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Computer Simulations of Systems in Confined Geometries*

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Basic simulation methods in porous material are reviewed. The presentation is focused on different simulation techniques and interaction models, describing the forces between molecules of the fluid and the adsorbent walls. The basic simulation techniques, grand-canonical Monte Carlo, Gibbs ensemble Monte Carlo and buffering field Molecular Dynamics, are presented. The methods to calculate adsorbate-adsorbate and adsorbate-adsorbent interaction parameters have been discussed. Examples of the simulations of adsorption in carbon nanotubes and silicates are presented.

Key words: Monte Carlo, Molecular Dynamics, porous materials

1. Introduction

There is increasing number of different experimental and theoretical techniques, which allow one to interpret the adsorption data. Computer simulation methods form one group of them. In the last few years, a large number of computer simulation studies on the physisorption of molecules in zeolites have revealed the molecular simulation techniques as powerful and complementary tool to experimental techniques of adsorbate-adsorbent systems characterization. Their significance arises from the fact that the simulations methods, such as Monte Carlo and Molecular Dynamics, provide a direct insight into the microscopic states of the system. The details of the microscopic states are necessary for understanding the adsorption data and relevant mechanisms, particularly for micropore (diameter less than 2 nm) and mesopore (diameter 2–50 nm) size analysis and for their potential application.

Also, the simulations of the adsorption in the porous materials are an interesting and challenging scientific goal, because of variety of possible situations. It is evident that small variation in the surface morphology, chemistry and structure can substantially change the adsorption characteristics. So, the modeling of the interaction be-

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*Dedicated to the memory of Professor Krzysztof Pigoń.

tween the adsorbate particles and adsorbent material is a critical feature, particularly for the quantitative results of simulations and direct interpretation of the experimental data. Additionally, the results depend on the interplay and competition between the adsorbate-adsorbent and adsorbate-adsorbate interaction. The properties of wetting, the mechanism that underlines the separation of atom or molecules, the energy of atoms adsorbed in the porous materials – they are all very sensitive to the details of the interaction models. At the same time, adsorption means a two-phase system being in equilibrium or in metastable states. At the macroscopic level, the bulk gas phase is in equilibrium with the adsorbed system. However, at the microscopic level, the gas-like volume can be metastable and coexists with a liquid-like volume. The situations like this require special simulation techniques, like the Grand Canonical Monte Carlo, Gibbs Ensembles or other techniques, which allow one to include the influence of the gas state on the adsorbed system.

This article focuses on two aspects of the simulations of the adsorption in the porous materials: building the interaction models and methodologies of the simulation techniques. As examples we present selected cases of adsorption in aluminosilicates and in carbon nanotubes.

2. Adsorption in confined system

The confined systems are very interesting from a basic point of view, because the confined geometry changes the phase diagram of the adsorbed system in a very distinctive and non-trivial way (Fig. 1). The coexistence lines between vapor, liquid and solid states are shifted, the triple-point exists at a different temperature and the critical temperature is lower. A new mechanism for the condensation is observed, called the capillary condensation, with its own characteristic (pore) critical temperature T_{cp} and hysteresis critical temperature T_{ch} [1].

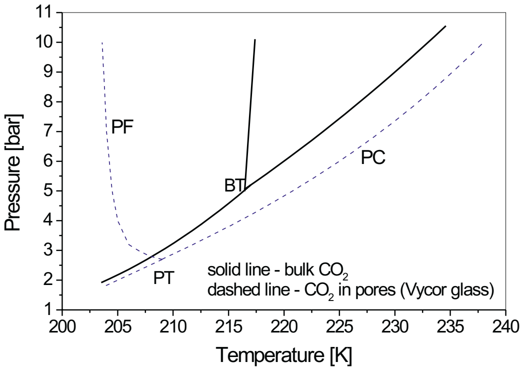

Figure 1. Phase diagram of CO_2 in bulk phase and in a confined system. BT and PT indicate bulk and pore triple points, PC and PF mean pore condensation and pore freezing lines, respectively [1].

The capillary condensations observed in real systems may be a sharp transition, signified by a sudden vertical jump in adsorption isotherm, when all the pores are of the same size and shape with homogeneous (smooth) walls. However, in many systems rather steeply rising adsorption is observed. Such behavior results from a continuous filling of pores, that can be due to one or more of the following factors: a distribution of pore size and shapes, connectivity among the pores or heterogeneity of the walls.

