Russian Chemical Reviews **67** (2) 93 – 108 (1998) © 1998 Russian Academy of Sciences and Turpion Ltd

UDC 541.138 : 548.4.001

Computer simulation of electrochemical processes on interfaces

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Abstract. The basic problems of computer simulation of mass and charge transfer in electrochemical processes such as electrocrystallisation and corrosion of metals are analysed. Three main approaches to the simulation of electrochemical problems are considered: the Ising (lattice gas) model, molecular dynamics (MD) and Monte Carlo (MC) methods. The principal equations used in simulation techniques and examples of the simulation of particular systems are presented. The bibliography includes 136 references.

I. Introduction

Computer simulation plays an important role in the solution of many physical problems. Certainly, the use of graphical two- (2*D*) and three-dimensional (3*D*) models obtained by computer simulation is interesting not only for physicists but also for chemists.[1] Primarily, these are simulation of phase transitions in chemical systems, construction of 'phase portraits' changing in time for these systems, and predictive assessment of the evolution of hierarchic near-the-surface crystal-electrolyte structures exposed to external factors. In computer simulation of electrochemical problems, reactions involving charge transfer are included in kinetic schemes along with chemical steps. The prerequisite for concentration and charge gradients to appear is the formation of fluctuations of the material density in the vicinity of reaction sites on the surface, where chemical reactions occur. Therefore, simulation of a metal – electrolyte interface is done taking account of the collective local degrees of freedom of a system.[2,3] Computer simulations of the dynamics of surface electrochemical processes are based on the lattice gas model (the Ising model) as well as on molecular dynamics (MD) and Monte Carlo (MC) methods. The simulation techniques are well developed and the corresponding application software is available.[4]

II. Lattice gas models

Corrosion-electrochemical systems described by computer simulations can be tentatively divided in two groups: processes involving the formation of a new crystalline phase on the substrate — crystallisation (*i*) and processes of dissolution — decrystallisation (*ii*).

Gilmer's approach is quite sufficient if the 'rigid' 2*D*-lattice Ising kinetic model is used for the computer-assisted description of the formal kinetics of growth and dissolution of ideal crystal lattices.[5,6] The following assumptions are made: (1) the atoms removed from the surface can only enter multi-centre adsorption states with maximum stability (*S*-positions); (2) the order of occupying the adsorption cells is fulfilled according to which cell can contain no more than one atom; (3) the van der Waals metal – metal (M – M) interaction is approximated by a pair Mie potential of the type $U(r) = A/r^n - B/r^m$, where A and B are constants characterising the attractive and repulsive forces, respectively, r is the distance between the particles, and $n > m > 0$. The Hamiltonian for a simple cubic Ising lattice taking account of interaction between the closest neighbours (*NN*) has the form:[7]

$$H = -J\sum_{\langle ij \rangle} \sigma_i \sigma_j \,, \qquad (1)$$

where J is the exchange energy; σ_i and σ_j are variables of the occupancy of cells i and j, respectively; the term $\sigma_i = \pm 1$ 'controls' the second assumption of the Ising model, and the symbol $\langle ij \rangle$ shows that summation is carried out over pairs of the closest neighbours. The formation of a step on this lattice (Fig. 1) is always accompanied by the formation of centres possessing excess charge and deficiency of mass, kinks, which are the most adsorption-active cells on a crystal surface (the TLK-model, from terrace T, step L, kink K). In these models, the solid is a Kossel – Stransky crystal †.[8]

The pair potential can be written in a form convenient for practical use:

$$U(r_{ij}) = \frac{E_1[a(B_a/r_{ij})^m - b(C_{lat}/r_{ij})^n]}{b-a} \,, \qquad (2)$$

where E_1 is the depth of the potential well; the a and b constants are the degrees of 'far-range action' and 'hardness' of the potential, respectively; B_a and C_{lat} are constants of attraction and repulsion interaction, respectively; and r_{ij} is the distance between the reacting particles i and j. The potential most commonly used for computer simulation of electrochemical systems is the Lennard-Jones potential, while the Buckingham potential

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Received 21 January 1997
Uspekhi Khimii **67** (2) 107 – 124 (1998); translated by S S Veselyi

† A defect-free crystal constructed according to Drude – Sommerfeld [9] (from ions oscillating in equilibrium positions with a Debye frequency of $\mu_D = 10^{13}$ s^{-1} near the equilibrium positions, and an electron subsystem).

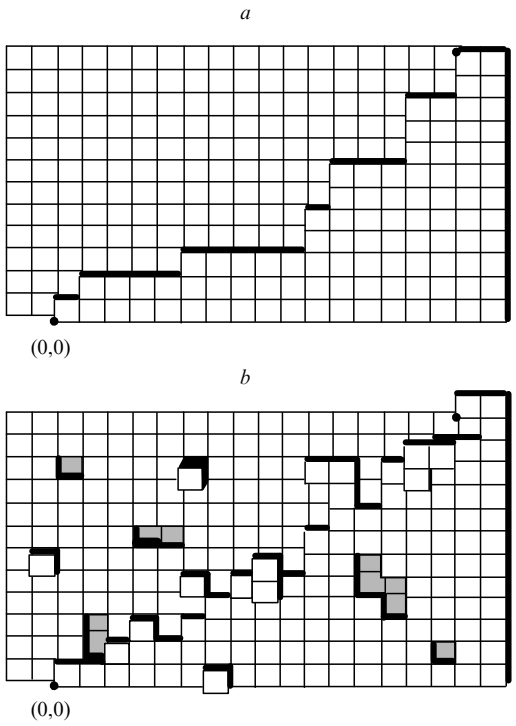


Figure 1. Typical stepped configurations on the (100) face of a simple cubic lattice; (*a*) $T = 0$ K; (*b*) $T > 0$ K.

and the anharmonic Morse potential are used more rarely. These potentials are written as follows:
the Lennard-Jones potential (pair potential 6–12)

$$U_{\mathrm{LJ}}(r_{ij}) = 4E_{\mathrm{l}}\left[-\left(\frac{C_{\mathrm{lat}}}{r_{ij}}\right)^6+\left(\frac{B_{\mathrm{a}}}{r_{ij}}\right)^{12}\right], \tag{2a}$$

the three-parameter Buckingham potential (if repulsion is determined by overlapping of wave functions)

$$U_{\mathrm{B}}(r_{ij}) = 4E_{\mathrm{l}}\left[-\left(\frac{C_{\mathrm{lat}}}{r_{ij}}\right)^6+B_{\mathrm{a}}\exp\left(-\frac{C_{\mathrm{lat}}}{r_{ij}}\right)\right], \tag{2b}$$

and the Morse potential

$$U_{\mathrm{M}}(r_{ij}) = \delta\{\exp[-2\alpha(r_{ij}-C_{\mathrm{lat}})]-2\exp[-\alpha(r_{ij}-B_{\mathrm{a}})]\}, \tag{2c}$$

where δ and α are empirical constants. The energy E_{l} is determined by the nature of interaction of particles and is as high as ~ 10 eV for the ionic bond, $\sim 1-5$ eV for the metal bond, ~ 0.5 eV for the hydrogen bond and ~ 0.1 eV for the van der Waals interaction.

The pair interaction potentials (2a) and (2b) are used in the case of nonspecific physical adsorption, when $E_{\mathrm{l}} < 0.5$ eV. The adsorption energy E_{ads} can be calculated from a relation obtained by integration of the Lennard-Jones potential (2a) assuming that atoms (the number of which in unit volume of a crystal equals the Avogadro number, N_{A}) form an averaged 'jelly'-background with mean parameters E_{l} and C_{lat}

$$E_{\mathrm{ads}} = \frac{\pi}{3}N_{\mathrm{A}}E_{\mathrm{l}}B_{\mathrm{a}}^3\left[\left(\frac{C_{\mathrm{lat}}}{r_{ij}}\right)^3-\frac{1}{15}\left(\frac{C_{\mathrm{lat}}}{r_{ij}}\right)^9\right]. \tag{3}$$

Models of the liquid mercury surface in contact with an electrolyte are in satisfactory agreement with the relationship (3).[10] An ideal flat condenser is formed in this case. The minimal distances between the particles

$$l \equiv r_{ij\,\min} \simeq \frac{C_{\mathrm{lat}}}{\sqrt[6]{5}}$$

have to be smaller for flat condenser models than for an actual surface M. Hence, it is necessary to take into account both the crystallographic features of adsorption and changes in the electronic structure of an adsorbate–adsorbent system (mixing of wave functions of valence electrons of the adsorbed particles with those of the metal adsorbent occurs).

The stability of two-dimensional lattices (usually, tetragonal, trigonal and hexagonal lattices incorporating 32×32, 64×64, 128×128, 256×256 *etc*. cells are analysed) depends on the total energy of the system. The dynamically unstable tetragonal lattice is transformed into the trigonal lattice, which is more energetically stable.[11] Dimers of a tetragonal lattice with antiparallel spins oriented along a particular crystallographic direction are rearranged in a simultaneous cooperative act[12] into a more stable Ising structure (Fig. 2). As a result, the density of dimers increases.

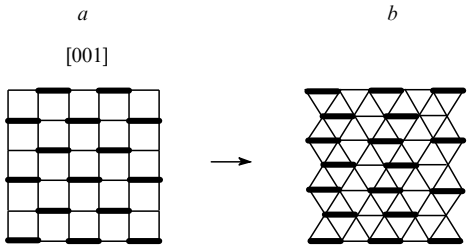


Figure 2. Transformation of simple tetragonal lattice (*a*) into triangular lattice (*b*).

The rearrangement occurs in the sequence: self-organising → high order → low entropy[13,14] and results in the generation of a low-entropy surface structure. The kinetics of destruction of two-dimensional lattices can follow their reversible nature, *i.e*., transition of rows or separate intermediates into solution with restoration of the coverage provided that the concentration of the surfactant in solution is sufficient. The equation for the destruction rate (current I) has the 'Arrhenius form' determined by the degree of coverage of the crystal with surfactant particles, θ_{surf}, which in turn depends on the external factors and internal state of the crystal surface–electrolyte system:

$$I = v_i(\theta_{\mathrm{surf}})\theta_{\mathrm{surf}}^n \exp\left[-\frac{E_{\mathrm{a}}(\theta_{\mathrm{surf}})}{kT}\right], \tag{4}$$

where $v_i(\theta_{\mathrm{surf}})$ is the pre-exponential frequency factor (vibration frequency of ith metal surface particles, $10^{13}-10^{14}$ s^{-1}), n is the order of the reaction between the adsorbed particles, and $E_{\mathrm{a}}(\theta_{\mathrm{surf}})$ is the activation energy of interaction of passivating particles in $2D$-structures. The $E_{\mathrm{a}}(\theta_{\mathrm{surf}})$ dependence is nonlinear: at $\theta \leqslant 0.2$, the interaction of the surfactant particles in the adsorbed layer can be neglected, but at $\theta > 0.8$ (under conditions of rapid increase in the B_{a} constant), an attraction correction should be made to determine $E_{\mathrm{a}}(\theta_{\mathrm{surf}})$. Usually, $E_{\mathrm{a}}(\theta_{\mathrm{surf}}) = E_{\mathrm{b}}-\Delta H_{\mathrm{ads}}$, where E_{b} is the bonding energy of the surfactant particles and ΔH_{ads} is their heat of adsorption on the crystal surface. The pre-exponential terms of kinetic equation (4) take account of the adsorption isotherm of a surfactant on the crystal surface, that is calculated within the scope of the Ising lattice model.[15] This determines changes in the rate of reorganisation of surface intermediates and, as a result, the current I across the interface.

