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Adsorption in Controlled-Pore Glasses: Comparison of Molecular Simulations with a Mean-Field Lattice Gas Model

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Abstract. We consider the possible *quantitative* application of a lattice-gas model approach to the calculation of adsorption isotherms. In order to validate such application, we use the lattice-gas approach to solve for the adsorption and desorption isotherms in model controlled-pore glasses that have previously been the subject of an extensive series of Grand Canonical Monte Carlo simulations. We find that the lattice-gas model augmented with longer-ranged interactions provides a quite good account of adsorption in some of these systems for appropriate choice of several system parameters, but that the quality of agreement depends on the pore size of the material.

Keywords: molecular simulation, statistical mechanics, capillary condensation

Introduction

Analysis of the adsorption isotherms of simple liquids such as argon and nitrogen remains the most commonly used method to obtain the porosity, surface area and pore size distribution of microporous and mesoporous materials (Gregg and Sing, 1982; Rouquerol et al., 1999). Methods for gas adsorption analysis involve fitting (either implicitly or explicitly) the morphological properties of an idealized model of the material (for instance, a collection of cylinders of varying size) to the measured adsorption data, and then reporting the fitted quantities (Gelb and Gubbins, 1998, 1999). For amorphous materials with a range of pore sizes and shapes connected in a "tortuous" network topology, it is not always clear how to construct such an idealized model.

We are working towards the extraction of structural data from adsorption isotherms by fitting the adsorption in an arbitrary three-dimensional porous matrix to experimental data. Such an extraction could in principle be accomplished using the same sort of integral equation as in standard analyses (Gregg and Sing, 1982; Rouquerol et al., 1999). This would require a fluid model for which the isotherm can be very quickly and cheaply calculated, since an iterative procedure with many thousands of model isotherm determinations would be required. Lattice-gas models (as described below) may be suitable for this purpose, but must first be tested and parameterized against adsorption data in nontrivial, three-dimensional structures before they could be applied reliably. In this paper we perform such a parameterization, using molecular simulations of xenon adsorption in controlled-pore glass materials as our reference data.

Models and Simulation Methods

The original preparations and characterizations of controlled pore glasses were done by Haller (1965). The starting material is 50–75% SiO_2, 1–10% Na_2O, and the remainder B_2O_3. The molten glass mixture is phase-separated by cooling to between 500 and 750°C; the time taken for this treatment determines the extent of

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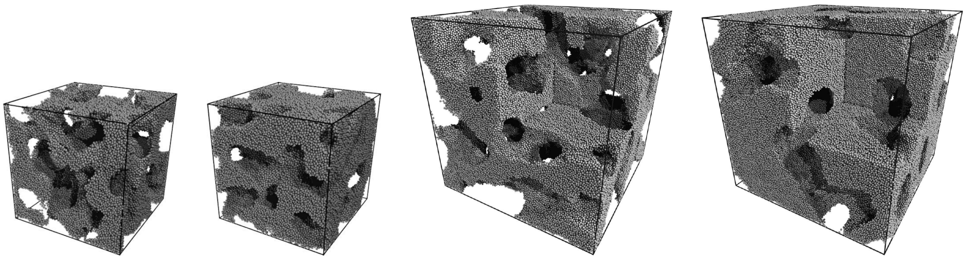

Figure 1. Molecular models used. From left to right, (a) 50% porous, 3.5 nm pore size, (b) 30% porous, 3.2 nm pore size, (c), 50% porous, 5.4 nm pore size, (d) 30% porous, 5.0 nm pore size. Materials (c) and (d) are shown with one corner removed.

phase separation and the resulting average pore size. The borate phase is leached out by acid solutions at high temperatures. The remaining glass contains colloidal silica particles, which are removed by treatment with NaOH followed by washing with water. The final glass has a porosity between 50 and 75%, an average pore size between 4.5 and 400 nm, and surface area between 10 and 350 m^2/g (Schnabel and Langer, 1991).

