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Modelling electrohydrodynamics in porous media

Fundamentals and model selection

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This report concerns a study which was conducted for Svensk Kärnbränslehantering AB (SKB). The conclusions and viewpoints presented in the report are those of the author. SKB may draw modified conclusions, based on additional literature sources and/or expert opinions.

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1 Preface

This report summarizes recent tasks and research conducted within the Pore Network Model project, without detailing specific findings. Previous results were documented in the memorandum Development of microstructural pore network models- Phase A. The primary objective of this document is to consolidate insights gained from modelling and research efforts to date. It aims to provide all stakeholders with a clearer understanding of the project's progress and support the planning of future tasks in alignment with SKB's objectives.

The document is structured as follows: Section 2 introduces the fundamentals of electrohydrodynamic modelling in microchannels. Section 3 outlines the core principles of the Pore Network Model, summarizes completed work, and proposes two potential directions for further development. Section 4 provides a brief overview of the Lattice Boltzmann Method (LBM), explores its applications in electrokinetic and electromigration modelling, and discusses its integration into electrohydrodynamic simulations for pores and porous media.

2 Electrohydrodynamics in microchannels

This chapter presents the fundamental physics of electrokinetic flow, with a focus on a modelling approach that couples the Navier-Stokes, Nernst-Planck and Poisson equations.

2.1 Basic concepts of electrokinetic flow

Electrohydrodynamics examines the influence of electrical forces on fluid dynamics, particularly in fluids containing charged particles, such as electrolytes. This field explores how these fluids respond to external electric fields and interact with charged surfaces. Electrokinetic phenomena commonly arise from:

- Ion motion under an external electric field (Electrophoresis in a stationary medium).
- Ion interaction with charged surfaces, forming the Electric Double Layer (EDL).
- Electrolyte motion driven by an external electric field (Electroosmosis near stationary charged surfaces).
- Induced electric potential due to an applied external force, such as a pressure gradient (Streaming Potential).

These phenomena will be briefly reviewed in the following sections.

2.1.1 Electrophoresis

Electrophoresis refers to the application of electric fields to move charged particles or ions in a stationary fluid. When an electric field is applied, charged particles experience an electrostatic force that drives their movement—Negatively charged particles (anions) migrate towards the positive electrode (anode), and positively charged particles (cations) migrates towards the negative electrode (cathode). However, their motion is opposed by two resistive forces. Frictional force arises as particles travel through the medium, with resistance depending on factors like particle size and the medium's viscosity—smaller particles face less friction and move faster than larger ones. Additionally, an electrophoretic retardation force comes into play due to the formation of an ionic cloud (or double layer) around each charged particle. This cloud, made up of oppositely charged ions from the surrounding fluid, creates a drag effect that slightly slows the particle's movement. The balance between these forces determines the particle's final velocity and migration behaviour during electrophoresis. Note that in electrophoresis, one does not apply any pressure gradients to cause a flow.



Figure 2-1. Illustration of electrophoresis.

2.1.2 Electrical double layers

When a charged object contacts an electrolyte, ions with an opposite charge to the object are attracted, while ions with the same charge are repelled. As a result, in a neutral electrolyte, an excess of counter-ions accumulates near the object, and an excess of co-ions forms at a distance. The region, where counter-ions accumulate, is known as the electrical double layer (EDL). The EDL consists of two distinct zones: the Stern layer, which includes adsorbed ions, and the diffuse layer, which contains mobile ions. Notably, the Stern layer is much thinner than the diffuse layer by several orders of magnitude, often leading to its exclusion in modelling considerations.



Figure 2-2. Illustration of electric double layers.

2.1.3 Electroosmosis

When a fluid carries a net charge, as in the diffuse layer of an EDL, an applied electric field exerts forces on the charged particles, causing them to move. This movement, in turn, drives the surrounding liquid, resulting in a phenomenon known as electroosmotic flow.



Figure 2-3. Illustration of electroosmosis.

2.1.4 Streaming potential

An electric field is generated when an electrolyte solution flows along a stationary charged surface under the influence of a pressure gradient. For example, a streaming potential develops when an electrolyte solution is pumped through a negatively charged capillary (as depicted in Figure 2-4). The electric field arises from the interaction between the charged surface and the electrolyte solution, with ion movement induced by the flow driven by the pressure gradient. The resulting charge imbalance at the interface between the bulk fluid and the charged surface creates the streaming potential. It is important to note that, this phenomenon occurs not due to an excess of free negatively charged particles in the bulk fluid, but rather due to the relative motion of ions near the surface during flow.



Figure 2-4. Illustration of streaming potential.

