Vacancy diffusion and stress relaxation in ^{4}He freezing in porous Vycor

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We report results of ultrasonic-attenuation and -velocity measurements during freezing of ^{4}He in porous Vycor glass. When solid helium is present, we observe attenuation peaks whose frequency and temperature dependences are characteristic of a thermally activated relaxation process. We identify the responsible mechanism as being the relaxation of ultrasonic stresses in the solid helium via vacancy diffusion. Since the pores of Vycor are very small ($\sim 10^{-6}$ cm), the relaxation time τ can be very short. For a sound wave with angular frequency ω, the resulting attenuation is largest at the temperature where $\omega\tau = 1$. The activation energy for diffusion and the diffusion rates extracted from our measurements are consistent with those determined in other experiments on solid helium. In interpreting other freezing experiments in Vycor, it is important to consider mass transport due to this vacancy-diffusion mechanism, since it can allow pressure equilibrium to be maintained between the helium in the pores and bulk helium outside.

When fluids are confined in small pores, they often remain liquid well below their bulk melting temperature and there may be considerable hysteresis between melting and freezing. The depression of the freezing temperature is usually attributed to the free energy required to create a liquid-solid interface (assuming the solid does not wet the pore surface). However, explaining the observed hysteresis requires further assumptions, for example, about the shape of the liquid-solid interface during freezing and melting. In the case of helium confined in porous media, a great deal of attention has recently been focused on the superfluid and liquid-vapor transitions, as well as on freezing and melting. In the pores of Vycor glass, for example, helium remains liquid at pressures well above the bulk melting curve[1] and has a sharp superfluid transition at a lower temperature than in bulk. Freezing of helium in Vycor was first observed in ultrasonic velocity measurements[2] which detected the increase in the shear modulus associated with solid in the pores. Specific heat, pressure,[3,4] NMR,[5] and torsional oscillator studies[6] have provided further information, but left some puzzles. For example, the latent heat and the volume change associated with freezing appear to be very different from their bulk values, possibly indicating that not all of the helium freezes, even at the lowest temperatures. In some of these experiments, it has not been clear whether the helium in the pores remained in pressure equilibrium with bulk helium outside, complicating their interpretation.

Ultrasonic measurements are particularly suited to the study of freezing in porous media, since the sound velocity is sensitive to the elastic properties as well as to the density of the material in the pores. When a fluid fills the pores, it causes a decrease in the transverse sound speed because it adds to the system's total density, ρ. When it freezes, however, it also contributes to the shear modulus, G, so that the sound velocity, $v = (G/\rho)^{1/2}$, increases. The ultrasonic attenuation provides further information since it reflects dissipation in the system. By making velocity and attenuation measurements over a range of sound frequencies we can probe the dynamics of the freezing transition.

In this paper we report the results of an ultrasonic study of the freezing and melting of helium in the pores of Vycor glass. The onset of freezing, marked by an increase in the transverse sound velocity, occurs at higher pressures than in bulk and is very sharp, without any of the time dependence which would be expected if the freezing was controlled by nucleation kinetics. As previously reported,[2,3] there is a well-defined hysteretic region associated with melting, beginning at a temperature somewhat below the onset of freezing and extending to the completion of melting in the pores. In addition, we find that freezing is accompanied by large increases in the sound attenuation. We discuss the temperature and frequency dependence of this attenuation and show that it is due to ultrasonic stresses in the solid helium relaxing via vacancy diffusion.

The porous Vycor (Corning 7930) used in these experiments was in the form of cylindrical rods about 0.3 cm in diameter and 1 cm long. We measured its porosity as $\phi = 29\%$ and its specific surface area $S = 105$ m^2/g. This gives an effective cylindrical pore radius $R \approx 35$ Å, somewhat larger than the neck radius of ≈ 19 Å determined by mercury intrusion porosimetry. The samples were cleaned by heating at 80 °C in a 30% hydrogen peroxide solution for 1 h, followed by rinsing in distilled water for a few hours. They were then air dried and evacuated at room temperature for several hours. After mounting 20-MHz $LiNbO_3$ shear transducers on the ends, the samples were sealed into a copper cell (volume about 7 cm^3) at-

tached to the mixing chamber of a small dilution refrigerator. The cell was reevacuated overnight and cooled. Temperatures were measured using calibrated Ge sensors. The ultrasonic velocity v and attenuation α were measured simultaneously at each temperature with a resolution of $\Delta v/v \approx 10^{-6}$ and $\Delta\alpha \approx 0.005$ dB/cm, respectively.[7] At each temperature, about 15 min were required to take data over the complete frequency range (from 5 to 140 MHz).

