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Effects of surface charge on the two-dimensional one-component plasma: I. Single double layer structure

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Abstract. The recent exact analysis of the canonical partition function and one- and two-particle distribution functions for a disc of classical one-component two-dimensional plasma of particle charge $-q$ with a uniform neutralising charged background is extended to consider the effects of surface charge and of having the dielectric constant outside the disc, ϵ_2 , different from that inside the disc, ϵ_1 . The system is characterised by bulk density ρ , the plasma parameter $\Gamma = q^2/\epsilon_1 kT$, the surface charge density σq and the parameter $\Delta = (\epsilon_1 - \epsilon_2)/(\epsilon_1 + \epsilon_2)$. For $\Gamma = 2$, $\Delta = 0$ or 1 and any value of ρ or σ , the canonical partition function and one- and two-particle distribution functions are calculated exactly. The bulk thermodynamic properties are independent of σ and Δ . The surface properties (surface excess free energy, density profile and two-particle correlation functions) are calculated in the thermodynamic limit and shown to depend strongly on both σ and Δ .

1. Introduction

The electrostatic double layer set up close to the surface of a charged electrode immersed in an electrolyte has been an object of study for many years. For a dilute electrolyte, the standard Debye–Huckel theory is capable of reproducing many experimental findings, but for a concentrated electrolyte there seems to be no complete theory as yet. Thus recourse is had to approximate analytic methods in statistical mechanics and to numerical simulations. Unfortunately the approximate methods have so far only given results for simple model potentials. This means that it is difficult to make meaningful comparisons with experiments on real systems. On the other hand, it is difficult to compare approximate methods with numerical simulations using the same model potential because there is no clear consensus on how to carry out the numerical simulations (Torrie and Valleau 1980). The problem is that the long-ranged nature of the ion–ion interaction in the electrolyte means that in a finite simulation sample, some account of the rest of an infinite system must be taken. There is some debate about how to take account of this. The situation with simulations of surface properties of ionic systems is even less clear. Thus it is clear that exact results for any simple model system would be of considerable value since they can be used to test any simulation procedure.

This paper provides such an example. The model is the classical two-dimensional one-component plasma. Recently Alastuey and Jancovici (1981) and Jancovici (1981) have published exact results for this system at a particular temperature in the thermodynamic limit. This paper extends those results to include the effects of a linear surface charge density on the surface of the system and some analysis of what happens when the

dielectric constant inside the system is different from that outside the system. This last point is of particular interest in the context of simulation of ionic systems.

Consider, then, a disc Ω of radius R with dielectric constant ϵ_1 immersed in a continuous medium of dielectric constant ϵ_2 . The disc contains N particles of charge $-q$ and a uniform background of charge density ηq . The edge of the disc contains a line charge density σq and the system is overall neutral so that

$$\pi R^2 \eta + 2\pi R \sigma = N. \tag{1.1}$$

The interaction potential between charges is a solution of the two-dimensional Poisson equation. For this system, with $\sigma = 0$ and $\epsilon_2 = \epsilon_1$, Hauge and Hemmer (1971) have shown that the thermodynamic limit of the pressure is given by

$$p = (kT - q^2/4\epsilon_1)\rho \tag{1.2}$$

where $\rho = N/\pi R^2$ is the bulk particle density. The system is characterised by the parameters ρ , $\Gamma = q^2/\epsilon_1 kT$, $\Delta = (\epsilon_1 - \epsilon_2)/(\epsilon_1 + \epsilon_2)$ and σ . Alastuey and Jancovici (1981) and Jancovici (1981) obtained expressions for the canonical partition function and one- and two-particle distribution functions for any value of ρ with $\Gamma = 2$, $\Delta = 0$, $\sigma = 0$. It may be noted that the pressure of equation (1.2) becomes negative for $\Gamma > 4$. Such a thermodynamically improbable event occurs because of the fixed charge background imposed on the system.

