Rotational diffusion of uniaxial probes in biaxial liquid crystal phases

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We discuss the reorientation of a cylindrically symmetric probe in a biaxial orthorombic medium, such as a biaxial nematic. We write down and solve for the first time the rotational diffusion equation for a rod-like or disc-like uniaxial probe reorienting in a medium of biaxial symmetry. We calculate first and second rank correlation functions both in the uniaxial and biaxial phase, giving the possibility of following the evolution of dynamic observables of interest (e.g. spectral densities) through the uniaxial–biaxial phase transition. Nonperturbative and approximate analytical solutions are provided.

I. INTRODUCTION

Smectics of biaxial symmetry have been known for a long time and biaxial phases of nematic liquid crystals, that were first theoretically predicted,[1–3] have recently been found experimentally in lyotropics,[4] polymer liquid crystals[5,6] and low molar mass thermotropics.[7–9] There is now a steadily growing number of mesogens leading to the formation of biaxial nematic phases.[10] Indeed a number of properties of these systems have been studied, such as their macroscopic elastic,[11,12] flow,[11,13–15] field alignment[16] behavior. Experimental investigations of lyotropic biaxial nematics have involved in particular optical,[17,18] deuterium NMR,[19,20] x-ray[21] studies, often with the purpose of establishing phase biaxiality, while comparatively little has been done on thermotropic systems. As more experimental systems become available it seems important to provide the tools for a molecular interpretation of dynamic spectroscopic properties, e.g., NMR,[22] fluorescence depolarization,[23,24] IR and Raman.[25] This involves calculating the orientational correlation functions [26–28] and spectral densities needed to analyze experimental data starting from a chosen model for molecular motion. In practice one of the most useful and successful models in describing the reorientation of solute molecules larger or comparable in size with those of the solvent is the diffusional model [28–41] that we shall adopt here.

The diffusional model is based on the assumption that the molecular reorientation can be considered as a stochastic Markov process that evolves in time as a sequence of small angular steps caused by collisions with the surrounding molecules as well as under the effect of torques originating from the long range order of the liquid crystal.[29–41] This process was studied by Favro[29] and first introduced in the study of reorientation in liquid crystals by Nordio and co-workers,[32] who considered cylindrical molecules in uniaxial phases. As far as the diffusional model is concerned the dynamic features of the probe molecule are described by its rotational diffusion tensor **D**, normally defined in the molecular frame. The ordering effect of the solvent, when present, is represented by an effective anisotropic potential. To the present time a number of models of increasing complexity have been studied; even if we limit ourselves to rigid molecules, as in the present paper, the reorientation of molecules with biaxial ordering matrix and uniaxial diffusion tensor in uniaxial phases has been considered.[35–39] More recently this treatment has been generalized to molecules with diffusion tensor of arbitrary symmetry.[36,40,41]

A description of the rotational diffusion of the molecule based on a laboratory frame representation, in terms of the anisotropic viscosity of the surrounding has also been discussed.[42] The more general combination of anisotropic rotation and anisotropic viscosity is very complex to treat and has so far not been solved completely even though some models exist.[42,43,44] If anything, this approach is going to be even more complicated in biaxial nematics where up to sixteen independent viscosity coefficients are predicted to exist.[14] Here we have chosen to define the diffusion tensor in the molecular frame, since in any case our interest is in discussing for the first time the consequences of introducing mesophase biaxiality, keeping the treatment at the same level it has been employed for uniaxial phases, rather than refining a description of diffusion in a more conventional and simple solvent.

The application of the diffusion model to orthorombic biaxial phases involves setting up and solving the diffusion equation for a probe molecule reorienting in an appropriate biaxial and uniaxial effective potential. Since the biaxial phase has a lower symmetry than the usual cylindrical nematic one, it is particularly interesting to study those correlation functions that are different from zero in the biaxial and vanish in the uniaxial phase. The effect of phase change can to some extent be monitored using a simple uniaxial probe, for instance deuterated benzene in a deuterium NMR study[45] and here we shall often concentrate on this example. In general we wish to examine what dynamic indicators (e.g. correlation times and spectral densities) can be associated to the uniaxial biaxial phase change using various techniques. Thus we shall present a rather extensive selection of first and second rank correlation functions.

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Molecules that tend to align with their symmetry axis parallel or perpendicular to the director may be influenced in a quantitatively different way by biaxiality simply because of geometric factors. For instance if we consider a biaxial[45] order parameter $\mathcal{R}e\langle D^2_{20}\rangle \equiv \sqrt{3/8}\langle \sin^2\beta \cos 2\alpha\rangle$ this will be, everything else being the same, smaller when the molecular axis aligns in such a way that β is close to zero and enhanced if β tends to be close to $\pi/2$. Similar considerations will also hold for dynamics, and since the effect of these geometric factors is not trivial to predict quantitatively we have considered two limiting cases, where the symmetry axis tends to be parallel (perpendicular) to the director, in the sense that $\langle P_2\rangle > 0$ ($\langle P_2\rangle < 0$). This is the typical situation obtained for a rod-like or disc-like probe and we shall name in this way the two cases, even if one cannot exclude that the same situation is obtained for differently shaped probes. Since approximately disc-like and rod-like probe molecules are normally used in the different spectroscopic methods we give results for both these prototype cases.

Our main attack to the problem is nonperturbative: We express the diffusion equation as a matrix representation in a sufficiently large basis set of Wigner rotation matrices[46] and solve the diffusion problem by diagonalization of the diffusion matrix[33,35,41] as discussed in the next sections. The calculations are performed at a set of temperatures in the biaxial and uniaxial phase by suitably relating the effective potential of the probe to that of the liquid crystal solvent undergoing the phase transition.

We also derive an approximate analytical solution for the rotational diffusion correlation functions, and we express the first derivative of the first and second rank diffusional correlation functions in closed analytical form. This approximate solution has not to our knowledge been used before and is here adopted for the problem of a uniaxial probe reorienting in a biaxial phase. Other approximate solutions for the diffusion problem have been presented in the literature[37,39,47,48] for simpler cases. Thus we have also compared our results, in the limit of diffusion in a uniaxial phase, with one of these earlier used approximation.[48] The results using the new approximation are also compared to those obtained from the numerical solution on both sides of the uniaxial–biaxial phase transition, testing when it is sufficient to use the simple analytic approximation rather than treating the full diffusional model. While a full numerical study is given for a selected value of molecular biaxiality, the analytical approximations show directly the dependence on the anisotropic potential, the order parameters and the diffusion tensor anisotropy. Thus they are very useful in allowing an easy extension of the results to different values of these parameters.

II. THEORY

A. Correlation functions

We are interested in dynamics experiments that probe the correlation functions of some relevant single particle properties **A**, **B** that we assume modulated by molecular reorientation. By writing the laboratory fixed spherical components of these properties in terms of their counterparts in a suitable molecular frame with orientation given by a collection of Euler angles $\omega=(\alpha,\beta,\gamma)$ (Ref. 46) one has

$$\langle A^{L,m}_{\mathrm{LAB}}(0)\, B^{L',m'*}_{\mathrm{LAB}}(t)\rangle$$

$$= \sum_{n,n'} \langle D^{L*}_{mn}(0)\, D^{L'}_{m'n'}(t)\rangle A^{L,n}_{\mathrm{MOL}} B^{L',n'*}_{\mathrm{MOL}}$$

$$= \sum_{n,n'} \phi^{LL'}_{mm'nn'}(t) A^{L,n}_{\mathrm{MOL}} B^{L',n'*}_{\mathrm{MOL}}, \tag{1}$$

with $D^{L*}_{mn}(t) \equiv D^{L*}_{mn}(\omega_t)$ a Wigner rotation matrix[46] depending on the angles connecting the two frames at time t and $\phi^{LL'}_{mm'nn'}(t)$ an orientational correlation function.

The number of potentially nonvanishing and of independent correlation functions is limited by the symmetry of the mesophase and by that of the observed ("probe") molecule.[49] Here we shall assume cylindrical symmetry of the probe molecule, while the mesophase can go from isotropic to uniaxial to biaxial.

In the simplest case of an isotropic liquid the requirement of invariance for an arbitrary rotation of the laboratory frame yields the constraint that only relative orientation correlation functions should be present (see, e.g. Ref. 50). Thus only correlation functions

$$\langle D^{L}_{nn'}(t)\rangle = \sum_{q} \phi^{LL}_{qqnn'}(t) \tag{2}$$

can be nonzero. Notice in particular that we have no coupling between properties of different rank.

In a uniaxial phase a rotation about the director, assumed to be the Z laboratory axis, should leave the system invariant. If the probe molecule has effective cylindrical symmetry a rotation around the z molecular axis should also leave the system invariant. Thus the potentially nonvanishing correlation functions are[50]

$$\phi^{LL'}_{mm'nn'} = \langle D^{L}_{mn}(0)\, D^{L'*}_{m'n'}(t)\rangle \delta_{m'm}\delta_{n'n}$$

$$\equiv \phi^{LL'}_{mn}, \tag{3}$$

where we have removed unnecessary subscripts. In liquid crystals we do not have a dependence on the relative orientations only. An immediate consequence is that as a system undergoes a transition from isotropic to nematic, the number of independent correlation functions becomes much higher than in an isotropic fluid. We also have that certain couplings between different rank properties can now be admissible. A new increase in the number of correlation functions takes place if the mesophase, e.g. by further cooling, becomes biaxial. The first new effect predicted is the possibility of observing correlation functions with $m \neq m'$. Here we deal with biaxial D_{2h} mesophases and application of group operations as well as the use of standard properties of Wigner rotation matrices[49] gives

$$\phi^{LL'}_{mm'n}(t) \equiv \phi^{LL'}_{mm'n'n}(t)\delta_{n'n}$$

$$= (-)^{L+L'}\phi^{LL'}_{-m-m'n}(t) \tag{4a}$$

$$= (-)^{L+L'-m-m'}\phi^{LL'}_{mm'-n}(t) \tag{4b}$$

$$= (-)^{m+m'}\phi^{LL'}_{m'mn}(t) \tag{4c}$$

$$= (-)^{m+m'}\phi^{LL'}_{-m-m'-n}(t). \tag{4d}$$

Since we assume a stochastic Markovian process, the orientational correlation function can be written as

$$\phi^{LL'}_{mm'n}(t) = \int\int d\omega_0 d\omega P(\omega_0) D^{L*}_{mn}(\omega_0)$$

$$\times P(\omega_0|\omega t) D^{L'}_{m'n}(\omega), \tag{5}$$

where $P(\omega_0|\omega t)$ is the conditional probability of finding a molecule at ω at time t if the orientation of the molecule was ω_0 at $t=0$. The equilibrium probability, $P(\omega)$ can be expressed as

$$P(\omega) = \frac{\exp[-U(\omega)/k_BT]}{\int d\omega \exp[-U(\omega)/k_BT]}$$

$$= \frac{\exp[-U(\alpha,\beta)/k_BT]}{\int d\omega \exp[-U(\alpha,\beta)/k_BT]}, \tag{6}$$

where k_B is the Boltzmann constant and T is the temperature. $U(\omega)$ is the potential of mean torque acting on the probe particle,[51] which has a symmetry determined by that of the particle and of the mesophase, as the distribution $P(\omega)$. In our case the molecule is assumed uniaxial and there will not be any dependence of the Euler angle γ, i.e. $U(\omega) = U(\alpha, \beta)$,[50] as written in Eq. (6).

The explicit form of the effective anisotropic potential $U(\omega)$ in the biaxial phase is obtained by a separate molecular field treatment,[1,3,51–53] but for the present time it suffices to expand it in Wigner matrices as suggested by symmetry considerations

$$\frac{U(\alpha,\beta)}{k_BT} = \sum_{Jp} a_{Jp} D^{J}_{p0}(\alpha,\beta). \tag{7}$$

Notice that in the same way the effective potential of a biaxial molecule in a uniaxial phase can only depend on the Euler angles β and γ,[54,55] and not α, as is the case already treated in Ref. 41.

If the molecular reorientation takes place through a sequence of small angular steps the evolution of the conditional probability, $P(\omega_0|\omega t)$ can be described by an equation that is local in angular space and in time, i.e. a differential equation. For a diffusion process[35] this evolution equation is

$$\frac{\partial P(\omega_0|\omega t)}{\partial t} = -\mathbf{LD}\left[\mathbf{L} + \mathbf{L}\frac{U(\omega)}{k_BT}\right]P(\omega_0|\omega t), \tag{8}$$

where $\mathbf{L} = (L_x, L_y, L_z)$ is a dimensionless angular momentum operator, and $\mathbf{D}$ is the diffusional tensor, which we take to be diagonal in the molecular frame where the ordering matrix is also diagonal. Assuming cylindrical symmetry we have components $D_\perp$, the diffusion coefficient of the z molecular axis, describing the "tumbling" of the molecule and $D_\parallel$ related to the "spinning" of the molecule around the molecular z axis. We shall also use the parameter η which describes the anisotropy of the diffusion tensor, expressed as the ratio $\eta \equiv D_\parallel / D_\perp$. We now obtain the following expression:

$$\frac{1}{D_\perp}\frac{\partial P(\omega_0|\omega t)}{\partial t} = -\left[L_x^2 + L_x\left(L_x\frac{U(\omega)}{k_BT}\right)\right]P(\omega_0|\omega t)$$

$$-\left[L_y^2 + L_y\left(L_y\frac{U(\omega)}{k_BT}\right)\right]P(\omega_0|\omega t)$$

$$-\eta\left[L_z^2 + L_z\left(L_z\frac{U(\omega)}{k_BT}\right)\right]P(\omega_0|\omega t) \tag{9a}$$

$$\equiv \mathbf{\Gamma} P(\omega_0|\omega t) \tag{9b}$$

where the diffusion operator $\mathbf{\Gamma}$ is introduced. The diffusion operator as written here is not symmetric because the anisotropic weighting of orientations existing in the mesophase but can, e.g. for the purpose of numerical calculations, be symmetrized by the similarity transformation:[33,35]

$$\hat{\mathbf{\Gamma}} = P^{-1/2}\mathbf{\Gamma}P^{1/2} \tag{10a}$$

$$= -\left[\nabla^2 + \frac{1}{2}\left(\nabla^2\frac{U(\omega)}{k_BT}\right) - \frac{1}{4}\left(L_+\frac{U(\omega)}{k_BT}\right)\left(L_-\frac{U(\omega)}{k_BT}\right)\right.$$

$$\left. - \frac{1}{4}\eta\left(L_z\frac{U(\omega)}{k_BT}\right)^2\right], \tag{10b}$$

where P is the equilibrium distribution already introduced, the nabla operator $\nabla^2 = L_x^2 + L_y^2 + \eta L_z^2$ and $L_\pm = L_x \pm iL_y$ is the angular momentum step operator.

