicting boundary conditions occurring, for example, in patterned confining walls, at the surfaces of suspended colloids or at the interface with an isotropic region.

The formation, the spatial organization and the reciprocal interactions of topological defects have been the subject of several experimental [26] and theoretical [29, 30, 31] studies with potential important applications such as the implementation of colloidal-nematic emulsions is the design and fabrication of photonic crystals [32].

Most papers, up to now, have focused on the topology of the director field close to the interface of the droplet: even when an external field is present, they often study only the dynamics of the defects [33] by keeping the droplet undeformed and static. The reason for it is that, at first approximation, we can expect the droplets to be spherical and undistorted by the nematic director, if their size is larger than the ratio between the elastic constant of the nematic and the surface tension of the isotropic-nematic interface, which is usually ≈ 1 nm [29]. If this ratio is much bigger than the droplet size, this approximation is not any more valid and the droplet deformation/motion must be taken into account in the overall dynamics of the system, as it is done in this thesis.

In this respect, about ten years ago a few important papers were published. Two of them constitute the work of Lishchuk *et al.* [99, 100], who investigated theoretically the shape of an isotropic droplet in a nematic matrix, assuming the director field as undistorted far from the interface and giving special attention to the role of surfactant. Sulaiman *et al.* [34], making a few less approximations, focus both on the structure of the director field and on the shape of a (two-dimensional) isotropic droplet, both at equilibrium and in presence of an electric field.

In the latter work, the authors adopted the Landau-de Gennes [25] form for the free energy (which has to be minimized) and employed a Lattice Boltzmann BGK scheme [35, 36, 78, 37] to solve numerically all the equations of motion. Although the approach is similar to the one used in [34], the algorithm I resorted to is slightly different. In particular, while the Lattice Boltzmann BGK scheme is used to solve the continuity and Navier-Stokes equations (i. e. for the local densities), for the equations of motion of the order parameter (Beris-Edwards equation, see [38]) and for the Cahn-Hilliard like equation of the two components of the emulsion (nematic and isotropic) [69]), an ordinary predictor-corrector finite difference method is implemented. This kind of approach, known as **hybrid Lattice Boltzmann algorithm**, has been shown in the past to be very effective in simulating several different complex fluids [84], binary mixtures [88, 89] and, of course, liquid crystals systems under different boundary conditions [85, 86, 87].

0.4 Organization of the thesis

The thesis is organized as follows. In Chapter 1 I give you the essential notions about liquid crystals and binary emulsions: the possible phases, the tensor order parameter, the various contributions to the total energy, the topological defects. Chapter 2 goes into detail about the hybrid Lattice

Boltzmann algorithm I adopted for my simulations. The other chapters are dedicated to the discussion of the calculations.

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Chapter 1

Liquid crystals and their emulsions

1.1 Introduction and historical overview

With the expression *liquid crystal*, we refer to any state of matter whose symmetric and mechanical properties are intermediate between a crystalline solid and an ordinary liquid [40].

In a crystalline solid, molecules are ordered in every direction, whereas the molecules of a liquid can glide freely over each other: their distances are distributed according to a particular law (radial distribution function), which is independent of the direction. There is no order along any direction (isotropy).

A liquid crystal has a partial order, i. e. their molecules, which are always anisotropic, have a crystal-like ordering at least along one spatial direction. There is a huge variety of substances whose phase diagram contains liquid crystalline phases: the first one to be observed was cholesteryl benzoate, an ester of cholesterol and benzoic acid, which is still employed in cosmetic industry and as a component of liquid crystal displays [40]. Friedrich Reinitzer [44], in 1888, noticed that this substance seems to have two distinct melting points: at room temperature it is a white powder, at 145°C it becomes a cloudy liquid, and turns clear at 179°C. The expression *fließender Kristall* (liquid crystal) was coined by Otto Lehmann, one year later [45], who identified “a new and distinct state of matter” .

After Merck AG fabricated and put some liquid crystals on the market (1904), and after Georges Friedel wrote the classification of the *mesomorphic states* (smectic, nematic, cholesteric) which we still refer to nowadays, liquid crystals were considered no more than a laboratory curiosity. The turning

point were the first prototypes of liquid crystal displays (1968) [40] and the work of Pierre-Gilles de Gennes [25], which culminated in his 1991 Nobel Prize.

Now, liquid crystals are one of the most popular fields of research in Soft Condensed Matter Physics, both experimentally and theoretically with a huge feedback in technical applications.

1.2 Liquid crystalline materials and mesophases

Today we know that the “cloudy liquid” observed by Reinitzer is the chiral nematic phase of the cholesteryl benzoate, a thermotropic organic compound. This is, however, just one of the several mesophases discovered in liquid crystals, most of which depend not only by physical parameters such as the concentration of molecules and the temperature, but also by the geometry of the molecules involved.

What do we mean with the word *mesophase*?

1.2.1 Classification of liquid crystalline compounds: molecular shape, chirality, physical parameters triggering transition between phases

As said previously, the molecules forming liquid crystalline substances are often strongly anisotropic, i. e. with one of their axes very different from the other two.

Although there is a lot of intermediate species, from this point of view liquid crystals can be divided into *calamitics* (rod-like molecules) and *discotics* (disc-shape molecules). The different geometry of such molecules (Fig. 1.1) reflects to the different mesophases that may occur in the system (see below).

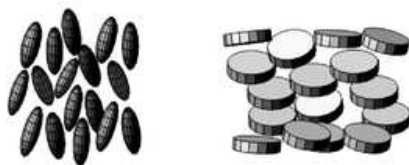


Figure 1.1: Schematic representation of calamitic (left) and discotic (right) liquid crystal molecules. Picture sourced from [41].

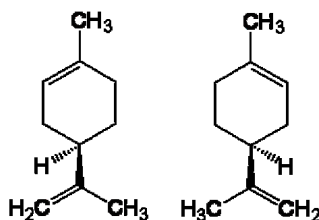


Figure 1.2: Structure of D-(+)-limonene (left) and L-(-)-limonene (right), enantiomers of limonene, a chiral dopant for liquid crystals [42]. The two molecules have the same chemical composition and chemical bonds, but they are non-superposable mirror images. Picture sourced from <http://www.icmab.es/resolve/what-is-an-enantiomer.html>.

Another important characteristic that may give rise to different mesophases is the chirality of the molecules: in a liquid crystal, the molecules can be *achiral*, *chiral* or a mixture of them. A chiral molecule has a non-superposable mirror image: this feature is often caused by the presence of an asymmetric carbon atom,¹ as pictured in Fig. 1.2. The presence of a given concentration of chiral molecules may give rise to equilibrium phases that are chiral, i. e. that lack inversion symmetry.

In general, different mesophases can occur in a liquid crystal and the transitions between the different phases are triggered either by a change in temperature (*thermotropic liquid crystals*) or because of a change in molecular concentration (*lyotropic liquid crystals*²). Cholesteryl benzoate is clearly thermotropic, while most lyotropic liquid crystals are formed by amphiphilic molecules in polar or non-polar solvents (soaps and phospholipides) [95].

1.2.2 Mesomorphic states

In a liquid crystal, the positional order, typical of a crystalline solid, disappears, either fully or partially, while a kind of orientational order remains. This orientational, and sometimes positional, order, does not hinder the molecular mobility: that means, the aspect is liquid-like.

For that reason such a phase is called mesomorphic (intermediate). Georges Friedel (see Sec. 1.1) opposed the name *liquid crystal*, since there is actually

¹Quite all liquid crystals are organic compounds.

²Recently, an important class of liquid crystalline inorganic materials, which are called *metallotropic liquid crystals*, has been developed. They are formed by exploiting cationic surfactant templating of molten divalent metal halides. See [46] and references therein.

a variety of mesomorphic phases, and each one has its own features.

What follows is a succinct classification of liquid crystal phases.

- The **isotropic** phase is a classical liquid phase. There is no long-range pair correlation and the orientation of the molecules is uniformly distributed in space.



Figure 1.3: Arrangement of the molecules of a calamitic, achiral liquid crystal in the nematic phase. Picture sourced from [43].

- The **nematic** phase (Fig. 1.3) is the simplest of all mesophases: it is the one which preserves the highest symmetry. In textbooks and papers, a nematic is usually a calamitic: there exist *discotic nematics*, too, with analogous properties (Fig. 1.6). The centres of mass of the molecules are spatially distributed as in a liquid, but their major axes tend to align along a particular direction. The coarse-grained average orientation $\hat{\mathbf{n}}$ (i. e., an average computed over a mesoscopic volume, like in the Ginzburg-Landau theory of ferromagnetism of spin-1/2 magnets), which is a function of space (and time), is called **director** (see Sec. 1.3 for more details). The space variation of the director, at rest, depends on the boundary conditions (see Sec. 1.5.3): in an infinite nematic, $\hat{\mathbf{n}}$ is uniform, because its distortions have an energy cost.
- The **cholesteric** (or **chiral nematic**) phase (Fig. 1.4) is the equivalent of the nematic phase for a chiral compound. The centres of mass are arranged as in a liquid, but the director is not uniform in space: the chirality of the molecules induces a twisting around an axis perpendicular to it: the rotation can be left- or right-handed, according to whether enantiomer is present³.

³The pitch of the helix usually decreases when a cholesteric LC is heated. Since the pitch

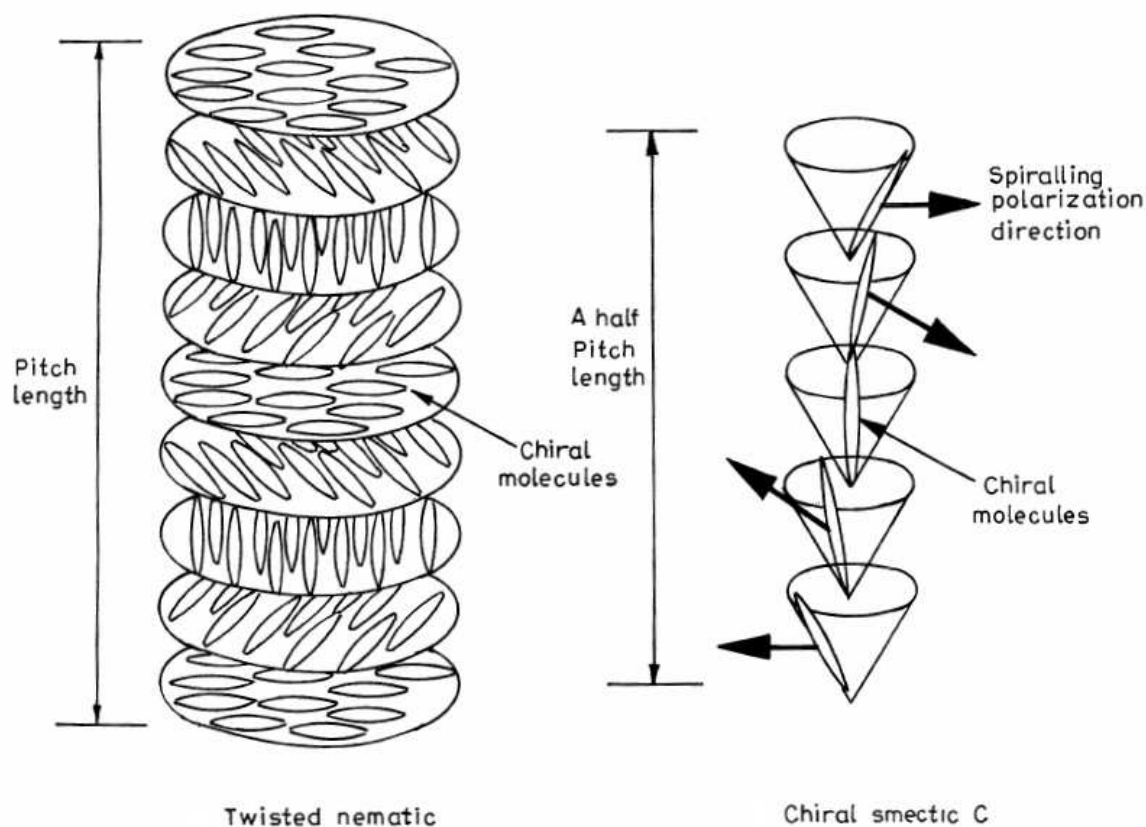


Figure 1.4: Arrangement of the molecules of a calamitic, chiral liquid crystal in the cholesteric phase (left) and in the Smectic-C* chiral phase (right). Picture sourced from [43].

- The **blue phases** occur only for chiral molecules, in a very narrow range of temperatures⁴ ($\approx 1^\circ \text{C}$ [47]) or concentration, between the isotropic and the chiral nematic phase. They are characterized by a simple cubic (BP1), body-centred cubic (BP2) or amorphous, locally cubic (BP3) arrangement of defects (see Sec. 1.6). Blue phases were first studied in the late 1970s, although, surprisingly enough, they had been already observed by Reinitzer himself, who wrote, in his first report [44], that “cholesteryl benzoate briefly turned blue when changing from clear to cloudy upon cooling.”

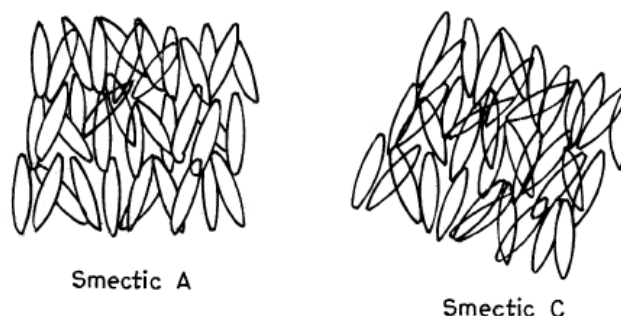


Figure 1.5: Arrangement of the molecules of a calamitic, achiral liquid crystal in the Smectic-A (left) and Smectic-C (right) phase. Picture sourced from [43].

- The **smectic** phases, either achiral or chiral, are closer to the solid phases than the nematic ones: while nematic is ordered only in one direction, smectics are ordered in two directions. More precisely, the molecules of a smectic phase are arranged in a layered structure, where the parallel layers can slide one on top of the other in a liquid fashion. Within each layer of the two most common smectic phases (Fig. 1.5), the centres of mass of the molecules are free to move as in a two-dimensional liquid. In a smectic-A, the average orientation of the molecules is perpendicular to the layer planes – and there is cylindrical symmetry around this direction, therefore; smectic-C breaks this symmetry by tilting the molecules.

determines which light frequencies are reflected, its colour changes, too: LC thermometers rely on this principle.

⁴Recently, materials whose phase diagrams show blue phases in a wider temperature range ($\approx 44^\circ \text{C}$), have been synthesized [48]: that paved the way to practical applications.

These two mesophases are achiral. For symmetry reasons, there does not exist any chiral phase akin to smectic-A⁵, whereas there exists chiral smectic-C* (Fig. 1.4).

Beside them, there is a wide variety of other smectic phases, in which the layers possess internal structure.

- The **columnar** phases are the equivalent discotic of the smectic phases: the molecules are arranged in stacks, along each one of which there is no long-range correlation. Also the smectic phases with internal structure within each layer have their discotic analogous: the *ordered columnar*. A snapshot of an ordered columnar might look like an ordinary crystal, but the stacks can glide one over another.

Figs. 1.7 and 1.8 show the phase diagrams of two thermotropic liquid crystals; Fig. 1.9 shows three phase diagrams of a ternary lyotropic liquid crystalline system (see captions).

1.3 Director, scalar and tensor order parameter for nematics

From now on, I will concentrate only on achiral, calamitic nematic phases and on the isotropic one, since these phases will be the essential constituents of the nematic emulsion I am going to study.

As mentioned in Sec. 1.2.2, in a nematic phase, the average orientation of the molecular major axes over a mesoscopic volume is different from 0. It is a unit length vector field – actually a headless vector field, because of the invariance under inversion of the major axis – it is commonly denoted with $\hat{\mathbf{n}}(\mathbf{r})$ and is called **director**:

The director, by the way, furnishes only the local average orientation of the liquid crystal: it does not quantify the local degree of ordering, i. e. the amount of molecules that within a mesoscopic volume are aligned along $\hat{\mathbf{n}}(\mathbf{r})$.

⁵Smectic-A (and smectic-C, too), however, can be frustrated into blocks of pure smectic material separated by parallel, regularly spaced grain boundaries, formed by a periodic array of screw dislocations which allows helical twist. This kind of phases are called *twist grain boundary* [49, 50, 51].

In a slightly narrower temperature range than for classical blue phases ($\approx 0.15^\circ \text{C}$), three *smectic blue phases* have been observed for the chiral material FH/FH/HH-18BTMHC. They are similar to classical blue phases, except for the positional order in one direction and for the hexagonal symmetry, at least for BP_{Sm2} [52, 53].

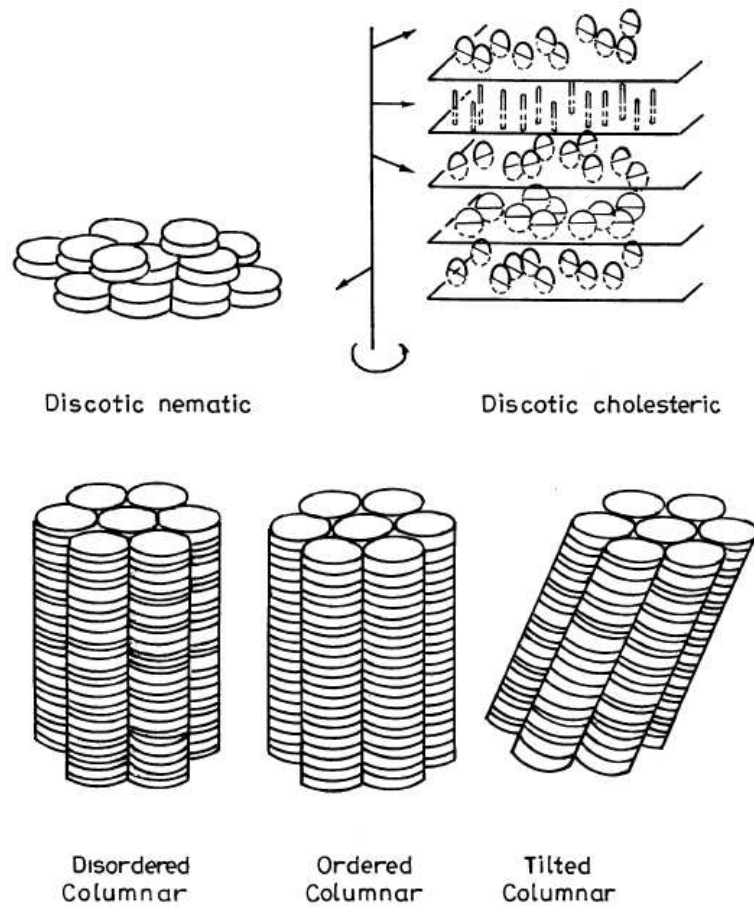


Figure 1.6: Arrangements of the molecules of a discotic, both achiral and chiral, liquid crystal. Picture sourced from [43].

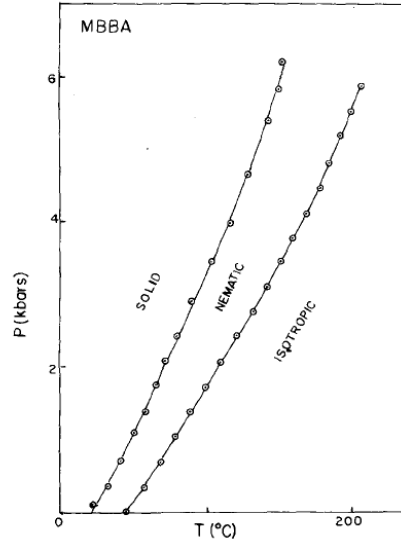


Figure 1.7: Phase diagram of N-(4-methoxybenzylidene)-4-butylaniline (MBBA), a thermotropic liquid crystal with solid, nematic and isotropic phases, sourced from [94].

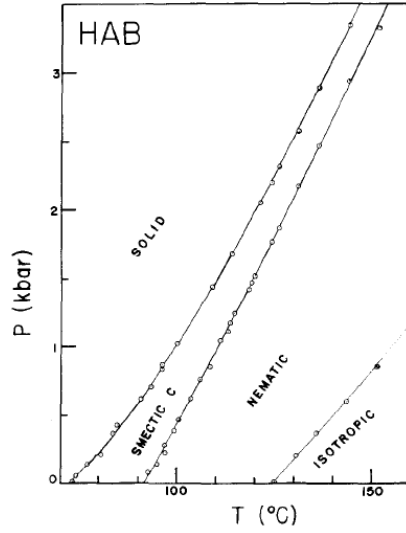


Figure 1.8: Phase diagram of 4,4'-bis(heptyloxy)-azoxybenzene (HAB), a thermotropic liquid crystal with solid, smectic-C, nematic and isotropic phases, sourced from [94].

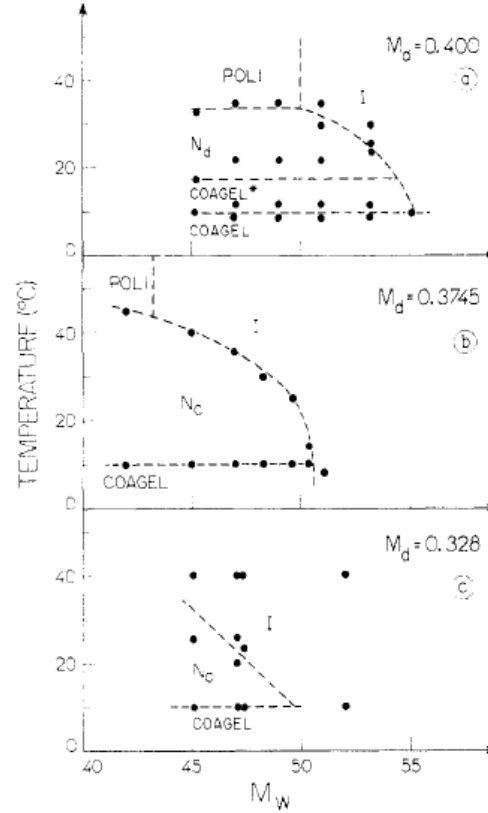


Figure 1.9: Phase diagrams of the lyotropic ternary sodium dodecyl (lauryl) sulfate/water/1-decanol system, as function of the water molar ratio (M_W), for three fixed values of the decanol molar ratio (M_d), sourced from [96]. N_c and I stand, respectively, for *calamitic nematic* and *isotropic*: we can think of the nematic-isotropic binary mixture investigated in Chapters 3 to 6 as a point on the upper dashed line in either the (b) or the (c) graph. N_D stands for *discotic nematic* – it is common, for lyotropic ternary systems, to have both calamitic and discotic phases [95]. POLI indicates a polyphase, and for information about coagel phase refer to [97].

A possible way to get this information consists in computing the average projection of the principal axis of the molecules on the director: if θ is the angle formed by the two directions, a natural **scalar order parameter** to compute would be:

$$q \equiv \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (1.1)$$

With this choice, if the nematic is perfectly ordered ($\langle \cos^2 \theta \rangle = 1$), we have $q = 1$. On the other hand, if the phase is fully disordered, i. e. the rod-like molecules are oriented randomly in space, one has $\langle \cos^2 \theta \rangle = 1/3$ and $q = 0$. It is interesting that a negative value of q is possible, corresponds to the situation in which the molecules tend to be confined to a plane perpendicular to the director.

Physical values of q belong to the interval $[-0.5, 1]$.

The introduction of a measure for the degree of alignment is one of the cornerstones of the Maier-Saupe theory of nematic phases [54], although, often, in a real system this quantity is not sufficient to fully describe the ordering. Indeed, one of the reasons for the discrepancies with the experimental values is that real nematogens do not have perfect cylindrical symmetry: this causes a significant, anisotropic alignment along a secondary axis. In this case, the nematic is **biaxial**, whereas in the more ideal case in which a secondary alignment axis is negligible, the nematic is **uniaxial** [59].

In order to account for biaxiality, too, the notion of director field $\hat{\mathbf{n}}$ and of scalar order parameter q must be generalized by defining the **tensor order parameter**⁶:

$$Q_{\alpha\beta} \equiv \langle u_\alpha u_\beta - \frac{1}{3} \delta_{\alpha\beta} \rangle \quad (1.2)$$

where u_α is the unit vector parallel to the principal axis of a single molecule, and $\delta_{\alpha\beta}$ is the Kronecker delta ($\alpha, \beta \in \{1, 2, 3\}$).

This tensor is symmetric and traceless, and at equilibrium it depends only on the director $\hat{\mathbf{n}}$. The most general form of such a tensor is [55]:

$$Q_{\alpha\beta} = q \left(n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta} \right) \quad (1.3)$$

and it follows from Eqs. (1.2) and (1.3) that q is the same q defined in Eq. (1.1), and is 1.5 times the biggest eigenvalue of $Q_{\alpha\beta}$.

⁶Throughout this whole thesis, the Einstein summation convention is adopted, i. e. when an index appears twice in a single addend, it implies summation of that term over all the values of the index.

With this approach we can say that if the second and third eigenvalue of $Q_{\alpha\beta}$ are equal (and smaller than the first one) the nematic is uniaxial; otherwise, it is biaxial. We will return to biaxiality in Sec. 1.7.2.

1.4 Bulk terms of the Helmholtz free energy

The systems we are going to investigate are lyotropic binary emulsions, with a nematic and an isotropic phase at coexistence: they are supposed to be at fixed temperature, volume and number of particles. With these constraints, the equilibrium phases correspond to the minima of the Helmholtz free energy $\mathcal{F}$.

In this section, we will go through the terms, constituting the Helmholtz free energy, which depend on the bulk properties of the system: the tensor field $\mathbf{Q}$ and the scalar field ϕ , the former defined in Sec. 1.3, the latter defined as the nematic concentration, more precisely its volume fraction.

In Sec. 1.5 we will enumerate the terms which depend on the gradients of $\mathbf{Q}$ and ϕ , i. e. on their distortions, together with the terms depending on the boundaries.

1.4.1 The Landau-de Gennes free energy

In order to approximate the Helmholtz potential (per unit volume) $\mathcal{F}_s$ for the liquid crystal under static conditions, in the spirit of Landau theories, we assume that it is an analytic function of the tensor order parameter $Q_{\alpha\beta}$. As long as $Q_{\alpha\beta}$ is a small parameter, we can expand it in power series: in particular, this expansion is expected to work well near the nematic-isotropic transition point.

Since the Helmholtz free energy must be invariant under rotations, the terms of the expansion have to be scalar:

$$\mathcal{F}_s = \mathcal{F}_0 + \frac{1}{2}A Q_{\alpha\beta} Q_{\alpha\beta} - \frac{1}{3}B Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{1}{4}C Q_{\alpha\beta} Q_{\alpha\beta} Q_{\gamma\delta} Q_{\gamma\delta} \quad (1.4)$$

The numerical coefficients are introduced for convenience, as well as the minus sign before the term of order 3. $\mathcal{F}_0$ is the free energy at $\mathbf{Q} = 0$ (isotropic state), and the expansion is truncated at order 4. We notice that the second term contains the trace of $\mathbf{Q}^2$ and the third term contains the trace of $\mathbf{Q}^3$. The trace of $\mathbf{Q}$ does not appear because it is 0, and a theorem of linear algebra states that, being $Q_{\alpha\beta}$ symmetric and traceless, $Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\delta} Q_{\delta\alpha}$, which in the general case would be another scalar containing a fourth power of the $Q_{\alpha\beta}$'s, equals $\frac{1}{2} Q_{\alpha\beta} Q_{\alpha\beta}$.

The Landau-de Gennes free energy can predict a first-order phase transition between a nematic and an isotropic phase. Since this point is central in my calculations, I will dedicate Sec. 1.4.2 to it.

1.4.2 The nematic-isotropic phase transition

It is observed experimentally that, when a liquid crystal is in the nematic mesophase and the temperature raises (for a thermotropic) or the concentration decreases (for a lyotropic), within the nematic range the order parameter decreases monotonically, and falls suddenly to zero at the transition point. That is, the transition is first-order, even if the latent heat is small (1.57 J/g for 5CB, see [60], compared to the 334 J/g for the liquid-solid transition in water, or 108 J/g for ethanol).

Let us denote by η the quantity whose variation may determine a transition from an isotropic to a nematic phase: an effective temperature, for a thermotropic, or an effective concentration, for a lyotropic. Nematic phase corresponds to higher η , isotropic phase to lower η values.

We next assume that only A depends strongly on η : $A = A_0 \left(\frac{1}{\eta} - \frac{1}{\eta_{\text{NI}}^*} \right)$, where η_{NI}^* is close to the transition value. a must be positive, since for low η the state $\mathbf{Q} = 0$ is a minimum of $\mathcal{F}_s$. B and C depend weakly on η .

The procedure to calculate the actual η_{NI} can be summarized as follows:

1. Assume that the state is uniaxial, and orient the coordinate axes in order that the director is parallel to z . The tensor order parameter is therefore diagonal, and the elements on the diagonal are $(-q/2, -q/2, q)$.
2. Assume that there is a minimum of $\mathcal{F}_s$ for a $\bar{q} \neq 0$. It follows that B and C must be positive, for a calamitic nematic.⁷
3. Impose $\left. \frac{\partial \mathcal{F}_s}{\partial q} \right|_{q=\bar{q}} = 0$. The solutions are: $\bar{q}_I = 0$ (isotropic), and:

$$\bar{q}_{\pm} = \frac{B}{4C} \left[1 \pm \sqrt{1 - \frac{24A_0C}{B^2} \left(\frac{1}{\eta} - \frac{1}{\eta_{\text{NI}}^*} \right)} \right] \quad (1.5)$$

4. Impose $\mathcal{F}_s = \mathcal{F}_0$ at the actual η_{NI} : the free energy of the nematic must equal the free energy of the isotropic, at coexistence.

For the order parameter in the nematic phase, it results $B\bar{q}_{\text{NI}}^3 = 3C\bar{q}_{\text{NI}}^4$. Two solutions are possible:

⁷For a discotic nematic, we should have imposed $B < 0$ in Eq. (1.4).

$$\bar{q}_{\text{NI}} = 0 \quad , \text{ with } \quad \eta_{\text{NI}} = \eta_{\text{NI}}^* \quad (1.6)$$

$$\bar{q}_{\text{NI}} = \frac{B}{3C} \quad , \text{ with } \quad \frac{1}{\eta_{\text{NI}}} = \frac{1}{\eta_{\text{NI}}^*} + \frac{B^2}{27A_0C} \quad (1.7)$$

The first solution corresponds to $\bar{q}_-$, the second solution corresponds to $\bar{q}_+$, at the values of η on the right.

Below the value η_{NI}^- satisfying

$$\frac{1}{\eta_{\text{NI}}^-} = \frac{1}{\eta_{\text{NI}}^*} + \frac{B^2}{24A_0C} \quad (1.8)$$

the square root in Eq. (1.5) is not defined, so no nematic phase is stable.

To sum it all up, there are four distinct behaviours, one for each of the following intervals of η :

- $\eta < \eta_{\text{NI}}^-$: the only minimum of the Helmholtz free energy corresponds to an isotropic phase;
- $\eta_{\text{NI}}^- < \eta < \eta_{\text{NI}}$: $\bar{q} = 0$ is the global minimum of $\mathcal{F}_s$ (isotropic stable state), $\bar{q}_+$ is a local minimum (nematic metastable state), and between them there is the local maximum $\bar{q}_-$. The potential barrier is 0 at $\eta = \eta_{\text{NI}}^-$ (critical point), while at $\eta = \eta_{\text{NI}}$ the free energy is the same at the two minima: the two phases coexist, and the potential barrier (which, for this system, is $B^4/11664C^3$) is the latent heat;
- $\eta_{\text{NI}} < \eta < \eta_{\text{NI}}^*$: the situation is similar to the previous case, but now the nematic state is stable, and the isotropic state is metastable;
- $\eta > \eta_{\text{NI}}^*$: the global minimum of $\mathcal{F}_s$ is $\bar{q}_+$, so the stable phase is nematic. $\bar{q}_-$ is a local minimum and $q = 0$ is a maximum (see Eq. (1.4)).

If [55] $a = B = C = \eta$,⁸ $\eta_{\text{NI}}^* = 3.0$:

$$\begin{aligned} \mathcal{F}_s = A_0 & \left[\frac{1}{2} \left(1 - \frac{\eta}{3} \right) Q_{\alpha\beta}^2 \right. \\ & \left. - \frac{\eta}{3} Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{\eta}{4} (Q_{\alpha\beta}^2)^2 \right] \end{aligned} \quad (1.9)$$

we obtain the popular reduced transition value: $\eta_{\text{NI}} = 2.7$.

⁸The equalities concern only the numerical values: B and C are measured with a different unit than a .

(1.9) is not yet the final form of $\mathcal{F}_s$, because it describes a single phase, not accounting for the presence of the scalar field $\phi(\mathbf{r})$ representing the nematic volume fraction. We will correct the formula in Sec. 1.4.4, after discussing the bulk energy term depending on ϕ .

1.4.3 The Landau-Brazovskii mixing energy

Since, as said at the end of Sec. 1.4.2, the system is characterized not only by the tensor field $\mathbf{Q}(\mathbf{r})$ representing the order parameter throughout the simulation box (*supercell*), but by the scalar field $\phi(\mathbf{r})$ representing the nematic volume fraction, we need to add a free energy term that governs a separation between two phases with different ϕ 's.

This can be done with a Landau free energy term for the mixture of an isotropic liquid and a liquid crystal. In the simplest mean field Landau approach⁹ this term is given by [64, 65]:

$$\mathcal{F}_m = \frac{A_m}{2} (\phi - \phi_0)^2 + \frac{B_m}{4} (\phi - \phi_0)^4 \quad (1.10)$$

where ϕ ($0 \leq \phi \leq 1$) is the nematic concentration and the coefficients $A_m < 0$ and $B_m > 0$ (their signs must be so, for two coexisting phases [34]) determine the properties of the bulk phases.

1.4.4 The Matsuyama correction to the L-dG free energy

The expression (1.9) for the Landau-de Gennes bulk free energy (Maier-Saupe, Doi-Edwards, [54, 55]) must be corrected (Matsuyama [82, 34]), taking into account that the system is a lyotropic binary emulsion, characterized by the volume fraction ϕ (Sec. 1.4.3), and that only the nematic phase contributes to $\mathcal{F}_s$:

$$\begin{aligned} \mathcal{F}_s = A_0 \phi^2 & \left[\frac{1}{2} \left(1 - \frac{\eta(\phi)}{3} \right) Q_{\alpha\beta}^2 \right. \\ & \left. - \frac{\eta(\phi)}{3} Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{\eta(\phi)}{4} (Q_{\alpha\beta}^2)^2 \right] \end{aligned} \quad (1.11)$$

⁹The energy cost of the phase separation is taken as the mean field free energy, which L. D. Landau derived for a continuous (second-order) phase transition. S. A. Brazovskii found that fluctuations effects lead to discontinuous (first-order) transitions.

The quantity η , which determines the phase (the nematic-isotropic transition occurs at $\eta = 2.7$, Sec. 1.4.2), is approximated as linear in the concentration [82, 34]:

$$\eta = \eta_0 + \eta_s (\phi - \bar{\phi}) \quad (1.12)$$

1.5 Gradient and boundary terms of the Helmholtz free energy

1.5.1 The Frank-Oseen distortion energy

In an ideal nematic, the director field $\hat{\mathbf{n}}(\mathbf{r})$ is uniform, as well as the tensor order parameter $Q_{\alpha\beta}(\mathbf{r})$.

In most practical circumstances, however, either the ideal configuration does not satisfy the boundary conditions, typically the anchoring constraints at the walls of a container (see Sec. 1.5.3), or is distorted by external fields, mostly electro-magnetic.

The deformations of the director field can be described by a continuum theory [25, 61, 62] because their length scale is much larger than the molecular dimension a :

$$\nabla \hat{\mathbf{n}} \ll \frac{1}{a} \quad (1.13)$$

wherefore we can expand $\mathcal{F}_d$ – denoting with this symbol the distortion energy – in powers of $\nabla \hat{\mathbf{n}}$.

There will not be any term linear in $\nabla \hat{\mathbf{n}}$, because $\mathcal{F}_d$ is invariant under rotations: and since $\hat{\mathbf{n}}$ and $-\hat{\mathbf{n}}$ represent the same state, $\mathcal{F}_d$ will be even in $\hat{\mathbf{n}}$ ¹⁰.

The distortion energy per unit volume, expanded up to the second-order terms in the gradients of the director field, takes, eventually, the following form:

$$\mathcal{F}_d = \frac{K_1}{2} (\nabla \cdot \hat{\mathbf{n}})^2 + \frac{K_2}{2} (\hat{\mathbf{n}} \cdot \nabla \wedge \hat{\mathbf{n}})^2 + \frac{K_3}{2} (\hat{\mathbf{n}} \wedge (\nabla \wedge \hat{\mathbf{n}}))^2 \quad (1.14)$$

K_1 , K_2 and K_3 , in Eq. (1.14), are elastic constants, and describe the response of the nematic to its three basic types of deformations: respectively,

¹⁰For chiral nematic LC's, which are not symmetric under the inversion of all the three axes, the term $\hat{\mathbf{n}} \cdot \nabla \wedge \hat{\mathbf{n}}$ is present.

splay, twist, bend (Fig. 1 in the Introduction). A general deformation can be seen as a combination of them.

The elastic constants have the dimensions of a force. To give you their order of magnitude, the elastic constants of N-(4-methoxybenzylidene)-4-butyraniline (MBBA) at 22°C, measured by Rondelez and Hulin [63] are:

- $K_1 = (5.3 \pm 0.5)$ pN (splay);
- $K_2 = (2.2 \pm 0.7)$ pN (twist);
- $K_3 = (7.45 \pm 1.10)$ pN (bend);

With a different meaning of the elastic constants, the Frank-Oseen distortion energy can be expressed in terms of the gradients of the tensor order parameter, too:

$$\mathcal{F}_d = \frac{L_1}{2} (\partial_\alpha Q_{\beta\gamma})^2 + \frac{L_2}{2} (\partial_\alpha Q_{\alpha\gamma}) (\partial_\beta Q_{\beta\gamma}) + \frac{L_3}{2} Q_{\alpha\beta} (\partial_\alpha Q_{\gamma\delta}) (\partial_\beta Q_{\gamma\delta}) \quad (1.15)$$

The one-constant approximation

Even though experimental measures point out that the three elastic constants of Eq. (1.14) are different – usually, the bend elastic constant is the largest one – since their order of magnitude is the same, they are often considered equal in order to simplify calculations.

In my calculations, I adopted the one-constant approximation. That corresponds to assume $K_1 = K_2 = K_3$ in Eq. (1.14) and imposing $L_2 = L_3 = 0$ in Eq. (1.15):

$$\mathcal{F}_d = \frac{L_1}{2} (\partial_\alpha Q_{\beta\gamma})^2 \quad (1.16)$$

1.5.2 The Cahn-Hilliard interfacial energy

According to Becker’s model of coherent interfaces [66] – the interface between two phases where the molecules can glide one over another is, reasonably, coherent, i. e. without misfits of lattice – the interface energy density between two immiscible phases characterized by two distinct concentrations is proportional to the concentration gradient across the interface.

The relation was definitely found in 1957, by J. W. Cahn and J. E. Hilliard [39], with an argument similar to those used for ferromagnetism, ferroelectric-

ity and superconductivity: it is valid for an isotropic system of nonuniform composition, like a binary emulsion¹¹.

Given the nonuniform property – in our case, it is the concentration ϕ – the authors stated that the local free energy is the sum of two contribution: one which is function of the local ϕ , and one which is function of ϕ in the immediate environment. Thus, the second contribution can be expanded in the derivatives of ϕ : the odd order terms and the terms containing mixed partial derivatives vanish in the expansion, because the free energy is invariant under inversion of an axis or under rotation about a fourfold axis. Hence, the interfacial free energy F_i in the volume V is:

$$F_i = N_V \int_V [a_0(\phi) + \kappa_1 \nabla^2 \phi + \kappa_2 (\nabla \phi)^2 + \dots] \quad (1.17)$$

where N_V is the number of molecules per unit volume.

The term proportional to $\nabla^2 \phi$ can be written as a surface integral, applying the divergence theorem; and it can be eliminated, because we are not interested in the effects related to the external surface:

$$F_i = N_V \int_V \left[a_0(\phi) + \frac{K}{2} (\nabla \phi)^2 + \dots \right] \quad (1.18)$$

In the above equation, $K = -d\kappa_1/d\phi + \kappa_2$. The bigger the K , the smoother the interface.

Assuming $a_0(0) = 0$ and truncating the expansion at the second-order term, we have the final form of the interfacial free energy per unit volume:

$$\mathcal{F}_i = \frac{K}{2} (\partial_\gamma \phi)^2 \quad (1.19)$$

1.5.3 Interaction with the boundaries: anchoring energy terms

Following de Gennes's argument [25], imposing an anchoring condition on the walls containing the nematic means adding an elastic term in the free energy. We can think of this condition as a spring on every lattice site:

$$\mathcal{F}_{aw} = \frac{\alpha_s}{2} (Q_{\alpha\beta} - Q_{\alpha\beta}^0)^2 \quad (1.20)$$

¹¹The reader could argue that, since the molecules of a liquid crystalline compound are anisotropic, as well as a mesophase, the equation does not hold. But the isotropy that Cahn and Hilliard are talking about acts on a much larger scale: in the system which I simulated, it is ensured by the periodic boundary conditions.

where α_s is a measure of the strength of the pinning and $Q_{\alpha\beta}^0 = q_0 (n_\alpha^0 n_\beta^0 - \frac{1}{3} \delta_{\alpha\beta})$ with q_0 the magnitude of surface order and $\hat{\mathbf{n}}^0$ the preferred orientation at the boundary.

A similar condition holds for the concentration (total wetting condition):

$$\mathcal{F}_{\phi w} = \frac{\alpha_w}{2} (\phi - \phi^0)^2 \quad (1.21)$$

in which ϕ^0 is the concentration at the boundary.

In an isotropic-nematic emulsion, the chemical structure of the molecules gives rise to an orientational condition at the interface between the two phases. This feature, which will be very important in the discussion of the behaviour of a droplet under a shear flow, translates into the following contribution to the free energy:

$$\mathcal{F}_{ai} = W (\partial_\alpha \phi) Q_{\alpha\beta} (\partial_\beta \phi) \quad (1.22)$$

$W > 0$ implies an anchoring of the nematic parallel to the interface; $W < 0$ implies an anchoring perpendicular to the interface.

1.6 Topological defects

A key role in determining the equilibrium or stationary configurations of a liquid crystal system is played by the defects. Defects are points or regions where the director field is ill-defined and where the average orientational order of the molecules drops sharply. Intuitively near a defect one can imagine that the director field change its orientation quite rapidly. More precisely one refers to *topological defects* since they can be seen as regions, of spatial dimension less than that of physical space, around which the configuration of the order parameter cannot be transformed into a homogeneous one via continuous deformations [29], just like a sphere cannot be continuously transformed into a torus. Defects in a vector field are characterized by their **topological charge** or **winding number** s , which is the number of times the vector field winds around a loop encircling the defect core in an anticlockwise sense. For example the hedgehog on the left of Fig. 1.10 has topological charge $s = +1$, as the director field winds around it fully once and the direction of the winding along a clockwise loop is also clockwise (positive sign). Similarly the vortex (Fig. 1.10, middle) the circular hedgehog (obtained from a radial hedgehog by rotating the director at every point through $\pi/2$ about the axis perpendicular to the page, Fig. 1.10, right), and the hyperbolic hedgehog (Fig. 1.11, left) have topological charge $+1$, $+1$ and -1 respectively.



Figure 1.10: From left to right: a radial hedgehog, a vortex and (a planar section of) a circular hedgehog. All the three topological defects are point defects, and have winding number $s = 1$. The solid lines draw the director field. Sourced from [98].



