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Microscopic model of the spontaneous polarization in ferroelectric liquid crystals

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A microscopic model is introduced which describes the coupling between the tilt of molecules from the normal to smectic layers in ferroelectric liquid crystals and the rotation of a molecule around its long axis. The single particle potential consists of a dipolar and a quadrupolar term. The microscopic model is shown to be consistent with the extended thermodynamic model, which takes into account the bilinear as well as the biquadratic coupling between the tilt of molecules and the induced transverse polarization, and which describes the anomalous thermodynamic behaviour of ferroelectric liquid crystals in the smectic C* phase. It is shown that close to the transition to the smectic A phase the thermodynamic description is exact, but overestimates the spontaneous polarization at lower temperatures. The results are compared with experimental data. It is demonstrated that the quadrupolar order is larger than the dipolar order except very close to the transition.

1. Introduction

Ferroelectric smectic C* liquid crystals [1, 2] are orientationally ordered liquids with a one dimensional density modulation. The smectic C phase is ferroelectric if the molecules are chiral and have a permanent dipole moment transverse to their long molecular axis. In the high temperature smectic A phase the molecules are arranged in smectic layers and their long axes are, on average, oriented perpendicular to the layers. They rotate freely around their long axes and there is no transverse ordering. In a smectic C phase the tilt of the long molecular axis from the normal to the smectic layers breaks the axial symmetry around the long molecular axis and a transverse ordering is induced, resulting in a transverse in-plane polarization perpendicular to the direction of the tilt. Because of the chirality of molecules in chiral smectic C* systems the molecular tilt as well as the in-plane polarization rotate slowly on going from one smectic plane to another, resulting in a helical structure.

The properties of ferroelectric smectic C* liquid crystals can be described by a Landau free energy expansion in two order parameters. These are the primary order parameter, the two component tilt vector $\boldsymbol{\xi} = (\xi_1, \xi_2)$ and the secondary order parameter, the two component in-plane polarization $\mathbf{P} = (P_x, P_y)$. For chiral systems the symmetry allows for two types of bilinear coupling between the molecular tilt and the molecular polarization [2, 3]. These types of coupling are the piezoelectric

$$P_x\xi_2 - P_y\xi_1 \tag{1}$$

and the flexoelectric

$$P_x\frac{d\xi_1}{dz} + P_y\frac{d\xi_2}{dz}, \tag{2}$$

where the z axis is perpendicular to the smectic layers. The piezoelectric coupling has a chiral nature and does not exist for achiral systems. The flexoelectric coupling exists for chiral as well as for achiral systems, but for achiral systems the molecules tilt homogeneously ($d\xi_1/dz = d\xi_2/dz = 0$) and the flexoelectric coupling has no effect. Therefore, the spontaneous polarization does not exist for achiral systems and is different from zero only for chiral systems. In the helicoidal smectic C* systems the spontaneous polarization induced by these two couplings is perpendicular to the direction of the tilt and is proportional to the magnitude of the tilt. Measurements [4, 5] do not confirm the predicted behaviour of the spontaneous polarization, and the predictions of the model for other thermodynamic properties of ferroelectric liquid crystals (pitch of the helix, dielectric susceptibility, critical electric and magnetic fields for unwinding the helicoidal structure, etc.) do not agree qualitatively with measured data [6, 7]. It was proposed therefore [8] that a biquadratic coupling

$$(P_x\xi_2 - P_y\xi_1)^2 \tag{3}$$

between the tilt and the polarization could be relevant in the smectic C* phase. The meaning of this coupling is that the tilt induces for chiral as well as for achiral systems a transverse quadrupolar ordering in the direction perpendicular to the tilt. This coupling is quadratic in the tilt and therefore has no effect close to the transition from the smectic A to the smectic C* phase, where only the bilinear couplings (see equations (1) and (2)) determine the properties of the system. At lower temperatures in the smectic C* phase the quadratic term becomes important and amplifies the effect of the bilinear couplings. The anomalous behaviour of thermodynamic properties of ferroelectric liquid crystals [4, 9] can be explained as a crossover behaviour between the two regimes.

