

## Modeling of adsorption in pores with strongly heterogeneous walls. Computer simulations approach\*

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We discuss the state of art in computer simulation of adsorption in nano-pores with strongly heterogeneous rough wall structures. As an example, we review the recent models used in simulations of MCM-41 adsorbent and discuss their capacity to reproduce experimental adsorption isotherms, in the whole range of relative pressures. The conclusions of previous studies are compared with our recent model of heterogeneous pores characterized by separately energetic or structural heterogeneity, or both of them. On this basis we identify the main factors responsible for the mechanism of adsorption and discuss their influence on the results of simulations of adsorption. Some possibilities of further improvements of the model are also suggested.

### 1. INTRODUCTION

During the last two decades the use of computer simulation methods to investigate properties of physisorbed systems has become a well-known and wide-spread methodology. The calculations based on grand canonical Monte Carlo (GCMC) or Density Functional Theory (DFT) simulations have proven their validity in modeling adsorption on external as well as internal (porous) a large variety of surfaces. Most of these the early calculations have studied focused on the adsorption on structured but regular surfaces (such as graphite,

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carbon nanotubes or zeolites); in cases of and for amorphous surfaces structures, an ideal smooth wall model was usually adopted. Numerical modeling of adsorption mechanism on heterogeneous surfaces is in the period of important development and a remarkable progress in concepts and techniques has been made during the last 10 years. The recent theoretical (numerical) treatments of such systems appear to be able to reproduce typical general features of experimental data in a better way than the smooth wall models [1-18]. However, there are many systems, in particular among porous materials, where the detailed influence of wall heterogeneity mechanism on adsorption is not yet fully understood.

Some aspects of adsorption of gases on flat heterogeneous surfaces have been reviewed in the book by Rudzinski and Everett [19]. In particular, it has been pointed out that an observation of smooth or stepped isotherms is not uniquely associated with the degree of heterogeneity of adsorbing surface. The first numerical studies of adsorption on heterogeneous plane surfaces, using simple lattice site models, have emphasized the importance of adsorbate-adsorbate potential as well [20,21]. The conclusion emerged from these papers emphasized. Of course, these two factors: surface heterogeneity and adsorption strength are never independent in real systems. As a consequence of this conclusion In reality, the temperature must be also considered as a factor modifying the mechanism of adsorption because it makes the effective adsorption energy surface as the well shallower. We discuss this aspect later in this paper.

Interesting studies of an influence of wall heterogeneity on the adsorption mechanism was proposed by Steele and co-workers. [22-25]. In their papers, computer simulations were used to model the relation between the shape of the isotherms and the surface structure. They demonstrated that the shape of an adsorption isotherm depends on two factors: the energetic heterogeneity and the geometric heterogeneity. Depending on the surface coverage, one or the other factor is predominant. At low coverage, in submonolayer regime, the shape of the isotherm is determined practically only by the energy distribution (over ? the adsorbing surface). of adsorption sites. Beyond the monolayer, as the distance from the wall increases and, as a consequence, the strength of the interaction with the wall decreases, this is geometric, structural roughness of the adsorbent that is of higher importance. Actually, the structural roughness of the wall is transmitted through the first to the second layer of adsorbed particles producing a distribution of adsorption sites for higher layers. As a consequence, the adsorption progresses smoothly through multilayer formation before a capillary condensation occurs. These conclusions are still valid in the case of adsorption on non-planar surfaces (in pores), as we discuss below.

Atomic level heterogeneity can be introduced in simulations in two different ways: either by an explicit construction of the atomic structure resembling the real amorphous/disordered situation or by (statistically) parametric definition of the energetic and/or structural adsorption sites distribution. Both approaches were explored in initial papers by Steele et al. [22-25], however, the methodology evolved during the last 5 years [2-18].

As an example, let us discuss the evolution of the model structures of nanoporous silica MCM-41 used in computer simulations. Early papers [1] proposed MCM-41 models obtained using the classical molecular dynamics simulations. The use of quantum molecular dynamics simulations [3] allowed one to improve short range order structure of the material as compared with the classical case. Monte Carlo simulations and energy minimization were also used to build either a relaxed silica surface or a randomly generated structure [4]. However, none of those models [1-4] tested the surface through adsorption simulations. The model structures were only compared to experimental data, either structural [1] or calorimetric (heat of adsorption and diffusion activation energy [4]). In general, the exact comparison of the models and the real surfaces was not possible because of lack of detailed relevant experimental data. Therefore, even the raw analysis [4] suggested a large distributions of the adsorption sites, both energetic (between -25 and -5 kJ/mol) and structural (surface roughness amplitude  $\cong \pm 3.5 \text{ \AA}$ ).