For sufficiently large pores the fluctuations in the density profile, due to the fluid-wall interaction, can be neglected and a macroscopic thermodynamic description of adsorbate – adsorbent system is possible. Assuming that the liquid wets the walls completely, it is possible to derive an equation for the pressure P corresponding to the capillary condensation [2]:

$$\ln(P/P_o) = -2\gamma/(RT\rho H)$$

where P_o is the saturated vapor pressure of the bulk fluid, γ is the gas-liquid surface tension for the bulk fluid, R is the gas constant, ρ is the density of the bulk liquid and H is the pore width. The equation is known as the Kelvin equation. It gives a qualitative interpretation of the capillary condensation phenomena and should be generally valid for large pores at temperatures well below the pore critical temperature, when a surface tension can be defined and the gas phase can be treated as an ideal gas. The microscopic properties of the wall-fluid interactions are related to the macroscopic phenomenon of wetting. The Kelvin equation fails to account for the layers strongly adsorbed on the pore walls. An analysis of the influence of wetting on corrections to the Kelvin equation shows that H should be replaced by a modified pore width, which accounts for the adsorbed layers that form prior to capillary condensation. Here, the role of the computer simulation methods is particularly important, because they are not limited by the assumptions existing in the macroscopic theories. Capillary condensation is often accompanied by a hysteresis (characterized by its own critical temperature T_{ch}): desorption starting from pores that are filled with a dense fluid phase occurs *via* a different path than adsorption. The appearance of reproducible and stable hysteresis implies the existence of well-defined metastable states. At present, it is recognized that there are many mechanisms responsible for the hysteresis generation [2]. If the temperature T_{ch} is above the triple point temperature of the bulk adsorbate, the hysteresis is interpreted as signature of the capillary condensation. The hysteresis appearing at temperatures lower than T_{BT} (see Fig. 1) is usually due to a fluid-solid or solid-solid transition. While the capillary condensation has been studied extensively, freezing and melting in porous media remains largely unexplored. However, freezing has been widely employed in the characterization of porous media. For example, the shift in freezing temperature is used to determine pore size distribution. The process of freezing in confined media depends on three main factors: strength of the pore-wall interaction forces (compressing effect), geometrical shape of the pore (geometrical hindrance) and equilibrium vapor-phase pressure (tensile effect). Depending on the strength of the attractive potential energy from the pore walls and/or the geometrical form of the pore, fluid in a pore in equilibrium with saturated vapor shows freezing point elevation as well as depression. The shift in freezing temperature T_f can be determined [1]:

$$T_f - T_{fb} = -2T_{fb}(\gamma_{ws} - \gamma_{wl})v/(H\lambda_{fb})$$

where T_{fb} is the bulk freezing temperature, γ_{ws}, γ_{wl} are the corresponding wall-solid and wall-fluid surface tensions, v is the molar volume of the liquid, λ_{fb} is the latent heat of melting in the bulk and H is the pore width. However, this model breaks down for small pores, for the same reasons as for the Kelvin equation. It is important that the layers adjacent to the pore walls behave differently than the rest of the fluid: the first few molecular layers close to the pore walls remained often amorphous, while the interior froze to a crystalline form. The computer simulations are very effective methods to study the influence of this local behavior on the freezing/melting transitions.

3. Computer simulations – methods

It is difficult to calculate adsorption isotherm using Monte Carlo simulations of the canonical ensemble because the Markov chains, being the method to generate the microscopic states, do not seem to converge for any reasonable length. This problem can be avoided by using the Grand Canonical ensemble Monte Carlo (GCMC) [3]. The obvious advantages are the rapid convergence of the average energy <U> and the mean number of molecules <N>. Additionally, the simulations produce the adsorption isotherm directly. The independent variable in this ensemble are the chemical potential μ, the volume of the system V, and the temperature T. At equilibrium, the chemical potential of the adsorbed phase is equal to the chemical potential of the bulk phase:

$$\mu_{ads} = \mu_{bulk}(T,P)$$

If the gas can be treated as ideal in the bulk phase, one can show that the chemical potential is a function of temperature T and pressure P in the bulk phase.

$$\mu_{bulk}(T,P) = -kT \cdot \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} kT\right] + kT \cdot \ln[P]$$

As a consequence, the independent variables in the simulation of the adsorption are the temperature, pressure of the bulk gas phase and the volume of the pore unit cell (m – the mass of gas molecule). The procedure outlined above is relatively simple only for simple fluids. For more complex fluids the equation of state may not be known a priori. Calculating the pressure of complex fluids in the simulations is not straightforward. So, in some cases the Gibbs ensemble (GEMC), which uses the pressure of the bulk gas as an input parameter, is an alternative method. It is worth remembering that in the standard Gibbs ensemble method, the chemical potential of the coexisting phases is not fixed. It is the difference $\Delta\mu$ that is equal to zero. Therefore, it is possible to define two intensive parameters, such as T and P.

