

Interface kinetics of freezing and melting with a density change

Peter M. Richards

Sandia National Laboratories, P.O. Box 5800, Albuquerque, New Mexico 87185-5800

(Received 19 January 1988)

The change in density between liquid and solid is shown to affect the interface velocity for rapid solidification or melting. The effect is asymmetric, being much more pronounced for freezing than for melting, regardless of whether the liquid is more or less dense than the solid. Freezing velocity is limited by the rate at which a density excess can be transported away from or into the interface, but melting speed can still approach the speed of sound or thermal velocity. It is argued that relaxation of the density excess should be viewed on the molecular level, whereby diffusive jumps take place. This leads to a much slower removal of the excess than if it were propagated away as sound and a corresponding much greater effect on the interface motion. A modified transition-state theory is presented which incorporates the density change. Comparison is made with experiments on silicon and with molecular-dynamics simulations of freezing of a Lennard-Jones liquid. Satisfactory agreement is obtained, particularly in regard to the large asymmetry between freezing and melting speeds observed near the melting point in silicon.

I. INTRODUCTION

The speed at which the liquid-solid interface moves during heterogeneous freezing or melting has been a problem of long-standing interest.¹ In early work the transformation rates were generally slow enough that quasiequilibrium conditions could be assumed and conventional transition-state theory^{1,2} (TST) applied. In TST the interface velocity v is driven by the difference between liquid and solid free energies at the interface temperature T , and v may also contain an activation factor if an intermediate "transition state" is required whose free energy is greater than that of the equilibrium liquid or solid. More recent techniques of rapid solidification and melting have produced speeds, however, where the equilibrium conditions and thus TST can well be questioned. It has been suggested,³ for example, that for pure metals v is limited only by the speed of sound c .

Of particular note and concern here are the pulsed-laser experiments^{2,4} on the melting and subsequent recrystallization of silicon. Although the reported speeds are still an order of magnitude less than c , there is a striking asymmetry between freezing and melting which cannot be explained by TST. (Asymmetry in this paper means the difference in a property such as $|v|$ between melting and freezing for the same absolute difference $|T - T_M|$ between T and the melting point T_M .) Although the melting speed is 190 m/s for what may be only moderate overheating,⁵ v for freezing into the crystalline state is only 15 m/s at the 240-K undercooling beyond which the amorphous phase is formed.⁶ More dramatic asymmetry is found in the x-ray studies⁴ which gave no evidence for overheating when $\langle 111 \rangle$ silicon melts with $v = -11$ m/s but 110-K undercooling for a freezing $v = 6$ m/s. (The usual² convention is adopted that $v > 0$ corresponds to freezing and $v < 0$ to melting.) These data are shown in Fig. 1. Recent transient conductance measurements⁷ have, however, failed to confirm the

strong degree of asymmetry seen in the data of Ref. 4; so there remains some question as to just how large the asymmetry really is. If it is manifested over as narrow a temperature range as the x-ray data suggest, it is difficult to explain by conventional TST. This is because for such small departures from the equilibrium crystal melting point $T_M = 1685$ K, the various kinetic coefficients of TST should have negligible temperature dependence and the free-energy differences should be much less than $k_B T$ so that one would expect $v \propto T_M - T$. That is, the speeds for given small amounts of undercooling and overheating should be the same, as seen for the TST curves in Figs. 1 and 3.

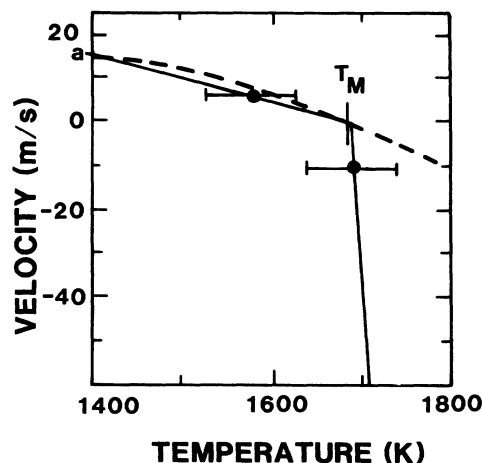


FIG. 1. Interface velocity vs temperature in silicon. Experimental points are from Ref. 4. Point a is freezing velocity from Ref. 6 at temperature below which amorphous phase is formed. Dashed curve is a fit to normal TST adjusted to give agreement at point a . Straight lines are guides to the eye only to emphasize asymmetry of data from Ref. 4.

The purpose of this paper is to show that asymmetry in v of the size found in silicon, even for the data of Ref. 4, might be accounted for by the sizeable change (8%) of density between liquid and solid. To achieve this end, a fairly detailed description is given of interface kinetics when there is an accompanying density change. Particular attention is paid to the rather crucial question of just how excess density is transported away from the interface (or conversely how density is transported into a deficient interface).

The situation is postulated to be shown in Fig. 2(a). The liquid is assumed to be much more compressible than the solid, so when a layer of liquid converts to solid in a substance such as silicon whose liquid is more dense than the solid, an excess number of molecules are forced

into the liquid ahead of the interface. Displacements of the order of the average intermolecular spacing a have occurred in a time a/v . This is assumed to produce "interstitial-like" defects (major molecular rearrangements leading to locally closer packing) in the liquid which cannot be relaxed by the small amplitude vibrations of a sound wave. Rather diffusive jumps are required. The more common case of a liquid less dense than the solid would lead, on freezing, to the formation of "vacancies" in the liquid ahead of the interface, and to the more familiar scenario of free-volume relaxation.⁸ In either case, I assume, largely by analogy with the known features of structural relaxation in glasses and free-volume effects,⁸ that a few diffusive hops are required before either the defects annihilate or the rearrangement be-

