Diffraction Patterns from Thin Hexatic Films

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On the basis of a "spin-wave" analysis of coupled hexatic layers, we propose a form for the diffraction patterns from thin liquid-crystal films. We note that the deviations from "two-dimensional behavior" observed in recent experiments on films of a few layers can in fact be used to extract the effective hexatic Frank constant, and to probe its temperature dependence. Our predictions are found to be quite consistent with the experimental observations.

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The elegant theories of defect-mediated transitions[1] provide an interesting scenario for the melting of two-dimensional crystals. In particular, they predict an intermediate phase with quasi-long-range orientational order, but no translational order: the *hexatic.*[2] However, observation of the crystal-hexatic-liquid sequence in either experiments or simulations has proved controversial[1]—the hexatic phase can be preempted by a direct discontinuous melting transition. Birgeneau and Litster[3] have observed that certain liquid-crystal phases can be regarded as three-dimensional stacked hexatic layers. The coupling of layers in the third dimension, however, endows them with true long-range orientational order, and changes the nature of the corresponding transitions.[4] However, by looking at successively thinner films of such liquid crystals one may hope to approach the two-dimensional limit, and indeed recently several groups have been engaged in such a pursuit.[5-7]

Diffraction studies of freely suspended liquid-crystal films[5-7] may indeed provide the most accurate and cleanest probe[1] of the two-dimensional melting sequence.[8] The diffraction pattern is isotropic in the liquid phase, but acquires a sixfold symmetry in the hexatic phase. In the latter, the 6nth Fourier component of the angular structure factor is given by[9,10] $C_{6n} = \mathrm{Re}\langle \psi_6^n \rangle$, with the orientational complex (two-component) order parameter $\psi_6(\mathbf{r}) = \psi_0 e^{6i\theta(\mathbf{r})}$, where $\theta(\mathbf{r})$ is the angle between the "bonds" and some reference axis. Using electron diffraction, Cheng *et al.*[11] recently studied films of two to six layers. For two layers, they found $C_{6n} = C_6^{n^2}$, as expected from two-dimensional scaling.[12] However, there remain two obstacles to further progress: One is the problem of extracting the behavior of interesting parameters (such as the hexatic stiffness, or Frank constant K_A) from the diffraction data. The other is to account for the observed deviations from the expected two-dimensional behavior in films of only four or six layers.[11]

Cheng *et al.*[11] fitted their diffraction patterns by $C_{6n} = C_6^{\sigma_n}$, with $\sigma_n = n + \lambda n(n-1)$. This form was theoretically suggested[9] on the basis of expansions about four dimensions, and is expected to hold only in the vicinity of the transition. It accounts very well for thicker three-dimensional films with a value[10] $\lambda = 0.3$. When forced to fit the data on thin films, λ becomes temperature dependent, and decreases to values smaller than 1 ($\sigma_n < n^2$) with increasing number of layers.[11] Thus it appears that even with four layers, describing the diffraction patterns requires a better understanding of the interlayer couplings. In this Letter we present a "spin-wave" (or harmonic) analysis of coupled hexatic layers that resolves the two problems posed earlier. The origin of deviations from the pure two-dimensional behavior[12] ($\sigma_n = n^2$) is attributed to the difference in fluctuations in the different layers. We propose that the diffraction patterns from l layers should be fitted by $C_{6n} = \sum_{i=1}^{l} \exp(-A_i^{(l)} n^2)/l$, where the sum contains $l/2$ (even l) or $(l+1)/2$ (odd l) independent terms (as $A_i^{(l)} = A_{l-i+1}^{(l)}$). Furthermore, since the coefficients $A_i^{(l)}$ are related to only *three independent parameters,* there are internal consistency checks for films of more than six layers. One of these three parameters is the Frank constant K_A, which is expected to have interesting critical behavior at both the hexatic-to-solid and hexatic-to-liquid phase boundaries (according to the theories of defect-mediated transitions[2]). Far away from both transitions, our theory predicts that the results for films of different thicknesses are all determined by the same three parameters. Our preliminary checks indicate that the observed patterns[11] are quite consistent with these predictions. Therefore it appears that explaining the "departure from two-dimensional behavior" can actually provide much valuable information about two-dimensional phase transitions. These results are also relevant to other realizations of two-dimensional quasi-long-range order.

