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When do like charges attract?

Yan Levin *

Instituto de Física, Universidade Federal do Rio Grande do Sul Caixa Postal 15051, CEP 91501-970, Porto Alegre, RS, Brazil

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Abstract

We study the interaction potential between two polyions in a colloidal suspension. It is shown that at large separation the interaction potential is purely repulsive, with the induced attractive interactions being doubly screened. For short separations the condensed counterions become correlated which leads to an effective attraction between two like-charged macromolecules. © 1999 Elsevier Science B.V. All rights reserved.

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Systems in which the interactions between the particles are predominantly due to long-range Coulomb force remain an outstanding challenge to classical statistical mechanics. Even such a basic question as the existence of a phase transition in a symmetric electrolyte has remained uncertain until quite recently [1]. Although the answer to this question has proven to be affirmative [2–4], the true nature of the transition as well as its universality class still remain unclear [5]. Surprisingly the theory that is in closest agreement with the Monte Carlo simulations is based on the old ideas first introduced by Debye, Hückel, and Bjerrum [6,7] more than seventy years ago. The fundamental insight of Debye was to realize that since the mean force inside the electrolyte is zero, it is the correlations in positions of oppositely charged ions that produce the main contribution to the free energy. A great advantage of the Debye–Hückel (DH) theory, besides its simplicity, is that its linear structure allows it to avoid the internal inconsistencies that are often present in the more complicated non-linear theories of electrolytes [8]. The price for linearity, however, is that DH theory cannot account for non-linear configurations, such as the formation of dipoles, which become important

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* Fax: +55-51-31-91-762; e-mail: levin@if.ufrgs.br.

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at low temperatures. It was an idea of Bjerrum, proposed only three years after the publication of the original DH paper, that the missing non-linearities can be reintroduced into the DH theory through the assumption of chemical equilibrium between monopoles and multipoles. The extended Debye–Hückel–Bjerrum (DHBj) theory has proven extremely successful in elucidating the underlying physics of symmetric electrolytes [5], polyampholytes [9], rod-like polyelectrolytes [10,11], and charged colloidal suspensions [12], with its validity extending far into the regime where the pure linear DH theory fails. In this paper, we shall use DHBj theory to explore a fascinating phenomena in condensed matter physics, namely the appearance of attraction between two like-charged polyions in a colloidal suspension.

The attractive interactions observed in a colloidal suspension have been attributed traditionally to the short range van der Waals forces, the relative magnitude of which is judged by the value of the phenomenological Hamaker constant. In order to explain various experimental data one is often led to use Hamaker constants which are much greater than can be justified theoretically [13–16]. This situation is quite unsatisfactory. Evidently, what is commonly denoted as the van der Waals force inside a suspension, is composed of two quite distinct interactions. The first is the usual van der Waals–London force produced by the quantum fluctuations in the charges of polyions, while the second and presumably much greater effect, is a dispersion force, of a purely classical origin, resulting from the correlations in the positions of counterions which compose the double layers of the macromolecules. It seems to us quite inconsistent to treat the correlational contributions to the dispersion force on a different footing from the other double layer effects, all being electrostatic in their origin. In the current work we present a unified view of various double layer interactions, in particular, obtaining corrections to the well known DLVO potential [17–19] at large and short distances.

To study a charged colloidal suspension we use a primitive model, in which the polyions are treated as hard spheres of radius a and uniform surface charge, $\sigma_- = -Zq/4\pi a^2$, and the counterions are point particles of charge zq. The solvent is modeled as a uniform medium of dielectric constant D. The bare interaction between any two macromolecules is purely repulsive. The question that we ask is, whether many-body effects are sufficient to produce an *effective* attraction without the need to invoke further nonclassical mechanisms.

In Ref. [12] it was demonstrated that the equilibrium state of a colloidal suspension consists of some free polyions of density ρ_0, free counterions of density ρ_f, and of clusters composed of *one* polyion and of $1 \leqslant n \leqslant Z/z$ associated counterions. The effective charge of an n-cluster is $Z_{\text{eff}} = -(Z - nz)q \equiv 4\pi a^2 \Delta\sigma$. The DHBj theory allows us to explicitly calculate the distribution of cluster densities $\{\rho_n\}$ [12].