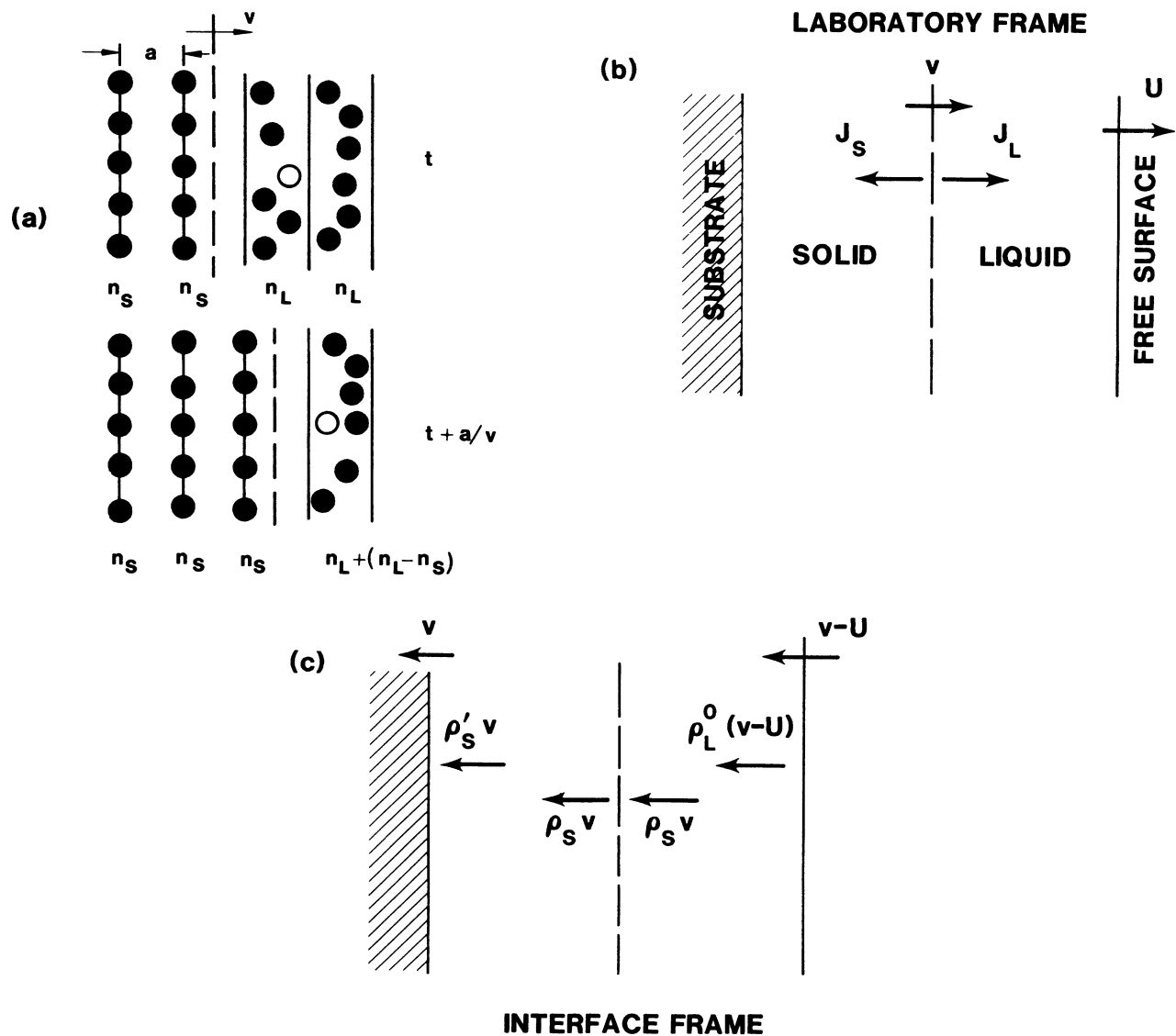


FIG. 2. Schematic of particle flow at interface with a density change. Freezing of a substance whose liquid is denser than solid is shown. (a) Arrangement of n_S solid atoms and average of n_L liquid atoms between planes separated by distance a . As interface moves distance a in time a/v molecule shown as open circle has to move back into liquid to accommodate density change. Illustration is for liquid 20% denser than solid. (b) Flows in laboratory frame of reference. Solid is fixed to an immobile substrate, but liquid has a free surface. J_L and J_S are particle currents away from interface. (c) Same as (b) but in interface frame of reference. Currents are now labeled as specific density times velocity.

comes so slight that it can be relaxed by generation of small-amplitude phonons. Consequently the time a/v for the interface to traverse the distance a can be no shorter than the order of a^2/D (D is the self-diffusion coefficient) in order for steady-state conditions to apply; so the limiting velocity is of the order of a/D . For relaxation of the excess density by sound, it takes only a time a/c for the interface density to equilibrate and thus the limiting velocity is c . For typical values $a=3 \text{ \AA}$, $D=10^{-4} \text{ cm}^2/\text{s}$, $c=4 \times 10^3 \text{ m/s}$, the time a^2/D is 2 orders of magnitude larger than a/c ; so diffusion provides a much more serious limitation.

I have no proof at present for the assumption that diffusive hops are required. Molecular-dynamics (MD) simulations on relaxation of vacancies in undercooled liquids⁹ show that diffusion time scales are involved. Although there are numerous MD treatments of self-diffusion in liquids, I am aware of none that specifically answer the question of how rapidly an increased density of molecules would be relaxed. That some diffusive hops are required seems reasonable, and it is at least worthwhile to explore the consequences on interface kinetics.

Heat flow^{10,11} can also limit the interface kinetics. But the present work assumes throughout that heat flow is sufficiently rapid and the necessary temperature gradients maintained to keep the interface temperature at a constant value T . This may seem inconsistent with the notion that excess density in the liquid relaxes by a slow diffusion process. The crucial point here is that, because of the large electronic contribution, the thermal diffusion coefficient of liquid silicon is estimated¹² to be almost 4 orders of magnitude greater than the self-diffusion coefficient D .

The steady-state densities on the liquid and solid sides of the interface are calculated in Sec. II by simple considerations of mass flow. Salient features are that these densities depend on v , and the dependence is asymmetric such that there is a much more profound effect on freezing than on melting. Section III presents a modified TST which is essentially just normal TST with a v -dependent free-energy difference. This dependence arises because the pertinent free energies are functions of the steady-state interface densities which depend on v as shown in Sec. II. Both the symmetric and entropy-limited growth versions² of TST are discussed. Appendix B shows how TST can further be modified to include fluctuations in interface densities from their steady-state values. Section II gives the density as a function $\rho(v)$ and Sec. III provides an independent relation for $v(\rho)$, so their combined equations can be solved numerically for v and the interface densities (and thus pressure) at a given interface temperature. Results are compared with experiment in Sec. IV for both silicon and the freezing of a Lennard-Jones liquid, the latter as obtained by molecular-dynamics simulation.¹³

II. STEADY-STATE INTERFACE DENSITIES

The densities on the liquid and solid sides of the interface, ρ_L and ρ_S , respectively, are derived in the steady-

state of the interface moving with velocity v as follows, with the aid of Fig. 2. The crystalline solid side of the interface consists of planes separated by a distance a . The liquid side is divided into layers of thickness a . Unit area is assumed. The language and sketches are explicitly for freezing with $\rho_L > \rho_S$, but the resulting equations are equally valid for melting and/or $\rho_L < \rho_S$.

Figure 2(a) illustrates that as the interface moves forward a distance a , $n_L = \rho_L a$ molecules of liquid are converted to $n_S = \rho_S a$ molecules of solid. Conservation of mass requires that $n_L - n_S$ molecules flow away from the interface. This excess is shown in Fig. 2(a) as all entering the liquid, but Fig. 2(b) shows a more general case of the excess as particle currents J_L and J_S into the liquid and solid, respectively, measured in the laboratory frame of reference. The sample, as shown, has a free surface which has been melted by the laser pulse, while the other surface which remains solid is fixed to an immobile substrate. The free surface can move with velocity U but, since it is under zero pressure, the density in the first few atomic layers from the free surface must have the equilibrium value ρ_L^0 . (In order to separate out the effects of density change only, temperature gradients are neglected in this illustration, so no distinction need be made between equilibrium densities at temperatures of the interface and surfaces.) Steady-state conditions demand $J_L = \rho_L^0 U$ and $J_S = 0$. The latter, which is a consequence of the fixed substrate, gives the useful conclusion that, as in Fig. 2(a), all excess molecules must go into the liquid if steady state prevails. Figure 2(c) shows the flows as viewed by an observer at rest with respect to the interface. The current entering the interface from the liquid is $\rho_L v$, while that leaving the interface into the liquid is $(\rho_L - \rho_S)v$, since, from the above, all excess molecules enter the liquid. The net flow from the liquid to interface is thus $\rho_S v$. In steady state this is balanced by the current entering from the free surface, which is $\rho_L^0(v - U)$ in the interface frame of reference. Hence we obtain

$$U = (1 - \rho_S/\rho_L^0)v \quad (1)$$

for the free-surface velocity. Similar consideration of the currents in the solid at the interface and substrate gives simply

$$\rho'_S = \rho_S, \quad (2)$$

where ρ'_S is the solid density at the substrate, since no excess enters the solid and the substrate surface moves away from the interface at v . Equation (1) is not used here, but it would be a consideration if the free-surface velocity could be measured in future experiments. Equation (2), however, is important for subsequent comparison with the x-ray data of Ref. 4. The implication is that, in the steady state, any departure of ρ_S from its equilibrium value ρ_S^0 is uniform from the substrate to the interface. That is, in the absence of temperature gradients, the solid is under uniform compression or tension. Such is not necessarily the case for the liquid. $\rho_L \neq \rho_L^0$ implies a pressure gradient which is possible since the excess molecules drifting toward the liquid free surface experience a friction force which balances the pressure differential.

Relaxation is accomplished by the defects or excess density migrating away from the interface region until they are annihilated or propagated away rapidly as phonons. The excess density is assumed to relax toward its equilibrium value at a rate Γ ,

$$\frac{d}{dt}\rho_L = -\Gamma(\rho_L - \rho_L^0). \quad (3)$$

Equating the rate at which excess density enters a layer of liquid from the interface to the rate at which it is transported away from the layer yields the steady-state condition

$$(\rho_L - \rho_S)v/a = \Gamma(\rho_L - \rho_L^0). \quad (4)$$

Departures of ρ_S and ρ_L from their equilibrium values ρ_S^0 and ρ_L^0 imply nonzero pressure at the interface. I assume this pressure p to be continuous on the liquid and solid sides of the interface, just as the temperature is assumed to be. Consequently one may write

$$\rho_S - \rho_S^0 = \gamma(\rho_L - \rho_L^0), \quad (5)$$

where, in the limit of small changes from equilibrium, $\gamma = (\rho_S^0 K_L / \rho_L^0 K_S)$ in which K_L and K_S are, respectively, isothermal bulk moduli of the liquid and solid. Use of Eq. (5) in (4) gives, with some manipulation,

$$\rho_L - \rho_L^0 = v(\rho_L^0 - \rho_S^0) / [\Gamma a - v(1 - \gamma)] \quad (6)$$

for the increase in liquid density at the interface. Although Eq. (6) was derived with language pertinent to freezing ($v > 0$) and liquid denser than solid ($\rho_L^0 - \rho_S^0 > 0$), it is also valid for $\rho_L^0 - \rho_S^0 < 0$ and/or melting ($v < 0$) provided account is taken of the sign of v . This may be seen by noting that the right-hand side of Eq. (4) is the same for melting or freezing while the left-hand side changes sign on going from freezing to melting. The latter holds because if the interface motion is reversed, a plane of solid is converted to liquid in the time a/v , requiring $(\rho_L - \rho_S)a$ molecules to be removed from adjacent layers.

