Modeling the Electric Double Layer in Finite Electrolyte Solutions

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INTRODUCTION: Electric double layers (EDLs) play a crucial role in many biophysical processes involving charged molecules (*e.g*. proteins, DNA), but are often a limiting factor in technological applications where charged conductors are brought in contact with electrolyte solutions. They form when charges in the conductor's surface layer (source charges) attract oppositely charged ionic species, which, in turn, modifies the electrostatic field generated by the source charges alone.

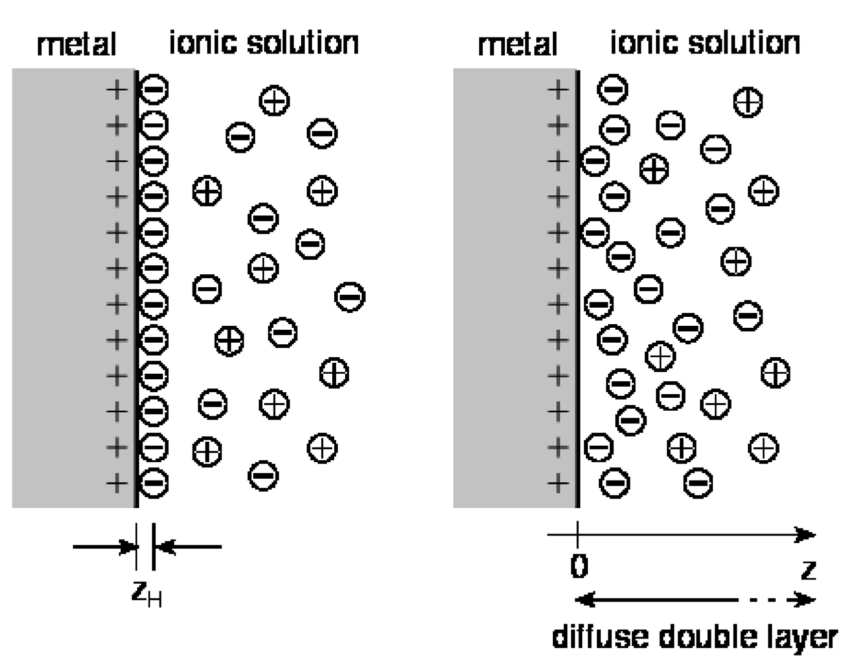

Figure 1. Simple EDL models. The Helmholtz model (**left**) assumes a compact layer of tightly bound counterions, while the Gouy-Chapman model (**right**) predicts a diffuse layer of counterions in solution.

POISSON-BOLTZMANN (PB) THEORY: Assuming a Boltzmann distribution, the particle density for ionic species *i* at distance *z* from a planar electrode at potential ϕ_0 is

$$n_i(z) = n_i^* \exp\left(-\frac{\nu_i e_0[\phi(z)-\phi_i^*]}{kT}\right),$$

where $$\phi_i^* = -\frac{kT}{\nu_i e_0}\ln\left[\frac{1}{d}\int_0^d \exp\left(-\frac{\nu_i e_0 \phi(z)}{kT}\right) dz\right].$$

n_i^*	bulk (average) ion density
ν_i	ion valency
e_0	elementary charge
$\phi(z)$	electrostatic potential at distance z
ϕ_i^*	electrostatic potential where $n_i(z) = n_i^*$
k	Boltzmann constant
T	absolute temperate
d	thickness of solution layer

GOUY-CHAPMAN (GC) THEORY:

- binary, symmetric electrolyte: $\nu_\oplus = -\nu_\ominus = \nu$
  $n_\oplus^* = n_\ominus^* = n^*$
- $n_i(z) = n_i^*$ at same *z* for *all* ionic species ("bulk")
  $\Longrightarrow\ \phi_i^* = \phi_j^* = \cdots = \phi^*$, *usually set to* 0.

Inserting the charge density

$$\rho(z) = \sum_i \nu_i e_0 n^* \exp\left(-\frac{\nu_i e_0[\phi(z)-\phi^*]}{kT}\right)$$

into Poisson's equation $\nabla^2\phi = -\rho/\epsilon$ leads to GC equation:

$$\frac{d^2\phi}{dz^2} = \frac{2n^*\nu e_0}{\epsilon}\sinh\frac{\nu e_0(\phi-\phi^*)}{kT}$$

Analytical solution:

$$\tanh\frac{u-u^*}{4} = \left(\tanh\frac{u_0-u^*}{4}\right)e^{-\kappa z} \quad \text{for } z < z^*$$

u	normalized potential $u(z) \equiv \frac{\nu e_0 \phi(z)}{kT}$
κ	reciprocal Debye length $\kappa = [2n^*\nu^2 e_0^2/(\epsilon kT)]^{1/2}$

PROBLEM: The implicit assumption that the reference potentials ϕ_i^* are *the same* for all ionic species ("bottomless bulk") leads to **unrealistic results** when the number of source charges is no longer small compared to the number of ionic charges (*i.e*. high applied potentials, low solution volumes, and/or low ion concentrations).

