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The inclusion of electrostatic and dispersion interactions into potentials of mean torque for solutes dissolved in uniaxial liquid crystal solvents

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A potential of mean torque is derived for a solute at infinite dilution in a uniaxial liquid crystal solvent, which contains terms originating from the dispersion interaction, and the electrostatic interaction between quadrupole moments on both molecules. It is shown that the electrostatic term is non-zero only if the solute–solvent vectors are distributed with lower than spherical symmetry. If this distribution has cylindrical symmetry then both the electrostatic and dispersion terms in the potential of mean torque are shown to depend on order parameters for the orientational distribution of the solute–solvent vectors, as well as on the order parameters of the solvent molecules.

1. Introduction

The basic idea of mean field theories of the orientational order of molecules in uniaxial liquid crystals, or of solutes dissolved in them, is to represent the average, anisotropic potential energy by a potential of mean torque, $U(\beta,\gamma)$, where β and γ are the polar angles made by the mesophase director in a molecule-fixed frame. A general approach to obtaining the angular dependence of $U(\beta,\gamma)$ is to recognize that it must be a continuous, well-behaved function of these variables, and so can be expanded as an infinite set of modified spherical harmonics, $C_{L,m}(\beta,\gamma)$, of even rank, thus [1]

$$U(\beta,\gamma) = -\Sigma_{L,\,\mathrm{even}}\Sigma_m \varepsilon_{L,m} C_{L,m}(\beta,\gamma). \tag{1}$$

Of course, to be useful the expansion must be terminated, and most theories have adopted the simplest form, that with $L=2$ and $m=0$, ± 2, giving

$$\begin{aligned} U(\beta,\gamma) &= -\varepsilon_{2,0}C_{2,0}(\beta,\gamma) - \varepsilon_{2,2}C_{2,2}(\beta,\gamma) - \varepsilon_{2,-2}C_{2,-2}(\beta,\gamma), \\ &= -\varepsilon_{2,0}C_{2,0}(\beta,\gamma) - 2\,\mathrm{Re}(\varepsilon_{2,2}C_{2,2}(\beta,\gamma)). \end{aligned} \tag{2}$$

The $\varepsilon_{2,m}$ are expansion coefficients to be obtained by comparison with experiment. To progress further it is usual to assume that the $\varepsilon_{2,m}$ depend on $\bar{C}_{2,m}$, the orientational order parameters of the liquid crystal molecules, so that

$$\varepsilon_{2,m} = \Sigma_n \bar{u}_{2mn} \bar{C}_{2,m}. \tag{3}$$

The coefficients $\bar{u}_{2mn}$ are dependent on the strength of the anisotropic intermolecular interactions. This is the simplest expression for the $\varepsilon_{2,m}$ which satisfies the necessary condition that these coefficients vanish if the sample is isotropic.

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A convenient way to test whether this truncated form of $U(\beta,\gamma)$ is indeed a reasonable approximate form for the potential of mean torque is to obtain values for the coefficients from observed values of the orientational order parameters, $\bar{C}_{2,m}$. Such studies on pure liquid crystals are complicated by the molecular flexibility that invariably exists. The importance of this factor can be reduced by studying the orientational order of solutes dissolved in liquid crystal solvents; the choice of a rigid solute confines the complication of non-rigidity to the solvent. The potential of mean torque, $U(\beta_2,\gamma_2)$, for a solute at infinite dilution in a uniaxial solvent has the same form as equation (2), and the $\varepsilon_{2,n}$ are still given by equation (3), with the $\bar{C}_{2,m}$ as the order parameters of the solvent [2], and the $\bar{u}_{2mn}$ being determined by the strength of anisotropic, solute–solvent interactions. Note that m refers to the solvent and n to the solute.

