Hexatic Order and Liquid Density Fluctuations

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We study the evolution of liquid structure factors with changing bond-orientational (hexatic) order. The *form* of the radial structure factor is found to depend strongly on the mean square amplitude of fluctuations in the hexatic order parameter. The effects of substrates on the hexatic ordering process in two dimensions are also examined. Our results apply not only to hexatic fluids, but also to other liquids whose local densities are coupled to x-y-like primary order parameters.

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Several years ago, Halperin and Nelson proposed that continuous melting of two-dimensional crystals occurs in two steps.[1] First, at a temperature $T = T_M$, there is a dislocation unbinding transition into a hexatic liquid phase, with quasi-long-range order in the orientations of the bonds between molecules. Subsequently, at $T = T_{H-I}$, there is a disclination unbinding transition to an ordinary liquid phase, without bond-orientational order.

The x-ray scattering technique, which measures the mean square of the Fourier-transformed liquid density $\rho_{\vec{q}}$, is sensitive to evolving hexatic order because of the coupling, first described by Bruinsma and Nelson,[2] between $\rho_{\vec{q}}$ and the hexatic order parameter. In this paper, we report on a study of the density fluctuations in the presence of such coupling. Beyond the well-known fact that the scattering pattern for hexatic fluids consists of diffuse spots rather than rings, as for isotropic fluids, we find that the form of the structure factor, $\langle |\rho_{\vec{q}}|^2 \rangle$, *as a function of* $q = |\vec{q}|$, changes as the isotropic to hexatic transition is approached. Furthermore, we show explicitly how, for T near T_{H-I}, both the mean intermolecular spacing and liquid correlation length are related to the specific heat. Finally, we estimate the influence of fields conjugate to the hexatic order parameter. The substrates used in studies of physisorbed gases[3] invariably give rise to such fields.

The results to be presented below are in excellent agreement with experiments on both liquid crystals[4] and xenon adsorbed on graphite.[3] They are also very general; indeed, they apply to a wide range of liquids whose local densities are coupled to other, primary order parameters. If these liquids are well correlated, measuring the position of a maximum in the x-ray structure factor can be a convenient method for determining the specific-heat exponent α. Our expressions for the $\vec{q}$ dependence of the structure factor are easily modified for arbitrary x-y-like primary order parameters, including that describing the biaxial nematic (N') phase.[5] Thus, the x-ray scattering technique is a useful tool in the search for new liquid phases, not only because of the singular behavior in easily measured parameters, such as the mean interlayer spacing, but also because of changes in the line shapes that the existence of such phases would entail.

To perform calculations, it is useful to divide the fluid into microscopic cells of sidelength Λ_0^{-1}, where Λ_0^{-1} is large compared to the liquid correlation length ξ. In each of these cells $V_{\vec{r}}$, labeled by their positions $\vec{r}$, we can calculate the Fourier-transformed density $\rho_{\vec{q}}(\vec{r})$ for $|\vec{q}| > \Lambda_0$. For an ordinary liquid, the free-energy functional governing $\rho_{\vec{q}}(\vec{r})$ is

$$F_\rho = \int_{\Lambda_0 < q} d^dq \int d^dr \, |\rho_{\vec{q}}(\vec{r})|^2 A_q. \tag{1}$$

In an x-ray experiment with $q = |\vec{q}| > \Lambda_0 > \xi^{-1}$, the cells scatter independently, and the corresponding structure factor is $S_{\vec{q}} = \int d^dr \langle |\rho_{\vec{q}}(\vec{r})|^2 \rangle = T/A_q$. If $S_{\vec{q}}$ reaches its maximum when $q = q_0$, A_q can be expanded near q_0 in powers of $\delta_q = |\vec{q}| - q_0$:

$$A_q = \kappa_0^2 + \delta_q^2 + \dots . \tag{2}$$

When higher-order terms in δ_q are ignored, the resulting x-ray scattering profile is a Lorentzian of width κ_0.

