Asymmetric Crystallization and Melting Kinetics in Sodium: A Molecular-Dynamics Study

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Computer-simulation studies of the crystallization and melting of a model of sodium have been carried out to determine the (001) steady-state velocity versus temperature relation in the temperature region 81 to 497 K. Using a form of transition-state theory there is an apparent slope discontinuity in the velocity versus temperature relation at the melting point, which is correlated with slope discontinuities in averaged order parameters for planes buried in the crystal; planes appear to soften more per unit temperature increase above the melting point, leading to larger melting velocities.

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In many cases crystallization and melting processes are heterogeneous, that is, they involve the motion of a liquid-solid interface. The velocity, v, of this interface as a function of deviations from the equilibrium melting temperature, T_E, is called the interface response function, and is a fundamental quantity describing the crystallization and melting processes. Most theoretical discussions of the interface response function use some generalization of the Wilson-Frenkel theory.[1,2] Such theories are often called transition-state theories since they assume the melting or solidification takes place through some intermediate or transition state.[3,4] In a simple version of the theory the interface response function is given by

$$v(T) = C_1 \exp(-Q/k_B T)$$
$$\times [1 - \exp(-L\Delta T/k_B T_E T)], \quad C_1 = \text{const}, \quad (1)$$

where Q is the activation energy for diffusion in the liquid, L is the latent heat of fusion per particle, and $\Delta T = T_E - T$ is the deviation from the equilibrium melting temperature. At temperatures below $T \approx T_E/2$ the diffusion-type term in Eq. (1), $\exp(-Q/k_B T)$, makes $v(T)$ decrease exponentially, whereas near T_E, $v(T)$ is linear with a slope proportional to $T_E - T$. For clarity of discussion we shall call crystal growth which is described by Eq. (1) with $Q \neq 0$ diffusion-limited growth, whereas if $Q = 0$ we shall call the growth non-diffusion-limited. Equation (1) correctly predicts the crystallization rates for various materials; as an example, for GeO_2, $v(T)$ is properly explained by Eq. (1) over a 400-K temperature range.[5]

Equation (1) has never been checked over a significant temperature range for monatomic simple metals, since the crystallization and melting rates are so high in these materials that they are difficult to determine experimentally. Turnbull,[6] Turnbull and Bagley,[7] and Spaepen and Turnbull[8] have suggested that the solidification of monatomic metals is non-diffusion-limited and is only limited by the frequency of collisions from the melt on the crystal face. The conjecture of Turnbull and coworkers is supported by various experiments including those of Ruhl and Hilsch[9] who showed that metal films deposited at 3 K undergo crystallization at 16 K, Will-

necker, Herlach, and Feuerbacher,[10] Walker,[11] and Colligan and Bayles[12] who found large solidification velocities ≈ 50 m/s in undercooled liquid metals undergoing dendritic growth, and MacDonald, Malvezzi, and Spaepen[13] who found large solidification velocities ≈ 100 m/s in picosecond-laser-melting experiments on metals. On the theoretical side Coriell and Turnbull's[14] analysis of the data of Walker[11] assumed a non-diffusion-limited growth model, and the analysis of MacDonald et al.[13] of their laser-melting data also assumed a non-diffusion-limited growth model.

Computer-simulation work by Broughton, Gilmer, and Jackson[15] using the Lennard-Jones potential to study fcc (100) crystallization clearly showed that crystal growth for this case is not diffusion limited. Their modification of the Jackson-Chalmers theory was to replace the diffusion term in Eq. (1), $\exp(-Q/k_B T)$, by the thermal velocity of the atoms which is proportional to $T^{1/2}$. This leads to the expression

$$v(T) = C_2 T^{1/2} [1 - \exp(-L\Delta T/k_B T_E T)], \quad C_2 = \text{const}. \quad (2)$$