The potential at r due to a unit positive charge at s is a solution of

$$\nabla_r^2 \phi(r, s) = -\frac{2\pi}{\epsilon(r)} \delta(r - s), \tag{1.3}$$

here $\epsilon(r) = \epsilon_1$ for $r \in \Omega$ and $\epsilon(r) = \epsilon_2$ for $r \notin \Omega$. This equation may be solved using the usual boundary conditions of continuity of the potential and the normal component of electric displacement at the edge of Ω , boundedness at $r = 0$ and the requirement that as $r \rightarrow \infty$, $\phi(r, s) \sim -\epsilon_2^{-1} \ln |r|$. The surface charges are assumed to be just inside the surface of the disc. For $r, s \in \Omega$, the solution to the boundary value problem for ϕ is

$$\begin{aligned} \phi(r, s) = & \frac{1}{\epsilon_1} \ln (|s - r|^2/R^2) - \frac{\Delta}{2\epsilon_1} \ln \left(1 - \frac{2s \cdot r}{R^2} + \frac{s^2 r^2}{R^4} \right) \\ & - \frac{1}{2\epsilon_2} \ln R^2. \end{aligned} \tag{1.4}$$

The energy of N particles at r_1, \dots, r_N and the background and surface charges may now be evaluated to give $E(\{r_i\}) = (q^2/2\epsilon_1)W(\{r_i\})$ with

$$\begin{aligned} W(\{r_i\}) = & -\frac{3}{4}N^2 + \Sigma(2N + \Sigma)/4 + N \ln R + N^* \sum_{i=1}^N r_i^2/R^2 - \Delta \sum_{i=1}^N \ln (1 - r_i^2/R^2) \\ & - \sum_{i < j} [\ln (r_{ij}^2/R^2) + \Delta \ln (1 - 2r_i \cdot r_j/R^2 + r_i^2 r_j^2/R^4)]. \end{aligned} \tag{1.5}$$

Here $r_{ij} = r_i - r_j$, $\Sigma = 2\pi R \sigma$ and $N^* = N - \Sigma$. The canonical partition function is, in its usual form

$$Z_N(\Gamma, \Delta, \sigma) = \frac{1}{N!} \prod_{i=1}^N \int_0^R r_i dr_i \int_{-\pi}^{\pi} d\theta_i \exp[-\frac{1}{2}\Gamma W(\{r_i\})]. \tag{1.6}$$

Some of the simplifying advantages of studying $\Gamma = 2$ and $\Delta = 0$ or 1 are immediately

apparent. The canonical distribution functions are

$$\rho_{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n; \Gamma, \Delta, \sigma) = [(N-n)! Z_N(\Gamma, \Delta, \sigma)]^{-1} \prod_{l=n+1}^N \int_0^R r_l dr_l \int_{-\pi}^{\pi} d\theta_l \exp[-\frac{1}{2}\Gamma W(\{\mathbf{r}_i\})]. \quad (1.7)$$

In the next section $Z_N(\Gamma, \Delta, \sigma)$, $\rho_{(1)}(\mathbf{r}; \Gamma, \Delta, \sigma)$ and $\rho_{(2)}(\mathbf{r}_1, \mathbf{r}_2; \Gamma, \Delta, \sigma)$ are evaluated exactly for $\Gamma = 2$ and $\Delta = 0$ or 1 . In § 3, the surface excess free energy is discussed in the thermodynamic limit and the density profiles close to the surface all derived for both $\Delta = 0$ and 1 , together with representations for the two-particle distribution functions close to the surface. The paper concludes with some discussion in § 4.

2. Exact results for $\Gamma = 0, \Delta = 0$ or 1

2.1. $\Delta = 0$

For this case the analysis repeats that of Alastuey and Jancovici (1981) and Jancovici (1981) very closely. The partition function is

$$Z_N(2, 0, \sigma) = \frac{(\pi R^2)^N}{N!} \exp(\frac{3}{4}N^2 - \Sigma(2N + \Sigma)/4 - N \ln R) \times \prod_{i=1}^N \left(\int_0^1 2z_i dz_i \exp(-N^* z_i^2) \int_{-\pi}^{\pi} \frac{d\theta_i}{2\pi} \right) \prod_{i < j} (z_j - z_i)^2. \quad (2.1)$$

