# Landau Model of the Smectic $C$ - Isotropic Phase Transition

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## Abstract

We propose a Landau model to describe the smectic $C$ - isotropic phase transition. A general Landau theory for the coupled orientational and translational order parameters and including the tilt angle is developed. The conditions for the smectic $C$ - isotropic phase transition and the stability conditions of the smectic $C$ phase are calculated. On the basis of this model it is argued that the smectic $C$ - isotropic phase transition is always first order. We present a detailed analysis of the question under which conditions a direct smectic $C$ - isotropic phase transition prevails in comparison to smectic $A$ - isotropic and nematic - isotropic transitions. The theoretical results are found to be in qualitative agreement with all published experimental results.

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## I. INTRODUCTION AND MOTIVATION

The smectic $A$ (SmA) and smectic $C$ (SmC) phases of liquid crystals can be regarded as stacked layers of two dimensional liquids. The molecules in the former are, on average, normal to the layers. In the SmC phase the director $\boldsymbol{n}$ is tilted by a fixed angle $\theta$ relative to the layer normal $\boldsymbol{k}$. The SmC order parameter has two degrees of freedom: the tilt angle (magnitude) and the azimuthal direction (phase).

In recent years the transitions from a smectic phase to an isotropic phase have attracted much experimental attention. Such transitions include smectic $A$ to isotropic (AI), smectic $C$ to isotropic (CI), smectic $C^*$ to isotropic ($C^*I$), smectic $E$ to isotropic (EI), smectic $I$ to isotropic and smectic $F$ to isotropic transitions. All the phase transitions described above are found to be more strongly first order than the nematic - isotropic (NI) transition. In this paper our interest is the study of CI transition. There are relatively few experimental papers[1–4] on the CI transition. The pretransitional behavior of terephthalylidene-bis-p-n-tetradecylaniline (TB14A) and terephthalylidene-bis-p-hexadecylaniline (TB16A) exhibits a direct CI transition[4] and the pretransitional effects are weaker at the CI transition than the AI and NI transitions. This means that fluctuations can grow less in intensity before the phase transition actually occurs. The large enthalpy and density jumps at the transition point indicate a strongly first order character of the CI transition. The CI transition is found to be more strongly first order than the AI and NI transitions. The orientational order in the SmC phase is higher than that in the SmA and the nematic phases.

There is practically no theoretical work on the CI transition although some theoretical studies on the AI transition are available in the literature. The purpose of the present paper is to examine the nature of and the factors governing the CI transition within a phenomenological Landau theory.

## II. MODEL

We start by describing the order parameters involved in the CI transition. The layering in the SmC phase is described by the order parameter $\psi(\mathbf{r}) = \psi_0 exp(-i\Phi)$, which is a complex scalar quantity whose modulus $\psi_0$, is defined as the amplitude of a one dimensional density wave characterized by the phase $\Phi$. The wave vector $\nabla_i \Phi$ is parallel to the director $n_i$ in the SmA phase. The layer spacing is given by $d = 2\pi/q_0$ with $q_0 = |\boldsymbol{\nabla}\Phi|$. The tilt angle in the SmC phase is described by the orientational order parameter

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

where $n_i$ is *not* parallel to $\nabla_i \Phi$. The quantity $S$ defines the strength of the nematic ordering and is zero (one) for complete disorder (order). Thus the tilt angle in the SmC phase is completely determined by the nematic order parameter. We point out that the modulus of the nematic order parameter in the SmC phase was measured experimentally by Bräuniger and Fung[5]. Gorodetskii and Podnek[6] constructed a model to describe the phase transitions between various liquid crystalline phases where they also described the behavior of the tilt angle by the nematic order parameter. The first order nature of the CI transition is characterized by a density jump $(\triangle\rho/\rho)_{CI} = 1.21 \times 10^{-2}$ in TB14A[4] which is slightly higher than that $(\triangle\rho/\rho)_{AI} = 10^{-2}$ in TB9A[4]. Thus in a broad sense the Landau model is still valid for the CI transition as well as for the AI transition.

