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A Hidden Assumption of Gouy-Chapman-Stern Model

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J Huang conceived and supervised this work. CK Li performed the mathematical derivation and calculation. J Huang and CK Li wrote this manuscript.

This PDF file includes:

Main Text
Figures 1 to 2

Abstract

Understanding the double layer at the electrode-electrolyte interface is of fundamental importance to electrochemistry, and also lays the basis for rational design of energy storage and conversion technologies. The prevailing Gouy-Chapman-Stern (GCS) model and its many derivatives invariably picture the double layer as a serial connection of a compact layer and a diffuse layer. We unravel that these models based on the serial connection tacitly prescribe a zero potential gradient at the solution-side boundary. This assumption is generally invalid, resulting in an incorrect expression for the double-layer impedance. Amendment of this deficiency gives out a revised analytical expression for the double-layer impedance at the potential of zero charge with new features. Specifically, the contribution of the compact layer now shows frequency dispersion. The deviation between the original and amended models is greater when the double layer is confined in narrower space. This work changes our basic understanding of double layer model and its impedance response.

Significance Statement

The double layer at the electrode-electrolyte interface is the cornerstone of the edifice of electrochemistry, and also arouses wide interest in various fields of physical sciences. Many theoretical models describe the double layer as a serial connection of a compact layer and a diffuse layer, originated from the celebrated Gouy-Chapman-Stern model. However, the assumption hidden in such serial connection has not been well acknowledged. Herein, we unravel that the serial connection assumes a zero potential gradient at the solution-side boundary, which is invalid under dynamic conditions. We amend this fundamental inconsistency and the amended model brings out new features that change our understanding of the double layer model and its impedance response.

Main Text

Research on the electrochemical double layer (EDL) has a long history dating back to the age of Helmholtz who viewed the EDL as a planar capacitor. Thereafter, a rich body of theoretical models have been developed.[1-4] Amongst them, the Gouy-Chapman-Stern (GCS) model is quintessential.[5-7] Improvements over the GCS model consider ion size,[8,9] specific adsorption,[10] solvent polarization,[11,12] nonlocal short-range correlations[13] and metal electronic effects.[14]

The GCS model is schematically illustrated in Figure 1 (a). The EDL is composed of a compact layer between the metal surface and the Helmholtz plane (HP), and a diffuse layer stretching toward the solution bulk. The HP is designated as the closest plane where solution species can approach the electrode surface, and the distance between the metal surface and the HP is usually ca. several Å. The diffuse layer is a non-electroneutral region where electrostatic interactions dominate over thermal motion, resulting in accumulation of counterions with charge of the sign opposite to the metal surface charge and depletion of coions with charge of the same sign. The diffuse layer has a characteristic thickness, termed the Debye length and given by, $\lambda_D = \sqrt{\epsilon_S RT / (2F^2 c_0)}$ (ϵ_S is the dielectric constant of the bulk solution, c_0 the bulk concentration, and other symbols have usual meanings), which is ca. 10 nm for an electrolyte solution with a concentration of 1 mM.

The impedance variant of the GCS model is shown in Figure 1. Within the electric circuit representation, the EDL is modeled as a serial connection of a compact capacitor, $C_H = \epsilon_H / \delta_H$ (ϵ_H and δ_H are the permittivity and thickness of the compact layer), and a diffuse layer part, Z_{GC} . It follows naturally to write the double layer impedance as,

$$Z_{dl} = \frac{1}{j\omega C_H} + Z_{GC} \quad (1)$$

with ω being the angular frequency of the perturbation. Most often, Z_{GC} is simplified as the impedance of a pure capacitor, $Z_{GC} = 1/j\omega C_{GC}$, [15] with,

$$C_{GC} = \frac{\epsilon_s}{\lambda_D} \cosh\left(\frac{U - U_{pzc}}{2}\right) \quad (2)$$

Here, $U = F\phi_M/RT$ is the electrode potential normalized with respect to thermal voltage, and U_{pzc} is the normalized potential of zero charge. Rigorously speaking, Z_{GC} may not be purely capacitive but show frequency dispersion, which will become clear later.

Herein, we will show that the canonical relation given in eqn (1) relies on a tacit assumption that the potential gradient at the solution-side boundary is zero, which is generally invalid, for instance, when the double layer is confined in narrow space or the double layer is under dynamic conditions. Removing this invalid assumption gives rise to a revised expression for the double-layer impedance, where the compact layer contribution is not given by $(j\omega C_H)^{-1}$ as in eqn(1), but a frequency-dependent one. The inaccuracy arose from the invalid assumption is more significant for double layers confined in narrower space.