The spontaneous polarization is usually measured for helicoidal ferroelectric liquid crystals [4, 5] in a state unwound by an external electric field. The corresponding Landau free energy density can be expressed as

$$g = -CP\theta - \tfrac{1}{2}\Omega P^2\theta^2 + \frac{1}{2\varepsilon}P^2 + \tfrac{1}{4}\eta P^4. \tag{4}$$

Here the molecules are taken to be tilted homogeneously in the x direction: $\xi = (\theta, 0)$, where θ is the magnitude of the tilt, and the polarization is induced in the y direction: $\mathbf{P} = (0, P)$. The first term in this free energy density is the piezoelectric coupling term. Its coefficient C is small because of its chiral nature and all of the chiral effects are expected to be small. The piezoelectric coupling is the only bilinear P–θ coupling because the flexoelectric coupling vanishes in a homogeneously ordered sample. The Ω term in equation (4) is the biquadratic P–θ coupling; here we take $\Omega > 0$. This means that the quadrupolar order is induced by the tilt in the same direction as the dipolar order and therefore the biquadratic coupling amplifies the effect of the bilinear coupling. For $\Omega < 0$ the quadrupolar order would be induced in the direction perpendicular to the direction of the dipolar order and would therefore reduce it [10]. In equation (4) ε, the coefficient of the harmonic term in P, corresponds to the high temperature dielectric susceptibility and the fourth order term with $\eta > 0$ is added to stabilize the system.

The free energy density g (see equation (4)) represents at a given tilt a non-equilibrium free energy density as a function of the polarization P. The square of the tilt represents an approximate measure for the temperature T, as it is expected within the Landau model that the tilt below the transition temperature T_c in the smectic C* phase increases monotonically and approximately as $(T_c - T)^{1/2}$. The equilibrium value of the polarization is obtained by minimizing the free energy density with respect to P:

$$\frac{dg}{dP} = \eta P^3 + \left(\frac{1}{\varepsilon} - \Omega\theta^2\right) P - C\theta = 0. \tag{5}$$

It is appropriate to introduce a dimensionless tilt ($\tilde{\theta}$) and a dimensionless polarization ($\tilde{P}$) as

$$\tilde{\theta} = (\varepsilon\Omega)^{1/2}\theta, \qquad \tilde{P} = (\varepsilon\eta)^{1/2}P. \tag{6}$$

Equation (5) can then be expressed as

$$\tilde{P}^3 + (1 - \tilde{\theta}^2)\tilde{P} - \beta\tilde{\theta} = 0, \tag{7}$$

where the only parameter β is defined as

$$\beta = \frac{\varepsilon\eta^{1/2}C}{\Omega^{1/2}} \tag{8}$$

and measures the relative importance of the chiral bilinear coupling coefficient C, which is expected to be small ($\beta < 1$). By solving equation (7) we obtain the dependence of the spontaneous polarization on the tilt and indirectly on the temperature, which agrees with measured dependences [4, 5]. Close to T_c, i.e. for $\tilde{\theta} \to 0$, the ratio, $\tilde{P}/\tilde{\theta} = \beta$. By lowering the temperature, i.e. by increasing $\tilde{\theta}$, the ratio $\tilde{P}/\tilde{\theta}$ increases and saturates at $\tilde{P}/\tilde{\theta} = 1$. By comparing the predictions of the model with the measured data [9] we obtain an estimate for the model parameters $\beta = 0{\cdot}17$, $(\varepsilon\Omega)^{-1/2} = 0{\cdot}2\,\mathrm{rad}$ and $(\varepsilon\eta)^{-1/2} = 1{\cdot}3 \times 10^{-5}\,\mathrm{A\,s\,m^{-2}}$.

Our aim is to introduce a microscopic model [7] for the influence of the molecular tilt on their transverse ordering. In §2 the model is described and its relationship to the Landau model is established. In §3 the spontaneous dipolar and quadrupolar transverse ordering are evaluated and the results are compared with the results of the Landau model, which, in contrast to the microscopic model, does not take thermal fluctuations into account.