The values of the $\varepsilon_{2,n}$ can be obtained from the experimental values of the two solute order parameters, S_{zz} and $S_{xx}-S_{yy}$, which are related to $U(\beta_2,\gamma_2)$ by

$$S_{zz}=Z^{-1}\int C_{2,0}(\beta_2,\gamma_2)\exp\{-U(\beta_2,\gamma_2)/kT\}\sin\beta_2\,d\beta_2\,d\gamma_2, \tag{4}$$

and

$$S_{xx}-S_{yy}=\sqrt{6}Z^{-1}\int C_{2,2}(\beta_2,\gamma_2)\exp\{-U(\beta_2,\gamma_2)/\mathrm{k}T\}\sin\beta_2\,d\beta_2\,d\gamma_2, \tag{5}$$

where

$$Z=\int\exp\{-U(\beta_2,\gamma_2)/kT\}\sin\beta_2\,d\beta_2\,d\gamma_2. \tag{6}$$

The biaxial order parameter $S_{xx}-S_{yy}$ vanishes if $\varepsilon_{2,2}$ is zero, and this occurs when the solute has an axis of at least threefold symmetry. There are advantages in choosing solutes for study for which $S_{xx}-S_{yy}$ is not zero, for this gives a unique insight into the nature of the potential of mean torque. The advantage in studying biaxial solutes is that the solvent order parameters $\bar{C}_{2,2}$ are only about 5 per cent of the major order parameter $\bar{C}_{2,0}$, so that the solute–solvent coefficients are to a good approximation both linear in $\bar{C}_{2,0}$

$$\varepsilon_{2,0}=\bar{u}_{200}\bar{C}_{2,0}, \tag{7}$$

$$\varepsilon_{2,2}=\bar{u}_{202}\bar{C}_{2,0}, \tag{8}$$

so that their ratio

$$\lambda=\varepsilon_{2,2}/\varepsilon_{2,0} \tag{9}$$

is simply

$$\lambda=\bar{u}_{202}/\bar{u}_{200}. \tag{10}$$

The order parameters contain most of the temperature dependence in equation (3), and so λ should have only a weak temperature dependence. Furthermore, if the potential of mean torque is dominated by a single, second rank interaction, such that

$$\bar{u}_{20n}=BA_{2,0}(\text{solvent})A_{2,n}(\text{solute}), \tag{11}$$

where B depends on the type of interaction, then

$$\lambda=A_{2,2}(\text{solute})/A_{2,0}(\text{solute}) \tag{12}$$

and λ should be independent of the solvent; we have assumed that B is independent of n. The values of $A_{2,n}$(solute) and $A_{2,0}$(solvent) are determined by the nature of the dominant interaction, so that for dispersion forces, for example, the polarizability tensor, $\boldsymbol{\alpha}$ is identified with $\mathbf{A}$.

Values of λ for a number of solutes dissolved in a range of liquid crystal solvents have been measured, and in all cases it is found that λ is temperature dependent, always decreasing as the transition to the isotropic phase is approached. This behaviour suggests a common origin for the temperature dependence, but the explanation for this phenomenon is as yet not clear; it may indicate that more than one interaction contributes to the magnitude of the $\bar{u}_{2mn}$, but it may also stem from the truncation of $U(\beta_2, \gamma_2)$ at second rank terms. It has also been found that λ is strongly solvent dependent, and this is strong evidence that a single type of interaction does not dominate the potential of mean torque for a particular solute in different liquid crystal solvents.

This same conclusion has been reached by studies [3–6] of both uniaxial and biaxial solutes by noting the orientational ordering of solutes in a particular pair of solvents, EBBA and ZLI 1132. This particular pair were chosen for study because of the observation that hydrogen molecules have their symmetry axes ordered such that S_{zz} is positive in ZLI 1132 and negative in EBBA, and passes through zero for a particular mixture of the two solvents. The suggested interpretation for this behaviour is that the orientational ordering of hydrogen in these solvents is dominated by the interaction between the electric quadrupole moment of hydrogen, $Q_{2,0}$, and an average electric field gradient, F_{zz}, produced at the solute by the solvent molecules. Data on hydrogen were used to obtain the values of F_{zz} for EBBA and ZLI 1132, which are found to be of opposite sign.

