

Guest Charges in an Electrolyte: Renormalized Charge, Long- and Short-Distance Behavior of the Electric Potential and Density Profiles

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Received April 27, 2005; accepted July 19, 2005; Published Online: 31 December 2005

We complement a recent exact study by L. Šamaj on the properties of a guest charge Q immersed in a two-dimensional electrolyte with charges $+1/-1$. In particular, we are interested in the behavior of the density profiles and electric potential created by the charge and the electrolyte, and in the determination of the renormalized charge which is obtained from the long-distance asymptotics of the electric potential. In Šamaj's previous work, exact results for arbitrary coulombic coupling β were obtained for a system where all the charges are points, provided $\beta Q < 2$ and $\beta < 2$. Here, we first focus on the mean field situation which we believe describes correctly the limit $\beta \rightarrow 0$ but βQ large. In this limit we can study the case when the guest charge is a hard disk and its charge is above the collapse value $\beta Q > 2$. We compare our results for the renormalized charge with the exact predictions and we test on a solid ground some conjectures of the previous study. Our study shows that the exact formulas obtained by Šamaj for the renormalized charge are not valid for $\beta Q > 2$, contrary to a hypothesis put forward by Šamaj. We also determine the short-distance asymptotics of the density profiles of the coions and counterions near the guest charge, for arbitrary coulombic coupling. We show that the coion density profile exhibit a change of behavior if the guest charge becomes large enough ($\beta Q \geq 2 - \beta$). This is interpreted as a first step of the counterion condensation (for large coulombic coupling), the second step taking place at the usual Manning–Oosawa threshold $\beta Q = 2$.

KEY WORDS: Coulomb systems; Cylindrical polyelectrolytes; Renormalized charge; Counterion condensation; Sine-Gordon model.

1. INTRODUCTION

In a recent paper⁽¹⁾, Šamaj studied the properties of one or two “guest” charges immersed in a classical (i.e. non-quantum) two-dimensional two-component charge-

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symmetric electrolyte. Using results from the (1+1)-integrable sine-Gordon model⁽²⁻⁴⁾, in particular the known expressions for the expectation value of the exponential field^(5,6) and for the form factors^(7,8) of this theory, and the exact solution for the thermodynamics of the two-dimensional two-component plasma⁽⁹⁾, he was able to determine exactly the excess chemical potential of a single “guest” charge immersed in the electrolyte, the long-distance behavior of the electric potential created by this guest charge and the long-distance behavior of the interaction energy between two guest charges, in the whole regime where the system of point charges is stable (i.e. when both the guest charges and the internal charges of the electrolytes are point particles).

An important result from Ref. [1] is for the electric potential created by a single guest charge Q immersed in the electrolyte. This potential $\psi(r)$ has a long-distance behavior, as the distance $r \rightarrow \infty$, similar to the screened potential predicted by Debye–Hückel theory,

$$\psi(r) \sim Q_{\text{ren}} K_0(m_1 r) \quad (1.1)$$

where m_1 is the inverse screening length (it is also the mass of the lightest breather of the sine-Gordon model), and it is given in terms of the inverse Debye length $\kappa = \sqrt{2\pi\beta n}$ in Eq.(4.15) of Ref. [1]. We shall use the same notations as in Ref. [1]: β is the Coulombic coupling, the electrolytes charges are $+1/-1$ and n is the density. In (1.1), K_0 is the modified Bessel function of order 0. However Q_{ren} is not the charge Q of the guest charge (as it would be in Debye–Hückel theory), but it is known as the renormalized charge. Šamaj found the following expression for the renormalized charge (Eqs. (5.8) and (5.9) of Ref. [1])

$$Q_{\text{ren}} = \frac{2 \exp \left[- \int_0^{\pi\beta/(4-\beta)} \frac{t dt}{\pi \sin t} \right]}{(4 - \beta) \sin \left(\frac{\pi\beta}{2(4-\beta)} \right)} \sin \left(\frac{\pi\beta Q}{4 - \beta} \right). \quad (1.2)$$

The concept of renormalized charge is very important in colloidal science⁽¹⁰⁻¹⁶⁾, thus Šamaj result is of extreme importance for colloidal science, in particular for the study of cylindrical polyelectrolytes, which can be reduced to a two-dimensional problem.

