Charge Renormalization of Cylinders and Spheres: Ion Size Effects

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The effect of counterion size on the degree of counterion condensation onto a cylindrical macroion and a spherical one is studied theoretically within a modified Poisson–Boltzmann approach. We find that excluded volume interactions reduce the degree of condensation. Using a simple variational free energy we show that this reduction can be attributed to an effective increase in the macroion size due to the contribution of the condensed counterions. We also find that for a charged cylinder, the reduction in charge renormalization vanishes at infinite dilution because of the extended nature of the condensed layer. In contrast, excluded volume interactions can reduce the degree of charge renormalization of a sphere even at high dilutions.

I. INTRODUCTION

The Poisson–Boltzmann (PB) equation (see, e.g., Refs. [1,2]) is the main tool for studying the behavior of ionic solutions. Its main advantages are its simplicity, which allows for analytical solutions in simple cases, and its surprisingly good agreement with experiments. In addition, its linearized form provides a simple description of screening effects in terms of the Debye–Hückel screening length.

An important implementation of the PB approach is the theoretical study of charged biopolymers, from the pioneering works of Katchalsky and Oosawa [3,4] to present day studies [2]. Since most biopolymers are sufficiently rigid and can be treated locally as charged cylinders, much effort was devoted over the years to studying the PB equation in a cylindrical geometry [3–9]. Perhaps the most important result that came out of these efforts was that mobile ions tend to condense strongly onto highly charged cylinders and reduce their apparent charge by a considerable amount [3,4,10–12]. The phenomena is often referred to as Manning condensation. The effect is indeed observed experimentally in DNA solutions although the quantitative features differ from the theoretical predictions [13,14]. An analogous phenomena of charge renormalization characterizes highly charged spheres immersed in ionic solutions [15–22,12].

Despite its success in describing a wide range of systems, the PB approach has certain limitations. First, the PB approach is a mean field approach in nature and as such does not include the effect of correlations and fluctuations [2,23]. These can lead to attractive interactions between equally charged surfaces in the presence of multivalent counterions. Second, the PB equation is purely electrostatic in nature and does not include non-electrostatic interactions such as short-range attractions or excluded volume repulsions. The latter can lead to the saturation of counterion densities near highly charged surfaces as was demonstrated recently by Cuvillier et al. [24]. This saturation and its consequences in the context of charge renormalization are the focus of this paper.

The simplest way of including the finite size of the ions in the Poisson–Boltzmann approach is to define a narrow layer close to the surface as impenetrable to the ions. This layer is usually referred to as the Stern layer [25–29] and its width is equal to the ion radius. Outside this layer the regular Poisson–Boltzmann equation is implemented. Here we use a modified Poisson–Boltzmann (MPB) approach [30–37] where the excluded volume interaction is incorporated into the PB equation. This approach allows the width of the saturated layer to depend on the surface charge and extend beyond a a single counterion layer. Ion distributions are then extracted from numerical solutions of the MPB equations and compared with solutions of the bare PB equation. One can also extract global properties such as the apparent charge of a cylindrical or spherical macroion immersed in an ionic solution. The results of the numerical calculation are then compared with simple variational approaches which provide additional insight on the behavior of the system.

Our main finding can be summarized as follows: (i) due to their repulsive nature, excluded volume interactions reduce the degree of counterion condensations. (ii) This reduction can be attributed to an effective increase in the macroion size due to the excluded volume of condensed counterions. (iii) Due to the extended nature of the condensed layer surrounding a cylindrical macroion, the effect of excluded volume interaction on the Manning condensation.

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II. THE MODIFIED POISSON–BOLTZMANN EQUATION

Consider an aqueous solution of dielectric constant $\varepsilon$ containing a symmetric electrolyte where the mobile ions are of valency $z$ and dimension $a$. The free energy of the system $F = U_{el} - TS$ can be expressed in terms of the local electrostatic potential $\psi(r)$ and the ion concentrations $c^\pm(r)$. The electrostatic contribution is

$$U_{el} = \int dr \left[ -\frac{\varepsilon}{8\pi} |\nabla\psi|^2 + zec^+\psi - zec^-\psi - \mu_+c^+ - \mu_-c^- \right]$$

(1)

The first term is the self energy of the electric field and the next two terms are the electrostatic energies of the ions. The last two terms couple the system to a bulk reservoir, where $\mu_\pm$ are the chemical potentials of the ions.

The entropic contribution is

$$-TS = \frac{k_BT}{a^3} \int dr \left[ c^+a^3 \ln(c^+a^3) + c^-a^3 \ln(c^-a^3) + (1 - c^+a^3 - c^-a^3) \ln(1 - c^+a^3 - c^-a^3) \right]$$

(2)

The first two terms are the translational entropies of the positive and negative ions, whereas the last term is the entropy of the solvent molecules. It is this last term that is responsible to the modification of the PB equation.

Minimizing the total free energy with respect to $\psi$ and $c^\pm$ yields the Poisson equation

$$\nabla^2 \psi = -\frac{4\pi}{\varepsilon} \left[ zec^+(r) - zec^-(r) \right]$$

(3)

where the ion concentrations are given by

$$c^\pm = \frac{c_0 e^{\pm z\beta\psi}}{1 - \phi_0 + \phi_0 \cosh(\beta z\psi)}$$

(4)

where $\phi_0 = 2c_0a^3$ denotes the bulk volume fraction of the small ions. Combining the above two expressions yields the modified PB equation.

In the presence of a large positively charged macroion and small mobile counterions (no added salt and hence no positive co-ions) a similar derivation leads to

$$\nabla^2 \psi = \frac{4\pi zec_0}{\varepsilon} \frac{e^{z\beta\psi}}{1 - \phi_0 + \phi_0 e^{z\beta\psi}}$$

(5)

where $\phi_0 = a^3c_0$ is the volume fraction at an arbitrary reference point $r_0$ where $\psi(r_0) = 0$ and $c(r_0) = c_0$. Note that the reference point of zero potential does not lie at infinity. The salt-free system contains only the counterions which neutralize the surface charges. Hence the concentration of counterions vanishes far away from the macroion. Since $c(r) = c_0 \exp(z\beta\psi)$ it follows that in this case potential must diverge to $-\infty$. Physically this divergence is not a problem because both the electric field and counterion density vanish.

A more formal derivation which relies on a lattice gas approach is presented elsewhere [33, 34]. Similar expressions were suggested earlier by Eigen [30] and later by Kralj-Iglić and Iglić [31, 37]. Analogous ionic distributions can be also obtained for solid electrolytes [38, 39].

This approach deviates significantly from the original PB equation for large electrostatic potentials $|\beta e\psi| \gg 1$. In particular, the ionic concentration is unbound in the standard PB approach, whereas here it is always bound by $1/a^3$ (“close packing”) as can be seen from eq. 5. This effect is pronounced when the macroion is highly charged.
III. ADSORPTION TO A CHARGED CYLINDER AND THE MANNING CONDENSATION

A. Introduction

We now proceed to study the case of a positively charged cylinder in the presence of an ionic solution. The model system is shown schematically in Fig. 1. The cylinder is assumed to be straight and infinitely long, carrying a uniform charge density per unit length $e/l_q > 0$. This model system has been used to describe the electrostatics of rigid polyelectrolytes such as DNA molecules where the persistence length is much larger than the molecular length scales. In the simple cell model [40], an ionic solution containing a finite concentration of charged cylinders is modeled by a single cylinder of radius $r_s$ inside a cylindrical cell of radius $R$. Thus, the volume fraction of charged cylinders is $\phi = r_s^2/R^2$ and $2R$ is the average inter-chain distance (center to center). The counterions are confined to the same cell and due to charge neutrality, the electric field must vanish at the cell boundary.

In the absence of salt the Poisson–Boltzmann equation was solved analytically by Fuoss, Katchalsky and Lifson [3]. Because of its importance to the understanding of the counterion layer structure, the analytical solution will be discussed in detail below. One of the main features of this solution is that at high charge densities the counterion distribution changes and more ions are located close to the surface.

![Schematic view of a charged cylinder in an ionic solution.](image)

**FIG. 1.** Schematic view of a charged cylinder in an ionic solution. The cylinder is uniformly charged with linear charge density $e/l_q$ where $l_q$ is the average separation (along the cylinder axis) between surface charges. The inner cylinder of radius $r_s$ and the outer cylindrical cell of radius $R$ are concentric. The cell contains only counterions of diameter $a$ (no added salt).

Manning [10] has proposed a simple model in which above a critical surface charge density the counterions condense onto the cylinder and reduce its charge density down to this critical value. This phenomenon is called the Manning condensation and it has been quite successful in predicting global properties, such as the osmotic pressure of the counterions [10]. However, as far as the structure of the condensed layer is concerned, this model is an over-simplification and the distinction between “condensed” and “free” ions is quite subtle and should be considered carefully [5,6,8]. Due to the delicate nature of the condensation phenomenon, it is of interest to discuss first in some detail the standard PB formulation for point-like ions ($a \to 0$) and only then proceed by adding excluded volume effects. For clarity, the discussion will be limited to monovalent ions only ($z = 1$).