In hexatic liquids, the positional correlation length remains finite, while there is long-range order in the intermolecular bond angles. Consequently, $S_{\vec{q}}$ will contain a sixfold modulation as a function of $\theta_{\vec{q}}$, the angle formed in a particular plane between a reference axis $\hat{a}$ and the scattering vector $\vec{q}$. The plane in question is defined by the substrates in the gas-monolayer experiments and by the smectic layers in the liquid-crystal work. In the remainder of this paper, we restrict our attention to those $\vec{q}$ with vanishing out-of-plane components. Using the order parameter $\rho_{\vec{q}}(\vec{r})$, which has an infinite number of components (indexed by $\vec{q}$), we can construct a two-component vector, or equivalently, a complex number, representing the hexatic order parameter:

$$\Psi(\vec{r}) = |\Psi(\vec{r})| \exp[6i\psi(\vec{r})] = \frac{\int_{\Lambda_0 < q < \Lambda_1} |\rho_{\vec{q}}(\vec{r})|^2 \exp(6i\theta_{\vec{q}}) d^d q}{\int_{\Lambda_0 < q < \Lambda_1} |\rho_{\vec{q}}(\vec{r})|^2 d^d q}. \tag{3}$$

Note that $\vec{q}$ is restricted to an annulus in reciprocal space surrounding the first maximum in the in-plane structure factor. $\Psi(\vec{r})$ can also be defined as $[\exp 6i\theta_6]$, where θ_6 represents the intermolecular bond orientation angles defined (in the smectic or substrate planes) with respect to $\hat{a}$, and the square brackets denote an average over the cell $V_{\vec{r}}$. Near the hexatic-isotropic transition, $\xi < \Lambda_0^{-1}$ remains finite and the cell-to-cell fluctuations in $\rho_{\vec{q}}(\vec{r})$ merely follow the fluctuations in $\Psi(\vec{r})$. Thus, the liquid's full free-energy functional, which includes terms coupling $\rho_{\vec{q}}(\vec{r})$ evaluated for different cells $V_{\vec{r}}$ and momenta $\vec{q}$, can be replaced by the effective functional $F_{\text{eff}} = F_\Psi[\Psi(\vec{r})] + F_\rho[\rho_{\vec{q}}(\vec{r})] + F_{\Psi-\rho}[\Psi(\vec{r}), \rho_{\vec{q}}(\vec{r})]$ where *only* F_Ψ couples different cells. Indeed, F_Ψ describes an x-y model:

$$F_\Psi = \int_{\Lambda_0 < q < \Lambda_1} d^d r \left(\tfrac{1}{2}|\nabla\Psi|^2 + r_6|\Psi|^2 + \tfrac{1}{4}u_6|\Psi|^4 + h_6\Psi + h_6^*\Psi_6^*\right). \tag{4}$$

A substrate, such as graphite, induces a field h_6 conjugate to the order parameter Ψ. For both liquid crystals and gas monolayers, ordering of other degrees of freedom,[2,6,7] such as molecular tilt, also produces nonvanishing effective fields h_6. The dimensionality $d = 3$ for bulk liquid crystals,[4,8,9] while $d = 2$ for thin liquid-crystal films and gas monolayers.[3,4]

Equation (3) defines the hexatic order parameter $\Psi(\vec{r})$ in terms of $\rho_{\vec{q}}(\vec{r})$. Consequently, the effective free-energy functional F_{eff} must include a coupling term

$$F_{\psi-\rho} = \int_{\Lambda_0 < q < \Lambda_1} d^d q \int d^d r\, f(q, |\Psi(\vec{r})|, \cos\{6[\theta_{\vec{q}} - \psi(\vec{r})]\}) |\rho_{\vec{q}}(\vec{r})|^2, \tag{5}$$

where f is a real-valued function of three variables. The following expansion of f is applicable for $T \gtrsim T_{H-I}$:

$$f(q, |\Psi(\vec{r})|, \cos\{6[\theta_{\vec{q}} - \psi(\vec{r})]\}) = B_q |\Psi(\vec{r})| \cos\{6[\theta_{\vec{q}} - \psi(\vec{r})]\} + C_q |\Psi(\vec{r})|^2. \tag{6}$$

