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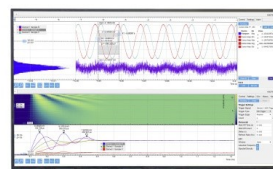
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# On the expected value of the electrostatic potential produced by a charged electrode neutralized by a Coulombic fluid: The capacitive compactness

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The extent of the electrical double layer surrounding a charged colloid is a measure of the neutralization of the bare or native colloidal charge and determines the colloidal stability properties of these macroparticles in solution. The effects of characteristic properties of Coulombic fluids in the electrical double layer have been widely studied in numerous experimental, theoretical, and simulation studies.<sup>1</sup> In particular, some of the present authors have shown that the electrical double layer can experience a peculiar shrinking and expansion in the presence of molten salts and simple charge-asymmetric electrolytes if coions are multivalent.<sup>2,3</sup> This observation was performed via simulation and theory by calculating the *capacitive compactness* of the electrical double layer.<sup>2-4</sup> By considering the global electroneutrality of an electrode–electrolyte system, it is possible to replace the real system by an effective capacitor in which the diffuse electrical double layer charge is placed in an electrode with a charge equal in magnitude to that of the real solid electrode but with opposite sign. The distance from the coordinate origin at which this electrode is located is, precisely, the capacitive compactness.<sup>2-5</sup> Note that if the location of the electrical double layer electrode is measured from the surface of the real solid electrode, then the capacitive compactness can be also interpreted as the separation distance between both electrodes. In the literature, it is very well known that the Debye length, and the associated electrical double layer, shrinks as a function of the ionic strength of the supporting electrolyte. However, the Debye length cannot take into account the influence of the surface

charge density of the electrode as well as other relevant properties of Coulombic fluids such as ion correlations, ionic excluded volume effects, polarization effects, and ionic specific adsorption. In this sense, the capacitive compactness is a generalization of the Debye length that has proven to be very useful to quantify the thickness or spatial extent of the ionic cloud neutralizing a charged surface. On the other hand, average potential theorems in electrostatics are very helpful to determine general properties of charge distributions typically found in electrified soft matter systems. By using general electrostatics and a normalized net charge density weight function, we show here that the expected value of the bare electrostatic potential  $V(\vec{r})$  produced by an electrode immersed in a continuum solvent in the absence of small charged particles—in planar, spherical, and cylindrical geometries—is equal to (i) the negative of the mean electrostatic potential  $\psi_0$  at the surface of an electrode immersed in a charged fluid with net charge density  $\rho_c(\vec{r})$  and the same surface charge density  $\sigma_0$ , and also to (ii) the bare electrostatic potential evaluated at the centroid of charge of the supporting Coulombic fluid (which is the so-called capacitive compactness of the electrical double layer). As a direct application of these results, we provide alternative explicit expressions of the capacitive compactness as the expected value of functions that depend on the specific geometry of the electrode.

Let us start by considering three types of charged electrodes: an infinite charged hard wall, an infinite solid cylinder of radius  $R_{cyl}$ ,

and a solid sphere of radius  $R$ . We will consider that these electrodes have a homogeneous surface charge density per unit area  $\sigma_0$  and are immersed in a medium with an average macroscopic dielectric constant  $\varepsilon = \varepsilon_0 \varepsilon_r$ . The bare electric field associated with 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  $\vec{E}(r) = \frac{\sigma_0 R^2}{\varepsilon r^2} \hat{r}$ , respectively. The bare electrostatic potential associated with each electrode in Cartesian, cylindrical, and spherical geometries can be written as

$$V_{wall}(x) = -\frac{\sigma_0 x}{\varepsilon} + C_{wall}, \quad (1)$$

$$V_{cylinder}(\rho) = -\frac{\sigma_0 R_{cyl}}{\varepsilon} \ln\left(\frac{\rho}{R_{cyl}}\right) + C_{cylinder}, \quad (2)$$

$$V_{sphere}(r) = \frac{\sigma_0 R^2}{\varepsilon} \left(\frac{1}{r} - \frac{1}{R}\right) + C_{sphere}. \quad (3)$$

Note that the first term on the right-hand side of Eq. (3) has been written in such a way that it becomes zero when  $r = R$ . If we choose that the bare electrostatic potential at the surface of each electrode vanishes, that is,  $V_{wall}(x = 0) = V_{cylinder}(\rho = R_{cyl}) = V_{sphere}(r = R) = 0$ , then  $C_{wall} = C_{cylinder} = C_{sphere} = 0$ .

Let us consider now the case in which each electrode is immersed in a charged fluid constituted by  $n$  species of charged hard particles with radius  $r_i$  and point charge  $q_i$  in their centers, in the so-called primitive model. Solvent particles are modeled as a continuous medium characterized by a macroscopic dielectric constant. All ionic species have a numerical concentration  $c_i$ , and there are no restrictions regarding their valences or radii, except that they must satisfy the electroneutrality condition in bulk,  $\sum_{i=1}^n q_i c_i = 0$ , very far away from the electrode's surface. As a result, the proposed method can be also applied to systems including charged colloids at finite concentration as well.

