

Surface Tension of a Metal-Electrolyte Boundary: Exactly Solvable Model

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An ideal conductor electrode in contact with a semi-infinite two-dimensional two-component plasma in an external potential is considered. The model is mapped onto an integrable sine-Gordon theory with Dirichlet boundary conditions. The information gained from the mapping provides an explicit form of the surface tension in the plasma-stability regime.

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

1. INTRODUCTION

In a previous paper,⁽¹⁾ hereafter referred to as I, the bulk thermodynamic properties (free energy, specific heat, etc...) of a model, the two-dimensional (2D) two-component plasma (TCP), or Coulomb gas, have been obtained, exactly. In the present paper, a surface property of the same model is considered: the surface tension, at a rectilinear interface between an ideal conductor and the Coulomb gas, is obtained, exactly, as a function of the bulk density, the applied electric potential, and the temperature, in the whole temperature range for which the point-particle model is stable. Like in I, a mapping onto a sine-Gordon field theory, now with a Dirichlet boundary condition, is made, and known results about that field theory are used. The

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resulting surface tension is checked on its high-temperature expansion derived from a renormalized Mayer expansion and on its singular behaviour close to the collapse point.

The model under consideration mimics the interface between an electrolyte (the two-component plasma, made of two species of point-particles, of opposite charges ± 1) and an electrode (the ideal conductor). 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. Instead of z_+ and z_- , it is convenient to use z and φ defined by $z_{\pm} = ze^{\pm\beta\varphi}$. 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 properties depend only⁽²⁾ on the chemical potential combination $\mu = (\mu_+ + \mu_-)/2$, i.e. on z , while $\mu_+ - \mu_-$ (or φ) is relevant only for the surface properties.⁽³⁻⁵⁾ The parameter φ has a physical meaning: it is the electric-potential difference between the bulk and the electrode. Indeed, if the potential of the electrode is taken as the zero and φ is the potential in the bulk, each chemical potential, i.e. the reversible work for adding a positive or negative particle into the bulk, has an electric part φ or $-\varphi$, respectively.

The point-particle model is stable against collapse of positive-negative pairs for $\beta < 2$. This is also the stability range in presence of a rectilinear ideal conductor wall. Indeed, a particle at a distance x from the wall interacts with its own image through a potential $(1/2)\ln(2x)$ and the corresponding Boltzmann factor $(2x)^{-\beta/2}$ is integrable at small x if and only if $\beta < 2$ (at large x , the interaction is screened).

The paper is organized as follows. In Section 2, the model is precisely defined and its mapping onto a sine-Gordon field theory is made. This field theory is described in Section 3. The desired surface tension is derived in Section 4. Its high temperature expansion is checked in Section 5. Its singular behaviour close to the collapse point $\beta=2$ is checked 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 electrode-electrolyte interface is localized along the y axis, namely at $\{r=(0, y)\}$. The half-space $x < 0$ is assumed to be occupied by an ideal conductor of dielectric constant $\epsilon \rightarrow \infty$, impenetrable to particles. 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 $= 1$. The interface is kept at zero potential while one assumes a given potential

φ in the bulk. Equivalently, there is a splitting of the fugacities of the \pm particles:

$$z_+ = z \exp(\beta\varphi), \quad z_- = z \exp(-\beta\varphi) \quad (1)$$

The system is translationally invariant in the y direction, so the position-dependent particle densities $n_{\pm}(\mathbf{r})$ 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. In the case $\varphi = 0$, $n_+(x) = n_-(x)$ everywhere.

In infinite space, the Coulomb potential v at spatial position \mathbf{r} , induced by a unit charge at the origin, is given by the 2D Poisson equation

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

The solution of (2) reads

$$v(\mathbf{r}) = -\ln(|\mathbf{r}|/r_0) \quad (3)$$

where the length constant r_0 , which fixes the zero point of energy, is set for simplicity to unity. Here, the interaction energy E of particles $\{q_j, \mathbf{r}_j = (x_j, y_j)\}$ consists of two parts (see, e.g., ref. 6):

(i) direct particle-particle interactions,

$$\sum_{i < j} q_i q_j v(|\mathbf{r}_i - \mathbf{r}_j|) \quad (4a)$$

(ii) interactions of particles with the images of other particles and with their self-images due to the presence of the conducting wall,

$$-\frac{1}{2} \sum_{i,j} q_i q_j v(|\mathbf{r}_i - \mathbf{r}_j^*|) \quad (4b)$$

where $\mathbf{r}^* = (-x, y)$. Introducing the microscopic charge density $\rho(\mathbf{r}) = \sum_j q_j \delta(\mathbf{r} - \mathbf{r}_j)$, the energy contributions (4a) and (4b) are expressible as follows

$$E = \frac{1}{2} \int d^2r \int d^2r' \rho(\mathbf{r}) [v(\mathbf{r}, \mathbf{r}') - v(\mathbf{r}^*, \mathbf{r}')] \rho(\mathbf{r}') - \frac{1}{2} N v(0) \quad (5)$$

where $v(0)$ is the self-energy. Introducing the microscopic charge + image charge density

$$\bar{\rho}(\mathbf{r}) = \sum_j q_j [\delta(x - x_j) - \delta(x + x_j)] \delta(y - y_j) \quad (6)$$

the energy (5) can be rewritten into a more convenient form

$$E = \frac{1}{4} \int d^2r \int d^2r' \bar{\rho}(r) v(r, r') \bar{\rho}(r') - \frac{1}{2} N v(0) \quad (7)$$

where the integrations over r and r' are now taken over the whole space.