In two dimensions, the fluctuations in the amplitude ψ_0 of ψ_6 [which led to the result[9] $\sigma_n = n + \lambda n(n-1)$] are negligible,[12] and we set $\psi_0 = 1$. For a film of l layers, we denote the angle at site $\mathbf{r}$ on the ith layer by $\theta_i(\mathbf{r})$. If we ignore topological defects, the energy cost of slowly varying fluctuations is described by the effective (spin-wave) Hamiltonian

$$\beta H = \int d^2r \left[\frac{K_A}{2} \sum_{i=1}^{l} (\nabla\theta_i)^2 + \frac{J}{2} \sum_{i=1}^{l-1} (\theta_{i+1}-\theta_i)^2 \right]. \quad (1)$$

K_A is the effective Frank constant[2] in each of the layers, while J measures the interplane coupling. Since we are dealing with a Gaussian theory, the normalized Fourier coefficients of the diffraction intensity are given by

$$C_{6n} = \frac{1}{l} \sum_{i=1}^{l} \langle e^{6i\theta_i(\mathbf{r})} \rangle$$

$$= \frac{1}{l} \sum_{i=1}^{l} e^{-18n^2\langle\theta_i^2\rangle} = \frac{1}{l} \sum_{i=1}^{l} e^{-A_i^{(l)}n^2}, \quad (2)$$

where $l^{-1}\sum_{i=1}^{l}$ explicitly deals with the average over the layers. Because of the free boundary conditions, the fluctuations $\langle\theta_i^2\rangle$ will differ from layer to layer ($\langle\theta_i^2\rangle$ is expected to decrease from outside layers to inside layers). Clearly, the scaling $C_{6n}=C_6^{\sigma_n}$ is no longer valid, and in fact (because of the symmetry $\langle\theta_i^2\rangle=\langle\theta_{l-i+1}^2\rangle$) C_{6n} should be fitted by the average of $l/2$ (l even) or $(l+1)/2$ (l odd) factors of $\exp(-A_i^{(l)}n^2)$. That the presence of a surface modifies the behavior of the order parameter in the layers close to it is quite well known in other liquid-crystalline phases. In fact, as observed in recent experiments by Ocko *et al.*[13] and explained theoretically by Selinger and Nelson,[14] the presence of a surface can induce smectic order in layers in its vicinity. Similar fluctuations in layer spacing could also, in principle, lead to variations in the interplanar coupling J. We have ignored such variations which appear to be small.[15]

To calculate $\langle\theta_i^2\rangle$ from Eq. (1), we need to construct the eigenmodes. It is easy to check that the transformation to normal modes,

$$\phi_0(\mathbf{r}) = \frac{1}{\sqrt{l}} \sum_{i=1}^{l} \theta_i(\mathbf{r}) \quad (3a)$$

and

$$\phi_m(\mathbf{r}) = \left(\frac{2}{l}\right)^{1/2} \sum_{i=1}^{l} \cos\left[\frac{m\pi}{l}\left(i-\frac{1}{2}\right)\right] \theta_i(\mathbf{r}) \quad (3b)$$

$$(m=1,2,\ldots,l-1),$$

leads to a Hamiltonian

$$\beta H = \int d^2r \sum_{m=0}^{l-l} \left[\frac{K_A}{2} (\nabla\phi_m)^2 + 2J\sin^2\left(\frac{m\pi}{2l}\right)\phi_m^2 \right]. \quad (4)$$

Inverting the transformation in Eq. (3) leads to

$$A_i^{(l)} = 18\langle\theta_i^2\rangle$$

$$= \frac{18}{l} \left\{ \langle\phi_0^2\rangle + 2\sum_{m=1}^{l-1} \cos^2\left[\frac{m\pi}{l}\left(i-\frac{1}{2}\right)\right] \langle\phi_m^2\rangle \right\}. \quad (5)$$

The averages of the normal-mode amplitudes are easily calculated from Eq. (4). For the zeroth mode

$$\langle\phi_0^2\rangle = \int \frac{d^2q}{(2\pi)^2} \frac{1}{K_Aq^2} = \frac{1}{4\pi K_A} \ln\left(\frac{L}{a}\right)^2, \quad (6a)$$

where L/a is the size of the system in units of molecular distance a. For the other modes

$$\langle\phi_m^2\rangle = \int \frac{d^2q}{(2\pi)^2} \frac{1}{K_Aq^2+4J\sin^2(m\pi/2l)}$$

$$= \frac{1}{4\pi K_A} \ln\left(\frac{1+\tilde{J}(l,m)}{(a/L)^2+\tilde{J}(l,m)}\right), \quad (6b)$$

