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Roto-translational diffusion of biaxial probes in uniaxial liquid crystal phases

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We discuss the problem of roto-translational diffusion of a rigid biaxial molecule dissolved in a uniaxial smectic liquid crystal phase. We examine distorted rod and disklike molecules and show how biaxiality and roto-translational coupling can produce significant effects on some of the correlation functions and spectral densities most useful in analyzing experimental observables. © *2000 American Institute of Physics.* [S0021-9606(00)50710-7]

I. INTRODUCTION

The description of molecular motions in liquid crystals is a subject of great importance both in its own right and as a tool for the interpretation of a variety of experimental results.[1–3] The problem has been treated in detail, as far as reorientation is concerned, assuming that the motion is diffusional and that it takes place in an effective (''molecular'') field potential describing the overall effect of the anisotropic solvent on the particle whose evolution is followed. The treatment has been pioneered by Nordio *et al.*[4] who dealt with uniaxial molecules reorienting in a uniaxial solvent but more recently a generalization to molecules of arbitrary symmetry reorienting in a uniaxial[5] or biaxial phase has been put forward.[6] A variety of experimental observables for biaxial molecules dissolved in liquid crystals, ranging from nuclear magnetic resonance spectral densities[7–9] to fluorescence polarized intensities,[10] have been interpreted using this approach, allowing the determination of the molecular rotational diffusion tensor components.

Similar problems arising in the reorientational kinetics of monodomain supermagnetic particles in external applied fields have recently been independently tackled.[11]

Translational motion in liquid crystals has also been experimentally[12–14] and theoretically[15–17] studied assuming a diffusional evolution. As far as translational dynamics is concerned, a liquid crystal behaves to a first approximation as an ordinary liquid in the nematic, where no long-range positional order exists, but not in a smectic phase, where molecules are instead distributed with their centers of mass being positioned, on average, on layers. It is worth noting that although in an idealized picture a smectic is represented as a collection of two-dimensional layers, molecules can actually migrate between layers. Accordingly, it can be assumed that in a smectic translational motion takes place in a molecular field corresponding to a periodic density distribution with a higher probability of finding molecules in layers.[18,19] At the same time the orientational distribution in a smectic *A* has, like that of a nematic, uniaxial symmetry, even if the constituent molecules are themselves biaxial. The simultaneous treatment of rotation and translation, needed in particular where roto-translational coupling exists, has been comparatively less treated. Thus the case of uniaxial molecules moving in a uniaxial smectic *A* phase has been treated by Moro and Nordio[20] and some applications to the analysis of experimental data have appeared,[21,22] but to the best of our knowledge the case, important in all practical applications of the rototranslation of less symmetric, biaxial, molecules has never been tackled. Here we wish to provide such a treatment for uniaxial mesophases. We shall discuss the problem in general first, considering the rototranslational evolution equation and its solution, that we shall provide employing a suitable matrix representation of the diffusion operator. Given the variety of experiments potentially sensitive to rotational–translational effects, and the fact that all of these are sensitive to roto-translational correlation functions, we have chosen to concentrate on the calculation of these quantities and on the examination of the effect of coupling on their behavior. We shall treat explicitly some typical cases both for elongated and flat biaxial molecules and examine how the correlation functions needed to interpret various experimental data are modified by the onset of roto-translational coupling.

II. THEORY

A. Description of the biaxial potential

We consider a uniformly aligned smectic *A* with layers perpendicular to the laboratory z axis and layers spacing d. The molecular field potential acting on a biaxial probe particle with position z and orientation ω in this liquid crystal phase has the same angular symmetry and spatial periodicity of the phase and may, in principle, be expanded in a product basis set of Wigner $D^{L}_{m,n}(\omega)$[23] and harmonic, cosine, functions:

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$$\frac{U(\omega,z)}{k_B T}=\sum_{L,n,p} u_{L,n;p}(D^L_{0,n}(\omega)+D^L_{0,-n}(\omega))\cos\frac{2\pi z}{d}p, \tag{1}$$

where k_B is the Boltzmann constant, T is the temperature, ω stands for the set of three Euler angles α,β,γ[23] and only $m=0$ Wigner matrices are employed here because of the assumed uniaxiality of the phase. It is important to note that only terms with L,n even need to be retained as a consequence of the fact that we assume to treat biaxial probe molecules that are invariant for a rotation of 180° about their principal axis. The coefficients $u_{L,n;p}$ determine the strength of interaction between the probe particle and its surroundings. In the particular case that the particle considered is a solute one, they will represent solute–solvent interactions. Notice also that the coefficients $u_{L,n;p}$ with $L\neq 0$, $p\neq 0$ cannot be factorized and correspond to a positional–orientational coupling. We shall use this potential for the general development (see Appendix). However, as far as numerical calculations go, we approximate the potential (1) retaining only the first few nonvanishing ordering terms allowed by the symmetry of the problem

$$\begin{aligned}\mathcal{U}(\omega,\xi)={}&u_{20,0}D^2_{0,0}(\omega)+u_{22,0}(D^2_{0,2}(\omega)+D^2_{0,-2}(\omega))\\&+u_{00,1}\cos\xi+u_{20,1}D^2_{0,0}(\omega)\cos\xi\\&+u_{22,1}(D^2_{0,2}(\omega)+D^2_{0,-2}(\omega))\cos\xi, \qquad (2)\\={}&u_{20,0}(1-\tfrac{3}{2}\sin^2\beta)+u_{22,0}\sqrt{\tfrac{3}{2}}\sin^2\beta\cos 2\gamma\\&+u_{00,1}\cos\xi+u_{20,1}(1-\tfrac{3}{2}\sin^2\beta)\cos\xi\\&+u_{22,1}\sqrt{\tfrac{3}{2}}\sin^2\beta\cos 2\gamma\cos\xi, \qquad (3)\end{aligned}$$

where we have introduced $\xi\equiv(2\pi/d)z$ and where to obtain this last expression we have used the explicit analytic expressions of the Wigner matrices.[24] This potential is the immediate generalization of the McMillan[18,19] smectic potential to the case of biaxial probes and it should be mentioned that the mean-field theory of uniaxial smectic phases formed of biaxial molecules has been studied by Averyanov and Primak.[25]

B. Roto-translational diffusion equation

The diffusion equation in the presence of a mean-field potential $U(\omega,z)$ is given[26–28] by:

$$\begin{aligned}\frac{\partial}{\partial t}P(\omega_0,r_0|\omega,r,t)={}&(-i\boldsymbol{L},\boldsymbol{\nabla}^T\boldsymbol{R}^T)\begin{pmatrix}\boldsymbol{D}_R & \boldsymbol{D}_{RT}\\ \boldsymbol{D}_{TR} & \boldsymbol{D}_T\end{pmatrix}\\&\times\begin{pmatrix}-i\left(\boldsymbol{L}+\boldsymbol{L}\dfrac{U(\omega,z)}{k_BT}\right)\\ \boldsymbol{R}\left(\boldsymbol{\nabla}+\boldsymbol{\nabla}\dfrac{U(\omega,z)}{k_BT}\right)\end{pmatrix}\\&\times P(\omega_0,r_0|\omega,r,t)\\={}&\boldsymbol{\Gamma}P(\omega_0,r_0|\omega,r,t),\end{aligned} \tag{4}$$

where $P(\omega_0,r_0|\omega,r,t)$ is the conditional transition probability of going from position–orientation r_0,ω_0 at time $t=0$ to r,ω at the time t, $\boldsymbol{L}$ is the dimensionless angular momentum operator written in the molecular frame[23] and $\boldsymbol{D}_R$, $\boldsymbol{D}_T$, $\boldsymbol{D}_{RT}$, $\boldsymbol{D}_{TR}$, represent rotational, translational and coupled diffusion tensors. The matrix $\boldsymbol{R}$ is the rotation matrix relative to the transformation form molecular to laboratory frame.[23]

Examining the evolution equation [Eq. (4)] we notice that the coupling between rotational and translational diffusions is due to the following three sources:

(1) Presence of terms that couple positional and angular degrees of freedom in the mean field potential. These terms are for instance of the type $D^L_{m,n}(\omega)\cos(2\pi/d)kz$, similar to those in the McMillan-type[19] mean field of potential valid for uniaxial probes [see Eq. (3)].

(2) Transformation of the diffusion tensor, as written in the laboratory frame, due to the rotation of the molecule. In fact we assume that the diffusion tensor is diagonal in the chosen molecular principal frame but the rotation of the molecule causes a transformation on the diffusion tensor which will be expressed as an *implicit angular dependence* of the translational motion. This contribution has been discussed, for instance, by Berne and Pecora[29] but seems to have been neglected in various other works.

(3) Presence of nonvanishing roto-translational diffusion coefficients (D_{RT} and D_{TR}) which correlate explicitly the rotations around an axis (e.g., z axis) to the translation along this or another one. Geometrical considerations lead to the conclusion that these terms are important mainly for chiral molecules, where propeller type effects can be expected,[30] and we will not consider their contribution here.

In practice the diffusion tensor $\boldsymbol{D}$ for the nonchiral molecules treated here is assumed to be diagonal in the molecular principal frame where it takes the form: $\boldsymbol{D}=\boldsymbol{D}_R\otimes\boldsymbol{D}_T$.

Performing the calculations implied in Eq. (4) the diffusion operator $\boldsymbol{\Gamma}$ can be written as a sum of two parts containing only orientational and positional differential operators

$$\boldsymbol{\Gamma}=\boldsymbol{\Gamma}_R+\boldsymbol{\Gamma}_T. \tag{5}$$

Here we consider smectic systems with one-dimensional positional order along the z direction and to obtain a simpler expression for the diffusion operator $\boldsymbol{\Gamma}_T$ it is convenient to take a projection of the transition probability over the only relevant degree of freedom, z.

$$P(\omega,z,t|\omega_0,z_0)=\int\int P(\omega,r,t|\omega_0,r_0)dxdy. \tag{6}$$

Performing this projection operation on both sides of the diffusion equation [Eq. (4)] and exchanging derivation and integration we obtain the *reduced diffusion operators* which do not contain any partial derivatives with respect to the x and y variables.

