A very mesoscopic approach to simulating the electrohydrodynamics of polyampholytes

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Abstract

The simulation of electrohydrodynamics is of great interest particularly with the widespread use of electrokinetics as a means of separating analytes. In order to generate realistic results one must simulate both electrohydrodynamics and electrodynamics which requires large amounts of computing time. We show that by using a novel coupling scheme to couple Molecular Dynamics simulations to a Lattice-Boltzmann fluid the large cost of electrostatic calculations can be eliminated while still providing realistic electrohydrodynamics. We then use this technique to show a variety of surprising counter-intuitive phenomena which arise due to the complex interplay between electrostatics and hydrodynamics.

Method

The method consists of hybrid Molecular Dynamics simulation with a standard D3Q19 Lattice-Boltzmann fluid. In contrast to other simulations we couple the MD beads to the LB fluid using:

\[ F_D = \xi(v - v_F - \mu_0 E) \]

This simple addition of the term \( \xi \), which represents the drag of the shear of the fluid between the bead and the bulk fluid as depicted below (taken from [1]) provides realistic electrohydrodynamics without any expensive electrostatic calculations.

Mobility and Diffusion

We ran simulations to make sure that the mobility is independent of the polymer length (see inset). We also tested to make sure that the diffusion coefficient obeys Zimm dynamics (D \( \propto \nu^{0.5} \)) and not House dynamics (D \( \propto \nu \)). This is the basic test for any simulation method attempting to reproduce realistic electrohydrodynamics for polyelectrolytes.

Net Neutral Polyelectrolytes

One interesting phenomena we simulated was how a net neutral polyelectrolyte can have a non-zero mobility when subjected to an electric field. The ring copolymer depicted schematically in the accompanying figure consists of a positive block (black section) and a negative block of equal length making it net neutral. If the polymer is cut where the two connect the mobility is zero since the distribution of positive and negative charges is identical. However the polymer is cut somewhere along the positive block the resulting mobility is positive since both ends of the polymer are positive and they contribute more to the mobility since they tend to be towards the outside of the polymer coil [1].

Stall Force of a Polyelectrolyte

One of the surprising consequences of the interplay between electrostatics and hydrodynamics is the force required to hold an object still when subject to an electric field. Despite the force on the polymer due to the electric field being \( F = \alpha \mu_0 E \), the electroosmotic flow causes the stall force to be proportional to the hydrodynamic radius \( R_D \), \( \alpha \propto R_D \). For a random walk polymer \( \alpha \propto R_D \propto N \), for a rod polymer as is clearly seen in the simulation results below.

Discussion

We have demonstrated that through a simple addition of the coupling between Lennard-Jones beads and a Lattice-Boltzmann fluid we are able to reproduce realistic electrohydrodynamics without expensive electrostatic calculations. This technique could be applicable to a wide variety of systems such as the electrohydrodynamics of soft interfaces, electrophoresis in microfluidic channels, and induced charge electrosorption and electrophoresis.

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