

LONG DISTANCE FORCES ACTING BETWEEN COLLOIDAL PARTICLES.

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The theory of the long distance force acting between the particles in a colloidal solution, more especially in the case where the particles are surrounded by an electrical double layer, was considered shortly before the war by several authors. Their results were contradictory in the main points. We have made an extensive investigation of the same problem,^{1, 2} and arrived at the conclusion that the theoretical considerations of the authors referred to above were all more or less unsatisfactory.

In section 1 of the present paper we shall give a brief critical discussion of this work. In sections 2 and 3 we shall then give a very brief summary of our own theoretical considerations and the results we obtained.

1. Work of Previous Authors.

The work of Corkill and Rosenhead³ and the extensive theory of Levine and Dube⁴ have this point in common that they both arrive at the conclusion that the interaction of the double layers of two parallel plates or two spherical particles leads to an attraction, at least at larger distances. From a theoretical point of view their treatments are closely analogous. Their considerations are, however, incorrect for two reasons:

(a) The main objection against their considerations of the case of two colloidal particles for which the particle charge is not altered by the interpenetration of the double layers is that they calculate the energy of the electrical field of the double layer system. In reality, however, the force between the particles due to the interaction of the double layers

¹ (a) Verwey, *Trans. Faraday Soc.*, 1940, **36**, 192; (b) *Chem. Weekblad*, 1942, **39**, 563 (in Dutch); (c) Contribution to a symposium held at Utrecht by the *Ned. Chem. Ver.*, July, 1944, (in Dutch); (d) *Philips Research Reports*, 1945, **1**, 33 (English translation of 1(c)).

² Verwey and Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1946).

³ Corkill and Rosenhead, *Proc. Roy. Soc. A.*, 1939, **172**, 310.

⁴ Levine, *ibid.*, **170**, 145, 165; Levine and Dube, *Trans. Faraday Soc.*, 1939, **35**, 1125, 1141; 1940, **36**, 215; *J. Physic. Chem.*, 1942, **46**, 239; *Phil. Mag.*, 1940, (7), **29**, 105.

is determined by the variation of the *free* energy of the system as a function of the distance. Accordingly these authors neglected the entropy associated with the thermal motion of the ions in the solution carrying the charge of the diffuse outer layer. We have been able to show that the two quantities (field energy and free energy) behave in an entirely different way as a function of the distance. The correct theory leads to a *repulsive* force between the particles for all particle distances.

(b) Usually—especially in lyophobic systems—the potential of the double layer will be independent of the distance between the particles. In this case the charge of the particles is altered by the interaction of the double layers (i.e. it decreases with decreasing distance between the particles). This possibility has also been considered by the authors mentioned above. In this case their erroneous results are mainly explained by the fact that they do not take into consideration the chemical changes associated with the variation of the charge. It can easily be shown, however, that the change in the chemical free energy is the predominant term if the distance between the particles is varied while keeping the surface potential constant. The correct theory again leads to a *repulsion* for all particle distances as a consequence of the interaction between the double layers.

The work of Langmuir⁵ has an entirely different character; he also arrives at the result that the ionic spheres of the particles are responsible for attractive forces between the particles. He considers the colloid as a whole (charged particles + dissolved ions) and applies the Debye-Hückel electrolyte theory to such a system. The result mentioned above, however, is entirely explained by the errors caused by the use of the linear Debye-Hückel approximation.

Derjaguin⁶ and also Langmuir in the last part of his paper, derives an equation for the force between two parallel plates covered by an electrical double layer. These force equations are fundamentally correct and can also be derived from free energy considerations. Derjaguin extends his theory to spherical particles. His theory of the stability of lyophobic colloids, however, is unsatisfactory for two reasons.

(a) In order to reduce the mathematical difficulties, he applies the double layer theory in its linear approximation, analogous to the Debye-Hückel theory of electrolytes. For colloid systems, however, especially if the particles are no longer small in comparison with the "thickness" of the ionic spheres, this approximation gives results which are quantitatively completely unsatisfactory.