In previous work (Gelb and Gubbins, 1998) we have developed models which have reasonable pore sizes, porosities and surface areas, and are similar in appearance to the real materials. For the study presented here, we used model materials with small and large pores of either 30% or 50% porosity. Simulation cells measured either 15.8 nm (small pores) or 27 nm (large pores) on each edge. The models are shown in Fig. 1; quoted pore sizes are the position of the PSD maxima obtained via geometrical analysis (Gelb and Gubbins, 1999).

Mean-Field Lattice Gas Model

In recent studies (Kierlik et al., 2001a, 2001b; Detcheverry et al., 2003) using the lattice-gas approach, the fluid is described by a model isomorphic with the nearest-neighbor Ising model. Following original work (De Oliveira and Griffiths, 1978), this can be thought of as a discretization of space into cells approximately the same size as a fluid molecule, with interactions between neighboring occupied cells given by a simple constant energy term. The Hamiltonian is written in the following form (Kierlik et al., 2001b):

$$\mathcal{H} = -w_{ff} \sum_{\langle ij \rangle} \tau_i \eta_i \tau_j \eta_j - w_{mf} \sum_{\langle ij \rangle} [\tau_i \eta_i (1-\eta_j) + \tau_j \eta_j (1-\eta_i)]. \quad (1)$$

$\tau_i = 0, 1$ and $(1-\eta_i) = 0, 1$ are the fluid and matrix occupation variables, and the sums run over distinct pairs of nearest-neighbor sites. w_{ff} and w_{mf} are the fluid-fluid and matrix-fluid interaction constants and μ is the fluid chemical potential. The η_i define the porous matrix, and are obtained from our molecular models (above) using a simple templating procedure; a lattice is placed "over" the molecular model, and each lattice point that falls within some σ of an atomic center is assigned $\eta = 0$ (occupied).

We have extended this fluid model slightly, by allowing interaction at distances up to two lattice spacings; this is accomplished by introducing u_{ij} terms which depend only on the distance between two lattice sites:

$$\mathcal{H} = -w_{ff} \sum_{\langle ij \rangle} u_{ij} \tau_i \eta_i \tau_j \eta_j - w_{mf} \sum_{\langle ij \rangle} u_{ij} [\tau_i \eta_i (1-\eta_j) + \tau_j \eta_j (1-\eta_i)]. \quad (2)$$

The lattice spacing Δ is set equal to the minimum position of a Lennard-Jones potential and the u_{ij} are determined from the values of that potential at the appropriate site-site distances. The sum of the u_{ij} around a given site is normalized to 6, as in the nearest-neighbor-only model; this leaves the bulk fluid phase diagram unchanged by the extension of the potential range. In this work the total number of sites within range of a given lattice site is 32.

The thermodynamics of this model is given by the solution of Eq. (2) in the Grand Canonical Ensemble. This could in principle be obtained through Monte Carlo simulation, but this would be prohibitively expensive. Instead, at conditions far from critical a mean-field approximation has been shown to be sufficient for describing many properties (Woo and Monson, 2003). In the mean field one obtains the following expression for the grand potential:

$$\begin{aligned}\Omega = &-w_{ff}\sum_{\langle ij\rangle} u_{ij}\rho_i\rho_j \\ &-w_{mf}\sum_{\langle ij\rangle} u_{ij}[\rho_i(1-\eta_j)+\rho_j(1-\eta_i)] \\ &+\frac{1}{\beta}\sum_i[\rho_i\log\rho_i+(\eta_i-\rho_i)\log(\eta_i-\rho_i)] \\ &-\mu\sum_i\rho_i \qquad (3)\end{aligned}$$