$$\begin{aligned}\boldsymbol{\Gamma}_R={}&-D_{R_x}[L_x^2+L_x(L_x\mathcal{U})]-D_{R_y}[L_y^2+L_y(L_y\mathcal{U})]\\&-D_{R_z}[L_z^2+L_z(L_z\mathcal{U})],\end{aligned} \tag{7}$$

$$\boldsymbol{\Gamma}_T=(D_{T_x}R_{13}^2+D_{T_y}R_{23}^2+D_{T_z}R_{33}^2)\left[\frac{\partial^2}{\partial z^2}+\frac{\partial}{\partial z}\frac{\partial\mathcal{U}}{\partial z}\right], \tag{8}$$

where $\mathcal{U}=\mathcal{U}(\omega,\xi)$ and $R_{i,j}$ are the elements of the Cartesian rotation matrix which will be expressed later in terms of Wigner matrices.[23] The roto-translational diffusion operator can be symmetrized with a similarity transformation constructed from the equilibrium distribution[5,6,31,32]

$$\hat{P}(\omega,z,t|\omega_0,z_0)=P^{-1/2}(\omega,z)P(\omega,z,t|\omega_0,z_0)P^{1/2}(\omega_0,z_0), \tag{9}$$

$$\hat{\mathbf{\Gamma}}=P^{-1/2}(\omega,z)\mathbf{\Gamma}P^{1/2}(\omega,z), \tag{10}$$

where we have used a ''hat'' to indicate a symmetrized quantity, and $P(\omega,z)$ is the equilibrium distribution, which we can write in terms of the mean field potential as:

$$P(\omega,z)=e^{-U(\omega,z)/k_BT}\bigg/\int e^{-U(\omega,z)/k_BT}d\omega dz. \tag{11}$$

It is convenient to redefine the diffusion coefficients as

$$\begin{aligned}&\rho=(D_{R_x}+D_{R_y})/2, \quad \rho_T=\left(\frac{2\pi}{d}\right)^2(D_{T_x}+D_{T_y})/2,\\ &\eta=2D_{R_z}/(D_{R_x}+D_{R_y}), \quad \eta_T=2D_{T_z}/(D_{T_x}+D_{T_y}),\\ &\epsilon=(D_{R_x}-D_{R_y})/(D_{R_x}+D_{R_y}),\\ &\epsilon_T=(D_{T_x}-D_{T_y})/(D_{T_x}+D_{T_y}).\end{aligned} \tag{12}$$

It is useful to notice that the coefficients η, η_T are connected to the axial anisotropy of the probe, while the coefficients ϵ and ϵ_T are related to its biaxiality and will vanish for uniaxial probes. Performing now the symmetrization in (10) gives the result

$$\hat{\mathbf{\Gamma}}=\rho(\hat{\mathbf{\Gamma}}_R+\mu\hat{\mathbf{\Gamma}}_T), \tag{13}$$

with

$$\begin{aligned}\hat{\mathbf{\Gamma}}_R=&-[\nabla^2+\tfrac{1}{2}(\nabla^2\mathcal{U})-\tfrac{1}{4}(L_+\mathcal{U})(L_-\mathcal{U})-\tfrac{1}{4}\eta(L_z\mathcal{U})^2\\ &+\epsilon(\tfrac{1}{2}(L_+^2+L_-^2)+\tfrac{1}{4}[(L_+^2+L_-^2)\mathcal{U}]\\ &-\tfrac{1}{8}[(L_+\mathcal{U})^2+(L_-\mathcal{U})^2])],\end{aligned} \tag{14}$$

$$\begin{aligned}\hat{\mathbf{\Gamma}}_T=&\left(\frac{1}{3}(2+\eta_T)+\frac{2}{\sqrt{6}}\epsilon_T(D^2_{0,2}+D^2_{0,-2})\right.\\ &\left.-\frac{2}{3}(1-\eta_T)D^2_{0,0}\right)\left[\frac{\partial^2}{\partial\xi^2}+\frac{1}{2}\frac{\partial^2\mathcal{U}}{\partial\xi^2}-\frac{1}{4}\left(\frac{\partial\mathcal{U}}{\partial\xi}\right)^2\right],\end{aligned} \tag{15}$$

$$\nabla^2=L^2+(\eta-1)L_z^2. \tag{16}$$

In Eq. (13) two important parameters appear; ρ which defines the overall time scale of the diffusive process, and $\mu=\rho_T/\rho$ which is a measure of the relative importance of the translational and rotational motions. Now the complete symmetrized diffusion equation reads:

$$\frac{1}{\rho}\frac{\partial}{\partial t}\hat{P}(\omega_0,z_0|\omega,z,t)=(\hat{\mathbf{\Gamma}}_R+\mu\hat{\mathbf{\Gamma}}_T)\hat{P}(\omega_0,z_0|\omega,z,t). \tag{17}$$

To solve this complicated equation, we proceed by expanding the transition probability over an orthonormal basis function set as in Refs. 4–6, 20, and 31. In this case the basis function set is chosen as a direct product of Wigner matrices (for the angular dependence) and harmonic plane waves (for the spatial dependence). The completeness and orthonormality of this basis are a direct consequence of those of the two basis sets employed.

$$\hat{P}(\omega_0,\xi_0|\omega,\xi,t)=\sum_{L,m,n,k}C_{L,m,n,k}|L,m,n,k\rangle, \tag{18}$$

where we have adopted the Dirac notation to indicate

$$\begin{aligned}|L,m,n,k\rangle&\equiv\mathcal{D}^L_{m,n}(\omega)\psi_k(\xi)\\ &\equiv\sqrt{\frac{2L+1}{8\pi^2}}D^L_{m,n}(\omega)\frac{e^{ik\xi}}{\sqrt{d}}.\end{aligned} \tag{19}$$

Inserting expansion (18) in the diffusion equation (17) multiplying both sides for $\langle L',m',n',k'|$ and using the orthonormality relations an infinite system of linear differential equations for the expansion coefficients is obtained. In practice we also assume that an approximate solution of the problem may be obtained to a certain level of accuracy simply by truncating the infinite summation in expression (18) after a certain, sufficiently large but finite number of terms. With this hypothesis the solution of the roto-translational equation is reduced to the solution of a finite system of linear differential equations

$$\frac{1}{\rho}\dot{\boldsymbol{C}}(t)=\hat{\boldsymbol{R}}\boldsymbol{C}(t), \tag{20}$$

where $\hat{\boldsymbol{R}}$ has elements

$$\begin{aligned}&\hat{R}_{L,m,n,k;L',m',n',k'}\\ &\quad=\langle L',m',n',k'|\hat{\mathbf{\Gamma}}|L,m,n,k\rangle\\ &\quad=\int d\omega d\xi\mathcal{D}^{L'*}_{m',n'}(\omega)\psi^*_{k'}(\xi)\hat{\mathbf{\Gamma}}\psi_k(\xi)\mathcal{D}^L_{m,n}(\omega).\end{aligned} \tag{21}$$

The solution can be expressed as an exponential matrix. The uniaxiality of the liquid crystal phase implies, as already mentioned, that the mean field potential $\mathcal{U}(\omega,\xi)$ cannot depend from the first Euler angle (α) and this causes the reducibility of the diffusion matrix $(\hat{\boldsymbol{R}})$, which does not contain elements with different values of the m indices

$$\begin{aligned}&\hat{R}^m_{L,n,k;L',n',k'}\\ &\quad=\int d\omega d\xi\mathcal{D}^{L'*}_{m,n'}(\omega)\psi^*_{k'}(\xi)\hat{\mathbf{\Gamma}}\psi_k(\xi)\mathcal{D}^L_{m,n}(\omega).\end{aligned} \tag{22}$$

The m index can thus be simply used to label blocks of the diffusional matrix. We can then write the formal solution to Eq. (20) as

$$\begin{aligned}c^m_{L,n,k}(t)=&\sum_{L',n',k'}\sum_K\hat{X}^m_{L,n,k;K}\\ &\times e^{t\rho\hat{r}^m_K}\hat{X}^{mT}_{K;L',n',k'}c^m_{L',n',k'}(\omega_0,\xi_0,0),\end{aligned} \tag{23}$$

where we have employed the solutions of the eigenvalue equation

$$\hat{\boldsymbol{R}}^m\hat{\boldsymbol{X}}^m=\hat{\boldsymbol{X}}^m\hat{\boldsymbol{r}}^m. \tag{24}$$

$\hat{\boldsymbol{X}}$ is the eigenvector matrix, and $\hat{\boldsymbol{r}}$ is the diagonal matrix containing the eigenvalues of $\hat{\boldsymbol{R}}$.

$$\begin{aligned}\hat{P}(\omega_0,\xi_0|\omega,\xi,t)=&\sum \mathcal{D}^{L}_{m,n}(\omega)\psi_k(\xi)\hat{X}^{m}_{L,n,k;K}\\&\times e^{t\rho\hat{r}^m_K}\hat{X}^{mT}_{K;L',n',k'}c^{m}_{L',n',k'}(\omega_0,\xi_0,0)\\=&\sum \mathcal{D}^{L}_{m,n}(\omega)\psi_k(\xi)\hat{X}^{m}_{L,n,k;K}\\&\times e^{t\rho\hat{r}^m_K}\hat{X}^{mT}_{K;L',n',k'}\mathcal{D}^{L'*}_{m,n'}(\omega_0)\psi^{*}_{k'}(\xi_0),\end{aligned}\tag{25}$$

where the initial values of the expansion coefficients are obtained from the condition:

$$\hat{P}(\omega_0,\xi_0|\omega,\xi,0)=\delta(\omega-\omega_0)\delta(\xi-\xi_0).\tag{26}$$

Equation (25) represents a formal solution for the conditional probability that we shall employ to calculate the relevant properties of the problem.

C. Roto-translational correlation functions

As dynamic observables can be typically described in terms of roto-translational correlation functions or of their Fourier transforms[5,6,31,33] we concentrate on the calculation of these quantities. The roto-translational correlation functions are defined in general as

$$\begin{aligned}\Phi^{LL'}_{m,nn',kk'}(t)=&\int d\omega d\xi\int d\omega_0 d\xi_0 D^{L}_{m,n}(\omega)\\&\times e^{ik\xi}P(\omega_0,\xi_0|\omega,\xi,t)D^{L'*}_{m,n'}(\omega_0)e^{-ik'\xi_0}\\=&\int d\omega d\xi\int d\omega_0 d\xi_0 D^{L}_{m,n}(\omega)e^{ik\xi}\\&\times P^{1/2}(\omega_0,\xi_0)P^{-1/2}(\omega,\xi)\\&\times\hat{P}(\omega_0,\xi_0|\omega,\xi,t)D^{L'*}_{m,n'}(\omega_0)e^{-ik'\xi_0}.\end{aligned}\tag{27}$$

