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The two-dimensional one-component plasma at $\Gamma = 2$: metallic boundary

P J Forrester

Department of Theoretical Physics, Research School of Physical Sciences, The Australian National University, Canberra, ACT 2601, Australia

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Abstract. The two-dimensional one-component plasma near a metal wall is exactly solvable at a special value of the coupling constant. We calculate the grand canonical partition function and correlation functions in strip geometry along the interface. By taking the strip width to infinity we obtain the exact statistical mechanics of a model of the metal-electrolyte boundary. Sum rules are discussed.

1. Introduction

The simplest model of a Coulomb system is the one-component plasma (OCP): N mobile particles of charge q immersed in a neutralising background charge density. The two-dimensional version (logarithmic potential), at the special value of the coupling constant $\Gamma \equiv q^2/k_B T = 2$, has the feature of being exactly solvable for a variety of different boundary conditions (Jancovici 1982a, Smith 1982, Rosinberg and Blum 1984, Alastuey and Lebowitz 1984).

One such instance is the ideally polarisable interface of Rosinberg and Blum (1984). This model consists of two OCPs of different background densities separated by an impermeable membrane. Despite the idealisations inherent in the model, it has the virtue of reproducing from a microscopic description some of the main features of the metal-electrolyte boundary. In particular, one deduces that the natural external variable of the system is the potential drop. This is contrary to the case of electrolytes near dielectric boundaries where the excess surface charge is the external variable.

In this paper further exactly solvable cases of the two-dimensional OCP at $\Gamma = 2$ are presented. We consider an explicit model of the metal-electrolyte boundary where the image forces induced by the conductor are written down in the Hamiltonian. The grand canonical partition function and distribution functions are first calculated for the plasma confined to strip of width W separted from the metal boundary by a distance ε. Also present inside the strip is a uniform background of variable charge density $-q\eta$ (the feature that the background charge density is variable instead of being fixed by charge neutrality is unique to the metallic boundary conditions). The two-dimensional model of the metal-electrolyte boundary is then obtained by taking the strip width to infinity.

In the strip geometry we can choose the background charge density to be equal to zero and take $W \to \infty$, permitting only a finite number of particles per unit length of the metal interface. We then obtain a model of bare charges confined in the vicinity of a metal interface by image forces.

2. Evaluation of the grand canonical partition function and N-particle correlations

2.1. The Hamiltonian

Two distinct geometries have been used in the exact calculations involving boundaries presented so far. The first and most used has been the disc, which in the exactly solvable cases allows integrations in the angular direction to be performed very easily (all references given in § 1 use the disc geometry). One is then left with a product of decoupled integrals in the radial direction, and the behaviour of these integrals in the thermodynamic limit is determined using Laplace's method. A second approach is to use semiperiodic boundary conditions (Choquard 1981, Choquard *et al* 1983). This again allows integrations in one direction to be performed very easily and again leaves us with a product of decoupled integrals. However, the integrals are such that determining their asymptotic behaviour requires no further manipulation, which is thus a simplification over the use of disc geometry. (In the formulation of Choquard *et al* (1983) it was necessary to order the integrations in the direction perpendicular to the periodic boundary conditions. This can be avoided as we will show here.)

Suppose that a perfect conductor occupies the half-plane $x<0$ in the xy plane. Let N particles of charge q occupy the rectangle $\varepsilon < x < W+\varepsilon$, $0<y<L$, and impose periodic boundary conditions in the y direction. Further suppose that the rectangle is filled with a uniform background of charge density $-q\eta$ (this background is not a neutralising background, but one independent of the N charges). The pair potential consists of a particle-particle and a particle-image term. We have (Choquard *et al* 1983)

$$\begin{aligned}\phi(\boldsymbol{x}, \boldsymbol{x}') = -\tfrac{1}{2}q \log[\![\{2\cosh[(2\pi/L)(x-x')] - 2\cos[(2\pi/L)(y-y')]\}(L/2\pi)^2]\!] \\ +\tfrac{1}{2}q \log[\![\{2\cosh[(2\pi/L)(x+x')] - 2\cos[(2\pi/L)(y-y')]\}(L/2\pi)^2]\!] \quad (2.1)\end{aligned}$$

where

$$\boldsymbol{x} = (x, y), \qquad \boldsymbol{x}' = (x', y'). \quad (2.2)$$

The constants in the terms corresponding to the particle-particle and particle-image interactions have been chosen so that in the limit $L\to\infty$ these terms reduce to

$$-\tfrac{1}{2}q \log[(x-x')^2+(y-y')^2] \qquad \text{and} \qquad -\tfrac{1}{2}q \log[(x+x')^2+(y-y')^2] \quad (2.3)$$

respectively.

Using (2.1) to compute the Hamiltonian H we find (taking special care of the self-energies)

$$\begin{aligned}H = -\tfrac{1}{2}q^2 \sum_{1\le j<k\le N} \log\left(\frac{(z_j-z_k)(z_j^*-z_k^*)}{(1-z_jz_k^*)(1-z_j^*z_k)}\right) + \tfrac{1}{2}q^2\sum_{k=1}^{N}\log(1-z_kz_k^*) + \tfrac{1}{2}q^2\left(\frac{2\pi}{L}\right)\sum_{k=1}^{N} x_k \\ + q^2\pi\eta\sum_{k=1}^{N}[x_k^2 - 2(W+\varepsilon)x_k + \varepsilon^2] + \tfrac{1}{2}q^2\pi\eta^2 L(\tfrac{2}{3}W^3 + 2\varepsilon W^2) \\ +\tfrac{1}{2}q^2 N\log(L/2\pi) \quad (2.4)\end{aligned}$$

where

$$z_k = \exp[-2\pi(x_k + \mathrm{i}y_k)/L]. \quad (2.5)$$

2.2. The grand canonical partition function and distribution functions in the finite system

In general the grand canonical partition function is defined as

$$\Xi = \sum_{N=0}^{\infty} \zeta^N I_{N,0} \tag{2.6}$$

and the distribution functions (in the grand canonical ensemble) are given by

$$\rho_n(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_n) = \frac{1}{\Xi} \sum_{N=n}^{\infty} \zeta^N I_{N,n} \tag{2.7}$$

where

$$I_{N,n} = \frac{1}{(N-n)!} \prod_{l=n+1}^{N} \int_{\Omega} \mathrm{d}\boldsymbol{x}_l \exp(-H/k_{\mathrm{B}}T) \tag{2.8}$$

and ζ denotes the activity.

