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Quantifying the thickness of the electrical double layer neutralizing a planar electrode: the capacitive compactness

Guillermo Iván Guerrero-García,[*,†] Enrique González-Tovar,[‡] Martín Chávez-Páez,[‡] Jacek Kłos,[¶] and Stanisław Lamperski[¶]

CONACYT-Instituto de Física de la Universidad Autónoma de San Luis Potosí, Álvaro Obregón 64, 78000 San Luis Potosí, San Luis Potosí, Mexico, Instituto de Física de la Universidad Autónoma de San Luis Potosí, Álvaro Obregón 64, 78000 San Luis Potosí, San Luis Potosí, Mexico, and Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61-614 Poznań, Poland

E-mail: givan@ifisica.uaslp.mx

[*]To whom correspondence should be addressed
[†]CONACYT-Institute of Physics, Autonomous University of San Luis Potosí, Mexico
[‡]Institute of Physics, Autonomous University of San Luis Potosí, Mexico
[¶]Faculty of Chemistry, Adam Mickiewicz University, Poland

The HNC/MSA integral equation for an infinite planar electrode

According to Carnie *et al.*,[1] the singlet profiles of charged particles modeled in the restricted primitive model around an impenetrable infinite charged wall can be written in terms of the mean electrostatic potential $\psi(x)$, and the direct correlation functions $c_{ij}^{MSA}(s)$ in the mean spherical approximations (MSA) as:

$$g_i(x') = \exp\left\{-\beta z_i e\psi(x') + \sum_j \rho_j \int_{x'-a}^{x'+a} c_{ij}^{MSA}(|x'-t'|)\ [g_j(t')-1]\ dt'\right\}, \tag{1}$$

if $x' \geq 0$; and $g_i(x') = 0$ if $x' < 0$, where $i, j = -, +$, and *the distances* x' *and* t' *are measured from the Helmholtz plane.* The interionic MSA direct correlation functions *in the bulk* are:

$$c_{ij}^{MSA}(s) = c^{PYHS}(s) + z_i z_j c^{ELEC}(s), \tag{2}$$

such as

$$c^{PYHS}(s) = 0, \quad \text{if} \quad s > a, \tag{3}$$

and

$$c^{PYHS}(s) = \frac{\pi a^2}{(1-\eta)^4}\left[-\frac{1}{5}\eta(1+2\eta)^2\left(1-\frac{s^5}{a^5}\right) + \eta(\eta+2)^2\left(1-\frac{s^3}{a^3}\right) - (1+2\eta)^2\left(1-\frac{s^2}{a^2}\right)\right], \tag{4}$$

if $s \leq a$, with $\eta = \frac{\pi a^3}{6}\sum_i \rho_i$, and

$$c^{ELEC}(s) = 0, \quad \text{if} \quad s > a, \tag{5}$$

and

$$c^{ELEC}(s) = \frac{2\pi\beta e^2}{\epsilon} a \left[\frac{B^2}{3}\left(1 - \frac{s^3}{a^3}\right) - B\left(1 - \frac{s^2}{a^2}\right) + \left(1 - \frac{s}{a}\right)\right], \tag{6}$$

if $s \leq a$. Notice the misprint in the B^2 term in Eq.(3.5) of Carnie *et al.*[1] Also,

$$B = (1 + \kappa a - (1 + 2\kappa a)^{1/2})/\kappa a, \tag{7}$$

with

$$\kappa = \frac{4\pi\beta e^2}{\epsilon} \sum_i \rho_i {z_i}^2. \tag{8}$$

For $x' \geq 0$, the expression for $g_i(x')$ can be formally written as:

$$\begin{aligned} g_i(x') = \exp\Bigg\{ & - \beta z_i e \psi(x') + \sum_j \rho_j \int_{x'-a}^{M} c_{ij}^{MSA}(|x' - t'|)\ [g_j(t') - 1]\ dt' + \\ & \sum_j \rho_j \int_{M}^{x'+a} c_{ij}^{MSA}(|x' - t'|)\ [g_j(t') - 1]\ dt' \Bigg\}, \end{aligned} \tag{9}$$

where $M \equiv \mathrm{Max}(x' - a\,,\, 0)$. Notice that

$$M = \begin{cases} 0 & \text{if } 0 \leq x' < a \\ x' - a & \text{if } a \leq x' < \infty. \end{cases} \tag{10}$$

