Nonlinear screening of charged macromolecules

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We present several aspects of the screening of charged macromolecules in an electrolyte. After a review of the basic mean field approach, based on the linear Debye–Hückel theory, we consider the case of highly charged macromolecules, where the linear approximation breaks down and the system is described by the full nonlinear Poisson–Boltzmann equation. Some analytical results for this nonlinear equation give some interesting insight on physical phenomena like the charge renormalization and the Manning counterion condensation.

Keywords: colloids; electrolytes; nonlinear Poisson–Boltzmann equation

1. Introduction and the linear Poisson–Boltzmann equation

A colloidal suspension is a system composed of two substances, one dispersed in the other. The dispersed phase is composed of macromolecules, with size of the order of $10^{-8}$ to $10^{-6}$ m, while the dispersion medium or the continuous medium is composed of small micromolecules and/or microions, with size of the order of nanometres. Of particular interest are the charge-stabilized colloids, where the dispersed macromolecules have ionizable sites and, when immersed into the dispersion medium, they acquire a surface electric charge that ensures repulsion between them and thus allows the colloid to stabilize and prevents aggregation.

Since the length and time scales of the microcomponents of the dispersion medium are much smaller than the ones of the dispersed phase, it is convenient to average over the degrees of freedom of the dispersion medium and treat the system as a one-component system composed of the macromolecules that interact via an effective potential. To understand the physical and thermodynamic properties of these systems, it is important to determine this effective interaction between the macromolecules, which results not only from the direct interaction between the macromolecules but also the interaction mediated by the microions of the dispersion medium.

The basic theory to find this effective interaction for charge-stabilized colloids was developed independently by Derjaguin & Landau [1] and Overbeek & Verwey [2], and it is known as the DLVO theory. It is based on the work of

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Debye & Hückel [3]. Let us consider a spherical charged macromolecule, with radius \( a \) and charge \( Z e \) (\( e \) is the elementary charge) immersed in an electrolyte with positive microions of charge \( z_+ e \) and average density \( n_+ \), and negative microions of charge \( -z_- e \) and average density \( n_- \). Without loss of generality we can suppose \( Z > 0 \). The idea of Debye & Hückel [3] is to treat the microions in a mean field approximation: at temperature \( T \), the local density of microions of charge \( q = \pm z \pm e \) at a distance \( r \) from the macromolecule can be approximated by

\[
n_\pm (r) = n_\pm e^{-\beta q_\pm \Psi(r)}, \tag{1.1}
\]

where \( \Psi(r) \) is the electrostatic potential, and \( \beta = 1/(k_B T) \) with \( k_B \) the Boltzmann constant. Replacing this into the Poisson equation of electrostatics yields the Poisson–Boltzmann equation

\[
\Delta \Psi = -\frac{4\pi e}{\epsilon} (z_+ n_+ e^{-\beta z_+ \Psi} - z_- n_- e^{\beta z_- \Psi}), \tag{1.2}
\]

where \( \epsilon \) is the relative dielectric constant of the dispersion medium.

It is convenient to introduce the following notations: the reduced potential \( y = \beta e \Psi \), the Bjerrum length \( l_B = \beta e^2/\epsilon \) and the Debye length \( \kappa^{-1} = (4\pi l_B (z_+^2 n_+ + z_-^2 n_-))^{-1/2} \). With these notations, the Poisson–Boltzmann equation reads

\[
\Delta y = \frac{\kappa^2}{z_+ + z_-} [e^{z_- y} - e^{-z_+ y}]. \tag{1.3}
\]

If the electrostatic coupling between the macromolecule and the microions is small, \( y(r) \ll 1 \), for any distance \( r \), the nonlinear Poisson–Boltzmann equation (1.3) can be linearized to obtain

\[
\Delta y = \kappa^2 y. \tag{1.4}
\]

For an impenetrable spherical macromolecule with uniform surface charge (total charge \( Z e \) and radius \( a \)), the solution of this equation is known as the DLVO potential

\[
y(r) = Z l_B \frac{e^{\kappa a} e^{-\kappa r}}{1 + \kappa a \frac{r}{a}}. \tag{1.5}
\]

From this equation, one can see that \( 1/\kappa \) is the screening length.

