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Surface Tension for the Two-Component Plasma at $\Gamma = 2$ near an Interface

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The grand partition function for the two-dimensional, two-component plasma at $\Gamma = 2$ is evaluated exactly in a finite system for various interfaces: a charged hard wall (the so-called primitive electrode model), a second two-component plasma of different fugacity separated by an impermeable membrane (the ideally polarizable interface), and a metal wall separated by an impermeable barrier. For each of these models the surface tension is calculated directly from the asymptotic expansion of the grand partition function.

KEY WORDS: Electrolyte; surface tension; exactly solved model; eigenvalue problem.

1. INTRODUCTION

The two-dimensional, two-component plasma is a model system of classical, oppositely charged point particles interacting via the logarithmic potential. In general the system is characterized by two dimensionless parameters—the coupling $\Gamma = q^2/kT$ (q is the magnitude of the charges) and the product of the density and the square of the hard-core diameter. A hard-core or similar short-distance regularization is necessary for couplings $\Gamma \geqslant 2$ to prevent collapse of the oppositely charged species. An alternative to regularizing the potential is to impose a lattice structure on the domain and constrain the oppositely charged particles to distinct sublattices.[1]

For $\Gamma < 2$, short-distance regularization of the logarithmic potential is unnecessary. The relevant density-like parameter is the fugacity ζ. The case $\Gamma = 2$ is special. Although collapse occurs, the resulting thermodynamic singularities are sufficiently weak (logarithmic) that the correlation

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functions are finite with ζ playing the role of the inverse correlation length.[2,3]

Another special feature of the isotherm $\Gamma = 2$ is that the system is exactly solvable: the pressure, density profiles, and correlation functions can all be computed,[1–6] The formalism is sufficiently general to allow for a variety interfaces.[2,6] Some examples are a charged wall[2,5] (the so-called primitive electrode model), a second two-component plasma of different fugacity separated by an impermeable membrane[2] (the ideally polarizable interface), and a metal wall separated by an impermeable barrier.[2,6]

Cornu and Jancovici[2] have provided the formalism necessary to calculate the density profiles and correlation functions ar $\Gamma = 2$. From the density profiles, an indirect calculation of the surface tension and equation of state is possible. This was given by Cornu and Jancovici for the primitive electrode and ideally polarizable interface models. However, the equation of state and surface tension should be obtainable directly from the grand partition function. Here we provide such a direct calculation of the surface tension for the primitive electrode, ideally polarizable interface, and metal wall models.

2. EVALUATION OF THE GRAND PARTITION FUNCTION FOR THE PRIMITIVE ELECTRODE AND IDEALLY POLARIZABLE INTERFACE

2.1. Reduction to an Eigenvalule Problem

Both the primitive electrode and the ideally polarizable interface models can be obtained from two-component plasma models with position-dependent fugacities.[2] We consider the two-dimensional, two-component plasma and for convenience choose the boundary conditions in the direction perpendicular to the wall (the x direction, say) to be periodic. The electrostatic potential $\phi(\mathbf{x}, \mathbf{x}')$ between a particle of charge q at $\mathbf{x} = (x, y)$ and a particle of charge q' at $\mathbf{x}' = (x', y')$ is then

$$\phi(\mathbf{x}, \mathbf{x}') = -qq' \log[|\sin(z - z')|(L/\pi)] \tag{2.1}$$

where the complex scaled coordinate z is defined by

$$z = \pi(x + iy)/L \tag{2.2}$$

and similarly for z'.

The Boltzmann factor for a symmetric mixture of N particles of charge q with scaled complex coordinates z_k and N particles of charge $-q$ with coordinates z'_k is thus

$$W_{N\Gamma} = \left(\frac{\pi}{L}\right)^{N\Gamma} \left| \frac{\prod_{1 \leqslant j < k \leqslant N} \sin(z_k - z_j) \sin(z'_k - z'_j)}{\prod_{j=1}^{N} \prod_{k=1}^{N} \sin(z_j - z'_k)} \right|^{\Gamma} \tag{2.3a}$$

$$= \left(\frac{\pi}{L}\right)^{N\Gamma} \left| \det \left[\frac{1}{\sin(z_j - z'_k)} \right]_{j,k=1,\ldots,N} \right|^{\Gamma} \tag{2.3b}$$

where to obtain (2.3b) a simple corollary of the Cauchy double alternative determinant formula has been used (see, e.g., ref. 4).

As commented in the Introduction, to obtain finite thermodynamics for couplings $\Gamma \geqslant 2$ it is necessary either to regularize the potential (2.1) at the origin for oppositely charged species or constrain the different species to distinct sublattices. The latter approach is required for exact calculations.

