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Charge reversal of colloidal particles

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Charge reversal of colloidal particles

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Abstract. – A theory is presented for the effective charge of colloidal particles in suspensions containing multivalent counterions. It is shown that if colloids are sufficiently strongly charged, the number of condensed multivalent counterion can exceed the bare colloidal charge leading to charge reversal. Charge renormalization in suspensions with multivalent counterions depends on a subtle interplay between the solvation energies of the multivalent counterions in the bulk and near the colloidal surface. We find that the effective charge is *not* a monotonically decreasing function of the multivalent salt concentration. Furthermore, contrary to the previous theories, it is found that except at very low concentrations, monovalent salt hinders the charge reversal. This conclusion is in agreement with the recent experiments and simulations.

Introduction. – When a colloidal particle is placed inside a suspension containing multivalent ions its electrophoretic mobility can become reversed [1,2]. If this happens, an applied electric field will produce a drift of a colloid in the direction opposite to the one expected based purely on its chemical charge [3–5]. Somehow an excessive number of counterions must become associated with the colloid forming an overcharged (charge reversed) complex [6–11]. What is the cause of this curious behavior?

There is a significant clue to the mechanism of charge reversal: the mean-field Poisson Boltzmann (PB) theory completely fails to account for its existence [12–15]. Since the PB theory does not take into account the ionic correlations, it is reasonable to suppose that they are the ones responsible for the colloidal charge reversal. Indeed, recently a number of theories have been advanced to establish the mechanism through which the counterion correlations lead to overcharging [3, 6, 7, 16, 17]. Unfortunately none of the theories can fully account for the experimental findings. While all the theories predict that addition of monovalent salt should greatly increase the amount of charge reversal, quite the opposite is found experimentally and in the molecular-dynamics simulations [4, 18, 19]. In fact it is observed experimentally that while small concentrations of 1 : 1 electrolyte have little effect on the charge reversal, larger concentrations destroy it completely [4]. Similar behavior has also been seen in recent molecular-dynamics simulations [18, 19]. In this paper we will present a theory of charge reversal which accounts for the behavior observed in the experiments and simulations.

The model. – Consider a colloidal particle of radius a and charge $-Zq$, distributed uniformly over its surface, inside a suspension containing monovalent salt at concentration C and α-valent salt at concentration C_α. All ions are modeled as hard spheres of diameter a_c. We shall assume that both salts are strong electrolytes so that in aqueous solution there will be α-valent (cation) counterions at concentration C_α, monovalent (cation) counterions

at concentration C and coions (anions) at concentration $C + \alpha C_\alpha$. For simplicity, we will assume that all the coions are identical. The solvent will be treated as a uniform continuum of dielectric constant ϵ. A strong electrostatic interaction between the colloid and the counterions will result in their mutual association. If the counterions are sufficiently strongly bound to the colloidal particle, a new entity —the colloid-counterion complex— will be formed. It is reasonable to suppose that for small electric fields the zeta potential at the colloidal shear plane will be proportional to the net charge of the complex. The Smoluchowski equation can then be used to find the electrophoretic mobility [20]. The goal of the present theory is then to calculate the number of condensed/associated counterions.

We will define the counterions as free (not-associated) if they are farther than distance δ from the colloidal surface. An "agglomerate" is then defined as a polyion with a δ-sheath of n surrounding counterions. For concreteness we shall take $\delta = 2\,\text{Å}$ which corresponds to the characteristic hydration radius of an ion.

Since the electrostatic attraction between the α-valent counterions and the colloid is much stronger than its interaction with the monovalent counterions and coions, it is the multivalent ions which are primarily responsible for the colloidal charge renormalization. The size of an agglomerate is then determined from the minimum of the grand potential function,

$$\Omega(n) = F(n) - n\mu_0\,, \tag{1}$$

where $F(n)$ is the Helmholtz free energy of the agglomerate and μ_0 is the bulk chemical potential of free α-ions defined later. The theory must provide the expressions for the Helmholtz free energy of the agglomerate and the bulk chemical potential of the free α-ions. Let us begin with the chemical potential.