where ρ_i are the average fluid densities $\langle\tau_i\eta_i\rangle$ and $\beta = 1/k_BT_L$, where T_L is the temperature in the lattice model. This can be arrived at by several routes, ranging from application of the Bragg-Williams approximation to the model (1) (Hill, 1956) to recasting the problem as a coarse-grained version of classical fluid Density Functional Theory (Kierlik et al., 2001b). By applying the variational condition $\partial\Omega/\partial\rho_i = 0$, a set of coupled equations is obtained

$$\rho_i = \frac{\eta_i}{1+e^{-\beta\{\mu+\sum_{j/i}u_{ij}[w_{ff}\rho_j+w_{mf}(1-\eta_j)]\}}}, \qquad (4)$$

which can be solved iteratively. The sum in (4) runs over the neighbors of i within potential range, e.g., with $u_{ij} \neq 0$.

It has been shown (Rosinberg et al., 2003; Salazar and Gelb, 2004) in similar systems that the usual periodic boundary conditions are not acceptable for the simulation of desorption isotherms, as they suppress nucleation of the low-density phase and therefore often display greatly exaggerated hysteresis. However, this effect appears to be due entirely to extension of the *desorption* branch; in this work we (safely) focus on *adsorption* branch data in comparison of simulated and lattice-gas systems.

As the slope of the isotherms can change rapidly, rather than use equally-sized steps in μ we attempt to choose μ intervals to yield a constant contour length along the isotherm. We calculate the absolute adsorption isotherm $\rho_f(\mu; T) = 1/N\sum_i\rho_i$ by varying the chemical potential μ^i to $\mu^{i+1} = \mu^i + \delta^i$ by the method presented in Salazar et al. (1999). Lattice-gas calculations have been performed for a very large number of temperatures, lattice spacings, and $y = w_{mf}/w_{ff}$ parameters, of which only a small selection will be shown.

Molecular Simulations

In order to simulate adsorption of xenon in these model pores, we represent xenon with a single Lennard-Jones sphere with potential parameters $\sigma_{\mathrm{Xe}} = 0.391$ nm and $\varepsilon_{\mathrm{Xe}}/k_B = 227$ K. The parameters for the substrate atoms are set to $\sigma = 0.27$ nm and $\varepsilon/k_B = 230$ K, which have been used to represent bridging oxygens in silica (Brodka and Zerda, 1996). The Lorenz-Berthelot mixing rules are used to give the inter-species parameters. Interactions between xenon atoms were truncated at $2.5\sigma_{\mathrm{Xe}}$, while interactions between xenon atoms and pore atoms were cut-and-shifted at the same radius. No long-range corrections were used (Allen and Tildesley, 1987).

Grand Canonical Monte Carlo is a stochastic scheme which simulates an *open* system with fixed temperature, chemical potential, and volume. It is the appropriate method to use for determining adsorption isotherms by computer simulation. The specific details can be found elsewhere (Allen and Tildesley, 1987). Adsorption calculations were performed using a GCMC algorithm parallelized by domain-decomposition (Heffelfinger and Lewitt, 1996); our implementation has been described previously (Gelb and Gubbins, 1999, 2001).

In this study, isotherm data in the large systems were obtained using a $3 \times 3 \times 3$ domain decomposition (27 processors) on IBM SP and Cray T3E computers. Points at low pressure and at pressures where the pores were filled with liquid were generally equilibrated for 200 million moves, followed by another 200 million moves for data collection; points on the capillary upswing of the adsorption branch and the shoulder of the desorption branch took as many as 2.4 *billion* moves for equilibration before a stable value of the density was reached. Isotherm data in smaller systems were run for correspondingly shorter times using either a single processor or a $2 \times 2 \times 2$ decomposition.

All simulation results will be given in Lennard-Jones *reduced units* appropriate for xenon. Simulated isotherms were obtained in the four models of Fig. 1 at reduced temperatures of 0.8085, 0.9270 and 1.025.