Thus, suppose the positive (negative) charged particles are confined to an $M_1 \times M_2$ lattice with scaled complex coordinates r_{ij} (s_{jk}), $j = 1,\ldots, M_1$, $k = 1,\ldots, M_2$, with $r_{jk} \neq s_{j'k'}$. The grand partition function with variable site fugacities $\zeta_+(r_{jk})$ and $\zeta_-(s_{jk})$ at each site of the sublattice available to the positive and negative charges, respectively, is then defined as

$$\Xi_\Gamma = \sum_{N=0}^{M_1 M_2} \left(\frac{\pi \tau_x \tau_y}{L}\right)^{2N} \sum_{z \in \{r\}} \sum_{z' \in \{s\}} \left[\prod_{l=1}^{N} \zeta_+(z_l) \zeta_-(z'_l) \right] W_{N\Gamma} \tag{2.4}$$

Here the sum over $z(z')$ consists of all distinct choices of N values of the scaled complex lattice coordinates r_{jk} (s_{jk}). The symbols τ_x and τ_y denote the average lattice spacing in the x and y directions, respectively.

At $\Gamma = 2$, using (2.3b), we recognise (2.4) as an expansion in minors of the determinants of a $2M_1M_2 \times 2M_1M_2$ matrix.[1] We have

$$\Xi_2 = \det(\mathsf{I}_{2M_1M_2} + \mathsf{K}) \tag{2.5a}$$

where

$$\mathsf{K} = \begin{bmatrix} \mathsf{O}_{M_1M_2} & \mathsf{K}_1 \\ \mathsf{K}_2 & \mathsf{O}_{M_1M_2} \end{bmatrix} \tag{2.5b}$$

with

$$\mathsf{K}_1 = \frac{\pi \tau_x \tau_y}{L} \frac{[\zeta_+(r_{jk})\, \zeta_-(s_{j'k'})]^{1/2}}{\sin \pi(r_{jk} - s_{j'k'})/L} \tag{2.5c}$$

and

$$\mathsf{K}_2 = \frac{\pi \tau_x \tau_y}{L} \frac{[\zeta_+(r_{j'k'})\, \zeta_-(s_{jk})]^{1/2}}{\sin \pi(s^*_{jk} - r^*_{j'k'})/L} \tag{2.5d}$$

In (2.5a), $\mathsf{I}_{2M_1M_2}$ denotes the identity matrix of order $2M_1M_2$, and in (2.5b), $\mathsf{O}_{M_1M_2}$ denotes the zero matrix of order M_1M_2.

Provided the position-dependent fugacities are real, the matrix K is anti-Hermitian. The corresponding eigenvalues λ_j are therefore pure imaginary and occur in complex conjugate pairs. Hence we have

$$\Xi_2 = \prod_{j=1}^{M_1M_2}{}^{*} (1 + |\lambda_j|^2) \tag{2.6}$$

where the asterisk in the product denotes the restriction $\mathrm{Im}(\lambda_j) > 0$, so the evaluation of the grand partition function at $\Gamma = 2$ has been reduced to the calculation of the eigenvalues of K.

2.2. The Continuum Limit

Suppose the lattice points r_{jk} and s_{jk} uniformly fill a rectangle of length L (the period) in the x direction and length $2W$ in the y direction. In the limit

$$M_1, M_2 \to \infty \qquad \text{(and thus } \tau_x, \tau_y \to 0) \tag{2.7}$$

the lattice structure becomes a continuum. Due to the short-ranged collapse of oppositely charged particles, the product (2.6) will diverge. However, the individual eigenvalues remain finite.

Explicitly, from (2.5), in the limit (2.7) the eigenvalue problem is to calculate the eigenvalues λ and eigenfunctions $(F(r, s),\ G(r, s))$ of the coupled integral equations

$$\frac{\pi}{L}\int_{-W}^{W} ds_1\, [\zeta_+(s_1)]^{1/2} \int_0^L dr_1 \frac{G(r_1, s_1)}{\sin \pi[r_2 - r_1 + i(s_2 - s_1)]/L} = \frac{\lambda F(r_2, s_2)}{[\zeta_-(s^2)]^{1/2}} \tag{2.8a}$$

and

$$\frac{\pi}{L}\int_{-W}^{W} ds_1\, [\zeta_-(s_1)]^{1/2} \int_0^L dr_1 \frac{F(r_1, s_1)}{\sin \pi[r_2 - r_1 - i(s_2 - s_1)]/L} = \frac{\lambda G(r_2, s_1)}{[\zeta_+(s_2)]^{1/2}} \tag{2.8b}$$

where we have written

$$\zeta_+(r, s) = \zeta_+(s) \qquad \text{and} \qquad \zeta_-(r, s) = \zeta_-(s) \tag{2.9}$$

and thus specialized to position-dependent fugacities which depend on the direction perpendicular to the interface—a valid choice for interface

models. The dependence on the difference variable in (2.8) and the periodicity of the sine function suggest that we seek eigenfunctions of the form

$$F(r, s) = e^{-2\pi i(p-1/2)r/L} X(s) \tag{2.10a}$$

$$G(r, s) = e^{-2\pi i(p-1/2)r/L} Y(s) \tag{2.10b}$$

where p is an integer.