It is also interesting to consider the case of cylindrical macromolecules, for instance, stiff polyelectrolytes, DNA, etc. As a first approximation, for an infinitely long cylinder with radius \( a \) and linear charge density \( e/\ell \), uniformly spread over its surface, the solution of equation (1.4) gives the electrostatic potential at a radial distance \( r \) from the cylinder

\[
y(r) = \frac{2\xi}{\hat{a} K_1(\hat{a})} K_0(\hat{r}), \tag{1.6}
\]

where \( K_0 \) and \( K_1 \) are the modified Bessel functions of order 0 and 1. We have defined the reduced linear charge density of the cylinder \( \xi = l_B/\ell \), and it is convenient to measure the distances in Debye length units: \( \hat{r} = \kappa r \) and \( \hat{a} = \kappa a \).
The boundary conditions that complement the differential equation (1.4) to yield the solution (1.6) are

\[
\lim_{r \to a} r \frac{dy}{dr} = -2 \xi \quad \text{and} \quad \lim_{r \to \infty} \nabla y(r) = 0.
\] (1.7)

It should be noticed that at large distances from the cylinder, compared with the Debye length, the potential exhibits again an exponential decay, as for the case of spherical macromolecules,

\[
y(r) \sim \frac{2 \xi}{\hat{a} K_1(\hat{a})} \sqrt{\frac{\pi}{2\kappa r}} e^{-\kappa r}, \quad r \gg \kappa^{-1}.
\] (1.8)

In the following sections, we turn our attention to the case of highly charged macromolecules, where the linear approximation breaks down and the full nonlinear equation (1.3) should be used. Several nonlinear effects appear, which we will review. In §2, we study the nonlinear phenomenon known as the charge renormalization [4,5], which is generic both for the spherical and cylindrical geometries. In §3, we focus our attention on the cylindrical case, where an analytical solution of the nonlinear Poisson–Boltzmann equation is available. From the analysis of this analytical solution we discuss the phenomenon of counterion condensation.

The scope of this review will be limited to the regime where the Poisson–Boltzmann equation is valid in its linear and nonlinear versions. This equation is based on a mean field approximation, which neglects the correlations between the microions of the electrolyte. The importance of the correlations between counternions can be characterized by the adimensional parameter \( \Gamma = z^2 l_B / d \), where \( d \) is the average distance of the counterions in the double layer. If \( \Gamma < 1 \), the mean field approach holds. At room temperature, and for a monovalent electrolyte in water, it is found that the mean field approach is valid, even for highly charged colloids. However, for multivalent electrolytes, the parameter \( \Gamma \) can become larger, thus requiring the use of more sophisticated theories to account for the microion correlations. An extensive discussion on the validity of Poisson–Boltzmann theory can be found, for instance, in Levin [6] and Levin et al. [7]. In the regime where correlation effects are important, some other interesting phenomena occur, for instance, overcharging [8,9] and like-charge attraction, which are reviewed elsewhere [6,10].

### 2. Charge renormalization

For a highly charged macromolecule, Poisson–Boltzmann equation (1.3) cannot be linearized near the macromolecule surface. However, owing to the screening effect, the potential will decay and become small, \( |y(r)| \ll 1 \), at large distances from the macromolecule surface, \( r - a \gg \kappa^{-1} \). In that far region, the linear version (1.4) of the Poisson–Boltzmann equation holds. Then, for a spherical macromolecule, the potential will behave as

