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The Stability of Colloid Systems (Theoretical Aspects)

B.V.Deryagin

After a brief description of the development of ideas concerning the nature of the stability of colloids, the main factors (ionic-electrostatic and molecular forces) whose balance determines the resistance of colloids to aggregation, are examined. An account is given of calculations of the free energy of charged particles in an electrolyte solution. The influence of the dense layer of adsorbed ions on the stability of colloids is discussed. The phase transitions in colloid systems, particularly coacervation and the formation of periodic colloid structures, are considered. The problem of thermodynamically stable colloid systems is analysed in connection with the properties of micellar solutions. A brief description is given of the problem of the stability of liquid layers and of the phenomenon of heterocoagulation.
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I. INTRODUCTION

Colloidal systems or colloids became the object of systematic study in the middle of the XIXth century. At that time they were considered as ordinary solutions of special glue-like substances—hence the origin of the term "colloidal solution". Only when the fundamental differences between colloid systems and glue solutions became understood, the science of colloids was established as an independent discipline. Traditionally it is still referred to as colloid chemistry, because of the earlier view that all the differences between colloidal and normal solutions are determined by the nature of "colloidal substances" and also because studies on such systems have been made mainly by chemists. However, in the course of development of the relevant research, the differences between normal and colloidal solutions were discovered and began to be investigated. These differences are largely physical and sometimes physicochemical. It is not fortuitous that the most important work in the study of colloid systems has been carried out by physicists: Helmholtz, Einstein, de Boer, Langmuir, Gibbs, Bernal, Onsager, Kirkwood, Rayleigh, Perrin, Smoluchowski, Gouy, Chapman, Debye, and others. The traditional term "colloid chemistry" has therefore now become, in essence, obsolete and the term "colloid science" is being increasingly used.

The principal difference between colloid systems and glue solutions is that the kinetic units in the former (colloid particles) consist in the general case of a large fairly indefinite number of molecules, and exhibit to a first approximation the properties of a phase separated from the adjoining phase (dispersion medium) by a very large interface. Hence the enormous role of surface phenomena at the boundary between particles of the disperse phase and the dispersion medium becomes understandable: the formation of an ionic double layer and ion exchange, electrokinetic phenomena, and adsorption. Without the consideration of the role of surface phenomena, the science of colloids would have been completely without theoretical foundation†. A distinction is frequently drawn between colloid and coarsely disperse systems: suspensions and emulsion. However, this difference is extremely arbitrary and depends on the particle size or on the area of interface and is largely qualitative.

All the foregoing considerations make it possible to define colloid science as the physical chemistry of disperse systems or systems with a large interface indissolubly linked to the physical chemistry of surface phenomena. In contrast to the science of solutions, the fundamental problem in this science is that of stability. Its importance is determined by the fact that colloid systems are in the main not in a state of thermodynamic equilibrium and an adequate stability of the colloid system constitutes a condition for its existence as such.

In contrast to solutions, the state of a colloid system can change in two significantly different ways—either by the dissolution of some particles and the growth of others, which are relatively more stable, or by the sticking together but not coalescence of the "primary" particles and the formation of aggregates with or without layers of the dispersion medium between the particle. A condition for equilibrium in a colloid system with respect to processes of the first type, i.e. the condition for the stability (constancy) of the composition of the disperse phase, is minimum free energy of the system relative to the distribution of particles with respect to size—the condition for thermodynamic equilibrium.

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†The role of surface phenomena in colloid science is indicated by the names of the international journals and semiperiodical publications as well as institutes: Journal of Colloid and Interface Science; Advances in Colloid and Interface Science; Institute of Colloid and Interface Science (USA); Surface and Colloid Science (Edited by E. Matijević).

The condition for equilibrium in the system relative to processes of the second type (stability in relation to aggregation) requires the existence of repulsion forces between particles approaching each other, which are capable of interfering with their cohesion under the influence of molecular attraction forces. A general condition for thermodynamic equilibrium may not in fact be fulfilled in this case. A characteristic of stability towards aggregation or of aggregation equilibrium in the system is constancy of the distribution of aggregates with respect to the number of "primary" particles in them. In the simplest case equilibrium can correspond to the absence of aggregates.

In mists and "unprotected" emulsions unhindered cohesion of particles may or may not be accompanied by coalescence. In the former case one should speak of the breakdown of the stability of the composition of the dispersion medium and not of stability with respect to aggregation.

The condition for the thermodynamic equilibrium of particles surrounded by electrical double layers was examined for the first time by March[1]. However, we incorrectly formulated the problem of thermodynamic equilibrium in relation to the changes in the degree of dispersion without the breakdown of monodispersity, i.e. with retention of identical surface curvatures by all the particles. Furthermore, when account is taken of the influence of the difference between the curvatures of the particles on their chemical potential, such a state (at any rate for particles containing one component soluble in the dispersion medium) is labile. On the other hand, it is pointless to consider the possibility or impossibility of a process in which such lability is maintained. This is entirely equivalent to considering from the standpoint of thermodynamics the possibility of the rolling of a sphere along a tightrope. A second error in March's work was failure to understand that the main thermodynamic condition which he considered has a bearing solely on the stability of the composition of the disperse phase and not on stability with respect to aggregation.

When the general condition for thermodynamic equilibrium in relation to changes in the composition of the disperse phase of the system holds, the possibility of the formation of aggregates whose particles are separated from one another by thin layers of the dispersion medium is not ruled out. However, whether this possibility does arise and, if it does, the state of the system (metastable, stable, or labile) are problems which must be solved for each specific case by a more detailed examination.

Thus it is necessary to distinguish two specific forms of stability of colloid systems, which are absent in glue solutions: the stability of the composition of the disperse phase and the stability of the aggregate composition or stability with respect to aggregation. Naturally if aggregation is accompanied by the coalescence of particles, then instability with respect to aggregation entails the instability of the composition of the disperse phase. The existence of two types of stability of colloid systems is one of the manifestations of the fundamental qualitative difference between them and true solutions for which the concept of the stability of the composition of the disperse phase and of stability with respect to aggregation lack significance. At the same time it is possible to consider also a third type of stability, which is common to true solutions and colloids. This is the stability with respect to the separation of the system into two phases or, in the case of colloids, quasi-phases, which differ in the concentrations of the kinetic units—molecules or colloidal particles—and also, possibly, in their distribution‡.

In the present review attention is concentrated on the stability with respect to aggregation, the changes in which are usually faster than the changes in the composition of the disperse phase and are therefore of practical importance. The nature of the stability of the aggregate composition is also important. If the condition of the constancy of the composition of the disperse phase does not hold but varies extremely slowly, the constancy of the composition of the aggregate may be referred to as partial equilibrium, since only some of the conditions for equilibrium are then maintained. Aggregation equilibrium can in this case be only temporary and will inevitably change as the composition of the disperse phase changes in direct functional relation to the latter. An exception is provided by a system where there are no aggregates owing to the operation of strong repulsion forces. Equilibrium in such systems can be maintained also during the variation of the disperse phase composition, at least until the size of the particles approaches molecular dimensions, which makes it easier for them to overcome the repulsion forces arising from other particles. At any rate aggregation stability can be considered independently of the possible instability of the disperse phase composition, ignoring the changes in the latter, provided that they are sufficiently slow.

With this stipulation, the aggregation stability can be of two kinds. Firstly it can be due to the slowness of the coagulation process (or the slowness of the decomposition of aggregates) and its nature is then purely kinetic. The aggregation quasi-equilibrium can be referred to in this instance as the relaxation of frozen or hindered non-equilibrium states (but not metastable equilibria). Secondly, a rigorous constancy of the aggregate composition can obtain when aggregation processes are balanced by the opposed deaggregation processes. As will be shown below (Section V), equilibria of this kind can break down also in consequence of the formation of larger aggregates; in this case one can speak of a metastable equilibrium.

Critical emulsions and micellar solutions (see Section VIII), which are colloid systems in complete thermodynamic equilibrium where the conditions of a constant disperse phase composition and the absence of aggregates are maintained, must be treated as a special case.

Equilibrium periodic colloid structures, formed, for example, by the tobacco mosaic virus or by spherical latex particles, merit a special discussion. This will be done later (see Section VII), where the problem of equilibria in colloid systems of the type of phase equilibria in the usual solutions is considered.

The foregoing considerations are based on the most general postulates and are used merely to throw light on the problem of the concept of stability of colloid systems. It is, however, impossible to reach fairly concrete conclusions about the nature of stability and its characteristics, solely on the basis of general considerations of this kind; concrete conclusions make it necessary to specify in greater detail the physical formulation of the problem, perhaps even at the expense of abandoning the generality of the conclusions. Colloid science entered this fruitful

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‡In considering the different types of stability of colloid systems, we are not concerned with kinetic or sedimentation stability, which is manifested by the presence of a sedimentation-diffusion equilibrium in the system.

path about forty years ago, which led to the development and general recognition and application of the physical theory of the stability of lyophobic colloids.

II. IONIC-ELECTROSTATIC AND MOLECULAR FORCES OF THE INTERACTION BETWEEN COLLOID PARTICLES

We shall now describe briefly the path traversed by colloid science and shall consider the factors which are either little known or have been incorrectly described in many monographs and articles to the detriment of the priority due to Soviet scientists§.

The sensitivity of many colloid systems, for example, metal sols, to electrolytes was noted a long time ago[2-5]. The concentrations of electrolytes for coagulating such systems are low, and decrease sharply with the increasing charge of the counterion[6-8]. Colloid systems of this class have been called lyophobic or electrocratic. Colloid systems which coagulate only at high electrolyte concentrations (of the order of several units on the molar scale), which depend little on the type of counterions, have been assigned to another class. A considerable proportion of such systems, referred to as lyophobic colloids, proved subsequently to be true solutions of polymers, whose particles (macromolecules) do not form an interace with the solvent. They ceased to be classified as colloid systems, because a fundamental feature of the latter is the existence of an interface. However, there remained many colloid systems, which, while not true solutions, are nevertheless fairly stable towards electrolytes. It must be emphasised that the same colloid may lose or acquire sensitivity to electrolytes depending on the state of the surface of its particles, which is determined by the absorption of surface-active molecules or ions[9,10]. It is therefore perhaps more correct to speak of the lyophobic or lyophilic state of colloid systems rather than lyophobic and lyophilic colloid systems. There also exist colloid systems, for example polysilicic acid hydrosols, which do not contain surface-active molecules or ions, and are at the same time relatively insensitive to electrolytes.

It was noted long ago that the stability of lyophobic colloids is as a rule correlated with the electrophoretic mobility of the particles, indicating their charge[11-15]. In considering the repulsion forces between charged particles as the cause of their aggregation stability, some workers attempted, following Freundlich[16], to explain the action of electrolytes by a decrease of the charge under the influence of the adsorption of ions of opposite sign. Together with this idea, Kruyt introduced the hypothesis of solvation as the second stability factor[17,18], apart from the charge, which explains the properties of lyophilic colloids. All these ideas, which remained largely qualitative, were completely inadequate for the creation of a full fledged theory of the stability of colloids with clearly formulated physical principles.

A breakthrough for this problem occurred when, firstly, a narrower problem was formulated: the elucidation of the mechanism of the stability and coagulation of lyophobic systems and, secondly, when the balance between molecular attraction and electrostatic repulsion forces between particles was adopted as a basis. In a qualitative form these forces, considered as responsible for the stability of lyophobic colloids, were examined by Kallmann and Willstatter[19]. The attempt to proceed to a quantitative allowance for such forces is due to Hamaker[21,22]. The latter (and independently de Boer[20]) summarised the London expressions for the energy of the pair interaction between all the molecules of two plates or spheres, as well as the dispersion medium, and found an expression for the energy of the molecular interaction between colloid systems as a function of their radii and the thickness of the layer separating them. However, Hamaker's calculations did not lead to the establishment of a theory of stability, because his empirical formula[23-25] for the energy of electrostatic repulsion was not subsequently confirmed theoretically.

A theoretically well founded method for the calculation of the force and energy of the interaction between colloid species, which depends on the overlap of their diffuse ionic atmospheres, is due to the author of the present review[26-29]. He based the calculation on the expression for the ponderomotive pressure P applied to a unit area of the surface of the colloid particle:

$$P = -\frac{\varepsilon}{8\pi} E^2 + p = -\frac{\varepsilon}{8\pi} |\operatorname{grad}\varphi|^2 + p, \qquad (1)$$

where ϵ is the dielectric constant, φ the electric potential, E the projection of the electric field strength vector at the surface of the particle on to the normal to the latter, and p the hydrostatic pressure at the surface in excess of the hydrostatic pressure in the region where there is no electric field¶. The pressure p at any place satisfies the equation for hydrostatic equilibrium taking into account the electric force acting on the space charge (allowance for the polarisation of the medium causes little change in the final results):

$$\operatorname{grad} p + \rho \operatorname{grad}\varphi = 0. \qquad (2)$$

According to the Boltzmann equation, the concentration of ions and hence the space charge density ρ are a function of the local potential φ:

$$\rho = \rho(\varphi). \qquad (3)$$

Therefore it follows from Eqn. (2) that

$$p = A - \int_0^{\varphi} \rho \, d\varphi, \qquad (4)$$

where the integration constant A is independent of the coordinates and is zero according to the definition of p. When a potential $\varphi = \varphi_0$ has been specified on the surface of the particles, it is the same at all sections of the surface, both internal and external. The force balancing the hydrostatic pressure on each particle is therefore zero regardless of the shape of the latter and the force balancing the ponderomotive forces is determined by the summation of the vector-Maxwell tensions $(\epsilon/8\pi)E^2 = f'$ applied to different sections of the surface. The Maxwell tension f' must be supplemented by the electrostriction number f'':

$$f'' = \frac{1}{8\pi} E^2 \frac{\partial \varepsilon}{\partial \rho} \rho. \qquad (5)$$

However, it is known from electrostatics[32] that this addition does not alter the total ponderomotive force acting on bodies immersed in a liquid or gaseous medium. The explanation is that the electrostriction terms should be

§ For example, in the well known book[85] edited by Kruyt.

¶ Langmuir[30] called this excess pressure the excess osmotic pressure. Verwey and Overbeek[31] point out that it is more rational to call it the excess hydrostatic pressure, with which one must agree.

introduced at the same time into Eqn. (2) and should cause a change in the electrostatic pressure p, acting in the vicinity of the surface, such that it compensates exactly the Maxwell tension. This demonstrates the gross error of Babchin's work [33], where an attempt was made to alter the principles of the theory of the stability of lyophobic colloids by introducing electrostriction terms. This work has been criticised by the present author [34,35] and by Levin [36].

If the surface charge densities have not been specified, the values of E at various sections of the surface of the particles must be determined (for a symmetrical electrolyte) by integrating the Poisson–Boltzmann equation:

$$\frac{4\pi}{\varepsilon}\rho = \Delta\varphi = a \operatorname{sh} \alpha\varphi, \tag{6}$$

where

$$a = \frac{8\pi}{\varepsilon} zec, \tag{7}$$

$$\alpha = \frac{ze}{kT}, \tag{8}$$

Here e is the electronic charge, c the electrolyte concentration (in equiv. cm^{-3}) outside the limits of the ionic double layers, k the Boltzmann constant, T the absolute temperature, z the ionic charge, and Δ the Laplace operator, indicating that the sum of the second derivatives of φ with respect to coordinates is considered:

$$\Delta\varphi = \frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + \frac{\partial^2\varphi}{\partial z^2}.$$

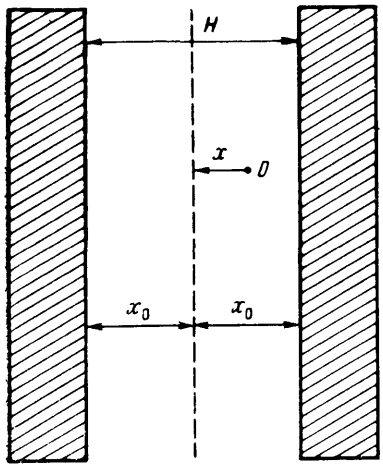


Figure 1. The distribution of potential in the electrolyte layer.

In this general formulation the calculation of the ionic-electrostatic interaction forces between the particles presents enormous mathematical difficulties even for two identical spherical particles.

The present author [26–29] examined initially the simpler case of the interaction of two parallel plates, whose dimensions are so much greater than the gap H separating them that the edge effects may be neglected (Fig. 1). The treatment was restricted initially to the case of low potentials satisfying the condition

$$\frac{ze\varphi}{kT} \ll 1. \tag{9}$$

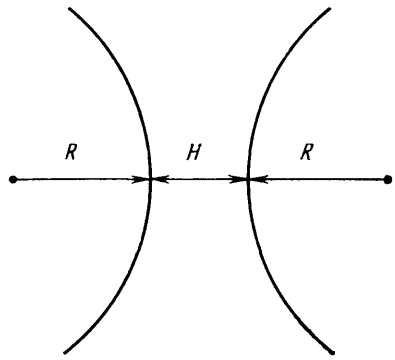


Figure 2. The interaction of two equal spheres.

In this case Eqn. (6) can be written approximately in the form

$$\Delta\varphi = \varkappa^2\varphi, \tag{10}$$

where κ is the reciprocal of the effective thickness d of ionic atmospheres and is given by

$$\varkappa = \frac{1}{d} = \sqrt{a\alpha} = \sqrt{\frac{8\pi}{\varepsilon}\frac{e^2z^2c}{kT}}. \tag{11}$$

In the general case of an arbitrary ionic composition cz^2 must be replaced by the ionic strength $\frac{1}{2}\Sigma z_i^2 c_i$, where c_i is the concentration (in gram-ion cm^{-3}) of the ions having the charge z_i. In the integration of Eqn. (10) it was assumed that a constant potential φ is maintained on the surfaces of the plates regardless of the thickness of the electrolyte layer H:

$$\varphi = \varphi_0, \tag{12}$$

The distribution of the potential between the plates has the following form:

$$\varphi = \varphi_0 \frac{\cosh \varkappa x}{\cosh \varkappa x_0}, \tag{13}$$

where x is the distance from the symmetry plane within the intervening layer to the zero point, where the potential has the required value φ, and $x_0 = H/2$.

