

Surface Tension of an Ideal Dielectric-Electrolyte Boundary: Exactly Solvable Model

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The model under consideration is a semi-infinite two-dimensional two-component plasma (Coulomb gas), stable against bulk collapse for the dimensionless coupling constant $\beta < 2$, in contact with a dielectric wall of dielectric constant $\epsilon = 0$. The model is mapped onto an integrable sine-Gordon theory with a “free” Neumann boundary condition. Using recent results on a reflection relationship between the boundary Liouville and sine-Gordon theories, an explicit expression is derived for the surface tension at a rectilinear dielectric – Coulomb gas interface. This expression reproduces the Debye-Hückel $\beta \rightarrow 0$ limit and the exact result at the bulk collapse border, the free-fermion point $\beta = 2$, where the surface tension keeps a finite value. The surface collapse, identified with the divergence of the surface tension, occurs at $\beta = 3$.

KEY WORDS: Two-component plasma; two dimensions; boundary sine-Gordon model; surface tension.

1. INTRODUCTION

In a previous paper,⁽¹⁾ the bulk thermodynamic properties (free energy, specific heat, etc...) of the two-dimensional (2D) two-component plasma (with logarithmic interactions), or Coulomb gas, have been obtained exactly in the whole temperature range for which the point-particle model is stable against collapse, i.e., for the dimensionless coupling constant (inverse temperature) $\beta < 2$. The mapping onto a bulk sine-Gordon field theory was made and recent results about that field theory,⁽²⁻³⁾ were used.

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In a next paper,⁽⁴⁾ a surface property of the same model in contact with an ideal conductor of dielectric constant $\rightarrow \infty$, impenetrable to particles, was considered. In particular, the surface tension at a rectilinear conductor—Coulomb gas interface was obtained exactly as a function of the bulk density, the applied potential and the temperature. A mapping onto an integrable boundary sine-Gordon theory⁽⁵⁾ with a Dirichlet boundary condition was established, and known results about that field theory,⁽⁶⁻⁷⁾ were used.

The model considered in the present paper is the 2D Coulomb gas in contact with an ideal dielectric wall of dielectric constant $=0$. The system is mapped onto an integrable sine-Gordon theory, now with a “free” Neumann boundary condition. Using very recent results on a “reflection” relationship between the boundary Liouville and sine-Gordon theories,⁽⁸⁻¹⁰⁾ an explicit expression is derived for the surface tension at a rectilinear dielectric—Coulomb gas interface as a function of the bulk density, or the fugacity, and the temperature. The surface tension is checked on its high-temperature expansion derived from a renormalized Mayer expansion and on the exact result at the bulk collapse border, the free-fermion point $\beta=2$, where it keeps a finite value.⁽¹¹⁾ The divergency of the surface tension occurs at $\beta=3$.

The model under consideration mimics the interface between an electrolyte (the 2D two-component plasma, made of two species of point particles, of opposite charges ± 1) and an ideal dielectric wall. Classical equilibrium statistical mechanics is used. In the grand-canonical formalism, the control parameters are the inverse temperature β and the two fugacities z_+ and z_- of the positive and negative particles, respectively. Due to the charge neutrality, the bulk properties of the plasma depend only on the combination $z=(z_+z_-)^{1/2}$.⁽¹²⁾ It is a specific feature of the present model that also its surface properties depend only on z .

In the bulk of the plasma, the interaction Boltzmann factor of a positive-negative pair of charges, $r^{-\beta}$, is integrable at small r if and only if $\beta < 2$ (at large r , the interaction is screened), with $\beta=2$ being the bulk collapse border of the plasma. In the region $\beta \geq 2$, one has to attach to particles a small hard core σ in order to prevent the collapse. As has been argued long time ago,⁽¹³⁾ in the limit $\sigma \rightarrow 0$, while the free energy and the internal energy per particle diverge, the specific heat, truncated correlation functions, etc. remain finite. In this sense one should also consider our exact result for the surface tension when $\beta \geq 2$. The stability range for surface properties of the model is $\beta < 3$. The surface collapse at $\beta=3$ is identified with the divergency of the surface tension.

