Lattice-Boltzmann simulations of driven transport in colloidal systems
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1 Introduction

Scientists have an effect upon society by finding out the details of how systems of practical interest work. The aim is either to obtain new knowledge, or learn how to use nature to our benefit. For this we need the basic rules of the systems, the governing equations, and we must know how to solve them for interesting conditions.

At the beginning of the twentieth century, scientists felt that, for macroscopic systems, all the relevant equations had been derived. Actually solving these equations for most practical problems is, however, a daunting task. Even though in the course of a few centuries, hundreds of talented scientists, including dozens of geniuses, worked on the solution of these equations, there are still many interesting practical situations and intriguing subtle interactions that lack a thorough understanding. It is not uncommon that areas of research that seemed exhausted suddenly regain the center of the scene. Perhaps a deeper understanding is needed to complement new experimental methods or for technological applications, or simply because new methods allow the solution of equations that previously seemed hopelessly intractable.

This thesis focuses mainly on electro-hydrodynamics. That is, systems where hydrodynamic (flow-induced) and electrostatic (charge-induced) interactions are of the same order of magnitude and are thus in competition. For applied purposes, a revival interest in this field has been driven by the practical needs of microfluidics and biophysics. On the theoretical side, electro-hydrodynamics is still challenging due to the inherent non-linearity of the relevant equations.

In microfluidics it was soon realized that the most efficient way to displace fluids in micro (or nano) capillaries is through electroosmosis. However, technological problems still remain unsolved. For example, the mixing of fluids at the extremely low Reynolds numbers that characterize very small scale flows remains an outstanding problem. In the context of biophysics, there is an additional question: living cells contain large numbers of charged (macro) molecules and large electric fields are maintained, in particular across membranes. Yet, little is known about the role of electrokinetic phenomena for molecular transport in cells.

The problem is, of course, that electrokinetic phenomena in all but the simples geometries cannot be treated analytically. One can imagine a protein in an electrolyte as a large charged particle surrounded by microions (of both signs) which rattle around while interacting with each other and with the protein, both electrostatically and hydrodynamically. The protein itself feels the environment and other proteins by means of forces, which can again being mediated by the solvent. However, all this complexity can actually help. Because the small particles move much faster than the large ones, they have time to explore so many configurations of phase space that they are, effectively, at equilibrium. To show this, let us estimate whether a microion is
able to follow the a colloidal particle in its most abrupt movement, a Brownian jump. We estimate the time of a Brownian jump of length \( l \) for a particle of mass \( m \) with friction coefficient \( \xi \) to be \( \tau_j = m/\xi \). On the other hand, the time it takes an ion \( \alpha \) of the electric double layer to relax to its equilibrium position in the layer is of the order \( \tau_\alpha = l^2/D_\alpha \), where \( D_\alpha \) is the diffusion coefficient of the ion. The electric double layer can be treated as approximately remaining in its equilibrium configuration if \( \tau_\alpha \ll \tau_j \). Estimating the length of a jump as \( l \approx u\tau_j \) and the particle velocity \( u \) as the root mean square value of one component of the thermal velocity \( u = \sqrt{k_B T/m} \) then, using the Stokes-Einstein relation \( D\xi = k_BT/\eta \), we find \( \tau_j/\tau_\alpha \sim \xi_j/\xi_\alpha \). Using Stokes law, \( \xi = 6\pi\eta a \), for the friction coefficient of a sphere of radius \( a \) in a fluid with viscosity \( \eta \), we see that this corresponds to \( a_{\text{ion}} \ll a_{\text{particle}} \). This condition is satisfied for colloidal particles.

Because retardation effects from the relaxation of the electric double layer are negligible, we can treat it “adiabatically”. In this context, an important role is played by new types of computer simulations usually referred to as “Mesoscopic simulations”. With this class of computer simulations one attempts a coarse graining procedure, recasting the microscopic description of a system, which would require solving the equations of motion for all the molecules, into a mesoscopic description where it is sufficient to follow the time evolution of the global properties of the system (mass and momentum density for example). There are several approaches to doing this, each with its own strategies, but the general procedure is to integrate out the fast degrees of freedom, reducing the actual simulation to only the slow ones. Among the mesoscopic simulations, the lattice-Boltzmann method (LB) (which I introduce in Chapter 2) has proved to have some very desirable properties for the study of the hydrodynamic interaction, especially from a computational point of view.

