

Chapter 5

Surface Nanophysics: Macro-, Meso-, Micro- and Nano-approaches

5.1 Surface: Thermodynamics, Anisotropy

The surface represents a geometric set of points in accordance with strictly formulated rules. The most common use of this term is to denote a two-dimensional (2D) submanifold of the three-dimensional (3D) Euclidian space (xyz). In geometry, 2D collection of points represents a flat surface according to Eq. (5.1):

$$\alpha \cdot x + \beta \cdot y + \gamma \cdot z + \Delta = 0. \quad (5.1)$$

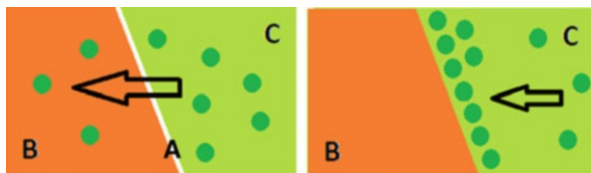
Quadratic, cubic, etc. equations describe the non-flat surfaces, which are important in many fields of natural sciences. The range of the surface could be expressed by the natural number (2,3) as well as by fractional (e.g. fractal surface).

In physics, a surface is a continuous boundary that separates a 3D space into two different subspaces. The phases of certain materials occur in the case when diffusion processes take place. Figure 5.1 represents a comparison of absorption and adsorption processes between two phases *B* and *C*. The absorption process represents the mixing of phase *C* into phase *B*: increasing the concentration of *C*-type particles in *B* volume without any chemical reaction. Gas particles penetrate the mass of a solid. Absorption processes in many cases are reversible, and it is possible to recover absorbed substance into the previous state. Substance *B* (liquid or gas) diffuses into liquid *C* to form a solution according to Fick's second law (1D form):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial t^2}, \quad (5.2)$$

where *c* represents the concentration of substance *B* into *C*, *x* is the reaction coordinate (physical distance from the interaction point), and *D* is the diffusion coefficient related to the substance behaviour. At intermediate states, concentration of *C*-type particles increases in *B* volume, and it is a time-dependent process. After

Fig. 5.1 Absorption and adsorption processes between phases *B* and *C*. *Left* – bulk phase *C* and absorbing phase *B*, *right* – bulk phase *C* and adsorbing phase *B*



established equilibrium, concentration of *C*-type particles in *B* volume is uniform (time-independent and distance-independent).

Otherwise, adsorption occurs in case when particles (extracted from liquid solute or gas) accumulate or concentrate at the surface of solid forming heterogeneous surface (mass transfer process). Adsorbent (also called substrate) represents the solid where adsorption takes place (covering the surface), adsorbate represents the substance adsorbed on the surface of solid (short distance to surface), and adsorptive represents the substance before the adsorption process (long distance to surface). Thus, the generated high-energy interface is located at a short distance to low-energy adsorptive system:



Diffusion processes (or more generally mass transfer processes) as well as adhesion processes create the region of particle accumulation at the liquid–solid or gas–solid interface. Adsorbed substance *B* creates an atomic or molecular film. Limited quantities of substance (in many cases – very small) are adsorbed (in comparison to absorption). Adsorption is a surface phenomenon, and geometrical area of surface could be treated as the main parameter for modelling. Saturation of covering is also limited by the surface. Surfaces of solids always express the tendency to attract the additional particles due to the presence of surface energy. In microparticle assumption, unbalances residual forces represent driving forces for adsorption.

Let us assume the existence of two phases – *B* and *C*. Two different approaches are presented in Fig. 5.1. with two bulk phases *B* and *C* with volumes V_B and V_C and the interface between phases (surface *A*). Figure 5.2 represents the dependence of concentration c of the bulk phase on the distance to the surface d . In the near surrounding, the concentration c rapidly increases.

Adsorbate (a substance adsorbed on the surface) and adsorbent (a substance which creates the region of increased concentration of adsorbate) could be treated as two interacting materials (the so-called phases).

An idealized model (Gibbs model) could be used in some cases, where the thickness of the surface phase is negligible, and two phases – *B* and *C* – are divided by Gibbs dividing plane, the so-called ideal interface.

The real alternative model (Guggenheim model) represents a quasi 3D surface, and the thickness of the surface phase is equal to z . The interfacial region is extended and its volume is significant. Figure 5.3 represents Gibbs (ideal) interface vs Guggenheim (real) interface between phases *B* and *C*.

Fig. 5.2 Adsorption processes between phases *B* (surface) and *C* (bulk solution). *Left* – dependence of concentration *c* of bulk phase on distance to surface *d*. *Right* – bulk phase *C* and adsorbing phase *B*

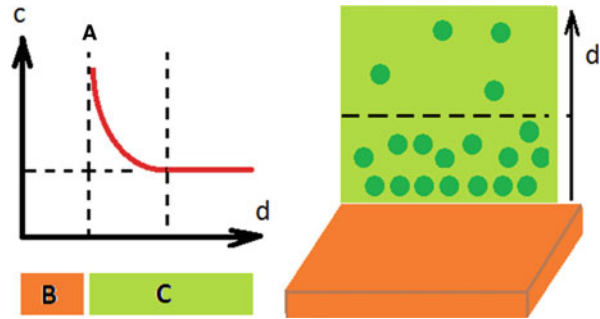
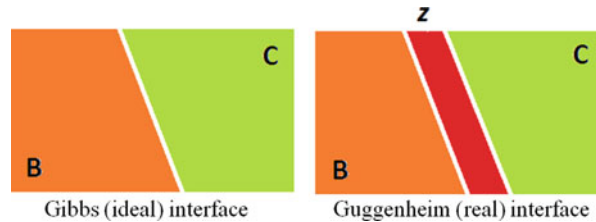


Fig. 5.3 Surfaces between phases *B* and *C*



Otherwise, Gibbs model as the first assumption allows interpreting the interface as ideally thin. The crystallographic surface as well as covered surface (thin film) and also the cell membrane may be considered similarly in the framework of the physical chemistry. The classical liquid surface can often be treated in the first assumption as a solid surface [1].

The adsorption processes must be analysed in two aspects: (1) thermodynamically, equilibrium of interfacial energy must be realized in the final phase of the processes; and (2) kinetically, the rate of adsorption process depends on the surface and substance behaviour as well as previously declared thermodynamic conditions.

Thermodynamically, many processes could be characterized through changes of arguments *T* and *p*, which results from Gibbs' free energy ΔG :

$$\Delta G = \Delta H - T\Delta S, \quad (5.4)$$

where ΔH represents the enthalpy and ΔS is the entropy. For adsorption, decreasing of free energy takes place (in the case if *T* and *p* are constants). Adsorption as a spontaneous exothermic process is characterized by the negative Gibbs energy. The so-called condition of spontaneity arises from Eq. (5.5)

$$\Delta G = \Delta H - T\Delta S < 0, \quad (5.5)$$

when particles of the adsorbate are fixed on the surface of the adsorbent (adsorption process is finished) the translational motion of the adsorbate is strongly limited in comparison with the bulk phase. It means that the freedom of the adsorbate strongly decreases and the entropy becomes negative:

$$\Delta S < 0, \quad (5.6)$$

$$\Delta G = \Delta H - T[-\Delta S], \quad (5.7)$$

$$\Delta G = \Delta H + T\Delta S. \quad (5.8)$$

According to Eq. (5.8), enthalpy ΔH should be negative, as determines the mentioned process as exothermic:

$$\Delta H < 0. \quad (5.9)$$

The so-called condition of exothermicity arises from Eq. (5.9).

Several parameters of Gibbs model will be described as the sum of partial parameters: total volume V , internal energy U , entropy S and number of particles of the i -th type N_i :

$$V = V_B + V_C, \quad (5.10)$$

$$U = U_B + U_C + U_A, \quad (5.11)$$

$$S = S_B + S_C + S_A, \quad (5.12)$$

$$N_i = N_{Bi} + N_{Ci} + N_{Ai}, \quad (5.13)$$

where indexed parameters belong to the mentioned phases B and C as well as interface A . Now it is necessary to estimate the exact phase contribution. Let us assume the energy density for both homogeneous phases as internal energy per unit volume: u_B and u_C .

The total energy U could be expressed as follows:

$$U = u_B V_B + u_C V_C + U_A, \quad (5.14)$$

where U_A represents an internal energy of interface A . Actually, the molecular amount at interfaces changes significantly. For i -th type of particles, molecular concentration represents the behaviour of two phases: c_{Bi} and c_{Ci} . According to Eq. (5.15), an additional quantity of particles is formed in two-phase system due to the interface is equal to N_{Ai} :

$$U_A = U - u_B V_B - u_C V_C, \quad (5.15)$$

$$N_{Ai} = N - c_{Bi} V_B - c_{Ci} V_C. \quad (5.16)$$

Now it is possible to determine the main parameter – interfacial excess Γ_i :

$$\Gamma_i = \frac{N_{Ai}}{A}. \quad (5.17)$$

In some cases, interfacial excess Γ_i could be treated as a molecular concentration on the surface (number of particles per unit area).

