The importance of hydrodynamic effects in polyelectrolyte electrophoresis

Kai Grass and Christian Holm

Electronic address: grau@ias.uni-frankfurt.de
Visit us at: http://www.ias.uni-frankfurt.de/

Frankfurt Institute for Advanced Studies
Max-Planck-Institut für Polymerforschung
Johann Wolfgang Goethe Universität
Max-von-Laue-Strasse 1
60438 Frankfurt am Main, Germany
55128 Mainz, Germany

Abstract

We investigate the electrophoretic mobility of polyelectrolytes in free solution under the influence of an applied DC electric field via coarse-grained molecular dynamics. The simulation method uses an implicit solvent model with an effective dielectric permittivity, but includes both long range hydrodynamic and full electrostatic interactions. The simulation results are compared to various sets of experimental data and to static and dynamic simulations disregarding hydrodynamic interactions. We investigate the influence on chain conformations and the corresponding counter-ion distribution around the chain which changes the electrophoretic mobility significantly.

The polyelectrolyte model

We use a bead-spring model to describe the polyelectrolyte.

![Polyelectrolyte model](image)

**Applied potentials**

- Truncated LJ potential: 
  \[ V_{LJ}(r_{ij}) = 4\epsilon \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} + \frac{1}{2} \]
- FENE potential: 
  \[ V_{FENE}(r_{ij}) = K \left( r_{ij} - r_{0} \right)^{2} \]
- Bond angle potential: 
  \[ V_{\angle}(r_{ij}) = \frac{1}{2} k_{\angle} \left( \theta_{ij} - \theta_{0} \right)^{2} \]
- Coulomb potential: 
  \[ V_{\text{Coul}}(r_{ij}) = \frac{q_{i} q_{j}}{4\pi\varepsilon_{0} r_{ij}} \]

**Reduced units**

We use the following reduced units:

- Length: \( \sigma \)
- Mass: \( \sigma^{2}/\epsilon \)
- Energy: \( \epsilon \)
- Time: \( \sigma^{2}/\epsilon \)
- Temperature: \( \epsilon/\sigma^{2} \)
- Electric field: \( \epsilon/\sigma^{2} \)

**Electrophoretic mobility \( \mu \)**

**Definition**

\[ \mu = \frac{q}{m} \]

**Steady state**

Two forces act on the polyelectrolyte-counter-ion-complex in the steady state:

- Electric driving force: 
  \[ F_{E} = q_{D} E \]
- Solvent friction force: 
  \[ F_{\text{Fr}} = \gamma_{D} \dot{\mathbf{r}}_{D} \]

Balancing these forces leads to the following equation:

\[ \mu = \frac{q_{D}}{m_{D}} \]

In the following we investigate the behavior of (2) in different regimes.

No hydrodynamics (Langevin)

**Langevin equation**

\[ \mathbf{v}_{i}(t) + \gamma \mathbf{v}_{i}(t) = F_{E}(t) - F_{\text{F}}(t) \]

The solvent-induced random forces \( F_{\text{F}}(t) \) fulfill the fluctuation-dissipation theorem.

Hydrodynamics (Lattice Boltzmann)

**Why include hydrodynamics?**

Hydrodynamic effects may lead to:

- Different scaling of effective friction coefficient \( \gamma_{D} \) with \( N \) ≠ different regimes.
- Alignment effects arising out of hydrodynamic instability.
- The increase of the electrophoretic mobility with polymerization as seen experimentally for polyelectrolytes such as PSS or DNA.

We use the O3Q8 scheme for the Lattice Boltzmann algorithm, i.e. at each grid node, we take 18 velocity vectors (neighbors and next neighbors) into account.

**Coupling between polymer and solvent**

The polymer beads and counter-ions are frictionally coupled to the solvent using a scheme by Alhorr and Dünweg [2]. The modified Langevin equation reads as follows:

\[ \mathbf{v}_{i}(t) + \gamma \mathbf{v}_{i}(t) = F_{E}(t) - F_{\text{F}}(t) - F_{\text{D}}(t), \]

where the additional term \( F_{\text{D}}(t) \) is the fluid velocity at the position of the monomer interpolated from the neighboring grid nodes. This coupling induces a momentum transfer between fluid and monomers.

**Electrophoretic mobility in simulations**

The standard way?

It is not recommendable to directly apply Equation 2 to obtain \( \mu \) from simulation. The small mobility of short polyelectrolytes requires either long simulation trajectories to determine \( \mu \) precisely enough, or artificial high external fields \( E \).

It has been shown ([3]), that external fields normally used in simulations lead to a conformational change and to a disturbed counter-ion distribution along the polyelectrolyte. Both effects lead to a changed electrophoretic behaviour, which is undesirable.

**Green-Kubo relation**

To avoid artificial conformational change by the electric field, the mobility can be determined from zero field simulations via a Green-Kubo relation.

\[ \mu = \frac{1}{k_{B} T} \int_{0}^{\infty} \langle \mathbf{v}_{i}(t) \cdot \mathbf{v}_{i}(t) \rangle \, dt \]

This approach has been successfully applied in simulations to determine the electrophoretic mobility of charged colloids [3].

**References**


Summary

In this contribution, we have shown the influence of hydrodynamic effects on the diffusion and the electrophoretic mobility of polyelectrolytes. The comparison with experimental observations shows that simulations disregarding hydrodynamic interactions fail to describe the dynamics of electrophoresis correctly, where as simulations based on the presented framework can quantitatively match the experimental data.

Visit us at: http://www.espresso.mpg.de/