Although the GCMC or GEMC simulations are most frequently used to simulate the adsorbed systems, other methodologies are also used, including the ones based on Molecular Dynamics algorithms [3]. However, in contrast to the Monte Carlo method, which handles particle variations by straightforward addition or removal, it is considerably more difficult to apply molecular dynamic scheme.

3.1. Grand Canonical ensemble Monte Carlo

The typical Monte Carlo simulation [3] in the grand canonical (μVT) ensemble consists of an attempted movement (translational or rotational) of a particle, taken in the usual Metropolis MC manner, and then either an attempted deletion of a randomly chosen particle or an attempted insertion of a particle at a random position. The probability of a move being accepted in a MC simulation is:

$$P(r \to r') = \min[1, \exp(-\Delta U^*/kT)],$$

where ΔU^* is the minimum reversible work required to bring the system from state r to state r′ (the pseudo-Boltzmann factor). For the simulation in the (μVT) ensemble:

$$\Delta U^* = U_{new}(r') - U_{old}(r)$$

for displacements of molecules, where U(r) is the configurational potential energy. In a typical grand canonical ensemble simulation, we impose the temperature and chemical potential. Experimentally, however, usually the pressure rather than the chemical potential of the gas is fixed. The pressure in the bulk gas phase is related to the chemical potential through:

$$\beta\mu = \beta\mu^o + \ln(\beta P_{id});$$

P_{id} denotes the pressure of an ideal gas. For insertion and removal of particles, the moves are accepted with the following probabilities [3]:

$$P(N \to N+1) = \min[1, (V\beta P_{id}/(N+1))\exp(-\beta(U(r,N+1) - U(r,N)))]$$

$$P(N \to N-1) = \min[1, (N/\beta P_{id} V)\exp(-\beta(U(r,N-1) - U(r,N)))]$$

So, if the experimental conditions are such that the system of interest is in equilibrium with a gas phase that behaves like an ideal gas, then only the pressure of this ideal gas enters into the acceptance rules. If the pressure in the reservoir is too high for the ideal gas law to hold, we have to use an equation of state to relate the chemical potential of the gas phase to its pressure by introduction the fugacity coefficient.

The examples of the applications of the GCMC methods are numerous. They have been discussed in [1]. An interesting example has been presented in a recent paper [4]. The authors have studied adsorption in the MCM-41 zeolite, which possesses a nearly monodisperse array of straight, unconnected pore channels with diameters that can be tailored in the range 1.6–10 nm. The pores are thought to be roughly cylindrical in shape. MCM-41 is an attractive system because its narrow pore size distribution and straight, unconnected channels make it an ideal model adsorbent for fundamental theoretical studies of confined system. The results of the simulations have shown that the heterogeneity of the wall structures is indispensable for quantitative description of a mechanism of the adsorption. The applied model reproduced the experimental adsorption isotherm very well, even in the low-pressure region. The reduced pressure, at which capillary condensation takes place, could be accurately reproduced. The important conclusion is that the simulated relationship between this pressure and the model pore diameters seems to be the most reliable way to estimate the pore diameters of experimental samples.

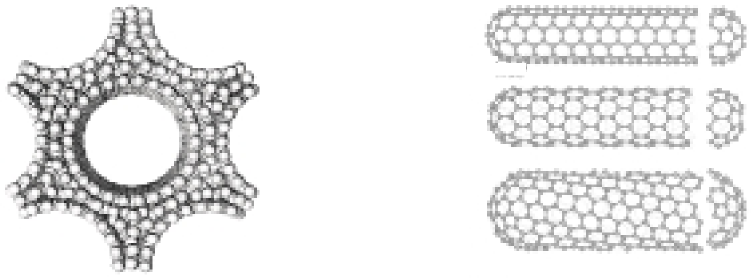

Figure 2. Schematic structure of the MCM-41 zeolite and three carbon nanotubes.