2.2 Mathematical formulation at pore scale

In modelling the motion of a charged fluid under the electrostatic forces, a coupled approach between various models is required. The electric field and its potential difference are determined by solving Poisson's equation (PE) with a specified charge density, which is derived from a set of Nernst-Planck (NP) equations. These equations account for the effects of the electric field, diffusion, and advection on the charge distribution, with one NP equation solved for each ion species in the solution. For example, in a 1:1 solution with equal concentrations of positive and negative ions, two equations are solved—one for positive ions and one for negative ions. The advective charge flux is obtained from the velocity field, determined by solving the Navier-Stokes (NS) equations. Additionally, forces arising from the electric fields acting on net charged regions of the fluid couple the NP equations with the NS equation. The interconnections between these equations are illustrated in Figure 2-5. The main transport equations to be solved are briefly discussed in the following sections.



Figure 2-5. Solving the complete physical model. Visualization depicting the interconnection between the three equations within the model: Poisson's equation (PE), the Nernst-Planck equation (NP), and the Navier-Stokes equation (NS). The dependencies are illustrated with arrows, indicating the quantities required from one equation to another (Bülling 2012).

2.2.1 Continuity equation

For an incompressible fluid, the continuity equation becomes:

 $\nabla \cdot \mathbf{u} = 0 \tag{2-1}$

Here, **u** represents the velocity vector field and ∇ denotes the divergence operator.

2.2.2 Navier-Stokes equation: motion of a fluid

The Navier-Stokes equation is a fundamental principle in hydrodynamics, governing the motion of a fluid under the influence of both internal and external forces. Its general form is derived from the principle of momentum conservation:

$$\frac{\partial(\rho \boldsymbol{u})}{\partial t} + \nabla \cdot (\rho \boldsymbol{u} \boldsymbol{u}) = -\nabla \mathbf{P} + \mu \nabla^2 \mathbf{u} + \mathbf{F}$$
(2-2)

In this equation, t represents time, ρ denotes density, P is pressure, μ is the dynamic viscosity and F accounts for external force contributions.

2.2.3 Nernst-Planck equation: transport of a charged particle

The charge concentration, c, within an electrolyte is influenced by several factors, including electrolyte advection, diffusion driven by concentration gradients, and the electric field generated by charged objects at the boundary or within the flow. These effects are described by the Nernst-Planck (NP) equation:

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(D \nabla c - \boldsymbol{u} c - \frac{D q_e}{k_B T} z c \nabla \psi \right)$$
(2-3)

In this equation, D is the diffusion coefficient, z is the ion species' charge number, qe is the fundamental charge, kB is the Boltzmann constant, and T is the fluid temperature. The final term represents the force exerted on charged particles by the electric field, driving positive ions toward negative potentials and vice versa. Here, ψ denotes the electric potential, and $\nabla \psi$ represents the electric field.

2.2.4 Poisson equation: distribution of the electrical potential ψ

To accurately model fluid flow dynamics in a pore with existing electrical double layers (EDLs), it is crucial to determine both the potential and charge distribution within the channel. These variables are interconnected, as described by Poisson's equation, Equation (2-4). In this context, ρe is the electrical charge density, ϵr denotes the relative permittivity, and $\epsilon 0$ is the vacuum permittivity. Under certain assumptions, the charge density can be derived explicitly as a function of the potential distribution, leading to the Poisson-Boltzmann equation.

$$\nabla^2 \psi = -\frac{\rho_e}{\varepsilon_0 \varepsilon_r} = \sum_i \frac{N_A z_i c_i e}{\varepsilon_0 \varepsilon_r}$$
(2-4)

2.2.5 Poisson-Nernst-Planck equations

The Poisson-Nernst-Planck (PNP) equations describe the transport of charged ions in an electrostatic environment by integrating diffusion, electromigration, and electrostatic interactions. This framework combines two fundamental equations:

- Nernst-Planck Equation Governs ion transport driven by diffusion and electromigration.
- Poisson Equation Determines the electric potential based on charge distribution.

This coupling introduces nonlinearity, as ion flux depends on the electric field, while the field itself is shaped by ion concentrations. The motivation for coupling these equations lies in the need for a self-consistent description of ion transport in electrostatically influenced systems. The Nernst-Planck equation alone describes ion motion but does not account for how ions alter the electric potential. Conversely, the Poisson equation computes the potential from charge distribution but does not track ion transport. The PNP model resolves this by capturing the two-way interaction: ion concentrations shape the electric field, which, in turn, governs ion movement.

2.3 Upscaling from pore scale to porous media scale

Scaling the conventional electrokinetic transport equations, such as the Poisson-Nernst-Planck (PNP) and Navier-Stokes (NS) equation, from the microscopic level, where the interactions take place, to the macroscopic scale, where most experiments are conducted, poses a significant modelling challenge. There are three primary approaches for upscaling pore-scale ion transport in charged porous media.

