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Influence of Strength of Atom-Wall Interactions on Adsorption Mechanism

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Abstract. The influence of the atom-wall interaction on adsorption in 4 nm cylindrical pores has been studied using Grand Canonical Monte Carlo simulations. A model with smooth ideal walls has been used to remove the influence of heterogeneous structures. It has been found that the layering transition pressures strongly depend on the atom-wall interaction. The interaction also defines the number of layers adsorbed below the capillary condensation pressure. It has been observed that the stability of adsorbed layers is modulated by the strength of the atom-wall interaction.

Keywords: adsorption mechanism, nanopores, Monte Carlo simulations, atom-wall interaction

1. Introduction

Adsorption is one of techniques used to characterize porous materials. At the same time, the process of adsorption is directly involved in various applications. Numerous examples (Rouquerol et al., 1999) show variety of mechanisms of in-pore adsorption that depend on many parameters such as thermodynamic conditions, surface structures, interactions between the adsorbed particles (adsorbate-adsorbate), between the surface and the particles (adsorbate-adsorbent), and many others. Adsorption isotherms in porous materials are generally of type IV in the IUPAC classification. They are characterized by a steep initial rise at low pressure, proving the strong affinity of the fluid for the pore, followed by a gradual increase in amount adsorbed up to a reduced pressure of around 0.4, where a sharp rise indicative of capillary condensation is observed (Rouquerol et al., 1999). Although these general features and mechanism of adsorption are well known, there is still not many studies to understand the exact role of the wall structures in the adsorption mechanism. In particular, the strength of atom-wall interactions and the role of heterogeneous pore wall compared to the smooth surface are of fundamental importance (Kuchta et al., 2003, 2004).

It has been known for a long time that adsorption isotherms on smooth surface, at relatively low temperatures, can show step-wise behavior. Methane adsorption on MgO, at 87.4 K and at 77 K is a typical example (Gelb et al., 1999). Similar stepwise adsorption has been found for methane in nanoporous graphite at 77 K (Larese et al., 1988), as well as on the exfoliated graphite and graphite foam (Bienfait et al., 1990). Oxygen adsorbed on graphite exhibits layering transitions, between crystalline layers below 43.8 K and liquid like

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at higher temperature (Youn and Hess, 1990). Argon is exhibiting a 're-entrant' layering behavior (Youn and Hess, 1990), in which layerwise transitions disappear near 69 K and then reappear around 74 K. In all these situations, adsorbing gas prefers to complete each successive layer before beginning the next one. In addition, the steps in these isotherms can be very sharp, suggesting a possible interpretation as phase transition type behavior. The shape of the steps and their number depend on the temperature and on the strength of the wall-atom interaction.

The microscopic mechanism of these transitions has been studied using theoretical methods and computer simulation techniques (Gelb et al., 1999). Layering transitions have been found in cylindrical pores of diameter 14σ (σ is the Lennard-Jones parameter) (Peterson et al., 1990), in models of carbon nanotubes with nitrogen and argon as adsorbed atoms (Maddox and Gubbins, 1997), in slit pores (adsorption of methane (Jiang et al., 1993)) and in argon films on graphite (Phillips et al., 1993). Experimentally, the microscopic mechanism of adsorption is always 'hidden' behind the macroscopic measurement. Similarities in the isotherms of adsorption do not mean that the underlying mechanism is the same. This mechanism can be easily modified by the sites distribution and the nature of the interaction of adsorbed atoms. So, the interaction models are the most important components of these approaches. The atom-wall interaction is essential for the adsorption phenomenon because it is competing with the inter-atomic, lateral forces determining the structural stability of the adsorbate.

In this paper we analyze an influence of the wall-pore interaction on mechanism of adsorption in ideal cylindrical pores with non-corrugated (smooth) walls using the Grand Canonical Monte Carlo (GCMC) simulation method. Although similar systems have been simulated before (Balbuena and K.E.Gubbins, 1993), there has not been much of analysis of the mechanism of the adsorption as a function of the interaction strength at different temperatures. In particular, a fundamental problem concerns differences in the mechanism of the layering transition in solid-like and liquid-like adsorbed layers. Also, cylindrical pore geometry, with nano-metric diameter has not been much studied. In such systems the behavior of the adsorbed atom is expected to be different from the one observed on plane surfaces or even in mesopores (Maddox and Gubbins, 1997).

