

MODELING OF DONNAN EQUILIBRIUM IN CHARGED POROUS MATERIALS - A SCALE TRANSITION ANALYSIS

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Summary. *Knowledge of location and magnitude of charge density, together with the pore morphology allows one to calculate the Donnan potential, characterizing ion exclusion in charged porous materials. Use of the electro-chemical potential together with Gauss' electrostatic theorem allows the computation of the ion and voltage distribution at the microscale. On the other hand, commonly used macroscopic counterparts of these equations allow the estimation of the Donnan potential and ion concentration on the macroscale. However, it turns out that the classical macroscopic equations describing phase equilibrium do not account for the non-homogeneous distribution of ion and voltage at the microscale, leading to inconsistencies in estimating the Donnan potential (at the macroscale) from microscale information. In this paper we derive a new generalized macroscopic equilibrium equation by means of volume averaging of the microscale electro-chemical potential.*

1 INTRODUCTION

A broad class of porous materials including clays, shales, polymer gels, and biological tissues are characterized by positive and/or negative charge on their surfaces [2]. The presence of surface charges leads to formation of diffuse double-layers characterized by high surface concentrations of anion or cations depending on the sign of the surface charge. In the case of phase equilibrium between a negatively charged porous material and an electrolytic solution the cation concentration is higher in the porous media phase (relative to the solution phase outside the porous material), whereas the opposite holds for anions. This phenomenon is often referred to as anion exclusion. In the following, we assume that the voltage difference $\Delta\bar{\psi}$ across an external electrolytic solution and the charged porous material is caused only by electrostatic effects. This voltage difference is commonly referred to as the Donnan Potential (E_{Don}).

The solution of the classic Poisson-Boltzmann equation describing ion and voltage distribution near charged particles (at the microscale¹) shows a highly nonlinear distribution

¹In the following we denote the scale where non-linearities in ion and voltage distribution are detected

of these quantities over a distance up to a few hundreds of nanometers (the so-called Debye length) depending on surface charge density and concentration of background electrolyte. However, most engineering applications only deal with the investigation of macroscopic quantities such as macroscopic concentrations and electric potentials. Macroscopic devices (like ion specific electrodes and volt meters) measure these macroscopic quantities. In this paper we address the following question: how are microscopic electro-chemical quantities such as cation and anion concentration, voltage distribution, and fixed surface charge density, related to the respective macroscopic (that is, measurable) quantities?

2 GOVERNING EQUATIONS

For a physical quantity $e(\mathbf{z})$ assigned to the α -phase (i.e., solid or liquid) there are two different spatial averages, namely the *apparent phase average* and the *intrinsic phase average*, as defined by [1]

$$\overline{e}_\alpha(\mathbf{x}, t) = \frac{1}{\mathcal{V}} \int_{\Omega(\mathbf{x})} \chi^0(\mathbf{z} - \mathbf{x}) \chi^\alpha(\mathbf{z}, t) e(\mathbf{z}, t) dV_z \quad (1)$$

$$\overline{e}_\alpha^\alpha(\mathbf{x}, t) = \frac{1}{\mathcal{V}_\alpha} \int_{\Omega_\alpha(\mathbf{x})} \chi^0(\mathbf{z} - \mathbf{x}) \chi^\alpha(\mathbf{z}, t) e(\mathbf{z}, t) dV_z \quad (2)$$

where \mathcal{V} and \mathcal{V}_α denote the total volume and the volume of the α -phase of the representative volume element (RVE) respectively. χ^0 and χ^α are indicator functions of $\Omega(\mathbf{0})$ and Ω_α (see [1] for details). It follows that apparent and intrinsic phase averages are related by:

$$\overline{e}_\alpha(\mathbf{x}, t) = \phi_\alpha \overline{e}_\alpha^\alpha, \quad (3)$$

where $\phi_\alpha = \mathcal{V}_\alpha/\mathcal{V}$ is the phase volume fraction.

2.1 Phase Equilibrium at the Microscale

The theory of thermodynamics provides the framework for the description of equilibrium of ionic species in different phases [2]. In the following, we consider phase equilibrium of ionic species between two phases. The distribution of the ions is assumed to be only controlled by differences in concentration and electric potential between the two phases (i.e., we neglect non-ideality and pressure effects). The electro-chemical potential of an ionic species (in solution) then is described by [2]

$$\mu_{i\beta} = \mu_{i0\beta} + RT \ln c_{i\beta} + z_i F \psi_\beta, \quad (4)$$

where the index i refers to the ionic species and the index β refers to the (electro-chemical) phase respectively. $\mu_{i0\beta}$ is a reference electro-chemical potential. $c_{i\beta}$ and ψ_β are the concentration of ion i and the voltage in the solution phase β . At equilibrium by definition,

as the microscale.

