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The Long-range Interaction between Colloid and other Particles and the Formation of Periodic Colloid Structures

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The general relations governing the formation of gel-like systems in electrolyte solutions have been formulated for particles of different size and shape. Comparison of the results of numerous experimental studies with data derived by theoretical analysis confirms the decisive role of long-range forces in the formation of periodic colloid structures and the extensive occurrence of these structures in nature and in technology. Peptisation, thixotropic processes, and syneresis as well as the phenomenon of reversibility in the formation of periodic colloid structures are examined and methods for estimating the interaction forces between dispersed particles are discussed on the basis of the rheological properties of periodic colloid structures.
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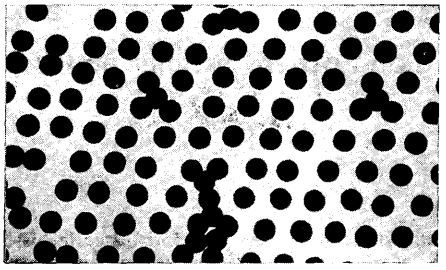
I. INTRODUCTION

By virtue of their unusual physicomechanical properties and characteristic capacity for thixotropic transformations, peptisation, and syneresis, periodic colloid structures (PCS), i.e. tactoids, heterogeneous gels, and gel-like systems, have for a long time attracted the continuous attention of investigators[1-9]. Examination of experimental and theoretical data established that the properties of disperse structures are to a large extent determined by the relative positions and orientation of the dispersed particles and also by the thickness of the liquid layers separating them[5-20]. Thus, over long quasiequilibrium distances (compared with atomic dimensions) between the particles, disperse structures consist of thixotropic and usually relatively unstable periodic colloid structures. However, when the particles stick together with retention of very thin liquid layers between them or when the adhesion process is accompanied by the appearance of direct contacts, fairly stable systems are formed, which have virtually no thixotropic properties and exhibit only a weak syneresis and a weak capacity for peptisation. Such relations have been observed, for example, for precipitates formed when metallic sols coagulate[21-23], for certain electrophoretic coatings[24], etc.

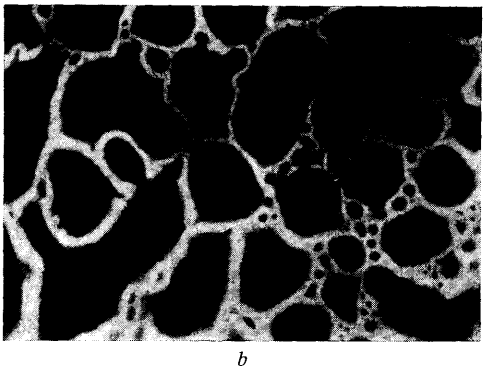
According to Rebinder's classification, thixotropic periodic colloid structures are reversible coagulation structures, while direct adhesion of particles and their further growth lead to the formation of irreversible condensation-crystallisation structures[14,25-27]. At the same time one must emphasise that the concept of periodic colloid structures is broader than that of coagulation structures and that not all periodic colloid structures (for example, equilibrium dispersions of swollen latex particles, micellar structures, etc.) can be classified as coagulations—thermodynamically non-equilibrium systems. The abundance of periodic colloid structures in nature and industry and their important role in various natural and industrial processes have been confirmed by the results of optical, X-ray diffraction, and electron microscope studies on a wide variety of disperse structures, including the results of direct observations on stabilised latex dispersions (Figs. 1 and 2).

The study of structure formation processes is associated with the development of concepts concerning surface forces of different types and acting over fairly long distances. The present advances in the theory of surface phenomena and also studies on coagulation (flocculation), gel formation, and the properties of gel-like systems have demonstrated the wide occurrence of long-range aggregation processes in which the characteristics of the particles and the relations governing their interactions are clearly manifested. In consequence of the predominance of attraction forces over long distances and the presence of a barrier preventing direct contact, in the mechanism of these processes the colloid particles are arranged in fixed relative positions with retention of liquid layers between them. On the other hand, in certain types of periodic colloid structures the fixation of particles is determined by the predominance of repulsion forces, as a result of which constrained conditions arise in the system.

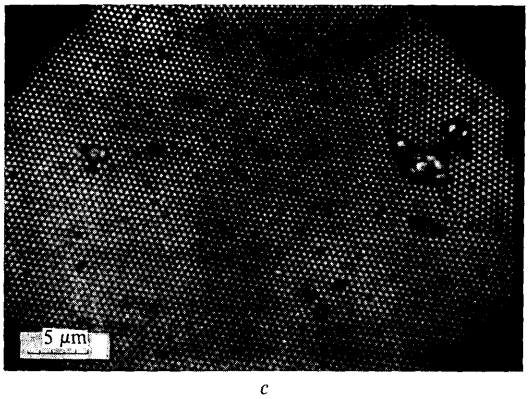
The concept of the decisive influence of long-range interaction on the formation of thixotropic structures was put forward for the first time by Freundlich[28]. Subsequently many further experimental and theoretical studies led to its thorough confirmation, amplification and extension to a wide variety of classes of colloid structures[5-7]. This review discusses the principal results of such studies, which are being particularly vigorously prosecuted at the present time.



a



b



c

Figure 1. Electron photomicrographs of periodic colloidal structures: *a*) polystyrene latex with a particle radius of 950 Å; *b*) particles of epoxy-resin; *c*) particles of a styrene–butadiene copolymer with a radius of 1400 Å–lattice defects and dislocations are visible[11].

II. LONG-RANGE SURFACE FORCES

It is known that attractive forces (van der Waals–London forces, forces due to permanent electric and magnetic dipoles, and forces due to dipoles induced by the polarisation of ionic double layers) and ionic–electrostatic repulsion forces can act between particles. The fact that these are long-range forces is responsible for the probability of further aggregation, i.e. the fixation of particles at a secondary potential minimum (Fig. 3).

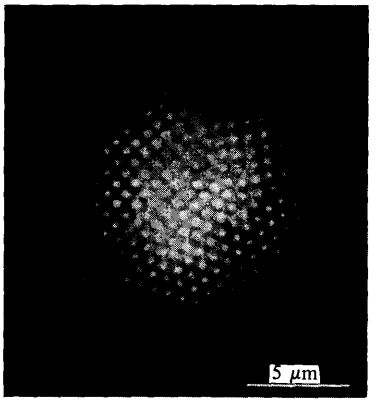


Figure 2. A photomicrograph of a polystyrene latex with a particle radius of 1700 Å for a solid phase concentration of 8 vol.%—the regions corresponding to the coexistence of the hexagonal and cubic lattices are clearly manifested[11].

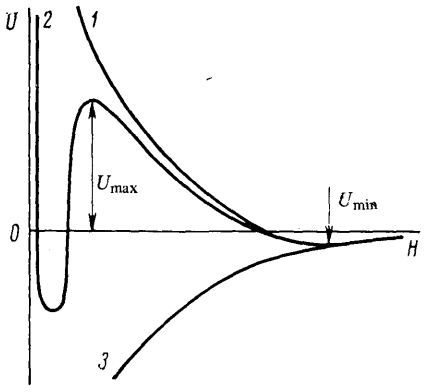


Figure 3. Various types of relations between the interaction energy of the dispersed particles and the distance between their surfaces.

Apart from molecular and dipole attraction forces as well as ionic–electrostatic repulsion forces, forces of a different type can also be manifested in the formation of periodic colloid structures.

Forces Due to the Viscoelastic Resistance of Anomalous Liquid Layers

Such forces offer resistance both to the mutual approach of the surfaces and to their separation from one another and, like ionic layers, influence the occurrence of a secondary minimum on the interaction energy curve for the particles[5,29–32]. The unusual relation between the disjoining pressure and the thickness of the film wetting the surface of quartz was recently explained in terms of the structural component and the three-layer model of a polar liquid film (presence of a layer with enhanced enthalpy or the so called partially fused layer)[33,34].

Forces Resisting the Rupture of Adsorption Layers Containing Surfactant or Polymer Molecules

The interaction between surfaces stabilised by adsorption layers (steric and entropy factors) has already been discussed[35-43].

One must also take into account the following factors: the thermal (Brownian) motion of particles[44-49]; gravitational[50,51], and centrifugal[52,53] forces which frequently appear to be equivalent to attraction forces and promote structure formation; mechanical compressive forces[29,54-55] and hydrodynamic[56-58] and capillary forces[59-62], which frequently have a marked influence on the properties of disperse and capillary-porous systems, as well as inertial, mirror image, and other forces[58].

