Exactly solvable model of the two-dimensional electrical double layer

L. Šamaj*
Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovak Republic

Z. Bajnok†
Theoretical Physics Research Group, Hungarian Academy of Sciences, Eötvös University, Pázmány Péter sétány 1/A, 1117 Budapest, Hungary

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We consider equilibrium statistical mechanics of a simplified model for the ideal conductor electrode in an interface contact with a classical semi-infinite electrolyte, modeled by the two-dimensional Coulomb gas of pointlike ± unit charges in the stability-against-collapse regime of reduced inverse temperatures $0 \leq \beta < 2$. If there is a potential difference between the bulk interior of the electrolyte and the grounded electrode, the electrolyte region close to the electrode (known as the electrical double layer) carries some nonzero surface charge density. The model is mappable onto an integrable semi-infinite sine-Gordon theory with Dirichlet boundary conditions. The exact form-factor and boundary state information gained from the mapping provide asymptotic forms of the charge and number density profiles of electrolyte particles at large distances from the interface. The result for the asymptotic behavior of the induced electric potential, related to the charge density via the Poisson equation, confirms the validity of the concept of renormalized charge and the corresponding saturation hypothesis. It is documented on the nonperturbative result for the asymptotic density profile at a strictly nonzero β that the Debye-Hückel $\beta \to 0$ limit is a delicate issue.

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I. INTRODUCTION

Asymmetric classical Coulomb mixtures, such as highly charged colloidal or polyelectrolyte suspensions, have attracted much attention in the last years due to the appearance of various anomalous phenomena; for a nice review, see Ref. [1]. The contemporary theoretical treatment of equilibrium statistical mechanics of asymmetric Coulomb mixtures is based on the concept of renormalized charge. This concept 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" [2–5]. The idea of renormalized charge is usually documented in the infinite dilution limit on a simplified model of a unique charged colloidal "guest" particle immersed in a symmetric weakly coupled electrolyte [6–9]. Plausible arguments were given to conjecture that the induced electric potential far from the guest colloid exhibits the form predicted by the Debye-Hückel (DH) theory [sometimes called the linear Poisson-Boltzmann (PB) theory], with a renormalized-charge prefactor. Within the framework of the *nonlinear* PB theory, the renormalized charge saturates at some finite value when the colloidal bare charge goes to infinity [8,9]. A more general phenomenon of the saturation of the induced electric potential at each point of the electrolyte region was studied in Ref. [10].

The idea of renormalized charge was developed within the linear and nonlinear versions of the PB theory, which are rigorously valid in the limit of the infinite temperature [11]. In order to treat correctly the Coulomb system at a finite temperature, one has to go beyond these mean-field approaches by incorporating electrostatic correlations among electrolyte particles. As concerns the large-distance asymptotic behavior of the electric potential induced by a guest charge, this should affect both the renormalized-charge prefactor (provided that the concept of renormalized charge remains valid) as well as the correlation length of electrolyte particles which is expected to govern the exponential decay of the electric potential. In spite of the existence of many phenomenological approximations based on heuristic extensions of the mean-field theories [1], there is no chance to solve exactly a three-dimensional (3D) Coulomb fluid at some finite temperature.

The situation is more optimistic in the case of 2D Coulomb fluids consisting of charged constituents with logarithmic pairwise interactions. These systems maintain many generic properties, like screening and the related sum rules [12], of "real" 3D Coulomb fluids. The 2D Coulomb gas of symmetric ± unit *pointlike* charges is stable against the collapse of positive-negative pairs of charges at high enough temperatures, namely for $\beta < 2$ where β is the (dimensionless) inverse temperature or the coupling constant. The collapse starts to occur at $\beta = 2$: interestingly, although the free energy and each of the species densities diverge, the truncated Ursell correlation functions are finite at this inverse temperature. The collapse $\beta = 2$ point is exactly solvable due to its equivalence with the free-fermion point of the Thirring fermionic representation of the 2D Coulomb gas [13,14]. The exact solution involves the bulk thermodynamics for an infinite system and special cases of the surface thermodynamics for a semi-infinite Coulomb gas in contact with an impermeable dielectric wall; for an exhaustive review, see Ref. [15].

*Electronic address: fyzimaes@savba.sk
†Electronic address: bajnok@elte.hu

Besides the Thirring fermion representation, the 2D Coulomb gas is equivalent to the 2D Euclidean, or $(1+1)$-dimensional quantum, sine-Gordon field theory with a conformal normalization of the cos field [16]. Although the bulk 2D sine-Gordon model has been known to possess the integrability property from the 1970s [17], the explicit exact solution of its ground-state characteristics was derived only quite recently due to a progress in the method of thermodynamic Bethe ansatz (TBA) [18,19]. Based on the equivalence with the sine-Gordon theory, the bulk thermodynamic properties (free energy, internal energy, specific heat, etc.) of the 2D Coulomb gas have been obtained exactly in the whole stability region of pointlike charges $\beta<2$ [20]. From a gnoseological point of view, this is the only exactly solvable case of a continuous (i.e., not on a lattice) fluid in more than one dimension. Later on, the form-factor approach [21,22] was applied to calculate the large-distance asymptotic behavior of the charge [23] and number density [24] pair-correlation functions in the bulk of the infinite 2D plasma. The integrability of the 2D sine-Gordon theory was shown to be preserved also in the half space geometry with specific types of boundary conditions [25]. The surface thermodynamic properties (surface tension) of the 2D Coulomb gas in contact with an ideal conductor wall [26] and an ideal dielectric wall [27] were obtained in the whole stability range of $\beta<2$ through the mappings onto the boundary sine-Gordon model with Dirichlet and Neumann boundary conditions, respectively, with the aid of the known TBA results [28,29] for these integrable boundary field theories.

The exact treatment of the 2D Coulomb gas was recently extended also to inhomogeneous situations of the present interest when one guest arbitrarily charged particle is immersed in the bulk of an electrolyte modeled by the 2D Coulomb gas. At the free-fermion (collapse) point $\beta=2$, the considered problem is solvable in the Thirring format [30] even for the guest Q-charged particle being of colloidal type, i.e., possessing a hard core of radius a which is impenetrable to the electrolyte ± unit charges. Based on an explicit formula for the electric potential induced by the charged colloid in the electrolyte region, the concept of the renormalized charge [6–9] was shown to fail in this strong-coupling regime. On the other hand, in the limit $Q\to\infty$, the anticipated phenomenon of the electric potential saturation [10] was confirmed at this free-fermion point. The special case of the *pointlike* ($a=0$) guest Q charge is solvable, within the framework of the sine-Gordon format, inside the whole stability interval of the electrolyte $\beta<2$ [31]. The explicit results for the asymptotic behavior of the induced electric potential confirm the adequacy of the concept of renormalized charge in this weak-coupling regime. The exact results are rigorously valid provided that $\beta|Q|<2$, i.e., when the guest Q charge does not collapse with an opposite unit charge (counterion) from the electrolyte. The possibility of an analytic continuation of the results beyond the stability border $\beta|Q|=2$ was conjectured [31], however, the validity of this "regularization hypothesis" is questionable [32]. The restricted rigorous validity of the exact results to the region $\beta|Q|<2$ prevents one from studying the saturation phenomena in the limit $Q\to\infty$.

In order to avoid the collapse of pointlike guest charges with electrolyte counterions, one has to search for another integrable 2D model with the guest charges uniformly smeared over a line manifold. The simplest system of this kind is the 2D half space Coulomb gas in contact with a plain hard wall carrying a uniform "line" charge density. Although this model is exactly solvable at the free-fermion $\beta=2$ point [14], it can be easily shown that its sine-Gordon formulation does not belong to the family of the boundary sine-Gordon theories integrable at arbitrary $\beta<2$ [25]. Another way of introducing an interface charge density is to consider a simplified model for an electrode in contact with a classical electrolyte: the half space Coulomb gas bounded by an ideal conductor wall, with a potential difference φ between the bulk interior of the electrolyte and the grounded interface [33,34]. As soon as $\varphi\neq 0$, the region of the Coulomb fluid close to the interface (known as the electrical double layer) carries some nonzero surface charge density. The 2D version of the model was mapped in Ref. [26] onto the integrable half-space sine-Gordon model with a specific φ-dependent Dirichlet boundary condition.

The present paper concentrates just on this integrable model of the 2D electrical double layer and has two main aims. The first aim is rather technical: we present a method for obtaining the charge and number density profiles of electrolyte particles at asymptotically large distances from model's interface. This task is equivalent to the calculation of one-point functions of bulk fields in the boundary sine-Gordon model with Dirichlet boundary conditions. Although the one-point functions of certain specific boundary field theories have already been analyzed using the truncated conformal space approach and the form-factor expansion [36,37], some additional generalizations and technicalities have to be developed for the present model. Among others we document on the exact nonperturbative asymptotic form of the *number density* profile at large distances from the interface that the DH $\beta\to 0$ limit is a delicate point which has to be taken with cautiousness. The second aim consists in pointing out physical consequences of the obtained exact results. The knowledge of the asymptotic behavior of the charge density at large distances from the interface enables us to derive the asymptotic large-distance tendency of the induced electric potential toward its bulk value φ. In the whole stability range of the electrolyte coupling $\beta<2$, the asymptotic form of the electric potential coincides, up to a renormalized-charge prefactor and the plasma correlation length, with the one obtained in the DH limit. This result supports the general validity of the concept of renormalized charge in the weak-coupling regime of the electrolyte. The saturation hypothesis of the induced electric potential is also confirmed.