The term $C_q|\Psi(\vec{r})|^2$ accounts for the increased density allowed by sixfold coordination, while the contribution proportional to B_q favors $\rho_{\vec{q}}(\vec{r})$ where $\vec{q}$ is along one of the hexatic axes determined by $\psi(\vec{r})$. Thus, f must display minima where $\theta_{\vec{q}} - \psi(\vec{r}) = n2\pi/6$, and so $B_q < 0$ for $q \approx q_0$. Like A_q, B_q and C_q can be expanded in powers of δ_q. To include the essential physics of the coupling between Ψ and $\rho_{\vec{q}}$, it suffices to consider only the constant B and the linear term $C + 2D\delta_q$ in the expansions for B_q and C_q, respectively. Note that $D < 0$ because hexatic order favors higher densities, and hence those Fourier components $\rho_{\vec{q}}$ of the density with larger $\vec{q}$.

Using the free-energy functional F_{eff}, we find that

$$\langle |\rho_{\vec{q}}(\vec{r})|^2 \rangle = \left\langle \frac{kT}{A_q + f(q, |\Psi(\vec{r})|, \cos\{6[\theta_{\vec{q}} - \psi(\vec{r})]\})} \right\rangle, \tag{7}$$

which is independent of $\vec{r}$ by translation invariance. The angular brackets denote a thermal average over the hexatic degrees of freedom. We perform this average exactly with respect to fluctuations in the phase of $\Psi(\vec{r})$, and to lowest order with respect to fluctuations in the amplitude $|\Psi(\vec{r})|$. In other words, $|\Psi(\vec{r})|$ is replaced by its root-mean-square value $\langle |\Psi|^2 \rangle^{1/2}$. The result is that

$$S_{\vec{q}} = N \sum_{p=-\infty}^{+\infty} S_q(p) \cos(6p\theta_{\vec{q}}) \langle \cos(6p\psi) \rangle, \tag{8}$$

where

$$S_q(p) = \frac{1}{2\pi/6} \int_{-\pi/6}^{+\pi/6} d\psi_0 \frac{\cos(6p\psi_0)}{A_q + f(q, \langle |\Psi|^2 \rangle^{1/2}, \cos(6\psi_0))} \tag{9}$$

and N is a $\vec{q}$- and $\langle|\Psi|^2\rangle^{1/2}$-independent prefactor proportional to the volume L^d. The averages in Eq. (8) must be computed using the following effective Hamiltonian for the phase variables:

$$H_{\text{eff}}=\tfrac{1}{2}K_A(T)\int d^dr\,|\nabla\psi|^2-\tilde{h}_6\int \cos 6\psi\, d^dr/a_0^d. \tag{10}$$

In (10), $-\pi/6\leq\psi(\vec{r})<\pi/6$, $K_A(T)$ is the Franck constant for phase fluctuations,[1] a_0^d is the volume per molecule, and $\tilde{h}_6=h_6\langle|\Psi|^2\rangle^{1/2}a_0^d$.

For temperatures above T_{H-I}, all terms with $p\neq 0$ in the series (8) vanish. Even below, but near T_{H-I}, where $|\langle\cos(6\psi)\rangle|\ll 1$, the series will converge rapidly because $\langle\cos(6p\psi)\rangle\approx\langle\cos(6\psi)\rangle^{p^2}$. Using the expansion (6) for f, and retaining only the first two terms in (8) yields

$$\frac{S_{\vec{q}}}{N}\cong\frac{1}{a}\left[1-\left(\frac{b}{a}\right)^2\right]^{-1/2}+\frac{2}{b}\cos(6\theta_{\vec{q}})\langle\cos(6\psi)\rangle\left\{1-\left[1-\left(\frac{b}{a}\right)^2\right]^{-1/2}\right\}, \tag{11}$$

where $a=A_q+C_q\langle|\Psi|^2\rangle$ and $b=B_q\langle|\Psi|^2\rangle^{1/2}$. If we perform the Fourier transform of $S_{\vec{q}}$ with respect to $\theta_{\vec{q}}$ we should recover the hexatic order parameter Ψ [Eq. (3)]. For small $\langle|\Psi|^2\rangle$, our choice for the coupling F_c is indeed consistent with the definition of Ψ if $B_q=-2A_q$.