the electro-chemical potentials of the ionic species i must be the same in both phases, i.e., $\mu_{i1} = \mu_{i2}$ which can also be expressed as:

$$\nabla \mu_{i\beta} = RT(1/c_{i\beta})\nabla c_{i\beta} + z_i F \nabla \psi_\beta = \mathbf{0} \quad (5)$$

In order to complete the set of equations describing phase equilibrium at the microscale we apply Gauss' electrostatic theorem (also known as Poisson equation) to relate the variation of the electric potential to the spatial distribution of the electric charges [2]:

$$-\nabla \cdot (\varepsilon_0 \varepsilon_\beta \nabla \psi_\beta) = F \sum_{i=1}^N z_i c_{i\beta} \quad \text{on } \Omega_f, \quad (6)$$

where we consider solid particles to have only surface charge. Hence, we assume that the voltage and volume charge density is defined over the fluid phase only. ε_0 is the permittivity of free space, ε_β is the relative permittivity of the fluid. $F \sum_{i=1}^N z_i c_{i\beta}$ is the volume charge density of the fluid respectively. The system of simultaneous partial differential Eqns. (5) and (6) must be solved over the domain of the RVE subject to appropriate boundary conditions (see [3] for details).

2.2 Phase Equilibrium at the Macroscale

Application of the intrinsic phase average rule (Eqn.(2)) to the microscale electro-chemical potential (Eqn.(4)) leads to the macroscopic equilibrium equations:

$$\begin{aligned} \overline{\mu_{i1}}^f &= \overline{\mu_{i2}}^f \\ RT \overline{\ln c_{i1}}^f + z_i F \overline{\psi_1}^f &= RT \overline{\ln c_{i2}}^f + z_i F \overline{\psi_2}^f = \text{const.} \end{aligned} \quad (7)$$

Now we introduce the concept of *intrinsic effective concentrations*, defined as,

$$\widehat{c}_{i\beta}^f := \exp(\overline{\ln c_{i\beta}}^f) \quad \text{with} \quad \overline{\ln c_{i\beta}}^f(\mathbf{x}) = \frac{1}{V_f} \int_{\Omega(\mathbf{x})} \ln(c_{i\beta}(\mathbf{z})) dV_z = \ln \widehat{c}_{i\beta}^f(\mathbf{x}) \quad (8)$$

Eqn.(7) can be rearranged to give the generalized Donnan potential:

$$E_{Don} := \overline{\psi_2}^f - \overline{\psi_1}^f = -\frac{RT}{z_i F} \left(\overline{\ln c_{i2}}^f - \overline{\ln c_{i1}}^f \right) = -\frac{RT}{z_i F} \ln \left(\widehat{c}_{i2}^f / \widehat{c}_{i1}^f \right) \quad (9)$$

This equation is a generalization of the standard equation describing the Donnan potential, i.e., $E_{Don} = -(RT/z_i F) \ln(\overline{c}_{i2}^f / \overline{c}_{i1}^f)$. Eqn.(9) is valid for any phase equilibrium (with uniform and non-uniform distribution of charge throughout the domain). For the special case of homogeneous charge distribution characterized by constant (microscopic) concentration and voltage distribution, the relation $\widehat{c}_{i1}^f = \overline{c}_{i1}^f$ and $\widehat{c}_{i2}^f = \overline{c}_{i2}^f$ holds. In other words, the generalized Donnan equation reduces to the usual Donnan potential.

The generalized Poisson equation provides a relation between electric potential and intrinsic effective ion concentration, i.e.:

$$-\nabla(\varepsilon_{eff\beta}\nabla\overline{\psi}_\beta^f) = F\sum_{i=1}^N z_i\overline{\hat{c}}_{i\beta}^f + F\omega\overline{\hat{X}}_\beta^f \quad (10)$$

where $\varepsilon_{eff\beta}$ is the effective permittivity, $\overline{\hat{c}}_{i\beta}^f$ are the intrinsic effective concentrations, and $\overline{\hat{X}}_\beta^f$ is an effective fixed charge concentration related to the surface charges σ on particles of the material phase (β). Note that the RHS of Eqn.(10) differs from the standard Poisson equation, i.e., $-\nabla(\varepsilon_{eff\beta}\nabla\overline{\psi}_\beta^f) = F\sum_{i=1}^N z_i\overline{c}_{i\beta}^f + F\omega\overline{X}_\beta^f$. Equilibrium at the macroscale implies electroneutrality within a material (β), and so the RHS of Eqn.(10) is zero within the considered material, i.e., $\sum_{i=1}^N z_i\overline{\hat{c}}_{i\beta}^f + \omega\overline{\hat{X}}_\beta^f = 0$. With the knowledge of the effective permittivity ($\varepsilon_{eff\beta}$) and (intrinsic) effective fixed charge concentration ($\overline{\hat{X}}_\beta^f$), the generalized macroscopic equations describing phase equilibrium (7) and (10) can be solved, and macroscopic measurable voltages estimated based on the knowledge of the microscale domain.

