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Two-Dimensional Models for an Electrode with Adsorption Sites

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Through a new method, the following model is solved exactly in the framework of classical equilibrium statistical mechanics of two-dimensional Coulomb systems, for the special value $\Gamma = 2$ of the coupling constant: the mobile charges of a one-component plasma are attracted by a line of equidistant sticky adsorption sites embedded in a background, the density of which varies in the direction orthogonal to the line. First the general expressions are given for the densities and correlation functions of nonadsorbed and adsorbed particles. Then these results are used to investigate two models of electrodes with localized adsorption: the externally charged hard wall and the impermeable polarized membrane. In each case the influence of the adsorption upon macroscopic features is studied: the potential drop across the interface, the contact theorem, and the Lippmann equation, which involves the surface free energy.

KEY WORDS: One-component plasma; localized adsorption; solvable model; impermeable membrane; potential drop; surface free energy.

1. INTRODUCTION

Using the framework of classical equilibrium statistical mechanics, I exactly solve models of polarized interfaces between two-dimensional charged systems when the interface bears equidistant adsorption sites. These interfaces are intended to mimic the electrical double layer which appears at the metal–electrolyte interface of an electrode; the adsorbed ions are in dynamical equilibrium with the electrolyte and the distribution of the adsorption sites reflects the periodic structure of the metallic adsorbent. Such a line of adsorption sites had previously been studied by Rosinberg *et al.*(1) in some special cases by a *tour de force* of expansion resummations.

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In this paper I solve the model in the general case by using a simpler method(2,3) and explicitly get the density profiles and the correlation functions. Thus, I am able to complete the work of Rosinberg *et al.* and to investigate a model of an ideally polarizable interface, which was introduced by Rosinberg and Blum,(4,5) when a line of adsorption sites is added on the interface.

The potential I use to describe either the chemisorption or the strong physisorption is the sticky short-range Baxter potential. Then the potential v_{ad} created at the position $\mathbf{r}$ by an adsorption site located at $\mathbf{R}$ is characterized by the Boltzmann factor $\exp(-\beta v_{\text{ad}}) = 1 + \lambda\delta(\mathbf{r}-\mathbf{R})$ (with β the inverse temperature): the positive parameter λ measures the strength of the adsorption force, while the delta "function" takes into account the contact nature of this force. The Boltzmann factor associated with a lattice of adsorption sites located at $\mathbf{R}_i$ is $\exp(-\beta V_{\text{ad}}) = 1 + \lambda \sum_i \delta(\mathbf{r}-\mathbf{R}_i)$. I model the conductive media by classical one-component plasmas (OCP): these are systems made up of mobile point charges embedded in a rigid background of opposite charge which ensures the global neutrality. This classical modeling is acceptable for the electrolytic fluid, but in principle the metal should be handled as a quantum mechanical OCP, which unfortunately is a far more intricate problem. In two dimensions the Coulombic potential between two particles of charges e separated by a distance r is $-e^2 \ln(r/L)$ (where L is an arbitrary length scale which fixes the origin of the potential), and models with various inhomogeneous backgrounds are exactly solvable for the special value of the dimensionless coupling constant $\Gamma = \beta e^2 = 2$. Since the fundamental property of Coulombic systems is the screening effect, which appears in two dimensions as well as in three dimensions, the behavior of electrolytes is very similar in both these dimensions. The method of solution and general results are given in Section 2.

I now turn to a simple modeling of the *polarized* metal–electrolyte interface (which is very complex for real systems). As long as the electrical potential drop $\Delta\phi$ between the electrolyte (which occupies the half-space $x>0$) and the electrode plate is not high enough to cause chemical reactions and a subsequent intense leakage current, the interface can be considered as an ideally polarizable one; in general, the two sides of it have opposite net surface charge densities $\pm\sigma e$. Since the equilibrium density profile of the surface layer of the plasma is determined by its net surface charge density σe, and since $\Delta\phi$ is proportional to the dipolar moment of the net charge density, there is a relation between σe and $\Delta\phi$. Consequently, one can choose either of them as the control parameter. In this paper I study two models for the electrode in greater detail. These models mainly differ in the treatment of the metal and will respectively be referred to as the charged hard wall and the impermeable membrane.

In the first model (Section 3), also called the "primitive electrode," only the electrolyte, which is modeled by an OCP, is treated at the microscopic level, whereas the *metal* is replaced by an insulating impenetrable *wall*. The only way of making a net surface charge appear is then to introduce an *external*, immobile, surface *charge* density $-\sigma e$ on the wall, which appears as the control parameter. Because of the property of perfect screening, a polarization charge density $(\rho - \rho_B) e$ is built by the plasma so that $\int_0^{+\infty} [\rho - \rho_B] \, dx = \sigma$. This model is the crudest one but it has the advantage of allowing simple calculations.

In the second model (Section 4), the ideally polarizable interface is described by two one-component plasmas of different background densities which are separated by an *impermeable membrane* of zero width; this impermeable surface prevents the charges from crossing the interface while allowing electrical interactions between all particles, which leads to the building of a double layer of opposite polarization charges. This model is better than the previous one, from two points of view: first, it deals with the *statistical mechanics of both sides*, which are thus both treated at a microscopic level, and second, the conducting nature of both the metal and the electrolyte is taken into account. This is more realistic, since Rosinberg *et al.*(5) have shown that the interaction between the metal particles makes a sizeable contribution to the differential capacity $\partial(\sigma e)/\partial \Delta\phi$. Moreover, the control parameter in this model is the potential drop $\Delta\phi$; this is a nice feature, since in the experimental situation the potential drop $\Delta\phi$ is the externally fixed variable, whereas the charge density σe is controlled by $\Delta\phi$ and is not measured directly. However, σ can be computed from other measurements such as either the curve of differential capacity versus $\Delta\phi$ or the electrocapillarity curve (surface tension γ versus $\Delta\phi$), since according to the Lippmann equation $\partial\gamma/\partial\Delta\phi = -e\sigma$.

In Section 2, I introduce the method of solution for the one-component plasma at $\Gamma = 2$ and give the general results (densities, correlation functions, potential drop, free energy) for a line of adsorption sites embedded in a background which varies only in the perpendicular direction. Thus, I complete the work of Rosinberg *et al.*(1) Then I investigate the density profiles, potential drop, contact theorem, and Lippmann equation for the primitive electrode (Section 3) and for the ideally polarizable membrane (Section 4). The formalism which allows for dealing with the impermeable membrane is introduced in Section 4.1, and it is used to establish a general demonstration of the Lippmann equation in the case of an impermeable membrane (Section 4.2).

2. METHOD

2.1. General Formalism for the Two-Dimensional OCP at $\Gamma = 2$

Consider N particles of charge e, the positions of which are alternatively described by $\mathbf{r}_i = (x_i, y_i)$ or $z_i = x_i + iy_i$, and which interact both with one another and with some background of opposite charge which makes the system globally neutral. The Hamiltonian of the system is

$$H_N = e^2 V_{\mathrm{BB}} + e^2 \sum_{i=1}^{N} V(\mathbf{r}_i) - e^2 \sum_{1 \leqslant i < j \leqslant N} \ln(|z_i - z_j|/L) \tag{2.1}$$

where $e^2 V$ is the background–particle interaction energy, plus possibly a contribution from some external potential, and $e^2 V_{\mathrm{BB}}$ is the background self-energy. For the inverse temperature β such that $\Gamma = \beta e^2 = 2$, the Boltzmann factor reads[2,3]

$$\exp(-\beta H_N) = C_N \exp(-\beta e^2 V_{\mathrm{BB}}) \times |\det\{\exp[-V(\mathbf{r}_i)]\, z_i^{j-1}\}_{i,j=1\cdots N}|^2 \tag{2.2}$$

where C_N is a constant. Thus, for the one-component plasma, the Boltzmann factor of the classical canonical partition function of N mobile charges may be written as the squared modulus of a Slater determinant; in other words, it has the same structure as the quantum probability density of a system made of independent N fermions which have orbitals of the type $(x+iy)^n \exp[-V(x, y)]$.

If we straightaway go to the thermodynamic limit, then the problem of obtaining the correlation functions reduces to the calculation of the projector P on the subspace $\mathscr{E}$ spanned by the entire functions of $z = (x+iy)$ times $\exp[-V(x, y)]$. If we are able to produce an orthogonal basis $\{\Psi_j(\mathbf{r})\}$ of the subspace $\mathscr{E}$, the projector P is merely given by

$$\langle \mathbf{r}_1 | P | \mathbf{r}_2 \rangle = \sum_j \frac{\Psi_j(\mathbf{r}_1)\, \bar{\Psi}_j(\mathbf{r}_2)}{\int d\mathbf{r}\, |\Psi_j(\mathbf{r})|^2} \tag{2.3}$$

(where $\bar{\Psi}$ is the complex conjugate of Ψ), and the truncated n-particle densities are

$$\begin{aligned} \rho(\mathbf{r}) &= \langle \mathbf{r} | P | \mathbf{r} \rangle \\ \rho^{(2)T}(\mathbf{r}_1, \mathbf{r}_2) &= -|\langle \mathbf{r}_1 | P | \mathbf{r}_2 \rangle|^2 \\ \rho^{(n)T}(\mathbf{r}_1, \ldots, \mathbf{r}_n) &= (-1)^{n+1} \sum_{(i_1 i_2 \cdots i_n)} \langle \mathbf{r}_{i_1} | P | \mathbf{r}_{i_2} \rangle \cdots \langle \mathbf{r}_{i_n} | P | \mathbf{r}_{i_1} \rangle \end{aligned} \tag{2.4}$$

where the summation runs over all cycles $(i_1 i_2 \cdots i_n)$ built with $\{1, 2, \ldots, n\}$.