Šamaj claims that the rigorous validity of his result (1.2) is for $\beta|Q| < 2$, which is the regime where the system of point particles is stable. However, he gives some arguments to support a conjecture he called “regularization hypothesis”. This conjecture states that the validity of (1.2) goes actually beyond $\beta|Q| = 2$. In the case $\beta|Q| > 2$, the regularization hypothesis says that Eq. (1.2) gives the value of the renormalized charge for a guest particle of charge Q and radius a in the limit $m_1 a \ll 1$.

In this article, we present some indications that suggest that the regularization hypothesis is not valid. These indications come from the small-coupling limit $\beta \rightarrow 0$ but when $\beta|Q|$ can be arbitrary large. This will be explained in Section 2.

In Section 3, follows a discussion on the short-distance behavior of the density profiles, near the guest charge. In particular, we show that the coion density have a change of behavior when $\beta|Q| = 2 - \beta$, which can be interpreted as a “precursor” of the counterion condensation.

2. THE MEAN FIELD LIMIT: POISSON–BOLTZMANN EQUATION

2.1. The case $a = 0$ and $\beta|Q| < 2$

Let $\psi(r)$ be the electric potential at a distance r from a single guest charge Q immersed in the electrolyte. The guest charge is an impenetrable disk of radius a with its charge spread over its perimeter. We shall use the dimensionless potential $y(\hat{r}) = \beta\psi(r)$ with $\hat{r} = \kappa r$.

For a three dimensional electrolyte in the presence of an arbitrary external charge distribution, it is rigorously proved in Ref. [17] that, in the limit $\beta \rightarrow 0$, the density and correlation functions of the electrolyte are given by the ones of an ideal gas in the presence of the external field $y(\hat{r})$ which is the solution of the nonlinear Poisson–Boltzmann equation with the external source charge. Based on this evidence, we conjecture that this is also valid for our problem, although in our case we consider a two-dimensional system, and in the case $a \neq 0$ we include a hard-core interaction between the external guest charge and the electrolyte (which is not considered in the proof of Ref. [17]). Thus, assuming the validity of this hypothesis, the mean field electric potential $y(\hat{r})$ for our problem is the solution of

$$\Delta_{\hat{r}}y(\hat{r}) = \sinh(y(\hat{r})) \quad \hat{r} > \hat{a} \tag{2.1}$$

$$\Delta_{\hat{r}}y(\hat{r}) = 0 \quad \hat{r} < \hat{a} \tag{2.2}$$

satisfying the boundary conditions

$$\lim_{\hat{r} \rightarrow \infty} y(\hat{r}) = 0 \tag{2.3}$$

$$\lim_{\hat{r} \rightarrow \hat{a}^+} \hat{r} \frac{dy(\hat{r})}{d\hat{r}} = -\beta Q \tag{2.4}$$

$$\lim_{\hat{r} \rightarrow \hat{a}^-} y(\hat{r}) = \lim_{\hat{r} \rightarrow \hat{a}^+} y(\hat{r}) \tag{2.5}$$

where $\hat{a} = \kappa a$ is the guest particle radius in units of $1/\kappa$ and the charge Q of the guest particle is supposed to be uniformly spread over its perimeter.

This is usually called the mean field approximation. Let us remind the reader that the mean field approximation corresponds to the classical treatment of the

sine-Gordon model: Poisson–Boltzmann equation is the stationary action equation of the sine-Gordon model. Let us also clarify, that the nonlinear Poisson–Boltzmann theory is correct in the limit $\beta \rightarrow 0$ when it is used to describe the density profiles of the electrolyte created by an *external* charge distribution, under the conditions considered in Ref. [17]. On the other hand, the linear Debye–Hückel theory should be used to describe the distribution functions of the *internal* charges of the bulk electrolyte in the limit $\beta \rightarrow 0$ ⁽¹⁸⁾.

The two-dimensional Poisson–Boltzmann Eq.(2.1) has been solved exactly^(19–21), and in particular the connexion problem has been studied extensively. This is the problem to relate the long-distance behavior of $y(\hat{r})$ with its short-distance behavior^(20,22,23). This connexion problem is essential for the determination of the renormalized charge.

