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Molecular biaxiality and reorientational correlation functions in nematic phases: Theory

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The molecular reorientation in nematic phases formed by rigid molecules with arbitrary shape is considered theoretically. In the framework of the small-step rotational diffusion model, the orientational correlation functions are obtained as fast converging series of exponentials. For cylindrical molecules our solutions are reduced to the results already reported in the literature. For molecules with effective D_{2h} symmetry we demonstrate that at reasonable values of the order parameter $\langle D_{02}^{2} \rangle$ the influence of the biaxiality on some correlation functions is significant and cannot be neglected.

I. INTRODUCTION

The most important feature of the mesomorphic state is the existence of long-range orientational order which determines the anisotropy of its properties. The orientational order is described by the distribution function $f(\Omega)$ where $\Omega=(\alpha,\beta,\gamma)$ are the set of Euler angles which connect the molecular to the laboratory frame (x,y,z). The distribution function can be expressed in terms of Wigner matrices $D_{0n''}^{n}(\Omega)$:[1]

$$f(\Omega)=\sum_{n,\text{even}} \frac{2n+1}{8\pi^2} \sum_{n''=-n} \langle (D_{0n''}^{n})^* \rangle D_{0n''}^{n}(\Omega) , \tag{1}$$

where the coefficients

$$\langle (D_{0n''}^{n})^* \rangle = \int f(\Omega)[D_{0n''}^{n}(\Omega)]^* d\Omega$$

are the parameters which describe the orientational alignment in the nematic phase. Very often in the theoretical and experimental investigations the mesomorphic molecules are assumed to have cylindrical symmetry. In this case

$$\begin{aligned} f(\Omega)&=f(\beta) \\ &=\frac{1}{4\pi^2}\sum_{n \text{ even}} \frac{2n+1}{2} \langle P_n \rangle P_n(\cos\beta) , \end{aligned} \tag{2}$$

where $P_n(\cos\beta)=D_{00}^{n}(\Omega)$ are the Legendre polynomials. The lower number of the orientational order parameters $\langle P_n \rangle = \langle D_{00}^{n} \rangle$ in Eq. (2) greatly simplifies the formulas while retaining the same level of information on the main orientational characteristic of the mesophase—namely, the alignment of the long molecular axis of the mesomorphic molecules. The order parameters may be obtained by writing the distribution function in terms of a cylindrically symmetric nematic pseudopotential $U(\beta)$,[2]

$$f(\beta)=\frac{\exp[-U(\beta)/kT]}{\int \exp[-U(\beta)/kT] d\Omega} . \tag{3}$$

The most simple physically acceptable expression of $U(\beta)$ is[3]

$$U(\beta)=-A\langle P_2 \rangle P_2(\cos\beta) . \tag{4}$$

The theory of Maier-Saupe based on this potential gives a correct semiquantitative description of the most of the liquid-crystal properties. The addition of another term to Eq. (4), proportional to $\langle P_4 \rangle P_4(\cos\beta)$ leads to quantitative coincidence with the experimentally determined temperature dependences of the orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$.[2] Approximation (2), however, implicates loss of information on the orientational statistics of the short axes of the mesomorphic molecules, connected to deviations from perfect cylindrical symmetry, which should be expected for real mesomorphic molecules. Some experimental results,[4–6] in fact, indicate that the order parameters $\langle (D_{0n''}^{n})^* \rangle$ for $n'' \neq 0$ and, in particular, $\langle (D_{02}^{2})^* \rangle$ are not negligible and must be taken into account. In Ref. 7 the orientational ordering of a nematic phase composed of rigid molecules with arbitrary shape is considered theoretically. The nematic pseudopotential $U(\Omega)$ in this case contains components proportional to $D_{0n''}^{n}(\Omega)$ and, in the simplest case for a molecule with effective D_{2h} symmetry, can be written as[7]

$$U(\Omega)=-kTa\{D_{00}^{2}(\Omega)+\lambda[D_{02}^{2}(\Omega)+D_{0-2}^{2}(\Omega)]\} . \tag{5}$$

For such potential $\langle (D_{0n''}^{n})^* \rangle = \langle D_{0n''}^{n} \rangle = \langle D_{0-n''}^{n} \rangle \neq 0$ for even n'' and n. From NMR data for nematic 4,4′-dimethoxyazoxybenzene (PAA) the results $\lambda \cong 0.2$ and $\langle D_{02}^{2} \rangle \leq 0.035$ are reported.[4]

The values of the relevant parameters determined by the use of different techniques, for example, EPR, fluorescence depolarization, dielectric relaxation, neutron scattering, etc., depend on the dynamics of the molecular reorientation too. All information on the molecular rotational dynamics is contained in the correlation functions of the Wigner matrices,[8]

$$\begin{aligned} \phi_{l'l''\,m'm''}^{l\,m}(t)&=\langle D_{l'l''}^{l}(\Omega_0)[D_{m'm''}^{m}(\Omega)]^* \rangle \\ &=\int d\Omega_0 D_{l'l''}^{l}(\Omega_0) f(\Omega_0) \\ &\quad \times \int d\Omega\, D_{m'm''}^{m}(\Omega) P(\Omega_0 \mid \Omega t) . \end{aligned} \tag{6}$$

Direct measurement of the correlation functions (6) is a difficult problem since the experimental results depend on many such correlation functions $\phi_{l'l''\,m'm''}^{l\,m}(t)$. Some simplification may be achieved by expressing $\phi_{l'l''\,m'm''}^{l\,m}(t)$ in terms of a small number of parameters describing the degrees of ordering and rotational diffusion of the molecules in the context of some reorientational models, for example, small-step rotational diffusion model,[9–12] strong collision model,[12,14] slowly relaxing local structure model,[5] etc. Only some EPR studies[5] of the molecular reorientation of nitroxide radical dissolved in liquid crystal have taken into account the biaxiality of the guest molecule. However, detailed studies of the influence of the molecular asymmetry on the reorientation of highly aligned mesomorphic molecules themselves are not available in the literature.

The purpose of the present work is to discuss molecular reorientation in nematic phases formed by rigid molecules with arbitrary shape. We adopt the small-step rotational diffusion model which is well known from the theoretical point of view and is widely applied to mesomorphic materials. In Sec. II we give the solution of the diffusion equation valid for liquid-crystal molecules with arbitrary shape. This solution consists of rapidly converging series of exponentials. Our method is equivalent to that employed in Ref. 15 for the case of molecules with cylindrical symmetry. In Sec. III we show how our solutions reduce to results[16] obtained for cylindrically symmetric molecules. We are therefore able to discuss the convergence of the solutions and to demonstrate that for the nematic phase in most cases $\phi^{lm}_{l'l''}{}_{m'm''}(t)$ may be approximated very well with no more than two exponentials. In Sec. IV we calculate the correlation functions for nematic molecules with effective D_{2h} symmetry.[17] We show that at reasonable values of $\langle D^2_{02} \rangle$ the influence of the biaxiality on some correlation functions is significant and cannot be neglected. We finally discuss the possible effects on the spectroscopic behavior of the nematic phase.