\[
y(r) \sim A e^{-\kappa r} r
\] (2.1)
at large distances from the macromolecule. To find the constant of integration $A$, one needs to enforce the boundary condition at the surface of the macromolecule that the normal component of the electric field is proportional to the surface charge density. However, the form (2.1) of the potential is not valid in that close region. One needs to find also the form of the potential close to the macromolecule surface, and connect it to the large-distance behaviour (2.1) to find explicitly the integration constant $A$. In analogy to the linear solution (1.5), one can write $A = Z_{\text{ren}} l_B e^{\kappa a}/(1 + \kappa a)$, defining a renormalized charge $Z_{\text{ren}}$. The large-distance behaviour of the potential then takes a DLVO familiar form

$$y(r) \sim Z_{\text{ren}} l_B \frac{e^{\kappa a}}{1 + \kappa a} \frac{e^{-\kappa r}}{r},$$

(2.2)

but replacing the bare charge $Z$ of the macromolecule by the renormalized one $Z_{\text{ren}}$. In the cylindrical geometry, the renormalized charge concept also applies. In that case, the large-distance behaviour of the potential is

$$y(r) \sim 2 \xi_{\text{ren}} \frac{d}{dK_1(\hat{a})} K_0(\hat{r}),$$

(2.3)

with a renormalized linear charge density $\xi_{\text{ren}}$. The determination of the renormalized charge requires knowledge of the short-distance behaviour of the solution of the nonlinear Poisson–Boltzmann equation (1.3). This can be done numerically, as in the original work of Alexander et al. [4]. In experimental situations, the unknown renormalized charge is often taken as an adjustable fitting parameter. There are also analytical approaches to find the renormalized charge [5,11,12] mostly based on approximations using the solution to the nonlinear Poisson–Boltzmann equation in the planar case.

Let us illustrate the concept of charge renormalization in the planar geometry where an explicit solution for the nonlinear Poisson–Boltzmann equation is known [13,14]. The system is an infinite charged plane, with charge density $\sigma > 0$, immersed in an electrolyte, which, for simplicity, we consider symmetric: $z_+ = z_- = 1$. Let Ox be the axis perpendicular to the plane, which we suppose to be located at $x = 0$, and the electrolyte occupies the region $x > 0$. The nonlinear Poisson–Boltzmann equation in this situation reads

$$\frac{d^2 y(x)}{dx^2} = \kappa^2 \sinh y(x).$$

(2.4)

It can be integrated once by multiplying by $dy/dx$,

$$\frac{dy(x)}{dx} = -2 \kappa \sinh \frac{y(x)}{2},$$

(2.5)

where the boundary condition $dy/dx \to 0$ when $x \to \infty$ has been used. This last equation is separable and can be integrated, finally obtaining

$$y(x) = 2 \ln \frac{1 + Ae^{-\kappa x}}{1 - Ae^{-\kappa x}},$$

(2.6)
where $A$ is a constant of integration, which is found using the boundary condition at the surface of the charged plane

$$\frac{dy}{dx}(0) = -\frac{4\pi l_B \sigma}{e}.$$ (2.7)

Notice that at large distances from the plane, $kx \gg 1$, the potential behaves as

$$y(x) \sim 4Ae^{-kx}.$$ (2.8)

This is the expected behaviour for the linear version of the Poisson–Boltzmann equation in this geometry: $y''_{\text{lin}}(x) - k^2 y_{\text{lin}}(x) = 0$. The linear solution is $y_{\text{lin}}(x) = 4\pi l_B \sigma e^{-kx}/(e\kappa)$. Comparing with the large-distance behaviour of the nonlinear solution (2.8), one can define the renormalized surface charge density $\sigma_{\text{ren}}$, by writing the constant of integration $A$ as

$$A = \frac{\pi l_B \sigma_{\text{ren}}}{e\kappa}.$$ (2.9)

Then, the large-distance behaviour of the potential is

$$y(x) \sim \frac{4\pi l_B \sigma_{\text{ren}}}{e\kappa} e^{-kx}.$$ (2.10)

