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ABSTRACT

Many processes in chemistry, physics, and biology depend on thermally activated events in which the system changes its state by surmounting an activation barrier. Examples range from chemical reactions to protein folding and nucleation events. Parameterized forms of the mean field potential are often employed in the stochastic modeling of activated processes. In this contribution, we explore the alternative of employing parameterized forms of the equilibrium distribution by means of symmetric linear combination of two Gaussian functions. Such a procedure leads to flexible and convenient models for the landscape and the energy barrier whose features are controlled by the second moments of these Gaussian functions. The rate constants are examined through the solution of the corresponding diffusion problem, that is, the Fokker–Planck–Smoluchowski equation specified according to the parameterized equilibrium distribution. Numerical calculations clearly show that the asymptotic limit of large barriers does not agree with the results of the Kramers theory. The underlying reason is that the linear scaling of the potential, the procedure justifying the Kramers theory, cannot be applied when dealing with parameterized forms of the equilibrium distribution. A different kind of asymptotic analysis is then required and we introduce the appropriate theory when the equilibrium distribution is represented as a symmetric linear combination of two Gaussian functions: first in the one-dimensional case and afterward in the multidimensional diffusion model.

I. INTRODUCTION

Arrhenius law[1] is a fundamental tool of chemical kinetics[2] and for the analysis of the rates of activated processes.[3] It allows their simple interpretation as dynamical processes controlled by the crossing of the energy barrier separating reactant and product states, like in the Transition State Theory.[4,5] Kramers in his article[6] of 1940 proposed a stochastic description as a convenient scheme for treating the relaxation to equilibrium in activated processes through frictional coupling with the environment. In this framework, he introduced the simplest and most insightful model for kinetics according to the one-dimensional diffusion equation in the presence of a mean field potential as described by the Fokker–Planck–Smoluchowski (FPS) equation.[7–9] In particular, he showed that the Arrhenius law is recovered in the limit of large barriers, with the pre-exponential factor controlled by the diffusion coefficient and the second derivative (curvature) of the mean field potential at the saddle point.

This Kramers asymptotic relation (KAR) has been highly appreciated in the literature and nowadays it appears as a standard tool in the field of physics, chemistry, and biophysics.[10,11] An important methodological issue then arises: Does KAR uniquely identify the large barrier behavior of one-dimensional diffusion models? In all generality, the answer is negative, and already Kramers[6] provided a counterexample for the case of mean field potentials with an edge-shaped barrier as obtained by matching two parabolic wells. Correspondingly, the second derivative of this potential at the top of the barrier is not defined and the standard KAR is out of the question.

Still, one might speculate that KAR is valid for the physically more realistic potential of having smooth behavior in all its derivatives. In this work, we intend to analyze the validity of KAR within this more restricted kind of model. We shall show that even in the presence of a smooth barrier, the asymptotic behavior of kinetic rates is not necessarily described by KAR. An enlightening example is provided by the mean field potential corresponding to the Two-Gaussian Distribution (TGD), which is a symmetric linear combination of two normal distributions having the same width for a given separation of their centers. The TGD was recently employed

for the analysis of tunneling splitting in light of the isomorphism between FPS operator and the Hamiltonian operator of Quantum Mechanics.[12] It might also be considered as a useful tool for modeling activated processes as long as the corresponding mean field potential displays a two-well profile separated by a smooth barrier whose height depends on the unique control parameter given by the ratio between the width and separation of the Gaussians. Indeed, larger potential barriers are recovered by decreasing the superposition between two Gaussians, that is, by decreasing their width or increasing their separation. We think that the mean field potential of TGD is a convenient candidate for a parameterized form to be employed in the characterization of activated processes like other standard models, for instance, polynomial potentials.[8,13–15]

Spectral analysis of the FPS operator can be performed numerically to obtain the exact value of rate constants for an increasing barrier height ΔU. This kind of computation shows that the asymptotic limit of the TGD model for large barriers ΔU is not described by KAR, more precisely that it requires a different pre-exponential factor in the Arrhenius representation. This provides clear evidence that KAR has no general validity even in the case of smooth potentials.

The issue has its origin in the very definition of asymptotic limits with respect to the barrier height ΔU. Analysis of the kinetic rate by increasing the barrier requires a change in the mean field potential and this can be done in different ways according to the parameterization of the stochastic model. Correspondingly, different asymptotic relations might be recovered for the rate constant.

The simplest asymptotic procedure is certainly that of scaling the mean field potential by multiplying it, as well as the potential barrier, by a scaling factor, thus leaving unmodified the overall shape of the potential as conveniently done, for instance, with polynomial potentials. This is considered in the literature as the standard procedure leading to KAR in the limit of large barriers.[3,10,11,16] However, it cannot be applied to the TGD model as long as the change in control parameter, i.e., ratio between the width and separation of the Gaussians, cannot be accounted by a scaling factor of the mean field potential. Thus, the TGD model calls for a different kind of asymptotic analysis that we present in this work and that leads to a pre-exponential factor of the Arrhenius form differing from that of KAR by $\sqrt{\pi/2}$, that is, an increase of about 25% in the rate. The peculiarity of the TGD model's asymptotic behavior is revealed by differences not only in the pre-exponential factor but also in the profile of the kinetic eigenmode of the diffusion (FPS) equation, that is, the eigenfunction of the evolution operator that describes the relaxation according to the kinetic rate. It should be mentioned that the kinetic eigenmode is strictly related to the committor function that in recent times has been recognized as a fundamental tool for describing the configuration dependence of rare events on the basis of the probability that a trajectory starting at a given point reaches the product state without visiting the reactant state.[17–21] While the error function profile is recovered from the potential scaling leading to KAR, asymptotic analysis of the TGD leads to a rather different kinetic eigenmode as specified by the integral of the inverse of the hyperbolic cosine.

One-dimensional diffusion models are appealing for the simplicity of their analysis, but a more profound and realistic interpretation of activated processes requires multidimensional diffusion representations in order to leave room for coupling between reactive and nonreactive coordinates. An extension of Kramers asymptotic analysis to multidimensional diffusion was performed by Langer[22] who derived a relation, in the following Kramers–Langer Asymptotic Relation (KLAR), which represents the multidimensional generalization of KAR. On the other hand, multidimensional TGD can be easily formulated on the basis of normal distributions and they generate a family of mean field potentials that are suitable to describe bistability and activated processes. We shall show that a similar scenario is recovered by moving from one-dimensional to multidimensional problems. In particular, like KAR for one-dimensional models, KLAR does not describe the large barrier limit of TGD models, which require a different kind of asymptotic analysis.

The article is organized as follows: In Sec. II, the one-dimensional TGD model is introduced and the exact numerical results for the rate constant are compared with the Kramers asymptotic relation for increasing barrier, providing evidence of the failure of KAR for this particular diffusion model. In Sec. III, we explain why the Kramers method should not be applied to one-dimensional TGD potentials and introduce the appropriate asymptotic analysis explaining the numerical results for such a model. In Sec. IV, we report the generalization of these results to multidimensional problems. Thus, we introduce the diffusion model with the multidimensional Two-Gaussian Distribution (mTGD) and we present its asymptotic analysis based on the scaling of the widths of the Gaussians. In order to verify such an asymptotic analysis, we also report a comparison with the numerical results for a two-dimensional realization of the mTGD model. In Sec. V, we summarize the results of our analysis.

II. RATE CONSTANT FROM ONE-DIMENSIONAL DIFFUSION

One-dimensional diffusion in the presence of a mean field potential is described by the following Fokker–Planck–Smoluchowski (FPS) equation[7–9] for the time-dependent probability density $\rho_t(x)$ on the coordinate x:

$$\frac{\partial}{\partial t}\rho_t(x) = -\hat{\Gamma}\rho_t(x), \tag{1}$$

where $\hat{\Gamma}$ is the time evolution operator specified as

$$\hat{\Gamma} = -\frac{\partial}{\partial x} D\rho_{eq}(x)\frac{\partial}{\partial x}\rho_{eq}(x)^{-1} \tag{2}$$

and D is the diffusion coefficient. The equilibrium distribution $\rho_{eq}(x)$ determines the infinite time limit of a generic probability density $\rho_t(x)$ and it can be specified according to the mean field potential $U(x)$ scaled by the thermal energy factor k_BT,

$$\rho_{eq}(x) = \frac{e^{-U(x)}}{Z} = \lim_{t\to\infty}\rho_t(x), \tag{3}$$

where Z is the suitable normalization. In this work, we consider bistable models with symmetric potentials $U(-x) = U(x)$ having a saddle point at $x = 0$ and two equivalent minima at $x = \pm x_0$. The energy barrier height, once scaled by k_BT, is then given as $\Delta U := U(0) - U(\pm x_0)$.

