Generalized lattice-gas model for adsorption of functional organic molecules in terms of pair directional interactions

S. S. Akimenko,[1] V. A. Gorbunov,[1] A. V. Myshlyavtsev,[1,2] and P. V. Stishenko[1]

[1]*Omsk State Technical University, Prospekt Mira 11, Omsk 644050, Russian Federation*

[2]*Institute of Hydrocarbons Processing SB RAS, 54 Neftezavodskaya, Omsk 644040, Russian Federation*

A generalized lattice-gas model that takes into account the directional character of pair interactions between the lattice sites is proposed. It is demonstrated that the proposed model can be successfully used to deeply understand the self-assembly process in adsorption monolayers of functional organic molecules driven by specified directional interactions between such molecules (e.g., hydrogen bonding). To illustrate the idea, representative cases of the general model with different numbers of identical functional groups in the chemical structure of the adsorbed molecule are investigated with Monte Carlo and the transfer-matrix methods. The model reveals that the phase behavior of the adsorption systems considered can be characterized as a hierarchical self-assembly process. It is predicted that in real adsorption systems of this type, the energy of hydrogen bonding sufficiently depends on the mutual orientation of the adsorbed molecules.

I. INTRODUCTION

Every year new methods of creating complex molecular structures on solid surfaces appear [1–5]. The phenomenon of molecular self-assembly is of special interest in this context. Usually, the term "molecular self-assembly" refers to spontaneous association of molecules in thermodynamically stable and ordered structures due to the noncovalent interactions between adsorbed molecules [6,7]. Resulting structures and the mechanism of the self-assembly process by itself depend on a large number of parameters, such as temperature, pressure, geometry and chemical nature of the surface, and structure of the adsorbed molecules. On the other hand, the availability of many control parameters in the adsorption systems indicates a significant diversity in the phase behavior. Even in relatively simple adsorption systems there are some complex effects, for example, a cascade of ordered structures [6]. In other cases, the adsorbed molecules tend to be combined into independent structural elements that act as building blocks for resulting ordered structures. Such behavior is often called hierarchical self-assembly [8–11]. It is rather difficult to predict a phase behavior of the adsorption layer. To date, the research process in this field looks like an accumulation of knowledge. Indeed, in recent years a huge amount of self-assembled monolayers has been discovered experimentally [6,7,12–15].

The main task of rational design of self-assembly processes is identification of the combination of the molecule, adsorption surface, and external conditions required to produce the adlayer with a desired ordered structure. A detailed understanding of the physicochemical processes occurring in the absorption layer is indispensable in this case. To this end, computer simulations can be useful for the ascertainment of general laws and subsequent prediction of the self-assembly.

To simulate self-assembled adsorption monolayers, the lattice-gas model (LGM) is often used. Conventionally, it is assumed that the energy of the intermolecular interaction does not depend on the mutual orientation of adsorbed particles [16–18]. However, self-assembly of molecules with complicated chemical structure on a solid surface in most cases is determined by directional intermolecular interactions such as hydrogen bonding, dipole-dipole interactions, and coordination interactions. There are several papers on modeling of such systems using the LGM [19–23]. In these works the Kronecker δ or tensor $\tau_i^{i,j,k}$ with similar structure is used to take into account the directional character of intermolecular forces.

The main goal of this study is to develop a general lattice-gas model of single-site adsorption in terms of pair directional interactions between adsorbed molecules and illustrate how it works in simple special cases. The paper is organized as follows. The general lattice model of single-site adsorption, which takes into account the directional nature of the interactions, is formulated in Sec. II. Section III briefly describes the methods for calculating thermodynamic characteristics of the constructed model. Further, in Secs. IV and V we show how to use the general model to analyze structural and thermodynamic properties of some adsorption monolayers of functional organic molecules. In Sec. VI general conclusions and perspectives for using the proposed model are formulated.

II. GENERAL MODEL

Since the main object of this study is directed intermolecular interactions in the adsorption layer, we will not directly take into account the size of adsorbate molecules. That is, only monomolecular adsorption will be considered in the model. The set theory language is the simplest and most intuitive way to describe the generalized model.

Let L be a set of lattice sites and Q be a set of all possible site states. Then the function $\xi : L \rightarrow Q$ maps each site to its state, i.e., ξ fully defines the state of the whole lattice. It is convenient to distinguish an empty site state $q_0 \in Q$. Then we can define the set of all occupied (not empty) sites $\Xi \equiv \{l|l \in L \wedge \xi(l) \neq q_0\}$. The lattice topology is defined with the function $\nu : L \rightarrow L^m$ that maps each lattice site to a tuple of its m neighbors. To avoid double accounting of site pairs it is convenient to define ν in such a way that $b \in \nu(a) \rightarrow a \notin \nu(b)$. Neighboring sites are linked by edges. Therefore, there is a set of possible types of edges E on the lattice. For example, for a two-dimensional square lattice with only nearest-neighbor

interactions there are two types of edges: horizontal (e.g., right) and vertical (e.g., down). Each pair of neighboring lattice sites is associated with an element from the set E. It is convenient to introduce the function $\varepsilon : L \times L \to E$, which yields the type of the edge between two sites of the lattice considered. Please note that $\varepsilon(a,b)$ is defined only for such a and b that $b \in \nu(a)$ and $a \notin \nu(b)$. Let W be a set of all possible values of interaction energies between neighboring sites. Then the model interactions can be defined by the function $g : Q \times Q \times E \to W$ that determines the energy of the interaction between two neighboring sites by their states and the edge type connecting the sites together. With the notions introduced above, the thermodynamic Hamiltonian for the open molecular system takes the following form:

$$H_{\text{eff}} = -\mu|\Xi| + \sum_{a \in \Xi} \sum_{b \in \nu(a)} g(\xi(a),\xi(b),\varepsilon(a,b)),$$

where $|\Xi|$ is the size of Ξ set and μ is the chemical potential.