Series expansions and exact results are rather rare for the present 2D configuration electrolyte—dielectric wall. More success was attained in the

case when the electrolyte is modeled by a one-component plasma, i.e., a system of moving point particles of the same charge embedded in a rigid neutralizing background. The $\beta \rightarrow 0$ limit was treated in ref. 14 and the $\beta=2$ free fermion case was solved by Smith⁽¹⁵⁾ (thermodynamics) and Jancovici⁽¹⁶⁾ (density profile, pair correlations, sum rules). When the electrolyte is modeled by a two-component plasma, at $\beta=2$, the exact solution was available only for a hard wall and an ideal conductor wall,^(17, 18) which admit a Thirring representation with an inhomogeneous mass going to 0 and to ∞ within the wall, respectively. Only recently,⁽¹¹⁾ an exact solution has been obtained also for the dielectric wall of interest by the method of pfaffians, and that solution offers via an explicit density profile a check of the surface tension formula at $\beta=2$.

One should emphasize that the present result was obtained due to recent progress in integrable field theories, in particular, a reflection relationship between the boundary Liouville and sine-Gordon theories.⁽⁸⁻¹⁰⁾ Mainly the work,⁽¹⁰⁾ providing an exact formula for the one-point function of an exponential boundary operator in the boundary sine-Gordon model with a general integrable boundary action, was crucial. The surface tension is obtained as a result of an integration from the conductor wall (Dirichlet boundary condition) with a known formula for the surface tension,⁽⁴⁾ to the dielectric wall (Neumann boundary condition), via a continuous class of integrable boundary field theories.

The paper is organized as follows. In Section 2, the mapping of the Coulomb gas in contact with an ideal dielectric onto a sine-Gordon field theory with a Neumann boundary condition is made. The reflection relationship between the boundary Liouville and sine-Gordon theories is briefly explained and basic formulae are written down in Section 3. The exact formula for the surface tension is derived in Section 4. Its high temperature expansion and the $\beta=2$ solution are checked in Section 5. Concluding remarks about a possible mechanism for the surface collapse are given in Section 6.

2. MAPPING

We consider an infinite 2D space of points $r \in R^2$ defined by Cartesian coordinates (x, y) . The model interface is localized at $x=0$, along the y axis. The half-space $x < 0$, impenetrable to particles, is assumed to be occupied by an ideal dielectric of dielectric constant $=0$. The electrolyte in the complementary half-space $x > 0$ is modeled by the classical 2D TCP of point particles $\{j\}$ of charge $\{q_j = \pm 1\}$, immersed in a homogeneous

medium of dielectric constant $\epsilon = 1$. Classical equilibrium statistical mechanics is used. In the grand-canonical formalism, the control parameters are the inverse temperature β and the fugacities z_+ and z_- of the positive and negative particles, respectively. For the dielectric wall of interest, only strictly neutral charge configurations survive and, therefore, the thermodynamics depends only on $z = (z_+ z_-)^{1/2}$ as will follow directly from the formalism presented here. Due to the translational invariance in the y direction, the particle densities $n_+(\mathbf{r}) = n_-(\mathbf{r})$ depend only on x . Let us denote their asymptotical $x \rightarrow \infty$ values by $n_+ = n_- = n/2$ where n is the total particle number density.

The interaction energy E of particles $\{q_j, \mathbf{r}_j = (x_j > 0, y_j)\}$ consists of two parts (see, e.g., ref. 19),

$$E = \sum_{i < j} q_i q_j v(|\mathbf{r}_i - \mathbf{r}_j|) + \frac{1}{2} \sum_{i,j} q_i q_j v(|\mathbf{r}_i - \mathbf{r}_j^*|) \quad (1)$$

where $\mathbf{r}^* = (-x, y)$ and $v(r) = -\ln(|r|/r_0)$ is the 2D Coulomb potential (r_0 will be set for simplicity to unity). The first term corresponds to direct particle-particle interactions, while the second one to interactions of particles with the images due to the presence of the dielectric wall. Introducing the microscopic charge + image charge density

$$\tilde{\rho}(\mathbf{r}) = \sum_j q_j [\delta(x - x_j) + \delta(x + x_j)] \delta(y - y_j) \quad (2)$$

the energy (1) can be written as

$$E = \frac{1}{4} \int d^2r \int d^2r' \tilde{\rho}(\mathbf{r}) v(\mathbf{r}, \mathbf{r}') \tilde{\rho}(\mathbf{r}') - \frac{1}{2} N v(0) \quad (3)$$

where the integrations over \mathbf{r} and \mathbf{r}' are taken over the whole 2D space and $-(N/2)v(0)$ is the self-energy.

