

Capillary Condensation of Phase Separated Liquid ^3He - ^4He Mixtures in Aerogel

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We have studied details of the phase separation of ^3He - ^4He mixtures in aerogel for ^4He concentrations between 13 - 36% and at pressures of 0 and 22 bar. Simultaneous measurements of the ^4He concentration (measured with a parallel-plate capacitor) and of the tortuosity of the ^4He -rich phase (using the period of the torsional oscillator) provide evidence for the diversity of configurations of the ^3He - ^4He interface as a consequence of capillary condensation. Thus, for the same ^4He content within the aerogel, the ^4He -rich phase can have different interconnectivities determined by preparation history.

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1. INTRODUCTION

It has been recently found that the phase diagram of liquid ^3He - ^4He mixture in highly open aerogels differs considerably from that of the bulk.¹ The novel feature is that even at zero temperature, phase separation seems to be completely suppressed at low ^4He concentrations.

For $x_4 \leq 20\%$, the ^4He -rich phase acts as a thick film that covers the aerogel surface below T_{ps} , the temperature of phase separation. Capillary condensation is known to cause metastability and hysteresis,² so different ^3He - ^4He interface configurations could be very long-lived. In Fig. 1 we illustrate how the morphology of the ^3He - ^4He interface can be rather different for identical volumes of ^4He -rich phase because of changes in the number of capillary condensed "bridges" between adjacent aerogel strands. These differences are manifested experimentally in the tortuosity of the ^4He film.

It is known that pressure changes the thermodynamics of the phase

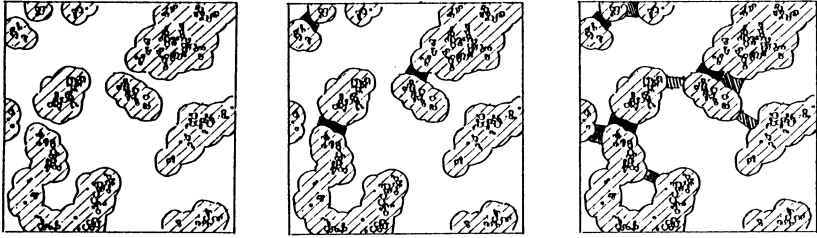


Fig. 1. Three configurations of ^4He -rich phase at the same x_4 . Left - film state (few “bridges”), right - capillary condensed state (many “bridges”).

separation of bulk ^3He - ^4He mixture.³ Therefore, we compare the phase diagram of ^3He - ^4He in aerogel at $p = 0$ and $p = 21.6$ bar.

2. EXPERIMENTAL TECHNIQUE AND RESULTS

We detect both the superfluid and phase-separation transitions by monitoring the resonant frequency and dissipation of a torsional oscillator (TO) that contains the aerogel sample. Providing the amount of ^4He in the cell is known, the period shift due to the decoupling of superfluid ^4He can be used to determine the tortuosity of the ^4He -rich film. A parallel-plate capacitor located in the head of the TO inside which the aerogel has been grown, allows us to determine x_4 , the molar fraction of ^4He . The 98.2 % porous aerogel (0.4 cm^3 open volume and 9.3 m^2 surface area), sintered powder (0.4 cm^3 open volume and 4.2 m^2 surface area) and a “dead” bulk volume (0.3 cm^3), about 10% of which is located in the torsion head constitute the experimental arrangement. When the temperature of the cryostat is cycled, the distribution of ^4He between the aerogel, sintered powder and filling line changes, making it important to monitor x_4 in the aerogel.

We were unable to make mixtures with ^4He concentrations in the range 4-10 % at low temperatures, since below T_{ps} the ^4He preferentially moved into the sinter (or filling line). To fill the cell with a mixture we first admitted pure ^4He to the empty cell at a temperature below 0.1 K. The ^4He coated the surfaces of the cell (including the strands of aerogel) with a thick ^4He film. This “film state” (with a different configuration of the ^3He - ^4He interface from that achieved by cooling a ^3He - ^4He mixture from 1K) persisted even after the remaining volume was filled with ^3He and the cell brought up to a pressure of 21.6 bar. If the cell was warmed above ~ 0.2 K, the system displayed a remixing transition and the result was a pronounced hysteresis in the amount and distribution of the ^4He in the aerogel.

