Phase behavior of short chains adsorbed on crystalline surfaces

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This review summarizes the results of the Monte Carlo simulation study of phase behavior of dimers and trimers on crystalline solids. The molecules are assumed to be composed of segments A and B. We discuss here the parameters relevant to vapor-liquid coexistence in adsorbed monolayers, including shapes of molecules, their chemical structure, a degree of flexibility, the strength of interactions between similar and dissimilar segments, a type of lattice and surface heterogeneity. The illustrative examples of phase diagrams are presented. The model is mapped on the Ising-like single-occupancy models used previously for magnetic systems and gas molecules with internal degree of freedom.

1. INTRODUCTION

Phase transitions are among the most intriguing phenomena exhibiting by condensed matter. The understanding of phase transitions and critical phenomena is challenge for researchers worldwide which is motivated by both industrial applications and scientific interest. For many years phase behavior of monolayers formed by adsorption of polyatomic molecules on solid surfaces has become an active field of research [1, 2]. In spite of considerable numbers of contributions it is not completely clear which parameters are responsible for the topology of the phase diagrams. However, in recent years molecular simulations have become an effective tool to generate phase diagrams for fluids consisting of short chains. The results allow us to present here a systematic analysis of vapor-liquid coexistence in such systems.

Theoretical models used to study thermodynamical properties of complex fluids involve two important elements: architecture of molecules and
intermolecular potentials. In the simple models a molecule is treated as a point source of the intermolecular potential. For molecules without internal degrees of freedom the category of phase diagram is determined by the range and strength of attractive and repulsive interactions [3-5]. Phase behavior of fluids with embedded anisotropic features such as, for example, magnetic or electric moments is much more complicated. The interrelations between internal and translational degrees of freedom lead to unusually rich diagram topologies [6-10]. The fluids can be described in the framework of the lattice models. The single-occupancy models in which one molecule occupies one lattice site can be easily mapped onto the Ising-like models formulated for magnetic systems [11].

In another group of models a molecule is assumed to be a chain of the same or different units linked together. Intermolecular forces are described by the multicenter potential. The simplest molecule of this sort is a dimer. The systems involving dimers have been often considered in terms of the lattice model. There is no a simple compatibility with the Ising model when a molecule occupies more than one lattice site. In this case occupation of a given site ensures that at least one of its nearest-neighbor sites is also occupied. There is no statistical equivalence between molecules and vacancies, which is characteristic for single-occupancy models. For these reasons a theoretical description of the system is very difficult. The key problem is to calculate a number of possible configurations for the system. The exact solution is known only for homonuclear dimers at a full surface coverage [12-14]. The lattices partially covered by the dimers have been also investigated and the structural ordering in such monolayers has been analyzed [15-19]. The heteronuclear dimers have been less intensively studied [20-27]. However, the results have shown a great variety of phase transitions in these systems. The aim of these works was to understand how the topology of phase diagram depends upon relative strength of interactions between segments and a character of the solid surface. Similar calculations have been carried out for various trimers, which seemed to be a very good model particles to study the influence of the geometrical shape and chemical structure of molecules on the vapor-liquid coexistence [28].

In this article we present a short overview of recent progress in the area of computer simulations of phase transitions in monolayers formed by adsorption of short linear molecules on crystalline solid surfaces. The review summarizes the results of our intensive research.

The article is organized as follows: in Section 2 the model is presented, Sec. 3 describes the Monte Carlo procedures, the results obtained for dimers are collected in Sec. 4, Sec. 5 contains the conclusions referring to trimers. The summary is given in Sec. 5.
2. MODEL

In our model molecules are composed of two types of segments A and B. We have considered dimmers and three kinds of trimers: homogeneous chains and trimers with the ‘functional group’ located at the end or at the midpoint of the molecule. In all cases we have studies molecules of different shapes: linear, L-shaped rigid rods and flexible chains.