II. SOLUTION OF THE SMALL-STEP ROTATIONAL DIFFUSION EQUATIONS FOR NEMATIC PHASES COMPOSED BY RIGID MOLECULES WITH ARBITRARY SYMMETRY

Molecular reorientation is a very complicated process even in isotropic liquids of simple molecules. Thus, in order to calculate the correlation functions or the conditional probability $P(\Omega_0 \mid \Omega t)$ we must adopt models which hopefully are a good approximation to the molecular reorientational dynamics. In the nematic phase, because of the existence of long-range orientational order and anisotropy of the big mesomorphic molecules, the reorientational process is even more complicated—the probability of the molecular reorientation depends not only on $\Omega - \Omega_0$ as in isotropic liquids, but on the initial orientation as well. As a result the number of the independent correlation functions increases and they become dependent on the order parameters $\langle (D^n_{0n''})^* \rangle$.

Recently some of the models for the molecular reorientation in simple isotropic liquids have been modified and applied to liquid crystals. We shall employ the small-step rotational diffusion model since it is based on solid physical background and has been used successfully to interpret many experimental results, e.g., ESR experiments,[5,12,14] dielectric relaxation,[10] fluorescence depolarization,[15,18,19] ir and Raman band-shape analysis.[20,21] This model is based on the hypothesis that the reorientation is a stochastic process which proceeds by angular jumps and for which the components of the angular momentum **J** relax with a correlation time τ_J which is much smaller than the relaxation time τ_Ω of the angular variables. In this case the probability for reorientation $P(\Omega_0 \mid \Omega t)$ does not depend on **J** but only on the initial and final molecular orientation. Obviously such a model does not describe correctly the dynamics at $t \lesssim \tau_J$ where inertial effects are expected to dominate.[22] Recent ir and Raman band-shape studies[20,21] indicate that in the liquid crystals $\tau_J \sim 0.2-0.5$ ps and is much less than τ_Ω which is usually between 5 and 40 ps. Therefore we believe that the small-step rotational diffusion model correctly describes the molecular reorientation in the nematic phase for the time domain 0.5–2.0 ps. We note that everywhere in this work where we discuss the behavior of the correlation functions in the short time limit we shall refer to the $\tau_J \lesssim t \ll \tau_\Omega$ range, for which the model is certainly valid.

The starting point in the small-step rotational diffusion model applied to uniaxial liquids is the generalized Smoluchowski equation[5,11,12]

$$\dot{P}(\Omega_0 \mid \Omega t) = \frac{d}{dt} P(\Omega_0 \mid \Omega t) = -\mathbf{J} \cdot \hat{D} \cdot \left[\mathbf{J} + \frac{\mathbf{J} U(\Omega)}{kT} \right] P(\Omega_0 \mid \Omega t) , \tag{7}$$

where **J** is the vector operator describing the infinitesimal rotations about the molecular axes and $\hat{D}$ is the rotational diffusion tensor defined in the molecular frame. This equation differs from the corresponding equation for the isotropic liquid by the term proportional to $\mathbf{J}U(\Omega)$ which takes into account the mean orientational torques. In the isotropic liquids the rotational diffusion tensor $\hat{D}$ is constant and can be diagonalized in the molecular frame, while for anisotropic systems in the most general case $\hat{D}$ depends also on the instantaneous molecular orientation, i.e., $\hat{D} = \hat{D}(\Omega(t))$. The Ω dependence of $\hat{D}$ reflects the lower macroscopic symmetry of the phase. The functional form of $D(\Omega)$ has been derived in Ref. 23 using a hydrodynamical model. Lin and Freed[24] have proposed that $\hat{D}$ can be decomposed as a sum of two tensors—one diagonal in the molecular frame and the other in the laboratory frame.

The Ω dependence of $\hat{D}$ can be very important and deserves further investigations. Here we shall neglect this dependence in order to avoid serious complication of the model together with proliferation of the adjustable parameters and will focus our attention on another problem—the influence of molecular asymmetry on the orientational correlation functions. So, as many other authors have done,[9,10,14,16] we shall assume that $\hat{D}$ is diagonal in the molecular frame

$$\hat{D} = \begin{bmatrix} D_1 & 0 & 0 \\ 0 & D_2 & 0 \\ 0 & 0 & D_3 \end{bmatrix} . \tag{8}$$

Equation (7) has been solved[9,10,12] under the assumption of cylindrical symmetry of the nematic molecules. This implies that

$$U(\Omega)=U(\beta) \tag{9a}$$

and

$$D_1=D_2=D_\perp\neq D_\parallel=D_3\ . \tag{9b}$$

The probability $P(\Omega_0\,|\,\Omega t)$ may then be obtained as a series expansion[18]

$$P(\Omega_0\,|\,\Omega t)=\sum_{I,J,K,m,n} b_{JKI}^{mn}\exp(D_\perp r_K^{mn}t)D_{mn}^{I}(\Omega_0)D_{mn}^{J}(\Omega)\ , \tag{10}$$

where the coefficients b_{JKI}^{mn} depend on the order parameters. The correlation functions obtained from Eq. (10) are a sum of exponential decays. A drawback of this solution is that the relaxation time cannot be obtained analytically but only by complicated numerical calculations. Another way to solve Eq. (7) is to use a set of nonorthogonal functions related to the equilibrium distribution function $f(\Omega)$ instead of Wigner matrices.[16] In this case the correlation functions can be derived to a good approximation as a sum of few exponentials. The same result has been reported in Ref. 15, where a different formalism was used.

Qualitatively, the reorientation of a rigid cylindrical molecule consists in (i) fast rotation around the long molecular axis 3 (spinning motion)[25] with time constant $\tau_\parallel\sim 1/D_\parallel$ and (ii) slow rotation around the short axes 1 and 2 of the molecule (tumbling motion) with time constant $\tau_\perp\sim 1/D_\perp$. Both these motions depend strongly on the degree of order. In the case of nematic molecules with lower than cylindrical symmetry Eq. (7) is the same but $D_1\neq D_2$ and $U(\Omega)=U(\beta,\gamma)$. The spinning motion in this case becomes order dependent [due to $U(\Omega)\neq U(\beta)$] and the tumbling rotational diffusions around both short axes are equivalent no more (due to $D_1\neq D_2$). As we shall demonstrate in Sec. IV the variation in the correlation functions due to the order-dependent spinning motion is proportional to $D_\parallel\langle D_{02}^2\rangle$. Taking into account the large value of $D_\parallel$, this change is important and in some cases can result in qualitative changes in the experimental data which are obtained. On the other hand, the change due to the anisotropic tumbling motion is proportional to $(D_1-D_2)\langle D_{02}^2\rangle$. Taking into account that D_1-D_2 depends on the anisotropy of the inertial motions and the steric hindrance for rotation about the short axes, we could expect $D_1-D_2\ll D_1+D_2\ll D_\parallel$, due to the small deviation of the nematic molecule from the effective cylindrical symmetry. Thus the asymmetry of the molecular tumbling motion will result only in minor quantitative change in the correlation functions. For this reason we will assume further that $D_1=D_2$ which will simplify the mathematics of the problem. Another reason for this assumption is that physically the asymmetry of the tumbling motion is equivalent to small changes in the Ω dependence of the diffusion tensor. As this dependence has already been neglected, it seems reasonable to neglect also D_1-D_2. In order to solve Eq. (7) under this assumption we develop the approach proposed in Ref. 15. First of all we transform Eq. (7) in

