Homogenization of the Nernst-Planck-Poisson-Boltzmann system by two-scale convergence

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Abstract:

This work focuses on performing the homogenization of the Nernst-Planck-Poisson-Boltzmann system, in order to obtain an efficient modelling of the ionic transfer and electrocapillary effects at the macroscopic scale for saturated porous media. The homogenization is performed with the powerful two-scale convergence method, which enables to obtain both the homogenized model and the associated convergence result.

1 Introduction

Ionic transfers in saturated porous media and the associated electrocapillary adsorption effect (electric double layer phenomenon) are generally modelled by the partial differential evolution system of Nernst-Planck-Poisson-Boltzmann with Cauchy and boundary conditions. The two equations of ionic transfer (for the cations and for the anions) are coupled with the Poisson-Boltzmann equation describing the electrical potential.

The main goal of this work is to deduce, from the micro-local Nernst-Planck-Poisson-Boltzmann equations, an efficient modelling of ionic transfers and electrocapillary effects at the macroscopic scale in saturated porous media. The homogenization is performed with the powerful two-scale convergence method. It enables to obtain both the search homogenized model and the convergence result, without assuming \textit{a priori} the form of the asymptotic expansion of the unknowns, as classically with periodic homogenization technique \cite{2}\cite{14}. Moreover, with this approach, it is not necessary to decompose the electrical potential into the bulk potential and the electrical double layer potential as it is generally the case in the literature. Furthermore, the present approach may be generalized to a multi-species formalism, without considering only monovalent cations and anions\textsuperscript{1}.

With the formalism proposed here, the electric potential due to the migration of ionic species, and the electrical double layer potential are contained in the total potential $\Psi^\ast_{\varepsilon}$. Once the homogenization performed and the efficient macroscopic model obtained by two-scale convergence method, with the

\textsuperscript{1}With valence $\pm 1$. 

associated convergence result, it is proved that the steady states have the form of the classical Poisson-Boltzmann expression of the ionic concentrations.

The originality of the present work lies on the consideration of electrocapillary adsorption effect: important phenomena occur on the boundaries of the pores and introduce into the model problem strongly nonlinear terms defined on a periodic surface and leading to memory effects, described by a macroscopic Grahame’s law.

2 The ionic drift-diffusion problem

2.1 The general framework

Using the classical notations of [1] for periodic homogenization problems, we denote by $Y$ the unit reference cube $[0,1]^d$, $Y_s$ an open set of $Y$ representing the solid phase, and $Y_f = Y \setminus Y_s$ its complementary (assumed to be connected) representing the fluid phase. The Lipschitzian boundary $\Gamma = \Gamma_{sf} \cup \Gamma_{ss}$ is composed of the internal boundary $\Gamma_{sf}$ between the fluid and the solid phases and of the boundary $\Gamma_{ss}$ between the solid parts of two adjacent unit cubes constituting the microstructure of the material (Figs. 1). Equivalently, we denote by $\Gamma_{ff}$ the boundary between the fluid phases of two adjacent unit cubes. Finally, in the sequel, we will still denote by $Y$, $Y_s$, $Y_f$ and $\Gamma_{sf}$ to $\mathbb{R}^d$ by $Y$-periodicity.

Introducing now a sequence $\varepsilon$ of positive reals converging to 0, we define the whole fluid phase where the fluid can circulate

$$\Omega_f^\varepsilon = \left\{ x \in \Omega, \frac{x}{\varepsilon} \in Y_f \right\}$$

(1)

and its complementary representing the whole solid phase

$$\Omega_s^\varepsilon = \left\{ x \in \Omega, \frac{x}{\varepsilon} \in Y_s \right\}$$

(2)

of the microstructure of the material (Fig. 1). We denote by $\Gamma_{sf}^\varepsilon$ the inner boundary of $\Omega$ between the fluid and the solid phases, periodic surface of dimension $(d - 1)$ such as:

$$\Gamma_{sf}^\varepsilon = \left\{ x \in \Omega, \frac{x}{\varepsilon} \in \Gamma_{sf} \right\}.$$  

(3)

Figure 1: Periodic microstructure constructed from the elementary reference cell considered.

