Tricritical Point and Superfluid Transition in ^{3}He-^{4}He Mixtures in Silica Aerogel

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We have ultrasonically studied ^{3}He-^{4}He mixtures in 87% porosity aerogel. We find only a single transition for ^{3}He-rich mixtures, in contrast to the detached phase separation curve seen in 98% porosity aerogel. However, it is a continuous transition, much like the superfluid transition seen in ^{4}He films on aerogels, rather than a first-order phase separation as seen in bulk mixtures. A kink occurs in the lambda line of the phase diagram at a ^{3}He concentration (corrected for the ^{4}He inert layer) of $X_c = 0.51$ and is accompanied by a change in the coupling to the superfluid component, indicating two distinct superfluid morphologies. [S0031-9007(98)06380-7]

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Phase transitions can be drastically changed by confinement in small pores and by disorder introduced by a porous matrix. Silica aerogels, with their tenuous structure and variable density, and helium, with its rich low temperature phase diagram, are particularly interesting for such studies. When measurements on pure ^{4}He [1,2] were extended to ^{3}He-^{4}He mixtures [3,4], the presence of 2% or 0.5% silica (i.e., aerogels with porosity ϕ of 98% or 99.5%) had even more dramatic effects. In bulk mixtures the lambda line terminates at a tricritical point (at ^{3}He concentration $X = 0.67$) but in aerogels it continues to low temperatures and high X, so superfluidity extends to dilute ^{4}He mixtures. Since other experiments [5] have observed superfluidity in pure ^{3}He in aerogels (at mK temperatures), there is a unique possibility of observing coexisting superfluids. Also, separate superfluid and phase separation transitions were seen for both high and low X mixtures; i.e., the phase separation curve was detached. Theoretical work [6,7] has shown that these features of the mixture phase diagram in aerogels can be qualitatively reproduced by introducing highly connected quenched disorder into the Blume-Emery-Griffiths model [8].

However, when we made preliminary ultrasonic measurements [9] on a denser ($\phi = 87\%$) aerogel, we found an apparently bulklike phase diagram, with a single transition at high ^{3}He concentrations. This has since been confirmed in torsional oscillator [10] and heat capacity [11] measurements. A very recent measurement [12] for an intermediate porosity (95%) found superfluid and phase separation transitions which were very close together at high X, but still distinct. The smaller effects of dense aerogels can be qualitatively understood if, because of its lower zero point energy, ^{4}He concentrates near the aerogel strands. As the temperature is lowered, ^{4}He will "condense" onto the strands, and the ^{4}He-rich layer will gradually thicken and become superfluid. Eventually, it will be thick enough to "capillary condense" (Phase separate into ^{4}He-rich domains). This should occur sooner in the smaller pores of high density aerogels.

Despite the progress made in understanding helium mixtures in aerogels, a number of important points are unresolved. One is the nature of the phase transitions in the high density aerogel. At low ^{3}He concentrations phase separation occurs well below the superfluid transition, which presumably takes place in a nearly homogeneous mixture. Is the single transition at high X a first-order phase separation, as in bulk, or does the disorder introduced by the aerogel convert it to a second-order transition, as suggested theoretically? If the ^{4}He is essentially all concentrated on the aerogel strands, the transition should resemble that in pure ^{4}He films on aerogels. Knowing how the ^{4}He is distributed is also important in understanding the phase separation itself. At low temperatures, where the interface is relatively sharp, the interfacial tension σ_{34} may drive a capillary condensation phase separation. At higher temperatures, however, the interface is not as well defined. Near a critical or tricritical point the interface's free energy disappears and its width diverges, so such a description is not applicable. This region is particularly interesting since low and high porosity aerogels behave differently. In 98% and 99.5% aerogels the phase separation curve detaches from the lambda line, and the tricritical point appears to be replaced by a conventional critical point. In the 87% porosity aerogel, the single transition at high ^{3}He concentrations suggests a more bulklike phase diagram. However, the experimental signature of phase separation disappears [10] as the phase separation line approaches the lambda line, so the expected tricritical point has not been observed.