The grand-canonical partition function is defined by

$$\mathcal{E} = \sum_{N_+=0}^{\infty} \sum_{N_-=0}^{\infty} \frac{z_+^{N_+}}{N_+!} \frac{z_-^{N_-}}{N_-!} \mathcal{Q}(N_+, N_-) \quad (4a)$$

where

$$\mathcal{Q}(N_+, N_-) = \int \prod_{j=1}^N d^2r_j \exp[-\beta E(\{q_j, \mathbf{r}_j\})] \quad (4b)$$

is the configuration integral of N_+ positive and N_- negative charges and $N = N_+ + N_-$. Since, in infinite space, $-\Delta/(2\pi)$ is the inverse operator of $v(r)$, the Boltzmann factor of the interaction energy is expressible as

$$\exp \left[-\frac{\beta}{4} \int d^2r \int d^2r' \tilde{\rho}(r) v(r, r') \tilde{\rho}(r') \right] = \frac{\int \mathcal{D}\phi \exp[\int d^2r (\frac{1}{2} \phi \Delta \phi + i \sqrt{\pi\beta} \phi \tilde{\rho})]}{\int \mathcal{D}\phi \exp(\int d^2r \frac{1}{2} \phi \Delta \phi)} \tag{5}$$

where $\phi(r)$ is a real scalar field and $\int \mathcal{D}\phi$ denotes the functional integration over this field. Inserting $\tilde{\rho}$ from (2), one recognizes in the action of the field theory (5) a nonlocal term $i \sqrt{\pi\beta} \sum_j q_j [\phi(x_j, y_j) + \phi(-x_j, y_j)]$. To make the field theory local, we shall reformulate it as a boundary problem by introducing two new fields⁽²⁰⁾

$$\phi_e(x, y) = \frac{1}{\sqrt{2}} [\phi(x, y) + \phi(-x, y)] \tag{6a}$$

$$\phi_o(x, y) = \frac{1}{\sqrt{2}} [\phi(x, y) - \phi(-x, y)] \tag{6b}$$

defined only in the positive $x \geq 0$ half-space. The even field has a Neumann boundary condition $\partial_x \phi_e|_{x=0} = 0$ and the odd field has a Dirichlet boundary condition $\phi_o|_{x=0} = 0$. Since it holds

$$\int d^2r \frac{1}{2} \phi \Delta \phi = \frac{1}{2} \int_{x>0} d^2r (\phi_e \Delta \phi_e + \phi_o \Delta \phi_o) \tag{7}$$

the odd field, contributing only by its free-field part $\phi_o \Delta \phi_o / 2$, disappears from (5) by the numerator-denominator cancelation. By integration per partes, the term $\phi_e \Delta \phi_e$ can be rewritten as $-(\nabla \phi_e)^2$, with a vanishing contribution from the boundary. The rhs of (5) is thus expressible as

$$\frac{\int \mathcal{D}\phi_e \exp\{\int_{x>0} d^2r [-\frac{1}{2}(\nabla \phi_e)^2 + i \sqrt{2\pi\beta} \sum_j q_j \phi_e(r_j)]\}}{\int \mathcal{D}\phi_e \exp[-\int_{x>0} d^2r \frac{1}{2} (\nabla \phi_e)^2]} \tag{8}$$

After inserting (8) via (5) into (4), one proceeds along the standard line⁽⁴⁾ and finally expresses \mathcal{E} in terms of the 2D Euclidean sine-Gordon theory formulated in the half-space $x > 0$:

$$\mathcal{E} = \frac{\int \mathcal{D}\phi \exp\{\int_{x>0} d^2r [-\frac{1}{2} (\nabla \phi)^2 + 2z \cos(\sqrt{2\pi\beta} \phi)]\}}{\int \mathcal{D}\phi \exp[-\int_{x>0} d^2r \frac{1}{2} (\nabla \phi)^2]} \tag{9}$$

with Neumann condition $\partial_x \phi(x, y)|_{x=0} = 0$ for the field at the boundary. Here, z is the fugacity $(z_+ z_-)^{1/2}$ renormalized by the self-energy term $\exp[\beta v(0)/2]$, and the uniformly shifted ϕ_e is renamed as ϕ ,

$$\phi = \phi_e + \frac{\ln(z_+/z_-)}{2i\sqrt{2\pi\beta}} \quad (10)$$

The dependence of the statistics exclusively on $(z_+ z_-)^{1/2}$ is now evident. The rescaling of the field $\phi \rightarrow \phi/\sqrt{2\pi}$ transforms (9) into the form