B. Point-like Ions: The Standard Poisson–Boltzmann Approach

1. Introduction

In the absence of salt and in cylindrical symmetry, the regular PB equation for the reduced potential $y = \beta e\psi$ reads:

$$\nabla^2 y = \frac{d^2 y}{dr^2} + \frac{1}{r} \frac{dy}{dr} = 4\pi l_B c_0 e^y$$

where $r$ is the distance from the cylinder axis and $c_0$ is a reference concentration which only determines the potential reference point. The Bjerrum length $l_B = e^2/\varepsilon k_B T$ is about 7Å for an aqueous solution at room temperature.

The linear charge density along the cylinder, $e/l_q$, corresponds to a surface charge density...
\[ \sigma = \frac{e}{2\pi r_s l_q} \]  

The electrostatic boundary condition at \( r = r_s \) can be written in the form:

\[ \left. \frac{dy}{dr} \right|_{r=r_s} = -\frac{2\xi_0}{r_s} \]  

where \( \xi_0 = l_B / l_q \) is the dimensionless Manning parameter proportional to the charge density on the cylinder. Because of charge neutrality the electric field must vanish at the external radius:

\[ \left. \frac{dy}{dr} \right|_{r=R} = 0 \]  

Onsager [10] was the first to notice that the cylindrical geometry contains an intrinsic irregularity which appears when \( \xi_0 \geq 1 \). This irregularity can be deduced from the following argument: close to the cylinder, at distances smaller than some distance \( \tau \), the Coulomb potential is unscreened and is thus logarithmic in \( r \):

\[ y(r) = -2\xi_0 \ln(r) \quad r_s \leq r \leq \tau \]  

Neglecting any ion–ion interactions, the contributions to the partition function of the nearest counter-ion located at a distance \( r_1 \) from the cylinder axis can be summed for all allowed values \( r_s \leq r_1 \leq \tau \) and is proportional to

\[ \int_{r_s}^{\tau} e^{y(r_1)2\pi r_1} dr_1 = \frac{2\pi}{2 - 2\xi_0} (\tau^2 - 2\xi_0 - r_s^2 - 2\xi_0) \]  

It is clear now that for \( \xi_0 > 1 \), this contribution to the partition function diverges as the inner radius vanishes (\( r_s \to 0 \)). Since the only two length scales in the problem are \( r_s \) and \( R \), the limit \( r_s \to 0 \) is equivalent to the limit \( R \to \infty \), corresponding to infinite dilution of the charged cylinders.

2. The Gouy–Chapman Layer

The opposite limit of a large internal radius \( r_s \) is also of interest since close to surface the effect of curvature is weak and to a good approximation the counterions feel the field of a flat surface. Therefore, it is instructive to discuss briefly the solution of the PB equation near a flat surface carrying a surface charge density \( \sigma \) given by eq. 7.

In a flat geometry the PB equation is (compare to eq. 6):

\[ \nabla^2 y = \frac{d^2 y}{dx^2} = 4\pi l_B e_0 e y \]  

where \( x \) is the distance from the surface. The boundary conditions are

\[ \left. \frac{dy}{dx} \right|_{x=0} = -4\pi l_B \frac{\sigma}{e} \]  

and

\[ y \big|_{x \to \infty} \to -\infty \]  

where the latter boundary condition ensures that the concentration of counterions vanishes at infinity.

The above differential equation can be easily integrated out yielding a logarithmic potential:

\[ y(x) = -2\ln (x + \lambda_{GC}) \]  

where \( \lambda_{GC} = e / 2\pi l_B \sigma \) is the Gouy–Chapman length inversely proportional to the surface charge density [41].

The electric field and the concentration of counterions are (recall that \( y = \beta e \psi \)):

\[ E(x) = -\frac{d\psi}{dx} = \frac{2}{\beta e (x + \lambda_{GC})} \]  

\[ c^-(x) = \frac{1}{2\pi l_B (x + \lambda_{GC})^2} \]
The concentration decays algebraically with the distance. Integrating eq. 17 it can be shown that exactly half of the counterions are in the layer \( x \leq \lambda_{GC} \).

From a more general point of view, the existence of this “confined” layer results from the competition between the Coulomb attraction to the surface and the translational entropy of the ions. In systems with one dimensional symmetry (such as a charged plane) the attraction is, basically, linear in \( x \) and dominates over the entropy which depends only logarithmically on \( x \). In our case, namely, cylindrical (two dimensional) symmetry, the attraction as well as the entropy are logarithmic. The result of this delicate competition depends on the numerical prefactors. At high surface charges we can expect a confined layer to form, while at lower surface charges we can expect the attraction to be too weak for keeping the counterions near the surface.

Since \( \lambda_{GC} \) is the characteristic “width” of the counterion layer in planar geometries, one might expect the curvature of the cylinder to become relevant for \( r_s \gtrsim \lambda_{GC} \). For the charged cylinder defined above (Fig. 1) the Gouy–Chapman length is

\[
\lambda_{GC} = \frac{e}{2\pi l_B \sigma} = \frac{r_s}{\xi_0} \tag{18}
\]

and the two opposite limits can be separated:

- High charge densities, \( \xi_0 \gg 1 \), where the Gouy–Chapman length \( \lambda_{GC} \) is much smaller than the cylinder radius \( r_s \). To leading order, the behavior should resemble that of a flat charged surface.
- Low charge densities, \( \xi_0 \ll 1 \), where the Gouy–Chapman length is larger than the cylinder radius. It is in this limit where the geometric properties of the cylinder become important.

3. The Analytical Solution [3,4]

The analytical solution to eq. 6 has three different forms depending on the boundary conditions eqs. 8, 9:

\[
y(r) = \begin{cases} 
- \ln \left( \frac{\kappa_0^2 \sigma^2}{2 B^2} \sinh^2 \left[ B \ln(r/R) - \tanh^{-1} B \right] \right) & \xi_0 < \xi^* \\
- \ln \left( \frac{\kappa_0^2 \sigma^2}{2} \left[ \ln(r/R) - 1 \right]^2 \right) & \xi_0 = \xi^* \\
- \ln \left( \frac{\kappa_0^2 \sigma^2}{2 B^2} \sin^2 \left[ B \ln(r/R) - \tan^{-1} B \right] \right) & \xi_0 > \xi^*
\end{cases} \tag{19}
\]

where

\[
\xi^* = \frac{\ln(R/r_s)}{1 + \ln(R/r_s)} \tag{20}
\]

\( \kappa_0^2 = 4 \pi l_B c_0 \), and \( B \) is an integration constant. In the limit of infinite dilution, \( \xi^* \to 1 \) as anticipated from the simple arguments presented above. The integration constant \( B \) is negative for \( \xi_0 < \xi^* \), positive for \( \xi_0 > \xi^* \) and zero for \( \xi_0 = \xi^* \). It can be calculated from the following implicit relations:

\[
\xi_0 = \begin{cases} 
1 - B \coth \left[ B \ln(R/r_s) + \tanh^{-1} B \right] & \xi_0 < \xi^* \\
1 - B \cot \left[ B \ln(R/r_s) + \tan^{-1} B \right] & \xi_0 > \xi^*
\end{cases} \tag{21}
\]

The relation between \( \xi_0 \) and \( B \) is plotted in Fig. 2a for several values of the radii ratio \( R/r_s \). The limiting behavior at infinite dilution is indicated as well. Note, that the curves are continuous at the crossover point \( B = 0 \).

Typical solutions for \( y(r) \) are presented in Fig. 2b for various values of the surface charge density: \( \xi_0 = 0.5 \) \((B = -0.48)\), \( \xi_0 = 1 \) \((B = 0.4)\) and \( \xi_0 = 4 \) \((B = 0.75)\). From the profiles plotted as function of \( \ln(r/r_s) \) it is apparent that the potential is almost linear in \( \ln(r/r_s) \) at low charge densities. Only at high charge densities the behavior close to the surface deviates from the linear behavior.
A useful quantity for describing the distribution of counterions is the accumulated charge parameter $\xi(r)$ which measures the total amount of charge inside a virtual cylinder of height $l_B$ and radius $r$. For monovalent negative ions:

$$\xi(r) = \xi_0 - l_B \int_{r_s}^r e^{-r_1} 2\pi r_1 \, dr_1$$  \hspace{1cm} (22)

The first term is the contribution of the fixed charges on the cylinder while the second term is the accumulated contribution of the mobile counterions. At the inner surface $\xi(r_s) = \xi_0$ and in the absence of positive ions in the solution it then decreases monotonously until it reaches zero on the cell outer boundary, $\xi(r) = 0$. The accumulated charge parameter is directly related to the electric field through Gauss law:

$$\xi(r) = -\frac{r \, dy}{2 \, dr}$$  \hspace{1cm} (23)

In analogy with eq. 21, the accumulated charge parameter can be calculated:

$$\xi(r) = \begin{cases} 
1 - B \coth [B \ln (R/r) + \tanh^{-1}(B)] & \xi_0 < \xi^* \\
1 - B \cot [B \ln (R/r) + \tan^{-1}(B)] & \xi_0 > \xi^*
\end{cases} \hspace{1cm} (24)$$

In Fig. 2c $\xi(r)$ is plotted for the same profiles of Fig. 2b. Note the qualitative difference between the low charge and the high charge limit. The steep decrease in $\xi(r)$ near the cylinder is the fingerprint of a condense counterion layer, which is similar to the Gouy–Chapman layer for the planar case.

