

Electric Field Driven Motion of Flexible Polyelectrolytes – A Molecular Dynamics Study

T.S. Lo*, B. Khusid**, A. Acrivos* and J. Koplik*

*The Levich Institute, City College of CUNY, New York, NY, 10031

**Department of Mechanical Engineering, NJIT, University Heights, Newark, NJ 07102

ABSTRACT

Our work aims to develop multi-scale computational procedures for simulating the dielectrophoretic behavior of biomolecules in micro/nano-fluidics, which combine electrohydrodynamics with molecular theories for the macromolecule polarization caused by the distortion of the counterion cloud. Molecular dynamics is used to simulate the transport of a flexible polyelectrolyte suspended in a solvent, with or without added salt, under the action of electric fields. We used a model with explicit solvent atoms that includes hydrodynamic interactions and finite atom size effects naturally. The polyelectrolyte is modeled as a negatively charged freely-jointed bead-spring chain and its responses in dc and ac fields are studied in details. We developed a procedure to compute the dipole moments of the molecule and the surrounding double layer, which are required for the multi-scale simulation of dielectrophoretic phenomena in nanochannels.

Keywords: multi-scale modeling, molecular dynamics, polarization, dielectrophoresis, nanochannels

1 INTRODUCTION

Compared to other available methods, electric fields are particularly well-suited for the nanometer scale manipulation of biologically relevant macromolecules such as DNA strands, because moving parts are not required and electrical forces are easily varied by changing the applied voltage. Although recent publications have extended our ability to model and fabricate micro- and nano-fluidic devices, very little has been achieved in mastering and quantifying electrohydrodynamic phenomena at the nanometer scales. A major unresolved issue concerns the proper method to simulate the behavior of bio-macromolecules under such conditions.

In contrast to most previous studies, our efforts [1] aim to develop multi-scale computational procedures for simulating the behavior of biomolecules in micro- and nano-electrofluidics, which combine electrohydrodynamics with molecular theories for the macromolecule polarization caused by the distortion of the surrounding counterion cloud.

To date, no attempt has been made to consider the coupling of hydrodynamic and electric effects in the polarization of a macromolecule subject to strong electric fields. To this end, we used a molecular dynamics (MD) model of a flexible polyelectrolyte molecule suspended in a solvent, with or without added salt, to investigate the responses of the polyelectrolyte in an external dc or ac electric field. In particular, our focus is on the extraction of the information on the polarization of the polyelectrolyte and its surrounding counterions. The main feature of the model which we used is that solvent atoms are represented explicitly, so all the hydrodynamic interactions are included naturally, with no ad hoc assumption required. Moreover, in an explicit solvent model, the effects of finite solvent atom size, which may be important in phenomena occurring at the nanometer scales, are also included.

2 SIMULATION METHODS

The MD simulations carried out here employ standard techniques [2] and a simple molecular model for a solvent, based on atoms interacting via the Lennard-Jones potential

$$V_{LJ}(r) = 4\epsilon \left[\left(\frac{r}{\sigma} \right)^{-12} - \left(\frac{r}{\sigma} \right)^{-6} \right]. \quad (1)$$

The interaction is cut off at $r_c = 2.5\sigma$, and shifted by a linear term so that the force vanishes smoothly there. The system consists of 32000 atoms of mass m inside a cubic box of length L . The average number density is $0.8\sigma^{-3}$, which gives $L \approx 34.2\sigma$. In this work, we use the so-called “MD units” derived from the above potential, with σ as the unit of length, ϵ as the unit of energy, and $\tau \equiv \sigma(m/\epsilon)^{1/2}$ as the unit of time.

We model the polyelectrolyte molecule as a group of N atoms joined in a freely-jointed chain using the FENE potential [3]

$$V_F(r) = -\frac{k_F}{2} R_0^2 \ln \left(1 - \frac{r^2}{R_0^2} \right). \quad (2)$$

The molecule carries a total charge $-Z_p e$ distributed uniformly along the chain. We used $k_F = 30\epsilon/\sigma^2$ and $R_0 = 1.5\sigma$, following [3].

