Sharp Heat-Capacity Signature at the Superfluid Transition of Helium Films in Porous Glasses

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We report the first observation of a sharp heat-capacity signature related to the superfluid transition in thin ^{4}He films adsorbed on porous Vycor and xerogel glasses. The transition temperatures of these films range from 0.14 to 1.1 K. This new feature is found in addition to the broad peak centered at a higher temperature reported in a number of earlier studies.

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The confinement of ^{4}He in a multiply connected geometry such as porous glass has received renewed experimental[1,2] as well as theoretical interest.[3-6] Superfluid density (ρ_s) measurements[1,2] of ^{4}He films in porous Vycor glass (pore diameter ~ 70 Å) reveal a sharp transition at T_c with an asymptotic power-law dependence similar to the bulk λ transition, i.e., $\rho_s(t) \sim t^{\zeta}$ with $\zeta = 0.67$, for $10^{-2} < t < 10^{-1}$, where $t = (T - T_c)/T_c$. This behavior was seen for films with $T_c > 70$ mK up to full pores where $T_c = 1.955$ K (Refs. 1 and 2). More recently, studies of ^{4}He in two other porous glasses have revealed different exponents: 0.89 for $10^{-3} < t < 10^{-1}$ in xerogel[7] and 0.813 for $10^{-4} < t < 10^{-2}$ in aerogel.[2] The pores in xerogel glass have a diameter near 100 Å and those in aerogel span a wide range in size. The power-law dependence in these systems suggests that the superfluid transition is sharp and indicative of genuine critical behavior.[2]

Previous heat-capacity measurements of confined ^{4}He have revealed a broad peak with a maximum at a temperature T_m, which is apparently higher than T_c.[8] As the confining dimension is descreased, the height of this broad peak decreases, whereas the width and $T_\lambda - T_m$ increase (T_λ is the bulk transition temperature). Some of these observations have been analyzed in terms of finite-size scaling.[9,10] No sharp signature at T_c has been observed. Qualitatively similar behavior has been seen for ^{4}He films in Vycor glass by Brewer.[8] For partial filling of the pores they found broad peaks with $T_m = 1.25$ and 1.75 K having widths of ~ 0.60 and 0.55 K (FWHM) at coverages which we calculate to be 32.1 and 40.9 μmole/m^2, respectively. From ρ_s measurements, T_c's for these films should be 0.4 and 1.1 K, respectively.[1] No signature at T_c was found in either film. At full pores, a broad anomaly 8 J/mol K in height and 0.40 K in width was observed at $T_m = 2.1$ K. Again, no signature was observed at $T_c = 1.955$ K. Similar results for filled pores were observed by Joseph and Gasparini.[11] To our knowledge, no sharp heat-capacity signatures have been observed for any thin helium films whether in Vycor or on a planar substrate. Broad heat-capacity peaks were observed by Yuyama and Watanabe[12] and Bretz[13] above 1.2 K in ^{4}He on graphite. These peaks appear to be similar to that seen in porous media, i.e., they are centered above T_c as determined by third-sound[12] and torsional-oscillator[14] measurements. However, Bretz's results show effects of capillary condensation as pointed out in Ref. 9. Indeed, the Kosterlitz-Thouless theory[15] (appropriate for planar films) predicts an unobservable essential singularity in the heat capacity at T_c.

If the superfluid transition for ^{4}He in Vycor and the λ transition in bulk ^{4}He belong to the same universality class, as is suggested by the ρ_s measurements, then the size of the anomaly in the He-Vycor system can be estimated with two-scale-factor universality arguments.[16] Such an estimate predicts the heat-capacity amplitude with filled pores to be roughly 10 times smaller than our experimental resolution and smaller yet in thin films.

Although no sharp anomaly was resolved, Tait and Reppy[17] observed a change in temperature dependence of the heat capacity at a temperature T_0 which roughly coincided with T_c for several ^{4}He films in porous Vycor. It was this result which motivated the work presented here.

