Adsorption (2013) 19:495–499
DOI 10.1007/s10450-013-9471-1

Devil’s staircase behavior of a dimer adsorption model

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Received: 4 November 2012 / Accepted: 7 January 2013 / Published online: 18 January 2013

Abstract We have constructed the simple two-dimensional adsorption model with short range non-competing interactions which demonstrates devil’s staircase of phase transitions. The main factor which leads to the appearance of infinite amount of ordered structures in our model is two competing forms of adsorption. The ground state properties of the model have been analyzed.

Keywords Devil’s staircase · Dimer adsorption · Phase transitions · Ground state

1 Introduction

The term «devil’s staircase» is usually used to describe the physical systems in which the amount of ordered structures in a finite range of phase space becomes formally infinite. Those systems occur fairly rare. For example, the formation of crystal facets (Pieranski et al. 2000), antiferroelectric, smectic and lyotropic liquid crystals (Wang and Taylor 1996; Bahr et al. 1995), magnetic structures (Shibata et al. 1995) and granular materials (Combe and Roux 2000). Recently, devil’s staircase of ordered phases was found experimentally in the adsorption system–trimesic acid on Au(111) (Ye et al. 2007).

Commonly, the devil’s staircase appears as a result of the competition between long-range repulsive and short-range attractive interactions. Even the simplest models in which devil’s staircase takes place include complex sets of interactions between particles. In the case of one-dimensional models it can be variable external field or long-range repulsive interactions, e.g. Frenkel–Kontorova model (Frenkel and Kontorova 1938) and one-dimensional Ising model (Bak and Bruinsima 1982); for three-dimensional models as a rule there are two or more competing interactions, e.g. well-known ANNNI model (Selke and Fisher 1979; Bak and Boehm 1980). As far as we know there are no Ising-like or lattice gas two-dimensional models with short range interactions that reveal the devil’s staircase behavior (Fefelov et al. 2012).

In this work we have constructed the simple two-dimensional adsorption model with short range non-competing interactions which demonstrates devil’s staircase of phase transitions in the ground state (at temperature equal zero). The main factor which leads to the appearance of infinite amount of ordered structures in our model is two competing forms of adsorption. The model under consideration is the simplest model of multisite adsorption with different orientations of adsorbed molecules with respect to surface and with respect to other adsorbed molecules–the dimer adsorption model (Fefelov et al. 2010a).

2 Model

Let us describe in detail the lattice-gas model of monolayer adsorption of homonuclear dimers in terms of the possibility of various orientations of dimers with respect to the surface. In our model the dimer molecule is presented as a linear array consisting of two identical elements with a fixed length of binding equal to the lattice constant. We do not consider the high-frequency stretching motion along

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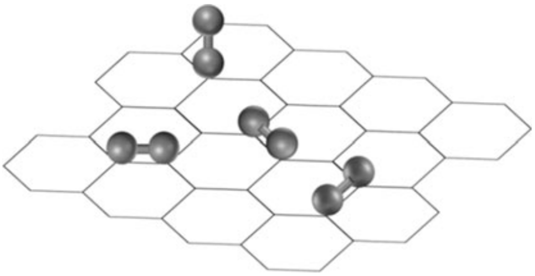

Fig. 1 Adsorption ways of dimer on hexagonal lattice

the molecule axis. Such molecule can adsorb perpendicularly (vertical orientation) or parallel (horizontal orientation) to the surface occupying one or two sites, respectively (Fig. 1). We allow for the orientation-dependent energies of interaction of the dimers with the surface h_1 (vertical orientation) and h_2 (horizontal orientation). To simplify the calculations, we use only the value of difference between them: $h = h_2 - h_1$. The substrate surface is represented as a hexagonal lattice. The infinite strong repulsive lateral interactions between nearest-neighbor particles are allowed for as well. It should be noticed that in the framework of our model there is the only kind of short range interactions.

The thermodynamic Hamiltonian of the model can be written as follows:

$$H_{eff} = -(h+\mu)\sum_i \frac{c_i}{2} - \mu \sum_i m_i, \tag{1}$$

where the occupation numbers c_i and m_i are equal to unity if the adsorption site i is occupied by the segment of the molecule adsorbed on two sites and one site, respectively, and zero in the case of a vacant site; μ is chemical potential. Thus, the model parameters are chemical potential, μ; value h.