In addition to the neutral solvent atoms and the polyelectrolyte, the system includes N_- coions of charge $-e$ and $N_+ = (N_- + Z_p)$ counterions of charge $+e$ so as to maintain electroneutrality. The salt free case corresponds to $N_- = 0$. The charges interact via the Coulomb potential, with the dielectric constant ϵ_r chosen to be that of water. Other interactions between the polyelectrolyte, solvent atoms, and ions are incorporated using the same Lennard-Jones potential in Eq. (1).

During the simulations, a Nosé-Hoover thermostat maintains a constant temperature $T = 1.0 \epsilon/k_B$ and periodic boundary conditions are used. We set the Bjerrum length $l_B = e^2/(4\pi\epsilon_r\epsilon_0k_B T)$ at 1.854σ (corresponding to $T = 300 K$ and assuming σ is similar to the size of a water molecule). We have benchmarked our model by computing the single chain structure factor and various pair correlation functions under equilibrium conditions, and comparing with simulation results available in the literature [4].

3 MOTION UNDER DC FIELD

To study the motion of the polyelectrolyte under the action of a dc electric field, we apply an uniform field of the form $\mathbf{E} = E_0 \mathbf{e}_x$ to the system after equilibration. The strength of the field, E_0 , is measured in $\epsilon/e\sigma$. A snapshot of a simulation of a 49-bead polyelectrolyte molecule in a salt solution is shown in Figure 1.

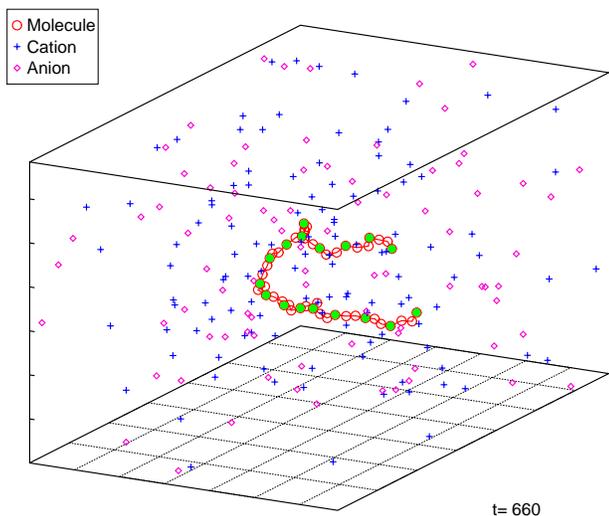


Figure 1: A snapshot of the simulation showing a 49-bead polyelectrolyte molecule and the ions (solvent atoms are not shown). The green beads are the positions where the charges of the molecule are located, each has a charge of $-e$. The constant electric field is applied in the positive x -direction, which is running from left to right and is parallel to the front edge in the figure.

In Figure 2, we show the x -coordinate of the center of mass of a 49-bead polyelectrolyte molecule in a salt

solution under fields of various strengths, after the field is turned on. The total charge on the chain is $-17e$ and N_- is 100. In this figure, each curve actually consists of 3000 data points, each one represents the average position of the molecule over a time interval of 1τ . This figure shows that the displacement of the molecule is linear in time, and hence, well-defined drift velocities can be obtained for different field strengths by fitting the curves to a straight line.

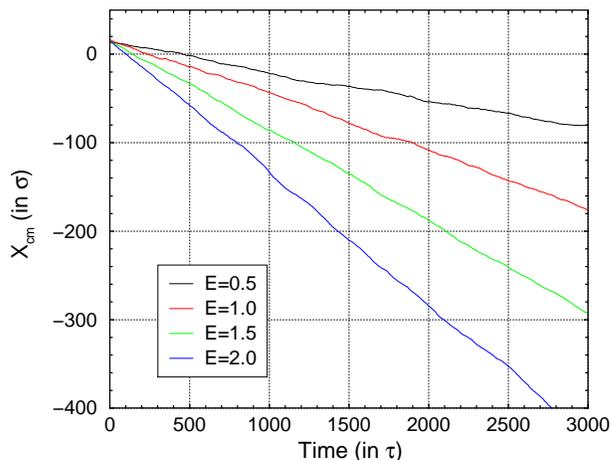


Figure 2: x -coordinate of the center of mass of a 49-bead long polyelectrolyte chain in a constant electric field vs. time. The field is applied in the positive x -direction and the strength varies. The charge on the molecule is $-17e$.