Figure 1.11: From left to right: a hyperbolic hedgehog (point defect, $s = -1$) and the cross section of two disclination lines, with winding numbers $s = -1/2$ and $s = 1/2$. The solid lines draw the director field. Sourced from [98].

All the defects listed up to now are **point defects**.

However, because of the head-tail symmetry of the director of a liquid crystal, it is not necessary for it to wind around a defect an integer number of times: half a turn is enough to have a defect. For this reason, also defects with charges $-1/2$ and $+1/2$ are possible: these are **disclination lines** (Fig. 1.11, middle and right).

It can be useful to remark that any closed loop or surface can be chosen to measure the topological charge, as long as no other defects are enclosed – as in the proofs of the Gauss and Ampère theorems.

1.6.1 Schlieren textures, disclination lines and point defects

An experimentally accessible way to look at defects in a liquid crystals is based on the so-called Schlieren textures. We can see these characteristic patterns when we look at a liquid crystal between crossed polarizers in a microscope.

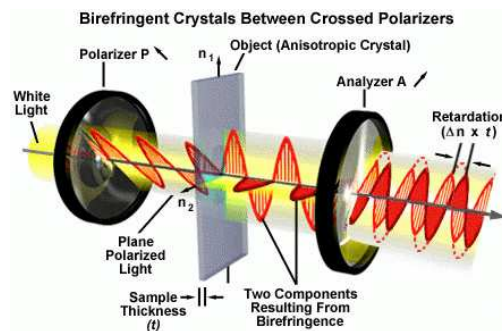


Figure 1.12: Scheme of polarized light microscopy in presence of a birefringent sample, sourced from <http://www.olympusmicro.com>. n_1 and n_2 are the refractive indexes.

When monochromatic linearly polarized light passes through an isotropic material, its polarization plane does not change, and it is completely absorbed by the analyzer. On the other hand, when the same light passes through a liquid crystalline sample, some light can pass through. This feature is due to the anisotropy of a nematic, which causes birefringence: linearly polarized light splits into two perpendicular components (ordinary and extraordinary) which experience two different refractive indexes¹². As the light

¹²The refractive indexes are two because a nematic is uniaxial (i. e. it is symmetric around its principal axis). If the phase were biaxial, the refractive indexes would be three.

passes through the sample, it becomes elliptically polarized; when it gets out, it turns back linearly polarized, but its polarization plane is rotated (optical activity), so a fraction of it is not absorbed by the analyzer (Fig. 1.12).

For a calamitic nematic, the local director (ordinary transmission axis) coincides with the local optical axis. On a consequence, if the local director $\hat{\mathbf{n}}(\mathbf{r})$ is either parallel or perpendicular to the polarizer axis, the light wave does not split, and a dark region is observed.

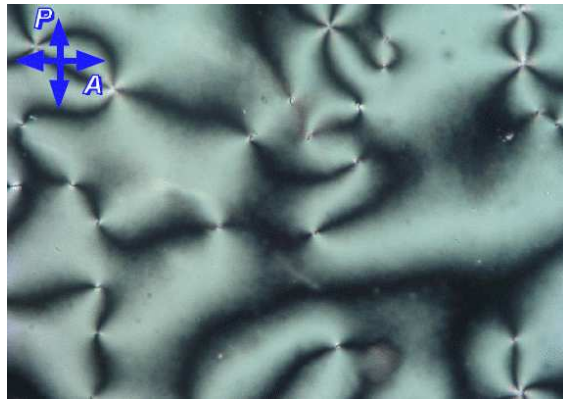


Figure 1.13: Schlieren texture of 4-Cyano-4'-pentylbiphenyl (5CB) coated with GLYMO, sourced from the slides of Y. Yi's talk at the 2010 ILCC.

In a typical Schlieren texture of a nematic phase with defects, one observes bright regions and dark brushes (*Schliere* means *streak*, in German), which meet in some points (Fig. 1.13). These points, where two or four brushes meet correspond to the director field singularities, and hence to the location of topological defects [56].

Considering that, when moving from a dark to a light brush, or vice versa, in a Schlieren texture, the director rotates of $\pi/4$, disclination lines correspond to the regions where two dark brushes meet, and point defects correspond to the points where four dark brushes meet.

1.6.2 Defects in nematic emulsions

The total topological charge in a system is determined by boundary conditions that can be either fixed at infinity or at the outer surface of an enclosed region (like the top and bottom walls of a nematic cell). In my simulations, I always imposed homeotropic anchoring of the nematic at both walls: this implies a total topological charge equal to zero.

On the other hand, if spherical particles, such as colloids or a droplet of isotropic phase, are included in the system, the local orientational order of the nematic is disrupted, and formation of defects is expected near the particle surface. This is because the director field typically aligns either normally or tangentially with respect to the surface (or interface) of the spherical intrusion. For example, if the anchoring at the surface is normal, a radial hedgehog ($s = 1$) is expected, both for two-dimensional and three-dimensional systems [26].

In this case, the conservation of the total topological charge requires the nucleation of a single topological defect of strength $s = -1$, or of an assembly of defects whose total charge is -1 .

In a two-dimensional system, we will see in Chapter 3 how this is achieved. In three dimensions, as for the experimental setup of Poulin and Weitz, it turns out that the two most stable defect configurations are either the one in which a hyperbolic hedgehog forms close to the particle (*elastic dipole*), or when a disclination line (*Saturn ring*) encircles the particle at its equator (*elastic quadrupole*). Basically, the former configuration is preferred by larger particles with stronger surface anchoring: smaller particles with weaker surface anchoring tend to arrange nematic in the second way [31, 57].

1.7 Detection of topological defects in numerical simulations

The configurations of the system in the simulations I am going to discuss in Chapters 3 to 6 are described in terms of the spatially varying $\mathbf{Q}$ -tensor order parameter.

Unfortunately, this is not the best format to visualize defects. The abrupt variation of the director $\hat{\mathbf{n}}$ is clearly a signal of the presence of a defect but, since $\hat{\mathbf{n}}$ fills the entire space, it is not the most efficient way to look for defects. The first simplest alternative one can think of relies on the spatial variation of the scalar order parameter q .

1.7.1 Detection by the scalar order parameter

The defect detection based on the scalar parameter is based on the following argument: as said in Sec. 1.6.1, at the core of a topological defect the orientation of the director field is not well-defined. In fact, in terms of Schlieren textures¹³ two or more domains with different orientation meet. In other

¹³It is possible, of course, to generate Schlieren textures by the simulation data [58].

words the nematic is locally disordered and one can say that it melts locally into the isotropic phase [30]. In this respect a drop almost to zero of the scalar order parameter (describing the degree of order) at the core of the defect is expected. Since away of the defects q assumes its bulk value corresponding to the equilibrium nematic phase, the isosurfaces of q are clearly a good way to visualize the defects.

1.7.2 Detection by biaxiality

Another way to locate and visualize defects is based on biaxiality, i.e. the property of a liquid crystals to have two axes of alignment – a stronger one, along the director, and a weaker one, along a secondary axis (see Sec. 1.3). Indeed, near a defect, the linear anisotropy decreases and the biaxiality, which is zero for the uniaxial phase in the bulk, can become significantly different from zero in proximity of a defect core.

An efficient way to measure biaxiality is based on the definition of the biaxiality parameter given by Westin *et al.*, and mentioned in [59]. This works as follows: if one adds the term $\delta_{\alpha\beta}/3$ to the tensor order parameter $Q_{\alpha\beta}$ (Eq. (1.2)), the resulting tensor $D_{\alpha\beta} \equiv Q_{\alpha\beta} + \frac{\delta_{\alpha\beta}}{3}$ is positive definite and symmetric. It can be then diagonalized and the relative eigenvalues can be sorted such that $\lambda_1 \geq \lambda_2 \geq \lambda_3 \geq 0$. With respect to the basis of the eigenvectors, the Westin tensor can be written:

$$D_{\alpha\beta} = \begin{pmatrix} \lambda_1 & & \\ & \lambda_2 & \\ & & \lambda_3 \end{pmatrix} \equiv \begin{pmatrix} \frac{1}{3}(2S+1) & & \\ & \frac{1}{3}(1-S+3b) & \\ & & \frac{1}{3}(1-S-3b) \end{pmatrix}. \quad (1.23)$$

Note that S is an effective scalar order parameter, which is different from q : indeed the latter one can be negative (e. g. for negative uniaxial nematics), while S is always nonnegative.

In Eq. (1.23), b is the biaxiality parameter: If $b = 0$, $\lambda_2 = \lambda_3$, the two minor eigenvalues of $Q_{\alpha\beta}$ are equal, and the liquid crystal is locally uniaxial. If, on the other hand, $b \neq 0$, biaxiality is locally present.

Following Westin, we can introduce the parameters

$$k_l = \lambda_1 - \lambda_2 = S - b \quad (1.24)$$

$$k_s = 3\lambda_3 = 1 - S - 3b \quad (1.25)$$

$$k_p = 2(\lambda_2 - \lambda_3) = 4b. \quad (1.26)$$

k_l, k_s, k_p form a barycentric space (i. e. their sum is 1) over all possible $D_{\alpha\beta}$. In particular:

- k_l is a measure of the positive uniaxiality;
- k_s is a measure of the isotropy;
- k_p is a measure of the biaxiality.

In my simulations, in addition to the profile of the order parameter q , I have chosen to look at the spatial variation of the parameter $k_p = 4b$ as a further tool to locate and follow defects. Often the two measures are both used and compared, to have a better resolution of the defects loops and points in the system.

Chapter 2

The equations of motion and the hybrid Lattice Boltzmann algorithm

2.1 Introduction: classical fluid dynamics

Classical theory of flowing fluids treats velocity $\mathbf{u}$, density ρ , pressure P_0 , temperature T and other relevant measurable quantities as continuous and differentiable functions of space. We know, from statistical mechanics, that pressure and temperature are not defined for a single particle: they are macroscopic concepts; and velocity and density have huge fluctuations on the molecular scale. In classical fluid dynamics, a point in space (*fluid particle*) is a volume, actually, and it must be big enough to define all the quantities properly (as averages, of course) and to eliminate the random fluctuations.

From classical fluid dynamics, we know that the time evolution of a simple flowing fluid is described by continuity and Navier-Stokes equations [67]:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (2.1)$$

$$\rho \frac{D\mathbf{u}}{Dt} = \nabla \cdot \mathbf{s} \quad (2.2)$$

where D/Dt denotes the material derivative, i. e. the rate of change of a physical quantity associated to a fluid particle, while following it in its flow:

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \quad (2.3)$$

and $\mathbf{s}$ is the *stress tensor*: thinking of an infinitesimal cube (fluid particle), its element $s_{\alpha\beta}$ is the component of the force, per unit area, acting on the α -th face (1: parallel to yz ; 2: parallel to xz ; 3: parallel to xy), in the β -th direction (Fig. 2.1).

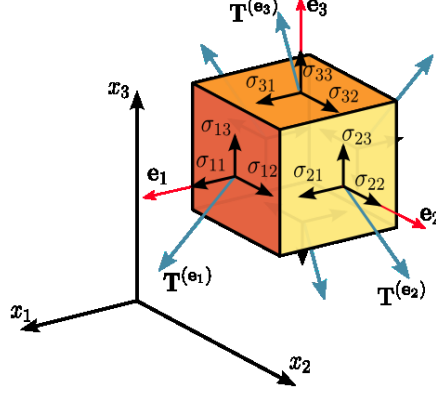


Figure 2.1: Components of the stress tensor $\mathbf{s}$ in Eq. (2.2).

The Navier-Stokes equation is the fluid-dynamical form of Newton's law. From the description of the stress tensor, it is clear that the diagonal components are the *normal stresses*, and the others are the *shear stresses*. The form for the stress tensor changes from fluid to fluid. A part of the normal stress is due to the hydrostatic pressure gradient ∇P_0 , defining the pressure as minus the mean normal stress and excluding all external forces. Usually, the hydrostatic pressure gradient and the external force field $\mathbf{f}$ are pointed out, as well as the viscosity terms.

As an example, this is the special form of the Navier-Stokes equation for a simple, incompressible fluid with viscosity η_V . I choose this example because the Navier-Stokes equation for a liquid crystal (2.18), as we shall see, is not so different from this:

$$\rho \frac{D\mathbf{u}}{Dt} = -\nabla P_0 + \eta_V \nabla^2 \mathbf{u} + \mathbf{f} \quad (2.4)$$

2.2 The Leslie-Ericksen model and the back-flow effect

Classical fluidodynamics stands as basis for studying the dynamics of a nematic liquid crystal, even though it must be deeply enriched, since a nematic

liquid crystal has internal microstructure, which makes it much more complicated to describe.

Leslie and Ericksen's model, developed in the 1960s, gained great success during the next decades, in describing the rheological behaviour of a low molecular-weight liquid crystal [38]. It is not the only model of nematodynamics developed since Reinitzer's discovery (Sec. 1.1), but it is worth to be sketched because the model employed in my simulation can be reduced to Leslie and Ericksen's, in particular conditions, not to mention its easy connection to experimental data.

Without having to spell things out, Leslie-Ericksen theory incorporates the elastic energy arising from inhomogeneities in the director field – the Frank-Oseen energy, in terms of $\hat{\mathbf{n}}$, (1.14) – and the effect of director rotation. It provides a Navier-Stokes equation and an evolution equation for the director field $\hat{\mathbf{n}}$, which are coupled. Better to say: the evolution of the velocity field has a dependence on the director field and the evolution of the director field has a dependence on the velocity field.

This is known as the **backflow effect**, and is a peculiar feature of liquid crystals.

In its constitutive equation, the Leslie-Ericksen stress tensor depends on six parameters $\{\alpha_1, \dots, \alpha_6\}$. Of them, only five are independent (Parodi relation), related to the same number of experimentally accessible quantities.

An example of set of five independent observables are:

- the three Mięsowicz viscosities [103], measured when a nematic is subject to a shear flow and is uniformly oriented
 - (a) along the shear velocity: $\bar{\eta}_1 = (\alpha_4 + \alpha_6 + \alpha_3)/2$;
 - (b) along the shear rate: $\bar{\eta}_2 = (\alpha_4 + \alpha_5 - \alpha_2)/2$;
 - (c) perpendicular both to shear velocity and to shear rate: $\bar{\eta}_3 = \alpha_4/2$;
- the Helfrich viscosity [104] $\bar{\eta}_{12} = 4\bar{\eta}_4 - 2(\bar{\eta}_1 + \bar{\eta}_2) = \alpha_1$, where $\bar{\eta}_4$ is the viscosity obtained for the director orientation within the plane where shear velocity and shear rate lie, which forms an angle of 45° with the direction of flow [105];
- the rotational (twist) viscosity $\gamma_1 = \alpha_3 - \alpha_2$, which reflects the rate of relaxation of the director from a twist deformation (Fig. 1) to a uniform configuration.

The relative ease which Leslie-Ericksen parameters can be measured with is one of the reasons for the success of the model in the decades which followed its publication.

The flaws start to show when we deviate from a perfectly oriented nematic, because Leslie-Ericksen model neither considers the variations in the degree of orientation (i. e. the scalar order parameter q) nor can describe a biaxial phase, i. e. a phase with two characteristic axes of orientation (Sec. 1.7.2) [38].

2.3 The Beris-Edwards equations of nematodynamics

The Beris-Edwards model (*conformation tensor theory*) [38] describes the dynamics of a nematic liquid crystals in terms of a generalized Hamiltonian formulation. The (quite long, and difficult) derivation is outlined in Appendix A.

Here, we will give you only the laws of motion descending from this theory, which have been employed in the simulations.

2.3.1 Evolution of the tensor order parameter

The evolution equation of the tensor order parameter $\mathbf{Q}$ (A.8) can be written in the following, relatively simple form:

$$(\partial_t + u_\gamma \partial_\gamma) \mathbf{Q} - \mathbf{S}(\mathbf{W}, \mathbf{Q}) = \Gamma \mathbf{H} \quad (2.5)$$

where

$$\begin{aligned} \mathbf{S}(\mathbf{W}, \mathbf{Q}) = & (\xi \mathbf{D} + \mathbf{Z})(\mathbf{Q} + \mathbb{1}/3) + (\mathbf{Q} + \mathbb{1}/3)(\xi \mathbf{D} - \mathbf{Z}) \\ & - 2\xi(\mathbf{Q} + \mathbb{1}/3) \text{Tr}(\mathbf{Q}\mathbf{W}) \end{aligned} \quad (2.6)$$

and

$$\mathbf{H} = - \left(\frac{\delta \mathcal{F}}{\delta \mathbf{Q}} - \frac{\mathbb{1}}{3} \text{Tr} \frac{\delta \mathcal{F}}{\delta \mathbf{Q}} \right) \quad (2.7)$$

$\mathbf{H}$ is the *molecular field*, and replaces the term in square brackets of (A.8). Given the formulas for the $\mathbf{Q}$ -dependent part of the free energy, with an obvious meaning of the indexes, $\mathbf{H}$ is the sum of the following contributions:

$$\begin{aligned} (H_s)_{\alpha\beta} = & A_0 \phi^2 \left\{ - \left(1 - \frac{\eta(\phi)}{3} \right) Q_{\alpha\beta} \right. \\ & \left. + \eta(\phi) \left[Q_{\alpha\gamma} Q_{\gamma\beta} - \left(Q_{\alpha\beta} + \frac{1}{3} \delta_{\alpha\beta} \right) Q_{\gamma\epsilon}^2 \right] \right\} \end{aligned} \quad (2.8)$$

$$(H_d)_{\alpha\beta} = L_1 \partial_\gamma \partial_\gamma Q_{\alpha\beta} \quad (2.9)$$

$$(H_{aw})_{\alpha\beta} = -\alpha_s (Q_{\alpha\beta} - Q_{\alpha\beta}^0) \quad (2.10)$$

$$(H_{ai})_{\alpha\beta} = -W \left(\partial_\alpha \phi \partial_\beta \phi - \frac{\delta_{\alpha\beta}}{3} \partial_\gamma \phi \partial_\gamma \phi \right) \quad (2.11)$$

$\mathbf{S}(\mathbf{W}, \mathbf{Q})$ replaces all the other terms in the right-hand side of (A.8), linear combination of the components of the velocity gradient tensor: $\mathbf{D} = (\mathbf{W} + \mathbf{W}^T)/2$ and $\mathbf{Z} = (\mathbf{W} - \mathbf{W}^T)/2$ are, respectively, the symmetric (*rate of strain*) and antisymmetric (*vorticity*) part of the velocity gradient tensor $W_{\alpha\beta} \equiv \partial_\beta u_\alpha$.

The constant ξ (function of β_8^m , Appendix A) is related to the molecular structure of the liquid crystal; the constant Γ (function of β_7^m , Appendix A) is a kind of collective rotational constant. We see, indeed, that in stationary conditions (constant field velocity) $\mathbf{S}(\mathbf{W}, \mathbf{Q}) = 0$, so (2.5) describes a simple relaxation towards equilibrium, governed by the constant Γ .

Recovery of the Leslie-Ericksen parameters

As said at the beginning of Sec. 2.2, the Leslie-Ericksen model can be seen as a special case of the Beris-Edwards model, namely assuming the orientational degree as uniform and a perfectly uniaxial phase. The following equations relate the scalar order parameter q , the bulk viscosity η_V and the constants Γ and ξ in (2.5) and (2.6) to the Leslie-Ericksen parameters. A derivation of these equations can be found in [78]:

$$\alpha_1 = -\frac{\frac{2}{3}q^2(3+4q-4q^2)\xi^2}{\Gamma} \quad (2.12)$$

$$\alpha_2 = \frac{-q(2+q)\xi - 3q^2}{3\Gamma} \quad (2.13)$$

$$\alpha_3 = \frac{-q(2+q)\xi + 3q^2}{3\Gamma} \quad (2.14)$$

$$\alpha_4 = \frac{4(1-q)^2\xi^2}{9\Gamma} + \eta_V \quad (2.15)$$

$$\alpha_5 = \frac{q(4-q)\xi^2 + q(2+q)\xi}{3\Gamma} \quad (2.16)$$

$$\alpha_6 = \frac{q(4-q)\xi^2 - q(2+q)\xi}{3\Gamma} \quad (2.17)$$

Since Leslie-Ericksen parameters are related to experimentally measurable quantities, these equations help us to map the simulation (reduced) units of length, time, mass...into real quantities. We will return on this point after discussing the simulation algorithm, in Sec. 2.8.

2.3.2 Evolution of the velocity field

The other central equation of Beris-Edwards model (A.7) describes the time evolution of the velocity field. It reads:

$$\rho (\partial_t + u_\beta \partial_\beta) u_\alpha = \partial_\beta \sigma_{\alpha\beta} + \partial_\beta \tau_{\alpha\beta} + \partial_\beta \Pi_{\alpha\beta} + \eta_V \partial_\beta [\partial_\alpha u_\beta + \partial_\beta u_\alpha + (1 - 3\partial_\rho P_0) \partial_\gamma u_\gamma \delta_{\alpha\beta}] \quad (2.18)$$

with η_V being the bulk viscosity.

We can recognize, in (2.18), a Navier-Stokes equation: the left-hand term is the material derivative of $\mathbf{u}$. The stress tensor (A.9) is the sum of three components:

$$s_{\alpha\beta} = \sigma_{\alpha\beta} + \tau_{\alpha\beta} + \Pi_{\alpha\beta} \quad (2.19)$$

- $\sigma_{\alpha\beta}$ is the symmetric part of the stress tensor which results from the liquid crystalline order (*backflow*). The hydrostatic pressure is taken to be $P_0 = \rho T - L_1 (\nabla \mathbf{Q})^2 / 2$ and is approximated, in the simulations, as a constant [37], because ρ and T are, and the gradient of $\mathbf{Q}$ is small by assumption (Sec. 2.6.3).

$$\begin{aligned} \sigma_{\alpha\beta} = & -P_0 \delta_{\alpha\beta} - \xi H_{\alpha\gamma} \left(Q_{\gamma\beta} + \frac{\delta_{\gamma\beta}}{3} \right) \\ & - \xi \left(Q_{\alpha\gamma} + \frac{\delta_{\alpha\gamma}}{3} \right) H_{\gamma\beta} + 2\xi \left(Q_{\alpha\beta} + \frac{\delta_{\alpha\beta}}{3} \right) Q_{\gamma\epsilon} H_{\gamma\epsilon} \end{aligned} \quad (2.20)$$

- $\tau_{\alpha\beta}$ is the antisymmetric part of the stress tensor which results from the liquid crystalline order:

$$\tau_{\alpha\beta} = Q_{\alpha\gamma} H_{\gamma\beta} - H_{\alpha\gamma} Q_{\gamma\beta} \quad (2.21)$$

- $\Pi_{\alpha\beta}$ is caused by distortions of the director field, and by the dependence of the free energy on the nematic volume fraction and on its gradient:

$$\Pi_{\alpha\beta} = - \left(\frac{\delta \mathcal{F}}{\delta \phi} \phi - \mathcal{F} \right) \delta_{\alpha\beta} - \frac{\delta \mathcal{F}}{\delta (\partial_\beta \phi)} \partial_\alpha \phi - \frac{\delta \mathcal{F}}{\delta (\partial_\beta Q_{\gamma\nu})} \partial_\alpha Q_{\gamma\nu} \quad (2.22)$$

2.4 The Cahn-Hilliard equation of motion for the concentration

[69, 70] If we define $\mathbf{h}$ as the mass current density, this quantity is related to the chemical potential μ :

$$\mathbf{h} = -M\nabla\mu \quad (2.23)$$

where M is a diffusion constant. The concentration ϕ and the mass current density are connected with a kind of continuity equation:

$$\frac{D}{Dt}\phi + \nabla \cdot \mathbf{h} = 0 \quad (2.24)$$

I said “a *kind of* continuity equation” because in Eq. (2.24) there is the material derivative. It would not be correct to put the ordinary partial time derivative, because the system is flowing, so at a fixed point in space the local concentration can change not only because of a chemical potential gradient, but because the fluid has moved, as well. Eq. (2.24) points out only the variation of ϕ due to the chemical potential gradient; combining it with Eq. (2.23), we obtain, indeed:

$$\partial_t\phi + \partial_\alpha(\phi u_\alpha) = M\partial_\alpha\partial_\alpha\mu \quad (2.25)$$

remembering that the chemical potential is the functional derivative, with respect to ϕ , of the total free energy [69]:

$$\begin{aligned} \mu = & \frac{\delta\mathcal{F}_s}{\delta\phi} + A(\phi - \phi_0) + B(\phi - \phi_0)^3 - \frac{K}{2}(\partial_\alpha\partial_\alpha\phi) \\ & - 2W[(\partial_\alpha\partial_\beta\phi)Q_{\alpha\beta} + (\partial_\alpha\phi)(\partial_\beta Q_{\alpha\beta})] \end{aligned} \quad (2.26)$$

2.5 Introduction to Lattice Boltzmann Methods: the Lattice Gas Automata

So, to put it briefly: to simulate a nematic-isotropic emulsion, we have to solve

- the Navier-Stokes equation, for the evolution of the velocity field (2.18);
- the Beris-Edwards equation, for the evolution of the tensor order parameter (2.5);

- the Cahn-Hilliard equation, for the evolution of the nematic volume fraction (2.25).

Apart from the Clay Millennium problem of existence and smoothness of global solutions of Navier-Stokes equations, these equations are very complicated, and even coupled.

The intention of the scientists who developed, in the late 1980s, Lattice Boltzmann methods (LBM), was specifically to find solutions, although approximate, of the Navier-Stokes equations.

Now, LBM are a very important class of computational schemes for fluid dynamics simulations [35].

To introduce you to them, I am giving a sketch of how their ancestors, the Lattice Gas Automata (LGA), work.

A **lattice gas** can be seen as a simplified version of a classical molecular dynamics [73], to simulate bigger systems than the ones which atomistic methods can model. In a lattice gas, space, time and particle velocities are all discretized: actually, the gas is represented by boolean particles, which evolve according to a set of rules [68].

If the lattice is cubic and Δr is the lattice spacing, every lattice site $\mathbf{r}$ is connected to z neighbouring lattice sites (z depends on the lattice topology) by z vectors (edges), whose length can be Δr (straight edge), $\sqrt{2}\Delta r$ (square-diagonal edge), $\sqrt{3}\Delta r$ (cube-diagonal edge). Dividing each of these vectors by Δt (discrete time step), and imposing, by convention, $\mathbf{e}_0 = 0$, we obtain $z + 1$ velocities: $\{\mathbf{e}_0, \dots, \mathbf{e}_z\}$.

Every lattice topology is denoted by $DnQ(z + 1)$, where n is the number of spatial dimensions and z is the number of edges starting from (and arriving to) every lattice site.

We define the boolean-valued functions $N_i(\mathbf{r}, t)$, $i = 0, \dots, z$. If $N_i(\mathbf{r}, t) = 1$, it means that, at the lattice site $\mathbf{r}$ and at the time t , a (fictitious) particle is moving with velocity $\mathbf{e}_i$ ($\mathbf{e}_0$ = particle at rest). They are called, for this reason, *particle occupation functions*.

Every iteration of a lattice gas automaton (LGA) is composed of:

- a *propagation step*: at each lattice site, every fictitious particle which is present at that site (i. e. which corresponds to a $N_i(\mathbf{r}, t) = 1$) moves towards the first site encountered in the direction of the velocity $\mathbf{e}_i$;
- a *collision step*: if two or more particles meet at a lattice site, they collide and are scattered, ending in one of a finite number of possible configurations.

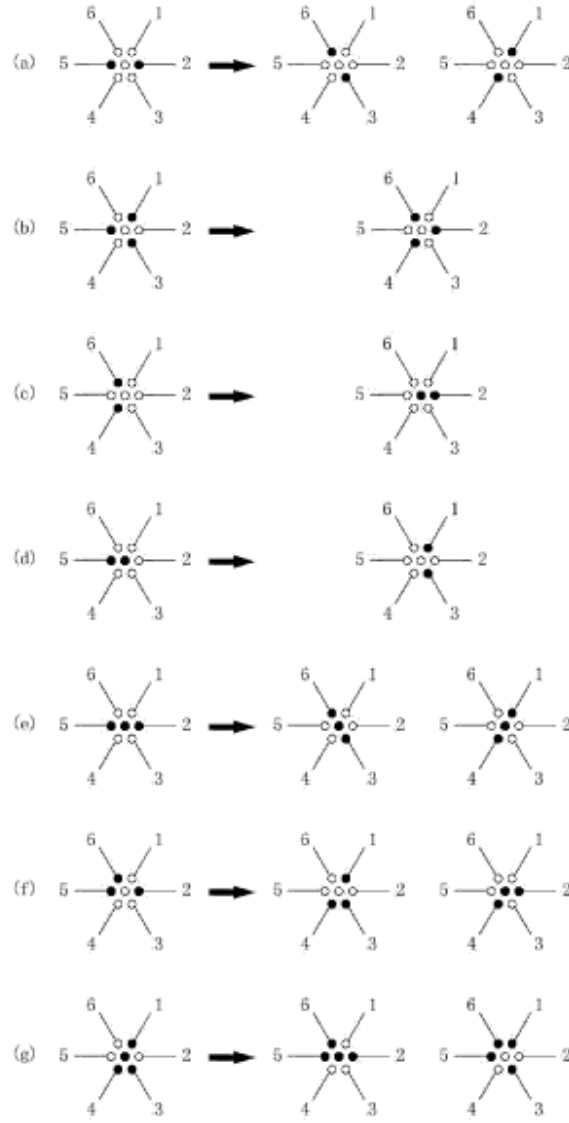


Figure 2.2: Rules for the collision step of the D2Q7 lattice gas automaton. The left column shows the situation before the collision step; the right columns shows the possible situations (they have equal probability) after the collision step. A black circle represents a $N_i(\mathbf{r}, t) = 1$; the central circle corresponds to N_0 . Picture sourced from [74].

The rules must be chosen according to the conservation principles of mass and momentum. An example is given in Fig. 2.2 for the D2Q7 lattice.

The keystone, when developing such a mesoscopic simulation method as a LGA, is to patch together the three levels on which a fluid can be described [68], well explained at any non-equilibrium statistical physics graduate course:

1. the molecular level, usually describable in a Hamiltonian fashion, at which the dynamics is reversible;
2. the kinetic level, whose basis is the Boltzmann transport equation: if $f(\mathbf{q}, \mathbf{p}, t) d^3\mathbf{q} d^3\mathbf{p}$ is the number of particles in the infinitesimal phase-space volume around the point $(\mathbf{q}, \mathbf{p})$,

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla f + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{p}} = \left(\frac{\partial f}{\partial t} \right)_c \quad (2.27)$$

where the index “c” stands for collision. The dynamics described by this equation is irreversible, because of the assumption of molecular chaos;

3. the macroscopic level, at which the continuum approximation holds, governed by the continuity (2.1) and Navier-Stokes equations (2.2).

The collision rules of the LGA reproduce the molecular chaos grounding the Boltzmann equation¹, while the link between (mesoscopic) kinetic and macroscopic levels is given by the Chapman-Enskog expansion², which will be sketched in Sec. 2.6.3 for a Lattice Boltzmann scheme.

2.6 The Lattice Boltzmann Bhatnagar-Gross-Krook scheme

While a LGA handles boolean-valued functions, yielding a strong statistical noise, a Lattice Boltzmann method (LBM) is defined in terms of a set of continuous functions [76]. The N_i ’s of the LGA are replaced by their ensemble

¹Of course, the name *Lattice Boltzmann*, given to the successors of LGA, adverts to the Boltzmann transport equation.

²Actually, not every LGA recovers the Navier-Stokes equation correctly. Frisch, Hasslacher and Pomeau [68] developed their D2Q7 (hexagonal) scheme after observing that the first LGA scheme, proposed by Hardy, de Pazzis and Pomeau [75] in 1972 and adopting the D2Q4 topology, was not good enough in this respect.

averages $f_i = \langle N_i \rangle$, which are single-particle distribution functions, then; and in the collision step, too, we calculate a mean-field effect, not the effects of single collisions anymore. In this way, the intrinsic statistical noise of a LGA is reduced.

Any iteration of the scheme can be summarized in the following equation ($i = 0, \dots, z$):

$$f_i(\mathbf{r} + \mathbf{e}_i \Delta t, t + \Delta t) = f_i(\mathbf{r}, t) + \Omega_i(\{f_i(\mathbf{r}, t)\}) \quad (2.28)$$

where Ω_i is the collision operator, function of all f_i 's in the collision site: if Ω_i was 0, we would have simple propagation. Ω_i is the “material difference quotient” (cf. the material derivative, Sec. 2.1) of f_i .

Seeing that

$$\rho(\mathbf{r}, t) = \sum_i f_i(\mathbf{r}, t) \quad (2.29)$$

is the local density, and

$$\rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t) = \sum_i f_i(\mathbf{r}, t) \mathbf{e}_i \quad (2.30)$$

is the local momentum density, conservation of mass and momentum are insured by the following conditions:

$$\sum_i \Omega_i = 0 \quad (2.31)$$

$$\sum_i \Omega_i \mathbf{e}_i = 0 \quad (2.32)$$

2.6.1 Linearization of the collision operator

In a 1989 paper [77], Higuera and Jiménez proposed a simplification of the collision operator Ω_i in (2.28), without which, actually, a LBM would be nothing but a mean-field version of a LBA.

In the spirit of Boltzmann approach, when the mean free path of the molecules is small, compared to the characteristic length of the system (small Knudsen number) and the mean particle speed is small, compared to the speed of sound³ in the fluid (small Mach number), the lattice spacing Δr and the time step Δt can be regarded as small parameters, of order ϵ , and

³The speed of sound, in a fluid with adiabatic index γ , molecular mass m and temperature T , is $\sqrt{\gamma k_B T / m}$.

the collision operator Ω_i can be simplified by expanding the local distribution functions about their local equilibrium values:

$$f_i = f_i^{\text{eq}} + \epsilon f_i^{\text{neq}} \quad (2.33)$$

and an expansion of (2.28) up to order $O(\epsilon)$ yields a linearized collision operator:

$$\Omega_i(f, t) = \frac{\partial \Omega_i(f^{\text{eq}})}{\partial f_j} (f_j - f_j^{\text{eq}}) \quad (2.34)$$

2.6.2 The Bhatnagar-Gross-Krook relaxation model

Already nearly 40 years before the development of Lattice Boltzmann schemes, P. L. Bhatnagar, E. P. Gross and M. Krook [36] presented a kinetic theory approach to collision processes in one-component ionized and neutral gases, to avoid the complicated nature of the collision term in the full Boltzmann equation (2.27) even for very simple physical problems.

The collision term in (2.27) is written as:

$$\left(\frac{\partial f}{\partial t} \right)_c \equiv \frac{f^{\text{eq}} - f}{\tau_f} \quad (2.35)$$

where τ_f is an average collision time. This expresses the fact that collisions tend to relax the distribution function to an equilibrium value [36]. It is interesting to remark that the authors developed the model to describe small amplitude oscillations: although the number of particles is instantaneously conserved in collisions, momentum and energy are not; if T_0 is the equilibrium temperature,

$$\int m \mathbf{v} \left(\frac{\partial f}{\partial t} \right)_c d^3 \mathbf{v} = -\frac{m}{\tau_f} \int \mathbf{v} f d^3 \mathbf{v} \quad (2.36)$$

$$\int m v^2 \left(\frac{\partial f}{\partial t} \right)_c d^3 \mathbf{v} = \frac{m}{2\tau_f} \left(\frac{3k_B T_0}{m} - \int v^2 f d^3 \mathbf{v} \right) \quad (2.37)$$

The equilibrium distribution functions must, of course, be chosen in accordance to the mass and momentum conservation principles

$$\sum_i f_i^{\text{eq}} = \rho \quad (2.38)$$

$$\sum_i f_i^{\text{eq}} e_{i\alpha} = \rho u_\alpha \quad (2.39)$$

and to the following condition concerning σ , the symmetric part of the stress tensor resulting from liquid crystalline order (2.19):

$$\sum_i f_i^{\text{eq}} e_{i\alpha} e_{i\beta} = -\sigma_{\alpha\beta} + \rho u_\alpha u_\beta \quad (2.40)$$

The relaxation time τ_f is related to the bulk viscosity η_V : $\eta_V = \rho\tau_f/3$.

We use (2.35) for the expression of the collision operator in (2.28), adding a forcing term, and applying it in a predictor-corrector fashion [78]:

$$\begin{aligned} f_i(\mathbf{r} + \mathbf{e}_i \Delta t, t + \Delta t) - f_i(\mathbf{r}, t) &= \\ &= \frac{\Delta t}{2} [\mathcal{C}_{fi}(\mathbf{r}, t, \{f_i\}) + \mathcal{C}_{fi}(\mathbf{r} + \mathbf{e}_i \Delta t, t + \Delta t, \{f_i^*\})] \end{aligned} \quad (2.41)$$

$$\mathcal{C}_{fi}(\mathbf{r}, t, \{f_i\}) = \frac{1}{\tau_f} [f_i^{\text{eq}}(\mathbf{r}, t, \{f_i\}) - f_i(\mathbf{r}, t)] + g_i(\mathbf{r}, t, \{f_i\}) \quad (2.42)$$

f_i^* is a first-order approximation to $f_i(\mathbf{r} + \mathbf{e}_i \Delta t, t + \Delta t)$, obtained imposing $f_i^* = f_i$ in (2.41). That is the reason why this formula resembles a predictor-corrector scheme: indeed, we can repeat it how many times we want, to improve the approximation. It can be proven [78] that this predictor-corrector form of the collision operator wipes out lattice viscosity effects to second order:

$$Df_i(\mathbf{r}, t) = \mathcal{C}_{fi}(\mathbf{r}, t, \{f_i\}) + \mathcal{O}(\Delta t^2) \quad (2.43)$$

The forcing terms g_i are subject to the following constraints, given $\mathfrak{m}_{\alpha\beta}$ the remaining part of the stress tensor ($\mathfrak{m}_{\alpha\beta} \equiv \tau_{\alpha\beta} + \Pi_{\alpha\beta}$, cf. Eq. (2.19)):

$$\sum_i g_i = 0 \quad (2.44)$$

$$\sum_i g_i e_{i\alpha} = \partial_\beta \mathfrak{m}_{\alpha\beta} \quad (2.45)$$

$$\sum_i g_i e_{i\alpha} e_{i\beta} = 0 \quad (2.46)$$

A way to satisfy the conditions (2.38)-(2.40), (2.44)-(2.46), is to write the equilibrium distribution function, in (2.42), as a polynomial expansion in the velocity [79, 80]:

$$f_i^{\text{eq}} = A_s + B_s e_{i\alpha} u_\alpha + C_s u_\alpha u_\alpha + D_s u_\alpha u_\beta e_{i\alpha} e_{i\beta} + E_{s\alpha\beta} e_{i\alpha} e_{i\beta} \quad (2.47)$$

and the forcing term as:

$$g_i = T_s \partial_\beta \Pi_{\alpha\beta} e_{i\alpha} \quad (2.48)$$

In the above equations, $s = |\mathbf{e}_i|^2 \in \{0, 1, 2, 3\}$: every coefficient identified by the same capital letter assumes a different value, according to which is the modulus of the $\mathbf{e}_i$ multiplied by it.

The set of coefficients depends on the system and on the lattice topology. A suitable choice of coefficients for D3Q15 – the lattice topology I used – will be given in Table 2.1 (Sec. 2.7.1).

2.6.3 The Chapman-Enskog expansion

As I said at the end of Sec. 2.5, the Lattice Boltzmann scheme works – in other words, it provides a solution, although approximate, of the fluid dynamics laws – if we can connect its equations, mesoscopic, to the continuity and Navier-Stokes equations, macroscopic.

This connection is actually achieved by the Chapman-Enskog expansion of the distribution functions.

The basic assumption of Chapman and Enskog is the following: *successive derivatives of the quantities at stake are of increasingly high order* [81].

If $f_i = f_i^{(0)} + f_i^{(1)} + f_i^{(2)} + \dots$, with the upper index denoting the order, from Eqs. (2.43) and (2.42) it follows that:

$$f_i^{(0)} = f_i^{\text{eq}} + \tau_f g_i \quad (2.49)$$

$$f_i^{(1)} = -\tau_f D f_i^{\text{eq}} - \tau_f^2 D g_i \quad (2.50)$$

$$f_i^{(2)} = \tau_f^2 D^2 f_i^{\text{eq}} + \tau_f^3 D^2 g_i \quad (2.51)$$

The procedure is explained extensively in [78]; its basic points are:

1. summing f_i over i ;
2. applying the constraints on f_i , f_i^{eq} and g_i ((2.38), (2.39), (2.40), and (2.44) to (2.46));
3. eliminating the higher-order terms;
4. multiplying the expansion of f_i by $e_{i\alpha}$ and repeating the three previous points;
5. combining the results, wiping out identical terms.

In the end, we obtain:

$$\partial_t \rho + \partial_\alpha (\rho u_\alpha) = 0 + o(\partial^3) \quad (2.52)$$

i. e. a continuity equation up to second order in derivatives, and:

$$\begin{aligned} \partial_t (\rho u_\alpha) + \partial_\beta (\rho u_\alpha u_\beta) &= \partial_\beta \sigma_{\alpha\beta} + \partial_\beta \Pi_{\alpha\beta} \\ &+ \tau_f \partial_\beta \left[-\partial_t \sigma_{\alpha\beta} + \partial_t (\rho u_\alpha u_\beta) + \partial_\gamma \sum_i f_i^{\text{eq}} e_{i\alpha} e_{i\beta} e_{i\gamma} \right. \\ &\left. + \tau_f \partial_\gamma \sum_i g_i e_{i\alpha} e_{i\beta} e_{i\gamma} \right] \end{aligned} \quad (2.53)$$

i. e. a Navier-Stokes equation up to first order in derivatives.

This is not the final form of the Navier-Stokes equation, yet. The final steps to get it are not common to any Lattice Boltzmann BGK scheme, but are peculiar to the lattice topology in use:

6. we need, namely, the explicit expressions of the equilibrium distribution functions f_i^{eq} 's (Eq. (2.47) and Table 2.1) and of the body force g_i (Eq. (2.48) and Table 2.1). We substitute these expressions in (2.53);
7. we assume that the fluid is incompressible, ignore third-order terms in the velocities and approximate as a constant $-P_0$ (hydrostatic pressure, see Sec. 2.3.2) the stress tensor within second-order terms.

Proceeding this way, we derive (2.18).

2.7 Hybrid Lattice Boltzmann algorithm

Of course, Lattice Boltzmann methods are suitable not only to solve the equations of fluid dynamics, although they were developed for this aim. Applying the same technique to the (five) independent components of the tensor order parameter, i. e. defining a set of distribution functions $\mathbf{G}_i$, writing a propagation-collision equation for each of them, assuming the collision operator as relaxation towards an equilibrium value, verifying that the Chapman-Enskog expansion gives us back the macroscopic equation... we can find an approximate discrete-time solution of the Beris-Edwards equation (2.5).

For a single nematic, that means calculating, in addition to the evolution (Eq. (2.28)) of the distribution functions f_i whose sum over i yields the

material density, the evolution of five extra distribution function sets, one for each of the five independent components of $\mathbf{Q}$.

If, instead of a single nematic, we have a binary emulsion, whose characteristic quantity is the nematic volume fraction ϕ , governed by the Cahn-Hilliard equation (2.25), another distribution function set is required. A Chapman-Enskog expansion can be performed for each of the distribution function set, to give back the macroscopic dynamical equation.

Anyway, this approach is considerably computationally expensive. Storing six (for a single nematic) or seven (for a binary nematic emulsion) sets of distribution functions requires a lot of memory, and that limits the size of the system we can simulate by a full LBM [85].

For that reason, following the approach used in studies of a thermal flow [84], cholesteric blue phases [85], colloids in liquid crystals [86], active liquid crystals⁴ [87], shear banding of fluids with a lamellar phase [88] and binary mixtures of simple fluids [90], *I applied the Lattice Boltzmann algorithm only for the continuity (2.1) and Navier-Stokes equations (2.18)*. The Beris-Edwards equation for the tensor order parameter (2.5) and the Cahn-Hilliard equation for the concentration (2.25) are solved by an ordinary finite-difference scheme (predictor-corrector).