Intermolecular van der Waals–London Forces

Despite the significant defects of the London–Hamaker microscopic theory[63], its equations are still widely used. The attraction energy between two identical spherical particles with a radius a and a distance R between their centres is given by the following expression when no account is taken of electromagnetic retardation:

$$U_m = -\frac{A}{6}\left(\frac{2a^2}{R^2-4a^2}+\frac{2a^2}{R^2}+\ln\frac{R^2-4a^2}{R^2}\right), \quad (1)$$

where A is the Hamaker constant; for low values of $H = R - 2a \ll a$ (H is the shortest distance between the interacting surfaces), we have

$$U_m = -\frac{A}{12}\left(\frac{a}{H}-2\ln\frac{a}{H}\right), \quad (2)$$

or in a still simpler form

$$U_m = -Aa/12H. \quad (2')$$

The corresponding formulae where account is taken of electromagnetic retardation were obtained by Schenkel and Kitchener[64] and for two spheres with radii a_1 and a_2 by Wiese and Healey[65]. Similarly, for $H \ll a_1$, a_2, we have[66]

$$U_m = -Aa_1a_2/6H(a_1+a_2). \quad (3)$$

For two identical plates with a thickness b and a separation H, the expression is[20,67]

$$U_m = -\frac{A}{12\pi}\left[\frac{1}{H^2}+\frac{1}{(H+2b)^2}-\frac{2}{(H+b)^2}\right]f(H), \quad (4)$$

where $f(H)$ is a function taking into account the electromagnetic retardation; its value for different H can be determined from tables and the graph quoted in Kruyt's book[67] and in the monograph of Sonntag and Strenge[36].

When $H \ll b$, we have

$$U_m = -\frac{A}{12\pi H^2}. \quad (5)$$

All these formulae are valid on the assumption that the interacting bodies are *in vacuo*. Allowance for the influence of liquid layers usually reduces to finding the effective Hamaker constant; the following simple relation is then frequently used[58,63]:

$$A = (\sqrt{A_{11}}-\sqrt{A_{22}})^2, \quad (6)$$

where A_{11} and A_{22} are constants for the particles and the medium *in vacuo*. However, Eqn. (6) is not rigorous[68] and, when the values of A_{11} and A_{22} are similar, the calculation leads to considerable errors.

The principal defects of the microscopic theory are as follows: (1) the applicability of the law of interaction of gas particles to condensed bodies is postulated; (2) the complete additivity of the electronic interactions is assumed; (3) the summation of such interactions over short distances between bodies is replaced by integration with respect to volume. The macroscopic theory of the intermolecular interaction of condensed bodies[69], based on the analysis of electromagnetic field fluctuations, is free from these defects. Dzyaloshinskii, Lifshits, and Pitaevskii[70,71] took into account the influence of the dispersion medium.

According to the macroscopic theory, the solutions of the problem of the interaction of bodies via a liquid layer assume a simple form for distances H which are both large and small compared with $\lambda_0/2\pi$ (λ_0 is the fundamental length in the absorption spectrum or the London wavelength). The following expression has been obtained for the force of the interaction between two plane-parallel particles *1* and *2* via a liquid layer *3* for large values of $H \gg \lambda_0/2\pi$ (for dielectrics, $\lambda_0/2\pi \simeq$ 20–30 nm):

$$P_m = \frac{3\hbar c}{16\pi^2H^4\sqrt{\varepsilon_{30}}}\int_1^\infty\left[\frac{(s_{10}-p)(s_{20}-p)}{(s_{10}+p)(s_{20}+p)}+\frac{(s_{10}-\alpha p)(s_{20}-\beta p)}{(s_{10}+\alpha p)(s_{20}+\beta p)}\right]\frac{dp}{p^2}, \quad (7)$$

where $s_{10} = (p^2 - 1 + \alpha)^{1/2}$, $s_{20} = (p^2 - 1 + \beta)^{1/2}$, $\alpha = \varepsilon_{10}/\varepsilon_{30}$, $\beta = \varepsilon_{20}/\varepsilon_{30}$ (ε_{10}, ε_{20}, and ε_{30} are the static dielectric constants of the plates and the liquid layer), $\hbar = h/2\pi$ is the Planck constant, c the velocity of light, and p the parameter with respect to which the integration is carried out.

Calculations based on Eqn. (7) can be carried out by a graphical procedure. The accuracy of the calculations is in many instances determined primarily by the appropriate choice of the static dielectric constants.

For two identical plates, $\varepsilon_{10} = \varepsilon_{20}$ and Eqn. (7) simplifies to

$$P_m = \frac{\hbar c\pi^2}{240H^4\sqrt{\varepsilon_{30}}}\left[\frac{\varepsilon_{10}-\varepsilon_{30}}{\varepsilon_{10}+\varepsilon_{30}}\varphi\left(\frac{\varepsilon_{10}}{\varepsilon_{30}}\right)\right]. \quad (8)$$

The function $\varphi(\varepsilon_{10}/\varepsilon_{30})$ has been calculated by Lifshits[69] and the calculation for $\varepsilon_{10} \neq \varepsilon_{20}$ has been carried out by Devereux and de Bruyn[72]. For two metallic plates in a medium with a dielectric constant ε_{30}, the function $\varphi(\infty) = 1$, since $\varepsilon_{10} = \varepsilon_{20} = \infty$. Then

$$P_m = \frac{\hbar c\pi^2}{240H^4\sqrt{\varepsilon_{30}}}. \quad (9)$$

The same equation was obtained by Casimir[73,74] on the basis of the microscopic theory with $\varepsilon_{30} = 1$.

Integration of Eqn. (8) leads to an expression for the attraction energy between two plates at a distance of 1 cm:

$$U_m = -\frac{\hbar c\pi^2}{720H^3}\left(\frac{\varepsilon_{30}-1}{\varepsilon_{30}+1}\right)\varphi(\varepsilon_{30}), \quad (10)$$

or

$$U_m = -\frac{K}{H^3}, \quad (11)$$

where K is the constant of the molecular attraction forces over long distances.

Using Deryagin's transformation[75], the formula for the attraction energy between two spheres can be obtained from Eqn. (11):

$$U_m = -\frac{\pi Ka}{2H^2}. \quad (12)$$

For two plates with $H \ll \lambda_0/2\pi$, we have

$$P_m = \frac{\hbar}{16\pi^2 H^3} \int_0^\infty \int_0^\infty x^2 \left[\frac{(\varepsilon_1 + \varepsilon_3)(\varepsilon_2 + \varepsilon_3)}{(\varepsilon_1 - \varepsilon_3)(\varepsilon_2 - \varepsilon_3)} \exp x - 1 \right] d\,x\,d\,\xi. \quad (13)$$

Neglecting unity compared with the term containing $\exp x$ and integrating with respect to x, we obtain

$$P_m = \frac{\hbar}{8\pi^2 H^3} \int_0^\infty \frac{(\varepsilon_1 - \varepsilon_3)(\varepsilon_2 - \varepsilon_3)}{(\varepsilon_1 + \varepsilon_3)(\varepsilon_2 + \varepsilon_3)} d\,\xi, \quad (14)$$

where ϵ_1, ϵ_2, and ϵ_3 are the dielectric constants as a function of the imaginary frequency $i\xi$. It follows from the above equation that the sign of the molecular interaction force is determined by the values of ϵ_1, ϵ_2, and ϵ_3. One must assume that, when the interacting surfaces approach one another, the sign of the quantity P_m may be reversed as a result of the different changes in the complex dielectric constant in them layers.

The microscopic and macroscopic theories of molecular forces yield [virtually] identical relations for the attraction forces *in vacuo* as a function of distance, differing only in the values of the constants. The experimental characteristics agree best with calculations based on the macroscopic theory[76-81].

The long-range nature of the molecular forces in condensed systems has been confirmed by the direct measurements of Abrikosova and Deryagin[76-81] as well as other investigators[82]. Many important studies have been made recently on the further development of the macroscopic theory, the improvement of the microscopic theory, and the development of methods for the calculation of the intermolecular attraction constants. This is because direct calculations of the forces of interaction via liquid layers are very complicated and have been carried out on the basis of Lifshits's theory for the simplest case of plates infinite in extent and separated by a planar gap the size of which must correspond to the limiting conditions ($H \gg \lambda_0/2\pi$ or $H \ll \lambda_0/2\pi$).

Van Kampen and coworkers[83-85] proposed a simpler method for the calculation of molecular forces equivalent in its approach to the Lifshits method; they considered the interaction between harmonic oscillators located at the interface. Using this method, Mitchell and Ninham[86] obtained the following expression for the attraction energies between two identical spheres in a liquid medium (for $H \ll a$):

$$U_m = -\frac{1}{12}\left(A_1 \frac{a}{H} - 2A_2 \ln \frac{a}{H}\right), \quad (15)$$

where A_1 and A_2 are constants.