The Gibbs approach is known as the Gibbs dividing surface (GDS). Let us assume the existence of the solution: any substance dissolved in a certain solvent. The interface is determined by the point of position, where the surface excess of solvent particles becomes zero.

The main phenomena of the surface could be titled as physical stability of the surface as well as the presence of the surface free energy [2]. The classical task (how to estimate the surface energy) starts from a crystal interface (*macro*-approach).

Let us assume the crystal of volume V , which consists of N particles. Let us assume the internal energy U as a function of entropy S , which is predetermined by temperature T , pressure P and chemical potential μ :

$$U = U(S, V, N), \quad (5.18)$$

$$dU = \left[\frac{\partial U}{\partial S} \right]_{V,N} dS + \left[\frac{\partial U}{\partial V} \right]_{S,N} dV + \left[\frac{\partial U}{\partial N} \right]_{V,S} dN, \quad (5.19)$$

$$dU = TdS - PdV + mdN. \quad (5.20)$$

In a specific case, if solid consists of one particle ($N = 1$), the chemical potential $\mu = m$, and Eq. (5.20) transforms to Euler equation for one particle (5.22):

$$U(IS, IV, IN) = IU(S, V, N), \quad (5.21)$$

$$U = TS - PV + mN. \quad (5.22)$$

For a conservative system, the particle energy U is a time-independent function:

$$\frac{dU}{dT} = 0, \quad (5.23)$$

$$SdT - PdV + Ndm = 0. \quad (5.24)$$

Equation (5.24) is called the Gibbs–Duhem equation.

Now it is necessary to evaluate the differences between macro- and microstructures. For large isotopic solids, the pressure inside is the same in all directions, but the pressure at the plane surface is anisotropic (anisotropy ratio is very high). It means that damaging the crystal surface (crystal cleavage along crystallographic planes) needs to consume additional energy which is proportional to the surface A . As a result, from Eq. (5.22), the additional member gA must be introduced, when the factor g is called the surface tension:

$$U = TS - PV + mN + gA, \quad (5.25)$$

$$g = \frac{dU}{dA}. \quad (5.26)$$

The surface tension is related to the surface formation energy when the main physical parameters (temperature T , volume V and the chemical potential of the particle m) are time independent. For microparticles, an additional condition must be established: the number of particles N does not change. The surface tension for a solid body corresponds to the gas pressure (two-dimensional analogue). The second term in Eq. (5.25) $p dV$ represents the work by increasing the volume V . The pressure p is always directed from surface (in normal direction). If the surface

Table 5.1 Size-scaled approaches in materials science

Pore size		Surface, %		Volume, %		
Macro		Negligible		30		
Meso		<5		<10		
Micro		>90		40 ÷ 50		
Nano		>95		100		
0.1 nm	Nanoscale	100 nm	Microscale	100 μm	Macroscale	1 mm
		2 μm	Mesoscale	20 μm		

area A increases when the volume V remains constant, the surface of the elastic vector is oriented parallel to the surface.

Now it is possible to determine four different approaches in materials science concerning the surface phenomena (see Table 5.1). A geometric surface can cover some amount of chemical substances, or otherwise, chemical substance could be formed in a certain cube containing pores. Significance of the surface according to surface thermodynamics could be treated as negligible (in case of macro-subjects) or significant (in case of micro-subjects). For practical estimation, the value of diameter d allows attributing the particles or pores into four groups: $d > 20 \mu\text{m}$ – macropores, $2 \mu\text{m} < d < 20 \mu\text{m}$ – mesopores, $800 \text{ nm} < d < 2 \mu\text{m}$ micropores and $d < 800 \text{ nm}$ – nanopores.

The ideal geometric surface contains any kind of pores. On the contrary, real surfaces are in pores of dimensions of molecular size and bigger. The real surface phenomena include two factors: (1) covering or adsorption as a slow mass transfer and (2) bonding capacity of the adsorbate.

5.2 Physical and Chemical Adsorption, Adsorption Kinetics

Adsorption is a surface-based process where adhesion of molecules from gas or liquid to a surface occurs. Attraction of adsorbate molecules to an adsorbent surface is a spontaneous process. Adsorption can occur at all surfaces. This term was first used in 1881 by a German physicist Heinrich Kayser (1853–1940). For the adsorbent surface and adsorbate molecules, adsorption processes start with the reorientation of molecules in the near environment to the surface and finish with the strong or soft fixation of molecules by short distances too. At the final position, attractive and repulsive forces become balanced when adsorption occurs. After finishing all steps, the free energy of the system decreases.

The surface forces of an adsorbent (substrate) are unsaturated, and according to the mentioned condition, the concentration of particles in the proximity of a surface arises (deposition takes place). The adsorbent surface and adsorbate gas (or liquid) could be treated as a thermodynamic system characterized by the total energy.

Table 5.2 Nature of adsorption forces for physical (PS) and chemical (CS) adsorption

Type	Definition
Van der Waals forces, London dispersion forces	PS
Inductive forces, dipole–dipole forces	PS, presence of significant induced dipole moment
Hydrogen bonding	Interactions between proton-donor group of adsorbate and nucleophilic polar surface of adsorbent
Covalent bonding	CS

Two types of adsorption can be found in materials science: physical adsorption and chemical adsorption. Exchange adsorption is always regarded as a special case of adsorption, when the strong electrostatic forces attract the particles to charged sites on the surface. Table 5.2 represents the comparison of adsorption forces.

Physical adsorption (additional terms *physisorption*, *van der Waals adsorption*) occurs in the case if attracting forces are of van der Waals type only. Chemical adsorption (additional terms *chemisorption*, *Langmuir adsorption*, *activated adsorption*) occurs in the case if attracting forces are of similar strength in comparison with chemical bonds.

Inductive forces such as intermediate forces could make a major contribution to the total adsorption energy on several metals such as alumina. Surprisingly, but this contribution is negligible for silica.

Due to the weak bonding forces, physical adsorption is the reverse process: increasing temperature or decreasing pressure can reduce the adsorbed amount of adsorbate. Van der Waals interactions are significant at low temperatures only. The attraction of particles is not fixed to a specific area. Individuality of both types of particles (adsorbent and adsorbate) is preserved. According to that, adsorbate is relatively free to move from the surface or along the surface. Surface covering and surface dissipation are limited by thermal motion.

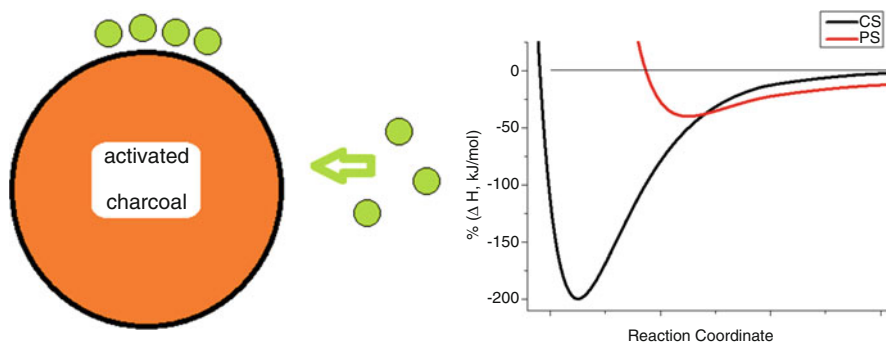
Otherwise, chemical adsorption is related to the creation of new chemical bonds while passing through the activation energy barrier. Due to unsatisfied vacancies of the surface and the existence of molecular fragments of the adsorbent, a solid surface can catalyze reactions. Table 5.3 represents a comparison of physical adsorption vs chemical adsorption processes.

Figure 5.4 presents the gas adsorption scheme on activated charcoal. Also, potential energy diagram of physical (PS) and chemical (CS) adsorption is presented. The dependence contains a minimum, which predetermines the condition of a stable point.

