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Effects of surface charge on the two-dimensional one-component plasma: II. Interacting double layers

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Abstract. The free energy density and one- and two-particle distribution functions for a two-dimensional one-component plasma of particles with charge q confined to a strip bearing charge densities on its surfaces are calculated exactly at the temperature for which $\Gamma = q^2/kT = 2$ (this parameter being dimensionless in two dimensions). The external dielectric constant is the same as that in the system interior so that there are no image forces. The density profiles look roughly like a sum of two independent double-layer profiles, except at extremely close separation. At large enough separation (more than the strip width) the two-particle distribution function decays with the inverse square of particle separation.

1. Introduction

An earlier paper (Smith 1982, hereafter referred to as I) discussed the two-dimensional one-component plasma of particles of charge q at a temperature given by $q^2/kT \equiv \Gamma = 2$. The system was confined to a disc, the edge of which carried a constant charge density $-\sigma q$, and there was a uniform background charge density $-\eta q$ in the disc with η chosen to make the system electrostatically neutral. The region outside the disc was a dielectric continuum with a dielectric constant of one (equal to that inside the disc) or zero (when images of the same sign and magnitude as the particles are generated). At the temperature $\Gamma = 2$ it is possible to obtain exact bulk and surface properties. In the limit of infinite disc radius (R), the surface properties are those of a straight surface edge bearing a finite charge density. In particular, as well as bulk properties, the excess surface free energy per unit length of surface and the one- and two-particle distribution functions close to the surface were obtained in closed form. With the external dielectric constant (ε_w) equal to one, a double layer is established which contains a net charge to cancel exactly the charge on the surface, and the first moment of the double-layer density profile obeys a sum rule derived by Blum *et al* (1981). For $\varepsilon_w = 0$ the double layer profiles are similar to those with $\varepsilon_w = 1$, but move out from the wall somewhat in response to a repulsive force on the particles excited by the images. The sum rule is again obeyed.

This similarity between the $\varepsilon_w = 0$ and $\varepsilon_w = 1$ cases does not extend to the two-particle distribution functions. Jancovici (1982a, b), in extending earlier exact studies of this system at $\Gamma = 2$ (Jancovici 1981, Alastuey and Jancovici 1981), has given a heuristic derivation of the result that along a wall of dielectric constant ε_w, the two-particle distribution function for two particles close to the wall but distant y from each other in a direction parallel to the wall will decay as $\varepsilon_w f(x_1, x_2)/y^\nu$. Here ν is the dimensionality of the system, x_1 and x_2 are the distances of the two particles from the wall and $f(x_1, x_2)$ is a function which remains finite while x_1 and x_2 are finite. His exact results for the two-dimensional one-component plasma at $\Gamma=2$ with $\varepsilon_w=1$ agree in giving a y^{-2} decay of the two-particle distribution function. On the other hand, he has shown that for $\varepsilon_w=0$, the exact results of I give an exponentially damped oscillatory behaviour.

These assorted general and particular results for single double layers make it of considerable interest to study the structure of two interacting double layers. There are many interesting features, of which the free energy per unit length of double layer, and the one- and two-particle distribution functions are examples. These are studied in this paper. They not only provide exact examples in the context of which general sum rules for the properties of electrostatic systems may be considered, but also provide examples on which approximate techniques in the theory of double layers may be tested. In this paper the case of a strip with external and internal dielectric constants equal is studied, so that there are no image forces. This simplification certainly makes the calculations simpler.

Section 2 of this paper introduces a finite system for which exact calculations may be performed at $\Gamma=2$. The system is not a strip but an annulus of width $2L$ with inner and outer radii $R-L$ and $R+L$ respectively. The annulus has appropriate fixed charge densities on both edges and a background charge density as well. There are N particles of opposite charge to the background in the annulus, and the system is exactly electrostatically neutral. The Hamiltonian for the system is written down and the canonical partition function and one- and two-particle canonical partition function calculated exactly for the annular system. In § 3 the limit of these expressions as $R\to\infty$ is discussed, giving distribution functions and a free energy per unit length of overlapping double layers. The range of interaction of double layers is seen to be small. In § 4 some consequences of these exact results are discussed, including a sum rule for the derivative of the free energy per unit length of a pair of interacting double layers with respect to an applied electric field.

