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## Modeling Fluid Behavior in Well-Characterized Porous Materials

ROGER F. CRACKNELL,<sup>†</sup> KEITH E. GUBBINS,<sup>\*,†,‡,§</sup> MICHAEL MADDOX,<sup>‡</sup> AND DAVID NICHOLSON<sup>†</sup>

*Department of Chemistry, Imperial College of Science, Technology & Medicine, London SW7 2AY, U.K., and School of Chemical Engineering, Cornell University, Ithaca, New York 14853-5201*

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### Introduction

The phenomenon of gas adsorption in porous solids has been recognized for over 200 years and today forms the basis of many industrial separation and reaction processes. Some porous solids, such as zeolites, are crystalline with regular well-defined pores, while others, e.g., activated carbons, contain a distribution of pore sizes and shapes. Scientific interest in the effects of confinement stems from the large effect of the fluid-wall forces in small pores; these lead to interesting new surface-driven phase transitions, hys-

teresis, strongly selective adsorption from mixtures, and novel transport properties.

The search for a theory of adsorption can be traced back over 100 years to Thomson (later Lord Kelvin). The Kelvin equation applies at subcritical temperatures and has its origins in thermodynamics. It relates the reduced pressure ( $P/P^\circ$ ) at which capillary condensation occurs in a cylinder ( $P^\circ$  is the vapor pressure of the bulk fluid) to the radius  $r_p$  and the vapor-liquid surface tension  $\gamma$  of the adsorbate:

$$RT \ln(P/P^\circ) = - \frac{2V_L \gamma}{r_p} \quad (1)$$

where  $V_L$  is the molar volume of the liquid phase,  $R$  is the gas constant, and  $T$  is the temperature. The derivation of Kelvin's equation rests on the assumptions that (a) the liquid phase is incompressible, (b) the gas phase is ideal, (c) there are well-defined gas and liquid phases separated by an interface, and (d)  $\gamma$  is unchanged on confinement. It predicts that the pressure difference across a curved meniscus leads to condensation in the capillaries at pressures below the bulk saturation value. The Kelvin equation fails for micropores and small mesopores, in part because it neglects the buildup of adsorbed layers on the walls prior to condensation, and particularly because the gas and liquid in the pore can no longer be treated as

Roger Cracknell was born in Shoreham-by-Sea, U.K., in 1965. He holds both his Bachelor's degree and Ph.D. from Imperial College (London University). After two years at Cornell University, he returned to Imperial College as a research associate in 1992. His research centers around molecular simulation of molecular fluids.

Keith Gubbins was born on January 27, 1937, in Southampton, England. He received his B.Sc. (Queen Mary College) and Ph.D. (King's College) from London University and then took a postdoctoral position at the University of Florida. After serving on the faculty at Florida he moved to Cornell University in 1976 as the Thomas R. Briggs Professor of Engineering. He has held visiting appointments at UC Berkeley (1982), at Oxford University (1986-1987) as a Guggenheim Fellow, and at Australian National University (1993) as a Fulbright Fellow. His research interests have been in applications of statistical mechanical theories and simulations to fluids and to interfacial properties.

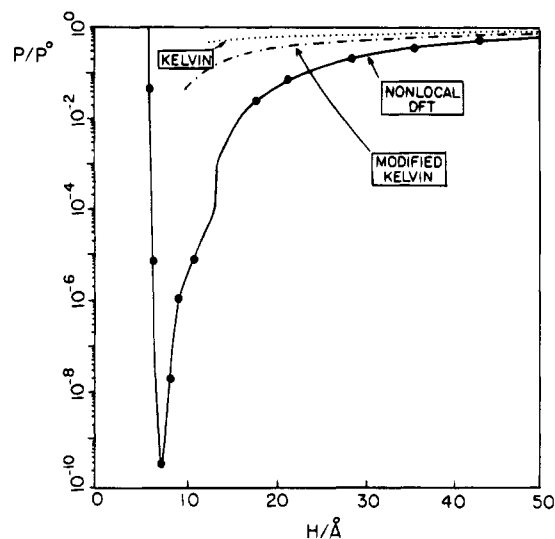
Michael Maddox was born in Ashton-under-Lyne, U.K., in 1967. He received his Bachelor's degree in chemistry from Bath University and a physical chemistry D.Phil. from Oxford University. He is currently a postdoctoral research associate at Cornell University. His research interests are in molecular simulation studies of fluid separations in novel porous materials.

David Nicholson was born in Hull, U.K., in 1936. He received his Bachelor's degree, Ph.D., and D.Sc. from the University of London. He is currently reader in physical chemistry at Imperial College. His early research involved experimental studies of physical adsorption and transport in porous materials. With Neville Parsonage he pioneered the application of simulation to adsorption systems and coauthored a monograph on the statistical mechanics and computer simulation of adsorption. His research interests are centered around the theory and simulation of interfacial systems.

<sup>†</sup> Imperial College of Science, Technology & Medicine.

<sup>‡</sup> Cornell University.

<sup>§</sup> Permanent address: Olin Hall, Cornell University, Ithaca, NY 14853.



