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ADVANCES IN ADSORPTION SEPARATION SCIENCE AND TECHNOLOGY

By

Li Zhong and Ye Zhenhua

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PREFACE

The Fourth China-Japan-USA Symposium on advanced in Adsorption Separation Science and Technology will be held during May 13~16, 1997 at Guangzhou, China. It follows the previous three symposiums in Hangzhou ('88), Hangzhou('91) and Dalian ('94), China.

I sincerely hope that the symposium can provide a forum for researchers and engineers from academia and industry to meet and to exchange ideas on the latest developments in Adsorption Separation Science and Technology and related technological areas.

The papers and abstracts collected in this proceedings, 88 in number, are presented at the plenary session, oral presentations and the poster session of the symposium, which represent the recent progress to some extent in the field of adsorption separation science and technology in three countries.

I would like to take this opportunity to express my heartfelt appreciation to Professor Kaneko, Professor Ma, Professor Wu and Professor Chen for their enthusiastic support and kind cooperation, and the National Natural Science Foundation of China and South China University of Technology for their financial supports. At the same time, I wish to express sincerely my personal appreciation to the authors from the three countries as well as UK, Korea, Indian, Germany and France. It is their contributions that make the proceedings of the symposium finished. My cordial appreciation is also due to all participants and staffs of the symposium for their collective efforts to making the symposium successful.

Z. Li (LI Zhong)

Zhong Li

Professor

South China University of Technology

Guangzhou, China

April 1997

CONTENTS

Computer Simulation of the Thermodynamic Properties of Films Adsorbed on Heterogeneous Surfaces

William A. Steele and M. J. Bojan
Department of Chemistry, Penn State University
University Park, PA 16802, USA

Abstract

The grand canonical Monte Carlo method for the computer simulation of adsorption thermodynamics is presented. A specific example of the sorption of krypton in a model rough-walled pore is given and it is shown that the simulation gives useful information about the atomic behavior in this system as well as the thermodynamic properties.

Introduction

The use of computers to simulate the thermodynamic and dynamical properties of molecular fluids (and solids) is now a well established technique. It began as a method to obtain these properties for simple molecular interaction laws in order to compare with approximate theories and, later, with experimental data. In its present state, it has proved its value as a tool to characterize complex biological and chemical systems which cannot be accurately treated with present theory. Physical adsorption on the surfaces of of heterogeneous solids is one such case. Because of its importance, there is a long history of attempts at quantitative theoretical treatments of this problem [1,2]. Most of these rest upon the idea that the surface can be represented as a regular array of sites having different adsorption energies. The global adsorption is then assumed to be sum of local isotherms for adsorption on the various sites that make up the adsorbing surface. The accuracy of these assumptions (sitewise adsorption and the representation of the global isotherm by local isotherms) is presently rather poorly known, but should be susceptible to testing via appropriately designed computer simulations.

After a brief presentation of a useful computer algorithm for simulating the thermodynamic properties of physically adsorbed molecules, results for physical adsorption on a specific model heterogeneous surface will be presented and their relevance to the understanding of molecular behavior in these systems will be discussed.

Fundamentals

Although there are several promising algorithms for use in problems in physical adsorption, it presently appears that the simulations that generate a grand canonical ensemble by Monte Carlo techniques (GCMC) are the most powerful and most useful. As is commonly done in simulations of adsorption, the computations are based upon the assumption that the adsorbent is a rigid solid whose role is to provide a field of force that causes adsorbate

molecules to adsorb on its surface. If the adsorbed molecules are in equilibrium with a vapor phase of pressure p and temperature T, the chemical potentials μ_{ads} and μ_{gas} of the two phases are equal. (This discussion can easily be extended from a pure adsorbate to a multi-component fluid if necessary.) For an ideal gas phase, one then has $\mu_{ads} = \mu_{gas} = \mu^o + RTlnp$, where μ^o is equal to $kTln(N\Lambda^3/V)$, with N=number of adsorbed molecules, V= the volume available to these molecules and $\Lambda = \sqrt{h^2/2\pi mkT}$, with m=atomic mass [3]. In the grand ensemble of statistical mechanics, fixed values of μ, T and V are taken and the energy E and number of particles N are fluctuating quantities whose averages $< E >$ and $< N >$ are to be evaluated. Evidently, this is a convenient ensemble for the calculation of isotherms ($< N >$ as a function of μ) and adsorption energies ($< E >$ as a function of $< N >$).

