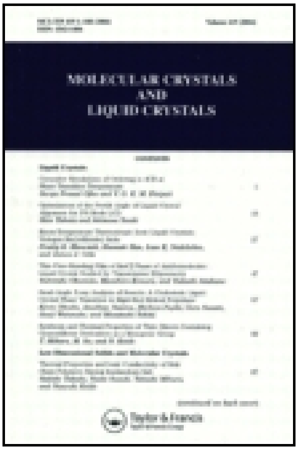

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Relations Between Rotational Diffusion and Frequency Spectra of Nematic Liquid Crystals

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A critical analysis of the frequency regime which contributes to rotational diffusion in nematic liquid crystals is made utilizing a rigorous molecular description and a frequency dependent friction constant. The equation of motion of a molecule is written in tensor form, since nematic liquids are anisotropic, and is that of a damped harmonic librator assuming a delta function external torque. A set of relaxation times is assumed and the role of different frequency regimes is analysed critically. The analysis shows that a high frequency cutoff in the hydrodynamic regime is inconsistent with experimental diffusion times. This result shows that high or intermediate frequencies are more significant than low frequency hydrodynamic modes in diffusion in nematics. The zero sound regime of frequencies, modified by molecular collisions, is found to be closer than the hydrodynamic regime to the predominant frequencies in rotational diffusion in nematics, which are in the range of 10^{11} to 10^{12} Hz—a frequency regime close to that known to predominate in translational and rotational diffusion in isotropic liquids. The possibility that the molecular mass dependence of the rotational diffusivity of cybotactic groups is $m^{-3/2}$ rather than $m^{-1/2}$, which is typical of monoatomic diffusion, is discussed.

I INTRODUCTION

The rotational motions of molecules and clusters of molecules in liquid crystals are complicated motions involving both hydrodynamic and molecular rotation modes, frequency dependent friction constants, different relaxation times for the three Euler angles, and effects of transitional–rotational interactions and of a cut-off frequency. There are also imposing effects on rotational diffusivities which result from the three Euler angles, molecular tail length, magnitude of the viscosity coefficients, type of mesophase, and critical phenomena. In addition, complexities are introduced by the presence of anharmonicities, nonlinearities in the rate equations for large electrochemical potential gradients, and the limited regimes of applicability of hydrodynamics, in the long wavelength regime, and molecular kinetics and high frequency collective modes in the short wavelength regime. In fact, the intermediate wavelength (and frequency) regime between hydrodynamic and high frequency collective mode behavior has not been solved for liquid crystals and could, possibly, contribute significantly to a thorough understanding of rotational diffusion. The statement by Gordon[1] in 1964 regarding rotational motions in isotropic liquids that "The angular dependence of intermolecular forces is one of the least-understood features of our knowledge of the ways in which molecules interact," certainly applies to liquid crystals as well. However, significant advances in the understanding of rotational motions in liquid crystals have been made recently which provide some reasonable approaches to this complicated problem.

The experimental observations and techniques in liquid crystals to which the theory of rotational diffusion applies are numerous and include thermal neutron scattering,[2,3] nuclear magnetic resonance,[4] band shapes in Raman and infrared spectroscopy, ultrasonic dispersion, and relaxation effects in the real and imaginary parts of the dielectric constants in microwave and radio attenuation.[5] Sinha[3] *et al.* and Töpler, Alefeld and Springer[2] found that the scattering of slow neutrons could be resolved into transitional and rotational parts[6] in the smectic B, nematic, and isotropic phases, provided that scattering angles were small. Doane *et al.*[4] showed that orientational order fluctuations are the dominant mode of relaxation for T_1 measurements in MBBA. It was also found that an adopted cut-off frequency in the frequency spectrum provided a fit for observed deviations from the $\omega^{-1/2}$ dependence of T_1 on frequency. The corresponding cutoff wavelength was about the length of the MBBA molecule. Subsequent work by Doane has however, raised some questions concerning the validity of the cutoff frequency model. Weise and Axmann[5] obtained a relaxation time of 4.3×10^{-9}s in PAA for orientational relaxation with the dipole moment parallel to both the director and external electric field. This is an important result which has been discussed by many authors.

