



Field theory for ionic systems. From fluctuations and structure at a hard wall to thermodynamics

Dung Di Caprio, J. Stafiej, J.P. Badiali

► To cite this version:

Dung Di Caprio, J. Stafiej, J.P. Badiali. Field theory for ionic systems. From fluctuations and structure at a hard wall to thermodynamics. *Electrochimica Acta*, 2003, 48 (20-22), pp.2967-2974. 10.1016/S0013-4686(03)00362-1 . hal-02354770

HAL Id: hal-02354770

<https://hal.science/hal-02354770v1>

Submitted on 20 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

Field theory for ionic systems. From fluctuations and structure at a hard wall to thermodynamics.

D. di Caprio ^{a,*} J. Stafiej ^b J.P. Badiali ^a

^a*Laboratoire d'Électrochimie et Chimie Analytique, UMR 7575, Université P. et M. Curie, Paris VI, Bât. F74, B.P. 39, 4, Place Jussieu, 75230 Paris Cedex 05, France*

^b*Department of Electrode Processes, Institute of Physical Chemistry of the Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland*

Abstract

We use a field theoretical approach to study ionic systems. In this paper we illustrate this formalism in a grand canonical ensemble for the long range Coulomb potential. For the inhomogeneous system near a hard neutral plane wall we go beyond the well known Debye - Hückel electrolyte results. The results are compared with well established sum rules for ionic systems and thermodynamic relations are verified. We also calculate the differential capacitance in a slab using the linear response theory. The capacitance is calculated from the charge – charge correlations for the neutral system using the fluctuation – dissipation theorem.

Key words: Statistical field theory, double layer, interfacial structure, surface tension, capacitance

1 Introduction

In a recent series of papers a considerable effort has been devoted to describe physicochemical systems with Coulombic interactions using alternative approaches to the classic statistical mechanics or density functional theories. These approaches are based on a field theoretical formalism [1,2]. The motivations for this interest are varied. In the case of systems with Coulomb potential there is a conviction that a field theoretical formalism is better suited to describe the effect of the long range Coulomb interaction. The other aspect is that in these approaches the fluctuations are treated in a different way. Some recent works [3–6] have shown that these fluctuations can be very important as they can lead to peculiar effects for instance the existence of charge induced attraction between likely charged objects.

The field theory presented here is simpler than the approaches [2] based on the Sine Gordon transformation which introduces an imaginary fluctuating field. As discussed by Fisher [7] the fluctuating imaginary field has no tangible physical meaning and it is difficult to develop intuitions about approximations based on the expansion of the Hamiltonian with respect to this field. In contrast we use fields which have a physical meaning and in the macroscopic limit they represent directly the ionic distributions coupled with the usual Coulomb potential.

In this paper we show that the field theoretical framework with a Hamiltonian based on ionic density fields provides a viable description of the system. Frusawa and Hayakawa [8] give a justification for such a treatment.

There is a set of basic relations characteristic for the field theoretical formalism which we show to acquire a new meaning when applied to the description of classical fluids. These relations appear to be similar to the well known relations in liquid state theory, like for instance the YBG equations [9] although as we will see the formulation is different.

Second, we show that the theory emphasizes different aspects in the physics of the system compared to other approaches such as the usual statistical me-

* Corresponding author

Email address: dicaprio@ccr.jussieu.fr (D. di Caprio).

chanics or density functional theories [10]. The resulting approximations and interpretations can lead to new insights into the physics of the system.

In the simple case of the neutral hard plane wall we show that the behavior of the charge fluctuations and their effect are non trivial. This is illustrated on the inhomogeneous charge – charge correlation functions at the level of the quadratic approximation. In the linear response theory we calculate the differential capacitance at the point of zero charge knowing the structure of the neutral system. We also go beyond the Debye approximation. Then as an effect of the fluctuations we have a desorption profile.

Another aim of this paper is to show that our approach is consistent with certain sum rules, thermodynamics and limiting laws. For instance the density profile is in agreement with the contact theorem [11] and the Gibbs adsorption isotherm. Differential capacitance at the point of zero charge is equal to the Gouy – Chapman value for small charges.

We use the grand canonical ensemble throughout the paper. In section 2 we present the field theoretical framework for ionic systems. In section 3 we apply the theory to the case of a slab geometry. We calculate the pressure as well as the inhomogeneous charge – charge correlation function. In the next section, we discuss on a few examples the effect of these fluctuations. Going beyond the Debye approximation, we calculate a desorption profile directly related to the charge fluctuations. The surface tension is obtained using the Gibbs adsorption isotherm. From the interfacial structure of the neutral system we calculate the differential capacitance. Finally we summarize the results in the conclusion.