Since the function g depends on three parameters for open molecular system, it can be represented as a third-rank tensor $\mathbf{G}$ with elements $G_{i,j,k}$. The size of the matrices $G_{i,j}$ depends on the number of states (including the vacancy state, hence the first row and the first column consist of zeros) and the matrix element at the cross section of two states describes the pair energy of two molecules along the k direction on the underlying lattice. The size of the interaction tensor along the third dimension k depends on the coordination number of the underlying lattice and interaction distance. For example, $k = 2$ for a square lattice and $k = 3$ for a triangular lattice. If the interactions between next-nearest-neighbor sites on square lattice are also taken into account, then $k = 4$. Thus, it is convenient to describe the interaction tensor as k square matrices that correspond to interactions along k directions on the underlying lattice. It is worth noting that different adsorption systems differ from one another only by the structure of the interaction tensor $G_{i,j,k}$.

The formulation of the model in terms of set theory explicitly shows the difference between the provided model and similar models with isotropic interactions, namely, the well-known q-state Potts model. The Potts model is the generalization of the Ising model, which was formulated primarily to describe the behavior of ferromagnets. Currently, it is widely used in physics [24,25], biology [26,27], medicine [25,28], sociology [29], etc. In particular, it is also known to be a fruitful model of adsorption phenomena [30]. The main difference between the q-state Potts model and the general model constructed in this paper is that the energy of interaction in the Potts model does not depend on the edge type connecting the sites. Therefore, if we replace the function $g : Q \times Q \times E \to W$ by $g_p : Q \times Q \to W$ we get the Potts model. In this case, the thermodynamic Hamiltonian of the generalized Potts model can be written as follows:

$$H_{\text{eff}} = -\mu|\Xi| + \sum_{a \in \Xi} \sum_{b \in \nu(a)} g_p(\xi(a),\xi(b)).$$

It is easy to see that the function g_p can be represented by a second rank tensor $\mathbf{G_p}$. In the simplest case of the Potts model, the function g_p can be represented as a diagonal matrix
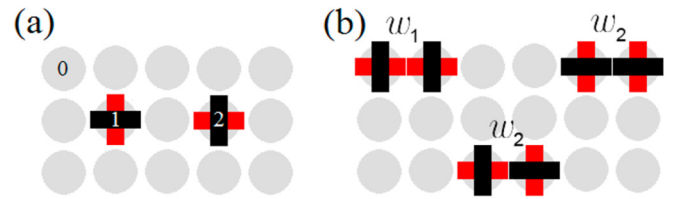

FIG. 1. Lattice model of adsorption of the cross-shaped molecules with two identical functional groups in the *trans* position: (a) possible states of the lattice site and (b) possible interaction energies between the molecules adsorbed on nearest-neighbor sites.

$\mathbf{G_p}$, with diagonal elements equal to the interaction energy J_p with indices running by all states of Q. There are also various generalizations and complications of the model that can be described in these terms. For example, the well-known chiral Potts model, which has no symmetry of interactions between neighboring sites, is characterized by the dense asymmetric matrix $\mathbf{G_p}$.

Therefore, the Potts model and some of its generalizations are the special cases of the proposed general model. It is obvious that a comprehensive study of the general model is very problematic. In this paper we consider some simple special cases concerning the adsorption of functional organic molecules. Let us consider cross-shaped molecules adsorbing on a simple square lattice. It is assumed that there are $n \leqslant 4$ special directions corresponding to the number of functional groups (FGs) in the molecule. Depending on the relative orientation of the molecules on the lattice, different types of interactions w_x may occur between the molecules. This model describes any molecule having C_4 symmetry and $n \leqslant 4$ different FGs capable of forming, for example, a hydrogen bond. Special cases of the model characterized by different numbers of FGs and their mutual arrangements are essentially the independent models. We believe that the study of these special cases provides a deeper understanding of the effect of directional intermolecular interactions on the behavior of self-assembled monolayers comprising functional organic molecules.

In the first special case, a molecule is assumed to have a single FG. All possible arrangements of FGs in the cross-shaped molecule are equivalent. Different states of the lattice site correspond to all possible orientations of the molecule (possible directions of FGs) along the primitive vectors of the lattice. Thus, there are four possible orientations of the
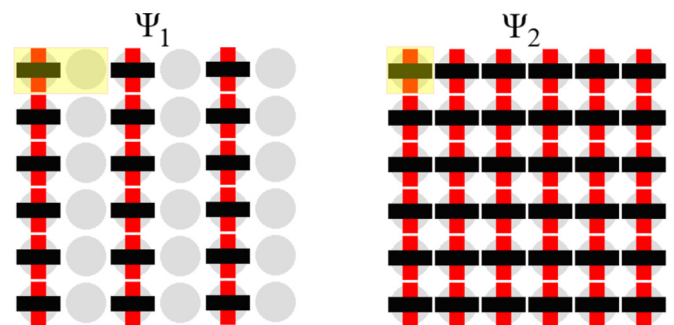

FIG. 2. Ordered structures found in the ground state of the adsorption layer of the cross-shaped molecules with two identical functional groups in the *trans* position on the square lattice.
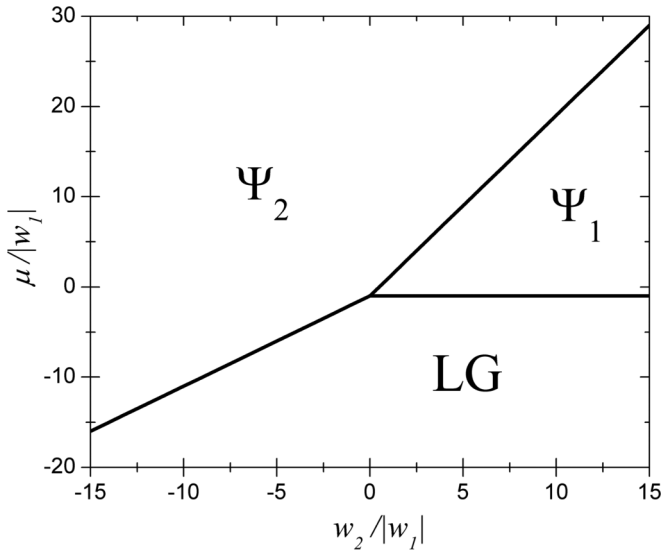
FIG. 3. Ground-state phase diagram of the adsorption layer of the cross-shaped molecules with two functional groups in the *trans* position on the square lattice in coordinates of $\mu/|w_1|$ and $w_2/|w_1|$.

molecule on the square lattice. This particular case of the model was studied earlier in Ref. [20]. The model revealed that the phase behavior of the system can be characterized as the hierarchical self-assembly process. The monodentate molecules tend to form dimers: the adsorbed molecules paired with a directional attractive interaction (e.g., hydrogen bonding). Then the dimers behave like building blocks for the stable phases occurring in the adlayer at higher surface concentrations of the adsorbed molecules. As it will be shown below, this feature of the self-assembly process apparently is common for this type of adsorption system.

