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Liquid-Vapor Critical Point of ^{4}He in Aerogel

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Thermodynamic studies of the liquid-vapor transition of ^{4}He confined in silica aerogel with a porosity of 95% is reported. In spite of the random nature of the pores, sharp heat-capacity signatures are seen. The positions of the sharp peaks are used to map out the liquid-vapor coexistence boundary, which is describable by a power law with an exponent $\beta = 0.28 \pm 0.05$.

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There has been a great deal of recent interest in the continuous phase transition of fluids confined in porous glasses. In spite of the highly complicated confining geometry, the superfluid transitions of ^{4}He adsorbed in Vycor and silica aerogel glasses were found to be sharp and to exhibit genuine critical behavior.[1,2] Depending on the nature of the disorder imposed by the host, the superfluid transition may or may not be in the same universality class as that of the λ transition in pure ^{4}He.[1,2] This is a subject of continuing theoretical and experimental interest. There are also substantial efforts in studying the effect of confinement in porous glass of fluid mixtures near their binary critical points.[3,4] These experiments, at the suggestion of de Gennes,[5] have been interpreted in terms of the random-field Ising-model (RFIM) transition.[6] Interestingly, but often not understood, hysteretic time-dependent effects probably related to metastability and slow kinetics in the experimental system were found.[3,4]

In this Letter, we report a heat-capacity and vapor-pressure isotherm study, inspired by the experiments reported above, of ^{4}He confined in porous silica aerogel glass near its liquid-vapor critical point. Although we expect this system to be similar to the confined binary-fluid systems, we found unexpected evidence of mesoscopic equilibrium liquid-vapor phase separation and a genuine critical point that is 31 mK below the bulk T_c at 5.198 K.

The silica aerogel used in this experiment has a porosity of 95%; it is obtained from the same source as that used in the superfluid experiment.[1] Small-angle neutron-scattering studies[7] indicate that the SiO_2 structure in silica aerogel exhibits no dominant length scale from 20 to 2000 Å and displays a volume fractal character. Transmission-electron-microscopy (TEM) studies on a similar aerogel sample show that the linear dimension of the void space between the SiO_2 aggregates ranges continuously from 20 to 5000 Å with no single characteristic pore size.[8] We have conducted N_2 and ^{4}He vapor-pressure isotherm studies and found the aerogel sample used in this experiment to have a surface area of 850 m^2/g. The isotherms indicate that the adsorption character of our sample is similar to that of the aerogel used in the TEM and small-angle diffraction studies.[7,8]

A schematic diagram of the calorimeter is shown in Fig. 1. The aerogel sample is shaped into a thin disk 1.07 cm in diameter by 0.025 cm in thickness. The sample is then encapsulated snugly in a brass cell with an indium O ring. Based on the vapor-pressure isotherm results to be presented below, roughly 8% of the space in the cell is not occupied by aerogel. The heat capacity of the sample is measured with an ac technique to a precision of 0.2%. In each run a desired amount of ^{4}He is introduced into the sample cell via a 0.01-cm-i.d. capillary and a room-temperature valve, and then heat capacity as a function of temperature is determined point by point. The amount of ^{4}He in the capillary (i.e., outside the cell) is less than 1% of the total sample. The amount of ^{4}He, and hence the average density of ^{4}He fluid inside the cell ($\bar{\rho}$), can be deduced from the change in the pressure in a room-temperature dosing volume before and after the introduction of ^{4}He into the cell. In order to improve the precision, the temperature oscillation at the heating frequency, which reflects the heat capacity of the sample, is averaged for 20 min for each data point. A typical run for each $\bar{\rho}$ takes approximately 30 h.

Figure 2 shows the temperature dependence of specific heat of confined ^{4}He at four different average densities. The heat capacity of the calorimeter is less than 35% of the total heat capacity. This addendum has already been

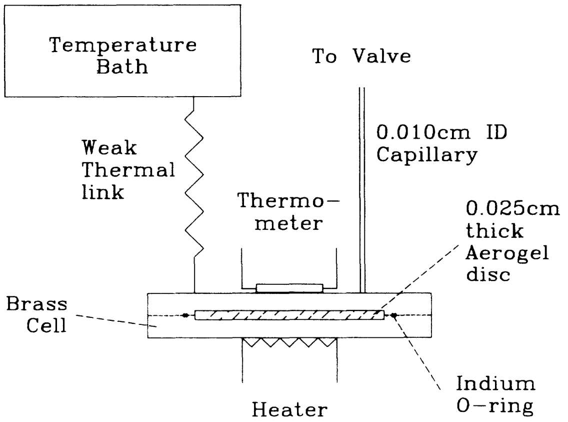

FIG. 1. Schematic diagram of the ac calorimeter.

