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# Orientation-Dependent Friction in Liquid Crystals

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The meaning of the rotational friction and diffusion tensor in liquid crystalline phases characterized by anisotropic viscosities is discussed, by generalizing the hydrodynamic Stokes–Einstein relationships. Corrections due to the viscosity anisotropy effects to the rotational correlation times, relevant for the interpretation of magnetic and dielectric relaxation experiments, have been computed by solving the appropriate Fokker–Planck equation.

## INTRODUCTION

In isotropic liquids, the diffusion tensor is essentially considered a molecular property, depending upon the molecular shape and symmetry. The effect of the surrounding medium enters only through a constant multiplicative factor, i.e. the isotropic viscosity. Obviously, this picture is untenable in liquid crystals, where the friction exerted upon a test molecule by the surrounding fluid must manifest the anisotropic character of both the molecular shape and the liquid crystalline phase. As a consequence, when the viscosity anisotropy of the mesophase is taken into account, the common knowledge of the diffusion tensor as a quantity diagonal in a molecular frame, is immediately lost. This situation was first recognized by Kutznetzov[1] who suggested to analyze the rotational diffusion of molecular probes in nematics by using a simple diffusion equation with the diffusion tensor assumed to be diagonal in the laboratory frame having the nematic director as $Z$-axis.

In a recent communication it has been stressed that the theory of rotational diffusion must allow the friction tensor for the solvent or solute molecules in oriented phases to be dependent upon the instantaneous molecular orientation[2] and an explicit form for the angular dependence of the tensor has been derived from hydrodynamical arguments, by assuming the elongated mesogen molecules to be approximated by a row of identical spheres. The resulting Fokker–Planck equation was then solved under conditions of diffusional regime, appropriate for the dense mesogen systems. In the present work we shall generalize the treatment to molecules of arbitrary shape, and we shall solve the diffusion equation to obtain the spectral density functions relevant for the interpretation of dielectric and magnetic relaxation experiments.

## DIFFUSION EQUATION IN ANISOTROPIC LIQUIDS

The inherent angular dependence of the diffusion tensor in anisotropic liquid phases can be immediately evidentiated by deriving the diffusion equation from the master equation for the orientational probability $P(\Omega, t)$:

$$\frac{\partial}{\partial t}P(\Omega, t) = \int d\Omega\left[W(\Omega', \Omega)P(\Omega', t) - W(\Omega, \Omega')P(\Omega, t)\right] \quad (1)$$

Here $W(\Omega, \Omega')$ is the transition rate for the reorientation from the initial orientation specified by the Euler angles $\Omega = (\alpha, \beta, \gamma)$ and the final orientation $\Omega'$, subjected to the condition of detailed balance.[3] If the system is thought to be rotated from $\Omega$ to $\Omega'$ through an angle $\phi$ about the direction specified by the unit vector $\mathbf{n}$, and $W(\Omega, \Omega')$ is rewritten as $W(\Omega, \boldsymbol{\phi})$ with $\boldsymbol{\phi} = \mathbf{n}\phi$, then the master equation becomes:

$$\frac{\partial}{\partial t}P(\Omega, t) = \int d\boldsymbol{\phi}\big[\exp(-i\boldsymbol{\phi}\cdot\mathbf{J})W(\Omega, -\boldsymbol{\phi})P(\Omega, t) \\ - W(\Omega, \boldsymbol{\phi})P(\Omega, t)\big] \quad (2)$$

where $\exp(-i\boldsymbol{\phi}\cdot\mathbf{J})$ is the operator generating rotations about the molecular axes. In the diffusional model, molecules are assumed to reorient through small angular steps, and so an expansion of the exponential operator up to the quadratic terms is appropriate. The result is:

$$\frac{\partial}{\partial t}P(\Omega,t) = -\sum_p J_p\left[iA_p(\Omega) + \sum_q J_q D_{pq}(\Omega)\right]P(\Omega,t) \tag{3}$$

with

$$A_p(\Omega) = \int d\phi\, \phi_p W(\Omega, -\phi) \tag{4a}$$

$$D_{pq}(\Omega) = \frac{1}{2}\int d\phi\, \phi_p\phi_q W(\Omega, -\phi) \tag{4b}$$

An internal relation between **A** and **D** is found by imposing that the diffusion equation has a time-independent solution $P(\Omega)$, and that the orientational distribution $P(\Omega)$ is derivable from a potential $U(\Omega)$ (in $kT$ units):

$$P(\Omega) = \exp[-U(\Omega)]/Z \tag{5}$$

$Z$ being the partition function. One finally obtains

$$\frac{\partial}{\partial t}P(\Omega,t) = -\mathbf{J}\cdot\mathbf{D}(\Omega)\cdot[\mathbf{J} + (\mathbf{J}U)]\,P(\Omega,t) \tag{6}$$