Using the result that for $p \geqslant 1$ $(p < 1)$

$$\frac{1}{L}\int_0^L \frac{e^{2\pi i(p-1/2)r/L}}{\sin \pi(r+i\alpha)}\, dr = \begin{cases} 2i \operatorname{sgn}(p-1/2) e^{\pi\alpha(2p-1)/L}, & \alpha < 0 \ (\alpha > 0) \\ 0, & \alpha > 0 \ (\alpha < 0) \end{cases} \tag{2.11}$$

we find for the eigenvalue equation (2.8), for $p \geqslant 1$,

$$\int_{s_2}^{W} ds_1 \, [\zeta_+(s_1)]^{1/2} \, e^{-\mu s_1} Y(s_1) = \frac{1}{\nu} \frac{e^{-\mu s_2} X(s_2)}{[\zeta_-(s_2)]^{1/2}} \tag{2.12a}$$

$$\int_{-W}^{s_2} ds_1 \, [\zeta_-(s_1)]^{1/2} e^{\mu s_2} X(s_1) = \frac{1}{\nu} \frac{e^{\mu s_2} Y(s_2)}{[\zeta_+(s_2)]^{1/2}} \tag{2.12b}$$

where

$$\frac{1}{\nu} = \frac{\lambda}{2\pi i} \tag{2.13a}$$

and

$$\mu = \pi(2p-1)/L \tag{2.13b}$$

These integral equations are equivalent to a pair of coupled differential equations with some appropriate boundary conditions. This step is best performed when specific interface models are being considered.

2.3. The Primitive Electrode

The primitive electrode is a charged hard wall with surface charge $q\sigma$ at a boundary, which we will take to be $s = 0$, and a neutralizing surface charge $q\sigma$ at the other wall, $s = W$. This corresponds to the choice

$$\zeta_\pm(s) = \begin{cases} 0, & s < 0 \\ \zeta e^{\mp 4\pi\sigma s}, & s > 0 \end{cases} \tag{2.14}$$

Substituting (2.14) in (2.12) and differentiating with respect s_2 gives the coupled differential equations

$$Y(s_2) = \frac{1}{\zeta v} [\hat{\mu} X(s_2) - X'(s_2)] \tag{2.15a}$$

$$X(s_2) = \frac{1}{\zeta v} [\hat{\mu} Y(s_2) + Y'(s_2)] \tag{2.15b}$$

where

$$\hat{\mu} = \pi(2p-1)/L + 2\pi\sigma \tag{2.16}$$

These equations must be solved subject to the boundary conditions

$$Y(0) = 0 \tag{2.17a}$$

$$X(W) = 0 \tag{2.17b}$$

Combining (2.15a) and (2.15b) gives the second-order equation

$$Y''(s_2) + [(\zeta v)^2 - \hat{\mu}^2]\, Y(s_2) = 0 \tag{2.18}$$

The solution of (2.18) with boundary condition (2.17a) is

$$Y(s) = A \sin[(\zeta v)^2 - \hat{\mu}^2]^{1/2} s \tag{2.19}$$

Substituting (2.19) in (2.15b) and using the remaining boundary condition (2.15b) then gives the equation

$$\hat{\mu} \frac{\sin W[(\zeta v)^2 - \hat{\mu}^2]^{1/2}}{[(\zeta v)^2 - \hat{\mu}^2]^{1/2}} + \cos W[(\zeta v)^2 - \hat{\mu}^2]^{1/2} = 0 \tag{2.20}$$

Repeating the above working for $p < 1$, from (2.12) on, gives the same equation except that $\hat{\mu}$ is to be replaced by $-\hat{\mu}$.

For each integer p, and thus from (2.16) the permitted value of $\hat{\mu}$, (2.20) specifies an infinite set of the possible values of v, which from (2.13a) and the discussion immediately before (2.6) are real. The solutions of (2.20) are also discrete, so as well as being labeled by p, can be labeled by a further discrete index q. Hence from (2.13a) and (2.6) we have

$$\Xi = \prod_{p=-\infty}^{\infty} \prod_{q} \left[1 + \left(\frac{2\pi}{v_{p,q}} \right)^2 \right] \tag{2.21}$$

where the product over q is restricted to values such that $v_{p,q} > 0$.