2 Field theory

2.1 The Field theoretical framework

The theory is based on a Hamiltonian which is a functional of the density fields $\rho_{i=\pm}(\mathbf{r})$ for anions and cations. Integrating over all possible density distributions we obtain the partition function of the system

$$\Xi = \mathcal{N} \int \prod_i \mathcal{D}\rho_i(\mathbf{r}) e^{-\beta H[\rho_i(\mathbf{r})] + \beta \mu_i \int \rho_i(\mathbf{r}) d\mathbf{r}_i} \quad (1)$$

where $\mathcal{N}$ is a normalization constant. Our formalism corresponds to the *grand canonical ensemble*, where μ_i are the chemical potentials of the ions and for symmetric ions we assume $\mu_+ = \mu_- = \mu$. An equivalent representation is in terms of charge density and overall ionic density : $q(\mathbf{r}) = \rho_+(\mathbf{r}) - \rho_-(\mathbf{r})$ and $s(\mathbf{r}) = \rho_+(\mathbf{r}) + \rho_-(\mathbf{r})$. The Hamiltonian is a functional of the fields :

$$\beta H[q(\mathbf{r}), s(\mathbf{r})] = \beta H^e[q(\mathbf{r}), s(\mathbf{r})] + \beta H^c[q(\mathbf{r})] \quad (2)$$

where the Coulomb contribution is given by

$$\beta H^c[q(\mathbf{r})] = \frac{1}{4\pi\epsilon} \int \frac{q(\mathbf{r})q(\mathbf{r}')}{\tilde{r}} d\mathbf{r}d\mathbf{r}' \quad (3)$$

where $\tilde{r} = |\mathbf{r} - \mathbf{r}'|$ and $\beta = 1/(k_B T)$ is the reciprocal temperature. $H^e[\rho_+(\mathbf{r}), \rho_-(\mathbf{r})]$ is the ideal entropy contribution functional used in [8,12]

$$\beta H^e[\rho_+(\mathbf{r}), \rho_-(\mathbf{r})] = \int \sum_{i=\pm} \rho_i(\mathbf{r}) \left[\ln \frac{\rho_i(\mathbf{r})}{\rho_{ref}} - 1 \right] d\mathbf{r} \quad (4)$$

which can be expressed alternatively in terms of q and s fields and ρ_{ref} is an unspecified reference density. The grand potential is defined as

$$\Omega \equiv -k_B T \ln \Xi$$

and we assume it corresponds to the thermodynamic definition $\gamma A - pV$ where p is the pressure, γ the surface tension A the area and V the volume of the system.

2.2 A new toolbox

Within the field theoretical framework we can find some general and useful equations. The first example is a relation similar to the equation of motion [13] obtained by requirement that Ξ be invariant under a shift of the dummy field integration variables : $\rho_i(\mathbf{r})$. The equation reads

$$\beta \left\langle \frac{\delta H}{\delta \rho_i(\mathbf{r})} \right\rangle - \beta \mu_i = 0 \quad (5)$$

$$\left\langle \ln \rho_i(\mathbf{r}) \right\rangle + \sum_j \int \beta V_{ij}(\mathbf{r}, \mathbf{r}') \left\langle \rho_j(\mathbf{r}') \right\rangle d\mathbf{r}' - \beta \mu_i = 0 \quad (6)$$

where $V_{ij}(\mathbf{r}, \mathbf{r}')$ is the potential coupling the fields $\rho_i(\mathbf{r})$ to $\rho_j(\mathbf{r}')$, and the average of any quantity A is defined

$$\langle A \rangle = \frac{\int \prod_i \mathcal{D}\rho_i(\mathbf{r}) A e^{-\beta H[\rho_i(\mathbf{r})] + \beta \mu \int \rho_i(\mathbf{r}) d\mathbf{r}_i}}{\int \prod_i \mathcal{D}\rho_i(\mathbf{r}) e^{-\beta H[\rho_i(\mathbf{r})] + \beta \mu \int \rho_i(\mathbf{r}) d\mathbf{r}_i}} \quad (7)$$

Equations (5) or (6) are exact relations different from the saddle point equations of the mean field theories [14]. They are also different from the density theory formalism [10], as H does not represent the free energy of the system. The Hamiltonian enters into the above equation through its average.

Deriving this equation with respect to $\mathbf{r}$ we obtain what can be seen as the equivalent of the YBG [9] equation for the field theory.

$$\frac{\nabla_{\mathbf{r}} \langle \rho_i(\mathbf{r}) \rangle}{\langle \rho_i(\mathbf{r}) \rangle} = \beta \nabla_{\mathbf{r}} V_i^{ext}(\mathbf{r}) + \beta \int \nabla_{\mathbf{r}} V_{ij}(\mathbf{r}, \mathbf{r}') \left\langle \rho_j(\mathbf{r}') \right\rangle d\mathbf{r}' \quad (8)$$

where we introduce $V_i^{ext}(\mathbf{r})$ as external fields. The equation is exact and distinct from the YBG equation. It is formally a closed relation in which only the one body distribution is involved and not the beginning of a hierarchy between correlation functions.

In an earlier paper [15] we have shown the analogy between the Ward Takahashi (WT) identities [14] which result from the invariance of the system under a symmetry of the fields and relations found in liquid state theory. In the case of the translational invariance we have shown that relations obtained in [16,17]

and sometimes known as Baxter relations for homonogeneous fluids have the equivalent WT type identities for the field theory.

The field theoretical framework can therefore be constructed around a few fundamental equations similar to well know relations in usual statistical mechanics although their detailed expression is different.