This equation is the generalized Smoluchowski equation derived by Hwang and Freed by means of a projection operator procedure, when the fluctuating torques acting on the molecules decay much faster than the angular variables.[4] This result differs from the usual form of the diffusion equation[5] in that $\mathbf{D}(\Omega)$ appears to be a function of the instantaneous molecular orientation. Note that the relation reported in Eq. (4b) gives no hints to the functional form of $\mathbf{D}(\Omega)$. Freed and coworkers[6] suggest that the diffusion tensor be decomposable in two parts, one diagonal in the molecular frame and the other in the laboratory frame. We shall resort here to hydrodynamical models to obtain an explicit form for the angular dependence of the friction tensors.

## HYDRODYNAMIC DERIVATION OF THE FRICTION TENSOR

Although hydrodynamics is in principle applicable only to a macroscopic description of fluids, it has been successfully used for evaluating microscopic properties in isotropic media. Thus, good estimates of the molecular rotational diffusion tensor are obtained from the application of the Stokes law to an ellipsoid approximating the shape of the molecule.[7]

Such a success has suggested more sophisticated ways of using hydrodynamics for the calculation of the diffusion tensor of molecules with arbitrary and complex shape. One of these is the solution of the hydrodynamic equations with the boundary conditions given by the actual shape of the molecule.[8] A second method consists in approximating the molecules as an ensemble of rigidly connected spheres, one for each atom or group of atoms.[9-11] A similar approach, sometimes referred to as "beads on a string" has been often exploited in the study of chains or polymers dynamics.[12]

The second method is not necessarily simpler than the first one because of the hydrodynamical interactions between spheres. However, if we neglect them, the problem is easily solved by summing the frictional forces **F** and torques **N** acting on each sphere[13] and by using the Stokes relations for **F** and **N**:

$$\mathbf{F} = -6\pi a \eta \mathbf{v} \tag{7a}$$

$$\mathbf{N} = -8\pi a^3 \eta \boldsymbol{\omega} \tag{7b}$$

where $\mathbf{v}$, $\boldsymbol{\omega}$ and $a$ are respectively the linear velocity, the angular velocity and the radius of the sphere, while $\eta$ is the viscosity of the medium. It has been shown by Knauss and coworkers[10] that this very simple approach predicts essentially correct values for the friction or diffusion tensors. Moreover, the hydrodynamical interactions, taken into account in an approximate way by means of the Oseen tensor, bring only minor modifications to the results.[11]

The above considerations suggest the application to nematic phases of the method of the hydrodynamically independent spheres, to derive a model of the angular dependence of the diffusion tensor. To our best knowledge, the full set of hydrodynamic equations describing a nematic liquid crystal[14] has not yet found solution even for the case of a moving sphere. Therefore we introduce a phenomenological extension of the Stokes law to the nematic phase by retaining the linear relations between force (torque) and velocity (angular velocity):

$$\mathbf{F} = -6\pi a \boldsymbol{\eta}^T \cdot \mathbf{v} \tag{8a}$$

$$\mathbf{N} = -8\pi a^3 \boldsymbol{\eta}^R \cdot \boldsymbol{\omega} \tag{8b}$$

We emphasize that the tensorial pseudoviscosity $\boldsymbol{\eta}^R$ and $\boldsymbol{\eta}^T$ are not actually properties of the medium, even if they must be somehow in relation to the true viscosity coefficients of a nematic.[14] It is more useful to think of them as related to the observed translational and rotational friction of a molecule with spherical shape. The above considerations suggest the following simplifying assumptions for $\boldsymbol{\eta}^R$:

$$\boldsymbol{\eta}^R = \eta^R \mathbf{1} \tag{9}$$

and a diagonal and axial form for $\boldsymbol{\eta}^T$ in the laboratory frame with the $Z$-axis parallel to the nematic director:

$$\boldsymbol{\eta}^T = \begin{pmatrix} \eta_\perp^T & 0 & 0 \\ 0 & \eta_\perp^T & 0 \\ 0 & 0 & \eta_\parallel^T \end{pmatrix} \tag{10}$$

