Supplementary Material of "Note: On the expected value of the electrostatic potential produced by a charged electrode neutralized by a Coulombic fluid: the Capacitive Compactness"

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Let us define ψ_0 and σ_0 as the mean electrostatic potential and the charge density per unit area, respectively, at the surface of a planar, a cylindrical, or a spherical electrode, next to a charged fluid with net charge local density per unit volume $\rho_c(\vec{t}) = \sum_{i=1}^{n} c_i(\vec{t}) q_i$, where q_i is the electric charge of the ionic species i and all ionic species have a numerical concentration c_i satisfying the electroneutrality condition in bulk, $\sum_{i=1}^{n} q_i c_i = 0$, very far away from the surface of a single electrode. In planar, cylindrical, and spherical geometries, the capacitive compactness τ_c, in the absence of a surface mean electrostatic potential of zero charge (i.e., provided that ψ_0 goes to zero in the limit when σ_0 goes to zero), can be written as[1–3]

$$\tau_c = \frac{\varepsilon\psi_0}{\sigma_0}, \tag{1}$$

$$\tau_c = R_{cyl} \exp\left(\frac{\varepsilon\psi_0}{R_{cyl}\sigma_0}\right), \tag{2}$$

or

$$\tau_c = R\left[1 - \left(\frac{\varepsilon\psi_0}{R\sigma_0}\right)\right]^{-1}, \tag{3}$$

respectively, where R_{cyl} and R are the radius of the cylindrical and spherical electrode, respectively, and the average macroscopic dielectric constant of the solvent is given by $\varepsilon = \varepsilon_0\varepsilon_r$. Macroscopically, these expressions can be obtained from the definition of an effective electrical double layer capacitor by replacing the difference of the electrostatic potential between the corresponding electrodes by the mean electrostatic potential ψ_0 at the surface of a single electrode with surface charge density σ_0, immersed in a Coulombic fluid.

On the other hand, let us consider a planar, a cylindrical, or a spherical electrode bathed by a continuum solvent with dielectric constant $\varepsilon = \varepsilon_0\varepsilon_r$ in the absence of small charged particles. The bare electric field associated to each electrode in cartesian, cylindrical, and spherical coordinates, can be written as $\vec{E}(x) = \frac{\sigma_0}{\varepsilon}\hat{i}$, $\vec{E}(\rho) = \frac{\sigma_0 R_{cyl}}{\varepsilon\rho}\hat{\rho}$, and $\vec{E}(r) = \frac{\sigma_0 R^2}{\varepsilon r}\hat{r}$, respectively. The corresponding bare electrostatic potentials $V(\vec{t})$ (in each geometry) are given by:

$$V_{wall}(x) = -\frac{\sigma_0 x}{\varepsilon} + C_{wall}, \tag{4}$$

$$V_{cylinder}(\rho) = -\frac{\sigma_0 R_{cyl}}{\varepsilon} \ln\left(\frac{\rho}{R_{cyl}}\right) + C_{cylinder}, \tag{5}$$

$$V_{sphere}(r) = \frac{\sigma_0 R^2}{\varepsilon}\left(\frac{1}{r} - \frac{1}{R}\right) + C_{sphere}. \tag{6}$$

Note that the first term on the right hand side of Eq. 6 has been written in such a way that it becomes zero when $r = R$. In the above equations, we have choosen that the bare electrostatic potential at the surface of each electrode vanishes, that is, $V_{wall}(x = 0) = V_{cylinder}(\rho = R_{cyl}) = V_{sphere}(r = R) = 0$, which implies that $C_{wall} = C_{cylinder} = C_{sphere} = 0$.

Let us define a normalized charge density weight function

$$w(\vec{t}) = \frac{\rho_c(\vec{t})}{\int_{all\ space} \rho_c(\vec{t}) d\vec{t}}, \tag{7}$$

associated to a charged fluid with net charge local density per unit volume $\rho_c(\vec{t}) = \sum_{i=1}^{n} c_i(\vec{t}) q_i$ in the presence of an electrode with homogeneous charge density per unit σ_0 and mean electrostatic potential ψ_0 at the surface, in planar, cylindrical and spherical geometries. The expected value of a function $f(\vec{t})$ averaged over the whole three-dimensional space is then defined as

$$< f(\vec{t}) > = \int_{all\ space} f(\vec{t}) w(\vec{t}) d\vec{t}, \tag{8}$$

where $d\vec{t}$ is a differential volume element in the corresponding geometry.

The expected value given by Eq. 8 is calculated explicitly in the next sections for the bare electrostatic potentials 4, 5, 6. Moreover, it is shown that

$$< V(\vec{t}) > = \int_{all\ space} V(\vec{t}) w(\vec{t}) d\vec{t} = -\psi_0, \tag{9}$$

in all geometries.

If the mean electrostatic potential ψ_0 is written in terms of the capacitive compactness τ_c and the surface charge density σ_0 (see Eqs. 1,2,3), it is shown here that the expected value $< V(\vec{t}) >$ is equivalent to evaluate bare electrostatic potential $V(\vec{t})$ at the centroid of charge of a Coulombic fluid, which is the so-called capacitive compactness of the electrical double layer, in the presence of an electrode with surface charge density and mean electrostatic potential σ_0 and ψ_0, respectively, next to a fluid with net charge local density per unit volume $\rho_c(\vec{t}) = \sum_{i=1}^{n} c_i(\vec{t}) q_i$ in the corresponding geometry.

Alternative explicit forms of the capacitive compactness as expected values of functions that depend on the geometry of the electrode are also provided in the following.

