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Fractal surface and cluster structure of controlled-pore glasses and Vycor porous glass as revealed by small-angle x-ray and neutron scattering

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Analysis of small-angle x-ray-scattering data from a series of controlled-pore glasses (nominal pore sizes from 75 to 2000 Å) and from Vycor porous glass has revealed the fractal nature of the surfaces of these materials. The controlled-pore glasses show a relatively low degree of surface irregularity, with a surface fractal dimension of $D=2.20\pm0.05$, regardless of pore size. Vycor glass, the fractal properties of which have been under some debate, has a rougher surface, with $D=2.40\pm0.10$. The D value for Vycor has been verified by small-angle neutron scattering. The fractal dimensions refer to surface irregularity in the range 10–100 Å. The scattering data suggest that the carriers of the fractal surface properties are interconnected units (particles, clusters) with an average diameter of 300 and 450 Å for the controlled-pore glasses of pore size 75 and 170 Å, respectively, and units with an average diameter of 350 Å for Vycor glass.

I. INTRODUCTION

Many physical and chemical processes in nature, in industry, and in the laboratory occur in porous environments. The long and continuous interest in these systems[1,2] has gained much momentum in recent years,[3] one of the reasons being the advent of new ideas which simplified the analysis of complex geometries.[4]

In this paper we focus our attention on a group of materials known as controlled-pore glasses (CPG's), of which Vycor® porous glass (VPG) is one example. This class of SiO_2 materials has the unique feature of having pore-size distributions (PSD's) which are much narrower[5] than those found in silica gels.[6] The most important use of controlled-pore glasses is in chromatography, where these glasses have offered practical solutions to many chemical, biochemical, biological, and medicinal chromatographic problems.[7–9] Another important application of both CPG and VPG is as intermediates in the preparation of silica glasses and optical fibers of high purity.[10,11]

The narrow pore-size distribution of VPG has made it the material of choice for many studies of the effects of a porous environment on diffusion, reaction, and physical properties. Because the pore size is of the order of 40 Å, many of these studies employed probes which during their lifetime can diffuse distances of this magnitude. Examples are studies which involved photochemical[12] and photophysical processes.[13] Among the electronic ground-state processes investigated in these porous environments are the superfluid behavior[14(a)] of ^{4}He and the kinetics of isotopic exchange,[14(b)] and of water adsorption.[14(c)]

There has been considerable interest in the question of whether or not VPG has fractal structural properties.[12(a),13(a),15–18] Values of the fractal dimension D in the range 1.7–2.45 have been suggested for this material. In particular, small-angle x-ray- and neutron-scattering (SAXS and SANS, respectively) data gave[17] $D=2.0$ and $D=2.45$.[18] Here we report a study of a series of CPG's of various average pore sizes (APS) in the range 75–2000 Å by SAXS, and of VPG by both SAXS and SANS. We obtained the following results: All of the CPG's which we studied have a fractal surface, with $D=2.20\pm0.05$, regardless of APS. For VPG we find that $D=2.40\pm0.10$; in the ongoing debate on the fractal properties of this material, our result is close to that of Sinha *et al.*[18] These fractal dimensions refer to a regime of length scales of approximately 10–100 Å. On length scales larger than about 100 Å, we find that VPG and the small-APS CPG's have a nonfractal structure that can be modeled as a random-packed assembly of particles or clusters with average diameters from 300 to 450 Å. (We conjecture a similar structure for the larger-APS CPG's, with an increasing particle diameter as the APS increases. In order to confirm this conjecture about these CPG's, however, one would have to measure intensities at smaller angles than those accessible in the present study.) This cluster structure agrees with the model for VPG proposed by Kadokura[15(a)] and amplified by Yang *et al.*,[15(b)] except that (a) the particles are not smooth but have a fractally rough surface, as borne out by our D values, and (b) the particle diameter is larger. As we explain in Sec. IV, the clusters and their fractal surface structure are in keeping with the mechanism of formation of these glasses. Our results about the cluster structure, as well as those in Ref. 15, leave little room for the idea[12(a),13(a)] that VPG has a fractal pore network on length scales above 40 Å.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Materials

Vycor porous glass is a Corning "Thirsty Glass" No. 7930, with average pore diameter 40 Å, N_2-Brunauer-Emmett-Teller surface area 250 m^2/g, and 28% porosity.[19,20] The other porous glasses which we studied were Electro-Nucleonics (USA) controlled-pore glasses CPG-10 (Refs. 8,9,21) with the following nominal and measured (in parentheses) average pore sizes (in Å): 75 (86), 170 (167), 500 (477), 700 (810), 1000 (962), and 2000 (2023). Below, we refer to these glasses by their nominal pore sizes (e.g., CPG-700). We verified the average pore size of VPG on a Quantachrome surface-area analyzer. The actual average pore size for each of the Electro-Nucleonics controlled-pore glasses was provided by the producer.[21] Typical pore-size distributions for these materials are shown in Refs. 5 and 8.

