

Heat Capacity Measurements of ^3He - ^4He Mixtures in Aerogel

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Heat capacity measurements of ^3He - ^4He mixtures in 98% porous aerogel show that, in this system, the coexistence boundary is detached from the superfluid transition line. Prominent heat capacity peaks are found deep inside the ^3He rich region. The resulting phase diagram is consistent with that based on the result of torsional oscillator superfluid density measurements.

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A recent torsional oscillator experiment [1] has shown that replacing 2% of the fluid by solid, in the form of a silica aerogel, has a profound effect on the topology of the ^3He - ^4He mixture phase diagram. In bulk mixtures, the superfluid transition temperature decreases with increasing ^3He concentration. The λ line terminates at a tricritical point at $T_{\text{tr}} = 0.872$ K and $X_{3,\text{tr}} = 0.669$ [2]. (X_3 is the molar ^3He concentration.) Below T_{tr} , the mixture separates into coexisting ^3He and ^4He rich phases. In the $T = 0$ limit, the ^4He rich phase contains approximately 6.4% ^3He , but on the other side of the phase diagram, ^4He is completely excluded from the ^3He rich phase [3]. Torsional oscillator measurements of the superfluid response of mixtures in aerogel show a rather different picture. The phase diagram based on those measurements is reproduced in Fig. 1. In contrast to the bulk, the superfluid transition line does not terminate at a tricritical point, but continues toward $T = 0$ on the ^3He rich side of the phase diagram. The coexistence region is completely contained within the superfluid part of the phase diagram; phase separation is now a transition between two superfluid phases. The tricritical point is replaced by a regular critical point, the top of the coexistence curve. The superfluid transition is marked by the decoupling of the superfluid from the motion of the oscillator. The coexistence boundary is deduced from excess damping and hysteresis inside the coexistence region. For ^3He concentrations greater than 81%, only the superfluid transition is seen. Aerogel, which takes the role of dilute quenched impurities, is a very porous solid [4]. It may be thought to consist of silica particles with a typical size of 20–30 Å which cluster together to form a network of interconnected strands. The specific surface area may be as high as 1000 m²/g. The mass and surface area distributions are highly nonuniform, the “pore” size, or rather the distance between the strands, ranges from the atomic scale up to a few thousand angstroms.

In this Letter we report the results of heat capacity measurements of ^3He - ^4He mixtures in aerogel. Our results appear to confirm the phase diagram based on the torsional oscillator measurements. The heat capacity (C) was measured using an ac technique [5]. To reduce the internal time constant of the sample, the aerogel was grown inside a silver sinter, made from a powder

with a grain size of 100 μm which was packed to 40% porosity. The remaining open volume of the cell was 0.32 cm³. The aerogel was grown under basic conditions via a two-step process [6], similar to the aerogel used in the torsional oscillator experiment. Both had a porosity of 98%. The surface area was determined to be 1000 m²/g from an adsorption isotherm performed with ^3He at 1.3 K. Because the aerogel is grown inside the cell, bulk volume is eliminated. We do not observe any features that can be attributed to bulk phase transitions. This puts an absolute upper limit on the space available for bulk fluid at 0.5%. The heat capacity of the empty cell is too small to be measured in our setup; we estimate it to be, at most, 1% of the heat capacity of the helium. The temperature response of the sample to a sinusoidal heat input at 0.08 Hz was measured with a calibrated germanium chip mounted on the sample. The sample cell was linked via a copper wire to a temperature controlled stage connected to the mixing chamber of a dilution refrigerator. The internal time constant of the sample

