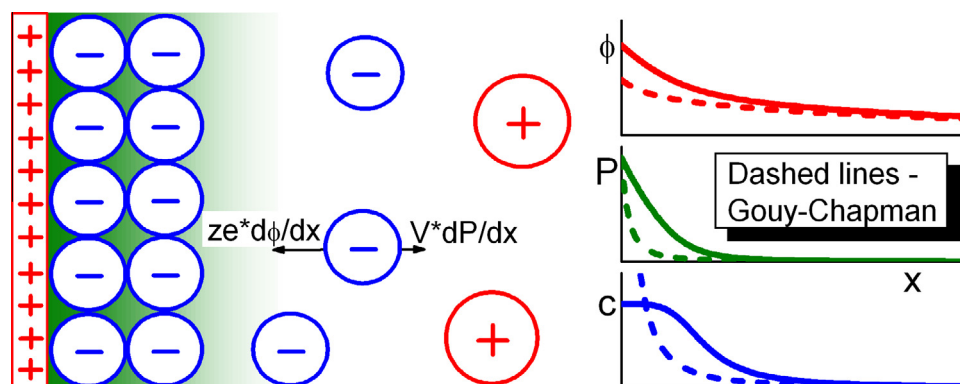# The interaction of electric field and hydrostatic pressure in an electrical double layer: A simple "first principle" model that accounts for the finite sizes of counterions

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GRAPHICAL ABSTRACT

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ABSTRACT

A simple model describing the influence of ion size in the electrical double layer (EDL) near a highly charged plane is proposed here. This model is based on the Poisson–Boltzmann equation with a single additional term representing the mechanical response of bulky ions to hydrostatic pressure. This pressure is produced by Coulomb forces, and increases to several kilobars in the vicinity of a highly charged plane. Numerical simulations demonstrate close packing as a limit for counterion concentrations. Differential capacity reaches maximum at 0.1–0.3 V and remains reasonably small in wide range of potentials.

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1. Introduction

One of the most widely used descriptions of the interaction between charged interfaces and the surrounding electrolyte solution is the Gouy–Chapman (GC) model [1] that uses a mean field approach, assuming point-like ions within an isotropic solvent that are affected by the mean electric field and remain in thermodynamic equilibrium with the bulk solution. The GC model has successfully predicted the electric potential distribution and the resulting surface forces near a charged surface. However, the GC model is found to greatly overestimate the differential capacity of a metallic electrode, easily observable experimentally.

Since the Poisson–Boltzmann (PB) equation does not take into account the finite sizes of ions, the calculated concentration of counter-ions close to a highly charged surface can exceed the maximum possible packing density of hydrated ions by one or more orders of magnitude. Various approaches have been proposed in order to introduce steric effects into the original GC model and improve consistency with experiment. One of the first such attempts was a "Stern layer" modification [1] of the GC model in which counterions were excluded from the first molecular layer close to the charged surface. Unfortunately, the resultant Gouy–Chapman–Stern model contains parameters that cannot be obtained by independent experiments.

Numerous later modifications rely on Monte Carlo simulations [2–5], or a "hypernetted chain" formalism [6,7]. In neither case is the mean field approximation used, which is a step forward compared with the GC approach, but at the cost of increased complexity. Models utilizing modified PB equations (MPB) to take into account finite ion size [8–14] may successfully describe experimental phenomena. It should be noted that, with certain limitations, MPB equations have been solved analytically [8]. MPB model was applied to spherical EDL demonstrating essential size effect for large counterions [15].

As far as the author is aware, most of the existing EDL models introduce ion finite size by consideration of excluded volume and steric interactions between ions. However, there exists another physical effect capable of accounting for finite ion size, namely the existence of significant non-uniform hydrostatic pressure within the EDL that tends to exclude bulky ions.

Hydrostatic pressure, generated by Coulomb forces within the EDL, is usually neglected, or at least not explicitly treated, by existing models. There are only a few exceptions, as far as we know: The first is the mean field model of Woelki and Kohler [16,17], which, unfortunately, is in poor agreement with experiment. Another approach to electrically generated hydrostatic pressure was introduced recently by Dreyer et al. [18,19], although resolution of important competing effects and their independent comparison with experiment, as a function of ion size, would appear to be rather complicated. Biesheuvel and Spruijt [20,21] include osmotic and hydrostatic pressure in a theory for transport of ions and colloids.