The constant C_2 is related to other constants by[15]

$$C_2 = a f_0 (3k_B/m)^{1/2}/\lambda, \quad (3)$$

where a is the interatomic distance, λ is the average distance a particle moves to reach the final growth position, f_0 is the interface-site distribution for the process being discussed, and $(3k_B/m)^{1/2}$ comes from the average thermal velocity. In Fig. 1 we show as small circles the simulation results of Ref. 15, assuming the system being described is argon, as well as Eq. (2) for the parameter values $T_E = 74$ K, $L/k_B T_E = 1.5$, and $C_2 = 16.9$ m/s K$^{1/2}$. The value for C_2 corresponds to the choice made in Ref. 15, $f_0 = 0.27$, $\lambda = 0.4a$. Using this value for $L/k_B T_E$ and the value of $T_E = 74$ K we find $L = 220$ cal/mol, whereas the experimental value for argon is 284 cal/mol. Figure 1 shows that the Broughton-Gilmer-Jackson modification of transition-state theory gives a satisfactory explanation of the crystallization of an fcc (001) Lennard-Jones system and supports the conjecture of Turnbull and coworkers that crystal growth of monatomic systems may not, in all cases, be diffusion limited. Note that any reasonable value of Q in Eq. (1) would make the velocity
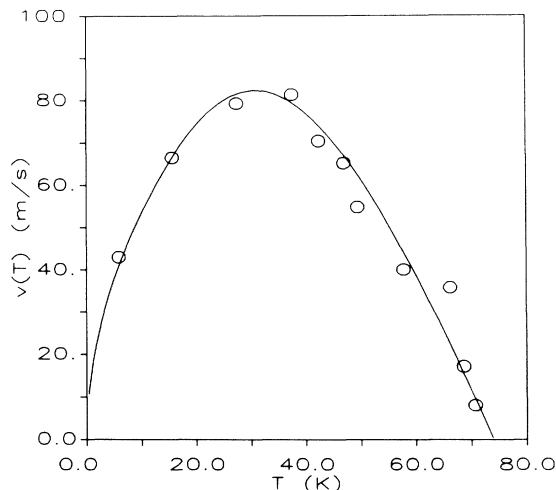
FIG. 1. The interface response function for crystallization as determined in Ref. 15. The circles are the simulation values while the full line is Eq. (2) with the parameter values given in the text. The values assume the system being discussed is argon.

too small at low temperatures. In these Lennard-Jones simulations no results were reported for melting. Thus, an important unanswered question is whether the excellent agreement between the crystallization velocities and Eq. (2) shown in Fig. 1 also occurs for melting.

In this paper we report on our studies of bcc (001) liquid epitaxial crystallization and melting of a model of sodium. The interaction potential energy between the atoms comes from pseudopotential perturbation theory and has been found to accurately model many of the thermodynamic properties of sodium.[16] Besides using a different crystalline structure than Broughton, Gilmer, and Jackson[15] (bcc), we also did extensive studies of the melting process.

The basic computational procedure used molecular dynamics following the successful strategy reported by Kluge and Ray[17] for growth and melting simulations of (001) silicon. Our simulations all started from a well equilibrated solid of 864 particles at 310 K interacting via the model potential. The particles were arranged in a bcc crystal lattice with the length of the system along the z direction being twice as long as either the x or y length. The solidification and melting took place along the z direction which was the [001] direction in the crystal. There were 24 (001) planes along the z direction with each plane containing 36 particles. The left-hand side of the crystal was at $z = 0$, and the right-hand side of the crystal ends near $z = 103$ bohrs (1 bohr $= 0.0529177$ nm). The first three planes on the left-hand side were held fixed to simulate a solid substrate. The next two planes (4 and 5) were used to control the temperature, energy being either added or removed every 20 iteration time steps in order to keep the temperature of the system nearly constant during the growth or melting process. The solidification or melting takes place in planes 13–24,

which were far enough removed from planes 4 and 5 so that the energy extraction or addition has a small disturbance on the dynamics of the solidification or melting processes. Periodic boundary conditions were imposed in the directions transverse to the z axis, while the boundary condition on the right-hand side of the sample was a free boundary. The size of the computational cell in the x and y directions was adjusted by using the experimental lattice constants at the given temperature and the interaction potential was chosen to be appropriate for that density. The iteration time step was set equal to 6.85 $\times 10^{-16}$ s and the range of the potential was set at 15.7 bohrs.