Let us recall some of the results from^(19–21,23) relevant for our discussion. For a point guest particle, $a = 0$, and $\beta|Q| < 2$, the electric potential has the long-distance behavior

$$y(\hat{r}) \sim 4\lambda K_0(\hat{r}), \quad \hat{r} \rightarrow \infty \quad (2.6)$$

and the short-distance behavior

$$y_{11}(\hat{r}) = -2A \ln \hat{r} + 2 \ln B + o(1), \quad \hat{r} \rightarrow 0. \quad (2.7)$$

The solution of the connexion problem^(19–20,22) states that the constant λ intervening in the long-distance behavior is related to the constants A and B of the short-distance behavior by

$$A = \frac{2}{\pi} \arcsin(\pi\lambda) \quad (2.8)$$

and

$$B = 2^{3A} \frac{\Gamma\left(\frac{1+A}{2}\right)}{\Gamma\left(\frac{1-A}{2}\right)} \quad (2.9)$$

where $\Gamma()$ is the Gamma function. In relation to the physical problem, one immediately recognizes that $2A = \beta Q$ is the bare charge of the guest particle and $4\lambda = \beta Q_{\text{ren}}$ is the renormalized charge. Thus, the renormalized charge is given by

$$\beta Q_{\text{ren}} = \frac{4}{\pi} \sin\left(\frac{\pi\beta Q}{4}\right). \quad (2.10)$$

Notice that (2.10) corresponds to the limit $\beta \rightarrow 0$ while keeping βQ arbitrary large (with $\beta|Q| < 2$) of Eq. (1.2). Indeed the mean field approximation for the study of single guest charge Q immersed in the electrolyte is asymptotically correct in the low coupling limit $\beta \rightarrow 0$ and βQ arbitrary.

2.2. The case $a \neq 0$ and $\beta|Q| > 2$

If $\beta|Q| > 2$ it is mandatory to consider that the guest particle is a disk with impenetrable radius $a \neq 0$, otherwise the charges of opposite sign of the electrolyte will collapse with the guest charge. Although it is not possible (yet) to obtain exact results when $a \neq 0$ for arbitrary values of β , in the limit $\beta \rightarrow 0$ we can obtain some results, under the hypothesis that the mean field approach is correct in that limit when $a \neq 0$. Thus, when $a \neq 0$, and $\beta \rightarrow 0$ and $\beta|Q| > 2$, we assume that the electric potential is given again by the mean field theory: it is the solution of Eqs. (2.1) and (2.2) and the boundary conditions (2.3), (2.4) and (2.5). We will consider the case $\kappa a = \hat{a} \ll 1$ but $a \neq 0$.

To formally solve this problem, let us introduce $y_0(\hat{r})$ the solution of Poisson-Boltzmann Eq. (2.1) *in the whole space*, for $\hat{r} \in \mathbb{R}^+$, and satisfying the boundary condition (2.6) when $\hat{r} \rightarrow \infty$. So far, λ in Eq. (2.6) can be seen as an integration constant. Then, the electric potential is given by

$$y(\hat{r}) = \begin{cases} y_0(\hat{a}) & \text{for } \hat{r} \leq \hat{a} \\ y_0(\hat{r}) & \text{for } \hat{r} > \hat{a} \end{cases} \tag{2.11}$$

Enforcing the boundary condition (2.4) at $\hat{r} = \hat{a}$ determines the integration constant λ .

To determine λ in the case $\hat{a} \ll 1$ we need to know the short-distance asymptotics of $y_0(\hat{r})$. Without loss of generality (because the electrolyte is charge symmetric), let us suppose that $Q > 0$. For $\beta Q < 2 + O(1/|\ln \hat{a}|)^2$, the short-distance asymptotics are the same as in the previous section, given in Eq. (2.7).

