Monatshefte für Chemie 113, 1263—1268 (1982)

Monatshefte für Chemie
Chemical Monthly

Monolayer Adsorption onto Triangular Lattice

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(Received 12 May 1982. Accepted 2 June 1982)

A simple model of monolayer adsorption on homogeneous solid surfaces of triangular symmetry is presented. This model takes into account the effects of three-fold positional degeneracy of adsorption sites and of partial mobility of adsorbed layer. The model predicts phase transitions in adsorbed layers analogous to those found in experimental systems.

(Keywords: Adsorption, partially mobile; Phase transitions in monolayers)

Einschichtadsorption auf triangularem Gitter

Es wird ein einfaches Modell für die Adsorption einer Schicht auf einer homogenen festen Oberfläche von triangularer Symmetrie präsentiert. Das Modell berücksichtigt den Effekt der dreifachen Positionsdegenierung von Adsorptionsstellen und auch den Einfluß der partiellen Mobilität der adsorbierten Schicht. Das Modell erlaubt die Voraussage von Phasenübergängen in der adsorbierten Schicht, die in Analogie zu experimentellen Systemen stehen.

The experimental realization of two-dimensional phase transitions in monolayers of gases adsorbed on homogeneous surfaces has attracted much interest and has become a field of intensive research[1–8].

From the volumetric measurements of adsorption of simple gases on graphite and boron nitride[1–3] it follows that monolayer films can undergo the phase transitions analogous to the gas—liquid—solid transitions observed in bulk matter, and also other transitions specific to adsorption systems. The properties of the two-dimensional phases are considerably affected by the structure of the solid substrate. Neutron scattering studies have shown that even at low temperature the molecules exhibit a partial mobility[9]. On the other hand, the lattice structure of solid substrate can favour the formation of the registered

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phase[10]. Another interesting property of two-dimensional films is that at a certain temperature, the two-dimensional liquid—solid transition becomes continuous[1,11].

Theory

The hitherto proposed theories of phase transitions in monolayers formed on surfaces of triangular symmetry have been mainly based on the lattice gas approach[12–15]. However, this does not seem to be an adequate approach to adsorption on such solids as graphite and boron nitride. The potential barriers between adsorption sites are rather shallow[16] and the mobility of adsorbed layer should be taken into account. Considering the geometry of the basal plane of graphite and the diameters of adsorbed atoms one can see that adsorption on adjacent hexagones is not possible even for relatively small argon atoms. Therefore, we can consider the graphite lattice as composed of three interpenetrating sublattices[17] as shown in Fig. 1. Therefore, the localized molecules can occupy sites belonging to different sublattices. The fraction of localized molecules adsorbed on a given sublattice depends, however, on the density of the monolayer and temperature. At low densities we expect uniform distribution of localized molecules among the sublattices. When the density of adsorbed layer increases the adsorbed molecules may be forced to shift their positions from one to another sublattice in order to reach a more stable state. Let N_l denote the total number of localized molecules on the surface, and by

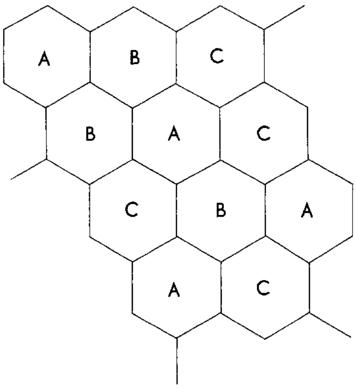

Fig. 1. The division of triangular lattice into three sublattices A, B, and C

N_{lk} $(K = A,B,C)$ we denote the number of localized molecules adsorbed on the K-th sublattice. When the molecules are distributed uniformly among the sublattices then

$$N_{lK} = (1/3) N_l, \; K = A,B,C \tag{1}$$

Now, we introduce the parameters Δ_A, Δ_B, and Δ_C which describe the deviations from the uniform distribution of localized molecules among the sublattices and generalize Eq. (1) writing

$$N_{lK} = (1/3)(N_l + \Delta_K), \; K = A,B,C \tag{2}$$

Only two Δ's are independent as they must satisfy the following condition:

$$\Delta_A + \Delta_B + \Delta_C = 0 \tag{3}$$

For simplicity and clarity of the physical picture we shall assume that the localized molecules are described in the framework of the *Bragg-Williams* approximation.

