MAIN FACTORS AFFECTING THE STABILITY OF COLLOIDS

B. V. DERJAGUIN

Institute of Physical Chemistry, USSR Academy of Sciences 117312 Moscow V-71, Leninskii pr. 31, USSR

Abstract—A general survey is given on the role that interparticular attraction forces play in the aggregative stability of colloidally dispersed systems. Special attention is paid to the disjoining pressure acting between interlayers. The importance of recent results obtained by the author using the so-called flow ultramicroscope method is emphasized as these data allow the interpretation of the kinetics of slow coagulation, not only in the initial stage as does Fuchs' theory, but also in the whole of the process.

It is well known that the stability of molecular or ionic solutions is a function of either the impossibility or slowness of the phase transition. The latter is understood to be a transition from either one concentration, or one crystalline structure, to another. Something similar is observed in the formation of coacervates or tactoids. Recently, the equilibrium between the colloidal phases and the transition from one to another, have been clearly demonstrated in the case of latexes, in works of Hachisu et al.[1] In one phase the particles formed a periodic lattice, while the other phase was amorphous and less concentrated, in accordance with the theory of Kirkwood[2] and Alder.[3] At an earlier date, the equilibrium between the anisotropic and the isotropic phases of sols containing elongated particles, e.g. the tobacco mosaic virus, was explained by Onsager's theory.[4] It is remarkable that the two theories do not conceive of attraction forces between particles. Here we have the essential difference between phase transitions in ordinary liquids and in colloidal solutions.

However, the main difference in properties between colloids and ordinary solutions, particularly in stability, is connected with the fact that the former are characterized by a certain degree of dispersity. This dispersity introduces an additional degree of freedom into the system, and causes special kinds of instability. The dispersity itself may vary in two ways. Firstly, owing to the difference in solubility of particles of different sizes, the small particles disappear, and the degree of dispersion continuously decreases. In the second case, with micellar solutions, such an ageing does not occur. With these solutions, the effect of curvature on solubility is different because micelles contain molecules with both lyophilic and lyophobic moieties, the molecules overall being amphiphilic. As a result, micellar solutions prove to be quite stable thermodynamically. Thermodynamic conditions for stability of disperse systems were formulated by a number of authors, in the most general form by Rusanov, Rehbinder and Schukin.[5] However, there is the more difficult question as to what real systems satisfy these conditions. This question requires the development of a molecular-statistical theory which takes into account the nature, for example, the amphiphility of molecules. This difficult problem has yet essentially to be solved.

Up to now, colloid research workers have directed their main attention to violations of stability arising from a variation in the degree of aggregation, first of all in the coagulation process. As opposed to phase transitions arising from collective interactions of particles, a change in aggregation is almost always determined by paired interactions. Therefore, the attempt of Langmuir[6] to extend to coagulation the coacervation theory he developed is in principle wrong.

The main factor accelerating both aggregation and disaggregation of particles is the Brownian motion. This is progressive in coagulation, but the process of disaggregation and peptization are oscillatory. Coagulation can be hindered or rendered impracticable by the repulsion forces acting between particles. At short distances, attraction forces hinder disaggregation, and may even lead to coalescence. However, the latter may be hindered in its turn by repulsion forces of still shorter range. Therefore, a theory of aggregative stability can only be developed after one has considered the nature of the aggregation processes, and taken into account the dependence upon distance of the forces acting between colloidal particles. These forces are very diverse in nature, and their study, which was started about 40 yr ago, is far from completion. The complexity of the problem arises from the necessity of studying these forces as a function of the spacing between particles.

To solve the problem, our laboratory has from the very beginning applied simultaneously three approaches as follows:

(1) Model experimental research into the interaction of surfaces separated by thin interlayers.

(2) Development of the theory of the interaction of surfaces and particles separated by thin interlayers.

(3) Research into the coagulation kinetics using the flow ultramicroscopy method, which facilitates study of the dependence of the number concentration upon time.

1. At first a model consisting of two plates separated by a plane-parallel layer of liquid was used.[7] It has been shown that water and some other liquids, while being drawn into a gap between two mica sheets, pushes them apart to a certain equilibrium spacing, which is an inverse function of the external pressure applied to the upper plate. Using this as a basis, the concept of an equilibrium disjoining pressure of thin liquid interlayers, which counterbalances the external pressure and is a function of the thickness of the interlayer has been developed. Recently, interesting results have been obtained by Peschel[8] in this context.

