

Pore Size Distributions in Porous Glasses: A Computer Simulation Study

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We have prepared a series of molecular models of porous glass using a recently developed procedure (Gelb, L. D.; Gubbins, K. E. *Langmuir* **1998**, *14*, 2097) that mimics the experimental processes that produce Vycor and controlled-pore glasses. We calculate nitrogen adsorption isotherms in these precisely characterized model glasses using Monte Carlo simulations. These isotherms are analyzed using the Barrett–Joyner–Halenda (BJH) method to yield pore size distributions, which are tested against exact pore size distributions directly measured from the pore structures. The BJH method yields overly sharp distributions that are systematically shifted (by about 1 nm) to lower pore sizes than those from our geometric method.

1. Introduction

Controlled-pore glasses (CPGs) and the related Vycor glasses are highly interconnected mesoporous silica materials that can be prepared with a wide range of porosities and pore sizes.^{1,2} Their preparation is based on the near-critical phase separation of a binary liquid mixture, which produces complex networked structures. The original preparations of CPGs were done by Haller,³ who partially phase-separated a mixture of SiO₂, Na₂O, and B₂O₃, and etched out the borosilicate phase, leaving a nearly pure silica matrix with a porosity between 50% and 75% and an average pore size between 4.5 and 400 nm.

Vycor (or “thirsty”) glasses are prepared by a similar procedure and have a porosity near 28% and an average internal pore diameter between 4 and 7 nm.^{2,4}

Characterization of amorphous networked solids is a difficult task. Most methods⁵ are based on two underlying assumptions: (a) that it is physically meaningful to divide the void volume into separate regions which can be analyzed independently, and (b) that these regions can be simply parametrized. These methods yield a *pore size distribution* (PSD), which is the distribution of a “size” parameter fitted to some experimental data. For porous glasses, one usually assumes that the material is composed of a collection of cylindrical pores and calculates a distribution of cylinder diameters that reproduces an experimental adsorption (or desorption) isotherm.

There are more rigorous measures for describing nanoscale amorphous systems, but they tend to be either difficult to obtain experimentally or difficult to interpret. X-ray scattering measurements provide information about the roughness of the pore surface and the average length-scale of the pore network⁴ but do not reveal the adsorptive or transport properties of the material. Quantities such as the topological connectivity of the network are not directly accessible by experiment.

It is difficult to evaluate the accuracy of isotherm-based methods for characterizing these adsorbents, because their structures cannot be exactly determined by *any* experiment. Computer simulation is an ideal tool for solving this sort of problem, since the results of isotherm analysis methods can be critically compared against exact results obtained from the simulated pore structure. If the computer model of the adsorbent is realistic, these comparisons ought to be relevant for experimental systems. We have previously used this approach to analyze methods for calculating adsorbent surface area;⁶ in this paper we consider the measurement of pore size distributions.

2. Preparation of Glass Models

The method we use to generate the glass models is outlined in Figure 1; the simulation details are given in our previous paper.⁶ The same procedure was followed here, except that the simulation cells in this work were all larger and measured 27 nm on each side; they contained initially 868 000 atoms of the quench mixture. These simulation cells are periodic in all three directions, so that surface effects are not present in this study. The initial mole fraction was $X = 0.7$, and the quench configurations were taken at 225 τ (sample “A”), 300 τ (“B”), 375 τ (“C”), and 450 τ (“D”) to prepare the four samples used in this study. Here $\tau = (\epsilon/m\sigma^2)^{1/2}t$ is the reduced time; 1 τ corresponds to 0.781 ps. (In the Lennard-Jones potential model used for the mixture, ϵ and σ are the potential well depth and diameter and m is the mass of one atom.) These samples all had porosities very near 30% and average pore sizes of approximately 3.3, 3.9, 4.5, and 5.0 nm, respectively. These models are fully connected, in that the void space is a single volume of very complex geometry, rather than several disconnected volumes.

