

# Bitransitions in molecule reorientation processes in an adsorption layer

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The possibility of pair phase transitions of reorientation (bitransitions) in a system of interacting particles adsorbed at the surface in two different orientations is predicted. The critical conditions for the onset of bitransitions are calculated.

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It is known that the condition for a first-order phase transition is the equality of the chemical potentials of the states between which the transition occurs.<sup>(1)</sup> This equality is achieved at the intersection point of the curves for the dependence of the chemi-

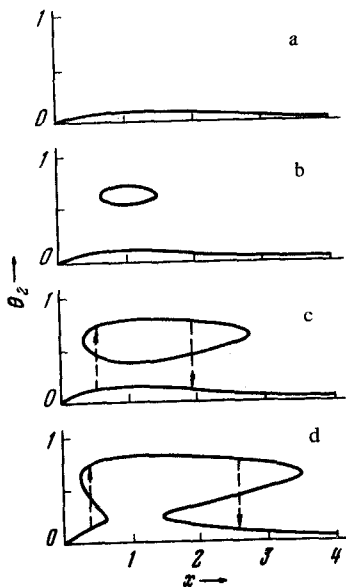


FIG. 1. The  $\theta_2(x)$  relations determined by Eq. (4), and diagrams of the phase transitions:  $m = 2$ ,  $n = 1$ ,  $\alpha = 3.5$ ; a)  $\beta = 5$ ; b)  $\beta = 4.3$ ; c)  $\beta = 3.5$ ; d)  $\beta = 3.1$ .

cal potentials on the thermodynamic variable (temperature, pressure, density). In this letter we report a study of the reorientation of molecules in an adsorption monolayer in which the dependence of the chemical potential on concentration of the particles under certain conditions is a multiply connected function with a loop branch. In this case the first-order phase transitions either are missing or are formed as pairs when appropriate critical conditions are fulfilled.

Let us examine a system of molecules in an adsorption monolayer, such that they can be arranged on the surface in two different orientations with degrees of covering (surface concentrations)  $\theta_1$  and  $\theta_2$  ( $0 < \theta_1 < 1$ ,  $0 < \theta_2 < 1$ , and  $0 < \theta_1 + \theta_2 < 1$ ). The free energy of the system can be calculated by the methods of statistical thermodynamics,<sup>(2,3)</sup> and in the average-field approximation (Bragg-Williams approximation) for a model which takes into account the pairwise interactions between the molecules in each orientation, it is given by

$$F = AT \left[ -\alpha_1 \theta_1^2 - \alpha_2 \theta_2^2 - 2\alpha_{12} \theta_1 \theta_2 + \frac{\theta_1}{n} \ln \frac{\theta_1}{B_1 c} + \frac{\theta_2}{m} \ln \frac{\theta_2}{B_2 c} \right. \\ \left. + (\mathbf{1} - \theta_1 - \theta_2) \ln (\mathbf{1} - \theta_1 - \theta_2) + \theta_1 \frac{n-1}{n} + \theta_2 \frac{m-1}{m} \right]. \quad (1)$$

Here  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_{12}$  are effective dimensionless constants (in units of temperature  $T$ ) of the interaction of molecules in orientation 1 or 2 and of the cross interaction,  $c$  is the volume concentration of the adsorbed molecules,  $B_1$  and  $B_2$  are adsorption-equilibrium constants for the appropriate orientations,  $n$  and  $m$  denote the number of adsorption sites occupied by one molecule in the orientations 1 and 2, respectively, and  $A$  is a

constant equal to the total number of adsorption sites per unit surface area. We can determine from Eq. (1) and from the conditions of thermodynamic equilibrium  $\partial F/\partial\theta_1 = 0$  and  $\partial F/\partial\theta_2 = 0$  the equation of state (adsorption isotherm), which in our problem is given by the set of equations<sup>1</sup>:

$$B_1 c = \frac{\theta_1}{(1 - \theta_1 - \theta_2)^n} \exp(-2\alpha_1 n \theta_1 - 2\alpha_{12} n \theta_2), \quad (2)$$

$$B_2 c = \frac{\theta_2}{(1 - \theta_1 - \theta_2)^m} \exp(-2\alpha_2 m \theta_2 - 2\alpha_{12} m \theta_1). \quad (3)$$

Equations (2) and (3) determine the dependence of the equilibrium degrees of covering  $\theta_1$  and  $\theta_2$  on the volume concentration  $c$ . The functions  $\theta_1(c)$  and  $\theta_2(c)$  in the region of relatively low concentrations are monotonically increasing and single-valued, and become multiple-valued with further increase of  $c$ . We can physically realize the case among the possible solutions of Eqs. (2) and (3) which corresponds to the minimum free energy  $F$ . The transition from one solution branch to another, which occurs spasmodically, is accompanied by a variation of the total number of molecules per unit surface area (two-dimensional condensation) and by a variation of the ratio of the number of molecules in the different orientations (reorientation).