Further, it is worthwhile to consider, within classical concepts, the interaction of a $2D$-film with a substrate leading to the formation of some new phases (layers). For example, this interaction is typical of the inhibition of metal dissolution.[16] If only the potentials of pair interactions 'a particle in film–a particle in substrate' are taken into account additively, then, according to Heitler and London,[17] the pair potential is expressed as:

$$U(r) = \sum_i U_i(r) = -\frac{K_L}{r^6}, \quad (5)$$

where $K_L = (3/4)\hbar v_0 \varepsilon^2$ is the London constant, $\hbar = h/2\pi$ is the Planck constant, v_0 is the characteristic frequency of vibration of charged particles, and ε is the polarisability of particles. Then, according to Ref. 18, one can write:

$$U(r) = -\int K_L r_{ij}^{-6} N_A \mathrm{d}V, \quad (5a)$$

where N_A is the number of particles per unit molar volume of the metal, $\mathrm{d}V$ is an element of the solid phase volume (in a particular case, the volume of the adsorbed particle) at a distance r_{ij} from a particle given by the r coordinate in the first near-surface layer of the substrate. If N_A = const, then

$$U(r) = -\frac{N_A \pi K_L}{6l^3}, \quad (5b)$$

where l is the shortest distance between the adsorbate and adsorbent particles. In the flat condenser model, the adsorbate and adsorbent are independent layers, and if the surfactant layer penetrates into the substrate, then to estimate $U(r)$ it is necessary to integrate over the depth l of the substrate. Integration gives

$$U(r) = -\frac{\Gamma_{\mathrm{surf,\,M}}}{12\pi l^2}, \quad (5c)$$

where $\Gamma_{\mathrm{surf,M}} = \pi^2 N_A^2 K_L$ is the Hamaker constant.[19] For example, such penetration occurs in the case of hydrogen adsorption. The size of the cell is close to that of the adsorbed hydrogen atom, that is, the use of the Ising model for the estimation of hydrogen adsorption is substantiated. If an electrical double layer appears and charges are transferred between the inhibiting surfactant film and the substrate, $\Gamma_{\mathrm{surf,M}}$ can be calculated by summing pair potentials for three-dimensional elements

$$\Gamma_1 = \frac{3}{4}\pi^2 N_{\mathrm{A,\,surf}}^2 \varepsilon_{\mathrm{surf}}^2 E_{i,\mathrm{surf}}, \quad (6)$$

where $N_{\mathrm{A,\,surf}}$ is the number of surfactant particles in unit molar volume of the film and $\varepsilon_{\mathrm{surf}}$ and $E_{i,\mathrm{surf}}$ are the polarisability of surfactant particles and the ionisation potential in the surfactant film, respectively. After the film–substrate interaction has occurred, the Hamaker constant in equation (5c) is determined by a superposition of constants for the film (Γ_{surf}) and the metal (Γ_M)

$$\Gamma_{\mathrm{surf,\,M}} = \Gamma_{\mathrm{surf}} - 2\sqrt{\Gamma_{\mathrm{surf}}\Gamma_M}\left(\frac{2\sqrt{E_{i,\mathrm{surf}}E_i}}{E_{i,\mathrm{surf}} + E_i}\right) + \Gamma_M, \quad (7)$$

where E_i is the ionisation energy of the metal.

If the ionisation energies in the inhibiting film and in the metal become equal, $E_{i,\mathrm{surf}} \simeq E_i$, relation (7) can be simplified

$$\Gamma_{\mathrm{surf,\,M}} = (\sqrt{\Gamma_{\mathrm{surf}}} - \sqrt{\Gamma_M})^2. \quad (8)$$

According to Frumkin,[20] the lateral interactions of adsorbed particles

$$E_a(T,\theta_{\mathrm{surf}}) = E_b + \Delta E_{\mathrm{lat}}(T,\theta_{\mathrm{surf}})$$

in a two-dimensional adsorption structure can also be of chemical or physical nature, and $E_a(T,\theta_{\mathrm{surf}})$ can be >0.5 eV or <0.5 eV. The Frumkin's correction factor $\Delta E_{\mathrm{lat}}(T,\theta_{\mathrm{surf}})$ decreases with an increase in temperature and increases for $\theta_{\mathrm{surf}} \geqslant 0.2$. Interactions in 'surfactant particles in solution–a surfactant in an inhibiting film' and 'surfactant particles in solution–substrate atoms' systems result in the formation of defects in the covering surfactant film because of the non-equivalence of energetic positions of the substrate atoms.

The interaction of particles in the 2*D*-structure of the covering film determines a hierarchy of defects and 3*D*-islands of the surfactant, which depends strongly on the structural features of the substrate. Within the scope of the linear elasticity theory, the contact of films with metal surfaces is considered taking account mostly of two parameters: the module of elasticity and the differences in the crystallographic parameters of film and substrate lattices. If the lattice parameter of an adsorbed covering 3*D*-film is larger than that of the substrate, the relaxation of strain in the film ends with the formation of discrepancy dislocations, and it is not deteriorated; in the absence of strain relaxation, the film is deteriorated.

Computer simulations use models that combine simultaneous formation of 2*D*- and 3*D*-structures on heterogeneous substrates. Analytical solutions of equations that describe inhibiting 2*D*-structures (on singular substrates) and 3*D*-islands on surfaces with uniformly distributed defects of the same nature are only possible in the lattice gas model.

The adsorption of an inhibitor on a non-uniform metal surface can be accompanied by the formation of both two-dimensional films and three-dimensional structures. The former case is less probable than the latter, but exact solutions are possible for it within the scope of the models considered. In the 2*D*-case, for the adsorption of light particles (H, O, N, CO, *etc.*) on singular single-crystal planes, the discreteness of charges of single, strongly bonded substrate atoms in an ensemble is described relatively accurately. However, it is impossible to simulate the behaviour of a big particle on the surface within the Ising model. The situation is similar to that when one has to play chess using chesspieces larger not only than the board squares but also than the board itself. Models are required that take into account the direction (correlated with the surface structure) of particle movement along the crystal surface (along definite preferred trajectories) and the presence of periodic extended surface and subsurface defects. When complex particles (large inorganic and/or organic molecules) are adsorbed, the field of extended surface and subsurface defects creates conditions for the formation of 3*D*-phase islets.[21,22] The three-dimensional adsorbed formations of inhibiting particles interact with each other both through the substrate and directly, creating their own hierarchic structure.

The study of the phase transition upon metal dissolution in the presence of surface 2*D*-films is an example of the classical approach to the consideration of the corrosion problem. Inhibiting layers on a non-uniform metal surface are formed more commonly as a superposition of 2*D*-films and 3*D*-structures. Two-dimensional films are formed on surfaces of crystallite (grain) terraces, which are, as a rule, non-singular stepped high-index planes. The expanse (surface area) of terraces on such stepped surfaces is sufficiently large to be treated as main structural elements (as regards surface area). The lattice gas model is quite applicable for the description of the adsorption of a metal dissolution inhibitor on densely packed ideal terraces. The corresponding Hamiltonian contains terms describing not only the surfaces of the metal and adsorbed particles of a surfactant but also exchange energies of their interactions, *i.e.*, the usual Ising Hamiltonian (1) becomes more complex

$$H = -E_{NN}\sum_{NN}\sigma_i\sigma_j - E_{NNN}\sum_{NNN}\sigma_i\sigma_j, \quad \sigma_i = \pm 1. \quad (9)$$

It contains exchange energies of interaction not only between the closest neighbours *NN*, but also between the next to the closest neighbours *NNN*. If one limits the consideration to $NN = 1$ and $NNN = 2$ and designates the *NN*- and *NNN*-interactions as E_1 and $E_2 = RE_1$, $R < 0$, then the parameter for the critical temperature (T_c) for the formation of a new phase on the surface is

$$\sinh\frac{2E_1}{kT_c}\sinh\frac{2E_2}{kT} = 1 \quad \text{or} \quad -\frac{2kT}{E_1}\ln\left(\tanh\frac{E_1}{4kT_c}\right) = \frac{E_2}{E_1}.$$

'Loose' steps and kinks on the steps have different adsorption characteristics from the terraces. Only in rare situations can adsorption be regarded as physical adsorption. The strength of bonds of adsorbed particles with kinks is high. The behaviour

(kinetics of movement and inhibition) of steps is described in terms of dislocation dynamics.

The formation of inhibiting covering 2*D*-films can be considered both from the viewpoint of the classical nucleation theory and taking account of the quantum-chemical nature of interaction in the adsorbate – adsorbent system.[23] In the classical variant, the surfactant particles that are adsorbed and form a uniform film are treated in the mean field approximation. The ratio of the density of this film (ρ) to the activity of spherically symmetrical particles in it (a_{surf}) is described by the equation:

$$\frac{\rho}{a_{\text{surf}}} = \mathrm{A}\left\langle \exp\left(-\frac{E_{\text{attr}}(T,\theta_{\text{surf}})}{kT} \right) \right\rangle ,$$

where $A = v_t(\theta_{\text{surf}})\exp(\Delta S/k)$ is the Einstein configurational term, ΔS is the entropy change in the adsorption ensemble, and $E_{\text{attr}}(T,\theta_{\text{surf}})$ is the attraction potential. When a uniform temperature-independent field of the inhibiting film is created, $E_{\text{attr}}(T,\theta_{\text{surf}})$ can be approximated by the mean field potential $E_{\text{mf}}(\theta_{\text{surf}})$, or $E_{\text{attr}}(T,\theta_{\text{surf}}) \simeq E_{\text{mf}}(\theta_{\text{surf}})$.

The classical models of new phase growth on a crystal surface (they can be divided in three groups, Fig. 3) are based on the formation of 2*D*-films and insular 3*D*-structures. According to the FVdM model, the growth of inhibiting films occurs by a mechanism involving a 'carpet' of a 2*D* inhibitor layer 'unrolling' over the crystal surface; the VW model assumes that flat disks arise and then coalesce; the SK theory involves a combination of 2*D*-films and 3*D*-islets. There is also a variant of the VW model in which the new phase grows as a column composed of adsorbed particles (see Fig. 3). This is the 'solid on solid' model, whose distinguishing feature is a high process rate (in a particular case, high cathodic current density, i_c), low supersaturation of reacting particles in the near-electrode layer $\Delta\gamma^{\neq}$, and high force field of the surface (subsurface) active centre where the new phase appears.

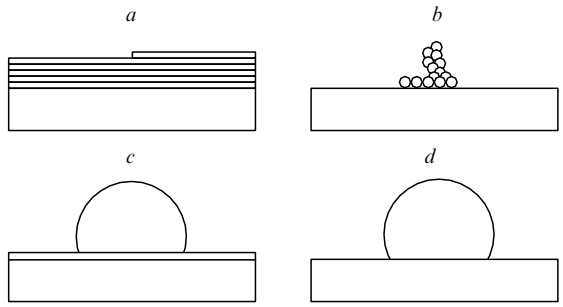


Figure 3. Scheme of growth of 2*D* and 3*D* structures on a crystal surface; (*a*) the Frank – Van der Merve model (FVdM); (*b*) 'column'; (*c*) the Stransky – Krastanov (SK) model; (*d*) the Volmer – Weber (VW) model.

The estimated specific surface energy change, $\Delta\sigma$, is the criterion of applicability of these models. Under conditions of heteroepitaxial growth of covering films (where the pseudomorphism mechanism operates), if the structure of the covering film is analogous to that of the structure of the substrate or maintains its symmetry upon minimisation of $\Delta\sigma$, the FVdM mechanism operates. Thus, at $\Delta\sigma = 0$ the FVdM mechanism, at $\Delta\sigma > 0$ the VW mechanism, and at $\Delta\sigma < 0$ the SK mechanism operates. The latter model (SK) is used in computer simulations more commonly than the two others. The growth models considered above (see Fig. 3) provide a reasonably good description of the structures observed in experiments.[24, 25] The phase transition considered in classical models is initiated by changes in surface tension, which appear because of disagreement between the lattice spacing of the substrate and the adsorbate.

Presently, the main difficulty in making a complete quantitative description of metal – electrolyte systems is the adequate representation of periodic 2*D*-structures at the level of regularly spaced particles (atoms, surfactant molecules) and accounting for the quantum-chemical nature of the interaction between the 2*D*-film and the substrate. The interaction mentioned above is described by model Anderson – Ising – Hubbard Hamiltonians [26] for each particular system 'M – inhibiting surfactant – electrolyte'. It should be noted that calculations using model Hamiltonian methods are often rather complicated, and Hamiltonians for electrochemical systems contain many uncertain parameters.

Let us analyse the 2*D*-nucleation process. We shall take the topological principle as the base and consider a series of main models, gradually complicating the dimensionality. It is reasonable at the beginning to give a description of a lattice gas model for singular defect-free surface crystals. Nucleation can also be considered in a classical approximation in which joining and formation of films occurs from fragments larger than separate atoms and molecules, surface clusters. In the lattice gas model, the degree of coverage of a crystal surface by inhibiting surfactant particles is expressed by the formula [27]

$$\theta_{\text{surf}} = \frac{1}{N_{\text{s}}}\sum_{i=1}^{N_{\text{a}}} \langle C_i \rangle_T , \qquad (10)$$

where N_{s} and N_{a} are the number of lattice points of substrate atoms and the number of occupied points, respectively; C_i is the variable of coverage ($C_i = 1$ if the surface points N_{s} are occupied and $C_i = 0$ if these points are not occupied). In formula (10), θ_{surf} is the molar fraction of occupied active centres on the crystal surface, and angle brackets henceforth denote statistical averaging over the main system state at a certain temperature T.

