Implicit Method for Simulating Electrohydrodynamics of Polyelectrolytes

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(Received 26 April 2010; published 29 September 2010)

We introduce a novel method to couple Lennard-Jones beads to a lattice-Boltzmann fluid by adding a term which represents the slip within the Debye layer with respect to the surrounding fluid. The method produces realistic electrophoretic dynamics of charged free chains, as well as the correct stall force in the limit of a thin Debye layer. Our simulations also demonstrate how a net-neutral polyampholyte can have a nonzero net force due to hydrodynamic interactions. This method represents an efficient way to simulate a wide variety of complex problems in electrohydrodynamics.

DOI: 10.1103/PhysRevLett.105.148301 PACS numbers: 82.35.Rs, 47.57.jd, 47.65.−d, 82.45.−h

Electrophoresis is of growing importance as a means to analyze charged particles and ions, colloids, and biomacromolecules such as DNA. In determining the velocity of the analyte the role of hydrodynamics is usually unimportant except at length scales of the order of the Debye length [1]. The long-ranged fluid velocity profile surrounding a sphere undergoing electrophoresis can be shown through a flow potential calculation to decay like $1/r^3$, where r is the distance to the center of the sphere [1,2]. The fast decrease in the hydrodynamic interactions with respect to r means that they can be neglected in certain cases and often are to save computation time [3–6]. In the case of electrophoresis of polyelectrolytes the conceptual framework of how hydrodynamics are screened on long length scales is called the local force or free-draining picture [7,8]. The mobility of a specific segment of a polyelectrolyte chain is seen as a balance between the electric force on the chain segment and the local hydrodynamic friction on the scale of the Debye length, λ_D.

Hydrodynamics do, however, play a crucial role in the electrophoresis of polyelectrolytes. For instance, Nkodo *et al.* [9] found that polyelectrolytes undergoing free-flow electrophoresis have diffusion coefficients which obey Zimm dynamics. Simulations have also shown the role of hydrodynamic interactions in determining the electrophoretic mobility of short polyelectrolytes [8,10–12].

Studies by Long, Viovy, and Ajdari [2,13–15] focused on the electrohydrodynamics of polyelectrolytes in the case where there is both a mechanical and an electrical force on the system. When the Debye length is much smaller than the other length scales in the system and at low Reynolds number (e.g., at moderate electric fields, $\zeta/\lambda_D \gg E$, where ζ is the zeta potential) they showed that one could simply superimpose the solutions for the flow field of the hydrodynamic problem (where a mechanical force, F_{ext}, is applied to a polyelectrolyte) to that of the electrophoretic problem (where an electric field E is applied to the charged object in solution). This yields the following general equation for the electrohydrodynamics of polyelectrolytes:

$$F_{\text{ext}} - \xi(v_{\text{polymer}} - \mu_0 E) = 0, \quad (1)$$

where $\xi = 6\pi\eta R_H$ is the drag coefficient, in which η is the viscosity and R_H is the hydrodynamic radius of the polymer conformation, v_{polymer} is the velocity of the polymer, and μ_0 is the electrophoretic mobility of the polymer. This equation yields some interesting results, most notably the force to hold a polyelectrolyte still in an electric field is not simply the external force applied to the polyelectrolyte QE (where Q is the charge on the polyelectrolyte) but rather $6\pi\eta R_H \mu_0 E$ [14]. There have been experimental studies on the stalling of a polyelectrolyte in an electric field [16–19] which support this conclusion, and it has been confirmed by computer simulations [20,21]. Recent experiments have also shown that Eq. (1) provides reasonable results for a colloid subjected to an electric field in an optical trap [22]. These results demonstrate that hydrodynamics can play an important role even on length scales much longer than the Debye length in contrast to prevailing views of how mobility is determined in free solution electrophoresis [7,8,10–12].

In this Letter we introduce a lattice-Boltzmann (LB) fluid model where the coupling to the classical molecular dynamics (MD) simulations is done via Eq. (1). The elimination of computationally demanding electrostatic calculations inherent in this method allows for the simulation of complex phenomena in mesoscopic systems in a wide range of applied field strengths, which would otherwise be impractical or take an extremely long time using explicit charges. First, we verify that the velocity of polymers in free solution electrophoresis is indeed $\mu_0 E$ and that their diffusion obeys Zimm dynamics for this model. We then show how long-ranged hydrodynamic interactions during free solution electrophoresis results in a polyampholyte with zero net charge having a nonzero mobility. Next we look at the stall force of a polyelectrolyte, and finally show how a special arrangement of charges can result in a net force perpendicular to the electric field.

