Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Interaction potentials and free energies for ferroelectric liquid crystals in the model of polar non-uniaxial molecules

K. Szumilin[a]; J. J. Milczarek[b]
[a] Institute of Physics, Warsaw Technical University, Warsaw, Poland [b] Institute of Atomic Energy, Otwock, Poland

To cite this Article Szumilin, K. and Milczarek, J. J.(1993) 'Interaction potentials and free energies for ferroelectric liquid crystals in the model of polar non-uniaxial molecules', Liquid Crystals, 14: 4, 1033 — 1038
To link to this Article: DOI: 10.1080/02678299308027810
URL: http://dx.doi.org/10.1080/02678299308027810

LIQUID CRYSTALS, 1993, VOL. 14, NO. 4, 1033–1038

Interaction potentials and free energies for ferroelectric liquid crystals in the model of polar non-uniaxial molecules

by K. SZUMILIN* and J. J. MILCZAREK†
Institute of Physics, Warsaw Technical University, Koszykowa 75,
00-662 Warsaw, Poland
†Institute of Atomic Energy, Świerk, 05-400 Otwock, Poland

The possible forms of the model interaction potentials are proposed for rigid polar non-uniaxial molecules with the molecular dipole moment making an arbitrary angle with the molecule's long axis. The molecule orientation is described by the direction of two molecular axes: its dipole moment and the long axis. The intermolecular potentials dependent on both molecular axes orientations are considered. The simple model interaction potentials between chiral molecules are used. It is shown that the form of the interaction potential determines the set of the relevant order parameters of the system. The free energy is calculated in the Landau expansion form in terms of the relevant order parameters.

1. Introduction

There is experimental evidence that ferroelectric liquid crystals are composed of mesogenic chiral molecules possessing a permanent electric dipole moment perpendicular to their long axes [1–3]. However, polar orderings are also observed in systems of uniaxial polar molecules [4]. Those facts necessitate the development of molecular models within which they can be described and explained. Another problem lies in the definition of the order parameters for systems described by the postulated interaction potential. In most molecular theoretical approaches [5–8] the order parameters are chosen on the basis of phenomenological considerations which lead to the conclusion that ferroelectric liquid crystals belong to the class of improper ferroelectrics [9, 10]. In this case the polarization vector is a secondary order parameter coupled to some primary one describing the tilt. This coupling makes the temperature behaviour of the polarization similar to that of the true order parameter. In this paper we formulate the theoretical approach which allows us to work out these problems in a more systematic way. We start from the postulated interaction potentials to show how its symmetry influences the definitions of the relevant order parameters. The method of calculation is based on the previously developed theory [11] which was also applied to the problem of ferroelectric-type orderings in the systems of uniaxial polar molecules [12]. In our approach, the coupling terms between various order parameters can be calculated allowing the discussion of secondary order parameters. One can then establish for which interaction potentials the ordering of the molecules' dipole moments may appear as a secondary effect.

2. Outline of the theory

We consider the system of identical rigid non-uniaxial molecules with the interaction described by the two-particle potential $U_2(x_1, x_2)$. The interaction energy

---

* Author for correspondence.

depends on the positions $\mathbf{r}_i$ of the centres of mass of the molecules and orientations Ω_i given by eulerian angles; $x_i = (\mathbf{r}_i, \Omega_i)$. V is the volume and $\bar{N}$ is the average number of molecules of the system.

The Helmholtz free energy of the system is considered in the lowest order of the diagram expansion method [12, 13]

$$\frac{F}{k_B T} = \frac{F_0}{k_B T} + \int dx \rho(x) \ln \rho(x) - \frac{1}{2} \iint dx\, dx' \rho(x) \rho(x') b(x, x'), \tag{2.1}$$

where $b(x, x')$ is the Meyer function

$$b(x, x') = \exp[-\beta_B U_2(x, x')] - 1 \tag{2.2}$$

($\beta_B = 1/k_B T$) and $\rho(x)$ is the one-particle distribution function of the system.