Statistical mechanics of asymmetric electrolytes still possess an outstanding challenge to physical chemistry [21]. It is possible, however, to gain a significant insight into the problem by appealing to the theories advanced by Debye, Hückel and Bjerrum more than 80 years ago. The fundamental insight of Debye and Hückel (DH) was that although the ions of electrolyte are *on average* uniformly distributed throughout the volume of solution, there are strong positional correlations between the ions of opposite sign [22]. Debye and Hückel suggested that these correlations can be studied using a linearized Poisson-Boltzmann equation (PB) —Poisson equation in which the ionic charge density is given by the Boltzmann distribution. Bjerrum, however, noted that when oppositely charged ions come into a close proximity forming dipolar pairs, linearization of the Boltzmann factor is no longer valid, and the DH theory fails [23]. Although for $1:1$ electrolytes in water at room temperature the Bjerrum dipolar formation is only marginally relevant, for multivalent ions it is the primary mechanism responsible for the failure of the linear DH theory. The non-linear configurations can be reintroduced into the DH theory as new species —dipoles and higher-order clusters containing an α-ion and $i = 0, \ldots, \alpha$ associated anions— the concentrations of which, c_i, is governed by the law of mass action

$$\mu_i = \mu_0 + i\mu_-\,, \tag{2}$$

where μ_0 is the chemical potential of free unassociated α-ions and μ_- is the chemical potential of anions. Particle conservation imposes constraints $C_\alpha = \sum c_i$ and $\alpha\,C_\alpha + C = c_- + \sum i c_i$, where c_- is the number of free anions.

The chemical potential of a cluster containing an α-ion and i associated anion is

$$\beta\mu_i = \ln\left(\frac{c_i \Lambda^{3(i+1)}}{\xi_i}\right) + \beta\mu_i^{ex}\,. \tag{3}$$

The first term of eq. (3) is the entropic contribution arising from the center of mass and internal motion of the clusters. $\Lambda = (h/\bar{m}k_B T)^{1/2}$ is the de Broglie thermal wavelength, where $\bar{m}$ is the geometric mean mass of the cluster, and ξ_i is the cluster internal partition function [24]. For free α-ions (0-clusters) $\xi_0 = 1$. The second term of eq. (3) is the excess chemical potential resulting from the electrostatic interaction between the cluster and other ionic species. At the level of the Debye-Hückel-Bjerrum (DHBj) approximation [24], only the interactions between charged entities contribute to the excess chemical potential. Thus, a neutral cluster will not have any excess chemical potential.

With the non-linearities taken into account through the process of cluster formation, the rest of the electrostatic interactions can be treated using the linearized PB equation

$$\nabla^2 \phi = \kappa^2 \phi, \tag{4}$$

where $\kappa = \sqrt{8\pi\lambda_B I}$ is the inverse Debye length, $I = \frac{1}{2}(\sum_{i=0}^{\alpha}(\alpha - i)^2 c_i + C + c_-)$ is the ionic strength and $\lambda_B = \beta q^2/\epsilon$ is the Bjerrum length. For example, the excess chemical potential of an anion can be obtained by integrating the Helmholtz equation (4) followed by the Güntelberg charging process [25],

$$\beta\mu_-^{ex} = -\frac{\lambda_B \kappa}{2(1 + \kappa a_c)} \ . \tag{5}$$

Similarly, the excess chemical potential of an i-cluster is found to be

$$\beta\mu_i^{ex} = -\frac{(\alpha - i)^2 \lambda_B \kappa}{2(1 + \kappa R_i)} \ , \tag{6}$$

where R_i is the effective radius of the cluster determined from its effective excluded volume, $R_0 = a_c$, $R_1 = 1.191 a_c$, $R_2 = 1.334 a_c$, etc. [24].

The internal partition function of an i-cluster is

$$\xi_i = \frac{1}{i!} \int dr_1^3 \ldots dr_i^3 e^{-\beta U}, \tag{7}$$

where U is the Coulomb potential. The integral is cutoff at short distance by the hard core of the ions and at large distance by some characteristic size at which the associated ions can be considered to belong to the same cluster. In the strong-coupling limit, $\alpha\lambda_B/a_c \gg 1$, the precise value of the upper cutoff is irrelevant [24], and the internal partition function can be evaluated explicitly. We find

$$\xi_1 = a_c^{\ 4} e^{\alpha\lambda_B/a_c} \frac{4\pi}{\alpha\lambda_B} \ , \tag{8}$$

$$\xi_2 = a_c^{\ 9} e^{(4\alpha-1)\lambda_B/2a_c} \frac{1024\pi^2}{(4\alpha - 1)^2 \lambda_B^3} \ , \tag{9}$$

$$\xi_3 = a_c^{\ 27/2} e^{(3\alpha-\sqrt{3})\lambda_B/a_c} \frac{2^{9/4}\pi^{9/2}}{3^{3/2}(\sqrt{2}\alpha - 1)^3 \lambda_B^{9/2}} \ . \tag{10}$$

