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Recent Progress in Molecular Modeling of Adsorption and Hysteresis in Mesoporous Materials

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Abstract. We review some recent progress in molecular modeling of the behavior of fluids confined in mesoporous materials. We address three issues. The first is the applicability of the grand canonical ensemble for studying adsorption and hysteresis in porous materials. Next we discuss models of complex pore structure and how these can be coarse grained using a lattice model. Then we consider the question of how hysteresis is related to a vapor-liquid phase transition for disordered mesoporous materials. In concluding we assess the prospects of developing a unified description of adsorption and hysteresis valid over the range of mesoporous materials.

Keywords: adsorption, hysteresis, mesoporous materials, molecular modeling, phase transitions

Introduction

A major challenge in the use of adsorption for characterization of porous materials has been to understand the precise influence of porous material microstructure upon the properties of confined fluids. Porous materials frequently have a complex interconnected void space, yet traditional approaches that engineers use to relate the adsorption behavior to the porous material structure largely ignore this fact, and seek to describe the microstructure in terms of a distribution of independent pores. In principle statistical thermodynamics offers the solution to this problem, provided that a sufficiently realistic model of the microstructure can be developed. However, implementation of this approach has been hampered by the computational expense of making Monte Carlo simulations on complex models or applying theories like density functional theory when the density distribution in the system is fully three-dimensional. Moreover the use of the grand canonical ensemble in modeling adsorption/desorption hysteresis has been subject to question because of uncertainty over the role of dynamics in these phenomena. This paper gives a short review of some recent progress in developing the statistical thermodynamic theory of adsorption and desorption in mesoporous materials. We first consider the applicability of the grand canonical ensemble for studying adsorption and hysteresis in porous materials. We also discuss the development of models of complex pore structure and how coarse-graining of these models using a lattice model leads to a computationally efficient theoretical and simulation methods for studying these systems. We consider the question of how hysteresis is related to a vapor-liquid phase transition for disordered mesoporous materials and also the role of dynamics in hysteresis. In our concluding section we assess the prospects of developing a unified description of adsorption and hysteresis valid over the range of mesoporous materials.

Can We Use the Grand Canonical Ensemble to Study Adsorption and Hysteresis?

As is very well known, the grand canonical ensemble of statistical mechanics should provide a natural framework for studying adsorption in porous materials since it is representative of a system of fixed chemical potential. On the other hand in this ensemble the variations in the local density of the fluid in the porous material are sampled without reference to the transport mechanism through which such variations would happen in nature. Thus when hysteresis between adsorption and desorption is observed in a grand canonical Monte Carlo (GCMC) simulation for a model fluid/pore system it is natural to raise the question of its significance as was done after the first observations of this type for fluids in slits and cylindrical pores (Schoen et al., 1989).

One way in which to address this issue in more detail is to develop a grand canonical simulation method for studying hysteresis that includes the transport mechanisms seen in real systems (Sarkisov and Monson, 2000, 2001). The resulting grand canonical molecular dynamics (GCMD) method has been used to show that the hysteresis in GCMC simulations of a model of adsorption in silica gel could be reproduced dynamically (Sarkisov and Monson, 2000). The method has subsequently be applied to simpler pore geometries (Sarkisov and Monson, 2001). As an illustration of the approach we consider results for a slit pore version of the inkbottle geometry with interactions modeled by Lennard-Jones 12-6 potentials (for details of the model parameters see Sarkisov and Monson, 2001). Figures 1 and 2 show adsorption/desorption isotherms from both GCMC and GCMD methods as well computer graphics visualizations for states of the system during adsorption and desorption. There are two important aspects to these results. The first feature is that the phenomenology seen here is different than that usually ascribed to an inkbottle pore. We see that on desorption the large cavity can empty even as the small pore remains filled. The second important feature is that the results from the two methods are essentially identical. This shows that simulations of hysteresis via the GCMC method can give physically significant results.