The thermodynamic characteristics of the system are determined by the grand partition function Ξ ,

$$\Xi = \sum_{N_+=0}^{\infty} \sum_{N_-=0}^{\infty} \frac{z_+^{N_+} z_-^{N_-}}{N_+! N_-!} Q(N_+, N_-) \quad (8a)$$

with

$$Q(N_+, N_-) = \int \prod_{j=1}^N d^2r_j \exp[-\beta E(\{q_j, r_j\})] \quad (8b)$$

being the configuration integral of N_+ positive and N_- negative charges and $N = N_+ + N_-$. To express Ξ in terms of a 2D Euclidean sine-Gordon theory, we first recall that $-\Delta/(2\pi)$ is the inverse operator of $v(r)$ [see eq. (2)]. The standard identity then follows

$$\exp \left[-\frac{\beta}{4} \int d^2r \int d^2r' \bar{\rho}(r) v(r, r') \bar{\rho}(r') \right] = \frac{\int \mathcal{D}\phi \exp \left[\int d^2r \left(\frac{1}{2} \phi \Delta \phi + i \sqrt{\pi\beta} \phi \bar{\rho} \right) \right]}{\int \mathcal{D}\phi \exp \left(\int d^2r \frac{1}{2} \phi \Delta \phi \right)} \quad (9)$$

where $\phi(r)$ is a real scalar field and $\int \mathcal{D}\phi$ denotes the functional integration over this field. Inserting $\bar{\rho}$ from (6), the second term in the action of the field theory (9) takes a nonlocal form $i \sqrt{\pi\beta} \sum_j q_j [\phi(x_j, y_j) - \phi(-x_j, y_j)]$. It is therefore convenient to reformulate the field theory (9) as a boundary problem using a procedure proposed in ref. 7. One introduces two new fields

$$\phi_e(x, y) = \frac{1}{\sqrt{2}} [\phi(x, y) + \phi(-x, y)] \quad (10a)$$

$$\phi_o(x, y) = \frac{1}{\sqrt{2}} [\phi(x, y) - \phi(-x, y)] \quad (10b)$$

defined only in the positive $x \geq 0$ half-space. Clearly, the even field has Neumann boundary conditions $\partial\phi_e(x, y)/\partial x|_{x=0} = 0$ and the odd field has Dirichlet boundary conditions $\phi_o(x=0, y) = 0$. It is straightforward to show that

$$\int d^2r \frac{1}{2} \phi \Delta \phi = \frac{1}{2} \int_{x>0} d^2r (\phi_e \Delta \phi_e + \phi_o \Delta \phi_o) \quad (11)$$

The even field contributes to the action only by its free-field part $\phi_e \Delta \phi_e / 2$, which is “cancelled” with its counterpart in the denominator of (9). By integration per partes, the term $\phi_o \Delta \phi_o / 2$ can be rewritten as $-(\nabla \phi_o)^2 / 2$, with a vanishing contribution from the boundary. Thus, when ϕ_o is renamed as ϕ , the rhs of (9) is expressible as a local field theory formulated in the half-space $x > 0$:

$$\frac{\int \mathcal{D}\phi \exp\left\{\int_{x>0} d^2r \left[-\frac{1}{2}(\nabla\phi)^2\right] + i\sqrt{2\pi\beta} \sum_j q_j \phi(r_j)\right\}}{\int \mathcal{D}\phi \exp\left[-\int_{x>0} d^2r \frac{1}{2}(\nabla\phi)^2\right]} \tag{12}$$

with Dirichlet boundary conditions $\phi(x=0, y)=0$. Now, defining by $\langle \dots \rangle$ the average over the field theory (12), one proceeds along the standard lines, i.e., express \mathcal{E} as follows

$$\begin{aligned} \mathcal{E} = & \sum_{N_+=0}^{\infty} \sum_{N_-=0}^{\infty} \frac{\bar{z}^{N_++N_-} e^{\beta\phi(N_+-N_-)}}{N_+! N_-!} \\ & \times \left\langle \left(\int_{x>0} d^2r e^{i\sqrt{2\pi\beta} \phi(r)} \right)^{N_+} \left(\int_{x>0} d^2r e^{-i\sqrt{2\pi\beta} \phi(r)} \right)^{N_-} \right\rangle \end{aligned} \tag{13}$$

where $\bar{z} = z \exp[\beta v(0)/2]$ is the fugacity renormalized by the self-energy term, and afterwards sum over N_+ and N_- . The final result reads

$$\mathcal{E} = \frac{\int \mathcal{D}\phi \exp\left\{\int_{x>0} d^2r \left[-\frac{1}{2}(\nabla\phi)^2 + 2\bar{z} \cos(\sqrt{2\pi\beta} \phi - i\beta\phi)\right]\right\}}{\int \mathcal{D}\phi \exp\left[-\int_{x>0} d^2r \frac{1}{2}(\nabla\phi)^2\right]} \tag{14}$$

with the fixed value of the field at the boundary, $\phi(x=0, y)=0$.

