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Striking World of Nanostructures

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Abstract—Two classes of nanostructures produced by comminution of macroscopic bodied and by aggregation of free molecules or ions are characterized. Interfacial phenomena in the nanostructures are described. The definition of surface tension as an excess surface stress is given and the condition of mechanical equilibrium at an arbitrarily curved interface is formulated. The influence of interfacial phenomena on the dependence of properties of nanoparticles on their size is discussed. Thermodynamic equations are derived describing first-order and second-order phase transitions in nanoparticles. Polymorphous transformations of solid phases in the comminution process are analyzed. A chemical approach to description of solid nanoparticles, based on introduction of the chemical potential of a supramolecule and the chemical affinity of a process, is characterized. A theory of polymorphous transformations and solution of solid nanoparticles is formulated on the ground of the chemical approach. In the section devoted to aggregative systems, unusual properties of micelles and vesicles of surfactants are described: the dualism of their liquid-like and solid-like behavior and the absence of their macroscopic analog; the universal (with respect to various properties of solution) abruptness of the transition to formation of nanostructures as the critical micelle concentration is attained; the qualitative difference in the thermodynamic properties of aggregates corresponding to a maximum and a minimum in the curve of equilibrium size distribution of aggregates; and the decrease in the concentration of a surface-active ion in a micellar solution at adding its mother substance, a strong electrolyte, to the solution. An approach to specifying thermodynamic relationships for description of the lamellar (onion-like) structure of micelles is proposed.

INTRODUCTION

Nanostructures are the structures of small forms of matter (nanos means a dwarf in Greek). This name itself implies that new structures can arise as matter is comminuted. Let us remind that a state and a structure is not the same. The state of a phase always changes at changing its size and is described by well-known thermodynamic relationships. Although structural changes, naturally, are also governed by thermodynamics, they are rather a unique phenomenon. Nevertheless, the phenomenon is reliably established in experiment (decades of types of such structural transformations have been discovered by the present time). This communication is devoted to that phenomenon.

Nanoparticles can be prepared in two ways: by comminution (disintegration) of a macroscopic phase of matter or by aggregation of free molecules (or ions) into clusters. Both the ways are easily realizable, the first being typically “forcible” (work is expended for breaking interparticle bonds), although spontaneous dispergation of bodies is also possible under certain conditions. The second way is based on a spontaneous mechanism. Only creation of a sufficiently high concentration for the actuation of a process is here a forcible element. As a result, equilibrium and stable structures are formed ((as, for example, at micellization), which sometimes is unattainable in the first way.

The notion of structure is often related to the notions of phase and of aggregative state. However, the latter notions, as well as phase diagrams, refer to macroscopic (strictly speaking, infinitely large) bodies and become the less definite (more diffuse) the smaller the body size. About a single particle, even possessing a pronounced structure, of 1 nm in size, it is hard to say in what aggregative state the particle is, although one can say (say, from spectroscopic data) about its liquid-like or solid-like behavior. For particles of one order higher in size, the X-ray diffraction analysis already discovers the types of crystalline (they are called nanocrystalline) structures incident to macroscopic bulk phases. Both amorphization and various polymorphous transformation of nanocrystalline structures are observed in the process of disintegration of a solid. The process of mechanical treatment of solid particles in a ball (vibration) mill or another disintegrating device is rather complex. The

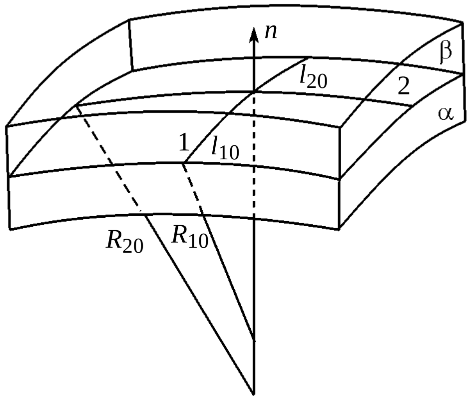

Fig. 1. Curved surface layer and dividing surface between phases α and β. (R_{10}, R_{20}) Principal curvature radii of the dividing surface.

parameters of mechanical action in this process (the duration and force of impacts, normal and tangential stresses and velocities) can be estimated [1]. High pressure itself can induce amorphization of matter (so it happens, for example, in SnI_4 [2]), and many factors of the disintegration process would manifest themselves as if we sledge-hammered a big piece of material. However, if we wish to distinguish nanosize effects, we should turn to the specificity of small systems: the smaller particles of matter the more they affected by surface phenomena. So we begin with surface phenomena.

1. NANOSTRUCTURES AND SURFACE PHENOMENA

Surface (interfacial) phenomena declare themselves, first of all, in the existence of a narrow transitional zone, a surface layer, at the boundary between adjacent phases. The properties of the surface layer differ from the properties of bulk phases. Far from the critical point, the effective thickness of the surface layer approaches molecular dimensions. Therefore, there should be observed very high gradients of those local properties that are different in the adjacent phases (for example, the thousandfold change in density at the boundary between a condensed phase and air occurs at a distance of about 1 nm). Such a strong nonuniformity of surface layers inevitably leads to their anisotropy. For instance, pressure in the surface layer of even liquid does not obey Pascal's law any more and depends on the orientation of unit area. In other words, the pressure tensor ceases to be spherical and acquires the set of components usually used for the description of mechanical state of solids. If one takes into account that, in addition, surface layer is not uniform, the specification of the whole field of the pressure tensor (or the stress tensor which only in sign differs from the pressure tensor) is needed for the full mechanical characterization of surface layer. A nanoparticle cannot contain a bulk phase inside if the nanoparticle size is comparable with the surface layer thickness. The spatial structure of such nanoparticle is different from the structure of the bulk phase and is rather closer to the structure of the curved surface layer (even if the structure type is maintained, the distances between the structure elements will be different as compared with the bulk phase). For example, at a reduced density of surface layer (it happens at the boundary of a codensed phase with its vapor), a nanoparticle will also be less dense as compared with condensed bulk phase, the whole nanoparticle generally being nonuniform. If, the reverse, the nanoparticle size appreciably exceeds the surface layer thickness, the bulk phase of matter is present inside the nanoparticle. However, surface layer influences the structure of the nanoparticle also in this case due to the existence of surface tension. The notion of surface tension is worthy to be discussed in detail. A real surface layer indeed possesses tangential stresses distributed in the surface layer thickness, and surface tension is real in this sense. However, Gibbs [3] suggested to replace the complex mechanical picture of surface layer by the simple model of two layers of adjacent bulk phases and, in-between, a membrane (this term was used by Gibbs as it is understood in the mechanics of continuous media and the theory of elasticity, i.e. as an infinitesimally thin elastic plate) of tension γ (surface tension). In other words, Gibbs replaced the real surface layer by an imaginary geometrical surface (dividing surface) supplied with surface tension. The location of the dividing surface is arbitrary, but it is advisable to place it inside the surface layer.

Generally, surface tension depends on the direction on the surface and is of a tensorial character. The components of the surface tension tensor can be defined as follows. Let us choose a system of orthogonal curvilinear coordinates (u_1, u_2, u_3) so that the coordinate line u_3 is directed along the gradients of loal properties inside the surface layer (i.e. along the normal to the surface). Then any coordinate surface (u_1, u_2) may be chosen as a dividing surface (this approach has been reasoned in detail in [4, 5]). We direct the coordinate lines u_1 and u_2 along the directions corresponding to the principal curvature radii of the dividing surface. Along these directions, we make two principal cross-sections of surface layer with the coordinate surfaces (u_2, u_3) and (u_1, u_3) (Fig. 1). In these cross-sections, we define the vectors of excess surface stresses (surface tensions), γ_1 and γ_2, respectively, as

$$\gamma_1 \equiv \frac{1}{l_{20}}\left[\int_{u_3^\alpha}^{u_{30}}(\mathbf{E_1}-\mathbf{E_1^\alpha})l_2h_3du_3+\int_{u_{30}}^{u_3^\beta}(\mathbf{E_1}-\mathbf{E_1^\beta})l_2h_3du_3\right], \tag{1.1}$$

$$\gamma_2 \equiv \frac{1}{l_{10}}\left[\int_{u_3^\alpha}^{u_{30}}(\mathbf{E_2}-\mathbf{E_2^\alpha})l_1h_3du_3+\int_{u_{30}}^{u_3^\beta}(\mathbf{E_2}-\mathbf{E_2^\beta})l_1h_3du_3\right], \tag{1.2}$$

where $\mathbf{E}_i(u_1, u_2, u_3)$ is the local stress vector in the cross-section perpendicular to the direction $i = 1, 2, 3$ (the vector of force acting on the unit area of the cross-section chosen), $\mathbf{E}_i^\alpha(u_1, u_2, u_3)$ and $\mathbf{E}_i^\beta(u_1, u_2, u_3)$ are its values inside adjacent bulk phases α and β (extrapolated values are taken for points inside the surface layer), l_i is the length of the coordinate line u_i ($dl_i = h_idu_i$ where h_i are Lame's coefficients), and u_3^α and u_3^β are the u_3 values for the boundaries of the surface layer on the sides of phases α and β, respectively (so that $\mathbf{E}_i(u_1, u_2, u_3) = \mathbf{E}_i^\alpha(u_1, u_2, u_3)$ and $\mathbf{E}_i(u_1, u_2, u_3) = \mathbf{E}_i^\beta(u_1, u_2, u_3)$, the additional subscript 0 means that a quantity refers to the dividing surface (in particular, the position of the dividing surface is given by the coordinate u_{30}).