In the study of active liquid crystals [87] we can find a comparison between a hybrid LB and two full LB schemes: the agreement is really good, at least for intermediate/long times ($\approx 10^5$ LB iteration).

Of course, every iteration of the algorithm, starting from $\{f_i, \mathbf{Q}, \phi\}$ defined at time t for every lattice site $\mathbf{r}$, calculates the value of the functions for each $\mathbf{r}$ at time $t + \Delta t$: the f_i 's, via the LBGK scheme; $\mathbf{Q}$ and ϕ , via the finite-difference solver. Since the points $\mathbf{r}$ are discrete and periodic boundary conditions are imposed (see Sec. 2.7.2), when translating the algorithm into an executable code, the f_i 's, the independent components⁵ of $\mathbf{Q}$ and ϕ are two- (for D2Qx lattice topologies) or three- (for D3Qx lattice topologies) dimensional arrays.

It is evident, now, why hybrid Lattice Boltzmann is less computationally expensive than a full LBGK: for a D2Q9 lattice topology, for instance, determining the volume fraction and the tensor order parameter requires 54 two-dimensional arrays altogether; for a D3Q15 lattice topology, the total number of arrays raises up to 90, and they are three-dimensional, too! On

⁴A liquid crystal is *active* if it consumes energy, being driven out of thermodynamic equilibrium even in absence of external forces [87]. Activity is given by an extra term $-\zeta Q_{\alpha\beta}$ in the stress tensor, where $\zeta > 0$ means that the (rod-like) molecules are extensible, $\zeta < 0$ means that they are contractile. Active liquid crystals are useful to model, for instance, flows of bacteria.

⁵Typically, physicists choose $Q_{xx}, Q_{xy}, Q_{xz}, Q_{yy}, Q_{yz}$.

the contrary, with the finite-difference scheme, the number of needed arrays for $\mathbf{Q}$ and ϕ is always 6.

2.7.1 Lattice topology and equilibrium distribution function

Even though I simulated both two-dimensional (Chapters 3 and 4) and three-dimensional (Chapters 5 and 6) systems, I chose a 15-velocity three-dimensional model for both geometries. For two-dimensional systems, I imposed one of the three dimensions of the simulation box (*supercell*) equal to 1.

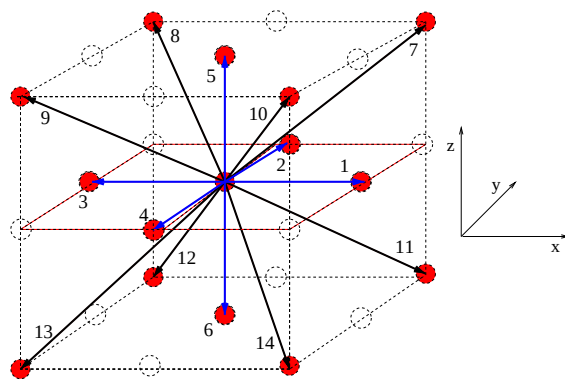


Figure 2.3: The D3Q15 lattice topology for a Lattice Boltzmann scheme.

The arrangement of the vectors are shown in Fig. 2.3. According to the definition given at page 40, the s index of the coefficients of the polynomial expansion of the equilibrium distribution functions f_i^{eq} (2.47) and of the body force g_i (2.48) can be:

- 0 for $\mathbf{e}_0 = (0, 0, 0)$;
- 1 for $\mathbf{e}_i = (\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1), i = 1, \dots, 6$;
- 3 for $\mathbf{e}_i = (\pm 1, \pm 1, \pm 1), i = 7, \dots, 14$.

A suitable choice of coefficients is given in Table 2.1.

	$s = 3$	$s = 1$	$s = 0$
A_s	$\sigma_{\gamma\gamma}/30$	A_3	$\rho - 14A_3$
B_s	$\rho/24$	$8B_3$	0
C_s	$-\rho/24$	$2C_3$	$-2\rho/3$
D_s	$\rho/16$	$8D_3$	0
$E_{s\alpha\beta}$	$(\sigma_{\alpha\beta} - \frac{1}{3}\delta_{\alpha\beta}\sigma_{\gamma\gamma})/16$	$8E_{3\alpha\beta}$	0
T_s	$1/24$	$8T_3$	0

Table 2.1: Coefficients of the equilibrium distribution functions f_i^{eq} defined in (2.47) and for the body force g_i defined in (2.48).

2.7.2 Settings of the simulations and boundary conditions

The supercell I defined at the beginning of every simulation is a rectangular box, of dimensions:

- $1 \times 100 \times 100$ lattice units, for two-dimensional systems (Chapters 3 and 4);
- $38 \times 38 \times 38$ lattice units, for three-dimensional systems (Chapters 5 and 6).

From now on, I will refer to these dimensions with $\{N_x, N_y, N_z\}$.

Non-sheared systems

As is customary in computer simulations, to avoid huge surface effects, I imposed **periodicity** at the boundaries.

Both in the two-dimensional and in the three-dimensional case, at first I simulated a single non-sheared isotropic droplets in a nematic environment, with periodic boundary conditions along all the three directions: in other words, if a fraction of matter goes out of the supercell through a face, it goes back into the supercell through the opposite face.

Technically, since every coordinate of a cubic lattice site (such as D3Q15) is an integer multiple of the lattice constant Δr (and, in simulation units, is an integer), to impose periodic boundary conditions means to replace the coordinate α with its least residue system modulo N_α .

This condition does not merely simulate a homogeneous⁶ emulsion of the two coexisting phases: as we will see in Chapter 3 and 5, the droplet changes its shape, and its aspect ratio, a very important role will be played by the elastic constant L_1 of the surrounding nematic (1.16) and by the anchoring coefficient W for the nematic near the interface (1.22).

The simulations without external shear flow started with the droplet at the centre of the supercell. That means,

$$\phi(\mathbf{r}, 0) = \begin{cases} \phi_{\text{iso}}^0 & \text{if } |\mathbf{r}| < R_0 \\ \phi_{\text{nem}}^0 & \text{if } |\mathbf{r}| \geq R_0 \end{cases} \quad (2.54)$$

where ϕ_{iso}^0 and ϕ_{nem}^0 are the initial values of the concentration for, respectively, the isotropic and the nematic phase, and R_0 is the initial radius of the droplet.

The interface, therefore, is a step function at $t = 0$. Comparing this initialization to a real situation, we could think of a nematic whereto isotropic droplets are injected all at once. During the simulation, the interface smoothes out⁷, and the concentration values for the two coexisting phases converge to the actual coexistence values, determined predominantly by the bulk free energy $\mathcal{F}_s + \mathcal{F}_m$ ((1.11) and (1.10)).

Having chosen $A_m = -0.016$ and $B_m = 0.8$, $\phi_0 = 0.5$ in (1.10), the only mixing energy $\mathcal{F}_m$ would give $\phi_{\text{iso}} \approx 0.359$ and $\phi_{\text{nem}} \approx 0.641$ as concentration values at coexistence (see Fig. 2.4).

I imposed two values almost close to them, for the starting configurations: $\phi_{\text{iso}} = 0.295$, $\phi_{\text{nem}} = 0.745$.

At the beginning of the simulation, the nematic director is set **parallel** to the z axis.

The initial **radius** of the isotropic drop is $R_0 = 22$ lattice units in the two-dimensional case, so the overall nematic volume fraction ≈ 0.677 ; it is $R_0 = 14$ lattice units in the three-dimensional case, so the overall nematic volume fraction ≈ 0.651 .

The overall nematic volume fraction is kept constant by a subroutine, called after every iteration of the hybrid Lattice Boltzmann algorithm, which offsets properly all values of $\phi(\mathbf{r}, t)$.

⁶Here, *homogeneous* means that all drops in the emulsion have the same size.

⁷It must be remarked that the regularity which the functions are required by a Lattice Boltzmann algorithm yields an interface much thicker than the interface of a real system.

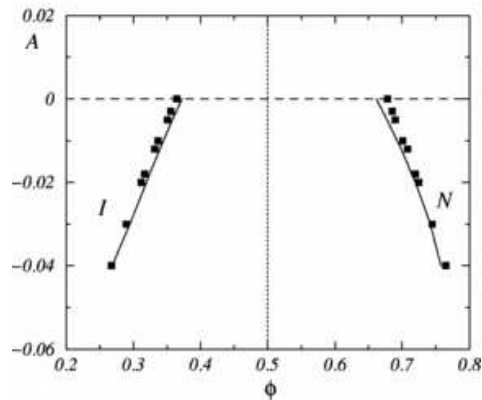


Figure 2.4: Phase diagram of the nematic-isotropic emulsion described by the bulk free energy $\mathcal{F}_s + \mathcal{F}_m$, with $\eta_0 = 2.7$, $A_0 = 1.5$, $\phi_0 = \bar{\phi} = 0.5$ ((1.11), (1.10) and (1.12)). The letter I stands for *isotropic phase*; the letter N stands for *nematic phase*; the A on the ordinate axis is the A_m of (1.10). The solid line joins the results of Lattice Boltzmann simulations, the black squares refer to a double-tangent calculation [83]. (Diagram sourced from [34].)

Sheared systems

In a shear flow experiment with a surface rheometer (Couette device), the fluid is sandwiched between two plates, moving one with respect to another. Either shear stress is imposed and strain rate is measured, or strain rate is imposed and shear stress is measured (Fig. 2.5). The configuration of my simulations resembles an infinitely long sliding-plate rheometer, where I can tune the strain rate – actually, I impose a velocity v , always parallel to the y axis, on the walls, which are set parallel to the xy plane. More precisely: the upper wall ($z = N_z - 1$) moves forward in the y direction, the lower wall ($z = 0$) moves backward in the y direction, and their speed is v .

The starting configuration of the two-dimensional system, for low values of the strain rate, is the same as for the unsheared system: hence, the situation can be depicted as a circular drop injected, very fast, in the rheometer, at the same moment when the plates start moving.

For high values of the strain rate, instead, every time I increased it, maintaining all the other parameters fixed, I let the simulation begin from the final configuration of the previous simulation, as though I sped up the plates of the Couette device.

Due to the long times needed for the equilibration, this latter option has been chosen for all the values of the strain rate of three-dimensional sheared

systems.

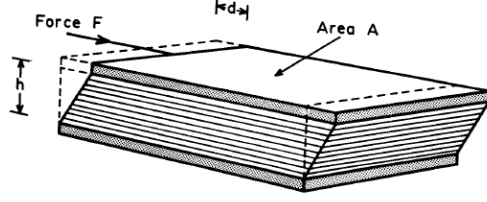


Figure 2.5: Shear flow for a simple fluid. Stress: F/A , strain: d/h .

In order to simulate an emulsion between parallel walls, I have to “turn off” the periodic boundary conditions along the z axis. In their place, I impose the **full way bounce-back boundaries** to the f_i 's at $z = 0$ and $z = N_z - 1$ (Fig. 2.3) [91, 37].

1. zero flux through the wall, i. e. $\sum_i f_i e_{iz} = 0$:

$$f_6 + f_{11} + f_{12} + f_{13} + f_{14} = f_5 + f_7 + f_8 + f_9 + f_{10} \quad (2.55)$$

2. no slip⁸ along x (fluid stuck to the surface), i. e. $\sum_i f_i e_{ix} = 0$:

$$f_1 + f_7 + f_{10} + f_{11} + f_{14} = f_3 + f_8 + f_9 + f_{12} + f_{13} \quad (2.56)$$

3. fixed velocity⁹ $\bar{v}$ along y , i. e. $\sum_i f_i e_{iy} = \rho \bar{v}$:

$$f_2 + f_7 + f_8 + f_{11} + f_{12} - f_4 - f_9 - f_{10} - f_{13} - f_{14} = \rho \bar{v} \quad (2.57)$$

For the lower wall, the unknown distributions – the ones corresponding to vectors coming from inside the wall – are $\{f_5, f_7, f_8, f_9, f_{10}\}$; for the upper wall, they are $\{f_6, f_{11}, f_{12}, f_{13}, f_{14}\}$. In either case, we need five equations, and up till now we have only three. To close the system, more than one solution

⁸The original idea of non-slip conditions is the following: fluid molecules that strike the wall are assumed to leave it with the Maxwellian velocity distribution corresponding to the temperature and velocity of the wall. Nevertheless, with this assumption, normally to the boundary we obtain the expected velocity, but along the boundary we do not. The difference between the actual and the expected velocities is the *slip velocity*: so, we let the unknown distribution functions (the ones corresponding to vectors coming from beyond the boundary) be equilibrium distribution functions with such a counter-slip velocity to compensate this difference [92, 93].

⁹ $\bar{v} = +v$ at $z = N_z - 1$, $\bar{v} = -v$ at $z = 0$.

can be adopted: we assume that the bounce-back rule is still valid for the non-equilibrium part of the distribution function *normal* to the boundary [91]:

$$f_5 = f_6 \quad (2.58)$$

and, for symmetry reasons [37]:

$$f_7 + f_9 = f_8 + f_{10} \quad \text{for } z = 0 \quad (2.59)$$

$$f_{11} + f_{13} = f_{12} + f_{14} \quad \text{for } z = N_z - 1 \quad (2.60)$$

At the walls, I imposed **homeotropic anchoring** for the nematic (1.20) with local scalar order parameter $q_0 = 0.3972$: it is the scalar order parameter for the nematic resulting in unsheared emulsions.

The elastic constant is $\alpha_s = 1.0$, and the same numerical value is set for α_w in the **wetting condition** (1.21).

The anchoring of the nematic at the interface (1.22) is always perpendicular. Its strength W , anyway, is a variable parameter, as well as the elastic constant L_1 of the nematic (1.15) and the shear velocity v , when the system is sheared.

Indeed, I studied the equilibrium configuration of an unsheared two-dimensional or three-dimensional droplet when varying the anchoring strength W and the nematic elastic constant L_1 ; and the deformation of the droplet under a shear flow when varying the anchoring strength W , the nematic elastic constant L_1 and the shear velocity v .

2.8 Fixed and variable parameters. Mapping of simulation units

In Table 2.2 I am giving you a summary of the values of all fixed parameters and the ranges of variable parameters.

In order to compare the simulation results with experimental data, anyway, we need to establish the relations between the simulation units and the measurable quantities.

The choice depends on the properties of the substance we want to simulate: in particular, it must allow for its Leslie-Ericksen coefficients, which are functions of experimentally measurable quantities (Sec. 2.2).

I chose the same mapping of [34]:

Parameter	Symbol	Value(s) for 2D	Value(s) for 3D
Supercell size	$N_x \times N_y \times N_z$	$1 \times 100 \times 100$	$38 \times 38 \times 38$
Density	ρ	2.0	
Temperature	T	0.5	
LBGK relaxation time (2.35)	τ_f	2.4 (time step $\Delta t = 1.0$)	
Bulk viscosity	$\eta_V = \rho\tau_f/3$	1.6	
Molecule-structural constant	ξ	0.7	
Rotational diffusion constant for $\mathbf{Q}$ (2.5)	Γ	0.2	
Diffusion constant for ϕ (2.25)	M	0.5	
Constants in Landau-de Gennes-Matsuyama bulk free energy (1.11), (1.12)	A_0	1.5	
	η_0	2.7	
	η_s	0.3	
	$\bar{\phi}$	0.5	
Constants in Landau-Brazovskii mixing energy (1.10)	A_m	−0.016	
	B_m	0.8	
Nematic elastic constant (one-constant approximation) (1.16)	L_1	$10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}$	
Interface energy coefficient (1.19)	K	0.1	
Coefficients for wall-nematic anchoring (*) (1.20)	α_s	1.0	
	q_0	0.3972	
Coefficients for wall-nematic wetting (*) (1.21)	α_w	1.0	
	ϕ_0	0.745	
Interface anchoring coefficient (1.22)	W	−0.040, −0.080, −0.133	
Initial radius of the droplet	R_0	22.0	14.0
Shear velocity (*)	v	$0 \div 0.016$	$0 \div 0.005$

Table 2.2: Fixed and variable parameters of the hybrid LB scheme for a nematic-isotropic emulsion at rest or under a shear flow. All values are in simulation units. The values of starred quantities hold only for sheared systems. Quantities which are not kept fixed during the simulations are shown in **bold**.

- the spacing between lattice sites is 10^{-7} m;
- the time step Δt is 10^{-6} s;
- a reduced density = 1 corresponds to 250 kg/m³.

With this mapping, a reduced elastic constant $L_1 = 0.01$ (1.16) corresponds to a real elastic constant = 20 pN, which is a typical value for liquid crystals (Sec. 1.5.1).

Chapter 3

Two-dimensional droplets at rest

As a check of the validity of my approach to the study of nematic-isotropic emulsions, I have tried to reproduce the results in [34] on the equilibrium shape of two-dimensional droplets of isotropic phase in a nematic host.

The system is two-dimensional, but because of the translational symmetry along x (Sec. 2.7.2), the system is, in fact, three-dimensional and the drops can be seen as the cross sections of cylindrical regions of isotropic phase.

The simulations have been carried out in a periodic box of size $1 \times 100 \times 100$ and for different combinations of the bulk elastic constant L_1 and anchoring coefficient W (see Eqs. (1.22) and (1.16)). These parameters and the surface tension parameter, that is set equal to $K = 0.1$, are the most important ones in controlling the shapes of the isotropic drops in the nematic host.

All the other quantities listed in Table 2.2 are kept fixed.

3.1 Simulation parameters and relevant dimensionless ratios

Among the several factors that may affect the equilibrium shape of the isotropic droplet, the *surface anchoring strength* at the drop surface (surface anchoring energy per unit area, cf. (1.22))

$$\frac{F_{ai}}{\Sigma} = \frac{\int \mathcal{F}_{ai} d^3x}{\int_{S_d} d\Sigma} = \frac{\int W (\partial_\alpha \phi) Q_{\alpha\beta} (\partial_\beta \phi) d^3x}{\Sigma}, \quad (3.1)$$

the *surface tension* (surface energy per unit area, cf. (1.19))

$$\frac{F_i}{\Sigma} = \frac{\int \mathcal{F}_i d^3x}{\Sigma} = \frac{\int \frac{K}{2} (\partial_\gamma \phi)^2 d^3x}{\Sigma} \quad (3.2)$$

and the *liquid crystal bulk elastic constant* L_1 (1.16 are the most relevant ones. In the above equations (3.1) and (3.2), Σ is the perimeter of the drop. Rigorously, since the system is two-dimensional, we should replace the words *per unit area* with *per unit length*, but remember: as said at the beginning of this chapter, the system is, in fact, three-dimensional, with the third dimension (x , with our choice of the axes) equal to 1, so Σ has the same numerical value as the droplet area.

Typical values of F_{ai}/Σ and F_i/Σ found in literature [106, 107] are $F_{ai}/\Sigma = 10^{-7} \div 10^{-3}$ J/m², $L_1 = 10^{-11}$ N and $F_i/\Sigma = 10^{-2}$ J/m². It is important to stress that, while the experimental values of F_{ai} and L_1 are accessible by our model, the values of the surface tension that can be reproduced by the LB simulations are $\approx 10^{-3}$ in simulation units. This corresponds to a physical value $\approx 2 \cdot 10^{-5}$ J/m², which is very small, if compared to the typical values considered in the literature, but that can be achieved experimentally by addition of a surfactant.

According to [34], a good dimensionless ratio to classify the possible equilibrium drop shapes is given by $F_{ai}R/\Sigma L_1$, where R is the drop radius.¹ This ratio measures the strength of the surface anchoring energy relative to the bulk director deformations [25]. Since typical sizes of the drops achieved in a nematic emulsions are within the range $1 \div 10$ μm , the possible values of $F_{ai}R/\Sigma L_1$ corresponding to experiments are within the range $10^{-2} \div 10^3$. When $F_{ai}R/\Sigma L_1 < 1$, the anchoring is considered to be weak. In this case the coupling between the nematic host and the isotropic drops through the interface is expected to be negligible and both the nematic director field and the interface would not be severely affected. In other words, undistorted drops and nematic field should be observed.

If, on the other hand, $F_{ai}R/\Sigma L_1 \gg 1$, the anchoring is strong and this would effect both the shape and the local orientation of the nematic close to the interface; in this regime, defects may be present, as well. In this case, another interesting dimensionless ratio to follow is given by F_{ai}/F_i , which measures the interface anchoring strength vs. the surface tension.

The ratio F_{ai}/F_i , together with $L_1\Sigma/F_iR$, constitute an alternative set of dimensionless numbers that can be used to classify the equilibrium properties of the isotropic drops, and is adopted in [99]. The latter ratio measures the strength of the elastic nematic distortion, relative to the surface tension.

In terms of our model (see Chapters 1 and 2) the ratios F_{ai}/F_i and $L_1\Sigma/F_iR$ can be equivalently represented respectively by the dimensionless parameters L_1/K and $|W|/K$.

¹N. B. Since $\mathcal{F}_{ai}$ is negative, from now on, with the symbol F_{ai} we will consider implicitly its absolute value.

The criterion for the choice of the values of L_1 , W and K is the same as in Sulaiman's paper [34]: namely, physical quantities comparable to the experimental values found in literature, and a wide enough range of the two dimensionless parameters to explore as much as we can the space of the equilibrium droplet shapes. Note, however, that the system we simulate is not identical to the one presented in [34] both because of the smaller supercell size we consider (Sulaiman *et al.* let the simulation run in a supercell of size $1 \times 200 \times 200$) and because of the difference in size of the initial drop (in [34], the starting radius is $R_0 = 60$ lattice constants).

Referring to Table 2.2, the set of relevant parameter values we choose in our simulations are

$$L_1 \in \{10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}\} \quad (3.3)$$

$$|W| \in \{0.04, 0.08, 0.133\} \quad (3.4)$$

in simulation units, corresponding to the dimensionless numbers

$$L_1/K \in \{10^{-3}, 10^{-2}, 10^{-1}, 1\} \quad (3.5)$$

$$|W/K| \in \{0.40, 0.80, 1.33\}. \quad (3.6)$$

3.2 Reaching equilibrium

For every combination of L_1 and W (K is fixed to 0.1), I let the simulations run until the total free energy of the system (the sum of all terms enumerated in Secs. 1.4 and 1.5) reaches a stable value, identified as the equilibrium value. In most of the cases this occurs after $2 \cdot 10^5 \div 8 \cdot 10^5$ hybrid LB iterations.

From Fig. 3.1, we can notice that the equilibrium value of F is not equal to its minimum value. This is essentially due to the different times needed by the system in responding to two different “stimuli” imposed by the initial condition, namely the time needed to the concentration field to reach its equilibrium profile and the time needed by the nematic to orient itself along the droplet interface.

In fact, as said at page 45, in the initial configuration the nematic is oriented parallel to the z axis and the concentration field ϕ is a step function, with approximately the nematic value outside a circle of radius $R_0 = 22$ centred on the centre of the supercell and approximately the isotropic value inside it.

Given this initial condition, since the surface energy coefficient K is nonzero, the interface smoothes out, reaching an equilibrium configuration

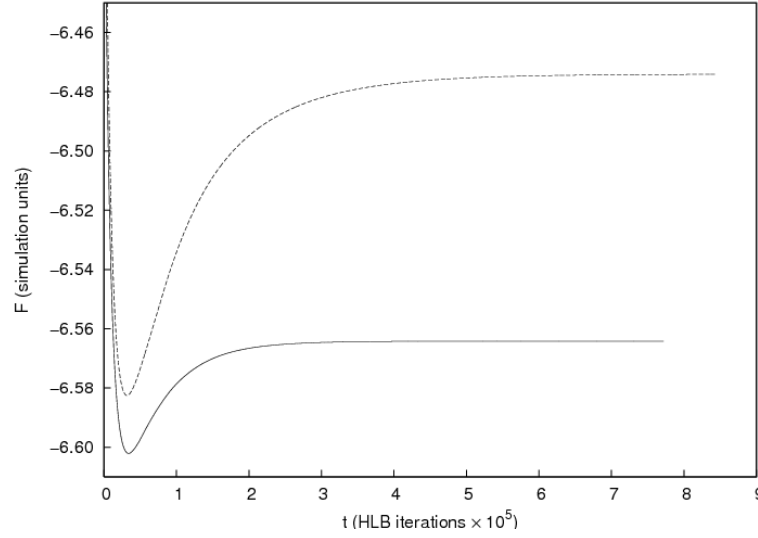


Figure 3.1: Time evolution of the free energy of a drop of isotropic phase within a nematic matrix. The values of the parameters considered are $W = -0.04$, $L_1 = 0.01$ (solid line) and $W = -0.133$, $L_1 = 0.1$ (dashed line).

similar to the one shown in Fig. 3.2. In this new state the values of ϕ inside and outside the drop converge to the actual coexistence values (Fig. 2.4) and, since the overall nematic volume fraction is constant (page 45), the initial droplet is contracted.

Once the droplet and its interface is formed, the nematic must orient perpendicular to the interface. The smoothing of the interface decreases the free energy, because the interface assumes the configuration which minimizes the surface tension, and is faster. The re-orienting of the director field is slower and increases the free energy, because if $\hat{\mathbf{n}} \parallel z$, $\mathcal{F}_d = 0$ at the beginning, but the equilibrium configuration usually requires $\mathcal{F}_d > 0$.

3.3 Characterizing two-dimensional droplets

Fig. 3.2 shows a profile of the concentration ϕ vs. the z coordinate at $y = 50$ (centre of the supercell) when the corresponding system has reached equilibrium, in two cases. The values of z where the concentration gradient differs significantly from 0 define the interface between the nematic matrix and the isotropic droplet.

In this respect, the interface is not a well-defined boundary. From a

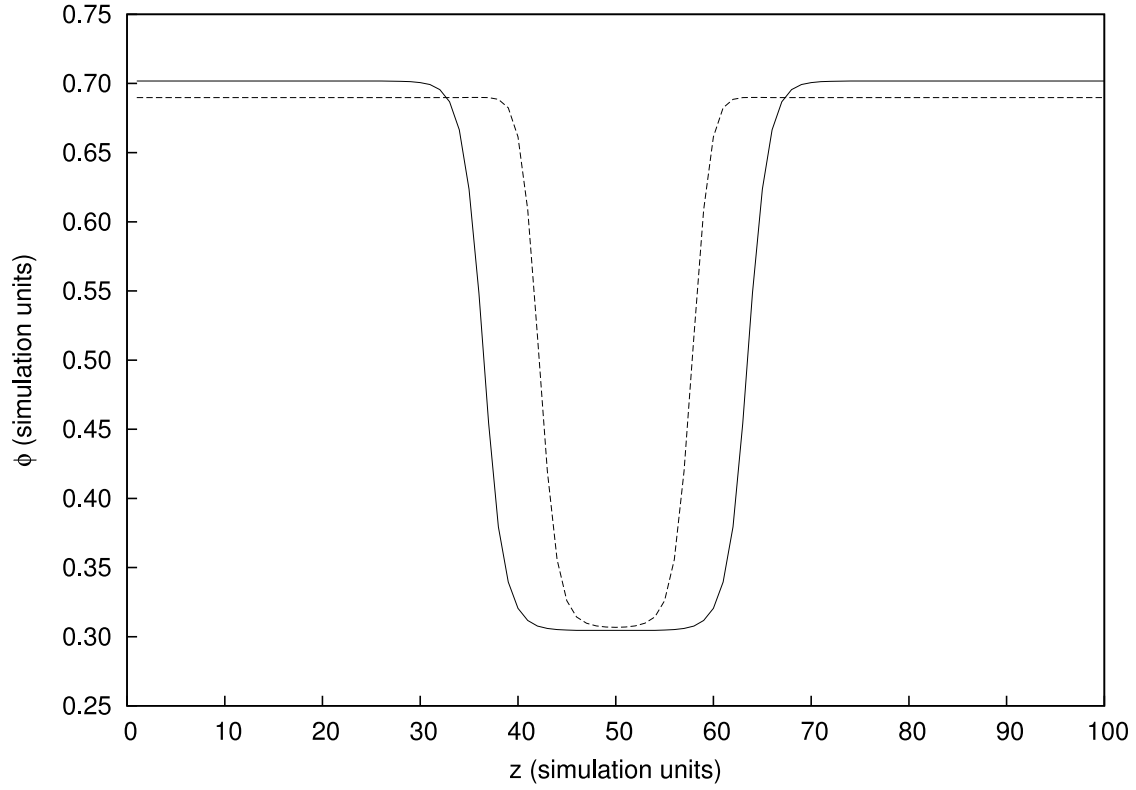


Figure 3.2: Equilibrium profile of the concentration ϕ along z taken at $y = 50$, for $W = -0.04$, $L_1 = 0.01$ (solid line), and for $W = -0.133$, $L_1 = 0.1$ (dashed line).

physical point of view, that is correct, because the interface is, actually, a region of space of nonzero volume; however, in order to define the shape and size of the droplet the interface has to be defined properly. As far as the shape of the droplet is concerned, we expect the droplet to assume a circular (spherical, in three dimensions) or a distorted circular shape. From previous studies one would expect that, at equilibrium, a two-dimensional Newtonian drop in a Newtonian immiscible matrix would be perfectly circular (spherical, in three dimensions) being the shape that, keeping the area (volume) constant, minimizes the interface energy. This is still almost true when both the anchoring strength-surface tension ratio and the nematic elastic constant are sufficiently small. On the other hand, by increasing either W or L_1 , the droplet contracts along z , the initial direction of $\hat{\mathbf{n}}$, and, especially when L_1 is big enough, the droplet looks like a rugby ball, sometimes with two bulges [99, 100].

To a first approximation, its shape can be considered *elliptical*.² and it is then convenient to assume an elliptical shape as the most general shape the drop can assume at equilibrium.

3.3.1 Approximation of the droplet shape as an ellipse

In order to calculate the ellipse which best approximates the boundary of the droplet, it is first convenient to compute a sort of “inertia tensor” of it, thinking of it as a two-dimensional rigid system of particles, with masses $\{m_i\}$, at the positions $\{(y_i, z_i)\}$, measured with respect to an origin O :

$$I = \begin{pmatrix} \sum_i m_i z_i^2 & -\sum_i m_i y_i z_i \\ -\sum_i m_i y_i z_i & \sum_i m_i y_i^2 \end{pmatrix} \quad (3.7)$$

The “mass” m_i of the i -th LB cell is related to the local nematic concentration ϕ_i as follows:

$$m_i = (1 - (\phi_i - \phi_{\min}) / (\phi_{\max} - \phi_{\min})) \quad (3.8)$$

where $\phi_{\min}$ and $\phi_{\max}$ are, respectively, the minimum and the maximum value of ϕ throughout the supercell. Note that with this definition $m_i \approx 1$ for an LB cell lying in the bulk of the droplet whereas $m_i \approx 0$ for an LB cell lying

²Lishchuk *et al.*, which discussed a very similar situation [99, 100], though they adopted a different model, never used the word *ellipse*. In fact, the analytical expression of the shape which they derived (3.10) is not the equation of an ellipse: it describes a droplet with sharp edges, depending on the anchoring strength vs. surface tension ratio. I approximated the shape as an ellipse for coherence with the description of the behaviour of the droplets under a shear flow.

in the nematic host. Clearly m_i assumes an intermediate value for an LB cell lying at the interface.

As reference point O for the computation of the inertia tensor, I chose the “centre of mass” of the droplet, calculated with the m_i ’s defined above.

I imposed a cut-off of 0.04 for the “mass” values, i. e. I set $m_i = 0$ if the value obtained with Eq. (3.8) is less than 0.04, because numerical noise in the nematic phase leads to an overestimate of the size of the supercell. As we can see from the definition of inertia tensor (3.7), a point particle located far from the origin “weighs” much more than a point particle located close to it. So, fluctuations in m_i within the nematic phase, especially far from the “centre of mass” of the droplet, can yield longer axes of the approximating ellipse (see below).

By diagonalizing the matrix I , we can find the principal axes of inertia: if the system is not sheared, they should coincide with the y and z axes; if a shear stress is applied, as we will see in Sec. 4, the droplet will be tilted and in this way the tilt angle can be computed, too.

The principal moments of inertia are $1/\sqrt{I_y}$ and $1/\sqrt{I_z}$, where I_y and I_z are the eigenvalues of I .

From classical mechanics, we know that the principal moments of inertia of an elliptical plate of mass M , with semiaxes a , b , are: $I_y = Mb^2/4$, $I_z = Ma^2/4$. With these relations, with M being the sum of all m_i ’s in the supercell, I can obtain the semiaxes a , b of the approximating ellipse ($a > b$), the aspect ratio a/b (as defined in [100]) and, through the Ramanujan formula [101], an estimate of the perimeter Σ :

$$\Sigma = \pi \left\{ (a + b) + \frac{3(a - b)^2}{10(a + b) + \sqrt{a^2 + 14ab + b^2}} \right\} \quad (3.9)$$

3.3.2 An alternative way to estimate the perimeter

Another way to estimate the perimeter of the droplet is the following.

We “draw” 12 straight lines passing through the “centre of mass” of the droplet, and (by linear interpolation) find their intersection with the boundary. Observing (see Fig. 3.2) that the concentration ϕ is quite uniform, both inside the bulk of the droplet ($\approx \phi_{\min}$) and in the surrounding nematic ($\approx \phi_{\max}$), we imagine a point moving along each straight line, starting from the centre. We select the two consecutive LB cells between which, ideally, lies the arithmetic mean $\bar{\phi} = (\phi_{\max} + \phi_{\min})/2$, and, by a linear interpolation, we estimate the coordinates where $\phi = \bar{\phi}$.

Once the 24 intersections (every straight line intersects the boundary of the droplet twice) are found, the calculation of the perimeter of the convex

24-gon whose vertices are the 24 intersections is straightforward.

In this way, we obtain always a value smaller than the estimate by the Ramanujan formula, of about 3.5%. (The perimeter of a regular 24-gon is 2.85% smaller than the circumscribed circumference.)

3.4 Results

During the simulations, the system was sampled every 10^5 hybrid LB iterations, and for every sample I computed the two semiaxes a , b of the ellipse which approximates best the real shape of the droplet, its perimeter Σ (Sec. 3.3.1) and the dimensionless ratio $F_{ai}R/\Sigma L_1$ where $R = \sqrt{ab}$.

I estimated the actual value of each mesoscopic quantity by a simple arithmetic mean, if the quantity fluctuates about the average. Sometimes, anyway, a quantity increases or decreases monotonically in time, and it would take too long to converge to the final value. In this case, I performed a power law regression and took the zero degree term.

3.4.1 Equilibrium shapes of the drops

The equilibrium shapes obtained at the end of the simulations are shown in Fig. 3.3. The black areas correspond to the isotropic phase, because in the isotropic phase $q \approx 0$. Comparing these shapes with the corresponding ones in [34], we find a qualitative similarity, which holds mostly for high elastic constants, i. e. when the dimensionless ratio $F_{ai}R/L_1\Sigma \lesssim 1$, corresponding to the condition of weak anchoring.

The combinations with the two lowest (absolute) values of the anchoring coefficient W and the two lowest values of L_1 (Fig. 3.3, panels a, b, e, f) yield a quite perfect circular shape of the droplet (Table 3.1). Both the ratio between the interface anchoring and the surface energy coefficient $|W|/K$ and the ratio between the elastic constant and the surface energy coefficient L_1/K (Sec. 3.1) are small ($K = 0.1$), so the system is dominated by the surface tension, which favours a circular shape, as brought forward in Sec. 3.3.

When we increase L_1 , the shape deviates from the quite perfect circle, because the elastic forces become comparable to the surface tension and the system converges towards the configuration which constitutes the best compromise between the two effects. If $W = -0.04$ (Figs. 3.3c and 3.6), the shape contracts simply along z (Table 3.1); if $W = -0.08$, the anchoring plays a more important role (in Fig. 3.6, relative to $W = -0.04$, $L_1 = 0.01$, we see that the director field is basically undistorted, except from the immediate

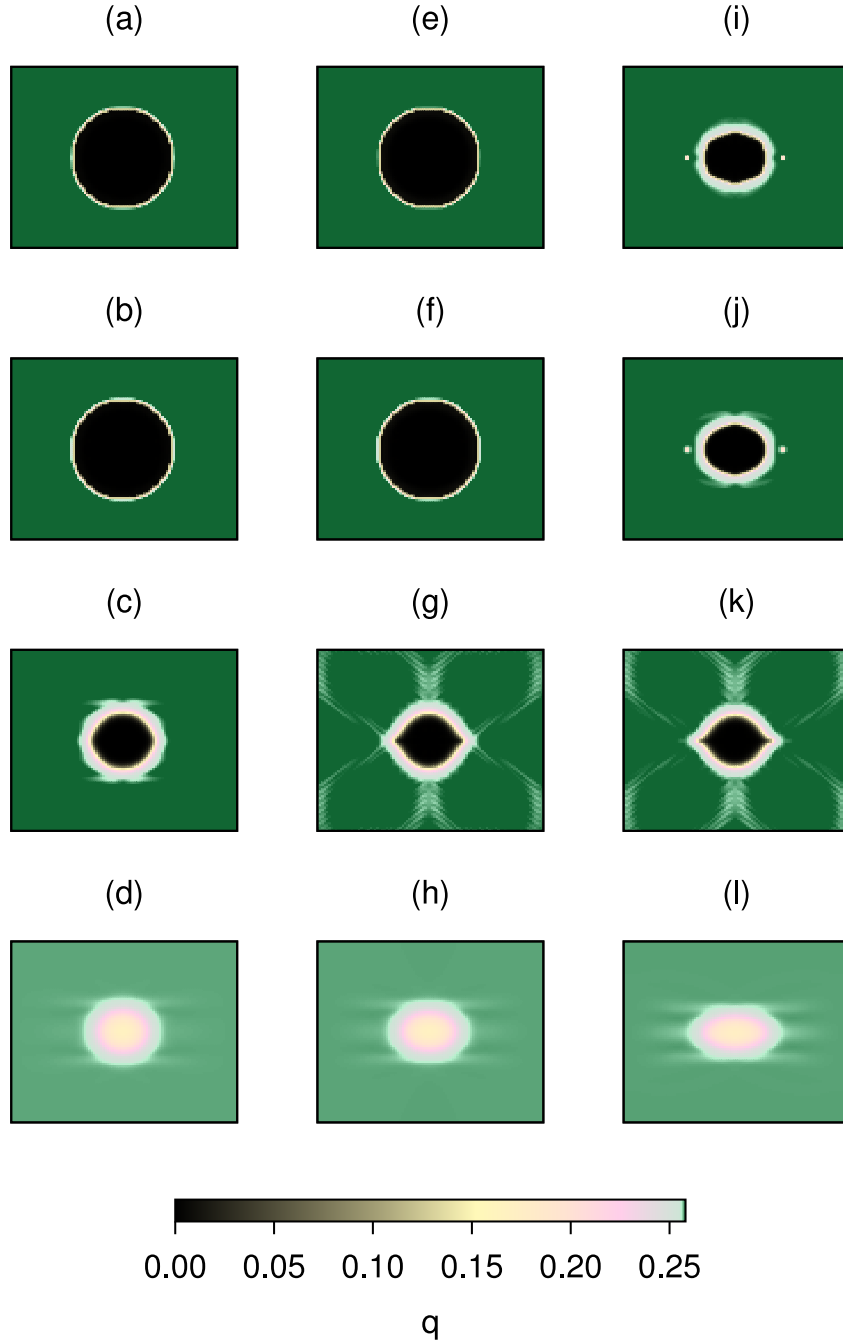


Figure 3.3: Equilibrium profiles of the scalar order parameter q of a drop of isotropic phase in a nematic host. The first column refers to $|W/K| = 0.4$, the second column to $|W/K| = 0.8$ while the last column to $|W/K| = 1.33$. The four panels of each column refer to four different values of the elastic constant L_1 . More precisely we have: (a) $L_1 = 10^{-4}$, $W = -0.04$; (b) $L_1 = 10^{-3}$, $W = -0.04$; (c) $L_1 = 10^{-2}$, $W = -0.04$; (d) $L_1 = 10^{-1}$, $W = -0.04$; (e) $L_1 = 10^{-4}$, $W = -0.08$; (f) $L_1 = 10^{-3}$, $W = -0.08$; (g) $L_1 = 10^{-2}$, $W = -0.08$; (h) $L_1 = 10^{-1}$, $W = -0.08$; (i) $L_1 = 10^{-4}$, $W = -0.133$; (j) $L_1 = 10^{-3}$, $W = -0.133$; (k) $L_1 = 10^{-2}$, $W = -0.133$; (l) $L_1 = 10^{-1}$, $W = -0.133$. See Eqs. (1.16), (1.22). The plots are taken over a box of size $1 \leq y \leq 100 \times 11 \leq z \leq 90$ centred around the drop.

	$W = -0.04$	$W = -0.08$	$W = -0.133$
$L_1=0.0001$	1.003 (*)	1.003 (*)	1.165
$L_1=0.001$	1.006 (*)	1.017 (*)	1.178
$L_1=0.01$	1.086	1.138	1.217
$L_1=0.1$	1.143	1.325	1.714

Table 3.1: Values of the aspect ratio a/b , where a and b are, respectively, the major and the minor semi-axes, for two-dimensional droplets in a nematic matrix, at rest. The values marked with (*) correspond to shapes where the major axis is parallel to z , whereas, normally, the major axis is parallel to y . However, considering their errors, the values marked with (*) are quite compatible with 1: we can consider these shapes as circular.

vicinity of the interface) and the droplet assumes a shape which resembles a rugby ball, with a bulge at each side of the major axis. I can argue, since the director field is parallel to z at the beginning, it should be perpendicular to the interface and its mobility is comparable to the mobility of the interface ($|W|/K = 0.8$), that the droplet tends slightly to extend perpendicularly to the initial direction of $\hat{\mathbf{n}}$ in order to favour its alignment.

This effect is more pronounced when $|W|/K = 1.33$ (Fig. 3.3k). The contraction of the droplet along z increases (the aspect ratio a/b decreases) when L_1 assumes the highest value (last row of Table 3.1).

With high anchoring coefficient $W = -0.133$, but low elastic constant ($L_1 = 10^{-3}$ or 10^{-4}), the interface must not deform too much (Fig. 3.3, panels i, j): we will see that this configurations implies two disclination lines of topological charge $s = -1/2$, corresponding to the bright points flanking the drop.

We can compare in a more quantitative way the shapes assumed by the drops that, as said at the beginning of Sec. 3.3, we approximate to be elliptical. In particular, we can compare their aspect ratio a/b , listed in Table 3.1, with the ones predicted by the theoretical study of Lishchuk and Care [100]. In their work, Lishchuk and Care discussed a very similar situation, although the model considered is much simpler than ours. In particular, they considered a uniform nematic director field at large distances from the drop (negligible elastic energy); the interface energy is assumed uniform across the drop surface; and the coupling between the director field and the interface is modeled by the simple Rapini-Papoular phenomenological formula [24]: if,

at the surface element $d\Sigma$, the angle between $\hat{\mathbf{n}}$ and the surface normal is α , we have $F_i = -\frac{W}{2} \int \sin^2 \alpha d\Sigma$, where the minus sign is put for consistency with (1.22) (homeotropic anchoring favoured by $W < 0$; note, however, that W has a different dimensionality than in (1.22)).

Their model predicts a drop with smooth edges if $F_{ai}/F_i \leq 2$, sharp edges (lens-shaped) otherwise.

From Fig. 3.4, we see that these simulations never yielded a ratio $F_{ai}/F_i > 2$, so the approximation of the droplet shape as an ellipse is acceptable: moreover, the axes of the approximating ellipse are very close to the axes calculated “manually”, i. e. intersecting the boundary with a horizontal and vertical line passing through the drop centre (cf. Sec. 3.3.2) and taking the distance between the two intersections.

The aspect ratio predicted by Lishchuk and Care is given by the following function:

$$A_{\text{LC}} = \begin{cases} 1 + \frac{F_{ai}}{2F_i} & \text{if } 0 \leq \frac{F_{ai}}{F_i} \leq 2 \\ 2\sqrt{\frac{F_{ai}}{2F_i}} & \text{if } \frac{F_{ai}}{F_i} > 2 \end{cases} \quad (3.10)$$

and in Fig. 3.4 we find a comparison between their prediction and my results.

