International Journal of Thermophysics, Vol. 15, No. 6, 1994

Molecular Simulation of Fluid Adsorption in Buckytubes and MCM-41[1]

M. W. Maddox[2,3] and K. E. Gubbins[2]

We report grand canonical Monte Carlo (GCMC) molecular-simulation studies of argon and nitrogen in models of two novel adsorbents, buckytubes and MCM-41. Buckytubes are monodisperse carbon tubes with internal diameters of 1–5 nm and a regular pore structure. MCM-41 is one member of a new family of highly uniform mesoporous aluminosilicates produced by Mobil. The pore size of MCM-41 can be accurately controlled within the range 1.5–1.0 nm. The adsorption of argon in a buckytube and the adsorption of nitrogen in two different MCM-41 pores are studied at 77 K. Both fluids are modeled as Lennard–Jones spheres, and an averaged fluid-wall potential, dependent only on the distance of the adsorbed molecule from the center of the tube or pore is used. Isotherms and isosteric heats are calculated. Layering transitions and a hysteresis loop are observed for the buckytube and good agreement is found between simulated and experimental isotherms for the MCM-41 systems.

KEY WORDS: adsorption; aluminosilicates; buckytubes; grand canonical Monte Carlo; isotherms; MCM-41; mesoporous.

1. INTRODUCTION

Microporous and mesoporous materials, including zeolites, aluminosilicates, activated carbons, and pillared clays, have a wide range of industrial applications including heterogeneous catalysis, purification of gas and water streams, and gas separation. The particular properties of any such material are closely related not only to its chemical composition but also to the size, shape, interconnectivity, and dispersity of its pores. The difficulty in assessing and controlling these physical properties has so far

---

[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

[2] School of Chemical Engineering, Cornell University, Ithaca, New York 14850, U.S.A.

[3] To whom correspondence should be addressed.

840 15 6-8

prevented the optimization of many useful processes. Two novel materials, buckytubes and MCM-41, may solve some of these problems. They are both monodisperse porous materials with accurately controllable pore sizes in the microporous and mesoporous ranges. The pore size can therefore be tailored to a particular application, and since all the pores are of the same size, the performance will not be diluted by nonoptimal pores.

Buckytubes are nanoscale carbon tubules, several different types of which have recently been reported by Iijima [1], Iijima and Ichihashi [2], and Bethune et al. [3]. These buckytubes have been synthesized by two methods: (i) vaporizing a carbon electrode in the presence of iron vapor, methane, and argon and (ii) covaporizing carbon and cobalt in a helium-filled arc generator. The structure of a buckytube is that of one or more graphite sheets, rolled up to form a tube. The direction of the rolling is such that each row of hexagons in the flat graphite sheet spirals helically around the rolled-up tube. A single buckytube is formed from one graphite sheet, a double buckytube from two graphite sheets, and so on. Multiply layered buckytubes, where the tubes are coaxial, and the spacing between graphite sheets is approximately the same as that in bulk graphite, have been reported with between 2 and 50 layers. The diameter of the cavity varies from 1 nm for a single buckytube to over 5 nm for multiply layered buckytubes.

MCM-41 is one member of a new family of silicate/aluminosilicate mesoporous materials [4, 5]. It exhibits an hexagonal arrangement of uniform mesopores whose diameter can be controlled in the range of 1.5 to over 10 nm. The class of materials is synthesized using a templating mechanism in which surfactant liquid crystal structures serve as organic templates.

Our main interest is the use of these materials as adsorbents for separating gas mixtures. Jiang et al. [6] recently showed that the selectivity of a gas mixture separation is extremely sensitive to the pore size of the adsorbent. By controlling the pore size, such separations can be greatly enhanced. While the synthesis and testing of many samples of adsorbents are a time-consuming and laborious undertaking, the same range of adsorbents can be studied cleanly and rapidly using computer simulation. In this way, we eventually hope to pinpoint the optimal pore size of both buckytubes and MCM-41 for a range of separations, in order to focus experimental research efforts. Materials such as buckytubes and MCM-41, which have regular structures that can be controlled synthetically, lend themselves particularly well to simulation, since the simplified models we use bear a close resemblance to the real systems they represent. In this paper we make a first attempt at modeling the adsorption of argon in buckytubes and of nitrogen in MCM-41. Our study of buckytubes is presently limited to predicting adsorption behavior which cannot yet be verified experimentally. However, since fluid adsorption in graphite slits is well understood, we can be fairly confident that our closely related buckytube model gives accurate results. In contrast, the precise structure of an MCM-41 pore is less certain, but the availability of some experimental isotherms allows us to postulate a model, fit one of the fluid-wall parameters, and produce isotherms in good general agreement with experiment.

