CHAPTER 4

ESR AND LIQUID CRYSTALS: STATISTICAL MECHANICS AND GENERALISED SMOLUCHOWSKI EQUATIONS

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ABSTRACT. A general overview of molecular dynamics in liquid crystals is presented, which will serve as the basis for our discussion of ESR experiments.

1. Introduction

In the last two decades, there have been numerous investigations of molecular structure and dynamics of liquid crystals using magnetic resonance techniques [1]. In analysing the magnetic resonance data we are primarily concerned with microscopic details such as rotational/translational diffusion coefficients and the local ordering of the liquid crystals. ESR spin probes have been utilised in extensive studies of thermotropic, lyotropic [1,2] and polymeric liquid crystals. Powerful numerical and analytical methods have been developed to interpret the molecular dynamics in liquid-crystalline phases from the ESR experiments [2-7]. More recently, new time domain techniques have been developed which show the promise of resolving subtle but important aspects of the motional models that are needed to describe the various liquid-crystalline phases [8]. Unlike ordinary liquids, the dynamics in liquid crystals involves cooperative motions extending over macroscopic distances [9,10]. Important manifestations of such motions appear near phase transitions, where near singularities in spin relaxation rates characterised by critical exponents are observed [7,11,12,13]. Thus, the statistical mechanics of liquid-crystalline phase transitions can also be explored through careful magnetic resonance studies [7,13].

We shall summarise the work that has been accomplished with emphasis on the results from our laboratory. We will cover the experimental as well as the theoretical aspects. However, we refer the reader to the original papers for further details.

2. Rotational and Translational Motion in Ordered Fluids

Our starting point for describing the diffusion of a probe molecule under the influence of an ordering potential, such as that due to a liquid-crystalline environment, is the Smoluchowski equation for the motion of a single molecule which undergoes rotational diffusion [5,14,15,16]:

$$\partial P_{\mathrm{R}}(\Omega,t)/\partial t = \left[\mathbf{J}\left\{.\mathbf{D}_{\mathrm{R}}(\Omega,t).\mathbf{J} + \left[\mathbf{J}\ U_{\mathrm{R}}(\Omega)\right]/k_{\mathrm{B}}T\right\}\right]P_{\mathrm{R}}(\Omega,t). \tag{1}$$

In this equation $P_{\mathrm{R}}(\Omega,t)$ is the time dependent probability distribution for the orientation of a molecule relative to a laboratory fixed coordinate frame; $\Omega(\equiv\alpha\beta\gamma)$ is the set of Euler angles specifying the orientation. $\mathbf{D}_{\mathrm{R}}(\Omega,t)$ is the rotational diffusion tensor, and it is usually defined in a molecule fixed frame. The operator $\mathbf{J}$ is the vector operator that generates an infinitesimal rotation of the molecule. In the simple case when $\mathbf{D}_{\mathrm{R}}(\Omega)$ is time independent in its molecular symmetry frame and is taken to be axially symmetric, this operator leads to:

$$\mathbf{J}.\mathbf{D}_{\mathrm{R}}(\Omega).\mathbf{J} = -\left[D_{\mathrm{R}}^{\perp}J^{2} + (D_{\mathrm{R}}^{\mid} - D_{\mathrm{R}}^{\perp})J_{z}\right], \tag{2}$$

where $D_{\mathrm{R}}^{\perp}$ and $D_{\mathrm{R}}^{\mid}$ are the components of $\mathbf{D}_{\mathrm{R}}(\Omega)$ perpendicular and parallel to the principal axis of the molecule. The explicit forms of J^{2} and J_{z} in terms of Euler angles are given by

$$J^{2} = -\left[\frac{\partial^{2}}{\partial\beta^{2}} + \cot\beta\,\frac{\partial}{\partial\beta} + \frac{1}{\sin^{2}\beta}\left(\frac{\partial^{2}}{\partial\alpha^{2}} + \frac{\partial^{2}}{\partial\gamma^{2}}\right) - 2\,\frac{\cos\beta}{\sin^{2}\beta}\,\frac{\partial^{2}}{\partial\alpha\,\partial\gamma}\right]$$

and

$$J_{z} = -i\,\frac{\partial}{\partial\gamma}. \tag{3}$$

The more general form for fully asymmetric diffusion tensors $\mathbf{D}_{\mathrm{R}}$ is given elsewhere [17]. In equation (1), the orienting potential $U(\Omega,t)$ is the potential of mean torque given by

$$\mathbf{T}(\Omega) = i\mathbf{J}\,U_{\mathrm{R}}(\Omega); \tag{4}$$

this is the actual torque exerted on the molecule with orientation Ω in the equilibrium fluid. More precisely, $\mathbf{J}$ is defined by

$$J^{2}\,\Phi_{km}^{L}(\Omega) = L(L + 1)\,\Phi_{km}^{L}(\Omega),$$

$$J_{\pm}\,\Phi_{km}^{L}(\Omega) = \left[(L \mp k)(L \pm k + 1)\right]^{\frac{1}{2}}\Phi_{k\pm 1m}^{L}(\Omega), \tag{5}$$

$$J_{z'}\,\Phi_{km}^{L}(\Omega) = k\Phi_{km}^{L}(\Omega),$$

where the eigenfunctions $\Phi_{km}^{L}(\Omega)$ and the operators $J_{\pm}$ are given by:

$$\Phi_{km}^{L}(\Omega) = \left[(2L + 1)/8\pi^{2}\right]^{\frac{1}{2}}D_{mk}^{L}(\Omega), \tag{6}$$

$$J_{\pm} \equiv J_{x'} \pm iJ_{y'}. \tag{7}$$

In equation (6) $D_{mk}^{L}(\Omega)$ are the Wigner rotation matrices also called the generalised spherical harmonics [18], and $J_{x'}$, $J_{y'}$ and $J_{z'}$ are the x', y' and z' components of $\mathbf{J}$ in the principal axis frame of the molecule.