2. The microscopic model and its relationship to the Landau model

We assume that the transverse molecular ordering does not originate from the interactions between their transverse dipole moments, but is a local property of a molecule which feels the average tilt of neighbouring molecules and therefore does not rotate freely around its long axis as in a smectic A phase. This assumption is already (implicitly) built into the Landau free energy expansion (see equation (4)). We describe the transverse orientation of a molecule by the angle ψ, which determines the orientation of the transverse molecular dipole. We measure the angle ψ from the direction which is perpendicular to the tilt. The single particle potential $V(\psi)$ for the rotation of a molecule around its long axis can be expressed as

$$V(\psi) = -a_1\theta\cos\psi - a_2\theta^2\cos 2\psi. \tag{9}$$

The first term is linear in θ and exists only for chiral molecules. It is analogous to the piezoelectric coupling term in the Landau expansion (see equation (1)). The tilt tends to induce the polar ordering in the direction $\psi = 0$ when the coefficient a_1 is positive. The second term is quadratic in θ and is not of chiral character. It leads to a quadrupolar ordering in the direction perpendicular to the tilt (for $a_2 > 0$) and is analogous to the biquadratic coupling in the Landau expansion (see equation (3)).

First we evaluate from the potential $V(\psi)$ the corresponding Landau free energy density expansion (see equation (4)). Such a free energy is a function of the spontaneous polarization P, which is proportional to $\langle\cos\psi\rangle$. It is also assumed implicitly that the induced quadrupolar moment, which is proportional to $\langle\cos 2\psi\rangle$ has been eliminated from the free energy by minimization. We therefore introduce an Ansatz for the density matrix

$$\varrho_{\mathrm{d}} = \frac{1}{Z}\exp\left(\frac{1}{kT}(A\cos\psi + B\cos 2\psi)\right), \tag{10}$$

where

$$Z = \int_0^{2\pi}\exp\left(\frac{1}{kT}(A\cos\psi + B\cos 2\psi)\right)d\psi \tag{11}$$

and A and B are the fields conjugate to $\langle\cos\psi\rangle$ and $\langle\cos 2\psi\rangle$, respectively, and are determined by the two equations for the average values:

$$\langle\cos\psi\rangle = \int_0^{2\pi}\cos\psi\,\varrho_{\mathrm{d}}\,d\psi, \tag{12 a}$$

$$\langle\cos 2\psi\rangle = \int_0^{2\pi}\cos 2\psi\,\varrho_{\mathrm{d}}\,d\psi, \tag{12 b}$$

as functions of $\langle\cos\psi\rangle$ and $\langle\cos 2\psi\rangle$: $A = A(\langle\cos\psi\rangle, \langle\cos 2\psi\rangle)$ and $B = B(\langle\cos\psi\rangle, \langle\cos 2\psi\rangle)$. The free energy per molecule is then evaluated as

$$\begin{aligned} G &= \langle V\rangle + kT\langle\ln\varrho_{\mathrm{d}}\rangle \\ &= -a_1\theta\langle\cos\psi\rangle - a_2\theta^2\langle\cos 2\psi\rangle + A\langle\cos\psi\rangle + B\langle\cos 2\psi\rangle - kT\ln Z, \end{aligned} \tag{13}$$

where $Z = Z[A(\langle\cos\psi\rangle, \langle\cos 2\psi\rangle), B(\langle\cos\psi\rangle, \langle\cos 2\psi\rangle)]$. We are interested only in the expansion of G in $\langle\cos\psi\rangle$ and $\langle\cos 2\psi\rangle$, which are small close to T_c. As a consequence the fields A and B are small and equations (12) can be expanded as

$$\langle\cos\psi\rangle = \tfrac{1}{2}\tilde{A} + \tfrac{1}{4}\tilde{A}\tilde{B} - \tfrac{1}{16}\tilde{A}^3, \tag{14 a}$$

