



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Physica A 357 (2005) 189–215

PHYSICA A

www.elsevier.com/locate/physa

Collective surface diffusion: An experimentalist's view

A.G. Naumovets*

Institute of Physics, National Academy of Sciences of Ukraine, 46 Prospect Nauki, Kiev UA-03028, Ukraine

Available online 11 July 2005

Abstract

Surface diffusion (SD) is a really ubiquitous phenomenon playing a highly important part in a wealth of natural and technological processes. The effect of SD is to move surface atoms, molecules and clusters and allow them to assemble into some desirable configurations or, vice versa, to destroy the configurations that have been purposely created. Growth of crystals and thin films; catalysis; sintering and powder metallurgy; capillary phenomena; corrosion; nanotechnologies of all kinds; strengthening of materials; soldering; a multitude of processes that occur on various biological interfaces, etc.— this is an incomplete list of scientific and practical areas where SD can be a rate-controlling stage. SD has much in common with volume diffusion from the point of view of the mathematical description, but at the same time some important differences between them are connected with the lower dimensionality of SD and the peculiarities of surface interactions. This review presents an introduction to experimental techniques used in SD investigations and to some theoretical challenges which arise in the interpretation of experimental results on SD. It is stressed that SD is basically a many-body (collective) phenomenon. Even in the case when one observes random walks of an individual atom, their kinetics depends on the interaction of the adatom with substrate atoms, concerted motions of the atoms, lattice dynamics, and energy exchange and dissipation. At low adatom concentrations, the lateral (interadatom) interactions can result in formation of clusters, which demonstrate an amazing diversity of SD mechanisms and substantially affect the kinetics. At dense (approaching a monolayer) coverages, the lateral interactions give rise to formation of various two-dimensional adatom structures in the SD zone. Actually, there occurs a self-organization of this zone: it represents a (nonequilibrium) phase portrait of the adsorbed layer. The adsorbate phases that provide fast SD occupy major areas in the SD zone.

*Tel.: + 380 44 265 09 27; fax: + 380 44 265 15 89.

E-mail address: naumov@iop.kiev.ua.

Surface diffusion is of the utmost importance in nano-objects and nanostructures, where its role may be either useful or adverse. An intriguing challenge are nonlinear processes in SD. The mechanisms of SD of large organic molecules in chemistry and biology also call for much more attention both from theoreticians and experimentalists.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Surface diffusion; Surface phase transitions; Self-organization; Adatoms; Clusters; Solitons

1. Introduction

In 2005, the diffusion community commemorates the anniversaries of two milestone achievements in the diffusion studies. One hundred and fifty years ago, A. Fick derived his classic diffusion equations. In 1905, Einstein [1] gave the statistical interpretation of diffusion interrelating the mean-square displacement of randomly walking particles, the time and the diffusion coefficient (diffusivity). Despite such a long history behind itself, diffusion still attracts much interest in all natural sciences. This omnipresent phenomenon remains in many points enigmatic and provides its researchers with an inspiring (although not an easy) job. The scientific history of surface diffusion, an important subarea of diffusion in general, is somewhat shorter (dating back to 1921 [2]), but encompasses already the activity of several generations of surfacists.

The aim of this article is to present, using some representative examples, a concise overview of experimental situation in surface diffusion (SD), especially in the investigations of collective effects in SD. As we shall see, this is a very important aspect of SD.

This review is organized as follows. In Section 2 we present some introductory arguments testifying the basically many-body nature of surface diffusion. Section 3 contains information on the main types of lateral interactions on surfaces. Section 4 is dedicated to a brief review of experimental techniques used in SD investigations. Diffusion coefficients and other parameters characterizing SD kinetics are discussed in Section 5. The correlation between SD kinetics and surface phase transitions is considered in Section 6. In Section 7 we discuss the processes of self-organization of SD zone, and Section 8 contains conclusions.

2. Many-body nature of surface diffusion

The main reason why diffusion, including surface diffusion, is a physically rich and intricate phenomenon, is its many-body (collective) nature. Let us hereafter concentrate on SD, which is our topic in this article.

Even in the case when we are able to trace the walks of a single surface atom, we should realize that its jumps occur in its continuous interaction with substrate atoms (Fig. 1). First, the atom receives fluctuatively some excessive energy from the substrate. This enables it to jump from one residence site to another. Second, the

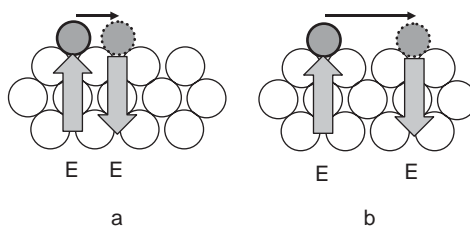


Fig. 1. Elementary (a) and “long” (b) jumps of an adsorbed atom (shadowed) on a substrate. E is an excess energy which the adatom receives and then gives back to the substrate.

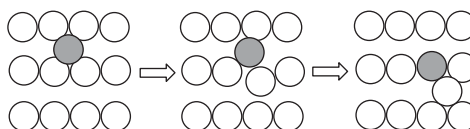


Fig. 2. A model of the exchange mechanism of surface diffusion. Adsorbed atom is shadowed.

jump ends as soon as the excessive energy is given back from the diffusing particle to the substrate (the heat bath). Besides, the potential barrier between the two sites can be substantially lowered if the jump occurs in a concerted motion with the adjacent substrate atoms. For example, in the exchange SD mechanism (Fig. 2), a number of atoms is displaced at a time [3].

Actually, the many-body character of SD is reflected in the very fact that it is meaningless to speak about SD parameters of some atoms or molecules. We always specify the diffusing particles *and* the substrate. The SD parameters depend both on the nature of the diffusing particle and on the substrate chemical nature (electronic structure), its atomic structure and dynamic properties. In other words, one always deals with *a system including a number of interacting particles*.

When we trace the random walks of a single diffusing atom, we have only to consider its interaction with an ensemble of substrate atoms. In the case of non-zero concentrations of the diffusing (adsorbed) particles, the interactions between them (lateral interactions) come into play. This makes the treatment of the diffusion even more complicated.

For brevity, in parallel with the absolute adatom (adsorbed atom) concentration n , we shall also use a relative adatom concentration θ defined as $\theta = n/n_s$, where n_s is the concentration of the substrate surface atoms. The value θ is commonly called *the coverage degree* (or simply *the coverage*). Thus, at low coverages (with respect to the full monolayer), one usually observes the coexistence of single atoms with clusters of various kinds. They migrate over the surface by manifold mechanisms which will be discussed in Section 6. Such dilute layers represent lattice gases, because most of the time the single atoms and clusters reside at the adsorption sites determined by the substrate potential relief.

As the coverage grows, transitions occur to denser (condensed) adsorbate phases. The phase diagrams of adsorbed layers are generally quite intricate

(see e.g. Refs. [4–7]), which results from the superposition of substrate potential relief and lateral interactions of adatoms. Let us consider this point in more detail.

3. Lateral interactions between adsorbed particles

Lateral interactions at surfaces have diverse physical origins [8–10]. One discerns the van der Waals, direct exchange, indirect (substrate-mediated) exchange and electrostatic (dipole–dipole and higher multipole) interactions. These interactions have different intensities, decay with distance more or less sharply and either monotonically or in an oscillating way, can be attractive or repulsive, and isotropic or anisotropic. Of course, the relative role of particular contributions depends on the nature of the adsorbate and the substrate.

Let us recall that the van der Waals interaction is attractive and its energy decreases with distance as r^{-6} . The exchange interaction caused by the direct overlap of electronic shells of adsorbed atoms diminishes with distance exponentially. The characteristics of the indirect (substrate-mediated) exchange interaction are much more diverse. The adatoms can exchange various kinds of quasiparticles excited in the substrate. The most intense interaction of this type is predicted to stem from the electronic exchange. Thus its parameters are determined by the electronic structure of the substrate in particular by its Fermi surface [11].

The energy of electronic indirect interaction oscillates with distance as the wave functions of interacting adatoms overlap in phase or antiphase (Fig. 3). The period of the oscillations is determined by k_F^{-1} , where k_F is the Fermi momentum of electrons (we consider here the case of a metal substrate). The amplitude of the oscillations falls with distance as $r^{-\alpha}$, where α ranges from 1 to 5 depending on the curvature of the Fermi surface normal to the axis connecting the two adatoms. This means that the indirect electronic interaction is generally anisotropic with the exception of the case when the Fermi surface can be approximated as a sphere. The slowest decay of the indirect interaction energy ($\propto r^{-1}$) occurs along the axes that are normal to flattened areas of the Fermi surface.

An important kind of the indirect interaction is connected with elastic strains induced in the substrate by the adsorbed layer. The strains arise due to lattice misfit between the substrate and the adlayer. This long-range interaction is believed to be responsible for the mesoscopic structural self-organization of thin films growing by the Stranski–Krastanov mechanism [12]. It is also important to note that surface strains can substantially affect the kinetics of surface diffusion [13].

