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Statistical Thermodynamics of Lattice Gas Models of Multisite Adsorption

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1. Introduction

The lattice models naturally arise in different fields of physics, chemistry and other sciences. First, it is physics of the solid state and physicochemistry of the surface. Among the many well-known lattice models the magnetic, alloys, liquid mixture, adsorption models are usually mentioned. The lattice models can be both classical and quantum. In this chapter only the classical lattice models focusing on models arising in physicochemistry of the surface will be considered. For the beginning let's give the most common formal definition of the classical lattice model.

Let there be given some finite or countable set M. Its elements will be called sites or nodes of the lattice and numbered index i. Each site is associated with the vector ($\vec{c_i}$) having k_i components. Each of the components can take a finite countable or uncountable number of values, i.e. without loss of generality, it can assume that the components of this vector take either integer or real values in some finite or infinite interval. The specific values of the $\vec{c_i}$ vector components determine the i-th site state. The M set state uniquely determines the state of all its elements. The system states can be divided into allowable and unallowable ones. Each allowable state of the $M\{\vec{c_i}\}$ set is match to the real number $E_M\{\vec{c_i}\}$ called the energy per lattice site. (Formally, unallowable state can be assigned value $E_M = +\infty$). Accepting the Boltzmann probability distribution of the system states as an additional postulate, one can receive object called a classical lattice model. All the models considered below are particular cases of the introduced generalized lattice model.

Determination of the lattice model dimension may be connected with the number of sites where can be the particle performing a random walk on the lattice in n steps. For d-dimensional regular lattice the number N is proportional to the volume of a box with an edge n, where $N \sim n^d$, i.e. the higher the dimension, the closer neighboring sites are located.

Following this approach 1,2,3,…, d-dimensional lattice models (for example, d-dimensional hypercubic lattices with interaction between the nearest-sites) are naturally obtained. 1,2 and 3-dimensional lattice models are of most importance for specific applications to the natural sciences. However, besides models whose dimension is equal to some natural number models which dimension defined the same way as above is fractional or infinite are of great interest. The simplest example of a model with a fractional dimension is the Ising model on the diamond-like lattice.

Concluding the general description of lattice models it is worth to introduce the concept of a homogeneous lattice model. Models properties of all their sites are identical are called homogeneous lattice models. It follows the obtained lattice model has a geometric realization possessing the property of translational invariance. As it is mentioned above, the models relating to physicochemistry of the surface are of main interest, respectively, these are primarily two-dimensional ones. It is readily to conclude that all the two-dimensional homogeneous models can be divided to three classes having in the basis the geometric realizations: the square, triangular and hexagonal lattice. Note that the lattice models having different types of sites but whose geometric realizations possess translational invariance can serve the generalization of concept of lattice model homogeneity. From the computational point of view these models are very similar to homogeneous ones. Thus, the most common definition of the classical lattice model, its dimension, homogeneity and translational invariance have been introduced.

Lattice gas model and its various generalizations are one of the most important lattice models of modern statistical physics. Despite its relative simplicity these shows fantastic variety of non-trivial physical phenomena. First, this refers to the phase transitions of various types whose study is of great interest from the standpoint of the general theory. Note that the adlayers on the monocrystal faces represent the physical realization of many interesting and important models for $d = 2$, in particular, these admitting exact solutions. The fact causes an increased interest of theorists to such systems.

Usually the lattice gas means the molecular system which differs from the continual gas following feature: molecules of such a system can occupy only such places in the space in which their centers are located at the sites of one-, two- or three-dimensional geometric lattice. The interaction energies of molecules located in different configurations respect to each other are the parameters of the model. In the general case, these parameters also depend on the relative orientation of the molecules. These interactions called lateral naturally can be divided to pairs and many-particle. Pair interactions are additive while many-particle ones are nonadditive.

It is easy to see from the standpoint of common definition of classical lattice model the lattice gas model (LGM) stated above refers to the same class of models as the Ising model. Indeed, considering the dependences of the energy of lateral interaction of molecules on their relative orientation one can obtain the lattice model in which the vector $\vec{c_i}$ is a scalar accepting two values (when all the molecules are the same type). From the above it immediately follows that the simplest LGM is isomorphic to the classical Ising model in the

sense of the common definition. The latter statement is a very important because the property of one model can be obtained that of another one.

One of the simplest examples of the system for which LGM is quite adequate model is the monomolecular adsorption model. It is well known that chemisorption has localized character as in this case there occurs chemical bond between the adsorbed molecule and the substrate. For substrate being face of monocrystal chemisorbed molecules are located in well defined places of the periodic lattice formed by the surface atoms. Therefore, the simplest LGM introduced above is completely adequate model of monomolecular chemisorption on monocrystal face.

The thermodynamic Hamiltonian of the simplest LGM with one type of particles on regular lattice (for example, hypercubic) has the form:

$$H = \varepsilon \sum_{\langle n,n \rangle} n_i n_j - \mu \sum_i n_i \,, \tag{1}$$

where ε is the lateral interaction energies of the nearest neighbors; μ is the chemical potential; the occupation number n_i is equal to unity if the adsorption site is occupied and zero in the case of a vacant site. The Hamiltonian (1) for $d = 2$ in the first approximation describes the monomolecular (one-center) adsorption on a monocrystal face.

In some cases this description corresponds to reality but in most cases it does not [1]. It is known that even at adsorption of the most simple gases such as Ar, Kr, Xe, nitrogen, carbon monoxide, oxygen and others the adsorbate molecule size is usually larger than the distance between neighboring active centers of adsorption [2-6]. In this connection at the adsorbate molecule adsorption on one active center it simultaneously occupies one or several neighboring active centers.

The assumption of one-center adsorption becomes even more inadequate at the description of adsorption of linear and quasilinear molecules such as the simple saturated and unsaturated hydrocarbons [7,8]. In the paper complete review of the experimental results on the adsorption of simple hydrocarbons on the surface of metal monocrystals (Pt, Pd) was given and, particularly, the adsorption of such molecules was shown to occur parallel to the solid surface in connection with which multicenter nature of the adsorption becomes apparent.

In addition in this review some types of ordered structures of adsorption monolayer $C_4 - C_8$ alkanes experimentally observed at low temperatyres on the surface of monocrystalline platinum are discussed. The necessity of describing of the n-alkane adsorption in the framework of the models with multisite adsorption is also supported by the fact that at the interpretation of experimental adsorption isotherms by using the known multisite Langmuir model and other analytical models there exists good correlation between the model parameter k (the number of active sites occupied by adsorbate molecule) and the real number of segments in the molecule of the adsorbate [7,8,10-12]. It should be noted that the above analytical models of multisite adsorption are used to determine the specific surface of porous solids and its topography (in the case of energetically heterogeneous surfaces).

Obviously that the adsorption of more complex (in regard geometry, the chemical structure – the presence of double/triple bonds or several functional groups) of molecules is even more nontrivial [14-25]. First of all this is manifested in that complex organic molecules (cyclic hydrocarbons, aromatic systems etc.) depending on their geometry and chemical structure can form set of different ordered structures on the solid surface.

Along with the possibility of multisite adsorption that of different orientations of molecules with respect to the interface is one of the most interesting features of these systems. Indeed, over the past ten years series of experimental works devoted to the study of organic self-assembled monolayers on metal surfaces has been published. The general conclusion of these studies is that the molecule orientation in the adlayer is a function of external parameters such as concentration, pressure, temperature, electrode potential and others[14-25]. Moreover, very interesting ordered structures have been experimentally found in some of similar systems. Those are structures which simultaneously contain the molecules with different orientations in the adlayer. For example, in [18] the authors investigated behavior of the adsorption monolayer of molecules p-Sexiphenil on the Au(111) surface in ultrahigh vacuum using the method of scanning tunneling microscopy. It was shown that five various ordered structures two of which contain molecules with different orientations in the adlayer – molecules oriented parallel to the surface and tilted to the surface at an angle can be formed. In [24] phase transitions in the adlayer of acid trimezin molecules on the Au(111) surface have been investigated using the method of scanning tunneling microscopy, and one of them proved to lead to formation of the ordered structure containing the acid trimezin molecules oriented both parallel and perpendicular to the surface. Another striking example of the adsorption system in which the adsorbate molecules can have different orientations with respect to the surface is the adsorption of cyclic unsaturated hydrocarbons on the reconstructed semiconductor surface especially on the reconstructed face of the Si(001) [25-27]. This is connected to the fact that cycloaddition reaction [2+2] with formation of di-σ bond Si-C with the silicon surface atoms results from chemisorption of unsaturated organic molecules on the silicon surface. In chemisorptions of more complex hydrocarbons containing several unsaturated bonds the particle adsorbed on the surface can have several configurations depending on the number of di-σ bonds Si-C [28]. Moreover, the stable π-complex being resulted from interaction between unsaturated hydrocarbon molecule and silicon atom has been experimentally discovered recently [29,30]. In light of the above it is clear that all specified features of the behavior arising at detail studying of adsorption of simple or complex molecules can be investigated only in the framework of models taking into account the multisite character of adsorption and the possibility of different orientation of molecules both with respect to each other and with respect to the solid surface.

Practically, theoretical study of organic self-assembled adsorption monolayers or thin organic films is of great interest generally in connection to the set of possible applications in which thin organic films are used anyway [31]. The potential field of application of such systems is an organic optoelectronics, in particular, electroluminescent devices [32], photovoltaics [33], organic field-effect transistors [34]. Similar systems are used as coatings on computer hard drives to provide protection against corrosion and low friction [35].

It is difficult to overestimate the applied significance of considered systems in the field of chemistry and biochemistry where they are used as active elements of chemical and biological sensors [36], in heterogeneous catalysis [37] and as coatings for biomedical implants [38]. Polymorphism of organic thin films and the ability of molecules to constitute different crystalline forms leads to is it is very difficult to control growth and properties of such systems. Moreover, it was recently shown that the structure of the organic film significantly affects epitaxial growth of crystals on the film [39]. This fact can be used to control the morphology of nanocrystalline systems.

In all these cases location of the molecules on the surfaces is a decisive factor that determines process of growth of the film and its physical properties. Therefore, a detailed understanding of elementary phisical and chemical processes occurring in such systems is the primary motivator at the investigation of molecular self-organization on the solid surface. The development of realistic models of such systems can allow completely to control the process of self-assembly of organic and other molecules on the solid surface and to come nearer to dream of nanotechnology – to gather material possessing the necessary properties with atomic precision. Based on the above it is clear why the interest of researchers specified both practical and theoretical considerations is now shifting towards more complex lattice models some of which will be discussed in this review.

Let's consider the class of lattice models describing the so-called multisite adsorption. The simplest LGM considered above in the two-dimensional case is a model of monosite adsorption (active centers of adsorption, generally speaking, do not coincide with the surface atoms). However, as noted above at the description of many adsorption systems one is forced to abandon from idea about the monosite adsorption. In the framework of the LGM multisite adsorption is described as a system of prohibitions on certain configurations. At the same time a relatively simple lattice geometrically equivalent to the crystal lattice of the surface is persisted but the number of possible states of the site determining which part of the complex molecule is located above this site and how adsorbed molecule is oriented is increased. Further, the main results obtained in the framework of the models with multisite adsorption will be presented.

