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Adsorption of triangular-shaped molecules with directional nearest-neighbor interactions on a triangular lattice

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Abstract Using Monte Carlo and transfer-matrix methods the lattice gas model of adsorption of triangular-shaped molecules on a triangular lattice is studied. The constructed model takes into account the directionality of pairwise nearest-neighbor interactions between the adsorbed molecules. It is shown that a predominant character of "tip-to-tip" attractive interactions w_1 always leads to the formation of the honeycomb structure in the adsorption monolayer with local density $\rho = 0.66(6)$. While, the values of "side-to-side" w_2 and "tip-to-side" w_3 interactions define the structure of close-packed phase. Depending on the values of the interactions the close-packed phase may have: (a) completely disordered structure; (b) frustrated honeycomb structure which is formed by Langmuir like adsorption onto 2D pores of the honeycomb structure; (c) ordered close-packed structure consisted of the molecules which all have the same orientation relative to each other and relative to the surface.

keywords Lattice gas model · Trimesic acid self-assembly · Molecular porous network Monte Carlo · Transfer-matrix

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1 Introduction

Structure and physicochemical properties of an adsorption monolayer significantly depend on type and energy of lateral interactions between adsorbed molecules. Nature of the lateral interactions may be different, but generally, these are non-covalent interactions such as van der Waals forces, dipole–dipole interactions, hydrogen bonds and indirect interactions through the substrate (Rudzinski et al. 1997; Liang et al. 2009). Recently, much attention is paid to the influence of hydrogen bonding on the structure and properties of adsorption monolayer. Substantially, it concerns of the adsorption monolayers of complex organic molecules with different functional groups (Liang et al. 2009; Bartels 2010; Cicoira et al. 2008; Gutzler et al. 2011).

In a typical donor-acceptor system, hydrogen bond is formed between the adsorbate molecules with different functional groups such as $-COOH$, $-OH$, $-NH_x$, ($x \geq 1$) and others. A distinctive feature of these systems is directionality of the interactions between the adsorbed molecules. It leads to a huge variety of ordered structures formed in the adsorption monolayer when varying the external parameters such as temperature, pressure, concentration or electrode potential (in the case of adsorption from electrolyte solution) (Gutzler et al. 2011; Liang et al. 2009; Li et al. 2005; Ishikawa et al. 2002; Ye et al. 2007). Therefore, the geometry of the adsorbate molecules and the arrangement of functional groups play a very important role in the process of self-assembly of the organic monolayers.

Stability of some ordered adsorption monolayers of the complex organic molecules and energy of the lateral interactions were successfully calculated using quantum-chemical methods and molecular dynamics (Nath et al. 2007;

Kannappan et al. 2007; Meier et al. 2005; Zhang et al. 2008; Classen et al. 2007). However, it is not possible to use density functional theory (DFT) for the entire adlayer of the complex organic molecules for the obvious reasons, and state-of-the-art research is limited by consideration of several molecules on the surface of small metal clusters or graphite. On the other hand, molecular dynamics method, despite its many advantages, has one serious "drawback"—with molecular dynamics we can calculate the evolution of the many-particle system in the time interval of a few nanoseconds, but many interesting phenomena such as self-assembly processes and phase transitions in adlayers have a much longer time scale (Binder et al. 2004). Apparently, the most appropriate method for study of the phase behavior of these adsorption systems is based on simulation of the lattice gas model (LGM). It is well established Monte Carlo method which allows us to consider almost any notion of physicochemical processes in the adsorbed monolayer. For example, in the papers (Pawin et al. 2006; Kim and Einstein 2011) the mechanism of spontaneous formation of the honeycomb structure in anthraquinone adsorption monolayer on Cu (111) was studied. It was shown that an important role in that process played by long-range interactions. A comprehensive analysis of the effect of anisotropic interactions in the melamine-PTCDA system on the phase behavior of the monolayer is given in the works (Silly et al. 2008; Weber et al. 2008). A LGM and Monte Carlo method were successfully used for the investigation of the formation process of honeycomb and close-packed phases in cyanuric acid and melamine adlayer at its different relative concentrations (Zhdanov 2007). In paper (Fortuna et al. 2010) the adsorption monolayers of dicarboxylic acids were studied. It has been shown that chemical structure of the molecule and the strength of intermolecular interaction sufficiently affect the phase behavior of the adlayer of the complex organic molecules.

In general, the analysis of papers on simulation of adsorbed monolayers of the complex organic molecules on the surface of metals and graphite has shown that in most cases the directional interactions between adsorbed nearest-neighbor molecules are not taken into account. The researchers usually do not consider the dependence of the interaction energy on relative orientation of the molecules at surface. And the appearance of ordered structures such as honeycomb or different close-packed ordered phases is determined by a complex set of lateral interactions in which apart from nearest-neighbor pairwise interactions there are multiparticle and long-range interactions.

Therefore, the main goal of this paper is the construction and investigation of the LGM of adsorption of triangular-shaped molecules on a triangular lattice taking into account the directionality of pairwise nearest-neighbor interactions between adsorbed molecules.

2 Model

Type of the functional groups determines how strong the molecule interacts with nearest-neighbor molecules. On the other hand, the arrangement of functional groups and the geometry of the molecule has a strong effect on symmetry of ordered organic monolayers and their structural parameters.

The simplest and therefore the well-studied system of this type is the adsorption monolayer of trimesic acid (TMA) on the surface of various metals and graphite (Cicoira et al. 2008; Liang et al. 2009). TMA molecule consists of benzene ring and three carboxyl groups disposed in the 1,3 and 5 positions (Fig. 1). This structure of the molecule allows us to consider the TMA adlayer as a model system for studying the mechanisms of supramolecular self-assembly in the organic adsorption monolayers which are stabilized by hydrogen bonding.

