ON THE DYNAMICS OF THE LYOPHOBIC COLLOIDS

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Abstract. According to the standard theory, a spatially-extended (diffuse) double layer is assumed to occur in charged colloids (suspensions), leading to repulsive forces that might compensate, at relevant distances, the attractive molecular forces. It is shown in this paper that a surface double layer of atomic dimensions is present at the surface of neutral condensed bodies, which originates in the cohesion of the condensed matter. This surface double layer generates exponentially small forces, with a (negative) exponent of the order of the ratio of the distance to the mean distance between the atomic constituents. Such colloids may be termed neutral colloids. The forces generated by the surface double layer are too small to compensate the attractive molecular forces and to ensure the equilibrium at relevant distances. The surface double-layer forces are calculated here explicitly for half-spaces and spheres, both in vacuum and in a material medium. The examination of the dynamics of the neutral colloids leads to the conclusion that, very likely, a (quasi-) equilibrium may be attained for mean separation distances between the colloidal particles much larger than their plasma wavelength, where the molecular forces become, practically, ineffective. For charged colloids (charged, for instance, by electrolyte dissociation) the electric interaction of the ions and colloidal particles requires the application of the cohesion theory of electrically-interacting particles, which may lead to particle stabilization, or even aggregation. The equilibrium mean separation distance is estimated here within this theory and the Hardy-Schulze-Ostwald law is obtained.

Key words: Lyophobic colloids; double layer; interface; molecular forces.

1. INTRODUCTION

It is well known that lyophobic colloids (and suspensions) are subject to attractive molecular forces (van der Waals-London-Casimir forces) [1, 2]. Other forces which may appear in these colloids are either particular or too small, such that they may be left aside in the present discussion. At the same time, the current DLVO (Deryagin-Landau-Verwey-Overbeek) theory of charged lyophobic colloids assumes that spatially-extended double layers generate repulsive forces which, combined with the attractive forces, may ensure equilibrium at relevant distances, at least for long periods of time [3, 4]. The interface which may appear at the contact of two condensed phases diminishes gradually the effects of the double layer [5] (as it is known

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in emulsions or, especially, in semiconductors). The DLVO theory is the current standard theory of lyophobic colloids (see, for instance, Refs. [6]-[9]); it is viewed as accounting satisfactorily for the stabilization, aggregation and, generally, dynamics of the colloidal suspensions, by means of the spatially-extended (diffuse) double layer, assumed to appear in charged colloids, as a consequence of the particle-medium interface. However, a number of issues are raised by this theory, which are discussed in this paper. A critical survey of the DLVO theory, partly from different perspectives, is given in Refs. [10, 11].

Our previous work [12]-[16] in the cohesion theory of the condensed matter shows that a double layer of atomic dimensions appears at the surface of the neutral condensed bodies (in vacuum or in a material medium), as a consequence of the cohesion forces. We call it a surface double layer, in order to distinguish it from the spatially-extended (diffuse, Gouy-Chapman) double layer. Its occurrence may already raise a problem for the theory of colloids. We analyze this surface double layer in the first part of the present paper; the charged colloids are treated in the second part. It is shown that the forces generated by the surface double layer are exponentially small, with a (negative) exponent of the order of the ratio of the distance to the atomic-scale distances. Consequently, these forces are much smaller than the attractive molecular forces for any distance much larger than atomic distances. We calculate in this paper the surface double-layer forces for half-spaces and spheres, both in vacuum and in a material medium. These forces are attractive for half-spaces and repulsive for spheres. While they are small for all distances of interest, they acquire high values over distances of the order of the atomic distances. The electric field of the surface double is limited to the atomic vicinity of the surface. In the bulk of the medium the forces generated by the surface double layer are vanishingly small. We call such a colloid a neutral colloid. It follows that the equibrium of the neutral lyophobic colloids (suspensions) cannot be attained without special conditions. The analysis of the dynamics of the neutral colloids made here leads to the conclusion that, very likely, a (quasi-) equlibrium may be attained for mean separation distances between particles much larger than their plasma wavelength, where the molecular forces become, practically, ineffective. The analysis of the surface double layer made here may help clarify results obtained usually in the diffuse double-layer theory.

In the presence of a small amount of electrolyte (or by various other means) the surface of the colloidal particles may acquire electric charges. The charged colloid particles and the in-between ions interact by electric forces. In this case it is necessary to resort to the cohesion theory mentioned above. The double layer theory is usually restricted to computing the interaction energy (forces) between a pair of particles, but, in order to estimate the equilibrium, we need the total energy of the ensemble, because the interaction implies long-range forces. For many, small particles, as in a colloidal ensemble, the total surface is comparable with the total volume, such that it brings an important contribution to the total energy ("surface energy" [17]). This contribution is taken into account by the cohesion theory. Within this theory we show here that the charged colloids may be stabilized (aggregated), or even flocculated at small distances (without resorting to attractive molecular forces). The equilibrium mean separation distance is estimated here in this case within the framework of the cohesion theory of electrically-interacting particles and the Hardy-Schulze-Ostwald law is obtained. We assume in this paper that the cohesion modifications of the interface occur over distances of the order of the atomic distances (as for a perfect contact), and the interface remains well-defined over distances of this order.

We include here a brief comment on the current use of the Debye-Huckel theory for colloids, where there are a few basic points which need attention. A density of positive and negative ions $n_{\pm}=ne^{\mp q\varphi/T}$ is usually assumed, where n is the concentration of ions, $\pm q$ are the ion charges, φ is the electric potential generated by these ions and T is the temperature. The Poisson equation is usually written as

$$\Delta\varphi=4\pi nq\left(e^{q\varphi/T}-e^{-q\varphi/T}\right)\simeq\kappa^{2}\varphi\ , \tag{1}$$

where $\kappa^2=8\pi nq^2/T$ and, for simplicity, $q\varphi/T$ is assumed to be much smaller than unity. First, we can see that there is an imbalance of charge in equation (1), which indicates that we need boundary conditions, as it is well known. The boundary conditions ensure the global charge neutrality. If we take as a boundary condition a point-like ion, then the solution has the well-known form $\varphi\sim e^{-\kappa r}/r$, where r is the distance from that ion. However, in that case the corresponding density of ions in equation (1) should be absent, since the source terms are distinct from boundary conditions, and they should not be counted twice. The solution is given in that case by the change caused by the potential φ in the density of the other type of ions, and the parameter κ^2 becomes $\kappa^2=4\pi nq^2/T$ [15]. The same is valid for ions placed on the surface of the domain, for instance on a plane surface, where the solution has the form $\varphi\sim e^{-\kappa x}$, x being the distance from the surface. In these cases there is only one species of ions in the charge distribution included in equation (1). More exactly, there is only the charge excess which is relevant as a source term in equation (1). Unfortunately, this misleading circumstance is often overlooked.