FPS Eq. (1) in the presence of large enough barriers displays two different kinds of motions: activated transitions between the two potential wells and intrawell dynamics.[3] A formal description of these motions is recovered according to the eigenmodes $\phi_n(x)$ of the FPS equation defined according to the eigenfunctions of $\hat{\Gamma}$,

$$\hat{\Gamma}\rho_{eq}(x)\phi_n(x) = \lambda_n\rho_{eq}(x)\phi_n(x), \tag{4}$$

for $n = 0, 1, 2, \ldots$, with $\lambda_n \leq \lambda_{n+1}$. Notice that eigenmode $\phi_0(x) = 1$ with $\lambda_0 = 0$ is associated with the stationary solution of Eq. (1), that is, the equilibrium distribution. The ensemble of these eigenmodes allows representation of the generic distribution $\rho_t(x)$ as their linear combination weighted by $\rho_{eq}(x)$, with coefficients depending on the time as $e^{-\lambda_n t}$, eigenvalue λ_n being the relaxation rate of eigenmode $\phi_n(x)$ (see Sec. A in the supplementary material for details).

For large enough barriers ΔU, the kinetic behavior emerges because of the spectral gap $\lambda_1 \ll \lambda_2, \lambda_3, \ldots$, which differentiates the relaxation rate λ_1 for transitions between the two potential wells and the ensemble of eigenvalues λ_n for $n \geq 2$ describing the relaxation rates of intrawell dynamics.[13,15] Correspondingly, one can identify the time scales of the model: $\tau_{kin} := 1/\lambda_1$ for the time scale of transition kinetics overcoming the potential barrier and $\tau_{lr} := 1/\lambda_2$ for the time scale of local relaxation (lr) within a potential well. For long enough times, to ensure local equilibration about each potential well, that is, for $t \gg \tau_{lr}$, only the first two eigenmodes $\phi_0 = 1$ and $\phi_1(x)$ are required to specify the time evolution of the probability density,

$$\rho_t(x) \simeq \rho_{eq}(x) + \langle\phi_1|\rho_0\rangle e^{-\lambda_1 t}\phi_1(x)\rho_{eq}(x), \tag{5}$$

with a single exponential decay along $\phi_1(x)$, which identifies the kinetic eigenmode.

On the other hand, also the reversible unimolecular mechanism, $A \xrightarrow{k} B$, $B \xrightarrow{k} A$, of chemical kinetics[2] leads to a single exponential decay e^{-2kt} of the concentrations. Thus, the FPS equation can be considered as a stochastic model explaining the kinetic behavior in terms of diffusion dynamics at times longer than those required by local equilibration, under the constraint of time scale separation $\tau_{kin} \gg \tau_{lr}$ due to the spectral gap. By matching the two exponential decays, $e^{-2kt} = e^{-\lambda_1 t}$, one gets a precise identification of the rate constant k according to the first nonvanishing eigenvalue of the FPS equation,

$$k = \lambda_1/2. \tag{6}$$

Such a relationship allows exact calculation of the rate constant k from numerical diagonalization of the FPS operator $\hat{\Gamma}$ once the potential $U(x)$ is chosen with a large enough barrier ΔU to ensure the spectral gap $\tau_{kin} \gg \tau_{lr}$.

Surely, Kramers[6] was the first to consider the large barrier behavior of the one-dimensional diffusion model and he derived an asymptotic form, in the following KAR for Kramers asymptotic relation, which in our notation is specified as

$$k_K^{\infty} = \frac{D}{2\pi}\sqrt{U_0^{(2)}\left|U_S^{(2)}\right|}\; e^{-\Delta U}, \tag{7}$$

where $U_0^{(2)}$ and $U_s^{(2)}$ are the second derivatives (curvatures) of the potential at the minima and the saddle point, respectively. The superscript in k_K^{∞} refers to the asymptotic validity of Eq. (7) with respect to the infinite barrier ΔU limit. By taking into account that ΔU denotes the energy barrier scaled by the thermal factor $k_B T$, KAR has the same structure of the Arrhenius equation with a precise identification of the pre-exponential factor. Therefore, the Kramers result instantiates the heuristic value of the Arrhenius law by validating it in a model of dynamics even if of simple diffusional type.

The simplicity of one-dimensional diffusion models allows their spectral analysis numerically and, therefore, exact calculation of the rate constant k according to Eq. (6). Then, the asymptotic values k_K^{∞} of Eq. (7) can be compared to the exact rate constants k in order to verify the validity of KAR by looking at the convergence of k_K^{∞} to k for an increasing barrier ΔU. This procedure will be applied to two different kinds of mean field potentials. As a reference case for which the convergence of KAR has been already verified in the past,[13,15] we consider the quartic polynomial potential that is conveniently specified as

$$U(x) = \Delta U[(x/x_0)^2 - 1]^2. \tag{8}$$

Furthermore, we examine the potential due to the Two-Gaussian Distribution (TGD) for the equilibrium probability density,[12]

$$\rho_{eq}(x) := \frac{1}{2}\mathcal{N}(x|x_0, \sigma^2) + \frac{1}{2}\mathcal{N}(x|-x_0, \sigma^2) = \frac{e^{-(x-x_0)^2/2\sigma^2} + e^{-(x+x_0)^2/2\sigma^2}}{\sqrt{8\pi\sigma^2}}, \tag{9}$$

that is, the symmetric linear combination of two normal distributions centered at $\pm x_0$ and having the same width σ. If x_0 is used as the unit of length, such a model has a unique control parameter specified as σ/x_0. We shall consider the situation of well-separated Gaussians so that the maxima of $\rho_{eq}(x)$ are nearly coincident with their centers $\pm x_0$, with deviations of the order of the superposition parameter $S := e^{-2x_0^2/\sigma^2}$.[12] In particular, we consider the control parameter in the range $0 < \sigma/x_0 < 1/2$, which ensures a negligible superposition parameter: $S < 10^{-3}$. The corresponding mean field potential is defined as[12]

$$U(x) = -\ln\left[\sqrt{8\pi\sigma^2}\rho_{eq}(x)\right] = \frac{x_0^2 + x^2}{2\sigma^2} - \ln\left[2\cosh\left(xx_0/\sigma^2\right)\right], \tag{10}$$

with the following barrier height by neglecting contributions of the order of S:

$$\Delta U = \frac{x_0^2}{2\sigma^2} - \ln 2. \tag{11}$$

Clearly, the previous equation allows identification of the control parameter σ/x_0 on the basis of a chosen value of the barrier ΔU.

In Fig. 1, we have represented the mean field potential together with the associated equilibrium distribution for both potentials with the same energy barrier of $\Delta U = 4.86$, corresponding to a control parameter $\sigma/x_0 = 0.3$ for the TGD model. It should be evident that the TGD potential provides a reasonable profile for bistable symmetric problems and that it can be employed as an alternative to the quartic potential.

We have evaluated the exact rate constant k according to the first nonvanishing eigenvalue λ_1 computed numerically with both

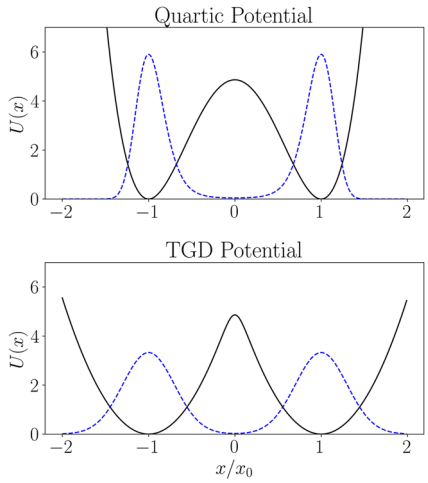

FIG. 1. Mean field potential $U(x)$ (continuous line) and equilibrium distribution $\rho_{eq}(x)$ (dashed line) for $\Delta U \simeq 4.86$. Upper panel: quartic potential of Eq. (8). Lower panel: TGD potential of Eq. (10).

potentials. The comparison with KAR is made in Fig. 2 in the form of the ratio k_K^∞/k as a function of the barrier height ΔU. In the case of a quartic polynomial potential (black line in Fig. 2), convergence to the asymptotic result of Kramers is detected by smooth approach to unity of the ratio k_K^∞/k with increasing barrier ΔU. A completely different behavior is recovered from the TGD potential (red line in Fig. 2) with, for large values of ΔU, k_K^∞/k approaching a constant value different from unity, like the one represented by the dashed line in Fig. 2. This provides clear evidence that KAR in Eq. (7) does not describe the asymptotic behavior correctly in the case of TGD potentials. In Sec. III, we analyze the reason for such a failure of the asymptotic Kramers relation.

