

## **Brownian Dynamics Simulation of Polymer Behavior in Nano- and Microfluidic Systems**

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### **Summary**

Brownian Dynamics (BD) is a stochastic simulation method that can quantitatively describe the behavior of polymers in flow and electric fields. With the increasing use of nano- and microfluidic devices for the handling of biopolymers such as DNA, BD has the potential to be a powerful design tool for the separation and transport processes carried out in these devices. As a coarse-grained simulation method, BD also serves as a natural bridge between atomistic and continuum modeling. In this talk, an introduction to the Brownian Dynamics simulation method will be given along with simulation results for some nano- and microfluidic systems of current interest. The introduction will review basic molecular models for polymers (bead-rod, bead-spring) and the stochastic differential equations used to describe their dynamics. The applications will focus on polymer stretching and transport in complex electroosmotic flows and polymer electrophoresis in narrow channels.

### **Molecular Models and Governing Equations**

The backbone of a polymer will perform a random walk in space if the polymer is placed in a solvent at the theta-temperature---the point where polymer-solvent attractions balance polymer-polymer repulsions (excluded volume effects). The characteristic step size of this random walk is called a Kuhn step (or Kuhn length), and can range from 1 to 100 nm. Thus, each Kuhn step represents a contiguous group of monomers. Typical polymers may have several thousand Kuhn steps, leading to backbone (contour) lengths exceeding 1 micron. A simple model for this random-walk behavior is the freely-jointed chain, a chain of  $N$  links where each link has the same length and is able to point in any direction independent of the other links. Using the tools of statistical mechanics, many of the equilibrium properties of the freely-jointed chain can be determined analytically [1].

In numerous situations of natural and practical importance, analytical solutions of certain equilibrium properties are very difficult to obtain and various nonequilibrium properties may also be of interest. An example of the former is the conformation of a polymer near a chemically and/or physically heterogeneous surface, while an example of the latter is the degree to which a polymer stretches when placed in a complex flow. In these cases, numerical simulation of molecular models is an extremely powerful tool for calculating the desired quantities. The model corresponding to the freely-jointed chain is

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the bead-rod model:  $N+1$  spherical beads connected by  $N$  links of constant length. The beads allow viscous drag to be felt by the polymer as it moves through the solvent and the rods form the polymer backbone. The force acting on a given bead will have several contributions: the viscous drag force due to its motion through the solvent, the tension forces exerted by the links on each of its sides, a stochastic Brownian force that represents collisions between solvent molecules and the bead, and forces due to imposed external fields (e.g., electric fields). A force balance can be written for each bead, and this leads to system of stochastic differential equations that describe the bead positions with respect to time [2-4]. Simulations are carried out by performing a set of runs and then averaging over the ensemble to obtain properties of interest. This is the essence of the Brownian Dynamics (BD) method

The viscous drag force is most simply calculated by assuming a Stokes-law relationship involving the difference between the bead velocity and the local solvent velocity due to an imposed external flow. More complicated relationships accounting for hydrodynamic interaction between different beads or between a bead and a solid boundary may also be used. The tension forces are calculated by imposing the constraint that the link lengths must remain constant. The form of the Brownian force is dictated by the fluctuation-dissipation theorem of statistical mechanics, which says that viscous drag forces and Brownian forces arise from the same source: collision of the bead (solute particle) with solvent molecules. This division is a coarse-graining in which the Brownian force represents the rapidly fluctuating character of bead-solvent interactions and the viscous drag represents bead-solvent interactions on a much longer time scale [5]. Often, bead inertia is neglected because the time scales associated with changes in the bead velocity ( $\sim 10^{-9}$  s) are much smaller than time scales of interest ( $\sim 1$  s). In this case, the time derivative in the problem comes from the term involving viscous drag, which is proportional to the bead velocity (change of position with respect to time).