In this paper we show some examples of exploitation of the general model to study the self-assembly processes in the adsorption layers of organic molecules with two identical FGs. There are two ways to arrange two FGs in the cross-shaped molecule: on opposite arms of the molecule (*trans* isomer) and on adjacent ones (*cis* isomer).
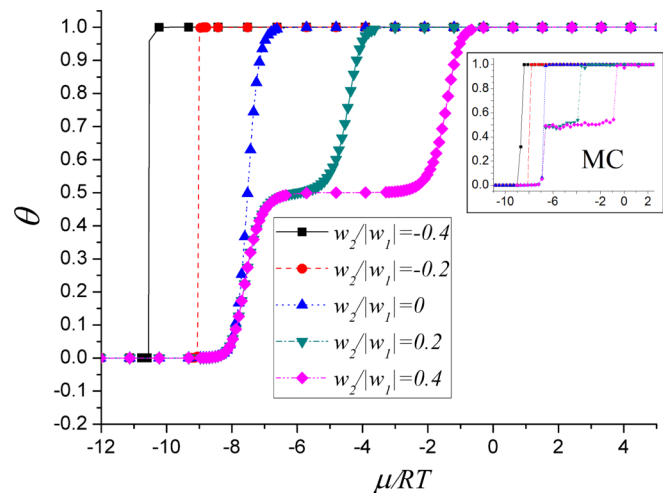
III. METHODS

All the constructed lattice-gas models were studied in the grand canonical ensemble with Monte Carlo [31] and transfer matrix methods [32]. By combining these two methods we can be sure that all calculated thermodynamic functions are equilibrium ones.

We have performed the Monte Carlo simulation using the standard Metropolis algorithm. Thermodynamic equilibrium at fixed chemical potential μ and temperature was achieved with adsorption-desorption dynamics and diffusion relaxation (Kawasaki dynamics). We simulated the adsorption on the square lattice with the linear size $L = 60$ and periodic boundary conditions. The size of the lattice was chosen in such a way that all ground-state ordered structures were not perturbed. Furthermore, it was found that the finite size of the lattice had no significant influence on the calculated thermodynamic characteristics. For each value of chemical potential $10^7 - 10^9$ Monte Carlo steps (MCSs) were used for relaxation and computation of thermal averages. Note that one MCS corresponds to one sweep over the entire lattice.

The idea of the transfer-matrix method is to replace the direct calculation of the grand partition function for the two-dimensional lattice-gas model with a much simpler problem of computing the largest absolute eigenvalue λ_1 and the corresponding eigenvector of the matrix. The transfer-matrix method gives the exact value of the grand partition function for the semi-infinite system considered ($\Omega = M^{-1} \ln \lambda_1$). It is obvious that thermodynamic characteristics calculated using the transfer-matrix method tend to exact values of the infinite two-dimensional lattice when increasing the stripe width M. In the case of transfer-matrix calculations, there is the well-known effect of M on the phases appearing on the surface with free edges [33]. In this paper, the lattice width M is chosen so that it is a multiple of the size of unit cells of all found in the ground-state phases. Periodic boundary conditions were imposed to reduce the influence of the finite size.

IV. *TRANS* POSITION OF FUNCTIONAL GROUPS

Due to the symmetry of the cross-shaped molecule, adsorption of the molecules with two functional groups in the
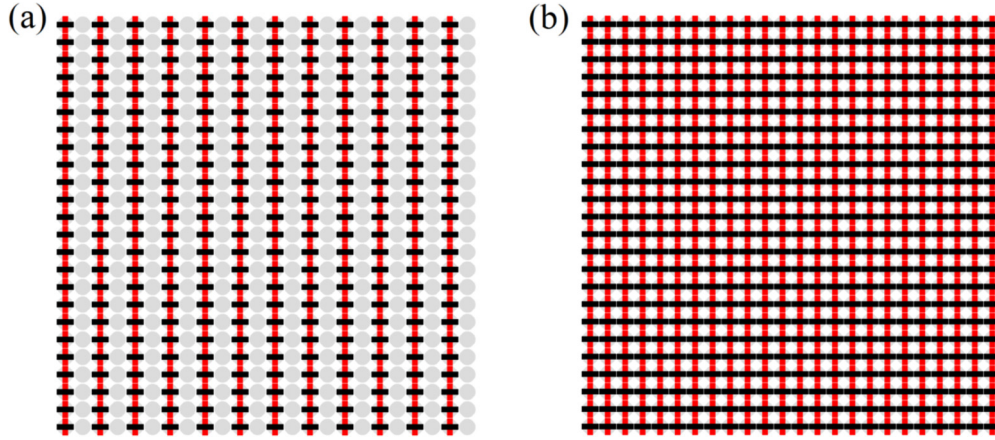

FIG. 4. Adsorption isotherms and entropy dependence on the surface coverage at $w_1/RT = 7.5$ and $M = 6$.
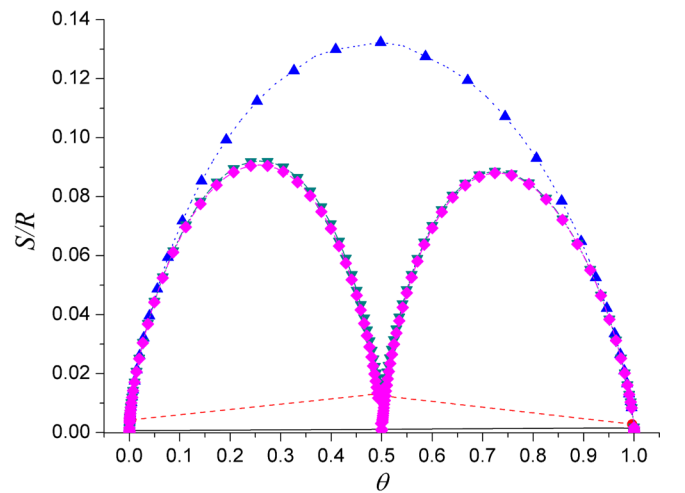
FIG. 5. Patterns of the lattice (24×24) obtained at (a) $\mu/RT = -4$ and (b) $\mu/RT = 2$.

trans position is the simplest case in terms of the model under consideration. There are only two possible orientations of such a molecule relative to the primitive vectors. Thus, there are three different possible states of the lattice site, including the empty sites [Fig. 1(a)].