**Figure 1.** Pore-filling pressure (relative to vapor pressure of bulk nitrogen) for nitrogen in slit graphite pores at 77 K. Points are Gibbs ensemble MC results; lines are theory calculations. In the Kelvin equation (eq 1), the pore radius is replaced by pore width,  $H$ , while in the modified Kelvin result it is replaced by  $(H - 2t)$ , where  $t$  is the film thickness on the walls at the condensation pressure, just before condensation. The sharp minimum in the NLDFT curve corresponds to the smallest pore width that can easily accommodate a nitrogen molecule; at this width the fluid-wall potential has its deepest minimum, due to overlap of the potential wells at the two walls. Based on ref 20.

uniform phases separated by an interface (assumption c above). Equation 1 can be modified in various ways<sup>1</sup> to take account of gas nonideality, adsorbate layers, and the adsorption field; for example, the pore radius  $r_p$  is often replaced by  $(r_p - t)$  in eq 1, to roughly account for the adsorbed layer of thickness  $t$ . Nevertheless, these modifications lead to only a modest improvement for small pores (see Figure 1 and discussion below). Despite its deficiencies, methods for determining pore size distributions based on the Kelvin equation are still in widespread use; they are discussed in the book by Gregg and Sing.<sup>1</sup>

In the well-known Brunauer-Emmett-Teller (BET)<sup>2</sup> model of adsorption on a nonporous surface, adsorption either occurs on specified surface sites or takes place on top of previously adsorbed molecules. The BET equation, although not appropriate for high pressures or for micropores, is much closer in spirit to modern theoretical approaches than the Kelvin equation, since it treats adsorption as a microscopic process. The original equation (like the Langmuir isotherm before it) was derived from the kinetics of adsorption and desorption, but Hill<sup>3</sup> later reformulated the BET equation in terms of a statistical mechanical lattice model of adsorption. To obtain the BET result it is necessary to subject the combinatorial term to certain restrictions<sup>4</sup> and to assume that, apart from the first adsorbed layer, all adsorbed molecules behave in the same way.

Classical methods for treating micropores have been more empirical than either the Kelvin or BET equations. Dubinin and Radushkevich (DR)<sup>5</sup> used the

concept of an adsorption potential (first proposed by Polanyi) to relate the fractional filling of a Gaussian distribution of micropores to the free energy change of the gas on adsorption. The logarithm of the amount adsorbed plotted against  $[\log(P^0/P)]^2$  should give a straight line, which when extrapolated to saturation pressure gives the micropore capacity. However, linearity is not observed in many cases,<sup>1</sup> and even when it is, the calculated micropore capacity is often different for probe molecules of different sizes. The empirical  $\alpha_s$  method,<sup>1</sup> due to Sing, provides an alternative and widely used method and is based on a comparison between experimental isotherms for the porous material and a chemically similar nonporous solid; it fares much better in giving the micropore capacity.

In the full statistical mechanical treatment considered here, one writes a Hamiltonian which is a function of the positions and momenta of all the atoms and molecules in the fluid-pore system. In the Monte Carlo technique of computer simulation, chains of actual system configurations (sets of molecular positions and orientations) are generated on the computer, the frequency of generation of each configuration being proportional to its Boltzmann weighting; equilibrium properties are obtained by taking average values over the run of the simulation. In molecular dynamics simulation the Newtonian equations of motion for the system are solved numerically, so that the positions, orientations, and velocities of each molecule are followed in time. In addition to equilibrium properties, diffusion coefficients and other transport properties can be found. These molecular simulation methods provide an exact (within statistical error) solution for a precisely defined model of the fluid-pore system.<sup>4</sup> Of the approximate statistical mechanical theories for adsorption, the most useful at present is the nonlocal density functional theory (NLDFT). These more rigorous simulation and theoretical methods are much more powerful than the older classical approaches described above; for example, they yield the full adsorption isotherm, isosteric heat of adsorption, phase diagram, etc. for the entire range of pressure, temperature, and composition. Various uses of the statistical mechanical treatment can be envisaged, for example: (a) the prediction of adsorption properties for models of real systems, and subsequent comparison with experiment where possible; (b) the prediction of optimal adsorbent characteristics for particular applications (e.g., methane storage, separations); (c) the analysis of experimental data to determine pore structure, e.g., pore size distributions. The present account focuses on the use of these methods for the study of fluid behavior in well-characterized meso- and microporous materials (uses a and b). We describe some recent simulation and NLDFT studies of the adsorption of simple fluids in various model materials, drawn from our own work.

