Lattice-Boltzmann simulations of driven transport in colloidal systems
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3 Introduction to electrokinetics

3.1 The Poisson–Boltzmann equation and the electric double layer

Consider an electrolyte composed of $k$ species of positive and negative ions dissolved in a neutral fluid. The ions create an electric field $\mathbf{E}(\mathbf{r}) = -\nabla \Phi(\mathbf{r})$, where $\Phi(\mathbf{r})$ is the electrostatic potential which, if we denote by $q(\mathbf{r})$ the charge density due to the ions, can be computed using the Poisson equation

$$
\nabla^2 \Phi(\mathbf{r}) = \frac{4\pi q(\mathbf{r})}{\epsilon},
$$

where $\epsilon$ is the dielectric constant of the (overall) neutral medium. If the electrostatic potential is not constant, the ions of species $k$ are subject to the electrostatic force $\mathbf{F} = z_k e \mathbf{E}$, where $z_k$ is their valency (with charge sign) and $e$ is the elementary charge. The effect of this electric force is counteracted by the thermal motion of the ions. A convenient way [16, 17, 18, 19, 20], [21, 22] to take the thermal equilibrium into account is to write the equilibrium distribution density of the ions as a Boltzmann equilibrium (which implies point sized ions)

$$
n_k(\mathbf{r}) = n_0 \exp(-z_k e \Phi(\mathbf{r})/k_B T).
$$

For specificity, let us consider a two species system. The charge density is then expressed in terms of the probability distributions of the two species

$$
q(\mathbf{r}) = e (z_+ n_+(\mathbf{r}) + z_- n_-(\mathbf{r})).
$$

In order to obtain a closed expression for the electrostatic potential, we can substitute Eq. (3.3) into Eq. (3.1) to get

$$
\nabla^2 \Phi(\mathbf{r}) = \frac{4\pi e}{\epsilon} (z_+ n_+(\mathbf{r}) + z_- n_-(\mathbf{r})).
$$

Finally, let us substitute Eq. (3.2) into Eq. (3.4) to obtain the so-called Poisson Boltzmann equation (PB) which, for a symmetric electrolyte (i.e. $z_+ = -z_- = z$), reads

$$
\nabla^2 \Phi(\mathbf{r}) = \frac{8\pi e n_0}{\epsilon} \sinh(ez \Phi(\mathbf{r})/k_B T).
$$

Unfortunately, solutions for this non-linear equation are only available for very simple geometries. However, if the electric potential is small, in other words if $e \Phi(\mathbf{r})/k_B T \ll $
1, the approximation $\exp(\pm z e \Phi(r)/k_B T) \simeq 1 \pm z e \Phi(r)/k_B T$ holds, and Eq. (3.5) is simplified by the linearized Poisson-Boltzmann equation (LPB)

$$\nabla^2 \Phi(r) = \frac{8\pi e^2 z^2 n_0}{\epsilon k_B T} \Phi(r) = \kappa^2 \Phi(r), \quad (3.6)$$

which can be solved analytically for many interesting geometries. In Equation (3.6), note that $\kappa = \sqrt{8\pi e^2 z^2 n_0 / \epsilon k_B T}$ has the dimension of an inverse length.

Let us now introduce a charged macroscopic particle in the electrolyte. The equilibrium density of microions in solution will still be given by Eq. (3.5), where now the macroscopic particle enters via a boundary condition for the electrostatic potential $\Phi(r)$. This equation, again, cannot be solved in general. Hence, to make it tractable, one must restrict the study to the case of small surface potentials (in other words, to weakly charged particles), in which the linearized Poisson-Boltzmann equation (3.6) provides a reasonable approximation. For simplicity, let us consider the case of a spherical macroscopic particle.

Intuitively, the like-charged microions (in the remainder coions) will be repelled, while the oppositely charged microions (counterions) will be attracted toward the sphere. While the electrostatic interaction favors an infinitesimally thin layer of counterions, which will immediately screen the charge of the sphere, entropy will prevent the counterions from condensing on the sphere. As a balance of the two forces, one could expect a cloud of counterions surrounding the sphere until the charge of the sphere is fully screened. Far beyond this length, called the Debye screening length, the sphere appears neutral. The layer of microions is usually referred to as the electric double layer (EDL). It is the presence of inhomogeneity and EDL that causes the distinctive electrostatic and hydrodynamic effects called electrokinetic phenomena, which I will briefly introduce below. For a rigorous description of the equilibrium distribution of the microions in terms of their free energy, I refer the reader to the book of Verwey and Overbeek [21].