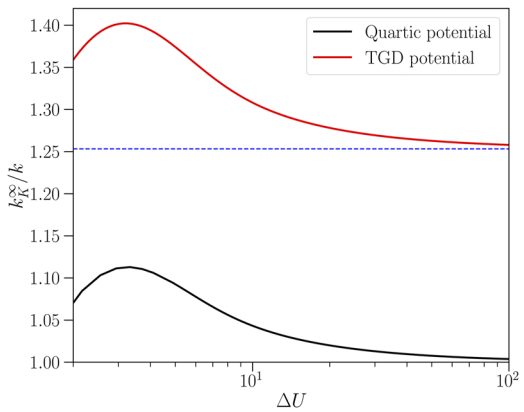

FIG. 2. Ratio k_K^∞/k between asymptotic Kramers relation (KAR) and the exact rate constant k for increasing barrier height ΔU. Black line: quartic potential; red line: TGD potential.

III. ASYMPTOTIC BEHAVIOR OF ONE-DIMENSIONAL DIFFUSION

Let us first recall the procedure employed by Kramers in his 1940s article.[6] He examined the stationary solution of the one-dimensional diffusion (FPS) equation by imposing source and sink boundary conditions at the potential minima. Then, the rate constant was evaluated according to the flux-over-population ratio. This procedure is commonly adopted in the literature concerning the asymptotic limit of rate constants for large barriers.[3,23,24] Here, we employ the alternative procedure of an asymptotic analysis performed directly on the first nonvanishing eigenvalue λ_1 of FPS operator, which according to Eq. (6) ensures exact identification of rate constants. In this way, results equivalent to those of Kramers are recovered without modifications of the diffusion model with *ad hoc* boundary conditions.

The central property to examine is the kinetic eigenmode $g(x) \equiv \phi_1(x)$, which is the eigenfunction of operator Eq. (2) that describes the barrier crossing process, and which we specifically identify with the symbol $g(x)$.[12] It has a step-like profile concentrated in a narrow domain about the saddle point, while far from the saddle point it is nearly constant with about ± 1 values.[15] We recall that by a suitable scaling, one recovers from $g(x)$ the committor function.[19,21] Because the spectral gap $\lambda_1/\lambda_2 \to 0$ for $\Delta U \to \infty$, in the scale of a typical eigenvalue of FPS equation, say λ_2, the contribution of λ_1 vanishes and the equation providing the kinetic component $g(x)$ is approximated as $\hat{\Gamma} g(x)\rho_{eq}(x) = 0$, which is equivalent to

$$\frac{\partial}{\partial x}\rho_{eq}(x)g'(x) = 0, \tag{12}$$

where $g'(x) := dg(x)/dx$. Such an equation is equivalent to the steady-state flux condition of the original Kramers treatment,[6] and it will be the starting point of our analysis of rate constants. It should be mentioned that a solution of Eq. (12) can be devised over the entire range of the stochastic variable, even if in a piecewise form, thus providing highly accurate approximations to the kinetic eigenmode $g(x)$ and to rate constants in the intermediate range of the potential barrier.[12,15,25] In particular, Berezhkovskii, Gopich, and Szabo in a recent publication[25] clarified the role of the Rayleigh–Ritz variational principle to justify the use of the steady-state flux solution of Eq. (12) as an approximation of the exact kinetic eigenmode. It should be recalled that such a piecewise global solution cannot be generalized to multidimensional diffusion problems, which instead can be solved by means of second-order expansion of the potential according to the Kramers–Langer procedure.

Our analysis, however, is devoted to the asymptotic behavior of rate constants for large values of the barrier, where $g'(x)$ is vanishing outside a small interval about the saddle point.[15] This motivates the replacement of the potential in $\rho_{eq}(x) \propto \exp\{-U(x)\}$ with its second-order Taylor expansion given by

$$U(x) \simeq U(0) - \frac{1}{2}\left|U_s^{(2)}\right|x^2 = U(0) - x_K^{\infty\,2}, \tag{13}$$

where

$$x_K^\infty := x\sqrt{\left|U_s^{(2)}\right|/2} \tag{14}$$

is the scaled coordinate according to the asymptotic method of Kramers. The parabolic approximation in Eq. (13) of the mean field potential is the key ingredient of the Kramers asymptotic result. Correspondingly, the solution of Eq. (12) with the proper symmetry, $g(-x) = -g(x)$, and the boundary conditions $\lim_{x\to\pm\infty} g(x) = \pm 1$ is readily found according to the error function given by

$$g_K^\infty = \mathrm{erf}(x_K^\infty). \tag{15}$$

Notice the universal character of this Kramers asymptotic form of the kinetic eigenmode as long as the parametric dependence on the diffusion model is taken into account only through the definition of the scaled coordinate x_K^∞. Finally, by evaluating λ_1 as the expectation value of the FPS operator according to the Kramers asymptotic form in Eq. (15) of the kinetic eigenmode, the KAR in Eq. (7) is recovered (see Sec. B of the supplementary material for details).

In order to understand why KAR in Eq. (7) works well in some cases but fails in others, like TGD potential, a deeper analysis of the asymptotic procedure is required. Let us first stress that in all generality, the first nonvanishing eigenvalue λ_1 and, therefore, the rate constant k according to Eq. (6) are proportional to the diffusion coefficient D but depend on the detailed shape of the mean field potential $U(x)$. This is specified in a formal sense as

$$k = D\, F[U(x)], \tag{16}$$

where $F[U(x)]$ denotes the functional dependence on $U(x)$. From this point of view, the numerical calculation of $\lambda_1 = 2k$ is a procedure for determining the value of the functional $F[U(x)]$ for a given potential $U(x)$. On the other hand, asymptotic analysis with respect to the barrier height ΔU requires that the rate constant be represented as an ordinary function of ΔU,

$$k = D\, f(\Delta U), \tag{17}$$

in order to be in the position to extract from $f(\Delta U)$ the leading contribution for $\Delta U \to \infty$. In conclusion, a preliminary step of asymptotic analysis is the conversion of functional $F[U(x)]$ into a function $f(\Delta U)$ of the barrier height and this can be done in different ways according to the kind of mean field potential we are dealing with. Correspondingly, different asymptotic relations could be found for the rate constant and, in the following, we discuss two cases that exemplify the difference in asymptotic predictions.

Let us consider first the scaling of the potential by the barrier, which can be considered the standard method leading to KAR.[16] It is based on the idea of multiplying the potential by a scalar factor that increases the barrier without modifying the overall potential profile. It can be applied to models of potential that can be represented as

$$U(x) = \Delta U\, s(x), \tag{18}$$

where $s(x)$ is the potential shape function corresponding to the mean field potential with a unitary barrier. The quartic potential in Eq. (8) belongs to this category with the shape function given as $s(x) = [(x/x_0)^2 - 1]^2$. Then, by definition, the functional $F[U(x)]$ becomes a function $f(\Delta U)$ of the potential barrier only if we consider the class of potentials in Eq. (18) for a fixed potential shape $s(x)$. In this framework, one can justify the truncation at the second-order Eq. (13) of the Kramers derivation because of the asymptotic limit $\Delta U \to \infty$. Indeed, according to the Taylor expansion of the potential Eq. (18) for $x \to 0$,

$$\begin{aligned} U(x) &= U(0) + \Delta U s_s^{(2)} x^2/2 + \Delta U O(x^4) \\ &= U(0) - x_K^{\infty\,2} + \frac{1}{\Delta U} O(x_K^{\infty\,4}), \end{aligned} \tag{19}$$

where $x_K^\infty = x\sqrt{\Delta U d^2\, s(x)/dx^2|_{x=0}/2}$, the limit $\Delta U \to \infty$ ensures the validity of the parabolic form Eq. (13)—because the fourth- and higher-order terms become negligible—as well as the validity of the Kramers asymptotic relation Eq. (7). Convergence to unity of k_K^∞/k for increasing ΔU as displayed in Fig. 2 for the quartic potential is strictly a consequence of this asymptotic behavior of potentials parameterized as in Eq. (18).

