

Modelling of electrokinetic flow using the lattice-Boltzmann method

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Abstract

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The lattice-Boltzmann method is used to model flow in electrokinetic systems. A modelling approach based on the coupling of Navier-Stokes, Nernst-Planck and Poisson's equation of electrostatics is utilised. Three lattice-Boltzmann methods are formulated for the three equations respectively.

The method is implemented in C++ with the aim of being high performing. Topics as locality, instruction pipelines and parallel computing are considered. The implementation is tested for a number of classic examples with known solutions, e.g. Taylor-Green vortex flow, an Helmholtz equation and an advection-diffusion situation. The computed solutions agree well with the analytic solutions.

The physical systems modelled consists mainly of various charged channel flows of ionic solutions. Electrokinetic effects, such as electroosmosis and the electroviscous effect are studied. This is done in thin channels where the thickness of the electrical double layers is comparable to the channel dimension. The electroviscous effect is shown to slow the flow down and a local minimum is found in the velocity profile for thick enough double layers. Other more complicated systems are also studied; electroosmotic flow in a channel with heterogeneously charged walls and flow in an array of charged squares.

Keywords: lattice-Boltzmann, electrokinetics, electrohydrodynamics, Nernst-Planck, Poisson-Boltzmann, high performance computing.

1 Introduction

This thesis deals with modelling of physical problems in the interdisciplinary field of hydrodynamics and electrostatics. The tool used for realising this is the new and promising but somewhat immature lattice-Boltzmann method. This is a method that is still under development but is today used in practical applications both in industry and academy.

1.1 Background

There is currently an ongoing project at the mathematics faculty of Chalmers University in producing a modelling package that should be able to deal with transport of various liquids and particles through complicated structures. The method of choice has fallen upon the lattice-Boltzmann method for its suitable characteristics in the systems of interest.

This work aims to investigate the possibility and procedure for taking electrical effects into account in the modelling of charged fluids. More theoretical questions about the method itself and of the physics involved is of interest as well as how the method may be effectively implemented on a computer.

From both industry and academy, there is a demand on the modelling of this kind of physics. For instance, in medical sciences, accurate modelling of transport of charged fluids is a fundamental ingredient in understanding biological systems and to be able to manipulate them. As a consequence of the always so present desire of more environmental friendly ways of using the planet, automotive industry are now engineering electrical cars. A great challenge is to produce high performing and durable batteries, the ability to accurately model the electrolytes in the batteries is indeed an advantage in achieving this.

1.2 Outline

The text is structured in five main chapters. In chapter ??, the physics involved and the equations of interest are presented. This is followed by chapter ?? where the lattice-Boltzmann method is formulated for the different equations of interest. Also an introduction to the method as well as some discussion on different boundary conditions is given here. In chapter ??, the implementation of the method is discussed together with some general aspects that is important to have in mind in order to produce a high performing code. The implementation is then tested for classic examples with known solutions in chapter ?. Finally some results in electrokinetics are presented and discussed in chapter ?. Here, the focus is rather on the physics of the simulated systems than on LBM aspects of the problems. These aspects, such as grid dimensions, how LBM parameters relate to physical quantities etc. are discussed for the problems in chapter ?.

1.3 Previous work

An extensive treatment of both theory and experiments in the field of electrokinetics is carried out in [1]. Mainly the Poisson-Boltzmann model is used in the modelling but

also in some situations, the model used in this work based on the coupling of Navier-Stokes, Nernst-Planck and Poisson's equation of electrostatics is discussed. Also in [2], this modelling approach is used. However, the computational model is not the Lattice-Boltzmann method (LBM).

There are a lot of formulations of the LBM for the Navier-Stokes equations as the method typically is used in the modelling of fluid dynamics. Not so common are formulations for the Nernst-Planck and Poisson's equation. However there are a few, e.g. in [3] and [4] formulations for the Poisson's equation is discussed. In [5] a complete formulation for the three equations are presented together with some example simulations of electrokinetic systems. The formulation presented in [5] will not be completely the same as the one used in this work as is discussed in later chapters of this text.

2 Physical model

Electrohydrodynamics involves the study of electric phenomena on fluid flow. How fluids carrying electrical charges (electrolytes) react upon external electrical fields or interact with charged objects are examples of problems that arise in this field.