The paper is organized as follows. In Sec. II, we introduce the notation and briefly summarize important aspects of the mapping of the infinite 2D Coulomb gas onto the bulk $(1+1)$-dimensional sine-Gordon theory. Sec. III deals with the 2D electrical double layer of interest and its mapping onto the semi-infinite sine-Gordon theory with Dirichlet boundary conditions. We would like to emphasize that Secs. II and III summarize previous results in the literature, so their presentation is sketchy; for a detailed study of some specific points, we quote relevant references. Our results are outlined in the rest of the paper. Section IV presents the mean-field theories for the 2D electrical double layer: the DH $\beta \to 0$ limit with the leading β correction, and the nonlinear PB theory. The crucial Sec. V is devoted to the derivation of the asymptotic charge and number density profiles for the 2D electrical double layer, in the whole stability region of inverse temperatures $\beta<2$. The Thirring free-fermion point $\beta=2$ is discussed in Sec. VI. A brief recapitulation and some concluding remarks are given in Sec. VII.

II. 2D COULOMB GAS IN THE BULK

A. Basic definitions

We start with a brief description of the classical Coulomb gas formulated in the infinite 2D space of points $\mathbf{r} \in \mathbb{R}^2$. It is realized as the limit of a finite system with periodic boundary conditions. The system consists of pointlike particles $\{i\}$ of charge $\{q_i = \pm 1\}$ (the elementary charge e is set for simplicity to unity) immersed in a homogeneous medium of dielectric constant $\epsilon=1$. The interaction energy E of a set of particles $\{q_i, \mathbf{r}_i\}$ is given by

$$E(\{q_i,\mathbf{r}_i\}) = \sum_{i<j} q_i q_j v(|\mathbf{r}_i - \mathbf{r}_j|), \tag{2.1}$$

where the electrostatic potential v is the solution of the 2D Poisson equation

$$\Delta v(\mathbf{r}) = -2\pi\delta(\mathbf{r}) \tag{2.2}$$

subject to the boundary condition $\nabla v(\mathbf{r}) \to 0$ as $|\mathbf{r}| \to \infty$. Explicitly, one has

$$v(\mathbf{r}) = -\ln\left(\frac{|\mathbf{r}|}{r_0}\right), \quad r \in \mathbb{R}^2. \tag{2.3}$$

The free length constant r_0, which fixes the zero point of the Coulomb potential, will be set to unity for simplicity. The Fourier transform of the 2D Coulomb potential (2.3) exhibits the form $1/|\mathbf{k}|^2$ with the characteristic singularity at $\mathbf{k} \to \mathbf{0}$. This maintains many generic properties (like screening and the related sum rules [12]) of 3D Coulomb fluids with the interaction potential $v(\mathbf{r}) = 1/|\mathbf{r}|$, $\mathbf{r} \in \mathbb{R}^3$.

The system is treated in thermodynamic equilibrium, via the grand canonical ensemble characterized by the (dimensionless) inverse temperature β and the couple of particle fugacities z_+ and z_-. Alternatively, chemical potentials μ_+ and μ_- can be defined by $z_\pm = \exp(\beta\mu_\pm)/\lambda^2$ where λ is the de Broglie thermal wavelength. The bulk Coulomb gas is neutral [38], and thus its bulk properties depend only on the chemical potential combination $\mu = (\mu_+ + \mu_-)/2$, i.e., on $\sqrt{z_+ z_-}$. It is therefore possible to set $z_+ = z_- = z$; however, at some places, in order to distinguish between the + and − charges we shall keep the notation $z_\pm$. The grand partition function is defined by

$$\Xi = \sum_{N_+=0}^{\infty} \sum_{N_-=0}^{\infty} \frac{z_+^{N_+}}{N_+!} \frac{z_-^{N_-}}{N_-!} Q(N_+,N_-), \tag{2.4a}$$

where

$$Q(N_+,N_-) = \int_{\mathbb{R}^2} \prod_{i=1}^{N} d^2 r_i \exp[-\beta E(\{q_i,\mathbf{r}_i\})] \tag{2.4b}$$

is the configuration integral of N_+ positive and N_- negative charges, and $N = N_+ + N_-$. For the considered case of pointlike particles, the singularity of the Coulomb potential (2.3) at the origin $\mathbf{r} = \mathbf{0}$ can cause the thermodynamic collapse of positive-negative pairs of charges. The stability regime against this collapse is associated with the 2D spatial integrability of the corresponding Boltzmann factor $\exp[\beta v(\mathbf{r})] = |\mathbf{r}|^{-\beta}$ at short distances, and therefore corresponds to small enough inverse temperatures $\beta<2$. At large distances, the Coulomb interaction is screened to a short-distance effective interaction of Yukawa type. The infinite system is homogeneous and translationally invariant. Denoting by $\langle \cdots \rangle_\beta$ the thermal average, the number density of particles of one charge sign $q(=\pm 1)$ is defined by $n_q = \langle \sum_i \delta_{q,q_i} \delta(\mathbf{r}-\mathbf{r}_i) \rangle_\beta$. Due to the charge symmetry, $n_+ = n_- = n/2$ where n is the total number density of particles. At the two-particle level, one introduces the two-body densities $n_{qq'}(|\mathbf{r}-\mathbf{r}'|) = \langle \sum_{i\neq j} \delta_{q,q_i} \delta(\mathbf{r}-\mathbf{r}_i) \delta_{q',q_j} \delta(\mathbf{r}'-\mathbf{r}_j) \rangle_\beta$, etc.

B. Sine-Gordon representation

The infinite 2D Coulomb gas is mappable onto the bulk sine-Gordon theory [16]. Using the fact that, according to Eq. (2.2), $-\Delta/(2\pi)$ is the inverse operator of the Coulomb potential v and renormalizing the particle fugacity z by the (divergent) self-energy term $\exp[\beta v(0)/2]$, the grand partition function (2.4a) and (2.4b) can be turned via the Hubbard-Stratonovich transformation into

$$\Xi(z) = \frac{\int \mathcal{D}\phi \exp[-S(z)]}{\int \mathcal{D}\phi \exp[-S(0)]}, \tag{2.5a}$$

where

$$S(z) = \int_{\mathbb{R}^2} d^2 r \left[\frac{1}{16\pi} (\nabla\phi)^2 - 2z\cos(b\phi) \right], \quad b^2 = \frac{\beta}{4} \tag{2.5b}$$

is the Euclidean action of the 2D sine-Gordon model. Here, $\phi(\mathbf{r})$ is a real scalar field and $\int \mathcal{D}\phi$ denotes the functional integration over this field. The one- and two-particle densities are expressible as averages over the sine-Gordon action (2.5b) in the following way

$$n_q = z_q \langle e^{iqb\phi} \rangle, \tag{2.6a}$$

$$n_{qq'}(|\mathbf{r}-\mathbf{r}'|) = z_q z_{q'} \langle e^{iqb\phi(\mathbf{r})} e^{iq'b\phi(\mathbf{r}')} \rangle. \tag{2.6b}$$

The renormalized fugacity parameter z gets a precise meaning when one fixes the normalization of the coupled cos field. In the Coulomb-gas format, the short-distance behavior of the two-body density for the oppositely charged particles is dominated by the corresponding Boltzmann factor of the Coulomb potential: $n_{+-}(\mathbf{r},\mathbf{r}') \sim z_+ z_- |\mathbf{r}-\mathbf{r}'|^{-\beta}$ as $|\mathbf{r}-\mathbf{r}'| \to 0$.

With respect to the representation (2.6b), in the sine-Gordon picture this corresponds to

$$\langle e^{ib\phi(\mathbf{r})} e^{-ib\phi(\mathbf{r}')} \rangle \sim |\mathbf{r}-\mathbf{r}'|^{-4b^2} \text{ as } |\mathbf{r}-\mathbf{r}'| \to 0. \quad (2.7)$$

Under this short-distance (conformal) normalization, the divergent self-energy factor disappears from statistical relations calculated in the sine-Gordon format.

The 2D Euclidean sine-Gordon action (2.5b) takes its minimum at a $\phi(\mathbf{r})$ constant in space. Due to a discrete symmetry $\phi \to \phi + 2\pi n/b$ (n being an integer), the action has infinitely many ground states $|0_n\rangle$ characterized by the associate expectation values of the field $\langle \phi \rangle_n = 2\pi n/b$. In the considered infinite-volume limit and for $b^2 < 1$, these ground states become all degenerate [17]. Equivalently, the discrete ϕ symmetry is spontaneously broken so it is sufficient to develop the sine-Gordon action (2.5b) around any one of its ground states, say the one $|0_0\rangle$ with $\langle \phi \rangle_0 = 0$.

In order to pass from the present Lagrangian formulation (2.5a) and (2.5b) to the Hamiltonian one, one chooses, say, the x direction to be the "Euclidean time" and associates a Hilbert space $\mathcal{H}$ to any equal-time section $\{x=\text{const}, y \in (-\infty,\infty)\}$. (Choosing the y direction to be the "Euclidean time" gives equivalent quantization.) General states are vectors in $\mathcal{H}$ whose evolution is governed by the Hamiltonian operator

$$H = \int_{-\infty}^{\infty} dy \left[4\pi \Pi^2 + \frac{1}{16\pi} (\partial_y \phi)^2 + 2z \cos(b\phi) \right]. \quad (2.8)$$

In the considered region $b^2 < 1$ with the spontaneously broken discrete ϕ symmetry, the sine-Gordon field theory is massive in the sense that $\mathcal{H}$ is the Fock space of massive multiparticle states. After rotation $x = it$ to the $(1+1)$ Minkowski time-space (t,y), these multiparticle states are interpreted as the asymptotic "in-" and "out-" scattering states (see below).