2.2. Background Inhomogeneous in One Direction

The background potential $eV_B(\mathbf{r})$ is determined by both the background density $\rho_B(\mathbf{r})$ (through the Poisson equation $\Delta V_B = 2\pi\rho_B$) and by the boundary conditions, even after these boundaries have receded to infinity. For instance, the description of a plane surface between two one-component plasmas with uniform backgrounds involves a potential V_0 which depends only on the direction orthogonal to the interface. In the following this direction will correspond to the x axis.

Since $V_0(x)$ is translationally invariant along the y axis, the functions $\exp[-V_0(x) + k(x+iy)]$, with $k \in \mathbb{R}$, are orthogonal because of the plane-wave factor $\exp(iky)$, and they form a basis of the subspace $\mathscr{E}$, at least in the sense of distributions. Thus, the projector $P^{(0)}$ associated with $V_0(x)$ is

$$\begin{aligned}\langle \mathbf{r}_1 | P^{(0)} | \mathbf{r}_2 \rangle = {} & \exp[-V_0(x_1) - V_0(x_2)] \\ & \times \int \frac{dk}{2\pi}\, g(k) \exp[k(x_1 + x_2)] \exp[ik(y_1 - y_2)] \end{aligned} \tag{2.5}$$

with

$$g(k) = \left\{ \int du \exp[-2V_0(u) + 2ku] \right\}^{-1} \tag{2.6}$$

and we retrieve Alastuey and Lebowitz's results,$^{(6)}$ for instance,

$$\rho^{(0)}(\mathbf{r}) = \int \frac{dk}{2\pi}\, g(k) \exp[-2V_0(x) + 2kx] \tag{2.7}$$

When the particles are confined to the half-space $x > 0$ by an impenetrable wall, the range of k must be restricted to $k > 0$, as can be seen by retrieving this case as the limit of the system where an impenetrable barrier separates two regions filled with the same one-component plasma.$^{(3)}$

The basis I have just exhibited will be useful for investigating the following problem.

2.3. Line of Equidistant Adsorption Sites (Method of Solution)

We are now able to study a system made of mobile charges which interact with a line of equidistant adsorption sites located along the y axis and with an electrical background which is inhomogeneous only in the x axis direction. The line of adsorption sites, with a distance between the nearest neighbors equal to ω, creates a Baxter potential V_{ad} such that

$\exp(-\beta V_{\mathrm{ad}}) = 1 + \lambda\delta(x) \sum_m \delta(y - m\omega)$, with m integer; the electrical potential V_0 created by the background is assumed to depend only on x. Thus, $e^2 V(\mathbf{r}) = e^2 V_0(x) + V_{\mathrm{ad}}$.

First we take advantage of the periodicity of V_{ad}. For that purpose, it is convenient to write $k = 2\pi(\zeta + n)/\omega$ (with $\zeta \in [0, 1]$ and n integer) and to introduce

$$\varphi_{\zeta+n}(z) = [g(\zeta + n)/\omega]^{1/2} \exp[2\pi(\zeta + n)\, z/\omega]$$

where $[g(\zeta + n)/\omega]^{1/2}$ is the normalization factor for the weight $\exp[-2V_0(x)]$ [see (2.6)]:

$$g(\zeta + n) \equiv g\left(\frac{2\pi}{\omega}(\zeta + n)\right) = \left\{\int dx \exp\left[-2V_0(x) + \frac{4\pi(\zeta + n)\, x}{\omega}\right]\right\}^{-1} \tag{2.8}$$

The functions $\varphi_{\zeta+n}$ are orthogonal and normalized for the weight $\exp(-2V_0)$. Then the periodicity of V_{ad} along the y axis ensures that, in this basis, the matrix of the scalar products with the weight $\exp[-2V(\mathbf{r})]$ is brought to a block-diagonal form:

$$\int d\mathbf{r}\, \bar{\varphi}_{\zeta+n}(z) \exp[-2V(\mathbf{r})]\, \varphi_{\zeta'+n'}(z) = \delta(\zeta - \zeta')\, A_\zeta(n, n') \tag{2.9}$$

If we are able to diagonalize the symmetric matrix $A_\zeta(n, n')$, that is, to find the eigenvalues α of $A_\zeta(n, n')$ and the corresponding orthogonal eigenvectors $(a_m^{(\alpha)})$ defined by

$$\sum_m A_\zeta(n, m)\, a_m^{(\alpha)} = \alpha a_n^{(\alpha)}$$

then the functions

$$\Psi_{\zeta,\alpha} = \exp[-V(\mathbf{r})] \times \left[\sum_m a_m^{(\alpha)} \varphi_{\zeta+m}(z)\right]$$

form an orthogonal basis of $\mathscr{E}$ and

$$\langle \mathbf{r}_1 |\, P\, | \mathbf{r}_2 \rangle = \int_0^1 d\zeta \sum_{\alpha(\zeta)} \frac{\Psi_{\zeta,\alpha}(\mathbf{r}_1)\, \bar{\Psi}_{\zeta,\alpha}(\mathbf{r}_2)}{\alpha \sum_p [a_p^{(\alpha)}]^2} \tag{2.10}$$

Now we use the peculiar form of the Baxter potential which implies that the matrix A_ζ has a very simple structure:

$$A_\zeta(n, n') = \delta_{nn'} + \mu \sqrt{g(\zeta + n)}\, \sqrt{g(\zeta + n')}$$

where $\mu = \lambda \exp[-2V_0(0)]/\omega$ and $V_0(0)$ is the value of $V_0(x)$ on the adsorption sites. A_ζ has only two eigenvalues, $\alpha_1 = 1 + \mu \sum_n g(\zeta + n)$, associated with the eigenvector $[a_n^{(1)} = \sqrt{g(\zeta + n)}]$, and $\alpha_2 = 1$, the eigenvectors of which span the subspace orthogonal to $(a_n^{(1)})$. As a result,

$$\begin{aligned}\langle \mathbf{r}_1 | P | \mathbf{r}_2 \rangle &= \exp[-V(\mathbf{r}_1) - V(\mathbf{r}_2)] \\ &\quad \times \int_0^1 \frac{d\zeta}{\omega} \sum_{n,m} \exp\left[\frac{2\pi(\zeta + n)\, z_1}{\omega}\right] \exp\left[\frac{2\pi(\zeta + m)\, \bar{z}_2}{\omega}\right] \\ &\quad \times g(\zeta + n) \left[\delta_{n,m} - \frac{\mu g(\zeta + m)}{1 + \mu G(\zeta)}\right]\end{aligned} \tag{2.11}$$

where $G(\zeta) = \sum_n g(\zeta + n)$. Moreover, one shows in the same way as for $V = V_0(x)$ that,[3] when the particles are confined to the half-space $x \geqslant 0$, the summation is restricted to $n \geqslant 0$. We can rewrite $\langle \mathbf{r}_1 | P | \mathbf{r}_2 \rangle$ as

$$\begin{aligned}\langle \mathbf{r}_1 | P | \mathbf{r}_2 \rangle &= \left[1 + \lambda \delta(x_1) \sum_m \delta(y_1 - m\omega)\right]^{1/2} \\ &\quad \times \left[1 + \lambda \delta(x_2) \sum_{m'} \delta(y_2 - m'\omega)\right]^{1/2} \\ &\quad \times \langle \mathbf{r}_1 | P^* | \mathbf{r}_2 \rangle\end{aligned} \tag{2.12}$$

with

$$\begin{aligned}\langle \mathbf{r}_1 | P^* | \mathbf{r}_2 \rangle &= \langle \mathbf{r}_1 | P^{(0)} | \mathbf{r}_2 \rangle \\ &\quad - \exp[-V_0(x_1) - V_0(x_2)] \\ &\quad \times \int_0^1 \frac{d\zeta}{\omega} \frac{\mu}{1 + \mu G(\zeta)} \sum_n g(\zeta + n) \exp\left[\frac{2\pi(\zeta + n)\, z_1}{\omega}\right] \\ &\quad \times \sum_m g(\zeta + m) \exp\left[\frac{2\pi(\zeta + m)\, \bar{z}_2}{\omega}\right]\end{aligned} \tag{2.13}$$

where $\langle \mathbf{r}_1 | P^{(0)} | \mathbf{r}_2 \rangle$ is the projector in the absence of adsorption sites, since, according to (2.5), $\langle \mathbf{r}_1 | P^{(0)} | \mathbf{r}_2 \rangle$ itself can be written as

$$\begin{aligned}\langle \mathbf{r}_1 | P^{(0)} | \mathbf{r}_2 \rangle &= \exp[-V_0(x_1) - V_0(x_2)] \\ &\quad \times \int_0^1 \frac{d\zeta}{\omega} \sum_n g(\zeta + n) \exp\left[\frac{2\pi(\zeta + n)(z_1 + \bar{z}_2)}{\omega}\right]\end{aligned} \tag{2.14}$$

