

Layer-by-layer ordering of ultrathin liquid crystal films on the three-level Potts model

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Abstract. – The three-level Potts model with variable coupling strengths is proposed to describe the newly observed smectic-A' to smectic-A phase transition in free-standing liquid crystal films. In a film of L molecular layers, the transition temperature for individual layers is determined separately by the bifurcation point of the free energy in the variational cumulant expansion (VCE), from which the heat capacity is also calculated analytically. By adjusting the interlayer and intralayer coupling between nearest-neighboring molecules, it is shown that the calculated heat capacity qualitatively reproduces the observed anomaly around transition temperatures in experiments on free-standing 54COOBC films of two and more molecular layers.

The characteristic behavior of liquid crystals (LC) has been one of the most interesting subjects of research in recent years. In particular, the free-standing LC film is perhaps the most ideal object for the study of two-dimensional (2D) melting. Experimentally, the first evidence of a “stacked” hexatic or hexatic-B (HexB) phase was observed in X-ray diffraction from a 65OBC thick film [1] and the 2D hexatic phase was established in electron diffraction from a two-layer free-standing film of a 65OBC mixture [2]. The X-ray diffraction study reveals two types of ordering: the short-range in-plane positional correlation but long-range, three-dimensional, six-fold bond-orientational order, and the local herring-bone order that assumes three distinct directions. The existence of herring-bone order in the HexB phase is also confirmed by electron diffraction studies [3]. Heat-capacity measurements and renormalization group calculation of the Landau-Ginsberg-Wilson free-energy model show that the SmA-HexB transition of 65OBC belongs to the universality class of the three-level Potts model [4, 5]. A series of simultaneous heat capacity and optical reflectivity measurements on free-standing nm OBC [6, 7] and 54COOBC [8] films of two and more molecular layers reveal a layer-by-layer ordering phenomenon. It is demonstrated that as the temperature decreases, the surface layer orders at a higher temperature than the interior one due to the surface tension as well as the highly anisotropic nature of smectic phases [9]. As a matter of fact, a qualitatively similar melting process behavior was also observed in other LC films [10–15]. These experiments show clearly that the LC films are not really 2D systems no matter how thin they are. Presumably

the monolayer film has a slightly higher transition temperature than a two-layer film. It is the interlayer coupling that results in the peculiar behavior of layer-by-layer melting. There is no theory, to our knowledge, that predicts the so-called thermal anomaly for LC films of finite thickness, although numerical attempts to account for the unusual behavior have been made either by analyses on the 2D Potts model [4] or by Monte Carlo simulation in 2D lattices [16].

Very recently, a new phase SmA' was observed in a series of experiments. It represents a phase with a higher degree of in-plane positional correlations than that in an ordinary liquid and similar to that found in a hexatic phase, but it lacks long-range bond-orientational order [17]. This seems to establish the sequence of phase transitions CryB - HexB - SmA' - SmA for the melting process of a two-layer film [18, 19]. The electron diffraction pattern at the transition temperature 66.3°C shows *no* long-range bond-orientational order, which appears after the transition to HexB phase at 63.0°C . Since no change in C_p is observed in the simultaneous high-resolution C_p and optical reflectivity measurements, SmA' - HexB and HexB - CryB are regarded as possible candidates for the phase transition of Kosterlitz and Thouless (KT) type. More data indicate that a similar situation exists for films of more than two layers, at least for the first few layers, implying that the heat capacity found for films of various thickness corresponds to the SmA - SmA' phase transition [20].