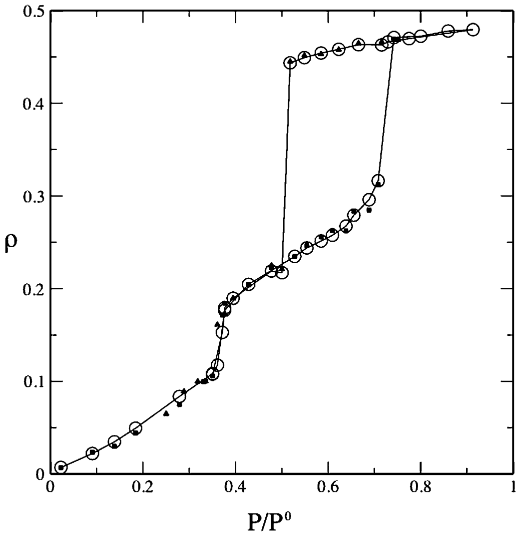

Figure 1. Adsorption/desorption isotherms of dimensionless density ($\rho\sigma^3$) vs. relative pressure for a model inkbottle geometry from grand canonical Monte Carlo (open circles) and molecular dynamics (filled squares—adsorption; filled triangles—desorption). (From Sarkisov and Monson, 2001).

Modeling Complex Pore Structure

Over the last decade researchers have built molecular models that address the microstructural complexity of porous materials while still being computationally accessible (Gelb et al., 1999). Efforts of this type include the model of silica gel that treats the adsorbent as a collection of spherical particles in a frozen configuration (Kaminsky and Monson, 1991). The void space between the spheres gives a complex interconnected pore structure. Complementary models of porous glasses have been built using mimetic simulations (Gelb and Gubbins,1998) and by reconstruction methods that reproduce experimentally determined structural information. GCMC simulations of adsorption in these systems give hysteresis loops of type II in the IUPAC classification hysteresis (Sing et al., 1985) and these correspond nicely with those seen experimentally. These models while accessible via computer simulation are quite computationally intensive. Moreover, the application of mean field density functional theory (DFT) that has been so useful for studying simple pore geometries such as slits and cylinders (Evans, 1990; Gelb et al., 1999) can only be applied to the complex pore models using sophisticated numerical techniques implemented on large scale computer systems (see e.g., Douglas Frink and Salinger, 2000).

Thus it is worthwhile to ask whether there might be a simplification of this approach that can still provide a useful framework for understanding the link between microstructure and adsorption/desorption behavior.

For fluids in mesoporous materials characterized by typical domain sizes much larger than molecular length scales, many of the microscopic details of the molecular interactions are expected to be less important to the qualitative behavior observed in experiments. A coarse-grained representation of the system based on a lattice model represents a useful approach under such circumstances. The application of lattice models to adsorption is almost as old as the field itself (if we consider that Langmuir's isotherm can be derived from the simplest lattice model of a monolayer). In recent years

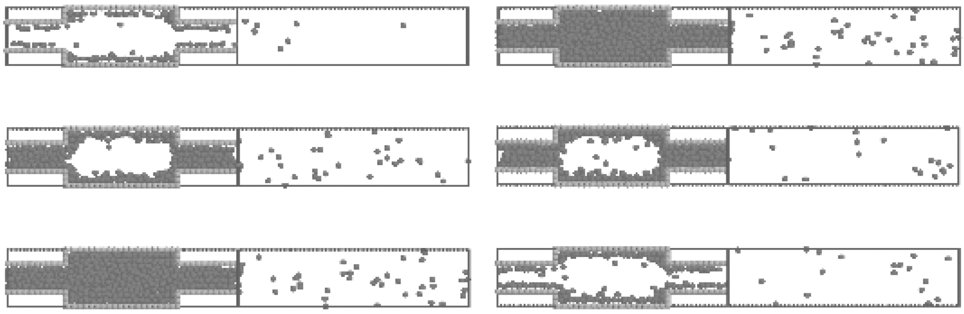

Figure 2. Configurations from GCMD simulations of an inkbottle geometry for states on adsorption (left) and desorption (right). (From Sarkisov and Monson, 2001).

lattice models have been applied to various problems in adsorption on surfaces and in porous materials. For example, wetting, prewetting and layering transitions on planar solid surfaces have been studied using mean field theory (Ebner, 1980) and Monte Carlo simulation (Nicolaides and Evans, 1989). Recently mean field lattice-gas models have been used to study the phase behavior of fluids confined between chemically corrugated substrates (Rocken and Tarazona, 1996; Bock and Schoen, 1999). A lattice model in combination with a mean field theory has been also applied to study hysteresis in narrow pores (Bettolo-Marini Marconi and van Swol, 1989). Lattice models have been used to model adsorption in zeolites for cases where the density distribution in the zeolite channels or cavities is thought to be highly localized (Snurr et al., 1994; Dukovski et al., 2000). Aranovich and Donohue (1998) have used DFT based on a formulation of Ono and Kondo (1960) for liquid-vapor interfaces to make calculations of adsorption at solid surfaces and in pores.