3 The model

The system we want to describe is an ionic solution confined by two hard plane walls of a surface A placed at $z = L_1$ and $z = L_2$ at a separation $L = L_2 - L_1$ from one another as shown in Fig. 1. The thermodynamic limit $A \rightarrow \infty$ is considered from the beginning while for the slab thickness L we take it finite

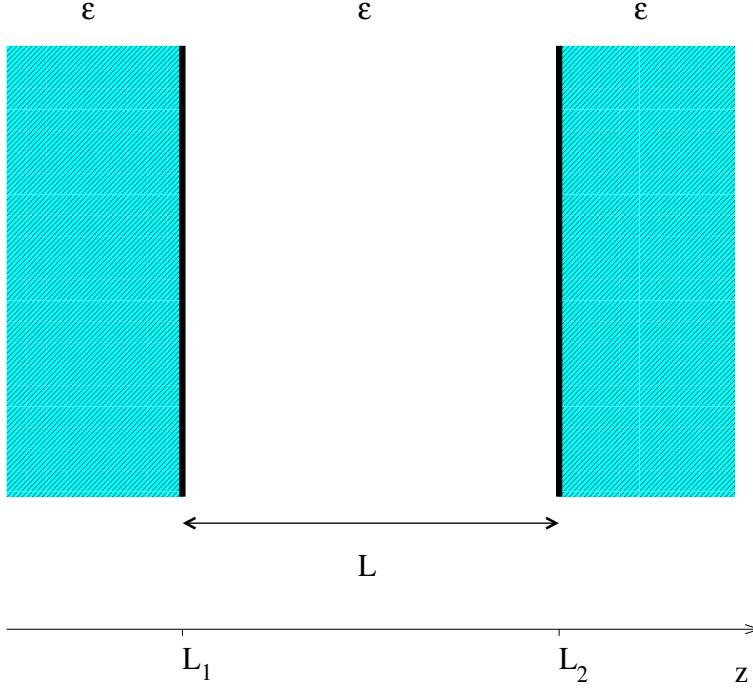


Fig. 1. Schematic representation of the model system.

first and then consider the limit $L \rightarrow \infty$. The dielectric constant is uniform throughout the whole space and it corresponds to the dielectric constant of the pure solvent ϵ .

3.1 The Hamiltonian

For the open system the chemical potentials of ions are fixed and the ionic densities fluctuate around their averages in an *a priori* unconstrained fashion. Hereafter, the Hamiltonian eq.(2) is expanded around the saddle point average values $\bar{q} = 0$ and $s = \bar{\rho}$, which will be specified in the following. The ideal entropy becomes

$$\begin{aligned}
\beta H^e = & \bar{\rho} \left(\ln \left(\frac{\bar{\rho}}{2\rho_{ref}} \right) - 1 \right) V + \int \delta s(\mathbf{r}) \ln \left(\frac{\bar{\rho}}{2\rho_{ref}} \right) d\mathbf{r} \\
& + \frac{1}{2\bar{\rho}} \int [\delta s^2(\mathbf{r}) + q^2(\mathbf{r})] d\mathbf{r} - \frac{1}{6\bar{\rho}^2} \int [\delta s^3(\mathbf{r}) + 3\delta s(\mathbf{r})q^2(\mathbf{r})] d\mathbf{r} \\
& + \frac{1}{12\bar{\rho}^3} \int [\delta s^4(\mathbf{r}) + 6\delta s^2(\mathbf{r})q^2(\mathbf{r}) + q^4(\mathbf{r})] d\mathbf{r} + \dots
\end{aligned} \tag{9}$$

where $\delta s = s - \bar{\rho}$. The Coulomb Hamiltonian is not modified in this expansion. The term related to the chemical potential is

$$\int s(\mathbf{r}) d\mathbf{r} = \bar{\rho} V + \int \delta s(\mathbf{r}) d\mathbf{r} \tag{10}$$

We reorder the terms in the Hamiltonian according to powers of δs . The term independent of δs is

$$\beta H_0 = \bar{\rho} \left(\ln \left[\frac{\bar{\rho}}{\rho_{ref}} \right] - 1 \right) V - \beta \mu \bar{\rho} V \tag{11}$$

The term linear in the fields is

$$\beta H_1 = \int_{L_1 < z_1 < L_2} \left(\ln \left[\frac{\bar{\rho}}{\rho_{ref}} \right] - \beta \mu \right) \delta s(\mathbf{r}_1) d\mathbf{r}_1 \tag{12}$$

Now we choose $\bar{\rho}$ such that the linear term βH_1 vanishes. This provides a relation between μ and $\bar{\rho}$

$$\beta \mu = \ln \left[\frac{\bar{\rho}}{\rho_{ref}} \right] \tag{13}$$

replacing μ in eq.(11), we then have $\beta H_0 = -\bar{\rho} V$.

The Hamiltonian is now

$$\begin{aligned}
\beta H = & -\bar{\rho} V + \beta H^c[q(\mathbf{r})] + \frac{1}{2\bar{\rho}} \int [\delta s^2(\mathbf{r}) + q^2(\mathbf{r})] d\mathbf{r} \\
& - \frac{1}{6\bar{\rho}^2} \int [\delta s^3(\mathbf{r}) + 3\delta s(\mathbf{r})q^2(\mathbf{r})] d\mathbf{r} \\
& + \frac{1}{12\bar{\rho}^3} \int [\delta s^4(\mathbf{r}) + 6\delta s^2(\mathbf{r})q^2(\mathbf{r}) + q^4(\mathbf{r})] d\mathbf{r} + \dots
\end{aligned} \tag{14}$$

We denote by H_2 the quadratic part of the Hamiltonian and treat it as the reference system. Subsequent terms will be treated perturbatively

$$\begin{aligned}\beta\delta H = & -\frac{1}{6\bar{\rho}^2} \int \left[\delta s^3(\mathbf{r}) + 3\delta s(\mathbf{r})q^2(\mathbf{r}) \right] d\mathbf{r} \\ & + \frac{1}{12\bar{\rho}^3} \int \left[\delta s^4(\mathbf{r}) + 6\delta s^2(\mathbf{r})q^2(\mathbf{r}) + q^4(\mathbf{r}) \right] d\mathbf{r}\end{aligned}\quad (15)$$

In the following we consider the quadratic Hamiltonian in which there is no coupling between the two fields $q(\mathbf{r})$ and $s(\mathbf{r})$.