In a fluid environment, the molecule is also engaged in translational diffusion which may be influenced by its precise location in the oriented liquid crystal. The appropriate Smoluchowski equation for this motion is [14]

$$\partial P_T(\mathbf{r},t)/\partial t = \nabla_r \cdot \mathbf{D}_T(\mathbf{r}) \cdot \left[\nabla_r + \nabla_r U_T(\mathbf{r})/k_B T \right]_T P_T(\mathbf{r},t) \tag{8}$$

where ∇_r is the gradient operator given by

$$\nabla_r = \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}.$$

In equation (8), $P_T(\mathbf{r},t)$ is the time dependent probability distribution in the position of the molecule and $\mathbf{D}_T(\mathbf{r})$ is the translational diffusion tensor. In a macroscopically aligned uniaxial liquid crystal we may write [19]

$$\nabla_r \cdot \mathbf{D}_T(\mathbf{r}) \cdot \nabla_r = D_T^{\perp} \nabla_r^2 + (D_T^{\parallel} - D_T^{\perp})\frac{\partial^2}{\partial z^2}, \tag{9}$$

where $D_T^{\parallel}$ and $D_T^{\perp}$ are the macroscopically measured components of the translational diffusion tensor. By analogy to equation (4) we may define a potential of mean force.

$$\mathbf{F}(\mathbf{r}) = -\nabla_r U_T(\mathbf{r}). \tag{10}$$

On a more microscopic level, we may anticipate the $D_T^{\parallel}$ and $D_T^{\perp}$ might still exhibit a spatial dependence (e.g. a dependence upon z in a smectic phase reflecting the location of the molecule in the smectic layer). This would be traceable to the dependence of the microscopic viscosities on the exact position of the molecule in the liquid crystal. In a similar sense, we may expect that $\mathbf{D}_R(\Omega)$ will also depend, in general, on the precise location of the molecule in the liquid crystal, whereas $\mathbf{D}_T(\mathbf{r})$ could well depend upon the molecular orientation Ω, e.g. a long rod-like molecule will diffuse more rapidly in a direction parallel to its long axis. Similar comments clearly apply to the potentials $U_R(\Omega)$ and $U_T(\mathbf{r})$, so that more generally we may wish to consider a single $U(\mathbf{r},\Omega)$ reflecting the combined orientational and positional potential experienced by the probe molecule. The possibility of combined orientational and positional coupling of the diffusion of a molecule does follow from general statistical mechanical considerations [14]. In fact, we should allow not only for $\mathbf{D}_T(\mathbf{r},\Omega)$ and $\mathbf{D}_R(\Omega,\mathbf{r})$ but a more general diffusion tensor:

$$\mathbf{D} \equiv \begin{pmatrix} \mathbf{D}_{TT} & \mathbf{D}_{TR} \\ \mathbf{D}_{RT} & \mathbf{D}_{RR} \end{pmatrix}. \tag{11}$$

In this equation we have let $\mathbf{D}_T(\mathbf{r},\Omega) \rightarrow \mathbf{D}_{TT}$, $\mathbf{D}_R(\mathbf{r},\Omega) \rightarrow \mathbf{D}_{RR}$, and $\mathbf{D}_{RT} = \mathbf{D}_{TR}$ is a cross diffusion coefficient. Such a cross-coupling can arise for example by propeller-like motion of an appropriately shaped molecule. This equation leads to a combined Smoluchowski equation for both rotational and translational diffusion [14,19]. We shall, for simplicity, ignore the cross-diffusion term, $\mathbf{D}_{RT}$, so that the Smoluchowski equation for the combined motion becomes:

$$\partial P(\mathbf{r},\Omega,t)/\partial T = \left(\left[\mathbf{J} \cdot \mathbf{D}_R(\mathbf{r},\Omega) \cdot \left(\mathbf{J} + [J\,U(\mathbf{r},\Omega)]/k_B T \right) \right] \right.$$
$$\left. + \left[\nabla_r \cdot \mathbf{D}_T(\mathbf{r},\Omega) \cdot \left(\nabla_r + \nabla_r [U(\mathbf{r},\Omega)]/k_B T \right) \right] \right) P(\mathbf{r},\Omega,t), \tag{12}$$

where $P(\mathbf{r},\Omega,t)$ is the combined probability distribution in orientation and position of the molecule, and it is not, in general, simply separable into the two equations (1) and (8).

The equilibrium solution to equation (12) is given by:

$$P(\mathbf{r},\Omega) = \exp(-U(\mathbf{r},\Omega)/k_B T)/\int d\Omega \, d\mathbf{r} \, \exp(-U(\mathbf{r},\Omega)/k_B T). \tag{13}$$

The ordering potential $U(\mathbf{r},\Omega)$ and its associated torque (and force) are allowed to be slowly varying in time. The form of the Smoluchowski equation (12) requires two additional assumptions [14]. First that the potential is not very large, so that angular and linear momentum relaxation can occur very rapidly compared to rotational or translational motion of the molecule. Secondly that rapidly fluctuating components of the torques or forces, which induce rotational reorientation or translational motion of the molecule, average to zero in times short compared to the molecular correlation rates due to rotation and translation. This assumption does not allow for localised coupled modes of reorientation of molecules such as a simultaneous flip of two neighbouring molecules. The latter effect can be introduced into the Smoluchowski equation (equation (1)) by introducing an **R** with a memory as described later in section 4.