The particle spectrum of the $(1+1)$-dimensional sine-Gordon field theory is the following [17]. The basic particles are the soliton S and the antisoliton $\bar{S}$ which form a particle-antiparticle pair of equal masses M. They correspond to specific ϕ configurations that interpolate between two neighboring ground states, say $|0_0\rangle$ and $|0_{\pm 1}\rangle$. Defining the "topological charge" q as

$$q = \frac{b}{2\pi} \int_{-\infty}^{\infty} dy \frac{\partial}{\partial y} \phi(x,y) = \frac{b}{2\pi} [\phi(x,\infty) - \phi(x,-\infty)], \quad (2.9)$$

$q = +1(-1)$ for the soliton (antisoliton). Since the theory is developed around the vacuum $|0_0\rangle$, allowed field configurations must start and end at $\langle \phi \rangle_0 = 0$, that is, the soliton and the antisoliton can coexist in the particle spectrum only in neutral pairs. The $S-\bar{S}$ pair can create neutral ($q=0$) bound states $\{B_i; i=1,2,\ldots < p^{-1}\}$; these particles are called "breathers." Their number depends on the inverse of the parameter

$$p = \frac{b^2}{1-b^2} \left(= \frac{\beta}{4-\beta} \right). \quad (2.10)$$

The mass of the B_i breather is given by

$$m_i = 2M \sin\left(\frac{\pi p}{2} i \right), \quad (2.11)$$

and this breather disappears from the particle spectrum just when $m_i = 2M$ (i.e., $p = 1/i$). Note that the breathers exist only in the stability region of the pointlike Coulomb gas $0 < \beta < 2$ ($0 < p < 1$); the lightest B_1 breather disappears just at the border $b^2 = 1/2$ ($\beta = 2$), which is the field-theoretical manifestation of the collapse phenomenon. The $S-\bar{S}$ pair remains in the spectrum up to the Kosterlitz-Thouless transition point $b^2 = 1$ ($\beta = 4$) beyond which the sine-Gordon model ceases to be massive. In what follows, we shall restrict ourselves to the stability region of pointlike charges $\beta < 2$.

Let $a \in \{S, \bar{S}, B_i (i=1,2,\ldots < p^{-1})\}$ denote the type of the given particle and m_a the corresponding particle mass. Since the sine-Gordon model is a relativistic field theory, the energy E and the momentum p of the particle can be parametrized as follows:

$$E_a = m_a \cosh\theta, \quad p_a = m_a \sinh\theta, \quad (2.12)$$

where $\theta \in (-\infty,\infty)$ is the particle rapidity. The asymptotic n-particle states $\{|n\rangle\}$ are generated by the "particle creation operators" $A_a^+(\theta)$,

$$A_{a_1}^+(\theta_1) A_{a_2}^+(\theta_2) \cdots A_{a_n}^+(\theta_n) |0\rangle, \quad (2.13)$$

where $|0\rangle \in \mathcal{H}$ is the ground state of the Hamiltonian H given by Eq. (2.8). The state (2.13) is interpreted as an in-state if the rapidities are ordered as $\theta_1 > \theta_2 > \cdots > \theta_n$ and as an out-state in the case of the reverse order $\theta_1 < \theta_2 < \cdots < \theta_n$. The in-state basis and the out-state basis are related via the scattering $n \to n$ S matrix. The $2 \to 2$ process is described simply by

$$A_{a_1}^+(\theta_1) A_{a_2}^+(\theta_2) = \sum_{b_1,b_2} S_{a_1 a_2}^{b_1 b_2}(\theta_1 - \theta_2) A_{b_2}^+(\theta_2) A_{b_1}^+(\theta_1). \quad (2.14)$$

Here, the momentum conservation demands $m_{a_1} = m_{b_1}$ and $m_{a_2} = m_{b_2}$, so that the inequalities $a_1 \neq b_1$ or $a_2 \neq b_2$ are allowed only for the soliton-antisoliton pair with the degenerate masses equal to M. Like for any integrable field theory, the $n \to n$ S matrix of the sine-Gordon model factorizes into a product of $n(n-1)/2$ two-particle S matrices. The two-particle S matrix possesses many symmetry constraints and its explicit form was obtained by exploring four general axioms: the Yang-Baxter equation; a unitarity condition; analyticity and crossing symmetry; the bootstrap principle [17].

The (dimensionless) specific grand potential ω of the sine-Gordon model (2.5a) and (2.5b), defined in the infinite-volume limit as

$$-\omega = \frac{1}{|\mathbb{R}^2|}\ln \Xi, \tag{2.15}$$

was found by using the TBA in Ref. [18]:

$$-\omega = \frac{m_1^2}{8\sin(\pi p)}. \tag{2.16}$$

Here, m_1 is the mass of the lightest B_1 breather [see formula (2.11) taken with $i=1$] and the parameter p is defined by Eq. (2.10). Under the conformal normalization (2.7), the relationship between the fugacity z and the soliton mass M was established in Ref. [19]:

$$z = \frac{\Gamma(b^2)}{\pi\Gamma(1-b^2)}\left[M\frac{\sqrt{\pi}\Gamma[(1+p)/2]}{2\Gamma(p/2)}\right]^{2-2b^2}, \tag{2.17}$$

where Γ stands for the gamma function. Since the total particle number density n of the 2D Coulomb gas is given by the obvious equality

$$n = z\frac{\partial(-\omega)}{\partial z}, \tag{2.18}$$

Eqs. (2.16) and (2.17) imply the explicit density-fugacity relationship, and consequently the complete bulk thermodynamics, of the 2D Coulomb gas in the whole stability region $\beta<2$ [20]. The mass m_1 plays the role of the inverse correlation length of the plasma particles [23,24]. Using Eqs. (2.16)–(2.18), it is expressible as

$$m_1 = \kappa\left[\frac{\sin(\pi p)}{\pi p}\right]^{1/2} = \kappa\left[1 - \frac{\pi^2}{192}\beta^2 + O(\beta^3)\right], \tag{2.19}$$

where

$$\kappa = \sqrt{2\pi\beta n} \tag{2.20}$$

is the inverse Debye length. In the DH limit $\beta\to 0$, m_1 reduces to κ as it should be.

III. 2D ELECTRICAL DOUBLE LAYER

A. Definition

We first introduce in detail the model of interest which describes an electrode in contact with a classical electrolyte. Let us consider an infinite 2D space of points $\mathbf{r}\in\mathbb{R}^2$ defined by Cartesian coordinates (x,y). The electrode-electrolyte interface is localized at $x=0$, along the y axis. The half space $\bar{\Lambda}=\{(x,y);x<0\}$ is occupied by an ideal-conductor wall of dielectric constant $\epsilon_W\to\infty$, impenetrable to electrolyte particles. The electrolyte is localized in the complementary half space $\Lambda=\{(x,y);x>0\}$. It is modeled by the classical 2D Coulomb gas of pointlike unit ± charges. The interface ($x=0$) is kept at zero potential while the bulk interior of the electrolyte ($x\to\infty$) is assumed to be at some electrostatic potential φ. The nonzero potential φ causes a splitting of the charge fugacities:

$$z_\pm = z\exp(\pm\beta\varphi). \tag{3.1}$$

As was mentioned in Sec. II, the fugacity z determines the bulk properties of the electrolyte. The difference of chemical potentials $\mu_+-\mu_-$ (or φ) is relevant only for the surface properties of the electrolyte region close to the interface (the electrical double layer) [33,34]; if $\varphi\neq 0$ the electrical double layer carries some surface charge density.

Here, we consider a simplified model of "inert" ideal-conductor wall which means that the electric potential is constant inside the wall, without any fluctuations. A realistic "living" ideal-conductor wall, made of a microscopic plasma system of charged particles with the correlation length going to zero, exhibits the electrostatic field fluctuations [39]; however, as was previously noted [40], the species density profiles and correlation functions are independent of these fluctuations. The presence of the ideal-conductor wall is described mathematically by charge images: the particle with charge q localized in the electrolyte region at the point $\mathbf{r}=(x>0,y)$ induces the image with the opposite charge $q^*=-q$ localized in the wall region at the point $\mathbf{r}^*=(-x,y)$. The interaction energy E of a set of particles $\{q_i,\mathbf{r}_i=(x_i>0,y_i)\}$ then consists of two parts (see, for example, Ref. [41]):

$$E(\{q_i,\mathbf{r}_i\}) = \sum_{i<j} q_iq_jv(|\mathbf{r}_i-\mathbf{r}_j|) + \frac{1}{2}\sum_{i,j} q_iq_j^*v(|\mathbf{r}_i-\mathbf{r}_j^*|); \tag{3.2}$$

the first term corresponds to direct particle-particle interactions, while the second term describes interactions of particles with the images of other particles and with their self-images. The grand partition function Ξ_{bry} is again given by

$$\Xi_{\mathrm{bry}} = \sum_{N_+=0}^{\infty}\sum_{N_-=0}^{\infty}\frac{z_+^{N_+}}{N_+!}\frac{z_-^{N_-}}{N_-!}Q(N_+,N_-), \tag{3.3a}$$

where the configuration integral

$$Q(N_+,N_-) = \int_\Lambda \prod_{i=1}^{N} d^2r_i \exp[-\beta E(\{q_i,\mathbf{r}_i\})] \tag{3.3b}$$

is now restricted to the half space $x>0$. The stability range of inverse temperatures for the surface thermodynamics is determined by the Coulomb interaction of the charged particle with its image [26]: the Boltzmann factor of a particle at a distance x from the wall with its own image, proportional to $(2x)^{-\beta/2}$, is integrable at small 1D distances x provided that $\beta<2$. Note that the bulk and surface thermodynamic stability intervals of β coincide.

Due to the translational invariance of the system along the y axis, the species densities depend only on the x coordinate: $n_\pm(\mathbf{r})\equiv n_\pm(x)$, $x\geq 0$. The electrolyte is neutral in the bulk interior of the electrolyte, i.e., it holds $\lim_{x\to\infty} n_\pm(x)=n_\pm=n/2$. The species densities determine the particle number density

$$n(x) = \sum_{q=\pm 1} n_q(x) = n_+(x) + n_-(x) \tag{3.4}$$

and the charge density

$$\rho(x) = \sum_{q=\pm 1} q n_q(x) = n_+(x) - n_-(x). \tag{3.5}$$

The induced (averaged) electrostatic potential $\varphi(x)$ in the electrolyte region is related to the charge density via the Poisson equation

$$\varphi''(x) = -2\pi\rho(x). \tag{3.6}$$

The potential satisfies the obvious boundary conditions $\varphi(0)=0$ and $\varphi(\infty)=\varphi$, and the regularity requirement (all derivatives φ', φ'', etc., vanish) at $x\to\infty$. Since we will be interested in the asymptotic approach of $\varphi(x)$ to its bulk value φ at large distance x from the electrode surface, it is natural to introduce the quantity

$$\delta\varphi(x) = \varphi(x) - \varphi \tag{3.7}$$

which vanishes as $x\to\infty$.