2. The system and its exact integrals

Consider a system of N particles of charge q at positions $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N$ in an annulus of inner radius $R-L$, outer radius $R+L$. There are charge densities $-\sigma_- q$ on the inner edge and $-\sigma_+ q$ on the outer edge while the annular region has a uniform background charge density $-\eta q$ as well as the particles. The system is exactly electrostatically neutral so that

$$N=2\pi(R-L)\sigma_- + 4\pi RL\eta + 2\pi(R+L)\sigma_+. \tag{2.1}$$

The pair interaction between charges is the solution of the two-dimensional Poisson equation, namely $-\frac{1}{2}q_\alpha q_\beta \log(\boldsymbol{r}_\alpha-\boldsymbol{r}_\beta)^2$ for two charges q_α at $\boldsymbol{r}_\alpha$ and q_β at $\boldsymbol{r}_\beta$. The Hamiltonian consists of a variety of terms, but may be written, after some integration,

$$H=-\tfrac{1}{2}q^2\sum_{k=1}^{N-1}\sum_{j=k+1}^{N}\log\frac{|\boldsymbol{r}_k-\boldsymbol{r}_j|^2}{(R+L)^2}-\tfrac{1}{2}q^2(N^*-\Sigma_B-\Sigma_-)\sum_{j=1}^{N}\log\frac{\boldsymbol{r}_j^2}{(R+L)^2}$$
$$+\tfrac{1}{2}q^2N^*\sum_{j=1}^{N}\boldsymbol{r}_j^2/(R+L)^2+\tfrac{1}{4}q^2N\log(R+L)^2$$

$$-\tfrac{1}{2}q^2\left[(N^*-\Sigma_B-\Sigma_-)^2\log\frac{R-L}{R+L}+NN^*-\tfrac{3}{4}\Sigma_B^2+\tfrac{1}{2}\Sigma_B N^*-\Sigma_B\Sigma_-\right] \quad (2.2)$$

where $N^*=\pi\eta(R+L)^2$, $\Sigma_\pm=2\pi(R\pm L)\sigma_\pm$ and $\Sigma_B=4\pi RL\eta$.

This Hamiltonian may be substituted into the usual integrals for the partition function and one- and two-particle distribution functions. An integral over the annulus may be written using an (r, θ) parametrisation of points in the annulus so that

$$\int \mathrm{d}^2\boldsymbol{r}=\int_{R-L}^{R+L} r\,\mathrm{d}r\int_0^{2\pi}\mathrm{d}\theta.$$

It is then convenient to use the change of variables $z_k=r_k/(R+L)$ and the usual van der Monde determinant representation for the Boltzmann factor in the integrand. The procedure works in exactly the same way as it does for a system confined to a disc. The canonical partition function for $\Gamma=2$ has the form

$$Z_N(2)=\frac{1}{N!}[\pi(R+L)^2]^N\exp\Big[-\tfrac{1}{2}N\log(R+L)^2+(NN^*-\Sigma_B-\Sigma_-)^2\log\frac{R-L}{R+L}$$
$$+NN^*-\tfrac{3}{4}\Sigma_B^2+\tfrac{1}{2}\Sigma_B N^*-\Sigma_B\Sigma_-\Big]$$
$$\times\prod_{l=1}^{N}\left[\int_{R-L/R+L}^{1}2z_l\,\mathrm{d}z_l z_l^{2(N^*-\Sigma_B-\Sigma_-)}\exp(-N^*z_l^2)\int_0^{2\pi}\frac{\mathrm{d}\theta_l}{2\pi}\right]|D_N|^2 \quad (2.3)$$

