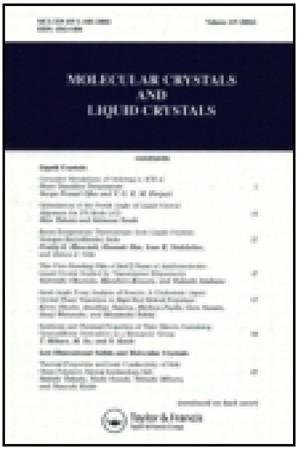

Molecular Crystals and Liquid Crystals

Roto-Translational Diffusion in Smectic-C Liquid Crystals

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ROTO-TRANSLATIONAL DIFFUSION IN SMECTIC-C LIQUID CRYSTALS

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Roto-translational diffusion of uniaxial molecules has been investigated in smectic-C (Sm-C) phases. A modified version of the McMillan mean-field potential has been adopted to describe the tilted monoclinic symmetry of the Sm-C domains with respect to the Sm-A. The roto-translational dynamics have been modeled as a diffusive stochastic process, and the relevant first- and second-rank rotational correlation functions used to describe spectroscopic experiments (dielectric relaxation and magnetic resonance respectively) have been calculated. The model calculations show that some peculiar features of the relaxation processes in Sm-C phases emerge in the comparison of the same observables evaluated for phases with different symmetry, and this could suggest new and specific methods of analysis for the experiments on biaxial smectics.

Keywords: smectics C; roto-translational diffusion; stochastic processes

1. INTRODUCTION

The molecular order in liquid crystals influences the molecular relaxation processes as detected with different spectroscopic techniques. For the nematic phase a well established theoretical interpretation is provided by the rotational diffusion equation [1] which allows a detailed analysis of the effects of the orientational order on the NMR relaxation times [2], on the ESR spectra [3] and on the dielectric relaxation [4,5]. The same rotational diffusion equation is often employed for smectic phases [6], even if a more complex theoretical analysis is in principle required because of the coupling between rotational and translational degrees of freedom due to the

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mean field potential. This appears quite evident if one considers the McMillan potential [7] for axial smectic (Sm-A) phases, whose cross-term precludes the factorization of the distribution function into translational and rotational contributions. The dynamical effects of such a coupling can be visualized as the translational modulation of orientational order between the (more ordered) core regions and the (less ordered) chain regions of the smectic layers. This is the qualitative picture derived from the solutions of the roto-translational diffusion equation for Sm-A phases [8]. Recently, the roto-translation diffusion equation for Sm-A phases has been solved by taking into account also the molecular biaxiality [9].

In the present work the effects of roto-translational coupling is analyzed in the case of biaxial smectic phases of Sm-C type characterized by a finite tilt angle between the main ordering axis and the layer normal. It should be recalled that in recent years the chiral forms of these phases have been intensively investigated for their ferroelectric behavior which might be exploited in the design of fast switching displays [10]. This contributes to motivate the efforts for understanding the molecular organization of biaxial smectic phases and its effects on dynamical observables detected by spectroscopic measurements.

An important ingredient of the diffusion model is the mean field potential specific for the examined phase. However, while for the Sm-A phase the McMillan potential [7] supplies a standard form of the mean field potential with a parameterized temperature dependence, an accepted counterpart for Sm-C phases is not available. This precludes the possibility of choosing the mean field potential appropriate for specific thermodynamic states of Sm-C samples. Thus we have generated the tilted versions of the McMillan potential with the symmetry appropriate to Sm-C phases without modifying the main orientational order parameter. This allows us to compare the dynamical observables (i.e., correlation functions) for phases with different symmetries (Sm-C and Sm-A primerily, but also the nematic phase for the sake of completeness) but with the same degree of orientational order, with the purpose of recognizing the specific effects of the layer organizations on the roto-translational coupling.

The paper is organized as follows: in Section 2 we describe the equilibrium distribution functions for the roto-translational degrees of freedom of a single molecule, which represents an important ingredient of the model for the stochastic dynamics, since it determines its *stationary limit*; in Section 3 the parameterized form of the mean field is introduced for the comparative analysis of nematic, Sm-A and Sm-C phases; in Section 4 we give the outlines for the modeling of the stochastic dynamics and for the calculation of the relevant rotational time-correlation functions describing spectroscopic experiments. Section 5 is dedicated to selected model calculations, and in Section 6 we draw the main conclusions.

2. EQUILIBRIUM DISTRIBUTIONS

The mean field potential acting on a molecule should be written by accounting for the symmetry of the phase and of the molecule (i.e., the mesogens themselves or a dissolved solute). First we introduce a Laboratory Frame (LF), (**x**, **y**, **z**) as the reference for the molecular coordinates and orientation. The **z** axis is chosen along the normal to the layers for the Sm-A and Sm-C phases, and along the orientational director for the nematic phase. In the cases of nematic and Sm-A domains, the transverse axes are arbitrarily chosen due to the axial symmetry about **z**, while in the case of Sm-C domain the **x** axis is taken along the two-fold axis of monoclinic symmetry. We do not consider ferroelectric Sm-C domains, i.e. we do not account for polarity on the transverse plane which differentiates the opposite orientations of the **x** axis. Secondly, we introduce a Molecular Frame (MF) rigidly attached to the probe molecule. In order to simplify the treatment, we shall consider in detail the case of solute with axial symmetry along the long molecular axis **l**. Correspondingly the **z** axis of MF is taken along **l**, while the transverse axes can be arbitrarily chosen. The molecular coordinates (i.e., the centre of MF) with respect to LF are indicated with $\mathbf{r} = (x, y, z)$, and the molecular orientation with $\mathbf{\Omega} = (\alpha, \beta, \gamma)$, i.e. the set of Euler angles [11] which specifies the transformation $LF \rightarrow MF$.

