A phenomenological theory of the isotropic to chiral smectic-C phase transition

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Abstract. In this paper we discuss the direct isotropic to chiral smectic C phase transition on the basis of a phenomenological theory. The model free energy is written in terms of the coupled order parameters including the spontaneous polarization. We present a detailed analysis of the different phases that can occur and analyze the question under which conditions a direct isotropic to chiral smectic-C phase transition is possible when compared to other phase transitions. On the basis of this model the isotropic - smectic-C* transition is always of first order. The theoretical predictions are compared with the available experimental results.

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1 Introduction and motivation

During the last two decades much progress has taken place in the field of ferroelectric liquid crystals. The smectic phases are organized in layers, where in the smectic C (SmC) phase the director $\mathbf{n}$ is tilted by a fixed angle θ relative to the layer normal $\mathbf{k}$. The chiral smectic (SmC*) phase represents a spatially modulated structure [1]. The SmC* phase shows in addition an intrinsic twist of the director from layer to layer. This additional symmetry breaking ($C_{2h} \rightarrow C_2$) allows microscopic electric dipoles to form a spontaneous electric polarization $\mathbf{P}$, which lies in the smectic planes.

While the research on the smectic A (SmA) to SmC* phase transition has attracted much attention, there is also increasing interest in the isotropic to SmC* (I-SmC*) transition. There are relatively few experimental works [2] - [6] on the I - SmC* phase transition. All these experiments showed the first order character of the I - SmC* phase transition. (S)-4'-(6-methyloctyl)resorcylidene 4-alkylanilines (MORA-n) are one such family of materials which show a direct I - SmC* phase transition. The enthalpy jump at the transition point indicates a first order character of the I - SmC* phase transition. The electrooptic measurements on the chiral derivative, denoted as A*B by Coles et al [6] show a weak temperature dependence of the spontaneous polarization in the SmC* phase and a finite value of the tilt angle and the spontaneous po-

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larization at the I - SmC* phase transition. The presence of a sharp peak and the small anomaly in the heat capacity measurements [7] also support a first order character of the I-SmC* phase transition.

There is practically no theoretical work on the I - SmC* phase transition because of the complexity of the system. The purpose of the present paper is to develop a phenomenological Landau model to examine the nature of and the factors governing the I - SmC* phase transition. Our approach will be similar to that used already for the investigations of the I - SmA and I - SmC phase transitions, which we analyzed before [8,9]. In the latter paper there is an algebraic error, which we correct here.

2 Model

2.1 Order parameter

The construction of the Landau free energy for the I - SmC* phase transition is rather complex, since one needs four different order parameters: the modulus of the orientational order parameter, S, the smectic order parameter characterizing the density wave, ψ, the tilt angle, θ and the spontaneous polarization, $\mathbf{P}$ as well as the wave vector q of the helix to describe the I - SmC* phase transition. All these order parameters jump simultaneously at the I - SmC* phase transition. First we start by describing the order parameters involved in the I - SmC* phase transition. The layering in the SmC* phase is described [10,11] by

the order parameter $\psi(\mathbf{r}) = \psi_0 \exp(-i\Phi)$, whose modulus ψ_0 is defined as the amplitude of a one dimensional density wave characterized by the phase Φ. The wave vector $\nabla_i \Phi$ is parallel to the director n_i in the smectic A phase. The layer spacing is given by $d = 2\pi/q_0$ with a nonzero $q_0 = |\nabla\Phi|$. It should be noted that d generally is of the order of the molecular length. Thus, the gradient expansion of ψ, in particular its truncation after the first few terms, is not of the same rigor as the gradient expansion of the nematic order parameter (see below). Nevertheless, we restrict ourselves to the lowest gradient terms of ψ for practical reasons. As a consequence, the q_0 dependences obtained by this procedure have to be taken with a grain of salt. However, since q_0 does not vary very much in most smectic phases, the q_0 dependence is not the most interesting one, anyhow. The tilt angle in the SmC* phase is described by the uniaxial orientational order parameter