Keeping homogeneous terms up to quartic order and gradients only to the lowest relevant order, the total free energy near the CI transition can be written as:

$$\begin{aligned} F = F_0 + \int \Big[ & \frac{1}{2} A Q_{ij} Q_{ij} - \frac{1}{3} B Q_{ij} Q_{jk} Q_{ki} + \frac{1}{4} C_1 (Q_{ij} Q_{ij})^2 + \frac{1}{4} C_2 Q_{ij} Q_{jk} Q_{kl} Q_{li} \\ & + \frac{1}{2}\alpha|\psi|^2 + \frac{1}{4}\beta|\psi|^4 + \frac{1}{2}\delta|\psi|^2 Q_{ij} Q_{ij} + \frac{1}{2} b_1 |\nabla_i \psi|^2 + \frac{1}{2} b_2 |\Delta\psi|^2 \\ & + \frac{1}{2} e_1 Q_{ij} (\nabla_i \psi)(\nabla_j \psi^*) + \frac{1}{2} f_1 Q_{il} Q_{jl} (\nabla_i \psi)(\nabla_j \psi^*) \Big] dV \end{aligned} \tag{2}$$

where $F_0$ is the free energy of the isotropic phase, $A = a(T - T^*_{NI})$ and $\alpha = \alpha_0(T - T^*_{AI})$. $T^*_{NI}$ and $T^*_{AI}$ are the critical temperatures for a hypothetical second order transition to the nematic and the SmA state, respectively, in the absence of any cross coupling. All other coefficients, as well as $a$ and $\alpha_0$, are assumed to be constants near the transition point. $\delta$ is a coupling constant. As we shall see, a negative value of $\delta$ favors the SmC phase over the nematic phase. Some higher order gradient terms involving $Q_{ij}$ as well as second order derivatives of $\psi$, have been disregarded in eq.(2), since such terms do not qualitatively change the physical picture. The isotropic gradient terms in (2) guarantee a finite wavelength $q_0$ for the smectic density wave. Symmetry would allow another term, $(b_3/2)|\nabla_i\nabla_j\psi|^2$, 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. The gradient terms $\sim e_1$ and $\sim f_1$ 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. A negative value of $e_1$ favors SmC and SmA phases over the nematic phase. The appearance of the SmC phase corresponds to $\delta < 0$ and $e_1 < 0$. The sign of the remaining constants is positive. There is no direct linear coupling term $\sim |\psi|^2 Q_{ij}$[7] in the free energy (2), since such a term cannot exist in the isotropic phase. Written in the full order parameter $Q_{ij}$ it would read $\xi_{ij}|\psi|^2 Q_{ij}$, which however is identically zero, since the material tensor $\xi_{ij}$ takes in the isotropic phase the form $\xi_{ij} = \xi\delta_{ij}$, and $Q_{ij}$ is traceless. However such a coupling term is allowed near the Smectic-A-nematic and Smectic-C-nematic transition.

Here we consider phases in which the nematic and smectic order are spatially homogeneous, $S = const.$ and $\psi_0 = const.$. We assume flat layers in the smectic phases and take the layer normal $q_0^{-1}\nabla_i\Phi = \delta_{iz}$ as the z-axis. Then $n_i$ is defined by

$$n_i = \delta_{iz}\cos\theta + \delta_{ix}\sin\theta \tag{3}$$

where $x$ is an arbitrary axis perpendicular to the layer normal and where $\theta$ is the angle between the layer normal and the nematic director $n_i$. In that case eq.(2) reads

$$\begin{aligned} F - F_0 = \int \Big[ & \frac{3}{4}AS^2 - \frac{1}{4}BS^3 + \frac{9}{16}CS^4 + \frac{1}{2}\alpha\psi_0^2 + \frac{1}{4}\beta\psi_0^4 + \frac{3}{4}\delta\psi_0^2 S^2 \\ & + \frac{1}{2}b_1\psi_0^2 q_0^2 + \frac{1}{2}b_2\psi_0^2 q_0^4 \\ & + \frac{1}{4}e_1\psi_0^2 S q_0^2(3cos^2\theta - 1) + \frac{1}{8}f_1\psi_0^2 S^2 q_0^2(3cos^2\theta - 1)^2\Big] dV \end{aligned} \tag{4}$$

with $C = C_1 + C_2/2$. To ensure stability of the isotropic phase at high temperatures, $\beta C - \delta^2 > 0$. The presence of the cubic terms ($\sim B$ and $\sim e_1$) describes the first order character of the NI, AI and CI transitions, respectively. Minimization of Eq.(4) with respect to $S$, $\psi_0$, $q_0$ and $\theta$ yields the following four phases:

$$Isotropic \ : \ S = 0, \quad \psi_0 = 0, \quad q_0 = 0, \quad \theta = 0 \tag{5}$$

$$Nematic \ : \quad S_N = \frac{B}{6C}\left[1 + \left(1 - \frac{24AC}{B^2}\right)^{1/2}\right], \quad \psi_0 = 0, \quad q_0 = 0, \quad \theta = 0 \tag{6}$$

$$\begin{aligned} &Smectic\ A \ : \quad S_A > 0, \quad \psi_0^2 = -\frac{1}{\beta}\left(\alpha_1 - e^* S_A + \frac{3}{2}\delta_1 S_A^2 - \frac{e_1 f_1}{2b_2} S_A^3\right), \\ &q_0^2 = -\frac{1}{2b_2}(b_1 + e_1 S_A + f_1 S_A^2), \quad \theta = 0 \end{aligned} \tag{7}$$

where $S_A$ is defined by:

$\frac{2\alpha_1 e^*}{3\beta} + 2A_1 S_A - B_1 S_A^2 + 3C_1 S_A^3 = 0$

$$\begin{aligned} &Smectic\ C \ : \quad S_C = \frac{B}{6C^*}\left[1 + \left(1 - \frac{24A^*C^*}{B^2}\right)^{1/2}\right], \\ &\psi_0^2 = -\frac{1}{\beta}\left(\alpha^* + \frac{3}{2}\delta S_C^2\right), \quad q_0^2 = -\frac{b_1^*}{2b_2}, \\ &\sin^2\theta = \frac{2}{3}\frac{(S_C - S_0)}{S_C} \end{aligned} \tag{8}$$

We use the abbreviations $\alpha_1 = \alpha - b_1^2/(4b_2)$, $\delta_1 = \delta - e_1^2/(6b_2) - f_1 b_1/(3b_2)$, $e^* = b_1 e_1/(2b_2)$, $\alpha^* = \alpha - b_1^{*2}/(4b_2)$, $b_1^* = b_1 - e_1^2/4f_1$, $S_0 = -e_1/(2f_1)$, $C^* = C - \delta^2/\beta$, $A^* = A - \delta\alpha^*/\beta$, $C_1 = C - \delta_1^2/\beta + \frac{2}{9}\frac{f_1}{\beta b_2}(f_1\alpha_1 - 4e_1 e^*)$, $B_1 = B - 3e^*\delta_1/\beta - \frac{e_1 f_1 \alpha_1}{\beta b_2}$ and $A_1 = A - \delta_1\alpha_1/\beta - e^{*2}/3\beta$.

The solutions of the nematic and SmA phase are the same as in our previous work[7,8] and the analysis will be similar as before. Since we have already discussed in detail the conditions for a direct AI transition in ref.[7,9], we will focus here on the CI transition.

From the solution of the SmC phase it is clear that a nonzero real value of $\psi_0$ exist only when $\delta < -\frac{2}{3}\alpha^* S_C^2$. Since there is a (small) temperature range where $\alpha^* > 0$, $\delta < 0$ in this region. Thus the degree of positional order $\psi_0$ increases in the SmC phase for $\delta < 0$. The layer wavelength $q_0$ in the SmC phase will be real for $b_1^* < 0$. Thus $f_1 > 0$, since $b_1 > 0$ and

$b_2 > 0$. The behavior of the tilt angle $\theta$ in the SmC phase is completely determined by the behavior of the orientational order parameter $S$. A non-zero value of the tilt angle $\theta$ exists for $S_C > S_0$. As temperature increases, the orientational order parameter $S_C$ decreases and the tilt angle $\theta$ decreases. This is possible only if $e_1 < 0$. As long as $S_C > S_0$ there is no SmA phase, and the SmC phase lies above the SmA phase. Thus $S_C > S_0$ is found to be a necessary condition for which a SmC phase exists. Thus for the SmC phase $\delta < 0$ and $e_1 < 0$. The condition for the SmA phase to appear and consequently for the SmC phase to disappear is $S_C \leq S_0$. This means that the orientational order parameter $S_C$ in the SmC phase is higher than the orientational order parameter $S_A$ in the SmA phase which is supported by experimental observations. The SmA phase disappears for $e_1 > 0$ and $\delta_1 > 0$. In this case a NI transition is possible for $\delta > 0$.

