

Correction to "Simulation of an Electrical Double Layer Model with a Low Dielectric Layer between the Electrode and the Electrolyte"

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Supporting Information

In a recent paper,¹ we reported a Monte Carlo (MC) simulation study on the properties of a model double layer with an inner layer (of width $\delta = 3$ Å) introduced between the electrode and the electrolyte (the diffuse layer). The ions were not allowed to enter the inner layer. We used different dielectric constants for the electrode ($\epsilon_1 \rightarrow \infty$), the inner layer (ϵ_2), and the diffuse layer ($\epsilon_3 = 80$). The double layer geometry is usually simulated in a planar geometry, where periodic boundary conditions are applied in the dimensions parallel to the electrode surface. This requires taking the effect of charges outside the central simulation cell into account in order to mimic an infinite homogeneous system in those dimensions. We used the charged sheet method² to handle these long-range corrections.

In the case of the three dielectric slabs geometry, however, extra care must be taken to collect all the polarization charges induced on the $\epsilon_1|\epsilon_2$ and $\epsilon_2|\epsilon_3$ dielectric boundaries. The polarization charge is computed by our Induced Charge Computation (ICC) method,³ which is a numerical procedure that considers only a finite segment of the dielectric boundary cut out by the central simulation cell (note that there are faster ways to handle this electrostatic problem; see the work of dos Santos and Levin⁴ and references therein). Corrections to the polarization charges that fall outside the simulation cell must be included, however, in order to achieve charge neutrality in the bulk region in the middle of the simulation domain. The corrections were computed by taking fundamentally well-established values of the total polarization charges (obtained from Gauss's law) and deducting the value given by ICC.

The total induced charges (sum rules), however, have been reported erroneously in our paper (eqs 7, 8, and 29).¹ The correct sum rules are

$$\alpha_1(0) = \alpha_1(\delta) = \alpha_1(\infty) = \frac{\epsilon_2 - \epsilon_1}{\epsilon_3 + \epsilon_1} \frac{1}{\epsilon_2} \quad (1)$$

$$\alpha_2(0) = \alpha_2(\delta) = -\frac{\epsilon_3 - \epsilon_2}{\epsilon_3 + \epsilon_1} \frac{1}{\epsilon_2} \quad (2)$$

$$\alpha_2(\infty) = \frac{\epsilon_1 \epsilon_3 - \epsilon_2}{\epsilon_2 \epsilon_3 + \epsilon_1 \epsilon_3} \frac{1}{\epsilon_3} \quad (3)$$

where $\alpha_i(0) = \alpha_i(\delta)$ and $\alpha_i(\infty)$ is the total polarization charge at interface i (1 and 2 denote the $\epsilon_1|\epsilon_2$ and $\epsilon_2|\epsilon_3$ boundaries, respectively) induced by a unit charge in the $0 < x < \delta$ and $\delta < x$ regions, respectively. For the special case of $\epsilon_1 \rightarrow \infty$, they are

$$\alpha_1(0) = \alpha_1(\delta) = \alpha_1(\infty) = -\frac{1}{\epsilon_2} \quad (4)$$

$$\alpha_2(0) = \alpha_2(\delta) = 0 \quad (5)$$

$$\alpha_2(\infty) = \frac{1}{\epsilon_2} - \frac{1}{\epsilon_3} \quad (6)$$

These errors influence our results and conclusions in the following way. All the general equations describing our procedure (eqs 1–6 and 9–22) are correct. The total surface charges on the dielectric boundaries (eqs 23 and 24 in ref 1), however, are influenced by the error. The correct equations are

$$\sigma_1 = \frac{\sigma}{\epsilon_2} \quad (7)$$

and

$$\sigma_2 = \sigma \left(\frac{1}{\epsilon_3} - \frac{1}{\epsilon_2} \right) \quad (8)$$

where σ is the electrode charge. These values are independent of ϵ_1 . The sum of these two terms ($\sigma_1 + \sigma_2 = 1/\epsilon_3$) is the same as in ref 1. Because the ions are restricted to the ϵ_3 region, the $\sigma_1 + \sigma_2$ sum determines the corrections to the induced charges. Because the sum is uninfluenced by the error, the MC simulations were correct and provided appropriate concentration profiles. The electric field and potential profiles ($E(x)$ and $\psi(x)$), however, are influenced by the error, but only in the inner layer. These profiles are calculated from eqs 25 and 26 of ref 1. Since $E(x)$ and $\psi(x)$ in the $x < \delta$ region depend on $\sigma_1 + \sigma_2$, they are correct in the contact layer ($\delta < x < \delta + R$, where R is the radius of the ions) and in the diffuse layer ($x > \delta + R$). They are incorrect, however, in the inner layer ($0 < x < \delta$), where they depend on σ_1 . The correct electric field (E_δ), potential drop ($\Delta\psi_\delta$), and the corresponding inverse capacitance (C_δ^{-1}) in the inner layer are larger than those reported in ref 1

