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# Modeling of adsorption in pores with strongly heterogeneous walls: parametric lattice-site wall model

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**Abstract** We present results of grand canonical Monte Carlo simulations of adsorption in cylindrical pores with rough surface modeled by a parametric lattice-site approach. The sites are randomly distributed over the pore walls. They could be attractive, neutral or repulsive with respect to the smooth pore model. Each site is characterized by two amplitudes (structural and energetic) which modify locally the structure and energetic properties of the surface. The results presented here show how different parameters of the model affect the mechanism of adsorption and, consequently, the form of the isotherm.

**Keywords** Pores · Heterogeneous walls · Lattice-site model

## 1 Introduction

Numerical modeling of adsorption mechanism on heterogeneous surfaces is in the period of important development and enormous progress has been made during the last 10 years. Consequently theoretical (numerical) treatments of such systems appear to be capable of reproducing typical features of experimental data in a better way than the smooth wall models (Feuston and Higgins 1994; Maddox et al. 1997; Patrikar 2004; Mischler et al. 2002; Stallons and Iglesia 2001; He and Seaton 2003; Vuong and Monson 1998; Sonwane et al. 2005; Kuchta et al. 2004, 2007; Puibasset 2005; Cao et al. 2004; Ravikovitch et al. 2006; Ravikovitch and Neimark 2006; Fox and Bates 2005; Coasne et al. 2006; Hung et al. 2007). However, there are many systems, in particular among porous materials, where the details of influence of wall heterogeneity on adsorption mechanism are not fully understood. It is the purpose of this paper to discuss the main factors which influence the mechanism of adsorption using a lattice-site model of pore heterogeneity.

The problem of adsorption of gases on flat heterogeneous surfaces has been reviewed and the existing theoretical models have been discussed in the book by Rudzinski and Everett (1992). The first numerical studies of adsorption on heterogeneous plane surfaces used simple lattice site models (Nicholson and Silvester 1977; O'Brien and Myers 1985). The conclusion emerging from these papers emphasized that an observation of either smooth or stepped isotherms is not uniquely associated with the degree of heterogeneity of adsorbing surface. The importance of adsorbate-adsorbate potential well has been emphasized. As a consequence of this conclusion, the temperature must be also considered as a factor modifying the mechanism of adsorption as it effectively makes the well shallower.

Interesting discussion of an influence of heterogeneity on the adsorption mechanism was presented by Steele et al. (Bojan and Steele 1988; Bakaev and Steele, 1992a, 1992b; Bojan et al. 1992). In their papers, the computer simulations were used to study the relation between the form of an adsorption isotherm and the surface structure. One of the conclusions stated that the shape of the isotherm in supermonolayer region depends on two factors: the energetic heterogeneity and the geometric heterogeneity of the adsorbent. In particular, the authors pointed out that the structural roughness of the adsorbing surface is transmitted to the first

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layer of adsorbed particles producing a distribution of adsorption sites for higher layers. As a consequence, the adsorption mechanism in mesopores shows smooth multilayer character before a capillary condensation. At the same time, the calculations showed that, at small coverage, the shape of the adsorption isotherm is determined practically only by the distribution of adsorption sites energy. It is the purpose of this paper to discuss all the mentioned factors using a model of heterogeneity in cylindrical pores proposed below.

## 2 Heterogeneity models

We propose a parametric model of pore surface based on a concept of lattice-site model and takes into account both, energetic and structural, distributions of the adsorption sites. It defines the surface heterogeneity as a modulation of the uniform potential given by the function $V_{smooth}(r)$ and representing smooth wall pore model. The variable r is the radial coordinate of the fluid atom with respect to the pore center.

The surface of the smooth cylinder with the radius R and the length $L_z$ has been divided into small areas (2-dimensional cells) of rectangular shape. $L_z$ is the length of the MC box in our simulations. The size of each rectangle is defined by two parameters: an angle $\Delta\phi$ and a length $\Delta z$ (see Fig. 1). The angle $\Delta\phi$ gives the length of the curved side of rectangle ( $= R^*\Delta\phi$) along the circumference and the value $\Delta z$ gives its length along the pore axis. Consequently, we have the lattice site elements $s_{i,j}$ ($i = 1, (2\pi/\Delta\phi)$ and $j = 1, (L_z/\Delta z)$) with the total number of the cells $s_{i,j}$ equal to $(2\pi/\Delta\phi) * (L_z/\Delta z)$.