2. The models of dimer and k-mer adsorption

The simplest model of multisite adsorption is a dimer adsorption model. In the first approximation the dimer model described adsorption of molecules consisted of two the same atoms, for example H_2, N_2, O_2 etc. when temperature is relatively low and molecules cannot dissociate.

Statistical thermodynamics of the dimers lattice models has a long history. This is one of the earliest lattice models which take into account the own size of molecules in the frame of the lattice gas model. Apparently, the first model of the dimer has been studied in the context of the entropy of the adlayer in 1937 [40]. As it turned out, the dimer model has deep connections with the Ising model and many other important models in statistical physics. In the early sixties of the twentieth century an exact solution of the dimer model on a square

lattice was obtained in the case of the so-called "close-packed limit", i.e. all lattice sites belong to one and only one of the dimers [41-43]. In particular, the entropy per one lattice site was calculated. Interest in the dimer model persists to this day. Exact solutions for the dimer model were recently obtained with close-packed limit in the case of the two-dimensional non-orientable surfaces, such as the Möbius strip and Klein bottle [44,45]. The problem of the packing of dimers in the presence of vacancies is much more complicated and largely solved numerically [46,47].This is mainly due to three factors: 1) there are no statistical equivalence between the particle and the vacancy, and 2) any occupied site indicates that at least one of the neighboring sites occupied too and 3) it is impossible to determine exactly whether there will be adsorption on the isolated vacancy. Exact solutions for the dimer model on lattices of dimension greater than two is currently unknown. For three- and more than three dimensional lattice models it is the overall situation characteristic not only for the dimer model, but also for the simpler one-centered model such as the classical Ising model and its many generalizations.

The dimer model in the framework of the lattice gas model can be described as follows. Let consider the lattice (for simplicity, a square) of the active sites. Each lattice site can be occupied by one of the segments of a dimer, or be empty. In addition, the orientation of the dimer should be specified. The last stage of building the lattice gas model is a complete listing of prohibited configurations. In this case, the system of prohibitions describes the continuity of the dimer. Just as in the simplest of the lattice gas model, different lateral interactions can be considered in the constructed model of dimer adsorption too. The dimer model is actively studied for decades because it is the simplest model of multisite adsorption and is of theoretical and practical interest.

A natural generalization of the dimer adsorption model is an adsorption model of rigid or flexible linear k-mers of having no thickness. The only difference from the dimer adsorption model is the assumption that the adsorbed molecule occupies now k lattice sites forming a certain configuration. Thus, k-mer is called the model of the adsorbate molecule, consisting of k equal-sized segments, and the bond length between the segments is equal to the lattice constant and does not change, and not broken in the process of modeling. In the case of dimers, k is equal to two. Thus, from a formal point of view the lattice gas model for the dimer adsorption does not differ from the lattice gas model for k-mers, so it makes sense to discuss the results obtained in the framework of these models together. Next, referring to the k-mers reader should keep in mind the dimers adsorption model, except where otherwise noted.

Depending on whether the same or different properties are segments of the molecule, k-mers differ by homonuclear and heteronuclear, respectively. Works devoted to the study of k-mers can be divided into two groups according to the shape of the molecule (flexibility), the first group is works devoted to the study of flexible k-mers [48-51], the second group is works studying the adsorption properties of rigid linear k-mers (rigid rods) [49,51,52]. Theoretical analysis of a multisite adsorption of linear molecules in the general case is rather complicated, and the exact solution for k-mers found only in the simplest one-dimensional case [52,53]. In these studies were obtained exact expressions for the free energy per active

site as a function of temperature and surface coverage. In this case, the most interesting is the dependence of the diffusion coefficient on the k-mer length and the surface coverage. Thus, with increasing size of the molecule the diffusion coefficient for noninteracting or attracting k-mers increases too, as in the case of repulsive interactions, the diffusion coefficient can either decrease or increase with the molecule length increasing, depending on the degree of coverage [52-54]. For more complex cases for the two-dimensional systems only approximate analytical expressions were obtained. The most well-known analytical approximation is: 1) the theory of Flory-Huggins [48,55-58], which is a generalization of the theory of binary solutions of polymer molecules in a monomolecular solvent for the two-dimensional case. The fact that in the framework of lattice gas model the problem of k-mer adsorption on homogeneous surfaces is isomorphic to the problem of binary solutions of polymer in a monomolecular solvent, 2) Guggenheim-DiMarzio approximation [59,60], which is based on calculating the number of possible ways of packaging rigid k-mers on lattices with different coordination numbers 3) the approximation based on the extension of the exact solution for a one-dimensional case [52,53] to higher dimensions [49,61], 4) well known quasichemical approximation [62] and mean-field approximation [63], 5) fractional statistical theory (FSTA) for the adsorption of polyatomic molecules, based on Holdan statistics [64], 6) semi-empirical model [61,65], etc. Unfortunately, none of these approximations is universal, and each shows quite good results, depending on the parameters of the model – a flexible or rigid k-mer, the length of k-mer, the presence or absence of lateral interactions between adsorbed molecules, etc. A brief description of the approximations and compare them with each other can be found in [49,65]. Generally, more recent analytical approximations for the k-mers adsorption include earlier ones as special cases. In this regard, let's consider the best of them – FSTA and semi-empirical approximation.

In ref. [51] the authors, by comparing experimental data with results obtained by means of analytical approximations and a Monte Carlo simulation, studied the adsorption of linear and flexible polyatomic molecules on honeycomb, square and triangular lattices. Data obtained by the FSTA model in the case of a square lattice are almost identical to the data obtained by the Monte-Carlo simulation. A similar analytical calculation by FSTA for the k-mers adsorption on triangular lattice gives an inaccurate result, because there are a larger number of possible configurations of a single k-mer on the surface.

In order to verify the accuracy of the proposed approach (FSTA) the authors have constructed and analytically calculated the two models of real processes. The first is a model of oxygen adsorption on 5A zeolite and the second one – a model of adsorption of propane on the 13X zeolite. The results of analytical calculations were almost identical to the experimental data. The principal difference FSTA from earlier models of multisite adsorption is that in addition to the size of molecules, it also takes into account their shape and surface geometry. Thereby FSTA can describe the adsorption of both rigid and flexible molecules.

Analyzing the results deviations for various approximations from the results of Monte Carlo, it was shown that the most accurate approximation is the semi-empirical model,

developed by Roma et al. Semi-empirical model is a combination of the exact solution for one-dimensional approximation and Guggenheim-DiMarzio approximation [65]. A new theoretical approach is significantly better than other existing approximations and allows fairly simple explaining the experimental data.

When comparing the adsorption isotherms of monomers and k-mers, it was found that in the second case the symmetry of the "particle-vacancy" is broken. The isotherms are shifted toward lower coverage with increasing coordination number of the lattice. In other words, for a given value of the chemical potential the surface coverage increases with the lattice coordination number.

As can be seen in most works devoted to the development of new analytical methods, the results are compared not only with the experimental data, but also with the results obtained by the Monte-Carlo, as the reference.

The Monte Carlo method has proved to be a very powerful tool in the study of k-mers adsorption. Using this method with different techniques (reweighing, finite-size scaling, and others [66,67]) many important parameters of the phase behavior for different k-mers adsorption systems were identified, such as the types of ordered phase structures, the points of phase transitions and critical indexes of phase transitions, etc. [68,69]. The appearance of ordered phases for the model k-mers in the presence of lateral interactions has its own specifics, this is due to the presence of orientation in the arrangement of the adsorbed molecules relative to each other.

In ref. [70] the authors, using the transfer-matrix method, investigated the ordered structures of the adsorption layer consisting of interacting dimers adsorbed on a square lattice. Analysis of the changes of the adlayer entropy and the surface diffusion coefficient showed that there is a finite number of ordered phases in case of repulsion lateral interactions between the nearest neighboring molecules.

Later in ref. [71] Ramirez-Pastor et al. using the Monte Carlo method have considered both attractive and repulsive interactions between adsorbed dimers on a square lattice. It was shown that in the case of attractive interactions, the phase diagram is similar to the diagram for a monoatomic gas, but the critical temperature is shifted to higher values. The most interesting case is repulsive interactions when a variety of ordered structures take place. In the case of dimers the symmetry of the "particle-vacancy", typical of monatomic particles, disturbed, that leads to the asymmetry of the adsorption isotherm with respect to the line θ = 0.5, on the isotherm two steps take place. When θ = 0.5 $c(2 \times 4)$ structure formed, which is characterized by the alternation of the adsorbed dimer and two adjacent vacancies. When the chemical potential μ increases and θ close to θ = 2/3, adsorbed dimers form parallel zigzag rows (ZZ phase) [71.72]. A similar phase behavior of adsorbed layer of dimers is observed in the case of triangular and honeycomb lattices [73] (Fig. 1). In addition, the scientific group of Ramirez-Pastor, using Monte Carlo method and finite-size scaling techniques, calculated the critical exponents and critical temperatures, and calculated a phase diagram for dimers with repulsive lateral interactions on a square [71] and triangular

[74] lattices. It was shown that the system does not belong to the universality class of two-dimensional Ising model.
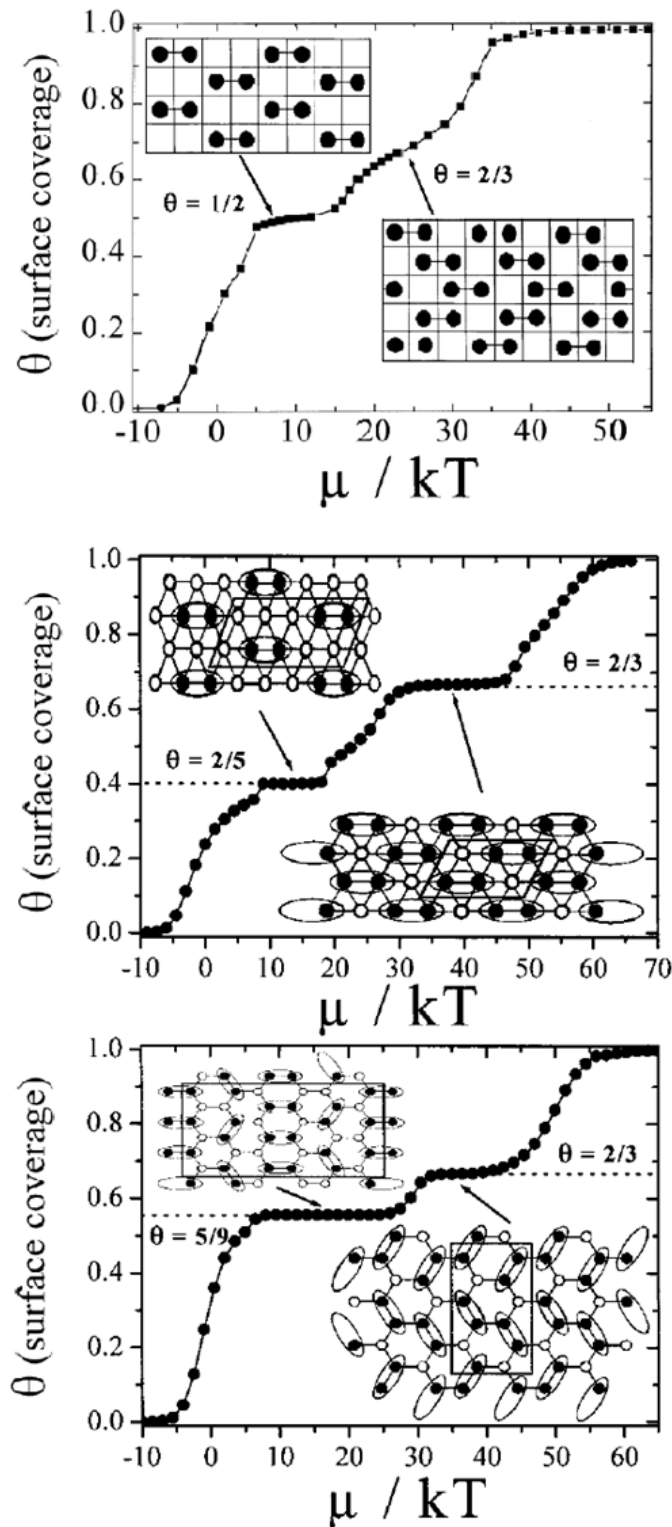

Figure 1. Adsorption isotherms of dimers on square, triangular and honeycomb lattices and corresponding ordered phases [71,73].

