

# UPSCALING ELECTROKINETIC TRANSPORT IN CLAYS WITH LATTICE BOLTZMANN AND PORE NETWORK MODELS

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A method for the numerical determination of the steady-state response of complex charged porous media to pressure, salt concentration, and electric potential gradients is presented here. The Pore Network Model (PNM), describing the porosity as a network of pores connected by channels, is extended to capture electrokinetic couplings which arise at charged solid–liquid interfaces and allows us to compute the macroscopic fluxes of solvent, salt, and charge across a numerical sample submitted to macroscopic gradients. On the channel scale, the microscopic transport coefficients are obtained by solving analytically (in simple cases) or numerically the Poisson-Nernst-Planck and Stokes equations. The PNM approach then allows us to upscale these transport properties to the sample scale, accounting for the complex pore structure of the material *via* the distribution of channel diameters. The Onsager relations between macroscopic transport coefficients are preserved, as expected. Electrokinetic couplings, combined with the sample heterogeneity, result in qualitative differences with respect to their microscopic counterparts for some macroscopic transport coefficients, however (*e.g.* permeability or electro-osmotic coefficient). This underlines the care that should be taken when accounting for transport properties based on a single channel of average diameter.

## 1. Introduction

Electrokinetic effects refer to the dynamic coupling between the solvent and charge flows which occur at a charged interface. The presence of surface charge in a porous medium has important practical applications in membrane technology (*e.g.* ion exchange and water desalination) and in environmental science, because most rocks and soils contain minerals (such as clays) that bear a permanent surface charge. As an example, electro-osmosis generates a solvent flow under an applied electric field, due to the driving of the electrically charged fluid in the vicinity of charged surfaces. Conversely, a pressure gradient induces the flow of a charged fluid; hence, an electric current. In geophysics, the electroseismic effect, by which an electromagnetic wave is

generated from the motion of underground fluids under an applied acoustic wave, is exploited to determine the properties of geologic formations (Thompson, 1936; Mizutani *et al.*, 1976; Pride and Haartsen, 1996). Streaming potentials and electro-osmotic flows can be measured in the laboratory to characterize the properties of porous media (Luong and Sprik, 2013).

The modeling and simulation of electrokinetic effects in porous media, and, more generally, of all coupled transport phenomena, including the osmotic solvent flow due to a salt concentration gradient, thus have been the subject of a large number of investigations, both on the pore scale where the couplings originate, and on the sample scale corresponding to the experimental measurements. From a mathematical point of view, this upscaling can be performed rigorously using the homogenization approach. The homogenization approach provides expressions of the macroscopic transport coefficients as solutions of coupled partial differential equations on the pore scale, which then have to be solved using simplifying assumptions or numerically. Some general results, such as Onsager's relations for the macroscopic transport coefficients, can be demonstrated without even resorting to the numerical resolution of the mathematical problem (Moyne and Murad, 2006a, 2006b; Allaire *et al.*, 2010, 2014).

For practical applications, most studies of electrokinetic couplings rely on an oversimplified idealization of the geometry, with single slit pores or cylinders with dimensions or surface-charge densities estimated from the macroscopic properties of the real system (Bresler, 2010; Gonçalves *et al.*, 2012). The heterogeneity of the material, combined with the electrokinetic couplings, may influence the overall behavior at the sample scale, however, so that such idealizations may not reflect the actual response of the medium. Direct numerical resolution of the coupled Poisson-Nernst-Planck (PNP) and Navier-Stokes (NS) equations in various complex systems (random packings, reconstructed and fractured porous media) has also been proposed by Adler and co-workers. Such an approach is usually difficult to implement for macroscopic samples, due to the lack of experimental data on the fine structure of the material over large distances (Coelho *et al.*, 1996; Marino *et al.*, 2001; Gupta *et al.*, 2006). The systematic study of a representative number of samples is also prevented by the computational cost of direct numerical simulation.