There are two parameters related to each site: structural amplitude $\Delta r$ and energetic relative amplitude $\Delta f$. They define the properties of site's rectangular surface. The distribution of the values $\Delta r$ characterizes the structural heterogeneity of the total surface. The positive values of $\Delta r$ shift locally the wall surface towards the center of the pore and the negative values in the opposite direction, making the pore locally a bit thinner or larger (see Fig. 2a). The energetic heterogeneity parameter $\Delta f$ is defined as a ratio of the heterogeneous amplitude with respect to the uniform $V_{smooth}(r)$ function (see Fig. 2b) and the lattice site energy is calculated as:

$$V_{smooth}(r) * (1 + \Delta f)$$

Finally, we have introduced a parameter $\lambda$ to define the spatial extend of the variation of the lattice site energy $\Delta f$. This parameter determines what is the 'energetic deepness' of specific lattice site. In the model, it is described using the exponential function. The final equation of the heterogeneous energy is the following:

$$V_{heter}(r)_{ij} = V_{smooth}(r + \Delta r_{ij}) * (1 + \Delta f_{ij} * \exp[-(R_{min} - r)/\lambda_{ij}])$$

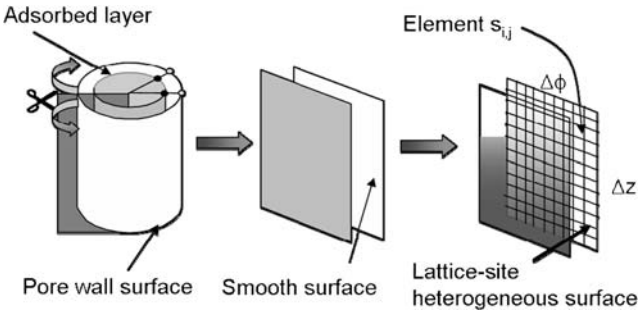


**Fig. 1** Definition of the lattice distribution sites on the surface of the cylindrical pores

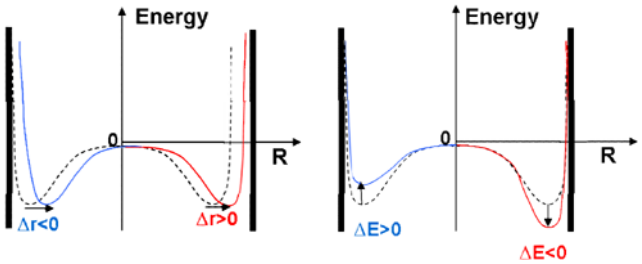


**Fig. 2** Local variation of the smooth potential $V_{smooth}(r)$ (*dashed line*) due to the structural amplitude $\Delta r$ and energetic amplitude $\Delta f$ (shown as the energy shift $\Delta E = V_{smooth}(r) * \Delta f$)

**Table 1** Parameters defining the surface heterogeneity in our model

| | |
|---|---|
| N | number of different types of lattice-sites (N-state model) |
| $\Delta\phi$, $\Delta z$ | dimension of the surface lattice-site (see Fig. 1) |
| $p_1, p_2, \ldots, p_N$ | probabilities corresponding to each type of lattice-site |
| $\Delta r_1, \Delta r_2, \ldots, \Delta r_N$ | structural amplitudes of each type of lattice-site |
| $\Delta f_1, \Delta f_2, \ldots, \Delta f_N$ | energetic amplitudes of each type of lattice-site |
| $\lambda_1, \lambda_2, \ldots, \lambda_N$ | energetic depth of lattice sites |

This formula represents the energy of the adsorbate-adsorbent interaction for a fluid particle located above the lattice site $s_{i,j}$ and at the distance r from the pore center. $R_{min}$ is the distance from the pore center where the $V_{smooth}(r)$ function has its minimal value. Table 1 gives all parameters defining the heterogeneous model.