where D_N is the determinant of the matrix with k, l element $(z_l\,\mathrm{e}^{\mathrm{i}\theta_l})^{k-1}$. If D_N and D_N^* are replaced by the usual expansions of determinants as sums over permutations of $(1,\ldots,N)$ then the θ_l integrals may be performed at once and, after a little thought, all the z_l integrals carried out in terms of differences of incomplete gamma functions. The standard definition

$$\gamma(s,x)=\int_0^x t^{s-1}\,\mathrm{e}^{-t}\,\mathrm{d}t \quad (2.4)$$

is used for the incomplete gamma functions. The canonical partition function at $\Gamma=2$ is then

$$Z_N(2)=[\pi(R+L)^2]^N\exp\Big[-\frac{N}{2}\log(R+L)^2+(N^*-\Sigma_B-\Sigma_-)^2\log\frac{R-L}{R+L}$$
$$+NN^*-\tfrac{3}{4}\Sigma_B^2+\tfrac{1}{2}\Sigma_B N^*-\Sigma_B\Sigma_-\Big](N^*)^{-N(N^*-\Sigma_B-\Sigma_-)}$$
$$\times\prod_{l=1}^{N}N^{*-l}\Big[\gamma(N^*-\Sigma_B-\Sigma_-+l,N^*)$$
$$-\gamma\Big(N^*-\Sigma_B-\Sigma_-+l,N^*\Big(\frac{R-L}{R+L}\Big)^2\Big)\Big]. \quad (2.5)$$

Once this method of integrating the canonical probability density has been sorted out, the integrals for the one- and two-particle distribution functions can be performed without too much effort. Large parts of the expression for $Z_N(2)$ cancel from these expressions and a relatively simple form remains. It is convenient to define the function

$$H(X)=(N^*X)^{N^*-\Sigma_B-\Sigma_-}\,\mathrm{e}^{-N^*X}\sum_{l=1}^{N}(N^*X)^{l-1}\Big[\gamma(N^*-\Sigma_B-\Sigma_-+l,N^*)$$

$$-\gamma\Big(N^*-\Sigma_B-\Sigma_-+l,N^*\Big(\frac{R-L}{R+L}\Big)^2\Big)\Big]. \tag{2.6}$$

In terms of this function

$$\rho_{(1)}(\boldsymbol{r})=\eta H[(r/R+L)^2] \tag{2.7}$$

and, with $\boldsymbol{r}_k=r_k(\cos\theta_k,\sin\theta_k)$,

$$\rho_{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2)=\eta^2\{H([r_1/(R+L)]^2)H([r_2/(R+L)]^2)$$

$$-\exp(-\pi\eta r_{12}^2)|H([r_1r_2/(R+L)^2]\exp[\mathrm{i}(\theta_1-\theta_2)])|^2\}. \tag{2.8}$$

These expressions for the one- and two-particle distribution functions have structures very similar to those reported in I for the same functions.

3. The large-radius limit

In the limit $R\to\infty$ with L fixed, the system becomes a pair of straight charged lines bearing linear charge densities $-\sigma_-q$ and $-\sigma_+q$ separated by a region of width $2L$ which contains a uniform background charge density $-\eta q$ and a one-component plasma of average particle density $\rho=\sigma_-+\sigma_++2\eta L$. The free energy per unit length of the system is then

$$f(L,\alpha_+,\alpha_-,\eta)=\lim_{R\to\infty}-(kT/2\pi R)\log Z_N(2) \tag{3.1}$$

where α_+ and α_- are the two dimensionless surface charge density parameters

$$\alpha_\pm=\sigma_\pm(2\pi/\eta)^{1/2}. \tag{3.2}$$

A 'Debye length' for the system is defined by $\lambda_D=1/\kappa$ with $\kappa^2=2\pi\eta$. The calculation of the free energy per unit length is rather tricky since the right-hand side of equation (3.1) with equation (2.5) substituted for $Z_N(2)$ contains a large number of potentially divergent terms as $R\to\infty$. In fact, these terms all cancel to zero when sufficient care is taken with the algebra and a finite free energy remains in the limit. The only non-obvious procedure is the replacement of the incomplete gamma functions by their uniform asymptotic expansions (see I). The sums of logarithms which arise may be conveniently written as integrals in the limit $R\to\infty$ and the final result for the free energy may be written in the form

