discussions with D. D. Osheroff, J. D. Reppy, D. M. Lee, W. P. Kirk, and J. M. Parpia. This work was supported in part by the National Science Foundation under Grant No. DMR 82-05697.

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[2] Actually, ^{3}He-A_1 exists only under an applied magnetic field, so the system must actually be polarized to some extent. While this *induced* magnetization may not be negligible in estimating the precise magnitudes of the effects discussed here, it is not *essential* to the *existence* of these effects. Thus for conceptual simplicity, we shall continue to describe these effects as if they are occurring in an idealized *unpolarized* superfluid ^{3}He-A_1 liquid, although all formulas derived at the end of each discussion shall be applicable even when the induced-magnetization effects are not negligible. (I.e., the correct ρ_s/ρ factor will take care of it.)

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[8] While we have derived Eq. (1) under the assumption $L_y \ll L_z$, the potential difference presented in Eq. (2) is actually also valid when this condition is not met. This may be easily seen from the viewpoint of a superposition principle. It should also be pointed out that the electric field and potential distributions discussed here cannot be understood in terms of flux cutting. Since all magnetic-flux lines must form closed loops, it can be seen that in a steady-state situation, no *net* flux could cut through, for example, the line located at $x = z = 0$, and extending from $y = -\infty$ to $y = +\infty$. On the other hand, if this infinitely long line is replaced by a finite line segment, then a net flux cutting in a steady state does exist, giving rise to an additional potential difference between the end points of the line segment.

[9] By using this empirical formula for ρ_s/ρ, which was obtained at the applied field of 8.46 kG, we have neglected the fact that ρ_s/ρ should actually be field dependent at any fixed $1-T/T_{c1}$.

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Crystallization Rates of a Lennard-Jones Liquid

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The crystallization of a Lennard-Jones liquid has been studied with molecular-dynamics techniques. In particular, the motion of the fcc (100) interface has been measured for a range of temperatures below the melting point. The crystallization rates are not limited by the mobility of atoms in the bulk liquid; measurable rates are even observed below the glass transition temperature. This result suggests the existence of a class of materials which is qualitatively different from conventional glass-forming materials.

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The properties of liquids made up of atoms which interact through a Lennard-Jones (LJ) potential have been studied extensively with molecular-dynamics methods.[1] Recently, the equilibrium properties of a LJ crystal-melt interface have been determined.[2] The initial crystallization kinetics of a slab of supercooled LJ liquid after contact with a crystal have also been reported.[3] In this Letter we report on a study of the steady-state crystallization rate of a LJ liquid measured at a series of temperatures below the melting point.

Most materials for which crystallization rates from the melt have been measured exhibit thermally activated growth. The temperature dependence of the crystallization rate is described by an equation similar to the form first proposed by Wilson[4] and later by Frenkel,[5]

$$v = (Da/\Lambda^2)f_0\{1 - e^{-\Delta\mu/kT}\}. \tag{1}$$

Here D is the diffusion coefficient in the liquid and Λ is the mean free path for this process. It is assumed that atoms in the adjacent liquid layer of thickness a impinge on the crystal surface at a rate proportional to D/Λ^2. A factor $f_0 < 1$ is included to account for the fact that some of these collisions are ineffective for crystallization; for example, they may occur far from crystal lattice binding sites. The transition from crystal to fluid is represented by the term $e^{-\Delta\mu/kT}$, where $\Delta\mu$ is the difference in chemical potential between the fluid and the crystal.

The diffusion coefficient in the liquid can usually be represented by the Arrhenius equation

$$D = D_0 \exp(-Q/kT) \qquad (2)$$

and the LJ liquid is no exception.[6] Figure 1 shows our data in reduced units[7]; note that the diffusion coefficient at $T = 0.25$ is smaller by about two orders of magnitude than its value at $T_m \cong 0.62$. Equation (1) correctly predicts the temperature dependence of the crystallization rate of GeO_2, for example, over a 400-degree temperature range, in which the viscosity changes by five orders of magnitude.[8] At large undercooling, the bracketed term in Eq. (1) changes slowly with temperature, so that the temperature dependence of the growth rate follows that of D, as has been observed experimentally in many glass-forming materials.

However, Eq. (1) has never been verified for a monatomic melt. These melts crystallize so rapidly that their true growth kinetics have never been measured experimentally. Turnbull and Bagley,[9] on the basis of the general difficulty of quenching pure metals into the glassy state, have argued that the crystallization of these melts should not be thermally activated. The observations of Ruhl and Hilsch,[10] indicating a transformation at temperatures as low as 16 K in Pb films deposited at 4 K, tend to support this view.

