Exact asymptotic expansions for the cylindrical Poisson-Boltzmann equation

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The mathematical theory of integrable Painlevé/Toda type systems sheds new light on the behavior of solutions to the Poisson-Boltzmann equation for the potential due to a long rod-like macroion. We investigate here the case of symmetric electrolytes together with that of 1:2 and 2:1 salts. Short and large scale features are analyzed, with a particular emphasis on the low salinity regime. Analytical expansions are derived for several quantities relevant for polyelectrolytes theory, such as the Manning radius. In addition, accurate and practical expressions are worked out for the electrostatic potential, which improve upon previous work and cover the full range of radial distances.

I. INTRODUCTION

Polyelectrolytes are polymer molecules bearing charged units. Within the associated relevant cylindrical geometry, the long range character of Coulombic interactions is responsible for the phenomenon of counterion condensation. In essence, the electric potential created by the charged polyion features a logarithmic dependence on radial distance. The competing entropy of confinement is of a similar functional form, which may result in a condensation of counterions onto the charged cylinder, when Coulombic interactions prevail, that is when the polyelectrolyte line charge exceeds a given threshold (see e.g. [1]). Strongly charged linear polyelectrolytes thereby effectively reduce their line charge density. This was realized by Onsager in the 1960s and formalized subsequently [2, 3]. It turns out that this phenomenon in detail [1, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14]. Unfortunately, even within mean-field, exact results are scarce, and one has to resort to numerical resolution or propose approximations.

This paper is dedicated to the derivation of exact results within PB theory. We will be interested in the behavior of a unique infinite charged cylinder of radius $a$ and uniform line charge density $e/b$, where $e > 0$ is the elementary charge and $b$ may be viewed as an equivalent average spacing between charges along the polyion. This macroion is immersed in an infinite electrolyte containing two species of microions (salt): their bulk densities $n_1$ and $n_2$ far from the cylinder define the Debye length $1/\kappa$ through $\kappa^2 = 4\pi\epsilon B (n_1 z_1^2 + n_2 z_2^2)$. Here, $z_i e$ denotes the charge of species $i$ and $\epsilon B = \beta e^2/\varepsilon$ is the Bjerrum length, which involves the solvent dielectric permittivity $\varepsilon$ and the inverse temperature $\beta$. We will focus on the three situations where analytical progress is possible: 1:1 electrolytes (or more generally symmetric $z:z$ electrolytes), together with the 1:2 and 2:1 cases. We denote by 1:2 the situation where coions are monovalent ($z_+ = 1$ for a positively charged polyion) and counterions are divalent ($z_- = -2$ or more generally, $z_- = -2z_+$). On the other hand, the notation 2:1 refers to divalent coions with monovalent counterions. To be specific, introducing the dimensionless radial distance $\tilde{r} = \kappa r$, the equations to be solved for the dimensionless electrostatic potential $y = \beta e \psi$ (\psi being the electric potential) read

\[
\frac{d^2y}{d\tilde{r}^2} + \frac{1}{\tilde{r}} \frac{dy}{d\tilde{r}} = \sinh(y) \quad (1:1) \quad (1.1a)
\]

\[
\frac{d^2y}{d\tilde{r}^2} + \frac{1}{\tilde{r}} \frac{dy}{d\tilde{r}} = \frac{1}{3} (e^{2y} - e^{-y}) \quad (1:2) \quad (1.1b)
\]

\[
\frac{d^2y}{d\tilde{r}^2} + \frac{1}{\tilde{r}} \frac{dy}{d\tilde{r}} = \frac{1}{3} (e^y - e^{-2y}) \quad (2:1) \quad (1.1c)
\]

The solution should satisfy the boundary conditions at $\tilde{a} = \kappa a$

\[
\lim_{\tilde{r} \to \infty} \tilde{r} \frac{dy}{d\tilde{r}} = -2\xi
\]

and $\lim_{\tilde{r} \to 0} y(\tilde{r}) = 0$. We have introduced here the dimensionless bare line charge $\xi = \ell_B/b$, that plays a key role below. It is understood that the cylinder is positively charged, without loss of generality [14].

We shall not comment here the well documented limitations of the mean-field approximation (see e.g. [16, 17, 18, 19, 20, 21]), but only summarize the main findings. In a solvent like water at room temperature, mean-field provides an accurate description in the 1:1 case for all existing polyelectrolytes. We also expect the 2:1 situation to be correctly described, while in the 1:2 case, micro-ionic correlations, discarded within mean-field, play an important role at large values of $\xi$. Schematically, the coupling parameter $\Gamma = z^{1/2} \sqrt{\xi \ell_B/(2\pi a)}$ allows to appreciate the importance of those correlations where $z$ stands for the counter-ions valency. When $\Gamma < 2$, mean-field holds.
The crux of our approach lies in the mapping between equations \[\text{1.1}\] and Painlevé/Toda type equations (see below), that are in particular relevant to describe the spin-spin correlator in the two-dimensional Ising model, and have been the subject of deep mathematical investigations \[\text{22, 23, 24}\]. It seems that this body of work has not been fully transposed in the language of polyelectrolyte physics, with the exception of the limit \(\kappa a \to 0\)\(^+\) (e.g. realized with a charged line of vanishing thickness at finite salt) where it allowed to show rigorously the existence of the condensation \[\text{4, 10}\] and also provided exact results for the electric potential \[\text{4, 11}\]. However, it will appear below that the limit \(\kappa a \to 0\)\(^+\) is approached logarithmically slowly so that finite salt correction cannot be neglected in practice. It also turns that to the best of our knowledge, the case of 2:1 electrolytes has not been considered in the physics literature, whereas some results have been reported in the reverse 1:2 case, but below the condensation threshold and again in the limit \(\tilde{a} \to 0\) \[\text{11}\].

Our aim is to fill these gaps. Our formulas will prove extremely accurate when compared to the numerical solutions of \[\text{1.1}\].

The paper is organized as follows. In section II, the formal solutions of Eqs. \[\text{1.1}\] will be given. As such, these relations are not useful in practice, and deriving “ready-to-use” and operational expressions will be the purpose of the subsequent analysis. Section III will then be devoted to the derivation of asymptotic expansions for the electric potential \[\text{1.1}\] for a given \(\kappa a \rightarrow 0\)\(^+\). Our aim is to fill these gaps. Our formulas will prove extremely accurate when compared to the numerical solutions of \[\text{1.1}\].

The solutions are expressed as determinants of certain integral operators on \(\mathbb{R}^+\) with kernel

\[
K_{\tilde{r}}(u, v) = \frac{e^{-\tilde{r}(u+u^{-1})/2}}{u + v}.
\]

In the 1:2 case the solution reads

\[
y_{12}(\tilde{r}) = \ln \det(1 - \Lambda K_{\tilde{r}}^{(1)}) - \ln \det(1 - \Lambda K_{\tilde{r}}^{(2)})
\]

while in the 2:1 situation it is

\[
y_{21}(\tilde{r}) = \ln \det(1 + \Lambda K_{\tilde{r}}^{(0)}) - \ln \det(1 + \Lambda K_{\tilde{r}}^{(1)})
\]

where

\[
K_{\tilde{r}}^{(0)} = (\zeta - \zeta^2)O_{\tilde{r}}^{(1)} + (\zeta^2 - \zeta)O_{\tilde{r}}^{(2)}
\]

\[
K_{\tilde{r}}^{(1)} = (\zeta^2 - 1)O_{\tilde{r}}^{(1)} + (\zeta - 1)O_{\til{r}}^{(2)}
\]

\[
K_{\til{r}}^{(2)} = (1 - \zeta)O_{\til{r}}^{(1)} + (1 - \zeta^2)O_{\til{r}}^{(2)}.
\]

Here \(\zeta = e^{2\pi/3}\) and \(O_{\til{r}}^{(1)}\) and \(O_{\til{r}}^{(2)}\) are integral operators on \(\mathbb{R}^+\) with kernel

\[
O_{\til{r}}^{(1)}(u, v) = \frac{e^{-\til{r}(1-\zeta)u+(1-\zeta^2)u^{-1})/(2\sqrt{3})}}{-\zeta u + v}.
\]

II. FORMAL SOLUTION TO THE PROBLEM

Poisson–Boltzmann equation \[\text{1.1}\] in the 1:1 case has been solved in Ref. \[\text{22}\] in the context of the Painlevé III theory, since \(e^{\nu/2}\) obeys a particular case of Painlevé III equation (see e.g. \[\text{26}\] and appendix A more details together with a relevant bibliography may be found in \[\text{22}\]). More generally, Eqs. \[\text{1.1a}, \text{1.1b}\] and \[\text{1.1c}\] are the first equations of the hierarchy of cylindrical Toda equations. In Ref. \[\text{22}\], a class of solutions to this Toda equations has been reported, hence the solutions to the Poisson–Boltzmann equations \[\text{1.1a}, \text{1.1b}\] and \[\text{1.1c}\]. These solutions obey a boundary condition at \(\tilde{r} \to \infty\), given in terms of a constant \(\lambda\) by

\[
y_{11}(\tilde{r}) \sim 4\lambda K_0(\tilde{r})
\]

for the 1:1 case,

\[
y(\tilde{r}) \sim 6\lambda K_0(\tilde{r})
\]

for both 1:2 and 2:1 cases.

