



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, in contrast with this standard double-layer theory, the electric interaction of the ions and the charged colloidal particles requires the application of the cohesion theory of electrically-interacting particles, which may lead to stabilization, or even aggregation of the colloid, independently of attractive molecular forces. The screened two-particle interaction which occurs in this case (in the dilute limit) is attractive at long distances and repulsive at short distances, with a negative minimum. Many-particle forces occur over short distances, which complicate considerably the situation. Solid and liquid phases are identified here in charged colloids (and even a non-ideal gaseous phase with attractive interaction), the equilibrium mean separation distance between the particles is estimated and the transition between various phases is discussed.

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. For instance, since we are not interested in the kinetics of these colloids (but only in their equilibrium phases), we may left aside the brownian and viscous (Stokes) forces. The current DLVO (Deryagin-Landau-Verwey-Overbeek) theory of charged lyophobic colloids assumes that spatially-extended double layers, which appear at the surface of the colloid particles, generate repulsive forces, which, combined with the attractive molecular forces, may ensure equilibrium at relevant distances, at least for long periods of time [3,4]. The DLVO theory is the current standard theory of lyophobic colloids (see, for instance, Refs. [5–8]); 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. [9,10].

Our work in the cohesion theory of the condensed matter [11–15] 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, assumed to appear in charged colloids. It may easily be shown (and, partly, it was shown in Refs. [13]) 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. In particular, 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 layer is practically 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. It follows that the surface double layer may be viewed as being irrelevant for the dynamics of the lyophobic colloids (though it may contribute to charging the surface of the particles).

The surface of the colloidal particles may acquire electric charges. The charged colloid particles and the in-between ions interact by electric forces. In order to assess the effect of these forces, it is necessary to resort to the cohesion theory mentioned above. Besides other difficulties (to be discussed below), 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

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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" [16]). 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. Solid and liquid phases are identified in charged colloids, and even a non-ideal gaseous phase, and the transition between these phases is discussed. The equilibrium mean separation distance between the particles is estimated. We assume in this paper that the cohesion modifications of the particle-medium 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 (a discussion of this point is given in Ref. [17]).

A few basic difficulties of the DVLO theory can be traced back to the application of the Debye-Huckel theory to colloids. 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

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

where; here, for simplicity, $q\varphi/T$ is assumed to be much smaller than unity (the dielectric constant of the medium may be included in the charge q). First, we can see that there is an imbalance of charge in Eq. (1), which indicates that we need boundary conditions, as it is well known. The boundary conditions ensure the global charge neutrality [18]. If we take as a boundary condition a point-like ion, then the solution has the well-known form $\varphi \sim e^{-x}/r$, where r is the distance from that ion. In that case the corresponding density of ions in Eq. (1) should be absent, since their contribution is included in the boundary conditions (source terms), 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 (counter-ions), and the parameter κ^2 becomes $\kappa^2 = 4\pi nq^2/T$ [14]. For external charges, placed, for instance, on a plane surface of the domain, the solution has the form $\varphi \sim e^{-\kappa x}$, x being the distance from the surface; in that case both species of ions are present in Eq. (1). If many external charges are present, all of them should act as boundary conditions. This makes the solution to depart appreciably from the usual solution, where only pairs of external charges are considered. This is shown explicitly below. Noteworthy, in all cases, it is the charge imbalance generated by the relative position of the ions with respect to one another which generate screening.

Second, there is a problem with the approximation of the type $n_{\pm} = ne^{\mp q\varphi/T} \simeq n \mp nq\varphi/T + \dots$ in the Debye-Huckel equation. It was shown [14] that the contribution of the constant term n may be absorbed in the potential and has no effect in the interaction energy. This reflects the average local neutrality for an infinite ensemble of charges. The higher-order terms in the expansion of n_{\pm} bring negligible contributions in the dilute (weak-coupling) limit. However, close to equilibrium, the interaction energy computed with this approximation may be overestimated by $\simeq 30\%$ [14].

