Effective charge versus bare charge: an analytical estimate for colloids in the infinite dilution limit

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We propose an analytical approximation for the dependence of the effective charge on the bare charge for spherical and cylindrical macro-ions as a function of the size of the colloid and salt content, for the situation of a unique colloid immersed in a sea of electrolyte (where the definition of an effective charge is non ambiguous). Our approach is based on the Poisson-Boltzmann (PB) mean-field theory. Mathematically speaking, our estimate is asymptotically exact in the limit $\kappa a \gg 1$, where $a$ is the radius of the colloid and $\kappa$ the inverse screening length. In practice, a careful comparison with effective charges parameters obtained by numerically solving the full non-linear PB theory proves that it is good down to $\kappa a \sim 1$. This is precisely the limit appropriate to treat colloidal suspensions. A particular emphasis is put on the range of parameters suitable to describe both single and double strand DNA molecules under physiological conditions.

I. INTRODUCTION

We know from the work of Debye and Hückel that elementary charges, $e$, immersed in an electrolyte solution interact through a screened Coulomb pair potential: $V(r) \sim e^2 \exp(-\kappa r)/r$, where the screening length, $\kappa^{-1}$, characterizes the thermodynamics of the ionic species. For highly charged macro-ions (bare charge $Z_{\text{bare}}e$, where $Z_{\text{bare}} \gg 1$), the strong electrostatic coupling between the macro-ion and the micro-ions results in an additional screening so that the actual Coulomb pair potential still writes $V(r) \sim Z_{\text{eff}}^2 e^2 \exp(-\kappa' r)/r$ at large distances (with possibly $\kappa' \neq \kappa$ [1]), but now $Z_{\text{eff}}$ is an effective (also called ”apparent”, or ”renormalized”) charge parameter, much smaller in absolute value than $Z_{\text{bare}}$. The idea is that the charged colloid retains captive a fraction of the oppositely charged micro-ions in its immediate vicinity, and therefore apparently behaves as a new entity of lower electric charge.

Because the effective charge is the relevant parameter to compute the electrostatics of the system at large inter-particle distances, the concept of charge renormalization plays a central role in the thermodynamics of highly charged colloidal suspensions. Several reviews have appeared recently which discuss this notion [1–4], see also [5]. In the colloid science field this concept has been introduced by Alexander et al. [6] in the context of the Poisson-Boltzmann (PB) cell model, but had been widely accepted since the fifties in the field of linear polyelectrolytes [7,8]. For an isolated macro-ion on the other hand, the definition of an effective charge from the far field potential created in an electrolyte is unambiguous [2,9–11].

In general the effective charge depends on the geometry of the particle, the concentration of macro-ions and the thermodynamics of the electrolyte. Within the non-linear Poisson-Boltzmann (PB) mean-field theory: $Z_{\text{eff}} \simeq Z_{\text{bare}}$ for low values of $Z_{\text{bare}}$, and $Z_{\text{eff}}$ saturates to a constant, $Z_{\text{sat}}$, when $Z_{\text{bare}} \to \infty$. Many studies have focused on finding an approximation for $Z_{\text{sat}}$. In particular, in the limiting case of infinite dilution, we have proposed a matching procedure for the electrostatic potential such that $Z_{\text{eff}}$ may be estimated at the level of the linearized PB theory only (the non linearity of the problem occurring only through an effective boundary condition, see [9,10]). This approach may be generalized to account for concentrated suspensions. In contrast, much less is known about the functional dependence of $Z_{\text{eff}}$ on $Z_{\text{bare}}$. This is because finding the exact analytical dependence $Z_{\text{eff}}(Z_{\text{bare}})$ involves solving the full non-linear PB system of equations, which is out of reach in general.