3.2 The quadratic Hamiltonian

3.2.1 Diagonal representation of the quadratic Hamiltonian

The fields are expanded on the basis which is written [18,19]

$$q(\mathbf{r}) = \sum_{\mathbf{K}, \nu > 0} e^{i\mathbf{K}\mathbf{R}} q_\nu \phi_\nu(z), \quad s(\mathbf{r}) = \sum_{\mathbf{K}, \nu > 0} e^{i\mathbf{K}\mathbf{R}} a_\nu \phi_\nu(z) \quad (16)$$

where q_ν and a_ν are the parameters defining the fields and

$$\phi_\nu(z) = \frac{e^{-i\nu(L_2-z)} \mp e^{i\nu(L_1-z)}}{\left[2L \left(1 \mp \frac{\sin(\nu L)}{\nu L}\right)\right]^{1/2}} \quad (17)$$

these functions are eigenfunctions of the electric potential operator and the + and – refer to even and odd functions.

$$V(\mathbf{r}) = \frac{e}{4\pi\epsilon} \int d\mathbf{r}' \frac{q(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (18)$$

$$= \frac{e}{\epsilon} \sum_{\mathbf{K}} e^{i\mathbf{K}\mathbf{R}} \sum_{\nu > 0} \lambda_\nu \tilde{q}_\nu(\mathbf{K}) \phi_\nu(z) \quad (19)$$

where $\lambda_\nu = 1/(K^2 + \nu^2)$ with the eigenvalues $\nu_\pm$ verifying

$$\tan\left(\frac{\nu_+ L}{2}\right) = -\frac{\nu_+}{K} \quad \text{and} \quad \tan\left(\frac{\nu_- L}{2}\right) = \frac{K}{\nu_-} \quad (20)$$

In this basis the quadratic Hamiltonian H_2 reads

$$\beta H_2 = \frac{A}{2\bar{\rho}} \sum_{\mathbf{K}, \nu(\mathbf{K})} \left[a_\nu a_\nu^* + q_\nu q_\nu^* (1 + K_D^2 [\bar{\rho}] \lambda_\nu) \right] \quad (21)$$

where $K_D[\bar{\rho}] = \sqrt{\beta\bar{\rho}e^2/\varepsilon}$ is the inverse Debye length with a ionic density $\bar{\rho}$.

3.2.2 Calculation of the pressure

From the grand potential eq.(5) we can calculate the pressure

$$\beta pV = \bar{\rho}V + \ln \mathcal{N} \int \mathcal{D}q \mathcal{D}s e^{-\beta H_2[q,s]}$$

As we focus on electrostatic effects we calculate the excess pressure relative to the uncharged system.

$$\beta \Delta pV = (\bar{\rho} - \rho_b)V + \ln \frac{\int \mathcal{D}q \mathcal{D}s e^{-\beta H_2[q,s]}}{\int \mathcal{D}q \mathcal{D}s e^{-\beta H_2[q,s]|_{e=0}}} \quad (22)$$

where Δp is the excess pressure of the system referred to the pressure of the corresponding ideal gas. The density of the ideal gas is taken as ρ_b the average density of the interacting gas. This density is different from $\bar{\rho}$ which corresponds only to the density of the saddle point approximation. $H_2[q, s]|_{e=0}$ is the Hamiltonian of the ideal gas, where the Coulomb interaction has been switched off. We then have

$$\beta \Delta pV = (\bar{\rho} - \rho_b)V + \frac{1}{2} \sum_{\mathbf{K}, \nu(\mathbf{K}) > 0} \ln \left[\frac{K^2 + \nu^2}{K^2 + \nu^2 + K_D^2[\bar{\rho}]} \right] \quad (23)$$

The sum in the above equation can be explicitly calculated [18]. In the limit $L \rightarrow \infty$ it becomes.

$$\begin{aligned} \sum_{\nu} \ln \left(\frac{K^2 + \nu^2}{K^2 + \nu^2 + K_D^2} \right) &= -2(\sqrt{K^2 + K_D^2} - K)L \\ &\quad -4 \ln \left(\frac{K + \sqrt{K^2 + K_D^2}}{2K} \right) \end{aligned} \quad (24)$$

The first term corresponds to the bulk contribution and we have

$$\beta \Delta p = \bar{\rho} - \rho_b + \frac{K_D^3[\bar{\rho}]}{12\pi} \quad (25)$$

The ionic density is different from that of the saddle point:

$$\begin{aligned}\rho_b V &\equiv \langle N \rangle \\ &= \frac{\partial \ln \Theta}{\partial \bar{\rho}} \frac{d\bar{\rho}}{d\beta\mu} = \bar{\rho} \frac{\partial \ln \Theta}{\partial \bar{\rho}}\end{aligned}\quad (26)$$