There are two sum rules which can be derived without solving explicitly the boundary problem. First, the consideration of Eq. (3.6) in the integral $\int_0^\infty dx\, \rho(x)$ implies

$$\int_0^\infty dx\, \rho(x) = \frac{1}{2\pi}\varphi'(0). \tag{3.8}$$

We note that a nonzero surface (more precisely "line") charge in the electrolyte $\int_0^\infty dx \rho(x)$ can appear only in the special case of an ideal-conductor wall where this charge is exactly compensated by the opposite surface charge σ of particle images, and the system as a whole is neutral. Since an isolated charged line at $x=0$, carrying a uniform charge σ per unit length, induces the electric potential such that

$$\varphi'(0) = -2\pi\sigma, \tag{3.9}$$

the sum rule (3.8) can be understood as the neutrality-type condition

$$\int_0^\infty dx\, \rho(x) + \sigma = 0. \tag{3.10}$$

Second, the consideration of Eq. (3.6) in the integral $\int_0^\infty dx\, x\rho(x)$ and the subsequent two integrations by parts lead to

$$\int_0^\infty dx\, x\rho(x) = \frac{\varphi}{2\pi}, \tag{3.11}$$

i.e., the dipole moment of the charge density is related to the potential difference across the electrical double layer. This relation follows from elementary macroscopic electrostatics [41].

At small distance from the wall $x\to 0$, the species densities are determined by the Boltzmann factors of the corresponding particle with its image [26]:

$$n_\pm(x) \sim \frac{z_\pm}{(2x)^{\beta/2}}, \quad x\to 0. \tag{3.12}$$

Consequently,

$$n(x) \underset{x\to 0}{\sim} 2z\frac{\cosh(\beta\varphi)}{(2x)^{\beta/2}}, \tag{3.13a}$$

$$\rho(x) \underset{x\to 0}{\sim} 2z\frac{\sinh(\beta\varphi)}{(2x)^{\beta/2}}. \tag{3.13b}$$

B. Boundary Sine-Gordon representation

The considered particle-image system is mappable onto a boundary sine-Gordon theory [26]. In particular, the grand partition function (3.3a) and (3.3b) can be written as

$$\Xi_{\rm bry}(z) = \frac{\int \mathcal{D}\phi \exp[-S_{\rm bry}(z)]}{\int \mathcal{D}\phi \exp[-S_{\rm bry}(0)]}, \tag{3.14a}$$

where

$$S_{\rm bry}(z) = \int_{x>0} d^2r\left[\frac{1}{16\pi}(\nabla\phi)^2 - 2z\cos(b\phi)\right], \quad b^2 = \frac{\beta}{4} \tag{3.14b}$$

is the 2D Euclidean action of the boundary sine-Gordon model defined in the half space $x\geqslant 0$ and the real scalar field $\phi(\mathbf{r})$ fulfills the following Dirichlet conditions at the $x=0$ boundary:

$$\phi(x=0,y) = \phi_0 = -4ib\varphi. \tag{3.15}$$

The fact that the boundary value of the field, ϕ_0, is a pure imaginary number makes no problem: as is usual in field theory, first one expresses the quantities of interest as functions of real ϕ_0 and then analytically continues the obtained results to complex values of ϕ_0. This procedure was successfully applied to the calculation of the surface tension (i.e., the surface part of the grand potential) for the present model [26]. ϕ_0 will usually appear in the combination

$$\eta = -\frac{\phi_0}{2b} = 2i\varphi. \tag{3.16}$$

Within the formalism developed in Ref. [26], the one-particle densities $n_\pm(x)$ in the electrolyte region $x\geqslant 0$ are expressible as averages over the boundary sine-Gordon action (3.14b) with Dirichlet boundary conditions (3.15) as follows:

$$n_\pm(x) = z\langle e^{\pm ib\phi(x,0)}\rangle_{\rm bry}. \tag{3.17}$$

Here, regarding the y invariance of the boundary mean values $\langle e^{\pm ib\phi(\mathbf{r})}\rangle_{\rm bry}$, we have set $y=0$ for simplicity. Thus the particle number density (3.4) and the charge density (3.5) read

$$n(x) = z[\langle e^{ib\phi(x,0)}\rangle_{\rm bry} + \langle e^{-ib\phi(x,0)}\rangle_{\rm bry}], \tag{3.18}$$

$$\rho(x) = z[\langle e^{ib\phi(x,0)}\rangle_{\rm bry} - \langle e^{-ib\phi(x,0)}\rangle_{\rm bry}], \tag{3.19}$$

respectively.

The specific case of Dirichlet boundary conditions in the semi-infinite sine-Gordon model does not spoil the integrability property of the bulk theory [25]. In passing from the Lagrangian formulation (3.14a) and (3.14b) to a Hamiltonian one, contrary to the bulk case, we have two different choices considering either x or y as the Euclidian time.

If y is taken to be the Euclidean time, then the boundary is in space, and a boundary Hilbert space $\mathcal{H}_B$ is associated to any time slices $\{x \in (0,\infty),\ y=\text{const}\}$. The time evolution is governed by the Hamiltonian

$$H_B = \int_0^\infty dy \left[4\pi\Pi^2 + \frac{1}{16\pi}(\partial_y \phi)^2 + 2z\cos(b\phi) \right], \tag{3.20}$$

where the boundary condition (3.15) is satisfied. The boundary Hilbert space consists of boundary bound states [35], and bulk multiparticle states:

$$A^+_{a_1}(\theta_1)A^+_{a_2}(\theta_2)\cdots A^+_{a_n}(\theta_n)|0\rangle_B, \tag{3.21}$$

where $|0\rangle_B \in \mathcal{H}_B$ is the ground state of the Hamiltonian H_B given by Eq. (3.20). The state (3.21) is interpreted as an in-state if the rapidities are ordered as $0>\theta_1>\theta_2>\cdots>\theta_n$ and as an out-state in the case of the reverse order $0<\theta_1<\theta_2<\cdots<\theta_n$. The in-state basis and the out-state basis are related via the reflection $n\to n$ R matrix. This matrix factorizes into the product of pairwise scatterings (2.14), and of $R_a^b(\theta)$'s, the individual one-particle reflections $A_a^+(-\theta)\to A_b^+(\theta)$ (θ positive) off the boundary. Owing to the energy conservation, $R_a^b(\theta)$ vanishes if $m_a \neq m_b$. The R amplitudes were obtained explicitly for the soliton-antisoliton pair in Ref. [25] and for the breathers in Ref. [42]. We shall need the Dirichlet R amplitudes for the lowest B_1 and B_2 breathers; with the notation $R_{B_j}^{B_j}(\theta) \equiv R_B^{(j)}(\theta)$, one has explicitly

$$R_B^{(1)}(\theta) = \frac{\left(\frac{1}{2}\right)\left(\frac{p}{2}+1\right)\left(\frac{\eta p}{\pi}-\frac{1}{2}\right)}{\left(\frac{p}{2}+\frac{3}{2}\right)\left(\frac{\eta p}{\pi}+\frac{1}{2}\right)} \tag{3.22a}$$

and

$$R_B^{(2)}(\theta) = \frac{\left(\frac{1}{2}\right)\left(\frac{p}{2}+1\right)(p+1)\left(\frac{p}{2}\right)}{\left(\frac{p}{2}+\frac{3}{2}\right)^2\left(p+\frac{3}{2}\right)} \times \frac{\left(\frac{\eta p}{\pi}-\frac{1}{2}-\frac{p}{2}\right)\left(\frac{\eta p}{\pi}-\frac{1}{2}+\frac{p}{2}\right)}{\left(\frac{\eta p}{\pi}+\frac{1}{2}-\frac{p}{2}\right)\left(\frac{\eta p}{\pi}+\frac{1}{2}+\frac{p}{2}\right)}, \tag{3.22b}$$

where we used the symbol

$$(x) = \frac{\sinh\left(\frac{\theta}{2}+\frac{i\pi x}{2}\right)}{\sinh\left(\frac{\theta}{2}-\frac{i\pi x}{2}\right)}. \tag{3.23}$$

The reflection amplitudes of breathers have simple poles at the imaginary rapidity $\theta = i\pi/2$. In the particular case of the first two breathers (3.22a) and (3.22b), one finds that

$$R_B^{(j)}(\theta) \sim \frac{i g_j^2}{2\theta - i\pi}, \quad j=1,2, \tag{3.24}$$

where the "boundary couplings" g_1 and g_2 are extracted in the form

$$g_1 = 2\tan\left(\frac{p\eta}{2}\right)\left[\frac{1+\cos\left(\frac{p\pi}{2}\right)-\sin\left(\frac{p\pi}{2}\right)}{1-\cos\left(\frac{p\pi}{2}\right)+\sin\left(\frac{p\pi}{2}\right)}\right]^{1/2}, \tag{3.25a}$$

$$g_2 = \frac{2\tan\left(\frac{p\pi}{4}-\frac{p\eta}{2}\right)\tan\left(\frac{p\pi}{4}+\frac{p\eta}{2}\right)}{\tan\left(\frac{p\pi}{4}\right)\left[\tan\left(\frac{p\pi}{2}\right)\tan\left(\frac{\pi}{4}+\frac{p\pi}{2}\right)\right]^{1/2}}. \tag{3.25b}$$

In the alternative Hamiltonian description one can take x to be the Euclidean time and associate with any equal-time section $\{x=\text{const},\ y\in(-\infty,\infty)\}$ the same Hilbert space $\mathcal{H}$ as in the bulk theory. The Hamiltonian operator is now given by Eq. (2.8). The boundary at $x=0$ appears as the initial condition described by the boundary state $|B\rangle \in \mathcal{H}$. In the $1+1$ Minkowski space-time, $|B\rangle$ can be written as a superposition of the bulk asymptotic states (2.13):

$$|B\rangle = \exp\left\{ \sum_a \tilde{g}_a A_a^+(0) + \int_0^\infty \frac{d\theta}{2\pi}\sum_{(a,b)} K^{ab}(\theta)A_a^+(-\theta)A_b^+(\theta)\right\}|0\rangle. \tag{3.26}$$

The amplitude $K^{ab}(\theta)$ is related to the reflection matrix as

$$K^{ab}(\theta) = R_{\bar{a}}^{b}\left(\frac{i\pi}{2}-\theta\right), \tag{3.27}$$

where $\bar{a}$ denotes the antiparticle of the particle a ($\bar{B}_j = B_j$). Ghoshal and Zamolodchikov [25] identified $\tilde{g}_a$ with the boundary coupling g_a, but Dorey *et al.* [36] found in the case of the Lee-Yang model the relation

$$\tilde{g}_a = g_a/2. \tag{3.28}$$

The strong evidence that this formula extends to any boundary $(1+1)$-dimensional quantum field theory, and in particular to the sine-Gordon one, was presented later in Ref. [37].