(b) In Derjaguin's theory the flocculation of a sol is considered to be induced by an infinitely large attraction force acting only when the particles are in direct contact. In our theory we have been able to show that the long distance action of the London-van der Waals attractive forces is an essential factor in determining the stability of colloids.

2. Outline of the Theory Presented Here.

The effect of the interaction of the double layers surrounding the particles is most easily found by considering the free energy of the systems as a function of the distance between the particles. This free energy can in principle be obtained in two different ways, which lead to the same result. The first is to start from a generalised Lippmann equation, giving the free energy as a function of the surface charges and the surface potential. For the simple case of two parallel plates we have per cm.²

$$F = - \int_0^{w_0} \sigma d\psi_0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

⁵ Langmuir, *J. Chem. Physics*, 1938, 6, 893.

⁶ Derjaguin and Kussakow, *Acta Psychicochim.*, 1939, 10, 25, 153. Derjaguin, *ibid.*, 1939, 10, 333. *Trans. Faraday Soc.*, 1940, 36, 203.

in which ψ_0 is the electrical potential of the plate surface and σ the surface charge density. For the integration of this equation we must know σ as a function of ψ_0 ; as we did not wish to apply the double layer theory in its linear approximation, this is a rather complicated function containing, for instance, the distance of the plates and the concentrations and the valencies of the ions in the medium.

The second way shows some analogy with the derivation of the free energy of an ion in its ionic sphere as given in Debye and Hückel's theory of electrolytes. According to this method the free energy of the double layer system is found as the total amount of work associated with the gradual discharge of all ions of the system, including the ions responsible for the surface charge. If this discharging process is carried out under such conditions that the surface potential is kept constant the chemical work exactly cancels the electrical work for the surface charge. The final expression, therefore, contains only the charge of the diffuse part of the double layer. Again, for the case of two parallel plates we have (when we only consider one half of the system between $x = 0$ and $x = H/2$, H being the distance between the plates)

$$F = \int_0^1 \frac{d\lambda}{\lambda} \int_0^{H/2} \rho' \cdot \psi' dx \quad . \quad . \quad . \quad (2)$$

in which ρ' and ψ' are respectively the space charge and the electrical potential in the solution corresponding to an ionic charge λe (during the discharging process λ decreases continually from 1 to 0). Accordingly ρ' and ψ' are functions of x (the distance from the surface), λ , and H .

Using the differential equation (for sake of simplicity we only consider symmetrical electrolytes, ionic valency = v) :

$$\Delta\psi = \frac{8\pi nve}{\epsilon} \sinh(v\psi/kT) \quad . \quad . \quad . \quad (3)$$

which also forms the starting point of the Gouy-Chapman theory for a single double layer, equation (2) can be solved and evaluated numerically. Thus we obtain F as a function of the distance between the plates, with v (the valency of the ions), n (the ionic concentration) and ψ_0 as variable parameters. From this we directly obtain the repulsive potential V_R per cm.² due to the double layer interaction

$$V_R = 2(F - F_\infty)$$

in which F_∞ is the free energy for $d = \infty$.

The theory shows that the most important part of the potential curve V_R is that for which $\frac{\kappa H}{2} < 1$, in which κ is the well-known Debye quantity.

$$\kappa = \left(\frac{8\pi n}{\epsilon kT} \right)^{\frac{1}{2}} \cdot ve.$$

For the distances in this region the repulsive potential function approaches an exponential decay function, exp. $(-\kappa H)$. The theory can also be extended to spherical particles by an approximative method already suggested by Derjaguin, applicable in those cases for which $\kappa a > 5$, if a is the particle radius. This condition is generally fulfilled in colloid systems containing some electrolyte in the sol medium. The potential curves obtained in this way do not differ much from those valid for the case of two flat plates.

