

Calculation of dipole correlation factors in liquid crystals with use of a semiempirical expression for the internal field

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The internal field expression given on a semiempirical basis in the preceding article, is applied in the generalization of the Kirkwood-Fröhlich theory for liquid crystals presented earlier by one of the authors. As an example correlation factors are calculated for two compounds in the nematic phase, and one in the smectic A phase.

I. INTRODUCTION

For isotropic liquids the Kirkwood-Fröhlich theory¹⁻⁴ provides a framework in which the permittivity of polar compounds can be evaluated in terms of molecular quantities, taking short-range correlation effects into account. In a previous article⁵ one of us gave a generalization of this theory to the case of liquid crystals. However, a satisfactory generalization appeared to be possible for two limiting cases only, i. e., for ideal orientational order ($S=1$, where S is the nematic order parameter) and for isotropic molecular polarizabilities ($\alpha_i = \alpha_t$, where α_i and α_t are the principal values of the molecular polarizability tensor, α_i being along the long molecular axis). This was due to the intricate problem of the relation between the internal field E_i experienced by a molecule and the macroscopic field E . The relation between these two fields can be written as $E_i = \mathbf{K} \cdot E$, where \mathbf{K} is the internal field tensor. In this paper it will be shown that the expression for \mathbf{K} derived by the authors in the preceding article⁶:

$$K_i = (1 - 4\pi N \alpha_i \Omega_i)^{-1}, \quad (1)$$

$$K_t = (1 - 4\pi N \alpha_t \Omega_t)^{-1},$$

makes it possible to generalize the Kirkwood-Fröhlich theory to a real liquid crystal, with nonideal orientational order and anisotropic polarizabilities. In Eq. (1) Ω_i and Ω_t are geometrical factors given in Eq. (14) of Ref. 6, while N is the particle density.

II. THEORY

The generalization of the Kirkwood-Fröhlich theory to the permittivity of liquid crystals yields⁵

$$\frac{(\epsilon_\lambda - \epsilon_\infty) [\epsilon_\lambda + (1 - \epsilon_\lambda) \Omega_\lambda]^2 v}{4\pi \epsilon_\lambda [\epsilon_\lambda + (\epsilon_\infty - \epsilon_\lambda) \Omega_\lambda]} = \frac{1}{kT} \langle M_\lambda^2 \rangle_0, \quad \lambda = \parallel, \perp, \quad (2)$$

where Ω_λ is a geometrical factor depending on the ratio $\epsilon_\parallel/\epsilon_\perp$, given by Eqs. (7) and (10) of Ref. 5, and M stands for the electric moment of a sphere with volume v in the sample for given positions and orientations of the molecules in it, the surrounding dielectric being treated on a continuum basis. The subscripts \parallel and \perp refer to the directions parallel and perpendicular to the director, respectively. In order to evaluate M we use the $3n$ -dimen-

sional formalism,^{7,8} n being the number of molecules in the sphere. The moment of the sphere for given positions and orientations of all molecules in it can then be written as:

$$\underline{m} = \underline{\mu} + \underline{\alpha} \cdot (\underline{e} E_c - \underline{T}' \cdot \underline{m}). \quad (3)$$

Here \underline{m} , $\underline{\mu}$, and \underline{e} are $3n$ -dimensional vectors whose projections on the subspace i are equal to \underline{m}_i , $\underline{\mu}_i$, and \underline{e} , respectively, i. e., the total dipole moment of molecule i , its permanent dipole moment, and the unit vector in the direction of the cavity field E_c ; $\underline{\alpha}$ is a $3n$ -dimensional tensor whose projection α_{ij} on the product of the subspaces i and j is equal to the polarizability tensor α_i of molecule i for $i=j$, and is zero otherwise,⁵ and \underline{T}' is a $3n$ -dimensional tensor whose projection on the product of the subspaces i and j accounts for the field at molecule i due to molecule j , both by the direct dipole-dipole interaction and via the reaction field.⁴

Equation (3) can be rewritten to obtain:

$$\underline{m} = \underline{A} \cdot (\underline{\mu} + \underline{\alpha} \cdot \underline{e} E_c), \quad (4)$$

with

$$\underline{A} = (\underline{I} + \underline{\alpha} \cdot \underline{T}')^{-1}, \quad (5)$$

where \underline{I} is the $3n$ -dimensional unit tensor. In Ref. 5 it was incorrectly stated that \underline{A} is a symmetric tensor. This holds only if $\underline{\alpha}$ is the same for all molecules, however, as for the two cases considered in Ref. 5, but not for the general case of a nonideal liquid crystal.

