

# Homogenization of the ionic transport equations in periodic porous media

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## 1 Introduction

The transport of electrolyte (salt solution) through porous media is a classical multiscale phenomenon with numerous applications in geophysics and bio-porous materials modeling. Phenomenological equations relating the transport of ions and solvent to electrical potential, pressure and concentration gradients have achieved widespread acceptance in the literature. These equations are assumed to be valid on the scale of the porous body (the macroscopic or Darcy-scale) and represent an average, in some sense, of the pore-scale (or microscopic) equations. Attempts at deriving macroscopic transport equations from microscopic equations have been successful under various somewhat restrictive assumptions. In this article, I demonstrate how Darcy-scale transport equations may be derived with minimal assumptions using homogenization theory. Without any additional assumptions, it can be shown that the transport coefficient tensors obey certain fundamental thermodynamic requirements, namely, Onsager's reciprocal relations and the positive definiteness of the diagonal coefficient tensors. Onsager's reciprocal relations state that the tensor relating the independent thermodynamic forces to their corresponding fluxes, must be symmetric [1].

I consider an  $N$ -component electrolyte in a dilute solvent flowing through a rigid porous body with a periodic microstructure, where the geometry of the porous medium ensures that the inertia of the flow may be neglected. The electrolyte flows in response to a static (d.c.) electric field and a constant surface charge density on the pore walls. The magnitude of the applied field is assumed to be sufficiently small to permit the linearization of the ionic transport (electrokinetic) equations.

Gross and Osterle [2] derived Darcy-scale transport equations for the case of a capillary model for charged wide-pore membranes. This simple geometry allowed for a complete analytical solution of the electrokinetic equations including the establishment of the Onsager relations. By assuming the distance from the pore walls over which electrostatic interactions are significant to be very small, Edwards [3] employed a volume averaging approach to derive macroscopic transport equations for a periodic porous body. However, Edwards did not succeed in establishing Onsager's reciprocal relations. The paper by Marino et al. [4] studies a periodic porous medium subjected to an external electric field, a pressure gradient and a concentration gradient. The well-known phenomenological equations are assumed to hold and, starting from the electrokinetic equations on the pore-scale, the transport coefficient tensors are calculated numerically for a number of different microstructural geometries. Moyne and Murad [5, 6] also considered a periodic porous medium but in addition, they permitted the porous body to swell. No linearization of the equation describing the conservation of ionic species on the pore-scale was carried out. However they effectively neglected pore-scale ionic

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convection. Under the assumption that the ionic concentrations in the pore water are uniform, Revil and Leroy [7] used volume averaging to derive macroscopic transport equations from linearized microscopic equations. The Onsager relations were established under these conditions. In all of the aforementioned articles, only a 1-1 electrolyte was considered.

In this article I show that all of the aforementioned assumptions are unnecessary and consequently, my analysis includes the effects of pore-scale ionic convection. No assumptions are made regarding the microstructure. Although we assume periodicity of the porous domain, there exists an equivalence between periodic and statistically homogeneous random porous media [8].

This work is stimulated by the author's interest in developing a theory for the electroacoustic characterization of suspensions of porous particles [9]. To determine the electrophoretic motion of a porous particle, the governing equations outside the particle, inside the particle and the boundary conditions coupling the two domains need to be specified. The governing equations exterior to the particle are the well-known electrokinetic equations [10]. It is therefore natural to upscale the electrokinetic equations to obtain a Darcy-scale model inside the particle. The author has used scaling arguments in conjunction with recent results in homogenization theory to develop a model for the hydrodynamics of an oscillating porous particle [11], since electroacoustic experiments generate oscillatory flows. To be consistent with this work, homogenization theory is employed to upscale the electrokinetic equations.

## 2 Homogenization

Homogenization theory exploits the fact that transport phenomena in porous media occur on two disparate length scales: a *macroscopic* scale (the scale of the reservoir,  $L$ ) and a *microscopic* scale (the pore scale,  $\ell$ ). Transport phenomena can then be characterized via the small dimensionless parameter  $\epsilon = \ell/L$ . In practice we only observe macroscopic transport phenomena and it is sufficient for information regarding the microstructure to be retained purely in the form of averaged quantities, such as porosity and permeability. The homogenization process transforms equations on the microscopic scale to effective equations on the macroscopic scale by determining the limiting behavior of the microscopic equations as  $\epsilon \rightarrow 0$ . For an extensive coverage of homogenization and porous media, see [12].