Thus, TMA adsorption monolayer was chosen as a basis for the construction of a simple lattice model, since the results obtained in the framework of this model apparently allow us to make some general conclusions valid for the entire class of adsorption systems. This model was formulated by us earlier (Fefelov et al. 2010), but for the sake of completeness of the material we present a short description here.

Analysis of the experimental data, in particular STM images of TMA adlayer, indicates that TMA molecules adsorbed on comparatively inert surface (for example, on Au (111) graphite) can form three major nearest-neighbor configurations (Fig. 2): "tip-to-tip" (w_1), "side-to-side" (w_2) and "tip-to-side" (w_3) depending on the orientation of the molecules and their relative positions. Taking into account the triangular symmetry of the adsorbate molecules, all the nearest-neighbor configurations can be addressed through a single-site adsorption model on triangular lattice when the adsorbed molecule can have two different orientations—"right" or "left" (see Fig. 2). Each

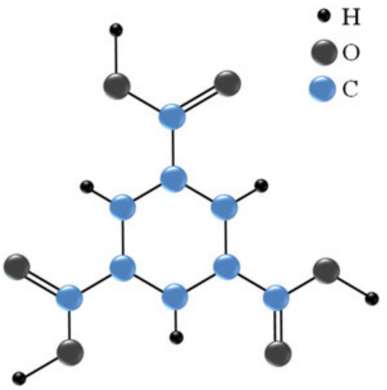

Fig. 1 Chemical structure of trimesic acid molecule

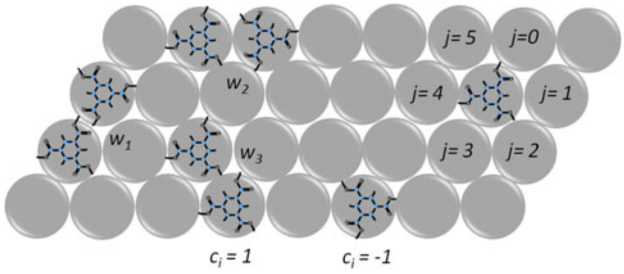

Fig. 2 Two possible orientations of the molecule on a triangular lattice—right-hand orientation and left-hand one with $c_i = 1$ and $c_i = -1$, respectively; and three major nearest-neighbor configurations: “tip-to-tip” (w_1), “side-to-side” (w_2) and “tip-to-side” (w_3); j denotes the number of nearest neighbor with respect to *i*th adsorption site

type of hydrogen bonding in the model has its own energy w_1, w_2 or w_3.

The thermodynamic Hamiltonian of the model can be written as:

$$\begin{aligned} H_{eff} = {} & \frac{1}{2}\sum_{i=1}^{M}\sum_{j=0}^{j=2} w_1\left(\delta_{c_i,1}\delta_{c_{2j},-1} + \delta_{c_i,-1}\delta_{c_{2j+1},1}\right) \\ & + \frac{1}{2}\sum_{i=1}^{M}\sum_{j=0}^{j=2} w_2\left(\delta_{c_i,1}\delta_{c_{2j+1},-1} + \delta_{c_i,-1}\delta_{c_{2j},1}\right) \\ & + \frac{1}{2}\sum_{i=1}^{M}\sum_{j=0}^{j=5} w_3\delta_{c_i,c_j} - \mu\sum_{i=1}^{M} c_i^2 + \Delta\sum_{i=1}^{M} c_i^2, \end{aligned} \tag{1}$$

where μ is the chemical potential, Δ the interaction energy between the molecule and adsorption site, $\delta_{i,\ j}$ the Kronecker symbol, and c_i is the occupation number such that $c_i = 1$ or $c_i = -1$ if adsorption site with number i is occupied by adsorbate molecule with right-hand or left-hand orientation, respectively (Fig. 2). If the *i*th site is empty $c_i = 0$. And *j* is the number of nearest neighbor with respect to *i*th adsorption site (Fig. 2). Since the interaction energy Δ between the molecule and adsorption site does not depend on any external parameters and the same for all adsorption sites in the proposed model, then it can be set equal zero without loss of generality.

It is worth to note that the model presented here can describe the behavior of whole class of similar adsorption systems, where the adsorbate molecule has three-fold symmetry in the functional groups arrangement. Examples of such systems include the adsorption monolayers of TMA derivatives such as 1,3,5-*tris*-(carboxymethoxy)-benzenbenzene (TCMB) (Cicoira et al. 2008; Yan et al. 2004) and 1,3,5-benzenetribenzoic acid (BTBA) (Liang et al. 2009; Cicoira et al. 2008) and cyanuric acid (CA) adlayer (Zhang et al. 2008; Kannappan et al. 2007). Based on the available data on the geometry and chemical structure of the above mentioned molecules we can expect that phase behaviors of the adsorbed monolayers consisting of these molecules will be alike.

Note that the special case of our model when $w_1 = w_2$ can be reduced to well-known and well-studied spin-1 models such as three-state Potts model and Blume–Emery–Griffiths model. In these models it is assumed that the occupation number S_i can take three different values: ±1 or 0 depending on the type of particle on *i*th site. Spin-1 model were built in the second half of the twentieth century and has since been used to solve various problems in condensed matter physics (Rzysko et al. 2005; Lajzerowicz and Sivardiere 1975; 1975a, 1975b). The difference between spin-1 models and our model is that our model is highly anisotropic because of the directionality of the intermolecular interactions.

It should be noted that in paper (Misiūnas and Tornau 2012) the same model has been developed. In spite of this, the study of influence of the nearest-neighbor pairwise interactions between adsorbed molecules on the phase behavior of the adlayer was not comprehensive. In particular, not all ordered structures which formation is determined only by the values of the nearest-neighbor pairwise interactions had been found. Mainly, the authors investigated the particular case of the model when $w_2 = w_3$. However, as will be shown below, the change in the balance between these interactions leads to the significant changes in the phase behavior of the adsorption monolayer. Additionally, the authors (Misiūnas and Tornau 2012) demonstrated that the phase behavior of the adlayer dramatically changes when next-nearest neighbor repulsions are taken into account. Namely, one more ordered structure of the “zig–zag” type appears in the adlayer.