If βQ is large enough (larger than 2) then $\lambda > 1/\pi$, and then the short-distance behavior of $y_0(\hat{r})$ changes drastically. It is now given by^(19,20).

$$y_0(\hat{r}) = -2 \ln \left(\frac{-\hat{r}}{4\mu} \right) - 2 \ln \left[\sin \left(2\mu \ln \frac{\hat{r}}{8} + 2\phi(\mu) \right) \right] + O(\hat{r}^4), \quad \hat{r} \rightarrow 0 \tag{2.12}$$

with

$$\phi(\mu) = \arg(\Gamma(1 - i\mu)). \tag{2.13}$$

Let us define

$$\varphi(\hat{r}, \mu) = 2\mu \ln \frac{\hat{r}}{8} + 2\phi(\mu) \tag{2.14}$$

which is the argument of the sine function in (2.12). The constant μ appearing in the short-distance behavior of $y_0(\hat{r})$ is related to λ (see Eq. (2.16) below) and can be determined by the boundary condition (2.4) at $r = a$. It is the solution of the

² When $a \neq 0$ there is a small (negative) correction of order $1/|\ln a|$ to the critical value $\beta Q = 2$, for details see [24].

transcendental equation

$$\beta Q = 2 + 4\mu \cot \left[2\mu \ln \frac{\hat{a}}{8} + 2\phi(\mu) \right]. \quad (2.15)$$

The solution of the connexion problem gives the following relation between λ and μ ^(19–20)

$$\mu = -\frac{1}{\pi} \cosh^{-1}(\pi\lambda) \quad (2.16)$$

Notice that we choose here $\mu < 0$. If $\beta Q > 2$ the argument of the cot function in Eq. (2.15) is in the range $[\pi/2, \pi]$. Eq. (2.16) allows us to obtain the renormalized charge Q_{ren} .

For $a \neq 0$, the definition of the renormalized charge comes from the long-distance behavior of the electric potential and its comparison with the solution from the linear Debye–Hückel theory

$$y(\hat{r}) \sim \frac{\beta Q_{\text{ren}}}{\hat{a} K_1(\hat{a})} K_0(\hat{r}), \quad \hat{r} \rightarrow \infty \quad (2.17)$$

where K_1 is the modified Bessel function of order 1. Comparing with (2.6) we have $\beta Q_{\text{ren}} = 4\hat{a} K_1(\hat{a})\lambda$. Notice the additional factor $\hat{a} K_1(\hat{a})$ in the renormalized charge. However this factor is not really important since if $\hat{a} \ll 1$, $\hat{a} K_1(\hat{a}) \sim 1$. We shall see that it is the behavior of λ which will be very different from the case when $a = 0$ and $\beta Q < 2$. Once μ has been determined from Eq. (2.15), using Eq. (2.16) we can find the renormalized charge

$$\beta Q_{\text{ren}} = \frac{4\hat{a} K_1(\hat{a})}{\pi} \cosh(\pi\mu) \quad (2.18)$$

Let us comment a few points on the small- \hat{r} behavior of the potential $y(\hat{r})$ and of $y_0(\hat{r})$. From Eq. (2.12), one can distinguish three special regions. Notice that $\varphi(\hat{r}, \mu)$ is a decreasing function of \hat{r} since $\mu < 0$. The first region is for $\hat{r} = 0$ up to a value r^* such that

$$\varphi(r^*, \mu) = \pi. \quad (2.19)$$

In this region, the formal solution $y_0(\hat{r})$ of Poisson–Boltzmann equation has no physical meaning, since $\varphi(\hat{r}, \mu)$ decreases from $+\infty$ to π , and then the argument of the logarithm of the second term of Eq. (2.12) oscillates around zero, changing of sign, thus $y_0(\hat{r})$ is not always real but can become complex. However this region is inside the guest charge ($r^* \leq \hat{a}$) and in this region the electric potential is a constant: $y(\hat{r}) = y_0(\hat{a})$.

The second region is for $\hat{r} \in [\hat{a}, r_M]$ where r_M is given by

$$\varphi(r_M, \mu) = \pi/2. \quad (2.20)$$

In this region $\pi/2 < \varphi(\hat{r}, \mu) < \pi$. If \hat{r} is close to \hat{a} (and \hat{a} is close to r^*), the second term of $y(\hat{r})$ in Eq. (2.12) can be very large because $\varphi(\hat{r}, \mu)$ is close to π . Then, as \hat{r} increases, $\varphi(\hat{r}, \mu)$ decreases from π down to $\pi/2$, and then, the second term of $y(\hat{r})$ in Eq. (2.12) decreases very fast. Since the counterion density is proportional to $e^{y(\hat{r})}$, this indicates that close to the guest charge there is a very large counterion density, which decreases quite fast as the distance \hat{r} increases. This is a manifestation of a widely known phenomenon in the theory of cylindrical polyelectrolytes, known as the Manning–Oosawa counterion condensation^(25,26). The layer of “condensed” counterions extends from $\hat{r} = \hat{a}$ to $\hat{r} = r_M$.