To find explicitly the renormalized charge, one needs to apply the boundary condition (2.7) at the surface of the charged plane. For this, one needs the short-distance behaviour of the potential. From the explicit solution (2.6), we find

$$y(x) = 2\ln \frac{1 + A}{1 - A} - \frac{4Ax}{1 - A^2} + O(x^2),$$ (2.11)

when $x \to 0$. Using this, we apply the boundary condition (2.7) to find

$$\frac{A}{1 - A^2} = \frac{\pi \sigma_{\text{ren}}}{e\kappa}.$$ (2.12)

Solving and using equation (2.9), we find the renormalized surface charge

$$\hat{\sigma}_{\text{ren}} = \frac{\sqrt{4\hat{\sigma}^2 + 1} - 1}{2\hat{\sigma}},$$ (2.13)

where we have defined reduced charge densities $\hat{\sigma} = \pi l_B \sigma/(e\kappa)$ and $\hat{\sigma}_{\text{ren}} = \pi l_B \sigma_{\text{ren}}/(e\kappa)$.

Figure 1 shows a plot of the renormalized charge as a function of the bare charge. When $\hat{\sigma} \ll 1$, the renormalized charge and the bare charge are the same $\sigma_{\text{ren}} \approx \sigma$, as expected, since the linear theory is valid when $\hat{\sigma} \ll 1$. But when the bare charge increases, the nonlinear effects take place, and the renormalized charge differs from the bare charge. Notice the saturation effect: when $\sigma \to \infty$, the renormalized charge approaches a finite value $\hat{\sigma}_{\text{ren}} \to 1$. This saturation effect can also appear in other theories obtained by modification of the Poisson–Boltzmann equation using a density functional formulation [15]. In that saturation regime,
the large-distance behaviour potential becomes independent of the bare charge of the plane

\[ y_{\text{sat}}(x) \sim y_0 e^{-\kappa x} = 4e^{-\kappa x}. \] (2.14)

The value \( y_0 = 4 \) plays an important role. It can be seen as an effective surface potential for the plane, if one wants to match the linear solution of the Poisson–Boltzmann equation with the nonlinear one in the close vicinity of the highly charged plane. This is also the starting point to find the renormalized charge at saturation for highly charged macromolecules of arbitrary shape. For these macromolecules, when they are highly charged, the linear Poisson–Boltzmann equation can be solved with an effective boundary condition of constant surface potential \( y_0 \), to find the behaviour of the potential at large distances and the corresponding renormalized charge, as explained in Bocquet et al. [16]. For instance, for a spherical macromolecule, the solution of the linear Poisson–Boltzmann equation with the effective constant potential boundary condition at the surface of the macromolecule \( y(a) = y_0 = 4 \), is

\[ y_{\text{sat, sphere}}(r) = y_0 e^\kappa a \frac{e^{-\kappa r}}{r}. \] (2.15)

The nonlinear solution, at large distances, has the behaviour given by equation (2.2). Comparing both equations (2.2) and (2.15), we find an approximate value for the renormalized charge in the saturation regime

\[ Z_{\text{ren}}^{\text{sat}} = \frac{a}{l_B} y_0 (\kappa a + 1) = \frac{a}{l_B} (4\kappa a + 4). \] (2.16)

This approximation is based on the planar solution of the nonlinear Poisson–Boltzmann equation, and therefore it is accurate for large macromolecules with \( \kappa a \gg 1 \), and only at the first order in \( \kappa a \). One can improve this estimate by developing a planar expansion of the solution of the spherical geometry, as done in Shkel et al. [11], Trizac et al. [17] and Téllez & Trizac [12]. Up to terms of
order $O(1/(\kappa a))$, the renormalized charge at saturation for spheres in a 1:1 electrolyte is [17]

$$Z_{\text{sat}}^{\text{ren}} = \frac{a}{l_B} (4\kappa a + 6).$$

(2.17)

