Pore-Space Correlations in Capillary Condensation in Vycor

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We use ultrasonic attenuation and light scattering to study spatial correlations in the pores of Vycor on filling and draining with hexane. On filling, the hexane initially adsorbs uniformly, but when capillary condensation occurs, vapor microbubbles are formed and persist until the sample is completely full. However, no long-range correlations of the bubbles are observed. By contrast, on drainage, the empty pores exhibit long-range correlations with a fractal dimension of 2.6. This results from the pore connectivity, suggesting that this behavior can be modeled by invasion percolation.

Vycor is a porous glass which is widely used as a proto-typic material for the study of the properties of fluids and molecules in highly confined geometries [1,2]. The pores in Vycor have an average radius r of about 30 Å, and are spaced about 190 Å apart, filling about 0.3 of the total volume of the material. The large internal surface area of Vycor effectively adsorbs molecules at low ambient vapor pressure, while the large pore volume effectively absorbs bulk fluids by capillary condensation at higher ambient vapor pressures. As such, it is often called "thirsty" glass. This propensity to absorb fluids is often characterized by the sorption isotherm, which is a measure of the amount of fluid absorbed as the ambient vapor pressure P is first increased to the saturated value P_S, and then decreased to zero. Like many porous materials, the isotherm of Vycor exhibits pronounced hysteresis, with adsorption and desorption occurring at markedly different reduced pressures $p = P/P_S$. The underlying origin of the hysteresis is generally believed to be a consequence of capillary condensation: Because of surface tension, the saturated vapor pressure in the pore is reduced as the curvature of the fluid surface is increased; this is described by the Kelvin equation [3]. The mean curvature of an empty cylindrical pore is $1/r$, where r is the pore radius, while that of a full pore is determined by its meniscus, and cannot exceed $2/r$. This difference results in hysteresis even in the simplest pore geometry. For more complex, random pore networks the hysteresis is less well defined. On adsorption, the isotherm does not rise sharply, but rather increases gradually, reflecting the combined effects of surface adsorption and capillary condensation in pores with a distribution of sizes. By contrast, on desorption, the isotherm falls sharply; this is often taken to indicate a narrow pore size distribution. Indeed, desorption isotherms are widely used for measurements of pore size distributions in porous materials [4].

Because of the extensive use of isotherms for pore size measurements, the origin of the discrepancy between the sharp drop on desorption and the gradual rise on adsorption is a critical, but still unresolved, question. One hypothesis for this sharp drop recognizes the importance of the connectivity of the interior pores to the surface [5]. It is not sufficient for p to be reduced below the pressure that drains a pore of a given radius; this pore must also have unrestricted access to the surface. If it is blocked by smaller pores, it cannot drain until a sufficiently low value of p is reached to empty the narrowest blocking pores. As a result, the random connectivity will lead to a disordered network of drained pores. A direct observation of the resulting fractal correlations on draining, but not on filling, would be the most convincing evidence in support of this hypothesis, and would enable a microscopic model of the role of pore connectivity to be established. While neutron scattering measurements have suggested that fractal correlations do exist, these data [6] were restricted to very short length scales, precluding any detailed understanding of the underlying physics.

In this Letter, we present direct evidence for the dramatic difference in the spatial correlations of the empty pores on filling and on draining, using a combination of ultrasonic and optical measurements. The ultrasonic velocity probes both the mass uptake and the change in the rigidity of the Vycor as it is filled with fluid. The ultrasonic attenuation probes both small and large scale spatial inhomogeneities in partially filled pores. The light scattering is a definitive probe of the long-range spatial correlations of the empty pores. We find that on filling, the fluid is first adsorbed uniformly on the pore walls and then, at higher ambient pressure, absorbed uniformly by capillary condensation. No evidence is found, either from the light scattering or the ultrasonic attenuation, for any long-range correlation. Instead, a large number of vapor bubbles, are observed just before the pore space is completely filled, confirming a theoretical prediction [7] and providing a measure of the size of the largest voids. We find dramatically different behavior on draining. We observe fractal correlations of the empty pores, providing conclusive proof of the validity of the connectivity hypothesis in accounting for the striking differences between the adsorption and desorption branches of the isotherm. We measure a fractal dimension of $d_f \approx 2.6$, suggesting that the drainage can be modeled by analogy to invasion

percolation [8–10].