The variable of coverage $C_i \equiv \sigma_i$ determines the Boltzmann factor

$$B = \exp\left(-\beta \sum_{i,j} \sigma_i \sigma_j \right) ,$$

where $\sigma_i = \pm 1$, $i \neq j$, $\beta = T^{-1}$. Equation (10) follows from the main relationship for the variable of coverage (S) in the Ising model

$$S = \frac{1}{N_{\text{s}}^d}\sum_{i=1}^{N_{\text{s}}^d} \sigma_i ,$$

where $d \geqslant 2$ is the fractal dimensionality ($d = 2$ in the two-dimensional model).

Summation in equation (10) is performed over all lattice points whose size is close to that of the adsorbing surfactant particles. When the sizes of adsorption cells are close to those of adsorbate particles, the Ising 2*D*-model employs a diagram technique.[28] At a certain average temperature T, the surfactant forms a monolayer, whose particles are bonded to the substrate particles with an energy E_{b}. This energy is determined by the sum of correlation functions of the spin on the crystal surface and the spins of the adequately conjugated surfactant monolayer with the surface layer of the substrate. The loss of mechanical stability of the flat frontier of growth (dissolution) of crystal surfaces results in the formation of a surface with a cellular structure. In this process, the growth of cells during self-organising is accompanied by avalanche-like changes in the overall distribution of spins.[29]

The energies of pair additive interactions of the neighbouring (E_{NN}), next-to-neighbouring (E_{NNN}) and third-to-neighbouring (E_3) adsorbed particles occupying highly coordinated *s*-states can be defined as shown in Fig. 4. In the case of unpaired interactions, the energy is $-2E_{NN} - E_{NNN} - E_t$ (E_t is the energy of interaction of the neighbouring, *NN*, and closest-to-neighbouring, *NNN*, points). The total (configurational) energy of the three-particle (i, j, k) system (potential as in the 2*D* lattice gas model) is:

$$U_0 = -E_{\text{b}}\sum_{i=1}^{N_{\text{a}}} C_i - \sum_{i\neq j} E_{ij} C_i C_j - \sum_{i\neq j\neq k} E_t C_i C_j C_k , \qquad (11)$$

where $E_{ij} = E_{NN}$, E_{NNN}, or E_3, if i and j are the neighbouring, the next-to-neighbouring, and third-to-neighbouring sites, respectively; C_i, C_j and C_k are variables of occupation. The second

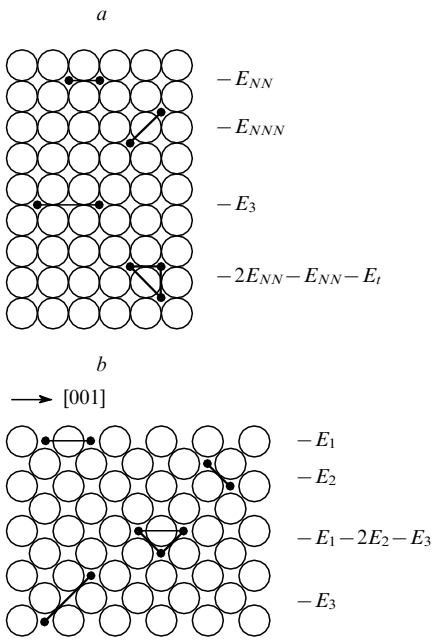


Figure 4. Energies of interaction of an adsorbed particle with a tetragonal (*a*) and centred rectangular lattice (*b*).

term in equation (11) describes all pair interactions, and the third term, all triple interactions. The prenucleation situation in the case of a centred rectangular lattice is analogous to that in the case of a square lattice (Fig. 5).

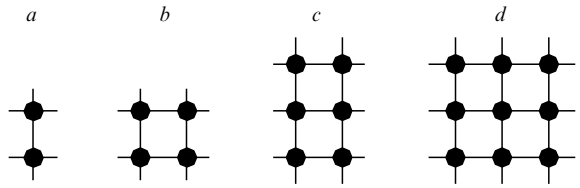


Figure 5. Completed ordered 2*D*-phases at $T = 0$ K; (*a*) c(2×2), $R < 0.5$; (*b*) *L*, $R > 0.5$; (*c*) $D_{0.25}$, $R > 0$; (*d*) $D_{0.25}$, $R > 0.5$.

The formation of condensed 2*D*-layers in the lattice gas model is described by statistical mechanics methods. Phases with low density (see Fig. 4) randomly distributed on a crystal surface are transformed into condensed phases due to the action of chemical and van der Waals forces. For example, on the (100) plane of a body-centred cubic (BCC) crystal (*c*) completed 2*D*-phases of various dimensionality are formed (see Fig. 5): *c*(2×2), *L*- and *D*-phases ($0 < R < 1$ is a dimensionless factor of confidence showing the divergence between experimental and calculated data). It should be noted that the Ising model for electrochemical contacts with charge transfer provides a good description of the results of *in situ* experiments performed by scanning tunneling electron microscopy in an electrolyte to study the initial steps of electrodeposition [30] and adsorption of solution particles on densely packed cubic crystal planes.[31]

Due to diversity of types of adsorption cells (Fig. 6) on the surface of the (100) plane, a type of unlimited percolation cluster can be formed in a 2*D*-structure.[32] The kinetics of its formation is determined by the probability of sticking of the surfactant particles to the crystal surface (*S*), which is described by the equation:

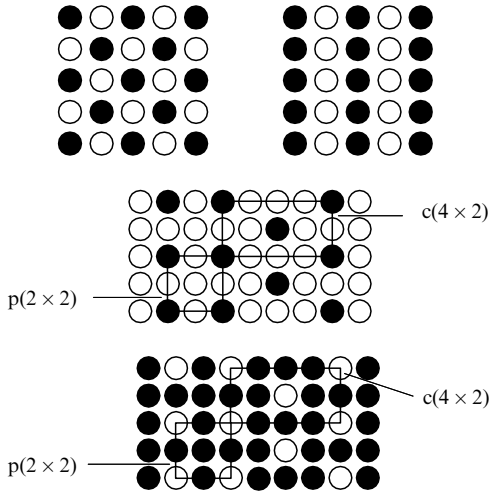


Figure 6. Types of adsorption cells on the (100) face of a body-centred cubic crystal. Here *c* and *p* are centred and primitive surface elementary cells, respectively; the black circle indicates a cell covered by an adsorbed particle.

$$S = S_0 K(E_{ij}, c_s) c_s^n ,$$

where S_0 is the initial sticking coefficient (at the degree of coverage $\theta_{surf} = 0$), K is the configurational factor determining the form of the adsorption ensemble (*e.g.*, $K = \pi$ for a dome-shaped ensemble and $K = 16\pi/3$ for a spherical ensemble), E_{ij} is the energy of interatomic (inter-particle) interaction, $c_s = f(N_s)$ is the surface concentration of vacant cells (unoccupied positions), which depends on the number of surface atoms of the substrate (total number of cells) N_s, and $n \simeq 0.3$ is a constant (degree) of nucleation of particles involved in the cluster.[33]

Computations of the probability of sticking usually employ relationships of the Arrhenius type

$$S = S_0(1 - \theta_{surf}) \exp\left(-\frac{E_{ads}}{RT}\right) , \tag{12}$$

where E_{ads} is the activation energy of adsorption of the surfactant particles on the metal surface. A particular dynamic three-dimensional percolation cluster with a high specific surface area is formed on the electrode surface. A percolation cluster can appear upon deposition of particles on the surface in the mode of underpotential deposition,[34] in the formation of composite electrochemical coatings [35, 36] and oxide structures.[37, 38] In these cases, the subsurface layer behaves as a dynamic 3*D*-electrode.

If a model takes into account only the flux of surfactant particles hitting the crystal surface and sticking to it and ignores the possibility of their diffusive movement (when the magnitudes E_b are high) along the surface, the coalescence of islets of condensed phases according to the VW model results in the formation of condensed layers. The particles in adsorbed layers interact through repulsive and attractive forces, which differently depend on the distance. As the distance decreases, the repulsive forces grow more quickly than the attractive forces.

Within the lattice gas model with account of the U_0 energy [from equation (11)], the adsorption energy E_{ads} can be determined as follows:

$$E_{ads} = \frac{\langle U_0 \rangle_T}{N_s} = -E_b \theta_{surf} - \frac{1}{N_s} \sum_{i \neq j} E_{ij} \langle C_i C_j \rangle_T - \tag{13}$$
$$- \frac{1}{N_s} \sum_{i \neq j \neq k} E_t \langle C_i C_j C_k \rangle_T ,$$

where N_s is the number of active lattice points to be occupied.

Equation (13) is written for a canonical ensemble at fixed independent T and θ_{surf}. If interaction of adsorbed particles occurs in a covering 2D-film, a term describing this should be added to equation (13), namely, $\mu_{surf}N_a$ (where μ_{surf} is the chemical potential of particles in the 2D-film, and N_a is the number of occupied points on the crystal surface). In the Ising model, the Hamiltonian for a crystal growing in an equilibrium mode has the form:[39]

$$H = 2E_b \sum_{\langle i,j \rangle} \left[C_i(1 - C_j) + (1 - C_i)C_j\right] + \mu \sum_i C_i \,, \qquad (14)$$

where E_b is the energy of cleavage of the interatomic bond between the closest NN-neighbours, summation $\langle i,j \rangle$ is carried out over pairs of NN-neighbours, and $\mu < 0$ is the energy of formation of a commensurate adsorbed 2D-phase 'not linked with the surface layer of the crystal'. The Hamiltonian for a system in which non-commensurate 'linked' films are formed from adsorbed layers, or the crystal lattice grows further, is more complex because it includes terms describing the interaction in 'linked' layers

$$H = U_0 - \mu_{surf}N_a = -(E_b + \mu_{surf}) \sum_{i=1}^{N} C_i - \qquad (15)$$

$$- \sum_{i \neq j} E_{ij}C_iC_j \; - \sum_{i \neq j \neq k} E_t C_iC_jC_k \,.$$

At T = const, the dependence of μ_{surf} on θ_{surf} is described by the adsorption isotherm

$$\mu_{surf} = \frac{1}{N_a}\left(\frac{\partial F}{\partial \theta_{surf}}\right)_T \,, \qquad (16)$$

where F is the Helmholtz free energy of the system

$$F = -kT \ln \mathrm{Tr} \exp\left[-\frac{H\{C_i\}}{kT}\right] , \; \mathrm{Tr} = \sum_{i=1}^{n} a_{ii} \,, \; C_i = 0.1 \,,$$

where the trace Tr means summation over all configurations (see Fig. 4). The condition $C_i = 0.1$ imposed on the Hamiltonian $H\{C_i\}$ means the absence of attraction–repulsion interactions in surface 2D-phases of adsorbed surfactant particles. In the Ising model taking account of the second limitation (see above), the variable of coverage C_i is given by the formula

$$C_i = \frac{1 - \sigma_i}{2} \,, \; \sigma_i = \pm 1,$$

where the spin is $\sigma_i = \pm 1$.

For particles of an adsorbing surfactant of the same type which do not interact, equation (13) is simplified when the temperature of the crystal increases to temperatures for desorption of the surfactant from the surface ($T \to \infty$):

$$E_{ads}(T \to \infty) = \qquad (17)$$

$$= -E_b\theta_{surf} - 0.5\theta_{surf}^2 \sum_{i(\neq j)} E_{ij} - \; 0.33\theta_{surf}^3 \sum_{i \neq j(\neq k)} E_t \,,$$

where $\theta_{surf}^2 = \langle C_iC_j \rangle$, $\theta_{surf}^3 = \langle C_iC_jC_k \rangle$.

If the following designations are introduced: the Jackson–Temkin parameter

$$\beta_{JT} = 0.5\frac{E_b}{kT},$$

$$m = \tanh\beta_{JT} \,, \;\; \beta_{JT} = \ln\frac{1+m}{1-m} = \ln\frac{1-\theta_{surf}}{\theta_{surf}} \,,$$

from equation (16) we obtain the Langmuir isotherm in the form

$$\frac{\mu_{surf} + E_{ads}}{kT} = \ln\frac{\theta_{surf}}{1 - \theta_{surf}} \,, \qquad (18)$$

where the bond energy $E_b = 2(\mu_{surf} + E_{ads})$.

