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Saturation of Electrostatic Potential: Exactly Solvable 2D Coulomb Models

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We test the concepts of renormalized charge and potential saturation, introduced within the framework of highly asymmetric Coulomb mixtures, on exactly solvable Coulomb models. The object of study is the average electrostatic potential induced by a unique "guest" charge immersed in a classical electrolyte, the whole system being in thermal equilibrium at some inverse temperature β. The guest charge is considered to be either an infinite hard wall carrying a uniform surface charge or a charged colloidal particle. The systems are treated as two-dimensional; the electrolyte is modelled by a symmetric two-component plasma (TCP) of point-like $\pm e$ charges with logarithmic Coulomb interactions. Two cases are solved exactly: the Debye–Hückel limit $\beta e^2 \to 0$ and the Thirring free-fermion point $\beta e^2 = 2$. The results at the free-fermion point can be summarized as follows: (i) The induced electrostatic potential exhibits the asymptotic behavior, at large distances from the guest charge, whose form is different from that obtained in the Debye–Hückel (linear Poisson–Boltzmann) theory. This means that the concept of renormalized charge, developed within the nonlinear Poisson–Boltzmann (PB) theory to describe the screening effect of the electrolyte cloud, fails at the free-fermion point. (ii) In the limit of an infinite bare charge, the induced electrostatic potential saturates at a finite value in every point of the electrolyte region. This fact confirms the previously proposed hypothesis of potential saturation.

KEY WORDS: Coulomb systems; colloids; charge renormalization; electrostatic potential saturation; solvable models.

1. INTRODUCTION

Asymmetric classical Coulomb mixtures, such as highly charged colloidal or polyelectrolyte suspensions, in the strong coupling regime, have

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attracted much attention in the last years (for a review of phenomenological approaches built on the base of mean-field theories, see ref. 1). The concept of renormalized charge has been introduced within the Wigner–Seitz cell models to describe an effective interaction between highly-charged "macro-ions" as a result of their strong positional correlations with the oppositely charged "micro-ions".[(2–6)]

The concept of renormalized charge can be documented in the infinite dilution limit of colloids.[(7–11)] The simplified model consists of a unique colloidal particle idealized as a hard sphere of radius a carrying charge Ze, Z is the valence and e the elementary charge, at its centre (any spherically symmetric charge distribution inside the colloid can be represented in this way). The colloid is immersed in an electrolyte modeled by a symmetric two-component plasma (TCP) of elementary $\pm e$ (if possible, point-like) charges. The system is defined in an infinite ν-dimensional space of points $\mathbf{r} \in R^\nu$, having for simplicity vacuum dielectric constant $\epsilon = 1$. The interaction energy of two particles of charges q and q' at the respective spatial positions $\mathbf{r}$ and $\mathbf{r}'$ is given by $qq'\phi(|\mathbf{r}-\mathbf{r}'|)$, where ϕ, the Coulomb potential induced by a unit charge, is the solution of the Poisson equation

$$\Delta\phi(\mathbf{r}) = -s_\nu \delta(\mathbf{r}), \tag{1.1}$$

s_ν is the surface area of the ν-dimensional unit sphere. This definition of the ν-dimensional Coulomb potential maintains many generic properties (e.g., screening sum rules ref. 12) of "real" three-dimensional (3D) Coulomb systems with the interaction potential $\phi(r) = 1/r, r \in R^3$. In particular, in 2D,

$$\phi(\mathbf{r}) = -\ln(|\mathbf{r}|/r_0), \quad \mathbf{r} \in R^2, \tag{1.2}$$

where r_0 is a free-length scale. Thermal equilibrium is treated in the grand canonical ensemble characterized by the inverse temperature $\beta = 1/(kT)$ and by the couple of bulk particle fugacities for electrolyte $\pm e$-charged particles, $z_+ = z_- = z$. The corresponding average bulk densities will be denoted by $n_+ = n_- = n/2$, n is the total number density. For the classical case of point-like particles, the singularity of the Coulomb potential $\phi(\mathbf{r})$ at the origin $\mathbf{r} = \mathbf{0}$ often prevents the thermodynamic stability against the collapse of positive–negative pairs of charges: in 2D, for small enough temperatures; in 3D, for any finite temperature.

We shall explain the concept of renormalized charge on the 3D mean-field theories, valid in the high-temperature limit and free from the collapse problem of point-like charges. Let us fix the colloidal particle at the origin **0** and denote by $\psi(\mathbf{r})$ the induced average electrostatic potential at point $\mathbf{r}$. Inside the colloidal hard-core region $0 < r \leqslant a$, $\psi(\mathbf{r})$ satisfies the Poisson equation

$$\Delta\psi_<(\mathbf{r}) = -4\pi Ze\delta(\mathbf{r}). \tag{1.3}$$

Inside the electrolyte region $r > a$, the Poisson equation takes the form

$$\Delta\psi_>(\mathbf{r}) = -4\pi\rho(\mathbf{r}), \tag{1.4}$$

where

$$\rho(\mathbf{r}) = e\left[n_+(\mathbf{r}) - n_-(\mathbf{r})\right] \tag{1.5}$$

is the charge density of electrolyte particles. Within the ordinary mean-field approach, the average particle densities at a given point are approximated by replacing the potential of mean force by the average electrostatic potential at that point, $n_\pm(\mathbf{r}) = n_\pm \exp[\mp\beta e\psi_>(\mathbf{r})]$. Eq. (1.4) then reduces to the non-linear Poisson–Boltzmann (PB) equation

$$\Delta\psi_>(\mathbf{r}) = 4\pi en\sinh\left[\beta e\psi_>(\mathbf{r})\right]. \tag{1.6}$$

