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INTERFACIAL MATERIAL CONSTANTS FOR SYSTEM OF FINE SIZES

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The properties of bulk and interfacial regions was presented in the paper taking onto account suspensions, colloids, micellar solutions, microemulsions and the so-called soft matter, which understanding is as important as the inorganic matter. A special attention was paid to the role and diversity of material constants necessary for delineation of the state and properties of the considered systems.

key words: material constants, suspension, colloid, micellar solution, microemulsion, soft matter

INTRODUCTION

The ratio between surface area and volume of any system changes substantially with the decreasing size. The same is valid for energy and other properties. As a result the interfacial regions are always different from the bulk regions.

Interfacial effects, resulting from the existence of surface, can frequently be neglected for large bulky systems while in finally divided systems their properties depend practically only on the interfacial regions properties. The interface accumulates the excess free energy of the system. The excess free energy is the source of the interfacial tension, the principal material constant of the interfacial regions as well as the reason of changing properties with the size of one and multi component substances. When we consider properties of individual atoms or molecules, knowing their atomic or molecular constants, we know that they do not allow directly describe the bulk properties build from the mentioned elements. Each bulk phase has however characteristic material constants, only when the bond lengths between atoms and molecules are very small in comparison with their location from the interface. The

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are very small in comparison with their location from the interface. The interfacial material constant (imc) become essential when this condition is not fulfilled. In this article nanometrically dispersed systems will be discussed. In finally divided systems practically all system properties are depended on the imc values.

HIERARCHY OF MATERIAL CONSTANTS

The material constants characterize the whole materialist world and differ in their generalization degree. The first category material constants occupying the top of a generalization pyramid are universal constants, including the speed of light in vacuum c , the Planck h , Boltzmann constants k as well as gravity constant g . They have always the same value and occur in equations dealing with properties of materials.

The second category of material constants is made of partial derivatives of different degree with respect to different parameters of chemical potentials of any type of material. The requirement is the thermodynamic equilibrium of the system with its surroundings. These constants are important parameters and are present in numerous textbooks and handbooks. The most important role, in his category of imc, is the excess molar free energy of interfacial regions ω^s .

The third category, still greater group of constants, characterizes matter in the course of transformation. We select from this group a category of processes running with a constant, limited velocity. They are called the steady state or stationary processes. They are very important for delineation of processes taking place in living organisms. These process are investigated by biochemists and biophysicists and the system in which they occur belong to the colloidal systems category. To realized the complexity of the issue it must be recalled how numerous and diversified are metabolic reactions in living organisms. For their description we need precise information on such systems as for example breathing and blood circulation. We need both qualitative and quantitative characteristics of colloids which form particular types of tissues and body fluids.

The fourth category, the lowest in the hierarchy, is formed by material constants which are normative and relative in their character.

PRINCIPLES OF MATERIAL CONSTANT CLASSIFICATION

Stating type and value of any material constant requires an additional and precise information on what material it represents. Therefore, formally, also the material constant name, being a kind of nickname, signaling its definition, is also a material constant. It represent the lowest level of the hierarchy of material constants because is defined relatively, and does not have any established value. For example the term gold means not only all gold isotopes of Au but also frequently its alloys of different

caratages. More precisely, the properties of gold ingots are different from those of gold used in jewelry as leaves and whiskers of colloidal dimensions. Therefore, besides name, we have to state precisely, parameters which allow to univocally define the considered material constant.

From the presented above example of gold results that besides common parameters of state such as pressure p , volume V , temperature T , and time t , also important is information on the size and shape of the considered piece of matter. The issue of shape and size is essential for understanding and description of the nature of matter.

Material, which is essential for development of living organism and technology is water. Most of the material constants of our interest is somehow connected with water and its solutions. It is a natural trend in science to qualitatively and theoretically delineate, starting from the foundations, the results of scientific observations. At the present level of development of science, the most general tool is the quantum mechanics and statistical thermodynamics, while modeling of real systems usually is based on the molecular dynamics. Systems, on which we are focused the most, are stable hydrophilic colloids at high concentrations. The principal type of bond, which determines the structure of colloid is the hydrogen bond. Until today, despite a dozen of models of water molecule, there is a lack of a uniform model describing the water structure and its solutions, due to lack of quantum approach to the hydrogen bond. Only properly modified existing principles of the quantum mechanics can fulfill this gap.

