Correlation of Charged Fluids Separated by a Wall

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It is shown that the concentration profile of a charged fluid, in contact with a planar electrode, is correlated with the charged fluid on the other side of the electrode. [S0031-9007(96)01638-9]

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If a charged fluid is next to a charged electrode of planar geometry, a charge concentration profile is induced on the fluid next to the plate. This charge concentration profile has a maximum at contact with the plate and decreases going away from the plate, to reach its minimum value of zero in the bulk fluid. This charge profile is known as the electrical double layer (EDL) in the liquid and colloidal dispersion fields. Since the classical work of Gouy [1] and Chapman [2], it has been universally accepted that the EDL formed by a charged fluid next to a planar, charged electrode is independent of the fluid that might be on the other side of the electrode. For example, this has been the case in liquid theory studies [3–14], numerical simulations [15–17], and classical monographs and textbooks on colloids [18–26]. To the best of our knowledge, all the literature in the field assumes either that there is no correlation between the fluids on both sides of the dividing wall or that the wall is infinitely thick.

In the case of the Poisson-Boltzmann equation [1,2] or theories based on charge moment expansions [3], they simply do not include proper boundary conditions in order to take into account the fluid on the other side of the wall. From the point of view of the integral equation theories the reason for this approach is probably due to the influential work of Henderson, Abraham, and Barker [4] and that of Henderson and Blum [5]. In these papers, a method for deriving integral equations for inhomogeneous fluids is proposed. In this method, the Ornstein-Zernike (OZ) equation [4] for a $(n + 1)$-component homogeneous fluid is generalized to study inhomogeneous fluids. The limits of infinite radius and zero concentration for the $(n + 1)$-species is taken in the OZ equation, the other n-species are left as the liquid species. Hence the field produced by the giant particle (assumed to be spherical) becomes the source of the external field, thus producing an inhomogeneity in the fluid. Because this central particle is giant, the fluid near it "sees" it as a planar wall. As we will show later, with a wall of infinite thickness there is no liquid-liquid correlation through the wall.

The equivalence between particles and fields is well established in physics, i.e., particles and fields are defined through their interaction with other particles or external fields. The various microscopic liquid theories are basically mathematical manipulations of the species probability densities, starting from a conservation equation or a probability density *ansatz.* Since there are no restrictions in these statistical mechanical theories in relation to the type of particles' interaction potential, the number of species in a fluid, and their concentrations, one can consider the external field in an inhomogeneous fluid to be just another particle in a homogeneous fluid. This very simple idea was used in the past by one of us to propose a method to derive theories for inhomogeneous liquids [27]. Here we will refer to this method as the direct method (DM). This method has been successfully applied to study inhomogeneous liquids next to external fields of several geometries [28]. The DM allows the study of an inhomogeneous fluid next to an electrode of planar geometry and a *finite* thickness.

With the DM [27] one can derive in a straightforward manner, for example, a hypernetted chain/mean spherical (HNC/MSA) equation for a two-component electrolyte next to the external field produced by a charged plate of thickness d, i.e.,

$$g_{pi}(x) = \exp\left\{-\beta u_{pi}(x) + \sum_{m=1}^{2} \rho_m \int c_{im}(s) h_{pm}(y)\, dv_3\right\}, \tag{1}$$

where ρ_m is the bulk concentration of the ions of species m; $c_{im}(s)$ is the MSA direct correlation function for ions of species i and m, a distant s apart; $\rho_i g_{pi}(x)$ is the local concentration of ions of species i, at a distance x from the center of the plate and perpendicular to the plate $(-\infty \leq x < \infty)$; $h_{pm}(y)$, defined as $h_{pm}(y) \equiv g_{pm}(y) - 1$, is the total correlation function; dv_3 is the volume differential; $\beta \equiv 1/KT$, where K is the Boltzmann constant and T is the system temperature; $u_{pi}(x)$ is the interaction potential between an ion of species i and the plate, represented by the subindex p. A widely used model for the electrolyte is the so-called restricted primitive model electrolyte (RPM). In this model the electrolyte is assumed to be a fluid of charged hard spheres of charge ez_i and diameter a in a dielectric continuum of dielectric constant ε, where e is the electronic charge and z_i is the valence of an ion of species i. In this Letter the plate is considered to be a flat, hard wall with a surface charge density σ_L on the left hand surface of the plate and a surface charge density σ_R on the right hand surface of the plate. The wall has a width d and is composed of a dielectric material with a dielectric constant chosen to be equal to that of the solvent, for simplicity,

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such that image forces need not be considered. This model for the electrode differs from others in the literature [1–26] in that the thickness of the plates is taken into account and in that its two surfaces need not be equally charged. As pointed out before, to the best of our knowledge, in the past this wall was explicitly or implicitly assumed to be infinitely thick.