The problem of the interaction of two spherical particles with a radius of the same order of magnitude as the double layer extension, or even smaller, cannot be solved in such a way, with the theory for two flat layers as a starting point. In this case it is unavoidable, for mathematical reasons, to simplify equation (3), and to introduce the linear approximation of Debye and Hückel, or, at best, the second or third approximation as has also been done by Levine and Dube. The free energy is now most

easily obtained by making use of equation (1). A less satisfactory point of this theory is the use of the linear approximation. Fortunately, however, when the particles are small in comparison to the "thickness" of the double layer, the error involved by this simplification is considerably smaller than for larger particles.

Having thus obtained a fairly complete picture of the repulsive potential resulting from the interaction of the double layers, based on the same principles as the Gouy-Chapman theory for a single double layer* (diffuse double layer), the theory of the stability of colloids and the long distance forces acting between the particles can be completed by considering also the van der Waals-London attractive potential V_A .

As a first approximation we used here the well-known London equation stating that the attractive potential between two atoms is proportional to r^{-6} , in which r is the distance between the atoms. A fundamental point of London's theory is that the attraction between all atoms is additive. The summation can be substituted by an integration. This integration shows that the attractive potential between two flat plates decreases according to H^{-2} and therefore considerably less steeply than between two atoms (de Boer).⁷ The attractive potential between two spheres is a rather complicated function (Hamaker);⁸ for small distances it approaches a H^{-1} law, if H now means the closest distance between the surfaces of the spheres; for very large distances it will again be proportional to R^{-6} , if R is the distance between the centres, or approximately to H^{-6} .

The force acting between two colloidal particles can then be read from a diagram containing the total potential curve

$$V = V_R + V_A$$

in which V_R and V_A are both functions of the distance between the particles; V_A is a negative quantity.

London's theory of the dispersion forces is based on the conception that the attraction is due to the polarisation of one atom as a consequence of the fluctuating dipole in a second atom. It does not take into account the finite time needed for the transmission of the electromagnetic field from the first atom to the second, and vice versa. This retardation will come into effect if the distance between the particles becomes of the order of the characteristic wavelengths of the participating atoms, i.e. of the order of 1000 Å. The van der Waals-London attractive potential between two colloidal particles some distance apart will generally contain many contributions of atomic pairs at such a distance or even at a larger distance. It can, therefore, be expected that the attractive potential especially at larger particle distances, will be appreciably smaller than suggested by the simple London-theory (Overbeek). Casimir and Polder have therefore reinvestigated the theory of dispersion forces (not yet published). They accounted for the effect mentioned above by applying the relativistic correction to the quantum mechanical theory. They found that for larger atomic distances the attractive potential between two atoms decays more rapidly than given by London's equation; the deviations become important for distances of the order of 500 Å. and their results show that for large distances the attractive potential approaches a r^{-7} law instead of a r^{-6} law.

This correction has not yet been applied in the potential curves to be discussed in the following section. It should be borne in mind, however, that it may have a perceptible influence upon these curves especially for larger particle distances.

* We have also extended our theory for the interaction of two double layers of the Stern-type, in which a correction has been applied for the finite dimension of the ions in the medium. For this extension we must refer to the book mentioned in ref. 2.

⁷ de Boer, *Trans. Faraday Soc.*, 1936, 32, 21.

⁸ Hamaker, *Physica*, 1937, 4, 1058.