$$\begin{aligned}\dot P(\Omega_0\,|\,\Omega t)=&-\mathbf{J}\cdot\hat{\mathcal{D}}\cdot\mathbf{J}P(\Omega_0\,|\,\Omega t)\\&+\mathbf{J}\cdot\hat{\mathcal{D}}\cdot[\mathbf{J}f(\Omega)]f^{-1}(\Omega)P(\Omega_0\,|\,\Omega t)\end{aligned} \tag{11}$$

using the definition for $U(\Omega)$

$$f(\Omega)=\frac{\exp[-U(\Omega)/KT]}{\int\exp[-U(\Omega)/kT]d\Omega}\ . \tag{12}$$

To simplify the indices, wherever it is possible we shall designate $D_{l'l''}^{l}$ with the main index L, etc., Therefore,

$$D^L(\Omega)=D_{l'l''}^{l}(\Omega),\quad \phi^{LM}(t)=\phi_{l'l''\,m'm''}^{l\,m}(t)\ ,$$

etc.

Let us define the functions

$$W^L(\Omega,t)=f^{-1}(\Omega)\int f(\Omega_0)D^L(\Omega_0)P(\Omega_0\,|\,\Omega t)d\Omega_0\ . \tag{13}$$

Then

$$\begin{aligned}\phi^{LM}(t)&=\langle W^L(\Omega,t)[D^M(\Omega)]^*\rangle\\&=\int W^L(\Omega,t)[D^M(\Omega)]^*f(\Omega)d\Omega\ .\end{aligned} \tag{14}$$

If we expand $W^L(\Omega,t)$ as a series of $D^I(\Omega)$ we obtain

$$W^L(\Omega,t)=\sum_I V^{LI}(t)D^I(\Omega)\ , \tag{15}$$

where

$$V^{LI}(t)=\frac{2i+1}{8\pi^2}\int W^L(\Omega,t)[D^I(\Omega)]^*d\Omega \tag{16}$$

and

$$V^{LI}(0)=\delta_{LI}=\delta_{li}\delta_{l'i'}\delta_{l''i''}\ . \tag{17}$$

Then

$$\begin{aligned}\phi^{LM}(t)&=\sum_I V^{LI}(t)\langle D^I(\Omega)[D^M(\Omega)]^*\rangle\\&=\sum_I V^{LI}(t)\phi^{IM}(0)\ .\end{aligned} \tag{18}$$

Multiplying Eq. (11) by $D^L(\Omega_0)d\Omega_0$ and integrating, we transform it into an equation for $W^L(\Omega,t)$ instead of $P(\Omega_0\,|\,\Omega t)$,

$$\begin{aligned}f(\Omega)\dot W^L(\Omega,t)=&-\mathbf{J}\cdot\hat{\mathcal{D}}\cdot\mathbf{J}[W^L(\Omega,t)f(\Omega)]\\&+\mathbf{J}\cdot\hat{\mathcal{D}}\cdot[\mathbf{J}f(\Omega)]W^L(\Omega,t)\ .\end{aligned} \tag{19}$$

After some transformation we obtain

$$\begin{aligned}f(\Omega)\dot W^L(\Omega,t)=\tfrac{1}{2}\{&\mathbf{J}\cdot\hat{\mathcal{D}}\cdot\mathbf{J}[W^L(\Omega,t)f(\Omega)]\\&+f(\Omega)\mathbf{J}\cdot\hat{\mathcal{D}}\cdot\mathbf{J}W^L(\Omega,t)\\&-W^L(\Omega,t)\mathbf{J}\cdot\hat{\mathcal{D}}\cdot\mathbf{J}f(\Omega)\}\ .\end{aligned} \tag{20}$$

This equation is very useful for our purpose since $\mathbf{J}\cdot\hat{\mathcal{D}}\cdot\mathbf{J}$ in the case of $D_1=D_2=D_\perp$ has the Wigner matrices as eigenfunctions,

$$\mathbf{J}\cdot\hat{\mathcal{D}}\cdot\mathbf{J}D^L(\Omega)=E^LD^L(\Omega)\ , \tag{21}$$

where the eigenvalues are given by

$$E^{L}=E^{l}_{l'l''}=l(l+1)D_{\perp}+l''^{2}(D_{\parallel}-D_{\perp}) \ . \tag{22}$$

Substituting Eq. (15) and Eq. (1) in Eq. (20) and using Eq. (21), we obtain for $V^{LI}(t)$ the following set of differential equations:

$$\sum_{I} b^{IM}\dot{V}^{LI}(t)=-\sum_{I} a^{IM}V^{LI}(t) \ , \tag{23}$$

where

$$b^{IM}=\sum_{N}(2n+1)\langle (D^{N})^{*}\rangle(-1)^{m'+m''} \times \begin{bmatrix} i & n & m \\ i' & 0 & -m' \end{bmatrix} \begin{bmatrix} i & n & m \\ i'' & n'' & -m'' \end{bmatrix} , \tag{24}$$

$$a^{IM}=\tfrac{1}{2}\sum_{N}(2n+1)\langle (D^{N})^{*}\rangle(-1)^{m'+m''} \begin{bmatrix} i & n & m \\ i' & 0 & -m' \end{bmatrix} \times \begin{bmatrix} i & n & m \\ i'' & n'' & -m'' \end{bmatrix}(E^{I}+E^{M}-E^{N}) \ . \tag{25}$$

Here

$$\begin{bmatrix} i & n & m \\ i'' & n'' & -m'' \end{bmatrix}$$

are the Wigner 3-j coefficients and $\langle (D^{N})^{*}\rangle=\langle (D^{n}_{0n''})^{*}\rangle$ are the order parameters defined in Eq. (1).

From definition (6) one can obtain at $t\to 0$

$$b^{IM}=\phi^{IM}(0) \ , \tag{26}$$

while the substitution of Eq. (23) in Eq. (18) yields

$$a^{IM}=-\dot{\phi}^{IM}(0) \ . \tag{27}$$

Equations (26) and (27) are very useful to approximate the behavior of $\phi^{IM}(t)$ at short time $t \ll \tau_{\Omega}$ and have already been used in Refs. 20 and 21 in the treatment of ir and Raman band-shape experiments.