3 Results and discussion

For the model under consideration we calculate exact phase diagram in (μ, h) plane in the ground state. At these conditions the grand thermodynamic potential for any ordered phase can be calculated from the Hamiltonian directly since each ordered phase is characterized by specific symmetry properties which determine the arrangement of differently oriented molecules over the surface. In this case stability of each phase is determined by minimum of the grand thermodynamic potential of the system at given value of chemical potential.

We consider the case when $h > 0$, i.e. dimer adsorption on two sites is energetically preferred then on one site, this case is the most interesting. To determine the ordered structures appearing on the surface and search for regularities of phase metamorphosis we developed the following algorithm:

(1) Initially, we found with the tip of the pen all as dense as possible surface structures composed of differently oriented dimers. (a) it is clear that the first structure (S_1) is formed by only horizontally oriented dimers for $h > 0$; (b) further structures were characterized by a gradual increase in the number of vertically oriented dimers; (c) the final structure (S_∞) is the most dense and consists of vertically oriented dimers.

(2) The unit cell structure was determined for each ordered phase and grand thermodynamic potential per one active center of the surface was calculated (directly from the Hamiltonian (1) for the unit cell).

(3) Next, by comparing the values of grand thermodynamic potential of each ordered structures for the entire range of the chemical potential we defined (a) the possibility of selected ordered structures existence and, if the phase exists, (b) the range of chemical potential in which that phase exists.

The analysis specified above of the ground state of the model demonstrates that as the chemical potential increases the transition from phase S_1 to the phase S_∞ goes through the infinite sequence of ordered structures (S_i) containing dimers with different orientation with respect to the surface (Fig. 2).

In Fig. 2 dimers adsorbed with horizontal orientation (adsorbed on two sites) are shown in black color, they form the "framework" of the phase or honeycomb cells. Dimers with vertical orientation (adsorbed on one adsorption site) are marked by light gray color and white color is used for empty adsorption sites. The size of unit cell is shown by frame and increases by two sites for each next ordered phase, excluding the S_∞ ordered phase which unit cell size equals two.

We have deduced the law of changing of the grand thermodynamic potential per one lattice site for the each ordered structure:

$$\Omega_n = -\frac{3n+2}{2(n+2)^2}h - \frac{n^2+2n+2}{2(n+2)^2}\mu, \tag{2}$$

where n is the serial number of the ordered phase. It is seen that when n tends to infinite the first and the second terms in right side of equation tends to zero and $-\mu/2$, respectively. Thus, the dimers adsorbed on two adsorption site are absent in ordered phase with serial number $n \to \infty$ (structure S_∞). The existence condition for ordered phase with serial number n at given value of chemical potential can be written as:

$$\Omega_n = \mathrm{Min}\{\Omega_1, \ldots, \Omega_\infty\} \tag{3}$$

Using the expressions (2) and (3) the ground state phase diagram of the model was calculated (Fig. 3). It is seen that the regions of existence of ordered phases are squeezed and tend to zero when chemical potential verges towards $3h/2$. When chemical potential achieves this value the ordered structure with maximal density forms on the surface (the