Outside the plate, the distribution of the potential is

$$\varphi = \varphi_0 e^{-\varkappa x'}, \tag{14}$$

where x' is the distance from the outer surfaces of the plates. It follows from Eqns. (1), (13), and (14) that the Maxwell tension acting on sections of the inner surfaces of the plates is

$$f_t = \frac{\varepsilon}{8\pi}\varkappa^2\varphi_0^2 \tanh^2 \varkappa x_0, \tag{15}$$

while that on the sections of the outer surface is

$$f_0 = \frac{\varepsilon}{8\pi}\varkappa^2\varphi_0^2. \quad (16)$$

The difference between these tensions is directed to the outside and is equal, according to the foregoing considerations, to the repulsion force N between the plates per unit area:

$$f_0 - f_l = N = \frac{\varepsilon}{8\pi}\varkappa^2\varphi_0^2 \cdot \frac{1}{\cosh^2 \varkappa x_0}. \quad (17)$$

Integration of both parts of Eqn. (17) with respect to x_0 can yield the energy of the interaction between the plates per unit area:

$$U_e = \frac{\varepsilon}{4\pi}\varkappa\varphi_0^2\left[1 - \tanh\left(\varkappa\frac{H}{2}\right)\right]. \quad (18)$$

When applied to the one-dimensional case under consideration, Eqn. (2) becomes

$$\frac{dp}{dx} + \rho\frac{d\varphi}{dx} = 0. \quad (19)$$

Having replaced ρ by $-(\epsilon/4\pi)(d^2\varphi/dx^2)$ and having integrated Eqn. (19), we obtain

$$p = \frac{\varepsilon}{8\pi}E^2 + C, \quad (20)$$

where C is the integration constant.

According to Eqn. (1), the repulsion pressure can be calculated, even if the potential of the surface of the plate changes when the two plates approach one another, by considering the differences between the constants C corresponding to the region between the plates and to the region outside, where $C = 0$. It is therefore sufficient to find the difference between the values of C for the region between the two plates. It is simplest to consider a point in the symmetry plane between the plates where $E = 0$. Then

$$N \equiv C = p_m = -\int_0^{\varphi_m}\rho\,d\varphi, \quad (21)$$

where φ_m is the potential in the symmetry plane.

Thus the force of repulsion between the plates (the "wedging" pressure of the layer between them) is equal to the excess hydrostatic pressure in the symmetry plane. On substituting in Eqn. (21) the expression found with the aid of the Poisson–Boltzmann equation [Eqn. (6)] instead of $\rho(\varphi)$, we find that p_m is equal to the excess osmotic pressure of the ions if it is assumed that the van't Hoff law applies (without the Debye–Hückel correction). In the analogous case of wetting films this led Langmuir to identify N with the excess osmotic pressure of ions at points where $E = 0$. However, as stated before, this is in essence incorrect, because formula (21) is essentially equal to the excess osmotic pressure only for extremely low electrolyte concentrations.

However, for identically charged surfaces, the wedging pressure can be expressed in terms of the potential φ_m, which has many mathematical advantages. The extension of Eqn. (21) to the interaction of spherical particles with the same absolute charges, but different signs of the latter, will be described below.

The transition from the interaction of planar particles to the interaction of spherical particles has been achieved[26–29] with the aid of the transformation proposed earlier by the present author[37]:

$$K = GU(H), \quad (22)$$

where K is an interaction force of any kind (belonging to the class of conservative forces) between convex surfaces, whose radii of curvature are much greater than the effective radii of action of the force (in the present instance twice the thicknesses of the ionic double layers), G a geometrical factor which depends on the radii of curvature of the normal sections of the surfaces near the region of the mutual approach of the particles, and U the energy of the interaction of planar surfaces of the same kind, separated by a plane-parallel layer of the same medium having a thickness H equal to the shortest distance between the convex surfaces under consideration (Fig. 2).

In the simplest case of two identical spheres with a radius R we have

$$G = \pi R. \quad (23)$$

Here it follows from Eqns. (15), (16), and (18) that

$$K = \frac{\varepsilon}{4}R\varkappa\varphi_0^2\left[1 - \tanh\left(\varkappa\frac{H}{2}\right)\right]. \quad (24)$$

Hence integrations with respect to H yields an expression for the energy of the interaction of spherical particles:

$$U(H) = \int_H^\infty K\,dH = \frac{\varepsilon}{2}R\varphi_0^2\ln(1 + e^{-\varkappa H}). \quad (25)$$

In order to estimate the extent to which the calculated repulsion is capable of stabilising the colloid, the present author used the formula for the rate of slow coagulation derived by Fuchs[38] in order to take into account the influence of charges on the rate of coagulation of aerosols:

$$\nu = \frac{4\pi Dc^2}{\int_0^\infty \left[e^{\frac{U(H)}{kT}}/(2R + H)^2\right]dH}, \quad (26)$$

where ν is the number of aggregation steps per unit volume per unit time, D the coefficient of Brownian diffusion of the colloid particles, and c their numerical concentration. In the derivation of Eqn. (26) it was postulated that the mutual approach up to contact leads to irreversible aggregation, and molecular long-range forces were neglected. Hence the stabilisation coefficient introduced by the present author is described by the expression

$$J = \frac{\nu_0}{\nu} = \int_0^\infty e^{\frac{U(H)}{kT}}\frac{2R}{(2R + H)^2}\,dH, \quad (27)$$

where ν_0 is the value of ν for $U(H) = 0$, i.e. in the absence of repulsion forces. Later J was called the retardation coefficient.

Eqn. (25) was supplemented[39,40] by a term defining the energy of attraction of the particles via van der Waals forces and assumed the following form:

$$U(H) = \frac{\varepsilon R\varphi_0^2}{2}\ln(1 + e^{-\varkappa H}) - \frac{AR}{12H}, \quad (28)$$

where A is the Hamaker constant. Analysis of Eqn. (28) showed[39,40] that, for values of the dimensionless parameter

$$m = \frac{1}{6}\frac{A\varkappa}{\varepsilon\varphi_0^2} < 0.3 \quad (29)$$

the function $U(H)$ has a shallow minimum and to the left of it a maximum whose height increases on further decrease of the parameter m (Fig. 3).

On substituting Eqn. (28) in Eqn. (27), it can be shown that the coefficient J is large, provided that

$$\frac{\varepsilon\varphi_0^2}{A\varkappa} > 1. \quad (30)$$

This criterion was introduced for $R \gg d$ and for low electrolyte concentrations where Eqns. (6) and (10) are applicable, subject to the condition that the dimensionless potential of the surface of the particles, corresponding to the coagulation threshold, is fairly small, i.e. that Eqn. (9) holds.

Inequality (30) is a modification and a refinement of the empirical rule of Eilers and Korff[41,42]. It agrees well with Powis's work[43], where observations on stability were accompanied by measurements of the electrokinetic potential ζ.

The substitution of the electrokinetic potential ζ instead of φ_0 in Eqn. (30) is permissible to a first approximation at low electrolyte concentrations. Inequality (30) in a modified form[44,45] proved to be applicable also to the determination of the limits of floatability of natural hydrophobic minerals[46-48].

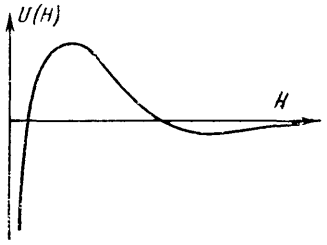


Figure 3. Dependence of the interaction energy between two particles U on the distance H.

An inconvenient aspect of the practical application of inequality (30) is that it includes, apart from the concentration (which determines the values of κ), a second unknown φ_0, which is difficult to measure accurately.

The present author[26-29] also considered another limiting case of the stability of lyophobic colloids corresponding to the condition

$$R \ll d, \tag{31}$$

which obtains either for highly disperse systems or at a very low ionic strength. If the van der Waals interaction is taken into account, then, instead of inequality (30), one must formulate the stability criterion [the condition for the maximum on the $U(H)$ curve] in the following form:

$$\frac{\varepsilon R \varphi_0^2}{A} > 1. \tag{32}$$

In order to ensure that the $U(H)$ maximum is much larger than the energy of the Brownian motion, it is necessary that an additional condition be fulfilled:

$$\frac{\varepsilon R \varphi_0^2}{kT} > 20, \tag{33}$$

which is infringed sooner for low values of A than condition (32).

Either condition [(32) and (33)] should be inevitably infringed for low values of K, i.e. for highly disperse systems, as observed in practice. Barriers preventing both the aggregation and deaggregation of particles are gradually lowered on passing from colloidally disperse systems to true solutions in which they are of the order of magnitude of the energy of Brownian motion or less.

III. THE FREE ENERGY OF CHARGED PARTICLES IN AN ELECTROLYTE SOLUTION

The first studies by the author of this review on the theory of stability were restricted to condition (9), i.e. to the condition where the potential φ_0 is small. The removal of this limitation and replacement of Eqn. (10) by the unsimplified Eqn. (6) was associated merely with computational conditions and was the subject of further studies[49-53]. However, the determination of the correct physical principles for calculations of the interaction between particles when their ionic double layers overlap and rigorous allowance for the van der Waals forces proved to be by no means trivial tasks, as shown by the errors in the 1939 publications by Levine[54-57] and Corkill and Rosenhead[58].

These workers adopted as their next task the calculation of the free energy of colloid particles. Knowing the dependence of the free energy on the distance between the particles, the interaction forces can also be found with some approximation by evaluating the derivative of the free energy with respect to distance. Many followers of these investigators concentrated initially on the calculation of the free energy of the system of charged particles in electrolyte solutions. In order to justify the advantages of this method of calculation on the interaction between colloid particles, Verwey and Overbeek wrote[59] "Serious difficulties arise in the subsequent integration (of the repulsive force) with respect to distance even for planar double layers. Indeed the force in the latter case is not a simple function of distance between the plates and it must therefore be integrated by numerical or graphical methods. In view of these difficulties, we investigated another simpler procedure: the determination of the free energy.... "

One cannot agree with these views, in the first place because the integration of the interaction force can be carried out analytically in terms of very general postulates, in particular when the potential is independent of the distance between the surfaces and when the density of the surface charge of the particles is independent of this distance[60-62]. If it were impossible to integrate analytically the expression for the force, it would also be impossible to obtain this expression in terms of the derivative of the free energy. The fundamental advantages of the "force method" are as follows:

1. The expression for the interaction force can be obtained very simply and rigorously from general and rigorous postulates of electrostatics and hydrostatics, using the familiar expression for the ponderomotive forces in an electric field.
2. The expression is independent of the type of variation of the potential for the surface charge with the distance between the particles and is therefore more general and fundamental.
3. It is easier to introduce corrections into this expression, taking into account the influence of dielectric saturation, the dense ionic layer, the mirror forces and the discrete nature of the ions, and the penetration of electric field into the bulk of the particles.

The history of the calculations of the free energy of the double layers surrounding particles showed that the establishment of the physical principles of these calculations involved considerable difficulties of both fundamental and mathematical kinds, and was fraught with many errors and obscurities. Apart from this, the expression for the free energy, in contrast to the expression for the interaction force, depends on the mechanism of the charging of

the surface particles and is of a different type, for example, in the two limiting cases where either the potential of the particles or the density of the surface charge is independent of the thickness of the intervening layer. It is particularly difficult to calculate the free energy in the case where the surface becomes non-isopotential as the particles approach one another, and the electric field penetrates into the bulk of the colloid particles.

It is therefore superfluous to calculate the free energy of the system in the theory of the interaction of colloid particles and the theory of the stability of colloids based on it, and it is incomparably simpler to employ directly the repulsion forces between particles.

However, the free energy of particles or electrodes immersed in an electrolyte solution is of independent interest. The history of the development of its calculation is extremely instructive and merits a critical consideration.

As stated above, the papers by Levine[54-57] and Corkill and Rosenhead[58] contain an incorrect expression for the free energy of ionic double layers and hence for the energy of the interaction between the particles when their ionic atmosphere overlap. It follows from the formulae derived that identically charged particles should attract one another over long distances, i.e. a qualitatively incorrect result was obtained.

The present paper[63,64] (1940) discovered the root cause of the error and indicated two correct methods for the determination of the free energy of charged particles in an electrolyte solution leading to the same expressions for the interaction forces as those found in his earlier studies[26,27].

The first, purely thermodynamic method is based on the expression for the differential of the free energy of the system of charged spheres immersed in an electrolyte solution. For simplicity, we shall assume that the surface of each sphere is isopotential and that each carries a charge e_i, which does not change in consequence of the ideal polarisability of the surface. Subsequently it will be shown that the combination of the requirements for an isopotential surface and the constancy of the overall charge can only apply approximately†. In a more rigorous treatment it is assumed that a constant potential has been specified on the surface of each particle and that the charge can vary when the ionic atmospheres overlap as the particles approach one another. This treatment corresponds to a different limiting case—the case of ideal non-polarisability of the surfaces of the particles, and obtains approximately if the potential is determined by the adsorbed ions for an extremely high specific energy of adsorption. Thus we can formulate an expression for the free energy of the system:

$$\mathrm{d}\Phi = \sum \varphi_i \mathrm{d}e_i - \sum (X_i \mathrm{d}x_i + Y_i \mathrm{d}y_i + Z_i \mathrm{d}z_i), \qquad (34)$$

where φ_i and e_i are respectively the potential and the charge of the ith spherical particle, x_i, y_i, and z_i are its coordinates, and X_i, Y_i, and Z_i are the components of the external forces acting on it. The charges and coordinates of the particles, determining the state of the system when it is in equilibrium, constitute a complete set of its generalised coordinates provided that the surface of each particle is isopotential and non-polarisable.

Terms corresponding to the charges of the ionic atmospheres should not be introduced into Eqn. (34) as was done by Levine, because the coordinates of the ions forming the ionic atmospheres are dependent quantities, in contrast to the coordinates of the particles in the present author's approach, and are established as a result of thermal equilibrium. By integrating Eqn. (34) for fixed positions of the particles, we obtain

$$\Phi = \Phi_0 + \sum \int_0^{e_i} \varphi_i \mathrm{d}e_i, \qquad (35)$$

where Φ_0 is the free energy corresponding to the state of the system with uncharged and non-interacting particles and therefore independent of the coordinates. Consequently the part of the free energy associated with the interaction forces is

$$F_e = \sum \int_0^{e_i} \varphi_i \mathrm{d}e_i. \qquad (36)$$

The derivatives of F_e with respect to the distances between the particles for e_i = const. give rise to forces of interaction between them and the work performed in the mutual approach of the particles from infinity is given by the following expression according to Eqn. (36):

$$A = F_e - F_\infty = \sum \int_0^{e_i} (\varphi_i - \varphi_\infty) \mathrm{d}e_i. \qquad (37)$$

For low potentials, when φ_i and e_i are proportional to one another, we obtain instead of Eqn. (36)

$$F_e = \frac{1}{2} \sum \varphi_i e_i. \qquad (38)$$

The free energy F_e can be expressed in terms of the electric fields in the ionic atmospheres. On differentiating Eqn. (36) for constant values of φ_i and ϵ and expressing $\mathrm{d}e_i$ in terms of the value of $\partial\varphi/\partial n$ at the surface‡, we obtain

$$\mathrm{d}F_e = \frac{\varepsilon}{4\pi} \int \varphi \, \mathrm{d}\left(\frac{\partial\varphi}{\partial n}\right) \mathrm{d}S, \qquad (39)$$

where n is the coordinate along the normal to the surface of the ith particle, and $\mathrm{d}S$ is an element of the surface; the integration is extended to the surface of all the particles.

Next, on transforming this expression with the aid of Green's theorem and Poisson's equation, we obtain

$$\mathrm{d}F_e = \frac{\varepsilon}{4\pi} \int \left[\frac{\partial\varphi}{\partial x} \mathrm{d}\left(\frac{\partial\varphi}{\partial x}\right) + \frac{\partial\varphi}{\partial y} \mathrm{d}\left(\frac{d\varphi}{\partial y}\right) + \frac{\partial\varphi}{\partial z} \mathrm{d}\left(\frac{\partial\varphi}{\partial z}\right)\right] \mathrm{d}n - \int \varphi \, \mathrm{d}\rho \, \mathrm{d}v; \qquad (40)$$

the integration is carried out with respect to the entire volume of the electrolyte (where φ or $\mathrm{grad}\,\varphi$ are non-zero). Integration of Eqn. (40) yields

$$F_e = \frac{\varepsilon}{8\pi} \int |\mathrm{grad}\,\varphi|^2 \mathrm{d}v - \int_0^{\rho} \int \varphi \, \mathrm{d}\rho \, \mathrm{d}v. \qquad (41)$$

The integral $\int_0^{\rho} \varphi \mathrm{d}\rho$ in the second term on the right-hand side of Eqn. (41) can be readily evaluated using the dependence of ρ on φ expressed by the Poisson–Boltzmann equation [Eqn. (6)]. When simplified Eqn. (10), used for low potential, is employed, Eqn. (41) becomes

$$F_e = \frac{\varepsilon}{8\pi} \int |\mathrm{grad}\,\varphi|^2 \mathrm{d}v + \kappa^2 \int \varphi^2 \mathrm{d}v. \qquad (42)$$

†Incidentally the results depend also on where the surface separating the surface charge from the diffuse ionic atmosphere is drawn.

‡It is assumed that there are no fields within the particles, for example, by virtue of the isopotential nature of the surfaces.

