The electrical double layer: A solvable model

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In classical equilibrium statistical mechanics, the two-dimensional two-component Coulomb gas is exactly solvable at the special value of the reduced inverse temperature $\Gamma = 2$. This is used for building an exactly solvable model of the electrical double layer. A charged hard wall (primitive electrode), a polarizable interface, an ideal conductor electrode, a semipermeable membrane are studied: the density profiles and correlation functions are computed. The differential capacity and the surface tension are also obtained.

I. INTRODUCTION

The electrical double layer is that arrangement of charges which forms at the interface between two conducting media[1] (for instance, at an electrode–electrolyte interface). Given some microscopic model (more and more sophisticated ones are being introduced), it can be studied by statistical mechanics, either by numerical simulation, or analytically; in the latter case, it is usually necessary to resort to some approximation method.

In recent years, a very simplified class of (two-dimensional) models has been considered, with the special feature of being exactly, analytically solvable. In these models, a conducting medium is represented by a two-dimensional classical one-component plasma, i.e., a system of point charges of one sign embedded in a continuous background of the opposite sign. At the special value of the coupling parameter (or reduced inverse temperature) $\Gamma = 2$, the particle density and all the correlation functions can be obtained exactly.[2-8] Models of the electrical double layer, based on the one-component plasma, have been studied.

It has now been found that the two-dimensional classical *two-component* plasma (the standard Coulomb gas), i.e., a system of positive and negative particles of opposite charges, is also a solvable model[9-11] at $\Gamma = 2$. In the present paper, we study models of the electrical double layer, based on the two-dimensional *two-component* plasma at $\Gamma = 2$.

Admittedly, a real electrical double layer is a complicated three-dimensional system with finite-size ions, a solvent which has a molecular structure, etc., and we do not expect our two-dimensional model of almost point particles to picture every detail of reality. However, many features of a Coulomb system essentially stem from the screening effect, which is itself a consequence of the harmonicity of the Coulomb potential. Therefore, we believe that our model can provide an insight into salient properties of electrical double layers. Also, our exactly solvable model can be used as a test bench for approximate methods.

In Sec. II, we define the model and we review the general method of solution. In Sec. III, we apply the general method to the calculation of density profiles and correlation functions in electrified interfaces. In Sec. IV, we study the differential capacity and the electrocapillarity. In Sec. V, we discuss the influence of the reduced dimensionality.

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II. MODEL AND METHOD OF SOLUTION

The model is a two-dimensional system of particles of charges $\pm e$. In two dimensions, the Coulomb interaction potential between two particles of charge e at a distance r from one another is logarithmic, of the form $-e^2 \ln(r/L)$, where L is some irrelevant length scale. We use classical equilibrium statistical mechanics. The dimensionless coupling constant is $\Gamma = \beta e^2$, where β is the inverse temperature. At $\Gamma = 2$, the model is exactly solvable. For the sake of completeness, we shall review the method of solution[9-11] (now avoiding some unnecessary complications of the original papers).

For $\Gamma \geqslant 2$, the point–particle model is unstable against the collapse of pairs of oppositely charged particles. This collapse can be prevented by introducing some short-distance cutoff, for instance, by representing the particles as charged hard discs of diameter R, and it will be seen that it is possible to obtain exact results near the limit $R \to 0$. Actually, if we take the correlation length as the control parameter, and keep it at some fixed value, the n-body ($n \geqslant 2$) correlation functions have well-defined limits as $R \to 0$; as to the one-body densities, they diverge as $R \to 0$, but their small-R behavior can be explicitly obtained.

We represent the position $\mathbf{r}$ of a particle by the complex number $z = x + iy$, where (x, y) are the Cartesian components of $\mathbf{r}$. For a system of N positive and N negative particles, the complex coordinates of which are u_i and v_i, respectively, the Boltzmann factor is, at $\Gamma = 2$,

$$\exp\left\{ 2\sum_{i<j}\left[\ln\left|\frac{u_i - u_j}{L}\right| + \ln\left|\frac{v_i - v_j}{L}\right|\right] - 2\sum_{i,j}\ln\left|\frac{u_i - v_j}{L}\right|\right\}$$

$$= L^{2N}\left|\frac{\Pi_{i<j}(u_i - u_j)(v_i - v_j)}{\Pi_{i,j}(u_i - v_j)}\right|^2$$

$$= L^{2N}\left|\left[\det\frac{1}{u_i - v_j}\right]_{i,j=1,\ldots,N^2}\right|^2, \qquad (2.1)$$

where the last equality stems from an identity of Cauchy.[12] It is convenient to start with a discretized model (for which there are no divergences). Two interwoven sublattices U and V are introduced. The positive (negative) particles sit on the sublattice $U(V)$; each lattice site is occupied by no or one particle. A possible external potential is described by posi-

tion-dependent fugacities $\lambda(u_i)$ and $\lambda(v_i)$. Then, the grand partition function (here defined as a sum including only neutral systems) is

$$Z = 1 + L^2 \sum_{\substack{u \in U \\ v \in V}} \lambda(u)\lambda(v) \left| \frac{1}{u-v} \right|^2 + L^4 \sum_{\substack{u_1,u_2 \in U \\ v_1,v_2 \in V}} \lambda(u_1)\lambda(u_2)\lambda(v_1)\lambda(v_2) \left| \left[\det \frac{1}{u_i - v_j} \right]_{i,j=1,2} \right|^2 + \dots \tag{2.2}$$

[the sums in Eq. (2.2) are defined with the prescriptions that configurations which differ only by a permutation of identical particles are counted only once]. It can be easily seen that this grand partition function is the determinant of an anti-Hermitian matrix involving all the lattice sites:

$$Z = \det \begin{vmatrix} 1 & 0 & \dots & \dfrac{L\lambda(u_1)}{u_1 - v_1} & \dfrac{L\lambda(u_1)}{u_1 - v_2} & \dots \\ 0 & 1 & \dots & \dfrac{L\lambda(u_2)}{u_2 - v_1} & \dfrac{L\lambda(u_2)}{u_2 - v_2} & \dots \\ & & \dots & & \dots & \\ \dfrac{L\lambda(v_1)}{\bar{v}_1 - \bar{u}_1} & \dfrac{L\lambda(v_1)}{\bar{v}_1 - \bar{u}_2} & \dots & 1 & 0 & \dots \\ \dfrac{L\lambda(v_2)}{\bar{v}_2 - \bar{u}_1} & \dfrac{L\lambda(v_2)}{\bar{v}_2 - \bar{u}_2} & \dots & 0 & 1 & \dots \end{vmatrix}. \tag{2.3}$$