Let us discuss this issue further. We know that matter is energy which permanently changes its forms. In addition to that, it is certain that its principal elements are electrical charges of opposite signs, while the principal element of structure is represented by the hydrogen atom. Mills (2002) proposed a change in the mathematical formalism presently used by the quantum mechanics. Even Newton noticed that we either measure or compare only forces acting in systems, while the existence of mass is only postulated. A statistical picture of the potential energy is given by the Coulomb law, which determines how a change of a distance between the charges, either of the same or opposite signs, increases, or decrease, the energy of the system. Mills (2002) defined the term of two-dimensional orbitsphere, which takes into account the mass of electron m_e , defined by a well experimentally determined de Broglie relation between electron linear momentum $m_e v_n$ through its materialistic wave of appropriate length $\lambda_n: \lambda_n = h/m_e v_n$. He also assumed that if an electron, having linear momentum $m_e v_n$, is present in the hydrogen atom on orbitspheres of Bohr radius r_n , then the energy is not emitted. The energy is either emitted or adsorbed only when the electron is transferred between orbitspheres of different n values. To define other quantum numbers he used the Maxwell equation for delineation of the electron on an orbitsphere and for connecting the motion of charges and magnetic field, getting as, a consequence, an expression for spin functions. The author claims that after taking into account the universal gravity constant g , his modified quantum mechanics provide quantitative description of matter starting from the hydrogen atom property, up to the average tem-

perature, and the expansion and shrinking period of the Universe as well as materialistic character of the black holes. Maybe this type of small modification of the principles of quantum mechanics will help to explain the nature of the hydrogen bond.

A point does not have any dimension. However, the point model of a neutral hydrogen atom has a mass, which is a sum of the mass of the electron and proton, and thus, the energy given by the Einstein formula. Having a collection of points in an infinite space we can, using the law of physics and mathematics build a model of a materialistic Universe. We need for it two types of parameters, material constants as well as the size and shape. We can build a sphere having the radius of Bohr's hydrogen atom up to complicated structures of nebulas and black holes. In other words, the shape is replaced with known rules of symmetry delineating systems of any size.

We can classified the systems into:

- 1) divided molecularly (angstrom scale)
- 2) divided nonometrically (nanometer scale)
- 3) divided colloiddally (micrometer scale)
- 4) suspensions (macro scale).

Regardless of system size, there are states of matter:

- gaseous
- condensed, including liquid, crystalline, hard, and soft matter.

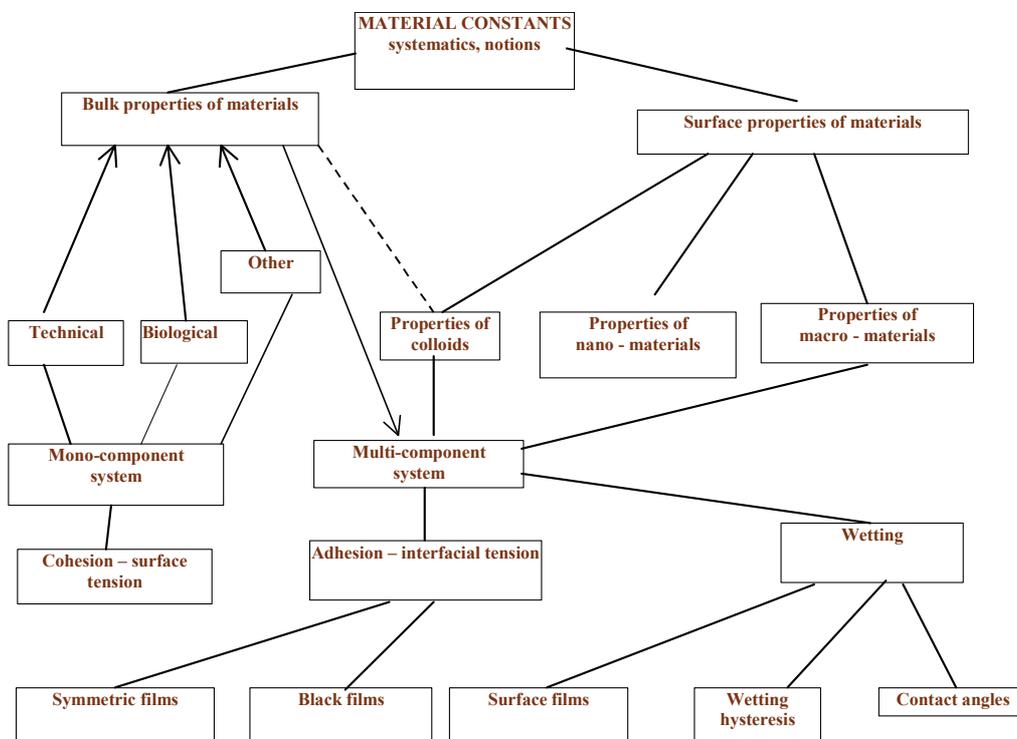
A system can be considered as:

- equilibrium state
- steady state
- non-steady state.

It depends on our choice how high in the hierarchy the material constant which characterizes the considered system is located.

At a constant temperature the surface tension is the excess specific change of the thermodynamic potential of a substance. In one-phase systems, regardless of their state of matter, the surface tension is defined as a half of maximum cohesion work needed for formation of a unit of free surface and is related only to the interface of a chemically pure substance at equilibrium with its saturated vapors. In practice the measurements are conducted in the presence of the so-called neutral gases, and their difficult-to-predict influence on the results, frequently significantly alters the properties of the interfacial regions.

A precise definition requires an additional decision whether or not the surface formation process is considered under constant volume, constant pressure, or constant potential of open systems ($\Omega = -pV$). Not always the excess free surface energy has one, well determined value, because in condensed phases it frequently becomes a tensor.



Another important material constant of a one-phase one-component material is connected with the density. It is viscosity, also called the internal friction, and lies at the border of equilibrium and stationary states. The detection and measurements of viscosity requires initiation in the liquid phase observable flow (motion). Due to permanent, at equilibrium, thermal motion of the molecules inside the liquids, the values of the viscosity are needed for delineation of their material constant called self-diffusion. The principal element needed for delineation of the stationary states is the thermodynamic driving force, that is a parameter which initiates the flow between reservoirs in which the system is kept at equilibrium. The other parameter is the intensity of the flux. For initiation of a flow of heat, a temperature **gradient** is needed. For electrical charge flow the **driving force** is the electrical potential **gradient**. Any flux, or generally an movement is accompanied by phenomena resulting from the specificity of the medium resistance in which the movement takes place. The nature of flux is based on interconnection of fluxes resulting from the nature of the medium. It is worthwhile to notice different characters of the force fields which cause formation, in the media, concrete **gradients**. A great variation of stationary material constants is connected with the character of the force fields determining the nature of the **appropriate gradient**, and is also connected with the character of resistance encountered by

the fluxes. The flow of charge causes, in a conducting medium, appearance of precisely determined magnetic field linked to the electrical field.

We know very well that equilibrium systems are not static. Its characteristic feature is a tremendous dynamics of matter movement but only on the atomic (molecular) scale. We know that the movement does not stop even at zero kelvin. They are characterized by the values of vibration energy at the so-called states also known as standard states. Great scientist Clausius offered a hypothesis of the so-called thermal death of the Universe. He based his hypothesis on the fact of increasing entropy of systems which dissipate their energy in non-reversible processes through transfer of the energy to the surrounding as heat. In contrary to the internal energy, portions of entropy are transport either as work or heat and they are not functions of state. Physically, their quantities are not total derivatives, and their values depend on the way the change occurs.

Introduction of time and defining the source of entropy density in thermodynamics allowed to consider the resistance, which dissipates energy, and provide a quantitative measure of the dissipation. It provided conditions for definition of the material constants for stationary systems as partial derivatives of volumetric source of entropy, while the stationary interfacial material constants are obtained as derivatives of quantities of original excess functions.