Let us include in the model only two types of intermolecular interactions with energies w_1 and w_2 [Fig. 1(b)]. The interaction energy w_1 is attractive and occurs between the molecules with FGs oriented towards each other, for example, a hydrogen bond between two carboxylic groups. The interaction energies for other relative arrangements of the adsorbed molecules are assumed to be the same and equal to w_2. The energy of the interaction w_2 ranges from negative to positive values under the condition $w_2 > w_1$, implying that the interaction between FGs is more thermodynamically favorable. In this case, the function g can be represented as the following tensor **G**:

$$G_h = \begin{pmatrix} 0 & 0 & 0 \\ 0 & w_2 & w_2 \\ 0 & w_2 & w_1 \end{pmatrix}, \quad G_v = \begin{pmatrix} 0 & 0 & 0 \\ 0 & w_1 & w_2 \\ 0 & w_2 & w_2 \end{pmatrix},$$

where G_h and G_v are the tensor cross sections corresponding to two types of edges on the square lattice, horizontal and vertical, respectively.

A. Ground-state analysis

The structures of the possible ordered phases and a sequence of their formation on the surface at $T = 0\,$K with increasing chemical potential (pressure in the gas phase) were determined using the principle of minimum grand thermodynamic poten-

tial. An analysis of the ground state has shown that there are only two ordered structures in the adsorption layer at surface coverages $\theta = 0.5$ and 1. For the sake of convenience, we denote them by Ψ_1 and Ψ_2 (Fig. 2).

Expressions for the grand thermodynamic potentials Ω of ordered structures per one lattice site can be written as follows:

$$\Omega_{LG} = 0, \quad \Omega_{\psi_1} = -0.5\mu + 0.5w_1, \quad \Omega_{\psi_2} = -\mu + w_1 + w_2,$$

where Ω_{LG} is the grand thermodynamic potential of the two-dimensional lattice gas, which is equivalent to the empty surface in the ground state of the system. The phase space of the model in the ground state is determined by three parameters μ, w_1, and w_2; therefore, it is not difficult to visualize it (Fig. 3). One can see that the phase behavior of the adsorption layer depends mostly on the energy w_2.

For $w_2 > 0$, an increase of the chemical potential leads to the following sequence of ordered structures: First, the $\Psi_1(-1 < \mu/|w_1| \leftarrow 1 + 2w_2/|w_1|)$ phase is formed from the lattice gas and then goes to the Ψ_2 phase at $\mu/|w_1| > -1 + 2w_2/|w_1|$. Similarly to the adsorption layer of the cross-shaped molecules with one functional group, the model considered at the specified parameters is also characterized by the hierarchical self-assembly [20]. A qualitative difference is that the cross-shaped molecules with two functional groups in the *trans* position tend to form chains, rather than dimers. Further, when the chemical potential increases, these chains combine to form the ordered structures found in the ground state (Fig. 2). If $w_2 < 0$, only the close-packed phase Ψ_2 appears at $\mu/|w_1| > -1 + w_2/|w_1|$.
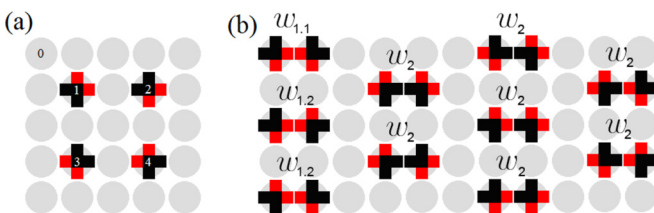

FIG. 6. Lattice model of adsorption of the cross-shaped molecules with two identical functional groups in the *cis* position: (a) possible states of the lattice site and (b) possible interactions between the molecules adsorbed on nearest-neighbor sites.
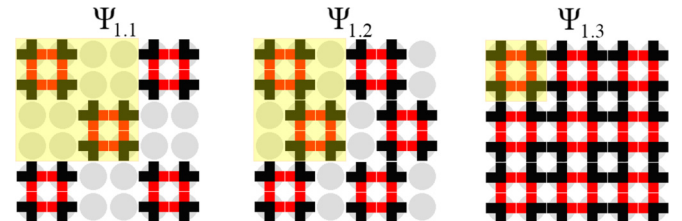

FIG. 7. Ordered structures appearing in the ground state of the adsorption layer of the cross-shaped molecules with two functional groups in the *cis* position on the square lattice. All structures are thermodynamically stable only at $w_{1.1} < w_{1.2}$.
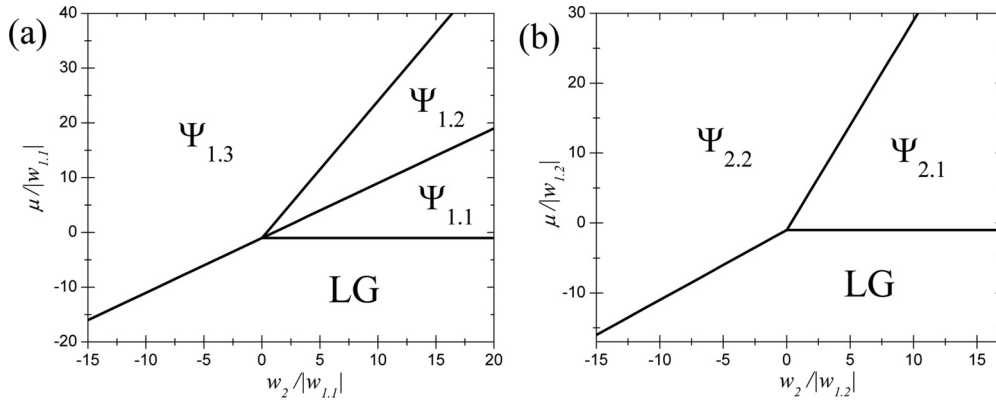
FIG. 8. Ground-state phase diagram of the adsorption layer of the cross-shaped molecules with two functional groups in the *cis* position on the square lattice in coordinates of $\mu/|w_1|$ and $w_2/|w_1|$ at (a) $w_{1.1} < w_{1.2}$ and (b) $w_{1.1} > w_{1.2}$.

