

Small-angle neutron scattering study of adsorbed water in porous Vycor glass: Supercooling phase transition and interfacial structure

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Small-angle neutron scattering by porous Vycor glass at scattering vectors above 0.025 \AA^{-1} decays as Q^{-n} . However, both intensity and power-law exponent differ markedly between a dry sample, which has a fractally rough surface with dimensionality $D \sim 2.5$, and a water-saturated sample with identical scattering contrast, implying that the pore surfaces undergo gross geometrical changes on drying. The temperature variation of intensity at constant Q confirms the existence of a diffuse supercooling transition centered at about 260 K.

There are many novel aspects of the behavior of fluids confined in small pores, e.g., in Vycor glass and other porous silicas, such as anomalous molecular diffusion¹⁻³ and electronic energy transfer,⁴⁻⁶ superfluidity,⁷ and supercooling.⁸⁻¹⁰ Recently there has been some discussion as to whether the anomalous scaling of diffusion and electronic energy-transfer processes in Vycor can be explained on the basis of fractal concepts.^{11,12} While small-angle neutron scattering (SANS) and small-angle x-ray scattering (SAXS) studies of porous Vycor glass by Schaefer *et al.*¹¹ and SANS measurements by Wiltzius *et al.*¹³ show no evidence for either volume or surface-fractal structures, recent measurements by Sinha *et al.*¹⁴ and Schmidt *et al.*¹⁵ suggest that the pore surfaces may be fractal with dimensionality $D \sim 2.4$ under dry conditions.

In the studies of Schaefer *et al.*¹¹ a broad peak centered at a scattering vector of $Q \sim 0.03 \text{ \AA}^{-1}$ was observed. This feature was attributed to the remnant of a spinodal decomposition process¹⁶ which involves the phase separation of SiO_2 and B_2O_3 on a scale of the order of 200 Å. Subsequent acid leaching of the B_2O_3 -rich phase creates the interconnected microporous structure evident in electron micrographs. At higher Q the scattered intensity was found to decay as Q^{-4} , the signature expected for a microscopically smooth surface.¹¹ These workers mention no attempt to control or monitor the moisture content of their sample. Wiltzius *et al.*¹³ presented SANS data for Vycor-containing mixtures of protonated (C_6H_{12}) and deuterated (C_6D_{12}) cyclohexane. In these studies a simple power-law behavior at Q values above that of the spinodal decomposition peak was not generally obtained, although one nominally dry sample (under nitrogen) gave a gradient of approximately -4 . The question of whether or not the pore surfaces of Vycor are fractal, therefore, appears to remain an unresolved issue.

Here we report SANS measurements on Vycor saturated with various mixtures of H_2O and D_2O . As in the study of Wiltzius *et al.*¹³ variation of the isotopic composition of the fluid enables the scattering contrast between the two phases to be varied, a technique which has been particularly exploited in studies of colloidal systems.^{17,18}

A sample of powdered Vycor glass (Corning 7930) was cleaned according to the manufacturer's prescription, then carefully outgassed for 24 h under vacuum at 180°C and divided into seven specimens, each of which was equilibrated at 95% relative humidity (RH) in airtight containers over saturated solutions of sodium sulphite in H_2O - D_2O mixtures with hydrogen atomic fractions X_{H} ranging from 0.5 to 0.9. The adsorption isotherm for water on Vycor indicates that the pore space is filled under these conditions. The choice of 95% RH and not 100% RH is motivated by minimizing scattering background arising from excess interparticle water. The samples were sealed in aluminum capsules fitted with a vacuum connection and Baratron absolute pressure transducer, and pumped down to a pressure equal to 95% of the saturated vapor pressure of water at 290 K (about 1.84 kN m^{-2}). One sample was later dried under high vacuum (rotary diffusion pump) at a temperature of 100°C . SANS data were recorded at 290 K on the D17 spectrometer at the Institut Laue Langevin, Grenoble at an incident wavelength of 12 \AA and scattering vector range $Q = 0.015\text{--}0.12 \text{ \AA}^{-1}$. After each run, the scattered intensities recorded by the two-dimensional multidetector were normalized to the same total incident neutron flux, corrected for instrument and sample capsule backgrounds, and radially averaged.