Using an integration procedure due to Gaudin (1966) we can obtain tractable expressions for the quantities (2.6) and (2.7) when H is given by (2.4) and $k_{\mathrm{B}}T$ by

$$q^2/k_{\mathrm{B}}T = 2. \tag{2.9}$$

Inserting (2.4) and (2.9) in (2.8) we have

$$I_{N,n} = \frac{AB^N}{(N-n)!} \prod_{l=n+1}^{N} \int_{\varepsilon}^{W+\varepsilon} \mathrm{d}x_l \int_0^L \mathrm{d}y_l \left(\prod_{j=1}^{N} f(x_j) \right) C(z) \tag{2.10}$$

where

$$A = \exp[\pi\eta^2 L(-\tfrac{2}{3}W^3 - 2\varepsilon W^2)] \tag{2.11}$$

$$B = (2\pi/L)\exp(-2\pi\eta\varepsilon^2) \tag{2.12}$$

$$f(x_j) = \exp\{-2\pi\eta[x_j^2 - 2(W+\varepsilon)x_j] + 2\pi x_j/L\} \tag{2.13}$$

$$C(z) = \prod_{1 \le j < k \le N} (z_j - z_k)(z_j^* - z_k^*) \left(\prod_{j,k=1}^{N} (1 - z_j z_k^*) \right)^{-1}. \tag{2.14}$$

However, $C(z)$ is the Cauchy double alternant. Thus

$$\begin{aligned} C(z) &= \det[(1 - z_j z_k^*)^{-1}]_N \\ &= \sum_{P=1}^{N!} \varepsilon(P) \prod_{l=1}^{N} (1 - z_l z_{P(l)}^*)^{-1} \end{aligned} \tag{2.15}$$

where $\varepsilon(P)$ denotes the parity of the permutation P. Substituting (2.5) for z_l in (2.15) and then Taylor expanding the denominator we have

$$\begin{aligned} C(z) &= \sum_{P=1}^{N!} \varepsilon(P) \sum_{\alpha_1,\ldots,\alpha_N \ge 0}^{\infty} \prod_{l=1}^{N} \exp[-2\pi(x_l + x_{P(l)})\alpha_l/L] \exp[-2\pi \mathrm{i}(y_l - y_{P(l)})\alpha_l/L] \\ &= \sum_{\alpha_1,\ldots,\alpha_N \ge 0}^{\infty} \sum_{P=1}^{N!} \varepsilon(P) \prod_{l=1}^{N} \exp[-2\pi x_{P(l)}(\alpha_{P(l)} + \alpha_l)/L] \\ &\quad \times \exp[-2\pi \mathrm{i} y_{P(l)}(\alpha_{P(l)} - \alpha_l)/L] \\ &= \sum_{\alpha_1,\ldots,\alpha_N \ge 0}^{\infty} \det[\exp[-2\pi x_j(\alpha_j + \alpha_k)/L] \\ &\quad \times \exp[-2\pi \mathrm{i} y_j(\alpha_j - \alpha_k)/L]]_N. \end{aligned} \tag{2.16}$$

Substituting (2.16) in (2.10) we can perform the y integrations row-by-row to obtain

$$I_{N,n}=\frac{AB^NL^{N-n}}{(N-n)!}\sum_{\alpha_1,\dots,\alpha_N\geq 0}\det[g_{jk}]_N \tag{2.17}$$

where for each $k=1,2,\dots,N$

$$g_{jk}=f(x_j)\exp[-2\pi x_j(\alpha_j+\alpha_k)/L]\exp[-2\pi \mathrm{i} y_j(\alpha_j-\alpha_k)/L] \qquad j=1,2,\dots,n \tag{2.18}$$

$$g_{jk}=\delta_{\alpha_j,\alpha_k}\left(\int_\varepsilon^{\varepsilon+W}\mathrm{d}x\, f(x)\exp[-2\pi x(\alpha_j+\alpha_k)/L]\right) \qquad j=n+1,\dots,N \tag{2.19}$$

where δ denotes the Kronecker delta. We observe that if $\alpha_a=\alpha_b$ for any $1\leq a,b\leq N$ $(a\neq b)$ in (2.17) then either the ath row and bth rows are identical, or the ath column and bth columns are identical. Thus the only non-zero contribution in (2.17) from the rows $n+1\leq j\leq N$ comes from the diagonal entries. Hence, after expanding out those terms we have

$$I_{N,n}=AB^NL^{N-n}\sum_{\alpha_1,\dots,\alpha_n\geq 0}\det[g_{jk}]_n \times\sum_{0\leq\alpha_{n+1}<\dots<\alpha_N}\prod_{j=n+1}^{N}\left(\int_\varepsilon^{W+\varepsilon}\mathrm{d}x\, f(x)\exp(-4\pi x\alpha_j/L)\right). \tag{2.20}$$

From (2.20) we obtain the result that $I_{N,n}$ is the coefficient of ζ^N in the power-series expansion of the function

$$A(\zeta B)^n\prod_{l=0}^{\infty}\left(1+\zeta LB\int_\varepsilon^{\varepsilon+W}\mathrm{d}x\, f(x)\exp(-4\pi xl/L)\right) \times\sum_{\alpha_1,\dots,\alpha_n\geq 0}\left[\prod_{l=1}^{n}\left(1+\zeta LB\int_\varepsilon^{\varepsilon+W}\mathrm{d}x\, f(x)\exp(-4\pi x\alpha_l/L)\right)^{-1}\right] \times\det[g_{jk}]. \tag{2.21}$$

But from (2.6) $I_{N,0}$ is the coefficient of ζ^N in the function Ξ. Hence equating (2.21) with $n=0$ to (2.6) we have

$$\Xi=A\prod_{l=0}^{\infty}\left(1+\zeta LB\int_\varepsilon^{\varepsilon+W}\mathrm{d}x\, f(x)\exp(-4\pi xl/L)\right) \tag{2.22}$$

where A, B and $f(x)$ are specified by (2.11), (2.12) and (2.13), respectively.