The second term, introduced by the present author[63], is absent from Levine's equation[54,55], which explains why Levine obtained an incorrect expression for the interaction forces. It was also shown[63] that the free energy of the charged particles satisfies the Gibbs–Helmholtz equation:

$$F_e - T\frac{\partial F_e}{\partial T} = U_e = \left(\varepsilon + T\frac{\partial \varepsilon}{\partial T}\right)\frac{\int |\operatorname{grad}\varphi|^2}{8\pi}\mathrm{d}v, \tag{43}$$

where U_e is the total internal energy—the increment in the total electrochemical energy which depends on the electric field. We shall now describe the derivation of Eqn.(43) for the simplest case of conducting particles whose charges have been specified. Denoting the temperature-dependent variation of the quantities by δ and applying Poisson's equation and Green's theorem, we obtain from Eqn. (41)

$$\delta F_e = \frac{\delta\varepsilon}{8\pi}\int |\operatorname{grad}\varphi|^2 \mathrm{d}v - \frac{1}{4\pi}\int \varphi\varepsilon\delta\Delta\varphi\,\mathrm{d}v - \tag{44}$$
$$-\int \varphi\delta\rho\,\mathrm{d}v - \int \mathrm{d}v\int_0^{\rho}\delta\varphi_\rho\,\mathrm{d}\rho\,\frac{1}{4\pi}\varphi\int\varepsilon\delta\left(\frac{\partial\varphi}{\partial n}\right)\mathrm{d}S$$

where $\partial\varphi/\partial n$ is the derivative with respect to the external normal to the surface of the particle and $\mathrm{d}S$ is an element of its surface. In the penultimate term on the right-hand side the integrand $\delta\varphi_\rho$, where φ_ρ is a function of ρ and T, corresponds to a constant value of ρ. We obtain from the Poisson equation

$$\frac{1}{4\pi}\delta(\varepsilon\Delta\varphi) + \delta\rho = 0. \tag{45}$$

The condition of a constant total charge on each particle yields

$$\int\delta\left(\varepsilon\frac{\partial\varphi}{\partial n}\right)\mathrm{d}S = 0. \tag{46}$$

With the aid of Eqns. (45) and (46), the expression for δF_e can be put in the following form:

$$\delta F_e = \frac{\delta\varepsilon}{8\pi}\int |\operatorname{grad}\varphi|^2\mathrm{d}v + \frac{\delta\varepsilon}{4\pi}\int\varphi\Delta\varphi\,\mathrm{d}v - \int\mathrm{d}v\int\delta\varphi_\rho\,\mathrm{d}\rho + \frac{\delta\varepsilon}{4\pi}\int\varphi\frac{\partial\varphi}{\partial n}\mathrm{d}S.$$

Application of the Green's theorem yields

$$\delta F_e = -\frac{\delta\varepsilon}{8\pi}\int |\operatorname{grad}\varphi|^2\mathrm{d}v - \int\mathrm{d}v\int\delta\varphi_\rho\,\mathrm{d}\rho; \tag{47}$$

whence

$$\frac{\mathrm{d}F_e}{\mathrm{d}T} = -\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}\cdot\frac{1}{8\pi}\int|\operatorname{grad}\varphi|^2\mathrm{d}v - \int\mathrm{d}v\int\frac{\mathrm{d}\varphi_\rho}{\mathrm{d}T}\mathrm{d}\rho. \tag{48}$$

The Boltzmann equation relates ρ and φ by an expression of the type

$$\rho = \omega\left(\frac{\varphi}{T}\right). \tag{49}$$

where ω is a function of φ/T. Consequently

$$\varphi = T\omega^{-1}(\rho), \tag{49'}$$

whence

$$\varphi - T\frac{\mathrm{d}\varphi_\rho}{\mathrm{d}T} = 0. \tag{49''}$$

Taking into account Eqn. (49), we obtain Eqn. (43) from Eqns. (41) and (48).

We shall now show that F_e, as given by Eqn. (41), is also obtained by an artificial procedure based on the consideration of an imaginary ion charging process and applied by Debye to the calculation of the electrical component of the free energy of strong electrolytes. The correct§ application of the Debye method for particles surrounded by ionic atmospheres has been described[63,64]. An analogous derivation (with certain differences) was described by Casimir[65]. The Debye method involves the consideration of the work of an imaginary process in which all the ions are charged simultaneously and at each instant the charges of the ions and of the particles are equal to the real charges multiplied by a parameter λ, which varies in the charging process from 0 to 1, but is independent of the coordinates of the given ion. As a result, the charge densities of the ionic atmosphere should vary in proportion to this parameter.

It is easy to show that, in calculations on the work of the charging process, which depends on the charges of the particles, it is sufficient to take into account only the macroscopic field around the charges (i.e. the average force potential), neglecting the microfields of the atmospheres around the individual ions, which are considered in the Debye theory of strong electrolytes. The elemental work $\mathrm{d}A$ of the charging process, corresponding to the increment $\mathrm{d}\lambda$ in the parameter λ, is then given by

$$\mathrm{d}A = \sum\varphi_i e_i\,\mathrm{d}\lambda + \int\varphi_\lambda\rho_\lambda\frac{\mathrm{d}\lambda}{\lambda}\mathrm{d}v, \tag{50}$$

where e_i are the charges of the particles; the subscript λ shows that the corresponding quantities refer to the instant of charging, corresponding to the given value of the parameter λ. If the surfaces of the particles are not isopotential, e_i denotes the charges of elementary sections of their surfaces, and the summation sign Σ should be replaced by the integration sign with respect to the surfaces of all the particles. The charges of the particles play a role analogous to the charges of the ions, i.e. the surfaces of the particles behave during the charging process as ideally polarisable electrodes and their charges cannot vary as a result of adsorption.

One can therefore write

$$e_i\mathrm{d}\lambda = e_{i\lambda}\frac{\mathrm{d}\lambda}{\lambda} = \mathrm{d}\,e_{i\lambda}. \tag{51}$$

On the other hand, one cannot put

$$\rho_\lambda\cdot\frac{\mathrm{d}\lambda}{\lambda} = \mathrm{d}\rho_\lambda \tag{52}$$

as in Levine's work[54-56], since the increment in the charge density in the ionic atmosphere with increasing λ takes place not only in consequence of the increase by $\mathrm{d}\lambda/\lambda$ of the charges of the ions forming part of the ionic atmosphere at a given instant, but also in consequence of a redistribution of the ions between the atmosphere and the bulk of the solution. This redistribution takes place with increase of λ owing to the change in the constants a and α which depend on the ionic charge and relate in accordance with the Boltzmann equation the concentration of the ions in the double layer and the potential φ.

We shall now prove the relation

$$\mathrm{d}A = \mathrm{d}F_{e\lambda}, \tag{53}$$

where $F_{e\lambda}$ is the value of F_e in a hypothetical fictitious case, where the charges are reduced by a factor λ. In calculating $\mathrm{d}F_{e\lambda}$ one must bear in mind that the relation

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§An incorrect use of the Debye method in this case[54-56] led to a value of F_e different from that of the present author and agreeing with the value obtained when only the first term is retained on the right-hand side of Eqn.(41).

$\varphi(\rho)$ is also modified by virtue of the change in the constants a and α, which depend on λ.

We obtain from Eqn. (40) [the derivation is the same as that of Eqn. (44) but it is now assumed that $d\epsilon = 0$]:

$$dF_{e\lambda} = -\frac{\varepsilon}{4\pi}\int \varphi_\lambda\, d\,\Delta\varphi_\lambda\, dv - \int \varphi_\lambda\, d\rho_\lambda\, dv - \\ -\int dv \int_0^{\rho_\lambda} d\varphi_\lambda\, d\rho_\lambda - \frac{\varepsilon}{4\pi}\int \varphi_\lambda\, d\left(\frac{\partial\varphi_\lambda}{\partial n}\right) dS, \quad (54)$$

or, taking into account the Poisson and Gauss equations

$$dF_{e\lambda} = -\int dv \int_0^{\rho_\lambda} d\varphi_\lambda\, d\rho_\lambda + \sum_i \varphi_{i\lambda}\, de_{i\lambda}. \quad (55)$$

Taking into account the identity

$$\left(\frac{\partial\varphi_\lambda}{\partial\lambda}\right)_{\rho_\lambda} = -\left(\frac{\partial\varphi_\lambda}{\partial\rho}\right)_\lambda \cdot \left(\frac{\partial\rho_\lambda}{\partial\lambda}\right)_{\varphi_\lambda}, \quad (56)$$

we obtain instead of Eqn. (55)

$$dF_{e\lambda} = \sum_i \varphi_{i\lambda}\, de_{i\lambda} + \int dv \int_0^{\varphi_\lambda} d\lambda \left(\frac{d\rho_\lambda}{d\lambda}\right)_{\varphi_\lambda} d\varphi_\lambda. \quad (57)$$

According to Eqn. (6), ρ depends on the ionic charge z and hence also on λ via the coefficients a and α in the equation

$$\rho = af(\alpha\varphi). \quad (58)$$

which are proportional to the ionic charge. One can therefore easily demonstrate the identity

$$z\left(\frac{\partial\rho_\lambda}{\partial z}\right)_\varphi = \lambda\left(\frac{\partial\rho_\lambda}{\partial\lambda}\right)_\varphi = \frac{\partial\rho_\lambda\varphi_\lambda}{\partial\varphi_\lambda}. \quad (59)$$

On substituting Eqn. (59) in Eqn. (57) and integrating the latter, we obtain finally,

$$dF_{e\lambda} = \sum \varphi_{i\lambda}\, de_{i\lambda} + \int \rho_\lambda\varphi_\lambda \frac{d\lambda}{\lambda} dv. \quad (60)$$

The validity of Eqn. (53) follows from a comparison of Eqn. (60) with Eqns. (50) and (51). On integrating the latter in the range from 0 to 1, we obtain

$$A = F_e. \quad (61)$$

Thus the correct generalisation of the Debye method leads to the same correct Eqn. (36) for the free energy of the particles in the electrolyte solution.

The function F_e, specified by Eqn. (36) is, by virtue of Eqn. (7), the potential of the interaction of the particles in the electrolyte solution at a constant charge on each particle. However, Eqn. (41) can be used to find F_e, integrating with respect to the volume of the dispersion medium only, subject to the condition that there is no field within the particles when their surfaces are isopotential. However, on the sections of the surfaces whose ionic atmospheres overlap with the atmospheres of neighbouring particles, the isopotential condition is incompatible with the condition of a constant surface charge density[66,67]. Because of this, the constancy of the overall charge of the particle can be maintained when it approaches another particle only as a result of a change in the charge density on the sections of the surface remote from the overlap zone. However, on these sections, the local surface charge density, which is a function of the local potential, cannot vary as a function of the situation on the sections of the surface remote from it. Thus we conclude that in the case of real colloid systems with an electrolyte solution as the dispersion medium, in which we are interested, where the function F_e should be used in the calculation on the interaction arising following the overlap of the ionic atmospheres, it is impossible to reconcile the conditions of a constant charge and a constant potential. This constitutes the profound difference between this case and classical electrostatics where conducting particles immersed in a liquid dielectric are considered.

In the absence of isopotential conditions, part of the work expended on the charging of the surface of the particles, which is equal to F_e, is consumed in creating an electrostatic field within the particles. In this case appropriate corrections must be applied to Eqns. (39) and (42). Eqns. (43) and (61) remain unchanged, but their derivation must be modified by taking into account the presence of the field within the particles. The cases with a constant potential and a constant charge have been compared[68].

We shall now consider the interaction potential F_φ of the particles at a constant potential (but not charge) of each, which applies particularly to metallic particles with a polarisable surface. The work performed to alter the configuration of the system for constant potentials φ_i is coupled with the work necessary to alter the charges and performed against forces maintaining a constant potential. Consequently we must write instead of Eqn. (37)

$$A_\varphi = \sum \varphi_i^0 (e_i^\infty - e_i^0) = \sum \int_0^{e_i^0} (\varphi_i)\, d\, e_i - \sum \int_0^{e_i^\infty} \varphi_i\, d\, e_i, \quad (62)$$

where the superscripts ∞ and 0 denote the states of the system where the particles are separated by distances for which the ionic atmospheres do not and do overlap respectively, and φ_i^0 is the constant potential applied to the ith particle. On transforming Eqn. (62), we obtain instead of Eqn. (37)

$$A_\varphi = -\sum \int_0^{\varphi_i^0} (e_i^0 - e_i^\infty)\, d\,\varphi_i = F_\varphi^0 - F_\varphi^\infty. \quad (63)$$

whence it follows that the free energy of the system for a constant potential of the particles is

$$F_\varphi = -\sum \int_0^{\varphi_i} e_i\, d\,\varphi_i. \quad (63')$$

On differentiating this expression and carrying out transformations analogous to those used in the derivation of Eqn. (39), we obtain

$$dF_\varphi = -\frac{\varepsilon}{4\pi}\int \frac{\partial\varphi}{\partial n}\, d\,\varphi\, dS. \quad (64)$$

Application of Green's theorem yields

$$dF_\varphi = -\frac{\varepsilon}{4\pi}\int \left(\frac{\partial\varphi}{\partial x}\, d\,\frac{\partial\varphi}{\partial x} + \frac{\partial\varphi}{\partial y}\, d\,\frac{\partial\varphi}{\partial y} + \frac{\partial\varphi}{\partial z}\, d\,\frac{\partial\varphi}{\partial z}\right) dv - \frac{\varepsilon}{4\pi}\int \Delta\varphi\, d\,\varphi\, dS, \quad (65)$$

or, taking into account Poisson's equation and integrating, we obtain

$$F_\varphi = -\frac{\varepsilon}{8\pi}\int |\operatorname{grad}\varphi|^2 dv + \int dv \int_0^{\varphi} \rho\, d\,\varphi. \quad (66)$$

Here ρ is a function of φ, specified by the Boltzmann equation (3) or Eqn. (58).

Eqns. (64) and (66) differ from Eqns. (39) and (41), which express the free energy of the electric field in the electrolyte, because they take into account, apart from the energy of the field, the energy of the source of the charge used to maintain a constant potential of the surfaces of the particles.

We shall now prove that Eqn.(41) or (66) is equivalent to the system of tensions of the Maxwell electric field tensor to which an excess isotropic hydrostatic pressure has been added:

$$p = \int_0^{\varphi} \rho \, d\varphi. \tag{67}$$

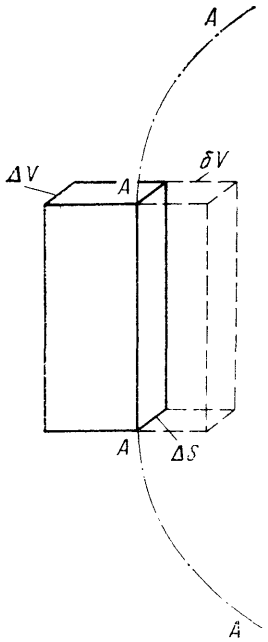


Figure 4. Derivation of the pressure tensor in an electrolyte surrounding charged particles.

We isolate from the total volume of the electrolyte a volume element Δv (Fig.4) and consider the virtual work performed in its expansion as a result of the displacement of a small section of its surface ΔS by a distance δh into the bulk of the remaining volume. The work expended in this process is converted into an increment of the free energy δF_{φ} of the remaining part of the system, in relation to which the volume V plays the role of the external medium:

$$\delta A = P\delta V = \delta F_{\varphi}, \tag{68}$$

where P is the total (including the corresponding component of the Maxwellian tensor) pressure on the given section of the surface of the volume and $\delta V = \Delta S \delta h$ is the volume increment ΔV when a section ΔS of its surface is displaced. The variation of δF_{φ} is given by the sum of two terms:

$$\delta F_{\varphi} = \delta_1 F_{\varphi} + \delta_2 F_{\varphi}. \tag{69}$$

The first term expresses the change in F_{φ} as a result of the loss of the field element δV and is therefore equal to

$$\delta_1 F_{\varphi} = +\frac{\varepsilon}{8\pi} |\operatorname{grad}\varphi|^2 \delta V - \int_0^{\varphi} \rho \, d\varphi \delta V. \tag{70}$$

The second term in Eqn.(69) expresses the change in F_{φ} occurring owing to the change in the potential φ over the entire volume of the system due to the shift of a section ΔS of the outer surface. The change $\delta_2 F_{\varphi}$ would be zero if, following the shift of the surface, its potential, having changed, acquires the value which existed hitherto at its new location, having received thereby the increment

$$\delta\varphi = \frac{\partial\varphi}{\partial n} \delta h, \tag{71}$$

where $\partial\varphi/\partial n$ is the derivative of φ with respect to the normal to the surface at the point under consideration.

However, the applicability of Eqn.(68) is determined by the maintenance on all the boundaries of the solution of the electrolyte AAAA (Fig.4) of a constant potential (this is recalled by the subscript φ in F_{φ}); in reality there is therefore no increment in the potential φ defined by Eqn. (71) and the new values of the potential at the new site on the surface S are reduced compared with the previous ones by an amount

$$\delta\varphi = -\frac{\partial\varphi}{\partial n} \delta h. \tag{72}$$

We can find from Eqn.(66) the change in F_{φ} caused by this factor:

$$\delta_2 F_{\varphi} = -\frac{\varepsilon}{4\pi} \int (\operatorname{grad}\varphi \cdot \operatorname{grad}\delta\varphi) \, dv + \int \rho\delta\varphi \, dv. \tag{73}$$

Application of Green's theorem yields

$$\delta_2 F_{\varphi} = \int \left(\frac{\varepsilon}{4\pi}\Delta\varphi + \rho\right) \delta\varphi \, dv + \frac{\varepsilon}{4\pi} \int \frac{\partial\varphi}{\partial n} \delta\varphi \, dS. \tag{74}$$

Taking into account Poisson's equation and Eqn.(72), we obtain

$$\delta_2 F_{\varphi} = -\frac{\varepsilon}{4\pi} \int \left(\frac{\partial\varphi}{\partial n}\right)^2 \delta h \, dS = \frac{-\varepsilon}{4\pi} \left(\frac{\partial\varphi}{\partial n}\right)^2 \delta V. \tag{75}$$

Finally, we find from Eqns.(75), (70), (69), and (68)

$$P = \frac{\varepsilon}{8\pi} |\operatorname{grad}\varphi|^2 - \frac{\varepsilon}{4\pi} \left(\frac{\partial\varphi}{\partial n}\right)^2 - \int_0^{\varphi} \rho \, d\varphi. \tag{76}$$

The last term on the right-hand side of Eqn.(76) expresses the excess isotropic hydrostatic pressure which is due to the electric field within the framework of the applicability of the Boltzmann equation and which depends on the field potential φ in accordance with the equation

$$p = -\int_0^{\varphi} \rho \, d\varphi = kT \sum c_i (e^{-\alpha_i \varphi} - 1), \tag{77}$$

which is applicable to any electrolyte including an asymmetric electrolyte.

The sum of the first two terms in Eqn.(76) expresses the pressure of the electrostatic field, which follows from the Maxwell tensor.

In the specific case of a plane parallel to the lines of force of the field, we have

$$P_{\parallel} = \frac{\varepsilon}{8\pi} |\operatorname{grad}\varphi|^2 + p. \tag{78}$$

The formula corresponding to a plane at right angles to the field vector is

$$P_{\perp} = -\frac{\varepsilon}{8\pi} |\operatorname{grag}\varphi|^2 + p. \tag{79}$$

It is important to emphasise that the values of the pressure P obtained are independent of the conditions governing the maintenance of the potential or charge when the surfaces

are displaced. Eqns.(78) and (79) can be undoubtedly obtained also by considering the function F_e.

Eqn.(79) agrees with Eqn.(1) which we used previously and confirms it.