B. X-ray-scattering measurements and analysis

The x-ray-scattering curves were recorded on a Kratky camera[22] with a position-sensitive detector. The measured curves were corrected for the distortions resulting from the length of the collimating slits by a modification of a method described some years ago.[23] To check for possible systematic errors in the scattering measurements, the curve for Vycor 7930 porous glass was also measured by neutron scattering at the National Center for Small-Angle Scattering Research, at Oak Ridge, Tennessee (USA), and at the University of Missouri Research Reactor. Since we measured the x-ray and neutron scattering from several samples of different thickness and obtained essentially equivalent scattering curves from all of the samples for *both* x-ray and neutron scattering, we can conclude that in spite of the high scattered intensity, multiple scattering is negligible. In our measurements, we were interested only in the dependence of the scattered intensity on the scattering angle and therefore did not determine the "absolute" scattered intensity (i.e., the scattering cross section).

For a porous material in which the internal surface has a fractal dimension D, the scattered intensity $I(q)$, at scattering angles large enough that $q\xi \gg 1$, can be approximated by[24–26]

$$I(q)=I_{00}q^{D-6} , \tag{1}$$

where $q=4\pi\lambda^{-1}\sin(\theta/2)$, θ is the scattering angle, λ is the wavelength, ξ is the upper limit of the length range in which the surface is fractal (i.e., the largest pore size in the fractal regime[27]), and I_{00} is a constant proportional to the surface area measured by yardsticks of a given size. The values of D were computed by least-squares fits of the regions of the scattering curves where (1) describes the scattering.

To make sure that these power-law regions were sufficiently far to the right of the peaks in Figs. 1 and 2 (i.e., that the measured exponent was independent of the line shape of the nearby peak), we developed a model that accounts for both the peak and the power law. The model is as follows.

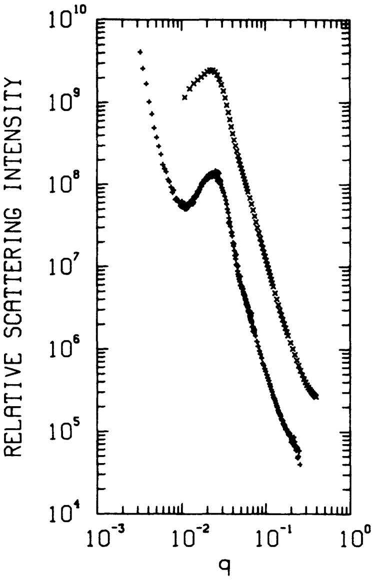

FIG. 1. The relative small-angle x-ray scattering (upper curve) and small-angle neutron scattering (lower curve) from Vycor® controlled-pore glass. On the abscissa, q is expressed in Å^{-1}. [The neutron-scattering curve was measured at the National Center for Small-Angle Scattering Research at Oak Ridge, Tennessee (USA).]

A peak at $q=q_0$ in the scattering curve is characteristic of the presence of structural units of diameter $L\sim 2\pi/q_0$ (a Bragg peak[28] broadened by irregular arrangement of units and by fluctuations in L). Since the values for $2\pi/q_0$ from Figs. 1 and 2 are much larger than the respective APS values, we conclude that these units (scatterers) are massive entities rather than pores. For simplicity, we refer to them as particles. (A more accurate term might be interconnected clusters.) This suggests modeling VPG and the CPG's as a hard-sphere "liquid," similar to the hard-sphere models used in scattering from microemulsions,[29] except that here the spheres are replaced by particles with a fractal surface. The corresponding scattered intensity is given by

$$I(q)=\rho S(q)P(q) , \tag{2}$$

where ρ is the particle number density, $S(q)$ is the interparticle structure factor, and $P(q)$ is the intensity from a single particle. The fact that for $S(q)$ we take the Percus-Yevick expression of a hard-sphere liquid[29,30] is of course not to say that our glasses are liquids in any way. This model simply serves as a convenient (minimal), thermodynamically consistent description of a random packing of spheres with diameter L and fraction η of volume occupied by the spheres. The spheres are the smallest spheres which circumscribe the particles. The intensity $P(q)$ for a single scatterer was computed from the equation[31]