2. THEORY

Grand canonical Monte Carlo (GCMC) molecular simulation is frequently used to model fluid adsorption, because the grand canonical ensemble fixes the chemical potential (related via the virial equation of state to the pressure of the gas surrounding the adsorbent), the volume, and the temperature of the system. Since these parameters are also fixed during experimental adsorption measurements, both systems yield the same results and can be easily compared. The GCMC method used here is that described by Woods and Rowlinson [7].

2.1. Intermolecular Potentials and Pore Models

For both argon and nitrogen the spherical Lennard–Jones model was used for the fluid–fluid potential, with the potential cutoff at a radius $r_c = 5.0\sigma$. The parameters used were taken from fits to second-virial-coefficient data and were as follows: argon, $\sigma = 0.341$ nm, $\varepsilon/k = 119.8$ K; and nitrogen, $\sigma = 0.375$ nm, $\varepsilon/k = 95.2$ K. For the fluid-wall potentials, a one-dimensional potential, $U_{\mathrm{fw}}(r)$, depending only on the distance r of the fluid molecule from the center of the pore, was obtained by averaging over the lateral wall structure. This potential was the analog of the 10–4–3 potential for planar graphite surfaces [8]. For argon in buckytubes, the fluid-wall parameters were derived from Lorentz–Berthelot mixing rules and were $\sigma = 0.3405$ nm, $\varepsilon/k = 57.92$ K. As usual when aluminosilicates are modeled, only the oxygen atoms of the MCM-41 pore were considered in the fluid-wall potential. An oxygen atom radius, $r = 0.1575$ nm, calculated by June et al. [9] for silicalite, was used. Lorentz–Berthelot mixing rules were again used to calculate the first fluid-wall parameter for spherical nitrogen in MCM-41: $\sigma = 0.328$ nm. In the absence of a reliable ε/k value for the Lennard–Jones interaction of spherical nitrogen which an MCM-41 oxygen atom, the parameter was estimated to be $\varepsilon/k = 250.0$ K by fitting simulated isotherms to experimental results.

3. RESULTS AND DISCUSSION

3.1. Argon Adsorption in a Buckytube

We have simulated the adsorption of spherical Lennard–Jones argon in a model double buckytube with an internal diameter of 4.78 nm, at 77 K. The adsorption isotherm is shown in Fig. 1 and the isosteric heat of adsorption, calculated in the usual way for GCMC simulations [10], is shown in Fig. 2. The coverages shown in Fig. 1 can be considered accurate to within plus or minus 1%. In our previous work [1], we presented a similar isotherm for argon adsorption in the same buckytube, showing chemical potential along the X axis. The longer fluid–fluid cutoff used here has enabled us to simulate a more realistic system and replace the chemical potential with the reduced pressure of the bulk fluid. In addition, the amount of argon adsorbed is shown in terms of its surface coverage. Both these changes allow easier comparison with future experimental results. The isotherm shows layering, capillary condensation (shown as a dashed line in Fig. 1), and a hysteresis loop; 77 K appears to be above the critical temperature for the layer formations seen here, which are all continuous. The layering critical temperature is the temperature below which the transition from one absorbed layer to two adsorbed layers (and two to three, etc.) is first order, and the isotherm is discontinuous. Three layers are observed before the onset of capillary condensation at a reduced pressure of around 0.38. On desorption, the capillary condensed state remains stable to a reduced pressure of around 0.09. The desorbed part of the isotherm passes directly from the condensed phase to the two-layered state, bypassing the third layer seen during adsorption. Such behavior has also been reported by Peterson et al. [12] for an idealized cylindrical pore. With reference to the IUPAC classification, which classifies adsorption isotherms according to their general shape [3], this isotherm is type IV, although the layering is also indicative of type VI behavior. Figure 2 shows the isosteric heat of adsorption as a function of coverage for the argon/buckytube system. At zero coverage the isosteric heat is simply a measure of the fluid-wall forces, but as the coverage increases, fluid–fluid interactions also contribute. The isosteric heat rises until the first layer of adsorbed molecules is complete. The next molecule to be added to the system is then forced to reside in a second layer, farther from the wall. The isosteric heat drops rapidly as a result. A similar pattern should be seen for the growth of the second and third layers, but the accuracy of the isosteric heat calculation is not great enough for these features to be obvious. The dashed line shows the capillary condensation transition. Balbuena and Gubbins [4] have reported similar isosteric heat curves for simple fluids in model slit pores.