2.4. The Ideally Polarizable Interface

The ideally polarizable interface consists of two distinct plasmas of different fugacities separated by an impermeable membrane. This can be obtained by the choice

$$\zeta_+(s)=\begin{cases}\zeta_+^{(a)}, & s<0\\ \zeta_+^{(b)}, & s>0\end{cases}\qquad \zeta_-(s)=\begin{cases}\zeta_-^{(a)}, & s<0\\ \zeta_-^{(b)}, & s>0\end{cases} \tag{2.22}$$

Differentiating (2.12) then gives

$$Y(s_2)=\frac{1}{\zeta_V^{(\chi)}}\left[\mu X(s_2)-X'(s_2)\right] \tag{2.23a}$$

$$X(s_2)=\frac{1}{\zeta_V^{(\chi)}}\left[\mu Y(s_2)+Y'(s_2)\right] \tag{2.23b}$$

where

$$\zeta^{(\chi)}=(\zeta_+^{(\chi)}\zeta_-^{(\chi)})^{1/2}$$

and $\chi=a$ for $-W\leqslant s_2<0$, while $\chi=b$ for $0<s_2\leqslant W$. Equations (2.23) are to be solved subject to the boundary conditions

$$Y(-W)=X(W)=0 \tag{2.24a}$$

and

$$\lim_{s\to 0^-}\frac{X(s)}{Y(s)}\left(\frac{\zeta_+^{(a)}}{\zeta_-^{(a)}}\right)^{1/2}=\lim_{s\to 0^+}\frac{X(s)}{Y(s)}\left(\frac{\zeta_+^{(b)}}{\zeta_-^{(b)}}\right)^{1/2} \tag{2.24b}$$

The condition (2.24b) follows from the conditions

$$X(0^+)/(\zeta_-^{(b)})^{1/2}=X(0^-)/(\zeta_-^{(a)})^{1/2} \tag{2.25a}$$

$$Y(0^-)/(\zeta_+^{(a)})^{1/2}=Y(0^+)/(\zeta_+^{(b)})^{1/2} \tag{2.25b}$$

which in turn follow from (2.12).

The method of solution of these differential equations and boundary conditions is the same as in the previous section. We find

$$Y(s)=A\sin([(\zeta^{(a)}v)^2-\mu^2]^{1/2}(s+W)),\qquad -W\leqslant s<0 \tag{2.26a}$$

$$X(s)=B\sin([(\zeta^{(b)}v)^2-\mu^2]^{1/2}(s-W)),\qquad 0<s\leqslant W \tag{2.26b}$$

Using (2.23) and (2.24b) then gives the equation

$$F(\zeta^{(a)}v)\,F(\zeta^{(b)}v)-\frac{\zeta^{(a)}}{\zeta^{(b)}}G(\zeta^{(a)}v)\,G(\zeta^{(b)}v)=0 \tag{2.27a}$$

where

$$F(t) = \mu \frac{\sin W(t^2 - \mu^2)^{1/2}}{(t^2 - \mu^2)^{1/2}} + \cos W(t^2 - \mu^2)^{1/2} \tag{2.27b}$$

$$G(t) = t \frac{\sin W(t^2 - \mu^2)}{(t^2 - \mu^2)^{1/2}} \tag{2.27c}$$

$$\hat{\zeta}^{(\chi)} = (\zeta_-^{(\chi)}/\zeta_+^{(\chi)})^{1/2} \tag{2.27d}$$

The same equation holds for $p < 1$ provided μ is replaced by $-\mu$ and $\hat{\zeta}^{(a)}$ is interchanged with $\hat{\zeta}^{(b)}$. Equation (2.27a) is analogous to (2.20) and thus the grand partition function can be written in terms of its solutions $v = v_{p,q}$ by (2.21).

3. ASYMPTOTIC EXPANSIONS AND THE SURFACE TENSION

3.1. The Surface Tension

With the grand potential defined by

$$\Omega = -\beta^{-1} \log \Xi \tag{3.1}$$

the surface tension γ is given by[2]

$$\gamma = \left(\frac{\partial \Omega}{\partial A} \right)_{\zeta, V, Q} \tag{3.2}$$

where A is the surface area which carries a uniform charge density $-q\sigma = -Q/A$.

For semiperiodic boundary conditions, with period L in the periodic direction and charged hard walls a distance W apart in the other direction, Ω has the large-volume expansion

$$\Omega \sim -LWp(\zeta) + 2L\omega_s(\zeta, \sigma) \tag{3.3}$$

where $p(\zeta)$ denotes the bulk pressure. From (3.2), and the dependence of σ on A, it follows from (3.3) that

$$\gamma = \left(1 - \sigma \frac{\partial}{\partial \sigma} \right) \omega_s(\zeta, \sigma) \tag{3.4}$$

Note from (3.3) that if we compute

$$\Omega_W := \lim_{L \to \infty} \frac{1}{L} \Omega \tag{3.5}$$

then the term independent of W in the large-W expansion of Ω_W is $2\omega_s(\zeta, \sigma)$.