The Monte Carlo method used together with the Metropolis algorithm is a powerful and rigorously correct method of generating such an ensemble for any set of molecular interaction energies [4]. Without going into the derivation, we will present the essence of the calculation as applied to adsorption on a rigid solid.

Starting with some number of molecules at arbitrary positions in the computer box of volume V that contains the adsorbent surface, one makes a series of attempted changes: a molecule is moved by a small but otherwise random amount and $\delta\mathcal{U}$, the change in the interaction energy of the molecule with its surroundings (solid and other adsorbate molecules) is evaluated. If the energy change is negative, the move is accepted; if it is positive, one generates a random number ξ between zero and one. Only if ξ is less than $exp(-\delta\mathcal{U}/kT)$ is the move accepted. Two other types of moves are also attempted: the creation of a new molecule at some randomly chosen point and the destruction of a molecule, also randomly chosen. In either case, the energy of the system changes by $\delta\mathcal{U}$, but the acceptance of the trial is governed by the values of the "creation function" $\delta\mathcal{C}$ and the "destruction function" $\delta calD$ that are defined by $\delta\mathcal{U} - \mu - ln[(N+1)\Lambda^3/V]$ for creation and $\delta\mathcal{U} + \mu + ln[N\Lambda^3/V]$ for destruction.

For atomic fluids, this completes the specification of the chain of trials that eventually generates the grand canonical ensemble; if the fluid is made up of non-spherical molecules, moves that change orientation must be included. In all cases, periodic boundary conditions are applied so that the small system (a few hundred molecules) will mimic a macroscopic adsorbed fluid.

At equilibrium, N and E fluctuate around constant values. Depending upon the starting conditions, the attainment of equilibrium can take several million moves. Once equilibrium is attained, as indicated by the constancy of the averages $< N >$ and $< E >$, the simulations is continued for another million moves (depending upon the system being studied) and data is gathered to obtain thermodynamic and other properties of interest.

Model solid

The simulation of thermodynamic and associated properties will be illustrated for krypton

adsorbed in a model cylindrical pore with atomically rough walls. The Kr/pore wall interaction is assumed to be the pair-wise sum of Lennard-Jones energies between the adsorbate atom and each of the atoms in the adsorbent. These atoms are spheres of diameter $2.30\mathring{A}$ that are randomly close packed [5] around a cylindrical cavity of radius $111\mathring{A}$ in the solid. The length of the pore is $41.4\mathring{A}$ but periodic boundary conditions are imposed in the direction parallel to the pore axis. The Kr atoms interact with each other via Lennard-Jones functions with known well-depth ϵ and size σ parameters [6]. Values for the gas/solid (gs) and gas/gas (gg) parameters are: $\epsilon_{gs}/k = 101.3K$; $\sigma_{gs} = 3.40\mathring{A}$; $\epsilon_{gg}/k = 170K$; $\sigma_{gg} = 3.60\mathring{A}$.

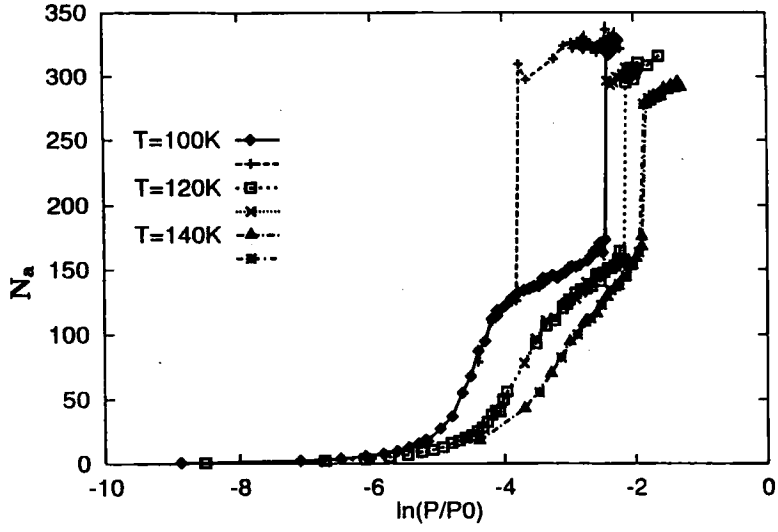

Figure 1: Simulated isotherms for krypton in a model cylindrical pore with atomically rough walls. Adsorption and desorption branches are shown which illustrate that hysteresis similar to that observed experimentally is also produced in simulations.