To measure the sound propagation, a 3.8-cm-long, 7-mm-diam rod of Vycor was pressed between two quartz delay rods using thin Teflon films for acoustic coupling. Ultrasonic transducers were bonded to the other ends of the delay rods. A short burst of longitudinal sound, with a frequency between 3 and 15 MHz, was generated with one transducer and detected with the second. The phase and amplitude of the transmitted signal were simultaneously measured using a quadrature phase detector, allowing the sound velocity and attenuation to be determined. The sample temperature was stabilized to better than 0.01 °C. The ambient pressure was measured by a baratron gauge, and was set by a temperature-controlled reservoir of hexane connected to the sample cell. All the measurements were made after the sample reached equilibrium and was uniformly filled.

Light scattering measurements were performed on a 6-mm-thick, 2.5-cm-diam disk of Vycor, using an Ar^+ laser, with a wavelength of 514.5 nm. The transmission through the sample was measured with a power meter, while the angular dependence of the scattered light was measured by placing a lens in front of the sample to focus the laser onto a diffusing screen where the central beam was blocked and the scattered light was imaged with a charge-coupled-device TV camera operated with linear gain [11]. The image was digitized, corrected for background, and radially averaged to obtain the scattered intensity as a function of wave vector $I(q)$. To extend the dynamic range of the measured intensity, images were recorded with two different incident intensities, the first ensuring no saturation of the brighter regions, and the second ensuring sufficient signal to noise in the weaker regions. The data were scaled by the incident intensity and combined. To extend the dynamic range in the scattering vector, data were recorded with two different lenses, having focal lengths of 35 and 192 cm. The data at different q were combined by normalizing the intensities of the regions that overlap. With this technique, $I(q)$ could be measured over about two and a half decades in q and four decades in intensity.

The sorption isotherms were determined gravimetrically for each sample. Slightly different behavior was observed for each sample, indicating small differences in their pore sizes. Thus we compare the behavior of the ultrasonic and light scattering measurements with the isotherms for each sample. To facilitate detailed comparisons with the ultrasonic data, concurrent volumetric measurements of the isotherm were also performed. They are in agreement with the gravimetric data and are shown in Fig. 1(a), where we plot the change in mass relative to the mass of the empty sample, $\Delta M/M_0$, as the hexane vapor pressure was varied. As with all data shown in this paper, the open points are obtained on filling, while the solid points are obtained on draining. The hysteresis in the isotherm between filling and draining is apparent, as is the marked difference in the shape
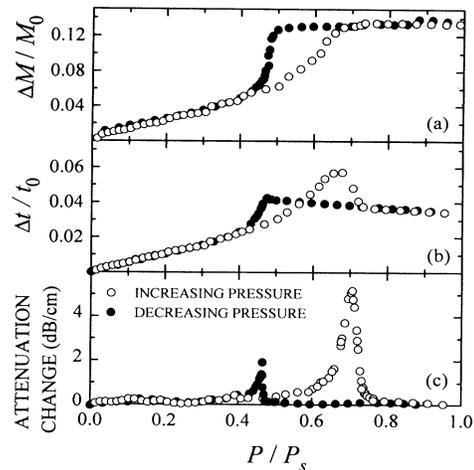

FIG. 1. (a) Hexane sorption isotherm, (b) relative change in the ultrasonic transit time, and (c) change in the ultrasonic attenuation for Vycor.

of the adsorption and desorption branches.

We compare the isotherm with the change in the ultrasonic transit time $\Delta t/t_0$ in Fig. 1(b), and with the change in attenuation in Fig. 1(c), both measured at a frequency of 6.2 MHz, and a wavelength of ~0.5 mm. The change in the transit time is a direct measure of the change in the velocity, $\Delta v/v_0 = -\Delta t/t_0$. Since $v = \sqrt{\beta/\rho}$, where β is the longitudinal elastic modulus and ρ is the density, the change in the transit time directly reflects the combined changes in density and modulus, $\Delta t/t_0 = \Delta\rho/2\rho_0 - \Delta\beta/2\beta_0$. By comparing Figs. 1(a) and 1(b), we see that, at low pressures, the increase in the relative transit time is exactly half that of the relative mass, implying that the modulus is unaffected by the fluid, thereby providing a direct measure of the amount of adsorbed fluid [12]. Remarkably, on adsorption, this behavior persists until the pores are almost completely filled; even though its mass has increased by more than 10%, the modulus of the Vycor remains unaffected. This behavior results from vapor voids which persist in the pore space at all stages, right until the filling is complete. The presence of voids dramatically weakens the fluid modulus, as can be understood within a simple effective medium model for the pore space wherein the compressibilities of the voids and the fluid are added in proportion to their volume fractions [13]; thus the effective modulus of the fluid mixture, which fills the pores, is dominated by the highly compressible voids and is so small that it makes a negligible contribution to the total Vycor modulus. It is only when the pores become about 99% filled that the transit time drops sharply, indicating a significant stiffening of the effective modulus.

