Theory of Two-Dimensional Melting

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The consequences of a theory of dislocation-mediated two-dimensional melting are worked out for triangular lattices. Dissociation of dislocation pairs first drives a transition into a "liquid crystal" phase with exponential decay of translational order, but power-law decay of sixfold orientational order. A subsequent dissociation of *disclination* pairs at a higher temperature then produces an isotropic fluid. The critical behavior, as well as the effect of a periodic substrate, is discussed.

Kosterlitz and Thouless[1] have proposed a model of two-dimensional melting, in which the "topological order" of a solid phase is destroyed by the dissociation of dislocation pairs. Similar ideas,[1] with vortices taking the place of dislocations, have led to a rather detailed theory[2] of the superfluid transition in two dimensions. In this Letter, we summarize the consequences of dislocation-mediated melting of triangular lattices, on both smooth and periodic substrates. A more detailed derivation will be given elsewhere.[3]

Consider the properties of a two-dimensional triangular solid on a smooth substrate. By definition, the solid has nonzero long-wavelength elastic constants. The structure factor exhibits[4] power-law singularities, $S(\vec{q}) \sim |\vec{q}-\vec{G}|^{2+\eta_{\vec{G}}}$, near a set of reciprocal lattice vectors $\{\vec{G}\}$, with exponents $\eta_{\vec{G}}$ related to the Lamé elastic constants $\mu_R(T)$ and $\lambda_R(T)$ by $\eta_{\vec{G}} = k_B T|\vec{G}|^2(3\mu_R+\lambda_R)/4\pi\mu_R(2\mu_R+\lambda_R)$. These singularities, which replace the δ-function Bragg peaks found in three-dimensional solids, reflect power-law decay at large distances of the correlation function $\langle \exp\{i\vec{G}\cdot[\vec{u}(\vec{r})-\vec{u}(\vec{0})]\}\rangle$, where $\vec{u}(\vec{r})$ is the lattice displacement at point $\vec{r}$. One can also define an order parameter (analogous to $e^{i\vec{G}\cdot\vec{u}}$) for bond orientations, namely $\psi \equiv e^{6i\theta}$, where $\theta(\vec{r})$ is the orientation, relative to the x axis, of a bond between two nearest-neighbor atoms at $\vec{r}$. In a solid, θ is given in terms of the displacement field, $\theta = \frac{1}{2}(\partial_y u_x - \partial_x u_y)$. The solid phase exhibits long-range orientational order, since $\langle \psi^*(\vec{r})\psi(\vec{0})\rangle$ approaches a nonzero constant at large $\vec{r}$.[5]

If melting is indeed characterized by an unbinding of dislocation pairs at a temperature T_m, one expects that a density $n_f(T)$ of free dislocations above T_m will lead to exponential decay of the translational order parameter $e^{i\vec{G}\cdot\vec{u}}$, with a correlation length $\xi_+(T) \approx n_f^{-2}$. This length diverges as $T \to T_m^+$ [see (6) below]. The structure factor $S(\vec{q})$ is now finite at all Bragg points, and the Lamé coefficients vanish at long wavelengths. We shall see, however, that orientational order persists, in the sense that bond-angle correlations now decay algebraically, $\langle \psi^*(\vec{r})\psi(\vec{0})\rangle \sim 1/r^{\eta_6(T)}$. This phase can be described as a liquid crystal, similar to a two-dimensional nematic, but with a sixfold rather than twofold anisotropy. The exponent $\eta_6(T)$ is related to the Franck constant $K_A(T)$, which is the coefficient of $\frac{1}{2}|\nabla\theta|^2$ in the free-energy density: $\eta_6(T) = 18k_B T/\pi K_A(T)$. We find that K_A is infinite just above T_m, but decreases with increasing temperatures, until a temperature T_i, where dissociation of *disclination* pairs drives a transition into an isotropic phase in which both the translational and orientational order decay exponentially.