If we define

$$2\pi\rho\, \alpha_i(x') \equiv \sum_j \rho_j \int_{x'-a}^{M} c_{ij}^{MSA}(|x' - t'|)\ [g_j(t') - 1]\ dt', \tag{11}$$

such that $\rho = \sum_i \rho_i$, we have

$$2\pi\rho\,\alpha_i(x') = \begin{cases} -\sum_j \rho_j \int_{x'-a}^{0} c_{ij}^{MSA}(x'-t')\;dt' & \text{if } 0 \le x' < a; \\ 0 & \text{if } a \le x' < \infty, \end{cases} \tag{12}$$

(observe that in the first case $|x'-t'| = x'-t'$). Thus, for $0 \le x' < a$,

$$2\pi\rho\,\alpha_i(x') = -\left\{ \Big(\sum_j \rho_j\Big) \int_{x'-a}^{0} c^{PYHS}(x'-t')\;dt' + z_i \Big(\sum_j \rho_j z_j\Big) \int_{x'-a}^{0} c^{ELEC}(x'-t')\;dt' \right\}. \tag{13}$$

Using the electroneutrality condition, $\sum_j \rho_j z_j = 0$, we obtain, for $0 \le x' < a$,

$$2\pi\rho\,\alpha_i(x') = 2\pi\rho\mathcal{A}(x'), \tag{14}$$

where

$$\mathcal{A}(x') = -\Big(\frac{1}{2\pi}\Big) \int_{x'-a}^{0} c^{PYHS}(x'-t')\;dt'. \tag{15}$$

Be aware that the function $\mathcal{A}(x')$ is independent of the ionic species. Inserting $c^{PYHS}(x'-t')$ in the last expression,

$$\mathcal{A}(x') = -\int_{x'-a}^{0} \left\{ \frac{c_1}{2}\big[a^2 - (x'-t')^2\big] + \frac{c_2}{3a}\big[a^3 - (x'-t')^3\big] - \frac{c_3}{5a^3}\big[a^5 - (x'-t')^5\big] \right\} dt'. \tag{16}$$

where

$$c_1 = -\frac{(1+2\eta)^2}{(1-\eta)^4}, \tag{17}$$

$$c_2 = 6\eta\frac{(1+\eta/2)^2}{(1-\eta)^4} \tag{18}$$

and

$$c_3 = -\eta \frac{c_1}{2}. \tag{19}$$

Reordering the terms we have

$$\mathcal{A}(x') = \int_{x'-a}^{0} (-a^2)\left(\frac{c_1}{2} + \frac{c_2}{3} - \frac{c_3}{5}\right) dt' + \int_{x'-a}^{0} \left(\frac{c_1}{2}\right)(x'-t')^2 \, dt' + \int_{x'-a}^{0} \left(\frac{c_2}{3a}\right)(x'-t')^3 \, dt' + \int_{x'-a}^{0} \left(-\frac{c_3}{5a^3}\right)(x'-t')^5 \, dt', \tag{20}$$

and, after a straightforward integration, we have that, for $0 \leq x' < a$,

$$\mathcal{A}(x') = -\left(\frac{c_1}{2} + \frac{c_2}{3} - \frac{c_3}{5}\right)(a - x')\, a^2 - \frac{c_1}{6}(x'^3 - a^3) - \frac{c_2}{12a}(x'^4 - a^4) + \frac{c_3}{30a^3}(x'^6 - a^6), \tag{21}$$

and $\mathcal{A}(x') = 0$, for $a \leq x' < \infty$. Hence, for $x' \geq 0$, we finally obtain

$$g_i(x') = \exp\left\{ -\beta z_i e \psi(x') + 2\pi\rho\mathcal{A}(x') + \sum_j \rho_j \int_M^{x'+a} c_{ij}^{MSA}(|x'-t'|)\ [g_j(t') - 1]\ dt' \right\}. \tag{22}$$

Explicit kernels for the HNC/MSA integral equations in planar geometry

Let us introduce the kernel

$$\mathcal{F}(x', t') = \frac{(a + x' + t') - |x' - t'|}{2}, \tag{23}$$

such that

$$\mathcal{F}(x',t') = \begin{cases} \frac{a}{2} + t' & \text{if } t' < x'; \\ \frac{a}{2} + x' & \text{if } t' \geq x'. \end{cases} \tag{24}$$