The mean field potential acting on the solute is now introduced for the Sm-C domain, i.e. for the phase with lowest symmetry. It can be expanded on the orthogonal basis of functions given as products of Fourier components for the z-dependence, and of Wigner rotational functions, $D^J_{m,0}(\mathbf{\Omega})$ with $m = 0, \pm 1, \ldots, \pm J$, to account for the orientational dependence [12]. By truncating up to the first-order on the Fourier components, and up to the second rank for the Wigner functions, the symmetry-adapted potential satisfying the monoclinic symmetry of the Sm-C domain for uniaxial molecules can be written as

$$\begin{aligned} V(z, \mathbf{\Omega})/k_B T = {} & 2c_{0,0}(1)\cos(2\pi z/d) \\ & + \left[c_{2,0}(0) + 2c_{2,0}(1)\cos(2\pi z/d)\right] D^2_{0,0}(\mathbf{\Omega}) \\ & + \left[c_{2,1}(0) + 2c_{2,1}(1)\cos(2\pi z/d)\right]\left[D^2_{-1,0}(\mathbf{\Omega}) + D^2_{1,0}(\mathbf{\Omega})\right] \\ & + \left[c_{2,2}(0) + 2c_{2,2}(1)\cos(2\pi z/d)\right]\left[D^2_{-2,0}(\mathbf{\Omega}) + D^2_{2,0}(\mathbf{\Omega})\right] \end{aligned} \tag{1}$$

where d is the layers' periodicity length. The symmetry of the phase requires that the coefficients $c_{J,m}(M)$ for even m (for odd m) should be real (purely imaginary). Symmetry arguments do not lead to constraints on the magnitude of these coefficients, unless a phase of higher symmetry is considered, for instance $c_{J,m}(M) = 0$ for $m \neq 0$ in the case of Sm-A phases so recovering the McMillan potential [7]. In general the coefficient $c_{0,0}(1)$ influences only the translational distribution, the coefficients $c_{2,0}(M)$ determine the strength of the nematic-like contribution to the orienting potential, coefficients $c_{2,1}(M)$ produce a *tilt* of the orientational director with respect to the layers' normal, and $c_{2,2}(M)$ give rise to a phase biaxiality of the orientational ordering.

Once the mean field potential is specified through the set of coefficients $c_{J,m}(M)$, the translational-rotational probability density can be calculated according to the Boltzmann distribution

$$P(z, \mathbf{\Omega}) = \frac{\exp\{-V(z, \mathbf{\Omega})/k_B T\}}{\int_0^d dz \int d\mathbf{\Omega} \exp\{-V(z, \mathbf{\Omega})/k_B T\}} \tag{2}$$

where the molecular orientation is integrated as $d\mathbf{\Omega} = d\alpha\, d\gamma\, d\cos\beta$. We also define the following *reduced* translational distribution function, $P_T(z)$:

$$P_T(z) = \int d\mathbf{\Omega}\, P(z, \mathbf{\Omega}), \qquad \int_0^d dz\, P_T(z) = 1 \tag{3}$$

and the conditional orientational distribution function $P(z \mid \mathbf{\Omega})$ for a given coordinate z:

$$P(z \mid \mathbf{\Omega}) = \frac{\exp\{-V(z, \mathbf{\Omega})/k_B T\}}{\int d\mathbf{\Omega} \exp\{-V(z, \mathbf{\Omega})/k_B T\}} \tag{4}$$

The complete average $\bar{F}$ of a function $F(z, \mathbf{\Omega})$ with respect to its translational and orientational degrees of freedom is given as

$$\bar{F} = \int_0^d dz \int d\mathbf{\Omega} F(z, \mathbf{\Omega}) P(z, \mathbf{\Omega}) \tag{5}$$

while its orientational average for a given molecular location z, in the following denoted by $\bar{F}(z)$, is defined by the relation

$$\bar{F}(z) = \int d\mathbf{\Omega} F(z, \mathbf{\Omega}) P(z \mid \mathbf{\Omega}) \tag{6}$$

Moreover we introduce the roto-translational order parameters $\bar{P}_{J,m}(M)$ as the averages

$$\bar{P}_{J,m}(M) = \overline{\exp\{-iM2\pi z/d\} D^J_{m,0}(\mathbf{\Omega})^*} \tag{7}$$

so that the equilibrium distribution function, Eq. (2) can be expanded as

$$P(z, \mathbf{\Omega}) = \sum_{M,J,m} \left(\frac{2J+1}{8\pi^2 d}\right) \bar{P}_{J,m}(M) \exp\{iM2\pi z/d\} D^J_{m,0}(\mathbf{\Omega}) \tag{8}$$