Let us consider monolayer film formed on a crystalline surface. We introduce the lattice model with a site occupied by one segment. Each lattice site is characterized by a pair of occupation variables \(c_A, c_B\). The occupation variable \(c_x\) (\(x\) denotes a kind of a segment (A or B)) can take values: \(c_x = 1\) when a site is occupied by atom \(x\) and \(c_x = 0\) in all other cases. We have taken into account only the near-nearest interactions. In the grand canonical ensemble the Hamiltonian of \(N\) molecules at a given temperature \(T\) can be written as

\[
H = u_{AA} \sum_{\sigma_i,j} c_A c_A + u_{BB} \sum_{\sigma_i,j} c_B c_B + u_{AB} \sum_{\sigma_i,j} c_A c_B - Nu^* - N\mu
\]

where \(\mu\) is the chemical potential of the fluid. The sums run over all pairs of nearest-neighbor lattice sites. The sum of the first three terms is the interaction energy for all possible pairs of segments, so we subtract the interactions between segments belonging to the same molecule \(Nu^*\) where: \(u^* = u_{AB}\) for dimers; \(u^* = 2u_{BB}\) for trimers \(BBB\); \(u^* = u_{BB} + u_{AA}\) for trimers \(ABB\); \(u^* = 2u_{AB}\) for trimers \(BAB\).

This Hamiltonian describes the multisite-occupancy lattice model in which molecule is a source of an multi-centre and short-ranged potential. In the above adsorption energy is assumed to be equal to zero. In a general case the Hamiltonian contains terms describing interactions of segments A and B with different adsorption sites:

\[
H' = H + \sum_i \left(V_{Ai} c_A_i + V_{Bi} c_B_i\right)
\]

where \(V_{Ai}\) and \(V_{Bi}\) are the adsorption potentials for a given active center and segments A and B, respectively [27].

3. MONTE CARLO PROCEDURES

We have performed series of Monte Carlo simulations in the grand canonical ensemble using the hyper-parallel tempering technique [29-34]. The hyper-parallel tempering allows us to study several thermodynamic states in a simple
run [34]. The method leads to faster convergence and lower fluctuations, as a consequence is more effective than independently carried out simulations at each state point. Thus, it is well suited to investigate the systems close to the transition points. The multiple-histogram reweighting technique was applied to analyze the results [33, 34]. According with the finite scaling theory the order-disorder transition in a finite system is rounded and shifted, so the critical parameters were determined from suitable scaling relationships [35, 36]. Readers seeking a more discussion of the methodological aspects pertaining to the simulation technique are referred to the original articles.

We have assumed that $u_{BB}$ is the unit of energy, the reduced temperature is defined as $T^* = k_B T / |u_{BB}|$.

4. DIMERS

For dimers $AB$ the particular sums in Eq. (1) are equal to numbers of particular pairs: $N_{AA}$, $N_{BB}$ and $N_{AB}$, respectively. This lattice-gas model Hamiltonian can be mapped onto the appropriate spin-1 lattice model Hamiltonian by the following variable transformation

$$S_i = \begin{cases} 1 & \text{for } cA_i = 1, cB_i = 0 \\ 0 & \text{for } cA_i = cB_i = 0 \\ -1 & \text{for } cA_i = 0, cB_i = 1 \end{cases}$$

(3)

One can express the Hamiltonian (1) as

$$H = \varepsilon \sum_{i>j>\sigma} S_i^z S_j^z + \varepsilon_1 \sum_{i>j>\sigma} S_i S_j + \varepsilon_2 \sum_{i>j>\sigma} (S_i^z S_j + S_i S_j^z) + H \sum_j S_j^z$$

(4)

where

$$\varepsilon = \frac{1}{4} (u_{AA} + u_{BB} + 2u_{AB})$$

(5)

$$\varepsilon_1 = \frac{1}{4} (u_{AA} + u_{BB} - 2u_{AB})$$

(6)

$$\varepsilon_2 = \frac{1}{4} (u_{AA} - u_{BB})$$

(7)
The first sum denotes the number of pairs of sites occupied by any segment, the second sum is equal to the difference between the numbers of pairs consisting the same and unlike segments, whereas the third sum is the difference in numbers of pairs \( AA \) and \( BB \). For dimers the following relationships hold

\[
\sum_j S_j = 0 \quad \text{and} \quad \frac{1}{2} \sum_j D_j = N = N_A = N_B
\]

where \( N_A, N_B \) denote numbers of segments \( A \) and \( B \).