The concentration, x_4 in aerogel is modified when a few distinct tem-

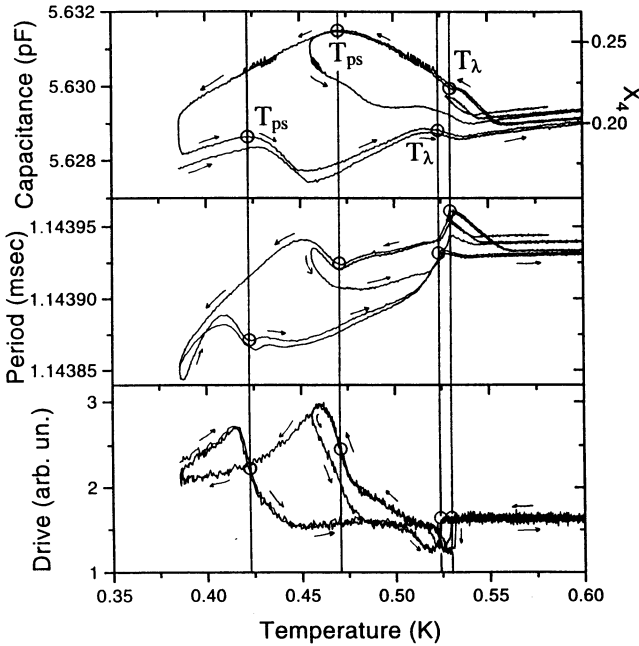


Fig. 2. An example of the capacitance, period and dissipation signals from a ^3He - ^4He mixture in aerogel during thermal cycling; $p = 21.6$ bar.

perature bands are traversed. These bands are typically separated by a phase transition in one of the cell parts. As we cooled from 0.8 K with 14 mmole of ^4He ($p = 21.6$ bar), we observed the sequence shown in Fig. 2 and summarized below:

1. $T > 0.56$ K. ^3He - ^4He solution ($x_4 \approx 21\%$) fills the cell.
2. 0.53 K. Superfluid transition of the ^4He in the aerogel.
3. 0.47 K. The phase separation transition in the aerogel ($x_4 \approx 25\%$).

These measurements were taken while ramping the temperature at ~ 10 $\mu\text{K}/\text{sec}$ and yielded sharp transitions. We ascribe T_{ps} and T_λ to the steepest parts of the oscillator drive vs temperature (marked by circles in Fig. 2). On warming, the values of T_{ps} and T_λ are different from the values while cooling and reflect changes in x_4 within the aerogel.

Fig. 3 shows the set of points, $T_{ps}(x_4)$, obtained in this way for $p = 0$ (\circ) and $p = 21.6$ bar (\bullet). At $x_4 > 20\%$, ($p=0$), our data are in good agreement with the results of Chan's group¹ for ^3He - ^4He in an aerogel of the same porosity (Δ). T_{ps} decreases when the pressure is increased from 0 to 21.6 bar in a manner similar to that in bulk ^3He - ^4He mixtures, reflecting the decrease of the energy of mixing over this pressure range.³

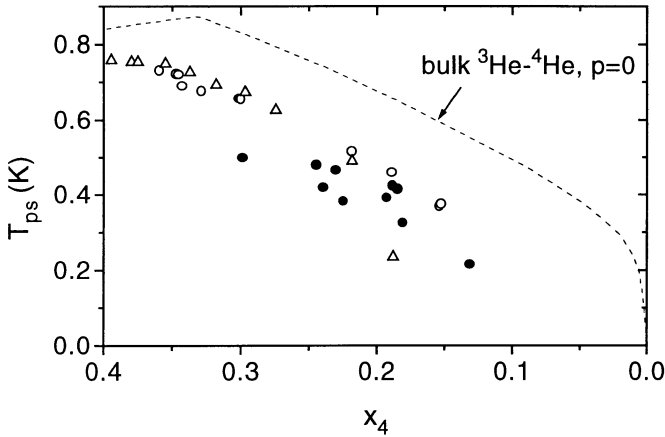


Fig. 3. Locus of T_{ps} vs x_4 obtained as in Fig. 2 (\circ - $p = 0$, \bullet - $p = 21.6$ bar). Also shown are the data from Kim *et al.*¹ at $p = 0$ (Δ).

The discrepancy between our $p = 0$ data and the low T point from Chan's group¹ at $x_4 < 20\%$ can either be ascribed to different microscopic structures of the aerogels *or* the diversity of metastable states in this region of x_4 . When we cooled a ${}^3\text{He}$ - ${}^4\text{He}$ solution through T_{ps} , or warmed it into the mixed state from $T \sim 0.2$ K, the scatter of the $T_{ps}(x_4)$ points was modest, and the data fall on a single curve on the phase diagram (circles in Fig. 3). However, this is not the case for the "cold-deposited" samples. The morphology of the "cold-deposited" ${}^4\text{He}$ films is expected to differ from that of those cooled from a mixed ${}^3\text{He}$ - ${}^4\text{He}$ solution. Thus T_{ps} depends not only on x_4 , but also on the particular morphology of the ${}^3\text{He}$ - ${}^4\text{He}$ interface. The dependence on morphology is also seen in adsorption isotherms in porous media when capillary condensation is important. We speculate that when a ${}^4\text{He}$ film is slowly deposited onto bare aerogel, it simply follows the strand's surface and has no opportunity to build capillary condensed "bridges" between adjacent strands. If ${}^3\text{He}$ liquid is gently added to fill the rest of the system at $T \ll T_{ps}$, the interface between ${}^3\text{He}$ -rich and ${}^4\text{He}$ -rich phases follows the shape of the ${}^4\text{He}$ film. In contrast, when a ${}^3\text{He}$ - ${}^4\text{He}$ mixture is cooled in aerogel, even at $T > T_{ps}$ domains of locally enhanced ${}^4\text{He}$ concentration occur between adjacent strands. After cooling through T_{ps} , the ${}^3\text{He}$ - ${}^4\text{He}$ interface probably forms near the regions of enhanced ${}^4\text{He}$ concentration, and stabilizes the "bridges".