The experimental evidence for more than one type of interaction making a significant contribution to $U(\beta_2, \gamma_2)$ is strong, and indeed our knowledge of the nature of the forces between molecules suggests that three types of force should be considered: dispersion and electrostatic interactions and short range repulsion. The question that is addressed here is whether it is possible to derive a potential of mean torque which includes the effects of these interactions, and which is simple enough to be characterized by comparison with experiment.

2. Theory

The first point to note is that short range interactions cannot be allowed for explicitly when attempting to derive a potential of mean torque with a simple, practical form, and whilst maintaining a consistent set of simplifying assumptions. Attempts have been made to include short range repulsion into potentials of mean torque, but these rely on assuming simplified forms for the potential and ad hoc assumptions about the separability of the variables involved in the averaging process. Thus, for short range interactions of any kind the separation between molecules r_{ij}, and the orientation of the molecules, Ω_i, relative to the mesophase director, are dependent variables, and this poses fundamental difficulties when attempting to perform the averages necessary to derive $U(\beta_2, \gamma_2)$.

The first contribution to the interaction between molecules that we shall consider are the electrostatic terms, since these give rise to an important problem which also has implications for the dispersion interaction. We start from a pair potential, $U_{12}(\Omega_1, \Omega_2, \Omega_{12}, r_{12})$; Ω_1, Ω_2, are the orientations of molecules 1 and 2, and Ω_{12} that of the intermolecular vector $\mathbf{r}_{12}$. The electrostatic contribution to $U_{12}(\Omega_1, \Omega_2, \Omega_{12}, r_{12})$

can be represented by coulombic forces between the charges on individual atoms in the two molecules, however, this is not a convenient form from which to derive a potential of mean torque. It is usual, therefore, to assume that the intermolecular separation, r_{12}, is large enough that the electrostatic potential can be expressed in terms of the interactions between sets of point multipoles located on each molecule. This is not to say that short range interactions are unimportant, indeed for liquid crystal molecules there is evidence in some cases for the importance of anti-parallel pairing of molecules, but that they cannot be written in a general form. These assumptions mean that the pair potential can be expressed as a product of a distance dependent and an angular dependent function, as discussed by Stone [7]. Thus,

$$U_{12}(r_{12}, \Omega_1, \Omega_2, \Omega_{12}) = \Sigma u_{LL'J}(r_{12}) S^{mn}_{LL'J}(\Omega_1, \Omega_2, \Omega_{12}), \tag{13}$$

where

$$S^{mn}_{LL'J}(\Omega_1, \Omega_2, \Omega_{12}) = -(i)^{L-L'-J} \Sigma \left(\begin{smallmatrix} L & L' & J \\ k & k' & M \end{smallmatrix}\right) D^L_{km}(\Omega_1) D^{L'}_{k'n}(\Omega_2) C_{J,M}(\Omega_{12}); \tag{14}$$

here $\left(\begin{smallmatrix} L & L' & J \\ k & k' & M \end{smallmatrix}\right)$ is a 3*j* symbol. The contributions to U_{12} from electrostatic terms have the form

$$U^{\mathrm{e}}_{12} = (4\pi\varepsilon_0)^{-1} \Sigma (-1)^{L+L'} [L; L'] r_{12}^{-t} Q^{(1)}_{Lm} Q^{(2)}_{L',n} S^{mn}_{LL'J}(\Omega_1, \Omega_2, \Omega_{12}), \tag{15}$$

where

$$[L; L'] = \{(2L + 2L' + 1)!/[(2L)!(2L')!]\}^{1/2} \tag{16}$$

and $J = L + L'$. The $Q^{(1)}_{L,m}$ are spherical tensor components of the 2^L multipole with respect to a frame fixed in molecule 1, a solvent molecule. The value of t is

$$t = L + L' + 1. \tag{17}$$

To derive a potential of mean torque from equation (13) we average first over the orientations of r_{12}. In the standard molecular mean field treatments this vector is assumed to be distributed uniformly over all orientations, and the average, $\bar{C}^{+}_{J,M}$, is

$$\bar{C}^{+}_{J,M} = \delta_{J0} \delta_{M0}, \tag{18}$$

where the superscript + is used to indicate that this is an order parameter for intermolecular vectors. For the electrostatic terms $J = L + L'$, and L and L' cannot be zero, so that from equation (18) it follows that all these terms vanish.