Inserting into this equation the expression previously found, Eq. (25), for $P(\omega_0,\xi_0|\omega,\xi,t)$ and noting the asymptotic condition

$$\lim_{t\to\infty}\hat{P}(\omega_0,\xi_0|\omega,\xi,t)=P^{1/2}(\omega_0,\xi_0)P^{1/2}(\omega,\xi),\tag{28}$$

and integrating we obtain the following explicit expression for the correlation functions:

$$\begin{aligned}\Phi^{LL'}_{m,nn',kk'}(t)=&\sum_{J,p,r}\sum_{J',p',r'}\sum_{J'',J'''}\sum_{K}(-1)^{p+p'}\sqrt{\frac{2J'+1}{2J'''+1}}\sqrt{\frac{2J+1}{2J''+1}}\hat{X}^{m}_{J,p,r;K}\hat{X}^{m}_{J',p',r';K}e^{t\rho\hat{r}^m_K}\hat{X}^{0}_{J'',n'-p,k-r;0}\\&\times\hat{X}^{0}_{J''',n-p',k-r';0}C(L,J',J''',m,-m)C(L,J',J''',n,-p')C(L',J,J'',m,-m)C(L',J,J'',n',-p),\end{aligned}\tag{29}$$

where $C(J_1,J_2,J_3,m_1,m_2)$ are Clebsch–Gordan coefficients.[23] This expression may be rewritten in a form more convenient for computational optimization by defining auxiliary vectors whose rotation may be performed at the same time of the diagonalization[5,6,31]

$$\begin{aligned}(V^{L}_{m,n,k})_{J',p',r'}=&(-1)^{p'}\sqrt{2J+1}\sum_{J'''}\frac{1}{\sqrt{2J'''+1}}\\&\times\hat{X}^{0}_{J''',n-p',k-r';0}C(L,J',J''',m,-m)\\&\times C(L,J',J''',n,-p'),\end{aligned}\tag{30}$$

$$\begin{aligned}\Phi^{LL'}_{m,nn',kk'}(t)=&\sum_{K}\left(\sum_{J,p,r}(V^{L}_{m,n,k})_{J,p,r}\hat{X}^{m}_{J,p,r,K}\right)\\&\times e^{t\rho\hat{r}^m_K}\left(\sum_{J',p',r'}(V^{L'}_{m,n',k'})_{J',p',r'}\hat{X}^{m}_{J',p',r',K}\right)\end{aligned}\tag{31}$$

$$=\sum_{K}(b^{LL'}_{m,nn',kk'})_K e^{t(a^{LL'}_{m,nn',kk'})_K}.\tag{32}$$

Limiting values: The initial and long time asymptotic values of the correlation functions are equilibrium, time independent, quantities and may be expressed in terms of order parameters, without going through the entire solution of the diffusion equation. This observation allows us to check the reliability of the previously done truncation, and provides an indication about the number of basis function to be retained in the expansion (18).

Initial value: At the initial time, $t=0$, the transition probability distribution is known and is simply given by a Dirac's delta distribution (26), so that

$$\begin{aligned}\Phi^{LL'}_{m,nn',kk'}(0)=&\langle D^{L}_{m,n}(\omega)D^{L'*}_{m,n'}(\omega)e^{ik\xi}e^{-ik'\xi}\rangle\\=&\sum_{J=|L-L'|}^{L+L'}(-1)^{m-n'}C(L,L',J,m,-m)\\&\times C(L,L',J,n,-n')\\&\times\langle D^{J}_{0,n-n'}(\omega)e^{i(k-k')\xi}\rangle,\end{aligned}\tag{33}$$

where the averages $\langle D^{J}_{0,n-n'}(\omega)e^{i(k-k')\xi}\rangle$ are orientational–positional order parameters.

Asymptotic value: In the long time limit the transition probability of the Markov process taking the state variable

TABLE I. Potential expansion coefficients [see Eq. (2)] and corresponding order parameters used for the disk and rodlike molecules discussed.

	$u_{20,0}$	$u_{22,0}$	$u_{00,1}$	$u_{20,1}$	$u_{22,1}$
Disklike	1.900	0.618	−0.108	2.149	0.519
Rodlike	−3.333	−0.222	−0.378	−0.760	−4.239
	$\langle \mathbf{D}^2_{00}\rangle$	$\langle \mathbf{D}^2_{02}\rangle$	$\langle \cos\xi\rangle$	$\langle \mathbf{D}^2_{00}\cos\xi\rangle$	$\langle \mathbf{D}^2_{02}\cos\xi\rangle$
Disklike	−0.300	−0.223	0.400	−0.200	−0.150
Rodlike	0.400	0.0693	0.400	0.200	0.150

from (ω_0,ξ_0) to (ω,ξ) tends to the equilibrium value of the arrival state (ω,ξ), so the asymptotic value of the correlation functions is given by expression (28)

$$\Phi^{LL'}_{m,nn',kk'}(\infty)=\langle D^L_{m,n}(\omega)e^{ik\xi}\rangle\langle D^{L'*}_{m,n'}(\omega_0)e^{-ik'\xi_0}\rangle\delta_{mo}. \tag{34}$$

1. Symmetries of the correlation functions

The correlation functions defined as in (27) are not all independent but obey symmetry relations which link some of them. These relations are important both to check the validity of the results obtained and to reduce the number of correlation function to be studied. The symmetry relations obtained implementing particle and mesophase symmetry are:

$$\Phi^{LL'}_{m,nn',kk'}(t)=\langle D^L_{m,n}(\omega_0)e^{ik\xi_0}D^{L'*}_{m,n'}(\omega)e^{-ik'\xi}\rangle \tag{35}$$

$$=\langle D^L_{-m,n}(\omega_0)e^{ik\xi_0}D^{L'*}_{-m,n'}(\omega)e^{-ik'\xi}\rangle$$

$$=\Phi^{LL'}_{-m,nn',kk'}(t) \tag{36}$$

$$=\langle D^L_{m,-n}(\omega_0)e^{ik\xi_0}D^{L'*}_{m,-n'}(\omega)e^{-ik'\xi}\rangle$$

$$=\Phi^{LL'}_{m,-n-n',kk'}(t) \tag{37}$$

$$=\langle D^L_{m,n}(\omega_0)e^{-ik\xi_0}D^{L'*}_{m,n'}(\omega)e^{ik'\xi}\rangle$$

$$=\Phi^{LL'}_{m,nn',-k-k'}(t). \tag{38}$$

We also have the asymptotic long time limit results

$$\Phi^{LL'}_{m,nn',kk'}(\infty)=0,\quad \text{for } m\neq 0, \tag{39}$$

$$\Phi^{LL'}_{m,nn',kk'}(\infty)=0,\quad \text{for } n,n' \text{odd}. \tag{40}$$

D. Correlation times and spectral densities

To provide a further characterization of the roto-translational dynamics two other quantities linked to experiment may be introduced. The first one is the correlation time, defined as the area comprised between a certain correlation function and its asymptotic limiting value.

$$\tau^{LL'}_{m,nn',kk'}=\int_0^\infty[\Phi^{LL'}_{m,nn',kk'}(t)-\Phi^{LL'}_{m,nn',kk'}(\infty)]dt$$

$$=\int_0^\infty\sum_K[(b^{LL'}_{m,nn',kk'})_K e^{t(a^{LL'}_{m,nn',kk'})_K}$$

$$-(b^{LL'}_{m,nn',kk'})_0]dt,$$

$$\tau^{LL'}_{m,nn',kk'}=\sum_{K\neq 0}\frac{(b^{LL'}_{m,nn',kk'})_K}{(a^{LL'}_{m,nn',kk'})_K}. \tag{41}$$

Another quantity, particularly helpful in various spectroscopies, is the spectral density, defined as the Fourier–Laplace transform of the correlation functions, subtracted of their long time asymptotic value, at a frequency $\hat{\omega}$.

$$J^{LL'}_{m,nn',kk'}(\hat{\omega})=\int_0^\infty\Phi^{LL'}_{m,nn',kk'}(t)e^{-i\hat{\omega}t}dt$$

$$=\int_0^\infty\sum_K(b^{LL'}_{m,nn',kk'})_K e^{t(a^{LL'}_{m,nn',kk'})_K}e^{-i\hat{\omega}t}dt$$

$$=\sum_{K\neq 0}\frac{(b^{LL'}_{m,nn',kk'})_K(a^{LL'}_{m,nn',kk'})_K}{(a^{LL'}_{m,nn',kk'})^2_K+\hat{\omega}^2}. \tag{42}$$

The correlation times are connected to zero frequency spectral densities. Having provided a general set of expressions for what we reckon are the relevant dynamic quantities of the problem, we now turn to numerical results.

III. RESULTS

A key question we are concerned with is the effect of roto-translational coupling on experimental observables. To try to answer this, we have investigated the dependence of some relevant rototranslational correlation functions on the molecular geometry of the probe for various smectic potentials. In particular we have studied two types of probes: Elongated (rodlike) probes which tend to align their axis of minimum biaxiality (taken as molecular z axis) parallel to the director, and oblate (disklike) probes which tend to align this axis perpendicular to the director of the phase.[34]

We have arbitrarily chosen to use for the coefficients of the biaxial potential in Eq. (3) values that yield the orientational order parameters $\langle D^2_{00}\rangle$, $\langle D^2_{02}\rangle$ used in Ref. 5 and a translational order parameter $\langle\cos\xi\rangle=0.4$. Moreover we use a geometric type mean for the mixed orientational–translational order parameters: $|\langle D^2_{00}\cos\xi\rangle|\sim\sqrt{|\langle D^2_{00}\rangle||\langle\cos\xi\rangle|}$; $|\langle D^2_{02}\cos\xi\rangle|\sim\sqrt{|\langle D^2_{02}\rangle||\langle\cos\xi\rangle|}$. The set of potential coefficients and of the order parameters corresponding to the cases that we have studied is reported in Table I.

As a check of our calculations we have first tried to reproduce already known results. Thus we have confirmed that in the case of purely rotational diffusion of our biaxial

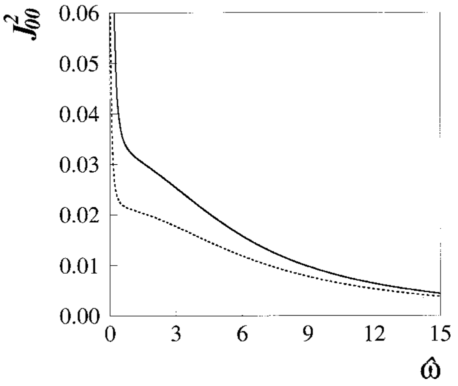

FIG. 1. Spectral densities $J^2_{00}(\hat{\omega})$ for the roto-translation of uniaxial probes in the case of (a) (full line) rodlike molecules as treated by Moro and Nordio (Ref. 20) for smectic potential coefficients: $u_{20,0}=-3.70$, $u_{00,1}=3.00$, $u_{20,1}=-1.30$ corresponding to order parameters $\langle D^2_{00}\rangle=0.564$, $\langle \cos\xi\rangle=-0.725$, $\langle D^2_{00}\cos\xi\rangle=-0.386$. (b) Disklike molecules (dotted line). We have used $u_{20,0}=0.137\times10^{-2}$, $u_{00,1}=-2.84\times10^{-2}$, $u_{20,1}=-1.10\times10$, corresponding to $\langle D^2_{00}\rangle=-0.300$, $\langle\cos\xi\rangle=-0.725$, $\langle D^2_{00}\cos\xi\rangle=0.466$. The diffusion parameters employed are: $\mu=0.088\,24$, $\eta=4.00$, $\eta_T=0.123\,53$. The frequency $\hat{\omega}$ is in ρ units.

molecules (that is when the translational contribution $\mu=0.$) we obtain indeed the same results presented in Ref. 5. We have then considered the case of roto-translation of uniaxial probes (that is the limit of vanishing rotational and translational diffusion biaxiality $\epsilon=0.$, $\epsilon_T=0.$) in smectics and we have found that the results for the spectral densities $J^2_{00}(\hat{\omega})=J^{22}_{0,00,00}(\hat{\omega})$ and for rodlike molecules, shown in Fig. 1, are in excellent agreement with the results obtained by Moro and Nordio[20] in this limiting case. As discussed in Ref. 20 the sharp peak at zero frequency is an effect of the slower translational motion. We have then also computed the similar spectral density for a disklike solute particle moving in a smectic, shown in Fig. 1 as the dotted line. The behavior is qualitatively similar, although the details are of course quite different, in particular at low frequencies ($\hat{\omega}\sim2.5$) where the translational effects are greater.