Vectors γ_1 and γ_2 are interpreted as forces applied to the unit length of lines l_{20} and l_{10}, respectively, situated on the dividing surface (Fig. 1), the forces being directed anyway (unnecessarily along the surface). At any point of the dividing surface, local values of γ_1 and γ_2 are related to bulk values of stresses $\mathbf{E_3^\alpha} \equiv \mathbf{E_3^\alpha}(u_1, u_2, u_{30})$ and $\mathbf{E_3^\beta} \equiv \mathbf{E_3^\beta}(u_1, u_2, u_{30})$, extrapolated to the same point, by the condition of mechanical equilibrium

$$\mathbf{E_3^\alpha} - \mathbf{E_3^\beta} = \frac{\partial\gamma_\mathbf{1}}{\partial l_{10}} + \frac{\partial\gamma_\mathbf{2}}{\partial l_{20}}. \tag{1.3}$$

At every point of the system, the triad of vectors $\mathbf{E_1}$, $\mathbf{E_2}$, $\mathbf{E_3}$ makes the local stress tensor $\hat{E}$ which is usually replaced by the pressure tensor $\hat{p} = -\hat{E}$ in the case of fluid systems (these tensors only differ in sign). In terms of the pressure tensor components, Eq. (1.3) is formulated as (Rusanov–Shchekin's equation [6, 7])

$$\mathbf{p_3^\alpha} - \mathbf{p_3^\beta} = \frac{\partial\gamma_\mathbf{1}}{\partial l_{10}} + \frac{\partial\gamma_\mathbf{2}}{\partial l_{20}}. \tag{1.4}$$

If it turns that the coordinate system chosen makes the pressure tensor of a diagonal form (this happens for fluid systems in the absence of external fields), and the bulk phases and the surface (in the two-dimensional sense) are mechanically isotropic, then, as it can be shown [6, 7], Eq. (1.4) leads, in particular, to the classical Laplace equation

$$p^\alpha - p^\beta = \gamma\left(\frac{1}{R_{10}} + \frac{1}{R_{20}}\right) = \frac{2\gamma}{R}. \tag{1.5}$$

where p^α and p^β are the hydrostatic pressures in bulk phases α and β, respectively, γ is the surface tension at their boundary, R_{10} and R_{20} are the principal curvature radii in directions 1 and 2, respectively, and R is the radius corresponding to the mean curvature of the dividing surface. In accordance with (1.5), a movable liquid surface spontaneously takes the shape corresponding to the condition of constancy of mean curvature when passing to mechanical equilibrium. A solid surface is unable to do this, but, in the isotropic case, Eq. (1.5) may be used as a local relationship. Strictly speaking, however, Eq. (1.5) is generally applicable to a solid only under the condition that the solid is a figure of constant mean surface curvature. In practice, the shape of a solid is dictated by its prehistory, but Eq. (1.3)–(1.4) is always valid. It is of note that vector quantities are differentiated in Eq. (1.3)–(1.4). The surface curvature leads to the vector turn, so that Eq. (1.3)–(1.4), like the Laplace equation, exhibits the influence of surface curvature on the pressure differential in the adjacent phases. For example, there is no such a differential at a flat uniform face of a monocrystal, but a pressure differential arises at the crystal edge (herewith the differential must be finite, which requires the edge to be microscopically rounded). Thus we see that, even in the case when a monocrystal is in a mechanically isotropic and uniform medium (for example, in air) and is not subjected to other actions, the internal mechanical state of the monocrystal is already nonuniform (nd, possibly, also anisotropic) due to surface tension.

It is readily seen from the Laplace equation that the closed surface compresses a particle if surface tension is positive and, inversely, expands the particle if surface tension is negative. Surface tension is always positive for fluids, and, therefore, pressure inside a drop or a bubble is always higher than outside. However, surface tension can be of any sign for solids. This can be explained as follows. Surface tension may be defined as the work of formation of unit surface area, but, as it was first noticed by Gibbs [3], it is necessary to distinguish between the work of formation of unit area, σ, of a new surface by cutting and the work of formation of unit surface, γ, by the dilatation of the old surface. There is no difference in these works for fluids since, at dilating the surface, new molecules come to the surface from the fluid bulk and restore the structure of surface layer. This occurs not to the full extent in solids since the species of the solid lattice (immobile components) are devoid of ability to move freely over the whole lattice volume. This is why $\sigma \neq \gamma$. As shown in [8], the nonuniformity of the chemical potentials of immobile components inside surface layer can serve as a measure of the difference between σ and γ.

The quantity σ is of adhesion (energetic) meaning (σ is surface free energy for one-component systems) and is a scalar. By contrast, the quantity γ is of a purely mechanical (force) origin and of tensorial nature (with the tensor components γ_ik). The relation between these quantities is given by Herring's equation [9, 10]

$$\gamma_{ik} = \sigma + \partial\sigma/\partial e_{ik}, \tag{1.6}$$

where e_{ik} are the components of the surface strain tensor. In the case of an isotropic surface, Eq. (1.6) is reduced to simple Shuttleworth's equation [11]

$$\gamma = \sigma + d\sigma/d\ln A, \tag{1.7}$$

where A is the surface area. According to the thermodynamic stability conditions, $\sigma > 0$ (otherwise, all bodies would disintegrate spontaneously). This is why $\gamma = \sigma > 0$ for fluids. As for solids, the sign of γ depends on the sign and value of the derivative standing in (1.6) and (1.7).

The excess stress created by surface tension in a solid particle, will inevitably lead to its deformation. In the simplest case of an elastic isotropic spherical particle, the relation between the pressure p^α inside the particle and the linear radial strain $\Delta R/R$ is given by the equation

$$p^\alpha = 3K\Delta R/R, \tag{1.8}$$

where K is the modulus of dilatation. Reckoning the pressure and strain from the standard state corresponding to a constant external pressure p^β and using (1.5), we transform Eq. (1.8) to the form

$$\Delta R = 2\gamma/3K. \tag{1.9}$$

It follows from Eq. (1.9) that the absolute radial deformation ΔR does not depend on the particle size at constant γ and K (i.e. for sufficiently large particles). Since ΔR is composed from the shift in intermolecular (interatomic) distances in the course of deformation, the shift will be the larger the smaller the particle size. This shift can be determined experimentally (for example, using the LEED method) for sufficiently small particles (lthough appreciably exceeding the surface layer thickness in size). If ΔR is determined from experiment, Eq. (1.9) allows us to calculate surface tension. In this way, γ values of 1.4, 1.2, and 2.6 H/m were found for small particles of silver, gold, and platinum, respectively [12–14].

Theoretical and experimental estimates for σ and γ for solids (see the reviews [15–17]) yield a wide spread in data. For example, for ionic crystals at the boundary with a vacuum, the range of values of γ extends from negative values to values of order of 1 H/m even exceeding the values of σ. Nevertheless, positive values of surface tension prevail for most solids [17]. If one takes γ of order 1 H/m, the Laplace equation yields a capillary pressure of order 10^9 Pa for particles of 1 nm in radius. Such pressures (10^9–10^{10} Pa) are also met at the mechanical treatment of solid particles [1]. However, particles of 1 nm in size do not contain already a bulk phase and are close to surface layer in structure. This is characterized by a drop in surface tension in the language of Gibbs' model. If one takes γ of order 0.1 H/m and the particle radius 10 nm, capillary pressure will already be of order 10^7 Pa and will be considerably smaller than the above values of pressure in the process of mechanical treatment. However, pressures of 10^9–10^{10} Pa are realizes there in the form of one-sided and short-term (of order 10^{-8}–10^{-9} s) pulses [1]. By contrast, surface tension produces all-round and permanent compression that can turn to be an important factor of structural transformations. Thus, we come to the conclusion that the effects of capillary pressure created by surface tension cannot be shrugged off when considering structural transformations in nanoparticles.

Summing up the above, we can imagine the influence of surface phenomena on the state of nanoparticles as follows. If a nanoparticle is large enough (typically larger than 10 nm) to speak about its surface tension, the surface tension will create, according to Eq. (1.3), the particle internal stresses whose complexity depends on the particle shape. In particular, positive surface tension will compress the particle and negative surface tension will dilate the particle. The region of an imaginary bulk phase subjected to the action of surface tension, is reduced as the particle size diminishes, and the particle (typically 1 nm in size) acquires the properties of surface layer. The surface layer is less dense than a bulk phase for particles in a gaseous medium. So we can imagine the case when a particle first constringes (to a positive surface tension) and then is loosened.

2. NANOSTRUCTURES AS THE RESULT OF PHASE TRANSFORMATIONS

A striking phenomenon was discovered at studying the process of comminution of solids: sometimes, quite another polymorphous modification was found in the disperse phase as compared with that taken for comminution. The formation of a polymorphous modification is a phase transition (of the first or second order). Therefore, we may conclude that phase transitions occur in the process of dispergation. By the time of publication of the review [18] in 1979, 16 cases of such transformations had been known already. It is of note that ordinary phase structures are implied. They are spoken as about nanostructures only because they are discovered in nanoparticles.