For thermodynamics of stationary states, the equivalent of Maxwell relation for the thermodynamics of equilibrium systems is the Onsager rule. Both deal with the so-called crossed effects between partial derivatives of total differentials.

The gradients of intensive parameters of state of a system are [thermodynamic driving forces](#) which cause flows of system's elements. Dissipative resistance of the medium which decides about the values of the phenomenological coefficients of flows are an essential source of entropy of irreversible processes taking place in the investigated systems. The most important two processes, defined in such a way irreversibility, and thus dissipation of energy, are diffusive fluxes of components of system, caused by gradient of their chemical potentials and fluxes of energy as heat under influence of temperature.

The smallest elements of macroscopic systems structure are atoms and individual molecules. If at least one of the dimension of the elemental component of the system: macromolecules, stable aggregation or association of molecules, particles, droplets of the dispersed condensed phase lies below 1 μm , the system is called colloid.

COLLOIDAL SYSTEMS

Non-dissipative, Newtonian character of movement in isolated ideal gases allowed to define the principal parameter of all materialistic systems, the absolute temperature T as a parameter describing energy state of gases resulting from elastic collisions of atoms, treated as materialistic points having certain momentum. When in the volume

V there is one such atom or molecule, then $T=pV/k$, because the number of atoms N_A is equal to the Avogadro number $T=pV/R$. In colloidal systems, tending to form coagula and precipitates, the process, leading to formation of still greater aggregates, is diffusion of molecules. Due to investigations of the Brownian motion, as a results of chaotic self-diffusive thermal movement of either molecules or particles, the rules regarding the particles diffusion were adopted from the terminology and laws established for diffusion of atoms. The change from the description of the movement of materialistic points to the properties and processes in real systems requires to give concrete sizes and shapes of the components and their interactions. Modeling colloidal systems, due to the ease of calculations, the simplest assumption is sphericity of the particles. Additional difficulty is, however, the polydispersity. A sample of a particular polyelectrolyte consists of a mixture of molecules differing in polymerization degree, thus in molecular mass. The molecular mass M_i , by definition, is the mass of $N_A=6.023 \cdot 10^{23}$ molecules of i type. A composition of the whole sample is determined by mole fractions x_i of all component i . Two methods are used to get average values. Number average $\bar{M}_n = m/n = (\sum_i n_i M_i)/(\sum_i n_i)$ or as weight average molecular mass $\bar{M}_w = \sum_i (m_i/m M_i)$, where m_i denotes the mass of a fraction having molecular mass M_i , while m is the mass of the whole sample $m = \sum_i m_i$.

In 1905/6, considering the nature of the Brownian motion, **independent** by Einstein and Smoluchowski found a relationship between diffusion coefficient D and the average value of the square of the shift $\bar{l}^2 = 2Dt$ for a colloidal particle in a certain direction at the same time intervals. Assuming sphericity of the colloidal particles Einstein derived a relation between particles radius and internal friction coefficient that is viscosity of the medium in which they are dispersed. The diffusive flux of the particles is caused by a gradient of their chemical potential in the investigated system. The stationary state of the flux stabilizes when caused by the existing gradient of chemical potential μ , the force acting on the particle is balanced by the force of medium resistance dependent on the values of its viscosity η , radius of the particle r and stationary velocity of its movement v , meaning a stationary flow, that is the movement of the particles of c_i concentration with a constant velocity v , hence $dc_i/dz = -v c_i (6\pi\eta r)/kT$, if $x_i = c_i$. The diffusion stream of colloidal particles is described by the first Fick law $j_i = -D dc_i/dz$, and therefore ($D = kT/6\pi\eta r$). The diffusion coefficient D is a phenomenological coefficient λ , while the concentration gradient is a stimulus of flow of the Onsager theory. The thermodynamic **forces** are gradients of intensive parameters of the state, and, when they appear in the system, they cause irreversible flows which act to restore the equilibrium. The intensity of the flux of any component j_i depends on the value of certain **gradient** w_m , and phenomenological coefficient λ_{im} , which characterizes the resistance of the medium $j_i = \sum_m \lambda_{im} w_m$. The fluxes are linear functions of **gradients** and the Onsager rule says that the source of entropy is the sum of products of combined fluxes (j_r) and thermodynamic **gradients** (w_r) $(\partial s/\partial t)_T = 1/T \sum_r j_r w_r$. The Onsager relations describe the phenomenon of symmetry existing between selected irreversible processes. The principle of the