The study of the adsorption monolayers consisting of heteronuclear dimers showed that the phase diagram of the system greatly influenced by the quantity of energy of lateral interactions between the different types of segments (it is about two different molecules). In the study of phase diagrams of these films interesting phenomena were found. In particular, the coexistence of three phases and a variety of structural transitions, and ordered linear type structure exists even at high temperatures [75].

Similar calculations were performed for the adsorption of homonuclear dimers on heterogeneous surfaces [1,10,76-79]. In the case where the surface is represented by heterogeneous clusters of active sites of one kind and another, the approximate solution is relatively simple (the solution for multisite adsorption on a homogeneous surface can be used). In describing the adsorption of dimers on heterogeneous surfaces, created at random, the task becomes more complicated. Slightly more than twenty years ago an approximate solution was suggested for this model [1,10,79]. However, the original approach of Nitta et al. could only be applied to surfaces with a discrete distribution of adsorption energy. Later on the basis of this approximation Rudzinski and Everett [1] obtained a solution for a model with continuous distribution of adsorption energy on the surface. However, the usable area of this and other approximations [78] is limited. For example, in [77], the authors investigated an analytical approximation by Monte Carlo method to describe the adsorption of homonuclear dimers on heterogeneous surfaces, created randomly (random heterogeneous surface). The calculation shows that this approximation yields accurate results when the difference between the energies of adsorption on active sites of one and other kind is small.

There are papers devoted to the description of the first order phase transition such as "surface gas – surface liquid" [75,76,80]. The most important conclusion from all these studies is that with increasing molecular size the critical temperature shifts to higher values. On the other hand, increasing of the molecule flexibility leads to decreasing of critical temperature. A very interesting phenomenon was observed in the study of phase transition "surface gas – surfacee liquid" in the adlayer consisting of heteronuclear trimers – namely, the coexistence of three phases (there is a second phase transition "liquid – liquid"). In this case, the phase diagram is asymmetric – there are a shift of the critical density to the unit and an increasing the critical temperature.

The findings in the study of dimers adsorption on heterogeneous surfaces with a sufficient degree of accuracy can be extended to the adsorption systems of k-mers [10,78,79]. However, as was shown in ref. [81], the calculation accuracy of the approximations developed for the adsorption of dimers on heterogeneous surfaces decreases with increasing molecular size.

Summarizing the results obtained in these works, one can conclude that the phase behavior of adlayer of dimers on heterogeneous surfaces defined by the following factors: 1) the distribution of the various active sites of adsorption, and 2) the relation between the k-mer length and the size of the local heterogeneity, 3) adsorption energy on different active sites.

It should be noted about the theoretical studies of percolation threshold in systems with multisite adsorption. Information on transitions "percolate region" – "nonpercolate area" on

the surface is of great interest both from the point of view of phase transitions science, as well as from the applied point of view, in particular the appearance of surface conductivity. In the case of the two-dimensional lattice gas model the percolation threshold is so minimum value of the coverage θ on an infinite surface, as infinitely large cluster of adsorbed molecules is formed. In ref. [82,83] it is shown that in addition to the dimension of the system and the lattice coordination number on the percolation threshold a size of k-mers has a significant effect. Influence of temperature on percolation in adsorption systems with flexible k-mers studied in ref. [50] by the Monte Carlo method. There was found an interesting phenomenon – a nonmonotonic behavior of the percolation threshold as function of temperature, i.e. there exists a temperature at which the percolation threshold is a minimum, and the position of the minimum does not depend on the length of k-mers.

Thus, all existing works on the k-mers adsorption, as in the case of dimers, are concentrated in four main areas: (1) study of the influence of the chemical structure of noninteracting adsorbed molecules on the behavior of their adsorption, (2) study of the influence of surface heterogeneity on the k-mers adsorption, (3) description of first order phase transition in the adlayer in the case of mutual attraction of the adsorbate – adsorbate. Only a small number of papers devoted to the study of phase transition "order-disorder", which takes places in the case of repulsive intermolecular interactions [69,70]. In particular, in ref. [69], using Monte Carlo simulation, two important characteristics of the critical properties of repulsive k-mers were identified: (1) the minimum critical temperature have on the value of k equal to 2 (dimers) and (2) for $k > 2$ the critical temperature increases monotonically with increasing k. Similar results (qualitatively) have been obtained from the analytical calculation of the mean field approximation and the principle of minimum free energy.

Additionally it should be noted that long before the above works, the study of the multisite adsorption was engaged by Soviet scientists in Temkin (1938 [84]), and Snagovski(1972 [85-87]). In ref. [84-87] the adsorption isotherms were analytically obtained in the case of multisite adsorption of two-center ($k = 2$), square ($k = 4$) and hexagonal ($k = 7$) complexes. Today's papers on multicenter adsorption are essentially the development, and sometimes repeating, of the works of Temkin and Snagovski.

As one can see, at present the theory of adsorption of k-mers are actively developing – adsorption isotherms are calculated, phase diagrams are constructed, percolation thresholds are determined, etc. This is due primarily to a large applied importance of such research. Already, it can be concluded that the behavior of adlayers consisting of molecules that occupy more than one active site of the surface is significantly different from the behavior of systems with monosite adsorption. However, it should be noted that in all these considered works the adsorbate molecule can adsorb only one way to the surface – is planar.

3. Multisite adsorption of orientable molecules

Today there is a small number of papers devoted to theoretical investigation of the behavior of adsorption monolayer consisting of molecules that can have a different orientation with respect to the surface [88-92]. Let's examine them in detail.

The earliest papers on theoretical study of molecular reorientation in the adsorption monolayer were carried out at MSU by Gorshtein and Lopatkin in 1971 [88,89]. They investigated one- and two-dimensional lattice models of diatomic molecules adsorption. It was assumed that the molecule can adsorb in two different ways with respect to the surface: vertically and horizontally. Each type of adsorption had its heat of adsorption, and adsorption energy of vertically oriented molecule was approximately two times smaller. The lateral interactions between adsorbed molecules were not taken into account. The authors derived an exact analytical expression for the adsorption isotherms in one-dimensional case and the approximate equation for two-dimensional lattice. It is shown that for the large values of adsorption heats at low pressures, most of the molecules adsorbed horizontally, and the number of vertically orientated molecules is very small. When coverage increasing the horizontally adsorbed molecules change the orientation, and the number of molecules adsorbed vertically grows fast. In addition, the authors had obtained expressions for isosteric heats of adsorption. Having analyzed calculated thermodynamic functions they concluded that the system exhibits two modes of adsorption: on two neighbor sites in the region of low pressure and on one site at high pressures.

The authors of [90] studied the adsorption of heteronuclear dimers (A-B) on a homogeneous surface with a mean-field approximation. In this case the dimer can be adsorbed on the surface in three different ways: horizontal adsorption with two segments at the same time and vertical adsorption with the A segment or vertical adsorption with the B segment. It was assumed that all three types of adsorption differed in the adsorption heat, and the interaction between adsorbed molecules were absent. The authors derived analytical expressions for the adsorption isotherms and isobars. In fact, the physical results obtained in this work are in qualitatively agreement with Gorshteyn and Lopatkin's ones and partially duplicate it.

There is the quite interesting model of spin-1 type, which can describe the adsorption of heteronuclear dimers on different lattices [91,92]. It is assumed in the model that all adsorbed molecules are oriented vertically to the surface only, and the energy of adsorption depends on what segment, A or B, molecule adsorb with. The authors of [91,92] considered the various sets of lateral interactions between dimers, in particular, they took into account not only interactions between nearest neighbors, but also between next-nearest neighbors. Such complex lateral interactions in the system led to the set of ordered surface structures and phase transitions. It had been shown that if the lattice is completely filled the "order-disorder" transition may occure via a continuous phase transition as well as the first-order phase transition depending on the model parameters. Moreover, the continuous phase transition is nonuniversal. It should be noted that the model does not take into account the possibility of horizontal orientation of the dimer and generally speaking this model can be attributed to the well-known Blume-Emery-Griffiths model [66].

In [93] authors proposed the general lattice gas model describing the adsorption of complex molecules. The model can be formulate by following: the molecule can be adsorbed on the surface by the k ways occupying the $m_1, m_2, \ldots, m_k$ active sites located in the corresponding configurations on homogeneous or heterogeneous lattice, respectively. The simplest model of this type is the model of homonuclear dimers adsorption. In this model it is assumed that dimer may have two different orientations in the adlayer – parallel (adsorption on two active