To simulate the adsorption of nitrogen in these model pores, we represent the nitrogen molecule with a single Lennard-Jones sphere, with potential parameters $\sigma_N = 0.375$ nm and $\epsilon_N/k_B = 95.2$ K.⁷ The parameters for the substrate atoms are set to $\sigma = 0.27$ nm and $\epsilon/k_B = 230$ K, which have been used to represent bridging oxygens in silica.⁸ The Lorenz–Berthelot mixing rules are used to give the interspecies parameters. All potential energy

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(1) Schnabel, R.; Langer, P. *J. Chromatogr.* **1991**, *544*, 137.

(2) Elmer, T. H. In *ASM Engineered Materials Handbook*; Schneider, S. J., Jr., Ed.; ASM: Materials Park, OH, 1991; Vol. 4, pp 427–432.

(3) Haller, W. *Nature* **1965**, *206*, 693.

(4) Levitz, P.; Ehret, G.; Sinha, S. K.; Drake, J. M. *J. Chem. Phys.* **1991**, *95*, 6151.

(5) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, 2nd ed.; Academic Press: London, 1982.

(6) Gelb, L. D.; Gubbins, K. E. *Langmuir* **1998**, *14*, 2097.

(7) Maddox, M. W.; Olivier, J. P.; Gubbins, K. E. *Langmuir* **1997**, *13*, 1737.

(8) Brodka, A.; Zerda, T. W. *J. Chem. Phys.* **1996**, *104*, 6319.

