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# Diffusion in *charged* porous media: macroscopic Poisson-Nernst-Planck equations through upscaling

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## ABSTRACT

The description of electro-diffusive ion transport through uncharged porous materials at the macroscale is frequently performed using the Poisson-Nernst-Planck (PNP) equations. Phenomenological formulations have been proposed for *charged* porous media like clays, usually disregarding their links to particle-level scale. In this paper we derive generalized macroscopic PNP equations for charged media using the volume averaging method on the microscale governing equations. Here we show that the macroscopic quantities are linked to so called “effective concentrations” rather than actual concentrations when one accounts for non-homogeneous electric charge distributions across the material. Numerical examples on thin clay membranes using the newly developed formulations are presented. We also highlight that diffusion through uncharged media can be treated as a special case within the generalized macroscopic PNP equations.

## 1 INTRODUCTION

Understanding of transport of ions through porous materials is essential for a number of engineering applications including movement of ions through soils in geotechnical engineering (Rowe et al., 2004; Shackelford and Daniel, 1991), penetration of chloride ions into reinforced concrete leading to chloride induced steel corrosion of civil engineering structures (Page and Treadaway, 1982; Samson et al., 2003), and even transport of nutrients through cell membranes in biomedical engineering (Honig and Nicholls, 1995). The Poisson-Nernst-Planck (PNP) system of equations can describe the above transport behaviour when there are no pressure gradients in the system. The key parameters are the ionic effective diffusion coefficient and permittivity. While macroscopic PNP equations have been successfully used in the description of ion transport through uncharged porous media, various modifications of PNP equations have been proposed to account for the electrostatic interactions of ions in the pore fluid and particles charges in the case of *charged* porous materials (e.g., clays, shales, polymer gels) (see (Samson et al., 2003) for details). However, the majority of these modified equations are phenomenological in nature, disregarding their relations to particle level scale. Therefore, transport parameters in these equations can not be directly linked to fundamental quantities such as ion self-diffusion coefficients, pore fluid permittivity, and surface charge density of particles. As a result, model parameters have to be calibrated for each application from respective experimental data.

In order to resolve uncertainties in the phenomenological macroscopic PNP equations, we derive generalized PNP equations for *charged* porous materials. We apply the method of volume averaging to upscale the respective microscale governing equations. The major advantage of using macroscopic equations based on up-scaling procedures is that detailed information from the microscale is incorporated into the macroscale governing equations.

## 2 UPSCALING OPERATIONS AND VOLUME AVERAGING RULES

The method of volume averaging is a mathematical technique which allows deriving governing equations for multi-scale systems. Hence, equations valid on a particular scale can be spatially smoothed to give equations valid on a larger one. In this paper we consider two distinct scales, where the position vector is denoted by  $\mathbf{z}$  at the microscale, while it is denoted by  $\mathbf{x}$  at the macroscale. A schematic representation of the separation of scale condition is given in Figure 1. Here  $L$  is the macroscopic length scale and  $d$  is the length of heterogeneities. The characteristic

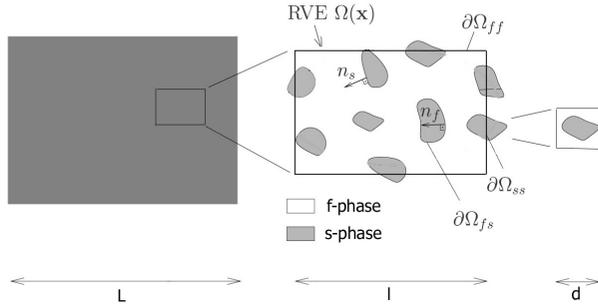


Figure 1. Separation of scales: macroscopic structure ( $L$ ); RVE ( $l$ ); heterogeneity ( $d$ ) of porous media ( $f$ -phase, electrolytic solution;  $s$ -phase, solid particles with surface charges  $\sigma$ ).

length  $l$  separates macro and micro scales ( $d \ll l \ll L$ ), and defines the minimum size of a representative volume element (RVE), where the tools of differential calculus are still valid.

Geometric quantities of the RVE in Figure 1 follow the notation by Bear and Bachmat (1991) (Bear and Bachmat, 1991),  $\Omega(\mathbf{x})$  is the volume of the RVE,  $\partial\Omega_{ff}$  and  $\partial\Omega_{ss}$  are the intersection of total area of boundary of the domain  $\Omega(\mathbf{x})$  with the fluid and solid phase respectively, and  $\partial\Omega_{fs}$  is the total area of the interface between the fluid and solid phase within  $\Omega(\mathbf{x})$ .