2.4. Line of Equidistant Adsorption Sites (General Results)

According to (2.12), the density $\rho(\mathbf{r})$ can be expressed as

$$\rho(\mathbf{r}) = \left[1 + \lambda\delta(x) \sum_m \delta(y - m\omega) \right] \rho^*(\mathbf{r})$$

where $\rho^*(\mathbf{r})$ obviously is the density of the particles which are not adsorbed:

$$\rho^*(\mathbf{r}) = \rho^{(0)}(\mathbf{r}) - \exp[-2V_0(x)] \int_0^1 \frac{d\zeta}{\omega} \frac{\mu}{1 + \mu G(\zeta)} \exp\left(\frac{4\pi\zeta x}{\omega}\right) \times \left| \sum_n g(\zeta + n) \exp\left(\frac{2\pi n z}{\omega}\right) \right|^2 \tag{2.15}$$

The change $\delta\rho(\mathbf{r}) = \rho^*(\mathbf{r}) - \rho^{(0)}(\mathbf{r})$ in the density of nonadsorbed particles which is due to the presence of the adsorption sites is a periodic function of y, with a period equal to ω. Thus, we have solved a problem where the density depends on both x and y: the interface has a genuine two-dimensional feature.

The occupation mean number n_{ad} of an adsorption site is $n_{\text{ad}} = \lambda\rho^*(0, 0)$ and, according to (2.14) and (2.15),

$$n_{\text{ad}} = \int_0^1 d\zeta \frac{\mu G(\zeta)}{1 + \mu G(\zeta)} \tag{2.16}$$

As Rosinberg *et al.*$^{(1)}$ had pointed out in a special case, $n_{\text{ad}} \leqslant 1$ because of the Coulombic repulsion between charges of the same sign. Moreover, n_{ad} is an increasing function of λ (which measures the strength of the adsorption) and the saturation is reached in the limit of an infinitely strong adsorption ($\lambda \to +\infty$). In the simplest case of a line of adsorption sites embedded in a homogeneous background of density ρ_0, $V_0(x) = \pi\rho_0 x^2$, $\mu = \lambda/\omega$, and

$$\mu g(\zeta + n) = \lambda\rho_0(\tau/\sqrt{\pi}) \exp[-\tau^2(\zeta + n)^2]$$

with $\tau = (2\pi/\rho_0\omega^2)^{1/2}$; then $\mu G(\zeta) = \lambda\rho_0\theta_3(\zeta, \tau)$, where $\theta_3(\zeta, \tau)$ is the Jacobi theta function defined by the series

$$\theta_3(\zeta, \tau) = (\tau/\sqrt{\pi}) \sum_{n \in \mathbb{Z}} \exp[-\tau^2(\zeta + n)^2]$$

and we retrieve the result of Rosinberg *et al.*

As for the "mean" surface polarization charge density

$$e\sigma_p = e\int_0^{+\infty} dx \left[\left(\int_0^{\omega} dy\, \rho(\mathbf{r})/\omega\right) - \rho_{\mathrm{B}}\right]$$

σ_p reads

$$\sigma_p = \sigma_p^{(0)} + \int_0^{+\infty} dx \frac{1}{\omega}\int_0^{y} dy\, \delta\rho(x, y) + \frac{n_{\mathrm{ad}}}{\omega} \tag{2.17}$$

where $e\sigma_p^{(0)}$ is the surface polarization charge density in the absence of adsorption sites, $\sigma_p^{(0)} = \int_0^{+\infty} dx[\rho^{(0)}(x) - \rho_B]$, and

$$\frac{1}{\omega}\int_0^{\omega} dy\, \delta\rho(x, y) = -\exp[-2V_0(x)] \int_0^1 \frac{d\zeta}{\omega} \frac{\mu}{1+\mu G(\zeta)} \times \sum_n \exp\left[\frac{4\pi(\zeta+n)\, x}{\omega}\right] [g(\zeta+n)]^2 \tag{2.18}$$

Because of the Poisson equation, the potential drop $\Delta\phi = \phi(+\infty) - \phi(-\infty)$ is related to the density profile via $\Delta\phi = 2\pi e \int_{-\infty}^{+\infty} dx\, x[\rho(x) - \rho_B]$. In the presence of adsorption sites we will use a "mean" potential drop

$$\Delta\phi = 2\pi e \int_{-\infty}^{+\infty} dx\, x \left[\left(\int_0^{\omega} dy\, \rho(x, y)/\omega\right) - \rho_B\right]$$

Since the term $\lambda\delta(x) \sum_m \delta(y - m\omega)$ does not contribute, $\Delta\phi$ may be written as

$$\Delta\phi = \Delta\phi^{(0)} + 2\pi e \int dx\, x \left(\int_0^{\omega} dy\, \delta\rho(x, y)/\omega\right)$$

where $\Delta\phi^{(0)}$ is the potential drop in the absence of adsorption sites. The calculation of $\Delta\phi - \Delta\phi^{(0)}$ is quite easy: after integrating upon y [see (2.18)], we interchange $\int d\zeta$ and $\int dx$ and we notice that

$$\int dx(x/\omega) \exp[-2V_0(x)] \exp[4\pi(\zeta+n)\, x/\omega] = 1/(4\pi)(\partial/\partial\zeta)\{[g(\zeta+n)]^{-1}\}$$

Then we obtain

$$\Delta\phi - \Delta\phi^{(0)} = \tfrac{1}{2} e[\ln[1+\mu G(\zeta)]]_0^1 \tag{2.19}$$

On the other hand, Rosinberg *et al.*(1) have shown that the canonical partition function of this system can be formally expressed as a grand canonical partition function, where λ plays the role of the fugacity of the adsorbed particles. Since the fugacity is defined up to a multiplicative constant, $n_{\text{ad}}/\omega = \mu(\partial/\partial\mu)(-\beta\,\Delta f)$, where Δf is the excess surface free energy density of the system compared to the system where there is no adsorption site. Since $\Delta f = 0$ when $\lambda = 0$, we get from (2.16)

$$-\beta\,\Delta f = \frac{1}{\omega}\int_0^1 d\zeta\,\ln[1+\mu G(\zeta)] \tag{2.20}$$

The negative sign of Δf means that the presence of the adsorption sites has a stabilizing effect.

As for the correlation function between the adsorbed particles

$$n_{\text{ad}}^{(2)T}(m_1, m_2) = -\lambda^2\,|\langle x_1 = 0,\, y_1 = m_1\omega\,|P^*|\,x_2 = 0,\, y_2 = m_2\omega\rangle|^2$$

it has a very simple form:

$$n_{\text{ad}}^{(2)T}(m_1, m_2) = -\left|\int_0^1 d\zeta\,\exp[i2\pi\zeta(m_1 - m_2)]\,\frac{\mu G(\zeta)}{1+\mu G(\zeta)}\right|^2 \tag{2.21}$$

We easily verify that $n_{\text{ad}}^{(2)T}(m_1, m_1) = -n_{\text{ad}}^2$: one site is occupied by at most one particle. Using (2.16) and (2.21), we readily see that the compressibility rule for the adsorbed particles is satisfied,(1)

$$\lambda\frac{\partial n_{\text{ad}}}{\partial\lambda} - n_{\text{ad}} = \sum_{m_2} n_{\text{ad}}^{(2)T}(m_1, m_2) \tag{2.22}$$

Moreover, the structure of $\rho(\mathbf{r})$ and $\rho^{(2)T}(\mathbf{r}_1, \mathbf{r}_2)$ in terms of the projector P implies that the first perfect screening sum rule is always satisfied:

$$\int d\mathbf{r}_2\,\rho^{(2)T}(\mathbf{r}_1, \mathbf{r}_2) = -\rho(\mathbf{r}_1) \tag{2.23}$$

A charge of the plasma is perfectly screened by the others, which is a fundamental property of a conductive medium.