A lattice model Hamiltonian for a fluid in a porous material is readily formulated (Kierlik et al., 2001). The sites of the lattice may be occupied by solid or fluid. There is an attractive interaction between nearest neighbor fluid sites as well as between each fluid site and any nearest neighbor solid sites. The configuration of the solid sites is fixed as in the off-lattice models of disordered porous materials. Among the possible variations in the model are: (i) the spatial arrangement of the solid sites; (ii) the ratio of the fluid-fluid and fluid-solid interaction parameters; and (iii) the coordination number of the lattice (e.g. simple cubic vs. bcc vs. fcc etc.,). A random distribution of solid sites on the lattice is an important base case and Kierlik et al. (2001) have used that model to discover important new phenomena in the hysteresis region.

We illustrate the approach for the case of Vycor glass (Woo et al., 2001; Woo and Monson, 2003). The structure of Vycor comes about through arresting the spinodal decomposition process of a molten mixture of silica and boron oxide. Etching out the boron oxide from the frozen configuration generates a porous glass structure. This can be modeled on a computer by arresting spinodal decomposition in a model binary mixture and removing one of the components (Gelb and Gubbins, 1998). An alternative and computationally more efficient method is to use Gaussian random field methods similar to those used to study the interfaces in spinodal decomposition (Woo et al., 2001). Figure 3 shows a typical Gaussian field configuration generated for Vycor using a porosity of 30% and the experimental structure factor. The surfaces shown represent the solid surfaces

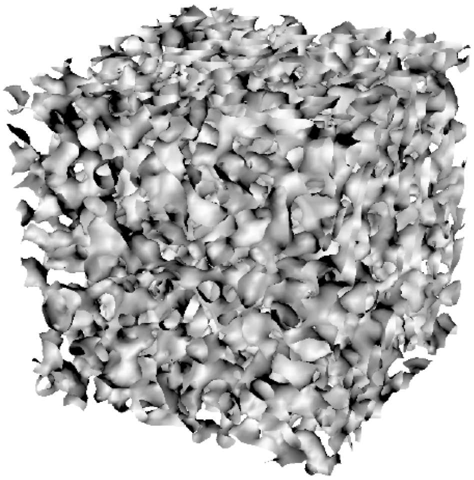

Figure 3. Isosurfaces of the Gaussian random field representing the internal surfaces of a model of Vycor glass. (From Woo et al., 2001).

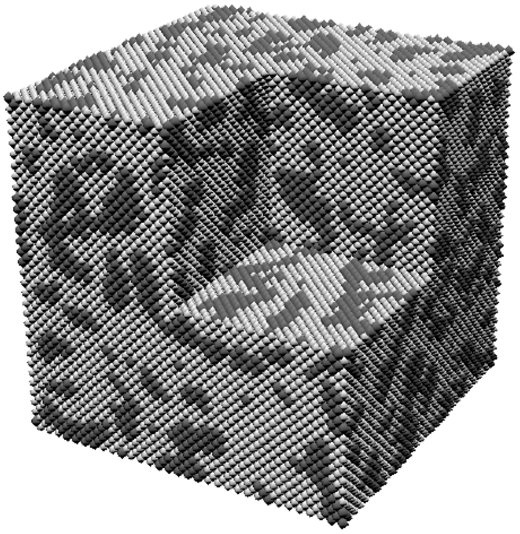

Figure 4. Visualization of the lattice model of Vycor obtained using the Gaussian random field method. Light areas represent the solid. (From Woo et al., 2001).

in the interior of the porous material. A lattice model developed by coarse graining this surface is shown in Fig. 4. DFT calculations with this model yield adsorption/desorption hysteresis behavior in remarkable qualitative accord with the classical experiments of Everett and coworkers (Everett, 1967).

Figure 5 shows the adsorption/desorption behavior for the lattice model described above at three temperatures (Woo et al., 2001). From Fig. 5 it is evident that the hysteresis in this model system narrows significantly as the temperature increases and will disappear once the temperature is sufficiently high, as has been seen in experiments (Burgess et al., 1989). The temperature at which the hysteresis disappears is sometimes referred to as the 'hysteresis critical temperature' (Burgess et al., 1989), although the precise relationship between this temperature and the critical temperature associated with a vapor-liquid phase transition has only recently emerged (Woo and Monson, 2003). In the following section we will address the question of the relationship between the hysteresis behavior and a vapor-liquid phase transition for the confined fluid.