In order to characterise the orientational order, we introduce the 3×3 matrix $\mathbf{S}$ with elements

$$S_{i,j} = \frac{3}{2}\overline{l_i l_j} - \frac{1}{2}\delta_{i,j} \tag{9}$$

where l_j for $j = x, y, z$ are the LF components of the long-molecular axis. Notice that, by specifying the orientational dependence of the l_j components according to the Wigner functions $D^J_{m,0}(\mathbf{\Omega})$, the elements of the $\mathbf{S}$ matrix can be rewritten in terms of the orientational order parameters Eq. (7) of second rank (i.e., for $M = 0, J = 2$). The set of (normalized) eigenvectors $(\mathbf{x_S}, \mathbf{y_S}, \mathbf{z_S})$ of $\mathbf{S}$ are chosen as the axes of the symmetry frame (SF). Because of the monoclinic symmetry of the potential Eq. (1), one of the eigenvectors coincides with the $\mathbf{x}$ axis of the Laboratory frame (LF). It will be labelled as $\mathbf{x_S} = \mathbf{x}$ and it corresponds to a negative eigenvalue for realistic choices of the potential. The axis $\mathbf{z_S}$ is referred to the largest positive eigenvalue, $S_{z_S,z_S} > 0$, having the meaning of the order parameter of (calamitic) orientational ordering, with $\mathbf{z_S}$ defining the orientation of the *tilted director*. In the following, we implicitly use the notation $\bar{P}_2 \equiv S_{z_S,z_S}$. The angle θ_T for the *clockwise* rotation about $\mathbf{x}$ which brings $\mathbf{z}$ into $\mathbf{z_S}$ is taken as the *tilt angle* of the Sm-C phase with respect to the layers' normal. The eigenvalues referred to the $\mathbf{x_S}$ and $\mathbf{y_S}$ axes are indicated with S_{x_S,x_S} and S_{y_S,y_S} respectively, and the absolute value $\left|S_{x_S,x_S} - S_{y_S,y_S}\right|$ is interpreted as a degree of biaxiality of the molecular orientational ordering with respect to the SF axes. Obviously, in case of Sm-A and nematic domains, one has $SF \equiv LF$ and $\theta_T = 0$ for the absence of the tilt.

It should be emphasized that complete averages have been employed in Eq. (9). On the other hand, if conditional averages Eq. (6) are performed, a position-dependent matrix $\mathbf{S}(z)$ is obtained. Then, by applying the previous procedure, one can obtain z-dependent parameters like the *tilt angle* $\theta_T(z)$ for the orientational director, the main order parameter $\bar{P}_2(z)$, as well as the position dependent biaxiality parameter.

In the following Section, a parameterization of the coefficients entering Eq. (1) is proposed. The aim is to generate a nematic, a Sm-A and a Sm-C phase with modulated tilt angle $\theta_T(z)$ by keeping the same order parameter $\bar{P}_2$ for all of them.

3. PARAMETERIZATION OF THE POTENTIAL

The starting point is the set of coefficients in column (b) of Table 1 for the McMillan potential, which has been already used in the past for the characterization of the roto-translational dynamics in Sm-A phases [7,8]. The

TABLE 1 Parameterization of the Single-molecule Potentials for Nematic (N), Sm-A and Sm-C Phases

	(a) N	(b) Sm-A	(c) Sm-C
$C_{0,0}(1)$	–	−0.20	−0.20
$C_{2,0}(0)$	−2.95	−2.30	−1.10
$C_{2,0}(1)$	–	−0.80	−1.00
$\mathrm{Im}[C_{2,0}(1)]$	–	–	1.34
$\mathrm{Im}[C_{2,1}(1)]$	–	–	0.24
$C_{2,2}(0)$	–	–	0.35
$C_{2,2}(1)$	–	–	0.35
$\bar{P}_2$	0.60	0.60	0.60
$\lvert S_{xs,xs} - S_{ys,ys}\rvert$	–	–	$\sim$0.00
$\bar{\theta}_T$	–	–	28°

corresponding translational distribution $P_T(z)$ and position dependent order parameter $\bar{P}_2(z)$ are displayed in Figure 1. It describes an uniaxial smectic phase with a significant confinement at the centre of the layers for $z = 0, \pm d, \pm 2d, \ldots$. The orientational order is large at the centre of the layers, but it is strongly reduced at $z = \pm d/2$ in correspondence of the more disordered aliphatic region between the layers. A value $\bar{P}_2 = 0.60$ is recovered for the average order parameter, which corresponds to a coefficient $c_{2,0}(0) = -2.95$ for the Mayer-Saupe potential of a nematic phase.