The field theory in (14) can be viewed as the ordinary 2D Euclidean sine-Gordon model in the half-space, defined by the action

$$\mathcal{A}_{sG} = \int_{x>0} d^2r \left[\frac{1}{2}(\nabla\phi)^2 - 2\bar{z} \cos(\beta_{sG} \phi) \right] \tag{15a}$$

with

$$\beta_{sG} = \sqrt{2\pi\beta} \tag{15b}$$

and Dirichlet boundary conditions $\phi(x=0, y)=\phi_0$,

$$\phi_0 = -i \sqrt{\frac{\beta}{2\pi}} \varphi \tag{15c}$$

The boundary value ϕ_0 usually enters into the formalism in the combination

$$\xi = \frac{4\pi}{\beta_{sG}} \phi_0 = -2i\varphi \quad (16)$$

which will also be used in what follows. For φ real (which is the case of interest), we assume that the solution of the present theory corresponds to an analytical continuation of the results of the theory with real Dirichlet boundary conditions.

Without going into details we mention that one can proceed as above also in the case of the 2D TCP in contact with a dielectric of dielectric constant $\epsilon = 0$. In that case, the images have the same charges as the source particles, the even field (10a) becomes the relevant one, and that gives a mapping onto an equivalent boundary sine-Gordon model with Neumann boundary conditions.

3. BOUNDARY SINE-GORDON MODEL

The integrability property of the bulk (infinite in both x, y -directions) sine-Gordon model along the standard lines of the Bethe ansatz technique is well known from the seventies.⁽⁸⁾ The discrete symmetry of the theory $\phi \rightarrow \phi + 2\pi n/\beta_{sG}$ (n integer) is spontaneously broken in the domain $0 < \beta_{sG}^2 < 8\pi$; one has to consider one of infinitely many ground states $\{|0_n\rangle\}$ characterized by $\langle \phi \rangle_n = 2\pi n/\beta_{sG}$, say the one with $n=0$. The spectrum of particles involves soliton S , antisoliton \bar{S} and soliton-antisoliton bound states (breathers) $\{B_j, j=1, 2, \dots < 1/q\}$ with masses

$$m_j = 2M \sin\left(\frac{jq\pi}{2}\right) \quad (17)$$

where M is the soliton mass. The parameter q , defined by

$$q = \frac{\beta_{sG}^2}{8\pi - \beta_{sG}^2} \quad (18)$$

ranges from 0 to ∞ : the breathers exist for $q \in (0, 1)$ (or in the plasma stability range $0 < \beta < 2$) and there are no breathers for q larger than 1 ($2 < \beta < 4$).

In the seminal work⁽⁹⁾ it was argued that the restriction of the sine-Gordon model to the half space ($x > 0, y$) does not break its integrability if one adds a boundary action term

$$(\mathcal{A}_{sG})_B = - \int_{-\infty}^{\infty} dy \, 2m \cos\left[\frac{\beta_{sG}}{2}(\phi_B - \phi_0)\right] \quad (19)$$

where m and ϕ_0 are free parameters, and $\phi_B(y) = \phi(x, y)|_{x=0}$. The underlying sine-Gordon theory (15) corresponds to the $m \rightarrow \infty$ limit of (19) which sets ϕ_B to ϕ_0 .

The free energy of the theory (15) is related to the ground state energy of the boundary quantum (1+1)-dimensional sine-Gordon model, defined by Lagrangian

$$\mathcal{L}_{sG} = \int_0^L dx \left[\frac{1}{2} (\partial\phi)^2 + 2\bar{z} \cos(\beta_{sG}\phi) \right] \quad (20)$$

$L \rightarrow \infty$, with boundary conditions $\phi(0) = \phi_0$ and $\phi(L) = \phi'_0$ considered in terms of ξ and ξ' , respectively [see eq. (16)]. There exists a lattice regularization of the theory (20), namely the XXZ model in boundary magnetic fields,⁽¹⁰⁾ defined by Hamiltonian

$$\mathcal{H}_{XXZ} = \epsilon \frac{\tau}{2\pi \sin \tau} \left\{ \sum_{j=1}^{N-1} [\sigma_j^x \sigma_{j+1}^x + \sigma_j^y \sigma_{j+1}^y - (\cos \tau) \sigma_j^z \sigma_{j+1}^z] + h\sigma_1^z + h'\sigma_N^z \right\} \quad (21)$$

with $\tau \in (0, \pi/2)$. Here, $\epsilon = 1$ and $\epsilon = -1$ correspond to the ferromagnetic and antiferromagnetic cases of the XXZ-chain, respectively. This model results as the hamiltonian limit of the inhomogeneous 6-vertex model on an open strip⁽¹¹⁾, with an alternating imaginary part $\pm iA$ added to the spectral parameter on alternating vertices. The continuum scaling limit is given by taking $A \rightarrow \infty$, $N \rightarrow \infty$, and the lattice spacing $a \rightarrow 0$, such that $L \equiv Na$ remains finite. In the bulk, the regularization fixes $\sqrt{\bar{z}} \propto (1/a) \times \exp(-\text{const} \times A)$ and

