

A Solvable Model for Localized Adsorption in a Coulomb System

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A model for an interface with localized adsorption is presented, in which the surface has a distribution of sticky adhesive sites in contact with a Coulomb fluid. Contrary to the current literature on the electrical double layer the surface charge is in dynamic equilibrium with the bulk fluid. The sum rules obeyed by the one- and two-body correlation functions are investigated. Explicit results are obtained for a solvable model, the two-dimensional one-component plasma at reduced temperature 2 . The effect of the granularity of the adsorbed charge on the adsorption isotherm is discussed.

KEY WORDS: Localized adsorption, Coulomb systems; one-component plasma; two dimensions; electrical double layer; sum rules.

1. INTRODUCTION

When a solid material such as an electrode plate or a colloid particle is in contact with an electrolyte solution or a plasma, it can acquire an electrical charge by specific adsorption of ions. This adsorbed surface charge modifies the distribution of the ions and the molecules in the vicinity of the surface and induces a surface potential. In the case of chemisorbed systems (or strong physisorption) the adsorbed ions are localized on adsorption sites with a distribution which reflects in some way the structure of the adsorbent, as for instance a periodic lattice. It is not an easy task to include

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this surface charge which is in dynamic equilibrium with the electrolyte in a statistical mechanical treatment of the interface. For this reason, in almost all works devoted to the study of Coulomb systems near a wall, the surface charge is a prescribed "external" charge, uniformly distributed on the wall.⁽¹⁾ In particular, the adsorbed charges cannot "react" to the bulk system.

In the present paper, we give an exact solution to a two-dimensional model of the true adsorption problem. The Coulomb fluid is the classical one-component plasma (OCP) at the special temperature T for which the coupling constant $\Gamma = \beta e^2 = 2$, $\beta = (k_B T)^{-1}$, and the specific (short range) adsorption potential is the sticky potential of Baxter.⁽²⁾

The one component plasma is the simplest model of a Coulomb fluid and recently various physically interesting inhomogeneous situations have been worked out exactly in two dimensions for $\Gamma = 2$.⁽³⁻¹⁰⁾ They are restricted, however, to the case where the background density or the external potential varies only in one direction.

We shall consider here the following three situations: (i) a semi-infinite plasma in the vicinity of an impenetrable wall (i.e., a line) with continuous adsorption; (ii) an infinite plasma in the vicinity of discrete adsorption sites regularly spaced on a line; (iii) a semi-infinite plasma in the vicinity of an impenetrable wall with discrete adsorption.

While (i) is a simple extension of the results obtained in References 3-5, (ii) and (iii) are real two-dimensional problems and the structure of the fluid (for instance, the one- and two-body distribution functions) will vary both in the directions perpendicular and parallel to the line of sites.

The method that we use for solving this problem involves infinite expansions in terms of the n -body correlation functions of the unperturbed fluid (i.e., without adsorption sites). While this solution is valid for any fluid subject to an external one-body potential of Baxter's type, this is so, however, only in a formal sense since the n -body correlation functions are generally unknown quantities. The two-dimensional OCP at $\Gamma = 2$ is a rare exception: the gaussian structure of the correlation functions^(4,11) makes the infinite expansions summable.

Our formal method of solution is described in Section 2 where, for the sake of simplicity, we restrict ourselves to the case of the two-dimensional OCP, but the generalization to any multicomponent fluid in two or three dimensions is immediate. We consider there also the sum rules that should be satisfied by a charged system.

In Section 3 we give the solution of case (i), using the direct method introduced by Jancovici^(3,4) and we discuss the effect of the nature of the surface charge (a prescribed external uniform charge against an adsorbed surface charge).

In Section 4, we work out the exact solution of case (ii) and consider some limit situations where it reduced to already known results. Finally, in Section 5, we give the solution of case (iii).

2. METHOD OF SOLUTION

We consider a two-dimensional system of classical particles of charge e and bulk number density ρ , embedded in a neutralizing uniform background of charge density $-e\rho$. The system is semi-infinite, confined to the half-space $x > 0$. The particles interact through the Coulomb potential

$$v(r) = -e^2 \ln \frac{r}{L} \quad (2.1)$$

where L is an irrelevant scale length.

The adsorption sites are located on the line $x = x_0$ and are regularly spaced with a linear density ω .

Following earlier work^(12,13) we model the adsorption potential $u_a(\mathbf{r} - \mathbf{R})$, created at \mathbf{r} by the site located at \mathbf{R} , by the sticky potential of Baxter⁽²⁾

$$\exp[-\beta u_a(\mathbf{r} - \mathbf{R})] = 1 + \lambda \delta(\mathbf{r} - \mathbf{R}) \quad (2.2)$$

where $\delta(\mathbf{r})$ is the Dirac delta function. The positive constant λ measures the strength of the adsorption and the delta function mimics the short-range nature of a specific adsorption potential. As we shall see later, this is equivalent to assigning a fugacity λ to the site B . We note that since the Coulomb potential becomes infinitely repulsive when r goes to zero, we expect that for a given λ the number of particles adsorbed on a site is smaller than one.

As mentioned earlier, we shall consider three cases: (i) and (iii) correspond to the limit $x_0 = 0$, respectively, in the continuous ($\omega \rightarrow \infty$, $\lambda \rightarrow 0$ such that $\lambda\omega$ goes to a finite value) and discrete version; (ii) correspond to the limit $x_0 \rightarrow \infty$ (i.e., the line of sites is located in the bulk plasma).

2.1. The Free Energy and the Density of Adsorbed Particles

Although we seek the free energy and the distribution functions of the (semi) infinite system, we first consider a finite system of N particles and M sites in a volume A . This could be, for instance, a system of circular symmetry as in Ref. 3, 4, e.g., a disk of radius R ($N = \pi\rho R^2$) with the sites located on the circle of radius R_0 ($M = 2\pi R_0\omega$). We do not need, however, to specify the geometry of the system in what follows.

The canonical partition function is

$$Z_N = \frac{1}{N!} \int_A e^{-\beta V^0(\mathbf{r}^N)} \prod_{i=1}^N \left\{ \left[1 + \lambda \sum_{m=1}^M \delta(\mathbf{r}_i - \mathbf{R}_m) \right] d\mathbf{r}_i \right\} \quad (2.3)$$

where V^0 is the potential energy of the unperturbed system (without adsorption sites, i.e., $\lambda = 0$) and \mathbf{R}_m is the position of site m .

Expanding the product in the integrand, we can rewrite Z_N in a more illuminating way

$$Z_N = \sum_{\{s\}} \frac{\lambda^s}{(N-s)! s!} \int_A e^{-\beta V^0(\mathbf{R}_{m_1}, \mathbf{R}_{m_2}, \dots, \mathbf{R}_{m_s}, \mathbf{r}_{s+1}, \dots, \mathbf{r}_N)} d\mathbf{r}_{s+1} \cdots d\mathbf{r}_N \quad (2.4)$$

where $\sum_{\{s\}}$ is a simplified notation for $\sum_s \sum_{m_1, m_2, \dots, m_s=1}^M$. The coefficient of λ^s corresponds to the sum over all the configurations where s particles are adsorbed. For instance, the term of the expansion corresponding to $s = 2$ is

$$Z_N^{(2)} = \sum_{m_1, m_2} \frac{\lambda^2}{2(N-2)!} \int_A e^{-\beta V^0(\mathbf{R}_{m_1}, \mathbf{R}_{m_2}, \mathbf{r}_3, \dots, \mathbf{r}_N)} d\mathbf{r}_3 \cdots d\mathbf{r}_N \quad (2.5)$$

It is clear from (2.4) that λ can be identified (up to a multiplicative constant) with the fugacity of the adsorbed particles with the average number of adsorbed particles $\langle N_a \rangle$ given by

$$\langle N_a \rangle = \frac{\partial \ln Z_N}{\partial \ln \lambda} \quad (2.6)$$

This also suggests that there should be the equivalent of a ‘‘compressibility’’ sum rule for the adsorbed particles (see Section 2.3).

Introducing in (2.4) the n -particle distribution functions of the unperturbed system defined as usual by

$$\rho_0^{(n)}(\mathbf{r}_1 \cdots \mathbf{r}_n) = \frac{1}{(N-n)!} \frac{1}{Z_N^0} \int_A e^{-\beta V^0(\mathbf{r}^N)} d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N \quad (2.7)$$

with $Z_N^0 = Z_N(\lambda = 0)$, Z_N can be written as

$$Z_N = Z_N^0 \sum_{\{s\}} \frac{\lambda^s}{s!} \rho_0^{(s)}(\mathbf{R}_{m_1}, \mathbf{R}_{m_2}, \dots, \mathbf{R}_{m_s}) \quad (2.8)$$

Since $\rho_0^{(s)}$ vanishes when any of the arguments coincide, we need consider only cases when there is no multiple occupancy of any site. One goes from

Z_N/Z_N^0 to its logarithm by replacing the distribution functions by their connected parts. This gives

$$\ln \frac{Z_N}{Z_N^0} = \sum_{s \geq 1} \frac{\lambda^s}{s!} T_s^{(0)} \quad (2.9)$$

where $T_s^{(0)} \equiv \sum_{m_1, m_2, \dots, m_s=1}^M \rho_0^{(s,T)}(\mathbf{R}_{m_1}, \mathbf{R}_{m_2}, \dots, \mathbf{R}_{m_s})$ and the truncated n -body correlation functions are defined as usual

$$\begin{aligned} \rho_0^{(1,T)}(\mathbf{r}_1) &= \rho_0(\mathbf{r}_1) \\ \rho_0^{(2,T)}(\mathbf{r}_1, \mathbf{r}_2) &= \rho_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho_0(\mathbf{r}_1) \rho_0(\mathbf{r}_2) \\ \rho_0^{(3,T)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \rho_0^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - \rho_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rho_0(\mathbf{r}_3) - \dots \end{aligned} \quad (2.10)$$

The excess free energy of the system (compared to the free energy of the unperturbed system) is given by

$$\Delta F = -k_B T \ln \frac{Z_N}{Z_N^0} = -k_B T \sum_{s \geq 1} \frac{\lambda^s}{s!} T_s^{(0)} \quad (2.11)$$

and since the number of sites is proportional to some ‘‘area’’ A (for instance $2\pi R_0$ in the circular geometry) and not to the ‘‘volume’’ V of the system, we expect that $\Delta F/A$ tends to a finite limit Δf^s in the thermodynamic limit ($N, M, A \rightarrow \infty$; ρ, ω fixed). We shall not discuss here the problem of proving the existence of this limit or of the convergence of the infinite expansion in the r.h.s. of (2.11) or in similar expressions. We shall simply assume that the ‘‘surface’’ properties have a well-defined limit. From (2.6) and (2.11) the average number of adsorbed particles is

$$\begin{aligned} \langle N_a \rangle &= -\beta \lambda \frac{\partial \Delta F}{\partial \lambda} \\ &= \sum_{s \geq 1} \frac{\lambda^s}{(s-1)!} T_s^{(0)} \end{aligned} \quad (2.12)$$

and in the thermodynamic limit $\langle N_a \rangle/M$ will tend to a finite number n_a , the average number of adsorbed particles per site, with $n_a \leq 1$.