In isotropic systems, $U(\mathbf{r},\Omega) = 0$, and the solutions of the diffusion equations (1) and (8) are well-known. Here $D_T^{\parallel} = D_T^{\perp} = D_T$, and the conditional probabilities are given by

$$P(\mathbf{r}_0,\mathbf{r},t) = (4\pi D_T t)^{-3/2} \exp(- \mid \mathbf{r} - \mathbf{r}_0 \mid^2 /4 D_T t), \tag{14}$$

and

$$P(\Omega_0,\Omega,t) = \sum_{Lmk} \left[(2L + 1)/8\pi^2 \right] D_{mk}^L(\Omega) \, D_{mk}^{L*}(\Omega_0) \exp(-t/\tau_{mk}^L), \tag{15}$$

where $D_{mk}^L(\Omega)$, the Wigner functions, are the eigenfunctions for the rotational diffusion operator (with $U = 0$) and $(\tau_{mk}^L)^{-1}$ are the associated eigenvalues which are given by

$$(\tau_{mk}^L)^{-1} = D_R^{\perp} L(L + 1) + (D_R^{\parallel} - D_R^{\perp}) k^2. \tag{16}$$

In utilising these expressions we are also assuming $\mathbf{D}_T(\mathbf{r},\Omega) \rightarrow \mathbf{D}_T(\mathbf{r})$. In a liquid crystal $U(\mathbf{r},\Omega) \neq 0$, and the dependence of $\mathbf{D}_R$ on position and $\mathbf{D}_T$ on molecular orientation may be significant. Let us, however, assume initially, for simplicity that equations (1) and (8) apply, and that the probability distribution function $P(\mathbf{r},\Omega,t)$ is such that it can be factored into spatial and orientational dependent parts.

3. Symmetries of the Liquid-Crystalline Potential

3.1 ORIENTATIONAL POTENTIAL

In liquid crystals for which $U(\mathbf{r},\Omega) \neq 0$, a probe molecule will experience cooperative torques (cf. equation (4)) which attempt to orient the probe along a preferred direction in space. This axis is usually referred to as the director and the liquid crystal medium is said to have uniaxial cylindrical symmetry. This director is represented by a unit vector **n** such that **n** = - **n**; thus the equilibrium properties of the molecule must be described in terms of an orientation dependent potential (or potential of mean torque) which satisfies cylindrical symmetry about the director as well as inversion symmetry [9]. First we distinguish between the laboratory frame (l) in which the z axis is taken parallel to B_0, the magnetic field, and the director frame (d) in which the z" axis is parallel to **n**. We shall let Ψ be the angle between **n** and B_0 [20]. When dealing with macroscopically aligned samples, it is usually possible to select this rotation angle in an experiment. (On the other hand, if the sample is microscopically ordered but macroscopically

disordered, then it is possible to perform a sequence of calculations at different director orientations Ψ, and model the composite spectrum as the appropriately weighted integral of the spectra calculated as a function of the director orientation [21].) The equilibrium orienting potential for the molecule may be expanded in a complete orthonormal set of functions $\Phi^L_{km}(\Omega_{D,d})$ (cf. equation (6)) [or alternatively, the orthogonal set $D^L_{mk}(\Omega_{D,d})$] where $(\Omega_{D,d})$ represents the rotation of the molecular (diffusion) frame into the director frame. This set of functions may be restricted by the following phase symmetries [5]. (1) The potential is cylindrically symmetric about $\mathbf{n}$, i.e., letting $\Omega_{D,d} = (\alpha\beta\gamma)$, then the potential must be independent of the angle α (rotation about $\mathbf{n}$). This can only be so if $m = 0$. (2) Inversion symmetry of the potential means that $D^L_{0k}(\Omega_{D,d}) \propto Y^L_k(\Omega_{D,d})$, the spherical harmonic of rank L and order k has L restricted to even values. Thus we can write:

$$\frac{U(\Omega_{D,d})}{k_B T} = -\sum_{L(even)}{}' \lambda_{Lk} D^L_{0k}(\Omega_{D,d}),$$ (17)

where the coefficients λ_{Lk} are dimensionless. Since $U(\Omega_{D,d})$ is real there is an additional requirement that $\lambda^*_{Lk} = (-1)\lambda_{L-k}$, and this is indicated by the prime on the summation in this equation. The equilibrium properties of the molecule experiencing the potential of equation (17) are usually described in terms of the ordering tensor defined by

$$<D^L_{mk}> = \int d\Omega\, P(\Omega)\, D^L_{mk}(\Omega),$$ (18)

with $L = 2$ and $m = 0$ and $P(\Omega)$ given by equation (13). It has the properties of a second rank irreducible tensor. (Note $P(\Omega)$ is obtained by first averaging over $\mathbf{r}$.)

Given that we may impose certain symmetry requirements upon the potential $U(\Omega)$ we may expect that $P(\Omega)$ given by equation (13) will have the same symmetry properties. In fact, we note that equation (13) may be written as $P(\Omega) = P[U(\Omega)]$, i.e., $P(\Omega)$ is a functional of $U(\Omega)$ such that whatever symmetry operation leaves $U(\Omega)$ invariant will also leave $P[U(\Omega)]$ invariant. That is, P must contain the same symmetries as $U(\Omega)$. We now observe that equation (1) may be rewritten as:

$$\partial P_R(\Omega,t)/\partial t = -\Gamma_R P_R(\Omega,T),$$ (19)

where the rotational diffusion operator Γ_R is just

$$\Gamma_R = \left[\mathbf{J} \cdot \left\{ \mathbf{D}_R(\Omega,t) \cdot \mathbf{J} + \left[\mathbf{J}\, U(\Omega) \right]/k_B T \right\} \right].$$ (20)