The method of integration is precisely that used by Alastuey and Jancovici (1981) and thus the partition function may be written

$$Z_N(2, 0, \sigma) = Z_N(2, 0, 0) \exp[-\Sigma(2N + \Sigma)/4] \left(\frac{N^*}{N}\right)^{-N(N-1)/2} \prod_{l=1}^N \frac{\gamma(l, N^*)}{\gamma(l, N)} \quad (2.2)$$

where

$$\gamma(s, x) = \int_0^x t^{s-1} e^{-t} dt \quad (2.3)$$

is the incomplete gamma function. The canonical one- and two-particle distribution functions have the form

$$\rho_{(1)}(R\mathbf{z}_1; 2, 0, \sigma) = \eta H_0(z_1^2, N^*, N) \quad (2.4)$$

and

$$\rho_{(2)}(R\mathbf{z}_1, R\mathbf{z}_2; 2, 0, \sigma) = \eta^2 [H_0(z_1^2, N^*, N) H_0(z_2^2, N^*, N) - \exp(-\pi\eta r_{12}^2) |H_0(z_1 z_2 \exp(i\theta_{12}), N^*, N)|^2] \quad (2.5)$$

where

$$H_0(X, N^*, N) = e^{-N^* X} \sum_{l=1}^N \frac{(N^* X)^{l-1}}{\gamma(l, N^*)} \quad (2.6)$$

and $r_{12} = R(z_1 - z_2)$, $\cos \theta_{12} = z_1 \cdot z_2 / z_1 z_2$. These results are identical to those of Jancovici (1981) for $\sigma = 0$, when $N^* = N$.

2.2. $\Delta = 1$

This choice of Δ is made in spite of its unphysical nature because it is the only other case for which a useful representation of the integrand in the partition function has been obtained. This representation is also a van der Monde determinant, this time of order $2N \times 2N$ (cf the $N \times N$ determinant used in deriving equations (2.3), (4) and (5)). Consider the determinant D_{2N} with elements

$$D_{2N_{l,j}} = a_j^{l-1}, l, j \in [1, 2N]. \tag{2.7}$$

The usual product representation of $\det D_{2N}$ may be rearranged in the form

$$\begin{aligned} \det D_{2N} &= \prod_{l=1}^{2N-1} \prod_{j=l+1}^{2N} (a_j - a_l) \\ &= \left\{ \prod_{l=1}^N (a_{2N+1-l} - a_l) \right\} \prod_{l=1}^{N-1} \prod_{j=l+1}^N (a_j - a_l)(a_{2N+1-j} - a_l) \\ &\quad \times (a_j - a_{2N+1-l})(a_{2N+1-j} - a_{2N+1-l}). \end{aligned} \tag{2.8}$$

Now let

$$a_j = z_j \exp(i\theta_j) \quad a_{2N+1-j} = z_j^{-1} \exp(i\theta_j). \tag{2.9}$$

Then $\det D_{2N}$ may be further rearranged to give

$$\begin{aligned} \det D_{2N} &= \prod_{l=1}^N \{z_l^{-(2N-1)} \exp[i\theta_l(2N-1)](1-z_l^2)\} \\ &\quad \times \prod_{l=1}^{N-1} \prod_{j=l+1}^N (z_j - z_l)^2 (1 - 2z_j \cdot z_l + z_l^2 z_j^2). \end{aligned} \tag{2.10}$$

Thus, using equation (1.5) the canonical partition function may be written

$$\begin{aligned} Z_N(2, 1, \sigma) &= \frac{(\pi R^2)^N}{N!} \exp \left[\frac{3}{4}N^2 - N \ln R - \Sigma(2N + \Sigma)/4 \right] \\ &\quad \times \left(\prod_{l=1}^N \int_0^1 2z_l dz_l z_l^{2N-1} \right. \\ &\quad \left. \times \exp(-N^* z_l^2) \int_{-\pi}^{\pi} \frac{d\theta_l}{2\pi} \exp[-i\theta_l(2N-1)] \right) \det D_{2N}. \end{aligned} \tag{2.11}$$

The determinant in this expression has the expansion

$$\det D_{2N} = \sum_{P=1}^{2N!} \varepsilon(P) \prod_{l=1}^N z_l^{P(l)-P(2N+1-l)} \exp \{i\theta_l[P(l) + P(2N+1-l) - 2]\} \tag{2.12}$$