We compare the results obtained with our parametric model with those for an atomistic amorphous silica surface generated using a stochastic distribution of the silicon and oxygen atoms in a ratio 2:1 (He and Seaton 2003). The atoms are randomly distributed to form the amorphous wall surface of the cylindrical shape. The wall is modeled in the same way as the heterogeneity of the parametric model presented above, that is, there is a distribution of structural amplitudes $\Delta r$ on the surface of the cylinder. This distribution is programmed as a constraint in the wall preparation procedure. In this way, we have two situations having similar

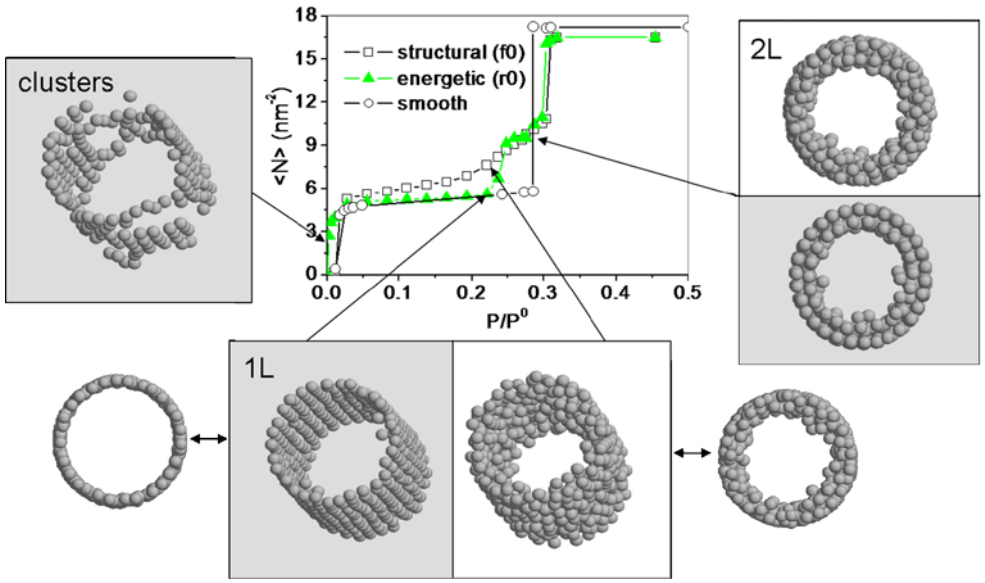


**Fig. 3** Adsorption in model heterogeneous pores. Two limiting isotherms are presented: with purely structural (f0) and purely energetic (r0) heterogeneity of the pore wall. The instantaneous configurations show characteristic structural features for each heterogeneity model (structural—*white background*, energetic—*grey background*). The image labeled '*clusters*' shows a typical low pressure structure in pore with energetic heterogeneity. The images labeled '*1L*' correspond to the region where the monolayer is still observed (in the pore with energetic heterogeneity). The images '*2L*' are the structures just before the capillary condensation

**Table 2** Parameters defining the surface heterogeneity of the 3-state model: structural amplitudes $\Delta r_i$ (in nm), energetic amplitudes $\Delta f_i$ and probabilities $p_i$ of finding the state $i = 1, 2, 3$. $\Delta f$'s are dimensionless as they are the fractions of the $V_{smooth}(r_{min})$ energy ($r_{min}$ is the distance along the pore radius corresponding to the minimal value of the $V_{smooth}(r)$ energy)

| | $(\Delta r_1,\ \Delta r_2,\ \Delta r_3)$ | $(\Delta f_1,\ \Delta f_2,\ \Delta f_3)$ | $p_1, p_2, p_3$ |
|---|---|---|---|
| Model smooth: | (0.0, 0.0, 0.0) | (0.0, 0.0, 0.0) | 0.4; 0.2; 0.4 |
| Model f0: | (−0.05; 0.0; 0.05) | (0.0, 0.0, 0.0) | 0.4; 0.2; 0.4 |
| Model r0: | (0.0; 0.0; 0.0) | (0.3; 0.0; −0.2) | 0.4; 0.2; 0.4 |

structural form of the pore surface. At the same time, it is clear that their energetic characteristics are different. In the parametric model it results from the distribution of energetic amplitudes whereas in the atomistic model it comes directly from the interaction with the silicon and oxygen atoms in the walls. Below we discuss these two approaches from the point of view of the adsorption mechanism in heterogeneous pores.