The anti-logarithm of isotherm (18) shows that the activation energy $\mu_{surf} + E_{ads}$ in the expression $\exp[(\mu_{surf} + E_{ads})/kT]$ is responsible for overcoming the potential difference in the double layer formed on the electrolyte side at the metal–electrolyte interface. This energy is related to variations in the Fermi energy of the metal, E_F, in the case of non-commensurate interaction in a film–substrate system and degree of solvation of surfactant particles in different phases that change the charge during the phase transition.

The Hamiltonian that describes the adsorption of surfactant particles within the Anderson–Newns model has the form:[40, 41]

$$H = H_{surf} + H_M + H_{surf-M} \,, \qquad (19)$$

where H_{surf} and H_M are Hamiltonians of the adsorbed particle and the pure substrate (metal), respectively; H_{surf-M} is the Hamiltonian of the bond between them. The sum $H_{surf} + H_{surf-M}$ in operator (19) is usually replaced by a Hamiltonian taking the adsorption of the surfactant into account

$$H = H_M + H_{ads} \,, \qquad (20)$$

where

$$H_{ads} = -kT \sum_{l,v} \ln\left\{1 + \exp[-\beta_{JT}(E_{l,v} - \mu_{surf})]\right\} .$$

Summation is done over all occupied adsorption cells N_s. Summation over l reflects the one-centre (on top) positions of the adsorbed surfactant particles, while summation over v corresponds to their bridging positions for a potential of the form

$$E_{l,v} = \sum_j \alpha_{lvj} \,,$$

where α_{lvj} is the constant of attraction–repulsion interaction between the surfactant and the metal surface.

When estimating the degree of coverage within the Ising model, one performs summation over all adsorption cells $\{l,v\}$, and formula (10) is reduced to a more concrete expression

$$\theta_{surf} = \left\langle \sum_{l,v} \frac{1}{\exp[(E_{l,v} - \mu_{surf})/kT] + 1} \right\rangle .$$

In almost all cases, the surfactant particles adsorbed on a crystal surface induce reorganisation in first near-surface layers (phase transition of second order, without a heat effect or change in the specific volume). If the electronic subsystem of the crystal lattice is only slightly affected by surfactant adsorption, computer simulation can use the Hamiltonian (15) in the form:[40, 41]

$$H = 0.5 \sum_{i \neq j} E_{ij}\langle C_iC_j \rangle_T \; + \sum_{i,j} C_iU(r_l^0 - r_l) \,, \qquad (21)$$

where E_{ij} is the energy of inter-particle interaction (adsorbate–adsorbent); U is the interaction potential, r_l^0 and r_l are the coordinates of a surface atom of the adsorbent before and after the reorganisation, respectively.

It should be noted that in electrolytes, the system 'metal surface–covering surfactant film' interacts with the solvent. The efficiency of interaction depends on the degree of coverage θ_{surf}. At $\theta_{surf} \ll 1$, it is necessary to take the predominating effect of interaction of particles in the film into account. Kornyshev and Schmickler [42] introduce into Hamiltonian (19) an additional term of the type $E_{sol}(q_a)\langle C_iC_j \rangle_T$, where $E_{sol}(q_a)$ is the energy of interaction of an adsorbed particle with a mean charge q_a with the solvent.

In accordance with the classical concepts, the adsorbed particles have vibrational, translational and rotational degrees of freedom. The potential part of the total energy of these slow movements is determined by the electronic part of the Hamilto-

nian. As new physical aspects of interaction in the adsorbate–adsorbent system are discovered, the structure of the model Hamiltonian changes.

The van der Waals attraction or repulsion is caused by overlapping and orthogonalisation of wave functions of electronic states for the substrate and the adsorbed atom. The interaction between the adsorbed particles can be of at least four types:[43] electrostatic (Coulomb or dipole–dipole), due to overlapping of orbitals of adsorbed atoms or through phonons of the substrate by direct interaction ($\theta_{surf} \leqslant 1$) and by indirect interaction through electronic states of the metal. For covering layers of a surfactant with very low degrees of coverage ($\theta_{surf} \ll 1$), the Anderson's model Hamiltonian is constructed using Hubbard operators.[41] The use of these operators makes it possible exactly to take into account the correlation of electrons on a doping (adsorbed) atom and to overcome the difficulties related to the need to combine the quantum character of an electronic subsystem with a classical representation (the Drude–Sommerfeld model[9]) of the crystal lattice.

A Hamiltonian for an adsorbate–adsorbent system in which reorganisation of the metal surface induced by adsorbed particles occurs has the form[44]

$$H = U - \mu_{surf} \sum_{i=1}^{N_a} \langle C_i \rangle \,, \tag{22}$$

where the operator C_i equals unity if the act of adsorption has occurred, and $C_i = 0$ otherwise. The interaction potential in equation (22) can be presented as a sum of four terms

$$U = U_0 + U_M + U_{surf} + U_{M-surf} \,, \tag{23}$$

where U_0 is the potential from the 2*D*-lattice gas model for adsorbed surfactant particles with no account of reorganisation of the metal surface [see equation (11)], U_M is the potential reflecting pair interactions of atoms in the bulk and on the surface of a crystal M; U_{surf} and U_{M-surf} are potentials composed taking account of the following effects of the substrate: lateral, dipole–dipole, those occurring due to overlapping of orbitals of adsorbed surfactant particles, electronic, and phononic.

In the case of 3*D*-nucleation at the interface, simulation requires 'cutting' of a definite volume including particles in the near-surface layer of the crystal, on the surface, and in the electrolyte. In this respect, lattice models have wider 'possibilities' in comparison with models based on the use of numerical methods. The cluster approach in the lattice gas model has been used for constructing equations that describe an equilibrium distribution of molecules in a multicomponent solution taking account of orientationally directed interactions.[45] To solve this problem, commensurate and non-commensurate layers of a surfactant are considered. The degree of commensurability depends on the sizes of surfactant particles and is primarily determined by the mean distance from adsorbing surfactant particles to the nearest adsorption points. Simulation of commensurability is performed by minimising the energy of additive interactions of atoms between each other $E(r_i - r_{i-1})$, which is very sensitive to the size of particles. If a commensurate phase of a protective inhibitor film has formed on a metal crystal surface ($\theta_{surf} \simeq 1$) that displays cooperative properties upon corrosive action of the medium, Hamiltonian (22) can describe the well-known Frenkel–Kontorova model[46]

$$H = \sum_i \left[E(r_i - r_{i-1}) + U(r_i) \right] , \tag{24}$$

where r_i is the coordinate of the ith atom and $U(r_i)$ is the periodic potential of substrate surface atoms in the form

$$U(r_i) \sim A \sin \frac{2\pi r_i}{\lambda} \,,$$

where A and λ are the amplitude and length of the potential disturbance wave, respectively. The periodic potential of the lattice, which is the sum of local potentials $U(r_i - r_{i-1})$ of additive interactions of the particles, equals

$$U(r) = \sum_i U(r_i - r_{i-1}) \,.$$

For simplification, one can accept

$$U(r) = U(r + 1)$$

and consider the action of this potential in a commensurate 'cross-linked' subsurface layer of the metal. Additive interactions $E(r_i - r_{i-1})$ occur in a commensurate M–surfactant 'sandwich'. In the physical sense, Hamiltonians (24) are practically equivalent for 3*D*- and 2*D*-layers. In this model, a monolayer of a surfactant undergoes the action of the periodic potential of the substrate that is a plane of an ideal crystal, while particles of the adsorbate (surfactant) in the 3*D*-structure elastically interact with each other. Naturally, a Hamiltonian of the type (24) describes a very limited number of real cases, since rather strict limitations are imposed on it: the similarity of sizes of metal atoms and surfactant particles, of the electrical and vibrational characteristics of the metal and the surfactant. Perhaps, covering of the surface of a single crystal of a 3*d*-metal (Fe, Co, Ni) with atoms of noble 4*d*- or 5*d*-metals (Ru, Rh, Pd, Os, Ir, Pt) corresponds to this model.

When a real crystal surface is represented by a combination of steps and terraces (Fig. 7), Hamiltonian (24) becomes more complicated, as it includes terms corresponding to covering of both the steps and the terraces and can be expressed[47] by parameters for a partial coverage of the adsorption centres

$$n(i,j) = \left(\frac{N_a}{N_s} \right)^d ,$$

where $2 < d < 3$ is the dimensionality.

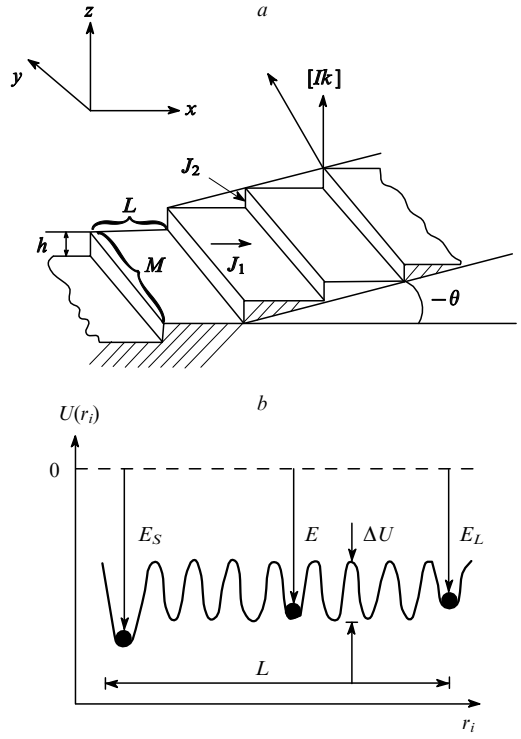


Figure 7. A model (*a*) and an energy diagram (*b*) for surfactant adsorption on a metal surface.

The complicated Hamiltonian has the form:

$$H = E_1 \sum_{j=1}^{M} n(1,j) - E_L \sum_{j=1}^{M} n(L,j) - E \sum_{i=2}^{L-1} \sum_{j=1}^{M} n(i,j) - \quad (25)$$

$$-0.5E_{\text{surf-surf}} \sum_{j=1}^{M} \{n(1,j)[n(1,j-1) + n(1,j+1) + n(2,j)] +$$

$$+ n(L,j)\big[n(L,j-1) + n(L,j+1) + n(L-1,j)\big] +$$

$$+ \sum_{i=2}^{L-1} n(i,j)\big[n(i,j-1) + n(i,j+1) + n(i+1,j) + n(i-1,j)\big]\},$$

where E_1, E_L, and E are energies of M – surfactant bonds at the end, at the beginning of a step, and on a terrace, respectively; $E_{\text{surf-surf}} = \mu_{\text{surf}} N_a$ is the energy of mutual repulsion in the adsorbate – adsorbent system. In relationship (25), the length of terraces is L, the length of steps is M, and the following condition is fulfilled: $M \gg L$. The step height is h, and the negative slope of the step face to the singular surface is $-\theta$ (see Fig. 7). A change in the sign of θ changes the dynamics of movement of the steps:[47] in one case, the adsorbed surfactant particles are forced back by the moving step, and in the other, they are absorbed in the crystal. The equidistant steps of finite length M take up the adsorbed surfactant particles, and the degree of coverage in a certain row l is determined by the relationship

$$\theta_{\text{surf}} = \langle n(l) \rangle_T = \frac{1}{M} \sum_{j=1}^{M} \langle n(l,j) \rangle_T . \quad (26)$$

As regards the retention of translational invariance in a bulk near-surface surfactant layer, since high-index planes of a single crystal with surface defects in the form of rectangular steps (without kinks) are considered, summation can be done over the index j of the coordinate y. Full coverage ($\theta_{\text{surf}} = 1$) of the terrace by the adsorbate is calculated using the formula

$$\theta_{\text{surf}} = \frac{1}{LM} \sum_{l=1}^{L} \sum_{j=1}^{M} \langle n(l,j) \rangle_T = \frac{1}{L} \sum_{l=1}^{L} \theta_{\text{surf}}. \quad (27)$$

The magnitude of θ_{surf} is considered to be a constant in this case.

The results of computer simulation using equations (25) – (27) agree satisfactorily with experimental data for well-characterised stepped planes of noble metal single crystals.[48] The growing steps maintain their faces in solutions where $\theta_{\text{surf}} \ll 1$. In the model of single step growth, the flux of surfactant from the terrace (J) that has higher kinetic coefficient or higher partial rate of direct reduction i_c [see relationships (29)] predominates. The flux of surfactant from the front terrace predominates,[49] *i.e.* $J_2 > J_1$ (see Fig. 7 *a*).