If we divide (2.21) with $n\geq 1$ by (2.22) and compare with (2.7) we see the resulting expression is the n-particle distribution function. Thus, after noting

$$\det[g_{jk}]_n=\det[a_{jk}]_n \tag{2.23}$$

where

$$a_{jk}=f(x_j)\exp[-2\pi(x_j+x_k)\alpha_j/L]\exp[-2\pi \mathrm{i}(y_j-y_k)\alpha_j/L], \tag{2.24}$$

we have

$$\rho_n(\boldsymbol{x}_1,\dots,\boldsymbol{x}_n)=\det[h_{jk}]_n \tag{2.25}$$

where

$$h_{jk}=\sum_{l=0}^{\infty}B\zeta a_{jk}\left(1+\zeta LB\int_\varepsilon^{\varepsilon+W}\mathrm{d}x\, f(x)\exp(-4\pi x\alpha_l/L)\right)^{-1}. \tag{2.26}$$

2.3. *The large-L limit*

In the limit $L \to \infty$ the periodic boundary conditions recede to infinity, and we obtain the statistical mechanics of an infinite strip (in length) of width W, separted from a metal wall by a distance ε.

Note that the boundary conditions are inhomogeneous, there being a metal wall on one side of the container and a hard wall on the other, which implies the pressure is anisotropic. The force per unit length exerted by the system on the wall closest to the metal boundary will be different from that exerted on the other wall. Thus the usual expression for the pressure of a two-dimensional system

$$(LW)^{-1} \log(\Xi) \tag{2.27}$$

is not applicable, since it assumes homogeneous boundary conditions.

If the strip width was taken to zero we could define the pressure p as

$$\beta p = \lim_{L \to \infty} L^{-1} \log(\Xi) \tag{2.28}$$

where, as usual, $\beta = 1/k_B T$. For the system with non-zero width we calculate (2.28) and call p the one-dimensional pressure. It represents the force the system exerts at one end of the strip. We have from (2.22), after noting that the sum resulting from taking the logarithm tends to a Riemann integral,

$$\beta p = -\pi\eta^2(\tfrac{2}{3}W^3 + 2W^2\varepsilon) + \frac{\eta}{\kappa}\int_{-W\kappa}^{\infty} dt \log\left(1 + \frac{\pi^{3/2}\zeta}{\kappa}\exp(t^2 - 2\kappa\varepsilon t)(\operatorname{erf}(t + \kappa W) - \operatorname{erf}(t))\right). \tag{2.29}$$

Here we have introduced the notation

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x \exp(-t^2)\, dt \tag{2.30}$$

and

$$\kappa = (2\pi\eta)^{1/2}. \tag{2.31}$$

Furthermore, in the limit $L \to \infty$,

$$h_{jk} = \kappa\zeta \exp\{-\kappa^2[x_j^2 - 2(W + \varepsilon)x_j] - (\kappa\varepsilon)^2\} \times \int_{-W\kappa}^{\infty} dt \frac{\exp\{-\kappa[(x_j + x_k) + i(y_j - y_k)](t + \kappa W)\}}{1 + (\pi^{3/2}\zeta/\kappa)\exp(t^2 - 2\kappa\varepsilon t)(\operatorname{erf}(t + \kappa W) - \operatorname{erf}(t))}. \tag{2.32}$$

Substituting (2.32) into (2.25) give the n-particle distribution functions in the limit $L \to \infty$.

In defining the potential (2.1) we have set the arbitrary length scale L' of the two-dimensional Coulomb potential equal to one. Keeping L' arbitrary merely has the effect of replacing ζ in the above working by ζ/L'. Thus we see the integrals in (2.29) and (2.32) are dimensionless.

3. Zero background charge density—charges near a metal wall

3.1. Thermodynamics

If we choose $\eta=0$ in the preceding results we obtain the statistical mechanics of charged particles in the vicinity of a metal interface. From (2.1) the pair potential for large distances r along the interface behaves as $1/r^2$. Thus in a strip of finite width W the potential is integrable and the system thus has well behaved thermodynamics. In particular the Mayer series and virial series are convergent for small enough activities and densities, respectively.

From (2.29) we have when $\eta=0$ and $\Gamma=2$

$$\beta p=\frac{1}{4\pi W}\int_0^\infty \mathrm{d}t\log\left(1+\frac{2\pi\zeta W}{t}\exp[-t(\varepsilon/W)](1-\exp(-t))\right) \tag{3.1}$$

and hence the linear density (i.e., the number of particles per unit length of the strip)

$$\mu=\zeta\frac{\partial}{\partial\zeta}(\beta p)=\frac{1}{2W}\int_0^\infty \mathrm{d}t\frac{\exp[-t(\varepsilon/W)](1-\exp(-t))}{(t/W\zeta)+2\pi\exp[-t(\varepsilon/W)](1-\exp(-t))}. \tag{3.2}$$

The expansion of (3.2) as a power series in ζ is known as the Mayer series. The radius of convergence is obvious from the integral representation (3.1). Denote

$$M=\max_{t\in[0,\infty)}\frac{\exp[-t(\varepsilon/W)]}{t}(1-\exp(-t)). \tag{3.3}$$

Then the Mayer series converge for all ζ such that

$$|\zeta|<\frac{1}{2\pi M}\left(\frac{L'}{W}\right) \tag{3.4}$$

where L' is the arbitrary length scale discussed in § 2.3.