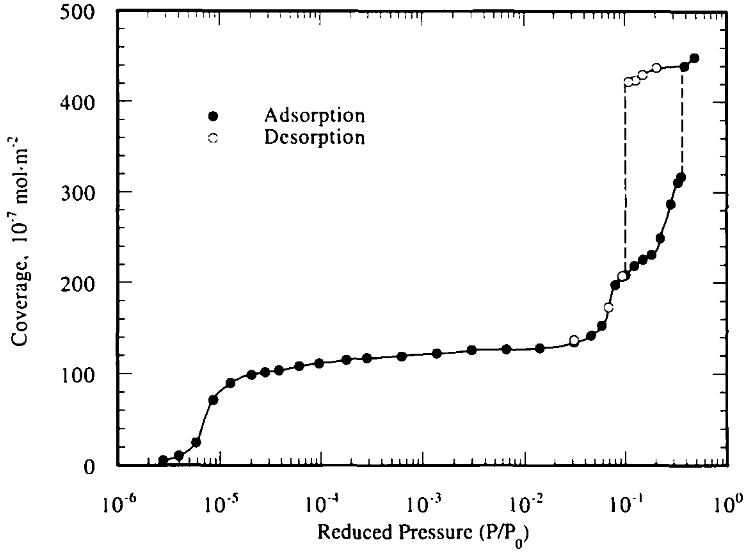

Fig. 1. Adsorption isotherm for argon in a 4.78-nm double buckytube at 77 K.

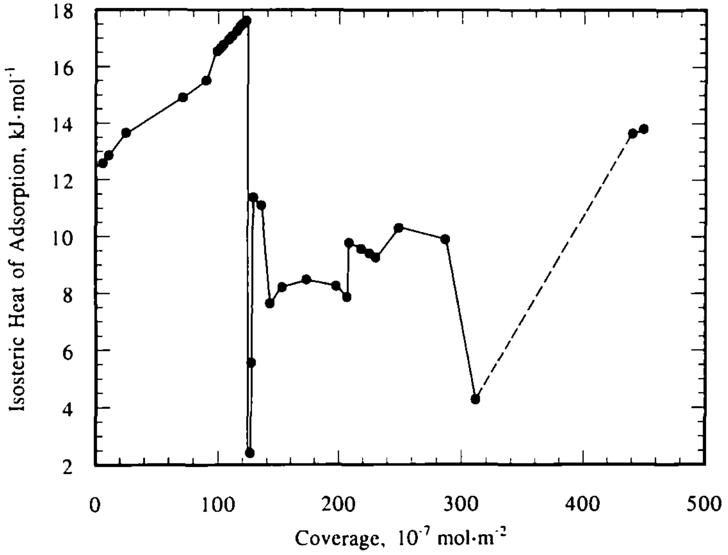

Fig. 2. Isosteric heats for argon in a 4.78-nm double buckytube at 77 K.

3.2. Nitrogen Adsorption in MCM-41

Two MCM-41 pores have been modeled, corresponding to those reported experimentally by Branton et al. [15] and Franke et al. [16]. Branton et al. show an adsorption isotherm for nitrogen at 77 K in an MCM-41 pore with an estimated diameter of 3.32 nm. Franke et al. show an adsorption isotherm for nitrogen at 77 K in an MCM-41 pore with an estimated diameter of 2.92 nm. These diameters correspond to simulated pore diameters of 3.60 and 3.20 nm, respectively, where the simulated diameter extends to the center of the first layer of wall atoms. Initial studies suggested that MCM-41 pores with these diameters would be too small to accommodate the amount of nitrogen adsorbed after condensation, as given by the experimental isotherms. Since the Kelvin and BET methods used to calculate the experimental pore diameters are known to underestimate the real pore size, larger model pores were employed. The model diameters were chosen so that the correct amount of nitrogen would be adsorbed after condensation. The values used were 4.10 nm for comparison with Branton et al. and 3.73 nm for comparison with Franke et al. A value of $\varepsilon/k = 250.0$ K was used in the Lennard–Jones interaction of spherical nitrogen with an MCM-41 oxygen atom. This was the only unknown parameter, and it was chosen to give the best fit between the experimental and the simulated isotherms. For both of the MCM-41 pore systems, our simulations show good agreement with the experimental isotherms in the region of capillary condensation (Figs. 3 and 4). The simulated coverages shown in Figs. 3 and 4 can be considered accurate to within $\pm 1\,\%$. The simulated isotherms show pronounced hysteresis loops, in contrast to the experimental isotherms, which exhibit no such behavior. A truly monodisperse system of pores, as modeled in our simulation, would normally be expected to produce a hysteresis loop. This leads us to believe that the samples of MCM-41 used in the experimental studies [15, 16] are not completely monodisperse. Away from the region of capillary condensation, the simulated isotherm exactly reproduces the experimental isotherm in Fig. 3 but shows some deviation at low pressure in Fig. 4. The linear shape of the experimental isotherm in this region is not at all representative of adsorption in a monodisperse array of mesopores. An isotherm of this shape suggests a range of pore sizes in the adsobent, including some in the microporous region (diameter, <2 nm). Figure 5 shows the isosteric heat of adsorption for the 4.10-nm-diameter pore. The isosteric heat curve for the 3.73-nm pore is qualitatively the same as that of the 4.10-nm pore. Figure 5 shows the same features seen in Fig. 2, including a large peak on completion of the first layer of adsorbed molecules and a large increase in isosteric heat at capillary condensation (shown by the dashed line).