- 1. **Homogenization**: This technique represents ion transport within a representative elementary volume (REV) and derives a macroscopic constitutive equation. The resulting partial differential equation (PDE) requires effective parameters such as effective diffusivity or conductivity to characterize ion transport. However, material heterogeneity and electrokinetic couplings may affect the sample-scale behavior, limiting the applicability of this approach in accurately reflecting the medium's actual response. This method has been used in safety assessment modelling and to interpret experimental results.
- 2. **Pore Network Modelling (PNM)**: This approach simplifies the complex topology of a porous media by representing the geometry as straight channels or pore networks. While computationally efficient for upscaling, it may require simplifications to facilitate analytical or semi-analytical solutions, particularly for the Poisson equation. Additionally, accurately capturing the geometric features of porous media within PNM can be challenging.
- 3. **Direct Numerical Solutions**: Solving the coupled PNP and NS equations within complex systems offers another upscaling method. However, this approach faces challenges due to limited experimental data on material fine structure over varying distances and the high computational cost of conducting systematic studies with a representative sample. Techniques like the lattice-Boltzmann method (LBM) can alleviate these challenges, particularly with the use of image scanning, numerical image creation, and parallelization.

The following sections provide an overview of the PNM and LBM frameworks proposed for electrokinetic modelling at both the pore and porous media scales.

3 Pore Network Model

3.1 Basic idea of the PNM

The Pore Network Model (PNM) conceptualizes porosity as a network of interconnected pores. This approach involves solving a set of conservation equations at the network nodes, similar to Kirchhoff's law for resistive networks. This solution is based on local fluxes through the pores connecting the nodes, influenced by external macroscopic gradient, such as pressure, salt concentration, and electric potential gradients. Figure 3-1 illustrates the main features of this PNM.



Figure 3-1. *T* Two-dimensional representation of a cubic network between two reservoirs, labelled 1 and N. Each node is characterized by a pressure P_i , a salt concentration c_i , and an electric potential V_i . The flows of solvent, salt, and charge between these nodes under the effect of pressure, salt concentration, and potential gradients are, in the linear response regime, determined by the transfer matrix (g)_{ij}, which depends on the surface charge density and on the salt concentration inside the corresponding pore (Obliger et al. 2014).

PNM-based models often consider the linear response of a macroscopic sample, such as a rock, initially in equilibrium with two solution reservoirs, to the macroscopic gradients. These gradients drive flows of solvent, cations, and anions (or equivalently, salt concentration and electric charge) on the macroscopic scale. The total flows of solvent, Q_0 , salt Q_1 and charge Q_2 through the network are proportional to the macroscopic gradients of pressure, P, salt chemical potential, C, and electric potential, V, respectively. The goal is to determine the macroscopic transfer matrix **K**, defined in Equation (3-1), by solving the underlying transport equations, namely Poisson's equation (PE), Nernst-Planck (NP), and Navier-Stokes (NS).

$$\begin{pmatrix} Q_0 \\ Q_1 \\ Q_2 \end{pmatrix} = \begin{pmatrix} K_P^0 & K_C^0 & K_V^0 \\ K_P^1 & K_C^1 & K_V^1 \\ K_P^2 & K_C^2 & K_V^2 \end{pmatrix} \begin{pmatrix} \nabla P \\ \nabla C \\ \nabla V \end{pmatrix}$$
(3-1)

The transfer matrix **K** is expected to be symmetric, in accordance with Onsager's reciprocity principle (Onsager 1931). At the pore scale, the linear response between two nodes *i* and *j* follows the same structure as the macroscopic response. Thus, the local flows of solvent, q_0 , salt, q_1 , and charge (electric current), q_2 , can be expressed as

$$\begin{pmatrix} q_0 \\ q_1 \\ q_2 \end{pmatrix}_{ij} = \begin{pmatrix} g_P^0 & g_C^0 & g_V^0 \\ g_P^1 & g_C^1 & g_V^1 \\ g_P^2 & g_C^2 & g_V^2 \end{pmatrix}_{ij} \begin{pmatrix} \nabla_{ij}P \\ \nabla_{ij}C \\ \nabla_{ij}V \end{pmatrix}$$
(3-2)

The coefficients in the matrix $G = g_{ij}$ in Equation (3-2) can be determined by analysing and solving the mechanisms underlying the coupling between solvent and ionic flows. These coefficients can, in principle, be calculated as a function of relevant parameters using both analytical and numerical techniques. The conventional description of these coupled solvent and ionic flows involves solving a set of coupled differential equations, (a) Navier-Stokes, which accounts for momentum conservation in the fluid and incorporates the effect of all local forces, including the electric force due to the local electric charge and electric field; (b) Nernst-Planck equation, which governs ion conservation and includes advection effect from the fluid flow; and (c) Poisson equation, which determines the electric potential distribution from the charge distribution. The fluxes of solvent and ions under gradients of pressure, salt concentration, and electric potential can then be solved for a given pore geometry and boundary conditions. It is important to note that simplifications are often required to solve these coupled systems for each pore. Local fluxes are computed at each node by ensuring the conservation of solvent, salt, and charge, resulting in a set of equations for the node variables P_i , C_i , and V_i . These equations are then solved to determine the distribution of these variables across the network. Finally, local, and macroscopic fluxes, as well as the elements of the macroscopic transfer function in the \mathbf{K} matrix, can be derived.