$$\Xi(z) = \frac{\int \mathcal{D}\phi \exp[-\mathcal{A}_{sG}(z)]}{\int \mathcal{D}\phi \exp[-\mathcal{A}_{sG}(z=0)]} \quad (11a)$$

with the action

$$\mathcal{A}_{sG}(z) = \int_{x>0} d^2r \left[\frac{1}{4\pi} (\nabla\phi)^2 - 2z \cos(2b\phi) \right] \quad (11b)$$

$$b = \frac{1}{2}\sqrt{\beta} \quad (11c)$$

and boundary condition $\partial_x \phi|_{x=0} = 0$, which is more convenient for our purpose. Hereinafter, the dependence of quantities on the temperature parameter b will be omitted in the notation.

The boundary sine-Gordon theory (11) is a member of integrable sine-Gordon theories defined in the half-space $x > 0$ ⁽⁵⁾:

$$\Xi(z, z_B) = \frac{\int \mathcal{D}\phi \exp[-\mathcal{A}_{sG}(z, z_B)]}{\int \mathcal{D}\phi \exp[-\mathcal{A}_{sG}(z=0, z_B)]} \quad (12a)$$

with the action

$$\mathcal{A}_{sG}(z, z_B) = \int_{x>0} d^2r \left[\frac{1}{4\pi} (\nabla\phi)^2 - 2z \cos(2b\phi) \right] - 2z_B \int_{-\infty}^{\infty} dy \cos(b\phi_B) \quad (12b)$$

Here, $\phi_B(y) = \phi(x=0, y)$ is the boundary field and z_B the boundary fugacity. The underlying sine-Gordon theory (11) with Neumann boundary condition $\partial_x \phi|_{x=0} = 0$ is known to correspond to the “free” case $z_B = 0$ (see, e.g., refs. 5 and 21). The model of the metal-electrolyte boundary studied in ref. 4 corresponds to the limit $z_B \rightarrow \infty$, fixing the value of the boundary field $\phi|_{x=0} = 0$ (Dirichlet boundary conditions for zero potential difference between the metal and the electrolyte).

The grand potential $\Omega = -\beta^{-1} \ln \Xi(z, z_B)$ is the sum of a volume part and a surface part:

$$\Omega = -Vp(z) + S\gamma(z, z_B) \quad (13)$$

where p is the bulk pressure, dependent only on z , and γ the surface tension, dependent on both z and z_B . For a strip $L \times R$, $R \rightarrow \infty$ in the y direction and L large in the x direction, the "specific" Ω/R is given by

$$\lim_{R \rightarrow \infty} \frac{\Omega}{R} = -Lp(z) + \gamma(z, z_B) \quad (14)$$

Thus, with regard to (12) and taking into account the crucial z_B -independence of p , one finds

$$\frac{\partial}{\partial z_B} \beta\gamma(z, z_B) = -2[\langle e^{ib\phi_B} \rangle_{z, z_B} - \langle e^{ib\phi_B} \rangle_{z=0, z_B}] \quad (15)$$

where the obvious symmetry relation

$$\langle e^{ib\phi_B} \rangle_{z, z_B} = \langle e^{-ib\phi_B} \rangle_{z, z_B} \quad (16)$$

implied by the invariance of the action (12b) with respect to the transformation $\phi \rightarrow -\phi$, was assumed. $\langle \cdots \rangle_{z, z_B}$ denotes the averaging with the sine-Gordon action (12b).

3. REFLECTION PROPERTY

The Liouville field theory, formulated in the half-space $x > 0$ with a conformally invariant condition at $x=0$, is defined by the action

$$\mathcal{A}_{Liou}(z, z_B) = \int_{x>0} d^2r \left[\frac{1}{4\pi} (\nabla\phi)^2 + ze^{2b\phi} \right] + z_B \int_{-\infty}^{\infty} dy e^{b\phi_B} \quad (17)$$

and the boundary condition on the field ϕ at infinity, $\phi(x, y) = -Q \ln(x^2) + O(1)$ as $x \rightarrow \infty$. The quantity

$$Q = b + 1/b \quad (18)$$

is called the “background charge”. The two-point function of the exponential of the boundary field behaves like

$$\langle e^{a\phi_B(y)} e^{a\phi_B(y')} \rangle_{Liouville} = \frac{d(a | z, z_B)}{|y - y'|^{2a(Q-a)}} \quad (19)$$