Measurements of the disjoining pressure between solid surfaces are, however, in the general case rendered difficult because of surface irregularity, and because of dust particles getting into the gap. It was much simpler to experiment with a liquid interlayer by pressing a bubble (or a droplet[6a]) to the surface of a solid. In this case, when in the state of thermodynamic equilibrium, the wetting

interlayer proves to be of uniform thickness. Observing the interference pattern by the reflected light, it was possible not only to measure the thickness of the film but also to control the presence of dust particles. The researches made according to this method by the author in conjunction with Kusakov,[9] allowed the accurate measurement of the disjoining pressure of thin liquid interlayers, having a thickness of up to several tenths of a micrometer.[10]

To explain the experimental results thus obtained, a theory of the ionic-electrostatic component of the disjoining pressure[11] has been developed using the Bradley, Hamaker and De Boer method, of summing paired London forces to express the dispersion component of the disjoining pressure.[12] The same calculations were used as a basis for developing the theory of stability of lyophobic colloids.[13]

This theory was further developed by Levine, Verwey and Overbeek, who started from an expression for the electrochemical free energy of a system including an interlayer of electrolyte. The electric component of the disjoining pressure was found by differentiating with respect to thickness. (This trend also was reflected in the general definition of the disjoining pressure., adopted by the IUPAC Commission on Colloid and Surface Chemistry). A strict and accurate calculation of the free energy of the system having single or overlapped double layers involves many difficulties and misunderstandings. Even after overcoming these difficulties, the differentiation operation demands knowing how the potential of a double layer depends upon the thickness of the interlayer. Now the direct and simple method for the calculation of the ionic-electrostatic repulsion yields an expression which is a function of the potential and charge of the double layer for any thickness of the interlayer. This method is based directly on the most general notions of electrostatics and hydrostatics. The calculations which are connected with the properties of ionic solutions in an electrostatic field were rendered more precise by Sanfeld and Defay.[14] The only misunderstanding that arose was connected with Babchin's[15] attempt to take into consideration the electrostriction contribution. This attempt was based on a serious mathematical error as I have shown.[16] In this connection, I stress additionally that in a number of problems connected with the swelling of montmorillonite and the flow of thin films, it is only necessary to know the disjoining pressure, and not the interaction energy.

The Journal of Colloid and Interface Science has recently published a paper which I wrote together with Dr. Churaev.[17] This paper shows that the dependence of the disjoining pressure upon the thickness of thick water films in contact with either fused quartz or mica is determined by the ionic-electrostatic component. However, the β-films referred to in the paper are metastable. When they break, they are changed into thinner α-films. Even in a semi-qualitative manner, their disjoining pressure cannot be attributed to the effect of the ionic-electrostatic repulsion forces plus Van der Waals forces. We are of the opinion that the above proves the existence of the structural component of the disjoining pressure, arising when the liquid interlayer is completely filled with a boundary layer (or layers) having a special structure.

This special structure is also revealed by an increase in the viscosity of films, an increase of as much as $5 \div 10$ times, which was detected by Churaev and Zorin,[18] by the thermoosmosis phenomenon,[19] and by the increased

thermal conductivity of water interlayers in mica laminations found by Metzik.[20] Especially convincing is the fact that all these effects disappear at the same temperature of about 70°C.[21] The same structural component of the disjoining pressure is able to explain the stability of secondary soap films, too.[22] One may also explain the changes of the disjoining pressure under the effect of a surface modification by adsorbed monolayers.[67]

However, an increase in the disjoining pressure under the effect of soluble surfactants, for example, caprylic acid in vaseline oil or heptane,[23] may be explained by the overlapping of adsorption layers; their diffuseness for a great number of solutions was proved through capillary osmosis measurements in our laboratory by Koptelova.[24] Using as a basis the Boltzmann equation and the Lifshits theory of Van der Waals forces, we have determined the distribution of molecules in overlapping diffuse adsorption layers. This, together with the application of thermodynamics enables the development of a theory for the adsorption component of the disjoining pressure, and to assess its value.[25] An analogous approach has been published by Everett[26] and coworkers. The effect was probably revealed in the experiments made by Sheludko and Exerova[27] with free films of aqueous solutions of acetic acid and other mixtures. Besides this effect, the structural component of the disjoining pressure may also exert its influence, this component being a function of the nature of the monolayer.[67]

Still more convenient as a model object are free films situated between two bubbles, which, when in the state of equilibrium, represent ideal plane-parallel slabs. In our laboratory the existence of the equilibrium state of these films was revealed for the first time.[28] Thus the concept of the disjoining pressure of thin liquid layers has been further generalized.[29] Later on, researches into free films have been extensively developed, first of all in the work of Sheludko[30] and his co-workers, then by Korkill, Goodman and Haydon,[31] Mysels,[32] Overbeek,[33] Lyklema[34] et al. The free films of hydrocarbon liquids have also been studied.[35,36] The presence of films of two types was first revealed by the research into free water films stabilised by soaps.