According to its derivation, Eqn.(76) is applicable to any plane selected within the bulk of the electrolyte. This makes it possible to calculate the interaction forces between two particles by the summation of the pressure, expressed by Eqn.(76), over all the sections of any surface incorporating one of the particles or with respect to any infinite plan BB′ separating them (Fig.5). Indeed, according to Stevin's solidification principle, equilibrium cannot be infringed if part of the liquid, included between this surface and the particle which it incorporates, "solidifies" (without change in charge density and distribution). The condition for equilibrium in the solidified part requires that the forces balancing the pressures on the outer and inner surfaces bounding this region should be equal since the introduction of the Maxwell tensor excludes from consideration the long-range electrical forces applied to the charges of the ionic atmospheres. However, the force balancing the pressure on the inner surface is equal to the force acting on the particle itself. Mathematically it is most convenient to select the symmetry plane normal to the line passing through the centres of two identical spherical particles (BB′ in Fig.5) as the separating surface for two such particles. In this case one must integrate with respect to this plane the pressure expressed by Eqn.(78), which was done by the present author [63,64] and by Dukhin et al. [69].

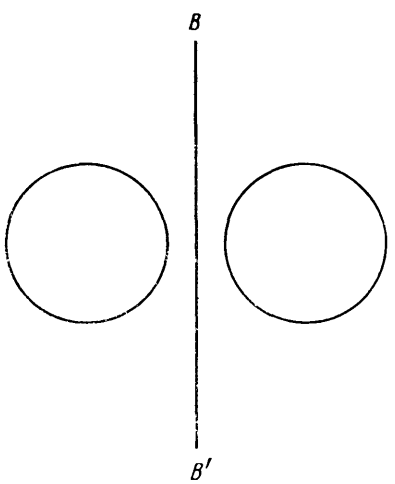


Figure 5. Calculation of the degree of interaction between spherical particles.

It follows from Eqn.(78) that the interaction of a sphere with a plane, which remains uncharged under all conditions, is the same as its interaction with another identical sphere. In addition one must take into account the fact that the boundary conditions in these problems are such that the distribution of the potential is the same in both instances. For two spheres charged to potentials which are equal but of opposite sign, it is possible to apply Eqn.(79) having put $p = 0$. Since the potential is zero at all points on the symmetry plane and p depends on φ in accordance with Eqn.(4) or (77), Eqn.(79) with $p = 0$ is also applicable to the calculation of the attraction is an electrolyte solution of a charged particle to the surface of a conductor with a zero potential. This case obtains, for example, in the electrophoretic coatings. We may note that Ikeda [70] arrived at the same expressions for the free energy and hence for the interaction forces of the particles in electrolyte solutions on the basis of a rigorously statistical method.

In conclusion of this section, we shall indicate a method for the calculation of the interaction forces between parallel plates in an electrolyte solution [72], which is based on a generalisation of the Gibbs–Duhem equation [71] in combination with the Poisson–Boltzmann equation. This method employs the most general postulates of thermodynamics and statistics, does not require the introduction of any additional assumptions, and does not use the Maxwell tension tensor and the distribution of the hydrostatic pressure in ionic double layers. For this reason, this is the most rigorous and general method, being at the same time very simple mathematically.

Further application of the above principles to the theory of the stability of lyophobic colloids has been described by the present author and Landau [52,53]. In contrast to previous reports, they calculated the repulsion forces from exact formulae obtained without linearising the Poisson–Boltzmann equation. At the same time, as in earlier studies [39,40], account was taken of the dispersion type attraction forces. For the interaction between plates separated by a plane-parallel layer of electrolyte, this implies that the wedging pressure of the layer [73–78] is considered as the sum of two terms—electrostatic and molecular (negative), which is characteristic of lyophobic systems. The degree of interaction between spherical particles was calculated on the basis of the interaction between plane surfaces by the integration method proposed previously [37].

It was shown that in the general case the curves describing the potential interaction energy can have, as before [26,29,39,40] (Fig.3), a potential barrier, which prevents particles from entering the potential well.

The present author and Landau [52,53] examined the limiting case of highly charged species and found conditions under which the potential and force barriers separating them vanish. The calculations were performed both for a symmetrical electrolyte and for electrolytes of the 1-2 and 2-1 valence types (the first numeral indicates the charge of the counterion). It was demonstrated by these examples that the charge of the coion has little effect on the stability of the sol. On the other hand, the charge of the counterion ez_1 determines the coagulation concentration m in accordance with the formula

$$m = C\frac{\varepsilon^3 (kT)^5}{A^2 e^6 z_1^6}, \qquad (80)$$

where A is the Hamaker constant and C a numerical coefficient, which depends only slightly on the valence of the coion. Thus the Hardy-Schulze rule, which states that the valence of the counterion has a dominant and a strong influence on the coagulation threshold, was explained.

The coagulation criterion (80), derived theoretically by the present author and Landau, is in good agreement with many experimental data which have accumulated in the last thirty years [79,80]. For convenience, it is frequently formulated in the form:

$$m \propto z_1^{-6}. \qquad (81)$$

In many instances deviations are observed, which can be accounted for by the lack of validity of the postulates underlying the derivation of this criterion: for example, the solvation of the surfaces of the particles and the failure of the condition that the Debye length is small compared with the radius of the particles. It is more difficult to explain why condition (80) is valid even when the dimensionless potential of the particle

$$\omega = \frac{z_i e\psi}{kT} \tag{82}$$

is small, so that one of the main conditions underlying its derivation does not hold. This question was considered particularly by Muller[81]. Glazman and Dykman[82,83] formulated the condition governing the applicability of the "law" defined by Eqn.(81) for moderate values of ω; this condition, which is of the form

$$\omega \propto z_i\varphi = \text{const}, \tag{83}$$

involves an inverse proportionality between the potential of the particle and the charge of the counterion. Us'yarov[84] demonstrated in relation to extensive experimental data that this condition holds satisfactorily in practice, and interpreted it theoretically.

It is noteworthy that the correct formulae for the repulsion forces between particles with a specified charge, separated by plane-parallel layers of electrolytes at any potential, have been developed by Bergmann et al.[49] in an attempt to explain the formation of the so-called "schiller" layers¶. These layers are formed after the sedimentation of lamellar particles of certain minerals in an electrolyte solution. The thicknesses of the layers separating the particles at different electrolyte concentrations can be determined from the interference colours visible in the light reflected from them. These thicknesses proved to agree more or less with theoretical calculations in which the pressure on the layer was calculated from the weight of the particles located above them. The effect of van der Waals forces was not taken into account, which apparently did not introduce a significant error. Bergmann et al.[49] confirmed experimentally the theory of the repulsion forces in electrolyte layers, but did not claim to have established a general theory of the stability of lyophobic colloids. The theory of the stability of lyophobic colloids was developed further by Verwey and Overbeek[31]. Their investigations were based on the principles described above. Apart from publication of a monograph on the subject, they can be credited with the study of the following problems:

1. The use of formulae for the repulsion forces between colloid particles charged to any potential.
2. The elucidation of the influence of the Stern correction, which takes into account the formation of a dense monolayer of adsorbed ions on the stability of colloids.
3. A theoretical determination of the principal characteristics of peptisation process.
4. Examination of the influence of the secondary (remote) potential well, first observed by the present author[39], on the aggregation and thixotropy of suspensions.

¶The name of these layers originates from the German word *schillern*, meaning to iridesce, which has apparently been long forgotten. On the erroneous assumption that this name is derived from the name of a scientist, they have come to be called Schiller layers.

IV. ALLOWANCE FOR MONOLAYER ADSORPTION

A correction taking into account the monolayer adsorption on the basis of the Stern or some other theory is of the most fundamental importance for the refinement of the theory of the stability of lyophobic colloids. On the basis of the Stern theory in a simplified form, Verwey and Overbeek arrived at the following conclusions.

In the Stern layer AA'SS' (Fig.6) there is a sharp decrease of potential (continuous UU' curve), which forces the potential of the diffuse layer to assume a Stern potential U' significantly smaller than the potential of the surface of the particle itself. This decrease of the potential eliminates objections to the employment in the theory of stability of the Boltzmann equation for potentials at which an unrealistically high concentration of ions is obtained. Furthermore, the introduction of the Stern correction improves the agreement between the theory and experiment, since it makes it possible to explain the dependence of the coagulating action of the counterions having the same charge on their chemical nature (their position in the lyotropic series). The Stern correction makes it possible to eliminate also a number of other contradictions, but some inconsistencies between theory and experiment nevertheless remained. Thus the Deryagin–Landau–Verwey–Overbeek (DLVO) theory explains the linear dependence of the logarithm on the concentration of the added indifferent electrolyte[86]. However, the experimental dependence of the slope of the plot of this function against the radius of the particles and the valence of the counterion does not agree with this theory[87].

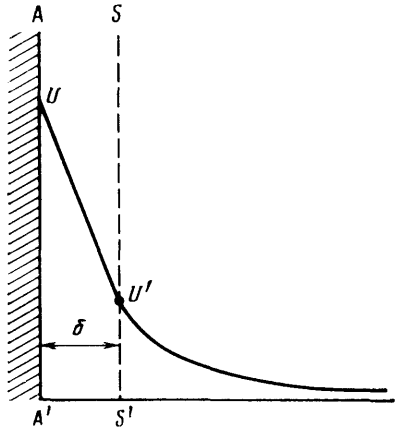


Figure 6. Distribution of the potential in the double layer near a charged surface.

An attempt to improve the DLVO theory by taking into account additional factors has been made by Martynov and Muller[88,89]. Their calculations include the earlier hypothesis that the presence of a molecular condenser shifts the plane corresponding to the beginning of the diffuse layer by a distance equal to its thickness δ relative to the interface (in their calculations the authors assumed that $\delta = 4$ Å). Thus the distance, inversely related to the van der Waals interaction, increases by 2 δ. The author's calculate that this can cause the near-by potential well to vanish

before the potential barrier under the influence of uni-univalent electrolytes. At a Stern potential exceeding 25–50 mV and at fairly high electrolyte concentrations, the near-by potential well disappears for similar values of the parameters for both planar surfaces and for spherical particles.

This conclusion conflicts with a multiplicity of experimental studies[6], which have firmly established the existence of two potential wells for electrolytes of different valence, including uni-univalent electrolytes, and for low concentrations and high potentials. The presence of a near-by potential well, protected by a potential barrier, has been observed particularly clearly in a study of the intracrystalline swelling of montmorillonite saturated beforehand by ion exchange with lithium, sodium, or potassium cations.[90] The problem has been studied theoretically by Serebrovskaya et al.[91] Comparison of the calculations with experiment showed that the quantitative discrepancies may be accounted for by the shear strength of the interlayer aqueous layers. Another possible cause, which reduces the thicknesses of the aqueous layers observed at low ionic strengths is, according to Van Olphen[92], adhesion of small crystals to the edges of other small crystals. Both explanations require further tests. There have also been a number of studies[93] indicating unambiguously the existence in various colloid systems of two wells separated by a barrier. For periodic colloid structures, the transfer of particles from the remote potential well to the near-by well is examined by direct microscopic observations[94,127].

The inconsistency between the conclusions in the literature[88,89] and experimental data is not surprising when the principles from which they were derived are examined more deeply. In the first place the concept of a molecular condenser whose charges are uniformly "smeared" over parallel planes is applicable in the introduction of a correction to the distribution of the potential (and hence to the repulsion forces) only at distances from the interfaces significantly exceeding the distance between neighbouring ions in the adsorption monolayer. Furthermore, the distance of the near-by potential well is known not to satisfy this necessary condition, particularly at electrolyte concentrations for which a barrier-free coagulation mechanism is said[88,89] to operate, because at these concentrations ($c \simeq 0.1$–0.15 M) the effective Debye thickness of the double layers becomes less than 10 Å. Furthermore, the limit of the applicability of the Poisson–Boltzmann equation, used for the double layer, is reached, since the distance between the surfaces and the near-by potential well becomes of the same order of magnitude as the distance between neighbouring ions of the molecular condenser, but with the thickness of the latter doubled. For this reason the use in this case of the concept of a molecular condenser with an arbitrary thickness in order to infer whether or not a near-by potential well is present is not justified.

This does not imply that the problem of the presence of the potential well cannot be the subject of theoretical calculations, but they must be performed differently taking into account in the first place the discrete nature of the structure of the monolayer of the adsorbed ions.

The last comment is of extremely general importance. The discrete nature of the adsorbed layer, made up of individual ions, must be taken into account also in other instances, for example, when the height of the potential barrier is considered at high electrolyte concentrations. The influence of the discrete structure of the surface charge on the interaction of the planes separated by a layer of electrolyte was taken into account for the first time by Yalamov[95], who used Levine's charging method as corrected by the present author. Using the same method, similar results were obtained recently by Richmond[96]. It was assumed in the above studies that ions are distributed on the surfaces in a strictly periodic arrangement among the sites of identical lattices, i.e. there is a rigorous correlation between the positions of the ions on both planes.

In contrast to these calculations, Deryagin and Muller[97] carried out an approximate stochastic calculation of the influence of the discrete nature of the structure of the dense part of the double layer on the interaction of parallel surfaces at short distances on the assumption that the correlation between the relative positions of the ions adsorbed on opposite surfaces are determined exclusively by the energy of the interaction of these ions in accordance with the Boltzmann equation. In other words, either the ions are adsorbed in a non-localised manner or the positions of the centres of adsorption on a single surface are in no way correlated with the positions of the centres of adsorption on the other surface.

Calculations performed on the assumption that the adsorption energy is small showed that the discrete but disordered distribution of adsorbed ions can reduce sharply the repulsion forces between surfaces over short distances and can thereby deepen the near-by potential well.

It is also important to take into account the discrete structure of the adsorption layer in the calculation of its influence on the Stern potential, i.e. on the potential in the plane from which the diffuse part of the double layer begins. Evidently this transition from the discrete lattice of the adsorption layer to the diffuse layer (treated in macroscopic terms), whose properties depend solely on one coordinate—the distance to the interface—cannot occur abruptly, especially directly on the surface of the outer plate of the condenser. Thus there should be a transitional layer between the molecular condenser and the diffuse ionic atmosphere with a thickness greater than that of the condenser itself. Its existence should alter the calculations of the potential outside its limits and in the diffuse double layer, especially within the transition layer. The thinner the layer of electrolyte, the greater the error in calculations where the effect of the discrete nature of the structure is ignored.

Without taking into account the discrete nature of the Stern layer, it is also impossible to devise a genuine quantitative theory of peptisation processes which, however, did not prevent a qualitative treatment of this phenomenon by Verwey and Overbeek[31] in accordance with experiments and a correct elucidation of its mechanism. Overbeek wrote later[98], "Quantitative studies in this field are lacking, which is to be regretted, since the peptisation phenomenon might yield information about the region of potential curves least accessible to study, corresponding to short distances between particles."

V. THE REVERSIBLE NATURE OF LONG-RANGE AGGREGATION

In their consideration of the problem of the role of the secondary (remote) potential well, Verwey and Overbeek[31] drew attention to the fact that it can be the cause of the formation of aggregates from primary particles only when the radius of the particle is approximately 1 μm and above, i.e. in suspensions. Only then is the depth of the remote

potential well sufficiently large compared with the energy of Brownian motion. Aggregation in the remote well is readily reversible owing to the absence of a barrier hindering the decomposition of aggregates. The aggregation process in the remote well is therefore rapidly balanced by the opposed deaggregation process and the authors used the Boltzmann equation in the following form in order to determine the degree of aggregation:

$$\Delta b = n_0 \int 4\pi a^3 s^2 e^{-V/kT} \, ds, \qquad (84)$$

where Δb is the fraction of aggregated particles, n_0 their total number, $s = d/2R$ (d is the distance between the centres of the particles and R their radius), and V is their interaction energy.

The authors[85] used $\Delta b \geqslant 0.1$ as the aggregation condition. On the basis of Eqn.(84), Martynov and Muller[88,89] found that rapid coagulation takes place when $\Delta b \gg 10$. However, they attribute a completely different significance to the concept of "rapid coagulation" in contrast to that associated with the kinetics of barrier coagulation. The degree of aggregation has been characterised[88,89] by the value of Δb, which depends significantly not only on the depth of the secondary potential well but also on the numerical concentration of the particles. We shall return to the problem of the role of the remote potential well in subsequent discussion of the question of quasi-equilibrium and equilibrium systems in which the particles are interrelated owing to these wells.

In principle, Eqn.(84) is applicable to the calculation of the degree of aggregation also due to the near-by potential well. The difference between the short-range aggregation and long-range aggregation consists in the fact that the corresponding equilibrium is established over a period the duration of which can be very large if the potential barrier is many times greater than the energy kT. Another, less fundamental difference is that the calculation of the interaction energy of the particles in the vicinity of the near-by potential well, for not unduly high electrolyte concentrations when the electrostatic interaction can influence its position and depth, is extremely difficult—one can actually say that so far it is virtually impossible. However, without such calculation, Eqn.(84) cannot be used for quantitative conclusions.

The calculation of the potential barrier and of the conditions for its disappearance is much easier. The results of our calculations, which have been introduced into Fuch's formula[26,38], made it possible to calculate the rate of slow coagulation. In order to test the theory, it is sufficient to measure the number of particles (including primary particles and aggregates) as a function of time. However, until recently these measurements were hindered by the lack of a sufficiently accurate, rapid, and convenient method for counting particles. The method based on the ultramicroscope counting of particles in a stationary volume is relatively unsuitable for this purpose. A number of new methods[99,100] are inconvenient because, owing to the low upper limit to the measurable concentrations, the measurement must be preceded by a high dilution of colloid systems with an optically clear solvent.

New possibilities arose after the development by the present author and Vlasenko of flow ultramicroscopy, initially for counting particles in aerosols[101-103]. Flow ultramicroscopes based on the same principle, for colloid systems with a liquid dispersion medium, have been developed by the present author and Kudryavtseva[104,105]. A series of studies on the kinetics of slow and rapid coagulation of red and blue gold sols have been carried out with the aid of a flow ultramicroscopic method[106,107] at different electrolyte concentrations; a version of the method using a laser has been published[108].

The results obtained permit the following conclusions.

At fairly high electrolyte concentrations the rate of coagulation expressed in terms of the variables $1/n$ and t, where n is the numerical concentration of the particles and t the time elapsed from the onset of coagulation, is expressed, in conformity with Smoluchowski's theory, by a straight line with a slope fairly close to the theoretical value. The deviations from theory can be explained in some cases by the operation of van der Waals forces and in others by deviations from Stokes' law when the particles which have approached one another to distances less than their radii move towards one another[109-111].

With decrease of the electrolyte concentration, the rate of coagulation not only falls but, "in conflict with both the Smoluchowski and Fuchs theories", the dependence of $1/n$ on t deviates increasingly from linearity, the curve becoming S-shaped. Fig. 7 illustrates examples of such relations. At a fairly low electrolyte concentration the reciprocal of the concentration of particles $1/n$, having increased with time by a factor of 2 or more, reaches fairly rapidly a value which remains constant for a long time. This time can increase to many days as the electrolyte concentration is reduced. After the elapse of a certain time, the quantity $1/n$ again begins to increase with t (at any rate for not unduly low electrolyte concentrations) and the curve rises more steeply. Towards the end, the slope of the curve tends to a more or less constant value.

