

Grain-Boundary Melting Transition in an Atomistic Simulation Model

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Molecular-dynamics simulations on the structure and energy of a bicrystal model reveal an interfacial melting transition at a temperature distinctly lower than bulk melting. Below the transition, thermal disorder occurs but interfacial width remains essentially unchanged; above the transition, the interfacial region behaves like a melt while its width grows significantly with temperature.

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The possibility that an internal interface such as a grain boundary can undergo a structural transition or an instability distinct from the bulk has long been recognized.¹ With the atoms in the grain-boundary core having a potential energy higher than that of the bulk atoms, it seems reasonable that the interface can become thermally disordered before the bulk or have its own melting transition. Although there exist theoretical considerations² and indirect experimental evidence³ for such behavior, the phenomenon of grain-boundary melting⁴ is at present not well understood.

Recent computer-simulation studies have revealed pronounced structural disorder in idealized bicrystal models at a temperature distinctly lower than that where the bulk lattice becomes disordered.⁵⁻⁷ The interpretation that this signifies grain-boundary melting is consistent with the predictions of a lattice-gas model⁸; it is also supported by results of direct free-energy calculations.⁹

In this Letter we report new molecular-dynamics results on thermal disordering in a bicrystal. These data provide compelling evidence that an atomistic model of a high-angle grain boundary will undergo a disordering process at the interface which has the characteristics of local melting. Our conclusion is based on the consistent behavior of the energy and the structure of the grain-boundary core, along with variations in atomic mobility. It points to an intrinsic property which we believe holds for all the bicrystal models of similar structure currently in use.¹⁰ A similar behavior is believed to occur in surface melting.¹¹

Our bicrystal model is a high-angle symmetric tilt boundary represented by a rectangular cell of 840 atoms with periodic border conditions along the x and y directions and fixed borders along the z direction (see Fig. 1). We have examined the vibrational amplitude of atoms as a function of distance from the fixed z borders, and have found that the constraining effects of the border extend about $\frac{1}{4}$ of the way into the cell. A larger cell of 3360 atoms obtained by expansion along the x direction by a factor of 4 was also studied

as discussed below. For interatomic interactions we use a Morse potential for aluminum with parameters chosen to fit the vacancy-formation energy.¹² Standard molecular-dynamics techniques are used to integrate Newton's equations of motion with an initially relaxed structure obtained by minimization of the energy while allowing rigid translations of the two halves of the bicrystal.⁷

We divide the simulation cell into 28 equal regions along the z direction, each containing thirty atoms at the outset. For each region we determine the potential energy U , the static structure factor $S(\mathbf{K})$, and the mean square displacement $\langle \Delta r^2 \rangle$, where

$$U = \frac{1}{2} \sum_{l \neq k} u(|\mathbf{r}_l - \mathbf{r}_k|),$$

$$S(\mathbf{K}) = (1/N) \langle |\sum_k \exp(i\mathbf{K} \cdot \mathbf{r}_k)|^2 \rangle,$$

where u is the interatomic potential, \mathbf{r}_k the position of atom k , N the number of atoms in a region, and summation is over these atoms. Through these properties one can decide whether a region is part of the interface

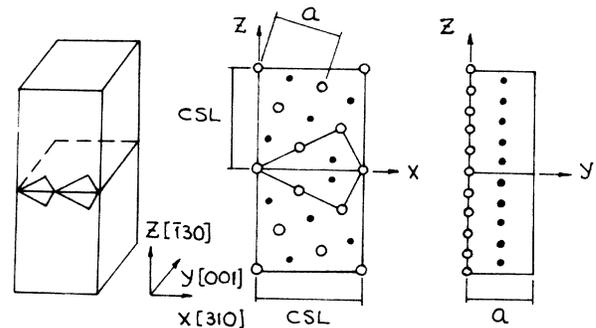


FIG. 1. Simulation cell showing the crystallographic orientation of the bicrystal with a $\Sigma=5[001](\bar{1}30)$ symmetric tilt boundary. Also shown are x - z and y - z plane projections of two adjacent layers of atoms (open and closed circles) in 2 CSL structural units. Entire cell is 14 CSL units along the z direction, 2 CSL units in the x direction, and $3a$, a being the lattice constant, along the y direction (1 CSL unit = $\sqrt{10}a/2$).

or belongs to the bulk.