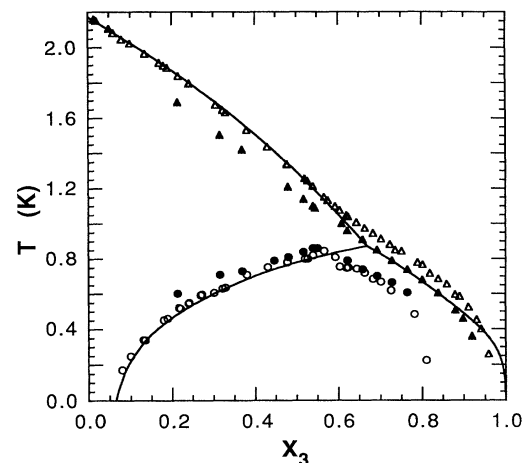


FIG. 1. The phase diagram of ^3He - ^4He mixtures in 98% porous aerogel. Triangles indicate the superfluid transition and circles indicate the phase separation. Solid symbols are obtained from heat capacity measurements and open symbols are obtained from a torsional oscillator experiment [1]. The bulk boundaries are shown as solid lines.

is less than 0.25 sec and the external time is of the order of 100 sec. Neither time constant varies much with temperature; the increase in the heat capacity with increasing temperature is evidently compensated by an increase in thermal conductivity of the sample.

The ^3He - ^4He mixture is introduced into the sample cell through a fill line with an inner diameter of 0.15 mm. To further reduce the contribution of the fluid inside the fill line to the heat capacity signal, a 0.14 mm diameter wire is inserted in the last 10 cm. By monitoring the pressure in the fill line, the cell was overfilled by approximately 1%. This was done in part to maintain a completely filled cell and to avoid rather serious heat leaks along a (superfluid) film in the capillary. Starting with pure ^3He , the concentration is changed by progressively replacing ^3He by ^4He . This is possible because of the much higher vapor pressure of ^3He . Superfluid film flow causes the ^4He concentration in the gas that is removed from the cell to be higher than the equilibrium concentration. To calibrate the concentration after repeated dilutions, we took four measurements on freshly prepared mixtures. The total uncertainty in the concentration is, at most, 2% for $X_3 > 0.5$ and proportionally smaller for higher ^3He concentration. In the process of changing the mixture ratio, we found that the density of the mixture in aerogel closely follows that of bulk mixtures [7]. Data are taken for each concentration by stepping the temperature of the control stage. The measured heat capacity is independent of the rate or direction in which the temperature is changed. This indicates that the sample is *macroscopically*, i.e., on length scales larger than a few thousand angstrom, homogeneous over its entire volume, and that no redistribution of the ^4He takes place after the dilution process is completed, a process that typically takes 30 min.

Figure 2 shows the heat capacity of mixtures at relatively low ^3He concentration. The results are very similar to those for bulk mixtures. For comparison, we reproduce the bulk data of Alvesalo *et al.* in Fig. 3 [8]. Cooling the sample down from the normal fluid phase, the superfluid transition is accompanied by a sharp peak in the heat capacity. On lowering the temperature further, the mixture phase separates with a corresponding discontinuity in the heat capacity. As expected, both the superfluid transition peak and the discontinuity diminish with increasing ^3He concentration; in bulk mixtures they vanish at the tricritical point. For $X_3 < 0.48$, the transitions in aerogel are sharp. At the superfluid transition, the heat capacity peak is rounded by less than 1 mK, and the jump in C at phase separation is less than 2 mK wide. The superfluid density measurements show the same sharp transitions with power law behavior in the superfluid density. With increasing X_3 , the heat capacity peaks become rounded; torsional oscillator data show a similar broadening.

It is at high ^3He concentration ($X_3 > 0.6$) that the heat capacity of the mixtures in aerogel differs dramati-

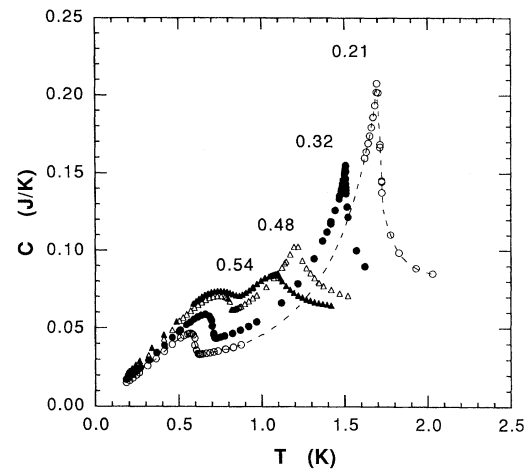


FIG. 2. The heat capacity of ^4He rich mixtures, $X_3 = 0.21, 0.32, 0.48,$ and 0.54 in 98% porous aerogel. The superfluid transition is accompanied by a sharp peak and phase separation is accompanied by a jump in C . The sample volume is 0.32 cm^3 . The curves are labeled with the corresponding concentrations.