A more compact notation can be used: each lattice site is characterized by its complex coordinate z and an isospinor which is $\binom{1}{0}$ if the site belongs to the positive sublattice U and $\binom{0}{1}$ if the site belongs to the negative sublattice V. The position dependent fugacities will be called $\lambda_+(z)$ for positive sites, $\lambda_-(z)$ for negative sites. We define a matrix M by

$$\langle z|M|z' \rangle = \frac{\sigma_x + i\sigma_y}{2} \frac{L}{z - z'} + \frac{\sigma_x - i\sigma_y}{2} \frac{L}{\bar{z} - \bar{z}'}, \tag{2.4}$$

where the σ's are 2×2 Pauli matrices operating in the isospinor space. Then, Eq. (2.3) can be written as

$$Z = \det \left\{ 1 + \left[\lambda_+(z) \frac{1 + \sigma_z}{2} + \lambda_-(z) \frac{1 - \sigma_z}{2} \right] \langle z|M|z' \rangle \right\}. \tag{2.5}$$

Ignoring the possible appearance of divergences for the time being, we now approach the continuum limit, letting the area S per lattice site become very small, and we show that Eq. (2.5) can be reexpressed in terms of a simple differential Dirac operator. Indeed, Eq. (2.4) can also be written as

$$\langle z|M|z' \rangle = L(\sigma_x \partial_x + \sigma_y \partial_y) \ln |r - r'| \tag{2.6}$$

and, since $\nabla^2 \ln r = 2\pi\delta(r)$, it is obvious that the inverse operator M^{-1} is

$$M^{-1} = \frac{S}{2\pi L} (\sigma_x \partial_x + \sigma_y \partial_y) \tag{2.7}$$

(S appears when discrete sums are replaced by integrals). Thus, an alternative form of Eq. (2.4) is

$$Z = \det \left\{ \left[\sigma_x \partial_x + \sigma_y \partial_y + m_+(r) \frac{1 + \sigma_z}{2} + m_-(r) \frac{1 - \sigma_z}{2} \right] [\sigma_x \partial_x + \sigma_y \partial_y]^{-1} \right\}, \tag{2.8}$$

where $m_\pm = (2\pi L/S)\lambda_\pm$ is a rescaled fugacity. Equation (2.8) expresses a well-known (?) equivalence between the two-dimensional Coulomb gas at $\Gamma = 2$ and a free Fermi field.[13]

From Eq. (2.8),

$$\ln Z = \mathrm{Tr} \left\{ \ln \left[\sigma_x \partial_x + \sigma_y \partial_y + m_+(r) \frac{1 + \sigma_z}{2} + m_-(r) \frac{1 - \sigma_z}{2} \right] - \ln[\sigma_x \partial_x + \sigma_y \partial_y] \right\} \tag{2.9}$$

and the one-particle densities and n-particle truncated densities can be obtained in the usual way by taking functional derivatives of Eq. (2.9) with respect to the fugacities $m_\pm(r)$. Marking the sign of the particle at r_i by an index $s_i = \pm 1$, and defining the matrix

$$G_{s_1 s_2}(r_1, r_2) = \langle r_1 s_1| \left[\sigma_x \partial_x + \sigma_y \partial_y + m_+(r) \frac{1 + \sigma_z}{2} + m_-(r) \frac{1 - \sigma_z}{2} \right]^{-1} |r_2 s_2\rangle, \tag{2.10}$$

we obtain the one-particle densities

$$\rho_{s_1}(r_1) = m_{s_1}(r_1) G_{s_1 s_1}(r_1, r_1), \tag{2.11}$$

the truncated two-body densities

$$\rho_{s_1 s_2}^{(2)T}(r_1, r_2) = -m_{s_1}(r_1) m_{s_2}(r_2) G_{s_1 s_2}(r_1, r_2) G_{s_2 s_1}(r_2, r_1), \tag{2.12}$$

and more generally the truncated n-body densities

$$\rho_{s_1 s_2 \dots s_n}^{(n)T}(r_1, r_2, \dots, r_n)$$
$$= (-1)^{n+1} m_{s_1}(r_1) m_{s_2}(r_2) \dots m_{s_n}(r_n)$$
$$\times \sum_{(i_1 i_2 \cdots i_n)} G_{s_{i_1} s_{i_2}}(r_{i_1}, r_{i_2}) \cdots G_{s_{i_n} s_{i_1}}(r_{i_n}, r_{i_1}), \tag{2.13}$$

where the summation runs over all cycles $(i_1 i_2 \cdots i_n)$ built with $\{1, 2, \dots, n\}$.

Therefore, the calculation of the one-body and n-body densities reduces to obtaining the Green function (2.10). This Green function G is the solution of a system of four coupled partial differential equations, which are, in a 2×2

matrix notation,

$$\left[\sigma_x \partial_{x_1} + \sigma_y \partial_{y_1} + m_+(\mathbf{r}_1)\frac{1+\sigma_z}{2}\right.$$

$$\left. + m_-(\mathbf{r}_1)\frac{1-\sigma_z}{2}\right]G(\mathbf{r}_1,\mathbf{r}_2) = 1\delta(\mathbf{r}_1 - \mathbf{r}_2). \quad (2.14)$$

By using the formal expansion of Eq. (2.10) in powers of $\sigma_x \partial_{x_1} + \sigma_y \partial_{y_1}$, it is easy to derive the useful symmetry relations

$$G_{ss}(\mathbf{r}_1,\mathbf{r}_2) = G_{ss}(\mathbf{r}_2,\mathbf{r}_1),$$

$$G_{s-s}(\mathbf{r}_1,\mathbf{r}_2) = - \overline{G_{-ss}(\mathbf{r}_2,\mathbf{r}_1)}. \quad (2.15)$$

It is convenient to define $m(\mathbf{r})$ and $V(\mathbf{r})$ by

$$m_s(\mathbf{r}) = m(\mathbf{r})\exp[-2sV(\mathbf{r})]. \quad (2.16)$$

This allows to take into account some external electrical potential: $se^2 V(\mathbf{r})$ is the energy of a particle of sign s in this potential[14]; if there is also a nonelectrical potential acting in the same way on particles of both sign, it is described by the $\mathbf{r}$ dependence of $m(\mathbf{r})$ (this will be a way of taking into account impenetrable walls for instance). It is also convenient to introduce the functions

$$g_{s_1 s_2}(\mathbf{r}_1,\mathbf{r}_2) = \exp[-s_1 V(\mathbf{r}_1)]G_{s_1 s_2}(\mathbf{r}_1,\mathbf{r}_2)\exp[-s_2 V(\mathbf{r}_2)] \quad (2.17)$$

[they obey symmetry relations similar to Eq. (2.15)]. Then, in terms of the operators $A = \partial_{x_1} + i\partial_{y_1} + \partial_{x_1} V(\mathbf{r}_1) + i\partial_{y_1} V(\mathbf{r}_1)$ and $A^+ = -\partial_{x_1} + i\partial_{y_1} + \partial_{x_1} V(\mathbf{r}_1) - i\partial_{y_1} V(\mathbf{r}_1)$, by combining the components of Eq. (2.14), one obtains decoupled equations for g_{++} and g_{--},

$$\{m(\mathbf{r}_1) + A^+[m(\mathbf{r}_1)]^{-1}A\}g_{++}(\mathbf{r}_1,\mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (2.18a)$$

$$\{m(\mathbf{r}_1) + A[m(\mathbf{r}_1)]^{-1}A^+\}g_{--}(\mathbf{r}_1,\mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (2.18b)$$

while

$$g_{-+}(\mathbf{r}_1,\mathbf{r}_2) = -[m(\mathbf{r}_1)]^{-1}A\, g_{++}(\mathbf{r}_1,\mathbf{r}_2). \quad (2.18c)$$