In this paper, we present results of an ultrasonic study of ^{3}He-^{4}He mixtures confined in an 87% porosity aerogel, with particular emphasis on the tricritical region. In ^{3}He-rich mixtures, we see only a single transition, but, in contrast to bulk mixtures, it is a continuous transition. The lambda line extends to low temperatures, but changes slope abruptly at an intermediate concentration, suggesting the phase separation line meets it at this point. The superfluid transition's qualitative features (continuous disappearance of ρ_s, critical attenuation peak) do not change through the tricritical region. However, the amount of superfluid that decouples (measured either at low temperature or near T_λ) changes suddenly at the concentration

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of the kink in the lambda line. This is the first measurement to see sudden changes in the properties of mixtures in an aerogel at an apparent tricritical point.

Ultrasonic measurements are well suited to probe the mixture-aerogel system [9]. The system's effective density ρ decreases if the helium becomes superfluid and decouples from the silica matrix. The resulting sound velocity increase (analogous to the period shift in a torsional oscillator) is proportional to the superfluid density ρ_s. The attenuation provides additional information, and previous measurements have shown that the onset of superfluidity in ^{4}He confined in porous glasses is accompanied by a critical peak in the attenuation.

The 87% porosity aerogel used in these measurements was from the same material used in the torsional oscillator measurements of Yoon *et al.* [10]. A 2.9 mm thick sample was cut, and 20 MHz $\mathrm{LiNbO_3}$ transducers were epoxied to the parallel faces. The aerogel-transducer assembly was encapsulated in epoxy to minimize the bulk helium present. A 0.25 mm inner diameter capillary was inserted to fill the sample, and the assembly was sealed into a copper cell attached to a dilution refrigerator with helium exchange gas to ensure thermal contact. The sample's surface $(1.39\ \mathrm{m^2/g})$ was determined from a nitrogen adsorption isotherm. Ultrasonic measurements were made for both transverse and longitudinal waves at frequencies around 10 MHz.

Initially, pure ^{4}He was admitted to the aerogel until a superfluid transition was seen in the adsorbed film (at around 250 mK) for a coverage of 34.5 $\mu\mathrm{mol/m^2}$. Enough ^{3}He was then added to saturate the remaining pore space, giving an initial ^{3}He concentration $X \approx 0.81$. Subsequent mixtures were prepared by removing vapor (primarily ^{3}He, because of its higher vapor pressure) at 1 K and replacing it with ^{4}He (taking care not to overfill the sample).

Figure 1 shows representative velocity data (11 MHz longitudinal) for mixtures with X between 0.69 and 0.06. Starting with the dilute (^{4}He-rich) mixture $X = 0.06$, we see a superfluid transition at $T_\lambda = 1.98$ K, marked by a sudden increase in velocity as the superfluid decouples. As in bulk mixtures at this concentration, there is no phase separation. In the next mixture, $X = 0.12$, T_λ is lower, and there is a second transition, which we identify as phase separation, at $T_{\mathrm{PS}} = 0.5$ K. Hysteresis also appears once the mixture phase separates, and we found that it begins slightly (about 50 mK) below the kink in the velocity curve which we identify as T_{PS}. Hysteresis is presumably the result of the interface between separated phases being pinned in different configurations and provides strong evidence that this is a first-order transition. It first appears for $X \approx 0.18$ and is most obvious in the $X = 0.27$ data. At higher concentrations, $X \approx 0.35$, it disappears again, although the phase separation is still obvious. As X increases further, phase separation becomes less distinct and cannot be seen at all for $X > 0.42$. The attenuation also has a kink at T_{PS} and shows hysteresis over the same concentration and temperature ranges.