3. DETERMINATION OF x_4 AND χ_4

The ^4He film's tortuosity can be characterized by a parameter χ_4 , the fraction of the ^4He superfluid inertially coupled to the oscillator. Thin ^4He films on aerogel have $\chi_4 \approx 0.90$, while liquid ^4He in full-pore aerogel has a $\chi_4 \approx 0.16$.⁴ We conclude that χ_4 decreases as the number of connections between the aerogel strands increase. Thus a small χ_4 must reflect an increased number of capillary condensed "bridges" between the aerogel strands.

The determination of χ_4 proceeds from a period measurement near 3 mK where almost all the ^4He is superfluid and the molar volumes of ^3He -rich and ^4He -rich phases are close to their bulk values V_3 and V_4 . When a sample contains N_3 (N_4) moles of ^3He (^4He) ($x_4 = N_4/(N_3 + N_4)$), the number density of the mixture is $(N_3 + N_4)/(N_3V_3 + N_4V_4)$. The mass density is $(m_3N_3 + m_4N_4)/(N_3V_3 + N_4V_4)$ (where $m_3 \approx 3$ g/mole and $m_4 \approx 4$ g/mole). The capacitance increment is given by

$$C_x - C_{emp} \propto \frac{N_3 + N_4}{N_3V_3 + N_4V_4} = \frac{1}{V_3 - \Delta V_{34}x_4}, \quad (1)$$

where $\Delta V_{34} = V_3 - V_4$. Hence,

$$x_4 = \frac{V_3}{\Delta V_{34}} \left(1 - \frac{1}{1 + \frac{C_x - C_0}{C_0 - C_{emp}}}\right) \approx \frac{V_3}{\Delta V_{34}} \frac{C_x - C_0}{C_0 - C_{emp}}, \quad (2)$$

where C_{emp} , C_0 and C_x , are the capacitances when the cell is empty, filled with ^3He , and filled with mixture respectively.

The period shift at 3 mK is related to x_4 and χ_4 through the expression

$$P_x - P_{emp} \propto \frac{3N_3 + 4N_4\chi_4}{N_3V_3 + N_4V_4} = \frac{3 + (4\chi_4 - 3)x_4}{V_3 - \Delta V_{34}x_4}. \quad (3)$$

Finally,

$$\chi_4 = \frac{3}{4} \left[\frac{P_x - P_{emp}}{P_0 - P_{emp}} \left(\frac{1}{x_4} - \frac{\Delta V_{34}}{V_3} \right) + 1 - \frac{\Delta V_{34}}{V_3} \right], \quad (4)$$

where P_{emp} , P_0 and P_x are the periods of the pendulum when it is empty, filled with ^3He and filled with mixture, respectively.

The values of x_4 , χ_4 calculated in this manner are shown in Fig. 4. It is generally true that at higher x_4 , χ_4 is smaller reflecting the greater likelihood of more connections between strands. However, it is crucial to realize that the scatter in Fig. 4 is not due to the uncertainty in determining x_4 and χ_4 . We found that χ_4 depends on the thermal history of a particular sample for a fixed x_4 . This is borne out by differences in the signature of the $\rho_s(T)$ of the ^3He superfluid.

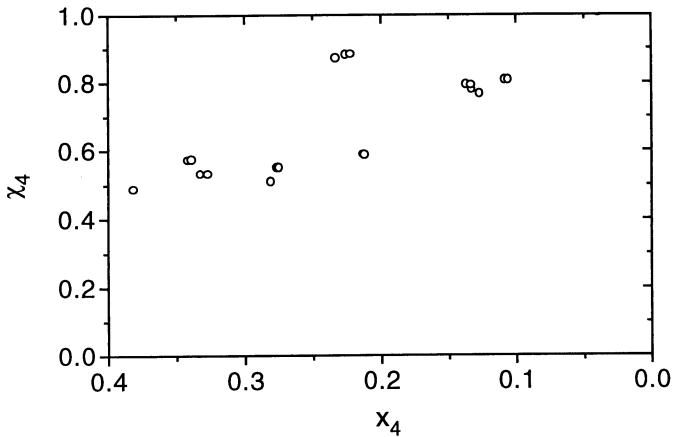


Fig. 4. Combinations of x_4, χ_4 determined for different samples at 21.6 bar.

4. SUMMARY

We have demonstrated that the coexistence region of ^3He - ^4He mixtures is detached from the λ -line at elevated pressures. Further, we have observed the metastability of the configuration of the interface between ^3He -rich and ^4He -rich phases in aerogel. We have used a torsional oscillator to probe the tortuosity of the ^4He -rich component and a capacitor to determine the ^4He content. The combined torsional oscillator - capacitor technique is ideal for probing this region of configurational and concentration metastability.

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