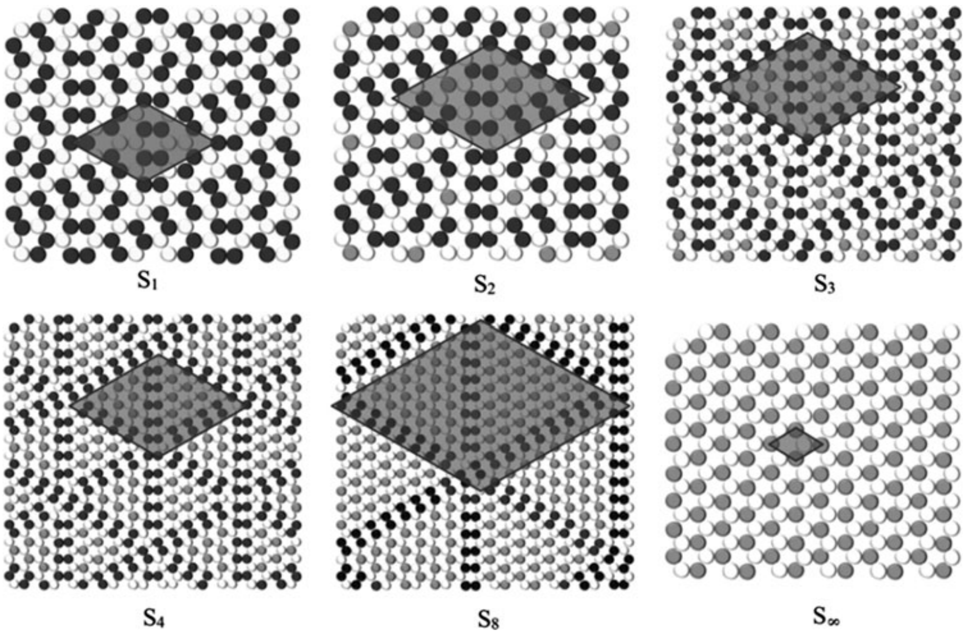

Fig. 2 The sequence of ordered structures of dimers on hexagonal lattice in ground state (see explanation in text)

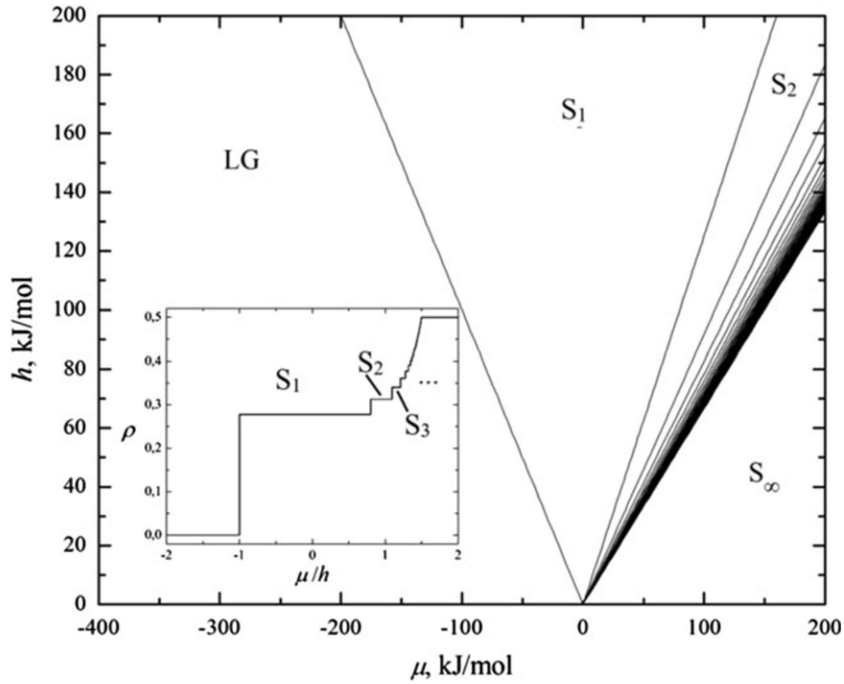

Fig. 3 Ground state phase diagram of dimers on hexagonal lattice and adsorption isotherm ρ (μ/*h*) at $T = 0K$

structure S_∞ consisted only with vertical oriented dimers adsorbed on one adsorption site). In addition, using the expressions (2) (3) and well-known thermodynamic relation for adlayer density

$$\rho = \left(\frac{\partial \Omega}{\partial \mu}\right)_{T=0,\,h} = \frac{n^2 + 2n + 2}{2(n+2)^2}, \tag{4}$$

One can derive the expression for ground state isotherm (amount of adsorbed dimers per site) which is shown on the inset of Fig. 3.

It should be noted that ground state coverage (reduced amount of occupied adsorption sites) dependence on reduced chemical potential θ (μ/*h*) is a nonmonotonous function, i.e. with chemical potential increasing, the amount of the vacant adsorption sites increases too. It seems to be a general property of systems where different molecule orientations and multisite occupancy are considered (Fefelov et al. 2009, 2010a, b, c). It is interesting that the highest value of coverage corresponds to the second ordered structure S_2 where vertical oriented dimers are appearing but not S_1 Fig. 4.