Note that at low values of $\xi_0$ the dependence of $\xi(r)$ on $\ln(r)$ is convex everywhere while for high values of $\xi_0$ it is concave near the surface and convex further away. By taking the second derivative of eq. 24 with respect to $\ln(r)$ it can be shown that indeed in the high charge limit ($\xi_0 > 1$) the function $\xi(\ln(r))$ is concave near the surface and convex further away. The crossover between these two regimes is exactly at the radial distance $r$ where $\xi(r) = 1$. It was therefore suggested [20,8] that this could provide a criterion for identifying the existence of a condensed layer.

In cylindrical symmetry the osmotic pressure is proportional to the concentration of the counterions at the external cell boundary [40]:

$$\Pi = k_B T c^- (R)$$  \hspace{1cm} (25)

The above expression can be compared to the osmotic pressure of an ideal gas consisting of the same amount of particles (non-interacting counterions) in the same cylindrical volume. In this case, the particles are uniformly distributed in space and the osmotic pressure reads
\[ \Pi_{id} = k_B T \langle c \rangle \]  

where \( \langle c \rangle = 1/[L_0 \pi (R^2 - r_s^2)] \) is the average concentration of counterions in the solution. The ratio between the osmotic pressure of the interacting system \( \Pi \) (eq. 25), and the ideal osmotic pressure \( \Pi_{id} \) (eq. 26) is defined as the activity coefficient \( \gamma \):

\[
\gamma = \frac{\Pi}{\Pi_{id}} = \frac{c^-(R)}{\langle c \rangle}
\]  

The activity coefficient \( \gamma \) reflects the influence of the charged cylinder at the outer boundaries of the cell. The effective amount of charge needed to produce only the counterions that contribute to the osmotic pressure is just \( \gamma \xi_0 \). It can be used do define an effective charge parameter of the cylinder [20],

\[
q_{\text{eff}} \equiv \gamma \xi_0 = \begin{dcases}
\frac{1-B^2}{2} \left[ 1 - \left( \frac{r_s}{R} \right)^2 \right] & \xi_0 < \xi^* \\
\frac{1+B^2}{2} \left[ 1 - \left( \frac{r_s}{R} \right)^2 \right] & \xi_0 > \xi^*
\end{dcases}
\]  

The behavior of \( \gamma \) and \( q_{\text{eff}} \) as calculated from the analytical solution is shown in Fig. 3.

![Activity coefficient and effective charge parameter](image)

**FIG. 3.** Activity coefficient \( \gamma \) (a) and effective charge parameter \( q_{\text{eff}} = \gamma \xi_0 \) (b) as functions of the bare charge parameter \( \xi_0 \). The different curves correspond to \( R/r_s = 10 \) (solid curve) and \( R/r_s = 100 \) (short dashes). The dot-dash line is the infinite dilution limit, \( R/r_s \to \infty \).

In the infinite dilution limit \( \xi^* \to 1 \) and

\[
\gamma \to \begin{dcases}
1 - \frac{\xi_0}{2} & \xi_0 \leq 1 \\
\frac{1}{\xi_0} & \xi_0 \geq 1
\end{dcases}
\]  

\[
q_{\text{eff}} \to \begin{dcases}
\xi_0 - \frac{\xi_0^2}{2} & \xi_0 \leq 1 \\
\frac{1}{2} & \xi_0 \geq 1
\end{dcases}
\]  

as can be seen in Fig. 3.

In order to understand better the structure of the counterion distribution around the cylinder in the high charge limit (\( \xi_0 > \xi^* \)) it is instructive to study \( r(\xi) \), the inverse of eq. 24 [5,6]. The function \( r(\xi) \) assigns to each value of \( \xi \in [0, \xi_0] \) the radius \( r \) which encloses a total amount of charge which is equal to \( \xi \). It can be readily obtained from eq. 24 and at high dilution \( (R \gg r_s) \) the large \( R \) behavior is the following:
\[
\begin{cases}
    r_s \exp \left( \frac{1}{\xi - r} - \frac{1}{\xi_0 - r} \right) & 1 < \xi < \xi_0 \\
    (r_sR)^{1/2} \exp \left( \frac{\xi - 2}{2(\xi_0 - 1)} \right) & \xi = 1 \\
    R \exp \left( -\frac{\xi}{r} \right) & 0 < \xi < 1
\end{cases}
\]

(31)

It is clear from the above expressions that in the high charge limit \(\xi_0 > 1\) and at high dilution \((R/r_s \to \infty)\), the space around the cylinder can be divided into two regions:

- Near the surface \(\xi > 1\) and the corresponding radius \(r(\xi)\) remains finite as the solution is diluted \((R \to \infty)\). This means that a fixed amount of counterions remains within a fixed distance from the charged cylinder. This layer can be considered as confined or condensed.

- Far from the surface \(\xi < 1\) and the corresponding radius \(r(\xi)\) diverges as the solution is diluted \((R \to \infty)\). In addition, this radius no longer depends on the amount of charge carried by the cylinder as characterized by \(\xi_0\). This layer can be considered as non-confined or free.

The crossover radius \(r^* \equiv r(\xi = 1)\) separating the two regions defines a virtual cylinder which encloses an amount of charge equivalent to \(\xi = 1\). This crossover radius is not finite but rather diverges as \(R^{1/2}\) upon dilution while for any fixed value of \(q\), \(\xi_0 > \xi > 1\), the corresponding asymptotic limit of \(r(\xi)\) remains finite. For example, for \(\xi = 1.001\) and \(\xi_0 = 4\) eq. 31 gives \(r(\xi) \to n_0 \exp(997)\), which is extremely large but finite.

The exact solution of the PB equation (eq. 19) can be extended by taking the infinite dilution limit \(R \to \infty\) [42]. The result is

\[
y(r) = \begin{cases}
    -2\xi_0 \ln(r/r_s) & \xi_0 \leq 1 \\
    -2\ln(r/r_s) - 2 \ln[1 + (\xi_0 - 1) \ln(r/r_s)] & \xi_0 \geq 1
\end{cases}
\]

(32)

where the zero of the potential was chosen to be at \(r = r_s\).

In the low charge limit, \(\xi_0 \leq 1\), the potential reduces to that of an unscreened charged rod. The physical meaning of this solution is that the electric field produced by the cylinder in the low charge limit is not strong enough to keep the counterions from escaping to infinity and gaining entropy.

In the high charge limit, \(\xi_0 \geq 1\), the potential has two contributions. The first term is the unscreened potential produced by a charged rod whose charge density was reduced down to the critical one by the “condensed” counterions. The second term is a logarithmic correction and is due to the actual distribution of these counterions which form a diffusive layer around the surface. This can be easily seen by looking at the accumulated charge parameter \(\xi(r)\) in the infinite dilution limit, \(R \to \infty\):

\[
\xi_\infty(r) = 1 + \frac{(\xi_0 - 1)}{1 + (\xi_0 - 1) \ln(r/r_s)}
\]

(33)

It should be noted, that in this limit the radius \(r^*\) separating the “free” counterions from the “condensed” ones is infinite. As a result, all the “free” counterions have left the system and only the condensed counterions remain. The overall charge in the system is no longer zero, as can be easily verified either by integrating the total amount of counterions in the system [42], or by looking at the value of \(\xi_\infty(r)\) for \(r \to \infty\).

4. The Manning Picture

A simple model which describes some of the properties of the ionic cloud around the cylinder was put forward by Manning [10,11]. Its main advantage is that it provides simple expressions for the global properties of the solution, which are in good agreement with experiments. The model can be easily generalized to include the presence of salt. It should be emphasized that the Manning picture gives the impression that the condensed layer is limited to a microscopically narrow region around the cylinder, while as seen from the solution of the PB equation, the counterions are much more spread out.
The Manning model is based on the fact that at the infinite dilution limit (eqs. 29, 30) the value of \( q_{\text{eff}} = \gamma \xi_0 \) above \( \xi_0 = 1 \) saturates to its value for \( \xi_0 = 1 \). Since \( q_{\text{eff}} \) is a measure of the amount of counterions far away from the cylinder, its saturation means that the amount of free ions remains constant even when the charge density on the cylinder increases. Manning interpreted this result as an outcome of the condensation of counterions onto the charged cylinder. Thus reducing the cylinder charge effectively from \( \xi_0 > 1 \) down to \( \xi_0 = 1 \).