For the ideally polarizable interface the independent variable is the potential drop $\Delta\phi$ and not the surface charge, so (3.2) is not directly applicable. In the semiperiodic boundary conditions of the exact calculation

$$\Omega \sim -LW(p(\zeta^{(a)}) + p(\zeta^{(b)})) + L[\omega_s(\zeta^{(a)}, \zeta^{(b)}, \Delta\phi) + \omega_s(\zeta^{(a)}, \sigma = 0) + \omega_s(\zeta^{(b)}, \sigma = 0)] \tag{3.6}$$

where the last two terms correspond to the surface term coming from the two hard walls. With the notation of (3.6), Cornu and Jancovici[2] have shown that the surface tension γ at the boundary between the two phases is given by

$$\gamma = \omega_s(\zeta^{(a)}, \zeta^{(b)}, \Delta\phi) \tag{3.7}$$

From (3.6), we see that, like $\omega_s(\zeta, \sigma)$, $\omega_s(\zeta^{(a)}, \zeta^{(b)}, \Delta\phi)$ can be obtained from the W-independent term of the large-W expansion of (3.5).

As commented in Section 2.2, the product over the eigenvalues (2.21) diverges in the continuum limit but each individual eigenvalue is finite. A way to avoid this divergence is to restrict the magnitude of p in (2.21) below some finite multiple, R say, of the length of the strip L. Then (3.5), (3.1), (2.1), (2.20), and (2.27) give

$$-\beta\Omega_W = \int_{-R}^{R} dt \sum_{q:\nu_{t,q}>0} \log\left[1 + \left(\frac{2\pi}{\nu_{t,q}}\right)^2\right] \tag{3.8}$$

where $\nu_{t,q}$ is the same as $\nu_{p,q}$, except $(p - 1/2)/L$ is replaced by t, and is thus given by (2.20) for the primitive electrode and by (2.27) for the ideally polarizable interface. It will be seen below that the surface tension is finite in the limit $R \to \infty$.

3.2. A Closed-Form Summation

The sum over the roots of Eqs. (2.20) and (2.27) in (3.8) can be obtained in a particularly simple closed form, which is a special case of the following result.

Theorem 1. Let $f(z)$ be an analytic function of z which has the large-$|z|$ behavior

$$\frac{f'(Re^{i\theta})}{f(Re^{i\theta})} \sim \begin{cases} c, & 0 < \theta < \pi \\ -c, & \pi < \theta < 2\pi \end{cases} \tag{3.9}$$

where c is a constant, and suppose $f(\gamma) \neq 0$ for $\gamma = it$, $-2\pi \leqslant t \leqslant 0$. Then

$$S := \sum_{\gamma : f(\gamma)=0} \log\left(1 + \frac{2\pi i}{\gamma}\right) \tag{3.10}$$

has the closed-from evaluation

$$S = \log[f(-2\pi i)/f(0)] \tag{3.11}$$

Proof. By the residue theorem

$$S = \lim_{r\to\infty} \lim_{\varepsilon \to 0^+} \frac{1}{2\pi i}\left(\int_{A_\varepsilon(r)} + \int_{B_\varepsilon(r)}\right) \frac{f'(z)}{f(z)} \log\left(1 + \frac{2\pi i}{z}\right) dz \tag{3.12}$$

where $A_\varepsilon(r)$ is the contour which runs from $ir + \varepsilon$ parallel to the imaginary axis to $-it + \varepsilon$ and then along a half-circle in the right half-plane back to $ir + \varepsilon$, while $B_\varepsilon(r)$ is the contour which runs from $-ir - \varepsilon$ parallel to the imaginary axis to $ir - \varepsilon$ and then along a half-circle in the left half-plane back to $-ir + \varepsilon$.

The value of the contour integrations along the half-circles can be obtained by replacing $\log(1 + 2\pi i/z)$ by its leading-order term $2\pi i/z$. Thus, in the limit $r \to \infty$, these contours contribute

$$i \int_0^{2\pi} \left(\lim_{r\to\infty} \frac{f'(re^{i\theta})}{f(re^{i\theta})}\right) d\theta \tag{3.13}$$

which, by hypothesis (3.9) of the theorem, equals zero.

In the limit $\varepsilon \to 0^+$, the contributions from the contours along the imaginary axis cancel for $\mathrm{Im}(z) > 0$ and $\mathrm{Im}(z) < -2\pi$ when the argument of the logarithm is positive. A nonzero contribution to (3.12) thus comes entirely from the integration along the imaginary axis, in the limit $\varepsilon \to 0^+$, for $-2\pi < \mathrm{Im}(z) < 0$. Since, for $-2\pi < t < 0$,

$$\lim_{\varepsilon \to 0^+} \log\left(1 + \frac{2\pi i}{it + \varepsilon}\right) = \pi i \tag{3.14}$$

while

$$\lim_{\varepsilon \to -0^+} \log\left(1 + \frac{2\pi i}{it - \varepsilon}\right) = -\pi i \tag{3.15}$$

we have

$$S = -i \int_{-2\pi}^{0} \frac{f'(it)}{f(it)}\, dt \tag{3.16}$$

The result (3.11) follows immediately.