For $A_1 = A_2$, this equation is transformed into Hamaker's equation [Eqn. (2)] [when the particles and the dispersion medium have similar spectroscopic characteristics (for example in the case of quartz and mica particles in water)]. For semiconductor and particularly metal dispersions in liquid dielectrics, A_1 and A_2 must differ significantly, so that Eqns. (1) and (2) cannot be used. Muller and Churaev[87] calculated the values of U_m for particles of metal hydrosols on the basis of the macroscopic theory using the spectroscopic characteristics of water and the metals. Churaev[88-90] calculated the molecular components of the disjoining pressure in terms of Lifshits's theory for thick and thin wetting films of nonpolar liquids. On the basis of a number of simplifying assumptions, he obtained recently an equation for the dependence of the molecular forces on distance for the entire range of film thicknesses and he also calculated the dispersion interaction forces in the transitional region[91]. A satisfactory agreement was achieved between the results of the calculations and experimental data.

The good agreement between the calculations based on Lifshits's theory and experimental molecular force constants has been pointed out in a number of interesting studies[69-81,92-98]. On the basis of the analysis of the equations of the macroscopic theory, Churaev[99] showed that Hamaker's constants for the interaction via a liquid layer cannot be obtained by the summation of the constants for the interaction *in vacuo*. The results of the calculations of the attraction forces between identical bodies via a liquid layer exhibit appreciable discrepancies for both theories.

Taking into account double and triple correlations, Renne and Nijboer[100] derived approximate formulae for the atom–wall and two plane-parallel plate models. The studies of Rusanov and coworkers[101-104] and other investigators[105-107] were devoted to the solution of the problem of the molecular interaction between colloid particles in a liquid dispersion medium. The problem of the interaction of coaxial cylindrical and concentric spherical surfaces has been solved[108] on the basis of Lifshits's theory. A number of studies[109-111] were devoted to problems of the shielding of van der Waals forces in electrolyte solutions. The influence of the molecular condenser (Stern layer) on the overall interaction forces between colloid particles and on the stability of sols has been examined by Martynov and Muller[112,113].

The Interaction Forces between Colloid Particles with Permanent Electric Dipole Moments

Studies on colloid solutions in the field of rectangular pulses (π-field) and in a rotating electric field (B-field) have shown that in many cases the colloid particle is a permanent electric dipole[114-119] due to the spontaneous unipolar orientation of the polar molecules (ions) adsorbed on the surface of the particle[114,115]. Measurement of the relaxation times for the orientation of the particles in the π-field and the determination of the angle by which the dichroic axis of the particle deviates from the direction of the B-field make it possible to calculate the dipole moment μ_p. The values of μ_p for various colloid particles amount to hundreds of thousands and millions of debyes[115].

The data compiled in Table 1 [120] demonstrate the surface nature of the dipole, the results being confirmed by the results of electron-optical studies on other suspensions and sols, for example the sols of various modifications of HgS. At the same time, these data do not of course constitute proof of the impossibility of the bulk-phase nature of the rigid dipole, which may arise as a result of the spontaneous orientation of the polar groups of the material of the disperse phase.

Identical particles of ferromagnetic materials behave similarly to the dispersed particles of dielectrics with permanent dipole moments[121-123].

The Interaction Forces between Induced Electric Dipoles

The deformation of the ionic double layer (DL) occurring under the influence of a particular factor produces an electric field with a radius of action of the order of the size of the dispersed particles, leading to their long-range interaction. The polarisation of the DL plays an important role in the electrophoretic precipitation of suspensions, determining the quality of the coating, in the

electrical treatment of cement pastes, electromelioration, vibrocondensation of dispersed materials, etc.

An approximate formula has been derived for the induced dipole moment[124,125]:

$$\mu_i = \frac{6a}{\sqrt{\pi}}\left[\left(\frac{\zeta\varepsilon_{30}}{2} + \frac{zeb_i}{3r_e}\right)\frac{\zeta\varepsilon_{30}r_e}{\Theta\varkappa^2}\right]E, \qquad (16)$$

where ζ is the electrokinetic potential, z and r_e are the valence and the effective radius of the counterions, e is the electronic charge, b_i a coefficient taking into account the anomalous mobility of the counterions, E the external electric field strength, and Θ the product of the Boltzmann constant and the absolute temperature. Eqn. (16) was obtained from the expression for the energy of the polarisation interaction derived using the insufficiently reliable Stauff formula[126], which does not take into account the tangential fluxes of the diffuse-layer ions.

Table 1. The molecular dipole moments (μ_p^0) of the liquid medium and specific (per cm^2) dipole moments (μ_p^s) of diamond (in CGSE units).

Dispersion medium	$10^{18}\mu_p^0$	$10^{14}\mu_p^s$	Dispersion medium	$10^{18}\mu_p^0$	$10^{14}\mu_p^s$
Water	1.85	1.7	Ethyl acetate	1.88	0.10
Methyl alcohol	1.64	1.1	Propyl acetate	1.88	0.12
Ethyl alcohol	1.70	1.1	Acetone	2.72	1.03
Propyl alcohol	1.59	1.1	Cyclohexanone	2.80	0.36
Butyl alcohol	1.64	1.1	Ethyl methyl ketone	2.75	0.82
Isobutyl alcohol	1.79	1.1	4-Methylisobutyl ketone	2.73	1.05
s-Butyl alcohol	1.70	1.1	Nitrobenzene	3.99	0.90
t-Butyl alcohol	1.66	1.1	Nitromethane	3.20	1.80
Pentyl alcohol	1.66	1.1	Acetonitrile	3.37	0.98
Dioxan	0.21	0.82	Dimethylformamide		0.43
Chlorobenzene	1.56	0.17	Acrylonitrile	3.40	1.26
Bromobenzene	1.53	0.16	Dimethyl sulphoxide	4.30	1.35
Methyl acetate	1.64	0.22			

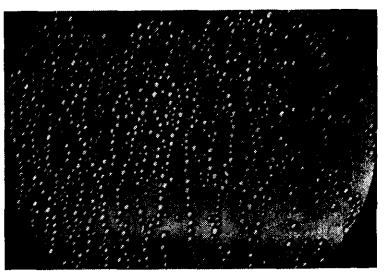


Figure 4. A photomicrograph of the aggregates formed in the latex under the influence of an external electric field.

The interaction of the induced dipoles usually leads to the appearance of chain aggregates (Fig. 4), which was first noted by Muth[127] and was subsequently studied in detail by many investigators[128-132]. Dukhin and coworkers[133-139] as well as other investigators[140-145] have made a major contribution to the development of concepts concerning the DL polarisation.

The following correct formula for the dipole–dipole interaction between two spherical particles has been proposed[139]:

$$V_{ip} = -4\varepsilon_{30}E^2B^2\frac{a^6}{(2+H/a)^3}, \qquad (17)$$

where $B = \frac{1}{2} - 3[\cosh(u_1/2) - 1]/[4\cosh(u_1/2) + \kappa a]$ and u_1 is the dimensionless potential of the Stern layer. In addition, the overall interaction energy of these particles in an external electric field was calculated. The energy of the overlapping of the ionic double layer was determined from the equation derived without restriction to the value of the u_1 potential[146].

The Ionic-Electrostatic Repulsion Forces Between Surfaces

These arise when diffuse ionic layers having identical charges overlap[147-158]. In some studies[148-152], the system of interacting ionic double layers is treated with some degree of approximation as corresponding to equilibrium and the corresponding forces are referred to as the equilibrium electrical surface forces. They are governed by the change in the energy density of the electrostatic field[152] and also by the variation of the chemical potentials of the ions and the solvent in the gap between the surfaces which have approached one another[5].

In recent studies undertaken to develop further the DL theory, account has been taken of the influence of the intrinsic volume of the ion and of pair correlations on the DL structure[159], of the DL polarisation on electrophoresis and diffusiophoresis[160], and of adsorbed ions on the DL structure and polarisability[161]; problems concerning the discrete nature of the DL,[162] the determination of the surface potential of the spherical particles[163], and the comparison of the constant surface potential and constant surface charge conditions in the Deryagin–Landau–Verway–Overbeek (DLVO) theory of the stability and coagulation of colloids[164] have also been examined. In addition the results of studies on the interaction of DL-charged surfaces have been published: in a solution of a mixture of electrolytes[165,166]; for planar particles in concentrated dispersions[167]; for spherical particles in concentrated dispersions containing a dispersion medium with a low dielectric constant[168]; for planar and spherical particles in an aqueous medium[169]; at constant surface potentials[170] and surface charges[65,171,172] and also at a constant potential of one surface and a constant charge of another[173,174]; for surfaces with energetic and geometrical inhomogeneities[175-177]. Calculations have been made on the DL interaction over long distances[165,166,178] and an equation has been proposed which can be used for weakly charged surfaces[178]:

$$U_i = \frac{\varepsilon_{30}\psi_0^2 a(R-a)}{R}\ln\left\{1 + \frac{a}{R-a}\exp[-\varkappa(R-2a)]\right\}, \qquad (18)$$

where R is the distance between the centres of the particles, ψ_0 the surface potential, and κ the Debye parameter.