We define the distribution function f as

$$f(x) = \frac{V}{\bar{N}} \rho(x) \tag{2.3}$$

and calculate the free energy ΔF due to deviation $\delta f(x) = f(x) - f_0$ from the isotropic liquid state, using the equation (2.1)

$$\begin{aligned} \Delta F = F(f) - F(f_0) &= \frac{n k_B}{4\pi} \left(\frac{1}{2} \int dx [\delta f(x)]^2 - \frac{1}{6} \int dx [\delta f(x)]^3 + \cdots \right) \\ &\quad - \frac{n^2}{2(4\pi)^2} k_B T \iint dx\, dx' \delta f(x) \delta f(x') b(x, x'). \end{aligned} \tag{2.4}$$

The theory of the phase transitions in the system should establish the set of the relevant order parameters. In our approach [11, 12] the crucial factor determining the order parameters is the interaction potential. We start with the expansion of the distribution function in the orthogonal function series

$$\delta f(x) = \sum_{\substack{l,m,n \\ \mathbf{q}}} \alpha^l_{mn}(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}) D^l_{mn}(\Omega), \tag{2.5}$$

where $D^l_{mn}(\Omega)$ are Wigner's D-functions. The coefficients $\alpha^l_{mn}(\mathbf{q})$ describe the orientational and translational ordering in the system and are the statistical averages

$$\alpha^l_{mn}(\mathbf{q}) = \frac{2l + 1}{8\pi^2} \langle D^{*l}_{mn}(\Omega) \exp(-i\mathbf{q} \cdot \mathbf{r}) \rangle. \tag{2.6}$$

With that assumption the free energy ΔF given by equation (2.4) becomes the power series in terms of the expansion coefficients $\alpha^l_{mn}(\mathbf{q})$. In general, the second order terms in $\alpha^l_{mn}(\mathbf{q})$ can be written in the form

$$\text{const.}\,(T - T^{*l}_{mn}(\mathbf{q}))\, |\alpha^l_{mn}(\mathbf{q})|^2. \tag{2.7}$$

Here the critical temperatures $T^{*l}_{mn}(\mathbf{q})$ are determined by the interaction potential

$$T^{*l}_{mn}(\mathbf{q}) = -\frac{\bar{n} k_B T}{8\pi} \int dx\, dx' \exp[i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')] D^l_{mn}(\Omega) D^{*l}_{mn}(\Omega') b(x, x'), \; (\bar{n} = \bar{N}/V). \tag{2.8}$$

The order parameters $\alpha^L_{MN}(\mathbf{q})$ are those $\alpha^l_{mn}(\mathbf{q})$ for which $T^{*l}_{mn}(\mathbf{q})$ reaches maximum.

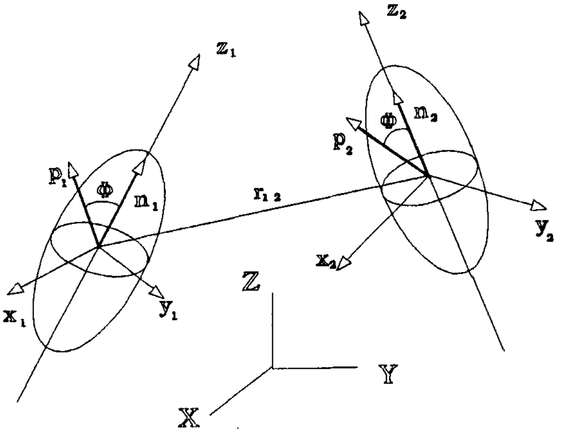

Figure 1. The model of interacting elongated non-uniaxial molecules with permanent dipole moment non-parallel to the long axis. The unit vectors **n** and **p** point in the directions of the long axes and dipole moments, respectively.