Second, there is a problem with the approximation of the type $n_+=ne^{-q\varphi/T}\simeq n-nq\varphi/T+...$ in the Debye-Huckel equation. It was shown [15] that the contribution of the constant term n may be absorbed in the potential and has no effect in the interaction energy, while higher-order terms in the expansion of n_+ bring negligible contributions in the dilute (weak-coupling) limit. However, close to equilibrium, the interaction energy computed with this approximation may be overestimated by $\simeq 30\%$ [15].

Third, it is usually assumed that the temperature in the expression of κ is the colloid temperature, while, in fact, it is the dissociation temperature, because the ionic dissociation occurs under the action of the electrical forces of the surrounding medium, not under the thermal action of the medium (though the thermal motion of the medium may help the effect of the electric forces to increase); it is easy to see that the dissociation process is a statistical process, with the temperature of the order $T \simeq q^2/a$, where a is a distance of the order of the atomic distance in the electrolyte molecule. This is why there is no need, in fact, to compute the free energy (the temperature T which enters the parameter κ and the mechanical energy is distinct from the colloid (medium) temperature). We note that the dissociation process is distinct from the thermal motion of the ions (electrolyte molecules) in the medium.

Finally, we note that the proper Debye-Huckel equation with proper boundary conditions may lead to a two-particle interaction energy which is attractive at long distances and has a negative minimum (without including molecular forces), in contrast with the standard results of the double-layer theory; this is shown in this paper for charged spherical colloidal particles. Although equation (1) is often used as a starting point for electrolytes or homogeneous weakly-interacting plasmas, its application to colloids (which originates with the work of Gouy [18] and Chapman [19]) can be misleading.

2. PLASMA MODEL

In a condensed phase (solid, liquid) the electrons and the ions are redistributed with respect to the neutral-atom (molecule) state. A similar situation occurs in a plasma. The Coulomb energy associated with this charge redistribution leads to cohesion. We may view such a condensed-phase model as consisting of N identical ions with charge q and N identical negative ions with charge $-q$, where q is connected with the chemical valency; the electrons may play the role of the negative ions. It is not necessary for our discussion to specify the valency, nor the number of ions in a dissociated (distorted) molecule; it is sufficient to impose the charge conservation. Similarly, we may extend the discussion to several species of ions. The charge redistribution generates an electric potential. At any point in the sample we are near an ion which is surrounded by a cloud of counter-ions; therefore, we may attribute a position $\mathbf{R}_i$ to that ion ($i = 1, 2, ...N$) and a density $n(\mathbf{r})$ to the surrounding counter-ions. The less-mobile q-ions are given positions $\mathbf{R}_i$ and the more mobile $-q$-ions (counter-ions) are described by density $n(\mathbf{r})$. The potential φ should satisfy the Poisson equation

$$\Delta\varphi = -4\pi q \sum_i \delta(\mathbf{r} - \mathbf{R}_i) + 4\pi q \delta n(\mathbf{r}) \ , \tag{2}$$

where $\delta n(\mathbf{r})$ is the (small) change in the density with respect to the neutral-atom (molecule) state.

For metals consisting of cations and electrons at high densities $\delta n(\mathbf{r})$ is the density of the collective electrons in the Fermi sea. The relationship $4\pi q\delta n(\mathbf{r}) = \kappa^2 \varphi(\mathbf{r})$ exists between this density and the potential, where κ is a variational parameter determined from the cohesion condition (minimum of the energy); it is found $\kappa a \simeq 1$, where a is the mean separation distance between the ions (concentration $n = 1/a^3$) [12]. For a classical plasma (where the temperature effects are relevant), consisting either of cations and electrons, or of both types of ions, the density is $n(\mathbf{r}) = ne^{q\varphi(\mathbf{r})/T}$ and $\delta n(\mathbf{r}) \simeq nq\varphi(\mathbf{r})/T$, where T is the temperature of the counter-ions; in this case $4\pi q\delta n(\mathbf{r}) = (4\pi nq^2/T)\varphi(\mathbf{r})$ and $\kappa^2 = 4\pi nq^2/T$ [15]. This is Debye-Huckel theory, where $1/\kappa = a\sqrt{Ta/4\pi q^2}$ is the Debye screening length. Therefore, in both cases equation (2) becomes

$$\Delta\varphi = -4\pi q\sum_i \delta(\mathbf{r}-\mathbf{R}_i) + \kappa^2\varphi(\mathbf{r}) \tag{3}$$

(to be compared with equation (1)). The solution of this equation is the screened Coulomb potential

$$\varphi = q\sum_i \frac{1}{|\mathbf{r}-\mathbf{R}_i|} e^{-\kappa|\mathbf{r}-\mathbf{R}_i|}\ ; \tag{4}$$

its vanishing at infinity ensures the charge conservation, which can readily be checked in equation (3). The ion-counter-ion attraction, the repulsion between counter-ions and the repulsion between the ions leads to the total interaction (potential) energy [12, 15]

$$E_{pot} = -\frac{3}{4}Nq^2\kappa - \frac{1}{4}q^2\kappa\sum_{i\neq j}\left(1 - \frac{2}{\kappa|\mathbf{R}_i-\mathbf{R}_j|}\right)e^{-\kappa|\mathbf{R}_i-\mathbf{R}_j|} \tag{5}$$

(the details of calculation are given below, for the more general case of charged colloids). We can see that the total potential energy given by equation (5) includes ionic self-energies $(-3q^2\kappa/4)$ and inter-ionic potentials (summation over $i \neq j$), which exhibit minima. At long distances these potentials are attractive, while at short distances they are repulsive. Therefore, at low ionic temperatures and high densities we may have solids, with a precursory liquid phase, *i.e.* we may have cohesion. The equilibrium of the ionic ensemble is obtained by minimizing (numerically) the total energy given by equation (5) with respect to $\kappa|\mathbf{R}_i - \mathbf{R}_j|$ [12, 15]. Similar results hold for distinct species of ions [16].