The aspect ratios of the simulated drops are not so far from the expected values, except for $L_1 = 0.1$. This is not surprising, since Lishchuk and Care neglected the elastic free energy [100]: the largest deviations from their model occur for the largest value of the elastic constant, precisely. Anyway, one of the other assumptions made by the authors was a large extrapolation length,³ compared to the size of the droplet, and this assumption is not valid at all in my simulations: the maximum extrapolation length was $K/|W| = 2.5$, while the order of magnitude of the radii of the drops is at least 10.

3.4.2 Anchoring strength vs. elastic forces

The values of the dimensionless ratio $F_{ai}R/L_1\Sigma$, which measures the anchoring strength with respect to the elastic forces, are listed in Table 3.2. For comparison we report in the same table the corresponding ratios calculated by Sulaiman *et al.* [34] for $|W/K| = 0.4$ and $\langle W/K \rangle = 0.8$ (they did not report this quantity for $|W/K| = 1.33$). As one can see, there is a good agreement for values of the elastic constant sufficiently high ($L_1 = 0.1$ and $L_1 = 0.01$). On the other hand, for very small values of L_1 ($L_1 = 10^{-4}$) the agreement is poor even for small values of W . It is interesting to remark that

³Even if in [25] the definition is slightly different, the extrapolation length is, roughly, the distance from a wall, or from an interface, beyond which, in absence of other boundaries, the director field is uniform and not influenced by the presence of the wall.

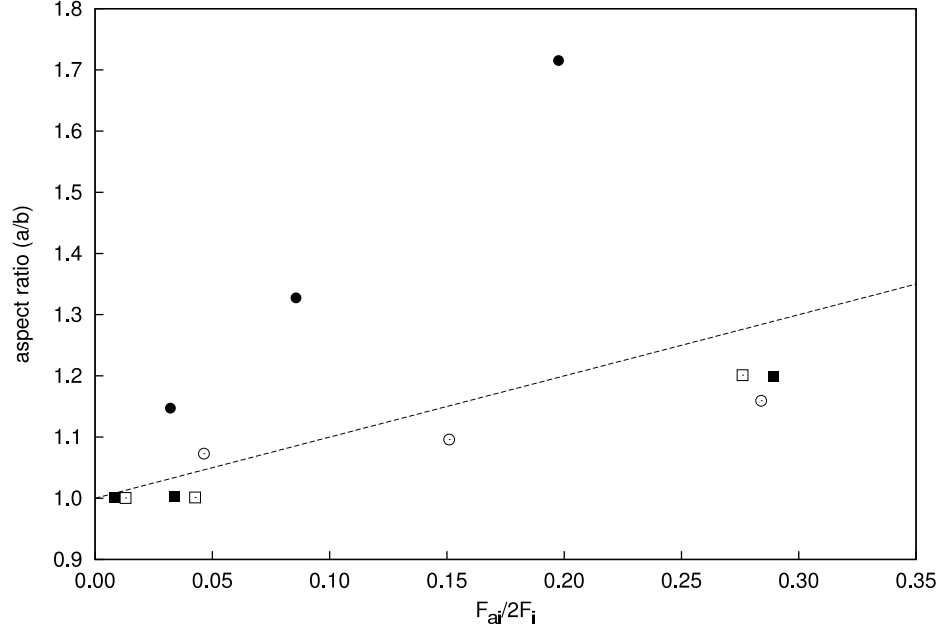


Figure 3.4: Comparison between the aspect ratio a/b of the simulated droplets ($\square$: $L_1 = 10^{-4}$, $\bullet$: $L_1 = 10^{-3}$, $\odot$: $L_1 = 10^{-2}$, $\blacksquare$: $L_1 = 10^{-1}$) and the aspect ratio predicted by Lishchuk and Care's model [100] (3.10) (dashed line).

	$W = -0.04$	$W = -0.08$	$W = -0.133$
$L_1=0.0001$	5.463 (27.1)	18.42 (68.7)	116.4
$L_1=0.001$	0.3450 (2.27)	1.426 (6.42)	12.25
$L_1=0.01$	0.1548 (0.154)	0.5475 (0.50)	1.074
$L_1=0.1$	$6.273 \cdot 10^{-3}$ ($9 \cdot 10^{-3}$)	$1.794 \cdot 10^{-2}$ ($2.6 \cdot 10^{-2}$)	$4.675 \cdot 10^{-2}$

Table 3.2: Values of the dimensionless ratio $F_{\text{ai}}R/L_1\Sigma$ for two-dimensional droplets in a nematic matrix, at rest. The values in bold-face, inside gray cells, correspond to a regime where the anchoring strength is not negligible, and which induce defects in the nematic phase. The values in light gray cells correspond to a regime where the “bulges” flanking the droplet are present. In brackets, for $W = -0.04$ and $W = -0.08$, the values calculated in [34] for droplets of radius 60, in a supercell $1 \times 200 \times 200$.

the values of ratio $F_{ai}R/L_1\Sigma$ considered in our simulations are well inside the range of values ($10^{-2} - 10^3$) that can be achieved experimentally. In Table 3.2 the values of $F_{ai}R/L_1\Sigma \gg 1$ have been highlighted in boldface, these values should correspond to the strong anchoring regime.

3.4.3 Profiles of $\hat{n}$ and of q . Defects

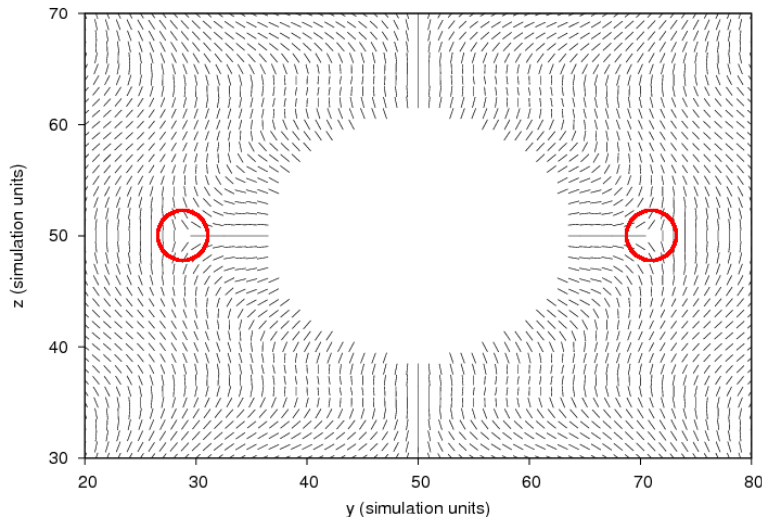


Figure 3.5: Director field of the nematic hosting an isotropic droplet, with interface anchoring coefficient $W = -0.133$ (1.22) and elastic constant $L_1 = 0.001$ (1.16). The circles are drawn around the defects, whose topological charge is $s = -1/2$ (Sec. 1.6).

Differently from isotropic emulsions, the viscoelastical properties of nematic emulsions come essentially from the elastic distorsion of the nematic phase and in particular on the presence of defects that interfere both with the flow field and with the shape of the droplet. In this respect an inspection of the director field profile and a localization of possible defects is crucial to understand the shape and rheological properties of the inverted nematic emulsion we are studying.

In our model, there is a clear competition between the anchoring energy of the director field at the interface of the drop, parametrized by W , and the bulk distorsion energy parametrized by L_1 . As said before, this competition can be quantified by the dimensionless ratio $F_{ai}R/L_1\Sigma$.

If $F_{ai}R/L_1\Sigma < 1$, the system is in the weak anchoring regime where the bulk distorsion energy dominates over the anchoring one and no distorsion is

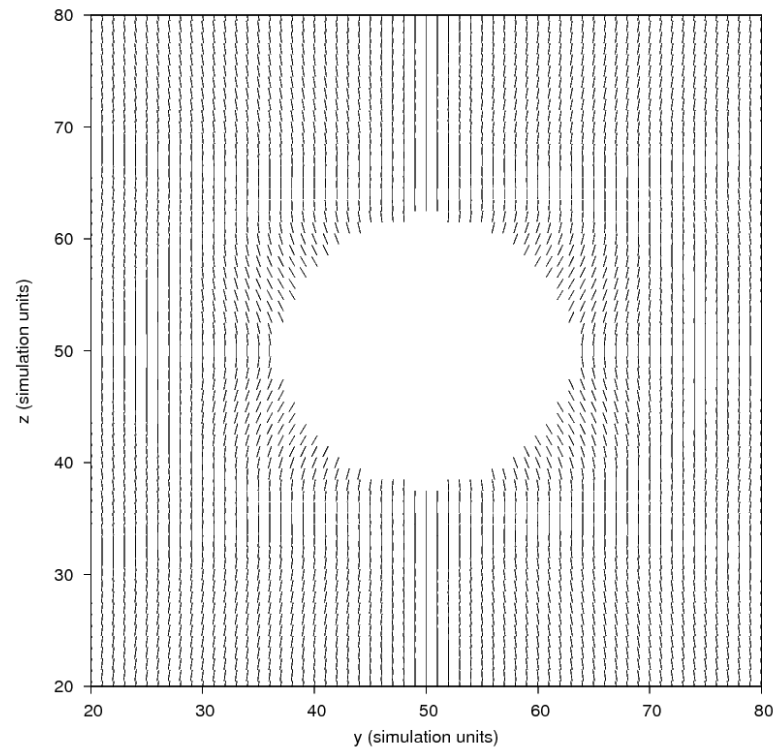


Figure 3.6: Director field of the nematic hosting an isotropic droplet, with interface anchoring coefficient $W = -0.04$ (1.22) and elastic constant $L_1 = 0.01$ (1.16).

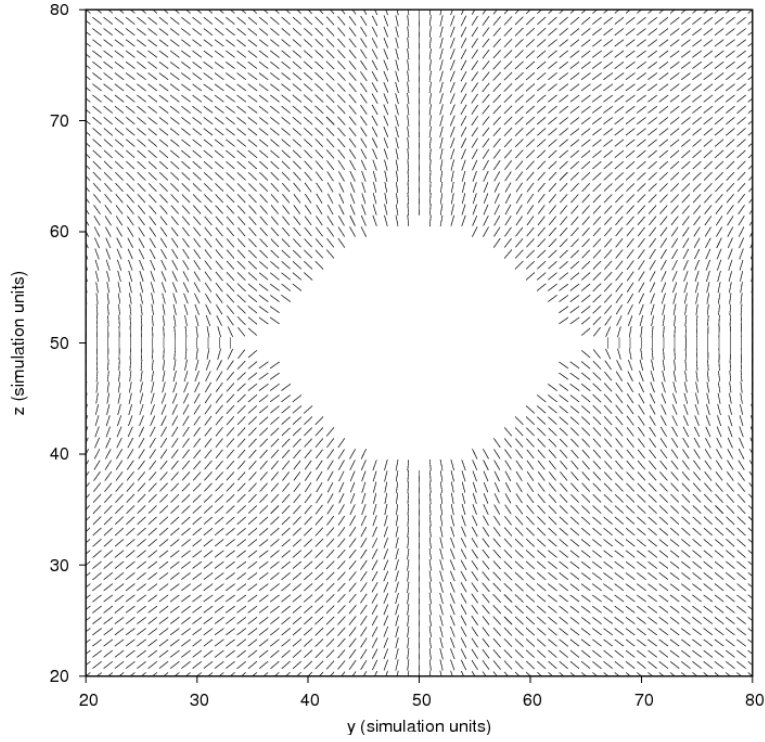


Figure 3.7: Director field of the nematic hosting an isotropic droplet, with interface anchoring coefficient $W = -0.04$ (1.22) and elastic constant $L_1 = 0.01$ (1.16).

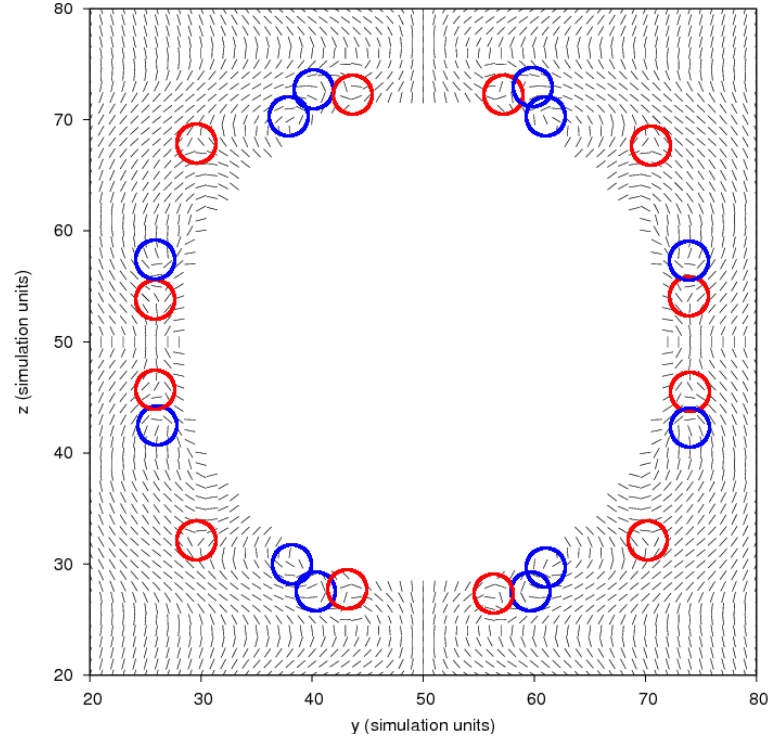


Figure 3.8: Director field of the nematic hosting an isotropic droplet, with interface anchoring coefficient $W = -0.04$ (1.22) and elastic constant $L_1 = 0.0001$ (1.16). The circles are drawn around the defects: blue when their topological charge $s = +1/2$, red when their topological charge $s = -1/2$ (Sec. 1.6). Note that the total topological charge of the marked defects is 0, and circumnavigating the interface, the director does not change, so the total topological charge of the system is 0, as required by the boundary conditions.

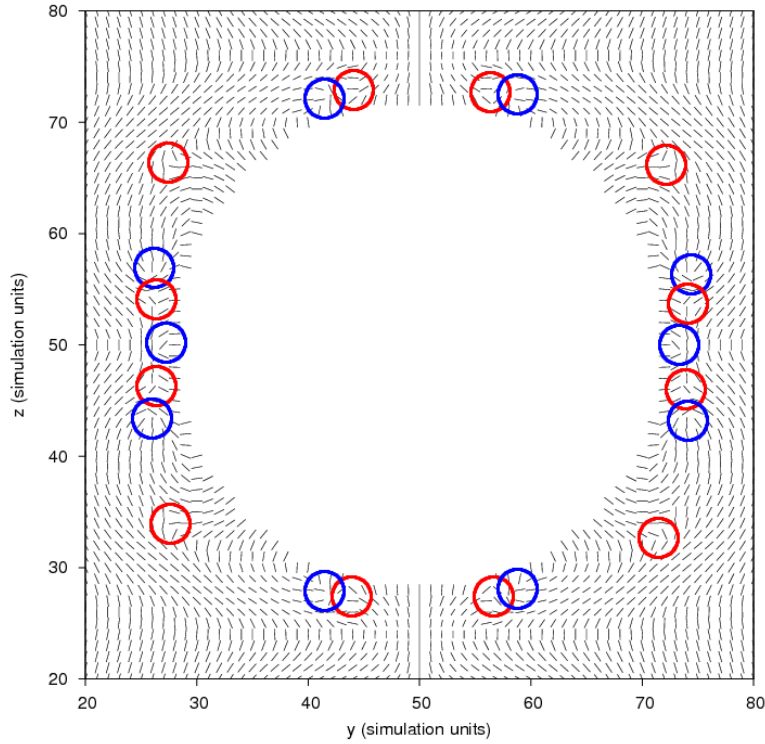


Figure 3.9: Director field of the nematic hosting an isotropic droplet, with interface anchoring coefficient $W = -0.08$ (1.22) and elastic constant $L_1 = 0.0001$ (1.16). The circles are drawn around the defects: blue when their topological charge $s = +1/2$, red when their topological charge $s = -1/2$ (Sec. 1.6). Note that the total topological charge of the marked defects is -1, and circumnavigating the interface clockwise, the director winds clockwise, too, so the total topological charge of the system is 0, as required by the boundary conditions..

observed either in the nematic phase or at the interface. This is for example the case for $L_1 = 0.1$, for any values of W considered as shown in Table 3.2. Indeed, in this case, the director field does not deform around the drop but it stays oriented tangentially to the drop at the equator.⁴ In the opposite case of strong anchoring, such as the combinations $L_1 = 10^{-3}$, $W = -0.133$ ($F_{ai}R/L_1\Sigma = 12.25$), or $L_1 = 10^{-4}$, $W = -0.133$ ($F_{ai}R/L_1\Sigma = 116.4$) the surface energy dominates over the bulk elastic energy and the director field is well anchored perpendicularly at the interface drop. In this case the drop is similar to a colloid in a nematic, i. e. it becomes a core of a defect whose topological charge is $+1$ (Sec. 1.6).

The conservation of the topological charge (see Sec. 1.6.2), since the total topological charge must be 0 (no defects at the beginning of the simulation), yields the formation of two defects of strength $-1/2$ that, for these values of the parameters, are well separated from the drop surface and positioned at opposite poles of the drop. The situation corresponds to a Saturn ring defect in 3D (see Sec. 1.7.1). and can be readily seen, for example, in the profile of the director field $\hat{\mathbf{n}}$ shown in Fig. 3.5, where the point defects are highlighted by two red circles.

The increase of the anchoring energy (at L_1 fixed) should move the defects further away from the drop.

If, on the other hand, the bulk elastic constant is very small ($L_1 = 10^{-4}$), the isotropic drop grows and the periodic boundary conditions produce an effective interaction between drops in contiguous supercells, giving rise to multiple defects. It is interesting to notice that, when $W = -0.04$, the defects are arranged in pairs of opposite topological charges ($s = \pm 1/2$), giving a total charge of zero (Fig. 3.8), and if one circumnavigates the interface, he does not detect any rotation of the director. Increasing the interface anchoring coefficient ($W = -0.08$, Fig. 3.9), instead, the sum of the topological charges of the defects gives -1 , and circumnavigating the interface the director rotates in a prograde motion ($s = +1$): the topological charge of the whole system is still 0.

The other combinations of W and L_1 correspond to intermediate cases, in which the anchoring surface strength is not sufficiently big with respect to the bulk elastic energy to force the director to be completely aligned perpendicularly to the interface (see Fig. 3.6 for the case $F_{ai}R/L_1\Sigma = 0.1548$). In this situation the defect charge of the drop, if computed at the interface,

⁴The case $L_1 = 0.1$, is almost special. Apparently, the interface fills the whole region of the bubble. Actually, the values of the nematic volume fraction ϕ inside and outside the line of maximum gradient of q are not dissimilar from the ones usually found in these simulations: nevertheless, it seems that such strong elastic forces yield an ordering even in the isotropic phase, like a shear flow [102].

is zero, and the situation can be described in terms of the presence of two $s = -1/2$ imaginary defects *inside* the drop [108].

If we slightly increase $F_{ai}R/L_1\Sigma$ up to the value 1.074, the two imaginary defects reach the drop surface at the equator and the resulting strong elastic deformation gives rise to the rugby like shape (“bulges” at the poles) previously discussed (see Fig. 3.7).

Chapter 4

Two-dimensional droplets under shear stress

After having looked at the equilibrium shape conformations of two-dimensional isotropic drops inside a nematic matrix, we now turn our attention on the effects that an imposed external flow may have on the system. We will focus on four typical combinations of the interface anchoring coefficient W (1.22) and bulk elastic constant L_1 (1.16) that were showing different behaviour at equilibrium (Chapter 3):

- $W = -0.04$, $L_1 = 0.01$ (Sec. 4.2, page 74): in this case $F_{ai}R/L_1\Sigma < 1$ and $|W|/K = 0.4$. The equilibrium configuration does not display defects, either imaginary (i. e. inside the drop) or real (i. e. two defects of charge $s = -1/2$) (Figs. 3.3c, 3.6). In this case we can anticipate that the drop under shear behaves qualitatively as a typical drop in a viscoelastic fluid, for sufficiently small values of the shear rate, while it presents some peculiarities for high shear rate, like the non-monotonic behaviour (as a function of the capillary number) of the tilt angle;
- $W = -0.133$, $L_1 = 0.001$ (Sec. 4.3, page 82): in this case $F_{ai}R/L_1\Sigma \gg 1$ and $|W|/K = 1.33$. The equilibrium configuration presents two real (i. e. out of the isotropic region) defects of charge $s = -1/2$ (Figs. 3.3j, 3.5). We will see that the presence of these defects will bring some instabilities in the system (for some values of the shear rate) due to their motion;
- $W = -0.133$, $L_1 = 0.01$ (Sec. 4.4, page 82): here $F_{ai}R/L_1\Sigma \approx 1$ and $|W|/K = 1.33$ and the equilibrium drop shows defects that are located at the interface, giving rise to a rugby ball-like shape with two

“bulges” (Figs. 3.3k, 3.7). As in the previous case, some instabilities are observed for some values of the shear rate; these are due to the imaginary defects that, under shear, move out of the drop becoming real defects;

- $W = -0.08$, $L_1 = 0.001$ (Sec. 4.5, page 92): here $F_{ai}R/L_1\Sigma \approx 1$ and $|W|/K = 0.8$ and the equilibrium drop, apparently, does not show any defect (Fig. 3.3f). Actually, we will see that two imaginary defects are present, although well inside the drop: as for the previous case, under shear, these defects move out of the drop yielding configurations with real defects.

4.1 Parameters of the system and measured quantities

To simulate the inverted nematic emulsion under shear, we sandwiched the system between two parallel walls, located at $z = 1$ and $z = 100$, to which the nematic is anchored homeotropically; on the other hand, along the x and y directions, periodic boundary conditions are imposed. As far as the velocity field is concerned, no-slip bounce-back conditions are set at the walls.

The shear flow is imposed by moving the walls in the opposite directions along the y axis (page 46). More precisely, the upper wall moves along y with velocity $v > 0$ while the lower wall moves along the same axis in the opposite direction (velocity $-v$) The shear rate is then $\dot{\gamma} = 2v/N_z = v/50$, in simulation units.

For low values of the shear rate, the initial configuration was the same as for the unsheared systems: a circular drop, of radius 22, of isotropic LC (initial $\phi_{\text{iso}} = 0.295$), surrounded by nematic (initial $\phi_{\text{nem}} = 0.745$), located at the centre of the supercell, with a step function interface. We can picture this situation as an isotropic drop injected into the rheometer simultaneously with the shear flow starting.

For high values of the shear rate, instead, searching for its maximum allowed value (Sec. 4.2.2), I increased progressively the shear rate, starting each simulation from the final configuration of the previous one.

Knowing the imposed shear rate, the radius of the droplet at rest ¹, the surface tension $\sigma = F_i/\Sigma$ (3.2) and the bulk viscosity η_V (page 39), one can

¹ R is taken as the geometric mean of the two semiaxes of the approximating ellipse: $R = \sqrt{ab}$ (Sec. 3.4)

define the dimensionless **capillary number**:

$$\text{Ca} = \frac{R\dot{\gamma}\eta_V\Sigma}{F_i}. \quad (4.1)$$

This number, that is often used in experiments of droplets under shear, relates the fluid viscosity to the interfacial forces. The range of the capillary numbers throughout these simulations is $\approx 0.1 \div 12$.

It is also interesting to notice that the maximum value of the Reynolds number

$$\text{Re} = \frac{\rho\dot{\gamma}R^2}{\eta_V} \quad (4.2)$$

achieved in our simulations is ≈ 0.17 ; in this respect our simulations operate in the Stokes regime ($\text{Re} \ll 1$) i. e. when the advective inertial forces are small compared with the viscous ones.

Being our system based on liquid crystals, besides the capillary number Ca , we should consider the two dimensionless numbers monitored in the equilibrium case: the ratio $F_{ai}R/L_1\Sigma$ (anchoring strength vs. bulk elastic forces) and the ratio $|W|/K$ (anchoring strength vs. surface tension), which have been introduced in Sec. 3.1.

If a similar investigation was carried out either for Newtonian [5] or viscoelastic [18] emulsions, one would expect that under shear the drop would deform and orient itself along the shear flow. Moreover, if the shear rate is large enough, the drop can deform widely and eventually breaks into smaller drops. Traditionally, as measure of the deformation, one takes the **Taylor deformation parameter** [2]:

$$D \equiv \frac{a-b}{a+b} \quad (4.3)$$

(a is the major semiaxis) and the **tilt angle**, α formed by the major axis with the shear direction.

In the Taylor model of drop deformation under shear, for a *small* deformation, D follows the law:

$$D = \frac{19\lambda + 16}{16\lambda + 16}\text{Ca} = (\lambda = 1) = \frac{35}{32}\text{Ca} \quad (4.4)$$

where λ is the viscosity ratio (viscosity of the matrix fluid / viscosity of the droplet fluid), which in our case is 1: within the Lattice Boltzmann scheme, $\eta_V = \rho\tau_f/3$ (Sec.), and there is no difference between an isotropic and a nematic phase, in this respect.

4.2 Small anchoring regime

4.2.1 Deformation and tilt for low shear rate

In this section, we will analyze the results of the simulations for $W = -0.04$ and $L_1 = 0.01$, corresponding to a ratio $F_{ai}R/L_1\Sigma < 1$ and $|W|/K = 0.4$.

We consider first the case of relatively small shear rates, corresponding approximately to the range of shear rates $[0, 10^{-4}]$. This is the simplest of all cases which we are going to consider: its phenomenology should be the closest to the one observed for Newtonian and/or viscoelastic emulsions.

Fig. 4.2 shows the effects of a shear rate $\dot{\gamma} = 4 \cdot 10^{-5}$ ($Ca = 1.098$, panel (b)) and $\dot{\gamma} = 10^{-4}$ ($Ca = 3.358$, panel (c)) on the shape of the isotropic drop inside the nematic matrix.

As one would expect, the droplet is stretched and tilted along the shear direction. The Taylor deformation parameter D and the tilt angle α vs. the capillary number Ca are shown in Fig. 4.3: they correspond respectively to the squares and to the diamonds symbols on the graph, from the first point on the left to the eighth point along the dashed line.²

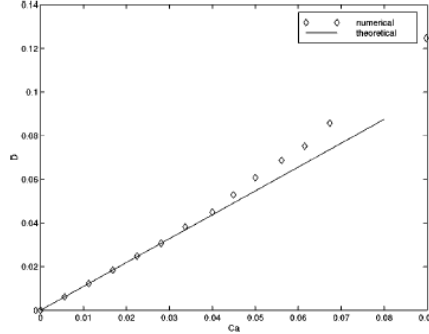


Figure 4.1: Taylor deformation parameter vs. capillary number for a Newtonian drop of initial radius equal to 10 lattice constants, in a Newtonian matrix, simulated by a Lattice Boltzmann algorithm. The diamonds represent the results of the calculations, the solid line is the theoretical Taylor result (for small deformations) for viscosity ratio = 1. Plot sourced from [112].

As expected, D increases with v (i. e. the droplet is more stretched) while α decreases with v (i. e. the droplet tends to be parallel to $\mathbf{v}$). The

²The non monotonic, or “inversion” behaviour, that occurs at the last points of the graphs (i. e. for higher shear velocities) will be discussed at the beginning of Sec. 4.2.2.

deformation D is much smaller than it would be expected, both for a Newtonian emulsion, for any viscosity ratio (4.4, Fig. 4.1), and for a viscoelastic emulsion [20, 15].

The diagram in Fig. 4.4 shows the variation of the dimensionless ratio $F_{ai}R/\Sigma L_1$, which relates the interface anchoring energy to the deformations of the bulk director. It is not surprising that this ratio falls when the shear rate $\dot{\gamma}$ increases, because the shear stress competes with the anchoring in forcing the nematic to follow different directions (respectively the one of the flow and the one perpendicular to the drop surface). The ratio can become even negative at high values of $\dot{\gamma}$, because the shear stress is so strong that overcomes the anchoring force and, therefore, the director does not orient perpendicular to the interface anywhere (see Fig. 4.5c corresponding to $\dot{\gamma} = 10^{-4}$).

4.2.2 Breakdown and “precession” at high shear rate

Looking at the curves in Figs. 4.3 and 4.4, we observe that, when the shear rate is sufficiently high, the capillary number decreases with $\dot{\gamma}$ (see captions). This is essentially due to the decrease of the drop radius $R = \sqrt{ab}$ (4.1) (Fig. 4.2d).

When the shear rate increases, the droplet becomes smaller and smaller until there is a value of $\dot{\gamma}$ above which the system does not reach a stationary state anymore and the phase coexistence of the isotropic droplet with the surrounding nematic disappears. In fact, during a simulation with a too high shear rate, the droplet keeps shrinking until eventually disappears, replaced entirely by the nematic phase.

This feature concerns all the combinations of interface anchoring coefficient and bulk elastic constants, with the only exception of $W = -0.04$, $L_1 = 0.001$, where the droplet, at very high shear, deforms into a stripe which crosses the supercell. Sometimes, the disappearance of the isotropic phase is preceded by a break-up of the droplet, a phenomenon which was widely investigated both for Newtonian [4, 5, 14] and for viscoelastic fluids [17].

In this respect, it is interesting to look at the time evolution of the free energy (see Fig. 4.6). Typically, when the droplet is about to vanish, the slope of the free energy vs. time curve is positive and increases, instead than approaching 0: simultaneously with the disappearance of the isotropic phase, there is a sudden fall of the total free energy F (Fig. 4.6), due to the vanishing both of the interface anchoring energy and of the interface energy (surface tension).

Moreover, as we can see for all the examined cases (Figs. 4.3, 4.10, 4.17,

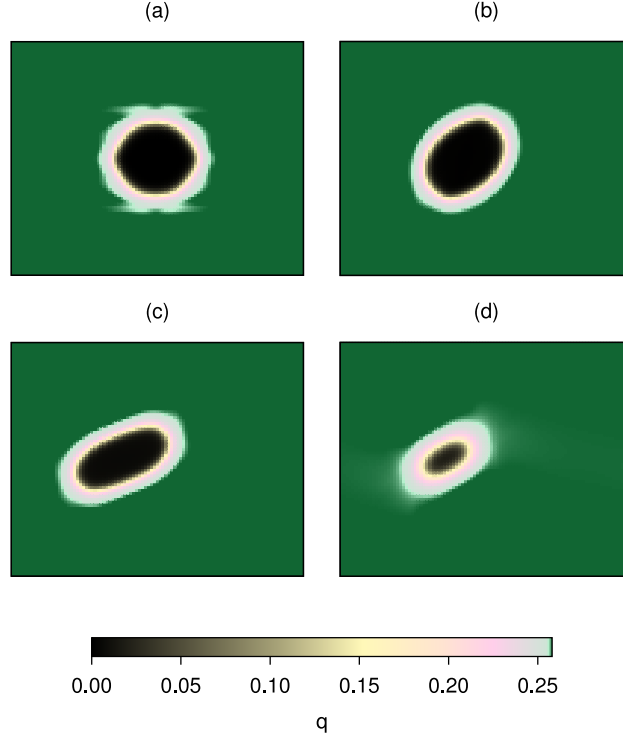


Figure 4.2: Profiles of the scalar order parameter q of an isotropic droplet in a nematic host, with interface anchoring vs. surface energy coefficients ratio $|W|/K = 0.4$ and bulk elastic constant $L_1 = 0.01$ (Eqs. (1.22), (1.19), (1.16)) (a) at equilibrium; (b) under a shear rate $\dot{\gamma} = 4 \cdot 10^{-5}$ ($\text{Ca} = 1.098$); (c) under a shear rate $\dot{\gamma} = 10^{-4}$ ($\text{Ca} = 3.358$); (d) under a shear rate $1.8 \cdot 10^{-4}$ ($\text{Ca} = 5.059$). The plots are taken over a box of size $1 \leq y \leq 100 \times 11 \leq z \leq 90$.

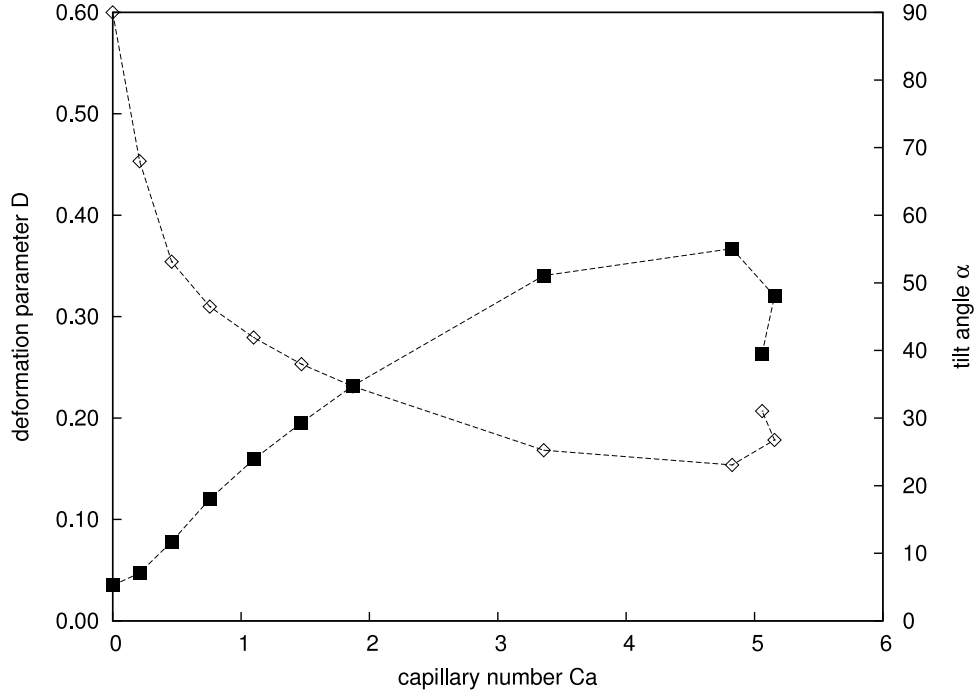


Figure 4.3: Taylor deformation parameter D (squares, left-hand vertical scale) and tilt angle α (diamonds, right-hand vertical scale), as a function of the capillary number of an isotropic droplet under shear flow, in a nematic host with interface anchoring vs. surface energy coefficients ratio $|W|/K = 0.4$ and bulk elastic constant $L_1 = 0.01$ (Eqs. (1.22), (1.19), (1.16)). Along the dashed lines, starting from the points lying on the left-hand vertical axis ($Ca = 0 \Leftrightarrow \dot{\gamma} = 0$), the points are ordered by increasing shear rate.

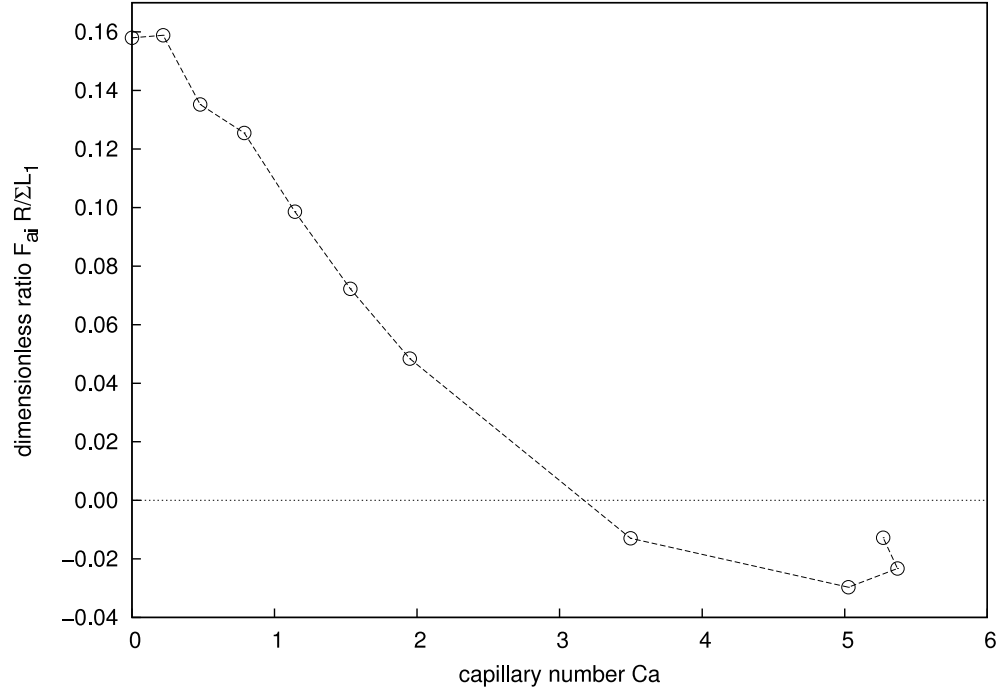


Figure 4.4: Dimensionless ratio $F_{ai}R/\Sigma L_1$, as a function of the capillary number of the flowing system, of an isotropic droplet under shear flow, in a nematic host with interface anchoring vs. surface energy coefficients ratio $|W|/K = 0.4$ and bulk elastic constant $L_1 = 0.01$ (Eqs. (1.22), (1.19), (1.16)). Along the dashed lines, starting from the points lying on the left-hand vertical axis ($Ca = 0 \Leftrightarrow \dot{\gamma} = 0$, the points are ordered by increasing shear rate.

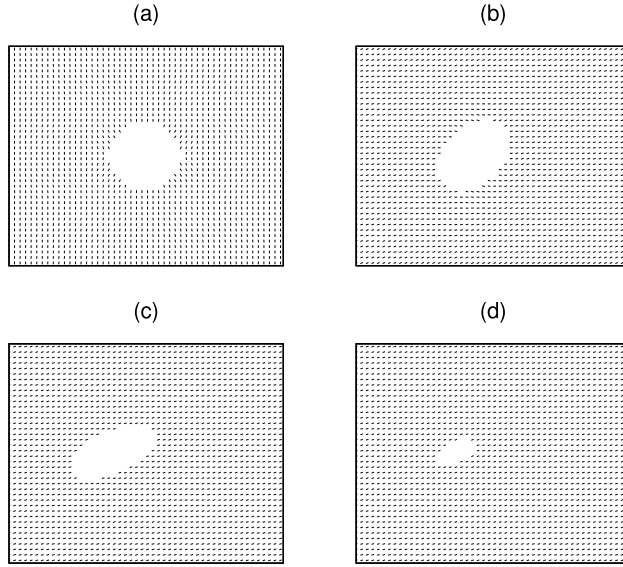


Figure 4.5: Profiles of the director field of the nematic hosting an isotropic droplet in a nematic host, with interface anchoring vs. surface energy coefficients ratio $|W|/K = 0.4$ and bulk elastic constant $L_1 = 0.01$ (Eqs. (1.22), (1.19), (1.16)) (a) at equilibrium; (b) under a shear rate $\dot{\gamma} = 4 \cdot 10^{-5}$ ($\text{Ca} = 1.098$); (c) under a shear rate $\dot{\gamma} = 10^{-4}$ ($\text{Ca} = 3.358$); (d) under a shear rate $1.8 \cdot 10^{-4}$ ($\text{Ca} = 5.059$). The plots are taken over a box of size $1 \leq y \leq 100 \times 11 \leq z \leq 90$.

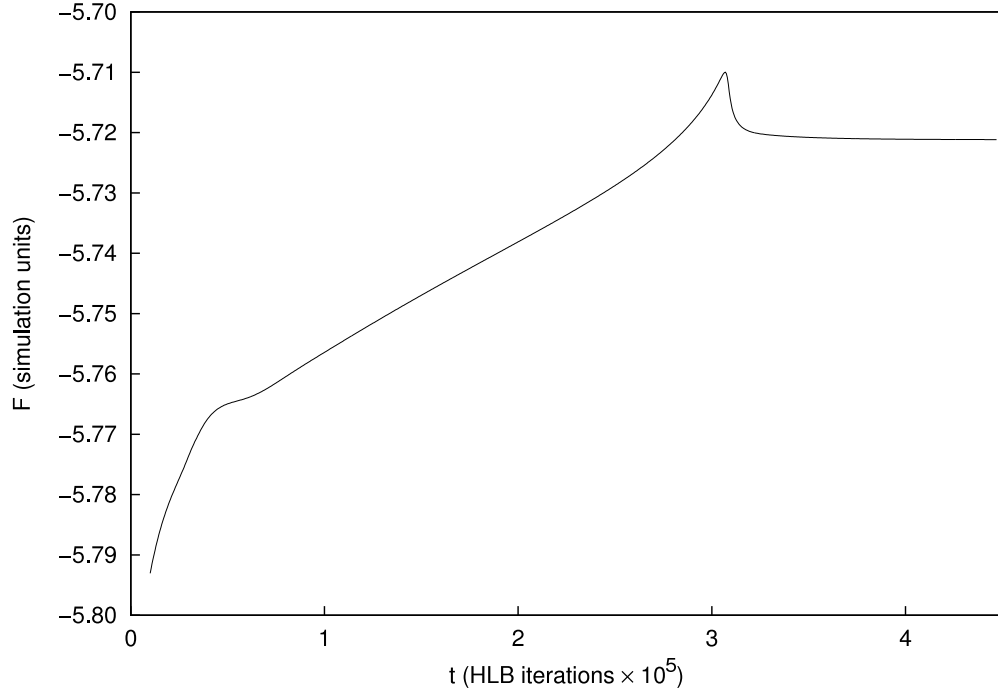


Figure 4.6: Time evolution of the free energy of a nematic-isotropic emulsion inside a $(1 \times 100 \times 100)$ simulation box, with interface anchoring vs. surface energy coefficients ratio $|W|/K = 0.4$, bulk elastic constant $L_1 = 0.01$ (Eqs. (1.22), (1.19), (1.16)), and shear rate $\dot{\gamma} = 2 \cdot 10^{-4}$ (higher than the breakdown value). The peak at $t = 3.07 \cdot 10^5$ (simulation units) and the subsequent decrease in the free energy, is the sign of the breakdown.

	$W = -0.04$	$W = -0.08$	$W = -0.133$
$L_1 = 0.001$	—	$2.60 \div 2.70 \cdot 10^{-4}$	$3.10 \div 3.12 \cdot 10^{-4}$
$L_1 = 0.01$	$1.80 \div 1.84 \cdot 10^{-4}$	$1.88 \div 1.90 \cdot 10^{-4}$	$2.4 \div 2.6 \cdot 10^{-4}$
$L_1 = 0.1$	$1.40 \div 1.44 \cdot 10^{-4}$	$1.52 \div 1.56 \cdot 10^{-4}$	$1.8 \div 1.9 \cdot 10^{-4}$

Table 4.1: Breakdown shear rates (in simulation units) for two-dimensional droplets under shear: i. e. the smallest shear rates at which the droplets disappear.

4.20), the configurations where the shear rate is just below the maximum allowed value $\dot{\gamma}_{\max}$ show an increase, rather than a decrease, of the tilt angle. We call this non-monotonic behaviour of α as (“drop precession”).

Comparing the thickness of the region of $q > 0$ for the high-shear rate configuration (Fig. 4.2d) with the one at rest, or at low shear rate (Fig. 4.2a, b, c), one can observe that this region is thicker in the former case. Shear-induced isotropic-nematic transition benefits of an abundant literature, both theoretical and experimental [109, 110, 111]. The shear stress induces an order in an isotropic LC, i. e. an increase in the scalar order parameter q , which normally would be 0. If q becomes comparable to the nematic value, the isotropic merges with the surrounding nematic becoming, in fact, nematic. If the shear rate is below the maximum allowed value $\dot{\gamma}_{\max}$, this phenomenon involves only the external region of the drop, making it become smaller; if we are above $\dot{\gamma}_{\max}$, it involves the whole drop, leading to its disappearance.