IV. MEAN-FIELD THEORIES

A. The Debye-Hückel limit

The position-dependent species densities in the electrical double layer can be evaluated systematically via an expansion in powers of β around the DH high-temperature limit $\beta\to 0$. The technique is based on a Mayer expansion of the free energy with series-renormalized bonds between each couple of field circles; for a detailed description of the method see Ref. [26].

In the lowest expansion order, the species concentrations are considered to be constant in the electrolyte region,

$n_\pm(x)=n/2$ ($x\geqslant 0$). Under this assumption, the renormalized bond is given by $K=K^{(0)}$ with

$$K^{(0)}(\mathbf{r}_1,\mathbf{r}_2) = -\beta K_0(\kappa r_{12}) + \beta K_0(\kappa r_{12}^*). \tag{4.1}$$

Here, κ is the inverse Debye length (2.20), K_0 is the modified Bessel function of second kind, $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$ and $r_{12}^*=|\mathbf{r}_1-\mathbf{r}_2^*|=|\mathbf{r}_1^*-\mathbf{r}_2|$. The first correction to the constant species densities can be obtained iteratively by inserting the lowest-order $K^{(0)}$ into a basic generating formula for the density profiles, with the result

$$n_\pm(x) = \frac{n}{2}\exp\left\{\pm\beta[\varphi-\varphi(x)] + \frac{\beta}{2}K_0(2\kappa x)\right\}. \tag{4.2}$$

Here, $\varphi(x)$ is the electric potential induced by the charge density $\rho(x)$ via the Poisson equation (3.6).

Expanding the exponential in Eq. (4.2) to order β gives for the charge density

$$\rho(x) = \beta n[\varphi-\varphi(x)]. \tag{4.3}$$

Inserting this into Eq. (3.6) and considering the boundary conditions for the electric potential, one gets

$$\delta\varphi_{\rm DH}(x) = -\varphi\exp(-\kappa x), \tag{4.4a}$$

$$\rho_{\rm DH}(x) = \beta n\varphi\exp(-\kappa x), \tag{4.4b}$$

where the deviation of the electric potential from its bulk value is defined by Eq. (3.7). The surface DH "image-charge" $\sigma_{\rm DH}$, defined by the couple of equivalent Eqs. (3.9) and (3.10), is obtained in the form

$$\sigma_{\rm DH} = -\frac{\kappa\varphi}{2\pi}. \tag{4.5}$$

In terms of $\sigma_{\rm DH}$, the relation (4.4a) is written as

$$\delta\varphi_{\rm DH}(x) = \frac{2\pi\sigma_{\rm DH}}{\kappa}\exp(-\kappa x). \tag{4.6}$$

Expanding the exponential in Eq. (4.2) to order β, the particle number density reads

$$n_{\rm DH}(x) = n + \delta n_{\rm DH}(x), \quad \delta n_{\rm DH}(x) = \frac{\beta n}{2}K_0(2\kappa x). \tag{4.7}$$

At large distances x from the wall,

$$\delta n_{\rm DH}(x) \sim \frac{\beta n}{2}\left(\frac{\pi}{4\kappa x}\right)^{1/2}\exp(-2\kappa x), \quad x\to\infty. \tag{4.8}$$

Note that this lowest-order relation is independent of φ.

B. Leading high-temperature correction

The next iteration for $n_\pm(x)$ is obtained by using the DH density (4.7) in the basic equation for the renormalized bond K and treating $\delta n(x)$ as a perturbation. Now $K=K^{(0)}+K^{(1)}$, where $K^{(0)}\propto\beta$ is defined by Eq. (4.1) and $K^{(1)}\propto\beta^2$ is given, to first order in the density perturbation, by the integral equation

$$K^{(1)}(\mathbf{r}_1,\mathbf{r}_2) = \int_{x_3>0} d^2r_3\, K^{(0)}(\mathbf{r}_1,\mathbf{r}_3)\,\delta n(x_3)K^{(0)}(\mathbf{r}_3,\mathbf{r}_2). \tag{4.9}$$

Taking also $K^{(1)}$ into account, instead of Eq. (4.2) we have

$$n_\pm(x) = \frac{n}{2}\exp\left\{\mp\beta\delta\varphi(x) + \frac{\beta}{2}K_0(2\kappa x) + \frac{1}{2}K^{(1)}(x)\right\}, \tag{4.10}$$

where $K^{(1)}(\mathbf{r},\mathbf{r})$, with $\mathbf{r}$ having the coordinate x, is renamed $K^{(1)}(x)$. Expanding the exponential in Eq. (4.10) up to order β^2, one obtains

$$\rho(x) = -\beta n\,\delta\varphi(x) - \frac{\beta^2 n}{2}K_0(2\kappa x)\,\delta\varphi(x), \tag{4.11}$$

$$\delta n(x) = \frac{\beta n}{2}K_0(2\kappa x) + \frac{n}{2}K^{(1)}(x) + \frac{\beta^2 n}{2}[\delta\varphi(x)]^2 + \frac{\beta^2 n}{8}[K_0(2\kappa x)]^2. \tag{4.12}$$

Inserting the charge density (4.11) into the Poisson equation (3.6) and considering the β expansion in the form

$$\delta\varphi(x) = -\varphi e^{-\kappa x} + \frac{\beta\varphi}{2}f(\kappa x), \tag{4.13}$$

the unknown f function is determined by the ordinary differential equation

$$f''(x) - f(x) = -e^{-x}K_0(2x) \tag{4.14}$$

with the zero boundary conditions $f(0)=f(\infty)=0$. In terms of the 1D Green function

$$G(x,x') = -e^{-x_>}\sinh(x_<) \tag{4.15}$$

with $x_<=\min\{x,x'\}$ and $x_>=\max\{x,x'\}$, the solution of Eq. (4.14) reads

$$f(x) = \int_0^\infty dx'\, G(x,x')[-e^{-x'}K_0(2x')]. \tag{4.16}$$

At large x, $f(x)$ behaves like $e^{-x}[(\pi/2)-1]/4$. Consequently,

$$\delta\varphi(x) \underset{x\to\infty}{\sim} -\varphi\left[1-\frac{\beta}{8}\left(\frac{\pi}{2}-1\right)\right]e^{-\kappa x}, \tag{4.17a}$$

$$\rho(x) \underset{x\to\infty}{\sim} \beta n\varphi\left[1-\frac{\beta}{8}\left(\frac{\pi}{2}-1\right)\right]e^{-\kappa x}. \tag{4.17b}$$

These formulas provide the pure exponential asymptotic decay of the DH results (4.4a) and (4.4b), in agreement with the concept of renormalized charge [6–9]. The renormalized image charge $\sigma_{\rm ren}$ is defined in analogy with Eq. (4.6) as

$$\delta\varphi(x) \underset{x\to\infty}{\sim} \frac{2\pi\sigma_{\rm ren}}{\kappa}\exp(-\kappa x); \tag{4.18}$$

note that there is no renormalization of the screening length κ^{-1} in the lowest order of the β expansion. The renormalized charge has the following weak-coupling expansion:

$$\sigma_{\rm ren} = -\frac{\kappa\varphi}{2\pi}\left[1 - \frac{\beta}{8}\left(\frac{\pi}{2} - 1\right) + O(\beta^2)\right]. \qquad (4.19)$$

From Eq. (4.16) one gets that $f'(0)=1/2$. Combining then Eqs. (3.9) and (4.13), the leading β correction to the surface "image-charge" (4.5) reads

$$\sigma = -\frac{\kappa\varphi}{2\pi}\left[1 + \frac{\beta}{4} + O(\beta^2)\right]. \qquad (4.20)$$

The problem of the number density deviation from its bulk value, $\delta n(x)$ given by Eq. (4.12), is more complicated because the function $K^{(1)}(x)$ is only defined implicitly as the solution of the integral equation (4.9). It can be shown after lengthy algebra that

$$K^{(1)}(x) \sim \frac{\pi^2\beta^2}{16}\exp(-2\kappa x) \text{ as } x \to \infty. \qquad (4.21)$$

Thus, at large distances from the wall,

$$\delta n(x) \underset{x\to\infty}{\sim} \frac{\beta^2 n}{2}\left(\varphi^2 + \frac{\pi^2}{16}\right)\exp(-2\kappa x). \qquad (4.22)$$

Note that this asymptotic behavior differs fundamentally from, and is superior to, that obtained in the DH limit (4.8). We conclude that, in contrast to the charge density, the DH theory does not provide an adequate description of the large-distance decay of the particle number density to its bulk value.