The application of this transformation allows rewriting the diffusion equation in its symmetrized form:[41]

$$\frac{1}{D_\perp}\frac{\partial \hat{P}(\omega_0|\omega t)}{\partial t} = \hat{\mathbf{\Gamma}}\hat{P}(\omega_0|\omega t). \tag{11}$$

The symmetrized form of the conditional probability, $\hat{P}(\omega_0|\omega t)$ is in turn defined as

$$\hat{P}(\omega_0|\omega t)=\exp\left(\frac{U(\omega)}{2k_BT}\right)P(\omega_0|\omega t)\exp\left(-\frac{U(\omega_0)}{2k_BT}\right) \tag{12a}$$

$$=P^{-1/2}(\omega)P(\omega_0|\omega t)P^{1/2}(\omega_0). \tag{12b}$$

The correlation functions are written in terms of the symmetrized quantities as

$$\phi^{LL'}_{mm'n}(t)=\int\int d\omega_0 d\omega D^{L}_{mn}(\omega_0)D^{L'*}_{m'n}(\omega) \times P^{1/2}(\omega_0)P^{1/2}(\omega)\hat{P}(\omega_0|\omega t). \tag{13}$$

The symmetrized diffusion Eq. (11) is given a matrix representation in a basis of normalized Wigner matrices,[41] $\mathscr{D}^{L}_{mn}(\omega)=\sqrt{2L+1/8\pi^2}D^{L}_{mn}(\omega)$, by expanding the symmetrized conditional probability $\hat{P}(\omega_0|\omega t)$

$$\hat{P}(\omega_0|\omega t)=\sum_{Lmn}C_{Lmn}(\omega_0,t)\mathscr{D}^{L}_{mn}(\omega). \tag{14}$$

The expansion coefficients, C_{Lmn}, are evaluated with the initial condition

$$C_{Lmn}(\omega_0,0)=\mathscr{D}^{L*}_{mn}(\omega_0), \tag{15}$$

which in turn ensures that

$$\hat{P}(\omega_0|\omega 0)=\delta(\omega-\omega_0). \tag{16}$$

By substituting Eq. (14) in Eq. (11), multiplying both sides on the left by $\mathscr{D}^{L'*}_{m'n}(\omega)$ and integrating over ω we obtain a system of linear differential equations

$$\frac{1}{D_1}\mathbf{C}(t)=\hat{\mathbf{R}}\mathbf{C}(t), \tag{17}$$

where $\hat{\mathbf{R}}$ is a matrix factorized in blocks labeled by n. This is because the potential is not dependent on the angle γ and there will not be any coupling between terms with different n, thus $(\hat{R}^n)_{L'm',Lm}\equiv\hat{R}_{L'm'n',Lmn}\delta_{n'n}$,

$$(\hat{R}^n)_{L'm',Lm}=\int d\omega\mathscr{D}^{L'*}_{m'n}(\omega)\hat{\Gamma}\mathscr{D}^{L}_{mn}(\omega). \tag{18}$$

In Appendix A we write down explicitly the matrix elements originating from the different operators contributing to the diffusion operator. The important case of a potential containing only second rank interactions is also presented. This expansion is of importance because the second order interactions are the simplest meaningful ones and are more amenable to theoretical treatment. Indeed they have been studied by mean field theory[1,3,51–54] and by computer simulation.[53,56] We can now introduce the unitary eigenvector matrix $\hat{\mathbf{X}}^n$ which diagonalizes the self-adjoint diffusional matrix $\hat{\mathbf{R}}^n$,

$$\hat{\mathbf{R}}^n\hat{\mathbf{X}}^n=\hat{\mathbf{X}}^n\hat{\mathbf{r}}^n, \tag{19}$$

where $\hat{\mathbf{r}}^n$ is the diagonal matrix of the eigenvalues of $\hat{\mathbf{R}}^n$. The formal solution is

$$\mathbf{C}^n(t)=\hat{\mathbf{X}}^n e^{tD_1\hat{\mathbf{r}}^n}(\hat{\mathbf{X}}^n)^T\mathbf{C}^n(0). \tag{20}$$

Considering the matrix elements and substituting the zero time coefficients in Eq.(15) we obtain

$$C_{Jpn}(\omega_0,t)=\sum_K\sum_{J'p'}(\hat{X}^n)_{Jp,K}e^{tD_1\hat{r}^n_K}(\hat{X}^n)_{J'p',K}\mathscr{D}^{J'*}_{p'n}(\omega_0), \tag{21}$$

where the single index K is used to label the eigenvalues of the diffusional matrix, $\hat{\mathbf{R}}^n$. We now use the solution of the differential equation to rewrite the expression of the symmetrized conditional probability given in Eq. (14) using un-normalized Wigner matrices

$$\hat{P}(\omega_0|\omega t)=\frac{1}{8\pi^2}\sum_{Kq}\sum_{Jp}\sum_{J'p'}\sqrt{2J+1}\sqrt{2J'+1} \times(\hat{X}^q)_{Jp,K}e^{tD_1\hat{r}^q_K}(\hat{X}^q)_{J'p',K} \times D^{J}_{pq}(\omega)D^{J'*}_{p'q}(\omega_0). \tag{22}$$

When $t\to\infty$ the unsymmetrized conditional probability reaches the equilibrium value, according to the asymptotic condition

$$\lim_{t\to\infty}P(\omega_0|\omega t)=P(\omega). \tag{23}$$

All the exponentials in Eq. (22) decay to zero at infinite time except for the one corresponding to the zero eigenvalue, $\hat{r}^0_0$. The long time behavior of the symmetrized conditional probability, Eq. (12), is then, according to Eq. (22) and Eq. (23), obtained as

$$\lim_{t\to\infty}\hat{P}(\omega_0|\omega t)$$

$$=P^{1/2}(\omega_0)P^{1/2}(\omega) \tag{24a}$$

$$=\frac{1}{8\pi^2}\sum_{J''p''}\sum_{J'''p'''}\sqrt{2J''+1}\sqrt{2J'''+1} \times(\hat{X}^0)_{J''p'',0}(\hat{X}^0)_{J'''p''',0}D^{J''}_{p''0}(\omega)D^{J'''*}_{p'''0}(\omega_0). \tag{24b}$$

It is now possible to rewrite the correlation function, Eq. (13), using the expressions of the conditional probability

given in Eq. (22) and Eq. (24b). The final expression for the correlation function of a uniaxial molecule undergoing rotational diffusion in a medium of biaxial symmetry is written as a sum of exponentials:

$$\phi^{LL'}_{mm'n}(t)$$

$$= \sum_K e^{tD_\perp \hat{r}^n_K} \sum_{Jp} \sum_{J'p'} \sum_{J''J'''} \sqrt{\frac{(2J+1)(2J'+1)}{(2J''+1)(2J'''+1)}}$$

$$\times (\hat{X}^n)_{Jp,K} (\hat{X}^n)_{J'p',K} (\hat{X}^0)_{J'',m'-p;0} (\hat{X}^0)_{J''',m-p';0}$$

$$\times C(L,J',J''';m,-p')\, C(L,J',J''';n,-n)$$

$$\times C(L',J,J'';m',-p)\, C(L',J,J'';n,-n) \qquad (25a)$$

$$\equiv \sum_K (b^{LL'}_{mm'n})_K e^{t(a^{LL'}_{mm'n})_K}, \qquad (25b)$$

where the result of the integrals including three Wigner rotation matrices have been expressed in terms of Clebsch–Gordan coefficients, $C(A,B,C;d,e)$.[46,57] In the calculations we have rewritten Eq. (25a) in a way that is more convenient from the point of view of programming,[41] that is,

$$\phi^{LL'}_{mm'n}(t) = \sum_K e^{tD_\perp \hat{r}^n_K} \Big(\sum_{Jp} (V^{L'm'n})_{Jp} (\hat{X}^n)_{Jp,K} \Big)$$

$$\times \Big(\sum_{J'p'} (V^{Lmn})_{J'p'} (\hat{X}^n)_{J'p',K} \Big), \qquad (26)$$

where we have introduced the vectors

$$(V^{Lmn})_{J'p'} = (-)^{p'} \sqrt{2J'+1} \sum_{J'''=|L-J'|}^{L+J'} \frac{1}{\sqrt{2J'''+1}}$$

$$\times C(L,J',J''';m,-p')$$

$$\times C(L,J',J''';n,-n) (\hat{X}^0)_{J''',m-p';0}. \qquad (27)$$

By handling the rotation of the vectors V^{Lmn} and $V^{L'm'n}$ at the same time as the diagonalization[58,59] of the matrix $\hat{\mathbf{R}}^n$ it is possible to avoid the explicit manipulation of the eigenvectors matrix, $\hat{\mathbf{X}}^n$ as discussed in Ref. 41.

B. Spectral densities

The spectral density $J^{(AB)}_{LL'mm'}(\hat{\omega})$ as a function of angular frequency $\hat{\omega}$ is given by a sum of Fourier–Laplace transforms of the correlation functions, Eq. (1):

$$J^{(AB)}_{LL'mm'}(\hat{\omega}) = \sum_{nn'} A^{Ln*}_{\mathrm{MOL}} B^{L'n'}_{\mathrm{MOL}} \delta_{nn'} \int_0^\infty \phi^{LL'}_{mm'n}(t) e^{-i\hat{\omega}t} dt, \qquad (28)$$

for a uniaxial probe. The correlation functions can be evaluated in terms of eigenvalues and eigenvectors of the diffusion matrix as we have discussed. A typical case where spectral densities rather than correlation functions enter is in the description of fast motion ESR[32,33] and NMR[22] experiments. In this last case $L=L'=2$ and $A=B$ is implied and the notation is accordingly simplified. We estimate the real part of the integral in Eq. (28) and write the tensor components in the molecular frame in terms of the principal component $A^{2,0}_A$ using the small Wigner matrices $d^2_{n0}(\vartheta)$, where ϑ is the angle between the molecular z axis and the principal z axis of the tensor $\mathbf{A}$, which is assumed to be cylindrically symmetric. The spectral densities for a uniaxial probe are then given by

$$J_{mm'}(\hat{\omega}) = A^{2,0}_A A^{2,0}_A \sum_n d^2_{n0}(\vartheta) d^2_{n0}(\vartheta)$$

$$\times \sum_K \frac{(b^{22}_{mm'n})_K (a^{22}_{mm'n})_K}{(a^{22}_{mm'n})^2_K + \hat{\omega}^2}. \qquad (29)$$

In the calculations presented later on we have considered in particular the case of $\vartheta=0$, appropriate, e.g. to a C–D bond parallel to the long axis and that of $\vartheta=\pi/2$ relevant to the case of a C–D perpendicular to the probe symmetry axis, as in perdeuterated benzene.

The zero frequency spectral densities are obviously related to correlation times. These are obtained by integrating the corresponding correlation functions over time after subtracting out the long time plateau, if any:

$$\tau^{LL'}_{mm'n} = \int_0^\infty [\phi^{LL'}_{mm'n}(t) - \phi^{LL'}_{mm'n}(\infty)]\, dt. \qquad (30)$$

Even though the detailed information about the evolution in time is lost they are of importance, because they are often the only quantities to be determined by experimental techniques. The easiest way to perform the integration, knowing all the eigenvalues and eigenvectors from the calculation of the correlation function, is to make the following summation picking out the zero eigenvalue, if $\phi^{LL'}_{mm'n}(\infty) \neq 0$

$$\tau^{LL'}_{mm'n} = \sum_K{}' \frac{(b^{LL'}_{mm'n})_K}{(a^{LL'}_{mm'n})_K}; \quad (a^{LL'}_{mm'n})_K \neq 0. \qquad (31)$$

III. ANALYTICAL EXPRESSIONS

The evaluation of correlation functions and of the related observable quantities described in the previous sec-

tions proceeds unavoidably through rather heavy numerical calculations. This has prompted various authors, even for the simpler case of probes reorienting in uniaxial mesophases, to propose approximate analytical solutions to the problem. Although they cannot represent a universal substitute for the full numerical solution, the analytic expressions have the advantage of showing the relation between correlation functions and order parameters, diffusion tensor anisotropy η and potential coefficients.

Here we wish to provide a set of analytic approximations for biaxial phases as well. We shall first propose a rather general approach that can be specialized to the simpler phases. We then compare the results with the numerical solutions to assess for which cases the approximation is good enough to be practically useful. We approximate the decay of the correlation functions with a single exponential that is obtained from the first derivative of the correlation function. Instead of the symmetrized form of the conditional probability we have found it more convenient to use for this purpose the unsymmetrized form, and then write the correlation functions as

$$\phi^{LL'}_{mm'n}(t)=\langle D^{L*}_{mn}(\omega_0)D^{L'*}_{m'n}(\omega)\rangle$$

$$=\sum_K\sum_{L''m''}\frac{2L''+1}{2L'+1}(X^n)_{L'm',K}e^{-r^n_K t}$$

$$\times(X^n)^{-1}_{L''m'',K}\langle D^L_{mn}D^{L''*}_{m''n}\rangle. \tag{32}$$

We are looking for a single exponential approximation such as

$$\phi^{LL'}_{mm'n}(t)\approx[m]\phi^{LL'}_{mm'n}(\infty)+b^{LL'}_{mm'n}e^{-ta^{LL'}_{mm'n}}, \tag{33}$$

where choosing

$$b^{LL'}_{mm'n}=\phi^{LL'}_{mm'n}(0)-\phi^{LL'}_{mm'n}(\infty), \tag{34a}$$

$$a^{LL'}_{mm'n}=\frac{\dot\phi^{LL'}_{mm'n}(0)}{\phi^{LL'}_{mm'n}(0)-\phi^{LL'}_{mm'n}(\infty)} \tag{34b}$$

ensures that the correlation functions have the correct value at time zero and at asymptotically long times as well as the derivative at time zero provided by the diffusional model. We can write the first derivative of the correlation functions as

$$\dot\phi^{LL'}_{mm'n}(t)=-\sum_K\sum_{L''m''}\frac{2L''+1}{2L'+1}(X^n)_{L'm',K}r^n_K e^{-r_K t}$$

$$\times(X^n)^{-1}_{L''m'',K}\langle D^L_{mn}D^{L''*}_{m''n}\rangle. \tag{35}$$

At $t=0$ the eigenvalues and eigenvectors can be recombined to give elements of the diffusional matrix, $(R^n)_{L'm',L''m''}$ [see Eq. (19)]

$$\dot\phi^{LL'}_{mm'n}(0)=-\sum_K\sum_{L''m''}\frac{2L''+1}{2L'+1}(X^n)_{L'm',K}r^n_K$$

$$\times(X^n)^{-1}_{L''m'',K}\langle D^L_{mn}D^{L''*}_{m''n}\rangle \tag{36a}$$

$$=-\sum_{L''m''}\frac{2L''+1}{2L'+1}(R^n)_{L'm',L''m''}$$

$$\times\langle D^L_{mn}D^{L''*}_{m''n}\rangle. \tag{36b}$$

In this way we can calculate the derivative of the correlation functions at $t=0$ directly by summing the matrix elements weighted by $\langle D^L_{mn}D^{L''*}_{m''m}\rangle$. These analytical expressions are listed in Appendix B, and because of their simplicity they could be useful in interpreting experimental data, but it should be stressed that the accuracy is not uniform for all the correlation functions, as discussed in the following section. Having this caveat in mind, we would like to stress that the analytical expressions are extremely useful to examine the effect of changing some of the parameters in the calculation without (or before) going to the complications of the full numerical solution. In Appendix B the expression of the unsymmetrized matrix elements are also given. It is clear that the procedure can be generalized to multi-exponential approximations if needed.