Consider two clusters separated by a distance $R = 2a + L$, each consisting of a polyion and n condensed counterions (see Fig. 1). It is convenient to set up a bipolar coordinate system with the two polyions located at $r_1 = 0$ and $r_2 = 0$, respectively. To calculate the effective potential between the two clusters we shall appeal to the DHBj theory [12]. The electrostatic potential, $\phi(\mathbf{r}_1, \mathbf{r}_2)$, inside the suspension satisfies the Poisson

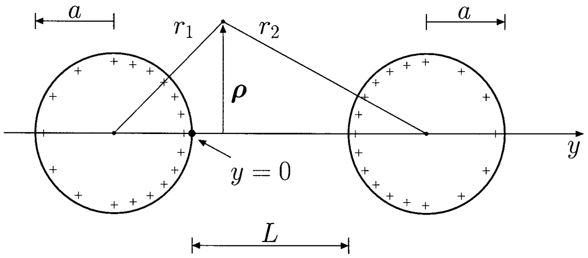

Fig. 1. Two clusters separated by a distance $R = 2a + L$. The polyions have a fixed uniform surface charge density σ_- and a mobile, nonuniform, surface charge σ_+ due to the condensed counterions, +. The overall imbalance of charge, $|\sigma_-| > |\sigma_+|$ is responsible for the polarization of clusters and for a decrease in the electrostatic energy relative to the uniform distribution of charge, $\Delta\sigma = \sigma_+ + \sigma_-$.

equation,

$$\begin{aligned}&\nabla^2\phi(\mathbf{r}_1,\mathbf{r}_2) = 0 \quad \text{for } r_1 < a \text{ or } r_2 < a\,,\\&\nabla^2\phi(\mathbf{r}_1,\mathbf{r}_2) = -4\pi\rho_q(\mathbf{r}_1,\mathbf{r}_2)/D \quad \text{for } r_1 \geqslant a \text{ and } r_2 \geqslant a\,.\end{aligned} \tag{1}$$

Within the DHBj theory the charge density is approximated by [12]

$$\begin{aligned}\rho_q(\mathbf{r}_1,\mathbf{r}_2) = {}& -\sum_{n=0}^{Z/z}(Z - zn)q\rho_n + zq\rho_f e^{-\beta zq\phi(\mathbf{r}_1,\mathbf{r}_2)} + \sigma_-\delta(r_1 - a)\\&+\sigma_+ e^{-\beta zq\phi(\mathbf{r}_1,\mathbf{r}_2)}\delta(r_1 - a) + \sigma_-\delta(r_2 - a)\\&+\sigma_+ e^{-\beta zq\phi(\mathbf{r}_1,\mathbf{r}_2)}\delta(r_2 - a)\,,\end{aligned} \tag{2}$$

where, $\beta = 1/k_B T$, and the average surface charge density of condensed counterions is $\sigma_+ = nzq/4\pi a^2$. As is usual in DH theory, the assumption is made that all the mobile microions will arrange themselves in accordance with the Boltzmann distribution. This is true both for the counterions in the bulk as well as for the counterions condensed on the surface of a polyion. As a second approximation [12], *linearization* leads to

$$\rho_q(\mathbf{r}_1,\mathbf{r}_2) = -(D/4\pi)\kappa^2\phi(\mathbf{r}_1,\mathbf{r}_2) + [\Delta\sigma - D\alpha\phi(\mathbf{r}_1,\mathbf{r}_2)/2\pi][\delta(r_1 - a) + \delta(r_2 - a)]\,, \tag{3}$$

where the inverse Debye and the Gouy–Chapman lengths are respectively $\kappa^2 = 4\pi\beta z^2 \times q^2\rho_f$, and $\alpha = 2\pi\sigma_+\beta zq/D$. Naively, one might think that linearization is valid only at high temperatures. This, however, is not the case, since the non-linearities are effectively included in the renormalization of the polyion charge by the formation of clusters [12,20]. The set of equations (1) is difficult to study due to non-trivial boundary conditions. Nevertheless some progress can be made in the two limiting cases, $L \gg a$ and $L \ll a$.

Let us consider first the case $L \gg a$ and $\kappa L > 1$. Using the Debye–Hückel theory [21,22] it is easy to demonstrate that the leading order interaction between the two n-clusters is given by the familiar DLVO potential [17–19,21,22],

$$W_{\mathrm{DLVO}}(R) = Z_{\mathrm{eff}}^2\theta^2(\kappa a)\frac{e^{-\kappa R}}{DR}\,, \tag{4}$$

where the geometric factor $\theta(x) = e^x/(1+x)$ appears as the result of the absence of screening inside the hard core exclusion region.