Unfortunately Γ_R is a non-symmetric operator when $U(\Omega) \neq 0$, but can be symmetrised by the following similarity transformation (which is *not* unitary). Let

$$\tilde{P}(\Omega,t) \equiv P^{-1/2}\, P(\Omega,t)$$ (21)

and

$$\tilde{\Gamma}_\Omega \equiv P^{-1/2}\, \Gamma_\Omega P^{1/2},$$ (22)

where $P^{1/2}$ is the square root of the function given by equation (13), but it is treated as an operator in equations (21) and (22). Then it is easy to show that Γ_Ω becomes the symmetric operator [4,5,22]:

$$\tilde{\Gamma}_{\Omega} = \mathbf{J} \cdot \mathbf{D}_{R} \cdot \mathbf{J} + \frac{(\mathbf{J} \cdot \mathbf{D}_{R} \cdot \mathbf{J}U)}{2k_{B}T} + \frac{(\mathbf{T} \cdot \mathbf{D}_{R} \cdot \mathbf{T})}{(2k_{B}T)^{2}}, \tag{23}$$

where the torque $\mathbf{T}$ exerted on the molecule is given by equation (4). For axially symmetric rotational diffusion we may rewrite this equation as:

$$\tilde{\Gamma}_{\Omega} = \Gamma_{iso} + \Gamma_{U} \tag{24}$$

with Γ_{iso} given by equation (2), and Γ_{U} is

$$\Gamma_{U} = (2k_{B}T)^{-1}\left[D_{R}^{\perp}(J^{2}\,U) + (D_{R}^{\parallel} - D_{R}^{\perp})(J_{z'}^{2}\,U)\right]$$
$$-(2k_{B}T)^{-2}\left[D_{R}^{\perp}(J_{+}U)(J_{-}U) + D_{R}^{\parallel}(J_{z'}U)^{2}\right]. \tag{25}$$

To proceed further, we simplify the form for $U(\Omega)$. First of all, if $U(\Omega)$ is to have a relatively simple dependence upon Ω, then we should consider retaining only the lowest even L values, (since spherical harmonics of increasing L will have an increasing number of nodes). Typically, we let $L = 2$ (and sometimes 4 as well). Then the λ_{2k} in equation (17) are the five components of a second rank irreducible tensor, while the λ_{4k} are the nine components of a fourth rank irreducible tensor. [These are due to the requirement that $U(\Omega_{D,d})$ in equation (16) transforms as a scalar function, so that the right hand side of this equation is to be regarded as a sum of scalar products of irreducible tensors]. There is always a principal axis of molecular orientation for the cartesian components of λ_{2k} (i.e., the λ_{ij}^{2}) such that they are diagonalised, and this means that only the irreducible tensor components λ_{20} and $(\lambda_{22} + \lambda_{2-2})$ are non-zero in this molecular axis system. This principal axis system for orientation need not, in general, coincide with that of the rotational diffusion tensor. We shall, for simplicity assume that there is sufficient molecular symmetry that the two axis systems do coincide. For simplicity, we also assume that the λ_{4k} may also be described by this principal axis system, which is equivalent to invoking D_{2} point group molecular symmetry. Then only λ_{40}, $(\lambda_{42}+\lambda_{4-2})$, and $(\lambda_{44}+\lambda_{4-4})$ are non-zero in the axis system. If the orientation tensor of the molecule has cylindrical symmetry (point group $D_{\infty h}$), then the potential must be independent of angle α in equation (17), i.e., we must restrict the expansion of $U(\Omega_{D,d})$ to terms for which $k = 0$. Then only λ_{20} (and λ_{40}) will be non-zero in our approximation of retaining just the lowest values of L. (We shall usually restrict the rotational diffusion tensor to be cylindrically symmetric as we have described. By equation (2) there is still a dependence upon the quantum number k (hence rotations by angle γ). It is often important to retain the $\lambda_{2\pm2}$ terms in the potential, giving rise to an asymmetric ordering tensor, since such orientational asymmetry does have significant effects which may be distinguished in the ESR spectrum.)

3.2. OTHER SYMMETRIES

The symmetries which we have noted are the ones most commonly used in the simulations of ESR experiments, but others may be necessary as various ordered phases are considered in more detail. We now consider examples of such situations.

3.2.1. *Director Tilt.* (a) In smectic phases such as S_{C} , the orientational or nematic director $\mathbf{n}$ is tilted from the normal to the smectic layers. In this case, if a well-aligned single-crystal-like sample is prepared, we should just continue to use the director frame in which z'' is parallel to $\mathbf{n}$

(but see later). Our orientation dependent ESR spectra in the aligned S_C phase of 4,4'-di-n-heptyloxyazoxybenzene using a highly ordered probe, which were performed by rotating the magnetic field to an angle close to the S_C tilt during the preparation in order to obtain true monodomains, showed no signs of director distribution that are typical of spectra due to macroscopic disorder in two dimensions, i.e., the plane containing the magnetic field and the director. Thus, our results were consistent with the S_C phase being rather similar to S_A, but with the director axis tilted from the normal to the layer (see also Chapter 15)

(b) Another model, suggested for lipid bilayers, is based on measured tilts of the hydrocarbon chain, whereas the region at or near the phospholipid head group is not tilted. Then we may conceive of a cooperative rotation of the chains in a cone. We may take the director n to be parallel to the layer normal, but we must recognise the fact that the chain axis prefers to be tilted by an angle β_t with respect to n, although all orientations in the $x'y'$ plane are equally likely. This may be achieved by a potential of the form $AY_{20}(\beta,0)+BY_{40}(\beta,0)$ or $a\cos^2\beta+b\cos^4\beta$ with B/A (or b/a) adjusted such that the potential minimum occurs at β_t. (Of course higher order $Y_{L0}(\beta,0)$ could be added if desired.

3.2.2. Biaxial Phases. A biaxial phase would imply that even a rod-like molecule would align with a preferential alignment along the laboratory x'' and y'' axes (or vice-versa), so that there would no longer be cylindrical symmetry in the laboratory frame about the mean director n (with n parallel to the smectic normal). We would have to impose another director $\hat{d}_c$ perpendicular to n. (Note that in the special case of smectic C alignment, case 3.2.1.(a), it was possible to remove this complication by a redefinition of n no longer parallel to the smectic normal). We now discuss some cases of this situation.