3 Methods

The model has been studied with two different methods that supplement each other—Monte Carlo method and transfer-matrix technique.

Monte Carlo method

The thermodynamic properties of the model were investigated using the standard grand canonical Monte Carlo method (Landau and Binder 2000). We consider a triangular lattice consisting of $M = L \times L$ sites with periodic boundary conditions as a model of the surface. The calculations were made with $L = 60$. The linear size of the lattice L is chosen to be comparable to the period of all the possible ordered structures in the model. As it was shown numerically the further increasing of the system size did not result in essential data change.

Thermodynamic equilibrium was achieved by adsorption–desorption dynamics (Glauber 1963) and diffusion dynamics (Kawasaki 1966). To define probabilities of the transition from one state of the system to another the standard Metropolis algorithm was used. The relaxation time of the system was varied from 10^6 to $5 \cdot 10^6$ Monte Carlo steps (MCSs) depending on the conditions. To compute the time averages of thermodynamic characteristics at fixed T and μ we used $5 \cdot 10^6$ MCSs. Note that 1 MCS corresponds to one sweep over the entire lattice. We calculated the thermodynamic quantities such as

the specific amount of adsorbed molecules (or adlayer density)

$$\rho = \frac{1}{M}\left(\sum_i \delta_{c_i,1} + \sum_i \delta_{c_i,-1}\right); \tag{2}$$

the specific internal energy of the adlayer

$$U = \frac{H + \mu N}{M}, \tag{3}$$

where H is numerical value of the Hamiltonian, and N total amount of adsorbed molecules;

the specific amount of molecules adsorbed with the right-hand orientation (see Fig. 2)

$$\rho_1 = \frac{1}{M}\sum_i \delta_{c_i,1}; \tag{4}$$

the specific amount of molecules adsorbed with the left-hand orientation (see Fig. 2)

$$\rho_{-1} = \frac{1}{M}\sum_i \delta_{c_i,-1}. \tag{5}$$

The differential heat of adsorption q_d (González et al. 2001) and the susceptibility of the adlayer density were defined as

$$q_d = \frac{\langle \rho \cdot U\rangle - \langle \rho\rangle \cdot \langle U\rangle}{\langle \rho^2\rangle - \langle \rho\rangle^2} \tag{6}$$

and

$$\chi_\rho = \frac{M}{RT}\left(\langle \rho^2\rangle - \langle \rho\rangle^2\right). \tag{7}$$

Analysis of the ground state of the system has shown that there are two ordered structures in the adsorption monolayer at least depending on the relation between the various directional interaction w_1, w_2 and w_3. These are the honeycomb structure and the close-packed structure where all molecules have the same orientation relative to each other and relative to the surface (Fig. 3a, b). To determine the region of the model parameter space in which the above mentioned ordered phases are stable it is convenient to consider the possible structure of adlayer and related order parameter.

The identification of the ordered structures appearing in our model was carried by dividing the original triangular lattice into three equivalent sublattices with corresponded coverages—θ_1, θ_2 and θ_3 (Fig. 3c). Here, we consider the sublattices covered only by molecules with the certain orientation, for example, only molecules adsorbed in the state $c_i = 1$. On the other hand, the sublattices coverage by molecules adsorbed in the state $c_i = -1$ was denoted as θ_1', θ_2' and θ_3'. The order parameters for the honeycomb structure and the close-packed structure can be written as

$$\psi_{hon} = \theta_1^2 + \theta_2^2 + \theta_3^2 - \theta_1\theta_2 - \theta_1\theta_3 - \theta_2\theta_3 \tag{8}$$

$$\psi_{cp} = |\theta_1\theta_2\theta_3 - \theta_1'\theta_2'\theta_3'|, \tag{9}$$

correspondingly.

The above-defined order parameters are complemented by the fourth-order cumulants (Landau and Binder 2000; Binder and Landau 1976)

$$U_\psi = 1 - \frac{\langle \psi^4\rangle}{3\langle \psi^2\rangle^2}, \tag{10}$$

where ψ denotes one of the order parameters.

Transfer-matrix method

The heart of this method is to replace the difficult problem of the grand partition function calculation for the two-dimensional lattice model with the simpler problem of calculation of the largest magnitude eigenvalue and the eigenvector corresponding to this eigenvalue for some matrix (Runnels and Combs 1966; Myshlyavtsev and Myshlyavtseva 2007; Myshlyavtsev et al. 1990; Rikvold et al. 1988; Bartelt et al. 1986; Kinzel and Schick 1981; Myshlyavtsev and Dongak 1997). In the framework of this method the two-dimensional lattice is replaced with a strip infinite in one direction and having a finite width W in the perpendicular direction. The transfer-matrix method (TMM) gives the exact value of the grand partition function for this semi-infinite system. Obviously, with increasing the value of W the calculated quantities tend to the exact values for the infinite two-dimensional lattice. According to concrete calculations even relatively small W values allows yielding practically exact results.

