

# SUMMARY OF DEVELOPMENT OF THE THEORY OF STABILITY OF COLLOIDS AND THIN FILMS\*

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*In this review, the research of the author in the field of colloidal systems is summarized. The factors influencing colloidal stability are systematized and analyzed. Examples are presented to illustrate the practical utilization of the theory of stability of colloids and thin films.*

**Keywords:** *stability of colloidal systems, thin films, electrostatic forces, disjoining pressure, boundary layers, structural forces, nucleation, thermoosmosis.*

Development of the theory of stability of colloids and thin films has gone through several stages that reflect different aspects of the phenomenon.

## ELECTROSTATIC FORCES

The first rigorous theory of stability of weakly charged and also highly dispersed lyophobic sols was advanced by the author of this review in 1937 [1]. Of primary importance was the method used for exact calculation of the forces arising in sufficiently thin interlayers as a result of overlapping of the diffuse ionic atmospheres that surround suspended disperse particles. These forces were termed the ionic-electrostatic component of the disjoining pressure ( $\Pi_e$ ) of thin interlayers.

Later, Levine [2] attempted to solve this same problem, but his solution, unfortunately, was erroneous. The same error was present in the simultaneously published article of Corkill and Rosenhead [3]. The solution proposed by Langmuir [4], based on calculation of the excess osmotic pressure in the plane of symmetry of the solution interlayer, was basically incorrect, as was shown later in the monograph of Verwey and Overbeek [5]. Moreover, Langmuir's approach is completely inapplicable to cases in which there is no plane of symmetry, for example in the convergence of two particles with different radii or nonidentical charges. The approach of the theoretical physicist March [6] to the theory of colloid stability, based on an unreal process of a simultaneous, identical change in size of all particles, likewise could not lead to any solution of the problem. In contrast, the approach proposed in [1] proved to be applicable in all cases.

The following expression was obtained in [1] for the electrostatic repulsion in plane interlayers:

$$H_e = \frac{\varepsilon}{8\pi} \kappa^2 \varphi_0^2 \left[ 1 - \operatorname{th}^2 \left( \frac{\kappa h}{2} \right) \right], \quad (1)$$

where  $\varepsilon$  is the permittivity of the interlayer;  $h$  is its thickness;  $\varphi_0$  is the potential at its boundary;  $1/\kappa$  is the thickness of the ionic atmospheres.

Whence, for the system stability  $L = 1/v$ , characterized by the reciprocal of the coagulation rate  $v$ , the following equation was derived:

$$\frac{L - L_0}{L_0} = \frac{1}{n} (e^n - 1). \quad (2)$$

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Here  $L_0 = 1/v_0$  is the stability of a system with particles having no surface charge, and

$$n = \frac{\epsilon r \varphi_0^2}{2kT}, \quad (3)$$

where  $k$  is the Boltzmann constant;  $T$  is the absolute (Kelvin) temperature;  $r$  is the particle radius.

According to Eq. (2), the stability, increasing sharply with increasing  $n$ , becomes significant when  $n > 7$ . This conclusion made it possible to refine the empirical rule of Eilers and Korff [7] to a considerable degree.

In these and all subsequent calculations of colloidal stability and the interaction of colloidal particles based on a calculation of the disjoining pressure  $\Pi(h)$  of a plane-parallel interlayer, an equation given in [8] was used to account for the influence of shape on the interaction of any convex bodies. This equation has been used in many studies over the past 55 years.

For the simplest case of two spheres with radii  $r_1$  and  $r_2$ , the force of their interaction is expressed as

$$N = 2\pi \frac{r_1 r_2}{r_1 + r_2} \int_H^\infty \Pi(H) dH, \quad (4)$$

where  $H$  is the shortest distance between the particle surfaces.

Subsequently, the theory of stability of lyophobic colloids was supplemented by an accounting for another component of the disjoining pressure — the molecular component.