In Table 4.1 we report the values of $\dot{\gamma}_{\max}$ for each combination of W and L_1 considered. We have got only an upper and a lower bound of $\dot{\gamma}_{\max}$, because I estimated it by trying different values and seeing if the system maintains the nematic-isotropic coexistence or not. The procedure is similar to the one usually adopted to find a root of an equation via the bisection algorithm.

Note also that $\dot{\gamma}_{\max}$ is smaller when either the nematic anchoring at the interface is weaker or the elastic constant is bigger. The dependence on L_1 could be explained by observing that, at $\dot{\gamma} = 0$ already, the scalar order parameter at the centre of the droplet deviates from 0 to a larger extent when L_1 is higher.

On a consequence, when L_1 is high, the droplet should not need a strong shear stress in order to merge with the nematic phase.

4.3 $|W|/K = 1.33$, $L_1 = 10^{-3}$: oscillating, non-periodic states

For these values of the parameters W and L_1 , we have $F_{ai}R/L_1\Sigma \gg 1$ and $|W|/K = 1.33$: at equilibrium, the system is in the strong anchoring regime and the anchoring strength dominates over both the elastic bulk deformation energy and the surface tension.

The two defects of charge $s = -1/2$ that are present at equilibrium (Fig. 3.5) move across the cell under the effect of the shear stress.

The motion of the defects, the high rotation mobility of the nematic (due to its relatively low elastic constant L_1) and the interactions with the drops in the neighbouring cells (Sec. 2.7.2) lead to complicated configurations with multiple distortions, even when the shear rate is low (Fig. 4.7b, $\dot{\gamma} = 10^{-5}$).

These distortions can give rise to further defects that form, move, and die. This causes the oscillations in the free energy, plotted in Fig. 4.9.

On the contrary, when the shear rate is increased (Fig. 4.7c, $\dot{\gamma} = 5 \cdot 10^{-5}$), the configuration becomes stable: apparently, the shear stress manages to “regularize” the director field (Fig. 4.8c) along its direction.

When the shear rate rises further (Fig. 4.7d, $\dot{\gamma} = 7.5 \cdot 10^{-5}$), the defects appear again quite clearly out of the drop, and we do not find any other stable stationary state before, after reaching the critical $\dot{\gamma}_{\max}$, the droplet disappears due to the “melting” of the isotropic into the nematic (Sec. 4.2.2).

If we look, moreover, at the time evolution of the free energy, we can see that no one of the oscillating states (the bigger points in Fig. 4.10) is periodic. For some time intervals we can observe quasi-periodicity (Fig. 4.9, dotted line), but never perfect periodicity. This is due, reasonably, to the complicated geometries of the distorted configurations.

The Taylor deformation parameter and the tilt angle are, for this case, reported in Fig. 4.10

4.4 $|W|/K = 1.33$, $L_1 = 10^{-2}$: pulsating states

If we maintain the interface anchoring coefficient W (1.22) equal to 0.133, but increase the bulk elastic constant L_1 (1.16) to 0.01, we know from Chapter 3 that the equilibrium shape of the drop is very deformed, resembling a “two-dimensional rugby ball with two bulges” at its poles (Fig. 4.11a). At page 68, we have argued that this shape is due to the presence of two “imaginary defects” i. e. two defects inside the isotropic drop.

The behaviour of this system under shear flow reinforces, to a given extent, this argument.

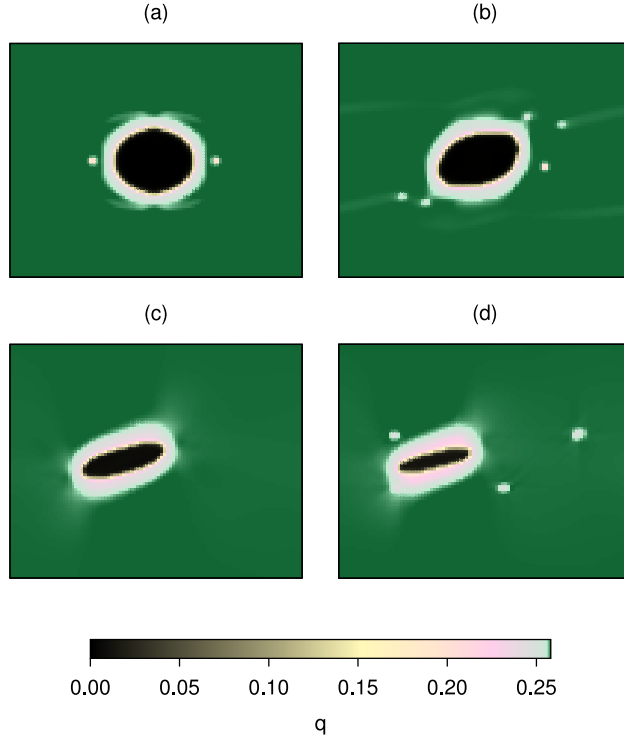


Figure 4.7: Profiles of the scalar order parameter q of an isotropic droplet in a nematic host, with interface anchoring vs. surface energy coefficients ratio $|W|/K = 1.33$ and bulk elastic constant $L_1 = 0.001$ (Eqs. (1.22), (1.19), (1.16)) (a) at equilibrium; (b) under a shear rate $\dot{\gamma} = 2 \cdot 10^{-5}$ ($\text{Ca} = 0.367$); (c) under a shear rate $\dot{\gamma} = 10^{-4}$ ($\text{Ca} = 2.010$); (d) under a shear rate $\dot{\gamma} = 1.5 \cdot 10^{-4}$ ($\text{Ca} = 3.135$). The plots are taken over a box of size $1 \leq y \leq 100 \times 11 \leq z \leq 90$. The plots at panels (a) and (c) refer to stable configurations; the plots at panels (b) and (d) are snapshots.

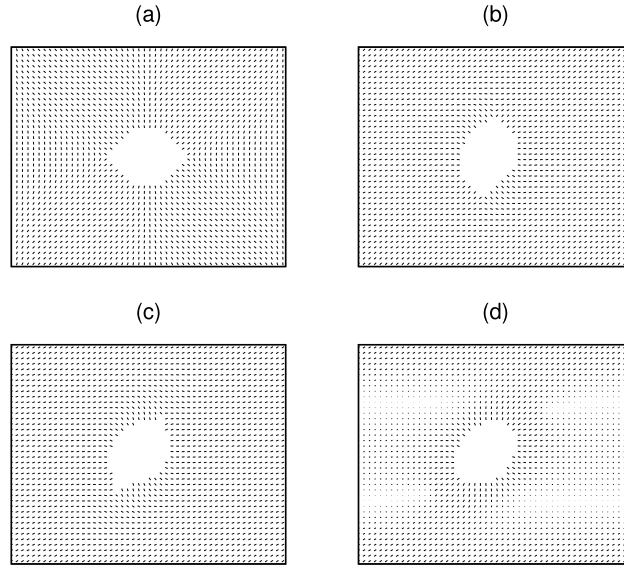


Figure 4.8: Profiles of the director field of the nematic hosting an isotropic droplet in a nematic host, with interface anchoring vs. surface energy coefficients ratio $|W|/K = 1.33$ and bulk elastic constant $L_1 = 0.001$ (Eqs. (1.22), (1.19), (1.16)) (a) at equilibrium; (b) under a shear rate $\dot{\gamma} = 2 \cdot 10^{-5}$ ($\text{Ca} = 0.367$); (c) under a shear rate $\dot{\gamma} = 10^{-4}$ ($\text{Ca} = 2.010$); (d) under a shear rate $\dot{\gamma} = 1.5 \cdot 10^{-4}$ ($\text{Ca} = 3.135$). The plots are taken over a box of size $1 \leq y \leq 100 \times 11 \leq z \leq 90$. The plots at panels (a) and (c) refer to stable configurations; the plots at panels (b) and (d) are snapshots.

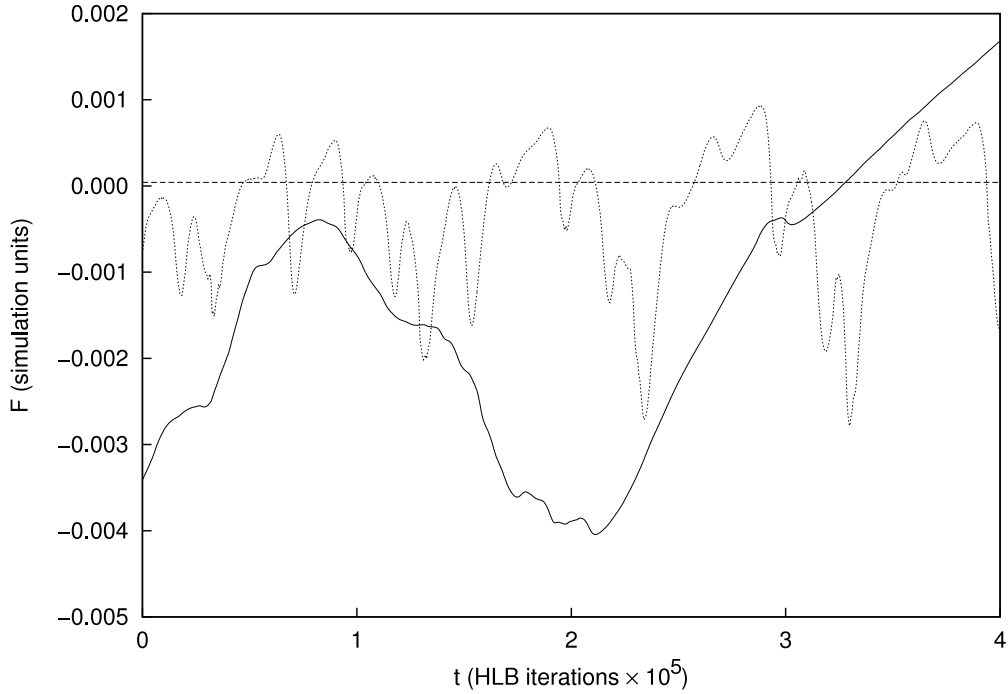


Figure 4.9: Time evolution of the free energy of a nematic-isotropic emulsion inside a $(1 \times 100 \times 100)$ simulation box, with interface anchoring vs. surface energy coefficients ratio $|W|/K = 1.33$, bulk elastic constant $L_1 = 0.001$ (Eqs. (1.22), (1.19), (1.16)), and shear rate $\dot{\gamma} = 2 \cdot 10^{-5}$ ($Ca = 0.367$, solid line), $\dot{\gamma} = 10^{-4}$ ($Ca = 2.010$, dashed line), $\dot{\gamma} = 1.8 \cdot 10^{-4}$ ($Ca = 3.135$, dotted line). All the three lines cover a time interval of $4 \cdot 10^5$ hybrid LB iterations, but the zero of the t axis is not $t = 0$: it is $t = 3 \cdot 10^5$ for the solid line and $t = 8 \cdot 10^5$ for the dashed and dotted lines. The energy scale is arbitrary, too: I had to offset the actual values because, otherwise, the oscillations in F would not be evident.

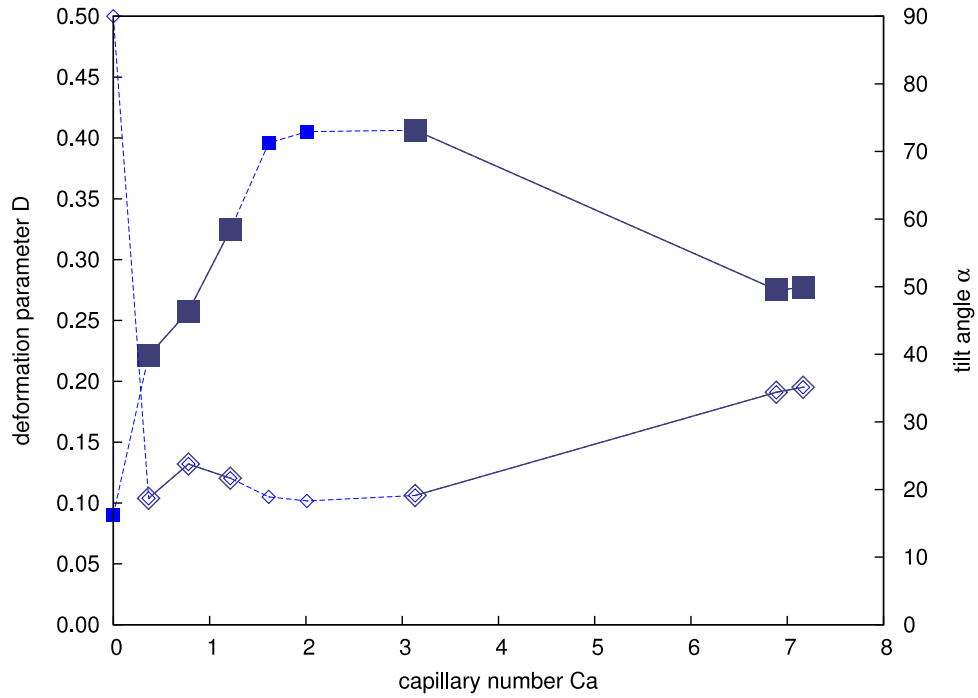


Figure 4.10: Taylor deformation parameter D (squares, left-hand vertical scale) and tilt angle α (diamonds, right-hand vertical scale), as a function of the capillary number of the flowing system, of an isotropic droplet under shear flow, in a nematic host with interface anchoring vs. surface energy coefficients ratio $|W|/K = 1.33$ and bulk elastic constant $L_1 = 0.001$ (Eqs. (1.22), (1.19), (1.16)). Along the dashed lines, starting from the points lying on the left-hand vertical axis ($Ca = 0 \Leftrightarrow \dot{\gamma} = 0$, the points are ordered by increasing shear rate. Bigger, darker points and solid lines indicate the oscillating states (see text).

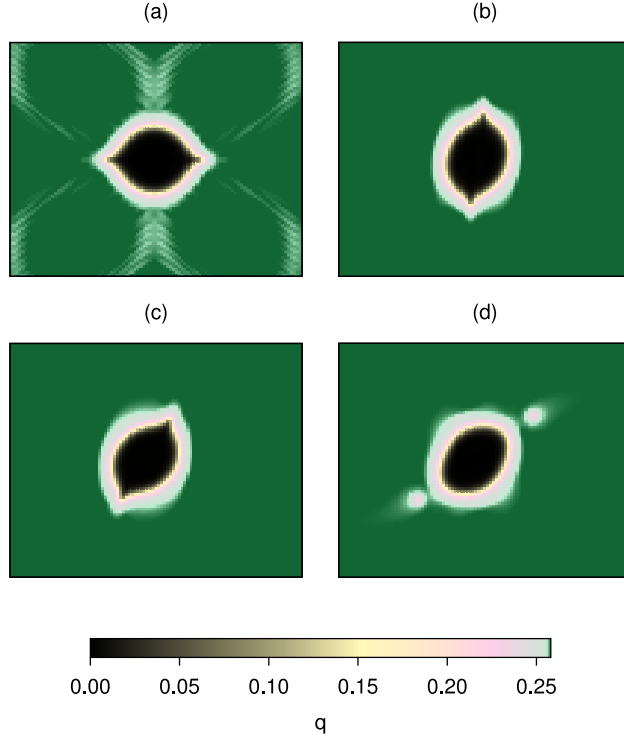


Figure 4.11: Profiles of the scalar order parameter q of an isotropic droplet in a nematic host, with interface anchoring vs. surface energy coefficients ratio $|W|/K = 1.33$ and bulk elastic constant $L_1 = 0.01$ (Eqs. (1.22), (1.19), (1.16)) (a) at equilibrium; (b) under a shear rate $\dot{\gamma} = 10^{-5}$ ($\text{Ca} = 0.042$); (c) under a shear rate $\dot{\gamma} = 2 \cdot 10^{-5}$ ($\text{Ca} = 0.396$); (d) under a shear rate $\dot{\gamma} = 2.5 \cdot 10^{-5}$ ($\text{Ca} = 0.095$: the capillary number is lower than for $\dot{\gamma} = 10^{-5}$ because of an increase in the surface tension). The plots are taken over a box of size $1 \leq y \leq 100 \times 11 \leq z \leq 90$. The plots at panels (a), (b) and (c) refer to stable configurations; the plot at panel (d) is a snapshot.

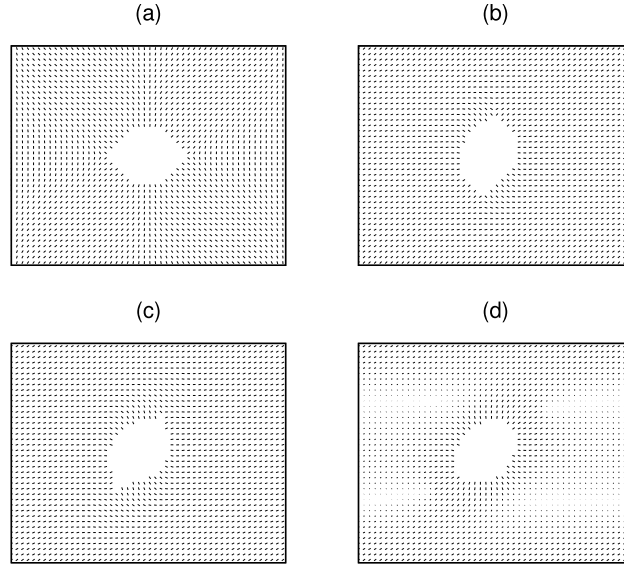


Figure 4.12: Profiles of the director field of the nematic hosting an isotropic droplet in a nematic host, with interface anchoring vs. surface energy coefficients ratio $|W|/K = 1.33$ and bulk elastic constant $L_1 = 0.01$ (Eqs. (1.22), (1.19), (1.16)) (a) at equilibrium; (b) under a shear rate $\dot{\gamma} = 10^{-5}$ ($\text{Ca} = 0.042$); (c) under a shear rate $\dot{\gamma} = 2 \cdot 10^{-5}$ ($\text{Ca} = 0.396$); (d) under a shear rate $\dot{\gamma} = 2.5 \cdot 10^{-5}$ ($\text{Ca} = 0.095$: the capillary number is lower than for $\dot{\gamma} = 10^{-5}$ because of an increase in the surface tension). The plots are taken over a box of size $1 \leq y \leq 100$ and $11 \leq z \leq 90$. The plots at panels (a), (b) and (c) refer to stable configurations; the plot at panel (d) is a snapshot.

In Figs. 4.11b and c we can see the effect of a low shear rate (respectively, $\dot{\gamma} = 10^{-5}$ and $2 \cdot 10^{-5}$) on the droplet shape: the shear induces a (clockwise) rotation of the bulges. In particular, the higher the shear rate, the wider the rotation angle.

These two values of the shear rate are too low to let the bulges (i.e. the imaginary defects) complete half a revolution (remember the symmetry of the system); but if we increase further the shear rate up to $\dot{\gamma} = 2.5 \cdot 10^{-5}$ (Fig. 4.11d), not only the bulges complete the half round, but the imaginary defects are “slung” away from the droplet, becoming real defects. It is worth noticing that, after the “leap” of the bulges, the droplet recovers an ellipsoidal shape since the excess of the elastic energy that previously was stored at the interface is now localized around the defects that lie in the bulk.

Once the defects are away from the drop, the velocity field move them far apart until they reach the image drop in the neighbouring supercell (Sec. 2.7.2). Eventually, they merge again in proximity of the interface, and the overall process just described repeats.

Note that, unlike the case described in Sec. 4.3, here the geometry of the system is much simpler (only two defects occur in the system) and the process has a (quite) perfect periodicity for any value of the shear rate $\geq 2.5 \cdot 10^{-5}$, provided it is not too high. In the latter case the strong flow field shifts the nematic-isotropic transition point and the droplet tends to disappear (Sec. 4.2.2).

Figs. 4.13 and 4.14 show a time sequence of the profile of q in the supercell covering a whole period of the process at shear rate $\dot{\gamma} = 6 \cdot 10^{-5}$ ($Ca = 0.224$):

- from panel (i) to panel (xiii) we see the bulges rotating;
- in panels (xiv) and (xv) we see the bulges leap from the interface and moving away as a pair of point defects of charge $s = -1/2$;
- in panels (xvi) to (xviii) we see them “re-enter” the supercell from the opposite side of their exit, because of periodic boundary conditions, and reach the droplet again;
- in panel (xix), the bulges have just merged with the interface;
- in panels (xx) to (xxiv), they are rotating again.

Following this picture, we can say that the droplet is undergoing a sort of oscillatory behaviour, or **pulsating state**.

Often, when there is a pulsating state the time evolution of the macroscopic quantities such as the deformation parameter and the tilt angle follows

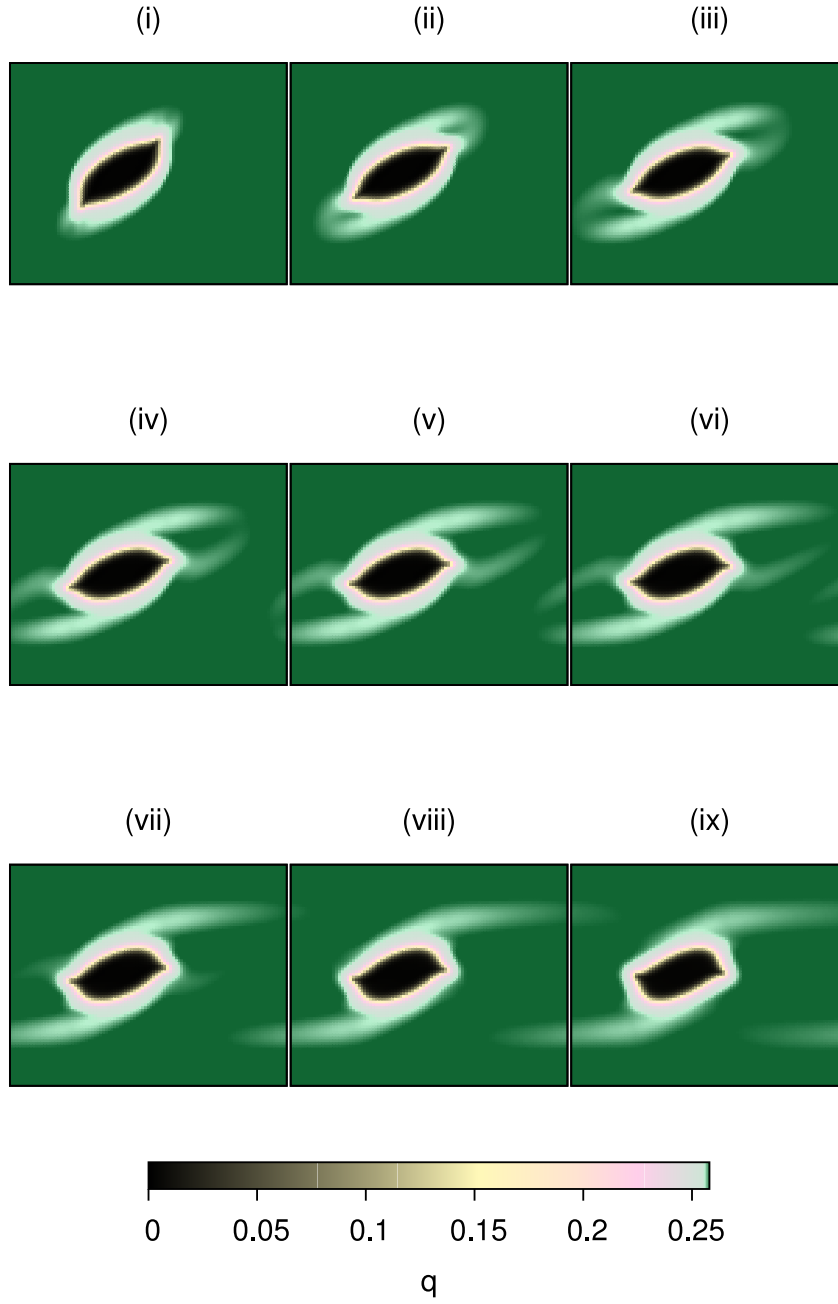


Figure 4.13: Profiles of the scalar order parameter q of an isotropic droplet in a nematic host, with interface anchoring coefficient $W = -0.133$ (1.22) and bulk elastic constant $L_1 = 0.01$ (1.16), at time intervals of 20000 HLB iterations, from (i) $t = 10^6$ to (xviii) $t = 1.16 \cdot 10^6$. The plots are taken over a box of size $1 \leq y \leq 100 \times 11 \leq z \leq 90$.

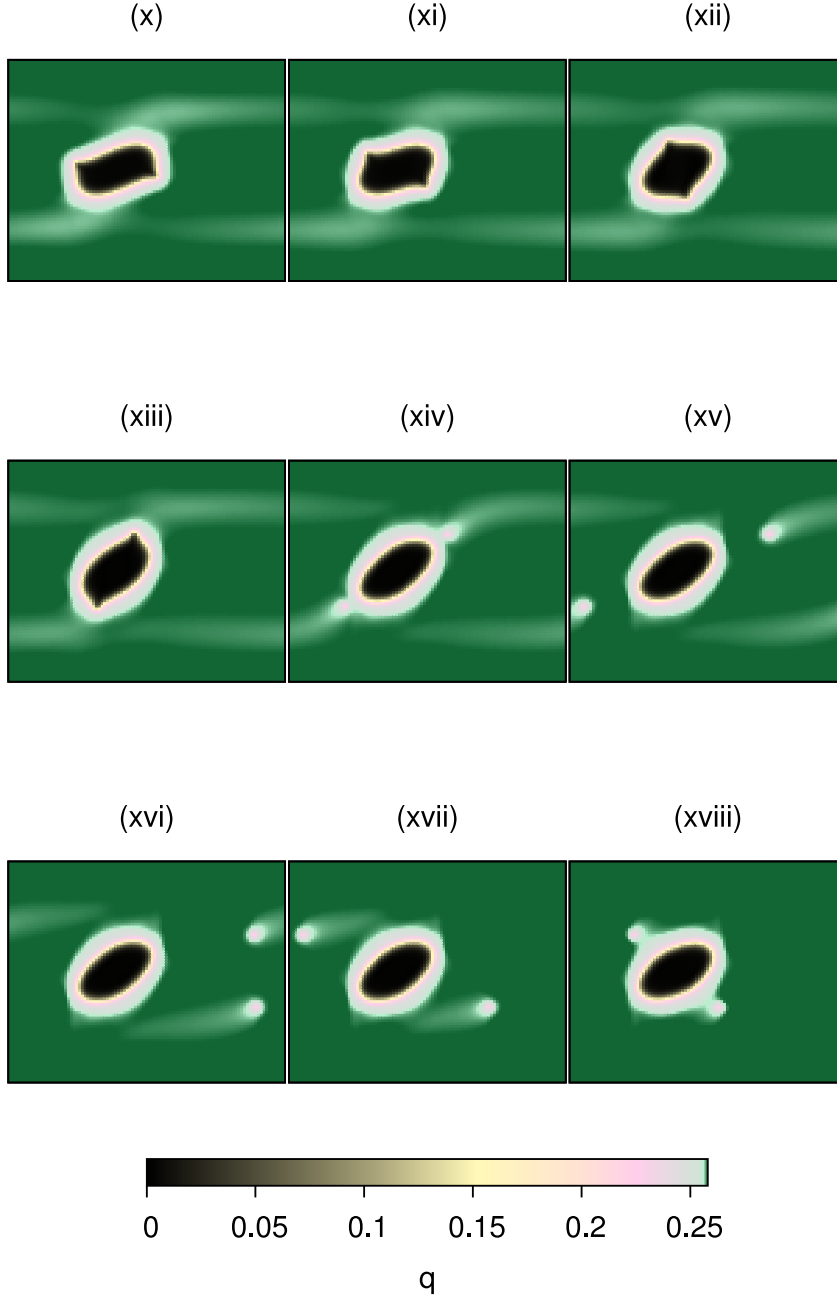


Figure 4.14: Profiles of the scalar order parameter q of an isotropic droplet in a nematic host, with interface anchoring coefficient $W = -0.133$ (1.22) and bulk elastic constant $L_1 = 0.01$ (1.16), at time intervals of 20000 HLB iterations, from (i) $t = 1.18 \cdot 10^6$ to (xviii) $t = 1.34 \cdot 10^6$. The plots are taken over a box of size $1 \leq y \leq 100 \times 11 \leq z \leq 90$.

the periodicity of the free energy (Fig. 4.15). Note also that the period of the pulse is a decreasing function of the shear rate (Fig. 4.16), because a higher shear stress induces a faster rotation of the bulges and a faster translation of the slung defects.

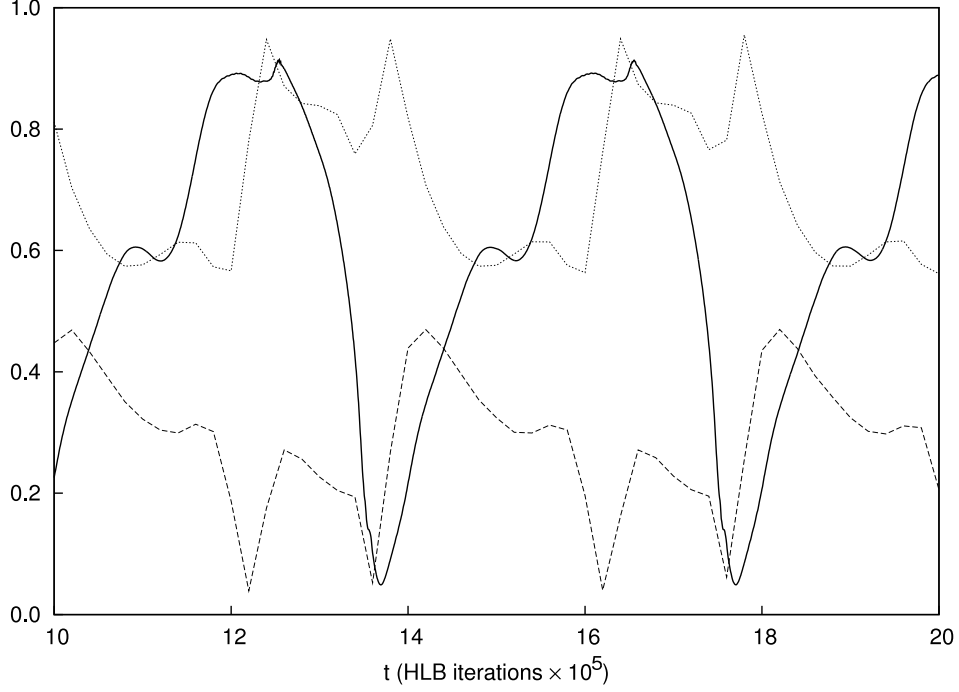


Figure 4.15: Time evolution of the free energy (solid line), Taylor deformation parameter (dashed line), tilt angle (dotted line) of an isotropic droplet inside a nematic, when $W = -0.133$, $L_1 = 0.01$, $\dot{\gamma} = 6 \cdot 10^5$. The units are arbitrary: this diagram has been drawn only to show the periodicity of the mesoscopic quantities following the periodicity of the free energy.

In Fig. 4.17 we report the Taylor deformation and the tilt angle for the values of the parameters W and L_1 discussed in this section.

4.5 $|W|/K = 0.8$, $L_1 = 10^{-3}$: imaginary defects revealed

As we saw in Sec. 3.4.3, the combination $|W|/K = 0.8$, $L_1 = 10^{-3}$ yields a ratio $F_{ai}R/\Sigma L_1 = 1.426$ which is not so big to produce defects in the

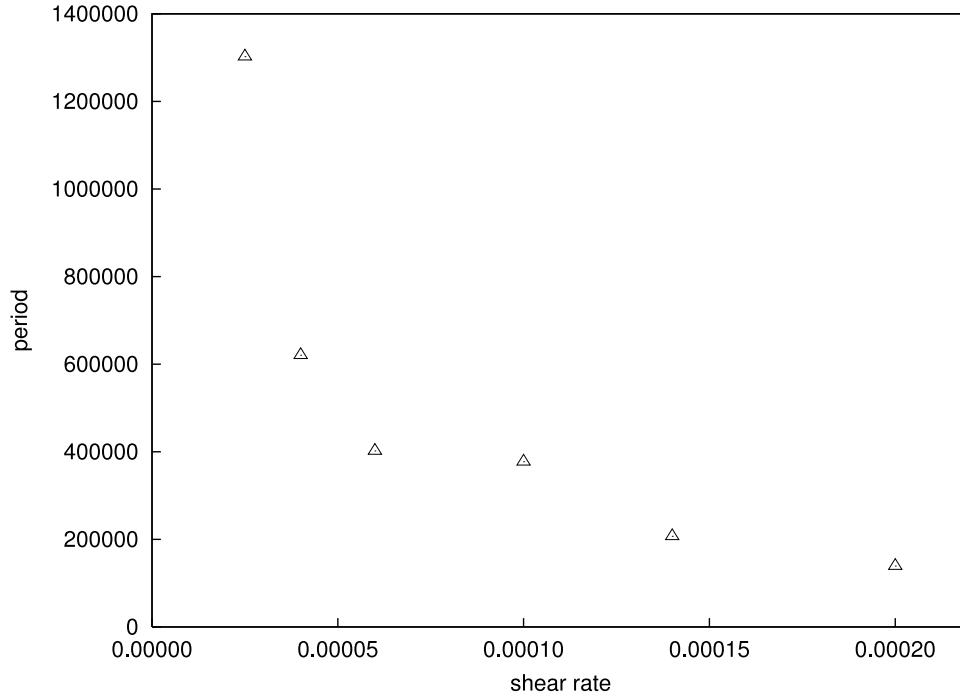


Figure 4.16: Periods of the pulsating states of an isotropic droplet inside a nematic, with $W = -0.133$, $L_1 = 0.01$, as a function of the shear rate.

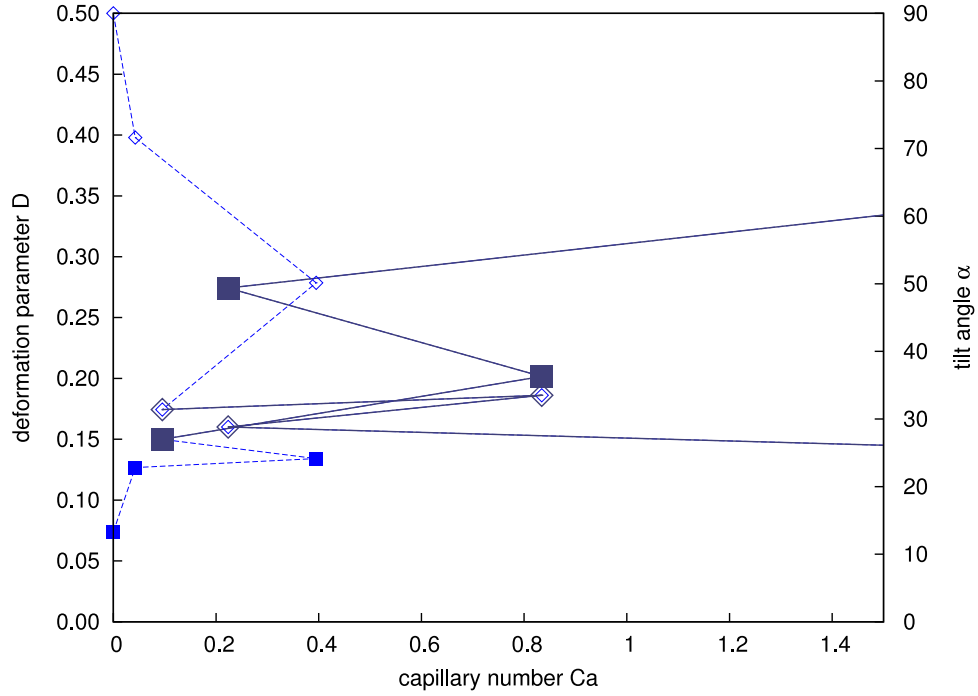


Figure 4.17: Taylor deformation parameter D (squares, left-hand vertical scale) and tilt angle α (diamonds, right-hand vertical scale), in function of the capillary number of the flowing system, of an isotropic droplet under shear flow, in a nematic host with interface anchoring vs. surface energy coefficients ratio $|W|/K = 1.33$ and bulk elastic constant $L_1 = 0.01$ (Eqs. (1.22), (1.19), (1.16)). Along the dashed lines, starting from the points lying on the left-hand vertical axis ($Ca = 0 \Leftrightarrow \dot{\gamma} = 0$, the points are ordered by increasing shear rate. Bigger, darker points and solid lines indicate the pulsating states. N. B. since in a pulsating state the droplet undergoes a sort of vibration, the macroscopic quantities can have huge errors. See text for details.

equilibrium configuration (Fig. 4.18a). This is confirmed by the profile of the director field (Fig. 4.19a).

Nevertheless, when we impose a weak shear flow ($\dot{\gamma} = 4 \cdot 10^{-5}$), something quite surprising occurs in the system. The droplet is tilted, the interface region has thickened (Sec. 4.2.2), but now, there are also two bulges, which in Fig. 4.18b are highlighted with two white circles.

As one can expect, after the discussion in Sec. 4.4, when the shear rate is large enough ($\dot{\gamma} = 6 \cdot 10^{-5}$), the bulges are able to jump out of the interface region (Fig. 4.18c) as real defects yielding an oscillating behaviour.

A good periodicity is observed, approximately, in the interval of shear rates $[6 \cdot 10^{-5}, 1.6 \cdot 10^{-4}]$: in this case, however, the period of the pulse is not always decreasing with $\dot{\gamma}$ (Fig. 4.21). Moreover, for high $\dot{\gamma}$, the system reaches a stable stationary state (Fig. 4.18d).

Also in this case the Taylor deformation parameter D and the tilt angle α is reported in Fig. 4.20.

4.6 Observations on the anchoring energy

In Sec. 4.2.1, we noticed, for $|W|/K = 0.4$ and $L_1 = 0.01$, that the dimensionless ratio $F_{ai}R/L_1\Sigma$, which throughout the whole discussion about the emulsions at rest (Chapter 3) has been used to discriminate the weak anchoring regime (vs. the elastic forces in the nematic), which does not yield defects, from the strong anchoring regime, which does, decreased with the shear rate.

Basically, with few exceptions, the same feature is observed for the systems whose behaviour is not so simple as the one mentioned above. This is not surprising, because the shear stress competes with the anchoring. After all is not a coincidence that $F_{ai}R/L_1\Sigma$ becomes negative either when the anchoring is already small or when the elastic constant is small, allowing the nematic to rotate more easily.

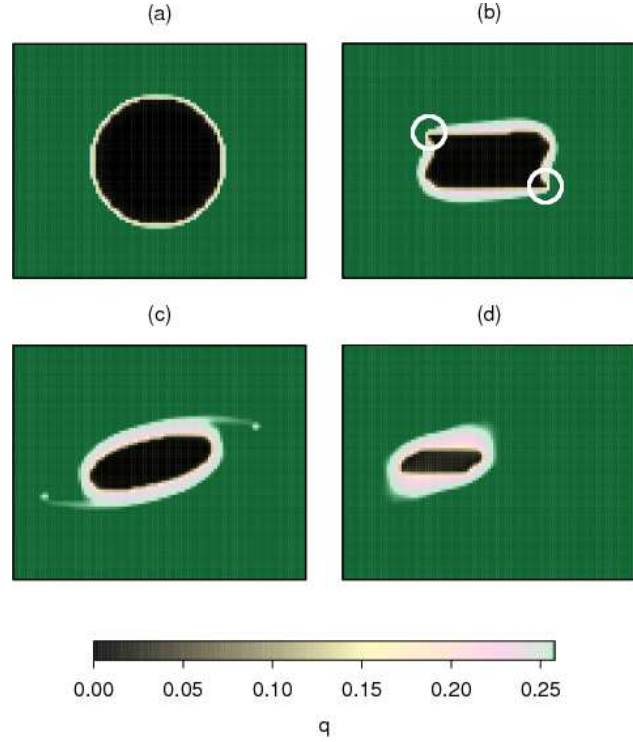


Figure 4.18: Profiles of the scalar order parameter q of an isotropic droplet in a nematic host, with interface anchoring vs. surface energy coefficients ratio $|W|/K = 0.8$ and bulk elastic constant $L_1 = 0.001$ (Eqs. (1.22), (1.19), (1.16)) (a) at equilibrium; (b) under a shear rate $\dot{\gamma} = 4 \cdot 10^{-5}$ ($\text{Ca} = 0.924$); (c) under a shear rate $\dot{\gamma} = 6 \cdot 10^{-5}$ ($\text{Ca} = 1.551$); (d) under a shear rate $\dot{\gamma} = 2 \cdot 10^{-4}$ ($\text{Ca} = 5.065$). The plots are taken over a box of size $1 \leq y \leq 100 \times 11 \leq z \leq 90$. The plots at panels (a), (b) and (d) refer to stable configurations; the plot at panel (c) is a snapshot. The white circles in panel (b) highlight two bulges which are invisible at rest.

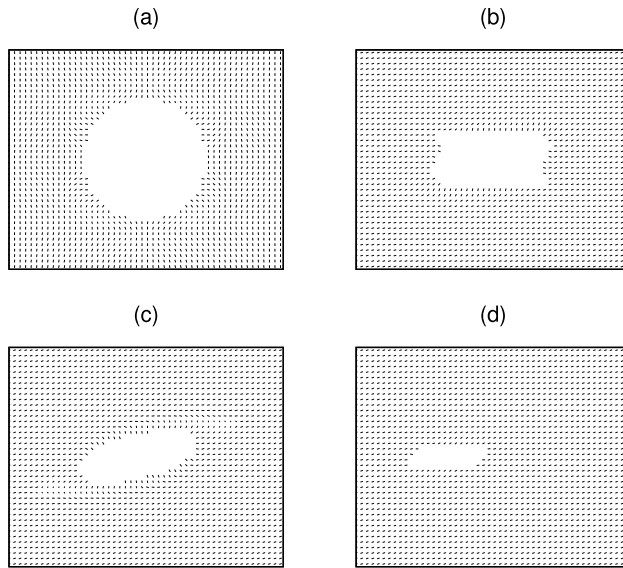


Figure 4.19: Profiles of the director field $\hat{\mathbf{n}}$ of an isotropic droplet in a nematic host, with interface anchoring vs. surface energy coefficients ratio $|W|/K = 0.8$ and bulk elastic constant $L_1 = 0.001$ (Eqs. (1.22), (1.19), (1.16)) (a) at equilibrium; (b) under a shear rate $\dot{\gamma} = 4 \cdot 10^{-5}$ ($\text{Ca} = 0.924$); (c) under a shear rate $\dot{\gamma} = 6 \cdot 10^{-5}$ ($\text{Ca} = 1.551$); (d) under a shear rate $\dot{\gamma} = 2 \cdot 10^{-4}$ ($\text{Ca} = 5.065$). The plots are taken over a box of size $1 \leq y \leq 100 \times 11 \leq z \leq 90$. The plots at panels (a), (b) and (d) refer to stable configurations; the plot at panel (c) is a snapshot. The white circles in panel (b) highlight two bulges which are invisible at rest.

