

## Thermodynamic Criteria for Grain-Boundary Melting: A Molecular-Dynamics Study

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Interface melting in various tilt boundaries between crystals of Lennard-Jones particles is predicted by a harmonic analysis of the ground-state configurations. Interface excess free energies obtained in this way are extrapolated to the triple point, and these values are compared with the crystal-melt excess free energy. The validity of the method is confirmed by direct comparisons with high-temperature structures obtained by molecular-dynamics techniques, and with excess free energies obtained from the same simulations. Systems containing boundaries that exhibit interface melting experience disorder at the melting point, whereas the others can be superheated.

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It is well known that self-diffusion rates at grain boundaries (GB) are often much higher than those in the crystalline bulk.<sup>1</sup> In fact, there is evidence that material near the GB assumes a liquidlike character, even at temperatures well below the bulk melting temperature ( $T_m$ ).<sup>2</sup> Further, GB's are expected to behave in a similar manner to crystal-vapor (CV) interfaces, in which the formation of a quasiliquid layer at high temperatures is well documented.<sup>3-5</sup> Experimental evidence for sudden changes in grain-boundary properties (migration rates, excess energies, etc.) with temperature has been observed, for example, by Aust<sup>6</sup> and by Gleiter.<sup>7</sup> These results do not necessarily imply a phase transition with an interface melting temperature below  $T_m$ , but that the GB structure may change appreciably over a narrow temperature range.

There is a large body of literature on the structures of model grain boundaries, and in most cases these calculations have been performed by use of two-body potentials and molecular-statics techniques. That is, they represent the ground-state configurations. Only recently have configurations been obtained for finite temperatures, and these calculations have been performed either by harmonic analyses based on the ground state, or by molecular-dynamics (MD) or Monte Carlo techniques.<sup>8-14</sup> Ciccotti, Guillope, and Pontikis<sup>12</sup> studied a Lennard-Jones (LJ) system at constant density. They observe gradual disordering of the atoms near the GB as the temperature approaches their estimated value of  $T_m$ , although the constraint of constant density may be expected to inhibit the disordering process. Diffusion occurred mainly by vacancy migration, even at the highest temperature studied,  $T/T_m = 0.76$ . In contrast, the MD simulation of Ho *et al.*<sup>14</sup> was performed at constant pressure and showed a highly disordered GB at temperatures as low as  $0.5T_m$ . However, their estimate of  $T_m$  was based on the melting of a single crystal without a free surface, and hysteresis effects may have increased the apparent value

of  $T_m$ . Lastly, we note that Kikuchi and Cahn<sup>11</sup> have observed GB disordering in a two-dimensional lattice gas model.

Several experimental measurements of the excess free energy of a GB have been performed.<sup>15,16</sup> Glicksman and Vold<sup>16</sup> studied the orientation dependence of  $\{01\bar{1}\}$  tilt boundaries in Bi at  $T_m$  by the GB grooving method. They found that the dihedral angle goes to zero for misorientations greater than  $15^\circ$ , implying that a quasiliquid layer is present in the boundary in this case. This is consistent with our LJ simulations, as discussed below.

Interface melting is favored if the excess free energy  $\gamma_{GB}^{(0)}$  of a "sharp" GB exceeds that of two crystal-liquid boundaries, i.e.,

$$\gamma_{GB}^{(0)} > 2\gamma_{CL}, \quad (1)$$

where  $\gamma_{CL}$  is the crystal-liquid (CL) free energy. Although the chemical potential of the liquid is higher than that of the crystal, the system can lower its free energy by forming a thin liquidlike film and two crystal-liquid interfaces. As  $T_m$  is approached, the film thickness is expected to diverge as either  $\log(T_m - T)$  or  $(T_m - T)^\beta$  depending upon the range of atomic interactions<sup>17,18</sup> Even for large inequalities of Eq. (1), the interface region can only attain liquidlike properties very close to  $T_m$ , where the thickness of the region is sufficiently large to minimize the influence of the adjacent crystals.