Another kind of the long-range lateral interaction has an electrostatic origin. The adsorption bonds have generally a polar (partially ionic) character. The charge distribution around an adatom can be rather complex, depending on the geometry of the adsorption site and the chemical nature (electronic structure) of interacting adatom and substrate atoms. This charge distribution can be decomposed into a series of multipoles. The dipole–dipole interaction, which arises because the adsorption bond may have a considerable dipole moment, decays with distance rather slowly ($\propto r^{-3}$) (Fig. 3) and plays an important role in many surface

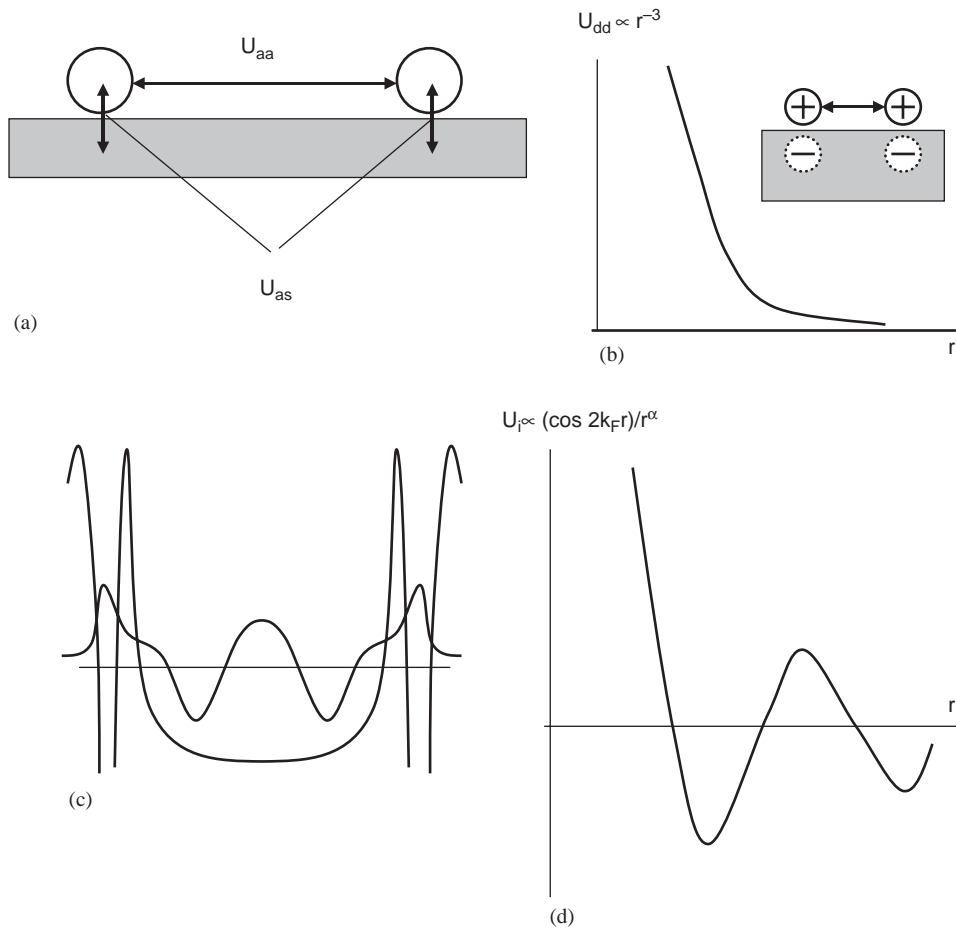


Fig. 3. Interactions of adatoms on a surface. (a) Interaction with the substrate (U_{as}) and lateral interaction (U_{aa}); (b) the dipole–dipole interaction as a function of distance; (c) schematic of the overlap of adatom wave functions in the indirect exchange interaction mediated by the substrate; (d) energy of the indirect exchange interaction as a function of distance (a case when $\alpha = 1$ is illustrated).

phenomena [4,6]. Of course, adsorbed molecules may possess permanent dipole moments, which also contribute to the dipole–dipole interaction. It is important to note that the dipole–dipole interaction of adatoms in one-component adsorbed layers is generally repulsive, because the dipoles have the same orientation. However, this interaction may turn to attractive at some critical coverage due to strong mutual depolarization of the adatoms [14] (Fig. 4).

The contact electrostatic fields that exist over the surface areas having different work functions can also be a driving force for the mesoscopic self-organization of the adlayer: the coverage may become nonuniform with some mesoscopic periodicity

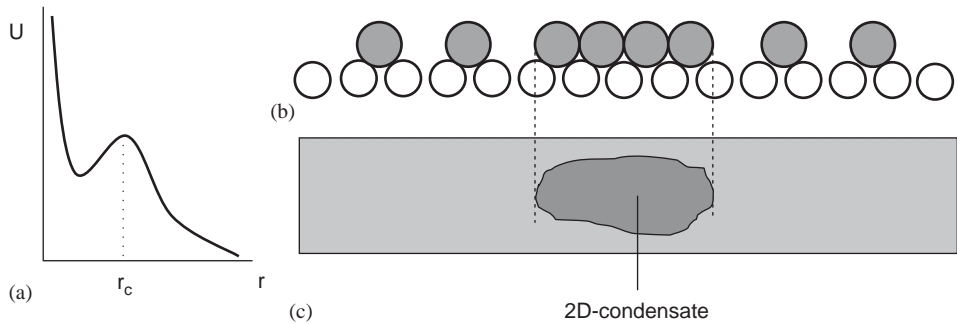


Fig. 4. First-order phase transition caused by mutual depolarization of adatoms. (a) Variation of the repulsive energy in the case of strong depolarization (r_c is a critical interadatom distance); (b) formation of the condensed phase on the background of the dilute phase; (c) top view on the two-phase adlayer.

[15]. The formation of a “patchy” adlayer reduces the energy of the contact electric fields in comparison with the case of a homogeneous layer.

This brief survey of interactions at surfaces makes it obvious that kinetics of SD must strongly depend on coverage. Variation of SD parameters should correlate with phase transitions that occur on surfaces, since these transitions are also determined by surface interactions, and the atomic structure as well as other properties of emerging surface phases affect the diffusion mechanisms.

The following conclusions can be drawn from the above considerations:

- (i) SD is basically a many-body process.
- (ii) The kinetics of SD cannot be understood without proper account for interactions between the diffusing particles.
- (iii) SD should be investigated in connection with surface phase transitions.

4. Experimental methods

For reasons of space, we shall restrict our survey of experimental techniques used in SD studies to giving a general idea about the kind of evidence provided by various methods. Technical details can be found in original works and earlier comprehensive reviews on this subject (see e.g. Refs. [16–23]) as well as in recent conference proceedings [24–26].

Existing techniques that detect SD processes can be grouped into two main categories. In the first of them experimentalists observe the processes of *equilibration* realized via surface diffusion in various nonequilibrium systems (nonequilibrium methods). In the second category of the methods, the systems are in equilibrium. There is no net mass transport on the macroscopic scale in this case, but the particles perform *thermal fluctuations around the equilibrium state*. These fluctuations are the source of information about the mobility of the particles in such “equilibrium methods”.

It is understood that each class of the methods gives evidence on particle mobilities in conditions that can be substantially different. This generally results in difference of the values of the diffusion parameters extracted from the equilibrium and nonequilibrium measurements. This point will be discussed in Section 5. But first let us consider a few examples of techniques belonging to the two classes.

4.1. Nonequilibrium methods

The task of such experiments is to record the kinetics of the transition, executed by surface diffusion, from a nonequilibrium state of the object to the equilibrium one.

Consider the case of surface self-diffusion, i.e., the situation when atoms diffuse over the surface of the same chemical nature. A typical example is the change of the shape of a crystal observed under annealing. Suppose the annealing temperature is low enough to preclude evaporation of the crystal and volume diffusion within it. Then the equilibration, i.e., the minimization of the surface free energy by a shape change, is attained through surface self-diffusion only. For instance, any sharp tip is getting blunter under annealing. Such experiments can be carried out with atomic resolution by field ion microscopy. Another possibility is to make a groove (or a system of grooves) on an initially flat surface and then to follow their healing up as the sample is heated. This process can be monitored, e.g. by electron microscopy or optical interferometry. The disadvantage of such methods is that their results relate to the surfaces whose atomic structure is changing during the experiment.

The nonequilibrium methods developed to investigate surface diffusion of adsorbates use one or another physical quantity sensitive to adparticle concentration (coverage) on the surface. The measurement of this quantity with an appropriate spatial resolution allows recording the time variation of the adsorbate surface distribution (coverage profile) as the adsorbed layer evolves from a nonequilibrium initial state to its equilibrium final state (Fig. 5). The process of evolution of the coverage profiles can be followed by scanning the surface with such probes as electron, ion and light beams, or a tip in various scanning probe microscopies [17,18,20,22–24,27–29]. The field emission and photoemission microscopies also are successfully employed to display the adsorbate distributions on the substrates

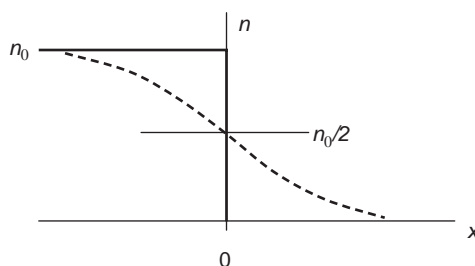


Fig. 5. Concentration profile (dashed line) in the case of diffusion of noninteracting particles from a step-like initial deposit.

[18,30]. Except for field-ion and scanning tunneling microscopies, which provide direct views of individual atoms and molecules on surfaces, the other techniques give some “raw” data, such as electron or ion currents, work function, intensity of atom or light beams, etc., that must be converted to coverage degree (adsorbate surface concentration). This is accomplished through corresponding calibration procedures that establish the relationship between the adatom concentration and the physical values immediately measured in concrete experiments. As an example, Fig. 6 shows the dependences of the work function on coverage for Li and Cu adlayers on W and Mo(112) surfaces [28,31]. Such dependences are used in scanning contact-potential microscopy [17,27,28].