3. Molecular model and interaction potentials

The molecules constituting the system are regarded as elongated forms with built-in permanent dipole moments at a given angle Φ to the main (long) axis of the molecule. Then each molecule can be represented by the set of two unit vectors $\{\mathbf{n}_i, \mathbf{p}_i\}$, where $\mathbf{n}_i$ is parallel to the long axis of the ith molecule and $\mathbf{p}_i$ points in the direction of its dipole moment (see figure 1).

The angle Φ between those two vectors turns out to be relevant in the present theory. Such a model enables us to discuss the interaction of non-uniaxial molecules (in case of $\Phi \neq 0$) and uniaxial ones when $\Phi = 0$. The widely discussed case of a permanent dipole moment perpendicular to the molecular long axis is also included here. We can also make use of this model to describe the interaction of chiral molecules.

Following standard theories of the orientational ordering we take the part of the interaction potential responsible for alignment of the long molecular axes proportional to $P_2(\mathbf{n}_1 \cdot \mathbf{n}_2)$ (here P_i denotes the Legendre polynomial of ith order) [14–15]. The simplest form of the dipole–dipole interaction can be described by the term proportional to $P_1(\mathbf{p}_1 \cdot \mathbf{p}_2)$. In the case when the appearance of the permanent dipole moment is associated with the existence of the short molecular axis (flat molecules), one can expect the ordering of those axes due to the interaction term proportional to $P_2(\mathbf{p}_1 \cdot \mathbf{p}_2)$. In general, the cross terms containing $P_2(\mathbf{p}_1 \cdot \mathbf{n}_2)$ can not be excluded on formal grounds, especially when chiral molecules are considered. Hence, the discussed potential can be written as

$$U_2(x_1, x_2) = \sum_{\substack{a_1 b_1 \\ a_2 b_2}} \sum_{l=0,1,2} V^l_{ab}(r_{12}) P_l(\mathbf{a}_1 \cdot \mathbf{b}_2), \quad (\mathbf{a}, \mathbf{b} = \mathbf{n}, \mathbf{p}), \qquad (3.1)$$

where $V^l_{ab}(r_{12})$ depends on the distances between the centres of masses of the molecules.

In the case of ferroelectric liquid crystals, being improper ferroelectrics, the spontaneous polarization really cannot be considered as the primary order parameter. This means that in the free energy ΔF of the system the quadratic terms in the polarization components $\mathbf{P}_\alpha$ ($\alpha = x, y, z$) are not relevant for the ferroelectric phase transition. Therefore, we would consider various possible forms of the interaction potential for chiral molecules, trying to find those leading to the ordering of the dipole moments; also there is the secondary effect resulting from the coupling between primary orientational order parameters and the polarization. It is generally accepted that the molecular chirality is responsible for ferroelectric behaviour observed in liquid crystals. The chirality of the molecule is understood as a lack of any centre of inversion or mirror plane in the symmetry group of the molecule [3, 16]. Hence by the chiral molecule we mean the molecule in which one can distinguish the 'up' and the 'down', the 'front' and the 'back' or the 'left hand side' and the 'right hand side'. In this sense the chirality is not identical with the helicity of the molecule [16]. The helical molecules are chiral, but chiral molecules must not necessarily be helical. The postulated interaction potential will describe the interaction of the chiral molecules with the assumption that the interaction between left handed molecules is the same as between the right handed ones.