Results

Simulated isotherms are shown in Fig. 1 for krypton adsorbed at three temperatures in a cylindrical pore with atomically rough walls. The amount adsorbed $< N >= N_a$ is plotted here as a function of $[\mu - \mu_{liq}]/kT = ln[p/po]$, where po is the vapor pressure of the bulk liquid. This logarithmic plot helps display the low-coverage behavior of the isotherm and also shows chemical potential, which is a fundamental thermodynamic property of the fluid. At each temperature, the vertical portions of the isotherms show condensation (or evaporation, for the desorption branches) from a pore containing $\sim$ one monolayer on the wall plus dilute gas in the interior of the cylinder to a state where the cylinder is essentially full of a dense fluid. This can be seen quite clearly in Figure 2, where the density of the adsorbate is plotted as a function of distance from the pore axis. A strong monolayer density peak at a distance of $10\mathring{A}$ from the axis is evident for both values of the pore loading, 127

and 302 atoms in a pore of approximate volume = 5470$\AA^3$. In the first case, the density

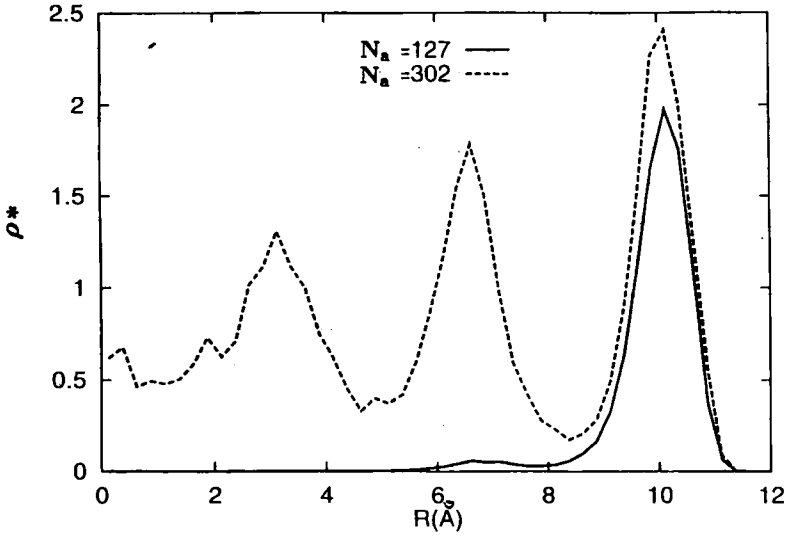

Figure 2: Simulations of the dependence of the density of the Kr in the pore (given in reduced units) upon distance from the pore axis are shown here for two pore loadings: 127 atoms, nearly a monolayer which occurs just before condensation begins (see Fig.1), and 302 atoms, a nearly filled pore.