A formula has also been obtained for the calculation of the energy U_i in the interaction of two similar spheres over long distances (for $\kappa a \gg 1$) without limitation as regards ψ_0.[146]

An interesting attempt has been made in a number of studies to examine from a single standpoint the energy of the interaction (the van der Waals attraction and the electrostatic repulsion energies) of charged surfaces.

Here a joint study was made of the low-frequency electromagnetic fluctuations and of the statistical charge distribution between two plates[179,180] and account was taken of the influence of the dielectric constant of the medium on the energy of the ions located near the interface[181]. The image method has been used[182] to calculate the interaction energy of two dielectrics *1* and *2* of different types separated by a layer of a dielectric *3*.

The dependence of the dimensionless potential u_1 of the Stern layer on the electrolyte concentration and the specific adsorption of the ion was studied recently[183]. It was concluded that the relation

$$n_c z^6 = \text{const}, \tag{19}$$

(where n_c and z are the critical concentrations and the valence of the counterions), established by Deryagin and Landau for dimensionless potentials $u_1 \geq 10$, should hold for arbitrary identical surface charges.

For different surface charges, the overlapping of ionic layers causes the mutual approach of the particles. For the same sign of the surface charges, but somewhat different potentials, the ionic-electrostatic forces P_i determine the repulsion of the particles over comparatively long distances and their attraction over short distances. The height of the maximum on the $P_i = f(H)$ curve depends on the lowest potential[184-186]. The interaction of the DL of inhomogeneous plates with different but constant charge densities has been studied[187], while another investigation[188] has dealt with the interaction of two plates immersed in ideal and non-ideal electrolyte solutions.

We may note that, as for molecular forces, the theoretical relations governing the action of surface ionic-electrostatic forces have been subjected to extensive experimental tests, the results of which basically confirmed their validity[29,36,37,147,189-196].

III. THE FIXATION OF PARTICLES AT A SECONDARY POTENTIAL MINIMUM AND THE FORMATION OF LOCAL PERIODIC COLLOID STRUCTURES

Under certain conditions, there is a fairly deep distant minimum on the curve for the interaction energy of colloid particles, $U(H) = U_m(H) + U_i(H)$, which determines the possibility of the mutual fixation of the particles with retention of the liquid layer between them. The probability of further aggregation and the lifetime of the aggregate formed depend on the depth of the minimum U_{min} and on the height of the potential barrier U_{max}, which reduces the frequency I of the effective collisions[66,197-199], as a result of which the particles are fixed at the primary minimum (short-range aggregation):

$$I = \frac{16\pi DaN}{2\int_2^\infty \exp(U/\Theta)\, ds/s^2} \simeq \frac{16\pi DaN}{\frac{1}{2\varkappa a}\exp(U_{max}/\Theta)}, \tag{20}$$

where N is the numerical concentration (the number of particles per unit volume) and D the diffusion coefficient.

The fixation of particles at a secondary minimum has been observed by numerous investigators[5-7] and confirmed by the results of many studies undertaken recently and designed to investigate the influence on the further aggregation of electrolytes[112,113,200-211] of the size, shape, and concentration of the colloid particles[5,65,212-217], and of the external force fields—electrical[124-128,139,218-223], magnetic[121,224-226], gravitational[50,51], centrifugal[52,53], hydrodynamic[56-58,227], etc.

A long-range interaction frequently occurs in processes involving the adhesion of the dispersed particles to a solid surface in the liquid medium. This has been confirmed by numerous experimental data[228-243]. Thus, when particles are deposited in air and also on a support in a liquid, the force required to strip them off, which is equal in absolute magnitude to the force of adhesion, is as a rule much greater in the former case[244-246]. Evidently the fixation of the particles at long distances corresponds to lower adhesion forces, while on deposition in air and the subsequent maintenance of the test specimens in the dispersion medium there are either no liquid layers between the particles and the macrosurface or their thickness is very low.

The theory of the collective interaction of particles has not as yet been duly developed. Therefore, in considering the problems associated with the formation and properties of periodic colloid structures, one usually begins with the relations governing the variation of the pair potential as a function of distance.

The Influence of Electrolytes on Long-Range Aggregation Processes

According to the DLVO theory, an increase of electrolyte concentration in the dispersion medium causes a contraction of the diffuse component of the DL and a decrease of the repulsion barrier. At the same time there is an increase in the depth of the secondary minimum U_{min} and a corresponding increase of the probability of long-range aggregation of particles, which is proportional to $\exp(U_{min}/\Theta)$.

Table 2. The exponents ν in the equation $nz^\nu = \text{const}$ for long-range aggregation processes.

Sol	ν	References	Sol	ν	References
V_2O_5	2.1—2.5	248	Latexes (a, μm):		
$Fe(OH)_3$	3.0—3.3	248	Polyacrylonitrile		
$Fe(OH)_3$	3.1	249	0.1	2.6—4.8	210
SiO_2	2.4	250	Polystyrene		
SiO_2	2.8	251			
CeO_2	4.3	252	0.1	3.3	261
H_2WO_4	2.0	253—255	0.19	3.3	200
S	3.0	256	0.17	3.2	212
S	3.6	257	0.21	3.4	212
AgI *	2.0	258	0.38	3.4	212
Au	2.7	259	0.54	3.5	212
Au	2.0	260	0.69	3.4	212
Ag	2.0	260	5.0	3.2	64
Cu	2.0	260	Polycaproamide		
			10	3.0	262
			Emulsions	3.1—3.3	203, 247

*Sol stabilised by poly(vinyl alcohol).

It has been known for a comparatively long time on the basis of experimental findings that gel-formation occurs at lower electrolyte concentrations than coagulation and the valence of the ions has a significant influence on the amount of electrolyte necessary for gel formation[247]. This relation has been demonstrated theoretically in studies[201,202] dealing with the interaction of two infinitely large plates and two spherical particles immersed in a symmetrical electrolyte.

It has been shown that, for a constant depth of the secondary force minimum, the following relation holds for the concentration and valence of counterions over a wide range of variation of the potential u_1:

$$nz^{2.5} = \text{const}, \quad (21)$$

and, when the effect of electromagnetic retardation for molecular forces is taken into account, we have

$$nz^{3.5} = \text{const}. \quad (22)$$

Both the limiting equations (21) and (22) and the intermediate equations with power exponents in the range 2.5–3.5 apparently hold in long-range aggregation processes.

The rate of gel formation and the stability of the gel usually depend on many factors (polydispersity, the presence of impurities, etc.), which are frequently difficult to take into account and this makes it difficult to obtain reliable results. For this reason, the relations between the valence and concentration of ions, derived from the results of many investigators and illustrated in Table 2, are approximate and depend on the methods used for the experimental determination of the PCS characteristics.

The concentrations of electrolytes required for coagulation and gel formation are compared in Table 3. Similar data were obtained by Kratochvil et al.[263] in a study of sols of microcrystalline cellulose and by Aleksandrova and Mochalova[264], as well as other investigators[265-268].

Table 3. The concentrations of electrolytes in the coagulation of an Fe_2O_3 sol and its conversion into a gel[28].

Content of disperse phase, g litre^{-1}	4,92	52,6
Electrolyte	Coagulation threshold, mmole litre^{-1}	gel-formation threshold, mmole litre^{-1}
NaCl	325.0	45.0
KCl	350.0	45.1
KBr	500.0	62.0
Na_2SO_4	3.25	12.0
$Na_2(COO)_2$	2.75	9.5
ν	7.1	2.3

Thus the results of the experimental investigation of the gel-formation processes in sols are consistent with the conclusions reached from the theoretical examination of the dependence of the depth of the secondary minimum on the concentration and valence of the ions. Calculation of the values of ν in the relation $nz^{\nu} = \text{const}$. can evidently yield information about the type of aggregation: $\nu = 6-7$ for short-range coagulation and $\nu = 2.5-3.5$ for long-range aggregation.

It has been shown[268] that, when the dispersed particles are fixed at long distances from the macrosurface, Eqn. (21) also holds; together with Eqn. (22), it must be regarded as a general criterion of the influence of electrolytes on long-range aggregation processes.