In order to start the simulations the particles in planes 4–12 were held fixed and the temperature in planes 13–24 was increased by velocity scaling until a temperature of ≈ 450 K was obtained. The system was then equilibrated for 40 000 time steps or 27.4 ps. The right-hand side of the system was then a well equilibrated liquid with a final temperature of 420 K. We then cooled this liquid to 310 K in 500 time steps. The particles in planes 4–12, whose positions had been held fixed during this melting and equilibration, were then allowed to move and participate in the dynamics. The system in this configuration consists of a hot solid (planes 4–12) in contact with a supercooled liquid at a temperature near 310 K. The entire system was then either heated or cooled to the desired temperature by carrying out velocity scaling over 500 time steps. After this the system was allowed to evolve in time on its own with the only outside interference being the velocity scaling for temperature control in planes 4 and 5 every 20 time steps.

Growth runs were made at twelve different temperatures between 81 and 369 K while melting runs were made at five different temperatures between 400 and 497 K. The velocity of crystallization can be obtained, for example, by studying the rate of arrival of particles into the positions occupied when the system was fully grown, since this relation has an approximately linear region during steady-state growth. For melting we determine the rate of departure of particles from these same positions. In Fig. 2 we show the growth of the system at an interface temperature of 340 K as a series of density plots along the z direction at different times. At time zero the right-hand side of the system was liquid and the left-hand side was crystalline as shown by the ordering into planes. As time proceeds crystal growth takes place as the atoms move into their crystalline positions. This shows up in Fig. 2 as a movement of the crystalline portion of the sample to larger values of z in time. The steady-state velocity of growth at this temperature of 340 K is 45.9 m/s. Figure 3 shows the number of particles grown versus time for the growth at 138 K. A linear least-squares fit to the linear portion of this growth curve gives a steady-state velocity of 132 m/s for the crystallization velocity at this temperature.
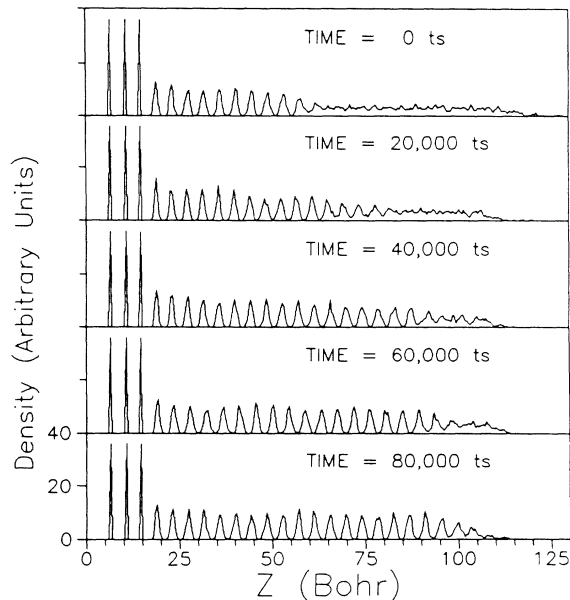
Figure 4 gives the simulation velocities versus inter-

FIG. 2. A series of plots of the density along the crystallization axis (z) at different numbers of time steps (ts) in one of our simulations of sodium.

face temperatures for all growth and melting simulations along with a fit of Eq. (2) to these points for the parameter values $C_2 = 15.6$ m/s K$^{1/2}$, $L/k_B T_E = 0.918$, and $T_E = 396$ K. The value for L was determined in the simulation by recording the energy extracted in holding the temperature nearly constant and the number of particles that are crystallized, and corresponds to a value of 722 cal/mol, whereas the experimental value for sodium is 622 cal/mol. Our choice for the constants making up C_2 are such that $af_0/\lambda = 0.48$. Although Eq. (2) fits the growth values very well it fails to even follow the general trend of the melting velocities which are much higher than the theory predicts. Thus, melting would appear as in Fig. 2 but with time reversed and increasing more rapidly.