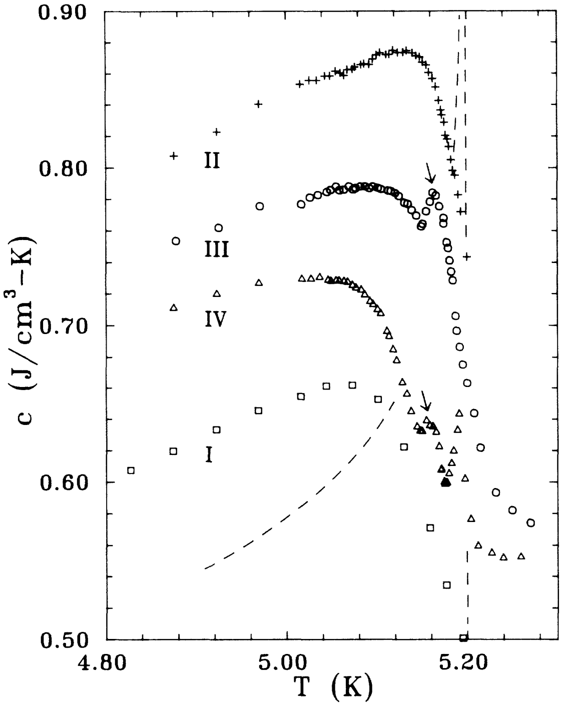

FIG. 2. Specific heat as a function of temperature at four different average densities of ^{4}He ($\bar{\rho}$). Arrows indicate the sharp peaks found for ^{4}He in aerogel. The dashed lines show the specific heat for bulk ^{4}He at $\bar{\rho}$ near $\rho_c = 0.0696$ g/cm^3 (see text). Curve I is shifted downward by 0.1 J/cm^{3}K, curve II is shifted upward by 0.04 J/cm^{3}K, and curve IV is shifted downward by 0.04 J/cm^{3}K for the sake of clarity. The $\bar{\rho}$ for the four curves are (□) 0.0682, (+) 0.0768, (○) 0.0802, and (△) 0.0818 g/cm^3, respectively.

subtracted from the curves in Fig. 2. For comparison purposes, the specific heat of bulk ^{4}He, near the liquid-vapor critical point as determined by Moldover,[9] is shown as dashed lines. The two curves at $\bar{\rho} = 0.0682$ and 0.0768 g/cm^3 represent all scans taken with $\bar{\rho}$ between 0.068 and 0.079 g/cm^3. These curves show only broad anomalies with a rounding of approximately ±0.15 K from the peak temperature. Rounding here is taken to be the temperature range over which the measured specific heat deviates from the idealized sharp peak of a bulk infinite system.[10] Finite-size considerations suggest that such a width is consistent with that of a finite system having a controlling linear dimension of $l \sim \xi_0 t^{-\nu} \sim 30$ Å. $\xi_0 = 3$ Å, $t = (0.15\ \mathrm{K})/(5.2\ \mathrm{K})$, and $\nu = 0.63$ are, respectively, the amplitude of the correlation length, the reduced temperature, and the correlation-length exponent for the bulk system. If the pores were all isolated from each other, this broad anomaly would be the only expected feature.

When $\bar{\rho}$ is increased to a value above 0.079 g/cm^3, a sharp peak in addition to the broad anomaly, as shown in curve III for $\bar{\rho} = 0.0802$ g/cm^3, appears. The sharp heat-capacity signature (indicated by an arrow) has a FWHM of approximately 15 mK and rounding (consistent with the definition given above) is apparent at ±2 mK from the peak position. One might suppose this sharp peak to be related to ^{4}He residing outside the aerogel sample undergoing a liquid-vapor transition. Such a proposition, however, is seen to be incorrect by examining curve IV for which $\bar{\rho} = 0.0818$ g/cm^3. Besides the sharp peak near 5.163 K, there is another one located at a temperature consistent with the bulk liquid-vapor T_c at 5.198 K. Above $\bar{\rho} = 0.083$ g/cm^3, heat-capacity scans show only the broad peak and the sharp peak near 5.198 K related to the bulk fluid.

It appears that only when $\bar{\rho}$ exceeds 0.081 g/cm^3 are the aerogel pores "saturated" and does excess liquid begin to condense in the cell volume outside the aerogel sample. The difference between the deduced value of $\bar{\rho}$ and the density of the excess fluid, which should be close to $\rho_c = 0.0696$ g/cm^3, is related to a substantial enhancement, resulting from van der Waals' attraction, of the density of the fluid that lies near the surface of the glass. Evidently, the first two layers of helium adsorbed on the glass substrate are solidlike with densities that are, respectively, 3 and 2 times that of ρ_c.[11] Since the compressibility of the fluid near the critical point is divergent, such a density enhancement is likely to extend beyond the first two layers. This effect is magnified in our system because the aerogel sample has an exceptionally large specific surface area of 850 m^2/g. A simple estimate based on these considerations shows that for the excess bulk to be near ρ_c, the average density $\bar{\rho}$ of helium inside the cell has to be close to 0.08 g/cm^3.