At the same time it follows from the analysis of Table 3 that the aggregation of particles is greatly influenced both by the concentration of the electrolyte in the system and by the concentration of the disperse phase. Thus it has been established[249] that, for an Fe_2O_3 concentration of 13.05 g litre^{-1} and a specific KCl consumption equal to 1.532×10^{-3} mole g^{-1}, the sol becomes turbid, the process being accompanied by local gel formation. Subsequently, with increase of the specific consumption of KCl, the individual gel-like regions are combined, giving rise to a thixotropic structure throughout the entire volume of the sol, which then breaks down owing to the short-range coagulation of the particles.

The Influence of the Size and Shape of the particles on their Mutual Fixation at Long Distances

Processes involving the formation of gel-like systems depend on the size and shape of the particles[5,65,212-217], which can be explained by taking into account quantitatively the forces operating in the system.

The interaction of homogeneous plates of different thicknesses for the same values of the parameters characterising their molecular attraction and ionic-electrostatic repulsion energies has been studied[20] and it has been shown that the rate of aggregation of large particles with one another and with small particles should be greater than the rate of the short-range coagulation of small particles. This conclusion has been confirmed by an experimental study of the kinetics of the formation of aggregates in suspensions[269]. At the same time the probability of the long-range aggregation of thick plates is higher than that of thin plates, since in the latter case the depth of the secondary energy minimum is smaller. Such relations have been noted in studies of gel formation in a number of disperse systems[270-274]. It has been established that a liquid is formed in gel formation primarily between large planar particles, while small particles remain predominantly in a free state and during syneresis are separated together with the syneretic liquid.

The method developed[20,45,46] for plotting curves characterising the interaction energy of three plates as a function of their relative positions made it possible to examine the influence of the concentration of the disperse phase on the short- and long-range aggregation processes[5]. It has been shown, that for fairly long distances between the surfaces, both thin and thick plates resist direct aggregation. This corresponds to a low bulk-phase (or weight) concentration of small planar particles and a high concentration of large particles. With increase of the content of the disperse phase, the distances between the surfaces and hence the resistance to aggregation diminish more sharply for thin plates, which is the reason for their coagulation at concentrations in the range where coarsely disperse systems can still be stable.

Consideration of potential curves for the interaction of three particles made it possible to explain qualitatively a number of the characteristic features of coagulation and gel formation in highly and weakly disperse colloid solutions. For example the rapid decrease of the depth of the minimum with increase of the content of thin plates is responsible for the difficulty of obtaining concentrated gels from highly disperse sols and, even if such gels are formed, rapid syneresis is their characteristic feature, as for gels containing coarsely dispersed particles. The interaction of plates of different types and dimensions is analogous although more complex.

In contrast to plates, the height of the ionic-electrostatic barrier and hence the resistance to aggregation of spherical particles increase with increase of their size (Fig. 5). In particular, this factor has been used by Oden[275] to fractionate sulphur sols. At the same time a fairly deep secondary energy minimum has been observed for large spherical particles and for large particles of

other shapes. For this reason, long-range aggregation processes should be particularly common in coarsely disperse systems[67]. This is confirmed by the existence of many concentrated periodic colloid structures, for example pastes, capable of peptisation and thixotropic transformations. Cement solutions (in the initial period of solidification)[276,277], silica[278-280] and Prussian Blue[274] gels, gel-like sulphur deposits[256], etc.

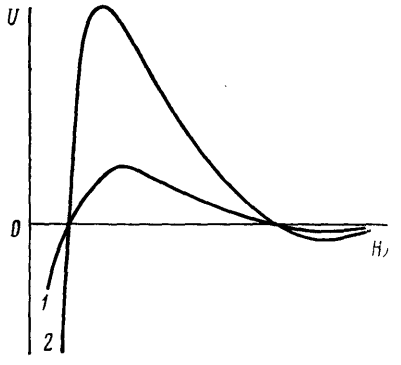


Figure 5. Dependence of the interaction energy of small (curve *1*) and large (curve *2*) spherical particles on the distance between their surfaces.

Furusawa and coworkers[212] investigated the aggregation of spherical polystyrene particles in different narrow fractions and established that, in the electrolytic coagulation of the most coarsely disperse system, the aggregation of particles occurs as a result of their fixation at a secondary minimum, because the stability of the system is restored after the removal of the electrolyte. Wiese and Healey[65] constructed a diagram (Fig. 6) where regions corresponding to the stable state of the system (region I) and to the unstable state leading to coagulation at the primary (region II) and secondary (region III) minima were defined as a function of the concentration of ions and the ratio of the radii of the particles. In the calculations, the dimensions of the particles, the surface charge, and other parameters were varied.

In connection with the wide occurrence of polydisperse systems, the question of interaction of particles of different size assumes particular importance. It has been shown[215] that fixation of small particles at long distances from relatively large particles can lead to the stabilisation of suspensions and emulsions for optimum electrolyte concentrations and a_1/a_2 ratios. Many experimental data confirming this conclusion are available. But it has been observed that small particles in rubber latexes execute "irregular" motions around large globules, behaving, as it were, as satellites of the latter[281,282]. Bethold and Snyder[278] patented a method for increasing the size of silica particles and for obtaining a stable sol containing 30 vol.% of the disperse phase by mixing suspensions with different degrees of dispersion.

Examination of the interaction of ellipsoids of rotation[215] showed that, in the presence of a repulsion barrier and a deep secondary minimum, the fixation of particles takes place preferentially for a parallel orientation of the symmetry axes (Fig. 7*a*). Since the size of the barrier is to a first approximation proporltional to the radius of curvature[75], the probability of aggregation of greatly extended ellipsoids via their vertices is high for a particular ratio of the attraction and repulsion forces and there is a possibility of aggregation over both short and long distances (Fig. 7*b*). The fixation of anisodiametric particles when anisotropic forces (for example, dipolar forces) operate between them should occur with a relative shift of the particles, i.e. for angles in the range $0 \leq \gamma < \pi/2$, where γ is the angle between the direction of the principal symmetry axis of the ellipsoids and the line joining their centres (Fig. 7*c*).

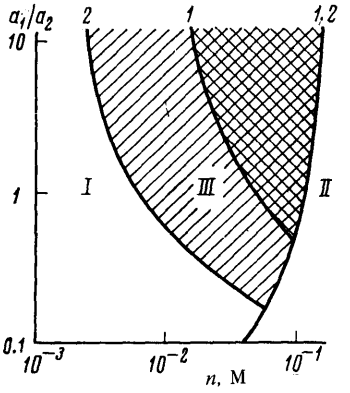


Figure 6. Stability diagrams of disperse systems consisting of particles of different sizes (a_2 = 0.1 μm) with (curve *1*) and without (curve *2*) allowance for the electromagnetic retardation effect: I) the region of the existence of stable systems; II) the region of short-range coagulation; III) the region of long-range coagulation.

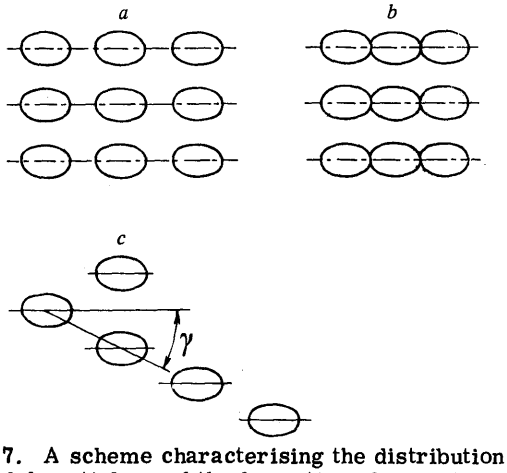


Figure 7. A scheme characterising the distribution of ellipsoidal particles and the formation of periodic colloid structures.

The structures arising as a result of the interaction of non-spherical (or spherical but non-polarised) particles usually possess anisotropic properties. Here one should mention in the first place a wide variety of periodic

tactoid structures consisting of particles in the form of plates and rods[67]. Chain aggregates or dendritic structures arise as a result of dipole–dipole interaction from spherical monodisperse systems of particles placed in an electric field (Fig. 4). Similar behaviour has been observed for many tactoids also in the absence of an external field (Fig. 8).

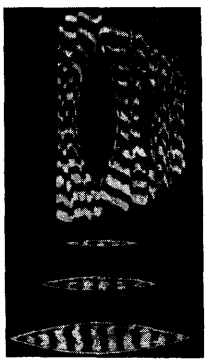


Figure 8. A scheme characterising the distribution of particles in tactoids.

Tactoids are the simplest (model) periodic colloid structures of the local type, the formation of which is determined by the fixation of the particles at a secondary minimum and is accompanied by the loss of potential energy ($\Delta U < 0$).[5-7,13,22,23] They are closely related, on the one hand, to liquid crystals and liquid-crystal phases in solutions of soaps, lipoids, and polymers† and, on the other hand, to gels, pastes, and gel-like systems. The similarity of the structures of local type, i.e. structures which usually do not arise throughout the volume of the dispersion‡, has been noted for a long time by many investigators[15-17,283,284].