Equation (4) implies that the moment of the sphere in the absence of the cavity field E_c is given by

$$\underline{m}^0 = \sum_i \underline{m}_i^0 = \sum_i \sum_j \underline{A}_{ij} \cdot \underline{\mu}_j = \sum_i \underline{\mu}_i \cdot \sum_j \underline{A}_{ji}. \quad (6)$$

The enlargement of the dipoles due to the external field, for fixed orientations of the molecules in the sphere, is given by:

$$\underline{p} = \underline{m} - \underline{m}^0 = (\underline{I} + \underline{\alpha} \cdot \underline{T}')^{-1} \cdot \underline{\alpha} \cdot \underline{e} E_c$$

$$= \underline{\alpha} \cdot (\underline{I} + \underline{T}' \cdot \underline{\alpha})^{-1} \cdot \underline{e} E_c = \underline{\alpha} \cdot \underline{\tilde{A}} \cdot \underline{e} E_c, \quad (7)$$

as can be seen from a series development for \underline{A} and $\underline{\tilde{A}}$. In three-dimensional notation Eq. (7) yields:

TABLE I. Dipole correlation factors in two liquid crystalline compounds.

Compound	$t(^{\circ}\text{C})$	phase ^a	S	ϵ_{\parallel}	ϵ_{\perp}	ϵ	ρ	g_{\parallel}	g_{\perp}	g
p, p' -heptylcyanobiphenyl	23	N	0.577	17.3	5.42		0.94	0.65	1.02	
$\mu_t = 4.34 \text{ D}$, $\mu_l = 0$	36	N	0.500	16.25	5.92		0.94	0.71	1.02	
$\alpha_t = 71 \text{ \AA}^3$	40	N	0.467	15.8	6.20		0.94	0.74	1.03	
$\Omega_t = 0.103$	43	I	0			9.82	0.94			0.98
p, p' -di- n -heptylazoxybenzene	36.3	S _A	0.747	3.36	3.57		0.991	0.36	0.83	
$\mu_t = 0.72 \text{ D}$, $\mu_l = 1.54 \text{ D}$	45.4	S _A	0.728	3.38	3.47		0.985	0.45	0.81	
$\alpha_t = 106 \text{ \AA}^3$, $\alpha_l = 43 \text{ \AA}^3$	55	N	0.636	3.46	3.34		0.976	0.74	0.76	
$\Omega_t = 0.067$	67	N	0.509	3.49	3.26		0.962	0.92	0.75	
	76	I	0			3.29	0.950			0.82

^aN=nematic, I=isotropic, S_A=smectic A.

$$\begin{aligned} \mathbf{p}_i &= \alpha_i \cdot \sum_j \bar{\mathbf{A}}_{ij} \cdot \mathbf{E}_c = \alpha_i \cdot \sum_j \mathbf{A}_{ji} \cdot \mathbf{E}_c \\ &= \alpha_i \cdot \sum_j \mathbf{A}_{ji} \cdot \boldsymbol{\epsilon} \cdot [\boldsymbol{\epsilon} + (\mathbf{I} - \boldsymbol{\epsilon}) \cdot \boldsymbol{\Omega}^e]^{-1} \cdot \mathbf{E}, \end{aligned} \quad (8)$$

where $\boldsymbol{\Omega}^e$ is a uniaxial tensor with its axis along the director and eigenvalues Ω_{λ}^e . The field \mathbf{E} is the macroscopic field in the surrounding dielectric, which should not be confused with the macroscopic field \mathbf{E}_2 in the cavity. For fixed positions and orientations of the molecules in the cavity, the field \mathbf{E}_2 is the same as if the cavity were filled with an anisotropic dielectric with permittivity tensor $\boldsymbol{\epsilon}_{\infty}$:

$$\mathbf{E}_2 = \boldsymbol{\epsilon} \cdot [\boldsymbol{\epsilon} + (\boldsymbol{\epsilon}_{\infty} - \boldsymbol{\epsilon}) \cdot \boldsymbol{\Omega}^e]^{-1} \cdot \mathbf{E}. \quad (9)$$

