Reentrant melting on an imperfect surface

R. A. Serota
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
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We study the reentrant melting, driven by the unbinding of dislocations, of a solid film on a substrate with quenched random imperfections. Phase boundaries are accounted for by an interplay of strong pair-breaking terms, induced via an interaction with substrate-generated random forces, and a cutoff for maximal separation of dislocations in a pair.

Since a dislocation model was proposed by Kosterlitz and Thouless,[1] a comprehensive understanding of melting in two-dimensional solids has been achieved.[2–4] Over the past few years quenched randomness, e.g., random impurities[5] and random topography of a substrate,[6] has been included into consideration. It was shown that at sufficiently low temperatures dislocation pairs unbind because of randomness, causing a reentrant transition into a hexatic phase.

As was mentioned by Nelson,[5] a different type of quenched disorder, breaking the translational symmetry, can occur in physiabsorbed monolayers on a glassy substrate. This disorder, similar to the symmetry-breaking fields in XY magnets,[7,8] has been recently studied by Chudnovsky[9] by modeling the quenched random imperfections of the substrate with a phenomenological substrate-generated random force $\mathbf{f}(\mathbf{r})$ which couples linearly to the lattice displacement $\mathbf{u}(\mathbf{r})$, as is given by the free energy

$$F=\tfrac{1}{2}\int d^2r(2\mu u_{ij}^2+\lambda u_{kk}^2-2f_iu_i)\ . \tag{1}$$

Here μ and λ are the usual isotropic elastic constants of a triangular lattice, $\mathbf{u}(\mathbf{r})$ is the displacement field, $u_{ij}(\mathbf{r})$ is the strain tensor, and a Gaussian distribution for the probabilities of different configurations of $\mathbf{f}(\mathbf{r})$ was assumed,

$$P[\mathbf{f}(\mathbf{r})]\sim\exp\left[-\frac{1}{2\sigma}\int d^2r[\mathbf{f}(\mathbf{r})]^2\right]\ . \tag{2}$$

It should be emphasized that in the case of quenched random impurities a fluctuation $\delta c(\mathbf{r})$ in the local concentration of impurities couples to the elastic *dilation*, $\nabla\cdot\mathbf{u}=u_{kk}$, as is seen from the free energy[5]

$$F=\tfrac{1}{2}\int d^2r(2\mu u_{ij}^2+\lambda u_{kk}^2-2w\delta cu_{kk})\ , \tag{1'}$$

where $w=(\mu+\lambda)\Omega_0$, Ω_0 being the change in the crystal area due to a defect. Direct coupling of the substrate-generated random force to the displacement in (1) is much stronger, which results in the different structural properties of a solid film.

With use of (1) and (2) it is straightforward to prove[9] that translational order (TO) and orientational order (OO) in a solid film on an imperfect surface decay exponentially and algebraically, respectively, at $T=0$. This result for TO is equivalent to that for the lack of long-range order in two-dimensional XY magnets with random symmetry-breaking fields.[10] However, as is argued by Goldschmidt and Schaub,[8] the vortex-unbinding mechanism, excluded in Ref. 10, is important for an understanding of the low-temperature phase. Therefore, the motivation for this work was to generalize the results of Ref. 9 for finite temperatures with subsequent introduction of dislocations in the model.

Following closely the technique used in the Appendixes of Ref. 5, it is easy to see that the correlation functions[3] for TO and OO in the harmonic approximation are given respectively by

$$C^{\mathrm{TO}}(\mathbf{r})=[\langle e^{i\mathbf{G}\cdot[\mathbf{u}(\mathbf{r})-\mathbf{u}(0)]}\rangle]_d \sim\frac{1}{r^{\eta_T}}\exp[-(\xi_{\parallel}^{-2}r_{\parallel}^2+\xi_{\perp}^{-2}r_{\perp}^2)\ln(L/r)]\ , \tag{3}$$

and

$$C^{\mathrm{OO}}(\mathbf{r})=[\langle e^{i6[\Theta(\mathbf{r})-\Theta(0)]}\rangle]_d \sim C(T)\frac{1}{r^{\eta_\sigma}}\ , \tag{3'}$$