Due to its small size, a nanoparticle changes its phase state practically instantaneously. So it is hard to imagine the state of equilibrium between two phases inside the particle and, all the more, at a flat interface (as in Kumazawa’s theory [18, 19]). In this case, it is more reasonable to compare the Gibbs energies for the nanoparticle as a whole before and after the phase transformation. Since the amount of matter in the particle does not change herewith, it is enough, for such consideration, the truncated variant of thermodynamics (without chemical potentials) usually used in the mechanics of continuum media (see, e.g., [20]). We only complement this variant with the account for surface phenomena.

We begin with the fundamental equation for the free energy F of a nanoparticle represented as a combination of a uniform bulk phase α and a piecewise smooth surface:

$$dF = -SdT - V_0 \sum_{i,k=1}^{3} p^{\alpha}_{ik} de^{\alpha}_{ik} + \sum_j A_{j0} \sum_{i,k=1}^{3} \gamma_{j(ik)} de^{\sigma}_{j(ik)}, \qquad (2.1)$$

where S is entropy; T is temperature; V_0 is the particle volume in a strainless state (constant quantity in the process of deformation); p^{α}_{ik} and e^{α}_{ik} are the components of the tensors of pressure and strain, $\hat{p}^{\alpha}$ and $\hat{e}^{\alpha}$, respectively, of bulk phase α; the subscript j numbers smooth parts of the surface, each possessing its own tensors of surface tension (excess surface stress) $\hat{\gamma}_j$ and of surface strain $\hat{e}^{\sigma}_j$ with the components $\gamma_{j(ik)}$ and $e^{\sigma}_{j(ik)}$, respectively; A_{j0} is the area of the jth surface part in the strainless state. Using tensorial notations, Eq. (2.1) is written as

$$dF = -SdT - V_0(\hat{p}^{\alpha} : d\hat{e}^{\alpha}) + \sum_j A_{j0}(\hat{\gamma}_j : d\hat{e}^{\sigma}_j), \qquad (2.2)$$

where the colon symbolizes a biscalar product of tensors.

If a nanoparticle is subjected to external mechanical actions characterized by the pressure tensor $\hat{p}^{\beta}$ (whose field is considered to be uniform for the sake of simplicity), the most stable state of the nanoparticle is a state with a minimum value of thermodynamic potential Φ (analog of Gibbs energy) defined through free energy F as

$$\Phi \equiv F + V_0(\hat{p}^{\beta} : \hat{e}^{\alpha}). \qquad (2.3)$$

Differentiating Eq. (2.3) and substituting (2.2) in (2.3), we obtain

$$d\Phi = -SdT - V_0(\hat{p}^{\alpha} - \hat{p}^{\beta}) : d\hat{e}^{\alpha} + V_0 \hat{e}^{\alpha} : d\hat{p}^{\beta} + \sum_j A_{j0}(\hat{\gamma}_j : d\hat{e}^{\sigma}_j) \qquad (2.4)$$

By the equilibrium conditions, the function Φ must have a minimum at given T and $\hat{p}^{\beta}$. Therefore, the second and fourth terms on the right-hand side of Eq. (2.4) should cancel each other, which forms the mechanical equilibrium condition [more general than (1.4)]

$$-V_0(\hat{p}^{\alpha} - \hat{p}^{\beta}) : d\hat{e}^{\alpha} + \sum_j A_{j0}(\hat{\gamma}_j : d\hat{e}^{\sigma}_j) = 0 \qquad (2.5)$$

(reader can easily verify that Eq. (2.5) is reduced to Eq. (1.5) in the case of a single isotropic surface and of isotropic pressures in both phases). Accounting for (2.5), Eq. (2.4) takes the simple form

$$d\Phi = -SdT + V_0 \hat{e}^{\alpha} : d\hat{p}^{\beta}. \qquad (2.6)$$

It is of note that Eq. (2.6) would be an ordinary fundamental equation for a mechanically anisotropic phase (α) if quantity $\hat{p}^{\beta}$ stood in place of $\hat{p}^{\alpha}$. However, Eq. (2.6) refers to a particle of any complex structure including its surface layer (according to Gibbs’ method, the action of the strain tensor $\hat{e}^{\alpha}$ is extended, as well as volume V_0, to include the whole particle).

Let phase α to have a polymorphous modification α'. We may write the same Eq. (2.6) for phase α'. Then subtracting one equation from the other, we obtain

$$d\Delta\Phi = -\Delta S dT + \Delta(V_0 \hat{e}^{\alpha}) : d\hat{p}^{\beta}, \qquad (2.7)$$

where Δ symbolizes the difference of a quantity for the two modifications ($\Delta\Phi \equiv \Phi - \Phi'$ etc.). Phase α is more stable at $\Phi < \Phi'$ and phase α' is more stable at $\Phi > \Phi'$. If, however, $\Delta\Phi = 0$, both the phases are equally stable, and, therefore, particles of both the modifications can exist with equal probability. Then Eq. (2.7) changes to the equation

$$\Delta S dT = \Delta(V_0 \hat{e}^{\alpha}) : d\hat{p}^{\beta}, \tag{2.8}$$

showing how the temperature of the polymorphous transformation of a particle depends on external mechanical actions. Since Eq. (2.7) acts at a constant amount of matter, all extensive quantities in Eq. (2.7) may be treated as molar quantities.

Let us first turn to the simplest case when the external action is isotropic: $\hat{p}^{\beta} = p^{\beta}\hat{1}$, where $\hat{1}$ is the unit tensor whose components are given by Kronecker's symbol δ_{ik}. Such a situation is realized, for example, when a particle is in a medium (liquid or air) with uniform pressure (the influence of gravity is negligible because of a small particle size). As is seen from Eq. (1.4), the only condition of isotropy of external action is not yet enough to make the particle internal phase α also mechanically isotropic. So the particle interior and, all the more, the surface layer of the particle can stay mechanically anisotropic. Substitution of the above isotropic value of $\hat{p}^{\beta}$ in Eq. (2.8) at using the standard relationship of the theory of elasticity (V is the real volume of a particle)

$$V_0 \hat{e}^{\alpha} : \hat{1} = V_0 \sum_{i,k=1}^{3} e_{ik}\delta_{ik} = V - V_0 \tag{2.9}$$

reduces Eq. (2.8) to the form

$$\Delta S dT = \Delta(V - V_0) dp^{\beta}. \tag{2.10}$$

If the initial volume of a particle in the strainless state V_0 is chosen the same for both the modifications (as did Coe and Paterson [21] in the analysis of polymorphous transformation in quartz), Eq. (2.10) is exactly reduced to the Clapeyron–Clausius equation

$$\frac{dT}{dp^{\beta}} = \frac{\Delta V}{\Delta S}. \tag{2.11}$$

This is a truly amazing fact. Why, we consider not the equilibrium of two phases at a flat interface (when the Clapeyron–Clausius equation acts in thermodynamics), but a polymorphous transformation in a nonuniform particle with a curved surface. The only condition of applicability of the Clapeyron–Clausius equation to this case turns to be the use of an external pressure p^{α} instead of a real pressure p^{β} whose action causes phase transition. However, external pressure is just that tool that is used by an experimentalist to influence the phase-transition process in a particle (in more general Eq. (2.8), the pressure tensor $\hat{p}^{\beta}$ includes kicks, impacts, shear stresses, all that happens with particles in the process of their comminution).

Like the initial Eq. (2.2), Eq. (2.8) is confined with the condition of the constancy of the number of molecules in a particle. Eq. (2.8) shows how external pressure influences the phase-transition temperature in a particle with a given number of molecules, but says nothing about the dependence of the particle structure on the molecule number. Regarding the question how the structure of matter changes in the process of its comminution, we should be guided by the reasoning of preceding section. In addition, we can similarly derive, for the separately-taken phase transformation α → α', the equation analogous to (2.8) ($\hat{p}^{\beta}$ is replaced by $\hat{p}^{\alpha}$):

$$\Delta S dT = \Delta(V_0 \hat{e}^{\alpha}) : d\hat{p}^{\alpha}. \tag{2.12}$$

For a mechanically isotropic state, Eq. (2.12), with the account for (2.9), is reduced to the relationship

$$\Delta S dT = \Delta(V - V_0) dp^{\alpha} \tag{2.13}$$

or, at the same choice of the initial volume V_0 for phases α and α', to the ordinary Clapeyron–Clausius equation

$$\frac{dT}{dp^{\alpha}} = \frac{\Delta V}{\Delta S}. \tag{2.14}$$

If bulk phase α exists inside a nanoparticle (due to its sufficiently large size), the application of Eq. (2.14) to the particle does not yet form a direct criterion of phase transformation of the particle. This occurs since surface properties are also important for the particle (for example, the transition predicted by Eq. (2.14) can be not realized because another modification has a too high surface tension). Although the reasoning of necessity of allowance for the anisotropy and surface properties of a particle was formulated in the literature long ago, the use of the Clapeyron–Clausius equation was the main element of analysis of phase transformations in the comminution process [18]. Actually, the Clapeyron–Clausius equation only indicates the tendency of the process (which, of course, is also useful). We explain this with an example. If surface tension is positive and the derivative dT/dp^{α} negative, we know that pressure inside particles increases and the phase-transition temperature decreases with decreasing particle size in the comminution process. When the phase-transition temperature becomes equal to the real temperature of the system, there can be no phase transition because of surface phenomena. However, we may think that phase transition will occur, sooner or later, in the process of further comminution.

