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Superheated melting of grain boundaries

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Based on a model of the melting of grain boundaries (GB), we discuss the possibility of the existence of a superheated GB state. The molecular dynamics simulation presented here shows that the superheated GB state can be realized in the high symmetric tilt GB. The sizes of liquid nuclei exceeding a critical size determined whether or not the superheating grain boundary melted. Our results also indicate that an increase of the melting point due to pressure is smaller than the superheating due to a nucleation mechanism.

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I. INTRODUCTION

Superheating has been found in a large number of systems such as surfaces,[1–3] small clusters,[4] confined thin films,[5] and particles covered by (or embedded in) material with a higher melting point.[6] Generally, the melting of solid material is a heterogeneous process with the nucleation mechanism at surfaces or interfaces.[7,8] Providing a heterogeneous nucleation could be avoided by means of suitable coating[6] or internal heating,[9] or the crystal materials can be in the superheated state, its melting is completed by a thermodynamic instability resulting in homogeneous disordering and catastrophic mechanism, with the stability limit from 0.2 T_m to 2.0 T_m.[10–14]

A large amount of research has contributed to the role of the surface for the melting of crystal. Superheated melting of fcc(110) and fcc(100) surfaces are virtually never observed.[15–17] The only example of a superheated surface is the small crystal strictly confined by high-symmetry fcc(111) facts.[1–3] Grain boundaries as another important quasi-two-dimensional defect also leads to the heterogeneous melting of solid material. Quite a number of studies have shown that GBs cannot melt below the T_m (not premelting).[18–28] Using the molecular dynamics (MD) simulation, Kikuchi and Cahn, as well as Ciccotti *et al.*, showed that the GB does not melt until the temperature reaches the melting point of bulk. Nguyen *et al.*, using the more accurate interatomic potential by embedded-atom methods (EAM), studied the high-temperature GB structure; they found that, close to melting point T_m, the GB structure was disordered, quite liquidlike, and metastable, and that the underlying crystalline order can reemerge over a long interval of simulation. Hsieh and Balluffi, using the HREM (High Resolution Electron Microscopy) methods, supported the above arguments and showed that aluminum GB did not melt below 0.999 T_m.[29]

It is more surprising that some of the simulations also hint that some high-symmetric GBs similar to the high-symmetric surface can probably melt by superheating.[24] In this work, parallel to Di Tolla's work[16] on surfaces, we study the possibility of a superheated high-symmetry GB by a theoretical model and MD simulation of a symmetric aluminum GB.

When temperature beyond the melting point of a crystal reaches the superheated state, all liquid nuclei must be smaller than a critical size. These liquid nuclei are unstable and able to recrystallize again. The liquid nuclei easily form at surfaces, grain boundaries, and other solid defects regions. So, to avoid a larger liquid nucleus, the crystal must be prepared with the lowest number of solid defects. It is easier to study the superheating of crystal in computer simulation than in experiment. We can construct prefect crystals using the periodic boundary condition in computer simulation. On the other hand, in experiment it is very difficult to obtain an infinite volume perfect crystal. We cannot eliminate the influence of surfaces, grain boundaries, dislocations, and other defects with complicated structures. All these defects have the potential to become liquid nuclei to melt crystal. However, surface effects can be partially removed by coating with other material with higher melting points or by internally heating the material. By these methods we can obtain superheated crystalline grains.

Additionally, the grain boundary itself may probably become a liquid nucleus near the melting point of crystal. Based on our theoretical model, it is possible that, under condition of the absence of critical nucleating cores, a grain boundary does not melt even if the temperatures beyond the melting point. We hope to find a superheated grain boundary in computer simulation, as it is difficult to find it in experiments due to the different kinds of unavoidable nucleation mechanisms. Our simulation will show that a high-symmetry grain boundary can be sustained above the melting point of crystal without other nucleation mechanisms. The superheated grain boundary is easily understood by proximity effects if we consider that the grain boundary is sandwiched between two superheated crystalline grains, while the superheated grains can be obtained by proper internal heating.

