When Do Like Charges Attract?

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We study the interaction potential between two polyions inside 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, what leads to an effective attraction between the two macromolecules.

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The systems in which the interactions between the particles are predominantly due to the long-ranged Coulomb force remain an outstanding challenge to classical statistical mechanics. Even such basic question as the existence of a phase transition in a symmetric electrolyte has remained uncertain until quite recently. Although the answer to this question has proven to be affirmative, the true nature of the transition as well as its universality class still remain unclear. Surprisingly the theory of phase transition in a symmetric electrolyte has proven extremely successful in elucidating the underlying physics of symmetric electrolytes. The price for linearity, however, is that the DH theory cannot account for the non-linear configurations, for instance formation of dipoles, which become important at low temperatures. It was an idea of Bjerrum, proposed only three years after the publication of original DH paper, that the missing non-linearities can be reintroduced into the DH theory through the assumption of chemical equilibrium between the monopoles and multipoles. The extended Debye-Hückel-Bjerrum (DHBj) theory has proven extremely successful in elucidating the underlying physics of symmetric electrolytes, polyelectrolytes, rod-like polyelectrolytes, and charged colloidal suspensions, with its validity extending far into the regime where the pure linearized DH theory fails. In this letter we shall use the DHBj theory to explore one of the most fascinating phenomena in condensed matter physics, the appearance of attraction between two like-charged polyions inside a colloidal suspension.

To model a charged colloidal suspension we use a restricted primitive model, in which the polyions are treated as hard spheres of radius $a$ and uniform surface charge, $\sigma_\pm = -Zq/4\pi a^2$, and the counterions are point particles of charge $zq$. The solvent is modeled as a uniform medium of dielectric constant $D$. In Ref. it was demonstrated that the equilibrium state of the colloidal suspension consists of some free polyions of density $\rho_0$, free counterions of density $\rho_f$, and of clusters composed of one polyion and of $1 \leq n \leq Z/z$ associated counterions. The effective charge of a $n$-cluster is $Z_{\text{eff}} = -\langle Z-nz \rangle q \equiv 4\pi a^2 \Delta \sigma$. The DHBj theory allows us to explicitly calculate the distribution of cluster densities $\{\rho_n\}$

\begin{equation}
\nabla^2 \phi = \begin{cases} 
0, & \text{for } r_1 < a \text{ or } r_2 < a, \\
-4\pi \rho_q(r_1, r_2)/D, & \text{for } r_1 \geq a \text{ and } r_2 \geq a.
\end{cases}
\end{equation}

FIG. 1. The two clusters separated by a distance $R = 2a + L$. The polyions have a fixed surface charge density $\sigma_-$ and the mobile surface charge $\sigma_+$ due to the condensed counterions, +. The overall imbalance of charge, $|\sigma_-| > |\sigma_+|$ is responsible for the polarization of clusters and for decrease in the electrostatic energy relative to the uniform distribution of charge, $\Delta \sigma = \sigma_+ + \sigma_-$. Consider two clusters separated by a distance $R = 2a + L$, each consisting of a polyion and $n$ condensed counterions. 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. The electrostatic potential inside the suspension satisfies the Poisson equation, within the DHBj theory the charge density is approxi-
mated by
\[
\rho_q(r_1, r_2) = -\sum_{n=0}^{Z/z}(Z - zn)q \rho_n + zq\rho_f e^{-\beta zq\phi(r_1, r_2)}
+ \sigma_-\delta(r_1 - a) + \sigma_+ e^{-\beta zq\phi(r_1, r_2)} \delta(r_1 - a)
+ \sigma_-\delta(r_2 - a) + \sigma_+ e^{-\beta zq\phi(r_1, r_2)} \delta(r_2 - a),
\]
where, \(\beta = 1/k_BT\), and the average surface charge density of condensed countermers is \(\sigma_+ = n zq/4\pi a^2\). Note that only the counterions are assumed to get polarized, while the polyions and clusters contribute only to the neutralizing background. As a second approximation, linearization leads to \(\rho_q(r_1, r_2) = -(D/4\pi)\kappa^2 \phi(r_1, r_2) + [\Delta \sigma - D \alpha \phi(r_1, r_2)/2\pi] [\delta(r_1 - a) + \delta(r_2 - a)]\), where the inverse Debye and the Gouy-Chapman lengths are respectively \(\kappa = \sqrt{4\pi z^2 q^2 \rho_f}\), 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 \([8,10]\). The set of equations \([1]\) is extremely difficult to study due to non-trivial boundary conditions. Nevertheless some progress can be made in the two limiting cases, \(L \gg a\) and \(L \ll a\). All the detail of calculations will be presented elsewhere, here we shall content ourselves with giving a simple and an intuitive explanation of the results.

In the limit \(L \gg a\) and \(\kappa L > 1\) one finds that the crucial small parameter is \(\epsilon = \exp(-\kappa L)/R\) \([1]\). It is then possible to show that the interaction potential between the two clusters is
\[
W(R) = Z_{\text{eff}}^2 \theta^2(\kappa a) e^{-\kappa R}/DR - Z_{\text{eff}}^2 \kappa^2 a^3 \theta^2(\kappa a) h(\alpha a) e^{-2\kappa R}/DR^2,
\]
where the two scaling functions are \(\theta(x) = e^x/(1 + x)\) and \(h(x) = \frac{\delta}{\delta x} [\ln(x + \frac{\delta}{\delta x})]\). The first term is just the usual DLVO potential between the two colloidal particles with the effective charge \(Z_{\text{eff}}^2\). The second term is the result of two types of interactions. First, presence of polyions produces holes in the ionic atmosphere. Since the charges of the holes have the same sign as the charges of the polyions, the holes interact repulsively with the polyions \([1]\). The second effect is that the mobile counterions confined to the surface are easily polarized. Thus, the electric field produced by the cluster \(C_1\) induces a dipole moment in the cluster \(C_2\), and vice versa. The polarizability of a \(n\)-cluster is found to be \(\gamma = 2\alpha a^3/(3 + 2\alpha a)\). The effective dipole moment interacts attractively with the charge that induced it. Since the scaling function \(h(x)\) changes sign, we see that the correction to the DLVO potential is repulsive (hole dominated) for \(\alpha a < 1.716\) and is attractive (dipole dominated) for \(\alpha a > 1.716\). However, we do note that this induced attraction is “doubly” screened and is dominated by the leading order DLVO term.