For a physical quantity  $e(\mathbf{z})$  assigned to the  $\alpha$ -phase (i.e.,  $s$ -solid or  $f$ -liquid) there are two different spatial averages: the *apparent phase average* and the *intrinsic phase average* (Dormieux, 2005):

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

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

where  $V$  denote the total volume and  $V_\alpha$ , the volume of the  $\alpha$ -phase,  $\chi^0$  and  $\chi^\alpha$  are the characteristic functions of  $\Omega(\mathbf{0})$  and  $\Omega(\alpha)$  respectively. Eq. (1) and (2) are related by the phase volume fraction  $\phi_\alpha = V_\alpha/V$  as  $\bar{e}_\alpha(\mathbf{x}, t) = \phi_\alpha \bar{e}_\alpha^\alpha(\mathbf{x}, t)$ . Application of volume averaging to the microscale equations requires knowledge of the mathematical operations summarized in Table 1.

### 3 MULTI-IONIC TRANSPORT GOVERNING EQUATIONS

The description of electro-diffusive multi ionic transport through uncharged porous materials at the macroscale is frequently performed using the Poisson-Nernst-Planck (PNP) equations. However, most geotechnical engineering applications deal with ion transport through clayey membranes (i.e., *charged* porous materials). Macroscopic transport properties generally have to be estimated from experiments (Jungnickel et al., 2004). One alternative is to understand the underlying behaviour of the system at a deeper level, deriving macroscopic equations by *up-scaling* or *homogenization*.

Table 1: Summary of volume averaging operations of a physical quantity  $e$  (over  $f$ -phase).

Operation	Averaging rule	Eq.
Summation	$\overline{e_1 + e_2}^f = \overline{e_1}^f + \overline{e_2}^f$	(T.1)
Product	$\overline{e_1 e_2}^f = \overline{e_1}^f \overline{e_2}^f + \overline{e_1 e_2}^{\circ f}$	(T.2)
Spatial derivative	$\overline{\nabla_z e(\mathbf{z}, t)} = \nabla_x \bar{e} + \frac{1}{V} \int_{\partial\Omega_{fs}} e(\mathbf{z}, t) \cdot \mathbf{n}(\mathbf{z}, t) dS_z$	(T.3)
Time derivative	$\frac{\partial \overline{e(\mathbf{z}, t)}}{\partial t} = \frac{\partial \bar{e}}{\partial t} - \frac{1}{V} \int_{\partial\Omega_{fs}} e(\mathbf{z}, t) \mathbf{u} \cdot \mathbf{n}(\mathbf{z}, t) dS_z$	(T.4)

Note:  $\hat{e}_i$ =deviation from average,  $V$ =RVE volume,  $\partial\Omega_{fs}$ =fluid-solid interface,  $\mathbf{n}$ =normal unit vector,  $\mathbf{u}$ =velocity

### 3.1 Particle level scale PNP equations

Two phases are considered on a clay membrane RVE: the micropore space filled with a solution containing solutes ( $f$ -phase in Figure 1) and the solid particles ( $s$ -phase). We assign an isotropic mobility  $u_{\alpha,i}$  to every solute. In the absence of pressure gradients, ion transport is driven by electrochemical potential  $\mu_{\alpha,i}$  gradients. The ion flux is given as (Cussler, 1997; Newman, 1991):

$$\mathbf{j}_{\alpha,i} = c_{\alpha,i} \mathbf{v}_{\alpha,i} = -c_{\alpha,i} u_{\alpha,i} \nabla \mu_{\alpha,i} \quad \text{on } \Omega_{\alpha} \quad (3)$$

where  $\mathbf{j}_{\alpha,i}$  is the molar flux density of the  $i^{\text{th}}$  ion in the  $\alpha$ -phase (i.e., fluid and solid phases),  $c_{\alpha,i}$  and  $\mathbf{v}_{\alpha,i}$  are the ion concentration and the relative ion velocity. Ion mobility can be found from the ion self-diffusion coefficient through the Nernst-Einstein equation (Newman, 1991):

$$u_{\alpha,i} = D_{\alpha,i} / RT \quad (4)$$

The electrochemical potential for ideal solutions can be expressed as (Helfferich, 1962):

$$\mu_{\alpha,i} = \mu_{\alpha,i}^0 + RT \ln c_{\alpha,i} + z_i F \psi_{\alpha} \quad (5)$$

where  $\mu_{\alpha,i}^0$  is a reference potential,  $z_i$  is the valence of the  $i^{\text{th}}$  ion, and  $\psi_{\alpha}$  is the voltage,  $F$ ,  $R$  and  $T$  are the Faraday constant, gas constant, and absolute temperature. Inserting Eq.(5) into Eq.(3) and making use of Eq.(4) leads to the well known Nernst-Planck equation,

$$\mathbf{j}_{\alpha,i} = -D_{\alpha,i} \left( \nabla c_{\alpha,i} + \frac{z_i F}{RT} c_{\alpha,i} \nabla \psi_{\alpha} \right) \quad \text{on } \Omega_{\alpha} \quad (6)$$