Below a version of Manning argument [11] is presented which may be somewhat more transparent than the original arguments [10]. This argument is similar to the two-phase approximation suggested in the past for cylindrical as well as spherical macroions [4,18] and it applies to the high dilution limit when \( R \to \infty \) or, equivalently, \( r_s \to 0 \).

We consider discrete charges located along the cylinder axis with a separation \( l_q \) between two neighboring charges. Each pair of charges \( i, j \) interacts via a screened Coulomb potential

\[
U_{ij} = \frac{(1 - \alpha)^2 e^2}{\varepsilon l_q |i - j|} e^{-\kappa l_q |i - j|}
\]

(34)

where \( \alpha \) is the average fraction of counterions that condense on each charge, \( \kappa^{-1} \) is the Debye–Hückel screening length. \( \kappa^2 = 4 \pi l_B c_{\text{tot}} \) where \( c_{\text{tot}} \) is total concentration of small ions in the solution (counterions as well as salt).

The sum of all pairs \( i, j \) can be carried out and the total electrostatic energy per lattice charge is:

\[
\beta U_{\text{el}} = -\xi_0 (1 - \alpha)^2 \ln \left( 1 - e^{-\kappa l_q} \right)
\]

(35)

Note that the exponential screened term became logarithmic. The reduction in the screening is a result of the overlap between the Coulomb fields surrounding each charge.

Assuming that the ions condensing onto one lattice site are restricted to a region of finite volume \( V_{\text{cond}} \) and that the non-condensed ions occupy a volume \( V_{\text{free}} \), the translational entropy of the ions per lattice site can be approximated by

\[
-S = \alpha \ln \left( \frac{\alpha a^3}{V_{\text{cond}}} \right) + (1 - \alpha) \ln \left( \frac{(1 - \alpha) a^3}{V_{\text{free}}} \right)
\]

(36)

The total free energy per lattice site \( f = U_{\text{el}} - TS \) is minimized with respect to \( \alpha \) and the result is the following implicit relation:

\[
-2\xi_0 (1 - \alpha) \ln \left( 1 - e^{-\kappa l_q} \right) = \ln \left( \frac{\alpha V_{\text{free}}}{(1 - \alpha) V_{\text{cond}}} \right)
\]

(37)

In the absence of salt the concentration of ions is \( c_{\text{tot}} = 1/(V_{\text{free}} + V_{\text{cond}}) \simeq 1/V_{\text{free}} \). At high dilution \( V_{\text{free}} \) is large, \( \kappa \) is small and the exponent on the right hand side of eq. 37 can be linearized yielding

\[
\xi_0 (1 - \alpha) \ln \left( \frac{4 \pi l_B^2}{V_{\text{free}}} \right) = \ln \left( \frac{1 - \alpha}{\alpha} \frac{V_{\text{cond}}}{V_{\text{free}}} \right)
\]

(38)

In the high dilution limit, \( V_{\text{free}} \to \infty \), the singularities on both sides can be balanced only if

\[
\alpha = \begin{cases} 
0 & \xi_0 \leq 1 \\
\frac{\xi_0 - 1}{\xi_0} & \xi_0 \geq 1 
\end{cases}
\]

(39)

The appearance of a condensed layer for \( \xi_0 > 1 \) is consistent with the results of the more elaborate Poisson–Boltzmann calculation. The difference in the current approach is that the volume of the condensed layer is now given by

\[
V_{\text{cond}} = 4 \pi l_B^2 \frac{\xi_0 - 1}{\xi_0}
\]

(40)

Consequently the radius of the cylinder which contains the condensed layer, \( r^* \), remains finite (on the order of \( l_B \)) as the solution is diluted. As pointed out above, this is in contrast with the exact solution of the PB equation where \( r^* \) diverges upon dilution. This represents the main difference between the Manning picture and the results of the Poisson–Boltzmann equation. Despite this difference, the Manning model appears to be in reasonable agreement with experiment as far as global properties, such as the osmotic pressure, are concerned. One should be careful, however when using the Manning model to describe the structure of the condensed layer.
C. Finite Ion Size: The Modified Poisson–Boltzmann Equation

After reviewing the behavior of point-like counterions around a charged cylinder, the ion-ion repulsion can be included (see also ref. [37]). Indeed, in many experimental systems the ion diameter is quite small, around 1-2 Å. Nevertheless, in some of them the finite size effects can become relevant.

![Graphs showing the effect of finite ion size on the ion concentration and electric potential.](image)

**FIG. 4.** Typical numerical solutions of the modified PB equation (eq. 41). The dashed curves were calculated for \( \alpha = 10 \). For comparison, the solution of the standard PB equation (eq. 6) are presented as well (solid curves). The reduced electric potential \( y = \beta e \psi(r) \) and the counterion concentration \( c^-(r) \) are plotted as function of \( \ln(r/r_s) \). The internal cylinder radius is \( r_s = 5 \) Å, while the external radius is \( R = 50 \) Å. Each pair of graphs corresponds to a different value of the charge parameter: \( \xi_0 = 0.5 \) (a), \( \xi_0 = 1 \) (b), \( \xi_0 = 2 \) (c) and \( \xi_0 = 4 \) (d). The dotted curve in (d) corresponds to the solution in the saturated region (eq. 42).

First, as discussed above, at high charge densities the concentration of ions near the charged cylinder can become very high. This is especially true in the Manning picture where the condensed layer occupies a finite volume around the cylinder.

Second, when the ions are immersed in an aqueous solution each ion is surrounded by an *Hydration shell* of (dipolar) water molecules which align around the ions. The driving force for the formation of this shell is the electrostatic interaction between the dipole moment of the water molecules and the electric field of the charged ion. The hydration shell can increase the effective diameter of the ions from 2 Å to 8 Å [6].

We start with the modified PB equation for the counterion-only case (eq. 5) with monovalent negative ions (\( z = 1 \)):

$$\frac{d^2y}{dr^2} + \frac{1}{r} \frac{dy}{dr} = \frac{4\pi l_B c_0 e^y}{1 - \phi_0 + \phi_0 e^y}$$  \hspace{1cm} (41)

where \( \phi_0 = \alpha^3 c_0 \) and \( c_0 \) is a reference concentration. Changing \( c_0 \) is equivalent to a constant shift in the electric potential \( y \) and does not affect the physical properties of the system. Of course, \( c_0 \) can not be larger than \( 1/\alpha^3 \) and
\( \phi_0 \) must be smaller than one. The same electrostatic boundary conditions as before (eqs. 8, 9) apply here and the system is well defined. It can be solved numerically for the electrostatic potential \( y(r) \), the small ion concentration \( c(r) \) and the accumulated charge parameter \( \xi(r) \).

Typical numerical solutions of eq. 41 for \( a = 10 \AA \) are presented in Fig. 4 for four different charge parameters \( (\xi_0 = 0.5, \xi_0 = 1, \xi_0 = 2 \) and \( \xi_0 = 4) \). The internal radius is \( r_s = 5 \AA \) while the external radius is \( R = 50 \AA \). For comparison, the solutions of the regular PB equation (eq. 6) are plotted as well.

At low charge densities \( (\xi_0 = 0.5, \text{Fig. 4a}) \) the potential is weak and the concentration of counterions remains low. The effect of the ion size on the concentration profile in this case is therefore negligible. At intermediate charge densities \( (\xi_0 = 1, \text{Fig. 4b}) \), small deviations from the regular PB solution appear only close to the surface.

At high charge densities \( (\xi_0 = 2, \text{Fig. 4c and } \xi_0 = 4, \text{Fig. 4d}) \) the effect of finite size becomes prominent. Near the surface the concentration of small ions saturates to its maximal value \( c^- \rightarrow 1/a^3 \) and the potential has the approximate form:

\[
y \simeq y(r_s) - 2 \left( \xi_0 + \frac{\pi l_B}{a^2 r_s^2} \right) \ln \left( \frac{r}{r_s} \right) + l_B \pi (r^2 - r_s^2) \frac{1}{a^3}
\]

(42)

This behavior is indeed verified by the dotted curve in Fig. 4d.

In the saturated layer the accumulated charge parameter (eq. 23) can be calculated from the derivative of the approximated potential and reads:

\[
\xi_{\text{sat}}(r) \simeq \xi_0 - \pi \left( r^2 - r_s^2 \right) \frac{l_B}{a^3}
\]

(43)

The above expression simply reflects the fact that in the saturated region the total amount of counterions enclosed in a ring of radius \( r \) around the cylinder is proportional to the ring area \( \pi (r^2 - r_s^2) \).

![Graph](image)

**FIG. 5.** The accumulated charge parameter \( \xi(r) \) as function of \( \ln(r/r_s) \) as calculated from the numerical solutions presented in Fig. 4. Same parameters and notations as in Fig. 4. The values of the charge parameter are \( \xi_0 = 1 \) (a) and \( \xi_0 = 4 \) (b). The dotted curve in (b) corresponds to the solution in the saturated region (eq. 43).