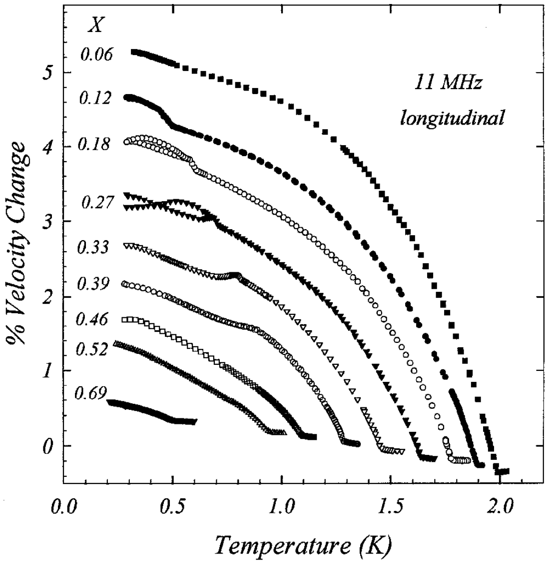

FIG. 1. Ultrasonic velocities (11 MHz, longitudinal) in aerogel containing ^{3}He-^{4}He mixtures. ^{3}He concentrations, $X = n_3/(n_3 + n_4)$, range from 0.06 to 0.69.

The behavior is quite different at the superfluid transition. There is a critical attenuation peak centered at T_λ, as expected for a continuous transition, and neither the velocity nor attenuation shows hysteresis. As X increases, T_λ decreases continuously (to below 0.5 K for $X > 0.69$) and the associated velocity increase becomes smaller (i.e., ρ_s decreases with the amount of ^{4}He present). For mixtures with $X \approx 0.8$, there is no sign of either superfluidity or phase separation down to the lowest temperature, 0.25 K. Figure 2 is the phase diagram from our measurements, showing T_λ and T_{PS} for a large number of mixtures. To compare to the bulk phase diagram (solid lines), we subtract an "inert layer" of ^{4}He tightly bound to the aerogel which does not participate in either superfluidity or phase separation. For pure ^{4}He films, we found an inert layer coverage of 30.7 $\mu\mathrm{mol/m^2}$, and in the mixtures we estimate it as 37 $\mu\mathrm{mol/m^2}$ [13]. Using the "corrected" concentrations, X_c, the superfluid transitions are shown as open circles and phase separations as open squares. The solid symbols are for the uncorrected concentrations X. This phase diagram agrees with that deduced from torsional oscillator [10] and heat capacity [11] measurements in aerogels of the same density. It resembles that of bulk mixtures in that there are two transitions (T_λ and T_{PS}) at low X but only a single transition at high X (in contrast to the situation in higher porosity aerogel [3,4,12]). For low X, superfluidity begins in an unseparated mixture. The phase separation at lower temperature requires nucleation of a normal ^{3}He-rich phase within the ^{4}He-rich superfluid; this should occur near the pore centers where the ^{3}He concentration is highest. During further cooling the ^{3}He-rich phase will grow until the interface between phases reaches the aerogel strands, at which point we expect it to

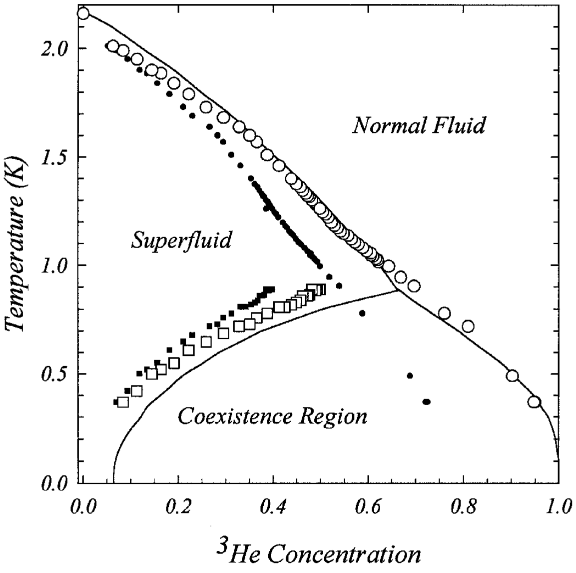

FIG. 2. Phase diagram for mixtures in 87% porosity aerogel showing superfluid transitions (T_λ, circles) and phase separation temperatures (T_{PS}, squares). Solid symbols are the overall ^{3}He concentrations, X; open circles are the concentrations, X_c, corrected for the ^{4}He inert layer.