$$\langle\cos 2\psi\rangle = \tfrac{1}{2}\tilde{B} + \tfrac{1}{8}\tilde{A}^2, \tag{14 b}$$

where $\tilde{A} = A/kT$ and $\tilde{B} = B/kT$. The inverse relationships can be obtained from equations (14) as

$$\tilde{A} = 2\langle\cos\psi\rangle - 2\langle\cos\psi\rangle\langle\cos 2\psi\rangle + 2\langle\cos\psi\rangle^3, \tag{15 a}$$

$$\tilde{B} = 2\langle\cos 2\psi\rangle - \langle\cos\psi\rangle^2 \tag{15 b}$$

and for the free energy per molecule we obtain the expansion in the two order parameters $\langle\cos\psi\rangle$ and $\langle\cos 2\psi\rangle$ as

$$\begin{aligned} G = {}& -a_1\theta\langle\cos\psi\rangle - a_2\theta^2\langle\cos 2\psi\rangle + kT\langle\cos\psi\rangle^2 - kT\langle\cos\psi\rangle^2\langle\cos 2\psi\rangle \\ & + \tfrac{1}{2}kT\langle\cos\psi\rangle^4 + kT\langle\cos 2\psi\rangle^2. \end{aligned} \tag{16}$$

By minimizing G with respect to the quadrupolar order parameter $\langle\cos 2\psi\rangle$ we obtain

$$\langle\cos 2\psi\rangle = \frac{1}{2}\frac{a_2\theta^2}{kT} + \tfrac{1}{2}\langle\cos\psi\rangle^2, \tag{17}$$

which means that the quadrupolar ordering consists of two contributions. The first is proportional to the square of the tilt and the second is proportional to the square of the dipolar ordering. By eliminating $\langle\cos 2\psi\rangle$ from equation (16) we obtain

$$G = -\frac{1}{4}\frac{a_2^2\theta^4}{kT} - a_1\theta\langle\cos\psi\rangle - \tfrac{1}{2}a_2\theta^2\langle\cos\psi\rangle^2 + kT\langle\cos\psi\rangle^2 + \tfrac{1}{4}kT\langle\cos\psi\rangle^4. \tag{18}$$

This expression for the free energy per molecule has the same structure as the Landau free energy density g (see equation (4)). Using the relationships $g = \varrho G$ and $P = \varrho\mu_d\langle\cos\psi\rangle$, where ϱ is the number of molecules per unit volume and μ_d is the molecular transverse dipole moment, we can express the coefficients of the Landau expansion in terms of the parameters of the microscopic model:

$$C = \frac{a_1}{\mu_d}, \quad \Omega = \frac{a_2}{\varrho\mu_d^2}, \quad \varepsilon = \frac{\varrho\mu_d^2}{2kT}, \quad \eta = \frac{kT}{\varrho^3\mu_d^4}. \tag{19}$$

We see that the parameters a_1 and a_2 determine the piezoelectric and the biquadratic coupling coefficients, respectively, and that the ε and η coefficients are of entropic origin. The ε coefficient is equal to the Curie free dipole susceptibility.

3. The results of the model

The spontaneous polarization is calculated as

$$P = \varrho\mu_d\langle\cos\psi\rangle = \varrho\mu_d\int\cos\psi\exp(-V/kT)\,d\psi\Big/\int\exp(-V/kT)\,d\psi, \tag{20}$$

where the potential $V(\psi)$ is given by equation (9). Introducing the dimensionless tilt ($\tilde{\theta}$) and the dimensionless polarization ($\tilde{P}$) in the same way as in the Landau model (see equation (6)) and using the equations (19), we obtain from equation (20)

$$\tilde{P} = \frac{1}{2^{1/2}}\frac{\int_0^{2\pi}\cos\psi\exp[2^{3/2}\beta\tilde{\theta}\cos\psi + 2\tilde{\theta}^2\cos 2\psi]\,d\psi}{\int_0^{2\pi}\exp[2^{3/2}\beta\tilde{\theta}\cos\psi + 2\tilde{\theta}^2\cos 2\psi]\,d\psi}, \tag{21}$$