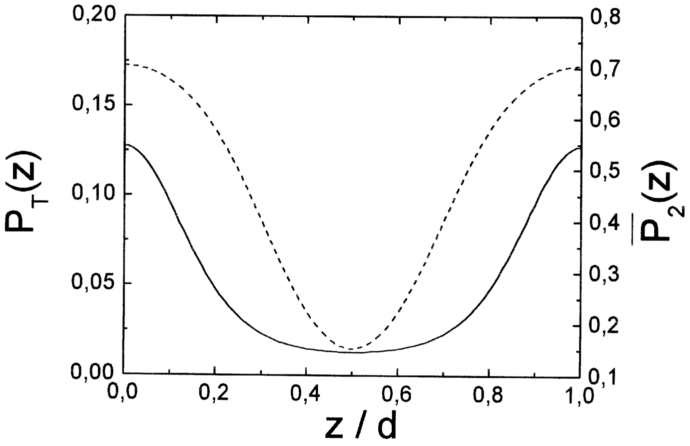

FIGURE 1 Longitudinal modulation of the *reduced* translational distribution function (solid line) together with the main order parameter (dashed line) for the Sm-A phase parameterized with the coefficients given in column (b) of Table 1.

The following guidelines have been assumed in order to generate a reasonable form of the Sm-C potential: 1) the average order parameter $\bar{P}_2 = 0.60$ of the Sm-A phase is conserved; 2) the tilt angle $\theta_T(z)$, with an average of $\bar{\theta}_T = 28°$, should reach its maximum value at the layers' boundaries where the orientational order is lower and the molecules are thought to tend to lay on the smectic planes; 3) a nearly vanishing biaxiality parameter should be recovered. By modifying the McMillan parameterization with the inclusion of coefficients $c_{2,m}(M)$ for $m \neq 0$, we have found that the mean field potential described in column (c) of Table 1 satisfies these requirements. The translational dependence of the main parameters as derived from these coefficients is shown in Figure 2. Notably, the spatial modulation of $\bar{P}_T(z)$ and of $\bar{P}_2(z)$ is very similar to that of the reference Sm-A phase (cf. Fig. 1), and the tilt angle has the expected behaviour.

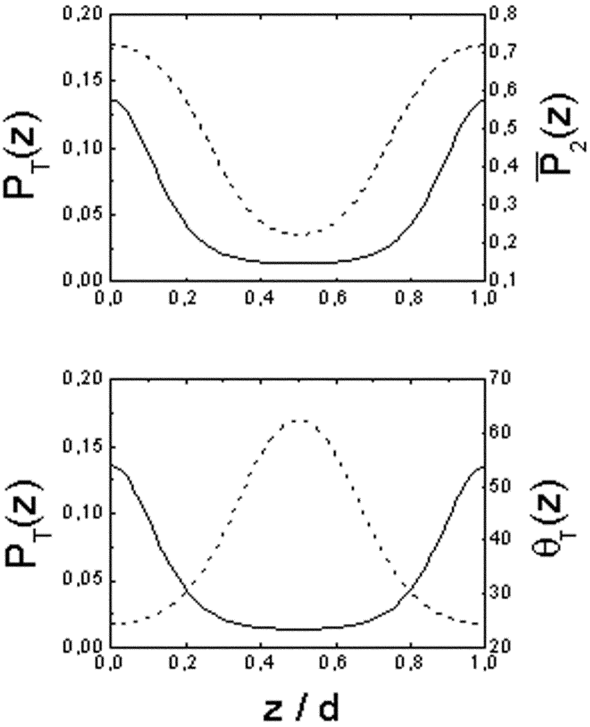

FIGURE 2 Longitudinal modulation of the *reduced* translational distribution function (solid lines), of the main order parameter and of the tilt angle (dashed lines) for the Sm-C phase parameterized with the coefficients given in column (c) of Table 1.

The single-molecule potentials so parameterized have been adopted to model the single-molecule dynamics in the investigated phases, as described in the following Section.

4. ROTATIONAL TIME-CORRELATION FUNCTIONS

The roto-translational dynamics of the uniaxial molecules has been described as a Markov stochastic stationary process in the diffusive regime of the motion for the molecular coordinates $\mathbf{r}$ and orientation $\mathbf{\Omega}$ with respect to LF. The basic formalism is provided by the Fokker-Planck-Smoluchowski equation,

$$\begin{aligned}&\frac{\partial}{\partial t}P(\mathbf{r}_0,\mathbf{\Omega}_0|\mathbf{r},\mathbf{\Omega},t)=-\hat{\Gamma}_{\mathbf{r},\mathbf{\Omega}}P(\mathbf{r}_0,\mathbf{\Omega}_0|\mathbf{r},\mathbf{\Omega},t)\\&P(\mathbf{r}_0,\mathbf{\Omega}_0|\mathbf{r},\mathbf{\Omega},0)=\delta(\mathbf{r}-\mathbf{r}_0)\delta(\mathbf{\Omega}-\mathbf{\Omega}_0)\\&\lim_{t\to\infty}P(\mathbf{r}_0,\mathbf{\Omega}_0|\mathbf{r},\mathbf{\Omega},t)=P(\mathbf{r},\mathbf{\Omega})\end{aligned} \tag{10}$$

which represents the differential form of the so-called Master Equation for small-steps diffusive dynamics [13]. It determines the time evolution of the conditional probability $P(\mathbf{r}_0,\mathbf{\Omega}_0\,|\,\mathbf{r},\mathbf{\Omega},t)$ of finding the molecule with position and orientation within an infinitesimal surrounding of $\mathbf{r},\mathbf{\Omega}$ at time t, if they had the values $\mathbf{r_0},\mathbf{\Omega_0}$ at the initial time $t=0$. The time evolution is controlled by the stochastic operator $\hat{\Gamma}_{\mathbf{r},\mathbf{\Omega}}$ acting on the stochastic variables, with the constraint that the equilibrium distribution $P(\mathbf{r},\mathbf{\Omega})$ should be recovered as the stationary solution.

