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# Mechanism of adsorption in cylindrical nanopores. The roles of adsorbate–adsorbate interactions in stabilizing the adsorbed phase

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Mechanism of adsorption in nanometric cylindrical pores has been analysed. Grand canonical Monte Carlo simulations were performed for two model systems: krypton and argon, adsorbed in an ideal (smooth) cylindrical silica pore of diameter $2R$ = 4 nm. The role of interatomic (adsorbate–adsorbate) interactions and atom–wall (adsorbate–adsorbent) forces in the mechanism of adsorption has been discussed. It has been shown that the correlation between these two energy components plays a crucial role in layering and capillary condensation transitions. The stability of different stages of adsorption has been analysed and discussed taking into consideration fluctuations of energy and number of adsorbed atoms during simulations.

Key words: *adsorption mechanism; nanopores; Monte Carlo simulations*

## 1. Introduction

Mechanism of adsorption of atoms and molecules on surfaces is a phenomenon that depends on many parameters such as thermodynamic conditions, the structure of the surface, interaction between adsorbed particles (adsorbate–adsorbate) as well as between the surface and the particles (adsorbate–adsorbent). Early theories of adsorption (e.g., Langmuir theory [1, 2]) and some of the most frequently used models (e.g., BET model [3]) ignored the lateral interaction between particles of adsorbate and explained the adsorption isotherms using only vertical components of the interaction. Although this seems to be rather important constrain that can result in underestimating

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monolayer adsorption [4], BET isotherms are still the most frequently used in the analysis of experimental adsorption data.

Smooth surfaces are important model systems that help to understand the underlying adsorption mechanism. On such surfaces, at relatively low temperatures, step-wise behaviour is observed experimentally. Methane adsorption on MgO [5, 6], (at 87.4 K and at 77 K), on nano-porous graphite [7] (at 77 K ), as well as on exfoliated graphite and graphite foam [8], are the examples. Oxygen adsorbed on graphite exhibits layering transitions, between crystalline layers below 43.8 K and liquid-like layers at higher temperature [9]. Argon exhibits a 're-entrant' layering behaviour [9], in which layerwise transitions disappear near 69 K and then reappear near 74 K. The microscopic mechanism of the transitions has been studied using theoretical models [10] and computer simulation methods. Layering transitions have been found in cylindrical pores of diameter $14\sigma$ ($\sigma$ is the Lennard–Jones parameter) [11], in models of nanotubes with nitrogen and Ar as adsorbed atoms [12], in slit pores (adsorption of methane [13]) and in argon films on graphite [14]. The interaction models are the most important components of the numerical approaches. Obviously, the atom–wall component of interaction is necessary for adsorption to take place but it is the interatomic, lateral interaction that determines structures of the adsorbed phase.

In this paper, we analyse the role of correlation between the lateral (interatomic) and vertical (atom–wall) components of interaction in the mechanism of adsorption in cylindrical nanopores. We use the Monte Carlo simulations to model a system of amorphous silica pore walls, with Kr or Ar atoms as the adsorbed species. To exclude any possible influence of the wall heterogeneity on the adsorption mechanism, we limited our analysis to a non-corrugated (smooth) wall. The adsorption was simulated at two temperatures: 77 K and 115 K. At 77 K (the temperature that is probably most frequently used in experimental characterization of porous systems) Kr forms solid layers and Ar liquid layers in silica pores. At 115 K, both Kr and Ar layers are liquid. We analyze the amplitude of fluctuations of adsorbed mass and energy to understand the mechanism of adsorption and we show that their character determines the stability of the system and its susceptibility to phase transformations. This information can be exclusively provided by simulation methods.

## 2. Monte Carlo ensemble and pore model

The simulation conditions were defined in the same way as in the previous papers [15–17]. The adsorbed gases were krypton or argon. We used a smooth cylindrical pore of nanometric size ($R$ = 2 nm). The interaction parameters [18] were chosen to describe interactions of Kr and Ar in the MCM-41 material. MCM-41 structure was modelled as an array of oxygen atoms, each one interacting with adsorptive atoms via a potential based on the Lennard–Jones (LJ ) [6–12] model:

$$V(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) \tag{1}$$

with $\varepsilon$ and $\sigma$ being constants. The skeletal density is assumed to be the same as that proposed by Maddox [20], that is 27 T-sites (Si atoms) per nm$^3$. We have not included inter-pore interaction because fluid–fluid interactions between atoms in adjacent pores proved to be negligibly small for the wall thickness of our system ($w$ = 1 nm).