### Intermolecular Potential Functions

The validity of the model calculation depends on the accuracy of the fluid-fluid and solid-fluid potential functions which are the input to the simulation. For the fluid-fluid interaction it is usual to use expressions that have been developed for the corresponding

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bulk fluid,<sup>6,7</sup> although as discussed below some care is needed in such an approach. The calculations are sensitive to the description of the solid–fluid potential. It is common to assume that this potential is pairwise additive, so that the potential between a fluid molecule  $i$  and the solid material is  $\sum_j u_{sf}(ij)$ , where the sum is over all solid atoms,  $j$ . This implies that the location of the solid atoms is known from experimental data (e.g., X-ray diffraction) or is defined in the model. At high temperatures the potential energy will be a smaller proportion of the total energy (potential plus kinetic) than at lower temperature, and it may be possible to neglect some of the details of the potential function without compromising the results. In such cases a treatment in which the solid is represented as a continuum will often suffice. An example of such a situation is the interaction of a spherical (e.g., argon or xenon) or quasi-spherical (e.g., methane) fluid molecule with a planar graphite surface. The sum of  $u_{sf}(ij)$  over lattice species  $j$  is replaced by an integral over a volume multiplied by the mean density of the adsorbent.<sup>8</sup> For example, for a slit-shaped pore of width  $H$ , often used to model carbon adsorbents, the potential is given in this approximation by

$$u_{\text{pore}} = u^{(1)}(z) + u^{(1)}(H - z) \quad (2)$$

where  $u^{(1)}$  is obtained by integrating a Lennard-Jones (12,6) pair potential over individual graphite atoms. Similarly, at this level of approximation, a zeolite cavity can be represented as a spherical shell, and pores in adsorbents such as AlPO<sub>4</sub>-5 or VPI5 by cylinder models. For methane adsorbed on a graphite surface, this continuum solid approximation has been shown to give good results for temperatures down to 80 K or less;<sup>9</sup> in this case the diameter of the methane molecule (3.81 Å) is large compared to the C–C spacing (1.42 Å) in the graphite plane; as a result, as the methane molecule moves parallel to the surface at constant  $z$ , the corrugations in the surface have little effect on the solid–fluid interaction.

Many adsorption studies are carried out at low temperatures (especially at 77 K, the normal boiling point of liquid nitrogen), where the continuum solid assumption becomes more questionable. A similar problem is encountered when adsorption of larger chain or nonspherical molecules is considered. In such cases a full-scale summation may be preferable, and the resulting potential will generally vary in three dimensions. For a fluid molecule close to a graphite surface, the C-hexagon centers form strong adsorption sites, but the corrugation attenuates rapidly as the molecule moves away from the surface. More complex potential surfaces are found from summation for molecules inside zeolite pores (see below), on ionic surfaces, or on other heterogeneous surfaces,<sup>10</sup> where several sites of different strength may exist.

Up to this point a two-body interaction between the fluid molecule and a single lattice species has been implicitly assumed. Often this interaction can be

satisfactorily represented by a Lennard-Jones function, provided that dispersion plus repulsion are the main contributions to the pair interaction. At a deeper level, however, several other aspects of the interaction may need to be considered.

In the first place, it is necessary to recognize that the inverse 6th power attraction term in the Lennard-Jones potential cannot be identified with the leading (dipole–dipole) term in the dispersion interaction. This is because both higher order two-body and three-body terms are approximated in the parametrization of the potential. These neglected terms not only represent a substantial part of the interaction (~15%) but also have different distance dependence from the inverse 6th power term, so that a parametrization based on isolated species, bulk properties, or plane surfaces cannot be guaranteed to transfer to the interior of a pore space such as a zeolite cavity. A large part of the interaction potential in physical adsorption usually comes from dispersion, which in turn depends on polarizability, and a second implicit assumption is that polarizability is isotropic. Clearly this assumption will not be valid for polyatomic adsorbate molecules, but the problem can be minimized in this case by resolving molecular polarizabilities onto isotropic atomic sites. The same problem arises in modeling carbon adsorbents, since the polarizability of graphite is certainly anisotropic. Some implications of this have been discussed elsewhere.<sup>4,11</sup>

Third, it is necessary to take account of the effects of charges on the adsorbent species. Charge effects are prominent in zeolites, where the importance of electrostatic and induced interactions has long been recognized. Quantum mechanical calculations can help in determining the magnitude of the partial charge which should be assigned to lattice species.<sup>12</sup> Another consequence of the increased or reduced electron density around a charged adsorbent species is the modification of polarizability and thus of the dispersion part of the interaction.

Electrostatic, induced, and dispersion energy terms can be handled successfully within the framework of quantum mechanical perturbation theory.<sup>6,11</sup> However, this is not the case for repulsion. Quantum mechanics suggests an exponential rather than an inverse 12th power decay for repulsive potentials, but accurate calculations for lattice-embedded species are problematic because the uncertainties associated with terminating clusters must be added to the usual difficulties of selecting basis sets. Here again, anisotropy of the interaction could be a significant factor,<sup>13</sup> and much remains to be done in this area.

Thus, although there is a large body of knowledge which can contribute to the determination of the general shape of a potential surface, some degree of parametrization using experimental data is nearly always necessary. Data for the zero coverage heat of adsorption and Henry law constants are particularly useful in refining the solid–fluid potential, since no fluid–fluid forces are present; Henry constants are especially sensitive to the more subtle details of the potential. In practice it turns out that, despite the many factors which contribute to an accurate potential, considerable success can frequently be obtained

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with relatively simple models and pairwise summation.