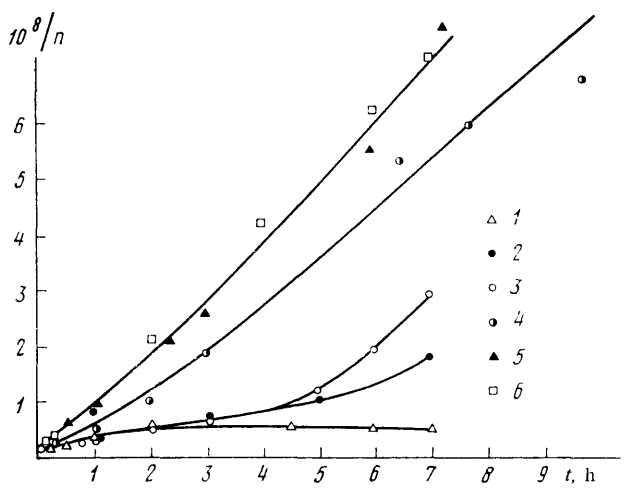


Figure 7. Relation between the reciprocal of the numerical concentration n and the time t. Silver iodide sol; $BaCl_2$ electrolyte; molar electrolyte concentration: *1*) $1.5 \cdot 10^{-3}$; *2*) $1.8 \cdot 10^{-3}$; *3*) $1.9 \cdot 10^{-3}$; *4*) $2.0 \cdot 10^{-3}$; *5*) $2.15 \cdot 10^{-3}$; *6*) $3.0 \cdot 10^{-3}$.

In order to explain this shape of kinetic coagulation curves, the present author and Kudryavtseva took into account the superposition of a deaggregation process on the aggregation process leading to the pairing of particles[106,107]. As a result, the kinetics of this stage of the

coagulation process become similar to those of a reversible bimolecular reaction and obey the differential equation

$$\frac{dn}{dt} = -kn^2 + l(n_0 - n), \quad (85)$$

where n_0 and n are respectively the number of particles at the initial instant and after time t and k and l are constants. The reasons why the equilibrium between the two process breaks down may be twofold:

1. At a certain instant an aggregate may be formed where the energy of the bonds between particles is greater than the energy of the bonds in the remaining aggregates as a result of a kind of collective interaction. For example, if each particle in an aggregate of three particles is linked to two others, then, as a result of the decreased probability of decomposition, the number of particles in the aggregate may subsequently increase rapidly. The growth of the aggregate may acquire the properties of an avalanche is each new particle added to the aggregate forms more than a single bond with any one particle in its condensation. The new state of aggregation equilibrium, at extremely low concentrations of individual particles, may be attained after a very long time.

2. Initially the pairing of particles may occur in the remote potential well. After some time they may pass to the near-by potential well, which sharply increases the bond energy. This facilitates the formation and growth of larger aggregates. It is noteworthy that the depth of the remote potential well for highly disperse sols is so small that the probability of such two-stage process is low.

The formation after a more or less prolonged "latent" period of larger aggregates, which serve, as it were, as effective coagulation nuclei, is clearly confirmed by visual observations in a flow ultramicroscope.

We may add that the cardinal difference between coagulation processes and typical processes involving the formation of new condensed phases consists in the possibility of bonds between particles in an aggregate corresponding to either the primary or secondary (remote) potential minimum. In the former case the barrier mechanism has no adequate analogue in condensation processes. Thus the activation energy for chemical condensation is not determined by the need to overcome repulsion forces as a result of thermal motion, but is caused by the low probability of collisions leading to the activated complex. This difference must be specially emphasised, since any attempt to minimise the fundamental differences between colloid and true solutions interferes with the development of colloid science as an independent discipline and with the discovery of its characteristics.

As stated at the beginning of this review, another characteristic difference between colloid systems and molecular solutions is the existence of two different types of equilibrium—the aggregation equilibrium and the equilibrium of the disperse phase composition. Kudryavtseva et al.[113] reported observations of equilibrium between the coagulant and single gold particles at a numerical concentration of the latter of the order of 10^6 cm^{-3}. However, this does not allow any general conclusions about the reversibility of hydrophobic sols, because, in view of the characteristics of the method developed by Sigmund for the preparation of the red gold sols, a certain degree of hydrophilisation of the surface of its particles due to the adsorption of organic molecules is probable. Owing to the high degree of dispersion of the gold sol, even when reversibility is observed, its aggregation under these conditions occurs after the passage through the barrier to the near-by potential well, including the process under the influence of univalent electrolytes. In other cases metal sols apparently coagulate virtually irreversibly.

An important further development of the theory of the stability of lyophobic colloids involves its application to a mixture of electrolytes. In view of lack of space, we refer the reader to the relevant literature[114-121].

VI. LANGMUIR'S THERMODYNAMIC CONCEPT OF COACERVATION AND COAGULATION PROCESSES

We shall now consider Langmuir's interesting attempt[122] at a thermodynamic approach to changes in the state of highly disperse colloid systems such as colloidal electrolytes. By analogy with the phase equilibria in molecularly disperse systems, for example, solutions, Langmuir considered temperature, numerical concentration, and osmotic pressure as the thermodynamic parameters of such systems. The expression borrowed from the Debye–Hückel theory of strong electrolytes is used for the osmotic pressure p:

$$p = kT\sum n_i - \frac{e^2\varkappa}{6\varepsilon}\sum_i n_i z_i^2, \quad (86)$$

where n_i is the concentration of ions with a valence z_i. The second term on the right-hand side of the equation expresses the decrease of the osmotic pressure caused by collective electrostatic interaction forces of all the charged particles and ions in which the influence of attraction forces predominates, which accounts for the sign of this term (because $\Sigma n_i z_i^2 > 0$).

Thus Langmuir treats colloid particles as large multicharged ions with a fixed charge. At the same time he considers the limiting case where no ions other than counterions are present in solution. However, Langmuir assumes that, with increase of the concentration of colloid particles, their charge falls owing to the conditions of a constant potential on the surface of the particles. As a result, Langmuir concluded that the dependence of the osmotic pressure on concentration is analogous in form to the van der Waals equation for real gases. From this, it follows immediately that, as the concentration of the sol increases, it may separate into two sols at different concentrations, which are in equilibrium. Langmuir postulates that one can explain in this way not only the coacervation of proteins but also the coagulation of lyophobic sols.

Langmuir's theory was subjected to a serious criticism in the book of Verwey and Overbeek[123], which was not answered. In particular, it was noted that, with increase of the charge of any ion, the applicability of the linearised Debye–Hückel equation is impaired. On the other hand, for the particles of a sol or a colloidal electrolyte, this equation leads to completely incorrect results. When Langmuir's theory is applied to ordinary electrolytes to determine their solubility, the ascending section of the $p(n)$ curve is determined by Born forces and not by the operation of ionic-electrostatic interaction forces.

The following may be added to Verwey and Overbeek's criticism of Langmuir's theory. Coagulation is a process in which a colloid system passes from one state to another under significantly non-equilibrium conditions and is characterised either by the aggregation of particles or by a decreased degree of dispersion as a result of their coalescence. The thermodynamic approach based on the

concentration dependence of the osmotic pressure cannot therefore be adopted for the determination of the rate of coagulation and for predicting its practical feasibility (when the rate is not unduly low).

Calculations on coagulation, according to Smoluchowski and Fuchs, must be based on a procedure taking into account the pair interaction forces between colloid particles approaching one another. In such approach of two particles the distances between the counterions surrounding them and between the counterions and colloid particles do not in any way change in the same proportions as in the phase transitions considered by Langmuir. The deformations of the ionic atmospheres around both particles are determined on the basis of the Boltzmann–Poisson equation taking into account the electrical interaction. In the approach of two identical colloid particles surrounded by ionic atmosphere repulsion is therefore never replaced by attraction.

The difference between the signs of the interaction in Langmuir's theory and in the theory of the pair interaction between particles can be explained by the fact that in the former case the interaction is regarded as a collective effect while in the latter it is a pair effect. The interaction force between particles in the former case is obtained by differentiating the Gibbs free energy of the system, for a constant volume of the dispersion medium, with respect to the concentration (or volume) of the entire system of particles including counterions. The interaction force in the latter case is obtained by the partial differentiation of the free energy of the system with respect to the distance between two isolated particles, assuming that the concentration of the surrounding particles and counterions is unchanged. Thus the difference between the signs of the two effects is not a contradiction. Hence it follows that Langmuir's approach is in principle inapplicable to the development of the theory of the coagulation of colloids. Despite this, Langmuir's work is valuable because he was the first to draw attention to the problem of phase equilibria and transitions in colloid systems. Consequently, it is appropriate to formulate the question of the existence not only of the aggregation equilibrium or equilibrium disperse phase composition, but also of the phase equilibrium, which may break down without a change in the degree of aggregation or dispersion owing to a change in the numerical concentration of particles—an increase in their density.

VII. THE FORMATION AND STABILITY OF PERIODIC COLLOIDAL STRUCTURES†

If one disregards the defects pointed out Verwey and Overbeek, Langmuir's thermodynamic approach can apparently be applied not only to the treatment of coacervation, i.e. the separation of a colloid system into two "phases" with different concentrations, but also to a number of other processes, for example, processes such as the formation of certain periodic colloidal structures (PCS). The question of the conditions governing the formation and stability of PCS is very complex and has been inadequately worked out. We shall therefore confine ourselves to the folowing general considerations without a detailed discussion, the reader being referred to the relevant literature[93,124-127].

†This chapter was written jointly with I. F. Efremov.

The fundamental characteristics of the formation and behaviour of different types of PCS were established as a result of the extension of the DLVO theory to processes involving the conversion of sols, suspensions, and emulsions into gels[128-130]. It was shown that, as a result of the interaction between micro-objects over long distances, different (depending on the conditions) regular structures are generated.

Periodic Colloidal Structures Filling the Entire Volume of the System

Their quasi-crystallinity has been confirmed by numerous experimental data, including direct observations of coexisting hexagonal and cubic lattices in concentrated latexes[131]. In these systems the repulsion forces between the particles, which are stable in relation to direct adhesion to one another, usually exceed the attraction forces[132-134]. Thus "constrained" conditions arise in the system, under which the average distance between the surfaces of the particles is smaller than that corresponding to the second minimum on the potential curve for their pair interaction[124].

The spontaneous transition of individual particles from the secondary to the primary minimum can gradually cause the breakdown of the regularity of the structure (Fig.8) up to the complete disappearance of "crystallinity". However, for very high potential barriers (of the ionic-electrostatic or solvation type), the state of the system approaches equilibrium, which is the reason for the prolonged maintenance of order in it.

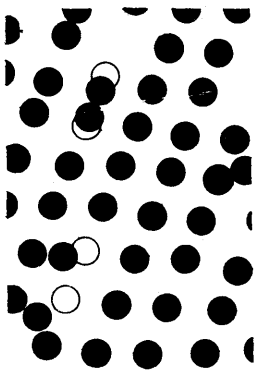


Figure 8. Defects in the periodic lattice of polystyrene particles with a radius of 950 Å caused by the transition of the particles through the potential barrier to the primary minimum.

Periodic Colloidal Structures Filling Part of the Volume of the System

These are tactoids—gel-like deposits. Under appropriate conditions, the local ordered structure in such formations coexists with a "phase" in which the particles are distributed at random, as in an ordinary dispersion medium (a sol or a suspension), but with a definite homogeneous numerical concentration. In some cases this

concentration is not much less than the numerical concentration of the PCS, while in others it is much less and sometimes becomes virtually zero.

The formation of local ordered structures is possible in two cases: when the attraction forces predominate over repulsion forces and when constrained conditions arise.

Owing to the predominance of attraction forces over repulsion forces at long distances and the maintenance of a force (potential) barrier, in the former case the particles may remain fixed for a long time relative to one another owing to the remote potential well. The fixation of micro-objects at the secondary minimum (long-range aggregation) has been observed a comparatively long time ago by numerous investigators and has been confirmed by the results of a large number of studies published recently and undertaken to investigate the influence on long-range aggregation by electrolytes, the size, shape, and concentration of colloid particles, and external electric and magnetic fields, which enhance the attraction forces between the particles [126]. The distribution of particles between the ordered and amorphous "phases" depends on the concentration and valence of ions, the concentration, size, and shape of the particles, the nature of the medium, etc.

The experimental data obtained by various investigators confirm the theoretical conclusions. In particular, the following law holds satisfactorily:

$$nz^{\chi}=\text{const},$$

where n and z are the concentration and valence of the counterions, expressing the influence of electrolytes on the aggregation threshold at the secondary minimum. The theoretical and experimental power exponents χ for both rapid coagulation ($\chi = 6$) and for long-range aggregation ($\chi = 2.5-3.5$) are in good agreement [127].

In the latter case the ordering of the structure takes place under the influence of external, including electrical, forces owing to the appearance of constrained conditions at some place in the stable dispersion, which is associated with the increase of the local concentration of colloid particles. Such PCS include "schiller" layers, gel-like deposits, formed in certain disperse systems, and also cream. In practice, such conditions are generated by the wide-scale application of centrifugal fields to dispersions [135, 136]. To a first approximation, one can assume that these fields do not alter the magnitude of the forces acting between surfaces which have approached one another. The structures arising under these conditions are analogous to the PCS with a limited volume of the medium and accordingly exhibit a ready reversibility; they can serve as model systems in the study of the formation and properties of PCS under constrained conditions.

It is of interest to investigate the distribution of particles between the ordered and disordered "phases" in the field of centrifugal forces as a function of the properties of the system and the field parameters. Concentrated "phases" (for example, electrophoretic coatings) with the required densities and other properties are obtained similarly with the aid of electrical and magnetic fields.

The possibility of equilibrium between a quasi-crystalline "phase" and an "amorphous phase" at a lower concentration has been demonstrated theoretically by Kirkwood [137] and confirmed by the results of the computer experiments of Alder et al. [138] According to these studies, a model system made up of identical solid spheres (or discs), between which there are no long-range forces (attraction or repulsion) of any kind, forms a periodic quasi-crystalline lattice when the volume of the system is half filled. According to Kirkwood's theory, this ordering is a paradoxical consequence of the purely random motion of individual particles. The authors noted that this quasi-crystalline "phase" can exist in equilibrium with the "amorphous phase" at a somewhat lower concentration.

Some investigators have used the purely statistical Kirkwood–Alder approach to explain the formation of quasi-crystalline structures in latexes. Thus aqueous dispersions of polystyrene with a volume fraction of the solid polymer less than 0.4 were found to separate into "phases" in the presence of an electrolyte [139]; in benzene dispersions of poly(methyl methacrylate), which swell appreciably in benzene, such layer formation occurred at a volume fraction of polymer particles of 0.1–0.2. [140] Finally, a highly concentrated polystyrene latex was obtained by the ultrafiltration (under a press) of the initial latex stabilised by surfactants and subsequent addition of large amounts of the electrolyte. At a KCl concentration of approximately 1 M an ordered "phase" with an effective volume fraction of the polymer of approximately 0.5 is formed. It is believed [141] that the results of these experiments confirm the validity of the Kirkwood–Alder theory.

Unfortunately the authors of these in general interesting studies [139–141] characterised a dispersion only to a very slight extent (the potential of the surface of the particles in dispersions with a low concentration of ions, the electrical conductivity of the medium, the degree of swelling of the particles, etc. are not indicated). Nor are there any data showing how the concentration of the disordered "phase" varies with time. A doubt therefore arises as to the reliability of the explanation of the results given by the authors on the assumption that there is no force interaction. Furthermore, in the presence of a lower electrolyte concentration, that of the quasi-crystalline phase diminishes. The authors nevertheless believe it possible to apply the Kirkwood–Alder theory to the systems investigated when the true volume of the particles is replaced by their "effective" volume, which exceeds the former owing to repulsion forces due to diffuse ionic layers.

This cannot be accepted, since the Kirkwood–Alder theory was derived for solid spheres in the absence of repulsion forces with a finite radius of action. Cases where the distances between neighbouring particles significantly exceed the distances indicated by the theory as a consequence of the ionic-electrostatic repulsion should evidently be interpreted in terms of another theory where the structure forming factor is the repulsion forces as well as molecular attraction forces. Such comparatively dilute periodic colloidal structures have been known for a long time [94, 125] and have been observed by the authors [143] themselves. Bernal and Fankuchen [142] observed in an early study, for example, that the average distance between the particles of the tobacco mosaic virus increases steadily with decrease of the electrolyte concentration, which is a consequence of the increasing radius of action of repulsion forces. They assume that in these periodic structures each particle executes an oscillatory Brownian motion about positions in which the repulsion forces, arising from neighbouring particles, are in mutual balance. Evidently particles located at the boundary with another much less concentrated "phase" cannot be in balance if they are acted upon only by repulsion forces from the side of neighbouring particles. The equal force opposing them will expel particles located on the boundary to the outside, i.e. to the less concentrated phase. However, equilibrium is possible if long-range attraction

forces operate together with repulsion forces. Quantitative calculations on conditions for such equilibrium, taking into account the theory of electrostatic repulsion forces and molecular attraction forces, have been described[127]. The separation into phases in the coacervation of sols consisting of rod-like particles, leads to the appearance of an anisotropic phase (tactoids) analogous to nematic liquid crystals. An example is provided by the quasi-crystals of the tobacco mosaic virus[142,144].

A theory of this phenomenon was described by Onsager[145], who also began with the calculation of the osmotic pressure and the chemical potential of the colloid system. This treatment is based on the general expression taken from statistical mechanics:

$$p = kT\frac{\partial \ln B}{\partial V}, \qquad (87)$$

where V is the volume of the system and B is given by

$$B(N, V, T) = \frac{1}{N}\int \exp\left(-\frac{W_N}{kT}\right)\prod_{i=1}^{i=N}(\mathrm{d}q_i); \qquad (88)$$

here N is the number of particles and W_N the potential energy of the interaction of the particles, which depends on their configuration, determined by the generalised coordinates q_i.