Planar geometry

First, let us consider an infinite solid charged hard wall with homogeneous surface charge density σ_0. The surface charge density and mean electrostatic potential at the electrode's surface can be written as:[3]

$$\sigma_0 = -\int_0^{\infty} \rho_c(x) dx, \tag{10}$$

and

$$\psi_0 = -\frac{1}{\varepsilon} \int_0^{\infty} x \rho_c(x) dx. \tag{11}$$

The expected value of $V_{wall}(x)$ can be written as:

$$< V_{wall}(x) >= \int_0^{\infty} -\frac{\sigma_0 x}{\varepsilon} w(x) A dx, \tag{12}$$

where

$$w(x) = \frac{\rho_c(x)}{\int_0^{\infty} \rho_c(x) A dx}, \tag{13}$$

is the normalized net charge density weight function in planar geometry, $d\vec{t} = Adx$, and A is the area of a section of the infinite planar electrode.

By using Eqs. 10 and 11 in Eq. 12, it is possible to write:

$$< V_{wall}(x) >= -\frac{\sigma_0}{\varepsilon} < x >= -\psi_0. \tag{14}$$

If we substitute Eq. 1 in Eq. 14 we obtain:

$$< V_{wall}(x) >= -\frac{\sigma_0}{\varepsilon}\tau_c, \tag{15}$$

that corresponds to $V_{wall}(x = \tau_c)$. If we compare Eqs. 14 and 15, we observe that:

$$\tau_c =< x >, \tag{16}$$

which is an alternative definition of the capacitive compactness in planar geometry.

Cylindrical geometry

Now, let us consider an infinite solid charged hard cylinder with homogeneous surface charge density σ_0. The surface charge density and mean electrostatic potential at the electrode's surface can be written as:[4]

$$\sigma_0 = -\frac{1}{R_{cyl}}\int_{R_{cyl}}^{\infty} \rho_c(\rho)\rho d\rho, \tag{17}$$

and

$$\psi_0 = -\frac{1}{\varepsilon}\int_{R_{cyl}}^{\infty} \ln\left(\frac{\rho}{R_{cyl}}\right)\rho_c(\rho)\rho d\rho. \tag{18}$$

The expected value of $V_{cylinder}(\rho)$ can be written as:

$$< V_{cylinder}(\rho) >= \int_{R_{cyl}}^{\infty} -\frac{\sigma_0 R_{cyl}}{\varepsilon}\ln\left(\frac{\rho}{R_{cyl}}\right) w(\rho) 2\pi\rho L d\rho, \tag{19}$$

where

$$w(\rho) = \frac{\rho_c(\rho)}{\int_{R_{cyl}}^{\infty} \rho_c(\rho) 2\pi\rho L d\rho}, \tag{20}$$

is the normalized net charge density weight function in cylindrical geometry, $d\vec{t} = 2\pi\rho L d\rho$, and L is the length of a section of the infinite cylindrical rod.

By using Eqs. 17 and 18 in Eq. 19, it is possible to write:

$$< V_{cylinder}(\rho) >= -\frac{\sigma_0 R_{cyl}}{\varepsilon} < \ln\left(\frac{\rho}{R_{cyl}}\right) >= -\psi_0, \tag{21}$$

If we substitute Eq. 2 in Eq. 21 we obtain:

$$< V_{cylinder}(\rho) >= -\frac{\sigma_0 R_{cyl}}{\varepsilon} \ln\left(\frac{\tau_c}{R_{cyl}}\right), \tag{22}$$

that is equal to $V_{cylinder}(\rho = \tau_c)$. If we compare Eqs. 21 and 22, we notice that:

$$\tau_c = R_{cyl} \exp < \ln\left(\frac{\rho}{R_{cyl}}\right) > . \tag{23}$$

which is an alternative definition of the capacitive compactness in cylindrical geometry.

Spherical geometry

Finally, let us consider an infinite solid charged hard sphere with homogeneous surface charge density σ_0. The surface charge density and mean electrostatic potential at the electrode's surface can be written as:[3]

$$\sigma_0 = -\frac{1}{R^2} \int_R^\infty \rho_c(r) r^2 dr, \tag{24}$$

and

$$\psi_0 = \frac{1}{\varepsilon} \int_R^\infty \left(\frac{1}{r} - \frac{1}{R}\right) \rho_c(r) r^2 dr. \tag{25}$$

The expected value of $V_{sphere}(r)$ can be written as:

$$< V_{sphere}(r) >= \int_R^\infty \frac{\sigma_0 R^2}{\varepsilon} \left(\frac{1}{r} - \frac{1}{R}\right) w(r) 4\pi r^2 dr, \tag{26}$$

where

$$w(r) = \frac{\rho_c(r)}{\int_0^\infty \rho_c(r) 4\pi r^2 dr}, \tag{27}$$

is the normalized net charge density weight function in spherical geometry and $d\vec{t} = 4\pi r^2 dr$.

By using Eqs. 24 and 25 in Eq. 26, it is possible to write:

$$< V_{sphere}(r) >= \frac{\sigma_0 R^2}{\varepsilon} \left(\left\langle \frac{1}{r} \right\rangle - \frac{1}{R} \right) = -\psi_0, \tag{28}$$

If we substitute Eq. 3 in Eq. 28 we obtain:

$$< V_{sphere}(r) >= \frac{\sigma_0 R^2}{\varepsilon} \left(\frac{1}{\tau_c} - \frac{1}{R} \right), \tag{29}$$

that corresponds to $V_{sphere}(r = \tau_c)$. If we compare Eqs. 28 and 29, we observe that:

$$\tau_c = \left\langle \frac{1}{r} \right\rangle^{-1}. \tag{30}$$

which is an alternative definition of the capacitive compactness in spherical geometry.

References

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