3.2 Developed PNM by Kemakta

In our initial attempt to develop and implement a PNM, we introduced certain simplifications based on Martin Löfgren's formulations in the Task Description document¹.



Figure 3-2. Illustration of a segment of the water-filled pore where the pore walls 1 and 2 are smooth parallel plates with uniform aperture, b_p .

- **Pore Geometry**: Pore segments are modelled as flat parallel plate structures, as illustrated in Figure 3-2.
- Fluid Flow: The pore water flow driven by a pressure difference ΔP (Pa) across the rock sample is approximated using the viscous flow assumption between parallel plates, consistent with channel-network models. For a rectangular pore segment, the cubic law equation describes the volumetric flow Q (m³/s) as:

$$Q = \frac{W_s}{\eta L_s} \frac{b_{ps}^3}{12} \cdot \Delta P \tag{3-3}$$

Where b_{ps} (m) is the segment's uniform aperture, L_s (m) is the length of the pore segment, W_s (m) is the width, and η (Pa·s) is the dynamic viscosity.

- **Electromigration:** In the first phase of the project, several assumptions are made to simplify electromigration modelling:
 - 1. The tracer bulk concentration is assumed to remain constant throughout the porous system.
 - 2. In the absence of a concentration gradient, diffusion is neglected in the Nernst-Planck equation, leaving the electrical potential gradient as the sole driving force.

Under these conditions, the anionic and cationic electrical current in the x-direction of each rectangular segment is given by:

$$I_{a,s} = b_{p,s} \kappa_{a,s} \cdot \frac{W_s}{L_s} \cdot \Delta U \tag{3-4}$$

$$I_{a,s} = b_{p,s} \kappa_{c,s} \cdot \frac{w_s}{L_s} \cdot \Delta U \tag{3-5}$$

¹ SKBdoc 1981119 ver 1.0, Svensk Kärnbränslehantering AB (internal document)

Where κ_a (S/m) and κ_c (S/m) is the average anionic and cationic conductivity within the pore water of the segment. For a two-component electrolyte the anionic and cationic conductivities are given by:

$$\kappa_a = \left(1 - \frac{2\lambda_s}{bp}\right) \frac{F^2}{RT} D_{w,a} z_a^{-2} \xi_{a,DL} c_a^B \tag{3-6}$$

$$\kappa_c = \left(1 - \frac{2\lambda_s}{bp}\right) \frac{F^2}{RT} D_{w,c} z_c^2 \xi_{c,DL} c_c^B$$
(3-7)

Here, it is assumed that cations sorbed in the Stern layer do not contribute to the cationic conductivity. In the above equations D_w (m²/s) is the diffusion coefficient of the ion in free water, $\xi_{a,DL}$ (–) and $\xi_{c,DL}$ (–) are the anion exclusion and cation enhancement factors for the diffuse layer, and λ_s (m) is the Stern layer thickness, F (C/mol) denotes the Faraday constant, z_i (–) is the charge number of the tracer, R (J/mol·K) is the gas constant, and T (K) is the temperature.

Hence, using similar notation as in Equation (3-1), we assumed Q_{θ} to be a function of the pressure gradient, while Q_2 is solely dependent on the electrical potential gradient. As a result, we considered only the diagonal elements in the matrix **G**. Additionally, Q_1 was neglected in this phase, and instead, a particle tracking technique was employed to monitor the transport of charged particles within the network.

During this initial phase, the following milestones were achieved:

- 1. Development of transport equations for a single pore.
- 2. Creation of pore-scale lattice network models.
- 3. Creation of pore-scale Voronoi network models.
- 4. Calculation of pore apertures based on the Weibull distribution
- 5. Establishment of a relationship between aperture and hydraulic conductivity, following the Cubic law.
- 6. Calculation of steady-state pore water flow and particle tracking.
- 7. Establishment of a relationship between aperture and electrical conductivity, utilizing the Poisson-Boltzmann equation with the Debye-Hückel approximation.
- 8. Calculation of steady-state anionic/cationic currents and cation/anion transport.
- 9. Statistical analysis of the network properties.

We concluded that it is relatively straightforward to create and solve pore network problems, provided the necessary input data are available. Furthermore, flow and transport problems can be efficiently addressed within this framework.

3.3 Future improvements

We propose the following steps for advancing the Pore Network Model:

- 1. Revisit and enhance the existing model:
 - Assess the simplifying assumptions, with particular focus on evaluating the feasibility of integrating the coupling between the different transport phenomena.
 - Enhance the model's accuracy and expand its applicability.
 - Implement the proposed upgrades within the current programming framework and tools.