The theory of rotational diffusion and relaxation in liquid crystals has been investigated by Martin, Meier, and Saupe,[7] Franklin,[8] and Kushik and Berne.[9] Martin *et al.* utilized the nematic potential to derive the deviation of the θ orientation from the ideal nematic configuration in an applied electric field through an extension of the Debye model for polar liquids. For the θ mode they found that a single relaxation time was sufficient. The theoretical results correlated reasonably well with the low frequency peak at 5×10^7 Hz and relaxation time of 4.3×10^{-9}s in the dielectric constant in PAA. Franklin[8] showed theoretically that the interaction between rotational and translational diffusion is expected to be significant in nematic liquids depending on the material parameters. Kushik and Berne[9] proved a useful relation for obtaining the rotational velocity autocorrelation function from light scattering data. Also, they simulated a nematic liquid crystal in a computer study of the momentum autocorrelation function of 100 ellipsoidal particles. The results of the computer study verified their theoretical predictions and gave reasonable results for the rotational velocity autocorrelation versus time for both the isotropic liquids and nematic phase.

It is important to note that the unmodified Stokes–Einstein equation does not give an accurate relationship between diffusivity and viscosity. The Oseen–Kirkwood molecular–hydrodynamic theory, which involves macroscopic viscosities, can be adapted for rotational diffusion as pointed out by Franklin[10] in a molecular–hydrodynamic theory of the anisotropy of translational diffusion. This theory would, however, involve the complexities of molecular chain space and Reimannian geometry and would not give as many useful results for rotational diffusion as the simpler approach taken here.

In isotropic liquids the theory of rotational diffusion and its applications has been developed in recent years by Steele,[11] Gordon,[1] Ivanov,[12] McClung,[13] and Hubbard.[14] Larrson[15] studied the contributions of rotational librations and diffusion on the scattering of slow neutrons. In addition, the research monographs by Egelstaff[16] and Fisher[17] deal substantively with both translational and rotational diffusion. Some theories have been developed regarding translational diffusion in liquids and solids which can be adapted to rotational diffusion. It is unnecessary to list these articles for our purposes except for the work of Martin and Yip[18] on a frequency dependent friction constant and the theory of solid state diffusion including anharmonicity by Franklin,[19] which are utilized in our calculations via adaption to rotational diffusion in nematic liquid crystals.

In the following section, we develop the theory of a dampled harmonic librator–rotator assuming a delta function external torque. The damping is provided by a frequency-dependent friction constant which is a tensor quantity in liquid crystals. In order to simplify the notation tensors will be denoted by $\overleftrightarrow{T}$ except where tensor products may be confusing. Then subscripts such as $T_{\alpha\beta}$ will be utilized where $\alpha, \beta = \theta, \phi, \psi$ (Euler angles).

II FREQUENCY-DEPENDENT FRICTION CONSTANT

A frequency-dependent friction constant allows a phenomenological description of diffusion in terms of a relaxation constant or constants and the average of the system's squared frequencies. A classical theory developed by Martin and Yip[18] for translational diffusion in isotropic liquids is rigorous and provides for an equally rigorous theory of rotational diffusion in nematic liquid crystals. The equation of motion combines the construct of a harmonic rotational oscillator of frequency ω_0 in a "cage" with that of a linear response function which is dependent on the system's spectrum of frequencies $S(\omega)$. All frequencies do not contribute equally to the migration process; contributions depend on frequency densities, linear combinations of frequencies, and the maximum frequency of the spectrum. As in the Debye spectrum in solids we might expect, on a physical basis, to have an approximate maximum wavevector k_c and associated frequency ω_c stemming from the short wavelength limit associated with molecular size.[4] In the high frequency regime, the high frequency collective modes of Kobayashi, Franklin, and Moroi[20] and the independent oscillator modes, which are also high frequency, rather than the hydrodynamic modes, are expected to contribute to molecular migration. In the low frequency regime, hydrodynamic modes make the larger contribution. Therefore, it is important to determine which wavevector regime contributes the most to rotational diffusion.