II. THE MODEL OF GB MELTING

The melting point T_m of a solid may be defined as a temperature with the coexistence of a solid phase and a liquid

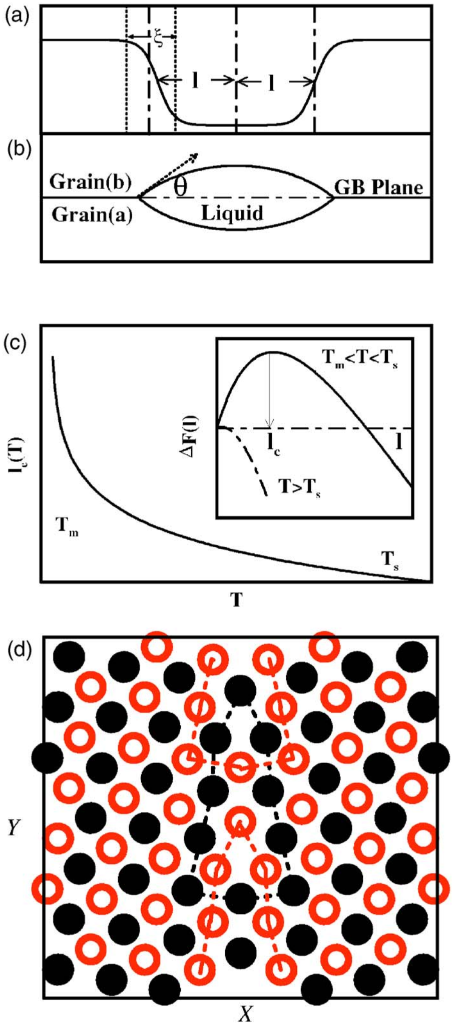

FIG. 1. (Color online) (a) The change of atomic density across the melting GB. (b) The schematic of a partly wetted GB. (c) Critical liquid thickness of a nonmelting GB vs temperature above T$_m$ (schematic). Inset: free-energy change upon conversion of a film of thickness l from solid to liquid. From T_m to T_s the solid GB is stable. (d) The structure Al $\Sigma=13$ GB. The solid and open circles show the I and II(001) planes of the $\cdots$I II I II$\cdots$ stacking sequence along z. The basic GB structural units are also shown with dashed-dotted lines. This figure illustrates only part of the region near the grain-boundary plane of our simulation cell.

phase. For a solid with surfaces or grain boundaries, melting is generally completed by the mechanism of heterogeneous nucleation. We consider that a liquid film with a thickness of $2l$ forms between two semi-infinite solids [Fig. 1(a)]. The change of free energy per unit area is taken as

$$\Delta F(l) = 2\rho L l(1 - T/T_m) + \Delta\gamma(l), \tag{1}$$

where ρ is the liquid density, L the latent heat of melting, and $\Delta\gamma(l)$ the difference between the overall free energy γ_{SL-SL} of two interacting solid-liquid interfaces separated by a distance l and the GB energy per unit area

$$\Delta\gamma(l) = \gamma_{SL-SL} - \gamma_{GB}. \tag{2}$$

By extending the Cahn's wetting theory to a solid-solid interface,[30] using $\Delta\gamma(0)=0$ and only considering the short-range interaction, we may obtain

$$\Delta\gamma(l) = \Delta\gamma_\infty(1 - e^{-l/\xi}), \tag{3}$$

where $\Delta\gamma_\infty = 2\gamma_{SL} - \gamma_{GB}$ is the difference of the interface energy of two isolated solid-liquid interfaces γ_{SL} and the GB energy γ_{GB}, and ξ is the width of solid-liquid interface.

The condition of GB melting is defined by the following process. We may create an image where there is a droplet in the GB region [Fig. 1(b)]; the equilibrium condition of the droplet is

$$\gamma_{GB} - 2\gamma_{SL}\cos(\theta) = 0, \tag{4}$$

where θ is the wetting angle. If $\Delta\gamma_\infty > 0$, i.e., $\gamma_{GB} < 2\gamma_{SL}$, θ is a finite value; the droplet can survive in the region of GB (partial wetting), and the whole GB cannot be wetted. As $\Delta\gamma_\infty < 0$, i.e., $\gamma_{GB} > 2\gamma_{SL}$, θ cannot be defined. A liquid film forms in the GB region (wetting) and the GB melts. Thus, $\Delta\gamma_\infty = 0$, i.e., $\gamma_{GB} = 2\gamma_{SL}$ and $\theta = 0$, and may be considered as the criteria of GB melting.

