Generalized Landau model of ferroelectric liquid crystals

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Using a generalized Landau type of free-energy density, we develop a theoretical model which, in a unified way, describes the general features of the tilt, polarization, pitch, dielectric susceptibility, and heat capacity of ferroelectric liquid crystals. Rewriting the equations into dimensionless form, we show that six parameters are needed in order to account properly for the temperature dependence of the quantities in question. It is also shown that the introduction of a biquadratic coupling between the tilt and the polarization in the free-energy density, which is an essential part of the model, implies a crossover behavior of the polarization when plotted as a function of temperature.

The chiral ferroelectric SmC^* phase represents a spatially modulated structure.[1-3] The tilt of the long molecular axis from the normal to the smectic layers precesses as one goes from one smectic layer to another, resulting in a helicoidal structure. Because of the chirality of molecules the tilt locally breaks the axial symmetry around the long molecular axis and induces a transverse in-plane polarization perpendicular to the direction of the tilt.

The Landau free-energy expansion used for the quantitative description of the system consists of the expansion in two order parameters. These are the primary-order parameter, the two-component tilt vector $\xi=(\xi_1,\xi_2)$, which is coupled to the secondary-order parameter, the two-component in-plane polarization $\mathbf{P}=(P_x,P_y)$.

Early ways of writing the free-energy density expansion have failed[2,3] to describe the experimental behavior of the system properly. By using a generalized[4-6] Landau expansion, where the most essential thing is the introduction of a biquadratic coupling between tilt and polarization, we are, however, able to describe the behavior of most of the quantities of interest of a ferroelectric liquid crystal. This coupling, which leads to a transverse quadrupole ordering, is of nonchiral character and can therefore be expected to be large compared to the bilinear coupling, which is of chiral character. Thus a crossover behavior can be expected from a regime close to T_c, where because of small tilt only bilinear coupling is important, to the regime far from T_c, where the tilt is large and the biquadratic coupling induces a transverse quadrupole ordering. This crossover manifests itself in such a way[6] that the graph of the polarization versus temperature can be expected to exhibit S-shaped behavior. This type of behavior has been observed[7] by us in p-(n-decyloxybenzylidene)-p-amino-(2-methyl-butyl)cinnamate (DOBAMBC), while other authors have presented[8] polarization measurements of DOBAMBC which are of non-S-shaped character.

It is the purpose of this report to show how the generalized Landau expansion of the free-energy density can be used to describe the SmA-SmC^* phase transition in a way which eliminates the shortcomings of previous[2,3] calculations. We shall present high-temperature resolution measurements of the spontaneous polarization, the pitch of the helix, and the dielectric constant of DOBAMBC and describe them qualitatively by our extended Landau model. The details of the experimental methods are presented elsewhere.[7,9-11] Using the parameters of the model determined from the experimental data, we shall calculate the tilt and the specific-heat temperature dependences.

The free-energy density describing the SmA-SmC^* transition can be expressed as[6]

$$g(z)=\tfrac{1}{2}a(\xi_1^2+\xi_2^2)+\tfrac{1}{4}b(\xi_1^2+\xi_2^2)^2+\tfrac{1}{6}c(\xi_1^2+\xi_2^2)^3-\Lambda\left[\xi_1\frac{d\xi_2}{dz}-\xi_2\frac{d\xi_1}{dz}\right]+\tfrac{1}{2}K_3\left[\left[\frac{d\xi_1}{dz}\right]^2+\left[\frac{d\xi_2}{dz}\right]^2\right]$$
$$-d(\xi_1^2+\xi_2^2)\left[\xi_1\frac{d\xi_2}{dz}-\xi_2\frac{d\xi_1}{dz}\right]+\frac{1}{2\epsilon}(P_x^2+P_y^2)+\tfrac{1}{4}\eta(P_x^2+P_y^2)^2-\mu\left[P_x\frac{d\xi_1}{dz}+P_y\frac{d\xi_2}{dz}\right]$$
$$+C(P_x\xi_2-P_y\xi_1)-\tfrac{1}{2}\Omega(P_x\xi_2-P_y\xi_1)^2\ , \qquad (1)$$

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where the z axis is normal to the smectic layers. Only the term quadratic in tilt is explicitly temperature dependent, $a=\alpha(T-T_0)$. K_3 is the elastic modulus, Λ the coefficient of the Lifshitz term responsible for the modulation, and μ and C are the coefficients of the flexo- and piezo-electric bilinear coupling. Ω is the coefficient of the biquadratic coupling term inducing transverse quadrupole ordering and the η term has been added to stabilize the system. The d term describes the monotonous increase of the pitch with temperature at low temperature. The sixth-order term in tilt (the c term) has been added to account for the specific-heat temperature dependence of the system.[12,13]

We are looking for a helicoidal solution

$$\xi_1=\theta_0\cos(qz),\quad \xi_2=\theta_0\sin(qz)\ , \tag{2a}$$

$$P_x=-P_0\sin(qz),\quad P_y=P_0\cos(qz)\ , \tag{2b}$$

which minimizes the free energy. Here $q=2\pi/p$ is the wave vector of the helix. Substituting this ansatz into Eq. (1) we obtain an expression for the free-energy density, which, when minimized with respect to θ_0, P_0, and q, respectively, gives three equations determining the tilt, the polarization, and the pitch of the system as functions of temperature.