Our computer simulations are carried out using the ESPRESSO simulation package [23]. The simulations consist of a coarse-grained bead spring model of the polyelectrolytes coupled to a mesoscopic fluid. The fluid is modeled as a lattice-Boltzmann fluid [8,10,24]. As in previous work we make use of the D3Q19 LB fluid model with a kinematic viscosity $v_{\text{kin}} = 3.0$, and a fluid density $\rho = 0.864$ yielding a dynamic viscosity of $\eta = 2.592$ [8,10]. The crucial difference in our model compared to other simulations is that we make use of Eq. (1) to couple the fluid to our polymer beads. Previous simulations have used a simple Stokes' drag term $F_D = \xi(v - v_f)$ [8,10,25], where v is the velocity of the Lennard-Jones bead and v_f is the local velocity of the fluid. In our simulations, a term representing the slip between the bead and the fluid, due to the electric field induced shearing in the Debye layer, is added to the total drag force:

$$F_D = \xi(v - v_f - \mu_0 E). \tag{2}$$

We show that this simple alteration of the coupling of an individual Lennard-Jones bead to the fluid provides realistic electrohydrodynamics for polyelectrolytes (in the limit of infinitely thin Debye layer) without needing to do any electrostatic calculations.

To test our approach we first model charged polymers undergoing free-flow electrophoresis. The nonbonded interactions between monomers are modeled by the Weeks-Chandler-Anderson (WCA) version of the Lennard-Jones potential with the standard energy (ϵ) and length (σ) parameters [3]. The bonded beads in the polyelectrolyte are linked via a finitely extensible nonlinear elastic (FENE) potential: $U_{\text{FENE}}(r) = -0.5kR_0^2 \ln[1 - (r/R_0)^2]$, where $R_0 = 1.5\sigma$ is the maximum extension of the bond and $k = 30\epsilon/\sigma^2$ is the energy scale for the interaction [3].

As a first test of the model, the velocity of polymers of lengths $N = 2$–30 and with values of $\mu_0 E = 0.0001$–1 was determined. The polymers were found to travel at $v = \mu_0 E$ regardless of the polymer length N (see inset of Fig. 1), as expected for free-draining polymers of size much larger than the Debye length [8,11,12]. Note that, had we simply applied a constant force to each bead, we would have found that $v \propto N^{1-\nu}$, where $\nu = 0.588$ is Flory's exponent. The main graph in Fig. 1 shows the diffusion coefficient D as a function of N, which fits a power law $D \propto N^{-0.54\pm0.02}$, consistent with Zimm dynamics, $D \propto N^{-\nu}$, rather than Rouse dynamics, $D \propto N^{-1}$. This result agrees with both MD simulations with explicit charges [8] as well as experimental results [9] and is, to the best of our knowledge, the first time both the correct mobility and diffusive behavior have been reproduced without the use of explicit charges.

As a second example we investigate the prediction made by Long *et al.* [15] that, depending on where it is cut, an overall neutral ring block copolymer can become a linear polymer with a nonzero mobility. The ring polymer consists of a positive and a negative block of equal length connected together to form a ring. If one cuts the ring polymer where the positive block connects to the negative block the resulting linear polymer has a net mobility of zero. If, however, one cuts the polymer in the middle of the positive block, the polymer will have a positive mobility. Monomers on the ends of the polymer matter more than those in the central portion for determining the overall mobility of the polymer. The results in Fig. 2 confirm the prediction that even an overall neutral polymer can have a nonzero mobility, and that the magnitude of the nonzero mobility depends on the charge layout along the backbone of the linearized polymer. The force is proportional to $\mu_0 E$, and by renormalizing the cut position by the total length N of our polymers (we used $N = 16$, 32), the results are largely insensitive to chain length. This is qualitatively consistent with the prediction of Long *et al.* [15], as

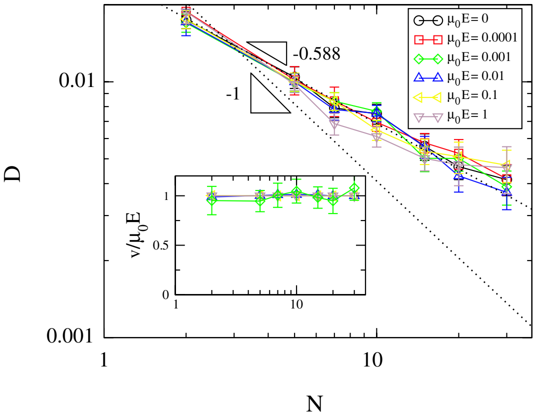

FIG. 1 (color online). The diffusion coefficient of polymers of various lengths N for several values of $\mu_0 E$. The dotted lines are slopes of -0.588 (the prediction for Zimm dynamics) and -1 (the prediction for Rouse dynamics). The inset shows the velocity renormalized by $\mu_0 E$.