For metallic solids the minimum of the total energv gives equilibrium positions for ions and $\kappa a \simeq 1$ [12]. Qualitatively similar results hold for covalent bonding. Also, the transition to a liquid followed by a solid state is shown by using equation (5) for a classical plasma [15]. In that case the transition to the liquid state, which also occurs for $\kappa a \simeq 1$, is predicted by a van der Waals equation of state for a plasma gas with interaction (non-ideal gas). The counter-ion temperature is sufficiently high in that case that the equilibrium condition $\kappa a \simeq 1$ is fulfilled; for slightly higher densities or lower ion temperatures a liquid-solid transition occurs. These results hold both for electron-ion and ion-ion plasma. The plasma becomes a liquid for $\kappa a = \sqrt{4\pi nq^2/T}a \simeq 1$, *i.e.* for a Debye length of the order of the mean separation distance a, where the coupling parameter q^2/aT is of the order unity ($q^2/aT \simeq 1$). For a Debye length slightly shorter than a, the plasma becomes a solid, first a classical ("plasmonic") solid, thereafter, for slightly higher densities, when the quantum-mechanical behaviour begins to dominate, a quantum solid [15]. For two species of ions the equilibrium positions given by the minimum of the interaction potentials in equation (5) are for one species of ions (q-ions), the counter-ions being distributed symmetrically in the screeaning cloud (which extends over a nearest-neighbour region), such as to minimize the repulsion energy when passing from a continuous density to a discrete one (ionic solids). The plasma model described here may be used as a representative model for the cohesion of solids and liquids. This model is applied to homo-atomic metallic clusters [12]-[14], classical two-component plasmas [15] metallic binary clusters [16], and heavy atoms [20]. Basically, it is a quasi-classical model, which admits (small) quantum-mechanical corrections. We show below that it can also be applied to charged colloids.

3. HALF-SPACE

For finite-size bodies the cohesion potential given by equation (4) gives rise to a surface double-layer. Let us consider a uniform distribution of ions in the half-space $x < 0$ with a plane surface at $x = 0$ (continuum approximation). The potential φ given by equation (4) is

$$\varphi = \begin{cases} \frac{4\pi nq}{\kappa^2}\left(1 - \frac{1}{2}e^{\kappa x}\right) \ , \ x < 0 \ , \\ \frac{2\pi nq}{\kappa^2}e^{-\kappa x} \ , \ x > 0 \end{cases} \tag{6}$$

and the potential energy (equation (5)) is

$$E_{pot} = -\frac{3}{4}Nq^2\kappa + \frac{\pi nq^2}{2a\kappa^3}N_s \ , \tag{7}$$

where N_s is the number of surface ions. The minimization of the energy with respect to κ brings a correction proportional to $N_s/N \ll 1$ to $\kappa a \simeq 1$, which may be neglected. Making use of $\Delta\varphi = -4\pi\rho$, we get the charge density

$$\rho = -\frac{1}{2}nq \cdot \mathrm{sgn}(x)e^{-\kappa|x|} \tag{8}$$

and, from $4\pi n_c q = \kappa^2\varphi$, the counter-ion density

$$n_c = \begin{cases} n\left(1-\frac{1}{2}e^{\kappa x}\right) \; , \; x<0 \; , \\ \frac{1}{2}ne^{-\kappa x} \; , \; x>0 \; . \end{cases} \tag{9}$$

We can see that the internal face of the surface ($x<0$) is depleted of counter-ions, which spill over its external face ($x>0$). This is a surface double layer, which extends over distances of the atomic-scale order ($\kappa \simeq 1/a$). The surface energy in equation (7) gives the surface tension. The energy needed for taking a counter-ion from the surface ($x=0$) to infinity, $q\varphi(x=0^+) = 2\pi nq^2/\kappa^2$, is the work function of the material [21, 22]. The vibrations of the surface double layer (perpendicular to the surface) are the surface plasmons with frequency $\omega_0/\sqrt{2}$, $\omega_0^2 = 4\pi nq^2/m$, where m is the mass of the counter-ion. Also, the double-layer potential gives rise to a surface scattering lifetime of the electrons. The tunneling of the ions through the double-layer potential barrier generates the structured interface at the contact of two condensed phases. The apparition of this interface diminishes gradually the effects of the surface double-layer [5].

Making use of the potential φ and the charge density ρ (equations (6) and (8)), we can compute the self-energy of a half-space; it is given by

$$E_s = \frac{1}{2}\int d\mathbf{r}\varphi\rho = \frac{\pi n^2q^2}{2\kappa^3}S = \frac{\pi nq^2}{2a\kappa^3}N_s \; , \tag{10}$$

where S is the area of the surface; we can see that the self-energy is the surface energy in equation (7) (in the continuum approximation the ion self-energy $-3Nq^2\kappa/4$ is lost). Similarly, the interaction energy between two (identical) half-spaces with parallel surfaces separated by distance d (in vacuum) is

$$U = -\frac{\pi n^2q^2S}{\kappa^3}(1+\kappa d)\,e^{-\kappa d} \; ; \tag{11}$$

the force acting between these two bodies is

$$F = -\frac{\pi n^2q^2S}{\kappa}de^{-\kappa d} \; . \tag{12}$$

We can see that the force is attractive, with a minimum for $d = 1/\kappa \simeq a$, which indicates the tendency of the two bodies to collapse into one body.

A comparison of this force with the van der Waals-London-Casimir force shows that the former is much smaller (in absolute value) for distances much larger than atomic distances. This is due to the abrupt exponential fall of the double-layer force, as shown in equation (12) ($\kappa \simeq 1/a \gg d$). However, for distances of the order of the atomic distance a the force given by equation (12) is large ($F \simeq q^2/a^2$ per atom). This force, together with the Coulomb repulsion of the ions (which is absent in the continuum approximation) ensures the cohesion [12–16].

The Casimir force between two identical (metallic) half-spaces is $F_C = -\pi^2 \hbar c S/240d^4$, valid for $d \gg c/\omega_0$ (where ω_0 is the plasma frequency); the van der Waals-London force is $F_W = -\hbar\omega_0 S/32\pi\sqrt{2}d^3$ (for dielectrics small numerical factors may appear) [23, 24]. For (not very small) colloid particles the plasma wavelength $\lambda = c/\omega_0$ (of the order 10^3Å for $\omega_0 = 10^{15}s^{-1}$) is much larger than the mean inter-ion separation distance, such that the van der Waals-London-Casimir force dominates the double-layer force. The maximum value of the double-layer force (equation (12)) is of the order q^2/a^2 per surface ion ($\kappa \simeq 1/a$), reached for distances of the order $d \simeq a$, and the van de Waals force for this distance is of the same order $\hbar\omega_0//a \simeq q^2/a^2$ (we take a of the order of the Bohr radius); at these distances the two forces are comparable, but at very small distances the van der Waals force is appreciably modified by other forces, like solvation, hydrophobic or steric forces, whose nature is only partially known [25]. At larger distance we should compare e^{-x} with $1/x^3$, where $x = d/a$; we can see that the inverse power dominates the exponential. This is due to the large scale factor κ in the exponent of the double-layer force in comparison with the lack of scale in the inverse-power laws of the molecular forces. The relevant distances considered throughout this paper are distances much longer than the atomic scale distances ($d \gg a$).