Following the procedure outlined by Happel and Brenner in their book,[13] we can now calculate the rotational friction acting on the composite body make up by $N$ rigidly connected spheres. The total force $\mathbf{F}$ and torque $\mathbf{N}$ acting on the body are simply given as:

$$\mathbf{F} = \sum_j \mathbf{F}_j \tag{11a}$$

$$\mathbf{N} = \sum_j (\mathbf{N}_j + \mathbf{r}_j \times \mathbf{F}_j) \tag{11b}$$

where $\mathbf{F}_j(\mathbf{N}_j)$ is the frictional force (torque) acting on the $j$th sphere according to the phenomenological Stokes law given in the Eqs. (8) and $\mathbf{r}_j$ is the position vector of the $j$-th sphere relative to the point of application of $\mathbf{F}$ and $\mathbf{N}$. If we express $\mathbf{N}$ and $\mathbf{F}$ with respect to the center of hydrodynamic reaction,[13] that is if we choose the origin for $\mathbf{r}_j$ such that:

$$\sum_j a_j \mathbf{r}_j = 0 \tag{12}$$

we obtain the following equations for the total force and torque

$$\mathbf{F} = -6\pi\left(\sum_j a_j\right)\boldsymbol{\eta}^T \mathbf{v} \tag{13a}$$

$$\mathbf{N} = -\left[8\pi\left(\sum_j a_j^3\right)\boldsymbol{\eta}^R + 6\pi\left(\sum_j a_j \mathbf{r}_j \times \boldsymbol{\eta}^T \times \mathbf{r}_j\right)\right]\boldsymbol{\omega} \tag{13b}$$

where $\boldsymbol{\omega}$ is the angular velocity of the body and $\mathbf{v}$ the linear velocity of the center of reaction:

$$\mathbf{v}_j = \mathbf{v} + \boldsymbol{\omega} \times \mathbf{r}_j \tag{14}$$

In Eq. (13b) $\mathbf{r}_j \times \boldsymbol{\eta}^T \times \mathbf{r}_j$ stands for a tensor whose $(i, k)$ component is given by the relation:

$$\left[\mathbf{r}_j \times \boldsymbol{\eta}^T \times \mathbf{r}_j\right]_{i,k} = -\sum_{m,n,p,q} \epsilon_{i,m,p}\epsilon_{k,n,q} \cdot (\mathbf{r}_j)_m (\mathbf{r}_j)_n (\boldsymbol{\eta}^T)_{pq} \tag{15}$$

with $\epsilon_{i,j,k}$ the Levi–Civita symbol. By recalling the usual form of the Langevin equation:

$$\mathbf{N} = -\boldsymbol{\xi} \cdot \boldsymbol{\omega} \tag{16}$$

Eq. (13b) defines implicitly the components of the rotational friction tensor $\boldsymbol{\xi}$.

In order to write down explicitly the angular dependence of the friction tensor, we separate out an isotropic contribution of the translational pseudoviscosity tensor:

$$\bar{\eta}^T = \frac{2\eta_\perp^T + \eta_\parallel^T}{3} \tag{17a}$$

from the anisotropic and traceless part

$$\delta\boldsymbol{\eta}^T = \boldsymbol{\eta}^T - \bar{\eta}^T\mathbf{1} \tag{17b}$$

Correspondingly $\boldsymbol{\xi}$ is written as the sum of two terms

$$\boldsymbol{\xi} = \boldsymbol{\xi}^0 + \boldsymbol{\xi}^1 \tag{18}$$

with $\boldsymbol{\xi}^0$ comprehensive of the purely rotational $(\eta^R)$ and isotropic translational $(\bar{\eta}^T)$ contributions.

The following relation for $\boldsymbol{\xi}^0$ is then derived

$$\boldsymbol{\xi}^0 = 8\pi\left(\sum_j a_j^3\right)\eta^R\mathbf{1} + 6\pi\bar{\eta}^T\left[(Tr\mathbf{M})\mathbf{1} - \mathbf{M}\right] \tag{19}$$

where **M** is a matrix with components:

$$M_{pq} = \sum_j a_j (\mathbf{r}_j)_p (\mathbf{r}_j)_q \tag{20}$$

The molecular frame that diagonalizes **M** shall be taken in the following as reference frame; moreover, we shall assume that the $z$ molecular axis coincides with a ternary or higher order rotation axis of symmetry, in order to recover an axially symmetric form for $\boldsymbol{\xi}$ in the isotropic phase. The principal components of $\boldsymbol{\xi}^0$ are therefore written as:

$$\xi_{\parallel}^0 = 8\pi \left( \sum_j a_j^3 \right) \eta^R + 12\pi \bar{\eta}^T M_{\perp} \tag{21a}$$

$$\xi_{\perp}^0 = 8\pi \left( \sum_j a_j^3 \right) \eta^R + 6\pi \bar{\eta}^T (M_{\parallel} + M_{\perp}) \tag{21b}$$

