

# Diffusion and phase transitions in films on crystal surfaces

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The diffusion of submonolayer films along crystal surfaces is studied theoretically. An explanation is given of experiments in which peculiar features were discovered in the behavior of the diffusion coefficient at concentrations corresponding to phase boundaries on the phase diagrams of multiphase films.

1. Although diffusion processes in solids have been rather well investigated experimentally and theoretically, new experiments studying the diffusion of atoms on metal surfaces<sup>1–3</sup> have directed attention again toward the unusual behavior of the diffusion coefficient for certain concentrations of surface atoms. In Refs. 1 and 2 the diffusion of submonolayer barium films on (110) molybdenum crystallites was investigated, and a strong correlation was observed between the behavior of the diffusion coefficient  $D$  and the surface structure of the film. In particular, near a phase transition for concentrations of surface atoms from  $C = 0.6$  in the  $C(2 \times 2)$  commensurate structure to the incommensurate structure ( $C > 0.6$ ) a sharply pronounced plateau is seen in the concentration profile of the film's atomic distribution. This corresponds to a strong enhancement ( $10^3$  to  $10^5$  times) of the diffusion coefficient  $D(C)$  in a narrow concentration interval.

In Ref. 3 the diffusion of gold films on the surfaces of (111) silicon crystallites was studied. A correlation was also noted between structural phase transitions and the magnitude of the diffusion coefficient, although the form of the correlation had a completely different character. For concentrations corresponding to boundaries between two surface phases (for instance,  $\sqrt{3} \times \sqrt{3}$  and  $5 \times 1$ , or  $7 \times 7$ ), the diffusional motion of the film edge was halted, and resumed only at the annealing temperature of the film. A fairly detailed review of work related to diffusion on the surfaces of semiconducting crystals can be found in Ref. 4.

The exactly opposite behavior of the diffusion coefficients at phase transitions in the two cases (a sharp increase in  $D$  in the first and a decrease to zero in the second) is connected, evidently, not with the different specific adsorption systems, but with the nature of the phase transition. The transition to the incommensurate phase proceeds continuously, while the structural transitions between surface phases of gold on (111) silicon are first-order (in the experiment, the region of two-phase coexistence is sharply fixed).

The anomalous behavior of the kinetic coefficients in the case of a continuous phase transition in three-dimensional systems has been quite well studied experimentally and theoretically (see, for example, Ref. 5). In particular, the critical behavior of the thermal conductivity coefficient of helium has been investigated at the transition to the superfluid phase. Its magnitude increases anomalously at the transition point  $T_c$ , and for  $\tau = T - T_c \rightarrow 0$  it is well described by a  $\kappa \propto \tau^{-1/3}$  dependence. Analogous behavior of both the mobility and the diffusion coefficient is seen at the critical point of the liquid-vapor transition.<sup>6</sup> In both cases the anomalous behavior of the kinetic coefficients is explained by saying that the coefficient in question is linked to

a critical mode; that is, is described by the relaxation of the order parameter of the system near the phase transition point. This property of the kinetic coefficients connected with a critical mode of the phase transition is, evidently, a general property of continuous phase transitions<sup>5,6</sup> and in this sense the transition to the incommensurate state is not an exception. The essential point is that for such a transition the order parameter is the soliton concentration, and consequently, coincides with the change in the concentration of atoms in the incommensurate phase, the diffusion coefficient describes the relaxation of the order parameter. Thus we expect its sharp increase in the vicinity of the transition point. In fact, as was shown in Ref. 7, such an increase can be linked to the formation in the film of lines of solitons, which in the incommensurate phase display a high mobility.

However, such an explanation does not include the peculiarities of behavior in diffusion coefficient connected with the fact that, along with the purely kinetic component (that is, mobility) it contains a "thermodynamic" part, equal to the derivative of the chemical potential with respect to concentration. We will see that, in contrast to the kinetic part, the thermodynamic part of the diffusion coefficient at the transition point in the incommensurate state goes to zero and limits the rapid rise in the diffusion coefficient.

In this work we show that the situation for second-order transitions can lead to the opposite case when the diffusion is not linked to the relaxation of a critical mode (that is, the concentration does not coincide with the order parameter). In this case there are no special reasons for an increased mobility at the transition point, although the renormalization of the thermodynamic part of the diffusion coefficient at the transition point can lead to its anomalous growth, which can be described by the corresponding critical index.