The moments \mathbf{p}_i are related to this field by:

$$\mathbf{p}_i = \alpha_i \cdot \mathbf{K}_i \cdot \mathbf{E}_2. \quad (10)$$

Equating this to Eq. (8), one obtains:

$$\sum_j \mathbf{A}_{ji} = \mathbf{K}_i \cdot [\boldsymbol{\epsilon} + (\mathbf{I} - \boldsymbol{\epsilon}) \cdot \boldsymbol{\Omega}^e] \cdot [\boldsymbol{\epsilon} + (\boldsymbol{\epsilon}_{\infty} - \boldsymbol{\epsilon}) \cdot \boldsymbol{\Omega}^e]^{-1}, \quad (11)$$

or, with Eq. (6):

$$(\mathbf{M}^0)_{\lambda} = \left(\sum_i \mu_i \cdot \mathbf{K}_i \right)_{\lambda} \frac{\epsilon_{\lambda} + (1 - \epsilon_{\lambda}) \Omega_{\lambda}^e}{\epsilon_{\lambda} + (\epsilon_{\infty\lambda} - \epsilon_{\lambda}) \Omega_{\lambda}^e}. \quad (12)$$

This expression can be substituted into Eq. (2):

$$\frac{(\epsilon_{\lambda} - \epsilon_{\infty\lambda}) [\epsilon_{\lambda} + (\epsilon_{\infty\lambda} - \epsilon_{\lambda}) \Omega_{\lambda}^e] v}{4\pi\epsilon_{\lambda}} = \frac{1}{kT} \left\langle \left(\sum_i \mu_i \cdot \mathbf{K}_i \right)_{\lambda}^2 \right\rangle. \quad (13)$$

At this stage it seems profitable to introduce molecular moments $(\mu_d)_i$, defined by:

$$(\mu_d)_i = \mu_i \cdot \mathbf{K}_i. \quad (14)$$

In the approximation that Eq. (1) holds, the components of these moments are given by:

$$(\mu_d)_i = \mu_i / (1 - 4\pi N \alpha_i \Omega_i), \quad (15)$$

$$(\mu_d)_t = \mu_t / (1 - 4\pi N \alpha_t \Omega_t). \quad (16)$$

For an isotropic system of molecules with an isotropic polarizability and spherical shape these expressions reduce to the one for the dipole moment in the liquid introduced by Fröhlich.² We use the symbol μ_d to conform to Refs. 5 and 3 (p. 25). Since the moments μ_d are fixed

in molecular coordinates, it is possible to introduce correlation factors g_{\parallel} and g_{\perp} for the components of μ_d parallel with and perpendicular to the director. We then obtain from Eq. (13) the final equations:

$$\frac{(\epsilon_{\parallel} - \epsilon_{\infty\parallel}) [\epsilon_{\parallel} + (\epsilon_{\infty\parallel} - \epsilon_{\parallel}) \Omega_{\parallel}^e]}{\epsilon_{\parallel}} = \frac{4\pi N}{kT} g_{\parallel} \langle \mu_d^2 \rangle_{\parallel}, \quad (17)$$

$$\frac{(\epsilon_{\perp} - \epsilon_{\infty\perp}) [\epsilon_{\perp} + (\epsilon_{\infty\perp} - \epsilon_{\perp}) \Omega_{\perp}^e]}{\epsilon_{\perp}} = \frac{2\pi N}{kT} g_{\perp} \langle \mu_d^2 \rangle_{\perp}, \quad (18)$$

with

$$\langle \mu_d^2 \rangle_{\parallel} = \frac{\mu_t^2 (1 + 2S)}{3(1 - 4\pi N \alpha_t \Omega_t)^2} + \frac{\mu_l^2 (1 - S)}{3(1 - 4\pi N \alpha_l \Omega_l)^2}, \quad (19)$$

$$\langle \mu_d^2 \rangle_{\perp} = \frac{2\mu_l^2 (1 - S)}{3(1 - 4\pi N \alpha_l \Omega_l)^2} + \frac{\mu_t^2 (2 + S)}{3(1 - 4\pi N \alpha_t \Omega_t)^2}. \quad (20)$$

