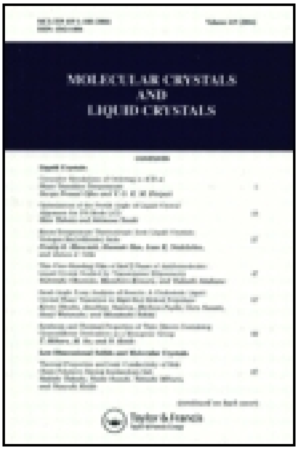

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Self-Diffusion in Uniaxial Liquid Crystals

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SELF-DIFFUSION IN UNIAXIAL LIQUID CRYSTALS

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Abstract Expressions are given for the translational diffusion parameters of non-spherical solutes in nematic and smectic-A phases, as measured by magnetic field gradient spin-echo NMR.

INTRODUCTION

In a previous paper [1], an exact expression has been derived for the diffusion parameters characterizing the translational motions of spherical solutes in uniaxial phases, for which detailed experimental data are available.[2] The theoretical treatment was based on a diffusion model, in which the coupling with the rotations could be avoided because of the symmetry of the problem.

In the present work, the theory is generalized to molecules of arbitrary shape, as are the real probes of most NMR experiments.[3] Although the solution of the full roto-translational problem is required in the case of smectics, analytical expressions are still obtainable if dealing with solutes whose dimensions are smaller than the characteristic layer spacings.

DIFFUSIONAL THEORY

The diffusion operator for non-spherical solutes in uniaxial liquid crystals is written in the form [4] :

$$\hat{R} = \hat{R}^R + \hat{R}^T$$
$$= \underline{M}\cdot\underline{\underline{D}}^R\cdot P\ \underline{M}\ P^{-1} - \underline{\nabla}\cdot\underline{\underline{D}}^T(\Omega)\cdot P\ \underline{\nabla}\ P^{-1} \tag{1}$$

where $\underline{M}$ are generators of infinitesimal rotations about the molecular axes, and $\underline{\nabla}$ is the gradient operator referred to the laboratory frame having the z-axis parallel to the mesophase director $\underline{n}$; $\underline{\underline{D}}^R$ and $\underline{\underline{D}}^T(\Omega)$ are the rotational and translational diffusion tensors, the latter being expected to be orientation-dependent in the fixed laboratory frame. The equilibrium distribution function is in general a non-factorizable function of the z-coordinate and the Euler angles, $P \equiv P(z,\Omega)$.

The translational diffusion parameter $D(\underline{u})$, as measured along the arbitrary laboratory direction $\underline{u}$ by NMR field gradient techniques [5], is defined in terms of the mean square displacement $\Delta\underline{r}(t) = \underline{r}(t) - \underline{r}(0)$ as:

$$D(\underline{u}) = \lim_{t\to\infty} \{|\underline{u}\cdot\Delta\underline{r}(t)|^2\}_{av} / 2t \tag{2}$$

The statistical average in Eq. (2) requires the evaluation of the correlation function $F_u(k,t)$:

$$F_u(k,t) = \int d\underline{r}\ d\Omega\ \exp(-ik\ \underline{r}\cdot\underline{u})\ \exp(-\hat{R}t)\ \cdot$$
$$\cdot\ \exp(ik\ \underline{r}\cdot\underline{u})\ P(z,\Omega) \tag{3}$$

In terms of the Laplace transform $F_u(k,s)$, the translation diffusion parameter $D(\underline{u})$ has the form :

$$D(\underline{u}) = \lim_{s\to o} \frac{s^2}{2} \left| -\frac{\partial^2}{\partial k^2} F_u(k,s)\right|_{k=0} \tag{4}$$

After some manipulation one obtains:

$$F_u(k,s) = \int d\underline{r}\, d\Omega \{ \hat{R}_u(k) + s\}^{-1} P(z,\Omega) \tag{5}$$

where:

$$\hat{R}_u(k) = \hat{R}^R + \hat{R}_z^{\,T} + k^2 D_{uu}^{\,T}(\Omega) - \\ -ik \{ \frac{\partial}{\partial z} D_{zu}^{\,T}(\Omega) + D_{uz}^{\,T}(\Omega)\, P \frac{\partial}{\partial z} P^{-1} \} \tag{6}$$

with:

$$\hat{R}_z^{\,T} = - \frac{\partial}{\partial z} D_{zz}^{\,T}(\Omega)\, P \frac{\partial}{\partial z} P^{-1} \tag{7}$$

By following the same procedure outlined in ref. 1 for the calculations of the derivatives with respect to k of the operator $\hat{R}_u(k)$, one obtains:

$$D(\underline{u}) = \int dz\, d\Omega \{ D_{uu}^{\,T}(\Omega) + \\ + D_{uz}^{\,T}(\Omega)\, P \frac{\partial}{\partial z} P^{-1} (\hat{R}^R + \hat{R}_z^{T})^{-1} \frac{\partial}{\partial z} D_{uz}^{\,T}(\Omega) \} P \tag{8}$$

In the next sections, the results for nematic and smectic phases shall be discussed separately.