where $\mathbf{G}$ is a reciprocal-lattice vector and $\Theta=\frac{1}{2}\epsilon_{ik}\partial_iu_k$, ϵ_{ik} being the antisymmetric tensor. The angle brackets denote the conventional thermal average, whereas the square brackets with the subscript d indicate a subsequent average over the disorder as described by Eq. (2). The longitudinal and transverse (with respect to $\mathbf{G}$) correlation lengths and the exponent η_σ were found in Ref. 9 and are given respectively by

$$\xi_{\parallel}^{-2}=\frac{\sigma|\mathbf{G}|^2}{32\pi}\left[\frac{1}{\mu^2}+\frac{3}{(2\mu+\lambda)^2}\right]\ , \tag{4}$$

$$\xi_{\perp}^{-2}=\frac{\sigma|\mathbf{G}|^2}{32\pi}\left[\frac{3}{\mu^2}+\frac{1}{(2\mu+\lambda)^2}\right]\ , \tag{4'}$$

and

$$\eta_\sigma=\frac{9\sigma}{2\pi\mu^2}\ . \tag{5}$$

L is the infrared cutoff in the logarithmically divergent integral[9,10] and is taken to be the size of the solid film here. Finally, η_T is the pure-system thermal exponent[3–5]

$$\eta_T=\frac{k_BT\,|\,\mathbf{G}\,|^2(3\mu+\lambda)}{4\pi\mu(2\mu+\lambda)}\ , \tag{6}$$

and $C(T)$ in Eq. (3') is the correlation function of the OO in a pure system (see Ref. 3 for the explicit form). In fact, we notice that in the limit $\sigma\to 0$, Eqs. (3) and (3') yield the pure-system results,[3] whereas at $T=0$ they coincide with the results of Ref. 9.

To simplify the problem, we neglect the anisotropy by introducing

$$R^{-2}=\tfrac{1}{2}(\xi_{\parallel}^{-2}+\xi_{\perp}^{-2})=\frac{\sigma\,|\,\mathbf{G}\,|^2}{16\pi}\,\frac{(2\mu+\lambda)^2+\mu^2}{\mu^2(2\mu+\lambda)^2}\ , \tag{7}$$

and we will also assume that $G=2\pi/a_0$, a_0 being the lattice constant. It is obvious then from Eqs. (3) and (7) that the TO order is confined to a distance of the order of R, i.e., strictly speaking there is only short-range translational order in the system. However, since $R\sim\sigma^{-1/2}$, the regions with crystalline order can be large for weak disorder. Therefore, it is relevant to ask what will be the effect of unbinding of dislocations coupled in pairs inside the crystalline regions.

Evidently, due to the absence of long-range translational order, one cannot expect a true phase transition to be triggered by the unbinding of dislocation pairs. Nevertheless, although the transitions are smeared, they separate rather distinct phases (as is discussed below) and in view of the considerable experimental interest in two-dimensional melting[11] at least a qualitative description of the effects of substrate imperfections on the dislocation-unbinding mechanism is definitely needed.

To introduce dislocations in the present model we notice that a solid film, subject to a quenched randomness, can be described in terms of a set of logarithmically coupled dislocations, each being exposed to the random potential.[5] The latter amounts to the coupling of the substrate-generated random force to the dislocation-induced displacement. For instance, $f_i(r)$ couples to the displacement[12]

$$u_i^{\rm disl}(\mathbf{r})=(a_0b_m/2\pi)\{[\tan^{-1}(y/x)]\delta_{im}+[\mu/(2\mu+\lambda)]\epsilon_{im}\ln(r/a)-[(\mu+\lambda)/(2\mu+\lambda)]\epsilon_{km}r_ir_k/r^2\}\ ,$$

induced by a dislocation at the origin, simply as $f_iu_i^{\rm disl}$, whereupon we conclude that the relevant effective free energy, $F_{\rm eff}=F_D+F_{\rm int}$, consists of the pure part[2-5] F_D and the interaction part $F_{\rm int}$ given respectively by

$$\frac{F_D}{k_BT}=-\frac{K}{8\pi}\sum_{\substack{i,j\\(i\neq j)}}\left[\mathbf{b}^i\cdot\mathbf{b}^j\ln(r_{ij}/a)-\frac{(\mathbf{b}^i\cdot\mathbf{r}_{ij})(\mathbf{b}^j\cdot\mathbf{r}_{ij})}{r_{ij}^2}\right]+\frac{E_c}{k_BT}\sum_j|\,\mathbf{b}^j\,|^2\ , \tag{8}$$

and

$$\frac{F_{\rm int}}{k_BT}=-\frac{a_0}{2\pi k_BT}\int d^2r\sum_j\left[\phi^jb_i^jf_i-\frac{\mu}{2\mu+\lambda}\epsilon_{mi}b_m^jf_i\ln(\,|\,\mathbf{r}-\mathbf{r}_j\,|/a)+\frac{\mu+\lambda}{2\mu+\lambda}\epsilon_{mk}b_m^jn_k^jn_i^jf_i\right]\ . \tag{9}$$