When \( H \) is replaced by \( H' = -\frac{1}{2}(\mu_A + \mu_B) \) the Hamiltonian (4) represents an equimolar two-component gas mixture [11]. Both of the models are formally similar but the phase behaviors of dimers and the mixture of monomers are completely different [37, 23-25].

In the case of symmetrical segment-segment interactions \( u_{AA} = u_{BB} \) the parameter \( \varepsilon_2 = 0 \) and the Hamiltonian becomes form of the Hamiltonian for the Blume-Emery-Griffiths model [38-40]. For \( \varepsilon = 0 \) and \( \varepsilon_2 = 0 \) it describes the Blume-Capel model [39, 40].

Two-dimensional fluid of dimers with \( \varepsilon_2 = 0 \) and \( \varepsilon, \varepsilon_2 < 0 \) has been discussed in the paper [23]. However, when \( u_{AB} = u_{BB} \) we have \( \varepsilon_1 = \varepsilon_2 \) and

\[
H = \varepsilon \sum_{\delta_i, j_p} S_i^z S_j^z + \varepsilon_1 \sum_{\delta_i, j_p} S_i S_j \left(S_i + S_j + 1\right)
\]
Such systems have been discussed in the articles [24-27].

Let us analyze the ground state for the Hamiltonian (4). When $\varepsilon < 0$ the model predicts that all possible ordered states correspond to the fully covered lattice. However, if $\varepsilon > 0$ ordered phases for lower densities are also observed [20, 21]. For a fully covered lattice the structure of the ordered phase depends only on the parameter $\varepsilon_l$. When $\varepsilon_l < 0$ the quasi-lamellar structure is formed by dimers lying parallel to the x or y-axes. The structure $A A B B$ is replicated to make alternating strips of $A$ and $B$ segments. The state has a fourfold degeneracy. There is the ordering of segments as well as the ordering of bounds. Conversely, if $\varepsilon_l > 0$ the chessboard structure (the antiferromagnetic phase AF [11]) is preferred. The segments are ordered but bounds can be randomly distributed over the lattice. The degeneracy of the state is very high [12]. The both ordered structures are shown in Figure 1. There is no any ordered structure for $\varepsilon_l = 0$.

The structural transition in a dimeric fluid is to some extent similar to demixing observed in binary mixtures of monomers $A$ and $B$ [36]. However, in a dimer molecule the the bond between segments cannot be broken. Therefore, differences in strengths of interactions between similar and dissimilar segments can only cause changes in orientation of molecules and, as a consequence partial separation of unlike segments.

Riccardo et al. [20] estimated the phase diagrams for homogeneous dimers on a square lattice. In the case of attractive interactions between segments they have obtained the phase diagram equivalent to that for a monoatomic lattice gas. However, for repulsive interactions the coexistence curve is asymmetrical and branches corresponding to two ordered structures are observed. We shall show below that phase behavior of heterogeneous dimers is much more complicated.

Figure 2 presents the phase diagrams estimated for symmetric dimers adsorbed on a square lattice. We consider systems with attractive segment-segment interactions ($u_{AA} = u_{BB} = -1$). The energy $u_{AB}$ is only parameter which controls the phase diagram topology. For a certain value of the energy $u_{AB}$ the phase diagram splits into two parts corresponding to two first-order transitions. The first transition is the usual vapor-liquid coexistence. The other is connected with the structural transition between two liquid phases. Both branches join together in the triple point. For weaker interactions between $A$ and $B$-segments the triple point moves toward the vapor-liquid critical point. On further reduction of these interactions the coexistence curve becomes a highly asymmetric form of a ‘neck swan’. We have carefully analyzed of the structure of all studied phases. For low temperatures dense fluids exhibit a high degree of the quasi-lamellar ordering. Coexistence between a disordered vapor and the ordered liquid has been found. For somewhat higher temperatures the liquid polymorphism is observed. The double criticality is found with a second liquid-liquid critical
point. There is a phase transition between disordered liquid and the quasi-lamellar liquid phase. The discussed group of dimers belongs to the universality class of the two-dimensional Ising model.

