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PROGRESS REPORT

Adsorption and Diffusion of Fluids in Well-Characterized Adsorbent Materials

DOE Grant No. DE-FG02-88ER13974

August 1, 1993 to July 31, 1994

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MASTER

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Summary Report on Work under DOE Grant DE-FG02-88ER13974, 8/1/93-7/31/94

During this period work under the grant has included molecular simulations for simple gases in well-characterized materials (carbons, aluminophosphates, buckytubes, pillared clays and MCM-41), water in carbons and aluminophosphates, and chain molecules in carbons.

1. Adsorbed Methane Monolayers on Carbon

We have completed a simulation study of methane adsorbed on non-porous graphite for the submonolayer region, and have made detailed comparisons with experimental data [1,2]. Simple Lennard-Jones models were used for the interactions, and this model was found to produce all of the monolayer phase transitions observed in the laboratory. Very large simulations (up to 8000 molecules) were carried out on the CM-2 at the Pittsburgh Supercomputer Center in order to study the vapor-liquid coexistence for the monolayer. The coexistence curve showed the flat top ($\beta=0.125$) characteristic of two-dimensional systems, and was in excellent agreement with experimental data of M.H.W. Chan and coworkers at Penn State.

2. Simple Fluids in Aluminophosphates, Buckytubes, Pillared Clays and MCM-41

A long range goal of our work is to develop molecular modeling techniques for well-characterized micro- and meso-porous materials. In particular, we are interested in materials which satisfy the constraints: (a) pores of uniform shape and size, with minimum structural defects, (b) pore size can be accurately controlled in manufacture, and (c) pore sizes in the range 8-100 Å (larger than most currently used zeolites). For such materials molecular modeling should be able to predict optimum pore sizes, materials and state conditions for particular purposes, e.g. removal of a particular constituent from a mixture. With this in mind we have begun studies of four classes of materials: aluminophosphates, buckytubes (tubular carbons), pillared clays and MCM-41 (a new zeolite first synthesized by Mobil in late 1992). For aluminophosphates we have completed a detailed simulation study (using GCMC and MD) for inert gases in VPI-5, ALPO₄-5 and ALPO₄-11 [3,4]. The most interesting results are for VPI-5, which has the largest pore (diameter 13 Å). The simulation results are in general agreement with the experimental results where available, but indicate a higher than expected number of lattice defects in the real material.

Results for adsorption isotherms, density profiles and heats of adsorption have been obtained [4] for argon in a model pillared clay with a pore width of 16 Å. The results show that capillary condensation occurs only below some critical density of pillars, which is found for a range of temperatures in the simulations. There seems to be qualitative agreement with experimental results. For buckytubes we have studied the adsorption of argon and nitrogen in tubes ranging in diameter from 10 to 50 Å. Tube sizes and walls were chosen to model buckytubes prepared by Iijima. The adsorption

isotherms and heats show several interesting phase transitions, including layering transitions (0 to 1, 1 to 2, 2 to 3) and capillary condensation [5]. There are no experimental data yet with which to compare our results, but these materials seem to be very promising for adsorption and separations. Preparation of buckytubes in sufficient quantities in a pure form (in the absence of other forms of carbon such as platelets, etc.) remains a problem.

Finally, we are commencing studies of gases in MCM-41. This new material seems especially promising as a new adsorbent, since it adsorbs strongly and selectively, and can be prepared with uniform cylindrical pores. Moreover, the pore diameter can be controlled in the range 15-100 Å. Our initial simulations are for a pore diameter of about 40 Å, and we find an adsorption isotherm in good agreement with a very recent experiment by K. Sing et al. In this work we expect to collaborate with Prof. J. White of Australian National University, who has a large experimental group working on synthesis of these materials, and their property measurement.

3. Water in Carbons and Aluminophosphates

Adsorbed water behaves very differently from simple fluids. In carbons the adsorption isotherms are usually of types III (non-porous materials) or V (mesoporous materials), with very little adsorption at lower pressures followed by a steep rise in adsorption at some higher pressure. In class V this rise is accompanied by capillary condensation. In materials with active groups on the surface (e.g. activated carbons, many silicas) a wide range of adsorption behavior is observed. The goal of our simulation work in this area is to understand the factors that govern such behavior, and particularly the role of temperature, type of surface, density and type of active groups on the surface, and pore width. We have carried out two studies of water in porous carbons [5]: (a) water in a porous graphitic carbon with slit pores of width 20 Å; (b) water in a model activated carbon with slit graphitic pores with carboxyl groups anchored to carbon atoms on the surface. In the case of the graphitic carbons we find adsorption isotherms of type V, in agreement with experiment [6]. The water molecules are forced to lose some of their H-bonded structure on entering the pores, and this leads to low adsorption except at higher pressures. In the case of the activated carbons, the density of COOH groups anchored to the surface is varied, as is the pore width [5]. For the higher densities of carboxyl groups the adsorption isotherm is strongly affected, with much more adsorption at low pressures. This is attributable to H-bonding between water molecules and the COOH groups on the surface. Two types of H-bonds are formed and these are clearly visible in the analysis of interaction energies and density profiles. We are now in the process of developing a GCMC code in which the active groups on the surface will be free to translate and reorient; this should enable us to determine the optimum arrangement of active groups for maximum water adsorption, and so suggest ways to design improved dessicants.

A second project involves the study of water in VPI-5 and other aluminophosphates. In this case there is strong experimental evidence of chemisorption of water to the aluminum atoms; thus, x-ray diffraction studies show a change from

tetrahedral to octahedral structure around the aluminum in the presence of water. We have carried out ab initio quantum mechanical calculations for the VPI-5 structure in the presence of, and in the absence of, water. These calculations show that the octahedral structure is stabilized by the presence of a water molecule, in agreement with the experimental results. We are in the process of calculating the intermolecular potential field for this system and will fit these results to a suitable equation for the potential. This potential will then be used in conventional GCMC simulations to determine the adsorption isotherm and heat of adsorption. Both of these properties have been measured experimentally, and comparisons of experiment and simulation will be made.

4. Chain Molecules in Pores

We have carried out Monte Carlo simulations of chain molecules (chains of up to 35 Lennard-Jones mers) in slit carbon pores of width 5.5σ , where σ is the diameter of a mer, for a range of fluid-wall interaction strengths [7]. The Chain Increment Method was used to calculate the chemical potentials of the polymers in the pore, and from these it was possible to calculate the adsorption isotherms. These are the first calculations of chemical potentials or adsorption isotherms for chain molecules in pores. For these narrow pores a strong bridging effect was observed. The incremental chemical potential due to the addition of mers to a chain is found to become independent of chain length for chains longer than about 8 mers. This work is being extended to other conditions and to include chains that H-bond to each other and to sites on the surface.

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