Figure 1 shows the effect of varying the H-to-D isotopic ratio, the data being recorded at a temperature of 290 K. The data are qualitatively similar to those obtained in other studies,^{11,13-15} the broad peak corresponding to the remnant of the spinodal process being centered at

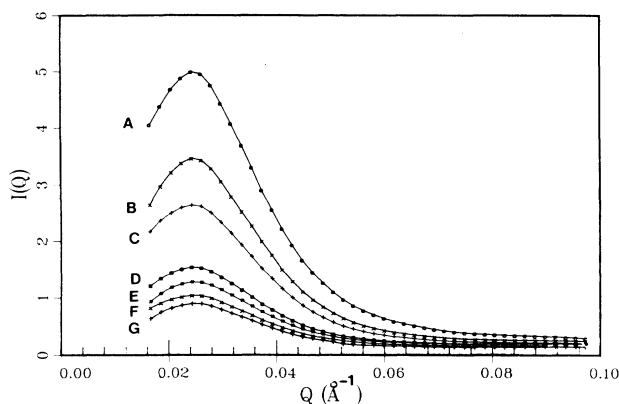


FIG. 1. SANS data for porous-Vycor-H₂O-D₂O system equilibrated at 95% relative humidity and 290 K for varying percentages of H₂O. A, 90%; B, 80%; C, 73%; D, 60%; E, 57%; F, 53%; G, 50%.

$Q \sim 0.025 \text{ \AA}^{-1}$, corresponding to a periodicity of about 250 Å. At higher scattering vectors, i.e., shorter observation distances, the scattering intensity decreases smoothly with increasing Q . At constant Q the scattered intensity decreases with decreasing X_H down to the minimum value at which measurements were made ($X_H = 0.5$).

For scattering from N interacting pores of identical geometrical shape and of volume V , the intensity of small-angle scattering is given by

$$I(Q) = A(\rho_g - \rho_w)^2 NV^2 P(Q) S(Q), \quad (1)$$

where A is an instrumental constant, ρ_g and ρ_w are the scattering amplitude per unit volume of the glass and adsorbed water, respectively, $P(Q)$ is the form factor for a single inhomogeneity, and $S(Q)$ is an interparticle structure factor representing interference scattering effects. For a polydisperse distribution of inhomogeneity sizes, Eq. (1) would include an integral over this size distribution, but nevertheless $I(Q)$ will depend independently on the contrast and on geometrical factors. Assuming macroscopic densities, the values of ρ_w for pure liquid H₂O and D₂O are -0.57×10^{10} and 6.36×10^{10} , respectively. For a matrix density of 2.2 g cm^{-3} , corresponding to fused silica, one may calculate for pure SiO₂ a value of $\rho_g = 3.46 \times 10^{10} \text{ cm}^{-2}$, close to the value of $3.35 \times 10^{10} \text{ cm}^{-2}$ obtained by Wiltzius *et al.*¹³ by contrast matching of Vycor with mixtures of cyclohexane and deuterocyclohexane. This scattering length density corresponds to an H₂O-D₂O mixture with $X_H = 0.43$, so that optimum contrast matching was not quite achieved in our measurements. However, from these values of ρ_g one may infer that the glass has a good phase separation, consistent with the manufacturer's quoted B₂O₃ content¹⁹ of 3%.

Figure 2 illustrates the temperature dependence of scattering for a sample equilibrated at 95% RH and $X_H = 0.57$ as its temperature was increased by stages from 230 to 279 K. The lines correspond to constant values of Q between 0.04 and 0.08 Å⁻¹. The main