To show more clearly the variation of the various order parameters (8) with temperature in the SmC phase we have plotted the order parameters ($S$, $\psi_0$, and $\theta$) *vs.* temperature $T$ in Fig. 1. This is done for a set of phenomenological parameters for which a direct isotropic to SmC transition is possible. Fig. 1 shows that the three order parameters $S_C$, $\psi_0$ and $\theta$ jump simultaneously at the CI transition point. Thus we see for $S_C > S_0$ there is always a direct first order CI transition. As can be seen from figure 1, the tilt angle is slowly varying with temperature ranging from 46.7° to 37.1°. For this fixed set of phenomenological parameter values, we find that the jumps of the order parameters at $T_{CI}$ are $S_{CI} = 0.44$ and $\psi_0|_{CI} = 0.23$. These values justify the validity of the Landau model for the first order CI transition. However, the values will be different for a different set of phenomenological parameters. To the best of the authors knowledge, there is no experiment which measures the jumps of the order parameters $S_{CI}$ and $\psi_0|_{CI}$ at the CI transition point.

Necessary conditions for the different phases to be stable are ($F = \int f dV$)

$$\frac{\partial^2 f}{\partial S^2} > 0, \qquad \frac{\partial^2 f}{\partial \psi_0^2} > 0, \qquad \frac{\partial^2 f}{\partial q_0^2} > 0, \qquad \frac{\partial^2 f}{\partial \theta^2} > 0,$$
$$\frac{\partial^2 f}{\partial S^2} \cdot \frac{\partial^2 f}{\partial \psi_0^2} - \Big(\frac{\partial^2 f}{\partial S \partial \psi_0}\Big)^2 > 0$$

$$
\begin{aligned}
&\frac{\partial^2 f}{\partial S^2}\cdot\frac{\partial^2 f}{\partial\theta^2}-\Big(\frac{\partial^2 f}{\partial S\partial\theta}\Big)^2>0,\\
&\frac{\partial^2 f}{\partial S^2}\cdot\frac{\partial^2 f}{\partial {q_0}^2}-\Big(\frac{\partial^2 f}{\partial S\partial q_0}\Big)^2>0,\\
&\frac{\partial^2 f}{\partial {\psi_0}^2}\cdot\frac{\partial^2 f}{\partial {q_0}^2}-\Big(\frac{\partial^2 f}{\partial \psi_0\partial q_0}\Big)^2>0,\\
&\frac{\partial^2 f}{\partial {\psi_0}^2}\cdot\frac{\partial^2 f}{\partial\theta^2}-\Big(\frac{\partial^2 f}{\partial \psi_0\partial\theta}\Big)^2>0,\\
&\frac{\partial^2 f}{\partial\theta^2}\cdot\frac{\partial^2 f}{\partial {q_0}^2}-\Big(\frac{\partial^2 f}{\partial\theta\partial q_0}\Big)^2>0,\\
&\det\left\|\frac{\partial^2 f}{\partial y_i\partial y_j}\right\|>0
\end{aligned}
\tag{9}
$$

were $y_i \in \{S, \psi_0, q_0, \theta\}$ and $i$,$j$ run from 1 to 4. In addition, all $(3\times 3)$ - subdeterminants must be positive as well. The derivatives in (9) have to be taken at the values (5-8) for the appropriate phases. For the SmA phase the stability conditions are

$$BS_A^2 - 6CS_A^3 + \frac{2}{3}e_1\psi_0^2q_0^2 < 0 \tag{10}$$

$$\alpha_1 - e^*S_A + \frac{3}{2}\delta_1 S_A^2 < 0 \tag{11}$$

$$b_1 + e_1S_A + f_1S_A^2 < 0 \tag{12}$$

$$3\beta(A - BS_A + \frac{9}{2}C_1S_A^2 + \delta\psi_0^2 + \frac{2}{3}f_1\psi_0^2q_0^2) > (e_1q_0^2 + 2f_1q_0^2S_A + 3\delta S_A)^2 \tag{13}$$

$$A - BS_A + \frac{9}{2}CS_A^2 + \psi_0^2\left(\delta_1 - \frac{f_1}{b_2}S_A(e_1 + f_1S_A)\right) > 0 \tag{14}$$