Applications of the GCMC simulations in carbon nanotubes are numerous as well. The general methodology is similar. However, in the case of the hydrogen adsorption, which has been widely studied, the quantum effects become important. In [5], the quantum effects are included through implementation of the path integral formalism of Feynman [6]. In the calculations, a classical ring of beads (polymer-like ring) replaces each quantum particle. The number of beads on the polymer is increases, until no further changes in the equilibrium properties are noted. The proper statistical mechanical averages of the classical ring polymer system yield the equilibrium properties of the quantum system of interest. In [5], the multiple-time step path integral hybrid Monte Carlo were combined with GCMC, giving a direct method for computing the adsorption of quantum fluids [7,8]. It has been shown that quantum effects for H_2 adsorption in tube interstices remain important even at 298 K. Path integral simulations are extremely CPU intensive. Therefore, as an approximation to adsorption in a full array of tubes, the authors computed adsorption in a single tube with the affective potential for a tube array. The average number of molecules ranged from 50–200. Periodic boundary conditions were applied in the z direction (tube axis). Adsorption in the interstice was evaluated through separate GCMC simulations of a single interstice bounded by three tubes.

3.2. Gibbs ensemble Monte Carlo

The standard Gibbs ensemble methods [3,9] have been proposed to simulate phase coexistence properties of fluids, in general, and to model adsorption and capillary condensation in cylindrical pores [10]. The basic idea is to simulate phase coexistence properties by following the evolution in phase space of a system composed of two distinct regions. Figure 3 shows a system consisting of two regions labeled 1 and 2.

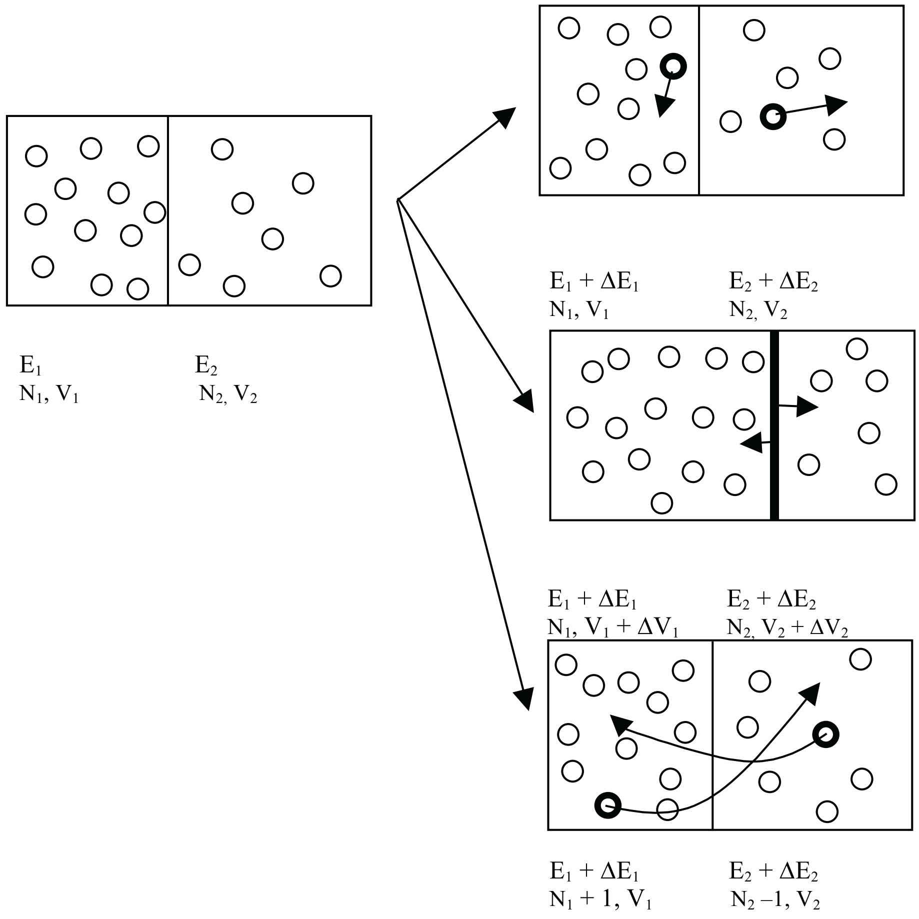

Figure 3. Schematic illustration of the possible steps for the GEMC simulations.