IV. THE INTERACTION OF PARTICLES UNDER "CONSTRAINED" CONDITIONS AND THE FORMATION OF PERIODIC COLLOID STRUCTURES WITH A LIMITED VOLUME OF THE MEDIUM

In stable colloid systems "constrained" conditions arise as a result of the increase of the concentration of the disperse phase. The increase of the number of particles involved in free Brownian motion prior to this leads to their mutual approach and to the overlapping of the ionic atmosphere or solvation shells and hence to the appearance of repulsion forces. In this case the average distance between the interacting surfaces becomes smaller than the coordinate H_0 corresponding to the secondary minimum on the pair potential curve (Fig. 9). A further increase of the concentration of the particles decreases the stability of the system in consequence of the decrease of the depth of the potential wells located in the region of positive values of the energy[45,46,285].

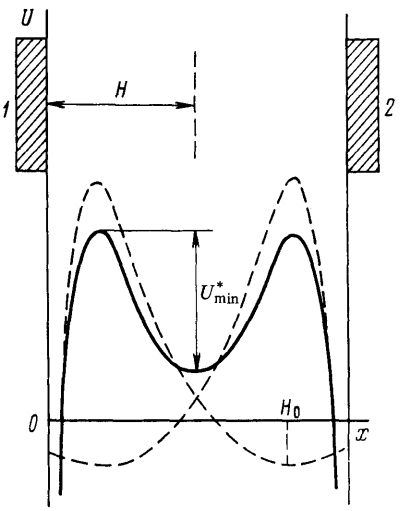


Figure 9. Dependence of the energy of interaction of particles *1* and *2* with a third particle on distance under restricted volume conditions. The dashed curves characterise the pair interaction potential.

For periodic colloid structures in a limited volume of the medium, an increase of potential energy is a characteristic feature ($\Delta U > 0$); they are formed throughout the volume of the system. The latter factor is responsible for the large-scale order in the distribution of the colloid particles, which can be readily observed from the bright iridescent colour of the dispersion[4,10,11,286]. In this case the periodic colloid structures play the role of a diffraction grating; the appearance of iridescence shows that the distances between the particles (and the dimensions of the particles themselves) are comparable to the wavelength of the transmitted light.

Numerous periodic colloid structures of the second type have been ovserved in latexes[4-8,10,11,210,286-291]. Many investigators have observed surprisingly regular lattices of latex particles (Figs. 1 and 2). In the stage preceding the formation of such quasicrystalline two-dimensional periodic colloid structures, the dispersion consisted of stable particles between which repulsion forces with a fairly large radius of action operated. "Constrained" conditions arose in such cases usually as a result of the evaporation of the liquid medium. In the Schiller layers, in deposits consisting of particles resistant to mutual aggregation, and also in creamy compositions, the restriction of the volume and "constrained" conditions are usually caused by gravitational or centrifugal forces.

†A comparative study of colloid particles and associated complexes of dissolved polyelectrolyte macromolecules has led to the conclusion that the interaction of these particles [as well as the interaction of the swelling latex particles (micelles) in surfactant solutions] is determined by general relations, which may be determined on the basis of unique physical principles.

‡ Under certain conditions and for a sufficiently high concentration of the disperse phase, a complete immobilisation of the system is possible.

Thus repulsion forces are responsible for the appearance of periodic colloid structures of the second type and attraction forces give rise to local periodic colloid structures.

The Influence of Electrolytes on the Interaction of Particles under "Constrained Conditions"

It has been shown[210,287] that, depending on a number of parameters, aqueous dispersions of polyacrylonitrile can exist both in the form of mobile suspensions and in the gel-like state. At a low electrolyte concentration and in the presence of a fairly high content of the disperse phase, periodic colloid structures are formed in which the particles are separated by quasiequilibrium liquid layers as a result of strong ionic-electrostatic interactions. Such systems possess viscoelastic and viscoplastic properties. With increase of the concentration of electrolytes, the radius of action of the ionic-electrostatic repulsion forces diminishes, which either gives rise to structures made up of locally ordered regions or causes a conversion of the gel into a mobile fluid state characterised by the absence of shear strength. In the former case the regularity of the structure is maintained in consequence of the fixation of the particles at distances corresponding to the coordinate of the second minimum. One should note that the "liquefying" action of small amounts of salts has been observed previously by Fryling[288] and also by Brodnyan and Lloyd Kelley[289,290] in studies of the rheological behaviour of a number of latexes.

Table 4. The exponents ν for polyacrylonitrile dispersions in the presence of different concentrations of electrolytes (τ_0 is the limiting shear stress).

τ_0, dyn cm^{-2}	10^2[NaCl], M	10^4[$MgCl_2$], M	ν	τ_0, dyn cm^{-2}	10^2[NaCl], M	10^4[$MgCl_2$], M	ν
10	0.2	4.10	2.6	75	1.00	8.40	3.6
20	0.3	4.90	2.8	100	1.50	10.0	3.8
25	0.4	5.40	2.9	200	5.30	19.0	4.8
50	0.6	7.50	3.0	τ_{max}	16.0	26.0	6.0

The transition from long-range to short-range aggregation (coagulation) with increase of the concentration of electrolyte in the dispersion medium takes place gradually and frequently these stages of the structure formation process cannot be very clearly distinguished§. For example, the exponent ν in the equation $nz^{\nu} = \text{const}$. for polyacrylonitrile dispersions in the concentration ranges 2.50×10^{-3}–1.00×10^{-2} M NaCl and 4.10×10^{-4}–8.40×10^{-4} M $MgCl_2$ amounts to 2.5–3.5, which demonstrates, according to Serebrovskaya and coworkers[201,202], the aggregation of particles with retention of the liquid layer separating them (Table 4).

§ The transition from long-range to short-range aggregation may be observed from the disappearance of iridescence[286,291].

The significant intensification of short-range aggregation at electrolyte concentrations close to the critical concentration n_c (5.30×10^{-2} M for NaCl and 1.90×10^{-3} M for $MgCl_2$) is responsible for the breakdown of the gel. The exponent $\nu = 6.0$ corresponds to this transition from the gel-like structure to a coagel, analogous to syneresis and accompanied by the evolution (displacement) of the syneretic liquid, which is consistent with the theory of the stability of lyophobic colloids[148–152], which has been used to prove the Schultze–Hardy rule in the form of Eqn. (19).

V. THE REVERSIBILITY OF PROCESSES INVOLVING THE FORMATION OF PERIODIC COLLOID STRUCTURES. PEPTISATION, THIXOTROPY, AND SYNERESIS

The mobility of the bonds between the elements of the quasicrystalline lattice, which is due to the comparatively small depth of the potential minimum, determines the most important properties of periodic colloid structures—the reversibility of the processes involving their formation and the possibility of peptisation and of thixotropic transformations.

A quantitative theory of these processes has not yet been devised. In discussing them, one must take into account the depths of the primary and secondary minima and also the changes in the conditions governing the mobile equilibrium (quasiequilibrium) between the particles fixed at the minima and existing in a free state in the bulk of the system. Indeed, experiment has shown that sol–gel transformations, induced by various physicochemical factors, can be regarded with some approximation as corresponding to equilibrium, as is assumed for crystallisation and dissolution processes. Naturally, this approach is justified only when coagulation and subsequent recrystallisation in the periodic colloid structures are very slow and do not have an appreciable influence on the aggregation equilibrium.

The existence of a mobile aggregation equilibrium in the aggregation of many colloid solutions has been observed by a number of investigators[5,22,23,52,53,209,242,253–255,292–299]. Thus, using an optical microscope, Okamoto and Hachisu[23] observed the Brownian movement of gold sol particles (forming aggregates) in the dispersion medium over a certain range of electrolyte concentrations. Using the method of the low-angle scattering of X-rays, Kratky et al.[299] measured the degree of aggregation of molecules in solutions of an azo-dye (Chlorantine Light Violet 2RLL) and established that the aggregation equilibrium depends on the concentration of the ions in solution, temperature, and the content of the dye. Similar relations were noted also in a study[297] of the coagulation of gold sols in a flow ultramicroscope.

In discussing the problem of the aggregation equilibrium in colloid solutions, Frens and Overbeek[294,295] concluded that the relation between the number of primary particles, the number of aggregates, and their size is determined by the minimum in the free energy of the system; for ion-stabilised dispersions, this minimum is related to the DL parameters. Thus there is a possibility in the DLVO theory of taking into account not only the processes involving the formation of aggregates but also their decomposition processes, determined by the finite depths of the primary and secondary minima.

