Roughening of Low-Angle Grain Boundaries

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The possibility of roughening in low-angle grain boundaries is investigated. By exhibiting an analogy between grain-boundary steps which do not have long-range strain and steps on solid surfaces, I argue that a grain-boundary roughening transition, of the same type as for solid surfaces, is possible. It is found that, as the grain-grain misorientation θ goes to zero, the energy of such a grain-boundary step diverges as $\ln(1/\theta)$. From this divergence I argue that, for sufficiently small θ, the solid will melt before the grain boundary has a chance to roughen as the temperature increases.

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The roughening transition (RT) is the most widely studied and commonly observed interfacial phase transition.[1] The RT temperature T_R separates two qualitatively distinct, equilibrium phases of the interface: the low-temperature "smooth" phase and the high-temperature "rough" phase. These phases are associated with distinct growth properties[2] and crystal morphologies.[3] For small driving force a nucleation barrier limits growth in the smooth phase (exponential growth) but not in the rough phase (linear growth). A facet in the equilibrium shape of a macroscopic crystal is present in the smooth phase but absent in the rough phase.

Traditionally, the RT is associated with the solid-vapor interface (thus, the terminology "*surface* roughening"). In fact, for the simplest models which have a RT, solid-on-solid models,[4,5] the vapor becomes a vacuum, the solid has no vacancies, and the only degrees of freedom are associated with positions of (nonoverhanging) steps which are allowed on the surface. Roughening of solid-liquid interfaces is also known to be possible,[6] although theoretical models seldom distinguish between liquid and vapor. Since the lattice-gas (Ising) model, which is known to have a RT,[7] corresponds directly to a binary alloy,[8] antiphase boundaries also roughen. For such solid-solid boundaries strain effects are not important, so that lattice models correctly describe the RT.

Here we wish to understand the RT for interfaces in which strain effects are important. The simplest such interface, the low-angle grain boundary (LAGB), is the focus of our attention. The LAGB is a natural candidate, since, as the angle of misorientation θ between the two grains goes to zero, the elastic strain energy of the LAGB is the dominant contribution to the interfacial energy.[9] In this paper I first argue that a LAGB RT is possible and then we investigate the dependence of T_R on θ. We find that T_R diverges as $\ln(1/\theta)$ as $\theta \to 0$. For a real material this divergence implies that, for $\theta < \theta_c$, the (bulk) grains will melt before roughening occurs. Although the methods I use are applicable only for θ less than some $\theta_{\max}$, I believe that for many materials $\theta_{\max}$ is larger than θ_c. We estimate below that, for copper, θ_c is roughly 2° while $\theta_{\max}$ is 5°, so that a RT is predicted to occur for $2° \lesssim \theta \lesssim 5°$ in copper.

Several parameters are necessary to characterize an arbitrary LAGB. For our purposes we choose a simple situation in which the fluctuations responsible for the RT are easy to picture. We thus restrict our attention to symmetric tilt boundaries in simple-cubic materials. In Fig. 1(a) I illustrate, on an atomic scale, a moderate-angle ($T=0$) symmetric tilt boundary with misorientation $\theta \simeq 19°$. As θ decreases, the matching of the two grains at the grain boundary becomes in-

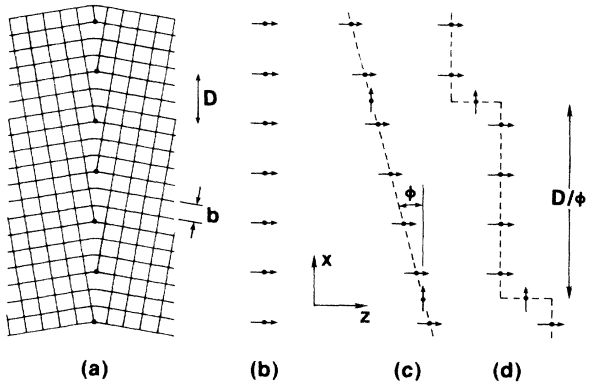

FIG. 1. (a),(b) Cuts through symmetric LAGB (boundary normal $\hat{\mathbf{z}}$). The dots of (a) indicate edges of planes descending from the top of (a). In the continuum limit, good for small θ, these defects of (a) become the edge dislocations of (b), oriented parallel to $\hat{\mathbf{y}}$, intersecting the x-z plane at the dots, with Burgers vectors as directed by the arrows. (c),(d) Cuts through nearly symmetric ($\phi \ll 1$) LAGB (boundary normal $\hat{\mathbf{z}}+\phi\hat{\mathbf{x}}$). Positions of the dislocations, strictly planar in (c), are partially relaxed (squared) to the stepped structure (d). Broken lines serve as guides to the eye.

creasingly good except near a series of parallel, equally spaced (spacing D), coplanar, linear defects which are readily identified[9] (by a Burgers circuit) as edge dislocations (Burgers vector $\mathbf{b}=b\hat{\mathbf{z}}$, $b=$ lattice constant). The small-θ ($\theta=b/D$, $D=$dislocation spacing) dislocation description is pictured in Fig. 1(b). In general, except for regions of order b from each dislocation (the "core"), the solid may be considered as an elastic medium, with local deformations determined from dislocation configurations by the use of dislocation theory.[10]