For first-order transitions the approach developed leads to a natural explanation for the observed vanishing of the diffusion coefficient.

In conclusion, it is shown that all the arguments can be transferred without difficulty to diffusion processes in the bulk in solids (for example, in alloys), which raises the possibility of seeing analogous phenomena in bulk samples.

2. To describe a continuous phase transition in the framework of the Landau theory, in the simplest case it is sufficient to study a system described by a scalar order parameter  $\eta$ . To study the phase change arising at a fixed temperature as the concentration  $n = N/V$  is changed it is convenient to look at the free energy functional  $F(V, T, N, \eta)$ , where  $V$  is the system volume and  $N$  the number of atoms in the system. We will assume that the order parameter  $\eta$  is not the independent variable thermodynamic density,  $n$ . If we

introduce the functional density  $f(T, n, \eta)$ :  $F = \int f dV$ , and the corresponding differential  $df = -s dT + \mu dn$  ( $s$  is the entropy per unit volume,  $\mu$  the chemical potential), it is not difficult to establish the dependence of chemical potential on concentration:

$$\mu = (\partial f / \partial n)_{T=\text{const}}. \quad (1)$$

The Landau expression for  $f(n, T, \eta)$  in the vicinity of the transition has the form

$$f = f_0(n, T) + A(n, T)\eta^2 + B(n, T)\eta^4 + \dots, \quad (2)$$

with

$$A(n, T) = a(T - T_c(n)) = a_1(n - n_c(T)).$$

We will further assume that the system is far from the "critical" point, where  $\partial T_c / \partial n_c = 0$ , so that the quantities  $a$  and  $a_1$  are connected by the relation  $a_1 = a \partial T_c / \partial n_c$ ; the derivative runs along the phase transition curve  $T_c(n_c)$ .

The condition of the functional minimum  $\partial f / \partial \eta = 0$  determines the value of the order parameter  $\eta^2 = a_1(n_c - n) / 2B$ , from which we can at once establish the dependence of  $\mu$  on  $n$  (see Eq. 1):

$$\mu = \left( \frac{\partial f}{\partial n} \right)_T = \mu_0 - \frac{a_1^2}{2B}(n - n_c). \quad (3)$$

The result allows us to reach several conclusions regarding the dependence of the diffusion coefficient on  $n$ . The diffusion current  $j$  arises as the result of the presence of a gradient in the chemical potential (see, for example, Ref. 8),  $j = -bn \nabla \mu$  ( $b$  is the mobility). Taking into account the  $\mu(n)$  dependence, it is not difficult to rewrite this expression in the form

$$j = -bn(\partial \mu / \partial n)_T \nabla n = -nD \nabla n. \quad (4)$$

Thus substituting in the definition of  $D$  the relation (3), we get

$$D = b \left( \frac{\partial \mu}{\partial n} \right)_T = b \left( \frac{\partial \mu_0}{\partial n} \right)_T - \frac{a_1^2}{2B} = D_0 - \Delta D, \quad (5)$$

where  $D_0$  is the value of the diffusion coefficient in the symmetric phase, and  $\Delta D$  is the discontinuity in the diffusion coefficient for the transition to the nonsymmetric phase.

Thus, within the Landau theory, we get a variation in  $D$  to its final value by means of a discontinuity at the phase transition boundary. Experimentally, such behavior should appear as a variation in the angle of deviation in the atomic distribution profile as a function of separation,  $n(x)$ .

However, up till now we have not taken account of the fluctuation region of the phase transition, in which application of the Landau theory is not justified and the behavior of the coefficient can vary substantially. The extent of the fluctuation region, determined by the Ginzburg criterion (see, for instance, Ref. 9), depends on the system parameters and often occupies a rather wide interval (in temperature or concentration), marked in experiment by a characteristic "lambda-type" singularity (or anomaly) in the second derivatives of the thermodynamic potentials (for example, the specific heat). The diffusion coefficient  $D$ , containing the second derivative of the free energy with concentration, is no exception to this.