The liquid-crystal phase is isomorphic to a two-dimensional superfluid, except that ±60° disclinations play the role of vortices. The transition at T_i should belong to the same universality class as the superfluid transition, and we expect, in particular, that[2] $\eta_6(T_i) = \frac{1}{4}$. Although disclination pairs are very tightly bound in the solid phase, screening by a gas of free dislocations produces a weaker logarithmic binding for $T_m < T < T_i$. It is interesting to note that an isolated dislocation can itself be regarded as a tightly bound disclination pair,[6] separated by one lattice constant.

To see the origin of these results, let us decompose the displacement field of a solid into a smoothly varying phonon field $\vec{\varphi}(\vec{r})$, and a part due to dislocations.[1] The Hamiltonian $\mathcal{H}_E$ for the solid, within continuum elasticity theory,[6] then breaks into two parts, $\mathcal{H}_E = \mathcal{H}_0 + \mathcal{H}_D$, with

$$\frac{\mathcal{H}_0}{k_B T} = \frac{1}{2}\int \frac{d^2r}{a_0^{\,2}}\left[2\bar{\mu}\,\varphi_{ij} + \bar{\lambda}\varphi_{ii}^{\,2}\right], \tag{1}$$

$$\frac{\mathcal{H}_D}{k_B T} = -\frac{1}{8\pi}\sum_{\vec{R}\neq\vec{R}'}\left[K_1\vec{b}(\vec{R})\cdot\vec{b}(\vec{R}')\ln\left(\frac{|\vec{R}-\vec{R}'|}{a}\right) + K_2\frac{\vec{b}(\vec{R})\cdot(\vec{R}-\vec{R}')\vec{b}(\vec{R}')\cdot(\vec{R}-\vec{R}')}{|\vec{R}-\vec{R}'|^2}\right] + \frac{E_c}{k_B T}\sum_{\vec{R}}|\vec{b}(\vec{R})|^2. \tag{2}$$

In (1), φ_{ij} is related to the smooth part of the displacement field, $\varphi_{ij}=\frac{1}{2}(\partial_i\varphi_j+\partial_j\varphi_i)$, and $\overline{\mu}$ and $\overline{\lambda}$ are "reduced" elastic constants, given by the usual Lamé coefficients μ and λ multiplied by the square of the lattice spacing, a_0^2, and divided by k_BT. In (2), $\vec{b}(\vec{R})$ is a dimensionless dislocation Burgers vector of the form $\vec{b}(\vec{R})=m(\vec{R})\vec{e}_1+n(\vec{R})\vec{e}_2$, where $m(\vec{R})$ and $n(\vec{R})$ are integers, and $\vec{e}_1$ and $\vec{e}_2$ are unit vectors spanning the underlying Bravais lattice. The sums in (2) are over, say, a square mesh with spacing a of sites in physical space, and the $\vec{b}(\vec{R})$ must satisfy a vector charge neutrality condition, $\sum_{\vec{R}}\vec{b}(\vec{R})=0$. The quantities K_1 and K_2 are equal, $K_1=K_2\equiv K=4\overline{\mu}(\overline{\mu}+\overline{\lambda})/(2\overline{\mu}+\lambda)$, and E_c is the core energy of a dislocation.

If dislocations only exist in bound pairs at low temperatures, one expects that they can be ignored, and that the long-wavelength properties of the solid will simply be given by (1), with suitably renormalized elastic constants. The properties of the solid phase quoted above follow directly from this observation.

