BROWNIAN DYNAMICS SIMULATIONS OF POLYMERS AND SOFT MATTER

The Brownian dynamics (BD) simulation technique is a mesoscopic method in which explicit solvent molecules are replaced instead by a stochastic force. The technique takes advantage of the fact that there is a large separation in time scales between the rapid motion of solvent molecules and the more sluggish motion of polymers or colloids. The ability to coarse-grain out these fast modes of the solvent allows one to simulate much larger time scales than in a molecular dynamics simulation. At the core of a Brownian dynamics simulation is a stochastic differential equation which is integrated forward in time to create trajectories of molecules. Time enters naturally into the scheme allowing for the study of the temporal evolution and dynamics of complex fluids (e.g. polymers, large proteins, DNA molecules and colloidal solutions). Hydrodynamic and body forces, such as magnetic or electric fields, can be added in a straightforward way. Brownian dynamics simulations are particularly well suited to studying the structure and rheology of complex fluids in hydrodynamic flows and other *nonequilibrium* situations.

Basic Brownian Dynamics

The technique of Brownian dynamics is used to simulate the dynamics of particles that undergo Brownian motion. Because of the small mass of these particles, it is common to neglect inertia. Using Newton's Second Law for particle i, $\mathbf{F}_i^{\mathrm{tot}} = m_i \mathbf{a}_i$, the neglect of inertia means that the total force is always approximately zero. The total force on a particle is composed of a drag force $\mathbf{F}_i^d$ from the particle moving through the viscous solvent, a Brownian force $\mathbf{F}_i^B$ due to random collisions of the solvent with the particle, and all non-hydrodynamic forces $\mathbf{F}_i^{nh}$

$$\mathbf{F}_i^{tot} = \mathbf{F}_i^d + \mathbf{F}_i^B + \mathbf{F}_i^{nh} \simeq 0 \ . \tag{1}$$

This total non-hydrodynamic force includes any external body forces, any spring forces, and any excluded volume interactions. In creeping flow and neglecting hydrodynamic interactions (free-draining), the drag force is taken as Stokes drag on a sphere

$$\mathbf{F}_i^d = -\zeta \left(\frac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}t} - \mathbf{u}^\infty(\mathbf{r}_i) \right) \tag{2}$$

where ζ is the drag coefficient and $\mathbf{u}^\infty(\mathbf{r}_i)$ is the unperturbed velocity of the solvent evaluated at the position of the particle. The differential equation governing the motion of the particle then becomes

$$\frac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}t} = \mathbf{u}^\infty(\mathbf{r}_i) + \frac{1}{\zeta}\left(\mathbf{F}_i^{nh}(\{\mathbf{r}_j\}) + \mathbf{F}_i^B(t)\right) \tag{3}$$

and is commonly called a *Langevin equation.* Note that the non-hydrodynamic force depends on the set of all particle positions $\{\mathbf{r}_j\}$. This is a stochastic differential equation because the Brownian force is taken from a random distribution. In order for the dynamics to satisfy the fluctuation-dissipation theorem, the expectation values of the Brownian force are

$$\langle \mathbf{F}_i^B(t) \rangle = \mathbf{0} \tag{4}$$

$$\langle \mathbf{F}_i^B(t) \mathbf{F}_j^B(t') \rangle = 2 k_B T \zeta \delta_{ij} \delta(t - t') \boldsymbol{\delta} \tag{5}$$

where k_B is Boltzmann's constant, T is the absolute temperature, δ_{ij} is the Kronecker delta, $\delta(t - t')$ is the Dirac delta function, and $\boldsymbol{\delta}$ is the unit second-order tensor. Equations (3), (4), and (5) are equivalent to the Fokker-Plank equation description, which is a diffusion equation for the phase space probability density (Öttinger, 1996).

Having developed the governing stochastic differential equation, one performs a BD simulation by integrating this equation forward in time. The stochastic nature means that one must produce many independent trajectories that are averaged together, producing the time-evolution of an ensemble-averaged property. The repetition of many independent trajectories is a time-consuming but necessary part to follow the time-evolution of a property. However, to calculate a steady state property, one uses the ergodic hypothesis to time-average a single trajectory.