From (3.2) we can readily calculate ζ as a function of μ to second order, and hence by substituting into the Mayer series deduced from (3.1) the virial expansion

$$\beta p=\mu+2\pi W\left(\frac{\int_0^\infty \mathrm{d}t\exp(-2t\varepsilon/W)(1-\exp(-t))^2/t^2}{[\int_0^\infty \mathrm{d}t\exp(-t\varepsilon/W)(1-\exp(-t))/t]^2}\right)\mu^2+\mathrm{O}(\mu^3). \tag{3.5}$$

In (3.1) and (3.2) we can take the strip width W to infinity provided we hold the linear density μ constant. We have

$$\beta p=\frac{1}{4\pi\varepsilon}\int_0^\infty \mathrm{d}t\log\left(1+\frac{2\pi\zeta\varepsilon}{t}\exp(-t)\right) \tag{3.6}$$

$$\mu=\frac{1}{2\varepsilon}\int_0^\infty \mathrm{d}t\exp(-t)/[(t/\varepsilon\zeta)+2\pi\exp(-t)]. \tag{3.7}$$

Clearly (3.6) and (3.7) are not analytic functions of ζ at $\zeta=0$. This is not surprising, since in the direction perpendicular to the interface the potential behaves logarithmically, and thus is not integrable in the half-plane domain.

Integrating (3.6) by parts and using (3.7) we see

$$\beta p\sim\mu+\zeta/2(1+\mathrm{o}(1)) \qquad \text{as } \mu,\zeta\to 0. \tag{3.8}$$

But from (3.7)

$$\mu \sim -(\tfrac{1}{2}\zeta)\log(\zeta) \qquad \text{as } \zeta \to 0. \tag{3.9}$$

Solving (3.9) for μ substituting into (3.8) we obtain

$$\beta p \sim \mu + f(\mu) \qquad \text{as } \mu \to 0 \tag{3.10}$$

where f is a non-analytic function of μ at $\mu = 0$, vanishing at that point along with all of its derivatives, and has the property

$$\lim_{\mu \to 0^+} \frac{f(\mu)}{\mu} = 0. \tag{3.11}$$

From (3.10) and (3.11) we see that the ideal-gas law is obeyed in the limit of zero density, but that the next-order correction term has an essential singularity at zero density, with all derivatives vanishing.

3.2. Correlation functions

From (2.25) and (2.32) the one- and two-particle distribution functions with zero background charge density in the strip of width W are

$$\rho_1(x) = \frac{\zeta}{W}\int_0^\infty \frac{\mathrm{d}t\,\exp(-2xt/W)}{1+(\zeta W\pi/t)\exp(-2\varepsilon t/W)(1-\exp(-2t))} \tag{3.12}$$

$$\begin{aligned}\rho_2(x_1, x_2) &\equiv \rho_2(x_1, x_2; y)\\ &= \rho_1(x_1)\rho_2(x_2) - |\rho_1[(x_1+x_2+\mathrm{i}y)/2]|^2.\end{aligned} \tag{3.13}$$

From (3.12) and (3.13) we deduce the asymptotic behaviour of the two-particle correlation along the interface:

$$\rho_2^{\mathrm{T}} \sim -\left(\frac{\zeta}{1+2\pi\zeta W}\right)^2\left(\frac{1}{(x_1+x_2)^2+y^2}\right) \qquad \text{as } y \to \infty. \tag{3.14}$$

The $1/y^2$ decay is in agreement with the general expectation that for integrable potentials the two-particle correlation will decay asymptotically as some multiple of the potential.

The correlation functions obey a sum rule applicable to compressible gases (Gaudin 1966):

$$\mu\left(\frac{\partial\rho_1(x)}{\partial(\beta p)}\right)_\beta = \rho_1(x) + \int_{-\infty}^{\infty}\mathrm{d}y\int_\varepsilon^{\varepsilon+W}\mathrm{d}x'\,\rho_2^{\mathrm{T}}(x, x'; y). \tag{3.15}$$

Recall one-component Coulomb systems without metallic boundary conditions are incompressible (Lieb and Narnhofer 1975), in which case the left-hand side of (3.15) is zero. The resulting sum rule is then known as the perfect screening sum rule.

Next consider the case $W \to \infty$. From (3.12) we have the one-particle correlation given by

$$\rho_1(x) = \frac{\zeta}{\varepsilon}\int_0^\infty \frac{\mathrm{d}t\,\exp(-2xt/\varepsilon)}{1+(\zeta\varepsilon\pi/t)\exp(-2t)} \tag{3.16}$$

and the two-particle correlation given by (3.13). This gives the asymptotic behaviour

$$\rho_1(x) \sim 1/4\pi x^2 \qquad x \to \infty \tag{3.17}$$

$$\rho_2^{\mathrm{T}}(x) \sim -\frac{1}{\pi^2[(x_1+x_2)^2+y^2]^2} \qquad x_1, x_2 \to \infty \text{ and/or } y \to \infty. \tag{3.18}$$

The correlations again obey the sum rule (3.15). They also obey the dipole moment sum rule (Blum *et al* 1981)

$$\int_{\varepsilon}^{\infty} \mathrm{d}x_1 \int_{-\infty}^{\infty} \mathrm{d}y\, x_1 \rho_2^{\mathrm{T}}(x_1, x_2; y) = -x_2 \rho_1(x_2). \tag{3.19}$$