To determine the critical index  $\Delta$  which defines the character of the diffusion coefficient anomaly near the phase transition line,

$$D \propto |n - n_c|^{-\Delta}, \quad (6)$$

we use the scale invariance hypothesis, written in the form

$$f \propto \xi^{-d}. \quad (7)$$

Here  $\xi$  is the system correlation radius,  $d$  is the dimensionality ( $d = 2$  or  $3$ ),

$$\xi \propto |T - T_c|^{-\nu} \propto |n - n_c|^{-\nu} \quad (8)$$

since

$$T - T_c \approx \frac{\partial T_c(n_c)}{\partial n_c}(n - n_c).$$

As a result we have for the diffusion coefficient

$$D \propto (\partial^2 f / \partial n^2)_T \propto |n - n_c|^{\nu d - 2}, \quad (9)$$

i.e., we have  $\Delta = -\nu d + 2$ , coinciding with the critical index  $\alpha$  for the dependence of the specific heat on  $|T - T_c|$ .

We consider now the fact that the index  $\alpha$ , measured for a fixed film concentration, can differ (even in sign) from the quantity  $\alpha'$  measured for a fixed chemical potential. According to the sign of the index  $\alpha$  the thermodynamic part of the diffusion coefficient vanishes or diverges in the fluctuation region of the phase transition.<sup>10</sup>

Experiments on the measured specific heat of adsorbed monolayers for second-order transitions have recorded different possible forms for the index  $\alpha$ .<sup>11-15</sup> In particular, in the experiment of Ref. 11 on disorder in helium films on graphite, carried out for various fixed adatom concentrations, intervals were detected on the continuous phase transition curve characterized by both negative and positive values of the specific-heat critical index  $\alpha$ . We note that in bulk systems measured specific heats also show various possible signs of the critical index (see, for example, Ref. 16).

According to our ideas, just such adsorbed systems, characterized for fixed concentration by positive values of the specific-heat critical index ( $\alpha > 0$ ), permit the observation of anomalous growth of the diffusion coefficient, leading to plateau formation in the concentration profile  $n(x)$ . In the opposite case; when  $\Delta = \alpha < 0$  and the diffusion coefficient vanishes at the transition point, a step should be seen in the concentration profile.

From the form of the plateau or step in  $n(x)$  in experiment, it is not difficult to obtain the value of the index  $\Delta$ . In fact, solving the diffusion equation in the case of a planar diffusion front,

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x} \left( D(n) \frac{\partial n}{\partial x} \right)$$

in quasistationary conditions (easy to produce due to the slow diffusion process, which holds the concentrations constant at the film extremities) for a narrow region in the vicinity of  $n_c$  where the  $D \propto |n - n_c|^{-\Delta}$  dependence is valid, it is easy to find the following dependence of  $n$  on  $x$ :

$$\ln |n - n_c| = \text{const} + (1 - \Delta)^{-1} \ln |x|, \quad (10)$$

The coordinate  $x$  is measured from the kink of the plateau or step where  $n = n_c$ .

We cannot completely exclude the possibility that peculiarities may arise in the kinetic part  $b$  of the diffusion coefficient near the transition point (see Eq. 5), which can alter the value found for the index  $\Delta$ . However, for the case studied so far, in which the diffusion mode describing the concentration relaxation is not critical, there are no special reasons for an anomalous increase in the mobility  $b$ . As was shown above, such an increase in the kinetic coefficient usually occurs as a result of dynamic renormalization in the neighborhood of the phase transition in the case when the concentration scales with the order parameter and the diffusion mode is critical.

Just such a situation occurs in the case of a phase transition in the incommensurate state. As shown in Ref. 7, the sharp increase in the diffusion coefficient in the neighborhood of a phase transition can be explained by the high mobility of soliton lines that arise in the incommensurate phase. We will show that consideration of the thermodynamic part of the diffusion coefficient in the vicinity of the phase transition complicates the picture resulting from analyzing only the kinetic properties of the system.