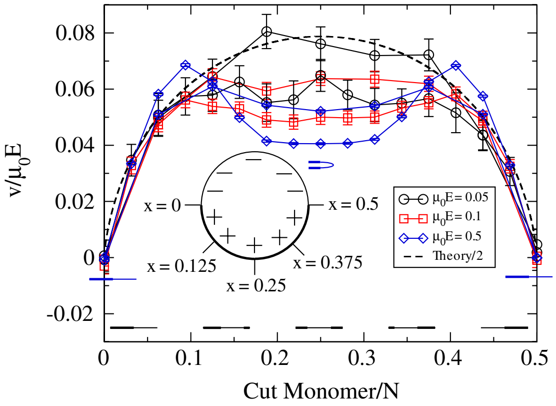

FIG. 2 (color online). The velocity of an overall neutral linear polymer renormalized by $\mu_0 E$ as a function of the charge distribution. The polymers are formed by taking the same ring copolymer and cutting it at different points along the positive block as depicted schematically. The dashed line represents the predictions of Long *et al.* [15] with a scaling factor.

shown rescaled by a factor of 2 in Fig. 2. For higher fields ($\mu_0 E = 0.5$), there is a dip in the middle of the curves. This is due to polymer chain extension causing the positive and negative sections of the polymer to hydrodynamically separate from each other, as has been discussed theoretically [26–28]. Essentially the two positive ends start to separate from the central negative segment due to stretching by the electric field as depicted schematically.

Next we reproduce, without the use of electrostatics, the MD results of Bertrand and Slater [20] that the stall force needed to hold a polyelectrolyte in place is $F = 6\pi\eta R_H \mu_0 E$ and not simply the electric force on the polyelectrolyte, $F_E = QE$. For these studies polymers are generated in both ideal random walk conformations (where $R_H \propto N^{0.5}$) and straight rod conformations (where $R_H \propto N/[\ln(2N/b) - 0.5]$). These polymer conformations are frozen and simulations are conducted in the absence of an LB thermostat similar to recent studies of electro-osmotic flow [29], to prevent stretching of the polymers by the electric field. This decoupling of electric field and polymer conformation allows us to focus on the electrokinetic phenomena associated with particular steady state chain conformations. Like Bertrand and Slater [20], we make a cylindrical channel of radius $R = 25\sigma$ of fixed Lennard-Jones beads in which we place the polymer. The wall beads are used to dissipate the linear momentum generated by the frozen monomers through the coupling of these beads to the LB fluid.

Figure 3 shows the stall force F divided by $\mu_0 E$ (which varies from 0.0001 to 1) as a function of the polymer length N, along with power law fits to the data. The data shows, that except for large values of N, the force on the polymer coil scales as $R_H \propto N^{0.5}$, and not as N, the total charge on the polymer. The discrepancy for larger values of N is due to R_H becoming on the order of the tube diameter, at which point the Stokes' velocity profile around the polymer is affected by the tube walls. The results in Fig. 3 for a rodlike polymer conformation along the center of the tube also support the Stoke's drag picture for the stall force. Data for $\mu_0 E = 0.0001$–1 are shown, and are identical for all values of $\mu_0 E$. The fits clearly show that the force to hold the polymer still in such a configuration is in agreement with the theoretical result for a rigid rod, $F/\mu_0 E \propto \xi_{\text{rod}} \propto N/[\ln(N/b) - 1]$.

Finally, we also applied our algorithm to the net-neutral, cross-charge configuration depicted in the bottom right of Fig. 4, and found that by choosing such a fixed configuration of charged beads, the net force in the direction of the field is exactly zero (due to symmetry) while there is a finite force perpendicular to it. This effect is caused by the electro-osmotic flow depicted by the curved arrows. Moreover, the magnitude of this transverse force was found to be a power law of the applied field, $F_\perp \propto (\mu_0 E)^3$, as shown in Fig. 4. This was a phenomenon proposed by Long and Ajdari [30], and has recently been observed experimentally [31]. Interestingly in the experimental work on asymmetric Janus particles [31] the velocity was also found to go like E^2. To our knowledge these results are the first computational evidence for such an effect.