Although it is, in principle, possible to calculate the internal partition function of higher-order clusters as well, the calculations become progressively more complex. Since in this paper we are interested only in the case $\alpha = 3$, the three internal partition functions given by eqs. (8)-(10) are sufficient for our purpose.

Substituting the expressions for μ_-, μ_0 and μ_i into the law of mass action yields

$$c_i = \xi_i c_0 c_-^i \, e^{-\beta\mu_i^{ex}+\beta\mu_0^{ex}+i\beta\mu_-^{ex}} \, . \tag{11}$$

Equation (10) is a set of α coupled algebraic equations which must be solved numerically to determine the distribution $\{c_i\}$ and the number of free coions c_-. With these in hand, the bulk chemical potential of free α-ions μ_0, needed for the minimization of the grand potential can be calculated using eq. (3). Since the electrostatic interactions are the strongest between the colloid and the free α-ions, we have assumed that it is their condensation which is primarily responsible for the colloidal charge renormalization.

Our next step is to calculate the free energy of an agglomerate containing a colloid and n condensed α-ions. The Helmholtz free energy can be written as a sum of three terms, $F_n = E_n + F_n^{solv} + F_n^{ent}$. E_n is the electrostatic free energy of an isolated agglomerate, F_n^{solv} is the solvation free energy that the agglomerate gains from being placed inside the suspension, and F_n^{ent} is the entropic free energy of the condensed counterions.

The energy of an isolated agglomerate is

$$\beta E_n = \frac{Z^2 q^2 \lambda_B}{2a} - \frac{Z\alpha q^2 \lambda_B}{a} + \beta F_n^{\alpha\alpha} \, . \tag{12}$$

The first term of eq. (12) is the electrostatic self-energy of the colloidal particle, the second term is the interaction energy between the colloid and n condensed counterions, and the last term is the electrostatic energy of interaction between the condensed α-ions. We can relate $F_n^{\alpha\alpha}$ to the free energy of a spherical one-component plasma (SOCP), defined as a plasma of n α-ions moving on the surface of a sphere with a *uniform neutralizing background*,

$$\beta F^{SOCP} = \beta F_n^{\alpha\alpha} + \frac{n^2\alpha^2 q^2 \lambda_B}{2a} - \frac{n^2\alpha^2 q^2 \lambda_B}{a} \, . \tag{13}$$

In the strong-coupling limit [6,26,27] the free energy of the $SOCP$ is very well approximated by $\beta F^{SOCP} \approx \alpha^2 \lambda_B M n^{3/2}/2a$, where $M = 1.104$ is the Madelung constant. Substituting eq. (13) into eq. (12), the energy of an isolated agglomerate becomes [28]

$$\beta E_n = \frac{(Z - \alpha n)^2 \lambda_B}{2a} - \frac{\alpha^2 \lambda_B M n^{3/2}}{2a} \, . \tag{14}$$

When the agglomerate is placed inside the electrolyte solution it gains an additional solvation free energy which, once again, can be obtained using the Debye-Hückel theory [6],

$$\beta F_n^{solv} = -\frac{(Z - \alpha n)^2 \lambda_B \kappa a}{2a(1 + \kappa a)} \, . \tag{15}$$

Finally, the entropic free energy of ions inside the agglomerate is $\beta F_n^{ent} = n \ln(\rho_n \Lambda^3) - n$, where $\rho_n = n/4\pi a^2 \delta$ is the concentration of multivalent counterions inside the δ-sheath.