In contrast to Langmuir, Onsager considers the case of non-spherical particles, in particular rods and discs. In the calculation of the function B Onsager uses the Mayer–Mayer method[146], neglecting, like Langmuir, the van der Waals forces and also, at the beginning of his exposition, the ionic-electrostatic repulsion forces, but he does take into account the repulsion forces arising on direct contact between the particles. At the end of fairly complex calculations, Onsager found that the system can separate into two stably coexisting "phases": isotropic and anisotropic. At equilibrium the concentration of the latter is higher than that of the former by a factor of 1.34, which is close to the experimental data. For such separation to occur, the volume fraction of the sol particles must be higher than a definite limit where the influence of the effective volume of the particles on the osmotic pressure becomes sufficiently significant. An important result of the Onsager theory is that the greater the deviation of the particle from the isometric shape (for which the effective volume is equal to four times the intrinsic volume of the particles), the lower the volume fraction of the particles in the system for which separation into "phases" is observed. Thus, for rod-like particles, the critical volume fraction, above which the differentiation of an anisotropic phase with oriented particles is observed, is inversely proportional to the ratio of the length of the particles to their diameter. The ability of a sol with extended particles to form tactoids was thus explained.

Later in his communication[145] Onsager takes into account the influence of the ionic-electrostatic repulsion forces, which he neglected at the beginning. For sols with rod-like particles, this leads to the conclusion that, in the calculation of the critical concentration for the onset of coacervation, the effective diameter of the particles must be increased by an amount δ, which is approximately proportional to the thickness of the ionic atmospheres. As a result, the "effective" volume fraction of particles increases to the critical theoretical value for a lower actual volume fraction. This effect, facilitating coacervation in systems with rod-like particles as the electrolyte concentration decreases, has also been observed experimentally.

This effect, discovered by Onsager, should depend, on the one hand, on the influence of the rotational Brownian motion of anisometric particles on the osmotic pressure and, on the other, it should depend on their orientation. Nevertheless, there is no quantitative agreement between the theory and experiment in terms of certain data[147]. Isachara developed the theory for systems with spherical particles[148,149].

It must be emphasised that colloidal quasi-phases, analogous to ordinary phases, constitute an unusual special case. Its manifestation requires primarily the maintenance of approximate monodispersity and certain concentration and temperature ranges. Its occurrence does not constitute a reason for underestimating the fundamental differences between disperse, typically heterogeneous systems, with the characteristic variability of the degree of dispersion and the decisive role of surface phenomena at interfaces, and ordinary single-phase systems.

VIII. MICELLAR SOLUTIONS

The fundamental difference between colloidal and true or molecular solutions noted above does not rule out the existence of semicolloid systems, occupying an intermediate position. These include micellar solutions. They are quite stable thermodynamically and at the same time exhibit a definite degree of dispersion, which can vary as the temperature and composition are altered. The micelles exhibit a certain scatter with respect to the molecular (more correctly micellar) weight, although it is frequently very small. In connection with the existence of micellar solutions, it is appropriate to consider the general problem of the possibility and conditions for the existence of thermodynamically stable disperse systems. This problem has been formulated in the following simplified form[150–153]. It is required to satisfy the conditions for the existence of a minimum in the free energy of a monodisperse system in relation to a virtual change in the latter such that the size of the particles is altered but the monodispersity is maintained. Naturally, this type of equilibrium has nothing in common with the equilibrium of periodic structures. Evidently the required conditions are necessary but not sufficient, since there remains the possibility of a spontaneous breakdown of monodispersity.

One of the conditions isolated by Kachanova et al.[161] is

$$\sigma \leqslant \frac{\gamma kT}{R^2}, \qquad (89)$$

where σ is the free energy per unit interface between particles with a radius R and the dispersion medium and γ is a numerical coefficient.

The significance of this condition is that, for fairly low values of σ, there is no tendency for the degree of dispersion in the system to decrease during ageing, since the decrease of the free surface energy in such a process is compensated by the increase of entropy. However low (but finite) is the value of σ, condition (89) can hold only if the radius of the particles is smaller than a certain value. The spontaneous dispersion of an arbitrarily coarse phase can therefore occur only as a result of the separation from the latter of sufficiently small particles, which can occur, in particular, as stated by Rebinder and coworkers[152,153], owing to internal stresses, the liberation of the energy of which makes it possible to overcome the activation energy barrier, which prevents such "colloidal dissolution".

However, it has been noted[151,154] that condition (89) must be supplemented by another condition, which, in contrast to the first, might hinder an unlimited increase of the degree of dispersion up to the formation of a true solution. This condition has been formulated[154] as follows:

$$-\frac{\partial \ln \sigma}{\partial \ln R} > 2. \qquad (90)$$

We shall consider the problem of the kind of systems for which this condition can hold. According to Shcherbakov[155] (see also Tolman[156]), the dependence of the free surface energy on the radius of spherical particles for one-component systems satisfies the relation

$$-\frac{\partial \ln \sigma}{\partial \ln R} = -1, \qquad (91)$$

which is incompatible with condition (90). At the same time this incompatibility with condition (90) may not obtain for three reasons. Firstly, condition (91) is valid only in the asymptotic case where $R \to \infty$. Secondly, both conditions may be modified in multicomponent systems. Thirdly, condition (91) has been derived for molecules interacting on the basis of central forces and is presumably inapplicable to diphilic molecules (for example, the molecules of soaps), the opposite ends of which exhibit affinity for phases of different polarity.

It is noteworthy that the derivation of equilibrium conditions was not accompanied by the analysis of the problem of the particular systems for which these conditions can be realised. This question is undoubtedly very difficult to resolve but is also the most important. We shall therefore now return to experimental results.

Only two types of fully (thermodynamically) stable colloidally disperse systems have now been firmly established—critical emulsions and micellar solutions. The theory of critical emulsions was first described by Volmer[157-159] and was improved by other workers[150,160,161]. However, the instability of the droplets of such emulsions has more in common with associated species in polar liquids than with stable colloid particles. Critical emulsions can therefore be hardly classified as colloid or even semicolloid systems.

Micellar solutions, to which soap solutions‡ belong, for example, are of great practical importance, being extremely varied and usually consisting of two or more components, at least one of which exhibits a high surface activity.

The literature devoted to micellar solutions is extremely extensive and contains many theoretical studies. In this review we are unable to discuss them and we shall confine ourselves solely to remarks of a general nature on the problem of the stability of disperse systems. Micelles are known to have different shapes, usually spherical, cylindrical, or lamellar[162]. The surface of cylindrical micelles is non-isotropic (has no circular symmetry) and the properties of the directions along the generatrices of the cylinder differ from those of the directions along the tangents to the perimeters of the normal sections. This can be explained in many instances by an orientation of the dipolar molecules on the surface such that the projection of the dipole moment of the molecules onto the surface of the micelle§ coincides with one of these two directions. For highly extended micelles, these projections should be tangential to the perimeters of sections of the cylindrical surface, according to the conditions for the free energy minimum[164], forming closed chains, and for this reason the external electrostatic field is extremely weak. At the same time if it is assumed by analogy with formula (90) that the formation of a micellar solution from a molecular solution is associated with the dependence of σ on the surface curvature, then, in order to apply Eqn.(91) to cylindrical micelles, it must be generalised by introducing the derivatives of the free interfacial energy with respect to the principal radii of surface curvature, one of which is zero and the other is equal to $1/r$ (r is the radius of the micelle).

IX. THE FORMATION AND STABILITY OF LIQUID FILMS

It is well known that many micellar solutions form liquid-crystal, for example smectic, phases in a particular range of concentrations and temperatures[167,168]. Such systems resemble a layer cake (Fig. 9). Some layers (*W*) consist of the polar, in most cases aqueous, phase, while others (*C*) consist of the hydrocarbon phase; at the interface there are layers of diphilic surface-active molecules oriented with the polar end towards the aqueous phase. The layers of hydrocarbon phase are frequently absent and only oriented bimolecular layers of diphilic molecules (analogous to lipid membranes) are located between adjoining layers of the aqueous phase. The system as a whole has a one-dimensional periodic structure.

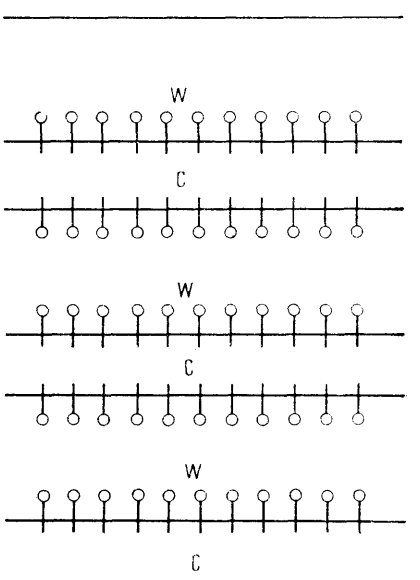


Figure 9. Schematic illustration of a one-dimensional periodic micellar solution.

‡Attention has recently been concentrated on stable microemulsions. They are in essence a variety of micellar solutions.

§The existence of this type of inclination of dipole monolayers is well known and in addition follows from the electro-optical studies of Tolstoi and Spartakov[163,164]; the theory of this phenomenon has been described by Deryagin and Shulepov[165,166].

The same solutions are capable of forming stable thin symmetrical films of the type of foam[169], whose thickness at equilibrium differs, however, from the repeat period of the above liquid-crystal structures even when the latter do not contain non-polar layers[170].

Evidently the task of the theory is to explain the cause of the formation and stability of both smectic structures of this kind and of isolated symmetrical films. The thermodynamic stability of free films, ensured by equilibrium between capillary suction and the wedging pressure, was first demonstrated by Deryagin and Titievskaya[171,172]. In the first place the problem arises of the nature of the repulsion forces which balance the van der Waals component of the wedging pressure, tending to make the layers thinner, and ensure thereby an equilibrium polymolecular thickness of the aqueous layers. The equilibrium thickness of the so-called primary free films, observed at low electrolyte concentrations, is largely determined by ionic-electrostatic repulsion forces and amounts to several hundreds of Angstroms. The primary films are metastable and under certain conditions are either ruptured or are abruptly converted into secondary or Perrin films. Under certain conditions both types of behaviour can coexist, being separated by an interface (in the form of a circle or its arc) at which the thickness of the film changes abruptly[174,175,195]. The secondary films observed at high electrolyte concentrations, at which the electrostatic component of the wedging pressure is infective, have a thickness of approximately 20–60 Å.[173-178]

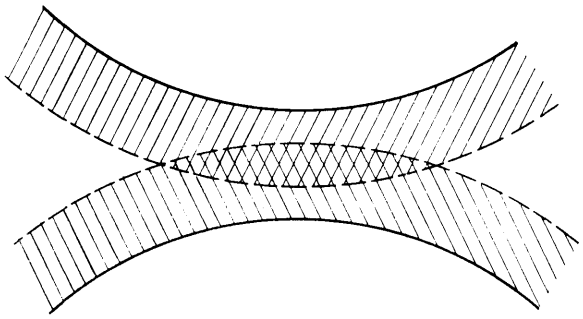


Figure 10. Schematic illustration of the overlap of surface layers.

In the light of the results of a series of experimental studies[179-182], one of the causes of aqueous layers retaining their thickness may be the structural component of the wedging pressure. In essence the same idea was put forward by Clunie et al.[183]. The origin of this component is as follows. The water layers at the interface between the aqueous phase and the hydrophilic surface or hydrophilic functional groups of the molecules adsorbed at the interface acquire under the influence of the latter a structure different from that in the bulk phase. The difference may consist, for example, in a modification of the network of hydrogen bonds and also in the polarisation of the molecular dipoles, which should be promoted by the oriented adsorption of diphilic molecules[184,185]. When the water layer becomes thinner, the boundary layers belonging to both surface layers may overlap (Fig. 10). This overlap should entail the disruption of the unusual structure of the peripheral parts of the boundary layers which leads to an increase in the amount of water with the properties of the bulk phase. This process initiates a change in the free energy of the system, which is inevitably associated with the generation of the wedging pressure. The role of the structural characteristics and the stability of secondary films is confirmed by the fact that aqueous solutions of surfactants, stabilising these films, are capable for forming liquid-crystal phases.

The secondary films are disrupted by the formation of a point break, or spontaneously, or under the influence of a spark, or on passing from α-rays.[169]

The theory of the rupture of secondary films, in the simplest case where the process is unaccompanied by local changes in thickness and takes place in only two dimensions, was developed by Gutop and Deryagin[197]. It is noteworthy that the assumption of a purely two-dimensional flow of all sections of the film during nucleation (the formation of a nuclear hole) constitutes a fairly rough first approximation. This approximation is altogether inapplicable to the primary thicker films, which greatly complicates the construction of a rigorous theory of their rupture or conversion into secondary films.

Theories permitting the calculation of the critical thicknesses and other conditions for the spontaneous conversion of primary films into secondary films have been developed in a number of studies[198-203], but these cannot be described here.

One of the important tasks of the theory of the stability of disperse systems consists in the development of a quantitative theory of the structural component of the wedging pressure. The main difficulty in this task is associated with the fact that the nature of the structure of water, even in the bulk phase, is controversial and cannot be regarded as reliably established.

Another example of a quasi-disperse system with a rigorously periodic structure in one direction is montmorillonite in the state of intracrystalline swelling[186]. The mechanism of the first stage of the swelling process, where the aqueous layer between elementary crystalline network layers, which has a thickness of the order of 10 Å, corresponding to a few molecular layers, may be compared with the formation of liquid-crystal smectic phases accompanied by the appearance of the components of the wedging pressure. At a low ionic strength of the surrounding solution, the second stage of the swelling process, referred to as osmotic, begins. Under the influence of the ionic-electrostatic component of the wedging pressure, aqueous layers can then be formed with an equilibrium thickness ranging from 10–20 to 300 Å, depending on the ionic strength[186]. Measurements of their thickness by X-ray diffraction may serve as a test (in terms of a model) of the theory of interaction of charged surfaces in electrolyte solutions and of the theory of the formation of colloid layer structures, including "schiller" layers.

For small thicknesses, the collective nature of the van der Waals interactions in closely spaced elementary crystalline layers (scales) constitutes in essence a complication, while for large thicknesses and low wedging pressures a complication arises from the mechanical jamming of the scales by the end faces of the adhering neighbouring scales[187]. The study of the state of equilibrium of free symmetrical films, first observed and investigated mainly by the present author and his coworkers[171-178], therefore has many advantages for model investigations. In this case it is possible to vary

the specified wedging pressure and to measure the thicknesses of the film and the aqueous layer by optical methods. A number of experimental studies made it possible to obtain a quantitative conformation of the theory of the electrostatic and van der Waals components of the cleaving pressure [189].

The most complete confirmation of this theory was obtained by Deryagin, Voropaeva, and Kabanov, who used crossed metallic wires in electrolyte solutions, whose potential could be varied by polarisation, as models of the interaction of particles in metal sols [190-194]. Apart from confirming the above theory, these measurements made it possible to determine the van der Waals interaction constant. At the same time lower values of the wedging pressure at the zero charge point and at high (of the order of several moles per litre) concentrations, which are not covered by the theory, were observed. Thus the theory of the wedging pressure of thin layers, which permits the calculation of their equilibrium thicknesses, has been confirmed in certain cases.

X. INTERACTION OF NON-IDENTICAL SURFACES

A theoretical treatment of the stability of disperse systems and thin films was described above for the interaction of surfaces of identical nature and having the same charge. The interaction of surfaces of different kinds and bearing different charges has been examined [204,205]. The following are the most significant theoretical conclusions.

The electrical component of the wedging pressure for surfaces bearing opposite charges is negative for all distances, i.e. corresponds to attraction. Surfaces charged to different potentials of the same sign alter the sign of the interaction from repulsion at long distances to attraction at short distances. The force barrier to mutual approach depends only on the potential of the surface which is charged to the lower potential. The van der Waals component of the wedging pressure of layers between bodies of different kinds may be positive (this conclusion was later confirmed [206,207] within the framework of the macroscopic theory of intermolecular forces). If the surfaces are simultaneously charged to very high potentials of different sign, then the inverse Hardy–Schulze rule is valid: the rapid coagulation threshold occurs as the concentration is decreased to a value inversely proportional to the ionic charge raised to the sixth power (for a symmetrical electrolyte).

This theory of heterocoagulation was developed further in other studies [208,209]. The case of surfaces with specified surface charge densities has also been examined [210-212]. Devereux and de Bruyn [213] published tables for the electrical components of the wedging pressure. Smilga [214] examined the case of an arbitrary mixture of electrolytes. The case of low potentials, examined initially by Deryagin and Levich [215], was later considered in greater detail [216,217].

The theory has received experimental confirmation in a number of studies; in particular, the inversion of the Hardy–Schulze rule was confirmed by Chernoberezhskii [218]. A rigorous quantitative comparison of experiment with theory is hindered mainly by the difficulty of determining the effective surface potential of the particles. Model experiments in which a study was made of the conditions for the mutual adhesion of two mercury drops polarised to different potentials [219, 220] as well as mercury and glass drops [221-223] are of interest in this respect. The mutual adhesion of mercury drops in a hydrocarbon medium was investigated by Srenge and Sonntag [224]. The wedging pressure of the electrolyte layer between the glass and the polarised mercury drop has also been investigated [225]. The theory of heterocoagulation was tested and confirmed [226,227] also by observing the adhesion of disperse particles to a rotating disc. It must be emphasised that heterocoagulation constitutes a wider range of phenomena than homocoagulation, which is its special case. Heterocoagulation constitutes the basis of such major problems as those of flotation [228-231], the purification of water in filters [232], dyeing, the adhesion of biological cells, etc. [233] The development, testing, and application of the heterocoagulation theory therefore undoubtedly merit further attention and efforts (see also Prieve and Ruckenstein [234]).

XI. CONCLUSION

The present review has shown that the theory of the stability of disperse systems and thin films is of the greatest importance for colloid science and for many fields involving surface phenomena. Despite the enormous literature on this problem, published during forty years, there is still much room for its further development and investigation, particularly as regards a quantitative test of the theory. It is also necessary to approach more rigorously the very definition of the concept of the stability of colloids, differentiating strictly its different varieties and aspects and avoiding a one-sided approach.

It must be emphasised that the development of the theory of the stability of colloids and the wedging pressure as its basis also led to progress in solving the purely physical problem of intermolecular forces and the electrochemical problem of the ionic double layer. This stimulating influence of the science of the stability of colloids merits its more detailed consideration in conclusion.

Although it had been known earlier that the molecular interaction in condensed media is non-additive, nevertheless up to 1955 it was generally accepted, following de Boer, Bradley, and Hamaker, that the degree of interaction between macro-objects should be found by integrating pair dispersion interactions with respect to their volumes. The first limitation of this procedure was pointed out by Casimir [235], who developed a more accurate quantum theory of dispersion interactions taking into account the finite rate of propagation of electromagnetic vibrations. As a result, molecular attraction over distances significantly greater than the characteristic length, where the electromagnetic lag is already fully manifested, begins to weaken more rapidly by a single power of the distance.