Quantitative predictions for the co- and counterion equilibrium-density-distributions are given by the Debye-Hückel theory [19, 20]. In their theory, Debye and Hückel assume that the electrostatic potential is much smaller than $k_B T$. Hence, instead of the full Poisson-Boltzmann equation, they use the approximate linearized Poisson-Boltzmann equation (3.6) for computing the electrostatic potential and, via Eq. (3.2), the co- and counterions equilibrium distributions.

For a sphere of radius $a$, Eq. (3.6) can be easily solved to give the Yukawa potential

$$\Phi(r) = \Phi_0 \frac{a}{r} e^{-\kappa(r-a)}, \quad (3.7)$$

where $r$ originates at the sphere center and $\Phi_0 = \Phi(0)$ is the electrostatic potential at contact with the sphere. By substituting the Yukawa potential into the linearized version of Eq. (3.2), the concentrations of co- and counterions are, respectively,

$$n_+(r) = n_0 \left( 1 - \frac{e z \Phi_0}{k_B T} \frac{a}{r} e^{-\kappa(r-a)} \right)$$

$$n_-(r) = n_0 \left( 1 + \frac{e z \Phi_0}{k_B T} \frac{a}{r} e^{-\kappa(r-a)} \right). \quad (3.8)$$
The counterion cloud in the vicinity of the charged sphere decays faster than exponentially over a distance of the order of $\lambda_D = \kappa^{-1}$, the Debye screening length. The coions, on the other hand, are expelled from the vicinity of the sphere and reach the bulk value with the same functional dependence. The symmetry of co- and counterions with respect to the bulk concentration [shown by Eq. (3.8)] is a typical signature of the validity of the Debye-Hückel approximation. The electrostatic potential at contact $\Phi_0$ is usually named the zeta potential $\zeta$. In electrokinetic phenomena, the relevant parameter is the relative size of the macroscopic particle to the extension of the EDL. Therefore, the Debye screening length $\lambda_D$ is the appropriate unit of length, and the electrokinetic phenomena are conveniently described in terms of the dimensionless length $\kappa a$.

In this description of the diffuse layer, I disregarded the so-called Stern layer [23, 24]. However, because this layer is thought to be inside the non-slip region of the fluid [23, 24], it is believed that it does not influence the hydrodynamic interactions with the fluid. It is possible to consider this layer as part of the sphere and model the system simply as an effective sphere plus an electric diffuse layer. Throughout this thesis I shall not consider the effect of a dynamic Stern layer, i.e. a Stern layer whose counterions are not glued on the particle surface but are free to move.

### 3.2 Electrokinetic phenomena

The term “Electrokinetic phenomena” refers to all phenomena in which the EDL is distorted from its equilibrium position via an external force, of electrical or other origin. Because of this distortion, the EDL reacts and consequently induces a relative motion between the suspended particles and the fluid. Many electrokinetic phenomena have been reported in the literature, but they can be grouped into two categories depending upon the nature of the perturbing force. On the one hand we have electrophoresis, where the macroscopic charged particle and its EDL are displaced by means of an electric field—here the specific particle velocity is due to the balance between the direct electrostatic interaction and the hydrodynamic friction, plus the counter-reaction of the EDL, which has the opposite charge. On the other hand, in a sedimenting sample, the driving force is gravitational and, because of the relative motion between the particles and the electrolyte, a local electric field is generated. The so-called sedimentation potential is the experimentally measured electrostatic potential difference between the top and the bottom of a sedimenting sample.