The fact that the correlations obey the dipole moment screening sum rule but not the perfect screening sum rule is anticipated by an obvious generalisation of an argument due to Jancovici (1982b). In a Coulomb system with image forces one must consider not just the charge-charge correlation (which we term the charge-screening cloud)

$$C^{\mathrm{T}}(x_1, x_2; y) = q\rho_1(x_1)\delta(x_1 - x_2)\delta(y) + q^2\rho_2^{\mathrm{T}}(x_1, x_2; y) \tag{3.20}$$

in the actual system, but also the induced charge-charge correlation in the dielectric medium due to the image forces. In the case of a metallic boundary, the induced charge-screening cloud is equal in magnitude but opposite in sign to the charge-screening cloud in the system itself. Thus the (modified) perfect screening sum rule which requires

$$\int_{\varepsilon}^{\infty} \mathrm{d}x_2 \int_{-\infty}^{\infty} \mathrm{d}y\, C^{\mathrm{T}}(x_1, x_2; y) + \int_{-\infty}^{-\varepsilon} \mathrm{d}x_2 \int_{-\infty}^{\infty} \mathrm{d}y\, C^{\mathrm{T}}(x_1, x_2; y) = 0 \tag{3.21}$$

is always obeyed since

$$C^{\mathrm{T}}(x_1, x_2; y) = -C^{\mathrm{T}}(x_1, -x_2; y). \tag{3.22}$$

However the dipole moment sum rule (3.19), which must hold in two-dimensional Coulomb systems whenever the correlations decay faster than $1/r^3$ in all directions (Blum *et al* 1981), is unaltered, by the same argument. Since both the monopole and dipole moments of the total charge-screening cloud vanish, the quadrupole moment must vanish by symmetry. Higher-order moments are not defined since the correlations only decay as $1/r^4$.

It is of some interest to compare the preceding results for the correlation functions in the half-plane with those obtained for a similar system by Jancovici (1984). Jancovici obtained the one- and two-particle correlations of two-dimensional charges attracted to an excess surface charge at $\Gamma = 2$. Since the system is neutral overall, there is only a finite number of particles per unit length of the interface, as is the case here. The correlations obeyed the usual perfect screening sum rule (since there are no image forces) and the dipole moment sum rule. Furthermore the asymptotic behaviour of the correlations was found to be precisely that given by (3.17) and (3.18) (excluding the y direction in (3.18)).

A plot of the density profile (3.16) for $\mu = 0.2$, $\varepsilon = 0.1$ is given in figure 1. (To compute ρ_1 from (3.16) it is first necessary to compute ζ from (3.7), which is specified from the values of ε and μ.)

4. The metal–electrolyte boundary

4.1. *Thermodynamics*

We now want to take the limit $W \to \infty$ with the background charge density η non-zero.

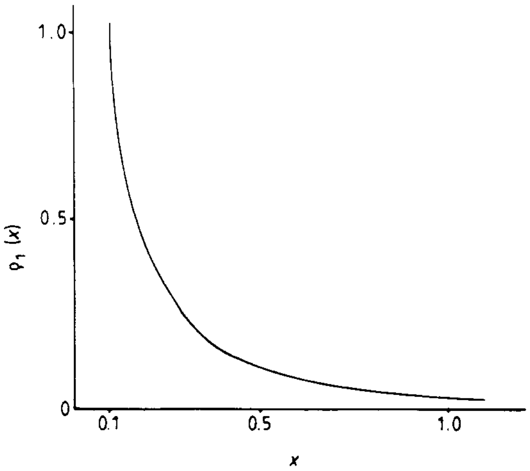

Figure 1. Density profile of charges near a metal wall.

However, first we consider the thermodynamics of the resulting system—the metal-electrolyte boundary—for general Γ.

Recall that in the grand canonical formalism the free energy per volume ψ is given by

$$\beta\psi = \rho \log(\zeta) - \log(\Xi)/LW. \tag{4.1}$$

Suppose we take $L \to \infty$. Now consider the system for W large but finite. For a one-component Coulomb system of background charge density $q\eta$ we must have

$$\rho \sim \eta + \frac{\sigma}{W} \tag{4.2}$$

where $q\sigma$ denotes the excess surface charge. However, in the grand canonical ensemble

$$\rho = \zeta\, \partial(\log(\Xi)/LW)/\partial\zeta. \tag{4.3}$$

Define g and g_s by

$$\lim_{L\to\infty} \log(\Xi)/LW \sim -\beta(g + g_s/W). \tag{4.4}$$

Then from (4.2), (4.3) and (4.4) we have

$$\zeta\, \partial(\beta g)/\partial\zeta = -\eta \tag{4.5}$$

and

$$\zeta\, \partial(\beta g_s)/\partial\zeta = -\sigma. \tag{4.6}$$

Substituting (4.2) and (4.4) into (4.1) we have

$$\beta\psi \sim \eta \log(\zeta) + \beta g + W^{-1}(\beta g_s + \sigma \log(\zeta)) \tag{4.7}$$

so that the surface free energy per unit length of the interface f_s is given by

$$\beta f_s = \sigma \log(\zeta) + \beta g_s. \tag{4.8}$$

Taking the partial derivative of (4.8) with respect to σ and using the sum rule (4.6) we immediately deduce

$$\partial(\beta f_s)/\partial\sigma = \log(\zeta). \tag{4.9}$$

The surface tension γ is defined by

$$\gamma = (\partial F/\partial A)_{\mu,T,V,Q} \tag{4.10}$$

where F is the total free energy of the system, A is the area of the interface, V the volume and Q the surface charge. But $F = F(A, \sigma(A))$ where $\sigma = Q/qA$, so using (4.6) in (4.10) we have

$$\gamma = g_s. \tag{4.11}$$

A further application of (4.6) gives

$$\zeta\, \partial\gamma/\partial\zeta = -\sigma/\beta. \tag{4.12}$$

Let us now calculate g and g_s (and thus, from (4.6), σ) at $\Gamma = 2$. From (2.28) and (2.29), after breaking the range of integration in (2.29) into two parts, one on $[0, \infty)$ and the other on $[-\kappa W, 0]$, we find

$$\beta g = -\eta \log[2\pi\zeta(1/2\eta)^{1/2}] \tag{4.13}$$

$$\begin{aligned}\beta g_s = -\frac{\eta}{\kappa}\Bigg(&\int_0^\infty dt \log\left(1 + \frac{\pi^{3/2}\zeta}{\kappa}\exp(t^2 - 2t\kappa\varepsilon)\,\mathrm{erfc}(t)\right)\\ &+ \int_0^\infty dt \log\left[1 + \left(\frac{\pi^{3/2}\zeta}{\kappa}\exp(t^2 + 2t\kappa\varepsilon)(1 + \mathrm{erf}(t))\right)^{-1}\right]\\ &- (4/\pi^{1/2})\int_0^\infty dt\, t \exp(-t^2)/(1 + \mathrm{erf}(t))\Bigg)\end{aligned} \tag{4.14}$$