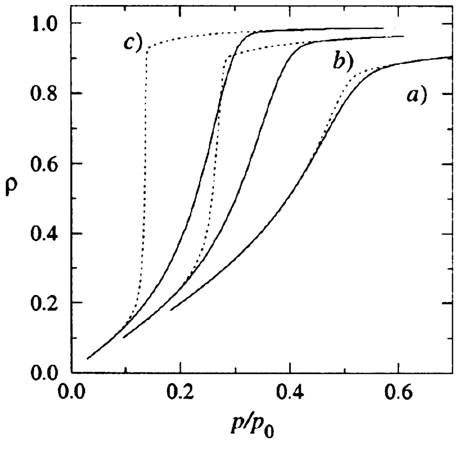

Figure 5. Adsorption desorption isotherms for the model of a fluid in Vycor at three temperatures relative to the bulk critical temperature: T/T_C- (a) 0.65, (b) 0.5, and (c) 0.4. (From Woo et al., 2001). The density here is the fractional occupancy of the void sites in the lattice.

Hysteresis and Phase Behavior

At first glance it is tempting to identify the hysteresis loops shown in Fig. 5 with the 'van der Waals loops' familiar to anyone who has worked with mean field theories or cubic equations of state for bulk vapor-liquid systems. However, as was shown in recent calculations for a lattice model with a random distribution of the solid (Kierlik et al., 2001) and subsequently for the lattice model of Vycor (Woo et al., 2001; Woo and Monson, 2003) this picture is an oversimplification. The calculations show that in the hysteresis region the system exhibits a very large (essentially infinite for a macroscopic sample of the porous material) number of local minima of the grand potential, which appear because of the roughness of the solid-fluid potential energy landscape generated by the disorder in the porous material microstructure. An immediate benefit of this analysis is a basis for understanding scanning curves in which reproducible traces of states in the hysteresis region are obtained experimentally (Everett, 1967). The scanning curves can be seen as loci connecting local minima of the grand potential (Kierlik et al., 2001; Woo et al., 2001).

Woo and Monson (2003) have presented results for the lattice model that clarify the relationship between the hysteresis and phase behavior of a fluid in Vycor. Figure 6 shows a temperature versus density diagram for a model with two sets of data. One is the locus of the upper and lower closure points of the hysteresis loops at each temperature. Such a locus has been referred to as the 'hysteresis phase boundary' (Burgess et al., 1989). The other is the actual vapor-liquid coexistence curve, which can be calculated directly in the mean field theory. In the familiar van der Waals picture,

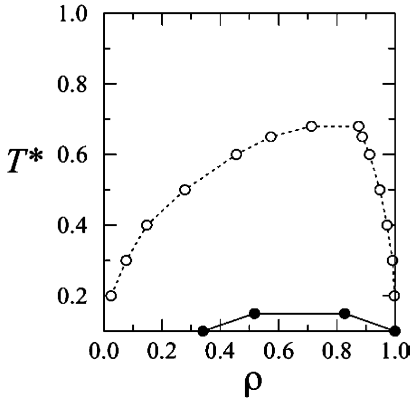

Figure 6. Hysteresis (open symbols) and equilibrium (filled symbols) phase diagrams for lattice model of a fluid in Vycor (From Woo and Monson, 2003). The temperature here is divided by the bulk critical temperature and density is the fractional occupancy of the void sites in the lattice.

the two curves should merge at the critical temperature. However, we see here that there is a large region of temperature above the actual critical temperature where the system still exhibits hysteresis. Over this range of temperatures the hysteresis is not associated with a vapor-liquid phase transition and the states of the fluid on and within the hysteresis loops do not in general represent thermodynamic equilibrium states of the system. Another question to be resolved is why the hysteresis seen in experiments is so reproducible. For that we must consider the dynamics of adsorption and desorption. Woo and Monson (2003) have made dynamic Monte Carlo calculations of the lattice model of a fluid in Vycor. These calculations suggest that the equilibration of the density in the porous material involves two kinds of processes operating on very different time scales. The first is a quasi-diffusional relaxation process at shorter times associated with the fluid entering and leaving the system via the external surfaces. The second is the relaxation of the density distribution of the fluid within the porous material at longer times and this involves barrier crossings between local minima of the grand potential—an intrinsically slower process. Experiments with sample times large enough to reach this longer time regime will exhibit an extremely slow dynamics such that density changes with time will be imperceptible. Thus the states measured in the hysteresis region are not at equilibrium but are changing so slowly that they appear equilibrated and will be quite reproducible. Another aspect of this is that even though we can calculate the vapor-liquid phase envelope for our model system this phase envelope will not be relevant experimentally since the vapor-liquid phase behavior cannot be equilibrated on an accessible time scale.