The TGD potential Eq. (10) cannot be assimilated to the form Eq. (18) since it has σ/x_0 as the only control parameter whose changes are not reproduced by a simple scaling of the potential. In other words, the scaling of Eq. (10) by a multiplicative factor does not define a mean field potential that can be generated by the Two-Gaussian-Distribution Eq. (9). Therefore, the previous asymptotic analysis cannot be applied to TGD potentials. On the other hand, the preliminary step in the reduction of the rate constant's functional dependence from Eq. (16) to Eq. (17) is not required with TGD potentials because it is parameterized according to the control parameter σ/x_0 that can be specified by the barrier height ΔU because of Eq. (11). This implies equivalence of the asymptotic limit $\Delta U \to \infty$ with a vanishing control parameter $\sigma/x_0 \to 0$. In conclusion, the functional dependence of the rate constant of the TGD model is specified by Eq. (17) by construction. Furthermore, one can easily show that the parabolic form Eq. (13) does not hold asymptotically in the case of TGD potentials since for $x \to 0$,

$$\begin{aligned} U(x) &= U(0) - \frac{x^2}{2\sigma^2}\left(\frac{x_0^2}{\sigma^2} - 1\right) + O(x^4 x_0^4/\sigma^8) \\ &= U(0) - x_K^{\infty\,2} + O(x_K^{\infty\,4}), \end{aligned} \tag{20}$$

where $x_K^\infty = x\sqrt{(x_0^2 - \sigma^2)/2\sigma^4}$ is the Kramers scaled coordinate evaluated according to Eq. (14). It is clear that in the limit $\sigma/x_0 \to 0$, the fourth- and higher-order terms are not negligible unlike in Eq. (19). This, for an increasing barrier, corresponds to a reduction in the range of validity of the second-order Taylor expansion, which is invoked in the Kramers theory, while in the case of the potentials parameterized like in Eq. (13), it is independent of the barrier height. Therefore, the asymptotic parabolic form in Eq. (18) of the potential, which might be considered as the basic ingredient of KAR, does not find justification in the case of TGD potentials.

A different procedure has to be developed in order to find the asymptotic behavior of the rate constant evaluated with TGD potentials. One can easily recognize that in the TGD potential given by Eq. (10), the hyperbolic cosine term prevails in the limit $\sigma/x_0 \to 0$ and this suggests taking its argument as the scaled variable of the asymptotic procedure,

$$x_{TGD}^\infty := x x_0/\sigma^2, \tag{21}$$

where we have inserted the subscript TGD to emphasize reference to such a model potential. By using x^{∞}_{TGD} as the independent variable, the TGD potential in Eq. (10) is rewritten as

$$U(x) - U(0) = \frac{\sigma^2}{2x_0^2} {x^{\infty}_{TGD}}^2 - \ln\left[\cosh\left(x^{\infty}_{TGD}\right)\right], \tag{22}$$

so that, in the asymptotic limit $\sigma/x_0 \to 0$, only the second term on the r.h.s. survives. Thus, instead of the Gaussian distribution $\rho_{eq}(x) \propto \exp\{-U(x)\}) \propto \exp\left(-{x^{\infty}_{K}}^2\right)$ derived with the Kramers procedure, a different asymptotic behavior specified by the hyperbolic cosine is recovered for the TGD potential given by

$$\rho_{eq}(x) \propto \cosh\left(x^{\infty}_{TGD}\right). \tag{23}$$

Correspondingly, by integrating Eq. (12), the following form is recovered for the kinetic eigenfunction of FPS:

$$g^{\infty}_{TGD} = \frac{2}{\pi}\int_0^{x^{\infty}_{TGD}} \frac{dy}{\cosh\left(y\right)}, \tag{24}$$

which replaces the result in Eq. (15) of the Kramers procedure in the case of TGD potentials. Notice that the proportionality coefficient in the previous equation has been chosen in order to ensure the limiting behavior $\lim_{x\to\pm\infty} g^{\infty}_{TGD}(x) = \pm 1$. Equation (24), like Eq. (15), has the structure of a universal form of the kinetic eigenfunction since it does not bear any reference to the parametric dependence of the model, which is taken into account only through the definition of the scaled variable, x^{∞}_{TGD} and x^{∞}_{K} in the two cases.

Equation (24) for the kinetic eigenmode of the FPS equation is the main result of our asymptotic analysis of TGD potentials. From the corresponding expectation value of the FPS operator (see Sec. B of the supplementary material for details), the following asymptotic rate constant is derived:

$$k^{\infty}_{TGD} = D\frac{x_0}{\sigma^3\sqrt{2\pi^3}}\, e^{-\Delta U}, \tag{25}$$

again of Arrhenius type with a pre-exponential factor determined by the control parameter. One might wonder what would be the result of the KAR in Eq. (7) if applied to TGD potentials. By inserting into Eq. (7) the second derivatives of potential in Eq. (10), in the asymptotic limit $\sigma/x_0 \to 0$, one obtains a pre-exponential factor different from that of Eq. (25) by a factor $\sqrt{\pi/2}$,

$$\lim_{\sigma/x_0\to 0} \frac{k^{\infty}_{K}}{k^{\infty}_{TGD}} = \sqrt{\pi/2}. \tag{26}$$

This explains the results for the ratio k^{∞}_{K}/k for TGD potential as displayed by the red line in Fig. 2. Such a ratio reaches the asymptotic value of $\sqrt{\pi/2}$ (the dashed line of Fig. 2) just because the Kramers relation overestimates by the same factor the asymptotic correct result Eq. (25) for TGD potential. On the other hand, the evidence from Fig. 2 that $\lim_{\sigma/x_0\to 0} k^{\infty}_{K}/k = \sqrt{\pi/2}$ for TGD potential can be considered as validation of the previous asymptotic analysis.

To summarize, we have shown that when dealing with TGD models, an asymptotic analysis different from that proposed by Kramers[6] is necessary and this leads to an asymptotic rate constant still of Arrhenius type but with a different pre-exponential factor. The difference, however, is not confined to the pre-exponential factor of Arrhenius form since a completely different asymptotic profile is derived for the kinetic eigenmode: the integral of the inverse hyperbolic cosine of Eq. (24) vs the error function profile of Eq. (15). As mentioned before, this implies a different behavior of the committor function[17–21] in the two cases. To illustrate this, Fig. 3 provides a comparison between these asymptotic forms g^{∞}_{K} of Eq. (15) and g^{∞}_{TGD} of Eq. (24) as a function of x^{∞}_{K} and x^{∞}_{TGD}, respectively. Their difference is evident in the approach to the asymptotes ±1.

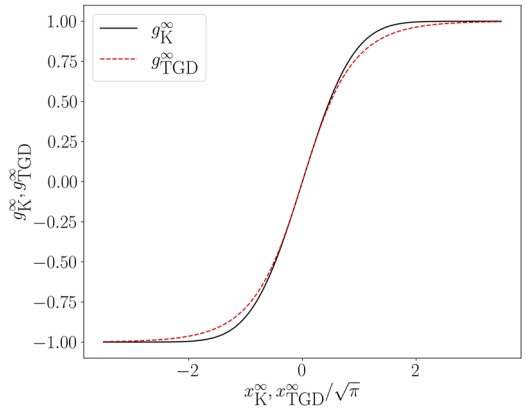

FIG. 3. Asymptotic forms of the kinetic eigenfunction g^{∞}_{K} and g^{∞}_{TGD} as function of x^{∞}_{K} and of x^{∞}_{TGD}, respectively, with the latter scaled as $x^{\infty}_{TGD}/\sqrt{\pi}$ in order to ensure in the graph the same first derivative at the origin.

IV. ASYMPTOTIC BEHAVIOR OF MULTIDIMENSIONAL DIFFUSION

In this section, we intend to generalize the previous analysis to multidimensional diffusion models. Even if these systems are in general much more complex, asymptotic behavior can still be reduced to the same one-dimensional forms for the kinetic eigenmode. Furthermore, it will be shown that the multidimensional Two-Gaussian Distribution (mTGD) model is characterized by an asymptotic rate constant different from the Kramers–Langer Asymptotic Relation (KLAR), which is the multidimensional generalization by Langer[22] of the Kramers result. The presentation is organized according to the following lines. First, we introduce the Fokker–Planck–Smoluchowski (FPS) description of diffusion in symmetric bistable multidimensional problems and the multidimensional Two-Gaussian Distribution (mTGD). Second, we recall the Langer analysis,[22] which, from normal mode analysis at the saddle point, allows one-dimensional reduction of the kinetic eigenmode to the form Eq. (15) with a suitable definition of the asymptotic reaction coordinate. Afterward, we tackle the asymptotic analysis for mTGD potentials leading to the kinetic eigenmode of the same form of Eq. (24). On this basis, a comparison is made between the asymptotic analysis of mTGD potentials and the predictions of KLAR. Finally, the results of our analysis are validated by examining the numerically exact rate constant for a two-dimensional realization of the mTGD model.

