Solidification and Superfluidity of ^{4}He in Porous Vycor Glass

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The onset of solidification of ^{4}He in porous Vycor is identified from changes in transverse sound velocity. From observed overpressures required to initiate freezing (ranging from 18 bars at 1.3 K to 30.7 bars at 2.38 K), the interfacial energy between liquid and solid ^{4}He was estimated. The superfluid transition up to 35.5 bars was also observed.

There has been considerable interest over the years in the behavior of ^{4}He in restricted geometries. Recently, observations[1] of the flow of liquid ^{4}He in packed powders of various sizes have shown that, in small pores, ^{4}He does not solidify up to a pressure somewhat greater than the bulk melting pressure. Freezing of ^{4}He in alumina (500-Å particle size) required overpressures of about 3.5 bars. Torsional-oscillator[2] and specific-heat[3] measurements have also been made in porous Vycor glass (a porous silica glass with a network of interconnected pores about 60 Å in diameter) at pressures above the bulk melting curve. These indicated that the ^{4}He in the pores remained liquid for overpressures as large as 15 bars and, in fact, no indications of freezing were observed.

In the experiments reported here, we made ultrasonic measurements of the transverse sound velocity in Vycor glass containing ^{4}He at pressures up to about 85 bars. The results indicate that the onset of solidification occurs at overpressures greater than about 18 bars. We also observed the λ transition inside the Vycor at pressures up to 35.5 bars.

The Vycor sample we used was a cylinder of diameter 0.36 cm and length 1.02 cm. The porosity was measured as ≈25%. The sample was mounted in a copper block and two 20-MHz LiNbO$_3$ shear transducers were bonded to the polished ends of the Vycor with high-viscosity silicone oil. The sample was inserted into the brass pressure cell (whose internal volume of 2.4 cm^3 was much larger than the 0.026 cm^3 pore volume of the sample). The transverse sound velocity in the Vycor was measured by using a pulse-echo overlap method with a resolution of 3 parts in 10^5.

The cryostat was a single-shot ^{3}He evaporation refrigerator capable of reaching 0.3 K. Temperatures were measured with a calibrated germanium resistance thermometer.

Figure 1 shows representative velocity meas-

urements. The points plotted with squares show the temperature dependence of the transverse sound velocity v_t in the empty Vycor (normalized by the maximum value of v_t). The temperature dependence of v_t is similar to that observed in fused silica.[4] However, both the transverse and longitudinal sound velocities in Vycor are considerably smaller than in fused silica because of the proosity of the Vycor. ($v_t = 2.4 \times 10^5$ cm/sec, $v_l = 3.7 \times 10^5$ cm/sec in Vycor compared with $v_t = 3.8 \times 10^5$ cm/sec, $v_l = 6.0 \times 10^5$ cm/sec in fused silica. It should also be noted that, at 20 MHz, the sound wavelength is 10^{-2} cm, much larger than the pore size.)
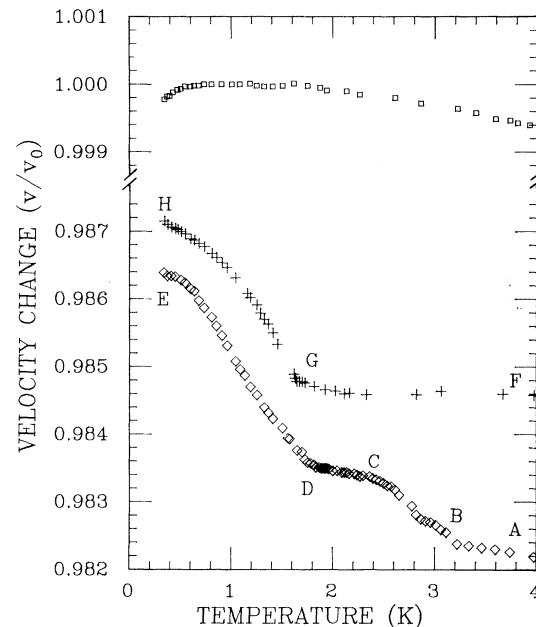

FIG. 1. Transverse velocity changes in empty and ^{4}He-filled Vycor as a function of temperature. Squares, for empty Vycor; crosses, for pressure of 25 bars; diamonds, for starting pressure (at 4.5 K) of 101 bars. The largest velocity of empty Vycor near 1.6 K is taken as the normalizing velocity v_0. Note the break in the vertical axis.