The RT is a defect-mediated transition.[1] The important defects, in the solid-vapor–interface context, are loops of steps (ledges) which encircle an interfacial island or depression. A step which is straight at $T=0$ will, for $T>0$, incorporate jogs (kinks) which increase the configurational step entropy per unit length. As $T\rightarrow T_R$ the step free energy per unit length $f_s(T)$ vanishes, so that large loops are created with little cost in interfacial free energy. Since step wandering is the only source of step entropy in *lattice* models, we expect that T_R should roughly scale as $f_s(0)$. From both solid-on-solid[5] and Ising[7] models we find $k_B T_R \simeq 1.3hf_s(0)$, where h is the step height. For systems not confined to a lattice other sources contribute to the step free energy, such as effects due the altered vibrations of atoms near the step (relative to atoms away from the step), with amplitudes less than a lattice spacing, and relaxation of atoms near the step off the sites extrapolated from average atomic positions deep in the bulk solid. We introduce the (bare) step free energy per unit length, $f_s^{(0)}(T)$, which includes such sources but excludes jogs along the step. This quantity is similar to the bare surface tension introduced in capillary-wave theory.[11] $f_s^{(0)}(T)$ may be calculated as the extra free energy of a step per unit length in the slab geometry, where the slab thickness, equal to the step length, is given by the closest approach to two jogs in the same step in an infinite system. In such more realistic systems we approximate[12] $k_B T_R$ by $1.3hf_s^{(0)}(T_R)$.

This Letter argues that a direct analogy between solid surfaces and LABG is possible so that, like surfaces, LAGB may roughen.[13-15] This RT, like that of a solid-fluid interface, would be in the Kosterlitz-Thouless universality class.[1,4] In developing this analogy we first identify the LAGB analog of the crystal-vapor step. In the crystal-vapor interface a slight change in boundary orientation introduces widely spaced steps. Suppose the LAGB normal of Fig. 1(b) is tilted by a small angle ϕ ($0<\phi$, $A\ll 1$) toward the x axis. (A tilt toward the y axis will be considered later.) Geometrical considerations require the introduction of "new" edge dislocations, parallel to the old ones, of spacing D/ϕ and $\mathbf{b}=b\hat{\mathbf{x}}$, in accord with Frank's formula.[9]

Originally, in such a tilted interface it has been assumed[9] that all (new and old) dislocations are confined to a strictly two-dimensional plane [Fig. 1(c)]. In that case a long-range strain field (energy density $\sim r^{-2}$) extends around each new dislocation. Since the new dislocation spacing D/ϕ provides the cutoff to this strain field, a simple integration shows that the extra elastic energy (over that of the symmetric LAGB) scales as[9,16] $\theta\phi\ln(1/\phi)$. Since the number of new dislocations scales as $\theta\phi$, the energy per unit length per dislocation $f_{sx}(T=0)$ diverges like $\ln(1/\phi)$, as $\phi\rightarrow 0$.

Both theory[17] and experiment[18] indicate that in asymmetric LAGB the dislocation positions are relaxed from a strictly two-dimensional plane. In the case of the slightly asymmetric LAGB, the energy is lowered by the local relaxation of the old dislocations around each new dislocation into a steplike structure, with step height equal to the old dislocation spacing D [Fig. 1(d)]. This structural relaxation of the old dislocations induces a long-range strain which exactly cancels that of the new dislocation for distances larger than a cutoff distance of order D.[19] The extra elastic energy now scales as $\theta\phi$, so that the *step energy per unit length* $f_{sx}(0)$ *is finite.* Such a single step, which incorporates a new dislocation without a long-range strain, is the desired analog of the crystal-vapor step.

Now suppose that the LAGB normal of Fig. 1(b) is tilted toward the y axis. The new, widely spaced, parallel dislocations are now *screw* dislocations, *perpendicular* to the old dislocations. An analysis similar to before identifies the LAGB step [Fig. 2(a)]. Again, the step height must be equal to D to relieve long-range strain. In this step structure each of the old (edge) dislocations must now jog [cf. Fig. 2(a)].

For either type of LAGB step, since the step height $D=b/\theta$ becomes increasingly large as $\theta\rightarrow 0$, it seems

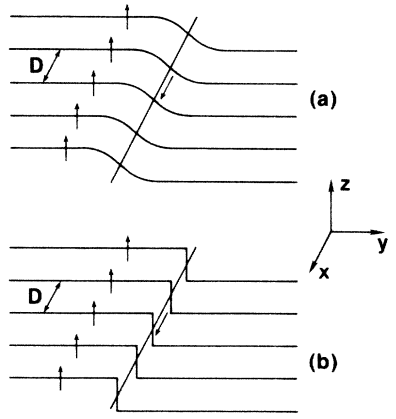

FIG. 2. Perspective of (a) relaxed and (b) partially relaxed (squared) "perpendicular" step. The new dislocation (Burgers vector $\mathbf{b}=b\hat{\mathbf{x}}$) intersects each of the old dislocations ($\mathbf{b}=b\hat{\mathbf{z}}$).

plausible that the step energy $f_s(0)$ diverges as $\theta \to 0$. The extra core energy per unit step length is independent of θ as $\theta \to 0$ and, therefore, not responsible for this divergence. On the other hand, the elastic energy of the new dislocation extends a distance D about each new dislocation and, therefore, accounts for this divergence. A simple integration of the elastic energy density suggests

$$f_s(0) = A_0 \ln(1/\theta) + B_0 + \ldots, \quad (1)$$

where the dots denote terms higher order in θ, and where core effects contribute solely to B_0 while elastic effects contribute to both A_0 and B_0.