4. MATERIAL INTERFACE. THE MEDIUM

Let us consider two half-spaces in contact with a plane separation surface $x = 0$. We denote all the quantities of the half-space $x > 0$ by the suffix 0 (material medium). The potential of this ensemble can be written straightforwardly by using equation (6). The self-energy per unit area of the surface is

$$E_s = \frac{\pi n^2 q^2}{2\kappa^3} + \frac{\pi n_0^2 q_0^2}{2\kappa_0^3} - \frac{2\pi n n_0 q q_0}{\kappa\kappa_0(\kappa+\kappa_0)} \; ; \qquad (13)$$

we can see that apart from the self-energies of the two bodies there appears an interaction surface energy, as expected (it contributes to the construction of the interface). We note that the potential of the interface given by equation (6), which includes two κ, κ_0-exponentials on each side ($x > 0$ and $x < 0$), differs from the potential given by the electromagnetism of the macroscopic bodies, which includes only one exponential on each side. This is due to the fact that the electromagnetism of the macroscopic bodies ignores the atomic structure of the interface. Also, the surface electric field generated by a half-space is exponentially low, such that the ions of the other half-space are not affected too much, except for those in the immediate neighbourhood of the interface (especially for a large disparity betweeen the parameters of the two half-spaces).

We consider now an ensemble of bodies, labelled by a, placed at $\mathbf{r}_a$. Each body generates a potential $\varphi_a(\mathbf{r}-\mathbf{r}_a)$, which can be calculated from equation (4). The total potential is $\varphi(\mathbf{r})=\sum_a\varphi_a(\mathbf{r}-\mathbf{r}_a)$ and the total electric field is $\mathbf{E}=-grad\varphi$, $\mathbf{E}=\sum_a\mathbf{E}_a$, $\mathbf{E}_a=-grad\varphi_a$ (the charge density ρ is gven by $\Delta\varphi=-4\pi\rho$). The total energy is given by

$$\mathcal{E}=\frac{1}{8\pi}\int d\mathbf{r}E^2(\mathbf{r})=\frac{1}{8\pi}\sum_{a,b}\int d\mathbf{r}\mathbf{E}_a\mathbf{E}_b\ , \tag{14}$$

where the summation over a and b extends to all bodies. We can separate the self-energy and the interaction energy $U=\sum_{a\neq b}U_{ab}$, where the pair-wise interaction energy can be written as

$$U_{ab}=\frac{1}{8\pi}\int d\mathbf{r}\mathbf{E}_a(\mathbf{r}-\mathbf{r}_a)\mathbf{E}_b(\mathbf{r}-\mathbf{r}_b)=\frac{1}{8\pi}\int d\mathbf{r}\mathbf{E}_a(\mathbf{r})\mathbf{E}_b(\mathbf{r}+\mathbf{r}_{ab})\ , \tag{15}$$

$\mathbf{r}_{ab}=\mathbf{r}_a-\mathbf{r}_b$ being the distance between the a-th body and b-th body; hence, we can calculate the force $\mathbf{F}_{ab}=-\partial U_{ab}/\partial\mathbf{r}_{ab}$ acting between two bodies.

The presence of the medium and the differences between the bodies complicate considerably the calculation. The complication arises from the finite spatial extension of the bodies and the inter-body spatial region occupied by the medium, which must be included in equation (4) for the calculation of the potentials. However, a great simplification is obtained by allowing the medium to occupy the whole space and writing the potential as

$$\varphi=\varphi_0+\sum_a(\varphi_a-\varphi_{0a})\ , \tag{16}$$

where φ_0 is the potential of the medium calculated as if the medium occupies the whole space and φ_{0a} is the potential of the medium calculated as if the medium occupies the volume of the a-th body. The potential φ_0 calculated from equation (4) is $\varphi_0=4\pi n_0q_0/\kappa_0^2$; it is a constant and does not contribute to the electric field. A further simplification is provided by the observation that the potential given by equation (4) depends on the parameters q and n (or q and κ, since $\kappa\simeq n^{1/3}$), which do not differ too much from body to body. Consequently, we calculate the difference of the potentials in equation (16) as the first-order differential $\varphi_a-\varphi_{0a}=\delta\varphi_a$ with respect to these parameters. This procedure is in accordance with the continuum approximation.

Let us apply this procedure to two identical half-spaces separated by a slab which occupies the region $0<x<d$. It is convenient to view the slab as a body immersed in a medium. We need the variation of the potential

$$\varphi=qn\int_{0<X<d}d\mathbf{R}\frac{1}{|\mathbf{r}-\mathbf{R}|}e^{-\kappa|\mathbf{r}-\mathbf{R}|}=\frac{2\pi qn}{\kappa}\int_0^d dXe^{-\kappa|x-X|}\ , \tag{17}$$

which generates the electric field

$$E = \frac{2\pi qn}{\kappa}\left[e^{-\kappa|x-d|} - e^{-\kappa|x|}\right] . \tag{18}$$

The interaction energy given by equation (15) is

$$\begin{gathered} U = -\pi \int dx \left[\delta(q\kappa^2) - q\kappa^2 \delta\kappa\, |x-d|\right] \cdot \\ \cdot \left[\delta(q\kappa^2) - q\kappa^2 \delta\kappa\, |x|\right] e^{-\kappa|x|} e^{-\kappa|x-d|} \end{gathered} \tag{19}$$

(per unit area), where we use $qn/\kappa = q\kappa^2$ ($n = 1/a^3 \simeq \kappa^3$). The main contribution to this integral comes from the $|x-d|\,|x|$-term; keeping only this contribution is in accordance with the continuum approximation. We get

$$U \simeq -\frac{1}{6}\pi q^2 \kappa (\delta\kappa)^2 (\kappa d)^3 e^{-\kappa d} , \tag{20}$$

where q and κ are the parameters of the slab and $\delta\kappa = \kappa - \kappa_0$, κ_0 corresponding to the half-spaces. The result is valid for $\kappa d \gg 1$. We can see that the force acting between the two half-spaces is an attractive force. By comparing equation (20) with equation (11) (the latter for two half-spaces in vacuum), we see that the effect of the medium is the replacement of κ^2 by $(\delta\kappa)^2$. We note that the use of a dielectric function (constant) of the medium is not appropriate, since the field varies spatially.