A. Multidimensional two Gaussian (mTGD) model

The N-dimensional diffusion problem for coordinates $\mathbf{x} = \{x_1, x_2, \ldots, x_N\}$ is described by the time-dependent probability density $\rho_t(\mathbf{x})$ normalized by integration on each coordinate in the full real axis and evolving in time as in Eq. (1) with the following Fokker–Planck–Smoluchowski operator:[7–9]

$$\hat{\Gamma} = -\frac{\partial}{\partial \mathbf{x}}^T \mathbf{D}\rho_{eq}(\mathbf{x})\frac{\partial}{\partial \mathbf{x}}\rho_{eq}(\mathbf{x})^{-1}, \tag{27}$$

where $\mathbf{D}$ is the $N \times N$ diffusion matrix supposed to be independent of coordinates. Let the operator $\hat{R}$ encode the binary symmetry, $\hat{R}^2 = \hat{1}$, of bistable symmetric systems with an invariant equilibrium distribution and a commuting evolution operator given by

$$\hat{R}\rho_{eq}(\mathbf{x}) = \rho_{eq}(\mathbf{x}), \qquad \left[\hat{\Gamma}, \hat{R}\right] = 0, \tag{28}$$

implying degeneracy of the properties and of the dynamics in the presence of an infinite barrier separating the two states. It is convenient to employ coordinates that are irreducible representations of the symmetry group, $(\hat{R}, \hat{I})$, of the problem. Thus, the coordinates are partitioned as $\mathbf{x} = (\mathbf{x}^+, \mathbf{x}^-)$, where $\mathbf{x}^+ = (x_1^+, x_2^+, \ldots, x_{N^+}^+)$ and $\mathbf{x}^- = (x_1^-, x_2^-, \ldots, x_{N^-}^-)$ are even and odd, respectively, with respect to symmetry operator $\hat{R}$,

$$\hat{R}x_n^{\pm} = \pm x_n^{\pm}. \tag{29}$$

N^+ and N^- denote the number of even coordinates and odd coordinates, respectively, with $N = N^+ + N^-$ being the overall number of coordinates. Then, the action of the symmetry operator $\hat{R}$ on a function $f(\mathbf{x})$ of the coordinates is algebraically reduced to multiplication of the array $\mathbf{x}$ by the square matrix $\mathbf{R}$,

$$\hat{R}f(\mathbf{x}) = f(\mathbf{R}\mathbf{x}), \tag{30}$$

with the matrix $\mathbf{R}$ block partitioned with respect to even and odd coordinates as

$$\mathbf{R} = \begin{pmatrix} \mathbf{R}^{++} & \mathbf{R}^{+-} \\ \mathbf{R}^{-+} & \mathbf{R}^{--} \end{pmatrix} = \begin{pmatrix} \mathbf{I}^+ & 0 \\ 0 & -\mathbf{I}^- \end{pmatrix}, \tag{31}$$

where $\mathbf{I}^+$ and $\mathbf{I}^-$ represent the identity matrix for the set of even coordinates and odd coordinates, respectively. Then, one easily derives that the commutation condition in Eq. (28) implies the constraint $\mathbf{RDR} = \mathbf{D}$, that is, the vanishing of the off-diagonal blocks of the diffusion matrix partitioned like in Eq. (31) with respect to even and odd coordinates,

$$\mathbf{D} = \begin{pmatrix} \mathbf{D}^{++} & 0 \\ 0 & \mathbf{D}^{--} \end{pmatrix}. \tag{32}$$

Like for the one-dimensional case, a fundamental tool for the analysis of rate constants is the kinetic eigenmode $g(\mathbf{x})$ which, in the limit of large barriers producing a large spectral gap, can be evaluated as solution of the equation

$$\frac{\partial}{\partial \mathbf{x}}^T \mathbf{D}\rho_{eq}(\mathbf{x})\frac{\partial}{\partial \mathbf{x}}g(\mathbf{x}) = 0, \tag{33}$$

which is the multidimensional generalization of Eq. (12). Once the asymptotic form $g^\infty(\mathbf{x})$ of the kinetic eigenfunction is determined, the rate constant can be evaluated according to the corresponding expectation value of the FPS evolution operator in Eq. (27).

In the following, as an example of a system that does not follow KLAR, we shall specifically consider the multidimensional generalization (mTGD) of the Two-Gaussian Distribution in Eq. (9) specified by a symmetric linear combination of two normal distributions,

$$\begin{aligned}\rho_{eq}(\mathbf{x}) &:= \frac{1+\hat{R}}{2}\mathcal{N}(\mathbf{x}|\mathbf{x}_0, \mathbf{\Sigma}) = \frac{1}{2\sqrt{(2\pi)^N \det(\mathbf{\Sigma})}} \\ &\times \left\{\exp\left[-(\mathbf{x}-\mathbf{x}_0)^T\mathbf{\Sigma}^{-1}(\mathbf{x}-\mathbf{x}_0)/2\right]\right. \\ &\left. + \exp\left[-(\mathbf{R}\mathbf{x}-\mathbf{x}_0)^T\mathbf{\Sigma}^{-1}(\mathbf{R}\mathbf{x}-\mathbf{x}_0)/2\right]\right\},\end{aligned} \tag{34}$$

characterized according to the positive definite matrix $\mathbf{\Sigma}$ of the second moments (covariance matrix) and their centers (first moments) at $\mathbf{x}_0 = (\mathbf{x}_0^+, \mathbf{x}_0^-)$ and at $\mathbf{R}\mathbf{x}_0 = (\mathbf{x}_0^+, -\mathbf{x}_0^-)$. In the following, the eigenvalues of the covariance matrix, $\mathbf{\Sigma}$, will be denoted by $\sigma_k^2 > 0$ for $k = 1, 2, \ldots, N$. Since the origin of even coordinates $\mathbf{x}^+$ is arbitrary, we choose it in correspondence of the centers of the two Gaussians: $\mathbf{x}_0^+ = 0$ so that $\mathbf{x}_0 = (0, \mathbf{x}_0^-)$ and $\mathbf{R}\mathbf{x}_0 = (0, -\mathbf{x}_0^-) = -\mathbf{x}_0$. Notice that the first moment cannot have a vanishing odd component $\mathbf{x}_0^-$ since otherwise the two Gaussians would be centered at the same location. The mean field potential of mTGD is defined in analogy to Eq. (10) as

$$U(\mathbf{x}) := -\ln\left[2\sqrt{(2\pi)^N \det(\mathbf{\Sigma})}\ \rho_{eq}(\mathbf{x})\right]. \tag{35}$$

We assume a weak superposition between the two Gaussians as quantified by negligible values of the superposition parameter $S := \exp\left[-2\mathbf{x}_0^T\mathbf{\Sigma}^{-1}\mathbf{x}_0\right]$, so that the minima of the potential are found at the centers of the Gaussians, that is, at $\mathbf{x}_0$ and $-\mathbf{x}_0$. The saddle point $\mathbf{x}_s = (\mathbf{x}_s^+, 0)$ has vanishing odd coordinates by symmetry, while its even coordinates are evaluated from the condition of vanishing gradient of the potential,

$$\mathbf{x}_s^+ = \left[(\mathbf{\Sigma}^{-1})^{++}\right]^{-1}(\mathbf{\Sigma}^{-1})^{+-}\mathbf{x}_0^-. \tag{36}$$

By neglecting terms of the order of the superposition parameter S, the barrier height is given as

$$\Delta U = U(\mathbf{x}_s) - U(\mathbf{x}_0) = \frac{1}{2}(\mathbf{x}_0^-)^T(\mathbf{\Sigma}^{--})^{-1}\mathbf{x}_0^- - \ln(2). \tag{37}$$

Furthermore, by employing the displacements $\delta\mathbf{x} := \mathbf{x} - \mathbf{x}_s$ from the saddle point, the potential Eq. (35) can be decomposed as

$$U(\mathbf{x}) = U_+(\delta\mathbf{x}) - \ln\{\cosh[U_-(\delta\mathbf{x})]\}, \tag{38}$$

with the two components $U_\pm$ with opposite symmetry, $\hat{R}U_\pm(\delta\mathbf{x}) = \pm U_\pm(\delta\mathbf{x})$, given as

$$\begin{aligned}U_+(\delta\mathbf{x}) &= U(\mathbf{x}_s) + \frac{1}{2}(\delta\mathbf{x}^+)^T(\mathbf{\Sigma}^{-1})^{++}\delta\mathbf{x}^+ + \frac{1}{2}(\delta\mathbf{x}^-)^T(\mathbf{\Sigma}^{-1})^{--}\delta\mathbf{x}^- \\ U_-(\delta\mathbf{x}) &= (\delta\mathbf{x}^-)^T(\mathbf{\Sigma}^{--})^{-1}\mathbf{x}_0^- - (\delta\mathbf{x}^-)^T(\mathbf{\Sigma}^{-1})^{-+}\delta\mathbf{x}^+\end{aligned} \tag{39}$$

(for details, see Sec. C of the supplementary material).