Since the interlayer coupling is very weak compared with the intralayer coupling, it is plausible to approximate the stacked hexatic LC films as a hexagonal close-packed (hcp) structure. Hence we propose to describe the hcp structure by the three-level Potts model. This is all right as long as there exists a weak herring-bone order in 54COBC [17]. Every molecule in the hcp structure has twelve nearest neighbors (nn) including six in-plane plus three on each side of the adjacent planes. The theory of variational cumulant expansion (VCE) was developed recently to determine the transition temperature of thin magnetic films [21]. It is *not* a mean-field approach but the first-order approximation yields the mean-field result. The advantage of the VCE is that the transition temperature can be calculated analytically as a function of the number of molecular layers in the film. It is shown that the convergence of the expansion is rather fast [22, 23]. It has also been demonstrated that a microscopic calculation by the VCE theory on the Ising model with variable exchange coupling constants is able to account for the transition temperatures measured on ultrathin $\text{Ni}(001)$ films in the region of dimensionality cross-over [24]. The three-level Potts model, on the other hand, predicts only first-order transitions except for a 2D monolayer in which the phase transition is second order [25]. Since a single-layer film is in practice unstable and ruptures quickly, there is no measurement available. Therefore we limit our discussion in the following to films of two and more molecular layers.

We consider the Hamiltonian

$$H = - \sum_{\langle i, j \rangle} J_{ij} \delta(\sigma_i, \sigma_j), \quad (1)$$

where σ_i and σ_j are parameters characterizing the herring-bone order. They can take the relative orientations 0° , 120° , 240° between the two molecules viewed from the top, and are labeled by 0, 1 and 2, respectively. The symbol $\langle i, j \rangle$ means summing only over the nn and the δ -function is defined as

$$\delta(\sigma_i, \sigma_j) = \begin{cases} 1, & i = j, \\ 0, & i \neq j. \end{cases} \quad (2)$$

The exchange coupling constant J_{ij} is allowed to vary, depending upon the relative positions of the nearest-neighboring molecules. For instance, the intralayer and interlayer coupling may be different from one another.

The action of the system is

$$S = -H/k_B T = \sum_{\langle i,j \rangle} \beta_{ij} \delta(\sigma_i, \sigma_j), \quad (3)$$

where $\beta_{ij} = J_{ij}/k_B T$. For the trial action, we assume

$$S_0 = \xi_0 \delta(\sigma_1, 0) + \xi_1 \delta(\sigma_1, 1) + \xi_2 \delta(\sigma_1, 2), \quad (4)$$

where we have defined $\xi_0 = 1 + 2\xi$, $\xi_1 = \xi_2 = 1 - \xi$ with the variational parameter ξ . As we shall see later, ξ plays the role of the order parameter. It is easily seen from (4) that ξ_0 , ξ_1 and ξ_2 are proportional to the probability of finding the system in the state $\sigma_j = 0, 1$ and 2 , respectively. The 6-fold symmetry implies that $\xi_1 = \xi_2$.

The partition function of the system is

$$Z = e^{-W} = \sum e^S = Z_0 \langle e^{S-S_0} \rangle_0, \quad (5a)$$

$$Z_0 = e^{-W_0} = \sum e^{S_0} = \prod [e^{\xi_0} + e^{\xi_1} + e^{\xi_2}] = [e^{\xi_0} + 2e^{\xi_1}]^N, \quad (5b)$$

where W_0 and Z_0 are, respectively, the free energy and partition function for the corresponding non-interacting system, and the Boltzmann ensemble average $\langle A \rangle_0 = \frac{1}{Z_0} \sum A e^{S_0}$ of a quantity A .

The free energy of the system is found from (5) as

$$W \approx W_0 - \sum_{n=1}^m \frac{1}{n!} \langle (S - S_0)^n \rangle_c = W_{\text{eff},m}. \quad (6)$$

In the second step of (6), we have defined the cumulant expansion to m -th order approximation. The cumulant average $\langle A \rangle_c$ is related to $\langle A \rangle_0$ by simply comparing the two series in (6).