Here $\mathbf{b}^j$ is the dimensionless Burger vector at $\mathbf{r}^j$, $\phi^j=\tan^{-1}[(y-y^j)/(x-x^j)]$, $n_k^j=(r_k-r_k^j)/|\,\mathbf{r}-\mathbf{r}^j\,|$, the dimensionless coupling[2-5] $K=4a_0^2\mu(\mu+\lambda)/[k_BT(2\mu+\lambda)]$, and E_c and a are the phenomenological dislocation core energy and size, the latter being of the order of a_0.

Knowledge of the free energy (8) allows us to calculate the correlation function

$$C^{\rm disl}(r)=\frac{1}{2\pi}\int_0^{2\pi}d\Theta[\langle\mathbf{b}(\mathbf{r})\cdot\mathbf{b}(\mathbf{0})\rangle]_d\ , \tag{10}$$

by performing a perturbation expansion in the dislocation fugacity, $y=\exp(-E_c/k_BT)$. To the leading order in y the thermal and disorder averages in (10) commute[5] and the disorder (random force) can be simply integrated out, as if it was annealed. The effective free energy which results has the following form:

$$\begin{aligned}\frac{F_{\rm eff}}{k_BT}=\sum_{\substack{i,j\\(i\neq j)}}&\left\{\mathbf{b}^i\cdot\mathbf{b}^j\left[-\frac{K}{8\pi}\ln\left[\frac{r_{ij}}{a}\right]+\frac{\sigma a_0^4}{8\pi(k_BT)^2}\left[\frac{r_{ij}}{a_0}\right]^2\ln\left[\frac{L}{r_{ij}}\right]\left[1+\frac{\mu^2+(\mu+\lambda)^2}{(2\mu+\lambda)^2}\right]\right]\right.\\&\left.+\frac{K}{8\pi}\frac{(\mathbf{b}^i\cdot\mathbf{r}_{ij})(\mathbf{b}^j\cdot\mathbf{r}_{ij})}{r_{ij}^2}-\frac{\sigma a_0^4}{8\pi(k_BT)^2}\left[\frac{r_{ij}}{a_0}\right]^2\ln\left[\frac{L}{r_{ij}}\right]\frac{(\mathbf{b}^i\cdot\mathbf{r}_{ij})(\mathbf{b}^j\cdot\mathbf{r}_{ij})}{r_{ij}^2}\frac{2(\mu+\lambda)^2}{(2\mu+\lambda)^2}\right\}\\&+\frac{E_c}{k_BT}\sum_i|\,\mathbf{b}^i\,|^2\ .\end{aligned} \tag{11}$$

As is clearly seen, the pair-breaking terms [the second and the fourth terms on the right-hand side of Eq. (11)], induced via the coupling to substrate-generated random forces, have a very strong r dependence. In fact, they are *proportional to the squared separation between the dislocations in a pair,* as opposed to the weak logarithmic coupling. However, disorder

causing a strong coupling provides also *a cutoff for the maximal separation of dislocations in a pair,* as is given by Eq. (7). Making use of the latter we see that $\sigma(r_{ij}/a_0)^2 \sim (r_{ij}/R)^2$ in the pair-breaking terms. This observation will be crucial in what follows.