We now turn to the introduction of biaxiality of the probe molecule and of the solute–solvent potential acting on this diffusing particle, which represents the main thrust of the paper. The problem we deal with involves a number of solute and solvent parameters, whose effects are difficult to disentangle. We have thus tried to examine some of the major effects one by one and we now present in turn our results for correlation functions of rod (in Figs. 2–4) and disk (in Figs. 5–7) solutes.

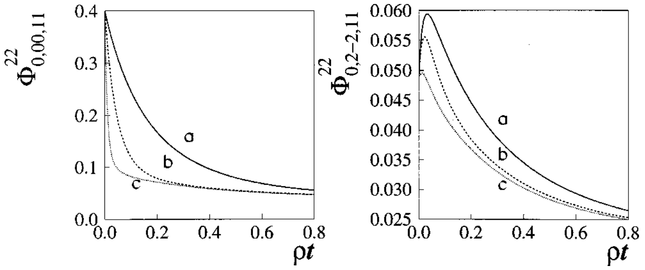

FIG. 2. Effect of the translational diffusion contribution parameter μ on the second rank correlation functions $\Phi^{22}_{0,00,11}$ and $\Phi^{22}_{0,2-2,11}$ and on their respective correlation times $\tau^{22}_{0,00,11}$ and $\tau^{22}_{0,2-2,11}$ for rodlike molecules. (a) (Full line) $\mu=0.2$ ($\tau^{22}_{0,00,11}=7.93\times10^{-2}$, $\tau^{22}_{0,2-2,11}=1.38\times10^{-2}$), (b) (dashed line) $\mu=1.0$ ($\tau^{22}_{0,00,11}=3.63\times10^{-3}$, $\tau^{22}_{0,2-2,11}=1.04\times10^{-2}$), (c) (dotted line) $\mu=5.0$ ($\tau^{22}_{0,00,11}=2.44\times10^{-2}$, $\tau^{22}_{0,2-2,11}=9.00\times10^{-3}$). $\eta_T=20.0$, $\epsilon=0.6$, $\epsilon_T=0.3$.

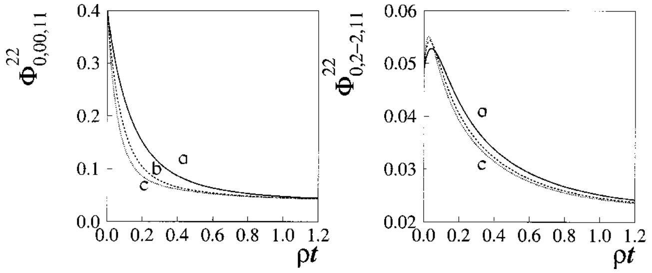

FIG. 3. Effect of the rotational and translational diffusion tensor anisotropy ratios η, η_T on the correlation functions for elongated molecules. The ratio (η/η_T) has been fixed at 4.0. (a) (Full line) $\eta=1.25$, $\eta_T=5.0$ (correlation times are $\tau^{22}_{0,00,11}=7.08\times10^{-2}$, $\tau^{22}_{0,2-2,11}=1.30\times10^{-2}$); (b) (dashed line) $\eta=2.5$, $\eta_T=10.0$ ($\tau^{22}_{0,00,11}=4.90\times10^{-2}$, $\tau^{22}_{0,2-2,11}=1.16\times10^{-2}$); (c) (dotted line) $\eta=3.75$, $\eta_T=15.0$ ($\tau^{22}_{0,00,11}=4.08\times10^{-2}$, $\tau^{22}_{0,2-2,11}=1.03\times10^{-2}$). The values of the other coefficients are: $\mu=1.0$, $\epsilon=0.6$, $\epsilon_T=0.3$.

In Fig. 2 we start examining the effect of increasing the relative importance of the translational motion, as obtained by varying the parameter μ, on two specific correlation functions: $\Phi^{22}_{0,00,11}=\langle P_2(\cos\beta_0)e^{-i\xi_0}P_2(\cos\beta_t)e^{i\xi}\rangle$ and $\Phi^{22}_{0,2-2,11}=\langle D^2_{02}(\omega_0)e^{-i\xi_0}D^{2}_{0-2}{}^{*}(\omega)e^{i\xi}\rangle$. The first only involves molecular tumbling, the second also depends on spinning around the molecule z axis. The effect of translation is noticeable in both cases, but larger in the first one that shows a much faster relaxation to equilibrium as μ increases and the combined effect of translation and rotation comes into play.

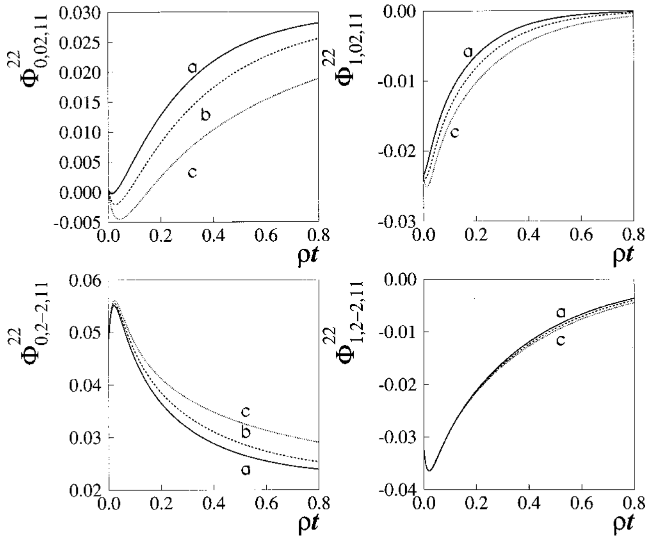

FIG. 4. Influence of the rotational and translational diffusion tensor biaxiality coefficients ϵ, ϵ_T [see Eq. (12)] for rodlike molecules. We consider the correlation functions on the second rank correlation functions $\Phi^{22}_{0,02,11}$, $\Phi^{22}_{1,02,11}$, $\Phi^{22}_{0,2-2,11}$, and $\Phi^{22}_{1,2-2,11}$. The ratio (ϵ/ϵ_T) has been fixed at 2.0: (a) (full line) $\epsilon=0.3$, $\epsilon_T=0.15$ ($\tau^{22}_{0,02,11}=-9.55\times10^{-3}$, $\tau^{22}_{1,02,11}=-3.68\times10^{-3}$, $\tau^{22}_{0,2-2,11}=8.18\times10^{-3}$, $\tau^{22}_{1,2-2,11}=-1.31\times10^{-2}$); (b) (dashed line) $\epsilon=0.6$, $\epsilon_T=0.3$ ($\tau^{22}_{0,02,11}=1.39\times10^{-2}$, $\tau^{22}_{1,02,11}=-4.50\times10^{-3}$, $\tau^{22}_{0,2-2,11}=1.04\times10^{-2}$, $\tau^{22}_{1,2-2,11}=-1.35\times10^{-2}$); (c) (dotted line) $\epsilon=0.9$, $\epsilon_T=0.45$ ($\tau^{22}_{0,02,11}=-2.62\times10^{-2}$, $\tau^{22}_{1,02,11}=-5.83\times10^{-5}$, $\tau^{22}_{0,2-2,11}=1.70\times10^{-2}$, $\tau^{22}_{1,2-2,11}=-1.40\times10^{-2}$).

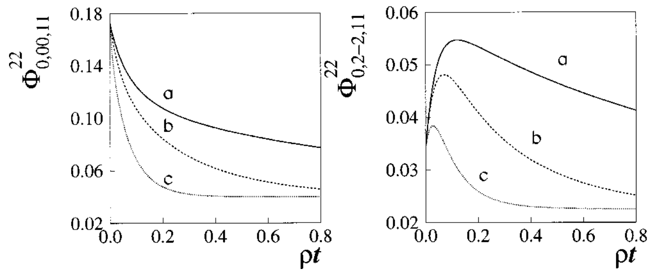

FIG. 5. Disklike molecules. Dependence of two correlation functions from the translational contribution parameter; (a) full line $\mu=0.20$ ($\tau^{22}_{0,00,11}=3.56\times10^{-2}$, $\tau^{22}_{0,2-2,11}=1.34\times10^{-3}$), (b) dashed line $\mu=1.00$ ($\tau^{22}_{0,00,11}=1.92\times10^{-2}$, $\tau^{22}_{0,2-2,11}=6.06\times10^{-4}$), (c) dotted line $\mu=5.00$ ($\tau^{22}_{0,00,11}=1.03\times10^{-2}$, $\tau^{22}_{0,2-2,11}=2.46\times10^{-4}$). The other diffusion coefficients have been fixed at the values $\eta=5.00$, $\eta_T=20.0$, $\epsilon=0.60$, $\epsilon_T=0.30$.

Moreover an increase of μ induces a decrease of the maximum of the functions $\Phi^{22}_{0,2-2,11}$. Both these effects can also be noticed looking at the correlation times which become shorter as μ increases.

We examine next the effect of anisotropy in the rotational and translational diffusion tensors by varying the ratios η, η_T defined in Eq. (12), while keeping a certain ratio of the translational to rotational contributions η/η_T fixed to 4.0 and assuming a certain translation–rotation ratio μ, here 1. This effect, that is related to a change in the molecule aspect ratio is shown in Fig. 3 to be not too big, at least for the chosen values of ϵ.

The consequences of changes in the rotational and translational biaxiality ϵ, ϵ_T are shown in Fig. 4 for various biaxial correlation functions. Here the effect of the biaxiality is larger for the first type of functions ($m=0$), while the second type ($m=1$) seems to be almost independent from these parameters. Notice also that for these correlations of different Wigner functions the starting value can be negative as it could be deduced directly from Eq. (33).

A similar type of study has also been performed on distorted disks and reported in the next three figures (i.e., Figs. 5–7). Also in the case of disklike molecules the effects of increasing the value of the parameter μ is to produce a faster decay of the correlations to their asymptotic values [Eq. (34)]. The effect seems to be particularly important for the spinning type correlation function $\Phi^{22}_{0,2-2,11}$ and should lead to observable results. No significative differences can be observed between the two rod and disk cases when varying the parameter η. Conversely the variation of the biaxial parameters ϵ and ϵ_T can be revealed only in the correlation functions with $m=1$ (see Fig. 7).