An even more coarse-grained model than the bead-rod chain is the bead-spring chain. It can be shown that the force it takes to separate the ends of a bead-rod chain by a certain distance obeys a so-called inverse Langevin function. This force arises from considering only the contribution of the entropy to the free energy of the chain, which is proportional to the number of different contributions the chain can adopt. Since the contribution of the internal energy is neglected, the resulting force law is sometimes referred to as an "entropic spring". Thus, one can effectively replace the bead-rod chain with two beads connected by a spring [6]. Of course, such a model will not be able to capture changes in orientation and conformation along the polymer backbone. Rather than replacing an entire chain by a single spring, a less coarse-grained model can be obtained by replacing groups of Kuhn steps by springs. Now the chain consists of a series of beads connected by springs, where each spring represents many Kuhn steps. Both bead-rod and bead-spring chains have been used extensively in BD simulations and can successfully predict many phenomena observed experimentally ; e.g., see [7]. Bead-bead interactions may be included to model the effects of excluded volume and solvent quality. Bending potentials

and various nonlinear spring laws can be used to account for stiffness along the polymer backbone.

### **Stretching and Transport in Complex Electroosmotic Flows**

Biopolymers like DNA are widely handled in microfluidic devices, which are increasingly being used to carry out a host of biotechnological experiments including DNA sequencing, proteome analysis, and screening of drugs. Electroosmosis is often used to drive fluid currents in microchannels and it is an important effect to take into consideration in electrophoretic separations. In order to explore the potential of electroosmotic flows to stretch and transport polymers in microfluidic devices, we have performed Brownian dynamics simulations using bead-spring chains whose model parameters are chosen to be representative of DNA.

The flows we consider are generated by prescribing a spatially periodic charge distribution on the walls of a parallel-plate channel and applying an electric field parallel to the direction of charge modulation. This gives rise to flows with inhomogeneous velocity gradients, in which there is a series of recirculation rolls separated by stagnation points. Simulations are performed for the cases of uncharged and charged polymers. For the uncharged case, it is found that the stagnation point in the center of the flow is not effective at stretching polymers because of the tendency of the flow to convect the polymer to regions where the velocity gradient is different. We observe that the polymers tend to become trapped in the recirculation rolls near that stagnation point, and that the amount of stretching which does occur is directly proportional to the residence time of the molecule near the stagnation point at the wall. For the charged case, it is found that the trapping persists below a critical charge density, but that above this threshold the polymer escapes from the rolls. This is a reflection of the competition between the electrophoretic force and the electroosmotically-induced drag force. Our observations suggest that while these complex flows may not be useful for stretching polymers far away from the channel walls, they may be useful for localizing the position of Brownian particles in microfluidic devices. In addition, they illustrate the rich dynamics that arise when polymers are placed in flows with inhomogeneous velocity gradients and when electroosmotic flow competes with electrophoresis.

### **Electrophoresis in Narrow Channels**

We use 2D BD simulations to study the electrophoresis of a bead-rod chain through a narrow slit. A constant electric field is assumed to act inside and outside of the slit, and each bead on the chain is assigned a constant uniform charge. We calculate the dependence of the polymer center-of-mass velocity on chain length, slit dimensions (length and width), and applied voltage. For sufficiently narrow slits, the center-of-mass velocity increases nonlinearly with the applied voltage for low voltages, whereas it increases linearly for high voltages. In the low-voltage region and for sufficiently narrow

slits, the center of mass velocity decreases rapidly for small chain lengths and then much less rapidly beyond a critical chain length,  $N^*$ . As the slit width increases, this critical length disappears and the center-of-mass velocity decreases with chain length in a more continuous manner. For sufficiently large slits, the center-of-mass velocity is much less dependent on chain length as expected. We also calculate the free energy of the polymer as it moves through the slit, and find that at  $N^*$  the free energy dramatically increases inside the narrow slit. Histograms reveal the heterogeneity in the degree to which different polymers stretch as they move down the slit. These results show the sensitivity of the center-of-mass velocity vs. chain length relationship to the slit dimensions and applied voltage. They may be useful for understanding the motion of biological polymers and for microfluidic separations.

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