The solutions are expressed as determinants of certain operators. For 1:1 salts, we have

\[
y_{11}(\tilde{r}) = 2\ln \det(1 + \lambda K_{\til{r}}) - 2\ln \det(1 - \lambda K_{\til{r}})
\]

with \(K_{\til{r}}\) an integral operator on \(\mathbb{R}^+\) with kernel

\[
K_{\til{r}}(u, v) = \frac{e^{-\til{r}(u+u^{-1})/2}}{u + v}.
\]

Before embarking on the analysis of the properties of Eqs. \[\text{1.1}\], we note that for a macroion with a small reduced linear charge density \(\xi_{\text{eff}}\), the problem may be linearized with solution

\[
y_{\text{lin}}(\tilde{r}) = \frac{2\xi_{\text{eff}}}{\til{a} K_1(\til{a})} K_0(\tilde{r}).
\]

Here \(K_0\) and \(K_1\) are the modified Bessel functions. Since the solution to the non-linear problem \[\text{1.1}\] vanishes when \(\tilde{r} \to \infty\) we necessarily have that for large distances \(\til{r}, y(\til{r})\) behaves as \[\text{1.3}\]. However in the non-linear case the constant \(\xi_{\text{eff}}\) is not the bare charge of the rod. This quantity is called the effective charge and depends on salinity conditions, bare charge, temperature etc. In the weak overlap approximation where the double–layers of different macroions are well separated (it is typically the case when their mutual distance is larger than \(1/\kappa\)), the (squared) effective charge governs the amplitude of the interaction free energy.
and $O^{(2)}_{\tau}(u,v) = O^{(1)}_{\tau}(u,v)$, the bar denoting complex conjugation. It can be shown \cite{22} that $\det(1 - \lambda K^{(1)}_{\tau}) = \det(1 - \lambda K^{(0)}_{\tau})$ (making use of a change of variable $u \to u^{-1}$), thus from the solution to the case 1:2, $y_{12}$, one can obtain the solution for the case 2:1 as $y_{21} = -y_{12}$ with the change $\lambda \to -\lambda$, as previously announced.

To solve completely the problem we are interested in, we should impose the boundary condition \cite{1,2} to express $\lambda$ in terms of the bare charge $\xi$. Notice that the constant $\lambda$ introduced above is closely related to the effective charge $\xi_{\text{eff}}$. Indeed,

\begin{align}
\xi_{\text{eff}} &= 2\tilde{a}K_1(\tilde{a}) \lambda \quad (1:1) \quad (2.8a) \\
\xi_{\text{eff}} &= 3\tilde{a}K_1(\tilde{a}) \lambda \quad (1:2) \quad (2.8b) \\
\xi_{\text{eff}} &= 3\tilde{a}K_1(\tilde{a}) \lambda \quad (2:1) \quad (2.8c)
\end{align}

The determination of the effective charge in terms of the bare one is interesting per se, since it allows to use, at large distances, the linear theory expression, provided that the bare charge is replaced by the effective one. Writing down the boundary condition \cite{1,2} gives the bare charge as a function of the effective one. In the limiting case $\tilde{a} \to 0$, this relation may be inverted since the associated (so-called) connection problem was solved: knowing the large-distance behavior \cite{22} of the solutions \cite{22}, \cite{24} and \cite{25}, the short-distance behavior for $r \to 0$ follows \cite{24}. The 1:1 and 1:2 cases for $\tilde{a} = 0$ were studied in detail by Tracy and Widom in Ref. \cite{11}. The 2:1 situation, even for $\tilde{a} = 0$, was not explicitly considered in Ref. \cite{11}, although it can be obtained following the same lines as those exposed in \cite{11}.

The situation with $\tilde{a} \neq 0$ is analytically more difficult, but we will show below that useful expressions may nevertheless be derived there, that rely on accurate approximations for certain key quantities related to the parameter $\lambda$. These expressions allow to fully cover the regime of thin cylinders and/or low salt $\tilde{a} < 1$, whereas the discussion of results valid at arbitrary salt content is deferred to section \ref{sec:VI}.

### III. ASYMPTOTIC EXPANSIONS

The results reported are obtained from the limit $\tilde{a} \to 0$ but turn out to be reliable for $\tilde{a} < 1$ (see below).

#### A. Short distance behavior

The general results of Ref. \cite{24} for the cylindrical Bullough-Dodd equation (which belongs to the Toda family and onto which the above asymmetric PB equation can be mapped) allow to find the small distance asymptotics of $y(r)$ given in Eq. \cite{24} for 1:2 electrolytes. Allowing for negative values of $\xi$ will therefore also provide the solution to the 2:1 case. Similarly, the 1:1 behavior encoded in Eq. \cite{22} follows from Theorem 3 of Ref. \cite{22} and its corollaries (in particular those derived in section IV.I of \cite{22}).

It turns that the parameter $\lambda$ plays an essential role here. Its position with respect to a threshold value $\lambda_c$ discriminates two different short scale behaviors. The threshold values read:

\begin{align}
\lambda_{(1:1)}^c &= \frac{1}{\pi} \quad (3.1a) \\
\lambda_{(1:2)}^c &= \frac{1}{2\sqrt{3} \pi} \quad (3.1b) \\
\lambda_{(2:1)}^c &= \frac{\sqrt{3}}{2 \pi} \quad (3.1c)
\end{align}

We will show that the condition $\lambda < \lambda_c$ is equivalent to $\xi < \xi_c$ where $\xi_c$ is some threshold charge. In the limit $\kappa a = \tilde{a} \to 0$, $\xi_c$ coincides with the known Manning parameter beyond which counterion condensation sets in:

\begin{align}
\xi_{\text{Mann}}^{(1:1)} &= 1 \quad (3.2) \\
\xi_{\text{Mann}}^{(1:2)} &= 1/2 \quad (3.3) \\
\xi_{\text{Mann}}^{(2:1)} &= 1 \quad (3.4)
\end{align}

However, as soon as $\tilde{a} \neq 0$, it will appear that $\xi_c$ significantly differs from $\xi_{\text{Mann}}$. For $\lambda < \lambda_c$, we have \cite{22,22}.

\begin{align}
y_{11}(\tilde{r}) &= -2A \ln \tilde{r} + 2 \ln B - 2 \ln \left[1 - \frac{B^2 2^{-2A}}{16(1-A)^2}\right] + O(\tilde{r}^{2+2A}) \quad (1:1) \\ 
y_{12}(\tilde{r}) &= -2A \ln \tilde{r} + \ln B - \ln \left[1 - \frac{B^2 2^{-4A}}{12(2A-1)^2}\right] + O(\tilde{r}^{2+2A}) \quad (1:2) \\ 
y_{21}(\tilde{r}) &= -2A \ln \tilde{r} + \ln B - 2 \ln \left[1 - \frac{\tilde{r}^{2-2A}B}{24(1-A)^2}\right] + O(\tilde{r}^{2+4A}) \quad (2:1)
\end{align}
where \( A \) is a function of \( \lambda \), see Eqs. (3.11) and (3.13) below, and

\[
B = \begin{cases} 
2^{3A} \left( \frac{\Gamma \left( \frac{1+4A}{2} \right)}{\Gamma \left( \frac{1-2A}{3} \right)} \right) & \text{(1 : 1)} \\
3^{3A}2^{2A} \left( \frac{\Gamma \left( \frac{1+4A}{2} \right)}{\Gamma \left( \frac{2-3A}{3} \right)} \right) & \text{(1 : 2)} \\
3^{3A}2^{2A} \left( \frac{\Gamma \left( \frac{1+4A}{2} \right)}{\Gamma \left( \frac{1-2A}{3} \right)} \right) & \text{(2 : 1)} 
\end{cases}
\]  

(3.6a, 3.6b, 3.6c)

Here \( \Gamma \) is the Euler gamma function.

On the other hand, for \( \lambda > \lambda_c \) (or equivalently \( \xi > \xi_c \)), the short distance behavior is characterized by a parameter \( \mu > 0 \) and we have

\[
e^{-y_{1/2}} \simeq \frac{\tilde{r}}{4\mu} \sin \left[ -2\mu \log(\tilde{r}) - 2\mu C^{(1:1)} \right] \quad (3.7a) \\
e^{-y_{1/2}} \simeq \frac{\tilde{r}}{3\sqrt{3}\mu} \sin \left[ -3\mu \log(\tilde{r}) - 3\mu C^{(1:2)} \right] \quad (3.7b) \\
e^{-y_{2/2}} \simeq \frac{\sqrt{2}\tilde{r}}{3\sqrt{3}\mu} \sin \left[ -3\mu \log(\tilde{r}) - 3\mu C^{(2:1)} \right] \quad (3.7c)
\]

For the sake of notational simplicity, we do not explicitly mention that \( \mu \) depends on the situation 1:1, 1:2 or 2:1 considered. The constants \( C \) appearing above are defined as

\[
C^{(1:1)} = \gamma - 3 \log 2 \simeq -1.502 \\
C^{(1:2)} = \gamma - \frac{1}{3} \log 2 - \frac{3}{2} \log 3 \simeq -1.301 \\
C^{(2:1)} = \gamma - \log 2 - \frac{3}{2} \log 3 \simeq -1.763
\]

(3.8, 3.9, 3.10)

where \( \gamma \simeq 0.5772 \ldots \) is the Euler constant. We emphasize that expressions (3.7) do not have the same status of mathematical rigor as their counterparts (3.6) valid for \( \lambda < \lambda_c \), as appears in Appendix B. The constants \( C \) in (3.7) arise from the linearization of a \( \mu \)-dependent function, which is justified from a practical point of view since for physically relevant situations, \( \mu \) is small enough to allow for the corresponding Taylor expansions. For the exact expressions see Appendix B.

We note here that the relation between surface potential and surface charge follows from the expressions given in the present section. At this point, the electric potential depends on a parameter \( A \) for \( \lambda < \lambda_c \) or on a parameter \( \mu \) for \( \lambda > \lambda_c \). These two parameters are related to the bare reduced charge \( \xi \) of the cylindrical polyion through the boundary condition (1.2). Before clarifying this relation, we precise the connection between small \( \tilde{r} \) and large \( \tilde{r} \) behavior.

B. Connecting short and large scale features

For 1:1 electrolytes, the connection problem was solved in [9, 22], with the result

\[
\lambda = \frac{1}{\pi} \sin \left( \frac{\pi A}{2} \right) \quad \text{for} \quad \lambda < \pi^{-1} \quad \text{(3.11)} \\
\lambda = \frac{1}{\pi} \cosh(\pi\mu) \quad \text{for} \quad \lambda > \pi^{-1} \quad \text{(3.12)}
\]

Since \( \lambda \) is related to the effective charge with governs the far field behavior [see (2.5)], the above expressions realize an interesting connection between small and large \( \tilde{r} \) features.