In equilibrium, the number of α-ions, n^*, inside the agglomerate is determined from the minimization of the grand potential function, eq. (1), given by $\delta\Omega_Z = 0$. The minimization is performed at fixed Z. It is important, however, to keep in mind that not all of the α-ions inside the agglomerate are really associated with the polyion. The way the theory is constructed, the region near the colloidal surface is treated separately from the rest of electrolyte. This leads to an artificial excess of the multivalent ions inside the δ-sheath. The number of truly condensed counterions (α-ion which are inside the δ-sheath precisely due to their electrostatic coupling with the colloid) is $n^* - n_0^*$, where the excess n_0^* can be found by minimizing the grand potential function at $Z = 0$, $\delta\Omega|_{Z=0} = 0$. The effective charge of the polyion-α-ion complex (in units of $-q$) is then $Z_{eff} = Z - \alpha n^* + \alpha n_0^*$.
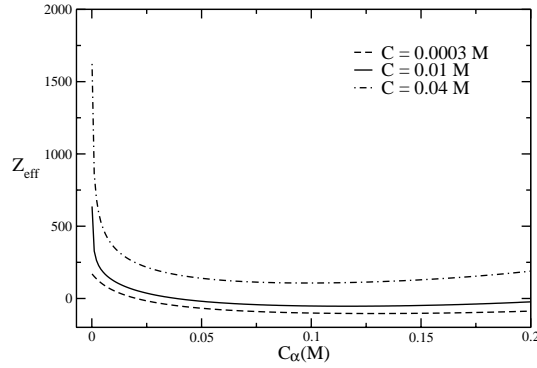
Fig. 1 – The effective charge as a function of concentration of trivalent ions ($\alpha = 3$) for a suspension containing colloidal particles with $Z = 4000$ and $a = 300$ Å. The curves correspond to different values of monovalent salt concentration with $\lambda_B = 7.2$, $\delta = 2$ Å, $a_c = 4$ Å.

Results and conclusions. – In fig. 1, we present the effective colloidal charge as a function of concentration of trivalent counterions ($\alpha = 3$) for a suspension containing particles with $Z = 4000$ and $a = 300$ Å and various concentrations of monovalent salt. It should be noticed that the charge reversal occurs only for sufficiently small concentrations of monovalent salt.

The overcharging found in fig. 1 is a consequence of strong positional correlations between the condensed counterions. We can quantify the strength of electrostatic correlations at the isoelectric point (when the number of condensed counterions completely neutralizes the colloidal charge) by the plasma parameter [6]

$$\Gamma_{iso} = \frac{\alpha^2 q^2}{\epsilon d k_B T}, \tag{16}$$

where d is the average separation between $n = Z/\alpha$ condensed α-ions. Furthermore, since $n\pi(d/2)^2 = 4\pi a^2$, the coupling strength becomes

$$\Gamma_{iso} = \alpha^{3/2}\lambda_B \frac{\sqrt{Z}}{4a} = \frac{1}{2}\alpha^{3/2}\lambda_B\sqrt{\pi\sigma}, \tag{17}$$

where $\sigma = Z/4\pi a^2$ is the colloidal surface charge density. Figure 2 shows the effective colloidal charge as a function of concentration of trivalent ions for colloids with $Z = 4000$ and
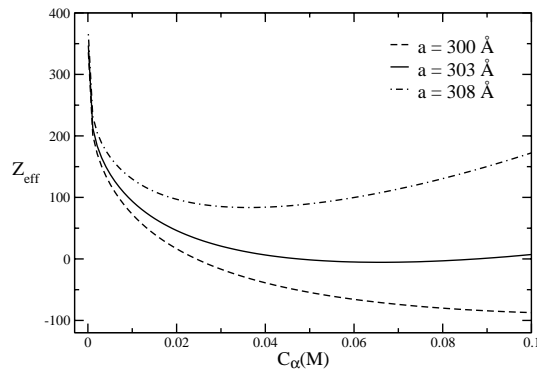