As a charged object is brought into contact with an electrolyte it is, qualitatively, easily deduced that ions with a sign of charge opposite to that of the object will be attracted to the object and ions with the same sign of charge will be repelled. These two distinct categories of ions will from hereon be referred to as counter- and co-ions respectively. In this case, for a neutral electrolyte, a surplus of counter-ions will be present in the direct vicinity of the object and a surplus of co-ions will be present at some other location further from the object. The part of the net charged fluid nearest to the charged boundary is often referred to as an electrical double layer (EDL) [1].

Traditionally, the physical description of EDLs and electrokinetics in general is based on the Poisson-Boltzmann model. However the PB model includes some crude assumptions on the system and is sometimes not an accurate choice, see section ?? for a brief description. Therefore, more sophisticated modelling approaches has been proposed e.g. in []. This paper is based on such an approach which is described further in this section.

2.1 Model overview

To model the fluid motion of a charged fluid under influences of electrostatic forces, a coupling between different models is considered.

The electric field and potential in the system are obtained from solving Poisson's equation (PE) for electrostatics (section ??) with a given charge density. This charge density is obtained from a set of Nernst-Planck (NP) equations (section ??) by including effects on the charge distribution from the electric field previously mentioned, diffusion and advection. One NP equation is solved for each different ion species in the solution. For instance in a 1:1 solution, two equations are solved one for the positive and one for the negative ions respectively. advective charge flux is given from the velocity field in the fluid that is obtained by solving the Navier-Stokes (NS) equations (section ??).

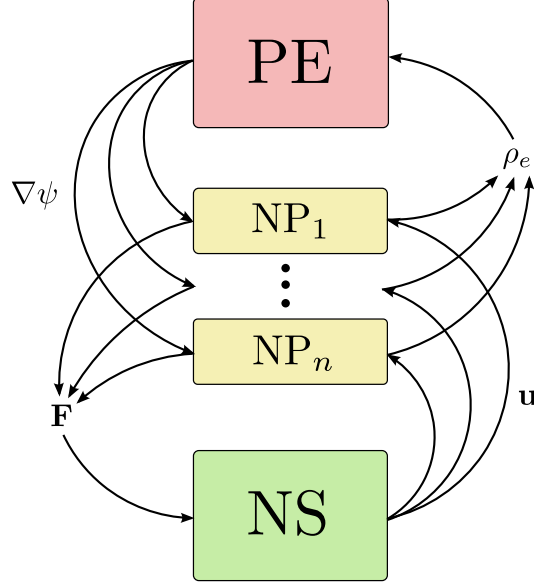


Figure 1: Visualisation of the coupling between the three equations present in the model. Poisson’s equation (PE), the set of Nernst-Planck equations (NP₁ ... NP_n) for the different ion species and the Navier-Stokes equations (NS). The dependencies have also be marked with arrows indicating what quantities for a certain equation that are needed from an other.

Forces due to present electric fields on net charged areas of the fluid also couples the NS equations to the NP equation. More about the force coupling is discussed in sections ?? and ?. The coupling between the different equations are visualised in fig. ?.

2.2 The potential - Poisson’s equation

To be able to model the flow dynamics of liquids in a channel with present EDLs, the potential and charge distribution in the channel must be determined. These quantities are mutually related through Poisson’s equation for electrostatics:

$$\nabla^2\psi = -\frac{\rho_e}{\epsilon_r\epsilon_0} \quad (1)$$

where ψ is the electrical potential, ρ_e the electrical charge density, ϵ_r is the relative permittivity and ϵ_0 the vacuum permittivity. Under certain assumptions, the charge density may be explicitly determined as a function of the potential distribution, one such result is the so called Poisson-Boltzmann equation, further discussed in section ?.

2.2.1 Boundary conditions

At the charged boundaries, most physical situations may be covered by either specifying the potential or the surface charge density. The former would be a boundary condition

of Dirichlet type:

$$\psi(\mathbf{x}) = \zeta(\mathbf{x}) , \quad \mathbf{x} \in \Gamma \quad (2)$$

and the latter a boundary condition of Neumann type:

$$\nabla\psi(\mathbf{x}) \cdot \mathbf{n} = -\frac{\sigma(\mathbf{x})}{\epsilon_0\epsilon_r} , \quad \mathbf{x} \in \Gamma \quad (3)$$

where Γ denotes the boundary of the domain and \mathbf{n} is the normal to the boundary surface. [?]