As in the case of interaction between two molecules, adsorbate–adsorbent interactions could be modelled by means of Lennard–Jones (LJ) potential:

Table 5.3 Physical (PS) vs chemical (CS) adsorption

Different aspects of adsorbent (AT) and adsorbate (AE)	
Physisorption (PS)	Chemisorption (CS)
Requiring of suitable PT conditions in any gas–solid system	Chemical bonding between AT and AE
Relatively low temperature required	Wide interval of temperature is possible
PS accelerates with decreasing of temperature	CS accelerates with increasing of temperature until extremum point, then decreases
High pressure P favours PS, low pressure causes desorption	High pressure P is favourable, low pressure does not cause desorption
No activation energy barrier	Activation energy takes place
Equilibrium rapidly	Equilibrium slowly
Reversible	Mostly irreversible
Longer distance between AT and AE	Shorter distance between AT and AE
Long range, weak bonding between AT and AE (van der Waals interactions)	Short range, strong bonding between AT and AE (usually covalent)
No decomposition of adsorbate	Possible breakage of adsorbate into radicals (or atoms) which will be bounded separately
No significant MO overlap	MO overlap takes place
No electron transfer	Electron transfer takes place
No sharing of electrons	Sharing of electrons takes place
No chemical reactions	Chemical reaction occurs
PS begins as a monolayer	CS begins as a monolayer
Multilayer or monolayer covering	Monolayer covering only
Any canalization	Canalization of reactions
Enthalpy in range $[5 \div 50]$ kJ/mol	Enthalpy in range $[40 \div 800]$ kJ/mol
Dissociation energy up to 0.5 eV	Dissociation energy $[1 \div 10]$ eV
Exothermic	Exothermic

**Fig. 5.4** Gas adsorption on activated charcoal (*left*). Energy diagram of physical (PS) and chemical (CS) adsorption

$$V_{L,J} = E \left[\left[\frac{R_m}{R} \right]^{12} - \left[\frac{R_m}{R} \right]^6 \right], \quad (5.27)$$

where E represents the depth of the potential well, R is the distance between the particles, and R_m is the distance of minimal potential. Buckingham potential looking similar to LJ-potential contains repulsive part as an exponential function:

$$V_B = E \left[\exp\left(-\frac{R_m}{R}\right) - \left[\frac{R_m}{R} \right]^6 \right]. \quad (5.28)$$

Near the equilibrium point and especially for chemical adsorption, Morse potential could be useful:

$$V_M = D_E [1 - \exp(-\alpha(R - R_m))]^2, \quad (5.29)$$

$$\alpha = \sqrt{\frac{k}{2D_E}}, \quad (5.30)$$

where D_E represents dissociation energy and k is the force constant at the minimum of the well.

In many cases, chemical adsorption and physical adsorption could occur at the same time but at different distances. CS always is dominating at short distances, in comparison to PS. At long distances, PS starts to dominate over CS.

Some differences between chemical adsorption and physical adsorption could be explained by energy exchange. Heat of adsorption, ΔH , could be derived from Clausius–Chaperon equation:

$$\left[\frac{\partial \ln P}{\partial T} \right]_V = - \frac{\Delta H_{AD}}{RT^2}. \quad (5.31)$$

Especially for physical adsorption, enthalpy of adsorption H_{ADS} is approximately equal to enthalpy of condensation Q_{CON} :

$$\Delta H_{ADS} \approx Q_{CON}. \quad (5.32)$$

For chemical adsorption, such two values can differ in orders. Tables 5.4 and 5.5 represent several structures with energies typical for process.

Many popular adsorbents are grouped into three classes:

- (i) Carbon-based compounds: activated carbon, graphite and graphene. Such materials are typically hydrophobic and non-polar.
- (ii) Oxygen-containing compounds: silica gel and zeolites. Such materials are typically hydrophilic and polar.
- (iii) Polymer-based compounds: functional polar groups in a porous polymer matrix. Figure 5.5 represents model of silica surface covered in different ways. Free hydroxyl and bounded hydroxyl on silica surface are the simplest

Table 5.4 Enthalpies of processes

Process	Motion	Adsorbate/adsorbent	ΔH , kJ/mol
Physisorption	Condensation	N2/Fe	−6
Physisorption	Adsorption	N2/Fe	−10
Physisorption	Adsorption	N2/graphite	−12
Chemisorption	Adsorption	N2/Fe	−150

Table 5.5 Physical (PS) vs chemical (CS) adsorption. Comparison on energies

Physisorption (PS)	Energy, kJ/mol	Chemisorption (CS)
	200 ÷ 400	Covalent bonding
	100 ÷ 200	Donor-acceptor interactions
	70 ÷ 150	CT interactions
Acid-base interaction with proton transfer	60 ÷ 80	
$\pi - \pi$ intermolecular complexes	30 ÷ 40	
Hydrogen bonding	<20	
Dipole–dipole interactions	10	
Van der Waals interactions	5	

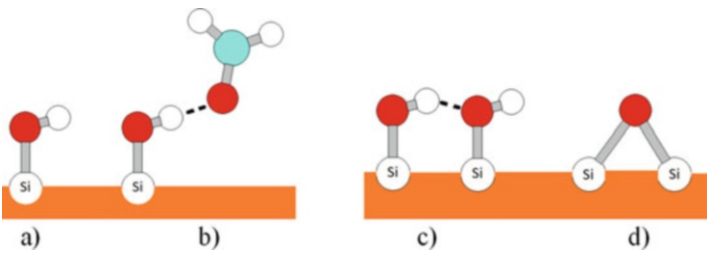
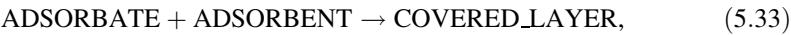


Fig. 5.5 Silica (Si) surface covered by hydroxyls [−OH]: (a) free hydroxyl; (b) bounded hydroxyl by [O = CH₂]; (c) reactive and bound hydroxyl; (d) surface siloxane

case in layer formation. Otherwise, mixed bounding could create more stable structures when reactive and bound hydroxyl forms several bonds. In addition, ‘molecular’ structure, so-called surface siloxane, could form in special case.

Adsorption process could be characterized as *cp* dependency (amount or concentration of adsorbate on the adsorbent surface as function of adsorbate gas pressure *p* at constant temperature *T*).

This type of graph is called the adsorption isotherm. The reversible process as behaviour of two types of chemical reactions (adsorption and desorption at the same time) could be characterized by Eqs. (5.33) and (5.34):



Chemisorption is always followed by charge transfer (CT) processes, in which adsorbate and adsorbent occur (reactant R and catalyst). Let us assume the existence of initial reaction of electron accepting:



If the reactant R is placed outside the surface, a partial charge transfer between the reactant R and the catalyst could be formed (corresponds to a chemisorption bond). If the reactant R is placed on the surface, a complete charge transfer between the reactant R and the catalyst initiates the creation of a charged area (hole layer) following a flow of electrons. This process is called depletive chemisorption.

Equilibrium of both processes could be achieved at a certain temperature, but in the transition period, equilibrium will shift in the direction where the number of particles decreases. After saturation, the increase of pressure does not affect the covered amount of the adsorbent. Figure 5.6 represents the saturation phenomena in physical adsorption. Dependency of adsorbed amount of adsorbate on adsorbate pressure is not linear but becomes linear after saturation pressure *PS*. Figure 5.7 represents adsorption isobars for both processes: physical adsorption (PS) and chemical adsorption (CS).

Generally, four factors are significant to describe the phenomena of adsorption effect:

1. The nature of the adsorbent and adsorbate (molecular structure of gas and crystalline or polycrystalline structure of surface). Actually, vacant electronic states on the surface represent the additional potential. The possibility to catalyze many chemical reactions occurs due to the mentioned condition.
2. The surface area of the adsorbent. Geometrically, the area of 2D surface gives the smallest value. For metal clusters of different diameters, the surface area is more fractal than plane; the surface area increases (e.g. from 2 to 2.3). For smaller clusters, absorbance on surface interface increases significantly, in orders.
3. Temperature. Le Chatelier's principle (or the principle of response reactions) claims that any change in status quo of chemical substance prompts an opposing reaction in the responding system. Initially, the system must be presented at equilibrium, and any changes in temperature induce the readjustment processes to counteract the effect of the applied change. Finally, a new equilibrium is established. For adsorption as an exothermic process, it means that magnitude of adsorption increases when temperature decreases (case of physical adsorption). The rise of temperature can switch physical adsorption to chemical adsorption (passing to the activation barrier, formation of strong bonding).
4. Pressure. Increasing pressure, the adsorption reaction yield increases – until a certain saturation level is exceeded (see Fig. 5.6). The decrease of pressure causes a reverse process – desorption.

Fig. 5.6 Saturation phenomena in physical adsorption. Dependency of amount of adsorbate n on adsorbate pressure p , when $T = \text{const}$

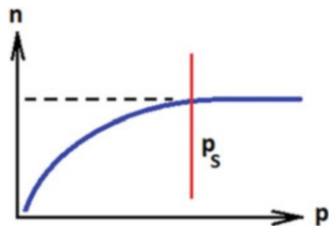
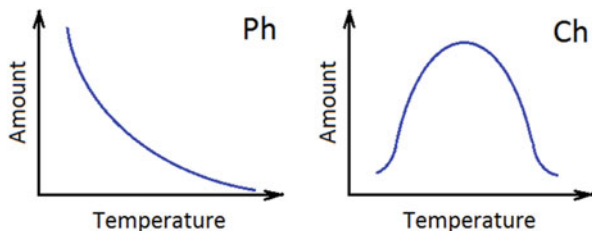


Fig. 5.7 Adsorption isobars: dependencies of adsorbate amount on temperature. *Left*, physical adsorption (PS); *right*, chemical adsorption (CS)



Adsorption could be characterized through isotherms – dependency of the amount of the adsorbent on its pressure (in case of gas) or concentration (in case of liquid), when temperature is constant.

5.3 Gibbs Adsorption Isotherms

Now it is necessary to estimate a near-surface layer. Particles of substances may form several sub-layers as thin films in the processes of accumulation. Let us assume the existence of two-phase systems consisting of B and C – see previous Fig. 5.1. Separation of phases is obtained by the surface A (cross-sectional area of the dividing surface). Total Gibbs free energy of a system could be obtained as a sum:

$$G = G^B + G^C + G^A, \quad (5.36)$$

where G^B and G^C represent Gibbs free energy of phase B and phase C, respectively, and G^A represents Gibbs free energy of a cross-sectional area (surface A) which separates the mentioned phases B and C.