The realistic models of the plane amorphous silica surfaces with potential application in adsorption modeling were usually prepared using one of four techniques [4]: (1) an ordered surface was created by cutting of a known silica polymorph; (2) an unrelaxed amorphous surface was obtained by cutting bulk amorphous silica; (3) a relaxed amorphous surface was created by relaxing the amorphous surface; and (4) a random surface was created by Monte Carlo simulations. All these approaches are general and may be applied to prepare plane surfaces but also to model porous materials. The review of these models leads to the important conclusion: models assuming ideal cylindrical geometry of the pore, regardless its smoothness (ideally smooth or atomistic, disordered crystalline or stochastic), cannot be used as a representation of the true structure of MCM-41.

The new atomistic models of the structure of MCM-41, based on the method previously described by Feutson and Higgins [1] and incorporating surface roughness were proposed in the recent paper by Sonwane et al. [7]. The new approach consists in incorporating bulk heterogeneity: structure of the interstitials between the pores and wall indentations to reproduce the shape of the surface. The authors suggested that structural heterogeneity on a scale larger than the interatomic distances is probably necessary to reproduce the real structures of many porous materials, not only MCM-41. In the case of this

material, the validity of the model was confirmed through comparison with X-ray diffraction experimental results [7]. It is worth emphasizing that this conclusion is in general agreement with earlier Steele's et al. suggestions [22-25].

The studies of He and Seaton [5] explored three other models of MCM-41 pore structure, including different degree of heterogeneity of the silica wall. The first model consisted in a structure built up by three concentric cylinders of oxygen atoms. This model was homogeneous at atomic scale. The second model was based on  $\alpha$ -quartz structure in which the atoms were removed from a cylindrical volume to form the pore. The third model included the surface heterogeneity at the highest degree. In this model, the amorphous matrix of MCM-41 walls was generated using a stochastic procedure. Oxygen and silicon atoms were first randomly generated in a cylindrical simulation box and then allowed to move according to an energy minimization algorithm, keeping the coordination numbers of silicon and oxygen atoms constant and equal to their physical values (4 and 2, respectively).

The results of simulations using the above described models confirmed the general conclusions [7] pointing at the heterogeneity of the surface as a primary factor affecting the shape of isotherms. In all three models, the calculated adsorption isotherms fit quite well the experimental ones in the high pressure (multilayer) range. However, important differences between the models were reported at low pressure where the energy distribution plays the most important role. Only the last model gave accurate results across the whole range of pressures (for adsorption of ethane and ethane-carbon dioxide mixtures at temperature above 264.6 K). Unfortunately, most of simulations have been performed at relatively high temperatures where the details of the surface structure are less important due to the thermal disorder. Lower temperatures have not been studied and in consequence the full evaluation of the models cannot be established.

Atomistic, strongly disordered models of structural heterogeneity in MCM-41 materials have also been proposed [26-28]. These models allowed one to analyze numerically the adsorption as a function of different type of atomistic walls, from relatively regular cylinders up to very irregular pores that mimic morphological features of the original template mesoporous materials [26,27]. Some of these situations are studied in papers by Coasne et al. [14,15,16] and give an interesting analysis of the influence of the wall heterogeneity on the isotherms shape, capillary condensation pressures and heat of adsorption. Many features of modeled systems (Ar and Xe in MCM-41) reproduced the experimental observations. The authors analyze the differences between calculated and experimental data and find that the adsorption is much faster than the experimental one although the adsorbed mass increases continuously in the

multilayer adsorption region. Obviously, the simulated situation stabilizes more layers before the capillary condensation occurs than the real system. Such behavior suggests that a competition between the strength of the fluid-wall interaction and the degree of structural heterogeneity is probably not totally correct in the model. One more time, the low temperature study (simulations and experiments) could help to rectify this point and give more insight into the mechanism of initial stages of adsorption. Comparing the results obtained for two models of the wall (differing by the degree of their structural heterogeneity) the authors advance the idea of two scales of structural heterogeneity that could be important in mechanism of adsorption: molecular and nanometric. This notion is interesting and should be explored.