For asymmetric electrolytes and \( \lambda < \lambda_c \),

\[
A = -\frac{1}{4} + \frac{3}{2\pi} \arcsin \left( \frac{1}{2} + \frac{\lambda}{2\lambda_c} \right) \quad \text{(1 : 2)} \quad (3.13a) \\
A = -\frac{1}{4} + \frac{3}{2\pi} \arcsin \left( \frac{1}{2} + \frac{3\lambda}{2\lambda_c} \right) \quad \text{(2 : 1)} \quad (3.13b)
\]

In these two expressions, the values of \( \lambda_c \) differ \( \lambda_c^{(1:2)} = 3\lambda_c^{(2:1)} \) see (3.11) in such a way that expressing \( A \) as a function of \( \lambda_c^{(1:2)} \) in both cases would provide the same expression, but a change in sign in \( A \) and in \( \lambda \). This reflects the original symmetry of 1:2 and 2:1 situations, when \( \xi \) is allowed to change sign. This symmetry is broken here by the choice \( \xi > 0 \) in both cases, which illustrates the practical difference between them.

From a more formal point of view, the expressions (3.11) and (3.13) hold even for complex parameters, provided by

\[
\lambda \notin (-\infty, -\lambda_c^{(1:1)}) \cup [\lambda_c^{(1:1)}, \infty) \quad \text{(1 : 1)} \quad (3.14a) \\
\lambda \notin (-\infty, -\lambda_c^{(2:1)}) \cup [\lambda_c^{(2:1)}, \infty) \quad \text{(1 : 2)} \quad (3.14b) \\
\lambda \notin (-\infty, -\lambda_c^{(1:2)}) \cup [\lambda_c^{(1:2)}, \infty) \quad \text{(2 : 1)} \quad (3.14c)
\]

Alternatively, for \( \lambda > \lambda_c \), we have

\[
\frac{\lambda}{\lambda_c} + 1 = 2 \cosh(\pi\mu) \quad \text{(1 : 2)} \quad (3.15a) \\
\frac{3\lambda}{\lambda_c} - 1 = 2 \cosh(\pi\mu) \quad \text{(2 : 1)} \quad (3.15b)
\]
C. Applying the boundary condition at polion contact

In order to have a closed problem, we need to impose the boundary condition (1.2) at \( \tilde{r} = \tilde{a} \) which relates \( A \) to \( \xi \) (and therefore \( \lambda \) to \( \xi \) from the connection formulae) if \( \lambda < \lambda_c \), and similarly relates \( \mu \) to \( \xi \) if \( \lambda > \lambda_c \).

A straightforward computation gives in the 1:1 situation

\[
\xi = A - \frac{(2 - 2A)(\kappa a)^{2 - 2A}}{16(1 - A)^2 B^2 - (\kappa a)^{2 - 2A}} \tag{3.16}
\]

\[
(\xi - 1) \tan \left[ 2\mu \log(\kappa a/8) + 2\mu \gamma \right] = 2\mu \tag{3.17}
\]

where it is understood that the first line holds for \( \lambda < \lambda_c \) while the second is relevant for \( \lambda > \lambda_c \), in which case \( \mu \) is the smallest positive root of the equation. Here again, \( \gamma \) denotes the Euler constant. The dependence of \( \mu \) and \( A \) upon \( \xi \) is shown in Figures 1 and 2.

![Figure 1: Short scale exponent \( A \) (relevant for \( \lambda < \lambda_c \)) as a function of bare charge for a 1:1 salt. Four salinities are displayed: from left to right, \( \tilde{a} = 10^{-2}, 10^{-3}, 10^{-6} \) and \( 0^+ \), the latter coinciding with the first bissectrix. The values of \( \xi \) where \( A = 1 \) correspond to an end point which defines the threshold bare charge \( \xi_c \).
](image)

In addition for the 1:2 situation, we get

\[
\xi = A - \frac{(1 - 2A)(\kappa a)^{2 - 4A}B^2}{12(2A - 1)^2 - B^2(\kappa a)^{2 - 4A}} \tag{3.18}
\]

\[
(2\xi - 1) \tan \left[ 3\mu \log(\kappa a) + 3\mu C^{(1:2)} \right] = 3\mu \tag{3.19}
\]

while for the 2:1 case

\[
\xi = A - \frac{2(1 - A)(\kappa a)^{2 - 2A}B}{24(1 - A)^2 - (\kappa a)^{2 - 2A}B} \tag{3.20}
\]

\[
(\xi - 1) \tan \left[ \frac{3}{2}\mu \log(\kappa a) + \frac{3}{2}\mu C^{(2:1)} \right] = \frac{3}{2}\mu \tag{3.21}
\]

The values of \( B \) are given in (3.4).

At this point, we emphasize that the above expressions are not mathematically exact, since use was made of the asymptotic expansions given in section III A to compute \( dy/d\tilde{r} \) in (1.2). They nevertheless become asymptotically exact for \( \kappa a \rightarrow \tilde{a} \rightarrow 0 \) \( \Gamma \), and will be shown to provide excellent results for the full range of thin cylinders \( \tilde{a} < 1 \).

Finally, it is important to remember that

\[
A \rightarrow \xi_{\text{Manning}} \quad \text{for} \quad \lambda \rightarrow \lambda_c^- \quad \text{(or} \quad \xi \rightarrow \xi_{c}^-) \tag{3.22}
\]

\[
\mu \rightarrow 0 \quad \text{for} \quad \lambda \rightarrow \lambda_c^+ \quad \text{(or} \quad \xi \rightarrow \xi_{c}^+) \tag{3.23}
\]

In the vicinity of the threshold \( \xi_{c} \), it can be checked that

\[
A - \xi_{\text{Manning}} \text{ and } \mu \text{ scale like } \sqrt{\xi - \xi_{c}}, \text{ as may be expected from Figures 1 and 2.}
\]

D. What are the associated threshold potentials and charges ?

To understand the change of behavior of the electrostatic potential below or above \( \lambda_c \), it is instructive to compute the associated threshold charge \( \xi_{c} \). There are several ways to perform such a computation, either from below taking the limit \( \lambda \rightarrow \lambda_c^- \) and considering the relations between \( A \) and \( \xi \), or from above \( (\lambda \rightarrow \lambda_c^+) \) manipulating \( \mu \). By construction (see Appendix B for the details of the analytic continuation method used), these two routes provide the same short distance potentials, that read for the three different electrolytes.
\[
y_{11}(\tilde{r}) \stackrel{\lambda = \lambda_c}{=} -2 \log \left( \frac{\tilde{r}}{2} \right) - 2 \log \left[ - \log(\tilde{r}) - C^{(1:1)} \right]
\]
(3.24a)
\[
y_{12}(\tilde{r}) \stackrel{\lambda = \lambda_c}{=} - \log \left( \frac{\tilde{r}}{\sqrt{3}} \right) - \log \left[ - \log(\tilde{r}) - C^{(1:2)} \right]
\]
(3.24b)
\[
y_{21}(\tilde{r}) \stackrel{\lambda = \lambda_c}{=} -2 \log \left( \frac{\tilde{r}}{\sqrt{6}} \right) - 2 \log \left[ - \log(\tilde{r}) - C^{(2:1)} \right]
\]
(3.24c)

Limiting ourselves to the region \( \tilde{a} < 1 \) (as for all the results reported in this section) ensures here that the previous expressions are real. Equations (3.24a) and (3.24b) were already given in Ref. [11] and are repeated here for the sake of completeness (expression (3.24b) appeared under number (3.2) with misprints in Ref. [11], where the notation 21 used there corresponds to our 1:2 case [46]). From Eqs. (3.24), it is straightforward to compute the integrated charge \( q(\tilde{r}) \) in a cylinder of radius \( r \) which reads \( q(\tilde{r}) = -(\tilde{r}/2)dy/d\tilde{r} \) from Gauss' law. Evaluating this expression at \( \tilde{r} = \tilde{a} \), we recover [12] hence the value of \( \xi \) associated to \( \lambda_c \)

\[
\xi_{c}^{(1:1)} = 1 + \frac{1}{\log(\kappa a) + C^{(1:1)}}
\]
(3.25a)
\[
\xi_{c}^{(1:2)} = 1 + \frac{1}{2 \log(\kappa a) + 2 C^{(1:2)}}
\]
(3.25b)
\[
\xi_{c}^{(2:1)} = 1 + \frac{1}{\log(\kappa a) + C^{(2:1)}}
\]
(3.25c)

where the constants \( C \) are given in Ref. [11]. We will see in section IV.A that these threshold values, which discriminate \( \lambda < \lambda_c \) behavior from that at \( \lambda > \lambda_c \), can be associated with the phenomenon of counterion condensation.

Expressions (3.25a) correspond to the leading order behavior of \( \xi_c \) and may be improved from the accurate expressions obtained in Refs. [22, 24]. In the 1:1 case, inclusion of the so far omitted dominant correction leads to

\[
e^{-y_{11}/2} = \frac{\tilde{r}}{2} \Omega(\tilde{r}) + \frac{\tilde{r}^5 \Omega(\tilde{r})}{2^9} + O(\tilde{r}^3 \log^2(\tilde{r}))
\]
(3.26)

with

\[
\Omega(\tilde{r}) = - \log(\tilde{r}) - C^{(1:1)}.
\]
(3.27)

Equation (3.26a) corresponds to truncating the right hand side of (3.26) after the first term. The integrated charge \( q(\tilde{r}) \) associated to (3.26a) reads, only including the dominant correction to the \( q(\tilde{r}) \) leading to (3.26a)

\[
q(\tilde{r}) = 1 - \frac{1}{\Omega(\tilde{r})} + \frac{\tilde{r}^4 \Omega^2(\tilde{r})}{16} + O(\tilde{r}^3 \Omega^3(\tilde{r}))
\]
(3.28)

From \( q(\tilde{a}) = \xi \), we get that the error made in (3.26a) — which corresponds to the first two terms on the right hand side of (3.28) — is of order \( \tilde{a}^4 \log^2(\tilde{a}) \). More quantitatively, the terms neglected in (3.25a) are below \( 2 \times 10^{-3} \) and are therefore irrelevant given that the term in \( 1/\log \tilde{a} \) in (3.25a) may be of order 0.1 or larger under reasonable salt conditions. A similar analysis could be performed to improve over expressions (3.25a) and (3.25b).