To ensure that we can properly identify the bulk region, a parallel simulation is carried out on a reference system, an identical cell with atoms arranged in the single-crystal structure and fixed borders having the same orientation of atom arrays at both ends. The reference-system behavior is that which is expected of the bulk region of the bicrystal cell if the latter cell is large enough for such a region to exist.

We consider first the reference-system results. Two series of simulation runs are made. In the first series, which we denote as the heating series, the first run starts at 400 K and in each succeeding run the temperature is increased in increments of 100 K (up to 1200 K). Constant temperature is maintained by re-scaling of the atomic velocities once every ten time steps. Each run, which consists of 10^4 time steps, is made at constant volume with the lattice constant set at the experimental value for that temperature, and the initial atomic configuration is taken from the end of the preceding run. With this procedure the system pressure is found to rise somewhat with increasing temperature; this can be attributed to inadequacy of the potential to give the correct pressure at a given temperature. We believe that it is more important to do the simulation at the correct lattice constant than to keep the pressure strictly constant, and in any case the pressure increase is less than a factor of 2 over a range 400–900 K.

As Fig. 2 shows, the internal-energy results for this

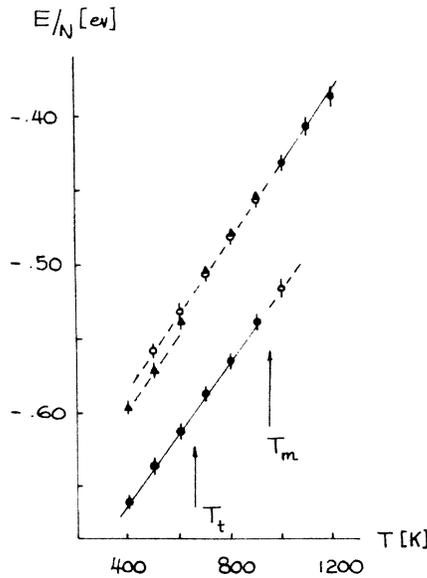


FIG. 2. Internal energy per particle from heating and cooling series: reference-system results, when system is equilibrated (closed circles) and where system is either superheated or undercooled (open circles), and bicrystal results (triangles).

series follow a straight-line behavior up to 900 K. At 1000 K the energy initially continues along the straight line, but after 8×10^3 time steps it increases to a distinctly higher value as the system becomes structurally disordered [as indicated by $S(\mathbf{K})$]. At the same time the mean square displacement also increases sharply and appears to become unbounded. We regard this behavior as indicating melting and estimate that the transition should occur at about 950 K for the present model. It should be noted that the known melting point of aluminum is 933 K.

In the second series of simulations, which we call the cooling series, all the runs start with the initial configuration of a well-equilibrated liquid (melt) obtained at 1000 K in the heating series, and the system is simulated at those temperatures studied in the heating series. During each run the system is found to crystallize, but the solidification is slow enough to obtain meaningful measures of the internal energy of the crystallized region and that of the disordered zone which is not yet crystallized. We find the former to agree with the results at the corresponding temperatures obtained in the heating series, while the latter falls on a straight-line extrapolation from the liquid curve (open circles) in Fig. 2. Even though the disordered zone is not stable in time, we think it is useful to show its internal energy in Fig. 2; for the purpose of interpreting the bicrystal results it can be regarded as the energy of an undercooled melt.