2.2. The One- and Two-Body Densities

The n -body distribution functions of our system are defined by

$$\begin{aligned} \rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_N) &= \frac{1}{(N-n)! Z_N} \int_{\mathcal{A}} e^{\beta V^0(\mathbf{r}^N)} \prod_i \\ &\times \left[1 + \lambda \sum_m \delta(\mathbf{r}_i - \mathbf{R}_m) \right] d\mathbf{r}_{n+1}, \dots, d\mathbf{r}_N \end{aligned} \quad (2.13)$$

They can be also expressed in terms of the distribution functions of the unperturbed system, by expanding the product in the integrand of (2.13). This will contain a continuous part (i.e., without delta functions) which corresponds to the distribution of the nonadsorbed particles and a singular part corresponding to the adsorption of at least one particle.

We shall only consider the one- and the two-body densities. We see immediately from (2.13) that $\rho(\mathbf{r}_1)$ has the form

$$\rho(\mathbf{r}_1) = \left[1 + \lambda \sum_m \delta(\mathbf{r}_1 - \mathbf{R}_m) \right] \rho^*(\mathbf{r}_1) \quad (2.14)$$

where the continuous part $\rho^*(\mathbf{r}_1)$ is given by

$$\rho^*(\mathbf{r}_1) = \rho_0(\mathbf{r}_1) + \sum_{s \geq 1} \frac{\lambda^s}{s!} T_s^{(1)} \quad (2.15)$$

where

$$T_s^{(1)} \equiv \sum_{m_1, m_2, \dots, m_s=1}^M \rho_0^{(s+1, T)}(\mathbf{r}_1, \mathbf{R}_{m_1}, \dots, \mathbf{R}_{m_s})$$

The average number of adsorbed particles is given by the integral of the singular part of $\rho(\mathbf{r}_1)$

$$\langle N_a \rangle = \lambda \int_A \sum_m \delta(\mathbf{r}_1 - \mathbf{R}_m) \rho^*(\mathbf{r}_1) d\mathbf{r}_1 \quad (2.16)$$

so that we have, in the thermodynamic limit, the exact relation

$$n_a = \lambda \rho^*(\mathbf{R}_m) \quad (2.17)$$

which relates the average density of adsorbed and nonadsorbed particles at one site. A similar result was given in Refs. 12, 13 where the specific ionic adsorption on a wall is treated in the hypernetted-chain (HNC) approximation.

Note also that (2.14) and (2.16) give, in the finite system

$$N = \langle N_a \rangle + \int_A \rho^*(\mathbf{r}_1) d\mathbf{r}_1 \quad (2.18)$$

which can also be written (since $N = \rho A$) as

$$\int_A [\rho^*(\mathbf{r}_1) - \rho] d\mathbf{r}_1 = -\langle N_a \rangle \quad (2.19)$$

The truncated two-body density can be written as

$$\rho_T(\mathbf{r}_1, \mathbf{r}_2) = \left[1 + \lambda \sum_{m_1} \delta(\mathbf{r}_1 - \mathbf{R}_{m_1}) \right] \left[1 + \lambda \sum_{m_2} \delta(\mathbf{r}_2 - \mathbf{R}_{m_2}) \right] \rho_T^*(\mathbf{r}_1, \mathbf{r}_2) \quad (2.20)$$

where the continuous part $\rho_T^*(\mathbf{r}_1, \mathbf{r}_2)$ is given by

$$\rho_T^*(\mathbf{r}_1, \mathbf{r}_2) = \rho_0^{(2,T)}(\mathbf{r}_1, \mathbf{r}_2) + \sum_{\substack{\{s\} \\ s \geq 1}} \frac{\lambda^s}{s!} \rho_0^{(s+2,T)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}_{m_1}, \dots, \mathbf{R}_{m_s}) \quad (2.21)$$

The truncated correlation function between two adsorbed particles (i.e., the coefficient of the product of the two delta functions in (2.21)) satisfies the relation (similar to (2.17))

$$R_T(\mathbf{R}_{m_1}, \mathbf{R}_{m_2}) = \lambda^2 \rho_T^*(\mathbf{R}_{m_1}, \mathbf{R}_{m_2}) \quad (2.22)$$

Noting that $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_1) = 0$, we must have

$$R_T(\mathbf{R}_m, \mathbf{R}_m) = -n_a^2 \quad (2.23)$$

2.3. Sum-Rules and the Decay of the Correlations

We know from Ref. 14 that, in Coulomb systems, the one- and two-body correlation functions satisfy in the thermodynamic limit a set of sum rules (multipole sum rules) whenever there is good asymptotic decay of the correlations. If the adsorption sites are located in the bulk phase, we can expect a fast decay (i.e., nonalgebraic) of $\rho_T(\mathbf{r}_1, \mathbf{r}_2)$ in all directions, similar to the behavior of the correlation functions of the unperturbed system. The situation is more delicate in the vicinity of a wall (cases (i) and (iii)) where $\rho_0^{(2,T)}(\mathbf{r}_1, \mathbf{r}_2)$ decays only as $(y_1 - y_2)^{-2}$ (in two dimensions) in the direction parallel to the wall.⁽⁴⁾ (Note, however, that

$$\int_{-\infty}^{+\infty} \rho_0^{(2,T)}(x_1=0, x_2=0, y) dy \quad \text{or} \quad \sum_{m_1, m_2} \rho_0^{(2,T)}(\mathbf{R}_{m_1}, \mathbf{R}_{m_2})$$

is still defined.) We shall, therefore, assume in general only the existence of the perfect screening sum rule

$$\int \rho_T(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -\rho(\mathbf{r}_1) \quad (2.24)$$

which, using (2.19) and (2.20), implies

$$\int d\mathbf{r}_2 \rho_T^*(\mathbf{r}_1, \mathbf{r}_2) + \lambda \sum_m \rho_T^*(\mathbf{r}_1, \mathbf{R}_m) = -\rho^*(\mathbf{r}_1) \quad (2.25a)$$

$$\lambda \int d\mathbf{r}_2 \rho_T^*(\mathbf{R}_m, \mathbf{r}_2) + \sum_{m_1} R_T(\mathbf{R}_m, \mathbf{R}_{m_1}) = -n_a \quad (2.25b)$$

Because of Eqs. (2.17) and (2.22), (2.25b) can be readily deduced from (2.25a).

Finally, $R_T(\mathbf{R}_{m_1}, \mathbf{R}_{m_2})$ should satisfy another sum rule which is the equivalent of the compressibility equation for homogeneous systems. It can be easily deduced from (2.4) where λ plays the role of the fugacity of the adsorbed particles. In the finite system we have

$$\langle N_a^2 \rangle - \langle N_a \rangle^2 = \lambda \frac{\partial \langle N_a \rangle}{\partial \lambda} \quad (2.26)$$

and the normalization

$$\sum_{m_1, m_2} R_T(\mathbf{R}_{m_1}, \mathbf{R}_{m_2}) = \langle N_a^2 \rangle - \langle N_a \rangle^2 - \langle N_a \rangle \quad (2.27)$$

Then in the thermodynamic limit

$$\begin{aligned} \sum_{m_1} R_T(\mathbf{R}_m, \mathbf{R}_{m_1}) &= \lambda \frac{\partial n_a}{\partial \lambda} - n_a \\ &= \frac{\beta \lambda^2}{\omega} \frac{\partial^2 \Delta f^s}{\partial \lambda^2} \end{aligned} \quad (2.28)$$

This relation unlike (2.25) is not restricted to Coulomb systems. But if (2.25) holds we get also

$$\int d\mathbf{r}_2 \rho_T^*(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\partial n_a}{\partial \lambda} \quad (2.29)$$

or, using (2.17), (2.22), and (2.25a)

$$\begin{aligned} \sum_{m_1} \rho_T^*(\mathbf{R}_m, \mathbf{R}_{m_1}) &= -\frac{\beta}{\omega} \frac{\partial^2 \Delta f^s}{\partial \lambda^2} \\ &= \frac{\partial \rho^*(\mathbf{R}_m)}{\partial \lambda} \end{aligned} \quad (2.30)$$

3. CONTINUOUS ADSORPTION ON A WALL ($\Gamma = 2$)

All the results of the preceding section remain valid when the density of the adsorption sites increases indefinitely ($\omega \rightarrow \infty$). However, in order to get finite quantities we must at the same time take the limit $\lambda \rightarrow 0$ such that $\lambda\omega \rightarrow \lambda_c$ finite. We then have a “continuous” adsorption on the line $x = x_0$ and all the sums over the sites must be replaced by integrals along the line. Thus, the one-body density for the nonadsorbed particles is now

$$\rho^*(x_1 - x_0) = \rho_0(x_1 - x_0) + \sum_{s=1}^{\infty} \frac{\lambda_c^s}{s!} \int \rho_0^{(s+1,T)}(\mathbf{r}_1, \mathbf{r}_2 \cdots \mathbf{r}_{s+1}) \times \delta(x_2 - x_0) \cdots \delta(x_{s+1} - x_0) d\mathbf{r}_2 \cdots d\mathbf{r}_{s+1} \quad (3.1)$$

and depends only on $x_1 - x_0$ since the adsorption potential varies only in the x direction. The density of adsorbed particles on the line is $\nu_a = \lim_{\omega \rightarrow \infty, \lambda \rightarrow 0} (\omega n_a)$.