Finally, note that exactly at \( \xi = \xi_c \), effective charges take a particularly simple form [making use of Eqs. (2.8) and (3.11)] since then \( \lambda = \lambda_c \).

IV. A FEW LIMITING CASES

A. \( a = 0 \) and arbitrary \( \xi \)

It is instructive to discuss first the case \( a = 0 \) (at fixed \( \kappa > 0 \)) where the analytical solutions take simple forms and \( \lambda \) can be found explicitly. From Eqs. (3.10), (3.18) or (3.20) we find \( A = \xi \) and

\[
\lambda = \frac{1}{\pi} \sin \frac{\pi \xi}{2}
\]
(1 : 1) (4.1a)
\[
\lambda = \frac{1}{2 \sqrt{3} \pi} \left[ 2 \sin \left( \frac{\pi}{3} \left( \xi + \frac{1}{4} \right) \right) - 1 \right]
\]
(1 : 2) (4.1b)
\[
\lambda = \frac{1}{2 \sqrt{3} \pi} \left[ 2 \sin \left( \frac{\pi}{3} \left( \xi - \frac{1}{4} \right) \right) + 1 \right]
\]
(2 : 1) (4.1c)

From these results we obtain the effective charge of the rod. For \( a = 0 \), we simply have [see Eq. (2.8)] \( \xi_{\text{eff}} = 2 \lambda \) (1:1) and \( \xi_{\text{eff}} = 3 \lambda \) (1:2) or (2:1), thus

\[
\xi_{\text{eff}} = \frac{2}{\pi} \sin \frac{\pi \xi}{2}
\]
(1 : 1) (4.2a)
\[
\xi_{\text{eff}} = \sqrt{3} \left[ 2 \sin \left( \frac{\pi}{3} \left( \xi + \frac{1}{4} \right) \right) - 1 \right]
\]
(1 : 2) (4.2b)
\[
\xi_{\text{eff}} = \sqrt{3} \left[ 2 \sin \left( \frac{\pi}{3} \left( \xi - \frac{1}{4} \right) \right) + 1 \right]
\]
(2 : 1) (4.2c)

Eqs. (4.2a) and (4.2b) may be found in Refs. [3] and [11]. These formulas are valid only if the conditions (3.14) on \( \lambda \) are satisfied. Given that, for \( a = 0 \), the threshold
the Manning-Oosawa threshold is for $\xi$ and $\xi^2$.

Check that in the linear regime (weak charges, in the 1:2 case). In the symmetric 1:1 electrolyte case, charges (3.25) read

$$\xi = \frac{1}{\pi}$$

is given by

$$\xi_{\text{Manning}} = 1$$

and beyond this threshold the effective saturated charge expressions (4.2) hold provided

$$\xi < 1 \quad (1:1)$$

$$\xi < 1/2 \quad (1:2)$$

$$\xi < 1 \quad (2:1)$$

or, in the most general case allowing for negative values of the bare charge:

$$-1 < \xi < 1 \quad (1:1)$$

$$-1 < \xi < 1/2 \quad (1:2)$$

$$-1/2 < \xi < 1 \quad (2:1)$$

We recover here the Onsager-Manning-Oosawa criterion for counterion condensation [2, 3, 10, 13, 15, 25]. Strictly speaking, if $\xi$ does not satisfy (4.3), there is no physical solution of the Poisson–Boltzmann equation for $a = 0$. As explained in [2], if the bare charge $\xi$ is above the Manning-Oosawa threshold given in Eqs. (4.1), the Boltzmann factor of the interaction between the rod and a counterion is not integrable at short distances, and thus would lead to a collapse between the macroion and the counterions. The situation is similar to the one in the theory of two-dimensional Coulomb systems [28, 29], with logarithmic interaction, where a system of point particles is stable only if the charge of the particles is small enough so that the Boltzmann factor of the interaction between two oppositely charged particles is integrable. Otherwise only a system with hard-core particles (or with other short-distance regularization of the Coulomb potential) is stable.

For the 1:2 electrolyte, the value $\xi = \xi_{\text{Manning}} = 1/2$ corresponds to Manning-Oosawa threshold [2, 3]. Beyond the threshold ($\xi \geq 1/2$), the effective charge $\xi_{\text{eff}}$ attains its saturation value, $\xi_{\text{sat}}^{\text{eff}} = \sqrt{3}/(2\pi) \approx 0.275$. One may check that in the linear regime (weak charges, $\xi \ll 1$), $\xi_{\text{eff}}$ and $\xi$ coincide, as they should. For the 2:1 electrolyte, the Manning-Oosawa threshold is for $\xi = \xi_{\text{Manning}} = 1$ and beyond this threshold the effective saturated charge is given by $\xi_{\text{sat}}^{\text{eff}} = 3\sqrt{3}/(2\pi)$; it is three times larger than in the 1:2 case. In the symmetric 1:1 electrolyte case, the Manning-Oosawa threshold is for $\xi = \xi_{\text{Manning}} = 1$ and the corresponding effective saturated charge is $\xi_{\text{sat}}^{\text{eff}} = 2/\pi \approx 0.636$. We note that this result is in harmony with exact bounds derived by Odijk in [30]: $0.59\xi_{\text{sat}}^{\text{eff}} < 0.67$.

This analysis clarifies the relationship between two different notions, the Manning-Oosawa threshold for counterion condensation and the notion of effective charge. The key point here is that the Manning-Oosawa threshold $\xi_{\text{Manning}}$ for the bare charge is different from the value of the saturated effective charge $\xi_{\text{sat}}^{\text{eff}}$. The fact that $\xi_{\text{sat}}^{\text{eff}} < \xi_{\text{Manning}}$ is of course a non-linear effect which means that even accounting correctly for counterion condensation, the remaining layer of “uncondensed” or “free” microns cannot be treated within a linearized (Debye-Hückel-like) theory. This exact result contrasts with common belief in the field, which possibly takes its roots in the work of Manning [2].

In Figs. 3 and 4, we compare the result of Eqs. (4.2a) and (4.2c) for a 1:2 and 2:1 electrolyte, respectively, with numerical data, for two low values of $\kappa a$. All numerical PB data have been obtained following the method discussed in [31]. One may conclude that the limiting behavior $\kappa a \rightarrow 0$ is reached very slowly, in fact, logarithmically, as we will show below.
It is interesting to notice in Fig. 1 that in the 2:1 electrolyte we have the overshooting effect, previously reported in Ref. 32, where the effective charge becomes larger than the bare charge for intermediate values of the latter. Indeed for $|\xi| \ll 1$, from Eqs. (4.2), we have for a 2:1 electrolyte

$$\xi_{\text{eff}} = \xi + \frac{\pi \xi^2}{3\sqrt{3}} - \frac{2\pi^2 \xi^3}{27} + O(\xi^4)$$

(2:1) (4.6)

and for a 1:2 electrolyte

$$\xi_{\text{eff}} = \xi - \frac{\pi^2 \xi^2}{24} + O(\xi^5).$$

(4.7)

The first deviation of the effective charge from linear behavior is positive in the 2:1 case (overshooting effect) and negative in the 1:2 case (no overshooting). For a 1:1 electrolyte,

$$\xi_{\text{eff}} = -\frac{\pi^2}{24} \xi^3 + O(\xi^5).$$

(4.8)

The first deviation of the effective charge from the bare one is of order $\xi^3$ (as in the case $\kappa a \gg 1$) and negative (thus no overshooting). There is no term in $\xi^2$ as opposed to the charge asymmetric electrolytes 1:2 and 2:1. The physical origin of the overshooting effect lies in the fact that in the 2:1 case, the divalent coions are expelled further away in the double layer than the monovalent ones in the 1:1 situation, which results in a stronger electrostatic potential at large distances. Similarly, the screening for 1:2 electrolytes is more efficient since divalent counterions are available, which not only results in the fact that $\xi_{\text{eff}} < \xi$, but also in the lower value of $\xi_{\text{eff}}$. We therefore speculate that the overshooting effect is generic in a $\varepsilon:z'$ electrolyte, with coions of valency $z$ larger than that of counterions ($\varepsilon'$).

B. $\xi \to 0$ and arbitrary $\bar{a} < 1$

In the limit where $\xi \to 0$, the solution (4.9) becomes exact for all distances, and one has $\xi_{\text{eff}}/\xi \to 1$, as was simply checked for $a = 0$ in section B.1 (A). At finite salt however, the requirement $\xi_{\text{eff}}/\xi \to 1$ when $\xi \to 0$ provides quite a non trivial benchmark for our analytical expressions. It turns that the results of sections B.1 and B.2 are not sufficient –at finite $\bar{a}$— to show $\xi_{\text{eff}}/\xi \to 1$. This is because in Eqs. (4.9) we neglected terms of order $r^{2+4A}$ in the 1:1 and 1:2 cases and terms of order $r^{2+2A}$ in the 2:1 case. As $\xi \to 0$, we have $A \to 0$, thus these terms become of order $r^2$ and are of the same order of the last term in the logarithms of Eqs. (4.8). Then, to properly compute the short-distance asymptotics as $\xi \to 0$, we need the next order terms in Eqs. (4.9). These can be easily obtained by replacing the small-$r$ asymptotics (3.5) into the Poisson–Boltzmann differential equation (3.1). For example for the 1:1 case, we obtain, if $A < 1$,

$$e^{-y_{11}/2} = \frac{\hat{r}^A}{B} \left[ 1 - \frac{\hat{r}^2}{16} \left( B^2 \hat{r}^{-2A} - \frac{\hat{r}^{2A}}{B^2(1+A)^2} \right) + O(\hat{r}^{2(2+2A)}) \right]$$

(4.9)

Notice the expected symmetry in the two terms when one changes $A \to -A$ (in which, from the definition of $B$, gives $B \to B^{-1}$). Taking the limit $A \to 0$ we obtain

$$y_{11}(r) = -2A \left[ \frac{\ln \hat{r}}{2} + \frac{\hat{r}^2}{4} \left( \gamma + \ln \hat{r} - 1 \right) \right] + O(\hat{r}^4)$$

(4.10)

We recognize the small-$r$ expansion of the Bessel function $K_0(\tilde{r})$. On the other hand (3.4) says that for $A \to 0$, $A = 2\lambda = \xi_{\text{eff}}/(\bar{a}K_1(\bar{a}))$. We conclude that the small-$r$ expansion (4.10) is the small-$r$ expansion of the linear solution (3.3) and that, clearly, imposing the boundary condition (3.2), at $r = a$ will yield $\xi = \xi_{\text{eff}}$.