Let us assume the existence of several homogeneous components (total number j) with the chemical potential μ_i and concentration c_i . Each phase (phases B, C and interface A) could be characterized by Gibbs free energy for a phase:

$$G^B = U + pV - TS + \sum_{i=1}^{j_B} \mu_i n_i, \quad (5.37)$$

$$G^C = U + pV - TS + \sum_{i=1}^{j_C} \mu_i n_i, \quad (5.38)$$

$$G^A = U + pV - TS + \sum_{i=1}^{j_A} \mu_i n_i, \quad (5.39)$$

where pVT represents thermodynamic parameters: pressure, volume and temperature, U is the internal energy, and S is the entropy.

The total derivative according to Eq. (5.36) includes three types of factors:

$$dG = \sum_{B,C,A} [X_1 + X_2] + X_3, \quad (5.40)$$

where

$$X_1 = dU + p dV + V dp - T dS - S dT, \quad (5.41)$$

$$X_2 = \sum_{i=1}^j \mu_i dn_i + \sum_{i=1}^j n_i d\mu_i, \quad (5.42)$$

$$X_3 = Adg + g dA. \quad (5.43)$$

Actually, gdA factor must be treated as negligible (in case of stable surface area). Factor g represents the surface tension.

All chemical or physical processes related to the covering of surfaces and creation of interface are reversible. According to the first law of thermodynamics, dU represents behaviour of heat energy Q and work W (non-pressure volume work, surface energy is considered):

$$dU = Q + W. \quad (5.44)$$

In Eqs. (5.40) and (5.41) presented dU can be expressed as follows:

$$dU = Q + W = \sum_{B,C,A} [TdS - pdV - W]. \quad (5.45)$$

By substituting Eqs. (5.45, 5.46, 5.47, 5.48, 5.49 and 5.50):

$$dG = \sum_{B,C,A} \left[V dp - S dT + \sum_{i=1}^j \mu_i dn_i + \sum_{i=1}^j n_i d\mu_i \right] + Adg, \quad (5.46)$$

$$dG = V dp - S dT + \sum_{i=1}^j \mu_i dn_i. \quad (5.47)$$

Properties of B , C phases and interface A are related by Eq. (5.48):

$$\sum_{i=1}^j n_{iB} d\mu_i + \sum_{i=1}^j n_{iC} d\mu_i + \sum_{i=1}^j n_{iA} d\mu_i + Adg = 0. \quad (5.48)$$

Let us assume the phases B and C as bulk phases. Let us establish the equilibrium ($T = \text{const}$, $p = \text{const}$). First two members in Eq. (5.48) are negligible:

$$\sum_{i=1}^j n_{iB} d\mu_i = \sum_{i=1}^j n_{iC} d\mu_i \rightarrow 0. \quad (5.49)$$

According to Eq. (5.49)

$$\sum_{i=1}^j n_{iA} d\mu_i + Adg = 0. \quad (5.50)$$

The Gibbs isotherm equation (Eq. 5.50) is called the adsorption isotherm that related surface tension g of a solution with the concentration of the solute n .

Foo et al. [3] presented a great number of different models for researches. Table 5.6 represents several models of adsorption isotherms which are important from the historical point of view or due to real acceptance in the surface chemistry – advantages and disadvantages are pointed out.

Freundlich Adsorption Isotherm. In 1909, Herbert Freundlich derived a primitive empirical relation which allows predicting the adsorption capacity on adsorbate pressure. This model has been useful so far as the relation of the first order assumption. In the case when identity of solute is unknown, it is possible to postulate the deposition model as simple as possible: adsorbate forms a monomolecular layer on the surface.

The quantitative dependence of the adsorption capacity (the amount of deposited particles of substance) was related to the equilibrium pressure of the adsorbate p :

$$\frac{x}{m} = k \cdot p^{\frac{1}{n}}, \quad (5.51)$$

$$\log \left[\frac{x}{m} \right] = \log k + \frac{1}{n} \log p, \quad (5.52)$$

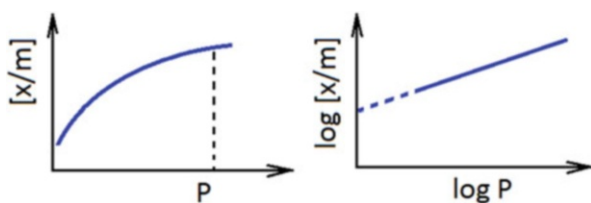
where x is the mass of the adsorbate and m is the mass of the adsorbent. Constants k and $n > 1$ are characteristic for a particular gas and the surface (adsorbate and adsorbent, respectively). Equation (5.70) as a logarithmic dependence shows that the adsorbate amount increases slowly in comparison with pressure.

Figure 5.8 represents Freundlich isotherm, which explains idealized adsorption in first assumption as a linear dependence.

Slope $n - 1$ is distributed practically in range $[0.1 \div 0.5]$. In a special case (at high pressure) if $n - 1 = 0$, Eq. (5.70) becomes:

Table 5.6 Physical (PS) vs chemical (CS) adsorption. Comparison on models

Model of isotherm	Advantages	Disadvantages
Freundlich	Monolayer on surface	Any interactions between adsorbate particles
Langmuir	One-layer model	Empirical model, any physics
BET	Three-layer model	Semi-empirical model
Lattice gas	Complete description of interactions between adsorbate particles	Big computer resources required

Fig. 5.8 Freundlich adsorption isotherms

$$\log \left[\frac{x}{m} \right] = \log k, \quad (5.53)$$

$$\frac{x}{m} = k = \text{const.} \quad (5.54)$$

Equation (5.54) expresses the process of adsorption independent of pressure. In the next case, if $n - 1 = 1$, Eq. (5.70) becomes:

$$\log \left[\frac{x}{m} \right] = \log k + \log p, \quad (5.55)$$

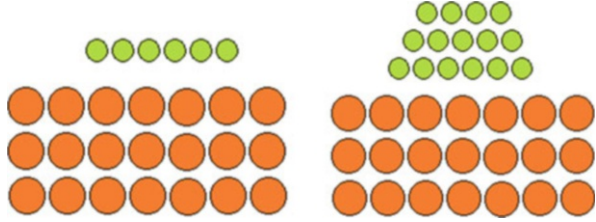
$$\frac{x}{m} = kp. \quad (5.56)$$

Adsorption is pressure dependent. It is necessary to point out that the Freundlich isotherm correctly represents the adsorption capacity at equilibrium pressure of the adsorbate only at low pressure.

Langmuir Adsorption Isotherm. In 1916, Irving Langmuir (Nobel Prize winner in 1932) presented a simple model for the adsorption of substance onto simple surfaces. Let us assume ideal gas to be adsorbed on surface, and adsorbed molecules are fixed at surface (immobile). All adsorbate regions are identical energetically. This model is suitable when surface is homogeneous and uniform, and only monolayer adsorption occurs. Figure 5.9 represents the surface structure of Langmuir adsorption: adsorbate – monolayer. Interactions between adsorbed molecules are absent, and adsorbed and desorbed (free) molecules exist in equilibrium.

The presented model is suitable for the analysis of reaction mechanisms in chemisorption as well as physisorption [4]. According to the model, reaction yield is independent of the amount of the adsorbed substance. Heat of the adsorption is a constant.

Fig. 5.9 Langmuir adsorption (adsorbate – monolayer) and BET adsorption (three-layer)



Let us assume the existence of the surface covered by adsorbate at pressure of adsorbate P . The total number of adsorption sites is equal to N , number of occupied sites – n . The fraction q of the surface (as covered by substance):

$$q = \frac{n}{N}. \quad (5.57)$$

At equilibrium of adsorption and desorption processes:

$$k_A P(N - n) = k_D n \quad (5.58)$$

The equilibrium constant K_{eq} is equal:

$$K_{eq} = \frac{k_A}{k_D} = \frac{n}{P(N - n)}, \quad (5.59)$$

where k_A and k_D are adsorption and desorption rate constants. From thermodynamics:

$$K_{eq} = \exp \left[-\frac{\Delta H}{RT} \right], \quad (5.60)$$

where ΔH represents heat of adsorption at standard pressure, P_{ST} , and temperature T . Equation (5.59) could be rewritten in the form of value q (see Eq. 5.57):

$$K_{eq} = \frac{n}{P(N - n)} = \frac{1}{P \left(\frac{N-n}{n} \right)} = \frac{1}{P \left(\frac{N}{n} - 1 \right)} = \frac{1}{P \left(\frac{1}{q} - 1 \right)}, \quad (5.61)$$

$$q = \frac{K_{eq} P}{1 + K_{eq} P} = \frac{P}{K_{eq}^{-1} + P}. \quad (5.62)$$

Taking into account Eq. (5.60):

$$q = \frac{P}{K_{eq}^{-1} + P} = \frac{P}{P_{ST} \exp \left[+\frac{\Delta H}{RT} \right] + P}, \quad (5.63)$$

$$n^{-1} = N^{-1} + [K_{eq} N P]^{-1}, \quad (5.64)$$

$$\frac{P}{V} = \frac{P}{V_m} + \frac{1}{\alpha V_m}. \quad (5.65)$$

BET, Brunauer–Emmett–Teller Adsorption Isotherm. In 1938, Stephen Brunauer, Paul Hugh Emmett and Edward Teller published the first article about the BET theory [5]. Development of BET theory was related with the tasks of industry, especially in solid catalysis. BET theory applies to systems of multilayer physisorption and is useful in surface area determination. Figure 5.9 represents the surface structure of the BET adsorption when the three-layer covering is made. The BET theory usually utilizes an adsorbate that does not react chemically with the adsorbent.