With the pressure cell at a temperature be-
tween 4 and 6 K, ^{4}He was admitted. The sound
velocity then decreased as the ^{4}He entered the
pores. After about 10 min, the velocity reached
a constant value. The velocity responded within
seconds to further changes in the ^{4}He pressure.
After the cell had been pressurized, the fill line
was cooled to approximately 1.6 K and therefore,
for pressures greater than 27 bars (the melting
pressure at 1.6 K), the line was blocked and the
mass of ^{4}He in the cell remained constant.

The lower points in Fig. 1 (diamonds) show the
velocity for an initial pressure (at 4.5 K) of 101
bars. The corresponding path in the P-T dia-
gram is shown in Fig. 2. Between A and B, the
liquid in the cell cools at nearly constant density
and the changes in v_t are essentially the same
as in empty Vycor. At point B, the bulk ^{4}He sur-
rounding the Vycor sample begins to freeze. This
point is determined from the sharp decrease in
the cooling rate due to the latent heat of freezing.
The bulk ^{4}He is completely frozen at point C, as
identified by an increase in cooling rate. At this
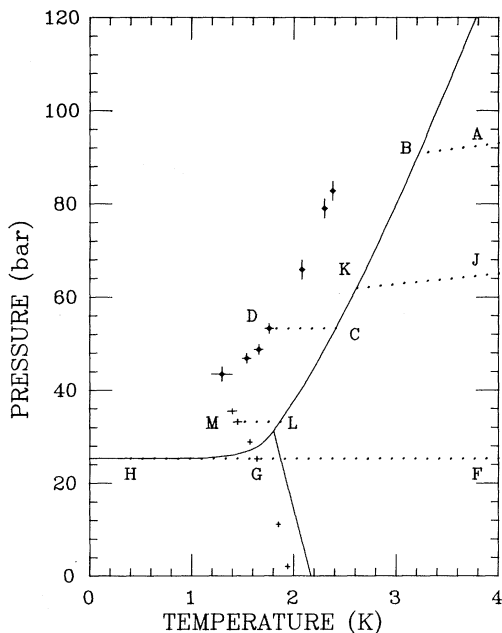point, the pressure in the cell is just the bulk

melting pressure at that temperature. When the
sample is cooled further, the sound velocity re-
mains nearly constant. At point D, the sound
velocity begins to increase and continues to in-
crease to low temperatures. We identify the
change in slope at D as the initiation of freezing
of the ^{4}He in the pores, and attribute the increase
in velocity to the contribution of the shear modu-
lus of the solid ^{4}He.

When different starting pressures were chosen,
similar velocity curves were obtained. The tem-
peratures that correspond to point D, the onset
of freezing inside the pores, are shown in Fig. 2
for seven different pressures (determined from
the bulk melting pressure at all points such as
C). It is apparent that the resulting freezing
curve for ^{4}He in Vycor is roughly parallel to the
bulk melting curve. The values of pressure and
temperature of the points D are listed in Table I.

We made similar measurements at lower pres-
sures. The points plotted as crosses in Fig. 1
show the results for a constant pressure of 25.3
bars (below the bulk melting curve and therefore
for an open fill line). When the sample was
cooled, v_t at first remained nearly constant and
then, at point G, began to increase. We identify
point G as the superfluid transition inside the
Vycor. This identification was confirmed by the
presence of a characteristic peak in the ultrason-
ic attenuation.

When we followed a path such as J-K-L-M in
Fig. 2, the bulk ^{4}He surrounding the Vycor again
solidified starting at K and ending at L. When
the sample was cooled further, the ^{4}He in the
Vycor underwent a superfluid transition at point
M, similar to that labeled G. The superfluid
transitions thus found at pressures up to 35.5
bars are also shown in Fig. 2.

