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Grain-boundary melting transition in a two-dimensional lattice-gas model

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A two-dimensional lattice-gas model that is capable of producing gas, liquid, and two orientations of a solid phase is adopted to study properties of a boundary between two crystalline grains by use of a nine-site cluster approximation of the cluster-variation method. At a temperature far below the melting temperature T_m, a gradual but well-defined transition is discovered between the low- and high-temperature structures of the boundary; this transition signals the onset of a liquidlike phase inside the boundary. The thickness of the boundary increases with T; the excess entropy due to the boundary diverges as $-\ln(T_m - T)$ near T_m; and the grain boundary is completely wet with liquid at T_m.

Recent calculations of some two-dimensional lattice-gas models have led to low- and high-density disordered phases (called vapor and liquid) and ordered phases (called crystalline).[1,2] Moreover, in some of the models the same crystalline phase can occur in different orientations. Such models can be used in studying linear interfaces between all pairs of phases as well as the grain boundary between two crystals of the same solid phase differing in orientation. The particular model we use is shown in Fig. 1. Using a nine-site cluster approximation of the cluster-variation method, we have found two singularities in the behavior of the grain boundary:

(i) Well below the melting point of the crystal there is a gradual, but clearly defined, transition in the structure and thermodynamic properties of the boundary.

(ii) At the melting point T_m of the crystal, the excess entropy per unit length of the boundary diverges as $-\ln(T_m - T)$, while the excess free energy remains finite and equals twice the solid-liquid interfacial free energy.

These two transitions are related. At the lower transition, the boundary changes from its low-temperature structure into a high-temperature structure, which continues to evolve and becomes at T_m a liquid layer bounded by two solid-liquid interfaces, with the thickness of the liquidlike layer diverging as $-\ln(T_m - T)$. Therefore, since the change of state starting from the low-temperature transition gradually leads to the melting of the boundary, we call the transition in (i) a melting transition even though the structure at that temperature is still far from T_m for the bulk phase.

Our model is a two-dimensional square lattice-gas model with interaction potentials chosen to match a prior computer simulation.[1] We used the cluster-variation method (CVM)[3] and natural iteration (NI)[4] to calculate the equation of state and the phase diagram. Figure 2 indicates that the phase diagram so calculated matches that obtained by the computer study. The properties of interphase interfaces were calculated along the appropriate two-phase coex-

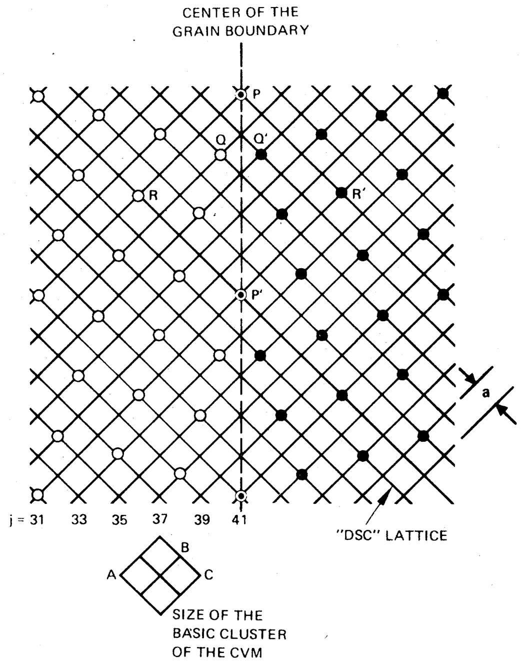

FIG. 1. A two-dimensional model of a grain boundary. Positions of atoms in the crystalline state are shown by circles. This illustration is for the unrelaxed state, and thus is schematic.