quench time

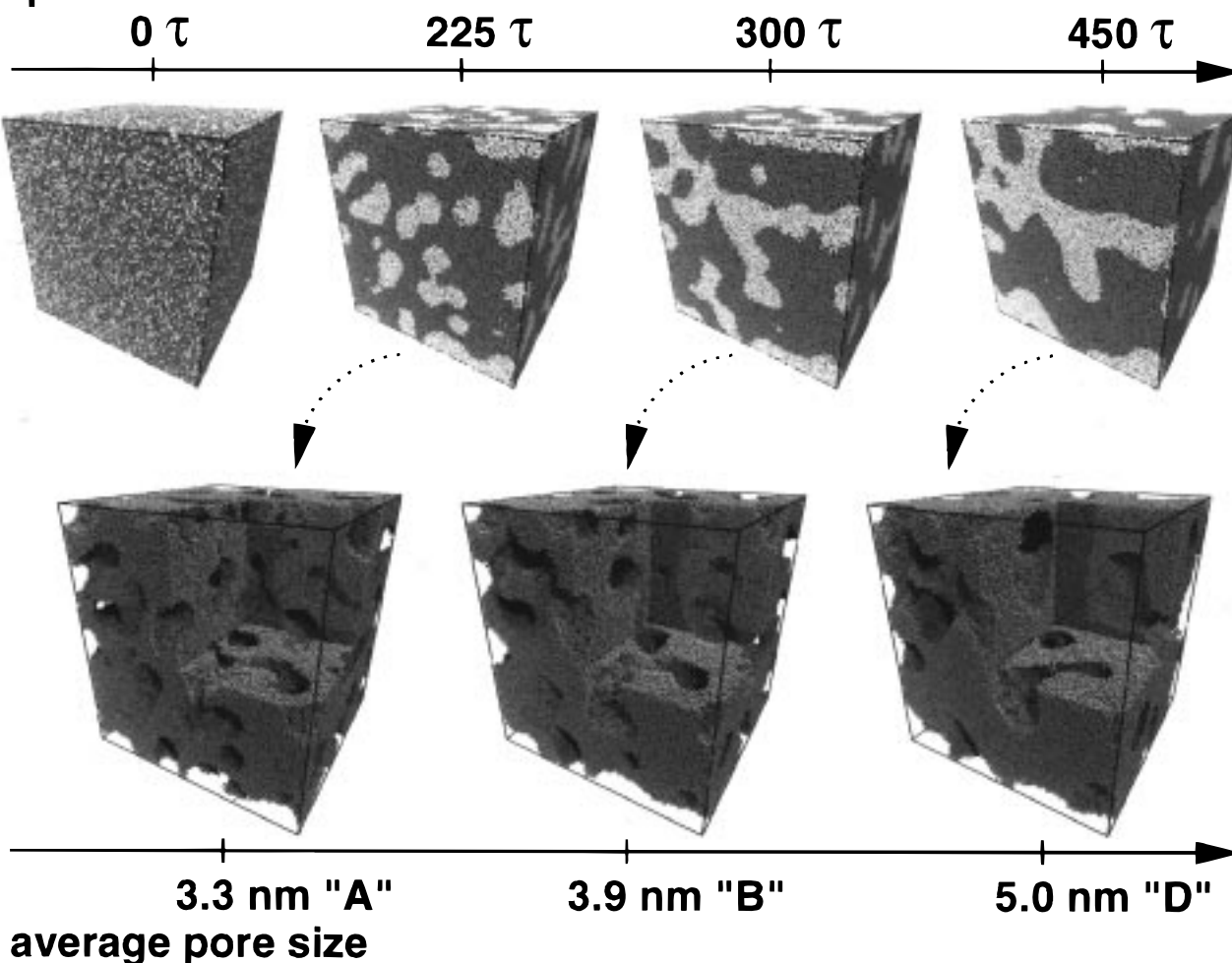


Figure 1. Generation of model materials. Quench molecular dynamics simulations of a binary mixture (top) produce a series of networked structures which are processed into adsorbent models. Snapshots taken at later stages in the phase separation are made into porous samples (bottom, shown in cut-away view) with increasing average pore size. Only samples "A", "B", and "D" are shown. Simulation time is given in reduced units (τ).

functions in the adsorption simulations were cut and shifted at a radius of 3.5σ ; no long-range corrections were used.⁹

3. Geometric Pore Size Distributions

Consider the subvolumes of the system accessible to spheres of different radii. Let $V_{\text{pore}}(r)$ be the volume of the void space "coverable" by spheres of radius r or smaller; a point x is in $V_{\text{pore}}(r)$ only if we can construct a sphere of radius r that overlaps x and does not overlap any substrate atoms (see Figure 2). (This volume is equivalent to that enclosed by the pore's "Connolly surface".¹⁰) $V_{\text{pore}}(r)$ is a monotonically decreasing function of r and is easily compared with the "cumulative pore volume" curves often calculated in isotherm-based PSD methods.¹¹ The derivative $-dV_{\text{pore}}(r)/dr$ is the fraction of volume coverable by spheres of radius r but not by spheres of radius $r + dr$ and is a direct definition of the pore size distribution.¹² The $V_{\text{pore}}(r)$ function can be calculated by a Monte Carlo volume integration.⁹

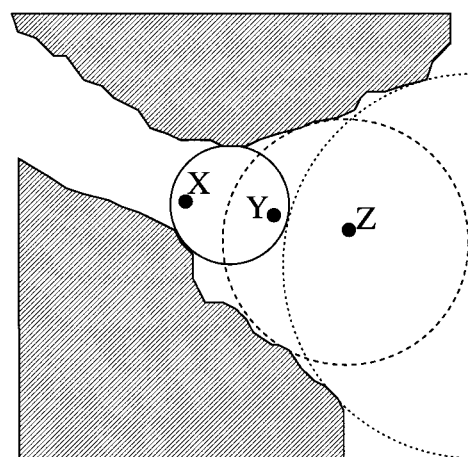


Figure 2. Two-dimensional illustration of the geometric derivation of the pore size distribution. Point "X" is only coverable by the smallest (solid) circle, while point "Y" is coverable by the smallest and midsize (dashed) circles, and point "Z" is coverable by all three circles. By determining the largest covering circle for every point in the void volume, we obtain a cumulative pore volume curve.

For a material composed of spherical, cylindrical, or slit-shaped pores, this analysis would give the exact distribution of pore sizes. For an irregular material this

(9) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon Press: Oxford, 1987.

(10) Connolly, M. L. *J. Appl. Crystallogr.* **1983**, *16*, 548.

(11) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 373.