The equation of angular motion of an average molecule of moment of inertia $\overleftrightarrow{I}$ relates angular acceleration $\ddot{\vec{\Omega}}$ to internal and external torques $\vec{\Gamma}$ via the microscopic description

$$\overleftrightarrow{I}\langle\ddot{\vec{\Omega}}(t)\rangle + \overleftrightarrow{I}\omega_0^2\langle\vec{\Omega}(t)\rangle = \langle\vec{\Gamma}^{\mathrm{int}}(t)\rangle + \vec{\Gamma}^{\mathrm{ext}}(t) \tag{1}$$

where $\vec{\Gamma}^{\mathrm{ext}}$ vanishes for $t < t_0$ and $\langle\quad\rangle$ denotes thermal averaging for times prior to t_0. Since this is a microscopic molecular description the long range orientational order parameter S does not appear in these equations. The effects of local order enter the theory via three relaxation times for different modes in the anisotropic description of the medium. A linear response of $\langle\dot{\vec{\Omega}}(t)\rangle$ is adequate for a weak external torque and we write

$$\langle\Omega_\alpha(t)\rangle = \int_{-\infty}^{\infty} \mathrm{d}t'\tilde{\chi}_{\alpha\beta}(t-t')\Gamma_\beta^{\mathrm{ext}}(t') \tag{2}$$

where the tilde is used to distinguish the time-dependent function from its Fourier transform

$$\tilde{\overleftrightarrow{\chi}}(t-t') = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi}\,\overleftrightarrow{\chi}(\omega)e^{-i\omega(t-t')} \tag{3}$$

where $\overleftrightarrow{\chi}(\omega) = \overleftrightarrow{\chi}'(\omega) + i\overleftrightarrow{\chi}''(\omega)$. We assume an impulsive external torque

$$\vec{\Gamma}^{\mathrm{ext}}(t) = \vec{\Gamma}_0^{\mathrm{ext}}\delta(t-t_0) \tag{4}$$

and a friction tensor approximation for the thermodynamic average internal torque

$$\langle\Gamma_\alpha^{\mathrm{int}}(t)\rangle \cong -I_{\alpha\beta}\gamma_{\beta\gamma}\langle\dot{\Omega}_\gamma(t)\rangle. \tag{5}$$

Later we will introduce a frequency dependent friction constant $\gamma(\omega)$. Letting $\vec{\Omega} = \vec{\Omega}_0 \exp(-i\omega t)$ Eq. (1) becomes

$$I[(\omega_0^2 - \omega^2)\vec{\delta} - i\vec{\gamma}\omega]\langle\vec{\Omega}(t)\rangle = \vec{\Gamma}^{\text{ext}}(t) \tag{6}$$

where $\vec{\delta}$ is the Kronecker delta. The frequency spectrum for nematic fluctuations stems from the Nyquist theorem and is given by $\vec{S}(\omega) = (2/\beta\omega)\vec{\chi}''(\omega)$ where $\beta = 1/k_BT$ The equilibrium thermodynamic average of the squared velocity has two representations given by

$$\langle\vec{\Omega}^2(t)\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega\, \omega^2\vec{S}(\omega) = \frac{1}{\beta\vec{I}} \tag{7}$$

and the moments of the frequency spectrum in terms of $\vec{\chi}''$ stem from

$$\frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega\, \omega^{2n+2}\frac{\vec{\chi}''(\omega)}{\omega} = \langle\omega^{2n}\rangle\vec{I}^{-1} \tag{8}$$

where $n = 0, 1, 2, \ldots$ and $\langle\omega^{2n}\rangle$ denote rotational frequencies thermally averaged over the nematic rotational spectrum.