Additional insight is provided by the attenuation, which exhibits a large, asymmetric peak. The pronounced maximum and its sharp, high-pressure cutoff coincide with the drop in the transit time, while its low-pressure shoulder extends down to $p \approx 0.5$ where capil-

lary condensation in the smallest pores probably first occurs. Near the maximum, the attenuation varies approximately as $\omega^{1.4}$ for frequencies between 3 and 15 MHz. This rules out any scattering mechanisms, which would have an ω^4 dependence at long wavelengths, and suggests instead an absorption mechanism for ultrasonic frequencies relatively near some resonant or relaxation frequency. We believe that this attenuation is caused by vapor-filled voids or bubbles in the pore space. In bulk fluids the high compressibility of bubbles results in a large absorption of sound [14]. Here, the interaction between a sound wave and vapor bubbles is modified by the presence of the solid Vycor frame and by the destabilizing effect of the large negative pressures exerted on the fluid by the capillary pressure; sound absorption must also occur, although a detailed model is lacking. In addition, the high compressibility of the vapor may allow fluid to flow in the pores, with viscous damping causing the attenuation. The striking maximum in the attenuation probes the microbubbles remaining in the largest pores just before the sample is completely filled. Moreover, from the Kelvin and Young-Laplace equations, we estimate the mean radius of curvature to be ~ 50 Å for these voids. This is significantly larger than the characteristic pore size, and presumably reflects those regions where several pores meet. These data suggest that the attenuation is a very sensitive probe of the largest pores even though they represent only about 1% of the pore space. Indeed, it may ultimately be possible to determine the distribution of pore sizes from the ultrasonic attenuation. Furthermore, the sharp cutoff of the attenuation unambiguously identifies the pressure at which the pores become completely filled.

The ultrasonic data on draining are markedly different. As p decreases, the transit time initially exhibits a small increase of about 0.5%. While the behavior is identical to that on filling down to $p \approx 0.75$, the sharp change in $\Delta t/t_0$ seen at this pressure in adsorption is completely absent in drainage. From this we conclude that there are no voids formed in the draining fluid, all the way down to $p \approx 0.48$. Instead, the slight rise in $\Delta t/t_0$ must result from the very large negative pressures, down to -130 atm, in the fluid. These negative pressures cause a reduction in the density of hexane, accounting for the decrease in $\Delta M/M_0$ observed in the isotherm, and confirming that the pores remain completely full for this range of pressures. However, this decrease in the density would result in a decrease in the transit time; the slight increase observed implies that the dominant effect is instead a weakening of the modulus. The contribution of the hexane can be estimated by extrapolating velocity data obtained at positive pressures [15]; this accounts for roughly half the observed increase in $\Delta t/t_0$. The larger increase may reflect an excess softening of the hexane modulus due to the approach towards the spinodal line where $\beta \rightarrow 0$ [13]. The negative pressure probably also weakens the Vycor frame.

As p is reduced from 0.48 to 0.47, $\sim 30\%$ of the fluid is drained, while $\Delta t/t_0$ remains practically unchanged. Thus the modulus must decrease precipitously to balance the sharp decrease in density as the initial fluid draining occurs. This confirms that voids in the emptying pore space are formed over a very narrow range of pressure. At $p = 0.47$, $\Delta t/t_0$ becomes equal to half of $\Delta M/M_0$, whereupon it exhibits a very sharp drop following the behavior of the isotherm. This precipitous drop in $\Delta t/t_0$ is accompanied by a very sharp increase in the attenuation over a very narrow range in p. The variation of the attenuation with frequency suggests that it is caused largely by the interference of ultrasonic waves traveling at different speeds in different regions of the sample, giving rise to phase cancellation effects in the detecting transducer [16]. This occurs because inhomogeneities in density, and hence in velocity, arise as the drainage proceeds radially from the outer surface towards the center.

To elucidate the physics of the drained pore space, we first show the light transmission through the second piece of Vycor in Fig. 2 where it is compared to the sorption isotherm. Because the pores are small, Vycor is homogeneous on length scales comparable to the wavelength of light, and scatters light very weakly. However, because of the reflections at the interfaces, the measured transmission of dry Vycor is ~ 0.8. On filling, the measured transmission is roughly independent of p, although the scattering becomes even weaker since the hexane-filled pores are better index matched to the glass. However, the voids which cause the large ultrasonic absorption peak are too small to scatter light significantly. By contrast, on draining, the transmission exhibits a very sharp and narrow dip due to strong scattering of light, as evidenced by the white appearance of the Vycor. The scattering occurs initially at the surfaces, and ultimately extends through the whole sample as the draining proceeds. The transmission dip occurs exactly at the sharp step in the isotherm and corresponds to the peak in the ultrasonic attenuation.