We use a LJ potential smoothly truncated at  $2.5\sigma$  as described in Ref. 4. All interactions and thermodynamic quantities are given in reduced units. This is the only system (experimental or simulated) for which the excess interfacial properties are known for each combination of the three phases at  $T_m$ .<sup>17</sup> Further, we know  $T_m$  very accurately by free-energy analysis to be 0.617 and we know the thermodynamic and dynamic properties of the bulk system along the CV coexistence curve.<sup>2</sup>

We consider the following three boundaries (additional cases are considered in greater detail elsewhere) chosen to lie on either side of inequality (1): (a) (310)  $\Sigma=5$ ,  $\langle 001 \rangle$ ,  $\theta=36.86^\circ$  boundary with 1920 particles, (b) (332)  $\Sigma=11$ ,  $\langle 01\bar{1} \rangle$ ,  $\theta=20.05^\circ$  boundary with 1848 particles, and (c) (443)  $\Sigma=123$ ,  $\langle 01\bar{1} \rangle$ ,  $\theta=14.65^\circ$  boundary with 1440 particles. The systems were set up with periodic boundary conditions in each Cartesian direction. Each system contains two equivalent boundaries with sufficient particles present to produce bulk properties between the boundaries. The minimum energy configuration of each GB is found by extensive conjugate gradient searches at  $T=0$ . The normal-mode frequencies (giving the  $T=0$  entropy) of each system were obtained by diagonalization of the Fourier-transformed dynamical matrix. Knowing the  $T=0$  GB stress ( $f$ ) and entropy ( $S$ ) we linearly extrapolate  $\gamma_{GB}^{(0)}$  to  $T_m$  by use of the zero-temperature gradient of

$$\frac{d\gamma_{GB}}{dT} = -\frac{S_{GB}}{A} + (f_{GB} - \gamma_{GB}) \frac{d(\log A)}{dT}, \quad (2)$$

where  $A$  is the area of the boundary. Our analysis of CV interfaces showed this to be a valid procedure.<sup>17</sup> Figure 1 shows the results. From inequality (1) we expect the (310) and (332) boundaries to exhibit interface melting as  $T \rightarrow T_m$ , whereas the (443) is a marginal case. At a given temperature the melt thickness ( $l$ ) of the (310) should be greater than that of the (332). An analysis of  $\gamma_{GB}^{(0)}(T_m)$  as a function of  $\theta$  for a complete range of  $\langle 01\bar{1} \rangle$  boundaries suggests that interface melting should occur for  $\theta > 15^\circ$  (see Broughton and Gilmer<sup>19</sup>), and this criterion is consistent with the (443) retaining a stable ordered structure at  $T_m$ .

The trajectory plots shown in Fig. 2 tend to support

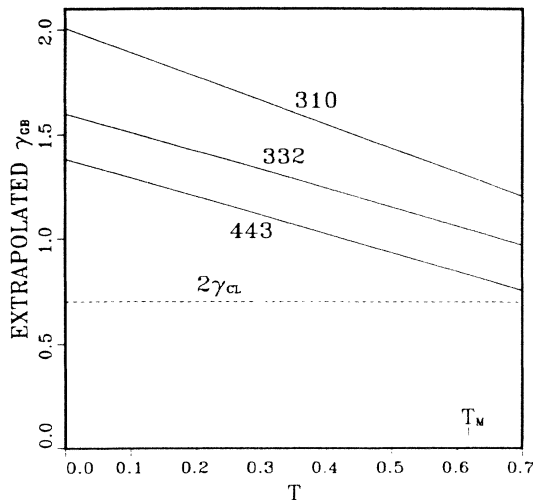


FIG. 1. Extrapolated excess grain-boundary free energies for (310), (332), and (443) tilt boundaries.

