Small Angle X-ray Scattering Study of He^4 Adsorption into Silica Aerogel

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INTRODUCTION

Recent adsorption isotherm measurements of He into porous silica aerogel have indicated the existence of a unique two-phase coexistence region at vapor pressures just slightly below the bulk coexistence point. It has been postulated that this is comprised of a coexistence between a film of He adsorbed onto the silica strands of the aerogel and regions of completely He filled pores [1]. Up to the present, however, there have been no microscopic structural measurements that could directly test the validity of this hypothesis.

METHODS AND MATERIALS

We have performed small angle x-ray scattering measurements along adsorption isotherms of He in aerogel which should be able to probe structural correlations between He and aerogel. Measurements were performed at a number of temperatures ranging from just above the lambda point to the liquid vapor critical point. The sample consisted of a 98% porous aerogel grown into silver sinter and then pressed into a temperature controlled copper cell. The cell was held within a custom, vapor cooled x-ray cryostat. Isotherms were performed by dosing He gas from a reservoir of known volume. Between doses the sample was allowed to thermally equilibrate and an x-ray scattering pattern was collected.

RESULTS

Fig. 1 shows a typical adsorption isotherm measured at 4.5K. At low coverage the vapor pressure increases rapidly with He density as would be expected for growth of a film in the presence of a Van-der-Walls field. Just below the bulk equilibrium point further addition of He results in no change in pressure. This indicates the presence of a distinct two phase equilibrium region. The pressure in the cell remains constant until the aerogel has been completely filled with He, at which point the pressure rises to the bulk vapor pressure as liquid fills the small excess volume of the sample chamber.

X-ray measurements were performed using 23 keV x-rays produced from the third harmonic of the the APS Undulator-A at sector 8 of the Advanced Photon Source. The x-ray beam was monochromatized by reflection from a diamond 111 monochromator. Passage through an aluminum filter removed the lower energy first harmonic of the undulator radiation. The use of high energy x-rays minimized absorption within the sample and the consequent heating and charging. To verify that no such effects were present the x-ray flux onto the sample was attenuated by a factor of 10. No measurable change in scattering could be discerned. Data sets were normalized to the direct beam intensity by inserting a current integrating silicon PIN diode before the sample and were were accurate to of order one percent. X-ray access to the sample was through beryllium windows on the sample cell and vacuum can of the cryostat.

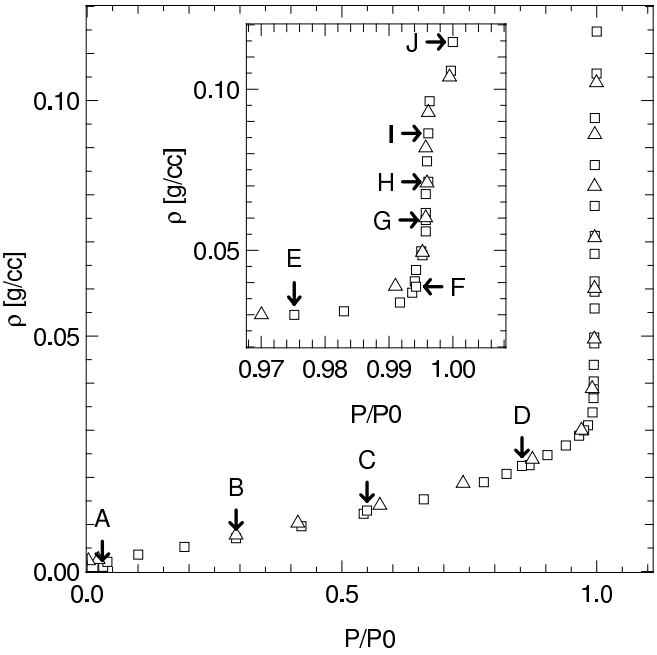

FIG. 1. Adsorption isotherm data from He^4 adsorbed into a 98% porous aerogel at 4.5K. The vertical scale shows the amount of He adsorbed per cm^3 of pore volume. Squares represent pressure measured during filling and triangles during draining of the sample. The positions of the arrows indicate the points along the isotherm where the SAXS measurements displayed in Fig. 3 were made.

Fig. 2 shows the x-ray scattering from the bare aerogel sample at 4.5K as a function of wavevector transfer $Q = 4\pi\sin(\theta/2)/\lambda$ where θ is the angle of the scattered radiation relative to the incident beam and λ the x-ray wavelength. The scattering was measured using a Princeton Instruments SCX/CCD optically coupled CCD detector. The azimuthally symmetric images were circularly averaged over regions of equivalent wavevector in order to produce a two dimensional plot. The bare aerogel scattering could be well described using a model for the the structure factor of a mass fractal with

dimension 1.38 [2].