The general theory of sound propagation in fluid-
filled porous media has been treated by Biot[5]

FIG. 2. P-T diagram of bulk ^{4}He (solid curves); so-
lidification (diamonds with error bars, points above 43
bars) and superfluid transition (plusses, points below
36 bars) of ^{4}He contained in the pores of Vycor glass.
The size of the symbol (error bars) represents the size
of errors. A-B-C-D, J-K-L-M, and F-G-H are the
paths of the cooling procedure for starting pressures
of 101, 72, and 25 bars, respectively.

TABLE I. Freezing points of ^{4}He in Vycor.

P (bars)	T (K)	ΔP (bars)	α_{LS} (erg/cm^2)
43.5 ± 1.5	1.3 ± 0.1	18.0 ± 1.5	0.31 ± 0.03
46.9 ± 1	1.54 ± 0.04	20.0 ± 1.5	0.29 ± 0.02
48.8 ± 1	1.66 ± 0.04	20.6 ± 1	0.27 ± 0.01
53.3 ± 1	1.76 ± 0.04	23.3 ± 1	0.29 ± 0.01
65.9 ± 2	2.08 ± 0.02	25.4 ± 3	0.30 ± 0.04
79.0 ± 2	2.30 ± 0.02	30.2 ± 3	0.34 ± 0.03
82.8 ± 2	2.38 ± 0.02	30.7 ± 3	0.34 ± 0.03

and further discussed with reference to liquid helium by Johnson.[6] Our results, however, can be understood by simply considering the shear modulus and the density of the ^{4}He-filled Vycor. The transverse sound velocity in an isotropic medium is given by $v_t = (\mu/\rho)^{1/2}$, where μ is the shear modulus and ρ the density. For the case of a fluid-filled porous medium, in this case helium-filled Vycor, the liquid does not contribute to the shear modulus and so $\mu = \mu_{\text{Vycor}}$. If the viscous penetration depth in the liquid δ $\{ = [2\eta/(\rho\omega)]^{1/2}$, where η is the shear viscosity and ω is the sound frequency$\}$ is much larger than the pore size, then the liquid moves with the porous matrix and the effective density becomes $\rho = \rho_{\text{Vycor}} + \varphi\rho_{\text{He}}$, where φ is the porosity ($\varphi \simeq 0.25$). For ^{4}He above the superfluid transition, $\delta > 500$ Å at 20 MHz, compared with a pore radius of ~ 30 Å in Vycor. Thus the density ρ_{He} can be obtained from the difference in sound velocity between empty Vycor and Vycor filled with liquid ^{4}He. Our measurements indicate that, at 4 K, $\rho_{\text{He}} = 0.169$ g/cm^3 at 1 bar, increasing to 0.207 g/cm^3 at 35 bars. This is to be compared with bulk helium densities of 0.125 at 1 bar and 0.176 at 35 bars. Differences in ρ_{He} for bulk ^{4}He and that contained in pores have been attributed to dense layers at the pore walls.[7] The sound velocity thus provides us with a measure of the density of normal liquid ^{4}He in the pores. For example, the velocity change when the bulk ^{4}He in the cell solidifies (between points B and C) reflects the drop in the ^{4}He density in the pores corresponding to the drop in pressure in the bulk ^{4}He outside the Vycor.

When the sample is cooled below the superfluid transition, a fraction of the superfluid component in the pores decouples from the Vycor (analogous decoupling is observed in torsional-oscillator experiments[2,8]). From the velocity change below point G, the fraction of the ^{4}He which decouples can be determined. At low temperatures we found this fraction to be 0.17 at 2.1 bars, dropping to less than 0.13 at 35.5 bars. For comparison, in torsional-oscillator measurements using Vycor, Brewer et al.[2] found this fraction to be 0.16 at 1 bar and to decrease with increasing pressure.

The depression of the superfluid transition temperature in small pores from its bulk value is well known.[9] By comparing the observed depression (0.21 K at low pressures) to those measured[10] in Vycor samples whose pore sizes were determined by nitrogen adsorption, we infer an average pore radius of 34 Å for our sample.