One of the first heterogeneous MCM-41 model defined by a distribution of adsorption energy sites and applied to simulations of adsorption of nitrogen was proposed by Maddox et al. [18]. The authors showed that a one-dimensional homogeneous potential predict poorly the adsorption of nitrogen in 4 nm pore at low pressure and  $T = 77.4$  K, whereas a heterogeneous, two-dimensional potential that greatly fluctuates around the pore wall give an excellent agreement for low-pressure adsorption data. It is interesting to note that even the smooth model represented the higher-pressure, super-monolayer adsorption in a reasonable way. We will address this fact later, showing that the multilayer adsorption becomes more sensitive to heterogeneity of adsorbing surfaces at lower temperatures. Apparently, the temperature of 77.4 K is high enough to smear out the effect of wall heterogeneity for nitrogen adsorption in 4 nm wide MCM-41 pore.

Similar approach was applied by Ravikovitch et al. [11] for simulation of adsorption of toluene in MCM-41. As the initial homogeneous model was not able to reproduce the low pressure adsorption, the authors introduced a heterogeneity of the adsorbing surface by placing at random over the surface attractive and repulsive sites. Such procedure introduced an adsorption sites distribution and, as a consequence, improved the low pressure adsorption. At the same time, this procedure seems do not introduce large structural heterogeneity. However, to test this feature one would need some lower temperature simulations and comparison with experimental data, not referenced in the paper.

Very recently, Density Functional Theory has also been used to model the influence of structural heterogeneity on the adsorption [12]. Although this approach, called by the authors *quenched solid density functional theory* cannot directly help us to understand the mechanism of adsorption in heterogeneous pores, it shows that using an appropriately averaged models one can reproduce the most characteristic features of isotherms. This conclusion seems to be very important for potential application in rapid industrial characterization of porous materials.

In summary, the general picture emerging from the recent studies of adsorption in mesopores with rough, heterogeneous walls is the following: (i) Although several models of heterogeneous walls have been proposed, there is no unique model which reproduces all features observed in experiments. (ii) The energetic site distribution is the primary factor determining the low pressure adsorption. (iii) The structural roughness seems to be the most important factor responsible for multilayer adsorption. (iv) Both molecular scale and nano-scale heterogeneity is probably necessary to reproduce continuous increase of adsorption in multilayer regime. (v) Low temperature adsorption is testing the heterogeneity models more rigorously.

In the following chapter we present our heterogeneity model that try to reproduce the adsorption isotherm the both sub- and super-monolayer regimes and to give a better microscopic insight into adsorption mechanism. The model is defined by a parametric adsorption sites distribution. We discuss the main qualitative results which compliment and summarize the general conclusions of the review presented above. Detailed and more quantitative analysis is presented in other authors' papers [8,17,29,30].

## 2. HETEROGENEITY MODEL

Our model of the heterogeneous pore wall assumes distributions, both energetic and structural, of the adsorption sites. As a starting point to define surface heterogeneity in the pore we have used a lattice-site model. It is defined as a modulation of the uniform potential given by the function  $V_{\text{smooth}}(r)$ , representing the interaction of the fluid atom or molecule with the pore that the wall is smooth. The variable  $r$  is the radial coordinate of the fluid atom with respect to the pore center. To prepare the lattice model of the pore wall, we proceed as follow. 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 Figure 1). The angle  $\Delta\phi$  gives the length of the curved side of the rectangle ( $= R*\Delta\phi$ ) along the cylinder circumference and the value of  $\Delta z$  gives its length along the pore axis. Consequently, we obtain the lattice site elements  $s_{i,j}$  ( $i = 1, (2\pi/\Delta\phi)$  and  $j = 1, (L_z/\Delta z)$ ). The total number of the cells  $s_{i,j}$  is equal to  $(2\pi/\Delta\phi)*(L_z/\Delta z)$ .