The conditional probability allows one to calculate the time-correlation between functions of the stochastic variables. The full dependence on the position coordinates $\mathbf{r}$ has in principle to be considered. However, in the case of time-correlation between functions of the molecular orientation $\mathbf{\Omega}$ only, e.g. Wigner rotational functions and their generic linear combinations, the transverse and the longitudinal translational diffusion can be decoupled, and only the variables z and $\mathbf{\Omega}$ need to be explicitly considered. Then one can employ the following simplified form of the evolution operator [8]

$$\hat{\Gamma}_{z,\mathbf{\Omega}}=-D^T\frac{\partial}{\partial z}P(z,\mathbf{\Omega})\frac{\partial}{\partial z}P(z,\mathbf{\Omega})^{-1}+\hat{\mathbf{J}}^{Tr}P(z,\mathbf{\Omega})\cdot\mathbf{D^R}\cdot\hat{\mathbf{J}}P(z,\mathbf{\Omega})^{-1} \tag{11}$$

where the first term accounts for the longitudinal translational motion (along the layers' normal) controlled by the diffusion coefficient D^T, and the second term describes the orientational dynamics according to the rotational diffusion tensor $\mathbf{D^R}$ (specified along the principal molecular axes), $\hat{\mathbf{J}}$ being the angular momentum operator which generates infinitesimal rotations about the molecular axes. Rotations and translations are dynamically coupled by the equilibrium distribution $P(z, \mathbf{\Omega})$ as long as its dependence on z and $\mathbf{\Omega}$ cannot be factorized.

In the derivation of the stochastic evolution operator Eq. (11), one has invoked several assumptions in the following *hierarchy*: (i) the frictional roto-translational coupling in the full 6×6 diffusion matrix has been neglected, (ii) we assume that the translational $\mathbf{D^T}$ and the rotational $\mathbf{D^R}$ diffusion tensors have constant components when they are expressed in the molecular frame MF [14] and finally (iii) an isotropic tensor $\mathbf{D^T} = D^T\mathbf{1}$ is employed for the translational diffusion. It should be emphasized that, even if the full problem can in principle be solved, these simplifications allow one to recognise the main features of the roto-translational dynamics without a substantial loss of generality. For instance, the use of an isotropic translational diffusion tensor might appear unrealistic in the case of molecules with elongated shape. However, it will be shown that the effects of the rototranslational coupling on the reorientational observables are controlled by the magnitude of the elements of the translational diffusion tensor and, therefore, their small differences have a secondary role.

We now express the time self-correlation of Wigner rotational functions of the molecular orientation with respect to the SF frame, i.e. the set $\mathbf{\Omega}'$ of Euler angles defining the axes transformation $MF \rightarrow SF$. Such a choice allows the comparison of the rotational relaxation processes in phases with different symmetries (i.e., nematic, Sm-A and Sm-C) for the same direction of the orientational director. Thus we shall examine the time-correlation functions:

$$G_m^J(t) = \overline{\delta D_{m,0}^J(\mathbf{\Omega}'(0))^* \delta D_{m,0}^J(\mathbf{\Omega}'(t))} \tag{12}$$

where $\delta F = F - \bar{F}$ is the displacement of the function F from its average. The second projection number of the Wigner functions is set to zero because we focus the attention on the relaxation dynamics of uniaxial molecules. In particular, correlation functions of first rank ($J = 1$) can be used to describe dielectric relaxation experiments [4,5] while those of second rank ($J = 2$) account for the observable in magnetic resonances, NMR [2] and ESR [3]. By introducing the Euler angles $\mathbf{\Omega_T} = (\pi/2, -\theta_T, -\pi/2)$ defining the axes rotation for $SF \rightarrow LF$, and by using the properties of transformations of Wigner functions under rotations of the reference system [11], one writes

$$D_{m,0}^J(\mathbf{\Omega}') = \sum_p D_{m,p}^J(\mathbf{\Omega_T})^* D_{0,p}^J(\mathbf{\Omega}) \tag{13}$$

Then, the correlation function Eq. (12) is specified as

$$G_m^J(t) = \sum_{p,q} D_{m,p}^J(\mathbf{\Omega_T}) D_{m,q}^J(\mathbf{\Omega_T})^* \overline{\delta D_{0,p}^J(\mathbf{\Omega}(0))^* \delta D_{0,q}^J(\mathbf{\Omega}(t))} \tag{14}$$

with each time-correlation in the summation calculated as [5]:

$$\overline{\delta D^J_{0,p}(\mathbf{\Omega}(0))^* \delta D^J_{0,q}(\mathbf{\Omega}(t))} = \langle \delta D^J_{0,p}(\mathbf{\Omega})| \exp\{-\hat{\Gamma}_{z,\mathbf{\Omega}} t\} | P(z,\mathbf{\Omega}) \delta D^J_{0,q}(\mathbf{\Omega})\rangle \tag{15}$$

where the ***bra-ket*** convention is adopted for the complex-conjugation in the hermitean scalar product defined as the integration on the stochastic variables z and $\mathbf{\Omega}$. The symmetry of a given phase allows one to reduce the number of independent non-vanishing contributions Eq. (15) which are required to compute the correlation function Eq. (14).