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. The ionic dissociation occurs under the action of the electric forces of the surrounding medium, and the dissociation process is a statistical process with its own temperature T of the order q^2/a , where a is a distance of the order of the atomic distance in the dissociating molecule. Indeed, the dissociation occurs when the Debye length $a\sqrt{aT/q^2} (\simeq 1/\kappa)$ is of the order a , such that $T \simeq q^2/a$ [11,14]. 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 statistical dissociation process is distinct from the thermal motion of the molecules (ions) 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. Eq. (1) is the standard starting point for electrolytes or homogeneous weakly-interacting plasmas, but its application to colloids (which originates with the work of Gouy [19] and Chapman [20]) can be misleading sometimes.

2. Charged colloids

The colloid particles may acquire electric charges on their surface by various means. 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

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

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 (outside region) there is a concentration n of ions with charges $\pm q$ (dissociated ions). The total potential φ satisfies the Poisson equation

$$\Delta\varphi = - \sum_i \frac{Q_i}{r_{0i}^2} \delta(|\mathbf{r} - \mathbf{R}_i| - r_{0i}) + 4\pi nq(e^{q\varphi/T} - e^{-q\varphi/T}) \quad (3)$$

(we assume the same temperature for both species of ions). This equation is to be compared with Eq. (1). Not too close to the bare particles, we may replace the exponentials in Eq. (3) by their first-order expansion. The Poisson Eq. (3) becomes

$$\Delta\varphi = - \sum_i \frac{Q_i}{r_{0i}^2} \delta(|\mathbf{r} - \mathbf{R}_i| - r_{0i}) + \kappa^2\varphi, \quad (4)$$

where $\kappa^2 = 8\pi nq^2/T$. We can see that the potential of the bare particles is screened by the change $\delta n = 2nq\varphi/T$ in the ion density. According to Eq. (4), the equilibrium may be achieved for particle density of the order δn , which is itself of the order n (as it is shown explicitly below). The particle charges are screened for all relevant distances and the exponent $|q\varphi/T|$ is at most of the order unity, such that the approximations used in deriving Eq. (4) are valid, except for very small inter-particle distances; the value of the potential at equilibrium may be affected by $\simeq 30\%$ an error [14].

Eq. (4) 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

$$\varphi = \sum_i Q_i^* \frac{e^{-\kappa|\mathbf{r} - \mathbf{R}_i|}}{|\mathbf{r} - \mathbf{R}_i|}, \quad (5)$$

where the constants Q_i^* (effective charges) are determined from the charge conservation. Indeed, by integrating Eq. (4) over the whole space, we get

$$4\pi Q_i = \kappa^2 Q_i^* \int d\mathbf{r} \frac{e^{-\kappa|\mathbf{r} - \mathbf{R}_i|}}{|\mathbf{r} - \mathbf{R}_i|}, \quad (6)$$

where the integration in Eq. (6) is performed over the whole outside region (i.e., avoiding all the particles). It is convenient to integrate over the whole space in Eq. (6) and subtract the integration over all the particles. The integrals are elementary, and we get

$$Q_i^* = \left[(1 + \kappa r_{0i})e^{-\kappa r_{0i}} - \sum_j (\kappa r_{0j} \cosh \kappa r_{0j} - \sinh \kappa r_{0j}) \frac{e^{-\kappa R_{ij}}}{\kappa R_{ij}} \right]^{-1} Q_i, \quad (7)$$

where the prime on the summation over j means $j \neq i$. The first term on the right in Eq. (7) 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 in Eq. (4), 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. It is worth noting that the ion concentration n , entering the screening parameter κ , affects the renormalized charge Q_i^* (not the bare charge Q_i , of course). 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) [21,22]. Although the potential given by Eq. (5) looks like a superposition of double-layer potentials, it can be viewed in fact as a multiple-layer potential, due to the summation over i and the effective charges Q_i^* , which depend on all the particles.