3.3. The Exact Evaluations

First consider the primitive electrode. Theorem 1, (2.20), and the remark after (3.5) give

$$-2\beta\omega_s(\zeta,\sigma)=\int_0^R dt\,\log\left(\{1+(t+\sigma)/[\zeta^2+(t+\sigma)^2]^{1/2}\}/2\right)$$
$$+\int_0^R dt\,\log\left(\{1+(t-\sigma)/[\zeta^2+(t-\sigma)^2]^{1/2}\}/2\right) \tag{3.17}$$

As commented in Section 3.1, these integrals are convergent in the limit $R\to\infty$ and thus the surface tension is cutoff-independent. Also, the integrals can then be evaluated explicitly, and we obtain

$$\omega_s(\zeta,\sigma)=\pi\zeta/2+\sigma\sinh^{-1}(\sigma/\zeta)-(\zeta^2+\sigma^2)^{1/2} \tag{3.18}$$

Identifying $2\pi\zeta$ with m, we see that this result is identical to that obtained by Cornu and Jancovici[2] [Eq. (4.11)] using an indirect approach.

For the ideally polarizable interface, Theorem 1, (2.27), (3.6), and (3.18) with $\sigma=0$ give

$$\beta\omega_s(\zeta^{(a)},\zeta^{(b)},\Delta\phi)$$
$$=-\int_0^\infty dt\,[\log F(t,\zeta^{(a)},\zeta^{(b)},\hat\zeta^{(a)}/\hat\zeta^{(b)})$$
$$+\log F(t,\zeta^{(a)},\zeta^{(b)},\hat\zeta^{(b)}/\hat\zeta^{(a)})]+(1-\pi/2)(\zeta^{(a)}+\zeta^{(b)}) \tag{3.19a}$$

where

$$F(t,\zeta^{(a)},\zeta^{(b)},\hat\zeta^{(a)}/\hat\zeta^{(b)})$$
$$=(\{1+t[(\zeta^{(a)})^2+t^2]^{-1/2}\}\{1+t[(\zeta^{(b)})^2+t^2]^{-1/2}\}$$
$$+\zeta^{(a)}\zeta^{(b)}\frac{\hat\zeta^{(a)}}{\hat\zeta^{(b)}}[(\zeta^{(a)})^2+t^2]^{-1/2}[(\zeta^{(b)})^2+t^2]^{-1/2})/4 \tag{3.19b}$$

The quantity $\hat\zeta^{(a)}/\hat\zeta^{(b)}$, defined in terms of the fugacities by (2.27d), is related to $\Delta\phi$ by[7,8]

$$\hat\zeta^{(a)}/\hat\zeta^{(b)}=e^{\beta q\Delta\phi} \tag{3.20}$$

In general the integral in (3.19a) cannot be evaluated explicitly. However, the special case of equal bulk fugacities $\zeta^{(a)}=\zeta^{(b)}=\zeta$ does allow an explicit evaluation. This is accomplished by substituting (3.20) in

(3.19b) and the taking the partial derivative of (3.19a) with respect to $\beta q \Delta\phi$. Changing variables $t = \sinh s$ gives

$$\frac{\partial \beta\omega_s(\zeta, \zeta, \Delta\phi)}{\partial(\beta q \Delta\phi)} = -\zeta \sinh \beta q \Delta\phi \int_0^\infty ds \frac{\cosh s}{\cosh 2s + \cosh \beta q \Delta\phi} \tag{3.21a}$$

$$= -\tfrac{1}{2}\pi\zeta \sinh(\beta q \Delta\phi/2) \tag{3.21b}$$

where (3.21b) follows from (3.21a) by using contour integration. Since $\omega_s(\zeta, \zeta, 0) = 0$ [this can be shown directly from (3.19a)] we thus have

$$\beta\omega_s(\zeta, \zeta, \Delta\phi) = -\pi\zeta(\cosh(\beta q \Delta\phi/2) - 1) \tag{3.22}$$

in agreement with the result obtained by Cornu and Jancovici [Eq. (4.22), with $m = 2\pi\zeta$] using an indirect approach.

4. THE METAL WALL

Here we will consider the two-dimensional, two-component plasma at $\Gamma = 2$ separated by an impermeable wall of thickness ε from a metal wall which occupies the half-plane $y < 0$. Suppose the positive (negative) particles are confined to an $M_1 \times M_2$ sublattice with complex coordinates r_{jk} (s_{jk}), $j = 1,..., M_1$, $k = 1,..., M_2$, and $\mathrm{Im}(r_{jk})$, $\mathrm{Im}(s_{jk}) \geqslant \varepsilon$, which uniformly fill a $L \times W$ rectangle separated by a distance ε from the metal wall. A formula for the grand partition function in terms of a determinant, analogous to (2.5), can be given.