The drift velocities at various field strengths for two 49-bead long polyelectrolytes of different charge in a salt solution ($N_- = 100$) are shown in Figure 3. From the figure, we can see that the variation of the drift velocity with respect to the field strength is roughly linear, defining a roughly constant mobility. The slight curvature in the curves mainly show up in the strong field region and is more significant for the higher charge case. For field strengths at or below 1, the curves are almost linear. Therefore, we shall restrict the maximum field strength to be at or below 1 from now on in order to ensure the simulations are in the linear regime.

4 MOTION UNDER AC FIELD

We investigated the response of a polyelectrolyte plus salt system under an applied ac electric field. The goal is to extract information on the dipole moments (or equivalently, the polarizability) of the molecule and the surrounding double layer, which is required for the multi-scale simulation of dielectrophoretic phenomena in nanochannels of the micrometer lengths. To achieve this goal, we first conduct a simulation of a salt solution (without polyelectrolyte) with an ac field and extract the dielectric response function $\epsilon_{sol}^*(\omega)$ of the system. Here ω is the angular frequency of the ac field. Next, we per-

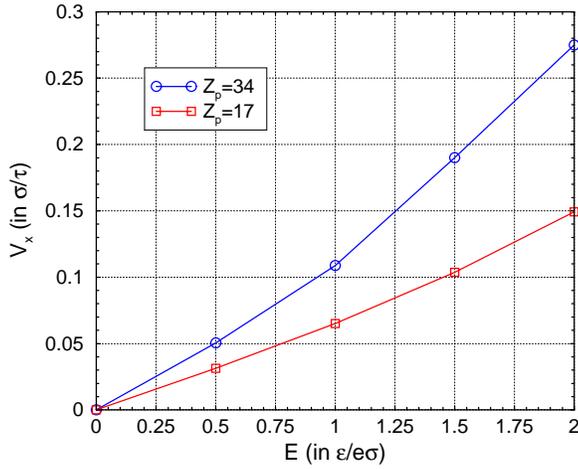


Figure 3: Drift velocity of two 49-bead long polyelectrolyte molecules with different charges under constant electric field of various strengths.

form the same simulation to the same system including a polyelectrolyte molecule and extract the dielectric response function $\epsilon^*(\omega)$. We then use theory of dilute solution to calculate the polarizability of the molecule plus counterion system.

4.1 AC Response of Ionic Solution

We performed a simulation of a system consists of 100 cations and 100 anions (i.e. $N_+=N_-=100$) and the neutral solvent atoms. An electric field of the form $\mathbf{E} = E_0 \sin \omega t \mathbf{e}_x$ is turned on after equilibration. The field strength is set at $E_0 = 1$ and ω is chosen to be $\frac{2\pi}{300} \tau^{-1}$ here. The total simulation time is 3000τ and the average current density $\langle \mathbf{J} \rangle$ due to the motion of the ions is calculated from the velocity data. At this frequency, the current density is almost in phase with the applied field. We extract the coefficients of the $\sin \omega t$ and $\cos \omega t$ components of this current signal by performing a Fourier transformation and obtain the ionic contribution to the dielectric response $\epsilon_{\text{sol}}^*(\omega)$ by using the relation $\langle \mathbf{J} \rangle = i\omega \epsilon_0 \epsilon^*(\omega) \mathbf{E}$ [5]. After accounting for the dielectric constant of the solvent, we find $\epsilon_{\text{sol}}^*(\omega) = (0.998 - 0.366i)\epsilon_r$.

4.2 AC Response with Polyelectrolyte

We now turn to the simulation of a salt solution with a polyelectrolyte molecule in an ac field. The system is a 25-bead long chain with a total charge of $-25e$; together with $N_+=125$ counterions, $N_-=100$ coions and the solvent atoms. This system is the same as the one in the last subsection, except that a polyelectrolyte and the corresponding counterions to maintain charge neutrality are added. The same ac electric field as in the last subsection is applied after equilibration and the simulation was run for 3000τ . The position of the center of mass of the molecule is shown in Figure 4. We can see

that the molecule oscillates back and forth at the same frequency of the applied field in the x -direction, which is the direction of the applied field. Note that the net drift in the x -direction is comparable to the drift in the other two directions along which no field is applied. This drift is caused by the Brownian motion of the molecule which is the result of the random kicks of the solvent atoms on the molecule due to thermal motion. The average current density due to the motion of all the charged particles in the system is similarly obtained from the velocity data as before. After performing the same analysis to the current density data, the dielectric response of the system is found to be $\epsilon^*(\omega) = (1.009 - 0.466i)\epsilon_r$.