Eq. (4) and the solution given by Eq. (6) are specific to the Debye-Huckel theory. The potential φ accounts for the Coulomb attraction between particles and the ions and (partly) the Coulomb repulsion between the ions, such that, in computing the total interaction energy we should add the particle-particle Coulomb repulsion E_p given above. The density of the ion charge imbalance is

$$\rho = -q\delta n = -\frac{2nq^2}{T}\varphi = -\frac{\kappa^2}{4\pi}\varphi \quad (8)$$

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

$$E_{pot} = \int d\mathbf{r} \rho \left(\varphi - \frac{1}{2} \varphi_i \right) + E_p = \frac{1}{2} \int d\mathbf{r} \rho \varphi + \frac{1}{2} \int d\mathbf{r} \rho \varphi_p + E_p, \quad (9)$$

where $\varphi_i = \varphi - \varphi_p$ is the potential generated only by ions; the term $\frac{1}{2} \varphi_i$ should be subtracted in Eq. (9) because the interacting term $\rho \varphi$ counts twice the ion repulsion. The integration in Eq. (9) is extended to the whole outside region. It is convenient to integrate in Eq. (9) over the whole space and subtract the contribution of the regions occupied by particles. We introduce the notation $E_{pot} = E_{pot}^w + E_{pot}^p$, where

$$\begin{aligned} E_{pot}^w &= \frac{1}{2} \int d\mathbf{r} \rho \varphi + \frac{1}{2} \int d\mathbf{r} \rho \varphi_p + E_p = -\frac{\kappa^2}{8\pi} \int d\mathbf{r} (\varphi^2 + \varphi \varphi_p) + E_p = \\ &= -\frac{\kappa^2}{8\pi} \sum_{ij} Q_i^* Q_j^* \int d\mathbf{r} \frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_i|}}{|\mathbf{r}-\mathbf{R}_i|} \frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_j|}}{|\mathbf{r}-\mathbf{R}_j|} - \\ &\quad - \frac{\kappa^2}{8\pi} \sum_{ij} Q_i^* Q_j \int d\mathbf{r} \frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_i|}}{|\mathbf{r}-\mathbf{R}_i|} \frac{1}{|\mathbf{r}-\mathbf{R}_j|} + \frac{1}{2} \sum_{i \neq j} \frac{Q_i Q_j}{R_{ij}} \end{aligned} \quad (10)$$

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

$$E_{pot}^p = \frac{\kappa^2}{8\pi} \sum_i \int_{|\mathbf{r}-\mathbf{R}_i| < r_{0i}} d\mathbf{r} (\varphi^2 + \varphi \varphi_p) \quad (11)$$

is the part corresponding to the integration over the region occupied by the particles. The integrals in Eq. (10) are double-centre integrals which can be effected by using elliptic coordinates [11,14]. They are given by

$$\int d\mathbf{r} \frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_i|}}{|\mathbf{r}-\mathbf{R}_i|} \frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_j|}}{|\mathbf{r}-\mathbf{R}_j|} = \frac{2\pi}{\kappa} e^{-\kappa R_{ij}} \quad (12)$$

and

$$\int d\mathbf{r} \frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_i|}}{|\mathbf{r}-\mathbf{R}_i|} \frac{1}{|\mathbf{r}-\mathbf{R}_j|} = \begin{cases} \frac{4\pi}{\kappa} \frac{1 - e^{-\kappa R_{ij}}}{\kappa R_{ij}}, & i \neq j, \\ \frac{4\pi}{\kappa}, & i = j. \end{cases} \quad (13)$$