The most important features of the experimental techniques applied to study SD are their spatial resolution and accuracy of coverage determination. The spatial resolution ranges from the atomic scale ($\sim 10^{-8}$ cm) in field-ion and scanning tunneling microscopies (STM) to 1–10 μm in photoelectron and other types of electron microscopies as well as in scanning contact-potential microscopy. The latter technique provides an accuracy in coverage determination to about 10^{-2} of a monolayer in the coverage intervals where the work function strongly depends on θ as in Fig. 6. It should be noted that STM technique can be adapted to measure the

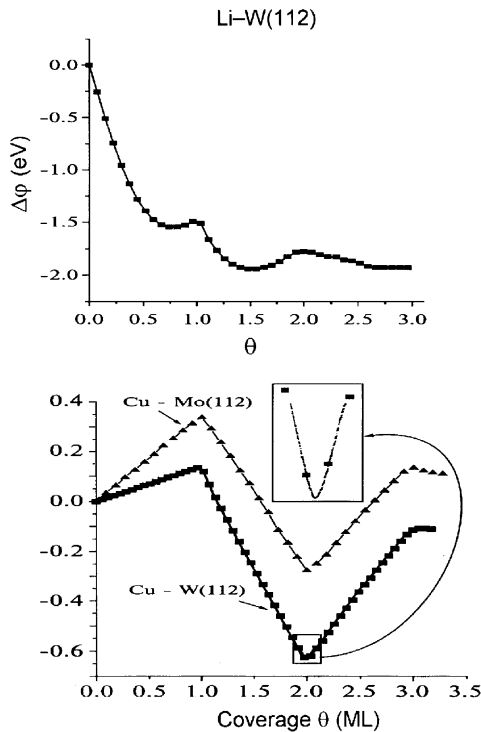


Fig. 6. Work function change $\Delta\phi$ versus coverage θ (in monolayers) for Li and Cu on W and Mo(112) surfaces.

spatial work function changes (or, more strictly, the changes of a local near-surface potential) with an atomic resolution (see e.g. Ref. [32]).

In general, the higher is the spatial resolution the better, but only if other advantages are equal. Unfortunately, this is almost never the case. For instance the field ion microscopy (FIM) provides the atomic resolution and is very efficient in following surface diffusion of single atoms and small clusters (oligomers) [19,21,33]. On the other hand, the FIM technique is only applicable to materials which can withstand high electric fields of $\sim 10^8$ V/cm. Besides, the small size of the crystal planes on sharp tips used in field ion microscopes makes impracticable quantitative recording of the evolution of coverage profiles and investigations of phase effects in surface diffusion.

Going to the STM, one can state that this is an excellent technique which offers a unique possibility to directly visualize the surface atomic structure of very wide variety of conducting objects. However, one should keep in mind that the rather high electric fields under the tip and the high-density tunneling current can sometimes induce a specific mobility of the adparticles [17,34,35].

The much more modest resolution of such methods as photoelectron microscopy and scanning contact-potential microscopy (1–10 μm) is rewarded with a high accuracy of coverage determination, nondestructive character of the measurements and the possibility to observe phase effects in surface diffusion over rather large distances. Of course, it should be understood that experiments in which surface diffusion is followed over macroscopic distances (say, $> 1 \mu\text{m}$) relate actually to surfaces with some quantity of defects. Existing technologies cannot ensure preparation of defect-free macrocrystal surfaces.

The point-like defects such as vacancies, single impurity atoms, etc. act as traps (attracting sites) or antitraps (repulsing sites) for diffusing particles. A trap can be filled by a diffusing atom which then may either attract or repulse the other diffusing atoms. In the former case the trap acts as a nucleation center if the temperature and the adatom density correspond to the region of a first-order phase transition in the diffusing overlayer. In contrast, if the point-like defect (either empty or filled) is a repulsive center, the other diffusing atoms will bypass it.

In the particular case when surface potential corrugation is strongly anisotropic and the diffusion predominantly proceeds along the atomic troughs (channels), the point-like defects situated within the channels can dramatically block the diffusion [36]. A similar strong suppression of surface diffusion by point-like defects is observed in the case of soliton diffusion mechanism [4,37]. This mechanism has a pronounced collective character: the mass transport is effected by solitons, which represent linear many-particle objects (domain walls) and can be effectively pinned by point-like defects (see Section 6).

Linear surface defects such as atomic steps and grain boundaries can have a strong impact on surface diffusion, because the diffusing particles cannot bypass them. The character of this impact depends on the interaction of the diffusant with the linear defect and on the orientation of the diffusion jumps with respect to the defect. For instance, surface diffusion is generally impeded across the steps and enhanced along them [30,38,39]. Uebbing and Gomer [40] simulated the impact

of atomic steps on surface diffusion kinetics for various possible combinations of interaction of adparticles with each other as well as with the steps and the atomic terraces. The implication of their analysis is that the atomic steps may generally exert a strong and diverse effect both on the diffusion kinetics and on the shape of the diffusion front.

Broadly speaking, diffusion on surface with defects presents a particular case of diffusion in (for our situation, *on*) disordered media. This is a complicated theoretical problem which is approached by involving such concepts as a certain hierarchy of defects according to their scale, percolation; possible fractal structure of the medium, etc. The diffusion in (on) disordered media differs by some unusual features. For example, the mean-square displacement of the diffusing particles increases in this case nonlinearly versus time. This gave grounds to term such diffusion *anomalous* in contrast to *normal* diffusion where (on defect-free surfaces) one has $\langle x^2 \rangle \propto t$ [41].

The substrates with uncontrollable defects are obviously not the best objects for investigating mechanisms and other regularities of surface diffusion which are very sensitive to the surface atomic structure. On the other hand, most if not all of the substrates used in practice do contain more or less defects. If for no other reason than this, the understanding of the impact of surface defects on diffusion is highly important. It is clear that in order to gain insight into essential physics of this impact, experimentalists must work with surfaces that possess controllable (intentionally created and well characterized) defects. Such works are yet few in number. As has already been noted, the collective character of SD is evidently an important factor for understanding the mechanisms through which defects can influence the adatom mobility in various diffusion regimes.

For other nonequilibrium SD techniques, the reader is referred to reviews cited above.

4.2. *Equilibrium methods*

Let us now discuss the character of information on surface diffusion that is provided by the equilibrium methods. We shall start with the FIM, a method that ensures the possibility to trace random walks of individual atoms and small clusters [19,33]. To prevent the effect of the high electric field existing near the tip in the imaging regime on diffusion, the field is switched off while heating the tip to diffusion temperatures. The result of diffusion is imaged on the microscope screen after cooling the tip.

A few spectacular collective effects were discovered in surface diffusion with the aid of the FIM technique.

(i) Bassett and Webber [3] found that atom jumping over saddle points on the surface is not necessarily the energetically favorable way of diffusion. Instead, the atoms may exchange their positions on the surface so that diffusion occurs as a relay process (Fig. 2). The exchange can be achieved by a concerted motion of a group of atoms. This diffusion mechanism is widely occurring in metal-on-metal systems, especially on surfaces with an open atomic structure.

(ii) A careful analysis of the positions consecutively occupied by diffusing atoms in their random surface walks led to the conclusion that some atomic jumps may be *long* [22,23]. It means that a particle which fluctuatively receives a sufficient energy from the substrate may overcome not just one, but several potential barriers before it gives back its excessive energy to the substrate (Fig. 1). It is understood that such long jumps can only be treated in terms of the models that consider the dynamic coupling of the diffusing particle with lattice vibrations and electronic excitations in the substrate.

(iii) The pronounced collective mechanisms were observed, both experimentally (using also electron microscopy and STM) and by computer simulations, in diffusion of atomic clusters. Depending on the number of atoms in the cluster, the mechanisms may be remarkably diversified: from sequential shear and “reptation” displacements [19,33,42–44] to gliding of the cluster as a whole [45], formation and relay motion of solitons (dislocations) [46,47], rolling [48], so-called leapfrog mechanism [49], etc. (Fig. 7). A more systematic review of this topic is given in Ref. [29].

Schwartzentruber [50] developed a STM analogue of FIM technique for studying surface diffusion, in which the coordinates of diffusing particles are automatically tracked in time. This is undoubtedly a very promising method because it substantially broadens the range of the objects for which surface diffusion can be studied in detail on atomic scale.

Another equilibrium method of surface diffusion investigation is based on recording thermal density fluctuations in adsorbed layers. Two of its versions, using, respectively, the field emission microscopy (FEM) [51] and STM [52,53], were elaborated in detail. By way of example we shall consider some possibilities of the FEM fluctuation technique. It is pertinent to recall here an important contribution to its development made cooperatively by the Leipzig and Wroclaw schools of surfacists [54,55]. The original physical quantity recorded in this technique is the field emission current collected from a small (≤ 100 Å in size) surface area. The current fluctuations stem mainly from the fluctuations of the number of adatoms within the probed area, which cause local work function variations. In turn, the density fluctuations in the adlayer can only occur thanks to the existence of a mobility of adatoms. Thus, the investigation of the process of building-up and decay of the adatom density fluctuations gives a possibility to extract the diffusion coefficient from the autocorrelation function of the fluctuations. The physical meaning of this (collective, or chemical) diffusion coefficient will be discussed in Section 5.

The inherent feature of this method is that it allows the determination of the surface diffusion parameters only in the presence of a high electric field of $\sim 10^7$ V/cm oriented normally to the surface (the tip being charged negatively). This peculiarity must be taken into account when comparing the diffusion data obtained from the field emission fluctuations and from other (field-free) measurements. Of course, the effect of high electric field on surface diffusion kinetics may be of interest by itself. It should also be noted that this effect can be negligible when the dipole moment and the polarizability of adsorbed particles are not large. This seems to be the case for most chemisorbed gases, but not for electropositive adsorbates like alkali, alkaline-earth and rare-earth elements.