Modifying the results of ref. 6 to account for semiperiodic boundary conditions, we have

$$\Xi_2 = \det\left(\mathsf{I}_{2M_1M_2} + \frac{\pi\tau_x\tau_y}{L}\begin{bmatrix}\mathsf{K}_1 & \mathsf{K}_2\\ \mathsf{K}_3 & \mathsf{K}_4\end{bmatrix}\right) \tag{4.1a}$$

where

$$\mathsf{K}_1 = i\zeta_+\left[\frac{1}{\sin(\pi(r_{jk} - r^*_{j'k'})/L)}\right], \qquad \mathsf{K}_2 = i\zeta_+\left[\frac{1}{\sin(\pi(r_{jk} - s_{j'k'})/L)}\right]$$

$$\mathsf{K}_3 = -i\zeta_-\left[\frac{1}{\sin(\pi(s^*_{jk} - r^*_{j'k'})/L)}\right], \qquad \mathsf{K}_4 = -i\zeta_-\left[\frac{1}{\sin(\pi(s^*_{jk} - s_{j'k'})/L)}\right] \tag{4.1b}$$

In terms of the eigenvalues λ_j of the block matrix in (4.1a), we therefore have

$$\Xi_2 = \prod_{j=1}^{2M_1M_2}(1 + \lambda_j) \tag{4.1c}$$

Unlike (2.5a), the block matrix in (4.1a) is not anti-Hermitian, so no pairing of the eigenvalues in (4.1c) is possible.

Analogous to (2.8a), in the continuum limit the eigenvalue problem takes the form of calculating the eigenvalues λ and the eigenfunctions $(F(r, s), G(r, s))$ of the coupled integral equations

$$\frac{\pi}{L}\int_{\varepsilon}^{\varepsilon+W} ds_1 \int_0^L dr_1 \frac{F(r_1, s_1)}{\sin \pi[r_2 - r_1 + i(s_2 + s_1)]/L} + \frac{\pi}{L}\int_{\varepsilon}^{\varepsilon+W} ds_1 \int_0^L dr_1 \frac{G(r_1, s_1)}{\sin \pi[r_2 - r_1 + i(s_2 - s_1)]/L} = \frac{\lambda}{i\zeta_+} F(r_2, s_2) \tag{4.2a}$$

and

$$\frac{\pi}{L}\int_{\varepsilon}^{\varepsilon+W} ds_1 \int_0^L dr_1 \frac{F(r_1, s_1)}{\sin \pi[r_2 - r_1 - i(s_2 - s_1)]/L} + \frac{\pi}{L}\int_{\varepsilon}^{\varepsilon+W} ds_1 \int_0^L dr_1 \frac{G(r_1, s_1)}{\sin \pi[r_2 - r_1 - i(s_2 + s_1)]/L} = -\frac{\lambda}{i\zeta_-} G(r_2, s_2) \tag{4.2b}$$

The method of solution of these equations is very similar to that of (2.8) specified from (2.10) above. The eigenfunctions are again of the form (2.10). Defining v and μ by (2.13a) and (2.13b), respectively, and writing

$$\zeta = (\zeta_+ \zeta_-)^{1/2}, \qquad \hat{\zeta} = (\zeta_-/\zeta_+)^{1/2} \tag{4.3}$$

we find that for $p \geqslant 1$ the allowed values of v are specified by the equation

$$(iv\zeta\hat{\zeta}e^{-2\mu\varepsilon} + \mu)\frac{\sin \pi W[(v\zeta)^2 - \mu^2]^{1/2}}{[(v\zeta)^2 - \mu^2]^{1/2}} + \cos \pi W[(v\zeta)^2 - \mu^2]^{1/2} = 0 \tag{4.4}$$

For $p < 1$ the same equation holds except that μ is to be replaced by $-\mu$ and $\hat{\zeta}$ by $1/\hat{\zeta}$.