IV. CALCULATIONS AND RESULTS

In order to put to practical use the expressions we have derived in the previous sections, we need to choose a potential of mean torque. Moreover if we intend to investigate the temperature dependence of the dynamics and the changes at the biaxial transition a set of order parameters has to be available. In the calculations presented here we investigate the simplest and most important case of a uniaxial probe subject to a biaxial potential containing only second rank interactions. The explicit form of this potential is then

$$\frac{U(\alpha,\beta)}{k_BT}=a_{20}(T)P_2(\cos\beta)$$

$$+a_{22}(T)[D^2_{20}(\alpha,\beta)+D^2_{-20}(\alpha,\beta)]$$

$$=a_{20}(T)(\tfrac{3}{2}\cos^2\beta-\tfrac{1}{2})$$

$$+a_{22}(T)\sqrt{3/2}\sin^2\beta\cos 2\alpha \tag{37}$$

and it is characterized only by the coefficients, $a_{20}(T)$ and $a_{22}(T)$, if we assume that $a_{2-2}=a_{22}$.[53] Since our aim is to study the changes in reorientational dynamics associated with a change of phase that is driven by a temperature variation it is important to find a way of producing a plausible set of coefficients $a_{20}(T)$ and $a_{22}(T)$ at various temperatures.

TABLE I. Order parameters and effective potential coefficients for the probes used in the calculations.

	Biaxial Phase							*Uniaxial Phase*			
$T^* = kT/\epsilon$	0.36	0.48	0.61	0.85	0.97	1.10	1.136	1.22	1.34	1.47	1.59
Order parameters of the solvent, $\lambda_s = 0.3$.											
$< P_2 >_s$	0.958	0.947	0.935	0.909	0.896	0.884	0.881	0.869	0.852	0.833	0.812
$< D^2_{20} >_s$	0.00657	0.00853	0.0104	0.0123	0.0112	0.00646	0.00000	0.0000	0.0000	0.0000	0.0000
$< D^2_{02} >_s$	0.00659	0.00859	0.0106	0.0142	0.0136	0.0130	0.0126	0.0138	0.0159	0.0181	0.0206
$< D^2_{22} >_s$	0.445	0.422	0.393	0.307	0.237	0.117	0.00001	0.0000	0.0000	0.0000	0.0000
a_{2p} *and* $< D^2_{p0} >$, $\lambda_s = 0.3$.											
Rod-like molecule, $c_{200} = -2.88\epsilon$											
a_{20}	-7.71	-5.69	-4.48	-3.11	-2.68	-2.34	-2.25	-2.07	-1.85	-1.66	-1.50
a_{22}	-2.19	-1.56	-1.17	-0.665	-0.455	-0.202	-0.00001	0.0000	0.0000	0.0000	0.0000
$< P_2 >$	0.853	0.795	0.732	0.607	0.552	0.502	0.488	0.454	0.409	0.369	0.334
$< D^2_{20} >$	0.0149	0.0209	0.0266	0.0308	0.0267	0.0143	0.00000	0.0000	0.0000	0.0000	0.0000
$< P_4 >$	0.599	0.488	0.392	0.252	0.204	0.166	0.156	0.134	0.109	0.0886	0.0724
$< D^4_{20} >$	0.0375	0.0415	0.0409	0.0298	0.0212	0.0095	0.00000	0.0000	0.0000	0.0000	0.0000
$< D^4_{40} >$	0.0010	0.0018	0.0026	0.0025	0.0017	0.0004	0.00000	0.0000	0.0000	0.0000	0.0000
$< P_6 >$	0.353	0.242	0.165	0.0792	0.0560	0.0403	0.0365	0.0291	0.0211	0.0155	0.0114
$< D^6_{20} >$	0.0440	0.0385	0.0304	0.0152	0.0093	0.0036	0.00000	0.0000	0.0000	0.0000	0.0000
$< D^6_{40} >$	0.0029	0.0035	0.0034	0.0019	0.0010	0.0002	0.00000	0.0000	0.0000	0.0000	0.0000
Disc-like molecule, $c_{200} = 2.88\epsilon$											
a_{20}	7.71	5.69	4.48	3.11	2.68	2.34	2.25	2.07	1.85	1.66	1.50
a_{22}	2.19	1.56	1.17	0.665	0.455	0.202	0.00001	0.0000	0.0000	0.0000	0.0000
$< P_2 >$	-0.457	-0.423	-0.399	-0.350	-0.325	-0.301	-0.294	-0.281	-0.262	-0.244	-0.228
$< D^2_{20} >$	-0.445	-0.387	-0.318	-0.193	-0.133	-0.059	0.00000	0.0000	0.0000	0.0000	0.0000
$< P_4 >$	0.255	0.217	0.183	0.126	0.104	0.0855	0.0805	0.0719	0.0611	0.0520	0.0444
$< D^4_{20} >$	0.226	0.174	0.130	0.0655	0.0412	0.0168	0.00000	0.0000	0.0000	0.0000	0.0000
$< D^4_{40} >$	0.196	0.128	0.0819	0.0287	0.0135	0.0027	0.00000	0.0000	0.0000	0.0000	0.0000
$< P_6 >$	-0.140	-0.102	-0.0738	-0.0377	-0.0270	-0.0194	-0.0175	-0.0145	-0.0111	-0.0086	-0.0066
$< D^6_{20} >$	-0.122	-0.0874	-0.0533	-0.0209	-0.0117	-0.0043	0.00000	0.0000	0.0000	0.0000	0.0000
$< D^6_{40} >$	-0.0889	-0.0512	-0.0290	-0.0082	-0.0035	-0.0006	0.00000	0.0000	0.0000	0.0000	0.0000

If we consider a probe particle dissolved at very low concentration in a biaxial mesophase, the coefficients are, at mean field level, proportional to the solvent order parameters .[51,54,55] The single particle orientational potential at second order can be written in this case as

$$U(\omega) = \sum_{pq} c_{2pq} \sum_{m} \langle D^2_{|m|p} \rangle_s D^2_{mq}(\omega), \tag{38}$$

where the subscript s indicates the solvent and c_{2pq} are solute–solvent coefficients. For a uniaxial probe we have no dependence on the angle γ and thus $c_{2pq} = c_{2p0}\delta_{q0}$. A knowledge of the order parameters of the mesophase $\langle D^2_{|m|p} \rangle_s$ gives us the possibility of making calculations of the effective potential and thus ultimately of the correlation functions at various temperatures, and in particular when the order parameters of the solution vary from a phase of biaxial symmetry to uniaxial symmetry. The order parameters have the following symmetry, if we assume a orthorombic biaxial phase formed of D_{2h} molecules: $\langle D^L_{mn} \rangle = \langle D^L_{-mn} \rangle$ and $\langle D^L_{mn} \rangle = \langle D^L_{m-n} \rangle$, with m,n even. Moreover we also have an additional symmetry due to the properties of Wigner functions, that is, $\langle D^{L*}_{mn} \rangle = (-)^{m+n} \langle D^L_{-m-n} \rangle$. An expansion of Eq. (38) up to rank two then gives the effective potential acting on a uniaxial probe as

$$U(\alpha,\beta) = [c_{200}\langle P_2 \rangle_s + 2c_{220}\langle D^2_{02} \rangle_s] P_2(\cos\beta)$$

$$+ [c_{200}\langle D^2_{20} \rangle_s + 2c_{220}\langle D^2_{22} \rangle_s]$$

$$\times [D^2_{20}(\alpha,\beta) + D^2_{-20}(\alpha,\beta)]. \tag{39}$$

Comparing this expression for the potential with Eq. (37) the coefficients $a_{2p}(T)$ in the general form of the potential are given by

$$a_{20}(T) = \frac{1}{k_B T}[c_{200}\langle P_2 \rangle_s + 2c_{220}\langle D^2_{02} \rangle_s], \tag{40}$$

$$a_{22}(T) = \frac{1}{k_B T}[c_{200}\langle D^2_{20} \rangle_s + 2c_{220}\langle D^2_{22} \rangle_s]. \tag{41}$$

The solute–solvent interaction coefficients can be factorized in a number of cases and in particular if the interactions are due to dispersion forces,[54] i.e. $c_{2pq} \propto \alpha^{(s)}_{2p}\alpha^{(p)}_{2q}$. It is then possible to define a biaxiality of the probe molecule studied, λ_p, and a biaxiality of the solvent, λ_s,

$$\lambda_p = \frac{\alpha^p_{22}}{\alpha^p_{20}}, \tag{42}$$

TABLE II. The initial values of the correlation functions for $L=L'=1$ and $L=L'=2$ calculated from $\phi^{LL'}_{mm'n}(0)=\langle D^{L}_{mn}D^{L'*}_{m'n}\rangle=(-)^{m'-n}\Sigma^{L+L'}_{J=\lvert L-L'\rvert}C(L,L',J;m,-m')C(L,L',J;n,-n)\langle D^{J}_{m-m',0}\rangle$.

$mm'\backslash n$	0	1	2
		FirstRank : $(L=L'=1)$	
00	$\frac{2}{3}<P_2>+\frac{1}{3}$	$-\frac{1}{3}<P_2>+\frac{1}{3}$	–
1-1	$-\sqrt{\frac{2}{3}}\mathcal{R}e<D^2_{20}>$	$\frac{1}{\sqrt{6}}\mathcal{R}e<D^2_{20}>$	–
11	$-\frac{1}{3}<P_2>+\frac{1}{3}$	$\frac{1}{6}<P_2>+\frac{1}{3}$	–
		SecondRank : $(L=L'=2)$	
00	$\frac{18}{35}<P_4>+\frac{2}{7}<P_2>+\frac{1}{5}$	$-\frac{12}{35}<P_4>+\frac{1}{7}<P_2>+\frac{1}{5}$	$\frac{3}{35}<P_4>-\frac{2}{7}<P_2>+\frac{1}{5}$
1-1	$-\frac{6}{7}\sqrt{\frac{2}{5}}\mathcal{R}e<D^4_{20}>-\frac{\sqrt{6}}{7}\mathcal{R}e<D^2_{20}>$	$\frac{4}{7}\sqrt{\frac{2}{5}}\mathcal{R}e<D^4_{20}>-\frac{\sqrt{6}}{14}\mathcal{R}e<D^2_{20}>$	$-\frac{1}{7}\sqrt{\frac{2}{5}}\mathcal{R}e<D^4_{20}>+\frac{\sqrt{6}}{7}\mathcal{R}e<D^2_{20}>$
11	$-\frac{12}{35}<P_4>+\frac{1}{7}<P_2>+\frac{1}{5}$	$\frac{8}{35}<P_4>+\frac{1}{14}<P_2>+\frac{1}{5}$	$-\frac{2}{35}<P_4>-\frac{1}{7}<P_2>+\frac{1}{5}$
2-2	$\frac{3\sqrt{70}}{35}\mathcal{R}e<D^4_{40}>$	$-\frac{2\sqrt{70}}{35}\mathcal{R}e<D^4_{40}>$	$\frac{1}{\sqrt{70}}\mathcal{R}e<D^4_{40}>$
20	$\frac{3}{7}\sqrt{\frac{3}{5}}\mathcal{R}e<D^4_{20}>-\frac{2}{7}\mathcal{R}e<D^2_{20}>$	$-\frac{2}{7}\sqrt{\frac{3}{5}}\mathcal{R}e<D^4_{20}>-\frac{1}{7}\mathcal{R}e<D^2_{20}>$	$\frac{1}{14}\sqrt{\frac{3}{5}}\mathcal{R}e<D^4_{20}>+\frac{2}{7}\mathcal{R}e<D^2_{20}>$
22	$\frac{3}{35}<P_4>-\frac{2}{7}<P_2>+\frac{1}{5}$	$-\frac{2}{35}<P_4>-\frac{1}{7}<P_2>+\frac{1}{5}$	$\frac{1}{70}<P_4>+\frac{2}{7}<P_2>+\frac{1}{5}$

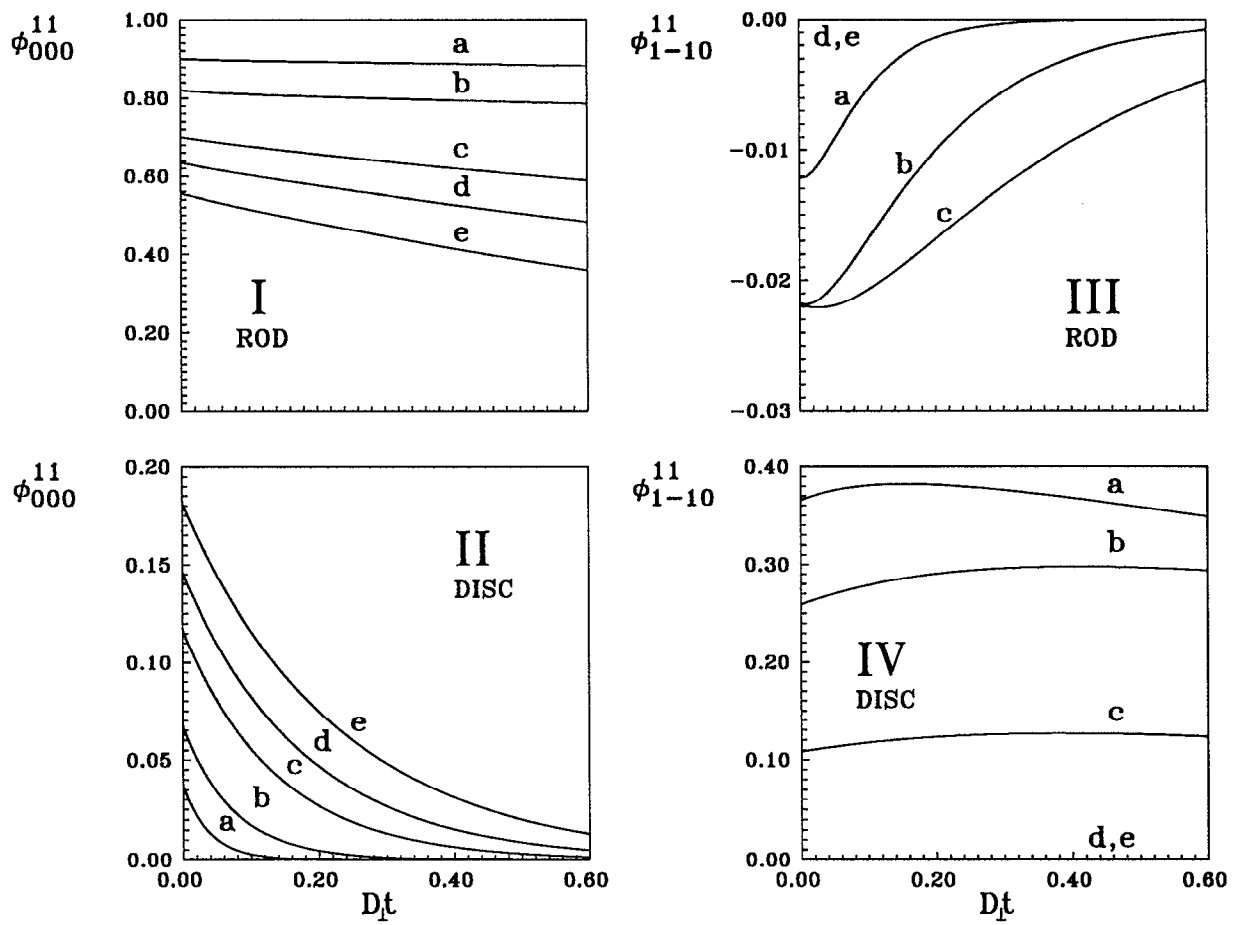

FIG. 1. The correlation functions $\phi^{11}_{000}(t)$ and $\phi^{11}_{1-10}(t)$ for rod- and disc-like molecules at various reduced temperatures in the biaxial phase: $T^*=0.36$ (a), 0.61 (b), 0.97 (c), and in the uniaxial phase: $T^*=1.22$ (d), 1.59 (e).