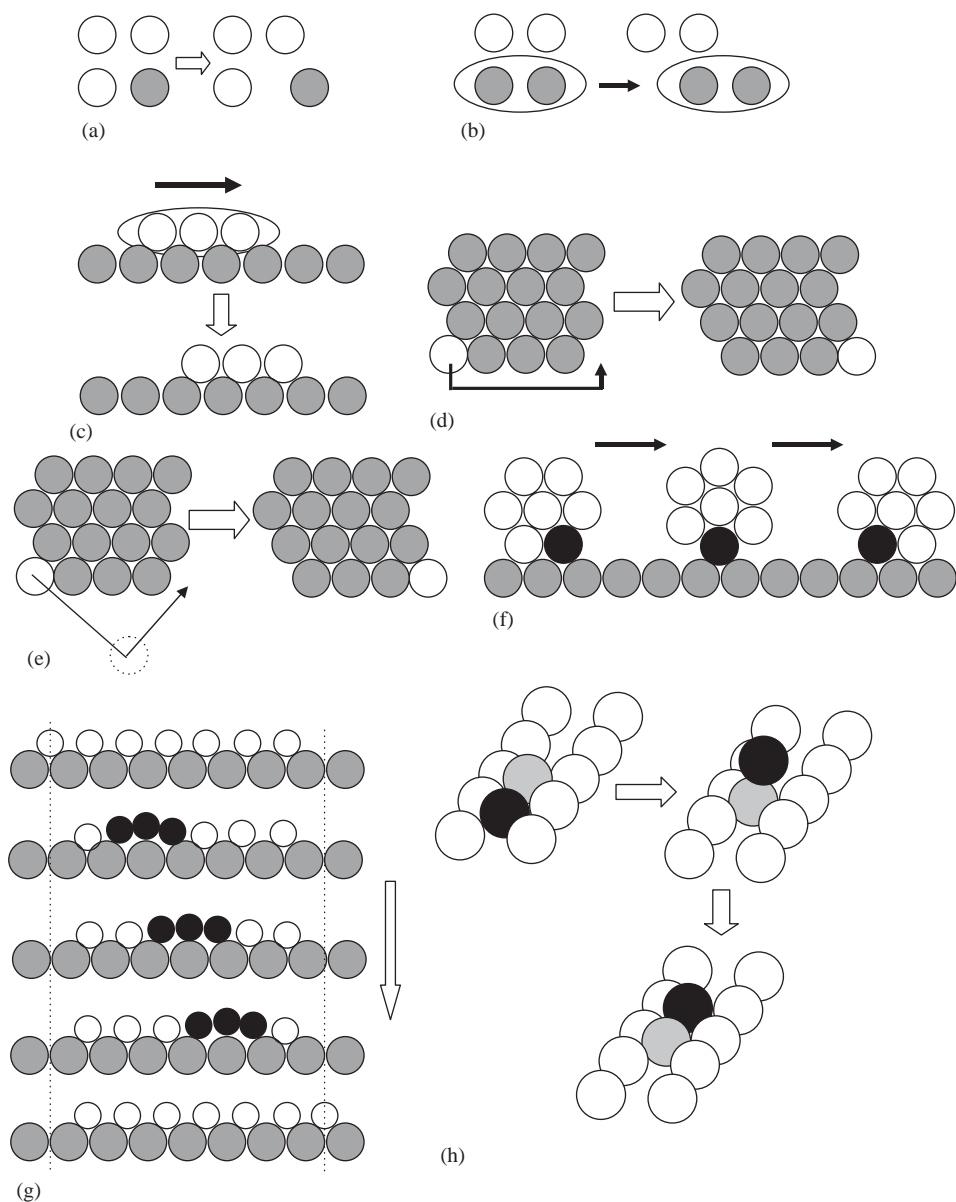


Fig. 7. Schematics of some diffusion mechanisms for clusters and atomic islands. (a) Sequential displacement of individual atoms. (b) The dimer shearing mechanism. (c) The gliding mechanism: the cluster glides as a whole from one position to the next. (d) The edge diffusion mechanism: the motion of an adatom along the island edge causes a shift of the center of mass of the island. (e) The evaporation + condensation mechanism. (f) Schematic of the rolling mechanism. (g) The dislocation (soliton) mechanism: adatoms in the dislocation (soliton) are shown as black balls. (h) Diffusion of a dimer in an atomic channel by the leapfrog mechanism.

In the STM version of the fluctuation technique, one records the fluctuations of the tunneling current caused by passing the diffusing particles under an immobile tip.

Among the equilibrium SD methods we shall also mention the quasielastic helium atom scattering [56] and the decay-detected nuclear magnetic resonance employed to measure the spin-lattice relaxation rate [57].

In the next section we shall discuss the basic ways of quantitative description of surface diffusion and the meaning of physical characteristics of this process evaluated from the experimental data.

5. Diffusion coefficients and other diffusion parameters

The first quantitative description of diffusion on a macroscopic level given by A. Fick was based on the assumption of a close analogy between this process and heat transfer. Equations expressing the regularities of the heat flow had been derived earlier by J. Fourier. Thus the first Fick's law relates the diffusion flux \vec{J} to the concentration gradient as

$$\vec{J} = -D\nabla n, \quad (1)$$

where n is the particle concentration and D is the diffusion coefficient (we consider here the simplest case of isotropic diffusion).

In 1905, A. Einstein explained diffusion as a result of random walks (Brownian movement) of individual particles [1]. His theory predicted that a diffusion coefficient, which as we presently understand is different from D in Eq. (1) and is now commonly termed *tracer diffusion coefficient* D_t , can be determined in the one-dimensional case from the ratio

$$D_t = \langle x^2 \rangle / 2t, \quad (2)$$

where $\langle x^2 \rangle$ is the mean-square displacement of a particle along axis x during the time t . This prediction was verified by J. Perrin (1908) whose experiments also gave decisive evidence for molecular structure of substances. It is also pertinent to recall that a recognized contribution to the theory of Brownian movement and theory of fluctuations in equilibrium systems belongs to Marian Smoluchowski, a prominent Polish physicist (see e.g. Ref. [58]).

A. Einstein clearly formulated the assumptions under which Eq. (2) is valid. He wrote: "*Es muß offenbar angenommen werden, daß jedes einzelne Teilchen eine Bewegung ausführe, welche unabhängig ist von der Bewegung aller anderer Teilchen; es werden auch die Bewegungen eines und desselben Teilchens in verschiedenen Zeitintervallen als voneinander unabhängige Vorgänge aufzufassen sein, solange wir diese Zeitintervalle nicht zu klein gewählt denken*" (Obviously, it is necessary to assume that each individual particle performs a motion which is independent of the motion of all other particles; besides, the motions of one and the same particle in different time intervals will be treated as independent processes as long as we imply that these time intervals are not too short.) (Ref. [1, p. 556]).

Thus, if like in an ideal gas there were no interaction between the diffusing particles and no “memory effects” between successive jumps, the diffusion coefficients in the first Fick’s law (1) and in Einstein’s formula (2) would be identical. However, the presence of interactions in all real systems brings about drastic changes in the situation. It is valid to say that interactions in the ensemble of diffusing species impart a rich physical content to diffusion, rendering it at once challenging and intricate. As has already been noted (Section 2), the diffusion is a many-body process, which adds much complexity to its description. In particular, the meaning of the diffusion coefficient and its value become ambiguous and depend on the conditions of diffusion.

If there exists a possibility to track individual random walks of each particle (atom or molecule) in an ensemble on the surface, one can apply Einstein’s formula to evaluate the tracer diffusion coefficient as

$$D_t = \lim_{t \rightarrow \infty} \frac{1}{4Nt} \sum_{i=1}^N \langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle . \quad (3)$$

Here we consider a *two-dimensional system* (hence coefficient 4 in the denominator) which consists of N noninteracting particles. Vectors $\vec{r}_i(t)$ and $\vec{r}_i(0)$ determine the positions of the i th particle at time t and the initial moment, respectively. The system is assumed to be in equilibrium, so the random walks may continue infinitely long. If we label some atoms in a system and follow their diffusion for a rather long time, we shall find out just the tracer diffusion coefficient. The “labelled” atoms (radioactive isotopes in the diffusion experiments, which explains the term *tracer* in the definition of D_t) have the same chemical properties as the other atoms (stable isotopes). Thus the energy of the system does not change during the mixing of the labelled and unlabelled atoms, and the only factor that causes their mixing is the maximization of entropy. For this reason the diffusion coefficient evaluated from the spreading of the concentration profile of labelled (radioactive) atoms (i.e., in a *nonequilibrium* system) appears equal to D_t that characterizes the random walks of a single labelled atom in an *equilibrium* system. D_t is often termed also the *coefficient of self-diffusion*.

D_t is the simplest of all diffusion coefficients introduced to quantify the diffusion processes in various situations. According to the random walk theory, its value in the two-dimensional case is

$$D_t = \frac{1}{4} \Gamma \langle l^2 \rangle , \quad (4)$$

where Γ is the jump rate and l is the length of the elementary particle jumps effecting the diffusion. However, this simplicity is only apparent and should not obscure the complex many-particle effects behind each jumping act. As it was noted above, the particles receive from the substrate the energy sufficient to jump over the potential barrier, and the jump finishes as this energy is given back to the substrate. Depending on the ratio of the vibration frequencies of the diffusing particle and of the substrate lattice, the energy transfer from the particle to the substrate may occur mainly through either the phonon or electron excitations [34].

For example, hydrogen atoms, due to the large difference between their mass and the mass of atoms of most substrates, lose their energy mainly via the electronic channel. This channel is less efficient than the phonon channel, which may result that such atoms jump over a longer distance than one substrate lattice period. The long jumps are possible, although with a lower probability, for heavier atoms, too. The relative contribution of the long jumps to the diffusion rate varies with temperature becoming larger as temperature grows [23].