5. SPHERE

A spherical uniform distribution of ions in equation (4) gives the potential

$$\varphi = \begin{cases} \frac{4\pi nq}{\kappa^2}\left[1 - (1+\kappa r_0)\, e^{-\kappa r_0} \frac{\sinh \kappa r}{\kappa r}\right] , \ r < r_0 , \\ \frac{4\pi nq}{\kappa^2}\left(\kappa r_0 \cosh \kappa r_0 - \sinh \kappa r_0\right) \frac{e^{-\kappa r}}{\kappa r} , \ r > r_0 , \end{cases} \tag{21}$$

where r_0 is the radius of the sphere. For $\kappa r_0 \gg 1$, equations (21) can be simplified to

$$\varphi \simeq \begin{cases} \frac{4\pi nq}{\kappa^2} - \frac{2\pi nq}{\kappa^2} \frac{r_0}{r} e^{-\kappa(r_0 - r)} , \ r < r_0 , \\ \frac{2\pi nq}{\kappa^2} \frac{r_0}{r} e^{-\kappa(r - r_0)} , \ r > r_0 . \end{cases} \tag{22}$$

This expression is similar with that corresponding to a half-space double-layer (equation (6)), except for the factor r_0/r, as expected. The dynamics of the spherical double layer gives the surface (dipole) plasmons, with the frequency $\omega_0/\sqrt{3}$, where ω_0 is the frequency of the bulk plasmons.

Let us consider two identical spheres, one placed at the origin (0) and the other $\mathbf{R}$, separated by distance R and immersed in a medium. The leading contributions to the change they bring in the electric field in the limit $\kappa R \gg \kappa r_0 \gg 1$ are

$$\begin{gathered}\delta\mathbf{E}_0 = -\tfrac{2\pi nq}{\kappa} r_0 \delta\kappa e^{-\kappa r} \tfrac{\mathbf{r}}{r} \,, \\ \delta\mathbf{E}_R = -\tfrac{2\pi nq}{\kappa} r_0 \delta\kappa e^{-\kappa|\mathbf{r}-\mathbf{R}|} \tfrac{\mathbf{r}-\mathbf{R}}{|\mathbf{r}-\mathbf{R}|} \,.\end{gathered} \qquad (23)$$

The leading term in the interaction energy (equation (15)) is

$$U \simeq \frac{5\pi^2}{3} q^2 \kappa (\delta\kappa)^2 r_0^2 (\kappa R)^2 e^{-\kappa R} \,; \qquad (24)$$

the force acting between the two spheres is a repulsive force. This force is much smaller than the van der Waals-London force for distances much larger than the atomic distances. Indeed, the van der Waals-London potential can be written as $U_W = -C/R^6$; for distances much larger than the dimension of the spheres the constant C is $C \simeq 3\hbar\omega_0 v^2/64\pi^2$, where ω_0 is the plasma frequency and v is the volume of the sphere [26]. By comparing U_W with U given by equation (24) we get $U < |U_W|$ at least for $r_0 \gtrsim 10a$.

We include here the interaction energy of a half-space and a sphere (same material) separated by distance d ($\kappa d \gg \kappa r_0 \gg 1$),

$$U \simeq -\frac{\pi^2}{3} q^2 r_0 (\delta\kappa)^2 (\kappa d)^3 e^{-\kappa d} \,; \qquad (25)$$

the force is attractive, a feature specific to the infinite extension of the half-spaces.

6. DYNAMICS OF A NEUTRAL COLLOID

The separation regime between the van der Waals-London and the Casimir forces is governed by the so-called plasma wavelength $\lambda = c/\omega_0$. A typical plasma frequency for solids is $\omega_0 = 10^{15} s^{-1}$, which gives $\lambda = 3 \times 10^{-5}$ cm (0.3μm). If the mean separation distance between the colloidal particles is larger than λ, the van der Waals-London forces are ineffective; it remains the Casimir forces, which are very small. For such distances the particles may be approximated by point-like particles. In this case the Casimir forces are repulsive and go like $3\hbar\omega_0 v^2/32\pi^2\lambda^4 d^3$, for $d \gg \lambda$ and identical particles, where v is the particle volume and d is the separation distance between the particles [26]. For intermediate distances, the exact Casimir forces are not known, but it is known that they are very small. In these circumstances we may say that the colloidal particles are quasi-free.

If the mean separation distance between the particles is smaller than λ, the van der Waals-London attractive force acts between the particles. This force can be written as A/d^7, where we may take approximately $A \simeq 9\hbar\omega_0 v^2/32\pi^2$ (for identical particles; $A = 6C$, where C is introduced above) [26]. The total force acting upon a particle is practically vanishing, due to the rapid decreasing with the distance, except for those particles placed inside a spherical shell of thickness λ at the periphery of the spatial region occupied by the particles. This total force can be estimated as $\simeq (C/\lambda^7)(\lambda^3/d^3)$. Under the action of this force the border of the spatial region occupied by the colloid, placed initially at R_0, shrinks, such that we may write $N/R^3 = 1/d^3$, where N is the total number of particles and R is the radius of the spatial region of the colloid at any moment. Indeed, the contraction of the colloidal region is very slow, such that the osmotic pressure ensures the thermal equilibrium at any moment. The equation of motion of the radius R is $M\ddot{R} = -CN/\lambda^4 R^3$, where M is the particle mass; the solution is

$$R = R_0\left(1-\frac{4CN}{M\lambda^4 R_0^4}t^2\right)^2 = R_0\left(1-\frac{9\hbar\omega_0 v^2}{8\pi^2 M\lambda^4 R_0 d_0^3}t^2\right)^2 , \tag{26}$$

where d_0 is the initial mean separation distance between the particles. The result is valid for $R_0 \gg \lambda \gg d_0 \gg v^{1/3}$. In the limit $v \longrightarrow 0$ the rate coefficient of the time variation in equation (26) is very small, such that the ensemble can be at quasi-equilibrium. However, for more realistic values of the parameters in equation (26) the conditions of (quasi-) equlibrium are difficult to be met, and, very likely, the ensemble is unstable (and collapse). We are led to conclude that the more realistic condition of (quasi-) equlibrium is $d \gg \lambda$, *i.e.* the mean separation distance between the particles is much larger than the plasma wavelength.

7. CHARGED COLLOIDS

We have discussed above neutral colloids. If a small amount of electrolyte is added to the solution, an amount of dissociated ions tends to adhere to the colloidal particles. Also, the colloid particles may acquire electric charges by various other agencies. The interaction between these particles is now governed by potentials similar with those given by equation (5), which may lead to quasi-bound states (according to the cohesion theory).