A conventional grand canonical MC ensemble was applied. The simulation box (5.0 nm long, with periodic boundary conditions along the axis of the pore) was assumed to be in equilibrium with the bulk gas obeying the ideal gas law. This allowed us to use the external gas pressure as the thermodynamic parameter instead of the chemical potential [19]. Trial moves included translations of atoms, insertion of new atoms and removal of existing ones. The system typically contained 1000–1300 adsorbed atoms in the MC box. Typical runs consisted of ~$10^6$ MC steps per atom. The main results were extracted from the previously equilibrated runs.

## 3. Results and discussion

We started the analysis of adsorption in our model pore assuming a hard-core interatomic interaction and a LJ potential describing the atom–wall interactions. Such situation may be considered as a Langmuir-like model with physical adsorption, with all adsorption sites having the same energy and with no activation energy for the adsorption process. Once a site is occupied, the hard-core potential excludes other atoms from this site. The first layer completed, the adsorption is stopped unless the wall interaction is strong enough to initiate adsorption of atoms in the next layer.

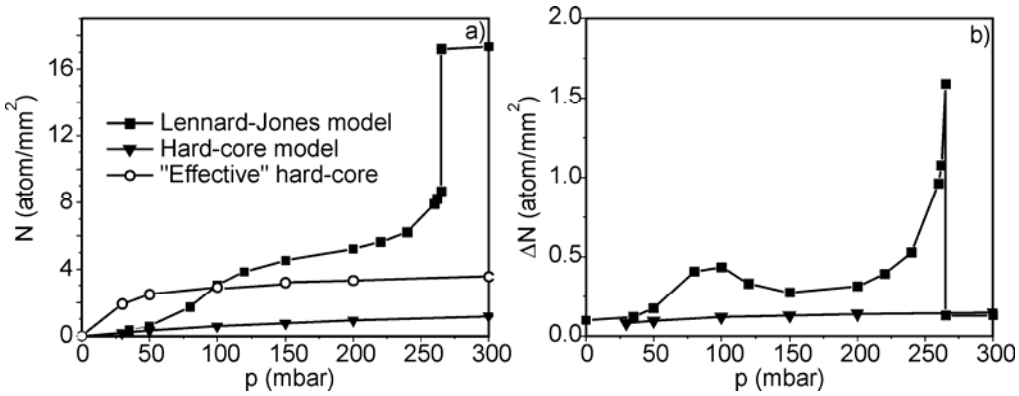


Fig. 1. Krypton adsorption at 115 K in a cylindrical pore of the radius $R$ = 2 nm. "Effective'' hard-core means the effective atom–wall interaction that gives the average energy per atom comparable with the LJ interaction model: a) isotherms, b) fluctuations of the number of adsorbed atoms

Figure 1 shows isotherms of adsorption of krypton at $T$ = 115 K, the simulated using hard core and LJ intermolecular potentials. A simple comparison proves that the intermolecular interaction plays a crucial role in the mechanism of adsorption and, on the microscopic level, it is impossible to substitute intermolecular interaction by effective vertical forces. The difference between the hard-core and the soft LJ interaction models becomes even more pronounced at lower temperatures ($T$ = 77 K) where the adsorbed layers are solid (Fig. 2). In this case, the layers are formed in a very abrupt way. Such a behaviour could never be observed when only atom–wall interaction were taken into account because, obviously, it is induced by the interatomic energy, responsible for the collective adsorption phenomenon. Therefore, such a mechanism cannot be deduced from classical Langmuir nor BET adsorption theoretical models. As could be expected, the lower the temperature, the more important are differences between isotherms generated with soft and hard type interaction models. These differences are easily seen when fluctuations of the adsorbed amount are compared. Contrary to the hard-core model, the system modelled with the LJ interaction exhibits enormous fluctuations when krypton undergoes the layering transition at 77 K (Fig. 2b). At a higher temperature (Fig. 1b), the fluctuations are smaller but still there exist maxima around the pressure of the first layer formation and when the capillary condensation is initiated. The magnitude of the latter fluctuations suggests that the increasing number of the adsorbed atoms (Fig. 1a) above the first layer cannot be stabilized in the layered structure (even as a metastable phase) hence the capillary condensation occurs.