$$P(q)=I_eN_e^2\frac{\int_0^L g(r)\frac{\sin qr}{qr}r^2dr}{\int_0^L g(r)r^2dr} , \tag{3}$$

where for SAXS, I_e is the scattered intensity per electron, and N_e is the number of electrons per scatterer. For the electron-density correlation function $g(r)$ we used the expression

$$g(r)=1-a(r/L)^{3-D}+b(r/L)^{\gamma} \ . \tag{4}$$

In (4) the first two terms are the leading-order terms for a scatterer with a fractal surface dimension D,[24] and the last term takes account of the finite size (diameter L) of the scatterer. The constant a depends on the overall shape of the scatterer, and b and γ are constants which are fixed by the conditions that $g(r)$ and dg/dr vanish at $r=L$. These conditions give $b=a-1$ and

$$\gamma=(3-D)\frac{a}{a-1} \ .$$

Also, $a \geq \frac{3}{2}$. For $D=2$ and $a=\frac{3}{2}$, Eqs. (3) and (4) yield the scattering equation for a sphere of diameter L.

Thus, the only parameters entering our model, which is given by Eq. (2), are the packing fraction η, the particle diameter L, the fractal dimension D, and the shape coefficient a. Figure 3 shows the intensity computed from (2) for parameter values that were chosen to reproduce the principal features of the VPG scattering curve (see Sec. III). The position of the main peak in Fig. 3 is identical to the location[30]

$$q_0 \simeq 7/L \quad (\text{for } \eta=0.5) \tag{5}$$

of the first maximum in the Percus-Yevick interparticle structure factor $S(q)$, and the slope at q values $\geq 5\times 10^{-2}$ Å^{-1} coincides with the slope $D-6$ of the single-particle intensity $P(q)$. This agreement proves the point in question, namely that the power law in $I(q)$ is unaffected by the peak and that, conversely, the position of the main peak is not affected by the power-law tail.

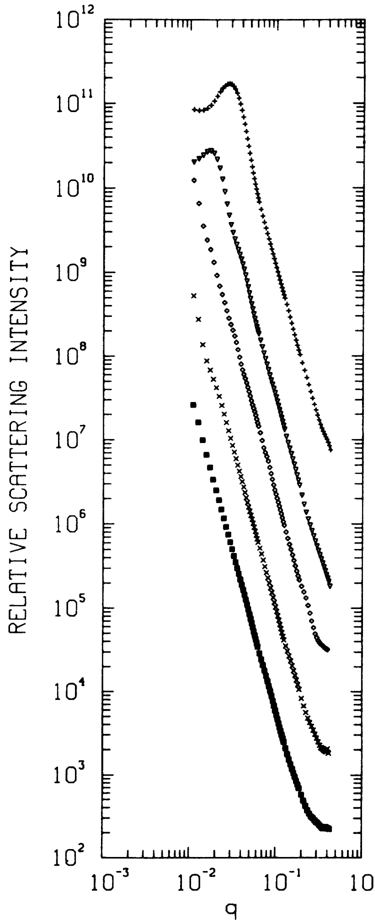

FIG. 2. Small-angle x-ray scattering curves for Electronucleonics, Inc. controlled-pore glasses with measured average pore sizes (from top to bottom): 86, 167, 477, 810, and 2023 Å. The values of q are given in Å^{-1}.

The purpose of the model (2), as it stands, is only to reproduce the correct peak position and the correct power-law tail. If one wants better agreement between the model curve and the experimental curves in Fig. 1, one has to allow for a distribution of particle diameters L. Such polydispersity will broaden the peak in Fig. 3 and, as is well documented in Ref. 29(b), will wash out all oscillations to the right of the peak [these maxima come from higher-order peaks in $S(q)$ and also from oscillations in $P(q)$ similar to those in the scattering from a sphere].

III. RESULTS

Figure 2 shows the corrected small-angle x-ray-scattering curves for the CPG's. The same fractal dimension, $D=2.20\pm0.05$, is obtained from the power-law region of the scattering curves in Fig. 2 regardless of pore size. (The scaling behavior observed for porous silicas[26,32] is not found here. In other words, the ratio of po-