In the past, it was believed that GBs could not melt below the melting temperature, that is, at certain temperature below T_m, $\Delta\gamma_\infty < 0$. In this paper we only consider the possibility of GB superheated melting, that is, as $T > T_m$, $\Delta\gamma_\infty > 0$.

For superheated melting, the insert of Fig. 1(c) show that $\Delta F(l)$ has a local minimum at $l=0$, and approaches negative infinity as l approaches infinity. There is a maximum at l_c, which is

$$l_c = \xi Ln\left(\frac{\Delta\gamma_\infty T_m}{2L\rho\xi(T - T_m)}\right). \tag{5}$$

Figure 1(c) shows the temperature dependence of l_c. According to Fig. 1(c), at a certain temperature $T(>T_m)$ and $l < l_c$, the system can reduce its free energy by decreasing the thickness of liquid film until the thickness reaches zero, that is, until the system crystallizes. When $l > l_c$, the system can reduce its free energy by increasing the thickness of liquid film until the thickness reaches infinity, and the GB melts. l_c is the critical thickness at T. If at a temperature $l_c=0$, any small thickness can lead to the melting of the GB. The temperature is named as the maximum superheated temperature T_s, expressed as

$$T_s = T_m\left(1 + \frac{\Delta\gamma_\infty}{2L\rho\xi}\right), \tag{6}$$

and l_c can also be expressed as

$$l_c = \xi Ln\left(\frac{T_s - T_m}{T - T_m}\right). \tag{7}$$

The critical nucleus is extremely large for $T \approx T_m$ and reduces rapidly with the increase of the superheating degree. At T_s, $l_c=0$ [Fig. 1(c)] and spontaneous melting happens. Between T_m and T_s the superheated states is metastable, although the melting does not occur. In following several sections, by MD simulations of aluminum GB melting and the above model, we prove that a GB can preserve its crystalline structure even above T_m until the temperature reaches the maximum superheated temperature T_s. Our simulation shows the behavior of a superheating GB; that is, for $T_m < T < T_s$, there exists a critical width l_c of liquid film. When the width of the artificially added liquid is larger than l_c, the GB melts or the liquid film is reduced and the effect of crystallization is dominant.

III. THE MOLECULAR SIMULATION OF GRAIN BOUNDARIES

Molecular dynamic simulations of crystal[31] and high-symmetry surfaces[16] have shown the superheating crystal without critical nuclei such as point defects and liquid drops. By internal heating, crystals with high-symmetry fcc(111) surfaces will superheat. This is because the process of nucleation is homogeneous in the surface region. For some low-symmetry surfaces such as fcc(110) surfaces, the anisotropy leads to heterogeneous nucleation and high concentration of defects, and superheating is extremely difficult to achieve.

Reconstruction and roughening are two main structural transitions for a surface when increasing the temperature. The behavior of grain boundaries is more complicated than that of surfaces, including the migration, bending, sliding, zigzag, and faceting transitions. Our simulations show that it is difficult to control the homogeneous nucleation in computer simulation to obtain a superheated grain boundary. However, we can use symmetric grain boundaries to make atoms homogeneously distribute in the GB region. Instead of a periodic boundary, we have fixed two boundaries of simulation cells parallel to the GB plane to decrease the possibility of grain-boundary sliding.