Hydrodynamic Interactions

As a particle moves along its trajectory, it exerts a force on the solvent which changes the velocity field from its undisturbed value. The disturbance velocity changes the viscous drag force exerted on the *other* particles. This interaction between particles mediated by the solvent is called hydrodynamic interaction (HI). The hydrodynamic interactions are included in Brownian dynamics through the use of an interaction tensor $\boldsymbol{\Omega}_{ij}$ included as part of the diffusion tensor $\mathbf{D}_{ij}$ (Öttinger, 1996). The two tensors are related by

$$\mathbf{D}_{ij}(\mathbf{r}_i, \mathbf{r}_j) = \frac{k_B T}{\zeta} \left(\delta_{ij} \boldsymbol{\delta} + \zeta \boldsymbol{\Omega}_{ij}(\mathbf{r}_i, \mathbf{r}_j) \right) \tag{6}$$

where $\boldsymbol{\Omega}_{ii} = \mathbf{0}$. The stochastic differential equation including HI then becomes

$$\frac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}t} = \mathbf{u}^\infty(\mathbf{r}_i) + \frac{1}{k_B T} \sum_{j=1}^{N} \mathbf{D}_{ij}(\mathbf{r}_i, \mathbf{r}_j) \cdot \mathbf{F}_j^{nh}(\{\mathbf{r}_k\}) + \sqrt{2} \sum_{j=1}^{N} \mathbf{B}_{ij}(\{\mathbf{r}_k\}) \cdot \mathbf{n}_j(t) \tag{7}$$

where $\mathbf{n}_j$ are random vectors with expectation values

$$\langle \mathbf{n}_j(t) \rangle = \mathbf{0} \tag{8}$$

$$\langle \mathbf{n}_i(t)\mathbf{n}_j(t')\rangle = \delta_{ij}\delta(t-t')\boldsymbol{\delta} \tag{9}$$

and the weighting factors $\mathbf{B}_{ij}$ must be calculated from the diffusion tensor in order to satisfy the fluctuation-dissipation theorem

$$\mathbf{D}_{ij}(\mathbf{r}_i,\mathbf{r}_j) = \sum_{p=1}^{N} \mathbf{B}_{ip}(\{\mathbf{r}_k\}) \cdot \mathbf{B}_{jp}^T(\{\mathbf{r}_k\}) \ . \tag{10}$$

This can be inverted to calculate $\mathbf{B}_{ij}$ by Cholosky decomposition. However, a more efficient method has been developed by Fixman (1986) and implemented in BD simulations.

The interaction tensor in an unbounded solvent is taken as the Rotne-Prager-Yamakawa tensor, which is a regularized version of the Oseen-Burgers tensor. The Oseen-Burgers tensor represents the disturbance due to a point-force in creeping flow. However, it results in a non-positive-definite diffusion tensor if particle separations are comparable to the particle radius. The Rotne-Prager-Yamakawa tensor modifies the small separation disturbance such that the diffusion tensor is always positive-definite.

Polymer Models used in Brownian Dynamics

The choice of polymer model is intrinsically a modeling decision which depends upon the real polymer one wants to model and the level of fine-scale molecular detail one needs to retain or can computationally afford to simulate. Polymers can be broadly separated into flexible and semiflexible chains. The flexibility of a chain is determined by the ratio L/l_p where l_p is the persistence length and L the contour length of the chain. Flexible chains have $L/l_p \gg 1$ and semiflexible chains have $L/l_p \sim 1$.

The most common coarse-grained models for flexible polymers are the freely-jointed bead-rod and bead-spring chains. The polymer is modeled as a series of beads connected by either rods or springs, as shown in Figure 1. The frictional drag on the chain is distributed at bead centers. The term ‘freely-jointed’ implies that there is no energetic penalty to rotating a spring or rod about a bead center. The spirit of these mesoscopic models is to coarse-grain out molecular details smaller than the finest length scale in the given model (rod or spring).