where

$$\tilde{J}(l,m) = 4(J/K_A)(a/\pi)^2\sin^2(m\pi/2l).$$

Equations (2), (5), and (6) summarize our results for the coefficients C_{6n} needed to fit the diffraction pattern; they are completely characterized by the three parameters K_A, Ja^2, and L/a. For systems of five layers or more (with three or more $A_i^{(l)}$'s) it is therefore in principle possible to extract the effective Frank constant K_A, and to follow its temperature dependence. This information can then be used to test predictions of defect-mediated transition theories.[2] For example, the exponent η_6 for the decay of correlations [$\langle\psi_6(r)\psi_6^*(0)\rangle \sim r^{-\eta_6}$] can be obtained from the L dependence of C_6 in Eqs. (5) and (6) and equals $\eta_6=18/\pi l K_A$. Close to the hexatic-to-liquid transition, it should have a universal drop[2] from $\eta_6^- = [1-b(T_c-T)^{1/2}]/4$ to $\eta_6^+=0$. Near the hexatic-to-solid transition, η_6 should vanish as ξ^{-2}, where ξ is the diverging correlation length at this transition[2]; $\xi \sim \exp[b'|T-T_m|^{-0.369634}]$.

To obtain some insight into the behavior of $A_i^{(l)}$, we examine the limit of weak interplane coupling, $(a/L)^2 \ll Ja^2/K_A \ll 1$. In this limit

$$A_i^{(l)} \simeq \frac{9}{2\pi l K_A} \left[2\ln\left(\frac{L}{a}\right) + (l-1)\ln\left(\frac{K_A\pi^2}{4Ja^2}\right) + a_i^{(l)} \right], \quad (7a)$$

with

$$a_i^{(l)} = -4\sum_{m=1}^{l-1} \cos^2\left[\frac{m\pi}{l}\left(i-\frac{1}{2}\right)\right] \ln\left[\sin\left(\frac{m\pi}{2l}\right)\right]. \quad (7b)$$

From Eq. (7a) we see that on increasing the number of layers a crossover to three-dimensional behavior ($A_i^{(l)}$ independent of l) occurs for

$$l \gtrsim l_x \sim 2\ln\left(\frac{L}{a}\right) \Big/ \ln\left(\frac{K_A\pi^2}{4Ja^2}\right).$$

However, the coefficients $A_i^{(l)}$ in Eq. (7b) decay slowly as $1/i$ on moving away from the surface. This is the characteristic decay of correlation functions in *three-dimensional* Gaussian models. In order to study the full crossover to the three-dimensional result C_{6n}

$\sim C_6^{n+\lambda n(n-1)}$ close to the transition, one must also include amplitude fluctuations.[9]

Another interesting crossover involves the variation of the transition temperature with J. For $J=0$, the layers are decoupled and topological defects (occurring independently in each layer) become relevant when $\eta_6 = 18/\pi K_A = \frac{1}{4}$, independent of l. For $J \rightarrow \infty$, all layers behave as one and $\eta_6 = 18/\pi l K_A$; the defects now extend over all layers and the critical value of $K_A = 72/\pi l$ decreases with l. Note, however, that K_A is the effective rigidity after renormalization by topological defects. Since the experimental transition temperatures do not vary strongly with the number of layers l, we expect that renormalization of K_A by defects is quite strong, and depends on l. How does the crossover from independent defects in each layer at $J=0$ to a line of defects crossing through l layers as $J \rightarrow \infty$ occur? For small J, the interplane energy cost of an isolated defect (on a single plane) increases roughly as $J\lambda^2$ over a distance λ. Equating this result with the energy cost of $2\pi K_A \ln(\lambda)$ for creating vortices in neighboring layers leads to the conclusion that between two layers a "defect line" can move at most by $\lambda \sim (K_A/J)^{1/2}$. Naturally as $J \rightarrow 0$, λ increases and eventually saturates to L. The partition function for a single defect now behaves as

$$Z_1 \sim (L/a)^{-\pi l K_A/36} (L/a)^2 (K_A/J)^{l-1},$$

where the first factor is the energy cost, the second factor is a center-of-mass entropy, and the final term comes from the entropy of fluctuations of the defect line in between layers. The transition condition is obtained roughly by setting $Z_1 \sim 1$: For $L \gg \lambda$, $K_A^c = 72/\pi l$ at the transition, while for $\lambda \sim L$, $K_A^c = 72/\pi$; and in between the result is effected by the finite size L. Note that similar strong fluctuations of a vortex line have also been proposed[16] for the high-temperature superconducting materials that have weak interplanar couplings.