The existence of electrostatically generated pressure is widely recognized for typical electrical capacitors, in which two metallic electrodes are separated by a dielectric material that is affected by anisotropic mechanical stress for a solid dielectric, or by isotropic (hydrostatic) pressure in a liquid dielectric. Because the EDL near a charged plane is analogous to a capacitor in which the distributed counter-ion charges play the role of an oppositely charged plate, a pressure due to electrostatic forces should exist within the EDL. Likewise, one can envision the hydrostatic pressure within the EDL induced by a monolayer of charged amphiphilic molecules at the interface between an electrolytic solution and a gas [22,23]. Each charged molecule within such a monolayer is affected by a combination of balancing forces, since the molecule does not move. In-plane forces of various types originating from neighbouring molecules within the monolayer should be balanced, based on symmetry considerations. The remaining electrostatic force due to the effect of mean field on molecular charge, directed into the solvent, should be balanced by some other force of equal magnitude and opposite direction. Hydrostatic pressure in the EDL seems to be the single candidate for this role.

In this paper we propose a simple "first principle" model that accounts for the finite size of counter-ions. This model is an extension of the classic GC model to which has been added only the hydrostatic pressure within the EDL, and which reduces to the parent model whenever the charge density or the counterion size is vanishingly small.

2. Theoretical considerations

For a flat, charged surface in contact with a semi-infinite aqueous electrolyte solution, the original Poisson equation is:

$$\varepsilon\varepsilon_0 \nabla^2 \phi = -\rho$$

where ε is dielectric permittivity of water, ε_0 is the electrical constant, ϕ is the electrostatic potential and ρ is the charge density. Elimination of in-plane coordinates and integration gives:

$$E(x) = -\frac{1}{\varepsilon\varepsilon_0} \int_x^\infty \rho(\xi) d\xi \tag{1}$$

where x is the coordinate normal to the interface, and $E(x)$ is the electric intensity. This equation can also be obtained from the Gauss theorem. The electric potential is related to the electric intensity by:

$$\phi(x) = \int_x^\infty E(\xi) d\xi. \tag{2}$$

The charge density in Eq. (1) depends on the local concentrations, $n_i(x)$, of all types, i, of ions in the electrolyte, as well as their charges, z_i:

$$\rho(x) = e \sum_i z_i n_i(x). \tag{3}$$

Local concentrations of ions are related to their bulk concentrations using the Boltzmann equation:

$$n_i(x) = n_i(\infty) \exp[-(z_i e\phi(x) + P(x)V_i)/kT]. \tag{4}$$

with the added "hydrostatic" term, $P(x)V_i$. This latter term is the mechanical work necessary to transfer an incompressible body, in the present instance an ion having a volume, V_i, from a region of zero hydrostatic pressure (the bulk solution) to another region having hydrostatic pressure $P(x)$. The external pressure is assumed to be zero. The hydrostatic pressure at a position x in the EDL is simply the accumulated Coulomb force affecting layers of solution located to the right of x:

$$P(x) = \int_x^\infty \rho(\xi)E(\xi) d\xi = \sigma^2(x)/2\varepsilon\varepsilon_0 \tag{5}$$

where the surface charge density, $\sigma(x)$ is given by Eqs. (5) and (6). The second equality in Eq. (5) results from the Gauss theorem.

$$\sigma(x) = \int_x^\infty \rho(\xi) d\xi \tag{6}$$

Although Eqs. (1)–(6) could, in principle, be combined into one modified PB equation, the result would be cumbersome and probably impossible to solve analytically. Therefore, we will solve this set of equations numerically.

The integration procedure begins at a distant point x_0 where the electric potential is vanishingly small: $\phi(x_0) \ll kT/e$. Since the potential is relatively small throughout the entire range to the right of x_0, the GC model should be strictly valid. Thus, the surface charge density, $\sigma(x_0)$ can be found for any electrolyte composition by use of the Grahame equation:

$$\sigma^2 = 2\varepsilon\varepsilon_0 kT \sum_i n_i[\exp(-z_i e\phi/kT) - 1]$$

where n_i is the numerical bulk ionic concentration of ion type i, of charge equal to z_i [21]. Using Eqs. (4) and (5), we can calculate the hydrostatic pressure, P, the electric intensity, E, and ionic concentrations at the starting point, x_0. We then step the value of x by the increment Δx in the direction of the charged plane, calculating the values of ϕ, P and σ, using Eqs. (1)–(3) and (6). The incremental calculations are repeated until σ reaches the given surface charge density of the charged plane. The coordinate x