Debye and Hückel proposed a linearization of this equation by considering the small-argument expansion of $\sinh(\beta e\psi_>) \sim \beta e\psi_>$ valid in the high-temperature limit. The linear PB equation then reads

$$\left(\Delta - \kappa^2\right)\psi_>(\mathbf{r}) = 0, \tag{1.7}$$

where $\kappa = \sqrt{4\pi\beta e^2 n}$ is the 3D inverse Debye length of the electrolyte particles. Due to the spherical symmetry of the problem, $\Delta = \partial_r^2 + (2/r)\partial_r$. Eqs. (1.3) and (1.7), subject to the condition of regularity at $r \to \infty$ and the boundary conditions of continuity of the electrostatic potential and the electric field across the colloid surface $r = a$, imply that, in the linear Debye–Hückel theory,

$$\psi_<(r) = Ze\left(\frac{1}{r} - \frac{\kappa}{1+\kappa a}\right), \tag{1.8}$$

$$\psi_>(r) = \frac{Ze}{1+\kappa a}\frac{\exp\left[-\kappa(r-a)\right]}{r}. \tag{1.9}$$

The charge density of electrolyte particles is given by

$$\rho(r) = -\beta e^2 n \psi_>(r), \quad r > a. \tag{1.10}$$

Strictly speaking, the linearization of Eq. (1.6) is only valid if $\beta e \psi(\mathbf{r}) \ll 1$, and this is indeed true for asymptotically large distances r where the screened potential $\psi(\mathbf{r})$ vanishes. As a consequence, at large r, the solution of the non-linear PB equation (1.6) must also take the Yukawa form

$$\psi_>(r) \sim A \frac{\exp[-\kappa(r-a)]}{r}, \quad r \to \infty \tag{1.11}$$

with A being an r-independent constant. The non-linearity of the problem is reflected only through an effective boundary condition at the colloid surface determining the constant A. Comparing (1.11) with (1.9) one sees that A is related to the renormalized colloid valence, Z_{ren}, as follows

$$A = \frac{Z_{\text{ren}} e}{1 + \kappa a}. \tag{1.12}$$

The renormalized charge reflects the screening effect of the electrolyte cloud, and can further be used to establish an effective interaction for a system of guest charges immersed in the electrolyte. Since the exact solution of the non-linear PB equation (1.6) for the sphere geometry is not available, the constant A can be determined only approximately, i.e., in the limiting case $\kappa a \gg 1$, by matching with the exact solution of the non-linear PB for the charged-plane geometry.(9,10) An important feature is that, as expected from the Manning condensation theory,(2) the renormalized valence saturates at some finite value $Z_{\text{ren}}^{\text{sat}}$ when the colloidal bare valence Z goes to infinity.

More refined approaches, which go beyond the mean-field approximation and incorporate electrostatic correlations among the electrolyte particles, were developed in refs. 13 and 14. Monte-Carlo simulations(13) indicate the existence of a maximum in the plot of the renormalized charge versus the bare colloidal charge.

As was correctly mentioned by Téllez and Trizac,(15) the definition of renormalized charge requires that the average electrostatic potential behaves far from the colloid as it would within the linearized Debye–Hückel theory, up to the constant prefactor. This is not at all ensured for a finite temperature. To avoid this artificial limitation in the saturation problem, one considers the possibility of a more general phenomenon of *potential* saturation: the question is whether, in the limit of the infinite bare colloidal charge $Ze \to \infty$, the induced average electrostatic potential $\psi^{\rm sat}(\mathbf{r})$ is finite inside the whole electrolyte region $r > a$.[2] We would like to emphasize that the potential saturation, if it exists, is a pure non-linearity effect: there is no potential saturation within the linear Debye–Hückel theory, (see Eq. (1.9)).

It is well known that the linearized Debye–Hückel theory correctly describes the small-coupling (high-temperature) limit $\beta e^2 \to 0$ in the sense that the basic screening properties of the charged system in the conducting regime are preserved. For an infinite homogeneous system, the zeroth and second moments of the truncated charge–charge correlation function are fixed by the Stillinger–Lovett sum rules.[12] In the present case one can readily verify by using Eqs. (1.9) and (1.10) that the screening cloud of the electrolyte particles compensates exactly the bare charge of the "guest" colloid:

$$Ze + \int_a^\infty dr\, 4\pi r^2 \rho(r) = 0. \tag{1.13}$$

This counterpart of the bulk zeroth-moment (electroneutrality) sum rule can be derived directly from the Poisson Eq. (1.4) by applying the Gauss' law and then considering the boundary conditions for the electric field $-\mathrm{d}_r \psi|_{r=a} = Ze/a^2$ and $-\mathrm{d}_r \psi|_{r\to\infty} = 0$. The electroneutrality sum rule (1.13) thus holds within the non-linear PB theory, too.

The present work aims to put the concept of charge renormalization and the hypothesis of the electric potential saturation on a rigorous basis. As a test model for the electrolyte, we use the 2D symmetric TCP of point-like $\pm e$ charges with logarithmic pairwise interactions (1.2). The 2D plasma of point-like charges is stable against the collapse of positive–negative pairs of charges provided that the corresponding Boltzmann factor $r^{-\beta e^2}$ is integrable at short distances in 2D, i.e. for the (dimensionless) coupling constant $\beta e^2 < 2$. In this stability range of couplings, the equilibrium statistical mechanics of the plasma (the bulk thermodynamics, special cases of the surface thermodynamics and the large-distance behavior of the two-body correlation function) is exactly solvable via an equivalence with the integrable 2D Euclidean sine-Gordon field theory (for a short review, see ref. 16). The complete exact information about correlation functions is available in two special cases: in the high-temperature Debye–Hückel limit $\beta e^2 \to 0$, and just at the collapse point $\beta e^2 = 2$,[17,18] which corresponds to the free-fermion point of an equivalent 2D Thirring model (although the free energy and the particle density diverge at the collapse point, the

[2] Based on simple electrostatics, the potential is infinite at the colloid surface $r = a$.

truncated Ursell correlation functions are finite). We examine the above-outlined problems in these two exactly solvable cases, for two particular geometries: the charged line and the charged circular colloid. Based on the exact results we show that the concept of renormalized charge does not apply to the studied 2D microscopic Coulomb system. On the other hand, the anticipated phenomenon of electric potential saturation is confirmed.

The paper is organized as follows. Section 2 deals with the charged-line geometry. Section 2.1 is devoted to a short recapitulation of the Debye-Hückel limit. In Section 2.2, the known exact results at the free-fermion point[18] are analyzed from the point of view of the studied subjects. Section 3 deals with the colloidal-charge geometry. As before, Section 3.1 concerns the Debye–Hückel limit, while Section 3.2 is devoted to an original derivation of the exact solution at the free-fermion point. A recapitulation and some concluding remarks are given in Section 4.