Equation (6), which forms one of the foundations of the theory, is thus quite general as long as the algebraic nature of v is noted (i.e., $v < 0$ for melting). Consequently there is an inherent asymmetry between melting and freezing. For the liquid relatively more compressible than the solid, $\gamma < 1$ ($\gamma \approx \frac{1}{3}$ for silicon) so that the freezing velocity $v > 0$ must be kept below $\Gamma a / (1 - \gamma)$ to avoid a catastrophic divergence. No such limit is imposed on the melting velocity $v < 0$, however. A physical interpretation of this asymmetry is that for freezing the interface and excess density are both moving into the liquid. The excess will pile up at an unacceptable rate unless the interface is slowed to an acceptable pace. On melting, the interface moves away from the liquid; so the density can only go to zero rather than pile up. This assumes most of the density change occurs in the liquid ($\gamma < 1$). The situation would be reversed, with the divergence occurring for melting, if $\gamma > 1$.

It is interesting to compare the above results which assume simple relaxation of the excess density with those for propagation and diffusion. If the excess propagates away from the interface at speed c into the liquid, it is

easy to show that Eq. (6) remains valid with $\Gamma = c/a$. This neglects reflection from the free surface back to the interface and thus assumes an infinite medium. The case of diffusion combined with relaxation is described by the equation

$$\frac{\partial \delta \rho}{\partial t} = D \frac{\partial^2 \delta \rho}{\partial x^2} - \Gamma \delta \rho, \quad (7)$$

where $\delta \rho$ is the departure of liquid density from ρ_L^0 . The resulting steady-state density when a source term is added at the interface is derived in Appendix A. A noteworthy feature is that no steady-state solution exists for pure diffusion, $\Gamma = 0$, and a highly incompressible solid.

III. TRANSITION-STATE THEORY WITH DENSITY CHANGE

Section II gave an expression (5) for the steady-state interface densities in terms of the velocity v . Since the goal is to obtain v for a given temperature T , completion of the theory requires a second, independent, relation for v in terms of the densities and temperature. This is provided by rate equations which describe transformation of molecules of liquid to solid and vice versa. The simplest approach, taken here, is to use conventional TST but with the liquid and solid free energies g_L and g_S evaluated at the steady-state interface densities. It is first helpful to review briefly the salient features of TST, especially since different forms of it have been shown^{2,14} to possess different asymmetry—albeit not over the narrow temperature range of the x-ray data on silicon.⁴ It is generally agreed that the interface velocity is given by

$$v = a(W_{LS} - W_{SL}), \quad (8)$$

where W_{LS} (W_{SL}) is the rate to transfer a layer of liquid (solid) of thickness a to solid (liquid), and that the rates should be in the ratio

$$W_{LS}/W_{SL} = \exp[\beta(g_L - g_S)], \quad (9)$$

with $\beta = 1/k_B T$; and g_L and g_S are Gibbs free energies per molecule of liquid and solid, respectively, evaluated at the interface temperature T and pressure p . The latter expression of detailed balance or microscopic reversibility is not, however, satisfied by a recent modification¹⁵ of TST. Since only the ratio is given by Eq. (9), there remains considerable flexibility which can lead, among other things, to ambiguities in the limiting speeds of freezing and melting. Two forms in common use² are the "symmetric" and "entropy-limited growth." The former takes

$$W_{LS} = v \exp[-\beta\theta(g_S - g_L)], \quad (10)$$

$$W_{SL} = v \exp[-\beta\theta(g_L - g_S)]. \quad (11)$$

The function $\theta(x)$ is defined as $\theta(x) = x$ for $x > 0$ and $\theta(x) = 0$ for $x < 0$. This definition guarantees that only transitions which involve an increase of free energy are activated so that the prefactor v represents a maximum transition rate. Use of Eqs. (10) and (11) in Eq. (8) allows the speed to be expressed as

$$|v| = v_0 a \exp(-\beta h) [1 - \exp(-\beta |\Delta g|)], \quad (12)$$

where $\Delta g = g_L - g_S$ and v has been written as $v_0 \exp(-\beta h)$ with h an activation enthalpy. We see that, for temperatures such that $\beta h \ll 1$, the freezing and melting speeds have the same maximum value $v_0 a$ and are the same for a given $\beta \Delta g$; hence, Eqs. (10) and (11) are called the symmetric version. For entropy-limited growth it is assumed that there is an intermediate state with free energy $g^* > g_S, g_L$ through which transitions proceed. Thereby

$$W_{LS} = v \exp[-\beta(g^* - g_L)], \quad (13)$$

$$W_{SL} = v \exp[-\beta(g^* - g_S)]. \quad (14)$$

In order to have $g^* > g_L, g_S$ at all temperatures requires $s^* < s_S$ and $h^* > h_L$, where the s 's and h 's are entropies and enthalpies of the various states ($h_L > h_S, s_L > s_S$). The frequency v is not necessarily the same in Eqs. (13) and (14) as in Eqs. (10) and (11). With some rearrangement the velocity resulting from Eqs. (13) and (14) can be written as

$$v = v_0 a \exp(-\beta h) \{ \exp[-(s_L - s_S)] - \exp[-\beta(h_L - h_S)] \} \quad (15)$$

with $v_0 = v_{00} \exp(s^* - s_S)$, $h = h_0 - h_L + h^*$, where v_{00} and h_0 are, respectively, prefactor and enthalpy associated with v in Eqs. (13) and (14), and the s 's are in units of k_B . Equation (15) is highly asymmetric in that, for $\beta h \ll 1$, the ratio of maximum melting speed [obtained for $\beta(h_L - h_S) \ll 1$] to maximum freezing speed [$\beta(h_L - h_S) \gg 1$] is $\exp(s_L - s_S) - 1 = 35$ for silicon. As noted above and seen in Fig. 1, Eq. (15) is, however, symmetric near T_M . The factor $a v_0$ in either Eq. (12) or (15) is a maximum speed and therefore usually taken as either the speed of sound c or proportional to the thermal velocity. Although Eq. (15) is useful for displaying the asymmetry, it is more convenient for subsequent discussion to factor out the entropy term and rewrite it as

$$v = v_0 a \exp(-\beta h) \exp[-(s_L - s_S)] [1 - \exp(-\beta \Delta g)]. \quad (16)$$

A final comment on conventional TST is that a factor $f < 1$ often multiplies v_0 in Eqs. (12) or (16). f is described as a fraction of sites which participate in the transition, and is generally an adjustable parameter. No such factor is included in the present work, i.e., $f = 1$ is used throughout; and I take $v_0 = c/a$ unless noted otherwise.

A straightforward modification of Eqs. (12) and (16) is to replace the free-energy difference Δg with $g_L(\rho_L) - g_S(\rho_S)$, i.e., evaluated at the steady-state interface densities. For simplicity I assume the interface g 's may be calculated as if the liquid and solid were uniformly compressed at the interface pressure p . This neglects the fact that a more realistic picture might have $g_L(\rho_L)$ calculated on the basis of interstitial-like defects, which would result in a greater increase in g_L from its equilibrium value for the same average interface density. That is, it generally costs more energy to change the volume of a

fixed number of particles by forming defects than by having uniform contraction or expansion. As might be expected from the general principle that nature always conspires against you, the magnitude of the driving force $|\Delta g| = |g_L(\rho_L) - g_S(\rho_S)|$ is always less than the equilibrium

$$|\Delta g^0| = |g_L(\rho_L^0) - g_S(\rho_S^0)|.$$

This may be seen from the relation $dg = V dp$ at constant temperature and the fact that the pressure p is continuous across the interface. ($V =$ volume per molecule $= 1/\rho$.) It follows that for changes $\delta\rho_L; \delta\rho_S$ in interface densities at fixed temperature T resulting in a pressure change δp ,

$$\delta(g_L - g_S) = (\rho_L^{-1} - \rho_S^{-1}) K_L (\delta\rho_L / \rho_L), \quad (17)$$

where K_L is the isothermal bulk modulus of the liquid and, as noted under Eq. (5), use has been made of