(a) Quasi-biaxiality: Hexagonal Packing. Smectic B phases involve positional order within the smectic layer corresponding to hexagonal packing [25]. Such six-fold symmetry about n would imply that $U(\Omega)$ be expanded in $D_{mk}^L(\Omega)$ such that $m = 6n$, $n = 0, \pm1, \pm2$, since these are invariant to the C_6 group operations. However, whereas this reduces the symmetry from cylindrical, there is sufficient symmetry that there is no preferential axis of alignment in the $x''y''$ plane [i.e., $< D_{k\pm2} >$ of equation (18) is zero], so this is not a true case of biaxiality from the molecular point of view. In fact, for a potential expandable in D_{mk}^L with $L \le 4$, there will be no distinction between six-fold and cylindrical symmetry; we would have to include $L \ge 6$ terms, and they are very likely to be small [25].

(b) True biaxiality: e.g., lipid bilayers with aligned head groups. When there are distinct laboratory x'' and y'' axes for alignment such that both n || z'' and $\hat{d}_c$ || x'' need to be specified, then in this axis frame we may again invoke D_2 symmetry, but in the laboratory frame. Thus, we would utilise $D_{mk}^L(\Omega)$ with $m = 0, \pm2, \pm4$ ... in this principal laboratory axis system, and the extent of biaxiality on the molecular alignment would be measured by $< D_{k\pm2}^2 >$, for example.

3.3. COMMENTS

This discussion and these examples are based upon the fact that the $D_{mk}^L(\Omega)$ functions for $(\alpha\beta\gamma)$ transform as spherical harmonics $Y_{Lk}^*(\beta,\gamma)$ in the molecular frame and also as spherical harmonics $Y_{Lm}(\beta,\alpha)$ in the laboratory frame, so that we can simultaneously impose laboratory frame and molecular symmetries upon the $U(\Omega)$ expandable in these functions. This is specifically related to the property of the $D_{mk}^L(\Omega)$ that they transform as double tensors [26].

3.4. ANISOTROPIC VISCOSITY

Because of this double tensor property of the $D_{mk}^{L}(\Omega)$, we can by analogy to equation (2) introduce $\hat{\mathbf{J}}$, the vector operator for infinitesimal rotation with respect to the laboratory coordinates. Then, for an ordered fluid, there can be an anisotropic viscosity even for a spherical molecule. Equation (2) becomes

$$\Gamma_\Omega = \hat{\mathbf{J}} \cdot \mathbf{D}_R \cdot \hat{\mathbf{J}}, \tag{26}$$

where

$$\hat{J}^2 \, \Phi_{km}^L(\Omega) = L(L + 1) \, \Phi_{km}^L(\Omega)$$

$$\hat{J}_\pm \, \Phi_{km}^L(\Omega) = \left[(L \mp M + 1)\right]^{1/2} \, \Phi_{km\pm1}^L(\Omega) \tag{27}$$

$$\hat{J}_{z'} \, \Phi_{km}^L(\Omega) = M\Phi_{km}^L(\Omega).$$

In a uniaxial laboratory frame we have $D_R^{z'z'} = D_R^{\parallel}$ and $D_R^{x'x'} = D_R^{y'y'} = \hat{D}_R^{\perp}$ and equation (26) becomes

$$\Gamma_\Omega = \hat{D}_R^{\perp} \hat{J}^2 + (\hat{D}_R^{\parallel} - \hat{D}_R^{\perp}) \hat{J}_{z'}^2 \tag{28}$$

with the eigenfunctions $\Phi_{km}^L(\Omega)$ of equation (26) and eigenvalues

$$(\hat{\tau}_{mk}^L)^{-1} = \left[\hat{D}_R^{\perp} L(L + 1) + (\hat{D}_R^{\parallel} - \hat{D}_R^{\perp}) m^2\right]. \tag{29}$$

The problem of combined anisotropic diffusion and anisotropic viscosity is difficult to treat in the general case. Lin and Freed [27] have discussed some general properties of such a diffusion equation and Moro et al. have discussed a hydrodynamic model [19,31].

3.5. SMECTIC POTENTIAL AND ORIENTATIONAL-POSITIONAL COUPLING

We now consider positional order that exists in smectic phases, and how to introduce the appropriate symmetries for $U_T(\mathbf{r})$. In these phases there is a characteristic repeat distance d, the smectic layer thickness, which is of molecular dimensions. Thus, we can Fourier analyse $U_T(\mathbf{r})$ along the z'' axis [28,29]:

$$U_T(\mathbf{r})/k_B T = \sum_{m=1}^{\infty} a_m \cos\left[(2m\pi z''/d) - \phi\right], \tag{30}$$

where $\phi \equiv 2\pi z_0''/d$, is a phase shift which specifies the origin of the coordinate system. For example, the arbitrary zero of $U_T(\mathbf{r})$ may be chosen to be at $z'' = md$, where $m = 0, 1, 2, ...,$ by selecting $\phi = \pi/2$, so $z_0'' = d/4$. Usually, only the leading terms, e.g., a_1, are taken as non-zero. When we consider the total potential $U(\mathbf{r},\Omega)$, then we should expand it in products of $D_{mk}^L(\Omega)$ and $\cos[(2m\pi z''/d)-\phi]$. A simple form for the S_A phase, that is suggested by McMillan's molecular field theory of the smectic phase transition [30], has been used by Moro and Nordio [19,32]; it is

$$U(\beta,z'')/k_B T = [A + B\cos(2m\pi z''/d)]D_{00}^2(\Omega) + C\cos(2m\pi z''/d). \qquad (31)$$

The A term reflects the molecular potential for an axially symmetric molecule relative to the nematic director, and the C term is the smectic potential. The significant new feature is the B term, a coupled orientational-positional potential term representing the idea that the orientational (positional) potential of the probe molecule should depend upon the probe location (orientation) within the smectic layer.