Simulation of non-equilibrium single atomic steps showed [50] that the critical supersaturation

$$\Delta\gamma_c^{\neq} = \ln \frac{c_{\text{surf,c}}}{c_{\text{surf,0}}}$$

[where $c_{\text{surf,0}}$ and $c_{\text{surf,crit}}$ are the equilibrium and critical (causing a phase transition) surfactant solution concentrations, respectively, at which the step starts growing linearly] depends on its inverse length M^{-1} for lattice spacing $k < 300$. Figure 7 *a* shows a tetrahedral lattice with $\{Ik\}$ surface, where I is the number of steps and k is the lattice spacing (number of lattice sites along axis x on a densely packed terrace). As k grows, the surface ever more approximates a singular plane. At $k > 500$, critical supersaturation in the vicinity of the interface is not observed. However, actual steps in solutions containing surfactants have no distinct crystallographic faceting and non-uniformly move over the surface.

A particle that is adsorbed disturbs the electron density at the metal surface when it approaches the substrate. This disturbance propagates according to the law

$$\bar{n} = \bar{n}_0 + K_a \exp(-K_p z) ,$$

where $\bar{n}_0$ is the mean bulk concentration of electrons, K_a and K_p are coefficients of intensity and decay of electron density, and z is the coordinate on an axis normal to the metal surface. The magnitudes of K_a and K_p are determined by the nature of the metal, primarily by the work function of an electron and the Fermi level.

The interaction energy of the particles adsorbed on the substrate [$E_{ij} = E_{i,j}(T,\theta_{\text{surf}}) = E_{\text{surf-surf}}(r)$] is determined by Friedel oscillations of electron density and depends on the shape of the Fermi surface [51]

$$E_{\text{surf-surf}}(x) \sim \frac{\sin(2\vec{k}_F r + m)}{r^n} , \quad (28)$$

where $\vec{k}_F$ is the Fermi wave vector, r is the distance between interacting surfactant particles, and the constants m and n depend on the nature of the metal. The Fermi surface, *i.e.*, the surface of constant energy in a multidimensional space, is described by the $\vec{k}_F$ vectors, local Fermi levels (energies) E_F. At 0 K, all states 0.07 eV lower than E_F will be occupied, while the states higher than E_F by the same value will be vacant. The function $\phi = m/r^n$ is introduced in equation (28) to take into account the additional indirect (exchange of electrons in the surfactant – metal system through the conduction band of the substrate) contribution into the energy of the surfactant – surfactant interaction. The values of m and n depend on the shape of the Fermi surface. In terms of graphical 3*D*-models, the Fermi surface characterises a definite metal with fixed topology and constant energy in inverse space (in a particular three-dimensional case, in an inverse lattice; for example, see Ref. 52) with wave vector $\vec{k}_F$ of the electron angular momentum. A classical surface of a solid is a direct analogue of the quantum-mechanical Fermi surface for conductivity electrons in inverse space.[53] The Fermi surface is transformed to a usual classical surface as the relativistic mass of electron increases. Transition to a state of Fermi surface instability is accompanied by a second-order phase transition and, eventually, desorption of the surfactant from the crystal surface.[54] For an amorphous material, the Fermi surface is spherical, *i.e.* analysis of the Fermi surface topology affords the possibility of predicting the high chemical resistance (low corrosion rate) of solids in an amorphous state.

The Fermi surfaces of compounds that exist in the crystalline state contain cylindrical regions. In this case, the energy of interaction in the direction perpendicular to the cylinder axis (when $m = 0, n = 2$) is inversely proportional to the square of the distance r between the interacting particles

$$E_{\text{surf-surf}}(r) \sim \frac{\sin(2\vec{k}_F r)}{r^2} ,$$

while for planar regions of the Fermi surface, in the direction perpendicular to them (when $m = 0, n = 1$),

$$E_{\text{surf-surf}}(r) \sim \frac{\cos(2\vec{k}_F r)}{r} .$$

In Hubbard's model,[41, 55] the penetration depth of the electric field of an adsorbed particle into a metal substrate depends on the Thomas – Fermi length of shielding [9]

$$l_{TF} = \left(\frac{E_F}{6\pi \bar{n}_0 |e^-|^2} \right)^{1/2} ,$$

where n_0 is the bulk concentration of electrons in the conduction band. Such adsorbents as Fe, Ru and Os, which have considerably higher Fermi energies than Cu, Ag and Au, have better chemisorption characteristics with respect to particles that are adsorbed with charge transfer. In the series of transition *d*-metals, elements occupying the middle of a series have higher E_F than the elements with *d*-shells filled (Cu, Ag, Au).

The chemisorption activity of transition metals is considerably affected by light particles implanted in the near-surface layer; either these particles are local harmonic oscillators, or they create their own sublattice as a result of self-organisation (provided that they have high diffusion mobility). Absorption of hydrogen by the near-surface layer of the metal or 'poisoning' of the metal by other light chalcophilic elements change both the E_F and $\bar{n}_0$. Programmes are available for modelling the ionic implantation into crystals, which provide the possibility of building concentration profiles [56] and subsequently of assessing changes in the corrosion resistance of the crystals subjected to a treatment.

On translation-invariant substrates, the adsorption of solution particles (the primary act in metal dissolution) can be rather strictly described (in analytical form) within the Ising model. The formation of ordered adsorption structures determines the kinetics of the corrosion dissolution of a metal whose surface is homogeneous (and/or the structural defects of the near-surface layer of the metal are blocked). For computer simulation purposes, the rates of partial cathodic and anodic reactions (cathodic and anodic current densities, i_c and i_a) occurring in non-saturated solutions can be expressed by equations that follow from formula (4),

$$i_c = v_i \exp\frac{\mu_e}{kT}, \tag{29}$$

$$i_a = v_i \exp\frac{-n_{ads}E_b}{kT}, \tag{30}$$

where v_i is a frequency factor (of the order of the Debye frequency, 10^{13} s^{-1}), μ_e is the equilibrium chemical potential in solution, n_{ads} is the number of bonds of an adsorbed atom with other lattice atoms and E_b is the energy required for the cleavage of one M – M bond. In the absence of charge transfer, the equilibrium chemical potential μ_e and the chemical potential of surfactant particles on the interface, μ_{surf}, are related to the solution concentration c_{surf} and activity a_{surf} by the equation

$$\mu_{surf} - \mu_e = kT\ln\frac{c_{surf}}{c_e} = kT\ln\frac{a_{surf}}{a_e},$$

where c_e and a_e are the equilibrium concentration and activity of the surfactant in solution, respectively.

When a quasi-equilibrium stationary state accompanied by inter-phase transfer of charged particles has been established in a system, the well-known Nernst equation, which describes the inter-phase distribution of particles, is applicable in the thermodynamic description:

$$\mu_e = 0.5WE_b + \frac{RT}{n\mathrm{F}}\ln\frac{c_{surf}}{c_e}.$$

Here W is the number of the closest neighbours of an atom (in bulk metal, $W = 12$ for a face-centred lattice and $W = 8$ for a body-centred lattice), n is the number of electrons transferred in an elementary discharge act, and F is the Faraday constant. The factor of 0.5 is introduced in the first term of the right-side expression (the two-particle potential $\mu_0 = 0.5WE_b$) in order to avoid counting the interaction of each pair of particles twice.

The coordination number W is determined by the topology of an adsorbed particle on the crystal surface. The magnitude of W on the crystal surface is considerably smaller (by a factor of two in a semi-crystalline position) than in the crystal bulk. The adsorption energies expressed according to Kaishev – Stransky [57] for different crystal faces (ΔE_{ads}) and the energies of semi-crystalline positions ($E_{1/2}$) depend strongly on the reticular density of the surface (the packing density of surface atoms) of the crystal, S_{hkl}. The magnitude of ΔE_{ads} for atomic-planar F-faces is 0.3 to 0.5 of the heat of sublimation ΔH; the $E_{1/2}$ values increase along the series: body-centred, face-centred, hexagonal close packed crystal.

Analysis of equations (29) and (30) shows that the frequency factor

$$v_i = k_0 a_a^0 \equiv k_0 a_k^0,$$

[here $k_0 = (kT/2\pi h)(z^{\neq}/z)$, where h is the Planck constant, $z^{\neq}$ and z are the partition functions per unit volumes of the active complex and the reagents in the electrolyte, respectively] most strongly depends on the activities of the cathodic and anodic surface complexes a_c^0 and a_a^0, which change in parallel with the concentration of Ox- and Red-particles in solution. The smaller W the easier it is to block the crystal surface element (cell) by an inhibiting surfactant. Conversely, adsorbed (mostly, semi-crystalline) particles have higher tendency to ionisation (dissolution). The excited state of an atom undergoing ionisation exists for a sufficiently long time ($\leqslant 10^{-8}$ s), that rapid transition of the surface atom to an unstable state is necessary. The characteristic times of electrochemical reactions ($\sim 10^{-11}$ s) are considerably longer [58] than the characteristic times of redistribution of bound charges of the solvent at the interface (10^{-14}–10^{-15} s). Hence, metal dissolution becomes possible. Increasing the electrochemical dissolution rate (decreasing the time t to 10^{-12}–10^{-13} s) by application of anodic current to an activated surface considerably decreases the contribution of surface defects to the overall balance of mass loss by the crystal due to dissolution. This provides the opportunity to use the classical formal kinetics approach based on the Langmuir isotherm (18) in the computer simulation. It is assumed in equations (29) and (30) that the dependence of the equilibrium concentration c_e on the surface coverage by adsorbed particles obeys the Langmuir isotherm.

According to the classical concepts, an act of dissolution is preceded by the transition of a surface atom to a metastable state, which occurs with a frequency differing from the Debye frequency v_D (which is characteristic of the bulk of the crystal), $v_i = 10^{13}$–10^{14} s^{-1}. This frequency v_i [the pre-exponential factor in kinetic equations (4) and (29)] depends on the Debye frequency v_D according to the formula

$$v_i = v_D \exp\left(\frac{-\Delta G}{RT}\right) = v_D \exp\left(\frac{\Delta S}{k}\right)\exp\left(\frac{-\Delta H}{RT}\right), \tag{31}$$

where the product $v_D \exp(S/k)$ ‡ is an insignificant deviation of a local volume of the system from the equilibrium state; ΔG, ΔS, and ΔH are the Gibbs free energy, the entropy and the enthalpy, respectively, required for the transfer of the atoms under consideration to the peak of the potential barrier between two equilibrium states of the structure.

Thus, in covering layers (commensurate or non-commensurate) on the surface and in the crystal bulk, a certain phonon mismatch (mechanical resonance) appears, which is, strictly speaking, the origin of phase transitions in these layers.

III. Models using the Monte Carlo method

In its canonical distribution variant, the MC method, which is based on statistical sampling of configuration mean values, calculates the mean values ($\bar{M}$) according to the formula

$$\bar{M} = \frac{\sum_i M_i \exp(-E_i/kT)}{\sum_j \exp(-E_j/kT)} = \sum_i M_i P_i,$$

where M_i is one of physical characteristics of the ith configuration, E_i is its energy, and P_i is the probability that the ith configuration would appear.

$$P_i = \frac{\exp(-E_i/kT)}{\sum_j \exp(-E_j/kT)}.$$

‡ The Einstein formula describing the fluctuation probability in the first near-surface metal layer.

The MC method is a method of numerical experiment; it is versatile and provides highly reliable results.[59] The MC technique can be used for the $2D$ Ising model for which exact solutions can be obtained,[60] in particular, for the formation of fluctuations of material density (drops) at the interface.[61,62] The stability of mesoscopic water clusters (small drops) and thin films is being studied intensively.[63] Ultra-thin water films on solid surfaces form crystal-like structures. The nucleation of small water clusters in the electrolyte bulk far from the interface occurs on ions of dissolved salts. The instability range of small water clusters results from the relative weakness of long-range electrostatic interactions. Large clusters form mesoscopic bubbles in polar liquids. Their shape is calculated using the MC method.[64] Calculations in independent sets (several hundred MC steps per adsorption cell) make it possible to access continuous thermodynamic functions of continuous thermodynamic variables. A stable state of a multiparticle system containing N particles corresponds to a minimum of the functional of inter-particle effective (resulting in the formation of chemical bonds) potentials $U_{ef}(r_i,r_j)$ of the type (2)

$$U_{ef}(r_i,r_j) = \int \ldots \int \left[\exp(\beta_{JT,E_b}) - \exp(\beta_{JT,U_{ef}})\right]^2 dr_1 \ldots dr_N .$$

Here the Jackson–Temkin parameter is

$$\beta_{JT,E_b} = \frac{-0.5E_b(r_1,\ldots,r_N)}{kT} \text{ and } \beta_{JT,U_{ef}} = \frac{-0.5\sum_{i<j}^{N} U_{ef}(r_i,r_j)}{kT} .$$

Naturally, the order in which problems are solved by MC simulation depends on the level of development of mathematical methods and computational means. Using the simplest pair potentials, electrochemical problems on the adsorption of chalcophilic particles on various faces of single crystals of noble transition metals were solved. Complication of the pair potentials is required if the act of adsorption involves more complex particles, such as water molecules.[65,66] In this case, the effective potential $U_{ef}(r_i,r_j)$ also becomes more complex. For example, the Raman–Stillinger potential[67] contains a spherically symmetric term [Lennard-Jones potential (2a), $U_{LJ}(r_{ij})$] and an electrostatic potential [$U_{el}(r_i, r_j)$] of point charges displaced from the geometric centre of the molecule

$$U_{ef}(r_i,r_j) = U_{LJ}(r_{ij}) + \sigma(r_{ij})U_{el}(r_i,r_j) . \quad (32)$$

Here $\sigma(r_{ij})$ is a smoothing function for correction of the interactions at small interatomic distances.