$$Q_{ij} = \frac{S}{2}(3n_i n_j - \delta_{ij}) \tag{1}$$

where n_i is not parallel to $\nabla_i \Phi$. We assume flat layers in the smectic phases and take the layer normal $q_0^{-1}\boldsymbol{\nabla}\Phi = \mathbf{e}_z$ as the z−axis. Then $\mathbf{n}$ is defined by

$$\mathbf{n} = \mathbf{e}_x \sin\theta\cos\phi(z) + \mathbf{e}_y \sin\theta\sin\phi(z) + \mathbf{e}_z \cos\theta \tag{2}$$

where θ is the angle between the layer normal and the director n_i. The azimuthal angle ϕ describing the average position of the molecules on the cone changes with the coordinate z as $\phi = qz$. The wave vector of the helix, q, is much smaller than the wave vector of the density modulation *i.e.* $q \ll q_0$. The quantity S defines the strength of the orientational ordering and is zero (one) for complete disorder (order). Thus the tilt angle in the SmC* phase is determined by the orientational order parameter. We point out that the modulus of the orientational order parameter in the SmC* phase was measured experimentally by Dollase and Fung [12]. In the main body of this manuscript we neglect the small biaxiality [13] in the orientational order parameter for simplicity, but discuss its main implications in the Appendix.

The in-plane spontaneous polarization is defined as

$$\mathbf{P} = P_0(-\sin\phi(z), \cos\phi(z), 0) \tag{3}$$

Here P_0 is the magnitude of the spontaneous polarization in the unwound ferroelectric state.

2.2 The free energy

Considering the order parameters described above we will now construct the free energy density near the I - SmC* phase transition. Keeping homogeneous terms up to quartic order and gradients only to lowest relevant order, the free energy density near the I - SmC* phase transition can

be written as:

$$\begin{aligned}
F = F_0 &+ \frac{1}{2}AQ_{ij}Q_{ij} - \frac{1}{3}BQ_{ij}Q_{jk}Q_{ki} \\
&+ \frac{1}{4}C_1(Q_{ij}Q_{ij})^2 + \frac{1}{4}C_2 Q_{ij}Q_{jk}Q_{kl}Q_{li} \\
&+ \frac{1}{2}\alpha|\psi|^2 + \frac{1}{4}\beta|\psi|^4 + \frac{1}{2\chi_0}\mathbf{P}^2 \\
&+ \frac{1}{2}\delta Q_{ij}Q_{ij}|\psi|^2 + \gamma Q_{ij}P_iP_j + \frac{1}{2}L_1\nabla_i Q_{jk}\nabla_i Q_{jk} \\
&+ \frac{1}{2}L_2\nabla_i Q_{ik}\nabla_j Q_{jk} + L_3\varepsilon_{ijk}Q_{il}\nabla_k Q_{jl} \\
&+ \frac{1}{2}b_1|\nabla_i\psi|^2 + \frac{1}{2}b_2|\Delta\psi|^2 + \frac{1}{2}eQ_{ij}(\nabla_i\psi)(\nabla_j\psi^*) \\
&+ \frac{1}{2}fQ_{il}Q_{jl}(\nabla_i\psi)(\nabla_j\psi^*) + \frac{1}{2}g_{ijkl}P_l\nabla_k Q_{ij} \\
&+ \frac{1}{2}hQ_{ij}Q_{kl}(\nabla_i\nabla_j\psi)(\nabla_k\nabla_l\psi^*) \tag{4}
\end{aligned}$$