In this work we chose an Al symmetric $\Sigma 13$ (320) [001] tilt grain boundary [Fig. 1(d)] as our simulation cell with a misorientation of 67.8°, the tilt axis of the boundary is along the z direction, the fixed-boundary conditions is used in the x direction perpendicular to the GB plane, and periodic boundary conditions are used in the y and z directions. The widths along x, y, z are 100 Å, 43 Å, 12 Å, respectively. Interatomic potential plays the most important role in molecular dynamics simulations. In this paper, we use a more realistic potential—a glue potential developed by Ercolessi and Adams.[32] The glue potential has been used in a large number of the simulations of surface, cluster, liquid, and crystal, and the simulation results are perfectly consistent with experimental results.[1,16,33–35] The lattice constant a_0 for Al at 0 K is 4.032 Å. For the glue potential, the melting point is about 936 K,[36] which is close to the experimental melting point of aluminum (about 933 K). The MD simulations are carried out at a constant temperature, constant volume, and constant atomic number. The time step is 0.06 (about 0.003 ps), and at each temperature the runs are made about 20 000 time steps (about 60 ps).

The static-structure factor $S(\mathbf{K})$ for specific reciprocal-space vector $\mathbf{K}$ [Eq. (8)] represents a quantitative measure for the long-range order and can be used as an order parameter describing the transition between disorder and order

$$S(\mathbf{K}) = \left\langle \left| \sum_{i \in GB} \exp[i\mathbf{K} \cdot \mathbf{r}_i(t)] \right|^2 \right\rangle \Big/ N_{GB}^2, \qquad (8)$$

where $\mathbf{r}_i(t)$ is the position of the ith atom at time t, $\langle \cdots \rangle$ is indicative of the time average, and N_{GB} is the number of atoms in the grain-boundary region. For a crystal the $S(\mathbf{K})$ is approaching 1; for liquid, it approaches 0. In order to study the stability and the nature of a disordered grain boundary, we define a distribution function of $P(S)$ which is the statistics of the value of $S(\mathbf{K})$ $[\mathbf{K}=2\pi/a_0(0,0,1)]$ of all molecular-dynamics time steps. Figure 2 shows the distribution functions at several temperatures from 400 K to 1050 K. The centers of the peaks represent the degree of disorder and order; the widths of the peaks as a measure of the fluctuation of $S(\mathbf{K})$ represent the instability of the GB structure. From Fig. 2, the peak is very narrow and the center of the peak is very near 1 in a low-temperature regime ($T \leqslant 400$ K), and this implies that the structure of the grain boundary is very ordered and stable in a low-temperature regime. At 850 K, the peak is broad (the minimum is at about 0.5 and the maximum is at about 0.9) and the center of the peak is much less than 1, which implies that the GB structure is disordered in this temperature. At about 950 K, the width of the peak is extremely broad (the minimum reaches 0.1 and the maximum still remains at about 0.9), which implies that the structure of the grain boundary is rather unstable. Sometimes the structure of the grain boundary is rather disordered (like a liquid) because of the $S(\mathbf{K})$ approaching 0, and sometimes it is just like a crystal structure with a long-range order because the $S(\mathbf{K})$ is probably approaching 1. This shows that at this temperature the coexistence of a liquid phase and a solid phase is reached. The above results show that the melting point of this system is

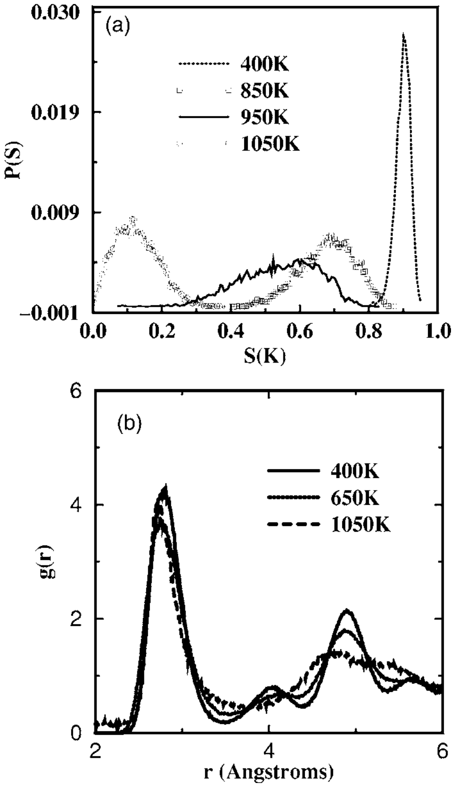

FIG. 2. The distribution functions $P(S)$ (a) and the pair-correlation functions (b) at various temperatures. The flat and wide distribution of $S(\mathbf{K})$ at 950 K represents the coexistence of liquid and solid.