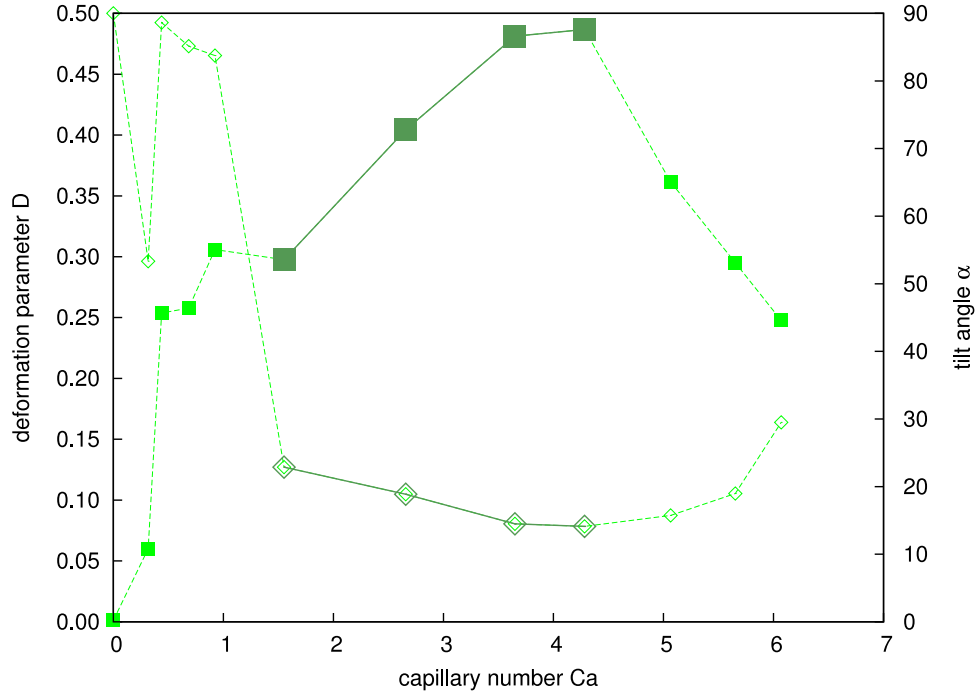


Figure 4.20: Taylor deformation parameter D (squares, left-hand vertical scale) and tilt angle α (diamonds, right-hand vertical scale), in function of the capillary number of the flowing system, of an isotropic droplet under shear flow, in a nematic host with interface anchoring vs. surface energy coefficients ratio $|W|/K = 0.8$ and bulk elastic constant $L_1 = 0.01$ (Eqs. (1.22), (1.19), (1.16)). Along the dashed lines, starting from the points lying on the left-hand vertical axis ($Ca = 0 \Leftrightarrow \dot{\gamma} = 0$), the points are ordered by increasing shear rate. Bigger, darker points and solid lines indicate the pulsating states. N. B. since in a pulsating state the droplet undergoes a sort of vibration, the macroscopic quantities can have huge errors. See text for details.

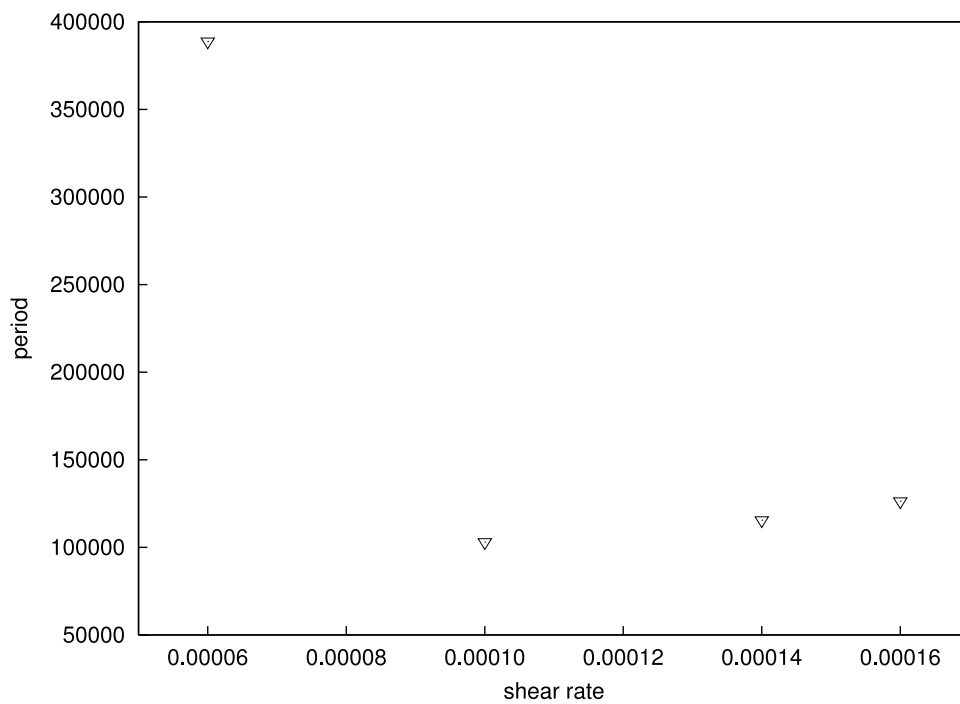


Figure 4.21: Periods of the pulsating states of an isotropic droplet inside a nematic, with $W = -0.08$, $L_1 = 0.001$, as a function of the shear rate.

Chapter 5

Three-dimensional droplets at rest

In this and in the following chapter, we extend the analysis of the drop shape at equilibrium and under shear to a fully three-dimensional system.

Because of the higher computational cost, the Lattice Boltzmann supercell had to be downsized to $38 \times 38 \times 38$ (Table 2.2) and, consequently, the initial radius of the droplets is reduced to 14 lattice constants.

Apart from that, the fixed parameters of the simulations are the same as in the two-dimensional case (Chapters 3 and 4), as well as the set of values of the interface anchoring coefficient $W \in \{-0.04, -0.08, -0.133\}$ (1.22) and of the bulk elastic constant $L_1 \in \{10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}\}$ (1.16).

5.1 Characterizing three-dimensional droplets

5.1.1 Approximation of the droplet shape as an ellipsoid

As the boundary of a two-dimensional droplet can be approximated to an ellipse (Sec. 3.3), to furnish some measure of the shape of a three-dimensional droplet we approximate it as an *ellipsoid*.

The procedure to calculate the principal axes and the tilt angles (polar and azimuthal) of the approximating ellipsoid is analogous to the one outlined in Sec. 3.3.1 for the two-dimensional case: to the i -th LB cell in the simulation box we assign a weight m_i , according to the formula (3.8). To minimize the effect of the numerical noise we set to zero any weight m_i less than 0.04. This procedure allows us first to evaluate the coordinates (x, y, z) of the centre of the droplet, through the definition of centre of mass of a set of bodies of mass m_i .

To calculate the lengths of the semi-axes a , b , c , instead than using the formula adapted for a two-dimensional space (3.7) we make use of the customary definition of inertia tensor:

$$I = \begin{pmatrix} \sum_i m_i (y_i^2 + z_i^2) & -\sum_i m_i x_i y_i & -\sum_i m_i x_i z_i \\ -\sum_i m_i x_i y_i & \sum_i m_i (x_i^2 + z_i^2) & -\sum_i m_i y_i z_i \\ -\sum_i m_i x_i z_i & -\sum_i m_i y_i z_i & \sum_i m_i (x_i^2 + y_i^2) \end{pmatrix} \quad (5.1)$$

The relations between the semi-axes of an ellipsoidal rigid body of mass M (which, here, is the sum of all m_i 's) and its principal axes of inertia I_x , I_y , I_z , are:

$$a = \sqrt{\frac{5}{2M} (-I_x + I_y + I_z)} \quad (5.2)$$

$$b = \sqrt{\frac{5}{2M} (I_x - I_y + I_z)} \quad (5.3)$$

$$c = \sqrt{\frac{5}{2M} (I_x + I_y - I_z)} \quad (5.4)$$

Let us suppose to order the principal axes such that $a \geq b \geq c \geq 0$. We see immediately the analogy to the eigenvalues of the offsetted (Westin) tensor order parameter of a liquid crystal (1.23).

As a consequence, we can characterize the shape of a three-dimensional droplet, approximated as an ellipsoid, in the same way as the Westin metrics can describe local biaxiality in a nematic liquid crystal.

To this purpose we define the three parameters

$$c_l = \frac{a - b}{a + b + c}, \quad (5.5)$$

$$c_s = \frac{3c}{a + b + c}, \quad (5.6)$$

$$c_p = \frac{2(b - c)}{a + b + c}, \quad (5.7)$$

which have respectively the following meanings:¹

¹Note that, unlike k_l , k_s , k_p (Sec. 1.7.2), these three parameters must be divided by the sum of the eigenvalues, otherwise their sum is not 1 and they do not form a barycentric space.

- c_l is a measure of the degree of **prolateness** of the ellipsoid: the extreme case is $c_l = 1$, in which there is only one eigenvalue > 0 , i. e. the ellipsoid degenerates into a segment. c_l must be compared to c_p – not to c_s – to establish whether the ellipsoid is nearer to the prolate shape than to the oblate shape.² Remember that the adjectives *prolate* and *oblate* refer to spheroids, i. e. to ellipsoids with a symmetry axis or, equivalently, where two of the three axes are equal. If $c_l > c_p$, the ellipsoid tends to be prolate, and c_p is a measure of the deviation from a perfect prolate shape (scalenity);
- c_s is a measure of the **sphericity**: c_s can be 1 only if the three eigenvalues are equal, i. e. the ellipsoid is a sphere. It must be $\neq 0$, otherwise the ellipsoid is, in fact, a two-dimensional ellipse;
- c_p is a measure of the **oblateness**: the extreme case is $c_p = 1$, where we have $a = b > 0$ and $c = 0$, i. e. the ellipsoid degenerates into a two-dimensional circle. c_p must be compared to c_l – not to c_s – to establish whether the ellipsoid is nearer to the oblate shape than to the prolate shape. If $c_p > c_l$, the ellipsoid tends to be oblate, and c_l is a measure of the deviation from a perfect oblate shape (scalenity).

Notice that (c_l, c_s, c_p) form a barycentric space over all possible shapes of an ellipsoid.

5.1.2 Knud Thomsen’s formula for the area

To estimate the area of the surface of the drop Σ , we rely on the Knud Thomsen’s approximate formula³ for the area of an ellipsoid with semiaxes a, b, c :

$$\Sigma = 4\pi \left(\frac{(ab)^p + (ac)^p + (bc)^p}{3} \right)^{1/p} \quad (5.8)$$

where $p = 1.6075$.

²For example, let us have $a = 0.4$, $b = 0.3$, $c = 0.3$. The ellipsoid is undoubtedly prolate, but $c_l = 0.1$, $c_s = 0.9$, $c_p = 0$.

³<http://home.att.net/~numericana/answer/ellipsoid.htm#thomsen>; in lieu of traditional peer review, this approximation has been discussed and analyzed by Sigma Xi mathematician David W. Cantrell in the sci.math newsgroup (search with keywords “knud thomsen” and “ellipsoid”) [Xu *et al.*, 2009]

5.2 Results and comparison to the two-dimensional case

5.2.1 Equilibrium shapes of the three-dimensional droplets

All the shape parameters c_l , c_s , c_p for the three-dimensional droplets at equilibrium, as functions of the simulation parameters W , L_1 , are listed in Tables 5.1, 5.2, 5.3.

In the panels of Fig. 5.1 we report the equilibrium isosurfaces $\phi = 0.6$, for all the combinations of W and L_1 listed in Table 2.2 (all the other parameters of the simulations are kept fixed) and at the beginning of this chapter. I chose $\phi = 0.6$ as representative of the drop surface, considering that, at equilibrium, $\phi_{\text{iso}} \approx 0.30$ and $\phi_{\text{nem}} \approx 0.69$ respectively for the isotropic and the nematic phase.

As in the two-dimensional cases, the equilibrium drop configurations are the result of the competition of three energy terms: the surface tension, the bulk elastic energy of the nematic and the anchoring energy of the nematic orientation at the interface. The relative strength of these terms can be again classified in terms of the dimensionless numbers $F_{ai}R/L_1\Sigma$ and $|W|/K$.

From Figs. 5.1a to 5.1e, the equilibrium configurations refer to values of W and L_1 corresponding to the weak anchoring regime ($F_{ai}R/L_1\Sigma < 1$), i. e. when the anchoring energy is too small to force the nematic to align perpendicularly. Under this condition, since, in addition, the surface tension dominates over the anchoring energy ($|W|/K \leq 0.8$), the drop is nearly spherical.

This is confirmed quantitatively by the values of the sphericity c_s (Sec. 5.1.1), listed in Tables 5.1 and 5.2 that are extremely close to 1 (sphere). As in the two-dimensional case (Sec. 3.4.1, Fig. 3.3, the deviation from the spherical shape occurs either by increasing W , with respect to K , or by increasing L_1 .

In particular, when $W = -0.133$ and the elastic constant is still at its lowest value (10^{-4} , Fig. 5.1i), the droplet is contracted along the initial orientation of the nematic in the bulk (the z axis), and c_p is a measure of this contraction. The relative low value of L_1 allows the nematic to rotate quite freely in the bulk, but the strong anchoring value W forces the interface to “adapt” to the nematic orientation in the bulk. Note that this is essentially the only case in the 3D simulations which we can be referred as a clear example of strong anchoring regime: see Table 5.5.

We should expect that an increase of L_1 , which strengthens the elastic contribution to the free energy, to the detriment of the surface tension, would

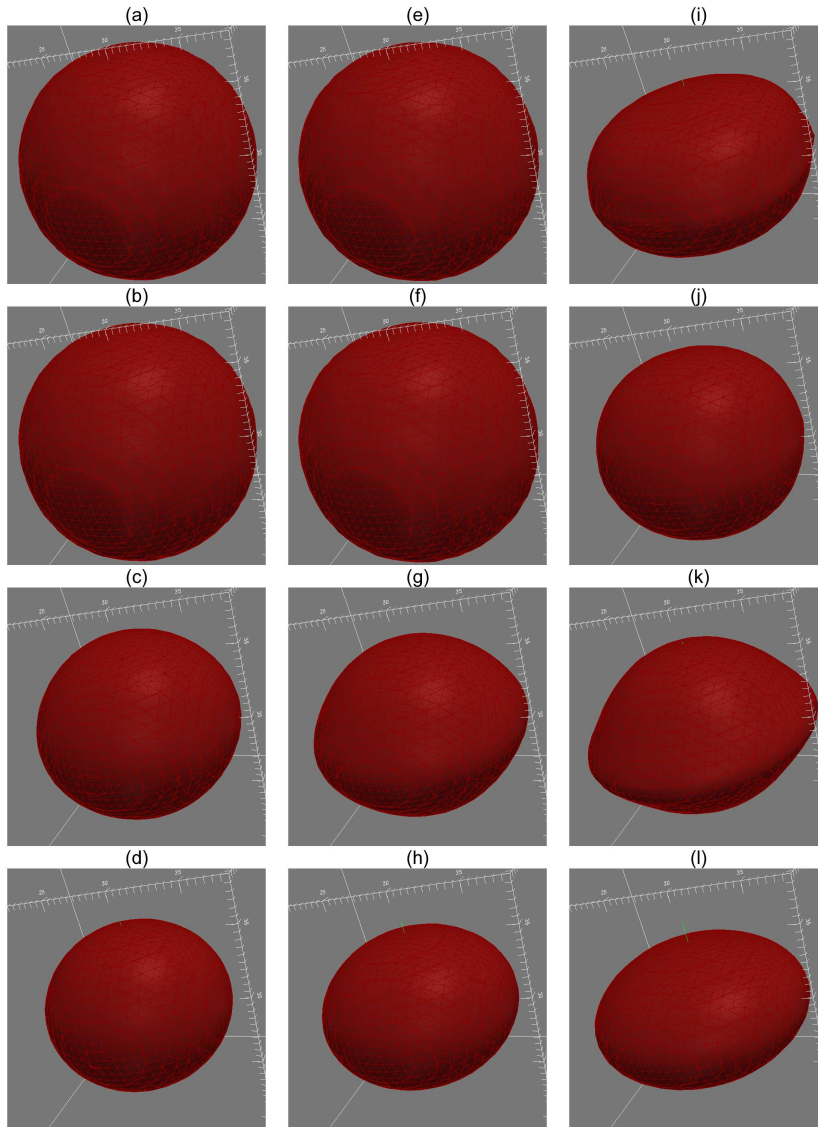


Figure 5.1: Isosurfaces $\phi = 0.6$ of three-dimensional isotropic droplets, with initial radius 14 (simulation units), in a nematic host, with initial director field parallel to z , at equilibrium. Interface anchoring coefficient (1.22) vs. surface energy coefficient (1.19): from the first to the third column, $|W|/K = 0.4, 0.8, 1.33$. Bulk elastic constant (Eq. (1.16)): from the first to the fourth row, $L_1 = 0.0001, 0.001, 0.01, 0.1$.

	c_l	c_s	c_p
$L_1 = 0.0001$	$2.37696 \cdot 10^{-4}$	0.999261	$3.48926 \cdot 10^{-4}$
$L_1 = 0.001$	$4.44 \cdot 10^{-5}$	0.999192	$7.639 \cdot 10^{-4}$
$L_1 = 0.01$	$2.102 \cdot 10^{-3}$	0.93071	$6.7187 \cdot 10^{-2}$
$L_1 = 0.1$	$1.952 \cdot 10^{-3}$	0.917002	$8.1047 \cdot 10^{-2}$

Table 5.1: Values of the shape parameters c_l , c_s , c_p (Sec. 5.1.1) for three-dimensional droplets in a nematic matrix, at rest, with $|W|/K = 0.4$ (Eqs. (1.22), (1.19)).

make the droplet shrink along z (an increase of c_p). Actually, that happens only for the lowest anchoring energy vs. surface tension ratio: $|W|/K = 0.4$: for $|W|/K = 0.8$, the oblateness c_p does not change significantly (Table 5.2); for $|W|/K = 1.33$, the droplet is exceptionally close to the spherical shape (Table 5.3). We will explain this apparent anomaly in Sec. 5.2.3, when we will discuss defects.

To observe a visible contraction along z , we must raise L_1 at least to the value 0.01 (Figs. 5.1c, 5.1g): the effect is more evident for $W = -0.08$, but in both cases the drop is slightly oblate. For $W = -0.133$ and $L_1 = 0.01$ (Fig. 5.1k), the oblateness parameter c_p is still bigger, and the drop takes the shape of a disc aircraft, which reminds us of the “rugby ball with bulges” observed in the two-dimensional case for the same set of values of $|W|$ and L_1 (Fig. 3.3k). Much less discernible is such a shape when $W = -0.08$ (see Fig. 5.1g) but the relative large value of c_p suggests that the effect is still there.

If the elastic bulk term L_1 is further increased to 0.1, the equilibrium drop assumes the shape of a Smartie, whose oblateness increases with W (Figs. 5.1d, 5.1h, 5.1l). This is again quantified by the rise of c_p , which is about 21%, bigger than the value measured at $L_1 = 0.01$, for $W = -0.04$ and -0.08 , and about 46% bigger for the corresponding value at $W = -0.133$.

Notice, at $W = -0.133$, the shape transition from the disc-aircraft situation for $L_1 = 0.01$ to the oblate spheroid at $L_1 = 0.1$.

It is interesting to look at the L_1 dependence of the shape parameters for different anchorings W , which are reported in Figs. 5.2, 5.3, 5.4.

Note the non-monotonic behaviour of the curves c_l for $W = -0.133$ and $L_1 = 0.01$, and of c_p and c_l for $W = -0.133$ and $L_1 = 10^{-4}$. This behaviour is related to the presence of defects in the systems, as we will discuss in Sec. 5.2.3.

	c_l	c_s	c_p
$L_1 = 0.0001$	$5.35824 \cdot 10^{-4}$	0.995417	$4.04725 \cdot 10^{-3}$
$L_1 = 0.001$	$6 \cdot 10^{-5}$	0.997787	$2.154 \cdot 10^{-3}$
$L_1 = 0.01$	$2.43293 \cdot 10^{-3}$	0.855623	0.141944
$L_1 = 0.1$	$2.6486 \cdot 10^{-3}$	0.825639	0.171713

Table 5.2: Values of the shape parameters c_l , c_s , c_p (Sec. 5.1.1) for three-dimensional droplets in a nematic matrix, at rest, with $|W|/K = 0.8$ (Eqs. (1.22), (1.19)).

	c_l	c_s	c_p
$L_1 = 0.0001$	$1.547 \cdot 10^{-2}$	0.792166	0.192367
$L_1 = 0.001$	$7.08571 \cdot 10^{-3}$	0.942773	$5.03883 \cdot 10^{-2}$
$L_1 = 0.01$	$7.2 \cdot 10^{-4}$	0.787717	0.211563
$L_1 = 0.1$	$7.18 \cdot 10^{-3}$	0.684449	0.30837

Table 5.3: Values of the shape parameters c_l , c_s , c_p (Sec. 5.1.1) for three-dimensional droplets in a nematic matrix, at rest, with $|W|/K = 1.33$ (Eqs. (1.22), (1.19)).

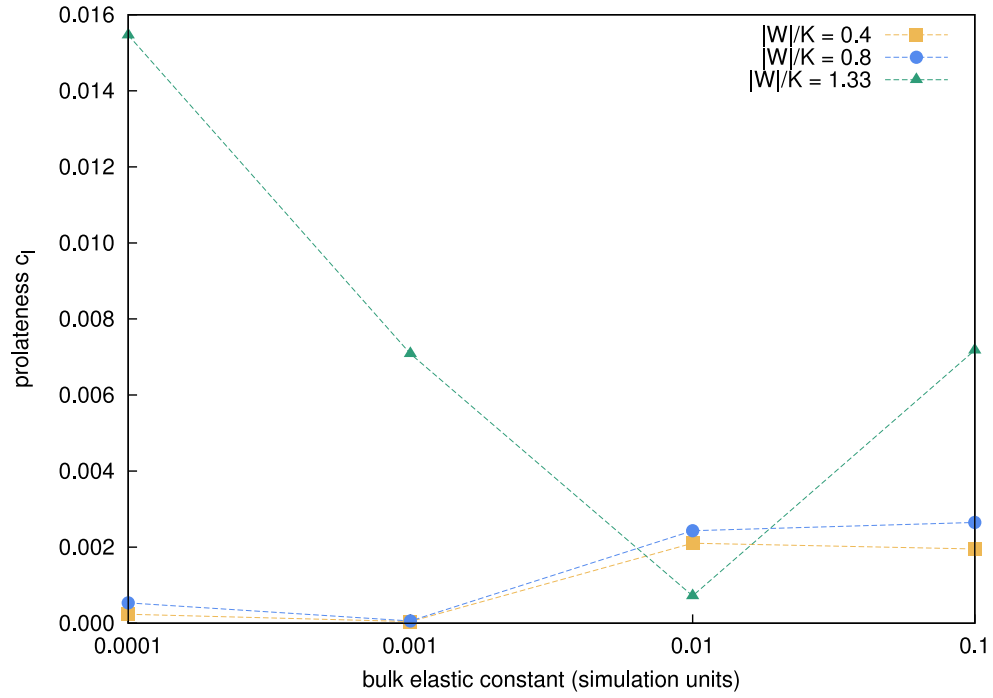


Figure 5.2: Plots of the prolateness parameter c_l for three-dimensional droplets in a nematic matrix, at rest, with $|W|/K = 0.4$ (ochre squares), $|W|/K = 0.8$ (blue circles), $|W|/K = 1.33$ (green triangles) (Sec. 5.1.1, Eqs. (1.22), (1.19)).

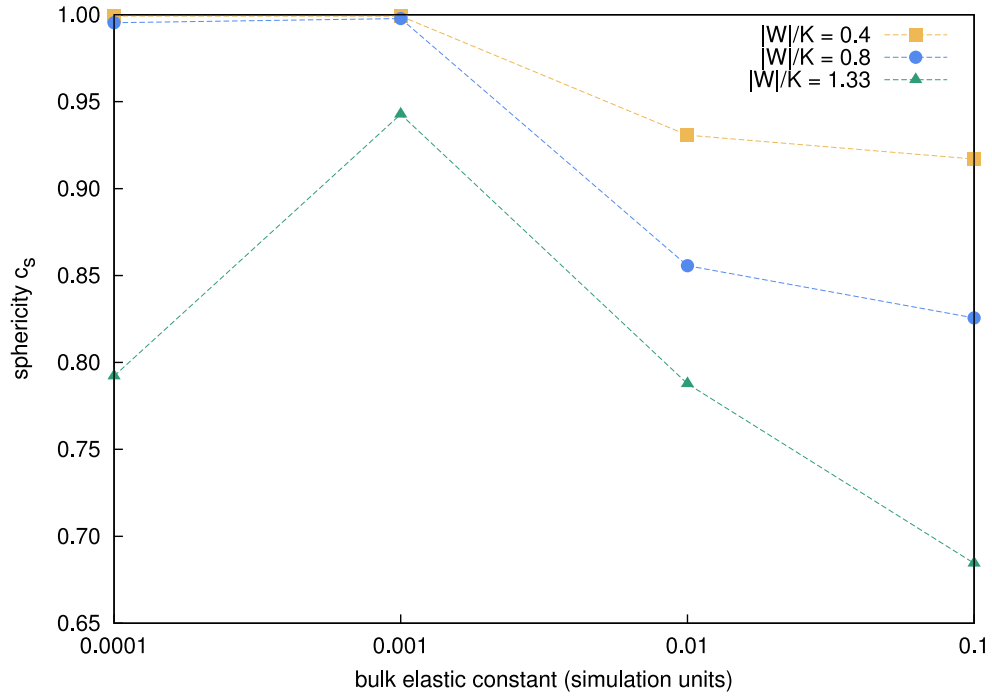


Figure 5.3: Plots of the sphericity parameter c_s for three-dimensional droplets in a nematic matrix, at rest, with $|W|/K = 0.4$ (ochre squares), $|W|/K = 0.8$ (blue circles), $|W|/K = 1.33$ (green triangles) (Sec. 5.1.1, Eqs. (1.22), (1.19)).

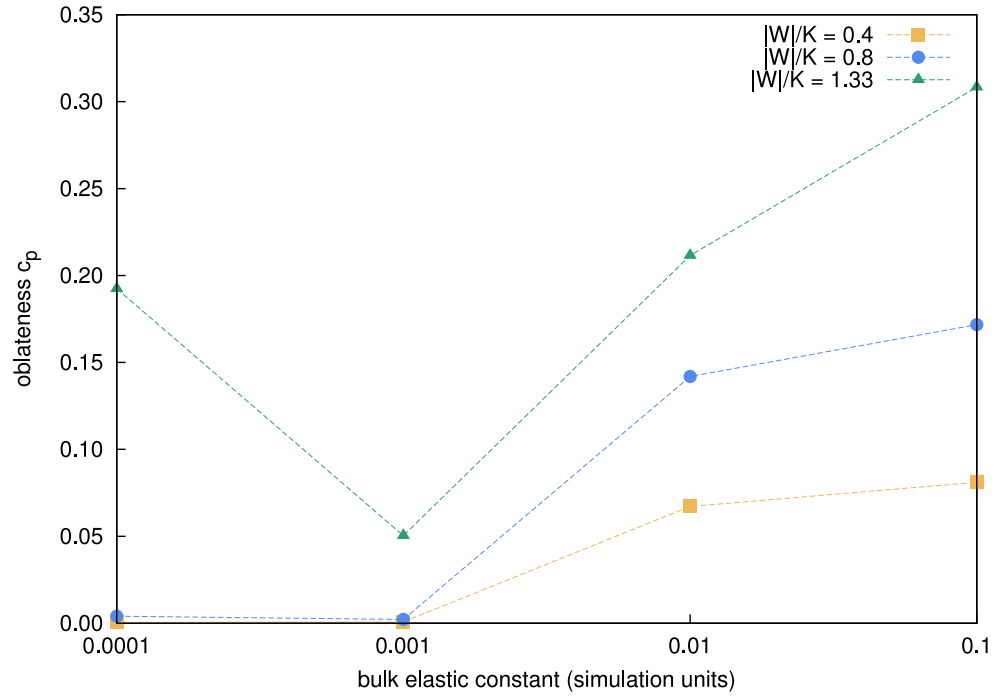


Figure 5.4: Plots of the oblateness parameter c_p for three-dimensional droplets in a nematic matrix, at rest, with $|W|/K = 0.4$ (ochre squares), $|W|/K = 0.8$ (blue circles), $|W|/K = 1.33$ (green triangles) (Sec. 5.1.1, Eqs. (1.22), (1.19)).

Finally, it is interesting to compare again the aspect ratios of the simulated drops with the values predicted in [100] (see Fig. 5.5): the agreement between our simulations and their theory suffers roughly of the same issues found in the two-dimensional case, and discussed in Sec. 3.4.1.

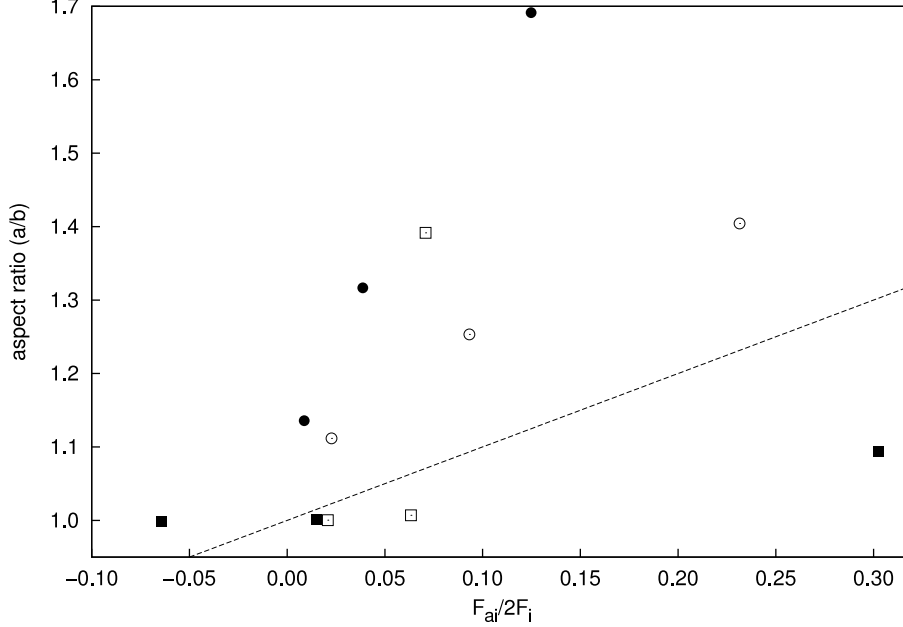


Figure 5.5: Comparison between the aspect ratio a/b of the simulated droplets ($\square$: $L_1 = 10^{-4}$, $\bullet$: $L_1 = 10^{-3}$, $\odot$: $L_1 = 10^{-2}$, $\blacksquare$: $L_1 = 10^{-1}$) and the aspect ratio predicted by Lishchuk and Care's model [100] (3.10) (dashed line).

The aspect ratios of the droplets in the two- and the three-dimensional case, for the same values of W and L_1 , are then compared in Table 5.4. The agreement between the two dimensions, that is in general reasonable, is best for $L_1 = 0.001, 0.1$ and worst for $L_1 = 0.01$.

5.2.2 Anchoring strength vs. elastic forces

Comparing the dimensionless ratios $|F_{ai}R/L_1\Sigma|$ calculated for these geometries⁴ – and listed in Table 5.5 – with the ones found in the two-dimensional case (Sec. 3.4.2), we find a similar trend, although the values, in the same conditions of interface anchoring and bulk elastic constant (remember that all

⁴The only difference with the two-dimensional case, in the calculation of $|F_{ai}R/L_1\Sigma|$, is that now R is evaluated as the geometric mean of the three semiaxes, instead of two.

W	−0.04		−0.08		−0.133	
	(2D)	(3D)	(2D)	(3D)	(2D)	(3D)
$L_1=0.0001$	1.00049	1.00052	1.00122	1.00610	1.20111	1.36426
$L_1=0.001$	1.00203	1.00115	1.00229	1.00324	1.09594	1.08017
$L_1=0.01$	1.07279	1.10829	1.09594	1.24884	1.15935	1.40287
$L_1=0.1$	1.14724	1.13258	1.32746	1.31196	1.71520	1.67579

Table 5.4: Comparison between the aspect ratios (horizontal axis / vertical axis) of the simulated droplets in two and in three dimensions, with all the same parameters in the code.

	$W = -0.04$	$W = -0.08$	$W = -0.133$
$L_1=0.0001$	$4.072 \cdot 10^{-1}$	1.297	$\gtrsim 12.3$
$L_1=0.001$	$2.985 \cdot 10^{-2}$	$-6.985 \cdot 10^{-1}$	$8.178 \cdot 10^{-1}$
$L_1=0.01$	$3.904 \cdot 10^{-3}$	$1.765 \cdot 10^{-2}$	$5.445 \cdot 10^{-2}$
$L_1=0.1$	$1.042 \cdot 10^{-4}$	$4.875 \cdot 10^{-4}$	$1.798 \cdot 10^{-3}$

Table 5.5: Values of the dimensionless ratio $|F_{ai}R/L_1\Sigma|$ for three-dimensional droplets in a nematic matrix, at rest.

the other parameters are fixed, Table 2.2), were bigger in the two-dimensional case. In fact, since the anchoring is considered weak if $|F_{ai}R/L_1\Sigma| \lesssim 1$, only in one of the three-dimensional systems the anchoring is strong, namely $W = -0.133$, $L_1 = 0.0001$.

In the three-dimensional case, too, the ratio between the highest and the lowest value of $|F_{ai}R/L_1\Sigma|$ is bigger when $W = -0.133$ (≈ 6841) than when $W = -0.04$ (≈ 3907), suggesting that the anchoring strength (i. e. anchoring energy per unit area) is not linear in W . Anyway, the data set for $W = -0.08$, whose ratio between the highest and the lowest value of $|F_{ai}R/L_1\Sigma|$ is about 2661, constitute an exception.

But $W = -0.08$ is a notable exception for another, more stunning, reason. When $L_1 = 0.001$, F_{ai} is even positive (it should be negative, see Eq. (1.22)), meaning that the director is not perpendicular to the interface, at least across parts of the interface. This point will be discussed in more details in Sec. 5.2.3.

5.2.3 Profiles of $\hat{n}$, q and k_p . Defects

Detecting point and line defects, in three-dimensional binary emulsions, is more difficult than in the two-dimensional case. For instance, examining the behaviour of the scalar order parameter q (Sec. 1.7.1) is not always sufficient to detect defects and one has to look either at the profiles of the biaxiality parameter k_p (Sec. 1.7.2) or directly at the orientation of the director field.

Fig. 5.6 shows the isosurfaces of k_p (at $k_p = 0.007$, solid green contours) and, for reference, the interfaces, taken as $\phi = 0.6$ (Fig. 5.1) at different values of W and L_1 . From the equilibrium configurations, one can observe that:

- when $|F_{ai}R/L_1\Sigma| \ll 1$ (Sec. 5.2.2), as in the two-dimensional case (Sec. 3.4.3), we are in the weak anchoring regime and there are no defects at all. The values of $|F_{ai}R/L_1\Sigma|$ in Table 5.5 suggests us an even weaker anchoring than in the two-dimensional case. The elastic forces, proportional to L_1 , are so strong with respect to the anchoring energy, proportional to $|W|$, that the director is quite uniform throughout the supercell and around the three-dimensional drops, too.
- When $L_1 = 0.01$, although the ratio $|F_{ai}R/L_1\Sigma|$ increases, the director and the scalar order parameter profiles, neither for $W = -0.04$ (Fig. 5.7) nor for $W = -0.08$, still show the presence of defects. The director is indeed still quite uniform in the cell. Note that this behaviour differs from the one observed in the two-dimensional drops where, for the same

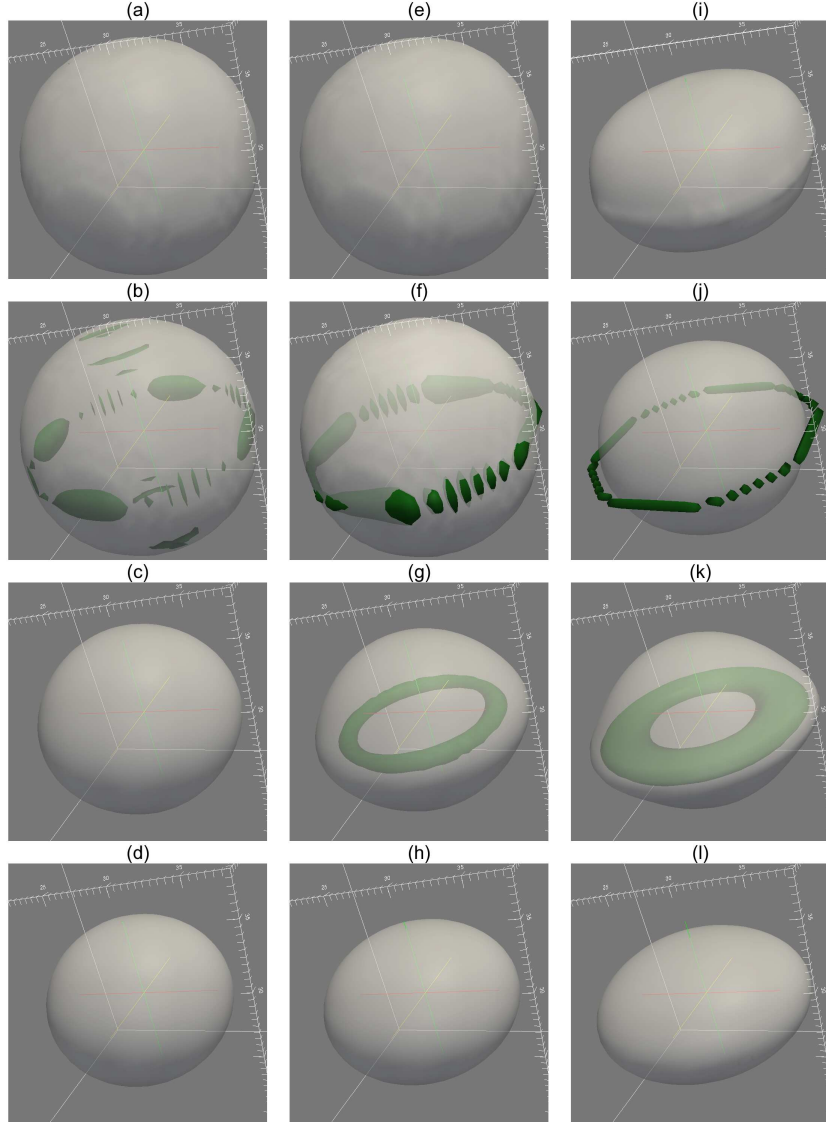


Figure 5.6: Isosurfaces (green contours) of the biaxiality $k_p = 0.007$ of three-dimensional isotropic droplets, with initial radius 14 (simulation units), in a nematic host, with initial director field parallel to z , at equilibrium. Interface anchoring coefficient (1.22) vs. surface energy coefficient (1.19): from the first to the third column, $|W|/K = 0.4, 0.8, 1.33$. Bulk elastic constant (Eq. (1.16)): from the first to the fourth row, $L_1 = 0.0001, 0.001, 0.01, 0.1$. The isosurfaces $\phi = 0.6$ (semi-transparent contours) are drawn for reference.

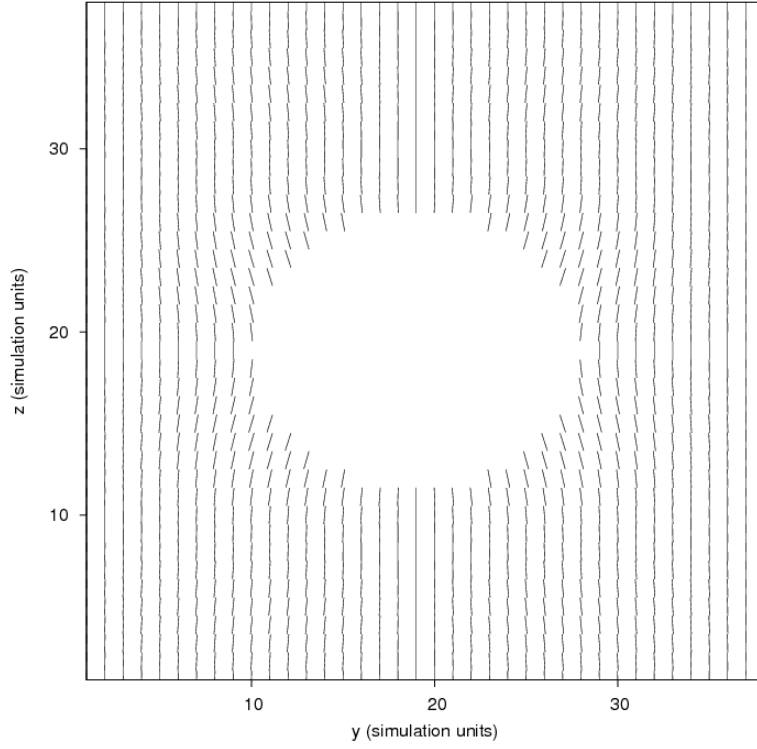


Figure 5.7: Profile of the nematic director for $W = -0.04$, $L_1 = 0.01$, along the plane $x = 19$.

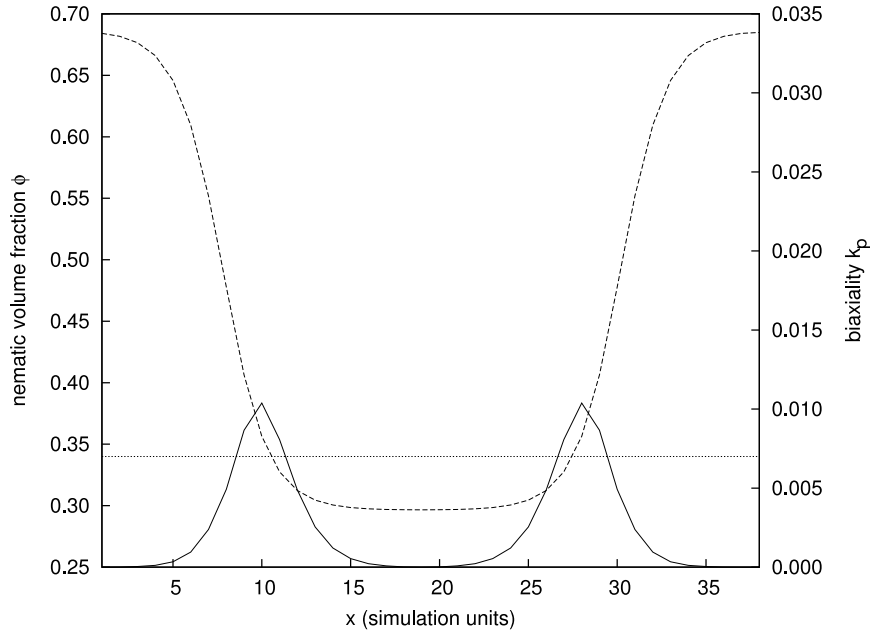


Figure 5.8: Concentration ϕ (dashed line, left-hand vertical scale) and biaxiality parameter k_p (solid line, right-hand vertical scale) along the line $y = 19, z = 19$ in the supercell, with $W = -0.08$ and $L_1 = 0.01$. The horizontal dotted line marks $k_p = 0.007$, the threshold value chosen to identify defects. The scalar order parameter q is not plotted in this graph because, apart from the difference in scale, its variations are indistinguishable from the variations of ϕ .

parameters, the anchoring strength is higher (see Tables 3.2 and 5.5). However, at $W = -0.08$, under the isosurface $\phi = 0.6$, a toroidal region in which the biaxiality is greater than 0.007 (the threshold value which I chose to detect defects) appears in the equatorial plane (Fig. 5.6g). More precisely, the toroid lies between the isosurface $\phi = 0.33$ (very close to the isotropic concentration) and the isosurface $\phi = 0.43$: in Fig. 5.8 we can see the profiles of k_p and ϕ along the straight line parallel to the x axis, passing through the centre of the supercell. As in the two-dimensional case, one can think in terms of an imaginary line of defects located inside the drop, the reason being that the anchoring is not strong enough (with respect to the nematic elastic energy) to force the director to orient perpendicularly to the drop surface where the nematic phase is important. On the other hand, inside the drop, where the nematic phase is negligible, the biaxiality may be non-negligible. Note that in this case the profile of scalar order parameter q (not shown in Fig. 5.8) seems unaffected as we cross the drop surface.