The set of Eqs. (23) can be solved by the method of Laplace transformation. If we denote by $\tilde{V}^{LI}(s)$ the Laplace transform of $V^{LI}(t)$ we obtain a set of linear algebraic equations

$$\sum_{I}\tilde{V}^{LI}(s)(a^{IM}+sb^{IM})=b^{LM} \tag{28}$$

and

$$\tilde{\phi}^{LM}(s)=\sum_{I} b^{IM}\tilde{V}^{LI}(s) \ . \tag{29}$$

An approximate solution of Eqs. (28) can be obtained if expansion (15) is truncated after a given term $\tilde{V}^{LI}(s)$. Then from Eq. (29) we can obtain $\phi^{LM}(t)$ as a sum of exponentials by an inverse Laplace transformation. The number of the exponentials in $\phi^{LM}(t)$ will depend on the number of the coefficients $\tilde{V}^{LI}(s)$ retained in Eqs. (28). Obviously the utility of these solutions depends on how fast they converge—if the correlation functions can be obtained to a good approximation using only a few exponential terms, then it is possible to derive analytical expressions for them. In general, the discussion on convergence of the solutions is a difficult problem due to the great number of independent order parameters in the coefficients in Eqs. (28). For this reason we shall consider the convergence of the solutions in the case of cylindrically symmetric and biaxial nematic molecules separately.

III. CORRELATION FUNCTION FOR MOLECULAR REORIENTATION IN CYLINDRICALLY SYMMETRIC POTENTIAL $U(\beta)$

As we already noted, the cylindrically symmetric potential has been considered in a number of papers[9,10,12] and the behavior of the correlation functions is well known. Thus we will focus our attention on the convergence of the approximate solutions in order to demonstrate that a few exponential terms are enough to yield good approximation to the correlation functions. Since in this case $f(\Omega)$ is independent on both α and γ the selection rules for $\Phi^{LM}(t)$ are very simple,[8]

$$\phi^{l\,m}_{l'l''\,m'm''}(t)=\delta_{l'm'}\delta_{l''m''}\phi^{l\,m}_{l'l''\,l'l''}(t) \ . \tag{30}$$

For simplicity we shall adopt the following notations:

$$\phi^{lm}_{l'l''}(t)=\phi^{l\,m}_{l'l''\,l'l''}(t) \ . \tag{31}$$

The symmetry relations

$$\phi^{lm}_{l'l''}(t)=\phi^{ml}_{l'l''}(t)=\phi^{lm}_{-l'-l''}(t)=(-1)^{l+m}\phi^{lm}_{-l'l''}(t) \tag{32}$$

enable us to diminish further the number of independent correlation functions.

Many experiments are sensitive only to the self-correlation functions $\phi^{ll}_{l'l''}(t)$ and among them the most important ones are $\phi^{11}_{l'l''}(t)$ and $\phi^{22}_{l'l''}(t)$. Here we shall consider the convergence of $\phi^{11}_{l'l''}(t)$ which is very representative because it is well known that the correlation function $\phi^{11}_{00}(t)$ converges very slowly.[26] For $l=m=1$

$$\tilde{\phi}^{11}_{l'l''}(s)=\sum_{i} b^{i1}_{l'l''}\tilde{V}^{1i}_{l'l''}(s) \tag{33}$$

and

$$\sum_{i}\tilde{V}^{1i}_{l'l''}(s)(a^{im}_{l'l''}+sb^{im}_{l'l''})=b^{1m}_{l'l''} \tag{34}$$

for $m=1,2,\ldots$. The coefficients $a^{im}_{l'l''}$ and $b^{im}_{l'l''}$ depend on the order parameters $\langle P_{2n}\rangle$ for $|i-m| \leq 2n \leq |i+m|$ [see Eqs. (24) and (25)]. For any physically acceptable potential $U(\beta)$, e.g., for the Maier-Saupe potential defined in Eq. (4), $\langle P_{2n}\rangle$ decreases with increasing n. Taking into account that $\langle P_{2m}\rangle \lesssim \langle P_{2}\rangle^{m}$ we obtain that $b^{im}_{l'l''}$ is of the order of $\langle P_{2}\rangle^{|i-m|/2}$. Similar conclusions can be drawn for $\tilde{V}^{im}_{l'l''}(s)$. Then the error in the approximate solution

$$\phi^{(k),11}_{l'l''}(s)=\sum_{i=1}^{k}\tilde{V}^{i1}_{l'l''}(s)b^{i1}_{l'l''} \tag{35}$$

is of the order of $\langle P_{2}\rangle^{k+1}$ and the precise solutions can be obtained with increasing k. If l' and/or l'' are zero then i can take only odd values in Eqs. (33)–(35) [see Eqs. (24) and (25)] and

$$\tilde{\phi}^{11}_{l'l''}(s)-\tilde{\phi}^{(k),11}_{l'l''}(s)\lesssim\langle P_{2}\rangle^{2k+1} \ , \tag{36}$$

while for $l'=l''=1$

$$\tilde{\phi}\,{}^{11}_{11}(s)-\tilde{\phi}\,{}^{(k)\,11}_{11}(s)\lesssim\langle P_2\rangle^{k+1}\ , \tag{37}$$

where k is the number of the exponentials retained in the approximate solution. The error estimated in Eqs. (36) and (37) is only an upper limit. We have calculated $\phi^{(k),11}_{l'l''}(t)$ for $D_{\parallel}=D_{\perp}$ and $k=1$ to 3. The order parameters have been calculated using a Maier-Saupe potential

$$U(\beta)=-kTaP_2(\cos\beta)\ , \tag{38}$$

for $a=2,3,6$ corresponding to $\langle P_2\rangle=0.43$, 0.62, and 0.82. To obtain $\tilde{\phi}\,{}^{(k),11}_{l'l''}(s)$ we truncate Eq. (34) up to $i=k$ and $m=k$, substituting further the solutions of this kth order system of linear algebraic equations in Eq. (33). Then by inverse Laplace transformation we obtain the functions $\phi^{(k),11}_{l'l''}(t)$ presented in Figs. 1–3. In all cases the highest-order approximation presented on the figures is undistinguishable, in the scale of the figure, from the exact solution. Except for the case $l'=l''=0$, the second-order approximation is excellent and the first order is reasonable. The function $\phi^{11}_{00}(t)$ is known to converge very slowly,[16,26] but even in this case a reasonable approximation is obtained for $k=2$ at small $\langle P_2\rangle$ and for $k=3$ at large $\langle P_2\rangle$.