For simplicity, we limit ourselves to the case when only one interaction constant, say  $\alpha_2$ , is nonvanishing, and  $\alpha_{12} = \alpha_1 = 0$ ; moreover, we take  $\alpha_2 > 0$ , which corresponds to effective attraction between the molecules in orientation 2. Thus, Eqs. (2) and (3) reduce to a single equation which determines the  $\theta_2(x)$  dependence, where  $x = B_1 c$ :

$$x = \{1 - \theta_2 - [\beta \theta_2 e^{-2\alpha \theta_2/x}]^{1/m}\} / [\beta \theta_2 e^{-2\alpha \theta_2/x}]^{n/m} \quad (4)$$

Here  $\beta = B_1/B_2$  and  $\alpha = \alpha_2 m$ .

Analysis of Eq. (4) shows that when  $m > n$  and in a certain range of parameters  $\alpha$  and  $\beta$  its solution of  $\theta_2(x)$  has two disconnected branches, which causes a peculiar behavior of the adsorption system as a result of variation of the concentration. Figure 1 shows the calculated  $\theta_2(x)$  dependences for  $m = 2$  and  $n = 1$  for different regions in the plane of the parameters  $\alpha, \ln \beta$  (Fig. 2). For the parameters in region 1 in Fig. 2 the  $\theta_2(x)$  dependence is a single-valued function for all the values of  $x$  (Fig. 1a). In region 2, which is separated from region 1 by the critical curve  $\alpha_1(\ln \beta)$ , and in region 3 the solution of Eq. (4) is described by two branches—a curve with a maximum which starts at the origin and a closed loop-shaped curve above it. In region 4, which is separated from region 3 by the critical curve  $\alpha_{11}(\ln \beta)$ , the  $\theta_2(x)$  dependence has two  $S$ -shaped sections in which two successive first-order phase transitions should occur (Fig. 1d). Region 4 is separated from region 1 by the line  $\alpha = \alpha^* = (3 + \sqrt{8})/2$ , which corresponds to the generation of the  $S$ -shaped sections in the function  $\theta_2(x)$ .

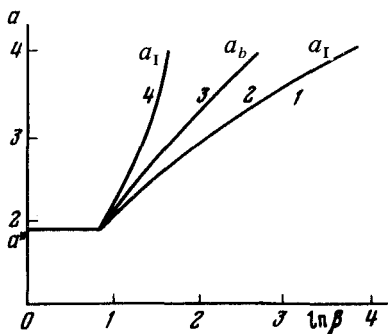


FIG. 2. The plane of the parameters  $a = \ln \beta: \alpha_{11}$ , the critical curve for transition from the loop solution to the solution with two  $S$ -shaped sections;  $a^*$ —the line for disappearance of the  $S$ -shaped sections;  $\alpha_b$ , the critical curve for generation of the bitransitions.

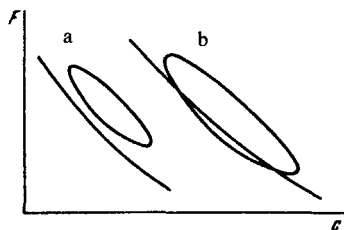


FIG. 3. Diagram for the relative position of the main and the loop-shaped branch of the  $F(c)$  function: a—no crossing and no transitions, b—a crossing and a bitransition occur.

It is clear from topological considerations that when the solution  $\theta_2(x)$  and hence the function  $F(x)$  have a loop-shaped branch (Figs. 1b and 1c), either there are no phase transitions or they appear in pairs. These situations correspond either to nonintersection of the two disconnected branches of the  $F(c)$  function or to their crossing at two points (Fig. 3). The critical condition for the onset of a bitransition<sup>2)</sup> corresponds to the point of tangency of the two disconnected  $\alpha_b$  branches of  $F(c)$ . This condition makes it possible to calculate the critical curve  $\alpha_b(\ln \beta)$  in Fig. 2, which divides regions 2 and 3. In region 2, in which the loop is sufficiently small, the states corresponding to it are metastable and there are no transitions. A bitransition, however, occurs in region 3 (for sufficiently large loops).

It is interesting to note that, although a systematic reorientation of molecules (the  $\theta_1/\theta_2$  ratio varies from large to small values and then back to large values) occurs in each transition that produces a bitransition, the total number of molecules adsorbed per unit surface area (in both orientations) increases as a result of each transition; thus, the two-dimensional condensation in this case has a two-stage nature.

In conclusion, we note that the predicted singularities of the phase transitions of reorientation should also apply to the general case  $\alpha_1 \neq 0$  and  $\alpha_{12} \neq 0$ , if the interaction  $\alpha_2$  is dominant.

<sup>1)</sup>Equations (2) and (3) for the isotherm were obtained for the first time by Parry and Parsons<sup>(4)</sup> by a phenomenological generalization of the Flory-Huggins isotherm.

<sup>2)</sup>Another example of a system in which two branches of the free energy touch is the model of cation disorder in the superionic crystals.<sup>(5)</sup>

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