We shall now consider situation (i) ($x_0 = 0$) where the line of adsorption coincides with the boundary of the semi-infinite system. The case $x_0 \rightarrow \infty$ (continuous adsorption in the bulk phase) will be treated in the next section as a limit of situation (ii).

At $\Gamma = 2$ we know from Jancovici⁽⁴⁾ how to compute the n -body correlation functions of the unperturbed semi-infinite system. It is, however, much easier to calculate directly by Jancovici’s method the properties of the system with adsorption, since the problem is only one dimensional. As in Ref. 4 we start with a finite disk of radius R and represent \mathbf{r}_i by a complex number in polar coordinates. The canonical partition function is now

$$Z_N = \frac{1}{N!} \int_{\mathcal{A}} e^{-\beta V^0(\mathbf{r}^N)} \prod_i \{ [1 + \lambda_c \delta(r_i - R)] d\mathbf{r}_i \} \quad (3.2)$$

Expanding the Boltzmann factor in terms of a Vandermonde determinant and performing the angular integration we get

$$Z_N = Z_N^0 \prod_{l=0}^{N-1} \left\{ 1 + \frac{2\lambda_c}{a} \frac{e^{-R_a^2} R_a^{2l+1}}{\gamma(l+1, R_a^2)} \right\} \quad (3.3)$$

where $a = (\pi\rho)^{-1/2}$ is the mean interparticle distance and $R_a = R/a$.

$$\gamma(l+1, R_a^2) = \int_0^{R_a^2} e^{-u} u^l du \quad (3.4)$$

is the incomplete gamma function. The excess free energy is

$$\Delta F = -k_B T \sum_{l=0}^{N-1} \ln \left[1 + \frac{2\lambda_c}{a} \frac{R_a^{2l+1} e^{-R_a^2}}{\gamma(l+1, R_a^2)} \right] \quad (3.5)$$

In the limit of the plane hard wall ($R \rightarrow \infty$) it can be shown as in Ref. 4 that the dominant values of l in the sums are close to R_a^2 and the incomplete gamma function can be replaced by its asymptotic form

$$\gamma(l+1, R_a^2) = \left(\frac{\pi}{2}\right)^{1/2} R_a \exp[-l + \ln l] \left[1 + \Phi(t) + O\left(\frac{1}{R}\right) \right] \quad (3.6)$$

where $t = (R_a^2 - l)/R_a \sqrt{2}$ and $\Phi(t)$ is the error function

$$\Phi(t) = \frac{2}{\sqrt{\pi}} \int_0^t \exp(-u^2) du \quad (3.7)$$

Then, in this limit

$$\frac{R_a^{2l+1} e^{-R_a^2}}{\gamma(l+1, R_a^2)} \rightarrow \sqrt{\frac{2}{\pi}} \frac{e^{-t^2}}{1 + \Phi(t)} \quad (3.8)$$

and the sum upon l can be replaced by an integral upon t . The surface excess free energy $\Delta F/2\pi R$ tends to the finite value

$$\Delta f^s = -k_B T (\rho/2\pi)^{1/2} \int_0^\infty \ln \left[1 + 2\lambda_c \sqrt{2\rho} \frac{e^{-t^2}}{1 + \Phi(t)} \right] dt \quad (3.9)$$

The surface density of adsorbed particle is given by a relation similar to (2.6) or (2.12)

$$v_a = -\beta \lambda_c \frac{\partial \Delta f^s}{\partial \lambda_c} = \frac{2\lambda_c \rho}{\sqrt{\pi}} \int_0^\infty \frac{e^{-t^2}}{1 + \Phi(t) + 2\lambda_c \sqrt{2\rho} e^{-t^2}} dt \quad (3.10)$$

Equation (3.10) gives an adsorption isotherm relating the surface charge density $\sigma_a = ev_a$ to the bulk density ρ and to the strength of the adsorption λ_c . For this two-dimensional model the relevant dimensionless parameter is $\lambda_c \rho^{1/2} \sim \lambda_c/a$. At low coverage ($\lambda_c \rightarrow 0$) we obtain at once

$$\sigma_a = e\lambda_c \rho_0(0)$$

or

$$\rho^{-1/2} \sigma_a = e\lambda_c \rho^{1/2} \ln 2 \quad (3.11)$$

where $\rho_0(0)$ is the contact value of the one-body density in the absence of adsorption.⁽³⁾

In the strong adsorption limit ($\lambda_c \rightarrow \infty$) we must be more careful with the integral in (3.10). First we break up the integral into

$$\int_0^{t_0} dt + \dots + \int_{t_0}^{\infty} dt, \dots \quad \text{where} \quad t_0^2 = \ln(2\lambda_c \sqrt{2\rho})$$

The second integral is bounded above by

$$\int_{t_0}^{\infty} \frac{e^{-t^2}}{1 + \Phi(t)} dt = -\frac{\sqrt{\pi}}{2} \ln \frac{1 + \Phi(t_0)}{2}$$

which goes to 0 like $e^{-t_0^2}/4t_0$ when $t_0 \rightarrow \infty$. The first integral diverges like $t_0/2\lambda_c \sqrt{2\rho}$. Therefore, we have

$$\rho^{-1/2} \sigma_a \sim e \left[\frac{1}{2\pi} \ln(2\lambda_c \sqrt{2\rho}) \right]^{1/2} \quad (3.12)$$

which shows that the adsorbed surface charge density will not saturate. This is clearly related to the fact that we are considering point particles, without any excluded volume interactions in the adsorbed layer. It is interesting to note that a linear theory such as the Mean Spherical approximation (MSA) would give a saturation effect even in the limit of point particles:⁽¹²⁾ this is obviously an artifact of the linearization.⁽¹³⁾

The one- and two-body densities can be calculated as in Refs. 3, 4. We find

$$\rho^*(x) = \rho \frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{e^{-(t-x/a\sqrt{2})^2}}{1 + \Phi(t) + 2\lambda_c \sqrt{2\rho} e^{-t^2}} dt \quad (3.13)$$

and

$$\rho_T^*(x_1, x_2, y) = -\rho^2 e^{-((x_1-x_2)/a)^2} \times \left| \frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{\exp \left\{ -\left(t - \frac{x_1+x_2}{a\sqrt{2}} \right)^2 - ity \frac{\sqrt{2}}{a} \right\}}{1 + \Phi(t) + 2\lambda_c \sqrt{2\rho} e^{-t^2}} dt \right|^2 \quad (3.14)$$

where $y = y_1 - y_2$. These results can be also derived from the expressions given in Reference 9. We readily see that

$$v_a = \lambda_c \rho^*(0) \quad (3.15)$$

while the truncated correlation function between two adsorbed particles is given by (see Eq. (2.22))

$$R_T(y) = \lambda_c^2 \rho_T^*(0, 0, y) \quad (3.16)$$

Introducing a convergence factor $\exp(-\delta x)$ we can also easily check the global electroneutrality relation

$$\int_0^{\infty} [\rho^*(x) - \rho] dx = -v_a \quad (3.17)$$

The perfect screening sum rule (2.24) and the ‘‘compressibility’’ relations (2.28), (2.29), or (2.30) also follow. By an analysis similar to that of Jancovici⁽⁴⁾ we find that the correlations along the wall decay only as y^{-2} when $y \rightarrow \pm\infty$ for fixed values of x_1 and x_2 . This suggests that the polarization cloud induced by a charge e located near the wall has a finite electrical dipole moment in the direction normal to the wall. Indeed we can check that

$$\begin{aligned} & \int_{x_2 \geq 0} (x_2 - x_1) \rho_T(x_1, x_2, y) d\mathbf{r}_2 \\ &= -\frac{1}{2\pi} \frac{\sqrt{2\rho} e^{-2\pi\rho x_1^2}}{1 + 2\lambda_c \sqrt{2\rho}} [1 + \lambda_c \delta(x_1)] \end{aligned} \quad (3.18)$$

or

$$\begin{aligned} & \int_{x_2 > 0} (x_2 - x_1) \rho_T^*(x_1, x_2, y) d\mathbf{r}_2 - \lambda_c x_1 \int_{x_2 > 0} \rho_T^*(x_1, 0, y) dy \\ &= -\frac{1}{2\pi} \frac{\sqrt{2\rho}}{1 + 2\lambda_c \sqrt{2\rho}} \quad (x_1 \geq 0) \end{aligned} \quad (3.19)$$

Another quantity of interest in the electrical double layer theory is the surface potential

$$\begin{aligned} \psi(0) &= -2\pi e \int_0^{\infty} x [\rho(x) - \rho] dx \\ &= -2\pi e \int_0^{\infty} x [\rho^*(x) - \rho] dx \end{aligned} \quad (3.20)$$

(where we have taken $\psi(\infty) = 0$). Introducing again a convergence factor $\exp(-\delta x)$ we find after some manipulations

$$\psi(0) = e \left[\frac{1}{4} + \frac{1}{2} \ln \frac{1 + 2\lambda_c \sqrt{2\rho}}{2} \right] \quad (3.21)$$

It is interesting to compare this result with that obtained when the surface charge σ_a is not an *adsorbed* charge but a smeared out charge density

on the wall, i.e., one which is rigid and not free to move and exchange with the charges in the system. We recall that this is a common assumption in the electrical double layer theory⁽¹⁾ and leads to the results⁽⁵⁾ for $\psi_{\text{rigid}} = \psi_r$

$$\psi_r(0) = e \left[\frac{1}{4} + \pi^2 v_a^2 a^2 + \frac{1}{2} \ln \left(\frac{1 + \Phi(\pi v_a a \sqrt{2})}{2} \right) \right] \quad (3.22)$$

For small surface charge (i.e., low coverage) we obtain, using (3.11) and (3.21)

$$\psi(0)/e = \frac{1}{4} - \frac{1}{2} \ln 2 - v_a \frac{a \sqrt{2\pi}}{\ln 2} + \dots \quad (3.23)$$

while (3.22) yields

$$\psi_r(0)/e = \frac{1}{4} - \frac{1}{2} \ln 2 - 2v_a a \sqrt{2\pi} + \dots \quad (3.24)$$

The corresponding differential capacitances at $\sigma_a = 0$ (potential of zero charge) defined by $C^{-1} = -\partial\psi(0)/\partial(\sigma_a a)$ are, respectively

$$C = \frac{\ln 2}{\sqrt{2\pi}} \quad (3.25a)$$

$$C_r = \frac{1}{2\sqrt{2\pi}} \quad (3.25b)$$

On the other hand, for high surface charge ($\lambda_c \rightarrow \infty$) we obtain

$$\psi(0)/e \sim \psi_r(0)/e \sim (v_a a \pi)^2 \quad (3.26)$$

where we have used (3.12).