The explicit form of the function d was found in ref. 10

$$d(a|s) = \left[\frac{\pi z \Gamma(b^2) b^{2-2b^2}}{\Gamma(1-b^2)} \right]^{(Q-2a)/2b} \frac{G(Q-2a)}{G(2a-Q)} \times \exp \left\{ - \int_{-\infty}^{\infty} \frac{dt}{t} \left[\frac{\sinh[(Q-2a)t] \cos^2(st/b)}{\sinh(bt) \sinh(b/t)} - \frac{(Q-2a)}{t} \right] \right\} \quad (20a)$$

$$\ln G(x) = \int_0^{\infty} \frac{dt}{t} \left[\frac{e^{-Qt/2} - e^{-xt}}{(1-e^{-bt})(1-e^{-t/b})} + \frac{(Q/2-x)^2}{2} e^{-t} + \frac{(Q/2-x)}{t} \right] \quad (20b)$$

where Γ denotes the Gamma function. The auxiliary variable s depends on z and z_B as follows

$$\cosh^2(\pi s) = \frac{z_B^2}{z} \sin(\pi b^2) \quad (21)$$

It is either real or pure imaginary. Writing

$$s = u + iv \quad u, v \in R \quad (22)$$

one has namely

$$\frac{z_B^2}{z} \sin(\pi b^2) > 1 \quad v=0, u \in (0, \infty) \quad (23a)$$

$$\frac{z_B^2}{z} \sin(\pi b^2) < 1 \quad u=0, v \in (0, 1/2) \quad (23b)$$

The function d clearly fulfils the unitarity relation

$$d(a | s) d(Q-a | s) = 1 \quad (24)$$

It is straightforward to show from (19) that the boundary exponential operators exhibit the following reflection property

$$e^{a\phi_B(y)} = d(a | s) e^{(Q-a)\phi_B(y)} \quad (25)$$

The associated boundary sinh-Gordon model is defined by the action

$$\mathcal{A}_{shG}(z, z_B) = \int_{x > 0} d^2r \left[\frac{1}{4\pi} (\nabla\phi)^2 + 2z \cosh(2b\phi) \right] + 2z_B \int_{-\infty}^{\infty} dy \cosh(b\phi_B) \tag{26}$$

The vacuum expectation value $\langle e^{a\phi_B} \rangle_{shG}$ is conjectured⁽⁸⁻¹⁰⁾ to satisfy a reflection relation similar to (25)

$$\langle e^{a\phi_B} \rangle_{shG} = d(a | s) \langle e^{(Q-a)\phi_B} \rangle_{shG} \tag{27}$$

This relation, together with the obvious symmetry

$$\langle e^{a\phi_B} \rangle_{shG} = \langle e^{-a\phi_B} \rangle_{shG} \tag{28}$$

determines the expectations up to a periodic function; the solution of interest is a ‘‘minimal solution’’ to the functional equations (27) and (28).

The boundary sine-Gordon model with the action (12b) results as an analytical continuation of (26) via the substitutions $b \rightarrow ib, z \rightarrow -z, z_B \rightarrow -z_B$. The final result for $\langle e^{ia\phi_B} \rangle_{sG} \equiv \langle e^{ia\phi_B} \rangle_{z, z_B}$ reads [see eqs. (4.10) and (4.11) of ref. ⁽¹⁰⁾, add a missing factor 1/2 to $\ln g_S(a)$]

$$\langle e^{ia\phi_B} \rangle_{z, z_B} = \left[\frac{\pi z \Gamma(1-b^2)}{\Gamma(b^2)} \right]^{\frac{a^2}{2(1-b^2)}} g_0(a) g_S(a) \tag{29}$$

where

$$\ln g_0(a) = \int_0^\infty \frac{dt}{t} \left\{ \frac{2 \sinh^2(abt) [e^{(1-b^2)t/2} \cosh(t/2) \cosh(b^2t/2) - 1]}{\sinh t \sinh(b^2t) \sinh((1-b^2)t)} - a^2 e^{-t} \right\} \tag{30a}$$

$$\ln g_S(a) = \int_0^\infty \frac{dt}{t} \frac{2 \sinh^2(abt) \sin^2(st)}{\sinh t \sinh(b^2t) \sinh((1-b^2)t)} \tag{30b}$$

where we have taken into account that $s^* = u - iv = \pm s$. This result holds under the conformal normalization of the bulk and boundary fields corresponding to the short distance asymptotics

$$e^{2ia\phi}(\mathbf{r}) e^{-2ia\phi}(\mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|^{4a^2}} \quad \text{as } |\mathbf{r} - \mathbf{r}'| \rightarrow 0 \tag{31a}$$