where β is defined in equation (8). In figure 1 the calculated dependence of the ratio $\tilde{P}/\tilde{\theta}$ on $\tilde{\theta}^2$, which is a measure for $T_c - T$, is shown for some values of β together with the corresponding results of the Landau model. The two results agree close to T_c at small $\tilde{\theta}$ where the potential $g(P)$ (see equation (4)) is almost harmonic, and thermal fluctuations, which are taken into account in the microscopic model but not in the Landau model, have no effect on the average value of the polarization. For larger $\tilde{\theta}$ the fluctuations diminish the average value of the polarization and the polarizations obtained from the microscopic model are below the Landau model values. At large θ the ratio P/θ decreases because of polarization saturation effects, which are not included in the Landau model. The dependence of P/θ on θ^2 is always convex, in contrast with the Landau model, where it shows for small β an S-shaped behaviour.

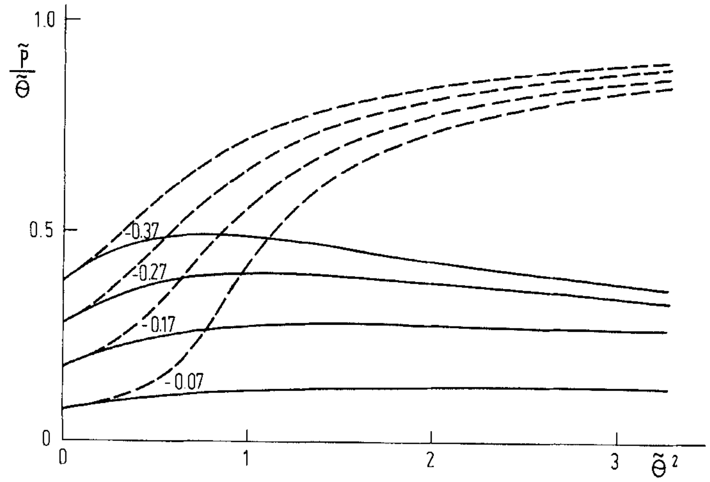

Figure 1. The dependence of the ratio $\tilde{P}/\tilde{\theta}$ on $\tilde{\theta}^2$ for four values of β. The corresponding results of the Landau model are also shown (broken curves).

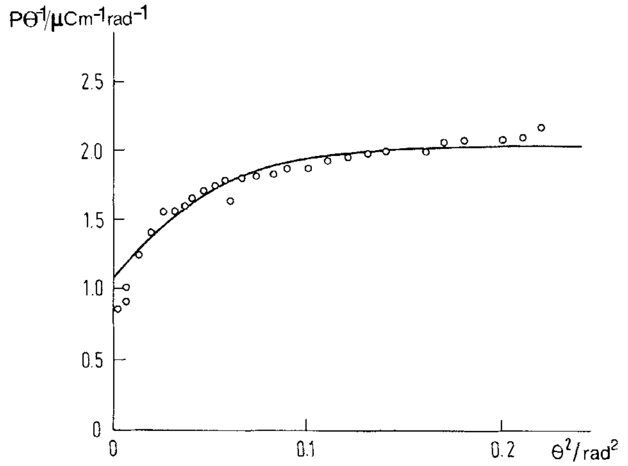

Figure 2. The fit of the results of the microscopic model to measured [4] values of P/θ. In the fit $\theta^* = 0{\cdot}260\,\mathrm{rad}$, $P^* = 7{\cdot}01 \times 10^{-6}\,\mathrm{A\,s\,m^{-2}}$ and $\beta = -0{\cdot}0400$.

As a consequence the temperature dependence of the spontaneous polarization (see equation (20)) is always convex.