One of us[7] has studied the properties of (2) in the absence of the dot product or angular terms ($K_2=0$). It was found that dislocations are indeed unimportant at low temperatures (large K_1), and that a dislocation-unbinding transition was controlled by the terminus of a fixed *surface*, parametrized by K_1 and $\vec{e}_1\cdot\vec{e}_2$. Here, we restrict ourselves to the triangular lattice ($\vec{e}_1\cdot\vec{e}_2=\frac{1}{2}$), and extend this treatment to the full dislocation Hamiltonian $\mathcal{H}_D$, taking into account the neglected angular terms. Recursion relations for K and $y\equiv\exp(-E_c/k_BT)$ can in fact be obtained rather straightforwardly, by considering the renormalization of elastic constants due to dislocation pairs, in analogy to calculations of the effect of vortices on the superfluid density in a ^{4}He film.[8] Integrating over mesh sizes between a and ae^l, we obtain partially dressed parameters $\overline{\mu}(l)$, $\overline{\lambda}(l)$, $y(l)$, and $K(l)$, which satisfy, to $O(y^2(l))$,

$$\frac{d\overline{\mu}^{-1}}{dl}=3\pi y^2e^{-K/8\pi}I_0\left(\frac{K}{8\pi}\right), \tag{3}$$

$$\frac{d[\overline{\mu}+\overline{\lambda}]^{-1}}{dl}=3\pi y^2e^{-K/8\pi}\left[I_0\left(\frac{K}{8\pi}\right)+I_1\left(\frac{K}{8\pi}\right)\right], \tag{4}$$

$$\frac{dy}{dl}=\left(2-\frac{K}{8\pi}\right)y+2\pi y^2e^{-K/16\pi}I_0\left(\frac{K}{16\pi}\right), \tag{5}$$

where $I_0(x)$ and $I_1(x)$ are modified Bessel functions of the first and second kind. We find that

$$K^{-1}(l)=\tfrac{1}{4}\{\overline{\mu}^{-1}(l)+[\overline{\mu}(l)+\overline{\lambda}(l)]^{-1}\}$$

for all l, so that its recursion relation can be obtained trivially from (3) and (4).

As in Ref. 7, $y(l)$ is driven to zero at large l, for all temperatures below a critical value T_m. Above T_m, $y(l)$ is ultimately driven toward large values and $K(l)$ is driven towards zero, an instability we associate with dislocation-pair unbinding.

Following Kosterlitz[2] and Ref. 7, we determine the behavior near T_m by studying Eqs. (3)–(5) near the critical value $K_c=16\pi$. We identify the correlation length $\xi_+(T)$ with ae^{l^*}, with l^* chosen such that $K(l^*)\approx\frac{1}{2}K_c$. In this way, we find that

$$\xi_+(T)\approx a\exp[b/(T/T_m-1)^{0.44817\cdots}], \tag{6}$$

as $T\to T_m^+$, where b is a constant, and 0.44817... can be expressed in terms of the roots of a quadratic equation with Bessel-function coefficients. The specific heat exhibits only an essential singularity, $C_p\sim\xi_+^{-2}$, while the structure factor at the Bragg points is given by $S(\vec{G})\sim\xi_+^{2-\eta_{\vec{G}}}$. Taking over the discussion for the superfluid density in Ref. 8, we find that the reduced shear modulus in the solid phase is

$$\overline{\mu}_R(T)=\lim_{l\to\infty}\overline{\mu}(l).$$

It follows from Eqs. (3)–(5) that $\mu_R(T)$ approaches a finite limiting value as $T\to T_m^-$. Just below T_m we find $\mu_R(T)=\mu_R(T_m)[1+\mathrm{const}(T_m-T)^{0.44817\cdots}]$, with a similar result for $\lambda_R(T)$. There is a universal relationship involving the elastic constants at T_m,

$$\lim_{T\to T_m^-}\left\{\frac{1}{\mu_R(T)}+\frac{1}{\mu_R(T)+\lambda_R(T)}\right\}=\frac{a_0^2}{4\pi k_BT_m}. \tag{7}$$

This corresponds to the critical value $K_c=16\pi$, and is also suggested by the "entropy argument" of Kosterlitz and Thouless.[1]