The bicrystal model is also studied in a heating and a cooling series of simulations. In the heating runs, the time required for the interface to become stable can be 4×10^4 time steps or more. For the interpretation of

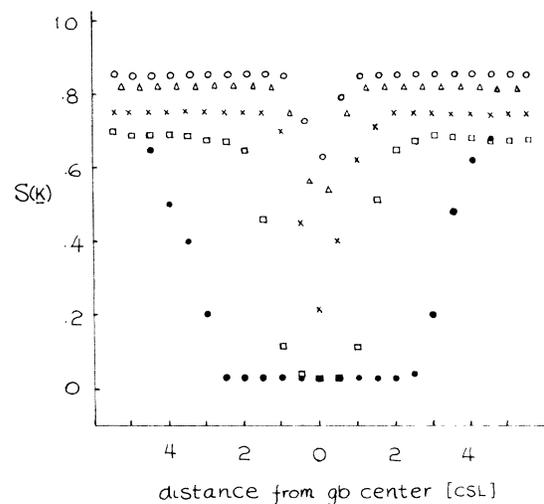


FIG. 3. Profile of $S(\mathbf{K})/N$, $\mathbf{K} = (4\pi/a)(0, 1, 0)$, of the bicrystal system at various temperatures: 400 K (open circles), 500 K (triangles), 600 K (crosses), 700 K (squares), and 800 K (closed circles).

the internal-energy results which are shown in Fig. 2, it is useful to keep in mind the profile of the static structure factor given in Fig. 3. One sees that at 600 K and below the grain-boundary core is quite well defined; although the interfacial region is less ordered than the bulk, as is expected, $S(\mathbf{K})$ still has a value indicating a certain amount of structural order. The internal energy in this region is higher than in the bulk (which is the same as in the reference systems) and lower than that of the undercooled melt. Above 600 K $S(\mathbf{K})$ in the center of the interfacial region has decreased essentially to zero; this onset of complete disorder is directly verified by plotting the detailed atomic configurations. Correspondingly, the energy in the interfacial region increases to that of the undercooled melt. We interpret the behavior at 700 K as melting at the interface. Notice that the energy in the bulk regions of the bicrystal, regions where $S(\mathbf{K})$ is still greater than ~ 0.5 , continues to follow the heating curve previously established by the reference system.

In the cooling runs the simulation proceeds until a stable interface is established, and then the run is continued for another 10^4 time steps for measuring properties. We find that above 600 K the resulting interfacial region is disordered, while at 600 K and below the interfacial structure is quite similar to that found in the heating runs. A comparison of the corresponding configurations obtained in the two series is shown in Fig. 4. The fact that heating and cooling runs produce essentially the same interfacial region with regard to both structural disorder and spatial extent implies that our runs are long enough for either disordering or ordering processes to take place, and therefore these

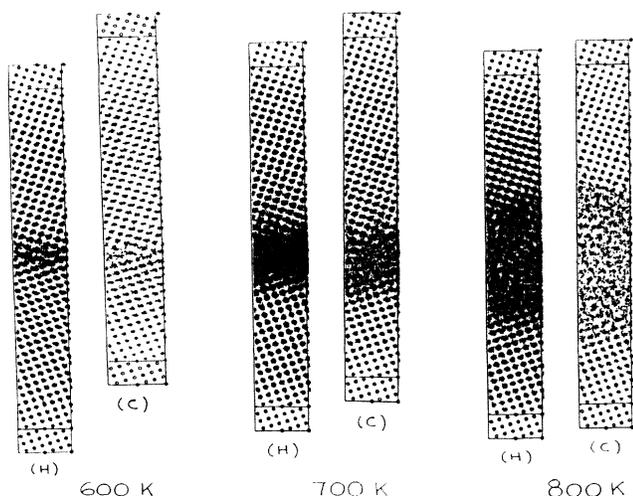


FIG. 4. Comparison of atomic-trajectory plots, each over a duration of approximately 5×10^3 time steps, obtained during heating (H) and cooling (C) runs when the system appears to have stabilized over a period of at least 10^4 time steps.

results are the intrinsic behavior of the bicrystal model. If we take interfacial melting to commence between 600 and 700 K, then we obtain a thickness of the melted layer for 700, 750, and 800 K. At 900 K thermal disordering spreads so decisively over the entire cell that we can only conclude that the cell length along the z direction, 14 coincidence-site-lattice (CSL) units, is a lower bound. These results are plotted in Fig. 5. A two-dimensional lattice-gas model has been used to show the existence of a grain boundary transition.⁸ From the calculated excess entropy it was inferred that the thickness of the liquidlike layer should diverge as $-\ln(T_m - T)$. Our limited data are consistent with a variation of this form; clearly further data on the growth of this layer will be of value.