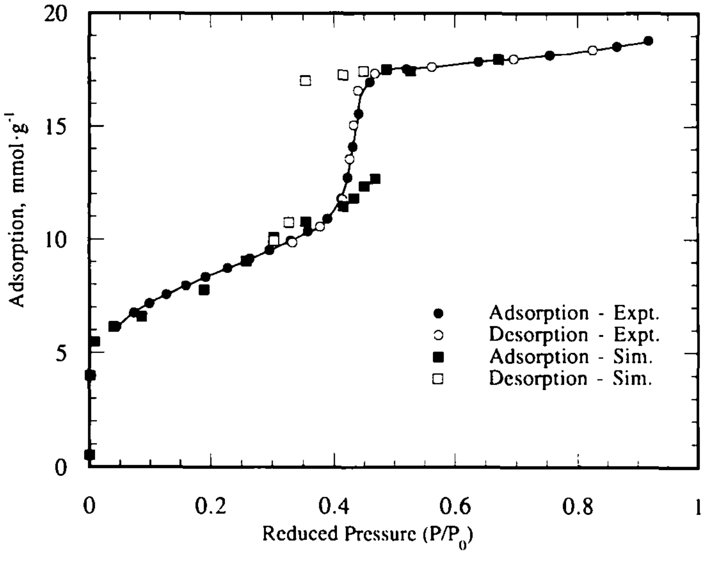

Fig. 3. Simulated and experimental isotherms for nitrogen in a 4.10-nm pore of MCM-41 at 77 K.

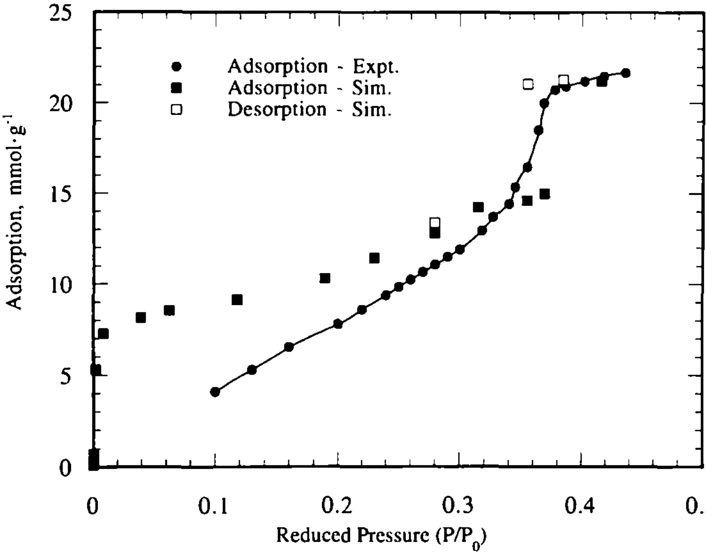

Fig. 4. Simulated and experimental isotherms for nitrogen in a 3.73-nm pore of MCM-41 at 77 K.