The matrix representation of $\boldsymbol{\xi}^1$ in the molecular frame has then the final form in units of $\xi_{\perp}^0$ :

$$\begin{pmatrix} \Delta_{\parallel}\left(\frac{1}{3} - n_x^2\right) + (\Delta_{\perp} - \Delta_{\parallel})\left(n_z^2 - \frac{1}{3}\right) & -\Delta_{\parallel} n_x n_y & -\Delta_{\perp} n_x n_z \\ -\Delta_{\parallel} n_y n_x & \Delta_{\parallel}\left(\frac{1}{3} - n_y^2\right) + (\Delta_{\perp} - \Delta_{\parallel})\left(n_z^2 - \frac{1}{3}\right) & -\Delta_{\perp} n_y n_z \\ -\Delta_{\perp} n_z n_x & -\Delta_{\perp} n_z n_y & \Delta_{\perp}\left(\frac{1}{3} - n_z^2\right) \end{pmatrix} \tag{22}$$

where $n_x = -\sin\beta\cos\gamma$, $n_y = \sin\beta\sin\gamma$, $n_z = \cos\beta$ are the direction cosines of the director of the nematic phase with respect to the molecular frame. The parameters $\Delta_{\parallel}$ and $\Delta_{\perp}$ are defined according to the equations:

$$\Delta_{\parallel} = \frac{\eta_{\parallel}^T - \eta_{\perp}^T}{\bar{\eta}^T} \frac{M_{\parallel}}{M_{\parallel} + M_{\perp} + \frac{4}{3}(\eta^R/\bar{\eta}^T)\Sigma_j a_j^3} \tag{23a}$$

$$\Delta_{\perp} = (M_{\perp}/M_{\parallel})\Delta_{\parallel} \tag{23b}$$

## FOKKER-PLANK EQUATION

A diffusional regime is certainly adequate to describe the rotational motions in liquid crystals, since the angular momenta, already thermally randomized in the isotropic phase, are more effectively quenched in the oriented phase owing to the action of the orientational torques.

However, it does not appear to be convenient to use a diffusion equation in the form given by the Eq. (6), because it would require the inversion of the matrix representing the friction tensor, according to the Einstein relation:

$$\mathbf{D} = kT\boldsymbol{\xi}^{-1} \tag{24}$$

For this reason, we prefer to use a Fokker–Planck (F.P.) equation[15, 16], whose "collisional" term is linear in the friction tensor components, and to solve it under the limiting conditions appropriate to the diffusional regime. Therefore, we shall adopt the following simplifying modifications, with respect to the standard form of the F.P. equation:

(i) The precessional term is neglected;

(ii) An isotropic inertial tensor **I** is used, the diffusion tensor anisotropy being determined only by $\boldsymbol{\xi}$.

In addition, it is convenient to use, in place of the angular momentum **L**, its adimensional counterpart **Q**.

$$\mathbf{Q} = (2kTI)^{1/2}\mathbf{L} \tag{25}$$

In this way, the equilibrium distribution function is given by the expression:

$$P = e^{-(U+Q^2)}/Z \tag{26}$$

The autocorrelation function $g(t)$ for any function $f(\Omega)$ of the molecular orientation is written as:

$$\begin{aligned} g(t) &= \overline{f(t)^* f(0)} = \langle fP^{1/2} | e^{-\Gamma_s t} | fP^{1/2} \rangle \\ &= \int d\mathbf{Q} \int d\Omega P^{1/2} f(\Omega)^* e^{-\Gamma_s t} f(\Omega) P^{1/2} \end{aligned} \tag{27}$$

where $\Gamma_s$ is the symmetrized Fokker–Planck operator, which under the conditions mentioned above assumes the form:

$$\begin{aligned} \Gamma_s = {} & i(2kT/I)^{1/2}\left[\mathbf{Q} \cdot \mathbf{J} - \tfrac{1}{2}(\mathbf{J}U)\frac{\partial}{\partial \mathbf{Q}}\right] \\ & -(2I)^{-1} P^{-1/2} \frac{\partial}{\partial \mathbf{Q}} \cdot \boldsymbol{\xi} P \cdot \frac{\partial}{\partial \mathbf{Q}} P^{-1/2} \end{aligned} \tag{28}$$