For large volumes, the grand potential (3.1) should have the behavior

$$\Omega \sim -LWp(\zeta) + L(\omega_s(\zeta, \Delta\phi) + \omega_s(\zeta, \sigma = 0)) \tag{4.5}$$

Thus, to calculate $\omega_s(\zeta, \Delta\phi)$, which due to its functional dependence on $\Delta\phi$ rather than σ is related to the surface tension by (3.7), we again want the term independent of W in the large-W expansion of

$$-\beta\Omega_W = \int_{-R}^{R} dt \sum_{q: f(\gamma_{t,q})=0} \log\left(1 + \frac{2\pi i}{v_{t,q}}\right) \tag{4.6}$$

where $f(\gamma_{t,q})$ denotes the LHS of (4.4) and the meaning of t, q, and R is the same as in Section 3.1. Thus sum in (4.6) can be evaluated using Theorem 1. We thus obtain

$$\beta\omega_s(\zeta, \Delta\phi) = -\int_0^\infty dt\,[g(t, \hat{\zeta}) + g(t, 1/\hat{\zeta})] + (1 - \pi/2)\zeta \tag{4.7a}$$

where

$$g(t, \hat{\zeta}) = \log\left\{\frac{1}{2}\left[1 + \frac{\zeta\hat{\zeta}e^{-4\pi t\varepsilon} + t}{(\zeta^2 + t^2)^{1/2}}\right]\right\} \tag{4.7b}$$

and the quantity $\hat{\zeta}$ is related to $\Delta\phi$ by

$$\hat{\zeta} = e^{-\beta q \Delta\phi} \tag{4.7c}$$

5. COMPARISON OF RESULTS

The ideally polarizable interface and metal wall are natural functions of the potential drop $\Delta\phi$, whereas the charged wall is a natural function of the excess surface charge density $q\sigma$. In the latter system the two quantities are related by the general sum rule[2,9]

$$\frac{\partial\omega_s(\zeta, \sigma)}{\partial q\sigma} = \Delta\phi \tag{5.1}$$

which from (3.19) gives

$$\sigma = \zeta \sinh(2\Delta\phi/q) \tag{5.2}$$

This is in agreement with the formula obtained obtained by calculating $\Delta\phi$ directly from the particle densities [ref. 2, Eq. (4.1)].

The excess charge densities for the ideally polarizable interface and the metal wall can be calculated from the exact expressions (3.20) and (4.7) for the surface tension by using the Lippmann equation

$$\frac{\partial\gamma}{\partial\Delta\phi} = -q\sigma \tag{5.3}$$

In general, no explicit evaluation of the resulting integrals is possible. An exception is the ideally polarizable interface with equal bulk densities, in which case we obtain

$$\sigma = (\pi\zeta/2)\sinh(\Delta\phi/q) \tag{5.4}$$

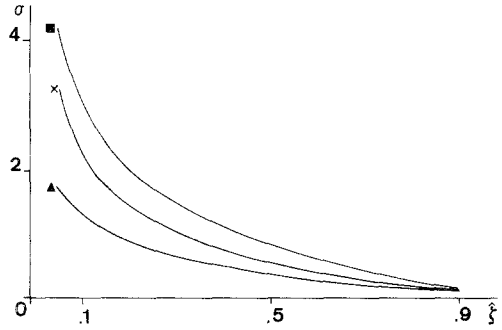

Fig. 1. Plot of the excess surface density σ as a function of $\hat{\zeta} = e^{-\beta q \Delta\phi}$ for the ideally polarizable interface with equal bulk densities (crosses) and the metal wall with an impermeable barrier of size $4\pi\varepsilon = 1$ (triangles) and $4\pi\varepsilon = 0.25$ (squares). In both cases $\zeta = 1$.

in agreement with ref. 2 [Eq. (4.17)]. A comparison of the dependence of σ on the quantity $\hat{\zeta}$, (4.7c), is given in Fig. 1 for the ideally polarizable interface with equal bulk densities and the metal wall.

The differential capacity is defined as

$$C = \frac{\partial q\sigma}{\partial \Delta\phi} \tag{5.5}$$

For the primitive electrode and the ideally polarizable interface with equal bulk fugacities we have from (5.2) and (5.4)

$$C = 2\zeta \cosh(2\Delta\phi/q) \tag{5.6a}$$

and

$$C = (\pi\zeta/2) \cosh(\Delta\phi/q) \tag{5.6b}$$

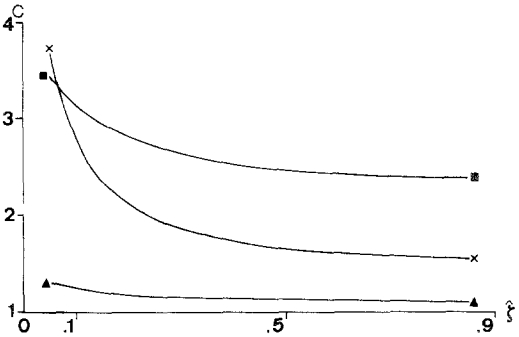

Fig. 2. Plot of the differential capacity C as a function of $\hat{\zeta} = e^{-\beta q \Delta\phi}$. The particular systems and notation are the same as for Fig. 1.

respectively [these results are also given in ref. 2, Eqs. (4.2) and (4.18)]. For the metal wall C can be calculated by using (4.7), (5.3), and (5.5). A comparison with (5.6b) is given in Fig. 2.

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