Lattice gas models can be realised in the $3D$ variant for the estimation of phase transformations at interfaces: these are Brunauer–Emmett–Teller generalised kinetic models, both in discrete and diffusion forms.[65] For example, problems on the absorption of electrolytic hydrogen by crystals are solved by numerical MC methods in three-dimensional systems[66] using $3D$ lattices with $> 10^6$ positions for occluded hydrogen and with variable parameters of the Gaussian distribution of equilibrium states and middle points between them. Subsequently, more complex systems were studied, such as M–chalcophilic particles, adsorption of CO, H_2O and halides, co-adsorption of CO and hydrogen on noble metal surfaces.[67,68]

In early studies on the simulation of water adsorption on metal electrodes by the MC method,[69,70] the crystal surface was simulated as a hard wall of a 'jelly'-metal. The surface charge was distributed uniformly, and the interface was simulated as a 'flat condenser', d being the distance between the plates; the ions located in the water layer were approximated by spherically symmetrical particles.[71] The inter-ionic interaction was described within the Poisson–Boltzmann model

$$U(r_{ij}) = \frac{n_i n_j |e^-|^2}{4\pi\varepsilon_0\varepsilon_r r_{ij}} \quad \text{for } r_{ij} > d ,$$

$$U(r_{ij}) = \infty \quad \text{for } r_{ij} < d ,$$

where r_{ij} is the distance between ions i and j; n_i and n_j are the concentrations of ions (of the kind i and j, respectively); ε_0 and ε_r are the dielectric constants of the solvent and the solution, respectively; and the interaction between the solvent layer and the 'jelly'-metal surface was described as

$$U(r_{ij}) = \frac{q_i n_i |e^-| \Delta z_i}{2\varepsilon_0\varepsilon_r} .$$

Here q_i is the surface charge density; Δz_i is the normal distance (along the z axis) between the charged surface of the 'jelly'-metal and an ion with a radius of r_i. It should be noted that Δz_i is the major factor determining the formation of commensurate and non-commensurate covering adsorbed layers.

When an interface is simulated, a cylinder, which contains a certain number of chalcophilic particles, is 'cut out' of the electrolyte so that some of the particles are located at the interface. For example, various models of hydrogen bond networks in $3D$ water have been constructed using the MC method. Three variants of the model were considered in Ref. 72: with 125 and 343 particles in the unit cell and with two different starting conditions. The differences between the variants are almost not discernible in the pair correlation functions, *i.e.* atom–atom radial distribution functions, which reveal the specifics of orientation order at sufficiently long distances (> 10 nm). The use of radial distribution functions is caused by the impossibility of obtaining exact solutions from equations, which operate in terms of particle coordinates and atom–atom interaction potentials. When one starts calculations, it is important to make a correct selection of the pair potential $U(r_{ij})$, which is different in adsorption $2D$ layers and in the bulk of the liquid phase. A model Hamiltonian of the system should certainly involve the mapping effects (for transition metals, the distance from the mapping plane to the crystal surface, which correlates with reticular density variation and decreases on changing from a 'loose' face to a densely packed one), the reconstruction of the near-surface metal layer due to adsorption and the evolution of non-equilibrium defects in this layer under the action of an electrolyte.

In the Kossel–Stransky model (TLK model), equations resembling (29) are used at moderate solution oversaturations for computer MC calculations of growth and dissolution of crystals under the above assumptions.[73–75] During the growth of an ideally smooth surface of a cubic crystal, the sticking probability of the particles that are deposited, P_a, is determined by the product of the probability of existence of n closest neighbours at one cell [$P_g(n)$] and the probability that the electrode potential E assumes a certain value, $P_\eta(E)$

$$P_a(n,E) = P_g(n)P_\eta(E) .$$

In metal corrosion, the probability of detachment of an atom from the first (n_1) and second (n_2) closest neighbours $P(n_1,n_2)$ for the {001} faces of a cubic crystal depends on the energy of cleavage of M–M bonds due to corrosion according to an Arrhenius-type equation:[76]

$$P(n_1,n_2) = \nu_i(n_1,n_2)\exp\frac{-E_b(n_1,n_2)}{RT} .$$

The bond energy, $E_b(n_1,n_2) \equiv n_{ads}E_b$, depends on solution undersaturation, as well as on the charge, ion size and concentration of an inhibitor if present. The physical meaning and structure of the equation presented above are similar to those of equation (30): the activation energy (energy of cleavage of one M–M bond) is $E_b(n_1,n_2) = n_2E_2 - n_1E_1 = -n_{ads}E_b$, and the frequency factor $\nu_i(n_1,n_2)$ is determined by equation (31). The values of E_1 and E_2 (bond energies for the first and second closest neighbours, respectively) can be calculated using pair potentials.

The MC method can be used for the computer description of both the development of local forms of corrosion (formation and

growth of a single pit) and the evolution of non-singular (diffusion) surfaces of crystals with surface defects in the form of steps and kinks. The growth of an ideally smooth (singular) single crystal surface is simulated by the MC method within the cellular automata model,[77] which takes the adsorption of discharging particles, their movement on the surface, incorporation, chemical reactions and desorption into account.[78, 79] The discrete growth of a new monolayer in a unit cell (Fig. 8) starts from the centre (single cell). A single cell is filled by an adsorbing particle in the case if two neighbouring sites are also vacant. The process is controlled [80] by a pair correlation function $\sigma(r,t)$, which changes with time (provided that the adsorption acts occur randomly)

$$\sigma(r,t) = \frac{-0.5\exp(-2A)\sum_{n=0}^{\infty}(-2A)^{2n+r+1}}{(2n+r+1)!},$$

where $A = 1 - \exp(-t)$.

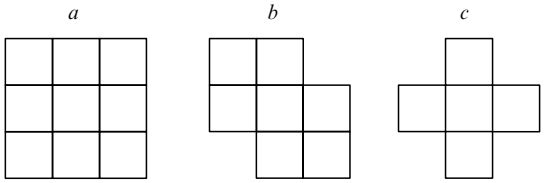
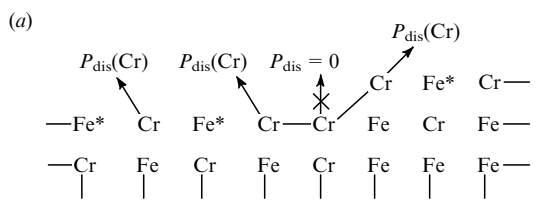


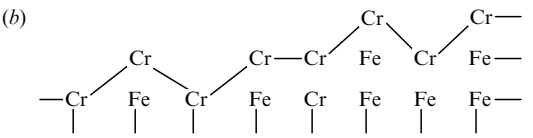
Figure 8. Types of elementary cells; (*a*) square (Neumann vicinity); (*b*) hexagon; (*c*) rhombus (Moore vicinity).

The distribution of adsorbed particles in a lattice that consists of cells with N_{ac} active centres on the surface has the dispersion $N_{ac}A\exp(-4A)$ at high N_{ac}. The cellular automata model is applicable to the description of selective dissolution of crystals occurring by generation of dissolution steps.[81]

The computer simulation of changes in the morphology of a pit growing at a dislocation exit on an 'atomically-smooth' surface is based on the concept that atoms with higher energies are preferentially removed from the crystal. In the first step, a 2*D* nucleus of the pit is formed. In the model suggested in Ref. 82, the authors considered the bonding of the atom being removed with the neighbouring metal atoms located in four types of positions at the closest distances. Computer calculations determine the energy of each atom along the perimeter of the 2*D* nucleus and select the atom with the weakest bonding to the substrate. After removal of this atom, the calculation of energies of perimeter atoms is repeated.

It has to be noted that this approach ('removal' of the most weakly bound atoms from the near-surface layer of a crystal) is also quite acceptable for the computer simulation of alloy corrosion or dissolution of high-index surfaces of pure metals.[83] Numerous experiments on the study of alloy corrosion [84] show that the most electronegative component is the first to be removed from the surface during alloy dissolution. For example, in modelling of the dissolution of an Fe–Cr alloy,[85] the percolation process is taken into account; this process can be visualised as follows in the 2*D* variant:





Here P_{dis} is the dissolution probability. At step *a*, the surface contains oxidised atoms of both iron and chromium. Removal of an iron atom from the surface (step *b*) results in the formation of a continuous surface coating by chromium, *i.e.*, a percolation 2*D* cluster is formed. The percolation leading to enrichment of the surface by chromium atoms results in surface passivation, structural stabilisation of the alloy and a decrease in the dissolution rate. A similar procedure of 'removal' of the most weakly bound atom in the 3*D* model of metal corrosion makes it possible to simulate the movement of dissolution steps on high-index crystal planes.

Eventually, corrosion stabilises the surface layers of crystals. The stabilisation occurs not only by percolation but also by forming a near-surface layer with particular grain composition. Problems of grain growth in near-surface metal layers were successfully solved using recrystallisation MC models.[86]

In the scheme of layered growth (dissolution) by the FVdM mechanism, the computer simulation of the TLK model (Fig. 9) uses a MC principle in the random formation of the growth (dissolution) centres.[87] This eventually results in the formation of a quasi-stationary surface topography characterised by the Gaussian distribution of layer coverage. The mean rate of tangentially moving atom chains ($\overline{V}$) is proportional to the degree of surface coverage by adsorbed atoms (θ_{ads})

$$\overline{V} = \frac{L}{t}\theta_{ads},$$

where L is the distance between atom chains (steps) and t is the time of incorporation of an adsorbed particle into a step. Of course, the rate $\overline{V}$ also depends on the density of active centres on the step, N_{ac}

$$\overline{V} = \frac{L}{N_{ac}\Delta t},$$

where $\Delta t = t/N_s\theta_{ads}$ is the time (the Monte Carlo time) till a successful attempt to incorporate an adsorbed particle at a functioning active centre and N_s is the number of substrate surface atoms. It is important that the Monte Carlo time Δt matches the increment of real time (or time step in numerical simulation).[88] Of major importance are the transition probabilities $P_a(n, E)$ describing a system in the MC model. The sums

$$\sum_{1}^{n} P_a(n, E)$$

determine the trajectories of the system transition into the equilibrium state. The main mechanism of the growth of adsorbed layers in the MC model is diffusion of an adsorbed particle until it incorporates itself in an active centre. The role of active centres is usually played by kinks.

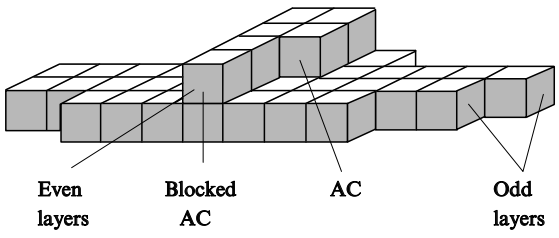


Figure 9. Scheme of increase in the crystal surface in the TLK model by the mechanism of anisotropic growth of 'orthogonal strings' (atomic chains); AC is the active centre.

The model of consecutive coverage by monolayers (see Fig. 9) is not the only one or the simplest one of TLK models. The following models have also been considered:[75,89] the random deposition model in which an adsorbing particle striking the crystal surface is instantly attached to a stable position of a tetragonal lattice (substrate); the model of locally-perfect layer-by-layer growth on a tetragonal lattice in whose each cell 'perfect' (not correlated with other cells) layer-by-layer growth of a non-commensurate phase occurs; the local islets model in which the diffusing adsorbed particles are attached in highly-coordinated positions on a crystal surface.

