Adsorption 2, 5–7 (1996)

Introduction

P.A. MONSON
Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003

This issue of ADSORPTION has been dedicated to the topic of molecular modeling of adsorption phenomena. This is one of the most important emerging efforts in the field of adsorption and the papers in this issue illustrate the kinds of efforts being made. While molecular theory of adsorption has a history of over seventy five years going back to the work of Langmuir, the last two decades have seen an enormous growth in the scope and success of calculations based on molecular theory. This has in large part paralleled significant developments in statistical mechanical theory together with the availability of high speed computers at low cost. A hallmark of this progress has been a more realistic treatment of the microscopic physics of the adsorption process.

There are a variety of goals to be achieved by a program in molecular modeling of adsorption phenomena. Some of these are: i) to formulate microscopic mechanical models of adsorption systems which give a physically correct description of the behavior of real adsorption systems at the molecular level; ii) calculation of the equilibrium and/or dynamical properties of the system; iii) development of insights into microscopic behavior of the system and how this is reflected in experimental measurements of equilibria and dynamics; iv) provide a fundamental basis for improving empirical mathematical models used in applications such as separation system design.

In formulating molecular models of adsorption there are two important aspects. In the first case it is necessary to start with information about the microstructure of the adsorbent. Adsorbent structures can be highly ordered as in the case of exfoliated graphite or zeolites. Although even in such cases as these there are usually significant variations in microstructure between different samples. On the other hand there are highly disordered structures as in the case of materials like activated carbons and silica gels.

The second aspect of molecular model formulation is a description of the intermolecular forces in the system. We have first of all the interactions between the adsorbed molecules (adsorbate) and the adsorbent. These are the most sensitive to the adsorbent microstructure. Also important are the adsorbate-adsorbate interactions which are qualitatively similar to the interactions between the molecules in the bulk, although they may be significantly modified in the presence of the adsorbent.

It can be argued that a real weak point in the molecular modeling of adsorption systems is the status of our quantitative knowledge of intermolecular forces. While it is true to say that we have a good qualitative understanding of physics involved in these forces, accurate quantitative information is very limited even for molecules in bulk phases (Maitland et al., 1981). Descriptions of intermolecular interactions used in adsorption are given in terms of empirical potential energy functions. The parameters in these functions are generated by a combination of estimation methods and fits to experimental data. For adsorbate-adsorbent interactions the most useful experimental information is the Henry's law constant. This is obtained from low pressure adsorption isotherm data and can be calculated from the adsorbate-adsorbent intermolecular potential. A common starting point for the adsorbate-adsorbate intermolecular potential is to assume that this is the same as in the bulk. Molecular theory calculations which seek to obtain close agreement with experimental data often use quite complex potential functions to model the different aspects of the interactions.

In addition to detailed molecular models with complex molecular interactions there are other simpler kinds of models which although not fully realistic can provide significant insights into the microscopic behavior. These include site-wise adsorption or lattice models, the simplest of which is the Langmuir model. Two dimensional fluid models of monolayers

are another example. Adsorption in pores can be modeled using idealized pore geometries such as slits and cylinders. Models such as these have the advantage that calculations are much simpler and analytic solutions are sometimes possible. Moreover, they are sufficiently simple that the relationship between the molecular level physics and the interactions is relatively clear.

The calculation of the properties of an adsorption system from a molecular model can pose special challenges. The central difficulty both for thermodynamics and transport phenomena is that a fluid adsorbed in a porous material or in contact with a free solid surface is intrinsically inhomogeneous, i.e., the density is spatially nonuniform. This nonuniformity can be so extreme as to lead to simplification of the problem through the lowering of dimensionality. For example, a low temperature monolayer on a strongly adsorbing surface can be treated as a two dimensional system as can a fluid in a narrow slit pore, while an adsorbed fluid in a narrow cylindrical channel can be treated as a one dimensional system. In general, however, the inhomogeneity must be confronted directly. The thermodynamic problem can be recast into that of determining the equilibrium molecular density distribution in the system (Rowlinson and Widom, 1982; Hansen and McDonald, 1986). The problem of transport phenomena involves issues such as the mechanism for diffusion in porous materials and the correct formulation of constitutive equations for inhomogeneous fluids.

Statistical mechanics provides a large arsenal of techniques which can be used to determine the properties of a molecular model of adsorption. Some of these techniques can be used in building approximate solutions to the properties of an adsorption system. In addition to the insights which emerge from the process of making approximations, this approach leads to generally the most tractable calculations and sometimes the possibility of analytical solutions. Moreover the approach offers the prospect of deriving new functional forms which can be used to develop new empirical correlations for practical applications.

Traditional approaches have been built upon idealizations of the surface phenomena and are well reviewed in a monograph by Steele (1973). These include lattice theories and two dimensional equation of state theories mentioned earlier. More recently approaches which directly address the thermodynamics of a system with nonuniform density have been developed. The most widely used of these approaches are the density functional theories (Hansen and McDonald, 1986; Evans, 1979) and these theories have been especially useful in understanding the phase behavior of fluids in porous materials (Evans, 1990; Balbuena and Gubbins, 1993). Integral equation theories developed for calculating the microstructure of bulk fluids are now being applied to the study of fluids in disordered porous materials (Madden and Glandt, 1988; Vega et al., 1993; Lomba et al., 1993; Rosinberg et al., 1994).