$$f(L,\alpha_+,\alpha_-,\eta)=(kT\kappa/2\pi)[Y\log(2\eta/\pi^2)-\tfrac{8}{3}Y^3$$

$$+(\alpha_++\alpha_-)(\alpha_+\alpha_-+4\kappa LY)+\tfrac{8}{3}(\kappa L)^3+F_\Delta(\kappa L,\alpha_+,\alpha_-)] \tag{3.3}$$

where $Y=\frac{1}{2}\alpha_++\frac{1}{2}\alpha_-+\kappa L$ and

$$F_\Delta(\kappa L,\alpha_+,\alpha_-)=-\int_0^Y \mathrm{d}t\,\log\{[\mathrm{erf}(t+Y-\alpha_-)-\mathrm{erf}(t-Y+\alpha_+)]$$

$$\times[\mathrm{erf}(t+Y-\alpha_+)-\mathrm{erf}(t-Y+\alpha_-)]\}. \tag{3.4}$$

Here erf(x) is the standard error function. Figure 1 shows plots of

$$\Delta f=(2\pi/kT\kappa)[f(L,\alpha_+,\alpha_-,\eta)-f(L,0,0,\eta)-\tfrac{1}{2}(\alpha_++\alpha_-)\log(2\eta/\pi^2)-\tfrac{1}{3}(\alpha_+^3+\alpha_-^3)] \qquad (3.5)$$

as a function of κL for $\alpha_-=\alpha_+=1.5$ and for $\alpha_-=-\alpha_+=-1.5$. In these plots, κ is considered fixed so that L, the distance between the charged walls, is being varied. It may be seen that for $\kappa L\geqslant 1.0$ the system has a free energy corresponding to two non-interacting double layers and this gives an estimate of the range over which the double layer interaction is significant.

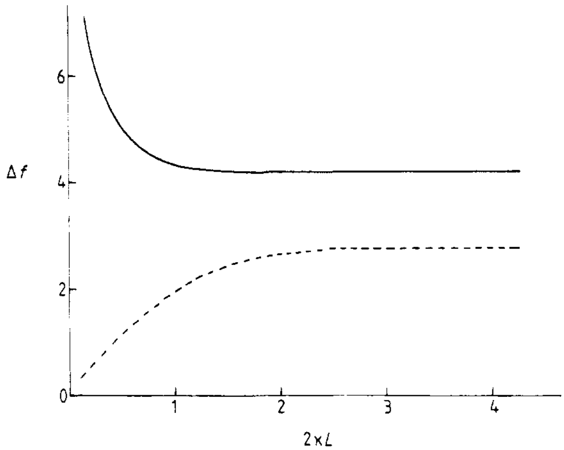

Figure 1. Plots of $\Delta f=(2\pi/kT\kappa)[f(L,1,1,\eta)-F(L,0,0,\eta)-\tfrac{1}{2}(\alpha_++\alpha_-)\log(2\eta/\pi^2)-\tfrac{1}{3}(\alpha_+^3+\alpha_-^3)]$. Full curve, $\alpha_-=\alpha_+=1.5$; broken curve, $\alpha_-=-\alpha_+=-1.5$.

A similar procedure using the uniform asymptotic expansion of the incomplete gamma functions involved may be used to estimate the function $H(X)$ in the limit $R\to\infty$. It is convenient to measure distances from $x=0$ at the surface leaving charge density $-\sigma_+q$ to $x=2L$ at the surface bearing charge density $-\sigma_-q$. The density profile across the pair of interacting double layers has the representation

$$\rho_{(1)}(x)=\eta h(x) \qquad (3.6)$$

where

$$h(x)=\frac{2}{\sqrt{\pi}}\int_0^Y \mathrm{d}t\left(\frac{\exp[-(t+Y-\alpha_++\kappa x)^2]}{\operatorname{erf}(t+Y-\alpha_+)-\operatorname{erf}(t-Y+\alpha_-)}+\frac{\exp[-(t-Y+\alpha_++\kappa x)^2]}{\operatorname{erf}(t+Y-\alpha_-)-\operatorname{erf}(t-Y+\alpha_+)}\right).$$