where P is one of the $(2N)!$ permutations $P\{1, \dots, 2N\} = \{P(1), \dots, P(2N)\}$ and $\varepsilon(P)$ is its parity. If equation (2.12) be substituted into equation (2.11), then integrations over the θ_l may be performed immediately to give zero unless $P(l) + P(2N+1-l) = 2N+1$ for all $l \in [1, N]$, when the integral is one. These contributing permutations may all be derived from permutations of $\{1, \dots, N\}$. They may be classified according to whether (a) $1 \leq P(l) \leq N$ and $N+1 \leq P(2N+1-l) \leq 2N$ or (b) $N+1 \leq P(l) \leq 2N$ and $1 \leq P(2N+1-l) \leq N$. If $P(l), P(2N+1-l)$ are of type (b) they may be derived from a permutation with $P(l), P(2N+1-l)$ of type (a) by one interchange and hence an extra

factor -1 in the parity of the permutation. These considerations allow the partition function to be written

$$Z_N(2, 1, \sigma) = (\pi R^2)^N \exp \left[\frac{3}{4} N^2 - N \ln R - \Sigma(2N + \Sigma)/4 \right] N^{*-N(N+1)/2} \prod_{l=1}^N G(l, N^*, N) \tag{2.13}$$

where

$$G(l, N^*, N) = \gamma(l, N^*) - N^{*-(2N+1-2l)} \gamma(2N+1-l, N^*). \tag{2.14}$$

The one-particle distribution function may be computed from its representation (equation (1.7)) by first using equations (2.12) and (2.10). It may be averaged over θ_1 (since it is radially symmetric), so that all the θ_i variables may be integrated out in the same way as for the partition function. The integration over the $(N-1)$ z_l variables then gives

$$\rho_{(1)}(Rz_1; 2, 1, \sigma) = \eta H_1(z_1^2, N^*, N) \tag{2.15}$$

with

$$H_1(x, N^*, N) = e^{-N^*x} \sum_{k=1}^N \frac{(N^*x)^{k-1}}{G(k, N^*, N)} (1 - x^{2N+1-2k}). \tag{2.16}$$

An immediate consequence of this result is that the density at the surface of the disc is zero. This is in accord with the notion that the interaction of a particle with its own image (of like sign) in the surface should give a strong repulsion from the surface.

The two-particle distribution function may be evaluated in the same way, though the counting of contributing permutations is complicated by the fact that only the angle variables $\theta_3, \dots, \theta_N$ are integrated out. The final result is

$$\begin{aligned} \rho_{(2)}(Rz_1, Rz_2; 2, 1, \sigma) &= \eta^2 \{ H_1(z_1^2, N^*, N) H_1(z_2^2, N^*, N) \\ &\quad - \exp(-\pi\eta r_{12}^2) [H_1(z_1 z_2 \exp(i\theta_{12}), N^*, N)]^2 \\ &\quad - z_2^{2(2N-1)} \exp[2N^*(z_1/z_2)(1-z_2^2) \cos \theta_{12}] \\ &\quad \times H_1(z_1/z_2 \exp(i\theta_{12}), N^*, N)^2 \}. \end{aligned} \tag{2.17}$$

It will be shown below that for $|x| < 1$, the functions $H_0(x, N^*, N)$ and $H_1(x, N^*, N)$ have a limit of one as $N \rightarrow \infty$. This means that $\rho_{(1)}(r; 2, \Delta, \sigma) = \rho$ and $\rho_{(2)}(r_1, r_2; 2, \Delta, \sigma) = \rho^2 [1 - \exp(-\pi\rho r_{12}^2)]$ for all values of σ and $\Delta = 0$ or 1 , in the bulk of the plasma. The thermodynamic limit of the free energy is precisely that obtained by Alastuey and Jancovici (1981) for all σ and $\Delta = 0$ or 1 .

3. Surface properties

The thermodynamic limit of the excess free energy per unit length of surface due to increasing the surface charge density from zero σq is defined by

$$\Delta F(\Gamma, \Delta, \sigma) = \lim_{r \rightarrow \infty} - \frac{kT}{2\pi R} \ln \{ Z_N(\Gamma, \Delta, \sigma) / Z_N(\Gamma, \Delta, 0) \}. \tag{3.1}$$

The density profile in the thermodynamic limit for $\Gamma = 2$ is given by

$$D_\Delta(x; \alpha) = \lim_{R \rightarrow \infty} \rho_{(1)}(R - x; 2, \Delta, \sigma) \tag{3.2}$$

while the two-particle correlation function for two particles placed at the points shown in figure 1 is defined in the thermodynamic limit for $\Gamma = 2$ as

$$D_\Delta(x_1, y, x_2; \alpha) = \lim_{R \rightarrow \infty} \rho_{(2)}((R - x_1)t, (R - x_2)t + yf; 2, \Delta, \sigma). \tag{3.3}$$

Here $\alpha = \sigma(2\pi/\rho)^{1/2}$ is a useful dimensionless parameter.