For our model, this potential can be separated into a hard sphere-hard wall term $u^{*}_{pi}(x)$ and an electrostatic part $u^{\mathrm{el}}_{pi}(x)$. The hard sphere-hard wall potential simply takes into account the fact that the ions cannot penetrate or deform the walls. From Gauss law, the electrostatic potential can be found to be

$$-\beta u^{\mathrm{el}}_{pi}(x) = \frac{2\pi\beta e z_i}{\varepsilon}(\sigma_L + \sigma_R)x \,. \tag{2}$$

Equation (1) is a non-linear integral equation that we solved numerically with advanced finite element techniques. The solution of Eq. (1) gives the concentration profile $\rho_i g_{pi}(x)$ to the left and right of the wall.

The charge profile in the solution is given by

$$\rho_{\mathrm{el}}(x) = \sum_{m=1}^{2} e z_m \rho_m g_{pm}(x) \,. \tag{3}$$

The electroneutrality condition for the plate plus the electrolyte system states that the charge induced in the liquid by the wall must cancel that on the wall; that is $\sigma_L + \sigma_R = -\sigma'_L - \sigma'_R$, where σ'_L and σ'_R are the induced charges in the liquid to the left and right of the plate, respectively. Mathematically this condition is expressed as

$$\sigma_L + \sigma_R = -\int_{-\infty}^{-d/2} \rho_{\mathrm{el}}(y)\,dy - \int_{+d/2}^{\infty} \rho_{\mathrm{el}}(y)\,dy \,, \tag{4}$$

where the first and second integrals define σ'_L and σ'_R, respectively.

In Fig. 1 the fluid is a 2:2, 0.971*M* electrolyte. The wall has a surface charge density on its left side of $\sigma_L = -0.136\ \mathrm{C/m^2}$ and on its right surface of $\sigma_R = 0.68\ \mathrm{C/m^2}$. Two thicknesses of the wall are considered, $d = a$ and $d = 5000a$. In Fig. 1(a) we show the positive ion reduced concentration profile (PIRCP), induced by the wall in the solution. In Fig. 1(b) the negative ion reduced concentration profile is shown (NIRCP). On the left side of the wall, near the wall and for $d = a$, the PIRCP is lower than in the bulk solution, whereas the NIRCP is clearly above its bulk value (far from the wall, i.e., in the bulk $g_{p-}(x) = g_{p+}(x) = 1$, since the wall's electrical field is screened by the charged fluid). This is an unexpected behavior because the left side of the wall is negatively charged. On the right hand side of the wall, still for $d = a$, an apparently normal behavior is observed near the wall, i.e., the PIRCP is lower than one and the NIRCP is well above one. Since the right surface of the wall is positively charged, this is to be expected. For a wall thickness of $d = 5000a$, a physically appealing result is obtained on both sides of the wall, i.e., the PIRCP is well above one on the left side of the wall and lower than one on the right side, whereas the NIRCP is lower than one on the left and higher than one on the right. A calculation for a symmetrically charge wall [with Eq. (1)] or with traditional methods [7] with charge density equal to $-0.136\ \mathrm{C/m^2}$ will show a PIRCP and a NIRCP equal to those shown in Fig. 1 for the left side of the wall with $d = 5000a$. A similar result is observed from a calculation for a symmetrically charged wall, with charge density equal to $0.68\ \mathrm{C/m^2}$, i.e., its NIRCP and PIRCP agree with those shown in Fig. 1 for the right hand size of the $d = 5000a$ wall. For a symmetrically charged plate the NIRCP and PIRCP are independent of the width of the plate.