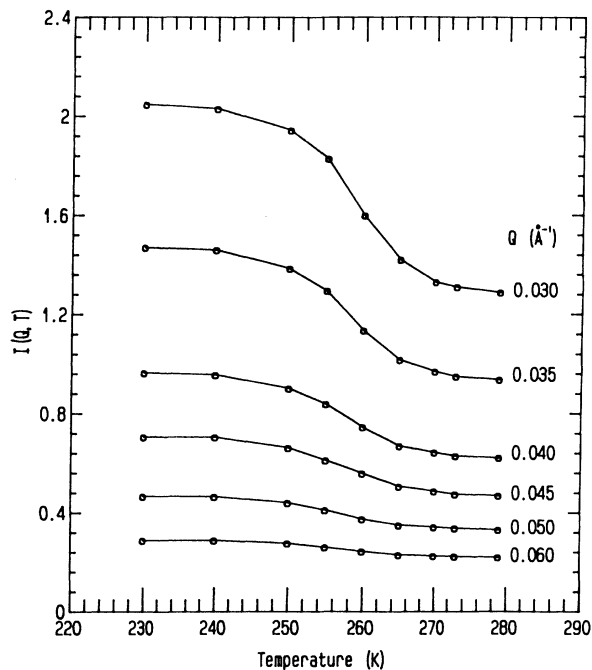


FIG. 2. Variation of SANS intensity with temperature for constant scattering vectors Q between 0.04 \AA^{-1} (uppermost curve) and 0.08 \AA^{-1} (lower curve).

change of intensity apparent between 250 and 265 K is attributed to the observation of a diffuse melting transition accompanied by a change of the relative density of glass and pore fluid.

The two curves in Fig. 3 illustrate the parabolic dependence on X_H of the factor $(\rho_g - \rho_w)^2$ from Eq. (1) for silica containing either liquid water or ice, calculated assuming mass densities of 1.000 and 1.105 for liquid H₂O and D₂O and a density decrease on freezing of 8% in both

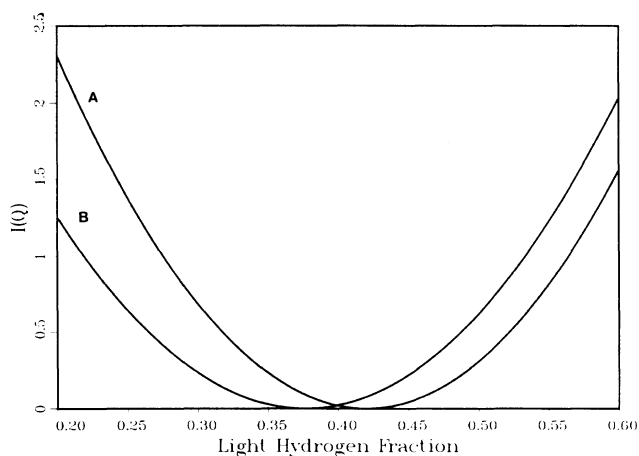


FIG. 3. Scattered intensity $I(Q)$ vs atomic hydrogen fraction X_H for Vycor-liquid-water (curve A) and Vycor-ice (curve B), assuming bulk densities for water and ice (1.0 and 0.92 g/cm^{-3} , respectively).

cases. The density of silica is assumed to be as quoted above. Differential freezing effects due to the differences of freezing point of H_2O and D_2O are neglected. Since $X_H=0.57$ is on the hydrogen-rich side of the contrast match point for both Vycor-ice and Vycor-liquid-water systems, where $\rho_g > \rho_w$ in both cases, it follows from Eq. (1) that a decrease in ρ_w , corresponding to a decrease in bulk density, will increase the SANS intensity at constant Q , and vice versa. The SANS data, therefore, indicate a contraction on melting, as for bulk water. Comparison of the two curves at $X_H=0.57$ gives a predicted relative increase of scattering intensity from high to low temperatures of about 45%. At the lower Q values in Fig. 2 the increase of intensity between 279 and 230 K is about 50–60%, which may reflect either a somewhat larger density change between solid and liquid phases than in the bulk state, or alternatively a significant compression of the silica matrix as freezing occurs.

The temperature range of the phase transition is in good agreement with previous evidence for a diffuse melting transition at about 262 K based on measurements of macroscopic volume changes.⁸ Adsorbed water in various porous silicas such as Spherisorb (pore diameter 90 Å) and Gasil (pore diameter 20 Å) have been found to exhibit a similar degree of supercooling from wide-angle neutron-diffraction measurements.^{9,20} In principle, comparison of macroscopic volume changes with the changes in small-angle scattering intensities enables the change in density of both the glass matrix and the pore-filling solution to be evaluated.