Up to this point, the theory is general. Let us now consider a film of L molecular layers labeled by l . For simplicity, we assume the uniform intralayer coupling $J_{ij} = J$ for $1 < l < L$. Because of the surface tension, a slightly stronger coupling for pairs in the surface layer is assumed. On the other hand, we assume a much weaker coupling for interlayer nn pairs as the average interlayer distance is about a molecular length or ~ 25 Å, which is much larger than the mean intermolecular distance in the layer. The weak nature of the interlayer coupling has in fact been found experimentally from measurements of the thickness dependence of the transition temperatures [4, 5]. Thus, we take the intralayer coupling $J_{ij} = aJ$ with $a > 1$ for $l = 1, L$ and $J_{ij} = bJ$ with $b \ll 1$ for interlayer coupling. The free energy up to the first order is, according to (6),

$$W_{\text{eff},1} = -\ln(e^{3\xi} + 2) + 3\xi y - \frac{\beta}{2} D_1(l, L, a, b) V_2. \quad (7)$$

The structure factor $D_1(l, L, a, b)$ depends on the lattice structure and for hcp is given by

$$D_1(l, L, a, b) = \begin{cases} 6a + 3b & \text{for } l = 1, L, \\ 6 + 6b & \text{for } l = 2 \leq l \leq L - 1. \end{cases} \quad (8)$$

The function V_m for m -th order with $m \geq 2$ is defined by

$$V_m = y^m + (1 - y)^m / 2^{m-1}, \quad (9a)$$

$$y = e^{3\xi} / (e^{3\xi} - 2). \quad (9b)$$

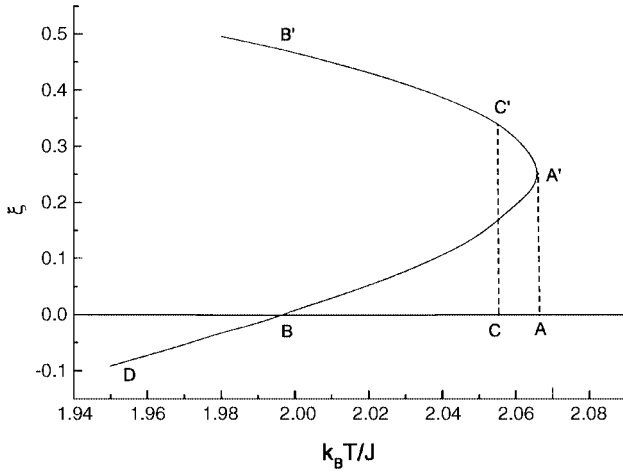


Fig. 1

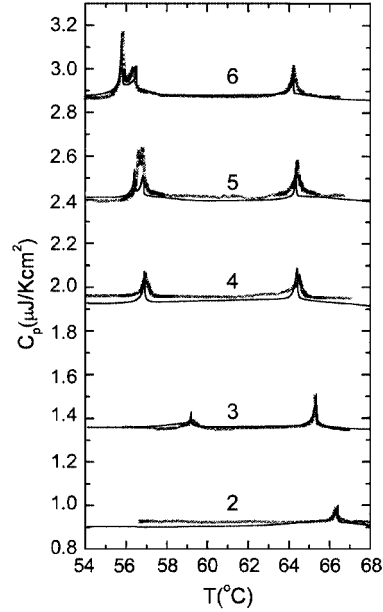


Fig. 2

Fig. 1 – Trace of extrema and analytic properties of the free energy as projected on the $\xi\tau$ -plane.

Fig. 2 – Heat capacity at constant volume calculated for LC films of $2 \leq L \leq 6$ are plotted as solid lines. The numeral indicates the number of molecular layers in the film. The high-temperature peak represents the transition for the surfaces or $l = 1, L$. The middle peak indicates the transition for the next-to-surface layers, and the peak at the low-temperature end stands for the interior transition. The shaded thick line represents experimental data measured at constant pressure on LC films of 54COOBC.

