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Adsorption and phase transitions in adsorbed systems: structural properties of CCl$_4$ layers adsorbed on a graphite surface

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Abstract We present the results of simulations of a CCl$_4$ monolayer adsorbed on a graphite surface. The CCl$_4$ molecule was represented either by a shapeless superatom or by its atomic sites. The simulations were carried out over a large range of temperatures, from 20 K up to 340 K. We address the following problems: (1) the influence of molecular shape on the structure and stability of phases (particularly at low temperatures), and (2) the influence of the graphite corrugation on layer stability and mechanism of phase transitions. In particular, we discuss the possibility and conditions of the appearance of hexatic phase in the system.

Keywords Graphite surface · Adsorption · CCl$_4$ · Monte Carlo

Introduction

Carbon tetrachloride (CCl$_4$) is widely used in many industrial processes as a raw material, a solvent (for example in petrochemical refining, catalysis and separation processes), and even as an agricultural fumigant. CCl$_4$ is an environmentally harmful substance and its release after use into the environment should be controlled. One way to limit

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the presence of CCl$_4$ in the human environment is to confine it in porous matrices. Therefore, investigations into adsorption mechanisms, structures and phase transformations of CCl$_4$ confined in nanopores are interesting not only from a fundamental point of view, but also as a source of new ideas in areas related to protection of the global environment.

Confinement of CCl$_4$ in nanoporous materials has recently been studied extensively, both experimentally and using computer simulations [1–8]. There is evidence that CCl$_4$ exhibits a rich phase diagram [9–14]. However, models of potential used in such calculations usually approximate the molecules by spherical super-atoms. Although this type of representation may be reasonable at higher temperatures, some aspects of molecular interactions are always neglected. As a consequence, not all phases can be observed in computer simulations.

This problem is even more pronounced when we try to calculate the phase diagram of a confined fluid. When the size of a confining pore does not exceed a few nanometers, the structure of the adsorbate that results from the delicate balance between the adsorbate–adsorbate and adsorbate–wall interaction may be totally different from the structure of the bulk material. A large variety of complicated, inhomogeneous structures, existing in three-dimensional (3D) systems can be stabilized by the pore walls. To simulate such situations, a knowledge of the details of the interaction model becomes crucial.

In this paper, we present the results of grand canonical Monte Carlo simulations of CCl$_4$ adsorption on a graphite surface. Two models of the CCl$_4$ molecule will be used: a superatom shapeless approximation and a tetrahedral crystallographic model taking into account the real positions of all atoms in the molecule. We analyzed the influence of the choice of molecular model on the structure

and stability of the adsorbed monolayer. In particular, we focused our studies on monolayer structure evolution with temperature and analyzed the mechanism of orientational and translational phase transitions within the monolayer. In addition, we also investigated how the atomic corrugation of the graphite surface influences the adsorbate structure and the phase transition temperature.

Methods

Simulation details

The CCl_4–CCl_4 interaction is modeled by two different potentials: a single site (superatom) potential [5] and the five sites potential proposed by McDonald et al. [15]. In the superatom model, the intermolecular interaction between structureless molecules of fluid was modeled using typical Lennard-Jones (LJ) potential. We used the following parameters: $\sigma_{ff} = 0.514$ nm, $\varepsilon_{ff}/k_B = 366$ K. These values have been used by many authors to simulate the properties of CCl_4 confined in nanopores of different shapes and wall structures [1, 5–8]. However, we emphasize that this model was optimized to fit correctly the freezing point of bulk CCl_4 [5], and it failed in the prediction of other properties of the 3D solid, namely the bulk crystal structure, even at relatively high temperatures (T > 250 K).

The more realistic McDonald's model (McD) represents the CCl_4 molecule as a rigid, regular tetrahedron with a central carbon atom and four chlorine atoms in the corners. The carbon–chlorine distance is $R_{C–Cl} = 1.766$ Å [15]. The intermolecular interaction is represented in terms of site-to-site potentials of the LJ form:

$$U(r_{ij}) = \sum_{\alpha=1}^{5} \sum_{\beta=1}^{5} 4\varepsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}} \right)^{6} \right]. \qquad (1)$$

where r_{ij} is the distance between centers of molecule i and j, and $r_{\alpha\beta}$ the distance between sites α and β on molecules i and j, respectively. We used: $\sigma_{CC} = 0.46$ nm, $\varepsilon_{CC}/k_B = 51.2$ K, $\sigma_{ClCl} = 0.35$ nm, $\varepsilon_{ClCl}/k_B = 102.4$ K. The values of mixed terms $\sigma_{\alpha\beta}$ and $\varepsilon_{\alpha\beta}$ were calculated using Lorentz–Berthelot mixing rules. To describe the interaction of CCl_4 with the graphite surface, we used a two-dimensional (2D) 10-4-3 potential of Steele [16]:

$$U(x, y, z) = U_0(z) + U_1(z)f(x, y) \qquad (2)$$

where $U_0(z)$ and $U_1(z)$ are non periodic terms, depending only on the distance of the interaction site from the average (smooth) graphite surface, and totally neglecting graphite atomic rugosity, and $f(x,y)$ is a term that takes into account the triangular arrangement of carbon atoms in the graphene structure and the resulting periodic modulation of fluid-

graphite potential [17] (a=2.46 Å is the graphite lattice spacing):

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

To evaluate the influence of pore wall heterogeneity on the adsorbate structure and the phase transition temperature, both models of the fluid–graphite interaction (smooth and corrugated) were tested.

Grand canonical Monte Carlo simulations were performed in a box of dimensions $a = 14$ nm, $b = 14$ nm, $c = 7$ nm. The angle between the a and b directions was $\alpha = 60°$. Periodic boundary conditions were applied in the (a, b) plane. During the simulations a hard wall was placed at a distance $z = 7$ Å from the top of the graphite surface to avoid multilayer adsorption. The adsorbed system was assumed to be in equilibrium with the bulk gas, which obeyed the ideal gas law. All calculations were performed at constant pressure (P = 1 atm) over a wide temperature range, from 20 K to 340 K. The overall number of molecules in the box oscillates at around 430 or 580 particles for McD and LJ models, respectively. The cut-off radius for energy calculations was 18 Å for McD and 12 Å for LJ models.

Results and discussion

The deviation of the planar layer of spheres from the ideal triangular packing can be measured by the structural order parameter Φ_6 [1, 6, 20]

$$\Phi_6 = \langle |\Psi_6(r)| \rangle = \left\langle \left| \frac{1}{N_b} \sum_{k=1}^{N_b} \exp(i6\theta_k) \right| \right\rangle \qquad (3)$$

Here, θ_k is the angle between the vector joining the two neighboring molecules and an arbitrary axis; the sum runs over all pairs of molecules in the layer. The parameter Φ_6 is usually employed to detect structural phase transformations in 2D systems as one expects $\Phi_6=1$ in the ideal triangular (solid) layer and $\Phi_6=0$ when the layer is totally disordered (fluid). However, as Φ_6 is a statistical average over the whole system, it cannot account for correlations between molecules of fluid. Therefore, we also used the orientation pair correlation function $G_6(r)$, which measures correlations between bond order parameter Ψ_6 of two molecules at the distance r:

$$G_6(r) = \langle \Psi_6^*(0) \Psi_6(r) \rangle \qquad (4)$$
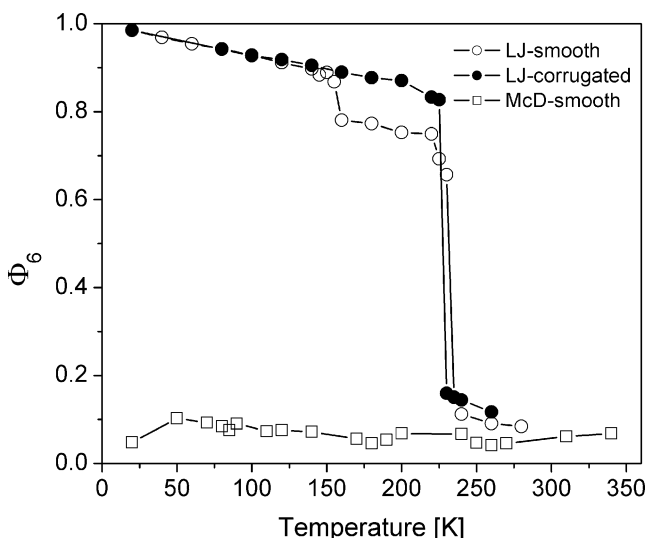
Fig. 1 Temperature dependence of Φ_6 order parameter for a CCl_4 monolayer adsorbed on a smooth or corrugated surface, in the spherical Lennard Jones (LJ) approximation. For comparison, the order parameter calculated for MacDonald's five-site potential is also presented