These results are not unexpected: it is clear that the effect of the nature of the surface charge must be more pronounced at low coverage. In other words, the approximation which replaces the adsorbed surface charge by a uniform external charge is better when the density of the adsorbed particles increases.

We can also treat the case where the surface carries both an adsorbed charge σ_a and a rigid surface charge σ_r .⁽¹⁵⁾ The preceding expressions for Δf^s , v_a , $\rho^*(x)$, and $\rho_T^*(x_1, x_2, y)$ are then modified in the following way: the lower limit of the integrals upon t is $-\pi\sigma_r(a\sqrt{2}/e)$ instead of 0. (see Ref. 4 for a similar calculation.)

We then have a sum rule similar to that of Blum *et al.*⁽¹⁶⁾

$$\frac{\partial \rho^*(x_1, \sigma_r)}{\partial \sigma_r} [1 + \lambda_c \delta(x_1)] = -2\pi\beta e^2 \int_{x_2 \geq 0} (x_2 - x_1) \rho_T(x_1, x_2, y) \, d\mathbf{r}_2 \quad (3.27)$$

which reduces to (3.18) when $\sigma_r = 0$.

4. ADSORPTION ON A LINE OF DISCRETE SITES ($\Gamma = 2$)

We now consider the case of an infinite two-dimensional plasma in which are embedded attractive sites regularly spaced on a line with a density ω (case ii)).

4.1. The Free Energy and the Density of Adsorbed Particles

For the finite unperturbed system in circular geometry the n -body distribution functions are given by Jancovici:⁽³⁾

$$\rho_0^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \rho^n \exp\left(-\sum_{i=1}^n z_i^2\right) \text{Det}[K_N(Z_i Z_j^*)]_{i,j=1 \dots n} \quad (4.1)$$

where $Z_i = z_i \exp(i\theta_i)$, $z_i = r_i/a$ and

$$K_N(Z_i Z_j^*) = \sum_{l=0}^{N-1} \frac{(Z_i Z_j^*)^l}{\gamma(l+1, N)} \quad (4.2)$$

In the thermodynamic limit $K_N(Z_i Z_j^*) \rightarrow \exp(Z_i Z_j^*)$ and Jancovici has explicitly calculated the 1, 2, 3, and 4 body distribution functions. Introducing the truncated correlation functions defined by (2.10), we have

$$\begin{aligned} \rho_0^{(2,T)}(\mathbf{r}_1, \mathbf{r}_2) &= -\rho^2 \exp(-\pi\rho r_{12}^2) \\ \rho_0^{(3,T)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= 2\rho^3 \exp[-\pi\rho(r_{12}^2 + r_{23}^2 + r_{31}^2)/2] \cos[2\pi\rho(A_{123})] \\ \rho_0^{(4,T)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) &= -2\rho^4 \left\{ \exp\left[-\frac{\pi\rho}{2}(r_{12}^2 + r_{23}^2 + r_{34}^2 + r_{41}^2)\right] \right. \\ &\quad + \exp\left[-\frac{\pi\rho}{2}(r_{12}^2 + r_{24}^2 + r_{43}^2 + r_{31}^2)\right] \\ &\quad \left. + \exp\left[-\frac{\pi\rho}{2}(r_{13}^2 + r_{32}^2 + r_{24}^2 + r_{43}^2)\right] \right\} \cdot \cos[2\pi\rho(A_{1234})] \end{aligned} \quad (4.3)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and A_{123} , (A_{1234}) is the area of the polygon formed by the vertices 1, 2, 3 (1, 2, 3, 4).

For the higher order functions it can be shown that all the Gaussian factors have the same "circular" structure $\{12, 23, 34, \dots, n1\}$ and one has to sum over all the nonequivalent cycles. The argument of the cosine is related to the area of the polygon formed by the particles (1, 2, 3 \dots n) and it is clear that the calculation of this area becomes a formidable task when n increases.

Fortunately, in order to compute the excess free energy due to the adsorption (Eq. (2.11)) we only need to know the truncated functions when the n particles are located on the sites. Since all the sites are equivalent and aligned, we find easily that

$$T_s^{(0)} = (-1)^{s-1} (s-1)! \rho^s \sum_{m_1, m_2, \dots, m_s} e^{-t[(m_1 - m_2)^2 + (m_2 - m_3)^2 + \dots + (m_s - m_1)^2]} (s \geq 2) \quad (4.4)$$

where $t = \frac{1}{2}\pi\rho/\omega^2$. For a large system these sums are proportional to the length L of the line ($M = \omega L$) and by a change of variable we obtain

$$\frac{1}{L} T_s^{(0)} \sim (-1)^{s-1} (s-1)! \rho^s \omega \sum_{m_1, m_2, \dots, m_{s-1}} e^{-t[m_1^2 + m_2^2 + \dots + m_{s-1}^2 + (m_1 + m_2 + \dots + m_{s-1})^2]} \quad (4.5)$$

where $m_i \in \mathbb{Z}$

Consider now the Jacobi theta function $\theta_3(\zeta, t)$ defined by the series⁽¹⁷⁾

$$\theta_3(\zeta, t) = \sum_{m \in \mathbb{Z}} e^{-tm^2} e^{2im\zeta} \quad (4.6)$$

For real values of the variable ζ , $\theta_3(\zeta, t)$ is a positive real function of period 1 which reaches its maximum in $[0, 1]$ for $\zeta = 0$. (To simplify the notation we shall write $\theta(\zeta, t)$ instead of $\theta_3(\zeta, t)$ in the rest of this paper). For real ζ we have

$$\int_0^1 \theta(\zeta, t) d\zeta = 1 \quad (4.7)$$

and

$$\int_0^1 \theta^n(\zeta, t) d\zeta = \sum_{m_1, m_2, \dots, m_{n-1}} e^{-t[m_1^2 + m_2^2 + \dots + m_{n-1}^2 + (m_1 + m_2 + \dots + m_{n-1})^2]} \quad (4.8)$$

Therefore

$$\frac{1}{L} T_s^{(0)} \sim (-1)^{s-1} (s-1)! \rho^s \omega \int_0^1 \theta^s(\zeta, t) d\zeta \quad (4.9)$$

and from (2.11) the excess surface free energy Af^s has the expression

$$Af^s = -k_B T \omega \sum_{s=1}^{\infty} (-1)^{s-1} \frac{(\lambda\rho)^s}{s} \int_0^1 \theta^s(\zeta, t) d\zeta \quad (4.10)$$

When $|\lambda\rho\theta(0, t)| < 1$ the series in (4.10) is absolutely summable for $\zeta \in [0, 1]$ and we get the final result

$$\Delta f^s = -k_B T \omega \int_0^1 \ln[1 + \lambda\rho\theta(\zeta, t)] d\zeta \quad (4.11)$$

By analytic continuation we assume that this is the correct result for any value of λ , ρ , and ω . Note that Δf^s has a constant negative sign and that we have now two independent dimensionless parameters $\lambda\rho$ and $t = \frac{1}{2}\pi\rho/\omega^2$. (Remember that λ has the dimension of an area while λ_c before had the dimension of a length). From Δf^s we get the average number of adsorbed particles per site

$$\begin{aligned} n_a &= -\beta \frac{\lambda}{\omega} \frac{\partial \Delta f^s}{\partial \lambda} \\ &= \lambda\rho \int_0^1 \frac{\theta(\zeta, t)}{1 + \lambda\rho\theta(\zeta, t)} d\zeta \end{aligned} \quad (4.12)$$

As expected this number is always smaller than 1 and saturates to 1 when the adsorption becomes infinite ($\lambda \rightarrow \infty$).