Here, we propose an analytical approximation for the dependence of $Z_{\text{eff}}$ on $Z_{\text{bare}}$ for spherical and cylindrical macro-ions as a function of the size of the colloid and the salt content. We restrict ourselves to the infinite dilution limit where an exact analytical representation of the electrostatic potential, $\psi$, solution of the non-linear PB theory has been recently obtained [12]. Our estimate is asymptotically exact in the limiting case when $\kappa a \gg 1$. In practice however, it is an accurate approximation of the exact solution in the whole colloidal domain: $\kappa a \gtrsim 1$, where $a$ is the typical size of the colloid.
II. EFFECTIVE CHARGE DEPENDENCE

We consider the situation of an isolated macro-ion of given bare charge in a symmetrical, mono-valent electrolyte of bulk density $n_0$ (no confinement). The solvent is considered as a medium of uniform dielectric (CGS) permittivity $\varepsilon$. Within Poisson-Boltzmann theory, micro-ions/micro-ions correlations are discarded and the potential of mean force identified with the electrostatic potential $\psi$. Accordingly, the reduced electrostatic potential ($\phi = e\psi/kT$), assumed to vanish far from macro-ion, obeys the equation

$$\nabla^2 \phi = \kappa^2 \sinh \phi,$$

where the screening factor $\kappa$ is defined as $\kappa^2 = 8\pi \ell_B n_0$ and the Bjerrum length quantifies the strength of electrostatic coupling: $\ell_B = e^2/(e kT)$ ($kT$ is the thermal energy). Far away from the colloid, $\phi$ obeys the linearized PB (LPB) equation $\nabla^2 \phi = \kappa^2 \phi$. The far field within PB is thus the same as that found within LPB, provided the charge is suitably renormalized in this latter case. In particular, for infinite rods (radius $a$, bare line charge density $\lambda_{\text{bare}}e$), we have

$$\phi(r) \sim A_{00} \left( \frac{2}{\pi} \right)^{1/2} K_0(\kappa r)$$

where $K_0$ is the zero order modified Bessel function (the symbol $\sim$ stands for “asymptotically equal”). In Eq. (2), the prefactor $A_{00}$ is a function of both the thermodynamics of the electrolyte and the characteristics of the macro-ion: $A_{00}(\lambda_{\text{bare}}, \kappa a)$. With these notations, the effective line charge density, $\lambda_{\text{eff}}$, is such that

$$2\ell_B \lambda_{\text{eff}} = A_{00} \left( \frac{2}{\pi} \right)^{1/2} \kappa a K_1(\kappa a)$$

where $K_1$ is the first order modified Bessel function.

Using the method of multiple scales, Shkel et al were able to propose an approximate expression for $A_{00}(\lambda_{\text{bare}}, \kappa a)$ up to the second order in $(\kappa a)^{-1} \ll 1$ [12]. This result can be translated into an approximate form for the functional dependence of $\lambda_{\text{eff}}(\lambda_{\text{bare}})$ through Eq. (3). After some algebra, we find, again for cylinders and up to order $O(1/(\kappa a))$

$$\lambda_{\text{eff}} \ell_B = 2\kappa a t_\lambda + \frac{1}{2} \left( 5 - \frac{t_\lambda^4 + 3}{t_\lambda^2 + 1} \right) t_\lambda$$

where

$$t_\lambda = T \left( \frac{\lambda_{\text{bare}} \ell_B}{\kappa a + 1/2} \right)$$

and the function $T$, also useful in spherical geometry (see below), is defined as

$$T(x) = \sqrt{\frac{1 + x^2}{x}} - 1$$

In the limit of diverging bare charge $\lambda_{\text{bare}} \to \infty$, $t_\lambda \to 1$ so that the saturation value for the line charge density reads

$$\lambda_{\text{sat}} \ell_B = 2\kappa a + \frac{3}{2} + O \left( \frac{1}{\kappa a} \right).$$

In the opposite limit where $\lambda_{\text{bare}} \to 0$, Eq. (4) yields $\lambda_{\text{eff}} = \lambda_{\text{bare}}$ as expected.

Similarly, for spheres (radius $a$, bare charge $Z_{\text{bare}}e$) we find that

$$\frac{Z_{\text{eff}} \ell_B}{a} = 4\kappa a t_z + 2 \left( 5 - \frac{t_z^4 + 3}{t_z^2 + 1} \right) t_z$$

where now

$$t_z = T \left( \frac{Z_{\text{bare}} \ell_B/a}{2\kappa a + 2} \right)$$
and the function $T(x)$ is still defined by Eq. (6). The corresponding saturation value for the effective charge is

$$\frac{\ell_B}{a} z_{\text{sat}} = 4\kappa a + 6 + O\left(\frac{1}{\kappa a}\right),$$

while for low bare charges, we have

$$\lim_{z_{\text{bare}} \to 0} \frac{Z_{\text{eff}}}{Z_{\text{bare}}} = 1.$$

Expressions (4)-(7) [resp. Eq. (8)-(10)] provide the first analytical estimate of the functional dependence of the effective charge on the bare charge for cylindrical (resp. spherical) macro-ions in an electrolyte solution. They are the exact expansions of the correct result in the limit of large $\kappa a$. In practice however, they are accurate as soon as $\kappa a > 1$, as we now show.