sites) or perpendicular (adsorption on one active site) to the surface. In the language of this general model homonuclear dimers adsorption model belongs to the class of models with $k = 2$, $m_1 = 1$, $m_2 = 2$, and heteronuclear dimers adsorption model [90] – to the class with $k = 3$, $m_1 = 1$, $m_2 = 1$, $m_3 = 2$. The model studied in [91,92] belongs to the class of $k = 2$, $m_1 = 1$, $m_2 = 1$. It should be noted that all these simple classes of models have a single representative and the set of numbers $k, m_1, m_2, ..., m_k$ uniquely identifies the type of model.
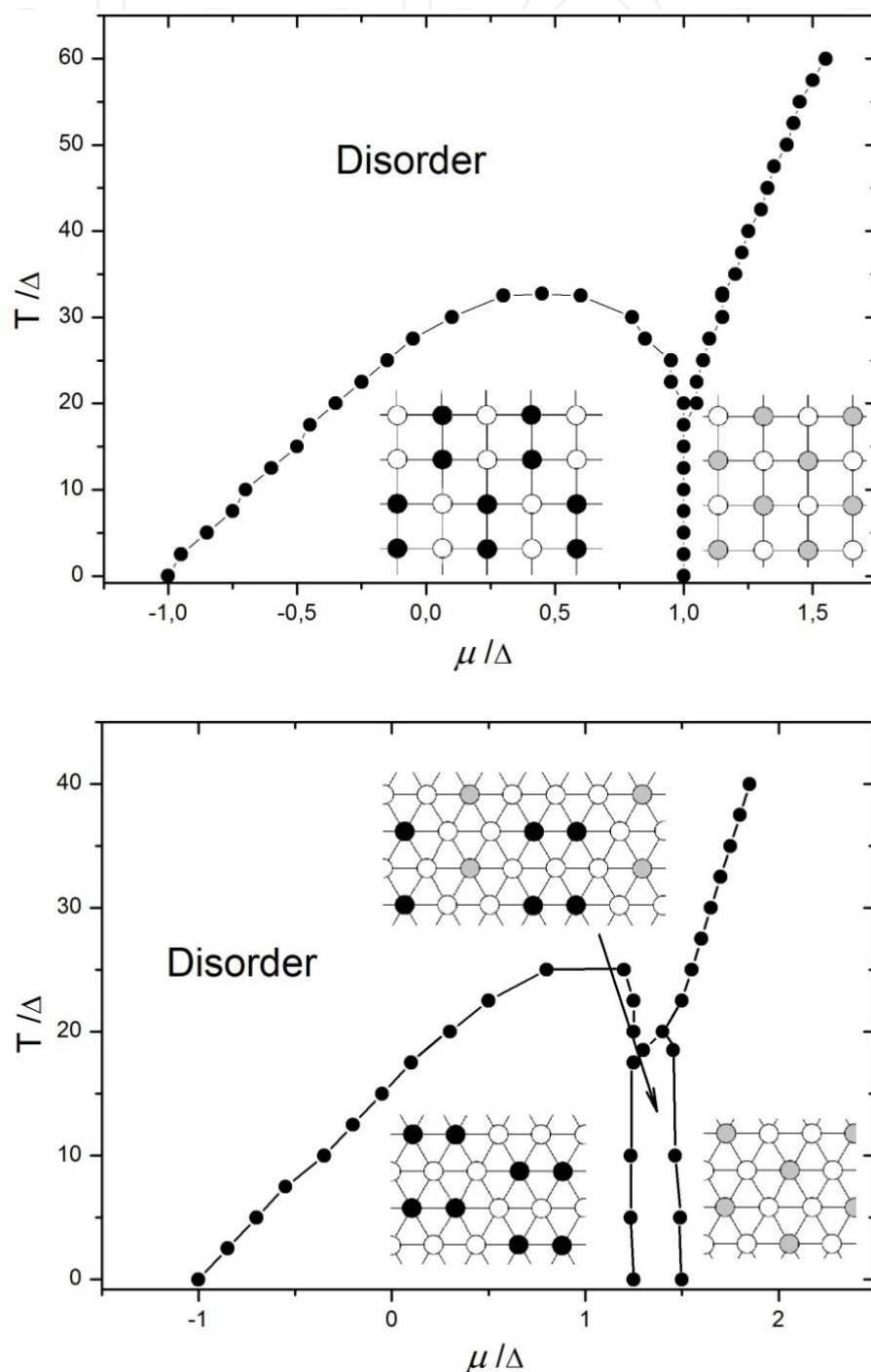
Figure 2. Phase diagrams for dimers on square and triangular lattices. Ordered structures: black circles are site occupied by dimers adsorbed on two sites; gray circles are sites occupied by dimers adsorbed on one site.

As it noted in [90], the results obtained for adsorption of complex molecules can be extended also to the gas mixtures. In other words, the general model can be considered as a special case of gas mixtures adsorption model. In this case the number of mixture components will be characterized by a number k and the molecule kind by value m. So if one consider the simplest representative of the general model – dimer adsorbed on two or one active site, it would be analogous to a binary mixture of dimers and monomers. These systems will be equivalent to each other if the model of binary mixture has the fixed difference between the chemical potentials of the components. From a physical point of view this means that the adsorbed molecules of one kind, and the behavior of the system is very similar to the adsorption of the gas mixture. Indeed, when the adsorption properties of complex molecules [93-97] was studed, it was discovered the phenomenon of non-monotonic changes in surface coverage with the chemical potential increasing, and a similar phenomenon was observed in the study of adsorption of binary mixtures [98,99].

In order to evaluate the influence of surface geometry on the phase behavior of adsorbed monolayer the model of orientable dimers on the square and triangular lattice was studied [100,101]. It was shown that the influence of the coordination number (the number of nearest neighbors) plays an important role in the phase formation process. Namely, in the case of square lattice only two ordered structures consisting of dimers adsorbed only vertically or only horizontally can form, in the case of triangular lattice except for the phases of this type another phase consisting of differently oriented molecules appears. Phase diagrams are presented in Fig.2.

The simplest special case of the general model of adsorption of molecules with different orientations in the adsorbed monolayer is the lattice model of dimers adsorption discussed in detail above. Extending the model of dimers adsorption on molecules with more complex form (cyclic hydrocarbons, aromatic systems, etc.) one can get the lattice model of complex organic molecules adsorption, which takes into account, firstly, the possibility of different orientations with respect to the solid surface and, secondly, the diversity and complicated structure of surface complexes (non-linear shape of the adsorbate molecules). Further, a special case of the generalized model, which allows to study the effect of varying the orientation of the complex organic molecules on the behavior of the adsorbed layer in «pure form» will be considered. The fact is the model of dimers adsorption along with the possibility of different orientations of the molecules with respect to the surface takes into account the ability to the different orientation of molecules relative to each other *a priori*. Indeed, in the case of square lattice, the dimer adsorbed parallel to the surface can have two different orientations which does not allow us, in the framework of this model, to focus on studying the effect of varying the orientation of the molecule with respect to the solid surface on the structure and thermodynamic properties of the adlayer.

As model of solid surface homogeneous square lattice is considered and it is assumed that the molecule can be adsorbed in two different ways: 1) on four active sites (Fig. 3a) and 2) on one active site (Fig. 3b). In the first case the four active sites involved in adsorption process form the square. Thus, for the constructed model one have $k=2$, $m_1=1$, $m_2=4$. In addition, an
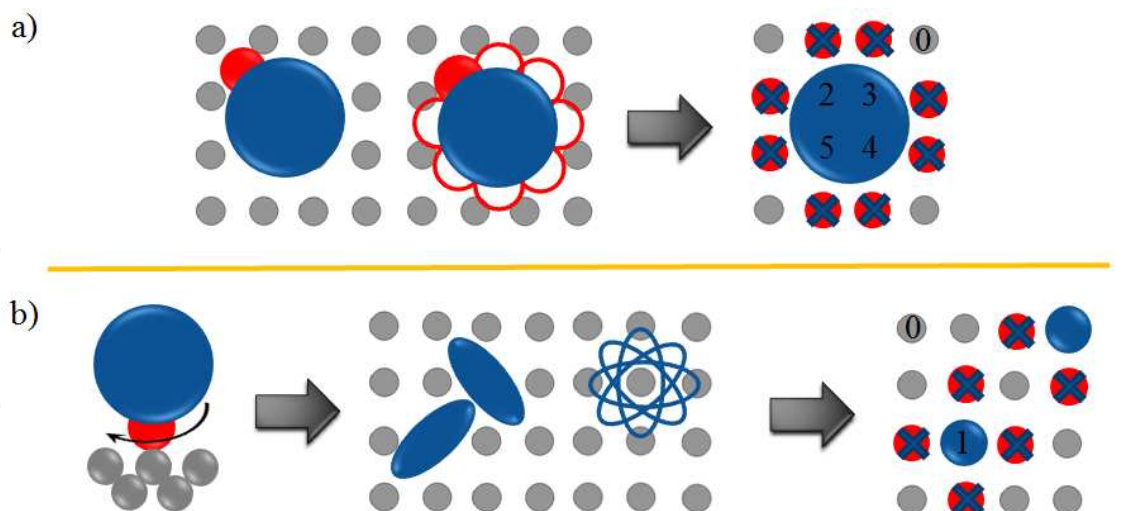
Figure 3. Possible configurations of the adsorbed molecules. The small circles represent molecules adsorbed on one active site, and the large ones – molecule adsorbed on the four active sites. The numbers from 0 to 5 correspond to all possible states of the active site (cell).

infinitely strong repulsion between the nearest neighboring molecules in the model (a nearest neighborhood between two adsorbed molecules independently of the adsorption way is prohibited as well) are assumed, which in a first approximation, take into account the complex structure of the molecule. Active sites prohibited for the adsorption, in the case of two different orientations of the adsorbed molecules are indicated on Fig. 3 by the cross. It is seen that the proposed model of multisite adsorption eliminates the effect of varying the orientation of molecules relative to each other on the structure and thermodynamic properties of the adsorbed layer, since all possible orientations of the molecules in the plane parallel to the interface are taken into account simultaneously (Fig. 3). Thus, this model is the simplest model, which allows to study the effect of varying the orientation of complex organic molecules relative to the interface on the structure and properties of the adsorbed layer regardless of other factors. To reduce the dimensionality of the model the value $\Delta = q_2 - q_1$ is introduced as the difference between the heats of adsorption of the four-site location and the mono-site one. The effective Hamiltonian of the model under consideration can be written as

$$H = -\frac{\Delta}{4}\sum_i n_i - \mu\left(\frac{1}{4}\sum_i n_i + \sum_i c_i\right) \qquad (2)$$

where the occupation numbers c_i and n_i are equal to unity for occupied by molecule adsorbed on one and four sites respectively and zero for empty sites; μ is the chemical potential of the adsorbed particles.

The thermodynamic properties of the model have been investigated with standard importance sampling Monte Carlo method [93]. The calculations of the isotherms and the surface coverage as the function of the gas phase pressure (chemical potential) are carried out with the linear size of the lattice $L = 96$ and $L = 24, 36, 48, 60$ used for finite-size scaling procedures. The linear lattice size was chosen for the adlayer structures to be not perturbed.

Thermodynamic equilibrium is reached by spin-flip (Glauber) dynamics [102] and diffusion relaxation (Kawasaki dynamics) [103]. To calculate thermodynamic functions successive configurations of the adlayer are generated using Metropolis transition probabilities [104] in the grand canonical ensemble.

