

## 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.

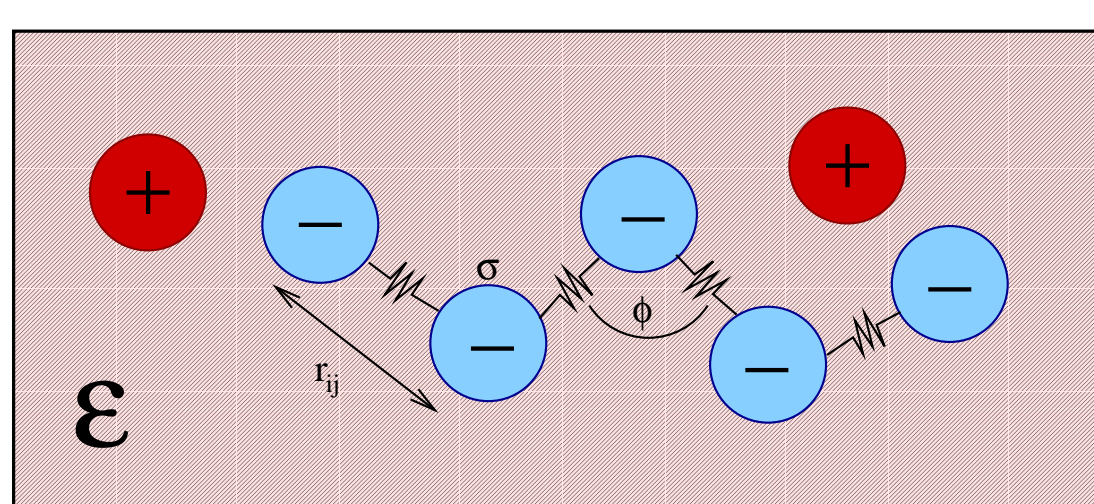


FIGURE 1: Polyelectrolyte model.

## Applied potentials

- Truncated LJ potential:  $V_{LJ}(r_{ij}) = 4\epsilon \left( \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 + \frac{1}{4} \right)$
- FENE potential:  $V_{FENE}(r_{ij}) = \frac{1}{2}kR^2 \ln \left( 1 - \left( \frac{r_{ij}}{R} \right)^2 \right)$
- Bond angle potential:  $V_{BA}(r_{ij}) = \frac{1}{2}\kappa (\phi - \phi_0)^2$
- Coulomb potential:  $V_{COU}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 \epsilon r_{ij}}$

## Reduced units

We use the following reduced units:

Length	Mass	Energy	Charge	Time	Temperature	Electric field
$\sigma$	$m$	$\epsilon$	$q$	$\sigma \sqrt{\frac{m}{\epsilon}}$	$\frac{\epsilon}{k_B}$	$\frac{\epsilon}{q\sigma}$

FIGURE 2: Reduced units.

FIGURE 3: Derived units.