4.2. The One-Body Density

Let us choose the site corresponding to $m=0$ as the origin of the coordinates (x, y) . In order to calculate the one-body density of the non-adsorbed particles $\rho^*(\mathbf{r}_1)$ (Eq. (2.15)) we need to compute the n -body truncated correlation functions $\rho^{(n,T)}(\mathbf{r}_1, \mathbf{R}_{m_1}, \dots, \mathbf{R}_{m_{n-1}})$. The n points $(\mathbf{r}_1, \mathbf{R}_{m_1}, \dots, \mathbf{R}_{m_{n-1}})$ are not aligned anymore but they form a triangle and the explicit calculation is still feasible. We find

$$\begin{aligned} T_s^{(1)} &= (-1)^s s! \rho^{s+1} e^{-2t\omega^2(x_1^2 + y_1^2)} \sum_{m_1 \cdots m_s} e^{-t[m_1^2 + (m_1 - m_2)^2 + \cdots + (m_{s-1} - m_s)^2 + m_s^2]} \\ &\quad \times e^{2iy_1\omega(m_1 + m_s)} \cos[2t\omega x_1(m_1 - m_s)] \end{aligned} \quad (4.13)$$

It is convenient to represent \mathbf{r}_1 by the complex number $z_1 = x_1 + iy_1$. After some variable changes among the m_i we get

$$\begin{aligned} T_s^{(1)} &= (-1)^s s! \rho^{s+1} e^{-\pi\rho|z_1|^2} \sum_{m_1 \cdots m_s} e^{-t[m_1^2 + m_2^2 + \cdots + m_s^2 + (m_1 + m_2 + \cdots + m_s)^2]} \\ &\quad \times \cos[2t\omega(m_1 z_1 + m_s z_1^*)] \end{aligned} \quad (4.14)$$

We now consider the theta function of second order $F(\zeta, z_1, t)$ defined by

$$F(\zeta, z_1, t) = \frac{1}{2} \left[\theta \left(\zeta + \frac{t\omega}{\pi} z_1, t \right) \theta \left(\zeta + \frac{t\omega}{\pi} z_1^*, t \right) + \theta \left(\zeta - \frac{t\omega}{\pi} z_1, t \right) \theta \left(\zeta - \frac{t\omega}{\pi} z_1^*, t \right) \right] \quad (4.15)$$

Clearly $F(\zeta, z_1, t)$ is real for real ζ . Using the definition (4.6) of $\theta(\zeta, t)$ we get

$$\int_0^1 \theta^{s-1}(\zeta, t) F(\zeta, z_1, t) d\zeta = \sum_{m_1, m_2, \dots, m_s} e^{-t[m_1^2 + m_2^2 + \dots + m_s^2 + (m_1 + m_2 + \dots + m_s)^2]} \cos[2\omega t(m_1 z_1 + m_s z_1^*)] \quad (4.16)$$

Thus

$$T_s^{(1)} = (-1)^s s! \rho^{s+1} e^{-\pi\rho|z_1|^2} \int_0^1 \theta^{s-1}(\zeta, t) F(\zeta, z_1, t) d\zeta \quad (4.17)$$

and from (2.15) we get

$$\rho^*(\mathbf{r}_1) = \rho + \rho e^{-\pi\rho|z_1|^2} \sum_{s=1}^{\infty} (-1)^s (\lambda\rho)^s \int_0^1 \theta^{s-1}(\zeta, t) F(\zeta, z_1, t) d\zeta \quad (4.18)$$

Again, when $\lambda\rho\theta(0, t) < 1$, the series in (4.18) is absolutely summable for $\zeta \in [0, 1]$ and we obtain the final result

$$\rho^*(\mathbf{r}_1) - \rho = -\lambda\rho^2 e^{-\pi\rho|z_1|^2} \int_0^1 \frac{F(\zeta, z_1, t)}{1 + \lambda\rho\theta(\zeta, t)} d\zeta \quad (4.19)$$

which can be extended by analytic continuation to other values of λ, ρ , and ω .

We can check at once the relation (2.17) since $F(\zeta, 0, t) = \theta^2(\zeta, t)$ and from (4.15) we have the expected symmetry

$$\rho(x_1, -y_1) = \rho(-x_1, y_1) = \rho(x_1, y_1) \quad (4.20)$$

We also expect $\rho^*(\mathbf{r}_1)$ to be a periodic function in y_1 with period $1/\omega$. This is shown in the Appendix together with the electroneutrality relation (2.19).

Since $F(\zeta, z_1, t)$ is a theta function of second order, we can use the addition formulas for θ functions⁽¹⁷⁾ to find another integral representation

of $\rho^*(\mathbf{r}_1)$ which has the nice feature of separating the variable x_1 and y_1 . Consider the theta function $\theta_1(\zeta, t)$ defined by

$$\theta_1(\zeta, t) = -i \sum_{m \in \mathbb{Z}} (-1)^m e^{-(m+1/2)^2 t} e^{(2m+1)\pi i \zeta} \quad (4.21)$$

We have the following addition formula⁽¹⁷⁾

$$\theta^2(0, t) \theta(\zeta + \eta, t) \theta(\zeta - \eta, t) = \theta^2(\zeta, t) \theta^2(\eta, t) + \theta_1^2(\zeta, t) \theta_1^2(\eta, t) \quad (4.22)$$

Thus (4.15) can be rewritten as

$$\begin{aligned} F(\zeta, z_1, t) = & \frac{1}{2} \frac{1}{\theta^2(0, t)} \left\{ \theta^2 \left(\frac{i t \omega y_1}{\pi}, t \right) \right. \\ & \times \left[\theta^2 \left(\zeta + \frac{t \omega}{\pi} x_1, t \right) + \theta^2 \left(\zeta - \frac{t \omega}{\pi} x_1, t \right) \right] \\ & \left. + \theta_1^2 \left(\frac{i t \omega y_1}{\pi}, t \right) \left[\theta_1^2 \left(\zeta + \frac{t \omega x_1}{\pi}, t \right) + \theta_1^2 \left(\zeta - \frac{t \omega x_1}{\pi}, t \right) \right] \right\} \quad (4.23) \end{aligned}$$

and we have

$$\begin{aligned} \rho^*(\mathbf{r}_1) - \rho = & -\frac{\lambda \rho^2}{2\theta^2(0, t)} e^{-\pi \rho(x_1^2 + y_1^2)} \\ & \times \left\{ \theta^2 \left(\frac{i t \omega}{\pi} y_1, t \right) \int_0^1 \frac{\theta^2 \left(\zeta + \frac{t \omega x_1}{\pi}, t \right) + \theta^2 \left(\zeta - \frac{t \omega x_1}{\pi}, t \right)}{1 + \lambda \rho \theta(\zeta, t)} d\zeta \right. \\ & \left. + \theta_1^2 \left(\frac{i t \omega y_1}{\pi}, t \right) \int_0^1 \frac{\theta_1^2 \left(\zeta + \frac{t \omega x_1}{\pi}, t \right) + \theta_1^2 \left(\zeta - \frac{t \omega x_1}{\pi}, t \right)}{1 + \lambda \rho \theta(\zeta, t)} d\zeta \right\} \quad (4.24) \end{aligned}$$

This representation is convenient for numerical computation, and in Fig. 1 we have drawn up the normalized density profile $\rho^*(\mathbf{r}_1)/\rho$ as a function of x_1 for some values of y_1 and for $\lambda = 10$, $\omega = \frac{1}{2}$ (the unit length if $a = (\pi \rho)^{-1/2}$). $\rho^*(x_1, y_1)$ approaches the background density ρ like a gaussian when $x_1 \rightarrow \pm \infty$ for fixed y_1 .

4.3. The Pair Correlation Function for the Adsorbed Particles

The calculation of the two-body correlation function $\rho_T(\mathbf{r}_1, \mathbf{r}_2)$ as given by (2.20) and (2.21) is very tedious and we shall explicitly calculate

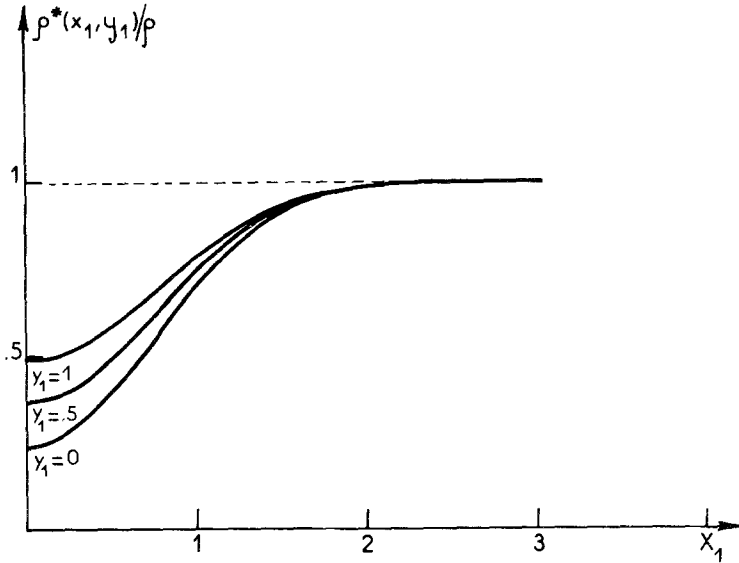


Fig. 1. The density profile $\rho^*(x_1, y_1)/\rho$ near a line of adsorption sites; $\lambda = 10$ and $\omega = \frac{1}{2}$ (the unit length is $a = (\pi\rho)^{-1/2}$).

only $R_T(\mathbf{R}_{m_1}, \mathbf{R}_{m_2})$, when the two particles are adsorbed. (The complete expression of $\rho_T^*(\mathbf{r}_1, \mathbf{r}_2)$ is given in Section 4.4 in the limit of continuous adsorption.)

In the thermodynamic limit $R_T(\mathbf{R}_{m_1}, \mathbf{R}_{m_2})$ depends only on the distance $y = (1/\omega)(m_1 - m_2)$ so we take the two particles located, respectively, at \mathbf{R}_0 (the origin) and \mathbf{R}_m .

In computing the n -body truncated correlation functions $\rho_0^{(s+2,T)}(\mathbf{R}_0, \mathbf{R}_m, \mathbf{R}_{m_1}, \mathbf{R}_{m_2}, \dots, \mathbf{R}_{m_s})$ there is some complication due to the fact that we must count separately each cycle $\{0m_1, m_1m_2, m_2m_3, \dots, m_i m, mm_{i+1} \dots m_{s-1} m_s\}$ according to the position of m .