For 2D triangular crystal phases exhibiting long range bond orientation order, $G_6(r)$ has a constant, finite value even at large distances. In a liquid layer there is no bond orientation order, and $G_6(r)$ decays exponentially with r. In structures without positional order, but which exhibit quasi-long range bond orientation order (hexatic phases [18–20]), $G_6(r)$ decreases much more slowly; an algebraic decay with r is expected.
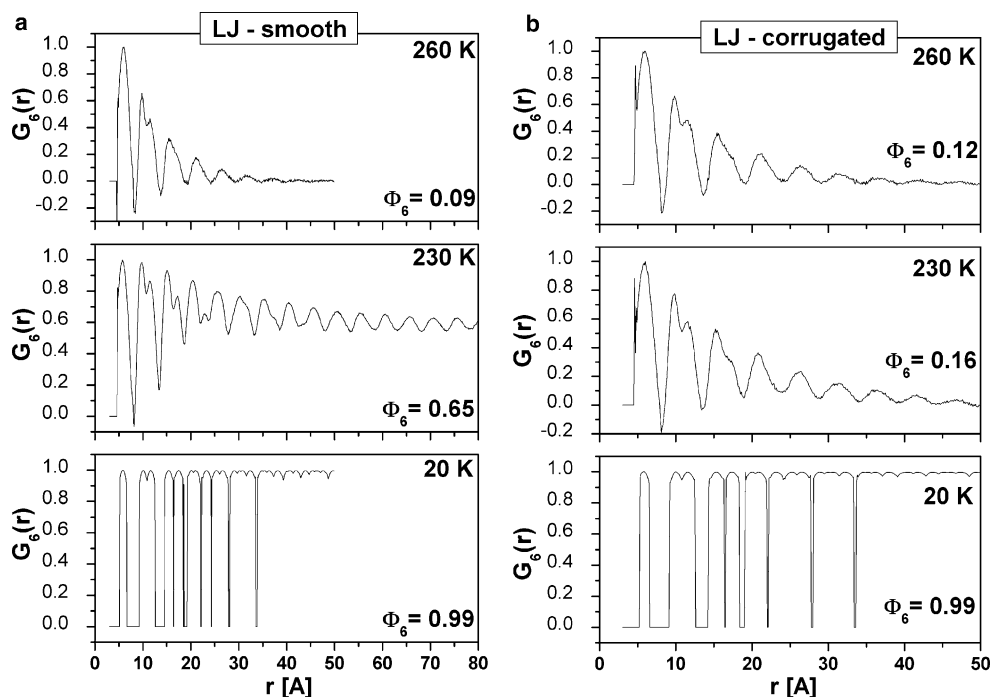
Figure 1 shows the temperature dependence of Φ_6 calculated for a CCl_4 monolayer adsorbed on smooth or

corrugated graphite using the superatom model of fluid. In both cases the monolayer melts at 230–235 K. However, on the smooth surface the layer loses its symmetry progressively and an additional step in Φ_6 is observed. Above 150 K the order parameter decreases by about 10% and then remains stable up to 230 K, at which point the transformation to the liquid phase is complete. Such behavior can act as a signature of a solid–hexatic–liquid sequence of transformations in the layer.

To test this hypothesis, we calculated the value of the orientational order parameter $G_6(r)$ at three temperatures T=20 K, T=230 K and T=260 K (Fig. 2a). The orientational $G_6(r)$ pair correlation functions show that the adsorbed monolayer is solid below 150 K and liquid above 230–235 K. Between these two temperatures the positional order parameter $g(r)$ (not shown here) does not correspond exactly to the isotropic situation and the $G_6(r)$ function has only a very slow algebraic decay. This suggests that the adsorbed monolayer may have some characteristics similar to those of the hexatic phase. Whether this structure is really hexatic or not requires more detailed studies. For now we can say that the system shows the possibility of stabilizing the hexatic order only in this range of temperatures.

The hexatic phase does not appear on the corrugated surface. The layer remains solid up to ~230 K and then melts (Figs. 1, 2b). We noted that the Φ_6 values at low temperatures are surprisingly similar regardless of whether the graphite surface is considered as smooth or corrugated. Therefore, as the diameter of the CCl_4 superatom ($d=$ 5.14 Å) is incommensurate with the graphite lattice constant