2. CHARGED LINE

We consider an infinite 2D space of points $\mathbf{r} \in R^2$ defined by Cartesian coordinates (x, y). The half-space $x < 0$, impenetrable to particles, is assumed to be a vacuum hard wall. The electrolyte of $\pm e$ point-like charges is confined to the complementary half-space $x > 0$. The model interface is the line localized at $x = 0$, along the y-axis. The line, which carries a uniform charge σe per unit length, models an electrode. There is another electrode of opposite charge density localized at $x = +\infty$. The electrostatic potential induced by the two electrodes is 0 for $x < 0$ and $-2\pi\sigma e x$ for $x > 0$. The boundary condition for the electric field reads

$$-\left.\frac{d\psi(x)}{dx}\right|_{x=0} = 2\pi\sigma e. \tag{2.1}$$

2.1. Debye–Hückel Limit

The average electrostatic potential at distance x form the interface satisfies the 2D Poisson equation

$$\frac{d^2\psi(x)}{dx^2} = -2\pi\rho(x), \quad x \geqslant 0. \tag{2.2}$$

In the spirit of the Debye–Hückel theory valid in the limit $\beta e^2 \to 0$, the charge density of the electrolyte particles is approximated, in close analogy with Eq. (1.10), as $\rho(x) \sim -\beta e^2 n \psi(x)$. The linear PB equation thus reads

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}x^2} - \kappa^2 \right) \psi(x) = 0, \quad x \geqslant 0, \tag{2.3}$$

where $\kappa = \sqrt{2\pi\beta e^2 n}$ is the 2D inverse Debye length. The solution of (2.3), subject to the requirement of regularity at $x \to \infty$ and the boundary condition (2.1), takes the form

$$\psi(x) = \frac{2\pi\sigma e}{\kappa} \exp(-\kappa x), \quad x \geqslant 0. \tag{2.4}$$

The consequent charge density

$$\rho(x) = -\sigma e \kappa \exp(-\kappa x), \quad x \geqslant 0, \tag{2.5}$$

fulfills the following analogue of the screening sum rule (1.13):

$$\sigma e + \int_0^\infty dx\, \rho(x) = 0. \tag{2.6}$$

2.2. The Free-fermion Point

Since the particle density diverges at the collapse point $\beta e^2 = 2$, the available thermodynamic parameter is the fugacity z. It will be considered in a rescaled form, $m = 2\pi r_0 z$ [r_0 is the length scale considered in (1.2)], having dimension of an inverse length. The density profiles of electrolyte particles near the charged plain hard wall were obtained in ref. 18 by solving the Green-function problem of the corresponding boundary Thirring model at its free-fermion point. The result is

$$\begin{aligned} n_\pm(x) = n_\pm &+ \frac{m^2}{4\pi} [K_2(2mx) - K_0(2mx)] \\ &- \frac{m^2}{2\pi} \left[\frac{1}{2mx} + \frac{1}{(2mx)^2} \right] \exp(-2mx) \\ &+ \frac{m^2}{2\pi} \int_0^{\mp 2\pi\sigma} \frac{\mathrm{d}t}{\sqrt{m^2+t^2} - t} \exp\left(-2\sqrt{m^2+t^2}\, x \right), \end{aligned} \tag{2.7}$$

where K_l are the modified Bessel functions of order l. The divergent bulk particle densities $n_+ = n_- = n/2$ can be regularized, for example, by considering a small hard core around each particle;[18] since we are interested in the charge density $\rho(x)$ defined by the difference $e[n_+(x) - n_-(x)]$, we avoid this regularization procedure. After some simple algebra, one gets

$$\rho(x) = -\frac{e}{\pi} \int_0^{2\pi\sigma} \mathrm{d}t \, \sqrt{m^2+t^2} \exp\left(-2\sqrt{m^2+t^2}x\right). \tag{2.8}$$

It is easy to check that the screening sum rule (2.6) is fulfilled by this charge density.

The corresponding electrostatic potential, determined by the Poisson equation (2.2) and the requirement of regularity at $x \to \infty$, reads

$$\psi(x) = \frac{e}{2} \int_0^{2\pi\sigma} \frac{\mathrm{d}t}{\sqrt{m^2+t^2}} \exp\left(-2\sqrt{m^2+t^2}x\right). \tag{2.9}$$

The boundary condition (2.1) is evidently satisfied for this potential. In order to obtain the large-x expansion of $\psi(x)$, we first make in (2.9) a change of the integration variable t into $u = x[\sqrt{1+(t/m)^2} - 1]$, and then expand the integrated function in powers of $1/x$. In the leading order

$$\psi(x) \sim \frac{e}{4} \left(\frac{\pi}{mx}\right)^{1/2} \exp(-2mx), \quad x \to \infty \tag{2.10}$$

for all $\sigma \neq 0$ [$\sigma = 0$ implies the trivial result $\psi(x) \equiv 0$]. The independence of the leading asymptotic term (2.10) on the (non-zero) charge density σ is a special feature of the present geometry. Comparing (2.10) to the Debye–Hückel result (2.4) characterized by the pure exponential decay in x, and identifying the respective inverse lengths $2m$ and κ, one sees that the large-x behaviors differ one from the other. The idea of renormalized charge density thus fails. On the other side, increasing in Eq. (2.9) the dimensionless ratio $\sigma/m \to \infty$, the induced electric potential saturates monotonically at the x-dependent value

$$\psi^{\mathrm{sat}}(x) = \frac{e}{2} K_0(2mx). \tag{2.11}$$

It follows from the basic properties of K_0 that $0 \leqslant \psi^{\mathrm{sat}}(x) < \infty$ for all $x > 0$, in full agreement with the saturation hypothesis.[15]

3. CHARGED CIRCULAR COLLOID

As in the 3D case discussed in Section 1, we fix at the origin one colloid of charge Ze and disk hard core with radius a. There is an infinite 2D TCP of $\pm e$ point-like charges in the complementary outer space. The analog of the boundary condition (2.1) for the electric field now reads

$$-\left.\frac{\partial\psi(\mathbf{r})}{\partial r}\right|_{r=a} = \frac{Ze}{a}. \tag{3.1}$$