(12) Pfeifer, P.; Johnston, G. P.; Deshpande, R.; Smith, D. M.; Hurd, A. J. *Langmuir* **1991**, *7*, 2833.

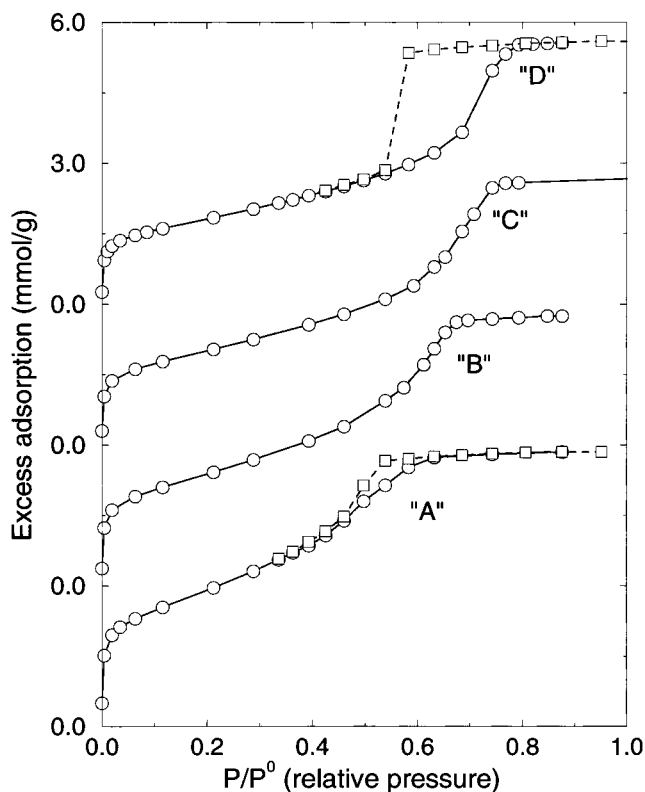


Figure 3. Simulated isotherm data for four systems of different pore size. The adsorption data are shown as circles; desorption data for the largest and smallest systems are shown as squares. Lines are guides to the eye; the isotherms are vertically displaced for clarity. Uncertainties in data are smaller than the symbols used.

geometric pore size definition is still fully applicable, while the assumptions that underly many isotherm-based methods may not apply.

4. Isotherm Calculations and Analysis

We have generated adsorption isotherms in a series of four materials of different pore size, and desorption isotherms in two of these materials, using Grand Canonical Monte Carlo (GCMC) simulations. GCMC is a stochastic method which simulates an *open* system with fixed temperature, chemical potential, and volume, and is the appropriate method to use for obtaining adsorption isotherms by computer simulation. The specific details and mathematics of a parallel-computer GCMC algorithm can be found elsewhere.^{13,14} All of these calculations were run on 28 processors of either IBM SP2 or Cray T3E supercomputers. The total cost of the simulations presented in this study was approximately 20 000 CPU hours.

For the simulations at low relative pressures all calculations were run for 60 million equilibration moves, followed by 60 million moves for data collection. For higher pressures, we used at least 100 million equilibration moves, and for points on the capillary upswing of the isotherm equilibrations longer than 500 million moves were often necessary. Simulations were deemed equilibrated after the density showed no detectable drift over a sequence of at least 60 million moves. At pore filling each system contained approximately 100 000 adsorbed molecules. The isotherms are shown in Figure 3. A virial

equation of state was used to convert between chemical potentials and pressures. As the average pore size increases across the four samples, the capillary upswing of the isotherm moves to larger relative pressures and becomes steeper, and the hysteresis loop becomes more pronounced. Uncertainties in the adsorption data are statistical and arise from performing only a finite number of Monte Carlo steps. This uncertainty has been estimated by variance analysis⁹ and is less than 1% for all the points plotted.