For the stepped surface in the TLK model (see Fig. 7), the flux of adsorbing particles striking the crystal surface should consist of, at least, three components:[90]

$$J = J_S + J_i + J_r ,$$

where J_S is the flux of surfactant particles attaching themselves to a step; J_i is the flux of surfactant particles directed to active centres (2D-islets); and J_r is the flux of desorbing surfactant particles.

The MC method was used for the surface of a simple cubic crystal in a study of surface covering with an epitaxially growing film.[90,91] It was shown that concentration oscillations appearing in the simulation of layer-by-layer film growth mechanism do not correspond to the exact filling of monolayers. As the length of surface migration of adsorbed atoms, λ ($\lambda < L$), increases, the oscillation region shifts from the region of high degree of coverage, $\theta_{surf} > 1$, to the region of small degree of coverage, $\theta_{surf} < 1$. It should be noted that concentration oscillations near the electrode surface in homogeneous nucleation have been reported as early as in Refs 92 and 93, which dealt with an MC simulation of polynuclear crystal growth. Concentration oscillations in solution give rise to non-uniformity of layer growth in galvanic coatings.

The electrodeposition of metals was studied using computer simulation methods.[94,95] It was assumed that the new phase growth occurred under the conditions of simultaneous coverage of adsorption cells with various particles and that depolarisation on both components occurred due to changes in the free energies of the components.[96] In a model predicting the alloy composition, the shift of the equilibrium potential for each component of a two-component alloy was used as the main characteristics for computer simulation [94,95]

$$E_i = \frac{RT}{n\mathrm{F}} \ln c_i - (1 - c_i)^2 E ,$$

where c_i is the molar fraction of the ith component in the alloy, $E = \Delta H/nF$, and ΔH is the integral enthalpy of mixing. In computer simulation of the formation of binary alloys AB in an electrochemical process by the VW mechanism, the work of formation of 2D-nuclei is determined taking account of the energy of elastic deformation of the crystal lattice

$$W_{hkl} = 6\pi \left(\frac{r_A - r_B}{r} \right)^2 r^3 \frac{c_B(1 - c_B)}{k_1 + k_2 C_B} ,$$

where r_A and r_B are the atomic radii of metals A and B, $r = (r_A + r_B)/2$ is the mean atomic radius, k_1 and k_2 are coefficients:

$$k_1 = \frac{3}{4} G_A + K_B ,$$

$$k_2 = \frac{3}{4} K_B + G_A - \frac{3}{4} K_A - G_B ,$$

G_A and G_B are the shear moduli of metals A and B, K_A and K_B are the deformability (compressibility) coefficients of metals A and B, respectively.

MC computer simulation was used in studies of the electrochemical growth of crystals, both in the form of islets [97–99] and in vicinal form (pack of monoatomic steps).[83,100,101] It was shown that surface evolution is in good accord with morphological patterns of the growth of continuous galvanic deposits and with the structural features of insular coatings. For example, computer simulation using Lennard-Jones potentials (2a) showed [98] that on the surface of a crystal with a simple cubic lattice, subcritical size nuclei of the new phase have body-centred cubic structure, while after reaching the critical size, they have face-centred cubic (FCC) structure. This result totally agrees with experimental estimates of actual heteroepitaxial systems 'crystal surface – galvanic deposit'.

The use of the vicinal growth model on a crystal surface [102] assumes correlated movement of not only monoatomic steps but also [taking account of equation (4)] electrochemically active adsorbed particles. The energy of the diffusion barrier $E(\theta_{surf})$ is expressed as the sum

$$E(\theta_{surf}) = E_s(\theta_{surf}) + nE_N(\theta_{surf}) ,$$

where $E_s(\theta_{surf})$ and $E_N(\theta_{surf})$ are contributions of interaction with the surface and with the closest neighbours, respectively; $n = 1–4$. The rate of movement of vicinals during crystal dissolution primarily depends on their height.[103–106] Splitting of vicinals from a chain of atoms, which belong to a step and are transferred into solution, occurs in a correlated way. Consideration of corrosion of a crystal face having linearly-stretched defects is possible either in the classical variant or with account of wave cooperative features of the interaction of adsorbed particles and surface atoms on the interface.[16]

In the classical Kossel-Stransky's theory of attachment (separation) of particles to a monoatomic step of a crystal, the rates (currents) of the direct and reverse processes ($\vec{i}$ and $\overleftarrow{i}$, respectively) obey equations of the type (31)

$$\vec{i}\ (\overleftarrow{i}) = \nu_D \exp\left(\frac{\Delta S}{k}\right) \exp\left[\frac{-(E_a + \Delta E_{lat}(T))}{kT}\right] , \qquad (33)$$

in which $E_a + \Delta E_{lat}(T) = \Delta H$, $\Delta E_{lat}(T)$ is the energy of lateral interaction of particles in a step (the Frumkin correction factor). An equation has been suggested for the estimation of the rate of movement of a single monoatomic step (V_L) containing kinks:

$$V_L = 0.5 \exp\ \frac{\Delta G^{\neq}}{RT} a_0 \left(\frac{2\mathrm{ch}(3\sigma_L)}{RT} - 1 \right) \left(\exp\ \frac{\Delta\mu}{RT} - 1 \right) , \qquad (34)$$

where $\Delta G^{\neq}$ is the free activation energy of dissolution in a kink on the step; a_0 is the activity of the substance in a saturated solution; σ_L is the specific free surface energy per atom located in the step; $\Delta\mu$ is the difference between the chemical potentials of the material of the crystal that is dissolved in supersaturated and saturated solutions.

Estimates using equation (34) show that an increase in σ_L should increase the rate of step movement, V_L. If a step and/or kinks on crystal steps in a Kossel – Stransky crystal are blocked by a corrosion inhibitor, σ_L and probabilities of detachment of an atom from the surface, $P(n_1,n_2)$, change. The reasons for this are as follows: first, a decrease in the number of 'free bonds' of an atom in a certain position; second, a decrease in the number of bonds between the inhibitor atoms and the crystal lattice; third, attenuation of electronic vibrational modes (changes in the electronic and phonon spectra of the surface atomic layer of the crystal) due to the adsorption of solution particles. The attenuation of vibrations due to the inhibiting adsorption of small chalcophilic particles is stronger in the direction tangential to the surface than in the perpendicular direction.[107] The decrease in the probability of exit of an atom from a kink due to dissolution inhibition can be determined from the equation

$$\frac{\Delta P(n_1, n_2)}{P(n_1, n_2)} = 1 - K \exp(n_{M-M} + n_{surf-M} + n'_{M-M}), \qquad (35)$$

where K is the metal deformability constant; n_{surf-M} is the number of bonds between the inhibitor particles and the lattice atoms; n_{M-M} and n'_{M-M} are the numbers of free bonds of an atom in a

typical lattice position with and without an inhibitor, respectively. According to equations (2) and (34), each bond has distinct energetic characteristics, and the maximum contribution to its realisation in inhibiting adsorption is made by the electronic interaction in the adsorbate–adsorbent system [the third term $H_{\text{surf}-\text{M}}$ in Hamiltonian (19)]. In an adsorbed dipole, the attenuation of stretching vibrations of the M–surfactant bond is primarily caused by changes in the density of states at the Fermi level of the transition metal, E_{F}, due to the adsorption of an inhibiting particle.

Simulation of adsorption by MC methods showed [47] that mutual attraction of particles on a stepped surface strongly affects the adsorption isotherm, which leads to the separation of the system into phases with low and high degree of coverage. For example, the authors [108] who made a calculation of the effective interaction potential of the simplest adsorbing particle (hydrogen) also noted that the Hamiltonian for the full energy of an adsorbed hydrogen atom similar to Hamiltonian (20) consists of the energy of hybridisation of one-electron states with *d*-electrons of the adsorbent, the adsorption energy of hydrogen on a uniform surface, and the short-range attraction forces between the adsorbed atoms and the ion framework of the metal. The Hamiltonian for a hydrogen molecule desorbing from a metal surface and not bound to it by chemical forces is expressed by the sum (in atomic units)

$$\hat{H}_{\text{H}_a\text{H}_b} = \underbrace{-0.5\nabla_1^2 - r_{1a}^{-1}}_{\substack{\text{Hamiltonian}\\ \text{of the}\\ \text{atom H}_a}} \underbrace{- 0.5\nabla_2^2 - r_{2b}^{-1}}_{\substack{\text{Hamiltonian}\\ \text{of the}\\ \text{atom H}_b}} \underbrace{- r_{1b}^{-1} - r_{2a}^{-1} - r_{12}^{-1} - R_{ab}^{-1}}_{\substack{\text{Hamiltonian}\\ \text{of the}\\ \text{molecule H}_a\text{H}_b}} . \quad (36)$$

Here the subscripts 1 and 2 signify the arbitrary numbers of 1*s* electrons of the H_a and H_b atoms; r_{1a}, r_{2a} and r_{1b}, r_{2b}; r_{12} and R_{ab} are the electron–nucleus, nucleus–nucleus distances and the distance to the adsorption point, respectively.

When atoms H_a and H_b are remote from each other, they can be considered non-interacting, and the electronic state of each of them can be described by wave functions $G_{\text{a}}(1)$ and $G_{\text{b}}(2)$ of isolated atoms H_a and H_b

$$G_a(1) \equiv 1S_a(1) = \frac{1}{\sqrt{\pi}}\exp(-r_{1a}), \quad (37)$$
$$G_b(2) \equiv 1S_b(2) = \frac{1}{\sqrt{\pi}}\exp(-r_{2b}).$$

The spins in the H_2 molecule are anti-parallel; hydrogen atoms adsorbed on a metal (with parallel spins) interact through van der Waals forces (repulsion).

A thermodynamic estimation of surface states shows that the lowest equilibrium chemical potential μ_e for surface states is realised for the most loosely packed {110} FCC and {111} BCC faces. This ensures their preferential filling with adsorbed particles within the model of hard spheres with uniform charge ('jelly'-spheres).

Results of computer simulation by methods of statistical selection of configurations (MC method) based on the concepts described above, with the assumption that E_{b} in a crystal does not depend on the direction $\langle hkl \rangle$, lead to certain conclusions on new phase formation on singular and low-index single crystal faces. This approach is quite satisfactory for the problem of corrosion inhibition, since films formed on the surface are two-dimensional and comply to the pre-phase formation condition. For example, on a face-centred crystal under monoepitaxy conditions (direct continuation of the solid phase lattice into solution) and with the Jackson–Temkin parameter $\beta_{\text{JT}} = 0.5E_{\text{b}}/kT = 0.3$ ($\Delta\mu \simeq 0.01kT$ for crystal growth from solution), the rate of new phase formation depends considerably on the reticular density of the face.[92, 93] It is lower on the most densely packed (111) FCC face than on the 'loose' (110) FCC face. According to Gilmer,[5, 6] this follows even from simple geometric considerations: an atom adsorbed on the (111) face of an FCC crystal is bound to three substrate atoms, as compared to four on the (001) FCC face and five on the (011) FCC face, *i.e.* the reverse process (dissolution) on an FCC crystal will not occur as easily on the densely packed (111) face as on the 'loose' (110) face.

IV. Molecular dynamics models

The molecular dynamics (MD) method is less widespread than the MC method. Both methods provide information on the structures of phases interacting in electrolytes; it is impossible to obtain such data by statistical methods. The MD method is based on calculations of trajectories for separate adsorbed particles on a crystal surface and for groups of interacting atoms. The calculation of new positions occupied by the particles moving on the surface is made using classical equations of motion. Pair potentials (2b) are used; for densely packed structures, the Lennard-Jones potential summed over all atom pairs

$$U_{\text{LJ}}(r_{ij}) = \sum_{i<j} U(r_{ij}) = \sum_{i<j} 4E_{\text{L}}\left[\left(\frac{B_{\text{a}}}{r_{ij}}\right)^{12} - \left(\frac{C_{\text{lat}}}{r_{ij}}\right)^{6}\right], \quad (38)$$

where $r_{ij} > 2.5(C_{\text{lat}},B_a)$, is used most commonly. If $r_{ij} \leqslant 2.5(C_{\text{lat}},B_{\text{a}})$, potential (38) is complicated by introducing a Coulombic correction when solving electrochemical problems [109, 110]

$$\sum_{i<j} U(r_{ij}) = \sum_{i<j} 4E_{\text{L}}\left[\left(\frac{B_{\text{a}}}{r_{ij}}\right)^{12} - \left(\frac{C_{\text{lat}}}{r_{ij}}\right)^{6}\right] + \frac{n_i n_j |e^-|^2}{4\pi\varepsilon_0\varepsilon_r r_{ij}}.$$

For loose structures, the Stillindger–Weber (SW) potential,[111] which takes three-particle interactions into account, is used. The SW potential for a triplet of atoms (*i*,*j*,*k*) has the form [112] (if $B_{\text{a}} = C_{\text{lat}}$)

$$U_{\text{CB}}(r_{ijk}) = \text{f}\left(\frac{r_{ij}}{\sigma}\right)\text{f}\left(\frac{r_{ik}}{\sigma}\right)\left(\cos\theta_{ijk} + \frac{1}{3}\right)^2.$$

In this expression, the smoothing nonparametric function $\text{f}(r/\sigma)$, which is common at small interatomic distances *r*, approaches zero at $r \to 1.8\sigma$, and θ_{ijk} is the internal angle of the triplet.