$$\delta p = K_L \delta\rho_L / \rho_L = K_S \delta\rho_S / \rho_S.$$

For the example most used here of freezing a liquid with $\rho_L > \rho_S$, Eq. (6) shows that $\delta\rho_L > 0$ so that the right-hand side of Eq. (17) is negative. But freezing requires $g_L > g_S$, so the net effect is a decrease in $|\Delta g|$. Table I lists the signs for all combinations of freezing or melting and liquid or solid being the denser phase. As seen, Eqs. (6) and (17) give a decreased $|\Delta g|$ in all cases. Integration of Eq. (17) together with the above relation between $\delta\rho_S$ and $\delta\rho_L$ gives

$$\Delta g = \Delta g^0 - (K_L / \rho_L^0) (\delta\rho_L / \rho_L^0) (\rho_L^0 / \rho_S^0 - 1) \quad (18)$$

to first order in the density change. The expression (5) may then be used to obtain a relation between Δg and v which, when inserted into Eq. (12) or (16), provides a transcendental equation for the interface response $v(T)$ in the symmetric or entropy-limited model. The prefactor in Eq. (16) contains an explicit thermodynamic term $s_L - s_S$ whose density dependence is given by the relation¹⁶ $(\partial s / \partial V)_T = \alpha K$ with α the coefficient of thermal expansion and K the bulk modulus. But since the density dependence of the prefactor is not overly important and since the original prefactor $v_0 \exp(-\beta h)$ may well have as strong a density dependence as has $\exp[-(s_L - s_S)]$, I choose simply to ignore density dependence except as it occurs in Δg .

The above gives a prescription for calculating $v(T)$ in what might be called the average density scheme. That is, there is a tacit assumption that liquid at average (steady state) density ρ_L transforms directly to solid at average density $\rho_S \neq \rho_L$ without going through intermediate densities. Or at least the rate can be calculated

TABLE I. Signs of terms in Eq. (17) for change in free-energy difference with velocity [see also Eq. (6)].

Denser phase	Transition	Δg	$(\rho_L^{-1} - \rho_S^{-1}) \delta\rho_L$	$\delta \Delta g $
Liquid	Freezing	+	-	-
Liquid	Melting	-	+	-
Solid	Freezing	+	-	-
Solid	Melting	-	+	-

without having to consider such effects. A possibly more realistic model is treated in Appendix B. There fluctuations in density are allowed, and transitions occur by a molecule of liquid (solid) at some local density ρ' transforming to solid (liquid) at the *same* local density ρ' . The local density of newly formed solid (liquid) then relaxes to the steady-state value. Numerical results from this method do not differ significantly from those of the simpler average density scheme, however.

IV. COMPARISON WITH EXPERIMENT

Comparison is made below both with the pulsed-laser experiments on silicon^{2,4} and molecular dynamics “computer experiments” on a Lennard-Jones (LJ) system.¹³ In both cases rapid interface motion has been studied, but only in the former has both freezing and melting been observed so that asymmetry could be investigated. The former provides an example of liquid denser than solid, whereas the latter has the solid denser than the liquid. Thus both positive and negative density changes can be compared and contrasted. The following notation is employed for the theoretical curves: $v(0,\text{sym})$ and $v(0,\text{asym})$ are Eqs. (12) and (16), respectively, with $\Delta g = \Delta g^0$, i.e., densities at their equilibrium value, and allowing for a finite activation enthalpy h ; $v(\rho,\text{sym})$ and $v(\rho,\text{asym})$ are Eqs. (12) and (16) with Δg given by Eq. (18) and $\delta\rho_L$ given by Eq. (6) and always having $h = 0$.

A. Silicon

Various curves are displayed in Fig. 3 for the interface velocity versus temperature computed for silicon. All these have limiting speed $v_{0a} = c$, the speed of sound. Figure 3(a) shows $v(\rho,\text{sym})$ and $v(\rho,\text{asym})$ together with data from Refs. 2 and 4. Values of parameters used are given in Table II. Where possible, these parameters are taken from experimental data on silicon. In the case of the liquid diffusion coefficient D , where data do not exist to my knowledge, values have been taken from a recent molecular-dynamics simulation of silicon.¹⁷ The relaxation rate in Eq. (6) has been taken as $\Gamma = D/\lambda^2 a^2$. λ thus represents approximately the distance in units of the average intermolecular spacing which must be diffused away from the interface¹⁸ in order to relax the density fluctuation, and is the only adjustable parameter used in the fit. Its value was fixed by requiring the freezing velocity to be about 15 m/s at 1450 K, the observed v at the point⁶ where the liquid freezes to the amorphous rather than crystalline state. Neither v for the liquid-amorphous transition nor the important question of *why* the amorphous state should form under these conditions are considered in this paper. Strong asymmetry of $v(\rho,\text{asym})$ is apparent for $|T - T_M| > 40$ K, but it should be noted that the theory is symmetric very near T_M (i.e., the slope of v versus T is continuous at T_M).

An ironic twist seen in Fig. 3(a) is that when the “symmetric” Eq. (12) is used with a density-dependent Δg , it produces a much more asymmetric curve than when the “asymmetric” Eq. (16) is used. The reason is that, except very near T_M , the freezing velocity is approximately the limiting value given in Eq. (6) as $\Gamma a/(1-\gamma)$, and in-

dependent of the prefactor. But the density change has much weaker effect on melting, so the melting speed is almost the same as in normal TST [see Figs. 3(b) and 3(c)]. Thus asymmetry defined as the ratio $|v_{\text{melt}}|/v_{\text{freeze}}$ for the same $\beta|\Delta g|$ is nearly proportional to the melting speed calculated with normal TST. Although the limiting melting speed is the same in both Eqs. (12) and (16), the melting speeds are seen to be in the ratio

$$v_{\text{melt}}(0,\text{sym})/v_{\text{melt}}(0,\text{asym}) = \exp(s_L - s_S) \exp(-\beta|\Delta g|),$$

which, for small overheating, is much greater than unity. Hence the “symmetric” theory turns out to give the greater asymmetry when $v(0,i)$ is replaced by $v(\rho,i)$ (i stands for “sym” or “asym”).

Thermal activation of D makes Γ decrease with decreasing temperature and thus accentuates reduction of the freezing velocity. In order to see how big an effect this aspect of the temperature dependence has, curves are shown both in which D is held at its value $D(T_M)$ for the melting point and in which an activated form

$$D = D(T_M) \exp[-E_a(\beta - \beta_M)] \quad (19)$$

is used. The activation energy for diffusion E_a was computed in Ref. 17. Over the temperature range of interest, there is almost negligible difference between using Eq. (19) and a constant D , as long as λ is adjusted to maintain the fit at 1450 K, as indicated in the figure caption. Such is not the case for the large temperature range over which freezing of the LJ liquid is studied in the following subsection.

The predictions of conventional TST, $v(0,\text{sym})$, and $v(0,\text{asym})$ are compared with the present theory, $v(\rho,\text{sym})$, and $v(\rho,\text{asym})$, in Figs. 3(b) and 3(c). $v(0,i)$ is shown both for $h = 0$ and h chosen so as to make $v = 15$ m/s at 1450 K, which gave $h = 0.59$ and 0.14 eV for the symmetric and entropy-limited models, respectively. Both $v(0,\text{sym})$ and $v(0,\text{asym})$ can fit the data of Ref. 2 shown in Fig. 3(a) as the point a and line b provided h is properly chosen. However, it was argued in Ref. 2 that only $v(0,\text{asym})$ could also account for melting of the amorphous phase (not considered here). This led the authors to favor the entropy-limited-growth model and reject $v(0,\text{sym})$. Use of a finite h in $v(0,i)$ ($i = \text{sym}$ or asym) gives about the same results for freezing as the present theory $v(\rho,i)$ with $h = 0$; so the advantages of this work might be questioned, at least for treatment of solidification only. My defense would be that the density effect provides a physical basis for the low freezing velocity, whereas the physical origin of the largely phenomenological h is not well understood. It is also clear that the density effect combined with the *symmetric* model has a chance of explaining the very large asymmetry seen in Ref. 4, which is not possible with normal TST.