At this stage we return to the development of the response function and utilize a frequency dependent friction constant, following Martin and Yip,[18] with the end in view of deriving a form for the rotational diffusivity $\vec{D} = (\beta\vec{I}\vec{\gamma})^{-1}$ in terms of $\langle\omega^{2n}\rangle$ and relaxation times τ. From Eqs. (2) and (6) for $\langle\vec{\Omega}(t)\rangle$ we obtain

$$\langle\Omega_\alpha t)\rangle = \int_{-\infty}^{\infty} \mathrm{d}t'\, \tilde{\chi}_{\alpha\beta}(t - t')\Gamma_\beta^{\text{ext}}(t') = \{I_{\alpha\beta}[(\omega_0^2 - \omega^2)\delta_{\beta\gamma} - i\gamma_{\beta\gamma}\omega]\}^{-1}\Gamma_\gamma^{\text{ext}}(t) \tag{9}$$

Using the Dirac delta function representation for $\vec{\Gamma}^{\text{ext}}(t)$ in Eq. (2) we obtain $\langle\vec{\Omega}(t)\rangle = \vec{\chi}(\omega)\vec{\Gamma}_0^{\text{ext}}$. Then from Eqs. (3) and (9) we have,

$$\int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi}\vec{\chi}(\omega)e^{-i\omega(t-t')} = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi}\frac{e^{-i\omega(t-t')}}{\vec{I}[(\omega_0^2 - \omega^2)\vec{\delta} - i\vec{\gamma}\omega]} \tag{10}$$

where $\vec{\chi}(\omega)$ can be separated into real and imaginary components. We note that for rotation, as for translation,[18] a frequency independent γ is not physically reasonable and does not satisfy the moment equations since the internal torque is out of phase with the angular displacement whereas, as Martin and Yip[18] note, at short times, it must be in phase. Therefore, we adopt the following forms for $\langle\vec{\Gamma}^{\text{int}}(t)\rangle$ and $\gamma(\omega)$

$$\langle\vec{\Gamma}^{\text{int}}(t)\rangle = \vec{I}\int_{-\infty}^{\infty} \mathrm{d}t'\, \vec{\gamma}(t - t')\langle\vec{\Omega}(t')\rangle \tag{11}$$

where

$$\overleftrightarrow{\gamma}(t-t') = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \overleftrightarrow{\gamma}(\omega) e^{-i\omega(t-t')} \tag{12}$$

and

$$\overleftrightarrow{\gamma}(\omega) = \overleftrightarrow{\gamma}'(\omega) + i\overleftrightarrow{\gamma}''(\omega) = \int_{-\infty}^{\infty} dt'\, \overleftrightarrow{\gamma}(t-t') e^{i\omega(t-t')} \tag{13}$$

Utilizing a Kramers–Kronig relation the response function follows from Eqs. (1), (9), (11) and (12)

$$\chi_{\alpha\beta}^{-1}(\omega) = I_{\alpha\gamma}[(\omega_0^2 - \omega^2)\delta_{\alpha\beta} - i\omega\gamma_{\gamma\beta}(\omega)] \tag{14}$$

which has a dissipative part given by

$$\overleftrightarrow{\chi}''(\omega) = \frac{\omega\overleftrightarrow{\gamma}'(\omega)}{\overleftrightarrow{I}\{[(\omega_0^2 - \omega^2)\overleftrightarrow{\delta} + \omega\overleftrightarrow{\gamma}''(\omega)]^2 + [\omega\overleftrightarrow{\gamma}'(\omega)]^2\}} \tag{15}$$

We note that $\overleftrightarrow{\chi}''(\omega)$ is real and odd and that $\omega\overleftrightarrow{\chi}''(\omega) \geqq 0$. We expect the dissipative response to be positive for rotation as it is for translation. This depends, in part, on the definition of $\overleftrightarrow{\gamma}(\omega)$ which we define as follows

$$\overleftrightarrow{\gamma}(\omega) = \frac{\overleftrightarrow{\gamma}_R}{1 - i\omega\tau_R} = \overleftrightarrow{\gamma}'(\omega) + i\overleftrightarrow{\gamma}''(\omega) \tag{16}$$

where

$$\overleftrightarrow{\gamma}'(\omega) = \frac{\overleftrightarrow{\gamma}_R}{1 + (\omega\tau_R)^2} \qquad \overleftrightarrow{\gamma}''(\omega) = \frac{\omega\overleftrightarrow{\gamma}_R\tau_R}{1 + (\omega\tau_R)^2} \tag{17}$$