The simplest case of a uniform TCP is described by taking constant fugacities $m_+ = m_- = m$ [thus, $V(\mathbf{r}) = 0$]. In that case $G_{++} = G_{--}$, and Eqs. (2.17) and (2.18a) become

$$(m^2 - \nabla_1^2)G_{++}(\mathbf{r}_1,\mathbf{r}_2) = m\,\delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (2.19)$$

with the solution

$$G_{++}(\mathbf{r}_1,\mathbf{r}_2) = \frac{m}{2\pi}K_0(m|\mathbf{r}_1 - \mathbf{r}_2|). \quad (2.20a)$$

From Eq. (2.18c), one obtains

$$G_{-+}(\mathbf{r}_1,\mathbf{r}_2)$$

$$= \frac{m}{2\pi}\frac{(x_1 - x_2) + i(y_1 - y_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}K_1(m|\mathbf{r}_1 - \mathbf{r}_2|). \quad (2.20b)$$

K_0 and K_1 are modified Bessel functions. These functions decay at large distances, on a characteristic length scale m^{-1}: the rescaled fugacity m is an inverse correlation length. As announced in the above, for a given value of the correlation length m^{-1}, the n-body ($n \geq 2$) truncated densities (2.12) and (2.13) are well-defined quantities for the point–particle system; the two-body truncated densities, for in-

stance, have the simple forms

$$\rho_{++}^{(2)T}(r) = -\left(\frac{m^2}{2\pi}\right)^2[K_0(mr)]^2, \quad (2.21a)$$

$$\rho_{+-}^{(2)T}(r) = \left(\frac{m^2}{2\pi}\right)^2[K_1(mr)]^2. \quad (2.21b)$$

The one-body densities, however, as given by Eqs. (2.11) and (2.20a), are infinite since $K_0(mr)$ diverges logarithmically as $r \to 0$. This divergence can be suppressed by a short-distance cutoff R: we replace the point particles by small charged hard discs of diameter R and use a regularized form of Eq. (2.11),

$$\rho_\pm = \frac{m^2}{2\pi}K_0(mR) \sim \frac{m^2}{2\pi}\left[\ln\frac{2}{mR} - \gamma\right], \quad (2.22)$$

where $\gamma = 0.5772$ is Euler's constant. Near the limit $mR \to 0$ (i.e., in the low-density limit $\rho_\pm R^2 \to 0$), we can keep the point–particle expression for the correlation functions, for separations larger than R. It can be checked that this way of implementing the cutoff is a consistent one, in that sense that the perfect-screening rule

$$\rho_\pm = \int_{r>R} d^2\mathbf{r}[\rho_{+-}^{(2)T}(r) - \rho_{++}^{(2)T}(r)] \quad (2.23)$$

is satisfied. Either by integrating Eq. (2.22), or by using the regularized form of Eq. (2.9), one obtains for the pressure p,

$$\beta p = \frac{m^2}{2\pi}\left[\ln\frac{2}{mR} - \gamma + \frac{1}{2}\right]. \quad (2.24)$$

The equation of state is

$$\beta p = \frac{1}{2}(\rho_+ + \rho_-) + \frac{m^2}{4\pi}. \quad (2.25)$$

In the limit $mR \to 0$, one finds $\beta p/(\rho_+ + \rho_-) \to 1/2$. This is the expected result for an ideal gas of collapsed neutral pairs.

III. INTERFACES

We want to compute the one-body and n-body densities near an interface. The interface is assumed to be along the y axis, and the system is translationally invariant in the y direction, i.e., the position-dependent fugacities $m_\pm(\mathbf{r})$ actually depend only on x. Our problem is to solve Eq. (2.14) or (2.18) in this geometry. The standard technique is to Fourier-transform $g(\mathbf{r}_1,\mathbf{r}_2)$ with respect to $y_2 - y_1$ (g depends on y_1 and y_2 only through their difference):

$$g(\mathbf{r}_1,\mathbf{r}_2) = \int_{-\infty}^{\infty}\frac{dl}{2\pi}\hat{g}(x_1,x_2,l)\,e^{il(y_1 - y_2)}. \quad (3.1)$$

We also define

$$\hat{G}_{s_1 s_2}(x_1,x_2,l) = \exp[s_1 V(x_1)]\hat{g}_{s_1 s_2}(x_1,x_2,l)\exp[s_2 V(x_2)]. \quad (3.2)$$

In terms of $\hat{G}$ or $\hat{g}$, one obtains ordinary differential equations, in one variable x_1, such as

$$m_+(x_1)\hat{G}_{++}(x_1,x_2,l)$$

$$+ \left(\frac{d}{dx_1} + l\right)\hat{G}_{-+}(x_1,x_2,l) = \delta(x_1 - x_2), \quad (3.2a)$$

$$\left(\frac{d}{dx_1} - l\right)\hat{G}_{++}(x_1,x_2,l) + m_-(x_1)\hat{G}_{-+}(x_1,x_2,l) = 0, \quad (3.2b)$$

or

$$\left\{ m(x_1) - \left[\frac{d}{dx_1} - V'(x_1) + l \right] [m(x_1)]^{-1} \left[\frac{d}{dx_1} \right. \right.$$
$$\left. \left. + V'(x_1) - l \right] \right\} \hat{g}_{++}(x_1,x_2,l) = \delta(x_1 - x_2), \quad (3.3a)$$

$$g_{-+}(x_1,x_2,l) = -[m(x_1)]^{-1} \left[\frac{d}{dx_1} + V'(x_1) - l \right]$$
$$\times g_{++}(x_1,x_2,l). \quad (3.3b)$$

In general, the fugacities $m_{\pm}(x_1)$ will be discontinuous on the interface $x_1 = 0$. Since Eq. (3.2) is a first-order system, its solutions in the regions $x_1 > 0$ and $x_1 < 0$ must be connected by the conditions that $\hat{G}_{++}$ and $\hat{G}_{-+}$ be continuous at $x_1 = 0$.

We now consider specific models.

A. Charged hard wall (primitive electrode)

We assume the half-space $x < 0$ to be impenetrable to the particles: the fugacities $m_{\pm}(x)$ vanish in that region. The Coulomb gas is confined to the region $x > 0$. We want to solve Eq. (3.2) or (3.3), assuming the source point x_2 to be in the Coulomb gas region, $x_2 > 0$. The boundary conditions are that $\hat{g}_{++}$ and $\hat{g}_{-+}$ must vanish at $x_1 = \pm \infty$.