In [9], the case of interaction of particles charged to limiting values of potential was examined, and a theory was constructed for the stability of the corresponding lyophobic sols. From this theory it followed that coagulation begins when the electrolyte concentration  $\gamma$  (moles/cm<sup>3</sup>) reaches the value

$$\gamma \geq C \frac{\epsilon^3 (kT)^5}{A e^6 z_1^6}, \quad (5)$$

where  $\epsilon$  is the permittivity;  $A$  is the Hamaker constant of molecular attraction;  $e$  is the charge of the electron;  $z_1$  is the valence of the primary ion;  $C$  is a constant that depends solely on the "asymmetry" of the electrolyte. This equation demonstrated the qualitative correctness of the empirical Schulze-Hardy rule, according to which the coagulating concentration of electrolyte decreases sharply with increasing valence of the counterion.

The theory developed in [9] was subsequently acknowledged as classical, and in 1987 it was placed in a collection of commentaries on classical works.

Later, in the monograph of Verwey and Overbeek [5], the theory of stability of lyophobic colloids was supplemented by an accounting for the Stern correction and by considering not only small and large potentials, but also intermediate potentials (subsequently, Verwey and Overbeek acknowledged the priority of Soviet scientists in the development of this theory).

An accounting for the influence of mechanical properties of thin interlayers on the coagulation of sols was given in [10].

The theory of irreversible coagulation that was developed for this case [11] is distinguished by an accounting for the increase of viscous resistance upon approach of particles to distances that are small in comparison with their radii. By accounting for not only viscous resistance but also the energy of interaction of the particles, it became possible to rectify the error of Smoluchowski in his theory of slow coagulation.

Subsequently published was a different version of the derivation of the electrical component of the disjoining pressure, based solely on thermodynamics and the Poisson-Boltzmann equation [12]. In the course of further development of the theory, it was used in calculating the interaction of unlike surfaces and particles charged to nonidentical potentials [13], thus expanding the field of its application (theory of heterocoagulation). Such phenomena as the coagulation of mixtures of sols, coacervation, dyeing, flotation, and so on, for which it was necessary to consider specifically the asymmetric case of nonidentical surfaces, are covered by the theory of heterocoagulation. One of the most important applications of the theory of heterocoagulation and stability of thin wetting films is its use in the theory of flotation, which was accomplished in [14, 15].

By using the method of "isodynamic curves," the problem of calculating electrostatic forces was also solved for any electrolyte and for any constant value of the surface potential. The existence of a maximum value of the repulsion at a certain width of the gap between surfaces is an extremely important property of the electrical repulsion of surfaces with charges of the same sign, this value being independent of the potential of the more strongly charged surface. This rule is observed rigorously, and it does not depend on the surface configuration of the interacting bodies.

Two fundamentally different cases were examined, in which molecular interactions lead to mutual attraction or repulsion of two bodies. In the first case, a modification of the rule of Eilers and Korff was obtained, when one surface remains strongly charged and the charge of the other surface may take on any value.

In the second case, adhesion of surfaces or coagulation is possible only when the charges of the two surfaces have different signs, and when the electrolyte concentration is not extremely high. If, in addition, both surfaces are strongly charged, an equation is obtained for a critical concentration below which the coagulation process begins. This equation is very similar in form to that derived in [9], which includes the refined Schulze–Hardy rule. In contrast to this rule, however, the valences of the anions and cations enter into the equation symmetrically.

In the review article [16], in addition to a critical review of research on the theory of colloidal stability, there appeared for the first time certain general and rigorous calculations of the free energy of charged particles in an electrolyte solution. Evidence was presented that the expression derived for the free energy  $F_e$  satisfies the Gibbs–Helmholtz equations:

$$F_e - T \frac{\partial F_e}{\partial T} = u_0 \quad (6)$$

where  $u_0$  is the total intrinsic energy.

It was proved simultaneously that the expression for the free energy  $F_e$  is equivalent to a system of Maxwell's stress tensors of the electric field, to which has been added an excess hydrostatic pressure.

For the distribution of the pressure tensor in a dispersion medium the following expression was obtained in [11]:

$$P = -\frac{e}{8\pi} [\text{grad } \varphi]^2 - \frac{e}{4\pi} \left( \frac{\partial \varphi}{\partial n} \right)^2 - \int_0^q \rho dq \quad (7)$$

where  $\varphi$  is the electric potential;  $\partial\varphi/\partial n$  is the gradient of electrical potential in the direction of the normal to the area on which the pressure  $P$  is acting;  $\rho$  is the charge density at this location. The first two terms of the equation express Maxwell's electrostatic field tensor, the last term  $\int_0^q \rho dq$  the excess hydrostatic pressure related to the ionic atmospheres around the particles.