The interface densities and pressure are shown in Fig. 4. Here, as with calculation of the Gibbs functions, a linear pressure versus density relation was assumed. The deviation from linearity¹⁹ in about a 20% increase in pressure for $\rho_S/\rho_S^0 = 1.03$. As noted in connection with Eq. (2), the solid density is predicted to be uniform, and thus the solid under uniform compression for freezing and uniform tension for melting. But the liquid den-

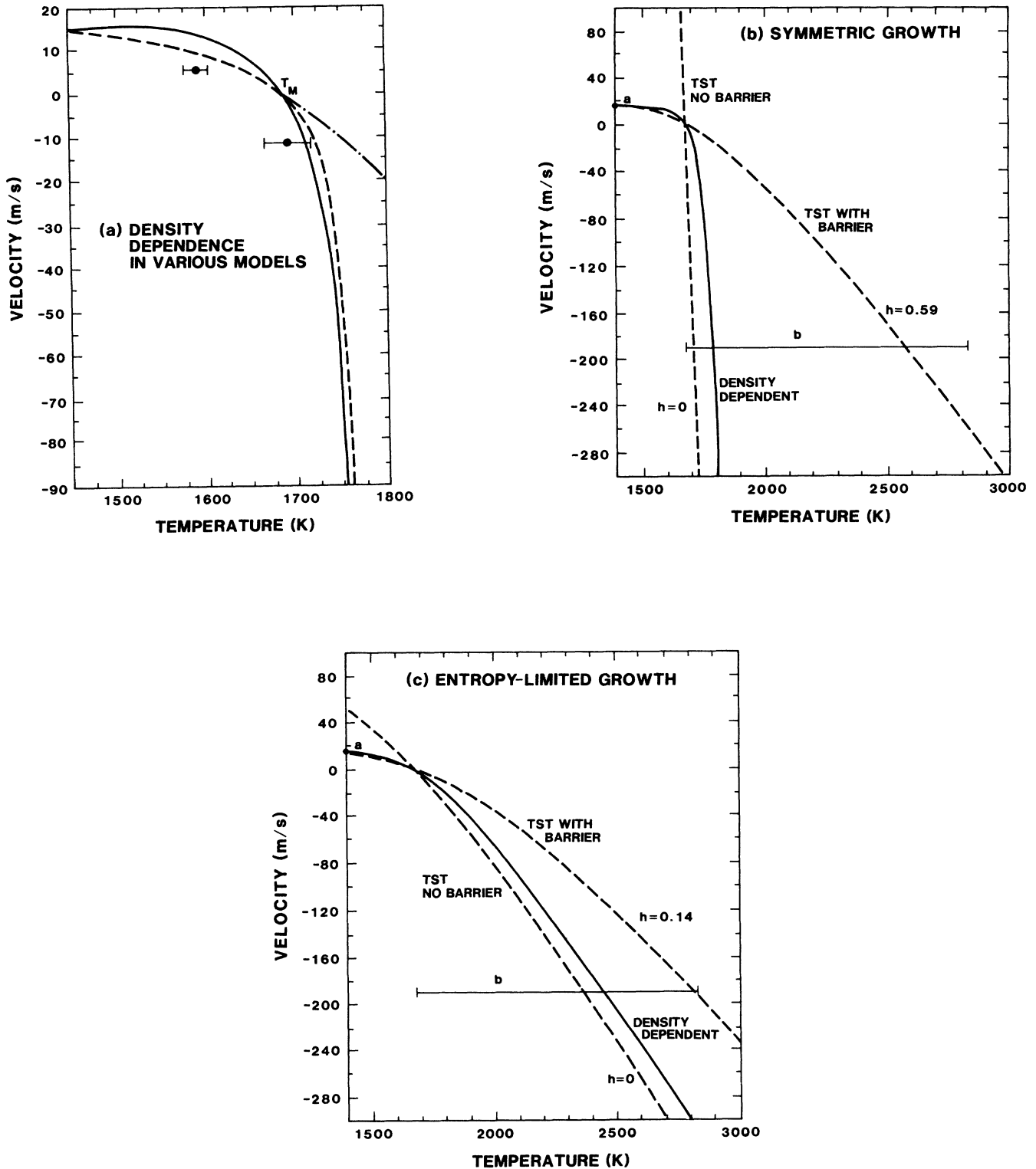


FIG. 3. Interface velocity vs temperature for silicon for various models. Values of parameters are given in Table II. Definitions of $v(\rho, \text{sym})$, etc., are given at beginning of Sec. IV. (a) Present theory together with data from Ref. 4. Solid curve is $v(\rho, \text{sym})$ for an activated diffusion coefficient D and $\lambda=0.88$. Dashed curve is $v(\rho, \text{sym})$ with D temperature independent $D(T_M)$ and $\lambda=1.2$. Dash-dot curve is $v(\rho, \text{asym})$ with an activated D and $\lambda=0.92$. For $T < T_M$ dash-dot and dashed curves are nearly indistinguishable. (b) Solid curve is $v(\rho, \text{sym})$ with activated D [same as solid curve in Fig. 3(a)]. Dashed curves are $v(0, \text{sym})$ for values of h shown. Point a is the same as in Figs. 1 and 3(a). Line b represents melting velocity at a temperature whose upper limit was found to be 2870 K in Ref. 5, but which could be as low as T_M . (c) Solid curve is $v(\rho, \text{asym})$ with an activated D [same as dash-dot curve of Fig. 3(a)]. Dashed curves are $v(0, \text{asym})$ for values of h shown. Point a and line b same as in Fig. 3(b).

TABLE II. Parameters for calculating v in silicon. Values are experimental found in standard references and tables except where noted. Only values actually used are quoted, thus accounting for blank spaces.

Property	Liquid value	Solid value	Difference between liquid and solid
Density ρ (10^{22} atoms/cm ³)	5.38	4.98	
Intermolecular distance $a = \rho^{-1/3}$ (Å)	2.65		
Bulk modulus K (10^{12} dynes/cm ²)	0.36	1.0	
Sound velocity c (10^3 m/s)	3.79 ^a		
Free energy $g_L - g_S$ (eV/atom, $T_M = 1685$ K)			$0.52(1 - T/T_M)$
Diffusion coeff. at T_M , $D(T_M)$ (10^{-5} cm ² /s)	6.9 ^b		
Activation energy for diffusion E_a (eV)	0.42 ^c		

^aCalculated from bulk modulus.

^bFrom molecular-dynamics calculation of Ref. 17.

^cFrom Ref. 17 and converting normalized units there to eV. Dr. Broughton is acknowledged for enlightening me on this point and providing data not given in Ref. 17.

sity decays to its equilibrium value at the free surface.

Although $v_0 = c/a$ was used whereby the speed of sound represents maximum interface speed, an equally plausible choice for v_0 could be the inverse of the average time for a molecule going at thermal velocity to travel from the center of a random position within the unit cell.

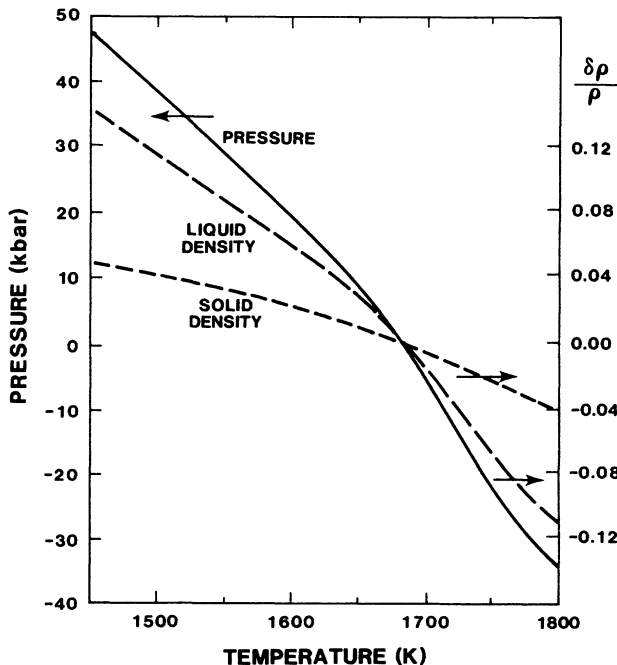


FIG. 4. Pressure and density changes at interface corresponding to solid curves in Figs. 3(a) and 3(b).

This was used in Ref. 13 to estimate

$$v_0 a = 2.5(3k_B T/m)^{1/2} = 3.2 \times 10^3 \text{ m/s}$$

for silicon at T_M , not significantly different from the $c = 3.8 \times 10^3$ m/s used here. In any event, as noted, the freezing velocity is quite insensitive both to v_0 and to the assumed dependence of free energy on density, since it is controlled by the rate Γ at which excess density is transported from the interface.