We consider a set of spherical colloidal particles labelled by i, each placed at $\mathbf{R}_i$, with a radius r_{0i} and a surface charge Q_i. The particle charge density is

$$\rho_p = \sum_i \frac{Q_i}{4\pi r_{0i}^2}\delta\left(|\mathbf{r}-\mathbf{R}_i| - r_{0i}\right) ; \tag{27}$$

this charge density generates a potential $\varphi_p = \sum_i Q_i/|\mathbf{r}-\mathbf{R}_i|$ in the region comprised between the particles (outside region); inside the particles $\varphi_p = 0$. The interaction energy between the particles (Coulomb repulsion) is $E_p = \frac{1}{2}\sum_{i\neq j} Q_i Q_j / R_{ij}$, as expected, where $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$.

We assume that in-between the particles there is a concentration n_c of undissociated charges (electrolyte molecules); they may dissociate in pairs of $\pm q$-charges. The q-charges go to the surface of the particles (irrespective of the sign of q), while the $-q$-charges remain in-between the particles; we call these latter charges counter-ions. All these charges generate a potential φ, such that a local change $\delta n_c = n_c q\varphi/T$ occurs in the counter-ion density. The potential φ satisfies the Poisson equation

$$\Delta\varphi = -\sum_i \frac{Q_i}{r_{0i}^2}\delta\left(|\mathbf{r}-\mathbf{R}_i| - r_{0i}\right) + \kappa^2\varphi \ , \tag{28}$$

where $\kappa^2 = 4\pi n_c q^2/T$. This equation is valid in the region comprised between the particles (outside region), where the first term on the right plays the role of a boundary condition (in a multiply-connected domain). Inside the particles the potential is zero. The solution vanishing at infinity can be written as

$$\varphi = \sum_i Q_i^* \frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_i|}}{|\mathbf{r}-\mathbf{R}_i|} \ , \tag{29}$$

where the constants Q_i^* (effective charges) are determined from the charge conservation. Indeed, by integrating over the whole space, we get

$$4\pi Q_i = \kappa^2 Q_i^* \int d\mathbf{r} \frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_i|}}{|\mathbf{r}-\mathbf{R}_i|} \ , \tag{30}$$

where the integration in equation (30) is performed over the whole outside region (*i.e.*, avoiding all the particles). It is convenient to integrate over the whole space in equation (30) and subtract the integration over all the particles. The integrals are elementary, and we get

$$\begin{gathered} Q_i^* = [(1+\kappa r_{0i})e^{-\kappa r_{0i}} - \\ -\textstyle\sum_j' (\kappa r_{0j}\cosh\kappa r_{0j} - \sinh\kappa r_{0j})\frac{e^{-\kappa R_{ij}}}{\kappa R_{ij}}]^{-1} Q_i \ , \end{gathered} \tag{31}$$

where the prime on the summation over j means $j \neq i$. The first term on the right in equation (31) comes from the i-th particle, while the summation over $j \neq i$ comes from all the other particles. We note that the finite size of the particles renormalizes the charge Q_i into an effective charge Q_i^*. This renormalization arises from the boundary condition to the potential in equation (28), imposed at the surface of the particles. The renormalization factor for each particle depends on all the particles, such that these factors give rise to many-particle forces in the ensemble. Also, we note that the assumption of spherical particles simplifies greatly the calculations (for particles with a general shape, the terms in the superposition of the potential φ are not spherically-symmetric anymore). Although the potential given by equation (29) looks like a superposition of double-layer potentials, it can be viewed in fact as a multiple-layer potential, due especially to the effectve charges Q_i^*, which depend on all the particles.

Equation (28) and the solution given by equation (30) are specific to the Debye-Huckel theory (compare with equations (3) and (4)). The potential φ accounts for the Coulomb attraction between particles and the counter-ions and the Coulomb repulsion between the counter-ions, such that, in computing the total interaction energy we should add the particle-particle Coulomb repulsion E_p given above. The charge density of the counter-ions is

$$\rho_c = -q\delta n_c = -\frac{n_c q^2}{T}\varphi = -\frac{\kappa^2}{4\pi}\varphi \tag{32}$$

in the outside region and zero inside the particles. The total potential (interaction) energy of the ensemble is given by

$$E_{pot} = \int d\mathbf{r}\rho_c\left(\varphi - \frac{1}{2}\varphi_c\right) + E_p = \frac{1}{2}\int d\mathbf{r}\rho_c\varphi + \frac{1}{2}\int d\mathbf{r}\rho_c\varphi_p + E_p \ , \tag{33}$$

where $\varphi_c = \varphi - \varphi_p$ is the potential generated only by the counter-ions; the term $\frac{1}{2}\varphi_c$ should be subtracted in equation (33) because the interacting term $\rho_c\varphi$ counts twice the counter-ions repulsion. The integration in equation (33) is extended to the whole outside region. It is convenient to integrate in equation (33) over the whole space and subtract the contribution of the regions occupied by particles. We introduce the notation $E_{pot} = E^w_{pot} + E^p_{pot}$, where

$$\begin{gathered}
E^w_{pot} = \tfrac{1}{2}\int d\mathbf{r}\rho_c\varphi + \tfrac{1}{2}\int d\mathbf{r}\rho_c\varphi_p + E_p = \\
= -\tfrac{\kappa^2}{8\pi}\int d\mathbf{r}\left(\varphi^2 + \varphi\varphi_p\right) + E_p = \\
= -\tfrac{\kappa^2}{8\pi}\sum_{ij} Q_i^* Q_j^* \int d\mathbf{r}\tfrac{e^{-\kappa|\mathbf{r}-\mathbf{R}_i|}}{|\mathbf{r}-\mathbf{R}_i|}\tfrac{e^{-\kappa\left|\mathbf{r}-\mathbf{R}_j\right|}}{|\mathbf{r}-\mathbf{R}_j|} - \\
-\tfrac{\kappa^2}{8\pi}\sum_{ij} Q_i^* Q_j \int d\mathbf{r}\tfrac{e^{-\kappa|\mathbf{r}-\mathbf{R}_i|}}{|\mathbf{r}-\mathbf{R}_i|}\tfrac{1}{|\mathbf{r}-\mathbf{R}_j|} + \tfrac{1}{2}\sum_{i\neq j}\tfrac{Q_i Q_j}{R_{ij}}
\end{gathered} \tag{34}$$

is the part of the energy correspoding to the integration over the whole space, and

$$E^p_{pot} = \frac{\kappa^2}{8\pi}\sum_i \int_{|\mathbf{r}-\mathbf{R}_i|,<r_{0i}} d\mathbf{r}\left(\varphi^2 + \varphi\varphi_p\right) \tag{35}$$

is the part corresponding to the integration over the region occupied by the particles. The integrals in equation (34) are double-centre integrals which can be effected by using elliptic coordinates [12, 15]. They are given by

$$\int d\mathbf{r}\frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_i|}}{|\mathbf{r}-\mathbf{R}_i|}\frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_j|}}{|\mathbf{r}-\mathbf{R}_j|} = \frac{2\pi}{\kappa}e^{-\kappa R_{ij}} \tag{36}$$

and

$$\int d\mathbf{r}\frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_i|}}{|\mathbf{r}-\mathbf{R}_i|}\frac{1}{|\mathbf{r}-\mathbf{R}_j|}=\begin{cases}\frac{4\pi}{\kappa}\frac{1-e^{-\kappa R_{ij}}}{\kappa R_{ij}}\ ,\ i\neq j\ ,\\ \frac{4\pi}{\kappa}\ ,\ i=j\ .\end{cases}\tag{37}$$