From Eqs. (8), (15), and (17) we utilize the relationship between $\overleftrightarrow{\chi}$ and $\overleftrightarrow{\gamma}$ plus an integration of $\omega^{2n}\overleftrightarrow{\gamma}'(\omega)$ to obtain

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \overleftrightarrow{\gamma}'(\omega) = (\langle\omega^2\rangle - \omega_0^2)\overleftrightarrow{\delta} = \frac{\overleftrightarrow{\gamma}_R}{\tau_R} \tag{18}$$

$$\begin{aligned}\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \omega^2\overleftrightarrow{\gamma}'(\omega) &= [\langle\omega^4\rangle - (\langle\omega^2\rangle - \omega_0^2)]\overleftrightarrow{\delta} \\ &= \frac{\pi^2}{2\tau_R^2}(\langle\omega^2\rangle - \omega_0^2)\overleftrightarrow{\delta}\end{aligned} \tag{19}$$

where the quantity $(\langle\omega^2\rangle - \omega_0^2)/\tau_R^2$ has three values in the general case corresponding to the three dispersion relations in lattice vibration theory in solids, for example.[21] These relationships can be utilized in the evaluation of the diffusivity, which is given by

$$\overleftrightarrow{D} = (\beta \overleftrightarrow{I} \overleftrightarrow{\gamma}_R)^{-1} = [\beta \overleftrightarrow{I}(\langle \omega^2 \rangle - \omega_0^2)\tau_R \overleftrightarrow{\delta}]^{-1} \tag{20}$$

using Eq. (18) for $\overleftrightarrow{\gamma}_R$. If Eq. (19) is used for τ_R an expression for $\overleftrightarrow{D}$ in terms of $\overleftrightarrow{I}$, ω_0^2, $\langle \omega^2 \rangle$ and $\langle \omega^4 \rangle$ is obtained.

From the defining relationships the rotational velocity autocorrelation function can be written as

$$\begin{aligned}\overleftrightarrow{F}(\omega) &= \frac{2}{\pi} \int_0 \mathrm{d}t \cos \omega t \, \frac{\langle \vec{\Omega}(t) \vec{\Omega}(0) \rangle}{\langle \Omega^2(0) \rangle} \\ &= \frac{\beta \omega^2 \overleftrightarrow{I}}{\pi} \overleftrightarrow{\delta}(\omega) = \frac{2\omega \overleftrightarrow{I}}{\pi} \overleftrightarrow{\chi}''(\omega)\end{aligned} \tag{21}$$

Following Martin and Yip[18] simple expressions for $F(\omega)$ can be obtained using Eqs. (21) and (17) with Eq. (15) for $\overleftrightarrow{\chi}''$.

$$\begin{aligned}\overleftrightarrow{F}(\omega) &= \frac{\dfrac{2\omega^2 \overleftrightarrow{\gamma}_R}{\pi[1 + (\omega\tau_R)^2]}}{\left[(\omega_0^2 - \omega^2)\overleftrightarrow{\delta} + \dfrac{\omega^2 \tau_R \overleftrightarrow{\gamma}_R}{1 + (\omega\tau_R)^2}\right]^2 + \left[\dfrac{\omega \overleftrightarrow{\gamma}_R}{1 + (\omega\tau_R)^2}\right]^2} \\ &= \frac{\dfrac{2\omega^2 \tau_R \overleftrightarrow{\delta}(\langle \omega^2 \rangle - \omega_0^2)}{\pi[1 + (\omega\tau_R)^2]}}{\left[(\omega_0^2 - \omega^2)\overleftrightarrow{\delta} + \dfrac{(\omega\tau_R)^2 \overleftrightarrow{\delta}(\langle \omega^2 \rangle - \omega_0^2)}{1 + (\omega\tau_R)^2}\right]^2 + \left[\dfrac{\omega\tau_R(\langle \omega^2 \rangle - \omega_0^2)\overleftrightarrow{\delta}}{1 + (\omega\tau_R)^2}\right]^2}\end{aligned} \tag{22}$$