The diffusion coefficient of adsorbed particles on the crystal surface is calculated using the Einstein's equation

$$D_{\text{surf}} = \frac{\{\langle[\vec{R}_i''(t_2) - \vec{R}_i''(t_1)]^2\rangle_i\}_c}{4(t_2 - t_1)},$$

where $\vec{R}_i''(t_1)$ and $\vec{R}_i''(t_2)$ are radius-vectors of the *i*th surface-adsorbed surfactant particle at instants t_1 and t_2 after the equilibrium state has been reached; $\vec{R}_i'' = (x_i, y_i)$ are vector projections on the 2*D* crystal surface; the angle brackets $\langle ... \rangle_i$ and braces $\{...\}_i$ mean statistical averaging over all *i* particles (on the surface and in the bulk of the 3*D* layer at the metal–electrolyte interface). A diffusing surfactant particle comes to an equilibrium position on the crystal surface by crossing the quasi-stable bridging positions. This crossing occurs through thermal activation. The minimum path, l_{min}, that has to be overcome along a crystal surface with a surface concentration of active lattice sites N_{s} (10^{18}–10^{19} m^{-2} for cubic crystals) is controlled by the well-known 'directed movement of a salesman' relationship

$$l_{\text{min}} = \frac{1}{N_{\text{s}}} + \frac{1}{L_l}\frac{2[2P_{\text{a}}(n,E) - 1]}{N_{\text{s}}^2},$$

where L_l is the characteristic size of the substrate tetragonal lattice and $P_{\text{a}}(n,E)$ is the probability of occupying a point by the *i*th surfactant particle to be adsorbed.

The equations for D_{surf} and l_{min} presented above are also valid under conditions of self-diffusion of particles, adsorbed on a metal crystal, along its surface. Adsorbed surfactant particles (including large organic molecules) can form structures 'cross-linked' with the near-surface metal layer. Calculation by the MD method of the height of surface barriers upon intrusion of surfactant particles into thin channels (pores) of a metallic adsorbent makes it possible

to assess the steric factor.[113] The surface layer itself is considered within the MD method as a non-commensurate 'cross-linked' adsorption layer of particles of the same type as the crystal atoms.

Finally, the MD method determines the position of a surface-adsorbed particle with a local minimum of potential energy. Along one of the pathways for the formation of adsorption layers, minimisation of energy as a function of position of the adsorbed particle occurs through thermal activation. An increase in temperature accelerates the attainment of low-entropy surfactant state (self-organisation) on the crystal surface. Computer simulation by the MD method showed [114] that in the temperature range close to the melting point, non-commensurate and adsorbed surfactant layers are transformed to a particular state that precedes melting. In this case, a correction for the attraction of particles, $\Delta E_{\rm attr}(T,\theta_{\rm surf})$, similar to the Frumkin's correction factor[20] for the description of adsorption in the double electric layer, should be introduced to the Arrhenius equation for the diffusion coefficient

$$D_{\rm surf}(T) = D_0 \exp\left\{\frac{-[E_{\rm a} + \Delta E_{\rm attr}(T,\theta_{\rm surf})]}{kT}\right\},$$

The value of $\Delta E_{\rm attr}(T,\theta_{\rm surf})$ depends on the degree of coverage of the crystal surface by surfactant particles and on the force of interaction of these particles between each other.

Combining the MD and MC methods provides a possibility of separating the first-kind phase transition as such [115] from processes of rapid but continuous changes in the physical parameters measured. This possibility is particularly important in the simulation of non-commensurate surfactant particles on crystal surfaces in the electrochemical contact with an electrolyte. Computer simulation by the MC method (using the Lennard-Jones potential) of the near-surface layer of the (100) face of a FCC crystal showed [116] that the temperature of non-commensurate first surface atomic layer is lower than that in the bulk of the crystal. Thus, non-commensurate adsorption layers stabilise or 'slow down' the near-surface crystal layers thus increasing its dynamic stability in a corrosive medium.

The MD method is widely used in the description of the movement of light particles (particularly, hydrogen [117]) on the surface and in the bulk of metal crystals.[118] The diffusion of hydrogen is simulated by the MD method taking account of the reticular density of near-surface metal layers.[119] It was found that light surfactant particles quickly form commensurate and non-commensurate phases on the crystal surface. As MD simulation shows,[120] non-commensurate islets are formed from particles in the first stage, in agreement with the VW model (see Fig. 3). In the crystal bulk, the hydrogen atoms which get into the metal due to an electrochemical process occupy tetra- or octahedral interstices. Comparison of results obtained using lattice gas models with MD results [121, 122] makes it possible to identify reliably the topology of hydrogen absorbed by the crystal.

The vast majority (95%) of atom jumps from one interstice to another in the crystal bulk occur in a non-correlated Brownian way. For example, the movement of adsorbed hydrogen on the surface of a metal saturated with hydrogen occurs in a directed (correlated with the potential energy surface) way, along valley bottoms of the potential pattern. Computer simulations of this process virtually always use the lattice gas model, and calculations using this model are carried out by the MC method.[123]

Hydrogen absorbed by a metal crystal changes the hierarchy of internal defects of various dimensionality, particularly near interfaces.[123–125] 2*D*-Models of external and internal interfaces of polycrystals that form a lattice of coinciding points or densely-packed hexagons are used for the description of changes in macroscopic deformation characteristics, as well as the evolution of dislocation ensembles in terms of the monoatomic steps model by Frenkel–Kontorova.[126–128] Computer simulation of dislocation rearrangements on a metal surface in the 3*D*-variant and assessment of the topology of the electric pattern of the process [129] make it possible to predict the adsorption coverage of not only singular but also diffuse surfaces.

The pair potentials used in MD computer simulations are relatively simple. For example, the following potentials are used in the description of hydrogen behaviour in palladium:[121]

$$U_{\rm Pd-Pd}(r) = \begin{cases} \sum_{S=0}^{6} K_S r^S, & r < r_0 \\ 0 \end{cases}, \qquad (39)$$

$$U_{\rm Pd-H}(r) = \begin{cases} K_S \exp\left(-\frac{r}{\rho}\right), & r < r_1 \\ 0, & r > r_1 \end{cases},$$

$$U_{\rm H-H}(r) = U_{\rm Pd-H}(r),$$

where $K_{\rm S}$ is the volume factor characterising the height of the energy barrier (when a hydrogen atom passes through it) of a surface Pd-cluster (up to six Pd atoms); r is the interstice (pore) radius; r_0 is the radius of pore 'cutting' in the formation of a 2*D* lattice of surface Pd atoms; r_1 is the radius of an adsorbed hydrogen atom (it is smaller than that of a hydrogen atom, $r_{\rm H} = 0.46$ nm, and depends on the nature of the transition metal adsorbent); the constants for palladium are as follows: $\rho = 0.05$ nm, $r_1 = 0.38$ nm, $K_{\rm S} = 15.3$ eV.

The MD method is successfully used for the simulation of the co-adsorption of chalcophilic particles on surfaces of transition metal single crystals;[128–130] it is also convenient for the simulation of water/metal interfaces.[131] In early studies, lattice 3*D*-models of H_2O adsorption on a homogeneous metal surface (Hg) were calculated by the MC method using asymmetric multi-particle pair potentials.[132–134] All calculation models are based on the Gouy–Chapman theory of the double layer structure. In analytical form, the pair potentials for the system water–platinum are represented as follows:

$$U_{\rm H_2O-Pt} = U_{\rm O-Pt}(r_{\rm O-Pt}, \vec{R}_{\rm O-Pt}) + U_{\rm H-Pt}(r_{\rm H_a-Pt}) + U_{\rm H-Pt}(r_{\rm H_b-Pt}), \qquad (40)$$

where $U_{\rm O-Pt} = [1894\exp(-1.1004r) - 1886.3\exp(-1.0966r)]f(\vec{R}) + 10^6\exp(-5.3568r)[1-f(\vec{R})]$,

$$U_{\rm H-Pt} = 1.7142\exp(-1.2777r),$$

where $f(\vec{R}) = \exp(-0.5208\,\vec{R}^2)$, r is the distance between adsorption cells on the metal surface (pore radius), $\vec{R}$ is the projection of the vector of displacement of an adsorbed H_2O molecule on the metal surface; $\vec{R}$ and r are expressed in nm, and the potentials are in eV. In adsorbed water layers on single crystal faces, a periodic structure with a definite oscillation period was observed. The interaction energy $E_{\rm b} \equiv U_{\rm H_2O-M}$ for water–metal contacts is 51.1 (Al), 33.7 (Ni), and 36.6 kJ mol^{-1} (Cu). Based on results of MD simulations,[131] four main configurations can be suggested for the geometry of a water molecule on an ideal metal 'jelly-surface' (Fig. 10); they do not differ much from the well-known Okamoto's model [135] in which water molecules, whose 'oxygen ends' form an angle of 10–35° with the crystal surface.

Consideration of this process within the Ising model suggests the formation of periodic surface low-entropy water structures [136]

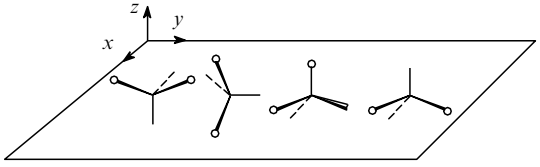


Figure 10. Variants of location of adsorbed water molecules on an ideal metal surface (according to results of the MD method).

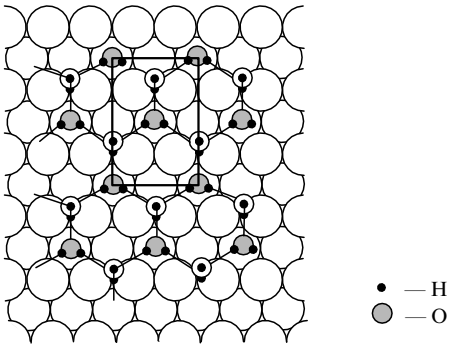


Figure 11. Schematic crystallographic model of adsorbed water on the (110) surface of a face-centred crystal.

(Fig. 11). On stepped crystal surfaces, water structures with a certain fractal dimensionality are formed.[124]

It has been shown [31] that water molecules are displaced from 'loose' steps to densely packed terraces by HSO_4^- or SO_4^{2-} ions, which have larger surface areas; a portion of water molecules are moved into the second adsorption layer.

V. Conclusions

Physicochemical patterns obtained by computer simulation of corrosion-electrochemical processes on metal – electrolyte interfaces satisfactorily describe many features of these complex phenomena. The computer models used now have good predicting ability. Although model Hamiltonians for the systems in question have many drawbacks, consideration of the main physical features of crystallisation – decrystallisation mechanisms provides the possibility to determine the types of materials that would be most stable in corrosive environments, to obtain information on the kinetics of corrosion-electrochemical processes, to predict the character of anticipated metal degradation and the structure of a galvanic coating to be formed.

Irrespective of the simulation method, the main direction of studies on computer simulation of electrochemical processes is related to the description of collective phase transitions. The speed and amount of memory available in modern computers make it possible to take into account not only the behaviour of separate particles in an ensemble (nearest environment) and the evolution of ensembles (clusters) in translation-invariant structures on the surface, but also mass and charge transfer of a material in a continuous medium. Therefore, the computer description of the behaviour of commensurate (floating) and non-commensurate (cross-linked) adsorption layers is based on non-linear relationships, which take into consideration the wave character of processes in these layers. One of the features of computer simulations is that they take into account correlated movements of adsorbed particles on the crystal surface involved in the formation of certain structures of adsorbed layers with fractal dimensionality and in adsorption-induced rearrangements (second-order phase transitions) in the crystal near-surface layer. It is believed that the development of mathematical methods and the coming of new-generation computers will make it possible to simulate the cooperative behaviour of resonance-linked double electric layers on the sides of the crystal and the electrolyte (the Frumkin double plane-parallel capacitor).

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