B. Lennard-Jones (argon)

Broughton, Gilmer, and Jackson¹³ (henceforth referred to as BGJ) did a molecular dynamics simulation of rapid solidification of an LJ fluid, usually taken as a good model for argon, from which the interface velocity for freezing was deduced. Other features of the LJ liquid needed for comparison with theory have also been calculated²⁰ by MD. The BGJ data are shown in Fig. 5. A striking feature is that v is quite large for reduced temperature T^* as low as 0.1 (dimensionless MD units as found in Refs. 13 and 20 are also used in this subsection to facilitate comparison with BGJ). Since MD gives^{13,20} an activated $D = D_0 \exp(-T_a^*/T^*)$ with $D_0 = 0.9$ and $T_a^* = 2.1$, BGJ reasonably argued that the limiting frequency v_0 would be many orders of magnitude too low if it were related to diffusion. A similar problem occurs in the present theory. If Γ were so strongly activated as suggested by the above D , the density catastrophe in the denominator of Eq. (6) would much too severely limit the freezing velocity at $T^* = 0.1$. BGJ were thus led to fit the data to Eq. (12) using the above-mentioned

$$v_0 a = 2.5(3k_B T/m)^{1/2} f$$

(converted to MD units), $h = 0$ and the "availability factor" f taken as 0.27 for a best fit, shown by the dashed

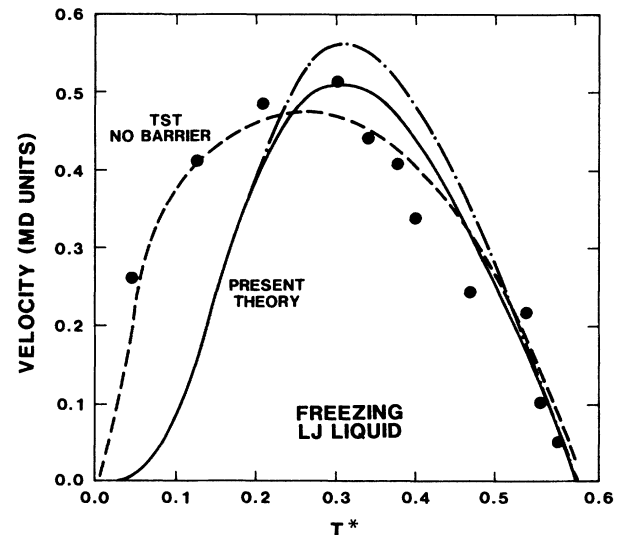


FIG. 5. Interface velocity for freezing of Lennard-Jones liquid. Experimental points are data of Ref 13 (BGJ), and dashed curve is BGJ's fit to data. Solid curve is $v(\rho, \text{asym})$ with D as discussed in text and parameters given in Table III; and $v_0 a = 2.5(3k_B T/m)^{1/2}$. Dash-dot curve is same as solid curve except for $v_0 a = c$.

curve in Fig. 5.

In order to salvage the theory, I argue that the activation energy for Γ can be considerably smaller than that for D in a system, such as the LJ, which contracts on freezing. D reflects the rate for a molecule to jump in an environment which is randomly fluctuating. It is generally accepted that such a jump cannot occur until the "cage" which contains the molecule opens up by a free-volume fluctuation⁸ or such a fluctuation allows the cage as a whole to move.²¹ Thus a major contribution to the activation energy for D is that required to form the free volume. But for the scenario of freezing a liquid to a denser solid state, the arguments of Sec. II show that molecules must diffuse into a density-deficient region, that is one which effectively contains vacancies. Thus a more reasonable estimate of the activation energy for Γ might be obtained by considering the time for a molecule to migrate into a region containing vacancies. Such MD studies have been performed on a supercooled LJ liquid.⁹ No quantitative estimate was given for the activation energy, but the authors state that after 40 time steps (88 ps) of the MD: "At 6 K there was no net displacement of the atoms. At 12 K there is a considerable motion, and . . . 24 K shows most of the vacant volume has annealed out." I deduce from this that the relaxation time for vacancies to anneal out is of the order of 40 time steps at 12 K. By assuming diffusion into a vacancy has the same prefactor D_0 as quoted above from Ref. 20 and converting their units, I thereby conclude that the reduced activation temperature should be $T_a^* \approx 0.37$ instead of 2.1.

The solid curve in Fig. 5 is $v(\rho, \text{sym})$ with $T_a^* = 0.37$ and $\lambda = 1.3$ chosen to reproduce the maximum v at $T^* = 0.3$ (λ is defined in the same way as described above for silicon). Other parameters such as densities and compressibilities are taken from Ref. 20 for the modified LJ potential and shown in Table III. The solid curve has $v_0 a = 2.5(3k_B T/m)^{1/2} = 4.3/T^*$ in MD units, as used by BGJ. For comparison, $v_0 a = c = 5.7$ in MD units is also shown. As noted above in the discussion on silicon, there

TABLE III. Parameters for calculating v in Lennard-Jones system. Values are in normalized units defined in Refs. 13 and 20, and are taken from results quoted in Ref. 20 for the modified LJ potential ϕ_m except where noted. Only values actually used are shown.

Property	Liquid value	Solid value	Difference between liquid and solid
Density ρ			
at T_M	0.83	0.95	
at 0 K	1.02	1.07	
Bulk modulus K	10.7	23.8	
Sound velocity v	5.7 ^a		
Free energy $g_L - g_S$			$\Delta\mu(T)^b$
Diffusion coeff., prefactor D_0	0.86		

^aFrom D. Levesque and L. Verlet, Phys. Rev. A 7, 1690 (1973).

^bGiven as a polynomial in T by expression in footnote 12 of Ref. 13.

is not much difference since the freezing velocity is controlled by the rate Γ at which the density change can be relaxed. By modifying the activation energy as discussed above, the theory is seen to give reasonable agreement for T/T_M greater than about 0.3 ($T^* > 0.2$), which is likely to include any undercooling possible for "real" studies of interface motion. But only a virtually nonactivated Γ could explain the MD data for $T^* < 0.1$, and this is inconsistent with the results of Ref. 9 on vacancy relaxation in the supercooled liquid.

V. SUMMARY AND DISCUSSION

The change of density between liquid and solid has been shown to impose a severe limitation on interface velocity v for heterogeneous freezing but not for melting. Consequently there can be a sizable asymmetry (defined as the difference between freezing and melting speeds for the same $|T - T_M|$) between freezing and melting. If the excess density can be propagated away from the interface at the speed of sound c , such asymmetry is not manifested unless the interface itself moves at close to c . But freezing velocity is much more strongly affected if the excess must initially relax by diffusive jumps. I have argued that this may be the case if a molecular, rather than hydrodynamic, viewpoint is taken, and developed the theory accordingly. The interface densities ρ_L and ρ_S were shown to depend on v and the rate Γ for relaxation of the excess density. This dependence was incorporated into transition-state theory to yield v as a function of temperature T .

Comparison was made with the pulsed-laser experiments on silicon and molecular dynamics simulation on a Lennard-Jones system. Strong asymmetry was shown to occur for silicon, in rough agreement with the x-ray data⁴ and much stronger than found in conventional TST. The only adjustable parameter was the average distance λ a molecule had to diffuse away from the interface in order to relax the excess density. To obtain the observed freezing speed in silicon of $v = 15$ m/s at 1450 K, the temperature below which the amorphous phase is formed, required $\lambda \approx 0.9$ in units of the average distance between molecules. The very large asymmetry occurred by using a modified form of the "symmetric" TST. Modification of the entropy-limited model produced much less asymmetry.

Agreement with MD data on freezing of the LJ liquid down to temperatures less than $T_M/2$ was possible if the activation energy for Γ was substantially less than that found in the MD simulation of diffusion. I argued that this was not unreasonable in view of the fact that, for freezing of the LJ liquid, Γ is characteristic of the rate for a molecule to hop into a region in which vacancies have *already* been formed. The present theory, however, cannot explain the apparent total lack of an activated process evidenced by the large freezing velocity at very low temperature.

Direct confirmation of this theory would require measurement of the liquid density profile. Departure from equilibrium of about 14% at the interface is predicted for silicon at 1450 K. A more feasible study might be that of

the density on the solid side of the interface. For silicon this density is predicted to be decreased by about 2% between freezing at 6 m/s and melting at 11 m/s. These are the velocities at which x-ray measurements were made⁴ to deduce the amounts of undercooling and overheating. Some comment is in order on whether the expected density changes should have been observed in Ref. 4. Strain, the difference between interatomic spacing near the interface and its value at the substrate, was monitored in that experiment. If a 1% change in lattice constant between $v=0$ and a few m/s were manifested as strain, it would have easily been detected—indeed overwhelmed the observed thermal strain from the temperature gradient. But as discussed in connection with Eq. (2), theory gives a uniform density change in the solid and hence no strain. Thus an absolute determination of the lattice constant is needed.