We used the strip with $W = 3$ and $W = 6$ for all calculations with periodic boundary conditions that provided the translational invariance of the system and, therefore, the complete identity of the lattice sites. In fact, we obtained a triangular lattice on infinite cylinder. The elements of the transfer-matrix $\mathbf{T}$ calculated as

$$T_{i,j} = \exp\left(\frac{1}{2}u_i + \frac{1}{2}u_j + v_{i,j}\right) \tag{11}$$

$$\begin{aligned} u_i = \mu \sum_{i=1}^{W} c_{i,k}^2 - w_1 \sum_{k=1}^{k=W} \delta_{c_{i,k},-1}\delta_{c_{i,k+1},1} \\ - w_2 \sum_{k=1}^{k=W} \delta_{c_{i,k},1}\delta_{c_{i,k+1},-1} - w_3 \sum_{k=1}^{k=W} \delta_{c_{i,k},c_{i,k+1}} \end{aligned} \tag{12}$$

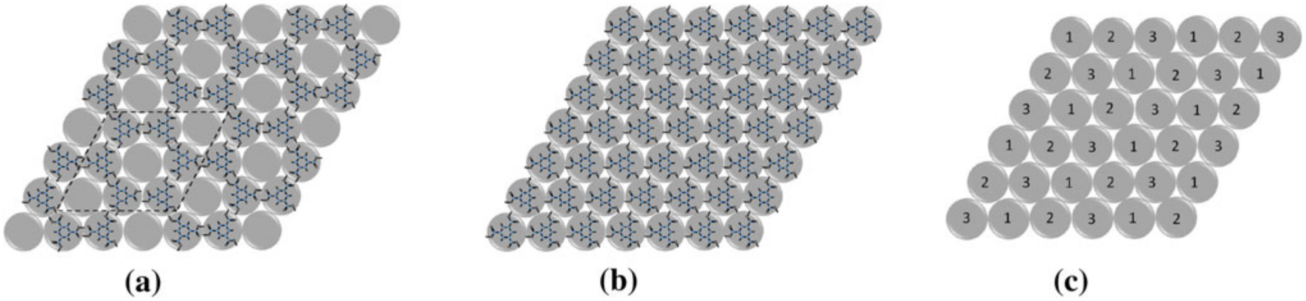

Fig. 3 The ground state ordered structures of the adlayer: **a** honeycomb and **b** close-packed; **c** the decomposition of a triangular lattice into three equivalent sublattices 1, 2, 3

$$\begin{aligned} v_{i,j} = {} & -w_1 \sum_{k=1}^{k=W} (\delta_{c_{i,k},-1}\delta_{c_{j,k},1} + \delta_{c_{i,k+1},1}\delta_{c_{j,k},-1}) \\ & - w_2 \sum_{k=1}^{k=W} (\delta_{c_{i,k},1}\delta_{c_{j,k},-1} + \delta_{c_{i,k+1},-1}\delta_{c_{j,k},1}) \\ & - w_3 \sum_{k=1}^{k=W} (\delta_{c_{i,k},c_{j,k}} + \delta_{c_{i,k+1},c_{j,k}}), \end{aligned} \tag{13}$$

where operator u_i gives the interaction energy along the ith ring; operator $v_{i,j}$ describes the interaction energy between ith and jth rings; k the number of site that belongs to ith or jth ring.

Eigenvalues of the matrix were computed with Krylov–Schur method (Stewart 2002, 2002) which can be considered as improved version of conventional Krylov subspace methods such as Arnoldi or Lanczos techniques (Arnoldi 1951; Lanczos 1950). As a software implementation of the method we used the SLEPc framework (the Scalable Library for Eigenvalue Problem Computations).

After the calculation of eigenvalues of the matrix we obtained the following thermodynamic characteristics as

$$\Omega = -\frac{RT}{W} ln\lambda_{max} \tag{14}$$

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{\mu} \tag{15}$$

$$\rho = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T} \tag{16}$$

where Ω is the grand thermodynamic potential per one lattice site; λ_{max} is the largest magnitude eigenvalue of matrix $\mathbf{T}$; μ chemical potential, S entropy per one lattice site and ρ specific amount of adsorbed molecules (adlayer density).

4 Results and discussion

Values of the directional interactions between the adsorbed molecules were chosen in such way that $w_1/RT = -7.5$ and w_2, w_3 are ranged from negative (attractive) to positive(repulsive). As we know from experimental data, this assumption is justified. Indeed, "tip-to-tip" interaction w_1 is negative and has a predominant character compared to other types of the pairwise nearest-neighbor interactions (Ye et al. 2007; Cicoira et al. 2008).

Due to the features of obtained results it is convenient to analyze it when pre-divided into two groups depending on the value of the interactions $\{w_1, w_2, w_3\}$:

1. *Case 1*—$w_1/RT = -7.5$, $w_3/RT = 0$, $w_2/w_1 = \{0; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6\}$
2. *Case 2*—$w_1/RT = -7.5$, $w_2/RT = 3$, $w_3/w_1 = \{0; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6\}$

Phase behavior of the adsorption monolayer in the first group of parameters $\{w_1, w_2, w_3\}$ is qualitatively different from its behavior in the second group. In this paper we consider the *Case 2* more completely then *Case 1* because the main features of *Case 1* were revealed in the article (Misiūnas and Tornau 2012), but here we also have some important additions. Let's discuss both cases in consecutive order.

4.1 Case 1

In this case "tip-to-tip" interaction w_1 is more attractive than "side-to-side" interaction w_2. And "tip-to-side" interaction w_3 is negligible in this case.