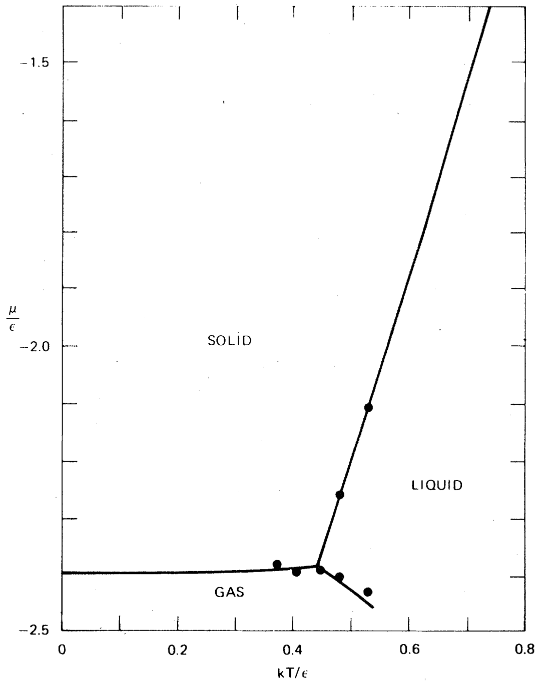

FIG. 2. The equation of state (μ vs T) of the homogeneous phase diagrams derived from the present model. Black circles are the values obtained by the computer-simulation method in Ref. 1.

istence of Fig. 2 and for the grain boundary between two solid-state grains of different orientations, as in Fig. 1. The CVM and NI were used as they had been in our previous studies of antiphase domain boundaries in ordered structures.[5–7]

If we consider crystallization in this model to be an ordering of holes (V) and atoms (A) into a V_4A structure, then the grain boundary is indeed a boundary between two ordered domains. The model is then also a model of antiphase domains in an adsorbate layer that can crystallize into a ($\sqrt{5}\times\sqrt{5}$) crystalline structure with a rotation of $\pm\tan^{-1}\frac{1}{2}$ with respect to the underlying substrate.[8,9]

The particular grain boundary in Fig. 1 is a symmetric tilt boundary. With this much tilt, a $\Sigma=5$ coincidence lattice exists in which one atom in five (e.g., P and P') occupies a site that could belong to either crystal structure. The underlying lattice is known as the DSC lattice.[10] If we let a be the lattice constant of the DSC lattice, the lattice constant of the crystal (as marked by white or black circles in Fig. 1) is $a\sqrt{5}$.

For the CVM, we use the basic nine-site cluster shown at the bottom of Fig. 1. We used the same potentials as the earlier study.[2] Pairs of atoms are not allowed closer than AB, and the energies of pairs at distances AB and AC are assumed attractive, being, respectively, -1.2ϵ and $-\epsilon$.[1,2] There is no interaction between atoms separated by more than the distance AC. We calculate the equilibrium state of the entire system including the boundary and obtain the probabilities of encountering each of 20 possible arrangements of atoms on the nine-site clusters centered on each site in a strip of width PP' along the grain boundary and extending from $j=1$ to 81 (sometimes 61 or 41) into each grain. The boundary conditions are so chosen that on the two end lines, $j=1$ and 81, the probability distributions of nine-site cluster configurations are those of the homogeneous phases. Both the nature of the approximation and this boundary condition prevent the boundary from experiencing the wandering that has been predicted by us[5] and proved by Gallavotti.[11] We will define the unit length along the boundary to be the distance $PP'=5\sqrt{2}a$, and will calculate thermodynamic quantities for a strip of the unit width across the boundary.

From the cluster probabilities, we computed for this strip excesses of the energy $[E]$, entropy $[S]$, number of atoms $[N_a]$, and grand potential σ (excesses compared to an equilibrated single crystal with the same number of lattice points at the same temperature T and chemical potential μ):

$$\sigma=[E]-T[S]-\mu[N_a] \ . \tag{1}$$

Thermodynamic self-consistency requires that[5,7,12]