The variational parameter $\xi = \xi(T)$ is determined by the condition of minimum free energy, namely, $\delta W_1 / \delta \xi = 0$ which yields

$$3\xi - \frac{1}{2}\beta D_1(l, L, a, b)(3y - 1) = 0. \quad (10)$$

Equation (10) is a transcendental equation which, for given values of a and b , has in general different solutions in different temperature ranges. Let us now examine the analytic properties of these solutions. As an example, we consider the particular case of $L = 2$, and the basic feature remains the same for other cases. The function $\xi(T)$ that satisfies (10) is illustrated in fig. 1. It has only one solution with $\xi = 0$ in the region $\tau > \tau_A$, where $\tau = k_B T/J$. This solution corresponds to a minimum W_1 as is seen from the second-order variation. When $\tau < \tau_A$, there are three solutions for each τ , depending on ξ . It is easy to show that the solution corresponds to minimum W_1 for $\xi > \xi_{A'}$ along $A'C'B'D'$, for $\xi = 0$ along ACB and for $\xi < \xi_B$ along BD . On the other hand, the solution is a maximum for $\xi_B < \xi < \xi_{A'}$ along the curve $A'B$ and for $\xi = 0$ along the straight line $B0$. Our numerical work indicates further that W_1 along AC is lower than that along $A'C'$, while it takes the same value at C and C' . When the temperature decreases, the system follows the route specified by $\xi = 0$ till τ_C , it jumps to C' with a change in its internal energy. Hence ξ has the characteristics of the order parameter which changes abruptly at C from zero to $\xi_{C'}$. Thus we expect a phase transition of the first

order at τ_C . After this transition, the system remains in the upper branch C'B' because of the minimum free energy. It cannot reach B as the free energy is maximum along A'B. It is important to emphasize once more that for a single molecular layer, the 2D three-level Potts model predicts a second-order phase transition independent of other parameters.

To find the transition temperature to m -th order, we start with the calculation of moments $(S - S_0)$ up to m -th order from which the cumulants are found by comparing the corresponding terms of the two series in (6). The evaluation of higher-order cumulants involves summing over graphs that are topologically equivalent. With the variable coupling, this may be tedious and usually results in cumbersome expressions. Here we just outline the second-order calculation as an illustration. Higher-order calculations can be carried out in a similar fashion.

Three cumulants are involved in the second-order calculation, namely,

$$\langle S_0^2 \rangle_c = 9\xi^2(y - y^2), \quad (11a)$$

$$\langle SS_0 \rangle_c = \xi \frac{\delta}{\delta\xi} \langle S \rangle_c \quad (11b)$$

and

$$\langle S^2 \rangle_c = \beta^2 \left[\frac{1}{2} D_{21}(l, L, a, b)(V_2 - V_1)^2 + D_{22}(l, L, a, b)(B_3 - V_2)^2 \right]. \quad (11c)$$

Substituting (11) into (6), we find the second-order free energy

$$\begin{aligned} V_{\text{eff},2} = & -\ln(e^{3\xi} + 2) + 3\xi y - \frac{\beta}{2} D_1(l, L, a, b) V_2 - \frac{9}{2} \xi^2 (y - y^2) + \xi \frac{\delta}{\delta\xi} \langle S \rangle_c - \\ & - \frac{\beta^2}{2} \left[\frac{1}{2} D_{21}(l, L, a, b)(V_2 - V_1)^2 + D_{22}(l, L, a, b)(B_3 - V_2)^2 \right], \end{aligned} \quad (12)$$

where V_2 is given by (9a) for $m = 2$. The structure factors D_{21} and D_{22} are defined through

$$\sum_{\langle i,j \rangle} \beta_{ij}^2 = \beta^2 D_{21}, \quad (13a)$$

$$\sum_{\langle i,j,k \rangle} \beta_{ij} \beta_{jk} = \beta^2 D_{22}, \quad (13b)$$

in which one has to evaluate the sum over all nearest neighbors j of i on the l -th layer of the film. The free energy $V_{\text{eff},2}$ is minimized to determine the variational parameter $\xi = \xi(T)$. We obtain, by requiring $W_{\text{eff},2}(\xi = 0) = W_{\text{eff},2}(\xi = \xi(T))$, the transition temperature $T_c^{(2)}(l, L, a, b)$ to the second order in VCE. The relative coupling strengths a and b are then fixed by fitting the data.