$$\beta_{sG}^2 = 8\tau \quad (\epsilon = 1) \quad (22a)$$

$$\beta_{sG}^2 = 8(\pi - \tau) \quad (\epsilon = -1) \quad (22b)$$

As $\tau \in (0, \pi/2)$, the ferromagnetic regime corresponds to $q \in (0, 1)$ and the antiferromagnetic regime to $q \in (1, \infty)$. As concerns the interrelation between the ‘‘surface’’ quantities,⁽¹²⁾ one defines the function

$$f(a, b) = -i \ln \left(\frac{\sinh((ib - a)/2)}{\sinh((ib + a)/2)} \right) \quad (23a)$$

and

$$H \equiv \frac{1}{\tau} f(i\tau, -i \ln(h + \cos \tau)) \quad (23b)$$

Then, introducing an auxiliary variable

$$t = \frac{\pi}{\tau} \quad t \geq 2 \quad (24)$$

one has

$$\xi = \frac{\pi}{2} (t - 1 - H) \quad (\epsilon = 1) \quad (25a)$$

$$\xi = \frac{\pi}{2} \left(1 - \frac{H}{t-1} \right) \quad (\epsilon = -1) \quad (25b)$$

The same formula hold for ξ' in terms of H' , resp. h' .

To study boundary effects in the XXZ model (21), one looks for the solutions of the Bethe equations which correspond to a wave-function localized at $j=0$ or $j=N$ and exponentially decreasing away from the boundary. These boundary bound states were identified with new boundary strings in the Bethe ansatz^(13, 14) (for a review see ref. 15). In the thermodynamic limit $N \rightarrow \infty$, when the left and the right boundaries can be treated independently and the overlap of the corresponding wave-functions is negligibly small, the lattice ground state energy was found as a function of the parameter A of the related 6-vertex model. In the continuum limit $A \rightarrow \infty$ corresponding to the (1+1)-dimensional sine-Gordon model (20), the ground state energy of the last (minus the ground state energy of the free-field model with the same boundary condition) was obtained in the form

$$E_{ground} = E_{bulk} + E_{bdries} + O(1/L) \quad (26)$$

where

$$E_{bulk} = -L \frac{M^2}{4} \tan \left(\frac{\pi}{2(t-1)} \right) \quad (27a)$$

$$E_{bdries} = -\frac{M}{2} \left[\frac{\sin(H\pi/[2(t-1)])}{\sin(t\pi/[2(t-1)])} + \frac{\sin(H'\pi/[2(t-1)])}{\sin(t\pi/[2(t-1)])} \right. \\ \left. - \cot \left(\frac{t\pi}{4(t-1)} \right) - 1 \right] \quad (27b)$$

for the ferromagnetic case $\epsilon = 1$ ⁽¹³⁾ (note a different notation in this reference) and

$$E_{bulk} = L \frac{M^2}{4} \cot\left(\frac{t\pi}{2}\right) \tag{28a}$$

$$E_{bdries} = -\frac{M}{2} \left[\frac{\sin((t-H)\pi/2)}{\sin(t\pi/2)} + \frac{\sin((t-H')\pi/2)}{\sin(t\pi/2)} - \cot\left(\frac{t\pi}{4}\right) - 1 \right] \tag{28b}$$

for the antiferromagnetic case $\epsilon = -1$.⁽¹⁴⁾ In terms of the sine-Gordon parameters, “bulk” q (18) and “boundary” ξ, ξ' (25), both Eqs. (27) and Eqs. (28) take the same form

$$E_{bulk} = -L \frac{M^2}{4} \tan\left(\frac{q\pi}{2}\right) \tag{29a}$$

$$E_{bdries} = -\frac{M}{2} \left\{ \frac{1}{\cos(q\pi/2)} [\cos(q\xi) + \cos(q\xi') - 1] + \tan\left(\frac{q\pi}{2}\right) - 1 \right\} \tag{29b}$$

4. SURFACE TENSION OF THE PLASMA

For a Coulomb gas of volume V bounded by a surface of area S , the grand potential $\Omega = -\beta^{-1} \ln \Xi$ is the sum of a volume part and a surface part:

$$\Omega = -Vp(z, \beta) + S\gamma(z, \beta) \tag{30}$$

where p is the pressure and γ the surface tension. For a strip $L \times R$, $R \rightarrow \infty$ and L large, the “specific” Ω/R is given by

$$\lim_{R \rightarrow \infty} \frac{\Omega}{R} = -Lp(z, \beta) + \gamma(z, \beta)|_{x=0} + \gamma(z, \beta)|_{x=L} + O(1/L) \tag{31}$$

The thermodynamics of (14) is mapped onto the ground state of (20) according to

$$\beta\Omega = RE_{ground} \tag{32}$$

In the considered $L \rightarrow \infty$ limit, the boundary energy (29b) is the sum of two clearly separated contributions coming from the boundaries at $x=0$ and

$x=L$. To calculate the surface tension, one keeps only the contribution at $x=0$, and identifies ξ with the bulk potential φ via eq. (16). Thus, one gets

$$\beta p = \frac{M^2}{4} \tan\left(\frac{q\pi}{2}\right) \quad (33a)$$

$$\beta\gamma = -\frac{M}{4} \left\{ \frac{1}{\cos(q\pi/2)} [2 \cos(q\xi) - 1] + \tan\left(\frac{q\pi}{2}\right) - 1 \right\} \quad (33b)$$