Another test might be to measure the free-surface velocity U . As given in Eq. (1), if ρ_S were increased over its equilibrium value ρ_S^0 by 5%, corresponding to freezing in silicon with $v=15$ m/s, U would be reduced from about 1.2 m/s to 0.5 m/s.

The theory has treated steady-state conditions only. Higher velocities could be obtained before the interface density grows to produce the limiting effects. The characteristic rate for the interface density to build up to its steady-state value is $\Gamma - v/a \approx 5 \times 10^{10} \text{ s}^{-1}$ from the fit to silicon for freezing at 15 m/s at 1450 K. This should be fast enough to have allowed steady state in Refs. 2 and 4 where the time scale was 10–100 ns. But it would not allow density to build up in pulse experiments on the ps time scale. It is thus interesting and perhaps suggestive to note that significantly higher freezing velocities have been reported for pulsed experiments in the 10 ps range.²²

A final caveat is that the most appealing feature of this theory is probably its ability to produce large asymmetry. The major evidence for such asymmetry comes from the data of Ref. 4, and very large asymmetry was also indicated in Refs. 2 and 5. However, the most recent transient conductivity results⁷ do not show much asymmetry. Thus it is not clear whether a theory which gives high asymmetry near T_M is really needed. But in any event it seems useful to quantify the density effect which at the very least has to be important for the very high interface velocities approaching the speed of sound which have been postulated for simple metals.

ACKNOWLEDGMENTS

J. Tsao suggested the analogy with structural and free-volume relaxation. I am also grateful to him and to S. Myers, P. Peercy, M. Thompson, and K. Schweizer for helpful discussions on other aspects of the problem. The work at Sandia National Laboratories was supported by the U. S. Department of Energy under Contract No. DE-AC04-76DP00789.

APPENDIX A: COMBINED DIFFUSION-RELAXATION

We consider solutions to the diffusion-relaxation Eq. (7). With addition of a source injecting particles into the liquid ($x > vt$) it becomes

$$\frac{\partial \delta \rho}{\partial t} = D \frac{\partial^2 \delta \rho}{\partial x^2} - \Gamma \delta \rho + R \delta(x - vt) \quad (\text{A1})$$

for $x > vt$. The condition that there is no current of excess particles into the solid is expressed by $\delta \rho = \text{const}$ for $x < vt$. Here x and vt are, respectively, positions of a particle and the interface measured in the laboratory frame, and the rate R is given by $R = (\rho_L - \rho_S)v$, consistent with the left-hand side of Eq. (4). In the steady-state $\delta \rho$ is a function only of $z = x - vt$ whereby Eq. (A1) reduces to

$$D \frac{d^2 \delta \rho}{dz^2} + v \frac{d \delta \rho}{dz} - \Gamma \delta \rho = -R \delta(0) \quad (\text{A2})$$

The solution for $z > 0$ is $\delta \rho = C \exp(-\xi z)$ with

$$\xi = -v/2D + [(v/2D)^2 + \Gamma/D]^{1/2} \quad (\text{A3})$$

since only a decaying exponential is allowed. The constant C is determined by integrating Eq. (A2) from 0^- to 0^+ (called 0) and using $d \delta \rho / dz |_{0^-} = 0$ since there is no current into the solid $z < 0$; and $\delta \rho(0^-) = \gamma \delta \rho(0)$ as in Eq. (5). Thus

$$C = R / \{ [v^2/4 + \Gamma D]^{1/2} - v(1 - 2\gamma)/2 \} \quad (\text{A4})$$

With $C = \delta \rho(0)$ and, from above, $R = [(1 - \gamma)\delta \rho(0) + \rho_L^0 - \rho_S^0]v$ where, as in the main text, $\gamma = \delta \rho_S / \delta \rho_L$, Eq. (A4) becomes

$$\delta \rho(0) = v(\rho_L^0 - \rho_S^0) / [\Gamma_{\text{eff}} a - v(1 - \gamma)] \quad (\text{A5})$$

with

$$\Gamma_{\text{eff}} = (\Gamma D + v^2/4)^{1/2} / a - v(1 - 2\gamma)/2a \quad (\text{A6})$$

Equation (A5) is the same as Eq. (6) with Γ replaced by Γ_{eff} . For $v \ll (2\Gamma D)^{1/2}$ and, as in the main text, $\Gamma = D/\lambda^2 a^2$, we have $\Gamma_{\text{eff}} = \Gamma \lambda$. The limiting velocity for which the denominator of Eq. (A5) goes to zero is

$$v_{\text{max}} = \Gamma D a^{-1} / (2 - 6\gamma + 4\gamma^2)^{1/2} \quad (\text{A7})$$

For either $D=0$ or $\Gamma=0$, the denominator of Eq. (A5) is negative unless $\gamma > \frac{1}{2}$ which means that no steady-state solution is possible for a relatively incompressible solid ($\gamma \ll 1$). D must be nonzero since otherwise there is no transport away from the small region into which the finite excess of particles is injected. That Γ must also be nonzero means that diffusion by itself is ineffective. This is because of the well-known property of one-dimensional diffusion that the probability of a particle remaining at the origin decays only as $t^{-1/2}$. It follows that if particles are continuously injected at a *stationary* plane, the number remaining at the plane grows as $t^{1/2}$ instead of reaching a steady-state value. If the plane (interface) moves into the medium in which the particles are injected, and no density is allowed to build up on the other side, the rate of growth of density at the origin plane can only be greater. This differs from the case, as in heat flow with both the solid and liquid having finite thermal conductivity, where the excess can build up freely on either side of the plane, which corresponds to $\gamma=1$ here. Then a steady-state solution is possible for finite v , but not for $v=0$. This is because excess can now move ballistically away from the moving source into the medium behind it,

as is known from the problem of heat flow into a moving medium.²³

APPENDIX B: TRANSITION THEORY WITH DENSITY FLUCTUATIONS

We assume here that not only are the steady-state densities altered from equilibrium as in Eq. (6), but fluctuations cause the local density in the region of a molecule undergoing transition to depart from the steady-state value. This latter effect is similar to the free-volume fluctuations important for diffusion and structural relaxation in disordered systems.⁸ I therefore write, analogous to Eqs. (10) and (11),

$$W_{LS}(\rho') = \nu \exp\{-\beta\theta[g_S(\rho') - g_L(\rho')]\}, \quad (\text{B1})$$

$$W_{SL}(\rho') = \nu \exp\{-\beta\theta[g_L(\rho') - g_S(\rho')]\}, \quad (\text{B2})$$

for transition rates when the local density is ρ' . Note that the individual transitions are assumed to take place *without* a change in density. That is, the local density stays at ρ' , as reflected by the arguments of the g 's, during the local phase transformation. The density difference is reflected in the different dependences of g_L and g_S on ρ' . For example, at the assumed constant interface temperature and pressure corresponding to steady state, $g_L(\rho')$ is a minimum when $\rho' = \rho_L$ while $g_S(\rho')$ is minimized for $\rho' = \rho_S$. Consequently $g_S(\rho') - g_L(\rho')$ can have either sign, thus making the θ functions necessary, even though the steady-state difference $g_L(\rho_L) - g_S(\rho_S)$ is fixed to be positive or negative by the respective conditions of net freezing and net melting. The condition of transition at constant density gives rise to an effective activated transition state for the following reason, illustrated in Fig. 6. Consider freezing and suppose first that the g difference in Eq. (B1) was the steady-state $g_S(\rho_S) - g_L(\rho_L)$, contrary to what is given. This difference is negative for freezing, so there would then be no activation barrier or transition state. But the difference given in Eq. (B1), $g_S(\rho') - g_L(\rho')$ can well be positive and thus produce an activation barrier. This is most evident for small density fluctuation, $\rho' \approx \rho_L$, and a highly incompressible solid, as seen in Fig. 6. In such cases the solid would have to be formed at liquid density at a large cost in free energy, i.e., $g_S(\rho_L) > g_L(\rho_L)$ even though $g_S(\rho_S) < g_L(\rho_L)$, owing to the assumed strong density dependence of g_S for a relatively incompressible solid. Figure 6 also illustrates that a barrier does not have to be

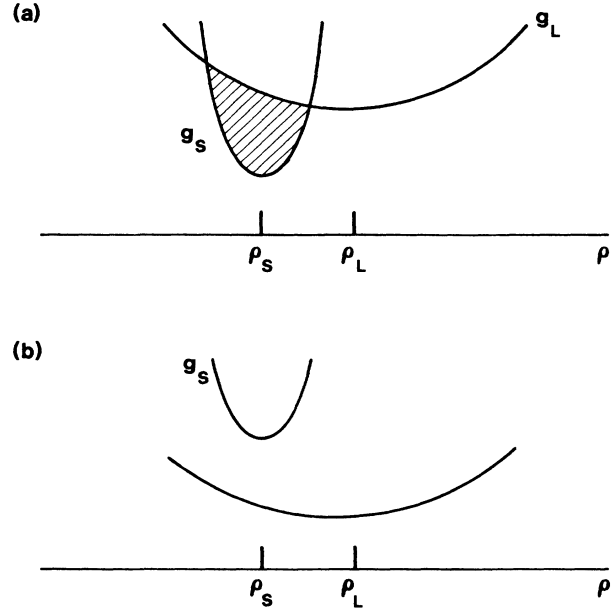


FIG. 6. Free energies vs density. (a) Freezing. Shaded region corresponds to region 1 for the integrations in Eqs. (B6) and (B7). (b) Melting.

present for melting, leading to a further source of asymmetry.