Non-vanishing electrostatic terms can contribute to the potential of mean torque only if the distribution of r_{12} is non-spherical, and indeed in the nematic phase the symmetry of the distribution need be no higher than $D_{\infty \mathrm{h}}$. Potentials of mean torque consistent with this symmetry were derived by Humphries *et al.* [8] for cylindrically symmetric liquid crystal molecules, but without considering the contributions of specific interactions. Chandrasekhar and Madhusudana [9] also derived a potential of mean torque which assumed cylindrical symmetry for the distribution of the $\mathbf{r}_{12}$ vector, but although they did consider electrostatic interactions, they neglected the quadrupole–quadrupole term, which in fact is the only term which gives a contribution to $U(\beta_2, \gamma_2)$. This arises because with the assumption of cylindrical symmetry for the distribution of $\mathbf{r}_{12}$, J must be even, and $L = L'$. If we also assume cylindrical symmetry about r_{12} then M is zero. The only terms in equation (15) which need be considered are, therefore, the dipole–dipole ($J = 2$) and quadrupole–quadrupole ($J = 4$) terms. Averaging over the orientations of the solvent molecules eliminates the dipole–dipole term because the first rank order parameters, $\bar{C}_{1,m}$, of the solvent molecules are zero. The quadrupole–quadrupole term in equation (15) has the form

$$U_{QQ} \propto r_{12}^{-5} Q_{2,m}^{(1)} Q_{2,n}^{(2)} S_{224}^{mn}, \tag{19}$$

with

$$S_{224}^{mn} = \binom{224}{000} C_{2,m}(\Omega_1) C_{2,n}(\Omega_2) C_{4,0}(\Omega_{12}). \tag{20}$$

Averaging over the orientations of the solvent molecules and the solute–solvent separations gives the contribution to the potential of mean torque as

$$U^{\mathrm{e}}(\Omega_2) = \Sigma \bar{u}_{2mn}^{\mathrm{e}} C_{2,n}(\Omega_2) \bar{C}_{2,m}, \tag{21}$$

where

$$\bar{u}_{2mn}^{\mathrm{e}} = \mathrm{A}^{QQ} \overline{r_{12}^{-5}} Q_{2,m}^{(1)} Q_{2,n}^{(2)} \bar{C}_{4,0}^{+}; \tag{22}$$

A^{QQ} is a constant whose magnitude can be derived from the general expression given by Stone [7], and $\bar{C}_{4,0}^{+}$ is a fourth rank order parameter for the solute–solvent vectors. Note that if cylindrical symmetry about r_{12} is still assumed for the solvent molecules, then λ is still predicted to be independent of solvent and temperature if the quadrupole–quadrupole term is the only contribution to the potential of mean torque. Note too that $\bar{C}_{4,0}^{+}$ is expected to depend on temperature, so that the temperature dependence of $U^{\mathrm{e}}(\beta_2, \gamma_2)$ is determined by $\bar{C}_{4,0}^{+}\bar{C}_{2,0}$. Equation (21) is equivalent to the contribution to $U(\beta_2, \gamma_2)$, proposed by Patey *et al.* [3], from the interaction between a solute quadrupole and the electric field gradient F_{zz} produced by the solvent molecules. F_{zz} is

$$F_{zz} = \mathrm{A}^{QQ} \overline{r_{12}^{-5}} Q_{2,0}^{(1)} \bar{C}_{4,0}^{+} \bar{C}_{2,0} \tag{23}$$

and is dependent on both the solute and solvent.