4. Relative Translational Diffusion: The Pair Correlation Function

The ESR techniques for measuring microscopic translational diffusion actually examine the relative diffusion of two probe molecules A and B [33]; i.e., $U(r_A,r_B)$, and there is a general diffusion tensor [14]:

$$\mathbf{D}_T \equiv \begin{pmatrix} \mathbf{D}_{AA} & \mathbf{D}_{AB} \\ \mathbf{D}_{BA} & \mathbf{D}_{BB} \end{pmatrix}, \qquad (32)$$

where $\mathbf{D}_{BA} = \mathbf{D}_{AB}$. If we focus on the relative motion of these two molecules, and ignore any other effects such as external fields or ordering potentials, then we can write the Smoluchowski equation for the motion of the relative coordinate $\mathbf{r} = \mathbf{r}_A - \mathbf{r}_B$ as

$$\partial P_T(\mathbf{r},t)/\partial t = \nabla_r \cdot \mathbf{D}_T(\mathbf{r}) \cdot [\nabla_r + F(\mathbf{r})/k_B T]P_T(\mathbf{r},t) \qquad (33)$$

which has the same form as equation (8), but now

$$D_T(\mathbf{r}) = \mathbf{D}_{AA} + \mathbf{D}_{BB} - \mathbf{D}_{AB} + \mathbf{D}_{BA} \qquad (34)$$

and the mean relative force

$$\mathbf{F}(\mathbf{r}) = -\nabla_{r_A} U(\mathbf{r}) = \nabla_{r_b} U(\mathbf{r}) = -\nabla_r U(\mathbf{r}) \qquad (35)$$

with $U(\mathbf{r})$ denoting the potential of mean force between molecules A and B. We may obtain $U(\mathbf{r})$ from the equilibrium radial distribution function g(r) [34], i.e.,

$$\ln g(\mathbf{r}) \equiv -U(\mathbf{r})/k_B T \qquad (36)$$

so that the effective force becomes:

$$\mathbf{F}(\mathbf{r}) = \nabla_r \ln g(\mathbf{r}). \qquad (37)$$

This means that in the limit $t \to \infty$, $P_T(\mathbf{r},t)$ will yield the equilibrium value g(r), whereas for finite times, $F(\mathbf{r})$ is the driving force acting to restore this equilibrium. Relative translational diffusion in both three and two dimensions [35] has been studied in this context (but with $\mathbf{D}_{AB} = 0$) displaying the importance of the radial distribution function on the motion.

5. Fluctuating Torques and Slowly Relaxing Local Structures

The spin probe dissolved in a liquid crystal environment is oriented with respect to the solvent

molecules surrounding it. Besides the potential of mean torque, it also experiences fluctuating torques from the time dependent interactions with the surrounding molecules. In particular, the rapid random components of the fluctuating torques give rise to the frictional resistance to rotational motion, from which the diffusion tensor D_R may be calculated in the brownian motion limit. Our development in the preceding sections assumed the basic validity of this brownian motion limit. When, however, the probe molecule is not much larger than the solvent molecules, it experiences fluctuating torques with relaxation times not much faster than that of the probe molecule, and this can lead to non-brownian effects on the molecular motion.

A general approach to this problem was provided by Hwang and Freed [14]. We shall use a somewhat simpler approach [15], wherein we consider only rotational motion, to illustrate two general cases that arise depending upon the time scale of the fluctuating torques. What is observed, after the incorporation of the effects, is non-exponential relaxation behaviour with Fourier transforms yielding non-Debye types of spectral densities. We begin with the generalised Fokker-Planck equation and reduce it to its Smoluchowski form. Then we consider the two limiting situations corresponding to fluctuating torque modes that are fast compared to $R_\parallel^{-1}$ or $R_\perp^{-1}$ and modes that are slow compared to τ_R. We refer to these cases as the fluctuating torques and the slowly relaxing local structure models, respectively.

The generalised Fokker-Planck equation for probe molecule B in the liquid crystal may be written for the distribution function $f_B(\Omega,L_B,t)$ as

$$\left[\frac{\partial}{\partial t} - i\omega_B . \mathbf{J} + L_B . (\nabla_L)_B + <T_B> . (\nabla_L)_B \right] f_B(t)$$

$$= (\nabla_L)_B . \int_0^t d\tau\, G(t - \tau) . \left[\omega_B/k_B T + (\nabla_L)_B\right] f_B(\tau), \tag{38}$$

where ω_B is the angular velocity of molecule B, L_B is its angular momentum, and $\mathbf{J}$ is again the vector operator that generates infinitesimal rotations. The third term $(L_B.(\nabla_L))$ is the inertial (or precessional term whereas $<T_B>$ represents the mean torque experienced by particle B. (The instantaneous torque is just $T_B(t)$, and the angular brackets imply ensemble averaging). Also, $G(t - \tau)$ is the operator equivalent of the correlation function for the fluctuating or random torques on particle B, and its calculation is, in principle, a many body problem. The random part of the torque has a zero time average. If we assume that $G(t)$ relaxes extremely rapidly so that it has a white noise spectrum [i.e., $G(t) = G_0\delta(t)$], then equation (38) becomes the typical Fokker-Planck equation for rotational reorientation of a brownian particle.

Assuming that the angular momentum L_B relaxes on a much shorter time scale compared to both D_R^{-1} and any fluctuations in the $<T_B>$ term, we may proceed to obtain the generalised Smoluchowski form by integrating over the angular momenta after a generalised perturbational approach, based upon the rapidity of angular momentum relaxation, is introduced. We obtain [5,14]:

$$\partial P(\Omega,t)/\partial t = \int_0^t d\tau\, i\mathbf{J} . \mathbf{D}_R(t - \tau) . \left[i\mathbf{J} + <T_B(t,\Omega)>/k_B T\right] P(\Omega,\tau), \tag{39}$$

where $\mathbf{D}_R(t)$ is a time dependent rotational diffusion tensor defined by its Fourier-Laplace transform $\mathbf{D}_R(s)$ (where $s = i\omega$):

$$\mathbf{D}_R(s) = (k_B T)^2\, \mathbf{K}^{-1}(s) \tag{40}$$

and $\mathbf{K}(t)$ is given by

$$K(t) = \left\langle \left(T_B(t = 0) - \langle T_B \rangle\right)\left(T_B(t) - \langle T_B \rangle\right)\right\rangle \qquad (41)$$