A similar conclusion is reached for the asymmetric cases. For the 2:1 case the small-$r$ expansion, for $A < 1$, reads

$$e^{-y_{21}/2} = \frac{\hat{r}^A}{B} B^{-1/2} \left[ 1 - \frac{\hat{r}^{2-2A}B}{24(1-A)^2} + \frac{\hat{r}^{2+4A}}{24B^2(2A + 1)^2} + O(\hat{r}^{2(2+4A)}) \right]$$

(4.11)

while the one for $y_{12}$ can be obtained from the preceding expression through the substitution $A \to -A$ and $B \to B^{-1}$. It is direct to verify that in the limit $A \to 0$, the asymptotics (4.11) yield again (4.10), that is the small-$r$ asymptotics of $y_{12}$ and $y_{21}$ are those of the Bessel function $K_0(\tilde{r})$, solution of the linear problem.

C. $\xi = \xi_{\text{Manning}}$ and arbitrary $\bar{a} < 1$

It is in general not possible to find analytically the solution to the transcendental equations satisfied by the parameter $\mu$, which quantifies the behavior at short distances above the salt dependent threshold, ie for $\xi > \xi_c$. However, if $\xi = \xi_{\text{Manning}}$ (which is always beyond $\xi_c$), the relevant roots of Eqs. (3.17), (3.19) and (3.21) read

$$\mu^{(1,1)} = -\frac{\pi}{4[\log \bar{a} + C(1:1)]}$$

(4.12a)

$$\mu^{(1,2)} = -\frac{\pi}{6[\log \bar{a} + C(1:2)]}$$

(4.12b)

$$\mu^{(2,1)} = -\frac{\pi}{3[\log \bar{a} + C(2:1)]}$$

(4.12c)

These expressions will be useful in section V.
D. $\xi > \xi_{Manning}$ and arbitrary $\hat{a} < 1$

The limit of large enough $\xi$ allows to derive a useful approximation for $\mu$, that will turn important from a practical point of view. Coming back to Eqs. (3.17), (3.19) and (3.21), we note that for diverging $\xi$, the arguments of the tangent functions should be close to $-\pi$, so that the tangent functions vanish, to be compatible with a finite value of $\mu$. Expanding then the tangent to first order, we obtain

$$\mu^{(1,1)} \approx \frac{\pi}{2[\log \hat{a} + C^{(1:1)} - 1/(\xi - 1)]}$$

$$\mu^{(1,2)} \approx \frac{\pi}{3[\log \hat{a} + C^{(1:2)} - 1/(2\xi - 1)]}$$

$$\mu^{(2,1)} \approx \frac{2\pi}{3[\log \hat{a} + C^{(2:1)} - 1/(\xi - 1)]}$$

The domain of validity of these relations is estimated to be $\xi > \xi_{Manning} + O(1/\log \hat{a})$, as may be observed in Fig. 2 in the 1:1 case. In the vicinity of $\xi_{Manning}$ where (4.13) fails, one should resort to expressions (4.12). We finally note that when $\xi$ diverges, $\mu$ saturates to a finite value [twice those reported in (3.12)]

$$\mu_{sat}^{(1,1)} = \frac{\pi}{2[\log \hat{a} + C^{(1:1)}]}$$

$$\mu_{sat}^{(1,2)} = \frac{\pi}{3[\log \hat{a} + C^{(1:2)}]}$$

$$\mu_{sat}^{(2,1)} = \frac{2\pi}{3[\log \hat{a} + C^{(2:1)}]}$$

From Eq. (3.12) and (3.15) we conclude that $\lambda$ does also saturate: a corollary is that effective charges –directly related to $\lambda$ through (3.8)– saturate, a generic feature of mean-field theories [33].

V. RESULTS AT FINITE SALT AND DISCUSSION

The results reported in sections III and IV are based on asymptotic expansions in the limit $\hat{a} \to 0$. This limit is approached logarithmically slowly, so that finite $\hat{a}$ corrections should always be important in practice. We now therefore address the question of the reliability of our expressions at finite salt, by confronting them with the numerical solution of the non-linear PB equation (1.1).

A. Counterion condensation and Manning radius

One of the most interesting features emerging here is that it is possible to generalize the notion of counterion condensation to finite salt systems. It is important however to emphasize here that condensation is not an all or nothing process, that would occur precisely at $\xi_c$. Instead, it is a gradually built phenomenon. This is particularly true at finite salt density but already in the limit of vanishing salt $\kappa a \to 0$, it is noteworthy that non linear effects play an important role for $\xi < \xi_c$, as revealed by the fact that $\xi_{eff}/\xi \neq 1$.

We concentrate here on a 1:1 salt, but the same analysis also holds for 1:2 and 2:1 salts. The value $\xi_c$ discriminates between the short distance behaviors (3.13a) for $\xi < \xi_c$ and (3.17a) for $\xi > \xi_c$. As may be observed in Fig. A $A$ is close to $\xi$ except in the vicinity of the threshold charge $\xi_c$, so that to dominant order, $y_{11}$ behaves as $-2\xi_c \log \hat{r}$, which corresponds to the potential of a bare cylinder with reduced charge $\xi_c$ unaffected by screening. At $\xi = \xi_c$, the potential develops an additional log $\log$ $\log$ term (see section III D), while for $\xi > \xi_c$, the behavior stemming from (3.17a) is more complex. For high enough $\xi$ (more precisely, for $\xi > \xi_{Manning} + |O(1/\log \hat{a})| > \xi_{Manning}$ (which is itself larger than $\xi_c$), one may resort to approximation (4.13) and after some manipulations, rewrite (3.7) as

$$e^{-y_{11}/2} \approx \frac{\hat{r}}{2} \left[\log \left(\frac{\hat{r}}{a}\right) + \frac{1}{\xi - 1}\right].$$

Here, we have used the fact that

$$2\mu \left(\log \hat{r} + C^{(1:1)}\right) = -\pi + 2\mu \log \left(\frac{r}{a}\right) + \frac{2\mu}{\xi - 1}$$

so that Eq. (5.1) holds for $\log(r/a) \ll O(1/\mu)$. Eq. (5.1) had already been derived by Ramanathan [7] (see also appendix A of [34]) and implies that to dominant order, the potential behaves like $-2\log \hat{r}$ at short distances, which corresponds to the bare potential of a polaron with $\xi = \xi_{Manning} = 1$, and is the fingerprint of counterion condensation. We also note that for high $\xi$, Eq. (5.1) yields a total concentration of ions close to the rod that is proportional to the square of the surface charge density, as in the planar case [35]. To complement the above results that assume $\xi > \xi_{Manning} + |O(1/\log \hat{a})|$, we also mention that for $\xi = \xi_{Manning}$ (i.e. above the threshold), the results of section IV C yield

$$e^{-y_{11}/2} \approx \frac{\hat{r}}{2 \pi} \left[\log \hat{a} + C^{(1:1)}\right].$$

The dominant behavior for $y_{11}$ is therefore again $-2 \log r$. Finally, decreasing further $\xi$ to investigate the regime where it is close to the threshold $\xi_c$ (but still larger than $\xi_c$), one may take advantage that $\mu$ vanishes at $\xi = \xi_c$ to get Eqs. (3.24)

$$e^{-y_{11}/2} = -\frac{\hat{r}}{2} \left[\log \hat{r} + C^{(1:1)}\right]$$

$$e^{-y_{12}} = -\frac{\hat{r}}{\sqrt{3}} \left[\log \hat{r} + C^{(1:2)}\right]$$

$$e^{-y_{21}/2} = -\frac{\hat{r}}{\sqrt{6}} \left[\log \hat{r} + C^{(2:1)}\right].$$

The dominant behavior at short scales is again $y \simeq -2\xi_{Manning} \log \hat{r}$, which is the unscreened potential created by a rod of reduced charge $\xi_{Manning}$. This is quite
remarkable given \( \xi_c < \xi_{\text{Manning}} \) since it holds in particular for a cylinder with \( \xi \) verifying \( (\xi_c <) \xi < \xi_{\text{Manning}} \). Such a remark is nevertheless quite misleading since at finite values of \( \kappa a \), the requirement \( r > a \) does not allow to take the limit \( r \to 0 \) where the different leading and sub-leading contributions to the potential can be identified: “corrections” to the “leading” term are important. In other words, the full expression is required to approximate \( y \) in (5.3) and the “dominant” term \(-2\xi_{\text{Manning}} \log r\) is in practice a bad approximation.