2.3 The transport of charges - Nernst-Planck equation

The charge concentration in an electrolyte is indeed affected by its environment. In the model proposed here, influences from: advection of the electrolyte, diffusion due to concentration gradients and effects from the electric field originating from charged objects placed at the border or in the flow is considered. Charge conservation without any external sources of the ion density, $c(\mathbf{x}, t)$, gives:

$$\frac{\partial c}{\partial t} + \nabla \cdot \mathbf{J} = 0 \quad (4)$$

where $\mathbf{J}(\mathbf{x}, t)$ is the net flux induced by the effects described above. Explicit expressions for the fluxes due to advection and diffusion respectively are

$$\mathbf{J}_{adv} = c\mathbf{u} \quad (5)$$

and

$$\mathbf{J}_{dif} = -D\nabla c \quad (6)$$

where \mathbf{u} is the advective velocity and D is a diffusion coefficient. The ionic flux due to the presence of an electric potential, $\psi(\mathbf{x}, t)$, is given by the Nernst equation [1]:

$$\mathbf{J}_{ele} = -\frac{zq_e D}{k_B T} c \nabla \psi \quad (7)$$

where z is the relative charge of the ion species, q_e is the fundamental charge, k_B is the Boltzmann constant and T is the temperature of the fluid.

Summing up the fluxes and putting them into eq. (??) gives

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[D\nabla c - c\mathbf{u} + \frac{zq_e D}{k_B T} c \nabla \psi \right] \quad (8)$$

which is a known result often referred to as the Nernst-Planck equation. This is the equation for the transport of *one* species of ions, if several are present one NP equation for each species needs to be solved. The advective velocity, \mathbf{u} , and the potential gradient, $\nabla\psi$, are obtained from couplings to the Navier-Stokes and Poisson's equation respectively. More about the coupling between the equations is discussed in section ??.

2.3.1 Boundary conditions

Depending on the physical situation being modelled, different conditions may be imposed at the boundaries of the domain. Throughout this work, at hard boundaries (walls), the charge flux through the boundary is set to zero, i.e.:

$$\mathbf{J} \cdot \mathbf{n} = 0, \quad \mathbf{x} \in \Gamma \quad (9)$$

where \mathbf{n} denotes the normal to the surface and Γ is the boundary of the domain.

2.4 Poisson-Boltzmann equation

Consider a system consisting of an electrolyte in contact with a (flat) charged wall. Under certain assumptions, it is possible to explicitly determine the charge density in eq. (??) as a function of the electric potential. E.g. if there is no advection present and if the system has reached a steady state, i.e. $\partial c / \partial t = 0$ and $\mathbf{u} = \mathbf{0}$ we have:

$$D \nabla c + \frac{z q_e D}{k_B T} c \nabla \psi = \mathbf{J}_0 \quad (10)$$

where \mathbf{J}_0 is a constant flux. Due to the steady state assumption, what the equation above actually says is that the net flux of charge in the system is constant. Since no charges are wanted to flow through the wall boundary, the flux is set to zero on the wall and since the flux is constant it will therefore be zero everywhere in the liquid, i.e. $\mathbf{J}_0 = \mathbf{0}$.

Considering only a one-dimensional situation with a position variable y varying in a direction out from the wall into the liquid, eq. (??) reads

$$\frac{1}{c} \frac{dc}{dy} + \frac{z q_e}{k_B T} \frac{d\psi}{dy} = 0. \quad (11)$$

The charge density is determined by solving eq. (??) for c , i.e. integrating the equation. In order to avoid introducing additional unknown quantities, the equation is integrated to far away from the wall where the potential from the EDL is assumed to have decreased to zero and where the concentrations, c^∞ , of the electrolyte is known.

$$\int_y^\infty d \ln(c(y')) = -\frac{z q_e}{k_B T} \int_y^\infty d\psi(y') \quad (12)$$

This gives an expression for $C(y)$:

$$c(y) = c^\infty \exp \left(-\frac{z q_e \psi(y)}{k_B T} \right). \quad (13)$$

In a general case, there may be several species of ions in the electrolyte, the net charge density, ρ_e , is then given by simply summing up the contributions from the different species:

$$\rho_e = q_e \sum_i z_i c_i. \quad (14)$$

Summarising eqs. (??), (??) and (??) gives the Poisson-Boltzmann equation in one dimension

$$\frac{d^2\psi(y)}{dy^2} = -\frac{q_e}{\epsilon_r \epsilon_0} \sum_i z_i c_i^\infty \exp\left(-\frac{z_i q_e \psi(y)}{k_B T}\right). \quad (15)$$

2.4.1 The Debye–Hückel approximation

Historically, the non-linear nature of eq. (??) complicated for those wanting to solve it. This was a major difficulty in the past when the computational power at hands were rather limited. A linearisation is therefore sometimes done, this linear version of the PB equation is often referred to as the Debye–Hückel approximation. The solution of the linearisation gives, something to compare with and is usually used when defining a characteristic length scale of the EDL.