irreversible processes. The principle of the description of these relations is the relation $(\partial j_r / \partial w_m) = (\partial j_m / \partial w_r)$ where j_r is the flux of the component, j_m is the flux of thermal energy, ∂w_m denotes the chemical potential gradient of a component, and ∂w_r is the temperature gradient.

HYDROPHILIC COLLOIDS AND MICELLIZATION

Typical hydrophilic colloids are formed during preparation of solution of substances which are called surfactants. Surfactant molecule possesses in its structure an organic hydrophobic group while the other part is polar with certain affinity towards water. In a wide range of temperatures, above the Kraft temperature, and also above the critical temperature, when the solution is enough concentrated, there is a spontaneous process leading to the formation of thermodynamically stable colloidal solution. The process is called micellization. Initially micelles are spherical in which the hydrocarbon chains occupy the interior of micelle while the polar groups form the outer sphere and are directed towards the surrounding medium. As a result of compensation of entropic and enthalpic components of the free energy, a state of its minimum value is established. A further addition of the surfactant causes neither further change in the solution nor noticeable changes of the surface tension nor monomer concentration. There is an increase of spherical micelles concentration. There is no saturation of the solution with the micelles. At certain, appropriate for a given system, surfactant concentration, micelles change their shape. The concentration of the spherical micelles decreases while the population of the cylindrical micelles increases. The cylindrical micelles, with increasing concentration, change into flat structures. In each micellar system there are many such shape transformations. An average spherical micelle contains from a dozen to hundreds of surfactant molecules. An appearance of other than spherical shapes makes that more and more regions of the system are ordered. The micellization equilibrium constant is the result of the minimization of the free energy of the whole system. The entropy decreases due to increased ordering of system elements while enthalpy changes as a result of replacement of contacts of the groups as a result of replacement of contacts of hydrophobic groups of individual surfactant molecules with water for the interactions of hydrocarbon groups between themselves in the interior of each micelle.

Rehbinder at the conference in Berlin (1966) showed that the presence of fragments of different hydrophobicities in the molecules structure alone is not enough to form micellar solutions. Using German terminology he proposed to reserve the term real or true tensides only for substances able to form micelles. Presently they are called surfactants. He noticed that surface activity in the sense of different molecular compositions of the interfaces and bulk is a universal phenomenon regarding all systems. Micellization is formation of a new phase characteristic only for systems fulfilling special conditions. Among material constants characterizing micellar systems, the

main role is played by the already mentioned Kraft temperature, below which surfactant has, as any substance, a limited solubility in water and does not form micelles. The phase transition is possible above the Kraft temperature. Rehinder (1966), analyzing the complexity of the affinity of different fragments of complex structure towards water, noticed a low value of the enthalpy component as a characteristic feature of micellization process. The higher temperature, the greater probability of free energy minimalization due to the formation of new phases. Different temperature relations of entropic components and enthalpic local ordered states lead to the formation of structures beneficial for attaining minimum. The system gathers the whole reserve of energy in their significantly developed interfacial regions.

INVERSED MICELLES

Discussing micellization we paid attention to aqueous surfactant solutions and characteristic structures of surface active substances, which greatly decrease the surface tension of water. They, due to the presence of hydrophobic groups in their structure, manifest also certain solubility in typical organic solvents. The molecules of surface active substances are gathered in these solutions at the interfaces and are oriented with the hydrophobic groups towards medium of lower polarity. This property is utilized for formation of colloidal systems called reversed micelles. In a hydrophobic medium, as the concentration increases, the aggregation is not taking place as fast as in water. Small amount of water may help the aggregation. The formed inversed micelles have, as a rule, greater diameter than the micelles in the aqueous medium. The reason is solubilization, relying on incorporation of a number of water molecules inside of each micelle. Their number depends on the nature of the polar groups in the surface active molecule directed towards the center of each reversed micelle. The knowledge of material constant values characterizing the equilibrium of solubilization has a great importance in technology.