Fig. 2 – The effective charge as a function of concentration of trivalent ions ($\alpha = 3$) for a suspension of particles with $Z = 4000$. The curves correspond to different values of a with $\lambda_B = 7.2$, $\delta = 2$ Å, $C = 0.003M$ Å, $a_c = 4$ Å.
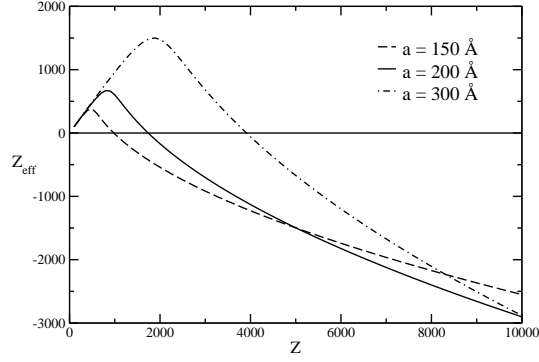
Fig. 3 – The effective colloidal charge as a function of bare charge Z, for a suspension containing monovalent salt at concentration $C = 0.002M$ and trivalent salt at $C_3 = 0.05M$. The curves correspond to different values of a with $\lambda_B = 7.2$, $\delta = 2\,\text{Å}$ and $a_c = 4\,\text{Å}$.

various sizes. As expected, overcharging is possible only for sufficiently large colloidal surface charge density [29]. For trivalent ions of $a_c = 4\,\text{Å}$, we find that the charge reversal can take place *if and only if* $\Gamma_{iso} > 1.95$ or, equivalently, when the colloidal surface charge density is $\sigma > \sigma_{cr} \equiv 0.18/\lambda_B^2$. This is a *necessary* but *not sufficient* condition. For colloids with Z and a satisfying $\sigma > \sigma_{cr}$, the overcharging will occur only if the monovalent salt concentration is below the critical threshold $C < C_{cr}(Z, a)$. The critical salt concentration $C_{cr}(Z, a)$ is a function of *both* colloidal charge and size, and is not simply a function of σ. Figure 3 shows the effective colloidal charge as a function of the bare charge. We note that the effective charge does not saturate, as predicted by the PB theory [12], but instead reaches a maximum and then falls off sharply eventually going through the isoelectric point.

Finally, the dependence of Z_{eff} on the amount of monovalent salt is presented in fig. 4. We see that for $\sigma < \sigma_{cr}$ (in the absence of overcharging), screening of electrostatic interactions by $1:1$ electrolyte results in a diminished counterion-colloid association. On the other hand if, in the absence of $1:1$ electrolyte the colloid-counterion complex is already overcharged, addition of a small amount of monovalent salt results in a slight increase of the charge reversal, see the inset of fig. 4. A further rise of the concentration of $1:1$ electrolyte, however, leads to a decline of the overcharging. This behavior, also observed experimentally [4], is different from
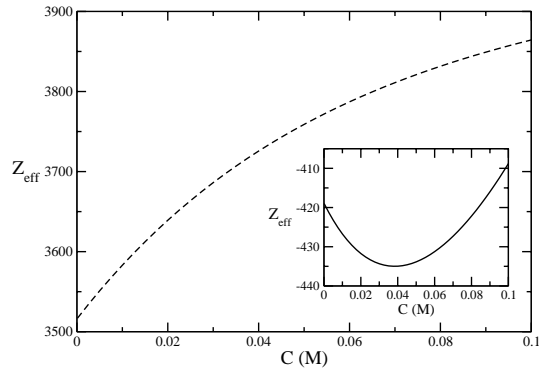

Fig. 4 – The effective charge of colloidal particle with $Z = 4000$ and $a = 500\,\text{Å}$ ($\sigma < \sigma_{cr}$) at $C_3 = 0.04M$, as a function of concentration of monovalent salt C. The inset shows variation of Z_{eff} for colloid with $Z = 4000$ and $a = 200\,\text{Å}$ ($\sigma > \sigma_{cr}$) at $C_3 = 0.01M$, $\lambda_B = 7.2$, $\delta = 2\,\text{Å}$, $a_c = 4\,\text{Å}$.

the predictions of other theories. For example, Nguyen *et al.* find that addition of large concentrations of monovalent electrolyte should lead to a giant charge reversal resulting from the screening of the electrostatic self-energy of the overcharged polyion-counterion complex [8]. Contrary to this, we see that for large salt concentrations the multivalent ions prefer to be solvated in the bulk electrolyte instead of the colloidal surface. In the bulk they gain favorable correlational energy from the interactions with the oppositely charged coions which are depleted from the colloidal surface [18,19]. Thus, in order for a theory to consistently predict the conditions of colloidal overcharging, it must first account well for the thermodynamics of the bulk electrolyte solution.

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