The most striking aspect of the present study is shown in Fig. 4. This illustrates double logarithmic plots of intensity versus Q for two samples, one equilibrated at $X_H=0.9$ and 95% RH, and the dry sample. There is a dramatic reduction in peak intensity, by a factor of about 7, on going from the dry to the wet sample. This is re-

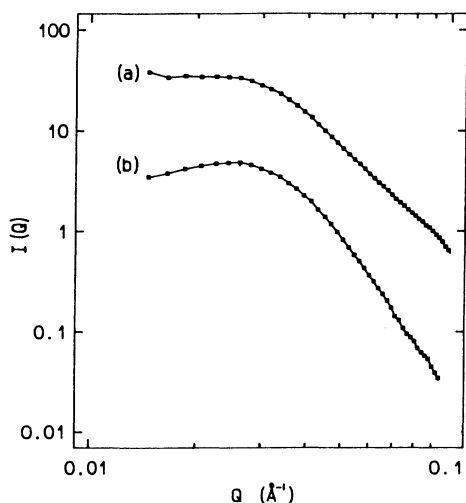


FIG. 4. Double-logarithmic plot of $I(Q)$ vs Q for (a) dry Vycor, (b) Vycor equilibrated at an atomic hydrogen fraction $X_H=0.9$ and at 95% relative humidity.

markable since at $X_H=0.9$ the value of ρ_w is quite close to zero, so that from Eq. (1) both the shapes and intensities in dry and wet samples would be expected to be identical. Since the contrasts are identical, the implication of the large differences between the two curves is that there are gross geometrical differences between dry and water-saturated samples.

Above the spinodal peak, both log-log plots exhibit a linear region, characteristic of power-law scattering. Three-parameter least-squares fits of the high- Q data were made using the equation

$$I(Q) = A Q^{-n} + B, \quad (2)$$

where B represents a Q -independent incoherent scattering background, which for both samples is quite small. The values of the exponent n differ significantly both from one another and from ideal Porod behavior $I(Q) \sim Q^{-4}$. For the dry sample $n = 3.5 \pm 0.1$ characteristic of a surface-fractal behavior^{18,20} with dimensionality $D = 6 - 3.5 \sim 2.5$, a result consistent with recent independent studies on dry Vycor.^{14,15} Similar surface-fractal behavior has been observed in a wide range of porous materials by small-angle scattering or gas adsorption studies.^{21–25} For the fully saturated sample having $\rho_w=0$, $n = 4.3 \pm 0.1$. Gradients in the range 4.2–4.5 were also observed at numerous other values of X_H and relative humidity.

Such negative deviations from strict Porod ($I \sim Q^{-4}$) behavior have previously been observed in SAXS data for polymer solutions, and are interpreted in terms of a diffuse boundary between the two phases across which the scattering amplitude density $\rho(r)$ varies gradually with no abrupt interfacial discontinuity.^{26,27} Although these models do not predict pure power-law scattering, to first order the effect often appears as a steepening of the negative gradient. In Vycor glass such a diffuse boundary could arise from (1) a spatial variation of composition within the glass, (2) a modification of water structure and density near pore surfaces, or (3) the presence of a mixed phase, e.g., a hydrated gel, at pore surfaces. The first of these explanations was invoked by Wiltzius *et al.*¹³ to explain some features of their data. However, neither of the first two explanations would account for the large difference in intensity between the dry and 90% H_2O samples, whereas the removal of water from a surface gel phase on drying, producing a rough pitted or cracked pore surface, would account for the both the differences in scattered intensities and power-law gradients between the wet and dry samples.

None of our SANS data give any indication of volume-fractal behavior,^{22,28} implying that anomalous scaling of molecular dynamics or electronic energy-transfer kinetics requires a different, nonfractal interpretation (see, e.g., Yang *et al.*²⁹).

In conclusion, our SANS data show the Vycor-water system to be neither a volume or a surface fractal, but to exhibit a diffuse liquid-solid boundary. Fractal surface roughness was observed only in an extremely dry sample. The latter finding apparently contradicts previous data,^{11,13} however, we have employed rather more

stringent drying conditions, likely to have removed the about 3% chemisorbed water remaining at 0% RH.¹⁹ It is clear that in porous Vycor there is a significant chemical interaction between the absorbed water and the pore surfaces, possibly formation of a gel-like state which significantly modifies the surface morphology of the pores. As the temperature is varied, we observe directly

a supercooling phase transition, confirming earlier macroscopic measurements.⁸

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