The fluid–fluid potential energy also needs special consideration in accurate modeling of adsorption. The commonly used Lennard-Jones parametrizations are often optimized using properties of the homogeneous, isotropic fluid, and three-body contributions are approximated implicitly within the parametrization. Adsorbed fluids, on the other hand, are nonuniform and are in a heterogeneous environment, so there is a measure of uncertainty about the transferability of fluid–fluid potentials from bulk properties. Since three-body effects are usually important only at the 5–10% level, this uncertainty is not expected to be very serious. A particular problem which has received much attention is the so-called “mediated” three-body interaction, involving two adsorbate molecules and a substrate atom.<sup>11</sup> Some care must be exercised if it is intended to include such interactions in simulation studies, since *effective* fluid–fluid potentials already include some compensation for three-body interactions, and mediation through the adsorbent should only be implemented with *true* two-body potentials. If these mediated three-body interactions are incorporated, then the appropriate three-body interactions for three fluid molecules should also be included for consistency; this greatly lengthens simulation times.

## Methods

**1. Grand Canonical Monte Carlo (GCMC).** The grand canonical Monte Carlo method is particularly convenient for studying adsorption, because the chemical potential ( $\mu$ ), volume ( $V$ ), and temperature are fixed in the simulation. Since the chemical potential and temperature of the bulk and adsorbed phases are equal at equilibrium, the knowledge of  $\mu$  enables the bulk gas pressure to be calculated from an equation of state. The ensemble average of the number of molecules in the system (equivalent to the amount adsorbed) is taken directly from the simulation. By running the simulation at various values of  $\mu$ , a simulated adsorption isotherm is readily obtained. In the usual way of carrying out such simulations, three types of trial are attempted:<sup>14</sup> attempts to move a particle within the system, attempts to create a new particle, and attempts to delete an existing particle. The acceptance criteria for the trials are such that configurations are generated in the grand ensemble with probabilities proportional to their Boltzmann weighting.

In addition to the adsorption isotherm and density profiles, it is possible to also calculate the isosteric heat of adsorption (the differential enthalpy of adsorption) in these simulations; the latter can be determined most directly from ensemble averages of the configurational energy of the fluid in the pore and in the bulk.<sup>15</sup>

**2. Molecular Dynamics (MD).** Conceptually, the MD technique is very straightforward. The forces and torques acting on each adsorbed molecule are calculated, and the system evolves in time dynamically. A number of algorithms exist for implementing MD;<sup>14</sup> each involves recalculating forces and velocities after

small time intervals (of the order of  $10^{-14}$  s). Molecular dynamics is most conveniently carried out in the microcanonical (constant  $N$ ,  $V$ ,  $E$ ) ensemble. Total energy (i.e., kinetic plus potential) is conserved. The temperature is calculated from the ensemble average of the kinetic energy via the equipartition principle. It is often convenient to rescale the velocities of the particles prior to collecting averages, so that the simulation can be run at a desired temperature. Alternatively, methods are available<sup>14</sup> for running the simulation at constant  $N$ ,  $V$ ,  $T$ . By using the potential distribution theorem,<sup>16</sup> it is possible to obtain values for the chemical potential, and hence by running simulations at various values of  $N$  an adsorption isotherm can be obtained. This tends to be less convenient than GCMC, however. An important advantage of MD is that diffusion rates in the pores can be calculated by determining molecular mean square displacements or velocity autocorrelation functions.

**3. Nonlocal Density Functional Theory (NLDFT).** An alternative to full-scale simulation that is much less demanding computationally is to introduce approximations that yield more tractable equations. The nonlocal density functional theories<sup>17</sup> are particularly useful for adsorption problems, and we briefly describe this approach here. Such theories are primarily useful for simple fluids and pore geometries (e.g., slits, cylinders); they are much more difficult to apply to more complex systems, e.g., zeolites.

We consider a fluid confined in a pore and adopt the grand canonical ensemble (constant  $\mu$ ,  $V$ ,  $T$ ). The appropriate free energy quantity for this ensemble is the grand free energy,  $\Omega$ ; for a bulk, homogeneous fluid  $\Omega = -PV$ , but for a fluid in a pore there will be an additional surface contribution. This free energy can be regarded as a functional of the density profile in the pore,  $\rho(\mathbf{r})$ . If the functional  $\Omega[\rho(\mathbf{r})]$  can be minimized with respect to variations in  $\rho(\mathbf{r})$ , then the equilibrium density profile can be determined. The surface excess number of molecules adsorbed, which corresponds to the experimentally measured property, is then given by  $\int[\rho(\mathbf{r}) - \rho_B] d\mathbf{r}$ , where the integral extends over the internal volume of the pore, and  $\rho_B$  is the density which the fluid would have in a bulk phase at  $(\mu, T)$ . Repetition of this procedure for various values of  $\mu$  yields an adsorption isotherm. The accuracy of this method rests on the expression used for the grand free energy functional. The usual approach is to split the fluid–fluid potential into repulsive and attractive parts and to treat the repulsive part as a hard sphere interaction, and the longer ranged attractive interaction in a mean field fashion, in the spirit of van der Waals theories. The problem is then reduced to one of finding an expression for the non-ideal gas part of the Helmholtz free energy density,  $a_{HS}(\mathbf{r})$ , of an inhomogeneous hard sphere fluid;  $a_{HS}$  is nonlocal, i.e., it depends on the density at positions near  $\mathbf{r}$ , and not just on that at  $\mathbf{r}$  itself. This excess free energy density at  $\mathbf{r}$  is equated to that of a *uniform* hard sphere fluid at some density which is an average of the true density over a volume around  $\mathbf{r}$ , with the average weighted so as to allow for correlations. A number of different methods exist to implement this;<sup>17</sup>