A kinetic interpretation can be attributed to the coordinates $\mathbf{x} = (\mathbf{x}^+, \mathbf{x}^-)$ on the basis of the critical points of the mean field potential $U(\mathbf{x})$. If we associate the two minima $\mathbf{x}_0$ and $-\mathbf{x}_0$ to the two species of the kinetics, then the odd coordinates $\mathbf{x}^-$ assume the character of collective coordinates of reaction as long as their values change in the transition. On the contrary, the even coordinates $\mathbf{x}^+$ can be interpreted as variables of non-reaction since they are not modified by a jump from one minimum to the other. However, the off-diagonal blocks of the variance matrix $\mathbf{\Sigma}$ introduce a coupling between these two kinds of coordinates, which is responsible for displacement $\mathbf{x}_s^+$ of the saddle point from the origin. In the absence of such a coupling for $\mathbf{\Sigma}^{+-} = \mathbf{\Sigma}^{-+} = 0$, the saddle point is at the origin midway between the two minima and the transition would not be affected by the displacement of even coordinates. On the contrary, for $\mathbf{\Sigma}^{+-} \neq 0$ the activated process is controlled also by the displacement of the coordinates of non-reaction.

As a simple example of mTGD, we shall consider here and in the following the two-dimensional model with one coordinate of even and odd type, $\mathbf{x} = (x^+, x^-)$. To parameterize the 2×2 variance matrix $\mathbf{\Sigma}$, we employ its principal values, σ_1^2 and σ_2^2, and the angle θ between the principal direction for σ_1^2 and the axis of coordinate x^+. For $\theta = 0$, the x^+ and x^- coordinates are independently distributed and also dynamically uncoupled since according Eq. (32), the diffusion matrix is diagonal. In this case, the activated process is described by the diffusion of odd coordinate x^- alone like in the analysis of Sec. III. A nonvanishing angle, $\theta \neq 0$, for the variance matrix introduces a coupling between the two coordinates that requires an intrinsically two-dimensional description of the diffusion. In Fig. 4, we have represented by means of a color code both the equilibrium distribution $\rho_{eq}(\mathbf{x})$ (upper panel) and the corresponding potential $U(\mathbf{x})$ (lower panel) for the particular case described by parameters: $\theta = \pi/6$, $\sigma_1/x_0^- = 0.25$, $\sigma_2/x_0^- = 0.35$. This is a situation of weakly superimposed Gaussians, as clearly seen in the upper panel, which leads to a significant potential barrier of $\Delta U = 3.958$. In the lower panel for the potential, the displacement of the saddle point (star symbol) from the origin is also evident, as a consequence of the coupling of the two coordinates induced by the variance matrix $\mathbf{\Sigma}$ for $\theta \neq 0$.

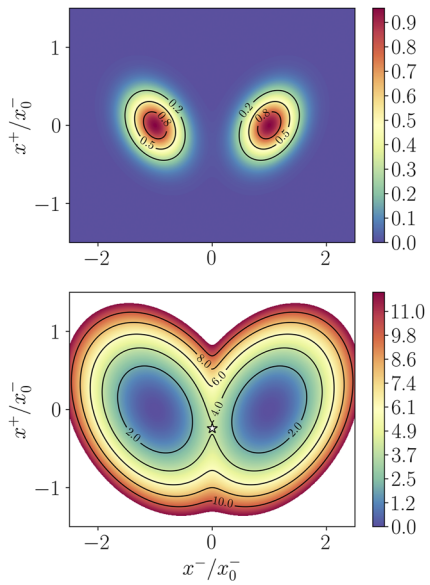

FIG. 4. Color code representation of the equilibrium distribution $\rho_{eq}(\mathbf{x})$ (upper panel) and of the corresponding potential $U(\mathbf{x})$ (lower panel), for the two-dimensional mTGD model with $\mathbf{x} = (x^+, x^-)$ coordinates and parameters: $\theta = \pi/6$, $\sigma_1/x_0^- = 0.25$, $\sigma_2/x_0^- = 0.35$. The star symbol in the lower panel denotes the position of the saddle point $\mathbf{x}_s$.

B. Asymptotic analysis

Before analyzing the asymptotic behavior of the mTGD model, for the sake of comparison, we recall the essential elements of the Kramers–Langer theory of the kinetic rate in multidimensional diffusion systems.[3,16,22] It is based on the second-order expansion of the potential at the saddle point,

$$U(\mathbf{x}) - U(\mathbf{x}_s) = \delta\mathbf{x}^T \mathbf{U}_s^{(2)} \delta\mathbf{x}/2, \tag{40}$$

where $\delta\mathbf{x}$ is the displacement from the saddle point and $\mathbf{U}_s^{(2)}$ is the second derivative matrix of the potential at the saddle point: $[\mathbf{U}_s^{(2)}]_{j,j'} := \partial^2 U(\mathbf{x})/\partial x_j \partial x_{j'}|_{\mathbf{x}=\mathbf{x}_s}$. Like in one-dimensional problems, replacement of the full potential $U(\mathbf{x})$ with Eq. (40) is justified in the asymptotic limit $\Delta U \to \infty$ if we scale the potential according to ΔU, that is, if we consider potentials of the form

$$U(\mathbf{x}) = \Delta U \, s(\mathbf{x}) \tag{41}$$

for increasing barriers ΔU but with a fixed potential shape $s(\mathbf{x})$. A simple picture of the diffusion dynamics near the saddle point is recovered from the normal modes defined according to the following eigenvalue problem:

$$\mathbf{D}\, \mathbf{U}_s^{(2)}\, \mathbf{u}_j = \xi_j \mathbf{u}_j, \tag{42}$$

with only one negative eigenvalue ξ_1 for the unstable (reactive) mode. The eigenvectors of the nonsymmetric matrix $\mathbf{D}\mathbf{U}_s^{(2)}$ supply a bi-orthonormal basis as $\mathbf{u}_j^T \mathbf{u}^{j'} = \delta_{j,j'}$, with $\mathbf{u}^j = \mathbf{D}^{-1}\mathbf{u}_j$ defining the displacements $z_j := \delta\mathbf{x}^T \mathbf{u}^j$ along the normal modes. With such a coordinate representation, $\delta\mathbf{x} = \sum_j z_j \mathbf{u}_j$, the FPS operator in Eq. (27) in the asymptotic limit is decomposed into independent contributions for each normal mode. In the Kramers–Langer (KL) procedure, this allows one-dimensional reduction of the asymptotic kinetic eigenmode g_{KL}^∞ depending only on the reaction coordinate z_1,

$$\frac{\partial}{\partial z_1} e^{|\xi_1| z_1^2/2} \frac{\partial}{\partial z_1} g_{KL}^\infty = 0. \tag{43}$$

The solution of this equation has the same form of Eq. (15),

$$g_{KL}^\infty = \mathrm{erf}(x_{KL}^\infty), \tag{44}$$

with the scaled reaction coordinate given as $x_{KL}^\infty := z_1 \sqrt{|\xi_1|/2}$. Finally, from the expectation value of FPS evolution operator (see Sec. D in the supplementary material), the Kramers–Langer Asymptotic Relation (KLAR) is derived for the rate constant,

$$k_{KL}^\infty = D_{KL} \frac{|U_{KL}^{(2)}|}{2\pi} \sqrt{\det(\mathbf{U}_0^{(2)})/|\det(\mathbf{U}_s^{(2)})|}\; e^{-\Delta U}, \tag{45}$$

where D_{KL} and $U_{KL}^{(2)}$ are the diffusion coefficient and the saddle point curvature, respectively,

$$\begin{aligned} 1/D_{KL} &:= (\mathbf{v}_{KL})^T \mathbf{D}^{-1} \mathbf{v}_{KL}, \\ U_{KL}^{(2)} &:= (\mathbf{v}_{KL})^T \mathbf{U}_s^{(2)} \mathbf{v}_{KL}, \end{aligned} \tag{46}$$

along the normalized direction, $(\mathbf{v}_{KL})^T \mathbf{v}_{KL} = 1$, of the reaction mode $\mathbf{v}_{KL} \propto \mathbf{u}_1$ of the Kramers–Langer theory. Notice that, taking into account that $\mathbf{D}^{-1}$ is proportional to the friction matrix, D_{KL} is inversely proportional to the friction along the reaction mode.