In Fig. 5 the accumulated charge parameter \( \xi(r) \) is plotted from the numerical solutions presented in Fig. 4. The charge parameter is \( \xi_0 = 1 \) in Fig. 5a and \( \xi_0 = 4 \) in Fig. 5b. In the first case, the ion concentration is far from being saturated and the difference between each pair of curves is only minor. In the latter case the ion concentration is saturated near the surface and the difference from the regular PB case is pronounced. As demonstrated in Fig. 5b, in the saturated layer \( (\ln(r/r_s) \lesssim 0.5) \) the profile of the accumulated charge parameter agrees well with eq. 43 (dotted curve).

From eq. 43 and from the fact that \( \xi_{\text{sat}}(r) \) must be positive, one can obtain an upper limit on the width of the saturated layer

\[
l^* < \left( r_s^2 + \frac{\xi_0 a^3}{\pi l_B} \right)^{1/2} - r_s
\]

(44)

We note that in the limit \( r_s \gg a \) the width \( l^* \) becomes comparable with an ion size when \( a^2 \xi_0 / l_B \gtrsim 2\pi r_s \). This condition simply means that a closely-packed ion monolayer exactly neutralizes the charged cylinder.
Perhaps a more significant crossover occurs when the width of the saturated layer becomes comparable with the cylinder radius. The condition $l^* \gtrsim r_s$ can be expressed as

$$\zeta_2 = \frac{\xi_0 a^3}{l_B^2 \pi r_s^2} \gtrsim 1 \quad (45)$$

which provides a qualitative criterion for the importance of excluded volume interactions in the cylindrical case. Note, that eq. 45 simply states that the total volume of the ions in the saturated layer is comparable with the volume occupied by the cylinder.

In addition, another criterion is given from the solution of the planar case [32–34]. In a planar geometry the PB equation can be integrated once and the surface potential expressed in terms of the surface charge. The dimensionless parameter $\zeta_1$ emerges which is a measure of the importance of excluded volume interactions. It can be written as a ratio between the volume of a single ion and an electrostatic volume

$$\zeta_1 = \frac{a^3}{\Sigma \lambda_{GC}} \quad (46)$$

where $\Sigma = e / \sigma$ is the area per surface charge. In the cylindrical case the condition that ion size becomes important becomes

$$\zeta_1 = \frac{\xi_0^2 a^3}{l_B^2 2 \pi r_s^2} = \frac{\xi_0^2}{2} \zeta_2 \gtrsim 1 \quad (47)$$

The two crossover curves $\zeta_1 = 1$ and $\zeta_2 = 1$ are illustrated in Fig. 6 for the same parameters of the numerical example presented above. Note, that for the ion size chosen in our numerical solution, $a = 10\,\text{Å}$, the point were $\xi_0 = 0.5$ is in the weak regime while the point where $\xi_0 = 4$ is in the strong regime.

![Steric (MPB) vs Non-Steric (PB)](image)

**FIG. 6.** Schematic diagram of the adsorption regimes of large ions to a charged cylinder. The horizontal axis is the charge parameter $\xi_0$, and the vertical axis if the ion size $a$. The dashed line ($\zeta_1 = 1$) and the dotted one ($\zeta_2 = 1$) illustrate the two criteria for the relevance of steric effects. The lower of the two curves marks the point were steric effects become important.

As expected, at high charge densities the planar crossover point is lower than the cylindrical one. On the other hand, at low charge densities the geometry of the charged object becomes important. The condition that $\zeta_1 = \zeta_2$ occurs at $\xi_0 = 2$ and is independent of the cylinder radius $r_s$.

For DNA molecules $\xi_0 \simeq 4$ and $r_s = 10\,\text{Å}$. In an aqueous solution at room temperature ($l_B \simeq 7\,\text{Å}$), the size of the counterions will become an important factor when $a \gtrsim 6.5\,\text{Å}$ which is rather large. The size of the ion is not very well defined, especially in an aqueous solution where the hydration layer has to be taken into account as contributing to the effective size of the ion.

It should be emphasized that the saturated layer is different from the condensed layer. In the former, the ion density reaches its maximal value and its definition is more or less straightforward (e.g., eq. 44). In contrast, the condensed layer is more extended and its definition is quite ambiguous. For example, it has been suggested that an inflection point in the dependence of $\xi(r)$ on $\ln(r)$ can be used for its definition [20,8]. The existence of a saturated
layer is not necessarily related to the existence of a condensed layer. It is more likely to form above the Manning threshold, i.e. at high values of $\xi_0$ (see eqs. 45, 47) but if the counterions are large enough it can also form at lower charge parameters. We proceed now to consider the effective charge parameter $q_{\text{eff}} = \gamma\xi_0 = \xi_0c^-(R)/\langle c \rangle$. The effect of the ion size is shown in Fig. 7a where $q_{\text{eff}}$ is plotted as a function of the charge parameter $\xi_0$. The dashed curves are calculated from the numerical profiles, similar to those presented in Figs. 4, 5. The dotted curve is the infinite dilution limit of the analytical solution (eq. 30).

The solid curves are calculated from the analytical solution (eq. 28) where the parameter $B$ is obtained from eq. 21 with a slight modification. Instead of using the bare cylinder radius $r_s$, it is assumed that as a result of the excluded volume repulsion the volume available for the small ions is reduced. This effect is important only for high charge parameters, $\xi_0 \geq 1$, when the concentration close to the surface is high. In other words, when Manning condensation occurs, the reduction in the volume is mostly due to the ions which are considered as condensed and can be estimated by

$$\Delta V = (\xi_0 - 1) \frac{\pi}{6} a^3$$

(48)

As a result, the effective cylinder radius is now

$$r_s^* = r_s^2 + (\xi_0 - 1) \frac{a^3}{6B}$$

(49)

It is $r_s^*$ and not $r_s$ which is used in eq. 21 to calculate $B$. The agreement between the numerical calculations and the empirical approach is quite good considering this crude approximation. Note, that due to the limited accuracy of the numerical solution there is also a slight discrepancy between the numerical and analytical solutions of the regular PB case.

In Fig. 7b the effect of dilution is demonstrated. The curves are all calculated using the modified radius $r_s^*$ (instead of $r_s$) for calculating $B$. The increase from $r_s$ to $r_s^*$ is independent of the external radius $R$. It therefore follows that as the system is diluted ($R \to \infty$) the behavior approaches the same limit as the analytical solution, where excluded volume are neglected.

![Fig. 7](image)

**FIG. 7.** (a) Effective charge parameter $q_{\text{eff}} = \gamma\xi_0$ as function of the bare charge parameter $\xi_0$ for various ion sizes. The internal and external radii are $r_s = 5\AA$ and $R = 50\AA$, respectively. The dashed curves are calculated from the numerical solutions, similar to those presented in Figs. 4, 5. The solid curves were constructed from the analytical solution (eq. 28), where $B$ was calculated from eq. 21 with a modified cylinder radius eq. 49. (b) Effective charge parameter $q_{\text{eff}} = \gamma\xi_0$ as function of the bare charge parameter $\xi_0$ for various dilution (changing $R$). The curves are constructed from the analytical solution where $B$ is calculated with a modified internal radius $r_s^*$. The ion size is $a = 10\AA$.

The excluded volume effect can be explained qualitatively by returning to Manning version of the two-phase approximation presented above. The contribution of the excluded volume repulsion can be added to the free energy per charge which now reads:

$$\beta f = -\xi_0(1 - \alpha)^2\ln(1 - e^{-N}) + \alpha\ln \left( \frac{\alpha a^3}{V_{\text{cond}}} \right) + (1 - \alpha)\ln \left( \frac{(1 - \alpha)a^3}{V_{\text{free}}} \right) + \frac{1}{2} q^2 \frac{a^3}{V_{\text{cond}}}$$

(50)
where we have assumed that outside the condensed layer the excluded volume interaction can be neglected. Recall that \( V_{\text{cond}} \) and \( V_{\text{free}} \) are the volumes available for the condensed and free counterions, respectively, per cylinder charge.