Products of Wigner rotation matrices[17] $D^j_{lm}(\Omega)$ and Hermite functions of the components of **Q** are chosen as basis functions, but only zero and first order Hermite polynomials need actually to be considered. To take advantage of the spherical tensor algebra, we introduce the orthonormal functions $\psi_{p,q}$ defined as:

$$\psi_{0,0} = (\pi)^{-3/2}\exp(-Q^2/2) \tag{29}$$

$$\psi_{1,q} = 2^{1/2}T_{\mathbf{Q}}^{(1,q)}\psi_{0,0} \tag{30}$$

where $T_{\mathbf{A}}^{(k,m)}$ stands for the components of the $k$-th rank spherical tensor[17] associated to the Cartesian tensor **A**. In order to show how $\Gamma_s$ operates on the basis functions $D^j_{l,m}(\Omega)\psi_{p,q}(\mathbf{Q})$, the following relation for scalar product is used:

$$\mathbf{V}\cdot\mathbf{A}\cdot\mathbf{V}' = \sum_{K,M,m',m''} C(1,1,K;m',m'',M)T_{\mathbf{V}}^{(1,m')}T_{\mathbf{A}}^{(K,M)*}T_{\mathbf{V}'}^{(1,m'')} \tag{31}$$

After some manipulation, we obtain:

$$\begin{aligned}\Gamma_s D^j_{l,m}\psi_{p,q} = {} & i(kT/I)^{1/2}\sum_k(-1)^{k+q}\Big[\tfrac{1}{2}(-1)^p D^j_{lm}\big(T_{\mathbf{J}}^{(1,k)}U\big) \\ & -f_k^{(j,m)}D^j_{l,m+k}\Big]\psi_{1-p,q-k} + \frac{1}{I}\delta_{p,1}\Big[\big(\xi^0_q + \tfrac{1}{3}Tr\,\boldsymbol{\xi}^1\big)\psi_{p,q} \\ & + \sum_k(-1)^q C(1,1,2;k,-q,k-q)T_{\boldsymbol{\xi}^1}^{(2,k-q)}\psi_{p,k}\Big]D^j_{lm} \\ & + \text{higher order Hermite polynomials}\end{aligned} \tag{32}$$

where $\xi^0_0 \equiv \xi^0_{\parallel}$, $\xi^0_{\pm1} \equiv \xi^0_{\perp}$, and the coefficients $f_k(j,m)$ are defined as:

$$f_0(j,m) = m \tag{33a}$$

$$f_{\pm1}(j,m) = \mp\left[\frac{j(j+1)-m(m\pm1)}{2}\right]^{1/2} \tag{33b}$$

The spherical components of $\boldsymbol{\xi}^1$ expressed in the molecular frame and corresponding to the Cartesian tensor shown in the Eq. (22), have the form:

$$Tr\,\boldsymbol{\xi}^1 = \tfrac{2}{3}\xi_\perp^0\,(\Delta_\perp - \Delta_\parallel)\,D_{00}^2 \tag{34a}$$

$$T_{\boldsymbol{\xi}^1}^{(2,0)} = \tfrac{1}{3}\left(\tfrac{2}{3}\right)^{1/2}\xi_\perp^0\,(\Delta_\parallel - 4\Delta_\perp)\,D_{00}^2 \tag{34b}$$

$$T_{\boldsymbol{\xi}^1}^{(2,\,\pm 1)} = -\left(\tfrac{2}{3}\right)^{1/2}\xi_\perp^0\,\Delta_\perp\,D_{0,\,\pm 1}^2 \tag{34c}$$

$$T_{\boldsymbol{\xi}^1}^{(2,\,\pm 2)} = -\left(\tfrac{2}{3}\right)^{1/2}\xi_\perp^0\,\Delta_\parallel\,D_{0,\,\pm 2}^2 \tag{34d}$$

An important feature can be derived from eq. (32) as a consequence of the particular form of $\boldsymbol{\xi}^1$: the *F.P.* operator conserves the "quantum numbers" $l$ and $(q + m)$ of the product function $D_{lm}^j \psi_{pq}$. Therefore, if we wish to calculate the autocorrelation function of $D_{l,m}^j$, only the orthonormal basis functions $|kpq\rangle \equiv (2k + 1)/(8\pi^2)^{1/2} \cdot D_{l,m-q}^k \psi_{p,q}$ are required.