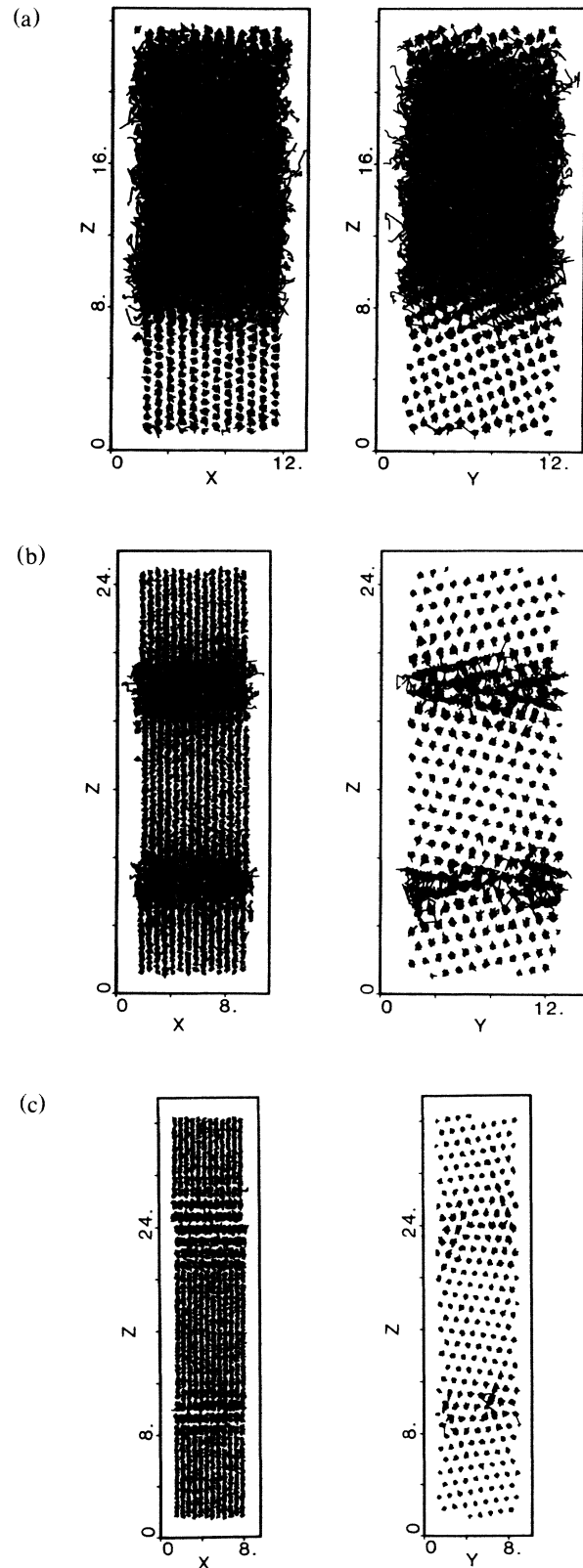


FIG. 2. Trajectory plots of (a) (310), (b) (332), and (c) (443) boundaries at  $T=0.617$ , the measured value of the triple point.

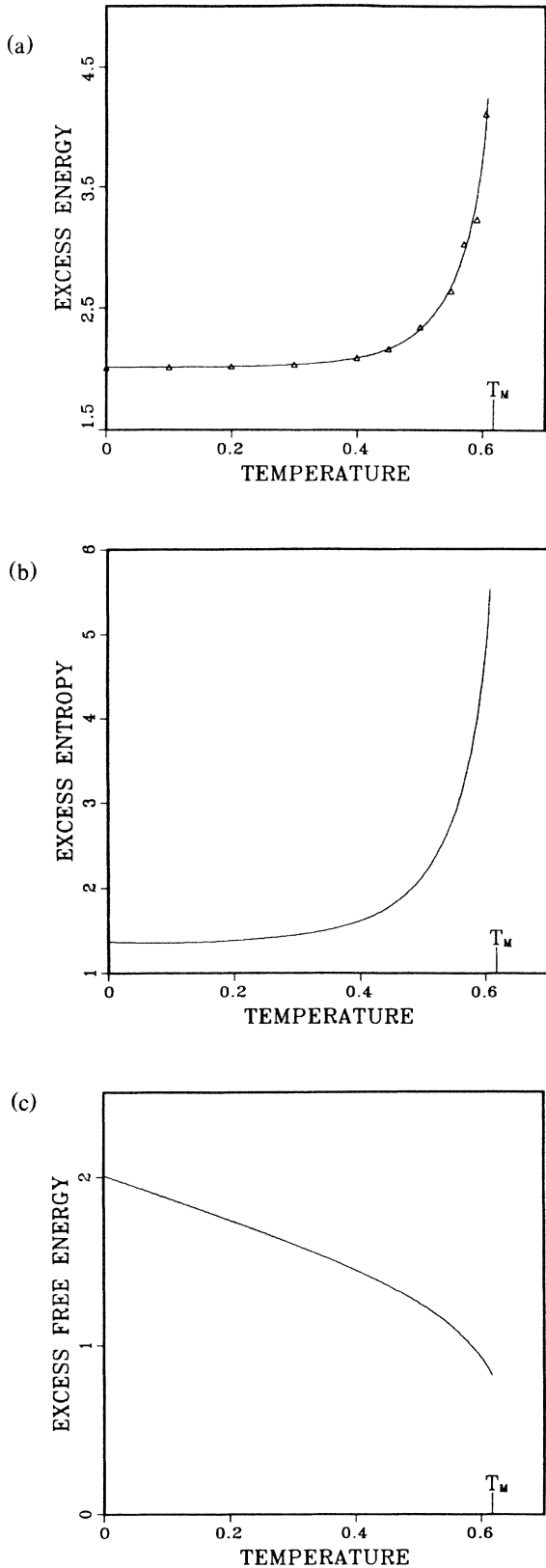


FIG. 3. Excess (a) energy, (b) entropy, and (c) free energy of the (310) system as a function of temperature.