In this Letter, in contrast to expectations, we report the observation of a sharp heat-capacity signature at T_c for thin ^{4}He films adsorbed on Vycor and xerogel glasses. The transition temperatures range from 0.14 to 1.1 K. For films with T_c's above 0.4 K, a broad anomaly well above T_c similar to that seen in earlier Vycor experiments[8] was also found.

A steady-state ac heat-capacity technique is used in our study.[18] To minimize the internal equilibration time, the sample cells are small pieces of Vycor (9 mm diam by 0.6 mm thick) and xerogel ($10 \times 5 \times 0.5$ mm^3). The surface areas are 5 m^2 and 3.2 m^2, respectively. The xerogel sample came from the same source and is almost identical, in terms of porosity and pore size, to that used in the recent torsional-oscillator measurements.[2] The heat-capacity data shown here have been corrected for the empty-cell contribution but otherwise represent the total heat capacity of mobile and immobile layers of He. Because of the small open volume of these cells, the desorption correction is less than a few percent for the coverages reported here.

In Fig. 1 we show the heat capacity per unit area for

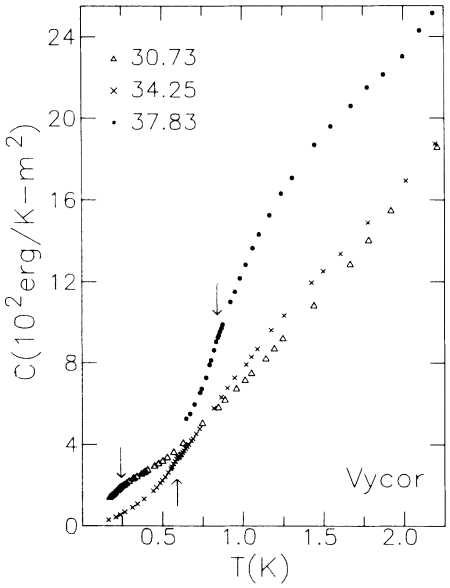

FIG. 1. Heat capacity per unit area vs temperature for three coverages of ^{4}He (in μmole/m^2) on Vycor. Arrows indicate the sharp signature at T_c. The lowest coverage (Δ) is shifted upward by 100 ergs/K m^2 while the highest coverage (●) by 200 ergs/K m^2.

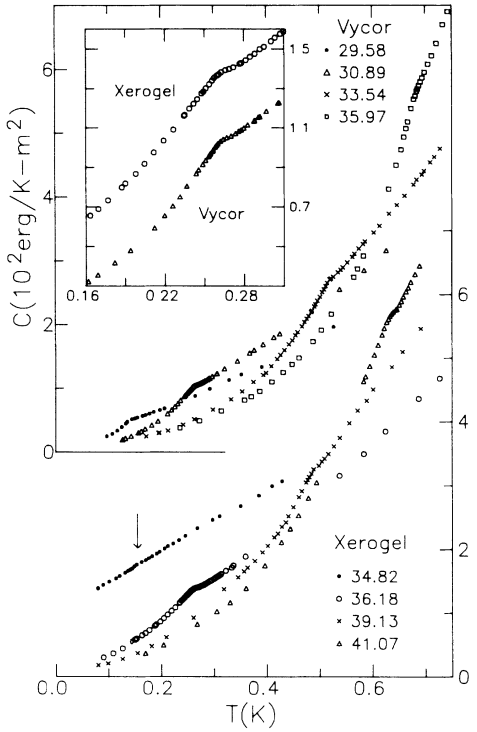

FIG. 2. Low-temperature heat capacity per unit area for various coverages (in μmole/m^2) on Vycor and on xerogel. The 34.82-μmole/m^2 scan in xerogel (●) is shifted upward by 100 ergs/K m^2. Some data have been deleted for clarity. Inset: The transition region for the coverages with $T_c \simeq 0.26$ K on both substrates.