cally from that of bulk. For $X_3 > X_{3,\text{tr}}$ in bulk, there is only one transition, phase separation with its characteristic jump in C . In mixtures in aerogel, the superfluid transition peak persists. As shown in Fig. 4, this peak can be observed down to a ^3He concentration of $X_3 = 0.92$ at $T = 0.35 \text{ K}$. We use the position of this peak to lo-

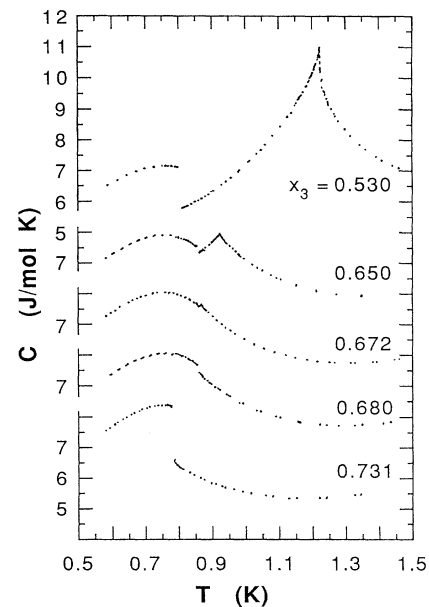


FIG. 3. The molar specific heat of bulk ^3He - ^4He mixtures for concentrations close to the tricritical point. Note the shifts along the vertical scale (after Ref. [8]).

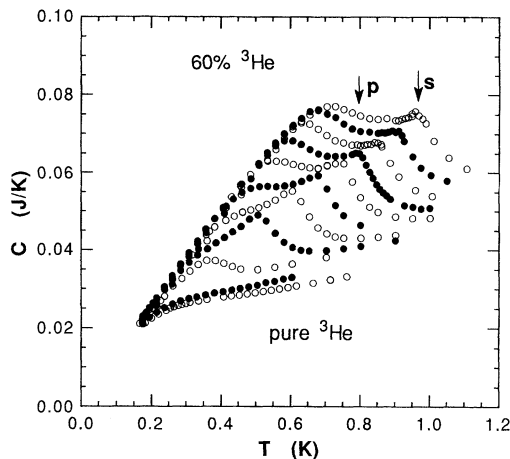


FIG. 4. The heat capacity for mixtures with $X_3 > 0.60$. The ^3He concentration is decreased in steps of 4% from pure ^3He to 60% ^3He . For ^3He concentrations equal to and less than $X_3 = 0.92$, there is a prominent peak associated with the superfluid transition. The arrows indicate the temperature of the phase separation (p) and the superfluid transition (s) for $X_3 = 0.60$.

cate the superfluid transition line in the phase diagram, (Fig. 1). At $X_3 = 0.6$ the height of the heat capacity peak is reduced by a factor of ~ 40 compared to pure ^4He . Surprisingly, on further increase of the ^3He concentration, its magnitude does not change very much, while, on the other hand, the superfluid density continues to drop. Only at very high ^3He concentration, $X_3 > 0.9$, does the heat capacity peak rapidly vanish. At temperatures below the superfluid transition, we find a region with $dC/dT < 0$. We interpret this as the signature of a broadened phase separation. This broadening is probably due to the fact that phase separation takes place in the rather heterogeneous environment close to the silica strands, whereas, on the ^4He rich side, the phase separation is nucleated far away from the silica network. For $X_3 > 0.76$, there is no obvious feature that can be attributed to phase separation. From the torsional oscillator measurements, it appears that there is no phase separation for $X_3 > 0.81$. A small but sharp heat capacity peak was found at the liquid-vapor critical point of ^4He in 94% porous aerogel [9]. Within our resolution (0.1% in C and with concentration steps of $\Delta X_3 = 0.005$), we did not find this at the mixture critical point.