Figure 1 shows the velocity and attenuation data at 16 MHz during a cooling run. The entire cell was filled with helium at a pressure of about 100 bar and a temperature of 4.2 K. When the cell was cooled, the fill line blocked almost immediately. At the bulk melting temperature, the fluid outside the Vycor began to freeze at essentially constant density, so the pressure in the cell dropped. Some helium then left the pores, reducing the density of the Vycor-helium system which, in turn, caused the transverse sound velocity to increase. The onset of bulk freezing outside the Vycor thus appears as a kink in the velocity data of Fig. 1 (point 1 at 3.38±0.02 K). The second kink (point A at 2.60±0.01 K) corresponds to the completion of bulk freezing in the cell. Below this temperature, the liquid helium within the pores cooled at nearly constant pressure until it began to freeze. The slight increase in the velocity below A is a background variation due to the "two-level systems" (TLS) which characterize the glass itself. Freezing of the helium in the pores appears as the third kink in the velocity (point B at 1.94±0.01 K) due to the added elastic modulus contribution of solid helium in the pores. Thus, confinement in the pores of Vycor depresses the freezing temperature by 0.66 K at this density. The various features in Figs. 1 and 2 (points 1, A, B, C, T_m) also appeared in the work of Adams *et al.*,[3] whose notation we have adopted. In their work, these features are shifted to slightly lower temperatures, because of their lower pressure, but otherwise agree well with our measurements. The onset of freezing seen in Figs. 1 and 2 was very sharp, since the kink occurred between data points spaced 20 mK apart, and did not depend on cooling rate (waiting just above B for several hours had no effect, but cooling slightly below B resulted in immediate freezing). Measurements were made simultaneously at frequencies of 5, 8, 16, 30, 83.3, and 140 MHz. The data at each frequency showed the features 1, A, and B at the same temperatures, as expected since they directly reflect the density and elastic modulus of the helium in the pores. The total sound velocity change during freezing was about 0.35%, consistent with estimates[8] of the total modulus change expected for complete freezing of the helium in the pores.

We also made measurements as the sample was warmed, to look for the expected hysteresis. The sensitivity of these measurements allowed us to look at the freezing and melting regions in some detail, as shown in Fig. 2. The velocity during warming matched the cooling data up to the point labeled C (at 1.75±0.05 K), but then deviated. The warming curve eventually rejoined the cooling curve when melting in the pores was complete (point T_m at 2.27±0.02 K). As in the work of Adams *et al.*, the warming data does not show any sharp feature which can be clearly identified as the beginning of melting. Note that, at temperatures just below T_m, the velocity during warming actually dropped *below* that on

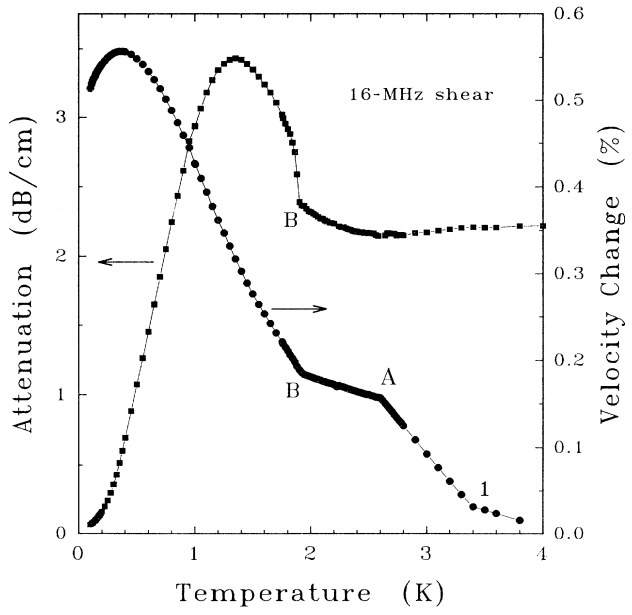

FIG. 1 Velocity and attenuation of 16-MHz shear waves in helium-filled Vycor glass. Bulk freezing occurs between points 1 and A, while helium in the pores begins to freeze at point B.