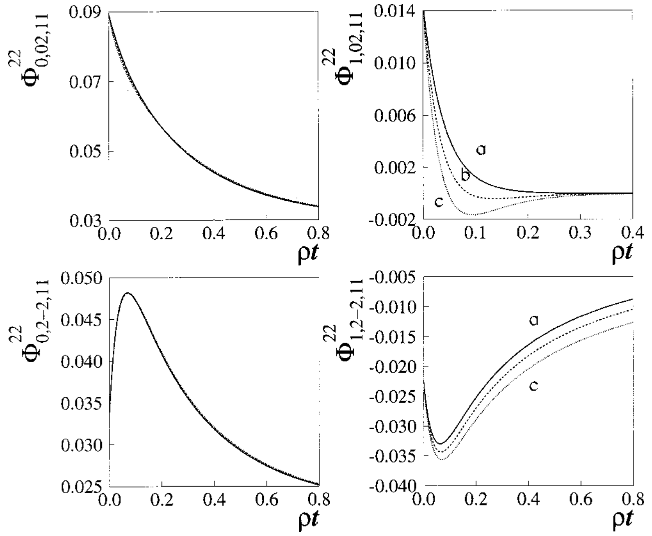

FIG. 7. Disklike molecules. Dependence of the correlation functions from the biaxiality coefficients [see Eq. (12)] ϵ, ϵ_T for the rotational and translational diffusion tensor. The ratio (ϵ/ϵ_T) has been fixed at 2.00: (a) full line $\epsilon=0.30$, $\epsilon_T=0.15$ ($\tau^{22}_{0,02,11}=1.62\times10^{-2}$, $\tau^{22}_{1,02,11}=5.83\times10^{-4}$, $\tau^{22}_{0,2-2,11}=1.00\times10^{-2}$, $\tau^{22}_{1,2-2,11}=-2.23\times10^{-2}$); (b) dashed line $\epsilon=0.60$, $\epsilon_T=0.30$ ($\tau^{22}_{0,02,11}=1.62\times10^{-2}$, $\tau^{22}_{1,02,11}=2.92\times10^{-4}$, $\tau^{22}_{0,2-2,11}=1.01\times10^{-2}$, $\tau^{22}_{1,2-2,11}=-2.69\times10^{-2}$); (c) dotted line $\epsilon=0.90$, $\epsilon_T=0.45$ ($\tau^{22}_{0,02,11}=1.63\times10^{-2}$, $\tau^{22}_{1,02,11}=1.72\times10^{-5}$, $\tau^{22}_{0,2-2,11}=1.02\times10^{-2}$, $\tau^{22}_{1,2-2,11}=-3.40\times10^{-2}$). The other coefficients have been fixed at $\mu=1.00$, $\eta=5.00$, $\eta_T=20.0$.

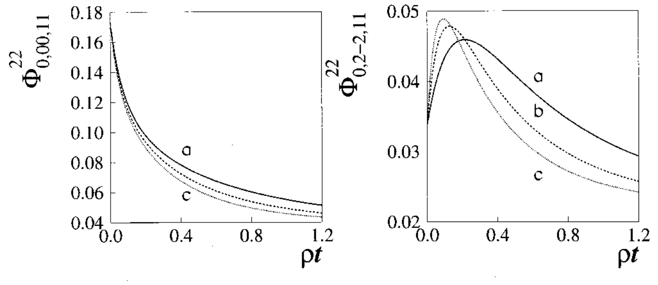

FIG. 6. Disklike molecules. Dependence of the correlation functions from the anisotropy ratios η, η_T in the rotational and translational diffusion tensors. The ratio (η/η_T) has been fixed at 4.0: (a) (full line) $\eta=1.25$, $\eta_T=5.0$ ($\tau^{22}_{0,00,11}=5.11\times10^{-2}$, $\tau^{22}_{0,2-2,11}=2.35\times10^{-2}$); (b) (dashed line) $\eta=2.50$, $\eta_T=10.0$ ($\tau^{22}_{0,00,11}=3.97\times10^{-2}$, $\tau^{22}_{0,2-2,11}=1.66\times10^{-2}$); (c) dotted line $\eta=3.75$, $\eta_T=15.0$ ($\tau^{22}_{0,00,11}=3.33\times10^{-2}$, $\tau^{22}_{0,2-2,11}=1.33\times10^{-2}$). The values of the other coefficients are: $\mu=1.00$, $\epsilon=0.60$, $\epsilon_T=0.30$.

In order to provide quantities more directly related to experimental observables we have also investigated the effect of the relative importance of the rotational and translational motion denoted by the parameter μ on the behavior of the frequency dependent spectral density $J^2_{00}(\hat{\omega})$. To do this we have calculated $J^2_{00}(\hat{\omega})$ for various values of the coefficient μ for both cases of prolate and oblate biaxial molecules, generalizing the results shown in Fig. 1 for uniaxial rod and disklike molecules. The results are reported in Fig. 8

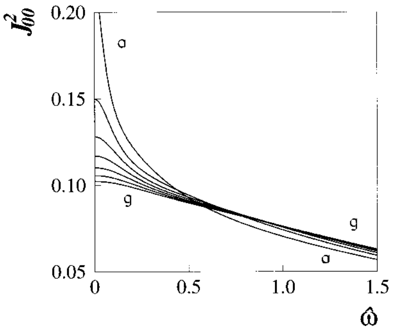

FIG. 8. Spectral densities $J^2_{00}(\hat{\omega})$ behavior for rodlike molecules of table 1: (a) $\mu=0.25$, (b) $\mu=0.50$, (c) $\mu=0.75$, (d) $\mu=1.0$, (e) $\mu=1.25$, (f) $\mu=1.50$, (g) $\mu=1.75$. The other diffusion coefficients are the same employed in Fig. 1: $\eta=4.00$, $\eta_T=0.123\,53$, $\epsilon=0.6$, $\epsilon_T=0.018\,53$.

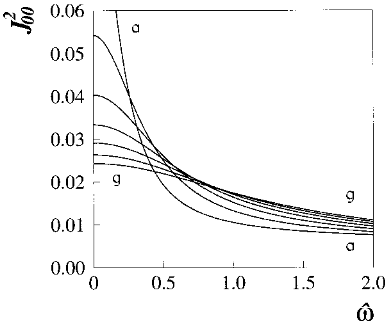

FIG. 9. Spectral densities $J^2_{00}(\hat{\omega})$ behavior for disklike molecules of table 1: (a) $\mu=0.25$, (b) $\mu=0.50$, (c) $\mu=0.75$, (d) $\mu=1.0$, (e) $\mu=1.25$, (f) $\mu=1.50$, (g) $\mu=1.75$. The other diffusion coefficients are the same employed in Fig. 1: $\eta=4.00$, $\eta_T=0.123\,53$, $\epsilon=0.6$, $\epsilon_T=0.018\,53$.

for rods and in Fig. 9 for disks, plotted as a family of curves using seven different values of μ. In both cases as the translational contribution μ increases the overall relaxation to equilibrium becomes more effective and the faster decay to equilibrium gives a broader spectral density.

IV. CONCLUSIONS

We have developed a theory for roto-translational diffusion of a rigid biaxial molecule in a uniaxial smectic liquid crystal. We have considered elongated or flat particles and we have shown that the coupling of rotations and translations can have significant effects on correlation functions that, in turn, have a direct influence on experimental observables for these molecules. The theory should be useful in the planning of experiments particularly sensitive to roto-translational effects such as those involving diffusion studied by optical,[12] neutron scattering,[14] and magnetic resonance techniques.[13,35,36] Another application should be in allowing the proper determination of rotational and translational diffusion tensor components for molecules of arbitrary shape dissolved in smectics by employing in the analysis of experimental data[9,37] this more general theory instead of one purely based on rotational motions such as that in Ref. 5. We also mention that computer simulations data on molecular diffusion in smectics are starting to be available[38] and that the analysis of these molecular dynamics virtual experiments will provide, for selected model systems, roto-translational correlation functions such as the ones directly investigated here. This should allow a test of the present diffusional theory in models with specific molecular interactions, contributing to an investigation of the relation between molecular features such as size and shape anisotropy and the type of motion observed in smectic phases.

ACKNOWLEDGMENTS

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APPENDIX A: MATRIX ELEMENTS OF THE DIFFUSION OPERATOR

Here we present, for the convenience of a reader interested in investigating smectic potentials different from the one studied here, explicit expressions for the various terms contributing to the diffusion operator matrix elements presented in Eqs. (13), (15), (21), and (22).

1. Rotational part

$$\langle L',m,n';k'|\nabla^2|L,m,n;k\rangle = [L(L+1)+(\eta-1)n^2]\,\delta_{L,L'}\,\delta_{n,n'}\,\delta_{k,k'}, \tag{A1}$$

$$\begin{aligned}\langle L',m,n';k'|\nabla^2\mathcal{U}|L,m,n;k\rangle &= \frac{1}{2}\sqrt{\frac{2L+1}{2L'+1}}\sum_{L'',n'',p''} u_{L''n'';p''}[L''(L''+1)\\ &\quad +(\eta-1)n''^2]C(L,L'',L',m,0)C(L,L'',L',n,n'')\\ &\quad \times(\delta_{k-k',p''}+\delta_{k-k',-p''})\,\delta_{n,n'-n''},\end{aligned} \tag{A2}$$

$$\begin{aligned}\langle L',m,n';k'|(L_+\mathcal{U})(L_-\mathcal{U})|L,m,n,k\rangle &= \frac{1}{4}\sqrt{\frac{2L+1}{2L'+1}}\sum_{L'',n'',p''}\ \sum_{L''',n''',p'''} u_{L''n'';p''}u_{L'''n''';p'''}[L''(L''+1)-n''(n''+1)]^{1/2}[L'''(L'''+1)-n'''(n'''-1)]^{1/2}\\ &\quad \times\sum_J C(L'',L''',J,0,0)C(L,J,L',m,0)C(L'',L''',J,n''+1,n'''-1)C(L,J,L',n,n''+n''')\,\delta_{n,n'-n''-n'''}\\ &\quad \times[\delta_{k-k',p''+p'''}+\delta_{k-k',-p''-p'''}+\delta_{k-k',p''-p'''}+\delta_{k-k',-p''+p'''}],\end{aligned} \tag{A3}$$

$$\begin{aligned}\langle L',m,n';k'|(L_z\mathcal{U})^2|L,m,n,k\rangle &= \frac{1}{4}\sqrt{\frac{2L+1}{2L'+1}}\sum_{L'',n'',p''}\ \sum_{L''',n''',p'''} n''n'''u_{L''n'';p''}u_{L'''n''';p'''}\sum_J C(L,J,L',m,0)C(L'',L''',J,0,0)\\ &\quad \times C(L,J,L',n,n''+n''',n')C(L'',L''',J,n'',n''')[\delta_{k-k',p''+p'''}+\delta_{k-k',-p''-p'''}+\delta_{k-k',p''-p'''}+\delta_{k-k',-p''+p'''}],\end{aligned} \tag{A4}$$