3.1. Debye–Hückel Limit

Inside the colloidal hard-core region $0 < r \leqslant a$, the electrostatic potential $\psi(\mathbf{r})$ satisfies the 2D Poisson equation

$$\Delta\psi_<(\mathbf{r}) = -2\pi Ze\delta(\mathbf{r}). \tag{3.2}$$

Inside the electrolyte region $r > a$, the consideration of the linear mean-field prescription $\rho(\mathbf{r}) \sim -\beta e^2 n\psi(\mathbf{r})$ in the Poisson equation implies

$$\left(\Delta - \kappa^2\right)\psi_>(\mathbf{r}) = 0. \tag{3.3}$$

Due to the circular symmetry of the problem, $\Delta = \partial_r^2 + (1/r)\partial_r$. Eqs. (3.2) and (3.3), subject to the requirement of regularity at $r \to \infty$ and the usual boundary conditions of continuity across the colloid boundary $r = a$, imply

$$\psi_<(r) = Ze\left[-\ln\left(\frac{r}{a}\right) + \frac{K_0(\kappa a)}{\kappa a K_1(\kappa a)}\right], \tag{3.4}$$

$$\psi_>(r) = \frac{Ze}{\kappa a K_1(\kappa a)} K_0(\kappa r). \tag{3.5}$$

The boundary condition (3.1) is trivially satisfied. Note that, after defining the surface charge density $\sigma e = Ze/(2\pi a)$ and going to the limits $a, r \to \infty$ with a fixed difference $r - a = x > 0$, (3.5) reduces to the straight-line result (2.4) as it should be. At large r, using the asymptotic formula for K_0,[19] the average electrostatic potential (3.5) behaves like

$$\psi_>(r) \sim \frac{Ze}{\kappa a K_1(\kappa a)} \left(\frac{\pi}{2\kappa r}\right)^{1/2} \exp(-\kappa r), \quad r \to \infty. \tag{3.6}$$

The electrolyte charge density, given by

$$\rho(r) = -\frac{Ze\kappa}{2\pi a K_1(\kappa a)} K_0(\kappa r), \quad r > a, \tag{3.7}$$

fulfills the screening sum rule

$$Ze + \int_a^\infty \mathrm{d}r\, 2\pi r \rho(r) = 0. \tag{3.8}$$

3.2. The Free-fermion Point

According to the general formalism established in ref. 17 and 18, in order to obtain density profiles of electrolyte $\pm e$ particles at coupling $\beta e^2 = 2$, one has to solve the Green function problem of a 2×2 matrix $\mathbf{G}(\mathbf{r},\mathbf{r}')$. Its matrix elements $G_{qq'}(\mathbf{r},\mathbf{r}')$ ($q, q' = \pm$ denote the charge sign) are determined by a system of four coupled partial differential equations (PDE), written in a 2×2 matrix notation as follows

$$\left[\sigma^1 \partial_x + \sigma^2 \partial_y + m_+(\mathbf{r}) \frac{\mathbf{1}+\sigma^3}{2} + m_-(\mathbf{r}) \frac{\mathbf{1}-\sigma^3}{2}\right] \mathbf{G}(\mathbf{r},\mathbf{r}') = \mathbf{1}\delta(\mathbf{r}-\mathbf{r}'). \tag{3.9}$$

Here, $\mathbf{1}$ and σ^i ($i = 1, 2, 3$) denote the 2×2 unit and Pauli matrices, respectively, and

$$m_q(\mathbf{r}) = m(\mathbf{r}) \exp[-2qv(\mathbf{r})], \qquad q = \pm \tag{3.10}$$

is the position-dependent (rescaled) fugacity for some external electric potential $v(\mathbf{r})$ (in units of e); a non-electric potential which acts in the same way on both kinds of particles, like an impenetrable hard wall or core, is described by the region-dependence of $m(\mathbf{r})$. Four Eqs. (3.9) split into two independent sets of equations, the one for the pair (G_{++}, G_{-+}) and the other for the pair (G_{--}, G_{+-}). We shall present a detailed derivation of the results for the pair (G_{++}, G_{-+}), given by

$$m_+(\mathbf{r})G_{++}(\mathbf{r},\mathbf{r}') + \left(\partial_x - \mathrm{i}\partial_y\right) G_{-+}(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}'), \tag{3.11}$$

$$\left(\partial_x + \mathrm{i}\partial_y\right) G_{++}(\mathbf{r},\mathbf{r}') + m_-(\mathbf{r})G_{-+}(\mathbf{r},\mathbf{r}') = 0. \tag{3.12}$$

Based on a similar derivation procedure, we shall only present the final results for the pair (G_{--}, G_{+-}). As concerns the boundary conditions, since Eq. (3.9) is a first-order system, all matrix elements $G_{qq'}(\mathbf{r},\mathbf{r}')$ must be continuous when crossing a boundary between two different regions. The requirement of regularity is obvious. The one-particle densities are given by

$$n_q(\mathbf{r}) = m_q(\mathbf{r}) \lim_{\mathbf{r}'\to\mathbf{r}} G_{qq}(\mathbf{r},\mathbf{r}'), \quad q=\pm. \tag{3.13}$$

In the bulk regime with $m(\mathbf{r})=m$ for all points $\mathbf{r}\in R^2$, one has[18]

$$G_{qq}(\mathbf{r},\mathbf{r}') = \frac{m}{2\pi} K_0(m|\mathbf{r}-\mathbf{r}'|), \qquad q=\pm \tag{3.14}$$

so the one-particle densities diverge logarithmically as $\mathbf{r}'\to\mathbf{r}$ in (3.13). This divergence can be suppressed by introducing a short-distance cut-off R,

$$n_\pm = \lim_{mR\to 0} \frac{m^2}{2\pi} K_0(mR) \sim \frac{m^2}{\pi}\left[\ln\left(\frac{2}{mR}\right) - C\right], \tag{3.15}$$

where C is Euler's constant.