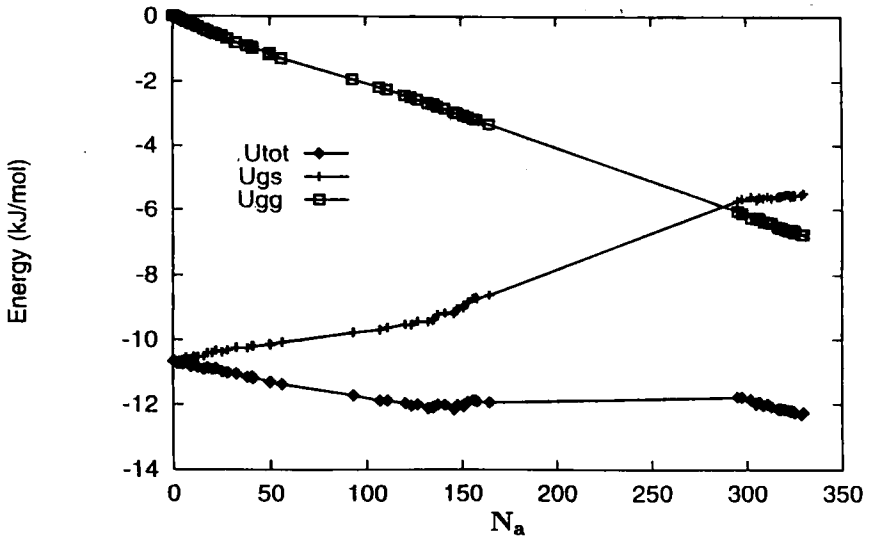

Figure 3: The coverage dependence of the average interaction energies of Kr atoms in the pore. Shown are the gas/solid (gs), the gas-gas (gg) and the total (tot) energies.

shows a very small number of atoms in the second layer and then is essentially zero in the space that is more distant from the pore wall. For the nearly full pore, the adsorbed fluid is structured, showing a series of three layers as one goes from the wall toward the pore axis.

The average energies of interaction of the sorbed Kr with neighboring Kr atoms (U_{gg}) and with the walls (U_{gs}) are plotted as a function of pore loading for T=120 K in Figure 3. The straight-line portions without points are energies within the vertical parts of the isotherm in Fig. 1 where simulations are not possible. The effect of heterogeneity is clearly shown in the decaying curve for U_{gs} in the monolayer regime ($N_a <\sim 130$ atoms; the decay at larger N_a is due to atoms that are not on the surface, but rather in the second and higher layers within the pore. Note finally that the total energy (U_{tot}) is nearly constant with increasing amount in the pore. This is often thought to be a sign of a homogeneous surface, but actually means only that the decay in U_{gs} is canceled by the changing U_{gg} as pore loading increases.

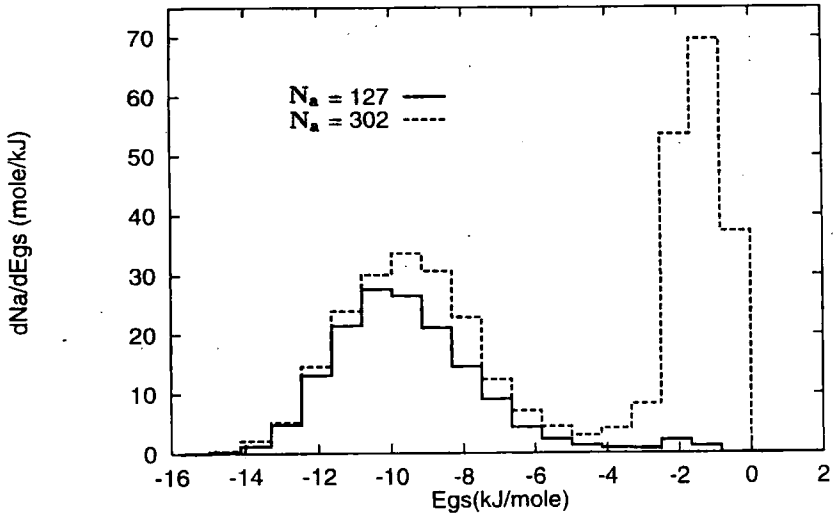

Figure 4: Histograms of the gas/solid energies of adsorbed Kr atoms. The distributions of the adsorbed atoms over the gas/solid energy are plotted as a function of this energy. Approximately, atoms in the first layer have energies that range from -5 to -14 kJ/mole and, for second layer atoms, from -1 to -2.5 kJ/mole.

A more detailed picture of the Kr adsorption energies is shown in Figure 4. Here, the distribution of the gas/solid energy for a given amount of Kr in the pore is shown; that is, the plots give $\Delta N_a/\Delta E_{gs}$, the number of atoms with gas/solid energy between E_{gs} and E_{gs}+0.8 kJ/mole, as a function of E_{gs}. In the plot for $N_a = 127$, the energies for the atoms adsorbed in the monolayer ranges from ~ -5 to ~ -14 kJ/mole, with a most probable value of -10 kJ/mole. A small number of second layer atoms is present that have gas/solid energies of ~ 2 kJ/mole. In the nearly full pore with $N_a = 302$ atoms, the gas-solid energies and