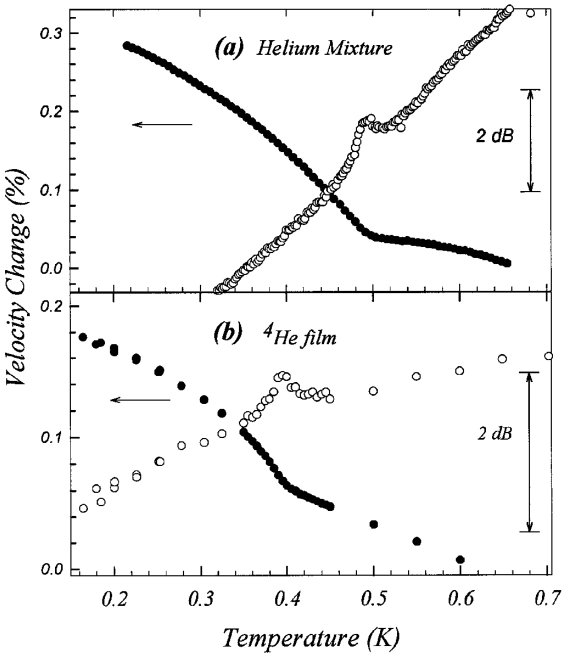

FIG. 3. Critical behavior of superfluid density (velocities, solid circles) and dissipation (attenuation, open circles). (a) ^{3}He-rich mixture $X = 0.69$; (b) ^{4}He film.

be randomly pinned, producing the hysteresis seen in the ultrasonic and torsional oscillator [3] data. Very recent measurements [14] indicate that the pinned interface can result in different metastable configurations.

The nature of the single transition in ^{3}He-rich mixtures in our aerogel is quite different from that in bulk mixtures where a first-order phase separation produces a minority superfluid phase and a normal ^{3}He-rich phase. In bulk, the nucleated ^{4}He-rich phase shows no critical behavior as it is well below its lambda temperature. If the transition in our aerogel is similar, we would expect ρ_s to vary as the fraction of the mixture in the ^{4}He-rich phase (i.e., linearly) and no critical attenuation peak. However, for ^{3}He-rich mixtures in the 87% porosity aerogel we find continuous transitions. The data for $X = 0.69$ are shown in Fig. 3(a). The superfluid density is not linear in temperature near T_λ, there is no hysteresis, and, most conclusively, there is a critical attenuation peak centered at T_λ. Figure 3(b) shows analogous data for a pure ^{4}He film on the same sample. The striking similarities support the idea that, for ^{3}He-rich mixtures, superfluidity occurs in a filmlike ^{4}He layer concentrated near the aerogel strands. The critical behavior of ^{4}He films in aerogels has been thoroughly studied in torsional oscillator measurements [15].

Given the different nature of the transitions at low and high X and the contrast with bulk ^{3}He rich mixtures, it is natural to ask how the crossover occurs as X is varied. In bulk mixtures, the lambda line meets the two branches of the first-order phase separation curve at a tricritical point (the lines meet linearly, with different slopes). Since we see only a single transition at high X, we might also expect a modified tricritical point; it would be a single first-order phase separation line meeting a continuous lambda line. It has proved difficult to verity the existence of an actual tricritical point because the signatures of phase separation in torsional oscillator and ultrasonic measurements disappear before the curves meet. However, since the superfluid transitions remain sharp at all concentrations, a tricritical point may appear as a change in the slope of the lambda line.

Figure 4(a) is a blowup of the lambda line between $X_c = 0.40$ and 0.65. Although the qualitative features of the superfluid transition do not change through this concentration region, the kink in Fig. 4(a) may mark a crossover between different mixture morphologies. This interpretation is supported by the behavior of the velocity. The open symbols in Fig. 4(b) are the velocity changes between T_λ and 0.25 K ($\Delta v/v_c$, a measure of the total amount of superfluid that decouples at low temperature). Although $\Delta v/v_0$ varies continuously with concentration, there is an abrupt change in slope at $X_c = 0.51$, where the kink appears in the lambda line. For comparison, we show the corresponding data for pure ^{4}He films in the same aerogel sample (solid symbols). The filling fraction for the films is plotted as an equivalent "concentration," again corrected for the inert layer. The decoupling for thick films is similar to that in ^{4}He-rich mixtures (i.e., at low X_c) but varies smoothly through the tricritical region where the mixtures show a kink. The film decoupling has a kink at higher $X_c \approx 0.75$, which corresponds to the onset of capillary condensation in the films (as seen in ^{4}He adsorption isotherms). The kink at $X_c = 0.51$ in the mixtures may indicate a similar change in the microscopic distribution of the ^{4}He at low temperature,