In the case of the studied model, the colloidal particle at the origin induces the electrostatic potential (in units of e) $v(\mathbf{r}) = -Z\ln(r/r_0)$. The rescaled fugacity $m(\mathbf{r})=0$ inside the hard-core region $0<r\leqslant a$ and $m(\mathbf{r})=m$ in the electrolyte region $r>a$. Thus,

$$m_\pm(\mathbf{r}) = \begin{cases} 0 & \text{for } 0<r\leqslant a, \\ m(r/r_0)^{\pm 2Z} & \text{for } r>a. \end{cases} \tag{3.16}$$

For our purpose it will be sufficient to consider the source point $\mathbf{r}'$ in Eqs. (3.11) and (3.12) to be localized only in the electrolyte region, so, without writing it explicitly, in what follows we shall assume that $r'>a$. As concerns the point $\mathbf{r}$, let us first assume its localization in the colloidal hard-core region, i.e. $r\leqslant a$. Taking $m_\pm(\mathbf{r})=0$ in Eqs. (3.11) and (3.12), one gets

$$\left(\partial_x + \mathrm{i}\partial_y\right) G_{++}(\mathbf{r},\mathbf{r}') = 0, \quad r\leqslant a, \tag{3.17}$$

$$\left(\partial_x - \mathrm{i}\partial_y\right) G_{-+}(\mathbf{r},\mathbf{r}') = 0, \quad r\leqslant a. \tag{3.18}$$

This means that, as functions of $\mathbf{r}$, G_{++} depends only on $z=r\exp(\mathrm{i}\varphi)$ and G_{-+} depends only on $\bar{z}=r\exp(-\mathrm{i}\varphi)$. The general solutions of Eqs. (3.17) and (3.18), regular at $r=0$, can be therefore written as the expansions of the forms

$$G_{++}(\mathbf{r},\mathbf{r}') = \frac{m}{2\pi}\sum_{l=0}^{\infty} f_l(mr',\varphi')(mr)^l \exp(\mathrm{i}l\varphi), \quad r\leqslant a, \tag{3.19}$$

$$G_{-+}(\mathbf{r},\mathbf{r}') = \frac{m}{2\pi}\sum_{l=0}^{\infty} h_l(mr',\varphi')(mr)^l \exp(-\mathrm{i}l\varphi), \quad r\leqslant a, \tag{3.20}$$

where the functions $\{f_l, h_l\}$ are determined by the boundary conditions at $r=a$. When the point $\mathbf{r}$ is localized in the electrolyte region, i.e. $r>a$, taking $m_\pm(\mathbf{r})=m(r/r_0)^{\pm 2Z}$, we first express by using Eq. (3.12) G_{-+} in terms of G_{++}:

$$G_{-+}(\mathbf{r},\mathbf{r}')=-\frac{1}{m}\left(\frac{r}{r_0}\right)^{2Z}\left(\partial_x+\mathrm{i}\partial_y\right)G_{++}(\mathbf{r},\mathbf{r}'), \quad r>a. \tag{3.21}$$

The consequent substitution of G_{-+} into (3.11) implies the only PDE determining G_{++}. After lengthy but simple algebra, in terms of the auxiliary two-point function

$$g_{++}(\mathbf{r},\mathbf{r}')=-\frac{1}{m}\left(\frac{r}{r_0}\right)^{Z} G_{++}(\mathbf{r},\mathbf{r}')\left(\frac{r'}{r_0}\right)^{Z} \tag{3.22}$$

this PDE is obtained in the form

$$\left(-m^2-\hat{H}\right)g_{++}(\mathbf{r},\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}'), \quad r>a, \tag{3.23}$$

where

$$\hat{H}=-\Delta_{\mathbf{r}}-\frac{2Z\mathrm{i}}{r^2}\left(x\partial_y-y\partial_x\right)+\frac{Z^2}{r^2}. \tag{3.24}$$

It is clear that $g_{++}(\mathbf{r},\mathbf{r}')=\langle\mathbf{r}|(-m^2-\hat{H})^{-1}|\mathbf{r}'\rangle$ is nothing but the Green-function two-point matrix element associated with the one-particle quantum Hamiltonian $\hat{H}$ and the spectral parameter $-m^2$. In polar coordinates (r,φ), the Hamiltonian (3.24) reads

$$\hat{H}=-\frac{\partial^2}{\partial r^2}-\frac{1}{r}\frac{\partial}{\partial r}-\frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}-\frac{2Z\mathrm{i}}{r^2}\frac{\partial}{\partial\varphi}+\frac{Z^2}{r^2}. \tag{3.25}$$

According to elementary quantum mechanics, the periodicity requirement under the shift $\varphi \to \varphi + 2\pi$ implies that the eigenfunctions of $\hat{H}$ have a trivial dependence on the angle φ: $\Psi_l \propto \exp(\mathrm{i}l\varphi)$, where $l = 0, \pm 1, \ldots$ is the "magnetic" quantum number. It follows from Eq. (3.25) that the radial part of the eigenfunction with a given l is then determined by

$$\hat{H}_l = -\frac{\partial^2}{\partial r^2} - \frac{1}{r}\frac{\partial}{\partial r} + \frac{(l+Z)^2}{r^2}. \tag{3.26}$$

This is the radial Hamiltonian of a free quantum particle in 2D, where the presence of the colloidal charge Ze manifests itself as the shift of the quantum number l by the integer Z. The standard Green-function technique implies an explicit form of g_{++}. Using then the relation (3.22), $G_{++}(\mathbf{r}, \mathbf{r}')$ with $r, r' > a$ is found to be

$$G_{++}(\mathbf{r}, \mathbf{r}') = \frac{m}{2\pi}\left(\frac{r_0}{r}\right)^Z \left(\frac{r_0}{r'}\right)^Z \sum_{l=-\infty}^{\infty} \exp\left[\mathrm{i}l(\varphi - \varphi')\right] \times [I_{l+Z}(mr_<)K_{l+Z}(mr_>) + c_l K_{l+Z}(mr)K_{l+Z}(mr')]. \tag{3.27}$$