In order to analyze the rate constant of the mTGD model, we have first to introduce the asymptotic limit adequate for the multidimensional Two-Gaussian Distribution. Given the structure Eq. (34) of the distribution, this limit is defined by considering a homogeneous narrowing of the Gaussians as obtained by replacing the second moments $\mathbf{\Sigma}$ by $\epsilon\mathbf{\Sigma}$ with a vanishing parameter ϵ. This scaling of the second moments given by

$$\mathbf{\Sigma} \;\rightarrow\; \epsilon\mathbf{\Sigma} \tag{47}$$

for $\epsilon \to 0^+$ produces a concentration of the two Gaussians about their centers, which correspondingly reduces their superposition at the saddle point, thus leading to an increasing barrier as $1/\epsilon$ according to Eq. (37). It should be stressed that the scaling of the second moments by a scalar parameter does not modify the anisotropy of matrix $\mathbf{\Sigma}$. Of course, parameter ϵ is instrumental in order to recognize the asymptotic form of the rate constant for increasing barrier and, once it has been found, the original problem is restored by using a unitary ϵ.

In the next step, we recognize the suitable coordinates for the asymptotic limit. Like with the one-dimensional problem previously analyzed, the odd component U_- of the potential has a critical role in determining the asymptotic form of the kinetic eigenmode. According to Eq. (39), U_- includes two kinds of contributions: the first is linear on the odd coordinates $\delta\mathbf{x}^-$ and the other one is given by a bilinear product of even $\delta\mathbf{x}^+$ and odd $\delta\mathbf{x}^-$ coordinates. Only the first contribution survives in the one-dimensional problem and, because of its structure of linear combination, it determines a particular coordinate that can be taken as the reaction coordinate of mTGD problems. To formalize it, we introduce an orthonormal set of vectors $\mathbf{v}_1, \mathbf{v}_2, \ldots, \mathbf{v}_{N^-}$, with $(\mathbf{v}_j)^T \mathbf{v}_{j'} = \delta_{jj'}$, for the space of odd coordinates, with the following choice of the first vector according to the coefficients of the linear combinations of $\delta\mathbf{x}^-$ in U_-:

$$\mathbf{v}_1 = \frac{1}{a}\left(\mathbf{\Sigma}^{--}\right)^{-1} \mathbf{x}_0^-, \tag{48}$$

where $a := \sqrt{(\mathbf{x}_0^-)^T (\mathbf{\Sigma}^{--})^{-2} \mathbf{x}_0^-}$ to ensure normalization. Correspondingly, we introduce a different representation of odd coordinates as displacements along vectors $\mathbf{v}_j$,

$$y_j := \mathbf{v}_j^T \delta\mathbf{x}^-. \tag{49}$$

Then, the linear contribution in U_- becomes proportional to y_1 and such a coordinate can be employed as the reaction coordinate of the problem, vanishing at the saddle point and taking opposite values by acting on the coordinates with symmetry operator $\hat{R}$. The potential components, after the scaling in Eq. (47), become

$$\begin{aligned} U_+ &= U(\mathbf{x}_s) + \frac{1}{2\epsilon}\left(\delta\mathbf{x}^+\right)^T \left(\mathbf{\Sigma}^{-1}\right)^{++} \delta\mathbf{x}^+ \\ &\quad + \frac{1}{2\epsilon} \sum_{j,j'=1}^{N^-} \mathbf{v}_j^T \left(\mathbf{\Sigma}^{-1}\right)^{--} \mathbf{v}_{j'} y_j y_{j'}, \\ U_- &= \frac{a}{\epsilon} y_1 - \frac{1}{\epsilon} \sum_{j=1}^{N^-} \mathbf{v}_j^T \left(\mathbf{\Sigma}^{-1}\right)^{-+} \delta\mathbf{x}^+ y_j. \end{aligned} \tag{50}$$

In order to recognize the asymptotic form of the potential, the following scaling of the coordinates according to parameter ϵ has to be employed:

$$\begin{aligned} y_1^\infty &:= y_1/\epsilon, \\ y_j^\infty &:= y_j/\sqrt{\epsilon} \quad \text{for } j = 2, 3, \ldots, N^-, \\ \delta\mathbf{x}^{+\infty} &:= \delta\mathbf{x}^+/\sqrt{\epsilon}. \end{aligned} \tag{51}$$

Then, by imposing the limit $\epsilon \to 0^+$ to the potential components of Eq. (50) after the change to variables in Eq. (51), one obtains their asymptotic forms,

$$\begin{aligned} U_+^\infty &= U(\mathbf{x}_s) + \left(\delta\mathbf{x}^{+\infty}\right)^T \left(\mathbf{\Sigma}^{-1}\right)^{++} \delta\mathbf{x}^{+\infty} \\ &\quad + \frac{1}{2} \sum_{j,j'=2}^{N^-} \mathbf{v}_j^T \left(\mathbf{\Sigma}^{-1}\right)^{--} \mathbf{v}_{j'} y_j^\infty y_{j'}^\infty, \\ U_-^\infty &= a y_1^\infty - \sum_{j=2}^{N^-} \mathbf{v}_j^T \left(\mathbf{\Sigma}^{-1}\right)^{-+} \delta\mathbf{x}^{+\infty} y_j^\infty. \end{aligned} \tag{52}$$

Notice that direct scaling of the reaction coordinate as y_1/ϵ is dictated by its linear term contributing to U_- in Eq. (50). On the other hand, the different scaling by $\sqrt{\epsilon}$ for the other coordinates $y_2, y_3, \ldots, y_{N^-}$ and $\delta\mathbf{x}^+$ is imposed by the need to recover an equilibrium distribution that can be integrated on these variables. This is the case of the potential components in Eq. (52) because of the contribution by $\exp(-U_+^\infty)$ since U_+^∞ is a positive definite bilinear form of these coordinates.

The final step is the calculation of the asymptotic kinetic eigenfunction g_{MTGD}^∞ for the mTGD model. After substitution in Eq. (27) of the original $\mathbf{x}$ coordinates with the scaled variables of Eq. (51), the leading term in the limit $\epsilon \to 0^+$ should be retained. In this way, only the contribution with the derivative with respect to y_1^∞ survives,

$$\frac{\partial}{\partial y_1^\infty} \cosh\left(U_-^\infty\right) \frac{\partial}{\partial y_1^\infty} g_{mTGD}^\infty = 0, \tag{53}$$

with U_-^∞ specified by Eq. (52) (see Sec. D of the supplementary material). Since this is a differential equation on the variable y_1^∞ only, the dependence of U_-^∞ on the other variables should be treated like for constants of integration and, therefore, the same functional form given by Eq. (24) of the one-dimensional TGD problem is recovered by imposing the boundary conditions $\lim_{y_1^\infty \to \pm\infty} g_{mTGD}^\infty = \pm 1$,

$$g_{mTGD}^\infty = \frac{2}{\pi} \int_0^{x_{mTGD}^\infty} \frac{dy}{\cosh(y)}, \tag{54}$$

where $x^{\infty}_{mTGD} \equiv U^{\infty}_{-}$ is the scaled variable for the asymptotic mTGD kinetic eigenmode, which is linearly dependent on the reaction coordinate y^{∞}_{1} but also bears dependence on the other coordinates,

$$x^{\infty}_{mTGD} = a y^{\infty}_{1} - \sum_{j=2}^{N^-} \mathbf{v}_j^T \left(\boldsymbol{\Sigma}^{-1}\right)^{-+} \delta \mathbf{x}^{+\infty} y^{\infty}_{j}. \tag{55}$$

By evaluating in the asymptotic limit $\epsilon \to 0^+$ the expectation value of the FPS operator in Eq. (27) with the previous result for the kinetic eigenmode (for details, see Sec. D of the supplementary material), the asymptotic rate constant of the mTGD model is found,

$$k^{\infty}_{mTGD} = D_{mTGD} \sqrt{\frac{\left(\mathbf{x}_0^-\right)^T \left(\boldsymbol{\Sigma}^{--}\right)^{-2} \mathbf{x}_0^- / (2\pi^3)}{\det\left(\boldsymbol{\Sigma}\right) \det\left(\mathbf{B}\right) \det\left[\left(\boldsymbol{\Sigma}^{-1}\right)^{++}\right]}}\, e^{-\Delta U}, \tag{56}$$

where we have restored the original mTGD model by attributing a unitary value to parameter ϵ. In the above equation, D_{mTGD} is the diffusion coefficient along the reaction coordinate y_1,

$$D_{mTGD} := \mathbf{v}_1^T \mathbf{D} \mathbf{v}_1, \tag{57}$$

while matrix $\mathbf{B}$ of dimension $(N^- - 1) \times (N^- - 1)$ has elements

$$B_{j,j'} := \mathbf{v}_j^T \left(\boldsymbol{\Sigma}^{-1}\right)^{++} \mathbf{v}_{j'} \tag{58}$$

for $j, j' = 2, 3, \ldots N^-$.