B. Results at finite temperature and discussion

Based on the results of the ground-state analysis, the following set of interactions had been used for a comprehensive study of the phase behavior of the system at finite temperatures: $w_2/|w_1| = \{-0.4, -0.2, 0, 0.2, 0.4\}$, where $w_1/RT = -7.5$. As can be seen in Fig. 3, the specified set of interaction parameters $w_2/|w_1|$ covers both areas of the phase space corresponding to qualitatively different phase behaviors of the adsorption layer. Figure 4 shows the adsorption isotherms and entropy dependence on the surface coverage calculated by the transfer-matrix method at $M = 6$.

It should be noted that adsorption isotherms obtained with the Monte Carlo method are characterized by minor fluctuations of the surface coverage, but are essentially the same within the error limit. There are two horizontal plateaus at $\theta = 0.5$ and 1 on the adsorption isotherms in Fig. 4. In addition, there are entropy minima at the same values of the surface coverage. These facts both indicate the formation of ordered structures in the adsorption layer. Analysis of the lattice snapshots (Fig. 5) shows that (i) all the adsorbed molecules in these ordered phases have the same orientation with respect to each other and combine into chains through the attractive interaction between FGs and (ii) two ordered phases revealed in the ground-state analysis, namely, Ψ_1 and Ψ_2, also appear in the adlayer at finite temperatures. Thus, the phase behavior of the adsorption layer within the considered case of the general model is quite obvious. On the other hand, the phase behavior of the system at $w_2/|w_1| > 0$ is similar to the adsorption overlayer comprising the molecules with a single FG [20]. Indeed, the hierarchical nature of the self-assembly process is observed in both cases. When the adsorbed molecule has only one FG, the building blocks of all ordered structures are the dimers; in the case of two FGs, the building blocks are the linear chains of the adsorbed molecules.

Real life analogs of such a system are essentially planar molecules with a C_4 axis and two FGs in *trans* position, for example, bifunctional derivatives of porphyrins, phthalocyanines, etc. [34–38]. In particular, it is established experimentally that an ordered phase similar to Ψ_2 emerges in adsorption layers of the above-mentioned molecules on the Au(111) surface [34].

V. *CIS* POSITION OF FUNCTIONAL GROUPS

In this section we consider the lattice model of adsorption of the cross-shaped molecules with two FGs in the *cis* position. Within the constructed general model the molecule considered has four possible orientations on the square lattice with respect to the primitive vectors (Fig. 6).

Unlike the previous model, there are two different orientations of the molecules with FGs directed to each other: $w_{1.1}$ and $w_{1.2}$ interactions [Fig. 6(b)]. These interaction energies are assumed to be different. Interaction energies for other mutual orientations of the adsorbed molecules are set to w_2. In this case, cross sections of the tensor **G** that correspond to horizontal and vertical edges types have the following form:

$$G_h = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & w_2 & w_2 & w_{1.2} & w_{1.1} \\ 0 & w_2 & w_2 & w_{1.1} & w_{1.2} \\ 0 & w_2 & w_2 & w_2 & w_2 \\ 0 & w_2 & w_2 & w_2 & w_2 \end{pmatrix},$$

$$G_v = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & w_2 & w_2 & w_2 & w_2 \\ 0 & w_{1.1} & w_2 & w_2 & w_{1.2} \\ 0 & w_{1.2} & w_2 & w_2 & w_{1.1} \\ 0 & w_2 & w_2 & w_2 & w_2 \end{pmatrix}.$$

A. Ground-state analysis

It was found that the phase behavior of the adlayer at $T = 0\,\mathrm{K}$ is determined by the type of dominant interaction
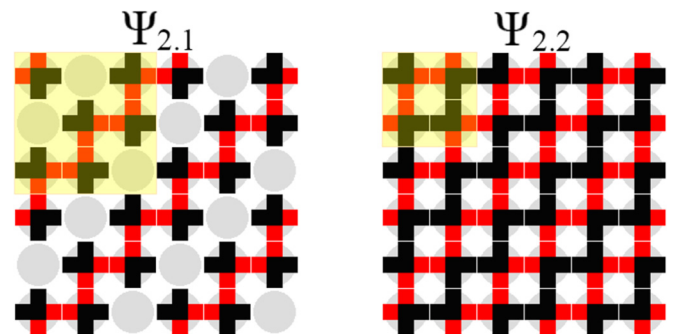

FIG. 9. Ordered phases formed in the ground state of the model at $w_{1.1} > w_{1.2}$.
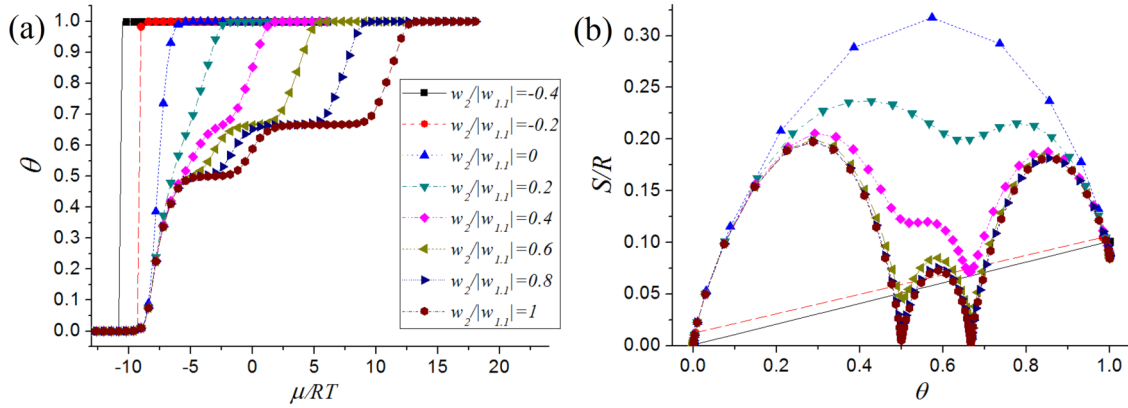
FIG. 10. Adsorption isotherms and entropy dependence on the surface coverage computed with the transfer-matrix method at $w_{1.1}/RT = -7.5$, $w_{1.2}/w_{1.1} = 0.5$, and different values of $w_2/|w_{1.1}|$.