We shall now turn our attention to the opposite limit \(L \ll a\) and \(\kappa L < 1\). Under these conditions the relevant small parameter is \(\epsilon = L/a\), and the Debye screening due to unassociated countermers can be neglected. It is convenient to define a cylindrical coordinate system, \((\rho, y)\), with the \(y\) axis passing through the centers of the two clusters, 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, \(V_{\text{MF}}\), arising from the overall imbalance of charge on the two clusters, and the attraction coming from the correlations among the condensed countermers. It is evident that the repulsive energy satisfies, \(V_{\text{MF}} \leq Z_{\text{eff}}^2/DR\). In what follows we shall approximate \(V_{\text{MF}}\) by the upper bound, \(V_{\text{MF}} = Z_{\text{eff}}^2/DR\), that is, we shall treat the mobile charge, \(\sigma_+\), 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 energy, see Fig. 1. With this in mind, to leading order in \(\epsilon\), the geometry can be replaced by that of two plates located at \(y = 0\) and \(y = L\), each with a fixed surface charge, \(\sigma_-\), and the mobile charge, \(\sigma_+\). The free energy can be calculated using the \(DH\) theory. Let us fix one counterion at \((0,0)\). The equations \([1]\) may now be integrated to give
\[
\phi(\rho, y) = \frac{\pi \Delta \sigma}{D} L - \frac{2\pi \Delta \sigma}{D} (|y| + |y - L|) + \Delta \phi_0(\rho, y),
\]
where the correlation potential can be written in terms of the zero-order Bessel function,
\[
\Delta \phi_0(\rho, y) = \begin{cases} 
\int_0^\infty A(k)e^{ky}J_0(k\rho)dk, & \text{for } y \leq 0, \\
\int_0^\infty B(k)e^{ky} + C(k)e^{-ky}J_0(k\rho)dk, & \text{for } 0 < y < L, \\
\int_0^\infty E(k)e^{-ky}J_0(k\rho)dk, & \text{for } y \geq L.
\end{cases}
\]
The coefficients, $A, B, C, E,$ 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 $y = L$. $\sigma(0, 0) = \Delta \sigma - \sigma_+ z q \beta \phi(\rho, 0) + z q \phi(\rho)/2\pi \rho$ and $\sigma(\rho, L) = \Delta \sigma - \sigma_+ z q \beta \phi(\rho, L)$, respectively. For our purpose it is sufficient to determine only the coefficient $A(k)$, since this is the only one that will enter into the calculation of free energy. We find $A(k) = [k(k + 1) - k e^{-2kL}]/[(k + 1)^2 - \alpha^2 e^{-2kL}]$. The electrostatic potential of the counterion due to the presence of other charges is $\lim_{\rho \to 0}(\phi(\rho, 0) - z q / D \rho)$. The regularized 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.

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

The force per unit area that each polyion exerts on the other is $F = -\partial f_R / \partial L$. Performing the differentiation we find $F = \frac{\pi(\Delta \sigma)^2}{D} + \frac{g(\alpha L)}{2\lambda L}$, with the scaling function $g(x)$ plotted in Fig 2. The first term is the repulsion due to excess charge on the two clusters, while the second term is the correlation-induced attraction. If $x \gg 1$, $g(\infty) = -\zeta(3)/8\pi$, where $\zeta$ is the Riemann zeta function. For small $x$, $g(x) \approx -x^2/4\pi$, 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 will only favor the attraction by decreasing the repulsive contribution, $V_{MF}$, and increasing the correlations ($\alpha$) between the induced counterions on the two hemispheres facing each other, Fig 1. Let us now make some estimates. Suppose that the condensed counterions neutralize a fraction of fixed charge, $|\sigma_{+}| = f |\sigma_{-}|$. We shall see attraction when $\mu \equiv z^2 \lambda_B f^2 / (1 - f)^2 > L$, where the Bjerrum length, $\lambda_B = \beta q^2 / D$, is 7.2 Å in water. Consider a colloidal suspension of polystyrene particles with characteristic size 700 Å and charge $Z = 1000$. In Ref. it was found that the average cluster size is $< n > = 400$ or $f = 0.4$, what 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 $Z = 3000$, $f = 0.73$, the attractive interaction will dominate for $L < 53$ Å and may be observable experimentally. If a multivalent salt is added to the colloidal suspension, due to a strong electrostatic attraction the multivalent counterions will be preferentially adsorbed to the polion surface, leading to even stronger fluctuation-induced attraction. We like to emphasize that a 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. Nevertheless the metastable effects connected with the presence of attractive forces might explain the unusual observations connected with the charged colloidal suspensions. Finally, we should stress that the attraction predicted by the $DHBj$ theory is 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 phenomenon. This should be contrasted with the 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, making it viable to study just two polyions with their counterions.

![FIG. 2. The scaling function $g(x)$.](image-url)

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