Inserting (15b) into (18) and considering (16), the sine-Gordon parameters are expressible in terms of the Coulomb ones as follows

$$q = \frac{\beta}{4 - \beta}, \quad \xi = -2i\varphi \quad (34)$$

As concerns the link between the soliton mass M and the fugacity z , the formalism of section 2 showed us that z renormalizes multiplicatively. To give z a precise meaning, one has to fix the normalization of the field $\cos(\beta_{sG}\phi)$. The conformal normalization proposed in refs. 16 and 17 corresponds to the short-distance limit of the two-point correlation function

$$\langle \cos(\beta_{sG}\phi)(x) \cos(\beta_{sG}\phi)(y) \rangle \rightarrow \frac{1}{2} |x-y|^{-\beta_{sG}^2/(2\pi)} \quad (35)$$

This normalization, equivalent to a well known leading short-distance behaviour of the positive-negative pair correlation in the Coulomb gas, fixes the z - M relationship as follows

$$z = \frac{\Gamma(q/(q+1))}{\pi\Gamma(1/(q+1))} \left[M \frac{\sqrt{\pi} \Gamma((q+1)/2)}{2\Gamma(q/2)} \right]^{2/(q+1)} \quad (36)$$

The total particle number density, generated via

$$n = z \frac{\partial(\beta p)}{\partial z} \quad (37)$$

is related to M as follows

$$n = \frac{1}{4} M^2 (1+q) \tan\left(\frac{\pi q}{2}\right) \quad (38)$$

The n - z relationship is given in paper I, Eqs. (49), (50). The singular behaviour of n as $\beta \rightarrow 2$ (z fixed) can be deduced from these formulae:

$$n \sim \frac{4z^2\pi}{2-\beta} \quad (39)$$

Finally, we have

$$\beta p = n \left(1 - \frac{\beta}{4} \right) \quad (40)$$

and

$$\begin{aligned} \beta \gamma = & -\frac{1}{2} \left[\frac{n(4-\beta)}{2 \sin(\pi\beta/(4-\beta))} \right]^{1/2} \left\{ 2 \cosh \left(\frac{2\beta\varphi}{4-\beta} \right) - 1 \right. \\ & \left. + \sin \left(\frac{\pi\beta}{2(4-\beta)} \right) - \cos \left(\frac{\pi\beta}{2(4-\beta)} \right) \right\} \end{aligned} \quad (41)$$

$\beta\gamma$ has the small β -expansion

$$\beta\gamma = -\frac{1}{8} (2\pi\beta n)^{1/2} \left\{ 1 + \left[\frac{\pi}{16} + \frac{2\varphi^2}{\pi} \right] \beta + \left[\frac{\pi}{64} \left(1 + \frac{\pi}{6} \right) + \frac{\varphi^2}{2\pi} \right] \beta^2 + \dots \right\} \quad (42)$$

With regard to (39), for z fixed, p and γ exhibit the same type of collapse singularities as $\beta \rightarrow 2^-$:

$$p \sim \frac{z^2\pi}{2-\beta} \quad (43)$$

and

$$\gamma \sim -\frac{z \cosh(2\varphi)}{2-\beta} \quad (44)$$

5. HIGH-TEMPERATURE EXPANSION

As a check of the exact expression (41) of the surface tension, the beginning of its high-temperature expansion [expansion in powers of β , eq. (42)] will now be compared to a direct evaluation of the two first terms of this expansion derived from the renormalized Mayer expansion of the free energy of the Coulomb system. In the following, all functions and integrals are defined in the half-space $x \geq 0$.

The surface tension γ can be defined as the boundary part per unit length of the grand potential Ω . The total numbers of positive and negative particles, respectively, are $N_+ = -\beta z_+ \partial\Omega/\partial z_+$ and $N_- = -\beta z_- \partial\Omega/\partial z_-$. Going to the variables z and φ defined by $z_{\pm} = ze^{\pm\beta\varphi}$ gives for the total

number of particles $N = N_+ + N_- = -\beta z \partial \Omega / \partial z$. The boundary part of this relation is

$$-\beta z \frac{\partial \gamma}{\partial z} = \int_0^\infty dx [n(x) - n] \quad (45)$$

Since, as recalled in I, z is proportional to $n^{1-\beta/4}$, (45) can be rewritten as

$$-\beta n \frac{\partial \gamma}{\partial n} = \left(1 - \frac{\beta}{4}\right) \int_0^\infty dx [n(x) - n] \quad (46)$$

This relation (46) will be used for computing the surface tension γ from the density profile $n(x)$ which will be determined as a function of the bulk density n , the electric potential φ in the bulk, and the inverse temperature β .