Here we propose to describe the interaction of two chiral molecules with fixed unit vectors **n** and **p** in terms of the following products of these vectors:

$$U_2^{\mathrm{ch}}(x_i, x_j) \sim (\mathbf{n}_i \times \mathbf{p}_i) \cdot (\mathbf{n}_j \times \mathbf{p}_j). \tag{3.2}$$

This kind of interaction can be expressed in terms of the Legendre polynomials

$$U_2^{\mathrm{ch}}(x_i, x_j) = V_s^{\mathrm{ch}}(r_{ij})(P_1(\mathbf{n}_i \cdot \mathbf{n}_j)P_1(\mathbf{p}_i \cdot \mathbf{p}_j) - P_1(\mathbf{n}_i \cdot \mathbf{p}_j)P_1(\mathbf{p}_i \cdot \mathbf{n}_j)) \tag{3.3}$$

Parity conservation requires that the function $V_s^{\mathrm{ch}}(r_{ij})$ should be a scalar; so it does not distinguish between a right and left hand helix. In reality the interaction energy depends not only on mutual molecular orientations, but also on their postions with respect to the intermolecular vector $\mathbf{r}_{12}$. In such cases, four types of potential, including **r** dependence, can be considered [6]. The first one is related to the elongated molecular shape [6, 15]

$$U_2^{\mathrm{sh}}(x_1, x_2) = \sum_{\substack{l \\ i=1,2}} V_{\mathrm{sh}}^l(r_{12}) P_{2l}(\mathbf{r}_{12} \cdot \mathbf{n}_i). \tag{3.4}$$

The effect of the molecular chirality is usually represented in the uniaxial molecular model by the interaction potential of the form [6, 17]

$$U_2^{\mathrm{chr}}(x_1, x_2) = V_p^{\mathrm{chr}}(r_{12})(\mathbf{n}_1 \times \mathbf{n}_2) \cdot \mathbf{r}_{12} P_1(\mathbf{n}_1 \cdot \mathbf{n}_2). \tag{3.5}$$

In this form of the interaction potential, the chirality of the molecules is reduced to helicity. Here the function $V_p^{\mathrm{chr}}(r_{12})$ is a pseudoscalar quantity. One should notice that, as we stated before, in general the chiral molecule is not always helical. In this respect the biaxial molecular model seems to be more general for discussion of possible molecular orderings in the system. The interaction of the biaxial noncentrosymmetric molecules can also be described in terms of $\mathbf{n}_i$, $\mathbf{p}_i$ and $\mathbf{r}_{12}$ vectors [6].

4. Free energies and order parameters

The scope of the theory presented in §1 enables us to calculate the free energy F of the system given the interaction potential. In the simplest case we take the molecular interaction potential in the form of

$$U_2(x_i, x_j) = V^0(r_{ij})P_0(\mathbf{n}_i\mathbf{n}_j) + V_{pp}^1(r_{ij})\, P_1(\mathbf{p}_i\mathbf{p}_j) + V_{nn}^2(r_{ij})\, P_2(\mathbf{n}_i\mathbf{n}_j). \tag{4.1}$$

For the calculation of the interaction term in equation (2.4) in the lowest order approximation in $\beta_{\mathrm{B}} U$ (when $b = -\beta_{\mathrm{B}} U$), the following formula is important:

$$P_l(\mathbf{a}_1 \cdot \mathbf{a}_2) = \sum_{m=-l}^{l} D_{-m0}^l(\Omega_1) D_{-m0}^{*l}(\Omega_2), \tag{4.2}$$

where $\Omega_i = \{\phi_i, \theta_i, \chi_i\}$ are the eulerian angles for the unit vectors $\mathbf{a}_i$ ($i = 1, 2$).

Now we can calculate the free energy ΔF of the system for the potential given by equation (4.1) using equations (2.4) and (2.5). Considering the angle Φ between the molecular vectors $\mathbf{n}$ and $\mathbf{p}$ we express their orientations in the same reference system using properties of the Wigner D-functions. The second order terms in the expansion coefficients $\alpha^l_{mn}(\mathbf{q})$ of the equation (2.5) can be written in the form

$$\Delta F^{[2]} = \sum_{\substack{l=0,2;m\\ \mathbf{q}}} (T - T_l^*(\mathbf{q}))|\alpha^l_{m0}|^2 + \sum_{\substack{m=-1,0,1\\ \mathbf{q}}} (T - T_1^*(\mathbf{q}))|\beta_m(\Phi,\mathbf{q})|^2, \quad (4.3)$$

where the critical tempertures $T_l^*(\mathbf{q})$ $(l = 0, 1, 2)$ are given by Fourier transforms of the functions $V^l(r)$ from equation (4.1).