We get

$$\begin{aligned} E_{pot}^w &= -\frac{\kappa}{4} \sum_i (Q_i^{*2} + 2Q_i^* Q_i) - \\ &\quad - \frac{\kappa}{4} \sum_{i \neq j} \left(Q_i^* Q_j^* - \frac{Q_i^* Q_j + Q_j^* Q_i}{\kappa R_{ij}} \right) e^{-\kappa R_{ij}} - \\ &\quad - \frac{\kappa}{4} \sum_{i \neq j} (Q_i^* Q_j + Q_j^* Q_i - 2Q_i Q_j) \frac{1}{\kappa R_{ij}}. \end{aligned} \quad (14)$$

In the limit of identical point-like charges ($r_{0i} = 0$) the energy given by Eq. (14) acquires the expression

$$E_{pot}^w = -\frac{3}{4} \kappa q^2 - \frac{1}{4} \kappa q^2 \sum_{i \neq j} \left(1 - \frac{2}{\kappa R_{ij}} \right) e^{-\kappa R_{ij}} \quad (15)$$

given in Refs. [11–15]. That result is generalized here to charged spherical-shells.

The calculation of the integrals in Eq. (11) (i.e. the integrals in Eqs. (12) and (13) where the integration is restricted to a finite domain) is more difficult. It is easy to see that the energy E_{pot}^p in Eq. (11) 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 \bar{R}_{ij} is larger than the mean radius \bar{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 Eq. (7) we may neglect the contribution of the summation over j , which leads to an effective charge

$$Q_i^* \simeq [1 + (\kappa r_{0i})^2] Q_i \quad (16)$$

(this is a self-particle renormalization). In the most unfavourable case $\kappa r_{0i} \simeq 1$ the contribution of the j -summation in Eq. (7) is of the same order of magnitude as the self-particle contribution $(\kappa r_{0i})^2$ in Eq. (16). Making use of this approximation we may calculate E_{pot}^p 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 $(\kappa r_{0i})^2 Q_i = Q_i^* - Q_i$, we get

$$\begin{aligned} E_{pot}^p &= \frac{\kappa}{2} \sum_i (\kappa r_{0i}) Q_i^2 + \\ &\quad + \frac{3\kappa}{4} \sum_{i \neq j} (Q_i^* Q_j + Q_j^* Q_i - 2Q_i Q_j) \frac{e^{-\kappa R_{ij}}}{\kappa R_{ij}} - \\ &\quad + \frac{\kappa}{4} \sum_{i \neq j} (Q_i^* Q_j + Q_j^* Q_i - 2Q_i Q_j) \frac{1}{\kappa R_{ij}}, \end{aligned} \quad (17)$$

such that the total potential energy is

$$\begin{aligned} E_{pot} &= E_{pot}^w + E_{pot}^p = -\frac{\kappa}{4} \sum_i (Q_i^{*2} + 2Q_i^* Q_i) + \frac{\kappa}{2} \sum_i (\kappa r_{0i}) Q_i^2 - \\ &\quad - \frac{\kappa}{4} \sum_{i \neq j} \left[Q_i^* Q_j^* - 2 \frac{2(Q_i^* Q_j + Q_j^* Q_i) - 3Q_i Q_j}{\kappa R_{ij}} \right] e^{-\kappa R_{ij}}, \end{aligned} \quad (18)$$

we note that the bare Coulomb term does not appear in the total energy, as expected for a screened interaction. Apart from the particle self-energy in Eq. (18) (the first two terms on the right), we get the pair-wise interaction potentials

$$\Phi_{ij} = -\frac{\kappa}{2} \left[Q_i^* Q_j^* - 2 \frac{2(Q_i^* Q_j + Q_j^* Q_i) - 3Q_i Q_j}{\kappa R_{ij}} \right] e^{-\kappa R_{ij}} \quad (19)$$

(in the interaction energy $\frac{1}{2} \sum_{i \neq j} \Phi_{ij}$). In contrast with the double-layer theory, the two-particle interaction potentials given by the cohesion theory in Eq. (19) are attractive at infinity, where they go like $(\kappa Q_i^* Q_j^*/2) e^{-\kappa R_{ij}}$, in agreement with Langmuir’s original observation [23] and subsequent discussions [10,24–31]. The total potential energy given by Eq. (18) and the pair-wise potentials given by Eq. (19) 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 $\bar{R}_{ij} \gg \bar{r}_{0i}$. 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 treatment presented here differs from the standard double-layer theory by including the boundary conditions arising from all the particles and by computing the interaction energy for the whole ensemble (not only for pairs of particles).