When $\hat{r} = r_M$ the second term of Eq. (2.12) vanishes. At this point the total charge $Q_{\text{guest+condens}}$ of the guest particle plus the condensed counterion layer is such that $\beta Q_{\text{guest+condens}} = 2$, as it can be seen from the first term of Eq. (2.12). We recover here another characteristic of the Manning–Oosawa counterion condensation^(25–27): the layer of condensed counterions reduces the bare charge of the guest charge to $\beta Q_{\text{guest+condens}} = 2$. Above r_M , we enter a third region, outside the condensed layer of counterions, where \hat{r} starts to become large enough such that the small- \hat{r} behavior (2.12) is no longer valid.

From a physical argument we can now see that as βQ becomes larger than 2, the renormalized charge is not given anymore by Eq. (2.10) (which is valid only for $a = 0$ and $\beta Q < 2$). Indeed, from the discussion above, we know that in the region $r^* > r_M$, just outside the counterion condensed layer, the guest charge “dressed” with the condensed counterions can be seen as an object with a charge $Q_{\text{guest+condens}} = 2/\beta$. Thus its renormalized charge will be close to the prediction of Eq. (2.10) for $\beta Q = 2$, that is βQ_{ren} is close to $4/\pi$.

The bare charge could be arbitrary large (with $\beta Q > 2$), but the renormalized charge will remain close to $4/\pi$, because of the Manning–Oosawa counterion condensation phenomenon. In particular, the renormalized will not oscillate and become eventually negative as predicted by (2.10) for $\beta Q > 2$, if the regularization hypothesis was valid.

This argument can also be justified from a more rigorous point of view. If \hat{a} is small enough, the solution of Eq. (2.15) for μ is small (of order $1/|\ln(\hat{a}/8)|$). The renormalized charge is given by the correct formula (2.18) when $\beta Q > 2$. If $\mu \ll 1$ and $\hat{a} \ll 1$, we see from (2.18) that βQ_{ren} is close to $4/\pi$. It is actually slightly larger than $4/\pi$.

This is verified numerically in figure 1, where we computed the renormalized charge from a numerical resolution of Poisson–Boltzmann equation, using the method described in Ref. [28]. We confirm numerically that the renormalized charge, for $\beta Q > 2$, is slightly above $4/\pi$ (for $\hat{a} \ll 1$). This can be contrasted with the prediction of the regularization hypothesis, shown in dashed line in Fig.1, where Q_{ren} is expected to decay when $\beta Q > 2$ and even vanish and change its sign at $\beta Q = 4$. The numerical results show that this is not true: Q_{ren} is always an increasing function of Q , and eventually saturates to a finite value for large values of Q .