i.e., the actual time correlation function of the fluctuating part of the torque averaged over the ensemble of solvent molecules. Using the fluctuation-dissipation theorem we may relate $K(s)$ to a friction tensor

$$K(s) = I k_B T \beta(s), \qquad (40a)$$

where $\beta(s)$ is the friction tensor, and I is the moment of inertia tensor. Hence $D_R(s)$ may be looked upon as the generalised rotational diffusion coefficient which is frequency dependent because of the fluctuations in $T(\Omega,t)$. If the memory in $D_R(t)$ is extremely short [i.e., $D_R(t) = D_R^0 \delta(t)$, with $\delta(t)$ the Dirac delta function], then equation (39) becomes just the rotational Smoluchowski equation given by equation (1). To proceed further, we must know the time scale of the various fluctuation modes. We decompose the effects of the spectrum of fluctuating torques into two parts for simplicity: (i) the faster components for which $\tau_m < \tau_R$, that lead to the diffusive type reorientations and which are included in equations (40) and (41), and (ii) the more persistent components, which represent systematic local torque effects over time scales greater than τ_R, but which average out in times $\tau_x > \tau_R$. They are included in a slow time varying mean $\langle T_B(t) \rangle$ with correlation time τ_x. The components relaxing on the order of τ_R will contribute both types of effects, but, because of the greater complexity of their analysis, we implicitly include them in both types of effects.

5.1. FLUCTUATING TORQUE INDUCED REORIENTATION

It is important to remember that the $\langle T_B \rangle$ is non-zero in liquid-crystalline phases due to the presence of an average orienting potential felt by the probe molecule. Further, assuming a single exponentially decaying correlation function,

$$K(t) = I k_B T V^2 \exp(-t/\tau_m)$$

we obtain for $D_R(\omega)$:

$$D_R(\omega) = (k_B T / I V^2)(-i\omega + \tau_m^{-1}) = D_R(0)(1 - i\omega\tau_m^{-1}). \qquad (42)$$

This equation can easily be generalised to take into account the anisotropic nature of D_R. It is convenient to Fourier-Laplace transform equation (39) to give

$$\left[-i\omega - D_R(-i\omega)\right]\left[J^2 - iJ \langle T_B \rangle / k_B T\right]P(\Omega, -i\omega) = P(\Omega, t = 0) \qquad (43)$$

and solve this equation by expanding $P(\Omega,-i\omega)$ in the complete orthonormal set of functions Φ_{km}^L given by equation (6); further details may be found elsewhere [5,14]. Because of the complexity of the results, we only give here that for $\langle T_B \rangle = 0$:

$$J_{mk}^L(\omega) = \frac{\tau_{mk}^L}{1 + \varepsilon_{mk}^L (\tau_{mk}^L)^2 \omega^2}, \qquad (44)$$

where the τ_{mk}^{L-1} are given by equation (16) corresponding to the eigenfunctions Φ_{km}^L, and

$$\varepsilon_{mk}^{L} = \left(1 + \tau_m/\tau_{mk}^{L}\right)^2.$$ (45)

The parameter ε_{mk}^{L} represents the correction to the Debye spectral densities. It is also possible to consider anisotropy in the fluctuating torques as well as $<T_B> \neq 0$ [5,14]. Added in proof: A recent general analysis of this case by the multi-dimensional Fokker-Planck-Kramer's method shows that the range of validity of equation (45) is limited to $(\tau_m/\tau_{mk}^{L}) \ll 1$. This new work gives the complete numerical solution; [cf. Polimeno, A. and Freed, J. H. (1990) Chem. Phys. Lett., **174**, 338.]

5.2. FLUCTUATIONS IN THE LOCAL STRUCTURE

In this case we neglect any memory in $\mathbf{D}_R(t)$ and assume that it becomes time independent in either a body fixed or a laboratory fixed frame. In the body fixed case

$$\partial P(\Omega,t)/\partial t = -i\mathbf{J} \cdot \mathbf{D}_R(\Omega) \cdot \left[i\mathbf{J} - <\mathbf{T}_B(t,\Omega)>/k_B T\right]P(\Omega,t).$$ (46)

Now we decompose $<\mathbf{T}_B(t,\Omega)>$ as:

$$<\mathbf{T}_B(t,\Omega)> = \mathbf{T} + \mathbf{T}'(t,\Omega),$$ (47)

where $\mathbf{T}$ is the true mean component and $\mathbf{T}'$ is a slowly fluctuating time dependent component with relaxation time τ_x such that $\tau_x \gg \tau_R$. This means $<\mathbf{T}_B(t,\Omega)>$ remains essentially constant over time intervals in which molecular reorientation of particle B occurs. We may regard $\mathbf{T}'$ as quasistatic, and calculate an ESR lineshape due to the combined effect of $\mathbf{T} + \mathbf{T}'$. Then we consider the effects of $\mathbf{T}'$ on a longer time scale. (More complicated cases of cooperative hydrodynamic modes of fluctuation near phase transitions fall under this category and are treated in detail in Chapter 14). We shall assume $|\mathbf{T}'| \neq 0$, and define the local director orientation with respect to the laboratory z axis by Euler angles Θ. It is further necessary to define the local order parameter Q_m:

$$Q_m = S_1 D_{0m}^{L}(\Theta).$$ (48)

We then calculate the spectral densities as a function of Θ and average them over an isotropic reorientation of Θ with the slow relaxation time τ_x [5,12,36]. It leads to the prediction that the spectral densities become:

$$J_{mk}^{L}(\omega) = \frac{\tau_{mk}^{L}}{\left(1 + \omega^2 (\tau_{mk}^{L})^2\right)}(1 - S_1^2) + \frac{S_1^2 \tau_x}{1 + \omega^2 \tau_x^2}.$$ (49)

Note that spectral densities of this form may be written down quite generally for any relaxation process whose correlation function is expressed as the sum of two exponential decays, and the slowly relaxing local structure model is one such case that is believed to be relevant in molecular dynamics in ordered fluids. Added in proof: This model has now been studied in great detail including the range of validity of equation (49); [cf. Polimeno, A. and Freed, J. H. (1990) Chem. Phys. Lett. **174**, 481.]