Analysis of the ground state (T = 0K) of the model allowed to conclude that in the adlayer due to the infinitely strong repulsive interactions between nearest-neighbor molecules the set of chessboard type ordered structures forms: $c(4\times4)_4$, $c(3\times3)_{4-1}$ and $c(2\times2)$. The structures are schematically shown in Fig. 4. In addition, the lattice gas phase (LG) with zero coverage exists in the ground state of the system. The corresponding phase diagram of the adsorption monolayer in the ground state of the system shown in Fig. 5.
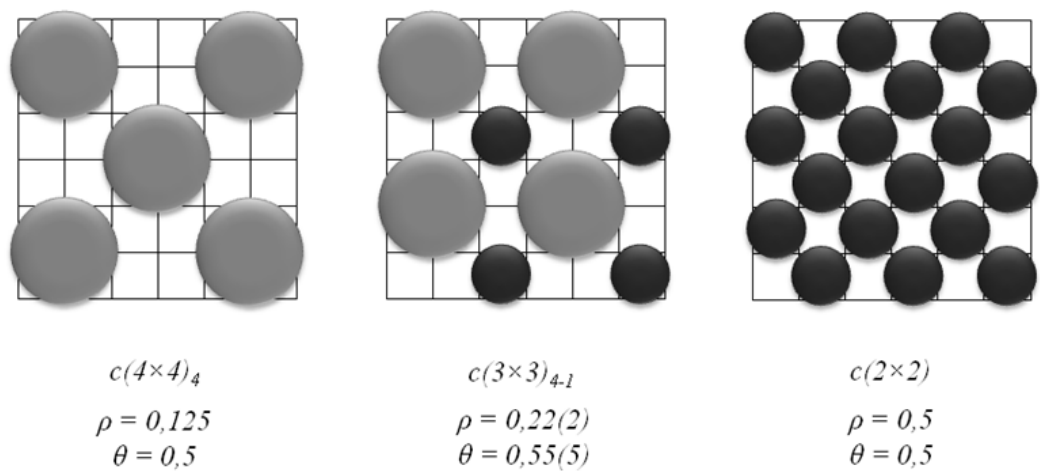

$c(4\times4)_4$
$\rho = 0,125$
$\theta = 0,5$

$c(3\times3)_{4-1}$
$\rho = 0,22(2)$
$\theta = 0,55(5)$

$c(2\times2)$
$\rho = 0,5$
$\theta = 0,5$

Figure 4. Ordered structure of the adlayer. Gray circle denotes a molecule adsorbed on the four active sites, and the black circle – molecule adsorbed on one active site. The structures are shown in order of their formation with the chemical potential increasing.
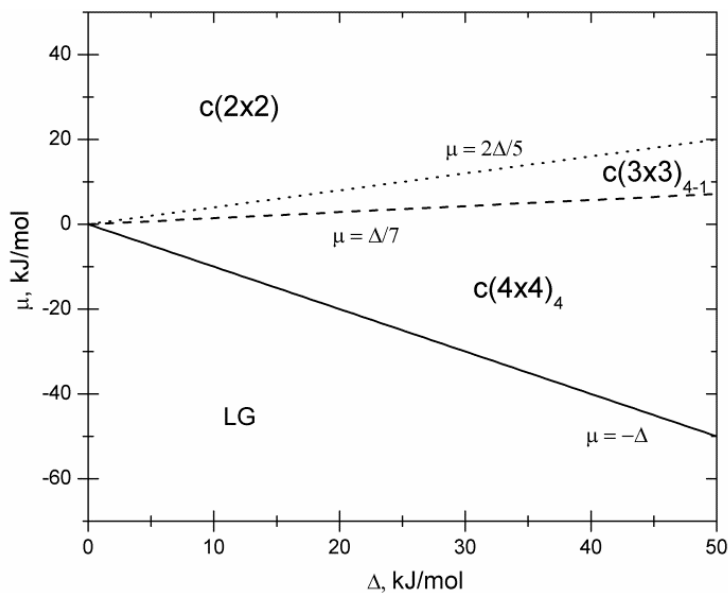

Figure 5. Phase diagram of the adlayer in the ground state. The solid line separates the stability region of the LG phase and stability region of phase $c(4\times4)_4$, while the dashed and dotted lines separate the stability region of phases $c(4\times4)_4 - c(3\times3)_{4-1}$ and phases $c(3\times3)_{4-1} - c(2\times2)$, respectively.

The adsorption isotherms calculated for different values of the ratio Δ/RT are shown in Fig. 6. It is seen that for sufficiently large values of Δ/RT there are three distinct plateaus on the isotherms, which correspond to thermodynamically stable phases of the adsorption monolayer at $\rho=0,125$, $\rho=0,22(2)$ и $\rho=0,5$, where ρ is density of the adlayer (the amount of adsorbed molecules per site). Based on the values of ρ corresponded to each horizontal plateau one can conclude that the first plateau determines the existence region of the ordered phase $c(4{\times}4)_4$, the second plateau – the existence region of the phase $c(3{\times}3)_{4{-}1}$, and the third – the existence region of the phase $c(2{\times}2)$. In addition, according to the shape of the adsorption isotherms it can be assumed that the ordered structure $c(4{\times}4)_4$ is formed from disordered lattice gas phase via second-order phase transition, which associated with the origin of a new symmetry element in the system. On the other hand, the phase transitions $c(4{\times}4)_4 - c(3{\times}3)_{4{-}1}$ and $c(3{\times}3)_{4{-}1} - c(2{\times}2)$ are the first-order phase transitions which associated with sharp changing in the first derivatives of the free energy of the system, in this case it is expressed by the sharp changing in the number of adsorbed molecules in the system. It is worth to note that along with an abrupt changing in the number of adsorbed molecules in the system, phase transitions $c(4{\times}4)_4 - c(3{\times}3)_{4{-}1}$ and $c(3{\times}3)_{4{-}1} - c(2{\times}2)$ are also attended by the reorientation of the adsorbed molecules with respect to the solid surface.
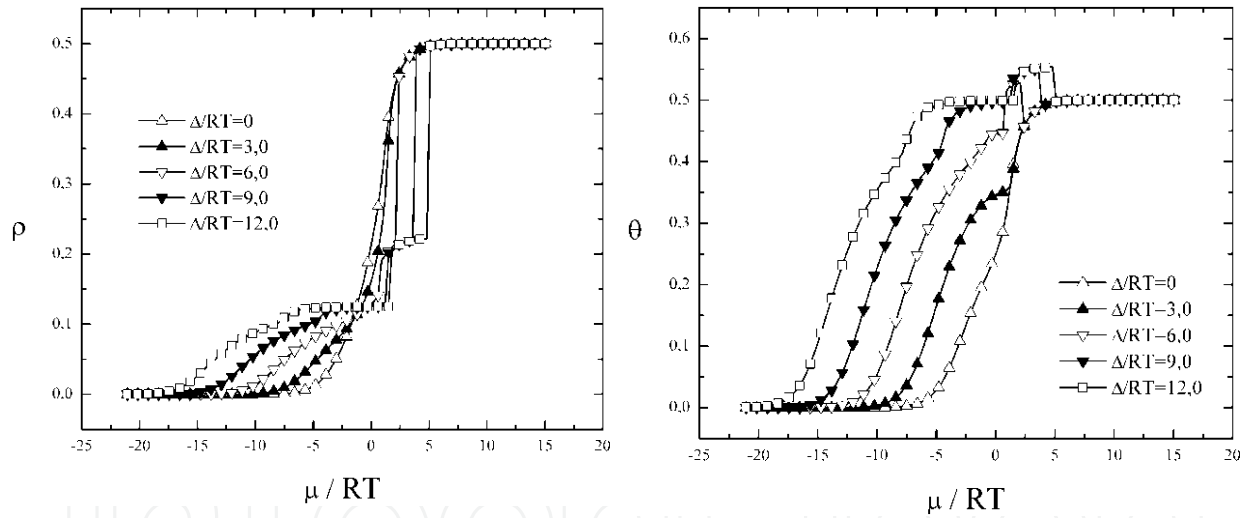

Figure 6. Adsorption isotherms (left) and the dependencies of surface coverage on reduced chemical potential (right) calculated for different values of Δ/RT.

The dependencies of surface coverage on reduced chemical potential Δ/RT demonstrate the same phase behavior of adsorbed monolayer (Fig. 6). Namely, there are three horizontal plateaus on the surface coverage curves at $\theta=0,5$, $\theta=0,55(5)$ and $\theta=0,5$ for sufficiently large values of the ratio Δ/RT. These values of surface coverage, as in the case of the adsorption isotherms, coincide with the values of surface coverage for the above mentioned phases $c(4{\times}4)_4$, $c(3{\times}3)_{4{-}1}$ and $c(2{\times}2)$, respectively . However, there is one significant difference between the adsorption isotherms and the dependencies of surface coverage on reduced chemical potential: the isotherm is not only coincides with the curve of surface coverage, but

even out of proportion to it. Indeed, the dependencies of surface coverage on the reduced chemical potential are non-monotonic function for sufficiently large values of Δ/RT. While the adsorption isotherms in accordance with the general conditions of stability of thermodynamic systems

$$(\delta\Omega)_{Tp\mu} = \delta\left(G - \mu N\right)_{Tp\mu} = \left(\frac{\partial G(T,p,N)}{\partial N} - \mu\right)\delta N + \frac{1}{2!}\frac{\partial^2 G}{\partial N^2}\left(\delta N\right)^2 +$$
$$+ \frac{1}{3!}\frac{\partial^3 G}{\partial N^3}\left(\delta N\right)^3 + \frac{1}{4!}\frac{\partial^4 G}{\partial N^4}\left(\delta N\right)^4 + \ldots + \frac{1}{m!}\frac{\partial^m G}{\partial N^m}\left(\delta N\right)^m + \sum_{n=m}^{\infty}\frac{1}{n!}\frac{\partial^n G}{\partial N^n}\left(\delta N\right)^n > 0, \qquad (3)$$

$$\mu = \frac{\partial G(T,p,N)}{\partial N}, \quad \left(\frac{\partial \mu}{\partial N}\right)_T > 0,$$

are monotonically increasing functions for all values of Δ/RT, where Ω – grand potential, G – Gibbs free energy, μ – chemical potential, N – amount of adsorbed molecules, T – temperature and p – pressure in gas phase. The same effect is observed in the dimer adsorption models on square and triangular lattices. Apparently, this effect takes a place in any adsorption monolayer of molecules with different orientations with respect to the interface.

In order to uniquely identify the ordered structures appearing in the adsorption monolayer the authors of [93] calculated the curves of partial surface coverage by molecules adsorbed on one and four active sites as functions of the reduced chemical potential μ/RT (Fig. 7). It is seen the phase with coverage $\theta = 0,5$ formed at low values of μ/RT consists only of molecules adsorbed on four active sites, so it is obvious that it has the structure of $c(4\times4)_4$. Then, with increasing chemical potential (gas phase pressure) or decreasing in temperature of the substrate, the system undergoes the phase transition from phase $c(4\times4)_4$ to the phase with coverage $\theta=0,55(5)$. It is clear from Fig. 7 that this phase consists of both molecules adsorbed on four active sites and on one active site. Therefore, this phase has the structure of $c(3\times3)_{4-1}$. With further increase of the chemical potential or when the temperature decreases the system undergoes the phase transition from phase $c(3\times3)_{4-1}$ to the phase $c(2\times2)$ with $\rho=0,5$ and $\theta=0,5$ which is formed only by molecules adsorbed on one active site.