- If we increase the anchoring strength up to 0.133) the toroidal region of non-negligible biaxiality moves outward closer to the surface drop (see Fig. 5.10), placing itself between $\phi = 0.3$ (the isotropic concentration) and $\phi = 0.51$. By sweeping the director field around the interface, we can count a zero topological charge: in this respect we can argue that, as in the two-dimensional droplet with the same parameter values (Fig. 3.3k), the distortion of the liquid crystal within the interface region (the “imaginary Saturn ring” mentioned above [108]) deforms considerably the interface itself, giving rise to a disc aircraft-like shape. Note that the distortions do not occur in the region of the full nematic phase because of the high value of L_1 .
- If, on the other hand, we fix the anchoring strength to $W = -0.133$, and decrease the bulk elastic constant to $L_1 = 0.001$, the Saturn ring forms out of the drop surface and separates from it, the same way as the two line defects flank the droplet for the same anchoring coefficient and elastic constant, in the two-dimensional case (Figs. 3.3j, 3.5). This behaviour is evident both from the profile of the scalar order parameter (Fig. 5.12, section at $z = 19$) and from the profile of the director (Fig. 5.11, section at $x = 19$). In particular we can see that, along the plane $z = 19$, which contains the Saturn ring, between the interface and the disclination line the director is parallel to the xy plane (and perpendicular to the interface), whereas outside the Saturn ring the director is parallel to the z direction, i. e. it is parallel to the

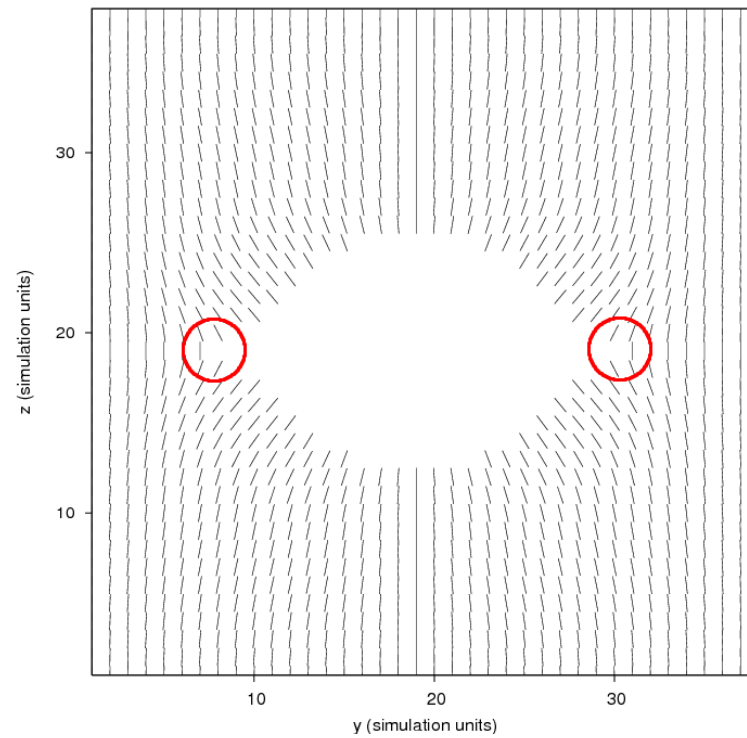


Figure 5.9: Profile of the nematic director for $W = -0.133$, $L_1 = 0.01$, along the plane $x = 19$. The red circles mark the alleged evidence of two defects, intersections, with the plane $x = 19$, of an “image Saturn ring” within the interface region.

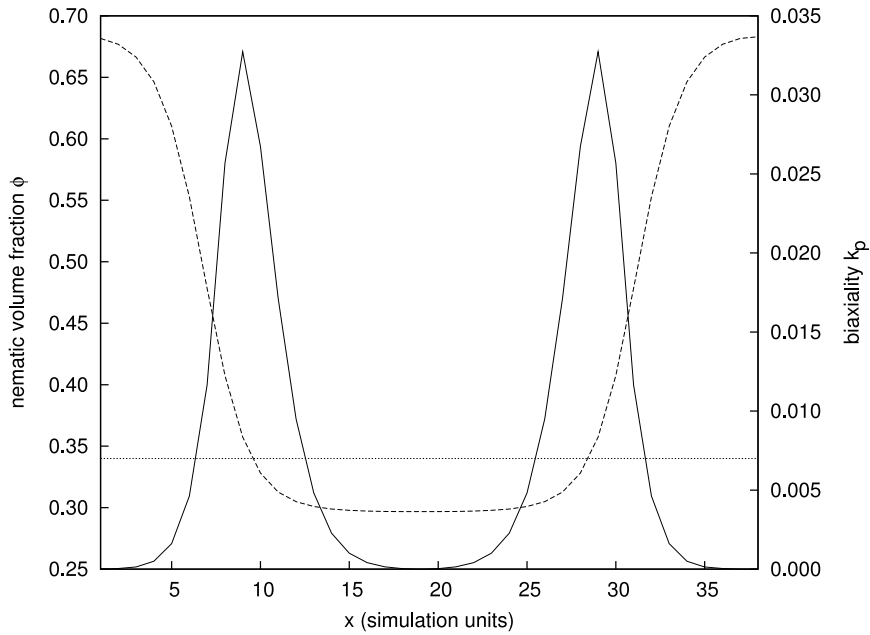


Figure 5.10: Concentration ϕ (dashed line, left-hand vertical scale) and biaxiality parameter k_p (solid line, right-hand vertical scale) along the line $y = 19, z = 19$ in the supercell, with $W = -0.133$ and $L_1 = 0.01$. The horizontal dotted line marks $k_p = 0.007$, the threshold value chosen to identify defects. The scalar order parameter q is not plotted in this graph because, apart from the difference in scale, its variations are indistinguishable from the variations of ϕ .

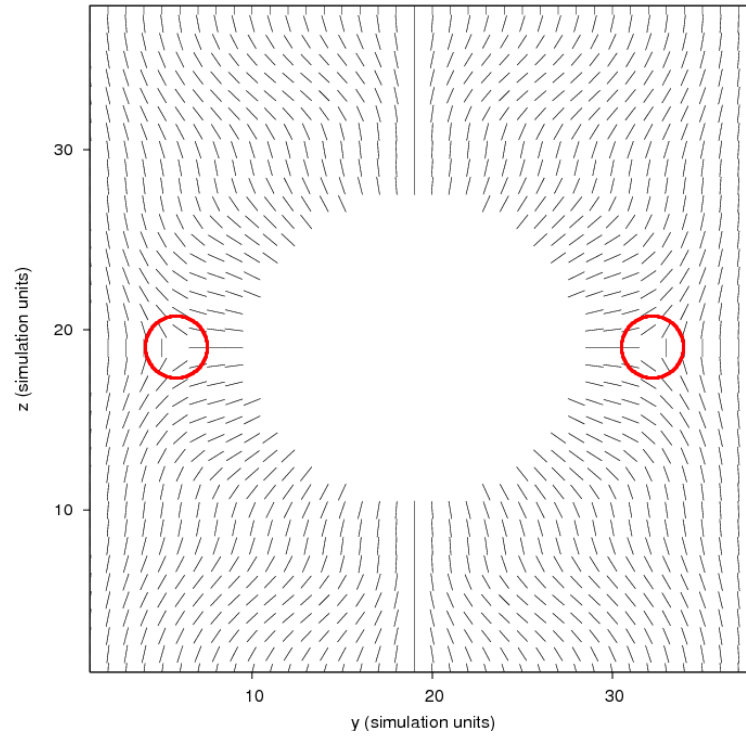


Figure 5.11: Profile of the nematic director for $W = -0.133$, $L_1 = 0.001$, along the plane $x = 19$. The red circles mark the defects.

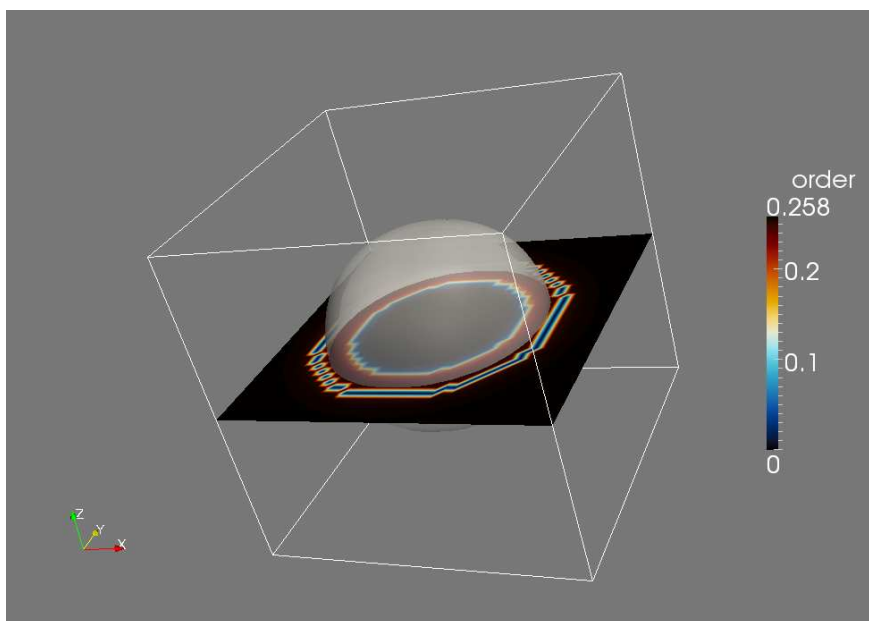


Figure 5.12: Profile of the scalar order parameter q for $W = -0.133$, $L_1 = 0.001$, along the plane $z = 19$. The semi-transparent contour is the isosurface $\phi = 0.6$ (Fig. 5.1j).

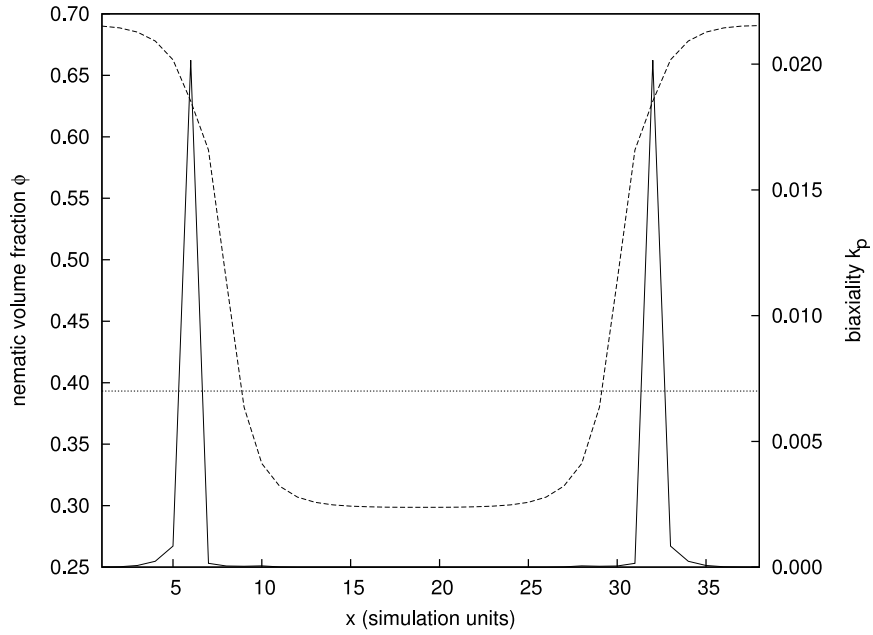


Figure 5.13: Concentration ϕ (dashed line, left-hand vertical scale) and biaxiality parameter k_p (solid line, right-hand vertical scale) along the line $y = 19, z = 19$ in the supercell, with $W = -0.133$ and $L_1 = 0.001$. The horizontal dotted line marks $k_p = 0.007$, the threshold value chosen to identify defects. The scalar order parameter q is not plotted in this graph because, apart from the difference in scale, its variations are indistinguishable from the variations of ϕ .

interface, just as when the elastic constant is $L_1 = 0.01$ (Fig. 5.11). That corroborates the assertion according to which, when $L_1 = 0.01$, there is a Saturn ring “inside” the droplet.

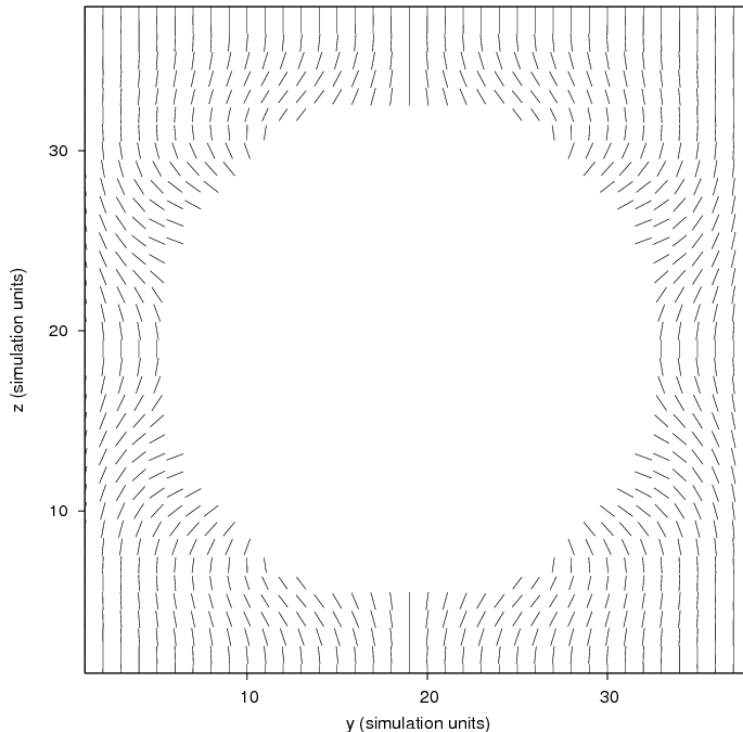


Figure 5.14: Profile of the nematic director for $W = -0.04$, $L_1 = 0.001$, along the plane $x = 19$. We can observe that this configuration does not show defects in the nematic phase.

- When $L_1 = 0.001$ and $W = -0.08$ or -0.04 , the profile of k_p still reveals a Saturn ring, or at least the semblance of a Saturn ring, even for weak anchoring. Indeed, as when $L_1 = 0.01$ and $W = -0.133$, the director is parallel to the interface along the equator (Fig. 5.14, section $x = 19$. This picture shows the profile for $W = -0.04$, but the profile for $W = -0.08$ is very similar to it). Near each pole of the droplet, the competition between anchoring forces and elastic forces causes the director not to orient perfectly perpendicular to the interface, but to “wrap” around it – (Figs. 5.15 and 5.16) – and the effect is more evident when the anchoring is weaker. We can try to explain, in this way, the anomaly in the anchoring en-

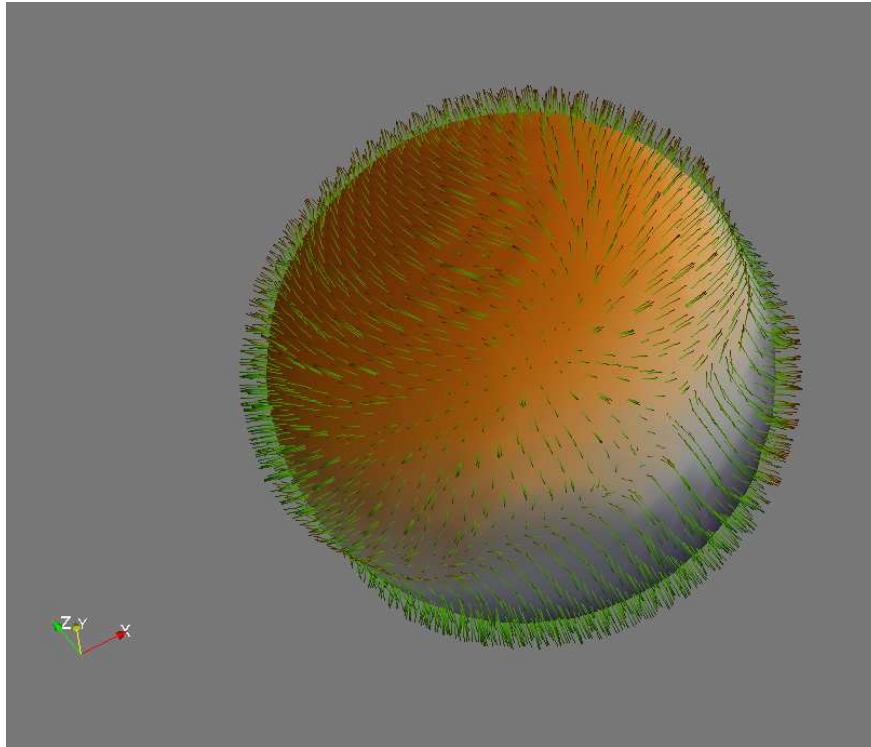


Figure 5.15: Profile of the director $\hat{\mathbf{n}}$ for $W = -0.04$, $L_1 = 0.001$. The contour is the isosurface $\phi = 0.6$ (Fig. 5.1b): the golden part is the half above the equator, the light violet part is the half below it.

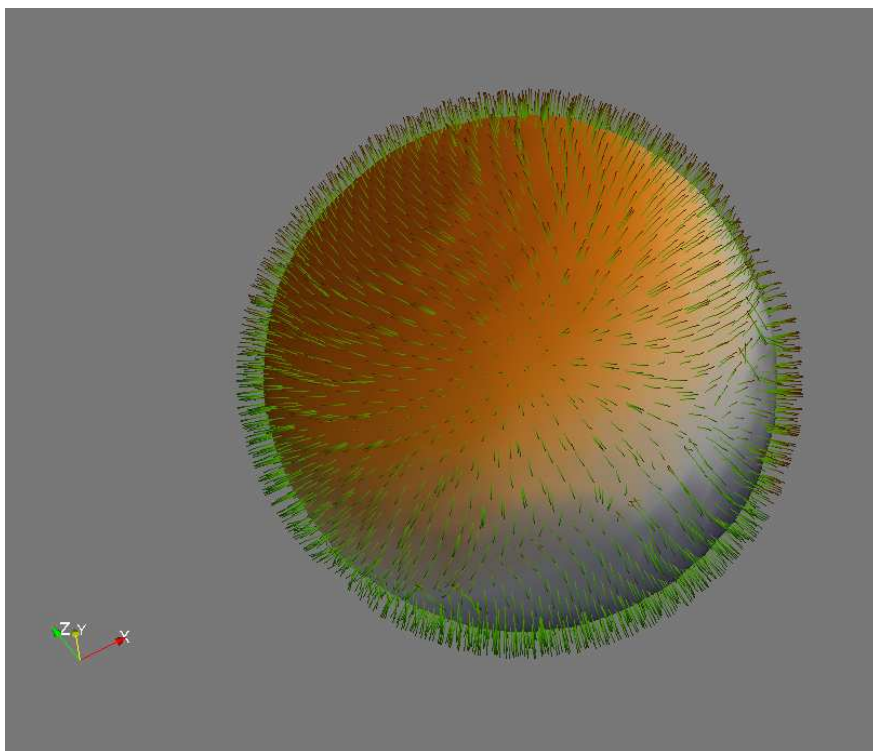


Figure 5.16: Profile of the director $\hat{\mathbf{n}}$ for $W = -0.08$, $L_1 = 0.001$. The contour is the isosurface $\phi = 0.6$ (Fig. 5.1f): the golden part is the half above the equator, the light violet part is the half below it.

ergy, mentioned at the end of Sec. 5.2.2. The director parallel to the interface in the equatorial zone, due to the presence of the Saturn ring, conflicts with the anchoring condition $W < 0$, which favours perpendicular anchoring. The imperfect homeotropic anchoring across the rest of the interface compensates this effect when $W = -0.04$, but is not able to compensate it when $W = -0.08$.

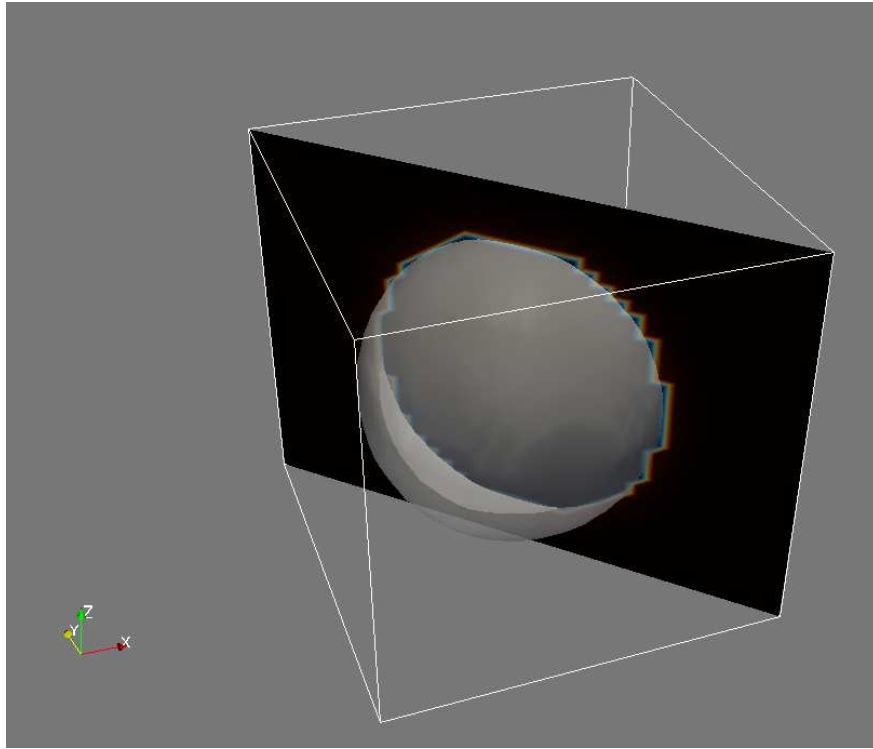


Figure 5.17: Section $y = x$ of the simulation box of an isotropic drop in a nematic matrix with interface anchoring coefficient $W = -0.04$, bulk elastic constant $L_1 = 0.00001$. The semi-transparent contour is the isosurface $\phi = 0.6$ (Fig. 5.1a).

- The profile of q , for the two cases discussed in the previous point, resembles a soccer ball (Fig. 5.19 for $W = -0.08$), which appears in the profiles of q at the same two values of the anchoring coefficient ($W = -0.04$ or -0.08), at $L_1 = 0.0001$, as well. With this low elastic constant, the Saturn ring is no more present: instead, the director profile (Figs. 5.17 and 5.18: plane $y = x$) is as weird as the analogous one for the two, two-dimensional combinations $W = -0.04, L_1 = 0.0001$ and $W =$

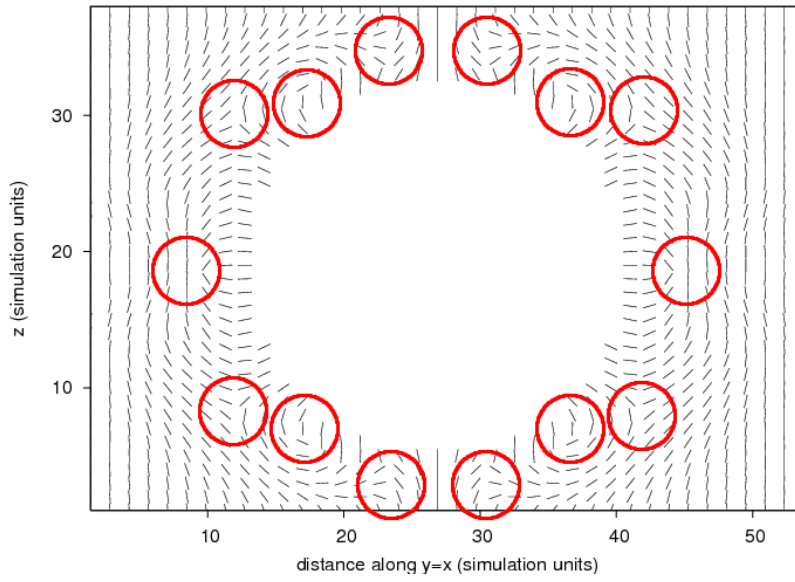


Figure 5.18: Profile of the nematic director for $W = -0.04$, $L_1 = 0.0001$, along the plane $y = x$. The red circles mark the defects.

-0.08 , $L_1 = 0.0001$ (Fig. 3.8), with a bunch of defects all around the interface.

- We can find several defects around the interface when $W = -0.133$, too, even though there is still the Saturn ring. The “satellite defects” are located especially on two circles, close to the interface, parallel to the xy plane.

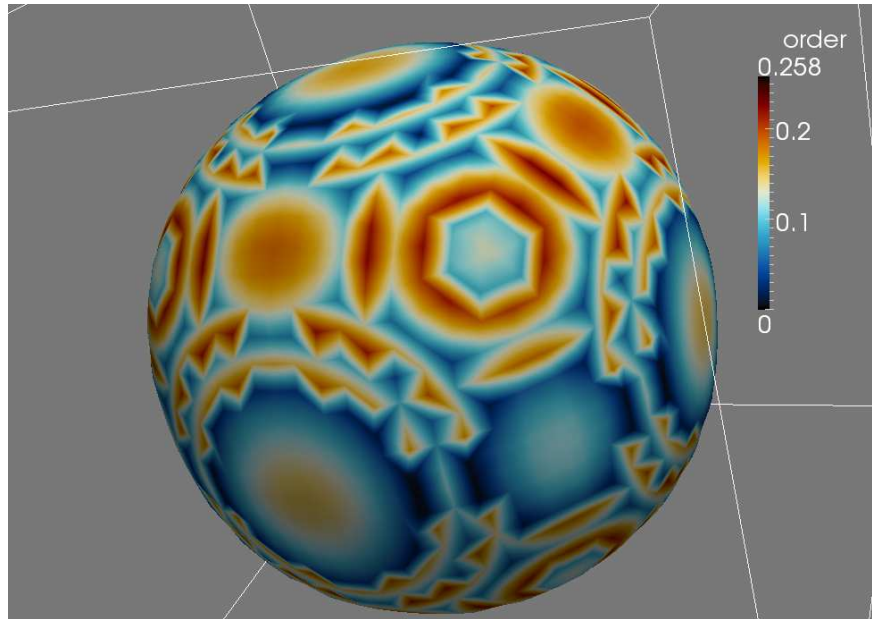


Figure 5.19: Isosurface $\phi = 0.6$ of an isotropic drop in a nematic matrix with interface anchoring coefficient $W = -0.08$, bulk elastic constant $L_1 = 0.0001$. The contour is colour-mapped, according to the scale on the right, to draw the profile of the scalar order parameter q across the interface.

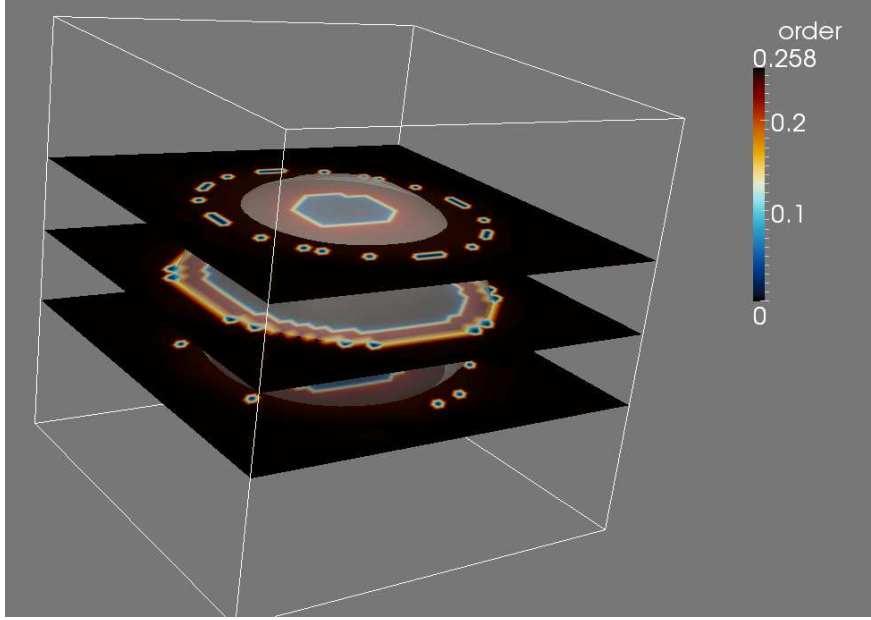


Figure 5.20: Sections $z = 13$, $z = 19$, $z = 26$ (lattice constants) of the simulation box of an isotropic drop in a nematic matrix with interface anchoring coefficient $W = -0.133$, bulk elastic constant $L_1 = 0.00001$. The semi-transparent contour is the isosurface $\phi = 0.6$ (Fig. 5.1i).

Chapter 6

Three-dimensional droplets under shear stress

As mentioned in the beginning of the previous chapter, the last part of this numerical study deals with three-dimensional isotropic drops hosted in a nematic phase and subject to a shear stress.

We can anticipate that, while often the two-dimensional drop under (small) shear behaves similarly to Newtonian drops (see Chapter 4), the three-dimensional case presents unexpected and peculiar features due to the complex interplay between the presence of defects and the shear field.

As in Chapter 4, we will examine a few (three) representative examples of three-dimensional droplets, each one corresponding to a different combination of the interface anchoring coefficient W (1.22) and nematic elastic constant L_1 (1.16). It is worth to remind that in all our simulations the interface energy coefficient K (1.19) is kept fixed at 0.1:

- $W = -0.133$, $L_1 = 10^{-4}$ (Sec. 6.2, page 133): here we are in the strong anchoring regime and at equilibrium, the droplet is surrounded both by a Saturn ring and by some “satellite defects”. In this case, under shear the droplet deforms with the velocity field, but the main disclination line (i.e. the Saturn ring) tends to stay still with respect to the flow, while the satellite defects disappear;
- $W = -0.04$, $L_1 = 10^{-4}$ (Sec. 6.3, page 138): at equilibrium the system displays many defects around the interface (a soccer ball-like profile of q across the interface). In this situation, under shear, the drop seems “pinned” to an imaginary defect inside it;
- $W = -0.04$, $L_1 = 10^{-2}$ (Sec. 6.4, page 141): here the anchoring is so weak that the equilibrium configuration shows no defects. On the other

hand the system under shear display planes of non negligible biaxiality that cross the whole supercell.

6.1 Parameters of the system and measured quantities

The boundary conditions imposed for the simulations of the three-dimensional droplets subject to a shear flow are the same as in the two-dimensional case, and treated in Sec. 4.1: periodic boundary conditions along x and y ; no-slip, bounce-back conditions at the walls, which are parallel to the xy plane; symmetric shear flow, with the upper wall moving parallel to the y axis with velocity $v > 0$, and the lower wall moving with the same velocity in the opposite direction. In this latter respect, since the size of the supercell, now, is $38 \times 38 \times 38$, the shear rate is $\dot{\gamma} = 2v/38$. According to the terminology of fluid mechanics, yz is the *shear plane* and x is the *vorticity direction*.

Apart from the overall size of the three-dimensional system (the radii of the droplets are smaller, as well), the other important difference with the simulations described in Chapters 3 and 4 concerns the starting configuration. Due to the longer time needed by the system to relax, I started every simulation either (low shear rates) from the equilibrium configuration of the system, or (high shear rates) from the final stationary configuration of a system with the same parameters but with a slightly lower shear rate.

In general, both for a Newtonian [113, 112, 14] and for a viscoelastic emulsion [13, 20], the deformation of the droplet occurs only along the shear plane and no observations (as far as we know) of a drop tilted along a different direction has been reported for such systems.

In our case, on the contrary, a nonzero tilt angle of the droplet towards the vorticity direction is observed: we will see later that this peculiar behaviour is the result of a complex interplay between the imposed velocity field and the defects which have a bigger inertia than the droplet to respond to the shear stress.

In order to measure the degree of deformation of a three-dimensional droplet under shear stress, we still approximate its shape by an ellipsoid. Moreover, besides the three Westin shape parameters $\{c_l, c_s, c_p\}$ (Sec. 5.1), we need to compute the polar and the azimuthal angles of each of the three axes of the ellipsoid.

For a better comparison with the two-dimensional case, instead of the usual definition of the polar angle (i. e. the angle formed with the z axis), we will quantify the orientation of the droplet in space through the angle

θ formed with the xy plane. Finally, since the shear direction is y and, in the Newtonian and viscoelastic case, the droplet would not be inclined with respect to y , we will use the word *azimuth* to denote the angle ψ formed by the droplet axis and the y axis, instead of the customary x axis.¹

6.2 $|W|/K = 1.33$, $L_1 = 10^{-4}$: oscillating, non-periodic states

Among all the systems studied in Chapter 5, the one characterized by a ratio $|W|/K = 1.33$ between the anchoring and the surface forces and by a bulk elastic constant $L_1 = 10^{-4}$ is the only one that corresponds to the strong anchoring regime where real defects are expected. Indeed, at equilibrium, the system displays a Saturn ring in the bulk encircling the equator of the droplet, whose shape is similar to an oblate spheroid.

In Sec. 4.3 we saw a two-dimensional example of an isotropic droplet with defects in the bulk, which only for a narrow interval of shear rates did not respond to the shear with oscillations in the free energy.

Here, on the contrary, for any value of the shear rate considered the long time states are oscillating and, as in the two-dimensional case, they do not display a perfect periodicity.

Figure 6.1 shows the drop shape under shear for the case considered in this section: with no shear (panel (a)), as we remember from Fig. 5.20, the droplet is surrounded by a well-defined Saturn ring and a set of “satellite defects”, located mostly on two circles parallel to the Saturn ring. When a weak shear stress is applied (panel (b)), the satellite defects essentially vanish. The Saturn ring, on the other hand, seems quite unaffected both by the shear flow and by the deformation of the droplet, which becomes prolate (see Fig. 6.4 for the shear-induced variations of the Westin shape parameters). In this respect, it is worth noticing that the rise of the prolateness c_l , when the shear rate increases, is compensated by a decrease of the degree of oblateness c_p . With few exceptions, one of the two parameters is always quite negligible, i. e. the droplet is always, approximately, a spheroid.

Moreover, except for the highest allowed values of the shear rate, where a “drop precession” (a sudden rise of the polar tilt angle θ , Sec. 4.2.2) is observed, the polar and the azimuthal tilt angles (since the droplet is prolate,

¹Maybe the attentive reader is wondering why, in these paragraphs, we never specified which of the three axes we are talking about. As we will see throughout the discussion, usually it is the major axis that characterizes the orientation of the droplet: in a bunch of cases, however, it is the intermediate one.

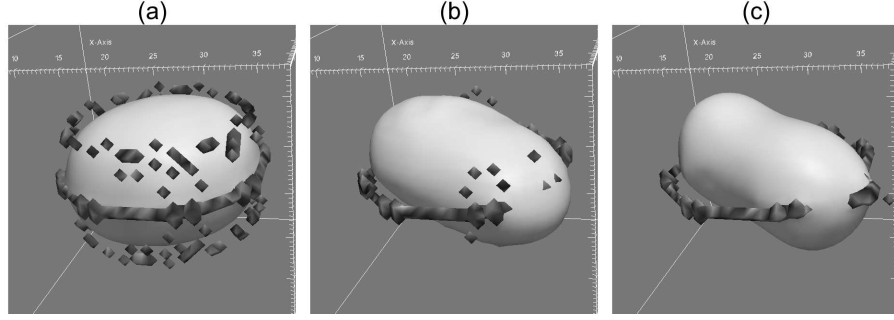


Figure 6.1: Isosurface of the nematic volume fraction $\phi = 0.6$ (white contour) of an isotropic droplet in a nematic matrix with anchoring vs. surface forces ratio $|W|/K = 1.33$ and nematic elastic constant $L_1 = 10^{-4}$ (Eqs. (1.22), (1.19),(1.16)), and isosurfaces of the scalar order parameter $q = 0.22$ (gray contours), (a) at equilibrium; (b) under a shear rate $\dot{\gamma} = 5.26 \cdot 10^{-5}$ ($Ca = 0.128$), (c) under a shear rate $\dot{\gamma} = 2.11 \cdot 10^{-4}$ ($Ca = 0.563$). The isosurfaces of q identify defects: we can see that, while the droplet extends, the Saturn ring remains approximately in its original position, whereas the satellite defects tend to vanish.

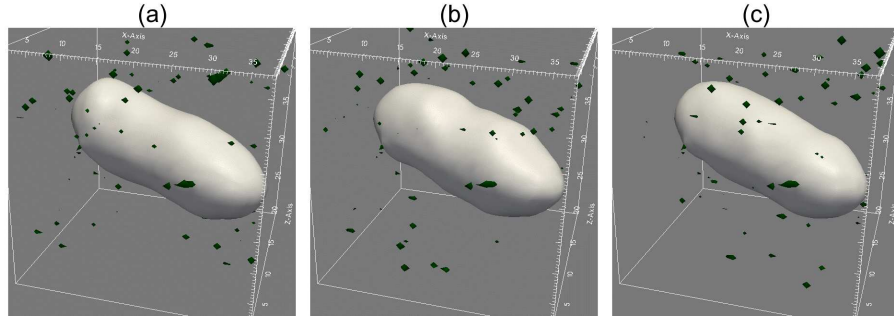


Figure 6.2: Isosurface of the nematic volume fraction $\phi = 0.6$ (white contour) of an isotropic droplet in a nematic matrix with anchoring vs. surface forces ratio $|W|/K = 1.33$ and nematic elastic constant $L_1 = 10^{-4}$ (Eqs. (1.22), (1.19),(1.16)), and isosurfaces of the biaxiality parameter $k_p = 0.02$ at three different instants, which are separated one from another by 10^4 hybrid LB iterations, under a shear rate $\dot{\gamma} = 1.18 \cdot 10^{-4}$ ($Ca = 1.552$).

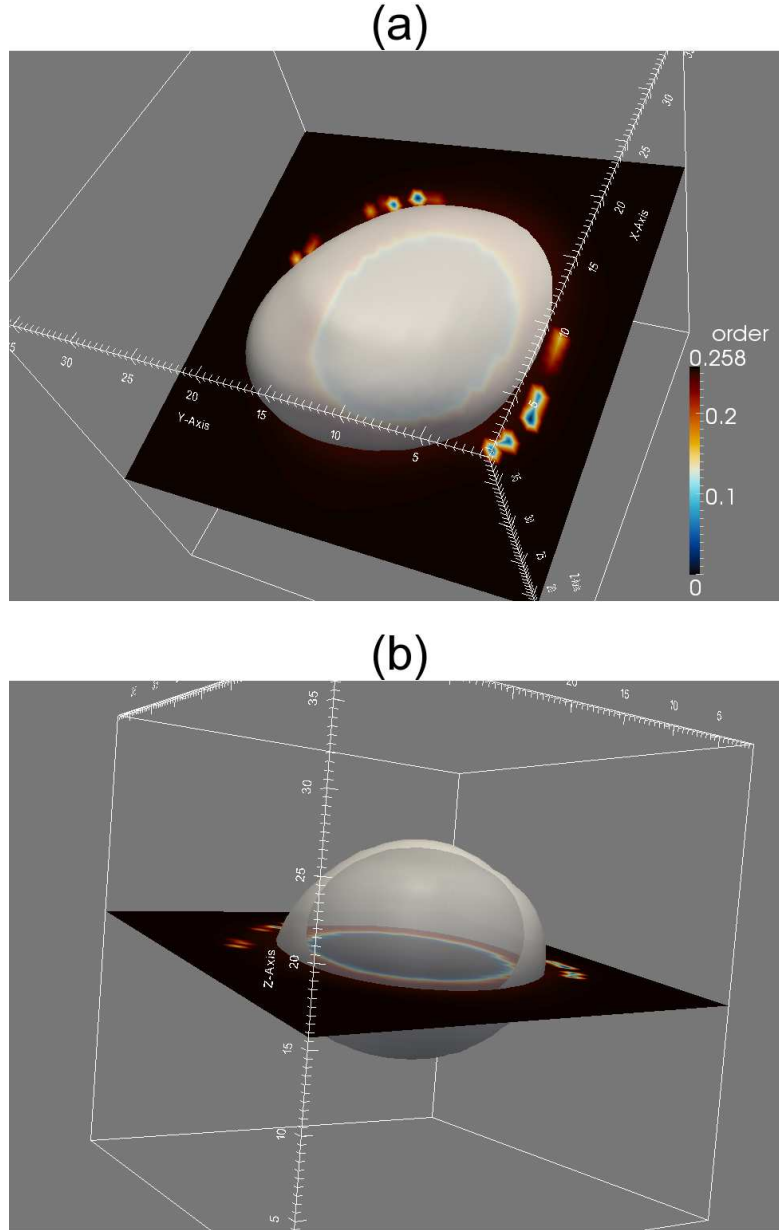


Figure 6.3: Isosurface of the nematic volume fraction $\phi = 0.6$ (white contour) of an isotropic droplet in a nematic matrix with anchoring vs. surface forces ratio $|W|/K = 1.33$ and nematic elastic constant $L_1 = 10^{-3}$ (Eqs. (1.22), (1.19),(1.16)), and profile (coloured map) of the plane containing the original Saturn ring, tilted by the shear stress, whose shear rate is $\dot{\gamma} = 5.26 \cdot 10^{-5}$ ($Ca = 0.651$).

we take the angles of the major axis) are approximately the same during the whole shear process and respectively equal to $\theta \approx 12.6^\circ$ and $\psi \approx 22.3^\circ$.

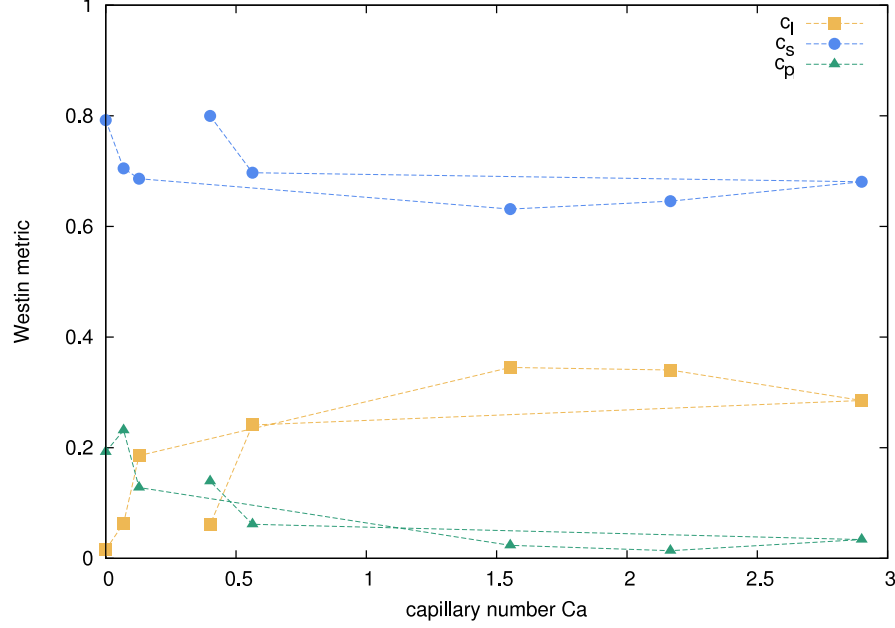


Figure 6.4: Westin shape parameters as functions of the capillary number for an isotropic droplet in a nematic matrix with anchoring vs. surface forces ratio $|W|/K = 1.33$ and nematic elastic constant $L_1 = 10^{-4}$ (Eqs. (1.22), (1.19), (1.16)). Following the dashed lines from the points on the left, we encounter points of increasing shear rate.

At low shear rate, as in the two-dimensional case, there are defects which move across the supercell, which are detectable by looking at the biaxiality parameter (Fig. 6.2), and which yield the fluctuations in the free energy.

Also when the shear rate is high (Fig. 6.1c), i. e. $\dot{\gamma} = 2.11 \cdot 10^{-4}$ the Saturn ring is still at its place (see for comparison Fig. 6.3 which shows a similar situation for $|W|/K = 1.33$, $L_1 = 10^{-3}$) whereas no satellite defects are observed. Remembering the discussion in Secs. 4.3 and 4.4, one could think that the energy should be stationary. Instead, it still fluctuates: presumably, the fluctuations are due to the conflict between the shear stress, which tends to align the nematic along a given direction² and the interface anchoring force, which tends to align it perpendicularly to the droplet surface. Fig. 6.5 shows the profile of the nematic director at different times: one can see signals

²The Leslie-Ericksen theory predicts a tilt angle $\arctan \sqrt{\alpha_3/\alpha_2}$ (Sec. 2.2).