Let us now dwell on the value of the jump frequency Γ in Eq. (4). According to the transition state theory (TST), termed also *activated complex theory* [59], it can be expressed as

$$\Gamma = \frac{kT}{h} \kappa e^{\Delta S/k} e^{-E_d/kT}, \quad (5)$$

where k is the Boltzmann constant, h the Planck constant, T the temperature, κ a transmission coefficient (see below), ΔS the entropy of activation and E_d the energy of activation of surface diffusion. TST is an equilibrium statistical theory which assumes that a particle, while moving along the so-called reaction coordinate, can reach the top (or saddle point) of a potential barrier (the transition state) if its energy is $E \geq E_d$. From this state, which is the point of no return, it passes into another stable (or metastable) state. The pre-exponential factor

$$\Gamma_0 = \frac{kT}{h} \kappa e^{-\Delta S/k} \quad (6)$$

determines the attempt frequency of overcoming the barrier. The transmission coefficient $\kappa < 1$ is introduced semiempirically to fit the calculated Γ_0 value to experimental one. It is actually a correction for the approximations of TST such as neglecting of the anharmonicity of the particle vibrations, of memory effects (i.e., of correlation in the direction of successive jumps [23]) and others. Again, the neglected effects are mainly of many-particle origin.

Using Eqs. (4) and (5), we can present the diffusion coefficient D_t in the well-known Arrhenius form

$$D_t = D_0 e^{-E_d/kT}. \quad (7)$$

Assuming that the jump length equals the substrate lattice period a , one obtains the following value for the pre-exponential factor:

$$D_{0t} = a^2 \Gamma_0. \quad (8)$$

Expression (7) is a widely used (and the most liked by experimentalists) way of presentation of data on the diffusion coefficients. Being convenient indeed, it is unfortunately not always well-justified.

Let us now discuss another definition of the diffusion coefficient which is used to describe the diffusion in the presence of a concentration gradient. This situation corresponds to the first Fick's law [Eq. (1)]. It should be noted that various terms are used in the literature to name this coefficient: *chemical diffusion coefficient*, *heterodiffusion coefficient* or, most frequently in current publications, *collective*

diffusion coefficient. We shall stick to the last term, although it is not irreproachable. Its flaw is that it gives an erroneous impression that the process of tracer diffusion (self-diffusion) is noncollective.

The particle flux in the case of collective (chemical) diffusion of interacting particles can be written as

$$\vec{J} = -L\nabla\mu, \quad (9)$$

where L is the transport coefficient and $\nabla\mu$ is the gradient of chemical potential [60]. Let us memorize that this expression presents a linear approximation with respect to $\nabla\mu$. It is actually a generalization of the first Fick's law [Eq. (1)] to the case of interacting particles. The attractive interaction slows down and the repulsive interaction enhances the diffusion rate in comparison with the case when interaction is absent and only the entropy growth drives the diffusion [61].

Eq. (9) can be cast in a form similar to the Fick's law:

$$\vec{j} = -D(n)\nabla n, \quad (10)$$

where $D(n)$, the collective (chemical) diffusion coefficient, is

$$D(n) = L(n)\frac{\partial\mu}{\partial n} = D_j(n)\frac{\partial(\mu/kT)}{\partial \ln n}. \quad (11)$$

The factor $D_j(n)$ in this expression, named either *the jump diffusion coefficient* [62] or *the kinetic factor* [63], is defined as

$$D_j(n) = L(n)kT/n. \quad (12)$$

It contains information on the frequency and length of the jumps. Proceeding from semiempirical considerations, Reed and Ehrlich [62] proposed to present $D_j(n)$ in a form analogous to (4):

$$D_j(n) = \Gamma(n)l^2(n). \quad (13)$$

As we see, both Γ and l are meant to depend on particle concentration. This dependence arises not only from the trivial blocking of the free sites by adjacent adatoms, but also from the lateral interactions, which can influence the shape of the potential well and the energy exchange (the friction) between the diffusing particle and the substrate.

The derivative $\partial(\mu/kT)/\partial \ln n$ in Eq. (11) is termed *the thermodynamic factor* (TDF). It includes contributions from both the energy and the entropy terms in the chemical potential and quantifies the impact of lateral interactions on D .

In the limit of low concentrations ($n \rightarrow 0$), the TDF is equal to 1 and obviously one has

$$D_t = D = D_j.$$

However, as we argued above, even in this limit the surface diffusion does not cease to be collective in nature.

6. Concentration dependence of D and phase transitions in the diffusion zone

It should be noted that surface diffusion experiments belong to the most laborious in surface science. The experiments must be carried out on the samples whose surface is prepared as perfect as possible; high spatial resolution as well as high accuracy in coverage and temperature determination are necessary; the requirements to purity of adsorbates and to vacuum conditions are extremely severe, because the diffusion parameters are very sensitive to impurities and the measurements may last for ~ 10 h; the experiments must be repeated many times, etc. Then a procedure of data evaluation is performed which should give the values of the diffusion coefficients at various temperatures, coverages and, sometimes, at various initial conditions. To correlate the diffusion parameters with the adlayer structure (and without this any sound judgements on the diffusion mechanisms would be impossible), it is also necessary to investigate the atomic structure and the phase diagram of the adlayer.

By way of example let us consider the Boltzmann–Matano (BM) method, which allows extraction of the concentration dependence $D(n)$ from the concentration profiles recorded after diffusion out of a step-function initial deposit [17,18,23,60,64]. It should be stressed that if D is coverage dependent, Fick's equations become nonlinear even if only the first approximation with respect to ∇n is used for the diffusion flux (1). Actually the BM method of finding $D(n)$ from the coverage profiles represents a semiempirical approach, since it may be applied only if the coverage profiles recorded experimentally at different times coincide with each other when replotted against the variable x/\sqrt{t} (this variable was suggested by L. Boltzmann in 1894). For a number of systems this was found to be the case with an acceptable accuracy (see, e.g. the data for the system Dy–Mo(112) [65] shown in Fig. 8). However, if this is not the case, other methods of solution of the inverse problem should be applied.

Thus, using the BM method, the diffusion coefficient at some coverage $\theta = \theta'$ can be evaluated from a coverage profile $\theta(x)$ as

$$D(\theta') = -\frac{1}{2t(d\theta/dx)_{\theta'}} \int_0^{\theta'} x(\theta) d\theta. \quad (14)$$

The advantage of the BM method is that it, in principle, it allows evaluation of the coverage dependence of D in a broad coverage range even from a single coverage profile measured experimentally. However, its accuracy is not very high at low and high coverages, where the accuracy of determination of the integral and derivative in Eq. (14) from the recorded profiles may be rather poor.

There is also a more basic difficulty in applying the BM method. This method relies on the second Fick's equation

$$\partial n/\partial t = \partial/\partial x[D\partial n/\partial x], \quad (15)$$

which is derived in the assumption that the concentration gradient is sufficiently small and that so-called hydrodynamic approach is applicable. This implies that it should be less steep than the gradient in thermal concentration fluctuations, which

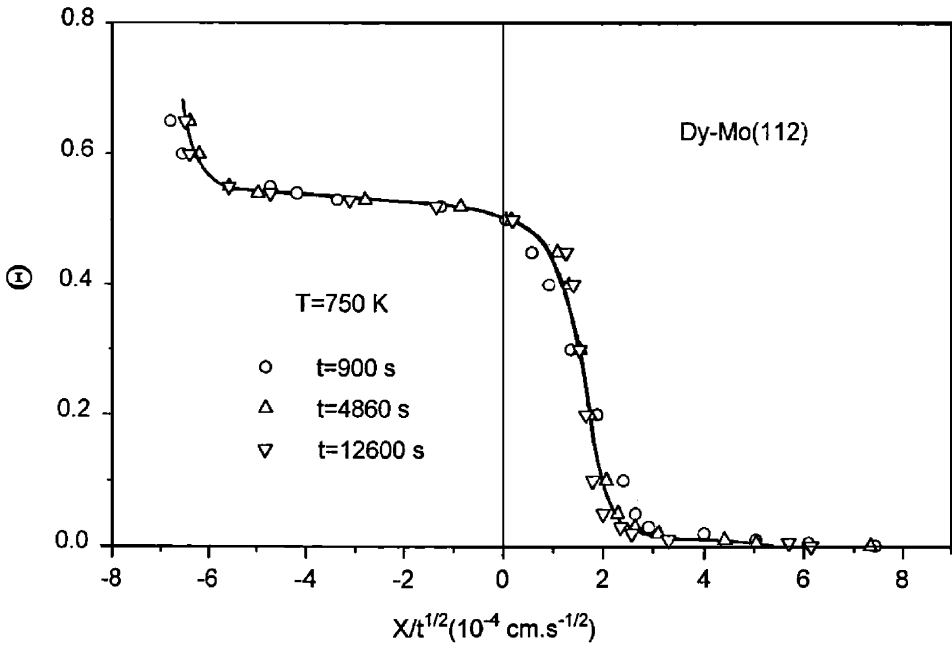


Fig. 8. Coverage profiles recorded in surface diffusion of Dy on Mo(112) and plotted against $x/t^{1/2}$ [65].

extend at least over a few lattice periods. Gomer [18] quantified the criterion as

$$\frac{d\theta}{dx} \leq 10^5 \theta^{1/2} \text{ cm}^{-1} . \tag{16}$$

In real experiments, it is reliably satisfied in the single-phase coverage regions, but not in the two-phase regions where the boundaries between phases of different density are atomically sharp. However, such distances are beyond the spatial resolution of the macroscopic techniques, which are currently employed to record the profiles analyzed by the BM method. It is anyway clear that a two-phase adlayer cannot be strictly characterized by a single diffusion coefficient. The D coefficients obtained in such conditions by macroscopic methods are some averaged (effective) values, which usually appear lower than in the single-phase regions (Fig. 9) [66]. This may mirror the operation of a complex mechanism of mass transport which includes the stages of 2D evaporation of adatoms from the dense islands, their migration within the dilute phase and finally their condensation at other islands (or their capture by defects). This is actually an interesting case of adlayer ripening in the concentration gradient [67]. Its concrete scenario should substantially depend on boundary conditions (which may vary in time if the diffusion process under study is nonstationary), on temperature, the presence of defects, on the self-organization of islands due to substrate-mediated elastic interactions, on the attainment of percolation limit, etc.