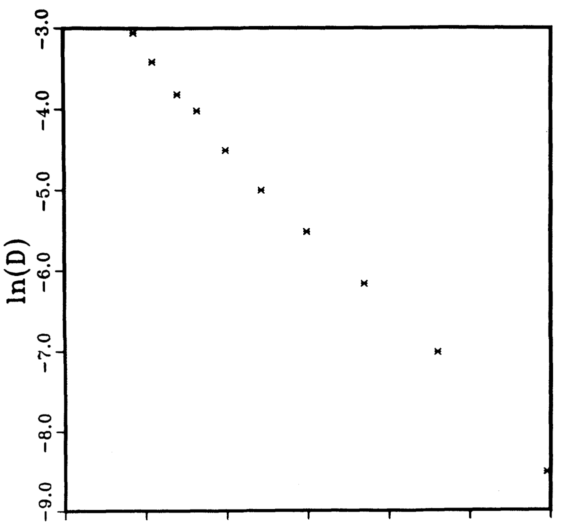

FIG. 1. Arrhenius plot of the atomic diffusion coefficent in the Lennard-Jones liquid at zero external pressure.

Simulations of the steady-state interface motion were performed by supplying "liquid" particles at a rate approximately equal to the crystallization rate. The coordinates of these particles were derived from a liquid at $T = 0.6$ which was cooled to zero kelvin in 200 time steps[7] by a series of velocity renormalizations. During this quench, periodic boundary conditions were applied at the vertical bounding planes and across planes A and B illustrated in Fig. 2(a). (No interactions with particles above plane B were included.)

Crystallization occurs in the "dynamic" zone in Fig. 2(a), which has a square cross section and periodic boundary conditions at the vertical planes. The lateral dimensions were chosen to fit a 7×7 array of atoms in the fcc (100) face; changes in the interface temperature were accompanied by a contraction or expansion to match the new lattice constant of the LJ crystal at zero pressure.

During a crystallization run the particles in the quenched liquid are translated with a common velocity v_L in the vertical direction. Particles reaching plane B are inserted into the dynamic region, and they are also introduced at the corresponding position at plane A in the quenched liquid. In this way an inexhaustible source of liquid particles is provided.

Particles at either end of the dynamic zone are coupled to a "heat bath" at temperature T by the application of random and dissipative forces. This method has been discussed elsewhere.[11] A coupling parameter $\beta = 10$ for the dissipative force $\vec{F}_d = -\beta\vec{v}$ gave ample equilibration with the heat bath without drastically affecting the motion of the particles. (The amplitude of the random force is proportional to the product βT.) The particles entering the dynamic zone across plane B are assigned initial random velocities with a Maxwellian distribution relative to the center of mass. During steady-state crystallization, evolution of the latent heat of the transformation produces a higher temperature at the interface as indicated in Fig. 2(b).

The growth rates and corresponding interface temperatures obtained are shown in Fig. 3. They do not correspond to Eq. (1) which has also been

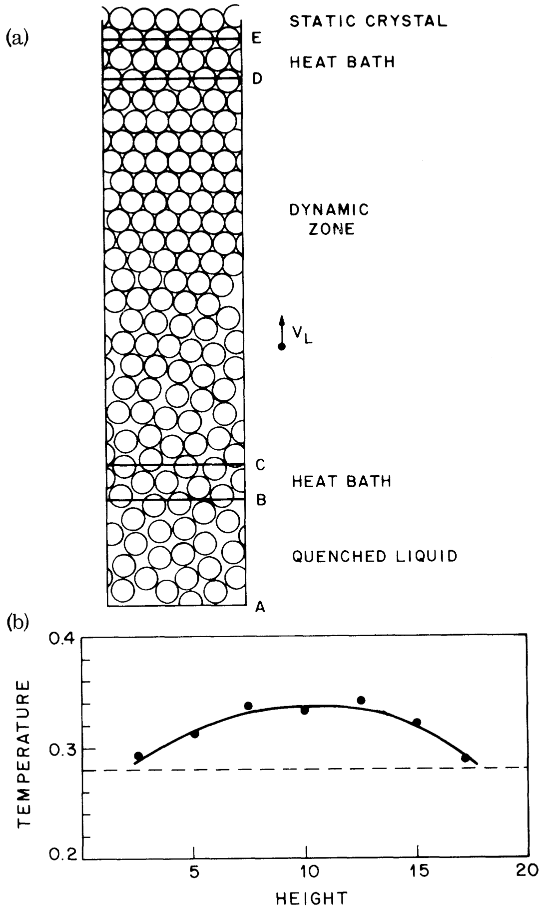

FIG. 2. (a) Schematic diagram of the crystallization system. (b) Steady-state temperature distribution in the dynamic zone with the heat baths set at $T = 0.28$.