We consider first the flexible bead-rod chain. Physically, the rod in a bead-rod chain corresponds to a Kuhn length l_k (twice the value of the persistence length). Mathematically, the rods act as a constraint on the system which ensures that adjacent beads in the chain are maintained at a constant separation at all times. How one achieves this constraint is important as there is a subtle difference between a completely rigid constraint and the approximation of that constraint using a very (infinitely) stiff potential (Morse, 2004). For example, the equilibrium distribution of a bead-rod chain using stiff constraints yields a

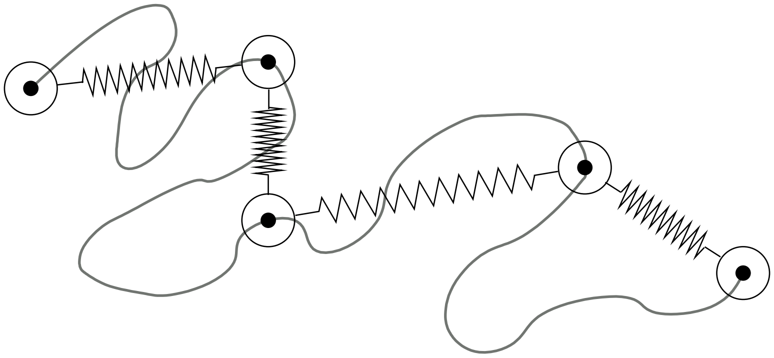


Figure 1: Schematic of the canonical polymer model used in Brownian dynamics simulations: a bead-spring chain. The continuous curve is the ‘real’ polymer that the bead-spring chain is meant to represent.

random walk configuration while imposing rigid constraints gives rise to correlations in the rod directions, even in the absence of bending forces. Physically, one would argue that the random walk configuration is more realistic. However, rigid constraints are attractive from a computational standpoint as they freeze out the usually uninteresting rapid bond fluctuations. In practice, one chooses to simulate the stiff system, but does so by imposing rigid constraints (which introduces a new tension force $\mathbf{F}^{tens}$) and adding a corrective pseudo-potential metric force $\mathbf{F}^{met}$ which makes the system equivalent to imposing an infinitely stiff potential. A recent detailed review of constrained Brownian motion and the implementation of bead-rod BD algorithms can be found in Morse (2004). With current computers typically one can only simulate chains with up to $\sim 100-200$ Kuhn steps which corresponds to a low molecular weight polystyrene polymer ($\sim 75,000 - 150,000$ Daltons).

Large flexible polymers are more commonly modeled as a series of N_s springs connected by beads. Each spring models a portion of the full chain and has a contour length $L_s = L/N_s$. The spring represents the entropic restoring force associated with stretching a subsection of the chain. The entropic force can be calculated starting from a fine-scale micromechanical model (e.g. freely-jointed bead-rod chain) using equilibrium statistical mechanics and calculating the extension of a chain when subject to a constant force. The force-extension response of a freely-joined chain is exactly described by the inverse Langevin function which is closely approximated by the more convenient FENE force law

$$F^{FENE}(r) = \frac{3k_BT}{l_k}\frac{r/L_s}{[1-(r/L_s)^2]} \tag{11}$$

where r is the spring extension and L_s is the spring length when fully stretched (Bird et al., 1987). A slightly more accurate approximation to the inverse Langevin function can be obtained using a Padé approximation (see for example Hsieh et al. (2003)). Most flexible synthetic polymers (polystyrene, poly(ethylene oxide) etc.) and single stranded DNA have significant bond rotations and should be modeled using the FENE force law. However, many biopolymers resist local bond torsion (e.g. duplex DNA) and are more accurately described by a wormlike chain model which for $L_s/l_p \gg 1$ is well approximated by the Marko-Siggia spring law (Marko and Siggia, 1995)

$$F^{wlc}(r) = \frac{k_B T}{l_p}\left[\frac{1}{4}\left(1 - \frac{r}{L_s}\right)^{-2} - \frac{1}{4} + \frac{r}{L_s}\right]. \tag{12}$$

It is important to note some limitations and assumptions when using common spring force laws such as Equations (11) and (12). These relations are derived assuming a large number of persistence or Kuhn lengths are contained in the spring. More refined calculations show however that corrections to the spring laws must be made when the spring has a contour length less than $\sim 20l_k$. Furthermore, if the underlying micromechanical model is freely-jointed at each node connecting the springs (e.g. freely-jointed chains), then spring force laws can be derived for springs containing an arbitrarily small number of Kuhn lengths which will exactly reproduce the force extension response of the micromechanical model. The use of *equilibrium* statistical mechanics to derive spring forces also raises a subtle point when using a bead-spring model in flow or other *nonequilibrium* situations. In such cases it is implicitly assumed that the springs are deformed slowly enough such that the micromechanical model describing the spring would be able to fully sample it's configuration space; in a sense achieving a local equilibration in phase space. Lastly, it is important to note that parameters in the spring force are *directly* related to the physical polymer system being modeled (e.g. a certain subsection of a polymer chain of length L_s with a given persistence length l_p). An extensive discussion of these and other issues on the coarse-graining polymers into bead-spring chains is given in Underhill and Doyle (2004).