Eq. 22 can be written as

$$g_i(x') = \exp\Bigg\{ -\beta z_i e \psi_0 + 2\pi\rho\mathcal{A}(x') - \beta z_i e \left(\frac{4\pi e}{\epsilon}\right) \int_0^\infty \mathcal{F}(x',t') \Bigg(\sum_j \rho_j z_j h_j(t') \Bigg)\, dt' + \sum_j \rho_j \int_M^{x'+a} c_{ij}^{MSA}(|x'-t'|)\, [g_j(t') - 1]\, dt' \Bigg\}. \tag{25}$$

In this last equation we have used the definition of the mean electrostatic potential and the electroneutrality condition. Employing the definitions of c_1, c_2 and c_3, it can be shown that

$$c^{PYHS}(|x'-t'|) = 2\pi\mathcal{K}(x',t'), \tag{26}$$

where the kernel $\mathcal{K}(x',t')$ is

$$\mathcal{K}(x',t') = \begin{cases} \frac{c_1}{2}[a^2 - |x'-t'|^2] + \frac{c_2}{3a}[a^3 - |x'-t'|^3] - \frac{c_3}{5a^3}[a^5 - |x'-t'|^5] & \text{if } |x'-t'| \leq a; \\ 0 & \text{if } |x'-t'| > a. \end{cases} \tag{27}$$

Introducing the quantity

$$\Gamma = \frac{(1+2\kappa a)^{1/2} - 1}{2a}, \tag{28}$$

it can be proved that

$$B = \frac{\Gamma a}{(1+\Gamma a)}. \tag{29}$$

Thus,

$$c^{ELEC}(|x'-t'|) = \frac{2\pi\beta e^2}{\epsilon}\mathcal{M}(x',t'), \tag{30}$$

such that the kernel $\mathcal{M}(x',t')$ is

$$\mathcal{M}(x',t') = \begin{cases} a - |x'-t'| - \frac{\Gamma}{(1+\Gamma a)}[a^2 - |x'-t'|^2] + \frac{1}{3}\left(\frac{\Gamma}{1+\Gamma a}\right)^2[a^3 - |x'-t'|^3] & \text{if } |x'-t'| \leq a; \\ 0 & \text{if } |x'-t'| > a. \end{cases} \tag{31}$$

Substituting all the kernels, and give Eq. 35, we obtain

$$\begin{aligned} g_i(x') = \exp\Bigg\{ &- ez_i\beta\psi_0 + 2\pi\rho\mathcal{A}(x') + 2\pi\sum_j \rho_j \int_0^\infty h_j(t')\ \mathcal{K}(x',t')\ dt' + \\ &\frac{2\pi\beta e^2 z_i}{\epsilon}\sum_j z_j\rho_j\int_0^\infty h_j(t')\Big[\mathcal{M}(x',t') - 2\mathcal{F}(x',t')\Big]\ dt'\Bigg\}. \end{aligned} \tag{32}$$

Defining the kernel $\mathcal{L}(x',t') = \mathcal{M}(x',t') - 2\mathcal{F}(x',t')$, or equivalently,

$$\mathcal{L}(x',t') = \begin{cases} -2t' - a & \text{if } t' < x' - a; \\ -x' - t' - \frac{\Gamma}{(1+\Gamma a)}[a^2 - |x'-t'|^2] + \frac{1}{3}\left(\frac{\Gamma}{1+\Gamma a}\right)^2[a^3 - |x'-t'|^3] & \text{if } x' - a \leq t' \leq x' + a; \\ -2x' - a & \text{if } x' + a < t', \end{cases} \tag{33}$$

we arrive to

$$g_i(x') = \exp\Bigg\{ - ez_i\beta\psi_0 + 2\pi\rho\mathcal{A}(x') + 2\pi\sum_j \rho_j \int_0^\infty h_j(t')\ \mathcal{K}(x',t')\ dt' + \frac{2\pi\beta e^2 z_i}{\epsilon}\sum_j z_j\rho_j \int_0^\infty h_j(t')\mathcal{L}(x',t')\ dt' \Bigg\}, \tag{34}$$

for $x' \geq 0$.