The Barrett–Joyner–Halenda (BJH) method for calculating pore size distributions¹¹ is one of a family of methods⁵ based on a model of the adsorbent as a collection of cylindrical pores. The method accounts for capillary condensation in the pores using the classical Kelvin equation. In each pore the total excess adsorption is given by a surface layer thickness $t(P)$ plus a pore-filling term; the pore is filled if the pressure satisfies

$$\ln \frac{P}{P^0} \geq \frac{-2\gamma V_L}{RT} \frac{1}{r_c} \quad (1)$$

where $r_c = r - t(P)$ and r is the radius of the pore. V_L is the molar volume of the liquid, γ is the surface tension, and P^0 is the vapor pressure. Thus, the Kelvin equation is only applied to the “core” fluid in this treatment. In the original BJH formulation, a simplification is introduced in which the parameter “ c ”, the ratio of core radius to pore radius, is assumed constant. In our calculations this assumption is relaxed; this is our only deviation from the original approach.¹¹

This analysis requires independent determination of γ , V_L , P^0 , and the reference isotherm $t(P)$. We have determined V_L and P^0 using Gibbs Ensemble Monte Carlo simulations of the bulk fluid. The surface tension was interpolated from previous simulations of the Lennard-Jones liquid;^{15,16} the value used was $\gamma^* = 0.389$ at $T^* = 0.809$, in reduced units.⁹ We have measured a reference isotherm by simulation of adsorption on a planar system comparable with the glass models.⁶ These data were fitted with a modified BET isotherm¹⁷ to provide an analytical function for $t(P)$.

In this study, only the *adsorption* branch of each isotherm was analyzed. The desorption branch data obtained from GCMC simulations show very sharp hysteresis loop closures (Figure 3) which lead to unphysical PSD data. Sharp loop closures in computer studies are a consequence of finite simulation times in systems with thermodynamically metastable states¹⁸ and should not be used to obtain PSDs.

The results of our BJH calculations and geometric analyses are shown in Figure 4. For all four systems, the peak is located at smaller diameters in the isotherm-derived data than in the geometric data. The peaks also tend to be sharper in the isotherm data. In each case, the discrepancy in position is approximately 1 nm. The isotherm-derived data are also somewhat rougher than the geometric data; this is due principally to noise in the adsorption isotherms.

(15) Holcomb, C. D.; Clancy, P.; Zollweg, J. A. *Mol. Phys.* **1993**, *78*, 437.

(16) Chapela, G. A.; Saville, G.; Thompson, S. M.; Rowlinson, J. S. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1133.

(17) Brunauer, S.; Skalny, J.; Bodor, E. E. *J. Colloid Interface Sci.* **1969**, *30*, 546.

(18) Schoen, M. *Computer Simulation of Condensed Phases in Complex Geometries*; Springer-Verlag: Berlin, 1993.

(13) Papadopolou, A.; Becker, E. D.; Lupkowski, M.; van Swol, F. *J. Chem. Phys.* **1993**, *98*, 4897.

(14) Heffelfinger, G. S.; Lewitt, M. E. *J. Comput. Chem.* **1996**, *17*, 250.