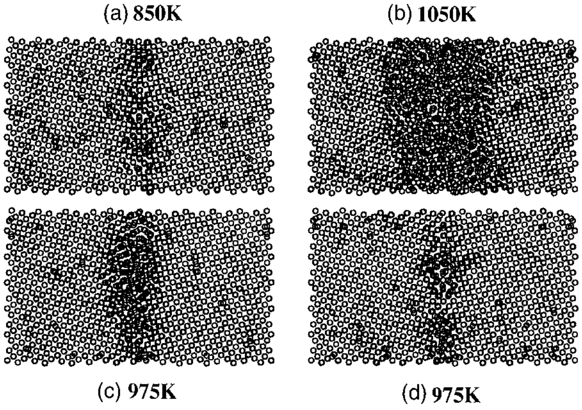

FIG. 3. The configuration of GB at high temperature. (a) The GB structure at 850 K (high-temperature disordered state). (b) The GB structure at 1050 K (melting state). (c) and (d) The GB structure at 975 K (superheated state) with unstable liquid film.

very close to 950 K. In our simulation, the large $S(\mathbf{K})$ fluctuation near 950 K indicates the signal of solid-liquid phase transition. At 1050 K the peak moves to the left and become narrow. When the position of the peak is close to zero, the GB is melting. Our results also show that the maximum superheated temperature T_s is close to 1050 K. We also calculated the pair-correlation functions $g(r)=1/4\pi\rho N\langle\Sigma_{i\neq j}\delta(r-r_{ij})\rangle$ at various temperatures that show the liquid behavior at 1050 K. Figures 3(a) and 3(b) illustrate the GB structures at 850 K and 1050 K.

Our model shows that between T_m and T_s, the GB will enter a new superheated state. The new state is characterized by (1) the coexistence of liquid and solid, and (2) the smaller size of the liquid nucleus than that of the critical nucleus at that temperature, which prevents the melting of the GB although $T>T_m$. Figures 3(c) and 3(d) show the competition of liquid and solid phase at 975 K in a superheated state. Sometimes there exists a liquidlike layer in the grain-boundary region [Fig. 3(c)] but it is metastable and may disappear, and the crystalline phase reemerges following time steps [Fig. 3(d)]. We will show that the superheated state (975 K) is rather different from the high-temperature disordered state at 850 K.

As the nucleus, melts a liquid layer can be artificially added to the GB region by the following methods: At a certain temperature T, we sample some layers with width $2l$; the atoms in these layers are heated up to an appropriate temperature $T_a(>T)$ until a liquid layer forms. By allowing all atoms to relax at temperature T again, we can obtain a new equilibrium structure at temperature T. Figure 4 shows that both the initial GB configurations [Figs. 4(a), 4(c), and 4(e)] have already added a liquid film with widths $2l$, and the final equilibrium configurations [Figs. 4(b), 4(d), and 4(f)] at 975 K and 850 K, respectively. At 850 K, for $2l=30$ Å, the liquid layer disappears after the relaxation about 50 ps [Figs. 4(a) and 4(b)]. However at 975 K for $2l=20$ Å, the liquid layer disappears [Figs. 4(c) and 4(d)] and for $2l=30$ Å the layer of liquid is still existent [Figs. 4(e) and 4(f)] after relaxation about 50 ps. Therefore, we can obtain 20 Å$<2l_c<$30 Å at $T=975$ K.