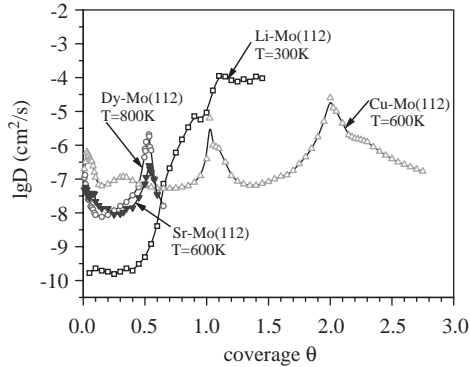


Fig. 9. Surface diffusion coefficients versus coverage for Li, Sr, Dy and Cu on the Mo(112) surface [66].

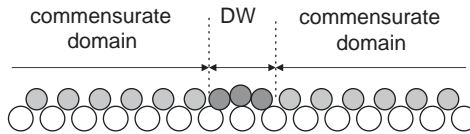


Fig. 10. Incommensurate domain wall (soliton) between two commensurate domains.

Unfortunately, the method of field emission fluctuations is also inadequate to study the mass transport in the regions of phase coexistence [18]. However, a useful information on this issue can be extracted from the observations of 2D evaporation and growth of small islands of adatoms in the field emission microscope [68]. It may also be expected that STM technique will shed more light on this problem.

On the whole, experimental investigations of surface diffusion in concentration gradients show that the diffusion coefficient can vary, in most cases nonmonotonically, over a few orders of magnitude as the coverage is changing from $\theta \rightarrow 0$ to a few monolayers (Fig. 9).

In addition to the low (effective) diffusivity in regions of first-order phase transitions which have been discussed above, some other general regularities were also found out [27,29]. The diffusion coefficients are usually high at low coverages (where the mass carriers are most probably single atoms and oligomers, see Fig. 7) as well as in the regions of commensurate-incommensurate (C-I) phase transitions. In the latter case the commensurate domains in the adlayer are separated by incommensurate walls, which do not conform to the substrate atomic relief (Fig. 10). The existence of such domain walls, which are actually the misfit dislocations in two-dimensional adlayers, is confirmed experimentally by LEED and STM techniques (see e.g. Refs. [69,70]). In mathematical terms, the walls represent topological solitons which can move rather easily within the adlayer [4,37].

Their motion proceeds by a typical collective (relay) mechanism in which all adatoms are in turn displaced by a substrate lattice period as the soliton passes through the commensurate adlayer as illustrated in Fig. 7g.

The solitons (domain walls) form at the high-coverage side of the θ profile (Fig. 11). Viewed from above, they appear as linear objects. The displacement of a soliton starts with emergence (due to thermal fluctuation) of an elementary protrusion, which represents a pair kink–antikink [4,71]. The motion of the kink and antikink in opposite directions results in the displacement of a section of the soliton by one substrate lattice period. Since these motions occur fluctuatively, the soliton meanders and actually performs a kind of “random windings”. Due to existence of a soliton concentration gradient, there is a flux of the solitons through the commensurate phase. When coming to the end of this phase, the soliton shifts its edge by a lattice period and disappears. Such is the essence of the soliton diffusion mechanism [4,37]. One can easily find its similarity to the known crowdion mechanism in volume diffusion [60] and to the mechanism of conductivity in ionic superconductors. Their common feature is the formation of some incommensurate configurations that serve as mass (or charge) carriers and have a high mobility. The difference is that solitons (domain walls) in adlayers are linear objects while crowdions are usually considered as point-like objects (actually, also solitons) moving along some densely packed rows (chains) of atoms. In fact, a similar situations can also exist on surfaces, e.g. when they have a furrowed atomic relief.

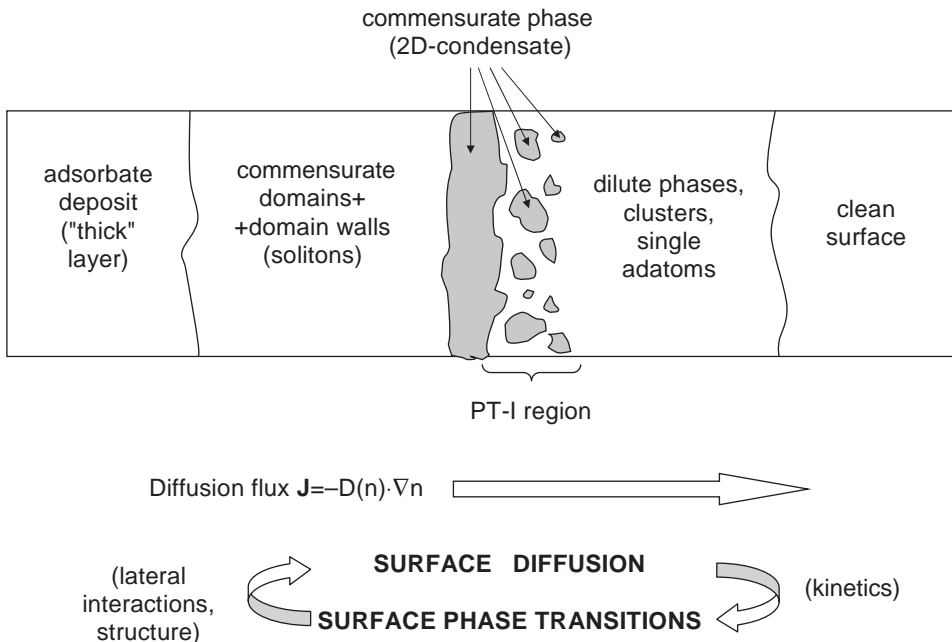


Fig. 11. A schematic of the phase states in the diffusion zone illustrating interrelation between surface diffusion and phase transitions in the diffusing layer.

It is understood that the pronounced collective character of the soliton diffusion mechanism should make it sensitive to the presence of defects, which can pin the solitons and thus slow down the diffusion. This effect was confirmed experimentally [37,72].

In general, experimental data show that D value is intimately linked with the phase state of the adlayer (Fig. 11). The extrema in D versus θ dependences usually correlate with phase transitions in the adlayers. This was to be expected, since singularities of the chemical potential that are responsible for the phase transitions must also affect the thermodynamic factor in Eq. (11). However, it is impossible to predict the behavior of D taking into account solely the value of TDF. The changes in the atomic structure that occur in the course of the phase transitions (which can also be accompanied by substantial changes in electronic structure, e.g. by a nonmetal–metal transition) can cause strong changes in the kinetic factor D_j .

Actually, the frequency of the jumps, their length and even the diffusion mechanism itself can depend on the character of order which changes in the phase transitions. These qualitative considerations are supported by computer simulations [24,25,41,63,73–75]. The common contribution of both thermodynamic and kinetic factor can account for the sharp changes in D that amount sometimes to a few orders of magnitude (Fig. 9).

It should be noted again that the substantial changes in the arrangement of adatoms in the course of phase transitions make questionable the possibility of presentation of the diffusion coefficient in the Arrhenius form, at least in a broad temperature interval. The raising of temperature in the region of a phase transition changes the order in the adlayer and thereby changes the system itself. In particular, it was shown that the memory effects in the diffusion jumps are sensitive to the order and can strongly affect the Arrhenius barriers [23,76]. Thus the observed changes in the diffusivity may not be attributed solely to the growth of the probability of overcoming some fixed potential barrier between the adsorption sites.

This question has a long history starting from investigations of volume diffusion kinetics in the region of a second-order phase transition in Cu–Zn alloy (see e.g. Refs. [77,78]). The Arrhenius plot $\lg D$ versus $1/T$ shows in this case a break at the point of order–disorder transition. Similar results were obtained for surface diffusion of Sr on W(112) [79]. For other systems, situations are possible when no clear-cut break is seen in the Arrhenius characteristics, but the pre-exponential factor D_0 can differ from its “normal” value of $\sim 10^{-3}–10^{-2} \text{ cm}^2 \text{ s}$ by a few orders of magnitude. The difference may be attributed, at least in part, to the contribution of activation entropy and/or to low transmission coefficient κ in Eq. (6), or to the existence of long jumps in Eq. (13). However, it cannot be ruled out that “anomalous” D_0 values appear from the unjustified application of the Arrhenius equation to systems whose state substantially changes with temperature. In addition to order–disorder transitions, where the changes in the short-range rather than in long-range order may appear most important to surface diffusion, one should also consider the possibility of such effects as surface reconstruction and roughening transition, surface alloying and surface segregation. In such cases, the forcing of experimental

results into the procrustean bed of the simple exponential dependence may lead to results which make little physical sense.

7. Self-organization of the diffusion zone

Now let us have a look at the diffusion zone from the standpoint of its macroscopic organization. Consider the case of diffusion from a step-like initial deposit (Fig. 5). If D is independent of concentration, the concentration profile in the diffusion zone is given by the well-known equation [60]:

$$n(x, t) = \frac{n_0}{2} \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right]. \quad (17)$$

Here, n_0 is the concentration in the initial ($t = t_0$) deposit ($n = n_0$ at $x < 0$ and $n = 0$ at $x > 0$) and erf is the error function.

This profile is smooth and does not show any peculiarity. However, it has little in common with the profiles recorded experimentally (see e.g. Fig. 8), which can exhibit a number of plateaus, precipices and, sometimes, even nonmonotonic variations (hollows) in $n(x)$ [27,65]. Intuition suggests, and the BM solution (14) confirms quantitatively, that the concentration plateaus correspond to the n regions where D is at its maxima.