Next, we assume that besides the localized molecules there also are mobile molecules in the monolayer. If the total number of molecules in the monolayer is N, then the number of mobile ones is $N_m = N - N_l$. These mobile molecules will be assumed to behave as a two-dimensional *van der Waals* gas. Now, let S be a surface area of solid and B denote the number of adsorption sites accessible for localized molecules. Then, the canonical partition function for the monolayer can be written in the following form:

$$Q(N,S,T) = \sum_{N_l=0}^{N} \; \sum_{|\Delta_A + \Delta_B| \leftrightharpoons N_l} \hat{Q}(\Delta_A, \Delta_B, N_l, N, S, T) \tag{4}$$

where

$$\hat{Q}(\Delta_A, \Delta_B, N_l, N,S,T) = \binom{B}{N_l} W(N_l, \Delta_A, \Delta_B)\, q_l^{N_l} q_m^{(N-N_l)} \frac{(S - \beta N)^{(N-N_l)}}{(N-N_l)!}$$

$$\times \exp[R(N, N_l, \Delta_A, \Delta_B, S)] \tag{5}$$

with

$$\binom{B}{N_l} = \frac{B!}{(B-N_l)!\, N_l!},$$

$$W(N_l, \Delta_A, \Delta_B) = \frac{3^{-N_l} N_l!}{[(1/3)(N_l + \Delta_A)]!\,[(1/3)(N_l + \Delta_B)]!\,[(1/3)(N_l - \Delta_A - \Delta_B)]!}$$

and

$$R(N, N_l, \Delta_A, \Delta_B, S) = -\frac{\Psi N^2}{2SkT} - \frac{\Phi}{2BkT} N_l^2 - \frac{\Phi^*}{2BkT}(\Delta_A^2 + \Delta_A \Delta_B + \Delta_B^2)$$

Next, q_l and q_m denote the molecular partition functions for the localized and mobile molecules, respectively, β is the area occupied by a single molecule in the monolayer, whereas the exponential term $R(N, N_l, \Delta_A, \Delta_B, S)$ is related to the attractive interactions in the monolayer. The parameters Ψ, Φ, and Φ^* are determined when the pair potential is specified. For the case of the surface with only two sublattices and for the (6-12) *Lennard-Jones* potential these parameters can be found in Ref.[18].

Applying the maximum term method to the canonical partition function (3), we obtain the following expressions defining the values of N_l, Δ_A, and Δ_B which produce the largest contribution to the sum (3):

$$(\theta_l + \delta_A) = (\theta_l - \delta_A - \delta_B) \exp [D (2\,\delta_A + \delta_B)] \tag{6a}$$

$$(\theta_l + \delta_B) = (\theta_l - \delta_A - \delta_B) \exp [D (2\,\delta_B + \delta_A)] \tag{6b}$$

$$K(T) = \frac{(1-\theta_l)(\theta-\theta_l)}{(1-\theta)\,[(\theta_l+\delta_A)(\theta_l+\delta_B)(\theta_l-\delta_A-\delta_B)]^{1/3}} \exp (\Delta\alpha\,\theta_l) \tag{7}$$

where

$$\theta = N/B,\ \theta_l = N_l/B,\ \delta_K = \Delta_K/B = \Delta_K/B\ (K = A, B) \tag{8}$$

$$K(T) = q_m \beta / q_l,\ D = \Phi^*/kT,\ \Delta\alpha = \Phi/kT \tag{9}$$

Finally, the adsorption isotherm corresponding to our model is obtained by the standard method[19] and takes the form

$$\ln p = \ln K_H(T) + \ln \frac{\theta-\theta_l}{1-\theta} + \frac{\theta-\theta_l}{1-\theta} - \alpha\theta \tag{10}$$

where

$$K_H(T) = (1/q_m \beta) \exp (-\mu^\circ/kT) \tag{11}$$

with μ^0 = the standard chemical potential of bulk phase, and

$$\alpha = \Psi/kT \tag{12}$$

Results and Discussion

A more detailed discussion of the predictions of our model will be given elsewhere. Presently we shall only mention the most interesting properties of the model and concerning the predicted phase transitions in the monolayer. The solution of equations (6) and (7) with respect to θ_l, δ_A, and δ_B gives that when $D < 1$ the monolayer remains disordered, i.e., $\delta_A = \delta_B = 0$, for any $\theta < 1$. Under this condition the model predicts only one first-order phase transition which can be considered as the 2 *D* gas—liquid transition (see Fig. 2*a*). When, however, $D > 1$ we find a