Let us assume the volume of the adsorbed vapour V , the monolayer capacity V_m , both at the standard pressure, P_{ST} , and partial pressure of the adsorbate P , as well as the saturation vapour pressure of the adsorbate P_0 . According to the first assumptions that Langmuir theory can be applied to each layer:

$$\frac{P}{V[P_0 - P]} = \frac{1}{V_m C} + \frac{(C - 1)P}{V_m C P_0}. \quad (5.66)$$

The constant C is called the BET constant (adsorbate and adsorbent dependent), where ΔH_A and ΔH_L represent the heat of adsorption for the first and second layers, respectively:

$$C \approx \exp \left[\frac{\Delta H_A - \Delta H_L}{RT} \right]. \quad (5.67)$$

In case, if $P_0 \gg P$:

$$\frac{C - 1}{C} \rightarrow 1. \quad (5.68)$$

The BET isotherm is transformed to the Langmuir isotherm:

$$\frac{P}{V P_0} = \frac{1}{V_m C} + \frac{P}{V_m P_0}. \quad (5.69)$$

The BET method is one of the most frequently used in the surface science when the surface area of solids must be calculated from the data of physisorption of some gas.

5.4 Hydrogen Adsorption

The problem of hydrogen storage belongs to one of the more complicated technical tasks of the contemporary humanity. Hydrogen as a source of energy could be suitable for many areas of technical activities. However, gas form storage is not safe; liquid form storage requires the cryogenic equipment (some sort of tank). Liquid hydrogen boils at around 20.27 K (−252.88 °C).

There are two methods for the hydrogen storage: physical and chemical.

The physical storage could be organized as the behaviour of two physical processes: compressing under high pressure (700 bar) and/or liquefaction (<20 K) of molecular H₂. All processes are reversible. Cryogenic equipment consists of the high-pressure pumps and well-isolated tanks.

Chemical storage is dissociative according to Eq. (5.70):



Decomposition of molecular hydrogen into the atomic one allows organizing the deposition of the substance onto an activated surface as well as following long-time storage. Processes of deposition can be both reversible (using metal hydrides as adsorbents) and nonreversible (hydrolysed fuel, decomposed fuel).

Figure 5.10 represents the general scheme of molecular hydrogen adsorption on a metal surface. Molecular hydrogen as adsorptive and adsorbate could be deposited on a metal surface (physical adsorption). The reaction yield is very low. But after the decomposition of molecular hydrogen, atomic hydrogen can be placed as an adsorbate directly on the surface (3) as well as into pores (4).

This way is preferable taking into consideration two circumstances. Thomas K [6] reported results of fuel cells useful for hydrogen storage for transport applications. Author discussed the tasks of adsorption of hydrogen on porous materials, ranging from activated carbons to metal organic framework materials. The advantage is formulated as follows: at temperature 77 K, up to 5 and 7.5 wt% of hydrogen can be stored on porous carbon and metal organic framework materials, respectively. Ströbel et al. [7] studied the hydrogen adsorption on carbon materials at ambient temperature. Hydrogen adsorption reached values of 1.5 wt.% at ambient temperature and 125 bars.

Generally, storage of solid-state materials could be realized through two interfaces: metal hydrides and porous materials. Metal hydrides, such as palladium hydride, TiFeH₂, MgH₂, LiAlH₄, LiH, etc., could be used as storage media of low degree efficiency. Porous materials such as carbons, metal organic framework, porous polymers and zeolites are more prominent materials for storage media.

Bianco S et al. [8] reported the study of the hydrogen adsorption in several kinds of carbon nanotubes (CNT). Morphological microstructure and physical properties of CNT were examined in order to establish microstructure–process–property relationships. Several types of carbon nanotubes (SWCNT and five MWCNT) were examined using different methods, including Brunauer–Emmett–Teller

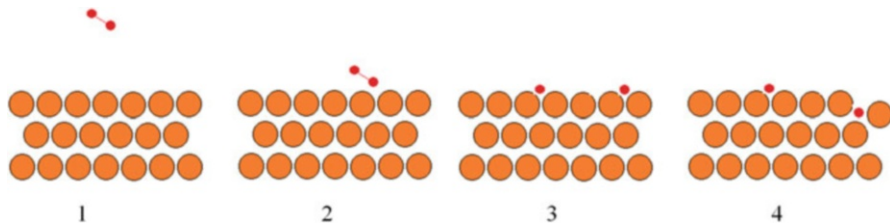


Fig. 5.10 Four stages of hydrogen (red) adsorption on a metal surface. Molecular hydrogen as adsorptive (1) and an adsorbate (2) at long and short distances from the surface, respectively. Atomic hydrogen as an adsorbate near the surface (3 and 4)

(BET) analysis for the surface area. The experimental measurements demonstrate a direct correlation between the exposed surface area and adsorbed hydrogen capacity, which confirms their linear relationship observed previously. SWCNT with surface area density of $800 \text{ m}^2/\text{g}$ has shown hydrogen storage of approximately 1.7 wt% at a pressure of 35 atm. Adsorption process seems to be perfectly reversible.

Meisner G P et al. [9] reported the previous results of novel synthesized carbon materials with microporous of high surface area. Specific surface area value was distinguished up to nearly $2000 \text{ m}^2/\text{g}$ and an excess hydrogen storage capacity of 4.2 wt% was observed. Authors claim that a strong correlation between the BET values of the specific surface area and the excess hydrogen adsorption capacity was observed.

5.5 Electronic Structure of Surface

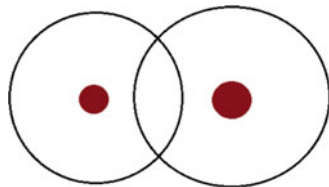
The Molecular System. First form of material complexation is a certain atomic or molecular system (molecule, dimer, cluster, etc). Electronic properties of molecular system could be established by solving the Schrödinger equation. The solution of the differential wave equation describes particle systems as well as macroscopic systems. The fundamental postulate of quantum mechanics claims that the wave function Ψ_0 describes all energetic properties of the system.

The time-independent Schrödinger equation for a simple molecular system contains Hamilton operator $\hat{H}_0$ which acts on a wave function $\Psi_0(\mathbf{r})$ representing stationary state. Proportionality constant E represents energy of the mentioned stationary state:

$$\hat{H}_0 \Psi_0(\mathbf{r}) = E \cdot \Psi_0(\mathbf{r}). \quad (5.71)$$

Hamiltonian $\hat{H}_0$ includes Laplacian Δ (as second derivative) and potential energy $U_0(\mathbf{r})$ as simplest case of Coulomb expression. For one-dimensional case:

Fig. 5.11 Simplest molecular system: two protons and two electrons. Overlap of two σ -orbitals



$$\hat{H}_0(x) = -\frac{\hbar^2}{2m} \cdot \frac{\partial^2}{\partial x^2} + U_0(x). \quad (5.72)$$

The simplest equation of the wave function is presented below as a plane wave with the amplitude A , wave vector $\mathbf{k}$ and angular frequency ω :

$$\Psi_0(\mathbf{r}, t) = A \cdot \exp[i(\mathbf{k}\mathbf{r} - \omega t)]. \quad (5.73)$$

The solution of the Schrödinger equation for a molecular system depends on the properties of the model. One of the simplest systems is a hydrogen molecule H_2 – a molecular system that consists of two protons and two electrons (see Fig. 5.11). In the framework of the molecular orbital (MO) as a linear combination of the atomic orbital (LCAO), the solution of the Schrödinger equation gives two and more possible states with different energies.

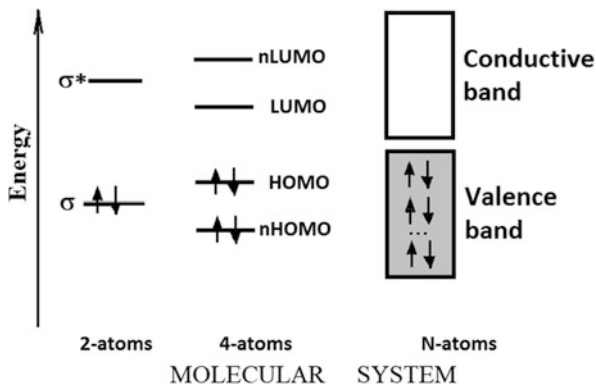
Figure 5.12 represents energy diagrams of the two-atom system, four-atom system and N -atom system. Such three systems could be treated as the main assumption of material organization starting from molecular. Practically evaporated molecular beam arranges on the surface in some periodicals. Formation of crystals is based on the lattice template.