C. Nonlinear Poisson-Boltzmann theory

In the nonlinear PB theory, one keeps the deviation of the electrostatic potential from its bulk value, $\varphi(x)-\varphi$, in the exponential form (4.2). The DH expression for the charge density (4.3) then takes the nonlinear form

$$\rho(x) = n\,\sinh\{\beta[\varphi - \varphi(x)]\}. \qquad (4.23)$$

The corresponding Poisson equation

$$\varphi''(x) = -2\pi n\,\sinh\{\beta[\varphi - \varphi(x)]\} \qquad (4.24)$$

is subject to the obvious boundary conditions $\varphi(0)=0$ and $\varphi(\infty)=\varphi$. We recall the well-known fact that, with the identifications $\phi_{\rm st}(x)=-4ib\varphi(x)$ and $z=n/2$, the nonlinear PB equation (4.24) corresponds to the static equation (ϕ does not depend on "time" y) of the "classical" variational treatment of the boundary sine-Gordon action (3.14b), $\delta S_{\rm bry}[\phi_{\rm st}(x)]=0$.

For the present semi-infinite geometry, the solution of the nonlinear PB equation (4.24) can be derived explicitly:

$$\delta\varphi(x) = -\frac{2}{\beta}\ln\left[\frac{1 + e^{-\kappa x}\tanh(\beta\varphi/4)}{1 - e^{-\kappa x}\tanh(\beta\varphi/4)}\right]. \qquad (4.25)$$

At asymptotically large distance x from the wall,

$$\delta\varphi(x) \underset{x\to\infty}{\sim} -\frac{4}{\beta}\tanh\left(\frac{\beta\varphi}{4}\right)e^{-\kappa x}. \qquad (4.26)$$

This behavior is again in full agreement with the idea of renormalized charge. The renormalized image charge $\sigma_{\rm ren}$, defined by Eq. (4.18), reads

$$\sigma_{\rm ren} = -\frac{2\kappa}{\pi\beta}\tanh\left(\frac{\beta\varphi}{4}\right). \qquad (4.27)$$

In the $\beta\to 0$ limit and for a finite φ, the DH result (4.5) is reproduced as it should be. On the other hand, the leading β correction to the DH result in Eq. (4.19) is not reproduced at this level. We shall show in the next section that the nonlinear formula (4.27) describes correctly the scaling regime of limits $\beta\to 0$ and $\varphi\to\infty$ with the product $\beta\varphi$ being finite.

The surface "image-charge" σ, defined by either Eq. (3.9) or Eq. (3.10), is obtained as follows:

$$\sigma = -\frac{\kappa}{\pi\beta}\sinh\left(\frac{\beta\varphi}{2}\right). \qquad (4.28)$$

For a nonzero β and in the limit of the infinite σ charge, which is equivalent in view of Eq. (4.28) to the limit $\varphi\to\infty$, the renormalized $\sigma_{\rm ren}$ [Eq. (4.27)] saturates at the finite value

$$\sigma^*_{\rm ren} = -\frac{2\kappa}{\pi\beta}. \qquad (4.29)$$

More generally, for a nonzero β and in the limit $\varphi\to\infty$, Eq. (4.25) reduces to

$$\delta\varphi^*(x) = -\frac{2}{\beta}\ln\left[\frac{1 + \exp(-\kappa x)}{1 - \exp(-\kappa x)}\right], \qquad (4.30)$$

i.e., the electric potential deviation from its bulk value saturates at a finite value in every point of the electrolyte region $x>0$, in accordance with the hypothesis of the potential saturation [10]. Note that the potential saturation is a pure nonlinear effect: there is no saturation in the DH relation (4.4a).

The nonlinear PB ("classical" in field theory) equation arises as the zeroth-order term in a loop expansion of the grand partition function [43]. While the high-temperature β expansion is a perturbative expansion, the loop expansion is a nonperturbative one. The relations between the two are described in field theoretical books; see, e.g., Ref. [44].

V. ASYMPTOTIC CHARGE AND NUMBER DENSITY PROFILES FOR $\beta<2$

A. Boundary one-point functions: General formalism

Let us consider a general integrable 2D boundary field theory, defined in the half space $x>0$ and possessing an integrable boundary condition at $x=0$. For the time being, the spectrum of the corresponding bulk theory is supposed to contain only one particle of mass m. We aim at calculating formally the mean values $\langle\mathcal{O}(x,0)\rangle_{\rm bry}$ (due to the translational y invariance, y is set to 0 for simplicity) of some, as yet unspecified, local field operator $\mathcal{O}$. As is explained in Sec. III B, in the 1+1 Minkowski x time and y space, the boundary condition at $x=0$ acts as the initial-time condition described by the boundary state

$$|B\rangle = \exp\left\{\frac{g}{2}A^{+}(0) + \int_0^{\infty}\frac{d\theta}{2\pi}K(\theta)A^{+}(-\theta)A^{+}(\theta)\right\}|0\rangle \tag{5.1}$$

which belongs to the bulk Hilbert space $\mathcal{H}$. Thus

$$\langle\mathcal{O}(x,0)\rangle_{\text{bry}} = \frac{\langle 0|\mathcal{O}(x,0)|B\rangle}{\langle 0|B\rangle}; \tag{5.2}$$

note that the normalization is $\langle 0|B\rangle=1$.

A systematic expansion for the one-point function (5.2) can be obtained by using a complete system of the bulk n-particle states $\{|n\rangle\}$ forming $\mathcal{H}$ as follows:

$$\langle 0|\mathcal{O}(x,0)|B\rangle = \sum_{n=0}^{\infty}\langle 0|\mathcal{O}(x,0)|n\rangle\langle n|B\rangle. \tag{5.3}$$

In the rapidity representation, this formula reads

$$\begin{aligned}\langle 0|\mathcal{O}(x,0)|B\rangle &= \langle 0|\mathcal{O}(x,0)|0\rangle + \int_{-\infty}^{\infty}\frac{d\theta}{2\pi}\langle 0|\mathcal{O}(x,0)|\theta\rangle\langle\theta|B\rangle \\ &+ \int_{-\infty}^{\infty}\frac{d\theta_1}{2\pi}\int_{\theta_1}^{\infty}\frac{d\theta_2}{2\pi}\langle 0|\mathcal{O}(x,0)|\theta_1,\theta_2\rangle\langle\theta_1,\theta_2|B\rangle \\ &+ \cdots,\end{aligned} \tag{5.4}$$

where $|\theta\rangle=A^{+}(\theta)|0\rangle$, $|\theta_1,\theta_2\rangle=A^{+}(\theta_1)A^{+}(\theta_2)|0\rangle$, etc.

The matrix elements $\langle\theta|B\rangle$, $\langle\theta_1,\theta_2|B\rangle$, etc., which depend on the given boundary condition, can be calculated by using the explicit form of the boundary state (5.1). The normalization condition for the two-particle scattering

$$A(\theta_1)A^{+}(\theta_2) = 2\pi\delta(\theta_1-\theta_2) + S(\theta_2-\theta_1)A^{+}(\theta_2)A(\theta_1) \tag{5.5}$$

implies that

$$\langle\theta|B\rangle \equiv \langle 0|A(\theta)B\rangle = \frac{g}{2}2\pi\delta(\theta). \tag{5.6}$$

Analogously, we have

$$\begin{aligned}\langle\theta_1,\theta_2|B\rangle &\equiv \langle 0|A(\theta_2)A(\theta_1)B\rangle \\ &= \int_0^{\infty}\frac{d\theta}{2\pi}K(\theta)(2\pi)^2\delta(\theta_1+\theta)\delta(\theta_2-\theta),\end{aligned} \tag{5.7}$$

and so on.

The matrix elements $\langle 0|\mathcal{O}(x,0)|\theta\rangle$, $\langle 0|\mathcal{O}(x,0)|\theta_1,\theta_2\rangle$, etc., which do not depend on the given boundary condition, are known as the bulk multiparticle form factors. Their x dependence can be factorized out by means of a translation on the operator $\mathcal{O}(x,0)$ [21]:

$$\langle 0|\mathcal{O}(x,0)|\theta\rangle = e^{-mx\cosh\theta}F_1, \tag{5.8a}$$

$$\langle 0|\mathcal{O}(x,0)|\theta_1,\theta_2\rangle = e^{-mx(\cosh\theta_1+\cosh\theta_2)}F_2(\theta_1-\theta_2), \tag{5.8b}$$

and so on. The bulk form factors $F_1=\langle 0|\mathcal{O}(0,0)|\theta\rangle$, $F_2(\theta_1-\theta_2)=\langle 0|\mathcal{O}(0,0)|\theta_1,\theta_2\rangle$, etc. can be obtained explicitly in an axiomatic way, similarly to the case of the two-particle scattering S matrix.

Finally, using the formulas (5.6), (5.7), (5.8a), and (5.8b) in the expansion (5.4), the form-factor representation of the one-point function reads

$$\begin{aligned}\langle\mathcal{O}(x,0)\rangle_{\text{bry}} &= \langle 0|\mathcal{O}(x,0)|0\rangle + \frac{g}{2}F_1e^{-mx} \\ &+ \int_0^{\infty}\frac{d\theta}{2\pi}K(\theta)F_2(-2\theta)e^{-2mx\cosh\theta} + O(e^{-3mx}).\end{aligned} \tag{5.9}$$

This formula is particularly useful for large distances x from the wall since it provides a systematic large-distance expansion. The first term is nothing but the bulk expectation value of the operator $\mathcal{O}$, $\langle\mathcal{O}\rangle$, which is indeed dominant in the limit $x\to\infty$. The leading correction term comes from the one-particle state, with the particle mass m playing the role of the inverse correlation length. The next-to-leading correction term decays at large x as $\exp(-2mx)$ multiplied by an inverse-power of mx, and so on.