In the wall region, $x_1 < 0$, Eqs. (3.2) reduce to

$$\left(\frac{d}{dx_1} + l \right) \hat{G}_{-+}(x_1,x_2,l) = 0, \left(\frac{d}{dx_1} - l \right) \hat{G}_{++}(x_1,x_2,l) = 0 \quad (3.4)$$

with the general solution

$$\hat{G}_{++} = A(x_2,l) \exp(lx_1), \hat{G}_{-+} = B(x_2,l) \exp(-lx_1). \quad (3.5)$$

The boundary conditions at $x_1 = -\infty$ can be satisfied only by taking $A = 0$ if $l < 0$, $B = 0$ if $l > 0$. There is a continuity requirement at $x_1 = 0$. Thus the solution in the region $x_1 > 0$ must obey the following boundary conditions at $x_1 = 0$: $\hat{G}_{++}(x_1 = 0,x_2,l) = 0$ if $l < 0, \hat{G}_{-+}(x_1 = 0,x_2,l) = 0$ if $l > 0$. These are the boundary conditions to be satisfied at a hard wall.

Let us now consider the Coulomb gas region $x > 0$. We assume that the wall may carry a uniform external "surface" charge density, i.e., there will be a charge $-e\sigma$ per unit length on the line $x = 0$; this charged wall models an electrode. This electrode, and another one of opposite charge assumed to be at $x = +\infty$, generate an electrostatic potential which is 0 for $x < 0$ and $2\pi e\sigma x$ for $x > 0$ (in two dimensions, the numerical factor is 2π rather than 4π); correspondingly, the fugacities are of the form $m_{\pm}(x) = m \exp(\mp 4\pi\sigma x)$, i.e., $m(x) = m$, $V(x) = 2\pi\sigma x$. Equations (3.3) take the simple form

$$\left[m^2 + (l - 2\pi\sigma)^2 - \frac{d^2}{dx_1^2} \right] \hat{g}_{++}(x_1,x_2,l) = m\delta(x_1 - x_2), \quad (3.6a)$$

$$\hat{g}_{-+}(x_1,x_2,l) = \frac{1}{m} \left[l - 2\pi\sigma - \frac{d}{dx_1} \right] \hat{g}_{++}(x_1,x_2,l). \quad (3.6b)$$

This system must be solved with the boundary conditions
$$\hat{g}_{++}(x_1 = \infty,x_2,l) \qquad = \hat{g}_{-+}(x_1 = \infty,x_2,l) = 0,$$

$\hat{g}_{++}(x_1 = 0,x_2,l) = 0$ if $l < 0, \hat{g}_{-+}(x_1 = 0,x_2,l) = 0$ if $l > 0$. This is easily done by adding an appropriate "reflected wave" to the free space Green function solution of Eq. (3.6a) (the calculation is facilitated by noting that $\hat{g}_{++}$ has to be symmetrical in x_1 and x_2). The result is

$$\hat{g}_{++}(x_1,x_2,l) = \frac{m}{2\kappa(l)} \{ \exp[-\kappa(l)|x_1 - x_2|]$$
$$- \exp[-\kappa(l)(x_1 + x_2)] \}, \quad l < 0, \quad (3.7a)$$

$$\hat{g}_{++}(x_1,x_2,l) = \frac{m}{2\kappa(l)} \left\{ \exp[-\kappa(l)|x_1 - x_2|] \right.$$
$$+ \frac{\kappa(l) - l + 2\pi\sigma}{\kappa(l) + l - 2\pi\sigma}$$
$$\left. \times \exp[-\kappa(l)(x_1 + x_2)] \right\}, \quad l > 0, \quad (3.7b)$$

where

$$\kappa(l) = [m^2 + (l - 2\pi\sigma)^2]^{1/2}. \quad (3.8)$$

$\hat{g}_{-+}$ is given by Eq. (3.6b). By a similar calculation, one obtains

$$\hat{g}_{--}(x_1,x_2,l) = \frac{m}{2\kappa(l)} \left\{ \exp[-\kappa(l)|x_1 - x_2|] \right.$$
$$+ \frac{\kappa(l) + l - 2\pi\sigma}{\kappa(l) - l + 2\pi\sigma}$$
$$\left. \times \exp[-\kappa(l)(x_1 + x_2)] \right\}, \quad l < 0, \quad (3.7c)$$

$$\hat{g}_{--}(x_1,x_2,l) = \frac{m}{2\kappa(l)} \left\{ \exp[-\kappa(l)|x_1 - x_2|] \right.$$
$$\left. - \exp[-\kappa(l)(x_1 + x_2)] \right\}, \quad l > 0. \quad (3.7d)$$

Using Eq. (3.7) in Eq. (3.1) gives an integral representation for $g(\mathbf{r}_1,\mathbf{r}_2)$; one can obtain the n-body correlations by Eqs. (2.13) and (2.17).

The first term on the right-hand side of Eqs. (3.7) gives to $mg_{ss}(\mathbf{r}_1,\mathbf{r}_2)$ a contribution $(m^2/2\pi) \exp[i2\pi\sigma(y_1 - y_2)] K_0(m|\mathbf{r}_1 - \mathbf{r}_2|)$, which is the bulk result, except for an irrelevant phase factor. For calculating the one-body densities

$$\rho_s(x) = mg_{ss}(\mathbf{r},\mathbf{r}), \quad (3.9)$$

one must use for the bulk contribution the regularized form Eq. (2.22). After the change of variable $l - 2\pi\sigma = t$, rearrangements, and the explicit calculation of some integrals, one obtains

$$\rho_{\pm}(x) = \rho_{\pm} - \frac{m^2}{4\pi} K_0(2mx) + \frac{m^2}{2\pi} \left\{ \frac{1}{2} K_2(2mx) \right.$$
$$\left. - \left[\frac{1}{2mx} + \frac{1}{(2mx)^2} \right] e^{-2mx} \right\} + \frac{m^2}{2\pi}$$
$$\times \int_0^{\pm 2\pi\sigma} \frac{dt}{(m^2 + t^2)^{1/2} - t}$$
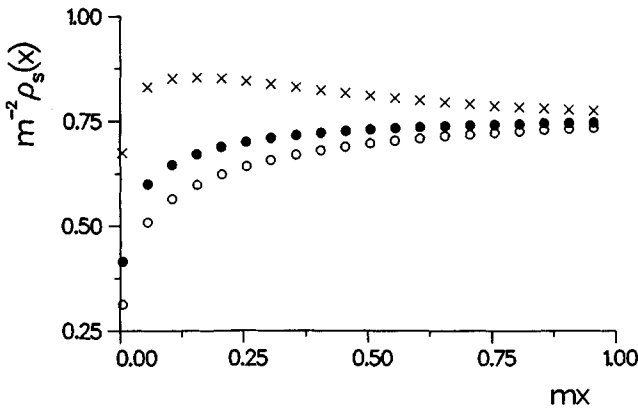$$\times \exp[-2(m^2 + t^2)^{1/2}x], \quad (3.10)$$