C. Comparison with the exact numerical rate constants

In order to characterize the convergence of the kinetic eigenvalue λ_1 of the FPS operator to the asymptotic form $2k^{\infty}_{mTGD}$, we have considered two-dimensional realizations of the mTGD model on coordinates $\mathbf{x} = (x^+, x^-)$ like in Fig. 4. More specifically, in order to calculate the exact kinetic eigenvalue λ_1, we have solved numerically the FPS equation with an isotropic 2×2 diffusion matrix given by Eq. (32), that is for $D^{++} = D^{--} = D_0$, and with a 2×2 covariance matrix Σ with fixed values of the angle, $\theta = \pi/6$, and of the first eigenvalue, $(\sigma_1/x_0^-)^2 = 0.04$, for decreasing values of the second eigenvalue $(\sigma_2/x_0^-)^2$ in the range [0.04, 0.25] in order to reproduce an increasing barrier ΔU evaluated according to Eq. (37). In the upper panel of Fig. 5, we have represented both the kinetic eigenvalue λ_1 of the FPS operator (red dots) and its asymptotic counterpart $2k^{\infty}_{mTGD}$ of Eq. (56) (blue dots), both scaled by $D_0/(x_0^-)^2$, as a function of the barrier height ΔU. Clearly, by increasing the barrier height, the kinetic eigenvalue λ_1 gets closer to its asymptotic estimate $2k^{\infty}_{mTGD}$. The convergence of the kinetic eigenvalue to its asymptotic limit is more directly verified in the lower panel of Fig. 5 where the relative difference $(2k^{\infty}_{mTGD} - \lambda_1)/\lambda_1$ is represented for increasing barriers in a logarithmic scale.

The results reported in Fig. 5 show that our analysis of mTGD models supplies the correct asymptotic form of the rate constant. On the other hand, one might apply the Kramers–Langer asymptotic rate constant in Eq. (45) to mTGD models by simply evaluating the curvature matrices according to Eq. (38), but an Arrhenius form with a different pre-exponential factor would result. Indeed, the Kramers–Langer method and our analysis of the mTGD model are

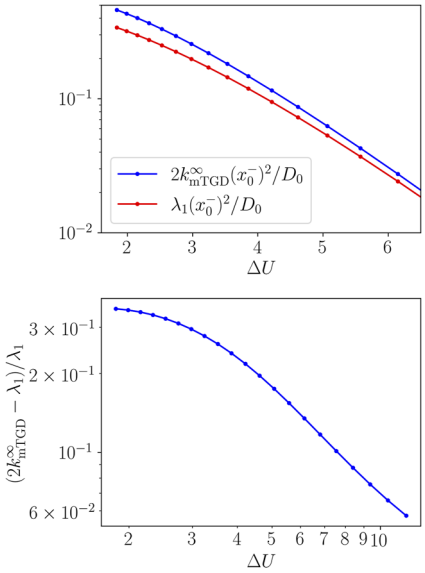

FIG. 5. Comparison between the kinetic eigenvalue λ_1 of the FPS operator with its asymptotic counterpart $2k^{\infty}_{mTGD}$ for a two-dimensional realization of the mTGD model. The calculations have been done for an isotropic diffusion matrix, $D^{++} = D^{--} = D_0$, and fixed angle $\theta = \pi/6$ and first eigenvalue $\sigma_1^2 = (x_0^-/5)^2$ of the covariance matrix $\boldsymbol{\Sigma}$ with a variable second eigenvalue σ_2^2 to produce an increasing potential barrier height ΔU. Upper panel: comparison of λ_1 with $2k^{\infty}_{mTGD}$ scaled by $D_0/(x_0^-)^2$ as a function of the barrier height ΔU. Lower panel: relative difference $(2k^{\infty}_{mTGD} - \lambda_1)/\lambda_1$ as a function of the barrier height ΔU in a logarithmic scale.

intrinsically different procedures just because they are based on different definitions of the asymptotic limit: the scaling Eq. (41) of the potential by the barrier height in the former and the scaling Eq. (47) of the second moments of the Gaussian distributions in the latter. In both cases, however, the kinetic eigenmode in the asymptotic limit is described by one-dimensional functional forms even if of different nature, Eqs. (44) and (54) in the two cases. Identification of the reaction coordinate exemplifies the difference of these two procedures. In the Kramers–Langer method, the reaction coordinate is determined by the unstable normal mode at the saddle point, depending on both the diffusion matrix and the curvature matrix according to Eq. (42), while in the case of the mTGD model it is independent of the diffusion matrix since it is derived from the asymptotic limit of the potential, which leads to Eq. (48) for the direction of the reaction coordinate. The reaction coordinates resulting from the two methods, however, are the same in the particular case of mTGD models with one odd coordinate only $(N^- = 1)$ because both the diffusion matrix $\mathbf{D}$ and the curvature matrix $\mathbf{U}_s^{(2)}$ at the saddle point, to be employed for the determination of the unstable normal model, are block separated with respect to even/odd coordinates. Still, different results for the asymptotic rate constant are recovered from the two methods, very much like the one-dimensional case that has been initially considered.

V. CONCLUSIONS

A large part of the literature about the stochastic analysis of activated processes is based on models of the mean field poten-

tial specified through suitable parameterized forms.[3] In this work, we follow the alternative route of modeling directly the equilibrium distribution through the linear combination of two Gaussians parameterized according to their second moments describing their widths. Even if the link between equilibrium distribution and mean field potential is clearly established by the Boltzmann relation, the two procedures are not equivalent from the point of view of the parametric space of the models. In particular, the linear scaling of the mean field potential is not in general allowed by parameterized forms of the equilibrium distribution. By using the stochastic description provided by the Fokker–Planck–Smoluchowski equation, we have characterized the diffusion models deriving from the parameterized Two-Gaussian Distribution, first in one-dimensional problems (the TGD model) and afterward in multidimensional problems (the mTGD model). The definition of the stochastic model through direct parameterization of equilibrium distributions becomes necessary when a physical model of the corresponding potential is not available as in the case of quantum tunneling.[12] However, we have shown here that this model also provides a flexible and convenient tool for studying the rate of activated processes as an alternative to the more conventional parameterized forms of mean field potential. In particular, the parameterization of equilibrium density in terms of a linear combination of Gaussian functions allows a straightforward generalization to multidimensional problems and facilitates the evaluation of expectation values.

A peculiarity of this kind of modeling activated processes through equilibrium distributions is that the large barrier limit is not reproduced by the Kramers (KAR) and the Kramers–Langer (KLAR) Asymptotic Relations. The one-dimensional case of TGD is particularly illuminating since in practice it has only one control parameter, which can be identified with the barrier height. The comparison with the exact numerical values of the rate constant provides clear evidence that the Kramers asymptotic result (KAR) does not supply the right pre-exponential factor of the Arrhenius form. The origin of the discrepancy resides in the fact that the Kramers and the Kramers–Langer asymptotic analysis are justified by linear scaling of the mean field potential, a procedure that is not allowed in the case of TGD and mTGD models. In the latter case, the barrier region described by a quadratic form of the potential is too narrow to guarantee the Kramers and Kramers–Langer asymptotic results. Then, one needs a different asymptotic procedure, which we have presented in this contribution together with its validation by comparison with the numerical results for one- and two-dimensional realizations of the proposed models.

Asymptotic results, even if they provide only approximations to the rate constants in the applications of stochastic theories necessarily dealing with finite barriers, are important tools for the identification of features of the model that control the kinetic process.

SUPPLEMENTARY MATERIAL

See the supplementary material for additional details on formal derivations.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Pierpaolo Pravatto: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Barbara Fresch**: Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Giorgio J. Moro**: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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