Minimizing the free energy with respect to \( \alpha \), and assuming that \( V_{\text{free}} \gg V_{\text{cond}} \) (in the expression for \( \kappa \)) as well as weak screening (\( \kappa l_q \ll 1 \)) we obtain the following relation between \( \alpha \) and \( V_{\text{cond}} \) (see also section III B 4):

\[
\xi_0 (1 - \alpha) \ln \left[ \frac{4\pi l_B^2}{V_{\text{free}}} \right] = \ln \left[ \frac{1 - \alpha}{\alpha} \frac{V_{\text{cond}}}{V_{\text{free}}} \right] - \frac{\alpha a^3}{V_{\text{cond}}} \tag{51}
\]

As before, above the Manning threshold (\( \xi_0 \geq 1 \)) and in the high dilution limit \( V_{\text{free}} \to \infty \) the above equation implies that

\[
\alpha = \frac{\xi_0 - 1}{\xi_0} \tag{52}
\]

The equation for \( V_{\text{cond}} \) is however slightly modified and reads

\[
V_{\text{cond}} = 4\pi l_B^2 \frac{\xi_0 - 1}{\xi_0} \exp \left( -\frac{\alpha a^3}{V_{\text{cond}}} \right) \tag{53}
\]

If the size of the counterions \( a^3 \) is still much smaller than the available volume \( V_{\text{cond}} \) the correction will be small. As a first order approximation we can use the zero order value of the volume \( V_{\text{cond}}^{(0)} = 4\pi l_B^2 (\xi_0 - 1)/\xi_0^3 \) on the right hand side of eq. 53. Expanding the exponent we obtain

\[
V_{\text{cond}} = V_{\text{cond}}^{(0)} \exp \left( -\frac{\alpha a^3}{V_{\text{cond}}} \right) \simeq V_{\text{cond}}^{(0)} - \alpha a^3 \tag{54}
\]

where \( \alpha \) is given by eq. 52. We see that as a result of the excluded volume repulsion the condensed counterions contribute to a decrease of the volume of the condensed layer. Up to numerical prefactors the above equation recovers the same behavior as in eq. 49 where the volume occupied by the condensed counterions is added to the volume of the charged cylinder itself. In the next section we shall see a similar effect in the case of a charged sphere.

To summarize this section, following a review of the condensation phenomena of point-like counterions onto a charged cylinder, we have studied the effect of ion size. It was demonstrated both numerically and using a simple two-phase approximation that the short range repulsion is not strong enough to cancel the condensation effect. Instead, it was shown that adding excluded volume interactions is equivalent to increasing the volume of the cylinder by an amount given by the total volume of the condensed counterions.

IV. ADSORPTION TO A SPHERE AND CHARGE RENORMALIZATION

A. Introduction

Colloids are an important ingredient in many industrial applications, such as ink and paint preparation as well as paper making [43]. In many cases the colloids acquire surface charges when immersed in an aqueous solution and these charges strongly affect the colloid–colloid interactions and the properties of the colloidal suspension. It is therefore of particular interest to study the behavior of a charged sphere in an ionic solution. Once again we will adapt the cell model where the colloid is located in the center of a spherical cell of radius \( R \) so that the volume fraction of the colloids is \( \phi = r_s^3/R^3 \) where \( r_s \) is the radius of the colloid. The local properties depend only on one coordinate, \( r \), being the distance from the center of the sphere. At low volume fractions this model keeps the important features while simplifying the geometry of the system. Another simplification is to put the charged colloid in a salt free solution containing counterions only (Fig. 8).

As discussed earlier, in the planar case the electrostatic attraction dominates over the translational entropy of the ions. As a result, the counterions can be considered as confined to the surface and the Gouy–Chapman layer is formed. In the cylindrical case, both the electrostatic attraction and the entropic contribution to the free energy are logarithmic with the distance from the cylinder axis. The formation of a confined layer near the surface depends therefore on the balance between these two contributions. At low charge densities the counterions can be considered as free and the cylinder is basically unscreened. At high charge densities a large portion of the counterions is confined to the vicinity of the cylinder thus reducing the apparent charge density down to a critical surface charge density which is independent of the bare charge density of the cylinder.
In the spherical case, however, the entropy is expected to dominate over the electrostatic attraction to the surface. Nevertheless, we will see below that at high charge densities a condensed layer is formed around the colloid. As noticed by Alexander et al. [16] the effect of this layer is to renormalize the surface charge and strongly reduce it. In contrast with the cylindrical case, the renormalized charge density does not saturate at high charge densities. In the following the behavior of point-like counterions surrounding a charged sphere is briefly discussed and then the effect of ion size will be examined [32–34].

![Schematic view of a charged colloid in an ionic solution](image)

**FIG. 8.** Schematic view of a charged colloid in an ionic solution. The total charge of the colloid is $Z_0e$ and it is uniformly distributed on the colloid surface. The colloid radius is $r$, and it is located at the center of a spherical cell of radius $R$. The cell contains only counterions (no added salt) of diameter $a$.

### B. Point-like ions: The Standard Poisson–Boltzmann Approach

In three dimensions and assuming spherical symmetry, the standard PB equation reads:

$$\nabla^2 y = \frac{d^2 y}{dr^2} + \frac{2}{r} \frac{dy}{dr} = 4\pi l_B c_0 e^y \tag{55}$$

where $r$ is the distance from the center of the sphere and $c_0$ is a reference concentration which only determines the potential reference point. Despite what seems to be a minor difference in the numerical prefactor of the first derivative term between the PB equation in cylindrical and spherical symmetry (eqs. 6 and 55, respectively) the behavior is considerably different.

If the total charge carried by the spherical colloid is $Z_0e$, where $Z_0$ is the macro-ion valency, then the average surface charge density on the colloid will be

$$\sigma = \frac{Z_0 e}{4\pi r_s^2} \tag{56}$$

The electrostatic boundary condition at the colloid surface is, therefore,

$$\frac{dy}{dr} \bigg|_{r=r_s} = -\frac{2}{\lambda_{GC}} = -\frac{Z_0 l_B}{r_s^2} \tag{57}$$

where the Gouy–Chapman length is defined as usual:

$$\lambda_{GC} = \frac{e}{2\pi l_B \sigma} = \frac{2r_s^2}{Z_0 l_B} \tag{58}$$

In the cell model the electric field must vanish at the external radius due to charge neutrality

$$\frac{dy}{dr} \bigg|_{r=R} = 0 \tag{59}$$
The PB equation (eq. 55) together with the two boundary conditions (eqs. 57, 59) constitute a well defined problem that can be solved numerically. Typical solutions will be presented below together with solutions of the modified PB equation. Fortunately, some of the characteristics of the system can be studied using the following simple arguments.

We have already seen in the previous section that in a planar geometry \( \lambda_{GC} \) characterizes the width of the diffusive layer of counterions near the surface. The importance of the spherical geometry depends therefore on the ratio between \( r_s \) and \( \lambda_{GC} \). In the large radius (low curvature) limit \( r_s \gg \lambda_{GC} \) we can expect some sort of counterion layer to form near the colloid surface as a reminiscence of the condensed layer that forms near a planar surface. In terms of the colloid charge, this condition corresponds to \([16-18,20,12]\)

\[
Z_0 \gtrsim 2 \frac{r_s}{l_B}
\]

(60)

In terms of the area per surface charge \( \Sigma \) this condition corresponds to

\[
\Sigma \lesssim 2 \pi r_s l_B
\]

(61)

For a small colloid of radius \( r_s = 50\AA \) in an aqueous solution with \( l_B = 7\AA \) this condition reads \( \Sigma \lesssim 2200\AA^2 \) and can be easily satisfied. In the opposite limit the curvature of the colloid plays an important role. In fact, it turns out that at these low charges the electrostatic attraction is not strong enough to keep the counterions close to the surface.

Assuming that a diffusive or condensed counterion layer exists at high charge densities it is now possible to describe the behavior of the system in the following semi-quantitative way. We have chosen to present a slightly modified version of the original argument presented by Alexander et al. \([16]\) which is compatible with the simple arguments used in the cylindrical case (Sec. III B 4) and which can be easily generalized to include the excluded volume interaction. This approach is sometimes referred to as the two phase approximation \([4,18]\) as it divides the counterions into two populations: condensed (or confined) and free. The main idea is to compare the entropy of the small ions with the electrostatic energy and calculate how the population of counterions splits between these two phases.

Assuming that a fraction \( \alpha \) of the counterions condense on the sphere, its effective valency can be written as \( Z_{\text{eff}} = (1 - \alpha) Z_0 \). The electrostatic energy of an unscreened sphere of radius \( r_s \) and valency \( Z_{\text{eff}} \) per unit charge can be therefore written as

\[
\frac{\beta U_{\text{el}}}{Z_0} = \frac{l_B (1 - \alpha)^2 Z_0}{2 r_s}
\]

(62)

while the translational entropy of the ions is

\[
-\frac{S}{Z_0} = \alpha \ln \left( \frac{\alpha a^3}{V_{\text{cond}}} \right) + (1 - \alpha) \ln \left( \frac{(1 - \alpha) a^3}{V_{\text{free}}} \right)
\]

(63)

where \( V_{\text{cond}} \) is the volume of the condensed shell and \( V_{\text{free}} \) is the volume available for the free counterions.

Minimizing the free energy \( F = U_{\text{el}} - T S \) with respect to \( \alpha \) yields the following implicit relation for \( Z_{\text{eff}} \):

\[
Z_{\text{eff}} = l_B \frac{Z_0}{Z_{\text{eff}} V_{\text{cond}}} \ln \left( \frac{Z_0 - Z_{\text{eff}} V_{\text{free}}}{Z_{\text{eff}} V_{\text{cond}}} \right)
\]

(64)

This result will be compared below with the numerical results.