$$C_\delta^{-1} = \frac{\Delta\psi_\delta}{\sigma} = -\frac{E_\delta \delta}{\sigma} = \frac{\sigma_1 \delta / \epsilon_0}{\sigma} = \frac{\delta}{\epsilon_0 \epsilon_2} \quad (9)$$

as opposed to the erroneous result $C_\delta^{-1} = 2\delta/\epsilon_0(\epsilon_2 + \epsilon_3)$ (eq 28 in ref 1).

Our electric field and potential profiles are influenced in a way that $E(x)$ is larger (in absolute value) in the inner layer and that the slope of $\psi(x)$ is larger (in absolute value) in the inner layer compared to the wrong data (note that the potential profiles as appeared in the original paper¹ should be divided by 10). Here we show only one example (Figure 1) to illustrate

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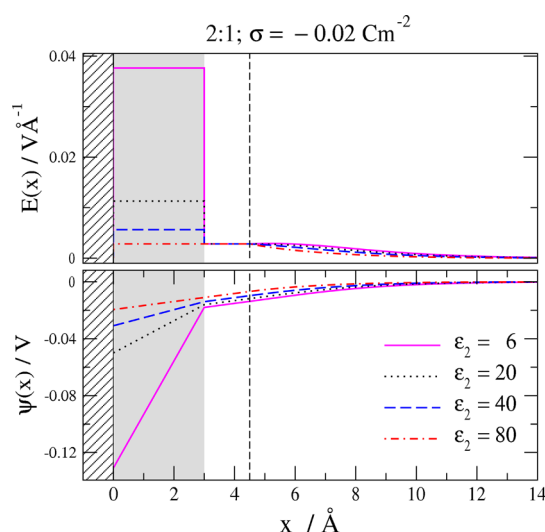


Figure 1. (Old Figure 10) Electric field and potential profiles for the DL of a 2:1 electrolyte formed near a ϵ_2 inner layer for electrode charge $\sigma = -0.02 \text{ Cm}^{-2}$ for different values of ϵ_2 .

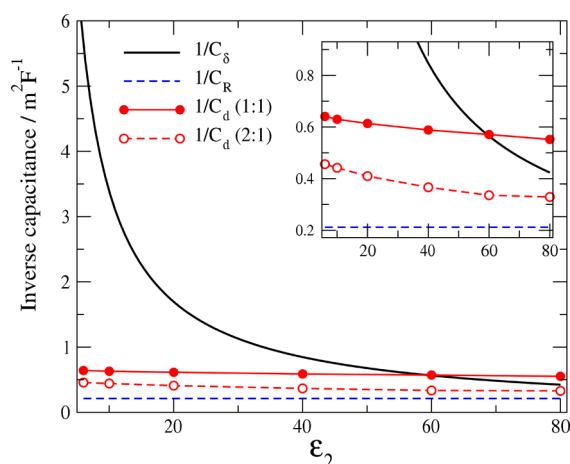


Figure 2. (Old Figure 12) The terms of the inverse capacitance associated with the inner layer (C_δ^{-1}), the contact layer (C_R^{-1}), and the diffuse layer (C_d^{-1}) as functions of the inner layer dielectric constant.

this (all the other corrected figures are found in the [Supporting Information](#)). The corrected equations confirm the traditional result that the capacitance of the inner layer scales with ϵ_2 . We erroneously stated that the traditional result is wrong. The discussion around eqs 29 and 30 and the first main conclusion in the Summary of ref 1, therefore, are wrong.

Our other main conclusion, however, that the diffuse layer capacitance is influenced by the value of ϵ_2 remains correct, although this dependence is smaller in light of the new data. For a typical value of the inner layer dielectric constant ($\epsilon_2 = 6$), for example, the inner layer capacitance dominates over the diffuse layer capacitance. For larger values of ϵ_2 , however, this dominance is weaker as shown in [Figure 2](#). The influence of ϵ_2 is better seen in the inset of this figure.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpcc.5b07719](https://doi.org/10.1021/acs.jpcc.5b07719).

The derivation of the sum rules and the corrected figures (PDF)

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■ REFERENCES

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