In both cases, the macro particles move. If, instead, the macroscopic objects are fixed, as, for example walls, slits, or a fixed obstacles, there are two equivalent electrokinetic phenomena. If an electric field is applied to, for example, a charged slit containing an electrolyte, the fluid will start moving generating a quasi plug flow. Although this phenomenon is called electro-osmosis, the physics is essentially the same as in electrophoresis due to Galilean invariance. If, instead, we displace the electrolyte in a charged porous medium by means of (for example) a pressure gradient, we will measure an electrostatic potential difference between the two sides, called the “streaming potential”. Again, a second of thought will show the equivalence of this potential with the sedimentation potential.
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For more details I refer the reader to the vast literature present; for a general introduction see, for example, [3, 25, 2], for a manuscript focused on colloidal suspensions see [23, 26], and for a nice recent review of the recent achievements see [24].

3.2.1 Onsager relation

In the previous section, I divided the electrokinetic phenomena into two categories. As the careful reader already suspects, there is a close relation also among the two basic electrokinetic phenomena. In one case, we displace the (overall neutral) fluid by means of an electric field; in the other, we generate an electrostatic potential by displacing particles (which together with the EDL are, again, neutral). This symmetry finds its formalization in an Onsager relation. For charged particles, the mass current $J_M$ is generated by two mechanisms: a force $\mathbf{G}$ which acts onto the particles because they have a mass, and the electrostatic forces $\mathbf{E}$ that displace mass because particles possess charge. Conversely, the electric current $J_e$ is generated by the action of a direct, electrostatic, force plus a non electrostatic force that, by displacing the charged particles, also contributes to the electric current. More formally

\[
J_M = A \mathbf{G} + \mathcal{L}_{ge} \mathbf{E},
\]

\[
J_e = B \mathbf{E} + \mathcal{L}_{eg} \mathbf{G},
\]

where $A$, $B$, and $\mathcal{L}_{ge}$ and $\mathcal{L}_{eg}$ are the relevant transport coefficients. The symmetry of the electrokinetic phenomena is formalized by the equality $\mathcal{L}_{eg} = \mathcal{L}_{ge}$.

3.2.2 Sedimentation velocity

Below, I briefly review the classical theories for sedimentation and electrophoresis. In a sedimentation experiment, charged colloids sediment under the influence of the gravitational force. The sedimentation velocity of a charged sphere (for example) is slightly less than that of a neutral one of the same size and weight because, while sedimenting, a charged sphere has to drag the (distorted) electrical double layer along. The amount of friction exerted by the EDL depends upon its spatial extension (measured by the dimensionless length $\kappa a$, where $a$ is the radius of the spheres) and upon the total charge of the sphere. In the two limits $\kappa a \to 0$, and $\kappa a \to \infty$ the EDL exerts no extra friction. In the first case, the EDL is extremely diffuse and, because in this limit the Yukawa potential reduces to a constant, the electrostatic potential exerts no force. In the second case, the layer is so thin and so close to the colloid that the no-slip boundary condition prevents any force generation. For intermediate values of $\kappa a$ the EDL, distorted by the flow field near the particle, will try to restore its equilibrium shape. In doing so, the EDL exerts a force on the fluid which opposes the perturbing, gravity, force; hence it will reduce the sedimentation velocity.

Booth [27] and later Ohshima [28] gave analytical formulae for the reduction of the sedimentation velocity $U(Z)/U_0$ in the limit of a single weakly-charged spherical colloid. In this limit, they predict that the sedimentation velocity, $U_0(Z)$ can be expressed as

\[
\frac{U_0(Z)}{U_0} = 1 - c_2 Z^2.
\]
where $U_0$ is the sedimentation velocity of a neutral sphere, and $c_2$ is a constant that can be computed analytically in the Debye-Hückel limit. For monovalent co- and counterions, i.e. when $z_+ = -z_- = 1$, which also have the same diffusivity, $D_+ = D_- = D$, the expression for $c_2$ is

$$c_2 = \frac{k_BTl_B}{72\pi a^2\eta D}f(\kappa a), \quad (3.11)$$

where $f(\kappa a)$ is the following function

$$f(\kappa a) = \frac{1}{1 + (\kappa a)^2}\left[ e^{2\kappa a} (3E_4(\kappa a) - 5E_6(\kappa a))^2 + 8e^{\kappa a} (E_3(\kappa a) - E_5(\kappa a)) \right. $$

$$- e^{2\kappa a} (4E_3(2\kappa a) + 3E_4(2\kappa a) - 7E_8(2\kappa a))] \quad (3.12)$$

of the integral functions

$$E_n(x) = x^{n-1} \int_x^\infty dt \ t^{-n} \exp(-t). \quad (3.13)$$

In the remainder of this thesis we repeatedly refer to this theory.