3. Results.

The total potential curves obtained according to the theory outlined in section 2 generally have the shapes indicated in Fig. 1 and 2. Fig. 1 gives a set of potential curves for different values of ψ_0 for two parallel plates in a rather concentrated solution of a monovalent electrolyte. Fig. 2

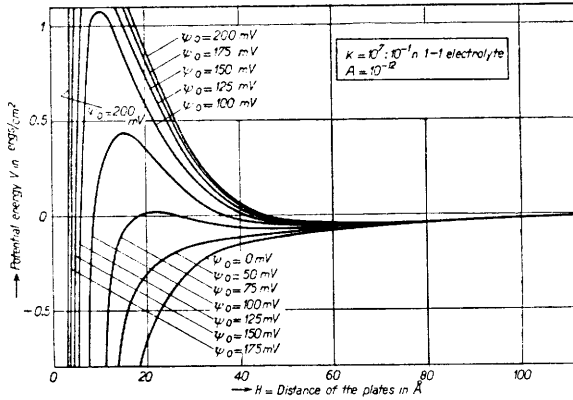


FIG. 1.

gives similar curves for two spherical particles in a more diluted electrolyte solution. The constant A is a proportionality factor determining the magnitude of the attractive potential; according to the quantum mechanical theory it will depend somewhat on the material of the particles and the sol medium but should be of the order of 10^{-12} erg. It is seen that

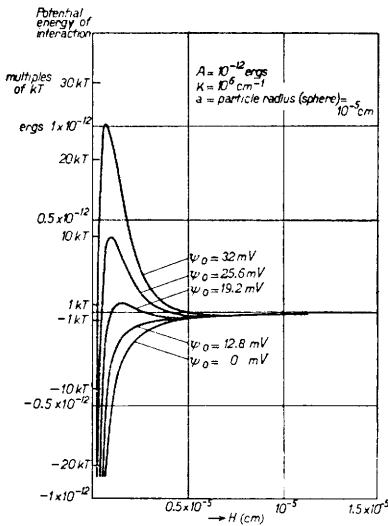


FIG. 2.

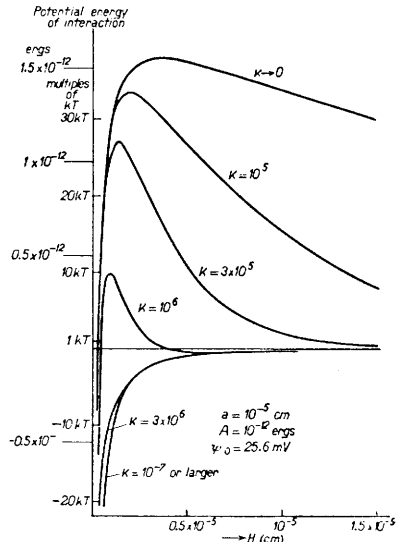


FIG. 3.

the double layer potential must have a certain minimum value in order to obtain a potential curve with a maximum; in the more dilute solution the potential required is lower than in the more concentrated electrolyte. This can also be read from Fig. 3, showing potential curves for $a = 10^{-5}$ cm. and $\psi_0 = 25.6$ mv. for varying values of κ (κ is proportional to \sqrt{n}).

The theory for the kinetics of slow coagulation shows that in stable sols the potential barrier preventing the agglomeration must be at least 20 to 25 times kT . Hence in such a sol the particles cannot approach each other completely, and each particle is surrounded by a spherical liquid shell where a second particle of a similar kind never penetrates. The distance between the particle surfaces at which the potential curve has a maximum depends on the concentration and the valency of the ions in the sol medium, and also on the dimensions of the particles. If the particles are large in comparison with the "thickness" of the double layer the maximum is reached for a particle distance equal to about 1 to 2 times the characteristic length $1/\kappa$ (see Fig. 1 and 2); in "salt-free" water $1/\kappa$ is of the order of 1000 Å., in 10^{-1} N solution 10 Å. If the particles are smaller the maximum is reached for a smaller distance between the particle surfaces (see Fig. 3, curve for $\kappa = 10^5$). The presence of such a protective layer caused by the interaction of the double layers, which determines the stability of lyophobic colloids, is apparent from many other phenomena in colloid chemistry as e.g. in the so-called electroviscous effect of lyophobic sols,* in the special arrangement in sediments from sols containing disc-shaped particles, in the phenomena observed in the formation of a deposit by electrophoresis, etc.