Calculation of the thermal and angular averages can be made with the help of Eq. (11) using the methods of Ref. 3. This yields

$$C^{\rm disl}(r) \sim \exp\left[-\frac{K}{4\pi}(C+1) - \frac{K}{4\pi}\ln\left[\frac{r}{a}\right] + \frac{K^2}{16\pi^2}\frac{(2\mu+\lambda)^2}{(\mu+\lambda)^2}\left[\frac{r}{R}\right]^2 \ln\left[\frac{L}{r}\right]\right] I_0\left[\frac{K^2}{16\pi^2}\frac{(2\mu+\lambda)^2}{(2\mu+\lambda)^2+\mu^2}\left[\frac{r}{R}\right]^2 \ln\left[\frac{L}{r}\right]\right], \tag{12}$$

where we used $2E_c/k_BT = (C+1)K/4\pi$, C being a positive phenomenological constant, whose value depends on the lattice structure.[2,3] Below we will use a plausible assumption that C is large, i.e.,

$$C+1 \approx C \gg 1 , \tag{13}$$

which simplifies the further analysis without affecting its generality. We also note that the Bessel function $I_0(x)$ assumes an exponential form only for the large values of its argument, i.e., $I_0(x) \sim x^{1/2}\exp x$ for $x \to \infty$. On the other hand, as will be explicitly seen below, the argument of I_0 should be bound. For this reason we will neglect I_0 in Eq. (12) and concentrate on the exponent on the right-hand side of this equation.

For a meaningful perturbation theory one has to satisfy an obvious condition that $C^{\rm disl}(r)$ is limited from above (by unity). Consider first the case of exponentially weak random forces, that is, in accordance with (7), of an exponentially large correlation length of TO, $C \ll \ln(R/a)$. Then as is evident from (12), the above condition for $C^{\rm disl}(r)$ cannot be satisfied for large K (small temperatures). Since the exponent is maximal at $r \sim R$, we demand that

$$K\ln(R/a)/4\pi > K^2(2\mu+\lambda)^2/[16\pi^2(\mu+\lambda)^2] ,$$

whereof a rough estimate of the temperature above which dislocations are paired inside large crystalline regions ("solid" phase) is obtained using the definition of K as

$$T_{\rm SH}^{(1)} \approx \frac{a_0^2\mu(2\mu+\lambda)}{\pi k_B(\mu+\lambda)\ln(R/a)} . \tag{14}$$

A breakdown of the perturbation expansion in the dislocation fugacity is a sign of proliferation of unbound dislocations.[5] Hence, $T_{\rm SH}^{(1)}$ is interpreted as the temperature of the reentrant transition into a low-temperature hexatic phase [the solid-hexatic (SH) transition]. Below $T_{\rm SH}^{(1)}$ coupled dislocations unbind, which presumably forces $r^{-\eta_T}$ in (3) to be replaced by an exponential $\exp[-r/\xi(T)]$ with the temperature-dependent correlation length $\xi(T)$.[5] Eventually the latter becomes smaller than the exponentially large R, thus taking over as a major factor defining the range of the TO. No further speculations on the nature of the reentrant hexatic phase will be made here. We stress though the limit $T_{\rm SH}^{(1)} \to (-\ln\sigma)^{-1}$ as $\sigma \to 0$, following from (7) and (14). It gives $dT/d\sigma \to \infty$, which means that the transition to the reentrant hexatic phase is much eased in comparison, say, with the case of quenched random impurities.[5] This is not surprising provided the very-long-range character of the pair-breaking interaction.

At higher temperatures we study the convergence of the inverse response function[1] $\epsilon^{-1}(q \to 0)$ given by[5]

$$\epsilon^{-1}(q \to 0) - 1 \sim \int^R dr\, rC^{\rm disl}(r) . \tag{15}$$

Since the condition $T > T_{\rm SH}^{(1)}$ is satisfied, one can neglect the term $\sim K^2$ in the exponent in (12). Our first— and trivial—observation is that in the limit $\sigma \to 0$, (15) yields a pure Kosterlitz-Thouless condition[2-5] for the stability of the solid phase, $K > K_{\rm KT} = 16\pi$. Performing the integration in (15) we obtain that, in the lowest order in σ, the condition of stability of the solid phase becomes $K > K_{\rm KT}/[1 + C/\ln(R/a)]$, whereof we find that a transition to the high-temperature hexatic phase occurs roughly at

$$T_{\rm SH}^{(2)} \approx T_{\rm KT}[1 + C/\ln(R/a)] . \tag{16}$$

Since the random force is assumed to be exponentially weak, the second term in parentheses is only a small correction to unity. Knowing that $R \sim \sigma^{-1/2}$, we conclude that as in the transition to the reentrant hexatic phase, $dT/d\sigma \to +\infty$ as σ tends to zero and T to $T_{\rm KT}$. We note that the slope of the transition line is positive, as opposed to the case of random impurities,[5] which is a distinct effect of the cutoff.