At low electrolyte concentration the equilibrium state of the film is mainly ensured by the forces of repulsion between two diffuse ionic atmospheres. In accordance with theory the equilibrium thickness of films of this type decreases comparatively rapidly as the pressure rises. These films are designated primary films. As the electrolyte concentration rises, these primary films lose their stability, and their thickness, in parts, drops to a value of 5–10 nm.

The analogy with the β and α wetting films[17] is striking. The thinnest areas eventually coalesce to form a film of uniform thickness which is so thin that the film appears to be black. The thickness of these free films varies little, as the effective capillary pressure of menisci increases. Their stability cannot be considered to have been completely clarified. They are generally termed secondary black, or Perrin films. Sometimes, the secondary films reveal tremendous stability over a large area, and even under conditions where they are at equilibrium with water vapour at a pressure which is substantially lower than that of saturation. Now, the stability of the primary black films is considerably smaller. Therefore, when the secondary films do not form, there is only a first defence line available, and the free films are easily broken through.

These facts show that two potential energy wells and two potential barriers may exist on the curve showing the dependence of the interaction energy upon thickness. The walls and barriers that correspond to the thinner, or secondary black, films are usually deeper and higher respectively. In the case of secondary black films with an aqueous core, the existence of a stabilizing potential barrier is probably connected with the structural component of the disjoining pressure. In favour of this hypothesis stands the fact that solutions of surfactants which produce stable secondary films are also able to form liquid–crystalline, smectic phases in the bulk. A similar observation can be made about thin interlayers hindering the coalescence of droplets of an oil emulsion in water; this in particular follows from the researches done by Friberg[37] and his coworkers at the Swedish Institute for Surface Chemistry.

A characteristic universally present is the dispersion component of the disjoining pressure; for symmetrical films it is always negative, and, therefore, when other components are absent, free films are unstable, tending to thin out. Sheludko,[38] nonetheless, succeeded in assessing that component of the disjoining pressure, by measuring the rate of thinning out of the free film.

2. Of special interest in proving the applicability of Hamaker's calculations, is the direct measurement of the molecular attraction between two solid bodies as a function of an air (or vacuum) gap separating them. The first correct measurements of that kind were carried out by myself[39] in collaboration with Abrikosova, by applying a negative feedback to the forces measurement. (This method, earlier suggested by myself, to be applicable to an ordinary analytical balance,[40] is now being extensively used by many firms.) These measurements were carried out for distances greater than 30 nm. For making the measurements a weighing operation was carried out. The measured values of the forces proved to be much smaller than expected on the basis of the calculations and the formulae of Hamaker. This might be explained qualitatively by the effect of electromagnetic retardation, which was first studied by Casimir.[68]

For the quantitative interpretation of the data we obtained, a macroscopic theory of the molecular interaction of macro-objects was developed by Lifshits.[41] This theory relates the molecular interaction of macro-objects to their absorption spectrum, and proves the non-additive nature of the paired dispersion interactions. The formulae derived proved to be in good agreement with our experimental results.

It should be noted that the magnitudes of the attraction forces, measured by Overbeek and Sparnay,[42] on the contrary proved to be much greater than one would expect from the Hamaker formulas. This has prompted a modification of the theory in another direction.[43] In fact, it appears that the measured forces resulted from the interaction of occasional surface charges.[44]

Further to this, similar measurements were carried out, both by us and by other authors (Kitchener,[45] Sparnay,[46] Overbeek, Black, de Jongh,[47] van Silfhout,[48] Wittman,[49] Tabor and co-workers[50] et al.). These measurements substantiated both the formula for small distances when the electromagnetic retardation is absent, and the formula for the limiting case of "full" retardation. Later on, Dzyaloshinsky, Lifshits and Pitaevsky[51] generalized the theory for the case of two different bodies with an arbitrary liquid interlayer in between. This essentially involved finding a method for the calculation of the molecular component of the disjoining pressure for any case, including vacuum and liquid interlayers. Further progress is due to Ninham, Parsegian, Langbein, and others who generalized the approach to systems of different geometry, including multilayers.