Where we have used the definition of $\bar{\rho}$ given in eq.(13) With the expression of $\ln \Theta$ derived from eq.(25), we have

$$\rho_b = \bar{\rho} + \frac{K_D^3[\bar{\rho}]}{8\pi} \quad (27)$$

Finally the excess pressure is

$$\Delta p = -\frac{k_B T K_D^3[\bar{\rho}]}{24\pi} \quad (28)$$

At the lowest order in the expansion we can replace $\bar{\rho}$ by ρ_b in K_D . The result we obtain for the pressure is the same as in the canonical ensemble [18]. We emphasize that the density ρ_b is not an external parameter of the system but has to be calculated perturbatively at each level of approximation as illustrated by eq.(27).

3.2.3 Charge – charge correlation functions

The interest of the field theoretical approach is to stress the importance of fluctuations and of the resulting structure as given by the correlation function. We calculate the charge – charge correlations in the vicinity of a plane hard wall. The quadratic Hamiltonian is the same as the one used in [18,19] and the results are the same except that the density is replaced by $\bar{\rho}$. The bulk correlation function does not depend on the distance to the walls:

$$\langle q(\mathbf{r})q(\mathbf{r}') \rangle_b = \bar{\rho} \left[\delta(\mathbf{r} - \mathbf{r}') - \frac{K_D^2[\bar{\rho}]}{4\pi} \frac{e^{-K_D[\bar{\rho}]\tilde{r}}}{\tilde{r}} \right] \quad (29)$$

The surface contribution is

$$\begin{aligned}\langle q(\mathbf{r})q(\mathbf{r}') \rangle_s = \sum_{i=1,2} \left[\frac{\bar{\rho} e^{-K_D[\bar{\rho}]\tilde{r}_i^*}}{2\pi} \left(\frac{K_D^2[\bar{\rho}]}{2r_i^*} + \frac{K_D[\bar{\rho}]}{r_i^{*2}} - \frac{K_D^2[\bar{\rho}]\tilde{z}_i^2 - 1}{r_i^{*3}} \right. \right. \\ \left. \left. - 3 \frac{K_D[\bar{\rho}]\tilde{z}_i^2}{r_i^{*4}} - 3 \frac{\tilde{z}_i^2}{r_i^{*5}} \right) \right]\end{aligned}$$

$$+\frac{\bar{\rho}}{2\pi}\int K^2 dK J_0(K\rho)e^{-|\tilde{z}_i|\sqrt{K^2+K_D^2[\bar{\rho}]}}\Big] \quad (30)$$

where $\tilde{z}_1 = z + z' - 2L_1$, $\tilde{z}_2 = z + z' - 2L_2$, $\rho = |\mathbf{R} - \mathbf{R}'|$ and J_0 is a Bessel function [20]. The first contribution is screened over the Debye length and $\tilde{r}_i^*$ is the distance between the point $\mathbf{r}$ and the image $\mathbf{r}^*$ of the second point symmetric with respect to the wall at L_1 and L_2 respectively. It is similar to image contribution with screening however the dielectric constant is uniform across the system and there is no explicit image potential. The charge – charge correlations verify the asymptotic behaviour predicted in [21] and decay as $1/R^3$ parallel to the wall without screening as a consequence of the local dipole moments created by the deformation of the screening cloud in the vicinity of the wall. The coefficient $\bar{\rho}$ can be replaced by ρ_b in eq.(29) when we take into account the standard one loop correction due to the q^4 coupling term in δH [14]. As for the other $\bar{\rho}$'s which appear in $K_D[\bar{\rho}]$ they can be systematically replaced by ρ_b at the lowest order in the expansion. Integrating over $\mathbf{r}'$, we can check that the inhomogeneous correlation function verifies the electroneutrality condition.

4 From fluctuations to thermodynamics.

In this section we will see how the above calculated charge fluctuations give rise to a nontrivial desorption profile and to the electrostatic contribution to the surface tension for the neutral system. We will also calculate the differential capacitance of the system in the linear response theory.

4.1 Desorption density profile.

The expansion of the ideal entropy beyond the quadratic term [18] : $\delta H = -\frac{1}{2\bar{\rho}^2} \int \delta s(\mathbf{r}) q^2(\mathbf{r}) d\mathbf{r}$ couples charge and density fields, this term is treated as a perturbation. The average of any quantity with the full Hamiltonian is then written

$$\langle A \rangle = \langle A \rangle_0 - \langle A \beta \delta H \rangle_0 + \dots \quad (31)$$

where the averages $\langle \dots \rangle$ and $\langle \dots \rangle_0$ refer to the full Hamiltonian and to the quadratic Hamiltonian respectively. With the new Hamiltonian the density profile at the wall is modified. As we are interested in the profile at the wall we subtract the corresponding bulk contribution. Eq. (31) for the ionic density profile reads

$$\langle \delta s \rangle = \left\langle \frac{q(\mathbf{r}) \int q(\mathbf{r}') \delta s(\mathbf{r}')^2 d\mathbf{r}'}{2\rho_b^2} \right\rangle_0 - \left\langle \frac{q(\mathbf{r}) \int q(\mathbf{r}') \delta s(\mathbf{r}')^2 d\mathbf{r}'}{2\rho_b^2} \right\rangle_{0,bulk} \quad (32)$$