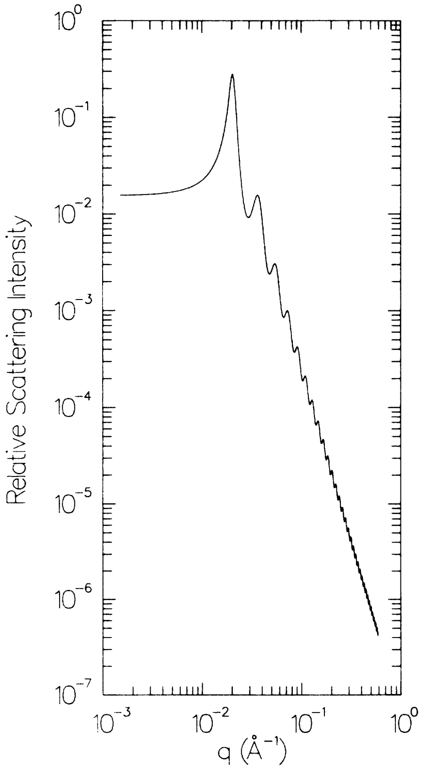

FIG. 3. Model scattering curve calculated from Eq. (2) for $\eta=0.5$, $D=2.4$, $a=1.5$, and $L=350$ Å.

sitions of the maxima in the scattering curves of CPG-75 and 170 is not equal to 170/75.) Figure 1 shows the results for VPG for both SAXS and SANS. As can be seen, the two techniques are in good agreement. The power-law region, extending over a range of about 100 in intensities, corresponds to $D = 2.40 \pm 0.10$. From the rough criterion[28] that a length π/q is associated with the scattering at a given q, one can estimate that the D values in Figs. 1 and 2 refer to surface features in the range 10–100 Å. The rise of intensity on the left of the SANS peak in Fig. 1 may be due to scattering from the grains of the powdered material; a monolithic piece of VPG used for the SANS measurements at the University of Missouri did not show this rise.

As mentioned in Sec. II, the parameter values for the model curve in Fig. 3 were chosen so as to portray both the fractal power law and the peak in Fig. 1. Since the position q_0 of the peak in the model depends only slightly on η (η controls the width of the peak, which is not at issue here), we arbitrarily put[33] $\eta = 0.5$. This makes q_0 a unique function of L [see Eq. (5)] and allows us to estimate L directly from the experimental value for q_0. For VPG we obtained $L = 350$ Å. The minimal value $a = 1.5$ in Fig. 3 was chosen because our numerical calculations have shown that larger a values shift the power-law regime to much larger values of q.

Thus the experimental values for D were obtained from least-squares fits of Eq. (1) to the power-law regions of the experimental curves, and the values of L were determined from insertion of the experimental peak positions q_0 into Eq. (5). In contrast, an accurate determination of all four parameters D, L, a, and η from a fit of Eq. (2) to the experimental data would require either *a priori* knowledge of the distribution of particle diameters L, or the introduction of an additional fitting parameter to allow for polydispersity (cf. Sec. II).

For CPG-70 and CPG-170, Eq. (5) gives $L = 300$ Å and $L = 450$ Å, respectively. These L values, above all the ones for VPG, explain why the fractal behavior does not stop at lengths corresponding to the average pore diameter as one might have expected if the fractal surface were an attribute of pores with average sizes of 40 Å, 86 Å, etc.: A particle of diameter L can have a fractal regime up to lengths as large as L. So, the estimated fractal regimes are well compatible with these results for L. An important corollary is that the pores of diameter 40 Å, 86 Å, etc. in these systems are of interstitial nature, as has been suggested previously for VPG.[15]

There is no reason not to expect a similar particle and pore structure for the higher CPG's. If we assume that the ratio of L to APS is the same for these glasses as for CPG-170, namely 2.7, we obtain the estimates $L \geq 1300$ Å and $q_0 \leq 0.005$ Å^{-1} [Eq. (5)] for CPG-500,. . . . . ,2000. In agreement with this estimate, the scattering curves for the higher CPG's do not exhibit a peak in the accessible range of q values.

IV. DISCUSSION

The preparation of porous silica glasses is based on the 1926 discovery of Turner and Wink,[34] and on the later patented development of Nordberg and Hood.[19] These glasses are made by a process based on acid-leaching of the phase-separated Na_2O and B_2O_3 produced in a heat treatment of a low-melting Na_2O-B_2O_3-SiO_2 glass. After the leaching is complete, a porous skeleton of SiO_2 remains. This process, which is a liquid-liquid phase-separation phenomenon, takes place when the melted borosilicate glass is cooled below a critical temperature. In low-viscosity liquids, such separations occur rapidly and are complete in the sense that two separate liquid layers are formed. In the borosiliate case there are two unique features. First, the high viscosity causes the separation to proceed very slowly; consequently one can stop the process by freezing when the separated phases have sizes of the order of nanometers. Second, the immiscibility gap is below the crystallization temperature. Therefore, the undercooled melt in which phase separation occurs is metastable. (The miscibility diagram is shown in Ref. 8.) The control of porosity is done in two stages: First, the melt is cooled to a chosen point near the maximum of the immiscibility curve. Phase separation is then quenched by freezing. The glass is then reheated for varying periods of time (10–100 h). During heating, the typical size of the separated phase domains increases with time (i.e., there is a slow approach to full equilibrium). Finally the glass is cooled again, crushed, and leached with warm dilute acid.