$$e^{ia\phi_B}(y) e^{-ia\phi_B}(y') = \frac{1}{|y - y'|^{2a^2}} \quad \text{as } |y - y'| \rightarrow 0 \tag{31b}$$

in ref. 2 and 3. This normalization is consistent with a well known leading short-distance behaviour of the positive-negative pair correlation in the Coulomb gas. For the case of interest $a=b$, using the integral representation

$$\ln \Gamma(x) = \int_0^\infty \frac{dt}{t} e^{-t} \left[x - 1 + \frac{e^{-(x-1)t} - 1}{1 - e^{-t}} \right], \quad \text{Re } x > 0 \quad (32)$$

one gets after some algebra

$$g_0(b) = \frac{1}{2\sqrt{\pi}(1-b^2)^2 \Gamma(b^2)} \Gamma\left(\frac{1-2b^2}{2-2b^2}\right) \Gamma\left(\frac{b^2}{2-2b^2}\right) \quad (33a)$$

$$g_s(b) = (1-b^2) \frac{\sinh\left(\frac{\pi s}{1-b^2}\right)}{\sinh(\pi s)} \quad (33b)$$

With the aid of (21), one then finds

$$\begin{aligned} \langle e^{ib\phi_B} \rangle_{z, z_B} &= \frac{1}{4\pi^{3/2}(1-b^2) z_B} \Gamma\left(\frac{1-2b^2}{2-2b^2}\right) \Gamma\left(\frac{b^2}{2-2b^2}\right) \left[\frac{2\pi z_B}{\Gamma(b^2)} \right]^{1/(1-b^2)} \\ &\times \left[\frac{1}{2 \cosh(\pi s)} \right]^{b^2/(1-b^2)} \frac{\sinh\left(\frac{\pi s}{1-b^2}\right)}{\sinh(\pi s)} \end{aligned} \quad (34)$$

According to (21), in the limit $z \rightarrow 0$ the real parameter s diverges and (34) yields

$$\langle e^{ib\phi_B} \rangle_{z=0, z_B} = \frac{1}{4\pi^{3/2}(1-b^2) z_B} \Gamma\left(\frac{1-2b^2}{2-2b^2}\right) \Gamma\left(\frac{b^2}{2-2b^2}\right) \left[\frac{2\pi z_B}{\Gamma(b^2)} \right]^{1/(1-b^2)} \quad (35)$$

in full agreement with formula (24) in ref. 8.

4. SURFACE TENSION

We first summarize the bulk thermodynamics of the 2D Coulomb gas.⁽¹⁾ The pressure is expressible in terms of the soliton mass M as follows

$$\beta p = \frac{M^2}{4} \tan\left(\frac{q\pi}{2}\right) \quad (36)$$

where $q = \beta/(4 - \beta)$. The normalization of the bulk field (31a) fixes the relationship between the fugacity z and M in the form

$$z = \frac{\Gamma(q/(q+1))}{\pi\Gamma(1/(q+1))} \left[M \frac{\sqrt{\pi} \Gamma((q+1)/2)}{2\Gamma(q/2)} \right]^{2/(q+1)} \quad (37)$$

The total particle number density n , generated via

$$n = z \frac{\partial}{\partial z} \beta p \quad (38)$$

is related to M as follows

$$n = \frac{1}{4} M^2 (1+q) \tan\left(\frac{\pi q}{2}\right) \quad (39)$$

Let us denote the surface tensions of the metal-electrolyte and of the dielectric-electrolyte boundaries by

$$\gamma_{met} = \lim_{z_B \rightarrow \infty} \gamma(z, z_B) \quad (40a)$$

$$\gamma_{diel} = \lim_{z_B \rightarrow 0} \gamma(z, z_B) \quad (40b)$$

respectively. In paper 4 [formula (33b) with zero bulk potential $\xi = 0$], we have found

$$\beta\gamma_{met} = -\frac{M}{4 \cos(q\pi/2)} \left[\sin\left(\frac{q\pi}{2}\right) - \cos\left(\frac{q\pi}{2}\right) + 1 \right] \quad (41)$$

With regard to the definitions (40) and eq. (15), it holds

$$\begin{aligned} \beta\gamma_{diel} &= \beta\gamma_{met} - \int_0^\infty dz_B \frac{\partial}{\partial z_B} \beta\gamma(z, z_B) \\ &= \beta\gamma_{met} + 2 \int_0^\infty dz_B [\langle e^{ib\phi_B} \rangle_{z, z_B} - \langle e^{ib\phi_B} \rangle_{z=0, z_B}] \end{aligned} \quad (42)$$