Casimir was also the first [236] to describe an example of a macroscopic theory of van der Waals forces, having devised it for the case of two metallic plates separated by distances over which the electromagnetic lag is fully manifested. The first study which demonstrated experimentally the inapplicability of the Hamaker method to the calculation of the attraction of macro-objects was that of Deryagin and Abrikosova [237-241]. The force of attraction of a glass (or quartz) lens to a similar plate was first correctly measured in their investigation as a function of the gap separating them¶. It was found that the experimental

¶ Owing to the incomplete elimination of random electrical charges, the measurements of Overbeek and Sparnay [242] published simultaneously were erroneous. They yielded attraction forces exceeding by a factor of thousands the true molecular attraction and were even greater than the value yielded by calculation without allowance for the electromagnetic lag.

attraction force in the range of gaps 500–5000 Å is much weaker than the value obtained when Hamaker's formula is applied. This result led Lifshits[243] to develop a macroscopic theory of van der Waals forces acting between macro-objects of any kind.

The experimental data agreed, within the limits of the error of the measurements, with data calculated from the formulae for the complete manifestation of the electromagnetic lag. Subsequently Deryagin and Abrikosova carried out measurements on another object (the quartz–chromium pair and the NaBr–NaI mixed crystal) and in all cases agreement between theory and experiment was demonstrated[244,245]. An analogous conclusion was arrived at later by experimenters using other methods. Recently it has been possible to extend the treatment also to the range of gaps for which the limiting laws neglecting the electromagnetic gap are valid[246,247]. In particular, measurements have been made for the first time on the molecular attraction between two metallic objects[248,249].

The reader is referred to reviews[250,277] of experimental studies and further theoretical developments, while here the following remarks will be made.

Dzyaloshinskii et al.[251] extended the theory to the case where the interacting plates are immersed in any medium, which is of particular interest for colloid science. Here it is important that the general formulae make it possible to calculate beforehand the interaction force, provided that the characteristic regions of the optical absorption spectra of both bodies and the medium are known. This possibility has been tested experimentally in many instances and is exceptionally valuable for the theory of the stability of disperse systems.

Recent studies, designed to develop further the theory of the electrical double layer (DL), took into account the influence of the intrinsic volume of ions and pair correlations on the DL structure[252], of the polarisation of DL on electrophoresis and diffusiophoresis[253], of adsorbed ions on the structure and polarisability of DL [254]; the problems of the discrete nature of DL [255], of the determination of the surface potential of spherical particles,[256] and of the comparison of the constant surface potential and constant surface charge conditions in the DLVO theory[257] have been examined. Furthermore, the results of studies of the interaction of DL of charged surfaces have been published: for a solution of a mixture of electrolytes[258], for planar particles in concentrated dispersions with a dispersion medium having a low dielectric constant[260], for constant surface charges[49,263], and for a constant potential of one surface and a constant charge of another[264,266].

In a number of studies an interesting attempt has been made at a unified treatment of the interaction energy (van der Waals attraction and electrostatic repulsion) of charged surfaces[267,268]; the low-frequency electromagnetic fluctuations and the statistical charge distribution between two plates have been examined jointly[269,270] and account has been taken of the influence of the dielectric constant of the medium on the energy of an ion near the interface[271]. The method of images has been used[272] to calculate the interaction energy of two different dielectrics separated by a layer of a third dielectric. The interaction of surfaces with energetic and geometrical inhomogeneities has been examined[273,274]. Reviews of the literature on the surface forces in disperse systems have been published[275-278]. The stability of black hydrocarbon films has been comprehensively examined in the monograph by Kruglyakov and Rovin[279]. Various questions of the stability of colloids have been discussed[280]. The wedging pressure of liquid-crystal films has been considered[281].

REFERENCES

1. A. March, Kolloid. Z., 45, 97 (1928).
2. H. Schulze, J. prakt. Chem., (2), 25, 431 (1882).
3. H. Schulze, J. prakt. Chem., 27, 320 (1883).
4. S. E. Linder and H. Picton, J. Chem. Soc., 67, 62 (1892).
5. S. E. Linder and H. Picton, J. Chem. Soc., 87, 1906 (1905).
6. H. Schulze, J. prakt. Chem., 27, 323 (1883).
7. W. B. Hardy, Proc. Roy. Soc., 66, 110 (1900).
8. W. B. Hardy, Z. phys. Chem., 33, 385 (1900).
9. Yu. M. Glazman, Kolloid. Zhur., 24, 275 (1962).
10. Yu. M. Glazman, Discuss. Faraday Soc., 42, 255 (1966).
11. W. B. Hardy, Proc. Roy. Soc., 66, 110 (1900).
12. W. B. Hardy, Z. phys. Chem., 33, 385 (1900).
13. E. F. Burton, Phil. Mag., 11, 425 (1906).
14. E. F. Burton, Phil. Mag., 12, 472 (1906).
15. E. F. Burton, Phil. Mag., 17, 583 (1909).
16. H. Freundlich, "Kappillarchemie", Akadem. Verlagsges., Leipzig, 1932, Vol. II.
17. H. R. Kruyt and H. G. Bungenberg de Jong, Z. phys. Chem., 100, 250 (1922).
18. H. R. Kruyt and H. G. Bungenberg de Jong, Kolloidchem. Beihefte, 28, 1 (1928).
19. H. Kallmann and M. Willstätter, Naturwiss., 20, 952 (1932).
20. J. H. de Boer, Trans. Faraday Soc., 32, 21 (1936).
21. H. C. Hamaker, Rec. Trav. chim., 55, 1015 (1936).
22. H. C. Hamaker, Rec. Trav. chim., 56, 727 (1937).
23. H. C. Hamaker, Chem. Weekblad., 35, 47 (1938).
24. H. C. Hamaker, Rec. Trav. chim., 55, 1015 (1936).
25. H. C. Hamaker, Rev. Trav. chim., 56, 3 (1937).
26. B. V. Deryagin, Izv. Akad. Nauk SSSR, OMEN, Ser. Khim., 1119 (1937).
27. B. V. Deryaguin, Acta Physicochim. URSS, 10, 333 (1939).
28. B. V. Derjaguin, Trans. Faraday Soc., 36, 730 (1940).
29. B. V. Deryagin, Kolloid Zhur., 6, 291 (1940).
30. I. Langmuir, J. Chem. Phys., 6, 885 (1938).
31. E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids, Elsevier Publ., New York–Amsterdam, 1948, p. 92.
32. I. E. Tamm, "Osnovy Teorii Elektrichestva" (Principles of the Theory of Electricity), Gos. Izd. Tekh.-Teor. Lit., Moscow, 1954 § 34.
33. A. J. Babchin, J. Colloid. Interface. Sci., 49, 390 (1974).
34. B. V. Derjaguin, J. Colloid. Interface. Sci., 56, 492 (1976).
35. B. V. Deryagin, Kolloid Zhur., 37, 1015 (1975).
36. G. Bell and S. Levine, J. Colloid. Interface Sci., 56, 218 (1976).
37. B. V. Derjaguin, Kolloid Z., 69, 155 (1934).
38. N. Fuchs, Z. Physik, 89, 735 (1934).
39. B. V. Derjaguin, Trans. Faraday Soc., 36, 731 (1940).
40. B. V. Deryagin, Kolloid Zhur., 7, 285 (1941).
41. H. Eilers and J. Korff, Chem. Weekblad., 33, 358 (1936).
42. H. Eilers and J. Korff, Trans. Faraday Soc., 36, 229 (1940).
43. F. Powis, Z. phys. Chem., 89, 186 (1915).
44. B. V. Derjaguin and S. S. Dukhin, Bull. Inst. Mining and Metallurg. (London), No. 651 (1961).

45. B.V.Derjaguin and S.S.Dukhin, Transact. Inst. Mining and Metallurg. (London), 70, pt 5, 221 (1960–1961).
46. B.V.Deryagin and N.D.Shukakidze, Dokl.Akad. Nauk SSSR, 134, 376 (1960).
47. B.V.Derjaguin and N.D. Chukakidze, Bull. Inst.Mining and Metallurg., No.656 (1961).
48. B.V.Derjaguin and N.D. Chukakidze, Trans. Inst. Mining and Metallurg.(London), pt 10, 569 (1960–1961).
49. P.Bergmann, P. Löw–Beer, and H. Zocher, Z.phys. Chem., A181, 301 (1938).
50. A.N. Frumkin, Trans. Faraday Soc., 36, 79 (1940).
51. J. Langmuir, Science, 88, 430 (1938).
52. B.V.Derjaguin and L.D. Landau, Acta Physicochim. URSS, 14, 633 (1941).
53. B.V.Deryagin and L.D. Landau, Zhur. Eksper. Teor. Fiz., 11, 802 (1941); 15, 663 (1945).
54. S. Levine, Proc.Roy.Soc., A170, 145, 165 (1939).
55. S. Levine, J. Chem. Phys., 7, 831 (1939).
56. S. Levine and G. P.Dube, Compt.rend., 208, 1812 (1939).
57. S. Levine and G. P.Dube, Trans. Faraday Soc., 35, 1125, 1141 (1939).
58. A.J. Corkill and L.Rosenhead, Proc.Roy.Soc., A172, 410 (1939).
59. E.J.W. Verwey and J.T.G. Overbeek, See Ref. 31, p. 51.
60. V.M. Muller, Symposium, "Issledovaniya v Oblasti Poverkhnostykh Sil" (Studies on Surface Forces), Izd. Nauka, Moscow, 1967, p. 270.
61. V.M. Muller, Kolloid Zhur., 31, 427 (1969).
62. V.M. Muller, Symposium, "Poverkhnostnye Sily i Ustoichivost' Kolloidov" (Surface Forces and Stability of Colloids), Izd. Nauka, Moscow, 1974, p. 245.
63. B.V. Deryagin, Trans. Faraday Soc., 36, 203 (1940).
64. B.V. Deryagin, Kolloid Zhur., 6, 293 (1940).
65. E.J.W. Verwey and J.T.G. Overbeek, See Ref. 31, p. 63.
66. V.N. Shilov, Kolloid Zhur., 34, 147 (1972).
67. V.N. Shilov, Kolloid Zhur., 37, 1143 (1975).
68. J.E. Jones and S. Levine, J. Colloid. Interface Sci., 30, 241 (1969).
69. S.S. Dukhin, B.V. Deryagin, and N.M. Semenikhin, Dokl. Akad. Nauk SSSR, 192, 357 (1970).
70. Y. Ikeda, J. Phys. Soc. Japan, 8, 49 (1953).
71. E. L. Mackor, Rec. Trav. chim., 70, 717 (1951).
72. B.V. Deryagin, Kolloid Zhur., 39, 1139 (1977).
73. B.V. Deryagin and E.V. Obukhov, Kolloid Zhur., 1, 385 (1935).
74. B.V. Derjaguin and E.V. Obuhov, Acta Physicochim. URSS, 5, 1 (1936).
75. B.V. Deryagin and M. M. Kusakov, Izv. Akad. Nauk SSSR, OMEN, Ser. Khim., 1121 (1937).
76. B.V. Derjaguin and M. M. Kusakov, Acta Physicochim. URSS, 10, 25, 153 (1939).
77. B.V. Deryagin and N.V. Churaev, Kolloid Zhur., 38, 438 (1976).
78. B.V. Derjaguin, Kolloid Z. u. Z. Polymere, 263, 492 (1975).
79. D.H. Napper and R. J. Hunter, in "MTP Internat. Rev. Sci. Phys. Chem.", Ser. 1, Vol. 7 (Edited by A. Buckingham and M. Kerker), 1972, p. 280.
80. R.H. Ottewill, in Annual. Rep. Progr. Chem., Sect. A, 66, 183 (1969) (publ. 1970).
81. V.M. Muller, Kolloid Zhur., 31, 548 (1969).
82. Yu. M. Glazman and I. M. Dykman, Kolloid. Zhur., 24, 382 (1962).
83. Yu. M. Glazman and I. M. Dykman, Kolloid Zhur., 25, 282 (1963).
84. O.G. Us'yarov, Kolloid Zhur., 37, 79 (1975).
85. H.R. Kruyt (Editor), "Colloid Science" Amsterdam, 1952, Vol. 1; Russian Translation Inostr. Lit., Moscow, 1955.
86. H. Reerink and J.T.G. Overbeek, Discuss. Faraday Soc., 18, 74 (1954).
87. B.V. Deryagin, Discuss. Faraday Soc., 42, 307 (1966) (Summary and Remarks).
88. G.A. Martynov and V.M. Muller, Kolloid Zhur., 34, 878 (1972).
89. G.A. Martynov and V.M. Muller, Symposium, "Poverkhnostnye Sily v Tonkikh Plenkakh i Dispersnykh Sistemakh" (Surface Forces in Thin Films and Disperse Systems), Izd. Nauka, Moscow, 1972, p. 7.
90. K. Norrish, Discuss. Faraday Soc., 18, 120 (1954).
91. M.V. Serebrovskaya, O.G. Us'yarov, and V.M. Muller, Kolloid Zhur., 34, 730 (1972).
92. H. Van Olphen, "An Introduction to Clay Colloid Chemistry", Interscience, New York, 1963.
93. Croat. Chem. Acta, 42, No. 2 (1970).
94. S. Okamoto and S. Hachisu, J. Colloid. Interface Sci., 62, 172 (1977).
95. Yu. I. Yalamov, Symposium, "Issledovaniya v Oblasti Poverkhnostykh Sil" (Studies on Surfaces Forces), Izd. Nauka, Moscow, 1964, p. 113.
96. P. Richmond, J. Chem. Soc. Faraday Trans. II, 71, 1154 (1975).
97. B.V. Deryagin and V.M. Muller, Dokl. Akad. Nauk SSSR, 225, 601 (1975).
98. J.T.G. Overbeek, in "Colloid Science", Vol. 1 (Edited by H.R. Kruyt), Elsevier Publ., Amsterdam, 1952, p. 333.
99. L.H. Princen and W.H. Kwolk, Rev. Sci. Instr., 36, 646 (1956).
100. P. Favelen and H. Smith, J. Colloid. Interface Sci., 45, 100 (1973).
101. B.V. Deryagin and G.Ya. Vlasenko, Dokl. Akad. Nauk SSSR, 63, 155 (1948).
102. B.V. Deryagin and G.Ya. Vlasenko, Kolloid Zhur., 13, 249 (1951).
103. B.V. Derjaguin and G.Ya. Vlasenko, J. Colloid Sci., 17, 605 (1962).
104. B.V. Deryagin and N.M. Kudryavtseva, Kolloid Zhur., 25, 739 (1963).
105. B.V. Derjaguin and Kudryavceva, J. Colloid Interface Sci., 17, 605 (1962).
106. B.V. Derjaguin and N.M. Kudryavceva, in "The Law of Mass-Action, A Centenary Volume", Oslo, 1964, p. 79.
107. B.V. Deryagin and N.M. Kudryavtseva, Kolloid Zhur., 26, 61 (1964).
108. P. Fadven and A. Smith, J. Colloid. Interface Sci., 45, 573 (1973).
109. B.V. Deryagin and V.M. Muller, Dokl. Akad. Nauk SSSR, 176, 869 (1967).
110. B.V. Derjaguin and V.M. Muller, J. Colloid. Interface Sci., 56, 154 (1976).
111. B.V. Derjaguin and V.M. Muller, J. Colloid. Interface Sci., 36, 97 (1971).
112. E.P. Honig, G.J. Roebersen, and P.H. Wiersoma, J. Colloid. Interface Sci., 36, 97 (1971).
113. N.M. Kudryavtseva, G.A. Martynov, B.V. Deryagin, and S.F. Vanaev, Kolloid Zhur., 36, 1173 (1976).