The average rates are obtained by weighting with the respective probabilities $P_L(\rho')$ and $P_S(\rho')$ of finding the molecule in an initial state of local density between ρ' and $\rho' + d\rho'$ for the LS and SL transitions and summing over all possible initial states. Thus we have

$$W_{LS} = \int d\rho' W_{LS}(\rho') P_L(\rho'), \quad (\text{B3})$$

$$W_{SL} = \int d\rho' W_{SL}(\rho') P_S(\rho'). \quad (\text{B4})$$

These average rates satisfy microscopic reversibility (8), as now shown. The probabilities are given by

$$P_i(\rho') = \exp[-\beta g_i(\rho')] / Z_i, \quad (\text{B5})$$

where the subscript i is either L or S and the partition function is $Z_i = \int d\rho' \exp[-\beta g_i(\rho')]$. The integrations in Eqs. (B3) and (B4) are over regions 1 and 2 where, respectively, $g_L(\rho') > g_S(\rho')$ and $g_L(\rho') < g_S(\rho')$. Use of Eqs. (B1), (B2), and (B5) thereby gives

$$W_{LS} = Z_L^{-1} \left\{ \int^1 d\rho' \exp[-\beta g_L(\rho')] + \int^2 d\rho' \exp[-\beta g_L(\rho')] \exp\{-\beta[g_S(\rho') - g_L(\rho')]\} \right\} \quad (\text{B6})$$

$$W_{SL} = Z_S^{-1} \left\{ \int^1 d\rho' \exp[-\beta g_S(\rho')] \exp\{-\beta[g_L(\rho') - g_S(\rho')]\} + \int^2 d\rho' \exp[-\beta g_S(\rho')] \right\}, \quad (\text{B7})$$

where the superscripts on the integrals refer to the regions 1 and 2. The terms in large parentheses are seen to be identical so that

$$W_{LS} / W_{SL} = Z_S / Z_L = \exp[\beta(G_L - G_S)]. \quad (\text{B8})$$

In the second equality G_L and G_S , are, respectively,

Gibbs free energies per molecule of liquid and solid evaluated at the steady-state interface temperature T and pressure p , and the fundamental thermodynamic relation¹⁶ between Gibbs free energy and partition function of a constant p, T ensemble has been used. An unfortunate feature of the notation is that, if density rather than pres-

sure is used as the thermodynamic variable, $G_L(\rho_L) \neq g_L(\rho_L)$. The right-hand side is the local free energy per molecule of a region whose density ρ' is allowed to fluctuate but happens to have exactly the steady-state value $\rho' = \rho_L$; the left-hand side is the average free energy on the liquid side of the interface whose average density ρ_L is related to the steady-state p and T by an equation of state. Similar statements apply to $G_S(\rho_S)$ and $g_S(\rho_S)$. The above Eq. (B8) is the proper realization of microscopic reversibility or detailed balance (8) when density fluctuations are accounted for.

Use of the average rates given by Eqs. (B3) and (B4) is valid only if the density ρ' fluctuates rapidly compared with the net rate $W_{LS} - W_{SL}$. The fluctuation rate for ρ' is characteristic of equilibrium fluctuations within liquid or solid regions within a layer and might be much faster than the previous Γ which is the rate for a "drastic" density change to be relaxed by motion out of a layer. With rapid variation of ρ' , the molecule experiences many different local densities during the course of transition, and it is appropriate to consider the average rate. Use below of Eqs. (B3) and (B4) should be valid for *all* freezing velocities because of the severe limitation Eq. (6) imposes when $v > 0$ and for melting speeds sufficiently great to illustrate the large asymmetry which is the main point of this paper. More careful analysis may be required for melting at still greater speeds when the rate to transform a layer becomes comparable to the rate at which density

fluctuates within a layer.

Analytic expressions for W_{LS} and W_{SL} in terms of ρ_L are possible if departures from equilibrium are small enough that the approximations

$$g_L(\rho') = g_L(\rho_L) + b_L(\rho'/\rho_L - 1)^2, \quad (\text{B9})$$

$$g_S(\rho') = g_S(\rho_S) + b_S(\rho'/\rho_S - 1)^2 \quad (\text{B10})$$

can be made. As mentioned under Eq. (B2), the density fluctuations take place at the steady-state pressure p for which g_L and g_S are minimized at ρ_L and ρ_S , so terms linear in $\rho'/\rho_L - 1$ and $\rho'/\rho_S - 1$ must vanish. That is, ρ' is a parameter in the expression $g_L(\rho') = F_L(\rho') + pV$ which is minimum at the fixed p and T when $\rho' = \rho_L$ (F_L is the Helmholtz free energy and $V = 1/\rho'$), with a similar statement for $g_S(\rho')$. Since $\partial F/\partial V = -p$ in equilibrium at constant temperature, the same interpretation of $g_L(\rho')$ shows that

$$b_L = K_L/2\rho_L \quad (\text{B11})$$

and similarly,

$$b_S = K_S/2\rho_S, \quad (\text{B12})$$

where, as in connection with Eq. (5), K_L and K_S are, respectively, bulk moduli of the liquid and solid. The result of using Eqs. (B9) and (B10) in Eq. (B6) is

$$W_{LS} = v[\text{erf}[\lambda_L(x_B - 1)] - \text{erf}[\lambda_L(x_A - 1)]] + e^{\beta(G_L - G_S)} \{ \text{erf}[\lambda_S] - \text{erf}[\lambda_S(1 - qx_A)] + \text{erfc}[\lambda_S(qx_B - 1)] \}. \quad (\text{B13})$$

Here $\lambda_{L,S} = (\beta b_{L,S})^{1/2}$, $q = \rho_L/\rho_S$, and x_A and x_B are the lower and upper values of ρ'/ρ_L which satisfy $g_L(\rho') = g_S(\rho')$. They are given by

$$x_{B,A} = \frac{qb_S - b_L \pm \{ [g_L(\rho_L) - g_S(\rho_S)](q^2 b_S - b_L) + b_S b_L (q - 1)^2 \}^{1/2}}{q^2 b_S - b_L}. \quad (\text{B14})$$

If Eq. (B14) has no real solutions, either region 1 or region 2 in Eq. (B6) shrinks to zero, whereby the result is simply

$$W_{LS} = v \exp[-\beta(G_S - G_L)]$$

[$g_S(\rho') > g_L(\rho')$ for all ρ' , which is likely for melting] or $W_{LS} = v$ [$g_S(\rho') < g_L(\rho')$ for all ρ' , which should not occur for freezing if the liquid is more compressible than the solid]. It is assumed that the g 's of Eqs. (B9) and (B10) are large enough at $\rho' < 0$ that the integration in Eq. (B6) may be extended to the unphysical region $-\infty < \rho' < 0$ without affecting the results. With this understanding, if Eq. (B14) gives a real $x_A < 0$, it may be used in Eq. (B13). Equality of pressures on the liquid and

solid sides of the interface shows, as in Eq. (5), that only ρ_L is an independent variable in the above expression for W_{LS} . The rate W_{SL} is obtained from the condition of microscopic reversibility (B8).

The above example is specifically for modifying the symmetric version Eq. (12). The entropy-limited version Eq. (16) would be handled in a similar way with similar final expressions. Although inclusion of fluctuations and having transitions take place without an immediate density change might seem to be quite a different physical picture than the average density approach described in the main text, the actual results for v versus T differ by no more than 10% between these two models for the solid curves shown in Fig. 3.

¹See F. Spaepen and D. Turnbull, in *Laser Annealing of Semiconductors*, edited by J. M. Poate and J. W. Mayer (Academic, New York, 1982), Chap. 2, for a general review and references to earlier work.

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