Our starting point is the relation obeyed by the density profiles:

$$\ln \left[\frac{n_\pm(1)}{z_\pm(1)} \right] = \frac{\delta \Delta[n]}{\delta n_\pm(1)} \quad (47)$$

where $\Delta[n]$ is the negative of the excess free energy times β , considered as a functional of the position-dependent densities, and $z_\pm(1)$ is the position-dependent fugacity at point 1. Since a particle at a distance x from the boundary has an interaction $(1/2) \ln(2x)$ with its own image,

$$z_\pm(x) = z \exp[\pm \beta \varphi - (\beta/2) \ln(2x)] \quad (48)$$

The relation (47) is exact. Here, the renormalized Mayer expansion, described in I, is used for expanding $\Delta[n]$ up to order β^2 , i.e., we keep only the contributions \bar{D}_0 (two field circles connected by a simple $-\beta v$ bond plus the sum of ring diagrams) and the graph D_1 . However the latter one will be shown to give no contribution to the density profiles at the desired order, and we shall be left with only \bar{D}_0 , which constitutes an approximation of the Debye-Hückel type. However, here, the interaction $v(1, 2)$ between particles 1 and 2 includes the contributions from the images, i.e., $v(1, 2) = -\ln r_{12} + \ln r_{12}^*$ where r_{12} is the distance between points 1 and 2, r_{12}^* is the distance between point 1 and the image of point 2. The contribution of \bar{D}_0 to the functional derivative in (47) is

$$\frac{\delta \bar{D}_0[n]}{\delta n_\pm(1)} = \mp \beta \int d2 v(1, 2) [n_+(2) - n_-(2)] + \frac{1}{2} [K(1, 1) + \beta v(1, 1)] \quad (49)$$

where $K(1, 2)$ is the renormalized bond defined by the integral equation

$$K(1, 2) = -\beta v(1, 2) + \int d3 [-\beta v(1, 3)] n(3) K(3, 2) \quad (50)$$

This integral equation (50) can be transformed into a partial differential equation by taking the Laplacian with respect to 1, Δ_1 , of both sides of (50), and using $\Delta_1 v(1, 2) = -2\pi\delta(1, 2)$, which gives

$$\Delta_1 K(1, 2) = 2\pi\beta\delta(1, 2) + 2\pi\beta n(1) K(1, 2) \quad (51)$$

Since $v(1, 2)$, the Coulomb interaction in presence of a conducting wall, vanishes when 1 is on the wall, the same boundary condition holds for $K(1, 2)$.

The above equations can be solved for the density profile $n(x)$ by iterations, starting with the lowest-order approximation of a constant $n(x) = n$ in (51). Then, the solution of (51), with its boundary condition, is

$$K^{(0)}(1, 2) = -\beta K_0(\kappa r_{12}) + \beta K_0(\kappa r_{12}^*) \quad (52)$$

where $\kappa^2 = 2\pi\beta n$ (κ is the inverse Debye length), and K_0 is the modified Bessel function of second kind. Using this lowest-order $K^{(0)}$ in (49), approximating $\Delta[n]$ by $\bar{D}_0[n]$ and using (48) in (47), gives

$$n_{\pm}(x) = z \exp\left\{ \pm \beta[\varphi - \varphi(x)] + \frac{1}{2} \lim_{r_{12} \rightarrow 0} [-\beta K_0(\kappa r_{12}) - \beta \ln r_{12}] + \frac{1}{2} \beta K_0(2\kappa x) \right\} \quad (53)$$

where, with point 1 at a distance x from the boundary,

$$\varphi(x) = \int d^2 v(1, 2) [n_+(2) - n_-(2)] \quad (54)$$

$\varphi(x)$ is the electric potential created at point 1 by the charge distribution (localized near the boundary) $n_+(2) - n_-(2)$. $\varphi - \varphi(x)$ is a finite quantity which goes to zero as $x \rightarrow \infty$. Since, at the Debye-Hückel order of approximation, the bulk fugacity and density are related by

$$n = 2z \exp\left\{ (1/2) \lim_{r_{12} \rightarrow 0} [-\beta K_0(\kappa r_{12}) - \beta \ln r_{12}] \right\} \quad (55)$$

(53) can be rewritten as

$$n_{\pm}(x) = \frac{n}{2} \exp\left\{ \pm \beta[\varphi - \varphi(x)] + (\beta/2) K_0(2\kappa x) \right\} \quad (56)$$

(56) has a simple physical interpretation: each particle feels a mean one-body potential made of two parts: $\varphi(x)$ is the electric potential created by the surface charge density in the plasma, $-(1/2) K_0(2\kappa x)$ is the screened

interaction of the particle with its image. The linearized form of (56) gives for the density profile

$$n(x) = n_+(x) + n_-(x) = n[1 + \frac{1}{2} \beta K_0(2\kappa x)] \quad (57)$$

In the following, the integrals

$$\int_0^\infty K_0(x) dx = \frac{\pi}{2} \quad (58a)$$

and

$$\int_0^\infty K_0^2(x) dx = \frac{\pi^2}{4} \quad (58b)$$

will be needed. Using (57) and (58a) in (46) gives the surface tension γ at lowest order in β :

$$\beta\gamma = -\frac{1}{8} (2\pi\beta n)^{1/2} \quad (59)$$

At this order in β , an explicit form of $\varphi(x)$ was not needed for computing the surface tension, neither does that surface tension depend on the parameter φ . However, $\varphi(x)$ will be needed in the following. It can be easily obtained by writing, from the linearized form of (56), $n_+(x) - n_-(x) = \beta n[\varphi - \varphi(x)]$ and using the Poisson equation $d^2[\varphi - \varphi(x)]/dx^2 = 2\pi[n_+(x) - n_-(x)]$ with the boundary condition $\varphi(0) = 0$. One obtains