For the SmC phase the first four stability conditions

$$-BS_C + 6CS_C^2 - \frac{b_1^*e_1^2}{6b_2f_1S_C^2}\psi_0^2 > 0 \tag{15}$$

$$\alpha^* + \frac{3}{2}\delta S_C^2 < 0 \tag{16}$$

$$b_1 < \frac{e_1^2}{4f_1} \tag{17}$$

$$S_C > \frac{|\, e_1 \,|}{f_1} \tag{18}$$

ensure $S_C$, $\psi_0^2$, $q_0^2$ and $\theta^2$ to be indeed positive quantities. The Cauchy conditions in (9) lead two additional stability criteria (since $\partial^2 f/\partial S \partial q_0 = 0$, $\partial^2 f/\partial\psi\partial q_0 = 0$, $\partial^2 f/\partial\psi\partial\theta = 0$ and $\partial^2 f/\partial\theta\partial q_0 = 0$)

$$-BS_C + 6C^* S_C^2 - \frac{b_1^* e_1^2}{6 b_2 f_1 S_C^2}\psi_0^2 > 0 \tag{19}$$

$$f_1(S_C - S_0)(S_C + 2S_0)(-BS_C + 6CS_C^2) > 0 \tag{20}$$

while the determinant condition is

$$f_1(S_C - S_0)(S_C + 2S_0)(-BS_C + 6C^* S_C^2) > 0 \tag{21}$$

The inequalities associated with the $(3 \times 3)$ - subdeterminants do not lead to any additional inequality. The stability conditions listed determine the stability of the different phases rather implicitly. The stability condition (16) is satisfied only for $\delta < 0$. The stability condition (17) shows that $f_1 > 0$ (since $b_1 > 0$).

## III. DIRECT ISOTROPIC TO SMECTIC C TRANSITION

The SmC phase is in competition with the isotropic, nematic and SmA phases, which are also possible. The existence ranges of all four phases generally overlap. The phase with the lowest free energy is the stable one. A (first order) transition takes place, when 2 free energies are equal. Since we have already predicted that the tilt angle in the SmC phase is completely determined by the modulus of the orientational order parameter, we will describe the direct CI transition in more detail as a function of $S$ only. Thus in order to study the direct CI transition, we substitute the solutions (8) for $\psi_0 \neq 0$, $q_0 \neq 0$ and $\theta \neq 0$ into the free energy (4). We get the free energy density for the SmC phase as a function of $S$ alone, which can be written as

$$f = f_0 - \frac{\alpha^{*2}}{4\beta} + \frac{3}{4}A^* S^2 - \frac{1}{4}BS^3 + \frac{9}{16}C^* S^4 \tag{22}$$

where the starred coefficients are defined after (8). Since $\delta < 0$, we can infer $C^* > 0$ from $\beta C > \delta^2$.

The temperature dependence of the orientational order parameter $S_C$ in the SmC phase can be expressed as

$$S_C = \frac{B}{6C^*}\left[1 - \sqrt{1 - \frac{24aC^*}{B^2}\Big(1 - \frac{\delta}{\delta_0}\Big)\Big(T - \Big(1 - \frac{\delta}{\delta_0}\Big)^{-1}T^*\Big)}\right] \tag{23}$$

where $T^* = T^*_{NI} - \frac{\delta}{\delta_0}(T^*_{AI} + b_1^{*2}/4b_2\alpha_0)$.

Equation (23) shows $S_C$ is real and a direct CI transition is possible when

$$T < \Big(1 - \frac{\delta}{\delta_0}\Big)^{-1}\Big(T^* + \frac{B^2}{24aC^*}\Big) \tag{24}$$

At the CI transition there are two minima ($\frac{\partial F}{\partial S} = 0$) at the same free energy $F = F_0 - \frac{\alpha^{*2}}{4\beta}$. One is the trivial one (the isotropic phase $S = 0$) and the other has $S > 0$ (the smectic $C$ phase). For the latter the jump of $S$ at the transition is given by

$$S_{CI} = \frac{2B}{9C^*} \tag{25}$$

This condition gives the minimum value of the order parameter $S_C$ in the smectic $C$ phase. In addition it yields the minimal tilt angle $\theta$ via the last equation in (8). From (8) we also read off a maximum tilt angle $\theta_{max} = 54.7°$. It is obvious that the CI transition is always first order (except for $B = 0$). The higher the value of $B$, the stronger will be the first order character of the CI transition. In the general case there is a jump in $S_C$, $\psi_0$ and $\theta$ at the CI transition temperature $T_{CI} > T^*_{CI}$, where $T^*_{CI}$ is the supercooling temperature. Equation (25) also shows that the jump of $S$ at the CI transition is higher than that at the NI transition ($S_{NI} = 2B/9C$) since $C^* < C$.