Here, I_l and K_l are the modified Bessel functions, and $r_<$ ($r_>$) is the smaller (the larger) of r and r'. G_{-+} is generated from G_{++} via Eq. (3.21). For the special case $a < r < r'$, it takes the form

$$G_{-+}(\mathbf{r}, \mathbf{r}') = \frac{m}{2\pi}\left(\frac{r}{r_0}\right)^Z \left(\frac{r_0}{r'}\right)^Z \sum_{l=-\infty}^{\infty} \exp\left[\mathrm{i}(l+1)\varphi - \mathrm{i}l\varphi'\right] \times [-I_{l+Z+1}(mr) + c_l K_{l+Z+1}(mr)]K_{l+Z}(mr'). \tag{3.28}$$

The unknown constants $\{c_l\}$ are determined by the requirements that G_{++} and G_{-+} be continuous at $r = a$. With regard to Eqs. (3.19) and (3.20), one gets

$$c_l = \begin{cases} -I_{l+Z}(ma)/K_{l+Z}(ma) & l < 0, \\ I_{l+Z+1}(ma)/K_{l+Z+1}(ma) & l \geqslant 0. \end{cases} \tag{3.29}$$

Applying the "summation theorem" for the modified Bessel functions[19]

$$K_0(m|\mathbf{r} - \mathbf{r}'|) = \sum_{l=-\infty}^{\infty} \exp[\mathrm{i}l(\varphi - \varphi')]I_l(mr_<)K_l(mr_>), \tag{3.30}$$

we conclude that, when both points $\mathbf{r}$ and $\mathbf{r}'$ are in the electrolyte region ($r, r' > a$),

$$G_{++}(\mathbf{r},\mathbf{r}') = \frac{m}{2\pi}\left(\frac{r_0}{r}\right)^Z \left(\frac{r_0}{r'}\right)^Z \Bigg\{ \exp\left[-iZ(\varphi-\varphi')\right] K_0(m|\mathbf{r}-\mathbf{r}'|) + \sum_{l\geqslant 0} \exp[il(\varphi-\varphi')] \frac{I_{l+Z+1}(ma)}{K_{l+Z+1}(ma)} K_{l+Z}(mr) K_{l+Z}(mr') - \sum_{l<0} \exp[il(\varphi-\varphi')] \frac{I_{l+Z}(ma)}{K_{l+Z}(ma)} K_{l+Z}(mr) K_{l+Z}(mr') \Bigg\}. \quad (3.31)$$

The matrix element $G_{--}(\mathbf{r},\mathbf{r}')$ can be deduced in the same way. It is expressible by formula (3.31) under the substitution $Z \to -Z$, which corresponds to the sign reversal of the colloidal charge.

The densities of electrolyte particles at $r > a$ follow from the relation (3.13):

$$n_{\pm}(r) = n_{\pm} + \frac{m^2}{2\pi} \sum_{l=\pm Z}^{\infty} \frac{I_{l+1}(ma)}{K_{l+1}(ma)} [K_l(mr)]^2 - \frac{m^2}{2\pi} \sum_{l=-\infty}^{\pm Z-1} \frac{I_l(ma)}{K_l(ma)} [K_l(mr)]^2. \quad (3.32)$$

Using the Wronskian relation[19]

$$I_l(x)K_{l+1}(x) + I_{l+1}(x)K_l(x) = \frac{1}{x}, \quad (3.33)$$

together with the symmetry properties $I_l = I_{-l}$ and $K_l = K_{-l}$ for integer l, the charge density in the electrolyte region is found in the form

$$\rho(r) = -\frac{me}{2\pi a} \sum_{l=1}^{Z} \frac{1}{K_{l-1}(ma)K_l(ma)} \left([K_{l-1}(mr)]^2 + [K_l(mr)]^2 \right), \qquad r > a. \quad (3.34)$$

It stands to reason that $\rho(r) = 0$ in the colloidal region $r \leqslant a$ due to the hard-core repulsion. With the aid of the integral formula

$$\int_a^{\infty} dr\, r[K_l(mr)]^2 = \frac{a^2}{2} \left(K_{l-1}(ma)K_{l+1}(ma) - [K_l(ma)]^2 \right) \quad (3.35)$$

and the recursion relation[19]

$$x[K_{l-1}(x) - K_{l+1}(x)] = -2l K_l(x), \tag{3.36}$$

taken at $l=Z$, the charge density (3.34) can be shown to fulfill the screening sum rule (3.8).

The average electrostatic potential is given by the couple of Poisson equations

$$\Delta\psi_<(\mathbf{r}) = -2\pi Ze\delta(\mathbf{r}), \quad r \leqslant a, \tag{3.37}$$

$$\Delta\psi_>(\mathbf{r}) = -2\pi\rho(\mathbf{r}), \quad r > a. \tag{3.38}$$

The circularly symmetric solution of Eq. (3.37) reads

$$\psi_<(r) = Ze\left[-\ln\left(\frac{r}{a}\right) + \text{const}\right]. \tag{3.39}$$

The circularly symmetric potential of Eq. (3.38) fulfills the differential equation

$$\frac{d}{dr}\left[r\frac{d\psi_>(r)}{dr}\right] = \frac{me}{a}\sum_{l=1}^{Z}\frac{1}{K_{l-1}(ma)K_l(ma)}\, r\left([K_{l-1}(mr)]^2 + [K_l(mr)]^2\right). \tag{3.40}$$

The first integration of Eq. (3.40) with respect to r can be performed easily. Using the regularity condition $\lim_{r\to\infty} r\, d_r\psi_>(r) = 0$, the integration formula of type (3.35) and finally the recursion relation (3.36), one arrives at

$$\frac{\mathrm{d}\psi_>(r)}{\mathrm{d}r} = -\frac{e}{a}\sum_{l=1}^{Z}\frac{K_{l-1}(mr)K_l(mr)}{K_{l-1}(ma)K_l(ma)}. \tag{3.41}$$

Note the obvious fulfillment of the boundary condition (3.1). The subsequent integration of Eq. (3.41) with respect to r is a bit more complicated problem. The regularity condition $\lim_{r\to\infty}\psi_>(r) = 0$ has to be combined with the integral formula [derivable by using the relation (3.52)]

$$m\int_r^{\infty}\mathrm{d}r'\, K_{l-1}(mr')K_l(mr') = (-1)^{l+1}\frac{1}{2}\sum_{j=0}^{l-1}(-1)^j\mu_j[K_j(mr)]^2, \quad l \geqslant 1, \tag{3.42}$$