where F_0 is the free energy of the isotropic phase. $A = a(T - T_1^*)$ and $\alpha = \alpha_0(T - T_2^*)$, T_1^* are T_2^* are the critical temperatures for a hypothetical second order transition in the absence of any cross-coupling and cubic terms. Here we take $T_1^* > T_2^*$. All other coefficients, as well as a_0, and α_0 are assumed to be temperature independent. δ and γ are coupling constants. A negative value of δ increases smectic ordering and favors the SmC* phase over the isotropic phase. χ_0 is the dielectric susceptibility. L_1, L_2 and L_3 are the orientational elastic constants. The isotropic gradient terms in Eq. (4) guarantee a finite wavelength q_0 for the smectic density wave. Symmetry would allow another term, $\frac{b_3}{2}|\nabla_i\nabla_j\psi|^2$, which however does not lead to any new contribution (compared to that $\sim b_2$) for the smectic phase and has therefore been omitted here. ε_{ijk} is the antisymmetric third-rank tensor. The chiral character of the SmC* phase results in the pseudoscalar first order spatial derivative term in the free energy. Thus the coefficient L_3 is analogous to the coefficient of the Lifshitz-invariant term and induces the helical modulation of the SmC* phase. We assume $L_3 < 0$. The gradient terms $\sim e, f$ and $\sim h$ involving Q_{ij} govern the relative direction of the layering with respect to the director and lead to the tilt angle of the SmC* phase. In general a negative value of e favors the stability of tilted smectic phases. Here g_{ijkl} takes the form $g_{ijkl} = g(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$. The coefficient g is analogous to the flexoelectric coefficient and would be negative for $\mathbf{P} > 0$ and positive for $\mathbf{P} < 0$. A coupling term $\sim \mathbf{P}^2|\psi|^2$ could also be added in the free energy (4).

Now we consider the phases in which the nematic and smectic order are spatially homogeneous, *i.e.* S =const. and ψ_0=const., and for the smectic phase a spatially constant wave vector q_0 characterizing the layering. The substitution of Q_{ij}, ψ and $\mathbf{P}$ in Eq. (4) leads to the free energy

density

$$F = F_0 + \frac{3}{4}AS^2 - \frac{1}{4}BS^3 + \frac{9}{16}CS^4 + \frac{1}{2}\alpha\psi_0^2 + \frac{1}{4}\beta\psi_0^4$$
$$+ \frac{1}{2\chi_0}P_0^2 + \frac{3}{4}\delta S^2\psi_0^2 - \frac{1}{2}\gamma P_0^2 S + \frac{9}{4}L'S^2q^2\sin^2\theta$$
$$- \frac{9}{8}L_2S^2q^2\sin^4\theta + \frac{9}{4}L_3S^2q\sin^2\theta + \frac{1}{2}b_1\psi_0^2q_0^2$$
$$+ \frac{1}{2}b_2\psi_0^2q_0^4 + \frac{1}{4}e\psi_0^2q_0^2S(3\cos^2\theta - 1)$$
$$+ \frac{1}{8}f\psi_0^2q_0^2S^2(3\cos^2\theta + 1) + \frac{3}{2}gSP_0q\sin\theta\cos\theta$$
$$+ \frac{1}{8}h\psi_0^2q_0^4S^2(3\cos^2\theta - 1)^2 \tag{5}$$

where $L' = (L_1 + L_2/2)$ and $C = (C_1 + C_2/2)$. The sign of the coefficients $a, \alpha_0, B, C, \beta, b_1, b_2, L_1$ and L_2 is assumed to be positive. The presence of the cubic terms ($\sim B, \sim \gamma$ and $\sim e$) signals the first order character of the I - SmC* transition.

Equilibrium values of S, ψ_0, P_0, q_0, q, and θ are determined from the condition that F should be a minimum with respect to all these variables. We obtain

I) Isotropic phase: $S = 0$, $\psi_0 = 0$, $P_0 = 0$, $q_0 = 0$, $q = 0$, $\theta = 0$.

II) Cholesteric (Ch) phase :
$S_{ch} = \frac{B}{6C}\left[1 + \left(1 - \frac{24A_1C}{B^2}\right)^{1/2}\right]$, $P_0 = 0$, $q_0 = 0$, $\psi_0 = 0$
$q_{ch} = (-L_3/2L_1)$, $\theta_{ch} = \pi/2$.