Our analytical expressions identify a mathematical change in the behavior of the electric potential at \( \xi = \xi_c \), that may be considered as being associated with condensation. Such a terminology may however be confusing since at finite \( \xi \), no singularity signals the crossing of the threshold value \( \xi_c \). This restriction should be borne in mind. Of particular interest is the condensate structure, completely encoded in Eqs. (5.7), and in particular the condensate thickness \( r_a \). Its definition is necessarily arbitrary. The so-called Manning radius is often considered when it comes to quantifying the condensate size. It is defined as the distance \( r_m \) where the integrated charge \( q(r) = -(r/2) dy/dr \) equals \( \xi_{\text{Manning}} \). Since we have seen that \( \xi_c < \xi_{\text{Manning}} \), it is clear that such a criterion in inoperant for \( \xi_c < \xi < \xi_{\text{Manning}} \), which constitutes quite a deficiency, but the corresponding value \( r_m \) nevertheless exhibits remarkable features within its domain of definition \( \xi > \xi_{\text{Manning}} \). We first compute \( q(r) \), that follows directly from Eqs. (3.4):

\[
q^{(1:1)}(r) = 1 + 2 \mu \tan \left[-2 \mu \log \left( \frac{r}{r_m^{(1:1)}} \right) \right] \tag{5.5a}
\]
\[
q^{(1:2)}(r) = 1 + \frac{3}{2} \tan \left[-3 \mu \log \left( \frac{r}{r_m^{(1:2)}} \right) \right] \tag{5.5b}
\]
\[
q^{(2:1)}(r) = 1 + \frac{3}{2} \tan \left[-3 \mu \log \left( \frac{r}{r_m^{(2:1)}} \right) \right] \tag{5.5c}
\]

with

\[
k r_m^{(1:1)} = \exp \left(-C^{(1:1)} - \frac{\pi}{4 \mu} \right) \tag{5.6a}
\]
\[
k r_m^{(1:2)} = \exp \left(-C^{(1:2)} - \frac{\pi}{6 \mu} \right) \tag{5.6b}
\]
\[
k r_m^{(2:1)} = \exp \left(-C^{(2:1)} - \frac{\pi}{3 \mu} \right) \tag{5.6c}
\]

In these expressions, one observes that \( q(r) = \xi_{\text{Manning}} \) for \( r = r_m \), which means that the \( r_m \) appearing in (5.5) are by definition Manning radii. When \( \xi = \xi_{\text{Manning}} \), then by definition the Manning radius should coincide with the polyon radius \( a \). This is indeed the case here, as a consequence of Eqs. (4.12). For large enough \( \xi \), we obtain an expression in closed form from approximation (4.13):

\[
k r_m^{(1:1)} \approx 2 \sqrt{2 \kappa a} \exp \left(\frac{-\gamma}{2} - \frac{1}{2(\xi - 1)}\right) \tag{5.7a}
\]
\[
k r_m^{(1:2)} \approx \frac{3^{3/4}}{2^{1/3}} \sqrt{2 \kappa a} \exp \left(-\frac{\gamma}{2} - \frac{1}{2(2(\xi - 1))}\right) \tag{5.7b}
\]
\[
k r_m^{(2:1)} \approx \frac{3^{3/4}}{2^{1/3}} \sqrt{2 \kappa a} \exp \left(-\frac{\gamma}{2} - \frac{1}{2(\xi - 1)}\right) \tag{5.7c}
\]

In the cell model, the previous definition

\[
q(r_m) = \xi_{\text{Manning}} \tag{5.8}
\]

offers a geometric construction to compute \( r_m \): \( q(r) \) plotted as a function of \( \log r \) displays an inflection point at \( r = r_m \) (see Ref. [13] where it was also shown that this criterion could be extended beyond mean-field and used in Molecular Dynamics simulations to define a fraction of condensed ions). From the functional form of Eqs. (5.6) —with a shifted tangent as a function of \( \log r \), i.e. the same form as in the salt-free cell model case— we see that a similar inflection point criterion holds here. This will be illustrated further in section V.C.

For a 1:1 electrolyte, (5.7a) is precisely the result obtained in Ref. [13]. The present work therefore precisely the domain of validity of this expression, and offers with (5.6a) supplemented with (5.7a) a better approximation (see Figure 6). By construction, the accuracy of our expressions improve upon decreasing \( \tilde{a} \). To test the worst cases, we therefore chose a relatively “high” value \( \tilde{a} = 0.01 \) in Fig. 5 where the agreement is seen to be very good, while (5.6a) fails when \( \xi \) is too close to \( \xi_{\text{Manning}} = 1 \). Fig. 6 illustrates the effect of increasing salinity and displays the results associated to three values of \( \tilde{a} \). It is observed that at high \( \xi \), the analytical predictions deviate all the more from the numerical results computed for PB theory as \( \tilde{a} \) is increased. For the highest value \( \tilde{a} = 0.3 \) of Fig. 6, the error made when \( \xi \to \infty \) is on the order of 30%. It also appears that even at relatively high \( \tilde{a} \), the analytical prediction is reliable for low \( \xi \) [bearing in mind that \( \xi \) must be larger than \( \xi_{\text{Manning}} \) to allow for the definition of \( r_m \) through Eq. (5.5)]. For completeness, we present results for the 1:2 case as well in Figure 7 changing \( \tilde{a} \) at fixed charge \( \xi = 0.55 \) which is just above the value \( \xi_{\text{Manning}} = 1/2 \). The results at saturation are also reported (dashed line and squares). One needs to push \( \tilde{a} \) beyond 0.1 to notice a difference between (5.6a) and the numerical PB result (see the inset). Figure 7 illustrates how finite salt effects influence the scaling exponent \( \alpha \) in the relation \( k r_m \propto (\kappa a)^{\alpha} \). If \( \xi > \xi_{\text{Manning}} + |O(1/\log \tilde{a})| \), that is at high enough \( \xi \) or low enough \( \tilde{a} \), we have \( \alpha = 1/2 \) as dictated by Eqs. (5.7) and evidenced by the dotted line in the main graph. If on the other hand one sits in the region \( \xi_{\text{Manning}} < \xi < \xi_{\text{Manning}} + |O(1/\log \tilde{a})| \), the exponent \( \alpha \) changes continuously, and increasing \( \tilde{a} \) at fixed \( \xi \) drives the system toward the regime \( \alpha = 1 \), a feature —visible for the data at \( \xi = 0.55 \) in Fig. 7, which simply reflects
the fact that $r_m \to a$. Finally, we emphasize that the behavior in all three 1:1, 1:2 and 2:1 situations are qualitatively very similar so that the conclusions reached and phenomena observed are transferable from one situation to another.

The inflection point feature stemming from (5.8) has the merit to unify the present infinite dilution/finite salt phenomenology with the finite density/vanishing salt situation of the cell model. It should be kept in mind however that (5.8) does not allow to define a Manning radius for $\xi_c < \xi < \xi_{\text{Manning}}$, where the condensation phenomenon is already present, at least from a mathematical point of view with a change in the short distance behavior of $y(r)$. In addition the scaling $r_m \propto (a/\kappa)^{1/2}$ valid for large enough $\xi$ [see (5.7)] is definition dependent. An alternative to (5.8) could be to define a characteristic radius of the condensate through $q(r^*) = \xi_c$. Making use of (1.13), then implies that for a 1:1 salt $\kappa r^* \propto (\kappa a)^{\alpha}$ with $\alpha = (\arctan \pi)/\pi \simeq 0.402$ instead of $\alpha = 1/2$ in (6.7). As (1.13), this is limited to high enough $\xi$. For $\xi = 1$, the results of section IV C allow for an analytical computation of $r^*$ and yield $\alpha = (2/\pi) \arctan(\pi/2) \simeq 0.639$.

Our expressions also allow to discuss several quantities that directly follow from the electric potential, such as the Bjerrum radius $r_B$ considered in Ref. [36] and defined as the locus of an inflection point in the integrated counterion density when plotted as a function of radial distance. For 1:1 and 2:1 salts, this definition implies $q(r_B) = 1/2$ while in the 1:2 case, we have $q(r_B) = 1/4$. Making use of Eqs. (5.7) provide a transcendental equation from which $r_B$ follows.

### B. Effective charges

Of particular interest to describe interactions at large distances (typically $r > \kappa^{-1}$ as will be discussed in section IV C) is the effective charge defined from the far field asymptotics (1.3). This quantity is given by Eqs. (2.8) where $\lambda$ follows from the expressions given in sections III B and III C. The results pertaining to the limit $\bar{a} \to 0$...
have been given in section IV A, but it is also possible to derive closed form relations in the saturation limit $\xi \to \infty$ where $\mu$ is given by (4.14). We therefore have (denoting $\xi_{\text{sat}}$ by $\xi_{\text{sat}}$):

$$
\xi_{\text{sat}}^{(1:1)} = \tilde{a} K_1(\tilde{a}) \frac{2}{\pi} \left[ \cosh \left( \frac{\pi^2}{2\text{log } \tilde{a} + C^{(1:1)}} \right) \right] \quad (5.9a)
$$

$$
\xi_{\text{sat}}^{(1:2)} = \tilde{a} K_1(\tilde{a}) \sqrt{3} \frac{\pi}{2} \left[ \cosh \left( \frac{\pi^2}{3\text{log } \tilde{a} + C^{(1:2)}} \right) - \frac{1}{2} \right] \quad (5.9b)
$$

$$
\xi_{\text{sat}}^{(2:1)} = \tilde{a} K_1(\tilde{a}) \sqrt{3} \frac{\pi}{2} \left[ \cosh \left( \frac{2\pi^2}{3\text{log } \tilde{a} + C^{(2:1)}} \right) + \frac{1}{2} \right] \quad (5.9c)
$$

Figures 8 and 9 show that the analytical expressions (5.9) are in good agreement with the numerical results for $\kappa a = \tilde{a} < 0.1$. For $\tilde{a} > 0.1$, deviations become apparent (see the inset of Fig. 8). We will propose in section VI an alternative approach that covers the whole range of $\kappa a$.

We have also checked that the effective charges are correctly described by the analytical predictions of section III, not only in the saturation regime but for arbitrary values of the charge $\xi$ provided $\tilde{a} < 0.1$.