Results and Discussion

A mapping of our molecular simulation parameters onto the mean-field model may be made as follows. First, in accord with the long-ranged interaction model described above, we choose the lattice spacing $\Delta = \sigma 2^{1/6}$, the potential minimum separation. For the small-pore simulation cells given above, this results in a lattice gas grid of 36^3 points. For the large-pore cells it results in a grid of 62^3 points.

Either of the ratio of energy units w_{ff}/ε or the ratio of temperatures T/T_L may be chosen arbitrarily and the other used as an adjustable parameter; this results from the scaling of energy and temperature in both models. We choose $w_{ff}/\varepsilon = 1$ and treat T_L as an adjustable parameter. The y parameter may be determined by fitting to the interaction between the fluid and a wall in the molecular model. For fluid molecules in a lattice cell adjacent to a wall, on average this should be $y = \rho_{\text{wall}} \times V_{\text{cell}} \times V_{\text{Xe-O}}(\Delta)$, where the last term is the Lennard-Jones potential between the fluid and pore-wall atoms evaluated at the lattice spacing. Here this works out to 2.065, which we round to 2.0.

Finally, because the simple lattice gas does not have a crystalline phase (which would unambiguously set the density scale of the model) the meaning of the density ρ in Eq. (3) is open to interpretation, and it is reasonable to apply a temperature-dependent scaling factor to the density in the lattice-gas model; in the results below we simply scale the lattice-gas adsorption to agree with molecular simulations at pressures above capillary condensation.

We will present isotherm data as relative pressures (P/P^0, where P^0 is the vapor pressure in each model), so that no conversion of pressures or chemical potential will be necessary; coexistence state data are obtained in auxiliary calculations (Gibbs Ensemble Monte Carlo in the case of the molecular system.)

In Fig. 2(a) we plot the results of this parameter estimation in fitting the lattice model to the 50% porous, small-pore model described above. The molecular model was "templated" onto a 36^3 grid, and the isotherms obtained over a range of lattice-gas temperatures. By inspection, the best agreement between the two models is found at a lattice temperature of 0.85; the difference between the lattice and simulation temperatures could equivalently be described as a difference between the energy scales in the two models. We see that, as expected, under all conditions the lattice model displays greatly enhanced hysteresis; this can be at least partly alleviated by using open boundary conditions as discussed earlier. Even the best fit isotherm somewhat overestimates adsorption in the monolayer and multilayer regions, which suggests an excessively large choice of the parameter y, above. In Fig. 2(b) we "float" the y parameter as well, and find that excellent agreement is found if the y parameter is chosen near 1.70.

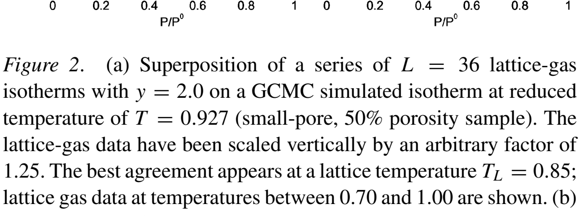

Figure 2. (a) Superposition of a series of $L = 36$ lattice-gas isotherms with $y = 2.0$ on a GCMC simulated isotherm at reduced temperature of $T = 0.927$ (small-pore, 50% porosity sample). The lattice-gas data have been scaled vertically by an arbitrary factor of 1.25. The best agreement appears at a lattice temperature $T_L = 0.85$; lattice gas data at temperatures between 0.70 and 1.00 are shown. (b) Superposition of two lattice-gas isotherms on the same simulation data. Here the y parameter is "floated" in order to obtain better agreement; the best results are obtained over a small range of y and T_L as shown.

In Fig. 3 we present "best fit" data at two different temperatures for both small-pore models. Good agreement is obtained using the same y and T_L parameters for both models, which is encouraging. In addition, the required temperature scale factor of approximately 0.90 (that is, the lattice model temperature is approximately 90% of the simulation temperature for a good fit) is the same for both temperatures. In both sets of data, at the lower temperature, the lattice model gives somewhat higher adsorption in the multilayer region than does the molecular simulation.