Recently, a similar phase behavior of adlayer of complex organic molecules was observed experimentally (Fig. 8). In [24] the authors investigated the behavior of the adsorption monolayer of trimesic acid on Au (111) with electrochemical scanning tunneling microscopy. It was shown that with increasing electrode potential the ordered structure of the adlayer consisting only of molecules oriented parallel to the surface changes into the ordered phase, which contains molecules adsorbed both parallel and perpendicular to the electrode surface. Further increasing in the electrode potential leads to the surface phase which is formed only by molecules oriented perpendicular to the surface.
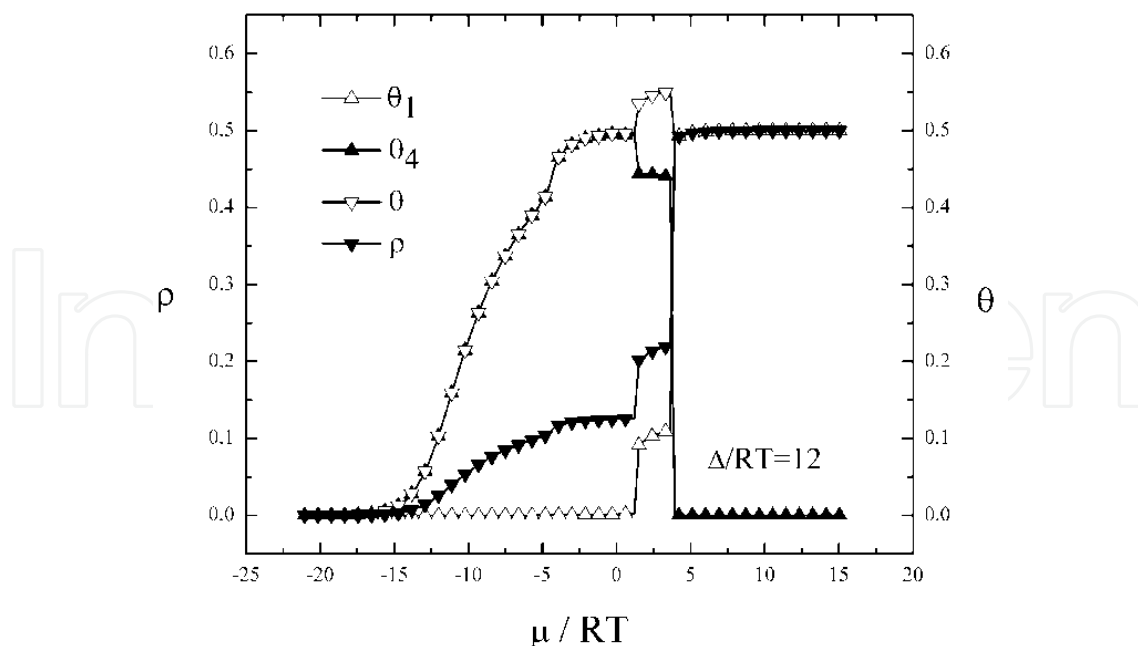
Figure 7. The curves of partial surface coverage calculated at $\Delta/RT = 12$. θ_1 – partial coverage of the surface by molecules adsorbed on one active site; θ_4 – partial coverage of the surface by molecules adsorbed on four active sites; θ – total surface coverage; ϱ – density of the adlayer (adsorption isotherm).
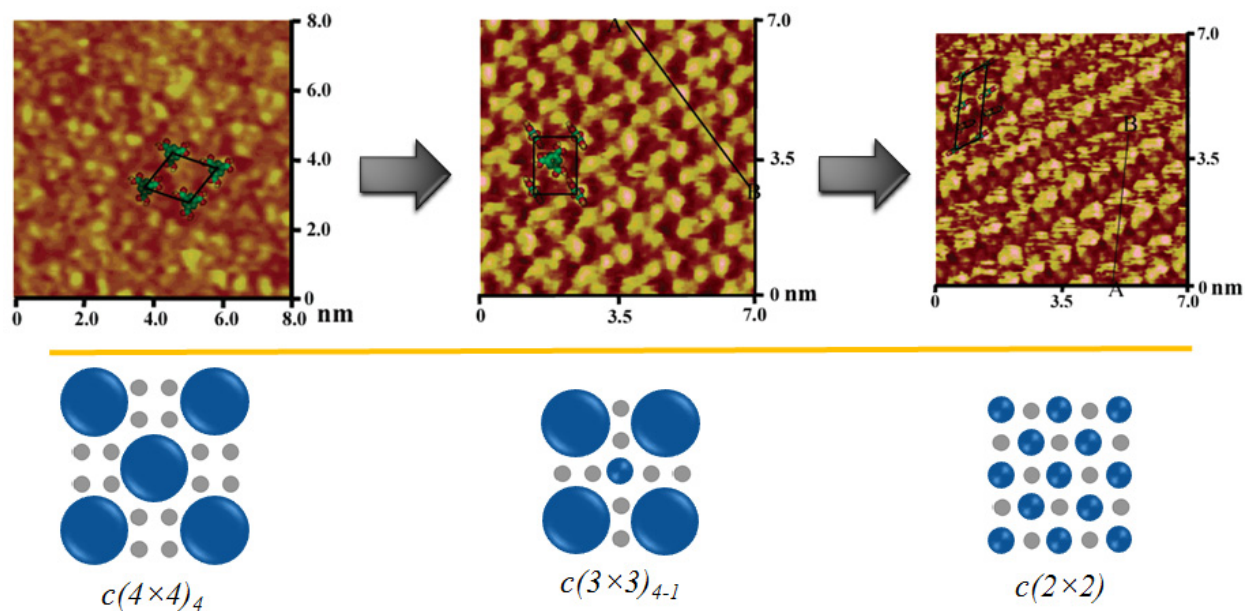

Figure 8. Ordered structure of the trimesic acid adsorption monolayer on Au (111) [21] and the corresponding structures calculated in the framework of the proposed model.

Analogous sequence of the ordered structures was also observed in other systems, in particular, in p-sexiphenyl [18] and pyridine adsorption monolayers [23] on Au (111). Thus, the phase behavior of monolayer adsorption which is realized in the model under consideration is qualitatively the same as the phase behavior of real adsorption monolayers of complex organic molecules on homogeneous surfaces. Therefore, a detailed study of the

model and models similar to that is very useful for deeper understanding of the thermodynamics of self-assembled monolayers of complex organic molecules.

In the framework of the model under consideration, the modern methods of theoretical physics such as the multiple-histogram reweighting and finite-size scaling techniques (the fourth-order cumulant of the order parameter) have been used to estimate the phase diagram (T, μ) of complicated organic molecules adsorbed on the homogenous square lattice (Fig. 9) [93].
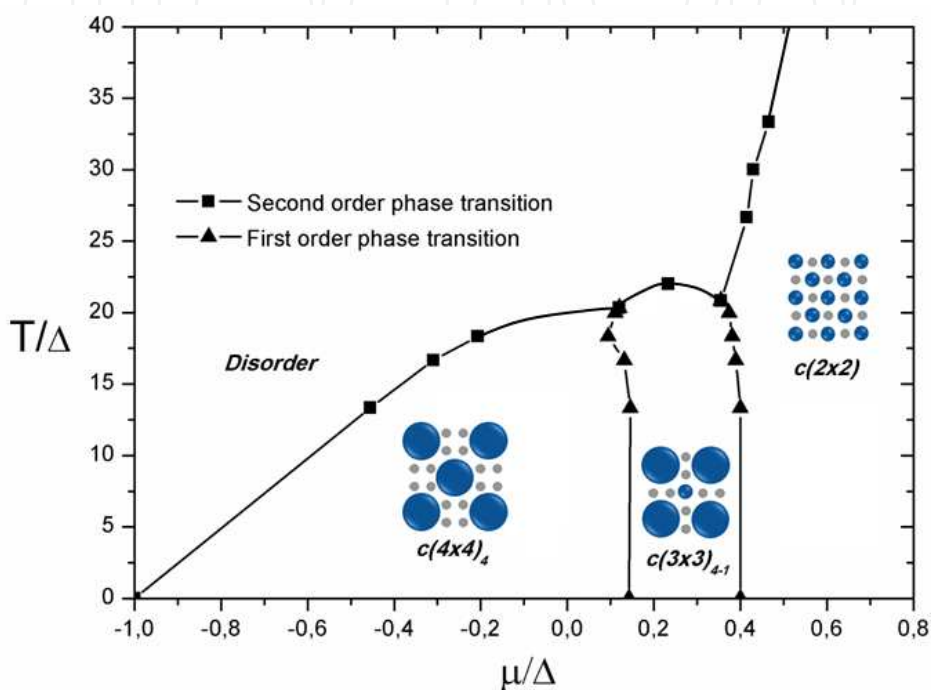

Figure 9. Phase diagram of adsorption monolayer of complex organic molecules on homogenous square lattice.

The phase diagram shown in Fig. 9 differs from the phase diagrams of dimers adsorption monolayer on square and triangular lattices that: 1) there is the phase consisting of molecules oriented in both ways (parallel and perpendicular to the solid surface) simultaneously, and 2) the critical temperature of this phase $(c(3{\times}3)_{4\text{-}1})$ is higher than the critical temperature of the ordered phase formed only by molecules adsorbed parallel to the surface. Indeed, the phase diagram of dimers adsorption on square lattice contains only two regions corresponding to the ordered phases due to the fact that when dimers adsorb on square lattice the ordered phase consisting of both dimers adsorbed parallel and perpendicular to the surface does not appear. In contrast, when dimers adsorb on triangular lattice that ordered phase is formed, but its critical temperature is lower than the critical temperature of the ordered structure formed only by dimers adsorbed parallel to the surface.

Thus, the numerical analysis of the thermodynamic properties of the lattice models which take into account the possibility of varying the orientation of the adsorbate molecules both with respect to each other and with respect to the solid surface showed that:

1. The phenomenon of non-monotonic changes of the surface coverage as function of the chemical potential is a general property of the systems under consideration and is not observed in models of single-site or multisite single-component gas adsorption which exclude different orientations in the adsorption monolayer.
2. There are ordered structures in the adsorption monolayer of complex organic molecules consisting of the molecules with different orientations relative to the solid surface, simultaneously.
3. The transition between the ordered structures of the adsorption monolayer occurs abruptly through the first-order phase transition.
4. The phase behavior of adsorption monolayer of complex organic molecules strongly depends on two factors: a) the geometry and chemical structure of the adsorbed molecule, and b) the geometry of the surface.

It is worth to note that the adsorption of single-component gas consisting of molecules with complex shape can exhibit the features which typical for the adsorption of multicomponent gas mixtures [90]. In particular, the model of adsorption of a gas mixture A (adsorb on m_1 active sites) and B (adsorb on m_2 active sites) is equivalent to the considered models (with $k = 2$) when the chemical potentials of the gas mixture components are the same, $\mu_A = \mu_B$.

4. Conclusion

Lattice gas model and its various generalizations are one of the most important models of modern statistical thermodynamics and are currently experiencing a new stage of development. On the one hand, it is related to the solution of some fundamental issues concerning the limiting behavior of two-dimensional lattice models, and, on the other hand, it is related to successful attempts to describe with the help of this model complex systems, in particular, multisite adsorption of various molecules on the solid surface.

Lattice models of multisite adsorption can take into account the number of characteristic features of complex adsorption systems, the most important of which is the possibility of the orientation varying of the adsorbate molecules, both with respect to each other and relative to the solid surface. Analysis of the thermodynamic properties of models of this type showed that despite its relative simplicity they exhibit a fantastic variety of non-trivial physical phenomena. First of all, it refers to the processes of self-assembly and phase transitions of various types, whose study is of considerable interest from the standpoint of the general thermodynamic theory. In addition, referring to the results of the experimental data, it can be argued that discussed in this chapter multisite adsorption model is firstly qualitatively, and in some cases quantitatively, reproduce the behavior of real systems and secondly have considerable predictive power. The results of study of multisite adsorption models can be summarized in following conclusions:

1. The adlayer of complex organic and inorganic molecules can form ordered structures consisting of molecules with different orientations simultaneously (both with respect to each other and relative to the solid surface).