The assumption of cylindrical rather than spherical symmetry for the distribution of the r_{12} changes the form of the contribution to $U(\beta_2, \gamma_2)$ of the dispersion interaction. The dispersion interaction is such that three terms survive the averaging over Ω_{12}, and we obtain [7]

$$U^{\mathrm{d}}(\beta_2, \gamma_2) = \Sigma \bar{u}_{2mn}^{\mathrm{d}} \bar{C}_{2,m} C_{2,n}(\beta_2, \gamma_2) \tag{24}$$

with

$$\bar{u}_{2mn}^{\mathrm{d}} = \overline{r_{12}^{-6}} \alpha_{2,m}^{(1)} \alpha_{2,n}^{(2)} (\mathrm{A}^{\mathrm{d}} + \mathrm{B}^{\mathrm{d}} \bar{C}_{2,0}^{+} + \mathrm{C}^{\mathrm{d}} \bar{C}_{4,0}^{+}), \tag{25}$$

where A^{d}, B^{d} and C^{d} are constants. Again the additional terms do not predict either a temperature or solvent dependence of λ.

The contribution of short-range repulsion to the intermolecular potential is a complicated function with strong interdependences of radial and angular variables. Of course, any continuous, well-behaved function of these variables can be expanded in the form of equation (13), but the expansion of the short-range repulsion interaction in this form contains many large terms. Therefore, it cannot be interpreted in the descriptive manner that we have used for the electrostatic and dispersion interactions. At the phenomenological level, however, such a contribution should exist, and we shall assume that there is a contribution to the magnitude of the $\bar{u}_{2mn}$ from this source which we shall represent simply as $\bar{u}_{2mn}^{\mathrm{r}}$. Thus, there are in general, three conditions to the $\bar{u}_{2mn}$,

$$\bar{u}_{2mn} = \bar{u}_{2mn}^{\mathrm{r}} + \bar{u}_{2mn}^{\mathrm{d}} + \bar{u}_{2mn}^{\mathrm{e}}. \tag{26}$$

For the solute the appropriate axes to be used for calculating the values of each of the contributions to $\bar{u}_{2mn}$ are the principal axes for the solute order matrix, which will usually be fixed by symmetry. The solvent molecules, however, will always have low symmetry which means that the principal axes for the total interaction tensor will not coincide necessarily with the principal axes for the individual interactions. In calculating the three terms in equation (26) it is necessary to use the principal frame for the total interaction tensor as the common axis system for the solvent molecules.

3. Conclusion

Electrostatic terms do contribute to potentials of mean torque, but only if the distribution of intermolecular vectors has less than spherical symmetry, in which case the $\bar{u}^{\mathrm{e}}_{2mn}$ depend on an order parameter $\bar{C}^{+}_{4,0}$ for the intermolecular vectors r_{ij}. The assumption of cylindrical symmetry for the r_{ij} also affects the form of the contributions to the potential of mean torque from the dispersion interaction, such that $\bar{u}^{\mathrm{d}}_{2mn}$ depends on order parameters $\bar{C}^{+}_{4,0}$ and $\bar{C}^{+}_{2,0}$ for the r_{ij}. The average electric field gradient, F_{zz}, produced at a solute by the solvent molecules, is predicted to depend on the product $Q^{(1)}_{2,0}\bar{C}^{+}_{4,0}\bar{C}_{2,0}$. It is difficult to understand, therefore, why F_{zz} obtained from experiment should apparently change sign consistently for different solutes in the pair of solvents EBBA and ZLI 1132. This point, and the general question of whether it is possible to identify, and understand, the importance of the electrostatic contribution to $U(\beta_2, \gamma_2)$ is discussed in the following paper, which reports on the orientational order of two solutes of different polar character dissolved in a range of liquid crystal solvents with different structures.

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