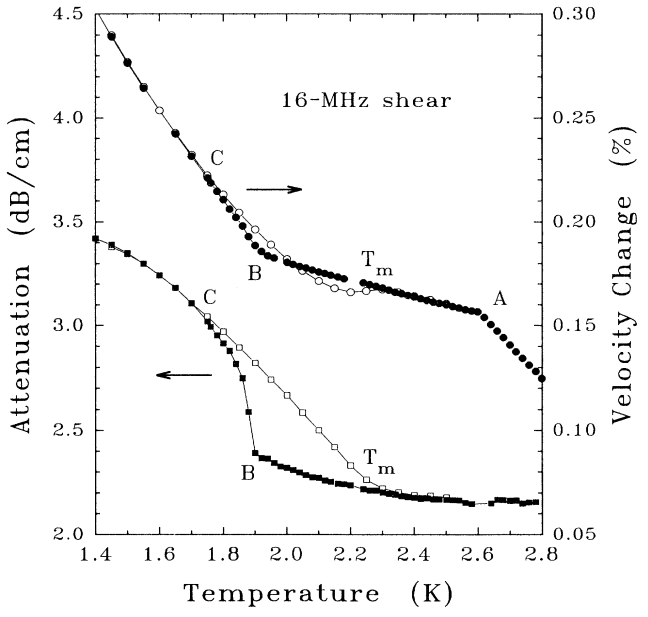

FIG. 2 Hysteresis between freezing and melting for helium in the pores of Vycor. During cooling (solid symbols) freezing begins at point B. During warming the velocity and attenuation rejoin the cooling curves at point T_m, where melting in the pores is complete.

cooling. Since any remaining solid helium cannot decrease the system's shear modulus, the density of the helium in this temperature range must be larger during warming than during cooling. This is expected since, at least in the initial stages of freezing, there must be percolating liquid paths along which helium flows into the pores to maintain pressure equilibrium with the bulk helium outside. As explained later, vacancy diffusion allows mass transport from outside the sample even when all the helium is frozen.

All of the sound-velocity features related to freezing and melting in the pores (points B, C, and T_m) are also obvious in the attenuation data of Figs. 1 and 2. However, since the attenuation is not related to the density as directly as the velocity, the beginning and end of freezing of bulk helium in the cell (points 1 and A) are not apparent in the attenuation data. The most striking feature in the attenuation is the rapid increase which begins at the onset of freezing and continues to form a large, broad peak at a lower temperature. This peak is superimposed on a background temperature dependence due to the TLS in the glass itself. The approximately constant attenuation seen above the onset of freezing is essentially the higher temperature plateau in the TLS attenuation[9] (it matches that found at higher temperatures in empty Vycor where, of course, there is no peak associated with freezing).

The mechanism responsible for the attenuation is not immediately obvious. The peak occurs at a temperature below the onset of hysteresis at point C. If this point does indeed mark the completion of freezing in the pores, as suggested by Adams *et al.*, then any mechanism involving the interface between liquid and solid helium is ruled out. A related question is why, if the helium is completely frozen, the sound velocity continues to increase below point C (in fact, about 90% of the total change ascribed to freezing occurs below this point). One possible alternative is that, rather than marking the completion of freezing, point C corresponds to the blocking of a sufficient number of pores by solid plugs to prevent liquid from flowing. Freezing in the pores would then continue, but at constant density rather than constant pressure. To help clarify the behavior we show in Fig. 3 the attenuation at several different sound frequencies. The exact peak heights are somewhat uncertain, because of the temperature-dependent background, but they grow approximately linearly with frequency. The peak maxima systematically shift to higher temperatures as the ultrasonic frequency increases. In fact, the frequency dependence is consistent with a relaxation mechanism governed by a thermally activated process. The data indicate an activation energy of approximately 14 K. Since this is roughly the activation energy for diffusion of vacancies in solid helium, we are led to consider their effects in our experiment.