- 2. Incorporate the multi-scale model (Alizadeh and Mani 2017) into the Pore Network Model:
 - **Model description**: This model employs a multi-scale approach to efficiently simulate nonlinear electrokinetic phenomena in micro- and nano-scale pore networks. Each pore is modelled as a one-dimensional element, with governing equations for fluid flow, charge transport, and ion transport derived through area-averaging. Assuming cross-sectional equilibrium, the model captures the electric double layer (EDL) effect, which induces non-uniform flow and concentration profiles. Instead of explicitly resolving these variations, the model incorporates their influence through tabulated transport coefficients, ensuring robust applicability across different surface charge densities and EDL thicknesses. This multi-scale framework enhances computational efficiency while maintaining the fundamental physics of electrokinetic transport in complex pore networks.
 - Code package: Dedicate time to thoroughly understanding the accompanying C++ code package, which is readily accessible in Alizadeh and Mani (2017). A simple example for a single pore has been successfully executed; however, a manual is missing, and there are no instructions on constructing a network of interconnected pores. Despite these challenges, gradually extending the code to handle pore networks is crucial for scaling the Pore Network Model (PNM) to more realistic and complex representations. Utilize an alternative analytical solution for cylindrical pores given in (Obliger et al, 2014):
 - Begin by reviewing the simplifying assumptions underlying this model and utilize the derived analytical solutions to construct networks of cylindrical channels.
 - Implement a new non-linear solver in Python to solve the system.

Feature	Pore Network Model
Representativeness	The model simplifies the geometry of porous media into straight channels or pore networks, but matching geometrical features of the porous media, such as porosity and BET surface area, can often be challenging.
Code availability	In (Alizadeh and Mani 2017), the code package is readily available, and a simple example for a single pore has been successfully executed. However, instructions for constructing a network of interconnected pores are not provided.
Analytical solutions and solver	In (Obliger et al. 2014), while the code is not available, analytical solutions for determining transfer functions are provided. To solve the system of equations, a non-linear Newton solver must be employed.
Anion exclusion effect	Anion exclusion effect can be incorporated using the Donnan model and the Poisson-Boltzmann equation.
Computational Efficiency	In the model presented in (Alizadeh and Mani 2017), pre-tabulated data is utilized to solve the coupled partial differential equations (PDEs). Additionally, the system of equations for a pore network can be solved using a linear solver and is suitable for parallelization.
	In contrast, the model presented by Obliger et al. (2014) employs analytical solutions at the pore scale. However, the formulation leads to a non-linear system of equations that requires a non-linear Newton solver for solving the pore network.

Table 3-1. Some features of Pore Network Model.

4 The lattice-Boltzmann method

4.1 Introduction

In fluid dynamics, discussions often span across microscopic, mesoscopic, and macroscopic perspectives. The 'microscopic' perspective refers to a molecular-level description, whereas 'macroscopic' viewpoint involves a continuous fluid model characterized by observable variables such as fluid velocity and density. At the microscopic scale, systems are governed by Newtonian dynamics, while the Navier-Stokes equation (NSE) describes the behaviour of fluid continua. Between these two extremes lies the 'mesoscopic' scale, which doesn't track individual molecules but rather focuses on distributions or representative groups of molecules. The kinetic theory provides the mesoscopic framework for fluid behaviour and forms the basis of the lattice Boltzmann method (LBM).

Currently, the lattice-Boltzmann method (LBM) is predominantly used in fluid dynamics to compute solutions for the macroscopic Navier-Stokes equation. However, its application extends beyond this domain. Recently, LBM has successfully employed to solve other macroscopic equations including the (coupled) Nernst-Planck and Poisson's equations. Several significant applications of LBM are discussed in Section 4.5.

4.2 Basic idea of the LBM

As previously mentioned, the lattice-Boltzmann method operates at a mesoscopic scale, which means that it does not model fluids at the microscopic level (e.g., Molecular Dynamics, MD) nor does it directly solve macroscopic equations (e.g. Computational Fluid Dynamics, CFD). Instead, LBM aims to solve a macroscopic equation *indirectly*, by employing a statistical model that uses mesoscopic variables. Under certain conditions, these variables mimic the behaviour of the macroscopic variables, ensuring that macroscopic conservation equations are satisfied through a specific scheme.