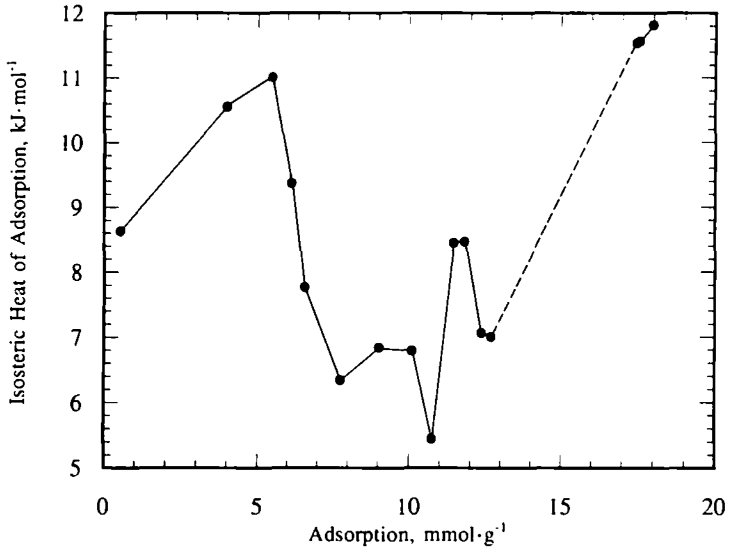

Fig. 5. Isosteric heats for nitrogen in a 4.10-nm pore of MCM-41 at 77 K.

4. CONCLUSIONS

The mesoporous buckytube shows characteristics of both type IV and type VI isotherms for argon adsorption, with layering and capillary condensation transitions, accompanied by hysteresis. The critical temperature for the layering transitions is below 77 K, while the critical temperature for capillary condensation is somewhat higher. Models of two MCM-41 pores of slightly different sizes show good general agreement with experiment for the adsorption of nitrogen at 77 K. The real pore diameters are thought to be greater than those suggested experimentally when the Kelvin or BET methods are used, and the samples produced so far show evidence of some polydispersity. Despite the lack of experimental results for comparison, the buckytube model shows all the features expected of the material, and the MCM-41 model does show fairly good agreement with experiment. Our future work will use these models to study the adsorption of simple fluid mixtures in order to assess their potential for gas separations.

ACKNOWLEDGMENTS

We thank the Department of Energy for a grant (DE-FG02-88ER13974) in support of this work. Supercomputer time was provided under a NSF Metacenter grant (MCA93S011P). Finally, we thank the Pittsburgh Supercomputer Center for the use of the C90 supercomputer.

REFERENCES

1. S. Iijima, *Nature* **354**:56 (1991).
2. S. Iijima and T. Ichihashi, *Nature* **363**:603 (1993).
3. D. S. Bethune, C. H. Kiang, M. S. deVries, G. Gorman, R. Savoy, J. Vasquez, and R. Beyers, *Nature* **363**:605 (1993).
4. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E.W. Sheppard, S. B. McCullen, J. B. Higgins, and J. L. Schlenker, *J. Am. Chem. Soc.* **114**:10834 (1992).
5. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature* **359**:710 (1992).
6. S. Jiang, K. E. Gubbins, and P. Balbuena, *J. Phys. Chem.* **98**:2403 (1993).
7. G. B. Woods and J. S. Rowlinson, *J. Chem. Soc. Faraday Trans. II* **85**:756 (1989).
8. W. A. Steele, *The Interaction of Gases with Solid Surfaces* (Pergamon Press, Oxford, 1974), Chap. 2.
9. R. L. June, A. T. Bell, and D. Theodorou, *J. Phys. Chem.* **94**:1508 (1990).
10. G. B. Woods, A. Z. Panagiotopoulos, and J. S. Rowlinson, *Mol. Phys.* **63**:49 (1988).
11. M. W. Maddox, D. Ulberg, and K. E. Gubbins, Proceedings of the International Symposium on Molecular Thermodynamics and Molecular Simulation, Kyoto, *Fluid Phase Equil.* (1994), in press.
12. B. K. Peterson, G. S. Heffelfinger, K. E. Gubbins, and F. van Swol, *J. Chem. Phys.* **93**:679 (1990).
13. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Roquerol, and T. Siemineiewska, *Pure Appl. Chem.* **57**:603 (1985).
14. P. B. Balbuena and K. E. Gubbins, *Langmuir* **9**:1801 (1993).
15. P. J. Branton, P. G. Hall, and K. S. W. Sing, *J. Chem. Soc. Chem. Commun.* 1257 (1993).
16. O. Franke, G. Schulz-Ekloff, J. Rathousky, J. Starek, and A. Zukal, *J. Chem. Soc. Chem. Commun.* 724 (1993).