3. THE PRIMITIVE ELECTRODE

3.1. Model

In a slab of plasma with a bulk density ρ_0 bounded by the two plates of a capacitor with opposite surface charge densities ($-\sigma e$ at $x = 0$ and σe

at $x = +L$), the potential created by these plates is equal to $+2\pi\sigma e x$ inside the capacitor and to constant values outside. Consequently, the potential in the vicinity of the plate located at $x=0$ (the other one being sent away to infinity) is $V_0(x) = (\pi\rho_0 x^2 + 2\pi\sigma x)\,\theta(x)$, where $\theta(x)$ is the step function $[\theta(x)=0$ for $x<0$, $\theta(x)=1$ for $x>0]$. The plate, which is modeled by a hard wall with a surface charge density $-\sigma e$, occupies the half-space $x<0$ so that the particles are confined to the region $x \geqslant 0$. Then $\mu = \lambda/\omega$ and, in terms of g_w defined in (2.8), we introduce $\tilde{g}_w$ by $\mu g_w(\zeta) = \lambda\rho_0\,\tilde{g}_w(\zeta - \sigma\omega)$ (in this section the index w refers to the charged hard wall). Thus,

$$\begin{aligned}\tilde{g}_w(\zeta) &= \left\{\rho_0\omega \int_0^{+\infty} dx \exp[-2\pi\rho_0 x^2 + 4\pi\zeta(x/\omega)]\right\}^{-1} \\ &= \frac{2\tau}{\sqrt{\pi}}\,\frac{\exp(-\tau^2\zeta^2)}{1+\mathrm{erf}(\tau\zeta)} \equiv \frac{1}{\tilde{h}_\tau(\zeta)}\end{aligned} \tag{3.1}$$

where $\tau = [2\pi/\rho_0\omega^2]^{1/2}$ and $\mathrm{erf}(u)$ is the error function:

$$\mathrm{erf}(u) = (2/\sqrt{\pi}) \int_0^u dt \exp(-t^2)$$

According to (2.13) and (2.14), the projector P^* becomes

$$\begin{aligned}\langle \mathbf{r}_1 |\, P_w^* \,| \mathbf{r}_2 \rangle &= \rho_0 \exp[-\pi\rho_0(x_1^2 + x_2^2) + i2\pi\sigma(y_1 - y_2)] \\ &\quad \times \int_{-\sigma\omega}^{-\sigma\omega+1} d\zeta \sum_{n=0}^{+\infty} \tilde{g}_w(\zeta+n) \exp\left[\frac{2\pi(\zeta+n)\,z_1}{\omega}\right] \\ &\quad \times \sum_{m=0}^{+\infty} \exp\left[\frac{2\pi(\zeta+m)\,\bar{z}_2}{\omega}\right]\left[\delta_{n,m} - \frac{\lambda\rho_0}{1+\lambda\rho_0\tilde{G}_w(\zeta)}\,\tilde{g}_w(\zeta+m)\right]\end{aligned} \tag{3.2}$$

with $\tilde{G}_w(\zeta) = \sum_{n=0}^{+\infty} \tilde{g}_w(\zeta+n)$.

3.2. Density Profile

According to (2.7), we immediately retrieve$^{(7)}$ that, in the absence of adsorption sites,

$$\rho_w^{(0)}(x) = \rho_0 \frac{2}{\sqrt{\pi}} \int_{-\sigma[2\pi/\rho_0]^{1/2}}^{+\infty} du \,\frac{\exp\{-[(2\pi\rho_0)^{1/2}x - u]^2\}}{1+\mathrm{erf}(u)} \tag{3.3}$$

Then the surface polarization charge density is $e\sigma_{p,w}^{(0)}$ with $\sigma_{p,w}^{(0)} = \int_0^{+\infty} [\rho_w^{(0)}(x) - \rho_0]\, dx = \sigma$.[7] Notice that, according to (2.14), $\rho_w^{(0)}(x)$ can be written as

$$\rho_w^{(0)}(x) = \rho_0 \exp(-2\pi\rho_0 x^2) \int_{-\sigma\omega}^{-\sigma\omega+1} d\zeta \sum_{n=0}^{+\infty} \tilde{g}_w(\zeta+n) \exp[4\pi(\zeta+n)\, x/\omega] \tag{3.4}$$

In the presence of the adsorption sites on the charged hard wall, according to (2.15), the density of the nonadsorbed particles is

$$\rho_w^*(\mathbf{r}) = \rho_w^{(0)}(x) - \rho_0 \exp(-2\pi\rho_0 x^2) \int_{-\sigma\omega}^{-\sigma\omega+1} d\zeta \frac{\lambda\rho_0}{1+\lambda\rho_0\tilde{G}_w(\zeta)} \exp\left(\frac{4\pi\zeta x}{\omega}\right) \times \left| \sum_{n=0}^{+\infty} \tilde{g}_w(\zeta+n) \exp\left(\frac{2\pi n z}{\omega}\right) \right|^2 \tag{3.5}$$

Since

$$\exp(4\pi\zeta x/\omega) \left| \sum_{n=0}^{+\infty} \tilde{g}_w(\zeta+n) \exp(2\pi n z/\omega) \right|^2 \leqslant B \exp(\pi\rho_0 x^2)$$

(where B is a constant) and since $\rho_w^{(0)}(x) - \rho_0$ goes to zero as a Gaussian when x goes to infinity,[7] $\rho_w^*(\mathbf{r})$ tends to the bulk density ρ_0 as a Gaussian whether there are adsorption sites or not.

Moreover, since the particles are confined to the half-space $x \geqslant 0$,

$$\int_0^{+\infty} dx \exp[-2V_0(x)] \exp[4\pi(\zeta+n)\, x/\omega] = [g_w(\zeta+n)]^{-1}$$

and, by using (2.18) and (2.16), we find

$$\int_0^{+\infty} dx \left[\int_0^{\omega} dy\, \delta\rho_w(\mathbf{r})/\omega \right] = -n_{\mathrm{ad},w}/\omega \tag{3.6}$$

so that, according to (2.17),

$$\sigma_{p,w} = \sigma_{p,w}^{(0)} = \sigma \tag{3.7}$$

This equality expresses the perfect screening of the external charge $-\sigma e$ in two models, where σ is the control parameter.

3.3. Potential Drop and Contact Theorem

(a) In the absence of adsorption sites, $\Delta\phi_w^{(0)}$ is easily calculated by writing it as

$$\Delta\phi_w^{(0)} = \lim_{s \to 0^+} -\pi e \int_0^{+\infty} dx\, x^2 \frac{d\rho}{dx} e^{-sx}$$

with the result that(8)

$$\Delta\phi_w^{(0)} = -\frac{e}{2}\left(\frac{1}{2} + 2\pi\frac{\sigma^2}{\rho_0} + \ln\left\{\frac{1}{2}\left[1 - \operatorname{erf}\left(\sigma\left(\frac{2\pi}{\rho_0}\right)^{1/2}\right)\right]\right\}\right) \tag{3.8}$$

(Recall that $-\sigma e$ is the surface charge density on the wall.)

On the other hand, the thermodynamic pressure p_{th} is given by a scaling argument(9) which leads to $\beta p_{\text{th}} = \rho_0(1 - \beta e^2/4)$ (which reduces to $\beta p_{\text{th}} = \rho_0/2$ at $\beta e^2 = 2$); moreover, the electrostatic pressure due to a surface charge density $-\sigma e$ is $p_\sigma = (2\pi\sigma e)^2/(4\pi)$, and, according to (3.3),

$$\rho_w^{(0)}(x=0) = \rho_0 \ln\{2/[1 - \operatorname{erf}(\sigma(2\pi/\rho_0)^{1/2})]\}$$

Thus, the relation (3.8) can be viewed as a contact theorem,

$$p_{\text{th}} = \beta^{-1}\rho_w^{(0)}(x=0) - p_\sigma - \rho_0 e\Delta\phi_w^{(0)} \tag{3.9}$$

This equation expresses the balance(10) of a slab of electrolyte submitted to the thermodynamic pressure, the kinetic pressure on the wall, the surface electrostatic pressure, and the electrostatic pressure due to the charged background. It can also be derived from the first hierarchy equation.(11)

(b) We now study the change in $\Delta\phi_w$ originating from the presence of the adsorption sites. In the case of the charged hard wall

$$\mu G(\zeta) = \lambda\rho_0 \sum_{n=0}^{+\infty} \tilde{g}_w(\zeta - \sigma\omega + n)$$

and, according to (2.19), the presence of the adsorption sites is responsible for the extra potential drop

$$\Delta\phi_w - \Delta\phi_w^{(0)} = \frac{e}{2}\ln\left[1 - \frac{\lambda\rho_0\,\tilde{g}_w(-\sigma\omega)}{1 + \lambda\rho_0\sum_{n=0}^{+\infty}\tilde{g}_w(-\sigma\omega + n)}\right] \tag{3.10}$$

The electrode potential $\phi_w(0) - \phi_w(+\infty)$ increases when there are adsorption sites.