Eq. (6) is a generalization of Fick's law that takes into account electrical effects. In addition, it is assumed that no adsorption on the fluid-solid interface takes place, i.e.,  $\mathbf{j}_{\alpha,i} \cdot \mathbf{n}_{\alpha} = 0$  on  $\partial\Omega_{fs}$ . Mass conservation for each conservative ion species is expressed by,

$$\frac{\partial c_{\alpha,i}}{\partial t} = -\nabla \cdot \mathbf{j}_{\alpha,i} \quad \text{on } \Omega_{\alpha} \quad (7)$$

where  $\nabla \cdot \mathbf{j}_{\alpha,i}$  is the divergence of the flux of the  $i^{\text{th}}$  ion in the  $\alpha$ -phase, and  $t$  is time. Substitution of the flux Eq. (6) into the mass conservation Eq. (11) leads to the governing differential equation for mass transport in the pore solution of the porous material.

The variation of the electric potential can be related to the spatial distribution of electric charges through the Poisson equation as (Newman, 1991):

$$-\nabla \cdot (\varepsilon_0 \varepsilon_{\alpha} \nabla \psi_{\alpha}) = \rho_{\alpha} \quad \text{on } \Omega_{\alpha} \quad (8)$$

where  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_{\alpha}$  is the relative permittivity of the  $\alpha$ -phase and  $\rho_f = F \sum_{i=1}^N z_i c_i$  in the fluid phase. We assume that the volume charge density of the solid particles is zero ( $\rho_s=0$ ) and the charge on the clay particle surfaces  $\sigma$  is constant on the fluid-solid interface  $\partial\Omega_{fs}$ , where the electrostatic boundary conditions are (Stratton, 1941) (pp 36):

$$(\mathbf{D}_f - \mathbf{D}_s) \cdot \mathbf{n}_f = \sigma \quad \text{on } \partial\Omega_{fs} \quad \text{with } \mathbf{D}_{\alpha} = -\varepsilon_0 \varepsilon_{\alpha} \nabla \psi_{\alpha} \quad (9)$$

$\mathbf{D}_f$  and  $\mathbf{D}_s$  are the electric displacement in the fluid phase and solid phase respectively and  $\mathbf{n}_f$  is a unit outward normal vector.

Eqs. (6), (7) and (8) are referred to as Poisson-Nernst-Planck (PNP) system of equations.

### 3.2 Macroscopic PNP equations

The overall average macroscopic flux through a RVE is the sum of the average macroscopic fluxes in the fluid and solid phases. Assuming that the solid phase does not contribute to ion transport ( $\mathbf{j}_s=0$ ), one can take the apparent average of Eq. (3) for the fluid phase and recognize the relationship between apparent and intrinsic averages. Then, applying the product averaging rule (T.2) gives:

$$\bar{\mathbf{j}}_i = \bar{\mathbf{j}}_{f,i} + \bar{\mathbf{j}}_{s,i} = -u_{f,i} \overline{c_{f,i} \nabla_z \mu_{f,i}} = -u_{f,i} \phi_f \overline{c_{f,i} \nabla_z \mu_{f,i}} = -u_{f,i} \phi_f \left( \overline{c_{f,i} \nabla_z \mu_{f,i}} + \overline{c_{f,i}^\circ \nabla_z \mu_{f,i}^\circ} \right) \quad (10)$$

where the last term is the deviation from the respective quantities around their average values (see Table 1), which are negligible over a sufficiently small chosen RVE. The gradient averaging rule (T.3) is applied to electrochemical potential term, yielding (we drop the  $f$  subscript for clarity):

$$\phi \overline{\nabla_z \mu_i} = \overline{\nabla_z \mu_i} = \nabla_x \bar{\mu}_i + \frac{1}{V} \int_{\partial\Omega_f} \mu_i \mathbf{n}_f dS_z = (\mathbf{1} + \mathbf{m}_i) \nabla_x \bar{\mu}_i = \boldsymbol{\tau}_i \nabla_x \bar{\mu}_i \quad (11)$$