In a formal thermodynamic approach micelle can be treated as a neutral particle because the stability of the system requires that eventual electrical charge its ionized polar groups was, in the interfacial region of the micelle, completely neutralized by ions of the opposite sign. Thus, the ions neutralize their charges within the micelle structure. The discussed neutral system is stable in the states determined by the material constant which is here the equilibrium constant of the dynamic micellization reaction.

A numerous group of hydrophilic colloids is formed by proteins. The principal elements of the proteins structure are amino acids. Sometimes large protein macromolecule containing hundreds or thousands of amino acid units can be prepared by suitable methods in crystalline form, as a chemical of well established composition. The material constant of proteins are type, number, and structure of amino acids. A biochemical activity is possessed only by native proteins which have secondary, ter-

ary and ternary structures which require, besides peptide bonds, also formation of hydrogen and disulfide bridges. Improper temperature, electrolytes concentration, the presence of additional substances or solution pH cause either partial or total loss of protein activity, that is temporary or irreversible denaturation. Biochemical monographs accumulate more and more material constants for proteins.

Historically important issue is proteins coagulation. Noticed many years ago salting out of protein, leading to the turbidity of the chicken egg white solutions in the presence of electrolytes. Such observations lead to classification of ions according to their salting out effect. The strongest are ions with great heat of hydration. At high, about molar, concentrations the ions compete for water, while the water-protein structures provide stability of the hydrophilic colloids. Most anions are much more hydrated than cations, hence popularity of the Hofmeister series in which anions are ordered according to their coagulation ability (citric > tartaric > SO_4^{2-} > acetate > Cl^- > NO_3^- > Br^- > I^- > SCN^-).

A change of type and concentration of electrolyte makes the weakly mutually interacting neutral particles of hydrophilic colloids to modify their distribution of potentials in the surrounding electrical double layer. Within a wide region of changes of system parameters it does not cause thermodynamic destabilization. The hydrophilic colloids can form thermodynamically stable systems, while hydrophobic ones always undergo destabilization.

MICROEMULSIONS

In contrast to emulsions, microemulsions are thermodynamically stable. Similarly to emulsions, microemulsions are formed by mixing water, or other polar liquid, with a non-polar liquid, also called oil. It can be a hydrocarbon such as octane, a long chain fatty acid, or aromatic hydrocarbon with a low affinity for polar liquid. There are two types of emulsions: oil in water and water in oil. In unstable emulsions, the interfacial tension between droplets of the dispersed phase and the dispersing medium is much above zero. A spontaneous coalescence causes a decrease of the interfacial area and the free energy of the system significantly decreases. To stabilize the emulsion system, we add a third component which strongly reduces the interfacial tension. This component, having the ability to be present in both phases can cause solubilization. An increase of the sorption in the interfacial regions decreases the interfacial tension while formed in the system new colloidal phases decrease further their free energy. When only one component aggregates, the surface tension of the colloidal solution does not drop below a dozen of mN/m, while in a multicomponent microemulsion system it decreases to one tenth of a mN/m and sometimes to one thousandth of a mN/m. To measure such low values of surface tension, a special device was constructed able to record changes of the shape of small droplets rotating with a precisely regulated velocity. Presently, a direct computer recording and graphical representation of equilib-

ria in the form of classic isothermal Gibbs triangle and a plot taking into account evolution of phase composition with temperature is possible.

A typical example (Miller and Neogi, 1985) of a multicomponent microemulsion system is the water/anionic surfactant/short chain alcohol/oil/sodium chloride system. Depending on the composition and temperature the system can, due to gravity, split into two or three, differing in densities, phases. When, in the presence of salt, the system containing equal amounts of oil and 1% aqueous alcohol solution (containing an anionic surfactant) is shaken, we observe initially two-phase system, and a third phase appears and next disappears. Traditionally it is called the middle phase.