The total system is considered under NVT conditions. The "surface" separating the two regions in Fig. 3 is devoid of any physical significance and does not represent any interface. Thus, unlike the two-phase methods, there is no real interface. It results in much shorter run time in simulations. Three types of fluctuations are considered. The first ones are conventional random displacements of molecules. The second is a perturbation, in which the volumes of the two regions are changed so as to keep the total system volume constant. Finally, the movement of a single molecule from region 2 to region 1 is possible. The transfer of a molecule from one region to the other does not take place through an interfacial region: in simulation one selects a molecule at random from one region to disappear and appear at a random point in the other region. The appropriate change in energy is:

$$\Delta U^* = \Delta E_1 + \Delta E_2 + kT \ln[V_2(N_1 + 1)/V_1N_2]$$

The last term in ΔU^* results from the ideal gas contribution to the change in system entropy. McGrother *et al.* [11] have recently proposed an interesting extension of the GEMC method. Here, two simulation cells are used, one representing the pore, and the other the coexisting bulk fluid. The number of particles N, the volume of the pore V_p and the temperature are fixed just as in simple GEMC simulations of confined system. However, rather than fixing the volume V_b of the bulk fluid we fix the pressure P. Thus, in this technique called Fixed Pressure GEMC (FP-GEMC), we must perform additional moves, namely random changes in the volume of the bulk fluid cell. The modified technique is particularly useful in the study of complex fluids, where the equation of state may not be known a priori, so the pressure cannot be directly related to the applied chemical potential (GCMC) or the bulk density (GEMC). The FP-GEMC method uses the pressure as an input parameter. The method has been applied to study the adsorption of water into slit-shaped pores and good qualitative correspondence with experiment has been obtained [11]. Further refinement of the model is expected to yield quantitative agreement.

3.3. Molecular dynamics methods

M. Miyahara *et al.* [12] has recently proposed an interesting example of the Molecular Dynamics scheme with an imaginary gas phase. At each end of the simulation cell (slit-shaped pore), distant from the center (called: Full Potential Field), a border plane is set, beyond which an imaginary gas phase is assumed to exist. Since the external potential energy in the gas phase must be zero, there should exist a connecting space with a potential energy smoothly varying between the gas phase and pore space values. It is called Potential Buffering Field and its role is to maintain the vapor-liquid or vapor-solid coexisting conditions. The results obtained with this method are consistent with the GCMC simulation. It has been also observed that the liquid in the cell shows almost no hysteresis in condensation/evaporation process. This seems to be an advantage over the MC methods because it has allowed the authors to determine easily solid-liquid coexistence line and observe the dependence of the freezing point as a function of small changes in the bulk vapor pressure. There are different Molecular Dynamics techniques that are used in phase equilibria situations [13]. Their applications in the area of adsorption are not very numerous or they do not exist at all. Their potential advantages in this area are to be tested.

4. Modeling interactions in confined systems

The main feature, which makes the pore adsorption more difficult and very diverse, is the existence of the walls of the porous material and their strong influence on the potential energy of the total system. Molecular simulations offer a prospect of a more rigorous treatment than analytic calculations, since they are based on the fundamental principles of statistical mechanics. However, it must be kept in mind that to solve the statistical mechanics Hamiltonian, it is necessary to know the exact positions of the force centers in the solid structure and also the potential functions that govern the solid-fluid and fluid-fluid interaction.

The existence of an adsorbent in general, or the walls in pores, affects the intermolecular interaction in two ways. First, it supplements the potential energy with an additional term describing direct interaction of atoms with the surface. Second, it screens the dispersion part of the interaction between adsorbed particles. In the latter case, the role of the substrate is analogous to that of the third body in the tree-body interaction; the substrate modifies the electromagnetic fields associated with the fluctuating dipole moments of a pair of adsorbed particles.

4.1. Slit-shaped pores

Relatively simple formulas have been computed for interactions between atoms and the plane graphite surfaces for both types substrate-dependent interaction [14,15]. In the first approximation, the structure of the solid surface is neglected:

$$u_{sf}(z) = 2\pi\rho_s\varepsilon_{sf}\sigma_{sf}^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{sf}}{z}\right)^{10} - \left(\frac{\sigma_{sf}}{z}\right)^4 - \left(\frac{\sigma_{sf}^4}{3\Delta(z + 0.61\Delta)^3}\right)\right] \tag{1}$$

z is the distance between a fluid particle and solid surface. The potential parameters ε_{sf} and σ_{sf} correspond a Lennard-Jones model. ρ is the solid density and $\Delta = 0.335$ nm. The potential (called 10-4-3) neglects the lateral (x,y) substrate structure, so, it is a function of z only. To include the effect of the substrate periodicity, a laterally varying function f(x,y) is included. The total potential V is given by:

$$V(x,y,z) = u_{sf}^{o}(z) + u_{sf}^{1}(z) \cdot f(x,y) \tag{2}$$

$u^{o}(z)$ is the same as (1) and $u^{1}(z)$ is

$$u^{1}_{sf}(z) = B\left[C\left(\frac{a_1}{z}\right)^5 K_5\left(\frac{4\pi\pi}{\sqrt{3}a_1}\right) - D\left(\frac{a_1}{z}\right)^2 K_2\left(\frac{4\pi\pi}{\sqrt{3}a_1}\right)\right]$$

with $a_1 = 0.246$ nm and constants B, C, D:

$$B = \frac{4\pi\varepsilon_{sf}\sigma_{sf}^{6}}{\sqrt{3}a_1^{6}} \qquad C = \frac{\sigma_{sf}^{6}}{30a_1^{6}}\left(\frac{2\pi}{\sqrt{3}}\right)^5 \qquad D = \frac{8}{3}\pi^2$$

K_2 and K_5 are modified Bessel functions of the second kind. The laterally periodic function f(x,y) is:

$$f(x,y) = -2\left[\cos\left(2\pi\left(\frac{x}{a_1} + \frac{y}{\sqrt{3}a_1}\right)\right) + \cos\left(2\pi\left(\frac{x}{a_1} - \frac{y}{\sqrt{3}a_1}\right)\right) + \cos\frac{4\pi y}{\sqrt{3}a_1}\right]$$

In view of the complexity of most porous adsorbents and its apparent influence on the interaction property, it is not surprising that most attention has been given to the adsorption of small, spherical molecules in pores of uniform geometry – particularly cylindrical or slit – shaped pores. In a slit pore, the particle will interact with both walls, so the total adsorbate-adsorbent interaction will be the sum of two terms of the type (1), (*i.e.* $u_{sf}(z) + u_{sf}(H\text{-}z)$, where H is the dimension of the slit pore) and (2).

4.2. Cylindrical pores

In a cylindrical pore the situation is more complicated because previous equation for $u_{sf}(z)$ is valid for a plane surface only. One way to model the solid would be simply to include a large number of molecules on lattice sites. This is realistic, but it greatly increases the number of interactions that must be calculated in the simulations. Instead, one simplifies the potential by "smearing" the wall molecules into a continuum of density ρ_s and then integrating over volume and producing one-dimensional potential. This potential is a function of the radial distance from the center of the pore [4,16,17,18]. Such models represent the majority of the simulations in zeolites materials [1] and nearly all simulations of adsorption in carbon nanotubes [18]. However, even within this cylindrical approximation, a special care must be taken for quantum behavior for particles such as hydrogen. This effect can be also taken into account using the Feynman (semi-classical) effective potential approximation. As described in

[6], the effective potential represents a smearing of the classical potential as a first quantum correction. In the case of a cylindrical symmetric potential, the averaging yields:

$$V_{eff}(r) = \frac{6}{l^2}\int_0^\infty d\rho\cdot\rho\cdot I_0(6\rho r/l^2)V(\rho)\exp[-3(\rho^2 + r^2)/l^2]$$

where $I_0(x)$ is the Bessel function of imaginary argument, $l^2 = (\beta h^2)/(24m\pi^2)$. At high T the quantum correction is proportional to l^2 and the second derivative of V with respect to r:

$$V_{eff}(r) \cong V(r) + \frac{l^2}{12}V''(r)$$

The surface roughness can be taken into account if one uses a two- or three-dimensional model. Two-dimensional potential is a function of the distance from the wall (along the pore radius) and the distance around the pore circumference, with the axial component averaged out over the length of the pore. The interaction energy at each point in such a two-dimensional grid is precalculated, and linear interpolation is used during a simulation run to calculate the potential at off-grid points. The excessive size of the three-dimensional potential grid, which is a function of the distance from the wall, the distance around the pore circumference and the distance along the pore axis, prohibits this approach in many cases. It seems that 2-dimensional grid must be used in most cases with possible analytical modulation of the third dimension.