### C. Electric potential

So far, we focused on several scalar quantities characterizing the electric potential, and thus the ionic distribution. It is also instructive to compare the analytical potentials to their “exact” PB counterparts. When $\xi > \xi_c$, the relevant short scale expressions are those of Eqs. (3.7). We take the 2:1 situation as an illustrative example. As expected from the results of section IV B, Figures 10 and 11 show that the far field behavior is well captured by (1.3), and it also appears that such an expression may be used in practice for $\kappa r > 1$. On the other hand, expansion (3.7c) is very accurate at small distances, and may be extended up to $\kappa r$ of order 1. For the low values of $\kappa a$ such as that of Fig. 10, expansion (3.7c) produces the correct potential with an exceptional accuracy for several orders of magnitude in $r$. For higher values of $\kappa a$, the short distance expansion (3.7c) is still useful and reliable up to $\kappa r$ of order unity (see Fig. 11). To illustrate the improvement over previous expansions, we come back to the 1:1 case in Fig. 12 and compare our formula with the classic one of Ramanathan [7], recalled in (5.1) and re-derived in the present work. Once the potential is known, one can compute the integrated charge $q(r) = -\frac{1}{2} r dy/dr$, displayed in Fig. 13. The coincidence between the $q$ versus $\log r$ inflection point and the Manning radius may be observed in the inset. The integrated charge—shown by the dotted line—following from (5.1) cannot reproduce such a feature, and we also
FIG. 10: Electrostatic potential in a 2:1 electrolyte as a function of radial distance for a rod with a high bare charge ($\xi \approx 11$) and $\kappa a = 10^{-3}$. The circles represent the numerical solution of PB theory, the dotted line is for the short distance formula (3.7c) and the dashed line is for the far field expression (1.3). In the inset, the same results are shown on a linear-log scale.

FIG. 11: Same as Fig. 10 with $\xi \approx 40$ and $\kappa a = 0.3$, on a linear scale.

observe that the most significant decay of $q(r)$ from its initial value ($\xi$ as requested by Gauss theorem, i.e. 25 in Figure 12) to unity occurs on a much shorter scale than the Manning radius.

VI. EFFECTIVE CHARGE AT SATURATION AND THE LARGEST EIGENVALUE OF THE OPERATORS $K_{\tilde{a}}$

The results of the previous sections are broadly speaking restricted to the regime $\kappa a < 1$. For the specific problem of the effective charge in the 1:1 situation, it is however possible to obtain expressions that hold for all salinities.

The effective charge at saturation, for any arbitrary value of $\tilde{a}$, has an interesting relation with the largest eigenvalue of the operators defined in Eqs. (2.3) and (2.6). To see this, consider first the 1:1 electrolyte, and the solution (2.2) to Poisson–Boltzmann equation. As the bare charge $\xi$ increases the parameter $\lambda$ (related to the effective charge $\xi_{\text{eff}}$) increases. At saturation ($\xi \to +\infty$), $\lambda = \lambda_{\text{sat}}$ is such that the electric field obtained from the solution (2.2) diverges at $\tilde{r} = \tilde{a}$. Clearly this happens if $\det(1 - \lambda K_{\tilde{a}}) = 0$, thus if $\lambda$ is the inverse of an eigenvalue of $K_{\tilde{a}}$. Now, since when $\xi = 0$, $\lambda = 0$ and it increases as $\xi$ increases, it appears that at saturation $\lambda = \lambda_{\text{sat}}$ is equal to the inverse of the largest eigenvalue of $K_{\tilde{a}}$.

The same analysis applies to the 1:2 and 2:1 elec-
trolytes. For a 1:2 electrolyte, for positive saturation \( \xi \to +\infty \), \( \lambda_{\text{sat}} \) is the inverse of the largest eigenvalue of \( K_{\text{a}}^{(2)} \), whereas for a 2:1 electrolyte, when \( \xi \to +\infty \), \( \lambda_{\text{sat}} \) is the inverse of the largest eigenvalue of \( -K_{\text{a}}^{(0)} \).

We have not been able to find explicitly the eigenvalues of the operators \( K_{\text{a}} \), \( K_{\text{a}}^{(0)} \) and \( K_{\text{a}}^{(2)} \), for any arbitrary value of \( \tilde{a} \). However one can use approximate methods to find estimates for the largest eigenvalue.

For the 1:1 electrolyte, it is shown in the appendix of [37], that for any function \( \phi \in L^2(0,\infty, e^{-\tilde{a}(u+u^{-1})}/du) \), the largest eigenvalue \( \lambda_{\text{sat}}^{-1} \) of \( K_{\text{a}} \) satisfies

\[
(\phi, K_{\text{a}}\phi) \leq \lambda_{\text{sat}}^{-1}
\]

where \((\cdot, \cdot)\) is the scalar product of \( L^2(0,\infty, e^{-\tilde{a}(u+u^{-1})}/du) \). Using the test function \( \phi(u) = 1/\sqrt{u} \), we obtain

\[
\lambda_{\text{sat}} \leq \frac{K_0(\tilde{a})}{\pi \Gamma(0, 2\tilde{a})}
\]

with \( K_0 \) the modified Bessel function and \( \Gamma(0, z) = \int_z^{+\infty} e^{-t}/t \,dt \). Using Eq. 28 in [37], this finally gives an upper bound for the effective charge at saturation, for a 1:1 electrolyte, for any arbitrary value of \( \tilde{a} \), \( \xi_{\text{sat}} \leq \xi_{\text{sat,up}} \), with

\[
\xi_{\text{sat,up}} = 2\tilde{a} K_1(\tilde{a}) K_0(\tilde{a}) / \pi \Gamma(0, 2\tilde{a})
\]

As \( \tilde{a} \to 0 \), \( \xi_{\text{sat,up}} \to 2/\pi \), thus has the same limit as the exact \( \xi_{\text{sat}}^{\text{eff}} \). This is expected since in the appendix [37], this upper bound was used to prove that the supremum of the largest eigenvalue of \( K_{\text{a}} \) as \( \tilde{a} \to 0 \) is \( \pi \).

Interestingly, when \( \tilde{a} > 1 \) we have

\[
\xi_{\text{sat,up}} = 2\tilde{a} + \frac{3}{2} + O(\tilde{a}^{-1})
\]

which is the same asymptotic behavior of the true effective saturated charge \( \xi_{\text{sat}}^{\text{eff}} \) obtained in [38] by a different approach than the present one. It is the effective charge of an infinite plane \((2\kappa a)\) plus a correction \((3/2)\) that is obtained using a small curvature expansion.

Figure 14 shows a comparison between \( \xi_{\text{sat,up}} \) from Eq. 6.3 in [38] and the effective charge at saturation \( \xi_{\text{sat}}^{\text{eff}} \) obtained numerically. Surprisingly, it turns out \( \xi_{\text{sat,up}} \) is not only an upper bound for \( \xi_{\text{sat}}^{\text{eff}} \) but also a very good estimate for \( \xi_{\text{sat}}^{\text{eff}} \) for any value of \( \tilde{a} \). If \( \tilde{a} > 10^{-1} \) it is in very good agreement with the numerical data. However, for very small radius \( \tilde{a} \ll 1 \), the estimate \( 10 \) \( \xi_{\text{sat,up}} \) of section IV is better than the ansatz (6.3) (see the inset of Fig. 14 and compare it to Fig. 8).

**VII. CONCLUSION**

The mathematical results derived in the framework of Painlevé/Toda type equations provides much insight into the screening behavior of microions in the vicinity of a charged rod-like macroion. Although the mapping between the Poisson–Boltzmann equation for a certain class of electrolytes (1:1, 1:2 and 2:1) onto a Painlevé/Toda equation is itself not new, previous analysis were concerned with the no salt limit where the ratio of macroion radius \( a \) to Debye length \( \kappa^{-1} \) vanishes, and the practical consequences and implications of a finite salt concentration had not been drawn. We have shown here that systematic logarithmic, and thus strong, corrections arise for various quantities of interest. All finite salt results reported here are new, and significantly improve previously available expressions. In addition, the 2:1 situation worked out here had not been considered before, even in the limit of vanishing salt content.

The experimental relevance of our findings has been sketched in the introduction. A rough criterion for the validity of our mean-field approach is that \( \Gamma = z^{3/2} \sqrt{\xi_{\text{FB}}^{\text{sat}}}/(2\pi a) < 2 \) where \( z \) denotes the valency of counter-ions. For 1:1 and 2:1 electrolytes, the criterion is fulfilled even by the most highly charged polymers, such as double-stranded DNA for which \( a \simeq 1 \) \( \text{nm} \) and \( \xi \simeq 4 \), at least in water where \( \ell_B \simeq 0.7 \) \( \text{nm} \). In the 1:2 case, we obtain for dsDNA \( \Gamma \simeq 2 \), for which it is difficult to weight the importance of microionic correlation against the mean-field effects reported here. In any case, our results apply to single stranded DNA and polymers of lower line charge such as hyaluronan. An upper limit should also be put to salt content \( (\kappa \ell_B < 1) \), but such a requirement is irrelevant for our purposes since only the low salt regime has been discussed.

Section I contains the core of our analysis. It appeared there that the short scale behavior of the electric potential depends on the position of the reduced bare charge \( \xi \) with respect to a threshold \( \xi_c \). One may consider that this threshold is a remnant of its vanishing
salt counterpart, which signals the onset of counter-ion condensation. It should be kept in mind however that counter-ion condensation is not an all or nothing process, but a gradually built phenomenon.

The charge $\xi_c$ is strongly salt dependent, and coincides with Manning critical value in the limit $\kappa a \to 0$. On the other hand, the large distance behavior is always of the same functional form [see (1.3)] and is governed by the effective charge $\xi_{\text{eff}}$. This latter quantity depends on a parameter $\lambda$ that also plays a crucial role in the description of the short distance behavior. We have proposed a simple approximation to compute explicitly $\lambda$ for 1:1, 2:1 and 1:2 electrolytes, from which all other quantities follow. The analytical predictions have been tested against the numerical solution of Poisson-Boltzmann theory, and shown to be remarkably accurate [of particular practical interest for highly charged polyelectrolytes are Eqs. (3.7) and (1.3) with $\mu$ given by (1.13) and where $\lambda$ is given as a function of $\mu$ in section IIIB. In particular, simple analytical results have been derived for the Manning radius, that is often used to quantify the lateral extension of the condensate that may form around a cylindrical polyelectrolyte. A few other measures of the condensate thickness have been commented upon.