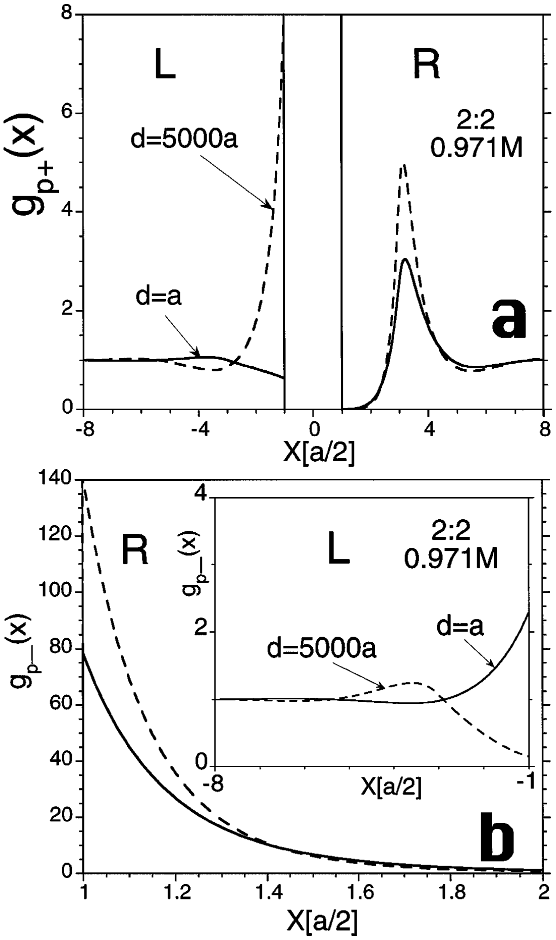

FIG. 1. Reduced concentration profiles (RCP) for a 2:2, 0.971*M* electrolyte, next to a charged wall, as a function of the distance to the wall. The wall has a surface charge density on its left side of $\sigma_L = -0.136\ \mathrm{C/m^2}$ and on its right surface of $\sigma_R = 0.68\ \mathrm{C/m^2}$. Two thicknesses of the wall are considered, $d = a$ and $d = 5000a$. In (a) we show the positive ion reduced concentration profile (PIRCP), induced by the wall in the solution. In Fig. (b) the negative ion reduced concentration profile is shown (NIRCP). The distance to the wall is measured in ionic radius. The zero of the x coordinate is located on the left surface of the wall for the left RCPs and on the right surface of the wall for the right RCPs, i.e., the thickness of the wall is not plotted.

In Fig. 2 the fluid and the charge of the plate is the same as that in Fig. 1. We plot the charge density induced in the fluid by the wall as a function of the wall's thickness. For $d = 0$, $\sigma'_L = \sigma'_R = 0.272\ \mathrm{C/m^2}$, this is equal to the average charge on the wall. As d increases, σ'_L decreases and σ'_R increases such that $\sigma'_L \rightarrow -0.136\ \mathrm{C/m^2}$ and $\sigma'_R \rightarrow +0.68\ \mathrm{C/m^2}$ for $d \rightarrow \infty$. Figures 1 and 2 show that there is a correlation of the liquid through the wall. Preliminary calculations show that this correlation seems to increase with lower charge on the plate and/or lower electrolyte's charge and concentration; these results are not shown. Hence there seems to be a higher correlation of the fluid, through the wall, for thicker EDLs. However, in the limit of zero charge the hard sphere fluid is recovered, as expected for this model. All the data were obtained for $T = 298$ K, $\varepsilon = 78.5$, $a = 4.25$ Å.

In the past it has been shown that in confined fluids there is a violation of the local electroneutrality condition (LEC) [29–31]. That is, the fluid between two plates, *symmetrically charged,* does not cancel the charge on the inside surfaces of the plates. This violation of the LEC is larger for thinner plates and greater confinement. However, the LEC is satisfied for large separations between the plates and for any thickness of the plates. In this paper, we certainly report a violation of some sort of electroneutrality conditions. However, here the fluid is not confined and the origin of this effect is due to a correlation of the fluid through the wall. This effect has not been recognized before, and we believe it could be of far-reaching consequences in the field of statistical mechanics of condensed matter systems, where boundaries between different kind of materials are present. In particular, this finding could be relevant in colloid, thin film, and biophysics studies.

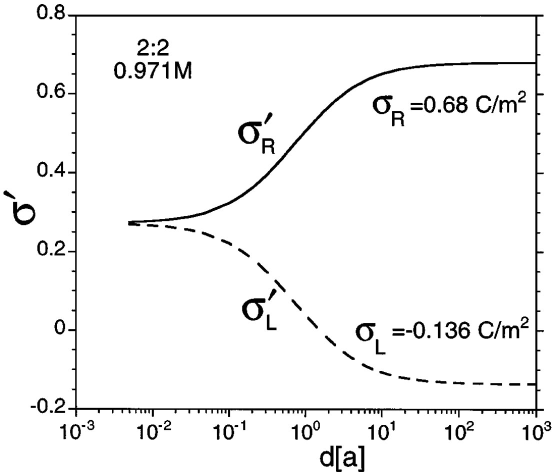

FIG. 2. Charge density induced in the fluid by the wall as a function of the wall's thickness (measured in ionic diameters). The fluid and the charge of the plate is the same as that in Fig. 1. σ'_L is the charge induced on the left side of the wall, whereas σ'_R is that induced on the right side of the wall.

The fluid correlation through the wall need not be limited to a charged wall. This effect could be present, for example, in Lennard-Jones fluids next to a wall with surfaces with unsymmetrical Lennard-Jones potentials.

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