$$\varphi - \varphi(x) = \varphi \exp(-\kappa x) \quad (60)$$

The next iteration for $n(x)$ is obtained by using the density (56) in the equation (51) for K and treating $n(x) - n = (1/2) n\beta K_0(2\kappa x)$ as a perturbation. Now $K = K^{(0)} + K^{(1)}$, where $K^{(0)}$ is defined by (52). To first order in the density perturbation, (51) and (52) give

$$(\Delta_1 - \kappa^2) K^{(1)}(1, 2) = 2\pi\beta\delta n(1) K^{(0)}(1, 2) \quad (61)$$

where $\delta n(1) = (1/2) n\beta K_0(2\kappa x)$ with x the distance of point 1 to the boundary. The solution of (61), with the boundary condition that $K^{(1)}(1, 2)$ vanishes when 1 is on the wall, is studied, by the method of Green functions, in the Appendix, where it is shown that $K^{(1)}(1, 1)$ is a function of the coordinate x_1 of 1 such that

$$\int_0^\infty dx_1 K^{(1)}(1, 1) = \frac{\beta^2}{16\kappa} \left(\pi - \frac{\pi^2}{4} \right) \quad (62)$$

It is a priori necessary to keep also the contribution from the graph D_1 to $\Delta[n]$. However, at the present order in β , $\delta D_1[n]/\delta n_{\pm}(1)$ can be evaluated for constant densities and then it vanishes. Taking also $K^{(1)}$ into account, we now have, instead of (56),

$$n_{\pm}(x) = \frac{n}{2} \exp\left\{ \pm \beta[\varphi - \varphi(x)] + \frac{1}{2} [\beta K_0(2\kappa x) + K^{(1)}(x)] \right\} \quad (63)$$

where $K^{(1)}(1, 1)$, when 1 has the coordinate x , is renamed $K^{(1)}(x)$. Expanding the exponential in (63) to order β^2 gives for the total density $n_+ + n_-$

$$n(x) - n = \frac{n\beta}{2} K_0(2\kappa x) + \frac{n}{2} K^{(1)}(x) + \frac{n\beta^2}{8} K_0^2(2\kappa x) + \frac{n\beta^2}{2} [\varphi - \varphi(x)]^2 \quad (64)$$

where it is sufficient to use for $\varphi - \varphi(x)$ the lower-order expression (60). Thus, using (58) and (62), one finds

$$\int_0^{\infty} dx [n(x) - n] = \frac{\kappa}{16} \left[1 + \frac{\beta}{4} \left(1 - \frac{\pi}{4} \right) + \frac{\beta\pi}{8} + \frac{2\beta}{\pi} \varphi^2 \right] \quad (65)$$

Using (65) in (46) gives the final result

$$\beta\gamma = -\frac{1}{8} (2\pi\beta n)^{1/2} \left[1 + \left(\frac{\pi}{16} + \frac{2\varphi^2}{\pi} \right) \beta + O(\beta^2) \right] \quad (66)$$

in agreement with (42).

6. COLLAPSE SINGULARITY

To check the singular behaviour of the surface tension γ near the collapse point $\beta = 2$, eq. (44), one starts with the exact $x \rightarrow 0$ limits

$$n_+(x) - n_+ \sim \frac{z_+}{(2x)^{\beta/2}}, \quad n_-(x) - n_- \sim \frac{z_-}{(2x)^{\beta/2}} \quad (67)$$

which can be derived directly by using the grand canonical or canonical formalisms, in analogy with the short-distance expansion of the positive-negative pair correlation in the bulk. At $\beta = 2$, the exact result for the density profile reads⁽⁴⁾

$$n_{\pm}(x) - n_{\pm} = \frac{m}{2\pi} \int_0^{\infty} dl \left[-\frac{m}{\kappa_l} + \frac{\kappa_l \exp(\pm \beta\varphi) + m}{m \cosh(\beta\varphi) + \kappa_l} \right] \exp(-2\kappa_l x) \quad (68)$$

where $m = 2\pi z$ and $\kappa_l = (m^2 + l^2)^{1/2}$ (note that in the original work⁽⁴⁾ there are some mistakes in the equation (3.25)). The $x \rightarrow 0$ limit of eq. (68)

$$n_{\pm}(x) - n_{\pm} \sim \frac{z_{\pm}}{2x} \quad (69)$$

still is of the form (67), even when the n_{\pm} densities diverge. Consequently, one can put

$$n(x) - n = \frac{2z \cosh(\beta\varphi)}{(2x)^{\beta/2}} f(2x) \quad (70)$$

where f is a function regular in β around $\beta = 2$, with

$$f(0) = 1 \quad (71a)$$

The density $n(x)$ is supposed to tend to its asymptotical $x \rightarrow \infty$ value n faster than any inverse power of x , so that

$$\lim_{x \rightarrow \infty} f(2x) \rightarrow 0 \quad \text{faster than any inverse power of } x \quad (71b)$$

According to (45), it holds

$$-\beta z \frac{\partial \gamma}{\partial z} = z \cosh(\beta\varphi) \int_0^{\infty} dt t^{-\beta/2} f(t) \quad (72)$$