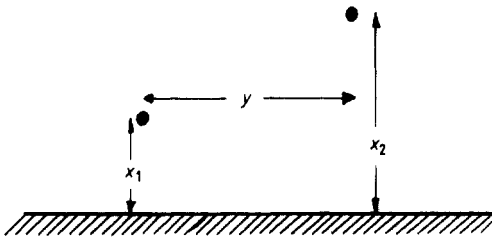


Figure 1. Sketch of position of particles with respect to the surface for calculating two-particle distribution functions.

The evaluation of equation (3.1) for $\Delta = 0$ from equation (2.2) requires the thermodynamic limit of a sum of logarithms of incomplete gamma functions. This sum may be evaluated using the uniform asymptotic expansion (Erdelyi 1953)

$$\gamma(1 + M, M + \sqrt{2My}) = \frac{1}{2}\Gamma(1 + M)(1 + \text{erf}(y) + O(M^{-1/2})) \tag{3.4}$$

with $\text{erf}(y)$ being the usual error function. In the limit $R \rightarrow \infty$, the sum reduces to a Riemann integral and gives

$$\Delta F(2, 0, \sigma) = -\frac{q^2}{4\epsilon_1} \left(\frac{\rho}{2\pi}\right)^{1/2} \left(\alpha(1 - 2 \ln 2) - \frac{2}{3}\alpha^3 + 2 \int_0^\alpha \ln(\text{erfc}(t)) dt \right). \tag{3.5}$$

A similar expansion of the logarithm of $G(k, N^*, N)$ may be used to give

$$\Delta F(2, 1, \sigma) = -\frac{q^2}{4\epsilon_1} \left(\frac{\rho}{2\pi}\right)^{1/2} \left[\alpha + \frac{2}{3}\alpha^3 + 2 \int_0^\infty \ln\left(\frac{P(t, \alpha)}{2\text{erf}(t)}\right) dt \right] \tag{3.6}$$

where

$$P(t, \alpha) = 1 + \text{erf}(t - \alpha) - e^{4\alpha t} \text{erfc}(t + \alpha). \tag{3.7}$$

Define $f(\Delta, \alpha) = \Delta F(2, \Delta, \sigma)[q^2(\rho/2\pi)^{1/2}/4\epsilon_1]^{-1}$. Plots of $f(0, \alpha)$ and $f(1, \alpha)$ are given in figure 2. The minima are at α_0 and α_1 where

$$1 + 2\alpha_0^2 = -2 \ln\left(\frac{1}{2} \text{erfc}(\alpha_0)\right) \tag{3.8}$$

and

$$1 + 2\alpha_1^2 = 8 \int_0^\infty \frac{t dt}{P(t, \alpha_1)} e^{4\alpha_1 t} \text{erfc}(t + \alpha_1). \tag{3.9}$$

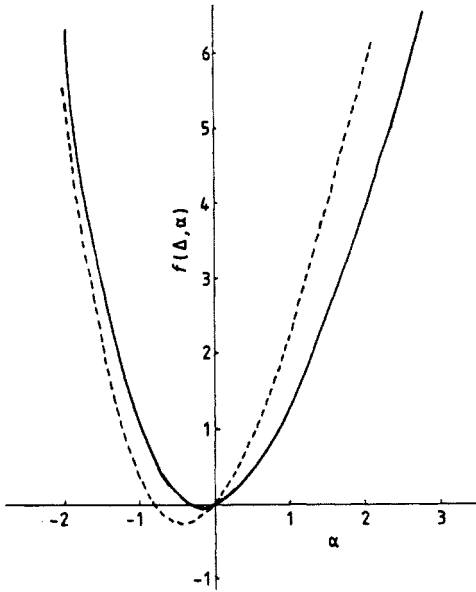


Figure 2. Plots of scaled excess free energy density: —, $f(0; \alpha)$; ----, $f(1, \alpha)$.