One can see in Figs. 1–3 that at a small t ($tD_{\perp}<0.1$) even the one exponential approximation is very good. This is due to the fact that

$$\phi^{(1),11}_{l'l''}(t)=b^{11}_{l'l''}\exp\left[-\frac{a^{11}_{l'l''}}{b^{11}_{l'l''}}t\right] \tag{39}$$

has the right initial value and first derivative [see Eqs. (26) and (27)]. This approximation is very useful for experiments which are sensitive to very short times and has been used to treat the Raman and ir band-shape data.[20,21] It is important also to check the behavior of the functions $\phi^{(k)\,11}_{l'1}(t)$ when $D_{\parallel}\neq D_{\perp}$ [the $\phi^{11}_{l'0}(t)$ functions do not depend on $D_{\parallel}$ because they are not sensitive to the spinning motion] taking into account that in the real nematic phases $D_{\parallel}\gg D_{\perp}$. It has been demonstrated by Nordio and Segre[8] that

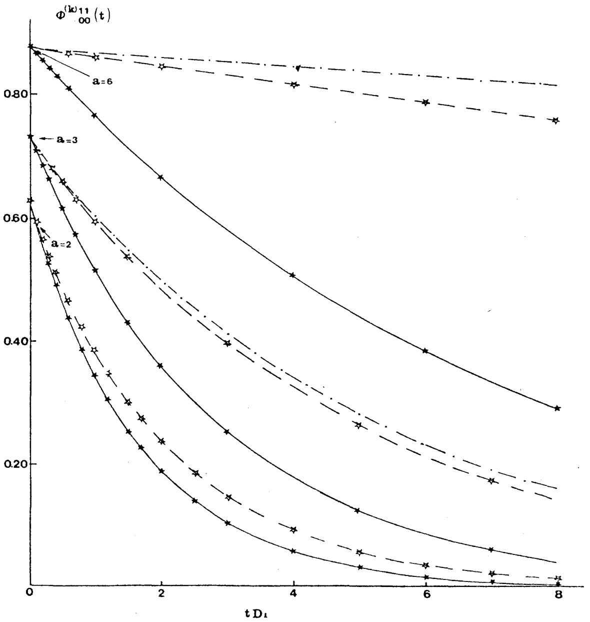

FIG. 1. Approximate solutions for the correlation function $\phi^{11}_{00}(t)$ calculated by using the Maier-Saupe potential from Eq. (39) at different values of a: —★—, one-exponential approximation ($k=1$); – –☆– –, two-exponential approximation ($k=2$); —·—·—·—, three-exponential approximation ($k=3$).

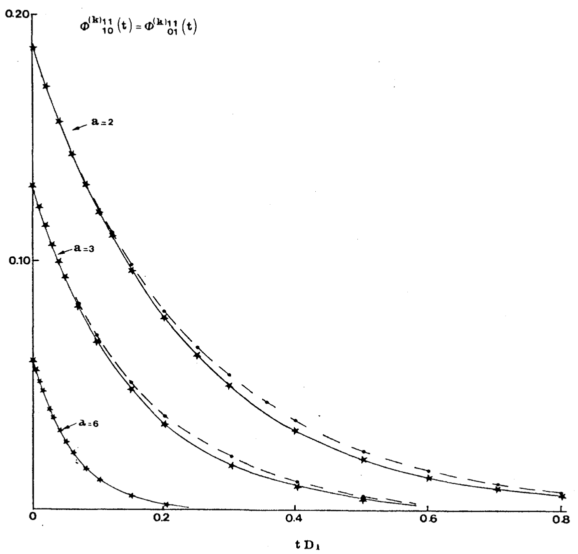

FIG. 2. One- (—★—) and two- (– – –) exponential approximations of the correlation functions $\phi^{11}_{01}(t)=\phi^{11}_{10}(t)$ ($D_{\parallel}=D_{\perp}$ is supposed).

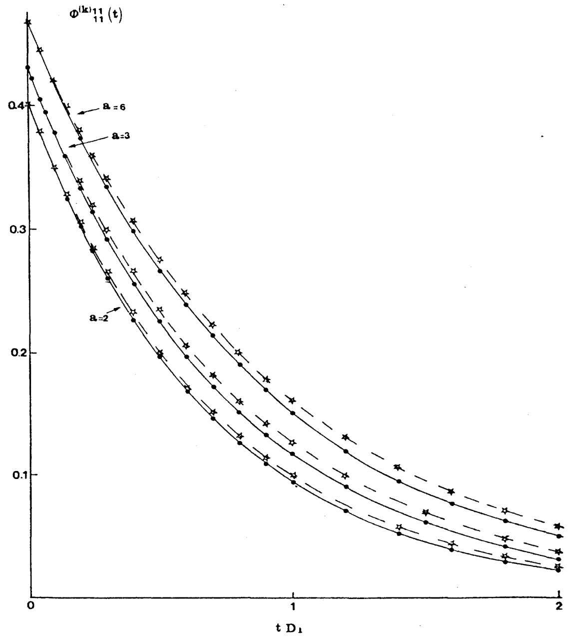

FIG. 3. One- (——) and two- (—☆—) exponential approximation of the correlation function $\phi^{11}_{11}(t)$ at $D_{\parallel}=D_{\perp}$.

$$\phi_{l'1}^{11}(t)=\phi_{l'1}^{11}(t)\,|_{D_{\parallel}=D_{\perp}}\exp[-(D_{\parallel}-D_{\perp})t] \tag{40}$$

and similar equations can be derived for the kth approximation. The correlation functions $\phi_{l'1}^{(1)\,11}(t)$ obtained for $D_{\parallel}-D_{\perp}=10D_{\perp}$ are presented in Figs. 4 and 5 and on the scale they coincide with the exact solution $\phi_{l'1}^{11}(t)$. This is due to the fact that for $t\sim 1/D_{\parallel}-D_{\perp}$ the error $\phi_{l'1}^{11}(t)-\phi_{l'1}^{(1)\,11}(t)$ is very small.

We have seen that the convergence of $\phi_{l'l''}^{(k)\,11}(t)$ is worse in the long-time domain. A good test for this region which is important for many experiments is the time integral of the correlation function

$$J_{l'l''}^{11}=\int_0^\infty \phi_{l'l''}^{11}(t)dt\ . \tag{41}$$

In Table I we present the approximate and exact values of these time integrals. Comparison with the results of Ref. 16 demonstrates that although the mathematical formalism in Ref. 16 is quite different from ours, the results are essentially the same for $k=1$ and for $k=\infty$ cases. One can see from Table I that for the correlation functions $\phi_{l1}^{11}(t)$ which are sensitive to the spinning motion, the single exponential approximation is very good even in the long-time region (under the realistic assumption that $D_{\parallel}\gg D_{\perp}$). For $J_{10}^{(1)\,11}$ the error is greater but still reasonable. Only in the case of $\phi_{00}^{11}(t)$ are several exponential terms needed to obtain a reasonable approximation.