These considerations suggest that the sharp peak found at 5.167 K and below for samples with $\bar{\rho}$ near 0.081 g/cm^3 is related to the confined fluid crossing the modified liquid-vapor coexistence boundary applicable in the aerogel. Unfortunately, the sharp peak is too small, as compared to the broad background, to be used for a quantitative analysis of the heat-capacity exponent α. By varying the fluid density, the value of the peak temperature is found to increase and then decrease with $\bar{\rho}$. This allows for the determination of the coexistence phase boundary in the $\bar{\rho}$-T plane,[12] as shown in Fig. 3. The absolute value of $\bar{\rho}$ has an uncertainty of ±3%, mostly due to the uncertainty in the determination of cell volume. The precision of the density difference of the data as shown in Figs. 3 and 4 is as good as ±0.2%. The precision of the temperature determination is ±1.5 mK; a typical error bar is shown in the inset of Fig. 3.

In order to confirm our interpretation of a liquid-vapor coexistence region of helium confined in the pores, we have also performed vapor-pressure isotherm studies. The results of these studies near the coexistence density and pressure are shown in Fig. 4. The average density of ^{4}He in the cell is used in this figure. The density of fluid in the aerogel is different from the fluid outside. A vertical step, or a region of constant pressure, in this figure is a signature of two-phase coexistence. The isotherm at $T = 5.174$ K taken between the bulk (5.198 K) and aero-

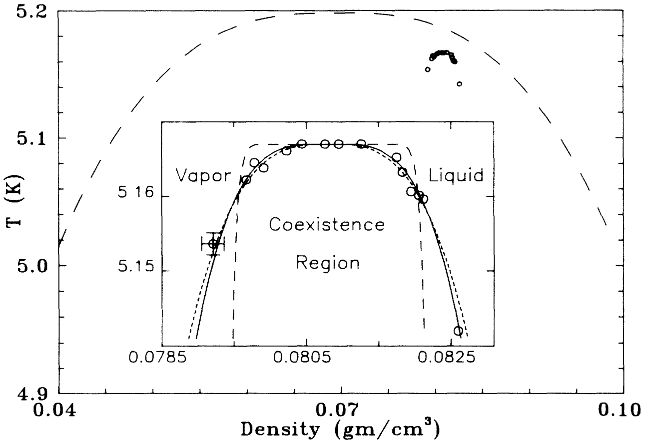

FIG. 3. Coexistence curve of liquid-vapor critical point of ^{4}He in aerogel. The circles depict the locations of sharp heat-capacity peaks related to the crossing of the coexistence boundary. Both the liquid and vapor densities found here include enhancement effects of the aerogel. The dashed line is that of bulk ^{4}He. The inset magnifies the coexistence boundary in aerogel. The solid line shows the best fit with $\beta = 0.28$, $B = 0.20$, $T_c = 5.167$ K, and $\rho_c = 0.0808$ g/cm^3. The dotted line shows the "best" fit with β fixed at 0.325; such a fit is marginally consistent with the data. The dashed line shows the "best" fit with an imposed β of 0.05.

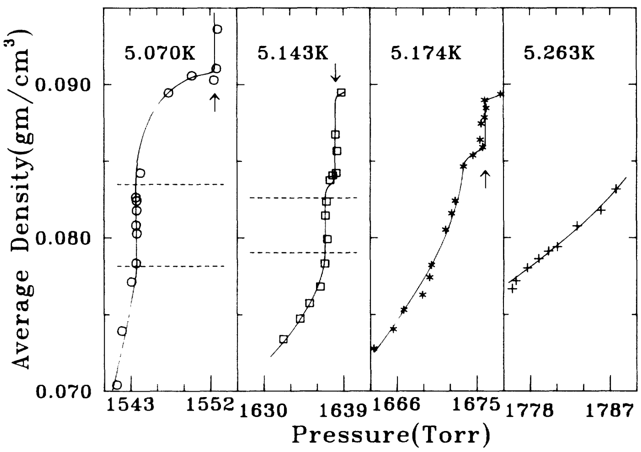

FIG. 4. ^{4}He vapor-pressure isotherms at four different temperatures. Vertical lines are drawn to highlight the vertical steps of bulk-liquid condensation at P_0 (marked with arrows) for the three isotherms below the bulk T_c at 5.198 K and the liquid-vapor coexistence of ^{4}He inside the aerogel below the aerogel critical point at 5.167 K. For easy comparison, the coexistence regions shown in Fig. 3 are marked by horizontal brackets.