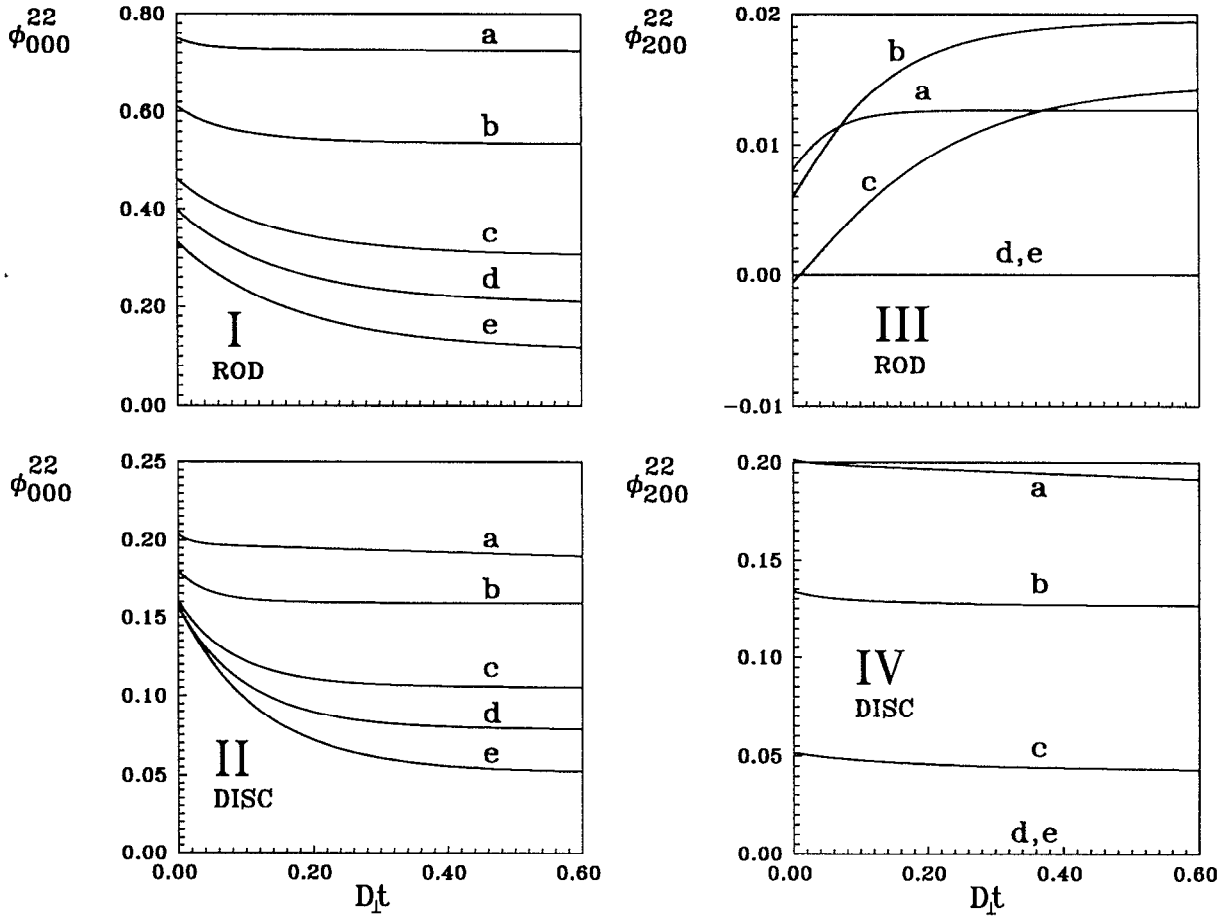

FIG. 2. The correlation functions $\phi^{22}_{000}(t)$ and $\phi^{22}_{200}(t)$ for rod- and disc-like molecules at various reduced temperatures in the biaxial phase: $T^*=0.36$ (a), 0.61 (b), 0.97 (c), and in the uniaxial phase: $T^*=1.22$(d), 1.59 (e).

$$\lambda_s=\frac{\alpha^s_{22}}{\alpha^s_{20}}. \tag{43}$$

In case of a uniaxial molecule $\lambda_p=0$, and the coefficient c_{220} is not an independent one once the biaxiality of the phase is fixed:

$$c_{220}=c_{200}\lambda_s. \tag{44}$$

In our calculations we have used temperature dependent order parameters of the biaxial solvent obtained from recent molecular field calculations.[53] These calculations have used the nearest neighbors pair potential [54,56]

$$U(\omega_{ij})=-\varepsilon\{P_2(\cos\beta_{ij})+2\lambda_s[R^2_{02}(\omega_{ij}) + R^2_{20}(\omega_{ij})]+4\lambda_s^2R^2_{22}(\omega_{ij})\}, \tag{45}$$

where ε is a positive constant determining the strength of the solvent–solvent interaction, ω_{ij} represents the relative orientation of the molecular pair and the R^L_{mn} are symmetry-adapted functions:[53]

$$R^L_{mn}(\omega)\equiv\tfrac{1}{2}\mathscr{R}e[D^L_{mn}(\omega)+(-)^mD^L_{-mn}(\omega)]. \tag{46}$$

This biaxial potential has now been fully studied and its phase diagram has been obtained not only with molecular field theory but also with Monte Carlo simulations.[53] In general various theories predict that the uniaxial to isotropic transition is a first order one whose character becomes weaker as the biaxiality increases until it vanishes when the three axis of the constituent particles become equivalent. The uniaxial to biaxial transition, that involves going from disordered to aligned short molecular axis is a continuous one [1,2,60,61] which is expected to resemble the so called XY transition .[62,63] For a biaxiality $\lambda_s=0.3$, as we assume here, the system has, according to mean field theory and when we assume a nearest neighbors number $z=12$,[53] a continuous biaxial–uniaxial transition at $T^*=1.136$ and a weak

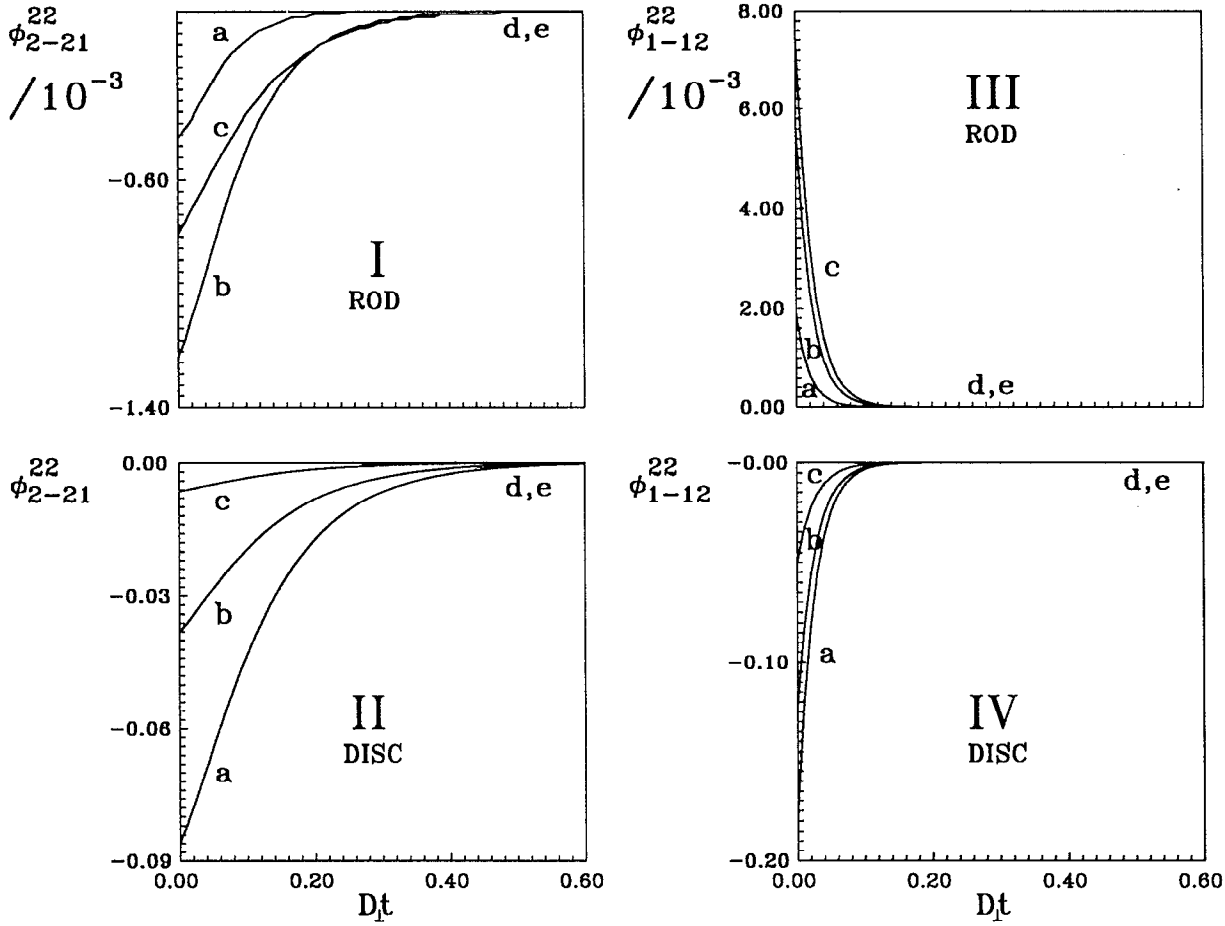

FIG. 3. The correlation functions $\phi^{22}_{2-21}(t)$ and $\phi^{22}_{1-12}(t)$ for rod- and disc-like molecules at reduced temperatures $T^*=0.36$ (a), 0.61 (b) and 0.97 (c) in the biaxial phase. The correlation functions vanish in the uniaxial phase; 1.22 (d) and 1.59 (e).

first order uniaxial–isotropic transition that takes place at $T^*=2.88$. Notice in particular that $\langle P_2\rangle_s$ is essentially continuous and that $\mathscr{R}e\langle D^2_{02}\rangle_s$ is different from zero on both sides of the uniaxial–biaxial transition, while $\mathscr{R}e\langle D^2_{22}\rangle_s$ and $\mathscr{R}e\langle D^2_{20}\rangle_s$ go to zero. Notice also that the limiting low temperature values of these two parameters are respectively $\frac{1}{2}$ and 0, so that it is the first one that provides the largest change, while the other increases from zero and then vanishes again. In Table I, the order parameters of the biaxial phase and of the rod-like and disc-like probes at a set of reduced temperatures selected between those studied here are given for $\lambda_s=0.3$.[53] The coefficients, $a_{Jp}(T)$ of the molecule, calculated from the solvent parameters, are also listed in Table I. The cases presented in Table I are (i) a uniaxial molecule with the z axis along the direction of maximum elongation, i.e. a rod-like probe, ($c_{200}=-2.88\epsilon$), (ii) a uniaxial molecule with the z axis perpendicular to the molecular plane, a disc-like probe, ($c_{200}=2.88\epsilon$). The change of sign of c_{200} makes the sign of $\langle P_2\rangle$ change according to the shape of the molecule,[24,54] as we see in Table I, where the second and fourth rank order parameters are listed for the two cases.

The order parameters of the probe have been calculated by integration of the distribution obtained from the potential Eq. (37), but they can also be obtained from the eigenvector corresponding to zero eigenvalue by[41]

$$\begin{aligned}\langle D^L_{m0}\rangle &= \int d\omega P(\omega)\, D^L_{m0}(\omega)\\ &= \frac{1}{8\pi^2}\sum_{Jp}\sum_{J'p'}(\hat{X}^0)_{Jp,0}(\hat{X}^0)_{J'p',0}\\ &\quad\times\sqrt{(2J'+1)(2J+1)}\\ &\quad\times\int d\omega D^{J'*}_{p'0}(\omega)\, D^J_{p0}(\omega)\, D^L_{m0}(\omega)\\ &= \sum_{Jp}(\hat{X}^0)_{Jp,0}\sum_{J'=|J-L|}^{J+L}(\hat{X}^0)_{J',p+m;0}\\ &\quad\times\sqrt{(2J+1)/(2J'+1)}\\ &\quad\times C(L,J,J';p,m)C(L,J,J';0,0).\end{aligned}\tag{47}$$

In our calculations we have evaluated the order parameters in both ways to check the accuracy in the calculations due to the chosen size of the basis set of the diffusional matrix.

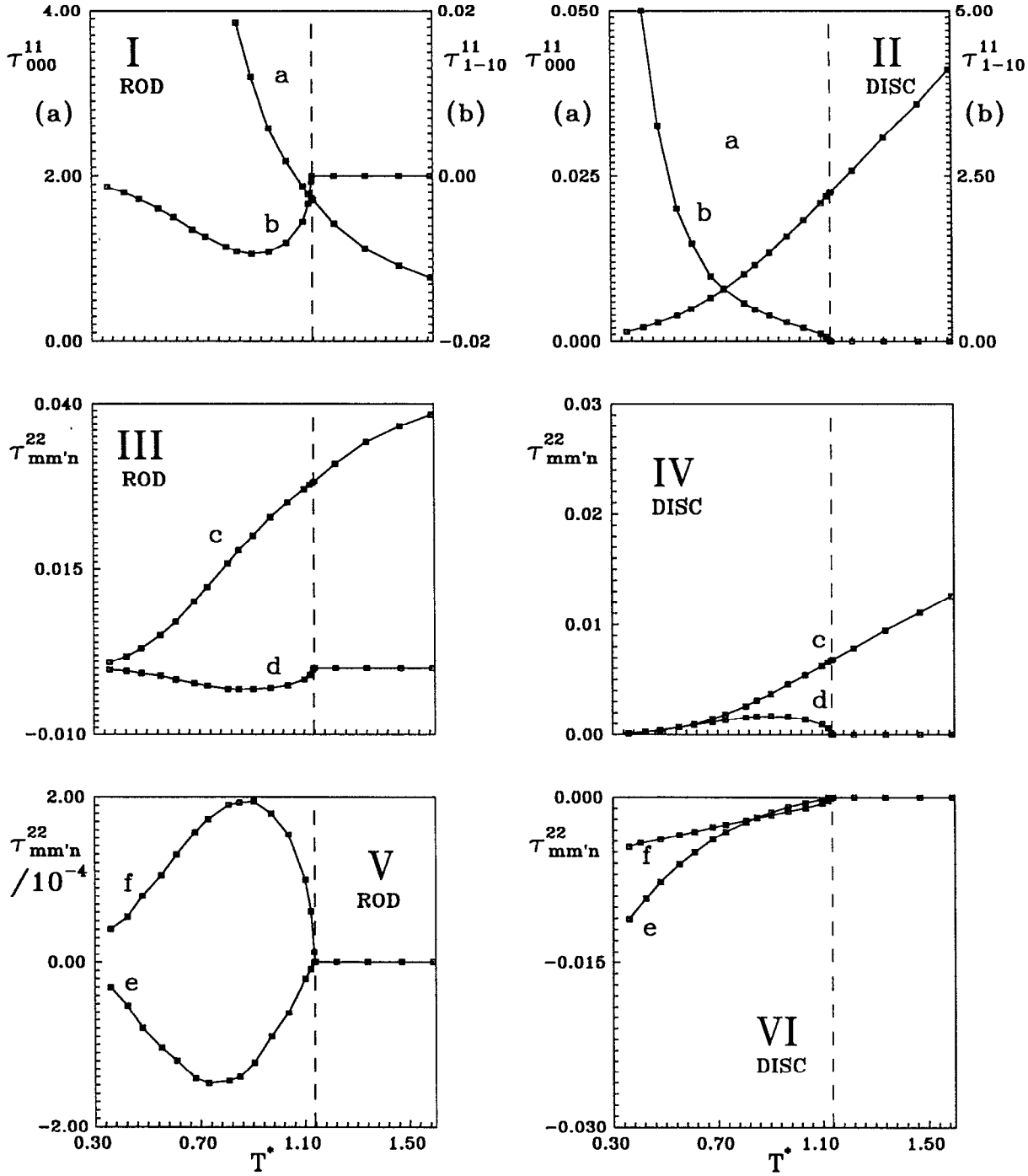

FIG. 4. Correlation times τ^{11}_{000} (a), τ^{11}_{1-10} (b), τ^{22}_{000} (c), τ^{22}_{200} (d), τ^{22}_{2-21} (e) and τ^{22}_{1-12} (f) (in units of $D_\perp^{-1}$), corresponding to the correlation functions plotted in figures 1–3, plotted versus reduced temperature. The vertical dashed line marks the uniaxial–biaxial transition.