The starting point to obtain estimates of the renormalized charge at saturation is the value $y_0$ of the effective surface potential at saturation in the planar geometry. This depends only on the constitution of the electrolyte. We propose now a simple formula that gives $y_0$ in the generic case of a multi-component electrolyte, composed of several species of ions with charges $\{q_\alpha e\}$ and densities $\{n_\alpha\}$. The nonlinear Poisson–Boltzmann equation in the planar geometry reads now

$$y''(x) + 4\pi l_B \sum_\alpha q_\alpha n_\alpha e^{-q_\alpha y(x)} = 0.$$

(2.18)

Multiplying this equation by $y'(x)$, it can be integrated once to find

$$(y'(x))^2 = 8\pi l_B \sum_\alpha n_\alpha (e^{-q_\alpha y(x)} - 1),$$

where the boundary condition $y'(x) \to 0$ when $x \to \infty$ has been used. Introducing the inverse Debye length $\kappa x = \int_0^{y(0)} \frac{du}{\sqrt{\sum_\alpha \frac{2}{q_\alpha^2 n_\alpha} \sum_\alpha n_\alpha (e^{-q_\alpha u} - 1)}}.$

(2.20)

Suppose the charged plane is located at $x = 0$ and positively charged, and we are in the saturation regime, therefore $y(0) \to +\infty$. At large distances from the plane, $\kappa x \gg 1$, the potential behaves as $y(x) \sim y_0 e^{-\kappa x}$, thus $\kappa x = \ln y_0 - \ln y(x) + o(\ln y(x))$ as $y(x) \to 0$. Replacing in equation (2.20) we find

$$\ln y_0 = \lim_{y \to 0} \left[ \int_0^y \frac{du}{\sqrt{\sum_\alpha \frac{2}{q_\alpha^2 n_\alpha} \sum_\alpha n_\alpha (e^{-q_\alpha u} - 1)}} + \ln y \right]$$

$$= \text{Pf.} \int_0^\infty \frac{du}{\sqrt{\sum_\alpha \frac{2}{q_\alpha^2 n_\alpha} \sum_\alpha n_\alpha (e^{-q_\alpha u} - 1)}}.$$

(2.21)

Thus, the value of $y_0$ is expressed as a Hadamard finite part (Pf.) of the integral (2.21). Alternatively, it can be computed from

$$\ln y_0 = \int_0^1 \left[ \frac{1}{\sqrt{\sum_\alpha \frac{2}{q_\alpha^2 n_\alpha} \sum_\alpha n_\alpha (e^{-q_\alpha u} - 1)}} - \frac{1}{u} \right] du + \int_1^\infty \frac{du}{\sqrt{\sum_\alpha \frac{2}{q_\alpha^2 n_\alpha} \sum_\alpha n_\alpha (e^{-q_\alpha u} - 1)}}.$$

(2.22)

In the case of a two-component electrolyte, $q_1 = z_+$ and $q_2 = -z_-$, the saturation value $y_0$ can be expressed as a function of the ratio $r = z_+/z_-$,

$$y_0 = \frac{1}{z_-} \exp \left[ \text{Pf.} \int_0^\infty \frac{du}{\sqrt{\frac{r}{2 (e^{-ru/(1+r)} + (e^u/(1+r-1)) - 1)}}} \right].$$

(2.23)

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Table 1. Value of the saturation potential for several electrolytes.

