Grain-Boundary Theory of Melting in Two Dimensions

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A quantitative theory of melting in two dimensions via the spontaneous generation of grain boundaries is presented. It is found that as the temperature is increased, grain boundaries are generated before the dislocations unbind. Also discussed are (a) the nature of the transition, (b) the coupling of the grain boundaries to a density change, (c) the existence of a hexatic phase, and (d) comparisions with recent computer simulations.

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Melting in two dimensions has been a subject of interest recently. Many computer simulations[1] have been done, but the results do not fit well with the calculations using the dislocation unbinding mechanism (DUM) by Kosterlitz and Thouless[2] and by Halperin and Nelson.[3] All computer simulations show a dramatic increase in the total number of dislocations as the system goes into the liquid phase, whereas the DUM predicts no change in the total number of dislocations. Also, the DUM predicts a gradual increase in the separation of some of the dislocation pairs, but this is not seen. Some computer simulations indicate a first-order phase transition, whereas the DUM produces a continuous phase transition. An alternative mechanism of melting via the spontaneous generation of grain boundaries was discussed thirty years ago,[4] but no detailed calculation was carried out. Recently Fisher, Halperin, and Morf[5] pointed out that the free energy required to generate a single small-angle grain boundary goes to zero at the temperature T_0 where the dislocations unbind. I have studied the statistical mechanics of a collection of grain boundaries on a hexagonal lattice and find the following features: (a) Grain boundaries are generated before T_0 is reached as the temperature is increased. (b) When the grain boundary is coupled to a finite density change a first-order transition always results. Without such coupling, a first-order transition results if the core energy is small enough. (c) A hexatic phase may exist if the temperature is less than the Kosterlitz-Thouless temperature. Since a grain boundary consists of an array of dislocations,[6] spontaneous generation of grain boundaries implies a dramatic increase in the total number of dislocations, a result more consistent with computer simulations.

Since a grain boundary consists of an array of dislocations, what then is the difference between the present mechanism and the DUM? Dislocations with Burgers vectors $\vec{b}$, $\vec{b}'$ interact with each other with a potential that consists of a logarithmic term as well as a dipolar term, viz.

$$V=-\frac{K}{4\pi}\left(\ln|\vec{r}-\vec{r}'|\,\vec{b}\cdot\vec{b}'-\frac{\vec{b}\cdot(\vec{r}-\vec{r}')\vec{b}'\cdot(\vec{r}-\vec{r}')}{|\vec{r}-\vec{r}'|^2}\right). \tag{1}$$

K here is a function of the elastic constants. For a finite number of dislocations, the first term always dominates the second term at a large enough distance. Hence in the DUM, the second term plays a much less significant role compared with the first term; the question of interest is whether the dislocations unbind.

For the grain boundary, a correlation among the Burgers vectors of an *infinite* array of dislocations is built in. The effective potential between grain boundaries a distance z apart becomes short ranged and one ends up with a potential of the form[6]

$$U(z,K)=\frac{L}{s}\frac{K}{4\pi}\left\{\ln\left(\sinh\pi\frac{z}{s}\right)-\frac{\pi z}{s}\coth\pi\frac{z}{s}+\ln\frac{s}{\pi}\right\}. \tag{2}$$

Here s is the separation between dislocations on a grain boundary in the unit of the lattice constant. The question of interest here is whether grain boundaries are generated. Note that $z\geq 1$. When $z=0$, the grain boundaries annihilate each other. This can be represented by a hard-core potential at $z=1$.

Because the cancellation between the logarithmic and the dipolar term is complete only for infinitely long grain boundaries, finite grain-boundary loops are neglected in the present calculation. I shall focus my attention only on hexagonal lattices here. The grain boundaries can

then have only three orientations. I have considered three different configurations of grain boundaries illustrated in Fig. 1 and have found that Fig. 1(b) is most favorable. Let me explain briefly why this is so.