4.3. General models

The adsorption phenomena in microporous materials depend critically on the details of the potential surface induced by the host system. It is a difficult task to develop a potential both physically meaningful and suitable for simulations. The general expression for the adsorbate-adsorbent potential function is given by:

$$U^{total} = U^{coul} + U^{ind} + U^{disp} + U^{rep}$$

The coulomb term is calculated classically, using the partial charges of each interacting species. The induction energy is given by the first term of the induction multipole expansion [18]. It depends on the dipole polarizabilities of atoms. The dispersion and repulsion energies are often described by the Lennard-Jones potential, although other forms are also used (*e.g.*, Buckingham 6-exp function [20]). In nanotubes, the adsorbent atoms and their structure are well defined. In zeolites and other aluminosilicates or aluminophosphates porous materials, many calculations have been based on effective two-body potential that acts between adsorbates and oxygen atoms of the host lattice only. Such an approximation neglects of silicon, assuming that the framework silicon atoms have a very small polarizability and, being further away from the pore center compared to the oxygen atoms, contribute very little to the total dispersion energy. However, as discussed in [21,22], the silicon dipole polarizability will be negligible only if one considers the structure as purely ionic, which is usually not the case.

The interaction between the adsorbing atoms or molecules is in most cases modeled by the Lennard-Jones (LJ) potential. The spherical model is usually chosen (even for molecules), because of the need to have an accurate equation of state and saturated vapor pressure for the chosen model fluid. These allow one to compare the results directly at the reduced pressure, at which capillary condensation occurs in the experimental system. A bulk fluid equation of state for diatomic LJ fluid (with a quadrupole) has not been reported yet.

An interesting method for deriving the parameters of interaction has been proposed by Pellenq *et al.* [20] for rare-gas/silicalite systems. It uses the atom polarizabilities (in-crystal) and effective number of electrons to calculate the two-body and three-body dispersion coefficients. The repulsive parameters for Ar atoms are fitted to zero coverage experimental data. No adjustable parameters were involved in extending the argon potential to Kr and Xe. The nice feature of this model is the potential transferability of the potential parameters among different systems. The repulsive potential is the Born-Mayer atom-atom term:

$$E_{rep} = \Sigma A \exp(-br_{ij})$$

The dispersion term is in the form of damped multipole expansion:

$$E_{disp} = -\sum_{n=3}^{\infty} f_{2n}\left(\frac{C_{2n}}{r_{ij}^{2n}}\right) \qquad \text{where} \qquad f_{2n} = 1 - \left(\sum_{k=0}^{2n}\frac{(br_{ij})^k}{k!}\right)\exp(-br_{ij})$$

The parameters (C_6, C_8, C_{10}, b and A) have been calculated for Atom-Atom, Atom-O, Atom-Si types of two-body and Atom-O-O and Atom-Si-O for three-body interaction contacts (Atom = Ar,Kr,Xe). The model has been used to simulate the adsorption of the atoms in silicalite-1 zeolite [22]. One of the most important conclusions from this work was that some of transitions observed in adsorption isotherms must be associated with changes in the adsorbent framework. In [21] the interaction model has been applied in NaY zeolite. Here, the adsorption of polar molecules was also studied and a model of interaction contained also the electrostatic and polarization energies. In the calculations of the adsorption in MCM-41 [4], the crucial influence of heterogeneous wall has been shown. The system of a pure silicate version of the materials has been used (the solid skeletal structure of MCM-41 has been also synthesized as aluminosilicates or titanosilicate). There are no net charges and therefore no chargebalancing cations in this version of the material, so the interaction with adsorptive molecules can be modeled using repulsion and dispersion forces alone. The LJ parameters used to model the interaction of an oxygen atom in a zeolitic adsorbent with a particular type of adsorptive atom depend on an environment (that is, on the precise chemical and physical structure of the adsorbent) in part, because the oxygen adsorptive parameters usually take some account of the neglect of the small silicon or aluminum atom contribution. In the simulation of the adsorption of nitrogen in MCM-41 material [4] two sets of parameters were used. The first one assumed that all O-N_2 interactions were the same, regardless of the location of O atoms in the wall. This produced a homogeneous surface potential. The second one produces a heterogeneous surface potential, mimicking a surface that contains a wide variety of attractive sites (from weakly attractive silica-type regions to highly attractive regions of unknown composition). The results have proven that a good representation of the fluid-wall interaction requires a two-dimensional inhomogeneous potential that fluctuates around the pore wall, indicating the diversity of attractive sites present on the surface of an MCM-41 pore wall. The one-dimensional, homogeneous potentials are not even qualitatively modeling the adsorption of nitrogen. At the same time, the inhomogeneous potential gives an excellent fit.