## 3 Results

Figure 3 presents the adsorption isotherms for methane, calculated within our heterogeneous model of the wall, for two limiting situations: first, pure structural corrugation (Model f0, Table 2) and, second, a pure energetic corrugation (Model r0, Table 2). In this paper we use a 3-state model (N = 3, in the Table 1). The characteristic feature of the adsorption with pure structural heterogeneity is a continuous increase of the amount of the adsorbed mass. It is observed between the pressure of the first layer formation and the pressure of the capillary condensation. The main factor which is responsible for such form of the isotherm is the disorder introduced by the structural heterogeneity. This structural roughness is transmitted to the first layer of adsorbed particles producing a distribution of adsorption sites for higher layers. One can easily see the difference looking at the instantaneous configurations shown in the Fig. 2 (indicated as 1L and 2L). They illustrate the fact that structurally heterogeneous wall does not support ordered layer formation. As a consequence, the adsorption mechanism shows continuous multilayer adsorption before the capillary condensation occurs. However, at low pressure, before the first layer formation, the behavior is similar to the smooth pore situation, that is, the adsorption is negligible (very low density, 2-dimensional gas).

In the second limit, one observes that the pure energetic heterogeneity is able to make the low pressure adsorption much stronger (one can observe a formation of clusters at low pressures, before the first layer is formed, see image in Fig. 3) but it cannot modify the step-wise adsorption at higher pressures. Low pressure adsorption is the consequence of strong attractive adsorption sites which induce formation of local cluster and rapid formation of the first layer at low pressure. At the same time, structurally the surface is smooth. Consequently, the first layer structure is ordered (see corresponding instantaneous configurations in the

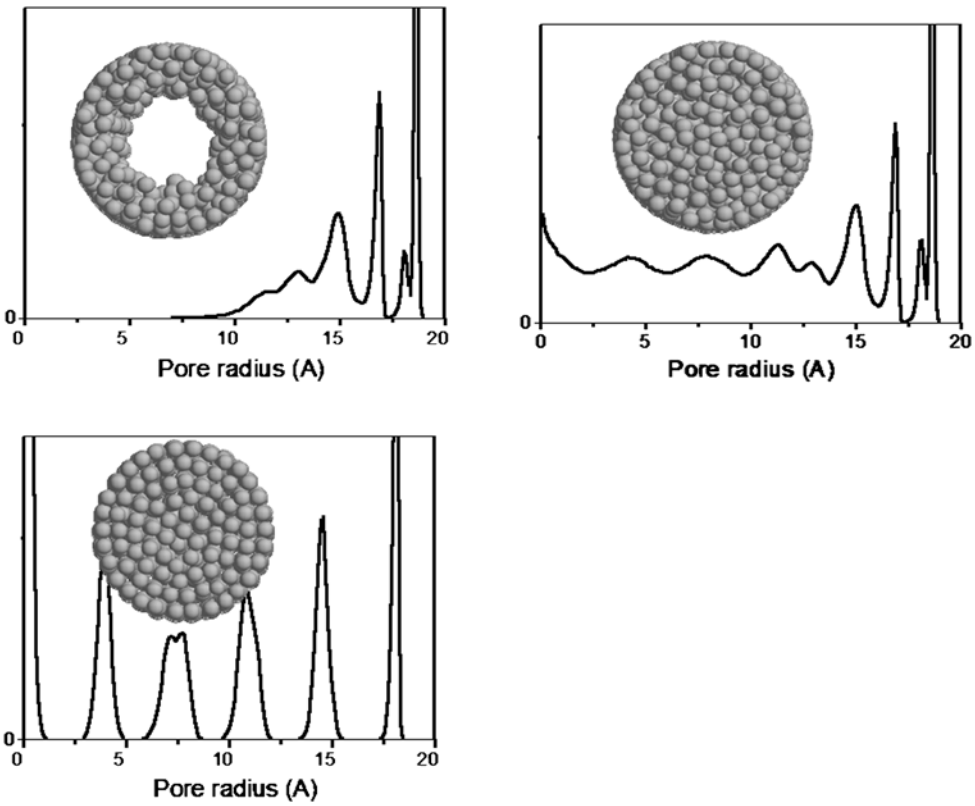


**Fig. 4** Radial density distribution in totally heterogeneous pore (**a**, **b**) and in a pore with limited (only energetic) heterogeneity (**c**)

Fig. 3) and the adsorption shows a typical step-wise character after the first layer is formed.