Fig. 2 Orientational order parameter $G_6(r)$ for a CCl_4 superatom monolayer adsorbed on a smooth or corrugated graphite surface
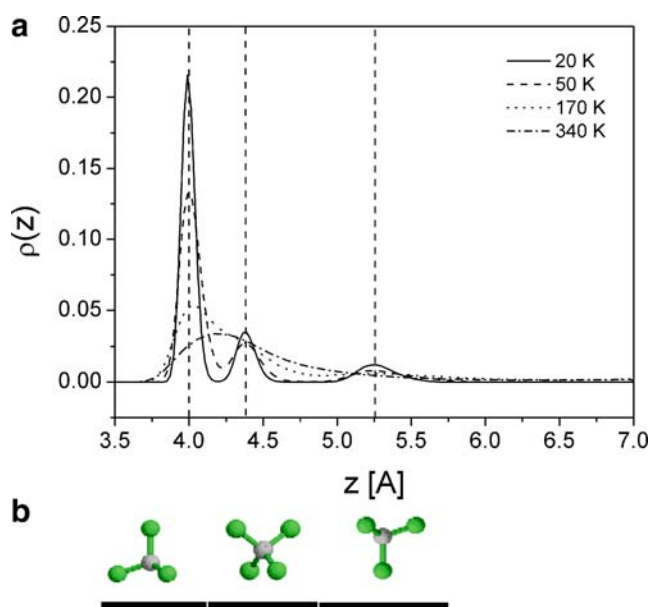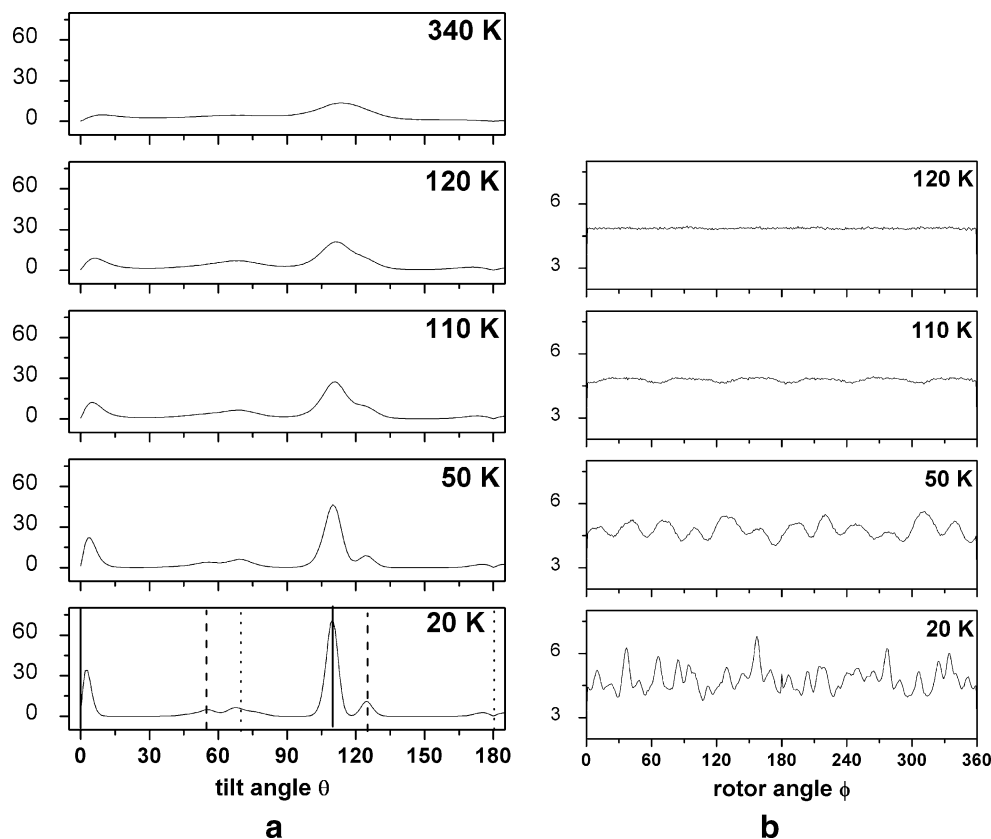
Fig. 3 The distribution of CCl$_4$ mass center positions above a smooth graphite surface. The *dashed lines* mark the distance corresponding to (from left to right) the tripod, dipod and anti-tripod orientation of molecules

(a=2.43 Å), a substrate-induced modulation of the adsorbent structure (and, as a consequence, a decrease in Φ_6 value) could be expected. However, as the intermolecular interaction with the substrate is ~4 times stronger than the fluid

interaction, the substrate has only a moderate influence on the layer structure. Consequently, at low temperature, Φ_6 evolves in the same way for a monolayer adsorbed on both corrugated and smooth graphite surfaces, at least when using the superatom model of CCl$_4$.