The energy of configuration 1(c) was computed using a Fourier series in a manner very similar to that used in electrostatics calculations. For the pair $ABCD\ldots$, $A_1B_1C_1D_1\ldots$, because of a modulation of period l, there is now an incomplete cancellation of the logarithmic and the dipolar term at a length scale of the order of l. Because of this,[7] it was found that this configuration contributes a term of the order of $1/n$ to the free energy. In the small-n expansion, this is very unfavorable and hence is discarded. Configuration 1(b) is found to be more favorable than configuration 1(a) because of a negative grain-boundary crossing energy which I shall explain in a moment.

I have calculated the free energy F of Fig. 1(b) in terms of the density n (of one orientation but including the two directions of the Burgers vector) as

$$F = -A(T - T')n + Bn^2 + Cn^3 + O(n^4). \quad (3)$$

These coefficients are given later. The term linear in n comes from consideration of noninteracting grain boundaries. The n^2 term comes from a grain-boundary crossing energy. The n^3 term comes from a strain-energy correction to the n^2 term.

To treat the thermal fluctuation of small deviations of the grain boundaries from their equilibrium positions, one needs the energy of distortion Y.

From Eq. (1), one gets

$$Y = \sum_i (|q|\gamma + \Delta)|\delta\vec{r}_{iq}|^2. \quad (4)$$

Here $\gamma = b^2K/8s$. $\delta\vec{r}_{iq}$ is the Fourier transform of the displacement of the ith boundary from its equilibrium position. Δ is significant only if the grain boundaries are close together. For two grain boundaries at a distance z from each other, $\Delta = (b^2K\pi/4s^2)\mathrm{csch}^2\pi z/s$ for longitudinal modes. For transverse modes, one has to use the short-range potential (2). When the grain boundaries are far apart so that Δ is negligible one gets the free energy G_1 of noninteracting grain boundaries, viz.

$$G_1 \cong -3T(n/s)[\ln s + (1 + \ln T/2\pi T_0], \quad T_0 = K/16\pi. \quad (5)$$

When the grain boundaries are close together,

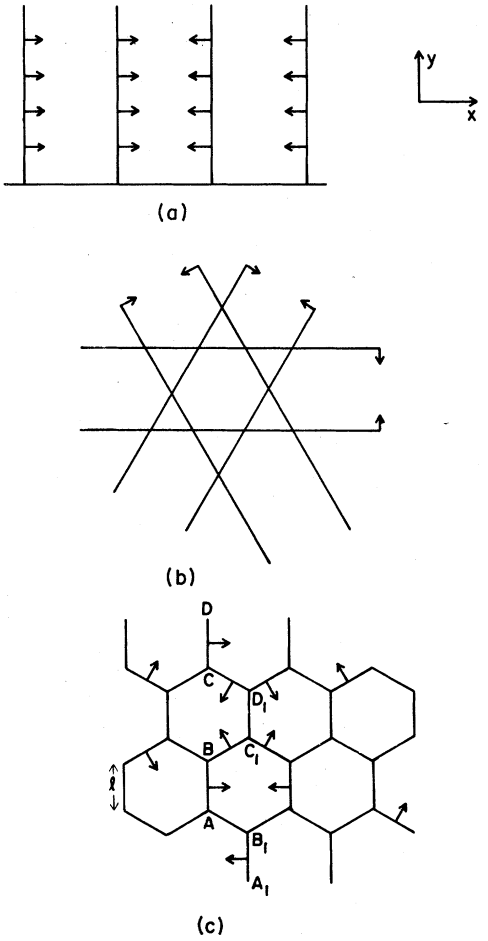

FIG. 1. Three possible configurations of grain boundaries that have been investigated in this paper.

this free energy is lost.

Because of the thermal fluctuation, two grain boundaries can come close together at certain places. Whenever this happens because of the hard-core repulsion between parallel grain boundaries, some entropy is lost. If the elastic energy Y were proportional to q^2 then this "entanglement" energy is of the order of n^3.[8] Now the grain boundary is stiffer so that the chances of entanglement and hence the loss in entropy is reduced. Estimates indicate that it is of the order of $n\exp(-\mathrm{const}/Tn^2)$. For small n this term is much smaller than the terms in Eq. (3). Hence it is neglected.