References

[1]   (a) Emsley, J. W. (1985) Nuclear Magnetic Resonance of Liquid Crystals, D. Reidel
       Publisher (ed.), Boston; (b) Freed, J. H. (1987) Rotational Dynamics of Small and
       Macromolecules in Liquids, T. Dorfmuller and R. Pecora (eds.), Springer Verlag
       Publishers, Berlin, pp. 89-142; (c) Emsley, J. W. and Linden J. C., (1975) NMR
       Spectroscopy Using Liquid Crystal Solvents, Pergamon Publishers, New York; (d)
       Luckhurst, G R. and Gray, G. W. (eds.) (1979) Molecular Physics of Liquid Crystals,
       Academic Publishers, New York; (e) Luckhurst, G. R. (1972) Electron Spin Relaxation
       in Liquids, L. T. Muus and P. W. Atkins (eds.), Plenum Publishers, New York, Ch.XV.

[2]   Freed, J. H. (1976) Spin Labeling: Theory and Applications, Berliner, L. J. (ed.), Academic
       Publishers, New York, Ch.3.

[3]   (a) Nordio, P. L. and Busolin, P. (1971) J. chem. Phys., 55, 5485; (b) Nordio, P. L., Rigatti,
       G. and Segre, U. (1972) J. chem. Phys., 56, 2117.

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

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

[6]   (a) Luckhurst, G. R., Setaka, M. and Zannoni, C. (1974) Molec. Phys., 28, 49;
       (b) Luckhurst, G. R. and Yates, R. N. (1976) J. Chem. Soc. Faraday Trans. II., 72, 996;
       (c) Luckhurst, G. R. and Zannoni, C. (1977) Proc. R. Soc. Lond. Ser A, 352, 87;
       (d) Kventsel, G. F., Luckhurst, G. R. and Zewdie, H. B. (1985) Molec. Phys., 56, 589.

[7]   Zager, S. A. and Freed, J. H. (1984) Chem. Phys. Lett., 109, 270.

[8]   Gorcester, J., Rananavare, S. B. and Freed, J. H. (1989) J. chem. Phys., 90, 5764.

[9]   de Gennes, P. G. (1974) The Physics of Liquid Crystals, Oxford, New York.

[10]   (a) Brochard, F. (1973) J. Phys. Paris, 34, 411. (b) Jahnig, J. and Brochard, F. (1974) J.
       Phys. Paris, 35, 301.

[11]   Doane, W. (1981) Magnetic Resonance of Phase Transitions, C. P. Poole (ed.), Wiley, New
       York.

[12]   Freed, J. H. (1977) J. chem. Phys., 66, 118.

[13]   Rao, K. V. S., Hwang, J. S. and Freed, J. H. (1976) Phys. Rev. Lett., 37, 515.

[14]   Hwang, L. P. and Freed, J. H. (1975) J. chem. Phys., 63, 118.

[15]   Hwang, J. S., Mason, R. P., Hwang, L. P. and Freed, J. H. (1975) J. phys. Chem., 79, 489.

[16]   Favro, L. D. (1965) Fluctuation Phenomena in Solids, R. E. Burgess (ed.), Academic, New
       York, pp. 79-101.

[17]   Freed, J. H. (1964) J. chem. Phys., 41, 2077.

[18]   Rose, M. F. (1957) Elementary Theory of Angular Momentum, Wiley, New York.

[19]   Moro, G., Segre, U. and Nordio, P. L. (1985) Nuclear Magnetic Resonance of Liquid
       Crystals, J. W. Emsley (ed.), D Reidel Publisher, Boston, Ch.9.

[20]   Schneider, D. J. and Freed, J. H. (1989) Biological Magnetic Resonance, L. J. Berliner and
       J. Reuben (eds.), Plenum, New York, Vol. 8, Ch.1.

[21]   Meirovitch, E., Nayeem, A. and Freed, J. H. (1984) J. phys. Chem., 88, 3454.

[22]   Meirovitch, E., Igner, D., Moro, G., Igner, E. and Freed, J. H. (1982) J. chem. Phys., 77,
       3915

[23]   Gray, G. W., [1(d)], Ch.12.

[24]   Doane, J. W., [1(a)], Ch.18, 19.

[25] Meirovitch, E. and Freed, J. H. (1980) J. Phys. Chem., **84**, 2459.

[26] Biedenharn, L. C. and Louck, J. D. (1981) Angular Momentum in Quantum Physics, Addison Wesley, Reading.

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

[28] Wojtowicz, P. J. (1975) Introduction to Liquid Crystals, E. B. Priestley, P. J. Wojtowicz and P. Sheng (eds.), Plenum, New York, Ch.7.

[29] Meyer, R. and Lubensky, T. (1976) Phys. Rev. A14, 2307.

[30] McMillan, W. L. (1971) Phys. Rev., A4, 1238.

[31] Moro, G. and Nordio, P. L. (1984) Molec. Crystals liq. Crystals, **104**, 361.

[32] Moro, G. and Nordio, P. L. (1985) J. phys. Chem., **89**, 997.

[33] Nayeem, A., Rananavare, S. B., Sastry, V. S. S. and Freed J. H. (1989) J. chem. Phys., **91**, 6887.

[34] Hwang, L. P. and Freed, J. H. (1975) J. chem. Phys., **63**, 4017.

[35] (a) Zientara, G. P. and Freed, J. H. (1979) J. chem. Phys., **71**, 3861. (b) Korb, J. P., Ahadi, M., Zientara, G. P. and Freed, J. H. (1987) J. chem. Phys., **86**, 1125.

[36] (a) Zager, S. A. and Freed, J. H. (1982) J. chem. Phys., **77**, 3344. (b) ibid, (1982) **77**, 3360.