2. The phase diagram of such systems is asymmetric. Its shape depends essentially firstly on the size and shape of the adsorbate molecules and secondly on the coordination number and type of heterogeneity of the substrate surface.

3. The critical temperature of the ordered phases of the adlayer on the one hand increases with the size of the molecule and on the other hand decreases with increasing coordination number of the lattice (entropy factor).

4. In models that take into account the possibility of the orientation varying of molecules adsorbed on the solid surface one can see the phenomenon of non-monotonic change in the coverage with increasing chemical potential, and the transition between the ordered structures of the monolayer adsorption occurs abruptly, through first order phase transition.

From applied point of view a theoretical study of such systems in general is of great interest because of the many possible applications in which used the adsorption monolayers one way or another (self-assembled monolayers adsorbed, thin organic films). The potential application range of such systems is an organic optoelectronics, the development of active elements of chemical and biological sensors, biomedical materials, heterogeneous catalysis. In this paper it is shown that the development of lattice models of these systems and study of its thermodynamic properties allows ones to understand and generalize laws of physical and chemical processes occurring in such systems, and brings the scientists closer to being able to fully control the phase behavior of monolayers of organic and other molecules on solid surfaces.

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5. References

[1] W. Rudzinski, D. H. Everett, Adsorption of Gases on Heterogeneous Surfaces; Academic Press: London, 1992.

[2] J. Morrison, J.J. Lander, Ordered physisorption of xenon on graphite // Surf. Sci. 5 (1966) 163.

[3] O.E. Vilches, Phase Transitions in Monomolecular Layer Films Physisorbed on Crystalline Surfaces // Annu. Rev. Phys. Chem. 31 (1980) 463.

[4] V.A. Bakaev, Towards the molecular theory of physical adsorption on heterogeneous surfaces // Surf. Sci. 198 (1988) 571.

[5]   J.L. Riccardo, A.J. Ramirez-Pastor, F. Roma, Multilayer Adsorption with Multisite Occupancy: An Improved Isotherm for Surface Characterization // Langmuir 18 (2002) 2130.

[6]   S. Cavenati, C.A. Grande, A.E. Rodrigues, Adsorption equilibrium of methane, carbon dioxide and nitrogen on zeolite 13X at high pressures// J. Chem. Eng. Data 49 (2004) 1095.

[7]   W. Rudzinski, K. Nieszporek, J. M. Cases, L. I. Michot, F. Villieras, A new molecular probe method to study surface topography of carbonaceous solid surfaces // Langmuir 12 (1996) 170.

[8]   D.S. Rawat, A.D. Migone, J.L. Riccardo, A.J. Ramirez-Pastor, F.J. Roma, Surface area measurements with linear adsorbates: an experimental comparison of different theoretical approaches // Langmuir 25 (2009) 9227.

[9]   J.F. Weavera, A.F. Carlssonb, R.J. Madix, The adsorption and reaction of low molecular weight alkanes on metallic single crystal surfaces // Surf. Sci. Rep. 50 (2003) 107.

[10] T.S. Nitta, M. Kurooka, T. Katayama, An adsorption isotherm of multi-site occupancy model for homogeneous surface // J. Chem. Eng. Jpn. 17 (1984) 39.

[11] J.A.C. Silva, A.E. Rodrigues, Multisite langmuir model applied to the interpretation of sorption of n-paraffins in 5A zeolite // Ind. Eng. Chem. Res. 38 (1999) 2434.

[12] G. Martinez, D. Basmadjian, Towards a general gas adsorption isotherm // Chem. Eng. Sci. 51 (1996) 1043.

[13] R. Otero, F. Rosei, F. Besenbacher, Scanning tunneling microscopy manipulation of complex organic molecules on solid surfaces // Annu. Rev. Phys. Chem. 57 (2006) 497.

[14] S.M. Barlow, R. Raval, Complex organic molecules at metal surfaces: bonding, organisation and chirality // Surf. Sci. Rep. 50 (2003) 201.

[15] T.R. Leftwich, A.V. Teplyakov, Chemical manipulation of multifunctional hydrocarbons on silicon surfaces // Surf. Sci. Rep. 63 (2008) 1.

[16] J.V. Barth, Molecular architectonic on metal surfaces // Annu. Rev. Phys. Chem. 58 (2007) 375.

[17] H. Liang, Y. He, Y. Ye, X. Xu, F. Cheng, W. Sun, et al., Two-dimensional molecular porous networks constructed by surface assembling // Coord. Chem. Rev. 253 (2009) 2959.

[18] C.B. France, F.A. Frame, B.A. Parkinson, Multiple two-dimensional structures formed at monolayer and submonolayer coverages of p-sexiphenyl on the Au(111) surface // Langmuir 22 (2006) 7507.

[19] Q.-M. Xu, H. Ma, N. Tucker, J.A. Bardecker, K-J. Jen, Controlled assembly of large π-conjugated n-type molecules on Au(111) // Nanotechnology. 18 (2007) 335302.

[20] Z. Li, B. Han, L.J. Wan, Th. Wandlowski, Supramolecular nanostructures of 1,3,5-benzene-tricarboxylic acid at electrified Au(111)/0.05M H2SO4 interfaces: An in situ scanning tunneling microscopy study // Langmuir 21 (2005) 6915.

[21] A. Dmitriev, N. Lin, J. Weckesser, J.V. Barth, K. Kern, Supramolecular assemblies of trimesic acid on a Cu(100) surface // J. Phys. Chem. B 106 (2002) 6907.

[22] F. Cunha, N.J. Tao, X.W. Wang, Q. Jin, B. Duong, J. D'Agnese, Potential-induced phase transitions in 2,2-bipyridine and 4,4-bipyridine monolayers on Au(111) studied by in

situ scanning tunneling microscopy and atomic force microscopy // Langmuir 12 (1996) 6410.

[23] W.-B. Cai, L.-J. Wan, H. Noda, Y. Hibino, K. Ataka, M. Osawa, Orientational phase transition in a pyridine adlayer on gold(111) in aqueous solution studied by in situ infrared spectroscopy and scanning tunneling microscopy // Langmuir 14 (1998) 6992.

[24] G.-J. Su, H.-M. Zhang, L.-J. Wan, C.-L. Bai, T. Wandlowski, Potential-induced phase transition of trimesic acid adlayer on Au(111) // J. Phys. Chem. B 108 (2004) 1931.

[25] H.S. Kato, M. Wakatsuchi, M. Kawai, J. Yoshinobu, Different adsorbed states of 1,4-cyclohexadien on Si(001) controlled by substrate temperature // J. Phys. Chem. C. 111 (2007) 2557.

[26] K. Oguchi, K. Mukai, Y. Yamashita, J. Yoshinobu, Low-Temperature STM and UPS Study of Adsorption States of 1,4-Cyclohexadiene on Si(100) – c(4×2) // J. Phys. Chem. C 112 (2008) 15009.

[27] R.J. Hamers, S.K. Coulter, M.D. Ellison, Cycloaddition chemistry of organic molecules with semiconductor surfaces // Acc. Chem. Res. 33 (2000) 617.

[28] N.A. Besley, J.A. Bryan, Partial hessian vibrational analysis of organic molecules adsorbed on Si(100) // J. Phys. Chem. C, 112 (2008) 4308.

[29] M. Nagao, H. Umeyama, K. Mukai and et al., Precursor mediated cycloaddition reaction of ethylene to the Si(001)c(4×2) surface // J. Am. Chem. Soc., 126 (2004) 9922.

[30] C.-H. Chung, W.-J. Jung, I.-W. Lyo, Trapping-mediated chemisorption of ethylene on Si(001) – c(4×2) // Phys. Rev. Lett., 97 (2006) 116102.

[31] J. Seto, N. Asai, I. Fujiwara, T. Ishibashi, T. Kamei, S. Tamura, Functional organic ultra-thin films for device applications // Thin Solid Films 273 (1996) 97.

[32] T. Sano, H. Fujii, Y. Nishio, Y. Hamada, H. Takahashi, K. Shibata, Organic electroluminescent devices doped with condensed polycyclic aromatic compounds // Synthetic Metals 91 (1997) 27.

[33] L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R.H. Friend, J.D. MacKenzie, Self-organized discotic liquid crystals for high-efficiency organic photovoltaics // Science 293 (2001) 1119.

[34] C.D. Dimitrakopoulos and P.R.L. Malenfant, Organic thin film transistors for large area electronics // Adv. Mater. 14 (2002) 99.

[35] D. H. Kim, J. K. Kim, and P. Hwang, Anisotropic tribological properties of the coating on a magnetic recording disk // Thin Solid Films 360 (2000) 187.

[36] A.N. Shipway, E. Katz, I. Willner, Nanoparticle arrays on surfaces for electronic, optical, and sensor applications // Chem. Phys. Chem. 1 (2000) 18.

[37] M.O. Lorenzo, C.J. Baddeley, C. Muryn, R. Raval, Extended surface chirality from supramolecular assemblies of adsorbed chiral molecules // Nature 404 (2000) 376.

[38] B. Kasemo, J. Gold, Implant surfaces and interface processes // Adv. Dent. Res. 13 (1999) 8.

[39] C.A. Mitchell, L. Yu, M.D.Ward, Selective nucleation and discovery of organic polymorphs through epitaxy with single crystal substrates // J. Am. Chem. Soc. 123 (2001) 10830.

[40] R.H. Fowler, G.S. Rushbrooke, An attempt to extend the statistical theory of perfect solutions // Trans. Faraday Soc., 33 (1937) 1272-1294.

[41] M.E. Fisher, Statistical mechanics of dimers on a plane lattice // Phys. Rev., 124 (1961) 1664.

[42] P.W. Kasteleyn, The statistics of dimers on a lattice // Physica 27 (1961) 1209.

[43] H.N.V. Temperley, M.E. Fisher, Dimer problem in statistical mechanics – An exact result // Phil. Mag. 6 (1961) 1061.

[44] W.T. Lu, F.Y. Wu, Dimer statistics on a Mobius strip and the Klein bottle // Phys. Lett. A 259 (1999) 108.

[45] W.T. Lu, F.Y. Wu, Close-packed dimers on nonorientable surfaces, Phys. Lett. A 293 (2002) 235.

[46] Y. Kong, Packing dimers on (2p+1)×(2q+1) lattices // Phys. Rev. E, 73 (2006) 016101.

[47] V.S. Poghosyan, V.B. Priezzhev, P. Ruelle, Jamming probabilities for a vacancy in the dimer model // Phys. Rev. E 77 (2008) 041130.

[48] P.J. Flory, Thermodynamics of high polymer solutions // J. Chem. Phys. 10 (1942) 51.

[49] F. Roma, A.J. Ramirez-Pastor, J.L. Riccardo, Multisite occupancy adsorption: Comparative study of new different analytical approaches // Langmuir 19 (2003) 6770.