For a 1:1 electrolyte solution with an equal amount of positive and negatively charged ions, eq. (??) reduces to

$$\frac{d^2\psi(x)}{dx^2} = \frac{2c^\infty q_e z}{\epsilon_r \epsilon_0} \sinh\left(\frac{z q_e \psi(x)}{k_B T}\right). \quad (16)$$

and the linearised equation is

$$\frac{d^2\psi(x)}{dx^2} = \frac{2c^\infty q_e^2 z^2}{\epsilon_r \epsilon_0 k_B T} \psi(x) = \kappa^2 \psi(x) \quad (17)$$

where κ^{-1} is the Debye length which is where the exponential solution has decayed to e^{-1} of the boundary value. This quantity gives therefore a measure for the characteristic thickness of the EDL.

2.5 The velocity field - Navier-Stokes equations

The Navier-Stokes equations are among the most fundamental corner stones of hydrodynamics. They describe the motion of a fluid under the influence of various internal and external forces.

For later convenience and for reference when it comes to deriving the Lattice-Boltzmann formulation of the NS equation, a brief sketch of a derivation will here be presented. A most general form of the Navier-Stokes equation follows from momentum conservation

$$\frac{\partial(\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) + \mathbf{Q} = 0 \quad (18)$$

where, ρ is fluid density, \mathbf{u} is velocity, \otimes represents the outer product and \mathbf{Q} is a momentum source term (force per volume). Expanding the time derivative and the divergence terms respectively gives

$$\mathbf{u} \left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) \right) + \rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) + \mathbf{Q} = 0. \quad (19)$$

To assure mass conservation (without sources) we have

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (20)$$

and eq. (??) reduces to

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) + \mathbf{Q} = 0 \quad (21)$$

which together with eq. (??) is a general formulation of the Navier stokes equations.

The force term \mathbf{Q} , is determined by the physical properties of the fluid and from its environment. In this work, only incompressible ($\rho = \text{constant}$) Newtonian fluids will be studied. The force contribution to \mathbf{Q} involved in that case is limited to viscous forces, pressure gradients in the fluid and to external force fields. Putting this into eqs. (??) and (??) gives

$$\nabla \cdot \mathbf{u} = 0 \quad (22)$$

and

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla P + \mu \nabla^2 \mathbf{u} + \mathbf{F} \quad (23)$$

where P is the pressure, μ the kinematic viscosity and \mathbf{F} is the contributions from external forces.

2.5.1 Boundary conditions

At hard boundaries (walls), the boundary conditions to eqs. (??) and (??) are set on the velocity of either a Dirichlet or Neumann type. In most physical situations the Dirichlet condition is used which corresponds to that there is a friction between the fluid and the wall, usually full friction, i.e. when no relative movement between fluid and wall is present and the velocity at the wall boundary is set to zero, i.e.

$$\mathbf{u} = 0, \quad \mathbf{x} \in \Gamma \quad (24)$$

where Γ denotes the boundary. The Neumann type conditions are used for no-friction walls where the normal component of the derivative of the velocity is specified, usually to zero.

At wet boundaries, inlets and outlets, of the domain various boundary conditions may be set. For instance the pressure or the velocity could be fixed. In the case of a fixed pressure boundary, a flow direction must also be specified for completeness. [?]]

2.6 Pressure-driven electrokinetic flow

As a charged fluid is driven by a pressure gradient, a movement of charges, i.e. an electrical current will be induced. Due to the charge flux, a potential gradient will build up along the flow direction. This potential is usually referred to as the streaming potential, $\phi(\mathbf{x})$, and its magnitude is determined from the induced current through Ohm's law

$$\mathbf{J} = -\sigma \nabla \phi \quad (25)$$

where σ is the conductivity of the fluid. In a perfectly conducting fluid there will be no potential differences. Also a complete neutral solution will carry no net current and also in this case there will be no potential differences.