Using the MO method, the number of stationary electronic states is equal to the number of electrons. According to the Pauli principle, one state could be populated by two electrons with different spins (presented by top-arrow and bottom-arrow). The two-atom two-electron system could be characterized by two electronic states, when the lowest is populated by both electrons with different spins (σ -state), and next is empty, virtual (σ^* – state).

The four-atom four-electron system could be characterized by four electronic states, when two lowest states are populated by four electrons (two pairs of electrons in state with different spins), and two highest states are empty, virtually. The highest occupied molecular orbital (HOMO) is related to the ionization energy, and the lowest unoccupied molecular orbital (LUMO) is related to the electron affinity. HOMO $\rightarrow$ LUMO transition denotes the electronic excitation dynamics of the system.

According to the mentioned assumption, N -atom N -electron system contains N states, which are overlapped in bands: the valence band (corresponds to the occupied MO) and the conductive band (corresponds to the virtual MO). This approach looks similar to the crystal definition.

Fig. 5.12 Energy diagram of different molecular systems: two atoms, four atoms, N -atoms



Crystal and Surface. The second form of material complexation is a solid formed in the form of an ordered (monocrystalline), partially ordered (polycrystalline, film based, etc.) or disordered system. According to the definition, a crystal represents a certain realization of the spatial distribution of a molecular system according to the rules of periodicals. A surface represents a two-dimensional behaviour of geometric localization of atoms.

Let us assume the existence of a cubic crystal with the lattice constant a – see Fig. 5.13. Vector $\mathbf{R}_n$ describes the coordinates of nuclear related to the lattice vector in three-dimensional space: $\mathbf{a}_i$, $i = 1, 2, 3$. The factor n_i represents the natural number.

$$\mathbf{R}_n = \sum_{i=1}^3 n_i \mathbf{a}_i, \quad (5.74)$$

$$\mathbf{a}_1 \rightarrow (a, 0, 0), \quad (5.75)$$

$$\mathbf{a}_2 \rightarrow (0, a, 0), \quad (5.76)$$

$$\mathbf{a}_3 \rightarrow (0, 0, a). \quad (5.77)$$

To describe the potential energy $U_1(\mathbf{r})$ of electrons in the crystal, operations of translation symmetry must be used. Vector $\mathbf{r}$ describes the coordinates of electrons related to the nuclear according to the Born–Oppenheimer assumption:

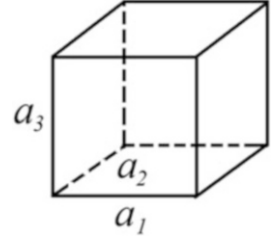
$$U_1(\mathbf{r} + n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3) = U_1(\mathbf{r}). \quad (5.78)$$

In the Schrödinger equation, Hamiltonian $\hat{H}_1$ includes Laplacian Δ (as second derivate) and mentioned potential energy $U_1(\mathbf{r})$:

$$\hat{H}_1 \Psi_1(\mathbf{r}) = E \cdot \Psi_1(\mathbf{r}), \quad (5.79)$$

$$\hat{H}_1(x) = -\frac{\hbar^2}{2m} \cdot \frac{\partial^2}{\partial x^2} + U_1(x). \quad (5.80)$$

Fig. 5.13 Cubic crystal lattice with lattice vectors a_1, a_2, a_3



Let us assume the existence of all electrons in the crystal as a behaviour of single isolated electrons (coordinate $\mathbf{r}$) belonging to the nuclear ($\mathbf{R}_n$). The complicated equation of the wave function is presented below as a product of the coefficient c and the wave function of the isolated electron $\phi(\mathbf{r} - \mathbf{R}_n)$:

$$\Psi(\mathbf{r}) = \sum_n c(n_1, n_2, n_3) \phi(\mathbf{r} - \mathbf{R}_n). \quad (5.81)$$

In that case, the wave function of the isolated electron ϕ must satisfy the Schrödinger equation, where s represents the energy of the stationary state of the isolated electron:

$$\hat{H}_2 \phi(\mathbf{r} - \mathbf{R}_n) = \varepsilon \cdot \phi(\mathbf{r} - \mathbf{R}_n), \quad (5.82)$$

$$\hat{H}_2(x) = -\frac{\hbar^2}{2m} \cdot \frac{\partial^2}{\partial x^2} + U_2(\mathbf{r} - \mathbf{R}_n). \quad (5.83)$$

The potential electronic energy $U_1(\mathbf{r})$ is expressed as the sum of potentials of isolated electrons and additional potentials δ :

$$U_1(\mathbf{r}) = \sum_n U_2(\mathbf{r} - \mathbf{R}_n) + \delta. \quad (5.84)$$

By solving the Schrödinger equation Eq. (5.79), assumptions of Born-von Karman type must be made. A crystal of infinity dimensions is divided into crystals of finite dimensions with $N > 1$ atoms. The condition of translational symmetry according to Eq. (5.78) must be applicable to coefficients $c(n_1, n_2, n_3)$:

$$c(n_1, n_2, n_3) = c(n_1 + N, n_2, n_3) = c(n_1, n_2 + N, n_3) = c(n_1, n_2, n_3 + N), \quad (5.85)$$

$$c(n_1, n_2, n_3) = \exp[i(k_1 n_1 + k_2 n_2 + k_3 n_3)a]. \quad (5.86)$$

After replacing, Eq. (5.81) becomes Eq. (5.87):

$$\Psi(\mathbf{r}) = \sum_n [\exp[i(k_1 n_1 + k_2 n_2 + k_3 n_3)a]] \phi(\mathbf{r} - \mathbf{R}_n). \quad (5.87)$$

The factor k_i represents the expression of the natural number $0 \leq u_i \leq N$:

$$k_i = \frac{2\pi}{Na} u_i. \quad (5.88)$$

Firstly, it is necessary to solve wave equations for isolated electrons and to receive the energy of the stationary state of the isolated electrons. Secondly, the equation Eq. (5.79) must be solved in any practical way using semi-empirical lattice atomic potentials. The solution of the Eq. (5.79) is presented below:

$$E = \varepsilon + \alpha + 2\beta(\cos n_1 a + \cos n_2 a + \cos n_3 a), \quad (5.89)$$

where α represents the Coulomb integral and β represents the exchange integral. Analysing Eq. (5.100), it is easy to establish the minimum and maximum energy, in case of $\cos \gamma = 1$ or $\cos \gamma = -1$:

$$E_{\max} = \varepsilon + \alpha + 6\beta, \quad (5.90)$$

$$E_{\min} = \varepsilon + \alpha - 6\beta. \quad (5.91)$$

Energetically, the width of the zone W increases with the decreasing lattice constant a (due to increasing of exchange integral β).

$$W = E_{\max} - E_{\min} = 12\beta. \quad (5.92)$$

Figure 5.14 represents the energy diagram of the isolated atom (single energy level) and atoms in crystal (many overlapped energy levels formed as zone). With $N \rightarrow \infty$, zone forms as quasi-continuous.

The task of forming the two-dimensional surface is related to the breaking of three-dimensional periodicity of the crystal. After mechanical motion, the absence of atoms initiates: (1) redistribution of the electronic charge inside the crystal and in the near-surface environment and (2) following the reformation of the damaged electronic states (formation of so-called surface states).

Let us assume the breaking operation of a cubic crystal ($n_3 = 0$) and arising of the surface (see Fig. 5.15). Vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are placed in a plane surface ($n_3 = 0$). Vector $\mathbf{R}_p$ describes the coordinates of any atom placed on the surface in a two-dimensional space: $\mathbf{a}_i$, $i = 1, 2$. The factor n_i represents the natural number (1, 2, 3, etc.).

$$\mathbf{R}_p = \sum_{i=1}^2 n_i \mathbf{a}_i. \quad (5.93)$$

The condition of the translational symmetry according to Eq. (5.78) must be applicable to coefficients $c(n_1, n_2, n_3)$:

$$c(n_1, n_2, n_3) = c(n_1 \pm N, n_2, n_3) = c(n_1, n_2 \pm N, n_3). \quad (5.94)$$

The condition for the surface $n_3 = N$ must be present in form:

Fig. 5.14 Energy diagram: energy levels of the isolated atom (IA) and atoms in the crystal (CR)

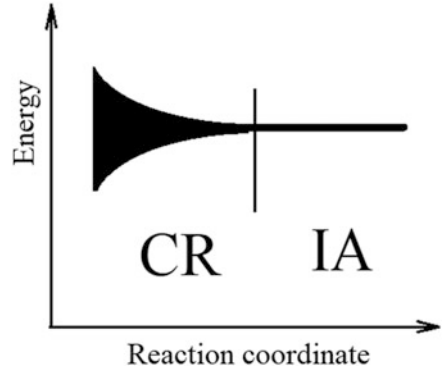
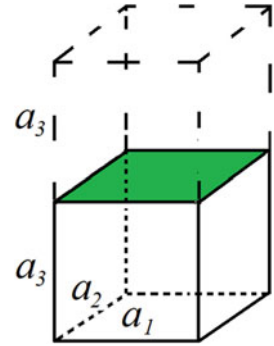