The results for orientational correlations above T_m follow from a calculation of the Franck constant K_A:

$$\frac{k_BT}{K_A}=\lim_{q\to0}q^2\langle\hat{\theta}(q)\hat{\theta}(-q)\rangle$$
$$=\lim_{q\to0}\frac{q_iq_j}{q^2}\langle\hat{b}_i(q)\hat{b}_j(-g)\rangle, \tag{8}$$

where $\hat{\theta}(q)$ and $\hat{b}_i(q)$ are the Fourier-transformed orientational and Burgers-vector fields, respectively. The second line of (8) follows because the contribution of $\vec{\varphi}(\vec{r})$ to K_A^{-1} is zero and because the dislocation part of $\hat{\theta}(q)$ is just[3,6] $\hat{\theta}(q)=-iq_j\hat{b}_j(q)/q^2$. To estimate K_A just above T_m, we use its transformation properties under the renormalization group, $K_A(K(0), y(0)) = e^{2l}K_A(K(l), y(l))$. Choosing $l = l^* = \ln(\xi_+/a)$, we can evaluate K_A using Debye-Hückel theory, which amounts to treating $\vec b(\vec R)$ as a continuous vector field, rather than restricting it to discrete points on a Bravais lattice. Upon Fourier transformation, $\mathcal{H}_D$ becomes

$$\frac{\mathcal{H}_D}{k_BT} = \frac{1}{2V}\sum_{\vec q}\left[\frac{K}{2q^2}\left(\delta_{ij} - \frac{q_iq_j}{q^2}\right) + \frac{2E_ca^2}{k_BT}\delta_{ij}\right]\hat b_i(\vec q)\hat b_j(-\vec q), \tag{9}$$

where V is the volume. Since the term proportional to the transverse projection operator in (9) does not contribute to (8), one obtains $K_A(K(l^*), y(l^*)) \approx 2E_c(l^*)a^2 = O(k_BT_m)$. It follows that the physical Franck constant is $K_A \sim \xi_+^2(T)$. The algebraic decay of orientational order above T_m and the relationship between $\eta_6(T)$ and $K_A(T)$ are straightforward consequences of this result.

Many experimental investigations of two-dimensional melting are carried out on films adsorbed onto a regular substrate,[9] and so it is important to determine the effect of a periodic potential on our results. One must now distinguish between a "floating solid," characterized by power-law Bragg singularities at reciprocal lattice vectors $\{\vec G\}$ which vary continuously with coverage and temperature, and an "epitaxial solid," having δ-function Bragg peaks at a lattice of vectors including the substrate reciprocal lattice $\{\vec K\}$ as a proper subset. The floating solid should be rather similar to the solid on a smooth substrate discussed in this paper. Figure 1 shows a schematic phase diagram with fluid, floating solid, and epitaxial phases. A region of two-phase coexistence is also shown, separating epitaxial phase I from a dilute fluid or "vapor."[8,10] We expect an increasing multiplicity and complexity of epitaxial phases with decreasing temperatures.

To understand Fig. 1, consider first the effect of a weak substrate potential commensurate with the lattice of the adsorbed film. Let $\{\vec M\}$ be the set of vectors common to $\{\vec G\}$ and $\{\vec K\}$, and let M_0 be the minimum length of nonzero vectors in $\{\vec M\}$. Let us expand the potential on the reciprocal lattice $\{\vec K\}$, and focus our attention on

$$\mathcal{H} = \mathcal{H}_E + \sum_{|\vec M| = M_0} h_{\vec M}\sum_{\vec r} e^{i\vec M\cdot\vec u(\vec r)}, \tag{10}$$

where $h_{\vec M}$ is the potential strength at $\vec M$; the terms displayed in (10) are the most important ones for weak potentials. The renormalization-group eigenvalue for $h_{\vec M}$ is easily shown to be $\lambda_{\vec M} = 2 - \frac{1}{2}\eta_{\vec G}|_{\vec G = \vec M}$, so that any commensurate perturbation becomes relevant at sufficiently low temperatures. If M_0 is sufficiently small ($M_0 \lesssim 8\pi/a_0$), λ_{M_0} remains relevant out to quite high temperatures and a floating solid can never exist; there is then a transition directly from a low-temperature expitaxial phase into a fluid, as shown for epitaxial phases I and III. For large enough M_0 ($M_0 \gtrsim 8\pi/a_0$), however, there is a temperature window where $\lambda_{M_0} < 0$ and $K_R > 16\pi$, indicating that a floating solid is stable to both substrate perturbations and dislocation unbinding. The dotted line in Fig. 1 shows a locus of such points, where the floating solid has the same periodicity as epitaxial phase II, which exists at lower temperatures.