Here new quantities β_m are introduced as linear combinations of $\alpha^1_{mn}(\mathbf{q})$

$$\beta_m(\Phi,\mathbf{q}) = \sum_{n=-1,0,1} \alpha^1_{mn}(\mathbf{q}) D^{*1}_{n0}(0,\Phi,0) \quad (4.4)$$

Those parameters describe the ordering of molecular dipole moments. In the case of uniaxial molecules ($\mathbf{n}\|\mathbf{p}$, *i.e.* $\Phi = 0$) the polar ordering is described by $\alpha^1_{m0}(\mathbf{q})$ $(m = -1, 0, 1)$ as was found in our previous work [12]. In the case when the dipole moment is perpendicular to the molecular long axis ($\Phi = \pi/2$), we obtain the different set of the polar order parameters

$$\beta_m(\pi/2,\mathbf{q}) = (\alpha^1_{m1}(\mathbf{q}) - \alpha^1_{m-1}(\mathbf{q}))/\sqrt{2}. \quad (4.5)$$

The set of polar parameters given by equation (4.4) is induced by the symmetry of the assumed molecular interaction. The existence of the polar interaction term $\sim P_1(\mathbf{p}_i\mathbf{p}_j)$ allows us to expand the distribution function δf in the reduced set of orthogonal functions

$$\delta f(x) = \sum_{\substack{m=-1,0,1\\ \mathbf{q}}} \beta_m(\Phi,\mathbf{q})\mathscr{D}_m(\Phi,\Omega)\exp(i\mathbf{q}\cdot\mathbf{r}) + \sum_{\substack{l\neq 1,m,n\\ \mathbf{q}}} \alpha^l_{mn}(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r})D^l_{mn}(\Omega), \quad (4.6)$$

where the set of nine Wigner functions $D^1_{mn}(\Omega)$ is reduced to three orthogonal functions $\mathscr{D}_m(\Phi,\Omega)$

$$\mathscr{D}_m(\Phi,\Omega) = \sum_n D^{*1}_{mn}(\Omega)D^{*1}_{n0}(0,\Phi,0). \quad (4.7)$$

Note that the reduction of the set of orthogonal functions takes place also due to the presence of the orientational interaction term in the potential in the form $\sim P_2(\mathbf{p}_i\mathbf{p}_j)$. The full set of orientational parameters $\alpha^2_{mn}(\mathbf{q})$ is here reduced to five parameters $\alpha^2_{m0}(\mathbf{q})$.

We have also calculated the second order terms in the free energy ΔF yielded by the chiral potential part given by equation (3.3). For example we found that the second order term containing $|\alpha^1_{01}(\mathbf{q})|^2$ is now introduced into ΔF. The assumed form of chirality makes the use of the polar parameters β_m impossible. Hence all parameters α^1_{mn} should be used in the expression for leading terms in the free energy. This potential does not yield mixed second order terms proportional to the product $\alpha^2_{m_2n_2}(\mathbf{q})$ $\alpha^1_{m_1n_1}(-\mathbf{q})$. Thus the chirality described in terms of such a potential is not sufficient to produce coupling between orientational order and polarization parameters.

The existing theoretical description of ferroelectric liquid crytals are based on the interaction potential given by equation (3.5) [6, 7], so we expect that application of our approach to systems with intermolecular potentials containing dependence on orientation of vectors $\mathbf{r}_{ij}$. Ω_i and Ω_j will introduce into the free energy the coupling terms between appropriate order parameters.