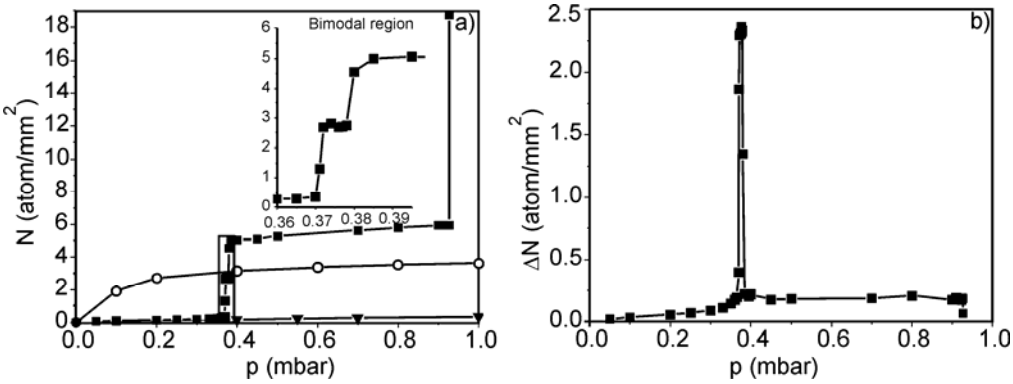


Fig. 2. Krypton adsorption at 77 K in a cylindrical pore, $R$ = 2 nm: a) isotherms, b) fluctuations of the number of adsorbed atoms. The insert in (a) shows details of the isotherm near the layering transition. The symbols as in Fig. 1

An analysis of energies and of their fluctuations provides an additional insight into the role of the inter-atomic interaction. At a higher temperature (115 K, Fig. 3), the adsorption starts at a relatively low pressure. Increasing pressure stabilizes the adsorbed layer: the total energy fluctuations decrease, being lower in the LJ model than in the hard-core model (Fig. 3a). At the same time, the fluctuations of two components

of the total energy in the LJ model behave in a non-monotonic way (Fig. 3b). The fluctuations of the interatomic energy show a stabilizing character when the first layer is formed and destabilizing before the initiation of the capillary condensation. At pressures corresponding to the first layer formation ($p$ ~ 100–150 mbar, Fig. 3b) the fluctuations of the atom–wall component of the energy also exhibit a minimum indicating its stabilizing influence on the layer structures. This shows that there is a correlation between interatomic and atom–wall interactions leading to a compensation between both components of the total energy. At a lower temperature (77 K, Fig. 4), the compensating effect is weaker. Here, fluctuations of the interatomic energy are so strong that they suppress the fluctuations of the other component. As a result, the total energy fluctuations increase when the layering transition is approaching. These results indicate that the mechanism of layering depends on the state of the adsorbed layer. For solid layers the layering has a character of a sharp transition whereas it is rather continuous in liquid layers.

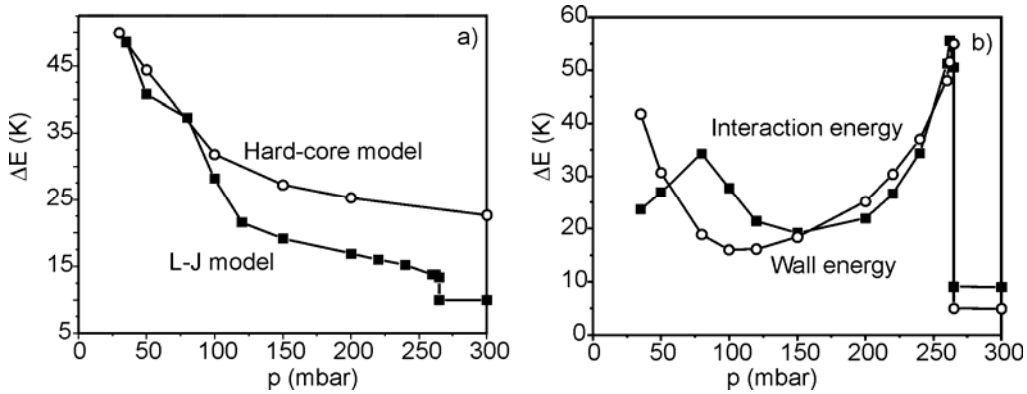


Fig. 3. Krypton adsorption at 115 K: a) total energy fluctuations, b) its components (wall and interaction) fluctuations in LJ model