COMPUTATIONAL METHODS: To avoid this problem, we use the accurate charge density for a binary, symmetric electrolyte

$$\rho(z) = \sum_i \nu_i e_0 n^* \exp\left(-\frac{\nu_i e_0[\phi(z)-\phi_i^*]}{kT}\right),$$

which can be rewritten as

$$\rho(z) = n^*\nu e_0 d\left[\frac{e^{-u(z)}}{Z_\oplus} - \frac{e^{+u(z)}}{Z_\ominus}\right]$$

where $$Z_\pm = \int_0^d e^{\mp u(z)}\, dz.$$

These last two equations were used in the **Electrostatics module** (*es*) and solved in COMSOL Multiphysics®.

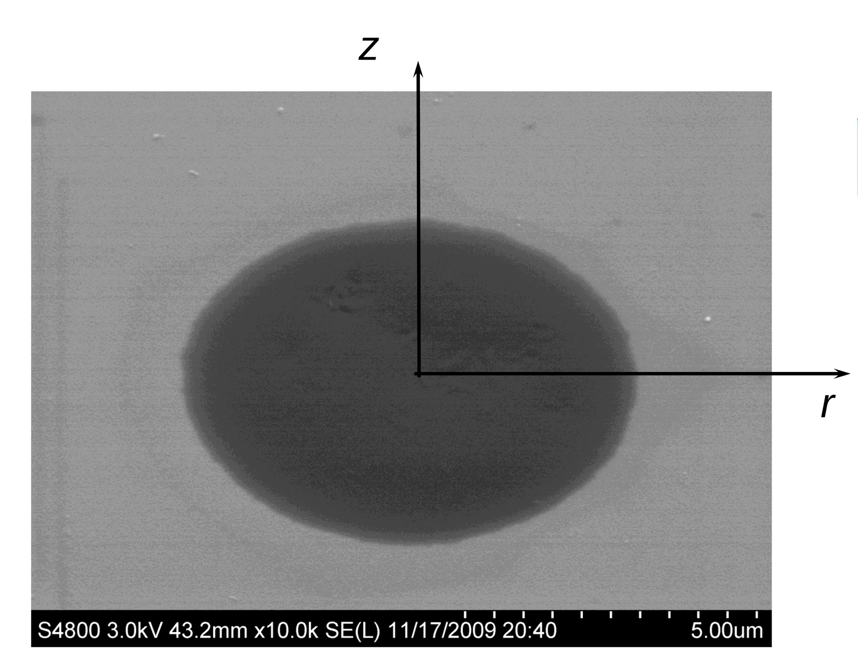

Figure 2. Bottom electrode. Uncoated area: glass; thickness of metal coating (Au/Pd): 5 nm.