It is known that the derivative dT/dp^{α} in the Clapeyron-Clausius equation can be of any sign, although molar volume always decreases with increasing pressure under isothermal conditions and molar entropy always increases with temperature under isobaric conditions. The case of a positive slope of the line of a polymorphous transformation in the state diagram $T–p^{\alpha}$ is accounted to be normal, and the case of negative slope is accounted to be abnormal. As stated in [18], belonging to this two cases also determines the character of phase transition of matter in the course of comminution: at comminution matter changes to a more dense modification in the normal case and to a less dense modification in the abnormal case. However, the relation of these phenomena seems to be problematic. It seems that the transition to a more dense modification at comminution is still more probable in the abnormal case than in the normal one, since the inevitable heating in the process of comminution now works in the same direction as increasing pressure in particles. The fact that, at comminution, $CaCO_3$ successively passes the stages of vaterite (density 2.64 kg/l), calcite (density 2.72 kg/l), and aragonite (density 2.95 kg/l) [18], can be explained by a positive value of surface tension and by compression of particles in the comminution process, rather than by that the phase transitions in $CaCO_3$ belongs to the normal case. As for the transformation of massicot (density 9.64 kg/l) into litharge (density 9.35 kg/l) at the comminution of PbO, this transition, although abnormal indeed for bulk phases, can be explained either by the negative surface tension (unless this will be controverted experimentally by independent surface tension measurements) or by the role of shear stresses and strains not taken into account in the Clapeyron–Clausius equation.

An interesting case is zirconia. Its synthetic tetragonal modification (density 5.86 kg/l) with the particle size 15 nm completely changes to the monoclinic modification (density 5.74 kg/l) at mechanical treatment. However, as the particle size decreases to 10 nm, the monoclinic modification is again consolidated to the tetragonal one [22], although this polymorphous transformation in the bulk refers to the abnormal case (the monoclinic modification of ZrO_2 transforms into tetragonal at heating up to 1100°C). Such a behavior of zirconia is explained as follows. The tetragonal modification is metastable at room temperature and should spontaneously transform into the monoclinic modification. Mechanical treatment activates this process. However, the pressure inside particles increases, and the polymorphous transformation temperature decreases as the particle size decreases, until (as it turns at a particle size of about 10 nm) the reverse process occurs, the transformation of the monoclinic modification into the more dense tetragonal modification.

The aforesaid relates to first-order phase transitions. For second-order phase transitions, $\Delta S = 0$ and $\Delta V = 0$, so that the Clapeyron–Clausius equation becomes indeterminate. Phases α and α' become identical at the point of a second-order phase transition. Therefore, not only the thermodynamic potentials of phases, but also any other quantities (the first derivatives of thermodynamic potentials are advisable to obtain nonzero values for the difference of the second derivatives of thermodynamic potentials) may be equated. Regarding the number of molecules in a particle to be fixed, we choose the particle volume V as such a quantity and as a function of temperature and of the components p^{β}_{ik} of the external pressure tensor $\hat{p}^{\beta}$:

$$dV = \left(\frac{\partial V}{\partial T}\right)_{\hat{p}^{\beta}} dT + \sum_{i,k}\left(\frac{\partial V}{\partial p^{\beta}_{ik}}\right)_{T,p^{\beta}_{lm\neq ik}} dp^{\beta}_{ik}$$

$$\equiv V\theta dT - V\sum_{i,k}\chi_{ik}dp^{\beta}_{ik}. \qquad (2.15)$$

Here the following designations were introduced for the sake of brevity: θ is the thermal dilatation coefficient, χ_{ik} are the isothermal compressibilities corresponding to the components of the pressure tensor (in bulk phases, molar volume is not sensitive to the off-diagonal components of the pressure tensor; in the case under consideration, however, any change in the particle shape means a change in its surface area accompanied by adsorption and the volume change).

Applying now Eq. (2.5) to phases α and α' and equating the resultant expressions, we obtain the equation of the hypersurface of a second-order phase transition in the state diagram

$$\Delta\theta dT = \sum_{i,k}\Delta\chi_{ik}dp^{\beta}_{\mathrm{ik}}. \qquad (2.16)$$

Similarly to Eq. (2.8), Eq. (2.16) describes the influence of external pressure on the phase transition temperature, but now for a second-order phase transition. As for the description of a second-order phase transition in an anisotropic bulk phase α in terms of its own pressure tensor $\hat{p}^{\alpha}$, the corresponding equations have been considered in detail in our preceding publication [23] to which we refer the reader, but with a certain limitation. Such equations with no account for surface phenomena are only capable of approximate pointing and do not yield such a rigorous description as that given by Eq. (2.16).

3. CHEMICAL INTERPRETATION OF SOLID NANOPARTICLES

The dictum “a crystal is a big molecule” is known to a chemist since the student time. At down-the-line holding this point of view (see, e.g., [24], not only crystalline, but also amorphous solid nanoparticles should be regarded as "supramolecules," their set of same nature and increasing size as homologous series, and nanoparticles of same composition but different structure as isomers. Up to the present time, however, such ideas have not yet embodied in a corresponding rigorous thermodynamic theory (in fact, they use traditional phase approach when the matter concerns thermodynamics). We will here show how to approach the formulation of such a theory.

Thus, let us forget that a nanoparticle is a piece of a phase. Now, it is a single but large molecule, however complex, or even an ion of multiple charge. Both is below called a supramolecule. Let a supramolecule include n_1 structural units of the first sort, n_2 structural units of the second sort, and so on. We denote the whole set of the numbers n_i as $\{n\}$. The set $\{n\}$ gives the composition of the supramolecule, as if being a supramolecule passport. The symbol $\{n\}$ will be used below as a subscript to indicate that a quantity belongs to a supramolecule of a certain type. As for any other chemical individuum, the chemical potential, the main quantity of chemical thermodynamics, should be introduced for supramolecules. We designate the supramolecule chemical potential $\mu_{\{n\}}$ and write, using known results of statistical mechanics for ordinary molecules, its detailed expression in the form

$$\mu_{\{n\}} = G^0_{\{n\}} + kT\ln(c_{\{n\}}\Lambda^3_{\{n\}}f_{\{n\}}), \tag{3.1}$$

where $G^0_{\{n\}}$ is the Gibbs energy of a supramolecule of sort $\{n\}$ with resting center of mass in a given medium (liquid or gas) in the absence of other supramolecules, k is Boltzmann's constant, $\Lambda_{\{n\}}$ and $f_{\{n\}}$ are the mean de Broglie wavelength and the activity coefficient of supramolecules, respectively. The mean de Broglie wavelength of a supramolecule is given by the expression

$$\Lambda_{\{n\}} \equiv h(2\pi m_{\{n\}}kT)^{-1/2}, \tag{3.2}$$

where h is Planck's constant and $m_{\{n\}}$ is the supramolecule mass compiled of the masses of supramolecule structural units m_i as

$$m_{\{n\}} = \sum_i m_i n_i. \tag{3.3}$$

The interaction of a supramolecule with a medium is taken into account in $G^0_{\{n\}}$. As for the activity coefficient $f_{\{n\}}$, it reflects the interaction of supramolecules with each other. It is possible to include the quantity $kT\ln f_{\{n\}}$ into $G^0_{\{n\}}$ and write Eq. (3.1) in the form

$$\mu_{\{n\}} = G^0_{\{n\}} + kT\ln(c_{\{n\}}\Lambda^3_{\{n\}}), \tag{3.4}$$

where $G^0_{\{n\}}$ is already understood as the Gibbs energy of a supramolecule of sort $\{n\}$ with resting center of mass in a dispersion medium containing other supramolecules ($G^0_{\{n\}}$ now accounts for the interaction of the supramolecule not only with the medium, but also with other supramolecules present in the system).

Bearing in mind the possibility of calculating the Gibbs energy $G^0_{\{n\}}$, it may be detailed as follows. First of all, one should take into account the difference in the energetic state of structural units on the surface of a supramolecule and inside the supramolecule. Let there be structural units of the ith sort on the surface where b_i is a numerical coefficient determined by the chemical structure and geometrical shape of a supramolecule. We now imagine that, in the initial state, the structural units of the supramolecule were separated and placed in a vacuum with the resting state of their centers of mass. The Gibbs energy of such a state is $\Sigma g^0_i n_i$ where g^0_i is the Gibbs energy of a separate structural unit of the ith sort with resting center of mass in a vacuum. The transfer of this structural unit into the interior of the supramolecule (we mark the supramolecule interior with the symbol α) will require the work w^α_i. Obviously, $w^\alpha_i < 0$, since the binding energy in a solid exceeds, in its absolute value, the positive kinetic energy of oscillatory motion acquired by the structural units as a result of such transfer. The subsequent transfer of a structural unit to the supramolecule surface requires an additional work $w^{\alpha\sigma}_i$ (σ symbolizes the surface region of a supramolecule, the sequence of the subscripts indicating the transfer direction). Since such transfer is accompanied by bond rupture, it is evident that $w^{\alpha\sigma}_i > 0$. We now may write the expression

$$G^0_{\{n\}} = \sum_i g^0_i n_i + \sum_i w^\alpha_i n_i + \sum_i w^{\alpha\sigma}_i b_i n_i^{2/3}, \tag{3.5}$$

and Eq. (3.4), after substitution of (3.5) in (3.4), takes the form

$$\begin{aligned}\mu_{\{n\}} = {} & \sum_i g^0_i n_i + \sum_i w^\alpha_i n_i + \sum_i w^{\alpha\sigma}_i b_i n_i^{2/3} \\ & + kT\ln(c_{\{n\}}\Lambda^3_{\{n\}}).\end{aligned} \tag{3.6}$$

In principle, the quantities w^α_i and $w^{\alpha\sigma}_i$, even in dilute systems, depend on $\{n\}$ and, in particular, on the supramolecule size. However, accounting for this dependence becomes necessary, firstly, only for very small (one can say small in the limit) particles and, secondly, only for weak chemical bonds (approaching ordinary molecular forces).

