Adsorption and Desorption of Helium in Aerogels

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Abstract

We have studied the adsorption and desorption of helium in a 95% porosity aerogel. The helium density in the aerogel was directly measured with a capacitive technique, while the pressure and bulk helium density were measured with in situ capacitive gauges. Thermal response is slow in aerogels, so we used a thin sample to minimize the time constant. The combination of high resolution and rapid equilibration allowed us to study the capillary condensation of helium, which in aerogels occurs very close to the bulk saturation pressure. We saw hysteresis between filling and emptying of the pores, even for very slow rates. The hysteresis becomes smaller as the critical temperature is approached. We discuss whether true two phase coexistence can be observed in the helium-aerogel system.

Key words: helium, liquid-vapor, critical behavior, aerogels, capillary condensation

1. Introduction and Experimental Details

Silica aerogels, with their tenuous structure and variable density, provide a unique opportunity to study the effects of disorder on phase transitions. Phase separation and the liquid-vapor transition in fluids confined in porous media have been suggested [1] as experimental realizations of the random field Ising model (RFIM). Heat capacity and light scattering measurements [2] near the critical point of ^{4}He and N_2 in 95% porosity aerogels showed suppressed critical temperatures and dramatically narrowed liquid-vapor coexistence curves, but with similar shapes to the bulk coexistence curve. We recently used acoustic techniques [3] to study the critical behavior of Ne in a similar aerogel but found a significantly broader coexistence region. Also, recent experiments [4] which used a low frequency mechanical oscillator to determine the density of ^{4}He showed features characteristic of capillary condensation rather than true two-phase coexistence, although long thermal time constants made it difficult to determine the equilibrium behavior.

In this paper we report direct capacitive measurements of pressure-density isotherms for ^{4}He in a 95% porosity aerogel grown in our lab. To reduce thermal time constants, a thin (0.6 mm) disc was cut from the 12 mm diameter aerogel cylinder. Copper electrodes (9 mm diameter) were evaporated onto both sides to form a 1.7 pF capacitor. This was sealed into a copper cell which included an *insitu* capacitive pressure gauge with a resolution of 100 μbar. Temperatures were measured and controlled with a resolution of about 100 μK using a calibrated Ge thermometer. The cell also contained a bulk density capacitor which allowed us to directly compare the behavior of bulk and confined ^{4}He. A room temperature gas handling system and flow controller allowed us to admit or remove helium at controlled rates down to 0.2 sccm (corresponding to filling over about 5 hours). Capacitance changes were proportional to the amount of fluid present and were converted to densities using the known properties of ^{4}He.

2. Results and Discussion

Isotherms were measured above and below the bulk critical temperature, T_c (5.195 K, checked using our

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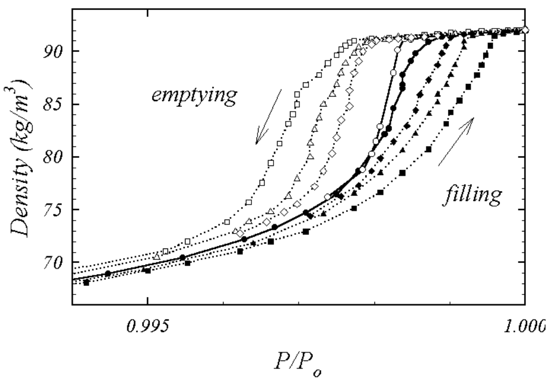

Fig. 1. Hysteresis loops in aerogel at 5.140 K. Equilibrium isotherm (solid lines with circles) and data taken during filling (solid symbols) and emptying (open symbols) at rates of 2, 1 and 0.5 sccm (dotted lines with squares, triangles and diamonds, respectively).

bulk ^{4}He capacitor). The isotherms for the confined ^{4}He differed from the bulk isotherms in several ways. The most obvious was the hysteresis between filling and emptying which appeared at temperatures below 5.155 K. The long time constants (due to the low thermal conductivity of the aerogel and the suppression of convection in its pores) resulted in thermal lags when gas was admitted or removed. This effect appears as a rate dependent hysteresis, so it was essential to check directly for equilibrium. Figure 1 shows isotherms taken at 5.140 K for three different filling/emptying rates. The effects of thermal lags are obvious, even at the slowest gas flow rate, so we also measured an isotherm by admitting the gas in steps and monitoring the relaxation towards equilibrium. The thermal time constant varied greatly along the isotherm, from less than a minute far from the bulk saturation pressure P_o to about 15 minutes in the steepest part of the isotherm. At each point we waited several time constants until the pressure and density had stabilized. The equilibrium isotherm (solid symbols) measured in this way had a small but reproducible hysteresis loop and did not exhibit the sharp vertical step characteristic of two phase coexistence, although the sample did fill and drain over a narrow pressure range. This behavior is characteristic of surface tension driven capillary condensation in a porous medium with a narrow range of pore sizes.

To see how the hysteresis evolved close to T_c (where the surface tension vanishes), we measured equilibrium isotherms at different temperatures. Figure 2 shows the filling and emptying isotherms at 4.880, 5.100 and 5.150 K. At lower temperatures the hysteresis loops are larger, steeper (with corresponding longer thermal relaxation times) and occur further below the bulk saturation pressure P_o. The hysteresis loop at 5.150 K is very small and isotherms taken at 5.155 K (still well below the bulk T_c of 5.195 K) and higher temperatures showed no hysteresis within our resolution.

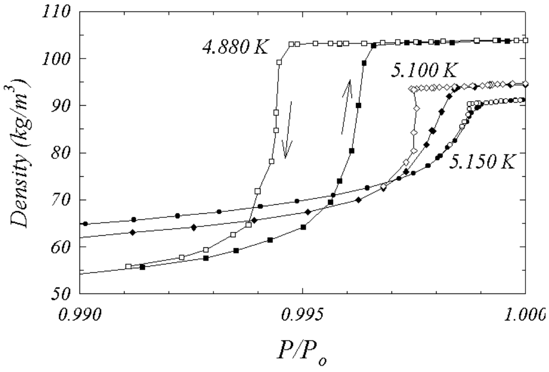

Fig. 2. Equilibrium isotherms at 4.88, 5.100 and 5.150 K taken during filling (solid symbols) and emptying (open symbols).

At low temperatures we observed hysteresis between filling and emptying, as expected for capillary condensation; this hysteresis disappeared above 5.155 K. The vanishing of the hysteresis may correspond to the critical temperature of the confined fluid (previous work [2] indicated that a similar aerogel suppressed ^{4}He's T_c by about 31 mK). However, this identification is not clear, since all our isotherms have finite slopes, while the diverging compressibility expected at a liquid-vapor critical point would correspond to infinite slope. Previous experiments on ^{3}He-^{4}He mixtures in porous media [5] have shown that two-phase coexistence in mixtures is closely related to capillary condensation and that this is much sharper in high porosity (98%) than low porosity (87%) aerogels. We are now extending our liquid-vapor measurements to lower density aerogels in addition to directly measuring the system's compressibility using acoustic methods.

Acknowledgements

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