The oily upper phase is transparent while the aqueous salt solution forms the lower phase. Practically the whole surfactant is gathered in the middle phase having not yet established structure.

An increase of the salinity leads to the transition of the microemulsion from the aqueous to oily continuous phase. At optimal salinity, a formation of a bicontinuous phase is postulated. It means that within the whole volume of the system it is possible, from a point selected in any of two phases, to go very near to any other point of that system. In any point of such a system the interfacial region has the saddle curvature shape which main radius of curvature is constant. Due to practical importance of the microemulsion for removal of remaining crude oil from the exploited deposits, the discussed systems are intensively investigated by physical chemists specializing in oil and mineral processing.

HYDROPHOBIC COLLOIDS AND THEIR INSTABILITY

A colloidal hydrophobic particle is stabilized, in a given dispersing medium, by the surface electrical charge. The greater is the charge, the more difficult, for accidental thermal motion, to cause the collision of the particles. The electrical field, regulated by the Coulomb law, causes an increasing, with the approaching particles, repulsion. The changes of the repulsion depend on the dielectric constant of the medium and the ions concentration. A direct collision is possible when the kinetic energy caused by thermal movement of a concrete pair of particles is greater than the potential energy of repulsion. Only a direct contact of both objects, especially when they have significant adhesion energy, make attractive forces come into play promoting onset of coagulation.

From the earliest period of colloidal systems investigation, they were conducted by means of two approaches. As a result, rules were created which describe the influence of electrolytes on the stability of system and the theory of the coagulation has been developing. Simple rules for the behavior of colloids were formulated by Hardy and Schulze. They established that ions can cause coagulation when their electrical charge was of opposite sign in relation to the electrokinetic potential of the colloid. The ions concentration initiating coagulation was found to change proportionally do

the 6th power of reciprocal of their valence. Organic ions with large sizes do not follow the rule. The Hardy and Schulze was confirmed theoretically (Hsu and Kuo, 1995).

The theoretical foundation of electrolytic coagulation (the so-called theory of fast coagulation) were provided independently by Einstein and Smoluchowski. Simple calculations of Smoluchowski, assuming that for a reaction which does not need activation after time t of sedimentation the concentration c_k of the aggregates containing k particles of a monomer is $c_k = c_0 (t/\tau)^{k-1}/(1+t/\tau)^{k+1}$, where τ denotes the time after which half of the initial number of colloidal particles aggregated. Thus, the total colloid concentration is $c = \sum c_k$ (sum for k from 1 do ∞) is $c = c_0/(1 + t/\tau)$.

The experiments of Zsigmondy and others confirmed rapid coagulation of colloids for which the absolute values of the electrokinetic potential is below a critical value of ζ_{kr} . However, not each collision of individual particles results in aggregation.

Coagulation requiring activation energy and when is sterically hindered by unsuitable orientation of the non-spherical particles at the moment of their touching is called slow coagulation. Then, the equation describing such coagulation require suitable modification.

SOFT MATTER

The definition of the soft matter assumes that its lowest size is that of molecules, and includes, as especially interesting group of substances, polymers and polyelectrolytes as well as mezosopic porous objects. All such systems are characterized, in contrast to the condensed crystalline phases, not only lack of macroscopic ordering at great distances, but also the presence of more or less ordered domains. In addition, a small change of the composition, pressure and/or temperature frequently leads to a phase transition having a great number of diverse structures. It confirms a great role of defining characteristic interfacial constants which would allow univocally determine the nature and properties of the discussed materials. A summary of the present state of art and literature data is available in the Internet at the web site of Robert Hołyst (2008). The most important features of matter, which cannot be classified as liquid or solid, he considers partial ordering of orientation or translation and topologic complexity or geometric structure. As a result of broken translation and/or rotational symmetry, the visco-elasticity and elastic deformation appear. The Young modulus of the liquid crystals is four orders smaller than that of the solids. Water, as a main component of soft matter, determines the temperature range of its existence. Although the structural effects appear in proper solutions only in the region of free surfaces, or interfacial regions, they are of decisive importance for the delineation of the soft matter of living organisms.