FIG. 1. The density profiles near a hard wall. For an uncharged wall $(\sigma = 0)$, $\rho_+(x) = \rho_-(x)$ (black circles). For a charged wall $(2\pi\sigma = m)$, $\rho_+(x)$ (crosses) and $\rho_-(x)$ (white circles). The cutoff is $mR = 0.01$.

where $\rho_\pm$ is the bulk density (2.22). In the limit $x \to 0$, $K_0(2mx)$ must be replaced by its regularized form $K_0(mR)$; the other terms in Eq. (3.10) have finite limits. One finds for the contact densities

$$\rho_\pm(0) = \frac{1}{2}\rho_\pm + \frac{m^2}{8\pi} + \frac{m^2}{4\pi}\left[\pm \sinh^{-1}\frac{2\pi\sigma}{m} \right.$$
$$\left. \pm \frac{2\pi\sigma}{m}\left(1 + \frac{4\pi^2\sigma^2}{m^2}\right)^{1/2} + \frac{4\pi^2\sigma^2}{m^2}\right]. \quad (3.11)$$

The density profiles are shown in Fig. 1, in the two cases $\sigma = 0$ and $2\pi\sigma = m$.

It is easy to check that Eq. (3.10) obeys the screening rule

$$\int_0^\infty [\rho_+(x) - \rho_-(x)]\, dx = \sigma. \quad (3.12)$$

Also from Eqs. (2.25) and (3.11), one checks that the contact theorem

$$\beta p = \rho_+(0) + \rho_-(0) - \beta\pi(e\sigma)^2 \quad (3.13)$$

is satisfied; this relation expresses the balance between the bulk pressure on one side and the kinetic plus electrostatic pressures at the wall on the other side.

B. Polarizable interface

The model is a Coulomb gas separated into two regions (a) (the half-plane $x > 0$) and (b) (the half-plane $x < 0$) by a membrane (the line $x = 0$) impermeable to the particles. In the grand canonical formalism, this membrane can be described by using different fugacities on each side.[5,8] In general, the densities have different given values far away on each side of the interface, and the potential drop across the interface is also a given quantity. Here, we take as our control parameters different constant fugacities on each side: In the general notation (2.16), the fugacities of the particles of sign s are $m_a \exp(-2sV_a)$ in region (a) and $m_b \exp(-2sV_b)$ in region (b); it will be seen that the physical quantities depend on V_a and V_b only through their difference $V_a - V_b$.

We want to solve Eq. (3.3). If, for instance, the source point x_2 is in region (a) $(x_2 > 0)$, $\hat{g}_{++}$ obeys

$$\left(m_a^2 + l^2 - \frac{d^2}{dx_1^2}\right)\hat{g}_{++}(x_1,x_2,l)$$
$$= m_a\delta(x_1 - x_2), \quad x_1,x_2 > 0, \quad (3.14a)$$
$$\left(m_b^2 + l^2 - \frac{d^2}{dx_1^2}\right)\hat{g}_{++}(x_1,x_2,l)$$
$$= 0, \quad x_1 < 0, x_2 > 0. \quad (3.14b)$$

We look for a solution, vanishing at $x_1 = \pm\infty$, of the form

$$\hat{g}_{++} = \frac{m_a}{2\kappa_a}\exp[-\kappa_a|x_1 - x_2|]$$
$$+ A\exp[-\kappa_a(x_1 + x_2)], \quad x_1,x_2 > 0, (3.15a)$$
$$\hat{g}_{++} = B\exp(\kappa_b x_1 - \kappa_a x_2), \quad x_1 < 0, x_2 > 0, \quad (3.15b)$$
where
$$\kappa_a = (m_a^2 + l^2)^{1/2}, \kappa_b = (m_b^2 + l^2)^{1/2}. \quad (3.16)$$

The constants A and B are determined by the conditions that $\hat{G}_{++}$ and $\hat{G}_{-+}$ be continuous at $x_1 = 0$, i.e., that $\exp(V)\hat{g}_{++}$ and $\exp(-V)m^{-1}[l - (d/dx_1)]\hat{g}_{++}$ be continuous at $x_1 = 0$. The same method applies to $x_2 < 0$ and to $\hat{g}_{--}$. The results are

(i) if $x_1,x_2 > 0$,

$$\hat{g}_{++}(x_1,x_2,l) = \frac{m_a}{2\kappa_a}\left\{\exp[-\kappa_a|x_1 - x_2|] + \frac{[(\kappa_a - l)/m_a] - \exp[2(V_a - V_b)][(\kappa_b - l)/m_b]}{[(\kappa_a + l)/m_a] + \exp[2(V_a - V_b)][(\kappa_b - l)/m_b]}\right.$$
$$\left. \times \exp[-\kappa_a(x_1 + x_2)]\right\}; \quad (3.17a)$$

(ii) if $x_1,x_2 < 0$,

$$\hat{g}_{++}(x_1,x_2,l) = \frac{m_b}{2\kappa_b}\left\{\exp[-\kappa_b|x_1 - x_2|] + \frac{[(\kappa_b + l)/m_b] - \exp[2(V_b - V_a)][(\kappa_a + l)/m_a]}{[(\kappa_b - l)/m_b] + \exp[2(V_b - V_a)][(\kappa_a + l)/m_a]}\right.$$
$$\left. \times \exp[\kappa_b(x_1 + x_2)]\right\}; \quad (3.17b)$$

(iii) if $x_1 x_2 < 0$,

$$\hat{g}_{++}(x_1,x_2,l) = \frac{\exp[-\kappa_1|x_1| - \kappa_2|x_2|]}{\exp(V_b - V_a)[(\kappa_a + l)/m_a] + \exp(V_a - V_b)[(\kappa_b - l)/m_b]}, \quad (3.17c)$$

where $\kappa_i = \kappa_a$ if $x_i > 0$, $\kappa_i = \kappa_b$ if $x_i < 0$. One obtains $\hat{g}_{--}(x_1, x_2, l)$ by changing the signs of V_a, V_b, l in the above expressions for $\hat{g}_{++}$. One obtains $\hat{g}_{-+}$ by

$$\hat{g}_{-+}(x_1, x_2, l) = \frac{1}{m_1}\left[l - \frac{d}{dx_1}\right]\hat{g}_{++}(x_1, x_2, l), \quad (3.17d)$$

where $m_1 = m_a$ if $x_1 > 0$, $m_1 = m_b$ if $x_1 < 0$. Using Eq. (3.17) in Eq. (3.1), one obtains an integral representation

which gives the n-body correlations by Eqs. (2.13) and (2.17).