In order to interpret Eq. (3.10) as a contact theorem, we come back to the calculation of $\Delta\phi - \Delta\phi^{(0)}$ which led to (2.19). Using the fact that

$$\frac{2\tau}{\sqrt{\pi}}\exp(-\tau^2\zeta^2) = \frac{d}{d\zeta}[1 + \operatorname{erf}(\tau\zeta)]$$

in order to rewrite

$$\frac{d}{d\zeta}([g_w(\zeta + n)]^{-1}) = \frac{1}{\omega\rho_0} + \frac{4\pi}{\rho_0\omega^2}(\zeta + n - \sigma\omega)[g_w(\zeta + n)]^{-1}$$

we finally get

$$\beta e[\Delta\phi_w - \Delta\phi_w^{(0)}] = -\int_0^1 d\zeta \frac{\mu}{1+\mu G_w(\zeta)} \left\{ \sum_n \frac{1}{\omega\rho_0} [g_w(\zeta+n)]^2 \right.$$
$$\left. + \sum_n \frac{4\pi}{\rho_0\omega^2} (\zeta+n-\sigma\omega)\, g_w(\zeta+n) \right\}$$

Then we recognize that, according to (2.18), the first term of the rhs is merely $(1/\rho_0)\{[\int_0^\omega dy\, \rho^*(0, y)/\omega] - \rho^{(0)}(x=0)\}$ and that, according to (2.14) and (2.15), when $-2V_0(x) = -2\pi\rho_0 x^2 - 4\pi\sigma x$, the second term is $-(\lambda/\omega\rho_0)(\partial\rho^*/\partial x)(x, 0)|_{x=0}$. We obtain

$$\beta e[\Delta\phi_w - \Delta\phi_w^{(0)}]$$
$$= \frac{1}{\rho_0} \left\{ \left[\frac{1}{\omega} \int_0^\omega dy [\rho^*(0, y) - \rho^{(0)}(x=0)] \right] - \frac{\lambda}{\omega} \frac{\partial\rho^*}{\partial x}(x, 0)|_{x=0} \right\} \tag{3.11}$$

This gives the interpretation of the expression of $e[\Delta\phi_w - \Delta\phi_w^{(0)}]$ given by (3.10), and the contact theorem now reads

$$p_{\text{th}} = \beta^{-1} \left\{ \frac{1}{\omega} \int_0^\omega dy\, \rho^*(0, y) - \frac{\lambda}{\omega} \frac{\partial\rho^*}{\partial x}(x, 0)|_{x=0} \right\} - p_\sigma - e\rho_0 \Delta\phi_w \tag{3.12}$$

This modified contact theorem was suggested by Blum *et al.*$^{(12)}$

3.4. Surface Free Energy and Lippmann Equation

Since our formalism straightaway deals with the thermodynamic limit, we cannot compute directly the surface free energy of a system (the subtle interplay between the background and particle contributions to electrostatic energies, which ensures the extensitivity of the free energy, can be exhibited only if one starts with a finite system).

(a) First we recall the surface free energy density $f_w^{(0)}$ of a charged hard wall, which was first derived through statistical mechanics calculations by Smith.$^{(8)}$ $f_w^{(0)}$, defined through an increase of the surface charge while keeping the area of the interface and the background density constant, is given at $\beta e^2 = 2$ by$^{(10)}$

$$f_w^{(0)} = \sigma\mu_0 - \frac{e^2}{2}\left[\frac{\sigma}{2} + \frac{2\pi}{3}\frac{\sigma^3}{\rho_0} + \left(\frac{\rho_0}{2\pi}\right)^{1/2} \int_0^{\sigma(2\pi/\rho_0)^{1/2}} dt \ln\frac{1-\text{erf}(t)}{2} \right] \tag{3.13}$$

where σe is the net surface charge density of the fluid and μ_0 is the bulk chemical potential. On the other hand, from the thermodynamic point of view, this variation of free energy which occurs when one raises the surface charge density of the wall from 0 to $-e\sigma$ while increasing the number of mobile charges in order to keep the system globally neutral is the sum of the following two terms: σ times the bulk free energy per mobile particle, plus

$$\int_0^{\sigma} (-e d\sigma')[\phi^{(0)}_{w,\sigma'}(0) - \phi^{(0)}_{w,\sigma'}(+\infty)]$$

which is the sum of the works needed to carry the external charge $-ed\sigma'$ from infinity to the wall across the potential drop created by the plasma. Using the expression (3.8) for $\phi^{(0)}_{w,\sigma'}$ when the external surface charge density on the wall is $-\sigma' e$, we retrieve (3.13).

(b) In the presence of the adsorption sites, according to (2.16) and (2.21), the occupation mean number is

$$n_{\text{ad}} = \int_{-\sigma\omega}^{-\sigma\omega+1} d\zeta \, \frac{\lambda \rho_0 \tilde{G}_w(\zeta)}{1 + \lambda \rho_0 \tilde{G}_w(\zeta)} \tag{3.14}$$

and the correlation function between the adsorbed particles is

$$n^{(2)T}_w(m_1, m_2) = -\left| \int_{-\sigma\omega}^{-\sigma\omega+1} d\zeta \, \exp[i2\pi(\zeta + \sigma\omega)(m_1 - m_2)] \, \frac{\lambda \rho_0 \tilde{G}_w(\zeta)}{1 + \lambda \rho_0 \tilde{G}_w(\zeta)} \right|^2 \tag{3.15}$$

An integration per parts shows that $n^{(2)T}_w(m_1 - m_2)$ decreases as $1/(m_1 - m_2)^2$ when $m_1 - m_2$ goes to infinity as it is expected in the vicinity of an insulating wall.[7] According to (2.20), the total surface free energy density is

$$f_w = f^{(0)}_w + \Delta f_w = f^{(0)}_w - \frac{e^2}{2} \int_{-\sigma\omega}^{-\sigma\omega+1} \frac{d\zeta}{\omega} \ln[1 + \lambda \rho_0 \tilde{G}_w(\zeta)] \tag{3.16}$$

(c) Let us now turn to the derivation of the Lippmann equation. For that purpose I introduce F_s, the surface free energy; A, the "surface" of the interface; Ω, the "volume" of the system; and $Q = A\sigma e$, the polarization charge. The interpretation of (3.13) implies that

$$\partial f^{(0)}_w / \partial \sigma \,|_{\rho_0} \equiv e(\partial F_s / \partial Q)\,|_{A,\Omega,\rho_0} = \mu_0 + e\Delta\phi^{(0)}$$

Moreover, using (2.19) and (3.16), we notice that $\partial(\Delta f)/\partial\sigma\,|_{\omega,\rho_0} = e[\Delta\phi - \Delta\phi^{(0)}]$. Therefore $f^{(0)}_w$ and f_w satisfy the same equation,

$$\left. \frac{\partial f_w}{\partial \sigma} \right|_{\omega,\rho_0} = \mu_0 + e\Delta\phi \tag{3.17}$$

On the other hand, the surface tension $\gamma = (\partial F_s/\partial A)|_Q$ is related to $f = F_s/A$ via

$$\gamma = f - \sigma(\partial f/\partial \sigma)|_{\rho_0} \tag{3.18}$$

γ is the Legendre transform of f with respect to σ and, according to (3.17), in the case of the charged hard wall the conjugate quantities are σ and $\mu(\beta, \rho_0) + e\Delta\phi$. This implies the following relation, known in electrochemistry as the Lippmann equation$^{(10)}$:

$$\left.\frac{\partial \gamma_w}{\partial \Delta\phi}\right|_{\rho_0} = -e\sigma \tag{3.19}$$

By means of (3.19), the experimental electrocapillarity curve (γ versus $\Delta\phi$) allows for the calculation of σ, where σe is the total polarization charge density, which includes the possibly adsorbed charge density.

4. THE IDEALLY POLARIZABLE INTERFACE

4.1. Description of a Polarized Impermeable Membrane

Dealing with a polarized impermeable interface is as easy as treating a permeable membrane if one notices that the grand canonical partition function of an impermeable surface Ξ_{imp}, when the particles on each side of it have different fugacities, may be viewed as the canonical partition function of a permeable surface Q_{perm}, where the particles are submitted to an external potential step when they cross the membrane, this external potential step being related to the polarization charge density.$^{(5,6)}$ On the other hand, the equivalence between the grand canonical ensemble and the canonical ensemble ensures that we can calculate the density and the truncated n-body densities for the impermeable membrane directly from the grand canonical partition function of the impermeable membrane $\Xi_{\text{imp}} = Q_{\text{perm}}$. The point is that Q_{perm} is far more easily tractable than Q_{imp}.