The leading correction to the DLVO potential comes from two main effects. First, the presence of polyions produces holes in the ionic atmosphere. The charge of a hole is equal to minus the charge of the counterions excluded from the region of space occupied by the polyion [21,22], namely,

$$Q_h(R) \approx \frac{1}{3}\kappa^2 a^3 \theta(\kappa a) Z_{\text{eff}} \frac{e^{-\kappa R}}{R} \,. \tag{5}$$

Since the charges of the holes have the same sign as the charges of the polyions, the holes interact repulsively with the polyions. The electrostatic energy of a hole is its charge times the potential that it feels.

The second major correction to the DLVO potential is the result of the polarization of the condensed layer of counterions surrounding a polyion. Thus, the electric field produced by the cluster $\mathscr{C}_1$ induces a dipole moment in the cluster $\mathscr{C}_2$, and vice-versa. The surface charge density of an n-cluster is found from Eq. (3) to be $\sigma(\mathbf{r}) = \Delta\sigma - D\alpha\phi(\mathbf{r})/2\pi$. It is a simple calculation in electrostatics [23] to show that the induced dipole moment of an n-cluster is,

$$\mathbf{p} = \frac{2\alpha a^4 D\mathbf{E}}{(3 + 2\alpha a)} \,. \tag{6}$$

Within the Debye–Hückel theory the electric field, $\mathbf{E}$, produced by an n-cluster at distance R from its center is,

$$\mathbf{E}(\mathbf{R}) = Z_{\text{eff}}\theta(\kappa a)\frac{e^{-\kappa R}(1+\kappa R)\mathbf{R}}{DR^3} \,. \tag{7}$$

The electrostatic energy of the induced dipole of $\mathscr{C}_2$ in the electric field produced by $\mathscr{C}_1$ is minus the inner product between the dipole moment and the electric field. This interaction is always attractive [24]. Clearly this argument can equally well be applied to the induced dipole moment of the cluster $\mathscr{C}_1$ in the field produced by the cluster $\mathscr{C}_2$. The electrostatic *free energy* due to the two effects described above can be easily calculated using the charging process in which both polyions are simultaneously charged from zero to Z_{eff}. In the limit $L \gg a$ and $\kappa L > 1$ the full interaction potential between the two n-clusters is found to be,

$$W(R) = Z_{\text{eff}}^2\theta^2(\kappa a)\frac{e^{-\kappa R}}{DR} - Z_{\text{eff}}^2\kappa^2 a^3\theta^2(\kappa a)h(\alpha a)\frac{e^{-2\kappa R}}{DR^2} \,, \tag{8}$$

where the new scaling function $h(x)$ is,

$$h(x) = \frac{2}{3} - \frac{3}{2x}\ln\left(1 + \frac{2x}{3}\right) \,. \tag{9}$$

We see from the form of Eq. (9) that the correction to the DLVO potential is repulsive (hole dominated) for $\alpha a < 1.716\ldots$ and is attractive (dipole dominated) for $\alpha a > 1.716\ldots$. However, one must note that this induced attraction is "doubly" screened and is so dominated at long distances by the leading order DLVO term.

We now turn our attention to the opposite limit $L \ll a$ and $\kappa L < 1$. Under these conditions the relevant small parameter is $\varepsilon = L/a$, and the Debye screening due to unassociated counterions can be neglected. It is convenient to define a cylindrical coordinate system, $(\boldsymbol{\rho}, y)$, with the y-axis passing through the centers of the two clusters: see Fig. 1. The two polyions are located at $y = -a$ and $y = a + L$, respectively. The interaction potential can be subdivided into two parts: the mean-field repulsion, V_{MF}, arising from the net charge on the two clusters, and the attraction coming from the correlations among the condensed counterions. It is evident that the repulsive energy satisfies, $V_{\mathrm{MF}} < Z_{\mathrm{eff}}^2/DR$. In what follows we shall approximate V_{MF} by the upper bound, $V_{\mathrm{MF}} = Z_{\mathrm{eff}}^2/DR$, that is, we shall treat the mobile charge, σ_+, as, on average, *uniformly distributed* on the surface of the two polyions. Clearly this assumption will *overestimate* the importance of repulsion, since it neglects the ability of the bound counterions to arrange themselves in the most efficient way to minimize the free energy, see Fig. 1. With this in mind, to leading order in $\varepsilon = L/a$, the geometry can be approximately replaced by that of two plates located at $y = 0$ and $y = L$, each with a fixed surface charge, σ_-, and the mobile charge, σ_+. The free energy can then be calculated using DH theory. Let us fix one counterion, say 0, at $(\mathbf{0}, 0)$. Eqs. (1) and (3) may now be integrated to give