2. Monte Carlo Ensemble and Pore Model

The simulation conditions have been defined in the same way as in our previous papers (Kuchta et al., 2003, 2004) including the applied interaction parameters (Siperstein and Gubbins, 2002). The adsorbed gases are krypton and argon in smooth pores that are used to model of the MCM-41 material, of diameter 4 nm (5σ–6σ). The conventional grand canonical MC ensemble has been applied. The simulation box (50 Å long, with periodic boundary conditions along the axis of the pore) is assumed to be in equilibrium with the bulk gas, which obeys the ideal gas law. This allows us to use the external gas pressure as the thermodynamic parameter instead of the chemical potential (Frenkel and Smit, 1996). Trial moves include translations of atoms, insertion of new atoms and removal of existing ones. The system typically contains in the box from 600 to1300 adsorbed atoms. Some runs have been carried out in the constant volume (with constant number of atoms, that is, NVT canonical ensemble) conditions where only the translations of atoms have been allowed. Typical runs contained the minimum number of MC steps of the order of 10^6 steps (per atom). The main results are extracted from the previously equilibrated runs.

By smooth (or not corrugated) ideal pores we understand perfect cylindrical geometry of walls with atom-wall potential energy which depends only on the distance from the center of the cylinder. Our simulations correspond to a single pore of diameter equal $D = 4$ nm and wall thickness $W > 1$ nm. We have not included inter-pore interaction because the fluid-fluid interaction between atoms in adjacent pores proved to be negligibly small for wall thickness of 1 nm. The choice of the pore diameter is for its nano-metric diameter range where the macroscopic approximation is not valid any more.

In this paper we use a parameter **s** that modifies the strength of atom-wall interaction, directly affecting the ε parameter of the initial (that is, before integration over the wall structure) atom-wall Lennard-Jones interaction. We define it as a coefficient which multiplied par ε gives the effective parameter of the atom-wall Lennard-Jones potential: $\varepsilon_{\text{eff}} = s\varepsilon$.

3. Results and Discussion

The direct influence of the strength of the atom wall interaction is seen from the simulations of the krypton

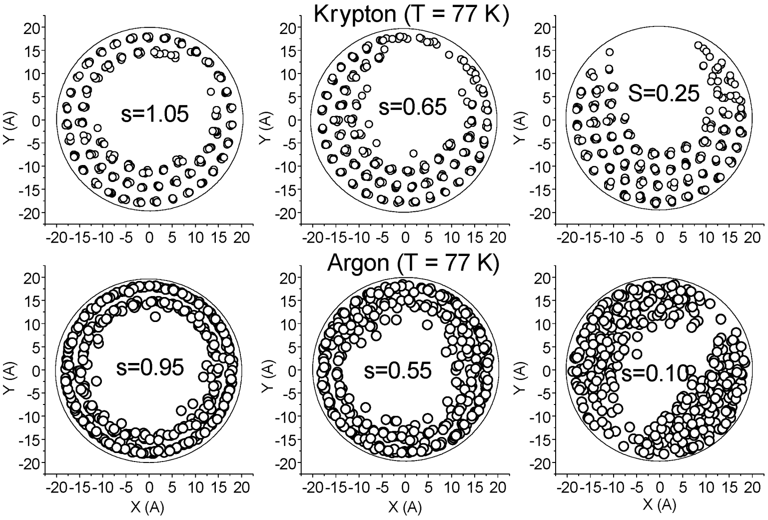

Figure 1. Instantaneous configurations of atoms adsorbed in a smooth wall closed pores calculated at temperature $T = 77$ K for several values of the atom-wall strength parameters s.

and argon (Fig. 1) layers in the pore, at 77 K, in NVT canonical ensemble. Krypton, which forms solid layers at this temperature, is very sensitive to the strength of the interaction. The simulations, performed with constant number of atoms, corresponding to a model of two layers structure in a closed pore, show that the krypton structure becomes much more compact and localized when the attractive forces of the wall decrease. In the same conditions, argon seems to prefer layered structure, even when wall interaction is relatively weak and starts to form more localized structure only when attractive interaction is below 10% of its initial ($s = 1$) value. It seems, that the liquid-like state of the argon layers is less sensitive to the strength of wall-atom interaction. So, one can see that the stability of the adsorbed layers is affected be the strength of atom-wall interaction. As will be seen below, it has important consequences for the mechanism of the layering formations (transitions).

The argon and krypton isotherms of adsorption in ideal smooth cylindrical pores, at 77 K, are shown in the Fig. 2. Obviously, they are very different. The only similarity between these two isotherms is the stepwise form and the low-pressure region (below the first layer formation) where adsorbed atoms form a very low-density structure (two-dimensional analog of gas state). At the same time, krypton isotherm exhibits very sharp formation of the first layer whereas argon shows a more continuous increase of the number of adsorbed atoms. It suggests that the mechanism of layering transition, at constant temperature, depends on the relative strength of the adsorbent-adsorbate particles interaction and interaction between adsorbed particles. The experimental isotherms of adsorption of krypton and argon in MCM-41 show a steep initial rise at low pressure, which is not observed in simulations on smooth walls. Possible reason is the heterogeneity of real walls, not discussed in this paper.