between the functional groups $w_{1.1}$ or $w_{1.2}$. When $w_{1.1} < w_{1.2}$, the adsorbed molecules tend to form tetramers, square-shaped clusters comprised of four molecules bonded with a $w_{1.1}$ attractive interaction (Fig. 7). It should be noted that all observed ordered structures at $w_{1.1} < w_{1.2}$ consist of such units. Therefore, in this case the self-assembly process of the adsorption layer is also hierarchical. Ordered phases observed in the adsorption layer at $T = 0$ K can be seen in Fig. 7.

Provided that $w_{1.1} < w_{1.2}$, the value of energy $w_{1.2}$ does not qualitatively affect the phase behavior of the system. Therefore, it is possible to construct a phase diagram in coordinates $\mu|w_{1.1}|$ and $w_2/|w_{1.1}|$ [Fig. 8(a)] ignoring the parameter $w_{1.2}$.

When $w_2 > 0$, the system is in a phase region where all ordered structures found in the ground state sequentially emerge with increasing chemical potential. In contrast, if $w_2 \leqslant 0$, only the close-packed phase $\Psi_{1.3}$ is formed. When the dominant energy is $w_{1.2}(w_{1.2} < w_{1.1})$, zigzag units become more stable. As a result, there are two ordered structures $\Psi_{2.1}$ and $\Psi_{2.2}$ in the ground state of the adsorption layer (Fig. 9). Such phase behavior is similar to the previously discussed case of adsorption of the molecules with two FGs in the *trans* position, wherein the linear structural elements are also observed (Fig. 5).

The effect of $w_{1.1}$ energy on the system phase behavior is negligible in the case considered. Hence we can construct

the ground-state phase diagram in coordinates $\mu|w_{1.2}|$ and $w_2/|w_{1.2}|$ without any loss of generality [Fig. 8(b)]. Here we have similar regularities. If $w_2 > 0$, then all phases found are formed in the adsorption layer depending on the value of the chemical potential. If $w_2 \leqslant 0$, only the close-packed phase $\Psi_{2.2}$ appears in the adsorption layer.

B. Results at finite temperatures and discussion

According to the results of the ground-state analysis, we considered the following sets of the interaction parameters to study the model at finite temperatures:

$$w_{1.1}/RT = -7.5, \quad w_{1.2}/w_{1.1} = 0.5,$$
$$w_2/|w_{1.1}| = \{-0.4, -0, 2, 0, 0.2, 0.4, 0.6, 0.8, 1\};$$
$$w_{1.2}/RT = -7.5, \quad w_{1.1}/w_{1.2} = 0.5,$$
$$w_2/|w_{1.2}| = \{-0.4, -0.2, 0, 0.2, 0.4\}.$$

It is easy to see that the main difference between them lies in the ratio between $w_{1.1}$ and $w_{1.2}$. Figure 10 shows the adsorption isotherms and adlayer entropy dependence on the surface coverage, when $w_{1.1}/RT = -7.5$ and $w_{1.2}/w_{1.1} = 0.5$.

In this case, the Monte Carlo relaxation time is significantly increased compared to the previous one. This is due to a large number of possible states of a lattice site and high degeneracy
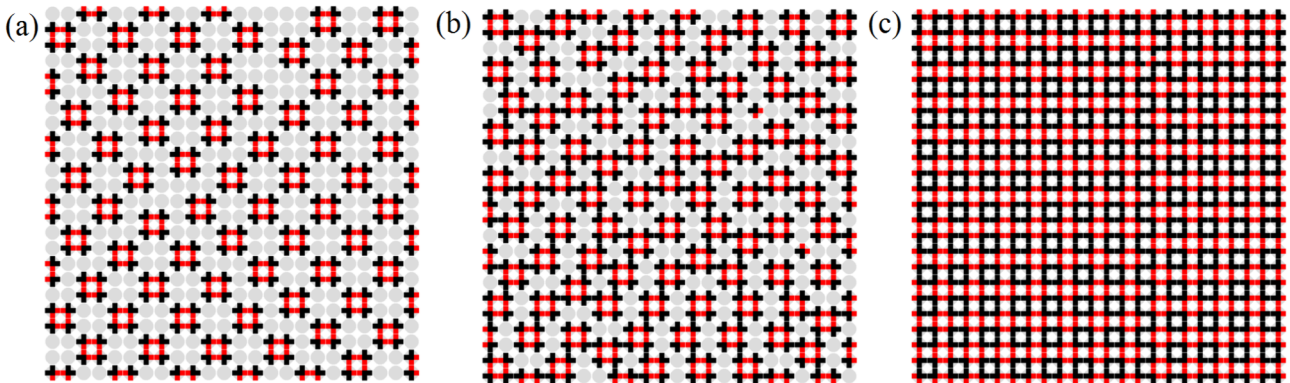