In Fig. 4 the isotherms of adsorption $\rho(\mu/RT)$ calculated with Monte Carlo method for the different values of w_2/w_1 relation are shown. Note that the same isotherms were calculated with transfer-matrix technique and they are in excellent agreement with Monte Carlo ones (discrepancy between the curves doesn't exceed the size of the symbols in Fig. 4). Therefore, we can guarantee that the calculated thermodynamic characteristics are equilibrium ones. It is seen that the phase behavior of the system changes significantly when "side-to-side" w_2 attraction decreases. Indeed, when "side-to-side" attraction is sufficiently strong the adlayer undergoes only one first-order phase transition

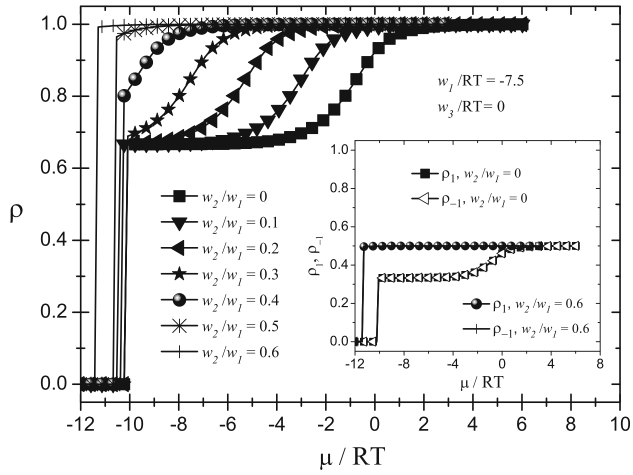

Fig. 4 The adsorption isotherms and partial isotherms (*inset*) at $w_1/RT = -7.5$, $w_3/RT = 0$ calculated with Monte Carlo method for the different values of w_2/w_1

from lattice gas phase with $\rho = 0$ to a close-packed one with $\rho = 1$. When “side-to-side” attraction gradually decreases one more ordered structure with coverage $\rho = 0.66(6)$ appears in the adlayer. Judging by abrupt changing of coverage that structure formed by the first-order phase transition from lattice gas.

Partial isotherms $\rho_1(\mu/RT)$ and $\rho_{-1}(\mu/RT)$ indicate that the phase with $\rho = 0.66(6)$ contains the same number of the molecules oriented in both ways that means $\rho_1 = \rho_{-1} = 0.33(3)$ (see inset in Fig. 4). So, if we take into account the snapshot of the adlayer in this region of chemical potential (Fig. 5a) we can conclude that the phase has honeycomb structure. The honeycomb structure is known to appear in real adlayers of TMA and it’s derivatives such as TCMB, BTBA and in adlayer of CA, irrespective of the substrate (Cicoira et al. 2008; Liang et al. 2009; Li et al. 2005; Ishikawa et al. 2002; Ye et al. 2007; Kannappan et al. 2007; Zhang et al. 2008).

When “side-to-side” attraction w_2 is relatively weak a frustrated close-packed structure is formed by Langmuir like adsorption onto 2D pores of the honeycomb structure on the basis of host–guest principle (Fig. 5b). It is exactly Langmuir adsorption in the limit case when $w_2 = w_3$ (Fig. 5c). It is due to (1) both orientations of the molecule adsorbed in the 2D pores are energetically equal (in limit case) and (2) the molecules adsorbed on these sites can not interact with each other. So, the adsorbed molecules can rotate on those sites. This phenomenon was observed experimentally in TMA adlayer on Au(111) (Li et al. 2005). If “side-to-side” attraction is strong the first-order phase transition from lattice gas leads the system to the structure where islands of honeycomb structure and disordered close-packed phase coexist.

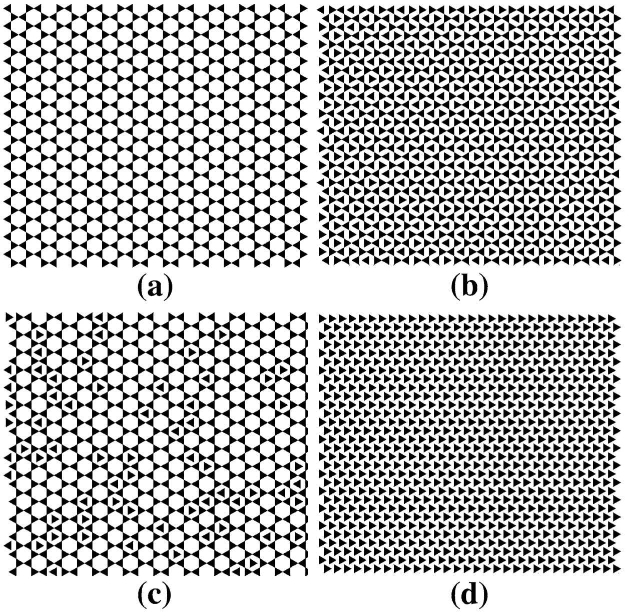

Fig. 5 The snapshots of the adlayer for *Case 1* at $w_2 = w_3 = 0$ in stable regions of **a** honeycomb structure ($\mu/RT = -8$), **b** frustrated close-packed structure ($\mu/RT = 6$), **c** in intermediate region ($\mu/RT = -2.1$) between the honeycomb and the close-packed structure; and **d** the snapshot of the adlayer for *Case 2* at $w_3/w_1 = 0.4$ in stable rigion of the ordered close-packed structure ($\mu/RT = 4$)

In Fig. 6 the specific internal energy $U(\rho)$ and the differential heat of adsorption $q_d(\rho)$ dependencies on the adlayer density are shown. These curves confirm the above mentioned phase behavior. Indeed, the position of inflection point on the internal energy curves and the step on the differential heat of adsorption curves at $\rho = 0.66(6)$ indicate that the honeycomb structure is formed in the adlayer. And the values of the internal energy $U/RT = -7.5$ and the differential heat of adsorption $q_d/RT = 0$ in close-packed structure confirm that Langmuir like adsorption onto 2D pores of the honeycomb structure takes place for weak “side-to-side” attraction w_2.

We had been calculated entropy per one lattice site as a function of the adlayer density with transfer-matrix technique (Fig. 7). It is seen the abrupt formation of the honeycomb structure is confirmed here as minimum of the entropy at $\rho = 0.66(6)$. On the other hand, the dynamic behavior of the close-packed structure for weak “side-to-side” attractions is revealed as constant non-zero value of the entropy at $\rho = 1$.