A disordered structure of the adsorbed system seems to be the key feature to understand the evolution of the step-wise form (observed in pores with wall having a regular structure) into continuous adsorption characteristic for amorphous walls existing in almost all real porous materials. The disorder has its source mainly in structural heterogeneity, amplified by the energetic distribution of adsorption sites.

As a consequence of the existing disorder, the properties of the adsorbed phase are different. Figure 4 compares the radial density distributions in heterogeneous pore, with both structural and energetic heterogeneity (Fig. 4a—before capillary condensation, Fig. 4b—after capillary condensation) with the limiting situation of only energetic heterogeneity (Fig. 4c—after capillary condensation). In the pore with energetic heterogeneity the layer are adsorbed in a very regular way, similar to the smooth wall situation. The subsequent layers are also very well defined. Only the presence of the structural heterogeneity make the adsorbed structure disordered. Even our model 3-state situation makes the first layer so disordered (layer thickness $\sim$4 Å, see Fig. 4a, 16 Å $<$ r $<$ 20 Å) that the final radial density distribution resembles more a liquid like state (see Fig. 4b). This assures a distribution of adsorption sites, for each layer, and leads to smooth, continuous adsorption in the multilayer range, as argued above.

## 4 Discussion and conclusions

We have shown that structural and energetic heterogeneities of pore walls in cylindrical pores, is well represented by our lattice-site model. An application of the model allows one to discuss different aspects of adsorption mechanism on microscopic level. In this paper we have analyzed the most simple, 3-state model, which exhibits many interesting features. First, the energetic heterogeneity or, in other words, the adsorption energy distribution on the wall surface plays the most important role in first stage of adsorption. It determines the pressure of the first layer formation, its kinetics and possible formation of a cluster structure at low pressures. However, it is the structural heterogeneity which is responsible for multilayer adsorption. Our model shows that the main difference between a step-wise and continuous isotherms stems from a degree of structural heterogeneity of the adsorbing walls as it is expected in real pores. Regular wall structure leads to step-wise adsorption. When they become more heterogeneous, continuous multilayer adsorption is observed. We conclude that the lattice site model represents the main features of real heterogeneous cylindrical pores.

Additionally, we verified validity of the presented parametric model of heterogeneity by comparison with an atom-based model. The most important observation was the following: the wall built from randomly distributed atoms around a cylindrical surface leads to step-wise adsorption. A continuous increase of the adsorbed mass in multilayer region could be obtained only if a distribution of structural amplitudes $\Delta r$, on a scale larger than a typical atomic size, was introduced. In other words, the atomic scale heterogeneity was not enough. It is a nanoscale corrugation which modifies mechanism of adsorption, as it is represented in our lattice site model. This comparison has shown why our simple lattice site model exhibits similar profile of adsorption as real heterogeneous pore surfaces. It is worth emphasizing that an application of the lattice site model does not depend on the source of heterogeneity. It could be due to an amorphous structure of the wall and a particular method of the pore synthesis, as in the case of MCM-41 pores. However, one can easily imagine that the same model could be applied on initially regular (crystalline) surface with an important distributions of defects. The details of simulations with atomistic walls will be presented elsewhere.

Finally, we want to emphasize another factor that introduces disorder on microscopic level, that is, the thermal energy. When temperature rises, the entropic effect makes the system more disordered and, apparently, its effect is similar to the influence of structural heterogeneity. As a consequence, at higher temperatures, even relatively smooth surface may show continuous adsorption. Therefore, high temperature adsorption cannot be considered as a rigorous test confirming the correct model of any surface. Although this comment may seem to be an obvious one on the base of general thermodynamic properties, the calculation carried out within our lattice site model showed precisely that the mechanism of adsorption is very different in both cases. It is only the low temperature adsorption simulation which can serve as a final verification of models used to represent different types of heterogeneity.

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