It turns out to be convenient to rewrite the equations governing the behavior of the system into dimensionless form. By doing so we reduce the 11 material parameters introduced in Eq. (1) to six independent dimensionless constants

$$\gamma=\frac{\tilde{b}\eta}{\Omega^2},\quad \beta=\frac{\eta^{1/2}\tilde{C}\tilde{\epsilon}}{\Omega^{1/2}},\quad \rho=\frac{\tilde{c}\eta}{\tilde{\epsilon}\Omega^3}\ ,$$
$$\lambda=\frac{\Lambda\eta^{1/2}\tilde{\epsilon}^{1/2}}{K_3^{1/2}\Omega^{1/2}},\quad \nu=\frac{\mu\tilde{\epsilon}^{1/2}}{K_3^{1/2}},\quad \delta=\frac{d\eta^{1/2}}{K_3^{1/2}\Omega^{3/2}\tilde{\epsilon}^{1/2}}\ , \tag{3}$$

where

$$\tilde{a}=a-\frac{\Lambda^2}{K_3},\quad \tilde{b}=b-\frac{4\Lambda d}{K_3}\ ,$$
$$\tilde{c}=c-\frac{3d^2}{K_3},\quad \frac{1}{\tilde{\epsilon}}=\frac{1}{\epsilon}-\frac{\mu^2}{K_3},\quad \tilde{C}=C+\frac{\Lambda\mu}{K_3}\ . \tag{4}$$

The physical quantities such as the polarization P_0, the tilt θ_0, the wave vector q, and the dielectric susceptibility χ will now be expressed in dimensionless form and will be denoted by a tilde above the corresponding symbol, while the characteristic units with which these are measured will be denoted by an asterisk (e.g., $\tilde{\theta}_0=\theta_0/\theta^*$). The reduced temperature, however, we denote by $\tau=(T_c-T)/T^*$. The characteristic units are chosen to be

$$\theta^*=\left[\frac{1}{\tilde{\epsilon}\Omega}\right]^{1/2},\quad P^*=\left[\frac{1}{\tilde{\epsilon}\eta}\right]^{1/2}\ ,$$
$$q^*=\frac{1}{z^*}=\left[\frac{\Omega}{\tilde{\epsilon}\eta K_3}\right]^{1/2}\quad \chi^*=\tilde{\epsilon},\quad T^*=\frac{\tilde{b}}{\tilde{\epsilon}\alpha\Omega}\ , \tag{5a}$$

$$g^*=\frac{P^{*2}}{\chi^*},\quad c_p^*=\frac{P^{*2}}{\chi^*T^*},\quad E^*=\frac{P^*}{\chi^*}\ . \tag{5b}$$

The original 11 parameters [Eq. (1)] can thus be transformed into six dimensionless constants [Eqs. (3) and (4)], which determine the shape of the temperature dependences of the physical quantities, and into five characteristic units [Eq. (5a)]. The characteristic units of the free-energy density, of the heat capacity, and of the electric field are not independent and are given in Eq. (5b) for completeness.

Eliminating q from the free-energy density, this can be written in dimensionless form as

$$\tilde{g}_0=\tfrac{1}{2}(\beta^2-\gamma\tau)\tilde{\theta}_0^2+\tfrac{1}{4}\gamma\tilde{\theta}_0^4+\tfrac{1}{6}\rho\tilde{\theta}_0^6+\tfrac{1}{2}\tilde{P}_0^2-\beta\tilde{P}_0\tilde{\theta}_0$$
$$-\tfrac{1}{2}\tilde{P}_0^2\tilde{\theta}_0^2+\tfrac{1}{4}\tilde{P}_0^4-\nu\delta\tilde{\theta}_0^3\tilde{P}_0\ . \tag{6}$$