After choosing the simple Maier-Saupe form $U = \lambda D_{00}^2$ for the orientational potential, the matrix elements of $\Gamma_s$ are constructed from Eq. (32), and the continued fraction representation of the required spectral density is computed by means of the Lanczos algorithm.[18]

## CALCULATIONS

The correlation functions $g_{lm}^j(t)$ for all components of the Wigner functions of rank one and two have been computed by solving the Fokker-Planck equation on a PDP 11/24 minicomputer. In general, the correlation functions are obtained as multiple exponential decays, and so the "effective" correlation times $\tau_{lm}^j = \tilde{g}_{lm}^j(0)/g_{lm}^j(0)$, in terms of the Fourier-Laplace transforms $\tilde{g}_{lm}^j(\omega)$ will be reported here. The numerical values of these correlation times are complicated functions of $\xi_\perp^0/\xi_\parallel^0$ and of the parameters $\Delta_\parallel$ and $\Delta_\perp$ given in the Eqs. (23), except in the case $l = m = 0$, for which the following expression holds:

$$\tau^j = \tau_0^j\left(1 + c_\parallel^j\Delta_\parallel + c_\perp^j\Delta_\perp\right) \tag{35}$$

Results at three different degrees of order are summarized in the Table I.

Since from Eqs. (23) we expect $\Delta_\perp$ to be smaller than $\Delta_\parallel$ for elongated molecules, as a first approximation we might neglect the $\Delta_\perp$ term in the expression (22) for the friction tensor. Results obtained in

TABLE I

Effect of the viscosity anisotropy on the effective correlation times of Wigner components $D^j_{lm}$ of rank one and two, and $l = m = 0$

| $\bar{P}_2$ | $\tau_0^1$ | $c_\parallel^1$ | $c_\perp^1$ | $\tau_0^2$ | $c_\parallel^2$ | $c_\perp^2$ |
|---|---|---|---|---|---|---|
| .34 | 1.40 | .490 | −.157 | .173 | .217 | .116 |
| .60 | 5.23 | .538 | −.204 | .128 | .180 | .152 |
| .82 | 151. | .602 | −.269 | .097 | .000 | .333 |

this way are shown in Table II, where the correction factors to the effective correlation frequencies $\alpha^j_{lm} = 1/\tau^j_{lm}$ are reported for $\Delta_\parallel = -1.49$, practically the highest value ($-1.5$) attainable for very anisotropic molecular shapes and viscosities. The results relative to the cases $l = m = 0$, and $j = 1$ and 2 are visualized in Figure 1 as functions of $\Delta_\parallel$.

In order to estimate the effect of the viscosity anisotropy in actual systems, the frictional parameters have been evaluated for benzonitrile and 4-cyano-biphenyl as test molecules having dimensions and shape typical for solutes or solvent mesogens. Standard bond lengths of 1.158 A for C—N, 1.40 A for C—C, and 1.084 A for C—H, have been chosen. For lack of better knowledge, we have identified $\eta^T_\perp$ and $\eta^T_\parallel$ with the Helfrich viscosities $\eta_1$ and $\eta_2$ reported by Kneppe and Schneider[19] for MBBA and equated $\eta^R$ with $\bar{\eta}^T$ in the Eqs. (21). This

TABLE II

Corrections to the effective correlation frequencies for $\Delta_\parallel = -1.49$, relative to $\Delta_\parallel = 0$, at three degrees of order. The values have been calculated for $\xi^0_\perp/\xi^0_\parallel = 1$ and 6 (in parenthesis)

| $j$ | $lm$ $\bar{P}_2$ | 0.34 | 0.60 | 0.82 |
|---|---|---|---|---|
| 1 | 0,0 | 3.7 | 5.0 | 9.75 |
| | 1,0 | 0.82 | 0.81 | 0.73 |
| | 0,1 | 0.92(0.96) | 0.89(0.92) | 0.75(0.81) |
| | 1,1 | 1.39(1.10) | 1.26(1.05) | 1.01(1.00) |
| 2 | 0,0 | 1.48 | 1.37 | 1.00 |
| | 1,0 | 1.65 | 1.00 | 0.72 |
| | 0,1 | 1.71(1.42) | 1.00(1.00) | 0.75(0.80) |
| | 1,1 | 1.64(1.22) | 1.30(1.07) | 1.00(1.00) |
| | 2,0 | 0.86 | 0.91 | 0.81 |
| | 0,2 | 1.03(1.01) | 1.02(0.99) | 0.86(0.91) |
| | 1,2 | 1.09(1.04) | 0.97(0.98) | 0.79(0.89) |
| | 2,1 | 0.95(0.98) | 0.87(0.91) | 0.74(0.79) |
| | 2,2 | 1.16(1.04) | 1.01(1.01) | 0.99(1.00) |