We now come to the demonstration of the relations between the descriptions of these two membranes. Let us consider a system Σ built with two OCPs Σ_a and Σ_b separated by an impermeable membrane. If the membrane carries adsorption sites which exchange particles with Σ_a, the following argument will remain unchanged. The background of Σ_a (Σ_b) has a charge $-N_B^a e$ ($-N_B^b e$). Since only globally neutral systems contribute to the thermodynamic limit,$^{(13)}$ we will at once deal with systems $\Sigma(n)$ where the number of mobile particles in Σ_a (Σ_b) is $N_B^a + n$ ($N_B^b - n$). Then the grand canonical partition function of the system where the fugacity of the particles in Σ_i is z_i $(i = a, b)$ reduces to

$$\Xi_{\text{imp}}(z_a, z_b) = z_a^{N_B^a} z_b^{N_B^b} \sum_{n=-N_B^a}^{N_B^b} (z_a/z_b)^n \, Q_{\text{imp}}(n) \tag{4.1}$$

where $Q_{\text{imp}}(n)$ is the canonical partition function of $\Sigma(n)$. I now introduce $\chi_i(\mathbf{r})$, the characteristic function of the region occupied by Σ_i. Since the Hamiltonian $H(\Sigma)$ of the system is invariant under the permutations of the mobile particles, one readily shows that

$$\begin{aligned}
&\Xi_{\text{imp}}(z_a, z_b) \\
&\quad = \frac{1}{(N_B^a + N_B^b)!} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \prod_i \left[z_a \chi_a(\mathbf{r}_i) + z_b \chi_b(\mathbf{r}_i) \right] \exp[-\beta H(\Sigma)] \\
&\quad = Q_{\text{perm}}(V_a, V_b)
\end{aligned} \tag{4.2}$$

where $Q_{\text{perm}}(V_a, V_b)$ is the canonical partition function of the system when the membrane is permeable and the particles are submitted to an external potential $eV_i = -(\beta e)^{-1} \ln z_i$ in the area occupied by Σ_i. Therefore, in the thermodynamic limit, if we denote

$$\tilde{Q}_{\text{perm}} = Q_{\text{perm}} / (z_a^{N_B^a} z_b^{N_B^b})$$

then

$$\ln[\tilde{Q}_{\text{perm}}(z_a/z_b)] = n^* \ln(z_a/z_b) + \ln Q_{\text{imp}}(n^*) \tag{4.3}$$

where n^* is a function of (z_a/z_b) such that

$$\left. \frac{\partial}{\partial n^*} [\ln(\tilde{Q}_{\text{perm}})] \right|_{z_a/z_b} = 0 \tag{4.4}$$

4.2. The Lippmann Equation

Let F be the free energy of the system with an interface. Let $F_a (F_b)$ be the free energy of region a (b) bounded by an uncharged hard wall without any external potential. Define the surface free energy density f as $f = (F - F_a - F_b)/A$, where A is the "area" of the interface. According to (4.3) and (4.4), the surface free energy densities f_{perm} and f_{imp} are Legendre transforms of each other with respect to σ, the other control parameters being kept constant,

$$f_{\text{perm}}\left(\frac{z_a}{z_b}\right) = f_{\text{imp}}(\sigma_a) - \sigma_a \left. \frac{\partial f_{\text{imp}}}{\partial \sigma_a} \right|_{z_a/z_b, \rho_a, \rho_b} = \gamma_{\text{imp}} \tag{4.5}$$

with

$$\left.\frac{\partial f_{\text{imp}}}{\partial \sigma_a}\right|_{z_a/z_b,\rho_a,\rho_b} = \beta^{-1} \ln \frac{z_a}{z_b} \tag{4.6}$$

where $\sigma_a e$ is the polarization surface charge density in region a and γ_{imp} is the surface tension of the impermeable membrane.

Moreover, the equilibrium criterion for the electrochemical potential is satisfied in the case of the permeable membrane with an external potential step (this will be verified on the exact model in Section 4.3):

$$\beta^{-1} \ln(z_a/z_b) = -e^2(V_a - V_b) = \mu_a - \mu_b + e(\phi_a - \phi_b) \tag{4.7}$$

where $\mu_i(\beta, \rho_i)$ is the chemical potential of a particle in the bulk with density ρ_i, and ϕ_i is the electrical potential in the bulk in region i. This macroscopic equality is satisfied whether there are adsorption sites or not because these create only a short-range potential.

Consequently, according to (4.6) and (4.7), σ_a and $\mu_a - \mu_b + e(\phi_a - \phi_b)$ are conjugate variables for the Legendre transformation, so that, according to (4.5),

$$\left.\frac{\partial \gamma_{\text{imp}}}{\partial \Delta\phi}\right|_{\rho_a,\rho_b} = -e\sigma_a \tag{4.8}$$

The Lippmann equation is valid for the impermeable membrane as for the charged hard wall and it is not altered by the presence of the adsorption sites.

4.3. Density Profile and Potential Drop

In this section we consider a permeable membrane located at $x = 0$ which separates two OCPs of background densities ρ_a for $x > 0$ and ρ_b for $x < 0$. The extra external potential is eV_a for $x > 0$ and eV_b for $x < 0$. The related fugacities are $z_a = \exp(-\beta e^2 V_a) = \exp(-2V_a)$ and $z_b = \exp(-2V_b)$. Then

$$\exp[-2V_0(x)] = \theta(-x)\, z_b \exp(-2\pi\rho_b x^2) + \theta(x)\, z_a \exp(-2\pi\rho_a x^2) \tag{4.9}$$

The adsorption sites exchange mobile particles with the fluid in the half-space $x \geqslant 0$, so that $\mu = (\lambda/\omega) \exp(-2V_a)$.

(a) *When there is no adsorption site* we straightaway retrieve from (2.7) the following formulas[5] (with $i = a$ if $x > 0$ and $i = b$ if $x < 0$),

$$\rho_i^{(0)}(x) = z_i \exp(-2\pi\rho_i x^2) \int_{-\infty}^{+\infty} \frac{dk}{2\pi}\, g_M(k) \exp(2kx) \tag{4.10}$$

where the index M refers to the impermeable menbrane and

$$g_M(k)=\frac{1}{h_a(k)+h_b(k)} \tag{4.11}$$

with

$$h_a(k)=\int_0^{+\infty} dx \exp[-2V_0(x)+2kx]$$

$$h_b(k)=\int_{-\infty}^0 dx \exp[-2V_0(x)+2kx]$$

As a matter of fact, $\rho_i^{(0)}(x)$ only depends on ρ_a, ρ_b, and $z_a/z_b=\exp[-\beta e^2(V_a-V_b)]$. The global neutrality of the double layer, which is an ingredient of the formalism developed to tackle with the impermeable membrane, is easily verified: the surface polarization charge density $e\sigma_a=e\int_0^{+\infty}[\rho_a^{(0)}(x)-\rho_a]\,dx$ is opposite to $e\sigma_b=e\int_{-\infty}^0[\rho_b^{(0)}(x)-\rho_b]\,dx$.

We now turn to the potential drop $\Delta\phi=\phi_a(+\infty)-\phi_b(-\infty)$ across the interface in order to interpret $e(V_a-V_b)$. As in Section 3.3, $\Delta\phi$ is calculated by using a convergence factor with the result that $z_a/z_b=(\rho_a/\rho_b)^{1/2}\exp(\beta e\Delta\phi)$ at $\beta e^2=2$.[5] Since, according to a scaling argument, the chemical potential $\mu_i(\beta, \rho_i)$ satisfies

$$\mu_a(\rho_a, \beta)-\mu_b(\rho_b, \beta)=\beta^{-1}[1-(\beta e^2/4)]\ln(\rho_a/\rho_b)$$

we get

$$-e^2(V_a-V_b)=\mu_a-\mu_b+e(\phi_a-\phi_b) \tag{4.12}$$

Thus, $-e^2(V_a-V_b)$ proves to be the difference between the electrochemical potentials on each side, and Eq. (4.12) is interpreted as an equilibrium relation for the permeable membrane with an external potential step equal to $e(V_a-V_b)$: at equilibrium, the total free energy is minimum and the work needed to make a particle cross the permeable membrane from side b to side a, $-e^2(V_a-V_b)$, is compensated by the variation of free energy when a particle is taken out of region a, $-\mu_a$, carried across the inner potential drop $\phi_b-\phi_a$, $e(\phi_b-\phi_a)$, and finally is embedded into region b, $+\mu_b$. Moreover, if $V_a=V_b$ ($z_a/z_b=1$), the density is continuous on the interface, $\rho_a^{(0)}(x=0)=\rho_b^{(0)}(x=0)$, while, from a macroscopic point of view, the electrochemical potential $\mu_i(\rho_i)+e\phi_i$ also becomes continuous (which actually is the equilibrium criterion for a permeable membrane) and the free energy densities f_{imp} and f_{perm} coincide: as expected, by letting V_a-V_b vanish, one recovers the case where the mobile particles are free to cross the interface.

Since the potential drop $\Delta\phi$ differs from $-e(V_a-V_b)$ by a known constant at $\beta e^2=2$, it does appear as the control parameter of the model and the density can be written as

$$\rho_a^{(0)}(x) = \sqrt{\rho_a}\exp(-2\pi\rho_a x^2) \times \int_{-\infty}^{+\infty} \frac{dk}{2\pi} \frac{\exp(2kx)}{\exp(-\beta e\Delta\phi)\, H_b(-k) + H_a(k)}$$

$$\rho_b^{(0)}(x) = \sqrt{\rho_b}\exp(-\beta e\Delta\phi)\exp(-2\pi\rho_b x^2) \times \int_{-\infty}^{+\infty} \frac{dk}{2\pi} \frac{\exp(2kx)}{\exp(-\beta e\Delta\phi)\, H_b(-k) + H_a(k)} \tag{4.13}$$

with

$$H_i(k) = \left(\frac{1}{2\pi}\right)^{1/2} \frac{\sqrt{\pi}}{2}\left[1 + \operatorname{erf}\left(\frac{k}{(2\pi\rho_i)^{1/2}}\right)\right]\exp\left(\frac{k^2}{2\pi\rho_i}\right) \tag{4.14}$$

[I have used that $\operatorname{erf}(-u) = -\operatorname{erf}(u)$ in order to define $h_a(k) = (z_a/\sqrt{\rho_a})\, H_a(k)$ and $h_b(k) = (z_b/\sqrt{\rho_b})\, H_b(-k)$.]