### 3.2.3 Electrophoresis

When charged spheres are immersed in an electrolytic solution in the presence of an external electric field, they begin to move under the effect of the electrostatic force. For a quantitative prediction of the translational velocity, one needs to explicitly consider the combined effect of the electric double layer and of hydrodynamics. Again, analytical formulae were obtained in the two limiting scenarios $\kappa a \to 0$, and $\kappa a \to \infty$. As we already observed in the sedimentation case, for $\kappa a \to 0$ the EDL does not couple with the external electric field and the electrophoretic mobility is given by the ratio of the electrostatic force $QE$ (acting directly onto the particle) to the Stokes drag $\xi = 6\pi\eta a$ and to the driving electric field $E$. The electrophoretic mobility is then simply

$$\mu_e = \frac{Q}{6\pi\eta a}, \quad (3.14)$$

which, in terms of the the zeta potential $\zeta$ (i.e. the electrostatic potential at contact) reads:

$$\mu_e = \frac{2}{3} \frac{\varepsilon}{\eta} \zeta. \quad (3.15)$$

This result was first derived by Hückel in 1924 [29]. In 1903, von Smoluchowski [30] showed that in the opposite limit, i.e. when $\kappa a \to \infty$, the electrophoretic mobility is increased by a factor $3/2$

$$\mu_e = \frac{\varepsilon}{\eta} \zeta. \quad (3.16)$$

Remarkably, the Smoluchowski result is valid regardless of the shape of the macroscopic particle and it is used daily in hundreds of laboratories in the world for separating many biologically relevant particles. Phenomenological descriptions of these results can be found in text books and reviews [25, 31, 32].
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3.3 Electrokinetic equations

In order to provide the general framework for the description of electrolyte dynamics, I first briefly review the dynamics of dilute mixtures—of which electrokinetic phenomena are a sub set—on hydrodynamic length and time scales. As in all hydrodynamic descriptions, the starting point of this discussion lies in the laws of conservation of mass and momentum.

3.3.1 Mass conservation

Every species of the fluid mixture satisfies the usual mass conservation law:

$$\frac{\partial \rho_k}{\partial t} + \nabla \cdot \rho_k \mathbf{v}_k = 0,$$  \hspace{1cm} (3.17)

where $\mathbf{v}_k$ is the velocity and $\rho_k$ the density distribution of the species labeled by $k$. The total density, $\rho = \sum_k \rho_k$, is also conserved, and satisfies an equation analogous to Eq. (3.17) with respect to the barycentric velocity $\rho \mathbf{v} = \sum_k \rho_k \mathbf{v}_k$, which describes the evolution of a fluid element. If we refer the motion of all species to this common velocity, then Eq. (3.17) can be expressed as

$$\frac{\partial \rho_k}{\partial t} + \nabla \cdot \rho_k \mathbf{v} = -\nabla \cdot \mathbf{j}_k,$$  \hspace{1cm} (3.18)

where I have introduced the relative current of species $k$, $\mathbf{j}_k = \rho_k(\mathbf{v}_k - \mathbf{v})$, which accounts for all dynamical effects arising from the mismatch in velocities between the different species. For mixtures composed of molecular constituents at low Reynolds number (as is usually the case in electrolytes), the inertial time scale is extremely small; hence the relative current can be assumed proportional to a thermodynamic driving force, which is proportional to the gradient of the chemical potential. As a result, the relative current of species $i$ becomes diffusive and can be expressed as [33]

$$\mathbf{j}_k = -\sum_k D_{ik} \rho_k \nabla \beta \mu_k,$$  \hspace{1cm} (3.19)