The first application in this thesis, and the only one unrelated to charged colloids, uses the LB method to study flow in random porous media. In Chapter 4 I show how velocity fluctuations decay in a simple model porous medium and how the use of approximate expressions, based on the pre-averaged properties of the flow, lead to large errors. This is contrary to the assumption underlying the existing theories for hydrodynamic dispersion. In an attempt to study flow in porous media, we introduce a highly simplified lattice-Boltzmann model for porous media. This model has the desirable property of possessing no excluded volume while allowing for friction on the fluid with a low density of obstacles. In my opinion, this model is ideally suited for studying the statistical properties of well behaved—in the sense that the spacial correlation functions decay exponentially—porous media. In the same chapter I show a simple way to obtain the largest possible Peclet numbers (in lattice simulations spurious diffusion always limits the Peclet number to small values).

Although the LB method is well established for the solution of flows in complex geometries, only recently has the study of the electrokinetic equations (Chapter 3), which couple electrostatics and hydrodynamics, been undertaken. In Chapter 5 I describe a novel method developed in the course of my PhD project that allows us to treat the electrokinetic equations and study previously unexplored flow conditions. Following the vogue, I should call the method a “hybrid” method because it couples a lattice-Boltzmann model of the neutral solvent with a discretization of the Smoluchowski description for the solutes. This combination of different methods is justified.
by our choice of the level of description to use for the various components of the system (possible because of the scale separation between large colloidal particle and small ions). An important characteristic of the new method is that it strictly conserves mass and momentum at the level of the single node, thus rules out, from the very beginning, spurious mechanisms of transport. It is also very easy to implement and it is fully parallelizable. To illustrate the advantages of this pragmatic approach, in Appendix A I present two technical problems which originated from a different lattice-Boltzmann model. Small imbalances generated spurious mass currents at the boundary with a macroscopic object, that proved capable of obscuring the subtle interactions we were trying to study. In summary, although the method can be improved, I believe that it is already very flexible and well suited for studying colloidal suspensions of charged particles and microfluidics. Although in this thesis I have not extensively applied the method to the latter, in my opinion, that is the field were one might exploit fully its potential.

The remainder of the thesis concerns exploratory studies of the electrokinetic properties of charged colloids in electrolytes by means of the lattice-Boltzmann model presented in Chapter 5. In selecting this system to study, we were motivated by questions such as: how do the shape and charge distribution of a particle affect its mobility?

In Chapter 6, I describe computer simulations of the sedimentation velocity of highly charged spheres. I show that the sedimentation velocity can be discussed in terms of the equilibrium properties of the electric double layer. Moreover, at high charge, the surface-charge dependence of the sedimentation velocity is affected by the accumulation of charge on the surface of the sphere, and the sedimentation velocity resembles that of a sphere in an electrolyte with no-added salt, where coions cease to affect the sedimentation velocity of the spheres and only the dynamics of the counte-

rions is relevant.

Another important aspect of the electrohydrodynamic interaction, which, once again, proves the flexibility of the method, is the study of the effect of the shape on electrodynamics. In Chapter 7 I study the role of shape, volume fraction, charge, and ionic strength on the sedimentation velocity of disks with non-zero thickness. They are relevant both practically and theoretically because they are a prototype for studying the effect of the shape and model real clay particles. I find that disk particles become hydrodynamically symmetric due to non-trivial interactions between the flow field near the particle and the electric double layer.

The last application I discuss concerns the electrophoretic mobility of a “patched” particle. In Chapter 8 I show how the electrophoretic mobility of such a sphere depends on the electric quadrupole moment and on the Debye screening length. I also show that if the particle undergoing electrophoresis is not exactly spherical (as occurs when representing a sphere on a lattice), one should consider also even electric multipole moments higher than the quadrupolar.
1 Introduction