$$d\sigma=-[S]dT-[N_a]d\mu \ , \tag{2}$$

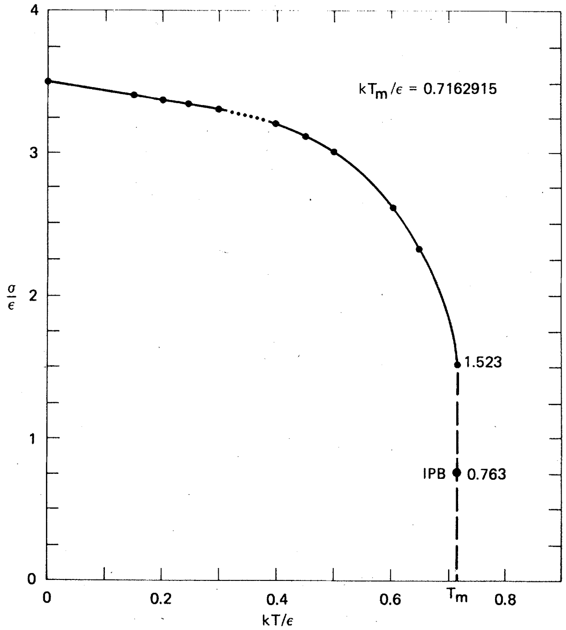

FIG. 3. The σ vs T of the present work for $\mu/\epsilon=-1.5$. The points are computed results; the one marked IPB is the σ for the solid-liquid interphase boundary at the melting temperature. Two solid curves are Eqs. (3) and (6), respectively.

which is a useful test for equilibrium and forms the basis for our extrapolation as we use it below.

Figure 3 shows σ calculated as a function of temperature for $\mu/\epsilon=-1.5$. The low-temperature behavior is readily understood by examining Fig. 1. The pair QQ' is forbidden, and either site must be empty. For the unit length of the boundary, this leads to $[S]=k\ln 2$, $[N_a]=-1$, and $[E]=5\epsilon_{AB}-\epsilon_{AC}$ at $T=0$. Hence, for low T,

$$\sigma=5\epsilon+\mu-kT\ln 2 \ , \qquad (3)$$

which agrees with the curve for $kT/\epsilon<0.3$.

The left half of the density profiles perpendicular to the boundary is shown in Fig. 4 for various temperatures. The low-temperature W shape (V shape for the half shown) near the center of the boundary is consistent with the expectation that the layer on either side of center is half occupied. As the melting point is approached, a low-density layer with liquid-like properties is formed near the center of the boundary, and the thickness of the layer approaches our computer capacity. The excess quantities $[S]$ and $-[N_a]$ tend to increase without limit as does $-\partial\sigma/\partial T$ as the melting point is approached.

Figure 5 plots $[S]$ versus $-\ln(T_m-T)$. For $\mu/\epsilon=-1.5$, T_m is $0.71629\epsilon/k$. The curve in Fig. 5 is made of two distinct portions. For low temperatures ($kT/\epsilon<0.20$), we see

$$[S]\simeq k\ln 2 \ ; \qquad (4)$$

for high temperatures ($kT/\epsilon>0.45$), $[S]$ is linear in $\ln(T_m-T)$ as

$$[S]/k=-3.681-4.1520\ln[k(T_m-T)/\epsilon] \ . \qquad (5)$$

Making use of these relations for $[S]$ in Fig. 5, we can integrate $\int[S]dT$ to obtain the estimate of $\sigma(T)$ for the high-temperature region:

$$\sigma_{\mathrm{HT}}=1.523\epsilon-k(T_m-T) \times\{-0.471+4.152\ln[k(T_m-T)/\epsilon]\} \ . \qquad (6)$$

This is shown as a solid curve for $kT/\epsilon>0.4$ in Fig. 3.

The good agreement between the solid curve σ_{HT} and individually computed σ values indicated by dots shown in Fig. 3 serves as a test of Eq. (2), the self-consistency of the formulation, but it also permits extrapolating σ to the melting temperature, where its value is 1.523ϵ.

We separately calculated the solid-melt interfacial properties for the orientation corresponding to that of our grain boundary. The value of its reduced σ was found to be 0.763ϵ, while its density profile closely matched that of either half of the grain boundary. We concluded not only that the grain boundary has become a melted layer at the melting point, but that