When a transverse ultrasonic wave propagates in a porous medium such as Vycor, an average shear strain is imposed which varies smoothly over a sound wavelength ($\lambda \approx 10^{-2}$–10^{-3} cm in these experiments). However, on the much smaller length scale of the pores ($\approx 10^{-6}$ cm) the strains can be larger, with both shear and compressional components. The strain in the solid helium within a pore is inhomogeneous because most of the deformation of the Vycor occurs in the weakest solid "bridges" and these have irregular distributions of shapes, sizes, and orientations with respect to the polarization of the sound wave. Strain gradients give rise to gradients in the chemical potential for vacancies (because of the energy σV added to or subtracted from the vacancy formation energy, where σ is the stress and V the vacancy volume). This means that the ultrasonic wave is accompanied by alternating vacancy concentration gradients and vacancy currents in the solid helium. Vacancy flow transports mass from compressed to expanded regions, relaxing the stress. This mechanism was first discussed by Nabarro and Herring in the context of creep.[10] In solid helium, plastic deformation experiments[11,12] have shown that this vacancy diffusion mechanism is important at very low strain rates. However, these measurements involved mass flow over macroscopic distances, while in our experiment the stress relaxes over a much smaller length scale, namely that of the pores. This makes relaxation by vacancy creep much more rapid, especially in view of the large number of mobile vacancies in helium near melting.

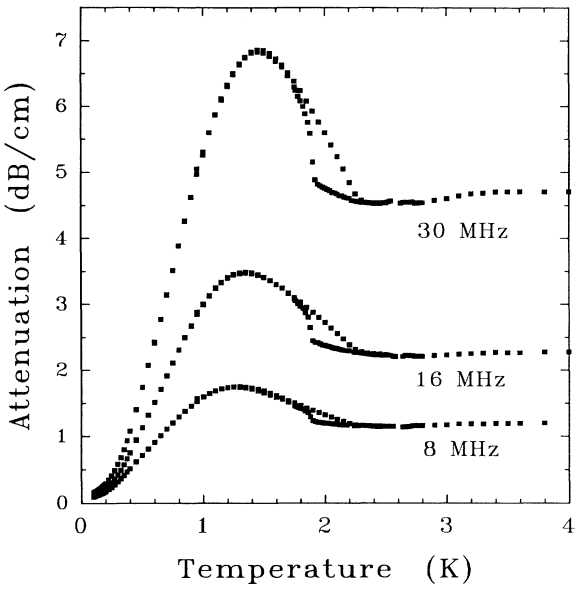

FIG. 3 Frequency dependence of the shear wave attenuation associated with freezing of helium in Vycor. Data is shown for both cooling and warming at frequencies of 8, 16, and 30 MHz.

If a stress is imposed on a crystal of size L, then the resulting vacancy flux will relax the stress in a time[10]

$$\tau = \frac{k_B T L^2}{2\alpha G V D} , \tag{1}$$

where α is a shape-dependent numerical factor and G is the shear modulus. The self-diffusion coefficient of solid helium, D, has the usual form

$$D = D_0 e^{-E_v/k_B T} , \tag{2}$$

where E_v is the activation energy for vacancy diffusion. For a relaxation process, the attenuation maximum corresponds to the condition $\omega\tau=1$ and, from Eqs. (1) and (2), we can write

$$\omega T_{\max}=\left[\frac{\alpha G V D_0}{k_B L^2}\right] e^{-E_v/k_B T_{\max}}, \quad (3)$$

where $T_{\max}$ is the temperature of the peak maximum at each frequency.

In Fig. 4 we plot $\ln(\omega T_{\max})$ versus $1/T_{\max}$ and find a straight line, as expected from Eq. (3). From the slope we find $E_v=14.2$ K, which can be compared to the vacancy activation energy for diffusion in bulk helium. The various x-ray, ^{3}He-impurity-diffusion, and ion-mobility measurements[13] give activation energies with considerable scatter, ranging at this pressure from close to our 14.2-K value up to above 25 K. We can also compare the relaxation time calculated using bulk ^{4}He parameters in Eq. (1) to that found from the sound frequency by assuming that $\omega\tau=1$ at the attenuation peaks. We take $\alpha=16$ (the appropriate value for spherical grains[10]), $V=3.2\times10^{-29}$ m^3, $G=1.9\times10^7$ Pa, $L=3.1\times10^{-9}$ m, and $D_0=1.4\times10^{-8}$ m^2/s. The value for L is the average pore radius minus the thickness of the first monolayer of helium, since the solid which nucleates in the pores does not appear to wet this high density layer. For D_0 we have used the value from plastic deformation experiments,[11,12] which is close to that observed in ion-mobility experiments. Using these values and our observed 14.2-K activation energy, we find a relaxation time of 1.4×10^{-9} s at 1.94 K where the helium in the pores begins to freeze. Since this is much less than the sound period, even at the highest ultrasonic frequencies used, we expect to see attenuation peaks at lower temperatures, where $\omega\tau=1$. At 16 MHz the peak occurs at 1.33 K. At this temperature, Eq. (1) predicts $\tau=2.8\times10^{-8}$ s, quite close to $1/\omega=1.0\times10^{-8}$ s.