Fig. 5.15 Plane surface of crystal lattice vectors a_1, a_2



$$c(n_1, n_2, N) = 0, \quad (5.95)$$

$$c(n_1, n_2, n_3) = \exp[i(k_1 n_1 + k_2 n_2)a] \sin(N - n_3)k_3 a. \quad (5.96)$$

After replacing, Eq. (5.81) becomes Eq. (5.97):

$$\Psi(\mathbf{r}) = \sum_n [\exp[i(k_1 n_1 + k_2 n_2)a]] \phi(\mathbf{r} - \mathbf{R}_n). \quad (5.97)$$

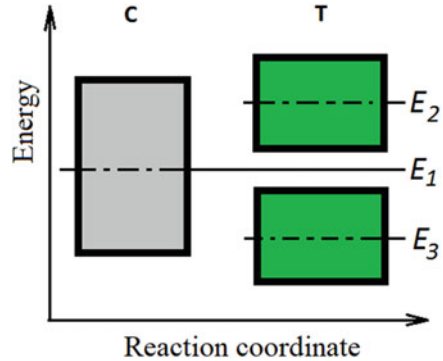
Solving the Schrödinger equation for the surface, the so-called Tamm states:

$$E_3 = \varepsilon + \alpha + 2\beta(\cos k_1 a + \cos k_2 a) + 2\beta \cosh \eta a, \quad (5.98)$$

$$E_3 = \varepsilon + \alpha + 2\beta(\cos k_1 a + \cos k_2 a) - 2\beta \cosh \eta a, \quad (5.99)$$

where α represents the Coulomb integral and β represents the exchange integral. Figure 5.16 represents distributions of energy levels of atoms in the crystal (C) and atoms on the surface (T). The energetic width of the zone W increases with the decreasing lattice constant a (due to increasing the exchange integral β):

Fig. 5.16 Energy diagram: energy levels of atoms in the crystal (C) and atoms on surface (T): $E_1 = c + \alpha$, $E_2 = c + \alpha + 2\beta \cosh \eta a$, $E_3 = c + \alpha - 2\beta \cosh \eta a$.



$$W = E_{\max} - E_{\min} = 2 \cdot 4\beta = 8\beta. \quad (5.100)$$

Local electronic states can be created on the surface of solids. There are three reasons why surface electronic states occur:

1. Damage of the periodic potential of the crystalline lattice due to the atomic dislocations.
2. The presence of uncompensated covalent bands on the surface.
3. Molecules or atoms of the adsorbate perturb the periodic potential created by the adsorbent in the lattice.

For the determination of the surface electronic states, two main assumptions are useful according to the presented model: the Tamm states and Shockley states. From the physical point of view, both models represent the same reality. The mathematical approach is different.

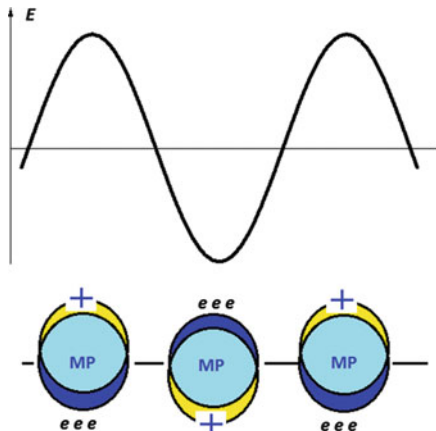
The Tamm states could be received by the following assumptions: (1) wave functions are of orbital-like type and (2) the tight-binding model for localized electrons. This method could be applied for semiconductors as well as for transition metals. The existence of the surface states was first shown by Igor Tamm in 1932.

The Shockley states could be received by the following assumptions: (1) wave functions are of crystal-like type and (2) the nearly free electron model. This method could be applied for narrow-gap semiconductors as well as many metals such as K, Al, etc.

Inglesfield [10] presented a very complete review of the electronic structure theory of clean metals and semiconductor surfaces. Effective methods how to solve the one-electron Schrödinger equation are described. Detailed calculations of the surface states of transition metals, s-p bonded metals and semiconductors are also explained and reviewed.

Zangwill [11] presented a detailed review of the surface electronics from different points of view: thermodynamic, crystallographic and phase transition. In addition, the review of Green [12] must be pointed out as one of significant classical reviews in the surface physics.

Fig. 5.17 Metal particles (MP) in electric field E : oscillations of E induce oscillations of electronic clouds



5.6 Surface Plasmon Resonance

Plasmon represents a collective oscillation of the plasma density at optical or near optical frequencies. According to this model, plasma must be treated as a free electron gas. Figure 5.17 represents metal particles (MP) in the electric field E when oscillations of E induce oscillations of electronic clouds. The surface plasmon resonance (SPR) is the basic method for the estimation of interactions between adsorbent (typically gold or silver) and adsorbate. The macro-surface or the surface of metal nanoparticles could be used for such purposes.

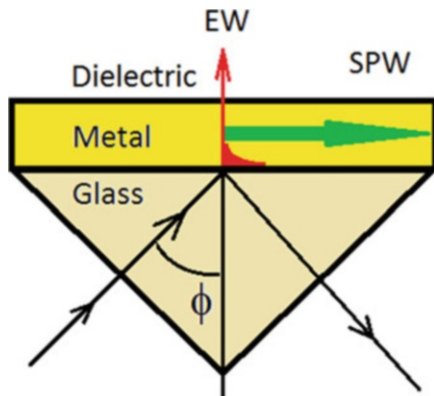
Figure 5.18 represents an experimental setup for the surface plasmon resonance (SPR) built up by the Kretschmann configuration. The glass prism is covered with a layer of Au (thickness $45 \div 55$ nm). The metal layer is covered with a dielectric (sample to investigate). The incident light beam passes through the glass prism (incident angle φ) and is reflected from the inner prism surfaces. If p-polarized light (the wavelength of the incident light λ) accesses metal layer at the total reflection angle, the charge density oscillations on the metal layer (evanescent field) occur. The surface plasmon represents transverse magnetic waves. Three different environments are present in this experiment. ϵ_d and ϵ_m represent a complex dielectric constant of dielectrics and the metal. ϵ_p is a dielectric constant of the prism, when the refractive index of the prism $n_p = \epsilon_p^2$.

Gwon et al. [13] presented resonance conditions for SPR experiments. The propagating vector of the surface plasmon wave k_{sp} and electromagnetic wave k_{em} must be equal:

$$k_{sp} = k_{em}, \quad (5.101)$$

$$k_{sp} = \frac{2\pi}{\lambda} \sqrt{\frac{\epsilon_m \cdot \epsilon_d}{\epsilon_m + \epsilon_d}}, \quad (5.102)$$

Fig. 5.18 Kretschmann configuration for SPR experiment. Surface plasmon wave (SPW) by *green* array, evanescence wave (EW) by *red*



$$\varphi = \sin^{-1} \sqrt{\frac{\varepsilon_m \cdot \varepsilon_d}{\varepsilon_p(\varepsilon_m + \varepsilon_d)}}. \quad (5.103)$$

The real SPR experiment could be organized using two techniques: (1) reflected beam changes intensity at the resonance angle (measuring of intensities at a fixed excitation wavelength); (2) resonance angle increases by the exciting metal layer covered by an active material (searching for the incidence angle at the lowest refraction index R).

The second way is more profitable:

1. Covering the surface of a sapphire prism by Au (thickness 50 nm).
2. Measuring the refractive index R_0 at different UV beam incident angles φ in the range of $[25 \div 45]^\circ$ – background curve $R_0 = R_0(\varphi)$.
3. Covering metal surface by an active organic material.
4. Measuring the refractive index R_x at different UV beam incident angles φ in the range of $[25 \div 45]^\circ$ – sample curve $R_x = R_x(\varphi)$.
5. The refractive index dependence on the incident angles φ contains the minimum at $[36 \div 37]^\circ$. A shift to higher angles for the active material takes place.

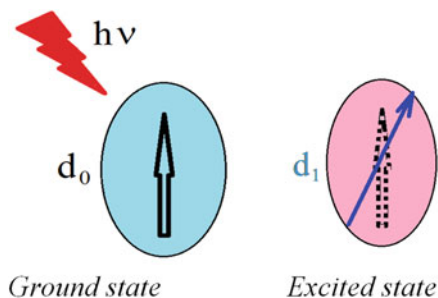
5.7 Interaction of Light and Nanoparticle

The Molecular Approach. Interaction of light and material could be understood using the approach of particle interaction. If the light absorption process is allowed, the main reaction could be written as follows:



The reactant (molecule, dimer, cluster, etc.) R interacts with the light quantum $h\nu$ and produces the reactant in the excited state R^* . After the internal conversion and different relaxation processes (luminescence, dark state depopulation, electron

Fig. 5.19 Schematic chart of material-light interactions (neutral π -conjugated molecule and light quantum $h\nu$). Essential change of the molecular dipole moment: $\mathbf{d}_0 \rightarrow \mathbf{d}_1$ at transition from the ground state to the excited state



transfer, etc.), the reactant returns to the ground state through energy Q dissipation processes. Eq. (5.104) represents only the energy balance according to the law of energy conservation in isolated systems. Figure 5.19 represents schematic chart of material-light interactions when the neutral π -conjugated molecule interacts with the light quantum $h\nu$. If the molecule absorbs the quantum, an essential change of the molecular dipole moment must occur. Dipole moments of ground and excited states $\mathbf{d}_0$ and $\mathbf{d}_1$, respectively, could be of different orientations or of different scalar values.