Assume for the moment that we have a stationary situation. Then the concentration gradient must adjust itself to the D -value to provide the continuity of the diffusion flux. The gradient can be the lower the higher the diffusion coefficient. The result is that the largest space in the diffusion zone is taken by the phase which is transporting the particles with the highest rate. Thus, if we treat the diffusion zone as some physical object, we may speak about its macroscopic self-organization. Actually, there is a source and a drain of the diffusing particles, so the system is open, nonequilibrium and nonlinear.

In a more general nonstationary type of experiment, the diffusion zone is evolving in time and space, but nonetheless the different phases appearing in the adlayer can manifest themselves quite clearly. The zone becomes a sort of exposition of the phases that form in the diffusing adlayer in the specific conditions of the experiment. It should be understood, however, that we are dealing with a nonequilibrium situation where some structurization may appear which cannot exist in equilibrium. It is also important to note that the scenario of the diffusion self-organization is sensitive to initial and boundary conditions (see e.g. Ref. [80]). The kinetics of nucleation in the concentration gradient is predicted to have a number of essential peculiarities [67].

Since the diffusion zone is obviously an unstable object which eventually disappears as the adlayer comes to equilibrium, the diffusion self-organization discussed here is actually a transient phenomenon. However, its duration depends on experimental conditions and may be long enough in practice.

Above, we have given some examples of self-organization in diffusing submonolayers. Interesting manifestations of self-organization are also revealed in

the diffusion from multilayer (three-dimensional) solid deposits and in spreading liquid droplets [17,18,81]. Here, the self-organization arises from the substantial difference of adatom mobility in the monolayers residing at different distances from the substrate. This stems in turn from the fact that the particle interactions, the dynamic characteristics and atomic (molecular) structure vary with the distance. In particular, the monolayers of a liquid closest to the solid/liquid interface are now known to possess an augmented (solid-like) degree of order in comparison with the short-range order in volume. The result is that the front of the spreading droplet can assume a stepped shape in which individual steps correspond to successive monatomic or monomolecular layers [81].

In conclusion, surface diffusion and surface phase transitions are closely interrelated and determine the kinetics of each other. Actually, the kinetics of phase transitions depends on the particle mobility, which in its turn depends on the properties (structure, dynamics, interactions) of the emerging phases (Fig. 11).

8. Conclusions

Current studies on surface diffusion are focused mainly on its important features which did not receive proper attention in the past. Actually almost all of them relate to many-body effects in surface diffusion such as lateral interactions and phase transitions, long jumps, memory effects, collective diffusion mechanisms, nonlinearities, etc.

It should be admitted that a more penetrating insight into the nature of surface diffusion is often achieved at the expense of lucidity of its description. Engineers who intend to use surface diffusion in technologies would prefer to have simple and reliable Arrhenius formulas which could be applied at all temperatures and independently of phase transitions, nonlinearities, nonequilibrium effects and other complications. Alas, we now understand that this is generally unattainable. It is pertinent to recall the message of Ecclesiastes: “With much wisdom comes much sorrow, the more knowledge, the more grief”.

On the other hand, physicists are now prepared to investigate increasingly complex systems and phenomena (physics of complexity) and consider them not as a burden, but as a challenge. In regard to surface diffusion, this is demonstrated by the fact that about one-fifth of the works in surface science are now related to this field. For decades, surface diffusion lagged behind volume diffusion both in the number of investigations and in the level of theoretical understanding. The advent of readily accessible ultra-high vacuum technologies and of a multitude of surface characterization techniques, together with the “openness” of surfaces, brought about the possibility to study SD processes at an unprecedented level of visibility, resolution and accuracy. One may even state that the technical arsenal available for SD studies is now more powerful and versatile than that for volume diffusion. It is also important that SD data is wanted by nanotechnologists developing nanoelectronic devices and nanomaterials [29]. Biology, medicine and the corresponding technologies are now the disciplines which are increasingly interested in the mechanisms of the mobility of large organic molecules at various surfaces and interfaces in animate

nature [82–84]. *Interaction* is one of the most frequently used terms in all natural sciences, and just interaction is the reason why most processes in nature bear a many-body and nonlinear character.

In SD, we now see a lot of effects that are yet poorly investigated experimentally. For the most part they are pronouncedly many-body and nonlinear in origin. The essential difficulty is that while the spatial resolution of the best modern SD techniques has attained a subnanometer level, their time resolution does not yet allow one to shoot moving pictures of the process of elementary diffusion jumps. However, this is possible in computer simulations, which became a very important and inseparable part of SD investigations and reveal such details of SD processes that are so far unobtainable in present experiments. Of course, it should be kept in mind that the reliability of simulations depends on the level of adequacy of physical models and parameters used in them.

The list of problems in SD that call for further detailed research, both experimental and theoretical, is rather long. In addition to those which have been discussed above (collective diffusion mechanisms, correlations with phase transitions, self-organization of the diffusion zone, manifestations of nonlinearities and nonequilibrium, role of surface defects and anomalous SD) other topical points are worthy of mention. For instance, SD in coadsorbed layers, which is almost unexplored, is highly important in catalysis [85]. Surface diffusion stimulated by electrons and photons (MIET—*migration induced by electronic transitions* [86]), or by high electric fields and high-density currents in STM, opens rich possibilities in controlling SD kinetics and manipulating individual atoms and molecules on surfaces (see e.g. [87] and references therein). An interesting particular case of such SD processes is surface electromigration [88–90]. It produces spectacular dissipative surface structures and opens new ways for controllable preparation of solid surfaces. Recent studies which demonstrated a specific ordering of liquids near liquid/solid interfaces show that some old concepts about spreading of liquid droplets on solids should be reconsidered on the basis of present knowledge of the interface structure. Interesting questions remain to be answered in tunneling surface diffusion [18,23]. They relate not only to hydrogen SD, but also to SD mechanisms of large organic molecules which contain many hydrogen atoms occupying various positions. Finally, let us mention the problems of modern tribology [91]. The behavior of lubricant nanolayers between two solid surfaces that rub against each other has much in common with processes of “traditional” surface diffusion driven by the chemical potential gradient.

As a basically collective (many-body) phenomenon, surface diffusion definitely needs concerted collective efforts of experimentalists and theoreticians to gain a deeper understanding of its complex mechanisms.

Acknowledgements

This work has been supported in part by the Ministry of Ukraine for Education and Science (Project No. F7/279-2001). I thank O.M. Braun for helpful discussions and O.L. Fedorovich for technical assistance.

References

- [1] A. Einstein, *Ann. Phys.* 17 (1905) 549.
- [2] M. Volmer, I. Estemann, *Z. Phys.* 7 (1921) 13.
- [3] D.W. Bassett, P.R. Webber, *Surf. Sci.* 70 (1978) 520.
- [4] I.F. Lyuksyutov, A.G. Naumovets, V. Pokrovsky, *Two-Dimensional Crystals*, Academic Press, Boston, 1992.
- [5] B.N.J. Persson, *Surf. Sci. Rep.* 15 (1992) 1.
- [6] R.D. Diehl, R. McGrath, *Surf. Sci. Rep.* 23 (1996) 43.
- [7] L.D. Roelofs, in: W.N. Unertl (Ed.), *Handbook of Surface Science*, vol. 1, Elsevier, Amsterdam, 1996, p. 713.
- [8] O.M. Braun, V.K. Medvedev, *Sov. Phys. Usp.* 32 (1989) 328.
- [9] T.L. Einstein, in: W.N. Unertl (Ed.), *Handbook of Surface Science*, Elsevier, Amsterdam, 1996, p. 577.
- [10] M. Scheffler, C. Stampfl, in: K. Horn, M. Scheffler (Eds.), *Handbook of Surface Science*, vol. 2, Elsevier, Amsterdam, 2000, p. 285.
- [11] T.B. Grimley, *Crit. Rev. Solid State Sci.* 6 (1976) 239.
- [12] V.A. Shchukin, D. Bimberg, *Rev. Mod. Phys.* 71 (1999) 1125.
- [13] M. Schroeder, D.E. Wolf, *Surf. Sci.* 375 (1997) 129.
- [14] L.A. Bolshov, *Sov. Phys. Sol. State* 13 (1971) 1404.
- [15] D. Andelman, F. Brochard, P.-G. de Jennes, J.-F. Joanny, *C.R. Acad. Sci. Paris* 301 (1985) 675.
- [16] E.W. Müller, T.T. Tsong, *Field Ion Microscopy, Principles and Applications*, Elsevier, New York, 1969.
- [17] A.G. Naumovets, Y.S. Vedula, *Surf. Sci. Rep.* 4 (1985) 365.
- [18] R. Gomer, *Rep. Prog. Phys.* 53 (1990) 917.
- [19] G. Kellogg, *Surf. Sci. Rep.* 21 (1994) 1.
- [20] H. Brune, *Surf. Sci. Rep.* 31 (1998) 121.
- [21] T.T. Tsong, *Progr. Surf. Sci.* 64 (2000) 199.
- [22] J.V. Barth, *Surf. Sci. Rep.* 40 (2000) 75.
- [23] T. Ala-Nissila, R. Ferrando, S.C. Ying, *Adv. Phys.* 51 (2002) 949.
- [24] M.C. Tringides (Ed.), *Surface Diffusion. Atomistic and Collective Processes*, Plenum, New York, 1997.
- [25] M.C. Tringides, Z. Chvoj (Eds.), *Collective Diffusion on Surfaces: Correlation Effects and Adatom Interactions*, Kluwer, Dordrecht, 2001.
- [26] M. Kotrla, N.I. Papanicolau, D.D. Vvedensky, L.T. Wille, *Atomistic Aspects of Epitaxial Growth*, Kluwer, Dordrecht, 2002.
- [27] A.T. Loburets, A.G. Naumovets, Yu.S. Vedula, in: M.C. Tringides (Ed.), *Surface Diffusion. Atomistic and Collective Processes*, Plenum, New York, 1997, p. 509.
- [28] A.T. Loburets, *Metallofiz. Noveishie Technol.* 21 (1999) 43.
- [29] A.G. Naumovets, Z. Zhang, *Surf. Sci.* 500 (2002) 414.
- [30] M. Snabl, M. Ondrejcek, V. Chab, Z. Chvoj, W. Stenzel, H. Conrad, A.M. Bradshaw, *J. Chem. Phys.* 108 (1998) 4212.
- [31] A.T. Loburets, *Metallofiz. Noveishie Technol.* 21 (1999) 47.
- [32] Y. Nakayama, H. Kondoh, T. Ohta, *Appl. Surf. Sci.* 241 (2005) 18.
- [33] G. Ehrlich, *Surf. Sci.* 299/300 (1994) 628.
- [34] O.M. Braun, E.A. Pashitskii, *Phys. Chem. Mech. Surf.* 3 (1985) 1989.
- [35] R.E. Walkup, D.M. Newns, Ph. Avouris, *J. Electr. Spectr. Rel. Phenom.* 64/65 (1993) 523.
- [36] A.T. Loburets, N.B. Senenko, A.G. Naumovets, Yu.S. Vedula, in: M.C. Tringides, Z. Chvoj (Eds.), *Collective Diffusion on Surfaces: Correlation Effects and Adatom Interactions*, Kluwer, Dordrecht, 2001, p. 97.
- [37] I.F. Lyuksyutov, A.G. Naumovets, Yu.S. Vedula, in: S.E. Trullinger, V.E. Zakharov, V.L. Pokrovsky (Eds.), *Solitons*, Elsevier, Amsterdam, 1986, p. 607.