We introduce the parameter  $\delta$  to express the degree of incommensurability  $\delta = (a - b)/b \ll 1$  of the film, where  $a$  and  $b$  are the periods of the film and of the substrate in the direction of incommensurability (see, for instance, Ref. 17). The concentration  $k$  of soliton lines in the incommensurate film is proportional to the variation in adatom concentration  $n - n_c$  and can be expressed in terms of  $\delta$  by the relationship

$$k \propto n - n_c \propto (\delta - \delta_c)^{1/2}. \quad (11)$$

The free energy of the system is expressed in terms of the concentration of soliton lines in the neighborhood of the phase transition by the relation (see Ref. 17)  $f = \varepsilon k + ck^3$ , where  $\varepsilon \propto (\delta - \delta_c)$  is the energy density per unit length of a soliton line, and the second term in the energy is connected with the system entropy increase due to kinks in the soliton lines. Using Eq. 11, it is not difficult to find that

$$f \propto (n - n_c)^3, \quad (12)$$

from which we can at once determine the behavior of the thermodynamic part of the diffusion coefficient;

$$D \propto \partial^2 f / \partial n^2 \propto (n - n_c) \xrightarrow{n \rightarrow n_c} 0, \quad (13)$$

that is, the critical index  $\Delta = -1$ . In experiments<sup>1,2</sup> the diffusion coefficient is seen to increase sharply, rather than vanishing; this, obviously, means that a strong dynamic renormalization of the kinetic part takes place, with a positive critical index exceeding one.

To conclude this section on the behavior of the diffusion coefficient in continuous phase changes, we note that at present there is a large number of adsorbed systems in which such a transition is observed. Apart from the systems already mentioned, disordered films of krypton forming a  $\sqrt{3} \times \sqrt{3}$  structure on a graphite substrate,<sup>18</sup> oxygen films forming a  $p(2 \times 2)$  structure on nickel (111),<sup>19</sup> hydrogen on iron (110) surfaces,<sup>20</sup> and many other adsorbed systems have been quite well studied. Investigation of diffusion of such films on crystal surfaces could confirm or disprove the discussion above regarding the dependence of the diffusion coefficient. One must bear in mind that the fluctuation region of some of these systems may be too narrow, since in

experiments only the final jump in the diffusion coefficient will be seen (in accordance with Eq. 5).

3. We now turn to the question of the behavior of the diffusion coefficient near a first-order phase transition. As we said above, such a situation arises in studying the diffusion of gold on silicon (111) surfaces.<sup>3</sup> Here, diffusion is observed to stop when a concentration is reached on the diffusion front corresponding to that for the coexistence boundary of two different surface phases for the given temperature. To explain this phenomenon we investigate how the free energy functional depends on concentration near a first-order phase transition. This functional has the form of a double-well curve, the minima of which correspond to the concentrations  $n_1$  and  $n_2$  of the two phases. At the point of phase equality the chemical potentials of the two phases are equal,  $\mu_1 = \mu_2$ . For a concentration change from  $n_1$  to  $n_2$  the film consists of a two-phase mixture with equal chemical potentials; as  $n$  is increased islets of the new phase grow in area and the transition is completed at the concentration  $n_2$ . Thus, in the concentration interval from  $n_1$  to  $n_2$  the system has the chemical potential  $\mu_0 = \mu_1 = \mu_2$ , which means that

$$D \propto (\partial \mu / \partial n)_T = 0. \quad (14)$$

We emphasize that in this case the issue in question is the effective coefficient characterizing the diffusional motion of the film boundary. The actual coefficient characterizing diffusional motion of the particles in each of the equilibrium phases remains at its final value.

Schematically, the system behavior is described by the diagrams in Fig. 1. We see that when the diffusion front reaches the concentration  $n_1$  (for fixed temperature) its movement ceases. For a variation  $\Delta T$  in film temperature the system will leave the state of two-phase thermodynamic equilibrium, so that  $\mu_1$  will be less than  $\mu_2$ . In the intermediate concentration region from  $n_1$  to  $n_2$ , corresponding to a two-phase mixture, the chemical potential grows linearly from  $\mu_1$  to  $\mu_2$ :

$$\mu(n) = \mu_1 + (\mu_2 - \mu_1)(n - n_1)/(n_2 - n_1), \quad (15)$$

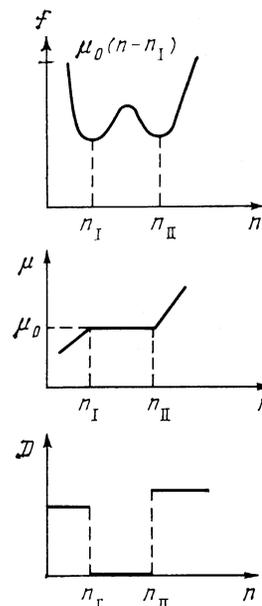


FIG. 1.