It is useful to consider

$$\frac{\partial \Delta F(2, 0, \sigma)}{\partial \alpha} = -\frac{q^2}{4\epsilon_1} \left(\frac{\rho}{2\pi}\right)^{1/2} [1 + 2\alpha^2 + 2 \ln(\frac{1}{2} \operatorname{erfc}(\alpha))] \tag{3.10}$$

and

$$\frac{\partial \Delta F(2, 1, \sigma)}{\partial \alpha} = -\frac{q^2}{4\epsilon_1} \left(\frac{\rho}{2\pi}\right)^{1/2} \left(1 + 2\alpha^2 - 8 \int_0^\infty \frac{t \, dt}{P(t, \alpha)} e^{4\alpha t} \operatorname{erfc}(t + \alpha)\right), \tag{3.11}$$

since, in addition to giving equations for α_0 and α_1 , these derivatives are connected below with properties of the density profile.

The density profiles resulting from equation (3.2) may be evaluated using the same uniform asymptotic expansion of the incomplete gamma functions as was used for the partition functions. The results may be written

$$D_0(x; \alpha) = \rho h_0(\kappa x; \alpha); D_1(x; \alpha) = \rho h_1(\kappa x; \alpha) \tag{3.12}$$

where $\kappa = (2\pi\rho)^{1/2}$ and

$$h_0(\xi; \alpha) = \frac{2}{\sqrt{\pi}} \int_{-\alpha}^\infty \frac{\exp[-(t-\xi)^2]}{1 + \operatorname{erf}(t)} \, dt \tag{3.13}$$

and

$$h_1(\xi; \alpha) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{dt}{P(t, \alpha)} \exp[-(t-\alpha-\xi)^2](1 - e^{-4\xi t}). \tag{3.14}$$

The contact values may be evaluated analytically in each case and are $D_0(0; \alpha) = -\rho \ln(\frac{1}{2} \operatorname{erfc}(\alpha))$ and $D_1(0; \alpha) = 0$. Figure 3 gives a plot of $D_0(0; \alpha)/\rho$ as a function of α . Figures 4 and 5 give plots of $h_0(\xi, \alpha)$ and $h_1(\xi, \alpha)$ respectively for several values of α .

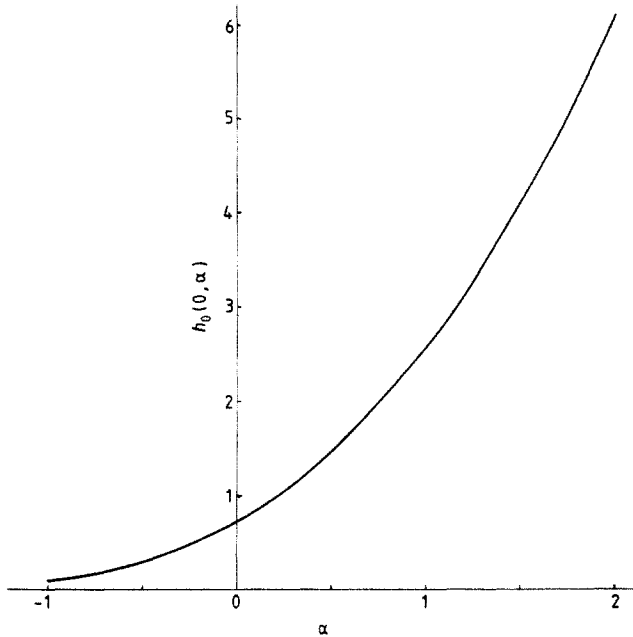


Figure 3. Plot of contact density for $\Delta = 0$ as a function of α .

The Gibbs adsorption isotherm

$$M_{\Delta}(\alpha) = \int_0^{\infty} (D_{\Delta}(x; \alpha) - \rho) dx \tag{3.15}$$

may be computed by using a convergence factor $\exp(-sx)$. The result is $M_{\Delta}(\alpha) = \sigma$ for both $\Delta = 0$ and $\Delta = 1$. This means that the net double layer is electrostatically neutral in each case. The convergence of the integral in equation (3.15) implies that $h_{\Delta}(x; \alpha) \rightarrow 1$ as $x \rightarrow \infty$ for both values of Δ , thus giving the results for the bulk distribution functions quoted in § 2. These representations of $h_{\Delta}(x; \alpha)$ are also useful in evaluating the two-particle distribution functions close to the wall. Reduction of the sums in equations (2.5 and 17) gives

