The ideally polarizable interface: The metallic boundary limit

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The ideally polarizable interface: The metallic boundary limit

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The model of a classical one-component plasma in the vicinity of a metallic hard wall is shown to be a limiting case of an ideally polarizable interface.

A simple model which simulates the behavior of ideally polarizable interfaces (IPI) has been proposed recently.[1] It consists of two classical one-component plasmas (OCP) of different background densities α_1/π, α_2/π separated by an impermeable membrane. An exact solution was found in two dimensions with a logarithmic interaction at the special value of the coupling constant $\Gamma=\beta e^2=2$, where e is the charge of the mobile ions and $\beta=1/kT$ is the thermal Boltzmann factor. In the limit $\alpha_2\to\infty$ we may expect that the corresponding region of the interface behaves as a perfect conductor since the screening length [typically $\lambda=(2\Gamma\alpha_2)^{-1/2}$] tends to zero and the excess charge stands close to the interface. In this limit and for a membrane of finite width we should then recover the solution obtained recently for the OCP–metal interface[2] where the image forces induced by the metal are explicitly included in the Hamiltonian. Since the technical methods used in Refs. 1 and 2 are quite different it is interesting to verify that they yield effectively the same solution.

First we must extend the results of Ref. 1 to the case of an impermeable membrane of finite width ϵ. This can be done quite easily by noticing that, in the limit of a large system, the introduction of ϵ only modifies the expression of the function $\chi(t)$ defined by Eq. (2.13). Since the partition function, the free energy, the one- and two-body distribution functions are given as functionals of $\chi(t)$ their formal expressions remain unchanged. After some simple manipulations we find

$$\chi(t)=me^{(m^2-1)t^2}\frac{\operatorname{erfc}(mt)}{\operatorname{erfc}(-t)}e^{-2t\epsilon\sqrt{2\alpha_1}}, \tag{1}$$

where $\operatorname{erfc}(t)$ is the complementary error function and $m=(\alpha_1/\alpha_2)^{1/2}$. As in Ref. 1 the key ingredient of the exact solution is the quantity $z_0=z_1/z_2$ where z_1 and z_2 are the fugacities of the particles on either side of the interface;

$$z_1=e^{\beta[\mu_1+e\varphi(+\infty)]},\quad z_2=e^{\beta[\mu_2+e\varphi(-\infty)]}. \tag{2}$$

φ is the electrostatic potential and μ_1 and μ_2 are the bulk chemical potentials of the two plasmas separated by the gap $0<x<\epsilon$ (to make easier the comparison between Refs. 1 and 2 the positions of regions 1 and 2 have been inverted).

We now consider the limit $\alpha_2\to\infty$, i.e., $m\to 0$. First we notice that in two dimensions the potential difference $\varphi(0)-\varphi(-\infty)$ does not become zero as it would be in an ideal conductor. For dimensional reasons it is of the form

$$\varphi(0)-\varphi(-\infty)=ef\left(\frac{\sigma}{\sqrt{\alpha_2}},\frac{\alpha_1}{\alpha_2}\right), \tag{3}$$

where σ is the surface charge density defined by Eq. (3.10) of Ref. 1.

When $\alpha_2\to\infty$ this potential difference becomes $ef(0,0)$ which can be also obtained by taking $\sigma=\alpha_1=0$ for α_2 finite. So $ef(0,0)$ is merely the potential drop across the surface of one OCP bounded by a hard uncharged insulating wall, which has already been computed at $\Gamma=2$ (Ref. 3):

$$ef(0,0)=-\frac{e}{2}\left(\ln 2-\frac{1}{2}\right). \tag{4}$$

Since

$$\beta\mu_2=\frac{1}{2}\left(\ln\frac{\alpha_2}{2\pi^3}+1\right) \tag{5}$$

we see that z_0/m tends to the finite value

$$\tilde{z}_0=\frac{\pi^{3/2}}{\sqrt{2\alpha_1}}e^{\beta(\mu_1+e\Delta\varphi)}, \tag{6}$$

where now $\Delta\varphi=\varphi(\infty)-\varphi(0)$. Also the quantity $\chi(t)/m$ tends to the finite value

$$\tilde{\chi}(t)=\frac{e^{-t^2-2t\epsilon\sqrt{2\alpha_1}}}{\operatorname{erfc}(-t)}. \tag{7}$$