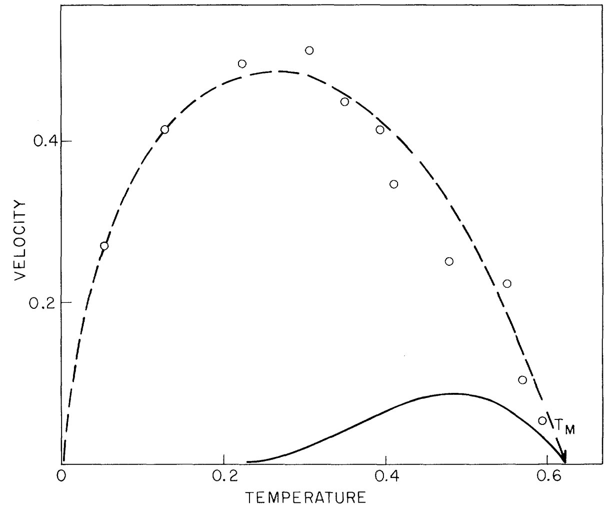

FIG. 3. Molecular-dynamics data (open circles) for the velocity of the crystal-liquid (amorphous) interface vs interface temperature. The solid curve represents Eq. (1), and the dashed curve Eq. (4); in both cases $f_0 = 0.27$.

plotted, with measured values for D and Λ, and values of $\Delta\mu$ calculated from measured internal energies.[12] The crystallization is apparently not thermally activated. Even a very small activation barrier would reduce the growth rate significantly at low temperatures.

To test for the presence of an energy barrier to crystallization, the two heat sinks were put at 0 K. The resultant growth rate is the point with the lowest interface temperature in Fig. 3. As a further test, the velocities of all particles were set equal to zero and the simulation restarted. The interface velocity increased to the same rate as before. Repeated applications of this procedure also failed to stop the interface motion. This indicates that there are no energy barriers which can prevent the liquid atoms from reaching the lattice sites.

The peak in the growth rate corresponds to a linear velocity of about 80 m/sec for argon (the time unit depends on mass), so that these are extraordinarily high rates compared to those obtained in the laboratory. For comparison, recrystallization of silicon following pulsed laser melting of a surface layer is usually in the range of a few meters per second. Splat cooling is usually a few magnitudes slower and normal crystal-growth rates are again several magnitudes slower.

Near T_m, the diffusion coefficient in the liquid is 1.6×10^{-5} cm^2/sec. At $v = 50$ m/sec, the interface moves one atomic diameter in $\sigma/v = 7.6\times10^{-12}$ sec. During this time, an atom in the liquid can move an average distance $(Dt)^{1/2} \approx 1.1\times10^{-8}$ cm. At $T = T_m/2$, the corresponding distance is 2.2×10^{-9} cm. This means that near the melting point these atoms can move a significant distance while the interface is in their vicinity. But at the lower temperatures, the liquid is nearly rigid on this time scale.

We suggest the following explanation of our results. Molecular-dynamics studies of this interface at the melting point show a smooth transition between the densities of the two bulk phases. There is no indication of large voids in this region, and the mobility of the interfacial atoms is approximately equal to that in the bulk liquid.[2] But enhanced diffusion of atoms at the interface between two solid phases is well documented. Grain-boundary diffusion *and* migration are observed at low temperatures where the bulk diffusion rate is essentially zero.[13] Molecular-dynamics studies[14] have demonstrated the presence of voids and their influence on the atomic mobility in the interface. Apparently the rigid lattices prevent relaxation to the degree that occurs at the crystal-melt interface. As the temperature of a crystal-melt interface is reduced below T_m, this interface should develop properties similar to those of an interface between two solid phases. The increased viscosity of the liquid and rapid crystallization prevent complete structural relaxation. Indeed, density profiles at low temperatures reveal densities in this region ~ 5% lower than that of the amorphous material. Thus, as the temperature is reduced, the amount of free volume available for atomic diffusion actually increases.

At the lowest temperatures studied, the liquid becomes a rigid glass. Our results imply that this material is unstable when placed in contact with a (100) crystal face. We note, however, that stable configurations of the amorphous-crystalline interface can be produced by other initialization procedures. Abraham, Tsai, and Pound[15] performed an instantaneous quench of a crystal-melt system by the Monte Carlo method. In this way an interface without a density deficit was frozen in place, and this configuration proved to be stable with respect to crystallization during subsequent Monte Carlo events at a low temperature. Since our intent was to measure steady-state kinetics, we reduced the temperature in small increments from T_m, and this procedure always resulted in finite crystallization rates. A reduced rate was occasionally observed during simulations performed after large changes in the interface temperature. A defect in one crystal layer near the interface was noted in most of these cases; one row of atoms was usually displaced by a distance $a/2$ parallel to the row. This defect was not trapped in the bulk crystal, but persisted in layers near the interface during the crystallization of several layers. Although we never observed the interface motion to be stopped by such defects, we cannot exclude the possibility that they would prevent growth at very low temperatures.