In the limit of high valency \( Z_0 \gg Z_{\text{eff}} \) and in high dilution the leading \( Z_0 \) dependence is logarithmic:

\[
Z_{\text{eff}} \approx \frac{r_s}{l_B} \left[ \ln Z_0 + \ln \left( \frac{V_{\text{free}}}{Z_{\text{eff}} V_{\text{cond}}} \right) \right]
\]

(65)

We see that the apparent charge of the colloid \( Z_{\text{eff}} \) can be much smaller than the bare charge \( Z_0 \). Unlike the cylindrical case it does not saturate to a fixed value but rather continues to increase as charges are added to the colloid surface.

Finally, a note should be made regarding the volumes available for the two ion species \( V_{\text{free}} \) and \( V_{\text{cond}} \). Whereas the first is basically the inverse of the macroion density, the second is open to interpretation. A simple estimate of \( V_{\text{cond}} \) can be obtained using the Gouy–Chapman length as an estimate to the width of the condensed layer around the sphere. This estimate is only valid as long as \( r_s \gg \lambda_{GC} \). The corresponding volumes are therefore:

\[
V_{\text{cond}} \approx 4 \pi r_s^2 \lambda_{GC} = \frac{8 \pi r_s^4}{Z_0 l_B}
\]

(66)

and

\[
V_{\text{free}} \approx \frac{4}{3} R^3 - V_{\text{cond}}
\]

(67)
C. Finite Ion Size: The Modified PB Equation

We proceed now to include the steric ion-ion interactions (see also Refs. [44,45]). In three dimensions and assuming spherical symmetry, the modified PB equation reads:

$$\frac{d^2y}{dr^2} + \frac{2}{r} \frac{dy}{dr} = \frac{4\pi l_B c_0 e^y}{1 - \phi_0 - \phi_0 e^y}$$  \hspace{1cm} (68)

where $\phi_0 = a^3 c_0$ and $c_0$ is a reference concentration defined as before. The electrostatic boundary conditions are given by eqs. 57, 59.

![Graphical representation of the modified PB equation solution.](image)

**FIG. 9.** Typical numerical solutions of the modified PB equation (eq. 68). The dashed curves were calculated for $a = 10\AA$ while the solid curves are the solutions of the standard PB equation for $a = 0$ (eq. 55). The reduced electric potential $y = \beta \psi(r)$ and the counterion concentration $c^-(r)$ are plotted as function of $r$, the distance from the center of the sphere. The internal sphere radius is fixed, $r_s = 50\AA$, while the outer cell radius is $R = 100\AA$. Each pair of graphs corresponds to a different amount of charge on the sphere: $Z_0 = 200$ (a) and $Z_0 = 500$ (b). The dotted curve in (b) corresponds to the solution in the saturated region (eq. 69).

Typical numerical solutions are presented in Fig. 9 for two charge densities: $Z_0 = 200$ (Fig. 9a) and $Z_0 = 500$ (Fig. 9b). The colloid radius is 50Å while the outer radius is 100Å. The Bjerrum length $l_B = 7\AA$. The numerical solutions of the modified PB equation (eq. 68) for $a = 10\AA$ are compared with the numerical solutions of the standard PB equation (eq. 55) for two values of the outer radius $R$. In the lower charge case ($Z_0 = 200$) the potential near the surface is not very high and the ion concentrations do not reach their saturated values. The concentrations are only slightly reduced because of the short range repulsion near the surface. In the higher charge case ($Z_0 = 500$) the potentials become high and the counterion concentration near the surface reaches its saturated value $c^- \rightarrow 1/a^3$. A saturated layer is formed near the surface where the counterion density is fixed at this saturated value. In this layer the Poisson equation can be integrated out and the potential reads

$$y \approx \frac{2\pi l_B}{3a^3} r^2 + \left( Z_0 + \frac{4\pi r_s^3}{3a^3} \right) \frac{l_B}{r} + \text{const.}$$  \hspace{1cm} (69)

In analogy with the cylindrical case studied above one can obtain some insight into the distribution of counterions by defining an accumulated colloid valency as

$$Z(r) = Z_0 - \int_{r_s}^r c^-(r_1) 4\pi r_1^2 dr_1$$  \hspace{1cm} (70)

This quantity measures the amount of charge contained inside a virtual sphere of radius $r$. The first term in eq. 70 is the bare colloid valency and the second term is the accumulated contribution of the free counterions. $Z(r)$ is maximal at the surface of the colloid where $Z(r_s) = Z_0$ and decreases monotonously as $r$ increases and more counterions are included in the virtual sphere. It follows from charge neutrality that $Z(r)$ must be zero at the external surface $r = R$.

Using Gauss law one can relate $Z(r)$ to the local electric field by
\[ Z(r) = \frac{r^2 \, dy}{l_B \, dr} \]  

(71)

In the saturated region the accumulated valency \( Z(r) \) can be obtained from the derivative of the potential:

\[ Z_{\text{sat}}(r) \simeq Z_0 - \frac{4\pi}{3} \left( r^3 - r_s^3 \right) \frac{1}{a^3} \]  

(72)

which is simply proportional to the volume of a spherical shell of external radius \( r \) enclosing the sphere.

![Graphs showing \( Z(r) \) as a function of \( r \) for different values of \( Z_0 \)](a) \( Z_0 = 200 \) (b) \( Z_0 = 500 \)

FIG. 10. The accumulated valency \( Z(r) \) as a function of \( r \) as calculated from the numerical solutions. Same parameters and notations as in Fig. 9. The dotted curve in (b) corresponds to the solution in the saturated region (eq. 72). The width of the saturated layer as estimated from eq. 73 is \( l^* \simeq 63 \lambda \).

In Fig. 10 the accumulated colloid valency \( Z(r) \) is plotted as function of the radius \( r \) as calculated from the numerical profiles of Fig. 9. In the low charge limit there is no saturated layer and the effect of the ion size is only minor. In the high charge limit a saturated layer can be clearly observed around the sphere. Indeed the behavior of \( Z(r) \) in the saturated layer agrees well with the saturated expression (eq. 72) which is plotted for comparison on Fig. 10b.

The existence of the saturated layer can be inferred by looking for the point where \( Z_{\text{sat}}(r) = 0 \). This provides an upper limit on the width of the saturated layer (similar to the one discussed in the cylindrical case):

\[ l^* \simeq \left( r_s^3 + \frac{3}{4\pi} Z_0 a^3 \right)^{1/3} - r_s \]  

(73)

In the limit \( r_s \gg a \) the width \( l^* \) becomes comparable with an ion size when \( Z_0 a^3 \gtrsim 4\pi r_s \). As before, this condition means that a closely-packed ion monolayer exactly neutralizes the spherical colloid.

The width of the saturated layer becomes comparable to the colloid size when \( l^* \gtrsim r_s \). Again, this crossover condition can be expressed in terms of the ratio of the accumulated volume of the ions in the saturated layer and the colloid volume (see also eq. 45):

\[ \zeta \equiv \frac{Z_0 a^3}{4\pi r_s^3/3} \gtrsim 1 \]  

(74)

Similarly, at high surface charge densities on the sphere, the planar criterion \( \zeta_1 \gtrsim 1 \) (eq. 46) applies. Using the sphere charge density \( \sigma \) (eq. 56) gives

\[ \zeta_1 = \frac{Z_0^2 a^3 l_B}{8\pi r_s^2} \gtrsim 1 \]  

(75)

As demonstrated in Fig. 9 steric effects indeed dominate at high values of \( \zeta_1 \). For the physical values of (a) one obtains \( \zeta_1 \simeq 1.8 \) and indeed the steric effects are weak. On the other hand in (b) steric effects are strong in agreement with the calculated value \( \zeta_1 \simeq 11 \).
The crossover curves $\zeta_1 = 1$ and $\zeta_3 = 1$ are illustrated in Fig. 11 where we have used $l_B = 7\,\text{Å}$ and $r_s = 50\,\text{Å}$. The qualitative behavior is similar to that of the cylindrical case: at low charge densities, $Z_0 \lesssim 6r_s/l_B$, the curvature of the colloid plays an important role and the spherical criterion dominates. For the parameters used in the figure, this case corresponds to relatively low surface charge densities ($Z_0 \lesssim 43$ or, alternatively, $\sigma \lesssim 1e/730\,\text{Å}^2$). At higher charge densities, $Z_0 \gtrsim 6r_s/l_B$ (or $\sigma/\varepsilon \gtrsim 6/4\pi r_s l_B$) the curvature is less important and the planar criterion dominates.