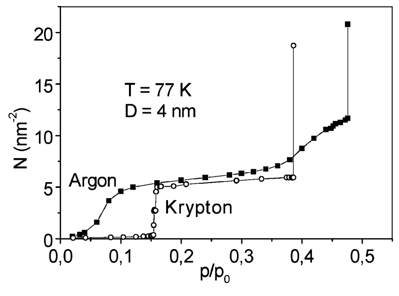

Figure 2. The isotherms of adsorption of Kr and Ar in the smooth wall pore of diameter 4 nm at 77 K. Number of atoms N gives the average number of adsorbed atom per nm^2 of the pore wall. The last reported points correspond to the capillary condensation. P_0's are the saturation pressures at 77 K.

The pressure of layering transition is a continuous function of the strength of the atom-wall interaction (Fig. 3). As could be expected, weaker interaction leads to higher transition pressure. In the limit of no atom-wall interaction (hard walls), the layering transition must disappear. However, weaker interaction also

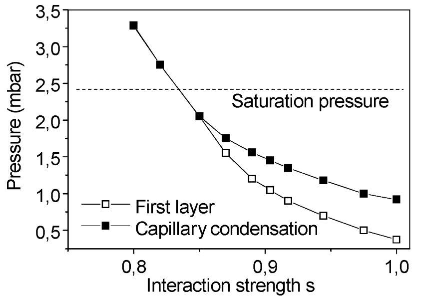

Figure 3. The pressure of the layering transition (first layer formation) and capillary condensation of krypton as a function of the strength parameter.

reduces the range of pressure where the first layer is stable. As it can be seen from the Fig. 3, the difference between the first layer formation and capillary condensation disappears below the saturation pressure of krypton. In such situation, only capillary condensation would be observed in the situation of weak atom-wall interaction. The formation of the first layer may be interpreted as an analog of the 3-dimensional gas-solid phase transition. At 77 K, in krypton, it is very discontinuous. In our Monte Carlo box we have observed a very narrow range of pressures where the system is jumping between gas-like (2D) and solid-like (adsorbed layer) phases. This bimodal behavior is well pronounced and easily observed from instantaneous fluctuations of the number of adsorbed atoms and from the energy fluctuation distribution (Fig. 4). It seems that the free energy barrier between these two states is negligible in these thermodynamic conditions. Remembering that the size of our Monte Carlo system is limited, it is impossible to decide whether this is like I-order or II-order transition. However, no hysteresis was observed. A stronger atom-wall interaction not only shifts the pressure of the transition but also makes it more discontinuous. The mechanism of this phase transition will be discussed in separate paper (Kuchta et al., in preparation). A similar layering transition in argon shows a different mechanism. It shows up in a gradual and continuous manner, in a finite range of pressures. There is no bimodal behavior, as has been observed in krypton, but still the intermediate states between gas-like phase and the full layer structure exhibit much higher fluctuations (in energy and in number of adsorbed atoms) than the initial and final states.

This influence of the atom-wall interaction on the adsorption properties could be seen from our simulations of argon adsorption as a function of the strength parameter s. Stronger interaction not only shifts the pressure of the first layer adsorption but also induces a higher layer formation at higher pressure, before the capillary condensation is observed (Fig. 5). However, the stronger atom-wall interaction is not monotonically increasing the stability of the adsorbed system. Obviously, the number of step-wise adsorption layers depends on the interaction strength. At the same time, it is interesting to observe that the fluctuations show a modulation indicating that the most stable structures correspond to the full layer coverage. The intermediate situations are less stable as can be seen from much higher fluctuations of the number of adsorbed atoms and energy fluctuations (not shown here).

In krypton, the influence of the strength of the atom-wall interaction on the number of adsorbed layers is similar, that is, a stronger interaction induces a formation of the two-layer structure below the capillary condensation pressure. However, no intermediate structure

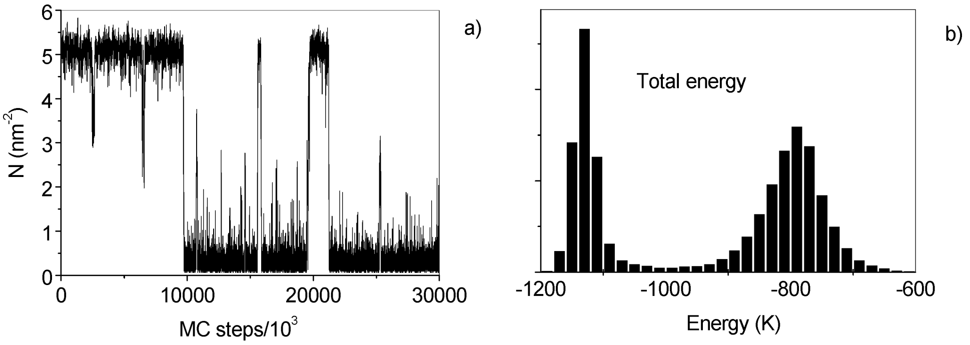

Figure 4. Adsorbed atoms and energy fluctuations at the pressure of the first layer formation of krypton atoms: (a) instantaneous numbers of adsorbed atoms (per nm^2 of the pore wall) as a function of the time of simulation (Monte Carlo steps) observed in a relatively long run, (b) the bimodal distribution of the energy fluctuations is a consequence of the behavior of the systems as shown in the (a).