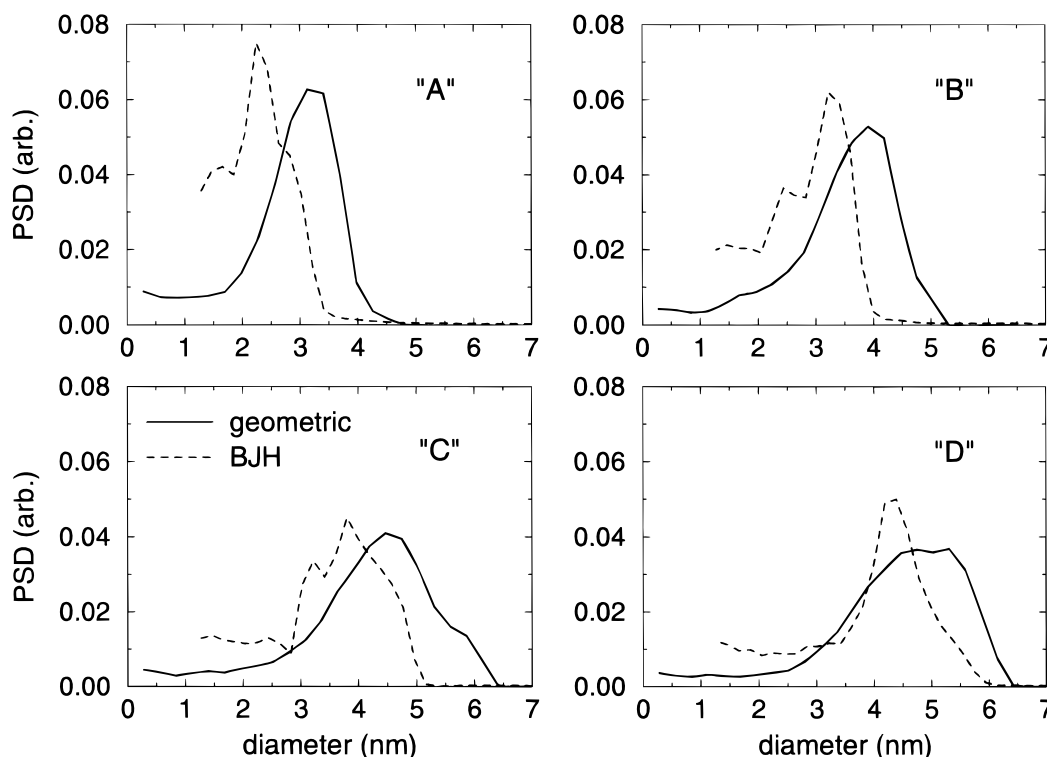


Figure 4. Pore size distributions from BJH analysis of adsorption data and our geometric analysis. Solid lines are the geometric data, and dashed lines are the results of BJH isotherm analyses.

5. Discussion

We have found that the distributions of void volume measured by the BJH method differ in systematic ways from those determined directly from the pore structure using spherical probes. The BJH method yields PSDs which are narrower, and have maximum pore diameters about 1 nm smaller, than the exactly known geometric PSDs. Nevertheless, the near agreement of these data is remarkable given the complexity of the pore geometries; the BJH method appears to be quite forgiving of pore nonideality. The systematic differences are due to several factors. The first is the use of the Kelvin equation, which is expected to give low estimates of the pore size in small pores.^{5,19–21} A second error is the use of a standard reference isotherm; in our previous study⁶ we showed that the surface adsorption in very small pores was systematically higher than that on a chemically identical planar surface. Last, since these pores are of nonideal geometry, we have no reason to expect these two measures to agree exactly!

Isotherm analysis methods have recently been augmented by the use of density functional theories to calculate adsorption in the model cylindrical pores, which is a considerable improvement over the use of a reference isotherm and the Kelvin equation.^{20,21} Such improvements may well bring our data into closer agreement; we have studied the classical theory here because it is widely used

and may be considered as a standard characterization method. While it is tempting to propose that some BJH-derived PSDs could be improved by a shifting of ca. 1 nm, we have not yet determined over what range of pore size and porosity this would be reliable, and such corrections are not advised. Our choice of potential model may influence the size of the observed shift, and determining the “transferability” of our quantitative findings will require considerable additional study.

Our principal conclusion is that this type of method is adequate for roughly estimating an average local “size” in the pore network but shows systematic errors in small pores. Furthermore, the width of the isotherm-derived PSD can be taken as a *qualitatively* reliable measure of the regularity of the material, but probably has little meaning apart from that. By comparing our PSDs with snapshots of the pore models (Figure 1), we see that the actual pore structures have a complexity which is completely obscured at this level of analysis; more sophisticated measures (either directly obtained or inferred from adsorption data) are required to fully understand these materials.

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(19) Tolman, R. C. *J. Chem. Phys.* **1949**, *17*, 333.

(20) Lastoskie, C.; Gubbins, K. E.; Quirke, N. *Langmuir* **1993**, *9*, 2693.

(21) Lastoskie, C.; Gubbins, K. E.; Quirke, N. *J. Phys. Chem.* **1993**, *7*, 4786.