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

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Abstract
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 κ is the inverse screening length. In practice, a careful comparison with effective charge parameters, obtained by numerically solving the full nonlinear PB theory, proves that our estimate 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.

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1. 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, κ^{-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_{eff} is an effective (also called 'apparent' or 'renormalized') charge parameter, much smaller in absolute value than Z_{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 it has been widely accepted since the 1950s 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 nonlinear PB mean-field theory, $Z_{\text{eff}} \simeq Z_{\text{bare}}$ for low values of Z_{bare}, and Z_{eff} saturates to a constant, $Z_{\text{eff}}^{\text{sat}}$, when $Z_{\text{bare}} \to \infty$. Many studies have focused on finding an approximation for $Z_{\text{eff}}^{\text{sat}}$. In particular, in the limiting case of infinite dilution, we have proposed a matching procedure for the electrostatic potential such that $Z_{\text{eff}}^{\text{sat}}$ may be estimated at the level of the linearized PB (LPB) theory only (the nonlinearity 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_{eff} on Z_{bare}. This is because finding the exact analytical dependence $Z_{\text{eff}}(Z_{\text{bare}})$ involves solving the full nonlinear PB system of equations, which is generally out of reach.

Here, we propose an analytical approximation for the dependence of Z_{eff} on Z_{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, ψ, solution of the nonlinear 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.

2. Effective charge dependence

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

$$\nabla^2 \phi = \kappa^2 \sinh \phi \tag{1}$$

where the screening factor κ is defined as $\kappa^2 = 8\pi \ell_B n_0$ and the Bjerrum length quantifies the strength of electrostatic coupling: $\ell_B = e^2/(\epsilon kT)$ (kT is the thermal energy). Far away from the colloid, ϕ obeys the LPB equation $\nabla^2 \phi = \kappa^2 \phi$. The far field within PB theory is thus the same as that found within LPB theory, 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

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

where K_0 is the zeroth-order modified Bessel function (the symbol $\sim$ denotes 'asymptotically equal'). In equation (2), the pre-factor 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, λ_{eff}, is such that

$$2\ell_B \lambda_{\text{eff}} = A_{00} \left(\frac{2}{\pi}\right)^{1/2} \kappa a \, K_1(\kappa a) \tag{3}$$

where K_1 is the first-order modified Bessel function.

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

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

where

$$t_\lambda = T \left(\frac{\lambda_{\text{bare}} \ell_B}{\kappa a + 1/2}\right) \tag{5}$$

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

$$T(x) = \frac{\sqrt{1 + x^2} - 1}{x}. \tag{6}$$

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

$$\lambda_{\text{eff}}^{\text{sat}} \ell_B = 2\kappa a + \frac{3}{2} + \mathcal{O}\left(\frac{1}{\kappa a}\right). \tag{7}$$

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

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

$$Z_{\text{eff}} \frac{\ell_B}{a} = 4\kappa a \, t_z + 2 \left(5 - \frac{t_z^4 + 3}{t_z^2 + 1}\right) t_z \tag{8}$$

where now

$$t_z = T \left(\frac{Z_{\text{bare}} \ell_B / a}{2\kappa a + 2}\right) \tag{9}$$

and the function $T(x)$ is still defined by equation (6). The corresponding saturation value for the effective charge is

$$\frac{\ell_B}{a} Z_{\text{eff}}^{\text{sat}} = 4\kappa a + 6 + \mathcal{O}\left(\frac{1}{\kappa a}\right) \tag{10}$$

while for low bare charges, we have

$$\lim_{Z_{\text{bare}} \to 0} \frac{Z_{\text{eff}}}{Z_{\text{bare}}} = 1. \tag{11}$$

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

In figures 1 and 2 we compare 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 $\kappa a \gtrsim 5$, and reasonable down to $\kappa a \approx 1$ (see also below).
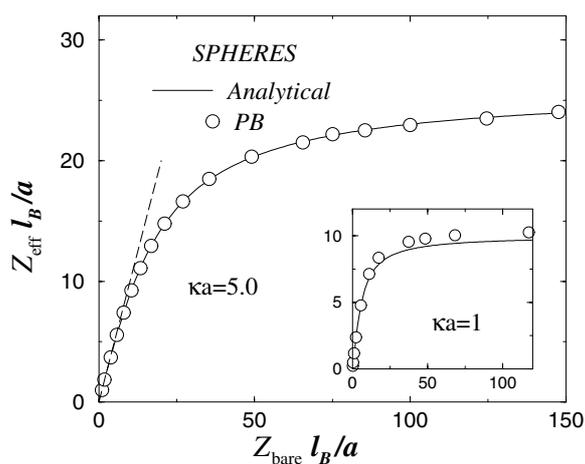
Figure 1. Rescaled effective charge, $Z_{\text{eff}}\ell_B/a$, versus rescaled bare charge, $Z_{\text{bare}}\ell_B/a$, for isolated spherical macro-ions in a symmetrical, monovalent electrolyte solution (for $\kappa a = 5$, where κ^{-1} is the Debye–Hückel screening length of the electrolyte, and a is the sphere radius). The solid curve is the analytical estimate of Z_{eff} (see equation (8)), whereas the open circles are the exact values of Z_{eff} found by numerically solving the full nonlinear PB problem. The dashed curve has a slope of unity to emphasize the initial linear behaviour. The inset shows $Z_{\text{eff}}(Z_{\text{bare}})$ for $\kappa a = 1$.
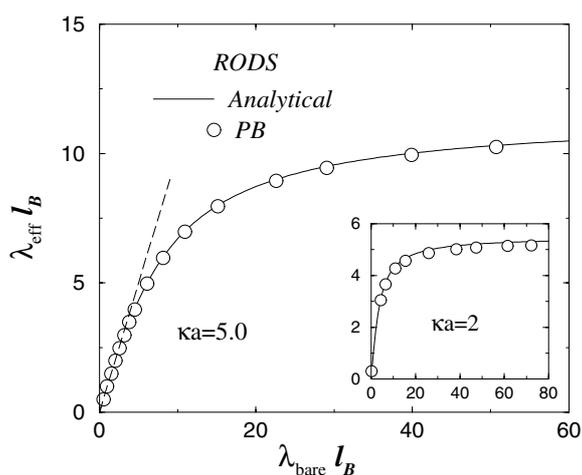