III) Smectic A (SmA) phase (for $h = 0$):
$S_A \neq 0$, $\psi_0^2 = -\frac{1}{\beta}\left(\alpha^* - e^*S_A + \frac{3}{2}\delta^*S_A^2\right)$,
$q_0^2 = -\frac{1}{2b_2}(b_1 + eS_A + fS_A^2)$, $P_0 = 0$, $q = 0$, $\theta = 0$.
where S_A is defined by:
$\frac{2\alpha^*e^*}{3\beta} + 2A_1^*S_A - B^*S_A^2 + 3C^*S_A^3 = 0$

IV) SmC* phase : $S_{C^*} \neq 0$, $\psi_0 \neq 0$, $P_0 \neq 0$, $q_0 \neq 0$, $q_{C^*} \neq 0$, $\theta_{C^*} \neq 0$ (for details cf. the following section).

We use the abbreviations $A_1 = A - \frac{3L_3^2}{4L_1}$, $\alpha^* = \alpha - (b_1^2/4b_2)$, $f^* = (fb_1)/(2b_2)$, $e^* = (eb_1)/(2b_2)$, $\delta^* = \delta - (e^2/6b_2) - (2f^*/3)$, $A_1^* = A - (\delta^*\alpha^*/\beta) - (e^{*2}/3\beta)$, $B^* = B - (3\delta^*e^*/\beta) - (ef\alpha^*/\beta b_2)$ and $C^* = C - \delta^{*2}/(\beta) + (2f/9\beta b_2)(\alpha^*f - 2ee^*)$. The renormalized coefficients B^* and C^* are now temperature dependent.

Eq.(5) seems to allow for two additional and unphysical phases, $S = 0$, $\psi_0 \neq 0$, $P_0 = 0$, $q_0 = 0$, $q = 0$, $\theta = 0$ and $S = 0$, $\psi_0 \neq 0$, $P_0 = 0$, $q_0 \neq 0$, $q = 0$, $\theta \neq 0$. The first is a pseudo-isotropic one that has a nonzero smectic order parameter modulus, but an infinite layer spacing. This phase is clearly ruled out by the condition that q_0 has to be finite, in order to describe any reasonable smectic phase. The second is a pseudo-smectic C one without a nematic order, but with a "universal" value of the tilt angle, $\cos^2\theta = 1/3$, that does not depend on the material nor on temperature and pressure. This phase is eliminated by using a general biaxial form for the nematic order parameter Q_{ij} (cf. appendix).

The necessary conditions for the different phases to be stable are :

$$\frac{\partial^2 F}{\partial S^2} > 0, \frac{\partial^2 F}{\partial\psi_0^2} > 0, \frac{\partial^2 F}{\partial P_0^2} > 0,$$
$$\frac{\partial^2 F}{\partial\theta^2} > 0, \frac{\partial^2 F}{\partial q_0^2} > 0, \frac{\partial^2 F}{\partial q^2} > 0,$$
$$\frac{\partial^2 F}{\partial y^2} \cdot \frac{\partial^2 F}{\partial z^2} - \left(\frac{\partial^2 F}{\partial y\partial z}\right)^2 > 0,$$
$$\det\left\|\frac{\partial^2 F}{\partial x_i\partial x_j}\right\| > 0 \tag{6}$$

where $y, z, x_{i,j} \in \{S, \psi_0, P_0, \theta, q_0, q\}, i, j = 1, ..., 6$. In addition, all the appropriate (5×5), (4×4) and (3×3)-subdeterminants must be positive as well.

For the isotropic phase the stability conditions are $\alpha > 0$ and $A > 0$. The cholesteric phase is stable if $2\alpha + 3\delta S_{ch}^2 > 0$, $24A_1C < B^2$, and $L_3 < 0$. The stability conditions of the SmA phase are the same as in our previous papers [8, 9]. Hence we will discuss only the stability conditions of the SmC* phase in the following.

By lowering the temperature from the isotropic phase, the above three liquid crystalline phases can appear sequentially or in partial sequence. Since however phase transitions like isotropic to cholesteric or to SmA or the transitions cholesteric to smectic A or to smectic C*, and the smectic A to smectic C* transition have already been discussed in the literature, we will concentrate on the direct isotropic to smectic C* phase transition in what follows.