The model for a semiflexible polymer is based on the premise that the polymer can be described as a homogeneous, isotropic elastic filament. The energy associated with bending a continuous filament described by a curve $\mathbf{r}(s)$ is $U^{bend} = \kappa/2 \int ds\, |\partial^2 \mathbf{r}/\partial s^2|^2$ where s is a contour distance along the chain. The bending rigidity κ is related to the persistence length by $l_p = \kappa/k_B T$. The chain is typically course-grained to a series of beads connected by rods which have a bending energy given by

$$U^{bend} = -\frac{\kappa}{a}\sum_{j=2}^{N-1} \mathbf{u}_j \cdot \mathbf{u}_{j-1} \tag{13}$$

where a is the length of the connecting rod and $\mathbf{u}_j$ is the unit vector directed from bead j to $j+1$. The bending force is $\mathbf{F}_i^{bend} = -\partial U^{bend}/\partial \mathbf{r}_i$. This description of a semiflexible polymer is commonly referred to as the wormlike chain or Kratky-Porod model (Yamakawa, 1997).

Systems with constraints (rods between beads) which ensure local inextensibility of a chain are computationally expensive and are sometimes replaced by stiff Fraenkel springs of the form $\mathbf{F}_i^s = H(|\mathbf{r}_{i+1} - \mathbf{r}_i| - a)\mathbf{u}_i$ where H is the spring constant and a is the equilibrium length of the spring. Pasquali and coworkers have shown that rigid constraints and stiff Fraenkel springs give similar results for the collapse of DNA in poor solvent (Montesi et al., 2004). They found typical time savings in using stiff springs over rigid constraints are on the order of $10 - 50$ fold. Most researchers use stiff springs *only* when simulating a polymer which is at or near equilibrium. Detailed comparisons between Fraenkel springs and constraints have not yet been performed for polymers in flow or under large tensions. In general, it is recommended to use rigid rods (with the corrective metric force discussed previously) unless one is certain stiff springs introduce no computational artifacts.

Numerical Algorithms

We have developed the stochastic differential equation and discussed the types of models and corresponding forces involved. To solve for the trajectory, one must integrate forward in time. A simple explicit Euler time integration scheme is widely used

$$\mathbf{r}_i(t + \delta t) \simeq \mathbf{r}_i(t) + \left(\frac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}t}\right)(t)\ \Delta t\ . \tag{14}$$

In this discrete version, the random vectors have an expectation value

$$\langle \mathbf{n}_i(t)\mathbf{n}_j(t')\rangle = \delta_{ij}\delta_{tt'}\boldsymbol{\delta}/\Delta t\ . \tag{15}$$

If the forces are steep, this would require very small time steps. This is particularly important for bead-spring chains with finitely extensible springs such as the FENE or Marko-Siggia force law. The above algorithm allows for the possibility of a spring being stretched beyond its fully-extended length. A semi-implicit predictor corrector method including HI has been developed that prevents this overstretching of springs (Hsieh et al., 2003).

The realization of a trajectory requires the sampling of random vectors with the appropriate expectation values. The calculation of these ‘random’ numbers is a significant computationally cost of BD simulations. Because of this cost, it is better to use uniform random numbers than Gaussian distributed. These random number generators should be used with care. Öttinger (1996) reviews important aspects of random number generators.

The use of random variables in the simulation and a finite number of trajectories in the ensemble means that there is intrinsic statistical noise to the method. The size of this error is proportional to $N_T^{-1/2}$ where N_T is the number of independent trajectories. An important technique for the reduction of this error by reducing the proportionality factor (not by increasing N_T) is called variance reduction. The exact way of performing variance reduction depends on the system of study. Two important types of variance reduction are importance sampling and subtracting off a control variable (Öttinger, 1996).