In practice we have typically used for each n block an expansion up to $L_{max}=20$ and $m_{max}=8$ in Eq. (14), corresponding to 149 basis functions. At the lowest temperatures we have found it necessary to use expansions up to $L_{max}=40$ and $m_{max}=8$ (329 basis functions) to ensure convergence.

Correlation functions have been calculated for the various temperatures in Table I. For the potential assumed, the correlation functions obey the symmetry relations of Eq. (4). It is important to notice that the initial values of the correlation functions are model independent quantities.[41] The explicit expressions for the initial values are

TABLE III. The average Wigner rotation matrix products contributing to the nonvanishing terms of Eq. (36 b) for $L''\neq L$ and $L=2$.

$\langle D^2_{mn} D^{L''*}_{m''n}\rangle = (-)^{m''-n}\sum_{J=|2-L''|}^{2+L''} C(2,L''J;m,-m'')C(2,L'',J;n,-n)\langle D_{m-m'',0}\rangle$

$L''=0$: $\langle D^2_{00} D^{0*}_{00}\rangle = \langle P_2\rangle$, $\langle D^2_{20} D^{0*}_{00}\rangle = \mathcal{R}e\langle D^2_{20}\rangle$,

$L''=1$: $\langle D^2_{\pm 11} D^{1*}_{\mp 11}\rangle = \mp\frac{1}{\sqrt{6}}\mathcal{R}e\langle D^{20}_2\rangle$, $\langle D^2_{11} D^{1*}_{11}\rangle = \frac{1}{2}\langle P_2\rangle$, $\langle D^2_{\pm 21} D^{1*}_{\mp 01}\rangle = \pm\frac{1}{\sqrt{3}}\mathcal{R}e\langle D^2_{20}\rangle$,

$L''=2$: Listed in Table II,

$L''=3$: Not included, because they are all to be multiplicated by matrix elements equal to zero in the terms of Eq. (36b).

$L''=4$: See table.

$mm''\backslash n$	0	1	2
00	$\frac{5}{11}<P_6>+\frac{20}{77}<P_4>+\frac{2}{7}<P_2>$	$-\frac{2\sqrt{30}}{33}<P_6>+\frac{\sqrt{30}}{77}<P_4>$ $+\frac{1}{7}\sqrt{\frac{10}{3}}<P_2>$	$\frac{\sqrt{15}}{33}<P_6>-\frac{6\sqrt{15}}{77}<P_4>$ $+\frac{1}{7}\sqrt{\frac{5}{3}}<P_2>$
1-1	$-\frac{4\sqrt{14}}{33}\mathcal{R}e<D^6_{20}>-\frac{9\sqrt{3}}{77}\mathcal{R}e<D^4_{20}>$ $+\frac{\sqrt{5}}{21}\mathcal{R}e<D^2_{20}>$	$\frac{16}{33}\sqrt{\frac{7}{15}}\mathcal{R}e<D^6_{20}>-\frac{27}{154\sqrt{10}}\mathcal{R}e<D^4_{20}>$ $+\frac{5}{21\sqrt{6}}\mathcal{R}e<D^2_{20}>$	$-\frac{4}{33}\sqrt{\frac{14}{15}}\mathcal{R}e<D^6_{20}>+\frac{81}{154\sqrt{5}}\mathcal{R}e<D^4_{20}>$ $+\frac{5}{42\sqrt{3}}\mathcal{R}e<D^2_{20}>$
11	$-\frac{2\sqrt{30}}{33}<P_6>+\frac{\sqrt{30}}{77}<P_4>$ $+\frac{1}{7}\sqrt{\frac{10}{3}}<P_2>$	$\frac{8}{33}<P_6>+\frac{3}{154}<P_4>+\frac{5}{21}<P_2>$	$-\frac{2\sqrt{2}}{33}<P_6>-\frac{9}{77\sqrt{2}}<P_4>$ $+\frac{5}{21\sqrt{2}}<P_2>$
2-2	$\frac{1}{11}\sqrt{\frac{70}{3}}\mathcal{R}e<D^6_{40}>-\frac{2}{11}\sqrt{\frac{6}{7}}\mathcal{R}e<D^4_{40}>$	$-\frac{4\sqrt{7}}{33}\mathcal{R}e<D^6_{40}>-\frac{3}{11\sqrt{36}}\mathcal{R}e<D^4_{40}>$	$\frac{3\sqrt{14}}{99}\mathcal{R}e<D^6_{40}>+\frac{9}{11}\sqrt{\frac{2}{35}}\mathcal{R}e<D^4_{40}>$
20	$\frac{\sqrt{70}}{33}\mathcal{R}e<D^6_{20}>-\frac{6\sqrt{15}}{77}\mathcal{R}e<D^4_{20}>$ $+\frac{1}{21}\mathcal{R}e<D^2_{20}>$	$-\frac{4}{33}\sqrt{\frac{7}{3}}\mathcal{R}e<D^6_{20}>-\frac{9}{77}\sqrt{\frac{1}{2}}\mathcal{R}e<D^4_{20}>$ $+\frac{1}{21}\sqrt{\frac{5}{6}}\mathcal{R}e<D^2_{20}>$	$\frac{1}{33}\sqrt{\frac{14}{3}}\mathcal{R}e<D^6_{20}>+\frac{27}{77}\mathcal{R}e<D^4_{20}>$ $+\frac{1}{42}\sqrt{\frac{5}{3}}\mathcal{R}e<D^2_{20}>$
02	$\frac{2}{11}\sqrt{\frac{14}{3}}\mathcal{R}e<D^6_{20}>+\frac{8}{77}\mathcal{R}e<D^4_{20}>$ $+\frac{\sqrt{15}}{21}\mathcal{R}e<D^2_{20}>$	$-\frac{8}{33}\sqrt{\frac{7}{5}}\mathcal{R}e<D^6_{20}>+\frac{2}{77}\sqrt{\frac{6}{5}}\mathcal{R}e<D^4_{20}>$ $+\frac{5}{21\sqrt{2}}\mathcal{R}e<D^2_{20}>$	$\frac{2}{33}\sqrt{\frac{14}{5}}\mathcal{R}e<D^6_{20}>-\frac{12}{77}\sqrt{\frac{3}{5}}\mathcal{R}e<D^4_{20}>$ $+\frac{5}{42}\mathcal{R}e<D^2_{20}>$
22	$\frac{\sqrt{15}}{33}<P_6>-\frac{6\sqrt{15}}{77}<P_4>$ $+\frac{1}{7}\sqrt{\frac{5}{3}}<P_2>$	$-\frac{2\sqrt{2}}{33}<P_6>-\frac{9}{77\sqrt{2}}<P_4>$ $+\frac{5}{21\sqrt{2}}<P_2>$	$\frac{1}{33}<P_6>+\frac{27}{77}<P_4>+\frac{5}{42}<P_2>$

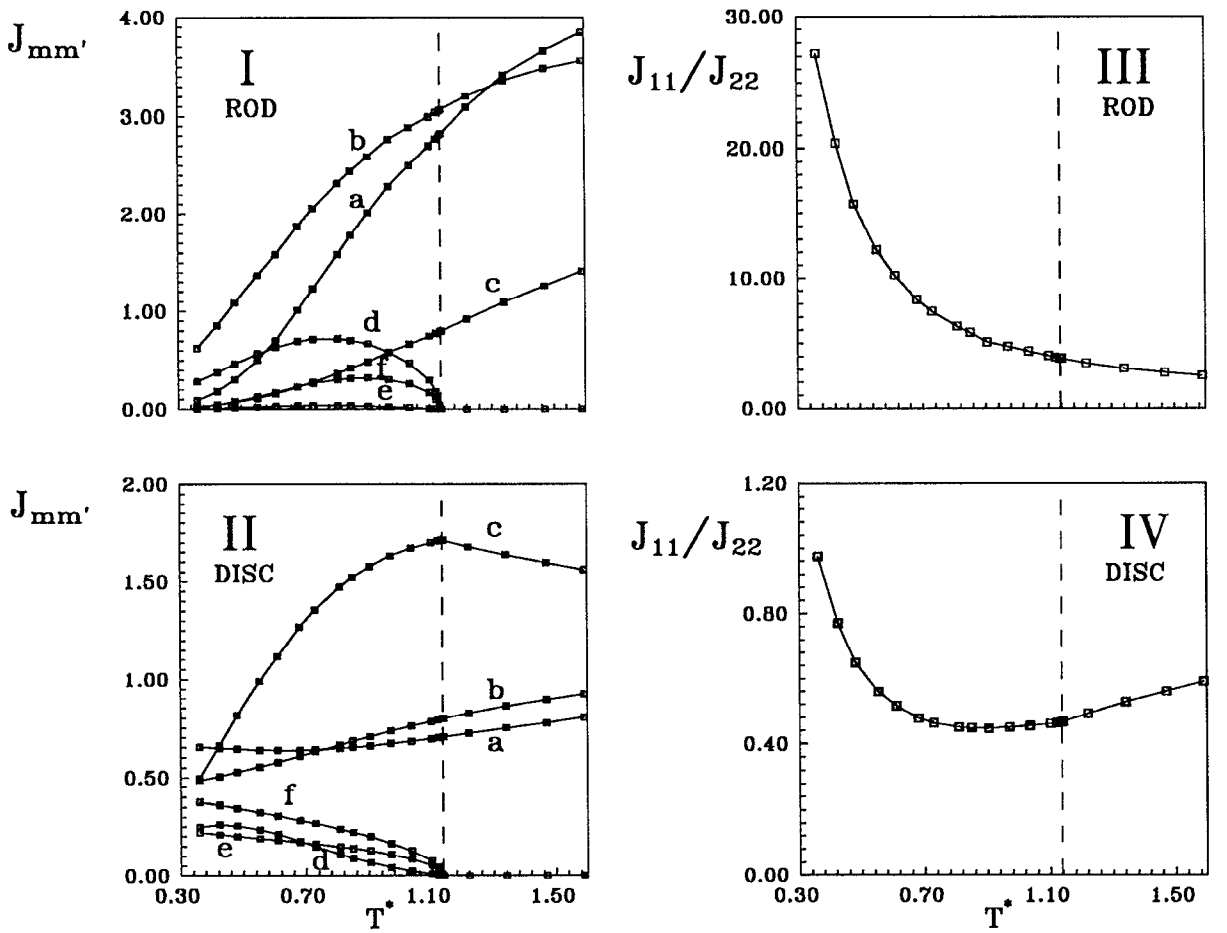

FIG. 5. In I and II the spectral densities [in units of $(A^{2,0})^2$] are given as functions of reduced temperature for a rod- and a disc-like molecule, respectively. J_{00} (a), J_{11} (b), J_{22} (c), J_{1-1} (d), J_{20} (e) and J_{2-2} (f). In III and IV the ratio J_{11}/J_{22} is plotted for the two cases. The vertical dashed line marks the uniaxial–biaxial transition.

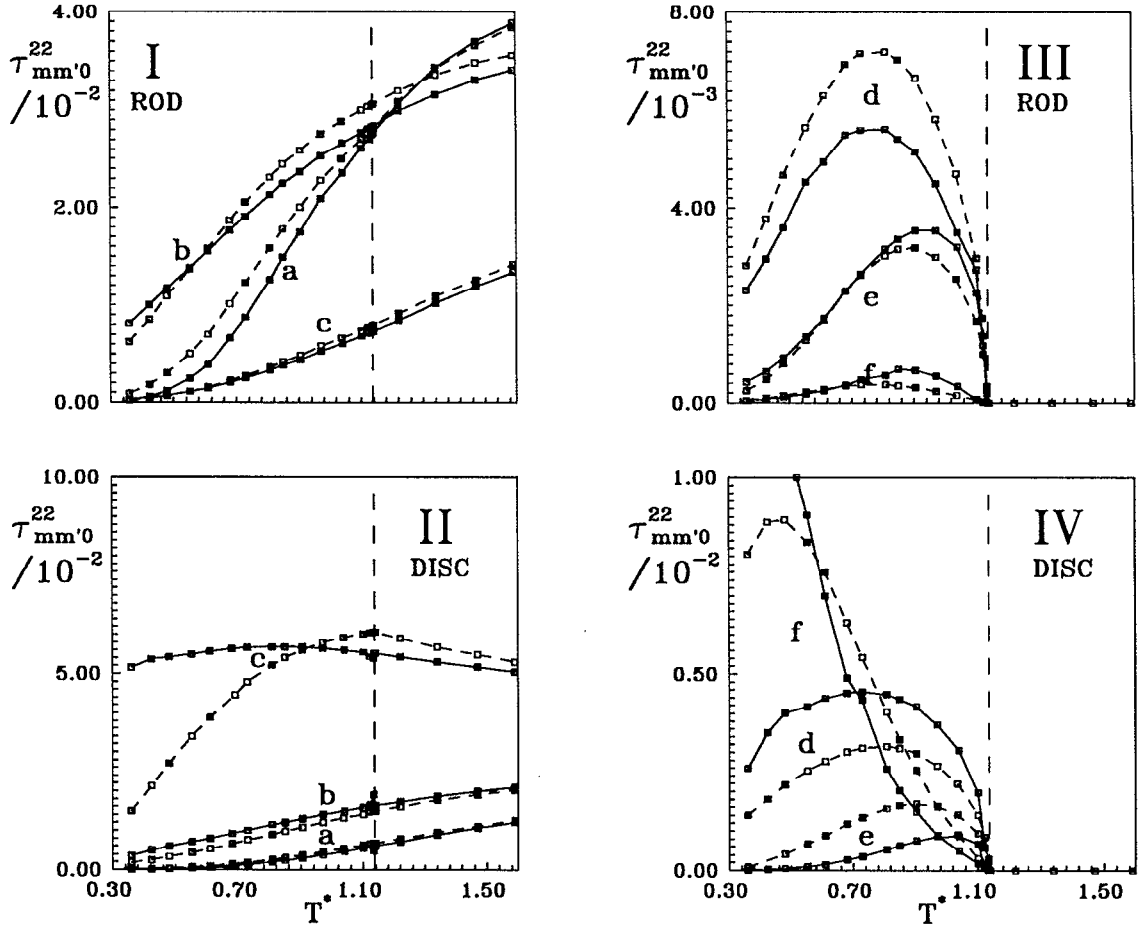

FIG. 6. Approximate values of the correlation times: τ^{22}_{000} (a), τ^{22}_{110} (b), τ^{22}_{220} (c), τ^{22}_{1-10} (d), τ^{22}_{200} (e), and τ^{22}_{2-20} (f) (in units of D_1^{-1}) and with solid lines as a guide to the eye, compared to these obtained from the numerical calculations (dashed lines). The vertical dashed line marks the uniaxial–biaxial transition.

given in Table II for correlation functions of first and second rank. The value of the correlation functions at long time is also model independent, since

$$\phi^{LL'}_{mm'n}(\infty) = \langle D^{L}_{mn} \rangle \langle D^{L'*}_{m'n} \rangle. \tag{48}$$

The correlation functions decay to products of order parameters, so if an order parameter goes from zero to a certain value at a phase transition the tail of the correlation function should correspondingly change. A correlation function labeled with $m \neq m'$ is always equal to zero in the uniaxial phase,[35,50] and the phase transition from biaxial to uniaxial phase are easily detected in the plotted series of correlation functions. In figures 1 (first rank) and 2, 3 (second rank) some examples of orientational correlation functions for both rod- (I,III) and disc- (II,IV) like molecules are plotted at various temperatures across the phase transition. The values of the order parameters corresponding to the temperatures in figures 1–3 are to be found in Table I. It is possible to verify that for the cases with $m' = m$ the qualitative appearance of the correlation function is not changed across the phase transition (I,II in figures 1–3), while those corresponding to the cross-correlation functions vanish in the uniaxial phase (III, IV in figures 1–3). It is worth noting that the values of the cross-correlation functions are considerably higher, and of the same order of magnitude of the autocorrelation functions, for the disc-like molecule (IV in figures 1–3) than for the rod-like molecule (III in figures 1–3). In figure 4 the correlation times corresponding to the correlation functions in figures 1–3 are plotted as a function of temperature for our chosen examples of rod- (I,III) and disc- (II,IV) like molecules. The transition temperature between uniaxial and biaxial phase is marked by the vertical dashed line. In case of cross-correlation the correlation time is zero in the uniaxial phase. To detect the phase transition by a dynamic spectroscopic method it might be preferable to perform an experiment which depends significantly on these cross-correlation contributions, because in this case the correlation times change from non-zero to zero at the phase transition.