The numerical calculation of the correlation functions has been performed (i) by introducing the symmetrized form of the stochastic operator, i.e. $\tilde{\Gamma}_{z,\mathbf{\Omega}} = P(z,\mathbf{\Omega})^{-1/2} \hat{\Gamma}_{z,\mathbf{\Omega}} P(z,\mathbf{\Omega})^{1/2}$, (ii) by representing it on the following basis of orthonormal functions:

$$|M,J,m\rangle = \left(\frac{2J+1}{8\pi^2 d}\right)^{\frac{1}{2}} \exp\{iM2\pi z/d\} D^J_{m,0}(\mathbf{\Omega}) \tag{16}$$

and (iii) by using the Lanczos algorithm [15] in order to generate iteratively subspaces of increasing dimension for the optimal representation of the correlation functions.

5. MODEL CALCULATIONS

In this section we present the results for the correlation functions by employing the mean field potentials described in Section 3 (see Table 1). The translational and rotational diffusive tensors have been parameterized according to the Stokes-Einstein-Perrin (SEP) model [16] for the case of ellipsoidal molecules with lengths 20 Å and 5 Å for the major and the minor axes (the reference compound is the ***p-azoxi-anisole*** molecule, PAA). On the other hand the translational diffusive coefficient $D^T = 3.7 \times 10^{-6}\,\mathrm{cm}^2\,\mathrm{s}^{-1} = 37\,\mathrm{Å}^2\,\mathrm{ns}^{-1}$ has been estimated by averaging the principal components of the macroscopic tensor for the translational self-diffusion of PAA in its nematic phase as reported in Ref. [17]. The SEP model determines the ratio between translational and rotational diffusion coefficients independently of the viscosity. Therefore, on the basis of the chosen value of D^T, one can derive the rotational diffusion elements, so obtaining the coefficients $D^R_{//} = 2.9\,\mathrm{rad\,ns}^{-1}$ and $D^R_{\perp} = 0.7\,\mathrm{rad\,ns}^{-1}$. These parameters will represent the standard set of diffusion coefficients for our calculations. For the sake of comparison, we have also employed an alternative set of parameters for a much slower translational motion, by setting $D^T = 0.1 \times 10^{-6}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, but keeping the same rotational diffusion coefficients.

In Figure 3 the first-rank correlation functions $G_0^1(t)$ and $G_1^1(t)$ are displayed for the standard set of diffusion coefficients. In this Figure and in the following ones, the solid, dashed and dotted lines represent the results for the set (c) (Sm-C phase), set (b) (Sm-A phase) and set (a) (nematic phase), respectively, of the potential coefficients reported in Table 1. In all the three cases it is evident that the longitudinal relaxation described by $G_0^1(t)$ is characterized by a much slower time scale than the transverse relaxation recovered from $G_1^1(t)$. This can be easily explained by taking into account that the correlation function for $D_{0,0}^1(\mathbf{\Omega}') \propto \cos\beta'$ is dominated by the activated process of the flipping motion of the long molecular axis between $\beta' = 0, \pi$[5]. For symmetry reasons such a process does not contribute to the transverse relaxation in uniaxial phases, which is controlled by the much faster tumbling motion within the local potential wells [18].

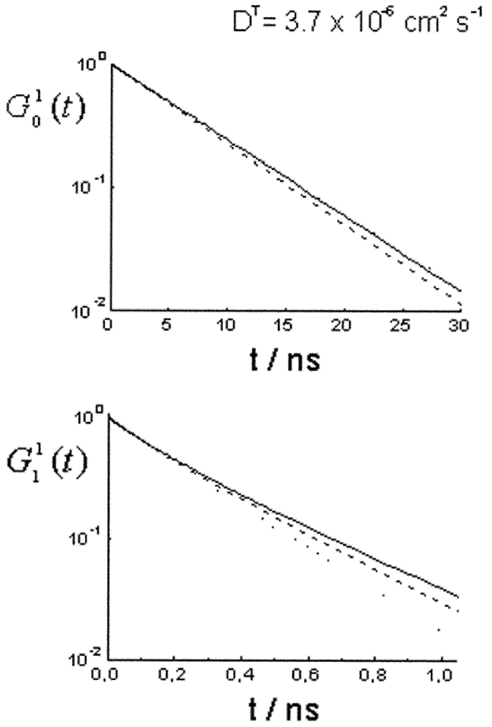

FIGURE 3 Rotational self-correlation functions of first rank for molecular orientation referred to the SF axes of the Sm-C (solid lines), Sm-A (dashed lines) and nematic (dotted lines) phases. The single-molecule potentials are parameterized as reported in Table 1, and $D_{//}^R = 2.9\,\mathrm{rad\,ns^{-1}}$, $D_\perp^R = 0.7\,\mathrm{rad\,ns^{-1}}$, $D^T = 3.7\times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$.