Figure 2. Effective line charge density, λ_{eff}, versus bare line charge density, λ_{bare}, for an isolated, infinitely long cylindrical macro-ion ($\kappa a = 5$). The solid curve is the analytical estimate of λ_{eff} (see equation (4)), whereas the open circles are the exact values of λ_{eff} found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

3. Cylindrical geometry and DNA

Because DNA (a rod-like polyelectrolyte in first approximation) is of paramount importance in biology, the cylindrical case deserves special attention. For typical parameters of double strand DNA ($a \cong 10$ Å, $\lambda_{\text{bare}}\ell_B \cong 4.2$), the domain $\kappa a \geqslant 1$, where we expect our estimate to be good enough, reads $n_0 \geqslant 0.1\ M$ for a monovalent symmetrical electrolyte. This is experimentally
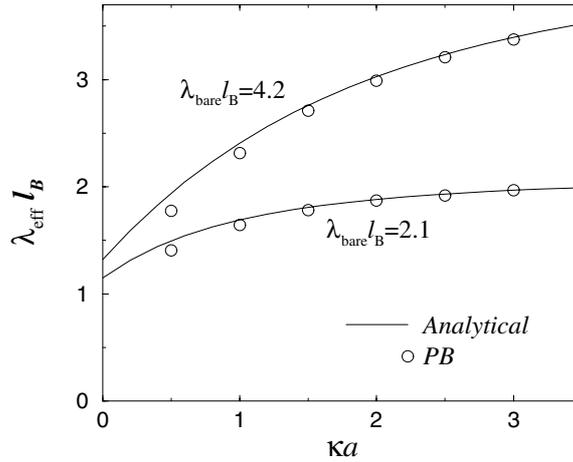
Figure 3. Effective line charge density, $\lambda_{\text{eff}}\ell_B$, versus κa for isolated, infinitely long cylindrical macro-ions of bare charge $\lambda_{\text{bare}}\ell_B = 2.1$ (lower sets) and $\lambda_{\text{bare}}\ell_B = 4.2$ (upper sets). The solid curve is the analytical estimate of λ_{eff} (see equation (4)), whereas the open circles are the exact values of λ_{eff} found by numerically solving the full nonlinear 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 and (b) by numerically solving the PB theory.

$\lambda_{\text{bare}}\ell_B$	κa	$\lambda_{\text{eff}}\ell_B$ (equation (4))	$\lambda_{\text{eff}}\ell_B$ (num)	$\lambda_{\text{eff}}^{\text{sat}}\ell_B$ (equation (7))	$\lambda_{\text{eff}}^{\text{sat}}\ell_B$ (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.

$\lambda_{\text{bare}}\ell_B$	κa	$\lambda_{\text{eff}}\ell_B$ (equation (4))	$\lambda_{\text{eff}}\ell_B$ (num)	$\lambda_{\text{eff}}^{\text{sat}}\ell_B$ (equation (7))	$\lambda_{\text{eff}}^{\text{sat}}\ell_B$ (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

relevant. Indeed, physiological conditions are found for $n_0 = 0.15\,M$ ($\kappa^{-1} = 8$ Å). For simple strand DNA ($a \cong 7$Å, $\lambda_{\text{bare}}\ell_B \cong 2.1$) the condition $\kappa a \geqslant 1$ is written $n_0 \geqslant 0.2\,M$. Figure 3 displays the effective charge, $\lambda_{\text{eff}}\ell_B$, against κa for $\lambda_{\text{bare}}\ell_B = 2.1$, and $\lambda_{\text{bare}}\ell_B = 4.2$. We observe that our estimate remains good 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 ($\lambda_{\text{eff}} \cong \lambda_{\text{bare}}$) and the asymptotic approximation $\left(\lambda_{\text{eff}} \cong \lambda_{\text{eff}}^{\text{sat}}\right)$ fail to be accurate, as shown in tables 1 and 2. In other words, both λ_{bare} and $\lambda_{\text{eff}}^{\text{sat}}$ provide a rather poor approximation for λ_{eff}. This justifies *a posteriori* our effort to find a good approximation for the full functional dependence of $\lambda_{\text{eff}}(\lambda_{\text{bare}})$.

4. Concluding remarks

In this paper, 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 charge parameters obtained by numerically solving the full nonlinear PB theory proves that our estimate is good down to $\kappa a \gtrsim 1$ (where a is the radius of the 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 PB 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, for example, [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].

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