NEMATIC PHASES

In a nematic phase, the second term in the integral is zero, and $D(\underline{u})$ can be easily calculated by assuming the translational diffusion tensor diagonal and axially symmetric in a molecular axis system. Denoting by θ the angle between $\underline{u}$ and $\underline{n}$, we have :

$$D(\theta) = D_{\parallel} \cos^2\theta + D_{\perp} \sin^2\theta \tag{9}$$

$$D_{\parallel} = \{ D_{\parallel}^{\,T} + 2D_{\perp}^{\,T} + 2(D_{\parallel}^{\,T} - D_{\perp}^{\,T})\, \overline{P}_2 \} / 3 \tag{10}$$

$$D_{\perp} = \{ D_{\parallel}^{\,T} + 2D_{\perp}^{\,T} - (D_{\parallel}^{\,T} - D_{\perp}^{\,T})\, \overline{P}_2 \} / 3 \tag{10'}$$

The principal values $D_{\parallel}^{T}$ and $D_{\perp}^{T}$ in the isotropic phase can in principle be evaluated from the Stokes-Einstein relationship for prolate ellipsoids.[6] The anisotropy ratio $D_{\parallel}^{T}/D_{\perp}^{T}$ is predicted to be:

$$D_{\parallel}^{T}/D_{\perp}^{T} = 2\,\{(2\rho^{2} - 3)\,F(\rho) + 2\rho\}\,\cdot\,\{(2\rho^{2} - 1)\,F(\rho) - 2\rho\}^{-1} \qquad (11)$$

$$F(\rho) = 2(\rho^{2} - 1)^{-\frac{1}{2}}\,\ln\{\rho + (\rho^{2} - 1)^{\frac{1}{2}}\} \qquad (12)$$

where $\rho \geq 1$ is the ratio between the semiaxes of the ellipsoid. The anisotropy ratio is then restricted to vary between one and two. The above formulation ignores the anisotropy of the viscosity, which would suggest to consider $\underline{\underline{D}}^{T}$ as diagonal in the laboratory frame. This anisotropy effect is clearly manifested by the experimental ratio $D_{\parallel}/D_{\perp} \neq 1$ for the quasi-spherical methane molecule.[2] As already done for the rotational diffusion,[7] a possible improvement of the theory might consist in the inclusion of viscosity anisotropy into the hydrodynamic friction coefficients.[8]

SMECTIC-A PHASES

In smectic phases, the angular dependence of the translational diffusion tensor introduces a roto-translational coupling into the problem even if the distribution function $P(z,\Omega)$ is factorized. Actually, if a McMillan[9] form for the mean-field potential is assumed, $P(z,\Omega)$ is not factorizable, and this gives rise to a more important coupling term. Therefore, a complete basis on the (z,Ω) variables is needed to represent the operator $\hat{R}^{R} + \hat{R}_{z}^{T}$, and thus to solve numerically, by inversion, the kernel in Eq. (8). A convenient basis is provided by the products of Wigner functions and the set of functions $\exp(2\pi imz/d)$ periodic in the layer spacing d. However, if the time scale for rotational motions can be assumed to be faster than the time scale for translations, i.e. if $|\underline{\underline{D}}^R| >> |\underline{\underline{D}}^T| / d^2$, then a projection of the diffusion operator onto the subspace of the slow variable z can be performed. From the Stokes-Einstein relations, the above condition is expected to be valid when the molecular dimensions are lesser than d, i.e. for the motion of small solute probes. With the following definitions for the orientational and spatial averages of a general function $f(z,\Omega)$:

$$\bar{f}(z)\, P^T(z) = \int d\Omega\, f(z,\Omega)\, P(z,\Omega) \tag{13}$$

$$<\bar{f}\, P^T> = \int_0^d dz\, \bar{f}(z)\, P^T(z) \tag{13'}$$

the expression for $D(\underline{u})$ becomes:

$$D(\underline{u}) = <\bar{D}^T_{uu}\, P^T> - <P^T\, \bar{D}^T_{uz} \frac{\partial}{\partial z} \left\{ \frac{\partial}{\partial z} \bar{D}^T_{zz}\, P^T \frac{\partial}{\partial z} \right\}^{-1} \cdot \frac{\partial}{\partial z} \bar{D}^T_{uz}\, P^T > \tag{14}$$

In the above equations, $P^T(z)$ represents the reduced translational distribution function, normalized in the d-interval. We again proceed in the same manner as in ref. 1 to calculate explicitely the second term at the right-hand side of Eq. (14), and to obtain the components $D_{\|}$ and $D_{\perp}$ of $D(\theta)$:

$$D_{\|} = d^2 \left[\int_0^d dz\, \frac{3 / P^T(z)}{D_{\|}^T + 2D_{\perp}^T + 2(D_{\|}^T - D_{\perp}^T)\, \bar{P}_2(z)} \right]^{-1} \tag{15}$$

$$D_{\perp} = \{ D_{\|}^T + 2D_{\perp}^T - (D_{\|}^T - D_{\perp}^T) <\bar{P}_2> \} / 3 \tag{15'}$$

Notice that $\overline{P}_2$, the orientationally averaged second-rank Legendre polynomial, is positionally dependent as a consequence of Eq. (13). If the z-dependence of $\overline{P}_2$ could be ignored, one would obtain for $D_{||}$ a result analogous to Eq. (10) for the nematics, except for the multiplying factor:

$$d^2 \{ \int_0^d dz \,/\, P^T(z) \}^{-1} \qquad (16)$$

In the limit of steep translational distributions, this factor assumes the Arrhenius-type form:[10]

$$\pi \, \Delta \, \exp \, (-\Delta) \qquad (17)$$

where Δ in kT units is the barrier height for a translational jump across the smectic layers.

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