3. Dynamics of colloids

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; the position of these minima is of the order $\bar{R}_{ij} \approx 1/\kappa$. 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 $Q_i^* Q_j^*/\bar{R}_{ij}$, which, usually, is higher than the energy of the molecular forces (in absolute value). The equilibrium configurations (which can be found numerically from Eq. (18)) 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 liquid colloidal phase [32].

In order to get an insight into the nature of the potentials Φ_{ij} we use mean values $r_0^2 = \bar{r}_{0i}^2$, $Q = \bar{Q}_i$, $R = \bar{R}_{ij}$ and introduce the notation $\alpha = 1 + (\kappa r_0)^2$ ($Q^* \approx \alpha Q$); the potentials Φ_{ij} can be written as

$$\Phi \approx -\frac{1}{2}\kappa Q^2 \left(\alpha^2 - 2\frac{4\alpha - 3}{\kappa R} \right) e^{-\kappa R}, \quad (20)$$

this potential has a zero for $\kappa R = 2(4\alpha - 3)/\alpha^2$ (≈ 2 for $\alpha \approx 1$) and a minimum for $\kappa R \approx 2.73$ ($\alpha \approx 1$), where the potential (energy) is $\Phi_0 \approx -10^{-2}\kappa Q^2 \approx -3 \times 10^{-2}Q^2/R$. For a qualitative discussion we may take a mean equilibrium distance between the particles of the order $\kappa R \approx 1$ and a minimum energy of the order $\Phi_0 \approx -Q^2/R$. 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 form of the Hardy-Schulze-Ostwald law [33–35]. We note that $\kappa R \approx 1$ implies $R \sim 1/\sqrt{n}$, a relation which has been known since long, both experimentally and theoretically [36,37].

In contrast with the cohesion theory for solids or plasmas [11–15], where the charge Q is equal to q (and there exists only one species of “ions” - the electrons), in colloid theory Q is a free parameter. Within the present approximations we may write the ion density as $n \approx Q/qR^3$ and $\kappa^2 \approx (aQ/qR^3)(q^2/aT) \approx 1/R^2$ (leaving aside numerical factors like $4\pi/3$ or 8π); since $q^2/aT \approx 1$, we get an estimation of the equilibrium mean separation distance of the order $R \approx a(Q/q)$, where a is a distance of the order of the atomic distance between the ions in the dissociating 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 is plausible to assume 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 $R \approx a(r_0^2/a_p^2)$. 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.

The condition $n \approx Q/qR^3$ reflects the local charge neutrality. At equilibrium we may take $\varphi \approx -10^{-2} \times Q/R$ (computed above), such that $|q\varphi/T| \approx 10^{-2} \times aQ/qR \ll 1$. This inequality holds for any other distance (not very close to particles). We can see that the first-order expansion of $e^{q\varphi/T}$ is justified. On the other hand, $\delta n = 2nq\varphi/T \ll n$; the

mean charge density nq of the q -ions (concentration) is cancelled out by the mean charge density $-nq$ of the counter-ions, while the local change $-q\delta n$ in the ion charge density screens the particle charges Q and leads to equilibrium.