three selected coverages of ^{4}He in Vycor versus temperature up to 2.4 K to emphasize both a sharp signature at T_c (arrows) and the broad anomaly centered at higher temperatures. This broad anomaly becomes visible for films with $T_c \gtrsim 0.4$ K, grows, and moves to higher temperature with increasing coverage. The area under the broad peak scales linearly with the amount of mobile fluid. It is worth noting that the heat-capacity scan at 37.8 μmole/m^2 (Fig. 1) and those at full pores[8,11] clearly show that the broad peak extends well below T_c. These features are in quantitative agreement with the broad peak observed by Brewer. For brevity we have not shown the broad anomalies of the He-xerogel system, as they are exceedingly similar to that in Vycor. We have investigated the heat capacity of He in Vycor with the pores full and found a broad peak centered at 2.1 K similar in size and shape to previous measurements.[8,11] In this case no signature larger than the maximum scatter in our data ($\sim$0.1%) was resolved at T_c.

Figure 2 shows more clearly the sharp signatures for four coverages on Vycor and xerogel, respectively, with T_c's between 0.1 and 0.8 K. It is striking that the sharp peaks remain prominent (in the Vycor case, more prominent) for coverages where the broad anomaly disappears (i.e., $T_c \lesssim 0.4$ K). The widths of all the small peaks shown in Figs. 1 and 2 are surprisingly coverage insensitive having values (FWHM) near 50 mK. In contrast, the width of the broad anomaly is highly dependent on the film thickness.[8-10]. The sharp peaks exhibit rounding within $\sim$5 mK of T_c. This is consistent with ρ_s measurements[2] and likely to be substrate related. Care was taken to limit the temperature oscillation in the calorimeter to less than 1 mK.

Note that for both substrates the heat capacity on the superfluid side *decreases* with increasing coverage, in contrast to the behavior above T_c. The heat capacity eventually drops below that of the localized layer (the coverage for which $T_c = 0$) making the separation of the mobile-film and localized-layer heat-capacity contributions inappropriate and impossible. Apparently, when the coverage is increased the excitation spectrum is changed in such a way that the entropy of the entire film is lowered. Hydrodynamically, however, the superfluid and localized-layer densities can apparently be distinguished by imposing a relative velocity between them as with a torsional oscillator.[1]

Two important differences between the two systems can be seen in Fig. 2. First, the size of the sharp signature for the lowest xerogel coverage is anomalously small when compared to the trend of the higher coverages, as well as the lowest Vycor coverage more clearly shown in Fig. 3. This behavior may be related to the anomalously small value for ρ_s at $T = 0$ for low coverages of ^{4}He in xerogel,[2] since the entropy of transition (i.e., the area under the heat-capacity peak) should scale with ρ_s. Second, the temperature dependence of the heat capacity

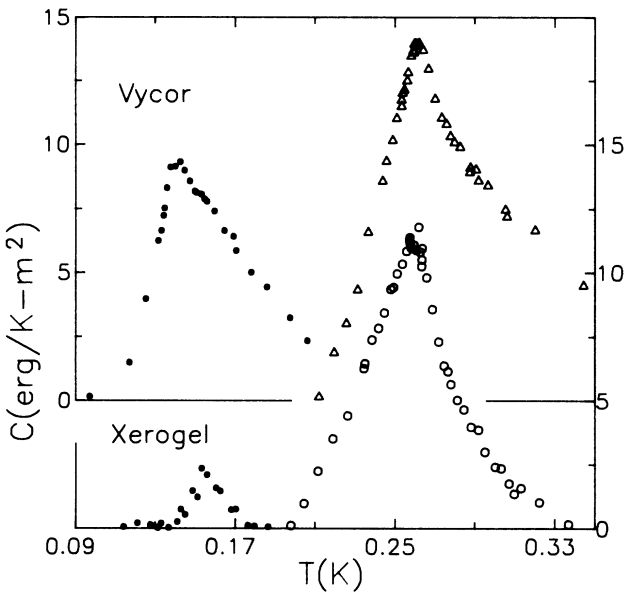

FIG. 3. Singular part of the heat capacity for the two lowest coverages on both substrates as shown in Fig. 2 after linear background subtractions.