I briefly describe the construction of a periodic porous domain with period  $\epsilon$ . A complete description of periodic porous media can be found in [8]. A standard cell consists of a three dimensional cube  $\mathcal{C}$  containing a standard obstacle  $\mathcal{S}$ , where the fluid part of the cell is  $\mathcal{Y} = \mathcal{C} \setminus \mathcal{S}$ , with boundary  $\partial\mathcal{C} \cup \partial\mathcal{S}$ . This cell is extended periodically, with period  $\epsilon$ , to all of three dimensional space. A domain  $\Omega$  is then intersected with the periodically extended standard cells to give the periodic porous domain. The fluid part of the periodic porous domain is given the symbol  $\Omega^\epsilon$ , with boundary  $\partial\Omega^\epsilon \setminus \partial\Omega$ . The limit  $\epsilon \rightarrow 0$  corresponds to the size of the cells becoming progressively smaller and greater in number until the fluid part is annihilated (or, the pore size goes to zero).

Under the assumptions stated in the introduction, the scaled linearized microscopic equations in  $\Omega^\epsilon$  are, for  $j = 1, \dots, N$  [13],

$$n_j = n_j^\infty \exp(-z_j \psi), \quad (1)$$

$$\epsilon^2 \nabla^2 \psi = -4\pi \sum_{j=1}^N z_j n_j, \quad (2)$$

$$\nabla^2 \Phi_j = z_j \nabla \psi \cdot \left( \nabla \Phi_j + \mathbf{E} + \frac{\lambda_j}{z_j} \mathbf{u} \right), \quad (3)$$

$$\epsilon^2 \nabla^2 \mathbf{u} = \nabla P + \sum_{j=1}^N z_j \nabla n_j (\Phi_j + \mathbf{E} \cdot \mathbf{x}), \quad (4)$$

$$\nabla \cdot \mathbf{u} = 0, \quad (5)$$

with boundary conditions on  $\partial\Omega^\epsilon \setminus \partial\Omega$ ,

$$\epsilon \hat{\mathbf{n}} \cdot \nabla \psi = -\sigma, \quad (6)$$

$$\hat{\mathbf{n}} \cdot \nabla \Phi_j = -\mathbf{E} \cdot \hat{\mathbf{n}}, \quad (7)$$

$$\mathbf{u} = \mathbf{0}. \quad (8)$$

The ionic parameters  $z_j$ ,  $\lambda_j$  and  $n_j^\infty$  represent the valency, drag and the bulk ionic number density of the  $j$ th ionic species, respectively. The physical constant  $\sigma$  is the surface charge density and  $\mathbf{E}$  is the applied electric field. The functions  $\psi$ ,  $n_j$ ,  $\Phi_j$ ,  $\mathbf{u}$  and  $P$  are the equilibrium electric potential, equilibrium number density of the  $j$ th ionic species, ionic potential of the  $j$ th ionic species, velocity of the solvent, and the partial pressure of the solvent. The vector  $\hat{\mathbf{n}}$  denotes the outward unit normal to  $\partial\Omega^\epsilon \setminus \partial\Omega$ . Observe that the boundary conditions are applied on the boundary of the pore walls, *not* on the boundary of the macroscopic domain  $\partial\Omega$ . For convenience, all functions and variables in (1)–(8) refer to dimensionless quantities. We shall adopt this convention for the remainder of the article.