our ( $T=0$ )-based extrapolations. Three systems were derived from the ground-state configurations described above, but were equilibrated at the triple point,  $T=0.617$ . The pressure was maintained at zero by dynamical adjustment of the box dimension normal to the interface ( $z$ ).<sup>20</sup> The crystal lattice parameter in the  $x$ - $y$  plane was fixed at the correct value for zero pressure in the bulk crystal. (CV coexistence corresponds closely to zero pressure in LJ systems.) Equilibration times of  $20\,000 \Delta t$  ( $\Delta t=0.005$ ) were used and the trajectories represent further elapsed times of  $4000 \Delta t$ .

The system that was prepared with the (310) boundaries has a large region of extensive disorder. In fact, it appears that one of the crystallites has melted. Initially the disorder was localized at the boundaries, but during the molecular-dynamics simulation at  $T_m$ , the disordered zones gradually expanded. At temperatures just below  $T_m$ , this boundary exhibits disordering only in its immediate vicinity. The (443) boundary is stable and highly ordered at  $T_m$ , and presumably it is metastable above  $T_m$ . The (332) system contains regions of high mobility and disorder at the two boundaries, but these regions did not expand significantly during extended simulations at  $T_m$ . The different behavior of the (332) and (310) boundaries may simply be a result of a smaller value of  $\gamma_{GB}^{(0)}$  for the (332) system, and hence a weaker driving force for the formation of a liquid film at  $T_m$ . On the other hand, it may indicate that  $\gamma_{GB}^{(0)}$  is somewhat lower than the extrapolated value, a result which is not too surprising in view of the fact that the grain-boundary structure changes significantly at high temperatures.

By increasing the temperature in steps from  $T=0$  (equilibrating and gathering statistics each time) for the (310) boundary, we have obtained the excess energy,  $E_{GB}$  [Ref. 4 gives  $E_{\text{bulk}}(T)$ ], and  $f_{GB}$  as a function of temperature up to  $\sim T_m$ . If we assume that this describes a reversible path (see below), evaluation of

$$S_{GB}(T) = S_{GB}(0) + \int_0^T (dE_{GB} - f_{GB}dA)/T \quad (3)$$

gives  $\gamma_{GB}(T)$  and  $S_{GB}(T)$ . We extrapolated  $E_{GB}$  to  $T_m$  by use of various analytic expressions. We find that  $\gamma_{GB}(T_m)$  is very insensitive to whether a power-law ( $\beta=0.25$ ) or logarithmic divergence is assumed for  $E_{GB}$ . This result is shown in Fig. 3. The behavior of  $E_{GB}$  and  $S_{GB}$  shows that very significant disordering is occurring in the GB as  $T \rightarrow T_m$ . The magnitude of  $\gamma_{GB}$  at  $T_m$  is somewhat higher than  $2\gamma_{CL}$ , although it is clearly not possible for the free energy of the boundary to exceed this value. This may indicate that some of the systems had not completely equilibrated since the energies are obtained from MD data taken from stepwise increasing temperature.

Our data indicate that grain-boundary melting is not a true phase transition that can be identified at a tem-

perature below  $T_m$ . The thermodynamic parameters are continuous functions of temperature, and the quasiliquid layer must retain some crystalline symmetry because of the finite layer thickness below  $T_m$ . Boundaries that do not exhibit interface melting can, in principle, be distinguished by the presence of metastable states above  $T_m$ .

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<sup>1</sup>*Grain-Boundary Structure and Kinetics*, American Society for Metals Materials Science Services (American Society for Metals, Metals Park, Ohio, 1979), and references therein.

<sup>2</sup>See Surf. Sci. **31**, (1972), and references therein.

<sup>3</sup>See, for example, J. W. M. Frenken and J. F. van der Veen, Phys. Rev. Lett. **54**, 134 (1985).

<sup>4</sup>J. Q. Broughton and G. H. Gilmer, J. Chem. Phys. **79**, 5095, 5105, 5119 (1983).

<sup>5</sup>E. W. Hart, in *The Nature and Behavior of Grain Boundaries*, edited by H. Hu (Plenum, New York, 1972).

<sup>6</sup>K. T. Aust, Can. Metall. Q. **8**, 173 (1969).

<sup>7</sup>H. Gleiter, Z. Metallkd. **61**, 282 (1970).

<sup>8</sup>M. Hashimoto, Y. Ishida, R. Yamamoto, and M. Doyama, J. Phys. F **10**, 1109 (1980), and Acta Metall. **29**, 1148 (1981).