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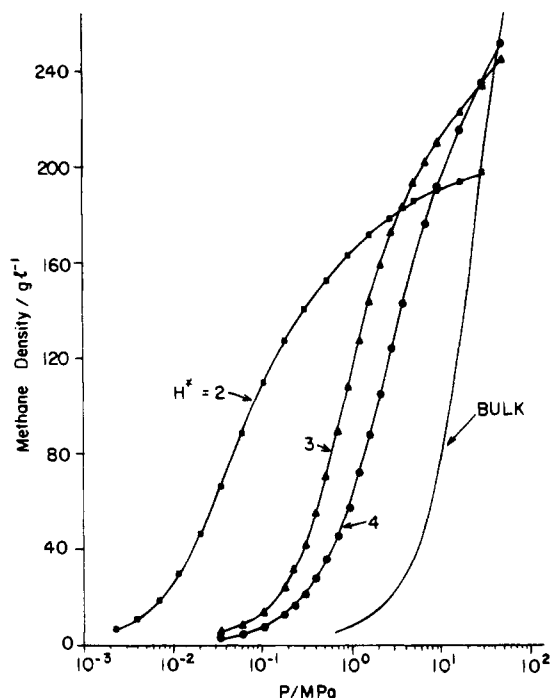
those due to Tarazona<sup>18</sup> and to Kierlik and Rosinberg<sup>19</sup> have proved particularly useful.

Applications of NLDFT have included inversion of experimental adsorption isotherm data to obtain pore size distributions,<sup>20</sup> tests of the classical equations,<sup>20,21</sup> and studies of mixture adsorption.<sup>22</sup> In Figure 1 are shown results for the pore-filling pressure for a model of nitrogen in slit graphite pores from NLDFT, simulations, and the Kelvin equation. In each case the theory is used to calculate the pressure  $P$  at which the pore fills with a dense, liquid-like phase of the adsorbate. Depending on the pore size, this may be a sharp capillary condensation transition or a steep rise in the isotherm. The NLDFT is found to be in excellent agreement with the exact simulation results for this model system. The Kelvin and modified Kelvin equations give good results for pore widths of 80 Å and above, but they give filling pressures that are too high for small pores.

## Results

In this section we give several examples of the use of molecular simulation to study adsorption in well-characterized materials.

**1. Supercritical Methane Adsorption in Porous Carbons.** Activated carbons of super-high surface area can be used for adsorptive storage of natural gas. Potential applications are natural gas transportation and natural gas driven vehicles. NLDFT calculations and molecular simulation have been used to determine the optimal pore size of the carbon;<sup>23</sup> a favorable model for such calculations is one where the pores are slits bounded by parallel single layers of graphite. Such a model porous carbon has the highest fraction of micropore volume to total volume. Both methane–methane and methane–graphite interactions were modeled using Lennard-Jones potentials, with the graphite layer a smooth continuum of carbon atoms, since it was found that the detailed structure has minimal influence at supercritical temperatures. GCMC adsorption isotherms for methane in three model pore sizes at 274 K are shown in Figure 2, where  $H$  refers to the distance between centers of carbon atoms in facing graphitic layers. Adsorption occurs in the smallest pore at very low pressure because adsorbed methane molecules are in the potential minima of both walls; this effect diminishes for wider pores. The pore which is optimal for adsorptive storage of methane can be seen to depend on the operating conditions; for a storage pressure of 34 atm (3.4 MPa) and a desorption pressure of 1 atm (proposed operating conditions), a pore of width  $H/\sigma_{\text{ff}} = 3$  ( $H = 11.4$  Å) is optimal; too much methane is retained at 1 atm in the  $H/\sigma_{\text{ff}} = 2$  pore, and too little methane is adsorbed at 34 atm for  $H/\sigma_{\text{ff}} = 4$ . A pore of width  $H/\sigma_{\text{ff}} = 3$  is just able to



**Figure 2.** Adsorption isotherms for methane in carbon slit pores of varying widths at 274 K. Here  $H^* = H/\sigma_{\text{ff}}$ , where  $H$  is the distance between the centers of C atoms in the first layer on opposite walls and  $\sigma_{\text{ff}}$  is the fluid–fluid LJ parameter. Reprinted with permission from ref 23c. Copyright 1993 American Chemical Society.

hold two layers of adsorbed methane. Recent experimental studies on a carbon with this pore width show superior adsorption to other existing carbons.<sup>24</sup>