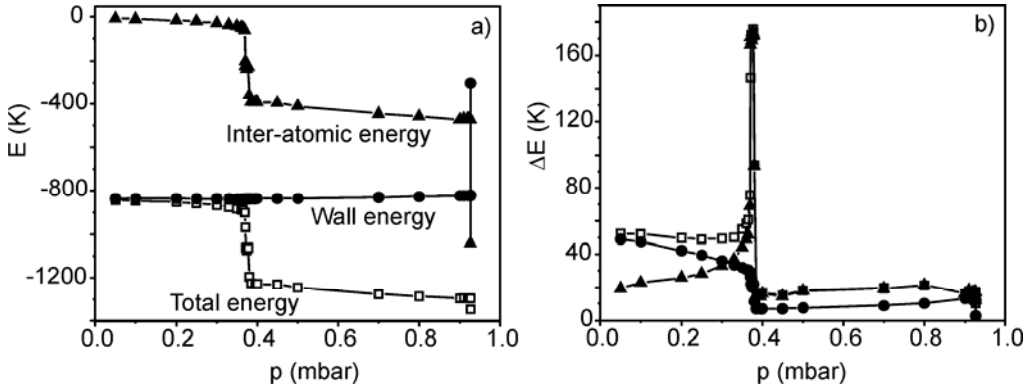


Fig. 4. Krypton adsorption at 77 K (LJ model): a) energies, b) energy fluctuations

The energy fluctuations give an important insight into the energy landscape of the system. Statistical thermodynamics shows that the square of the amplitude of the energy fluctuations defines the specific heat of the system, i.e., the amplitude of energy fluctuations characterizes the stability of the system. In other words, it indicates a susceptibility of a system to make a transition into another (meta)stable state. Figure 5a presents the energy fluctuations of the system near the layering transition. There is a dramatic decrease of the fluctuations when the system transforms from the 2D gas state into a solid monolayer structure because the system is stabilized by the interatomic energy. Such a transition is not possible when only vertical interactions are present (Fig. 5b) because there is no driving force which could rearrange the randomly distributed adsorbed atoms into another more stable structure.

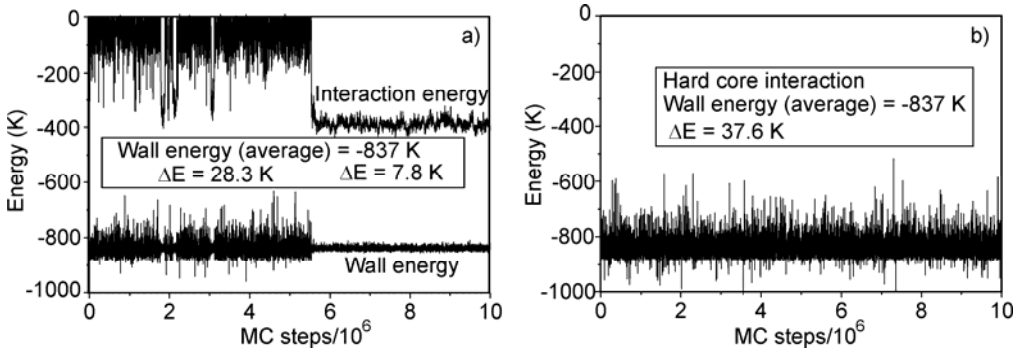


Fig. 5. Fluctuations of the interatomic and atom–wall energies during GCMC runs ($p$ = 0.379 mbar, $T$ = 77 K): a) LJ model, the transition between 2D gas phase and the first layer stabilizes the system, b) hard-core model, no transition is observed; $\Delta E$ values represent the mean amplitudes of fluctuations

The crucial role of the interatomic interaction can also be seen from our simulation of the Kr adsorption isotherm at 77 K. At pressures corresponding to formation of the first layer from the 2D gas ($p$ ~0.37–0.38 mbar, see insert in Fig. 2a), the system exhibits enormous fluctuations between gas-like and solid phases. Figure 6 shows two examples of typical MC runs observed at these conditions. Clearly, the system exhibits a bimodal behaviour: it jumps between two coexisting states being unable to stabilize any intermediate situation. Such a behaviour is a direct consequence of properties of the adsorbent model we used: smooth cylindrical walls and strong interatomic interactions. In these conditions, one can stabilize a full layer structure but not a partially adsorbed one. However, the temperature can modify the character of this step-wise behaviour: the higher the temperature, the more important is the entropy factor stabilizing the adsorbed structure and intermediate states between complete layer structures. The adsorption occurs in a more gradual way, although its general step-wise characteristic is always preserved. The isotherm at 115 K (Fig. 1a) shows such a characteristics. It is important to emphasize that an ideal smooth surface of the walls always prefers a step-wise adsorption in nanometric pores. As has already been discussed in our previous paper [15], a heterogeneous wall is necessary to observe more steady and gradual isotherms of adsorption.