## Electrophoretic mobility $\mu$

### Definition

$$\mu = \frac{v}{E} \quad (1)$$

### Steady state

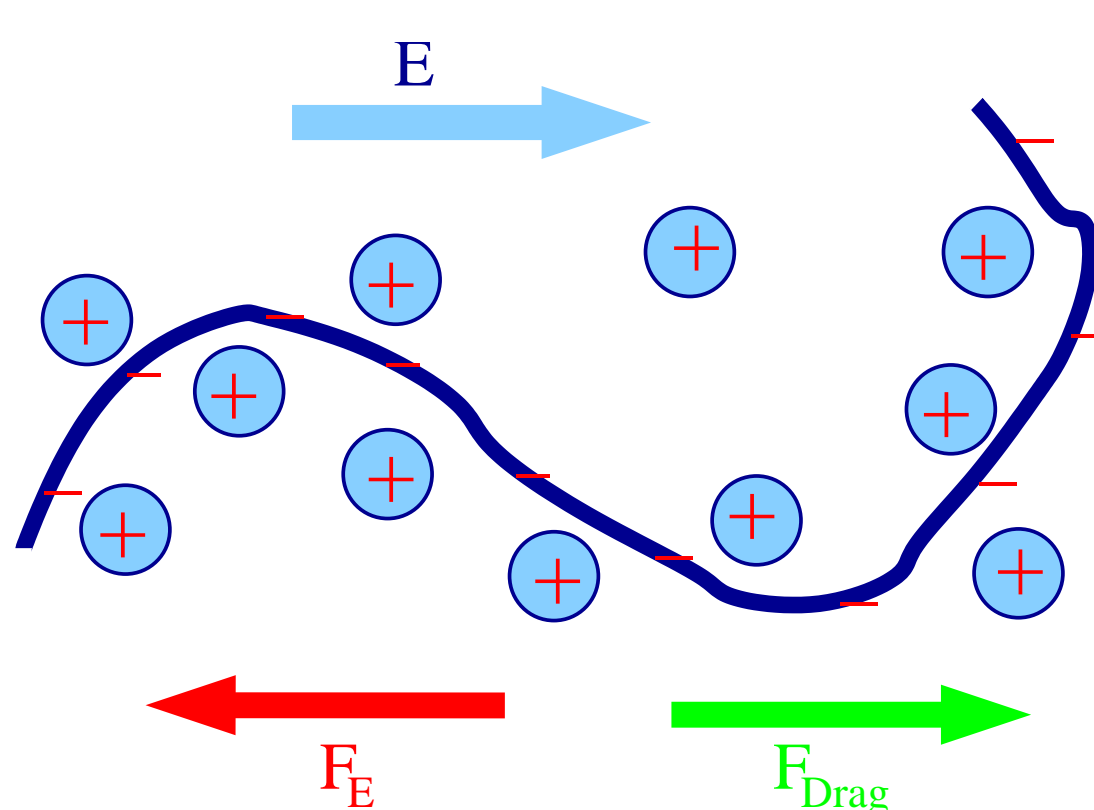


FIGURE 4: Electrophoretic mobility.

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

- Electric driving force:  $\vec{F}_E = q_{\text{eff}} \vec{E}$
- Solvent friction force:  $\vec{F}_{\text{Drag}} = \gamma_{\text{eff}} \vec{v}$

Balancing these forces leads to the following equation:

$$\mu = \frac{v}{E} = \frac{q_{\text{eff}}}{\gamma_{\text{eff}}} \quad (2)$$

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

## No hydrodynamics (Langevin)

### Langevin equation

$$m \frac{d\vec{v}_i}{dt} = \vec{F}_i - \Gamma \vec{v}_i + \vec{F}_r(t) \quad (3)$$

The solvent-induced random forces  $\vec{F}_r(t)$  fulfill the fluctuation-dissipation theorem.

## Hydrodynamics (Lattice Boltzmann)

### Why include hydrodynamics?

Hydrodynamic effects may lead to

- different scaling of effective friction coefficient  $\gamma_{\text{eff}}$  with  $N \Rightarrow$  different regimes
- alignment effects arising out of hydrodynamic instability ([6])
- the increase of the electrophoretic mobility with polymerization as seen experimentally for polyelectrolytes such as PSS or DNA

We use the D3Q18 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 Ahlrichs and Dünweg ([1]). The modified Langevin equation reads as follows:

$$m \frac{d\vec{v}_i}{dt} = \vec{F}_i - \Gamma (\vec{v}_i - \vec{u}(\vec{r}_i, t)) + \vec{F}_r(t), \quad (4)$$

where the additional term  $\vec{u}(\vec{r}_i, t)$  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  $v$  precisely enough, or artificial high external fields  $E$ .

It has been shown ([4]), 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.

$$\mu = \frac{1}{3k_B T} \sum_i q_i \int_0^\infty \langle \vec{v}_i(0) \cdot \vec{v}_i(\tau) \rangle d\tau \quad (5)$$

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

## References

- [1] P. Ahlrichs and B. Dünweg. Lattice-boltzmann simulation of polymer-solvent systems. *Int. J. Mod. Phys. C*, 9(8):1429–1438, Dec. 1998.
- [2] H. Cottet, P. Gareil, O. Theodoly, and C. E. Williams. A semi-empirical approach to the modeling of the electrophoretic mobility in free solution: Application to polystyrenesulfonates of various sulfonation rates. *Electrophoresis*, 21:3529–3540, 2000.
- [3] V. Lobaskin, B. Dünweg, M. Medebach, T. Palberg, and C. Holm. Electrophoresis of colloidal dispersions in the low-salt regime. *Phys. Rev. Lett.*, 98:176105, April 2007.
- [4] R. R. Netz. Nonequilibrium unfolding of polyelectrolyte condensates in electric fields. *Physical Review Letters*, 90(12):128104, Mar. 2003.
- [5] U. Scheler. private communication. 2006.
- [6] X. Schlagberger and R. R. Netz. Orientation of elastic rods in homogeneous stokes flow. *Europhysics Letters*, 70:129–135, 2005.
- [7] E. Stellwagen, Y. J. Lu, and N. C. Stellwagen. Unified description of electrophoresis and diffusion for dna and other polyions. *Biochemistry*, 42(40):11745–11750, Oct. 2003.