For even s ($s = 2p$) we find

$$\begin{aligned}
 T_s^{(2)} \equiv & \sum_{m_1 \dots m_s} \rho_0^{(s+2,T)}(R_0, R_m, R_{m_1} \dots R_{m_s}) = (-1)^{s+1} 2\rho^{s+2} s! \\
 & \times \sum_{m_1 \dots m_s} e^{-t[m^2 + (m-m_1)^2 + (m_1-m_2)^2 + \dots + m_s^2]} \\
 & + e^{-t[m_1^2 + (m_1-m)^2 + (m-m_2)^2 + (m_2-m_3)^2 + \dots + m_s^2 + \dots]} \\
 & + e^{-t[m_1^2 + (m_1-m_2)^2 + \dots + (m_{p-1}-m)^2 + (m-m_p)^2 + (m_p-m_{p+1})^2 + \dots + m_s^2]} \\
 & + \frac{1}{2} e^{-t[m_1^2 + (m_1-m_2)^2 + \dots + (m_p-m)^2 + (m-m_{p+1})^2 + (m_{p+1}-m_{p+2})^2 + \dots + m_s^2]}
 \end{aligned}
 \tag{4.25}$$

For odd s ($s = 2p + 1$) the factor of the last term in the r.h.s. of (4.25) is 1 instead of $\frac{1}{2}$.

After some changes of variable among the m_i , and noting that we have

$$\int_0^1 \theta(\zeta, t) e^{-2i\pi m\zeta} d\zeta = e^{-im^2} \tag{4.26}$$

and

$$\int_0^1 \theta^{n+1}(\zeta, t) e^{-2i\pi m\zeta} d\zeta = \sum_{m_1 \cdots m_n} e^{-t[m_1^2 + m_2^2 + \cdots + m_n^2 + (m - m_1 - m_2 \cdots - m_n)^2]} \tag{4.27}$$

for $n \geq 1$

we get for $s = 2p$

$$\begin{aligned} T_s^{(2)} = & (-1)^{s+1} 2\rho^{s+2} s! \left\{ \int_0^1 e^{-2i\pi m\zeta} \theta(\zeta, t) d\zeta \int_0^1 \theta^{s+1}(\zeta, t) e^{-2i\pi m\zeta} d\zeta \right. \\ & + \int_0^1 e^{-2i\pi m\zeta} \theta^2(\zeta, t) d\zeta \int_0^1 e^{-2i\pi m\zeta} \theta^s(\zeta, t) d\zeta + \cdots \\ & \left. + \frac{1}{2} \int_0^1 e^{-2i\pi m\zeta} \theta^{p+1}(\zeta, t) d\zeta \int_0^1 e^{-2i\pi m\zeta} \theta^{s-p+1}(\zeta, t) d\zeta \right\} \tag{4.28} \end{aligned}$$

and from (2.21) and (2.22) we obtain

$$\begin{aligned} R_T(m/\omega) = & -2\lambda^2 \rho^2 \sum_{s=0}^{\infty} (-1)^s (\rho\lambda)^s \\ & \times \left\{ \sum_{l=1}^{p+1} g_l \int_0^1 e^{-2i\pi m\zeta} \theta^l(\zeta, t) d\zeta \int_0^1 e^{-2i\pi m\zeta} \theta^{s-l+2}(\zeta, t) d\zeta \right\} \tag{4.29} \end{aligned}$$

with

$$g_l = 1 \quad \forall l \neq p+1$$

$$g_{p+1} = \begin{cases} 1 & s = 2p+1 \\ \frac{1}{2} & s = 2p \end{cases}$$

We recognize in (4.29) the expansion of $-\left[\lambda\rho \int_0^1 (\theta(\zeta, t) e^{-2i\pi m\zeta}) / (1 + \lambda\rho\theta(\zeta, t)) d\zeta\right]^2$ and we obtain finally the simple result

$$R_T(m/\omega) = -\left[\int_0^1 \frac{\lambda\rho\theta(\zeta, t) \cos(2\pi m\zeta)}{1 + \lambda\rho\theta(\zeta, t)} d\zeta \right]^2 \tag{4.30}$$

where we have used the fact that $\theta(\zeta, t)$ is an even periodic function with period 1.

We see immediately that (2.23) is satisfied

$$R_T(0) = -n_a^2 \tag{4.31}$$

and using the Parseval theorem for Fourier series we get

$$\begin{aligned} \sum_{m=-\infty}^{+\infty} R_T(m/\omega) &= -\int_0^1 \frac{\lambda^2 \rho^2 \theta^2(\zeta, t)}{[1 + \lambda \rho \theta(\zeta, t)]^2} d\zeta \\ &= \lambda \frac{\partial n_a}{\partial \lambda} - n_a \end{aligned} \tag{4.32}$$

which is the ‘‘compressibility’’ sum rule (2.28). Since $\theta(\zeta, t)/[1 + \lambda \rho \theta(\zeta, t)]$ is analytical on the real axis, $R_T(m/\omega)$ decays faster than any inverse power of m when $|m| \rightarrow \infty$.

4.4. The Limit of Continuous Adsorption

Although the case of a continuous adsorption on the line could be easily solved by the direct method used in Section 2, it is interesting to find the solution as a limit of the discrete case when $\omega \rightarrow \infty$. Consider first the series (4.6) which defines $\theta(\zeta, t)$. When $t \ll 1 (\omega \gg 1/a)$ the convergence is very slow. However, we can use the Jacobi identity⁽¹⁷⁾ to transform (4.6) into a rapidly convergent series

$$\sqrt{\frac{t}{\pi}} \theta(\zeta, t) = \sum_{m \in \mathbb{Z}} e^{-(\zeta - m)^2 (\pi^2/t)} \tag{4.33}$$

Hence

$$\lambda \rho \theta(\zeta, t) = \lambda \omega \sqrt{2\rho} \sum_{m \in \mathbb{Z}} e^{-(\zeta - m)^2 (\pi^2/t)} \tag{4.34}$$

and (4.11) can be rewritten as

$$\Delta f^s = -k_B T \sqrt{\frac{\rho}{2\pi}} \int_0^{\pi/\sqrt{t}} \ln \left[1 + \lambda \omega \sqrt{2\rho} \sum_{m=-\infty}^{+\infty} e^{-[u - m(\pi/\sqrt{t})]^2} \right] du \tag{4.35}$$

where we have made the variable change $\zeta = (\sqrt{t}/\pi) u$.

In the limit of continuous adsorption ($\omega \rightarrow \infty, \lambda \rightarrow 0, \lambda \omega \rightarrow \lambda_c$ finite) all the gaussian factors $\exp\{-[u - m(\pi/\sqrt{t})]^2\}$ go to zero except those corresponding to $m = 0$ and $m = 1$ (since $u \in [0, \pi/\sqrt{t}]$). We then break up the integral into $\int_0^{\pi/2\sqrt{t}} du \dots + \int_{\pi/2\sqrt{t}}^{\pi/\sqrt{t}} du \dots$ and make the variable change $u' = u - \pi/\sqrt{t}$ in the second integral. We find eventually

$$\Delta f^s = -k_B T \sqrt{\rho/2\pi} \int_{-\infty}^{+\infty} \ln[1 + \lambda_c \sqrt{2\rho} e^{-u^2}] du \tag{4.36}$$

which can be compared to the corresponding result for the semi-infinite plasma near a wall (Eq. (3.9)).

The density of adsorbed particle is

$$v_a = -\lambda_c \beta \frac{\Delta f^s}{\partial \lambda_c} = \frac{\lambda_c \rho}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \frac{e^{-u^2}}{1 + \lambda_c \sqrt{2\rho} e^{-u^2}} du \quad (4.37)$$

It is instructive to compare this adsorption isotherm to the one given by (4.12) ($v_a = n_a \omega$) in order to see the influence of the periodic structure of the adsorption potential. While ω varies it is sensible to keep the product $\lambda \omega$ constant so that the average of the Boltzmann factor (2.2) over the sites remains constant. The variation of v_a with ω is shown in Fig. 2 for $\lambda_c/a = \lambda \omega/a = 1$. We see that $v_a(\omega)$ is a monotonic increasing function of ω so that

$$v_a(\omega) < v_a(\infty) \quad (4.38)$$

This variation with the density of sites is lost in the usual approximation where the real three-dimensional solid-fluid potential is replaced by an effective one-dimensional potential varying only in the direction normal to the surface. We see, however, from Fig. 2 that $v_a(\omega) \neq v_a(\infty)$ as soon as $\omega a \simeq 1$, i.e., the distance between the sites is comparable to the mean interparticle distance.

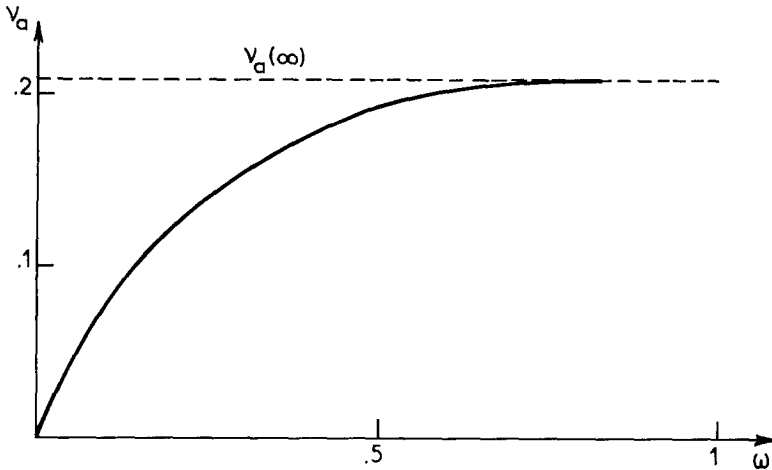


Fig. 2. The linear density of adsorbed particles as a function of the density of sites ω ; $\lambda_c = \lambda \omega = 1$ (same length unit as Fig. 1). $v_a(\infty)$ is the result for continuous adsorption ($\omega \rightarrow \infty$).