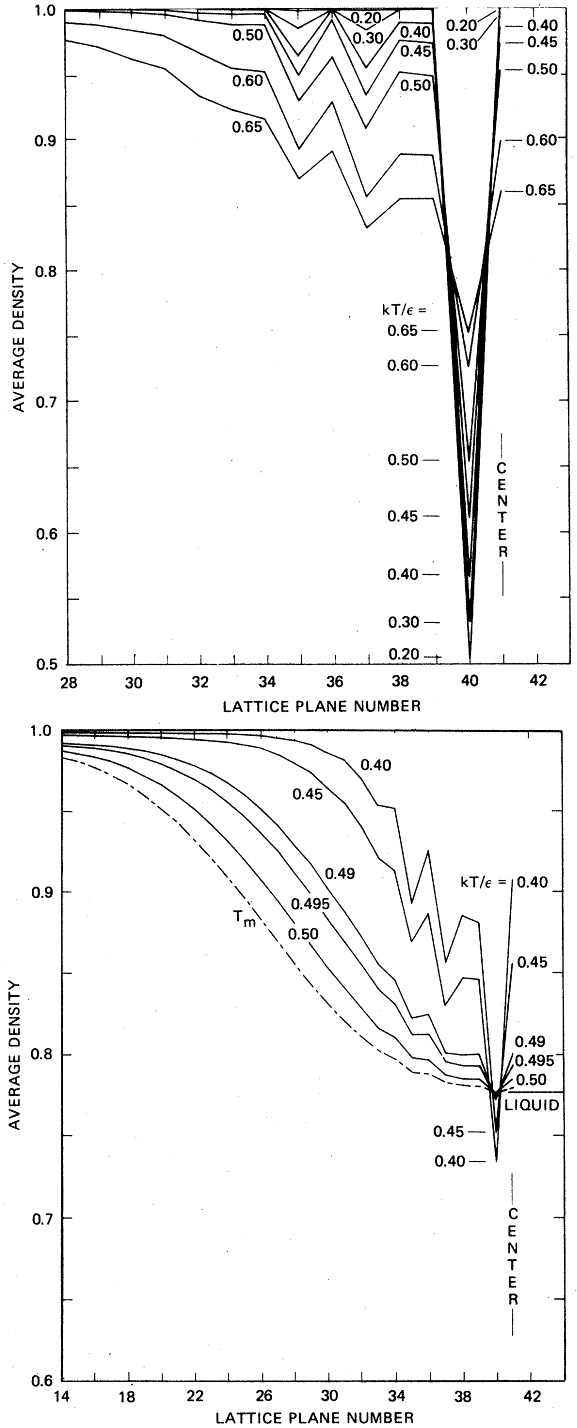

FIG. 4. Density profile across the grain boundary. The center of the boundary is chosen at the 41st lattice plane. The profile is repeated on the right of the 41st plane as a mirror image. (a) is for $\mu/\epsilon=-1.5$ and starts from a very low temperature. (b) is for $\mu/\epsilon=-2.2$ and shows how the profile changes near the melting temperature ($kT_m/\epsilon=0.5032$). The curve for T_m is for an intermediate stage of convergence.

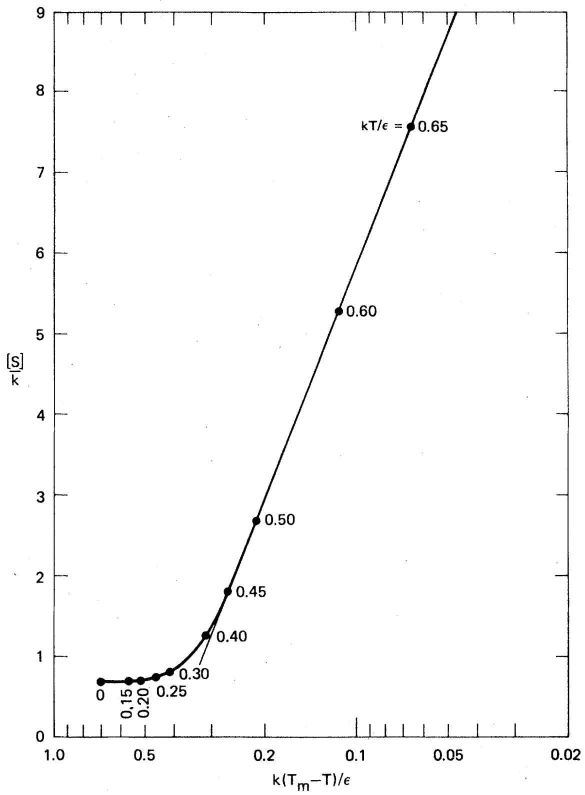

FIG. 5. The excess entropy S of the present work plotted against $-\log_{10}(T_m - T)$.

it behaves as if it is coated with a melted layer for a considerable temperature interval below the melting point. At some temperature near $0.35\epsilon/k$, there is a gradual transition in structure from the low-temperature profile to a structure that with increasing temperature increasingly tends to resemble a melted layer and that exhibits a singularity as T_m is approached. Since the grain boundary is completely wet with liquid at T_m, it is legitimate to call the gradual transition near $T=0.35\epsilon/k$ the melting transition.