<table>
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<th>$z_+ : z_-$</th>
<th>1:5</th>
<th>1:4</th>
<th>1:3</th>
<th>1:2</th>
<th>1:1</th>
<th>2:1</th>
<th>3:1</th>
<th>4:1</th>
<th>5:1</th>
</tr>
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<tr>
<td>$y_0$</td>
<td>0.56080</td>
<td>0.71742</td>
<td>0.99388</td>
<td>1.6077</td>
<td>4</td>
<td>6</td>
<td>8.7070</td>
<td>12.314</td>
<td>17.337</td>
</tr>
<tr>
<td>$z_+ : z_-$</td>
<td>2:3</td>
<td>3:2</td>
<td>2:5</td>
<td>5:2</td>
<td>3:5</td>
<td>5:3</td>
<td>1:10</td>
<td>10:1</td>
<td></td>
</tr>
<tr>
<td>$y_0$</td>
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<td>2.4611</td>
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<td>1.7544</td>
<td>0.26761</td>
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</tbody>
</table>

In the cases of electrolytes with $z_+ : z_-$ equal to 1:1, 1:2, and 2:1, the integral can be computed exactly to find the known values $y_{0}^{1:1} = 4$, $y_{0}^{1:2} = 6(2 - \sqrt{3}) \approx 1.6077$ and $y_{0}^{1:2} = 6$. Table 1 gives the value of the saturation potential for other electrolytes. In the table, we report the saturation potential even for highly multi-valent electrolytes (1:10), but it should be remembered that for highly multi-valent electrolytes, the mean field Poisson–Boltzmann theory is not valid at room temperature in water, because correlation effects are important, as discussed at the end of §1. Nevertheless, the results reported here can be useful in other situations, for instance, in a solvent with a very large dielectric constant, or in the context of dusty plasmas at high temperature, where the Bjerrum length $l_B$ can be much smaller than its counterpart in water at room temperature ($\approx 7$ Å), and the coupling parameter $\Gamma = z_+^2 l_B / d$ can remain small.

3. Cylindrical macromolecules

(a) Exact solution for Poisson–Boltzmann equation and the connection problem

In this section, we focus our attention on the study of the screening of a thin cylindrical macromolecule, with radius $a \ll \kappa^{-1}$. Besides the charge renormalization effect, another interesting phenomenon that occurs in this geometry is the counterion condensation. This was first realized by Onsager and studied by Manning [18] and Oosawa [19]. To understand this phenomenon, consider the Boltzmann factor between the macromolecule and an ion of opposite charge (counterion): $\exp(-2z_+ \xi \ln r) = r^{-2z_+ \xi}$. It diverges when $r \to 0$, and furthermore it is not integrable near $r \to 0$ if $\xi > 1/z_-$. This means that, for an infinitely thin macromolecule, with radius $a = 0$, the thermodynamics are not properly defined unless $\xi < 1/z_-$. In real situations $a \neq 0$. For $ka \ll 1$, when $\xi > 1/z_-$, the density of counterions will be very large near the surface of the macromolecule. These counterions are bound to the macromolecule: besides the diffuse screening cloud of ions around the macromolecule, there is also a thin layer of condensed counterions very near to the surface of the cylinder.

This counterion condensation effect can be studied quantitatively in the mean field approximation, since an analytical solution of the nonlinear Poisson–Boltzmann equation in the cylindrical geometry is available. For a 1:1 electrolyte, this solution was found by McCoy et al. [20], in a different context, in relation to the correlation functions of the two-dimensional Ising model. Later on, Widom [21] developed the solution for the asymmetric cases 2:1 and 1:2, and Tracy & Widom [22] studied the short-distance asymptotics of the solution and solved the problem of connecting the large-distance and the short-distance behaviours of the solution. The consequences of this mathematical work to the screening of...
cylindrical macromolecules were reported by McCaskill & Fackerell [23], Tracy & Widom [24] and Trizac & Téllez [25]. A more extensive study is presented in Téllez & Trizac [26]. We summarize here some of the main findings of that work.