For the calculation of the one-body densities $m_a g_{ss}(\mathbf{r}, \mathbf{r})$ or $m_b g_{ss}(\mathbf{r}, \mathbf{r})$, the first term on the right-hand side of Eq. (3.17a) or (3.17b) gives the bulk density $\rho_{\pm}^a$ or $\rho_{\pm}^b$, for which we must use the regularized expression (2.22) with $m = m_a$ or m_b. From Eq. (3.1), after some rearrangements, one obtains the integral representations

$$\rho_+(x) = \rho_{\pm}^a + \frac{m_a}{2\pi}\int_0^{l_0} dl\left\{-\frac{m_a}{\kappa_a} + \frac{\exp[-2(V_a - V_b)](\kappa_a/m_a) + (\kappa_b/m_b)}{\cosh[2(V_a - V_b)] + [(\kappa_a\kappa_b + l^2)/(m_a m_b)]}\right\}\exp(-2\kappa_a x), \quad x > 0, \quad (3.18a)$$

$$\rho_+(x) = \rho_{\pm}^b + \frac{m_b}{2\pi}\int_0^{l_0} dl\left\{-\frac{m_b}{\kappa_b} + \frac{(\kappa_a/m_a) + \exp[2(V_a - V_b)](\kappa_b/m_b)}{\cosh[2(V_a - V_b)] + [(\kappa_a\kappa_b + l^2)/(m_a m_b)]}\right\}\exp(2\kappa_b x), \quad x < 0; \quad (3.18b)$$

one obtains $\rho_-(x)$ by changing the signs of V_a and V_b in the above expressions for $\rho_+(x)$. When $x \to 0$, the integrals in Eq. (3.18) diverge at $l = +\infty$, and we must regularize them. We did it by introducing an ultraviolet cutoff l_0. This cutoff must be such that the first term on the right-hand side of Eq. (3.17a) or (3.17b) correctly gives the regularized bulk densities (2.22); this requirement determines

$$l_0 = \frac{e^{-\gamma}}{R}. \quad (3.19)$$

In general, the densities are discontinuous at $x = 0$. They are shown in Fig. 2, for $m_b = 0.5 m_a$ and $\exp[2(V_a - V_b)] = 4$.

Without a cutoff, $\rho_{\pm}(x) - \rho_{\pm}$ diverges only logarithmically; thus, relevant integrals on x can be calculated with the cutoff removed. With some algebra, one can check that the total charges on each side of the interface have opposite values:

$$\sigma = \int_0^\infty dx[\rho_+(x) - \rho_-(x)]$$

$$= -\int_{-\infty}^0 dx[\rho_+(x) - \rho_-(x)]. \quad (3.20)$$

Furthermore, one can compute explicitly the potential drop $\phi_a - \phi_b$ across the interface [$\phi_a(\phi_b)$ is the electrical potential at $x = +\infty(-\infty)$]:

$$\Delta\phi = \phi_a - \phi_b = 2\pi e\int_{-\infty}^\infty dx\, x[\rho_+(x) - \rho_-(x)]. \quad (3.21)$$

After some algebra, one finds

$$\Delta\phi = \phi_a - \phi_b = e(V_b - V_a). \quad (3.22)$$

This very simple result is not unexpected. Since the physical quantities depend on V_a and V_b only through their difference, we can choose $eV_a = -\phi_a$ and $eV_b = -\phi_b$. Therefore, if we define bulk chemical potentials μ_a and μ_b by $m_a = m_0 \exp(\beta\mu_a)$ and $m_b = m_0 \exp(\beta\mu_b)$ (where m_0 is some inverse length), in region (a), for instance, the fugacity $m_a \exp(-s\beta e^2 V_a)$ of the particles of sign s can be written as $m_0 \exp[\beta(\mu_a + se\phi_a)]$. This means that the total chemical potential $\mu_a + se\phi_a$ actually is an electrochemical potential, which includes the electrical part $se\phi_a$ in addition to that part μ_a which governs the bulk properties; the electrical part plays a role only in the surface region.

One can also check the contact theorem which expresses the balance between the bulk pressures p_a and p_b, and the kinetic pressures on the membrane:

$$\beta p_a - \beta p_b = \rho_+(0^+) + \rho_-(0^+) - \rho_+(0^-) - \rho_-(0^-). \quad (3.23)$$

C. Ideal conductor electrode

If, in the results for the impermeable membrane, we take the limit $m_b \to 0$, we retrieve the hard-wall expressions.

Another interesting limit is $m_b \to \infty$. Then, the correlation length m_b^{-1} in region (b) vanishes, and region (b) becomes an ideal conductor.[6] From Eq. (3.17a), we obtain in region (a) [we now omit the index a, and use the notation
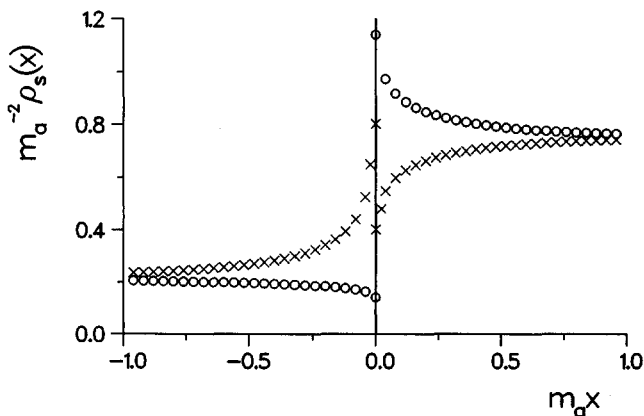

FIG. 2. The density profiles near a polarizable interface, for $m_b = 0.5 m_a$ and $\exp[2(V_a - V_b)] = 4$: $\rho_+(x)$ (crosses) and $\rho_-(x)$ (white circles). The cutoff is $mR = 0.01$.

(3.22)]

$$\hat{g}_{++}(x_1,x_2,l) = \frac{m}{2\kappa}\left\{\exp[-\kappa|x_1-x_2|]\right.$$

$$+\frac{\kappa - l - me^{-\beta e\Delta\phi}}{\kappa + l + me^{-\beta e\Delta\phi}}$$

$$\left.\times\exp[-\kappa(x_1+x_2)]\right\}, \qquad (3.24)$$

and from Eq. (3.18a),

$$\rho_+(x) = \rho_\pm + \frac{m}{2\pi}\int_0^{l_0} dl\left\{-\frac{m}{\kappa}\right.$$

$$\left.+\frac{\kappa e^{2\beta e\Delta\phi}+m}{m\cosh(2\beta e\Delta\phi)+\kappa}\exp(-2\kappa x)\right\};$$

$$(3.25)$$

one obtains $\rho_-(x)$ by changing $\Delta\phi$ into $-\Delta\phi$. Without the cutoff l_0 in Eq. (3.25), $\rho_\pm(x)$ would diverge at small x like $1/x$; this effect comes from the strong attraction of each particle by its image.

In the special case $\Delta\phi = 0$, one finds the explicit expression

$$\rho_\pm(x) = \rho_\pm + \frac{m^2}{2\pi}[K_1(2mx) - K_0(2mx)]. \quad (3.26)$$

D. Semipermeable membrane

As a special case of the impermeable membrane, we can obtain a solvable model of a membrane permeable to one species, say the positive particles, and impermeable to the other species. Now, there are only two control parameters, which can be chosen as the bulk fugacities on each side, m_a and m_b. We expect the electrochemical potential of the positive particles to be the same on both sides, since these positive particles can freely cross the membrane; this condition, $m_a \exp(\beta e\phi_a) = m_b \exp(\beta e\phi_b)$, then determines $\Delta\phi = \phi_a - \phi_b$ which is no longer a free parameter.