The Landau form of the free energy ΔF is obtained from the general expression given by equation (2.4) when the critical vectors $\mathbf{Q}$ are calculated as those wavevectors $\mathbf{q}$ for which the critical temperatures T^{*l}_{mn} reach their maxima. Then all $\alpha^l_{mn}(\mathbf{q})$ or $\beta_m(\mathbf{q})$ with $\mathbf{q} \neq \mathbf{Q}$ are neglected in the free energy ΔF which becomes the polynomial in chosen $\alpha^L_{MN}(\mathbf{Q})$ and $\beta_M(\mathbf{Q})$.

5. Conclusions

We have outlined the method of analysing the system orderings based on the expansion of the one-particle distribution function in the complete set of functions containing full rotation ($D^l_{mn}(\Omega)$) and translation group ($\exp(i\mathbf{q}\cdot\mathbf{r})$) functions. The order parameters are determined from the expansion coefficients in that series. The explicit form of the assumed interaction potential is the crucial factor in choosing the relevant order parameters.

The method was applied to the model of elongated molecules with the permanent dipole moment forming an arbitrary angle Φ with the long molecular axis. The simple interaction potential for a system of such molecules was proposed. We have shown that the definition of the polar order parameters contains the dependence on that angle.

The chiral part of the interaction potential for the given model of the molecules was postulated and its influence on the polar order parameters definition is demonstrated.

In this work we have limited the presentation to the results obtained from the potentials dependent on the molecular orientations only. These potentials do not give coupling between the long axes ordering and the polarization. The discussion of the potentials containing the intermolecular vector orientation will be presented in a forthcoming more comprehensive paper.

This work was supported by the Science Research Committee (Poland) under contract KBN No 2 0496 91 01.

References

[1] Martinot-Lagarde, P., 1988, *Ferroelectrics*, **84**, 53.
[2] Walba, D. M., Razavi, H. A., Horiuchi, A., Eidman, K. F., Otterholm, B., Haltiwanger, R. C., Clark, N. A., Shao, R., Parmar, D. S., Wand, M. D., and Vohra, R. T., 1991, *Ferroelectrics*, **113**, 21.
[3] Goodby, J. W., 1991, *J. mater. Chem.*, **1**, 307.
[4] Hardouin, F., Levelut, A. M., Achard, M. F., and Sigaud, G., 1983, *J. Chim. phys.*, **80**, 53, and references cited therein.
[5] Nakagawa, M., and Akahane, T., 1987, *J. phys. Soc. Japan*, **56**, 2653.
[6] Nakagawa, M., 1988. *Liq. Crystals*, **3**, 63.
[7] Osipov, M. A., 1984, *Ferroelectrics*, **58**, 305.
[8] Huang, C. C., 1987, *Molec. Crystals liq. Crystals*, **144**, 1.
[9] Pikin, S. A., and Indenbom, V. L., 1978, *Sov. Phys. Usp.*, **125**, 251 (Russian edition).
[10] Blinov, L. M., and Beresnev, L. A., 1984, *Sov. Phys. Usp.*, **134**, 391 (Russian edition).
[11] Szumilin, K., and Milczarek, J. J., 1985, *Molec Crystals liq. Crystals*, **127**, 289.
[12] Szumilin, K., and Milczarek, J. J., 1991, *Ferroelectrics*, **113**, 143.
[13] Morita, T., and Hiroike, K., 1961, *Prog. theor. Phys.*, **25**, 537.
[14] Kobayashi, K. K., 1970, *Physics Lett.*, A, **31**, 125; 1970, *J. phys. Soc. Japan*, **29**, 101; 1971, *Molec. Crystals liq. Crystals*, **13**, 137.
[15] Mederos, L., and Sullivan, D. E., 1989, *Phys. Rev.* A, **39**, 854.
[16] Cahn, R. S., Ingold, C. K., and Prelog, V., 1966, *Angew. Chem. Int. Ed. Engl.*, **5**, 385.
[17] Van der Meer, B. W., and Vertogen, G., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), p. 149.