The fundamental variable in LBM, is the particle distribution function $f(\mathbf{x}, \boldsymbol{\xi}, t)$, which serves as a generalized representation of mass density, $\rho(\mathbf{x}, t)$, while also incorporating microscopic particle velocities. While $\rho(\mathbf{x}, t)$, reflects mass density in physical space, $f(\mathbf{x}, \boldsymbol{\xi}, t)$ simultaneously describes mass density in both three-dimensional physical space and three-dimensional velocity space. The distribution function *f* is related to macroscopic variables such as mass density ρ and fluid velocity **u** through its moments. These moments are integrals of *f*, weighted by functions of particle velocity, $\boldsymbol{\xi}$, across the entire velocity space. For example, the macroscopic mass density can be determined as follows:

$$\rho(\mathbf{x}, \mathbf{t}) = \int f(\mathbf{x}, \boldsymbol{\xi}, \mathbf{t}) \, \mathrm{d}^{3}\boldsymbol{\xi} \tag{4-1}$$

By integrating over velocity space in this way, we are considering the contribution to the density of particles of all possible velocities at position x and time t. We can also account for the particles' contribution ξf to the momentum density. By considering all conceivable velocities, we derive the macroscopic momentum density as follows:

$$\rho(x,t)\boldsymbol{u}(x,t) = \int \boldsymbol{\xi} f(x,\boldsymbol{\xi},t) \,\mathrm{d}^{3}\boldsymbol{\xi}$$
(4-2)

The distribution function $f(x,\xi,t)$ evolves over time as particles move and interact. This evolution is governed by the Boltzmann equation.

$$\frac{\partial f}{\partial t} + \boldsymbol{\xi} \cdot \nabla_{\boldsymbol{x}} f + F \cdot \nabla_{\boldsymbol{\xi}} f = \Omega(f)$$
(4-3)

This can be perceived as a type of advection equation: the first two terms denote the distribution function being advected with the velocity ξ of its particles. The third term encapsulates forces influencing this velocity. On the right-hand side, we encounter a source term, which signifies the local redistribution of *f* due to collisions. Thus, the source term $\Omega(f)$ is referred to as the 'collision operator'.

Through statistical methods and appropriate averaging techniques, it can be shown that the macroscopic equations of fluid mechanics like the Continuity and Navier-Stokes equations can be derived directly from the Boltzmann equation. This derivation is crucial as it bridges the microscopic world of individual particle interactions with the macroscopic behaviours observed in (macroscopic) fluid flow.

Hence, it can be inferred that solving the Boltzmann equation yields the equations of fluid dynamics on the macroscale. Consequently, by obtaining a solution to the Boltzmann equation (*f*) for a specific case, we can derive a solution to the NSE for the same scenario. However, the challenge lies in the fact that the Boltzmann equation is even more complex to solve analytically compared to the NSE. This complexity arises because its fundamental variable, $f(x, \xi, t)$, is a function of seven parameters: *x*, *y*, *z*, ξ_x , ξ_y , ξ_z , and *t*. As a result, numerical solutions are often computationally demanding, necessitating access to large-scale computers and substantial programming efforts.

To mitigate this issue, the lattice Boltzmann equation (LBE) is formulated through a two-step process of discretizing the Boltzmann equation. Initially, velocity space is discretized by constraining the continuous particle velocity to a discrete set of velocities. Subsequently, physical space and time are discretized by integrating along characteristic paths of the discrete velocity set. These characteristic paths represent the trajectories that particles follow in a discrete time step based on their assigned discrete velocities, ensuring that particle movement aligns with the Lattice Boltzmann framework. The combination of these steps yields the lattice Boltzmann equation. In essence, the lattice Boltzmann equation solves a discretized version of the Boltzmann equation, Equation (4-3) to obtain the distribution functions, from which macroscopic quantities can be derived. This method discretizes both spatial positions and velocity space, enabling distributions to reside only at specific positions and to stream solely in certain directions to neighbouring locations. A simplistic way to envision the evolution of f is to regard the distribution functions at lattice nodes as pseudo-particles traversing the lattice and undergoing collisions. In the lattice Boltzmann method, the velocity space is discretized by limiting the continuous particle velocity $\boldsymbol{\xi}$ to a discrete set of velocities $\{\boldsymbol{\xi}_i\}$. There are various approaches to construct these velocity sets. The first is based on the Gauss-Hermite quadrature rule. These velocity sets are usually denoted by DdQq, where d is the number of spatial dimensions the velocity set covers, and q is the set's number of velocities. The most commonly used velocity sets to solve the Navier-Stokes equation are D1Q3, D2Q9, D3Q15, D3Q19 and D3Q27. In practice, the aim is to employ the minimum number of velocities feasible to reduce memory usage and computational demands. Nonetheless, there exists a trade-off between utilizing smaller velocity sets (e.g., D3Q15) and achieving higher accuracy (e.g., D3Q27). In three dimensions, the velocity set most frequently utilized is D3Q19.