$$D_0(x_1, y, x_2; \alpha) = \rho^2 [h_0(\kappa x_1; \alpha)h_0(\kappa x_2; \alpha) - \exp(-\pi\rho r^2)|h_0(\frac{1}{2}\kappa(x_1 + x_2 + iy); \alpha)|^2] \tag{3.16}$$

and

$$D_1(x_1, y, x_2; \alpha) = \rho^2 \{h_1(\kappa x_1; \alpha)h_1(\kappa x_2; \alpha) - \exp(-\pi\rho r^2)[|h_1(\frac{1}{2}\kappa(x_1 + x_2 + iy); \alpha)|^2 - \exp(-2\kappa^2 x_1 x_2 - 4\alpha\kappa x_2)|h_1(\frac{1}{2}\kappa(x_1 - x_2 + iy); \alpha)|^2]\} \tag{3.17}$$

where $r^2 = (x_1 - x_2)^2 + y^2$.

Finally, because qualitative discussions of double layer structure often refer to the dipole moment set up by charged layers at a surface, it is of interest to consider the

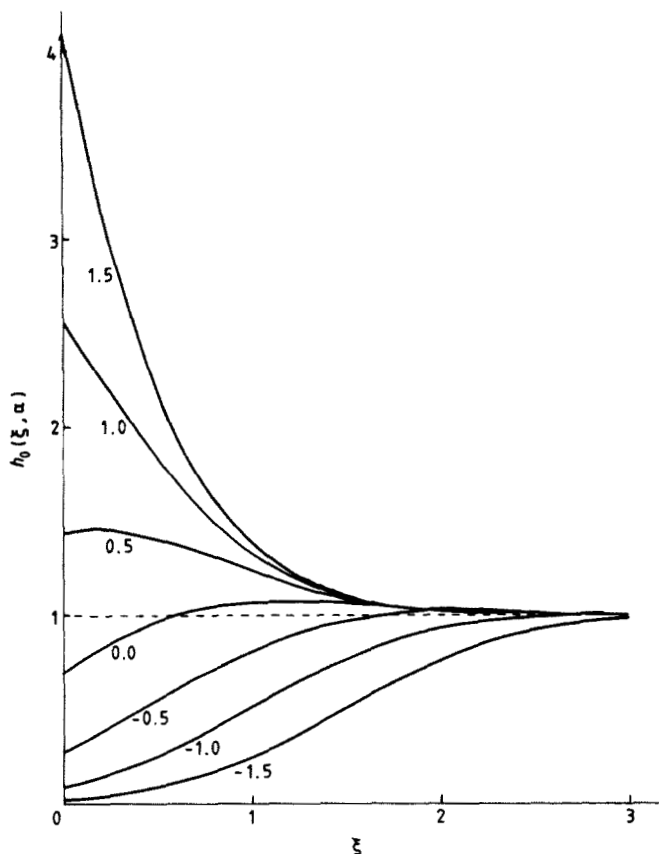


Figure 4. Plots of $h_0(\kappa x; \alpha) = D_0(x; \alpha)/\rho$ as a function of κx . Labels on curves refer to appropriate value of α .

quality

$$P_\Delta(\alpha) = -q \int_0^\infty x(D_\Delta(x; \sigma) - \rho) dx. \tag{3.18}$$

A strip of the system normal to the surface and of width ω has dipole moment $\omega P_\Delta(\alpha)$ about the $x = 0$ end of the strip. For both $\Delta = 1$ and $\Delta = 0$, this integral may be evaluated using a convergence factor $\exp(-sx)$.