In many cases, this general conclusion permits a very marked simplification of the calculation of colloidal particle interaction forces, reducing the calculation to a mere integration of the components of the stress tensor over sections of any surface covering one of the particles or a plane located between the particles. In the case of two identical spheres, it is convenient to use the symmetry plane normal to their line of centers.

One of the first confirmations of the theory of ionic-electrostatic repulsion in the presence of equal-thickness interlayers was the observation of iridescent layers formed by deposits of platelike particles of certain minerals. Analogous forces produce swelling of montmorillonite clays in electrolyte solutions. Also examined in their review [16] was the influence of monolayer adsorption and the Stern layer on colloidal stability.

Another significant advance was the development of an approach to quantitative explanation of coacervation processes, for example the separation of a colloidal sol into two layers with different concentrations. Here it was shown that Langmuir's attempt to carry over the interpretation of coacervation into the coagulation of colloids was erroneous.

An important role was played by the calculation of electrostatic interaction in the theory of formation of periodic colloidal structures, for example in tobacco mosaic virus.

Highly indicative in this connection are the experiments of Chernoberezhskii, who confirmed the reversal of the Schulz–Hardy rule in heterocoagulation, and also the experiments of Usui on the coalescence of mercury drops polarized to different potentials. The way in which the electrostatic component of the disjoining pressure and its free energy vary with the interlayer thickness are highly dependent on whether the charges or potentials remain constant as the surfaces bounding the interlayer approach each other. An exact solution of this problem for solutions of symmetric electrolytes and certain unsymmetric electrolytes was given by Muller [17].

Still more complex calculations were performed for the interaction in the case of overlap of spherical double layers, a case that is directly related to the interaction of colloidal particles. Also examined was a case that is of extreme practical importance, in which the solution contains a mixture of two electrolytes. This problem was solved for conditions under which both electrolytes are symmetric.

With thin interlayers, the disjoining pressure  $\Pi_e$  may be influenced considerably by the discreteness of charges of the dense layer of ions. The corresponding theory was constructed by Muller together with the present author [18] for the case of nonlocalized adsorption of ions, where correlation in the positions of the ions on both boundaries of the interlayer as a result of electrostatic interaction should be taken into account. As shown by the calculations, correlation of positions of the adsorbed ions, with thin interlayers, leads to a decrease of the repulsive forces, and in certain cases with very thin interlayers, even to a change in sign of  $\Pi_e$ , i.e., a change from repulsion to attraction.

## DISJOINING PRESSURE

In the monograph [11], principles of the theory of stability of colloids were set forth, and the concept of disjoining pressure of thin interlayers of both liquids and gases was introduced into physicochemical science. The generality and rigor of this approach are ensured by the introduction of the stress tensor at all points of the interlayer through the Maxwell electromagnetic tensor and the Lifshits theory of molecular forces. It was shown that the introduction of the Bakker stress tensor by Bakker and his followers involved an error, the magnitude of which is difficult to overestimate. The dependence of the disjoining pressure on the interlayer thickness that was established in [11] offers a means for constructing its thermodynamics and deriving conditions of equilibrium and disruption of stability, particularly for foam, emulsion, and wetting films. Thus, it becomes possible to explain the formation of secondary ultrathin black films in the initial primary black films, and to develop a theory of their stability with due regard for the molecular and electrostatic components of the disjoining pressure.

Even at the start of the 1960s [19], the first direct measurements of molecular attraction of solids as a function of gap thickness were performed, with the aim of testing the equations that had been proposed previously. We claim priority for these measurements, which were ahead of the work performed in other countries, some of which proved to be erroneous, for example, the measurements of Overbeek and Sparnaay [19], which gave values three orders of magnitude greater than the actual forces of molecular attraction, as a result of failure to eliminate random charges on the interacting surfaces [19].

