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## Ordering of $^3\text{He}$ – $^4\text{He}$ mixtures in aerogel

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**Abstract.** Silica aerogel is a highly porous glass consisting of a tenuous network of  $\text{SiO}_2$  strands interconnected at random sites. When a  $^3\text{He}$ – $^4\text{He}$  mixture is placed inside the aerogel, the coexistence region is found to be detached from the superfluid transition line, giving rise to a new miscible superfluid mixture at high  $^3\text{He}$  concentration and low temperatures.

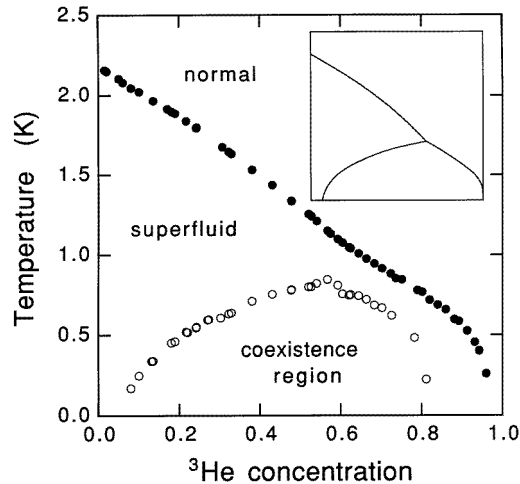
An important theme in phase transition studies is in elucidating the effect of randomness and disorder on the nature of the transition. For fluids, ‘quenched’ disorder can be introduced into a pure fluid system by placing the fluid in a porous medium (by quenched disorder, we mean the positions of the impurities are fixed). Recent studies found unexpected results near the superfluid [1] and liquid–vapour [2] transition of  $^4\text{He}$  entrained in silica aerogel. In spite of the random environment imposed by the aerogel, the transitions were found to be sharp and well defined. Although the silica network, the source of impurities, occupies as little as a few per cent of the total available volume, the nature of the transitions is completely changed. In this paper we will concentrate on the effect of aerogel on the phase separation of  $^3\text{He}$ – $^4\text{He}$  mixtures.

Aerogels are highly porous solids, formed by a sol–gel process [3]. After the formation of the gel network, the solvent is extracted by hypercritical drying to preserve the delicate structure. The porosity is controlled by the ratio between solid and solvent used in the gelation process, and can range from 85% to as much as 99.8%. In an aerogel of 99.8% porosity, only 0.2% of the volume is occupied by silica. The initial stages of the gelation process, in our case, consist of hydrolysis of tetramethoxysilane and polycondensation of small silica particles, typically 1–2 nm diameter. Gelation is thought to be the diffusion-limited aggregation of these particles. This leads to the formation of a very open structure that consists of silica strands that are interconnected at random sites. Transmission electron microscopy (TEM) and small-angle x-ray scattering (SAXS) studies on aerogel show no characteristic pore sizes [3]. The SAXS data show fractal-like correlations in the mass distribution, on length scales up to about 100 nm. At length scale larger than 100 nm, the mass distribution appears to be uniform.

Torsional oscillator experiments on  $^3\text{He}$ – $^4\text{He}$  mixtures in 98% porous aerogel produced a striking result [4]. They indicated that in this system the superfluid transition line in the phase diagram, instead of terminating at the tricritical point near 0.87 K, extends down to absolute zero. As shown in figure 1, the coexistence region is completely contained within the superfluid part of the phase diagram. Phase separation is now a transition between the usual  $^4\text{He}$ -rich and a new  $^3\text{He}$ -rich superfluid. The tricritical point is replaced by a

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**Figure 1.** The phase diagram of a  ${}^3\text{He}$ - ${}^4\text{He}$  mixture in 98% porous aerogel. The phase diagram of bulk mixture, i.e., without aerogel, is shown in the inset. The transition line separating the superfluid and normal phases in bulk mixture terminates at a tricritical point at 0.872 K and a  ${}^3\text{He}$  concentration of 0.669. Below 0.872 K, the bulk mixture with  ${}^3\text{He}$  concentration higher than 0.064 phase separates into  ${}^4\text{He}$ -rich superfluid and  ${}^3\text{He}$ -rich normal-fluid phases. Inside aerogel, the superfluid transition line is detached from the coexistence curves, and the coexistence region resides entirely within the superfluid part of the phase diagram. The top of the coexistence curve now corresponds to a regular critical point.