Further algorithm of constructing the theory suggests itself. Any physicochemical process, including chemical reactions, is governed by chemical affinity. If a process is symbolically depicted by the equation

$$\sum_{\{n\}} \nu_{\{n\}} \mathrm{B}_{\{n\}} \Rightarrow \sum_{\{n\}} \nu'_{\{n\}} \mathrm{B}'_{\{n\}}, \tag{3.7}$$

where the initial substances stand on the left and the process products (marked with a prime) on the right, $\nu_{\{n\}}$ are stoichiometric coefficients, the chemical affinity A of the process is given by the expression [25]

$$A \equiv \sum_{\{n\}} (\nu_{\{n\}} \mu_{\{n\}} - \nu'_{\{n\}} \mu'_{\{n\}}), \tag{3.8}$$

where $\mu_{\{n\}}$ are the chemical potentials of substances $\mathrm{B}_{\{n\}}$ that feature in Eq. (3.7). The initial and final states can be different in time and space. The sign of chemical affinity determines the process direction (“plus” corresponds to the direct process and “minus” to the reverse process) and the affinity value determines the process rate. If supramolecules (nanoparticles) participate in the process, their chemical potentials will enter Eq. (3.8). The subsequent analysis is carried out as it is generally accepted in the thermodynamics (both equilibrium and non-equilibrium) of chemical reactions.

For the sake of illustration, we consider two examples of physicochemical processes. As a first example, we take a polymorphous transformation considered above within the frames of the phase approach. A polymorphous transformation is now meant as a monomolecular isomerization chemical reaction of type

$$\mathrm{B}_{\{n\}} \Rightarrow \mathrm{B}'_{\{n\}}, \tag{3.9}$$

proceeding under the influence of external factors. We assume that factors to act simultaneously on all particles of the system, so that the polymorphous transformation simultaneously occurs in all particles of a given composition. The chemical affinity of the reaction expressed in Eq. (3.9) is

$$A = \mu_{\{n\}} - \mu'_{\{n\}}. \tag{3.10}$$

Substituting (3.4) in (3.10) and accounting for that the concentration and the mean de Broglie wavelength are the same for both isomers, we arrive at the expression

$$A = G^0_{\{n\}} - G'^0_{\{n\}} \equiv \Delta G^0_{\{n\}} \; (= \Delta G_{\{n\}}). \tag{3.11}$$

It is shown in Eq. (3.11) that the chemical affinity can also be represented as the difference of the total Gibbs energy $G_{\{n\}}$ for the two isomers of a supramolecule (the quantities $G^0_{\{n\}}$ and $G_{\{n\}}$ differ by $3kT/2$). If a supramolecule is so large as to obey the mechanics of continuous media, we can define $G^0_{\{n\}}$ as the function Φ by Eq. (2.3) and repeat all the derivations of the preceding section. In particular, by setting the affinity expressed in (3.11), equal to zero, we obtain equations for the equilibrium of the two isomers and again come to the Clapeyron–Clausius equation. It is of note, however, that the problem is now solved to a larger extent since $G^0_{\{n\}}$ also includes the interaction between a given supramolecule and other supramolecules (which can influence polymorphous transformations). Herewith, general thermodynamic equations preserve their form, but the values of the quantities standing there are implied to be more exact.

As the second example of a physicochemical process, we consider the dissolution of a nanoparticle. Chemically, this is the reaction of dissociation of a supramolecule into its constituents. For the sake of simplicity, we assume the supramolecule to consist of structural units of only one type (for example, we meet such situation at the dissolution of a molecular crystal). Then Eq. (3.6) is reduced to the form

$$\mu_n = g^0 n + w^{\alpha} n + \mathrm{w}^{\alpha\sigma} b n^{2/3} + kT \ln (c_n \Lambda_n^3), \tag{3.12}$$

where n is the number of the structural units in the supramolecule. As a result of dissociation, the structural units take on self-dependence. For them also, the chemical potential can be introduced

$$\mu = g^0 + w^{\beta} + kT \ln (c\Lambda^3), \tag{3.13}$$

where β symbolizes the solution phase and w^{β} is the work of transfer of a single structural unit with resting center of mass from a vacuum to a fixed point of the real solution (the sign of the work w^{β} is determined by the character of interaction of the structural unit with the solvent). Turning to Eqs. (3.2) and (3.3), we conclude that, in the case of the one-component supramolecule under consideration, the mean de Broglie wavelength of the supramolecule Λ_n and the mean de Broglie wavelength of a single structural unit Λ are related by the simple equation

$$\Lambda_n = \Lambda n^{-1/2}. \tag{3.14}$$

From the chemical point of view, the dissolution process is a sequence of dissociation reactions of the form

$$\mathrm{B}_n \Rightarrow \mathrm{B}_{n-1} + \mathrm{B}, \quad \mathrm{B}_{n-1} \Rightarrow \mathrm{B}_{n-2} + \mathrm{B}, \ldots \tag{3.15}$$

The corresponding chemical affinity (by the first reaction example) is

$$A_n = \mu_n - \mu_{n-1} - \mu. \tag{3.16}$$

When substituting Eqs. (3.12) and (3.13) in Eq. (3.16), we will consider the quantities w_i^{α}, $w_i^{\alpha\sigma}$ and b to be independent of n for the sake of simplicity. As a result, also accounting for Eq. (3.14), we obtain

$$A_n = w^{\alpha} - w^{\beta} + w^{\alpha\sigma}b[n^{2/3} - (n-1)^{2/3}] - kT\ln(c\Lambda^3) + kT\ln\frac{c_n n^{-3/2}}{c_{n-1}(n-1)^{-3/2}}. \tag{3.17}$$

Evidently, the work difference w^{α}–w^{β} is the work of transfer of a structural unit from solution to the interior of the supramolecule, $w^{\beta\alpha}$ (we remind that the subscript sequence indicates the direction of transfer). The quantity $w^{\beta\alpha}$ is negative, but the reverse quantity $w^{\alpha\beta}$ is positive (the transfer is accompanied by bond rupture in the supramolecule):

$$w^{\alpha} - w^{\beta} \equiv w^{\beta\alpha} = -w^{\alpha\beta}. \tag{3.18}$$

Using the binomial expansion, we come to the relationship

$$n^{2/3} - (n-1)^{2/3} \approx \frac{2}{3}n^{-1/3}, \tag{3.19}$$

that turns to be an acceptable approximation practically for all n. We now turn to the last term in Eq. (3.17). Let us assume that supramolecules of sort $n - 1$ were absent in the initial state and they all have been formed by removal of a structural unit from supramolecules of sort n. Then we may set $c_n = c_{n-1}$, neglecting the system volume change at dissolution. As a result, the last term in (3.17) will differ from zero only at the expense of the difference of the numbers n and $n - 1$, so that the last term will amount fractions of kT. Under such conditions, the last term in (3.17) becomes negligible and may be omitted. We now rewrite Eq. (3.17), accounting for (3.18) and (3.19), in the form

$$A_n \approx -w^{\alpha\beta} + \frac{2}{3}w^{\alpha\sigma}bn^{-1/3} - kT\ln(c\Lambda^3). \tag{3.20}$$

The augend on the right-hand side of Eq. (3.20) is negative and constant, whereas the addend is positive and n-dependent. The product $c\Lambda^3$ is of the meaning of a volume fraction (is close to the real volume fraction for structural units of atomic dimensions) and, therefore, is always smaller than unity. Hence, the last term on the right-hand side of (3.20) is also positive. At a fixed temperature, it depends only on concentration and increases with decreasing concentration. Evidently, irrespective of the supramolecule size, the last term will secure a positive value for the whole right-hand side of (3.20). So we arrive at the condition $A_n > 0$ that means that the dissolution process develops. We have $A_n = 0$ at equilibrium. Then Eq. (3.20) immediately yields the detailed expression for the solubility of a particle of size n:

$$c \approx \frac{1}{\Lambda^3}\exp\left\{\left[-w^{\alpha\beta} + \frac{2}{3}w^{\alpha\sigma}bn^{-1/3}\right]/kT\right\}. \tag{3.21}$$

It is seen form (3.21) that the particle solubility increases with decreasing the particle size. At passing to a macroscopic solid ($n \to \infty$), the solubility acquires a constant value determined by the work on escaping a structural unit form the solid bulk to the solution:

$$c \approx \frac{1}{\Lambda^3}\exp\left(-\frac{w^{\alpha\beta}}{kT}\right). \tag{3.22}$$

Thus, we see that Eq. (3.20) nicely describes all known regularities of dissolution.