We get

$$\begin{gathered}E^w_{pot}=-\frac{\kappa}{4}\sum\nolimits_i\left(Q_i^{*2}+2Q_i^*Q_i\right)-\\ -\frac{\kappa}{4}\sum\nolimits_{i\neq j}\left(Q_i^*Q_j^*-\frac{Q_i^*Q_j+Q_j^*Q_i}{\kappa R_{ij}}\right)e^{-\kappa R_{ij}}-\\ -\frac{\kappa}{4}\sum\nolimits_{i\neq j}\left(Q_i^*Q_j+Q_j^*Q_i-2Q_iQ_j\right)\frac{1}{\kappa R_{ij}}\ .\end{gathered}\tag{38}$$

This is precisely the potential energy given by equation (5) for point-like ($r_{0i}=0$) identical charges $Q_i^*=Q_i=q$. Equation (5), pertaining to the cohesion theory, is extended here to charge spherical-shells.

The calculation of the integrals in equation (35) (*i.e.* the integrals in equations (36) and (37) where the integration is restricted to a finite domain) is more complicated. It is easy to see that the energy E^p_{pot} in equation (35) implies, besides particle self-energy and pair-wise interaction potentials, many-particle interactions. Fortunately, a great simplification comes from the observation that the mean inter-particle distance $\overline{R}_{ij}$ is larger than the mean radius $\overline{r}_{0i}$ (and for a dilute ensemble it is much larger). Therefore, we may restrict ourselves to the approximation $\kappa r_{0i}\ll 1$. Within this approximation in the renormalization factor in equation (31) we may neglect the contribution of the summation over j, which leads to an effective charge

$$Q_i^*\simeq\left[1+(\kappa r_{0i})^2\right]Q_i\tag{39}$$

(this is a self-particle renormalization). In the worst case where $\kappa r_{0i}\simeq 1$ the contribution of the j-summation in equation (31) is of the same order of magnitude as the self-particle contribution $(\kappa r_{0i})^2$ in equation (39). Making use of this approximation we may calculate E^p_{pot} up to corrections of the order $(\kappa r_{0i})^2$. We note that the many-particle forces begin to appear with a third-order term $\sim(\kappa r_{0i})^3$. Using $(\kappa r_{0i})^2Q_i=Q_i^*-Q_i$, we get

$$\begin{gathered}E^p_{pot}=\frac{\kappa}{2}\sum\nolimits_i(\kappa r_{0i})Q_i^2+\\ +\frac{3\kappa}{4}\sum\nolimits_{i\neq j}\left(Q_i^*Q_j+Q_j^*Q_i-2Q_iQ_j\right)\frac{e^{-\kappa R_{ij}}}{\kappa R_{ij}}-\\ +\frac{\kappa}{4}\sum\nolimits_{i\neq j}\left(Q_i^*Q_j+Q_j^*Q_i-2Q_iQ_j\right)\frac{1}{\kappa R_{ij}}\ ,\end{gathered}\tag{40}$$

such that the total potential energy is

$$\begin{gathered}E_{pot}=E^{w}_{pot}+E^{p}_{pot}=-\tfrac{\kappa}{4}\sum\nolimits_{i}\left(Q^{*2}_{i}+2Q^{*}_{i}Q_{i}\right)+\tfrac{\kappa}{2}\sum\nolimits_{i}(\kappa r_{0i})Q^{2}_{i}-\\ -\tfrac{\kappa}{4}\sum\nolimits_{i\neq j}\left[Q^{*}_{i}Q^{*}_{j}-2\tfrac{2\left(Q^{*}_{i}Q_{j}+Q^{*}_{j}Q_{i}\right)-3Q_{i}Q_{j}}{\kappa R_{ij}}\right]e^{-\kappa R_{ij}}\ ;\end{gathered}\tag{41}$$

we note that unscreened Coulomb terms do not appear in the total energy, as expected. Apart from the particle self-energy, we get the pair-wise interaction potentials

$$\Phi_{ij}=-\frac{\kappa}{2}\left[Q^{*}_{i}Q^{*}_{j}-2\frac{2\left(Q^{*}_{i}Q_{j}+Q^{*}_{j}Q_{i}\right)-3Q_{i}Q_{j}}{\kappa R_{ij}}\right]e^{-\kappa R_{ij}}\tag{42}$$

(in the interaction energy $\frac{1}{2}\sum_{i\neq j}\Phi_{ij}$ in equation (41)). In contrast with the double-layer theory, the two-particle interaction potentials given by the cohesion theory in equation (42) are attractive at infinity, where they go like -$\left(\kappa Q^{*}_{i}Q^{*}_{j}/2\right)e^{-\kappa R_{ij}}$, in agreement with Langmuir's original observation [27] and subsequent discussions [10, 11, 28]-[34]. The total potential energy given by equation (41) and the pair-wise potentials given by equation (42) are valid up to the second-order terms $(\kappa r_{0i})^{2}\ll 1$ (first non-vanishing correction to the interaction potentials). This is a satisfactory approximation as long as $\overline{R}_{ij}\gg\overline{r}_{0i}$. Even in the unfavourable situation of a close contact $R_{ij}=r_{0i}+r_{0j}$ we still have $R_{ij}>r_{0i},r_{0j}$, especially for large particles. For small particles close to each other, the above approximation is not valid anymore; in particular many-particle forces appear in this case.