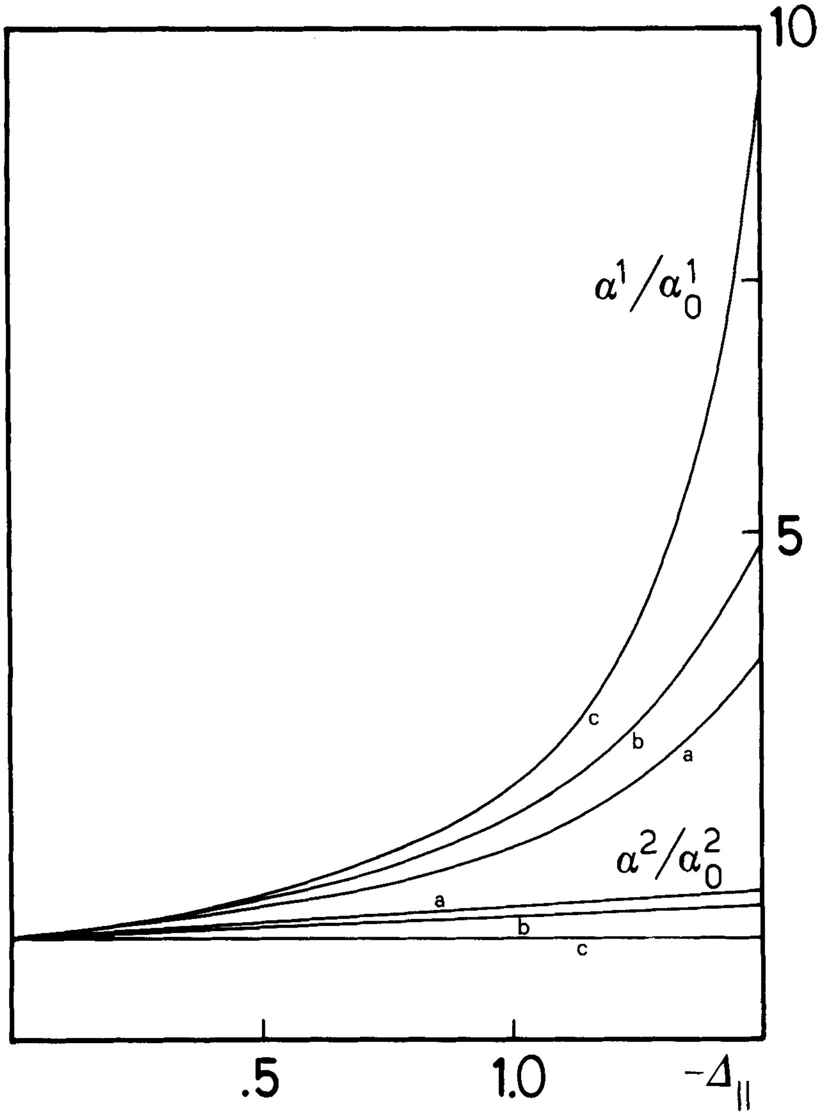

FIGURE 1 Correlation frequencies $\alpha^j = 1/\tau^j$ for first and second rank Wigner functions with $l = m = 0$, plotted as functions of the viscosity anisotropy parameter $\Delta_{\parallel}$, relative to their values $\alpha^j_0$ for $\Delta_{\parallel} = 0$. The labels $a$, $b$, $c$ refer to the three degrees of order $\overline{P}_2 = 0.34$, 0.60 and 0.82. The parameter $\Delta_{\perp}$ has been taken equal to 0.

TABLE III

Calculated frictional parameters for benzonitrile and 4-cyano-biphenyl

| | benzonitrile | 4-cyano-biphenyl |
|---|---|---|
| $\sum_j a_j^3(A^3)$[a] | 2.78 | 5.1 |
| $M_\perp(A^3)$[b] | 5.6 | 11.2 |
| $M_\parallel(A^3)$ | 22.6 | 106.8 |
| $M_\parallel/M_\perp$ | 4.0 | 9.5 |
| $\xi_\perp^0/\bar{\eta}^T(A^3)$ | 602. | 2350. |
| $\xi_\parallel^0/\bar{\eta}^T(A^3)$ | 281. | 550. |
| $\xi_\perp^0/\xi_\parallel^0$ | 2.1 | 4.2 |

[a] Sphere radii have been taken from bond length as 0.70 A for carbon, 0.458 A for nitrogen, and 0.384 A for hydrogen.
[b] Calculated as $(M_{xx} + M_{yy})/2$.

choice may be questionable, but it is useful to give upper limits to our correction factors. Table III gives the frictional parameters obtained in this way for the two molecules under examination. Since the highest values reported[19] for $\eta_1$ and $\eta_3$ are 0.189 and 0.031 Pa $s$ respectively, we conclude that $\Delta_\parallel$ is generally less than the unity in absolute value and $\Delta_\perp$ can indeed be neglected.