The CI transition temperature is given by

$$T_{CI} = \Big(1 - \frac{\delta_0}{\delta}\Big)^{-1}\left[T^*_{AI} - \frac{\delta_0}{\delta}\Big(T^*_{NI} + \frac{B^2}{27aC^*}\Big) + \frac{b_1^{*2}}{4\alpha_0 b_2}\right] \tag{26}$$

with $\delta_0 = a\beta/\alpha_0$. Having calculated $T_{CI}$ and $S_{CI}$ we can go back to eq.(8) and calculate the finite smectic order parameter $\psi_0(T_{CI})$ and the tilt angle $\theta(T_{CI})$ at the transition temperature. Of course, one has to check that $T_{CI}$ is within the existence range (9) of the SmC phase, e.g. that the resulting quantities $\psi_0^2$, $q_0^2$ and $\theta^2$ are positive. In that case there is a direct first order $CI$ transition possible within the framework and assumptions of our model.

Then the first order $CI$ transition line is given by

$$9^3\alpha^{*2}C^{*3} + 4B^2\beta(B^2 - 27A^*C^*) = 0 \tag{27}$$

In order to make the discussion of the temperature dependence of the transition more transparent, we plotted in Fig. 2 the free energy (22) as a function of the orientational order parameter $S$ for different temperatures taking a negative value for $\delta$ and $e_1$.

For $T > T_{CI}$, $S = 0$ is the absolute minimum. As $T$ approaches $T_{CI}$ from above, a shoulder at finite $S$ emerges that evolves into a minimum (SmC) below the superheated SmC temperature $T_{CI}^{**}$. This temperature is determined by the appearance of the $S \neq 0$ solution. At $T = T_{CI}$, the free energy of the SmC phase and the isotropic phase become equal. The two phases are separated by a barrier height. There is no third minimum either for the nematic or the SmA phase for these particular values of $\delta$ and $e_1$. For $T < T_{CI}$ the $S \neq 0$ (SmC) minimum represents the stable state. The isotropic state ($S = 0$) is a metastable one, and at even lower temperature $T < T_{CI}^*$, it becomes unstable (a local energy maximum). Thus there is a direct CI transition within the framework of our model for a range of parameter values and for $T_{CI} > T_{AI} > T_{NI}$.

## IV. DISCUSSION

We have presented here a Landau model for the CI transition. We have derived expressions of the conditions for the direct CI transition to occur. The coupling between the order parameters $S$, $\psi_0$ and $\theta$ is found to play a crucial role in determining the phase behavior and the order of the transition. The analysis shows that the CI transition is always a first order transition. It is always more strongly first order than the AI and NI transitions which agrees well with experimental results on the jumps in density and enthalpy[4]. We also see that $S_C > S_A > S_N$. Thus our results are in qualitative agreement with the experimental results we could find in the literature. A quantitative application of the theory is not possible yet due to the lack of experimental data.

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[9] We note that in the caption of Fig.1 of ref.[7] the values of $e_1$ and $b_1$ for the smectic A phase are missing and should read $e_1 = -0.1J$ and $b_1 = 0.03J$.