Perhaps the most widely used techniques from statistical mechanics in current use are those which come under the heading of molecular simulation techniques (Allen and Tildesley, 1987; Nicholson and Parsonage, 1982) and this is the route taken in most of the papers in this issue. In these techniques the properties of the system are solved by brute force on the computer. In the molecular dynamics technique the classical equations of motions for a system of interacting particles are solved numerically and the properties are obtained as a time average. The molecular dynamics method permits the study of transport phenomena. The Monte Carlo method provides a means for generating random states of the system with a probability determined by the distribution function for one of the statistical mechanical ensembles. The properties of the system are then obtained as ensemble averages over these states. Each of the methods provides an essentially exact numerical solution of the statistical mechanics for a given molecular model of an adsorption system.

These calculations serve a number of purposes. First of all comparison of the results obtained with experimental data provides a basis for testing the accuracy of the molecular model used in the simulations. Molecular simulations also provide a basis for systematic testing of approximate theories developed for the same molecular model. This is an important step in disentangling the effects of approximations in the statistical mechanics from the effects of inadequacies in the molecular model. Finally, molecular simulations allow us to probe directly molecular scale phenomena which are not readily accessible via experiment. For example, molecular simulations can be used to determine the molecular density distribution in a porous material and important insights can emerge from the analysis of such distributions.

The papers in this special issue cover a diverse array of topics in adsorption. The first three papers from the groups at Minnesota and Cornell are concerned with the use of molecular simulation to study the behavior of simple fluids and fluids mixtures in model pores.

A key feature of this work is that it shows the importance of the molecular packing in determining adsorption equilibria arising from the finite size of the molecules and the confinement effects produced by the porous material microstructure. This can be especially important in determining selective adsorption from mixtures. The paper by Dunne et al. is illustrative of the work being carried out in a large number of groups on molecular simulation of models of fluids in zeolites. An interesting feature of this work is the focus on adsorption from liquid mixtures and the simultaneous determination of the bulk vapor-liquid equilibrium. The paper by Bojan et al. describes studies of capillary condensation in model pores and how this is influenced by the form of the adsorbate-adsorbent interactions.

The next three papers are concerned with chain molecules. The paper from the Cornell group focuses on the behavior of chain molecules in pores and especially the effects of strong association forces between the molecules and with specific sites on the pore walls. The paper by Ballamudi and Bitsanis describes a study of a model of liquid *n*-octane squeezed between flat plates. This work is motivated by the need to understand the behavior of thin hydrocarbon and polymer films. The paper by Fichthorn deals with the diffusion of chain molecules on metal surfaces. This work is directed at understanding the nature of diffusive processes and their dependence on molecular structure, especially in the context of surface catalysis.

The paper by Talbot illustrates the kind of new developments that are emerging in the field of adsorption kinetics for non equilibrium systems. Such systems are common in the area of macromolecule adsorption. Statistical mechanical techniques can be used to determine information about the distribution of molecules on the surface in nonequilibrium adsorption and how this affects the adsorption kinetics.

The final paper in the issue deals with the molecular simulation of fluid transport through semipermeable membranes focusing on osmosis and reverse osmosis. Murad and his coworkers have developed a molecular dynamics technique for studying these phenomena. Although this paper is not strictly on the topic of adsorption it nicely illustrates the close relationship between transport through membranes and diffusion in porous materials.

References

Allen, M.P. and D.J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford, 1987.

Balbuena, P.B. and K.E. Gubbins, *Langmuir*, **9**, 1801 (1993).

Evans, R., *Adv. Phys.*, **28**, 143 (1979); Evans, R. in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson, Dekker, New York, 1992.

Evans, R., *J. Phys.: Condens. Matter*, **2**, 8989 (1990).

Hansen, J.-P. and I.R. McDonald, *Theory of Simple Liquids*, Academic Press, London, 1986.

Lomba, E., J.A. Given, G. Stell, J.-J. Weis, and D. Levesque, *Phys. Rev. E*, **48**, 233 (1993).

Madden, W.G. and E.D. Glandt, *J. Stat. Phys.*, **51**, 537 (1988).

Maitland, G.C., M. Rigby, E.B. Smith, and W.A. Wakeham, *Intermolecular Forces: Their Origin and Determination*, Clarendon Press, Oxford, 1981.

Nicholson, D. and N.G. Parsonage, *Computer Simulation and the Statistical Mechanics of Adsorption*, Academic Press, London, 1982.

Rosinberg, M.L., G. Tarjus, and G. Stell, *J. Chem. Phys.*, **100**, 5172 (1994)

Rowlinson, J.S. and B. Widom, *Molecular Theory of Capillarity*, Clarendon Press, Oxford, 1982.

Steele, W.A., *The Interaction of gases with solid surfaces*, Pergamon, Oxford, 1973.

Vega, C., R.D. Kaminsky, and P.A. Monson, *J. Chem. Phys.*, **99**, 3003 (1993).