**2. Adsorption and Diffusion of Ar in VPI-5.** VPI-5 is an aluminophosphate-based zeolite with a pore opening of 18 tetrahedral atoms (P or Al). Experimental isotherms for Ar at 77 K<sup>25</sup> show two steeply rising portions separated by a plateau, which GCMC simulations were successfully able to reproduce.<sup>26</sup> Following Kiselev et al.,<sup>27</sup> only interactions between argon and framework oxygen atoms were modeled explicitly. The Lennard–Jones Ar–O parameters were chosen by fitting simulated isosteric heats at low coverage for Ar in  $\text{AlPO}_4\text{-5}$  to experimental data. Thus the parametrization implicitly includes the interaction between the tetrahedral atoms and the argons. More recent experimental calorimetric measurements for Ar on VPI-5<sup>28</sup> are also in excellent agreement with predictions from simulation. The GCMC results are shown in Figure 3 together with self-diffusion coefficients ( $D$ ) taken from MD simulations. The results, when taken with density profiles from the simulations,<sup>26</sup> show that the beginning of the plateau region is associated with completion of the first adsorbed layer. Diffusion in the first adsorbed layer increases initially with adsorbate loading; the mechanism of diffusion is clearly quite different from bulk diffusion, where an increased Ar density would cause an increased collision frequency and a decrease

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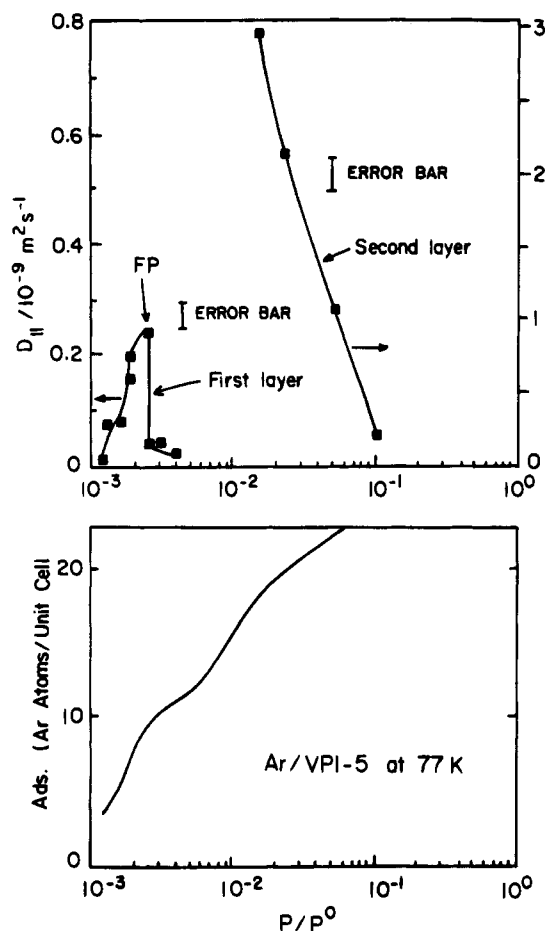
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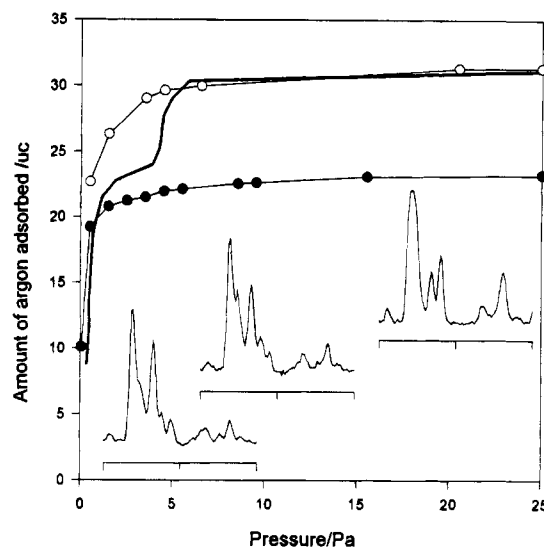
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**Figure 3.** Amount adsorbed (from GCMC) and self-diffusion coefficient (from MD) for Ar in VPI-5 at 77 K. Reprinted with permission from ref 26. Copyright 1993 American Chemical Society.

in  $D$ . At low temperatures collisions facilitate the escape of molecules trapped in strong local potential minima, and consequently self-diffusion is initially facilitated by increased sorbate loading. The decrease in self-diffusion in the second layer with loading is due to the type of bulk diffusion mechanism discussed above.

**3. Argon Adsorption in Silicalite-1.** Silicalite-1 is the all-silica form of the industrially important zeolite ZSM-5. The structure contains regular intersecting straight and sinusoidal channels, with pore diameters of about 5–6 Å. Experimental isotherms at 77 K for Ar, Kr, and N<sub>2</sub> all exhibit phase transitions (N<sub>2</sub> has two transitions), while those for Xe and CH<sub>4</sub> do not. When Kiselev's original Lennard-Jones potentials for the Ar–O interaction in silicalite<sup>27</sup> were used to calculate zero coverage isosteric heats and Henry's law constants, poor agreement was found with experimental measurements.<sup>29</sup> In light of this finding, a new model of the silicalite–fluid interaction potential was developed.<sup>30</sup> Lattice charges of –1 and +2 were assigned to O and to Si, respectively, in keeping with quantum mechanical calculations.<sup>12</sup> Unlike the Kiselev approach, both Si and O were modeled explicitly. Polarizabilities and effective electron numbers were obtained which are consistent with this assign-