As the electrostatic component is the main factor of stability of lyophobic colloids, let us consider in more detail the limits of applicability of its calculation. It is generally known that the Poisson–Boltzmann equation is inapplicable at the high local concentration of ions that are found close to fairly strongly charged surfaces. Another difficulty consists in an accurate establishment of the boundary conditions for integration of the Poisson–Boltzmann equation. Also the determination of both potential and field near to the surfaces of a liquid interlayer creates a further problem and this problem requires a knowledge of the mechanism by which interfaces are charged. In the case where a charge arises preponderantly from the specific adsorption of ions of one sign, the charging mechanism is described by Stern or Grahame. In any case the potential at the boundary between the dense and the diffuse ionic layer will be much lower than the potential of the surface itself. Therefore, the concentrations of ions at the diffuse layer boundary will in fact permit the use of Poisson–Boltzmann equation[52], and the boundary conditions will have to be assumed to be delineated by the Helmholtz plane. The excess values of both the Maxwellian stress and the hydrostatic pressure field will have to be determined as well.

In all these calculations, the charge of the dense part of the double layer is assumed to be uniformly smeared over the surface. This, however, cannot be done when calculating the depth of the primary potential well and, hence, discussing the problem of irreversibility of coagulation. Jalamov,[53] and later Richmond,[54] using the same method, considered the effect of a discrete, but strictly periodic arrangement of surface charges. We are, however, of the opinion that in the case where the colloidal particles are close to one another, a stochastic approach is more realistic. A theory was developed in collaboration with Muller[55] which showed in particular that if the charge of each surface of very thin interlayers has been neutralized owing to the adsorption of counterions, the surfaces are eventually attracted. This may be used to explain aging coaguluns It follows from the theory of Derjaguin and Landau,[12] that the concentration of coagulation is inversely proportional to the sixth power of the charge of the counterions when the surfaces are charged to a high potential. Now the rule also proves to be valid even at low potential, say, of the order of scores of millivolts. Moreover, it is frequently applicable to cases where the rule of Eilers and Korff[56] (whose theoretical derivation presupposes the ionic force is small) is valid. As was shown by Usyarov,[57] this seeming contradiction can be removed, if the laws of the adsorption of ions determining the surface charge are taken into account. So, in the theory of the stability of lyophobic colloids, the calculation of the disjoining pressure of charged particles can only be completed by considering the mechanism of their charging. Only then can one predict how the charge and the potential of particles approaching one another will change.

3. In the general case, the ratio of the rapid coagulation rate to the actually observed slow coagulation rate may be assumed to be the measure of the stability of a colloidal

system. As is well known, that ratio, later called the retardation coefficient, is defined according to Fuchs[58] by the following equation:

$$H = \frac{L_\infty}{L_0} = \int_0^\infty \frac{e^{U(H)/kT}2r \, dJ}{(2r+H)^2}. \tag{1}$$

In the literature, experimental facts were mentioned that do not agree quantitively with eqn (1). In a work by Muller and myself[59] a correction was suggested which should be inserted in the above expression, in order to take into consideration an increase in the viscous resistance offered to the approach of two particles at small distances apart.

Similar conclusions were drawn by Spielman,[60] who did not refer to our earlier work. However, the correction did not reconcile the differences between experiment and theory.

As shown by researches made using the flow ultramicroscope,[61] the character of slow coagulation does not agree with the calculation of Fuchs even qualitatively. The calculation procedure describes only the interaction of two particles under the influence of Brownian motion, until they completely stick to each other, without taking into consideration the reverse disaggregation process. It also fails to take into account the differences between the forces of interaction of aggregates with individual particles as compared to the interaction between primary particles. Therefore, Fuchs's theory is in principle able to describe only the initial stage of slow coagulation.

Figure 1 depicts the dependence of $1/n$ upon time τ, where n is the number concentration of the red gold sol at various concentrations of NaCl; these data were obtained using the flow ultramicroscope.[61] Straightening of the curves occurs only in the case of rapid coagulation. At low electrolyte concentrations a quasi-equilibrium is es-

tablished in a short period. This indicates that the processes of aggregation coupling are rapidly counterbalanced by the processes of decomposition or disaggregation. In a number of cases the aggregation does not proceed further but stops after the formation of pairs of particles. With higher concentrations of electrolyte, after a certain period of time the quasi-equilibrium state ends with a progressive rise in the curve. Simultaneously, comparatively large-size aggregates were detected with the microscope.

This process is to some extent similar to the formation of nuclei of a new phase after passing through a critical nucleus state. In the present case the ending of the state of equilibrium and the rise in the curve may be explained by the fact that when adding the third particle (or more, the bond energy is at least doubled, and the decomposition of aggregates becomes improbable.