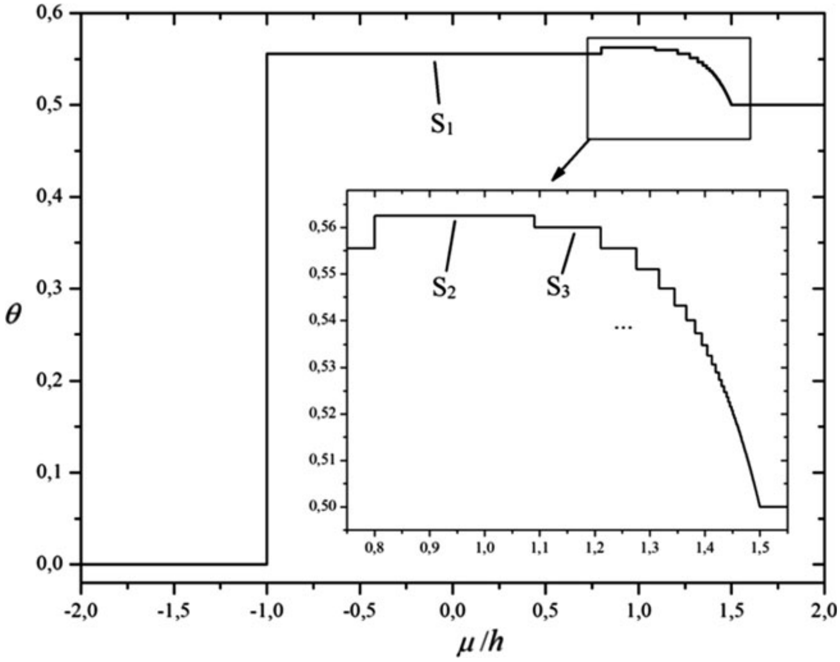

Fig. 4 Ground state coverage dependence of reduced chemical potential θ (μ/*h*)

Similar metamorphoses of adlayer ordered structures take place in the real adsorption systems of complicated organic molecules. For example, the same phase behavior was directly observed in the adsorption system of trimesic acid on Au(111) with scanning tunneling microscopy in ultra-high vacuum conditions (Ye et al 2007). It should be noted that the formation of honeycomb cells in that adlayer is attributed to specific (directed) lateral interactions between adsorbed molecules rather than surface geometry.

It should be note that our tentative results of modeling at finite temperatures show that devil's staircase takes place in the model at finite temperature too.

4 Conclusions

In this work we have constructed the simple two-dimensional adsorption model with short range non-competing interactions which demonstrates devil's staircase of phase transitions in the ground state. It is the model of oriented dimer adsorption on honeycomb lattice. It is shown that as the chemical potential increases in the model the transition from phase consisted of only horizontally adsorbed dimers to the phase formed by only vertical adsorbed dimers goes through the infinite sequence of ordered structures containing dimers with different orientation with respect to the surface.

It is interesting that the coverage dependence on reduced chemical potential θ (μ/*h*) is a nonmonotonous function and the highest value of coverage belongs to the second ordered phases.

At present we certainly know that at finite temperatures ordered structures S_1 and S_∞ can form on the surface, moreover structure S_1 had been obtained by Gonzalez et al. in (Gonzalez et al. 2001). Confirmation of existence or absence of other ordered structures $S_2 \ldots S_{\infty-1}$ at finite temperatures is our current task.

It is worth to note that our model may be considered as a special case of the model of binary gas mixture adsorption, in which the molecules of the first kind are adsorbed on two sites and the molecules of the second kind are adsorbed on one site (Du et al. 1998). These two models become equivalent when the difference between chemical potentials of components in the model of binary gas mixture adsorption is constant. Accordingly, the devil's staircase phase behavior observed in our model is expected to appear in binary gas mixtures adsorption systems as well [Dávila et al. 2009].

Recently, we had studied the adsorption model of orientable dimers on square and triangular lattices, and essentially this work is a continuation of our studies of the lattice coordination number effect on the phase behavior of the adsorption monolayer. The results obtained in this paper allow us to conclude that the phase behavior of the adsorption monolayer qualitatively changes with coordination number of the lattice and the phase behavior in the case of honeycomb lattice is the richest one, at least at lim $T \to 0$. It is important that the main factor which leads to the appearance of infinite amount of ordered structures in our model is two competing forms of adsorption. So, it is the first simple two-dimensional adsorption model with short range non-competing interactions which demonstrates devil's staircase of phase transitions in the ground state. Investigation of phenomenon of Devil's staircase in adsorption systems is in very beginning and requires further comprehensive studies.

Acknowledgments This work was financially supported by Federal program "Scientific and Scientific-Pedagogical Personnel of Innovative Russia in 2009–2013 years" and Analytical departmental target program "Development of Scientific Potential of Higher Education (2009–2011)".

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