The extension of the formula (5.9) to general integrable 2D field theories with many-particle spectrum $\{a\}$ is straightforward. We only write down the final result:

$$\begin{aligned}\langle\mathcal{O}(x,0)\rangle_{\text{bry}} &= \langle\mathcal{O}\rangle + \sum_a\frac{g_a}{2}F_1^{(a)}e^{-m_ax} \\ &+ \int_0^{\infty}\frac{d\theta}{2\pi}\sum_{\substack{(a,b)\\ m_a=m_b}}K^{ab}(\theta)F_2^{(ab)}(-2\theta)e^{-2m_ax\cosh\theta} \\ &+ \cdots.\end{aligned} \tag{5.10}$$

B. Electrical double layer

Since the number (3.18) and the charge (3.19) density profiles are determined by the boundary mean values of the exponential field, $\langle e^{iqb\phi(x,0)}\rangle_{\text{bry}}$ $(q=\pm1)$, the operator of interest is

$$\mathcal{O}_q(x,0) = \exp\{iqb\phi(x,0)\}, \quad q=\pm1. \tag{5.11}$$

In the spectrum of the 2D bulk sine-Gordon theory, the first two lightest neutral particles are the B_1 and B_2 breathers with the corresponding masses [see Eq. (2.11)]

$$m_1 = 2M\sin\left(\frac{\pi p}{2}\right), \quad p<1, \tag{5.12a}$$

$$m_2 = 2M\sin(\pi p), \quad p<\frac{1}{2}. \tag{5.12b}$$

The mass $m_2\leq 2m_1$, the equality taking place in the DH limit $p\to0$. Consequently, when applying the large-x expansion

(5.10) to the boundary sine-Gordon theory with Dirichlet boundary conditions (3.15), we have to consider the following leading terms:

$$\langle \mathcal{O}_q(x,0)\rangle_{\text{bry}} = \langle \mathcal{O}\rangle + \frac{g_1}{2}F_1^{(1)}(q)e^{-m_1x} + \frac{g_2}{2}F_1^{(2)}(q)e^{-m_2x} + \int_0^\infty \frac{d\theta}{2\pi}K^{11}(\theta)F_2^{(11)}(-2\theta;q)e^{-2m_1x\cosh\theta} + \cdots. \tag{5.13}$$

Here, the boundary couplings g_1 and g_2 are given by Eqs. (3.25a) and (3.25b), respectively, and $K^{11}(\theta) = R_B^{(1)}((i\pi/2)-\theta)$ where the reflection amplitude $R_B^{(1)}$ is given by Eq. (3.22a).

Our preliminary task is to write down the bulk form factors in Eq. (5.13) for the exponential operator (5.11). We start with the B_1 form factors which have been obtained in Ref. [22]. The one-particle B_1 form factor reads

$$F_1^{(1)}(q) = -iq\lambda\langle e^{iqb\phi}\rangle, \quad q=\pm 1, \tag{5.14}$$

where the parameter λ is defined by

$$\lambda = 2\cos\left(\frac{p\pi}{2}\right)\left[2\sin\left(\frac{p\pi}{2}\right)\right]^{1/2}\exp\left(-\int_0^{p\pi}\frac{dt}{2\pi}\frac{t}{\sin t}\right). \tag{5.15}$$

The two B_1-breathers form factor reads

$$F_2^{(11)}(\theta;q) = -\lambda^2 R(\theta)\langle e^{iqb\phi}\rangle, \quad q=\pm 1, \tag{5.16}$$

where the function $R(\theta)$ is given on the interval $-2\pi+p\pi < \mathrm{Im}(\theta) < -p\pi$ by the integral

$$R(\theta) = \mathcal{N}\exp\left\{8\int_0^\infty \frac{dt}{t}\frac{\sinh(t)\sinh(pt)\sinh[(1+p)t]}{\sinh^2(2t)} \times \sinh^2\left[t\left(1-\frac{i\theta}{\pi}\right)\right]\right\}, \tag{5.17a}$$

$$\mathcal{N} = \exp\left\{4\int_0^\infty \frac{dt}{t}\frac{\sinh(t)\sinh(pt)\sinh[(1+p)t]}{\sinh^2(2t)}\right\}. \tag{5.17b}$$

This function satisfies a useful relation,

$$R(\theta)R(\theta\pm i\pi) = \frac{\sinh(\theta)}{\sinh(\theta)\mp i\sin(p\pi)}, \tag{5.18}$$

which, together with $R(-\theta)=S_{11}(\theta)R(\theta)$, enables one to extend the definition of $R(\theta)$ to arbitrary values of $\mathrm{Im}(\theta)$. (Here S_{11} denotes the B_1B_1 scattering matrix, see below). The evaluation of the one-particle B_2 form factor can be based on a bootstrap procedure [21]. Namely, since the B_2 breather is a bound state of the two B_1 breathers (i.e., the B_1B_1 scattering matrix has the B_2 pole), the one-particle B_2 form factor can be calculated from the two-particle B_1 form factor (5.16) as follows [21]:

$$\Gamma F_1^{(2)}(q) = -i\,\mathrm{res}_{\epsilon=0}F_2^{(11)}\left(\theta+\frac{ip\pi+\epsilon}{2},\theta-\frac{ip\pi+\epsilon}{2};q\right), \tag{5.19}$$

where Γ is related to the residue of the B_2 pole in the B_1B_1 scattering as follows:

$$-i\,\mathrm{res}_{\theta=ip\pi}S_{11}(\theta) = \Gamma^2. \tag{5.20}$$

Explicitly, one has [17]

$$S_{11}(\theta) = \frac{\sinh(\theta)+i\sin(p\pi)}{\sinh(\theta)-i\sin(p\pi)}, \quad \Gamma = \sqrt{2\tan(p\pi)}. \tag{5.21}$$

The one-particle B_2 form factor thus reads

$$F_1^{(2)}(q) = -\lambda^2\left[\frac{\tan(p\pi)}{2}\right]^{1/2}\frac{1}{R[i\pi(1+p)]}\langle e^{iqb\phi}\rangle. \tag{5.22}$$

With regard to the bulk neutrality condition $\langle e^{ib\phi}\rangle = \langle e^{-ib\phi}\rangle$, under the transformation $q\to -q$ the form factor $F_1^{(1)}(q)$ changes the sign, $F_1^{(1)}(+1) = -F_1^{(1)}(-1)$, while the form factors $F_2^{(11)}(\theta;q)$ [Eq. (5.16)] and $F_1^{(2)}(q)$ [Eq. (5.22)] are unchanged, $F_2^{(11)}(\theta;+1)=F_2^{(11)}(\theta;-1)$ and $F_1^{(2)}(+1)=F_1^{(2)}(-1)$. Consequently, as is clear from the definitions (3.18) and (3.19), within the series representation (5.13), the term with $F_1^{(1)}$ contributes to the charge density ρ while the terms with $F_2^{(11)}$ and $F_1^{(2)}$ contribute to the particle number density n.

C. Asymptotic charge profile

The asymptotic large-x behavior of the charge density is obtained in the form

$$\rho(x) \underset{x\to\infty}{\sim} 2n\sqrt{\cos\left(\frac{p\pi}{2}\right)}\left[1+\cos\left(\frac{p\pi}{2}\right)-\sin\left(\frac{p\pi}{2}\right)\right] \times \exp\left(-\int_0^{p\pi}\frac{dt}{2\pi}\frac{t}{\sin t}\right)\tanh(p\varphi)\exp(-m_1x), \tag{5.23}$$

where $p=\beta/(4-\beta)$ and the mass m_1 of the lightest B_1 breather, given by the relations (2.19) and (2.20), is the renormalized inverse screening length. The formula (5.23) applies to the whole stability region $\beta<2$ which is simultaneously the region of the existence of the B_1 breather in the particle spectrum of the sine-Gordon model. With respect to the Poisson Eq. (3.6), the deviation of the induced electrostatic potential from its bulk value (3.7) behaves at large x as $\delta\varphi(x)\sim_{x\to\infty} -2\pi\rho(x)/m_1^2$. We conclude that the pure exponential asymptotic decay of the DH results (4.4a) and (4.4b), taken with the renormalization of the inverse screening length $\kappa\to m_1$, is recovered. This means that the concept of renormalized charge, which is meaningful only if it is introduced with the renormalization of the (inverse) screening length, is applicable to the present model. The renormalized image charge σ_{ren}, defined by Eq. (4.18) with the replacement $\kappa\to m_1$, is given by

$$\sigma_{\text{ren}} = -\frac{\kappa}{\pi\beta}\sqrt{\frac{p\pi}{2\sin(p\pi/2)}}\left[1+\cos\left(\frac{p\pi}{2}\right)-\sin\left(\frac{p\pi}{2}\right)\right] \times \exp\left(-\int_0^{p\pi}\frac{dt}{2\pi}\frac{t}{\sin t}\right)\tanh(p\varphi). \quad (5.24)$$

It can be readily verified that the β expansion (4.19) is reproduced by this formula. In the limits $\beta \to 0$ and $\varphi \to \infty$ such that the product $\beta\varphi$ is finite, Eq. (5.24) reduces to the result (4.27) of the nonlinear PB theory which is therefore adequate in such regime. For a given β, increasing the potential difference φ to infinity, σ_{ren} saturates monotonically at the finite value

$$\sigma^*_{\text{ren}} = -\frac{\kappa}{\pi\beta}\sqrt{\frac{p\pi}{2\sin(p\pi/2)}}\left[1+\cos\left(\frac{p\pi}{2}\right)-\sin\left(\frac{p\pi}{2}\right)\right] \times \exp\left(-\int_0^{p\pi}\frac{dt}{2\pi}\frac{t}{\sin t}\right), \quad (5.25)$$

in agreement with the saturation hypothesis.