Two parameters are 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  $\Delta r$  values characterizes the structural heterogeneity of the

total surface. The positive  $\Delta r$  values shift locally the wall surface towards the center of the pore and the negative values in the opposite direction, modifying locally the pore diameter. The energetic heterogeneity parameter  $\Delta f$  is defined as a ratio of the heterogeneous amplitude with respect to the uniform  $V_{\text{smooth}}(r)$  function and the site lattice site energy is calculated as:

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

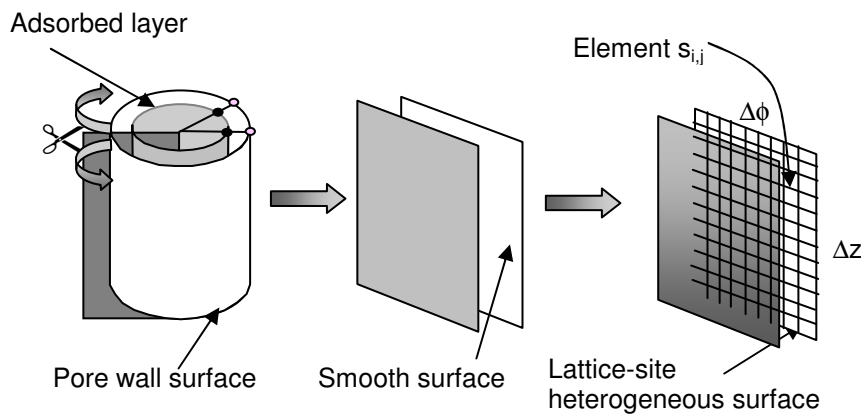


Fig. 1. Definition of the lattice sites on the surface of the cylindrical pores.

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 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:

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

This formula represents the energy of the adsorbate-adsorbent interaction for a fluid particle located above the lattice site  $s_{i,j}$  at the distance  $r$  from the wall surface.  $R_{\text{min}}$  denotes the distance from the pore center where the  $V_{\text{smooth}}(r)$  function minimal value.

### 3. ADSORPTION IN HETEROGENEOUS MODEL

It is more convenient to discuss the principal features of our model starting from simulations with limited heterogeneity. As an example, Figure 2 shows

calculated isotherms of methane adsorption in MCM-41 pore of the average diameter of 4 nm, in two limiting situations: first, assuming pure structural corrugation of the wall (Model f0) and second, considering only energetic corrugation (Model r0). In the first situation, we observe a continuous increase of the amount of the adsorbed mass. The main factor responsible for such form of the isotherm is the disorder introduced by the structural heterogeneity. The structural roughness of the wall results in a disordering of the adsorbed layer that, in his turn becomes a rough substrate for the particles adsorbed in second layer and producing a distribution of adsorption sites for higher layers (see Figure 3).

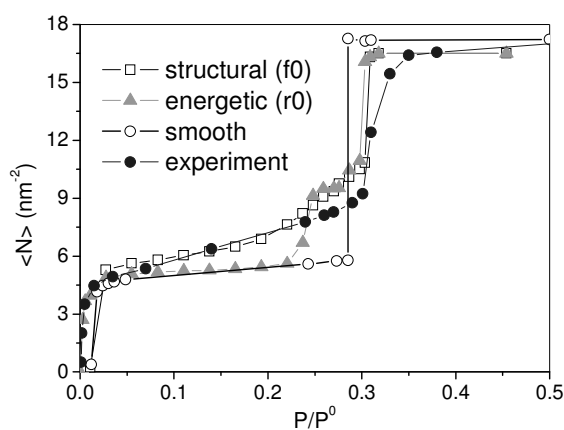


Fig. 2. Isotherms of methane adsorbed in heterogeneous MCM-41 pores calculated assuming two limiting models of heterogeneity: purely structural or purely energetic. For comparison, the isotherm calculated using smooth wall model and the experimental data are also presented.

On the contrary, the pure energetic heterogeneity (the second limiting case), is able to reinforce the adsorption at low pressure. It is the result of existence of strongly attractive sites which inhibit the nucleation of local clusters and rapid formation of the first layer. However, for the same reason, it cannot eliminate the step-wise adsorption at higher pressures.

Another insight into the influence of wall heterogeneity on the mechanism of adsorption comes from the analysis of the adsorbed layer structure. Figure 3 shows the radial distribution of adsorbed molecules in both limiting models of pores. Purely structural roughness (left panel) produces disordered first layer and this disorder is clearly transmitted to higher levels. The first three peaks next to the wall composing the first layer are clearly the consequence of our choice of



3-state model of structural roughness. Obviously, if higher,  $n$ -state model was applied, the first layer structure would be even more disordered. As a consequence of the disorder appearing in the first layer, starting from the second layer the adsorbed structure is totally disordered.