Similar but more detailed ideas were developed in a series of studies by Martynov and Muller[300–303] for long-range aggregation or, in the authors' terminology,

"barrierless coagulation"¶. It was shown that, under certain conditions, coagulation (aggregation) can occur only in consequence of a remote potential well[302]. Since the depth of this well is as a rule small, there is a comparatively high probability of the decomposition of the aggregate formed. One should note that the coagulation mechanism proposed by the authors[300-303] remains valid, subject to certain assumptions, also for systems a characteristic feature of which is the presence of a repulsion barrier between the particles: the relations established should hold also for a near potential well at electrolyte concentrations exceeding the critical value.

Analysis of the kinetics of slow coagulation[302], presupposing allowance for the decomposition processes of the aggregates formed, is of significant interest, since it has been found that the shape of the curves relating the total number of particles to time makes it possible to determine the decomposition coefficient and the depth of the potential well in which the fixation of the particles takes place. Furthermore, the height of the barrier can be found from the coefficient of the retardation of aggregation, and hence the fundamental parameters of the interaction between the particles may be calculated.

The decomposition of the aggregates and their formation take place spontaneously as quasiequilibrium processes; in contrast to this, peptisation and thixotropic transformations take place as a result of physicochemical and mechanical influences on the system.

Local Periodic Colloid Structures ($\Delta U < 0$)

Such structures, arising as a result of long-range aggregation, usually undergo peptisation comparatively readily; for example they consist of tactoids[18,19,22,23,241,253-255,283,304,305], freshly prepared gels and gel-like deposits[5,15-17,64,206-209,242,253-255,292-297], and flocculated emulsions[203,285,306-308]. Many disperse structures are peptised on simple contact with the dispersion medium containing stabilising ions or surfactant molecules, which occurs fairly frequently in the swelling of various argillaceous minerals[309-312] as well as pastes obtained from latexes, dyes, pigments[5], and colloid silver deposits[313].

However, one should bear in mind that peptisation is not usually quite complete (i.e. some of the precipitate remains)†. Thus the aggregation equilibrium in an AgI sol, observed on varying the concentration of the solid phase, changes with time: the aggregates are gradually stabilised and decompose to a lesser extent following dilution[313]. It is important to note that peptisation proceeds most completely when the electrolyte concentration in the intermicellar liquid in the initial state does not exceed the critical concentration causing the disappearance of the repulsion barrier[22,23,52,53].

¶ We believe that the term "barrierless coagulation" cannot be regarded as successful, since it corresponds merely to the model adopted by the authors in which infinitely large barriers and hence the absence of coagulation at the primary minimum are postulated.

† The periodic colloid structures corresponding to thermodynamic equilibrium as well as those in which the particles are separated by very high repulsion barriers, which brings the system closer to equilibrium, are apparently exceptions.

Periodic Colloid Structures with a Limited Volume of the Medium ($\Delta U > 0$)

Such structures are characterised by their capacity for almost complete peptisation, since, following the decrease of the content of the disperse phase (the numerical concentration), the system tends to pass to a lower energy level, which is accompanied by a simultaneous increase of entropy‡. This process has been studied experimentally[10,52,53,210,291].

Anomalous Liquid Layers

Anomalous liquid layers preventing direct contact between the particles play an important role in peptisation processes, like the adsorption of ions from solution at the interface, which alters significantly the ion-electrostatic interaction of the particles. The influence of these factors on peptisation can be followed in relation to the intracrystalline swelling of various argillaceous minerals in electrolyte solutions. Norrish[309] showed by the method of low-angle X-ray scattering that the interplanar spacings H_B in swollen montmorillonite are to a large extent determined by the position of the exchangeable cation in the lyotropic series and its concentration in solution. For H^+ and Li^+ ions, H_B varies linearly to a first approximation as a function of $1/\sqrt{n}$; Na-montmorillonite exhibits the same relation at electrolyte concentrations $n < 0.3$ M, while at a concentration of approximately 0.3 M the interplanar spacings can be simultaneously $H_B = 19$ and 40 Å.

The interplanar spacings in specimens of an argillaceous mineral placed in KCl, NH_4Cl, and CsCl solutions do not as a rule exceed 15 Å whatever the concentration of the electrolyte. However, it has been observed[309,317] that the capacity of K-montmorillonite specimens for swelling depends on the method of their preparation. K-Montmorillonite which had been kept in a concentrated KCl solution and then placed in a dilute KCl solution does not swell, in contrast to the Li- and Na-montmorillonites in LiCl and NaCl solutions. At the same time, when a clay specimen which had been subjected to preliminary treatment in a dilute NaCl solution is placed in a dilute KCl solution, the high values $H_B \simeq 100$ Å persist after the exchange of Na^+ ions for K^+ ions and the lattice does not undergo appreciable changes.

The experimentally observed intracrystalline swelling of various cationic forms of montmorillonite has been explained[318] on the basis of the theory of the interaction of dispersed particles and the values of H_B have been calculated as a function of the concentration of the electrolyte in the disperse medium and have been found to agree fairly well with the experimental data, qualitatively and quantitatively. It proved necessary to take into account the specific adsorption of the ions in the dense component of the DL as well as the limit of the plastic strength of water near the interface[319-321].

The shear strength of the liquid layers should lead to the appearance of hysteresis loops in swelling–contraction processes[320-323]. For example, when the concentration

‡ The conditions governing the formation and existence of spontaneously dispersable systems with low interfacial energies have been discussed[314-316].

of the electrolyte is varied, the volume of the sedimentation deposit of Oglanlinsk Na-bentonite varies as in intracrystalline swelling[322], but the branches of the curve corresponding to the decrease and increase of the concentration of ions in the dispersion medium do not coincide. This type of variation must be explained by the fact that, on swelling, the shear strength of the liquid prevents the mutual separation of the elementary packets of montmorillonite and on contraction it prevents their mutual approach.

The problem of the capacity for peptisation of local periodic colloid structures is closely related to the phenomenon of thixotropy, i.e. to the ability of the structure to be restored after its disturbance under the influence of mechanical stress (stirring, vibration, etc.). Such a transition is usually accompanied by a change of effective viscosity by several orders of magnitude. At the same time it is known that, together with ideal thixotropy, there are many instances of an incomplete restoration of the strength characteristics of periodic colloid structures: in each succeeding thixotropic transformation, the volume occupied by the gel diminishes to an increasing extent until the disperse phase separates in the form of a dense deposit. Under these conditions, the strength of the gel frequently increases and the restoration period shortens. However, in many systems there is a characteristic decrease of strength and a gradual liquefaction of the gel, leading to complete irreversibility. Many gels (as a rule dilute gels) have no thixotropic properties: their strength is not restored even after the first disruption of the structure. Thus there are intermediate types between ideal thixotropic systems and systems without thixotropic properties[5].

Various processes resulting in a decrease of the strength of colloid structures, i.e. in liquefaction, are frequently classified as thixotropic. However, liquefaction can also occur as a result of slow coagulation, which disrupts the gel lattice and causes a sharp decrease in strength. The latter evidently has no bearing on thixotropy and is more likely to be a syneretic process. In particular, this is frequently observed in periodic colloid structures with a limited volume of the medium: coagulation (fixation at the primary minimum) leads to an increase of the distances between the particles or their aggregates, which is responsible for the disruption of the lattice of the gel and hence for the decrease in its strength.

The processes occurring in syneresis may be examined on the basis of the theory of slow coagulation, where, however, one must take into account the cooperative effect, i.e. the influence of a single particle attached to the aggregate on the interaction of all the particles. This constitutes a very difficult task. The current theory of slow coagulation[197-199] is based on the concept of pair interaction between particles, which has been justified with adequate approximation for dilute systems. In gels, each particle is surrounded by neighbours and the energy of their collective interaction must be expressed by the exponent in Eqn. (20). The overall height of the barrier U^*_{max} for the pair interaction is defined, according to Wiese and Healy[65], as the arithmetical sum of the absolute height of the repulsion barrier U_{max} and the depth of the secondary minimum U_{min}.

Phenomena analogous to thixotropic recovery processes frequently occur in disperse systems under the influence of external force fields: electrical, magnetic, ultrasonic, etc. In dilute dispersions, these fields are responsible for the formation of structures, for example chain aggregates, which may decompose after the removal of the field, i.e. may be spontaneously peptised[121,124,125,128,324].