When the ^{4}He in the pores solidifies, the sound velocity increases, since the shear modulus of the ^{4}He now contributes to the stiffness of the system. The velocity change $\Delta v/v_0$ which we associate with this solidification (between points D and E in Fig. 1) increased from 2.1×10^{-3} to 3.8×10^{-3} for starting pressures of 43.5 and 82.8 bars, respectively. The largest velocity change corresponds to a change in effective shear modulus $\Delta\mu \simeq 7 \times 10^8$ dyn cm^2. Although the elastic moduli of filled porous media vary greatly depending on the structure of the porous matrix, limits can be placed on the moduli of the composite material.[11] A lower limit for the change in shear modulus due to filling empty pores with solid ^{4}He has the form $\Delta\mu \simeq \varphi\mu_{\text{He}}$. This expression is appropriate for low porosities. For weak porous structures, an appropriate upper limit to $\Delta\mu$ is $\Delta\mu \simeq (1/\varphi)\mu_{\text{He}}$. To compare our observed velocity change to that expected from these limits, we assume that the ^{4}He in the pores completely solidifies at constant density (so that the velocity change is solely due to the modulus change). With use of $\mu_{\text{He}} = 2 \times 10^8$ dyn/cm^2 (appropriate to solid ^{4}He at 40 bars) and $\varphi = 0.25$, the lower and upper limits on $\Delta\mu$ are 5×10^7 and 8×10^8 dyn/cm^2. The values of $\Delta\mu$ inferred from our velocity data fall in this range, further substantiating our interpretation of the observed velocity change as being due to solidification. The fact that the magnitude of the velocity change increases with increasing starting pressure is also consistent with this view.

The depression of the freezing temperature in small pores is not unique to helium. The simplest explanation of this effect involves the interfacial free energy, α_{LS}, between the liquid and solid phases. There is evidence[12] that solid ^{4}He does not wet the surfaces of some materials. In this case, freezing requires the formation of solid particles within the liquid contained in the pores. The excess pressure required to form a stable solid sphere of radius R is

$$\Delta P = (2\alpha_{LS}/R)V_S/(V_L - V_S), \qquad (1)$$

where V_S and V_L are the solid and liquid molar volumes. Since the solid particles cannot be larger than the pore size, this gives the overpressure required for solidification. Assuming the same values of V_S and V_L as in bulk ^{4}He at the same temperature, Eq. (1), combined with our measured overpressures, gives the values of α_{LS} shown in Table I. These values can be

compared to the value of 0.16 erg/cm² obtained by Landau *et al.*[13] for the interfacial energy between liquid and solid hcp ⁴He at temperatures below 1.5 K.

Dash[14] has proposed that the overpressure requred for solidification of ⁴He in small pores is due to the grain-boundary energy between small ⁴He crystallites growing in the pores. He estimates that solidification will occur for overpressures of $\Delta P = 0.05 \alpha \mu_{He} a/l$, where a is the interatomic spacing, l is the volume-to-surface ratio of the pores ($=R/2$ for Vycor), and α is a constant related to the surface roughness of the pores. Our observed overpressure of 18 bars at low pressures thus implies $\alpha \simeq 10$ for Vycor. The increase in ΔP which we observed at higher pressures is also consistent with this model, since the shear modulus of ⁴He increases with pressure. Dash also attributes the previously observed hysteresis[1] between the freezing and melting of the ⁴He in small pores to annealing of grain boundaries. We also observed some hysteresis in our measurements. On warming, the velocity varied smoothly around point D and did not match the cooling velocity until much closer to the bulk melting point C.

Both the idea of surface free energy between liquid and solid ⁴He and that of grain-boundary energy between crystallites qualitatively account for the overpressure required for solidification in small pores. Our measured solidification curve in Vycor is consistent with a value of the liquid-solid interfacial energy in ⁴He of approximately 0.3 erg/cm², comparable to that found in other experiments.[12,13] It is difficult to make quantitative comparison to Dash's grain-boundary model without an independent measure of the surface roughness parameter α.

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