FIG. 11. Lattice patterns obtained with the Monte Carlo method at $w_{1.1}/RT = -7.5$, $w_{1.2}/w_{1.1} = 0.5$, and $w_2/|w_{1.1}| = 1$: (a) $\mu/RT = -3$, (b) $\mu/RT = 4.2$, and (c) $\mu/RT = 16$.
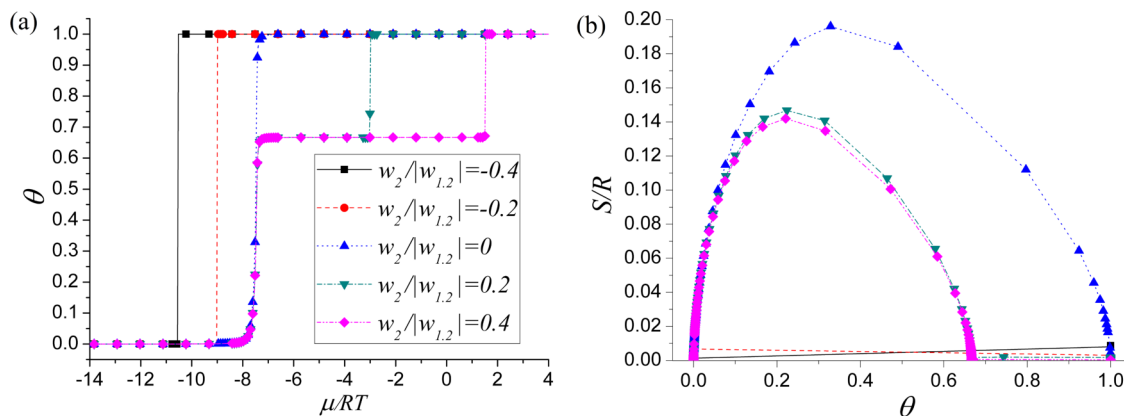
FIG. 12. (a) Adsorption isotherms and (b) entropy dependence on the surface coverage calculated with the transfer-matrix method at $w_{1.2}/RT = -7.5$, $w_{1.1}/w_{1.2} = 0.5$, and different values of the $w_2/|w_{1.2}|$ parameter.

of ordered structures. Therefore, the Monte Carlo method was used only to verify the results obtained with the transfer-matrix method. Namely, we performed the Monte Carlo simulation for a large number of MCSs (10^{10}) to calculate the equilibrium coverage of the lattice and made snapshots of the lattice state at interesting values of the chemical potential. The results provided by both numerical methods are in good agreement. The snapshots of the lattice (Fig. 11) confirm the formation of all ordered structures found in the ground state. Analysis of adsorption isotherms calculated at $w_2 > 0$ shows a sequential formation of $\Psi_{1.1}$, $\Psi_{1.2}$, and $\Psi_{1.3}$ ordered phases when the chemical potential grows. Positions of the entropy minima coincide with the formation of the identified ordered structures (Fig. 10).

It is worth noting that the ordered structure $\Psi_{1.2}$ is similar to the zigzag phase formed in the adsorption overlayer of cross-shaped molecules with a single FG [20]. However, in this case, the supramolecular building blocks of the $\Psi_{1.2}$ zigzag phase are the tetramers. It is clearly shown in the snapshots of the adsorption layer that all these ordered structures are highly degenerate at finite temperatures.

The adsorption isotherms and entropy dependence on the surface coverage calculated with the transfer-matrix method at $w_{1.2}/RT = -7.5$, $w_{1.1}/w_{1.2} = 0.5$, and different values of $w_2/|w_{1.2}|$ are shown in Fig. 12. As before, we used the Monte Carlo method just to verify the results in several special points on the adsorption isotherms.

The results are in good agreement with ones obtained for the ground state of the model. There are two plateaus on the adsorption isotherms at $\theta = 2/3$ and 1. In addition, the entropy of the adsorption layer at those coverages takes a minimum value. Note that the closed-packed phase is formed through the first-order phase transition as evinced in the abrupt changing of the surface coverage. As a result, there are no intermediate states between two minima of the adlayer entropy at $\theta = 2/3$ and 1 [Fig. 12(b)]. These data and snapshots of the adsorption layer (Fig. 13) indicate the formation of two ordered structures in full conformance with the ground-state analysis.

Thus, the adsorption layer of cross-shaped molecules with two FGs in the *cis* position is characterized by a rather complex phase behavior. In fact, depending on the value $w_{1.1}/w_{1.2}$, the considered special case of the general model
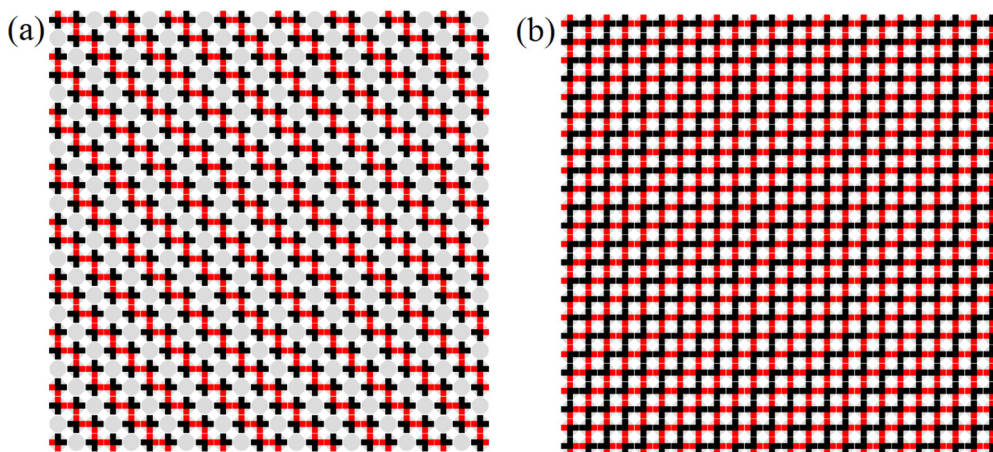

FIG. 13. Lattice patterns obtained in the Monte Carlo simulation at $w_{1.2}/RT = -7.5$, $w_{1.1}/w_{1.2} = 0.5$, and $w_2/|w_{1.2}| = 0.4$: (a) $\mu/RT = 0$ and (b) $\mu/RT = 6$.
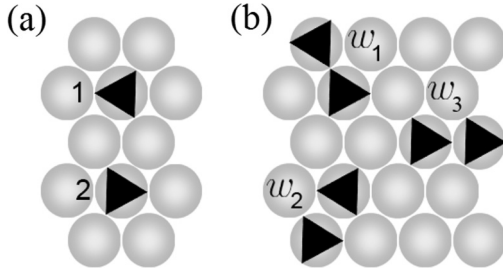
FIG. 14. Model of adsorption of triangular molecules with three identical functional groups on a triangular lattice: (a) possible states of the adsorbed molecule and (b) possible pair interactions between the molecules adsorbed on nearest-neighbor sites.