Fundamental studies of the forces of molecular attraction of glass and quartz surfaces were performed by the author together with Abrikosova [20]. For the first time, the author, in cooperation with Rabinovich, also measured molecular attraction between two metals [21], which was successful because of further improvement of a proposed feedback method. The results of the measurements confirmed the theory of Lifshits and provided impetus for its subsequent expansion. This theory in turn stimulated the design and performance of a number of subsequent experiments.

## ADSORPTION AND ELECTRONIC COMPONENTS OF DISJOINING PRESSURE

In the case of nonionic solutions, diffuse adsorption layers may be formed at boundaries between the solution and neighboring phases. Overlap of these layers gives an additional adsorption component of the disjoining pressure, which is not taken into account in the formulas of the Lifshits theory. In [22, 23], the theory of the adsorption component of the disjoining pressure was examined. For interlayer thicknesses considerably greater than the thickness of the adsorption monolayer, the disjoining pressure of an interlayer with thickness  $h$  from a solution with concentration  $c$  is given by the formula

$$\Pi = \frac{\hbar}{8\pi^2 h} \int_0^\infty \frac{(\epsilon_2 - \epsilon_3)}{(\epsilon_2 + \epsilon_3)} \left[ \frac{c}{\epsilon_2} \frac{\partial \epsilon_1}{\partial c} - \frac{(\epsilon_2 - \epsilon_3)}{(\epsilon_2 + \epsilon_3)} \right] d\xi, \quad (8)$$

where  $\hbar$  is the Planck constant;  $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon_3$  are the permittivities as functions of the imaginary frequencies  $i\xi$  of the solution, neighboring phases, and solvent, respectively. The actual adsorption components is  $\Pi_a = \Pi - \Pi_m$ , where  $\Pi_m$  is the value given by the Lifshits theory if dissolved molecules or their nonuniform distribution in the interlayer are neglected.

Let us note that if, following Langmuir, we set the difference  $\Pi - \Pi_m$  equal to the excess osmotic pressure in the symmetry plane, we obtain a value that is eight times the true value. The author has also examined the case in which an interlayer of a binary solution is located between two gas volumes (free film). For such a film to be stable, the solute must lower the permittivity of the solvent quite considerably; this is consistent with the stability of free films of aqueous solutions of butyric acid that had been observed by Scheludko and Exerowa.

In particular, analysis of the molecular and adsorption components of the disjoining pressure [16, 24] made it possible to derive the following conditions for stability of foam films:

$$1 < \varepsilon_1 < \frac{2\varepsilon_2}{1 + \varepsilon_2} < \varepsilon_2, \quad (9)$$

where  $\varepsilon_1$  and  $\varepsilon_2$  are the permittivities of the solution and solvent, respectively. The isotherm for the adsorption component of the disjoining pressure was derived analytically in [23].

Quite recently, an electronic component of the disjoining pressure was detected experimentally in the observation of stable free mercury films surrounded by octane [25]. A theory was developed in which this component is explained by overlapping of those regions of the boundary layers of mercury in which the electron wave functions differ from the values in the bulk. Thus, we are speaking of a quantum nature of an essentially macroscopic pressure. The quantitative theory that had been developed has also provided an explanation for the sharp dependence of the mercury film stability on the surrounding medium, even in the series of homologs of octane.

## BOUNDARY LAYERS OF LIQUIDS AND STRUCTURAL FORCES

Subsequent development of the theory of stability in its application to the case of lyophilic particles demanded first of all an explanation of the relationships involved in the structural component of the disjoining pressure of polar liquids [11a], which is created when structurally altered boundary layers overlap. The problem here is the inadequate state of development of the theory of polar liquids; as a result, no final theory of the structural component of the disjoining pressure has yet been developed.

Therefore, our cycle of works was devoted to experimental methods for studying this component and defining the conditions that influence the appearance of structural forces. The results of these studies were summarized in the article [26].

A review [27] covered the work of the author (together with V. V. Karsaev) on the use of an original blowoff method, with which viscosity could be determined as a function of the distance from a solid substrate, which could be either glass or metal — information that could not be obtained by any other method. The results obtained in these studies showed that nonpolar white mineral oil does not exhibit any changes in viscosity whatever, even at distances of only 10-20 Å from the substrate. Polar compounds or long-chain hydrocarbons exhibit viscosity changes even at much greater distances from the substrate, measured in microns.