Inserting the previously obtained formulae (34) and (35) into (42) and substituting $b = \sqrt{\beta/2}$ in accordance with (11c), one arrives at

$$\beta\gamma_{diel} = \beta\gamma_{met} + \frac{2}{\pi^{3/2}(4-\beta)} \left[\frac{2\pi}{\Gamma(\beta/4)} \right]^{4/(4-\beta)} \Gamma\left(\frac{2-\beta}{4-\beta}\right) \Gamma\left(\frac{\beta}{8-2\beta}\right) (I_1 + I_2) \quad (43)$$

where

$$I_1 = 2\pi \left[\frac{z}{4 \sin(\pi\beta/4)} \right]^{2/(4-\beta)} \times \int_0^\infty du \left\{ \sinh\left(\frac{4\pi u}{4-\beta}\right) - \sinh(\pi u) [2 \cosh(\pi u)]^{\beta/(4-\beta)} \right\} \quad (44a)$$

$$I_2 = 2\pi \left[\frac{z}{4 \sin(\pi\beta/4)} \right]^{2/(4-\beta)} \times \int_0^{1/2} dv \left\{ \sin\left(\frac{4\pi v}{4-\beta}\right) - \sin(\pi v) [2 \cos(\pi v)]^{\beta/(4-\beta)} \right\} \quad (44b)$$

Here, by using eq. (21) we have transformed the integration over z_B into integrations over the u, v -components of the auxiliary variable s (22); the split of the integral onto the I_1 and I_2 ones is due to the existence of the two regimes (23a) and (23b). Algebra gives

$$I_1 = \frac{1}{2} (4-\beta) \left[\frac{z}{4 \sin(\pi\beta/4)} \right]^{2/(4-\beta)} (2^{\beta/(4-\beta)} - 1) \quad (45a)$$

$$I_2 = \frac{1}{2} (4-\beta) \left[\frac{z}{4 \sin(\pi\beta/4)} \right]^{2/(4-\beta)} \left[1 - 2^{\beta/(4-\beta)} - \cos\left(\frac{2\pi}{4-\beta}\right) \right] \quad (45b)$$

Inserting I_1 and I_2 into (43), then using (37), applying simple operations with trigonometric functions and formula $\Gamma(x)\Gamma(1-x) = \pi/\sin(\pi x)$ and considering (41), one finally gets

$$\beta\gamma_{diel} = \frac{M}{4 \cos(q\pi/2)} \left[\sin\left(\frac{q\pi}{2}\right) + \cos\left(\frac{q\pi}{2}\right) - 1 \right] \quad (46)$$

where $q = \beta/(4-\beta)$ and M is related to the fugacity z by (37).

When M is expressed in terms of the particle density n by using eq. (39), (46) takes the form

$$\beta\gamma_{diel} = \frac{1}{2} \left[\frac{n(4-\beta)}{2 \sin(\pi\beta/(4-\beta))} \right]^{1/2} \left[\sin\left(\frac{\pi\beta}{2(4-\beta)}\right) + \cos\left(\frac{\pi\beta}{2(4-\beta)}\right) - 1 \right] \quad (47)$$

$\beta\gamma_{diel}$ has the small β -expansion

$$\beta\gamma_{diel} = \frac{1}{8} (2\pi\beta n)^{1/2} \left[1 - \frac{\pi}{16} \beta - \frac{\pi}{64} \left(1 - \frac{\pi}{6}\right) \beta^2 + \dots \right] \quad (48)$$

The singular behaviour of n as $\beta \rightarrow 2^-$ (z fixed) can be deduced from formulae (37) and (39):

$$n \sim \frac{4z^2\pi}{2-\beta} \quad (49)$$

On the other hand, the surface tension, expressed in terms of the fugacity z , remains finite at the bulk collapse point $\beta=2$,

$$\gamma_{diel} = \frac{\pi z}{4}, \quad \beta=2 \quad (50)$$

The function $\beta\gamma_{diel}$ increases monotonously up to $\beta=3$ where the surface tension diverges,

$$\gamma_{diel} \sim \frac{\pi}{12} \left[\frac{\Gamma(1/4)}{\Gamma(3/4)} \right]^2 \frac{z^2}{3-\beta}, \quad \beta \rightarrow 3^- \quad (51)$$

The singularity prevents from going beyond this point.