## DISCUSSIONS AND CONCLUSIONS

We have derived, on the basis of hydrodynamical concepts, an expression for the angular dependence, induced by the viscosity anisotropy, of the friction tensors of molecules in liquid crystals. We believe that this expression is qualitatively correct, and that it should be used in practical cases by considering $\xi_\perp^0/\xi_\parallel^0$ and $\Delta_\parallel$ as phenomenological parameters, because their relations to the actual shape of the molecule and the viscosity coefficients of the liquid crystal phase are not free from ambiguity. For example, the component of the "translational" viscosity perpendicular to the nematic director must be a combination of the two viscosity coefficients determined in shear-flow experiments with the director parallel to the velocity gradient or normal to the shear planes.[14,19,20]

The numerical results obtained with reasonable values of the parameters, compared with the experimental results for the translational diffusion coefficients for small solute molecules[21] or the mesogen molecules themselves,[22] show that the effect of the viscosity anisotropy on the friction tensors, although important in accurate calculations, does not alter drastically the picture obtained by the usual formulation of the diffusion equation including the orientational pseudopotential. In practice, the diffusion tensor may still be considered a molecular property as a first approximation.

A few words on the behaviour of the first rank correlation frequency $\alpha^1_{00}$ are now in order. The value of $\alpha^1_{00}$ is known to be related to the dipole relaxation frequency measured in dielectric relaxation experiments, when the electric field is parallel to the nematic director.[23] This relaxation frequency undergoes a large shift to lower values with the increase of the strength of the orientational potential.[24] It follows from Figure 1 that the effect of the viscosity anisotropy is that of counterbalancing this shift. Mathematically, the correction term diverges for the limiting values of $\Delta_{\parallel} = -1.5$ and $\overline{P}_2 = 1$, situation in which the dipole relaxation frequency tends to zero. Physically, this means that the friction acting on the dipole is determined, at high values of the orientational torque, by the component $\eta^T_{\parallel}$, parallel to the nematic director. In all other cases under the same limiting conditions, one has to expand the *F.P.* operator[25] about $\beta = 0$, and so the friction tensor becomes diagonal with $\xi_{\perp}$ proportional to $\eta^T_{\perp}$. The surprising result for $\alpha^1_{00}$ can be understood if one realizes that the dipole relaxation frequency, at high orientational torques, is determined by the frequency of passage across the potential barrier, whose asymptotic values[26] can be obtained by means of an expansion about $\beta = \pi/2$.

In conclusion, we expect the manifestation of a high viscosity anisotropy to be manifested experimentally by an apparent lowering of the potential barrier for the dipole orientation, and the consequent relative increase of the dipole relaxation frequency.

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## APPENDIX: ANGULAR DEPENDENT DIFFUSION TENSOR.

If the $\Delta_{\perp}$ terms are neglected in Eq. (22), the expression for the rotational friction tensor obtained in ref. 2 is recovered. In contrast to the previous treatment, one might now prefer to obtain directly the diffusion tensor $\mathbf{D}(\Omega)$ from the relation in Eq. (24), and to solve the resultant diffusion equation. One would obtain in this case:

$$\mathbf{D}(\Omega) = \mathbf{D}^0 + \mathbf{D}^1(\Omega) \tag{A.1}$$

where $\mathbf{D}^0$ is the angular-independent, axially symmetric tensor

$$\mathbf{D}^0 = \begin{pmatrix} (kT/\xi_\perp^0)(1-\Delta/3)^{-1} & 0 & 0 \\ 0 & (kT/\xi_\perp^0)(1-\Delta/3)^{-1} & 0 \\ 0 & 0 & (kT/\xi_\parallel^0) \end{pmatrix} \tag{A.2}$$

with $\Delta \equiv \Delta_\parallel$, and $\mathbf{D}^1(\Omega) = \mathbf{R}\mathbf{D}'\mathbf{R}^+$, $\mathbf{D}'$ having only one non-zero component $D'_{yy}$:

$$D'_{yy} = -\frac{(kT/\xi_\perp^0)\Delta\sin^2\beta}{(1-\Delta/3)(1-\Delta/3+\Delta\sin^2\beta)} \tag{A.3}$$

$\mathbf{R}$ being the Euler matrix for the rotation about the molecular symmetry axis.

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