The capacitive compactness can be calculated if the surface charge density  $\sigma_0$  and the mean electrostatic potential at the surface of the electrode  $\psi_0$  are known. In planar, cylindrical, and spherical geometries, the capacitive compactness  $\tau_c$  in the absence of a surface mean electrostatic potential of zero charge (i.e., provided that  $\psi_0$  goes to zero in the limit when  $\sigma_0$  goes to zero) can be written as<sup>2,3,5</sup>

$$\tau_c = \frac{\varepsilon \psi_0}{\sigma_0}, \quad (4)$$

$$\tau_c = R_{cyl} \exp\left(\frac{\varepsilon \psi_0}{R_{cyl} \sigma_0}\right), \quad (5)$$

$$\tau_c = R \left[1 - \left(\frac{\varepsilon \psi_0}{R \sigma_0}\right)\right]^{-1}. \quad (6)$$

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  $\psi_0$  at the surface

of a single electrode with surface charge density  $\sigma_0$ , immersed in a Coulombic fluid. It must be noted that relationships between the integer and the differential capacity, and the capacitive compactness and its first derivative have been derived elsewhere.<sup>2</sup>

In order to calculate the capacitive compactness in any of these geometries, it is necessary to know the ionic structure of the electrical double layer either via theory or simulations. If the surface charge density is chosen as the independent variable, the knowledge of the electrical double layer allows us to calculate the mean electrostatic potential at the colloidal surface and, as a result, the capacitive compactness via Eqs. (4)–(6). Let us suppose that we know the microscopic ionic concentration as a function of the distance in the planar, spherical, or cylindrical geometry. This allows us to write the net charge local density per unit volume of the Coulombic fluid as  $\rho_c(\vec{r}) = \sum_{i=1}^n c_i(\vec{r}) q_i$ . Depending on the geometry, the three-dimensional spatial dependency of  $\rho_c(\vec{r})$  can be simplified from three independent variables to only one if the electrode is an infinite planar wall, an infinite cylinder, or a sphere. Let us define now a normalized net charge density per unit volume weight function in the whole space as  $w(\vec{r}) = \frac{\rho_c(\vec{r})}{\int_{all\ space} \rho_c(\vec{r}) d\vec{r}}$ , where  $d\vec{r}$  is a differential of volume and the integral is performed in the whole space. Let us also define the expected value of a function  $f(\vec{r})$  in the three-dimensional space as  $\langle f(\vec{r}) \rangle = \int_{all\ space} f(\vec{r}) w(\vec{r}) d\vec{r}$ . We have the conjecture that in the particular case of the non-linear Poisson–Boltzmann theory, the normalized net charge density weight function  $w(\vec{r})$  is one signed if the closest approach distance between all charged particles and the electrode's surface is the same. Nevertheless, in general, the characteristic properties of charged fluids beyond the Poisson–Boltzmann viewpoint, such as the ionic size asymmetry, the ionic excluded volume effects, polarization effects, and ionic specific adsorption, may promote the appearance of oscillations of the net charge local density per unit volume, and, as a result, the weight function  $w(\vec{r})$  may display both negative and positive signs as a function of the distance to the surface of the charged electrode, which, in turn, can lead to a non-monotonic behavior of the averaged quantity.

The expected value of the bare electrostatic potential  $V(\vec{r})$  produced by a planar, a cylindrical, or a spherical charged electrode immersed in continuum dielectric solvent [see Eqs. (1)–(3)] can be calculated in the whole space regarding the normalized net charge density weight function  $w(\vec{r})$  in the corresponding geometry yielding  $\langle V(\vec{r}) \rangle = \int_{all\ space} V(\vec{r}) w(\vec{r}) d\vec{r} = -\psi_0$ . Specifically, in planar geometry, let us consider an infinite solid charged hard wall with homogeneous surface charge density  $\sigma_0$ . The surface charge density and mean electrostatic potential at the electrode's surface can be written as<sup>3</sup>  $\sigma_0 = -\int_0^\infty \rho_c(x) dx$  and  $\psi_0 = -\frac{1}{\varepsilon} \int_0^\infty x \rho_c(x) dx$ , respectively. The expected value of  $V_{wall}(x)$  can be written as  $\langle V_{wall}(x) \rangle = \int_0^\infty -\frac{\sigma_0 x}{\varepsilon} w(x) A dx = \frac{\int_0^\infty \rho_c(x) x dx}{\int_0^\infty \rho_c(x) A dx}$  is the normalized net charge density weight function in planar geometry,  $d\vec{r} = A dx$ , and  $A$  is the area of a section of the infinite planar electrode. From these equations, it is possible to write  $\langle V_{wall}(x) \rangle = -\frac{\sigma_0}{\varepsilon} \langle x \rangle = -\psi_0$ . If in this last equation the mean electrostatic potential at the surface  $\psi_0$  is written in terms of the surface charge density  $\sigma_0$  and the capacitive compactness  $\tau_c$  via Eq. (4), we obtain  $\langle V_{wall}(x) \rangle = -\frac{\sigma_0}{\varepsilon} \tau_c$ , which corresponds to  $V_{wall}(x = \tau_c)$ . As a result, we observe that  $\tau_c = \langle x \rangle$ , which is an alternative definition of the capacitive

compactness in planar geometry. Analogously, it is possible to show that  $\langle V_{cylinder}(\rho) \rangle = V_{cylinder}(\rho = \tau_c)$  and  $\langle V_{sphere}(r) \rangle = V_{sphere}(r = \tau_c)$ , wherefrom we can write the following alternative definitions of the capacitive compactness:  $\tau_c = R_{cyl} \exp(\ln(\frac{\rho}{R_{cyl}}))$  and  $\tau_c = \langle \frac{1}{r} \rangle^{-1}$  in cylindrical and spherical geometries, respectively. The above alternative definitions of the capacitive compactness are based on general electrostatics, and they are suitable to be used with modern liquid theories and accurate molecular simulations beyond the classical non-linear Poisson–Boltzmann theory in order to include the effects of the colloidal surface, ion correlations, ionic excluded volume effects, polarization effects, and ionic specific adsorption.

The explicit and detailed derivations in cylindrical and spherical geometries have been included in the [supplementary material](#).

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## DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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