4.2 Case 2

In this case “tip-to-tip” interaction w_1/RT is much more attractive than others and equals -7.5 as in *Case 1*, but “side-to-side” interaction w_2 is repulsive. “Tip-to-side” interaction is attractive and varied from $w_3/w_1 = 0$ to

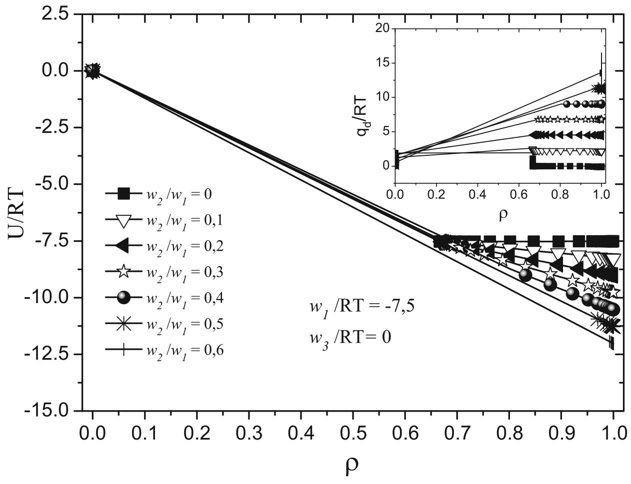

Fig. 6 The specific internal energy and the differential heat of adsorption (inset) vs adlayer density at $w_1/RT = -7.5$, $w_3/RT = 0$ for the different values of w_2/w_1 calculated with Monte Carlo method

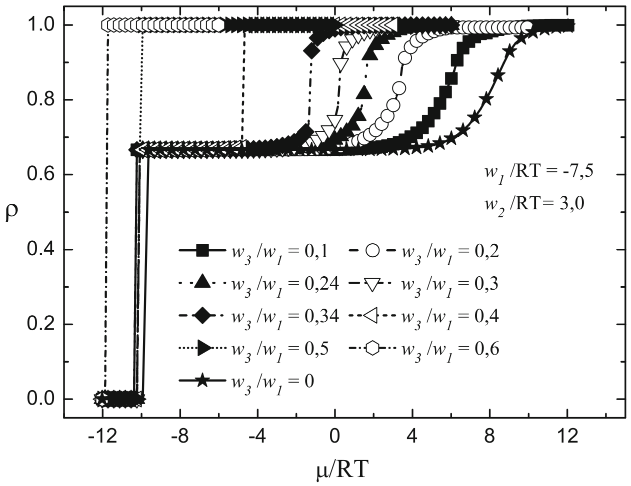

Fig. 8 The adsorption isotherms at $w_1/RT = -7.5$, $w_2/RT = 3$ calculated with Monte Carlo method for the different values of w_3/w_1

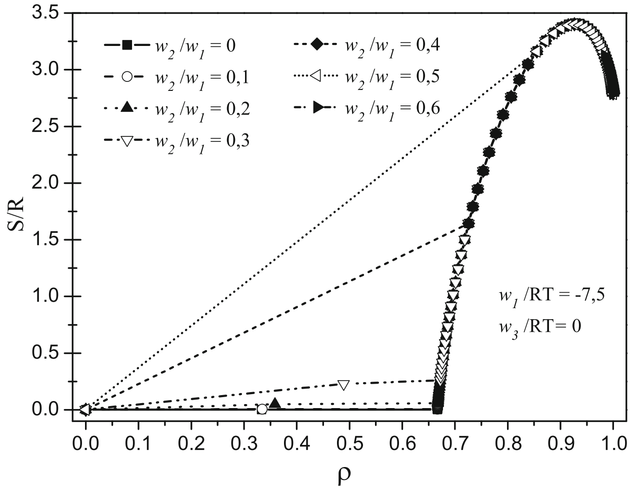

Fig. 7 Entropy (in units of R) as a function of the adlayer density at $w_1/RT = -7.5$, $w_3/RT = 0$ for the different values of w_2/w_1 calculated with transfer-matrix technique

$w_3/w_1 = 0.6$. In Fig. 8 the isotherms of adsorption calculated with Monte Carlo method for the different values of w_3/w_1 are shown. We can distinguish four different phase behaviors of the adlayer (or regimes of adsorption) depending on the relative value of "tip-to-side" interaction.

In the IV regime "tip-to-side" interaction is set to zero. This regime is pretty similar to *Case 1* with weak "side-to-side" interaction w_2. So, in this regime, after formation of the honeycomb structure there is Langmuir like adsorption onto 2D pores and the frustrated close-packed structure appears (Fig. 5b).

When "tip-to-side" interaction gradually increases up to $w_3/w_1 = 0.3$ the transition from the honeycomb structure to close-packed one becomes not Langmuir like because of discontinuous part on the isotherm (it is the III regime). In this regime the close-packed phase has completely disordered structure.

In the II regime at $0.3 < w_3/w_1 \leq 0.5$ there are two consecutive first-order phase transitions in the adsorption monolayer when chemical potential increases. The first phase transition leads to the honeycomb structure (Fig. 5a) as in *Case 1*. The second phase transition, in addition to the sharp changing of the adlayer density, accompanied by abrupt reorientation of a particular part of the already adsorbed molecules that leads to the close-packed structure consisted of molecules which all have the same orientation relative to each other and relative to the surface (Fig. 5d). Cross-lines on the partial isotherms mean that the close-packed structure of the adlayer can switch between two states which different by the orientation of all the molecules from $c_i = 1$ to $c_i = -1$ and contrariwise (Fig. 9). This close-packed structure has been experimentally observed using STM in real adsorption monolayers of TMA on Au (111) (Cicoira et al. 2008; Liang et al. 2009; Ye et al. 2007), BTBK on Ag (111) (Liang et al. 2009; Cicoira et al. 2008) and CA on graphite (Kannappan et al. 2007).