- [38] H. Wagner, in: Vu Thien Binh (Ed.), *Surface Mobilities on Solid Materials*, Plenum, New York, 1983, p. 161.
- [39] J.W. Ma, X.D. Xiao, M.M.T. Loy, *Surf. Sci.* 436 (1999) L661.
- [40] C. Uebing, R. Gomer, *Surf. Sci.* 306 (1994) 419 and 427;
C. Uebing, R. Gomer, *Surf. Sci.* 317 (1995) 165.
- [41] R. Kutner, A. Pekalski, K. Sznajd-Weron (Eds.), *Anomalous Diffusion. From Basics to Applications*, Springer, Berlin, 1999;
R. Metzler, J. Klafter, *Phys. Rep.* 339 (2000) 1.
- [42] S.C. Wang, U. Kurpick, G. Ehrlich, *Phys. Rev. Lett.* 81 (1998) 4923.
- [43] V. Chirita, E.P. Munger, J.E. Greene, J.-E. Sundgren, *Surf. Sci.* 436 (1999) L641.
- [44] O.S. Trushin, P. Salo, T. Ala-Nissila, *Phys. Rev. B* 62 (2000) 1611.
- [45] R. Kern, G. Le Lay, J.J. Metois, in: E. Kaldis (Ed.), *Current Topics in Materials Science*, vol. 3, North-Holland, Amsterdam, 1979, p. 131.
- [46] I. Markov, S. Stoyanov, *Contemp. Phys.* 28 (1987) 267.
- [47] J.C. Hamilton, *Phys. Rev. Lett.* 77 (1996) 885.
- [48] D.Y. Sun, X.G. Gong, *Surf. Sci.* 445 (2000) 41.
- [49] F. Montalenti, R. Ferrando, *Phys. Rev. Lett.* 82 (1999) 1498.
- [50] B.S. Schwartztruber, *Phys. Rev. Lett.* 76 (1996) 459.
- [51] R. Gomer, *Surf. Sci.* 38 (1973) 373;
M.C. Tringides (Ed.), *Surface Diffusion. Atomistic and Collective Processes*, Plenum, New York, 1997, p. 427.
- [52] M. Sumetskii, A. Kornyshev, *Phys. Rev. B* 48 (1993) 17493.
- [53] M.L. Lozano, M.C. Tringides, *Europhys. Lett.* 30 (1995) 537.
- [54] Ch. Kleint, *Solid State Phenom.* 12 (1990) 1.
- [55] R. Meclowski, *Solid State Phenom.* 12 (1990) 49.
- [56] A.P. Graham, J.P. Toennies, in: M.C. Tringides, Z. Chvoj (Eds.), *Collective Diffusion on Surfaces: Correlation Effects and Adatom Interactions*, Kluwer, Dordrecht, 2001, p. 1.
- [57] H.D. Ebinger, H. Arnolds, C. Polenz, B. Polivka, W. Preuss, R. Veith, D. Fick, H.J. Jaensch, *Surf. Sci.* 412/413 (1998) 586.
- [58] M. Smoluchowski, *Bull. Intern. de l'Acad. Sci. de Cracovie* 202 (1906);
M. Smoluchowski, *Ann. Phys.* 21 (1906) 756.
- [59] P. Atkins, *Physical Chemistry*, sixth ed., Oxford University Press, Oxford, 1998, p. 830.
- [60] J. Philibert, *Atom Movements. Diffusion and Mass Transport in Solids*, Les Editions de Physique, Les Ulis, 1991.
- [61] M. Bowker, D.A. King, *Surf. Sci.* 71 (1978) 583;
M. Bowker, D.A. King, *Surf. Sci.* 72 (1978) 208.
- [62] D.A. Reed, G. Ehrlich, *Surf. Sci.* 102 (1981) 588.
- [63] A.V. Myshlyavtsev, A.A. Stepanov, C. Uebing, V.P. Zhdanov, *Phys. Rev. B* 52 (1995) 5977.
- [64] C. Matano, *Japan. J. Phys.* 8 (1933) 109.
- [65] A.T. Loburets, A.G. Naumovets, Yu.S. Vedula, *Surf. Sci.* 399 (1998) 297.
- [66] A.T. Loburets, N.B. Senenko, A.G. Naumovets, Yu.S. Vedula, in: R. Kutner, A. Pekalski, K. Sznajd-Weron (Eds.), *Anomalous Diffusion. From Basics to Applications*, Springer, Berlin, 1999, p. 1.
- [67] A.M. Gusak, F. Hodaj, A.O. Bogatyrev, *J. Phys.: Condens. Matter* 13 (2001) 2767.
- [68] V.N. Shrednik, G.A. Odisharia, *Sov. Phys. Sol. State* 11 (1970) 1487.
- [69] T. Masuda, C.J. Barnes, P. Hu, D.A. King, *Surf. Sci.* 276 (1992) 122.
- [70] B.V. Andryushechkin, K.N. Eltsov, V.M. Shevlyuga, *Surf. Sci.* 472 (2001) 80.
- [71] I.F. Lyuksyutov, H.-U. Everts, H. Pfner, *Surf. Sci.* 481 (2001) 124.
- [72] Yu.S. Vedula, I.F. Lyuksyutov, A.G. Naumovets, V.V. Poplavsky, *JETP Lett.* 36 (1982) 88.
- [73] C. Uebing, R. Gomer, *J. Chem. Phys.* 100 (1994) 7759.
- [74] M.A. Zaluska-Kotur, in: M.C. Tringides (Ed.), *Surface Diffusion. Atomistic and Collective Processes*, Plenum, New York, 1997, p. 455.
- [75] C. Uebing, R. Gomer, *Surf. Sci.* 381 (1997) 33.
- [76] I. Vattulainen, *Surf. Sci.* 412/413 (1998) L911.

- [77] M.A. Krivoglaz, A.A. Smirnov, *The Theory of Order-Disorder in Alloys*, Macdonald, London, 1964.
- [78] L.A. Girifalco, *Statistical Physics of Materials*, Wiley, New York, 1973 (Chapter 9).
- [79] A.T. Loburets, A.G. Naumovets, N.B. Senenko, Yu.S. Vedula, *Zs. Phys. Chem.* 202 (1997) 75.
- [80] P. Nikunen, I. Vattulainen, T. Ala-Nissila, *Surf. Sci.* 447 (2000) L162.
- [81] N. Fraysse, M.P. Valignat, A.M. Cazabat, F. Heslot, P. Levinson, *J. Colloid Interface Sci.* 158 (1993) 23.
- [82] B. Kasemo, *Curr. Opin. Sol. State Mater. Sci.* 3 (1998) 451.
- [83] R.D. Tilton, in: M. Malmsten (Ed.), *Biopolymers at Interfaces*, M. Dekker, New York, 1998, p. 363.
- [84] V.P. Zhdanov, B. Kasemo, *Proteins Struct. Funct. Genet.* 39 (2000) 76.
- [85] R. Imbihl, G. Ertl, *Chem. Rev.* 95 (1995) 697.
- [86] A.G. Fedorus, E.V. Klimenko, A.G. Naumovets, E.M. Zasimovich, I.N. Zasimovich, *Nucl. Instrum. Methods B* 101 (1995) 207.
- [87] Y. Nakamura, Y. Mera, K. Maeda, *Surf. Sci.* 487 (2001) 127.
- [88] H. Yasunaga, A. Natori, *Surf. Sci. Rep.* 15 (1992) 205.
- [89] H. Emmerich, C. Misbah, K. Kassner, T. Ihle, *J. Phys. Condens. Matter* 11 (1999) 9985.
- [90] A.V. Latyshev, S.S. Kosolobov, D.A. Nasimov, V.N. Savenko, A.L. Aseev, in: R. Kutner, A. Pekalski, K. Sznajd-Weron (Eds.), *Anomalous Diffusion. From Basics to Applications*, Springer, Berlin, 1999, p. 281.
- [91] B.N.J. Persson, *Sliding Friction: Physical Principles and Applications*, Springer, Berlin, 1998.