We consider a heterogeneous saturated porous medium, whose microstructure contains two phases: a solid phase $\Omega_s^\varepsilon$ (of cement paste for example and eventually aggregates in case of mortars or concrete).
and a liquid phase $\Omega^f_\varepsilon$ (see Fig. 1). The boundary between the solid and the liquid phases is denoted $\Gamma^sf_\varepsilon$. The diffusion in the fluid phase is described by Nernst-Planck equation coupled with the Poisson equation characterizing the electrical field accelerating or slowing down the ionic transfer. Nernst-Planck equation is generally written for an isotropic diffusivity assumed in the fluid phase $[3][10][11][13]$

$$\frac{\partial c_{\pm,\varepsilon}}{\partial t} - \text{div} \left( D_{\pm} \nabla c_{\pm,\varepsilon} + D_{\pm} \frac{F}{\varepsilon} z_{\pm} c_{\pm,\varepsilon} \nabla \Psi^*_\varepsilon \right) = 0 \quad \text{in} \quad \Omega^f_\varepsilon, \quad t > 0,$$

where $c_{\pm,\varepsilon}$ denotes the concentration of the cations (respectively anions) of valence $z_{\pm}$, $D_{\pm}$ their molecular diffusion coefficient in the liquid phase$^2$, $E^*_\varepsilon = -\nabla \Psi^*_\varepsilon$ the total electrical field in the solution. Note that the electrical potential $\Psi^*_\varepsilon$ results both from the evolution of the repartition of concentrations of electrical species (cations and anions), and of the effect of the double electrical layer. When an external electrical potential is applied, it may be also included in the total potential $\Psi^*_\varepsilon$. Finally, $F$ and $R$ denote respectively, the Faraday and the ideal gas constant, and $\Theta$ the temperature of the fluid.

Let us denote $\varepsilon_f$ (resp. $\varepsilon_s$) the dielectric constant of the fluid phase $\Omega^f_\varepsilon$ (resp. of the solid phase $\Omega^s_\varepsilon$). In a general way, $\varepsilon_f$ et $\varepsilon_s$ may depend on $x$ for very heterogeneous media, with $\varepsilon_f > 0$, $\varepsilon_s \geq 0$. Introducing the function

$$\kappa = \varepsilon_f \chi Y_f + \varepsilon_s \chi Y_s,$$

representing the dielectric values on the whole domain $\Omega$ through the characteristic phase functions $\chi Y_f$ and $\chi Y_s$, the Poisson equation can be written in the global formulation in the sense of distributions as

$$\text{div} (\kappa (\frac{x}{\varepsilon}) \nabla \Psi^*_\varepsilon) = -F (z_+ c_{+,\varepsilon} - z_- c_{-,\varepsilon}) \chi \Omega^f_\varepsilon + g(\varepsilon, t, x) \delta_{(\Gamma^f_\varepsilon \setminus \Gamma^s_\varepsilon)} \quad \text{in} \quad \Omega, \quad t > 0,$$

where the last term denotes a measure, with support on $\Gamma^sf_\varepsilon$, governing the jump of the electrical flux through the interface $\Gamma^sf_\varepsilon$.

To complete equations (4)-(6), let us write the associated boundary conditions. First, we assume that we have homogeneous Neumann boundary conditions associated with Nernst-Planck equation on $\Gamma^sf_\varepsilon \cup \Gamma^f_\varepsilon$ where $\Gamma^f_\varepsilon$ denotes the external fluid boundary to $\Omega^f_\varepsilon$ and $n$ denotes the external unit normal to $\Omega^f_\varepsilon$. Moreover, as the system is assumed to be insulated with respect to the exterior, we have

$$\frac{\partial \Psi^*_\varepsilon}{\partial n} = 0 \quad \text{on} \quad \Gamma^f_\varepsilon \cup \Gamma^s_\varepsilon,$$

where $\Gamma^s_\varepsilon$ denotes the external solid boundary to $\Omega^s_\varepsilon$.

Finally, the electrical double layer phenomenon at the interface $\Gamma^sf_\varepsilon$ will be modelled through the boundary condition involving the surface charge density $\sigma$. In the general case, accounting for the jump of the electrical flux through the interface$^3$, $\Gamma^sf_\varepsilon$, noted $[[\kappa (\frac{x}{\varepsilon}) \nabla \Psi^*_\varepsilon (t, x)]] \cdot n$, we have:

$$\left[ \left[ \kappa (\frac{x}{\varepsilon}) \nabla \Psi^*_\varepsilon (t, x) \right] \cdot n = \varepsilon \sigma (\Psi^*_\varepsilon (t, x)), \quad x \in \Gamma^sf_\varepsilon, \quad t > 0. \right.$$

A bijective relation between the surface charge density $\sigma$ and the potential $\Psi^*_\varepsilon$ may be given by the Grahame relation coming from the Gouy-Chapman theory $[8]$. The electrocapillary adsorption

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$^2$The pore solution for cementitious materials for the concerned applications.

$^3$The unit normal vector $n$ is directed from $\Omega^f_\varepsilon$ to $\Omega^s_\varepsilon$. 