Moreover, for a number of polymers, for example Vinipol [poly(vinyl *n*-butyl ether)] and its solutions in turbine oil, in the wedge-shaped film obtained as a result of blowoff, zones of unstable thickness were manifested in the form of "ripples." It was found that these zones corresponded to thicknesses in the region of a few microns. Thicker sections of the wedge remained smooth. On the basis of thermodynamic considerations, such active instability means that, at these thicknesses, the derivative of the disjoining pressure with respect to thickness is positive. Even in itself, the manifestation of disjoining pressure at thicknesses on the order of microns is remarkable, all the more its nonmonotonic dependence on thickness.

Thus, the blowoff method has made it possible not only to study viscosity as an indicator of structural features, but also to study the behavior of the structural component of the disjoining pressure.

Let us add that the relationships between the viscosity and the distance from the substrate that are obtained by the blowoff method reveal the existence of very marked changes in viscosity at certain thicknesses, thus confirming the existence of the boundary phases that had been postulated and described in general terms as far back as 1952 [28].

Further data on the formation of boundary phases were set forth in [29]. A comprehensive review of results from studies of the effect of surface forces on the properties of boundary and thin layers of liquids was given in [30]. An extensive review of experimental evidence for the special anisotropic structure of boundary layers of liquids was presented in the article [31].

Analysis of the special features of the structural component of the disjoining pressure is based on direct measurements of the disjoining pressure of adsorption-wetting films and interlayers between solids, and also on data indicating the structural features of layers of polar liquids adjacent to lyophilic surfaces. For water, these features disappear at a temperature of 70° [11a], simultaneously with the disappearance of the structural component of the disjoining pressure that is generated by these features. Surface lyophilicity may be reinforced or even created as a result of the adsorption of polar molecules. This provides a scientific basis for an important practical method of regulating the structural component of the disjoining pressure, and through it the stability of the corresponding disperse systems of sols, foams, or emulsions.

Of still greater interest is a discovery made by the author together with Popovskii [32] — the existence of boundary phases in layers of nitrobenzene on glass, the layers having a homogeneous anisotropic structure with a boundary that is defined by a sharp transition to the bulk phase. The thickness of these layers decreases linearly with increasing temperature, and the heat of the transition to the bulk phase increases with increasing temperature, having the order of magnitude of phase transitions in the formation of liquid-crystal phases.

In [33], basic conclusions were set forth from a study of liquid-crystal phases of certain polar but not mesogenic liquids: nitrobenzene, aniline, acetophenone, *p*-chlorotoluene, and esters of benzoic acid. The theory that was developed provides an explanation for the homogeneity of the corresponding boundary layers, the sharp transition to the bulk phase at a certain distance from the substrate, the orientation of the molecules, and the decrease of thickness and "degree of ordering" of the boundary phases with increasing temperature. Also, the author studied, together with M. Snitkovskii, certain electrical properties of the boundary layers of a number of liquids (properties related to their special structure), as well as the influence of this structure of the lubricating action in boundary friction.

Research on liquid-crystal boundary phases was continued in cooperation with Altoiz and Nikitenko [33].

In research carried out with M. V. Golovanov on the behavior of elements of blood plasma diluted with a salt solution [35, 36], record-long-range forces of repulsion were discovered — up to  $100\ \mu$  — emanating from the leucocytes. This property was observed mainly for the leucocytes of cancer patients. These leucocytes, repelling the erythrocytes, form an erythrocyte-free "halo" around themselves. These halos are formed in 5-10 min. In the absence of erythrocytes, the leucocytes, over a period of 1 day, form a hexagonal network with a period up to  $100\ \mu$ .\*

The author advanced the hypothesis that these forces of repulsion are the result of coherent electromagnetic vibrations and the waves that they generate, with a wavelength on the order of millimeters. This concept was introduced to the scientific community by Frolich [37]. When the activity of the cells ends, these waves disappear.

## THEORY OF NUCLEATION

Theories of nucleation (new-phase formation) have been made considerably more rigorous by the author's use of the Gibbs grand ensemble [38, 39]. This method also made it possible to construct a theory of the rupture of bilayer membranes such as lipid membranes [40].