The equations for $\tilde{\theta}_0$ and $\tilde{P}_0$ are obtained by minimizing Eq. (6),

$$(\beta^2-\gamma\tau)\tilde{\theta}_0+\gamma\tilde{\theta}_0^3+\rho\tilde{\theta}_0^5-\tilde{\theta}_0\tilde{P}_0^2-(\beta+3\nu\delta\tilde{\theta}_0^2)\tilde{P}_0=0\ , \tag{7a}$$

$$\tilde{P}_0^3+(1-\tilde{\theta}_0^2)\tilde{P}_0-(\beta+\nu\delta\tilde{\theta}_0^2)\tilde{\theta}_0=0\ , \tag{7b}$$

while $\tilde{q}$ [obtained by minimizing Eq. (6) before the substitution] is given by

$$\tilde{q}=\lambda+\nu\frac{\tilde{P}_0}{\tilde{\theta}_0}+\delta\tilde{\theta}_0^2\ . \tag{8}$$

Our model also permits us to calculate[6,11] the dielectric susceptibility $\chi=\lim_{E\to 0}\langle P_i\rangle/E$. The electric field is assumed to be applied parallel to the smectic layers and $\langle P_i\rangle$ is the corresponding induced polarization. These calculations are, however, much too involved to be displayed here. The induced polarization consists of two contributions of different nature,[11] generally denoted as the soft mode (χ_1) and the Goldstone mode (χ_2), respectively. The soft mode contributes at T_c in a cusplike way and is rapidly suppressed as T_c-T increases. The Goldstone mode contributes in all the SmC^* phase and is thus the dominating part of χ, except in a temperature interval of a few tenths of a degree below T_c. By physical reasoning we have been able to derive[6,11] an expression of χ_2 which approximates the exact one with a relative error which is less than 10^{-3}. This reads

$$\tilde{\chi}_2=\frac{1}{8\pi^2}\left[\frac{\tilde{P}_0\tilde{p}}{\tilde{\theta}_0}\right]^2,\quad \chi_2=\frac{1}{8\pi^2K_3}\left[\frac{P_0p}{\theta_0}\right]^2\ , \tag{9}$$

where we have given the relation in both dimensionless and physical units. As the contribution to χ from the soft mode is negligible except close to T_c, the expression (9) can serve as a good approximation of χ in almost all the SmC^* phase.

In Fig. 1 we show the results of a calculation using the parameter values $\gamma=2.0$, $\beta=-0.17$, $\rho=0.9$, $\lambda=-0.062$, $\nu=-0.06$, and $\delta=-0.012$. These parameter values have been obtained by fitting the outcome of the calculations to our experimentally measured values of polarization, pitch, and dielectric susceptibility of DOBAMBC, which are shown as crosses in the figure. The signs of the four parameters β, λ, ν, and δ are chosen in such a way,[6] that the calculations describe a left-handed, "minus" compound. The fitting procedure, which involves altogether the six dimensionless parameters of Eqs. (3) and four of the scaling factors (T^*, P^*, q^*, and χ^*), is not straight-

forward and more effort has to be put to construct a scheme with which the parameters of the model can be determined unambiguously. Thus the curves in Fig. 1 do not represent the best fit, but just one fit which shows anyhow that our model gives a qualitative correct description of the system and has removed all the shortcomings of the previous simplified models.[2,3] By the parameters obtained above, we have calculated the tilt and the heat capacity $\tilde{c}_p = -(T_c/T^* - \tau)(d^2\tilde{g}_0/d\tau^2)_p$. By comparing these calculations with available data,[13,14] we obtained approximate values of θ^* and c_p^*. The full set of scaling factors has been determined to be $T^* = 0.92$ K, $P^* = 1.3 \times 10^{-5}$ C/m^2, $p^* = 1.46 \times 10^{-8}$ m, $\chi^* = 2.7 \times 10^{-13}$ C/V m, $\theta^* = 0.2$ rad and $c_p^* = 900$ J/m^{3}K. From Eqs. (5b) we have $c_p^* = P^{*2}/(\chi^* T^*) = 690$ J/m^{3}K. This number shall be compared with the value of c_p^* given above as a check of the consistency of the parameters we have chosen.

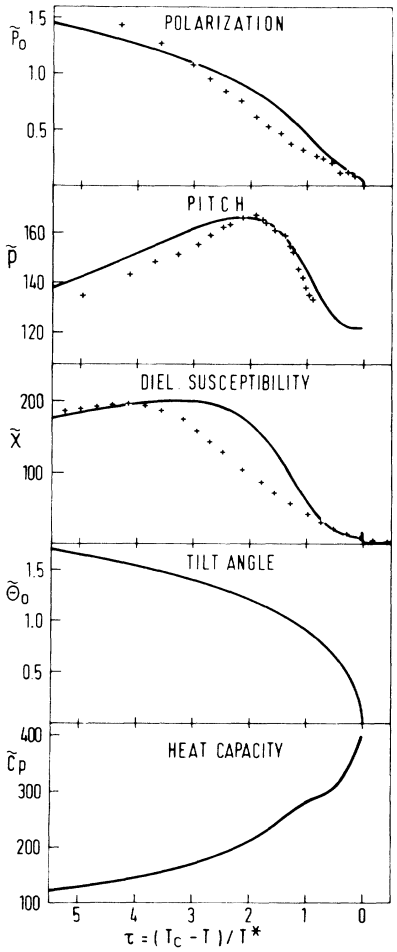

FIG. 1. Calculated $\tilde{P}_0$, $\tilde{p}$, $\tilde{\chi}$, $\tilde{\theta}_0$, and $\tilde{c}_p$ vs τ (solid lines). The crosses represent the experimental values.