(b) *In the presence of adsorption sites*, the potential drop is given by the general formula (2.19). Since in the case of the membrane $G_M(\zeta) = \sum_{n \in \mathbb{Z}} g_M(\zeta + n)$, $G_M(\zeta)$ is a periodic function of ζ with a period equal to 1 and

$$\Delta\phi_M = \Delta\phi_M^{(0)} \equiv \Delta\phi \tag{4.15}$$

so that the equilibrium criterion (4.12) is still satisfied. The existence of the adsorption sites does not modify the potential drop across the impermeable surface in the same way as it does not change the polarization charge in the case of the charged hard wall. This is not surprising, since $\Delta\phi$ is the control parameter in the formalism which deals with the impermeable membrane.

Then we write the projector in terms of $\Delta\phi$. For that purpose let us introduce $\tilde{g}_M$ defined in terms of g_M [see (2.8)] by $\mu g_M(\zeta) = \lambda\rho_a \tilde{g}_M(\zeta)$ [with $\mu = (\lambda/\omega)\exp(-2V_a)$]. Then

$$\tilde{g}_M(\zeta) = [\tilde{h}_{\tau_a}(\zeta) + (\rho_a/\rho_b)^{1/2}\exp(-\beta e\Delta\phi)\,\tilde{h}_{\tau_b}(-\zeta)]^{-1} \tag{4.16}$$

where $\tilde{h}_{\tau_i}$ is defined in (3.1) with $\tau_i = (2\pi/\rho_i\omega^2)^{1/2}$. Then, according to (2.13) and (2.14),

$$\langle \mathbf{r}_1 | P_M^* | \mathbf{r}_2 \rangle = \begin{cases} \rho_a \exp[-\pi\rho_a(x_1^2 + x_2^2)]\, D(\mathbf{r}_1, \mathbf{r}_2) \\ \qquad \text{if} \quad x_1 > 0, x_2 > 0 \\ \rho_b \exp(-\beta e\Delta\phi)\exp[-\pi\rho_b(x_1^2 + x_2^2)]\, D(\mathbf{r}_1, \mathbf{r}_2) \\ \qquad \text{if} \quad x_1 < 0, x_2 < 0 \\ (\rho_a/\rho_b)^{1/4}\,[\rho_a\rho_b\exp(-\beta e\Delta\phi)]^{1/2} \\ \times \exp(-\pi\rho_a x_1^2 - \pi\rho_b x_2^2)\, D(\mathbf{r}_1, \mathbf{r}_2) \\ \qquad \text{if} \quad x_1 > 0, x_2 < 0 \end{cases} \tag{4.17}$$

with

$$D(\mathbf{r}_1, \mathbf{r}_2) = \int_0^1 d\zeta \sum_{n=-\infty}^{+\infty} \tilde{g}_M(\zeta+n) \exp\left[\frac{2\pi(\zeta+n)\, z_1}{\omega}\right] \sum_{m=-\infty}^{+\infty} \left[\frac{2\pi(\zeta+m)\, \bar{z}_2}{\omega}\right]$$
$$\times \left\{\delta_{n,m} - \frac{\lambda\rho_a}{1+\lambda\rho_a \tilde{G}_M(\zeta)}\, \tilde{g}_M(\zeta+m)\right\}$$

Similarly, the density of the nonadsorbed particles is given by

$$\rho_M^*(\mathbf{r}) = \begin{cases} \rho_a \exp(-2\pi\rho_a x^2)\, D(\mathbf{r}) & \text{if} \quad x > 0 \\ \rho_b \exp(-\beta e \Delta\phi) \exp(-2\pi\rho_b x^2)\, D(\mathbf{r}) & \text{if} \quad x < 0 \end{cases} \tag{4.18}$$

where

$$D(\mathbf{r}) = D^{(0)}(x) - \int_0^1 d\zeta \frac{\lambda\rho_a}{1+\lambda\rho_a \tilde{G}_M(\zeta)}$$
$$\times \exp\left(\frac{4\pi\zeta x}{\omega}\right) \left| \sum_{n=-\infty}^{+\infty} \tilde{g}_M(\zeta+n) \exp\left(\frac{2\pi n z}{\omega}\right)\right|^2$$

with

$$D^{(0)}(x) = \int_0^1 d\zeta \sum_{n=-\infty}^{+\infty} \tilde{g}_M(\zeta+n) \exp[4\pi(\zeta+n)\, x/\omega]$$

As for the polarization charge density $e\sigma_a$ in the half-space $x \geqslant 0$, in the case of the membrane,

$$\int_0^{+\infty} dx \exp[-2V_0(x)] \exp[4\pi(\zeta+n)\, x/\omega] = h_a(2\pi(\zeta+n)/\omega)$$

is different from $[g_M(\zeta+n)]^{-1}$ so that, according to (2.16)–(2.18), $-n_{\mathrm{ad}}/\omega$ is now different from $\int_0^{+\infty} dx[\int_0^{\omega} dy\, \delta\rho(\mathbf{r})/\omega]$ and $\sigma_a \neq \sigma_a^{(0)}$. (This is analogous to the fact that $\Delta\phi \neq \Delta\phi^{(0)}$ for the charged hard wall.) However, the interface is globally neutral: the polarization charge density $e\sigma_b$ in the half-space $x < 0$,

$$\sigma_b = \sigma_b^{(0)} + \int_{-\infty}^{0} dx \left[\int_0^{\omega} dy\, \delta\rho(x, y)/\omega\right]$$

satisfies $\sigma_b = -\sigma_a$, since, using (2.18) and

$$\int_{-\infty}^{0} dx \exp[-2V_0(x)] \exp[4\pi(\zeta+n)\, x/\omega] = h_b(2\pi(\zeta+n)/\omega)$$

we obtain $\sigma_a + \sigma_b = \sigma_a^{(0)} + \sigma_b^{(0)} = 0$. Moreover, by using (4.16), we notice that

$$\sum_n [\mu g_M(\zeta + n)]^2\, h_b(\zeta + n)/\mu = \partial[\mu G_M(\zeta)]/\partial(\beta e \Delta\phi)\,|_\omega$$

and we find

$$\sigma_a - \sigma_a^{(0)} = -[\sigma_b - \sigma_b^{(0)}] = \frac{\partial}{\partial(\beta e \Delta\phi)} \left\{ \frac{1}{\omega} \int_0^1 d\zeta \ln[1 + \lambda \rho_a \tilde{G}(\zeta)] \right\} \Bigg|_\lambda \tag{4.19}$$

Actually, this equality can be deduced from the general formalism of the impermeable membrane, as will be shown in Section 4.5.

4.4. Contact Theorem

In the absence of the adsorption sites, the calculations for $\Delta\phi$ which lead to (4.12) also imply that

$$\begin{aligned} p_{\text{th}}^a - p_{\text{th}}^b = {} & \beta^{-1}[\rho_a^{(0)}(x=0) - \rho_b^{(0)}(x=0)] \\ & - e\{\rho_a[\phi^{(0)}(+\infty) - \phi^{(0)}(0)] - \rho_b[\phi^{(0)}(-\infty) - \phi^{(0)}(0)]\} \end{aligned} \tag{4.20}$$

The step of thermodynamic pressure at the interface is equal to the step of kinetic pressure plus an electrostatic contribution from the background.$^{(5)}$

In the presence of the adsorption sites, we show, as in Section 3.3, that, if we write $\delta\phi = \phi_M - \phi^{(0)}$,

$$\begin{aligned} & \beta e \rho_a[\delta\phi(+\infty) - \delta\phi(0)] \\ & \quad = -\int_0^1 \frac{d\zeta}{\omega} \frac{\mu}{1 + \mu G_M(\zeta)} \sum_n [g_M(\zeta + n)]^2 \left[z_a + \frac{4\pi}{\omega} (\zeta + n)\, h_a(\zeta + n) \right] \\ & \beta e \rho_b[\delta\phi(0) - \delta\phi(-\infty)] \\ & \quad = -\int_0^1 \frac{d\zeta}{\omega} \frac{\mu}{1 + \mu G_M(\zeta)} \sum_n [g_M(\zeta + n)]^2 \left[-z_b + \frac{4\pi}{\omega} (\zeta + n)\, h_b(\zeta + n) \right] \end{aligned}$$

Since $h_a(\zeta + n) + h_b(\zeta + n) = [g_M(\zeta + n)]^{-1}$, we get a result similar to (3.11),

$$\begin{aligned} & \beta e\{\rho_a[\delta\phi(+\infty) - \delta\phi(0)] + \rho_b[\delta\phi(0) - \delta\phi(-\infty)]\} \\ & \quad = \frac{1}{\omega} \int_0^\omega dy\, [\rho_a^*(0, y) - \rho_a^{(0)}(0)] \\ & \qquad - \frac{1}{\omega} \int_0^\omega dy\, [\rho_b^*(0, y) - \rho_b^{(0)}(0)] - \frac{\lambda}{\omega} \frac{\partial \rho_a^*}{\partial x}(x, 0) \Bigg|_{x=0} \end{aligned} \tag{4.21}$$

so that the contact theorem now reads

$$p^a_{\text{th}} - p^b_{\text{th}} = \beta^{-1}\left\{\frac{1}{\omega}\int_0^{\omega} dy\, \rho_a^*(0, y) - \frac{1}{\omega}\int_0^{\omega} dy\, \rho_b^*(0, y) - \frac{\lambda}{\omega}\frac{\partial \rho_a^*}{\partial x}(x, 0)\bigg|_{x=0}\right\}$$
$$- e\{\rho_a[\phi(+\infty) - \phi(0)] - \rho_b[\phi(-\infty) - \phi(0)]\} \tag{4.22}$$

Thus, the contact theorem is altered by the presence of adsorption sites in the same way for the impermeable membrane as for the charged hard wall.