## Results

### Diffusion of polyelectrolytes

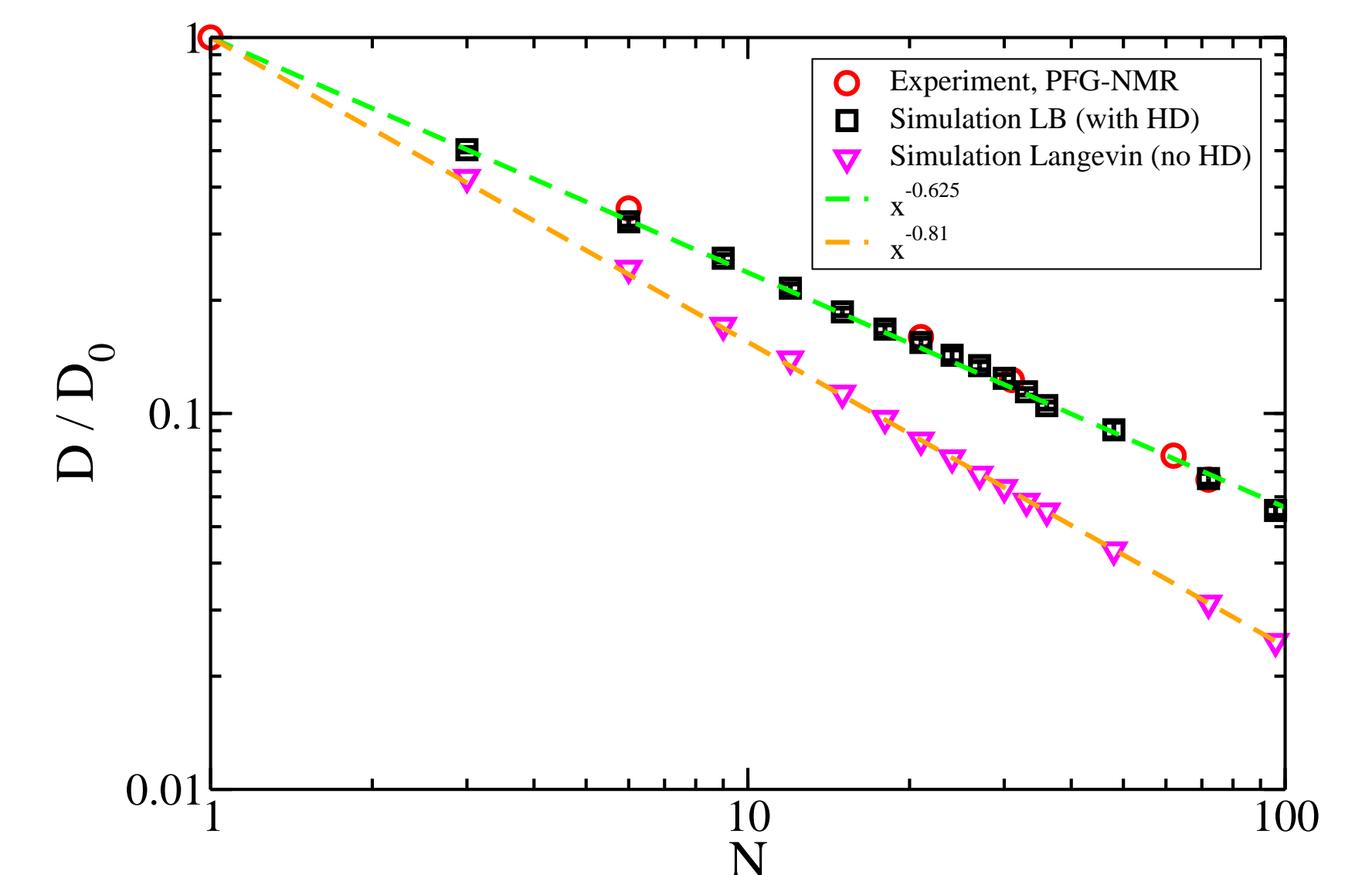


FIGURE 5: Polyelectrolyte diffusion measured by PFG-NMR ([5]) compared to simulations with and without hydrodynamics.

The dependence of the diffusion of PSS from the chain length can be approximated by a power law with a scaling exponent of -0.625. This is consistent with previous observations ([7]). When hydrodynamic interactions are neglected, the diffusion coefficient decreases significantly. Those simulations fail to reproduce the experimental data.