Summing up all Eqs. (3.16), we can write the affinity of complete dissolution of a particle consisting of n structural units as

$$A = \mu_n - n\mu. \tag{3.23}$$

By substituting Eqs. (3.12) and (3.13) in Eq. (3.23) and accounting for (3.14), we obtain

$$A = -w^{\alpha\beta}n + w^{\alpha\sigma}bn^{2/3} - nkT\ln(c\Lambda^3) + kT\ln(c_n\Lambda^3 n^{-3/2}). \tag{3.24}$$

Neglecting a change in the system volume at dissolution, we can write the mass balance condition as $c = c_n n$. Then we may neglect the last term in (3.24) at a sufficiently large n to obtain

$$A \approx -w^{\alpha\beta}n + w^{\alpha\sigma}bn^{2/3} - nkT\ln(c_n n\Lambda^3). \tag{3.25}$$

The process will develop at $A > 0$. Therefore, we may write the condition of complete dissolution of nanoparticles at a given concentration c_n as

$$-w^{\alpha\beta}n + w^{\alpha\sigma}bn^{2/3} - nkT\ln(c_n n\Lambda^3) > 0, \tag{3.26}$$

where c_n plays the role of a constant. The exact analytical solution of this inequality is problematic. If, however, we neglect the logarithmic term (at $w^{\alpha\beta} >> kT$ and $w^{\alpha\sigma} >> kT$), the approximate solution is found at once

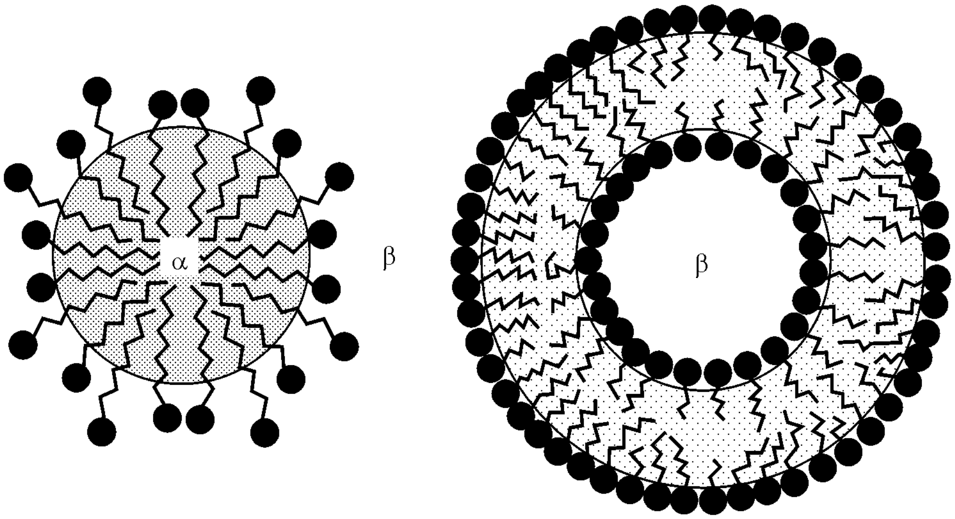

Fig. 2. Direct micell and direct vesicle in an aqueous solution of a surfactant. (α) Hydrocarbon (fluorocarbon) core and (β) aqueous phase.

$$n^{1/3} < \frac{bw^{\alpha\sigma}}{w^{\alpha\beta}}. \tag{3.27}$$

The particular final result depends on the value of the right-hand side of Eq. (3.27). However, the principal significance of this formula is that it shows the possibility of the particle size boundary below which the stable existence of the particles becomes impossible (they dissolve spontaneously). In the size region below the boundary, particles can arise only by fluctuations, and this statement is known to be the cornerstone of the whole physical theory of phase nucleation. Thus, we see that the chemical approach leads to the same conclusions as the phase approach.

In Eq. (3.17) we assumed the concentration of supramolecules of different size to be equal since they change to each other in a simultaneous dissolution process. We now consider the case of equilibrium between supramolecules of different size but then, evidently, of different concentration. Returning to Eq. (3.24), we should now set $A = 0$ and write the equilibrium condition as

$$c_n = c^n\Lambda^{3n-1}n^{3/2}\exp[(-w^{\alpha\beta}n + w^{\alpha\sigma}bn^{2/3})/kT]. \tag{3.28}$$

Now already the concentration c plays the role of a constant, and Eq. (3.28) shows that supramolecular homologs of various mass, each homolog being with its individual concentration c_n, can be in equilibrium with free structural units of a given concentration. We remind that the quantities $w^{\alpha\beta}$ and $w^{\alpha\sigma}$ include interaction between supramolecules, and, therefore, $w^{\alpha\beta}$ and $w^{\alpha\sigma}$ themselves are dependent on n and c_n. Only in the case of a dilute system when such interaction is negligible (this means that the activity coefficient $f_{\{n\}}$ in Eq. (3.1) is unity), the right-hand side of Eq. (3.28) is an explicit function of n and yields explicitly the equilibrium distribution of supramolecular homologues. Of course, an attentive reader has noticed that Eq. (3.28) contains the mass action law. Actually, our derivation was reduced to finding an expression for the mass-actionlaw constant in terms of the para meters of the system under investigation.

4. NANOSTRUCTURES IN AGGREGATIVE SYSTEMS

As was already noted, nanostructures form not only by dispergation of macroscopic phases, but also by spontaneous aggregation of free molecules or ions. In the series of structures of such type, there are most known the micelles (closed monolayers) and vesicles (closed bilayers) of amphiphilic compounds (Fig. 2), as well as their complexes with high-molecular compounds formed in a liquid medium. Among the nanostructures prepared by aggregative methods, micelles of surfactants are the most interesting. So we will pay most attention to micelles.

4.1. Peculiarity of Micelles

Micelles of surfactants may be called typical nanostructures both because of their size scale (4 nm and larger) and because of their characteristics. Micelles are truly equilibrium and stable structures in contradistinction to those molecular aggregates that are embryos of new phases and, therefore, can only be in unstable equilibrium with their mother phase (as well as also in contradistinction to vesicles which are unstable in principle, although are able to exist for a long time). Micelles can exist even in supersaturated solutions, and this again confirms that micelles are not embryos of any phases. When applied to micelles, the term "nanostructure" acquires its true sense since, unlike to the above solid nanoparticles with the structure of bulk phases, micelles have no macroscopic analog and exist only in small forms due to their unique structure.

Molecules of amphiphilic substances possess polar and nonpolar parts. In polar media and, first of all, in water, molecules of amphiphilic substances merge by their nonpolar parts to form direct micelles or vesicles (Fig. 2). Reverse micelles and vesicles of amphiphilic compounds form in nonpolar media as a result of mutual attraction of polar groups. Both micelles and vesicles exhibit a variety of geometrical shapes and, therefore, also of nanostructures. From the thermodynamic point of view, the equilibrium shape of a nanoparticle is dictated by the generalized Gibbs–Curie principle [26, 27]

$$\sum_j \sigma_j A_j - (kT/2)\ln(I_1 I_2 I_3) + kT\ln f = \min, \qquad (4.1.1)$$

where σ_j and A_j are the work of formation of unit surface and the surface area of the jth fragment of the fragmentary smooth surface of the nanoparticle, respectively; k is Boltzmann's constant, T is temperature, I_1, I_2, and I_3 are the principal inertia moments of the nanoparticle, f is the activity coefficient of the particle accounting for the mutual interaction of particles. The second and third terms in Eq. (4.1.1) play the role of corrections. They are negligible for particles with high values of σ, and then Eq. (4.1.1) is reduced to the classical Gibbs–Curie principle used for prediction of the equilibrium shape of monocrystals. However, the corrections can play their role in the case of micelles and vesicles with very low values of σ.

When applied to direct micelles and vesicles, the generalized Gibbs–Curie principle implies the constancy of volume, resulting from the dense packing of hydrocarbon radicals, as well as the dense packing of polar groups required by the minimization of the first term in Eq. (4.1.1). These factors are described by the equation of packing a monolayer of amphiphilic molecules [27–29]

$$\frac{v}{a} = l\left[1 \mp \frac{l}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + \frac{l^2}{3R_1R_2}\right], \qquad (4.1.2)$$

where v is the volume of the hydrocarbon part of a amphiphilic molecule, a is the parking area of its polar group, l is the thickness of the hydrocarbon part of the monolayer, R_1 and R_2 are the principal curvature radii for the hydrocarbon layer surface on which the polar groups are positioned. The double sign in Eq. (4.1.2) indicates the difference in packing on a convex (minus sign) and a concave (plus sign) surface. The usefulness of the packing equation is evidenced in that it can predict the geometrical shape of an aggregate from the geometrical parameters of a amphiphilic molecule.

The existence of the polymorphism of micelles seems to give evidence for a solid-like character of micellar structures. However, spectroscopic data argue in favor of a liquid-like behavior of micelles. Such dualism itself is striking. Indeed, oriented amphiphilic molecules in micelles and vesicles are able to move freely in the tangential direction (long the boundary between the polar and non-polar regions of a nanoparticle) and restricted only in their movement along the normal. Therefore, micelles and vesicles may be conditionally called two-dimensionally liquid and one-dimensionally (in the radial direction) solid bodies. This turns to be enough for nonspherical shapes of molecular aggregates (worm-like and disc-like micelles, vesicular nanotubes, etc.) to be realized.