The grain-boundary crossing energy comes about in the following manner. Dislocations inside a grain boundary can move. When two grain boundaries cross their dislocations stay closer together (further apart) if they attract (repel) each other. Even though a single grain boundary

crosses equal numbers of dislocations of opposite Burgers vectors, because of the special correlation mentioned there is a net energy gained. Carrying out the calculation, we get a contribution G_2 to the free energy of the form

$$G_2 \cong -\tfrac{1}{2}T(n/s)\ln\pi/\beta\gamma - n^2T_0\epsilon(s)(1-2sn/\pi),$$
$$\epsilon(s) = \ln(0.5s+0.27)+\ln(0.27)-1/2\pi. \quad (6)$$

Note that for large s, $\epsilon(s) \to \ln s$.

Dislocations inside a grain boundary are coupled to each other elastically. Such couplings provide for the factor $-1/2\pi$ in $\epsilon(s)$.

Collecting all the terms, we arrive at the following expression for the parameters in Eq. (3):

$$A = 6\ln s/s, \quad T' = T_0 + (E_c + 0.83T_0)/2\ln s,$$
$$B = -T\epsilon(s), \quad (7)$$
$$C = 2\epsilon(s)/\pi.$$

In the limit of large s, the free energy is of the form

$$F = nf(ns)\ln s/s. \quad (8)$$

The negative n^2 term in (3) only predicts that ns assumes a finite value at the phase transition but it does not predict that n alone goes through a discontinuous change. This "degeneracy" is broken only when coupling of grain boundaries to other degrees of freedom such as a finite density change or to bound dislocation pairs is considered. The details of this shall be relegated to a longer publication.

Let us next turn our attention to the so-called hexatic phase. In order for the hexatic phase to exist, it is necessary to have power-law correlation or some other long-range correlation for the bond orientational order parameter $e^{6i\theta}$. The orientation of a crystal changes as one goes from one side of a grain boundary to another. The direction of rotation is related to the "sign" of the Burgers vector of the grain boundary. It is obvious that the mean square fluctuation of θ is proportional to the mean square fluctuation of the net sum of the Burgers vectors of the grain boundaries. If the grain boundaries with opposite Burgers vectors form bound states, then there is long-range correlation in θ. This is because if one crosses a grain boundary and the orientation of the crystal is rotated, one always encounters a grain boundary with opposite Burgers vectors and the orientation is restored. If bound states are not formed then $\langle[\theta(0)-\theta(R)]^2\rangle \propto R$ and $\langle e^{6i[\theta(R)-\theta(0)]}\rangle \propto e^{-R\alpha}$ where α is some constant of proportionality. When parts of two grain boundaries are close they lose some entropy ΔF. The losses for the transverse and the longitudinal modes are calculated separately. For the longitudinal modes Δ in Eq. (4) is now finite. The resultant effective potential is the difference between Eq. (2) and the loss in entropy due to the gap. For small z, it is $U_{\rm eff} = (4T_0 - 2T)\ln ns/s + 0.466\,T_0$. For $z > s/\pi$, $U_{\rm eff}$ approaches zero exponentially fast. Using $U_{\rm eff}$, one can calculate the net gain in free energy for any part of the grain boundaries that are closer than s/π. This turned out to be $-(4T_0 - 4T)\ln s + 3.6T_0$. Hence for $\ln s \leq 0.9/(T_0 - T)$ no bound state can form.

In this Letter I have demonstrated that the grain-boundary mechanism (GBM) is more favorable than the DUM. The GBM also fits in better with computer-simulation results in that a dramatic increase in the total number of dislocations is predicted. I have not considered the possibility of grain-boundary loops here. I have not considered the interaction of grain boundaries with other point defects such as interstitials or vacancies. Nor can I rule out other possible mechanisms. There are certain predictions of the present theory which one should be able to compare with computer simulations. These include the dependence of the melting temperature on the core energy E_c, as well as the coupling to the elastic strain.

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