Figure 2 contains plots of $h(x)$ as a function of κx for $\alpha_-=-\alpha_+=1.0$ and several values of $2\kappa L$ while figure 3 contains similar plots but with $\alpha_-=\alpha_+=1.0$. Notice that the profiles look like two independent profiles for $2\kappa L\geqslant 2$, a rather small value consistent with the estimate of double-layer interaction range obtained from the free energy plots. For smaller separations, both figures show that the interaction causes gross distortion of the double layers.

The two-particle distribution function for particles at $(x_1,0)$ and (x_2,y) is given by

$$\rho_{(2)}(x_1,x_2,y)=\eta^2\{h(x_1)h(x_2)-\exp[-\pi\eta r_{12}^2]|h[\tfrac{1}{2}(x_1+x_2+\mathrm{i}y)]|^2\} \qquad (3.7)$$

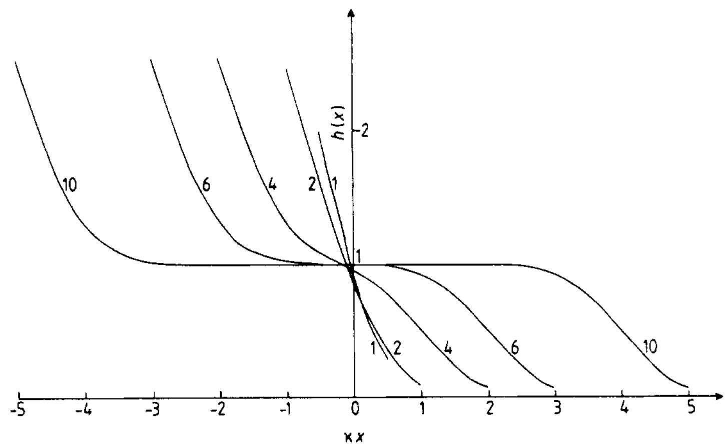

Figure 2. Plots of $\rho_{(1)}(x)/\eta$ as a function of κx with x measured from the centre of the layer with $\alpha_- = -\alpha_+ = 1$. Figures on curves refer to the appropriate values of $2\kappa L$.

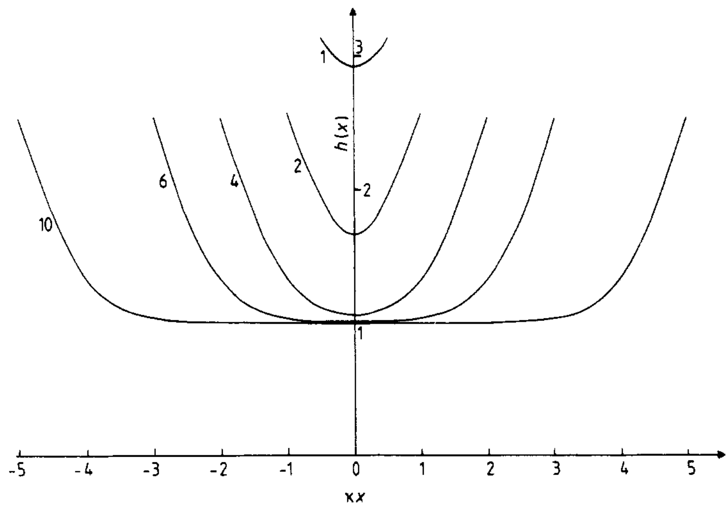

Figure 3. Plots of $\rho_{(1)}(x)/\nu$ as a function of κx with x measured from centre of layer with $\alpha_- = \alpha_+ = 1$. Figures on curves refer to the appropriate values of $2\kappa L$.