**Figure 4.** Adsorption of argon on silicalite at 77 K. Experimental,<sup>31</sup> —; simulated using Kiselev potential, ○; simulated using new potential,<sup>30</sup> ●. The inset neutron spectra,<sup>32</sup> taken with <sup>40</sup>Ar as the adsorbate, are, from left to right, empty silicalite, Ar loading at the top of the substep (24 molecules per unit cell), and Ar loading for the final plateau (31 molecules per unit cell).

ment, and two-body and three-body contributions up to terms in the quadrupole polarizability were included. The new potential gave results in close agreement with the experimental zero coverage data<sup>29</sup> for argon and, with the aid of combining rules, for other fluids including Kr, Xe, and N<sub>2</sub>.

Simulated adsorption isotherms are shown in Figure 4 for both the Kiselev and new potentials, together with experimental measurements.<sup>31</sup> Neither potential correctly predicts the transition (the new potential did correctly predict a lower pressure transition for N<sub>2</sub>-silicalite); however, the isotherm calculated from the new potential saturates at values close to the observed substep, while the Kiselev model is able to accommodate 30 molecules, which is close to the final loading in the experimental isotherm. It was concluded that the observed transitions result from a distortion of the silicalite lattice under the stress of the adsorbate. This conclusion is supported by an examination of heat of adsorption curves, aided by the separate fluid–solid and fluid–fluid components obtainable from simulation,<sup>30</sup> and also by neutron diffraction experiments. Parts of the relevant spectra are shown in Figure 4. These were obtained<sup>32</sup> using <sup>40</sup>Ar, which is nearly transparent to neutrons; any changes in the spectra are therefore attributable to changes in adsorbent structure. Structural changes are clearly evident in the third spectrum compared to the other two. Determination of the nature of the structural changes awaits further investigation. These adsorbent structural transitions have not been observed for methane or Xe adsorption, and it seems probable that their occurrence is determined by the ability of the adsorbent to exactly accommodate certain molecules, coupled with the partly covalent nature of the silicalite structure.

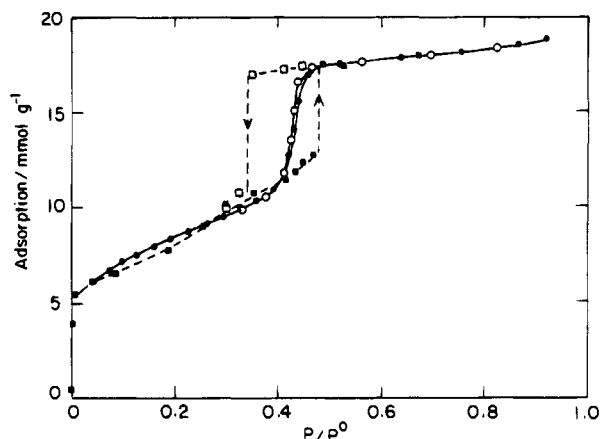
**4. Nitrogen Adsorption in MCM-41.** MCM-41 is a member of a newly-synthesized<sup>33</sup> family of silicate/aluminosilicate mesoporous molecular sieves, with

(29) Reichert, H. Private communication, 1991.

(30) (a) Pellenq, R. J.-M.; Nicholson, D. In *Fundamentals of Adsorption, Proceedings of the IVth International Conference*; Suzuki, M., Ed.; Kodansha: Kyoto, 1993; p 515; (b) *J. Phys. Chem.* **1994**, *98*, 13339; (c) *Langmuir*, in press.

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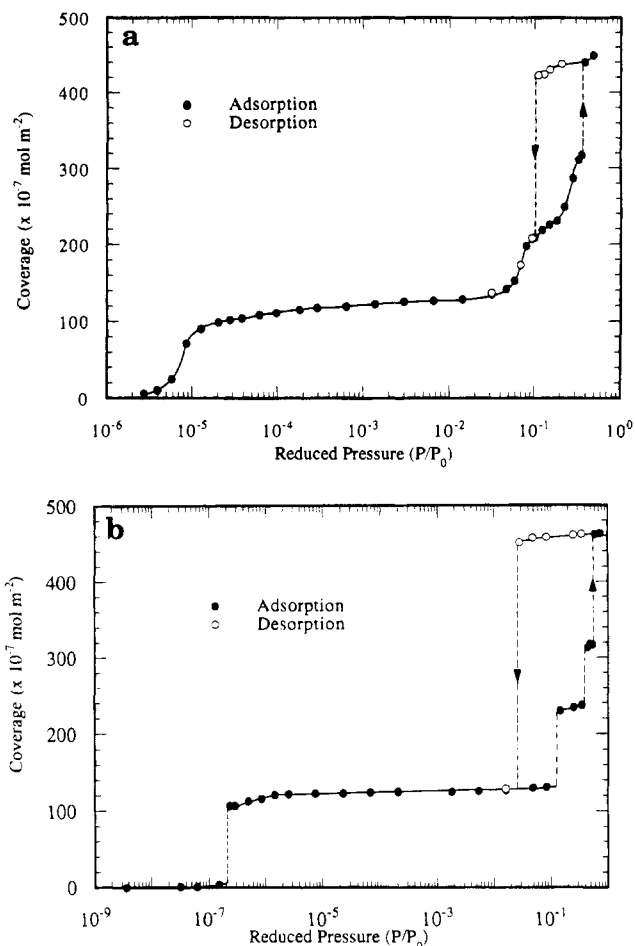
(32) Tosi-Pellenq, N. M.; Coulomb, J.-P. Private communication, 1993.