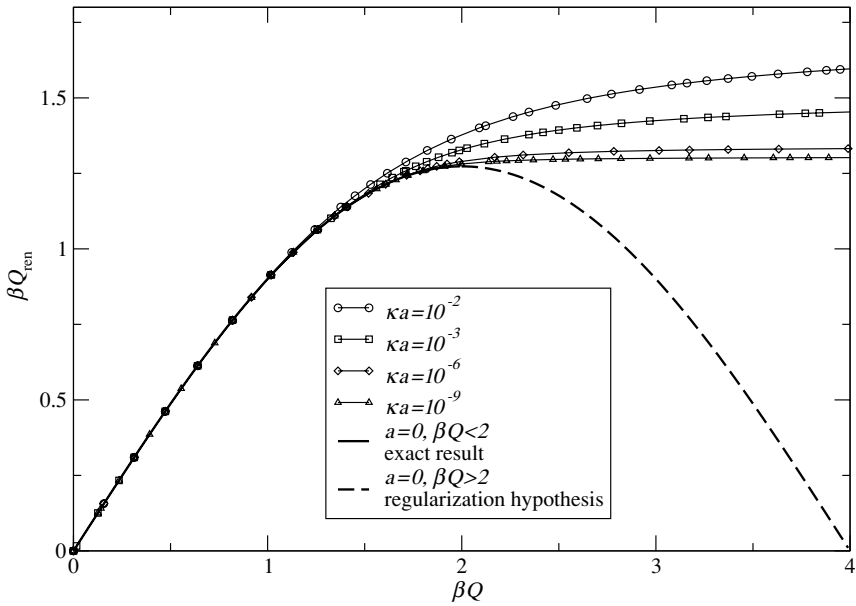


Fig. 1. The renormalized charge Q_{ren} as a function of the bare charge Q , in the mean-field limit $\beta \rightarrow 0$, for various values of the radius a of the guest charge. For $a = 0$, the exact result (2.10) is shown in full thick line for $\beta Q < 2$. In dashed line, the extension of (2.10) for $\beta Q > 2$ is shown: this is the prediction of the regularization hypothesis from Ref. [1]. The symbols correspond to values $a > 0$, obtained from a numerical resolution of Poisson–Boltzmann equation.

This saturation phenomenon⁽²⁷⁾ of the renormalized charge is quite usual in the nonlinear Poisson–Boltzmann approach to the problem. When the saturation phenomenon occurs we also have $\hat{a} = r^*$. Indeed, if $\hat{a} = r^*$, by the definition (2.19) of r^* we have $\varphi(\hat{a}, \mu) = \pi$ and one can verify that in Eq. (2.15), $Q \rightarrow +\infty$. Solving

$$\varphi(\hat{a}, \mu) = \pi \tag{2.21}$$

for μ and replacing in (2.18), allow us to obtain the saturation value of the renormalized charge. Eq. (2.21) is a transcendental equation, but since μ is small, of order $1/|\ln(\hat{a}/8)|$, if $\hat{a} \ll 1$, it can be solved in an expansion of powers of $1/|\ln(\hat{a}/8)|$. For example, up to order 4 in $1/|\ln(\hat{a}/8)|$, we find the renormalized charge at saturation⁽²³⁾

$$\beta Q_{\text{ren}}^{\text{sat}} = \frac{4\hat{a}K_1(\hat{a})}{\pi} \left[\cosh \frac{\pi^2}{2(\ln \frac{\hat{a}}{8} + \gamma)} + O(|\ln \hat{a}|^{-5}) \right] \tag{2.22}$$

where $\gamma \simeq 0.5772$ is the Euler constant.

In conclusion to this part, we notice the failure of the regularization hypothesis in the limit $\beta \rightarrow 0$ with $\beta Q > 2$ and $\hat{a} \ll 1$. The renormalized charge is not given by Eq. (1.2) in that limit as the regularization hypothesis claims.

3. SHORT-DISTANCE BEHAVIOR OF THE DENSITY PROFILES: A “PRECURSOR” OF THE COUNTERION CONDENSATION AT $\beta Q = 2 - \beta$

An important factor, which is responsible of the failure of the regularization hypothesis exposed in the previous section, is the change of behavior of the electric potential at short distances when $\beta Q > 2$. In this section we consider the general situation when $0 < \beta < 2$ and we return to the case of point particles $a = 0$. We study the short-distance behavior of the density profiles and show that there is a change of behavior in the asymptotic expansion at short distances of the coion density profiles when $\beta|Q| = 2 - \beta$.

The short-distance behavior of the density profiles, in the presence of the guest charge, can be obtained by adapting an argument presented in Refs. [29, 30] for the correlation functions. Let suppose, without loss of generality, that $Q > 0$. From the general principles of statistical mechanics we know that the short-distance behavior of the density profiles, near the guest charge at the origin, is dominated by the Boltzmann factor of the Coulomb potential $e^{-\beta Q q v_c(r)}$, with $v_c(r) = -\ln r$ the Coulomb potential. We have

$$n_q(r) \sim n_q c_{Qq} r^{\beta Q q}, \quad r \rightarrow 0 \tag{3.1}$$

with $q = \pm 1$, n_q is the bulk density of charges q , and the constant c_{Qq} is related to the excess chemical potentials (μ_q^{exc} , μ_Q^{exc} , μ_{Q+q}^{exc}) of the charges q , Q and $Q + q$, which can in turn be expressed as expectation values of exponentials of the sine-Gordon field ϕ ,