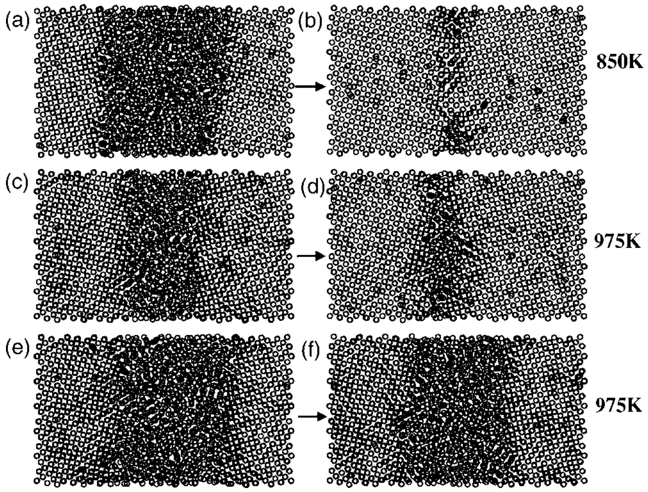

FIG. 4. The response of superheated state for adding liquid film. (a) and (b) at 850 K, $2l=30$ Å. (c) and (d) at 975 K, $2l=20$ Å. (e) and (f) at 975 K, $2l=30$ Å.

The above results also show that the superheated state (975 K) is very different in nature from the high-temperature disordered state (850 K). For high-temperature disordered states, the liquid film cannot induce the melting of GB; but for a superheated GB state, the GB melts only when the width of the liquid film is larger than the critical width l_c. In order to define the correlation length ξ and the thickness of the liquid film, we calculate the corresponding atom-density profile [Fig. 4(f)]. Our results show that at 975 K, the critical width $2l_c$ is between 20 Å and 30 Å and $\xi=10$ Å, thus $1.0<l_c/\xi<1.5$, which is consistent with the theory model $l_c/\xi=1.4$ with $T_m=950$ K and $T_s=1050$ K in Eq. (7) (see Fig. 5).

IV. DISCUSSION AND CONCLUSION

In summary, we study the possibility of a superheated GB state by both a theoretical model and MD simulation. Our results indicate that we can obtain superheated grain boundaries by having a properly controlled homogeneously nucleating precession when increasing temperature. If there are liquid nuclei whose sizes, are larger than a critical size, the

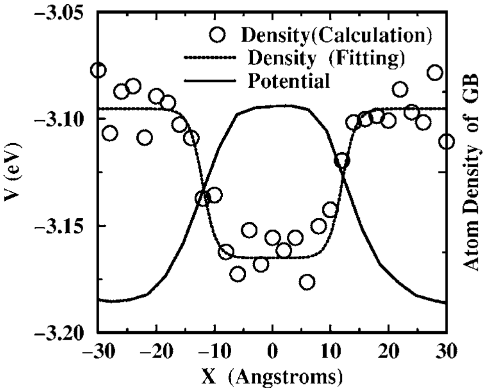

FIG. 5. The profile of potential and atomic density across the GB at 975 K.

superheated grain boundary melts, or the grain boundary waits for homogeneous melting when the temperature is higher than the maximum superheated temperature.

We must note that pressure plays an important role for the superheated grains in experiments and computer simulations. In experiments, both coating with high melting-point materials and internal heating induce internal pressure in the melting region. In our simulation there is also internal pressure in the melting region because the size of the simulation cell does not change with the increasing temperature. In this paper we only consider the superheated state due to the nucleation mechanism. The pressure mechanism and nucleation mechanism become intertwined and influence the melting of materials. Pressure leads to the increase of melting points. The melting point is about 950 K in our simulation and higher than the experimental melting points $T_{exp}=933$ K and $T_{glue}=936$ K[36] in simulation using glue potential without internal pressure. Pressure increases the melting point less than $T_m - T_{glue} \sim 950\text{ K} - 936\text{ K} = 14$ K. However, the nucleation mechanism leads to superheating about $T_s - T_m \sim 100$ K.

The proximity effects of the superheated grains are also important to induce the superheated grain boundary sandwiched between two properly superheating grains. Because the superheated state is a metastable state in the phase diagram, we do not expect it is long-lived. The superheated materials melt by the nucleation mechanism or homogeneously melt at higher temperature.

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