An interesting example of a modeling of the interaction in carbon nanotubes is an application of the electronic density-functional (DF) calculations to search for hydrogen adsorption sites [23]. In this paper, a self-consistent charge density-functional-based tight-binding method (SCC-DFTB) has been compared with the DF total energy calculations based on the local density approximation (LDA) and the generalized gradient approximation (GGA). The calculations showed that two hydrogen chemisorption sites exist; top sites at the exterior and interior of the tube wall. Adsorption of a hydrogen atom at the interior pulls inward the carbon atoms, enhancing sp^3 rehybridization. When the number of hydrogen atoms bonded to carbon atoms increases, the structure becomes unstable and results in formation of H_2 molecules existing in the vacant space inside the nanotubes.

5. Conclusions

A large part of the activity in the modeling of confined system is devoted to an understanding of the influence of the pore characteristics on the phase diagram of confined system. This problem is more general and relates to any finite system, for example, to clusters. The main difference between clusters and the confined system is in the boundary conditions; the most important resemblance is due to the existence of the edge particles. In cluster, the particles, which are close to the edge have more translational freedom that the particles inside the system. In confined geometry, situation may be similar or just opposite. It depends on the strength of the particle-wall interaction that may be weak (and repulsive) or strongly attractive. This factor may substantially change the conditions of the melting/freezing or condensation phenomena. It is obvious that smaller the system, larger the influence of the edge, or contact properties on thermodynamic properties of the whole system.

The situation in confined system is more complicated than in clusters, not only because of the variable strength of the interaction. The walls are usually heterogeneous, that is, they have the centers that attract more and other which are less preferable. This situation makes that the overall geometric factor is crucial for understanding the adsorption mechanism. The role of the computer simulation is not disputable [1]. Practically, there are no other theoretical or experimental techniques that could follow the microscopic picture of the phenomena. Adsorption in pores is very localized, after all, keeping in mind that the mean dimensions are of the order of few nanometers. Also, the influence of the media modifies the properties of layers adjacent to the walls.

It is important to remember, that idealized pore geometries are not easily related to experimental results for real materials. Apart from the heterogeneity mentioned above, other factors substantially affect the properties of the confined system. Complex pore geometries introduce a new spectrum of possible situations and properties, more challenging from the point of view of the simulation methodology. For example, pore-pore correlation effects may change the dimensionality of the confined system and lead to true phase transitions [24]. Additionally, the existence of a network of interconnected pores of different sizes has an important effect on the adsorption behavior. In particular, the mechanism of capillary condensation may change, because of the pore blocking effect, which happens when pores of large width are connected to the bulk phase only through narrower pores. This effect has been studied using rather DFT (Density Functional Theory) [25] than simulations. The reasons are not accidental: such complex geometry is still a challenge for simulations. Another perturbation is introduced in disordered porous media: the simulations of Monson and coworkers [26–28] are examples of applications of GCMC methodology in such systems. However, it is important to remember that it is difficult to perform reliable simulations for the disordered porous media, because the results are very sensitive to the size of the media represented in the simulations. Several studies have shown that, for example, the resulting phase diagram depends on the particular configuration of the solid media.

Studying the adsorption faces new challenges from the point of view of the application of the statistical physics in computer simulations methods. Two aspects are the most important. First, it is the proper implementation of the statistical ensemble. The multiphase coexistence, a typical situation in the adsorption phenomena, is not simple to simulate numerically. So, non-standard algorithms must be used, such as Gibbs ensemble or the Buffering Field Molecular Dynamics, discussed in this paper. However, the second aspect, the intermolecular interaction, is also crucial for quantitative predictions. These two aspects are strongly coupled; a more realistic interaction model becomes numerically more time consuming and the numerical algorithms must be more efficient. At the same time, the models of adsorbent particles should start taking into account their 3-dimensional structure and the walls of the pores and tubes must be described including their heterogeneous structure. The modern computers and algorithms allow one to build the models of the adsorption phenomena more and more realistic. However, still some balance is needed between the reality of the model and the software and hardware performance. A part of the computational research challenges is to find the right proportion among them and get a new insight into the understanding of the phenomena studied.

A comparison of the simulation results with experimental data and other theoretical models (like spin or lattice gas models) or approaches (like Density Functional Theory) are separate subjects that have been reviewed in recent papers and books [1,2,28,29]. However, we want to emphasize that computer simulation methods are unable to deal with phenomena, where a large length scale is involved. Finally we conclude, that although the available methodology provides many tools suitable for simulations of confined systems, new developments are necessary to deal with complicated geometries of real porous materials and a realistic model of interactions.

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