5. ANALYTIC CHECKS

The surface tension γ ($=\gamma_{diel}$) is the boundary part per unit length of the grand potential Ω . The total number of particles is given by $N = N_+ + N_- = -\beta z \partial \Omega / \partial z$. The boundary part of this relation is

$$-\beta z \frac{\partial \gamma}{\partial z} = \int_0^\infty dx [n(x) - n] \quad (52)$$

or, since $z \propto n^{1-\beta/4}$,

$$-\beta n \frac{\partial \gamma}{\partial n} = \left(1 - \frac{\beta}{4}\right) \int_0^\infty dx [n(x) - n] \quad (53)$$

These formulae will be used for computing the surface tension from the density profile.

5.1. High-Temperature Expansion

As a check of the exact expression (47) for the surface tension, its high-temperature expansion in β , equation (48), can be compared to a direct evaluation of the first two terms of this expansion by using a renormalized

Mayer expansion, in close analogy with section 5 of paper 4. Since the derivative of the interaction potential $v(\mathbf{r}, \mathbf{r}') + v(\mathbf{r}^*, \mathbf{r}')$ with respect to x vanishes when point \mathbf{r} is on the interface, the same boundary condition holds for the renormalized bond $K(\mathbf{r}, \mathbf{r}')$,

$$\frac{\partial}{\partial x} K(\mathbf{r}, \mathbf{r}')|_{x=0} = 0 \quad (54)$$

After some algebra, one finds

$$\int_0^\infty dx [n(x) - n] = \frac{(2\pi\beta n)^{1/2}}{16} \left[-1 - \frac{\beta}{4} \left(1 + \frac{\pi}{4} \right) + \frac{\beta\pi}{8} + \dots \right] \quad (55)$$

Consideration of (55) in (53) gives the final result

$$\beta\gamma = \frac{1}{8} (2\pi\beta n)^{1/2} \left[1 - \frac{\pi}{16} \beta + O(\beta^2) \right] \quad (56)$$

in agreement with (48).

5.2. Free Fermion $\beta=2$ Case

Using a Thirring-like representation of the Coulomb gas in presence of a dielectric wall at special inverse temperature $\beta=2$, the exact result for the density profile was obtained in the form⁽¹¹⁾

$$n_\pm(x) - n_\pm = -\frac{m^2}{2\pi} K_0(2mx) \quad (57)$$

where $m=2\pi z$ is the rescaled fugacity. Thus,

$$\int_0^\infty dx [n(x) - n] = -\frac{\pi z}{2} \quad (58)$$

Inserting this integral into equation (52), one immediately arrives at the exact formula (50).

6. CONCLUDING REMARKS

A two-dimensional model for the interface, the two-component plasma bounded by a rectilinear ideal dielectric wall, was considered. The surface tension as a function of fugacity is finite at any inverse temperature $\beta < 3$.

In general, the surface properties are supposed to be governed by the particle-image interaction. A particle at distance x from the dielectric wall interacts with its own image of the same sign through a repulsive potential $-(1/2) \ln(2x)$, and the corresponding Boltzmann factor $(2x)^{\beta/2}$ is always integrable at small x , and gives rise to a vanishing particle density at the interface. In spite of this, our exact solution for the surface tension predicts a surface collapse at $\beta=3$, identified with the divergence of the surface tension with a characteristic type of short-distance collapse singularity, see formula (51). Such a phenomenon might be explained by recalling an observation of Hansen and Viot⁽²²⁾ concerning the short-distance behavior of bulk pair distribution functions for two charges of the same, let us say plus, sign. The expected dependence $g_{++} \sim C_{++} r^\beta$ as $r \rightarrow 0$, where the pre-factor C_{++} is related to a difference of free energies, is changed to $g_{++} \sim \bar{C}_{++} r^{2-\beta}$ at $\beta \geq 1$ as a consequence of the divergence of C_{++} at point $\beta=1$. The weakening of g_{++} at short distance is caused by a pair formation of oppositely charged particles at low temperatures: the neutrality of a pair allows a third particle to approach very close to the pair. For $\beta \geq 2$, the strong clustering of positive-negative particles causes an effective short-distance attraction between particles of the same sign. Based on these plausible arguments it is tempting to conjecture that, at $\beta=3$, the surface tension diverges due to a paradoxical short-distance collapse of a particle with its own image of the same sign.

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