The simulation data above the melting point can be fitted in an *ad hoc* manner by using Eq. (2) with a different value of af_0/λ above T_E. We find that Eq. (2) with $af_0/\lambda = 1.85$ and the other parameters unchanged adequately fits the melting points in Fig. 2. If this is done then one finds a slope discontinuity at T_E; the slope being -0.72 m/s K on the low-temperature side and -2.77 m/s K on the high-temperature side. The ratio of these two slopes gives a value of 3.8.

Because of microscopic reversibility, it is generally believed that if molecules are added to or taken from similar interface sites, in crystallization and melting, respectively, then the curves of crystallization rate and melting rate versus temperature should be continuous with the same slope through the melting temperature.[18] One usually assumes that the interface-site distribution function for the (001) bcc face is the same for crystallization and melting and there should not be a slope discontinuity in
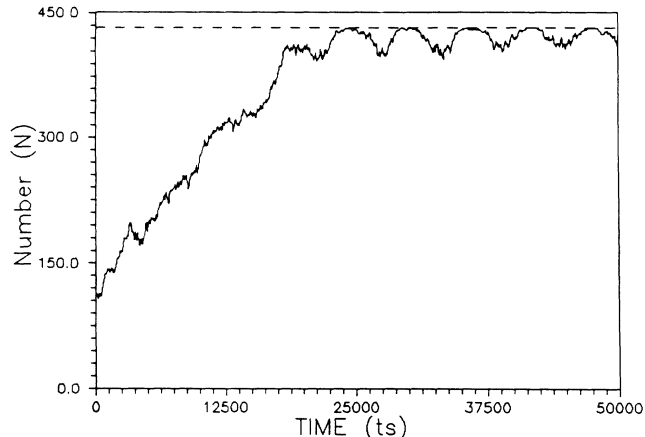
FIG. 3. The number of particles grown vs the number of times steps (ts) into the 138-K simulation.

the interface response function at the melting point.

We do not have a theoretical reason why there should be a slope change in the interface response function at the melting temperature for model sodium; however, we found an interesting correlation between this slope discontinuity and the slope discontinuities of the two-dimensional structure factors, $S(\mathbf{k})$, of planes buried deep in the crystalline portion of the system as a function of the temperature. The structure factor is an order parameter for the planes and is defined by

$$S(\mathbf{k}) = \left| \sum_{a=1}^{N} \exp(i\mathbf{k} \cdot \mathbf{r}_a) \right|^2 / N, \quad N = 36, \qquad (4)$$

where $\mathbf{k} = (2\pi/L)(n_x \hat{\mathbf{x}} + n_y \hat{\mathbf{y}})$, n_x, n_y are integers, and $\mathbf{r}_a$ is the position of particle a in the (001) plane. In Fig. 5 we show the average $S(\mathbf{k})$ of planes 6 and 8 for $\mathbf{k} = (2\pi/L)(6,0)$ as a function of the temperature of the planes. These planes are buried in the crystalline region of the system for the points shown in Fig. 5. For plane 6 a weighted linear least-squares fit of the data between 19 and 334 K gives a slope of -0.0158/K, whereas a fit on
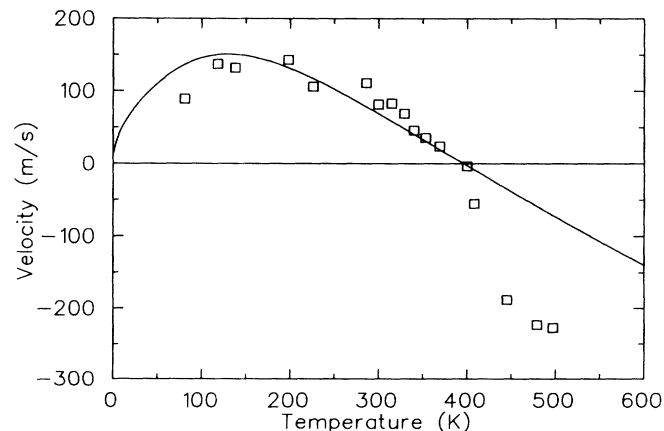