For each type of first-rank correlation function, one can clearly distinguish the behavior of the different phases. In particular, while a nearly mono-exponential decay is recovered for the nematic phase, some evidences of a distribution of decay rates are found in the case of smectic phases. The latter feature can be attributed to the fact the molecule, moving across the smectic layers, explores locations with different order strengths, as shown by the profiles of $\bar{P}_2(z)$ in Figures 1 and 2. In the absence of translational diffusion, this necessarily leads to a distribution of relaxation times in correspondence of molecules reorienting under the action of different mean fields. Of course, a fast translational dynamics tends to wash out such a distribution by averaging the effects of the position dependent orientational order [8]. On the basis of such an interpretation, one would expect that the relaxation dispersion should become more pronounced by slowing down the translational diffusion process. This is precisely the finding of our calculations, as shown by the comparison with Figure 4 where the first-rank correlation functions have been evaluated in the same conditions of Figure 3 except for the slower diffusion coefficient $D^T = 0.1 \times 10^{-6}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. Such an amplification of the dispersion on the relaxation rates is particularly evident in the case of the Sm-C phase. One can also recognize a significant slowing down of the flipping process in smectic phases as detected by the longitudinal relaxation. This should be attributed to the fact that, for the given $\bar{P}_2 = 0.6$, the molecule at the center of the layers experiences an orientational order higher than in the nematic phase, i.e. an higher barrier for the flipping between the two orientational potential minima. Moreover, the transverse relaxation for the Sm-C phase displays a slow component which is absent in the other phases. The analysis of the dispersion profile reveals that such a slow component has the characteristic rate of the flipping process. Our interpretation is that the position dependence of the tilt angle $\theta_T(z)$ produces a partial mixing between longitudinal and transverse relation so that the correlation function of $D^1_{1,0}(\mathbf{\Omega}')$ is affected also by the flipping process. On contrary, for the nematic and Sm-A phases the relaxation of $G^1_1(t)$ is entirely due to the fast motion of the long axis within the wells of the orienting potential. When the translational diffusion becomes faster, i.e. for $D^T = 3.7 \times 10^{-6}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, the effect of the tilt angle modulation tends to disappear, and the molecule feels the situation of an *effective* Sm-C phase with constant, dynamically-averaged, tilt angle $\bar{\theta}_T$. These features suggest that dielectric relaxation experiments could in principle reveal the presence of the longitudinal modulation of the tilting, if the translational diffusion is slow enough. In particular, experiments with the electric field perpendicular to the tilted (average) director are expected to be the most informative.

Let us now consider the correlation functions for second-rank rotational functions, which are shown in Figure 5 for the standard set of diffusion

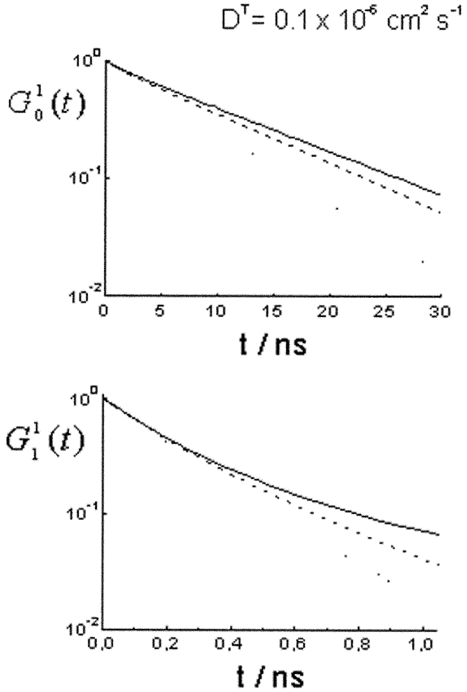

FIGURE 4 Rotational self-correlation functions of first rank for molecular orientation referred to the SF axes of the Sm-C (solid lines), Sm-A (dashed lines) and nematic (dotted lines) phases. The single-molecule potentials are parameterized as reported in Table 1, and $D^R_{//} = 2.9\,\mathrm{rad\,ns^{-1}}$, $D^R_{\perp} = 0.7\,\mathrm{rad\,ns^{-1}}$, $D^T = 0.1 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$.

parameters. In the case of the correlation function for $D^2_{0,0}(\mathbf{\Omega}')$, significant differences emerge between the nematic phase and the smectic phases. This derives from the existence of non-vanishing position-dependent average $\bar{D}^2_{0,0}(z)$ defined according to Eq. (6). As shown in Ref. [8], in the case of Sm-A phases this leads to a further relaxation mechanism operating at long times in correspondence of the translational averaging of $\bar{D}^2_{0,0}(z)$, and which is absent in nematic phases. The results here presented demonstrates that a similar mechanism is operating also in Sm-C phases. The corresponding relaxation rate should be controlled by the translational diffusion coefficient and, therefore, a slowing down of the long time tail of $G^2_0(t)$ of smectic phases is expected when D^T is decreased. This is confirmed by the results of calculation performed for $D^T = 0.1 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ without modification of the other parameters, and which are shown in Figure 6.