$$\begin{aligned}&\langle L',m,n';k'|(L_+^2+L_-^2)|L,m,n,k\rangle\\&\quad=([L(L+1)-n(n+1)]^{1/2}[L(L+1)-(n+1)(n+2)]^{1/2}\delta_{n',n+2}\\&\qquad+[L(L+1)-n(n-1)]^{1/2}[L(L+1)-(n-1)(n-2)]^{1/2}\delta_{n',n-2})\delta_{L,L'}\delta_{k,k'},\end{aligned}\tag{A5}$$

$$\begin{aligned}&\langle L',m,n';k'|[(L_+^2\mathcal{U})+(L_-^2\mathcal{U})]|L,m,n,k\rangle\\&\quad=\frac{1}{2}\sqrt{\frac{2L+1}{2L'+1}}\sum_{L'',n'',p''}u_{L''n'';p''}C(L,L'',L',m,0)[[L''(L''+1)-n''(n''+1)]^{1/2}[L''(L''+1)-(n''+1)(n''+2)]^{1/2}\\&\qquad\times C(L,L'',L',n,n''+2)\delta_{n,n'-n''-2}+[L''(L''+1)-n''(n''-1)]^{1/2}[L''(L''+1)-(n''-1)(n''-2)]^{1/2}\\&\qquad\times C(L,L'',L',n,n''-2)\delta_{n,n'-n''+2}][\delta_{k-k',p''}+\delta_{k-k',-p''}],\end{aligned}\tag{A6}$$

$$\begin{aligned}&\langle L',m,n';k'|[(L_+\mathcal{U})^2+(L_-\mathcal{U})^2]|L,m,n,k\rangle\\&\quad=\frac{1}{4}\sqrt{\frac{2L+1}{2L'+1}}\sum_{L'',n'',p''}\sum_{L''',n''',p'''}u_{L'',n'';p''}u_{L''',n''';p'''}\sum_{J}C(L,J,L',m,0)C(L'',L''',J,0,0)\\&\qquad\times[[L''(L''+1)-n''(n''+1)]^{1/2}[L'''(L'''+1)-n'''(n'''+1)]^{1/2}C(L,J,L',n,n''+n'''+2,n')C(L'',L''',J,n''+1,n'''+1)\\&\qquad+[L''(L''+1)-n''(n''-1)]^{1/2}[L'''(L'''+1)-n'''(n'''-1)]^{1/2}C(L'',L''',J,n''-1,n'''-1)C(L,J,L',n,n''+n'''-2,n')]\\&\qquad\times[\delta_{k-k',p''+p'''}+\delta_{k-k',-p''-p'''}+\delta_{k-k',p''-p'''}+\delta_{k-k',-p''+p'''}].\end{aligned}\tag{A7}$$

2. Translational part

$$\begin{aligned}&\langle L',m,n';k'|\left[\frac{1}{3}(2+\eta_T)+\frac{2}{\sqrt{6}}\epsilon_T(D_{0,2}^2+D_{0,-2}^2)-\frac{2}{3}(1-\eta_T)D_{0,0}^2\right]\frac{\partial^2}{\partial\xi^2}|L,m,n;k\rangle\\&\quad=-k^2\left[\frac{1}{3}(2+\eta_T)\delta_{L,L'}\delta_{n,n'}-\frac{2}{\sqrt{6}}\epsilon_T\sqrt{\frac{2L+1}{2L'+1}}C(L,2,L',m,0)(C(L,2,L',n,-2)\delta_{n,n'+2}+C(L,2,L',n,2)\delta_{n,n'-2})\right.\\&\qquad\left.-\frac{2}{3}(1-\eta_T)\sqrt{\frac{2L+1}{2L'+1}}C(L,2,L',m,0)C(L,2,L',n,0)\delta_{n,n'}\right]\delta_{k,k'},\end{aligned}\tag{A8}$$

$$\begin{aligned}&\langle L',m,n';k'|\left[\frac{1}{3}(2+\eta_T)+\frac{2}{\sqrt{6}}\epsilon_T(D_{0,2}^2+D_{0,-2}^2)-\frac{2}{3}(1-\eta_T)D_{0,0}^2\right]\left(\frac{\partial^2\mathcal{U}}{\partial\xi^2}\right)|L,m,n;k\rangle\\&\quad=-\sqrt{\frac{2L+1}{2L'+1}}\sum_{L'',n'',p''}p''^2u_{L''n'';p''}\left[\frac{1}{3}(2+\eta_T)C(L,L'',L',m,0)C(L,L'',L',n,n'')\delta_{n,n'}\right.\\&\qquad+\sum_{J}C(L,J,L',m,0)C(L'',2,J,0,0)\left\{\frac{1}{\sqrt{6}}\epsilon_T[C(L,J,L',n,n''+2)C(L'',2,J,n'',2)\delta_{n,n'-n''-2}\right.\\&\qquad\left.\left.+C(L,J,L',n,n''-2)C(L'',2,J,n'',-2)\delta_{n,n'-n''+2}]-\frac{2}{3}(1-\eta_T)C(L,J,L',n,n'')C(L'',2,J,n'',0)\delta_{n,n'-n''}\right\}\right.,\end{aligned}\tag{A9}$$

$$\begin{aligned}&\langle L',m,n';k'|\left[\frac{1}{3}(2+\eta_T)+\frac{2}{\sqrt{6}}\epsilon_T(D_{0,2}^2+D_{0,-2}^2)-\frac{2}{3}(1-\eta_T)D_{0,0}^2\right]\left(\frac{\partial\mathcal{U}}{\partial\xi}\right)^2|L,m,n;k\rangle\\&\quad=-\sqrt{\frac{2L+1}{2L'+1}}\sum_{L'',n'',p''}\sum_{L''',n''',p'''}p''p'''u_{L''n'',p''}u_{L'''n''',p'''}\sum_{J}C(L,J,L',m,0)\\&\qquad\times\left\{\frac{1}{3}(2+\eta_T)C(L,J,L',n,n''+n''')C(L'',L''',J,0,0)C(L'',L''',J,n'',n''')\delta_{n,n'-n''-n'''}\right.\\&\qquad+\sum_{J'}C(L'',J',J,0,0)C(L''',2,J',0,0)\left[\frac{2}{\sqrt{6}}\epsilon_T(C(L''',2,J',n''',2)C(L,J,L',n,n''+n'''+2)C(L'',J',J,n'',n'''+2)\right.\end{aligned}$$

$$
\begin{aligned}
&\delta_{n,n'-n''-n'''-2}+C(L''',2,J',n''',-2)C(L,J,L',n,n''+n'''-2)C(L'',J',J,n'',n'''-2)\,\delta_{n,n'-n''-n'''+2})\\
&\quad-\frac{2}{3}(1-\eta_T)C(L,J,L',n,n''+n''')C(L''',2,J',n''',0)C(L'',J',J,n'',n''')\,\delta_{n,n'-n''-n'''}\Bigg]\Bigg]\Bigg\}.
\end{aligned}
\tag{A10}
$$

Expressions (A1)–(A10) are general and independent from the number of functions retained in the expansion of the potential. Inserting in this expressions the explicit form of the potential (3) allows the expansion of the sums and the substitution of the explicit algebraic value for the Clebsch–Gordan coefficients and yields the following simplified form of the diffusion operator matrix elements:

$$
\begin{aligned}
R^{LL'}_{m,nn',kk'}=&\Bigg[\Bigg(-\frac{1}{3}(2+\eta_T)k^2-[L(L+1)+(\eta-1)n^2]+\lambda_1\Bigg)\delta_{n,n'}+\frac{\epsilon}{2}[L(L+1)-n(n+1)]^{1/2}[L(L+1)-(n+1)(n+2)]^{1/2}\\
&\times\delta_{n,n'-2}+\frac{\epsilon}{2}[L(L+1)-n(n-1)]^{1/2}[L(L+1)-(n-1)(n-2)]^{1/2}\delta_{n,n'+2}\Bigg]\delta_{L,L'}\delta_{k,k'}\\
&+\sqrt{\frac{2L+1}{2L'+1}}C(L,2,L',m,0)\Bigg[\Bigg(\lambda_2-\frac{2}{\sqrt{6}}\epsilon_T k^2\Bigg)C(L,2,L',n,2)\,\delta_{n,n'-2}+\Bigg(\lambda_3+\frac{2}{3}(1-\eta_T)k^2\Bigg)C(L,2,L',n,0)\,\delta_{n,n'}\\
&+\Bigg(\lambda_2-\frac{2}{\sqrt{6}}\epsilon_T k^2\Bigg)C(L,2,L',n,-2)\,\delta_{n,n'+2}\Bigg]\delta_{k,k'}+\sqrt{\frac{2L+1}{2L'+1}}C(L,4,L',m,0)[\lambda_4 C(L,4,L',n,4)\,\delta_{n,n'-4}\\
&+\lambda_5 C(L,4,L',n,2)\,\delta_{n,n'-2}+\lambda_6 C(L,4,L',n,0)\,\delta_{n,n'}+\lambda_5 C(L,4,L',n,-2)\,\delta_{n,n'+2}\\
&+\lambda_4 C(L,4,L',n,-4)\,\delta_{n,n'+4}]\delta_{k,k'}+\sqrt{\frac{2L+1}{2L'+1}}C(L,6,L',m,0)[\lambda_7 C(L,6,L',n,6)\,\delta_{n,n'-6}\\
&+\lambda_8 C(L,6,L',n,4)\,\delta_{n,n'-4}+\lambda_9 C(L,6,L',n,2)\,\delta_{n,n'-2}+\lambda_{10} C(L,6,L',n,0)\,\delta_{n,n'}+\lambda_9 C(L,6,L',n,-2)\,\delta_{n,n'+2}\\
&+\lambda_8 C(L,6,L',n,-4)\,\delta_{n,n'+4}+\lambda_7 C(L,6,L',n,-6)\,\delta_{n,n'+6}]\delta_{k,k'}+\lambda_{11}\delta_{L,L'}\delta_{n,n'}\delta_{|k-k'|,1}\\
&+\sqrt{\frac{2L+1}{2L'+1}}C(L,2,L',m,0)[\lambda_{12} C(L,2,L',n,2)\,\delta_{n,n'-2}+\lambda_{13} C(L,2,L',n,0)\,\delta_{n,n'}\\
&+\lambda_{12} C(L,2,L',n,-2)\,\delta_{n,n'+2}]\delta_{|k-k'|,1}+\sqrt{\frac{2L+1}{2L'+1}}C(L,4,L',m,0)[\lambda_{14} C(L,4,L',n,4)\,\delta_{n,n'-4}\\
&+\lambda_{15} C(L,4,L',n,2)\,\delta_{n,n'-2}+\lambda_{16} C(L,4,L',n,0)\,\delta_{n,n'}+\lambda_{15} C(L,4,L',n,-2)\,\delta_{n,n'+2}\\
&+\lambda_{14} C(L,4,L',n,-4)\,\delta_{n,n'+4}]\delta_{|k-k'|,1}+\lambda_{17}\delta_{L,L'}\delta_{n,n'}\delta_{|k-k'|,2}+\sqrt{\frac{2L+1}{2L'+1}}C(L,2,L',m,0)\\
&\times[\lambda_{18} C(L,2,L',n,2)\,\delta_{n,n'-2}+\lambda_{19} C(L,2,L',n,0)\,\delta_{n,n'}+\lambda_{18} C(L,2,L',n,-2)\,\delta_{n,n'+2}]\delta_{|k-k'|,2}\\
&+\sqrt{\frac{2L+1}{2L'+1}}C(L,4,L',m,0)[\lambda_{20} C(L,4,L',n,4)\,\delta_{n,n'-4}+\lambda_{21} C(L,4,L',n,2)\,\delta_{n,n'-2}+\lambda_{22} C(L,4,L',n,0)\,\delta_{n,n'}\\
&+\lambda_{21} C(L,4,L',n,-2)\,\delta_{n,n'+2}+\lambda_{20} C(L,4,L',n,-4)\,\delta_{n,n'+4}]\delta_{|k-k'|,2}+\sqrt{\frac{2L+1}{2L'+1}}C(L,6,L',m,0)\\
&\times[\lambda_{23} C(L,6,L',n,6)\,\delta_{n,n'-6}+\lambda_{24} C(L,6,L',n,4)\,\delta_{n,n'-4}+\lambda_{25} C(L,6,L',n,2)\,\delta_{n,n'-2}+\lambda_{26} C(L,6,L',n,0)\,\delta_{n,n'}\\
&+\lambda_{25} C(L,6,L',n,-2)\,\delta_{n,n'+2}+\lambda_{24} C(L,6,L',n,-4)\,\delta_{n,n'+4}+\lambda_{23} C(L,6,L',n,-6)\,\delta_{n,n'+6}]\delta_{|k-k'|,2}.
\end{aligned}
\tag{A11}
$$