### Electrophoretic mobility of polyelectrolytes

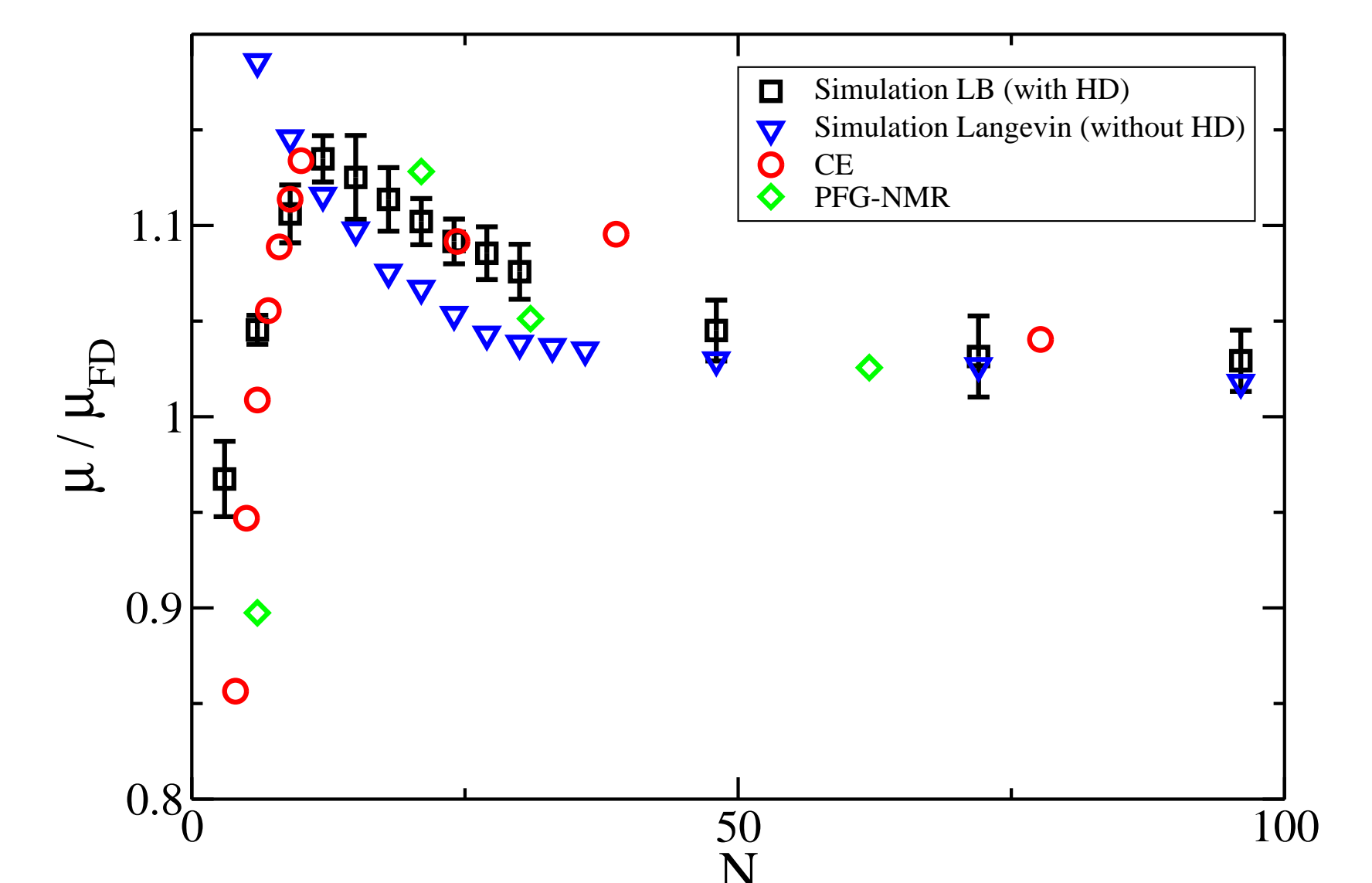


FIGURE 6: Polyelectrolyte electrophoretic mobility of PSS measured by PFG-NMR ([5]) and CE ([2]) compared to simulations with and without hydrodynamics.

The electrophoretic mobility also shows a non-monotonic dependence on the chain length with a characteristic maximum for intermediate chains. The Langevin simulation fails to reproduce the behaviour observed in experiments (see [2]), while as the Lattice Boltzmann simulations can be quantitatively matched to it.

## 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 frame work can quantitatively match the experimental data.