We also checked whether the height of the attenuation peak, α_p, is consistent with that expected for a relaxation process. For a single relaxation time, the peak height is related to the total velocity change $\Delta v/v_0$ (from low to high frequency or high to low temperature) by $\Delta v/v_0=2v_0\alpha_p/\omega$. The peak heights should scale linearly with frequency, as observed, but for a velocity change of 0.35%, the predicted magnitude α_p is larger than the experimental results. For example, at 16 MHz we expect $\alpha_p=7$ dB/cm from the above relation, compared to the observed value of about 1 dB/cm. However, we note that the peaks are substantially broader than would be expected for a single relaxation rate with an activation energy of 14.2 K. A distribution of relaxation rates could result from different pore geometries. In addition, the energy barriers for diffusion may depend on the distance from the pore surface. In any case, having a range of relaxation times at each temperature would broaden the attenuation peaks and reduce their amplitudes, but would not change the total velocity dispersion.

The vacancy-diffusion mechanism provides an explanation of the fact that, during warming, the sound velocity dips below its cooling values at temperatures above the freezing onset B (see Fig. 2). The contribution of the solid helium to the shear modulus must be larger during freezing than melting, even for the same amount of solid in the pores, since the velocity never decreases during freezing. This is expected, since vacancy diffusion is much more rapid at the higher temperature where the dip occurs during warming and will reduce the solid helium's effective modulus.

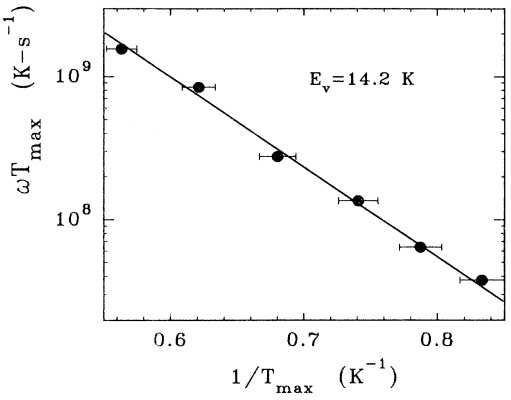

FIG. 4 Frequency dependence of the temperature $T_{\max}$ of the attenuation maxima.

Vacancy diffusion will also help to maintain pressure equilibrium with bulk helium outside the Vycor, even when all the helium in the pores is frozen. The relaxation time is still given by Eq. (1) but L is now the sample size. At 1.94 K, vacancy flow through the solid helium would allow pressure equilibrium to be established in our sample (radius 1.5 mm), in about 5 min. In measurements such as those of Adams *et al.*,[3] where the Vycor is ground into 74-μm powder, pressure equilibrium will be established in less than a second. It therefore appears that, unless the temperature is reduced quite rapidly, pressure equilibrium is maintained between the helium in the pores and that outside. In our experiment, where about 15 min is spent taking data at each temperature, this means that freezing occurs at essentially constant pressure, even when most of the pores are "blocked" by solid plugs. This makes Adams *et al.*'s identification of point C as the completion of freezing very plausible.

In conclusion, we have observed ultrasonic attenuation peaks, as a function of temperature, associated with the presence of solid ^{4}He in Vycor pores. The frequency dependence of the peak temperature indicates a thermally activated process which we identify as the relaxation of ultrasonic stresses in the helium via diffusion of vacancies. The observed activation energy and relaxation rates are in good agreement with those calculated using bulk helium parameters, indicating that the diffusion of vacancies in solid helium is not dramatically affected by confinement in the pores of Vycor.

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