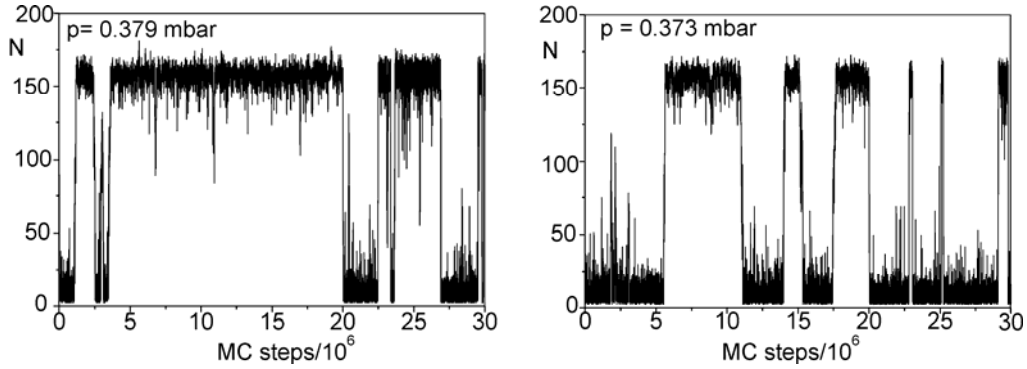


Fig. 6. Examples of fluctuations of the number of atoms
at pressures where a layering transition is observed in krypton at 77 K

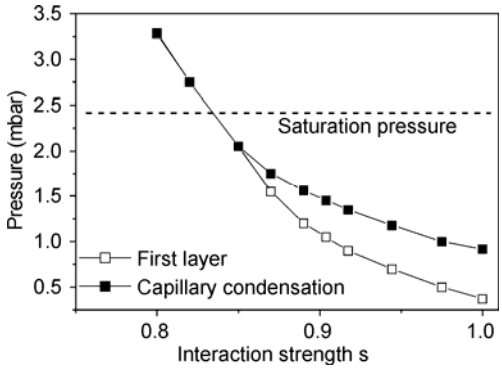


Fig. 7. The pressure of the layering transition (first layer formation) and capillary condensation of krypton as a function of the strength parameter *s* (*s* defines the effective parameter $\varepsilon_{\text{eff}}$ of the LJ atom–wall potential (Eq. (1)): $\varepsilon_{\text{eff}} = s\varepsilon$

Evidently, the pressure and the character of the layering transition depend on the atom–wall interaction. A stronger atom–wall interaction makes the layering transition sharper [17], at the same time lowering both the capillary condensation pressure and the layering pressure (Fig. 7). This general tendency is directly seen in Fig. 8 which presents a simulated isotherm of Ar adsorption at 77 K. The simulations performed for various strengths of the atom–wall interaction show that the vertical interaction affects all observed transitions: first layer formation (2D gas – solid layer), first-second layer transition and the capillary condensation pressure. All of them are shifted towards lower pressures when the atom–wall interaction becomes more attractive. This effect is well understood in the case of the first layer formation because stronger attractive forces facilitate the adsorption and allow the system to be adsorbed at a lower pressure. The influence of the atom–wall interaction strength on the second layer is not so obvious. Generally, from the structural and energetic point of view, the higher layer can be formed when: (i) the atom–wall interaction is still important at the second layer position or/and (ii) the structure of the previous layer is very different from the average liquid configuration. In the case of Kr, at 77 K, the second layer was observed only when the atom–wall interaction is sufficiently strong. Otherwise, the capillary condensation occurred directly, without a second layer formation (see

Fig. 7). In this case, the second (or any higher) layer is not stabilized but is followed by an immediate higher layers adsorption, up to a complete filling of the pore.