It can be shown[3] that the transitions from floating solid to fluid and from floating solid to epitaxial phase II (marked A and B in Fig. 1) are both describable at long wavelengths by a Hamiltonian of the form (2) with $K_1 \neq K_2$. Indeed, these transitions are essentially dual to each other.[3] The situation is very similar to the "$\cos p\theta$" perturbations discussed by José *et al.*[11] The transition from epitaxial phase II to a floating solid at points other than B may connect two phases with different periodicities; its nature is not yet known. We expect that the transition from floating solid to fluid will be everywhere qualitatively similar to our discussion of dislocation unbinding on a smooth substrate. The orientational bias imposed by the substrate, however, should alter or eliminate the liquid-crystal isotropic transition discussed above.

We wish to emphasize in closing that we have only explored consequences of the dislocation model of melting perturbatively in $y = \exp(-E_c/$

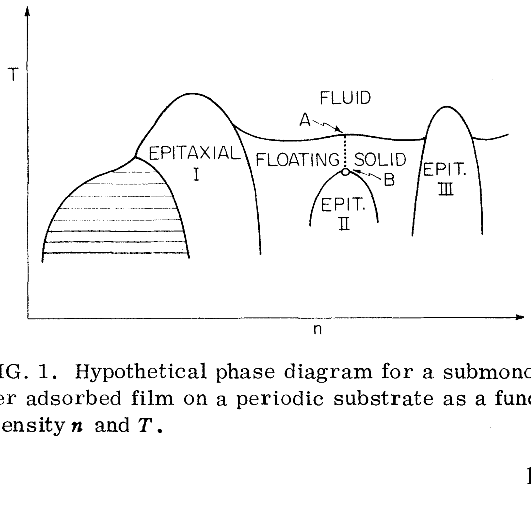

FIG. 1. Hypothetical phase diagram for a submonolayer adsorbed film on a periodic substrate as a function of density n and T.

k_BT). Although the theory is stable and self-consistent, we cannot rule out other mechanisms for melting, perhaps leading to a first-order transition. A "premature" unbinding of disclinations (before dislocations dissociate) might constitute such a mechanism.

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Mechanisms of Methyl-Group Rotation

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The dominant mechanism of methyl-group rotation in MDBP (4-methyl-2,6-ditertiary-butylphenol) between 4 and 15 K is a Raman process involving the scattering of optical phonons, rather than the usually assumed two-step process of methyl torsional excitation with phonon absorption and subsequent emission. The Raman process is positively identified for the first time by combining magnetic resonance measurements of tunnel splittings with inelastic neutron scattering spectra for both normal and partially deuterated MDBP.

There is a useful parallel between the rotation of molecular groups in solids at low temperature and the magnetic relaxation of paramagnetic ions, since both involve localized transitions occurring through interactions with lattice phonons. The temperature dependence of electron spin-lattice relaxation is discussed[1] mainly in terms of three mechanisms, the direct, Raman, and Orbach processes, which successively dominate relaxation as the temperature is increased, each type of process having a distinct temperature dependence which serves as its signature. By contrast, discussions of methyl-group rotation have mostly invoked one single process which is the analog of the Orbach process. The experimental reason for this is that the rotation rate τ^{-1} is very commonly found to obey an Arrhenius-type law,

$$\tau^{-1} = \sum_i \tau_i^{-1} \exp(-E_i/kT), \tag{1}$$

with just one or two terms describing the behavior over a wide range of temperature,[2-4] and this exponential temperature dependence is regarded as the signature of the Orbach process. The apparent failure of the Raman process to assert itself at low temperatures is mysterious, until one