where  $\boldsymbol{\tau}_i = \mathbf{1} + \mathbf{m}_i$  may be considered as a generalized tortuosity coefficient that requires information on the distribution of  $\mu_i$  (obtained solving the microscale governing equations) to be computed. Inserting Eq. (11) into Eq. (10) and using the definition of electrochemical potential in Eq.(5) together with the summation averaging rule (T.1) leads to the macroscopic flux equation:

$$\bar{\mathbf{j}}_i = -u_i \boldsymbol{\tau}_i \bar{c}_i \nabla_x \bar{\mu}_i = -u_i \phi \boldsymbol{\tau}_i \bar{c}_i \nabla_x \left( RT \ln \bar{c}_i + z_i F \bar{\psi} \right) \quad (12)$$

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

$$\bar{c}_i^f := \exp\left(\ln \bar{c}_i^f\right) \quad \text{with} \quad \ln \bar{c}_i^f(\mathbf{x}) = \frac{1}{V_f} \int_{\Omega(\mathbf{x})} \ln(c_i(\mathbf{z})) dV_z = \ln \hat{c}_i^f(\mathbf{x}) \quad (13)$$

Finally, the *generalized macroscopic Nernst-Planck equations* are found inserting Eqs. (4) and (13) into Eq. (12):

$$\bar{\mathbf{j}}_i = -\phi \hat{\mathbf{D}}_{eff,i} \left( \nabla_x \hat{c}_i^f + \frac{z_i F}{RT} \hat{c}_i^f \nabla_x \bar{\psi} \right) \quad (14)$$

where the *generalized effective diffusion coefficient* is defined as:

$$\hat{\mathbf{D}}_{eff,i} = D_{f,i} \boldsymbol{\tau}_i \left( \bar{c}_i^f / \hat{c}_i^f \right) \quad (15)$$

Therefore, the macroscopic quantities are linked to “effective concentrations” rather than actual concentrations as the standardly used NP equation does.

Similarly, volume averaging operations performed over Eq. (8) while accounting for the boundary conditions on the clay surfaces (Eq. (9)), leads to the *generalized macroscopic Poisson equation*:

$$\boldsymbol{\varepsilon}_{eff} \nabla_x \cdot \nabla_x \bar{\psi}_f = F \left( \bar{X} - \sum_{i=1}^N z_i \hat{c}_i \right) \quad (16)$$

where  $\boldsymbol{\varepsilon}_{eff}$  is the effective permittivity of the clay membrane,  $\bar{X}$  is an *effective fixed charge concentration* related to the negative constant clay surface charge  $\sigma$  and the background concentration. At the macroscale, a simplification of Eq. (16) is the electroneutrality condition:

$$\bar{X} - \sum_{i=1}^N z_i \bar{c}_i = 0 \quad (17)$$

Effective parameters and concentration distributions at the macroscale (Eqs. (14) and (17)) can be computed when knowing the concentration distribution at the microscale (Eqs. (6) and (8)).

#### 4 NUMERICAL ANALYSES OF THIN CLAY MEMBRANES

We use the newly developed governing equations in ionic electro-diffusive transport of a binary electrolyte through a thin membrane with cylindrical pores in order to be able compute microscale quantities such as flux density, ion concentration, voltage, and their gradients. For straight pores, the tortuosity  $\tau$  in Eq.(11) is one, reducing the number of variables involved in this example and thus facilitating tracking between scales. Effective ion diffusion coefficients can be explicitly computed either by using Eq. (15) or Eq. (14).

Table 2. Parameters used for microscale numerical analyses.

Microscale model		
$\varepsilon_0$	$8.85419 \times 10^{-12}$	$C^2/(J\ m)$
$\varepsilon_f$	78 (water)	-
$F$	96485.3	$C/mol$
$R$	8.3144	$J/(K\ mol)$
$T$	293	K
$D_{f,Ca^+}$	$1.334 \times 10^{-9}$	$m^2/s$
$D_{f,Cl^-}$	$2.032 \times 10^{-9}$	$m^2/s$

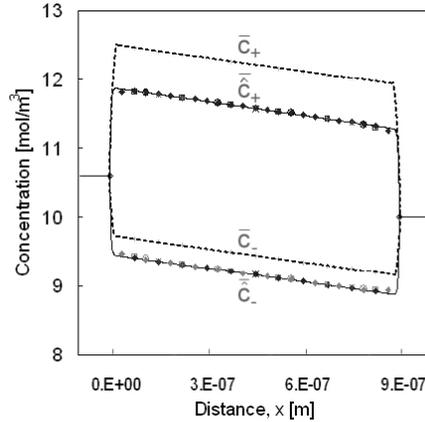


Figure 2. Average of actual concentrations and intrinsic effective concentrations. Dots: values computed for several RVE sizes. Continuous line: values from macromodel that uses upscaled parameters.