Consider the simplest case where the electrolyte is symmetrical, charge carriers are monovalent and have the identical diffusion coefficient, denoted D . The EDL is described by the Poisson-Nernst-Planck (PNP) theory in its standard form,

$$\frac{\partial C_p}{\partial \tau} = \frac{\partial}{\partial X} \left(\frac{\partial C_p}{\partial X} + C_p \frac{\partial U}{\partial X} \right) \quad (3)$$

$$\frac{\partial C_n}{\partial \tau} = \frac{\partial}{\partial X} \left(\frac{\partial C_n}{\partial X} - C_n \frac{\partial U}{\partial X} \right) \quad (4)$$

$$0 = \frac{\partial^2 U}{\partial X^2} + \frac{1}{2}(C_p - C_n) \quad (5)$$

Here, C_p and C_n are the concentration of positive and negative charge carriers referenced to the bulk concentration, X is the spatial coordinate normalized with respect to λ_D , $\tau = tD/\lambda_D^2$ is the dimensionless time. The PNP theory is closed by following boundary conditions. In solution bulk, $X = L$, $C_p = C_n = 1$ and

the potential is taken as the reference, namely, $U = 0$. At the HP, $X = 0$, no reaction is considered, prescribing zero fluxes of positive and negative charge carriers,

$$\frac{\partial C_p}{\partial X} + C_p \frac{\partial U}{\partial X} = 0 \quad (6)$$

$$\frac{\partial C_n}{\partial X} - C_n \frac{\partial U}{\partial X} = 0 \quad (7)$$

The potential at the HP is not an independent variable, but an implicit function of the electrode potential, U_M , an independent variable in experiments, given by,

$$\frac{\partial U}{\partial X} + \frac{\epsilon_H \lambda_D}{\epsilon_s \delta_H} (U_M - U_{pzc} - U) = 0 \quad (8)$$

which is readily obtained from the notion that potential distribution in the compact layer is linear, and that potential gradients at the HP on two sides are correlated as, $\epsilon_s \frac{\partial U}{\partial X} (X \rightarrow 0^+) = \epsilon_H \frac{\partial U}{\partial X} (X \rightarrow 0^-)$; both are guaranteed by the Gauss law as there is no net charge in the compact layer or at the HP, respectively.

By Fourier transform, eqn (3)-(5) can be analytically solved when the metal is initially held at U_{pzc} , namely, $C_p = C_n = 1$ and $U = 0$. With algebra manipulations detailed in the Supporting Materials, we obtain the following analytical solution,

$$Z_{dl} = \frac{1}{j\omega C_H} \frac{1 + \Omega}{1 - \text{sech}(L\sqrt{1 + \Omega})} + \frac{1}{j\omega C_{GC}^0} \frac{\frac{\tanh(L\sqrt{1 + \Omega})}{\sqrt{1 + \Omega}} + L\Omega}{1 - \text{sech}(L\sqrt{1 + \Omega})} \quad (9)$$

with $\Omega = j\omega \lambda_D^2 / D$ being the dimensionless imaginary frequency, and $C_{GC}^0 = \epsilon_s / \lambda_D$ the Gouy-Chapman capacitance at the pzc.

In the low frequency limit, $\omega \rightarrow 0$, we simply eqn(9) to,

$$Z_{dl} = \frac{1}{j\omega C_H} \frac{1}{1 - \text{sech}(L)} + \frac{1}{j\omega C_{GC}^0} \frac{\tanh(L)}{1 - \text{sech}(L)} \quad (10)$$

which is further reduced back to the classical GCS model,

$$Z_{dl} = \frac{1}{j\omega C_H} + \frac{1}{j\omega C_{GC}^0} \quad (11)$$

when $L \rightarrow \infty$, namely, when the solution phase is semi-infinite.

Compared to eqn(1), eqn(9) indicates that the contribution of the compact layer to Z_{dl} is not purely capacitive, given by $(j\omega C_H)^{-1}$, but shows frequency dispersion, which can be effectively described by a frequency-dependent capacitance,

$$C_H^{eff} = C_H \frac{1 - \text{sech}(L\sqrt{1 + \Omega})}{1 + \Omega} \quad (12)$$

which is asymptotic to C_H when $\omega \rightarrow 0$ and $L \rightarrow \infty$.