We compare on Figs. 1 and 2 the results for the effective charge against the bare charge obtained using: a) our estimate and b) the exact solution found by solving the full numerical PB problem. The results are displayed for two different values of the ionic strength of the solution. The agreement is seen to be excellent for $\kappa a > \sim 5$, and reasonable down to $\kappa a \approx 1$ (see also below).

III. CYLINDRICAL GEOMETRY AND DNA

Because DNA (a rod-like polyelectrolyte in first approximation) is of paramount importance in biology, the cylindrical case deserves a special attention. For typical parameters of double strand DNA ($a \approx 10 \text{ Å}$, $\lambda_{\text{bare}}\ell_B \approx 4.2$), the domain $\kappa a \geq 1$, where we expect our estimate to be good enough, reads $n_0 \geq 0.1 \text{ M}$ for monovalent symmetrical electrolyte. This is experimentally relevant. Indeed, physiological conditions are found for $n_0 = 0.15 \text{ M}$ ($\kappa^{-1} = 8 \text{ Å}$). For simple strand DNA ($a \approx 7 \text{ Å}$, $\lambda_{\text{bare}}\ell_B \approx 2.1$) the condition $\kappa a \geq 1$ writes $n_0 \geq 0.2 \text{ M}$. Fig. 3 displays the effective charge, $\lambda_{\text{eff}}\ell_B$, against $\kappa a$ for $\lambda_{\text{bare}}\ell_B = 2.1$, and $\lambda_{\text{bare}}\ell_B = 4.2$. We observe that our estimate remains decent down to $\kappa a = 0.5$, where the error is of the order of 7% (see also Tables 1 and 2).

Note that, for DNA in typical experimental conditions, the parameters are such that we find ourselves in the crossover regime where both the linear approximation ($\lambda_{\text{eff}} \approx \lambda_{\text{bare}}$) and the asymptotic approximation ($\lambda_{\text{eff}} \approx \lambda_{\text{sat}}^{\text{eff}}$) fail to be accurate, as shown in Tables 1 and 2. In other words, both $\lambda_{\text{bare}}$ and $\lambda_{\text{sat}}^{\text{eff}}$ provide a rather poor approximation for $\lambda_{\text{eff}}$. This justifies $a$ posteriori our effort to find a good approximation for the full functional dependence of $\lambda_{\text{eff}}(\lambda_{\text{bare}})$.

IV. CONCLUDING REMARKS

In this contribution, we have proposed an analytical approximation for the dependence of the effective charge on the bare charge for spherical and cylindrical macro-ions as a function of the size of the colloid and salt content. Mathematically speaking, our estimate is asymptotically exact in the limit $\kappa a \gg 1$. In practice, a careful comparison with effective charges parameters obtained by numerically solving the full non-linear PB theory proves that it is good down to $\kappa a \geq 1$ (where $a$ is the radius macro-ion). This is precisely the relevant range of parameters for colloidal suspensions.

An important example considered in some detail is the cylindrical geometry. This is because the infinitely long charged rod provides a simple model for DNA. While the simple asymptotical approximations fail for DNA in typical physiological conditions, we provide an estimate for the effective charge line density, which compares well with the numerical results.

We have performed the analysis at the level of the mean-field Poisson-Boltzmann theory. In spite of its limitations, this picture is excellent for all existing macro-ions in water at room temperature, when only monovalent micro-ions are present in the electrolyte (see e.g. ref [4] for an estimation of a relevant coupling constant quantifying the importance of the micro-ionic correlations). It may also hold for multivalent counter-ions, provided the surface charge density of the macro-ion is not too large. In general, for a given total charge of the macro-ion, micro-ionic correlation become irrelevant in the asymptotic limit where $a \gg \ell_B$ [13,14].