To further elucidate the structure of these correlated regions, we show the dependence of the scattered light intensity on the wave vector in Fig. 3. Because the scatter-
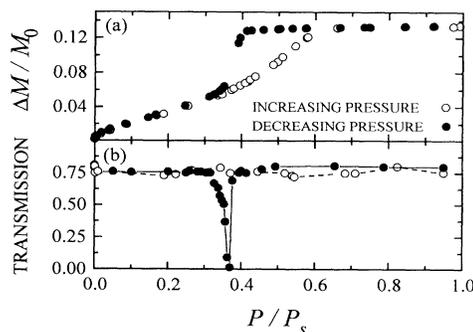

FIG. 2. (a) Hexane sorption isotherm and (b) transmission of light through Vycor. The lines are guides for the eye.
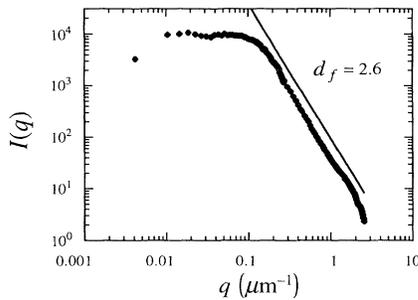
FIG. 3. Dependence of scattered light intensity on wave vector, illustrating the fractal correlations of the empty pores. The fractal dimension is $d_f \approx 2.6$, as indicated by the slope of the solid line.

ing is so large, we are able to obtain reliable data only when the scattering first appears and the transmission is reduced by less than 10%, at $p \approx 0.38$. Clear evidence of fractal correlations is observed: The data exhibit the characteristic power-law dependence at larger q, and are asymptotically constant at smaller q. The fractal dimension is $d_f \approx 2.6$, as indicated by the solid line. The correlation length of the fractal regions is determined by the crossover at $q \sim 0.1$ μm^{-1}, corresponding to $\xi \sim 10$ μm. The value of ξ could be even larger as multiple scattering may distort the data at very low q.

The large scattering in the Vycor must result from the contrast between the empty pores and the remaining Vycor, where the pores are still full. These empty pores must, therefore, have long-range fractal correlations. We emphasize, however, that our results do not imply that the pore space itself has a fractal structure, but only the drained pores. These correlations must arise from the randomness of the pore space: Even though p is sufficiently low to empty some of the larger pores, their access to the surface is blocked by narrow pores. Provided that the sample has no large scale inhomogeneities, ξ should increase as p is decreased until it is comparable in size to the sample itself. Then the remainder of the pores should begin to drain, causing ξ to decrease again and the scattering to be reduced. The initial portion of this behavior, while ξ is still increasing, is directly analogous to invasion percolation [8], which occurs when a nonwetting fluid is forced into a porous medium which is fully saturated with a wetting fluid, and when the invasion occurs sufficiently slowly that it is dominated by capillary forces. The pressure that must be applied to overcome the capillary pressure increases as the radius of the pore decreases. However, because of the randomness of the pore space and its connectivity to the surface, larger pores can be blocked by smaller pores, and fractal structures result. This process can be mapped onto bond percolation for which d_f is predicted to be 2.5 in three dimensions. Our results are in excellent accord with this prediction, clearly demonstrating that the drainage process is correctly de-

scribed by invasion percolation. By contrast, our results are at odds with the value of $d_f \approx 1.75$ obtained from neutron scattering from water-filled Vycor [6]. These measurements were performed at larger values of q, and may have been distorted by short-range correlations in the pore structure.

We expect the behavior observed for Vycor to be generic to porous materials. Thus our results are of particular significance for industrially important macroporous materials such as catalyst supports, sorbent particles, and ultrafiltration membranes. Desorption isotherms are frequently used to determine their pore size distributions, and the usual interpretation implicitly assumes that the pore space is fully connected to the sample surface, so that all pores of a given size drain at the same pressure. Our results demonstrate the fallacy of this assumption, and call into question the validity of some of the common methods used to determine the pore size distributions of porous materials. In addition, they indicate that a theoretical interpretation of the desorption data should begin through the use of invasion percolation to model the drainage.

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