To study the limit as  $\epsilon \rightarrow 0$  of (1)–(8), we postulate that  $\psi$ ,  $\mathbf{u}$ ,  $P$  and  $\Phi_j$  have formal two-scale asymptotic expansions of the form,

$$f(\mathbf{x}) = f_0(\mathbf{x}, \mathbf{y}) + \epsilon f_1(\mathbf{x}, \mathbf{y}) + \mathcal{O}(\epsilon^2),$$

where  $\mathbf{x} \in \mathbb{R}^3$  is the macroscopic (or slow) variable, and the  $f_i$  are  $\mathcal{Y}$ -periodic with respect to the microscopic (or fast) variable  $\mathbf{y} = \mathbf{x}/\epsilon$ . A  $\mathcal{Y}$ -periodic function has the same value on each opposite face of  $\partial\mathcal{C}$ . The two different length scales imply that the derivatives must be transformed according to,

$$\nabla = \nabla_x + \frac{1}{\epsilon} \nabla_y, \quad \nabla^2 = \nabla_x^2 + \frac{2}{\epsilon} \nabla_x \cdot \nabla_y + \frac{1}{\epsilon^2} \nabla_y^2.$$

The asymptotic expansions for  $\psi$ ,  $\mathbf{u}$ ,  $P$  and  $\Phi_j$  are substituted into (1)–(8) and terms of the same order of magnitude are compared, generating a cascade of equations. Solutions are sought in terms of products of macroscopic forcing terms and cell functions. Cell functions are defined only in  $\mathcal{Y}$  and are required to be  $\mathcal{Y}$ -periodic.

### 3 Non-Equilibrium Thermodynamics

After homogenization of the microscopic equations and integration over a cell, it is shown in [14] that the macroscopic fluid velocity and ionic flux of the  $j$ th species can be expressed as:

$$\mathbf{u}_{\text{eff}}(\mathbf{x}) = - \sum_{j=1}^N \mathbf{J}_j \cdot \nabla \mu_j^{\text{eff}}(\mathbf{x}) - \mathbf{K} \cdot \nabla p_{\text{eff}}(\mathbf{x}) \quad \text{in } \Omega, \quad (9)$$

$$\mathbf{j}_j^{\text{eff}}(\mathbf{x}) = -\mathbf{D}_j^s \cdot \nabla \mu_j^{\text{eff}}(\mathbf{x}) - \sum_{l=1}^N \mathbf{D}_{jl}^c \cdot \nabla \mu_l^{\text{eff}}(\mathbf{x}) - \mathbf{L}_j \cdot \nabla p_{\text{eff}}(\mathbf{x}) \quad \text{in } \Omega, \quad (10)$$

where  $\mu_j^{\text{eff}}$  and  $p_{\text{eff}}$  are the effective electrochemical potential and pressure, respectively. The electrochemical potential is a thermodynamic measure of how much work is required to return a system to equilibrium [15]; it is related to the ionic potential via,

$$\nabla \mu_j^{\varepsilon} = -z_j (\nabla \Phi_j + \mathbf{E}).$$

The tensors  $\mathbf{J}_j$  and  $\mathbf{L}_j$  are coupling tensors,  $\mathbf{K}$  is the permeability tensor,  $\mathbf{D}_j^s$  is a self electrodiffusion tensor and  $\mathbf{D}_{jl}^c$  accounts for cross electrodiffusion effects. Note that  $\mathbf{D}_{jj}^c \equiv \mathbf{0}$ . These transport coefficient tensors are expressed in terms of averages of cell functions that are solutions to given boundary value problems in  $\mathcal{Y}$ . For example, the  $\alpha\beta$  component of the permeability tensor is given by,

$$\{\mathbf{K}\}_{\alpha\beta} = \frac{1}{|\mathcal{Y}|} \int_{\mathcal{Y}} \{\mathbf{v}_{\beta}^1(\mathbf{y})\}_{\alpha} d\mathbf{y} + \sum_{j=1}^N \frac{1}{|\mathcal{Y}|} \int_{\mathcal{Y}} \{\mathbf{v}_{j\beta}^2(\mathbf{y})\}_{\alpha} d\mathbf{y},$$

for  $\alpha, \beta = 1, 2, 3$ , where  $|\mathcal{Y}|$  is the volume of  $\mathcal{Y}$ . The first term is the usual Darcy permeability tensor [12], but in the presence of ionic motion,  $\mathbf{K}$  contains extra contributions. The vectors  $\mathbf{v}_{\beta}^1$  and  $\mathbf{v}_{j\beta}^2$  represent microscopic solvent velocities:  $\mathbf{v}_{\beta}^1$  is nonzero in the absence of ions, while  $\mathbf{v}_{j\beta}^2$  arises purely from the pore-scale ionic convection of the  $j$ th species.