$$c_{Qq} = \exp \left[-\beta \left(\mu_{Q+q}^{\text{exc}} - \mu_Q^{\text{exc}} + -\mu_q^{\text{exc}} \right) \right] = \frac{\langle e^{ib(Q+q)\phi} \rangle}{\langle e^{ibQ\phi} \rangle \langle e^{ibq\phi} \rangle} \tag{3.2}$$

with the same conventions as in⁽¹⁾ for the normalization of the sine-Gordon field and $b^2 = \beta/4$. In the case $q = +1$ (coions, same sign as Q) this is valid provided βQ is small enough, as we will explain below.

Let $\Xi[Q]$ be the grand canonical partition function of the system composed by the electrolyte and the guest charge Q fixed at the origin, with fugacities z_+ and z_- for positive and negative particles respectively. The partition function is well defined for point particles if $\beta < 2$ and $\beta|Q| < 2$. The density of particles of charge q is

$$n_q(\mathbf{r}) = z_q r^{\beta Q q} \frac{\Xi[Q; q, \mathbf{r}]}{\Xi[Q]} \tag{3.3}$$

where $\Xi[Q; q, \mathbf{r}]$ is the partition function of the electrolyte in the electric field created by a guest charge Q fixed at the origin and a charge q fixed at \mathbf{r} .

When $r \rightarrow 0$, $\Xi[Q; q, \mathbf{r}]$ has a finite limit provided that $\beta|Q + q| < 2$, since $\Xi[Q; q, 0] = \Xi[Q + q]$ is the partition function of a system composed by the electrolyte and a guest charge $Q + q$ at the origin. Under this condition we can affirm that the short-distance behavior (3.1) for the density profile is valid. This can also be seen from (3.2): the expectation value $\langle e^{ib(Q+q)\phi} \rangle$ is finite provided $\beta|Q + q| < 2^{(1)}$.

For $Q > 0$ and $q = 1$, the above condition reads $\beta Q < 2 - \beta$. When $\beta Q > 2 - \beta$, Eq. (3.1) is no longer valid. We must return to the general expression (3.3), and study the short-distance behavior of $\Xi[Q; q, \mathbf{r}]$. If $\beta Q > 2 - \beta$, $\Xi[Q; q, \mathbf{r}]$ diverges as $r \rightarrow 0$. Its short-distance behavior is dominated by the approach of a charge -1 to the system of the charges Q and $+1$ which are separated by a distance $r^{(29)}$. This gives

$$\Xi[Q; q, \mathbf{r}] \sim \text{cst} \times r^{-\beta(Q+1)+2}, \quad r \rightarrow 0 \quad (3.4)$$

with cst some constant, which will not be needed for our analysis, but that can eventually be evaluated^(31,32). Thus, the short-distance behavior of the coion density profile, for $\beta Q > 2 - \beta$, is

$$n_+(r) \sim \text{cst} \times r^{2-\beta}, \quad r \rightarrow 0 \quad (3.5)$$

Notice that, on the other hand, the counterion density profile $n_-(r)$ behaves always as predicted by Eq. (3.1), since the corresponding $\Xi[Q; -1, \mathbf{r}]$ has always a finite limit at $r = 0$, provided $\beta < 2$ and $\beta Q < 2$.

The mean interaction potential $w_{+,Q}(r)$ of a coion (charge $+1$) with the guest charge Q and its polarization cloud, is defined by $n_+(r) = n_+ e^{-\beta w_{+,Q}(r)}$. From (3.5), we deduce that its short-distance behavior is

$$\beta w_{+,Q}(r) = \begin{cases} -\beta Q \ln r + O(1), & \text{if } \beta Q < 2 - \beta \\ -(2 - \beta) \ln r + O(1), & \text{if } \beta Q > 2 - \beta \end{cases}, \quad r \rightarrow 0 \quad (3.6)$$

Notice that, in particular, the short-distance leading behavior of $w_{+,Q}(r)$ is independent of Q when $\beta Q > 2 - \beta$. This situation can be interpreted as a “precursor” of the Manning–Oosawa counterion condensation. When βQ increases above $2 - \beta$, the counterion cloud near the guest charge reduces its bare charge so that the coions “see” a “dressed” object with charge $2/\beta - 1$, which is independent of Q .