where $\mathrm{erfc}(t)$ denotes the complementary error function, $\mathrm{erfc}(t) = 1 - \mathrm{erf}(t)$. From (4.6) and (4.14) we have

$$\begin{aligned}\sigma = \frac{\eta}{\kappa}\Bigg[&\left(\frac{\pi^{3/2}\zeta}{\kappa}\exp[-(\kappa\varepsilon)^2]\right)\int_0^\infty dt \frac{\exp[(t - \varepsilon\kappa)^2]\,\mathrm{erfc}(t)}{1 + (\pi^{3/2}\zeta/\kappa)\exp(t^2 - 2\kappa\varepsilon t)\,\mathrm{erfc}(t)}\\ &- \int_0^\infty dt \frac{1}{1 + (\pi^{3/2}\zeta/\kappa)\exp(t^2 + 2\kappa\varepsilon t)(1 + \mathrm{erf}(t))}\Bigg].\end{aligned} \tag{4.15}$$

Substituting (4.13) into (4.7) and taking the limit $W \to \infty$ we obtain

$$\beta\psi = -\eta \log[2\pi(1/2\eta)^{1/2}], \tag{4.16}$$

which is identical to the bulk free energy per unit volume of the two-dimensional OCP at $\Gamma = 2$ with hard-wall boundary conditions (Alastuey and Jancovici 1981).

Note that for a one-component Coulomb system the bulk free energy ψ is dependent only on the fixed background density η and the coupling constant Γ so that $\psi = \psi(\eta, \Gamma)$. The usual thermodynamic equation

$$\beta P = \eta \log(\zeta) - \beta\psi \tag{4.17}$$

where P denotes the bulk pressure is not applicable since for the metal-electrolyte boundary ζ is a surface variable independent of the bulk particle density $\rho = \eta$.

By defining the bulk pressure as

$$P = -\partial F/\partial V \tag{4.18}$$

where F denotes the total free energy ($F = V\psi$) we regain the known result at $\Gamma = 2$ (Alastuey and Jancovici 1981):

$$\beta P = \eta(1 - \tfrac{1}{4}\Gamma). \tag{4.19}$$

4.2. Interpretation of the activity

Note from (4.2) that in the limit $W \to \infty$ we have $\rho = \eta$ so the activity ζ does not change the bulk density. However, from (4.15) varying ζ does change the surface charge σ. In experimental electrochemistry variations in σ are made by varying the potential drop $\Delta\phi$ between the two metal electrodes (in our situation one of the metal electrodes is at infinity). Hence for our exactly solvable model to mimic the real metal-electrolyte boundary we require ζ to be related to the potential drop.

To show that this is indeed the case we must consider the correlation function $\rho_1(x)$. From (2.25) and (2.31) the one-particle density in the limit $W \to \infty$ with non-zero background charge density $q\eta$ is

$$\rho_1(x) = \zeta\kappa \exp[-\kappa^2(x-\varepsilon)^2] \int_{-\infty}^{\infty} \frac{\mathrm{d}t \exp(-2\kappa x t)}{1 + (\pi^{3/2}\zeta/\kappa)\exp(t^2 - 2\kappa\varepsilon t)\,\mathrm{erfc}(t)}. \tag{4.20}$$

Note we can use (4.20) as an independent check on (4.15), since by definition

$$\sigma = \int_{\varepsilon}^{\infty} \mathrm{d}x(\rho_1(x) - \eta). \tag{4.21}$$

To compute the integral (4.21) we introduce a convergence factor $\exp(-\delta x)$ and consider the ranges $t \in [0, \infty)$, $t \in (-\infty, 0]$ of (4.20) separately. We reclaim (4.15).

Using an integration technique similar to that used to compute (4.20), we find for the potential drop

$$\begin{aligned} \Delta\phi \equiv \phi(\infty) - \phi(0) &= 2\pi q \int_{\varepsilon}^{\infty} \mathrm{d}x\, x(\rho_1(x) - \eta) \\ &= \tfrac{1}{2} q \log[\pi\zeta(2/\eta)^{1/2}] - \tfrac{1}{4} q. \end{aligned} \tag{4.22}$$

At $\Gamma = 2$ we know the bulk chemical potential μ (not to be confused with the μ defined in § 3.1) is given by

$$\mu\beta = -\log[\pi(2/\eta)^{1/2}] + \tfrac{1}{2}. \tag{4.23}$$

Substituting (4.23) into (4.22) we have at $\Gamma = 2$

$$\zeta = \exp[\beta(\mu + q\Delta\phi)]. \tag{4.24}$$

We expect this relationship to be true in general for OCPs near metal boundaries.

Using (4.15) and (4.24) we can calculate the differential capacity

$$C = \partial(q\sigma)/\partial\Delta\phi. \tag{4.25}$$

In figure 2 we plot C as a function of $\Delta\phi/q$ for $\kappa = 1$, $\varepsilon = 1$. The curve is not symmetrical about the C axis since negative $\Delta\phi$ corresponds to an excess of uniform background while positive $\Delta\phi$ corresponds to an excess of mobile point charges, the latter being easier to obtain energetically.

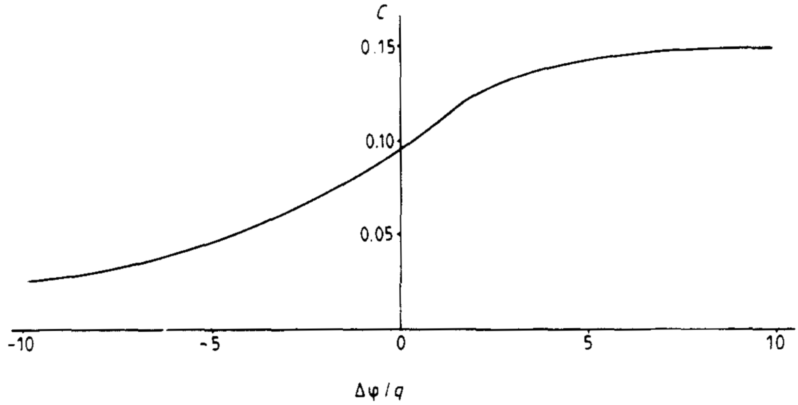

Figure 2. The differential capacity C as a function of the potential drop per charge $\Delta\phi/q$.