After the transition temperatures are determined, we can proceed to calculate the heat capacity. While the heat capacity is measured at constant pressure, we can only calculate the heat capacity at constant volume C_v from the free energy. The difference is not expected to have any significant influence on the qualitative behavior. Since the phase transition in the film takes place layer-by-layer, we have to calculate the specific heat for every layer l in a sample of L -layer film. The calculation is again tedious and here we just outline the procedure. For the surface, $l = 1$, we have $T_c(l = 1, L)$. When $T > T_c(l = 1, L)$, $\xi = 0$, then the internal energy U per site is given by

$$U = \partial W / \partial \beta \quad (14a)$$

and the corresponding heat capacity is

$$C_v = -k_B\beta^2(\partial U/\partial\beta). \quad (14b)$$

When $T < T_c(l = 1, L)$, the free energy depends on both ξ and β which are related by (10). As a consequence, we have

$$U_1 = \frac{\partial W}{\partial\beta} + \frac{\partial W}{\partial\xi} \frac{\partial\xi}{\partial\beta}, \quad T < T_c, \quad (15)$$

$$C_v(l = 1) = -k_B\beta^2 \left(\frac{\partial U_1}{\partial\beta} + \frac{\partial U_1}{\partial\xi} \frac{\partial\xi}{\partial\beta} \right), \quad T < T_c. \quad (16)$$

It is noted that the internal energy changes abruptly at T_c , implying the first-order phase transition of the system. The same procedure is repeated for the second and third layer with $l = 2$ and $L - 1$. Of course, both T_c and the structure factor D depend explicitly on l .

We now present the transition temperature and heat capacity for LC films of $2 \leq L \leq 6$ obtained from the third-order VCE of the free energy. This is sufficient because the convergence of VCE is fast as is illustrated in refs. [21–23]. For a film of given L , the transition temperature $T_c^{(3)}(l, L, a, b)$ is computed for every molecular layer l . It is numerically verified that the reflection symmetry is preserved. In other words, the transition temperature is the same for $l = 1, L$; $l = 2, L - 1$ and so on. Since what we have found is C_v for each site, the total heat capacity for a film of five layers, say, is given by

$$C_v(L = 5) = N[2C_v(L = 5, l = 1) + 2C_v(L = 5, l = 2) + C_v(L = 5, l = 3)]. \quad (17)$$

Because the coupling constant J is not known, we normalize our results in such a way that the surface T_c of a 6-layer film is taken to be unity, namely, $\tau_c = k_B T_c(l = 1, L = 6, a, b)/J = 1$. The relative coupling parameters a, b are determined by fitting the three T_c values with measurements after setting the surface T_c of the 6-layer film equal to the corresponding experimental value. The best fitting yields $a = 1.1$ and $b = 0.09$. The heat capacity is still in arbitrary units. In order to compare with data, we require that the heat capacity for a 6-layer film at 65°C matches the experimental point [26]. This is because the heat capacity is known more accurately at 65°C than at T_c . There is no other adjustment in the calculation. In fig. 2, the heat capacity calculated as a function of temperature for films of various thickness is compared with recent experiments. Theoretical results are represented by solid lines and experimental data by a shaded thick line. It is seen that the transition temperatures for each film agree quite well with measurements.

It is most interesting to note that the layer-by-layer ordering phenomenon is in agreement with experimental observations [9]. We have also calculated C_v for a seven-layer film, and found that it peaks at practically the same temperature for $l = 3, 4$ and 5 . It is thus reasonable to expect that all interior layers order at the same temperature. More explicit calculation for thicker films requires higher-order VCE of the free energy and hence much more labor, but we do not expect any qualitative change. These results suggest that the SmA'-SmA transition [27], which is responsible for the layer-by-layer melting, observed in quasi-two-dimensional LC films can be qualitatively understood by the three-level Potts model although it is not predicted by the strict 2D theory of topological order. The Potts model is not two-dimensional, however, it actually has interlayer coupling.

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