In Fig. 4, we attempt to transfer the scaling rules and y choice from the small-pore models to the large-pore ones. In the large-pore models, the lattice gas

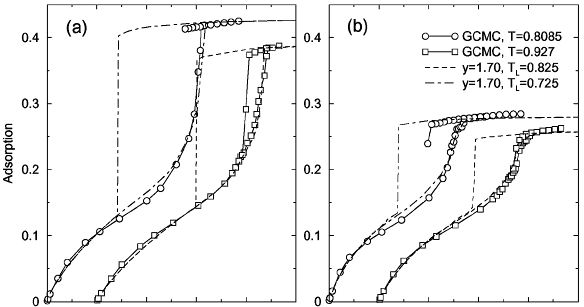

Figure 3. (a) "Best fit" of lattice model to the small-pore, 50% porous system at temperatures of 0.8085 (reduced) and 0.927. (b) The same, but for the small-pore, 30% porous system. Lattice-gas data have been scaled vertically by an arbitrary factor in each case so that total adsorption is similar at high pressure. The same y and T_L values are used to fit isotherms in the two materials.

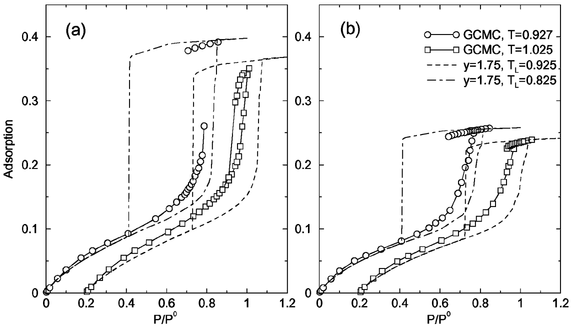

Figure 4. (a) Lattice-gas fit to the large-pore, 50% porous system with $L = 60$, at temperatures of 0.927 and 1.025, using y and T_L/T similar to that from Fig. 3. (b) The same, but for the large-pore, 30% porous system. The lattice-gas data have been scaled vertically by an arbitrary factor in each case. The same y and T_L values are used for isotherms in the two materials.

consistently overestimates the relative pressure of condensation, and consistently underestimates the adsorption in the multilayer region. These two errors are related via the "core" condensation model used in BJH analysis, for instance (Gregg and Sing, 1982). One possible reason for the poor fit observed here is that the roughness of the molecular pore surface is not preserved upon mapping to the η_i lattice (this will be influenced by the mean curvature of the surface, inversely related to the pore radius) which would lead to lower adsorption in the multilayer region and delayed condensation at higher pressures. Interestingly, using a different lattice spacing and a 48^3 grid with $T_l \simeq 1.05$ gives good agreement for the capillary condensation pressure, but large positive errors in the multilayer region due to thickening of the multilayer from the increased lattice spacing.

The lattice model approach is dramatically faster than the GCMC molecular simulations. To obtain adsorption and desorption data at forty pressures in the smaller $L = 36$ models required approximately 33 *seconds* of CPU time on an Athlon MP2000+ processor, while the $L = 60$ models took 96 seconds. This is between three and four orders of magnitude faster than the simulations, which often required thousands of CPU *hours* to complete.

It thus appears that the lattice-gas approach could *in principle* be applied in a quantitative fashion to the prediction of adsorption data in mesoporous materials, but that improvements will have to be made before it can be reliably used to do so. It remains to be determined whether the principal error is in the mapping of the molecular model onto the lattice or in the fluid model itself. If the lattice translation is at fault, a more complex mapping that preserves surface area will be implemented. If the fluid model is insufficiently realistic, it can be improved following previous work (Gelb, 1996) in this area. Finally, we note that the findings here clearly support a "microscopic" interpretation of the lattice-gas model in which the lattice parameter is on the scale of one atomic diameter.

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