Let us give also the one- and two-body densities in the continuous limit. We have

$$\rho^*(x) = \rho/\sqrt{\pi} \int_0^\infty \frac{e^{-[u - (x/a)\sqrt{2}]^2}}{1 + \lambda_c \sqrt{2\rho} e^{-u^2}} du \quad (4.39)$$

$$R_T'(y) = -\lambda_c^2 \rho^2 \left[\frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \frac{e^{-u^2}}{1 + \lambda_c \sqrt{2\rho} e^{-u^2}} \cos(\sqrt{2\pi\rho} uy) du \right]^2 \quad (4.40)$$

and, using the direct method of Section 2,

$$\rho_T^*(x_1, x_2, y) = -\rho^2 e^{-\pi\rho(x_1 - x_2)^2} \times \left| \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \frac{\exp \left\{ -\left[u - \frac{x_1 + x_2}{a\sqrt{2}} \right]^2 - \frac{iuy}{a} \sqrt{2} \right\}}{1 + \lambda_c \sqrt{2\rho} e^{-u^2}} du \right|^2 \quad (4.41)$$

We can check easily the “compressibility” sum rule

$$\begin{aligned} \int_{-\infty}^{+\infty} R_T(y) dy &= -\lambda_c^2 \rho^{(3/2)} \sqrt{2/\pi} \int_{-\infty}^{+\infty} \frac{e^{-2u^2}}{[1 + \lambda_c \sqrt{2\rho} e^{-u^2}]^2} du \\ &= \lambda_c \frac{\partial v_a}{\partial \lambda_c} - v_a \end{aligned} \quad (4.42)$$

The function $\rho^*(x_1, x_2, y)$ has an oscillating exponential decay when $|y| \rightarrow \infty$ (x_1 and x_2 fixed) and accordingly all the multipole moments vanish.⁽¹⁴⁾

4.5. The Limit of External Fixed Charges

When $\lambda \rightarrow \infty$ with ω fixed, $n_a \rightarrow 1$ and the adsorbed charges can be considered as *fixed* charges creating an external perturbing potential in the infinite plasma. This situation is interesting because this external potential is two dimensional. All previous work was restricted to a potential varying only in one direction⁽⁹⁾ or local.⁽⁴⁾

Since the M charges are fixed, the excess free energy of the system should not contain anymore the term $-k_B T M \ln \lambda$. In the thermodynamic limit we find from (4.11)

$$\Delta f = \lim_{\lambda \rightarrow \infty} (\Delta f^s + k_B T \omega \ln \lambda) = -k_B T \omega \int_0^1 \ln[\theta(\zeta, t)] d\zeta \quad (4.43)$$

(The integrand is always defined since $\theta(\zeta, t)$ has no real zeros.⁽¹⁷⁾)

Using the product representation of the theta function⁽¹⁷⁾

$$\theta(\zeta, t) = \prod_{n=1}^{\infty} (1 - e^{-2nt}) \prod_{n=1}^{\infty} [1 + 2e^{-t(2n-1)} \cos 2\pi\zeta + e^{-t(4n-2)}] \quad (4.44)$$

we get

$$\begin{aligned} \Delta f = & -k_B T \omega \left[\sum_{n=1}^{\infty} \ln(1 - e^{-2nt}) \right. \\ & \left. + \sum_{n=1}^{\infty} \int_0^1 \ln[1 + 2e^{-t(2n-1)} \cos 2\pi\zeta + e^{-t(4n-2)}] d\zeta \right] \quad (4.45) \end{aligned}$$

Since $t > 0$ we have $e^{-t(2n-1)} < 1$ and the integral in (4.45) vanishes ($(1/2\pi) \int_0^{2\pi} \ln(r_1^2 + r_2^2 + 2r_1 r_2 \cos \theta) d\theta = \ln(r_1^2)$ for $r_1 > r_2$). Thus finally

$$\begin{aligned} \Delta f = & -k_B T \omega \sum_{n=1}^{\infty} \ln(1 - e^{-2nt}) \\ = & -k_B T \omega \left[\frac{t}{12} + \ln \eta(t) \right] \geq 0 \quad (4.46) \end{aligned}$$

where we have introduced the Dedekind eta function⁽¹⁷⁾

$$\eta(t) = e^{-t/12} \prod_{n=1}^{\infty} (1 - e^{-2nt}) \quad (4.47)$$

For numerical computation it is convenient to use the Euler pentagonal number theorem⁽¹⁷⁾ which yields

$$\Delta f = -k_B T \omega \ln \left[\sum_{n=-\infty}^{+\infty} (-1)^n e^{-n(3n-1)t} \right] \quad (4.48)$$

For $t \gg 1$ ($\omega a \ll 1$) we have

$$\Delta f \sim k_B T \omega e^{-1/(\omega a)^2} \quad (4.49)$$

For $t \ll 1$ ($\omega a \gg 1$) the series converges very slowly but we can use the functional equation⁽¹⁷⁾

$$\eta(t) = \sqrt{\pi/t} \eta(\pi^2/t) \quad (4.50)$$

so that

$$\Delta f = -k_B T \omega \left[\frac{t}{12} - \frac{\pi^2}{12t} + \frac{1}{2} \ln(\pi/t) + \ln \left(\sum_{n=-\infty}^{+\infty} (-1)^n e^{-n(3n-1)\pi^2/t} \right) \right] \quad (4.51)$$

For $\omega a \neq 1$ Δf reaches its asymptotic behavior

$$\Delta f \sim k_B T \omega \left[\frac{\pi^2}{6} (\omega a)^2 - \ln(\omega a) - \frac{1}{2} \ln 2\pi \right] \quad (4.52)$$

The one-body density is readily obtained from (4.19)

$$\rho^*(\mathbf{r}_1) - \rho = -\rho e^{-\pi\rho(x_1^2 + y_1^2)} \int_0^1 \frac{F(\zeta, z_1, t)}{\theta(\zeta, t)} d\zeta \quad (4.53)$$

4.6. The Limit of the One-Dimensional Plasma

We now consider the limit $\rho \rightarrow 0$, $\lambda \rightarrow \infty$ such that the density n_a at each site goes to a finite value smaller than one. It is clear that this limit corresponds to the case of the one-dimensional plasma which has been studied in the past both in the continuous⁽¹⁸⁾ and in the discrete⁽¹⁹⁾ version.

Using again the Jacobi identity (4.33) we rewrite (4.12) as

$$\begin{aligned} n_a &= \int_0^1 \frac{d\zeta}{1 + [\lambda\omega \sqrt{2\rho} \sum_{n=-\infty}^{+\infty} e^{-(\zeta-n)^2 2\pi\omega^2/\rho}]^{-1}} \\ &= \int_0^1 \frac{d\zeta}{1 + [\sum_{n=-\infty}^{+\infty} e^{-2\pi\omega^2/\rho [(\zeta-n)^2 - t_0^2]}]^{-1}} \end{aligned} \quad (4.54)$$

where

$$t_0 = \{\rho/2\pi\omega^2 \ln(\lambda\omega \sqrt{2\rho})\}^{1/2} \quad (4.55)$$

and we consider the limit $\rho \rightarrow 0$, $\lambda \rightarrow \infty$ such that t_0 remains finite with $0 < t_0 < \frac{1}{2}$.

We first break up the integral (4.54) into $\int_0^{t_0} d\zeta + \int_{t_0}^{1-t_0} d\zeta + \int_{1-t_0}^1 d\zeta$. In the middle integral, it is easy to see that $\sum_{n=-\infty}^{+\infty} e^{-2\pi\omega^2/\rho [(\zeta-n)^2 - t_0^2]} \rightarrow 0$ when $\rho \rightarrow 0$ while the same sum is diverging in the two other integrals. Thus $n_a \rightarrow 2t_0$ in this limit and we have $0 < n_a < 1$ as required. Consider now the two-body correlation function $R_T(m/\omega)$. Using (4.33) in (4.30) we have

$$R_T(m/\omega) = - \left[\int_0^1 \frac{\cos(2\pi m\zeta)}{1 + [\sum_{n=-\infty}^{+\infty} e^{-2\pi\omega^2/\rho [(\zeta-n)^2 - t_0^2]}]^{-1}} d\zeta \right]^2 \quad (4.56)$$

and breaking again the integral into the same three parts we get in the same limit

$$R_T(m/\omega) \rightarrow - \frac{\sin^2(2\pi m t_0)}{\pi^2 m^2} = - \frac{\sin^2(\pi m n_a)}{\pi^2 m^2} \quad (4.57)$$

which is the result of Gaudin.⁽¹⁹⁾

In the continuous case ($\omega \rightarrow \infty$) a similar calculation would give

$$R_T(y) = -v_a^2 \frac{\sin^2(\pi y v_a)}{\pi^2 y^2 v_a^2} \quad (4.58)$$

which is the result of Dyson.⁽¹⁸⁾

These two-body correlation functions have the well-known algebraic decay of the two-dimensional Coulomb system near a wall. It is interesting to note that in the limit process ($\rho \rightarrow 0, \lambda \rightarrow \infty, n_a$ finite) the "compressibility" sum rule (2.28) reduces to the perfect screening sum rule (2.25)

$$\sum_{m=-\infty}^{+\infty} R_T(m/\omega) = -n_a \quad (4.59)$$

5. LOCALIZED ADSORPTION ON A WALL ($\Gamma = 2$)

In this last section we give the solution of case (iii) where the line of discrete sites coincides with the boundary of the semi-infinite system ($x_0 = 0$). For the sake of simplicity we shall only consider the excess free energy Δf^s and the average number of adsorbed particles per site n_a .

The n -body distribution functions of the unperturbed finite system are still given by Eqs. (4.1) and (4.2) but the distance of the particles to the circular wall must be kept to a constant value in the thermodynamic limit. Jancovici⁽⁴⁾ has computed the one- and two-body distribution functions of the semi-infinite system

$$\begin{aligned} \rho_0(\mathbf{r}_1) &= \rho \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{e^{-[u - (x_1/a)\sqrt{2}]^2}}{1 + \Phi(u)} du \\ \rho_0^{(2,T)}(\mathbf{r}_1, \mathbf{r}_2) &= -\rho^2 e^{-[(x_1 - x_2)/a]^2} \\ &\quad \times \left| \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\exp\left\{-\left(u - \frac{x_1 + x_2}{a\sqrt{2}}\right)^2 - iuy \frac{\sqrt{2}}{a}\right\}}{1 + \Phi(u)} du \right| \quad (5.1) \end{aligned}$$

where $\Phi(u)$ is the error function defined by (3.7).