where we use the fact that the profile $\langle \delta s \rangle_0$ for the quadratic Hamiltonian is zero. In the quadratic Hamiltonian the fields q and s are independent. The expression for the profile can be obtained in the form

$$\langle \delta s(\mathbf{r}) \rangle = -\frac{K_D^3}{8\pi} I[(z - L_1)K_D] \quad (33)$$

where $I(x) = \int_1^\infty dt e^{-2xt} / (t + \sqrt{t^2 - 1})^2$ is a fast decaying function. In the vicinity of one wall at $z = L_1$ the correction to the total density profile given by eq.(33) is plotted in figure 2. We have $I(0) = 1/3$ which yields the contact value of the corrected profile $\langle \delta s(z = L_1) \rangle = -\frac{K_D^3}{24\pi}$ consistent with the

contact theorem [11] and the Debye-Hückel correction for the ionic gas pressure eq.(28). *Vice versa* this shows that the quadratic Hamiltonian, where

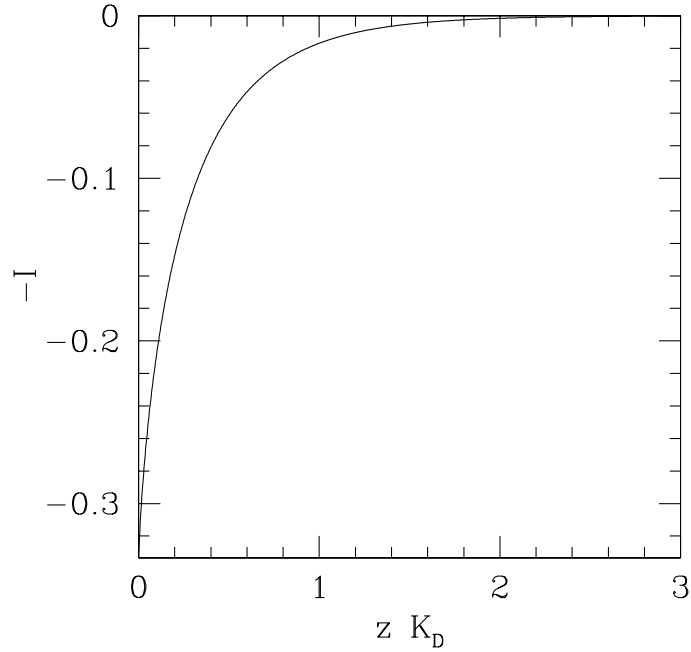


Fig. 2. Plot of the function I related to the total density profile correction across the interface.

the profile at the wall is constant, does not fulfill the mechanical equilibrium expressed by the contact theorem.

4.2 Surface excess free energy

The excess free energy due to the electrostatics has been calculated in the bulk [1] and the contribution due to the surface has been calculated in two ways in [18]. Let us recollect the results. The bulk contribution to the free energy is

$$\beta\mathcal{F}^b = -V \frac{K_D^3}{12\pi}. \quad (34)$$

And the surface contribution to the free energy can be obtained directly from the partition function

$$\beta\mathcal{F}^s|_{L \rightarrow \infty} = \frac{AK_D^2}{4\pi} \left(\frac{2 \ln 2 - 1}{4} \right). \quad (35)$$

An alternative way to calculate the free energy is using the charge – charge correlation functions and a charging process. We define

$$\beta\tilde{\mathcal{F}}_\lambda \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 \beta H^c(\mathbf{r}_1, \mathbf{r}_2; \lambda) g(\mathbf{r}_1, \mathbf{r}_2; \lambda) \quad (36)$$

where $\beta H^c(\mathbf{r}_1, \mathbf{r}_2; \lambda) = \frac{\lambda^2 \beta e^2}{8\pi\epsilon|\mathbf{r}_1 - \mathbf{r}_2|}$ and where we consider a charging process by which $g(\mathbf{r}_1, \mathbf{r}_2; \lambda)$ is the charge - charge correlation function for a system with elementary electric charge λe instead of e . The electrostatic contribution to the free energy for a system of elementary electric charges e is

$$\int_0^1 d\lambda \beta\tilde{\mathcal{F}}_\lambda = \beta\tilde{\mathcal{F}}|_e - \beta\tilde{\mathcal{F}}|_{e=0}. \quad (37)$$

The contribution from the bulk part of the correlation function eq. (29) yields

$$\beta\tilde{\mathcal{F}}^b = -V \frac{K_D^3}{12\pi} + A \frac{K_D^2}{16\pi}, \quad (38)$$

The contribution from the surface correlation given in eq. (30) is

$$\beta\tilde{\mathcal{F}}^s|_{L \rightarrow \infty} = A \frac{K_D^2}{8\pi} (\ln 2 - 1). \quad (39)$$

Summing the two contributions, we find that we have indeed $\mathcal{F}^b + \mathcal{F}^s|_{L \rightarrow \infty} = \tilde{\mathcal{F}}^b + \tilde{\mathcal{F}}^s|_{L \rightarrow \infty}$. This shows the consistency of the two ways of calculating the free energy.