Returning to D and its representation given by Eq. (20) we note that the tensor components are given by

$$D_{\alpha\beta} = \frac{\delta_{\alpha\beta}}{\tau} = kT[(\langle \omega^2 \rangle - \omega_0^2)\tau_R I_{\alpha\gamma} \delta_{\gamma\beta}]^{-1} \tag{23}$$

where the evaluation of $D_{\alpha\beta}$ depends on the three components

$$(\langle \omega^2 \rangle - \omega_0^2)\tau_R \delta_{\gamma\beta}.$$

τ_R has been evaluated experimentally for PAA for the ψ, ϕ and θ rotations so that these values can be utilized in Eq. (23). Theoretical derivations of τ_R can, of course, be compared with these experimental values. Eq. (23) is similar in structure to that obtained for isotropic liquids but displays the anisotropy in $[\overleftrightarrow{I} \overleftrightarrow{\delta} \tau_R]^{-1}$ caused by nematic symmetry. Upon the breaking of nematic symmetry it takes on the isotropic form. Both low frequency hydrodynamic[22] and high frequency collective mode[20] dispersion relations have been derived for nematic liquid crystals. The frequency regime of the latter ($\approx 10^{13}$ Hz) is similar in nature to that of the (high frequency) plasmon regime in solids. Since low frequencies in hydrodynamic theory correspond to long wavelengths, the relative motion of a single molecule with respect to its neighbors in the low frequency regime requires the Fourier superposition and interaction (anharmonic) of a large number of wavevectors giving rise to the resultant local relative motion.[19] On the other hand, the preponderance of high frequencies would preclude substantial contributions of low frequency hydrodynamic modes.

The question of high and low frequency cutoffs is an important consideration in frequency averaging and in the contributions made by different dispersions. In recent T_1 measurements, Doane, Tarr, and Nickerson[4] proposed that a cutoff frequency of 8×10^7 Hz for MBBA would fit the data for the frequency dependence of T_1^{-1}. The corresponding cutoff assumed for PAA was 2×10^8 Hz. Both of these cutoffs are well below the 10^{12}–10^{13} Hz regime of the high frequency collective modes.[20] In addition, they are within the range of frequencies utilized in light scattering studies, for which linearized hydrodynamic theory has been satisfactory.[22] For translational diffusion in isotropic liquids $\langle\omega^2\rangle$ is in the lower portion of the high frequency collective mode regime since Rahman's computer study of argon[23] gave $\langle\omega^2\rangle = 4.7 \times 10^{25}$. If liquid crystals are close to isotropic liquids in their diffusion properties, then the hydrodynamic modes are expected to contribute little to the diffusion mechanism. On the other hand, if $\langle\omega^2\rangle$ was in the hydrodynamic regime, then the slow or fast modes of nematic liquid crystals might contribute a unique hydrodynamic character to liquid crystal diffusion. Consequently, the determination of the frequency regime for $\langle\omega^2\rangle$ is important for the understanding of the nature of the migration process in nematic liquid crystals.

III CONCLUSIONS AND DISCUSSION

The evaluation of Eq. (23) gives important insights into the following items:

1) the consideration of a cutoff frequency and its regime,

2) relative magnitudes of D_ϕ, D_Θ, and D_ψ,

3) the possible role of rotation of molecular clusters in addition to individual molecules.

Since the temperature and moments of inertia are known, the evaluation of Eq. (23) for $\vec{D}(\vec{k})$ depends on the values of τ_R chosen as well as $\langle\omega^2\rangle$ and ω_0. Table I lists the values of $\vec{I}$, $\tau_{R\phi}$, $\tau_{R\Theta}$, and $\tau_{R\psi}$ used for the material PAA in its nematic phase at a temperature of 408°K. Eq. (23) represents three

TABLE I

Values of parameters used in evaluation of Eq. (23) for the rotational diffusivities of nematic PAA at 408°K.

