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SHORT TITLE: Upscaling electrokinetic transport in clays

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ABSTRACT

This contribution presents a method for the numerical determination of the steady-state response of complex charged porous media to pressure, salt concentration and electric potential gradients. 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. This 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. However, electrokinetic couplings combined with the sample heterogeneity result for some macroscopic transport coefficients (e.g. permeability or electro-osmotic coefficient) in qualitative differences with respect to their microscopic counterparts. This underlines the care that should be taken when accounting for transport properties based on a single channel of average diameter.

KEYWORDS: Electrokinetics, Coupled transport, Homogenization, Lattice Boltzmann, Pore Network Model, Upscaling

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, since 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 electro-magnetic wave is generated from the motion of underground fluids under an applied acoustic wave, is exploited to determine the properties of geological formations (Thompson, 1936; Pride and Haartsen, 1996; Mizutani *et al.*, 1976). 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 the mathematical point of view, this upscaling can be performed rigorously using the homogenization approach. This 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&b; 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, 1973; Gonçalvès *et al.*, 2012). However, the heterogeneity of the material, combined with the electrokinetic couplings, may influence the overall behavior on the sample scale, 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 on the intermediate scales, which is at the heart of this workshop. In the present contribution, we present a numerical homogenization scheme leading 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 Pore Network Model (PNM), which relies on the one hand on a simplified description of the electrokinetic transport on the pore scale and on the other hand on a statistical distribution of the geometry of the pores. This allows to investigate how the upscaled electrokinetic properties depend on the heterogeneity of the sample, in addition to the surface charge density and the salt concentration.

ELECTROKINETICS ON THE SAMPLE SCALE

On the macroscopic scale of a clay sample, pressure P, electric potential V and salt concentration gradients (or, equivalently, solvent, cation and anion chemical potentials 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:

$$\begin{pmatrix} \mathcal{Q}_0 \\ \mathcal{Q}_1 \\ \mathcal{Q}_2 \end{pmatrix} = -\frac{S}{\eta} \begin{pmatrix} K_0^P & K_0^C & K_0^V \\ K_1^P & K_1^C & K_1^V \\ K_2^P & K_2^C & K_2^V \end{pmatrix} \begin{pmatrix} \nabla P \\ \nabla C \\ \nabla V \end{pmatrix} \quad , \tag{1}$$

where the subscripts 0, 1 and 2 refer to solvent, cations and anions, respectively, Q indicate their fluxes, C is the logarithm of the salt concentration, η the solvent viscosity and S the cross-section 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?

ELECTROKINETICS ON THE PORE SCALE

Recently, significant progress has been made on the derivation of the macroscopic transport equations from the pore-scale ones. 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 one the one hand to the advection by the fluid and on the other hand to the local electrochemical potential gradients; they can be modelled 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.*, 2010&2013), will not be discussed here. Rather, the present discussion focusses on how to upscale this to the macroscopic scale, since 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 behaviour 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). For example, Capuani et al. proposed a hybrid lattice based approach (Lattice Boltzmann Electrokinetics, LBE) 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). Such Lattice Boltzmann simulations have already been applied, 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.

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, we have recently proposed a simplified description based on the Pore Network Model (PNM). Such a 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. It has been extensively used and extended by petrophysicists in various situations, such as capillarity and multiphase flow through porous media (Békri *et al.*, 2005; Blunt, 2001; van Dijke and Sorbie, 2002), or mineral dissolution and precipitation in the context of CO_2 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 latter 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). Therefore, the macroscopic problem to be solved numerically has a non-linear structure, contrary to most previous applications of the PNM approach. This can be achieved numerically using a non-linear Newton solver.

TRANSPORT COEFFICIENTS ON 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. However, it is also possible to introduce a distribution deduced from experimental data, if a reliable one can be provided.

For a given pore/channel diameter distribution, a sufficient number of networks must be generated. For each of 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. This general approach will be illustrated during the workshop on a number of test cases.

CONCLUSION

During the workshop, the various steps of the proposed PNM approach will be presented and its interest illustrated for charged porous materials. The influence of the surface charge density, the salt concentration in the reservoirs and of the channel diameter distribution will be 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 qualitatively behave as their microscopic counterpart for a channel with the average diameter. However, the combined effects of electrokinetic couplings on the local scale and of heterogeneity result in a decrease of the overall transport coefficients, in accordance with Le Châtelier's principle. Overall, the coupling between the complex pore structure of porous media and electrokinetic effects underlines the limitations of approaches based on idealized geometries (single slit pore or cylindrical channel) parametrized directly from the experimental macroscopic properties.

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

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