In figure 5 (I,II) the second rank spectral densities

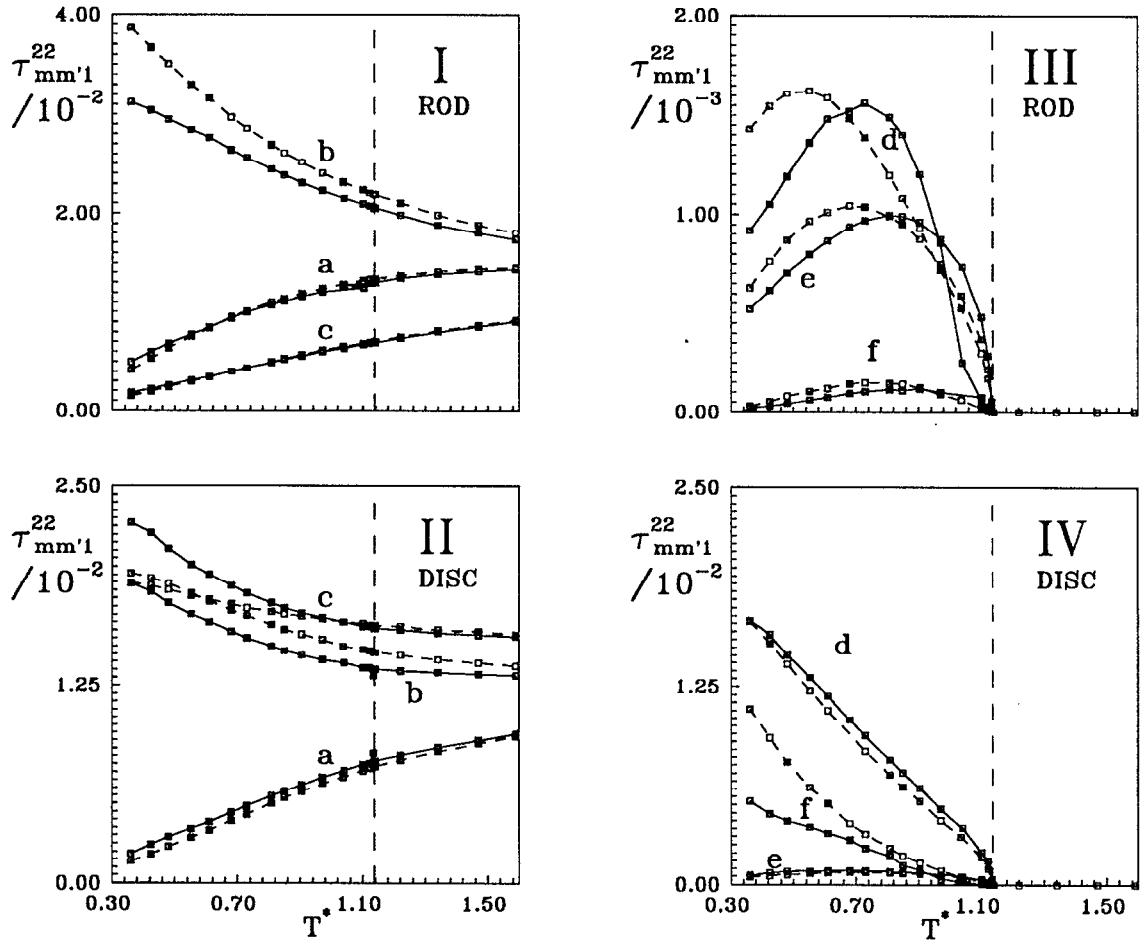

FIG. 7. Approximate values of the correlation times: τ^{22}_{001} (a), τ^{22}_{111} (b), τ^{22}_{221} (c), τ^{22}_{1-11} (d), τ^{22}_{201} (e) and τ^{22}_{2-21} (f), (in units of D_1^{-1}) and with solid lines as a guide to the eye, compared to these obtained from the numerical calculations (dashed lines). The vertical dashed line marks the uniaxial–biaxial transition.

defined in Eq. (29) are plotted as a function of temperature, and it is possible to notice that the values of the cross-correlation spectral densities are in the same range as those with $m'=m$ in the biaxial phase, and their contribution is not negligible, neither for the rod- (I) nor for the disc- (II) like probe. In figure 5 (III,IV) the ratio J_{11}/J_{22} is also presented for both the cases of a rod- and a disc-like molecule. We see that it does not seem possible to detect the biaxial phase transition, since the spectral density curves vary continuously across the transition. However, in the case of a disc-like probe (IV) the ratio changes from a decreasing to an increasing trend as the system moves well into the biaxial phase.

We also present, besides the numerical calculations, the results from the approximation Eq. (33) based on the analytical expressions given in Appendix B. The weighting factors, i.e. the values of the correlation function at $t=0$, are listed in Tables II and III. In the limit of uniaxial rotational diffusion in uniaxial phase the results of our approximate solutions have been compared to these obtained by using the approximation presented by van der Meer *et al.*[48] and they are found to be in good agreement at low values of the second rank order parameter.

We have further used our approximate solutions to calculate the correlation times through the uniaxial–biaxial phase transition. In figures 6, 7 and 8 the second rank correlation times are indicated with a solid line for the approximate solutions of the correlation time, while the numerical solution is indicated with a dashed line. The approximate solution is indeed satisfying for many of the correlation times. In general it can be noticed that the approximate results are less reliable at low temperatures, as could be expected. The more interesting point is to notice that the quality of the approximation is very sensitive to the chosen correlation function. Thus it should not be concluded that an approximation that has a high accuracy for some of the correlation functions, should have it for all. The accuracy of the approximation also changes with the type of chosen probe for the same correlation function (see, for example, c in I and II, figure 6).

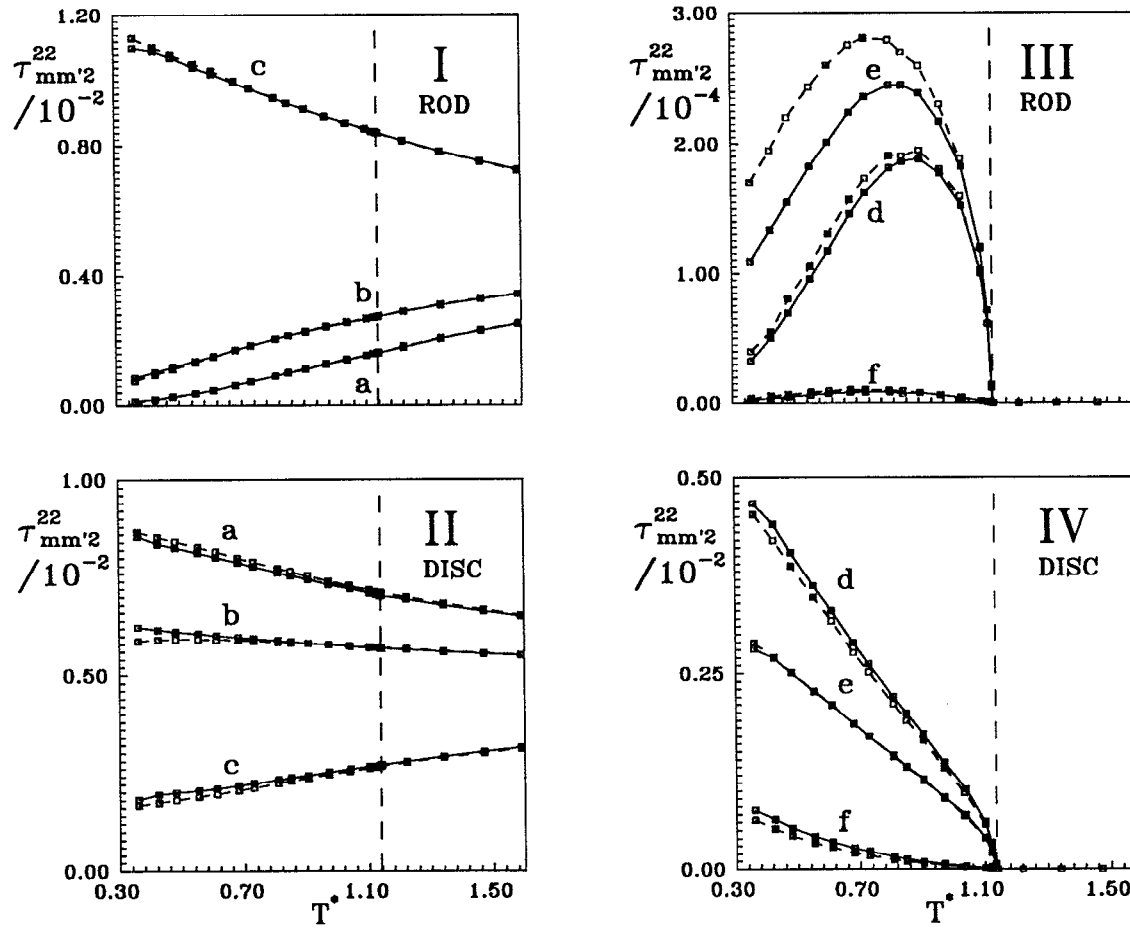

FIG. 8. Approximate values of the correlation times: τ^{22}_{002} (a), τ^{22}_{112} (b), τ^{22}_{222} (c), τ^{22}_{1-12} (c), τ^{22}_{202} (e) and τ^{22}_{2-22} (f), (in units of $D_\perp^{-1}$) and with solid lines as a guide to the eye, compared to these obtained from the numerical calculations (dashed lines). The vertical dashed line marks the uniaxial–biaxial transition.

V. CONCLUSIONS

We have treated the reorientation of uniaxial molecules in biaxial phases in detail. The solutions we have obtained could be used to probe the uniaxial–biaxial nematic phase transition with, for example, perdeuterated benzene dissolved in the liquid crystal phase.

The values of cross-correlation functions and spectral densities are all nonzero in the biaxial phase and zero in the uniaxial phase. Therefore, in order to observe the phase transition, an experiment dependent on cross correlation spectral densities should be preferred. We also found that observables due to the cross-correlations are higher for the disc-shaped probe than for the rod-like probe, at least for the solute–solvent parameters chosen here. Thus the use of say, deuterated benzene derivatives as NMR probes could also prove useful in view of its essentially disc-like shape.

In addition to the numerical calculations, we have performed an approximate calculation of the correlation times. It is of course desirable to be able to calculate the correlation functions and correlation times in a more simple and less time consuming way, but our results indicate also the weakness of an approximate solution as the only approach to be employed. Indeed the approximate forms might be, as we have seen, satisfactory in many cases, but clearly not in those cases where the correlation functions evolve in time in an inherently nonexponential way. Having this limitation clear, the approximate calculations could be useful in fitting experimental data as a first step, before making use of the more time consuming numerical calculations in a number of cases.

In any case it is hoped that the results presented in this paper will stimulate experimental studies of the dynamics in biaxial nematics.

ACKNOWLEDGMENTS

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sions on the biaxial model. A preliminary version of this work was presented at the XIV International Liquid Crystal Conference, Pisa, July 1992.

APPENDIX A: MATRIX ELEMENTS OF THE DIFFUSION OPERATOR

Here the explicit expressions of the elements of the diffusional matrix are given for the case of anisotropic diffusion in biaxial phase. First we evaluate the various terms contributing to the symmetrized diffusional operator given in Eq. (10), which are

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

$$\langle \mathscr{D}^{L'}_{m'n} | -\frac{1}{2}\nabla^2 \frac{U(\alpha,\beta)}{k_BT} | \mathscr{D}^{L}_{mn} \rangle = -\frac{\sqrt{2L+1}}{2\sqrt{2L'+1}} \sum_{Jp} a_{Jp}[J(J+1)] \times C(L,J,L';m'-p,p) \times C(L,J,L';n,0)\delta_{m,m'-p}, \tag{A2}$$

$$\left\langle \mathscr{D}^{L'}_{m'n} \left| \frac{1}{4}\left(L_+ \frac{U(\alpha,\beta)}{k_BT}\right)\left(L_- \frac{U(\alpha,\beta)}{k_BT}\right) \right| \mathscr{D}^{L}_{mn} \right\rangle = \frac{\sqrt{2L+1}}{4\sqrt{2L'+1}} \sum_{Jp} \sum_{J'p'} a_{Jp}a_{J'p'} \sqrt{J(J+1)}\sqrt{J'(J'+1)} \times \sum_{J''=|J-J'|}^{J+J'} C(J,J',J'';p,p')C(J,J',J'';1,-1) \times C(L,J'',L';m'-p-p',p+p') \times C(L,J'',L';n,0)\delta_{m,m'-p-p'}. \tag{A3}$$

In the derivation of the matrix elements the following relations have been used:

$$\nabla^2 \mathscr{D}^{L}_{mn} = [L(L+1)+(\eta-1)n^2]\mathscr{D}^{L}_{mn}, \tag{A4}$$

$$L_z \mathscr{D}^{L}_{mn} = n\mathscr{D}^{L}_{mn}, \tag{A5}$$

$$L_\pm \mathscr{D}^{L}_{mn} = \sqrt{L(L+1)-n(n\pm1)}\,\mathscr{D}^{L}_{m,n\pm1}. \tag{A6}$$