VI. ESTIMATION OF THE INTERACTION FORCES BETWEEN DISPERSED PARTICLES ON THE BASIS OF THE RHEOLOGICAL PROPERTIES OF PERIODIC COLLOID STRUCTURES

When specific deformation processes in colloidal dispersions, pastes, and deposits are considered, it is important to know the relation between the stresses operating in the system and its flow rate. Problems of this kind constitute the subject of rheology—the science of the fluidity of matter[325]. However, rheology, which is a component of physochemical mechanics[25,26], is restricted to phenomenological methods for the description of the deformation process without elucidating the relation between the strength of disperse systems and the surface forces of the interaction between particles. Furthermore, the latter problem, the solution of which is apparently still in its initial stage, is of great practical importance, primarily for the development of new methods whereby various materials with specified properties could be obtained[326].

Periodic colloid structures usually have a high yield point and they can therefore be regarded as plastic solids or, according to Rebinder's classification[14,327], as solid systems, in contrast to liquid systems (dilute sols, emulsions, etc.) for which the yield point is zero. The calculation of the strength of such systems is as a rule based on model concepts and certain assumptions concerning the parameters of the interaction of the particles. The models employed evidently constitute only a first approximation and do not fully reflect the real structure of the disperse material. This applies mainly to systems characterised by low equilibrium (quasiequilibrium) distances between individual particles and hence a significant non-uniformity of the distribution of particles in the bulk phase of disperse porous bodies. For periodic colloid structures of the local type and particularly for such structures formed under the conditions of a restricted volume, the introduction of model concepts is fully justified, although the methods of calculation in the case of short-range and long-range aggregation are not fundamentally different.

In most studies dealing with the strength of gels and gel-like systems, a uniform distribution of the particles of the disperse phase is postulated. For example, in a study of glyceryl tristearite suspensions in hydrocarbons, Nederveen[328] determined the average distance between the particles, assuming that van der Waals–London forces as well as Born repulsion forces operate between them, and calculated the moduli of elasticity of the dispersions from the formula proposed by van den Tempe[329]. The appreciable discrepancies between the experimental and calculated data were accounted for by the imperfection of the model.

Volarovich and Gutkin[330] showed that the limiting stresses due to the existence of periodic colloid structures, occurring in simple shear deformation, may be found from the expression

$$\tau_0 = \frac{4}{\pi} N U_0, \qquad (23)$$

where U_0 is the energy of the pair interaction of the particles. On the assumption that the fixation of the particles in the lattice takes place owing to long-range dipolar forces, the authors[331] calculated the values of τ_0, which were in the order of hundreds of dyn cm^{-2} and were close to the values of τ_0 observed experimentally for a number of suspensions[332].

A similar model was also used in another study[8], where the relation between the limiting shear stresses in periodic colloid structures was considered as a function of the concentration of the solid phase and of the electrolyte in the dispersion medium. Molecular and ionic-electrostatic interaction forces between the particles were taken into account, while the energy of the interaction of rigid electrical dipoles, which should probably be shielded by the counterdipoles in electrolyte solutions, were disregarded. The results of the calculations, which are in good qualitative and quantitative agreement with experimental data, explained many of the known facts, namely the decrease of the strength of periodic colloid structures of the second type with increase of the concentration of ions in the system[210], the parabolic relation between τ_0 and the numerical concentration of the particles[287], etc.

A chain model of disperse structures has been proposed by Rebinder et al.[326] It is designed mainly for the calculation of the strength of disperse materials such as catalysts, the porosity of which may vary within wide limits, although it can be used successfully also for estimating the mechanical properties of local periodic colloid structures. In constructing the model, the occurrence of chain aggregates consisting of spherical particles of identical size in contact was postulated. The chains are distributed along three mutually perpendicular directions and intersect, forming nodal points. In order to characterise the system, it is sufficient to know the diameter of the particles $2a$ and their number N_0 in the aggregate; its strength Q_m depends on the strength q_1 of a single contact and

$$Q_m \simeq 10^{10} q_1 \frac{1}{d^2} \beta, \qquad (24)$$

where d is the average pore diameter in angstroms, Q_m is expressed in kgf cm^{-2}, and $\beta = 4/\pi - 2/N_0 + 1/N_0^2$.

An experimental test of Eqn. (24), showed that the equation predicts fairly accurately the force of cohesion of the particles q_1, provided that Q_m is known[333]. At the same time, it has been stated[333] that the difference between the values of q_1, found from the results of microscopic and macroscopic measurements, may be attributed to some uncertainty in the estimation of q_1 from the measured strength of individual contacts, which varies within the limits of six orders of magnitude.

A somewhat modified model of disperse structures, consisting of a series of repetitions of the same unit cell (which is not necessarily closed), was proposed by Yakhnin and Taubman[334]. The basic element of the cell is a conventional edge containing N_0 particles having the same diameter $2a$. Then

$$Q_m = kq_1/a^2 N_0^2, \qquad (25)$$

where k is a dimensionless coefficient, which depends on the shape of the cell and the fraction of the effective (structural) units in the chain. It is important to note that the concepts developed by the authors[334] have been extended to the case of the particles of the disperse phase modified by surface-active substances, which alter the forces of interaction between the particles. Subsequently the distribution of the particles with respect to cohesive forces was taken into account within the framework of the model of Yakhnin and Taubman[335].

Considering the dissipation of energy of the flow of a plastic material, Michaels and Bolger[336] showed that the limiting shear stresses may be calculated from the equation

$$\tau_0 = \frac{3\varphi}{2\pi^2 a^3} U_0, \qquad (26)$$

where φ is the bulk-phase concentration of the solid. The derivation of Eqn. (26) is not associated with model concepts, is general, and does not involve any assumptions concerning the nature of the linkages between the particles. Using this approach, Hunter and coworkers[337-339] subsequently investigated the problem of the influence of electrical double layers, temperature, and steric stabilisation of suspensions on the energy of cohesion of the particles in the aggregate U_0.

Information about the interaction of the particles can be obtained from compression measurements[340,341] and also from data obtained by studying the elastic properties of dispersions[342]. For example, Ottewill and coworkers[340] found the interaction forces between the particles as a function of the distance H between their surfaces by determining the dependence of the elastic deformation of moisture-saturated Na-montmorillonite specimens and powders containing monodisperse polystyrene particles on the external load. The electron-microscope photographs of the latex quoted by the authors[340] permit the conclusion that the distribution of particles in the systems investigated is fairly rigorously ordered, and the systems can probably be classified as periodic colloid structures with a limited volume of the medium, since the range of variation of H for all loads amounted to several tens and hundreds of angstroms.

The application of external electrical and magnetic fields and the associated electrorheological[124-132] and magnetorheological[226,343] aggregation effects proved to be extremely promising for the estimation of the degree of interaction between dispersed particles. In contrast to spontaneously coagulated suspensions and sols, the aggregates arising under the influence of the fields are extended, which significantly facilitates the interpretation of experimental data. In consequence of the rapid development of a number of fields in chemical engineering, where electrical and magnetic treatment of disperse systems is being used on an increasing scale, such studies assume particular urgency.

The theoretical and experimental data concerning the long-range interaction of colloid particles confirm the validity of ideas about periodic colloid structures of the first and second types. In order to devise a rigorous theory of the processes involved in the formation of such systems, which is very important for the successful development of the science of surface phenomena and for the improvement of various technological processes, it is necessary to solve many complex problems, which arise primarily in consequence of the insufficiently complete investigation of the interaction forces between particles. Thus there are no methods for the calculation of the forces acting between surfaces having anomalous liquid layers or between surfaces separated by a layer or solution with a high concentration of ions; the theory of the interaction of surfaces stabilised by surfactants and polymers has been inadequately developed, and so on. Particular mention should be made of the necessity for the solution of the problem of the collective interaction of particles, which can occur in general under the influence of attraction and repulsion forces of different types.

Latexes containing virtually monodispersed spherical particles have been used recently with increasing frequency as model systems for the investigation of structure formation processes. The results for the study of such dispersions have been widely discussed in the present review. However, this does not mean that latexes occupy a dominant position among other periodic colloid structures, which are common in nature and

industry, although their importance is many respects incontrovertible. There is no doubt that certain sedimentary rocks, soils, cement pastes, ceramic and paper compositions, clay dispersions, gelled emulsions and foams, creams, etc. are of primary importance. Unfortunately their extensive investigation is complicated by the fact that they are usually polydisperse, the shape of the particles is irregular, many components, including various impurities, are present, and frequently also both chemical and physicochemical processes take place. It therefore appears to be necessary to investigate systematically and thoroughly real polydisperse systems for variable values of different parameters, which will help in the solution of theoretical and practical problems. The research must be directed primarily towards the study of the influence of electrolytes, temperature, and other factors on long-range aggregation, peptisation, thixotropic transformations, and syneresis, as well as the rheological properties of periodic colloid structures.

The determination of the relations governing the behaviour of particles in dispersions is possible on the basis of the theory of molecular and ionic solutions, the development and improvement of which constitutes a very complex and topical problem at the present time.

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