The one-exponential approximation given in Eq. (39) is of great utility in the treatment of the experimental data. This is due to the simple analytical form of $\phi_{l'l''}^{lm}(t)$ but also on the fact that it depends only on the order parameters $\langle P_n\rangle$ with $|1-m|<n<1+m$. Usually these order parameters can be obtained from the same experiments in which $\phi_{l'l''}^{lm}(t)$ are measured, thus leading to a complete determination of the relevant static and dynamic parameters. When the number of the exponentials used to approximate the correlation functions increases, we need more and more order parameters which are not always available from the experimental data. Then (as in the case of the exact numerical solutions[24]) we have to postulate an explicit nematic pseudopotential. Even if we suppose that the mean-field theory is accurate enough, only the first two terms of $U(\beta)$ are known for a real nematic. For this reason it is quite possible that the order parameters $\langle P_n\rangle$ obtained in this way might differ from the real ones, especially for large n. The accumulated error makes the practical utility of this procedure and of the "exact" solutions obtained in this way, doubtful.

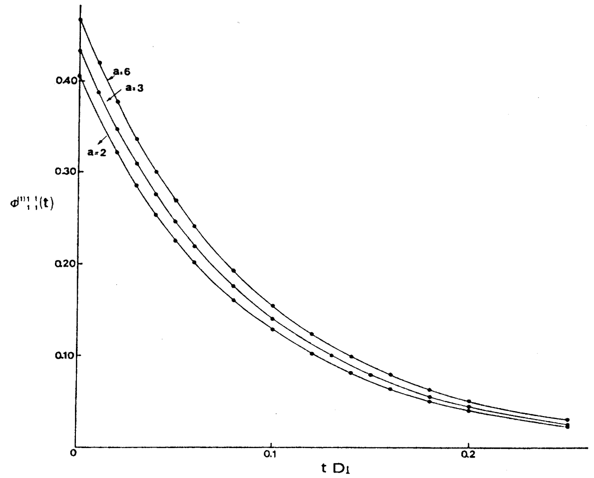

FIG. 5. One-exponential approximation of $\phi_{11}^{11}(t)$ at $D_{\parallel}=11D_{\perp}$.

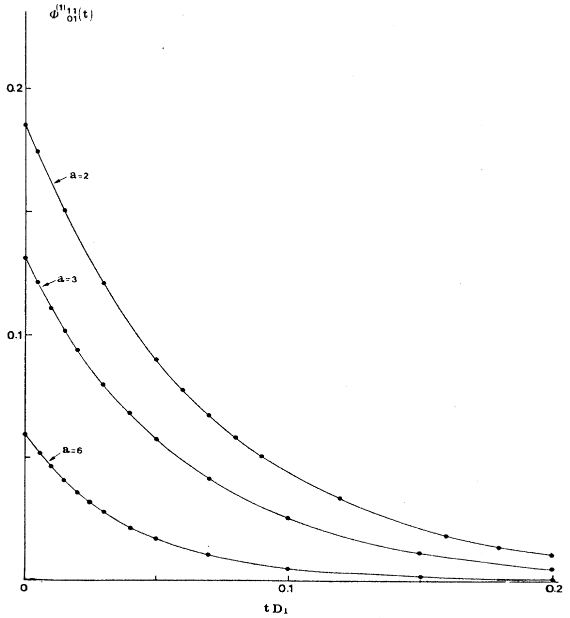

FIG. 4. One-exponential approximation of $\phi_{01}^{11}(t)$ at $D_{\parallel}=11D_{\perp}$.

IV. CORRELATION FUNCTIONS FOR THE MOLECULAR REORIENTATION IN BIAXIAL NEMATIC PSEUDOPOTENTIAL $U(\Omega)$

Equations (28) and (29) enable us to obtain the solutions in most general cases, i.e., the lack of any molecular symmetry. However, the great number of independent correlation functions even at small l and m and the great number of order parameters even for one-exponential approximation makes this approach unpractical. There are both theoretical[7] and experimental[4,6] evidences that in the nematic phase the mesomorphic molecules have effective D_{2h} symmetry,[17] and the only nonvanishing order parameters are $\langle D_{0n''}^{n}\rangle$ where n and n'' are even and $\langle D_{0n''}^{n}\rangle=\langle (D_{0n''}^{n})^*\rangle=\langle D_{0-n''}^{n}\rangle$. Assuming an effective D_{2h} symmetry for the nematic molecules, we obtain the following symmetry properties for the correlation functions:

$$\begin{aligned}\phi_{l'l''\,m'm''}^{l\,m}(t)&=\delta_{l'm'}\phi_{l'l''\,l'm''}^{l\,m}(t)\\&=(-1)^{l+m-l''-m''}\phi_{-l'l''\,-m'm''}^{l\,m}(t)\\&=(-1)^{l+m}\phi_{l'-l''\,m'-m''}^{l\,m}(t)\\&=(-1)^{l''+m''}\phi_{l'l''\,m'm''}^{l\,m}(t)\ ,\end{aligned} \tag{42}$$

TABLE I. Time integrals $J^{(k)\,11}_{l'l''}$ of the reorientational correlation functions (approximated by k exponentials).

				$(D_\parallel - D_\perp)/D_\perp = 0$				$(D_\parallel - D_\perp)/D_\perp = 10$		
a	$\langle P_2 \rangle$	l'	l''	$k=1$	$k=2$	$k=3$	$k=\infty$	$k=1$	$k=2$	$k=\infty$
2	0.43	0	0	1.049	1.297	1.306	1.307			
		0	1	0.0430	0.0453	0.0455	0.0456	0.0130	0.0131	0.0131
		1	0	0.0430	0.0453	0.0455	0.0456			
		1	1	0.2785	0.2889	0.2952	0.2976	0.0355	0.0356	0.0356
3	0.62	0	0	2.061	3.574	3.829	3.854			
		0	1	0.0200	0.0213	0.0215	0.0215	0.0079	0.0081	0.0081
		1	0	0.0200	0.0213	0.0215	0.0215			
		1	1	0.3332	0.3536	0.3617	0.3641	0.0384	0.0386	0.0386
6	0.82	0	0	6.408	48.54	101.7	132.8			
		0	1	0.0039	0.0040	0.0040	0.0040	0.0024	0.0024	0.0024
		1	0	0.0039	0.0040	0.0040	0.0040			
		1	1	0.4164	0.4433	0.4498	0.4510	0.0422	0.0424	0.0424

i.e., $\phi^{LM}(t)$ vanish if $l' \neq m'$ and if $l'' + m''$ is odd.

As in Sec. III we shall concentrate our attention on the case $l = m = 1$ which is of special interest for ir band-shape analysis (see the following paper). For the case l and/or $m \neq 1$, the solutions can be obtained in a similar way and there will be no qualitative change in their behavior.

