Acoustic Study of the Liquid-Vapor Critical Point of Neon and Helium in Aerogel

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Abstract

We used low frequency acoustic resonators to study the liquid-vapor coexistence curve and critical behavior of simple fluids in low density silica aerogels. Resonators provide direct measurements of sound speed at low frequency. Sound speeds exhibit sharp kinks at the liquid-vapor phase boundary that allow us to map out coexistence curves near the critical point. Our previous measurements showed that neon in 95% aerogel exhibits a narrowed coexistence curve shifted to higher fluid density, but were complicated by a significant quantity of bulk neon present in the cell. We discuss results from our current experiments on two different fluids (neon and helium). Results are compared to our earlier measurements and to studies by other groups.

Key words: Liquid-vapor critical point; helium; neon; aerogel

1. Introduction and Methods

Silica aerogels, extremely porous glasses with a very open structure and a wide distribution of effective pore sizes, provide an environment in which to measure the effect of impurities on phase transitions. Experiments on the liquid-vapor critical point in 95% aerogel using heat capacity and light scattering[1] methods show a narrowed coexistence curve shifted to lower temperature and higher density relative to the bulk. A study of helium in 95% porosity aerogel using a low frequency mechanical oscillator found hysteresis below the critical temperature, and extremely long equilibration times[2] suggesting that the transition may be closer to capillary condensation than liquid-vapor coexistence.

We have used low frequency acoustic resonance to study the liquid-vapor critical point in aerogel. A monolithic cylinder of aerogel, grown in our lab, is fitted into a cylindrical cavity. A thin circular membrane, driven by a piezoelectric transducer, in each end cap allows us to measure the lowest resonant frequency, and thus the sound speed, in the fluid. This allows a determination of transition temperature, manifested as a kink in resonant frequency as a function of temperature. Data are collected along isochores rather than isotherms, which minimizes any heat of adsorption. Aerogel is an exceptional insulator, leading to long equilibration times.

The samples discussed here are neon in 95% aerogel (about 20% bulk neon in cell) and helium in 95% aerogel (about 3% bulk helium in cell). Some results on the neon in 95% aerogel sample have been previously published[4].

2. Results and Discussion

In order to determine whether we observe true liquid-vapor coexistence or capillary condensation, we look at the transitions in detail. Figure 1 shows (frequency vs. temperature two isochores for neon in 95% porosity aerogel with similar transition temperatures. The transition appears as a sharp kink in resonant frequency

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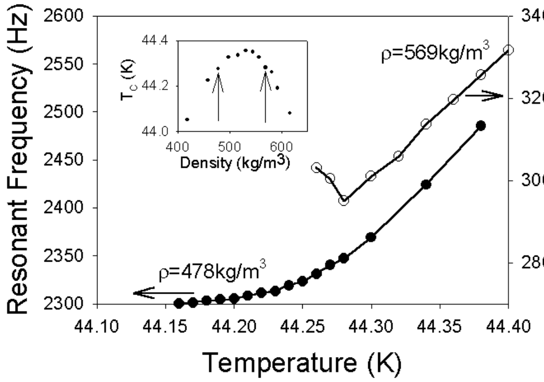

Fig. 1. Neon in 95% aerogel. Isochores are included for $\rho = 569kg/m^3 > \rho_c$ and $\rho = 478kg/m^3 < \rho_c$, indicated by arrows on the inset coexistence curve. The transition for $\rho > \rho_c$ is sharp, while that for $\rho < \rho_c$ is gradual.

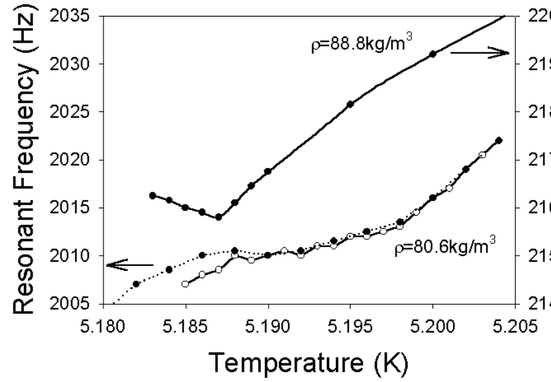

Fig. 2. Helium in 95% aerogel. Isochores are included for $\rho > \rho_c$ and $\rho < \rho_c$. As in neon, the transition for $\rho > \rho_c$ is sharp. For $\rho < \rho_c$ it is not obvious how to choose a transition temperature. For $\rho < \rho_c$, points are shown for data runs with equilibration times of 30min. (•) and 120min. (o). The temperatures shown are based on an approximate thermometer calibration – the transition in aerogel is actually about 40mK below the bulk T_c[3].

for $\rho > \rho_c$; in longer data runs at these densities, resolution is limited by temperature control. However, for $\rho < \rho_c$ the transition is gradual. To check whether the rounding is due to bulk fluid present in the sample cell, or specific to neon in 95% aerogel, a resonator with much less bulk volume was constructed for the helium measurements.

Figure 2 shows two frequency vs. temperature isochores for helium in 95% aerogel, above and below the critical density in 95% aerogel ($\rho_c \approx 85kg/m^3$). Again, the higher density ($\rho > \rho_c$) curve shows a sharp transition while the lower density ($\rho < \rho_c$) curve shows no obvious signature of a transition. One possible indicator of phase separation at this density is a rate dependence in resonant frequency – the appearance of liquid domains leads to a large increase in equilibration time. The lower density curve includes points taken with equilibration times of 30min (•) and 120min (o) and the appearance of deviations between these two data sets may be a marker of phase separation. The lack of a sharp transition is common to both neon and helium samples, and is not an artifact of bulk fluid in the cell.

Fluids in porous media tend to exhibit a narrowed coexistence curve, with a critical temperature lower than bulk and a critical density higher than bulk[5]. Indeed, the heat capacity measurements of liquid-vapor coexistence of helium in aerogel pointed to an extremely narrow coexistence curve completely contained within the bulk coexistence curve[1]. Nitrogen in aerogel also exhibits a narrowed coexistence curve[1]. Our results with neon in 95% aerogel also exhibited a narrowed coexistence region, although not as narrowed as the previous results[4].

Further examination of our results showed that there may not be a sharp liquid-vapor transition on the low density side of the "coexistence curve". This broadening is present in cells with very little bulk volume as well as cells with significant bulk volume. Capacitive measurements of pressure-density isotherms performed in our lab also show a sharp transition on the high density side and a gradual transition on the low density side of the coexistence curve[3]; hence the broadened transition appears to be a general feature of fluids confined in 95% porosity aerogels.

The gradual transitions on the low density site of the coexistence curve, combined with the appearance of hysteresis in pressure-density isotherms, supports an interpretation closer to capillary condensation than true liquid-vapor coexistence.

Experiments are currently also being performed on helium in 98% aerogel.

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