Material parameters used for the microscale numerical analyses are summarized in Table 2. We solve the PNP equations numerically using the finite element method. The boundary conditions are: upstream cation ( $Na^+$ ) and anion ( $Cl^-$ ) concentrations of  $10.6\ mol/m^3$  and downstream concentrations of  $10\ mol/m^3$ . For the voltage boundary conditions we assume that the system is electric short circuited, i.e.,  $\psi_1 = \psi_2 = 0$ . The surface charge density  $\sigma$  on the pore wall is set to  $-0.01\ C/m^2$ . Figure 2 summarizes the results corresponding to the numerical simulations at both scales. The fluxes calculated from the microscale and the macroscale are the same, validating our equations ( $\bar{J}_{Na^+} = 0.00105\ mol/(m^2s)$ ,  $\bar{J}_{Cl^-} = 0.00124\ mol/(m^2s)$ ).

It is interesting to explore the influence of concentration levels and clay surface charge on the macroscopically measured effective diffusion coefficient, since the intrinsic effective concentration depends on the actual distribution of the ionic species and the extent of their non-uniformity. Figure 3 summarizes these numerical results, with normalized effective diffusion coefficients being shown. The effective diffusion coefficient tends to the standardly used coefficient as the background electrolyte concentration increases indicating compression of the diffuse double layer. For lower concentrations, the discrepancies in diffusion coefficient values of the examples analysed here can be up to 40% for cations and 20% for anions. A similar effect is observed in the effective fixed charged concentration. Its absolute value increases with increasing surface charge density and its nonlinearity is more profound at low concentration levels.

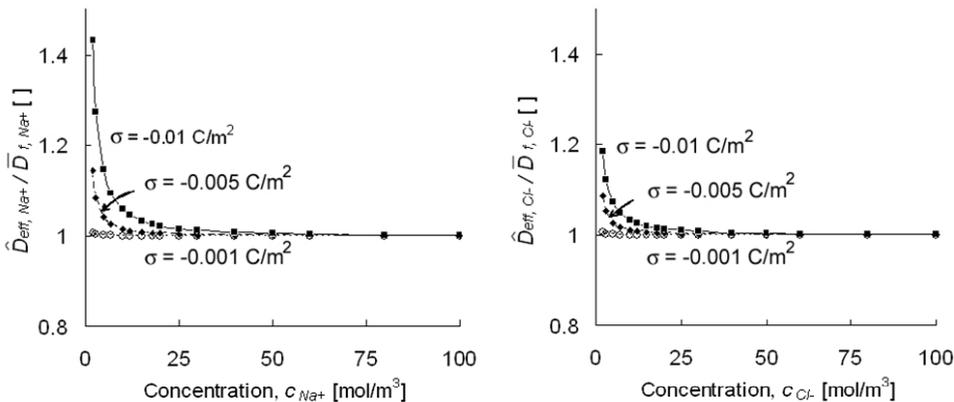


Figure 3. Influence of background concentration and surface charge density on diffusion coefficient estimations.

## 5 CONCLUSIONS

A new set of upscaled Poisson-Nernst-Planck equations has been proposed and numerically checked as ionic electro-diffusive transport governing equations. The key steps in the derivation of the macroscopic PNP equations, and numerical examples of a simple geometry have been included in this article. These equations successfully account for non-homogeneous ionic distributions at the particle level scale. Moreover, these equations can treat homogeneous charge distributions (i.e., uncharged porous media) as a particular case. The comparison between the standardly used macroscale governing equations with the ones obtained here from upscaling through volume averaging reveals that the discrepancies increases with decreasing electrolyte concentration and increasing surface charge density, as the ratio  $\bar{c}_i/\bar{c}_i^f$  becomes larger. The macroscopic ionic transport is linked to effective concentrations  $\bar{c}_i^f$  rather than actual concentrations  $\bar{c}_i$ .

This new theory gives insight on how the effective diffusion coefficients of ions can be estimated for ion transport in clays. Further work is in progress to apply this model toward more realistic clay particles geometries, such as flocculated or disperse clay particle arrangements where the estimation of porosity  $\phi$  and tortuosity  $\tau$  are crucial, and for transient responses.

## ACKNOWLEDGMENTS

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