In the case of clays, an additional difficulty arises due to the complex multiscale porosity of the material and the lack of experimental data at the intermediate scales. In the present contribution, a numerical homogenization scheme is presented which leads to a description of transport through macroscopic charged porous materials at low computational cost, thereby enabling the systematic study of the combined effects of electrokinetic couplings and sample heterogeneity. The algorithm to upscale the electrokinetic couplings is based on the PNM which relies, on the one hand, on a simplified description of the electrokinetic transport at the pore scale and, on the other hand, on a statistical distribution of the geometry of the pores. This allows investigation of how the upscaled electrokinetic properties depend on the heterogeneity of the sample, in addition to the surface charge density and the salt concentration.

## 2. Electrokinetics at the sample scale

At the macroscopic scale of a clay sample, pressure,  $P$ , electric potential,  $V$ , and salt concentration gradients (or, equivalently, solvent, cation, and anion chemical potential gradients), induce macroscopic fluxes of mass, electric charge, and salt (or, equivalently, solvent, cation, and anion chemical fluxes). For sufficiently small applied gradients, the response is linear and the fluxes can be expressed as a function of the applied gradients *via* a coupling matrix:

$$\begin{pmatrix} Q_0 \\ Q_1 \\ Q_2 \end{pmatrix} = -\frac{S}{\eta} \begin{pmatrix} K_0^P & K_0^C & K_0^V \\ K_1^P & K_1^C & K_1^V \\ K_2^P & K_2^C & K_2^V \end{pmatrix} \begin{pmatrix} \nabla P \\ \nabla C \\ \nabla V \end{pmatrix} \quad (1)$$

where the subscripts 0, 1, and 2 refer to solvent, cations, and anions, respectively,  $Q$  indicates their fluxes,  $C$  is the logarithm of the salt concentration,  $\eta$  is the solvent viscosity, and  $S$  is the cross-section area of the sample. Along the diagonal, one finds, for example, the sample permeability,  $K_0^P$ , and the electric conductivity,  $K_2^V$ . The fundamental question is, then, how do these coefficients emerge from the microscopic structure of the material, including heterogeneities on intermediate scales, and from the surface charge density of the solid matrix?

## 3. Electrokinetics on the pore scale

Recently, significant progress has been made on the derivation of the macroscopic transport equations from the pore-scale equations. These studies usually start from a continuous description of the fluid *via* transport equations, which are then upscaled to derive their average effect on the sample scale, which is quantified by a coupling matrix relating the solvent and ionic fluxes to the corresponding forces (pressure, potential, and concentration gradients). The solvent flow under applied local forces is accounted for *via* the NS equation (or even the Stokes equation), which includes a local force due to electrochemical potential gradients. The solute fluxes are due, on the one hand, to the advection by the fluid and, on the other hand, to the local electrochemical potential gradients; the fluxes can be modeled on this scale using the PNP equations. The limitations of such continuous descriptions to describe solvent and ion transport in clay nanopores, which can be assessed using molecular simulations (Botan *et al.*, 2011, 2013), will not be discussed here. Rather, the present discussion focuses on how to upscale this to the macroscopic scale, as the structure is too complex for a direct resolution on the whole sample.

The coupled Navier-Stokes and Poisson-Nernst-Planck equations can be solved numerically using finite element or volume methods. For example, Adler and co-

workers used this direct numerical resolution in various complex systems (random packings, reconstructed, and fractured porous media) (Coelho *et al.*, 1996; Marino *et al.*, 2001), demonstrating, in particular, a universal electrokinetic behavior if appropriate rescaled quantities are introduced (Gupta *et al.*, 2006, 2008). Recently, alternative methods have been proposed to simulate electrokinetic effects starting from a more fundamental description of the fluid than the PNP and NS equation (Pagonabarraga *et al.*, 2010). A hybrid lattice-based approach (Lattice Boltzmann Electrokinetics, LBE) has been proposed to capture the coupling of hydrodynamic flow with ion transport and the simulation of electrokinetic effects in colloidal suspensions (Capuani *et al.*, 2004; Pagonabarraga *et al.*, 2005). The Lattice Boltzmann simulations have been applied previously, without accounting for electrokinetic effects, to realistic rock geometries (Boek and Venturoli, 2010). In the context of the present numerical homogenization, LBE was recently used in a simple cylindrical geometry, in order to assess the validity range of the analytical solution of the linearized problem (Obliger *et al.*, 2013). This simpler analytical solution is then used in the PNM, even though in principle a numerical expression for the transport coefficient on the pore scale may also be used.