114. Yu. M. Glazman and I. M. Dykman, Dokl. Akad. Nauk SSSR, **100**, 299 (1955).
115. Yu. M. Glazman and I. M. Dykman, Kolloid Zhur., **18**, 13 (1956).
116. Yu. M. Glazman, I. M. Dykman, and E.A.Strel'tsova, Kolloid Zhur., **20**, 149 (1958).
117. V. M. Barboi, Yu. M. Glazman, and I. M. Dykman, Kolloid Zhur., **23**, 381 (1961).
118. V. M. Barboi and Yu. M. Glazman, Symposium, "Issledovaniya v Oblasti Poverkhnostykh Sil" (Studies on Surface Forces), Izd. Nauka, Moscow, 1967, p. 207.
119. E. F. Zhelovich, Yu. M. Glazman, V. M. Barboi, and V. B. Barboi, Kolloid Zhur., **31**, 831 (1969).
120. S. Levine and J. E. Jones, Kolloid. Z. u Z. Polymere, **230**, 306 (1969).
121. E. Bresler, J. Colloid. Interface Sci., **33**, 278 (1970).
122. I. Langmuir, J. Chem. Phys., 6, 893 (1938).
123. E. J. W. Verwey and J. T. G. Overbeek, "Theory of the Stability of Lyophobic Colloids", Elsevier Publ., 1948, p. 125.
124. I. F. Efremov, "Periodicheskie Kolloidnye Struktury" (Periodic Colloid Structures), Izd. Khimiya, Leningrad, 1971.
125. I. F. Efremov, Symposium, "Uspekhi Kolloidnoi Khimii" (Advances in Colloid Chemistry), Izd. Nauka, Moscow, 1973, p. 30.
126. I. F. Efremov, in "Surface and Colloid. Science" (Edited by E. M. Matijevic), Wiley, New York, 1975, Vol. 8, Chapter 2.
127. I. F. Efremov and O. G. Us'yarov, Uspekhi Khim., **45**, 877 (1976) [Russ. Chem. Rev., No. 5 (1976)].
128. I. F. Efremov and S. V. Nerpin, Dokl. Akad. Nauk SSSR, **113**, 846 (1957).
129. I. F. Efremov and S. V. Nerpin, Kolloid Zhur., **19**, 757 (1957).
130. G. M. Lukashenko, I. F. Efremov, and O. G. Us'yarov, Symposium, "Poverkhnostnye Sily v Tonkikh Plenkakh i Dispersnykh Sistemakh" (Surface Forces in Thin Films and Disperse Systems), Izd. Nauka, Moscow, 1972, p. 35.
131. A. Kose, M. Ozaki, K. Takano, J. Kobayashi, and S. H. Hachisu, J. Colloid. Interface Sci., **44**, 330 (1973).
132. J. F. Hamilton and F. A. Hamm, J. Appl. Phys., **27**, 190 (1956).
133. P. A. Hiltner and I. M. Krieger, J. Phys. Chem., **73**, 2386 (1969).
134. J. W. Vanderhoff, H. J. Van den Hul, R. J. M. Tausk, and J. T. G. Overbeek, "Clean Surfaces: Theory Preparation and Characterisation for Interfacial Studies" (Edited by G. Goldfinger), Marcell Decker, New York, 1970, p. 15.
135. S. Rohrsetzer, I. Kerek, and E. Wolfram, Kolloid. Z. u. Z. Polymere, **245**, 529 (1971).
136. M. S. El-Aasser and A. A. Robertson, Kolloid. Z. u. Z. Polymere, **251**, 241 (1973).
137. J. G. Kirkwood, J. Chem. Phys., 7, 919 (1939).
138. B. J. Alder, W. G. Hoover, and D. A. Young, J. Chem. Phys., **49**, 3688 (1968).
139. S. Hachisu, Y. Kobayashi, and A. Kose, J. Colloid. Interface Sci., **42**, 342 (1973).
140. A. Kose and S. Hachisu, J. Colloid. Interface Sci., **46**, 460 (1974).
141. S. Hachisu and J. Kobayashi, J. Colloid. Interface Sci., **46**, 470 (1974).
142. J. D. Bernal and J. Fankuchen, J. Gen. Physiol., **25**, 111 (1941).
143. S. Okamoto and S. Hachisu, J. Colloid. Interface Sci., **43**, 30 (1973).
144. I. B. Donnet, J. Polym. Sci., **12**, 53 (1954).
145. L. Onsager, Ann. New York. Acad. Sci., **51**, 627 (1949).
146. J. E. Mayer and M. G. Mayer, "Statistical Mechanics", John Wiley, New York, 1940.
147. V. Parsegian and S. Brenner, Nature, **259**, 632 (1976).
148. A. Isachara, J. Chem. Phys., 18, 1446 (1950).
149. A. Isachara, J. Chem. Phys., **19**, 1142 (1951).
150. E. D. Shchukin and P. A. Rebinder, Kolloid Zhur., **20**, 645 (1958).
151. A. V. Pertsov, L. I. Mirnin, N. V. Pertsov, and E. D. Shchukin, Dokl. Akad. Nauk SSSR, **158**, 1166 (1964).
152. V. M. Barboi, Yu. M. Glazman, P. A. Rebinder, G. I. Fuks, and E. D. Shchukin, Kolloid Zhur., **32**, 321 (1970).
153. A. I. Rusanov, E. D. Shchukin, and P. A. Rebinder, Kolloid Zhur., **30**, 573 (1968).
154. Yu. M. Glazman, Kolloid Zhur., **30**, 804 (1968).
155. L. M. Shcherbakov, Symposium, "Issledovaniya v Oblasti Poverkhnostykh Sil" (Studies on Surface Forces), Izd. Nauk, Moscow, 1964, p. 17.
156. R. C. Tolman, J. Chem. Phys., **16**, 758 (1948).
157. M. Volmer, Z. phys. Chem., **125**, 151 (1927).
158. M. Volmer, Z. phys. Chem., **135**, 281 (1931).
159. M. Volmer, Z. phys. Chem., **206**, 181 (1957).
160. E. D. Shchukin, N. P. Fedoseeva, L. A. Kachanova, and P. A. Rebinder, Dokl. Akad. Nauk SSSR, **189**, 123 (1969).
161. L. A. Kachanova, N. P. Fedoseeva, V. M. Kuchumova, A. V. Pertsov, and P. A. Rebinder, Kolloid Zhur., **35**, 838, 843 (1973).
162. P. A. Winsor, Chem. Rev., 68, 2 (1968).
163. N. A. Tolstoi, A. A. Spartakov, and A. A. Trusov, Symposium, "Issledovaniya v Oblasti Poverkhnostykh Sil" (Studies on Surface Forces), Izd. Nauka, Moscow, 1967, p. 56.
164. N. A. Tolstoi, E. L. Kitanina, A. A. Trusov, E. V. Rudakova, and A. A. Spartakov, Kolloid Zhur., **35**, 497 (1973).
165. B. V. Deryagin and Yu. V. Shulepov, Kolloid Zhur., **38**, 245 (1976).
166. Yu. V. Shulepov and B. V. Deryagin, Kolloid Zhur., **38**, 1143 (1976); Surface Sci., **81**, 149 (1979).
167. S. Friberg, in "Advances in Liquid Crystals", Acad. Press, New York, 1976, Vol. 2, p. 173.
168. S. Friberg, J. Colloid. Interface Sci., **55**, 614 (1976).
169. K. K. J. Mysels, J. Gen. Physiol., **52**, 113 (1968).
170. K. Roberts, Nature, **253**, 52 (1975).
171. B. V. Deryagin and A. S. Titievskaya, Dokl. Akad. Nauk SSSR, 89, 1041 (1953).
172. B. V. Derjaguin and A. S. Titijevskaia, Discuss. Faraday Soc., No. 18, 27 (1954).
173. B. V. Deryagin and A. S. Titievskaya, Kolloid Zhur., **22**, 398 (1960).
174. B. V. Derjaguin and A. S. Titijevskaia, "Proceedings of the IInd International Congress on Surface-Active Substances", Butterworths, London, 1957, Vol. 1, p. 211.
175. B. V. Derjaguin, J. Colloid. Interface Sci., 19, 119 (1964).
176. A. D. Sheludko, Dokl. Akad. Nauk SSSR, **123**, 1074 (1958).

177. J. M. Corkill, J. F. Goodman, D. K. Haisman, and S. P. Harrold, Trans. Faraday Soc., 57, 821 (1961).
178. J. M. Corkill, J. F. Hoodman, and C. P. Ogden, Trans. Faraday Soc., 6, 583 (1965).
179. B. V. Deryagin and Z. M. Zorin, Zhur. Fiz. Khim., 29, 1010, 1755 (1955).
180. B. V. Derjaguin and Z. M. Zorin, "Proceedings of the IInd International Congress on Surface-Active Substances", Butterworths, London, 1957, Vol. 2, p. 145.
181. B. V. Derjaguin, Chem. Scripta Acta (Sweden), 9, 97 (1976).
182. B. V. Derjaguin and N. V. Churaev, J. Colloid. Interface Sci., 49, 249 (1974).
183. J. S. Clunie, J. F. Goodman, and P. C. Symons, Nature, 216, 1203 (1967).
184. S. Friberg, J. Colloid. Interface Sci., 47, 291 (1973).
185. T. Waöler, J. Colloid. Interface Sci., 45, 372 (1973).
186. K. Norrish, Discuss Faraday Soc., 18, 120 (1954).
187. H. Van Olphen, J. Colloid. Interf. Sci., 17, 660 (1962).
188. A. D. Sheludko, Dokl. Akad. Nauk SSSR, 127, 149 (1959).
189. A. D. Scheludko, Adv. Colloid. Interface Sci., 1, 391 (1967).
190. B. V. Deryagin, T. N. Voropaeva, and B. N. Kabanov, Dokl. Akad. Nauk SSSR, 128, 981 (1959).
191. B. V. Deryagin, T. N. Voropaeva, and B. N. Kabanov, Kolloid Zhur., 24, 396 (1962).
192. B. V. Derjaguin and T. N. Voropaeva, J. Colloid. Interface Sci., 19, 113 (1964).
193. B. V. Deryagin and Ya. I. Rabinovich, Kolloid Zhur., 31, 47 (1969).
194. B. V. Deryagin, V. M. Muller, and Ya. I. Rabinovich, Kolloid Zhur., 31, 304 (1969).
195. M. Van den Tempel, J. Colloid. Interface Sci., 13, 125 (1958).
196. D. Exerova, Compt. rend. Acad. Bulg. Sci., 23, 547 (1970).
197. B. V. Deryagin and Yu. V. Gutop, Kolloid Zhur., 24, 431 (1962).
198. A. J. De Vries, Rec. Trav. chim., 77, 783 (1958).
199. A. Scheludko, Z. Elektrochem., 61, 220 (1957).
200. A. Scheludko, Proc. Konikl. Ned. Akad. Wet., B65, 87 (1962).
201. A. D. Sheludko, Symposium, "Uspekhi Kolloidnoi Khimii" (Advances in Colloid Chemistry), Izd. Nauka, Moscow, 1973, p. 51.
202. A. Vrij, J. Colloid Sci., 19, 1 (1964).
203. A. Vrij and J. Th. G. Overbeek, J. Amer. Chem. Soc., 90, 3074 (1968).
204. B. V. Deryagin, Kolloid Zhur., 16, 425 (1954).
205. B. V. Derjaguin, Discuss. Faraday Soc., 18, 85 (1954).
206. I. E. Dzyaloshinskii, E. M. Lifshits, and L. P. Pitaevskii, Zhur. Eksper. Teor. Fiz., 37, 229 (1959).
207. I. E. Dzyaloshinskii, E. M. Lifshits, and L. P. Pitaevskii, Uspekhi Fiz. Nauk, 73, 394 (1961).
208. O. F. Devereux and P. L. de Bruyn, J. Chem. Phys., 37, 2147 (1962).
209. O. F. Devereux and P. L. de Bruyn, J. Colloid. Sci., 19, 302 (1964).
210. S. Usui, "Heterocoagulation" in "Progress in Surface and Membrane Science", Acad. Press, New York, 1972, Vol. 5, p. 223.
211. G. R. Wiese and T. W. Healy, Trans. Faraday Soc., 66, 490 (1970).
212. R. J. Rugh and J. A. Kitchener, J. Colloid. Interface Sci., 35, 1656 (1971).
213. O. F. Devereux and P. L. de Bruyn, "Interaction of Plane-Parallel Double Layers", M. I. T. Press, Cambridge, Massachusetts, 1963.
214. V. P. Smilga, Kolloid. Zhur., 22, 615 (1960).
215. B. V. Deryagin and V. G. Levich, Dokl. Akad. Nauk SSSR, 98, 985 (1954).
216. R. Hogg, T. W. Healy, and D. W. Fuerstenau, Trans. Faraday Soc., 62, 1638 (1966).
217. A. Bleier and E. Matijevic, J. Colloid. Interface Sci., 55, 510 (1976).
218. Yu. M. Chernoberezhskii and E. V. Golikova, Kolloid Zhur., 36, 115 (1974).
219. A. Watanabe and R. Gotoh, Kolloid. Z. Polymere, 191, 36 (1963).
220. A. Watanabe, M. M. Matsumoto, and R. Gotoh, Kolloid. Z. Polymere, 201, 147 (1965).
221. S. Usui, T. Yamasaki, and J. Shimoiizaka, J. Phys. Chem., 71, 3195 (1967).
222. S. Usui and T. Yamasaki, J. Colloid. Interface Sci., 29, 629 (1969).
223. A. V. Gorodetskaya, A. N. Frumkin, and A. S. Titievskaya, Zhur. Fiz. Khim., 21, 675 (1947).
224. K. Strenge and H. Sonntag, Tenside, 6, 61 (1969).
225. B. V. Deryagin, A. V. Gorodetskaya, A. S. Titievskaya, and V. N. Yashin, Kolloid Zhur., 23, 535 (1961).
226. J. K. Marshall and J. A. Kitchener, J. Colloid. Interface Sci., 22, 342 (1966).
227. G. E. Clint, J. H. Clint, J. M. Corkill, and T. Walker, J. Colloid. Interface Sci., 44, 121 (1973).
228. B. V. Deryagin and V. D. Samygin, in "Sbornik Trudov Gintsvetmeta" (Collected Reports from the State Institute for Non-Ferrous Metals), Metallurgizdat, Moscow, 1962, No. 19, p. 240.
229. B. V. Deryagin and V. D. Samygin, Kolloid Zhur., 26, 179 (1964).
230. B. V. Deryagin, S. S. Dukhin, and N. N. Rulev, Kolloid Zhur., 38, 251, 1015 (1976).
231. A. Bleier, E. D. Gooddard, and R. D. Kulkarni, J. Colloid. Interface Sci., 59, 490 (1977).
232. S. S. Dukhin, O. D. Kurilenko, and V. D. Grebenyuk, Kolloid Zhur., 37, 859 (1975).
233. C. J. van Oss, R. J. Good, A. W. Neumann, J. D. Wieser, and P. Risenberg, J. Colloid. Interface Sci., 59, 505 (1977).
234. D. C. Prieve and E. Ruckenstein, J. Colloid. Interface Sci., 63, 317 (1978).
235. H. G. Casimir and D. Polder, Phys. Rev., 73, 360 (1948).
236. H. B. G. Casimir, Proc. Kon. Ned. Akad. Wetenschap., 51, 793 (1948).
237. B. V. Deryagin and I. I. Abrikosova, Dokl. Akad. Nauk SSSR, 90, 1055 (1953).
238. B. V. Derjaguin, J. Chem. Soc. Faraday Discuss., No. 18, 24 (1954).
239. B. V. Deryagin and I. I. Abrikosova, Dokl. Akad. Nauk SSSR, 108, 214 (1956).
240. B. V. Deryagin and I. I. Abrikosova, Zhur. Tekh. Fiz., 21, 945 (1951).
241. B. V. Deryagin and I. I. Abrikosova, Zhur. Eksper. Teor. Fiz., 30, 993 (1956); 31, 3 (1957).
242. J. T. Overbeek and M. J. Sparnay, J. Colloid. Interface Sci., 7, 343 (1952).
243. E. M. Lifshits, Zhur. Eksper. Teor. Fiz., 29, 94 (1955).
244. B. V. Deryagin, I. I. Abrikosova, and E. M. Lifshits, Uspekhi Fiz. Nauk, 64, 493 (1958).

245. B. V. Derjaguin and I. I. Abrikosova, J. Phys. Chem. Solids, 5, 1 (1958).
246. D. Tabor and R. H. S. Winterton, Nature, 219, 1120 (1968).
247. J. M. Israelachvili and D. Tabor, Nature, Phys. Sci., 236, 106 (1972).
248. Ya. I. Rabinovich, B. V. Deryagin, and N. V. Churaev, Dokl. Akad. Nauk SSSR, 233, 349 (1977).
249. B. V. Derjaguin, Ya. I. Rabinovich, and N. B. Churaev, Nature, Phys. Sci., 265, 520 (1977); 272, 313 (1978).
250. Yu. S. Barash and V. L. Ginzburg, Uspekhi Fiz. Nauk, 116, 5 (1975).
251. I. E. Dzyaloshinskii, E. M. Lifshits, and L. P. Pitaevskii, Uspekhi Fiz. Nauk, 73, 381 (1961).
252. G. A. Martynov, Symposium, "Uspekhi Kolloidnoi Khimii" (Advances in Colloid Chemistry), Izd. Nauka, Moscow, 1973, p. 86.
253. S. S. Dukhin, Symposium, "Uspekhi Kolloidnoi Khimii" (Advances in Colloid Chemistry), Izd. Nauka, Moscow, 1973, p. 98.
254. G. M. Bell and P. L. Levine, J. Colloid. Interface Sci., 41, 275 (1972).
255. I. S. Zhiguleva and V. P. Smilga, Symposium, "Poverkhnostnye Sily v Tonkikh Plenkakh i Ustoichivost' Kolloidov" (The Surface Forces in Thin Films and the Stability of Colloids), Izd. Nauka, Moscow, 1974, p. 220.
256. S. L. Brenner and R. E. Roberts, J. Phys. Chem., 20, 77 (1973).
257. J. E. Jones and S. Levine, J. Colloid. Interface Sci., 90, 241 (1969).
258. S. Levine and J. E. Jones, Kolloid. Z., Z. Polymere, 230, 306 (1969).
259. E. Bresler, J. Colloid. Interface Sci., 33, 278 (1970).
260. C. S. Chen and S. Levine, J. Chem. Soc. Faraday Trans., 11, 68, 1497 (1972).
261. C. S. Chen and S. Levine, J. Colloid. Interface Sci., 43, 599 (1973).
262. S. Levine, Croat. Chem. Acta, 42, 377 (1970).
263. R. Hogg, T. W. Healy, and D. W. Fuerstenau, Trans. Faraday Soc., 64, 1638 (1966).
264. R. G. Wiese and T. W. Healy, Trans. Faraday Soc., 66, 490 (1970).
265. N. F. H. Ho, H. Toguchi, and W. J. Higuchi, J. Pharm. Sci., 62, 851 (1973).
266. Hiroyuki Ohshima, Kolloid. Z. u. Z. Polymere, 252, 158 (1974).
267. G. M. Bell and G. C. Peterson, J. Colloid. Interface Sci., 41, 542 (1972).
268. G. Kar, S. Schandor, and T. S. Mika, J. Colloid. Interface Sci., 44, 347 (1973).
269. E. Barouch, J. W. Perram, and E. R. Smith, Stud. Appl. Math., 52, 175 (1973).
270. E. Barouch, J. W. Perram, and E. R. Smith, Proc. Roy. Soc., A334, 49 (1973).
271. J. W. Perram and M. N. Barber, Molec. Phys., 28, 131 (1974).
272. R. A. Graig, J. Chem. Phys., 60, 3523 (1974).
273. F. S. Kaplan, I. F. Efremov, and O. G. Us'yarov, Symposium, "Poverkhnostnye Sily v Tonkikh Plenkakh i Ustoichivost' Kolloidov" (The Surface Forces in Thin Films and the Stability of Colloids), Izd. Nauka, Moscow, 1974, p. 131.
274. F. S. Kaplan and O. G. Us'yarov, Kolloid Zhur., 36, 258 (1970).
275. I. N. Izraelashvili and B. W. Ninham, J. Colloid. Interface Sci., 58, 14 (1977).
276. I. Mahanty and B. W. Ninham, "Dispersion Forces", Acad. Press, London–New York, 1976.
277. V. A. Parsegian, in IUPAC Commission 1.6 Colloid and Surface Chemistry (Enriching Topics from Colloid and Surface Science) (Edited by H. van Olphen, and K. J. Mysels), La Jolla, New York, 1975.
278. R. H. Ottewill, J. Colloid. Interface Sci., 58, 357 (1977).
279. P. M. Kruglyakov and Yu. G. Rovin, "Fiziko-Khimiya Chernykh Uglevodorodnykh Plenok" (The Physical Chemistry of Black Hydrocarbon Films), Izd. Nauka, Moscow, 1978.
280. J. Chem. Soc. Faraday Discuss., No. 65 (1978).
281. E. Perez, J. Proust, L. Ter Minassian-Saraga, and E. Manev, Colloid Polymer Sci., 255, 1003, 1133 (1977).

Institute of Physical Chemistry,
USSR Academy of Sciences, Moscow