regular critical point at the top of the coexistence curve. This phase diagram is deduced from the following experimental observations. The frequency and amplitude of the torsional oscillator, which is operated at constant drive, are monitored as a function of temperature. After a temperature scan at a particular  ${}^3\text{He}$  concentration is completed, the concentration is changed and the next temperature scan is made. The superfluid transition in such a scan is marked by the decoupling of the superfluid from the motion of the oscillator. At high  ${}^3\text{He}$  concentrations,  $X_3 > 0.8$ , the superfluid decoupling is the only feature that is detected ( $X_3 = N_3/(N_3 + N_4)$ , with  $N_3$  and  $N_4$  being the numbers of  ${}^3\text{He}$  and  ${}^4\text{He}$  atoms in the mixture). At lower  ${}^3\text{He}$  concentration one finds, at a temperature below the superfluid transition, a second feature, namely a sharp dip in the amplitude of the oscillator. This is taken as the signature of the miscible mixture phase separation into  ${}^3\text{He}$ -rich and  ${}^4\text{He}$ -rich phases. This interpretation is reinforced by the observation of hysteresis in the oscillator frequency inside the coexistence region.

An interesting question is how the system organizes itself to be able to support superfluidity at high  ${}^3\text{He}$  concentrations, where this is normally not possible in mixtures without the aerogel. Because  ${}^4\text{He}$  has a smaller zero-point motion than  ${}^3\text{He}$ , it can profit more from the attractive van der Waals interaction between helium and silica. At high  ${}^3\text{He}$  concentration and temperature far below the  ${}^3\text{He}$ - ${}^4\text{He}$  critical point, the  ${}^4\text{He}$  atoms are plated out of the mixture onto the silica strands and form a solid-like layer, similar to that found in experiments of adsorbed  ${}^4\text{He}$  films. After completion of the localized solid layer, the  ${}^4\text{He}$  atoms are still expected to accumulate near the silica strands, instead of being homogeneously distributed among the  ${}^3\text{He}$ . At low temperatures, where the solubility of  ${}^4\text{He}$  in  ${}^3\text{He}$  is low, this should lead to the formation of a well defined  ${}^4\text{He}$ -rich film. The superfluid transition can now be thought of as taking place purely in this film [5].

The main argument against this picture for mixtures in aerogel comes from heat capacity measurements. Recently, superfluid transitions of  $^4\text{He}$  films adsorbed from vapour onto the silica strands in aerogel were studied using torsional oscillator and heat capacity techniques [6]. It was found that, based on the disappearance of the superfluid density, the transition is quite sharp, but not accompanied by any measurable peak in the heat capacity. With the mixtures in aerogel the situation is quite different [7]. At low  $^3\text{He}$  concentrations one finds a heat capacity peak at the superfluid transition, very similar to that in bulk mixtures. But whereas in bulk this peak decreases in size with increasing  $^3\text{He}$  concentration to vanish at the tricritical point, in aerogel it persists and can be observed all along the superfluid transition line. Indeed, the phase diagram for mixtures in 98% porous aerogel based on heat capacity results is consistent with that shown in figure 1. Recent density functional calculations and path integral Monte Carlo simulations of bulk mixtures found that the  $^3\text{He}$ - $^4\text{He}$  'interface' is of the order of 1 nm [8]. Such a diffuse interface increases substantially the effective thickness of the  $^4\text{He}$  film and thus enhances the three-dimensional connectivity established by the aerogel. This mechanism is most likely responsible for the 3-D-like superfluidity observed at low temperatures. In such a scenario, the coexistence region at low temperatures is likely to correspond to 'capillary condensation' of the  $^4\text{He}$  film from neighbouring silica strands into  $^4\text{He}$ -rich domains. With increasing  $^4\text{He}$  concentration, increasingly larger pockets are formed. On the  $^4\text{He}$ -rich side of the phase diagram, coexistence ends when the last  $^3\text{He}$ -rich domain, presumably situated farthest from any silica strand, shrinks out of existence. With increasing temperature,  $^4\text{He}$  atoms will progressively 'evaporate' into the  $^3\text{He}$ -rich domains, giving rise to a more homogeneous solution. The  $^3\text{He}$ - $^4\text{He}$  critical point marks the maximum temperature where  $^3\text{He}$ - and  $^4\text{He}$ -rich domains are found.

These results have stimulated a number of recent theoretical studies. Maritan *et al* [9] take the silicon strands as a source of quenched randomness that favours  $^4\text{He}$  atoms. Within the Blume-Emery-Griffiths (BEG) model, the tricritical point was found to be unstable, which can lead to a phase diagram that resembles the one shown in figure 1. By constructing a correlated random chemical potential model to mimic the connectivity of the aerogel, Falicov and Berker [10] obtained a mixture phase diagram remarkably similar to what is deduced from experiment.

To conclude, we have found that a minute amount of appropriately placed quenched impurities, as is the case of the silica network in aerogel, has unexpected effects on the ordering of  $^3\text{He}$ - $^4\text{He}$  mixture.

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