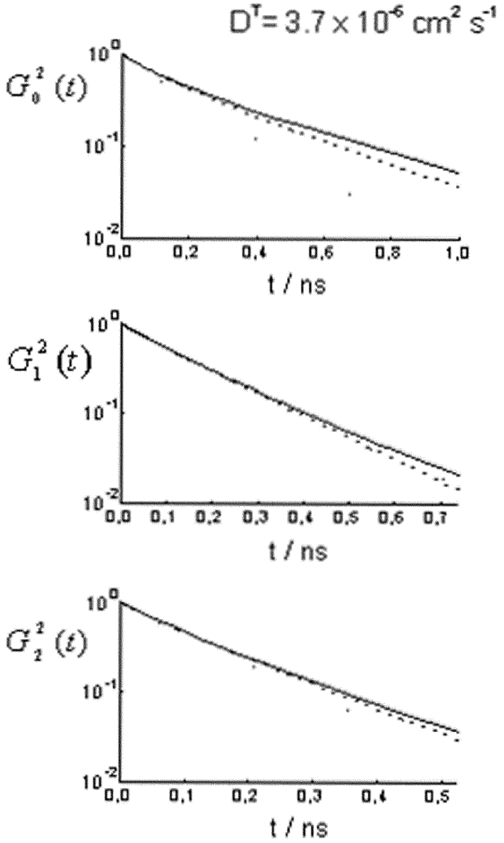

FIGURE 5 Rotational self-correlation functions of second rank for molecular orientation referred to the SF axes of the Sm-C (solid lines), Sm-A (dashed lines) and nematic (dotted lines) phases. The single-molecule potentials are parameterized as reported in Table 1, and $D^R_{//} = 2.9\,\mathrm{rad\,ns^{-1}}$, $D^R_{\perp} = 0.7\,\mathrm{rad\,ns^{-1}}$, $D^T = 3.7 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$.

6. CONCLUSIONS

The main point we would like to emphasise is that the analysis of the molecular roto-translational dynamics in layered structures, which in the past has been developed for uniaxial Sm-A phases [8,9], can be extended to biaxial Sm-C phases. This, however, requires appropriate models of the mean-field potential taking into account the molecular features and the peculiarities of the layer organization. As a matter of fact, their derivation on the basis of the molecular structure and interactions is still a very

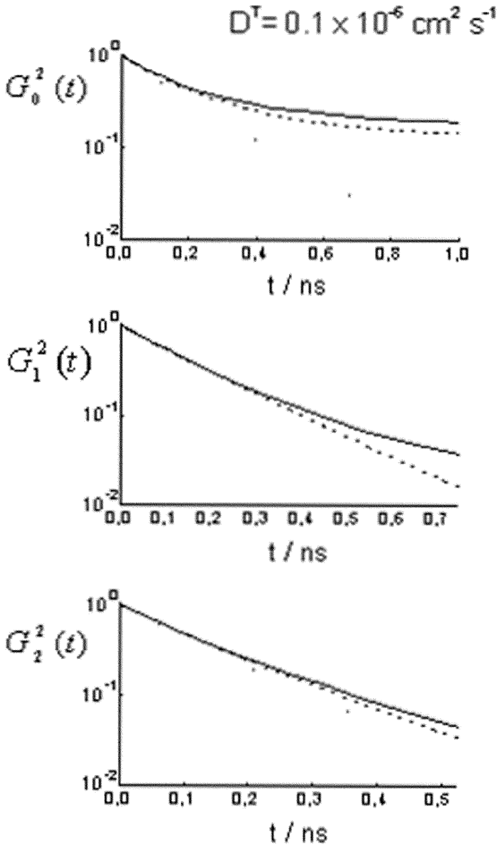

FIGURE 6 Rotational self-correlation functions of second rank for molecular orientation referred to the SF axes of the Sm-C (solid lines), Sm-A (dashed lines) and nematic (dotted lines) phases. The single-molecule potentials are parameterized as reported in Table 1, and $D^R_{//} = 2.9\,\mathrm{rad\,ns^{-1}}$, $D^R_{\perp} = 0.7\,\mathrm{rad\,ns^{-1}}$, $D^T = 0.1 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$.

difficult task. Thus we have adopted a more phenomenological procedure, by using for the mean field of Sm-C phases a parameterized form which is consistent with the expected behaviour of significant properties like the position dependence of the orientational order parameter and of the tilt angle of the director. Then, by assuming that such a mean field potential is realistic, we have analyzed the specific features of the relaxation processes induced by the biaxial organization of the smectic layers. This requires the solution of the Fokker Planck equation for the roto-translational diffusion and the calculation of the corresponding correlation functions. We have shown that such an objective can be fulfilled by computing explicitly the orientational correlation function of the first rank, relevant for the description of dielectric relaxation experiments, and of the second rank for the observables of magnetic relaxation experiments. Some peculiar features of the relaxation processes in Sm-C phases emerge in the comparison of the same observables evaluated for phases with different symmetry, and this could suggest new and specific methods of analysis for the experiments on biaxial smectics.

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