Consequently, in this case, slow coagulation differs from rapid coagulation in the character of kinetics rather than in the value of retardation coefficient. This difference may cause inconsistencies in the slow-coagulation theory. Martinov and Muller[62] developed the slow coagulation theory, taking into account the decomposition of aggregates and the existence of a secondary potential well. They found, however, no sharp coagulation threshold, and the coagulation process rapidly passed into a quasi-equilibrium state.

In conclusion let us consider certain results arising from the development of the theory of stability of symmetrical and non-symmetrical liquid films.

Let us consider a symmetrical (free) film comprising of a component 1 in an amount of Γ_1 mol/cm^2 which is not contained in the adjacent phases, and two other components 2 and 3, which are also contained in the other phases. Then the condition for stability of the film will be:[63]

$$\left(\frac{\partial \sigma}{\partial \Gamma_1}\right)_{T,\mu_2,\mu_3} < 0, \tag{2}$$

where σ is the film tension; μ_2 and μ_3 are the chemical potentials of components 2 and 3, respectively; and T is the absolute temperature.

It would be more convenient to express the condition for stable equilibrium of films in terms of their disjoining pressure π. This directly defines the equilibrium conditions for the film. The stability condition is expressed as follows:[63]

$$\left(\frac{\partial \pi}{\partial \Gamma_1}\right)^{T,\mu_2,\mu_3} < 0. \tag{3}$$

In the case where the film contains two components 1 and 2, which are only present in the film, and two other components 3 and 4, which are present in the adjacent phases also, the conditions (2) or (3) will be insufficient for equilibrium stability. An additional condition[64] has to be fulfilled, which will not be dealt with here.

The conditions for the stability equilibrium of non-symmetrical wetting films of a similar composition are identical to conditions (2) and (3).

The conditions for quasi-and stable equilibriums are considerably more complicated in the case where two wetting films coat the surfaces of a narrow, slit-shaped pore. In recent work[65] this case has been considered by taking into account the influence on the equilibrium of each layer, not only in terms of its interaction with the substrate, but also allowing for the effect of Van der Waals forces resulting from the layer coating the opposite
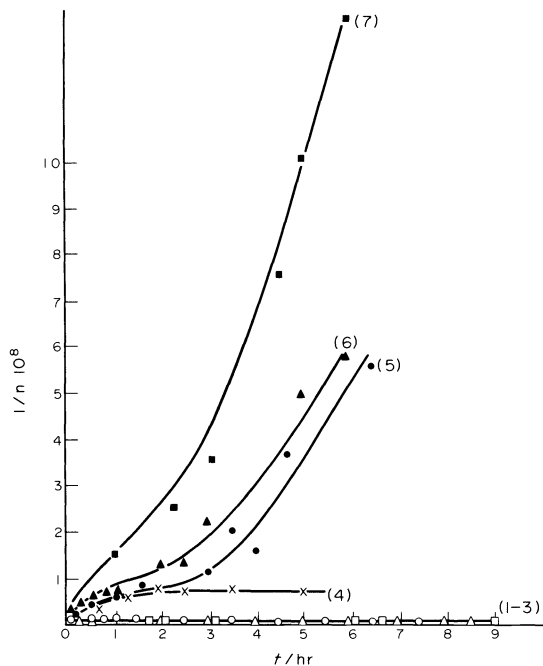

Fig. 1. The relationship between the inverse particle concentration and time. Red gold sol. Electrolyte: NaCl. (1–3) {$\triangle$ $1.0 \cdot 10^{-2}$ mol l^{-1}, $\bigcirc$ $1.5 \cdot 10^{-2}$ mol l^{-1}, $\square$ $1.6 \cdot 10^{-2}$ mol l^{-1}}, (4) $\times$ $1.8 \cdot 10^{-2}$ mol l^{-1}, (5) $\bullet$ $2.0 \cdot 10^{-2}$ mol l^{-1}, (6) $\blacktriangle$ $3.0 \cdot 10^{-2}$ mol l^{-1}, (7) $\blacksquare$ $6.0 \cdot 10^{-2}$ mol l^{-1}.

surface of a slit. It was shown that the equilibrium film thickness increases as the slit width decreases until on reaching a certain critical value of the width of the slit (or gap between the films), the latter lose their stability, coalescing together. It was demonstrated that taking into account this phenomenon enables one not only to render a more precise theory of capillary condensation and sorption of vapour in porous bodies, but also to explain sorption hysteresis on a very general basis.

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