On the other hand, the counterion mean interaction potential has always the behavior (provided $\beta < 2$ and $\beta Q < 2$)

$$\beta w_{-,Q}(r) \sim \beta Q \ln r + O(1), \quad r \rightarrow 0. \quad (3.7)$$

The counterions continue to “see” the bare guest charge Q even if $\beta Q > 2 - \beta$.

When $\beta Q \geq 2$, we arrive at the collapse of the charge Q with the counterions. In this case we need to consider that the guest charge is an impenetrable disk with radius $a \neq 0$. $\beta Q = 2$ corresponds to the well-known Manning threshold for counterion condensation.

We would like to stress that the above analysis is valid for large coupling $0 < \beta < 2$. The usual presentation of the counterion condensation phenomenon^(25,26) is done in a small-coupling approximation $\beta \rightarrow 0$. Notice that in this case both limits $\beta Q < 2 - \beta$ and $\beta Q < 2$ coincide. Here we have put in evidence that, at large coulombic coupling β , the counterion condensation might actually take place in two steps: first when $\beta Q = 2 - \beta$, where the coion density changes its short-distance behavior, but not the counterion density, and a second step, at the usual threshold $\beta Q = 2$.

Let us conclude this section with a conjecture, suggested by Šamaj⁽³³⁾. The mean field analysis of the previous section shows that the formula (1.2) for the renormalized charge is not valid beyond $\beta Q = 2$ in the limit $\beta \rightarrow 0$. For arbitrary values of β , the validity of (1.2) might be beyond $\beta Q = 2$. In the case $\beta \rightarrow 0$, the failure of (1.2) when $\beta Q > 2$ is accompanied by a change of behavior in the short distance asymptotics of the electric potential.

For arbitrary β , when $\beta Q > 2$ it is necessary to introduce a hard core for the guest particle. The coion density will certainly change its short distance behavior at $\beta Q = 2$. On the other hand there are indications that the counterion density will still behave at short distances as $r^{-\beta Q}$ up to $\beta Q < 2 + \beta$. This is because, as previously noted, $\Xi[Q; -1, \mathbf{r}]$ remains finite up to $\beta Q < 2 + \beta$, for small \mathbf{r} . Since the counterion density determines the dominant behavior at short distances of the electric potential, the electric potential might actually not change its short distance behavior until $\beta Q > 2 + \beta$. If this is true, the regularization hypothesis put forward by Šamaj, might be valid up to $\beta Q < 2 + \beta$ ⁽³³⁾. Interestingly, this leaves open the possibility of charge inversion (i.e. the renormalized charge becomes negative) if $\beta > 1$, when $\beta Q > 4 - \beta$.

4. CONCLUSION

As a complement to Ref. [1], we have studied the low-coupling, mean field situation, $\beta \rightarrow 0$, but $\beta|Q|$ arbitrary, in order to determine the behavior of the renormalized charge when $\beta|Q| > 2$ of a guest charge Q immersed in an electrolyte. We have shown that, at least in this mean field situation, the regularization hypothesis put forward by Šamaj in Ref. [1] is not valid: the formula (1.2) for the renormalized charge is not valid when $\beta|Q| > 2$.

We have also studied the short-distance asymptotics of the density profiles. The coion density profile exhibits a change of behavior if the guest charge Q is large, $\beta Q > 2 - \beta$, as shown in Eq. (3.6). Colloquially speaking, it is like if the coions “see” a “dressed” charge $2/\beta - 1$ instead of Q , when $\beta Q > 2 - \beta$. We

interpret this as a first step in the Manning–Oosawa counterion condensation when the coulombic coupling β is large, the second step taking place when $\beta Q = 2$ as it is usually explained in the literature^(25,26) for the small coupling $\beta \rightarrow 0$ situation.

ACKNOWLEDGMENTS

I thank L. Šamaj for a careful reading of this manuscript and for his comments and remarks. I also thank B. Jancovici for his comments.

This work was partially funded by COLCIENCIAS (project 1204-05-13625), ECOS-Nord/COLCIENCIAS, and Comité de Investigaciones de la Facultad de Ciencias de la Universidad de los Andes.

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