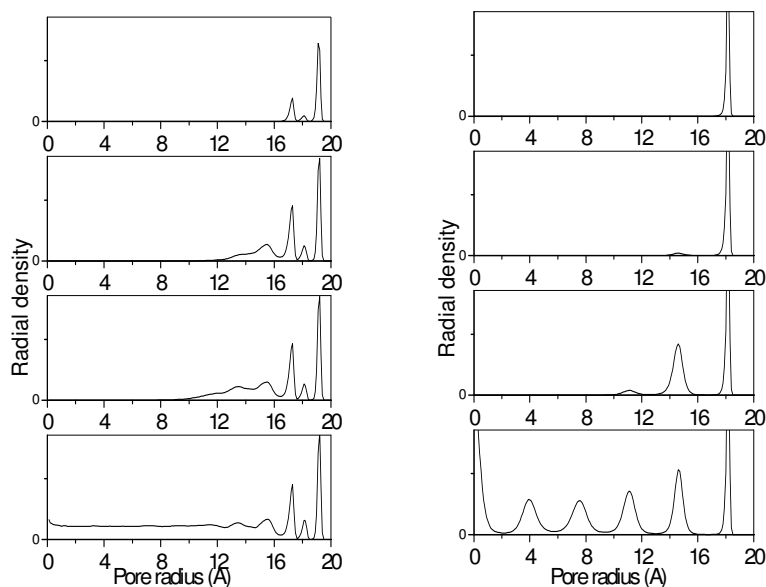


Fig. 3. Radial density in pores with purely structural (left) and energetic (right) heterogeneity. The simulations were done at  $T = 77$  K, and the pressure are (from the top to bottom)  $p = 0.05, 3.0, 4.0, 4.5$  mbar.

On the other hand, if only energetic heterogeneity is present (right panel), the layers are formed one by one and continuous adsorption in multilayer region is not possible. This situation does not differ from that observed in simulations using the smooth wall model: the layers observed in radial density distribution are very clearly defined and the inter-layer density very small.

Figure 4 shows typical instantaneous configurations in both models. The important structural differences, related to both types of heterogeneity, are clearly seen. We have to stress, that the partial layer coverage is always unstable when the structural heterogeneity is absent. On the other hand, a complete layer is always more stable in an ordered system. Energetically, it means, that if thermodynamic conditions allow the particles to adsorb in a new layer, it is more stable to adsorb the whole layer instead of partial one.

The above conclusion introduces immediately the question of the role of temperature in the adsorption process. Some elements of the answer come from

the analysis of Figure 5, where the isotherms simulated using smooth wall model, but at different temperatures are presented. When temperature increases, the form of the isotherm passes from a step-wise to a more continuous one. Although this effect is not a consequence of the structural heterogeneity, it is always superimposed on the corrugation of the adsorbing surface.

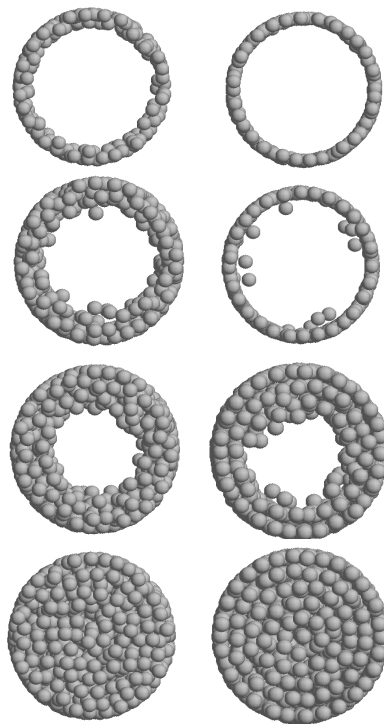


Fig. 4. Instantaneous configurations of fluid adsorbed in pores with structural (left) and energetic (right) heterogeneity. The snapshots correspond to the same thermodynamic conditions as presented in the Figure 3 ( $T = 77$  K, and the pressures, from the top to bottom,  $p = 0.05, 3.0, 4.0, 4.5$  mbar).