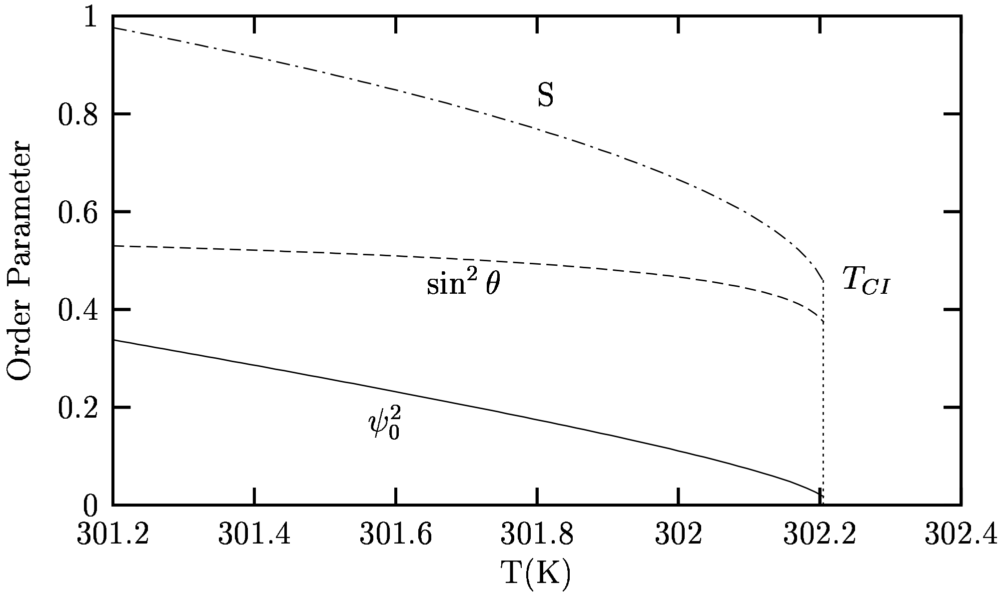


FIG. 1. The variation of the order parameters $S$, $\psi_0$ and $\theta$ is plotted as a function of temperature $T$ near the CI transition. The values of the parameters were taken to be $\alpha_0 = 0.1J/K$, $a = 0.1J/K$, $B = 0.6J$, $C = 0.32J$, $\beta = 1.5J$, $b_1 = 0.02J$, $b_2 = 0.4J$, $e_1 = -0.4J$, $f_1 = 1J$ and $\delta = -0.34J$.

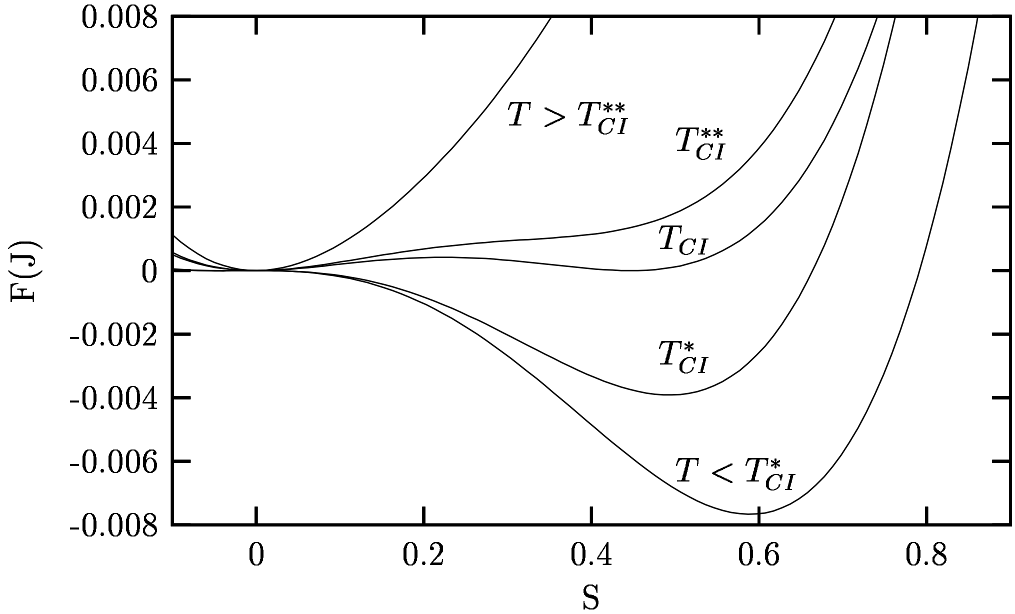


FIG. 2. The free energy $F$ as function of the orientational order parameter $S$ for the superheated smectic $C$ temperature $T = T_{CI}^{**}$, the transition temperature $T = T_{CI}$ and the supercooled temperature $T = T_{CI}^{*}$. The parameter values are the same as in Figure 1.