If we want to express the matrix elements, assuming only second rank contributions to the potential the matrix elements are given by

$$\begin{aligned}\langle \mathscr{D}^{L'}_{m'n} | \hat{\Gamma} | \mathscr{D}^{L}_{mn} \rangle = {} & [-L'(L'+1)-n^2(\eta-1)+K_0]\delta_{L'L}\delta_{m'm} + \frac{\sqrt{2L+1}}{\sqrt{2L'+1}} K_1 C(L,2,L';m',0)C(L,2,L';n,0)\delta_{m'm} \\ & + \frac{\sqrt{2L+1}}{\sqrt{2L'+1}} K_2[C(L,2,L';m'-2,2)\delta_{m,m'-2} + C(L,2,L';m'+2,-2)\delta_{m,m'+2}]C(L,2,L';n,0) \\ & + \frac{\sqrt{2L+1}}{\sqrt{2L'+1}} K_3 C(L,4,L';m',0)C(L,4,L';n,0)\delta_{m'm} + \frac{\sqrt{2L+1}}{\sqrt{2L'+1}} K_4[C(L,4,L';m'-2,2)\delta_{m,m'-2} \\ & + C(L,4,L';m'+2,-2)\delta_{m,m'+2}]C(L,4,L';n,0) + \frac{\sqrt{2L+1}}{\sqrt{2L'+1}} K_5[C(L,4,L';m'-4,4)\delta_{m,m'-4} \\ & + C(L,4,L';m'+4,-4)\delta_{m,m'+4}]C(L,4,L';n,0).\end{aligned} \tag{A7}$$

The following constants have been used in (A7):

$$K_0=-\frac{3}{5}\left[\frac{1}{2}a_{20}^2+a_{22}\right], \tag{A8}$$

$$K_1=-3a_{20}-\frac{3}{7}\left[\frac{1}{2}a_{20}^2-3a_{22}^2\right], \tag{A9}$$

$$K_2=-3a_{22}+\frac{3}{7}a_{20}a_{22}, \tag{A10}$$

$$K_3=\frac{6}{35}(3a_{20}^2+a_{22}^2), \tag{A11}$$

$$K_4=\frac{6}{7}\sqrt{\frac{3}{5}}a_{20}a_{22}, \tag{A12}$$

$$K_5=3\sqrt{\frac{2}{35}}a_{22}^2. \tag{A13}$$

The symmetry relation $C(2,2,J'';m,n)=(-)^{J''}\times C(2,2,J'';-m,n)$ has been used, and the Clebsch–Gordan coefficients have been substituted by explicit values, where possible. We have also assumed for the second rank interactions, that $a_{22}=a_{2-2}$.[53]

APPENDIX B: APPROXIMATE ANALYTICAL EXPRESSIONS

We give here the approximate analytical expressions of the first derivative of the correlation function at $t=0$. To obtain these expressions we have used the unsymmetrized form of the matrix[32,64] given by

$$\langle D^{L'}_{m'n}|\Gamma|D^{L}_{mn}\rangle = [-L'(L'+1)-n^2(\eta-1)]\delta_{L'L}\delta_{m'm} - \sum_{Jp}\frac{1}{2}a_{Jp}[L'(L'+1)-L(L+1)+J(J+1)] \times C(L,J,L';m'-p,p)C(L,J,L';n,0)\delta_{m,m'-p}, \tag{B1}$$

which is a straightforward application of (9) on the basis set of Wigner matrices. The analytical expressions of first derivatives of the second rank correlation functions $\dot{\phi}^{22}{}_{m'mn}$ obtained from Eq. (36b) using Eq. (B1) for the calculation of the matrix elements are listed below. The explicit expressions are rather complicated to work out and have been obtained with the help of the Mathematica[65] computer algebra package.

$n=0$:

$$\dot{\phi}^{22}_{000}(0)=\frac{6}{5}+\frac{6}{35}a_{20}+\frac{12}{7}\langle P_2\rangle+\frac{6}{7}a_{20}\langle P_2\rangle+\frac{108}{35}\langle P_4\rangle-\frac{36}{385}a_{20}\langle P_4\rangle-\frac{12}{11}\sqrt{\frac{3}{5}}a_{22}\mathscr{R}e\langle D^4_{20}\rangle-\frac{72}{77}a_{20}\langle P_6\rangle - \frac{48}{11}\sqrt{\frac{2}{35}}a_{22}\mathscr{R}e\langle D^6_{20}\rangle, \tag{B2}$$

$$\dot{\phi}^{22}_{110}(0)=\frac{6}{5}+\frac{3}{35}a_{20}+\frac{6}{7}\langle P_2\rangle-\frac{3}{7}a_{20}\langle P_2\rangle+\frac{2}{7}a_{22}\mathscr{R}e\langle D^2_{20}\rangle-\frac{72}{35}\langle P_4\rangle-\frac{108}{385}a_{20}\langle P_4\rangle+\frac{72}{77}\sqrt{\frac{3}{5}}a_{22}\mathscr{R}e\langle D^4_{20}\rangle + \frac{48}{77}a_{20}\langle P_6\rangle+\frac{16}{11}\sqrt{\frac{2}{35}}a_{22}\mathscr{R}e\langle D^6_{20}\rangle, \tag{B3}$$

$$\dot{\phi}^{22}_{220}(0)=\frac{6}{5}-\frac{6}{35}a_{20}-\frac{12}{7}\langle P_2\rangle+\frac{10}{7}a_{22}\mathscr{R}e\langle D^2_{20}\rangle+\frac{18}{35}\langle P_4\rangle+\frac{18}{55}a_{20}\langle P_4\rangle-\frac{18}{77}\sqrt{\frac{3}{5}}a_{22}\mathscr{R}e\langle D^4_{20}\rangle-\frac{12}{77}a_{20}\langle P_6\rangle - \frac{4}{11}\sqrt{\frac{2}{35}}a_{22}\mathscr{R}e\langle D^6_{20}\rangle, \tag{B4}$$

$$\dot{\phi}^{22}_{1-10}(0)=-3\frac{\sqrt{6}}{35}a_{22}-\frac{6\sqrt{6}}{7}\mathscr{R}e\langle D^2_{20}\rangle-\frac{\sqrt{6}}{7}a_{22}\langle P_2\rangle-\frac{\sqrt{6}}{7}a_{20}\mathscr{R}e\langle D^2_{20}\rangle-\frac{36}{7}\sqrt{\frac{2}{5}}\mathscr{R}e\langle D^4_{20}\rangle+\frac{48\sqrt{6}}{385}a_{22}\langle P_4\rangle + \frac{18}{77}\sqrt{\frac{2}{5}}a_{20}\mathscr{R}e\langle D^4_{20}\rangle+\frac{8\sqrt{6}}{77}a_{22}\langle P_6\rangle+\frac{32}{11}\sqrt{\frac{3}{35}}a_{20}\mathscr{R}e\langle D^6_{20}\rangle, \tag{B5}$$

$$\dot{\phi}^{22}_{200}(0) = -\frac{6}{35}a_{22} - \frac{12}{7}\mathcal{R}e\langle D^2_{20}\rangle + \frac{6}{7}a_{20}\mathcal{R}e\langle D^2_{20}\rangle + \frac{18}{7}\sqrt{\frac{3}{5}}\mathcal{R}e\langle D^4_{20}\rangle + \frac{18}{55}a_{22}\langle P_4\rangle + \frac{90}{77}\sqrt{\frac{3}{5}}a_{20}\mathcal{R}e\langle D^4_{20}\rangle$$
$$-\frac{18}{11}\sqrt{\frac{2}{35}}a_{22}\mathcal{R}e\langle D^4_{40}\rangle - \frac{12}{77}a_{22}\langle P_6\rangle - \frac{24}{11}\sqrt{\frac{2}{35}}a_{20}\mathcal{R}e\langle D^6_{20}\rangle - \frac{12}{11}\sqrt{\frac{2}{7}}a_{22}\mathcal{R}e\langle D^6_{40}\rangle, \tag{B6}$$

$$\dot{\phi}^{22}_{2-20}(0) = \frac{10}{7}a_{22}\mathcal{R}e\langle D^2_{20}\rangle - \frac{18}{77}\sqrt{\frac{3}{5}}a_{22}\mathcal{R}e\langle D^4_{20}\rangle + 18\sqrt{\frac{2}{35}}\mathcal{R}e\langle D^4_{40}\rangle - \frac{18}{11}\sqrt{\frac{2}{35}}a_{20}\mathcal{R}e\langle D^4_{40}\rangle - \frac{4}{11}\sqrt{\frac{2}{35}}a_{22}\mathcal{R}e\langle D^6_{20}\rangle$$
$$-\frac{12}{11}\sqrt{\frac{2}{7}}a_{20}\mathcal{R}e\langle D^6_{40}\rangle \tag{B7}$$

$n=1$:

$$\dot{\phi}^{22}_{001}(0) = 1 + \frac{3}{35}a_{20} + \frac{5}{7}\langle P_2\rangle - \frac{3}{7}a_{20}\langle P_2\rangle - \frac{2}{7}a_{22}\mathcal{R}e\langle D^2_{20}\rangle - \frac{12}{7}\langle P_4\rangle - \frac{108}{385}a_{20}\langle P_4\rangle + \frac{12}{77}\sqrt{\frac{3}{5}}a_{22}\mathcal{R}e\langle D^4_{20}\rangle + \eta\left[\frac{1}{5} + \frac{1}{7}\langle P_2\rangle\right.$$
$$\left. - \frac{12}{35}\langle P_4\rangle\right] + \frac{48}{77}a_{20}\langle P_6\rangle + \frac{32}{11}\sqrt{\frac{2}{35}}a_{22}\mathcal{R}e\langle D^6_{20}\rangle, \tag{B8}$$

$$\dot{\phi}^{22}_{111}(0) = 1 + \frac{3}{70}a_{20} + \frac{5}{14}\langle P_2\rangle + \frac{5}{14}a_{20}\langle P_2\rangle + \frac{11}{21}a_{22}\mathcal{R}e\langle D^2_{20}\rangle + \frac{8}{7}\langle P_4\rangle + \frac{6}{385}a_{20}\langle P_4\rangle - \frac{15}{77}\sqrt{\frac{3}{5}}a_{22}\mathcal{R}e\langle D^4_{20}\rangle$$
$$+\eta\left[\frac{1}{5} + \frac{1}{14}\langle P_2\rangle + \frac{8}{35}\langle P_4\rangle\right] - \frac{32}{77}a_{20}\langle P_6\rangle - \frac{32}{33}\sqrt{\frac{2}{35}}a_{22}\mathcal{R}e\langle D^6_{20}\rangle, \tag{B9}$$

$$\dot{\phi}^{22}_{221}(0) = 1 - \frac{3}{35}a_{20} - \frac{5}{7}\langle P_2\rangle - \frac{1}{7}a_{20}\langle P_2\rangle + \frac{22}{21}a_{22}\mathcal{R}e\langle D^2_{20}\rangle - \frac{2}{7}\langle P_4\rangle + \frac{48}{385}a_{20}\langle P_4\rangle + \frac{12}{77}\sqrt{\frac{3}{5}}a_{22}\mathcal{R}e\langle D^4_{20}\rangle + \eta\left[\frac{1}{5} - \frac{1}{7}\langle P_2\rangle\right.$$
$$\left. - \frac{2}{35}\langle P_4\rangle\right] + \frac{8}{77}a_{20}\langle P_6\rangle + \frac{8}{33}\sqrt{\frac{2}{35}}a_{22}\mathcal{R}e\langle D^6_{20}\rangle, \tag{B10}$$

$$\dot{\phi}^{22}_{1-11}(0) = -\frac{3}{35}\sqrt{\frac{3}{2}}a_{22} - \frac{5}{7}\sqrt{\frac{3}{2}}\mathcal{R}e\langle D^2_{20}\rangle + \frac{1}{3}\sqrt{\frac{3}{2}}a_{22}\langle P_2\rangle + \frac{1}{3}\sqrt{\frac{3}{2}}a_{20}\mathcal{R}e\langle D^2_{20}\rangle + \frac{20}{7}\sqrt{\frac{2}{5}}\mathcal{R}e\langle D^4_{20}\rangle - \frac{6}{55}\sqrt{\frac{3}{2}}a_{22}\langle P_4\rangle$$
$$+\frac{3}{11}\sqrt{\frac{2}{5}}a_{20}\mathcal{R}e\langle D^4_{20}\rangle - \eta\frac{1}{7}\left[\sqrt{\frac{3}{2}}\mathcal{R}e\langle D^2_{20}\rangle - 4\sqrt{\frac{2}{5}}\mathcal{R}e\langle D^4_{20}\rangle\right] - \frac{16}{77}\sqrt{\frac{2}{3}}a_{22}\langle P_6\rangle - \frac{64}{33}\sqrt{\frac{3}{35}}a_{20}\mathcal{R}e\langle D^6_{20}\rangle, \tag{B11}$$

$$\dot{\phi}^{22}_{201}(0) = -\frac{3}{35}a_{22} - \frac{5}{7}\mathcal{R}e\langle D^2_{20}\rangle - \frac{1}{7}a_{22}\langle P_2\rangle - \frac{1}{7}a_{20}\mathcal{R}e\langle D^2_{20}\rangle - \frac{10}{7}\sqrt{\frac{3}{5}}\mathcal{R}e\langle D^4_{20}\rangle + \frac{48}{385}a_{22}\langle P_4\rangle + \frac{6}{77}\sqrt{\frac{3}{5}}a_{20}\mathcal{R}e\langle D^4_{20}\rangle$$
$$+\frac{12}{11}\sqrt{\frac{2}{35}}a_{22}\mathcal{R}e\langle D^4_{40}\rangle - \eta\frac{1}{7}\left[\mathcal{R}e\langle D^2_{20}\rangle + 2\sqrt{\frac{3}{5}}\mathcal{R}e\langle D^4_{20}\rangle\right] + \frac{8}{77}a_{22}\langle P_6\rangle + \frac{16}{11}\sqrt{\frac{2}{35}}a_{20}\mathcal{R}e\langle D^6_{20}\rangle$$
$$+\frac{8}{11}\sqrt{\frac{2}{7}}a_{22}\mathcal{R}e\langle D^6_{40}\rangle, \tag{B12}$$

$$\phi^{22}_{2-21}(0) = -\frac{20}{21} a_{22} \mathcal{R}e\langle D^2_{20}\rangle + \frac{12}{77}\sqrt{\frac{3}{5}}\, a_{22} \mathcal{R}e\langle D^4_{20}\rangle - 10\sqrt{\frac{2}{35}}\, \mathcal{R}e\langle D^4_{40}\rangle + \frac{12}{11}\sqrt{\frac{2}{35}}\, a_{20} \mathcal{R}e\langle D^4_{40}\rangle - 2\sqrt{\frac{2}{35}}\, \eta \mathcal{R}e\langle D^4_{40}\rangle$$

$$+ \frac{8}{33}\sqrt{\frac{2}{35}}\, a_{22} \mathcal{R}e\langle D^6_{20}\rangle + \frac{8}{11}\sqrt{\frac{2}{7}}\, a_{20} \mathcal{R}e\langle D^6_{40}\rangle. \tag{B13}$$