Fig. 2. Phase diagrams for dimmers $AB$ adsorbed on a homogenous square lattice. Parameters: $u_{AA} = u_{BB} = -1$ and $u_{AB} = -0.375, -0.35, 0$. Simulation data from ref [23].

In the papers [20-27] we have studied another category of dimers, namely fluids, for which $u_{BB} = u_{AB} = -1$, and the $AA$-interactions vary from attractive to repulsive: $u_{AA} \in <-1,1>$. For all studied systems $\varepsilon_1 = \varepsilon_2 > 0$ so the ordered structure $AF$ is formed. In the considered cases the $\varepsilon_2 = u_{AA} + 1$, and the energy $u_{AA}$ is only free parameter that controls the phase behavior of the system. If energy $u_{AA}$ changes from -1 to 1 then the parameter $\varepsilon_1$ decreases from 2 to 0. The evolution of phase diagrams connected with an increase of the energy $u_{AA}$ is shown in Figure 3. For positive values of the parameter $\varepsilon_1$ there exists a line of critical points separating a disordered fluid from the ordered $AF$-fluid. This line
crosses the vapor-liquid coexistence curve. For very high values of $\varepsilon_1$, corresponding to strong repulsive AA-interactions, the line terminates at the tricritical point. In the case of lower values of $\varepsilon_1$ the critical line of the order-disorder transition crosses the coexistence curve below its critical point at a critical end point. If the parameter $\varepsilon_1$ decreases the critical end point moves towards lower temperatures. Obviously, for $\varepsilon_1 = 0$ the order-disorder transition is not observed. A critical behavior of these systems has been carefully investigated [25]. We have found an interesting crossover from the universality class of Blum-Capel model (for repulsive AA-interactions) to the universality class of the two-dimensional Ising model (for attractive AA-interactions).

![Phase diagram topologies for dimmers AB adsorbed on a homogeneous square lattice](image)

Parameters: $u_{BB} = u_{AB} = -1$, and $u_{AA} \in [-1,1]$. Solid lines represent the first order transitions, the dotted lines correspond to continuous transitions.

Fig. 3. Schematic representation of phase diagram topologies for dimmers AB adsorbed on a homogeneous square lattice. Parameters: $u_{BB} = u_{AB} = -1$, and $u_{AA} \in [-1,1]$. Solid lines represent the first order transitions, the dotted lines correspond to continuous transitions.
This completes our short discussion of a role of interactions between different segments in phase transitions in dimers adsorbed on crystalline surfaces.

It should be mentioned here that a type of lattice can strongly affects phase equilibrium in the system. These effects have been discussed in [26]. Nowadays it is quite obvious that surface heterogeneity of the solid surface is one of the most important parameters determining adsorption process. The problem of how surface heterogeneity affects phase transitions in adsorbed monolayers is still being explored [2]. The illustrative example of phase diagrams estimated for dimers AB adsorbed on energetically heterogeneous surface is shown in Figure 4. In this case it was assumed that the energy of interactions between a given surface site and both segments of the molecule are always the same ($V_{AB} = V_{BB} = V_i$). The lattice is composed of alternating strips of non-interacting ($V_1 = 0$) and attractive ($V_2 = 0$) sites. The sites of both types have the same contributions. Two parameters have been used to characterize the surface heterogeneity: the difference in adsorption energies of different adsorption centers ($\Delta V$), which describe the degree of energetical heterogeneity, and the width of the strips ($s$) characterizing the topography of the adsorbent. It has been shown that both of the parameters considerable affect the nature of phase transitions and critical behavior of the systems. Figure 4 shows the surprisingly strong influence of surface topography on a location of a critical point.

Fig. 4. Phase diagrams for dimmers AB adsorbed on a heterogeneous square lattice. The surface is composed of alternating strips of non-interacting and attractive segments. Parameters: $u_{BB} = u_{AB} = -1, u_{AA} = 1, \Delta V = 0.5, s = 3$ [27].
5. TRIMERS

Similar calculations have been performed for trimers [28]. Depending of the chemical structure and the shape of molecules the systems have different ground-states, and the possible ordered structures have different symmetries. As a consequence, their phase diagrams are also completely different.