If we now shift the origin of the coordinate system to coincide with the location of the electrode's surface (as it was considered in the present paper), the distances $x = x' + a/2$ and $t = t' + a/2$ are measured from the electrode's surface. In these new variables, the HNC/MSA integral equations for the single planar electric double layer of a binary RPM electrolyte are:

$$g_i(x) = \exp\Bigg\{ - ez_i\beta\psi_0 + 2\pi\rho A(x) + 2\pi\sum_j \rho_j \int_{a/2}^\infty \big[g_j(t) - 1\big]\ K(x,t)\ dt + \frac{2\pi\beta e^2 z_i}{\epsilon}\sum_j z_j\rho_j \int_{a/2}^\infty \big[g_j(t) - 1\big] L(x,t)\ dt \Bigg\}, \tag{35}$$

for $x \geq \frac{a}{2}$, $\psi_0 = \psi(x = 0)$, and $i, j = -, +$, where

$$A(x) = \begin{cases} -\left(\frac{c_1}{2} + \frac{c_2}{3} - \frac{c_3}{5}\right)\left(\frac{3a}{2} - x\right) a^2 - \frac{c_1}{6}\left[(x - \frac{a}{2})^3 - a^3\right] - \frac{c_2}{12a}\left[(x - \frac{a}{2})^4 - a^4\right] + \frac{c_3}{30a^3}\left[(x - \frac{a}{2})^6 - a^6\right] & \text{if } \frac{a}{2} \leq x < \frac{3a}{2}; \\ 0 & \text{if } \frac{3a}{2} \leq x < \infty, \end{cases} \tag{36}$$

$$K(x,t) = \begin{cases} \frac{c_1}{2}[a^2 - |x-t|^2] + \frac{c_2}{3a}[a^3 - |x-t|^3] - \frac{c_3}{5a^3}[a^5 - |x-t|^5] & \text{if } x-a \leq t \leq x+a; \\ 0 & \text{if } t < x-a \ \text{ or } \ x+a < t, \end{cases} \tag{37}$$

and

$$L(x,t) = \begin{cases} -2t & \text{if } t < x-a \\ a - x - t - \frac{\Gamma}{(1+\Gamma a)}[a^2 - |x-t|^2] + \frac{1}{3}\left(\frac{\Gamma}{1+\Gamma a}\right)^2 [a^3 - |x-t|^3] & \text{if } x-a \leq t \leq x+a \\ -2x & \text{if } x+a < t. \end{cases} \tag{38}$$

Finally, in terms of the total correlation functions $h_{ij}(x)$:

$$\begin{aligned} 1 + h_i(x) - \exp\Bigg\{ - e z_i \beta \psi_0 + 2\pi\rho A(x) + 2\pi \sum_j \rho_j \int_{a/2}^{\infty} h_j(t)\ K(x,t)\ dt + \\ \frac{2\pi\beta e^2 z_i}{\epsilon} \sum_j z_j \rho_j \int_{a/2}^{\infty} h_j(t) L(x,t)\ dt \Bigg\} = 0. \end{aligned} \tag{39}$$

The last equation, along with the definitions of $A(x)$, $K(x,t)$ and $L(x,t)$, coincide exactly with the HNC/MSA expression for the single planar electric double layer of a binary electrolyte in the restricted primitive model reported by Mier y Terán *et al.*[2]

Free energy of two charged plates in terms of the capacity compactness: a Gouy-Chapman calculation

In a general calculation of the free energy of a planar electrical double layer the following integral must be performed:[3]

$$\int_0^{\sigma_0} \psi_0'(\sigma_0')\, d\sigma_0'. \tag{40}$$

Consequently, if the relations $\psi_0(\sigma_0)$ and $\tau_c(\sigma_0)$ (or equivalently $\sigma_0(\tau_c)$) are known, the resulting free energy could be written, in principle, as a function of the capacity compactness. Unfortunately, except for the case of the Gouy-Chapman theory, analytical forms of the $\psi_0(\sigma_0)$ and $\sigma_0(\tau_c)$ relationships are not available for any of the current approaches to the electrical double layer, namely the mean electrostatic potential formalisms, integral equations and density functional theories. However, for the non-linearized Poisson-Boltzmann equation and the rest of the above mentioned approaches the free energy can still be obtained via a numerical integration of the tabulated functions $\psi_0(\sigma_0)$ and $\sigma_0(\tau_c)$.

For the well-known case of the Gouy-Chapman theory, the free energy per unit area for a $z : z$ electrolyte between two equally charged plates (in terms of the capacity compactness) is given by

$$A^{GCH} = \left(64\, k_B T \rho_+ \gamma^2\right) \tau_c \; e^{-D/\tau_c}, \tag{41}$$

where $\gamma = \tanh(ze\psi_0/4k_BT)$ and D is the interplanar separation. In the above expression the weak overlap approximation has been made. A^{GCH} is an essential ingredient in the DLVO theory of colloidal stability.

References

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