Finally the surface tension can also be calculated from the Gibbs adsorption isotherm

$$d\gamma = 2\Gamma^{salt}d\mu \quad (40)$$

where Γ^{salt} is the adsorption of the salt per unit surface area. The adsorption can be calculated from the density profile eq.(33). Integrating the isotherm from zero density to the final density of the system we have that the surface tension is

$$\beta\gamma = \frac{K_D^2(2\ln 2 - 1)}{32\pi} \quad (41)$$

This result is consistent with the results above.

4.3 Differential capacitance.

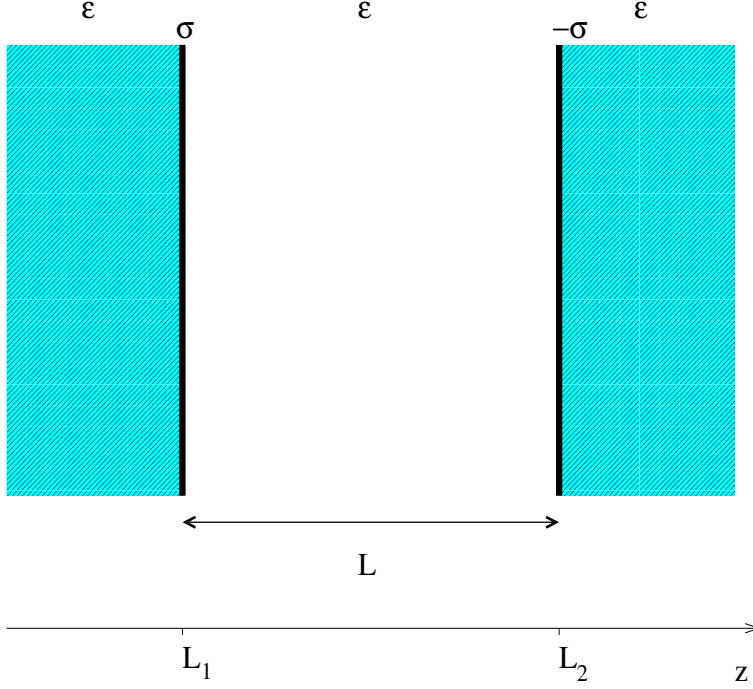


Fig. 3. Schematic representation of the model system with wall with surface charge σ .

In this section the Coulomb Hamiltonian includes an external contribution accounting for the fact that the walls can be charged

$$\beta H^c[q(\mathbf{r})] = \frac{\beta e^2}{4\pi\epsilon} \int \frac{q(\mathbf{r})q(\mathbf{r}')}{\tilde{r}} d\mathbf{r}d\mathbf{r}' + \beta e \int q(\mathbf{r})V^{ext}(\mathbf{r})d\mathbf{r}, \quad (42)$$

$V^{ext}(\mathbf{r})$ is the potential created by the surface charge densities σ and $-\sigma$ on the walls. This contribution is

$$V^{ext}(\mathbf{r}) = -\frac{\sigma e}{\epsilon} \left(z - \frac{L_1 + L_2}{2} \right) \quad (43)$$

where the zero for the electric potential is set in the middle of the system. To calculate the capacitance of the system we consider the linear response theory for a small surface charge density σ . The Hamiltonian can be rewritten

$$H = H_{\sigma=0} + H_{\sigma} \quad \text{with} \quad H_{\sigma} = e \int q(\mathbf{r})V^{ext}(\mathbf{r})d\mathbf{r} \quad (44)$$

All averages are then performed with the Hamiltonian $H_{\sigma=0}$ and H_{σ} replaces

δH as the perturbation in eq.(31). The potential difference between the two walls can then be written in the following way :

$$\begin{aligned}
V(L_2) - V(L_1) &= \left\langle \left(V^{ext}(r) + \frac{e}{4\pi\epsilon} \int \frac{q(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right) \right. \\
&\quad \left. \left(1 - \beta e \int q(\mathbf{r}'') V^{ext}(\mathbf{r}'') d\mathbf{r}'' \right) \right\rangle_{0,z=L_2} - \left\langle \dots \right\rangle_{0,z=L_1} \\
&= \delta V^{ext} + \frac{e}{4\pi\epsilon} \left[\left\langle \int \frac{q(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right\rangle_{0,z=L_2} - \left\langle \dots \right\rangle_{0,z=L_1} \right] \\
&\quad - \frac{\beta e^2}{4\pi\epsilon} \left[\left\langle \int \frac{q(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \int q(\mathbf{r}'') V^{ext}(\mathbf{r}'') d\mathbf{r}'' \right\rangle_{0,z=L_2} - \left\langle \dots \right\rangle_{0,z=L_1} \right] \\
&\quad - \beta e \left[\left\langle V^{ext}(L_2) \int q(\mathbf{r}'') V^{ext}(\mathbf{r}'') d\mathbf{r}'' \right\rangle_{0,z=L_2} - \left\langle \dots \right\rangle_{0,z=L_1} \right] \quad (45)
\end{aligned}$$

where for each quantity its difference for $z = L_2$ and $z = L_1$ is taken. The first term is $\delta V^{ext} = V^{ext}(z = L_2) - V^{ext}(z = L_1) = -\sigma e L / \epsilon$ the potential difference due to the electric charges on the wall. The second term is the average of the Coulomb potential created by the charges in the ionic solution but taken for neutral walls, in this case electric potential is constant throughout the system and this difference is zero [12,22]. The last term is proportional to σ^2 and can be neglected in the linear response regime. Finally we have [23]

$$\begin{aligned}
V(L_2) - V(L_1) &= \delta V^{ext} + \frac{\sigma e L}{\epsilon} - \frac{2\sigma e}{\epsilon K_D} [1 - e^{-K_D L}] \\
&= -\frac{2\sigma e}{\epsilon K_D} [1 - e^{-K_D L}] \quad (46)
\end{aligned}$$