One feature which comes as a natural consequence out of our model is the tendency of the polarization curve to exhibit S-shaped behavior. This behavior, which is experimentally observed by us for DOBAMBC, as is seen from Fig. 1, has also been observed by other authors[15,16] for other compounds. However, Dumrongrattana and Huang[8] strongly argue against S-shaped polarization curves for experimental as well as theoretical reasons. We have therefore investigated the polarization equation (7b) in detail and have shown how the behavior of the polarization can be analyzed essentially by the use of the parameter β only. From theoretical reasoning we expect[6] $|\nu\delta| \ll |\beta|$, a behavior which is also verified by our choice of parameters of DOBAMBC. Thus, neglecting the $\nu\delta\tilde{\theta}_0^2$ term and dividing Eq. (7b) by $\tilde{\theta}_0^3$, we conclude that the ratio $\tilde{P}_0/\tilde{\theta}_0$ plotted as a function of $\tilde{\theta}_0^2$ depends on the parameter β only. In Fig. 2 we have plotted $\tilde{P}_0/\tilde{\theta}_0$ and $\tilde{P}_0$ as functions of $\tilde{\theta}_0^2$ for three different values of the parameter β. The lesson we learn from Fig. 2 is that the S-shaped behavior of the polarization is connected to the "anomalous" behavior of $\tilde{P}_0/\tilde{\theta}_0$. As we can easily derive $\lim_{\tilde{\theta}_0 \to 0} \tilde{P}_0/\tilde{\theta}_0 = \beta$ and $\lim_{\tilde{\theta}_0 \to \infty} \tilde{P}_0/\tilde{\theta}_0 = 1$ from Eqs. (7b), we conclude that the S shape of the polarization curve is connected to the dip of $\tilde{P}_0/\tilde{\theta}_0$ close to T_c, i.e., to the smallness of β. This in turn means that the polarization curve becomes S shaped if the biquadratic coupling (Ω term) is strong enough compared to the bilinear coupling (C term) as $\beta \sim \tilde{C}/\Omega^{1/2}$. We have calculated[6] the critical value of β for producing S-shaped polarization curves to be between 0.3 and 0.5, depending on the values of γ and ρ. It is easy to show[17] that S-shaped as well as non-S-shaped polarization curves are well contained within the realistic sets of parameters, but it is obvious that the solutions of Eqs. (7) exhibit a crossover behavior, the magnitude of which is determined by β.

In conclusion, we have shown that our extended Landau model is capable of describing the features of the SmA-SmC^* phase transition qualitatively correctly. We have demonstrated that the experimentally observed S shape of the polarization curve is an inherent quality of

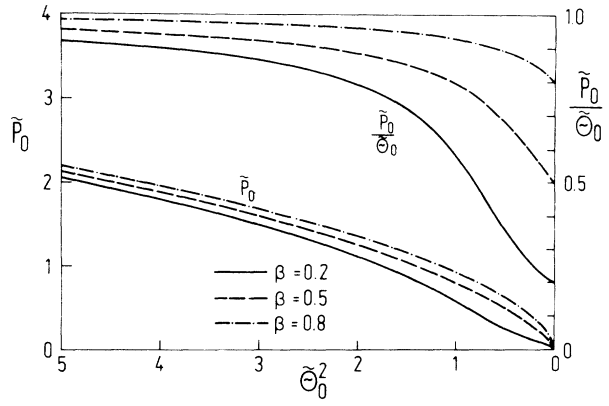

FIG. 2. Calculated $\tilde{P}_0/\tilde{\theta}_0$ and $\tilde{P}_0$ vs $\tilde{\theta}_0^2$.

the polarization equation (7b) for strong enough biquadratic coupling (small enough β). Still we must admit that the fitting of the model to the experimental data is not a straightforward problem and more work has to be done in the future concerning this.

Further, as the polarization equation is a cubic equation, two solutions of which correspond to a local minimum (for certain values of τ) of g_0, we believe that the incorporation of thermal fluctuations is also essential in future development of the model.

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