An influence of a geometrical shape of homogeneous trimers on the vapor-liquid coexistence is shown in Figure 5. The coexistence curve for L-shaped trimers lies below the curve estimated for linear molecules. The flexible trimers exhibit similar phase behavior as the L-shaped rigid rods.

![Phase diagrams for various homogeneous trimers adsorbed on a homogenous square lattice: rodlike linear (circles), rodlike L-shaped squares) and flexible (diamond). Simulation data from ref [28].](image)

Fig. 5. Phase diagrams for various homogeneous trimers adsorbed on a homogenous square lattice: rodlike linear (circles), rodlike L-shaped squares) and flexible (diamond). Simulation data from ref [28].

In the case of heterogeneous trimers a shape of rodlike molecules is even more significant for phase transitions. The spectacular example of shape effects is presented in Figure 6. The comparison of phase diagrams for the linear and L-shaped trimers $ABB$ leads to conclusion that they belong to different categories. For linear $ABB$ molecules the quasi-lamellar structure, similar to that depicted in Figure 1, is strongly preferred. The symmetry of the ordered fluid consisting of $L$-shaped trimers is diverse. This can explain the difference in phase diagram topology [28]. It has been also found that a position of segment $A$ in a trimer decides on physical properties of a fluid. For linear $BAB$ molecules the coexistence curve is less asymmetric than for trimers $ABB$. Moreover, the second-order transition between a disordered and the ordered fluid is observed at high temperatures. The system exhibit the tricritical point behavior.
6. CONCLUSIONS

The described above model allows us to formulate some conclusions referred to the influence of various parameters on phase behavior of the two-dimensional films. One of the most important parameters determining a nature of phase transitions are, of course, interactions between particular segments. They decide about the category of the phase diagram. However, our studies have clearly shown that the molecular structure of molecules also plays a crucial role in phase transitions in one-component fluids consisting of short chains. The shape of molecules affects the phase diagrams for homogeneous, as well as, heterogeneous trimers. Similarly, the phase diagrams estimated for “chemical isomers’ (e.g., the linear rigid rods: $ABB$ and $BAB$) can be completely different.

Another important parameter is the structure of solid surface. For energetically homogeneous surfaces a type of crystalline lattice affects a nature of vapor-liquid coexistence in thin films consisting of heteronuclear dimers. In the case of heterogeneous adsorbents an influence of the surface is more visible. The phase diagrams and critical parameters depend on the degree of energetical heterogeneity and the geometrical topology of the surface.

The picture of phase transitions in monolayers formed by short ‘heterosegment’ chains on crystalline surfaces appeared to be much more complicated than was previously expected.
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CURRICULA VITAE

Małgorzata Borówko was born in 1952 in Lublin. After graduating in chemistry she was employed in Department of Maria Curie Skłodowska University (1976). She received her Ph.D. from Maria Curie-Skłodowska University in 1980 and in 1989 she completed her habilitation. She received the title of professor in 2001. She organized, together with prof. S. Sokołowski, Department for the Modelling of Physicochemical Processes. Since 1995 she had been the head of this department until now. Her areas of research include theoretical chemistry, statistical thermodynamics, computer modeling, interface and colloid science, adsorption and chromatography. She is the author or co-author about 90 scientific papers. She edited the monograph “Computational Methods in Colloid and Surface Science”, Surfactant Science Series, M. Dekker, vol. 89, New York, 2000. This comprehensive reference presents modern methods for mathematical modeling of physical processes used in surface science. She was the member of the Advisory Board of Journal of Colloid and Interface Science (2001–2004). She was awarded two times by the Polish Ministry of Education and five times by the Rector of M. Curie-Skłodowska University. In 2001 she received the Langmuir Lecture Award from American Chemical Society (Division of Colloid and Surface Science). She had the Langmuir Lecture entitled ‘Monte Carlo simulations of adsorption’ on the 222nd Fall Meeting of American Chemical Society in Chicago.

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