splits into two models having significantly different phase behaviors. The appearance of the tetramers at $w_{1.2} > w_{1.1}$, which further act as independent structural elements, is similar to the formation of the dimers in the adsorption layer of the cross-shaped molecules with a single FG on a square lattice [20]. On the other hand, the behavior of linear chains at $w_{1.2} < w_{1.1}$ has significant similarities to the phase behavior of the adsorbed layer of the molecules with two FGs in the *trans* position. The phase behavior of the adsorption layer with increasing chemical potential can be characterized as hierarchical by nature for all the studied lattice models. Thus, the hierarchical character of the self-assembly process seems to be a common feature of the adsorption systems under consideration. The reason for that behavior is the dominance of the attractive interaction between FGs in the chemical structure of the molecules adsorbed on the nearest-neighbor sites. This interaction leads to the formation of the stable primary structural units such as the dimers or tetramers, further acting as building blocks for more complicated structures.

Empirical examples of adsorption systems, with cross-shaped adsorbate molecules with two FGs in the *cis* position, are bifunctional derivatives of porphyrin or phthalocyanine on metal and graphite surfaces. In Refs. [34,38] the scanning tunnel microscope (STM) snapshots of such adsorption layers at different surface coverage were analyzed. The tetramers of the adsorbed molecules were observed at low coverages, which is in good agreement with our lattice model at $w_{1.1} < w_{1.2}$ (Fig. 7). However, the zigzag phase or another ordered structure comprising the tetramers was not observed in those experiments. In the real adsorption systems, only

linear ordered structures are formed with increasing surface coverage. It is interesting that the linear ordering is observed in our model at $w_{1.1} > w_{1.2}$ (Fig. 13). Thus, the energy of hydrogen bonding sufficiently depends on the mutual orientation of the adsorbed molecules. For example, in the adsorption systems considered the hydrogen bond of $w_{1.1}$ type is energetically more favorable than $w_{1.2}$ (Fig. 6).

It is worth noting that one more interesting lattice model of this type has attracted much attention in recent years [19,22]. This is the model of adsorption of triangular molecules (C_3 axis) with three FGs on a triangular lattice (Fig. 14). The model can also be described as a special case of the general model proposed in this paper.

The simplest and most well-studied system of this type is the adsorption layer of trimesic acid and its derivatives (1,3,5-tricarboxy-methoxy-benzene, 1,3,5-benzene-tribenzoic acid, etc.) on the metal and highly oriented pyrolytic graphite surfaces. It is important to note that the thermodynamic Hamiltonian of this model in terms of the general model remains unchanged. The tensor **G** in this case is as follows:

$$G_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & w_3 & w_1 \\ 0 & w_2 & w_3 \end{pmatrix}, \quad G_2 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & w_3 & w_2 \\ 0 & w_1 & w_3 \end{pmatrix},$$

$$G_3 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & w_3 & w_1 \\ 0 & w_2 & w_3 \end{pmatrix},$$

where G_i are the tensor cross sections corresponding to three types of edges on the triangular lattice. This case of the general model was recently studied separately as an independent model [19]. Taking into account only pairwise interactions, only three ordered structures might found (Fig. 15).

The effect of multisite interactions on the phase behavior of this model was studied by Ibenskas and Tornau [39]. It was shown that an infinite number of ordered structures can appear in the adlayer with increasing chemical potential. Some of them are observed experimentally in the adsorption layer of trimesic acid on Au(111) [6].

VI. CONCLUSION

We have developed a general lattice model that takes into account pair directional interactions between lattice sites. We have demonstrated how to exploit this general model to analyze structural and thermodynamic properties of adsorption
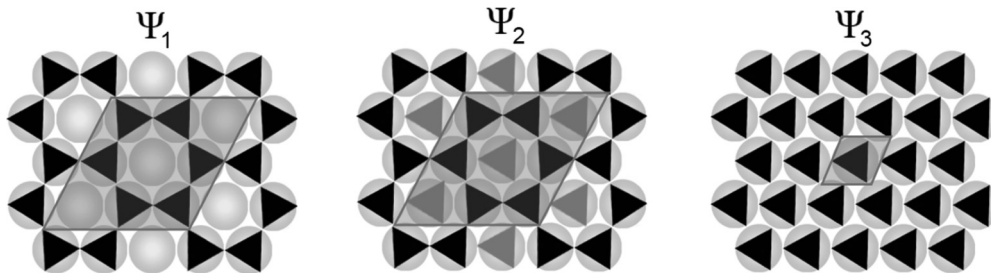

FIG. 15. Ordered structures of the adsorption overlayer comprising the molecules with triangular shape and three FGs on a triangular lattice. Black triangles denote stable (fixed) molecules and gray triangles the molecule that rotates in the two-dimensional pore due to the energetic equivalence of all the positions. A rhombus highlights the cell units.

monolayers comprising functional organic molecules of different symmetry and with different numbers of functional groups. In this approach, different adsorption systems are fully described with the interaction tensor. Rules of the tensor construction are also discussed in detail, using a few simple examples. With the Monte Carlo and transfer-matrix methods we have demonstrated that the special cases of the constructed model considered qualitatively reproduce some important features of the large class of real adsorption systems and therefore can be used for a better understanding of the self-assembly mechanisms in such systems. For example, it was shown that self-assembly process in the adsorption monolayers comprising functional organic molecules is hierarchical by its nature. The adsorbed molecules tend to be combined into independent supramolecular structural elements (dimers, tetramers, and linear chains) that further act as building blocks for resulting ordered structures. Apparently, this feature of the self-assembly process is common for this type of adsorption system. Comparing results obtained for adsorption of the cross-shaped molecules with two identical functional groups in the *cis* position with the STM images of *cis*-carboxyphenyl substituted porphyrin on the Au(111) surface, it has been revealed that in the real adsorption systems of this type, the energy of hydrogen bonding sufficiently depends on the mutual orientation of the adsorbed molecules. In particular, the hydrogen bond of $w_{1.1}$ type in the adsorption systems considered is energetically more favorable than $w_{1.2}$.

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