2.3 The SmC* phase and the I-SmC* phase transition

$S_{C^*} \neq 0$, $\psi_0 \neq 0$, $P_0 \neq 0$, $q_0 \neq 0$, $q_{C^*} \neq 0$, $\theta_{C^*} \neq 0$ are the equilibrium conditions for the SmC* phase. The SmC* phase is in competition with possible isotropic, cholesteric and SmA phases. As usual, the phase with the lowest free energy is the stable one.

After minimizing the free energy (5) with respect to P_0, the spontaneous polarization in the SmC* phase can be expressed as

$$P_0 = -\frac{3}{4}gSq\chi_0M\sin 2\theta \tag{7}$$

where $M = (1 - \gamma\chi_0 S_{C^*})^{-1}$. Equation (7) shows that a positive value of P_0 can only be obtained for $g < 0$. After minimization of Eq. (5) with respect to q and inserting the value of P_0 from Eq. (7), the temperature dependence of the wave vector of the helix in the SmC* phase can be written as

$$q = -\frac{L_3}{2L_1 + (L_2 - g^2\chi_0M)\cos^2\theta} \tag{8}$$

where the temperature enters through the temperature dependent tilt angle and through S_C^* in M. For a non-chiral material, $L_3 = 0$, hence $q = 0$. Equation (8) shows

that $L_3 < 0$, since the denominator is always positive. The pitch of the helix of the SmC* phase is

$$Z = -\frac{2\pi}{L_3}[2L_1 + (L_2 - g^2\chi_0 M)\cos^2\theta] \qquad (9)$$

Equation (9) shows that the pitch does not diverge at the I-SmC* phase transition. Measurements in most of the SmC* phases showed a temperature dependence of the ratio P_0/θ. For the special case of a small tilt angle ($\sin\theta \approx \theta \ll 1$) the ratio P_0/θ can be expressed as

$$\frac{P_0}{\theta} = \frac{3}{2}g\chi_0 L_3 \frac{S_{C^*}}{2L'M^{-1} - g^2\chi_0} \qquad (10)$$

showing that the variation of P_0/θ with temperature in the SmC* phase depends on the temperature variation of the orientational order parameter S_{C^*}.

The value of the smectic ordering and the wave vector of the density modulation in the SmC* phase can be expressed as

$$\psi_0^2 = -\frac{1}{\beta}\left(\alpha + \frac{3}{2}\delta S_{C^*} - \frac{x^2}{4u}\right) \qquad (11)$$

$$q_0^2 = -\frac{x}{2u} \qquad (12)$$

with

$$x = b_1 + eS_{C^*}(1 - \frac{3}{2}\sin^2\theta) + fS_{C^*}^2(1 - \frac{3}{4}\sin^2\theta)$$

$$u = b_2 + hS_{C^*}^2(1 - \frac{3}{2}\sin^2\theta)^2$$

Equation (11) shows that a negative value of the coupling constant δ increases the positional ordering ψ_0 in the SmC* phase. The variation of the tilt angle θ in the SmC* phase can be calculated after minimizing Eq. (5) with respect to θ and partially inserting the values of ψ_0, P_0, q_0 and q. This results in a complicated algebraic equation for $\sin^2\theta$,

$$\sin^2\theta = \frac{2}{3} + \frac{2e + fS_{C^*}}{6h\,q_0^2\,S_{C^*}} + \frac{q^2}{2h\,\psi_0^2\,q_0^4}(2L' - g^2\chi_0 M) \quad (13)$$

which is implicit, since q^2, q_0^2, and ψ_0^2 depend on θ, Eqs.(8)-(12).