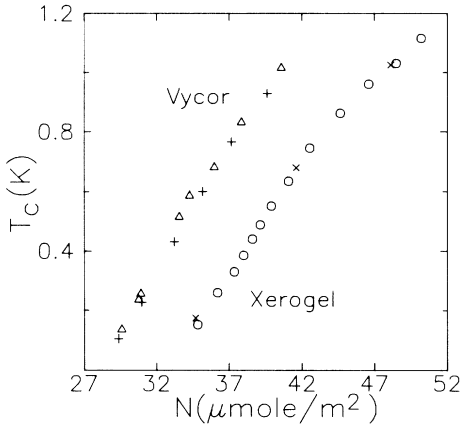

FIG. 4. Superfluid transition temperature vs coverage for ^{4}He on porous Vycor and xerogel from ρ_s torsional-oscillator measurements taken from Ref. 1 (+) and Ref. 2 (×). Also shown are the temperatures of the sharp signatures from this work (Δ,○).

below T_c appears to be stronger on Vycor than on xerogel for coverages with similar transition temperatures (see Fig. 2). We have not been able to fit the data with any simple and interpretable functional form (i.e., rotonlike or phononlike). Figures 1 and 2 show that as the coverage is increased the broad peak grows and washes out the sharp anomaly. This trend might explain why we did not see the sharp anomaly when the Vycor pores were full.

We have attempted an analysis of the sharp signature at T_c without arriving at any quantitative conclusion on the value of the specific-heat critical exponent. Three problems were encountered: (1) our sensitivity (0.1%), although quite good, is not sufficient for functional analysis on such a small peak; (2) our lack of knowledge of the regular part of the heat capacity makes the separation of the singular signature ambiguous; and (3) the rounding within $\sim$5 mK of T_c and the influence of the broad peak above and below T_c limits the temperature range for the analysis. Despite these difficulties, we have subtracted a linear background from the heat capacity for the two lowest coverages on both substrates to illustrate the sharpness of the singular contribution. The result is shown in Fig. 3. The background term corresponds to a line tangent to the data outside the peak region. The cusplike character of all the coverages, as well as the anomalously small signature for the lowest xerogel coverage, mentioned previously, can be easily seen in this subtracted data. Detailed analysis of the singular contribution will be presented in a forthcoming paper.

Figure 4 shows T_c versus coverage for both He in Vycor and He in xerogel, where we have defined T_c as the temperature of the sharp heat-capacity signature as well as where ρ_s vanishes.[1,2] The excellent correlation suggests that the sharp signature may coincide with the superfluid transition. A simultaneous heat capacity and ρ_s measurement is needed to confirm this suggestion. The coverage scale for the He-xerogel data was determined by vapor pressure isotherms performed in our laboratory on both the heat-capacity and torsional-oscillator cells. The He-Vycor coverage scale was normalized to ρ_s data of Refs. 1 and 17. For both substrates, the coverage scale reproduces within 5% upon repeated thermal cyclings. The minimum coverages needed for superfluidity (localized layers) are 27.5 μmole/m^2 for Vycor and 32 μmole/m^2 for xerogel.

There are a number of new models of the superfluid transition of films in porous media focusing on the role of vortices on a lattice of interconnected cylinders.[4-6] The common feature of these models is that the transition has some three-dimensional character, and thus a sharp heat-capacity peak at T_c is expected. In particular, the area under the peak in the model of Machta and Guyer[19] is expected to be of order aNk_BT_c, where N is the number of cylinder intersections and a is a number of order unity. When our data are compared with this prediction, we find the value of a ranges from 5 to 50 with no obvious trend with T_c. The value of N is estimated from the knowledge of the pore size, surface area, open volume, and the assumption of a square lattice.