This influence infers from general thermodynamics: when temperature increases, the entropic effect results in increased disorder. As a consequence, adsorption mechanism is less sensitive to details of the structural heterogeneity at higher temperature. From the point of view of methodology of computer modeling of adsorption on heterogeneous surfaces, this obvious conclusion should be interpreted as following: a quality of any model of adsorbing wall can be reliably tested only at temperature low enough to avoid thermodynamic smoothing of the effective energy surface seen by adsorbing fluid. In practice, it means that we

have to test model surfaces at temperatures below and above the bulk melting temperature of the adsorptive. In the case of methane adsorption in a smooth pore (Fig. 5) only monolayer is stable at 77 K, but above 95 K multilayer structure is stable too. However, increasing temperature cannot enhanced the low pressure adsorption. Strong adsorption in this region, experimentally observed in real MCM-41 pores, can be modeled only assuming the heterogeneous distribution of strong energetic sites of adsorption, as discussed above.

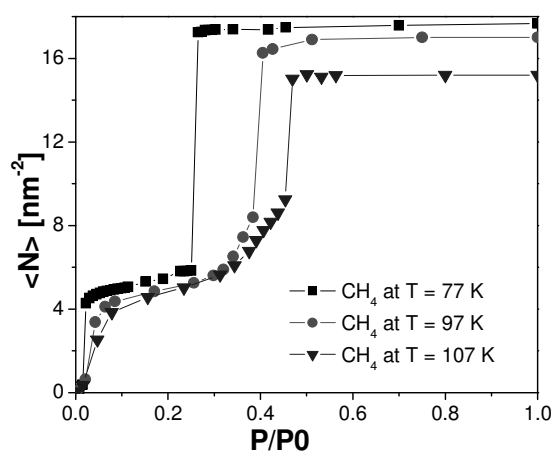


Fig. 5. The calculated isotherms of methane adsorption in smooth wall pores. Notice the multilayer adsorption at temperature above 95 K.

#### 4. CONCLUSIONS

The general conclusion that comes out from our study as well as from the review of literature presented in the first part of this paper can be formulated as follows: whatever is the model of the roughness of the adsorbing surface, it must include in some cooperative way both aspects of surface heterogeneity: energetic and structural. It means, that during the numerical construction of the wall it is crucial not only the way we design the structural corrugation (spatial distribution, amplitudes and spatial extend), but also the way we associate to it the energy sites distribution; This correlation must be not only logical but, first of all, physically meaningful.

It is clear that the final form of the isotherm in multilayer region depends not only on the energetic adsorption sites distribution but also on the geometrical corrugation which we call 'geometrical heterogeneity'. If the adsorbate forms ordered layers, the adsorption isotherms are always step-wise. This classical behavior is observed when adsorption occurs on smooth or ordered crystalline surfaces. The continuous isotherms are observed if a geometrical heterogeneity

of the wall leads to a formation of shallow micropores of irregular shape on the surface. If the sizes of these surface imperfections are greater than the dimensions of the adsorbate, the wall roughness, is transmitted to the second (and possibly higher) layer of adsorbed molecules, producing a new rough surface for adsorption of distribution of adsorption energies for the consecutive layers. However, to ensure a rapid increase of the adsorbed amount at submonolayer coverage and the completion of the first layer at the low pressure, some minimal number of strong (energetic) adsorption sites must be distributed over the wall. It means, that at low pressure the sites energy distribution is more important than the structural disorder. The latter one becomes dominant only after the first layer is formed, as it determines adsorption sites distribution for the next layers.

Additionally, the temperature is a crucial parameter that influences the form of the adsorption isotherm. The models of the surface roughness should always be carefully tested at low temperature. At higher temperatures adsorption calculations are less sensitive to the surface heterogeneity details and the thermal disorder smoothes out the shape of isotherm in a similar way that the structural heterogeneity.

Further improvement of the modeling methodology is possible. First of all, it seems justified to follow both options for surface modeling: atomistic and parametric approach. An advantage of parametric approach consists in much less time consuming algorithms. At the same time, the influence of the energetic and structural corrugation is not so directly correlated as it is in atomistic models. It seems that the parametric model could be defined starting from the atomistic model. It means, that the parametric corrugation may mimic the atomistic structure by using structural and energetic parameters calculated directly from an atomistic wall.

The other area is the capillary condensation region.

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