Another issue to be noted for the implementation of BD algorithms concerns the neglect of mass, which is a singular limit. This limit is discussed in detail by Grassia et al. (1995). We note here that one consequence of this singular limit is a drift that results if the diffusivity depends on position. To correct for this drift, a term with the gradient of the diffusivity must be added to the algorithm. However, if a higher order scheme is used such as a midpoint method or predictor corrector method, the extra term *should not* be added.

Computing Stress

The rheology of most complex fluids is not described well by simple constitutive relations. Central to the study of rheology then is the calculation of the bulk stress tensor $\boldsymbol{\sigma}$ in a simulation. The bulk stress of the mixture is a linear combination of the solvent contribution $\boldsymbol{\sigma}^s$ (typically a simple Newtonian fluid) and the polymer/colloid contribution $\boldsymbol{\sigma}^p$. The exact form of the stress tensor depends upon the details of the microstructural model. However, the most common model for a polymer or colloid is a collection of discrete beads (with positions $\mathbf{r}_i$) for which the particle contribution to the bulk stress is given by the Kramers-Kirkwood expression

$$\boldsymbol{\sigma}^p = -\frac{1}{V}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \mathbf{F}_i^h \right\rangle \tag{16}$$

where $\mathbf{F}_i^h$ is the total hydrodynamic force exerted on bead i, V is the volume of the simulation box and $\langle \cdots \rangle$ denotes an ensemble average. Equation (16) is a quite general result and is still applicable for systems with constraints (e.g. bead-rod chains) and when hydrodynamic interactions are taken into account (Bird et al., 1987; Morse, 2004).

While it is important to establish Equation (16) as a rather general form for the stress tensor, it useful to consider the specific form of the tensor for restricted classes of models and other commonly encountered cases. Consider first the canonical model employed in Brownian dynamics for a polymer: a series of N beads connected by springs. The polymer contribution to the stress is then

$$\boldsymbol{\sigma}^p = n_p \left\langle \sum_{i=1}^{N} \left(\mathbf{F}_i^s + \mathbf{F}_i^{other}\right) \mathbf{R}_i \right\rangle + n_p N k_B T \, \boldsymbol{\delta} \tag{17}$$

where $\mathbf{R}_i$ is the position of a bead relative to the center of mass of the chain, n_p is the number density of polymer molecules, $\mathbf{F}_i^s$ the net force by springs on bead i and $\mathbf{F}_i^{other}$ is the sum of all the non-hydrodynamic and non-spring forces exerted on bead i, such as bead-bead excluded volume interactions or bending forces. Equation (17) is valid both when hydrodynamic interactions are accounted for or neglected. The last term in Equation (17) is the familiar ideal gas-like internal energy contribution from each bead which is a direct result of applying the usual 'equilibration in momentum space' and assuming an isotropic friction tensor for a bead (Bird et al., 1987).

There can be computational advantages to using certain formulas over others to calculate the stress tensor in particular simulations. To gain some appreciation of this consider the *steady-state* rheology of a bead-rod (or bead-spring) chain in a simple shear flow $u_x^\infty(\mathbf{r}) = \dot{\gamma} r_y$ and neglect hydrodynamic interactions between beads. Using the Giesekus stress formula the polymer contribution to the shear viscosity ($\eta^p = -\sigma_{xy}^p/\dot{\gamma}$) can be written

$$\eta^p = -\frac{n_p \zeta}{2\dot{\gamma}} \frac{d}{dt} \left\langle \sum_{i=1}^{N} R_x^i R_y^i \right\rangle + \frac{n_p \zeta}{2} \left\langle \sum_{i=1}^{N} R_y^i R_y^i \right\rangle . \tag{18}$$

However, because in this example we are only interested in the stress of the system at *steady-state* we can immediately set the first term on the right side of Equation (18) to zero and eliminate it from our simulation code. Not only is this a great simplification, but now one has a simple expression which gives physical insight into the connection between polymer viscosity and molecular configurations. For this example, the effective width of the chain in the shear-gradient direction is directly related to the contribution to the viscosity. Furthermore, simplifying the formula for the stress tensor can aid in the development of scaling relations which generalize the trends (Doyle et al., 1997).

An extensive discussion of the various forms of the stress tensor can be found in Bird et al. (1987). We note that extra care must be taken when handling polymers containing constraint forces. In this case, a brute force calculation of the stress using Equation (16) will contain some contributions which fluctuate about zero but are quite large (order $\Delta t^{-1/2}$). Various efficient algorithms have been developed specifically for this case which essentially filter out these uninteresting 'noise' terms (Doyle et al., 1997; Morse, 2004).