The short-distance behaviour of the potential can be obtained by a physical argument. Very close to the charged cylindrical macromolecule, one would expect the potential to be the bare Coulomb potential $-2A \ln \hat{r} + \text{constant}$, with $A$ some constant related to the charge of the macromolecule. By replacing this ansatz into the Poisson–Boltzmann equation (1.3), one can compute systematically the following terms of the short-distance expansion, to find [22,26,27]

$$y(\hat{r}) = -2A \ln \hat{r} + 2 \ln B - 2 \ln \left[1 - \frac{B^2 \hat{r}^{1-2A}}{16(1-A)^2}\right] + O(\hat{r}^{2+2A}).$$  (3.1)

We consider here a 1:1 electrolyte. For the general case of a $z_+ : z_-$ electrolyte, see Trizac & Téllez [27]. $A$ and $B$ are some constants of integration. The constant $A$ can be related to the charge density of the electrolyte by writing the first boundary condition (1.7)

$$\xi = A - \frac{(2-2A)(\kappa a)^{2-2A}}{16(1-A)^2 - B^2(\kappa a)^{2-2A}}.$$  (3.2)

From §2, we already know the large-distance behaviour of the potential, it is the screened potential (2.3)

$$y(r) \sim 4\lambda K_0(\hat{r}),$$  (3.3)

where $\lambda$ is some constant related to the renormalized charge by

$$\xi_{\text{ren}} = \hat{a} K_1(\hat{a}) \lambda/2.$$  (3.4)

By using the explicit analytical solution of the nonlinear Poisson–Boltzmann equation from McCoy et al. [20], Widom [21] and Tracy & Widom [22] were able to solve the connection problem of relating the constants of integration from the short-distance behaviour $A$ and $B$ to the one of the large-distance behaviour $\lambda$. To satisfy the boundary condition $y'(r) \to 0$ when $r \to \infty$, the constants $A$ and $B$ need to satisfy

$$B = 2^{3A} \frac{\Gamma\left(\frac{1+A}{2}\right)}{\Gamma\left(\frac{1-A}{2}\right)},$$  (3.5)

where $\Gamma$ is the gamma function, and $A$ and $\lambda$ need to satisfy

$$\lambda = \frac{1}{\pi} \sin\left(\frac{\pi A}{2}\right).$$  (3.6)

The first physical consequence of these relations is that we can obtain an analytical expression for the renormalized charge, by combining equations (3.2), (3.4) and (3.6). In the simplest situation, when $a = 0$, this gives $A = \xi$ and

$$\xi_{\text{ren}} = \frac{2}{\pi} \sin\left(\frac{\pi \xi}{2}\right).$$  (3.7)
Figure 2. Short-distance expansion of the potential (3.9) (solid line) compared with $-2 \ln(\hat{r}/(4\mu))$ (dashed line). Parameter $\mu = 0.2$.

(b) Counterion condensation

The previous discussion, and in particular equation (3.1) are only valid provided that $A < 1$. Indeed, if $A = 1$, equation (3.1) becomes singular: the last term becomes of the same order as the second, and besides, the constant $B$ from equation (3.5) becomes undefined. This is the mathematical signature of the counterion condensation phenomenon. Notice that for $a = 0$, the constant $A$ is the linear charge of cylinder $A = \xi$, and the value $\xi_{\text{Manning}} = 1$ is precisely the threshold for counterion condensation discussed earlier.

For a cylinder with non-zero radius $a \neq 0$, notice that, using equation (3.2), the threshold $A = \xi_{\text{Manning}} = 1$ corresponds for the linear charge to the threshold

$$\xi_c = 1 + \frac{1}{\ln \hat{a} + C}, \tag{3.8}$$

where $C = \gamma - 3 \ln 2 \simeq -1.502$, with $\gamma$ the Euler constant. Note that there is a negative logarithmic correction in the radius $a$ of the cylinder to the Manning value $\xi_{\text{Manning}} = 1$ for the threshold for condensation: $\xi_c \leq 1$.