At lower temperatures, hexatic order will be well developed and $|\langle\cos(6p\psi)\rangle|\cong 1$ for many values of p, with the result that the series (8) will converge slowly. However, we can take advantage of the fact that for $T\ll T_{H-I}$, the mean square fluctuations $\langle|\delta\psi|^2\rangle$ in ψ are small. Thus, $\langle\cos(6p\psi)\rangle\cong\exp(-18p^2\times\langle|\delta\psi|^2\rangle)$, and summing the series (8) yields the spin-wave result,

$$S_{\vec{q}}\simeq S_{\vec{q}}^{\text{sw}}=\frac{N}{(2\pi\langle|\delta\psi|^2\rangle)^{1/2}}\int_{-\infty}^{\infty}\frac{\exp(-\frac{1}{2}\psi^2/\langle|\delta\psi|^2\rangle)\,d\psi}{A_q+f(q,\langle|\Psi|^2\rangle^{1/2},\cos 6(\theta_{\vec{q}}-\psi))}, \tag{12}$$

where $\langle|\delta\psi|^2\rangle=(2\pi)^{-d}T\int d^dq/(K_aq^2+36\tilde{h}_6)$.

We now discuss the evolution of $S_{\vec{q}}$ with T for $h_6=0$. At high temperatures $(T\gg T_{H-I})$, $b=B\times\langle|\Psi|^2\rangle^{1/2}$ is small and $S_{\vec{q}}$ assumes the usual Lorentzian form $(\kappa_0^2+\delta_q^2)^{-1}$ near q_0. Furthermore, $S_{\vec{q}}$ will be independent of $\theta_{\vec{q}}$. In contrast, for $T<T_{H-I}$, the structure factor, when measured as a function of $\theta_{\vec{q}}$, will display the sixfold modulation characteristic of hexatic order. For $T\ll T_{H-I}$, Eq. (12) applies and near the maxima (at $\theta_{\vec{q}}=\psi_n=2\pi n/6$) of the structure factor, we can make the expansion $f=f_0+\frac{1}{2}f_0''(\theta_q-\psi-\psi_n)^2$. If $f_0+\kappa_0^2\gtrsim\frac{1}{2}f_0''\langle|\delta\psi|^2\rangle$, radial scans through the maxima will be Lorentzians of half-width $\kappa'=(f_0+\kappa^2+\frac{1}{2}\langle|\delta\psi|^2\rangle f_0'')^{1/2}$. Transverse scans are given by the convolution of a Gaussian with a Lorentzian; if, again, $f_0+\kappa^2\gtrsim\frac{1}{2}f_0''\langle|\delta\psi|^2\rangle$, the corresponding *angular* half-width will be $\kappa'/(\frac{1}{2}f_0'')^{1/2}$. Consequently, radial and angular half-widths should have a T-independent ratio for $T\ll T_{H-I}$, as is indeed observed[3] near the melting temperature T_M for xenon on graphite. For $d=2$, $h_6=0$, and T very close to T_M, these results agree with those of Ostlund and Halperin.[6]

The most interesting behavior occurs for $T\approx T_{H-I}$, where the first term in the expansion (8) dominates. Using the expansions for A_q, B_q, and C_q, we find from Eq. (11) that

$$S_{\vec{q}}/N=[(q-q_0')^2+\kappa_+^2]^{-1/2}[(q-q_0')^2+\kappa_-^2]^{-1/2}. \tag{13}$$