The possibility that a grain boundary would have a liquid layer at the melting point was first discussed by Gibbs.[13] Whenever σ for the grain boundary has a tendency to exceed twice the σ for the solid-liquid interface, the transition we found is expected to occur. Smith[14] attempted to formulate the temperature behavior of a melted-layer model of the grain boundary. The value of σ for the melted-layer model was assumed to consist of three terms

$$\sigma_{\mathrm{ML}} = 2\sigma_{\mathrm{SL}} + \lambda \Delta S (T_m - T) + E(\lambda) \ , \tag{7}$$

where $2\sigma_{\mathrm{SL}}$ is the contribution of the two solid-melt interfaces, $\lambda\Delta S(T_m - T)$ is the contribution of a melted layer of thickness λ, ΔS is the entropy of fusion per unit volume, and $E(\lambda)$ is an unknown repulsive energy; the latter is between the two liquid-solid surfaces and keeps the melted layer from collapsing below the melting point. In the analysis, σ_{SL}, ΔS, and $E(\lambda)$ are assumed to be independent of temperature. Minimizing σ_{ML} with respect to λ at a fixed temperature, we obtain a relation for

$$dE/d\lambda + \Delta S (T_m - T) = 0 \ . \tag{8}$$

When this relation holds, we can further obtain

$$d\sigma_{\mathrm{ML}}/dT = -\lambda \Delta S \ . \tag{9}$$

Since $\lambda\Delta S$ in Smith's model is readily identified with $[S]$, our finding in Fig. 5 and Eq. (5) implies that λ linearly depends on $-\ln(T_m - T)$, and integrating Eq. (8) leads to an expression for Smith's $E(\lambda)$ in the lattice-gas grain-boundary model as

$$E(\lambda) = C_1 \exp(-C_2\lambda) \ . \tag{10}$$

This indicates the reasonable nature of the repulsive term in Smith's formulation, Eq. (7). It is generally known, and is verified in our Fig. 4, that the density profiles have exponential tails. The exponential repulsion in Eq. (10) strongly suggests that it arises from the overlap of exponential tails of profiles. When we use Eq. (10) together with the temperature dependence of λ, we can write σ_{ML} in Eq. (7) in the form

$$\sigma_{\mathrm{ML}} = 2\sigma_{\mathrm{SL}} - (T_m - T)[C_3 + C_4 \ln(T_m - T)] \ , \tag{11}$$

which has the same $(T_m - T)$ dependence as does Eq. (6).

In the present paper, we used a two-dimensional lattice-gas model, and thus the grain boundary is essentially one dimensional. Gradual transitions are expected for such one-dimensional systems. For a three-dimensional system with a two-dimensional grain boundary, it is expected that the transition from low- to high-temperature behavior may be a sharper one. A second-order phase transition has been found in a theoretical three-dimensional antiphase boundary.[7]

A melting transition in real metals has been observed[15] as a function of orientation difference and explained in terms of a dislocation model with liquid cores.[16] The temperature dependence of such a model might show several transitions.

Although the computational method used in the paper is approximate, we believe the qualitative conclusions (i) and (ii) stated at the beginning of the paper are reliable. Three pieces of supporting evidence are as follows: First, the good agreement in the homogeneous phase diagram (Fig. 2) with the computer simulation; second, the agreement between the computed σ with the rigorous estimate Eq. (3) near $T=0$; and third, the agreement of our σ in Eq. (6)

near $T = T_m$ with Eq. (11), which is derived based on Smith's theory. It is true that when the CVM uses a finite-size cluster as its base, the method cannot take into account very large fluctuations and thus gives an incorrect answer near a second order transition point. The present treatment, however, is free from such shortcomings because the entropy is diverging at a first-order melting point, the divergence being caused by the fact that the thickness of the liquid layer caught between two solid phases increases to infinity as T_m is approached.

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