4.5. Surface Free Energy

(a) First we recall the expression for the surface free energy density in the absence of adsorption sites derived by Rosinberg and Blum,[5] who started with a *finite* system. With our notations [see (4.14)],

$$-\beta f^{(0)}_{\text{imp}} = \int_{-\infty}^{0} \frac{dk}{2\pi} \ln\left[1 + \frac{H_a(k)}{\exp(-\beta e \Delta\phi)\, H_b(-k)}\right]$$
$$+ \int_0^{+\infty} \frac{dk}{2\pi} \ln\left[1 + \frac{\exp(-\beta e \Delta\phi)\, H_b(-k)}{H_a(k)}\right] \tag{4.23}$$

This formula is not surprising, since, according to (2.2) and Section 2.2, the surface density $f^{(0)}_{\text{perm}}$ involves the difference between

$$\int_{-\infty}^{+\infty} dk \ln\left\{\int_{-\infty}^{+\infty} dx \exp[-2V_0(x) + 2kx]\right\} = \int_{-\infty}^{+\infty} dk \ln[h_a(k) + h_b(k)]$$

and the contribution $\int_0^{+\infty} dk \ln[h_a(k)] + \int_{-\infty}^{0} dk \ln[h_b(k)]$ from the reference states defined in Section 4.2.

(b) Second, we formally study the excess surface free energy due to the presence of the adsorption sites. When there are adsorption sites, the surface free energy density f can be viewed as the sum of two contributions: $f_{\text{imp}} = f^{(0)}_{\text{imp}} + \Delta f_{\text{imp}}$, with Δf_{imp} defined at constant potential drop:

$$\beta \Delta f_{\text{imp}} = -\ln[Q_{\text{imp}}(n, \lambda)/Q^{(0)}_{\text{imp}}(n^{(0)})]/A$$

where $Q_{\text{imp}}(n, \lambda)$ is the canonical partition function of the impermeable membrane in the presence of the adsorption sites when there is a total excess charge ne in the region $x > 0$, and $Q^{(0)}_{\text{imp}}(n^{(0)})$ is the canonical partition function in the absence of the adsorption sites when the excess charge is $n^{(0)}e$; n and $n^{(0)}$ are functions of the same $\Delta\phi$, i.e., of the same z_a/z_b. We define $\Delta f_{\text{perm}}(z_a/z_b, \lambda)$ in the same way as Δf_{imp} by

$$\beta \Delta f_{\text{perm}} = -\ln[\tilde{Q}_{\text{perm}}(z_a/z_b, \lambda)/\tilde{Q}^{(0)}_{\text{perm}}(z_a/z_b)]/A$$

Since the argument which leads to (4.3) is still valid in the presence of the adsorption sites, we can use it for Q_{imp} and $Q_{\text{imp}}^{(0)}$ and we find, as in Section 4.2, that the variation of the surface tension of the impermeable membrane due to the presence of the adsorption sites is

$$\Delta\gamma_{\text{imp}} = \Delta f_{\text{perm}}(\Delta\phi, \lambda) = \Delta f_{\text{imp}}(\Delta\phi, \lambda) - (\sigma_a - \sigma_a^{(0)})(\mu_a - \mu_b + e\Delta\phi) \tag{4.24}$$

with the Lippmann equation

$$e(\sigma_a - \sigma_a^{(0)}) = -\frac{\partial}{\partial(\Delta\phi)}(\Delta f_{\text{perm}})\Big|_{\lambda} \tag{4.25}$$

Moreover, according to the study by Rosinberg *et al.*,(1) the occupation mean number of an adsorption site is

$$\begin{aligned} n_{\text{ad}} &= \omega\beta(\partial\Delta f_{\text{imp}}/\partial \ln \lambda)|_n \\ &= \omega\beta(\partial f_{\text{imp}}(n, \lambda)/\partial \ln \lambda)|_n \end{aligned}$$

and, since $f_{\text{imp}}(n, \lambda)$ and $f_{\text{perm}}(\Delta\phi, \lambda)$ are Legendre transforms of each other with respect to the conjugate variables n and $\mu + e\Delta\phi$, we get

$$\frac{n_{\text{ad}}}{\omega} = -\frac{\partial}{\partial \ln \lambda}[\beta\Delta f_{\text{perm}}(\Delta\phi, \lambda)|_{\Delta\phi} \tag{4.26}$$

Thus, the change in the nonadsorbed excess charge density is

$$e\left[\sigma_a - \sigma_a^{(0)} - \frac{n_{\text{ad}}}{\omega}\right] = -\frac{\partial}{\partial\Delta\phi}(\Delta f_{\text{perm}})\Big|_{\lambda} + \lambda\beta e\frac{\partial}{\partial\lambda}(\Delta f_{\text{perm}})\Big|_{\Delta\phi} \tag{4.27}$$

Now we come back to our model at $\beta e^2 = 2$. The general formula (2.20) was derived when keeping the control parameters of the model, but λ, constant, and Δf vanishes when λ goes to zero. Thus, we get the identification

$$-\beta\Delta f_{\text{perm}}\left(\frac{z_a}{z_b}, \lambda\right) = \frac{1}{\omega}\int_0^1 d\zeta \ln[1 + \lambda\rho_a\tilde{G}_M(\zeta)] \tag{4.28}$$

and using (4.25), we recover (4.19). The occupation mean number is [see (4.26) and (4.28)]

$$n_{\text{ad}} = \int_0^1 d\zeta \frac{\lambda\rho_a\tilde{G}_M(\zeta)}{1 + \lambda\rho_a\tilde{G}_M(\zeta)} \tag{4.29}$$

as was expected from (2.16) and from the equivalence between the canonical partition function Q_{imp} and the grand canonical partition function $\Xi_{\text{imp}} = Q_{\text{perm}}$ for the calculation of the density and correlation functions. In the same way, according to (2.21), the correlation function between the adsorbed particles is

$$n_M^{(2)T}(m_1, m_2) = -\left| \int_0^1 d\zeta \exp[i2\pi\zeta(m_1 - m_2)] \frac{\lambda\rho_a \tilde{G}_M(\zeta)}{1 + \lambda\rho_a \tilde{G}_M(\zeta)} \right|^2 \tag{4.30}$$

Since $\tilde{G}_M(\zeta) = \sum_{n=-\infty}^{+\infty} \tilde{g}_M(\zeta + n)$ and all its derivatives are periodic functions of ζ with a period equal to 1, $n_M^{(2)T}(m_1, m_2)$ decreases faster than any power of $(m_1 - m_2)^{-1}$ when $m_1 - m_2$ goes to infinity, as expected near the boundary between two plasmas.(15)

Finally we get

$$f_{\text{imp}} = f_{\text{imp}}^{(0)} - \frac{1}{\beta\omega} \int_0^1 d\zeta \ln[1 + \lambda\rho_a \tilde{G}_M(\zeta)] + (\sigma_a - \sigma_a^{(0)})(\mu_a - \mu_b + e\Delta\phi) \tag{4.31}$$

with $\sigma_a - \sigma_a^{(0)}$ given by (4.19).

5. CONCLUSION

A salient feature of this paper is the description of an impermeable membrane by means of a permeable one with an external potential step on the surface; this description is very convenient for the statistical mechanics approach. Moreover, the two-dimensional OCP at $\Gamma = 2$ in an inhomogeneous background which varies in only one direction is exactly solvable. Thus, one has at hand a solvable model for an ideally polarizable electrode, a model which, according to Rosinberg and Blum's survey,(5) accounts for the main features of experimental curves.

Using a new method, I have exactly solved this two-dimensional model at $\Gamma = 2$ when there are adsorption sites on the interface. I have checked that the screening effect, which is the fundamental property of Coulombic fluids, is unaffected by the presence of the adsorption sites.

For the first time, using the present model, the modified contact theorem suggested by Blum *et al.*(12) has been verified: the kinetic pressure on the interface is increased by a contribution from the gradient of the mobile charge density at an adsorption site.

Finally, I have shown quite generally that the Lippmann equation is valid for the impermeable membrane whether there are adsorption sites or not: it is derived from the Euler–Lagrange relation which connects the descriptions of the permeable membrane and the impermeable one, and from the equilibrium criterion for the electrochemical potential.

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