The expressions for σ (Eq. 2.34), $\rho(x)$ (Eq. 3.4), and $\rho_T(x_1,x_2,y)$ (Eq. 3.15) of Ref. 1 are all functions of $\chi(t)/m$ and z_0/m. Thus their limiting value is obtained by simply replacing $\chi(t)/m$ and z_0/m by $\tilde{\chi}(t)$ and $\tilde{z}_0$, respectively. In each case we regain the results of Ref. 2. For example, the density profile for $x>\epsilon$ (Eq. 3.4) tends to the limit

$$\rho(x)=\frac{2\alpha_1}{\pi^{3/2}}\tilde{z}_0\int_{-\infty}^{+\infty}dt\frac{\exp\{-[t+(\epsilon-x)\sqrt{2\alpha_1}]^2\}}{\tilde{z}_0\operatorname{erfc}(-t)+e^{-t^2-2t\epsilon\sqrt{2\alpha_1}}} \tag{8}$$

which is precisely the result of Ref. 2 (Eq. 4.20 with $\zeta=(\sqrt{2\alpha_1}/\pi^{3/2})\tilde{z}_0$). For α_2 finite the surface excess free ener-

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gy can be written

$$f^s = f_1^s + f_2^s + \Delta f^s + \epsilon e^2\sigma^2/\pi, \tag{9}$$

where f_1^s and f_2^s denote the surface free energy of the OCP near an insulating wall, Δf^s is the correction term due to the correlations between the two sides, and the last term is due to the gap ϵ. When $\alpha_2 \to \infty$ f_2^s will not tend to a finite limit. However, the excess free energy of the limiting system defined as

$$f^s = f_1^s + \Delta f^s + \epsilon e^2\sigma^2/\pi \tag{10}$$

is a function of z_0/m and $\chi(t)/m$ and thus tends to a finite limit. This limit is identical to the corresponding expression for f^s in Ref. 2 [Eqs. (4.8) and (4.14)] provided we note that the latter contains an extra contribution $f_1^s(\sigma = 0)$; it is due to the other uncharged wall located at $x = W + \epsilon$. Thus, as expected, the OCP–metal interface can be considered as a limiting case of the IPI model.

The correlation functions can be also obtained by a third method described in Ref. 4 which gives the exact solution for the 2D OCP in an arbitrary nonuniform background and submitted to an arbitrary non-Coulomb external potential $V_{\text{ext}}(x)$.

An important consequence of the OCP–metal interface being a limiting case of the IPI model is that the sum rules proved in Ref. 1 also hold for the metallic boundary. Thus we have the Lippmann equation [Eq. (5.13) of Ref. 1] which is true for any charged interface and the sum rule

$$\left.\frac{\partial f^s}{\partial \alpha_1}\right|_\sigma = -e\int_\epsilon^\infty [\varphi(x) - \varphi(\infty)]dx, \tag{11}$$

which is restricted to the case of jellium.

We can also derive a contact theorem, expressing the balance of forces across the interface: it is not very useful because it requires the knowledge of the two-body correlation function.[5] Let us indicate a last sum rule

$$\left.\frac{\partial f^s}{\partial \epsilon}\right|_\sigma = kTp(\epsilon) + \frac{\alpha_1}{\pi}e[\varphi(\epsilon) - \varphi(\infty)] - P, \tag{12}$$

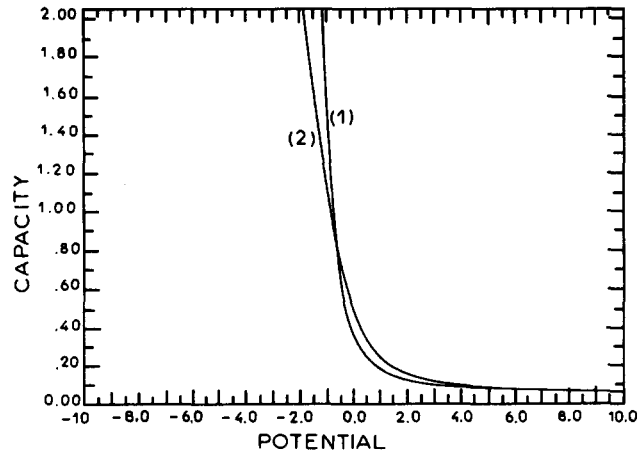

FIG. 1. Differential capacity vs potential drop: (1) insulating wall, (2) metallic wall.

where P is the bulk pressure. It can be derived by the general method indicated in Sec. V C of Ref. 1.

Finally, let us compare the differential capacity C of the interface to that corresponding to a "primitive" electrode, i.e., the plasma near a charged *insulating* wall. Since the impermeable gap $0 < x < \epsilon$ gives a constant contribution $1/(2\pi\epsilon)$ to C it is sensible to compare only the "diffuse" contribution, i.e., $C_D = \partial(e\sigma/\pi)/\partial[\varphi(\epsilon) - \varphi(\infty)]$. Figure 1 shows the dependence with the potential drop $\Delta\varphi$ and corresponds to $\epsilon = 1$ (units are $e = \alpha_1 = 1$). Here we can see the influence of an exact treatment of metallic image forces.

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