To extend the solution beyond the condensation threshold, Tracy & Widom [22] suggested to write $A$ as a complex number $A = 1 - i\mu/2$. Replacing into equation (3.1), the short-distance expansion of the potential now reads

$$y(r) = -2 \ln \hat{r} - 2 \ln \frac{\sin(-2\mu \ln \hat{r} - 2\mu C)}{4\mu}. \tag{3.9}$$

The constant $\mu$ can be expressed in terms of the bare linear charge density $\xi$ by using the first boundary condition (1.7), and connected to the large-distance expansion of the potential and the renormalized charge by means of equation (3.6), replacing $A = 1 - i\mu/2$; for details see Téllez & Trizac [26].
Notice the first term of expansion (3.9): \(-2 \ln \hat{r}\). It is the bare Coulomb potential of a charged line with linear charge density \(\xi_{\text{Manning}} = 1\). This a characteristic of the counterion condensation phenomenon. At intermediate distances of the charged cylinder, one ‘sees’ a cylinder with an effective charge \(\xi_{\text{Manning}} = 1\), if the bare charge exceeds the threshold value \(\xi_c\). The second term of equation (3.9) can become very large in the close proximity of the cylinder. This second term represents the thin layer of condensed counterions located at the surface of the cylinder. Figure 2 shows a plot of the potential close to the cylinder, and compares it to the bare term \(-2 \ln \hat{r}\).

4. Concluding remarks

To summarize and conclude the review presented here, we would like to stress the differences between the different linear charge densities that we presented for cylindrical macromolecules: renormalized charge, Manning charge, threshold charge for counterion condensation.

The renormalized charge characterizes the behaviour of the potential far from the charged macromolecule. At those large distances, \(r \gg \kappa^{-1}\), the potential exhibits an exponential decay. The prefactor of this exponential decay is proportional to the renormalized charge, as shown in equation (2.3).

At short distances, there are two possible behaviours, depending on the value of the bare linear charge density \(\xi\) compared with the threshold value \(\xi_c\) given by equation (3.8). If \(\xi < \xi_c\), the potential behaves as given by equation (3.1). It is a bare Coulomb potential with a prefactor given in terms the bare charge of the macromolecule. If \(\xi > \xi_c\), the counterion condensation takes place. The short-distance behaviour of the potential is now given by equation (3.9). A thin layer of counterions is bound to the surface of the cylinder, which makes the potential very large in that region. Beyond this layer, the potential behaves as \(-2\xi_{\text{Manning}} \ln r\): the bare Coulomb potential for a charged line but with an effective charge \(\xi_{\text{Manning}} = 1\), the Manning charge for counterion condensation (figure 2). Notice that if the radius of the cylinder \(a \neq 0\), the Manning value differs from the threshold value: \(\xi_{\text{Manning}} > \xi_c\).

The counterion condensation phenomenon can be only noticed at close proximity to the charged cylinder by the change of the short-distance behaviour of the potential from equations (3.1) to (3.9). At large distances, the potential is always given by equation (2.3), regardless of whether the counterion condensation has taken place or not. When \(\xi = \xi_c\), no singularity appears in equation (2.3), nor in the renormalized charge \(\xi_{\text{ren}}\) that characterizes only the large-distance behaviour of the potential. Also, notice that \(\xi_{\text{ren}} \neq \xi_{\text{Manning}}\) and \(\xi_{\text{ren}} \neq \xi_c\). This has caused some confusion in the past, since in the original work of Manning [18], in the condensed phase, the diffuse screening cloud of the remaining uncondensed counterions around the charged cylinder was treated using the linear Poisson–Boltzmann equation and using an effective charge of the cylinder given by \(\xi_{\text{Manning}} = 1\) to account for the counterion condensation. It turns out that this picture is not completely correct, since besides the counterion condensation, there are also additional nonlinear effects in the uncondensed cloud that are
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responsible for an additional charge renormalization. As a result $\xi_{\text{ren}} \neq \xi_{\text{Manning}}$. For example, in the limiting case $a = 0$, from equation (3.7), we obtain $\xi_{\text{ren}} = 2/\pi \simeq 0.63662 < \xi_{\text{Manning}} = 1$.

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