μ_j is the Neumann factor: $\mu_0 = 1$ and $\mu_j = 2$ for $j \geqslant 1$, to get

$$\psi_>(r) = -\frac{e}{2} \sum_{j=0}^{Z-1} (-1)^j \mu_j f_j(ma)[K_j(mr)]^2, \tag{3.43}$$

where

$$f_j(ma) = \sum_{l=j+1}^{Z} (-1)^l \frac{1}{ma} \frac{1}{K_{l-1}(ma) K_l(ma)}. \tag{3.44}$$

With regard to the Wronskian relation (3.33), f_j can be simplified as follows

$$\begin{aligned} f_j(ma) &= \sum_{l=j+1}^{Z} (-1)^l \left[\frac{I_l(ma)}{K_l(ma)} + \frac{I_{l-1}(ma)}{K_{l-1}(ma)} \right] \\ &= (-1)^Z \frac{I_Z(ma)}{K_Z(ma)} - (-1)^j \frac{I_j(ma)}{K_j(ma)}. \end{aligned} \tag{3.45}$$

Thus, in the electrolyte region $r > a$,

$$\begin{aligned} \psi_>(r) &= \frac{e}{2} \sum_{j=0}^{Z-1} \mu_j \frac{I_j(ma)}{K_j(ma)} [K_j(mr)]^2 \\ &\quad + \frac{e}{2} (-1)^{Z+1} \frac{I_Z(ma)}{K_Z(ma)} \sum_{j=0}^{Z-1} (-1)^j \mu_j [K_j(mr)]^2. \end{aligned} \tag{3.46}$$

Before analyzing the result (3.46), let us recall some basic properties of the modified Bessel functions $I_l(x)$ and $K_l(x)$ $(l = 0, 1, \ldots)$ when the argument x belongs to the interval $0 \leqslant x < \infty$. $I_l(x)$ and $K_l(x)$ satisfy the same differential equation,

$$\frac{d^2 f}{dx^2} + \frac{1}{x} \frac{df}{dx} - \left(1 + \frac{l^2}{x^2}\right) f = 0, \quad f = I_l(x) \text{ or } K_l(x) \tag{3.47}$$

but exhibit different asymptotic behaviors:

$$I_l(x) \sim \frac{1}{\sqrt{2\pi x}} e^x, \quad K_l(x) \sim \left(\frac{\pi}{2x}\right)^{1/2} e^{-x} \quad \text{for } x \to \infty \tag{3.48}$$

and

$$I_l(x) \sim \frac{1}{l!}\left(\frac{x}{2}\right)^l, \quad K_l(x) \sim \frac{(l-1)!}{2}\left(\frac{x}{2}\right)^{-l} \quad \text{for } x \to 0 \tag{3.49}$$

except for the special $l = 0$ case of $K_0(x) \sim -\ln(x/2) - C$. Both $I_l(x)$ and $K_l(x)$ are positive for $x \geqslant 0$. In particular: $I_l(x)$ starts from 0 at $x = 0$ [except for the special case of $I_0(0) = 1$] and monotonously increases to infinity at $x \to \infty$; $K_l(x)$ is infinite at $x = 0$ and monotonously decreases to zero at $x \to \infty$.

For finite Z, at large r, the average electrostatic potential (3.46) behaves like

$$\psi_>(r) \sim \frac{\pi e}{4}\left[\sum_{j=0}^{Z-1} \mu_j \frac{I_j(ma)}{K_j(ma)} + \frac{I_Z(ma)}{K_Z(ma)}\right] \frac{1}{mr} \exp(-2mr), \quad r \to \infty. \tag{3.50}$$

This asymptotic behavior differs from the large-distance prediction (3.6) of the Debye–Hückel theory by the factor $r^{-1/2}$, which is in contradiction with the concept of renormalized charge.

In order to resolve the saturation problem in the limit $Z \to \infty$, we first use the integral formula (3.42) to rewrite the last term on the rhs of Eq. (3.46) as follows

$$\begin{aligned}\psi_>(r) &= \frac{e}{2}\sum_{j=0}^{Z-1} \mu_j \frac{I_j(ma)}{K_j(ma)}[K_j(mr)]^2 \\ &\quad + e\frac{I_Z(ma)}{K_Z(ma)} m \int_r^\infty dr'\, K_{Z-1}(mr')K_Z(mr').\end{aligned} \tag{3.51}$$

The positivity of the modified Bessel functions then ensures that, for every Z, $\psi_>(r) \geqslant 0$ in the whole region $r > a$. In order to establish an upper bound for $\psi_>(r)$, we first use the relation[19]

$$K_{l-1}(x) + K_{l+1}(x) = -2\frac{dK_l(x)}{dx} \tag{3.52}$$

to establish the equality

$$m\int_r^\infty dr'\, K_{Z-1}(mr')K_Z(mr') = [K_Z(mr)]^2 - m\int_r^\infty dr'\, K_Z(mr')K_{Z+1}(mr'). \tag{3.53}$$

The consideration of this equality in Eq. (3.51) leads to

$$\psi_{>}(r) \leqslant \frac{e}{2} \sum_{j=-Z}^{Z} \frac{I_j(ma)}{K_j(ma)} [K_j(mr)]^2, \quad r > a \tag{3.54}$$

In the considered region $r > a$, the inequality $K_j(mr)/K_j(ma) < 1$ implies that

$$\psi_{>}(r) < \frac{e}{2} \sum_{j=-Z}^{Z} I_j(ma) K_j(mr), \quad r > a. \tag{3.55}$$

In the limit $Z \to \infty$, the application of the summation theorem (3.30) with $\varphi = \varphi'$ finally gives

$$0 \leqslant \psi^{\text{sat}}(r) < \frac{e}{2} K_0 \left(m(r-a) \right), \quad r > a. \tag{3.56}$$

The existence of the lower and upper bounds for ψ^{sat} in the electrolyte region confirms once again the validity of the potential saturation hypothesis.[(15)]

4. CONCLUSION

We have studied the average electrostatic potential induced by a unique "guest" charge immersed in an infinite electrolyte, the electrolyte being modelled by the classical TCP of elementary $\pm e$ point-like charges. The primary motivation came from the predictions of the two basic 3D mean-field theories described in the Introduction: the Debye–Hückel theory based on the linear PB equation and the non-linear PB theory. The important point is that both mean-field theories predict the same type behavior of the induced electrostatic potential at asymptotically large distances from the guest charge, only the constant prefactors are different. Within the non-linear PB theory, this fact permits one to introduce the renormalized guest charge which involves the non-linear screening effect of the electrolyte cloud, and can further be used to establish an effective interaction for a system of guest charges immersed in the electrolyte. When the bare guest charge goes to infinity, the renormalized charge saturates at a finite value.