It is worth noting that the colloidal stabilization (and coagulation) 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 Eq. (18) we have a configurational equilibrium for $\kappa_0 R_0 \approx 1$, with an energy minimum of the order $-Q^2\kappa_0$; the temperature of the medium may be sufficiently high to overpass this minimum, such that we have a gaseous phase, with an attractive interaction between particles (a non-ideal gas, which obeys a van der Waals equation [14]; it seems that this equation was highlighted for the first time in Refs. [38,39]). The ensemble may begin 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 $R \approx a(Q/q)$; if Q is small, the colloid may even be flocculated (coagulated). 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. If the coagulation process is not very much developed, peptization cannot be excluded, if the charges are removed, or mechanical means are applied. This holds also for the stabilized phase, though it is difficult to assess the precise conditions of reversibility/irreversibility of these phase transitions. (This is so because this is a statistical problem with interacting particles and the interaction effects, which should be solved first, are treated only approximately).

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 mainly 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), at a distance governed by the particle charge Q , as described above (with only one species of counter-ions), or may acquire a liquid phase around these equilibrium positions, depending on the temperature of the medium.

4. Concluding remarks

The cohesion theory is employed here to estimate the stability and aggregation conditions of charged colloids. 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 solid and liquid phases are identified (even a non-ideal gaseous phase). The transitions between these phases, or to a flocculated (coagulated) phase, are discussed. The theory presented here differs from the standard double-layer theory by including all the particles (not only particle pairs) in solving the Debye-Huckel (Poisson) equation and computing the interaction energy.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] A.J. Stone, *The Theory of Intermolecular Forces*, Oxford University Press, Oxford, 2013.
- [2] J. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, NY, 1929.
- [3] B.V. Deryagin, L. Landau, A theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes, *Acta Physicochim. USSR* 14 (1941) 633–662.
- [4] E.J.V. Verwey, J.Th.G. Overbeek (with collab. of K. van Nes), *Theory of the Stability of Lyophobic Colloids (The Interaction of Sol Particles having an Electric Double Layer)*, Elsevier, Leiden, 1948.
- [5] D. Myers, *Surfaces, Interfaces and Colloids, Principles and Applications*, Wiley, NY, 1999.
- [6] R.J. Hunter, *The Double Layer in Colloidal Systems*, in: J.O'M. Bokriss, B.E. Conway, E. Yeager, (Eds.), *The Comprehensive Treatise of Electrochemistry*, vol. 1, *The Double Layer*, Springer, NY, 1980.
- [7] S. Durand-Vidal, J.-P. Simonin, P. Turq, *Electrolytes at Interfaces*, Kluwer, NY, 2002.
- [8] W.B. Russel, D.A. Saville, W.R. Schowalter, *Colloidal Dispersions*, Cambridge University Press, 1989.
- [9] V. Uskokovic, Theoretical and practical aspects of colloid science and self-assembly phenomena revisited, *Revs. Chem. Eng.* 23 (2007) 301–372.
- [10] M.B. McBride, A critique of diffuse double layer models applied to colloid and surface chemistry, *Clays Clay Miner.* 45 (1997) 598–608.
- [11] L.C. Cune, M. Apostol, Ground-state energy and geometric magic numbers for homo-atomic metallic clusters, *Phys. Lett. A* 273 (2000) 117–124.