The constants that appear in this expression have been defined as:

$$
\begin{aligned}
\lambda_1=&-\tfrac{1}{5}(u^2_{22,0}+\tfrac{3}{2}u^2_{20,0}+\tfrac{1}{2}u^2_{22,1}+\tfrac{3}{4}u^2_{20,1})-\eta\,\tfrac{1}{5}(2u^2_{22,0}+u^2_{22,1})-\epsilon\frac{\sqrt{6}}{5}(u_{22,0}u_{20,0}+\tfrac{1}{2}u_{22,1}u_{20,1})\\
&+\mu\Bigg[\tfrac{1}{2}(-\tfrac{1}{6}u^2_{00,1}+\tfrac{1}{15}u_{00,1}u_{20,1}-\tfrac{1}{42}u^2_{20,1}-\tfrac{3}{35}u^2_{22,1})-\eta_T\,\tfrac{1}{2}(\tfrac{1}{12}u^2_{00,1}+\tfrac{1}{15}u_{00,1}u_{20,1}+\tfrac{11}{420}u^2_{20,1}+\tfrac{1}{70}u^2_{22,1})\\
&+\epsilon_T\frac{1}{5\sqrt{6}}(-u_{00,1}u_{22,1}+\tfrac{2}{7}u_{20,1}u_{22,1})\Bigg],
\end{aligned}
\tag{A12}
$$

$$\begin{aligned}\lambda_2 ={}& (-u_{22,0} + \tfrac{3}{7}u_{22,0}u_{20,0} + \tfrac{3}{14}u_{22,1}u_{20,1}) - 2\eta u_{22,0} + \epsilon\frac{\sqrt{6}}{2}(-u_{20,0} + \tfrac{3}{14}u_{20,0}^2 + \tfrac{3}{28}u_{20,1}^2 + \tfrac{1}{14}u_{22,1}^2 + \tfrac{1}{7}u_{22,0}^2)\\ &+ \mu\left[\tfrac{1}{14}(-3u_{00,1}u_{22,1} + u_{20,1}u_{22,1}) + \eta_T\tfrac{1}{28}u_{00,1}u_{22,1} + \epsilon_T\frac{1}{\sqrt{6}}(-\tfrac{1}{4}u_{00,1}^2 + \tfrac{1}{7}u_{00,1}u_{20,1} - \tfrac{1}{28}u_{20,1}^2 - \tfrac{3}{14}u_{22,1}^2)\right],\end{aligned}\tag{A13}$$

$$\begin{aligned}\lambda_3 ={}& -(\tfrac{1}{7}u_{22,0}^2 + 3u_{20,0} + \tfrac{3}{14}u_{20,0}^2 + \tfrac{1}{14}u_{22,1}^2 + \tfrac{3}{28}u_{20,1}^2) + \eta\,\tfrac{2}{7}(2u_{22,0}^2 + u_{22,1}^2) - \epsilon\sqrt{6}(u_{22,0} + \tfrac{1}{7}u_{22,0}u_{20,0} + \tfrac{1}{14}u_{22,1}u_{20,1})\\ &+ \mu\left[\tfrac{1}{2}(\tfrac{1}{6}u_{00,1}^2 - \tfrac{5}{21}u_{00,1}u_{20,1} + \tfrac{1}{42}u_{20,1}^2 + \tfrac{1}{7}u_{22,1}^2) - \eta_T\tfrac{1}{3}(\tfrac{1}{4}u_{00,1}^2 + \tfrac{11}{28}u_{00,1}u_{20,1}\,\tfrac{1}{7}u_{20,1}^2) + \epsilon_T\frac{1}{7\sqrt{6}}(2u_{00,1}u_{22,1} - u_{20,1}u_{22,1})\right],\end{aligned}\tag{A14}$$

$$\lambda_4 = \eta 3\sqrt{\tfrac{2}{35}}(\tfrac{1}{2}u_{22,1}^2 + u_{22,0}^2) + \mu\left[-\tfrac{3}{22}\sqrt{\tfrac{5}{14}}u_{22,1}^2 - \eta_T\frac{3}{44\sqrt{70}}u_{22,1}^2 + \epsilon_T\sqrt{\tfrac{3}{35}}(-\tfrac{1}{2}u_{00,1}u_{22,1} + \tfrac{2}{11}u_{20,1}u_{22,1})\right],\tag{A15}$$

$$\begin{aligned}\lambda_5 ={}& \tfrac{3}{7}\sqrt{\tfrac{3}{5}}(2u_{22,0}u_{20,0} + u_{22,1}u_{20,1}) + \epsilon\,\tfrac{3}{7}\sqrt{\tfrac{2}{5}}(u_{22,0}^2 + \tfrac{3}{2}u_{20,0}^2 + \tfrac{1}{2}u_{22,1}^2 + \tfrac{3}{4}u_{20,1}^2) + \mu\sqrt{\tfrac{3}{5}}[\tfrac{1}{14}(u_{00,1}u_{22,1} - \tfrac{13}{11}u_{20,1}u_{22,1})\\ &- \eta_T\tfrac{1}{2}(\tfrac{1}{7}u_{00,1}u_{22,1} + \tfrac{1}{22}u_{20,1}u_{22,1}) + \epsilon_T\tfrac{1}{7}\sqrt{\tfrac{3}{2}}(-\tfrac{1}{2}u_{00,1}u_{20,1} + \tfrac{1}{22}u_{20,1}^2 + \tfrac{3}{11}u_{22,1}^2)],\end{aligned}\tag{A16}$$

$$\begin{aligned}\lambda_6 ={}& \tfrac{3}{35}(4u_{22,0}^2 + 6u_{20,0}^2 + 2u_{22,1}^2 + 3u_{20,1}^2) - \eta\,\tfrac{3}{35}(2u_{22,0}^2 + u_{22,1}^2) + \epsilon\,\tfrac{6}{35}\sqrt{6}(2u_{22,0}u_{20,0} + u_{22,1}u_{20,1})\\ &+ \mu\,\tfrac{2}{7}[3(\tfrac{1}{5}u_{00,1}u_{20,1} - \tfrac{1}{22}u_{20,1}^2 - \tfrac{9}{110}u_{22,1}^2) - \eta_T\tfrac{3}{5}(\tfrac{1}{7}u_{00,1}u_{20,1} + \tfrac{23}{308}u_{20,1}^2 - \tfrac{1}{44}u_{22,1}^2) + \epsilon_T\tfrac{1}{35}\sqrt{\tfrac{3}{2}}(u_{00,1}u_{22,1} + \tfrac{8}{11}u_{20,1}u_{22,1})],\end{aligned}\tag{A17}$$

$$\lambda_7 = -\mu\,\tfrac{1}{4}\sqrt{\tfrac{3}{77}}\epsilon_T u_{22,1}^2,\tag{A18}$$

$$\lambda_8 = \mu\frac{1}{22\sqrt{14}}[u_{22,1}^2 - \eta_T u_{22,1}^2 - \epsilon_T\sqrt{6}u_{20,1}u_{22,1}],\tag{A19}$$

$$\begin{aligned}\lambda_9 ={}& \mu\,\tfrac{1}{11}\sqrt{\tfrac{2}{35}}[u_{20,1}u_{22,1} - \eta_T u_{20,1}u_{22,1}\\ &- \epsilon_T\tfrac{1}{4}\sqrt{\tfrac{21}{2}}(2u_{20,1} + u_{22,1})],\end{aligned}\tag{A20}$$

$$\begin{aligned}\lambda_{10} ={}& \mu\,\tfrac{1}{154}[(3u_{20,1}^2 + u_{22,1}^2) - \eta_T(3u_{20,1}^2 + u_{22,1}^2)\\ &- \epsilon_T\tfrac{1}{77}\sqrt{6}u_{20,1}u_{22,1}],\end{aligned}\tag{A21}$$

$$\begin{aligned}\lambda_{11} ={}& -\tfrac{1}{10}(2u_{22,0}u_{22,1} + 3u_{20,0}u_{20,1}) - \tfrac{2}{5}\eta u_{22,0}u_{22,1}\\ &- \epsilon\frac{\sqrt{6}}{10}(u_{22,0}u_{20,1} + u_{22,1}u_{20,0}) - \mu\,\tfrac{1}{6}\Big[(u_{00,1} + \tfrac{1}{5}u_{20,1})\\ &+ \eta_T(\tfrac{1}{2}u_{00,1} + \tfrac{1}{5}u_{20,1}) + \epsilon_T\frac{\sqrt{6}}{5}u_{22,1}\Big],\end{aligned}\tag{A22}$$