Summary and Outlook

We have presented a brief review of some key developments in our understanding of the adsorption and hysteresis behavior in mesoporous materials. This work establishes important points of principle. For example we now have a clearer idea of the significance of hysteresis loops calculated in GCMC simulations. Moreover a modeling framework for understanding the properties of fluids confined in complex pore structures has been established.

We should also ask whether the lessons learned from the work reviewed here can be applied to other systems. In this regard the outlook is quite promising. As an illustration of this the work on Vycor is being extended to controlled pore glass (CPG). CPG is similar in overall morphology to Vycor but with higher porosity and substantially larger pore sizes. Experiments reveal that CPG systems exhibit type I hysteresis (see e.g., Thommes et al., 2002). This reflects the smaller influence of the solid-fluid potential on the fluid properties in the system and a more bulk-like behavior. Results from DFT calculations for a model of CPG are shown in Fig. 7 compared with the corresponding model of

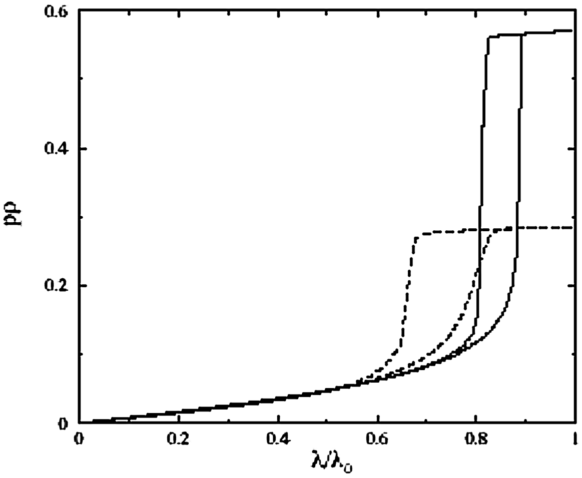

Figure 7. Adsorption/desorption isotherm for the lattice model of a fluid in CPG (full line) compared with those for Vycor (dashed line) (Porcheron et al., 2004). In order to compare the results for the two systems the density, ρ expressed as the lattice occupancy is multiplied by the porosity, p.

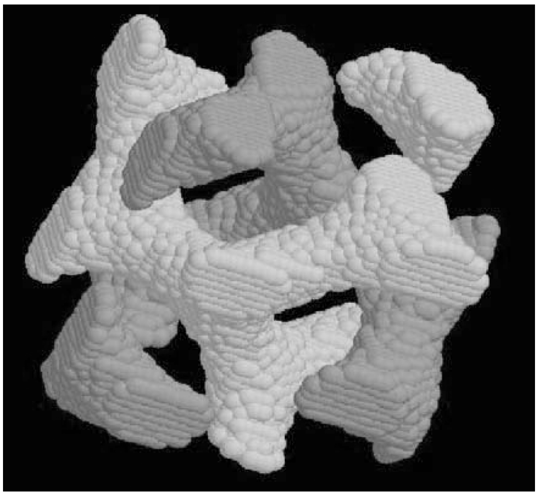

Figure 8. The lattice model of MCM-48. The pore structure consists of two interpenetrating pore networks. For clarity only the solid on the pore walls is shown and one of the pore networks is shaded differently (Libby and Monson, 2004).

Vycor. We see that the model calculations are able to capture the change from type II to type I between the Vycor and CPG. Recent work has also been done in extending the approach to ordered mesoporous materials. As an illustration of this Fig. 8 shows a visualization of the lattice model of MCM-48 (Beck et al., 1992). This was obtained by making a coarse graining of the double gyroid minimal surface, which has been suggested as the structure for MCM-48 (Alfredsson and Anderson, 1996). Adsorption/desorption isotherms for this model exhibit similar behavior to those measured experimentally.

In conclusion it appears that the kind of approaches reviewed here represent significant progress towards a comprehensive theory of adsorption and hysteresis in mesoporous materials. Of course, much remains to be done including, for example, the development of more efficient methods for studying off-lattice versions of these models and understanding the role of dynamics in the hysteresis for more ordered mesoporous adsorbents.

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