Micelles possess a number of other striking properties. First of all, they do not grow gradually, but arise almost by jump as the critical micelle concentration is attained. This is explained by that to escape maximally from the contact of hydrocarbon radicals with water (as the hydrophobic effect requires) is possible only in a sufficiently large aggregate (including several decades or hundreds of molecules). The rigorous theory of micellization is based on the mass action law. The aggregation of n molecules of a substance B into a micelle M is regarded similarly to the reaction

$$n\,\mathrm{B} \Leftrightarrow \mathrm{M}, \qquad (4.1.3)$$

where the micelle plays the role of a supramolecule. In reality, the process involves consecutive addition stages B + B = B_2, B_2 + B = B_3, etc. If we ascribe the same mass-action-law constant K to each stage, the mass action law for the whole reaction expressed in (4.1.3) can be written as

$$\frac{\alpha}{(1-\alpha)^n} = (Kc)^{n-1}, \qquad (4.1.4)$$

where α is the micellization degree (the fraction of matter in the micellar state) and c is the total concentration of substance B.

The aggregation number n plays the role of a stoichiometric coefficient. It is of order of several units for ordinary chemical reactions, but is huge in the case under consideration. This causes a sharp change of the micellization degree as the product Kc passes though unity (if the exponent of a power is large, every number smaller than unity in this power is almost zero, while every number larger than unity in this power is very large; for example, we have $0.9^{100} \approx 2.6 \times 10^{-5}$ and $1.1^{100} \approx 13781$ at $n = 101$). Although the change itself is continuous, its high rate creates the illusion of a break in the curves of the concentration dependence of various properties of solutions at passing through the critical micelle concentration (Fig. 3). Such a universal behavior at changing concentration can be explained as follows. The particle concentration in solution increases proportionally to the number of molecules added before the critical micelle concentration and proportionally to the number of molecular packets (micelles) above the critical micelle concentration, every packet having the number of molecules equal to the aggregation number. Within the narrow region of the critical micelle concentration, it happens as if the scale of the concentration axis changed, which itself should cause a break in any concentration curves.

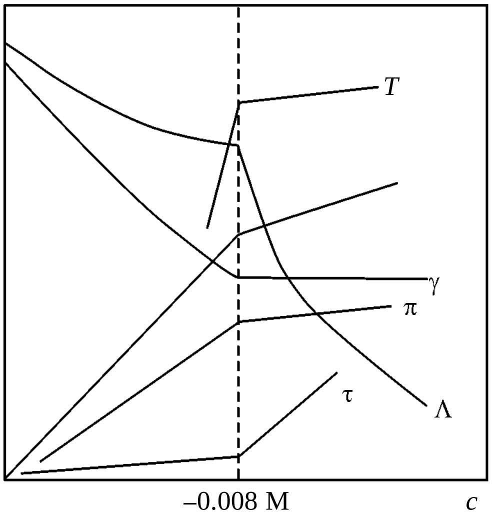

Fig. 3. Concentration dependences of different properties of aqueous sodium dodecyl sulfate at passing through the critical micelle concentration. (*T*) Equilibrium temperature with solid phase {[*s*(*T*)] solubility curve}, (κ) specific electrical conductivity, (γ) surface tension, (π) two-dimensional pressure of absorption monolayer, (Λ) equivalent electrical conductivity, and (τ) turbidity (light diffusion).

One more striking property of micelles is that, as experiment shows, the chemical potential of molecules in a micelle, changes in the same direction as the aggregation number. Treating the concentration of free molecules in equilibrium with the micelle as micellar solubility, we may formulate this observation in the form of a rule: the solubility of a micelle increases with its size. However, this contradicts to what we were taught by thermodynamics! By contrast, the classical Kelvin equation for the vapor pressure of a small drop and the Ostwald–Freundlich equation for the solubility of a small particle predict a decrease in solubility with growth of a molecular aggregate. Could it be true that micelles do not obey thermodynamics? The paradox is resolved by the thermodynamics of aggregative equilibrium that essentially complements the thermodynamics of heterogeneous systems [27, 30]. First of all, it is of note that the above equations of classical thermodynamics are asymptotic relationships for large particles nowise of nanodimensional range. Basically, these relationships represent the first term of the expansion with respect to the interfacial curvature and can be complemented by terms of higher orders (the adjusted equations of Kelvin and Ostwald–Freundlich have been obtained already [31]). As for small molecular aggregates, one must distinguish between two their classes in terms of their location in the curve of equilibrium size distribution for the aggregates (Fig. 4). Critical nuclei of a new phase, of micelles, and of liquid crystals (consisting of ready micelles) are located in minima and correspond to unstable phase equilibrium with the medium. By contrast, micelles are positioned in maxima and are the most stable in the whole distribution curve. The points of extremes in the aggregate equilibrium distribution curve simultaneously are the points of the phase equilibrium of the aggregates with the medium. The extreme type determines the type of dependence of the solubility of a molecular aggregate on its size in accordance with the thermodynamic formula [27, 31]

$$\frac{d\ln c_1}{dn_e} = -kT\left(\frac{d^2\ln c_n}{dn^2}\right)_{n=n_e}, \tag{4.1.5}$$

where c_1 is the equilibrium concentration of monomers, c_n is the concentration of a molecular aggregate with the aggregation number n, and n_e is the aggregation number at an extreme point. Eq. (4.1.5) itself is striking: the derivative on the left refers to the physical dependence of solubility on the particle size (in course of which the size distribution of aggregates changes), whereas the derivative on the right characterizes the shape of the distribution curve. It turns that, having a look at the distribution curve for a certain one fixed state of a system, we can predict the behavior of the system at changing its state. The sign of the derivative on the right depends on the extreme type: "plus" is for a minimum and "minus" for a

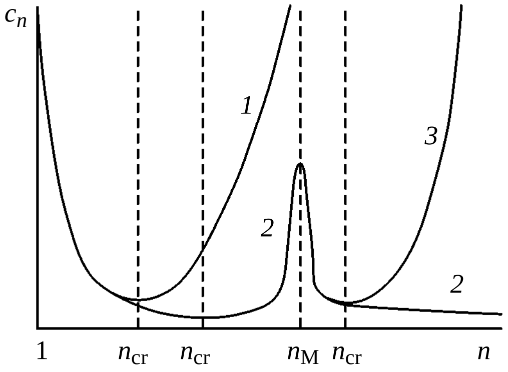

Fig. 4. Distribution of molecular aggregates by aggregation numbers: (*1*) Nuclei of a new phase, (*2*) molecular aggregates in a micellar system, and (*3*) liquid crystal nuclei. The minima relate to critical nuclei (the first to phase, the second to micellar, and the third to liquid crystal), and the maximum relates to micelles.

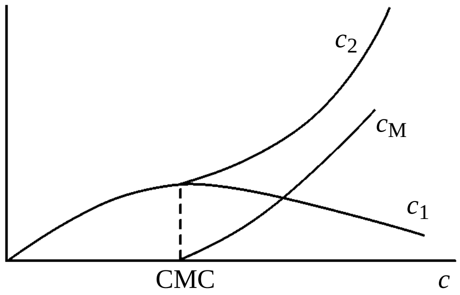

Fig. 5. Concentrations of surface-active ions (s_1), counterions (s_2), and micelles (s_M) vs. total concentration of an ionic surfactant in solution.

maximum. It just follows from here that the character of size dependence of particle solubility turns to be opposite for nuclei and micelles.

It is of note that critical nuclei, although being in unstable equilibrium with the medium, play an especially important role in kinetics. The kinetic theory of micellization can be formulated using the same scheme as for the nucleation kinetics and exhibits the necessity of studying such a class of nanoparticles as critical nuclei of micelles [32–34]. Unfortunately, practically nothing is known about critical nuclei of micelles, and this “blind-spot” remains to be a serious challenge both to theoreticians and experimentalists.

Proceeding our review of striking properties of micelles, we now turn to the behavior of ionic micellar solutions. A chemist can scarcely imagine that adding a new portion of a strong electrolyte to its solution can be accompanied by a concentration drop at least for one of the ions of the electrolyte. However, just this is observed in micellar solutions of ionic surfactants. The concentration of the surface active ion naturally increases with the total surfactant concentration before to the critical micelle concentration. In the region of the critical micelle concentration, the concentration of the surface-active ion passes through a maximum and then falls, whereas the counterion concentration invariably increases (Fig. 5). The speculative prediction of such kind was made still in 1935 [35], but seems to be not estimated seriously until the effect was discovered experimentally. It can be shown that the joint use of the mass action law and the condition of electroneutrality of an electrolyte solution is enough for qualitative explanation of the effect [36]. However, we here again meet an apparent contradiction with thermodynamics. The stability conditions require that the chemical potential of a surfactant in solution should increase with its total concentration, the electrolyte chemical potential being composed from the chemical potentials of ions. This requirement, however, does not touch the concentration of single ions but demands the mean activity of the electrolyte to increase with its total concentration in solution. Indeed, experiment shows that, although the activity of the surface-active ion falls with its concentration, the activity of the counterion increases so rapidly that the mean activity of the electrolyte slowly increases.