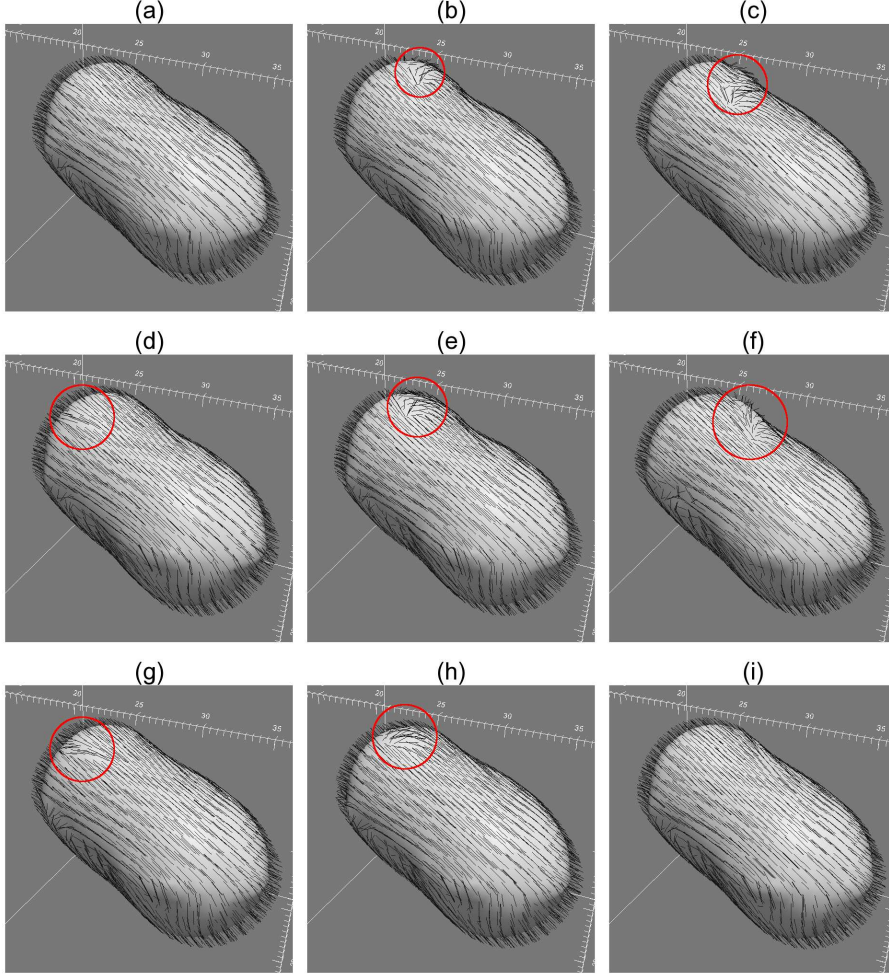


Figure 6.5: Profile of the director field on the isosurface of the nematic volume fraction $\phi = 0.6$ (white contour) of an isotropic droplet in a nematic matrix with anchoring vs. surface forces ratio $|W|/K = 1.33$ and nematic elastic constant $L_1 = 10^{-4}$ (Eqs. (1.22), (1.19),(1.16)), at nine successive instants separated by 10^4 hybrid LB iterations, under a shear rate $\dot{\gamma} = 2.11 \cdot 10^{-4}$ ($Ca = 0.563$).

of frustration in the nematic orientation, in a little region of the interface, which yield oscillations in the free energy.

6.3 $|W|/K = 0.4$, $L_1 = 10^{-4}$: “pinning” at an imaginary defect

Despite all the peculiarities of a liquid crystalline substance, in Sec. 6.2, where we have described the behaviour of a liquid crystal emulsion which, at rest, is in the strong anchoring regime ($F_{ai}R/L_1\Sigma \gg 1$), we saw the deformation of the droplet shape by shear stress (Fig. 6.4) as expected from our knowledge of ordinary liquids [112].

The behaviour of a droplet under shear with the same elastic constant the before ($L_1 = 10^{-4}$) but a much smaller ratio $|W|/K$ is in some way less predictable, although few similarities can be found with the previous case.

The process can be basically summarized by relying on Fig. 6.6: at equilibrium, since both the surface anchoring and the nematic elastic forces are weak, the droplet is spherical, being dominated by the surface tension (Sec. 5.2.1). The director field, at equilibrium, has many defects around the interface (Fig. 5.18) and that yields the “soccer ball-like” profile of q (Fig. 6.6a).

After turning the shear stress on, the “soccer ball-like” profile looks smeared (Fig. 6.6b). Not shown in the picture are some distortions in the nematic – detectable, as in the case studied in Sec. 6.2, by an analysis of the profile of the biaxiality – which move across the supercell, causing noise in the time evolution of the free energy.

Unlike the strong anchoring case, however, the shear stress does not make the droplet prolate. At least for low shear rate (Fig. 6.7), it is only the oblateness parameter c_p that increases: only when the shear rate is sufficiently large, and the isotropic droplet is about to dissolve into the nematic phase (shift of the nematic-isotropic transition point induced by shear), the prolateness parameter c_l increases slightly. On the other hand, with this particular combination of physical parameters, the approximation of the drop shape as an ellipsoid is not as good as before. The reason of this behaviour (and the reason why c_p grows so much, too) is the “pinning” of the droplet at a plane, parallel to the xy plane and located halfway between the two walls sandwiching the system. This effect is observed for every value of the shear rate and is clearer if we look at the droplet from a view direction parallel to the xy plane (Fig. 6.6e).

By looking at the profile of the biaxiality parameter k_p (Figs. 6.6e,f) (see

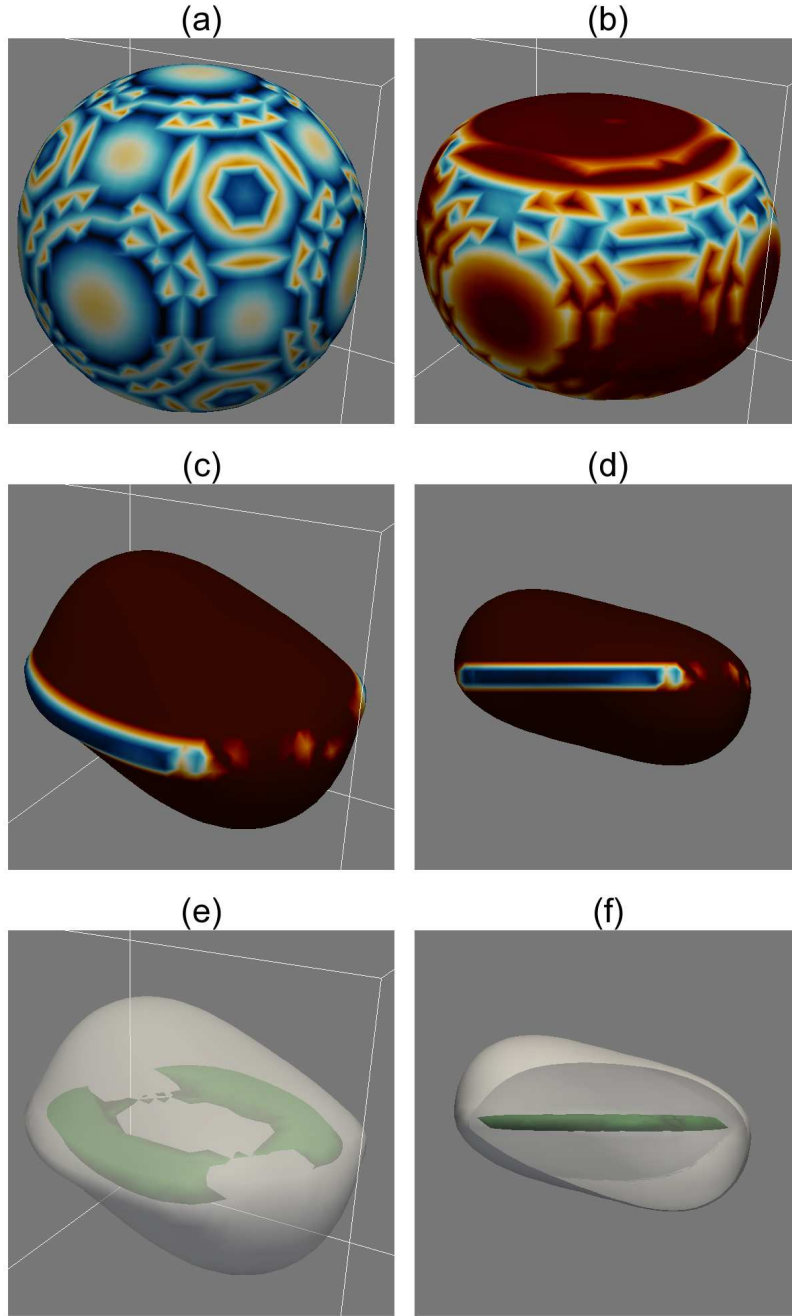


Figure 6.6: (a) Isosurface of the nematic volume fraction $\phi = 0.6$ of an isotropic droplet in a nematic matrix with anchoring vs. surface forces ratio $|W|/K = 0.4$ and nematic elastic constant $L_1 = 10^{-2}$ (Eqs. (1.22), (1.19),(1.16)), at equilibrium; (b) under a shear rate $\dot{\gamma} = 5.26 \cdot 10^{-5}$ ($Ca = 0.167$); (c) under a shear rate of $\dot{\gamma} = 2.11 \cdot 10^{-4}$ ($Ca = 0.540$); (d) same as (c), lateral view; (e) same as (c), with the isosurface $k_p = 0.02$ in green; (f) same as (e), lateral view. The scale of the colour map on panels (a), (b) and (c) is the same as in Fig. 5.19.

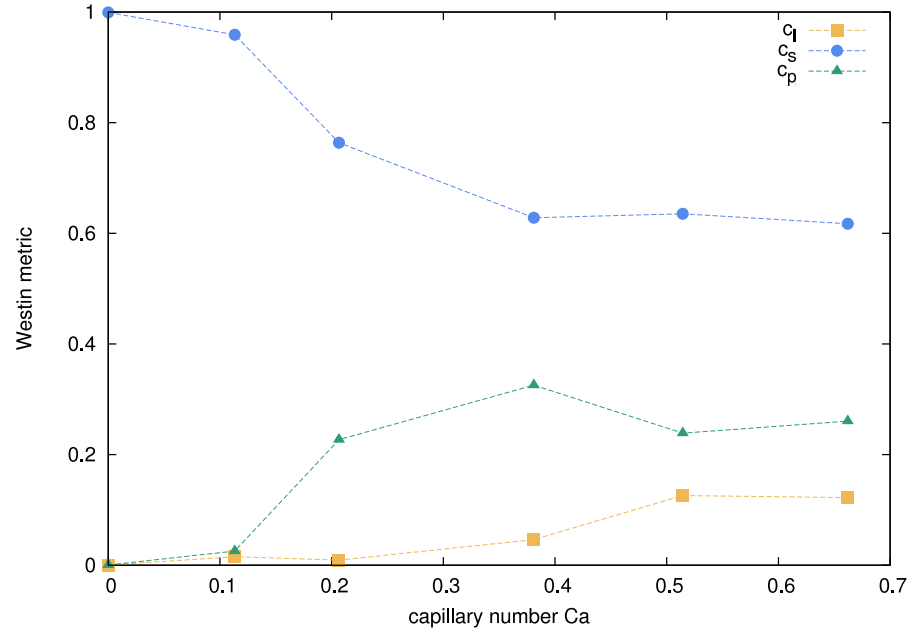


Figure 6.7: Westin shape parameters as functions of the capillary number for an isotropic droplet in a nematic matrix with anchoring vs. surface forces ratio $|W|/K = 0.4$ and nematic elastic constant $L_1 = 10^{-4}$ (Eqs. (1.22), (1.19), (1.16)). Following the dashed lines from the points on the left, we encounter points of increasing shear rate.

Sec. 1.7.2), one can notice a considerably wide region, under the surface of the droplet and extending exactly across the horizontal plane at the centre of the supercell, where the biaxiality is nonnegligible – the green contour in Figs. 6.6e,f corresponds to $k_p = 0.02$. Note that in other pictures such as Fig. 5.1, we had chosen $k_p = 0.007$ to identify a defect.

This situation is another example of “imaginary defect” inside the droplet: as the real Saturn ring seen in the previous case, this imaginary line of defects does not move with the flow field. Another similarity with the case described in Sec. 6.2 is the regularity of the tilt angles: here, $\theta \approx 11.9^\circ$ and $\psi \approx 62.5^\circ$. Note that while the stronger anchoring conditions allows the interface to move rather independently (Sec. 6.2) from the Saturn ring, in this case the imaginary defect seems to hinder its deformation.

6.4 $|W|/K = 0.4$, $L_1 = 10^{-2}$: “hornet-like” states

The last case that we are going to examine concerns an isotropic drop whose interface anchoring coefficient (1.22) is $W = -0.04$ and bulk elastic constant $L_1 = 0.01$ (1.16).

At equilibrium, this system is in the low anchoring regime ($F_{ai}R/L_1\Sigma = 3.904 \cdot 10^{-3}$) and the nematic maintains, substantially, the originally imposed orientation, that in our case is parallel to the z axis throughout the whole supercell. As said in Sec. 5.2.3, and as you can see in Figs. 6.9 (panels (a) and (b)), the nematic is quite perfectly parallel to z everywhere, even though the anchoring term of the free energy (1.22) favours an anchoring perpendicular to the interface.

I said *quite* perfectly, and the reason becomes clear if we look at Fig. 6.9b. At page 123, we discussed the “wrapping” of the nematic near the poles of the drop, due to the competition between anchoring and elastic forces. We focused on this feature for $L_1 = 10^{-3}$, but it occurs, to a smaller extent, for $L_1 = 10^{-2}$, as well.

When a shear stress is applied, it induces a stretching and a counterclockwise rotation of the interface (see the the panels in the right-hand column of Fig. 6.9, where the drop is shown from above). This latter feature occurred also in the two cases treated in Secs. 6.2 and 6.3: ψ , the azimuthal tilt angle (calculated with respect to the y axis, the shear direction), was positive.

If the shear stress is very weak, the droplet is simply tilted (Fig. 6.8a). But it is sufficient a shear rate $\dot{\gamma} = 5.26 \cdot 10^{-5}$ and the equilibrium breaks: the system tumbles down into a new state where the droplet is stretched quite perpendicularly, with respect to the weak-shear bending direction, becoming considerably scalene (see Fig. 6.11 for the variation of the shape parameters

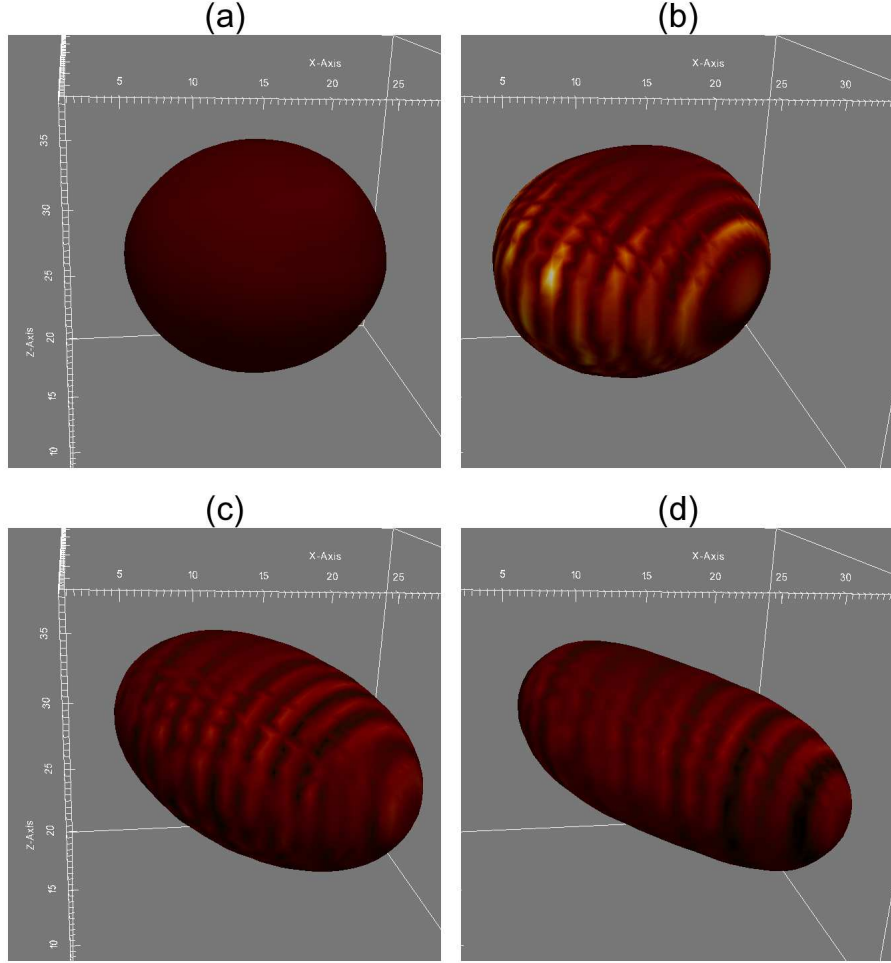


Figure 6.8: Isosurface of the nematic volume fraction $\phi = 0.6$ of an isotropic droplet in a nematic matrix with anchoring vs. surface forces ratio $|W|/K = 0.4$ and nematic elastic constant $L_1 = 10^{-2}$ (Eqs. (1.22), (1.19), (1.16)): (a) under a shear rate $\dot{\gamma} = 2.6 \cdot 10^{-5}$ ($\text{Ca} = 0.560$); (b) under a shear rate $\dot{\gamma} = 5.26 \cdot 10^{-5}$ ($\text{Ca} = 0.212$); (c) under a shear rate of $\dot{\gamma} = 1.31 \cdot 10^{-4}$ ($\text{Ca} = 3.412$); (d) under a shear rate of $\dot{\gamma} = 2.11 \cdot 10^{-4}$ ($\text{Ca} = 5.873$)

defined in Sec. 5.1) and a colour map of the scalar order parameter q across the interface (Fig. 6.8b) reminds us of the body of a hornet. For this reason, I call this state “**hornet-like**”.

In Fig. 6.9 we can see the transition from the original configuration to the hornet-like configuration. The argument according to which this transition is induced by the tendency of the nematic to “wrap” around the poles of the droplet, frustrated by the shear stress, is based on the fact that it begins near the poles (panels (e)-(f)), extending, later, to the whole surface. And not only to the surface: the profile of the biaxiality parameter k_p , in Fig. 6.10, reveals planes on non-negligible biaxiality which cross the whole supercell, such that the “stripes” of the hornet-like profile of q across the surface are the intersections of those planes with it.

By increasing the shear rate further, the shear-induced bending becomes stronger and the droplet assumes a cigar-like shape (Figs. 6.8c, d), maintaining the hornet-like profile of q . When the shear rate is big enough it aligns the director uniformly along a given direction – according to Leslie-Ericksen theory (Sec. 2.2), the angle formed by the director and the flow direction is $\arctan \sqrt{\alpha_3/\alpha_2}$, and with our parameters (Table 2.2 it is $\approx 30.3^\circ$ – and the profile of q is regular again (Fig. 6.12).

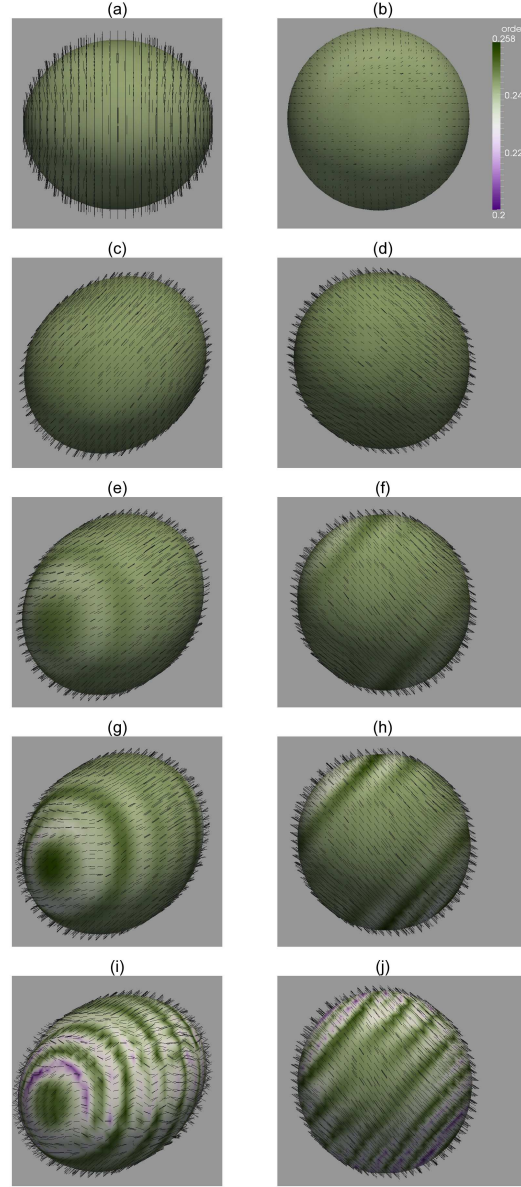


Figure 6.9: Snapshots of the time evolution of the isosurface of the nematic volume fraction $\phi = 0.6$ and of the director field $\hat{\mathbf{n}}$, across the isosurface, of an isotropic droplet in a nematic matrix with anchoring vs. surface forces ratio $|W|/K = 0.4$ and nematic elastic constant $L_1 = 10^{-2}$ (Eqs. (1.22), (1.19), (1.16)), under a shear rate $\dot{\gamma} = 7.89 \cdot 10^{-5}$ ($\text{Ca} = 0.212$; it is smaller than for $\dot{\gamma} = 5.26 \cdot 10^{-5}$ because of a fall of the surface tension). Panels (a), (c), (e), (g), (i): snapshots at, respectively, $t = 0$ (equilibrium), $t = 10^4$, $t = 1.7 \cdot 10^4$, $t = 1.8 \cdot 10^4$, $t = 2.0 \cdot 10^4$ hybrid LB iterations; direction of view parallel to the x axis. Panels (b), (d), (f), (h), (j): snapshots at, respectively, the same instants as the panels on the left-hand side, seen from a direction of view parallel to the z axis.

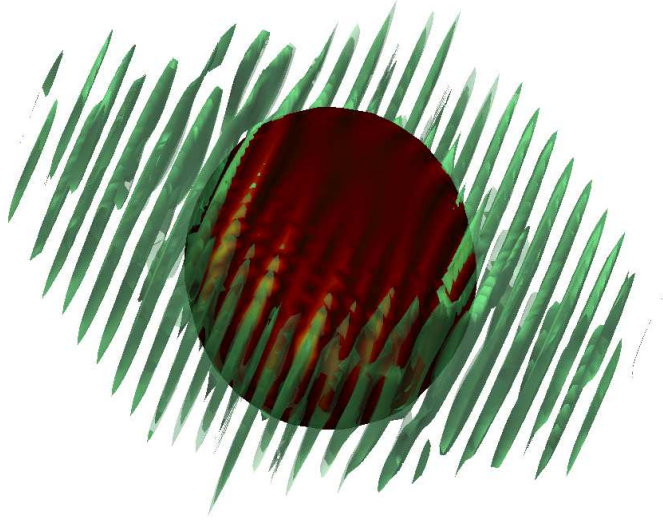


Figure 6.10: Black/red: isosurface $\phi = 0.6$ of a three-dimensional isotropic droplet inside a nematic matrix, with initial radius 14 (LB cells), elastic constant $L_1 = 0.01$, anchoring coefficient $W = -0.04$ and shear rate $\dot{\gamma} = 5.26 \cdot 10^{-5}$. Red areas correspond to lower q ($0.112 \div 0.2$, where the maximum value is 0.258). Green, semi-transparent: isosurfaces of k_p (biaxiality, see Sec. 1.7.2) $= 0.008$. The direction of view is parallel to the isosurfaces of k_p .

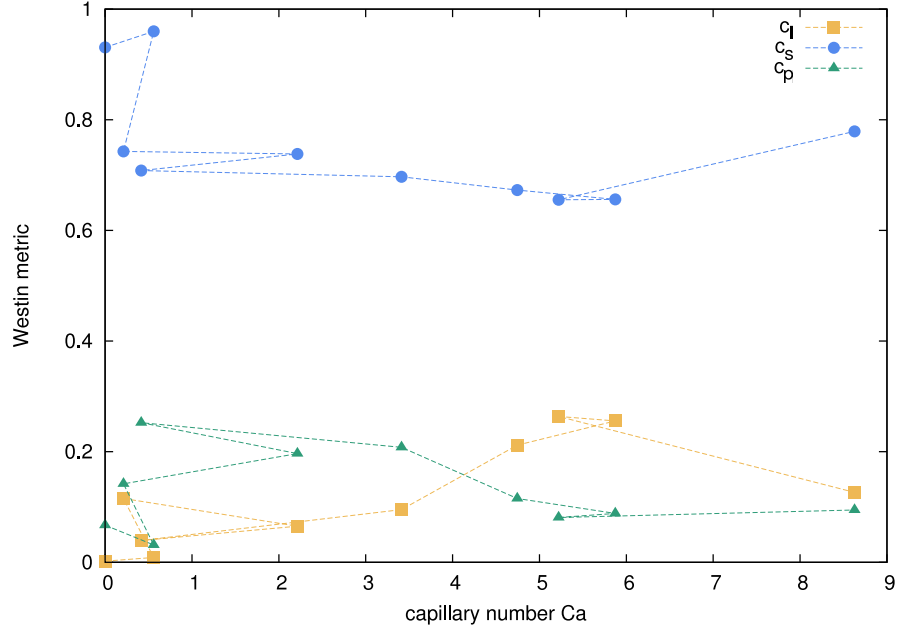


Figure 6.11: Westin shape parameters as functions of the capillary number for an isotropic droplet in a nematic matrix with anchoring vs. surface forces ratio $|W|/K = 0.4$ and nematic elastic constant $L_1 = 10^{-2}$ (Eqs. (1.22), (1.19),(1.16)). Following the dashed lines from the points on the left, we encounter points of increasing shear rate.

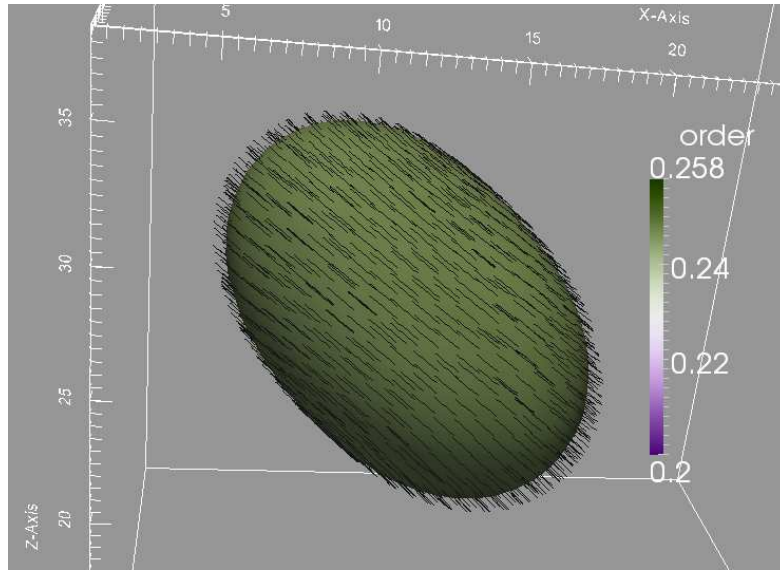


Figure 6.12: Isosurface of the nematic volume fraction $\phi = 0.6$, and profile of the director field $\hat{\mathbf{n}}$ across it, of an isotropic droplet in a nematic matrix with anchoring vs. surface forces ratio $|W|/K = 0.4$ and nematic elastic constant $L_1 = 10^{-2}$ (Eqs. (1.22), (1.19),(1.16)), under a shear rate $\dot{\gamma} = 2.37 \cdot 10^{-4}$ ($\text{Ca} = 8.627$).

Conclusions

In this thesis I have studied the behaviour of a two-dimensional and a three-dimensional drop of isotropic phase in coexistence with the nematic phase of a liquid crystal system. In particular, I have been interested in looking at how some physical parameters such as the elastic energy of the nematic, the surface tension of the drop and the anchoring energy of the nematic at the drop surface may influence the equilibrium properties and the response under shear of the system described in terms of the drop shape and the orientation of the nematics.

Unlike the more studied systems of Newtonian and viscoelastic emulsions, inverted nematic emulsions have additional degrees of freedom such as the local orientation of the nematic phase that induces further stress at the interface of the droplet. That affects, sometimes in a quite unpredictable way, the overall behaviour of the system.

Because of its extreme richness, inverted nematic emulsions are quite complicated to be described and studied properly, and I had to rely on numerical simulations based on the hybrid Lattice Boltzmann algorithm that in the past has been proved to be very efficient in simulating liquid crystals systems.

The equilibrium shapes of a two-dimensional droplet (Chapter 3), simulated at different values both of the coefficient governing the nematic anchoring at the nematic-isotropic interface W (1.22) and of the bulk elastic constant L_1 (1.16) which quantifies the energy cost of the distortions in the nematic phase, are coherent with the results and the observations of Sulaiman *et al.* [34], to which this work was inspired.

To a smaller extent, the results of the simulations are also comparable with the ones obtained using the simple theoretical model of Lishchuk and Care [100], the deviations being due to the strong approximations assumed in [100] to allow analytical computations.

The competition between the surface tension, the interface anchoring energy and the nematic elastic forces is the key to explain both the different shapes of the droplets and the presence (or the absence) of defects in the

nematic phase. Some particularly distorted shapes, moreover, have been explained in terms of the presence of “imaginary defects” located in proximity of the droplet interface, i. e. strong local distortions of the nematic orientation in a region where both nematic and isotropic phases coexist.

These arguments have been particularly valid also to interpret the results of the three-dimensional droplets at equilibrium (Chapter 5) that have been simulated using the same set of parameters used in the two-dimensional case. When the anchoring is strong enough, the geometry of the observed defects matches the one found both in the experiments of Poulin and Weitz [26] on inverted emulsions and in system of colloidal suspensions in nematic phases, although in this case the particles (colloids) cannot be deformed by the surrounding nematic.

The application of a shear flow, both to a two-dimensional and to a three-dimensional emulsion, confirmed the extreme richness and complexity of an inverted nematic emulsion in responding to an external ordering field. In two dimensions (Chapter 4), similarities with an emulsion of Newtonian or viscoelastic fluids were found only when the particular combination of the physical parameters neither yielded defects nor a sufficiently strong anchoring at the interface, so the system was essentially governed by the shear stress and the surface tension.

On the other hand, when the values of the parameters considered gave rise to defects (either real or imaginary) in the systems, several interesting and novel features have been observed.

In particular, it turns out that defects have a stronger tendency to oppose to the shear flow than the droplet. This inertial difference gives rise to several features such as the oscillation of the free energy and of other observables that characterize the response of the system under shear (pulsating states). More precisely, when the bulk elastic constant is particularly small, the defects, either real (i. e. within the bulk) or imaginary (i. e. at the droplet interface) tend to maintain their original positions in the system and remain undeformed; this is true with almost any value of the shear rate considered. The defects in this case act as pinning points for the drop that deforms accordingly. When the bulk elastic constant is larger, the competition between the shear stress, the anchoring strength and the elastic forces is stronger at the poles of the droplet, and the system acquires a new stationary state, characterized by a “hornet-like” profile of the scalar order parameter across the interface.

Another interesting feature that we have observed is that, unlike simple fluid emulsion, the three-dimensional droplets in our simulations present deformations not only along the shear direction but also along the vorticity direction (Chapter 6). This feature that, as far as we know, has not been

observed yet, should be the result of a complex interplay between the orientational field of the shear and the arrangement of the nematic anchored at the drop surface. Further investigations are however necessary to better understand this response to the shear that has no counterparts in simple emulsions.

Since this is the first numerical study on the response of two- and three-dimensional inverted nematic emulsions under shear, the results that have been obtained have certainly furnished more questions than answers, and additional investigations are necessary. In particular it would be nice to better explore the stability of the pulsating states and the deformation/orientation of the droplet along the vorticity direction. Another issue that has not been explored here is the phenomenology that can occur when, instead that flow aligning, a flow tumbling nematic is considered.

Appendix A

Summary of the derivation of the Beris-Edwards equations of nematodynamics

N. B. This appendix is a recap of Sec. 11.5 of Beris and Edwards's book [38]. Here, I adopt the same notation adopted by the authors, which is a lot different from the notation adopted throughout the rest of this thesis.

The dynamics of a liquid crystal, because of its anisotropy above all, is much more complicated than the dynamics of a simple fluid; and is much more complicated than the statics of a liquid crystal at rest, too.

In my simulations, I refer to the **conformation tensor theory** [38, 71], developed in the early 1990s by A. N. Beris, B. J. Edwards and M. Grmela. It describes the dynamics of the liquid crystals in terms of a generalized Hamiltonian formulation.

The $\{\mathbf{q}, \mathbf{p}\}$ (coordinates and conjugate momenta) of the classical Hamiltonian theory are replaced, here, with the velocity vector $\mathbf{v}$, and two tensor fields, $\mathbf{m}$ and $\mathbf{w}$.

$\mathbf{m}$ is the structure tensor; $w_{\alpha\beta} \equiv \sigma^m \dot{m}_{\alpha\beta}$ where the dot denotes the material derivative; and σ^m is an inertial constant.

$\mathbf{m}$, here, satisfies the constraint $m_{\alpha\alpha} = 1$, so the usual tensor order parameter (Eq. (1.2)) does not suit fine: instead, it can be the Westin tensor defined in Sec. 1.7.2.

An arbitrary functional of these fields can be written as:

$$F[\mathbf{v}, \mathbf{m}, \mathbf{w}] \equiv \int_{\Omega} f(\mathbf{v}, \mathbf{m}, \nabla \mathbf{m}, \mathbf{w}) d^3x \quad (\text{A.1})$$

where Ω is the phase space. Its dynamical equation is:

$$\begin{aligned} \frac{dF}{dt} &= \int_{\Omega} \left[\frac{\delta F}{\delta \mathbf{v}} \cdot \frac{\partial \mathbf{v}}{\partial t} + \frac{\delta F}{\delta \mathbf{m}} : \frac{\partial \mathbf{m}}{\partial t} + \frac{\delta F}{\delta \mathbf{w}} : \frac{\partial \mathbf{w}}{\partial t} \right] \\ &= \{F, H_m\} + [F, H_m] \end{aligned} \quad (\text{A.2})$$

H_m is the Hamiltonian: the first term on the last line of Eq. (A.2) is a Poisson bracket, defined as an extension of the classical Poisson bracket (it has to be bilinear and antisymmetric, and to satisfy the Jacobi identity); the second term accounts for dissipation [72].

The Hamiltonian is given by:

$$H_m[\mathbf{v}, \mathbf{m}, \mathbf{w}] \equiv \int_{\Omega} \left[\frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} + \frac{1}{2\sigma^m} \mathbf{w} : \mathbf{w} + W + \Psi_m \right] d^3x + H_b[\mathbf{m}] \quad (\text{A.3})$$

In the square brackets, we recognize the first two terms as, respectively, a kinetic translational term and a kinetic rotational term. W is defined as:

$$W \equiv \frac{1}{2} b_1 (\partial_{\gamma} m_{\alpha\beta}) (\partial_{\gamma} m_{\alpha\beta}) + \frac{1}{2} b_2 (\partial_{\alpha} m_{\alpha\beta}) (\partial_{\gamma} m_{\gamma\beta}) \quad (\text{A.4})$$

where b_1 and b_2 are constants. It reduces easily to the Frank-Oseen distortion energy (1.14).

Ψ_m contains the effect of the magnetic field¹ $\mathbf{B}$, and H_b is the bulk free energy, which Beris and Edwards take as the Landau-de Gennes energy (1.4).

After defining the Poisson and the dissipation bracket, it is possible to write the functional derivatives of the Hamiltonian with respect to the three variable fields; the derivation of the evolution equation of the fields is straightforward.

The next step consists in taking the limit $\sigma^m \rightarrow 0$. In a previous section of [38], the authors took this approximation for the continuum-mechanic Leslie-Ericksen model, which was initially (early 1960s) developed in an inertial form, on the following ground: *for very viscous materials, in which rotation of the director is largely inhibited, this approximation is probably not overly restrictive.*

In (A.1) and (A.2), the tensor $\mathbf{w}$ and the rotational term respectively disappear.

¹Denoting it with $\mathbf{B}$ is a little abuse, because it is the H-field, in fact. I use $\mathbf{B}$ to avoid confusion with the Hamiltonian.

Just for information (I am not willing to get into details of the calculations), I am giving you the form of the Poisson bracket of two functionals $\{F, G\}$ depending on a vector field and a tensor field. Here, the tensor field $\mathbf{m}$ is taken as unconstrained (actually, it is: $m_{\alpha\alpha} = 1$).

$$\begin{aligned} \{F, G\} = & - \int_{\Omega} v_{\alpha} \left[\frac{\delta F}{\delta v_{\gamma}} \partial_{\gamma} \frac{\delta G}{\delta v_{\alpha}} - \frac{\delta G}{\delta v_{\gamma}} \partial_{\gamma} \frac{\delta F}{\delta v_{\alpha}} \right] d^3x \\ & - \int_{\Omega} m_{\alpha\beta} \left[\frac{\delta F}{\delta v_{\gamma}} \partial_{\gamma} \frac{\delta G}{\delta m_{\alpha\beta}} - \frac{\delta G}{\delta v_{\gamma}} \partial_{\gamma} \frac{\delta F}{\delta m_{\alpha\beta}} \right] d^3x \\ & - \int_{\Omega} m_{\alpha\gamma} \left[\partial_{\gamma} \left(\frac{\delta F}{\delta v_{\beta}} \right) \frac{\delta G}{\delta m_{\alpha\beta}} - \partial_{\gamma} \left(\frac{\delta G}{\delta v_{\beta}} \right) \frac{\delta F}{\delta m_{\alpha\beta}} \right] d^3x \\ & - \int_{\Omega} m_{\beta\gamma} \left[\partial_{\gamma} \left(\frac{\delta F}{\delta v_{\alpha}} \right) \frac{\delta G}{\delta m_{\alpha\beta}} - \partial_{\gamma} \left(\frac{\delta G}{\delta v_{\alpha}} \right) \frac{\delta F}{\delta m_{\alpha\beta}} \right] d^3x \end{aligned} \quad (\text{A.5})$$

The dissipation bracket, instead, is:

$$\begin{aligned} [F, G] = & - \int_{\Omega} R_{\alpha\beta\gamma\epsilon}^m \partial_{\alpha} \left(\frac{\delta F}{\delta v_{\beta}} \right) \partial_{\gamma} \left(\frac{\delta G}{\delta v_{\epsilon}} \right) d^3x \\ & - \int_{\Omega} P_{\alpha\beta\gamma\epsilon}^m \frac{\delta F}{\delta m_{\alpha\beta}} \frac{\delta G}{\delta m_{\gamma\epsilon}} d^3x \\ & - \int_{\Omega} L_{\alpha\beta\gamma\epsilon}^m \left[\partial_{\alpha} \left(\frac{\delta F}{\delta v_{\beta}} \right) \frac{\delta G}{\delta m_{\gamma\epsilon}} - \partial_{\alpha} \left(\frac{\delta G}{\delta v_{\beta}} \right) \frac{\delta F}{\delta m_{\gamma\epsilon}} \right] d^3x \\ & - \int_{\Omega} L_{\eta\zeta\gamma\epsilon}^m m_{\alpha\beta} \left[\partial_{\eta} \left(\frac{\delta F}{\delta v_{\zeta}} \right) \frac{\delta G}{\delta m_{\alpha\beta}} - \partial_{\eta} \left(\frac{\delta G}{\delta v_{\zeta}} \right) \frac{\delta F}{\delta m_{\alpha\beta}} \right] d^3x \end{aligned} \quad (\text{A.6})$$

where $R_{\alpha\beta\gamma\epsilon}^m$, $P_{\alpha\beta\gamma\epsilon}^m$ and $L_{\alpha\beta\gamma\epsilon}^m$ are (phenomenological) tensors which are linear combinations of powers of the $m_{\alpha\beta}$'s, with eight parameters: $\{\beta_1^m, \dots, \beta_8^m\}$.

Using (A.2), we can write the equations of motion of $\mathbf{v}$ and $\mathbf{m}$:

$$\dot{v}_{\alpha} = F_{\alpha}^m - \partial_{\alpha} P - \partial_{\beta} \left(\partial_{\alpha} m_{\gamma\epsilon} \frac{\partial W}{\partial (\partial_{\beta} m_{\gamma\epsilon})} \right) + \partial_{\beta} T_{\alpha\beta}^m \quad (\text{A.7})$$

$$\begin{aligned} \dot{m}_{\alpha\beta} = & - \frac{1}{\beta_7^m} \left[\frac{\delta H_m}{\delta m_{\alpha\beta}} + 3m_{\gamma\epsilon} \frac{\delta H_m}{\delta m_{\gamma\epsilon}} \left(m_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \right) \right] \\ & + \frac{1 + \beta_8^m}{2} [m_{\alpha\gamma} \partial_{\gamma} v_{\beta} + m_{\beta\gamma} \partial_{\gamma} v_{\alpha}] \\ & - \frac{1 - \beta_8^m}{2} [m_{\alpha\gamma} \partial_{\beta} v_{\gamma} + m_{\beta\gamma} \partial_{\alpha} v_{\gamma}] \\ & - 2\beta_8^m m_{\alpha\beta} m_{\gamma\epsilon} \partial_{\epsilon} v_{\gamma} \end{aligned} \quad (\text{A.8})$$

in which $F_\alpha^m = \chi_a B_\beta \partial_\alpha B_\gamma m_{\beta\gamma}$ is the magnetic force vector (χ_a is the magnetic susceptibility parallel to $\hat{\mathbf{n}}$, and $\mathbf{T}$ is the extra stress:

$$\begin{aligned} T_{\alpha\beta}^m = & R_{\beta\alpha\gamma\epsilon}^m A_{\gamma\epsilon} + (\beta_8^m + 1) m_{\beta\gamma} \frac{\delta H_m}{\delta m_{\gamma\alpha}} \\ & + (\beta_8^m - 1) m_{\alpha\gamma} \frac{\delta H_m}{\delta m_{\gamma\beta}} \\ & - 2\beta_8^m m_{\alpha\beta} m_{\gamma\epsilon} \frac{\delta H_m}{\delta m_{\gamma\epsilon}} \end{aligned} \quad (\text{A.9})$$

with $\mathbf{A}$ the velocity gradient tensor.

Of course, (A.7) is a Navier-Stokes equation: the coupling with the tensor order parameter is evident, as well as the influence of the velocity field in the evolution of $\mathbf{m}$ (A.8).

This coupling is known as the **backflow effect** and is a peculiar feature of liquid crystals.

In the inertial form of the theory, as well, there were eight phenomenological parameters $\{\alpha_1^m, \dots, \alpha_8^m\}$: the β_i^m 's can be set as function of the α_i^m 's in order that the inertial form and the non-inertial form match at $\sigma^m \rightarrow 0$.

These parameters play the same role as the six (although only five of them are independent) α_i 's of the famous Leslie-Ericksen model, based on a continuum theory for a perfectly uniaxial nematic. The α_i 's are related to quantities which can be experimentally measured, relatively easily: for example, the Mięsowicz viscosities, i. e. the viscosities of a fully oriented nematic sandwiched between two parallel walls and subject to a shear flow, according to which orientation is imposed to the nematic. Beris-Edwards model has three more free parameters because the conformation tensor contains more information: the Leslie-Ericksen model can be obtained as a special case of the Beris-Edwards model.

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