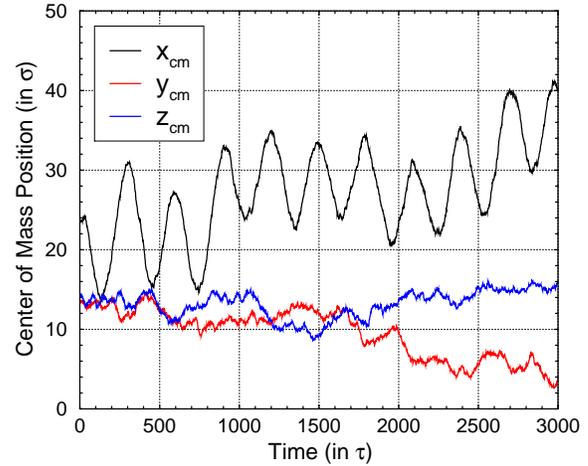


Figure 4: Center of mass position of a 25-bead long polyelectrolyte with charge $-25e$ in an ac field.

For a dilute polyelectrolyte solution, the polarizability (α) of a molecule and its associated double layer is related to the dielectric response functions as follows:

$$\frac{\epsilon^*(\omega)}{\epsilon_{\text{sol}}^*(\omega)} = 1 + \frac{n}{\epsilon_0 \epsilon_{\text{sol}}^*(\omega)} \alpha \quad (3)$$

Here n is the number density of the polyelectrolyte in the solution and is equal to $1/L^3$ in our system. From Eq. (3) and the results from the simulations above, we get $\alpha = (20.01 - 171.64i) e^2 \sigma^2 / \epsilon$.

5 CONCLUSIONS

In this work, we studied the motion of a flexible polyelectrolyte suspended in an ionic solution driven by dc or ac electric fields using molecular dynamics in detail. In the case of dc fields, we found that the polyelectrolyte moves with a constant drift velocity on the average and well-defined mobilities can be obtained. We are in the progress of investigating the dependence of the mobility on various parameters, such as the length and the charge of the polyelectrolyte, and the concentration of the ions. In the case of ac fields, we investigated the

dielectric responses of the polyelectrolyte/salt solution and developed a procedure to compute the polarizability of a single molecule and its surrounding counterion atmosphere from MD simulations. This information would be useful for developing multi-scale approach to simulate dielectrophoresis in nanochannels. At this point, more systematic investigations are needed and it would be interesting to compare simulational results with theory and/or experiments. Works along these lines are in progress.

ACKNOWLEDGEMENT

We are grateful to German Drazer for his valuable suggestions during the development of the code. This work was supported in part by grants from NSF (CTS-0307099), and NSF/Sandia (NTRT/NER-0330703).

REFERENCES

- [1] G. Drazer, B. Khusid, J. Koplik, and A. Acrivos, *Phys. Rev. Lett.* **95**, 016102, 2005; *Phys. Fluids* **17**, 017102, 2005; *Phys. Rev. Lett.* **89**, 24450, 2002.
- [2] M.P. Allen and D.J. Tildesley, “*Computer Simulation of Liquids*”, Clarendon Press, Oxford, 1987; D. Frenkel and B. Smit, “*Understanding Molecular Simulation*”, 2nd ed., Academic Press, San Diego, 2002.
- [3] G.S. Grest and K. Kremer, *Phys. Rev. A* **33**, 3628, 1986.
- [4] M.J. Stevens and K. Kremer, *J. Chem. Phys.* **103**, 1669, 1995; S. Liu and M. Muthukumar, *J. Chem. Phys.* **116**, 9975, 2002; S. Liu, K. Ghosh and M. Muthukumar, *J. Chem. Phys.* **119**, 1813, 2003.
- [5] F. Bordini, C. Cametti and R.H. Colby, *J. Phys.: Condens. Matter* **16**, R1423, 2004.