Ordering decreases entropy, therefore it is not usually spontaneous. Minimization of thermodynamic potential is based on the sum of the enthalpic and entropic compo-

nents. For states of matter covered by the definition of soft matter, the domain structure dominates. Frequently, when the parameters of the system change, in the volume of homogenous structure there is a spontaneous phase transition and two or more domain regions having different structure can appear. Ordering of some of them can visible increase. Locally, there is a drop of entropy, which is compensated by an appropriate enthalpy change. For the whole system, the rule of minimum free energy is preserved.

Richness of phases of different structures is characteristic for soft matter and results from a tremendous role played in such systems by structural interactions of short range, especially those which are called hydrophobic forces. It emphasizes an urgent necessity of development of the hydrogen bonding theory. Depending on the affinity towards water present in the system, the molecule (or surface), breaks locally, depending on the domain structure, certain number out of four hydrogen bonds, which are at disposal of each water molecule in the uninterrupted net of these bonds. The local strength of the hydrogen bonds is therefore the principal material constant, which characterizes a concrete type of the soft matter.

Unfortunately, a lack of a proper description of the quantum mechanics prevents us from creation of a full and quantitative definition of the soft matter. Literature on bio-chemical and bio-physical issues shows that this is a key point of development of these disciplines. This situation can be easily justified by comparing, in kT units, the energy of principal interactions deciding about the structure of matter. The energy of hydrogen bond is a dozen-fold greater than the energy of thermal movement of particles and by one order greater than that resulting from the DLVO theory for particles approaching the separation of a bond length. So, the hydrophobic interactions, which do not have much importance in comparison with long-range interactions, however they determine the domain structure of the soft matter.

In the system of nanometric size, the surface curvature of the domains, according to the thermodynamic condition determined by the Kelvin equation, leads to local pressure tensors approaching even 0.1 gigapascals. Under such conditions, valid is only the description based on the third Gibbs chemical potential $\Omega = -pV$. At the same time, gases present in systems with nano-bubbles being at equilibrium, must have local densities characteristic for critical states, similar to the liquid water, and can exist solely at the border with highly hydrophobic surfaces.

Making summary, let us compare our state of knowledge on material constants of the hard matter resulting, according to crystallography, from the 32 symmetry classes of crystalline matter, with the present description of the soft matter. Periodical arrangement, providing ordering of long range of atoms and molecules, is possible only within the frame of the mentioned classes. The domain structure of soft matter, not having ordered structure of long range, breaks the condition of the symmetry. A classification of such systems was initiated with research of the so-called glassy phases and liquid crystals. The structure of phases, characteristic for these systems, is called

mezomorphic or partially ordered, and such phases as smectic, nematic and cholesteric are distinguished.

The base for delineation of the pieces of soft matter ordering was provided, half a century ago, by Landau (Kleman et al., 2003), as a function of density distribution ρ . Mutual orientation of molecules in each, determined by vector \mathbf{r} , point of the phase, is given by the value of three Euler angles ω and $\rho(\mathbf{r}, \omega) = \langle \sum \delta(\mathbf{r} - \mathbf{r}_i) \delta(\omega - \omega_i) \rangle$. Averaging summation regards all positions of the molecules from $i = 1$ to $i = M$, within the domain of each phase.

From the given above relations, taking into account the size and structure of a given molecule forming the soft matter and, according to the statistical mechanics rules, a great number of symmetry classes was established as the characteristic material constants. Rules were presented which decide about the possibility of transformation between the phases belonging to different classes.

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W pracy szeroko scharakteryzowano właściwości materii i obszarów granicznych pomiędzy elementami materii o różnym rozdrobnieniu biorąc pod uwagę zawiesiny, koloidy, roztwory micelarne, mikroemulsje oraz tzw. materię miękką, której znajomość jest tak samo ważna jak materii nieożywionej. Szczególną uwagę zwrócono na rolę i różnorodność stałych materiałowych niezbędnych do opis stanu i właściwości rozpatrywanych przykładów.

słowa kluczowe: stałe materiałowe, zawiesina, kolloid, roztwór micelarny, mikroemulsja, materia miękka