$$\phi_0(\rho, y) = \frac{\pi \Delta\sigma}{D} L - \frac{2\pi \Delta\sigma}{D}(|y| + |y - L|) + \Delta\phi_c(\rho, y)\,, \tag{10}$$

where the correlation potential can be written in terms of the zero-order Bessel function as

$$\begin{aligned}
\Delta\phi_c(\rho, y) &= \int_0^\infty A(k) e^{ky} J_0(k\rho)\, dk \quad \text{for } y \leqslant 0\,,\\
\Delta\phi_c(\rho, y) &= \int_0^\infty [B(k) e^{ky} + C(k) e^{-ky}] J_0(k\rho)\, dk \quad \text{for } 0 < y < L\,,\\
\Delta\phi_c(\rho, y) &= \int_0^\infty E(k) e^{-ky} J_0(k\rho)\, dk \quad \text{for } y \geqslant L\,.
\end{aligned} \tag{11}$$

The coefficient functions, A, B, C, E, are determined through the conditions of continuity of the potential and discontinuity of the normal component of the electric field related to the presence of surface charge at $y = 0$ and $y = L$, namely

$$\sigma(\rho, 0) = \Delta\sigma - \sigma_+ zq\beta\phi(\rho, 0) + zq\delta(\rho)/2\pi\rho\,, \tag{12}$$

and

$$\sigma(\rho, L) = \Delta\sigma - \sigma_+ zq\beta\phi(\rho, L)\,, \tag{13}$$

respectively. For our purpose it is sufficient to determine only the coefficient $A(k)$, since it is the only one that enters into the calculation of free energy. We find

$$A(k) = \frac{[k(k+\alpha) - k\alpha e^{-2kL}]}{[(k+\alpha)^2 - \alpha^2 e^{-2kL}]}\,. \tag{14}$$

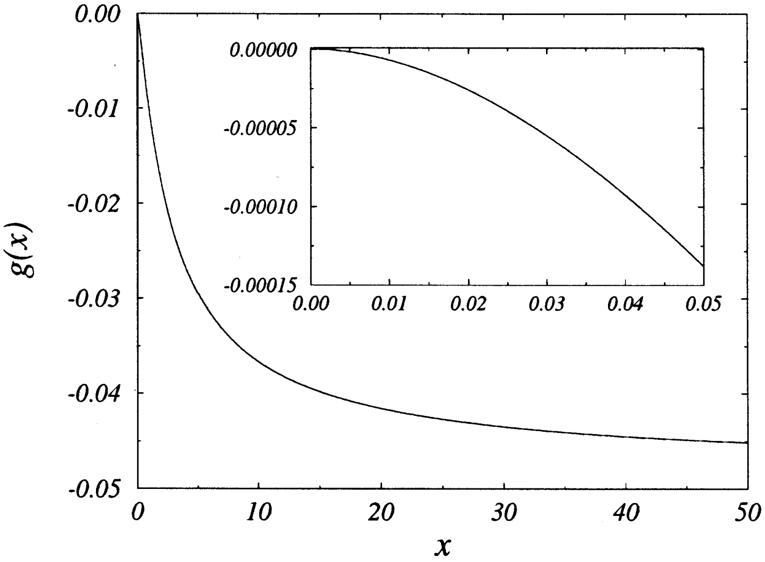

Fig. 2. The scaling function $g(x)$: see text.