For both $\Delta = 0$ and $\Delta = 1$, comparison of the result of this evaluation with equations (3.10 and 11) gives

$$\frac{\partial \Delta F(2, \Delta, \sigma)}{\partial \alpha} = -q(2\pi\rho)^{1/2} P_\Delta(\alpha). \tag{3.19}$$

Thus the surface excess free energy is minimal when $P_\Delta(\alpha) = 0$. This result, together with the condition $F(2, \Delta, 0) = 0$ also gives

$$\Delta F(2, \Delta, \sigma) = -2\pi q \int_0^\sigma P_\Delta(\sigma'(2\pi/\rho)^{1/2}) d\sigma'. \tag{3.20}$$

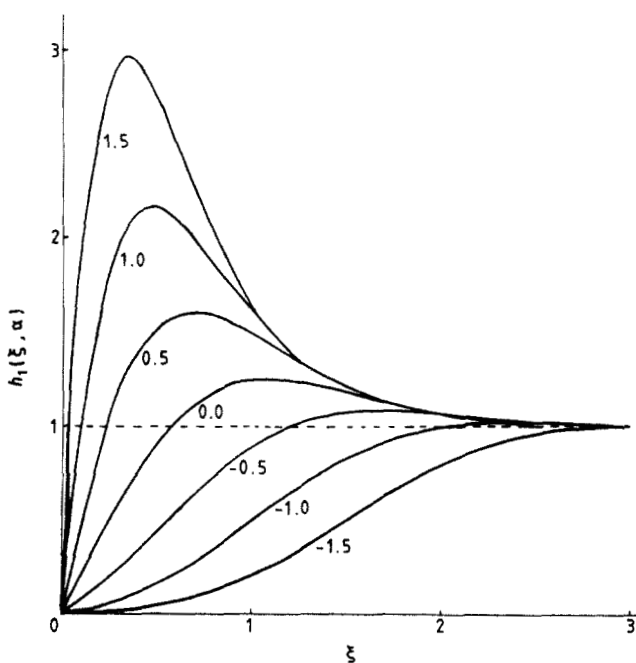


Figure 5. Plots of $h_1(\kappa x; \alpha) = D_1(x; \alpha)/\rho$ as a function of κx . Labels on curves refer to appropriate values of α .

4. Discussion

The first point to note is that the excess free energy per unit length of surface considered as a function of σ at a fixed bulk density ρ has a minimum for non-zero surface charge σ . These minima are not at zero surface charge because, as figures 4 and 5 show, the surface layer contains considerable structure even for $\sigma = 0$. Adjusting this surface structure significantly requires $\sigma \neq 0$ (since $M_\Delta(\alpha) = \sigma$), and such adjustment turns out to be capable of lowering the surface free energy.

Jancovici (private communication) has pointed out that equation (3.19) in fact holds for all Γ and may be generalised to higher dimensions and multicomponent systems. For this system he considers the plasma in a parallel plate condenser with surface charge densities $\pm\sigma q$ giving an electric field $E = 2\pi\sigma q$. The Hamiltonian for this system may be written, for plates of unit area at $x = \pm L$

$$H(E) = H(0) + qE(x_1 + \dots + x_N) - qE\rho \int_{-L}^L x \, dx. \quad (4.1)$$

The total free energy

$$F = -kT \ln \int \exp\left(-\frac{1}{kT}H(E)\right) dr_1 \dots dr_N \quad (4.2)$$

then has derivative

$$\frac{\partial F}{\partial E} = q \int_0^\infty x(\rho_{(1)}(x) - \rho) \, dx \quad (4.3)$$

where $\rho_{(1)}(x)$ is the density at x . Equation (4.3) reduces to equation (3.19). Similar sum rules have been derived in great generality by Gruber *et al* (1981).

The density profiles shown in figures 4 and 5 have some simple features worth mentioning. Firstly, when the surface bears positive charge, a well developed layer of negative particles is constructed adjacent to the surface. For $\Delta = 1$ repulsion of particles from the surface by interaction with their own images is particularly clear. For negative surface charge there is a depleted region close to the surface for both $\Delta = 0$ and $\Delta = 1$, as might be expected. While the bulk properties of the system are apparently insensitive to surface characteristics such as Δ and σ , the surface properties show clear and explicit dependence on these characteristics. The length κ^{-1} which scales distances in these systems is, of course, a Debye length but the shape of the density profiles is not the linear exponential decay predicted by the simple Debye-Huckel theory. This is to be expected since $\Gamma = 2$ corresponds to a temperature too low for weak coupling theory to apply. On the other hand the quadratic exponential behaviour in the distribution functions is somewhat surprising. It may occur here because $\Gamma = 2$ is a singular temperature for the system. This possibility has been raised by Jancovici (1981). The recent result of Fröhlich and Spencer (1981) that a classical two-component plasma has a transition from Debye (exponential) behaviour to a different form of screening behaviour reinforces the suggestion.

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