In conclusion, we report the first observation of a sharp heat-capacity signature at the superfluid transition of helium film on porous glasses in addition to a broad anomaly centered at higher temperatures. The broad anomaly is generally attributed to finite-size rounding of the λ transition. The sharp heat-capacity signature at T_c supports the suggestion that the superfluid transition in

porous media is a phase transition with genuine critical behavior.[2] However, the size of the sharp signature seen for T_c near 0.5 K is about 2 orders of magnitude larger than that predicted by two-scale-factor universality.[16] It is an interesting theoretical challenge to produce a model which includes the disappearance of long-range order at T_c and gradual decrease of short-range order, possibly associated with finite-size rounding of the λ transition at much higher temperatures.

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[1]C. W. Kiewiet, H. E. Hall, and J. D. Reppy, Phys. Rev. Lett. **35**, 1286 (1975); J. E. Berthold, D. J. Bishop, and J. D. Reppy, Phys. Rev. Lett. **39**, 348 (1977); B. C. Crooker, B. Hebral, E. N. Smith, Y. Takano, and J. D. Reppy, Phys. Rev. Lett. **51**, 666 (1983).

[2]K. I. Blum, S. Q. Murphy, M. H. W. Chan, D. D. Awschalom, and J. D. Reppy, Jpn. J. Appl. Phys. **26**, 275 (1987); M. H. W. Chan, K. I. Blum, S. Q. Murphy, G. K. S. Wong, and J. D. Reppy, preceding Letter [Phys. Rev. Lett. **61**, 1950 (1988)].

[3]P. B. Weichman, M. Rasolt, M. E. Fisher, and M. J. Stephen, Phys. Rev. B **33**, 4623 (1986).

[4]T. Minoguchi and Y. Nagaoka, Jpn. J. Appl. Phys. Pt. 1 **26**, 327 (1987).

[5]J. Machta and R. A. Guyer, Phys. Rev. Lett. **60**, 2054 (1988).

[6]F. Gallet and G. A. Williams, unpublished.

[7]Also known as sol-gel glass. See M. W. Shafer, D. D. Awschalom, J. Warnock, and G. Ruben, J. Appl. Phys. **61**, 5438 (1987).

[8]D. F. Brewer, J. Low Temp. Phys. **3**, 205 (1970), and references therein.

[9]T. P. Chen and F. M. Gasparini, Phys. Rev. Lett. **40**, 331 (1978), and Phys. Lett. **62A**, 231 (1977); F. M. Gasparini, T. P. Chen, and B. Bhattacharyya, Phys. Rev. B **23**, 5797 (1981).

[10]W. Huhn and V. Dohm, Phys. Rev. Lett. **61**, 1368 (1988).

[11]R. A. Joseph and F. M. Gasparini, J. Phys. (Paris), Colloq. **39**, C6-310 (1978). These authors did not find the data to be in quantitative agreement with finite-size scaling.

[12]J. Yuyama and T. Watanabe, J. Low Temp. Phys. **48**, 331 (1982).

[13]M. Bretz, Phys. Rev. Lett. **31**, 1447 (1973).

[14]Y. Takano and J. D. Reppy, private communication.

[15]J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973); J. M. Kosterlitz, J. Phys. C **7**, 1046 (1974).

[16]P. C. Hohenberg, Physica (Amsterdam) **109&110B**, 1436 (1982), and references therein.

[17]R. H. Tait and J. D. Reppy, Phys. Rev. B **20**, 997 (1979).

[18]P. Sullivan and G. Seidel, Phys. Rev. **173**, 679 (1968).

[19]J. Machta and R. A. Guyer, private communication.