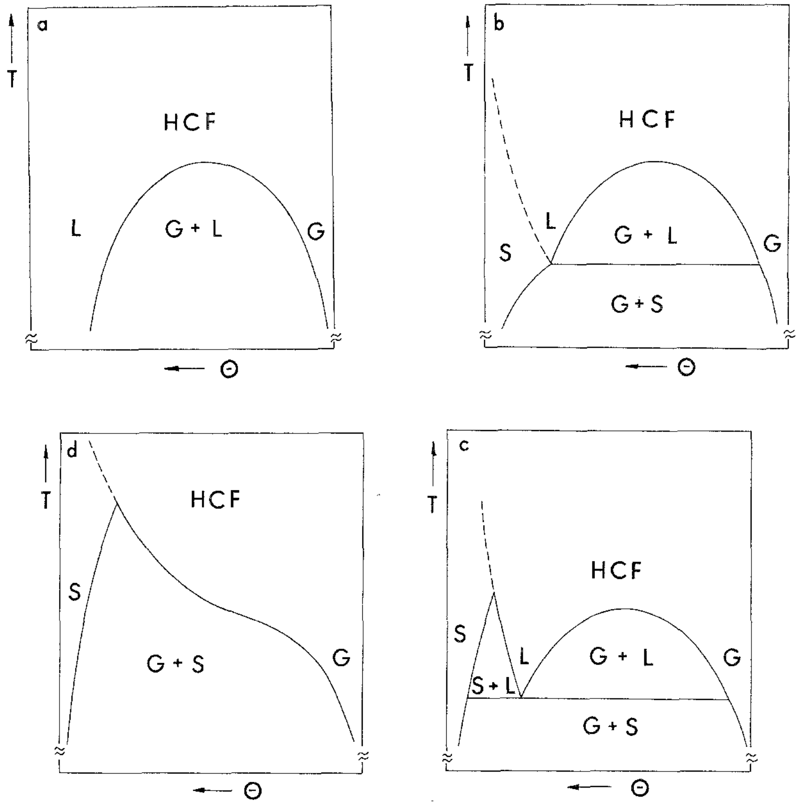

Fig. 2. The possible phase diagrams predicted by the model. The solid lines represent the first-order transitions and the dashed lines represent the continuous transition. The symbols *G*, *L*, *S*, and *HCF* denote a two-dimensional gas, liquid, solid, and hypercritical fluid phase respectively

certain value of $\theta = \hat{\theta}$ that for $\theta > \hat{\theta}$ the ordering of the localized molecules begins and we observe the formation of solid phase being in registry with the solid lattice. This transition, however, can be discontinuous or continuous depending on the particular values of D, $\Delta\alpha$, and $K(T)$. Besides, the order of this transition depends on the temperature as shown in Figs. 2*b* and 2*c*. These figures also show that for $D > 1$ we have a sequence of the phase transitions: gas—solid, gas—liquid and liquid—solid. Still another situation can be obtained when D becomes high enough and provided that $K(T)$ is low (see Fig. 2*d*). In this case, the ordering of the adsorbed layer starts at low coverages and the monolayer is localized to a high degree [small $K(T)$[20]]. It is noteworthy that the phase diagrams shown in Fig. 2 have all been found in experimental systems[1,21,22].

Concluding this communication we would like to emphasize that the above discussion gives only a qualitative picture of the most striking properties of our model. The calculations performed for a very similar model based on the assumption that the lattice is composed of two sublattices have shown[18,23] that the model predicts the dependence of 2 *D* critical and triple point temperatures on the dimensional incompatibility between adsorbent and adsorbate being in qualitative agreement with experimental data.

Of special interest is the appearance of the continuous transition in our model. This is analogous to the transition found in the spin-1 lattice gas model[24]. That the transition is of higher order results from the fact that the mechanism of this transition is mainly orientational as it begins at densities where the monolayer is already closely packed. Besides, symmetry considerations similar to the ones presented by *Lajzerowicz* and *Sivardiere*[24] lead to the conclusion that the odd order terms in the free energy expansion vanish what is a necessary condition for the continuous transition to occur.

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