<sup>9</sup>A. J. C. Ladd, W. G. Hoover, V. Rosato, G. Kalonji, S. Yip, and R. J. Harrison, Phys. Lett. **100A**, 195 (1984).

<sup>10</sup>G. Kalonji, P. Deymier, R. Najafabadi, and S. Yip, Surf. Sci. **144**, 77 (1984).

<sup>11</sup>R. Kikuchi and J. W. Cahn, Phys. Rev. B **21**, 1893 (1980).

<sup>12</sup>G. Ciccotti, M. Guillope, and V. Pontikis, Phys. Rev. B **27**, 5576 (1983).

<sup>13</sup>M. Guillope, G. Ciccotti, and V. Pontikis, Surf. Sci. **144**, 67 (1984).

<sup>14</sup>P. S. Ho, T. Kwok, T. Nguyen, C. Nitta, and S. Yip, Scr. Metall. (to be published).

<sup>15</sup>See, for example, S.-W. Chan and R. W. Balluffi, Acta Metall. **33**, 1113 (1985).

<sup>16</sup>M. E. Glicksman and C. L. Vold, Surf. Sci. **31**, 50 (1972).

<sup>17</sup>J. Q. Broughton and G. H. Gilmer, Acta Metall. **31**, 845 (1983).

<sup>18</sup>J. K. Kristensen and R. M. J. Cotterill, Philos. Mag. **36**, 437 (1977).

<sup>19</sup>J. Q. Broughton and G. H. Gilmer, to be published.

<sup>20</sup>J. Q. Broughton, G. H. Gilmer, and J. D. Weeks, J. Chem. Phys. **75**, 5128 (1981).

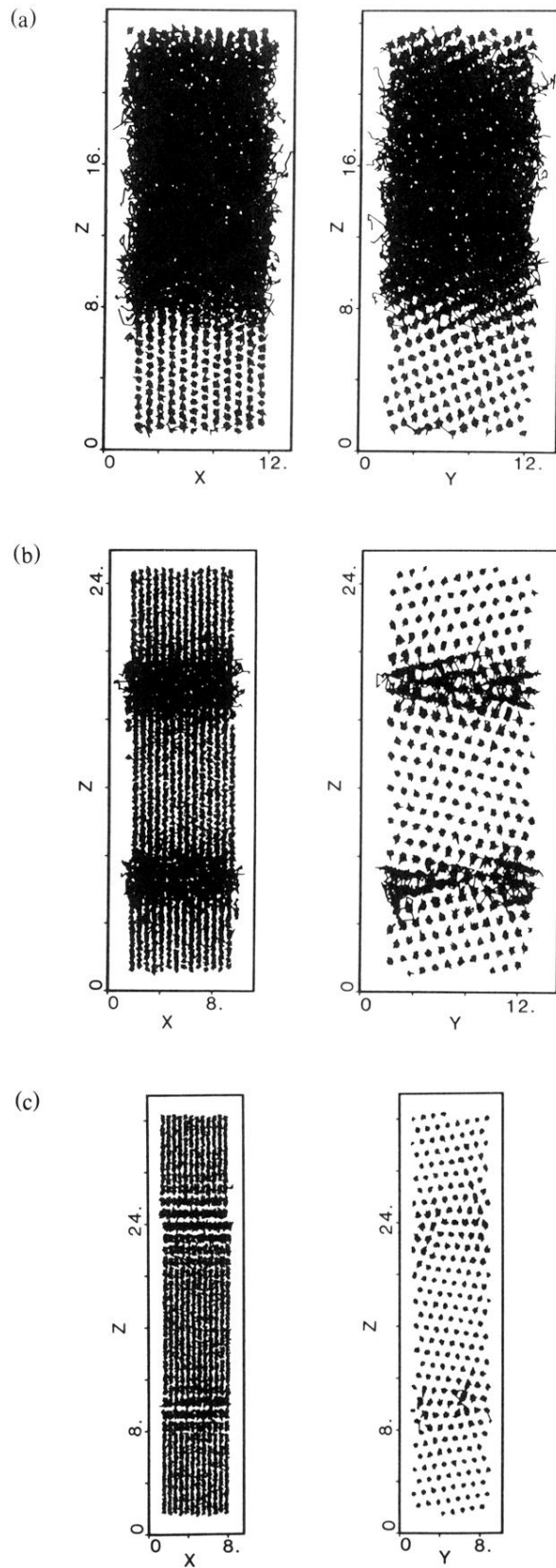


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