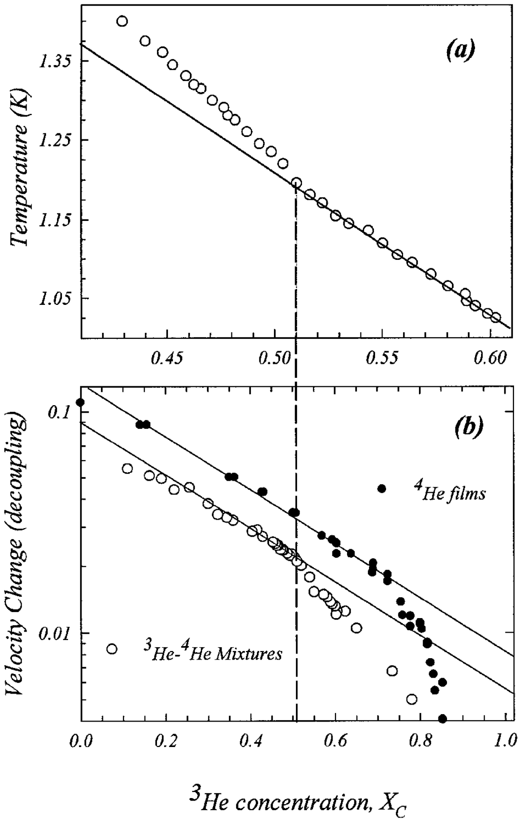

FIG. 4. Tricritical region for mixtures in 87% porosity aerogel. (a) Kink in lambda line at $X_c = 0.51$, $T = 1.18$ K; (b) velocity change due to superfluid decoupling at low temperature for mixtures (open circles) and for pure ^{4}He films (solid circles). Lines are guides to the eye.

from a thin filmlike distribution of ^{4}He at high X to a capillary condensed interface at low X [14].

At higher temperatures some of the ^{4}He dissolves into the ^{3}He; close to a tricritical point the interface width diverges, and its free energy disappears. The picture of a ^{4}He-rich film with a sharp interface which can cause capillary condensation of the ^{4}He-rich regions must break down. It is possible to obtain a measure of the superfluid decoupling at high temperatures by fitting the velocity data in the critical region near T_λ to form $\Delta v/v_0 = (\delta v/v_0)t^\zeta$, where t is the reduced temperature $(T_\lambda - T)/T_\lambda$. We found a superfluid density critical exponent ζ of about 0.75. It did not vary systematically with X but the "critical amplitude" $\delta v/v_0$ showed essentially the same behavior as the low temperature velocity changes shown in Fig. 4(b), including the kink at $X_c = 0.51$. The fact that the decoupling of mixtures changes suddenly along the lambda line, as well as at low temperatures, is consistent with recent theoretical work [7] which suggests that first-order phase separation can be converted to a continuous transition by disorder. The lambda line could then extend to zero temperature but be composed of two segments with different critical behavior [7].

Our measurements provide the first direct evidence of a sudden change in the morphology of helium mixtures in aerogel. We have observed a kink in the lambda line at $X_c = 0.51$ and, at the same concentration, a change in the velocity increase due to decoupling of the superfluid component. The fraction of ρ_s that decouples depends on the distribution of ^{4}He within the pores, and the crossover seen in the low temperature data may reflect the different tortuosities of homogeneous and localized ^{4}He arrangements. The disappearance of phase separation coincident with the kink in the lambda line is suggestive of a tricritical point. It occurs at 1.18 K, significantly higher than the bulk tricritical temperature (0.87 K) and also above an extrapolation of the first-order phase separation line in Fig. 2, but this may simply reflect uncertainty in picking $T_{\rm PS}$ from the data. Close to a true tricritical point the interface thickness will increase and eventually exceed the strand and pore sizes, but the nature of any tricritical point must still be affected by the disorder and preferential adsorption of ^{4}He introduced by an aerogel.

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