The coupling scheme we used for the case of an LB fluid might also be applicable for MD using multi-particle collision dynamics [11,12] or dissipative particle dynamics [32]. Applying the hydrodynamic tensor derived by Long *et al.* [13] could also be used in conjunction with Brownian dynamics simulations. One could also make the value of $\mu_0 E$ dependent on the local bond angle to incorporate the orientation dependent nature of μ_0 [18,33].

Certain aspects of electrohydrodynamics are neglected in this implicit method for thin Debye layers. Notably the lack of explicit charges in our approach makes it impossible to study the effect of charge condensation [34], an important phenomenon for both colloids and polyelectrolytes.

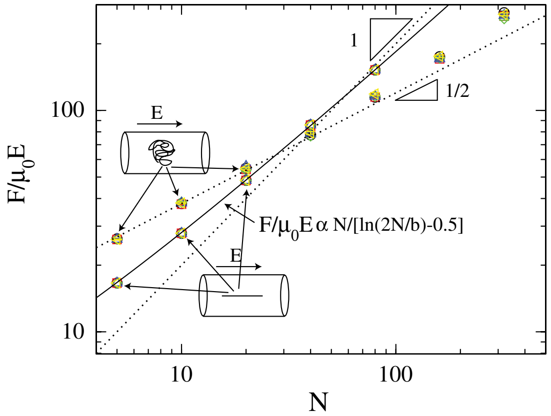

FIG. 3 (color online). Force needed to hold polymers of different lengths N stationary in a random walk or rod configuration for various values of the coupling constant $\mu_0 E$. Curves for $F \propto N^{0.5}$ and $F \propto N$ are shown as dashed lines, along with a solid line of the form $N/[\ln(2N/b) - 0.5]$ for the rod data.

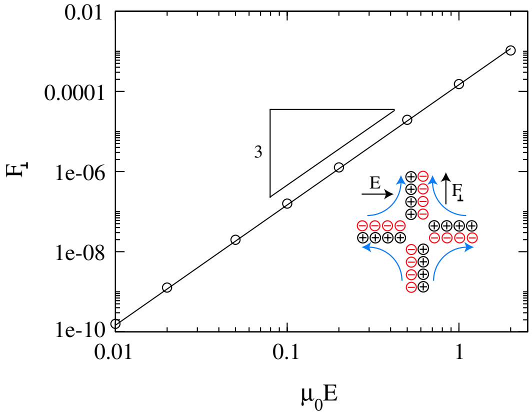

FIG. 4 (color online). The force perpendicular to the electric field on a cross of zero net charge as a function of the applied field $\mu_0 E$ showing $F_\perp \propto (\mu_0 E)^3$. The inset shows a schematic of the bead configuration along with the curved fluid flow lines which cause a force perpendicular to the electric field.

Swelling due to intramolecular electrostatic interactions in polyelectrolyte systems [35] would also not appear using our simulation technique. Our model would also miss important physics in polyelectrolyte solutions where intermolecular electrostatic interactions between chains are important. However, the focus of our method is on field-induced transport of individual polyelectrolytes or macroions in moderate-to-high ionic strength conditions. For such typical experimental conditions, the relevant physical parameters on the scale of the Debye layer (e.g., local charge densities and friction factors) are naturally combined into a single characteristic parameter, the mobility μ_0, that controls the response of a polyelectrolyte to an applied field in free solution. As such, the particular conditions governing the static chain properties (such as chain conformation, solvation, and charge distribution) are inputs required for the method, which may be separately determined experimentally or by complementary computational methods.

The simulation of electrohydrodynamics through our implicit coupling scheme in lieu of explicit electrostatic calculations allows for the simulation of much longer length and time scales. Moreover our method does not suffer from the fluctuations inherent in the response of finite systems to weak applied fields, thereby allowing the study of experimentally important electrokinetic conditions. This model thus has the potential to be applied to a wide variety of problems in electrohydrodynamics, and electrophoresis, in particular. The technique could be applied to the simulation of the separation of DNA using ELFSE techniques [28,36], charged polymer coatings for the modulation of electro-osmotic flow [37], the electrophoresis of colloids and other mesoscale objects [22], induced charge electrophoresis and induced charge electro-osmotic flow [38], the dynamics of polyelectrolytes in complex microfluidic structures [6,39–41], and the stall force of a polyelectrolyte within a nanopore [19,21].

The authors would like to thank Stefan Kesselheim and Florian Rühle. This work was supported through NSERC Discovery Grants to G. W. S and J. L. H. C. H. acknowledges financial contributions from the VW Foundation and the DFG through SFB 716. O. A. H. would like to acknowledge financial support from the NSERC-CGS program. The authors are grateful to Sharcnet for providing computational resources for this work.

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