It now becomes clear that the oft-used equivalent electric circuit based on the GCS model, depicted in Figure 1, is, rigorously speaking, invalid. The underlying cause of this fundamental error lies in the boundary condition for the PNP equation that is tacitly assumed in the GCS model. The serial connection of the compact layer and the diffuse layer implies that,

$$\frac{\epsilon_H}{\delta_H} \frac{\partial(\phi_M - \phi_{pzc} - \phi_H)}{\partial t} = - \frac{\partial q_{GC}}{\partial t} \quad (13)$$

where ϕ_H is the potential at the HP and q_{GC} the excess charge density stored in the diffuse layer. Equation (12) is transformed to,

$$\frac{Q_{GC}}{2} + \frac{\epsilon_H \lambda_D}{\epsilon_s \delta_H} (U_M - U_{pzc} - U) = 0 \quad (14)$$

where $Q_{GC} = 2q_{GC} F \lambda_D / RT \epsilon_s$ is the normalized excess charge density. The boundary conditions expressed in eqn (14) and (8) are equivalent only if,

$$Q_{GC} = 2 \frac{\partial U}{\partial X} (X \rightarrow 0^+) \quad (15)$$

which, as readily seen from eqn(5), relies on the assumption that,

$$\frac{\partial U}{\partial X} (X = L) = 0 \quad (16)$$

However, a zero potential gradient at $X = L$ is not guaranteed, generally. From the PNP equation, the Fourier-transformed potential gradient at the $X = L$ is given by,

$$\frac{\partial U}{\partial X} (X = L) = -U_M \frac{\text{sech}(L\sqrt{1+\Omega}) + \Omega}{\frac{C_{GC}^0}{C_H} \sqrt{1+\Omega} + \frac{\tanh(L\sqrt{1+\Omega})}{\sqrt{1+\Omega}} + L\Omega} \quad (17)$$

which becomes zero only when $\omega \rightarrow 0$ and $L \rightarrow \infty$. Otherwise, eqn(16) is not satisfied and the boundary condition written in eqn(14) is not true.

The impedance expression with eqn (14) as the boundary condition at the HP is written as,

$$Z_{dl}^{GCS} = \frac{1}{j\omega C_H} + \frac{1}{j\omega C_{GC}^0} \frac{\frac{\tanh(L\sqrt{1+\Omega})}{\sqrt{1+\Omega}} + L\Omega}{1 - \text{sech}(L\sqrt{1+\Omega})} \quad (18)$$

which varies from eqn(9) by a difference of,

$$\Delta Z = Z_{dl} - Z_{dl}^{GCS} = \frac{1}{j\omega C_H} \frac{\Omega + \text{sech}(L\sqrt{1+\Omega})}{1 - \text{sech}(L\sqrt{1+\Omega})} \quad (19)$$

which becomes zero only when $\omega \rightarrow 0$ and $L \rightarrow \infty$.

In the high frequency limit, $\omega \rightarrow \infty$, ΔZ is asymptotic to, $\Delta Z(\omega \rightarrow \infty) = \lambda_D^2 / DC_H$. Normalizing $\Delta Z(\omega \rightarrow \infty)$ with respect to the high-frequency asymptotic value of Z_{dl} , $Z_{dl}(\omega \rightarrow \infty) = \lambda_D^2 / DC_H + L\lambda_D^2 / DC_{GC}^0$ leads to,

$$\Delta Z^{nd}(\omega \rightarrow \infty) = (1 + L\xi)^{-1} \quad (20)$$

with $\xi = C_H / C_{GC}^0$. $\Delta Z^{nd}(\omega \rightarrow \infty)$ approaches zero when $L \rightarrow \infty$, and grows when L decreases.

In the low frequency limit, $\omega \rightarrow 0$, ΔZ is asymptotic to, $\Delta Z(\omega \rightarrow 0) = (j\omega C_H (\cosh(L) - 1))^{-1}$, and the dimensionless counterpart normalized with respect to the high-frequency asymptotic value of Z_{dl} expressed in eqn(10), reads,

$$\Delta Z^{nd}(\omega \rightarrow 0) = \frac{\text{sech}(L)}{1 + \xi \cdot \tanh(L)} \quad (21)$$

which approaches zero when $L \rightarrow \infty$, and grows when L decreases, namely, when the double layer is confined in narrower space.

As the magnitudes of Z_{dl}^{GCS} , Z_{dl} , and their difference, ΔZ , are infinitive when $\omega \rightarrow 0$, we define a dimensionless complex capacitance as, $C(\omega) = \left(j\omega C_H (Z(\omega) - Z(\omega \rightarrow \infty)) \right)^{-1}$. Figure 2 shows the Nyquist plots of $C(\omega)$, consisting of an arc in low frequency range and an inclined line in high frequency range. As regards Z_{dl}^{GCS} , $C_{dl}^{GCS}(\omega \rightarrow 0) = (1 + \xi \tanh(L) / (1 - \text{sech}(L)))^{-1}$, and $C_{dl}^{GCS}(\omega \rightarrow \infty) = 1$. As regards for Z_{dl} , $C_{dl}(\omega \rightarrow 0) = (1 - \text{sech}(L)) / (1 + \xi \tanh(L))$, and $C(\omega \rightarrow \infty) = 1$. These two $C(\omega)$ complex functions converge in high frequency range but differ in low frequency range, as shown in Figure 2.