In figure 2 a fit of measured data [4] is presented and the three parameters of the model are determined: $\theta^* = (\varepsilon\Omega)^{-1/2} = 0{\cdot}26\,\mathrm{rad}$, $P^* = (\varepsilon\eta)^{-1/2} = 7{\cdot}01 \times 10^{-6}\,\mathrm{A\,s\,m^{-2}}$ and $|\beta| = 0{\cdot}040$. The value of θ^* is only slightly larger than the corresponding Landau model value, whereas P^* is smaller by almost a factor of 2 and β by more than a factor of 4. We can conclude therefore that the Landau model can describe both qualitatively and quantitatively the properties of ferroelectric liquid crystals, but the values of the model parameters obtained in such a way have only an effective meaning. We can also observe in figure 2 that the predicted saturation regime, whereas P/θ decreases, does not seem to be accessible experimentally.

In figure 3 the quadrupolar and the dipolar order parameters $\langle\cos 2\psi\rangle$ and $\langle\cos\psi\rangle$, calculated from the microscopic model for these values of the parameters,

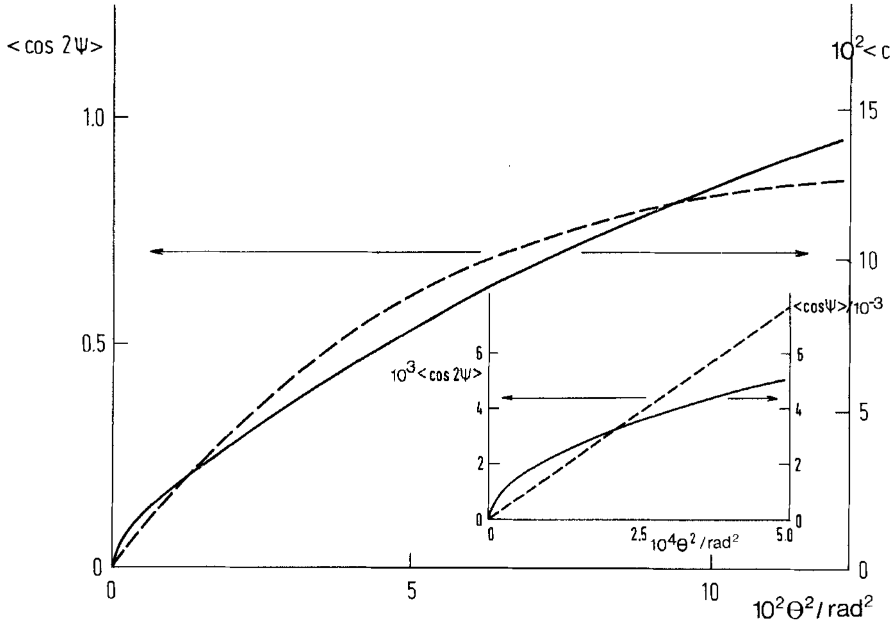

Figure 3. The dependence of $\langle\cos 2\psi\rangle$ and $\langle\cos\psi\rangle$ on θ^2. In the inset an enlarged part at small tilt angles is presented. The calculations used $\theta^* = 0{\cdot}260\,\mathrm{rad}$, $P^* = 7{\cdot}01 \times 10^{-6}\,\mathrm{A\,s\,m^{-2}}$ and $\beta = -0{\cdot}0400$.

are shown. We observe that the quadrupolar ordering is much larger than the dipolar ordering in the whole smectic C* phase expect close to T_c at very small tilt angles.

4. Conclusions

A microscopic model was introduced for the rotation of a chiral molecule around its long axis in a tilted smectic C phase. The potential consists of a dipolar term, which has a chiral character and is linear in the tilt, and a quadrupolar term, which is achiral and is quadratic in the tilt. The model is consistent with the extended thermodynamic model, which was shown recently to be capable of describing the properties of ferroelectric liquid crystals. It is shown that, for the values of the model parameters which describe the experimental data, the dipolar order parameter is much smaller than the quadrupolar ordering except very close to T_c.

In this model it is assumed that the three characteristic molecular directions, i.e. the direction of the chiral ordering, the direction of a molecular dipole and the quadrupolar molecular axis coincide. In a more general case the model could account also for the recently observed polarization sign reversal [11, 12].

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