where $\beta$ is $1/k_B T$, with $k_B$ the Boltzmann constant and $T$ the temperature. $\beta \mu_k = \log \rho_k + \beta \mu_k^{\text{ex}}$ is the chemical potential decomposed into an ideal and excess part, while $D_{ik}$ corresponds to the diffusion coefficient that determines the flux of species $i$ induced by spatial variations in the chemical potential of species $k$. For the sake of simplicity, I focus on the case where cross diffusion is neglected, and hence $D_{ik} = D_{i}\delta_{ik}$. By substituting the chemical potential in Eq. (3.19), I express mass conservation in the form of a set of convection-diffusion equations, expressing the two mechanisms that control density evolution for each species,

$$\frac{\partial \rho_k}{\partial t} + \nabla \cdot \rho_k \mathbf{v} = \nabla \cdot D_{k} \left[ \nabla \rho_k + \rho_k \nabla \beta \mu_k^{\text{ex}} \right].$$  \hspace{1cm} (3.20)

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3.3.2 Momentum conservation

Next, let us consider momentum conservation. On the same length and time scales, as I have already shown in Section 2.2.1, momentum conservation implies that the barycentric velocity, for low Reynolds number flows, follows the linearized Navier-Stokes equation,

$$\frac{\partial}{\partial t} (\rho \mathbf{v}) = \eta \nabla^2 \mathbf{v} - \mathbf{v} \cdot \nabla \rho + \mathbf{F}^{ext}, \quad (3.21)$$

where $\eta$ is the shear fluid viscosity, while $\mathbf{F}^{ext}$ is an external force density acting on a fluid element. The effect of the interactions among the different species enters as a net force acting on the fluid expressed as the gradient of the local pressure $p$. In the presence of spatial gradients, the pressure has in general a tensorial character, and can be derived from the free energy of the system. However, for ideal electrolytes, the local pressure can always be expressed as a scalar. Hence, for the sake of simplicity, we will consider this situation in what follows.

In general, the pressure gradient can be computed from the chemical potential as

$$\beta \nabla p = \sum_k \rho_k \beta \nabla \mu_k = \sum_k \left( \nabla \rho_k + \rho_k \beta \nabla \mu_k^{ex} \right) \quad (3.22)$$

and acts as a force. The first term of the pressure corresponds to the ideal-gas contribution, $\beta p^{id} = \sum_k \rho_k$ while the other two contain all the information of the interactions among the fluid species. If there is one majority neutral component, which only contributes to the ideal part of the pressure, then the excess component of the pressure can be identified as the osmotic pressure of the mixture.

Using Eq. (3.22) for the pressure gradient, the Navier-Stokes equation reads

$$\frac{\partial}{\partial t} (\rho \mathbf{v}) = \eta \nabla^2 \mathbf{v} - \mathbf{v} \cdot \nabla \rho + \sum_k \rho_k \nabla \mu_k^{ex} + \mathbf{F}^{ext}. \quad (3.23)$$

3.3.3 Electrokinetic equations

The electrostatic equations can be computed as a special case of Eqs. (3.20) and (3.23) by replacing $\mu_k^{ex} = z_k e \Phi$, where $z_k$ is the valency of the charged species $k$, and $\Phi$ is the electrostatic potential. The Smoluchowski equation (3.20) becomes

$$\frac{\partial \rho_k}{\partial t} + \nabla \cdot \rho_k \mathbf{v} = \nabla \cdot D_k \left[ \nabla \rho_k + e \beta z_k \rho_k \nabla \Phi \right], \quad (3.24)$$

while the Navier–Stokes equation (3.23) is

$$\frac{\partial}{\partial t} (\rho \mathbf{v}) = \eta \nabla^2 \mathbf{v} - \nabla p^{id} - \sum_k e z_k \rho_k \nabla \Phi + \mathbf{F}^{ext}. \quad (3.25)$$

We still need an additional equation that prescribes how the electrostatic potential is related to the local charge density. Since transport processes associated to mass and
momentum transfer in fluid mixtures are much slower than the propagation of electromagnetic waves, the electric field is completely determined by the Poisson equation

$$\nabla^2 \Phi = -\frac{4\pi e}{\epsilon} \left[ \sum_{k=\pm} z_k \rho_k + \rho_s \right], \quad (3.26)$$

where $\rho_s$ is for the charge density of the solid surfaces and accounts for possible confining walls or moving suspended particles in the electrolyte.