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phenomenon at the substrate interface may be modelled for a very general class of material by the
relation [4] via a strictly monotone Lipschitz-function $\tau$, with $\tau(0) = 0$,

$$\sigma(\Psi^*_\varepsilon(t,x)) = -\lambda \left( \frac{x}{\varepsilon} \right) \tau(\Psi^*_\varepsilon(t,x)), \ x \in \Gamma^{sf}_\varepsilon,$$

(9)

where $\lambda$ denotes the dielectric permittivity coefficient\(^4\) at the interface $\Gamma^{sf}$, possibly heterogeneous, ex
tented by $Y$–periodicity, verifying $\lambda \in L^\infty(\Gamma^{sf})$, $\lambda \geq \lambda_0 > 0$.

2.2 Associated weak formulation

The equivalent weak formulation associated to Eq. (4)-(8) takes the variational form:

Find $(c_{\pm,\varepsilon}) = (c_{+,\varepsilon}, c_{-,\varepsilon})$ in $L^\infty([0,T];H^1(\Omega^f_\varepsilon))^2 \cap H^1(Q^f_\varepsilon)$ and $\Psi^*_\varepsilon \in L^\infty([0,T];H^1(\Omega))$ verifying $\forall t > 0, \forall v \in H^1(\Omega^f_\varepsilon)$ and $\forall w \in H^1(\Omega)$:

$$\int_{\Omega^f_\varepsilon} \frac{\partial c_{\pm,\varepsilon}}{\partial t} v \, dx + D_\pm \int_{\Omega^f_\varepsilon} \nabla c_{\pm,\varepsilon} \cdot \nabla v \, dx + D_\pm \frac{F}{\Theta} \int_{\Omega^f_\varepsilon} z_{\pm} c_{\pm,\varepsilon} \nabla \Psi^*_\varepsilon \cdot \nabla v \, dx = 0,$$

$$\int_{\Omega} \kappa \left( \frac{x}{\varepsilon} \right) \nabla \Psi^*_\varepsilon(t) \cdot \nabla w \, dx + \varepsilon \int_{\Gamma^f_\varepsilon} \lambda \left( \frac{x}{\varepsilon} \right) \tau(\Psi^*_\varepsilon)(t) \, w \, ds_x$$

$$= F \int_{\Omega^f_\varepsilon} (z_+ c_{+,\varepsilon}(t) - z_- c_{-,\varepsilon}(t)) \, w \, dx,$$

$$c_{\pm,\varepsilon}(0) = 0, \forall t \geq 0, T[\times \Omega^f_\varepsilon], \ c_{\pm,\varepsilon}(0) = (c^0_{\pm,\varepsilon}) \ in \ \Omega^f_\varepsilon.$$

(10)

(11)

(12)

For the establishment of this weak formulation, let us notice that the integral of the left-hand side of the Poisson equation is on the whole domain $\Omega$ whereas the right-hand side only involves the integral on the fluid domain $\Omega^f_\varepsilon$.

The preliminary framework is stated by the following global well-posedness result whose proof can be found in [7], based on the Schauder-Tikhonov fixed-point method [5][6]:

**Proposition 1** If the boundary of $\Omega$ is smooth enough\(^5\), for all initial data $(c^0_{\pm,\varepsilon}) = (c^0_{+,\varepsilon}, c^0_{-,\varepsilon})$ in $L^\infty(\Omega^f_\varepsilon)^2 \cap H^1(\Omega^f_\varepsilon)^2$, such as $(c^0_{\pm,\varepsilon}) \geq 0$, problem (10)-(12) admits a unique solution $(c_{\pm,\varepsilon}, \Psi^*_\varepsilon)$ with $(c_{\pm,\varepsilon}) = (c_{+,\varepsilon}, c_{-,\varepsilon})$ in $L^\infty([0,T];H^1(\Omega^f_\varepsilon))^2 \cap H^1(Q^f_\varepsilon)^2$ and $\Psi^*_\varepsilon \in C^0([0,T];H^1(\Omega))$. The potential $\Psi^*_\varepsilon$ is continuous in time since the left-hand side of the Poisson equation is continuous in time $(c_{\pm,\varepsilon} \in C^0([0,T];\Omega^f_\varepsilon))$ and $(c_{\pm,\varepsilon})$ is bounded independently of $\varepsilon$ in $Q^f_\varepsilon$.

3 Homogenization by two-scale convergence of the Nernst-Planck-Poisson system

The homogenization method by two-scale convergence that will be used in the sequel has been de-
veloped first by G. Nguetseng [12] and then by G. Allaire [1]. This new type of convergence enables
to capture at the limit the oscillations of a function in resonance with another one of the type of
$x \rightarrow \varphi \left( x, \frac{x}{\varepsilon} \right)$. This method has the advantage to avoid to postulate the form of an asymptotic
expansion of the unknowns, and to obtain for non-linear problems in the same time both the limit
homogenized model and the result of convergence (see [9] for an overview).