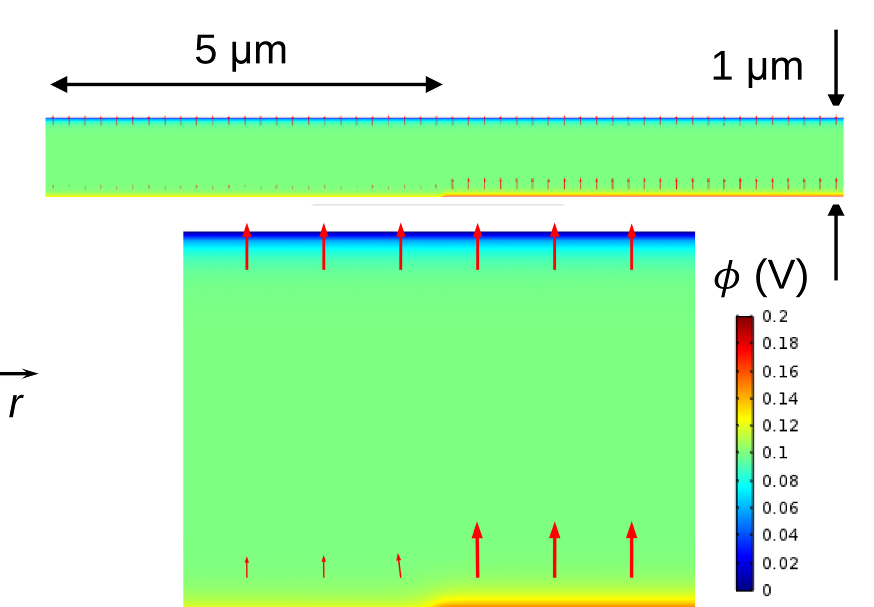

Figure 3. Model geometry (2D axisym.) and electrostatic potential in 10^{-4} M electrolyte at 20 °C (bottom electrode: 0.2 V; top: 0 V). Charge density on glass surface: 5000 $e_0/\mu\text{m}^2$.

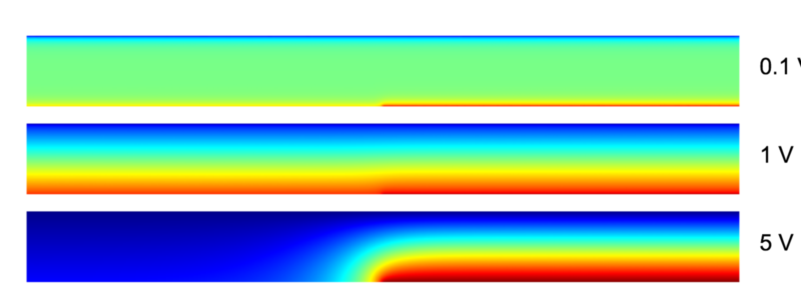

Figure 4 (above). Penetration of the electrostatic field into the solution with increasing applied potential.

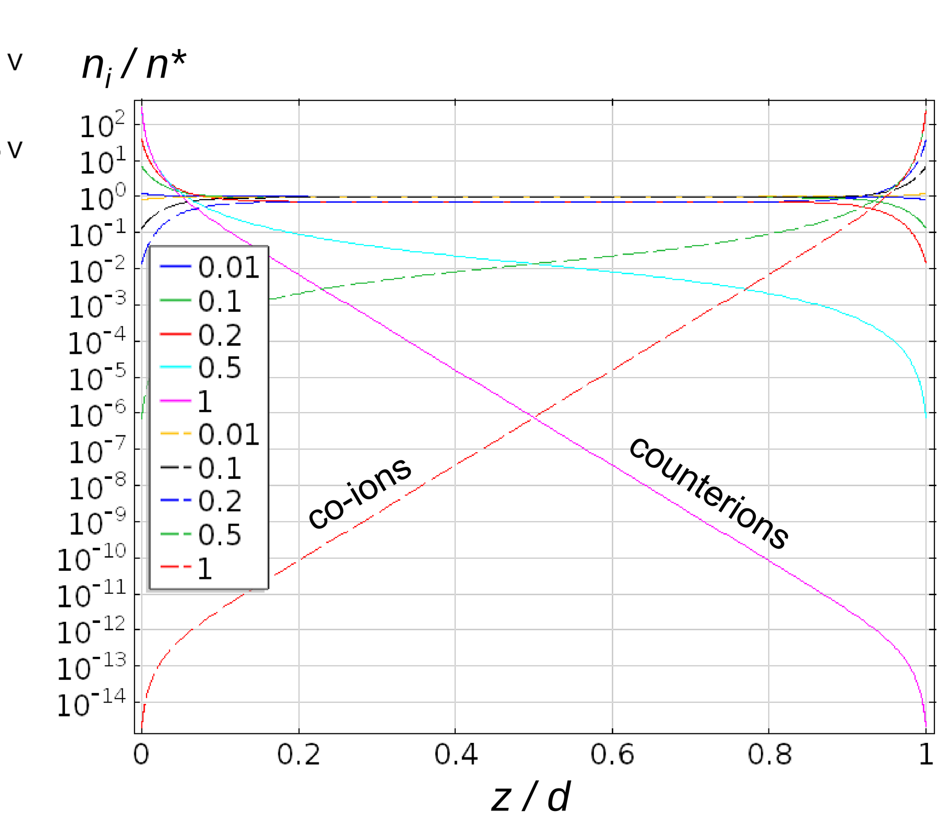

Figure 5 (right). Ion concentration profiles at different applied potentials.

CONCLUSIONS: In many cases of interest, such as in microfluidic device applications, the approximation of a "bottomless bulk" solution is not justified, and the classical GC equations fail to adequately describe the EDL. In these cases, *finite* GC theory must be employed using numerical simulations.

REFERENCES:

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