The electrostatic potential experienced by the counterion 0 due to the presence of other charges is $\lim_{\rho\to 0}(\phi_0(\rho,0) - zq/D\rho)$ [6,7,25]. The free energy per unit area is then obtained through the Debye charging process, in which all the particles in the system are charged from 0 to their final charge. We note, however, that in the absence of hardcores for the counterions this free energy has an ultraviolet divergence. A regularization scheme must then be used. In what follows we adopt the minimal subtraction scheme which allows for the clearest presentation of the scaling structure of the theory. The regularized free energy per unit area is found to be,

$$f_R = -\frac{2\pi(\Delta\sigma)^2}{D} L \int_0^1 \lambda\, d\lambda + \frac{2zq\sigma_+}{D} \int_0^1 \lambda\, d\lambda \int_0^\infty \left[\frac{(k+\lambda^2\alpha) - \lambda^2 \alpha e^{-2kL}}{(k+\lambda^2\alpha)^2 - \lambda^4\alpha^2 e^{-2kL}} - \frac{1}{k+\lambda^2\alpha} \right] k\, dk\,. \tag{15}$$

The force per unit area that each polyion exerts on the other is $F = -\partial f_R/\partial L$. Performing the differentiation we find

$$F = \frac{\pi(\Delta\sigma)^2}{D} + \frac{g(\alpha L)}{\beta L^3}\,, \tag{16}$$

where the scaling function $g(x)$ is plotted in Fig. 2. The first term here represents the repulsion due to the excess charge on the two clusters, while the second term is the correlation-induced attraction [26–28]. For $x \gg 1$ one finds $g(\infty) = -\zeta(3)/8\pi$, where ζ is the Riemann zeta function; for small x one has $g(x) \approx -x^2/4\pi$, and we note that for short enough separation the correlation-induced attraction will always dominate the excess charge repulsion. Furthermore, as was mentioned earlier, taking a better account of the spherical geometry should favor attraction by decreasing the repulsive contribution, V_{MF}, and increasing the correlations (α) between the induced counterions on the two hemispheres facing each other: see Fig 1. An attraction similar to the one discussed above has been recently observed in Monte Carlo simulations [29].

Let us now make some estimates. Suppose that the condensed counterions neutralize a fraction of the fixed charge so that $|\sigma_+| = f|\sigma_-|$. We should see a net attractive force when $\mu \equiv z^2\lambda_{\mathrm{B}} f^2/(1-f)^2 > L$, where the Bjerrum length $\lambda_{\mathrm{B}} = \beta q^2/D$, is 7.2 Å in water. Consider a colloidal suspension of polystyrene particles with characteristic size 700 Å and charge $Z = 1000$. In Ref. [12] it was found that the average cluster size is $\langle n \rangle = 400$. In that case a purely repulsive DLVO potential was used in order to estimate the cluster–cluster contribution to the overall free energy. It was found, however, that the cluster–cluster interaction is responsible for a very small part of the total free energy, of the order of few percent, and is completely dominated by the entropic contribution derived from the free, unassociated, counterions. We expect that the short range modification of the DLVO potential found above, will not significantly affect the total free energy and will not modify the average cluster size. Thus, for the polystyrene spheres considered above we find $f = 0.4$, which leads to $\mu = 3.2$ Å. This is smaller than the size of a hydrated counterion. We, therefore, do not expect that for colloids with $Z < 1000$ one will observe any attraction. However, for polyions with $Z = 3000$ we obtain $f = 0.73$, and the attractive interaction will dominate for $L < 53$ Å which may be observable experimentally. If a multivalent salt is added to the colloidal suspension, owing to the strong electrostatic attraction, the multivalent counterions will be preferentially adsorbed to the polyion surface, leading to even stronger correlation-induced attractions. We would like to emphasize that the presence of attraction does not imply the existence of a phase transition. The thermodynamic properties of a colloidal suspension are mostly determined by the counterions and their interaction with the polyions and clusters. The contribution of the cluster–cluster interaction to the osmotic pressure is minimal [12]. Nevertheless the metastable effects associated with the presence of attractive forces might explain the unusual observations connected with charged colloidal suspensions [13–16]. Finally, we should stress that the attractions predicted by the DHBj theory are intrinsically a finite-concentration result and will disappear at infinite dilution. The reason for this is that, in the case of spherical colloids, the formation of clusters is a purely finite-concentration phenomena. This should be contrasted with rod-like polyelectrolytes, for which the strong logarithmic potential existing between the polyions and the counterions allows for the condensed layer to persist all the way to zero density [10,11,30], making it viable to study just *two* polyions with their counterions [31–34].

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