where $r_{12}^2 = (x_1 - x_2)^2 + y^2$. Of course within the interacting double layers $0 \leq x_k \leq 2L$ so x_1 and x_2 remain bounded. The asymptotic expansion of the two-particle distribution function at large y displays the remarkable property of polynomial decay described first by Jancovici (1982a). Thus, as $y \to \infty$

$$\rho_{(2)}(x_1, x_2, y) = \rho_{(1)}(x_1)\rho_{(2)}(x_2) - \eta^2[A(x_1, x_2; y)/y^2](1 + O(y^{-1})) \qquad (3.8)$$

where $A(x_1, x_2; y)$ is a function which remains bounded away from zero for all x_1, x_2 in the range $[0, 2L]$. Thus the whole of the strip of interacting double layers is characterised by very long-ranged particle–particle correlations.

4. Conclusions

There are few surprises about the exact results presented in this paper. They do, however, allow tests to be made on more general exact and approximate theories of plasma systems. An example of this is to consider a strip of width $2L$ with charge densities σ_+ on one edge and $-\sigma_+$ on the opposite edge. This system may be interpreted as having an electric field

$$E = 2\pi\sigma q \tag{4.1}$$

imposed normal to the edge of the strip. The Hamiltonian for such a system may be written in terms of the Hamiltonian with zero field:

$$H(E) = H(0) + qE \sum_{k=1}^{N} x_k - 2q\eta EL^2 + \frac{1}{2\pi} qE^2 L, \tag{4.2}$$

the terms on the right-hand side of this equation being in order: $H(0)$, the interaction of the particles with the field, the interaction of the background with the field and the interaction of the surface charge densities with the field. The free energy per unit length of a strip of length W in the thermodynamic limit is then

$$f = \lim_{W\to\infty} -\frac{kT}{W} \int_0^W \mathrm{d}y_1 \int_0^{2L} \mathrm{d}x_1 \ldots \int_0^W \mathrm{d}y_N \int_0^{2L} \mathrm{d}x_N \exp(-H(E)/kT), \tag{4.3}$$

where, of course, N increases with W in the usual way. Assuming that the thermodynamic limit commutes with differentiation with respect to E then gives

$$\frac{\partial f}{\partial E} = q \int_0^{2L} \mathrm{d}x\, x[\rho_{(1)}(x) - \eta] + 2\sigma_+ qL, \tag{4.4}$$

a sum rule relating free energy and density profile, analogous to that derived in the same way for a single surface (Jancovici 1981, private communication). It may be checked by direct examination of equations (3.4) and (3.6) when it will be found that it holds. Another feature of this interpretation is given by the density profiles plotted in figure 2. They show that the electric field is in fact screened extremely rapidly by the double layers set up at the edges of the strip.

Another most interesting question which may be asked about this system is the way it changes when image forces act on it from one or both sides. In particular it would be of great interest to see how surfaces with dielectric constant zero on both sides of the strip might affect the considerations on two-particle distribution functions in Coulombic systems near surfaces introduced and developed by Jancovici (1982a, b) and the structural features in periodic strips uncovered by Choquard (1981) for this system. Work is in progress on these questions.

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Note added in proof. Jancovici (private communication) has pointed out that the form of the function $A(x_1, x_2; y)$ in equation (3.8), namely $A(x_1, x_2; y) = A(x_1, x_2) + \exp(-Y^2) B(x_1, x_2) \cos 2\kappa Y y$, gives two types of decay with large y. Here $A(x_1, x_2)$ and $B(x_1, x_2)$ are positive and bounded away from zero in $[0, 2L]$. The first type of decay, A/y^2, is that predicted by Jancovici's general theory at the surface of a half space (Jancovici 1982b). The second type, $\cos(2x^2 Ly)/y^2$, is not predicted by that theory this is because the theory estimates the singularity at $\boldsymbol{k} = \boldsymbol{0}$ in the Fourier transform with respect to $\boldsymbol{y}$ of the two-particle distribution function $h_{(2)}(x_1, x_2; \tilde{\boldsymbol{y}})$. It cannot predict the structure of singularities at $\boldsymbol{k} \pm \boldsymbol{0}$, as is the case here. This property of the system apparently reflects the one-dimensional nature of the system.

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