Polymer Solutions in Hydrodynamic Flows

The ability to predict the dynamics and rheology of dilute polymer solutions in simple linear flows is an important benchmark by which researchers evaluate BD simulations and mesoscopic polymer models. In recent years it has become possible to directly observe single polymer molecule dynamics in flow using double stranded DNA (Chu, 2003). DNA is a

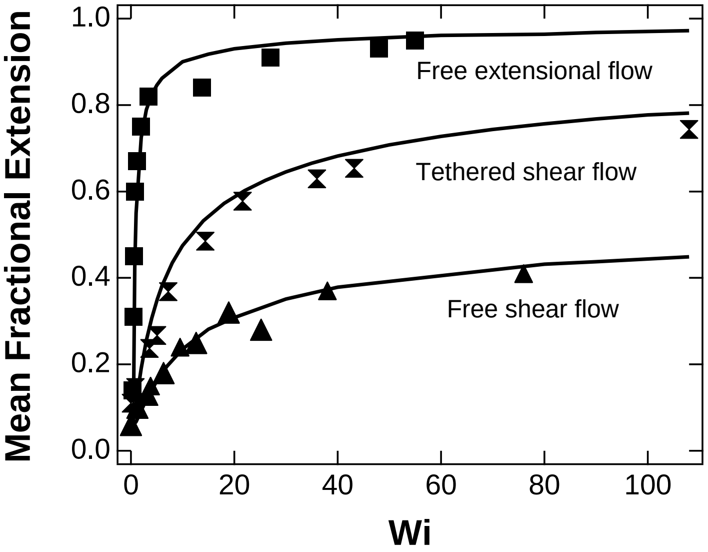


Figure 2: Comparison of Brownian dynamics simulations (lines) to single molecule DNA experiments (symbols). Mean fractional extension (stretch of the DNA scaled by the contour length of the molecule) versus Weissenberg number (Wi) is shown for tethered and free DNA in linear hydrodynamic flows. The Wi is the product of the shear rate (or elongation rate) and the longest relaxation time of the DNA. Figure adapted from Doyle et al. (2000).

unique polymer in that its force-extension relation (entropic spring-like force) has been well characterized and for large DNA is accurately described by the Marko-Siggia force law. To date most experiments have been performed with a particular commercially available DNA molecule, λ-DNA, which when stained with typical fluorescent dyes contains approximately 400 persistence lengths. Figure 2 shows a comparison between BD simulations using a free-draining (no HI) bead-spring chain (spring law given by Equation (12)) for free and tethered λ-DNA in simple linear flows. Excellent quantitative agreement between free-draining BD simulations and experiments of λ-DNA in shear, elongational and mixed flows has been attained (see for example Larson et al. (1999) and Doyle et al. (2000)). The ability to neglect HI in the BD simulations and obtain quantitative agreement with experiments is because λ-DNA contains a modest number of persistence lengths and so even when HI is included there is little difference in the drag on a coiled and fully extended chain. Recent experiments using extremely long DNA (genomic length, $\sim 20,000$ persistence lengths) have demonstrated conformational hysteresis in extensional flows (Schroeder et al., 2003). The authors show the qualitative nature of this behavior is captured only if HI is included in BD simulations.

As it stands now, quantitative description of most trends in the stretching of DNA with lengths up to $\sim$ 1000 persistence lengths can be captured without including HI in a simulation. Further simulations need to be done to quantitatively test HI when comparing to larger genomic length DNA. Furthermore, when polymers are placed near hard surfaces the hydrodynamic interaction between segments will change due to satisfying the no-slip boundary condition at the surface. These wall effects can be taken into account by numerically solving for the Green's function for creeping flow in an arbitrary geometry (Jendrejack et al., 2004). These modified hydrodynamic interactions are needed in a BD simulation to predict the correct trend of shear induced migration in channels. However, it has been shown that quantitative agreement between free-draining BD simulations and experiments for the stretch and fluctuations of tethered λ-DNA is obtained if the drag coefficient is merely adjusted (Doyle et al., 2000).