For $l = m = 1$ we have six independent correlation functions—the self-correlation functions —$\phi^{1\,1}_{l'l''\,l'l''}(t)$ for l', $l'' = 0$, and 1 which appear also in the cylindrical case and two additional new cross-correlation functions $\phi^{1\,1}_{l'1\,l'-1}(t)$ for $l' = 0$ and 1. Formally, Eqs. (28) and (29) are the same but the number of terms in these equations is higher due to the greater number of nonvanishing a^{LM} and b^{LM} coefficients. The first reasonable approximation can be obtained by truncating Eqs. (28) and (29) at $i = 1$. For $l'' = 0$ in this approximation (as well as in all other approximations) the correlation functions are the same as in the cylindrical case due to the independence of $\phi^{l\,m}_{l'0\,m'0}(t)$ on spinning motion. For $l'' = 1$, $l' = 0$, and 1, and $m'' = \pm 1$, we have

$$\tilde{\phi}^{(1)\,1\,1}_{l'1\,l'\pm 1}(s) = b^{1\,1}_{l'1\,l'\pm 1}\tilde{V}^{(1)\,1\,1}_{l'1\,l'1}(s) + b^{1\,1}_{l'1\,l'\mp 1}\tilde{V}^{(1)\,1\,1}_{l'1\,l'-1}(s)\ , \tag{43}$$

$$\begin{aligned} b^{1\,1}_{l'1\,l'\pm 1} = {} & \tilde{V}^{(1)\,1}_{l'1\,l'1}(s)(a^{1\,1}_{l'1\,l'\pm 1} + s b^{1\,1}_{l'\,1\,l'\pm 1}) \\ & + \tilde{V}^{(1)\,1\,1}_{l'1\,l'-1}(s)(a^{1\,1}_{l'1\,l'\mp 1} + s b^{1\,1}_{l'1\,l'\mp 1})\ . \end{aligned} \tag{44}$$

Defining

$$\tilde{\phi}^{(1)\,1}_{\pm\,l'1}(s) = \tfrac{1}{2}[\tilde{\phi}^{(1)\,1\,1}_{l'1\,l'1}(s) \pm \tilde{\phi}^{(1)\,1\,1}_{l'1\,l'-1}(s)] \tag{45}$$

and similarly for a, b, and $\tilde{V}^{(1)}$ we have

$$\tilde{\phi}^{(1)\,1}_{\pm\,l'1}(s) = 2b^{1}_{\pm\,l'1}\tilde{V}^{(1)\,1}_{\pm\,l'1}(s)\ , \tag{46}$$

$$b^{1}_{\pm\,l'1} = 2\tilde{V}^{(1)\,1}_{\pm\,l'1}(s)(a^{1}_{\pm\,l'1} + s b^{1}_{\pm\,l'1})\ . \tag{47}$$

We obtain

$$\begin{aligned} \phi^{(1)\,1\,1}_{l'1\,l'\pm 1}(t) = {} & b^{1}_{+\,l'1}\exp\left[-t\frac{a^{1}_{+\,l'1}}{b^{1}_{+\,l'1}}\right] \\ & \pm b^{1}_{-\,l'1}\exp\left[-t\frac{a^{1}_{-\,l'1}}{b^{1}_{-\,l'1}}\right]\ . \end{aligned} \tag{48}$$

The explicit form of the coefficients in this equation is reported in Table II. Let us now consider the convergence of the approximate solutions $\phi^{(k)LM}(t)$ obtained in this way. To calculate the order parameters we use the potential defined in Eq. (5). Taking into account that in this case $\langle D^{n}_{0n''} \rangle \lesssim \langle D^{n}_{02} \rangle^{n''/2} \sim \langle D^{2}_{02} \rangle^{n''/2}$ and that $\langle D^{2}_{02} \rangle$ is small [$\langle D^{2}_{02} \rangle \lesssim 0.035$ for PAA (Ref. 7)], a fairly good approximation can be obtained considering only the terms with $i'' - m'' = 0, \pm 2$ and $i'' - l'' = 0, \pm 2$ in Eq. (23). Neglecting the terms of order $\langle D^{2}_{02} \rangle^2$ in kth approximation, Eqs. (28) and (29) become

$$\tilde{\phi}^{(k)\,1\,1}_{l'1\,l'\pm 1}(s) = \sum_{i=1}^{k}\sum_{i''=\pm 1}\tilde{V}^{(k)\,1\,i}_{l'1\,l'i''}(s)\,b^{i\,1}_{l'i''\,l'\pm 1}\ , \tag{49}$$

$$b^{1\,1}_{l'1\,l'\pm 1} = \sum_{i=1}^{k}\sum_{i''=\pm 1}\tilde{V}^{(k)\,1\,i}_{l'1\,l'i''}(s)(a^{i\,1}_{l'i''\,l'\pm 1} + s b^{i\,1}_{l'i''\,l'\pm 1})\ , \tag{50}$$

and the solutions can be obtained in a similar way as a

TABLE II. Relation between the coefficients in Eq. (48) and the order parameters.

l	$b^{1}_{\pm\,l'1}$	$a^{1}_{\pm\,l'1}$
0	$\frac{1}{6}(1 - \langle P_2 \rangle \mp \sqrt{6}\langle D^{2}_{02} \rangle)$	$\frac{D_\perp}{6}(1 + 2\langle P_2 \rangle \pm \sqrt{6}\langle D^{2}_{02} \rangle) + \frac{D_\parallel - D_\perp}{6}(1 - \langle P_2 \rangle \pm \sqrt{6}\langle D^{2}_{02} \rangle)$
1	$\frac{1}{12}(2 + \langle P_2 \rangle \pm 6\langle D^{2}_{02} \rangle)$	$\frac{D_\perp}{12}(4 - \langle P_2 \rangle \mp \sqrt{6}\langle D^{2}_{02} \rangle) + \frac{D_\parallel - D_\perp}{6}(2 + \langle P_2 \rangle \mp \sqrt{6}\langle D^{2}_{02} \rangle)$

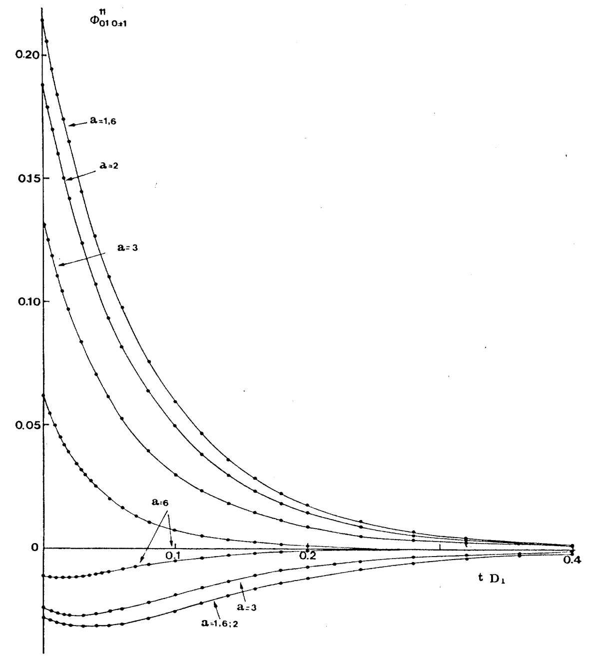

FIG. 6. Correlation functions $\phi^{1\,1}_{01\,0\pm1}(t)$ calculated using the potential from Eq. (5) at molecular biaxiality $\lambda=0.2$ and different values of a ($D_{\parallel}=11D_{\perp}$ is supposed).