$$\begin{aligned}\lambda_{12} ={}& \tfrac{1}{2}(\tfrac{3}{7}u_{22,0}u_{20,1} + \tfrac{3}{7}u_{22,1}u_{20,0} - u_{22,1}) - \eta u_{22,1}\\ &+ \epsilon\frac{\sqrt{6}}{2}(\tfrac{3}{14}u_{20,0}u_{20,1} + \tfrac{1}{7}u_{22,0}u_{22,1} - \tfrac{1}{2}u_{20,1})\\ &+ \mu\Big[-\tfrac{3}{14}u_{22,1} - \eta_T\tfrac{1}{28}u_{22,1}\\ &+ \epsilon_T\frac{1}{\sqrt{6}}(-\tfrac{1}{2}u_{00,1} + \tfrac{1}{7}u_{20,1})\Big],\end{aligned}\tag{A23}$$

$$\begin{aligned}\lambda_{13} ={}& (-\tfrac{1}{7}u_{22,0}u_{22,1} - \tfrac{3}{14}u_{20,0}u_{20,1} - \tfrac{3}{2}u_{20,1}) + \tfrac{4}{7}\eta u_{22,0}u_{22,1}\\ &- \epsilon\frac{\sqrt{6}}{2}(\tfrac{1}{7}u_{22,0}u_{20,1} + \tfrac{1}{7}u_{22,1}u_{20,0} + u_{22,1})\\ &+ \mu\,\tfrac{1}{6}[(u_{00,1} - \tfrac{5}{7}5\,u_{20,1}) - \eta_T(u_{00,1} + \tfrac{11}{14}u_{20,1})\\ &+ \epsilon_T\tfrac{2}{7}\sqrt{6}u_{22,1}],\end{aligned}\tag{A24}$$

$$\lambda_{14} = 3\sqrt{\tfrac{2}{35}}\eta u_{22,0}u_{22,1} - \mu[\tfrac{1}{2}\sqrt{\tfrac{3}{35}}\epsilon_T u_{22,1}],\tag{A25}$$

$$\begin{aligned}\lambda_{15} ={}& \tfrac{3}{7}\sqrt{\tfrac{3}{5}}(u_{22,0}u_{20,1} + u_{22,1}u_{20,0})\\ &+ \epsilon\,\tfrac{3}{7}\sqrt{\tfrac{2}{5}}(\tfrac{3}{2}u_{20,0}u_{20,1} + u_{22,0}u_{22,1})\\ &+ \mu\left[\tfrac{1}{14}\sqrt{\tfrac{3}{5}}u_{22,1} - \eta_T\tfrac{1}{14}\sqrt{\tfrac{3}{5}}u_{22,1} - \epsilon_T\frac{3}{14\sqrt{10}}u_{20,1}\right],\end{aligned}\tag{A26}$$

$$\begin{aligned}\lambda_{16} ={}& \tfrac{6}{35}(2u_{22,0}u_{22,1} + 3u_{20,0}u_{20,1}) - \eta\,\tfrac{6}{35}u_{22,0}u_{22,1}\\ &+ \epsilon 6\frac{\sqrt{6}}{35}(u_{22,0}u_{20,1} + u_{22,1}u_{20,0})\\ &+ \mu\,\tfrac{3}{35}\left[u_{20,1} - \eta_T u_{20,1} - \epsilon_T\frac{1}{\sqrt{6}}u_{22,1}\right],\end{aligned}\tag{A27}$$

$$\begin{aligned}\lambda_{17}={}&-\tfrac{1}{40}(2u_{22,1}^2+3u_{20,1}^2)-\eta\frac{1}{10}u_{22,1}^2-\epsilon\frac{\sqrt{6}}{20}u_{22,1}u_{20,1}\\&+\frac{\mu}{4}\Bigg[(\tfrac{1}{6}u_{00,1}^2-\tfrac{1}{15}u_{00,1}u_{20,1}+\tfrac{1}{42}u_{20,1}^2+\tfrac{3}{35}u_{22,1}^2)\\&+\eta_T(\tfrac{1}{12}u_{00,1}^2+\tfrac{1}{15}u_{00,1}u_{20,1}+\tfrac{11}{420}u_{20,1}^2+\tfrac{1}{70}u_{22,1}^2)\\&+\epsilon_T\frac{4}{5\sqrt{6}}(\tfrac{1}{2}u_{00,1}u_{22,1}-\tfrac{1}{7}u_{20,1}u_{22,1})\Bigg],\end{aligned}\tag{A28}$$

$$\begin{aligned}\lambda_{18}={}&\tfrac{3}{38}u_{22,1}u_{20,1}+\epsilon\frac{\sqrt{6}}{56}(\tfrac{3}{2}u_{20,1}^2+u_{22,1}^2)\\&+\mu\,\tfrac{1}{2}\Bigg[\tfrac{1}{14}(3u_{00,1}u_{22,1}-u_{20,1}u_{22,1})+\eta_T\,\tfrac{1}{28}u_{00,1}u_{22,1}\\&+\epsilon_T\frac{1}{\sqrt{6}}(\tfrac{1}{4}u_{00,1}^2-\tfrac{1}{7}u_{00,1}u_{20,1}+\tfrac{1}{28}u_{20,1}^2+\tfrac{3}{14}u_{22,1}^2)\Bigg],\end{aligned}\tag{A29}$$

$$\begin{aligned}\lambda_{19}={}&-\tfrac{1}{28}(u_{22,1}^2+\tfrac{3}{2}u_{20,1}^2)+\tfrac{1}{7}\eta u_{22,1}^2-\frac{\sqrt{6}}{28}\epsilon u_{22,1}u_{20,1}\\&+\mu\,\tfrac{1}{2}\Bigg[\tfrac{1}{2}(-\tfrac{1}{6}u_{00,1}^2+\tfrac{5}{21}u_{00,1}u_{20,1}-\tfrac{1}{42}u_{20,1}^2-\tfrac{1}{7}u_{22,1}^2)\\&+\eta_T(\tfrac{1}{12}u_{00,1}^2+\tfrac{11}{84}u_{00,1}u_{20,1}+\tfrac{1}{21}u_{20,1}^2)\\&+\epsilon_T\frac{1}{7\sqrt{6}}(-2u_{00,1}u_{22,1}+u_{20,1}u_{22,1})\Bigg],\end{aligned}\tag{A30}$$

$$\begin{aligned}\lambda_{20}={}&\tfrac{3}{4}\sqrt{\tfrac{2}{35}}\eta u_{22,1}^2+\mu\Bigg[\tfrac{3}{44}\sqrt{\tfrac{5}{14}}u_{22,1}^2+\eta_T\frac{3}{88\sqrt{70}}u_{22,1}^2\\&+\epsilon_T\sqrt{\tfrac{3}{35}}(\tfrac{1}{4}u_{00,1}u_{22,1}-\tfrac{1}{11}u_{20,1}u_{22,1})\Bigg],\end{aligned}\tag{A31}$$

$$\begin{aligned}\lambda_{21}={}&\tfrac{3}{14}\sqrt{\tfrac{3}{5}}u_{22,1}u_{20,1}+\tfrac{3}{28}\epsilon\sqrt{\tfrac{2}{5}}(u_{22,1}^2+\tfrac{3}{2}u_{20,1}^2)\\&+\mu\,\tfrac{1}{4}\sqrt{\tfrac{3}{5}}\Bigg[\tfrac{1}{7}(-u_{00,1}u_{22,1}+\tfrac{13}{11}u_{20,1}u_{22,1})\\&+\eta_T(\tfrac{1}{7}u_{00,1}u_{22,1}+\tfrac{1}{22}u_{20,1}u_{22,1})\\&+\epsilon_T\frac{\sqrt{6}}{7}(\tfrac{1}{2}u_{00,1}u_{20,1}-\tfrac{1}{22}u_{20,1}^2-\tfrac{3}{11}u_{22,1}^2)\Bigg],\end{aligned}\tag{A32}$$

$$\begin{aligned}\lambda_{22}={}&\tfrac{3}{35}(u_{22,1}^2+\tfrac{3}{2}u_{20,1}^2)-\eta\,\tfrac{3}{70}u_{22,1}^2+\epsilon 3\frac{\sqrt{6}}{35}u_{22,1}u_{20,1}\\&+\mu\Bigg[\tfrac{3}{14}(-\tfrac{1}{5}u_{00,1}u_{20,1}+\tfrac{1}{22}u_{20,1}^2+\tfrac{9}{110}u_{22,1}^2)\\&+\eta_T\,\tfrac{3}{10}(\tfrac{1}{7}u_{00,1}u_{20,1}+\tfrac{13}{308}u_{20,1}^2-\tfrac{1}{44}u_{22,1}^2)\\&+\epsilon_T\frac{\sqrt{6}}{35}(\tfrac{1}{4}u_{00,1}u_{22,1}-\tfrac{4}{11}u_{20,1}u_{22,1})\Bigg],\end{aligned}\tag{A33}$$

$$\lambda_{23}=\mu[\epsilon_T\,\tfrac{1}{8}\sqrt{\tfrac{3}{77}}u_{22,1}^2],\tag{A34}$$

$$\lambda_{24}=\mu\frac{1}{44\sqrt{14}}[-u_{22,1}^2+\eta_T u_{22,1}^2+\epsilon_T\sqrt{6}u_{20,1}u_{22,1}],\tag{A35}$$

$$\begin{aligned}\lambda_{25}={}&\mu\frac{1}{11\sqrt{70}}\Bigg[-u_{22,1}u_{20,1}+\eta_T u_{22,1}u_{20,1}\\&+\epsilon_T\frac{\sqrt{6}}{8}(u_{22,1}^2+2u_{20,1}^2)\Bigg],\end{aligned}\tag{A36}$$

$$\begin{aligned}\lambda_{26}={}&\mu\,\tfrac{1}{308}[-(3u_{20,1}^2+u_{22,1}^2)+\eta_T(3u_{20,1}^2+u_{22,1}^2)\\&+\epsilon_T\sqrt{6}u_{20,1}u_{22,1}].\end{aligned}\tag{A37}$$

The expansion of the sums presented in Eqs. (A1)–(A10) and the subsequent determination of constants (A13)–(A37) have been performed with the help of a Mathematica program.[39]

APPENDIX B: COMPUTATIONAL ASPECTS

The computational techniques employed for the storing and diagonalization of the diffusion matrix are essentially the same described in Refs. 5, 6, and 31. In particular we found the use of Polnaszek's routines[40] to perform the calculation of correlation functions without going through the entire diagonalization of the diffusive matrix particularly useful. The determination of the eigenvector corresponding to the zero eigenvalue ($\hat{X}^0_{L,n,k;K}$) which is necessary to initialize the auxiliary vectors (30) has been efficiently performed by the conjugate gradient method.[5,41] Furthermore because this eigenvector corresponds to the equilibrium distribution another optimization was possible by setting to zero the values of the diffusion coefficients with a consequently reduction of of the matrix bandwidth.[5] The calculations of the integrals needed to check the correctness of the asymptotic and initial limit values of the correlation functions (33) have been performed using an adaptive three-dimensional Gaussian quadrature routine.[42] The comparison between the two methods has shown that using an expansion up to $L=20$, $n=12$, $k=6$ basis function (corresponding to 2457 basis functions) is sufficient to guarantee agreement to at least the fourth significant figure in the results.

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