Again it is easy to get from (4.1) the expression of the s -body truncated correlation function when the s particles are located on the sites m_1, m_2, \dots, m_s . We find

$$\begin{aligned} T_s^{(0)} &= (-1)^{s-1} (s-1)! \rho^s \int_0^\infty \cdots \int_0^\infty \sum_{m_1, m_2, \dots, m_s} \\ &\quad \times e^{2i\sqrt{t}[u_1(m_1 - m_2) + u_2(m_2 - m_3) + \cdots + u_s(m_s - m_1)]} \prod_{i=1}^s \{R(u_i) du_i\} \quad (5.2) \end{aligned}$$

where

$$R(u) = \frac{2}{\sqrt{\pi}} \frac{e^{-u^2}}{1 + \Phi(u)} \tag{5.3}$$

For a large system we get, after some variable changes among the m_i

$$\begin{aligned} \frac{1}{L} T_s^{(0)} \sim & (-1)^{s-1} (s-1)! \rho^s \omega \int_0^\infty \cdots \int_0^\infty \sum_{m_1, m_2, \dots, m_{s-1}} \\ & \times e^{2i\sqrt{t}[m_1 u_1 + m_2 u_2 + \cdots + m_{s-1} u_{s-1} - (m_1 + m_2 + \cdots + m_{s-1}) u_s]} \prod_{i=1}^s \{R(u_i) du_i\} \end{aligned} \tag{5.4}$$

and from (2.11)

$$\begin{aligned} \Delta f^s = & -k_B T \omega \sum_{s=1}^\infty (-1)^{s-1} \frac{(\lambda \rho)^s}{s} \int_0^\infty \cdots \int_0^\infty \sum_{m_1, m_2, \dots, m_{s-1}} \\ & \times e^{2i\sqrt{t}[m_1 u_1 + m_2 u_2 + \cdots + m_{s-1} u_{s-1} - (m_1 + m_2 + \cdots + m_{s-1}) u_s]} \prod_{i=1}^s \{R(u_i) du_i\} \end{aligned} \tag{5.5}$$

Consider now the function

$$f(m, t) = \int_0^\infty R(u) e^{2im\sqrt{t}u} du \tag{5.6}$$

and the series

$$K(\zeta, t) = \sum_{m \in \mathbb{Z}} f(m, t) e^{2im\zeta} \tag{5.7}$$

For real ζ , $K(\zeta, t)$ is a real function of period 1 which can be rewritten as

$$K(\zeta, t) = \frac{\pi}{\sqrt{t}} \int_0^\infty R(u) \sum_{m \in \mathbb{Z}} \delta\left[u + \frac{\pi}{\sqrt{t}}(\zeta - m)\right] du \tag{5.8}$$

so that

$$\begin{aligned} K(\zeta, t) &= \pi/\sqrt{t} \sum_{m=1}^\infty R\left[\frac{\pi}{\sqrt{t}}(m - \zeta)\right] \\ &= 2\sqrt{\pi/t} \sum_{m=1}^\infty \frac{e^{(-\pi^2/t)(m - \zeta)^2}}{1 + \Phi[(\pi/\sqrt{t})(m - \zeta)]} \end{aligned} \tag{5.9}$$

for $0 < \zeta < 1$. This is a rapidly convergent series when $t \ll 1$ (compare to (4.33)).

From the definition (5.7) we have

$$\begin{aligned}
 \int_0^1 K^s(\zeta, t) d\zeta &= \sum_{m_1, m_2, \dots, m_s} f(m_1, t) f(m_2, t) \cdots f(m_s, t) \\
 &\quad \times \int_0^1 e^{2i\pi(m_1 + m_2 + \cdots + m_s)\zeta} d\zeta \\
 &= \sum_{m_1, m_2, \dots, m_{s-1}} f(m_1, t) f(m_2, t) \cdots f(m_{s-1}, t) \\
 &\quad \times f(-(m_1 + m_2 + \cdots + m_{s-1}), t) \\
 &= \int_0^\infty \cdots \int_0^\infty e^{2i\sqrt{t}[m_1 u_1 + m_2 u_2 + \cdots + m_{s-1} u_{s-1} - (m_1 + m_2 + \cdots + m_{s-1}) u_s]} \\
 &\quad \times \prod_{i=1}^s \{R(u_i) du_i\} \tag{5.10}
 \end{aligned}$$

Finally

$$\begin{aligned}
 \Delta f^s &= -k_B T \omega \sum_{s=1}^\infty (-1)^{s-1} \frac{(\lambda \rho)^s}{s} \int_0^1 K^s(\zeta, t) d\zeta \\
 &= -k_B T \omega \int_0^1 \ln[1 + \lambda \rho K(\zeta, t)] d\zeta \tag{5.11}
 \end{aligned}$$

and

$$n_a = \lambda \rho \int_0^1 \frac{K(\zeta, t)}{1 + \lambda \rho K(\zeta, t)} d\zeta \tag{5.12}$$

In the limit of continuous adsorption ($\omega \rightarrow \infty$, $\lambda \rightarrow 0$, $\lambda \omega \rightarrow \lambda_c$) and making the variable change $u = \pi/\sqrt{t} (1 - \zeta)$, we have

$$\lambda \rho K(\zeta, t) \rightarrow 2\lambda_c \sqrt{2\rho} \frac{e^{-u^2}}{1 + \Phi(u)} \tag{5.13}$$

so that

$$\Delta f^s \rightarrow -k_B T \sqrt{\rho/2\pi} \int_0^\infty \ln \left[1 + 2\lambda_c \sqrt{2\rho} \frac{e^{-u^2}}{1 + \Phi(u)} \right] du \tag{5.14}$$

and we recover the result obtained in Section 3 (Eq. (3.9)).

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APPENDIX

In this appendix we show that $\rho^*(\mathbf{r}_1)$ given by (4.19) is a periodic function in y_1 and satisfies the global electroneutrality relation (2.19).

In order to prove the periodicity of $\rho^*(\mathbf{r}_1)$ we shall use the fact that $\theta(\zeta, t)$ is also a quasi-periodic function⁽¹⁷⁾

$$\theta\left(\zeta \pm \frac{i t}{\pi}, t\right) = e^{\mp 2i\pi\zeta + t}\theta(\zeta, t) \quad (\text{A1})$$

Using (A1) in the definition (4.15) of $F(\zeta, z_1, t)$ we get

$$F(\zeta, z_1 + i/\omega, t) = e^{2t}e^{4t\omega y_1}F(\zeta, z_1, t) \quad (\text{A.2})$$

Thus, from (4.19)

$$\begin{aligned} \rho^*(z_1 + i/\omega) - \rho &= -\lambda\rho^2 e^{-2t\omega^2[x_1^2 + (y_1 + 1/\omega)^2]} e^{2t}e^{4t\omega y_1} \int_0^1 \frac{F(\zeta, z_1, t)}{1 + \lambda\rho\theta(\zeta, t)} d\zeta \\ &= \rho^*(z_1) - \rho \end{aligned} \quad (\text{A.3})$$

which shows that $\rho^*(\mathbf{r}_1)$ is periodic in y_1 with period $1/\omega$.

We now consider the relation (2.19). Using (4.6) we rewrite (4.19) as

$$\begin{aligned} \rho^*(\mathbf{r}_1) - \rho &= -\lambda\rho^2 e^{-\pi\rho|z_1|^2} \int_0^1 \frac{d\zeta}{1 + \lambda\rho\theta(\zeta, t)} \sum_{m_1, m_2} e^{-t(m_1^2 + m_2^2)} e^{2i\pi\zeta(m_1 + m_2)} \\ &\quad \times \cos[2\omega t(m_1 z_1 + m_2 z_1^*)] \end{aligned} \quad (\text{A.4})$$

Then, using the fact that $\rho^*(\mathbf{r}_1)$ is an even function in x_1

$$\begin{aligned} \int [\rho^*(\mathbf{r}_1) - \rho] d\mathbf{r}_1 &= -2\lambda\rho^2 \int_0^1 \frac{d\zeta}{1 + \lambda\rho\theta(\zeta, t)} \\ &\quad \times \sum_{m_1, m_2} e^{-t(m_1^2 + m_2^2)} e^{2i\pi(m_1 + m_2)\zeta} \\ &\quad \times \int_0^\infty dx_1 e^{-2t\omega^2 x_1^2} \cos[2\omega t(m_1 + m_2)x_1] \\ &\quad \times \int_{-\infty}^{+\infty} dy_1 e^{-2t\omega^2 y_1^2} e^{2\omega t(m_1 - m_2)y_1} \end{aligned} \quad (\text{A.5})$$

Since

$$\int_{-\infty}^{+\infty} dy_1 e^{-2t\omega^2 y_1^2} e^{2\omega t(m_1 - m_2)y_1} = \frac{1}{\omega} \frac{\sqrt{\pi}}{\sqrt{2t}} e^{(t/2)(m_1 - m_2)^2} \quad (\text{A.6})$$

we get, using the definition of t

$$\begin{aligned} \int [\rho^*(\mathbf{r}_1) - \rho] d\mathbf{r}_1 &= -\lambda\rho \int_0^1 \frac{d\zeta}{1 + \lambda\rho\theta(\zeta, t)} \sum_{m_1, m_2} e^{-t(m_1 + m_2)^2} e^{2i\pi\zeta(m_1 + m_2)} \\ &= \sum_m \left\{ (-\lambda\rho) \int_0^1 \frac{\theta(\zeta, t)}{1 + \lambda\rho\theta(\zeta, t)} d\zeta \right\} \end{aligned} \quad (\text{A.7})$$

which is the required result.

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