In figure 3 we plot $\rho_1(x)$ for $\kappa = 1$, $\varepsilon = 1$ and the three values of the surface excess $\sigma = -0.1$, 0 and 0.1.

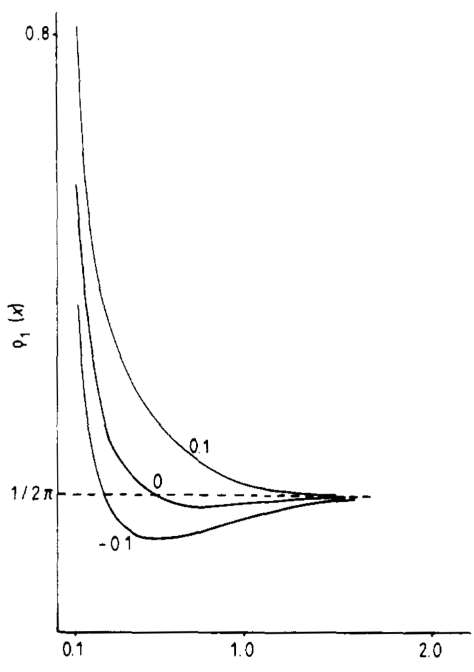

Figure 3. Density profile of the metal–electrolyte boundary for three different values of the surface excess σ.

4.3. Sum rules

The metal-electrolyte boundary (MEB) of this paper is compared with the ideally polarisable interface (IPI) of Rosinberg and Blum (1984) by considering the sum rules satisfied by the two systems.

First consider the MEB. Using the conjecture (4.24) we deduce from (4.9) the sum rules for general Γ:

$$\partial f_s/\partial\sigma = \mu + q\Delta\phi \tag{4.26}$$

$$\partial\gamma/\partial\Delta\phi = -q\sigma. \tag{4.27}$$

Equation (4.27) is known as Lippmann's equation (Brockris and Reddy 1970). Since (4.24) is true for $\Gamma=2$, (4.26) and (4.27) are true in this case. Figure 4 shows the surface tension in the case $\kappa=1$, $\varepsilon=1$, calculated from (4.11), (4.14) and (4.24), as a function of $\Delta\phi/q$. This is known as the electrocapillarity curve, and is similar in shape to that calculated by Rosinberg and Blum (1984) for the IPI.

The IPI satisfies Lippmann's equation, and the sum rule (4.26) in the form

$$\partial f_s/\partial\sigma = \mu_2 - \mu_1 + q\Delta\phi \tag{4.28}$$

where μ_1 and μ_2 denote the bulk chemical potential on either side of the interface.

Next we seek a sum rule analogous to (3.15). First we note from (2.25) and (2.31) that the two-particle correlation for the MEB is

$$\rho_2^{\mathrm{T}}(x_1, x_2; y) = -\exp\{-\kappa^2[(x_1+x_2)^2+y^2]\}|\rho_1[(x_1+x_2+\mathrm{i}y)/2]|^2 \tag{4.29}$$

where ρ_1 is given by (4.20). Since in the MEB the linear density and the one-dimensional pressure have no meaning, (3.15) is inapplicable in its present form. From the exact results (4.20), (4.24) and (4.29) we find

$$\left(\frac{\partial\rho_1(x)}{\partial(\beta q\Delta\phi)}\right)_\beta = \rho_1(x) + \int_{-\infty}^{\infty} \mathrm{d}y \int_{\varepsilon}^{\varepsilon+W} \mathrm{d}x'\, \rho_2^{\mathrm{T}}(x, x'; y), \tag{4.30}$$

which we conjecture to be a general property of the MEB.

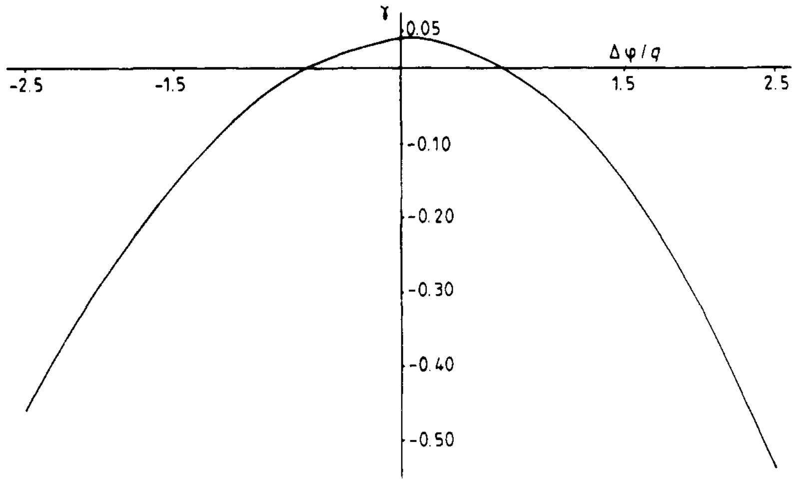

Figure 4. The electrocapillarity curve for the metal-electrolyte boundary.

Using an analysis due to Jancovici (1982b) we can show from (4.20) and (4.29) that ρ_2^{T} decays as an oscillating exponential along the wall and as a Gaussian into the system. This is qualitatively the same behaviour as that exhibited by the IPI.