$n=2$:

$$\phi^{22}_{002}(0) = \frac{2}{5} - \frac{6}{35} a_{20} - \frac{4}{7}\langle P_2\rangle + \frac{2}{7} a_{22} \mathcal{R}e\langle D^2_{20}\rangle + \frac{6}{35}\langle P_4\rangle + \frac{18}{55} a_{20}\langle P_4\rangle + \frac{30}{77}\sqrt{\frac{3}{5}}\, a_{22} \mathcal{R}e\langle D^4_{20}\rangle + \eta\left[\frac{4}{5} - \frac{8}{7}\langle P_2\rangle + \frac{12}{35}\langle P_4\rangle\right]$$

$$- \frac{12}{77} a_{20}\langle P_6\rangle - \frac{8}{11}\sqrt{\frac{2}{35}}\, a_{22} \mathcal{R}e\langle D^6_{20}\rangle, \tag{B14}$$

$$\phi^{22}_{112}(0) = \frac{2}{5} - \frac{3}{35} a_{20} - \frac{2}{7}\langle P_2\rangle - \frac{1}{7} a_{20}\langle P_2\rangle + \frac{1}{3} a_{22} \mathcal{R}e\langle D^2_{20}\rangle - \frac{4}{35}\langle P_4\rangle + \frac{48}{385} a_{20}\langle P_4\rangle - \frac{3}{11}\sqrt{\frac{3}{5}}\, a_{22} \mathcal{R}e\langle D^4_{20}\rangle + \eta\left[\frac{4}{5} - \frac{4}{7}\langle P_2\rangle\right.$$

$$\left. - \frac{8}{35}\langle P_4\rangle\right] + \frac{8}{77} a_{20}\langle P_6\rangle + \frac{8}{33}\sqrt{\frac{2}{35}}\, a_{22} \mathcal{R}e\langle D^6_{20}\rangle, \tag{B15}$$

$$\phi^{22}_{222}(0) = \frac{2}{5} + \frac{6}{35} a_{20} + \frac{4}{7}\langle P_2\rangle + \frac{1}{7} a_{20}\langle P_2\rangle + \frac{5}{21} a_{22} \mathcal{R}e\langle D^2_{20}\rangle + \frac{1}{35}\langle P_4\rangle - \frac{111}{385} a_{20}\langle P_4\rangle - \frac{3}{77}\sqrt{\frac{3}{5}}\, a_{22} \mathcal{R}e\langle D^4_{20}\rangle + \eta\left[\frac{4}{5} + \frac{8}{7}\langle P_2\rangle\right.$$

$$\left. + \frac{2}{35}\langle P_4\rangle\right] - \frac{2}{77} a_{20}\langle P_6\rangle - \frac{2}{33}\sqrt{\frac{2}{35}}\, a_{22} \mathcal{R}e\langle D^6_{20}\rangle, \tag{B16}$$

$$\phi^{22}_{1-12}(0) = \frac{3\sqrt{6}}{35} a_{22} + \frac{2\sqrt{6}}{7} \mathcal{R}e\langle D^2_{20}\rangle - \frac{2}{7}\sqrt{\frac{2}{3}}\, a_{22}\langle P_2\rangle - \frac{2}{7}\sqrt{\frac{2}{3}}\, a_{20} \mathcal{R}e\langle D^2_{20}\rangle - \frac{2}{7}\sqrt{\frac{2}{5}}\, \mathcal{R}e\langle D^4_{20}\rangle - \frac{3\sqrt{6}}{385} a_{22}\langle P_4\rangle$$

$$- \frac{30}{77}\sqrt{\frac{2}{5}}\, a_{20} \mathcal{R}e\langle D^4_{20}\rangle + \eta\frac{4}{7}\left[\sqrt{6}\langle D^2_{20}\rangle - \sqrt{\frac{2}{5}}\, \mathcal{R}e\langle D^4_{20}\rangle\right] + \frac{4}{77}\sqrt{\frac{2}{3}}\, a_{22}\langle P_6\rangle + \frac{16}{33}\sqrt{\frac{3}{35}}\, a_{20} \mathcal{R}e\langle D^6_{20}\rangle, \tag{B17}$$

$$\phi^{22}_{202}(0) = \frac{6}{35} a_{22} + \frac{4}{7} \mathcal{R}e\langle D^2_{20}\rangle + \frac{1}{7} a_{22}\langle P_2\rangle - \frac{2}{7} a_{20} \mathcal{R}e\langle D^2_{20}\rangle + \frac{1}{7}\sqrt{\frac{3}{5}}\, \mathcal{R}e\langle D^4_{20}\rangle - \frac{111}{385} a_{22}\langle P_4\rangle - \frac{51}{77}\sqrt{\frac{3}{5}}\, a_{20} \mathcal{R}e\langle D^4_{20}\rangle$$

$$- \frac{3}{11}\sqrt{\frac{2}{35}}\, \mathcal{R}e\langle D^4_{40}\rangle + \eta\frac{2}{7}\left[4 \mathcal{R}e\langle D^2_{20}\rangle + \sqrt{\frac{3}{5}}\, \mathcal{R}e\langle D^4_{20}\rangle\right] - \frac{2}{77} a_{22}\langle P_6\rangle - \frac{4}{11}\sqrt{\frac{2}{35}}\, a_{20} \mathcal{R}e\langle D^6_{20}\rangle$$

$$- \frac{2}{11}\sqrt{\frac{2}{7}}\, a_{22} \mathcal{R}e\langle D^6_{40}\rangle, \tag{B18}$$

$$\phi^{22}_{2-22}(0)=\frac{5}{21}a_{22}\mathcal{R}e\langle D^2_{20}\rangle-\frac{3}{77}\sqrt{\frac{3}{5}}a_{22}\mathcal{R}e\langle D^4_{20}\rangle+\sqrt{\frac{2}{35}}\mathcal{R}e\langle D^4_{40}\rangle-\frac{3}{11}\sqrt{\frac{2}{35}}a_{20}\mathcal{R}e\langle D^4_{40}\rangle+2\sqrt{\frac{2}{35}}\eta\mathcal{R}e\langle D^4_{40}\rangle$$

$$-\frac{2}{33}\sqrt{\frac{2}{35}}a_{22}\mathcal{R}e\langle D^6_{20}\rangle-\frac{2}{11}\sqrt{\frac{2}{7}}a_{20}\mathcal{R}e\langle D^6_{40}\rangle. \tag{B19}$$

In our calculations we have also used approximate values of the coefficients a_{20} and a_{22} derived from the first term of a power expansion of the rank two order parameters

$$a_{20}=-\frac{245\langle P_2\rangle+350\langle D^2_{20}\rangle^2+2450\langle P_2\rangle\langle D^2_{20}\rangle^2}{49+220\langle D^2_{20}\rangle^2}, \tag{B20}$$

$$a_{22}=-\frac{140\langle D^2_{20}\rangle}{14-20\langle P_2\rangle+25\langle P_2\rangle^2}. \tag{B21}$$

The expressions corresponding to Eqs. (B2)–(B19) for the special case of rotational diffusion of a uniaxial probe in a uniaxial phase are obtained by putting $\langle D^L_{m0}\rangle=0$ for $m\neq 0$, and the coefficients $a_{20}=-5\langle P_2\rangle$ and $a_{22}=0$, which evidently leads to the result that all $\dot{\phi}^{L'L}_{m'mn}$ with $m'\neq m$ become zero as expected in the limit of uniaxial mesophase symmetry.

[1] M.J. Freiser, Phys. Rev. Lett. **24**, 1041 (1970).
[2] R. Alben, Phys. Rev. Lett. **30**, 778 (1973).
[3] J.P. Straley, Phys. Rev. A **10**, 1881 (1974).
[4] L.J. Yu and A. Saupe, Phys. Rev. Lett. **45**, 1000 (1980).
[5] F. Hessel and H. Finkelmann, Polym. Bull. **15**, 349 (1986).
[6] A.H. Windle, C. Viney, R. Golombok, A.M Donald, and G.R. Mitchell, Faraday Discuss. Chem. Soc. **79**, 55 (1985).
[7] S. Chandrasekhar, B.R. Ratna, B.K. Sadashiva, and V.N Raja, Mol. Cryst. Liq. Cryst. **165**, 123 (1988).
[8] J. Malthête, L. Liébert, A.M. Levelut, and Y. Galerne, C. R. Acad. Sci. Paris **303**, 1073 (1986).
[9] K. Praefcke, B. Kohne, B. Gündoğan, D. Demus, S. Diele, and G. Pelzl, Mol. Cryst. Liq. Cryst. Lett. **7**, 27 (1990).
[10] K. Praefcke, B. Kohne, B. Gündoğan, D. Singer, D. Demus, S. Diele, G. Pelzl, and U. Bakowsky, Mol. Cryst. Liq. Cryst. **198**, 393 (1991).
[11] A. Saupe, J. Chem. Phys. **75**, 5118 (1981).
[12] U.D. Kini and S. Chandrasekhar, Physica A **156**, 364 (1989).
[13] E. Govers and G. Vertogen, Physica **133 A**, 337 (1985).
[14] D. Baalss, Z. Naturforsch. **45a**, 7 (1990).
[15] E.H. MacMillan, Arch. Rat. Mech. Anal. **117**, 193, 241 (1992).
[16] T. Carlsson and F.M. Leslie, Liq. Cryst. **10**, 325 (1991).
[17] M.B. Lacerda Santos and G. Durand, J. Phys. **47**, 529 (1986).
[18] A. Saupe, S.Y. Xu, S. Plumley, Y.K Zhu, and P. Photinos, Physica A **174**, 195 (1991).
[19] J.W. Doane, *Nuclear Magnetic Resonance of Liquid Crystals*, edited by J.W. Emsley (Reidel, Dordrecht, 1985), Chap. 16, p. 413.
[20] F.P. Nicoletta, G. Chidichimo, A. Golemme, and N. Picci, Liq. Cryst. **10**, 665 (1991).
[21] A.M. Figuereido Neto, Y. Galerne, and L. Liébert, Liq. Cryst. **10**, 751 (1991).
[22] *Nuclear Magnetic Resonance of Liquid Crystals*, edited by J.W. Emsley (Reidel, Dordrecht, 1985).
[23] C. Zannoni, Mol. Phys. **38**, 1813 (1979).
[24] A. Arcioni, R. Tarroni, and C. Zannoni, in *Polarized Spectroscopy of Ordered Systems*, edited by B. Samorì and E. Thulstrup (Kluwer, Dordrecht, 1988), p. 421.
[25] M.P. Fontana, B. Rosi, N. Kirov, and I. Dozov, Phys. Rev. A **33**, 4132 (1986).
[26] R.G. Gordon, *Advances in Magnetic Resonance*, edited by J.S. Waugh (Academic, New York, 1968), Vol. 3, p. 1.
[27] W.A. Steele, in *Transport Phenomena in Fluids*, edited by H.J.M. Hanley (Dekker, New York, 1968), p. 209.
[28] C. Zannoni, *The Molecular Dynamics of Liquid Crystals*, edited by G.R. Luckhurst and C.A. Veracini (Kluwer, Dordrecht, in press).
[29] L.D. Favro, in *Fluctuation Phenomena in Solids*, edited by R.E. Burgess (Academic, New York, 1965), p. 79.
[30] J.H. Freed, J. Chem. Phys. **41**, 2077 (1964).
[31] W. Huntress, Jr., Adv. Magn. Reson. **4**, 1 (1970).
[32] (a) P.L. Nordio and P. Busolin, J. Chem. Phys. **55**, 5485 (1971); (b) P.L. Nordio, G. Rigatti, and U. Segre, Mol. Phys. **25**, 129 (1973).
[33] C.F. Polnaszek, G.V. Bruno, and J.H. Freed, J. Chem. Phys. **58**, 3185 (1973).
[34] W.A. Steele, Adv. Chem. Phys. **34**, 1 (1976).
[35] P.L. Nordio and U. Segre, *The Molecular Physics of Liquid Crystals*, edited by G.R. Luckhurst and G.W. Gray (Academic, New York, 1979), Chap. 18, p. 411.
[36] J.M. Bernassau, E.P. Black, and D.M. Grant, J. Chem. Phys. **76**, 253 (1982).
[37] N. Kirov, I. Dozov, and M.P. Fontana, J. Chem. Phys. **83**, 5267 (1985).
[38] B. Rosi, M.P. Fontana, I. Dozov, and N. Kirov, Phys. Rev. A **36**, 2879 (1987).
[39] I. Dozov, N. Kirov, and B. Petroff, Phys. Rev. A **36**, 2870 (1987).
[40] J. Bulthuis and L. Plomp, J. Phys. France **51**, 2581 (1990).
[41] R. Tarroni and C. Zannoni, J. Chem. Phys. **95**, 4550 (1991).
[42] J.H. Freed, in *Spin Labeling Theory and Applications*, edited by L.J. Berliner (Academic, New York, 1971), Chap. 3, p. 53.
[43] R.R. Vold and R.L. Vold, J. Chem. Phys. **88**, 1443 (1988).
[44] I. Dozov and N. Kirov, J. Chem. Phys. **90**, 1099 (1989).
[45] (a) Z. Luz, D. Goldfarb, and H. Zimmermann, *Nuclear Magnetic Resonance of Liquid Crystals*, edited by J.W. Emsley (Reidel, Dordrecht, 1985), Chap. 14, p. 343; (b) D. Goldfarb, I. Belsky, Z. Luz, and H. Zimmermann, J. Chem. Phys. **79** , 6203 (1983); (c) D. Goldfarb, R. Poupko, Z. Luz and H. Zimmermann, J. Chem. Phys. **79**, 4035 (1983).
[46] M.E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).
[47] I. Dozov and I. Penchev, J. Lumin. **22**, 69 (1980).
[48] B.W. van der Meer, H. Pottel, W. Herreman, M. Ameloot, H. Hendrickx, and H. Schröder, Biophys. J. **46**, 515 (1984).
[49] C. Zannoni, in *The Molecular Physics of Liquid Crystals*, edited by G.R. Luckhurst and G.W. Gray (Academic, New York, 1979), Chap. 3, p. 51.
[50] C. Zannoni and M. Guerra, Mol. Phys. **44**, 849 (1981).
[51] G.R. Luckhurst, *The Molecular Physics of Liquid Crystals*, edited by G.R. Luckhurst and G.W. Gray (Academic, New York, 1979), Chap. 4, p. 85.
[52] D.K. Remler and A.D.J. Haymet, J. Phys. Chem. **90**, 5426 (1986).
[53] F. Biscarini, C. Chiccoli, P. Pasini, F. Semeria, and C. Zannoni, presented at the 14th International Liquid Crystal Conference, Pisa, 1992 (to be published).
[54] G.R. Luckhurst, C. Zannoni, P.L. Nordio, and U. Segre, Mol. Phys. **30**, 1345 (1975).
[55] çP. Palffy-Muhoray and G. Hoatson, Phys. Rev. A **44**, 5052 (1991).
[56] G.R. Luckhurst and S. Romano, Mol. Phys. **40**, 129 (1980).
[57] P. Pasini and C. Zannoni, INFN Bull. TC-83/19, 1 (1984).

[58] R.G. Gordon and T. Messenger, *Electron Spin Relaxation in Liquids,* edited by L.T. Muus and P.W. Atkins (Plenum, New York, 1972), Chap. 13, p. 341.
[59] G.H. Golub and C.F. Van Loan, *Matrix Computations* (North-Holland, Amsterdam, 1983).
[60] W.M. Gelbart, J. Phys. Chem. **86**, 4298 (1982).
[61] Z.-Y. Chen and J.M. Deutch, J. Chem. Phys. **80**, 2151 (1984).
[62] E.F. Gramsbergen, L. Longa, and W.H. de Jeu, Phys. Rep. **135**, 195 (1986).
[63] M.P. Allen, Liq. Cryst. **8** , 499 (1990).
[64] C. Zannoni, Mol. Phys. **42**, 1303 (1981).
[65] S. Wolfram, *Mathematica* (Addison-Wesley, New York, 1988).