As the hexatic-to-liquid transition is approached, K_A is renormalized by the topological defects, in a way that may depend on l. Therefore, it is not clear how to compare the values of $A_i^{(l)}$ for different l's. Away from this transition, the spin-wave approximation described above may give the correct answers for all l, with *the same* values of the parameters K_A, Ja^2, and L/a. This predicts strong relations between the C_{6n}'s for different layer thicknesses.

In order to make a rough comparison with the data of Ref. 11, we assume (a) the approximation of intermediate interplanar coupling, i.e., Eq. (7); and (b) the same values of K_A, Ja^2, and L/a for $l=2$, 4, and 6. Cheng *et al.*[11] fitted their data by $C_{6n} = C_6^{n+\lambda n(n-1)}$. From their figures, we read values of C_6 and λ at $T=47\,°\mathrm{C}$. For $l=2$, they found $\lambda=1$, and hence we identify $A_1^{(2)} = -\ln C_6 \simeq 0.78$. For higher l, in the limit of large n, their fit yields $C_{6n} \simeq C_6^{\lambda n^2}$. In the same limit, our Eq. (2) is dominated by the term with smallest $A_i^{(l)}$ ($i = l/2$ for l even). Thus, $\min\{A_i^{(l)}\}_i \simeq -\lambda \ln C_6$. At $T=47\,°\mathrm{C}$ this gives $A_2^{(4)} \simeq 0.40$. Equation (2) now yields

$$A_1^{(4)} \simeq -\ln[2C_{6n} - \exp(-A_2^{(4)} n^2)]^{1/n^2}.$$

Replacing C_{6n} by $(0.63)^{n+0.83n(n-1)}$ we indeed find that the right-hand side of this expression is practically independent of n, and yields $A_1^{(4)} \simeq 0.43$. Having extracted the values of $A_1^{(2)}$, $A_1^{(4)}$, and $A_2^{(4)}$ we now invert Eq. (7), and find $K_A \simeq 30$, $L/a \simeq 9 \times 10^6$, and $4Ja^2/K_A\pi^2 \simeq 1$, with large uncertainties. This value of J implies that we are on the borderline of the approximation (7). However, using these values we then obtained $C_6 \simeq 0.74$ for $l=6$, in reasonable agreement with the value 0.69 found in Ref. 11.

Since L/a is so large, the $A_i^{(l)}$'s are dominated by the first term in Eq. (7a), i.e., $A_i^{(l)} \simeq (9/\pi l K_A)\ln(L/a)$, implying that $lA_i^{(l)}$ is independent of l. Indeed, the values of $l\lambda \ln C_6$, representing the smallest $lA_i^{(l)}$ for each l, are within 15% of each other. Similar agreement is found at 43 and 45 °C. Such good agreement, in spite of the rough approximations, is quite encouraging. It would be very interesting to see a direct fit of the data with our theory.

Much of the existing experimental work is done on the smectic-I phase, in which the tilt of the molecules generates a weak ordering field on the hexatic order parameter ψ_6.[7,9,10] Such a field would add a term $\frac{1}{2} h \sum_i \theta_i^2 = \frac{1}{2} h \sum_m \phi_m^2$ to Eqs. (1) or (4), replacing Eq. (6a) by

$$\langle \phi_0^2 \rangle \simeq -\frac{1}{4\pi K_A} \ln \left\{ \left[\left(\frac{a}{L} \right)^2 + \frac{ha^2}{K_A \pi^2} \right] \Big/ \left[1 + \frac{ha^2}{K_A \pi^2} \right] \right\}$$

and shifting $4J \sin^2(m\pi/2l)$ everywhere by h. Our basic result, Eq. (2), remains unchanged. In the limit $4J/K_A \gg h/K_A \gg 1/L^2$, the only effect of the field is to replace the parameter L/a in Eq. (7a) by $K_A \pi^2/ha^2$.

Finally, we note that similar expressions should apply to the positional order in thin "solids," as well as to thin superconductors, etc. In the case of thin solid films, for example, the diffraction pattern $S(\mathbf{q})$ will have the usual[2] Bragg spots $\sum_G |\mathbf{q} - \mathbf{G}|^{-2+\eta_G}$ with $\eta_G = G^2 \times (3\mu + \lambda)/4\pi\mu l(2\mu + \lambda)$, where μ and λ are the Lamé coefficients, but with an additional Debye-Waller factor of the form $l^{-1} \sum_i \exp(-G^2 a_i^{(l)})$ due to the difference in fluctuations between different layers. It may also be instructive to look directly for these relative interplane fluctuations by doing diffraction experiments along the perpendicular direction.

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