An integration per partes gives

$$\int_0^{\infty} dt t^{-\beta/2} f(t) = \frac{1}{1-\beta/2} \left[t^{1-\beta/2} f(t) \Big|_{t=0}^{\infty} - \int_0^{\infty} dt t^{1-\beta/2} \frac{\partial f(t)}{\partial t} \right] \quad (73)$$

For $\beta < 2$, $t^{1-\beta/2} f(t)$ vanishes at $t=0$ as well as in the limit $t \rightarrow \infty$ due to the fast decay of $f(t)$. Then,

$$\beta \frac{\partial \gamma}{\partial z} = \frac{\cosh(\beta\varphi)}{1-\beta/2} \int_0^{\infty} dt t^{1-\beta/2} \frac{\partial f(t)}{\partial t} \quad (74)$$

When $\beta \rightarrow 2^-$, one can perform a $(2-\beta)$ expansion of the integral in (74),

$$\int_0^{\infty} dt t^{1-\beta/2} \frac{\partial f(t)}{\partial t} = f(\infty) - f(0) + O(2-\beta) \quad (75)$$

With regard to (71a) and (71b), one arrives at the desired formula (44).

7. CONCLUSION

A two-dimensional model for the interface between an electrolyte and an electrode has been considered: the 2D TCP bounded by a rectilinear ideal conductor wall. Previously, the surface tension γ in this model was known⁽⁵⁾ only at the special inverse temperature $\beta=2$ (in which case, for obtaining a finite result, a hard core repulsion between the particles and the wall had to be assumed). Now, the main result of the present paper, eq. (41), provides the surface tension for point particles at any temperature, in the stability range of the model $\beta < 2$.

The surface tension depends on the bulk density n as $n^{1/2}$, as a priori expected for dimensional reasons. Its temperature dependence is more complicated than the one of the bulk pressure but simpler than the temperature dependence of some bulk thermodynamic quantities derived in I.

As in the bulk case, the computation of particle distributions requires a new progress in the corresponding integrable sine-Gordon theory. As concerns a wall of general dielectric constant, we also succeeded in finding the temperature dependence of the surface tension for the particular case of an ideal dielectric (dielectric constant = 0). This result will be reported in a forthcoming publication. A generalization of the considered rectilinear conductor to other geometries would be nontrivial.

APPENDIX

In this Appendix, the correction $K^{(1)}$ to the renormalized bond is studied. In terms of the Green function $K^{(0)}$ which obeys

$$(\Delta_1 - \kappa^2) K^{(0)}(1, 2) = 2\pi\beta\delta(1, 2) \quad (\text{A1})$$

with the boundary condition $K^{(0)}(1, 2) = 0$ when point 1 is at $x=0$, the solution of (61) with the same boundary condition is

$$K^{(1)}(1, 2) = \int d^3 K^{(0)}(1, 3) K^{(0)}(3, 2) \delta n(3) \quad (\text{A2})$$

where $K^{(0)}$ is given by (52) and $\delta n(3) = (1/2) n\beta K_0(2\kappa x_3)$. Thus, the desired integral (62) is

$$\begin{aligned} \int_0^\infty dx_1 K^{(1)}(1, 1) &= \int_0^\infty dx_1 \int_{-\infty}^\infty dy_3 \int_0^\infty dx_3 [-\beta K_0(\kappa r_{13}) + \beta K_0(\kappa r_{13}^*)]^2 \\ &\quad \times \frac{\beta n}{2} K_0(2\kappa x_3) \end{aligned} \quad (\text{A3})$$

The integrals on x_1 and y_3 will be performed first. Since the integrand is an even function of x_1 , the integral on x_1 and y_3 is half that integral performed on the whole plane. Furthermore, y_3 can be shifted into y_1 . Therefore,

$$\begin{aligned} I(x_3) &= \int_0^\infty dx_1 \int_{-\infty}^\infty dy_3 [-K_0(\kappa r_{13}) + K_0(\kappa r_{13}^*)]^2 \\ &= \int d^2 r_1 [K_0^2(\kappa r_{13}) - K_0(\kappa r_{13}) K_0(\kappa r_{13}^*)] \end{aligned} \quad (\text{A4})$$

One now has a convolution integral which can be performed by going to Fourier space:

$$\begin{aligned} I(x_3) &= \int d^2 k \frac{1 - J_0(2\kappa x_3)}{(\kappa^2 + k^2)^2} = \frac{\pi}{\kappa^2} \left[1 + \kappa \frac{d}{d\kappa} \int_0^\infty \frac{dk k J_0(2\kappa x_3)}{\kappa^2 + k^2} \right] \\ &= \frac{\pi}{\kappa^2} \left[1 + \kappa \frac{dK_0(2\kappa x_3)}{d\kappa} \right] = \frac{\pi}{\kappa^2} [1 - 2\kappa x_3 K_1(2\kappa x_3)] \end{aligned} \quad (\text{A5})$$

Using (A5) in (A3) gives, using as a rescaled integration variable $x = 2\kappa x_3$,

$$\int_0^\infty dx_1 K^{(1)}(1, 1) = \frac{\beta^2}{8\kappa} \int_0^\infty dx [1 - x K_1(x)] K_0(x) \quad (\text{A6})$$

After an integration by parts using $K_1(x) = -dK_0(x)/dx$, and taking into account (58b), one finds (62).

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