D. Asymptotic number density profile

The asymptotic large-x behavior of the particle number density $n(x)$ is a more complicated topic. For the density deviation from its bulk value $\delta n(x)=n(x)-n$, the form-factor asymptotic expansion (5.13) gives

$$\delta n(x) \underset{x\to\infty}{\sim} \delta n^{(2)}(x) + \delta n^{(11)}(x), \quad (5.26)$$

where the B_2-breather term reads

$$\delta n^{(2)}(x) = -\frac{n}{2}\lambda^2 g_2\left[\frac{\tan(p\pi)}{2}\right]^{1/2}\frac{1}{R[i\pi(1+p)]}\exp(-m_2 x) \quad (5.27)$$

with g_2 given by Eq. (3.25b) taken at $\eta = i2\varphi$, and the B_1B_1 integral term reads

$$\delta n^{(11)}(x) = \int_0^\infty \frac{d\theta}{\pi}\chi(\theta)e^{-2m_1 x\cosh\theta}, \quad (5.28a)$$

$$\chi(\theta) = -\frac{1}{2}n\lambda^2 K^{11}(\theta)R(\theta). \quad (5.28b)$$

The presence of the B_2 term is restricted to $p<1/2$ ($\beta<4/3$), the B_1B_1 is present in the whole stability region $p<1$ ($\beta<2$). As soon as β (or, equivalently, p) has a strictly nonzero value, it can be shown from Eq. (5.28a) and (5.28b) that

$$\delta n^{(11)}(x) \propto \frac{e^{-2m_1 x}}{\sqrt{m_1 x}} \text{ at large } x, \quad (5.29)$$

with $2m_1 > m_2$ for any $\beta>0$. The B_1B_1 term thus becomes subleading in Eq. (5.26), while the B_2 term (5.27) dominates:

$$\delta n(x) \underset{x\to\infty}{\sim} \delta n^{(2)}(x), \quad \beta > 0. \quad (5.30)$$

As concerns the $\beta \to 0$ limit, considering $R(i\pi)\to -1$, $\lambda \to 2\sqrt{p\pi}$, $g_2 \to 8\sqrt{2p/\pi^3}[\varphi^2+(\pi^2/16)]$, $p\to \beta/4$, and $m_2 \to 2\kappa$ in Eq. (5.27) leads to the expression

$$\delta n^{(2)}(x) = \beta^2 n\left(\varphi^2+\frac{\pi^2}{16}\right)\exp(-2\kappa x) + O(\beta^3), \quad (5.31)$$

which is twice larger than the expected result (4.22) of the systematic β expansion. This means that the formula (5.30) does not reflect adequately the expansion of the asymptotic $\delta n(x)$ around the $\beta=0$ point. The reason for this inconsistency consists in the fact that, in the limit $p\to 0$, besides the important equality of inverse correlation lengths $m_2=2m_1=2\kappa$, the value of $\chi(\theta)$ as well as of all its derivatives go to infinity at $\theta=0$. As a consequence, also the B_1B_1 term (5.28a), which is subleading for a strictly nonzero β, contributes to the leading order of the pure-exponential large-x behavior [see the relation (5.35) below]. It is important to add that if we would be able to perform all β orders of the large-x decay of $\delta n^{(11)}(x)$, we should arrive at the exact asymptotic behavior (5.29), valid for $\beta>0$, which is no longer purely exponential. This mathematical technicality was observed in the study of finite-size effects for the (1+1)-dimensional sine-Gordon theory defined on a strip with Dirichlet-type boundary conditions [37]; the next analysis follows a regularization procedure presented in Ref. [37]. The dangerous singularity of $\chi(\theta)$, at $\theta=0$ in the limit $p\to 0$, can be isolated from $\chi(\theta)$ in the following way:

$$\chi(\theta) = \frac{\cosh\theta + \cos(p\pi/2)}{\cosh\theta - \cos(p\pi/2)}\chi_0(\theta), \quad (5.32)$$

where $\chi_0(\theta)$ is a regular function of θ around $\theta=0$:

$$\chi_0(\theta) = \chi_0(0) + \chi''_0(0)\frac{\theta^2}{2} + \cdots. \quad (5.33)$$

Here, $\chi_0(0)$ corresponds to the classical treatment, $\chi''_0(0)$ to the first quantum correction, etc. Within the regularized form (5.32) complemented by the regular expansion (5.33), the evaluation of the B_1B_1 integral (5.28a) can be carried out in close analogy with Ref. [37]. In particular, for very large x and small p, one uses the results of Ref. [37]:

$$\int_0^\infty \frac{d\theta}{\pi}\frac{\cosh\theta+\cos(p\pi/2)}{\cosh\theta-\cos(p\pi/2)}e^{-2mx\cosh\theta} \underset{x\to\infty}{\sim} \frac{\cos(p\pi/2)}{\sin(p\pi/4)}e^{-2mx}. \quad (5.34a)$$

Similarly, one can derive that

$$\int_0^\infty \frac{d\theta}{\pi}\frac{\cosh\theta+\cos(p\pi/2)}{\cosh\theta-\cos(p\pi/2)}\frac{\theta^2}{2}e^{-2mx\cosh\theta} \underset{x\to\infty}{\sim} 2\sin\left(\frac{p\pi}{4}\right)\cos\left(\frac{p\pi}{2}\right)e^{-2mx}. \quad (5.34b)$$

Regarding the explicit forms of $\chi_0(0)$ and $\chi''_0(0)$, the result for the B_1B_1 integral is such that

$$\lim_{p\to 0}\frac{\delta n^{(11)}(x)}{\delta n^{(2)}(x)} = -\frac{1}{2}. \quad (5.35)$$

In view of relation (5.31), the sum in Eq. (5.26) thus reproduces the needed result (4.22). To conclude, the small β

expansion around the $\beta=0$ point of the asymptotic number density profile involves artificial contributions from the B_1B_1 integral term, this term being totally absent at a strictly nonzero (possibly very small) value of β. In other words, the small-β expansion of the asymptotic density profile, when truncated at some finite β order, does not reflect adequately the asymptotic density profile at a nonzero value of β. From this point of view, the DH results for number density profiles have to be taken with caution also for other boundary Coulomb systems.

VI. FREE-FERMION β=2 POINT

For the sake of completeness, we summarize in view of the subjects of present interest the exact results for the 2D electrical double layer at the free-fermion $\beta=2$ point of the Thirring representation of the Coulomb gas [14]. The exact solution for the species density profiles at an arbitrary distance $x>0$ from the ideal-conductor wall reads

$$n_{\pm}(x) - n_{\pm} = \frac{m}{2\pi}\int_0^{\infty} dl \left[-\frac{m}{\kappa_l} + \frac{\kappa_l \exp(\pm\beta\varphi) + m}{m\cosh(\beta\varphi) + \kappa_l} \right] \times \exp(-2\kappa_l x), \tag{6.1}$$

where $m=2\pi z$ is the rescaled fugacity (equal to the soliton mass M, see formula (2.17) taken at $b^2=1/2$ and $p=1$), $\kappa_l=(m^2+l^2)^{1/2}$ and $n_{\pm}=n/2$ are the bulk densities regularized by considering a hard-core repulsion around each particle. The short-distance limit of Eq. (6.1),

$$n_{\pm}(x) \sim \frac{z_{\pm}}{2x} \text{ as } x \to 0, \tag{6.2}$$

is of the expected form (3.12). The charge density, calculated from Eq. (6.1), implies via the Poisson equation the following deviation of the electrostatic potential from its bulk value:

$$\delta\varphi(x) = -\int_0^{\infty} dl \frac{1}{2\kappa_l} \frac{m\sinh(2\varphi)}{m\cosh(2\varphi) + \kappa_l} \exp(-2\kappa_l x). \tag{6.3}$$

At asymptotically large distances from the wall,

$$\delta\varphi(x) \underset{x\to\infty}{\sim} -\frac{1}{4}\tanh\varphi \left(\frac{\pi}{mx}\right)^{1/2} \exp(-2mx). \tag{6.4}$$

This asymptotic behavior differs fundamentally from the purely exponential DH prediction (4.4a). The concept of renormalized charge is therefore not applicable at the free fermion point. The reason for the fundamental difference is obvious. The lightest B_1 breather disappears from the particle spectrum of the sine-Gordon model just at the free-fermion point $\beta=2$, and the asymptotic behavior of $\delta\varphi(x)$ starts to be governed by the soliton-antisoliton pair. Since $m_1 \to 2M$ ($\equiv 2m$) as $\beta \to 2$, the particle mass in the exponential decay on the right-hand side of Eq. (6.4) is a continuous function of β at $\beta=2$. On the other hand, the position-dependent prefactor $(mx)^{-1/2}$ in the formula (6.4), determined by the form factor of the soliton-antisoliton pair, has no "continuous" analog in the leading asymptotic behavior of $\delta\varphi(x)$ inside the stability region $\beta<2$. The basic qualitative features of the results at the $\beta=2$ point are expected to be present also for $\beta>2$, up to the Kosterlitz-Thouless point $\beta=4$ where the 2D sine-Gordon theory ceases to be massive.

In the limit $\varphi \to \infty$, $\delta\varphi(x)$ of Eq. (6.3) saturates at

$$\delta\varphi^*(x) = -\frac{1}{2}K_0(2mx). \tag{6.5}$$

This function is finite in the whole electrolyte region $x>0$, which confirms the validity of the hypothesis of the electric potential saturation [10].

VII. CONCLUSION

The main aim of this paper was to test basic concepts used in the theory of highly asymmetric Coulomb fluids on the exact solution of a 2D electrical double layer. This model is mappable onto the 2D semi-infinite sine-Gordon field theory with Dirichlet boundary conditions which do not break the integrability property of the bulk sine-Gordon model with the known particle spectrum. At large distances from model's interface, the induced electric potential has the pure exponential decay for small enough inverse temperatures (couplings) $\beta<2$, including the DH $\beta \to 0$ limit. This fact confirms the adequacy of the concept of renormalized charge for weak couplings. In the extreme case of an infinite potential difference between model's interface and the bulk interior of the electrolyte, the renormalized charge saturates at a finite value which is in agreement with the saturation hypothesis. Although the exact 2D results are not directly applicable to three dimensions, the presented verification of the basic concepts in two dimensions supports their general validity.

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