#### 4. Numerical homogenization *via* a pore network model

In order to investigate electrokinetic couplings on larger scales, including the effect of the heterogeneity of the material, a simplified description based on the PNM has been proposed. The model, originally developed by Fatt (1956) to predict multiphase flow properties in porous media, describes the porosity as a network of pores connected by channels and has been used extensively and extended by petrophysicists in various situations, such as capillarity and multiphase flow through porous media (Blunt, 2001; van Dijke and Sorbie, 2002; Békri *et al.*, 2005), or mineral dissolution and precipitation in the context of CO<sub>2</sub> sequestration (Algive *et al.*, 2010).

In a nutshell, the PNM approach amounts to solving a set of conservation equations on the nodes of the network (in analogy with Kirchhoff's law for a network of resistors), on the basis of local fluxes through the channels connecting the nodes, under the effect of an external, macroscopic gradient. For electrokinetics, the pressure, salt concentration, and electrical potential are introduced as pore variables on the nodes of the network. The fluxes through each link between nodes are determined locally using the transport matrix for a cylindrical channel, as determined in the previous section as a function of the channel diameter, the surface charge density of the solid, and the salt concentration inside the channel. The last of these is determined *via* the Donnan equilibrium with a fictitious reservoir corresponding to the properties of the pores at both ends of the channel (Obliger *et al.*, 2014); the macroscopic problem to be solved numerically has, therefore, a non-linear structure, which is contrary to most previous applications of the PNM approach. This can be achieved numerically using a non-linear Newton solver.

## 5. Transport coefficients at the sample scale

In addition to the transport coefficients on the channel scale, the crucial ingredient of the PNM is the distribution of pore/channel sizes and their spatial arrangement, describing in a very simplified manner the complex structure of the porous network. In order to demonstrate the feasibility of the approach and to investigate systematically the effect of heterogeneity, a model distribution (of the Weibull type) was considered first. A distribution deduced from experimental data may also be introduced if a reliable one can be provided.

For a given pore/channel diameter distribution, a sufficient number of networks must be generated. For each numerical sample, the macroscopic coefficients are determined by solving the conservation equations in the presence of applied gradients and by computing the macroscopic steady-state flux through the sample. In practice, three calculations must be done (one for each applied gradient) for which the three fluxes (mass, charge, salt concentration) are computed; this provides the nine macroscopic coefficients, which must then be averaged over the networks corresponding to the same diameter distribution.

## 6. Conclusion

The various steps of the proposed PNM approach are presented elsewhere in this volume with a focus on charged porous materials. The influence of the surface charge density, of the salt concentration in the reservoirs, and of the channel-diameter distribution was analyzed. The symmetry of the transport matrix is preserved by the present upscaling method, as required from Onsager's theory. In general, the coefficients of this matrix behave qualitatively as their microscopic counterpart for a channel with average diameter. The combined effects of electrokinetic couplings on the local scale and of heterogeneity, however, result in a decrease in the overall transport coefficients in accordance with Le Chatelier's principle. The coupling between the complex pore structure of porous media and the electrokinetic effects underlines the limitations of approaches based on idealized geometries (single slit pore or cylindrical channel) parameterized directly from the experimental macroscopic properties.

The relevance and limitations of this new strategy to the case of clay minerals are discussed. Experimental information on the pore network and its size distribution on intermediate (10–100 nm) scales is very desirable for the present method to provide more quantitative predictions. In the future, benefit should accrue from recent numerical (Tyagi *et al.*, 2013) and experimental (Levitz, 2007; Brisard *et al.*, 2012) developments for the generation of realistic numerical samples for the description of real materials. The diffusion of solutes in 3D images of a Callovo-Oxfordian clay-rich rock obtained by SEM and micro-CT experiments were simulated recently to investigate the effect of mineral distribution (Robinet *et al.*, 2012). Multiscale experiments using NMR also provide an ideal means of investigating the multiscale dynamics of mobile species in such complex materials (Porion *et al.*, 2013).

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