From Eq. (3.18) where now $\exp[2(V_a - V_b)] = m_a/m_b$, it is easy to check that the density of the positive particles is indeed continuous at

$x = 0$, as it should since the membrane is permeable to them. On the contrary, the density of the negative particles has a jump at $x = 0$ (at least in the nontrivial case $m_a \neq m_b$).

The density profiles are shown in Fig. 3, for $m_b = 0.5m_a$.

IV. DIFFERENTIAL CAPACITY AND SURFACE TENSION

These quantities are of central interest in experimental electrochemistry. They are related by the Lippmann equation.[15] We shall study them for our charged hard wall model and our polarizable interface model. Compared to previous work on the one-component plasma,[5,16] the present results for the two-component plasma are rather simpler and more explicit.

A. Charged hard wall

A given external surface charge density $-e\sigma$ on the wall induces a surface charge density $e\sigma$ in the Coulomb gas [see Eq. (3.12)]. From Eq. (3.10), it is easy to compute the potential drop across the interface:

$$\Delta\phi = 2\pi e \int_0^\infty dx\, x[\rho_+(x) - \rho_-(x)] = \frac{e}{2}\sinh^{-1}\frac{2\pi\sigma}{m}.$$

$$(4.1)$$

Therefore, the differential capacity C, defined by $C = \partial(e\sigma)/\partial\Delta\phi$, is

$$C = \frac{m}{\pi}\cosh\frac{2\Delta\phi}{e}. \qquad (4.2)$$

The shape of the curve $C(\Delta\phi)$ is in qualitative agreement with the usual experimental results.

For studying the surface tension, we first consider the general case of a Coulomb gas of volume V bounded by a surface of area A; the surface carries a total external charge $-Q$ with a uniform surface charge density $-e\sigma = -Q/A$, and the Coulomb gas has a surface charge density $e\sigma$ near its boundary. In the grand-canonical formalism, besides the temperature which here will be kept fixed, we use as independent variables V, A, Q, and the fugacity m which governs the bulk properties. In terms of the grand potential $\Omega = -\beta^{-1}\ln Z$, the surface tension is defined as[15-17]

$$\gamma = \left(\frac{\partial\Omega}{\partial A}\right)_{m,V,Q}. \qquad (4.3)$$

Ω is the sum of a volume part and a surface part:

$$\Omega = -Vp(m) + A\omega_s(m,\sigma). \qquad (4.4)$$

Therefore,

$$\gamma = \left(1 - \sigma\frac{\partial}{\partial\sigma}\right)\omega_s(m,\sigma), \qquad (4.5)$$

and we can compute the surface tension γ if we know the function $\omega_s(m,\sigma)$.

Rather than computing $\omega_s(m,\sigma)$ directly from the grand partition function, here we find more convenient to start with its derivatives. The total number of particles is $N = -\beta m(\partial\Omega/\partial m)$, and for the present semiinfinite ge-
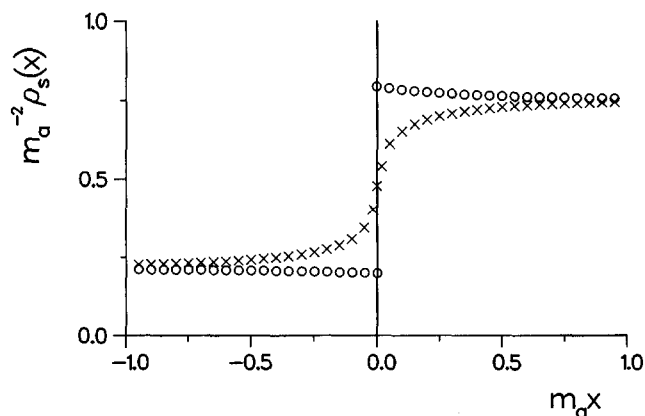
FIG. 3. The density profiles near a semipermeable membrane (permeable to the positive particle only), for $m_b = 0.5m_a$: $\rho_+(x)$ (crosses) and $\rho_-(x)$ (white circles). The cutoff is $mR = 0.01$.

ometry, the surface part of this relation gives

$$-\beta m \frac{\partial \omega_s}{\partial m} = \int_0^\infty dx[\rho_+(x) + \rho_-(x) - 2\rho_\pm] \ . \tag{4.6}$$

On the other hand, since the interaction between $-\sigma$ and a particle of charge $\pm e$, at a distance x from the wall, gives to the Boltzmann factor in Z a contribution $\exp[\beta 2\pi(\nu - 1)\sigma e^2 x]$ for a ν-dimensional system ($\nu = 2,3$), it is easy to show that

$$\frac{\partial \omega_s}{\partial(e\sigma)} = 2\pi(\nu - 1)e \int_0^\infty dx\, x[\rho_+(x) - \rho_-(x)] = \Delta\phi. \tag{4.7}$$

Equations (4.6) and (4.7) are of quite general validity, and do not depend on the detail of the present model. Equation (4.7) can also be obtained by a thermodynamical argument. By combining Eqs. (4.5) and (4.7), one obtains the Lippmann equation

$$\frac{\partial \gamma}{\partial \Delta\phi} = -e\sigma. \tag{4.8}$$

Incidentally, by writing $\partial^2\omega_s/\partial\sigma\partial m = \partial^2\omega_s/\partial m\partial\sigma$, one obtains from Eqs. (4.6) and (4.7) a relation of the Maxwell type.

For our present model, with the densities of Sec. III A, Eqs. (4.6) and (4.7) become

$$\beta m \frac{\partial \omega_s}{\partial m} = \frac{m}{4} - \frac{1}{2\pi}[m^2 + (2\pi\sigma)^2]^{1/2} \tag{4.9}$$

and

$$\beta \frac{\partial \omega_s}{\partial \sigma} = \sinh^{-1}\frac{2\pi\sigma}{m}\ . \tag{4.10}$$

Starting from the values $m = 0$, $\sigma = 0$, for which obviously $\omega_s = 0$, we can integrate Eqs. (4.9) and (4.10), first at constant $\sigma = 0$, and afterwards at constant m; the result is

$$\beta \omega_s = \frac{m}{4} + \sigma \sinh^{-1}\frac{2\pi\sigma}{m} - \frac{1}{2\pi}[m^2 + (2\pi\sigma)^2]^{1/2}\ . \tag{4.11}$$

Finally, the surface tension (4.5) is obtained as

$$\beta\gamma = \frac{m}{4} - \frac{1}{2\pi}[m^2 + (2\pi\sigma)^2]^{1/2}$$

$$= \frac{m}{4} - \frac{m}{2\pi}\cosh\frac{2\Delta\phi}{e}\ . \tag{4.12}$$

Qualitatively, the electrocapillarity curve $\gamma(\Delta\phi)$ has the usual shape. Since here the wall is a rigid one, γ is not necessarily positive.