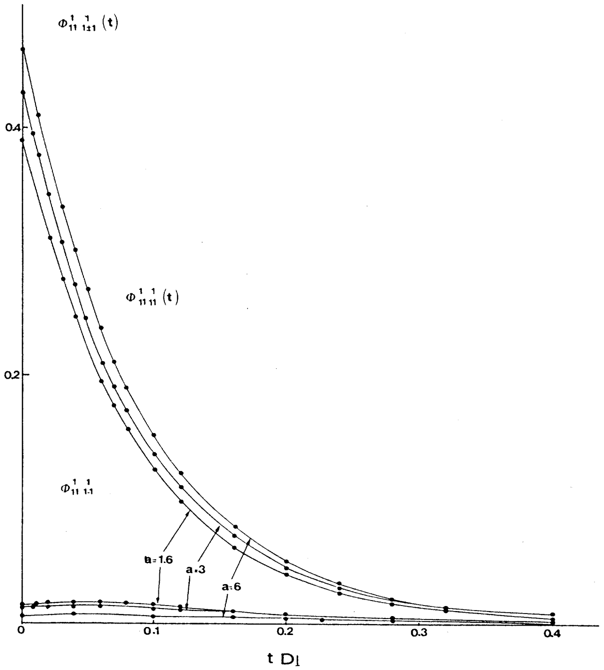

FIG. 7. Correlation functions $\phi^{1\,1}_{11\,1\pm1}(t)$ calculated using the potential from Eq. (5) at molecular biaxiality $\lambda=0.2$ and different values of a ($D_{\parallel}=11D_{\perp}$ is supposed).

sum of $2k$ exponentials. It can be demonstrated easily that the solutions for the correlation functions $\phi^{(k)\,1\,1}_{l'1\,l'1}(t)$ differ from the solutions $\phi^{(k)\,11}_{l'1}(t)$ obtained in Sec. III only by terms of order $\langle D^2_{02}\rangle^2 \ll 1$. So the main result of taking into account the biaxiality of $U(\Omega)$ is the appearance of the correlation functions $\phi^{l\,m}_{l'l''\,l'l''_{\pm2}}(t) \sim \langle D^2_{02}\rangle$.

In Figs. 6 and 7 we present the correlation functions obtained from Eq. (48) at $\lambda=0.2$, $a=1.6$, 2, 3, and 6 ($\langle P_2\rangle$ corresponding to 0.35, 0.43, 0.59, and 0.81) and $(D_{\parallel}-D_{\perp})/D_{\perp}=10$. We present only the first approximation because on the scale of the figure it cannot be distinguished from the exact solution. It is evident from the figure that for the cross-correlation functions $\phi^{1\,1}_{l'1\,l'-1}(t)$ a one-exponential approximation similar to Eq. (38) leads to unphysical behavior at $t\rightarrow\infty$. The cross-correlation functions are small compared to the self-correlation ones but they are not negligible. We shall demonstrate this experimentally in the following paper by analyzing the ir and Raman band shapes of some typically aligned nematic phases.

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[1] S. Jen, N. A. Clark, P. S. Pershan, and E. B. Priestley, J. Chem. Phys. **66**, 4635 (1977).

[2] R. L. Humphries, P. G. Games, and G. R. Luckhurst, J. Chem. Soc. Faraday Trans. II **68**, 1031 (1972).

[3] W. Maier and A. Saupe, Z. Naturforsch. A **13**, 564 (1958); **15**, 287 (1960).

[4] R. Alben, J. R. McColl, and C. S. Shin, Solid State Commun. **11**, 1081 (1972).

[5] C. F. Polnaszek and J. H. Freed, J. Chem. Phys. **79**, 2283 (1975).

[6] P. L. Bos, A. Shetty, J. W. Doane, and M. E. Neubert, J. Chem. Phys. **73**, 733 (1980).

[7] G. R. Luckhurst, C. Zannoni, P. L. Nordio, and U. Segre, Mol. Phys. **30**, 1345 (1975).

[8] P. L. Nordio and U. Segre, in *The Molecular Physics of Liquid Crystals,* edited by G. R. Luckhurst and G. W. Gray (Academic, New York, 1979), Chap. 18.

[9] P. L. Nordio and P. Busolin, J. Chem. Phys. **55**, 5485 (1971).

[10] P. L. Nordio, G. Rigatti, and U. Segre, J. Chem. Phys. **56**, 2117 (1972).

[11] J. H. Freed, J. Chem. Phys. **66**, 4183 (1977).

[12] C. F. Polnaszek, G. V. Bruno, and J. H. Freed, J. Chem. Phys. **58**, 3185 (1973).

[13] G. R. Luckhurst and A. Sanson, Mol. Phys. **24**, 1297 (1972).

[14] G. R. Luchurst, M. Setaka, and C. Zannoni, Mol. Phys. **28**, 1298 (1972).

[15] I. Dozov and I. Penchev, J. Lumin. **22**, 69 (1980).

[16] G. Moro and P. L. Nordio, Chem. Phys. Lett. **96**, 129 (1983).

[17] Although the mesomorphic molecules have much lower symmetry than D_{2h} point group, in the literature there are some evidences (see, e.g., Refs. 2, 3, and 7) that the pseudopotential $U(\beta)$ is dominated by second-rank terms. Then in the principal axes system of the corresponding interaction tensor all

orientational characteristics (e.g., the ordering matrix) have D_{2h} symmetry. Implicitly, we assume that both the interaction tensor and rotational diffusion tensor are diagonalized in the same frame of reference. In our opinion this is a reasonable approximation.

[18] C. Zannoni, Mol. Phys. **38**, 1813 (1979).

[19] A. Szabo, J. Chem. Phys. **72**, 4260 (1980).

[20] I. Dozov, N. Kirov, and M. P. Fontana, J. Chem. Phys. **81**, 2584 (1984).

[21] N. Kirov, I. Dozov, and M. P. Fontana, J. Chem. Phys. **83**, 5267 (1985).

[22] P. Pasini and C. Zannoni, Mol. Phys. **52**, 749 (1984).

[23] G. Moro and P. L. Nordio, Mol. Cryst. Liq. Cryst. **104**, 361 (1984).

[24] W. J. Lin and J. H. Freed, J. Chem. Phys. **83**, 379 (1979).

[25] The term "spinning" indicates molecular reorientation around the long molecular axis, while the "tumbling" signifies reorientation around the short axis. Both motions are reorientational, but they are usually decoupled—the spinning relaxation time is a few picoseconds, while the tumbling one is 30–50 ps. The terms spinning and tumbling have been introduced recently in order to explain the reorientational dynamics in aligned systems—mostly mesomorphic materials and uniaxially aligned polymers [see, e.g., the review by J. A. Janik, Adv. Liq. Cryst. **5**, 315 (1982)].

[26] P. L. Nordio, G. Rigatti, and U. Segre, Mol. Phys. **25**, 129 (1973).