gel (5.167 K) critical points shows only one vertical step for the consideration of bulk liquid at the saturated vapor pressure P_0. For temperatures below the aerogel critical point, there are two vertical steps, one related to the condensation of bulk liquid at P_0, and another at $P < P_0$ related to the liquid-vapor coexistence of ^{4}He in the aerogel. The density range of the step at P_0 indicates that the bulk liquid occupies up to 8% of the cell volume. In other words, 8% of the cell volume does not contain aerogel. The density range of the lower steps, i.e., the liquid-vapor coexistence region of ^{4}He in aerogel, is consistent with that shown in Fig. 3 mapped out by the locations of specific-heat peaks. The fact that this coexistence region is so much narrower than that in the bulk system indicates the extremely delicate nature of this transition.

It is interesting to note that the observed rounding in the sharp heat-capacity peak, at 2 mK or 4×10^{-4} in reduced temperature (t), is on the same order as but slightly larger than that found in the superfluid-density[1] and heat-capacity measurements[13] of ^{4}He in aerogel near the superfluid transition. The absence of rounding outside $t = 4\times10^{-4}$ indicates that the maximum value of the correlation length l' in this system, limited by some rounding mechanism (not completely clear to us), is 415 Å.[10] $l' \sim \xi_0 t^{-\nu}$ is estimated by assuming ξ_0 and ν to be, respectively, 3 Å and 0.63, i.e., the bulk values. If ν is taken to be 1, the RFIM value,[14] then l' will be an order of magnitude larger. Since there is no single characteristic pore size in aerogel and the minimum separation of the SiO_2 aggregates is on the order of 20 Å, the value of l' found for confined liquid-vapor and superfluid systems indicates that the critical fluctuation in these systems extends over many individual "pores."

In contrast to the binary-fluid[3,4] and dilute magnetic systems,[15,16] we found no evidence of hysteretic or dynamical effects. The temperature dependence of the specific heat is found to be reproducible upon cooling or warming to within the resolution of our technique, which is 0.2%. The data were obtained at the rate of one point every 20 to 30 min. A major difference between this experiment and the binary-fluid experiments is the porosity of glasses used. In contrast to a porosity of 95%, the Vycor glass used in binary-fluid experiments has a porosity of only 30%. In addition, critical slowing down in binary-fluid mixtures, being limited by mutual mass diffusion rather than by hydrodynamic equilibration, is known to be an order or even orders of magnitude slower than that of the pure liquid-vapor system. A careful quantitative comparison of the relevant time scale of these two systems should be interesting. Our system and the binary-fluid system differ from the dilute magnetic and the RFIM systems in that one phase preferentially wets the randomly distributed SiO_2 aggregates but there is no repulsion between the gel and the other (in our case, vapor) phase.

The coexistence region is assumed to be symmetric and is fitted by the form

$$\frac{|\rho_l - \rho_v|}{\rho_c} = B\left(\frac{T_c - T}{T_c}\right)^{\beta}. \tag{1}$$

ρ_l, ρ_v, and ρ_c are, respectively, the liquid, vapor, and critical densities of ^{4}He in aerogel. β and B are the coexistence curve exponent and amplitude. The result of the nonlinear least-squares analysis[17] is shown in the inset of Fig. 3 as the solid curve. The best-fit parameters are $B=0.200$, $T_c=5.167$ K, $\beta=0.28$, and $\rho_c=0.0808$ g/cm^3. The uncertainties, 1σ deviations, for B and β are 0.07 and 0.05, respectively. The uncertainties in T_c and ρ_c of the fit are comparable to the experimental precision quoted above. The corresponding parameters for the bulk system were determined in an equation-of-state experiment to be $B=2.7909$, $T_c=5.198$ K, and $\beta=0.355$.[18]

The value of β for a RFIM has been estimated by simulation studies to be 0.05.[14] As shown in the inset of Fig. 3, such a value of β is not consistent with our data. There are two possible interpretations of this result. The first is that the RFIM interpretation is still relevant; the discrepancy in β arises from the fractal characteristic[7] of the aerogel which imposes a correlated disorder on the confined fluid. In this case β is expected to be larger than 0.05.[19] For the reason given above, it is also possible that the RFIM interpretation is not applicable. The fact that the measured β is marginally consistent with the bulk value of 0.325 raises the possibility that in spite of confinement in a random host, the universality class of this liquid-vapor system is not changed. More experimental and theoretical information is needed before we can be certain of the proper interpretation for this remarkable finding of a sharp liquid-vapor transition for ^{4}He confined in a disordered environment.

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