[50] G. Kondart, Influence of temperature on percolation in a simple model of flexible chains adsorption // J. Chem. Phys. 117 (2002) 6662.

[51] F. Roma, J.L. Riccardo, A.J. Ramirez-Pastor, Application of the FSTA to adsorption of linear and flexible k-mers on two-dimensional surfaces // Ind. Eng. Chem. Res. 45 (2006) 2046.

[52] A.J. Ramirez-Pastor, T.P. Eggarter, V.D. Pereyra, J.L. Riccardo, Statistical thermodynamics and transport of linear adsorbates // Phys. Rev. B 59 (1999) 11027.

[53] A.J. Ramirez-Pastor, F. Roma, A. Aligia, J.L. Riccardo, Multisite-occupancy adsorption and surface diffusion of linear adsorbates in low dimensions: rigorous results for a lattice gas model // Langmuir 16 (2000) 5100.

[54] F. Bulnes, A.J. Ramirez-Pastor, G. Zgrablich, Surface diffusion of k-mers in one-dimensional systems // Surface Science 601 (2007) 569–577.

[55] P.J. Flory, Principles of polymers chemistry, Cornell University Press, Ithaca, NY, 1953.

[56] M.L. Huggins, Some properties of solutions of long-chain compounds // J. Phys. Chem. 46 (1942) 151.

[57] M.L. Huggins, Thermodynamic properties of solutions of long-chain compounds // Ann. N.Y. Acad. Sci. 43 (1942) 1.

[58] M.L. Huggins, Theory of solutions of high polymers // J. Am. Chem. Soc. 64 (1942) 1712.

[59] E.A. DiMarzio, Statistics of orientation effects in linear polymer molecules // J. Chem. Phys. 35 (1961) 658.

[60] E.A. Guggenheim, Statistical thermodynamics of mixtures with non-zero energies of mixing // Proc. R. Soc. London A 183 (1944) 203.

[61] P.M. Centres, A.J. Ramirez-Pastor, Configurational entropy of adsorbed rigid rods: theory and Monte Carlo simulations // Physica A 388 (2009) 2001.

[62] M. Davila, F. Roma, J.L. Riccardo, A.J. Ramirez-Pastor, Quasi-chemical approximation for polyatomics: statistical thermodynamics of adsorption // Surface Science 600 (2006) 2011.

[63] A.J. Ramirez-Pastor, J.L. Riccardo, V. Pereyra, Adsorption thermodynamics with multisite Occupancy at criticality // Langmuir 16 (2000) 10167.

[64] J.L. Riccardo, F. Roma, A.J. Ramirez-Pastor, Fractional statistical theory of adsorption of polyatomics // Phys. Rev. Lett. 93 (2004) 186101.

[65] F. Roma, J. L. Riccardo, and A. J. Ramirez-Pastor, Semiempirical model for adsorption of polyatomics // Langmuir 2006, 22, 3192.

[66] D.P. Landau, K. Binder, A Guide to Monte Carlo Simulation in Statistical Physics – Cambridge: Cambridge University Press, 2000 – p.432.

[67] M.E.J. Newman, G.T. Barkema, Monte Carlo Methods in Statistical Physics – NY: Oxford University Press, 2001 – p.475.

[68] D.A. Matoz-Fernandez, D.H. Linares, A.J. Ramirez-Pastor, Critical behavior of long linear k-mers on honeycomb lattices // Physica A 387 (2008) 6513.

[69] F. Roma, A. J. Ramirez-Pastor and J. L. Riccardo, Critical behavior of repulsive linear k-mers on square lattices at half coverage: Theory and Monte Carlo simulations // Phys. Rev. B 68 (2003) 205407.

[70] A.J. Phares, F.J. Wunderlicht, D.J. Curley, Jr. D.W. Grumbine, Structural ordering of dimers on square lattice // J. Phys. A: Math. Gen. 26 (1993) 6847.

[71] A.J. Ramirez-Pastor, J.L. Riccardo, V.D. Pereyra, Monte Carlo study of dimer adsorption at monolayer on square lattices // Surf. Sci. 411 (1998) 294.

[72] F. Roma, J.L. Riccardo, A.J. Ramirez-Pastor, Critical behavior of repulsive dimers on square lattices at 2/3 monolayer coverage // Phys. Rev. B. 77 (2008) 195401.

[73] J.E. Gonzalez, A.J. Ramirez-Pastor, V.D. Pereyra, Adsorption of dimer molecules on triangular and honeycomb lattices // Langmuir 17 (2001) 6974.

[74] P.M. Pasinetti, F. Roma, J.L. Riccardo, A.J. Ramirez-Pastor, Critical behavior of repulsive linear k-mers on triangular lattices // Phys. Rev. B, 74 (2006) 155418(8).

[75] W. Rzysko, M. Borowko, Phase diagrams of heteronuclear dimers adsorbed on a square lattice // J. Chem. Phys. 117 (2002) 4526.

[76] M. Borowko and W. Rzysko, Critical Behavior of Dimers in Monolayers Adsorbed on Heterogeneous Solid Surfaces // J. Colloid Interface Sci., 244 (2001) 1.

[77] M. C. Gimenez, F. Nieto, A. J. Ramirez-Pastor, Surface order-disorder phase transitions and percolation // J. Chem. Phys. – 125 (2006) 184707.

[78] A. J. Ramirez-Pastor, M. S. Nazzarro, J. L. Riccardo, G. Zgrablich, Dimer physisorption on heterogeneous substrates // Surf. Sci. 341 (1995) 249.

[79] T. Nitta, H. Kiriama, T. Shigeta, Monte Carlo simulation study for adsorption of dimers on random heterogeneous surfaces // Langmuir 13 (1997) 903.

[80] W. Rzysko, M. Borowko, Computer simulation of phase diagrams of trimers adsorbed on a square lattice // Phys. Rev. B 67 (2003) 045403.

[81] V.F. Cabral, C.R.A. Abreu, M. Castier, F.W. Tavares, Monte Carlo simulations of the adsorption of chainlike molecules on two-dimensional heterogeneous surfaces // Langmuir 19 (2003) 1429.

[82] V. Cornette, A.J. Ramirez-Pastor, F. Nieto, Dependence ofthe percolation threshold on the size of the percolating species // Physica A 327 (2003) 71.

[83] M. Quintana, I. Kornhauser, R. López, A.J. Ramirez-Pastor, G. Zgrablich, Monte Carlo simulation of the percolation process caused by the random sequential adsorption of k-mers on heterogeneous triangular lattices // Physica A 361 (2003) 195.

[84] M.I. Temkin, The transition state in surface reactions // Rus. J. Phys. Chem. 2 (1938) 169.

[85] Yu.S. Snagovski, Adsorption and catalytic reactions of multicenter molecules. I. in Ideal adlayer equilibrium // Rus. J. Phys. Chem. 9 (1972) 2367.

[86] Yu.S. Snagovski, Adsorption and catalytic reactions of multicenter molecules. II. Reaction kinetics in ideal adlayer // Rus. J. Phys. Chem. 10 (1972) 2584.

[87] Yu.S. Snagovski, Adsorption and catalytic reactions of multicenter molecules. III. Induced heterogeneity effect // Rus. J. Phys. Chem. 10 (1972) 2589.

[88] A.B. Gorshtein, A.A. Lopatkin, The influence of reorientation of adsorbed molecules on differential heat capacity // Rus. J. Phys. Chem. 1 (1974) 177.

[89] A.B. Gorshtein, A.A. Lopatkin, Lattice models of adsorption of diatomic molecules // Theor. Exp. Chem. 9 (1975) 148.

[90] W. Engl, L. Courbin, P. Panizza, Adsorption of asymmetric rigid rods or heteronuclear diatomic molecules on homogeneous surfaces // Phys. Rev. B. 70 (2004) 165407.

[91] W. Rżysko, A. Patrykiejew, K. Binder, Phase transitions in a two-dimensional lattice gas model of orientable diatomic molecules // Phys. Rev. B 72 (2005) 165416.

[92] W. Rżysko, A. Patrykiejew, K. Binder, Phase transitions in a two-dimensional lattice gas model of orientable diatomic molecules. II. Order-disorder transitions of superantiferromagnetic and c(2x2)AF phases // Phys. Rev. B. 76 (2007) 195409.

[93] V.F. Fefelov, V.A. Gorbunov, A.V. Myshlyavtsev, M.D. Myshlyavtseva, The simplest model of adsorption of molecules with different orientations of complex organic molecules. Monte Carlo and transfer-matrix techniques // Chem. Eng. J., 154 (2009) 107.

[94] V.A. Gorbunov, A.V. Myshlyavtsev, M.D. Myshlyavtseva, V.F. Fefelov, Simulation of complex molecules adsorption with different orientation in adlayer on square lattice // Omskiy nauchnyi vestnik 2 (2007) 19 (in russian).

[95] V.A. Gorbunov, A.V. Myshlyavtsev, M.D. Myshlyavtseva, V.F. Fefelov, Simulation of unsaturated cyclic hydrocarbons adsorption on reconstructed Si(001)–2×1 // Omskiy nauchnyi vestnik 1 (2009) 215 (in russian).

[96] V.A. Gorbunov, A.V. Myshlyavtsev, M.D. Myshlyavtseva, V.F. Fefelov, Monte Carlo study of phase behavior of complex organic molecules adlayer // Omskiy nauchnyi vestnik 3 (2009) 37 (in russian).

[97] V.F. Fefelov, V.A. Gorbunov, A.V. Myshlyavtsev, M.D. Myshlyavtseva, The simplest model of adsorption of molecules with different orientations in adlayer on the stepped surface // App. Surf. Sci., 256 (2010) 5298.

[98] P. Rinaldi, F. Bulnes, A.J. Ramirez-Pastor, G. Zgrablich, Monte Carlo study of multicomponent adsorption on triangular lattices // Surf.Sci. 602 (2008) 1783.

[99] F. Bulnes, A.J. Ramirez-Pastor, G. Zgrablich, Monte Carlo simulation of adsorption of binary gas mixtures on heterogeneous surfaces // Adsorpt. Sci. Technol. 23 (2005) 81.

[100] V.A. Gorbunov, A.V. Myshlyavtsev, M.D. Myshlyavtseva, V.F. Fefelov, Simulation of dimers adsorption on triangular lattice // Izvestiya vyschyh uchebnyh zavedeniy. Chimia I chimicheskaya, 9 (2010) 66.

[101] V.F. Fefelov, V.A. Gorbunov, A.V. Myshlyavtsev, M.D. Myshlyavtseva, Model of homonuclear dimer adsorption in terms of two possible molecule orientations with respect to surface: square lattice // Phys. Rev. E. 82 (2010) 041602.

[102] R.J. Glauber, Time-dependent statistics of the Ising model // J. Math. Phys. 4 (1963) 294.

[103] K. Kawasaki, Diffusion constants near the critical point for time-dependent Ising models // Phys. Rev. 145 (1966) 224.

[104] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.W. Teller, E. Teller, Equation of state calculations by fast computing machines // J. Chem. Phys. 21 (1953) 1087.