A simplification of these equations occurs if the dipole lies along the long axis of the molecule, as for the p, p' -alkylcyanobiphenyls.^{9,10} Then the correlation factors directly concern the components of the moment of the isolated molecule along and perpendicular to the director and are given by:

$$g_{\parallel} = \frac{3kT(1 - 4\pi N \alpha_l \Omega_l)^2 (\epsilon_{\parallel} - \epsilon_{\infty\parallel}) [\epsilon_{\parallel} + (\epsilon_{\infty\parallel} - \epsilon_{\parallel}) \Omega_{\parallel}^e]}{4\pi N \mu^2 (1 + 2S) \epsilon_{\parallel}} \quad (21)$$

$$g_{\perp} = \frac{3kT(1 - 4\pi N \alpha_t \Omega_t)^2 (\epsilon_{\perp} - \epsilon_{\infty\perp}) [\epsilon_{\perp} + (\epsilon_{\infty\perp} - \epsilon_{\perp}) \Omega_{\perp}^e]}{4\pi N \mu^2 (1 - S) \epsilon_{\perp}} \quad (22)$$

For ideal order Eqs. (17) and (18) are equivalent to the expressions derived in Ref. 5 for that case [Eqs. (27) and (30)]. For nonideal order, our calculation implies that the components of μ_d are the same as for ideal order, in spite of the difference in the surroundings of the molecule.

III. NUMERICAL EXAMPLES

In Table I values of g_{\parallel} and g_{\perp} have been calculated for p, p' -heptylcyanobiphenyl and p, p' -di- n -heptylazoxybenzene. For the former compound data by Davies *et al.*⁹ were used. Values of $\epsilon_{\infty\parallel}$ and $\epsilon_{\infty\perp}$ were obtained by multiplying the value of n_{\parallel}^2 and n_{\perp}^2 by 1.05, to account for the atomic polarization; from these values the value of α_l was calculated as indicated before.⁶ Values of S were

estimated from the Maier-Saupe theory.¹¹ For p, p' -di- n -heptylazoxybenzene data from previous articles were used.^{6,12,13} Values of α_i and α_e are from the measurements at 546 nm, with a correction of 5% for the atomic polarization. The dipole moment was taken to be 1.7 D, as obtained from azoxybenzene¹⁴ and the angle between the dipole and the long axis of the molecule was estimated from the molecular structure to be 65°.

Numerical results for the other dialkylazoxybenzenes will be given elsewhere.¹⁵

IV. DISCUSSION

For the isotropic liquid a value of g near unity is obtained for both compounds. These values deviate from the values that would be obtained with the original Kirkwood-Fröhlich equations, in view of the different assumption concerning the internal field, as appears from a comparison of Eq. (11) with Eq. (41) of Ref. 4.

For p, p' -heptylcyanobiphenyl it seems rather unlikely that there would be no net effect of the short-range correlation between the dipoles in the isotropic liquid, since one expects an antiparallel orientation of neighboring molecules to be favored for molecules where the dipole lies along the long axis. It should be mentioned, however, that the value $g = 0.98$ is calculated from the dipole moment in solution, and for molecules where the dipole is directed along the long axis this moment is known to be smaller than that of the isolated molecule. Furthermore, recently Lippens *et al.*¹⁶ reported a value of 5.1 D for the dipole moment of p, p' -heptylcyanobiphenyl, appreciably greater than the value we have used. This makes it plausible that if the correct dipole moment of the isolated molecule was used lower values of g would be obtained. Irrespective of the values of μ applied, the data show that for the dipole components along the director the tendency for antiparallel orientations increases with increasing nematic order.

For p, p' -di- n -heptylazoxybenzene, the value of g observed in the isotropic state is rather low. Here, apart from the uncertainty in the dipole moment of the isolated molecule, the uncertainty of the angle between the dipole and the long axis of the molecule plays a role, and also the uncertainty in the contribution of the atomic polariza-

tion to ϵ_∞ . For this compound $g_{||}$ decreases strongly with increasing order, whereas also an increase of g_{\perp} is observed. This can be explained from the formation of the smectic A phase, in which the distance between the molecules in the smectic planes is much smaller than the distance between different planes. In the case of central dipoles the dipole-dipole interaction energy then has a minimum for antiparallel orientation of the dipole components along the long axis of the molecule and for parallel orientation of the dipole components perpendicular to this axis.¹²

Finally we emphasize that the final justification of the equations for the internal field used is not in a molecular model, but in the experimental observation⁶ that the average dielectric permittivity shows for the induced polarization no discontinuity at the clearing point, and that the high-frequency dielectric anisotropy in the nematic phase is proportional to the product of density and order parameter.

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