The last necessary condition for the existence of the SmC* phase is $(\partial F/\partial S) = 0$ resulting in

$$0 = 2AS_{C^*} - BS_{C^*}^2 + 3CS_{C^*}^3 + 2\delta S_{C^*}\psi_0^2$$
$$-\frac{3}{2}\gamma q^2 g^2\chi_0^2 M^2 S_{C^*}^2 \sin^2\theta\cos^2\theta + 3L_3 qS_{C^*}\sin^2\theta$$
$$+\psi_0^2 q_0^2\Big(e\left[\frac{2}{3} - \sin^2\theta\right] + fS_{C^*}\left[\frac{4}{3} - \sin^2\theta\right]$$
$$+3hq_0^2 S_{C^*}\left[\frac{2}{3} - \sin\theta\right]^2\Big) \qquad (14)$$

which is implicit again.

Some of the stability conditions (6) for the SmC* phase read

$$e\psi_0^2 q_0^2(3\cos^2\theta - 1) < -3BS_{C^*}^2 + 18CS_{C^*}^3$$
$$+2\gamma P_0^2\frac{M+1}{M-1} \qquad (15)$$

$$\alpha + \frac{3}{2}\delta S_{C^*}^2 - b_2 q_0^4 < \frac{1}{4}hq_0^4 S_{C^*}(3\cos^2\theta - 1)^2 \qquad (16)$$

$$b_1 + eS_{C^*} + fS_{C^*}^2 < \frac{3}{4}(2eS_{C^*} + fS_{C^*}^2)\sin^2\theta \qquad (17)$$

$$L_2 q^2 \sin^2 2\theta < h\psi_0^2 q_0^4 \sin^2 2\theta + g^2 q^2\chi_0 M \quad (18)$$

$$\chi_0^{-1} > \gamma S_{C^*} \qquad (19)$$

$$2L_1 > L_2\cos^2\theta \qquad (20)$$

In order to get an explicit algebraic equation for S_{C^*} alone, we make the assumption that the influence of the chiral terms on the tilt angle is small. This is justified by $q^2 \ll q_0^2$ and allows to disregard the last contribution to $\sin^2\theta$ in Eq.(13). Then Eqs.(12) and (13) can be solved simultaneously by a systematic power expansion in S_{C^*} leading to

$$q_0^2 = -\frac{1}{4b_2}(2b_1 + fS_{C^*}^2) + O\left(\frac{q^2}{q_0^2}\right) \qquad (21)$$

$$\psi_0^2 = -\frac{1}{\beta}(\alpha^{**} - \frac{ef}{4h}S_{C^*} + \frac{3}{2}\delta^{**}S_{C^*}^2) + O\left(S_{C^*}^4, \frac{q^2}{q_0^2}\right) \quad (22)$$

$$q = -\frac{3}{2}\frac{L_3 h^*}{L_2' e}S_{C^*}\left(1 - f^{**}S_{C^*} + \left[\frac{f}{2b_1} + f^{**2}\right]S_{C^*}^2\right)$$
$$+O\left(S_{C^*}^4, \frac{q^2}{q_0^2}\right) \qquad (23)$$

with $\alpha^{**} = \alpha^* - e^2/4h$, $\delta^{**} = \delta - f^*/3 - f^2/24h$, $f^{**} = (1/2e)(f + h_6^*)$, with $h_n^* = h^*(1 + nL_1/L_2')$ and $L_2' = L_2 - g^2\chi_0 M$, $h^* = hb_1/b_2$ and the other singly 'starred' coefficients defined before Eq.(6). For the tilt angle we get

$$\sin^2\theta = \frac{1}{6h^*}(-4eS_{C^*}^{-1} + 4h^* - 2f + \frac{2ef}{b_1}S_{C^*}$$
$$+\frac{f^2}{b_1}S_{C^*}^2 - \frac{ef^2}{b_1^2}S_{C^*}^3) + O\left(S_{C^*}^4, \frac{q^2}{q_0^2}\right) \qquad (24)$$