To second order in $\langle|\Psi|^2\rangle^{1/2}$, the inverse lengths $\kappa_\pm$ are, when squared,

$$\kappa_\pm^2=\kappa_0^2\pm|B|\langle|\Psi|^2\rangle^{1/2}+C\langle|\Psi|^2\rangle. \tag{14}$$

Similarly, the inverse intermolecular spacing is, on average,

$$q_0'=q_0+|D|\langle|\Psi|^2\rangle. \tag{15}$$

Note that if κ_0^2 is comparable to $B\langle|\Psi|^2\rangle^{1/2}+C\times\langle|\Psi|^2\rangle$, $S_{\vec{q}}$ near q_0 is well approximated by the *square root* of a Lorentzian of width κ_-.[10] Because $(d/dT)\langle|\Psi|^2\rangle\approx C(T)$ where $C(T)$ is the specific heat, there will be singular contributions to q_0' and $\kappa_\pm$ for T near T_{H-I}. In particular, where α is the exponent and A_+/A_- the amplitude ratio characterizing the specific heat, $q_0'(T)-q_0'(T_{H-I})=-A_+|T-T_{H-I}|^{1-\alpha}$ and $+A_-|T-T_{H-I}|^{1-\alpha}$ for $T>T_{H-I}$ and $T<T_{H-I}$, respectively. Near T_{H-I}, the inverse correlation lengths behave similarly. Note, however, that for $T<T_{H-I}$, any inverse radial correlation length $\kappa_{\text{eff}}(T)$, derived, for example, from fits of Lorentzians to actual data, depends on $\theta_{\vec{q}}$, reaching its minimum for $\vec{q}$ parallel to any of the three axes defined by the hexatic order. Since Taylor expansions [based on Eq. (8)] for

such $\kappa_{\mathrm{eff}}(T)$ include terms proportional to $\langle\cos(6p\psi)\rangle$, $\kappa_{\mathrm{eff}}(T)$ will contain singularities characterized by the exponents $p\beta$ ($p = 1, 2, 3, \ldots$), with corrections of order η for $p > 1$, as well as $1-\alpha$. Fortunately, there are considerable simplifications when a powder average (integral with respect to $\theta_{\vec{q}}$) of $S_{\vec{q}}$ is performed. Upon averaging, all terms in the series (8) with $p \neq 0$ vanish and again Eqs. (13)–(15) define the structure factor.

We now consider the effects of substrate fields on the hexatic ordering process. Of course, the symmetry-breaking field h_6 eliminates the hexatic-isotropic phase transition, much as an applied magnetic field destroys second-order ferromagnetic-paramagnetic transitions. Nonetheless, as for ferromagnets, the field h_6 can be sufficiently small that the system will behave nearly as if $h_6 = 0$. Our object here is to make the phrases "sufficiently small" and "nearly" more precise for the case of greatest interest, gas monolayers adsorbed on graphite. For $T < T_{H-I}$ and small $\tilde{h}_6$, $\langle\cos 6\psi\rangle \approx (\tilde{h}_6/T)^{\eta/(4-\eta)}$, where $\eta = 18T/\pi K_A$.[11] Because $\eta = \frac{1}{4}$ for $T = T_c$, $\langle\cos 6\psi\rangle$ will be of order 0.5 or more as long as $\tilde{h}_6/T \gtrsim (0.5)^{(4-\eta)/\eta} > 3\times 10^{-5}$. If $T > T_{H-I}$, the linear response result, $\langle\cos 6\psi\rangle \cong \chi_6 \tilde{h}_6 = \xi_H^{2-\eta}\tilde{h}_6/T = \xi_H^{7/4}\tilde{h}_6/T$, will be valid provided that the hexatic correlation length $\xi_H < \xi_c = (\tilde{h}_6/T)^{-8/15}$. Thus, for xenon on graphite, where $\tilde{h}_6 \cong 0.2$ K/atom[12] and $T_M \approx 100$ K,[3] substrate effects on the hexatic order will be severe both above ($\xi_c \approx 30$ interatomic spacings) and below ($\tilde{h}_6/T \approx 10^{-3}$) T_{H-I}.

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