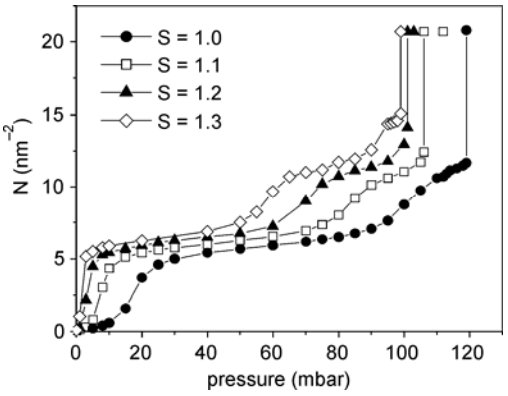


Fig. 8. The isotherms of adsorption of Ar in the pore ($T$ = 77 K) for various strengths of the atom–wall interaction

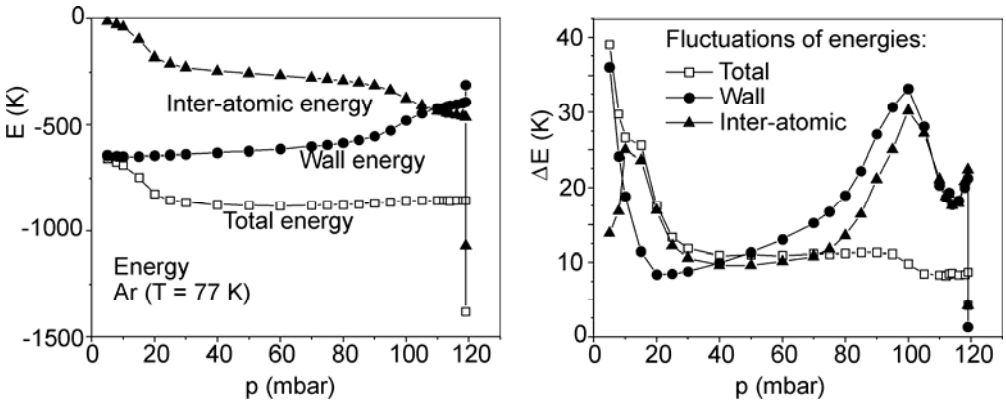


Fig. 9. The energies and energy fluctuations corresponding to the isotherm of adsorption of Ar atoms (see Fig. 8, $s$ = 1.0)

Figure 9 shows the energies and their fluctuations along the argon adsorption isotherm at 77 K. The energies do not exhibit any singular behaviour. The interatomic energy stabilizes the monolayer system. When the second layer starts to be adsorbed, the mean wall energy (per atom) becomes smaller (in absolute value) because the atoms are located farther from the surface. During the adsorption process the fluctuations of energies show very interesting features: the inter-atomic energy fluctuations show a maximum every time when a new layer is formed and when the capillary condensation approaches. At the same time, the wall energy fluctuates in a cooperative way to compensate the interatomic energy fluctuations, showing a minimum when the first layer is formed but exhibiting maxima when a higher layer is formed or capillary condensation is observed. As a consequence, total energy fluctuations decrease with increasing pressure.

## 4. Conclusions

Obviously, the analysis of both interatomic and atom–wall interactions is crucial for understanding the microscopic mechanism of adsorption, especially in a confined geometry. There exists a strong correlation between them leading to collective effects that are important for the mechanism of formation of the adsorbed system. We have shown that although the increasing pressure stabilizes the total system, the two components of energy may exhibit destabilizing behaviour, compensated by each other, but *in fine* facilitating the adsorption. It is a competition (but also a correlation) between intermolecular and atom–wall interactions that leads to transitions in adsorbed systems.

We found that the mechanism of the layering transition depends on the state of the adsorbed layer. A solid layer is formed as a sharp transition from a 2D adsorbed gas phase, at a well defined pressure. A liquid layer is formed in a continuous way, passing through intermediate stages of adsorption. It is a consequence of the interatomic interaction energy that determines the stable structure and usually prefers more ordered situations at lower temperatures. At higher temperatures, where the entropy contribution becomes more important, the intermediate situations become also more stable, although always exhibiting much larger fluctuations than the full monolayer structure. Obviously, fluid complete layers are always more stable than the intermediate structures.

We have shown that the fluctuation-based analysis provides new information allowing one to better understand the layer formation and phase properties in confined systems. Evidently, the free energy calculations would be desired to complement this approach.

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