Now the substitution of q, ψ_0, q_0 and $\sin\theta$ from Eqs. (21)-(24) into Eq. (14) leads to

$$0 = D + 2A^{**}S_{C^*} - B^{**}S_{C^*}^2 + 3C^{**}S_{C^*}^3 + O\left(S_{C^*}^4, \frac{q^2}{q_0^2}\right) \quad (25)$$

which determines the nematic order parameter in the SmC* phase and where

$$A^{**} = A + \frac{3L_3^2}{2L_2'} - \frac{1}{\beta}\left(\frac{e^2 f^2}{48h^2} + \alpha^{**}\delta^{**}\right)$$

$$B^{**} = B + \frac{9h_2^*}{2e}\frac{L_3^2}{L_2'} - \frac{3L_3^2}{2L_2'^2}\gamma g^2\chi_0^2 M^2 - \frac{3ef}{4\beta h}\delta^{**}$$

$$C^{**} = C + \frac{3}{2e}\frac{L_3^2}{L_2'}f^{**}h_2^* - \frac{3L_3^2}{4L_2'^2}h_4^*\gamma g^2\chi_0^2 M^2$$
$$+\frac{1}{\beta}\left(\frac{f^2}{18b_2}\alpha^{**} - \delta^{**2}\right)$$

and $D = ef\alpha^{**}/6\beta h$. Obviously, S_{C^*} cannot be zero and all expressions above, in particular $\sin^2\theta$, are well behaved. Eq.(25) is the extremum of an effective free energy in terms of S alone, which reads up to fourth order

$$F = F_0^* + \frac{3}{4}DS + \frac{3}{4}A^{**}S^2 - \frac{1}{4}B^{**}S^3 + \frac{9}{16}C^{**}S^4. \quad (26)$$

The spinodal of the SmC* phase is then given by

$$2A^{**} - 2B^{**}S + 9C^{**}S^2 = 0 \quad\quad (27)$$

We will now discuss the influence of the chiral terms on the tilt angle, neglected so far. For that purpose we put $f = 0$ for simplicity. Taking then into account the q^2 contribution in Eq.(13) we find that it does not influence the layer ordering ψ_0^2, nor does it change the explicit expression (23) for q. There are contributions $\sim L_3^2(2L_1 + L_2')/L_2'^2$ (with $L_2' = L_2 - g^2\chi_0 M$) to $\sin^2\theta$ in order S^2 and to q_0^2 in order S^3 and appropriate contributions to B^{**} and C^{**}. As expected they are of little influence.

Although in the original Landau-like expansion of the free energy for all order parameters no changes of the values of B and C are allowed as one approaches the transition temperature, the renormalized coefficients B^{**} and C^{**} are now temperature dependent, since all order parameters except for S_{C^*} have been eliminated. Equation (25) gives the temperature dependence of the orientational order parameter S_{C^*} in the SmC* phase.

The cubic coefficient B^{**} in the free energy (26) shows that the I-SmC* phase transition must always be first order in mean-field approximation. The transition is accompanied by a jump of the orientational order parameter S_{I-C^*} at T_{I-C^*}. In addition, there is also a jump in ψ_0, θ and P_0 at the I-SmC* transition temperature $T_{I-C^*} > T_{I-C^*}^*$, where $T_{I-C^*}^*$ is the supercooling temperature. All these order parameters jump simultaneously at the I - SmC* transition. Thus within the framework and assumptions of the presented Landau model there is always a direct I - SmC* transition for suitable parameter values.

In our previous paper on the direct I - SmC phase transition [9] instead of the f_1 term, an h term, as in Eq.(4) of the present paper, should have been used. This implicates minor corrections to the former paper, in particular the new assignments (in the notation of [9]) $b_1^* = b_1$, $\alpha^* = \alpha - (b_1^2/4b_2) - (e_1^2/4h)$, and $S_0 = e_1 b_2/hb_1$. This does not change the structure of the results, nor any of the conclusions drawn.

3 Conclusion

We have presented here a Landau-like theory analysis of the I-SmC* transition. We showed how different phases can be explained from a single model free energy expression. We have derived expressions of the conditions for the direct I - SmC* transition to occur. The coupling between the order parameters is found to play a crucial role in determining the phase behavior and the order of the transition. Although we have made some progress qualitatively

to compare the theoretical results with available experimental results, there is still a lack of basic data which would make possible a more complete quantitative comparison with the theory.