Charges under the influence of an electric field will be affected by a force. Charges moving due to this force will, in a liquid, also pull liquid (uncharged) molecules with them. In a macroscopic limit, the force density affecting the charges in the liquid is assumed to affect the liquid as a whole. The volumetric force affecting the fluid from the presence of the streaming potential is then given by:

$$\mathbf{F} = -\rho_e \nabla \phi \quad (26)$$

where ρ_e is the charge density. This is an example of how the charge density from the Nernst-Planck equation may couple to the force term in Navier-Stokes equations.

This force will always be affecting the fluid in a direction opposite to the net flux of charge, i.e. the force will slow the fluid down, this is illustrated in fig. ???. This effect that a moving net charged fluid is slowed down is called the *electroviscous effect*. The name originates from that a similar effect might be achieved by increasing the viscosity of the fluid.

2.7 Electroosmotic flow

Instead of driving the fluid flow through a pressure drop, a net charged fluid may be driven by an external electric field. This may be seen as the opposite case to that in section ?? where a current is induced by a pressure drop.

The volumetric force on the fluid from the external field, \mathbf{E}_{ext} , is given by

$$\mathbf{F} = \rho_e \mathbf{E}_{ext} \quad (27)$$

where ρ_e is the charge density. If the electric field is constant (or at least has the same direction) everywhere, the sign of the force is not in the same direction for a net charged positive area of the fluid as for a net charged negative. Thus the fluid may be either slowed down or sped up. This is a qualitative difference to pressure driven situation and is illustrated in fig. ??.

The electroviscous effect is in the case of pure electroosmotic flow usually neglected as the field due to the streaming potential is, in most physical cases, small in comparison to the applied external field. [3]

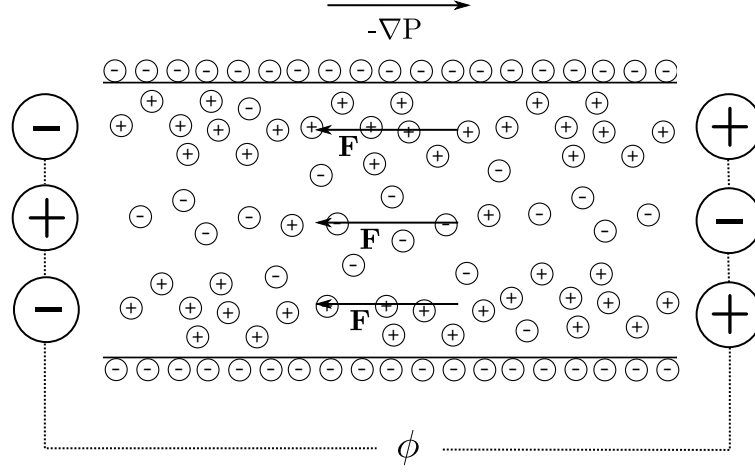


Figure 2: Example of an electroviscous system. The fluid is driven by a pressure gradient, ∇P . The directions of the forces on the fluid are always opposite to the flow direction. The force originates from the potential difference, ϕ , that builds up along the channel. The force is always opposite to the flow direction, thus slowing the flow down.

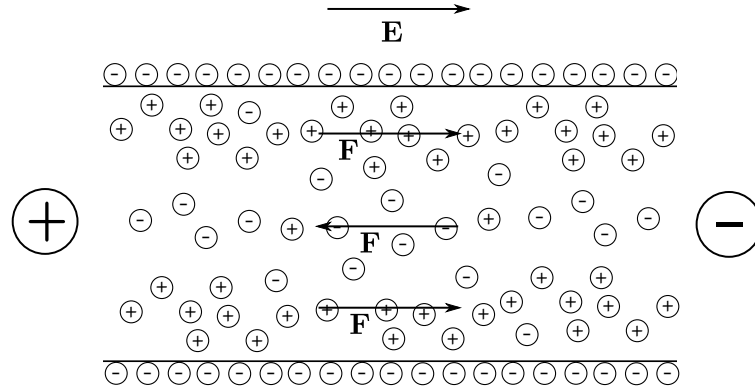


Figure 3: Example of an electroosmotic system. The fluid is driven by an external electric field, \mathbf{E} . The directions of the forces on the fluid from the electric field are indicated with arrows. Note however that the fluid does not necessarily has to flow in the direction of the force, this due to viscous effects in the fluid.

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