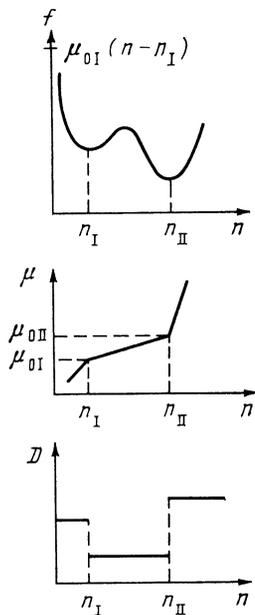


FIG. 2.

which is schematically depicted in Fig. 2.

For a small deviation  $\Delta T$  of the temperature from  $T_0$

$$\mu_1 \approx \mu_0 + \Delta T (\partial \mu_1 / \partial T) = \mu_0 + \Delta T s_1,$$

$$\mu_2 \approx \mu_0 + \Delta T (\partial \mu_2 / \partial T) = \mu_0 + \Delta T s_2,$$

so that

$$\mu_2 - \mu_1 \approx \Delta T (s_2 - s_1) = \Delta T Q / T, \quad (16)$$

where  $Q$  is the heat of transition.

Therefore, the dependence of the diffusion coefficient  $D'$  in the region of phase coexistence on  $\Delta T$  can be expressed as

$$D' \propto \frac{\partial \mu}{\partial n} = \frac{\Delta T}{T_0} \frac{Q}{n_2 - n_1},$$

which can be measured experimentally via the variation in angle of deviation of the concentration profile  $n(x)$  as a function of  $\Delta T$  and  $Q$ . As  $D'$  decreases the two-phase coexistence region occupies less area in the atomic surface distribution, and in the limit  $D' \rightarrow 0$  (throughout which  $D'$  has a finite value) a step should be evident in the concentration profile  $n(x)$ . In fact, under conditions of coexistence there is a non-zero diffusion current  $j = -nD'(\partial n / \partial x) \neq 0$  since  $D' \rightarrow 0$  as  $\partial n / \partial x \rightarrow \infty$ ; that is,  $n(x)$  jumps from  $n_1$  to  $n_2$ . It is possible that just such behavior has been observed for the diffusion of indium on a silicon (111) surface.<sup>4</sup>

We note that all the discussion carried out above on surface diffusion can be generalized to the case of diffusion of defects in the solid crystal. If, on the phase diagram showing the system state as a function of temperature and defect components, there are first-order or second-order phase transition lines, one should see the diffusion coefficient vanish or go to infinity at the corresponding concentrations. Such experiments are complicated by the difficulty of observing the diffusion front in the solid; however, they have been carried out. In Ref. 21 the propagation of the diffusion front of sodium in the crystal bulk in  $\alpha\text{-Al}_2\text{O}_3$  was observed. In these measurements the regions of sharp maxima and minima of

the diffusion coefficient  $D$  were very distinct; the authors note the correlation between the minima of  $D$  and the conversion between bulk phases of  $\text{Na}_2 \cdot 0.1 \text{Al}_2\text{O}_3$  and  $\text{Na}_2 \cdot 0.5 \text{Al}_2\text{O}_3$  for corresponding concentrations. It goes without saying that further investigations in this direction would be of great interest.

In conclusion, we will formulate the basic results of our work.

1. The observed experimental results on the anomalies of behavior of the diffusion front of adsorbed films (characterized by the vanishing of the diffusion coefficient) are explained for concentrations corresponding, on the equilibrium phase diagram, to a first-order transition.

2. For the case of a second-order phase transition anomalous behavior of the diffusion coefficient is discovered, characterized by a critical index coinciding with the critical index of the specific heat. Adsorption systems are indicated for which observation of a plateau in the concentration profile may be seen, in connection with the growth of the diffusion coefficient.

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