In the I regime when "tip-to-side" attraction is sufficiently strong ($w_3/w_1 > 0.5$) there is only one first-order phase transition from lattice gas to the close-packed structure, but in this regime as opposite to the IV regime and whole *Case 1* the close-packed structure consists of the molecules which all have the same orientation (Fig. 5d).

Thus, we come to an important conclusion that the predominant attractive interaction w_1 always leads to the formation of the honeycomb structure in the adsorption monolayer with local density $\rho = 0.66(6)$. While, the value w_3/w_1 defines the structure of close-packed phases. Comparative analysis of the experimental data and the results

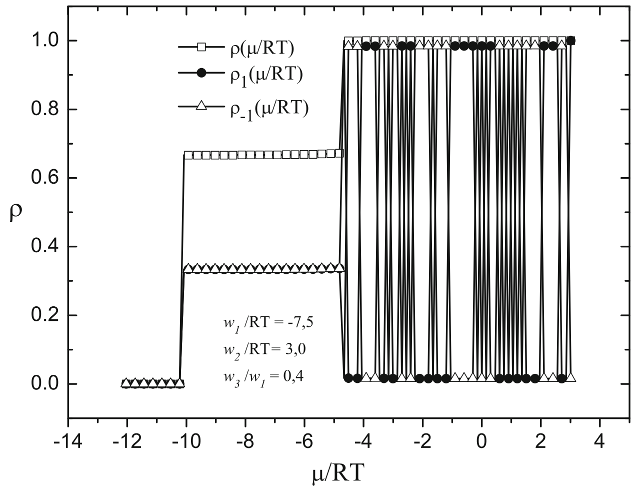

Fig. 9 The partial isotherms $\rho_1(\mu/RT)$ and $\rho_{-1}(\mu/RT)$ and the total isotherm $\rho(\mu/RT)$ calculated with Monte Carlo method at $w_1/RT = -7.5$, $w_2/RT = 3$ and $w_3/w_1 = 0.4$

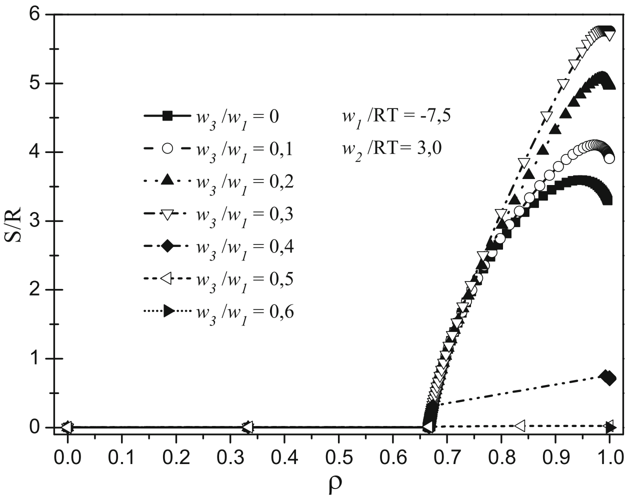

Fig. 11 Entropy per one lattice site (in units of *R*) as function of the adlayer density calculated with transfer-matrix technique at $w_1/RT = -7.5$, $w_2/RT = 3$ for the different values of w_3/w_1

obtained in the framework of the model allow us to conclude that for real adlayers $w_3/w_1 < 0.5$.

In Fig. 10 the specific internal energy $U(\rho)$ and the differential heat of adsorption $q_d(\rho)$ dependencies on the adlayer density calculated in the framework of *Case 2* are shown. These curves confirm the above mentioned phase behavior of the adlayer. It is seen that any stable phases except lattice gas with $\rho = 0$ and the close-packed phase with $\rho = 1$ are not observed in the system in the I regime. The values of the specific internal energy and the differential heat of adsorption are obviously equal to zero in the lattice gas phase and $U/RT \approx 3w_3$, $q_d/RT \approx 6w_3$ in the close-packed phase. Such values of the internal energy and the differential heat of adsorption indicate that the close-packed phase at $w_3/w_1 > 0.5$ consists of the molecules with the same orientation relative to each other and relative to the surface and has the above mentioned structure (Fig. 5d).

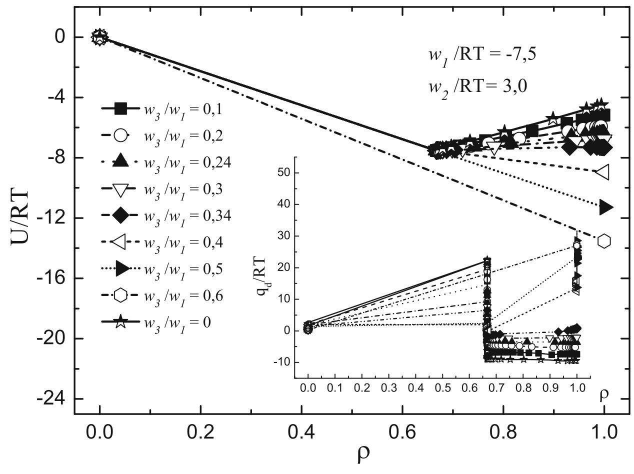

Fig. 10 The specific internal energy and the differential heat of adsorption (*inset*) versus adlayer density calculated with Monte Carlo method at $w_1/RT = -7.5$, $w_2/RT = 3$ for the different values of w_3/w_1

In other regimes, where $w_3/w_1 < 0.5$, there are the inflection point and the step on the plots $U(\rho)$ and $q_d(\rho)$ at $\rho = 0{,}66(6)$, respectively. This fact shows that the honeycomb structure appears in the adlayer. The formation of the honeycomb structure is also confirmed by the number values of $U(\rho = 0.66(6))/RT = w_1$ and $q_d(\rho = 0.66(6))/RT = 3w_1$.