Appendix A. Biaxial nematic order

Smectic C liquid crystals are generally biaxial due to the tilt of the nematic preferred direction n_i away from the layer normal $q_0^{-1}\nabla_i\Phi$. The biaxiality is rather small and often neglected. This is even more appropriate for smectic C* phases, where the helical structure somewhat reduces the biaxiality. Therefore, we have used an uniaxial nematic order (1) in the preceding sections. Here we will show that any finite biaxial order eliminates the unphysical pseudo-smectic C phase discussed in Sec. (2.2), even if this biaxial order is so small that is has no reasonable effect on the smectic C* phase. To that end we use the biaxial nematic order parameter [10]

$$Q_{ij} = \frac{S}{2}(3n_i n_j - 1) + \mu(m_i m_j - l_i l_j) \quad\quad (A.1)$$

with the biaxial order parameter modulus μ. The directions are defined as

$$\mathbf{n} = (\mathbf{e}_x \cos qz + \mathbf{e}_y \sin qz)\sin\theta + \mathbf{e}_z \cos\theta$$
$$\mathbf{l} = (\mathbf{e}_x \cos qz + \mathbf{e}_y \sin qz)\cos\theta - \mathbf{e}_z \sin\theta$$
$$\mathbf{m} = \mathbf{e}_x \sin qz - \mathbf{e}_y \cos qz \quad\quad (A.2)$$

where m_i is in-plane (perpendicular to both, n_i and $\nabla_i\Phi$, but along the polarization P_i), while $\mathbf{l} \equiv \mathbf{n} \times \mathbf{m}$.

With this form of the nematic order the free energy (4) gives

$$\begin{aligned}
F = & F_0 + A\left(\frac{3}{4}S^2 + \mu^2\right) - B\left(\frac{1}{4}S^3 - \mu^2 S\right) \\
& + C\left(\frac{3}{4}S^2 + \mu^2\right)^2 + \frac{1}{2}\alpha\psi_0^2 + \frac{1}{4}\beta\psi_0^4 + \frac{1}{2\chi_0}P_0^2 \\
& + \delta\psi_0^2\left(\frac{3}{4}S^2 + \mu^2\right) - \gamma P_0^2\left(\frac{1}{2}S - \mu\right) \\
& + (L_1 q^2 + L_3 q)\left(\left[\frac{9}{4}S^2 - 3S\mu - 3\mu^2\right]\sin^2\theta + 4\mu^2\right) \\
& - \frac{1}{2}L_2 q^2\left(\frac{3}{2}S + \mu\right)^2\sin^2\theta\cos^2\theta + \frac{1}{2}b_1\psi_0^2 q_0^2 \\
& + \frac{1}{2}b_2\psi_0^2 q_0^4 + \frac{1}{4}e\psi_0^2 q_0^2\left(S[3\cos^2\theta - 1] - 2\mu\sin^2\theta\right) \\
& + \frac{1}{8}f\psi_0^2 q_0^2\left(S^2[3\cos^2\theta + 1] + 4\mu[S + \mu]\sin^2\theta\right) \\
& + gqP_0\left(\frac{3}{2}S + \mu\right)\sin\theta\cos\theta \\
& + \frac{1}{2}h\psi_0^2 q_0^4\left(S[3\cos^2\theta - 1] - 2\mu\sin^2\theta\right)^2 \quad (A.3)
\end{aligned}$$

which is the biaxial generalization of Eq.(5).

If we now look for the pseudo-smectic C phase with $\psi_0 \neq 0$, $q_0 \neq 0$, $\theta \neq 0$, but $S = 0$, $P_0 = 0$, $q = 0$, the minimization of (A.3) with respect to S **and** μ leads to the conditions $3\cos^2\theta - 1 = 0$ and $\sin^2\theta = 0$, respectively, which cannot be fulfilled simultaneously and, thus, rule out such an unphysical solution.

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