Deriving eq.(46) with respect to σ

$$\begin{aligned}
C^{-1} &= \frac{\tilde{V}(L_2) - \tilde{V}(L_1)}{-\sigma e} \\
&= \frac{2}{\epsilon K_D} [1 - e^{-K_D L}] \quad (47)
\end{aligned}$$

which in the large L limit corresponds to the differential capacitance for the Gouy - Chapman theory.

5 Conclusion

In this paper on a specific example, an ionic system in a slab, we show that the field theoretical approach can be used for a coherent description. The specific features of systems with Coulomb potential are reproduced. The bulk charge correlation function obeys the required sum rules [22] and the inhomogeneous charge correlation function verifies the electroneutrality and the asymptotic behaviour parallel to the wall predicted by B. Jancovici [21].

The theory is based on fields which have a clear physical meaning. Our approach can be situated between the density functional theory and the usual statistical mechanics. As for the density functional theory the choice of ionic densities leads to a description closer to the macroscopic level and better understood. On the other hand with ionic densities as stochastic fields our treatment is close to the usual statistical mechanics and the assumptions at the level of the Hamiltonian are simpler than those at the level of the density functional.

With a simple extension of the Debye – Hückel theory we predict a nontrivial desorption profile at the interface of the ionic solution with a neutral hard wall. In contrast to the Debye – Hückel linear approximation, this result restores the consistency of the approach with the contact theorem and Gibbs adsorption thermodynamics.

Different tools and ways of thinking specific to the field theoretical approach yield new points of view. For instance the desorption profile is described as a result of the *coupling* between the charge and density fields due to the ideal entropy. This is a different point of view from the standard liquid state theory where the ideal entropy is usually written as an explicit and independent contribution to the free energy.

References

- [1] J. Stafiej and J. P. Badiali, J. Chem. Phys. **106** (1997) 8579.
- [2] R.R. Netz, Eur. Phys. J. E **5** (2001) 189.

- [3] R. Van Roij and J.P. Hansen, Phys. Rev. Lett. **79**, 3082 (1997).
- [4] M.N. Tamashiro and P. Pincus, Phys. Rev. E **60** (1999) 6549; R. Menes, P. Pincus and B. Stein, Phys. Rev. E, **62** (2000) 2981 and references therein.
- [5] D.G. Grier, J. Phys.: Condens. Matter **12** (2000) A85.
- [6] A. Diehl, M.N. Tamashiro, M.C. Barbosa et al., Physica A **274** (1999) 433.
- [7] M. E. Fisher, J. Chem. Phys., **96** (1992) 3352.
- [8] H. Frusawa and R. Hayakawa, Phys. Rev. E **60** (1999) R5048.
- [9] J. P. Hansen and I. R. Mc Donald, *Theory of simple Liquids* (Academic Press, New York, 1976)
- [10] R. Evans, Adv. Phys. **28** (1979) 143.
- [11] D. Henderson and L. Blum, J. Chem. Phys. **69** (1978) 5441.
- [12] D. di Caprio, J. Stafiej and J.P. Badiali, J. Chem. Phys. **108** (1998) 8572.
- [13] Feynman R.P. and Hibbs A.R., in *Quantum Mechanics and Path Integrals* (McGraw Hill, New York 1965).
- [14] J. Zinn Justin, *Quantum field theory and critical phenomena* (Clarendon Oxford 1989).
- [15] D. di Caprio, Q. Zhang and J.P. Badiali, Phys. Rev. E. **53** (1996) 2320-2325.
- [16] J.L. Lebowitz and J.K Percus, Phys. Rev. **122** 1675 (1961); J.L. Lebowitz and J.K Percus, J. Math. Phys. **4** (1963) 117.
- [17] R.J. Baxter, J. Chem. Phys. **41** (1964) 553.
- [18] D. di Caprio, J. Stafiej and J.P. Badiali, submitted to Phys. Rev. E.
- [19] D. di Caprio, J. Stafiej, J. P. Badiali and Z. Borkowska Electrochimica Acta, **46** (2001) 3051.
- [20] J. Spanier and K.B. Oldham, in *An Atlas of Functions*, (Edited by Hemisphere Publishing Corporation, Washington 1987); M. Abramowitz and I.A. Stegun, in *Handbook of Mathematical Functions with formulas, graphs and mathematical tables*, (Edited by National Bureau of Standards, Applied Mathematics Series 55, Washington 1965).
- [21] B. Jancovici, J. Stat. Phys. **28** (1982) 43; J. Stat. Phys. **29** (1982) 263 and J. Stat. Phys. **80** (1995) 445.

- [22] Stafiej J. and Badiali J.P., J. Chem. Phys. **106** (1997) 8579-8586.
- [23] D. di Caprio and J. Stafiej, Cond. Matt. Physics **4** (2001) 715-726.