I have succeeded in verifying Eq. (1) for the sharply squared steps in which the new dislocation is parallel [cf. Fig. 1(d)] or perpendicular [Fig. 2(b)] to the old dislocations. No terms diverging with the system size were found, so that the exact cancellation mentioned previously was confirmed. The core term, which I did not calculate, corresponds to the energy density integrated over the cylindrical volume surrounding each core. I have calculated the elastic term, from the volume outside the core, within isotropic linear elasticity theory using standard techniques.[10] The details of this calculation will be presented elsewhere.[20] For the step parallel to the old dislocations I find $A_0 = K/D$ and $B_0 \simeq (K/D)[\ln(\alpha) - 2.1]$, where the energy unit is $K = \mu b^3/[4\pi(1-\nu)]$ (μ is the shear modulus and ν is Poisson's ratio) and the (not calculated) dimensionless constant α, as used in Hirth and Lothe,[10] characterizes the core energy. For the perpendicular step, $A_0 = 2(K/D)(1-\nu)$ and

$$B_0 \simeq (K/D)\{(1-\nu)[2\ln(\alpha) - 5.2] - 1.3\}.$$

The fully relaxed structures [e.g., Fig. 2(a)] will have lower energies. For the parallel step A_0 is unaffected by relaxation, while for the perpendicular step relaxation may not reduce A_0 to less than $(K/D)(1-\nu)$. B_0 will be affected in each case.

Equation (1), with $A_0 > 0$, suggests that $T_R(\theta)$ will also diverge as $\ln(1/\theta)$ which, in practice, indicates that for sufficiently small θ, the crystal will melt before its interface roughens. However, as mentioned previously, the important parameter is not $f_s(0)$ but rather $f_s^{(0)}(T)$, the free energy of a step constrained not to have jogs. We expect

$$f_s^{(0)}(T) = A(T)\ln(1/\theta) + B(T) + \ldots, \quad (2)$$

where, as before, the dots denote terms higher order in θ. Also, $f_s^{(0)}(0) = f_s(0)$. Fluctuations on length scales less than D account for the difference $f_s^{(0)}(T) - f_s(0)$.

Might $A(T)$ of Eq. (2) vanish at some temperature T? The sources of entropy of the bulk solid, which may be included in the temperature dependence of the elastic coefficients (μ and ν) and core-energy parameter α, will not cause $A(T)$ to vanish, since $\mu(T) > 0$ and $\nu(T) < 1$. The most likely candidate that I envision is that associated with the many configurations of the new dislocation, wiggling with amplitude less than D and interacting with the old dislocations. Using the methods of Ref. 14, I have found that the energy ΔE of a sinusoidal fluctuation of amplitude a and wave vector k goes as $a^2k^2\ln(1/kD)$ for $k < 1/D$ and costs significantly more energy for $k > 1/D$. I find that such fluctuations contribute a term $-k_BT(\text{const})\theta\ln(1/\theta)$ to the free energy, so that they contribute to the higher-order terms of Eq. (2), not to $A(T)$. Therefore, I propose that $A(T)$ is positive for all T so that, for sufficiently small θ, a LAGB RT will not be found because of bulk melting.

The value of θ above in which roughening does not occur may be estimated as follows. We choose LAGB in copper, since the core energies may be deduced from experiments near its melting temperature ($T_m = 1356$ K). At 1338 K these experiments[21] indicate $\alpha \simeq 1.1$ (1.4) for an edge (screw) dislocation. The bulk elastic constants near T_m may be estimated to be[22] $\mu \simeq 1.4 \times 10^{10}$ N/m^2 and $\nu \simeq 0.4$, while $b(T_m) \simeq 2.6 \times 10^{-10}$ m. We find $Df_{sx}^{(0)} \simeq K \times [\ln(1/\theta) - 2.0]$ and $Df_{sy}^{(0)} \simeq K[1.2\ln(1/\theta) - 4.0]$, where $K \simeq 1.7k_BT_m$. Setting $Df_s^{(0)} \simeq 1.3k_BT_m$ yields $\theta_{crit} \simeq 2°$. This must be considered an order-of-magnitude estimate because of the uncertainty of the magnitude of entropic contributions to $B(T)$, our failure to allow full relaxation from the stepped configuration, and our choice of a simple-cubic lattice in the calculation (copper is fcc). Since the dislocation theory of LAGB appears[21] to be valid in Cu for $\theta \lesssim 5°$, a Cu LAGB should be rough near T_m for $2° \lesssim \theta \lesssim 5°$.

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