When the substrate-generated random force is not exponentially weak, i.e., $C \gg \ln(R/a)$, one can neglect the logarithmic term in the exponential of Eq. (12). Therefore, at lower temperatures we find the following estimate for the stability of the solid phase:

$$KC/4\pi > K^2(2\mu+\lambda)^2\ln(L/R)/16\pi^2(\mu+\lambda)^2 .$$

Note that $\ln(L/R)$ can be rather large here, unlike the case of an exponentially large R.

It is exclusively an artifact of the cutoff that the term $\sim\ln(r/a)$ has been neglected. An interesting consequence of the latter is the fact that the perturbation expansion is actually "better off" at higher temperatures. Hence, we conclude that the majority of dislocations within the crystalline regions stay in pairs until each of them disintegrates into freely moving disclinations. This indicates a possibility of a direct transition from a solid to a liquid phase, as well as of a "tricritical point."

The latter is also supported by the analysis of the hexatic phase above $T_{\rm SH}^{(2)}$. Presumably, as below $T_{\rm SH}^{(1)}$, a temperature-dependent correlation length[5] suppresses the exponentially large R, thus destroying the TO even on shorter scales. However, the OO can persist even in the absence of the TO. In this case one would expect a

nonzero stiffness K_A to enter an effective free energy for the OO.[3] Indeed, it was proposed by Chudnovsky[9] that the free energy of a hexatic takes the following form:

$$F_A = \tfrac{1}{2} K_A \int d^2r (\nabla\Theta)^2 + \frac{1}{2\mu} K_A \int d^2r \epsilon_{ij} f_j \partial_i \Theta \ . \quad (17)$$

Apparently, Eq. (17) almost exactly coincides with the Hamiltonian used by Rubinstein *et al.*[5] in their study of XY magnets with random Dzyaloshinskii-Moria interactions. Taking over the analysis of Ref. 5 we find the correlation function of the OO,

$$C^{OO}(r) \sim \left[\frac{1}{r}\right]^{\eta_T + \eta_\sigma} , \quad (18)$$

where η_σ is given by Eq. (5) and[3]

$$\eta_T = \frac{18 k_B T}{\pi K_A} \ . \quad (19)$$

Making use of (17) we also compute the stiffness K_A in the approximation of freely moving dislocations (Debye-Hückel approximation).[5] The result is

$$K_A = \frac{2E_c}{1 + 2\sigma a_0^2 / k_B T (2\mu + \lambda)} \ . \quad (20)$$

Evidently K_A decreases with the increase of σ, indicating that a hexatic can melt into a liquid when the strength of the random force is enhanced.

Our findings are summed up in a schematic phase diagram as is sketched in Fig. 1. At low temperatures the hexatic is predicted to become unstable[6] and transforms into a liquid via a disclination-unbinding transition. The effect of substrate-generated random forces on the process of disintegration of dislocations into freely moving disclinations was not a subject of this paper and will be considered elsewhere. It is also worth mentioning that our considerations become meaningless when the disorder is strong enough to reduce the correlation length to the value comparable with the lattice spacing. Finally, we emphasize that since the translational order decays exponentially even at zero temperature, solid-hexatic transitions must be smeared both at high and low temperatures. Smearing is expected to be larger for a stronger substrate-generated-random force.

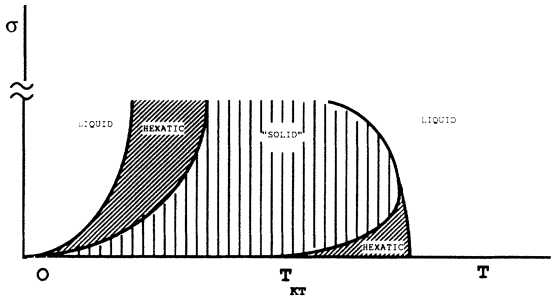

FIG. 1. "Solid," liquid, and hexatic phases as a function of temperature and the strength of the substrate-generated disorder σ. Solid refers here to a phase with large crystalline regions, inside which dislocations are bound in pairs (see text). The low-temperature instability of the hexatic phase (Ref. 6) was not studied in this work.

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