In summary, our bicrystal model shows a gradual onset of structural disorder up to a transition temperature T_i which we estimate to be about $0.7 T_m$. Below T_i there is only slight variation of interfacial width although grain-boundary migration does occur. Above T_i the interfacial region is fully disordered and its width grows rapidly with temperature. This conclusion is reinforced by the temporal behavior of the mean square displacements, which, when averaged over the particles in each region, show that the atoms in the locally melted regions acquire liquidlike mobility.

To check the validity of our results we have considered the effects of the potential function and system size. We have carried out substantial simulation runs on the same bicrystal model but using a pseudopotential derived for aluminum.¹³ Although a lower melting temperature was obtained with this potential, the ther-

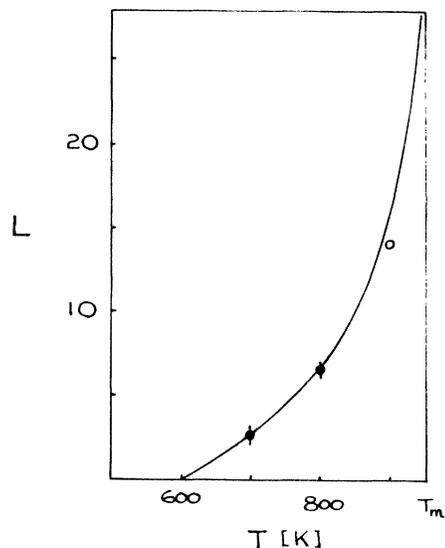


FIG. 5. Thickness of melted interfacial layer (in CSL units), present simulation results (closed circles), and a lower-bound estimate (open circle). Curve is an empirical fit, $L = -0.09[\ln(1 - T/T_m) + 1]$, with $T_m = 950$ K.

mal disordering behavior was essentially the same at the same value of $T/T_m \sim 0.7$. Since the Morse potential and the pseudopotential differ markedly in physical origin and even the qualitative shape, this suggests that the melting process discussed here is a general statistical mechanical property of the bicrystal system which is independent of the potential function.

We have investigated system-size effects by repeating some of the simulations with the Morse potential by use of a cell of 3360 atoms obtained by enlarging of the original cell four times in the x dimension. At 650 K, local regions of complete disorder were observed which indicated a state of metastability. At 600 K and 700 K the structural behaviors were similar to what we have observed for the cell of 840 atoms.

There are still other aspects of our simulation which could give rise to numerical artifacts, in particular the short-range cutoff between second and third neighbors which we have used and the fixed z borders. We have made only short simulation runs where the force cutoff up to the sixth nearest neighbor is considered and found no significant change; this effect will be investigated more thoroughly in future work. The fixed-border effect, if any, can only raise T_i , which would make the true transition temperature even lower than what we observed.

The experimental situation concerning the melting transition seems to be inconclusive. Measurements of grain-boundary sliding in high-angle zinc tilt bicrystals showed a transition at a temperature between $0.7T_m$ and $0.9T_m$; moreover, the effect of impurities was found to increase the transition temperature for the same tilt angle.¹⁴ Also, measurements¹⁴ and free-energy calculations¹⁵ showed that low-angle ($\theta < 15^\circ$) bicrystals do not undergo a transition. On the other hand, recent electron-microscopy study of diffraction contrast with use of $\Sigma=5$ Al tilt bicrystal showed no melting up to $0.9T_m$.¹⁶ We believe that at present it is still premature for simulation to address the experimental results directly. Issues such as the effect of impurities, dependence on the misorientation angle, and the effect of secondary grain-boundary dislocations have to be investigated.

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