The very derivation of Eq. (4.12) implies that the Lippmann equation (4.8) must be satisfied, and indeed it is.

It is amusing to consider the limit $m \to 0$ for a fixed nonzero value of σ. In this limit, the bulk densities $\rho_\pm$ vanish, while however near the wall, for say a negatively charged wall ($\sigma > 0$), the densities (3.10) become

$$\rho_-(x) = 0,$$

$$\rho_+(x) = \frac{1}{4\pi x^2}[1 - (1 + 4\pi\sigma x)\exp(-4\pi\sigma x)]. \tag{4.13}$$

Thus, the system becomes a negatively charged plate attracting in its neighborhood σ positive particles per unit "area"; indeed

$$\int_0^\infty \rho_+(x)dx = \sigma. \tag{4.14}$$

The limiting behavior of Eq. (4.11), as $m \to 0$, is

$$\beta\omega_s \sim \sigma\left[\ln\frac{4\pi\sigma}{m} - 1\right] \tag{4.15}$$

and the limit of $\beta\gamma$ is $-\sigma$. This peculiar one-component plasma (without a background) has been previously studied in the canonical ensemble,[18] and Eq. (4.13) was derived in this ensemble. Using the method of Ref. 18, one easily finds the free energy per unit area f_s and the grand potential per unit area ω_s, such that

$$\beta\omega_s = \beta f_s - \beta\mu\sigma = \sigma\left[\ln\frac{2\Lambda^2\sigma}{l} - 1 - \beta\mu\right], \tag{4.16}$$

where Λ is the thermal de Broglie wavelength, L the length scale of the logarithmic Coulomb potential, and μ the chemical potential. It is easy to see that our rescaled fugacity m is related to μ by $m = (2\pi L/\Lambda^2)\exp(\beta\mu)$, and therefore Eqs. (4.15) and (4.16) are identical, as they should.

B. Polarizable interface

Now, the control parameter is the potential drop $\Delta\phi$ rather than the charge; the surface charge density is defined by Eq. (3.20) as a function of $\Delta\phi$. In general, σ can be expressed only in terms of elliptic integrals. In the special case of equal bulk densities on each side of the interface, i.e., equal fugacities $m_a = m_b = m$, things are much simpler and one obtains from Eq. (3.18) [remembering Eq. (3.22)]

$$\sigma = \int_0^\infty dx[\rho_+(x) - \rho_-(x)] = \frac{m}{4}\sinh\frac{\Delta\phi}{e}; \tag{4.17}$$

the differential capacity is

$$C = \frac{\partial(e\sigma)}{\partial\Delta\phi} = \frac{m}{4}\cosh\frac{\Delta\phi}{e}\ . \tag{4.18}$$

For computing the surface tension, we can follow the same kind of approach as above. However the replacement of Q by $\Delta\phi$ as one of the independent variables brings some changes: For some given configuration, let N_a^+ be the number of positive particles in region (a), etc... . Then, each term in the grand partition function Z depends on ϕ_a and ϕ_b by the factor $\exp[\beta e\phi_a(N_a^+ - N_a^-)]$ $\times \exp[\beta e\phi_b(N_b^+ - N_b^-)] = \exp[\beta e\Delta\phi(N_a^+ - N_a^-)]$. As usual, Z can be replaced by its maximum term, and therefore the grand potential $\tilde{\Omega} = -\beta^{-1}\ln Z$ has a term $-Q\Delta\phi$. Had we used Q as an independent variable, the grand potential would have been Ω; now it is $\tilde{\Omega} = \Omega - Q\Delta\phi$. As a result of this Legendre transformation,

$$\gamma = \left(\frac{\partial\Omega}{\partial A}\right)_{m_a,m_b,V_a,V_b,Q} = \left(\frac{\partial\tilde{\Omega}}{\partial A}\right)_{m_a,m_b,V_a,V_b,\Delta\phi}. \tag{4.19}$$

Therefore, the surface part of $\tilde{\Omega}$ simply is $A\gamma(m_a,m_b,\Delta\phi)$.

The structure of Z gives the derivatives of γ as

$$-\beta m_a \frac{\partial\gamma}{\partial m_a} = \int_0^\infty dx[\rho_+(x) + \rho_-(x) - 2\rho_\pm^a],$$

(4.20)

$$-\beta m_b \frac{\partial\gamma}{\partial m_b} = \int_{-\infty}^0 dx[\rho_+(x) + \rho_-(x) - 2\rho_\pm^b],$$

(4.21)

plus the Lippmann equation (4.8).

For our model, we can, in principle, compute γ by starting from $m_a = m_b, \Delta\phi = 0$, in which case $\gamma = 0$, and integrating Eqs. (4.20), (4.21), and (4.8) to arbitrary values of the variables. However, for the sake of obtaining explicit results in terms of elementary functions, we shall content ourselves with sticking to equal bulk densities on each side of the interface, i.e., to $m_a = m_b = m$. Then, we obtain simply from Eqs. (4.8) and (4.17)

$$\beta\gamma = -\frac{m}{2}\left(\cosh\frac{\Delta\phi}{e} - 1\right).$$

(4.22)

Here too, γ is not positive, but this is not a problem for a rigid membrane.

It is remarkable that, except for numerical factors, the results (4.2) and (4.12) for the primitive electrode on one hand, and the results (4.18) and (4.22) for the polarizable interface (with equal bulk densities) on the other hand, have the same form.

V. CONCLUSION

In this paper, we have discussed at length the density profiles and the thermodynamics of several versions of our model for an electrified interface.

We can try to compare our two-dimensional exact results with the computer simulations[19,20] which have been performed in the three-dimensional case, for instance, for the density profiles near a charged hard wall. In both our two-dimensional case (Fig. 1) and the three-dimensional case, one sees the same qualitative feature: the counterions are attracted by the charged wall, while the coions are repelled. The detailed profiles, however, look different; in particular, as the wall is approached, the two-dimensional counterion density shows a maximum and then drops, while the three-dimensional counterion density rises monotonically.[19,20] We believe that these behaviors are different *not* because the dimensionality is different, but because the hard core is vanishingly small in our two-dimensional model. Indeed, in the zero hard core limit, the pressure has half the ideal gas value, and, from the contact theorem (3.13), the

densities at the wall have to be smaller than in the bulk, at least for moderate values of the surface charge density $e\sigma$. The three-dimensional calculations however, have been performed with sizeable hard cores, the pressure is close to its ideal gas value,[21] and there need not be a density drop near the wall.

Therefore, we consider that the main imperfection of our model is the absence of a hard core. On the contrary, we expect the reduced dimensionality to be rather unimportant, as long as we use, in ν dimensions, a ν-dimensional harmonic potential, i.e., a logarithmic potential in 2 dimensions.

We have also computed correlation functions. The correlations of any Coulomb system are supposed to obey a variety of sum rules[22] which are consequences of the screening effect. One should be able to check explicitly these sum rules for our model; this is left as an exercise for the reader.

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