4.2. Thermodynamic Relationships for a Single Molecular Aggregate in the Phase Approach

A rigorous theory of molecular aggregation and, in particular, of micellization relies on the mass action law [27, 37] which is known to be a consequence of the thermodynamic equilibrium condition for a chemical reaction. In such approach, a molecular aggregate is considered like a chemical compound, and the notion of the chemical potential of the molecular aggregate as a whole is introduced. However, molecular aggregates may be also considered as phase particles similarly to as nanoparticles obtained by the phase comminution are regarded as phase particles. A characteristic feature of the phase approach is the introduction of the chemical potentials of individual molecules in a molecular aggregate. It should be emphasized that we discuss the interpretation of a single molecular aggregate, but not the so called “pseudo-phase model” of micelles [38] in which the whole population of micelles is treated like a new phase. Since the mass-action-law constant includes the Gibbs energy of a molecular aggregate with resting center of mass, the thermodynamics of a single molecular aggregate was formulated in [27] just for this model. The thermodynamic relationships derived there for a micelle with resting center of mass also maintain their form (but not the values of parameters) for really moving molecular aggregates of surfactants in solution. We discuss such aggregates below.

Molecular aggregates of surfactants are of lamellar (onion-like) structures. For example, we can distinguish between at least five regions in direct micelles in aqueous solutions (Fig. 2): the hydrocarbon (fluorocarbon) core, the water–hydrocarbon (water–fluorocarbon) layer, the layer of polar groups, the hydrate layer of the solvent, and the bulk phase of solution. Let us ascribe the symbol α to the very internal phase (the phase of the hydrocarbon or fluorocarbon core in the case of direct micelles), and the symbol β to the very external phase (the solution surrounding the molecular aggregate). In between phases α and β, there are a number of layers, each possessing its own tension. However, irrespective of the complexity of this structure, for a molecular aggregate being in internal equilibrium and in the thermal and mechanical equilibrium with a medium, the equation always acts

$$dG_M = -SdT + Vdp^\beta - \sum_i N_i d\mu_i + \sum_i \mu_i^\alpha dn_i, \quad (4.2.1)$$

where G_M is a hybrid function related to the Gibbs energy G for the system of the molecular aggregate and its surrounding by the relationship

$$G_M \equiv G - \sum_i \mu_i N_i. \quad (4.2.2)$$

Here S and V are the entropy and volume of the system, respectively; T is temperature; p^β is external pressure; μ_i and N_i are the chemical potential and the number of molecules of the ith component in solution; μ_i^α is the chemical potential of the molecule of the ith component in the molecular aggregate (we here use the symbol α, although it can happen that only a part of the molecule of a surfactant falls into the region of phase α); n_i is the aggregation number. The Gibbs energy itself in Eq. (4.2.2) is defined through internal energy U by the identity

$$G \equiv U - TS + p^\beta V. \quad (4.2.3)$$

It is not implied in Eq. (4.2.3) that the chemical potentials μ_i and μ_i^α are equal.

At a constant state of a surrounding solution, the characteristic function G_M acts as Gibbs energy and yields the relationship

$$\mu_i^\alpha = (\partial G_M/\partial n_i)_{T, p^\beta, \mu_i}\ , \quad (4.2.4)$$

allowing us to calculate the chemical potential of a surfactant molecule in a molecular aggregate if an expression for G_M is known. The expression for G_M should account for the above lamellar structure of the molecular aggregate of a surfactant and can be derived as follows. For every layer k, we introduce a bulk phase with pressure p^k and a surface with tension γ_k. Then, for a sectoral part of the system under consideration inside a solid angle ω, we will have, instead of (4.2.1), the equation

$$dG_M = -SdT - \sum_k (p^k - p^\beta)dV^k + \sum_k \gamma_k dA_k + Vdp^\beta - \sum_i N_i d\mu_i + \sum_i \mu_i^\alpha dn_i, \quad (4.2.5)$$

where $k = \alpha$ ($\equiv 0$), 1, 2,: (phase α is reckoned as the zero phase layer, every phase layer has the number of its outer surface); V_k is the volume of the kth layer and A_k is the area of the kth surface inside the solid angle chosen. Herewith, for a spherically symmetrical molecular aggregate with concentric layers and surfaces of tension, the geometrical relationships are valid

$$V_M \equiv \sum_k V^k = V - V^\beta, \quad (4.2.6)$$

$$V_s \equiv \sum_{k=0}^{s} V^k = \omega r_s^3/3, \quad (4.2.7)$$

$$A_k = \omega r_k^2. \quad (4.2.8)$$

The pressures and tensions are related to each other by the Laplace equation (1.5) that, in the case under consideration, is of the form

$$p^k - p^{k+1} = 2\gamma_k/r_k, \quad (4.2.9)$$

where r_k is the radius of the kth surface.

Applying Eq. (4.2.5) to an element of the sector selected and integrating over the solid angle ω at a given state of the system, we obtain the expression

$$G_M = -\sum_k (p^k - p^\beta)V^k + \sum_k \gamma_k A_k + \sum_i \mu_i^\alpha n_i. \quad (4.2.10)$$

Using Eqs. (4.2.6)–(4.2.9) and the recursive relationship

$$\sum_{k=1}^{s} (p^k - p^{s+1})V^k = \sum_{k=1}^{s-1} (p^k - p^s)V^k + (p^s - p^{s+1})V_s, \quad (4.2.11)$$

it is easy to reduce Eq. (4.2.10) to the form

$$G_M = \sum_k \gamma_k A_k/3 + \sum_i \mu_i^\alpha n_i. \quad (4.2.12)$$

Eqs. (4.2.10) and (4.2.12) are valid at any value of the solid angle ω. At $\omega = 4\pi$, the thermodynamic function G_M standing in (4.2.10) and (4.2.12), is the same as in Eq. (4.2.1). Differentiating now (4.2.10) and (4.2.12) and comparing the result with (4.2.1), we arrive at two equivalent relationships of type of the Gibbs–Duhem equation

$$\sum_i n_i d\mu_i^\alpha = \sum_k V^k d(p^k - p^\beta) - \sum_k A_k d\gamma_k - SdT + Vdp^\beta - \sum_i N_i d\mu_i, \qquad (4.2.13)$$

$$\sum_i n_i d\mu_i^\alpha = -\sum_k d(\gamma_k 4\pi r_k^2/3) - SdT + Vdp^\beta - \sum_i N_i d\mu_i. \qquad (4.2.14)$$

It is seen from Eq. (4.2.13) that, except for pure external parameters (temperature, pressure, and the chemical potentials of a surrounding medium), the chemical potentials of components of a molecular aggregate μ_i^α are dependent only on the capillary pressure difference and tension of the layers of the molecular aggregate. Using Eq. (4.2.9), this dependence can be reduced to the dependence only on surface characteristics (tension and the curvature radius). Then Eq. (4.2.13) changes to Eq. (4.2.14).

For a one-component molecular aggregate, Eqs. (4.2.12) and (4.2.14) take the forms

$$G_\mathrm{M} = \sum_k \gamma_k A_k/3 + \mu^\alpha n, \qquad (4.2.15)$$

$$n d\mu^\alpha = -\sum_k d(\gamma_k 4\pi r_k^2/3) \quad (T,\ p^\beta,\ \mu_i - \text{const}). \qquad (4.2.16)$$

An alternative pair of relationships follow from Eqs. (4.2.10) and (4.2.13):

$$G_\mathrm{M} = -\sum_k (p^k - p^\beta)V^k + \sum_k \gamma_k A_k + \mu^\alpha n, \qquad (4.2.17)$$

$$n d\mu^\alpha = \sum_k V^k d(p^k - p^\beta) - \sum_k A_k d\gamma_k \quad (T,\ p^\beta,\ \mu_i - \text{const}). \qquad (4.2.18)$$

In the case of incompressible matter (usually the volume of a hydrocarbon chain is considered to be independent of the aggregation number), it is seen from (4.2.18) that the first sum on the right-hand side of Eq. (4.2.17) represent the contribution to the chemical potential μ^α from the capillary pressures of the phase layers of the molecular aggregate:

$$n(\mu^\alpha - \mu^{\alpha(\beta)}) = \sum_k V^k (p^k - p^\beta) \quad (T,\ p^\beta,\ \mu_i,\ \gamma_k - \text{const}). \qquad (4.2.19)$$

Here $\mu^{\alpha(\beta)}$ is the chemical potential of a surfactant molecule in the molecular aggregate under the condition that all the phase layers of the molecular aggregate have been reduced to the pressure p^β. The substitution of (4.2.19) reduces Eq. (4.2.17) to the form

$$G_\mathrm{M} = \sum_k \gamma_k A_k + \mu^{\alpha(\beta)} n. \qquad (4.2.20)$$

The additivity of the chemical potential μ^α with respect to the present surfaces is seen from Eq. (4.2.16). But, according to Eqs. (4.2.15) and (4.2.20), then also function G_M itself possesses additivity, i.e. the contributions of different surfaces may be calculated separately. This circumstance greatly simplifies the computational schemes for various models of molecular aggregates and micelles. One of such computations is given in another presentation in this issue.

CONCLUSION

In this communication the author aimed to describe the most interesting properties of nanostructures and to emphasize the role of surface phenomena. Naturally, the review is limited by the competence of the author and cannot be complete. It only outlines the topic of this issue where a reader will much learn the new about the striking world of nanostructures. Scientific problems are under consideration, but, due to their peculiarities, nanostructures are also widely applied in practice. Continually, new prospects of the use of nanostructures are open (for example, in the field of information technology). It has come the recognition of a great role of nanostructures in the future. “Dwarfs” advance!

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