FIG. 1. Rescaled effective charge, $Z_{\text{eff}} l_B/a$, versus rescaled bare charge, $Z_{\text{bare}} l_B/a$, for isolated spherical macro-ions in a symmetrical, monovalent electrolyte solution (for $\kappa a = 5$, where $\kappa^{-1}$ is the Debye-Hückel screening length of the electrolyte, and $a$ is the sphere radius). The solid line is the analytical estimate of $Z_{\text{eff}}$ [see Eq. (8)], whereas the open circles are the exact values of $Z_{\text{eff}}$ found by numerically solving the full non-linear PB problem. The dashed line has a slope of unity to emphasize the initial linear behaviour. The inset shows $Z_{\text{eff}}(Z_{\text{bare}})$ for $\kappa a = 1$. 

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FIG. 2. Effective line charge density, $\lambda_{\text{eff}}$, versus bare line charge density, $\lambda_{\text{bare}}$, for an isolated, infinitely long cylindrical macro-ion ($\kappa a = 5$). The solid line is the analytical estimate of $\lambda_{\text{eff}}$ [see Eq. (4)], whereas the open circles are the exact values of $\lambda_{\text{eff}}$ found by numerically solving the non-linear PB theory (the dashed line has a of slope unity). The inset shows $\lambda_{\text{eff}}(\lambda_{\text{bare}})$ for $\kappa a = 2$.

FIG. 3. Effective line charge density, $\lambda_{\text{eff}}\ell_B$, versus $\kappa a$ for isolated, infinitely long cylindrical macro-ions of bare charge $\lambda_{\text{bare}}\ell_B = 2.1$ (lower sets) and $\lambda_{\text{bare}}\ell_B = 4.2$ (upper sets). The solid line is the analytical estimate of $\lambda_{\text{eff}}$ [see Eq. (4)], whereas the open circles are the exact values of $\lambda_{\text{eff}}$ found by numerically solving the full non-linear PB theory. In the formal limit $\kappa a \to \infty$, these two curves would saturate to 2.1 and 4.2.
Table 1: Comparison of the effective charge and the saturation value for single strand DNA at physiological conditions as found a) by our analytical estimate, b) numerically solving PB theory.

| $\lambda_{bare} \ell_B$ | $\kappa a$ | $\lambda_{eff} \ell_B$ [Eq.(4)] | $\lambda_{eff} \ell_B$ (num) | $\lambda_{eff}^{sat} \ell_B$ [Eq.(7)] | $\lambda_{eff}^{sat} \ell_B$ (num) |
|-------------------------|------------|-------------------------------|-----------------------------|-----------------------------------|-----------------------------------|
| 2.1                     | 0.25       | 1.35                          | 1.20                        | 2.00                              | 1.61                              |
| 2.1                     | 0.5        | 1.50                          | 1.40                        | 2.50                              | 2.20                              |
| 2.1                     | 1          | 1.69                          | 1.65                        | 3.50                              | 3.27                              |
| 2.1                     | 1.5        | 1.81                          | 1.78                        | 4.50                              | 4.32                              |
| 2.1                     | 2          | 1.88                          | 1.87                        | 5.50                              | 5.35                              |

Table 2: Same as Table 1 for double strand DNA.

| $\lambda_{bare} \ell_B$ | $\kappa a$ | $\lambda_{eff} \ell_B$ [Eq.(4)] | $\lambda_{eff} \ell_B$ (num) | $\lambda_{eff}^{sat} \ell_B$ [Eq.(7)] | $\lambda_{eff}^{sat} \ell_B$ (num) |
|-------------------------|------------|-------------------------------|-----------------------------|-----------------------------------|-----------------------------------|
| 4.2                     | 0.25       | 1.65                          | 1.41                        | 2.00                              | 1.61                              |
| 4.2                     | 0.5        | 1.94                          | 1.78                        | 2.50                              | 2.20                              |
| 4.2                     | 1          | 2.40                          | 2.31                        | 3.50                              | 3.27                              |
| 4.2                     | 1.5        | 2.76                          | 2.71                        | 4.50                              | 4.32                              |
| 4.2                     | 2          | 3.02                          | 2.99                        | 5.50                              | 5.35                              |