$I_\phi = 59 \times 10^{-38}$ g cm^2	$^a\tau_{R\phi} = 4.3 \times 10^{-9}$ s	$I_\phi \tau_{R\phi} = 2.4 \times 10^{-45}$ g cm^2 s
$I_\theta = 45 \times 10^{-38}$ g cm^2	$^a\tau_{R\theta} = 3 \times 10^{-11}$ s	$I_\theta \tau_{R\theta} = 1.3 \times 10^{-45}$ g cm^2 s
$I_\psi = 42 \times 10^{-39}$ g cm^2	$\tau_{R\psi} = 2 \times 10^{-11}$ s	$I_\psi \tau_{R\psi} = 8.4 \times 10^{-49}$ g cm^2 s
Theor.		
$^bD_\phi = 5.2 \times 10^7$ s^{-1}	$^bD_\theta = 9.1 \times 10^9$ s^{-1}	$^bD_\psi = 1.5 \times 10^{11}$ s^{-1}
Obs.		
$^aD_\phi \cong 5 \times 10^7$ s^{-1}	$^aD_\theta \cong 6 \times 10^9$ s^{-1}	

[a] The experimental data is summarized in the theoretical paper by A. J. Martin, G. Meier, and A. Saupe, *Farad. Symp.*, **1A**, 327 (1971).

[b] Assuming $(\langle\omega^2\rangle - \omega_0^2)^{1/2} = 3.6 \times 10^{11}$ Hz.

equations for the three Euler angles in which $D_\phi \sim \tau_{R\phi}^{-1}$, $D_\Theta \sim \tau_{R\Theta}^{-1}$, and $D_\psi \sim \tau_{R\psi}^{-1}$. The values of $\tau_{R\phi}$ and $\tau_{R\Theta}$ are well known from experimental work[5] which preceeded the theoretical development of Martin, Meier, and Saupe.[7] The value of $\tau_{R\psi}$ was chosen after discussions with experimentalists in NMR[24], neutron scattering[25], and dielectric relaxation[26] and from a consideration of limits posed by free rotation times for PAA molecules. The value chosen is 2×10^{-11} s which is that reported recently by Conrad, Stiller, and Stockmeyer[25] and by Janik[26] which were obtained by neutron scattering and dielectric relaxation measurements, respectively, on PAA.

The cutoff frequency proposed by Doane *et al.*[4] for PAA was $\omega_c = 2 \times 10^8$ Hz. If it is assumed that $\langle\omega^2\rangle = \omega_c^2$ and that $\omega_0 = 0$, extremely high values are obtained for D. The three Euler-angle components of D obtained with these assumed values of ω are $D_\phi = 5.5 \times 10^{16}$ s^{-1}, $D_\Theta = 5.5 \times 10^{17}$ s^{-1}, and $D_\psi = 2.8 \times 10^{19}$ s^{-1}. If $\omega_0 > 0$ had been chosen the values of D would have been larger passing through infinity to negative values as ω_0 is increased. Since the D values are many orders of magnitude larger than the experimentally observed ranges of these material parameters for any value of ω_c chosen in the linearized hydrodynamic regime the important conclusion is reached that much higher frequencies, close to those used in isotropic liquid diffusion theory, pertain to the evaluation of the rotational diffusivity in nematics. A choice of $(\langle\omega^2\rangle)^{1/2} = 3.6 \times 10^{11}$ Hz and $\omega_0 = 0$ yields the more tenable results given in Table I. The close agreement obtained with the experimentally observed peak frequencies in microwave measurements of dielectric relaxation summarized by Martin, Maier, and Saupe[7] is a result of assuming that ω_c is in or near the high frequency collective mode regime of Kobayashi, Franklin, and Moroi.[20] Since the collective mode regime applies to frequencies of the order 10^{13} Hz whereas applications of linearized hydrodynamic theory are normally limited to $< 10^9$ Hz it is important to consider in future work the significance of the collective[20] and intermediate frequency regimes on rotational diffusion. Since the wavevector corresponding to the hydrodynamic cutoff frequency of 2×10^8 Hz for PAA has a wavelength equal to the length of the PAA molecule,[4] the wavelengths of frequencies in the 10^{11} to 10^{12} Hz regime would, under this argument, be clearly out of the hydrodynamic regime.