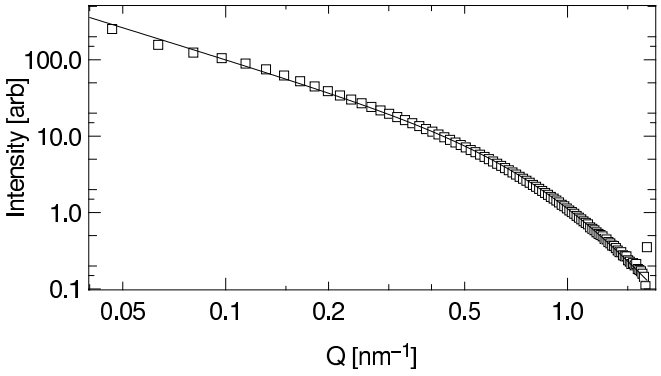

FIG. 2. Measured scattering intensity as a function of wavevector transfer, Q for empty aerogel. The squares are measured data and the line the fit described in the text.

Initial adsorption of He leads to only a small perturbation in the scattering due to its small electron density. In order to accentuate the effects of the He Fig. 3 displays scattering at points along the filling portion of the adsorption isotherm as the ratio $R = S_{He}/S_{Bare}$ of the scattering from the He filled to the empty aerogel. As He is added to the cell two trends become evident. The scattering at large Q decreases until it levels out at 86% of the scattering from the bare silicon. This decrease in scattering approximately corresponds to the expected decrease in contrast between the silica-vacuum interface and silica-He interface. It can be interpreted as the filling with He of the smaller pores in the aerogel. By contrast, at small Q a peak appears in the scattering which both grows in intensity and move in towards smaller wavevector with filling. As the sample becomes close to full the peak disappears, presumably moving in beyond the resolution of the spectrometer. This peak would be the expected behavior for scattering from He filled pores in the silica whose length scale increased as the gel filled.

DISCUSSION

Both the decrease in scattering at large wavectors and the presence of a scattering peak at small wavevectors lend support the model that the two phase equilibrium region involves the filling of aerogel pores with He. Not surprisingly larger and larger pores are seen to fill as the He dose increases. Measurements at other temperatures (not shown) also yield similar results. In principle, if the filled pore phase was in equilibrium with a phase in which aerogel strands were coated with He, one might also expect to see the effects of scattering from He layers of well defined thickness. A He film with a thickness $D = 6$nm would yield an oscillation with a period $T = 2\pi/D \sim 1\text{nm}^{-1}$. No such oscillation is observed, although it should be easily resolvable. It is possible that the film is significantly thinner and that the slight upturn in the data at $Q = 1.4$ could be evidence of interference oscillations from a thin film. Further analysis may resolve this issue. Alternately a thick film may exist but its thickness may not well defined due to sample inhomogeneity.

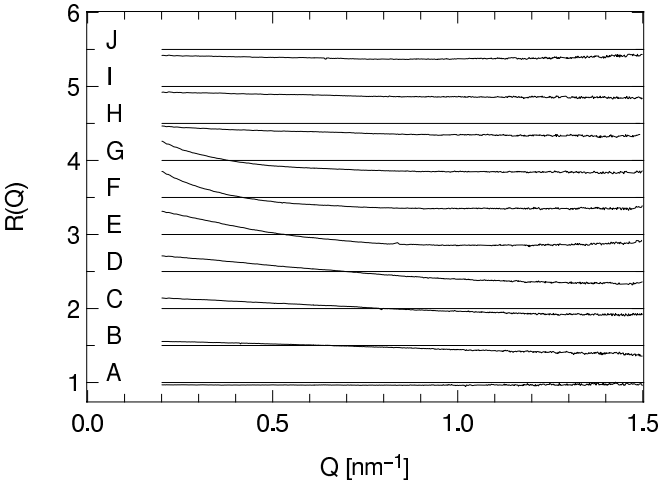

FIG. 3. Ratio, R, of scattering from He-filled aerogel to scattering from empty aerogel at 4.5K. The letters correspond to the points indicated in Fig. 1. Successive data sets are offset by 0.5 for clarity. The dashed lines, corresponding to an R of 1.0, are shown for reference

ACKNOWLEDGEMENTS

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