Our approach is free of the matching procedures [40, 41, 42] or ad-hoc though educated assumptions [43] underlying previous work, and therefore provides expansions with controlled error for the electric potential. The analysis of sections III to V requires that $\alpha < \kappa^{-1}$. For larger salinities, contributions that have been neglected here become relevant. However, the spectral analysis of section V provides for all values of $\kappa a$ an upper bound for the far field signature of the polyelectrolyte, from which an excellent approximation of the effective charge at saturation may be obtained.

The analytical results obtained emphasize the essential difference between the critical Manning charge for condensation and effective charge of the macroion, the latter being defined from the large scale electric behavior. A consequence is that within a simplified two state model where the population of microion is divided into a condensed region and a free population, free ions cannot be treated within a linearized theory, at variance with common belief and practice. Consistency with exact results requires that non linear effects are still at work in the free region and significantly decrease the effective charge compared to the critical one. In the 1:2 case at ultra low salt, for all bare charges $\xi$ larger than $\xi_c$, the ratio of $\xi_{\text{eff}}$ to $\xi_c$ (with $\xi_c$ equal to $\xi_{\text{Manning}}$ here since $\kappa a \to 0$) is equal to $\sqrt{3}/\pi \approx 0.55$. This ratio is closer to unity for 2:1 electrolytes [$3\sqrt{3}/(2\pi) \approx 0.83$], and intermediate for a 1:1 salt ($2/\pi \approx 0.64$). We therefore emphasize that the distinction between bound and free ions is not only arbitrary but also potentially misleading.

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APPENDIX A: PAINLEVÉ CLASSIFICATION, A BRIEF REMINDER

Polynomial non-linear differential equations of the form

$$A(x,y) \frac{d^2y}{dx^2} + B(x,y) \frac{dy}{dx} + C(x,y) \left( \frac{dy}{dx} \right)^2 + D(x,y) = 0,$$

(A1)

where the functions $A, B, C, D$ are polynomial in $y$ and analytic in $x$, have been classified with respect to the character of the singular points of the solutions. Of special interest are the equations for which branch points and essential singularities do not depend on initial conditions (hence the only movable singularities are poles). Fifty canonical types of equations with the above property have been uncovered, most of which (44) are integrable in terms of elementary functions. Solving the remaining 6 types requires the introduction of new (Painlevé) transcendental functions. The third member (Painlevé III) of this family of 6 corresponds to the generic form

$$xy \frac{d^2y}{dx^2} = x \left( \frac{dy}{dx} \right)^2 - y \frac{dy}{dx} + ax + by + cy^3 + dx^4. \quad (A2)$$

APPENDIX B: SHORT DISTANCE BEHAVIOR

For $\lambda > \lambda_c$, the asymptotics of $y(\tilde{r})$ are different, when $\xi > \xi_c$, than the ones given by Eqs. (55).

In [22] the asymptotics for $\lambda > 1$ in the 1:1 case were studied and in [21] the ones for the 1:2 case for $\lambda > \lambda_c$ were obtained. We will not reproduce those calculations here, but to illustrate the method from [22, 24], we will compute the small-$\tilde{r}$ asymptotics for the 2:1 case, for $\lambda > \lambda_c^{(2:1)}$, which has not been previously considered.

The asymptotic form (4.4) is actually valid even if $\lambda$ is complex, provided that it satisfies (5.14). To study the asymptotics when $\lambda > \lambda_c$ we can consider that $\lambda$
approaches the cut \([\lambda_c, +\infty)\) from below, for instance. Then we can rewrite \(6.16\) as

\[
A = 1 - \frac{3}{2}i\mu
\]  

(B1)

with

\[
\begin{aligned}
\mu &= \frac{1}{\pi} \ln \left[ \sqrt{\frac{3\lambda}{2\lambda_c} - \frac{1}{2}} - 1 - \frac{1}{2} + \frac{3\lambda}{2\lambda_c} \right] \\
&= \frac{1}{\pi} \cosh^{-1} \left( \frac{3\lambda}{2\lambda_c} - \frac{1}{2} \right) > 0
\end{aligned}
\]  

(B2a)

Replacing into \(3.5c\) and keeping only the first two dominant terms (which are of the same order) gives

\[
e^{-y_{21}/2} = \frac{-\tilde{r}}{3\sqrt{6\mu}} (z - \tilde{z}) + O(\tilde{r}^8)
\]  

(B3)

with

\[
z = \left( \frac{\tilde{r}}{6\sqrt{3}} \right)^{3i\mu/2} \left[ \Gamma \left( 1 - i\frac{\mu}{2} \right) \Gamma(1 - i\mu) \right]^{1/2} \left[ \Gamma \left( 1 + i\frac{\mu}{2} \right) \Gamma(1 + i\mu) \right]^{-1/2}
\]  

(B4)

If one chooses \(\lambda\) to approach the cut \([\lambda_c, +\infty)\) from above then \(\mu\) is changed into \(-\mu\) and the final result is unchanged.

Finally, the potential \(y_{21}\) is given by

\[
e^{-y_{21}/2} = \frac{2\tilde{r}}{3\mu\sqrt{6}} \sin \left[ -\frac{3\mu}{2} \ln \tilde{r} - \Psi^{(2:1)}(\mu) \right] + O(\tilde{r}^8)
\]  

(B5)

where

\[
\Psi^{(2:1)}(\mu) = \Im \left\{ \ln \left[ \Gamma \left( 1 - i\frac{\mu}{2} \right) \Gamma(1 - i\mu) \right] \right\}
\]  

(B6)

For the sake of completeness, we reproduce here smallerr asymptotics for the 1:1 and the 1:2 cases which were computed in Refs. \([22, 24]\), respectively. For the 1:1 electrolyte, when \(\lambda > \lambda^{(1:1)}\), the electric potential is given by

\[
e^{-y_{11}(\tilde{r})/2} = \frac{\tilde{r}}{4\mu} \sin \left[ -2\mu \ln \frac{\tilde{r}}{8} + 2\Psi^{(1:1)}(\mu) \right] + O(\tilde{r}^5)
\]  

(B7a)

with

\[
\mu = \frac{1}{\pi} \cosh^{-1}(\pi\lambda) > 0 \quad (1 : 1)
\]  

(B7b)

and

\[
\Psi^{(1:1)}(\mu) = \Im \left\{ \ln \left[ \Gamma(1 + i\mu) \right] \right\}
\]  

(B7c)

For the 1:2 electrolyte, when \(\lambda > \lambda^{(1:2)}\), the asymptotics are \([24]\)

\[
e^{-y_{12}(\tilde{r})} = \frac{\tilde{r}}{3\mu\sqrt{3}} \sin \left[ -3\mu \ln \frac{\tilde{r}}{6\sqrt{3}} - 2\Psi^{(1:2)}(\mu) \right] + O(\tilde{r}^4)
\]  

(1 : 2)

(B8)

now with

\[
\mu = \frac{1}{\pi} \cosh^{-1} \left( \frac{1}{2} + \frac{\lambda}{2\lambda_c} \right) > 0
\]  

(B9)

and

\[
\Psi^{(1:2)}(\mu) = \Im \left\{ \ln \left[ \Gamma \left( \frac{1}{2} - i\mu \right) \Gamma(1 - i\mu) \right] \right\}
\]  

(B10)

For practical purposes, since \(\mu\) is at most of order \(1/|\ln \tilde{c}|\), we can expand the functions

\[
\begin{align*}
\Psi^{(1:1)}(\mu) &= -\gamma\mu + O(\mu^3) \\
\Psi^{(1:2)}(\mu) &= \mu \left( \frac{3}{2} \gamma + \ln 2 \right) + O(\mu^3) \\
\Psi^{(2:1)}(\mu) &= 3\gamma\mu/2 + O(\mu^3)
\end{align*}
\]  

(B11) \quad (B12) \quad (B13)

The asymptotics presented in Eqs. \(3.7\) in the main text use this approximation for \(\Psi(\mu)\).

In principle this means that our expressions in the main text for \(\mu\) are accurate only to order \(O(1/|\ln \tilde{a}|^2)\). However, an explicit computation using further terms in the Taylor expansion of \(\Psi(\mu)\) shows that our results, in the form presented in the main text, are actually accurate up to order \(1/|\ln \tilde{a}|^3\) for \(\mu\) and order \(1/|\ln \tilde{a}|^4\) for the effective charges.

To illustrate this, consider, for example, the value of \(\mu_{\text{sat}}\) for the 1:1 case. Using a Taylor expansion of \(\Psi^{(1:1)}(\mu)\) up to order \(\mu^3\) gives

\[
\mu^{(1:1)}_{\text{sat}} = \frac{\pi}{2\ln \frac{8}{\tilde{a}}} \left[ 1 - \frac{\gamma}{\ln \frac{8}{\tilde{a}}} + \frac{\gamma^2}{(\ln \frac{8}{\tilde{a}})^2} - \frac{\gamma^3 - \frac{\gamma}{\ln \frac{8}{\tilde{a}}}}{(\ln \frac{8}{\tilde{a}})^3} \right] + O \left( (\ln \tilde{a})^{-5} \right)
\]  

(B14)

where \(\psi(x) = d\ln \Gamma(x)/dx\) is the digamma function and \(\psi^{(2)}(x)\) its second derivative. Replacing this expression into
Eqs. (3.12) and (2.8), yields the effective charge at saturation
\[ \xi_{\text{sat}}^{(1:1)} = \tilde{a}K_1(\tilde{a}) \left[ \frac{2}{\pi} + \frac{\pi^3}{4(\ln \tilde{a})^2} - \frac{\gamma \pi^3}{2 (\ln \tilde{a})^3} + \frac{144 \gamma^2 \pi^3 + \pi^7}{192 (\ln \tilde{a})^4} \right] - \frac{\pi^3(48 \gamma^3 + \gamma \pi^4 + \pi^7 \psi(2)(1))/48}{(\ln \tilde{a})^5} + O\left((\ln \tilde{a})^{-6}\right) \]

\[ (B15) \]

A direct comparison of Eqs. (B15) and (B14) with (114a) and (5.9a) shows that the (more compact) expressions presented in the main text are indeed accurate up to order 1/|ln a|^3 for µ and order 1/|ln a|^4 for ξ_{sat}.

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