In the absence of a potential-energy barrier, the rate at which liquid atoms in the interface approach the lattice sites is determined by the average thermal velocity, $(3kT/m)^{1/2}$. They travel a distance λ, which is, on average, only a fraction of the interatomic spacing a. Thus, Eq. (1) can be modified to give

$$v = (a/\lambda)(3kT/m)^{1/2} f_0 \{1 - e^{-\Delta\mu/kT}\}. \tag{3}$$

The dashed curve in Fig. 2 has been plotted with $\lambda = 0.4a$, the average distance from the center of points distributed randomly in a sphere of radius a, and $f_0 = 0.27$ was selected to give the best fit. This expression is in good agreement with the results of the simulations over the entire temperature range.

It is usually assumed that the glass-forming potential of different materials is only a matter of degree, and that the value of the glass transition temperature relative to the melting point provides a good measure of this property. The present result implies that there is a class of materials with unstable glassy states, since they crystallize even at very low temperatures when in contact with crystalline material. Network glasses require bond breaking for crystallization; big molecules must be reoriented to crystallize; some mixtures have to be sorted out to crystallize. Each of these requires rearrangement of the liquid structure, and so there is an activation barrier to crystallization for these materials.

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$$E_L = -7.1847 + 4.1896T + 0.2702T^2 + 0.78396T^3$$

and

$$E_c = -7.4487 + 3.0127T + 0.243917T^2 + 0.55607T^3 + 1.7928T^4 - 6.2339T^5$$

are polynomials representing the internal energies (per atom) of the liquid and crystalline phases, respectively. The expression relating $\Delta\mu$ to the internal energies is derived from the Gibbs-Helmholtz relation, and is valid only when the pressure is zero.

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Monochromatic Phonon Generation by the Josephson Effect

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ac-Josephson junctions of tin and lead were found to emit monochromatic phonons with Josephson frequency, rather than thermal phonons. This is a new tunable phonon source with high efficiency and prospectively extremely high frequency resolution.

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We have investigated the phonon emission spectra of ac-Josephson junctions[1] with a stress-tuned phonon spectrometer[2] whose resolution was greatly improved.[3] Surprisingly, we did not find the expected broad spectral distribution of phonons, but rather a sharp monochromatic peak. This peak is coincident with the Josephson frequency $\hbar\omega = 2eV$ and, accordingly, is tunable by the voltage. Thus, we have discovered a new tunable source of truly monochromatic phonons which is, at least with respect to frequency resolution, superior to the previous method of phonon "bremsstrahlung."[4] Since the phonons are excited by the electromagnetic waves in the junction, the new effect must also have some bearing on the noise resistance of Josephson junctions.

The Josephson junction was evaporated onto a silicon crystal of dimensions $2 \times 4 \times 15$ mm^3, doped with 5×10^{13} cm^{-3} boron acceptors [see inset (a) of Fig. 1]. The phonons emitted by the junction traveled ballistically through the crystal and were detected by a broadband detector (aluminum junction) on the far side. The boron acceptors have a fourfold-degenerate ground state

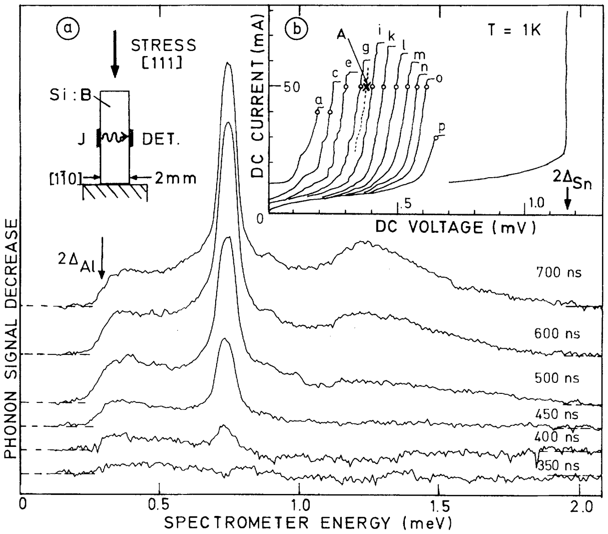

FIG. 1. Time evolution of the phonon spectrum for a fixed Josephson frequency. Insets: (a) geometry of spectrometer crystal, J is the Josephson junction; (b) I-V characteristic of the Sn junction at various magnetic fields.