The value of the three components of the rotational diffusivity obtained under the assumed frequency of $3.6 \times 10^{11}\ \mathrm{s}^{-1}$ are $D_\phi = 5.2 \times 10^7\ \mathrm{s}^{-1}$, $D_\Theta = 9.1 \times 10^9\ \mathrm{s}^{-1}$, and $D_\psi = 1.5 \times 10^{11}\ \mathrm{s}^{-1}$. The relative magnitudes of the rotational diffusivities for the three Euler angles are $D_\phi < D_\Theta < D_\psi$ which is the order expected from simple geometric arguments. One would expect for axial rotation with a very small activation energy that $D_\psi \approx \tau_{R\psi}^{-1}$ which is obtained from the theory. In diffusion with larger activation energies, such as that which occurs for the θ and ϕ components, smaller values of D and large values of τ_R are expected, which also obtains from the theory.

The possible role of cybotactic groups on D_ϕ and D_θ is dependent on the increase in $\overleftrightarrow{I}$ caused by molecular clusters and the mass dependence of the frequencies. Since $\overleftrightarrow{I}$ is directly proportional to mass while ω^2 is usually assumed to be approximately proportional to m^{-1}, the effect of mass changes cancels in the product $\overleftrightarrow{I}\omega^2$. If τ_R is proportional to $\sqrt{m}$ and if the frequencies that contribute to the diffusion process are altered only slightly from $m^{-1/2}$ dependence by local events, then a mass dependence similar to that in solids[19] will be observable. No unique differences from monomolecular rotation theory would be observed but an $m^{-1/2}$ mass dependence of D should be experimentally testable. It is important to note, however, that the *frequencies* which contribute to rotational diffusion may be *independent* of the mass in *molecular clustering*. In that case the mass dependence of D stems from $(I\tau_R)^{-1}$, which gives $m^{-3/2}$. This shows a *strong* dependence of D on the number of molecules together with their mass, in a cybotactic group. If the average number of molecules in a cluster can be controlled experimentally in a diffusion study the analysis of the mass dependence of D_ϕ and D_Θ should reveal whether or not local clustering is significant in rotational diffusion and whether a $m^{-1/2}$ or $m^{-3/2}$ mass dependence obtains.

Since the Martin–Yip theory[18] could also be extended to *translational* diffusion in nematic liquids[8] it could be used in a manner similar to that shown here to demonstrate that the zero sound frequency regime is much closer to the diffusion regime of frequencies than the range of applicability of hydrodynamic modes for translational as well as rotational diffusion.

In simple liquids and water both translational and rotational diffusion make their predominant contributions to the velocity autocorrelation functions at circular frequencies of $1\text{–}2 \times 10^{13}\ \mathrm{s}^{-1}$.[16,23] The cutoff frequency of $3.6 \times 10^{11}\ \mathrm{s}^{-1}$ found here is approximately 30 to 60 times less than this range for simple isotropic liquids. Since PAA molecules are larger, the mass dependence of ω^2, assuming $\omega^2 \sim m^{-1}$, accounts for a factor which is approximately four. The remaining factor of 7–15 difference from simple isotropic liquids may be accounted for by $\omega_0 \neq 0$, the form of the chosen dispersion which is integrated to give $\langle\omega^2\rangle$, experimental uncertainties in τ_R, or other possible causes such as molecular tails or anharmonicity. If we assume that the first factor is the most significant and choose a value of $\omega_0 = 2.5 \times 10^{12}$ Hz, then $[\langle\omega^2\rangle]^{1/2}$ turns out to be 2.53×10^{12} Hz. This value is close to that known for isotropic liquids and is the result of assuming a "cage" frequency of nearly the same value. Ordering in the liquid crystalline phases is expected to give rise to a significant contribution from ω_0—not negligible, as in isotropic liquids.[18] The evidence given here that high frequencies predominate in liquid crystal rotational diffusion indicates that a numerical analysis of the frequencies in the zero sound regime modified by molecular collisions in order to account properly for frequencies in the 10^{11} to 10^{12} Hz range must be done in order to assess the frequency spectrum of diffusion in nematic liquid crystals. The contributions from the frequencies was assumed to be isotropic here whereas they may, in reality, bear some anisotropy not accounted for by τ_R.

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