It is of interest now to consider the osmotic pressure of the counterions in a manner similar to that used in the cylindrical case. In spherical symmetry the osmotic pressure is proportional to the ion concentration at the outer cell boundary [40]

$$\Pi = k_B T c^-(R)$$

while the ideal osmotic pressure is now

$$\Pi_{id} = k_B T \langle c \rangle = k_B T \frac{Z_0}{4\pi (R^3 - r_s^3)}$$

It now follows that one can define an effective macro-ion valency $Z_{\text{eff}}$ which is a measure of the number of counterions that contribute to the osmotic pressure and could therefore be defined as “free”:

$$Z_{\text{eff}} = Z_0 \frac{\Pi}{\Pi_{id}} = \frac{4\pi}{3} \frac{(R^3 - r_s^3) c^-(R)}{c^-(R)}$$

The effect of the ion size on $Z_{\text{eff}}$ is shown in Fig. 12a, where the dependence of $Z_{\text{eff}}$ on the bare valency $Z_0$ and ion size $a$ is studied. The curves were calculated from the numerical profiles, similar to those presented in Figs. 9, 10. The dotted line $Z_{\text{eff}} = Z_0$ is drawn for comparison. At small values of $a$, the effective charge grows much slower than the bare colloid charge, indicating that the colloid charge is renormalized. This renormalization is a result of the competition between the electrostatic attraction of the counterions to the surface and their translational entropy.

When the ion size is included the behavior is somewhat different. It is encouraging that the point where the dashed curves ($a = 5\,\text{Å}$ and $a = 10\,\text{Å}$) deviate from the solid curve ($a = 0$) are consistent with the condition $\zeta_1 = 1$ (Fig. 11). Above this deviation point charge renormalization is much weaker than expected. This is especially true for $a = 10\,\text{Å}$ where the curve becomes almost linear at high values of $Z_0$. This effect is due to the fact that as the colloid charge increases the width of the condensed layer decreases and the concentration in this layer becomes much higher. At these high charge densities the excluded volume interaction is strong enough to reduce the amount of counterions in the condensed layer and consequently weaken the charge renormalization effect.
The two-phase approximation can be easily generalized to take into account the excluded volume interaction. The free energy per surface charge is now:

$$\frac{\beta F}{Z_0} = \frac{l_B}{2r_s}(1-a)^2Z_0 + \alpha \ln \left(\frac{\alpha a^3}{V_{\text{cond}}}\right) + (1-\alpha) \ln \left(\frac{(1-\alpha)a^3}{V_{\text{free}}}\right) + \frac{Z_0}{2} \alpha^2 \frac{a^3}{V_{\text{cond}}},$$

(79)

where the last term is the new addition approximating the effect of the excluded volume interaction in the condensed layer.

Minimizing the free energy with respect to $\alpha$ now yields a slightly modified equation for $Z_{\text{eff}}$:

$$Z_{\text{eff}} = \frac{r_s}{l_B} \left[ \ln \left(\frac{Z_0 - Z_{\text{eff}}}{Z_0} - \frac{Z_{\text{eff}}}{Z_0} \right) + \frac{Z_0 - Z_{\text{eff}}}{Z_0} \frac{a^3}{V_{\text{cond}}} \right].$$

(80)

The dependence of $Z_{\text{eff}}$ on $Z_0$ is depicted in Fig. 12b for the same values of the ion size $a$ as in Fig. 12a. We estimate the volumes $V_{\text{cond}}$ and $V_{\text{free}}$ by assuming that the condensed layer surround the colloid is of width $\lambda_{GC}$ (eqs. 66, 67). Indeed a weaker renormalization of the colloid charge is reproduced by this model. As can be seen from eq. 80, at high values of $Z_0$ the last term dominates over the logarithmic term and as a result $Z_{\text{eff}}$ increases faster than expected.

It should be noted, however, that in practice $Z_0$ cannot increase indefinitely as it is limited by the ability to pack a large amount of charges on the surface of the colloid. Roughly speaking, the maximal area per surface charge cannot be smaller than $\Sigma \approx 25\text{Å}^2$. For a colloid of radius $50\text{Å}$ the number of charges is limited by

$$Z_0 = \frac{4\pi r_s^2}{\Sigma} \lesssim 1300$$

(81)

We therefore conclude that in practical cases charge renormalization is still relevant but that it is reduced by the steric interactions. The increase in the effective colloid charge can be estimated by comparing the first and the third terms in eq. 80

$$\frac{Z_{\text{eff}}}{Z_{\text{eff}}(a = 0)} \approx \frac{(Z_0 - Z_{\text{eff}})a^3/V_{\text{cond}}}{\ln(Z_0 - Z_{\text{eff}})} \approx \frac{a^3}{4\pi r_s^4/l_B \ln(Z_0)}$$

(82)

For $r_s = 50\text{Å}$, $l_B = 7\text{Å}$, $Z_0 = 1000$ and $a = 5\text{Å}$ the ratio is about 1.6. In agreement with the data from Fig. 12b.

V. CONCLUSIONS

In this paper we have studied the effect of finite ion size on the distribution of counterions around charged objects, focusing on the simple cases of a single charged cylinder and a single charged sphere. A modified Poisson–Boltzmann equation which takes into account the saturation of ion concentration at high densities was used for this purpose.
We started by studying the adsorption of counterions onto a charge cylinder. In the cell model a single cylinder represents a solution of non-interacting charged rods at a finite concentration, and the results can then be related to electrostatic effects in DNA [3,4]. Much emphasis was given to the effect of the ion size on the Manning condensation phenomenon. The condensation picture reflects the fact that at high charge densities the electrostatic interaction of the counterions with the linear charge density along the cylinder dominates over the translational entropy of the counterions. The result is that above a critical charge density a layer of counterions is formed around the cylinder, which effectively reduces the charge density down to its critical value. It was demonstrated that when the size of the ions is taken into account the effective size of the cylinder is enlarged. Furthermore, only the ions in the condensed layer contribute to this enlargement. At high dilution, where the external volume becomes large, the effect of the ions size on the osmotic pressure becomes less pronounced, but it does affect the structure of the counterion layer.

We have also studied the adsorption of large ions to a charged sphere and how the short range repulsions affect the phenomenon of charge renormalization. The charged sphere was placed in a spherical cell which models a solution of charge colloids at a finite concentration. We have seen that the competition between the Coulomb attraction of the counterions to the surface and the translational entropy leads to a strong reduction of the apparent charge of the colloid. When the size of the ions is included, this reduction is weaker as the steric repulsion limits the ability of the counterions to pack in a narrow layer near the surface. This behavior can be explained semi-quantitatively using a simple two-phase model which takes into account the leading terms of the different interactions in the system.

In both cases one can introduce a dimensionless parameter $\zeta = a^3/\Sigma \lambda_{CC}$ where $a$ is the ion size, $\Sigma$ the specific area per surface charge and $\lambda_{CC} = \Sigma/2\pi l_B$ the Gouy-Chapman length, $l_B$ being the Bjerrum length. This parameter characterizes the importance of the excluded volume interactions in the following way: as long as $\zeta \lesssim 1$ the steric effects are weak. However, when $\zeta \gtrsim 1$ (large $a$, small $\Sigma$) they cannot be neglected any more and saturation appears in the adsorbed layer. The curvature of the adsorbing surface might also play a role in determining the structure of the saturated layer. Comparing the width of the saturated layer with the radius of the charged object introduces a second parameter: $\zeta_2 = 2a^3/\Sigma r_s$ for a charged cylinder of radius $r_s$ and charge and $\zeta_3 = 3a^3/\Sigma r_s$ for a charged sphere of the same radius. At low curvature (large radii) the structure of the saturated layer is almost unaffected by the geometry of the charged surface. This case is characterized by $\zeta_2 \lesssim 1$ ($\zeta_3 \lesssim 1$) for a charged cylinder (sphere). On the other hand, when $\zeta_2 \gtrsim 1$ ($\zeta_3 \gtrsim 1$), the curvature of the surface becomes important.

The two systems discussed above and the earlier studies of flat surfaces [32-34,31,37] demonstrate that the modified Poisson–Boltzmann equation provides a convenient framework to study steric effects in ionic solutions. The simplicity and clarity of this approach makes it a convenient tool in studying specific systems in a more quantitative way. Of particular interest are the interactions between charged objects, such as spheres or cylinders in the presence of large ions. These interactions have drawn a lot of interest in the last few years because theory and experiments suggest that these interactions can become attractive at short distances, of the order of a few Angströms [46-53,2]. These are the same distances where the steric interactions are expected to become relevant and it is therefore useful to have a simple way of including these interactions. Hopefully, other effects can also be included in the Poisson-Boltzmann equation in a similar way.

This study has focused on an attempt to understand how steric repulsions can be included in the standard PB picture and what are their main consequences. This is done by accounting for the entropy of the solvent molecules in an approximate way. It is of particular importance close to charged surfaces where the counterion densities can become very large. Other factors that might be important in certain experimental situations have been neglected here. Among them are short range attractive interactions (e.g. van der Waals) and the discrete nature of the ions and the solvent molecules [54-58]. The additional inclusion of such effects in the PB approach is left to future studies. The main advantage of our approach is its simplicity and the ability to obtain analytically corrections to well known PB results such as the Graham equation.

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