If the phase separation were carried out to completion (i.e., to produce two completely separated phases), then one would expect that at full equilibrium, the interface between the two phases would be completely flat, with $D = 2.0$. However, in porous glasses the phase separation is stopped before completion (i.e., "on the way" to equilibrium). Consequently there is (and must be) a certain width for the size and feature distribution of the tiny phase-separated zones. Because the glass froze close to, but not *at*, equilibrium, it is not unreasonable to expect D values which are close to but significantly above 2, just as we found (cf. also close-to-equilibrium Eden structures[35]). That is, the nonuniformity of the separated phases as evident from the very existence of a pore-size *distribution*,[5,8,20,21] and in particular the existence of the left tail of this distribution, is in one-to-one correspondence with the fact that we found a value of D higher than 2.0.

This picture offers a natural explanation of why we find that $D(\text{VPG}) > D(\text{CPG})$: The phase separation in VPG is stopped at an earlier stage than in the CPG's. (The leachable phase-separated volume is about 0.3 ml/g in the former and 0.5–1.0 in the latter; i.e., the former is farther from the smooth, ideal equilibrium state.)

Interconnected phases occurring in the process of phase separation are usually interpreted as indicative of spinodal decomposition as suggested by the theory of Cahn.[36] Haller,[8,37] however, pointed out that the observed morphology of interconnected pores for VPG may not be a sufficient criterion for spinodal decomposition, i.e., that a nucleation and growth mechanism ("intersecting growth mechanism"[38]) can equally lead to such morphologies.[39] Our observation of moderate surface roughness on a < 100-Å scale agrees with that mechanism.

Perhaps the most striking mechanistic support for our results comes from recent molecular dynamics simulations of phase separation of a two-dimensional Lennard-Jones fluid.[40] There it was found that interconnected clusters of rather uniform size are formed and that these clusters have a fractal dimension (mass dimension D_m) increasing slowly from 1.4 to higher values as time increases. The increase in D_m reflects that the clusters become increasingly compact. The surface morphology of the clusters, however, seems to change very little. The simulations thus indicate a transition from a mass fractal to a surface fractal ($D_m \rightarrow 2$) during which the surface dimension D remains essentially constant: $D \leq D_{m(\text{early})} \sim 1.4$. So if it is true that the simulated clusters are equivalent to cross sections of clusters in a three-dimensional fluid, the clusters in three dimensions will have a surface dimension D not exceeding about 2.4, which compares very well with our results for D. Furthermore, those simulations suggest that the value $\eta = 0.5$ in our calculation of the curve in Fig. 3 is not unreasonable. The conclusion that phase-separation clusters are surface fractals is also implicit in the theory of Klein[41] where it is shown that, below a critical length scale, the dominant fluctuations are compact and, above this length scale, ramified fluctuations dominate.

Finally, although different methods of fractal surface analysis need not, *a priori*, yield identical results (because of the possibility that different types of processes may probe different effective surfaces), we mention that preliminary comparison of D values from SAXS, electronic energy transfer[42] and adsorption of a series of molecules[43] for CPG-75 are in agreement with each other. This comparative work (analagous to Ref. 25) as well as an analysis of the width of the peak at 0.02 Å^{-1} for VPG will be presented elsewhere.

After this work had been completed, a SANS study of Vycor porous glass was published[44] by Wiltzius *et al.* Their results are in many ways complementary to ours: (a) These authors fit the small-q data, including the peak at $q = 0.02$ Å^{-1}, by the theory of Cahn[36] for spinodal decomposition, while our analysis of the peak is modelless, in the sense that instead of making specific hypotheses about the origin of the peak, we use the simplest possible structure factor for a random system of scatterers of fixed size L and density η. (b) Wiltzius *et al.* analyze the power law on the right of the peak without considering how the power law is affected by the finite size of the scatterers. In our treatment, the power law given by our $P(q)$ in Eqs. (3) and (4) explicitly includes a correction for finite-size effects. (c) Because of experimental uncertainties, Wiltzius *et al.* are unable to conclude whether Vycor porous glass has a fractal surface structure, whereas our combination of SANS and SAXS data gives unambiguous evidence for the fractal surface.

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