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

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

For $x_4 \leq 20\%$, the $^4$He-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 $^3$He-$^4$He interface configurations could be very long-lived. In Fig. 1 we illustrate how the morphology of the $^3$He-$^4$He interface can be rather different for identical volumes of $^4$He-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 $^4$He film.

It is known that pressure changes the thermodynamics of the phase
Fig. 1. Three configurations of $^4$He-rich phase at the same $x_4$. Left - film state (few "bridges"), right - capillary condensed state (many "bridges").

separation of bulk $^3$He-$^4$He mixture. Therefore, we compare the phase diagram of $^3$He-$^4$He 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 $^4$He in the cell is known, the period shift due to the decoupling of superfluid $^4$He can be used to determine the tortuosity of the $^4$He-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 $^4$He. 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 $^4$He 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 $^4$He concentrations in the range 4-10 % at low temperatures, since below $T_p$, the $^4$He preferentially moved into the sinter (or filling line). To fill the cell with a mixture we first admitted pure $^4$He to the empty cell at a temperature below 0.1 K. The $^4$He coated the surfaces of the cell (including the strands of aerogel) with a thick $^4$He film. This "film state" (with a different configuration of the $^3$He-$^4$He interface from that achieved by cooling a $^3$He-$^4$He mixture from 1K) persisted even after the remaining volume was filled with $^3$He 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 $^4$He 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 $^3$He-$^4$He mixture in aerogel during thermal cycling; $p = 21.6$ bar.

Temperature 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 $^4$He ($p = 21.6$ bar), we observed the sequence shown in Fig. 2 and summarized below:

1. $T > 0.56$ K. $^3$He-$^4$He solution ($x_4 \approx 21\%$) fills the cell.
2. 0.53 K. Superfluid transition of the $^4$He 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 $\sim 10$ $\mu$K/sec and yielded sharp transitions. We ascribe $T_{ps}$ and $T_\lambda$ to the steepest parts of the oscillator drive vs temperature (marked by circles in Fig. 2). On warming, the values of $T_{ps}$ and $T_\lambda$ 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 $p = 0$ (o) and $p = 21.6$ bar (●). At $x_4 > 20\%$, (p=0), our data are in good agreement with the results of Chan's group$^1$ for $^3$He-$^4$He in an aerogel of the same porosity (△). $T_{ps}$ decreases when the pressure is increased from 0 to 21.6 bar in a manner similar to that in bulk $^3$He-$^4$He 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.\textsuperscript{1} at $p = 0$ ($\triangle$).

The discrepancy between our $p = 0$ data and the low $T$ point from Chan’s group\textsuperscript{1} 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 $\chi_4$

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

The determination of $\chi_4$ proceeds from a period measurement near 3 mK where almost all the $^4$He is superfluid and the molar volumes of $^3$He-rich and $^4$He-rich phases are close to their bulk values $V_3$ and $V_4$. When a sample contains $N_3$ ($N_4$) moles of $^3$He ($^4$He) ($x_4 = N_4/(N_3 + N_4)$), the number density of the mixture is ($N_3 + N_4)/(N_3 V_3 + N_4 V_4$). The mass density is $(m_3 N_3 + m_4 N_4)/(N_3 V_3 + N_4 V_4)$ (where $m_3 \approx 3$ g/mole and $m_4 \approx 4$ g/mole).

The capacitance increment is given by

$$C_x - C_{emp} \propto \frac{N_3 + N_4}{N_3 V_3 + N_4 V_4} = \frac{1}{V_3 - \Delta V_{34} x_4}, \tag{1}$$

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

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

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

The period shift at 3 mK is related to $x_4$ and $\chi_4$ through the expression

$$P_x - P_{emp} \propto \frac{3 N_3 + 4 N_4 \chi_4}{N_3 V_3 + N_4 V_4} = \frac{3 + (4 \chi_4 - 3) x_4}{V_3 - \Delta V_{34} x_4}. \tag{3}$$

Finally,

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

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

The values of $x_4$, $\chi_4$ calculated in this manner are shown in Fig. 4. It is generally true that at higher $x_4$, $\chi_4$ 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 $\chi_4$. We found that $\chi_4$ 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 $^3$He superfluid.
Fig. 4. Combinations of $x_4, \chi_4$ determined for different samples at 21.6 bar.

4. SUMMARY

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

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REFERENCES