The two-particle interaction potentials Φ_{ij} exhibit negative minima, where the particles may accommodate, if the temperature of the medium is not too high. This would lead to the stabilization of the colloid. The attractive molecular forces contribute to a small extent, since the equilibrium energy is an electrostatic energy of the order $Q^{*}_{i}Q^{*}_{j}/\overline{R}_{ij}$, which, usually, is higher than the energy of the molecular forces (in absolute value). The equilibrium configurations (which can be found numerically) indicate a solid phase, in general disordered; for a large number of identical particles the phase can even be ordered. However, in general, there are many sets of equilibrium configurations, differing from one another by small amounts of energy (like an amorphous solid), such that there are large fluctuations between various equilibrium configurations. For higher temperature of the medium the solid melts, such that we have a colloidal liquid phase.

In order to get an insight into the nature of the potentials Φ_{ij} we use mean values $r^{2}_{0}=\overline{r^{2}_{0i}}$, $Q=\overline{Q}_{i}$, $R=\overline{R}_{ij}$ and introduce the notation $\alpha=1+r^{2}_{0}$; the potentials

Φ_{ij} can be written as

$$\Phi=-\frac{1}{2}\kappa Q^2\left(\alpha^2-2\frac{4\alpha-3}{\kappa R}\right)e^{-\kappa R}\,; \tag{43}$$

this potential has a zero for $\kappa R=2(4\alpha-3)/\alpha^2$ ($\simeq 2$ for $\alpha\simeq 1$) and a minimum for $\kappa R\simeq 2.73$ ($\alpha\simeq 1$), where the potential is $\Phi_0\simeq -10^{-2}\kappa Q^2\simeq -3\times 10^{-2}Q^2/R$. For a qualitative discussion we may take a mean equilibrium distance between the particles of the order $\kappa R\simeq 1$ and a minimum energy of the order $\Phi_0\simeq -Q^2/R$. If $Q^2/R>T_c$, where T_c is the temperature of the medium, we have a transition to the solid phase; this condition reads also $R^3=1/\gamma<Q^6/T_c^3$, where γ is the particle density; this is the familiar Hardy-Schulze-Ostwald law [35]-[37]. We note that $\kappa R\simeq 1$ implies $R\sim 1/\sqrt{n_c}$, a relation which has been known since long, both experimentally and theoretically [38, 39].

In contrast with the cohesion theory for solids or plasmas, where the charge Q is equal to q, in colloid theory Q is a free parameter. Within the present approximation we may write the counter-ion density as $n_c=Q/qR^3$ and $\kappa^2\simeq\left(aQ/qR^3\right)(q^2/aT)\simeq 1/R^2$ (leaving aside numerical factors like $4\pi/3$ or 4π); since $q^2/aT\simeq 1$ we get an estimation of the equilibrium mean separation distance of the order $R\simeq a(Q/q)$, where a is a distance of the order of the atomic distance between the ions in the electrolyte molecule (leaving aside the molecular forces). We can see that for large values of Q the distance R is large, while for small values of the particle charge Q the distance R is small and the colloid may be flocculated (coagulated). It may happen that the added electrolyte diminishes the particle charge, such that the equilibrium distance $R\simeq a(Q/q)$ decreases and the colloid becomes flocculated (aggregated). It is plausible to assume that that the charge Q attached to a particle of radius r_0 is proportional to the surface of the particle ($r_0\gg a_p$, where a_p is the mean separation distance between the atomic constituents of the particle). The maximum value of this charge is of the order $Q=q(r_0^2/a_p^2)$, such that we get $R\simeq a(r_0^2/a_p^2)$. We can see that small particles acquire a small charge and are more prone to aggregate at small distances (coagulate), while larger particles may be stabilized at larger distances, as expected.

It is worth noting that the colloidal stabilization (and aggregation) are discussed here at thermodynamic equilibrium, where solid and liquid phases are identified (and even a gaseous phase at large separation distance). Let us suppose that initially we have a dispersed colloid, with a (mean) particle charge Q and a large (mean) separation distance R_0. The initial counter-ion density is low and the initial value κ_0 of the parameter κ is small. From equation (41) we have a configurational equilibrium for $\kappa_0 R_0\simeq 1$, with an energy minimum of the order $-Q^2\kappa_0$; the temperature of the medium may be sufficiently large to overpass this minimum, such that we have a gaseous phase, with attractive interactions between particles. Therefore, the ensemble begins to shrink down to smaller values R of the separation distance, where the parameter κ has an enhanced value, which corresponds to a lower energy. If the temperature of the medium is still higher than this energy minimum, we have a (thermodynamically-stable) liquid phase; if, on the contrary, the energy minimum is sufficiently deep, we have a stable solid phase and we may say that the colloid is stabilized. In the solid phase the mean separation distance is given by $R \simeq a(Q/q)$; if Q is small, the colloid may even be flocculated (aggregated). At this stage, however, for very small separation distances, the cohesion theory as described above breaks down, because there appear many-particle forces, corrections to the energy minima and, in addition, attractive molecular forces may bring their important contribution. However, if the aggregation process is not very much developed, peptization can not be excluded, if the charges are removed, or mechanical means are applied. This applies also to the stabilization phase, though it is difficult to assess the precise conditions of reversibility/irreversibility of these phase transitions.

Another example is provided by a dense set of particles which get dispersed in the medium. At the initial moment the particles release counter-ions and acquire ionic charges. The counter-ions are placed initially outside the region occupied by the particle set, and the particles are dispersed under the action of the Coulomb repulsive forces. Thereafter, the counter-ionic atmosphere builds up around particles, which may acquire equilibrium positions (get stabilized), as described above, or may acquire a liquid phase around these equilibrium positions.

8. CONCLUDING REMARKS

It is shown here that a surface double layer of atomic thickness is a consequence of the cohesion forces for finite-size bodies. The surface double-layer forces are exponentially small, with the (negative) exponent of the order of the ratio of the distance to the mean distance between the atomic constituents. Consequently the repulsive forces generated by the surface double layer are too small to compensate the attractive molecular forces at relevant distances. We may call such a colloid a neutral colloid. It is likely that the stability of the neutral lyophobic colloids (suspensions) may be attained for mean separation distances between the particles much larger than the plasma wavelength, where the molecular forces become ineffective. The surface double-layer forces are estimated here for half-spaces (where they are attractive) and spheres, and the dynamics of the neutral colloids is analyzed.

For charged colloids the cohesion theory is employed to estimate their stability and aggregation conditions. We note that, in contrast with the double-layer theory, the cohesion theory predicts an attractive force between colloid particles placed at long distances. The inter-particle equilibrium distance is estimated by means of the cohesion theory and the Hardy-Schulze-Ostwald law is derived. Solid and liquid phases are identified in charged colloids, and even a transition towards a flocculated (aggregated) phase. The dynamics of the transitions towards these thermodynamically-stable phases is discussed.

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