For $X_3 > 0.64$, all heat capacity curves merge into a single straight line, the temperature below which they merge becoming progressively lower with increasing X_3 (Fig. 4). Since we show here the total heat capacity of the sample, this means that for sufficiently low temperature, in the phase separated region, the heat capacity *per unit volume* is independent of X_3 . Preliminary results of measurements on a much denser, 87% porous, aerogel

sample show the same result. This may or may not be unique to the mixtures in aerogel. To our knowledge, there are no data in this temperature and concentration range for the bulk system. However, heat capacity data by de Bruyn Ouboter *et al.*, at temperatures above 400 mK, indicate the possibility of similar behavior in bulk [10].

Figure 1 shows the mixture phase diagram based on the heat capacity measurements, and a comparison with the torsional oscillator results of Kim *et al.* As noted above, there is good qualitative agreement between the two measurements. The superfluid transition line, based on the heat capacity measurements, is shifted to lower ^3He concentration by approximately 4%. This is probably due to the much larger surface area of the heat capacity sample ($1000 \text{ m}^2/\text{g}$) as compared to the torsional oscillator sample ($580 \text{ m}^2/\text{g}$). The first layer adsorbed on the silica surface is expected to be a localized layer of pure ^4He , approximately $33 \mu\text{mol}/\text{m}^2$. Such a layer would effectively change the surface potential, but would otherwise play a minimal role in either the superfluid transition or the phase separation.

There have been a number of recent theoretical attempts to understand how aerogel can have such a profound effect on the mixture phase diagram. The bulk mixture is well described by the Blume-Emery-Griffiths (BEG) model [11]. Maritan *et al.* [12] take the silica strands in aerogel as a source of quenched randomness that favors the ^4He atoms. Within this framework the tricritical point was found to be unstable, which can lead to a phase diagram, at least near T_{tr} , similar to that shown in Fig. 1. Falicov and Berker [13] did their calculations also within the context of the BEG model. They constructed a lattice model that incorporated correlated randomness to mimic the connectivity of the aerogel network and found, by Monte Carlo simulation, a phase diagram remarkably similar to that shown in Fig. 1.

One of the most interesting questions raised by Fig. 1 is the nature of the superfluidity and hence the spatial distribution of the ^4He atoms in the high X_3 and low temperature region. In the limit of $T \rightarrow 0$ (i.e., $T < 0.2 \text{ K}$), they are expected to accumulate near the (solid layer ^4He coated) silica strands instead of being homogeneously dispersed among the ^3He . A complete phase separation, however, is not consistent with the observation of a 3D-like heat capacity peak for mixtures with X_3 as high as 0.92. Recent measurements on pure ^4He films on aerogel with transition temperatures up to 0.7 K show no heat capacity peak at the superfluid transition [14]. A likely scenario, first offered [1] as an interpretation of the torsional oscillator results, suggests that while the ^4He atoms tend to reside close to the silica strands, there is no well-defined interface separating the ^4He film from the ^3He rich liquid. Recent density functional calculations [15] for mixtures confined between parallel plates and path integral Monte Carlo simulations of bulk mixtures [16] ap-

pear to lend support for such a speculation. In both cases, it is found that the ^3He - ^4He "interface" is of the order of 10 Å, somewhat larger than the width of the liquid ^4He free surface, which is about 7 Å [17]. Such a diffuse interface increases greatly the effective thickness of the ^4He film, and perhaps is responsible for the 3D-like superfluidity observed in our experiment. In such a scenario, the coexistence boundary in the low temperature limit is likely to correspond to "capillary condensation" of the ^4He film from neighboring silica strands into ^4He rich domains. For a 98% porous aerogel, the condensation of the first domain occurs at a ^4He concentration of about 20%. With increasing ^4He concentration, increasingly larger pockets are formed. On the ^4He rich side of the phase diagram, coexistence ends when the last ^3He rich domain, situated presumably farthest from any silica strand, shrinks out of existence. It should be noted that, with increasing temperature, ^4He atoms will progressively "evaporate" into ^3He , giving rise to a thickening of the interface and a more homogeneous solution.

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