In order to go beyond the mean-field methods, we have have tested the concept of charge renormalization on the 2D Coulomb models. These system have advantage of being completely solvable not only in the

Debye–Hückel high-temperature limit $\beta e^2 \to 0$, but also at a finite temperature, namely the Thirring free-fermion point $\beta e^2 = 2$. Although just at this point the collapse of positive–negative pairs of point-like charges emerges, the charge-density profile in the electrolyte region (determining the average electrostatic potential through the Poisson equation) is a well-defined finite quantity which satisfies the electroneutrality sum rule. We have considered two geometries of the guest charge: the infinite hard wall carrying the uniform surface charge (Section 2) and the charged colloidal particle with a hard core (Section 3). For both geometries, the results at the free-fermion point can be summarized as follows. The asymptotic large-distance behavior of the induced electrostatic potential differs from that predicted by the linear Debye–Hückel theory, so the concept of renormalized charge does not apply. On the other hand, when the bare guest charge increases to infinity, the induced potential saturates monotonically at a finite value in each point of the electrolyte region. In the case of the infinite charged wall, the saturation potential was found explicitly, see Eq. (2.11). In the more complicated case of the charged colloidal particle, lower and upper bounds for the saturated potential were derived, see formula (3.56). These results confirm that the potential saturation hypothesis[(15)] is indeed true.

It is an open question whether the failure of the concept of renormalized charge is restricted to the free-fermion point or it is a more general phenomenon. The answer to this question probably lies in the particle spectrum of the integrable (1+1)-dimensional sine-Gordon model which is the field-theory equivalent of the 2D TCP. The particle spectrum consists of one soliton–antisoliton pair $(S, \bar{S})$ and of $S - \bar{S}$ bound states ("breathers") $\{B_j\}$.[(20)] According to the form-factor method,[(21)] the large-distance behavior of two-point correlation functions is determined by such particle from the sine-Gordon spectrum which has the lightest mass. In the whole stability region $0 \leqslant \beta e^2 < 2$, the role of the dominant particle is played by the lightest B_1-breather. The B_1-breather disappears from the particle spectrum (as the last from the breathers) just at the collapse point $\beta e^2 = 2$ where the soliton-antisoliton pair takes the dominant role. The soliton-antisoliton pair exists up to the Kosterlitz–Thouless transition point $\beta e^2 = 4$ at which the sine-Gordon model ceases to be a massive field theory. From this point of view, the qualitative characteristics of the large-distance behavior of the induced electric potential obtained at the free-fermion point $\beta e^2 = 2$ are supposed to be common for the whole strong-coupling interval $2 \leqslant \beta e^2 < 4$. It is likely that the weak-coupling interval $0 \leqslant \beta e^2 < 2$, "governed" by the lightest B_1-breather, exhibits the common large-distance characteristics of the Debye–Hückel type, and so the concept of renormalized charge might be applicable there. The rigorous treatment of the whole weak-coupling interval $0 \leqslant \beta e^2 < 2$ of the electrolyte via the equivalent sine-Gordon model will be reported soon.

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REFERENCES

1. Y. Levin, *Rep. Prog. Phys.* **65**:1577 (2002).
2. G. S. Manning, *J. Chem. Phys.* **51**:924 (1969).
3. S. Alexander, P. M. Chaikin, P. Grant, G. J. Morales, and P. Pincus, *J. Chem. Phys.* **80**:5776 (1984).
4. H. Löwen, *J. Chem. Phys.* **100**:6738 (1994).
5. E. Trizac, L. Bocquet, M. Aubouy, and H. H. von Grünberg, *Langmuir* **19**:4027 (2003).
6. E. Trizac, M. Aubouy, and L. Bocquet, *J. Phys: Condens. Matt.* **15**:S291 (2003).
7. L. Belloni, *Colloids Surfaces A* **140**:227 (1998).
8. A. Diehl, M. C. Barbosa, and Y. Levin, *Europhys. Lett.* **53**:86 (2001).
9. E. Trizac, L. Bocquet, and M. Aubouy, *Phys. Rev. Lett.* **89**:248301 (2002).
10. L. Bocquet, E. Trizac, and M. Auboy, *J. Chem. Phys.* **117**:8138 (2002).
11. M. Auboy, E. Trizac, and L. Bocquet, *J. Phys. A: Math. Gen.* **36**:5835 (2003).
12. Ph. A. Martin, *Rev. Mod. Phys.* **60**:1075 (1988).
13. R. D. Groot, *J. Chem. Phys.* **95**:9191 (1991).
14. M. C. Barbosa, M. Deserno, and C. Holm, *Europhys. Lett.* **52**:80 (2000).
15. G. Téllez and E. Trizac, *Phys. Rev. E* **68**:061401 (2003).
16. L. Šamaj, *J. Phys. A: Math. Gen.* **36**:5913 (2003).
17. F. Cornu and B. Jancovici, *J. Stat. Phys.* **49**:33 (1987).
18. F. Cornu and B. Jancovici, *J. Chem. Phys.* **90**:2444 (1989).
19. I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series, and Products*, 5th ed. (Academic Press, London, 1994).
20. A. Zamolodchikov and Al. Zamolodchikov, *Ann. Phys. (N.Y.)* **120**:253 (1979).
21. F. A. Smirnov, *Form-Factors in Completely Integrable Models of Quantum Field Theory* (World Scientific, Singapore, 1992).