Recall from the discussion of § 3.2 that the usual multipole sum rules (Blum *et al* 1981) must be modified to include the induced charge-screening cloud in the metal. Jancovici (1982b) has conjectured that if the two-particle correlation decays faster than a power law in each direction (as is the case here), then the 2^nth multipole moment of the charge-screening cloud must vanish. Continuing the argument used in § 3.2 for the 2^n, $n=0, 1, 2$ moments, this implies the 2^{2m-1}, $m=1, 2, \ldots$ multipole moments of the actual charge-screening cloud must vanish (the 2^{2m} multipole moments of the total charge-screening cloud then vanishing by symmetry). Thus we expect

$$\int_{\varepsilon}^{\infty} \mathrm{d}x' \int_{-\infty}^{\infty} \mathrm{d}y (x'+\mathrm{i}y)^{2m-1} \rho_2^{\mathrm{T}}(x, x'; y) = -x^{2m-1} \rho_1(x) \tag{4.31}$$

for each $m=1, 2, \ldots$. A proof of (4.31) is given in the appendix.

4.4. *Alternative derivations*

We have derived the results for the MEB from a 'first-principles' approach—the image forces have been included explicitly in the Hamiltonian (2.4). However, it has been shown recently that these results can be deduced as a limiting case of the IPI with an impermeable gap of width ε introduced between the two background densities η_1 and η_2, say. (This was conjectured by B Jancovici and checked by M L Rosinberg, private communications.) In the limit $\eta_1 \to \infty$ this region of the IPI tends to a perfect conductor, with the qualification, noted by A Alastuey (private communication), that there is a residual potential $\phi(0) - \phi(-\infty) = -\frac{1}{2}q(\log(2) - \frac{1}{2})$.

Furthermore, the results for both the MEB and the IPI can be obtained as limiting cases of a model recently presented by Alastuey and Lebowitz (1984).

A further discussion of the relationships between these models will be the subject of a forthcoming publication.

Acknowledgments

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Appendix

Here we prove (4.31) by adapting a technique due to Jancovici (1982b, appendix B). Denote

$$P_{2m-1} = \int_{\varepsilon}^{\infty} \mathrm{d}x' \int_{-\infty}^{\infty} (x'+\mathrm{i}y)^{2m-1} \rho_2^{\mathrm{T}}(x, x'; y) \tag{A1}$$

where ρ_2^{T} is given by (4.20) and (4.29). Further denote

$$F(t) = 1 + (\pi^{3/2}\zeta/\kappa) \exp(t^2 - 2\kappa\varepsilon t) \operatorname{erfc}(t). \tag{A2}$$

Then since

$$\frac{d^{2m-1}}{ds^{2m-1}}\exp[-\kappa s(x'+iy)]=\left(-\frac{1}{\kappa}(x'+iy)\right)^{2m-1}\exp[-\kappa s(x'+iy)] \quad (A3)$$

we have

$$\begin{aligned} P_{2m-1}=&-(\zeta\kappa)^2(-\kappa^{-1})^{2m-1}\exp[-2(\kappa\varepsilon)^2-\kappa^2(x^2-\varepsilon x)] \\ &\times\int_\varepsilon^\infty dx'\exp\{-\kappa^2[(x')^2-2\varepsilon x']\} \\ &\times\int_{-\infty}^\infty dy\int_{-\infty}^\infty dt\frac{\exp[i\kappa yt-\kappa(x+x')t]}{F(t)} \\ &\times\int_{-\infty}^\infty ds\frac{\exp(-\kappa xs)}{F(s)}\left(\frac{d^{2m-1}}{ds^{2m-1}}\exp[-\kappa(x'+iy)s]\right). \end{aligned} \quad (A4)$$

Noting

$$2\pi\zeta\exp[-(\kappa\varepsilon)^2]\int_\varepsilon^\infty dx'\exp\{-\kappa^2[(x')^2-2\varepsilon x']\}\exp[-\kappa x'(t+s)]=F[\tfrac{1}{2}(t+s)]-1 \quad (A5)$$

and

$$\int_{-\infty}^\infty dy\exp[i\kappa y(t-s)]=2\pi\delta(t-s)/\kappa, \quad (A6)$$

we have after changing the order of differentiation and integration in (A4)

$$\begin{aligned} P_{2m-1}=&-\zeta\kappa(-\kappa^{-1})^{2m-1}\exp[-(\kappa\varepsilon)^2-\kappa^2(x^2-\varepsilon x)]\int_{-\infty}^\infty dt\frac{\exp(-\kappa xt)}{F(t)} \\ &\times\int_{-\infty}^\infty ds\frac{\exp(-\kappa xs)}{F(s)}\frac{d^{2m-1}}{ds^{2m-1}}[(F[\tfrac{1}{2}(t+s)]-1)\delta(t-s)]. \end{aligned} \quad (A7)$$

In the s integration, integrate by parts $(2m-1)$ times and then use the delta function to combine the t and s integrations. This shows that

$$\begin{aligned} P_{2m-1}=&-\zeta\kappa(-\kappa^{-1})^{2m-1}\exp[-(\kappa\varepsilon)^2-\kappa^2(x^2-\varepsilon x)] \\ &\times\int_{-\infty}^\infty dt\frac{\exp(-\kappa xt)}{F(t)}(F(t)-1)\frac{d^{2m-1}}{dt^{2m-1}}\left(\frac{\exp(-\kappa xt)}{F(t)}\right). \end{aligned} \quad (A8)$$

But by the integration by parts

$$\int_{-\infty}^\infty dt\exp(-\kappa xt)\frac{d^{2m-1}}{dt^{2m-1}}\left(\frac{\exp(-\kappa xt)}{F(t)}\right)=(\kappa x)^{2m-1}\int_{-\infty}^\infty dt\frac{\exp(-\kappa xt)}{F(t)} \quad (A9)$$

$$\int_{-\infty}^\infty dt\frac{\exp(-\kappa xt)}{F(t)}\frac{d^{2m-1}}{dt^{2m-1}}\left(\frac{\exp(-\kappa xt)}{F(t)}\right)=0, \quad (A10)$$

where in (A10) we have made essential use of $(2m-1)$ being odd. Substituting (A9) and (A10) into (A8) and recalling the definition of $\rho_1(x)$ (4.6) proves (4.31).

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