If the light absorption process is forbidden, scattering processes takes place. Any significant changes of the molecule dipole moment occur. Several processes are significant in materials science: vaporization of the medium, heat transfer to the medium and generation of particle cavitation on the media surface.

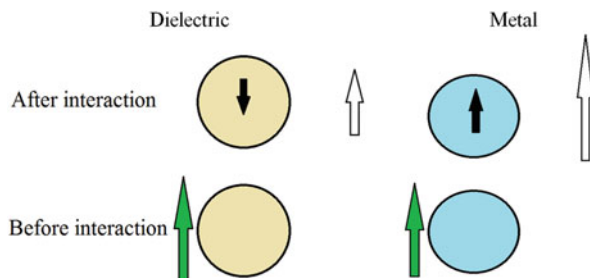
The Nanoparticle Approach. For particles, aspects related to quantum absorption are the same as in the case of molecules. If the light absorption process is allowed, the reaction according to Eq. (5.104) is realized. Otherwise, additional aspects related to the size of the particle (active nanosurface) sometimes are prior.

At the nanoscale, three types of nanoparticles could be accepted: (1) nanoparticles containing only several atoms; (2) small nanoparticles, diameter $1 \text{ nm} < d < 100 \text{ nm}$; and (3) large nanoparticles (diameter $d > 100 \text{ nm}$).

Figure 5.17 represents large metal particles (MP) in the electric field E when oscillations of E induce the oscillations of electronic clouds (plasmonic waves). Resonance conditions for such type oscillations could be distinguished in several ways. According to that, plasmonic nanoparticles could express higher reactivity in many scattering processes such as electron scattering, electron-phonon scattering, evaporation and melting of particle and fragmentation.

Figure 5.20 represents the scheme of interactions of light and a particle of a dielectric type and a metal type. Excitation could be produced by a light beam; the green arrow represents the vector of the incident electric field. The dielectric particle gives the response to the incident electric field by creating the induced dipole of the opposite direction. The metal particle gives the response to the incident electric field through oscillations of free electrons – the induced dipole in the same direction. Black arrows represent the vectors of induced dipoles. The vector of the resulting electric field after interaction (corresponds to the optical

Fig. 5.20 Interactions of light and dielectric particle (left) or metal particle (right) containing free electrons (right). Incident electric field, green arrow; inner electric field (induced), black arrow; resulting electric field, transparent arrow: green + black $\rightarrow$ transparent



response) is shown as a transparent arrow: for dielectric – a decreased length, for metal – an increased length. The directions of the resulting vector and the incident vector coincide.

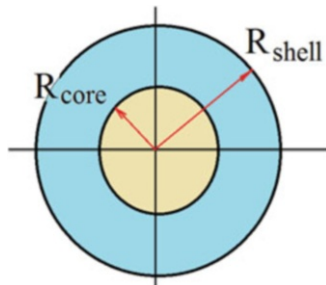
This effect could occur in macro-objects as well as in micro- or nanoobjects. A significant influence could be found only for nanoobjects. The Mie theory describes scattering processes of such type. The optical response for large metallic nanoparticles ($d > \lambda$) (near UV, VIS region) depends on the size of the particle (it means on the density of a free electron).

For small nanoparticles (diameter $1 \text{ nm} < d < 100 \text{ nm}$), several physical characteristics such as the refraction index and dielectric permittivity dramatically change. Kubo [14] established the refraction index dependence on the particle size when the size of a particle (50 nm Ag, Au) is comparable to the de Broglie wavelength for the electron. Predictions according the Mie theory are generally acceptable, but not exact. If the size of a particle (0.5 nm Ag, Au) is comparable with the Fermi wavelength for the electron, simulations of physical properties by means of the Mie theory are inaccurate. Several popular structures such as Au_{25} nanorods and Au_{25} nanospheres are useful as fluorescent nanoclusters.

For nanoparticles containing only several atoms, the size effects predominate over the steady-state electronic effects [15]. The properties of metallic nanoparticles are similar to molecules. Cesca et al. [16] studied a non-resonant broadband energy-transfer mechanism using sub-nanometric Au nanoclusters. It was found that small Au nanoclusters are very efficient sensitizers for the luminescent emission of $\text{Er}^{(3+)}$ ions in silica. It was concluded that the short-range nature of the interaction coincides with the non-radiative energy-transfer mechanisms.

Kubo [14] in 1962 decided that the energy level distribution in metallic nanoclusters is of discrete type but not continuing one. According to Fig. 5.20, interactions of light and a metallic particle induce charge density redistributions in the volume of the particle and also on the particle surface. Response depends on the free electron concentration which is related to the free path length of the electron. If the size of the metallic nanoparticle is more than the free path length of the electron, then the light absorption processes are related to the transition dipole moment. If the size of the metallic nanoparticle is less than the free path length of the electron, the light absorption energy is inverse proportional to the particle diameter [17]. According to Kubo [14], the energetic level distribution in metallic

Fig. 5.21 Geometry of metallic nanoshell



nanoclusters is of discrete type due to one condition: the size of a nanoparticle is equal to the Fermi wavelength (the so-called de Broglie wavelength for electron at the Fermi energy).

5.8 Nanoshells

A nanoshell represents a composite spherical nanoparticle which consists of a dielectric material covered by a thin Au shell (core and shell) [18]. Figure 5.21 represents a schematic chart geometry of metallic nanoshell. The sphere of radius R_{core} is covered by a metallic sphere of radius R_{shell} . The shell thickness t and nanoshell constant α are the main geometric parameters, which characterize the physical properties related to the plasmon excitation:

$$t = R_{\text{shell}} - R_{\text{core}}, \quad (5.105)$$

$$\alpha = \frac{t}{R_{\text{shell}}} = 1 - \frac{R_{\text{core}}}{R_{\text{shell}}}. \quad (5.106)$$

For practical purposes, $R_{\text{shell}} \approx 10$ nm, $t \approx 5$ nm and $\alpha = 0.5$.

A quasiparticle of such a type, called a nanoshell plasmon, represents a derivative where oscillations of electrons of the core and the shell are summarized: electrons simultaneously oscillate in relation to all ions. According to that, optical resonance of these nanoshells can be varied in the region from midIR to near UV, depending on the dimension.

Pena et al. [19] presented the study of the nanoshells linear optical responses. The plasmon resonance of metal nanoshells displays geometric tunability controlled by the ratio of the shell thickness either to the core radius or to the total radius of the particle. Considering the final $R_{\text{shell}} \approx 20$ nm by varying α parameter, several SPR peak positions can be shifted in the range of $510 \div 660$ nm for Au, $360 \div 560$ nm for Ag, and $553 \div 655$ nm for Cu. Authors claim that the intensity and position of the SPR peak strongly depends on the ratio α .

The advantages of metallic nanoshells are well-known in the area of biomedicine. Biocompatibility of nanoshells with tissues in vivo provides the specific applicability in the tumour therapy. Absorption and adsorption properties on

demand could be realized for the targeted displacing of nanoshells inside the tumour cells and killing the selected cells using appropriate therapeutical methods. Paithankar et al. [20] described several medical therapies for the treatment of diseases including atherosclerosis and thrombosis. The use of inorganic silica-gold nanoshells for various kinds of treatment is very prominent: core – SiO_x , shell – Au, $R_{\text{shell}} \approx 150$ nm, $t \approx 15$ nm and $\alpha = 0.1$. As excitation source infrared and red laser irradiation was used to thermally disrupt overactive sebaceous glands in the skin.

5.9 Organic–Nonorganic Interfaces

Polar molecular compounds represent a possibility to perform any conformational motion with the following charge transfer processes. After the external perturbation (laser light, current pulse, electron beam, etc.), electronic charge redistribution along the molecular axis is related to the occurrence of the transition dipole moment. Relaxation processes in a molecule are space limited (volume of a molecule) and time limited (up to several ns).

The possibility to manipulate the molecular charge distribution for informational purposes is strongly limited by the current contact problem: how to establish a true contact (in macro-approach resistiveless contact, in micro-approach junction according to the overlap of wave function).

Wang et al. [21, 22] studied the effect of metal–molecule contacts in molecular junctions and proposed a multibarrier tunnelling model. Sun et al. [23] presented an extensive review of the application of single molecules in electronics for the miniaturization purposes.

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