As discussed earlier, through discretizing the Boltzmann equation in velocity space, physical space, and time, we derive the lattice Boltzmann equation.

$$f_i(x + c_i\Delta t, t + \Delta t) - f_i(x, t) = \Omega_i(x, t)$$
(4-4)

This indicates that particles $f_i(x, t)$ move with velocity \mathbf{c}_i to a neighbouring point $x + c_i \Delta t$ at the subsequent time step $t + \Delta t$. Concurrently, particles are influenced by a collision operator $\Omega_i(x, t)$. This operator simulates particle collisions by redistributing particles among the populations f_i at each site. While there exists numerous collision operators Ω_i available, the simplest one that can be used for Navier-Stokes simulations is the Bhatnagar-Gross-Krook (BGK) operator:

$$\Omega(f_i) = -\frac{1}{\tau} \left(f_i - f_i^{eq} \right) \tag{4-5}$$

The equilibrium distribution function is given by:

$$f_{i}^{eq} = w_{i}\rho \left[1 + \frac{1}{c_{s}^{2}}c_{i} \cdot u + \frac{1}{2c_{s}^{4}}(c_{i} \cdot u)^{2} - \frac{1}{2c_{s}^{2}}u \cdot u\right]$$
(4-6)

With the weights w_i specific to the chosen velocity set, c_s is the denotes the speed of sound.

4.3 Computational algorithm

To solve the lattice Boltzmann, Equation (4-4), the distribution functions must be initialized to some initial value. The update in each time step is usually divided into two computational tasks. First, the new value that later will be propagated to a neighbouring node is computed, i.e.

$$f_i^*(x,t) = f_i(x,t) - \frac{1}{\tau} \Big(f_i(x,t) - f_i^{eq}(x,t) \Big)$$
(4-7)

This step will be referred to as the *collision* step since it is here the "collision" is computed. The second step consists of propagating the distribution functions to the neighbouring node in its corresponding direction, i.e.

$$f_i(x + c_i\Delta t, t + \Delta t) = f_i^*(x, t)$$
(4-8)

This step will be referred to as the *streaming* step. At each time step, the boundary conditions must also be handled.

4.4 Lattice Boltzmann Advection-Diffusion

The LBM is not only used for fluid dynamics; it is also a powerful method to solve advectiondiffusion problems. In fact, there is a growing interest in studying systems with coupled fluid dynamics and diffusion with LBM. Advection-diffusion problems are prevalent in natural phenomena. They encompass processes such as mixing and heat diffusion in fluids. The governing equation for such phenomena is the advection-diffusion equation (ADE) for a scalar field C, which may represent variables like concentration or temperature.

$$\frac{\partial C}{\partial t} + \nabla \cdot (\mathbf{u}C) = \nabla \cdot (D\nabla C) + q \tag{4-9}$$

The left-hand side describes the advection of C in the presence of an external fluid velocity **u**, while the right-hand side contains a diffusion term with diffusion coefficient D and a possible source term q. The advection-diffusion equation (ADE) and the Navier-Stokes equation share strong similarities. In fact, we can interpret the Navier-Stokes equation as an ADE for the fluid momentum density vector ρu . Therefore, it can be understood that the lattice Boltzmann method is readily adaptable to advection-diffusion equation. Similar arguments can be extended to the Nernst-Planck and Poisson equations using different change of variables.

4.5 LBM applications relevant to our objectives

In the following sections, we present a selection of applications of the Lattice Boltzmann Method in the literature, with a focus on electrokinetic and electromigration modelling. The reader is encouraged to consult the cited academic papers for further details. It is important to note that these papers represent just a portion of existing body of work, and additional relevant research can be found in the broader literature.

- **Diffusion (clay)**: Experiments on anion and cation diffusion along with pore-scale modelling in compacted clays were conducted. The purpose of these studies was to compare experimental and modelling (LBM) results and to quantify the extents of anion exclusion and cation sorption in various types of clay.
 - Anion Diffusion in Compacted Clays by Pore-Scale Simulation and Experiments (Wu et al. 2020)
 - Cation Diffusion in Compacted Clay: A Pore-Scale View (Yang and Wang 2019)
 - Upscaling scheme for long-term ion diffusion in charged porous media (Yang and Wang 2017)

- **Diffusion (cement): Pore-scale modelling of chloride ion diffusion in cement** microstructures was performed and the results were compared with experimental data.
 - Pore-scale modelling of chloride ion diffusion in cement microstructures (Yang and Wang 2018).
- Electrokinetic flows: Pore-scale modelling of electrokinetic flows (electroosmosis) in microchannels was conducted.
 - Lattice Poisson–Boltzmann simulations of electro-osmotic flows in microchannels (Wang and Wang 2006).
 - Modelling electrokinetic flows in microchannels using coupled lattice Boltzmann methods (Wang and Kang 2010).
- **Reactive transport**: A modelling framework is proposed for pore-scale fluid flow and reactive transport based on a coupled lattice Boltzmann model (LBM).
 - Coupled Lattice Boltzmann Modelling Framework for Pore-Scale Fluid Flow and Reactive Transport (Liu et al. 2023).