If the height of the maximum is decreased, which can be effected by decreasing ψ_0 (Fig. 1 and 2), or by increasing the electrolyte concentration (Fig. 3) the probability that a second particle crosses the potential barrier increases rapidly and the sol will show the phenomenon of a more or less "slow coagulation." For very low values of the maximum or for potential curves containing no maximum at all we finally reach the region of "rapid coagulation" in which every particle encounter leads to an agglomeration. In both cases the second particle enters the deep minimum for very short particle distances, i.e. the particles approach each other until the Born repulsive forces between the atoms of different particles come into action.

The theory shows that for short particle distances the van der Waals-London attraction potential generally prevails, causing the deep minimum which is responsible for the sticking together once the particles have come together within these small distances. All curves show however a second distance at which attraction always prevails. This is caused by the fact that the attractive potential, though decreasing more rapidly than the repulsive potential at short distances, decays more slowly at larger distances of the particles. Accordingly all curves containing a maximum at intermediate distances show a weak minimum at larger distances. This conclusion remains true if we apply the relativistic correction to the theory of dispersion forces, though the effect of this correction will be to lower the actual depth of these minima to an even lower level than suggested by the potential curves represented here. But even the minima occurring in Fig. 2 and 3 are so weak (the depth being less than kT) that they will normally escape experimental detection. Under very favourable conditions however, this minimum for large distances may come into effect and offer an explanation of certain phenomena observed in colloid chemistry. This may occur, for instance, for blade-shaped or linear particles oriented parallel to each other, as may be shown by comparing disc-shaped particles and spherical particles of the same radius. If we again take $\kappa = 10^6$, $a = 10^{-5}$ cm. and $\psi_0 = 25.6$ mV. we find for two spherical particles a minimum of about 2×10^{-14} erg (about $\frac{1}{2}kT$), and for two disc-shaped particles oriented parallel and facing each other 2×10^{-13} erg, or about $5 kT$ (calculated from the equations

* The strong decrease of the viscosity of many lyophilic colloids caused by small amounts of electrolytes, though determined by the same repulsive forces between different parts of the same "particle" (molecule), is slightly more complicated due to a variation of the shape of the particles (contraction to a less stretched form).

for two flat plates). This minimum, corresponding to a distance between the particles of about 1000 Å., has now sufficient depth to ensure that two particles with parallel orientation and at this distance from each other will travel together for a certain amount of time. There will also be a certain probability that this particle pair orients other particles in such a way as to form larger rows or groups in which the particles are captured in the field of two or more other particles. The depth of the minimum is proportional to a^2 , and will therefore be larger for larger discs.

A phenomenon as described in the foregoing paragraph has actually been observed in sols of Fe_2O_3 and V_2O_5 (a sol with lath-shaped particles) by Zocher.⁹ This phenomenon which has been called the formation of tactoids is especially observed in aged sols, i.e. sols with sufficiently large particles. Similar phenomena have been described by Bernal and Fankuchen¹⁰ for solutions of the tobacco mosaic virus, the particles of which have the shape of thin cylinders. Here the particles are arranged according to a two-dimensional hexagonal pattern. A parallel orientation, in such a way that the particles are in their weak potential minima, is in this case also favoured by the fact that each particle is surrounded by six direct neighbours. In order to test this hypothesis we have extended our theory to the interaction of cylindrical particles. A provisional calculation has shown that for a particle distance of 500 Å. and a particle length of 5000 Å. the minimum is at best of the order of magnitude of kT . As a somewhat deeper minimum seems to be required to explain the phenomena this might be an indication that the actual kinetic units are several times longer.

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⁹ Zocher, *Z. anorg. Chem.*, 1925, **147**, 91.

¹⁰ Bernal and Fankuchen, *Nature*, 1937, **139**, 923. *J. gen. Physiol.*, 1941, **25**, 111.