It is seen that the behavior of $U(\rho)$ and $q_d(\rho)$ changes when passing through the value $w_3/w_1 = 0.3$. In the III regime when $w_3/w_1 \leq 0.3$, there is continuous mode of adsorption which leads to the dynamic "host–guest" like close-packed structure (Fig. 5b). On the other hand, when $0.3 < w_3/w_1 \leq 0.5$, the values of $U(\rho = 1)/RT = 3w_3$ and $q_d(\rho = 1)/RT = 6w_3$ indicate that the close-packed phase has the structure shown in Fig. 5d.

Entropy as a function of the adlayer density calculated with transfer-matrix technique is shown in Fig. 11. There are two minima at $\rho = 0.66(6)$ and $\rho = 1$ those correspond to the honeycomb structure and the close-packed structure which consist of molecules with the same orientation. When $w_3/w_1 \leq 0.3$ there are few maxima at $\rho = 1$ relating to partially disordered honeycomb structure with molecules adsorbed in the 2D pores in some way.

The phase diagram of the adlayer in the framework of *Case 2* when $w_3/w_1 = 0.4$ is shown in Fig. 12. The positions of the phase transition points were determined by Monte Carlo calculations of the fourth-order cumulants U_ψ of related order parameters ψ_{hon} or ψ_{cp} and the location of the susceptibility peak for the given value of the lattice size. Typical behavior of the fourth-order cumulants $U_\psi(\mu/|w_1|)$

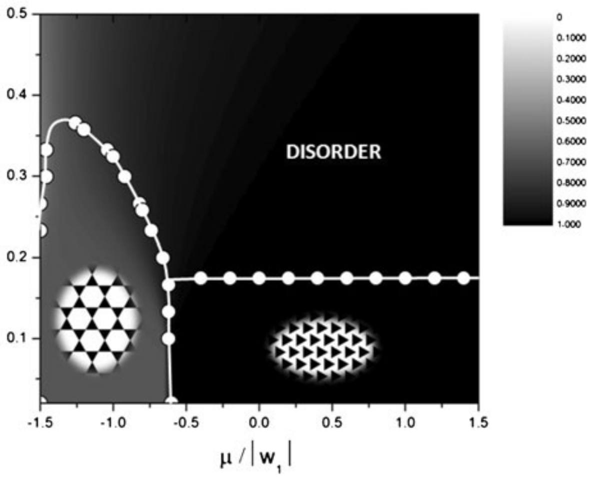

Fig. 12 The phase diagram (μ/|w_1|, |RT/w_1|) of the adlayer calculated with Monte Carlo method (*symbols*) and transfer-matrix technique (as projection of surface plot ρ(μ/|w_1|, |RT/w_1|), where scale of the adlayer density is shown on the *inset*) at $w_1/RT = -7.5$, $w_2/RT = 3$ and $w_3/w_1 = 0.4$. The *solid line* is just guide for eyes

of related order parameter ψ_{hon} and the susceptibility of the adlayer density χ_ρ(|RT/w_1|) are shown in Fig. 13. That allows us to obtain the estimation of the critical value of the chemical potential and temperature with error not exceeding the size of the symbols in the figure. Additionally, we calculated the set of adsorption isotherms ρ(μ/|w_1|) for different temperatures RT/w_1 and stacked them into the surface plot ρ(μ/|w_1|, |RT/w_1|) which corresponded to our phase diagram in (μ/|w_1|, |RT/w_1|) coordinates computed with Monte Carlo technique (Fig. 12). The qualitative agreement between both results is rather good.

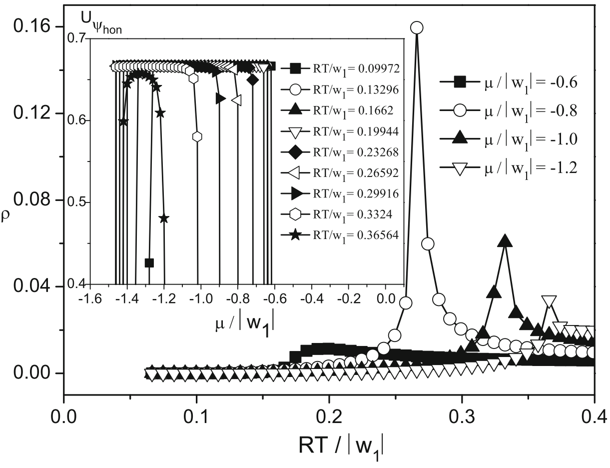

Fig. 13 Typical behavior of the forth-order cumulants U_{ψ_hon} as a function of μ/|w_1| calculated at different temperatures and the susceptibility of the adlayer density χ_ρ as a function of |RT/w_1| calculated at various chemical potentials μ/|w_1|

5 Conclusion

In this paper we have investigated the LGM of adsorption of triangular-shaped molecules on a triangular lattice taking into account the directionality of pairwise nearest-neighbor interactions between adsorbed molecules. The most important results of this study are as follows:

1. Pairwise nearest-neighbor interactions between adsorbed TMA molecules and molecules with the same symmetry in the arrangement of the functional groups can lead only to the honeycomb structure and the close-packed structure consisting of molecules with the same orientation relative to each other and relative to the surface.
2. All the adlayer ordered structures appear through the first-order phase transitions.
3. Sequential adsorption onto 2D pores of the honeycomb structure can be described by Langmuir isotherm.
4. Comparative analysis of the experimental data and the results obtained in the framework of the constructed model allows us to conclude that in real adlayers of this type the condition $w_3/w_1 < 0.5$ is true.
5. The constructed model reproduces qualitatively the most general features of the phase behavior of TMA adlayer, 1,3,5-benzenetribenzoic acid, 1,3,5-tris-(carboxymethoxy)-benzene, cyanuric acid adlayers and adlayers of other molecules with the same symmetry in the arrangement of the functional groups. In this regard, it is believed that the proposed model can be effectively used to better understand the physicochemical processes occurring in such systems and summarize all the experimental data.

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