\(^4\)Expressed in $F/m^3$.

\(^5\)Pathological edges are excluded. We consider a Lipschitz boundary without reentrant corners.
The homogenization by two-scale convergence of ionic drift-diffusion equations (4)-(9) or (10)-(12) leads to the results:

**Theorem 1** The concentrations of anions and cations in the solution \((c_\pm) = (c_+, c_-)\), and the electrical potential \(\Psi^*\) are solution of the homogenized ionic diffusion problem in \(Q = ]0, T[ \times \Omega\)

\[
\Phi \frac{\partial c_\pm}{\partial t} - D_\pm \text{div} \left( \Upsilon \nabla c_\pm + \frac{F}{R \Theta} z_\pm c_\pm \Upsilon \nabla \Psi^* \right) = 0 ,
\]

\[
- \text{div} [\Lambda \nabla \Psi^*(t)] + \left( \int_{\Gamma^f} \lambda(y) ds(y) \right) \tau(\Psi^*) (t) = F \Phi (z_+ c_+ (t) - z_- c_- (t)) ,
\]

where \(\Phi\) denotes the porosity of the material. The symmetric positive definite tensor of homogenized diffusion \(\Upsilon\) is defined as follows

\[
\Upsilon_{kl} = \int_Y (\nabla_y \omega_k + e_k) \cdot (\nabla_y \omega_l + e_l)(dy),
\]

where \((\omega_k)\) is the family of the solutions defined by the cell problem:

\[
E_c \left\{ \begin{array}{ll}
(\omega_k) \in H^1_\#(Y) \\
- \text{div}_y (\nabla_y \omega_k + e_k) = 0 \text{ in } Y_f \\
(\nabla_y \omega_k + e_k) \cdot n = 0 \text{ on } \Gamma^f_f.
\end{array} \right.
\]

In a similar way, the symmetric definite positive tensor \(\Lambda\) is defined as

\[
\Lambda_{kl} = \int_Y \kappa(y) (\nabla_y \varsigma_k + e_k) \cdot (\nabla_y \varsigma_l + e_l) dy ,
\]

where \((\varsigma_k)\) is the family of the solutions defined by the cell problem:

\[
E_\Psi^* \left\{ \begin{array}{ll}
(\varsigma_k) \in H^1_\#(Y) \\
- \text{div}_y (\kappa(y) (\nabla_y \varsigma_k + e_k)) = 0 \text{ in } Y.
\end{array} \right.
\]

The reader may refer to [7] for the detailed proof of this result.

4 Steady solutions and asymptotic solutions

The general expressions of the concentrations for a very long time (steady and asymptotic solutions of the homogenized Nernst-Planck-Poisson system) are given in the following result:

**Theorem 2** The steady solutions of the homogenized Nernst-Planck-Poisson system (13)-(14) can be written in the form

\[
C_\pm = \kappa_\pm \exp \left( - \frac{F}{R \Theta} z_\pm \Psi^{**} \right) , \quad \kappa_\pm > 0 ,
\]

where \((\kappa_\pm)\) are two strictly positive constants. The potential \(\Psi^{**} = \Psi^{**}_{\kappa_\pm}\) is the unique (steady) solution in \(L^\infty(\Omega) \cap H^1(\Omega)\) of the variational Liouville equation:

\[
\int_\Omega \Lambda \nabla \Psi^{**}(x) \cdot \nabla w dx - F \Phi \int_\Omega \left( \sum_\pm z_\pm \kappa_\pm \exp \left( - \frac{F}{R \Theta} z_\pm \Psi^{**}(x) \right) \right) w dx \\
+ \left( \int_{\Gamma^f} \lambda(y) ds(y) \right) \int_\Omega \tau(\Psi^{**})(x) w dx = 0 \quad \forall w \in H^1(\Omega).
\]

The reader may also refer to [7] for the detailed proof of this result.
5 Conclusion

The homogenization of Nernst-Planck-Poisson system by two-scale convergence enabled to obtained a consistent model describing the ionic transfers, coupled with the electrocapillary effects, at the macroscopic scale for saturated porous media. The electrocapillary effects are taken into account in the homogenized Poisson equation through a source or a well term (according to the sign of the potential). With the approach used, not only it is not necessary to assume a priori an asymptotic expansion of the unknowns of the problem (the concentrations and the potential), but also we obtain a convergence result associated with the homogenized model. Moreover, the Poisson-Boltzmann distribution of concentrations is recovered as the general form of the asymptotic steady solutions of the homogenized Nernst-Planck-Poisson system.

References