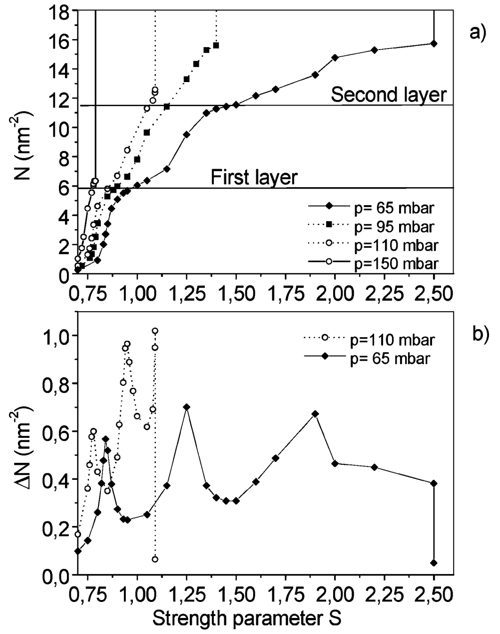

Figure 5. Adsorption of argon (a) as a function of the strength parameter for pressures of 65, 95, 110 and 150 mbar (respectively $p/p_0 = 0.26, 0.38, 0.44$ and 0.6). The fluctuations of the number of adsorbed atoms (b) are shown for two pressures: 65 and 110 mbar.

between first layer and two-layer system is observed. The transition from the one-layer to two-layer phase exhibits a large hysteresis. Also, two-layer structure easily undergoes the capillary condensation transition. Obviously, a detailed study of this behavior requires free energy calculations, which is beyond the scope of this paper.

4. Conclusions

Localized structures (Fig. 1) observed in closed pores for weak atom-wall interactions indicate partial or non-wetting properties, which make the adsorbed layers unstable and preferring to form clusters. In an open pore, the adsorption is not observed as it is shown from the Fig. 3, for the values of $s < 0.85$. It means, that in this range of the atom-wall interaction strength, increasing pressure leads directly to the capillary condensation. One may speculate, that depending on the adsorbate-adsorbate interaction properties, adsorption in the form of clusters may be observed in such situations. This problem requires more studies from the theoretical point of view.

It is obvious that the atom-wall interaction itself does not define stability of adsorbed atoms. It is rather the correlation between lateral and vertical interactions that stabilizes the final structure. However, the strength of the atom-wall interaction affects the properties of the adsorbed system, such as the number of adsorbed atoms, so it modifies indirectly the stability of the adsorbed system in defined thermodynamic conditions. Also, it changes the pressure of the layering transitions as well as the pressure of the capillary condensation.

At the same time, the variation of strength of the wall-atom interaction changes adsorbing properties in a non-monotonic way. As a result, the stability of adsorbed system is a modulated function of the interaction strength parameter s and one observes step-wise adsorptions on smooth (or regular, with small corrugation amplitude, as carbon nanotubes) surfaces of cylindrical pores. This behavior is a consequence of the fact that intermolecular interactions prefer some specific types of ordered structure (usually, compact full layer structures). So, the experimentally observed situations with gradual increase of adsorbed amount in pores must be a consequence of heterogeneous surface and possible micropores structure. It means, that smooth and regular isotherms are observed because of the structural disorder of adsorbing walls (structural as well as energetic), which induces some disorder on the first adsorbed layer and, consequently, destabilizes the ordered layer situation.

The mechanism of layer formation depends on the interaction strength and on thermodynamic conditions, particularly, on temperature. At temperatures where the first adsorbed layer is more solid like, one observes only a rapid layers formation, then the capillary condensation. All intermediate states are not stable. At temperatures where the layer is more like a liquid, one observes intermediate multilayer adsorption. As one could expect, the most stable are the structures corresponding to full layer coverage. So, we may conclude, that in adsorbing system there are at least two factors, which by inducing a disorder to the system, make isotherms more regular and continuous: heterogeneity of the wall structure and increased temperature. This conclusion suggests that observations of changes of the form of the adsorption isotherms, in the range of temperatures where the first layer is undergoing a solid-liquid phase transition, may be used as a complementary method in porous materials characterization. The analysis of the melting transition in layers adsorbed in pores will be presented in a future paper.

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