In conclusion, we have revealed that the serial connection involved in vast majority of double layer models requires that the potential gradient at the solution-side boundary is zero, which is generally invalid. This fundamental inconsistency has been amended, herein, resulting in a new expression of double-layer impedance with new features that change our understanding of the impedance response of the double layer.

Acknowledgments

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Figures

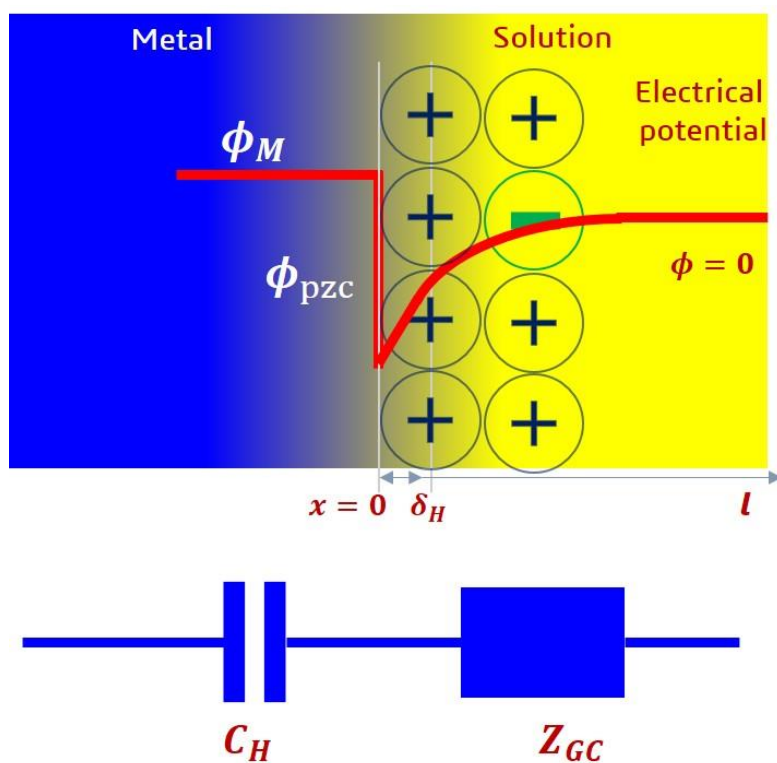


Figure 1. Schematic illustration of the double layer and its equivalent electric circuit according to the Gouy-Chapman-Stern model.

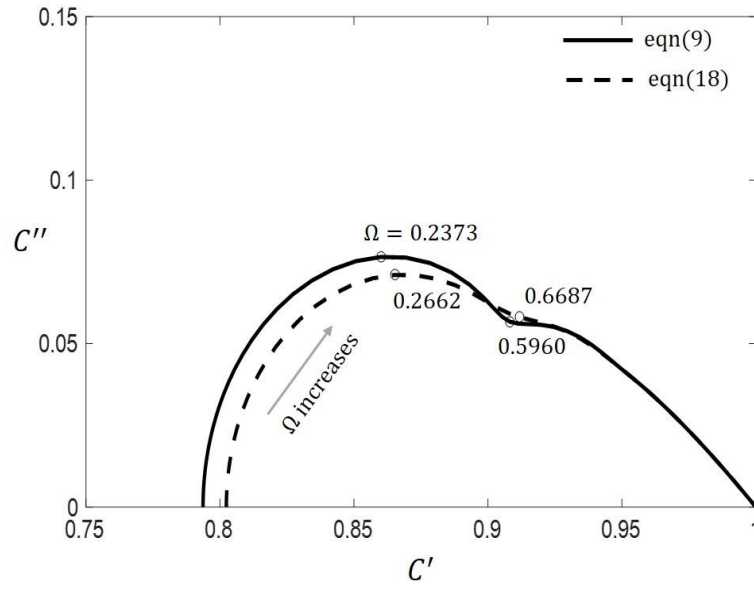


Figure 2. The dimensionless complex capacitance obtained from eqn(9) and eqn(18). Model parameters are: $c_0 = 0.1 \text{ mol} \cdot \text{L}^{-1}$, $\delta_H = 0.5 \text{ nm}$, $L = 5\lambda_D$, $D = 1 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$, $\epsilon_H = 10\epsilon_0$, $\epsilon_s = 80\epsilon_0$, $\epsilon_0 = 8.85 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$, $F = 96485 \text{ C} \cdot \text{m}^{-1}$, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$, $T = 298 \text{ K}$, $f = 10^{-4} \text{ Hz} \sim 10^{14} \text{ Hz}$.