An analysis was also made of the probability of nucleational rupture of ultrathin molecular films, including lipid films, as a consequence of local stretching. For a rigorous calculation, an original theory of nucleation was used [38, 39], through which it became possible to calculate the preexponential factor in the expression for the nucleation probability.

For the case of rupture of an ultrathin film, the probability  $\nu$  of its rupture was expressed by the equation [40]

$$\nu = \frac{s\rho_m}{4\pi r_c \eta} \sqrt{gkT} e^{-\pi\Delta^2/gkT}, \quad (10)$$

where  $s$  is the film area;  $\rho$  is the number of molecules in unit area;  $\sigma$  is the surface tension of the film;  $\gamma$  is the linear tension on its boundary with a hole;  $k$  is the Boltzmann constant;  $T$  is the absolute (Kelvin) temperature;  $\eta$  is the two-dimensional viscosity of the film;  $r_c$  is the radius of a critical hole.

In the work of D. Kaschiev and D. Exerowa, it was pointed out that a hole may be formed through the accumulation of vacancies. In the work of the author, together with A. Prokhorov, a general theory was constructed for the rupture of bilayer films as a result of simultaneous mechanical stretching and the diffusion of vacancies. It was shown [41] that in the special case where vacancies are absent, the theory as set forth by the author was obtained; and in the special case of an unstretched film with vacancies, the theory of Kaschiev and Exerowa was obtained, with certain refinements.

In [42], an analysis was made of certain features of coagulation kinetics that were discovered for the first time, as a result of opposing processes of aggregation and deaggregation. Simultaneously, an analogy of coagulation to the kinetics of new-phase formation was discovered experimentally by means of an original flow ultramicroscope, and the analogy was interpreted theoretically. Here the decisive factor is the existence of a distant (secondary) potential well when the particles approach. Its existence was first pointed out in a paper presented at the Faraday Society discussions on the coagulation of colloids in 1940. The combined analysis of experimental data and theory was continued in the papers [16, 24].

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\*According to a private communication from Hachisu, who is a specialist on periodic colloidal structures, such a scale of distances is many times greater than any of the cases known previously.

## THERMOOSMOSIS AND THERMOCRYSTALLIZATION FLOW

The structural and thermodynamic features of boundary layers of liquids provide an explanation for the phenomenon of thermoosmosis – the flow of a liquid through a capillary under the influence of a temperature gradient. In a formula derived by the author [43], the flux  $j$  through a slit capillary with width  $h$  is given by the formula

$$j = \kappa \frac{\text{grad } T}{T}, \quad (11)$$

where

$$\kappa = \int_0^{h/2} \frac{\Delta H(x) x (h-x) dx}{h\eta}, \quad (12)$$

and where  $\Delta H(x)$  is the excess specific enthalpy (in comparison with the bulk value) at a distance  $x$  from the wall;  $\eta$  is the viscosity.

As was observed in [44], with decreasing radius of a cylindrical capillary, the thermoosmotic flux first decreases, then changes sign, and, finally, increases sharply. This may indicate a special two-layer structure of the liquid boundary layer.

For thin, nonfreezing interlayers, a theory was developed for freeze-heaving of ground [45] – a global phenomenon in the northern regions of Siberia and Canada that creates enormous difficulties in the construction of buildings and other facilities and in the use of roads.

The mechanism of this phenomenon comes down to a cross-flow of unfrozen or moderately frosted moisture to the colder sections ("thermocrystallization flow") and to the appearance of disjoining pressure in the water interlayers between the ice phase and the soil particles. A theory based on nonequilibrium thermodynamics shows that the strength of the thermocrystallization flux is proportional to the heat of melting of ice, and this also serves as a source of its strength, with all of the consequences. For comparison, let us point out that, in contrast, the strength of thermoosmotic flux is proportional to the excess enthalpy of the boundary layers, which is several orders of magnitude smaller.

The material presented in this review demonstrates that the development of the theory of colloid and thin-film stability has led to the discovery of many new phenomena and practical applications in chemical technology, construction, soil science, mining, flotation, and ecology.

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