**Figure 5.** Simulated (---■--- for adsorption, ---□--- for desorption) and experimental (—●— for adsorption, —○— for desorption) adsorption isotherms for nitrogen in MCM-41 at 77 K. The pore diameter is 4.10 nm. Based on data from ref 35.

uniform pores of roughly cylindrical cross section, and with diameters that can be controlled in the range 1.5–10 nm. An experimental nitrogen adsorption isotherm at 77 K has been reported<sup>34</sup> for an MCM-41 material whose pore diameter has been estimated to be<sup>35</sup> 4.10 nm, and it is shown in Figure 5. It shows a narrow hysteresis loop, indicating capillary condensation. GCMC simulations have been carried out for this system,<sup>35</sup> using simple Lennard-Jones potentials for the fluid–fluid and solid–fluid interactions and a structureless wall approximation (cf. eq 3). The simulated isotherm is in good agreement with experiment at both the lower and higher pressures and predicts the capillary condensation transition at about the right pressure. The predicted hysteresis loop is more pronounced than the experimental one. However, such hysteresis loops are not true equilibrium effects, and differences between the model and experiment are not thought to be of any fundamental significance. The results suggest that the pores in the real material are not monodisperse and cover a range of pore sizes.

**5. Argon and Nitrogen in Buckytubes.** Nanoscale carbon tubules, consisting of one or more graphite sheets rolled up to form a tube, with internal diameters ranging from 1 to 5 nm, have recently been synthesized by vaporizing carbon under appropriate conditions.<sup>36</sup> These “buckytubes” have a regular tubular structure, monodisperse pore size, and large surface area, making them attractive as potential adsorbents and catalysts. At present, it is still difficult to synthesize large quantities of these materials in the absence of other forms of carbon, and there seem to have been no experimental adsorption studies so far. The structure of the tubules is known from scanning and transmission electron microscopy, and the solid–fluid potentials are known with some confidence for simple fluids, from studies of planar graphite surfaces. Simulations have been carried out for argon and nitrogen in such tubules for a range of subcritical



**Figure 6.** Simulated adsorption isotherms for argon in a double buckytube of 4.78 nm internal diameter at (a) 77 K and (b) 55 K.

temperatures,<sup>35</sup> using simple Lennard-Jones potentials and a structureless wall model that is the cylindrical analog of eq 3. The adsorption isotherm predicted for argon in a double buckytube (i.e., the wall has two graphite layers) of internal diameter 4.78 nm (one of the materials synthesized by Iijima<sup>36</sup>) is shown for two temperatures in Figure 6. At 77 K the adsorption isotherm has a step-like character, indicating the buildup of successive adsorbed layers on the walls, up to three layers, followed by capillary condensation; this temperature is clearly somewhat above the critical temperature for the layering transitions. Desorption exhibits the usual hysteresis behavior for monodisperse pores. At the lower temperature of 55 K the hysteresis loop becomes broader, and the layering occurs as sharp first-order transitions; the critical temperature for these transitions is  $58 \pm 2$  K. A two-dimensional freezing transition is observed in the first adsorbed layer at this temperature.

## Conclusions

Until recently the study of confined fluids has been an experimental science. Over the past 10 years there has been a rapid growth in interest and activity in modeling these phenomena, using the methods of statistical mechanical theory and molecular simulation. These methods are much more powerful than the old classical approaches and are now sufficiently advanced to be able to suggest new and optimal designs for materials and processes for particular

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applications, as well as providing new insight into the detailed behavior of the fluid. The main challenge in this area is to combine the modeling efforts with complementary experiments in a fruitful way. On the experimental side, a major need is to develop methods to synthesize porous materials that are highly regular in their pore geometry, that are thermally stable, and for which the pore size and geometry can be tailored to specific requirements. At present the small-pore zeolites largely satisfy these criteria, but the range of pore sizes is limited. Many of the other materials that are in common use (e.g., carbons, silicas, oxides) are amorphous and poorly characterized. Nevertheless, there have been encouraging advances in the synthesis of larger pore materials by sol-gel and electrolytic methods; MCM-41 and buckytubes are two examples. On the modeling side, most studies have been limited to simple fluids and pore geometries. There is a need now to extend the modeling effort to more complex

fluids (water, H-bonded fluids, chain molecules, etc.), to mixtures, and to more complex pore geometries. Molecular simulation should also prove of great value for investigating factors that are important in real materials, including nonrigid pore frameworks, chemically heterogeneous surfaces, pore networking, and the molecular structure and smoothness of the solid surface. Further advances in computing power should make it possible to investigate phenomena where chemisorption, as well as physisorption, are involved.

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