My aim is to establish the validity of these macroscopic equations. This shall be accomplished by proving, without any additional assumptions, that the above macroscopic system obeys one of the fundamental laws of non-equilibrium thermodynamics: Onsager's reciprocal relations. The primary reference for this section is [1].

Onsager's reciprocal relations are essentially a statement of time reversal invariance. That is, if a small perturbation to a system in some reference state is sent back in time, then the system will return to that reference state. If the system is expressed in the following format,

$$\mathcal{J} = \mathcal{M} \cdot \mathcal{F}, \quad (11)$$

where  $\mathcal{J}$  is a vector representing the fluxes and  $\mathcal{F}$  a vector of the independent thermodynamic forces, Onsager proved that the tensor  $\mathcal{M}$  must obey  $\mathcal{M} = \mathcal{M}^T$ , that is,  $\mathcal{M}$  must be symmetric. Recasting (9) and (10) into the form of (11) gives,

$$\begin{pmatrix} \mathbf{u}_{\text{eff}} \\ \mathbf{j}_1^{\text{eff}} \\ \vdots \\ \mathbf{j}_N^{\text{eff}} \end{pmatrix} = - \begin{pmatrix} \mathbf{K} & \mathbf{J}_1 & \cdots & \cdots & \mathbf{J}_N \\ \mathbf{L}_1 & \mathbf{D}_1^s & \mathbf{D}_{12}^c & \cdots & \mathbf{D}_{1N}^c \\ \vdots & \mathbf{D}_{21}^c & \ddots & & \vdots \\ \vdots & \vdots & & \ddots & \vdots \\ \mathbf{L}_N & \mathbf{D}_{N1}^c & \cdots & \cdots & \mathbf{D}_N^s \end{pmatrix} \cdot \begin{pmatrix} \nabla p_{\text{eff}} \\ \nabla \mu_1^{\text{eff}} \\ \vdots \\ \nabla \mu_N^{\text{eff}} \end{pmatrix}.$$

Symmetry of the coefficient tensor requires that:

$$\mathbf{K} = \mathbf{K}^T, \quad \mathbf{J}_j = (\mathbf{L}_j)^T, \quad \mathbf{D}_j^s = (\mathbf{D}_j^s)^T, \quad \mathbf{D}_{jl}^c = (\mathbf{D}_{lj}^c)^T, \quad (12)$$

must be true for each  $j, l = 1, \dots, N$  if the Onsager relations are to hold.

A necessary condition ensuring the entropy production of the system remains positive, is the positive definiteness of the diagonal tensors in  $\mathcal{M}$ . Therefore the permeability tensor  $\mathbf{K}$  and the self electrodiffusion tensor  $\mathbf{D}_j^s$  are required to be positive definite.

It is rigorously proven in [14] that (12) hold and the permeability and self electrodiffusion tensors are positive definite, for the transport coefficient tensors defined in this article. The proof follows directly from the ionic and fluid cell problems.

## 4 Discussion

Equations (9) and (10) are formally the same as the Darcy-scale equations modelling ionic transport in porous shales derived by Revil and Leroy [7], and are identical to the phenomenological transport equations presented in [1]. Explicit expressions for the transport coefficient tensors in terms of solutions to cell problems are presented in [14], where it is shown that all of the transport coefficient tensors have been influenced by the inclusion of pore-scale ionic convection in the present model.

This research constitutes a theoretical framework for a greater understanding of the assumptions underlying the phenomenological equations and similar models describing transport phenomena in porous media, however more work is required. For instance, computing the transport coefficient tensors numerically by solving the ionic and fluid cell problems will elucidate the relative importance of the terms in (9) and (10). Furthermore, making the underlying formal mathematical calculations rigorous by establishing the two-scale convergence [12] of the microscopic functions to their homogenized counterparts will further clarify the assumptions upon which (9) and (10) are based, and may be of independent mathematical interest.

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