FIG. 4. The squares are the velocity vs temperature data determined in our simulations for a model of sodium and the full line is Eq. (2) with the parameter values given in the text.
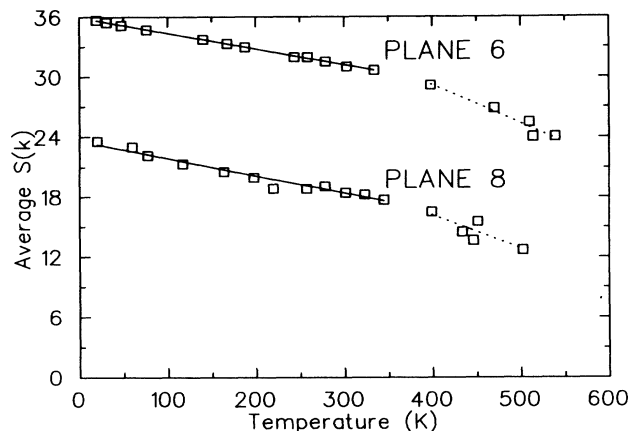
FIG. 5. The averaged two-dimensional structure factor of two planes buried in the crystal as a function of temperature. The lines are weighted least-squares fits to the simulation values.

the melting side from 398 to 539 K gives a slope of $-0.0383/K$. The two lines through the data cross at $T = 380$ K. The ratio of the slopes of the two straight lines gives 2.4 which is the same order of magnitude as found for the interface response function of Fig. 4. For plane 8 the ratio of the slopes is 1.9. Although we have not yet ruled out all possible reasons for the slope discontinuities in $S(k)$ shown in Fig. 5, we suggest they may be associated with anharmonic softening of the crystal because of the superheating. The softening of a plane, in the crystalline region of the system, for a given increase in temperature, is about twice (1.9 for plane 8 and 2.4 for plane 6) as great above the melting point as below the melting point. This increased rate of softening shows itself in the rapid increase of the velocity above the melting point and is consistent with the rapid increase in the melting velocities.

A possible slope discontinuity in the interface response function of systems for which the interface-site distribution function is thought to be the same for crystallization and melting has been discussed.[19-21] In nonequilibrium simulations of the laser melting of a Lennard-Jones system Chokappa, Cook, and Clancy[19] discussed a slope change in the velocity of growth and melting; however, it is difficult to relate their velocities to the steady-state velocities discussed in our work and those in Ref. 15, since the simulations in Ref. 19 were developed to model the actual nonequilibrium processes in the experiments. The experimental work by Larson, Tischler, and Mills[20] on silicon suggested a possible slope discontinuity in the interface response function at the melting point. Experimental work by Tsao et al.[21] on silicon reported no slope discontinuity in the interface response function at the melting point. Thus, the experimental situation for silicon is not clear and it is also not clear whether our simulations of sodium should have any simple relationship to silicon.

We discussed crystallization and melting simulations of model sodium and presented our calculation of the interface response function. The crystallization part of the interface response function is non-diffusion-limited and is explained by replacing the diffusion term in the transition-state theory by the average thermal velocity. This same equation does not fit the melting part of the interface response function determined in the simulations. The melting data can be fitted in an an hoc manner by increasing the parameter af_0/λ in Eq. (2) and thereby introducing a slope discontinuity in the interface response function at the melting point. This appears to place the standard theory, represented in this paper by Eqs. (1) and (2), of solidification and melting kinetics of a monatomic metal into conflict with the principle of microscopic reversibility. This may imply that a more comprehensive theory of rapid crystallization and melting, which includes more details of the processes taking place, is needed.

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