- [12] L.C. Cune, M. Apostol, Atomic clusters. Chemical bonds on condensed matter, in: A. Graja, B.R. Bulka, F. Kajzar, (Eds.), *Molecular Low-Dimensional and Nanostructured Materials for Advanced Applications*, Poznan, Poland 2001, NATO Science Series, Kluwer, Dordrecht, 2002, p. 221.
- [13] L.C. Cune and M. Apostol, Theory of atomic clusters. Metallic clusters deposited on surfaces, in: L.M. Liz-Marzan, M. Giersig, (Eds.), *Low-Dimensional Systems: Theory, Preparation and some Applications*, Puzszykovo, Poland 2002, NATO Science Series, Kluwer, Dordrecht, 2003, p. 1.
- [14] M. Apostol, L.C. Cune, On the stability of a classical plasma, *Phys. Lett. A* 383 (2019) 1831–1835.
- [15] L.C. Cune, Magic pairs and structural transitions in binary metallic clusters, *Chem. Phys. Chem.* 13 (2012) 2133–2141.
- [16] P.-G. de Gennes, Ultradivided matter, *Nature* 412 (2001) 385.
- [17] O.A. Dobrescu, L.C. Cune, M. Apostol, Ferromagnet-superconductor junction, *Roum. Repts. Phys.* 60 (2008) 353–359.
- [18] S. Kruchinin, *Problems and Solutions in Special Relativity and Electromagnetism*, World Scientific, Singapore, 2017.
- [19] G. Gouy, Sur la constitution de la charge électrique à la surface d'un électrolyte, *J. Phys. Radium* 9 (1910) 457–468.
- [20] D.L. Chapman, A contribution to the theory of electrocapillarity, *Philos. Mag.* 25 (1913) 475–481.
- [21] D. Chapot, L. Bocquet, E. Trizac, Interaction between charged anisotropic macromolecules: application to rod-like polyelectrolytes, *J. Chem. Phys.* 120 (2004) 3969–3982.
- [22] E. Allahyarov, H. Lowen, S. Trigger, Effective forces between macroions: the case of asymmetric macroions and added salt, *Phys. Rev. E* 57 (1998) 5818–5824.
- [23] I. Langmuir, The role of attractive and repulsive forces in the formation of tactoids, thixotropic gels, protein crystals and coacervates, *J. Chem. Phys.* 6 (1938) 873–896.
- [24] D.M.C. MacEwan, Adsorption by montmorillonite and its relation to surface adsorption, *Nature* 162 (1948) 935–936.
- [25] I. Sogami, Effective potential between charged spherical particles in dilute suspension, *Phys. Lett. A* 96 (1983) 199–203.
- [26] I. Sogami, N. Ise, On the electrostatic interaction in macroionic solutions, *J. Chem. Phys.* 81 (1984) 6320–6332.
- [27] N. Ise, I.S. Sogami, *Structure Formation in Solution*, Springer, 2005.
- [28] M.V. Smaley, Electrostatic interaction in macro-ionic solutions and gels, *Mol. Phys.* 71 (1990) 1251–1267.
- [29] J. Wu, D. Bratko, J.M. Prausnitz, Interaction between like-charged colloidal spheres in electrolyte solutions, *Proc. Natl. Acad. Sci.* 95 (1998) 15169–15172.
- [30] D.G. Grier, When like-charges attract: interactions and dynamics in charge-stabilized colloidal suspensions, *J. Phys.: Condens. Matter* 12 (2000) A85–A94.
- [31] D.G. Grier, Colloids: a surprisingly attractive couple, *Nature* 393 (1998) 621.
- [32] G.L. Hunter, E.R. Weeks, The physics of the colloidal glass transition, *Reps. Progr. Phys.* 75 (2012) 066501.
- [33] H. Schulze, Schwefelarsen in wässriger Lösung, *J. Prakt. Chem.* 25 (1882) 431–452.
- [34] W.B. Hardy, On the conditions which determine the stability of irreversible hydrosols, *Proc. R. Soc. London* 66 (1900) 110–125.
- [35] W. Ostwald, Elektrolytkoagulation schwach solvatisierter Sole und Elektrolytaktivität, *Koll. Z.* 73 (1935) 301–328; Neuere Ergebnisse und Anschauungen über die Elektrolytkoagulation hydrophober Sole, *Koll. Z.* 88 (1939) 1–17.
- [36] K. Norrish, The swelling of montmorillonite, *Disc. Faraday Soc.* 18 (1954) 120–134.
- [37] M.V. Smaley, Electrical theory of clay swelling, *Langmuir* 10 (1994) 2884–2891.
- [38] I. Langmuir, The nature of adsorbed films of Caesium on Tungsten. Part I. The space charge sheath and the image forces, *Phys. Rev.* 43 (1933) 224–251.
- [39] P. Debye, Osmotische Zustandsgleichung und Aktivität verdünnter starker Elektrolyte, *Phys. Zeit.* 25 (1924) 97–107.