3 NUMERICAL ANALYSIS

In the following we investigate phase equilibrium between two compartments containing a monovalent binary electrolyte separated by a charged clay membrane. A typical 2D representative volume element of clay ($a = 150\text{nm}$, $b = 300\text{nm}$) containing six clay platelets of 100nm length and 10nm width is shown in Figure 1 (for details on geometry and boundary conditions see [3]). The material parameters used for the microscale numerical analysis are: $\varepsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/(\text{J m})$, $\varepsilon_w = 78$, $F = 96500 \text{ C/mol}$, $T = 293 \text{ K}$, $R = 8.31 \text{ J/(K mol)}$, $\sigma = -0.01 \text{ C/m}^2$ (particle surface charge), $c_{i1} = 10 \text{ mol/m}^3$ (concentration of background electrolyte).

Figure 1 shows the distribution of voltage, cations, and anions. In the region around a particle the cation concentration is as high as 66.4 mol/m^3 (Figure 1(b)) whereas the anion concentration is as low as 1.51 mol/m^3 (Figure 1(c)) indicating that anions are excluded from the porous material.

The Donnan potential of the system can be computed by volume averaging (Eqn.(1)) of the respective microscale voltage, giving $E_{Don} = 3.89\text{mV}$. E_{don} can also be computed using the general definition for the Donnan potential Eqn.(9) leading the same value independent of the ion considered. On the other hand, using the standard Donnan potential equation leads different values for cations and anions ($E_{Don,+} = -5.43 \text{ mV}$ and $E_{Don,-} = -2.96 \text{ mV}$). Obtaining two different values for the Donnan potential is clearly incorrect, as only a single value for voltage is measured.

In order to perform a macroscopic analysis the effective permittivity and fixed charged concentration must be estimated from a microscale analysis. From the electroneutrality condition $\overline{\hat{X}}_\beta^f$ can be estimated as 3.09 mol/m^3 . Numerical solution of the macroscale

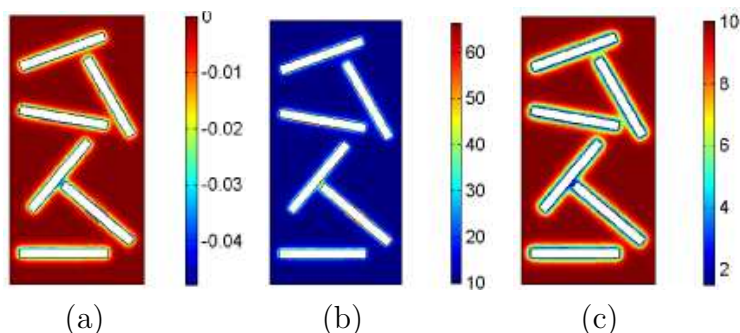


Figure 1: Distribution of (a) voltage (in V), (b) cation concentration (in mol/m³), and (c) anion concentration (in mol/m³) ($c_{i1} = 10$ mol/m³, $\sigma = -0.01$ C/m²)

governing equations leads the same Donnan potential as obtained from the microscale analysis. On the other hand using the standard fixed charge concentration, i.e., $\overline{X}_\beta^f = 3.51$ mol/m³ leads a wrong value for the Donnan potential.

4 CONCLUSIONS

In this paper a new theory for estimating the (macroscopic) Donnan potential in charged porous materials has been proposed. This theory incorporates information for a non-homogeneous (or lumpy) charge distribution at the microscale, into the macroscale governing equations. Comparison of the classical (macroscale) governing equations with the one obtained from upscaling indicate differences in terms of concentration and fixed charge concentration. In the classical equilibrium equations (intrinsic) voltage is linked to intrinsic actual ion concentrations. On the other hand, the new generalized equilibrium equations relates the (intrinsic) voltage to so-called (intrinsic) effective ion concentrations. The intrinsic effective concentrations are, for ideal solutions, logarithmic volume averages of concentrations. Regarding the Poisson equation, it turns out that the variation of the electric potential must be related to an effective fixed charge concentration.

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