The structure of the CCl$_4$ monolayer becomes more complicated when the five-site McD model of intermolecular interaction is used in the simulations. Figure 3 shows the distribution of molecular centers of mass in the layer adsorbed on a smooth graphite surface at T=20, 50, 170 and 340 K. At low temperatures there are three clearly distinguished peaks, located at 4.0 Å, 4.35 Å and 5.25 Å above the adsorbing surface. These correspond to three characteristic molecule orientations with respect to the surface: tripod, dipod and anti-tripod (Fig. 3a–c). The structure of the layer is clearly temperature-dependent. At low temperature the molecular orientations are frozen. Below 110 K most molecules stay in the tripod orientation. Increasing temperature allows the molecules to flip between preferential orientations. Even at the highest temperature studied, the reorientation of molecules does not become totally free; the tripod orientation is always more favorable than the others. Over the whole range of temperatures, the positional pair correlation function g(r) is isotropic-like, and the orientational correlation function G$_6$(r) exponentially decays. This indicates that, even at low temperatures, the system is disordered; it freezes into a statistically

Fig. 4 Distribution of tilt and rotor angles for CCl$_4$ molecules adsorbed on a smooth graphite surface

disordered, glass-like structure with no long-range translational order. When the temperature increases, an orientational order–disorder transition occurs at 110–120 K. To characterize this transition we defined two molecular angles: a rotor angle ϕ and a tilt angle θ. The rotor angle is the angle between the projection of a C–Cl bond on a graphite plane and the *x*-axis of the Monte Carlo box (of course, there are four rotor angles corresponding to the four different C–Cl bonds). This angle represents rotation of the CCl$_4$ molecule with respect to the axis that is perpendicular to the substrate. The tilt angle is the angle between the C–Cl bond vector and the *z*-axis and represents the rotation of CCl$_4$ molecules in the plane perpendicular to graphite. For the tripod orientation of molecules, θ=0°; for the bipod configuration, θ=55°; and for the anti-tripod orientation, θ=180°. Figure 4 shows the distributions of both angles over a large temperature range, from 20 K to 340 K. The distribution of the tilt angle confirms our previous conclusion that, over the whole temperature range, the preferred orientation of molecules is tripod. At the same time, the orientation of molecules characterized by the rotor angle shows a temperature evolution characteristic for an order–disorder transition. At low temperatures, the molecular orientations are statically disordered. This reflects the glass-like structure of the layer. With increasing temperature the molecules become dynamically disordered with respect to the rotor angle; they start to rotate freely at T=120 K. The system undergoes an in-plane order–disorder phase transformation. However, a 3D rotation of molecules is strongly hampered even at high temperatures.

Summary and conclusions

Simulations of a superatom CCl$_4$ monolayer adsorbed on a smooth graphite surface in the 20–340 K temperature range showed that the system undergoes a solid/liquid phase transformation at T=230–235 K. This value is similar to that reported in the study of phase transitions of CCl$_4$ within a slit-like graphite pore with smooth walls [6], but is higher then the experimentally determined value (T=195 K [21, 22]). We suggest that melting of the layer occurs in two steps, through crystal–hexatic and hexatic–liquid phase transitions [5, 6, 23]. The intermediate hexatic phase may exist over a wide temperature range (between 145 and 230 K); however, we consider that this finding requires further confirmation.

The addition of corrugation of the graphite surface to the substrate model does not have much effect on the temperature value of the solid/liquid phase transition. However, there is no sign of the hexatic phase in such a system. This is consistent with the fact that the existence of the hexatic phase was originally predicted for an ideal 2D situation.

The low temperature structure of the layer observed in our calculations with five-site potential is consistent with results published recently by Do and Do [24]. The three preferential orientations of CCl$_4$ molecules on a graphite surface and within a slit-like graphite pore, as well as their distance from the substrate, reported by the latter authors perfectly match our values.

However, the absence of a solid/liquid phase transition reveals a weakness in the existing five-site models. Although these models describe correctly the face-centered cubic plastic phase of the 3D CCl$_4$ crystal [15], and diffusion of liquid CCl$_4$ in pillared porous materials [25], they do not properly reproduce the properties of 2D structures of CCl$_4$ adsorbed on graphite.

Generally, our conclusions show that structural studies of CCl$_4$ adsorption will require a new potential model that will be able to reproduce the experimental situation, in particular at low temperatures. Obviously, a superatom-type model that can only be applied at temperatures above melting transition cannot be used. Also, new numerical procedures (such as parallel tempering methods [1] and special methods to analyze local liquid structures [26]) will be necessary to overcome potential metastability problems at low temperatures. Preliminary studies are in progress.

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