4.6 Steps in a healthy progression to incorporate LBM into our projects.

An extensive open-source LBM software package (LBPM 2020) is available for modelling transport problems in porous media in both two-dimensional (2D) and three-dimensional (3D) domains. The following progression steps are recommended for utilizing this software package:

1. Start with 2D models at pore scale:

• Begin by working with simpler 2D models at the pore scale. A basic example has been successfully executed but has not yet been fully validated. This initial phase allows for a foundational understanding of the LBM application in various pore representations.

2. Validation against analytical solutions and COMSOL:

• Validate the 2D models against analytical solutions under specific limiting conditions. Additionally, compare results with simulations in COMSOL. This step establishes confidence in the accuracy of your LBM simulations.

3. Progress to 3D models using rock properties:

- Transition to 3D models by incorporating rock properties like porosity and surface area.
- The LBM software package (LBPM 2020) is available, and several examples have been successfully executed. However, these models have not yet been validated.
- Utilize the Quartet Structure Generation Set (QSGS) method (Wang et al. 2007) to create realistic digital 3D rock models. QSGS is a stochastic approach that generates porous structures by simulating the nucleation and growth of solid grains within a voxel-based framework, allowing statistical control over properties such as porosity and surface area. These digital rock models can then be used in Lattice Boltzmann Method (LBM) simulations to evaluate flow accuracy and computational efficiency.
- This step will further enhance the realism and applicability of the LBM approach in capturing transport processes in realistic porous media.

4. Analysis and model evaluation:

• Run comprehensive analyses on the 3D models to understand their behaviour. Evaluate the accuracy of the LBM results against any available experimental data. This step helps assess the model's reliability in representing real-world scenarios.

5. Utilize micro-computed tomography (CT) data:

• Leverage the high-resolution imaging technique (Micro-CT) to capture detailed 3D structures of materials at the microscale. Convert these scans into digital models for simulation using LBM. This real-world data integration enhances the project's applicability to actual conditions.

6. Run 3D simulations and compare results:

• Conduct 3D simulations on the models derived from Micro-CT scans. Compare the results with both the 2D simulations and any available experimental data. This comparative analysis enhances the understanding of the system's behaviour in a 3D context.

Feature	Lattice Boltzmann Model
Representativeness	QSGS can create digital rock models that match the porosity and surface area of a given rock, accommodating both simple and complex porous structures, whether derived from scans or artificially generated.
Code availability	A comprehensive software package (LBPM 2020) is available, encompassing all Lattice Boltzmann (LB) schemes and fully parallelized, including GPU utilization. It has been successfully installed at Kemakta, with several examples executed successfully. However, the manual is currently limited and still under development.
Alternative code package	An alternative simpler code package (Bülling 2012) is also available. Several tests, including the electromigration example, have been successfully conducted. However, it is not fully parallelized and lacks proper packaging.
Anion exclusion effect	It can be directly incorporated through the coupled Poisson-Nernst–Planck equation.
Computational Efficiency	The coupled Poisson-Nernst-Planck (PNP) model can be computationally demanding without high-performance computing capabilities. However, this can be mitigated by employing parallel computing with the LBPM and GPU acceleration.

Table 4-1. Some features of Lattice Boltzmann model.

5 Final remarks

This report explores the fundamentals of electrohydrodynamic modelling and presents two approaches for further development. The first approach focuses on the Pore Network Model (PNM), which provides a scalable framework for modelling electrokinetic processes in porous media. The second approach utilizes the Lattice Boltzmann Method (LBM), a powerful tool for simulating electrokinetic flow and electromigration at the nano-scale. Both approaches are examined in terms of their capabilities, challenges, and potential for integration to enhance our understanding of electrokinetic phenomena across different scales.

While the PNM can be scaled up to model rock samples, it requires simplifying assumptions. However, the multi-scale model formulation proposed by Alizadeh and Mani (2017) can incorporate essential processes for electrokinetic modelling, ensuring an efficient yet computationally feasible approach. The software package for this model is available, but it lacks a comprehensive user manual.

The LBM, as a versatile and powerful numerical method, excels in modelling electrokinetic flow and electromigration in both 2D and 3D digital geometries. By leveraging techniques such as Micro-CT imaging and the Quartet Structure Generation Set (QSGS) method, challenges related to experimental data availability and fine-scale material structures can be addressed. Moreover, the high computational cost associated with LBM simulations can be mitigated through its parallelization capabilities. While an open-source software package for LBM modelling has been released, further investigation into its computational efficiency specific to our modelling cases is necessary, as hands-on experience in this area remains limited.

It is recommended to continue using both models in parallel. The LBM is ideal for modelling ion transport in single pores or nano-scale pore networks, offering valuable insights into electrokinetic phenomena in porous environments with diverse geometries, such as clay or cement structures. In contrast, the PNM can leverage the insights from LBM modelling to address larger-scale porous-media models, such as those representing rock samples. This dual approach can enhance the PNM by incorporating findings from LBM simulations, helping to refine assumptions and predict electromigration effects in scenarios involving complex pore intersections.

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