While the ability to observe single polymer molecules is very powerful, a measure of the polymer contribution to the stress is not attained in such experiments. Recently it has become possible to accurately measure transient extensional stresses of high molecular weight polymer solutions using filament stretching rheometers (McKinley and Sridhar, 2002). The stresses developed in these flows are challenging to model because the elongational nature of the flow leads to large deformation of the initially coiled polymer and brings with this a large contribution by the polymer to solution viscosity. Hsieh and Larson have performed the most detailed study of the role in HI in BD simulations of polystyrene and DNA in extensional flows (Hsieh et al., 2003). A method was developed to determine the HI parameters in the model which on one hand will keep the number of springs to a modest number while on the other hand will match the relaxation time or diffusivity of the experimental polymer system and the drag on the fully stretch polymer (estimated from Batchelor's formula). They confirmed that including HI has little effect for λ-DNA. Hsieh and Larson find that it is necessary to include HI in order to quantitatively match stress-strain behavior up to strains of $\sim$ 6 in filament stretching experiments of polystyrene with a molecular weight of 2 million ($\sim$ 5400 persistence lengths). However, the simulations do not properly predict the experimental values for the high strain plateau in the stress.

Outlook

Brownian dynamics is a powerful technique to simulate nonequilibrium dynamics of polymers and other soft matter. Efficient and stable algorithms have been developed which allow for the simulation of a wide class of polymer models ranging from flexible bead-spring chains to semiflexible bead-rod filaments. Furthermore, the strengths and deficiencies of springs representing a small number of persistence lengths is now well understood, at least for unconfined polymers. Quantitative comparisons of BD simulations to the rheology and dynamics of dilute polymer solutions show that our understanding of the importance and correct implementation of hydrodynamic interactions into a simulation is continuing to evolve.

With the growing importance of processing biological and other complex fluids in micro and even nanochannels, the BD simulation technique will continue to advance to properly treat molecules in tight spaces. Further *quantitative* comparisons to single molecule DNA experiments, both in ideal bulk flows and in microfluidic devices, will be critical in helping us to evaluate the state of the art in Brownian dynamics simulations.

Bibliography

Bird, R. B., Curtiss, C. F., Armstrong, R. C. and Hassager, O., 1987. *Dynamics of Polymeric Liquids, Volume 2*. 2nd edn. John Wiley and Sons, New York.

Chu, S., 2003. Biology and polymer physics at the single molecule level. *Phil. Trans. R. Soc. Lond. A* 361, 689.

Doyle, P. S., Gast, A. P. and Shaqfeh, E. S. G., 1997. Dynamic simulation of freely draining flexible polymers in steady linear flows. *J. Fluid Mech.* 334, 251.

Doyle, P. S., Ladoux, B. and Viovy, J. L., 2000. Dynamics of a tethered polymer in shear flow. *Phys. Rev. Lett.* 84, 4769.

Fixman, M., 1986. Construction of Langevin forces in the simulation of hydrodynamic interaction. *Macromolecules* 19, 1204.

Grassia, P. S., Hinch, E. J. and Nitsche, L. C., 1995. Computer simulations of Brownian motion of complex systems. *J. Fluid Mech.* 282, 373.

Hsieh, C.-C., Li, L. and Larson, R. G., 2003. Modeling hydrodynamic interaction in Brownian dynamics: simulations of extensional flows of dilute solutions of DNA and polystyrene. *J. non-Newtonian Fluid Mech.* 113, 147.

Jendrejack, R. M., Schwartz, D. C., de Pablo, J. J. and Graham, M. D., 2004. Shear-induced migration in flowing polymer solutions: simulation of long-chain DNA in microchannels. *J. Chem. Phys.* 120, 2513.

Larson, R. G., Hu, H., Smith, D. E. and Chu, S., 1999. Brownian dynamics simulations of DNA molecules in an extensional flow field. *J. Rheol.* 43, 267.

Marko, E. and Siggia, E. D., 1995. Stretching DNA. *Macromolecules* 28, 8759.

McKinley, G. H. and Sridhar, T., 2002. Filament stretching rheometry of complex fluids. *Ann. Rev. Fluid Mech.* 34, 375.

Montesi, A., Pasquali, M. and MacKintosh, F. C., 2004. Collapse of a semiflexible polymer in poor solvent. *Phys. Rev. E* 69, 021916.

Morse, D. C., 2004. Theory of constrained Brownian motion. *Adv. Chem. Physics* 128, 65.

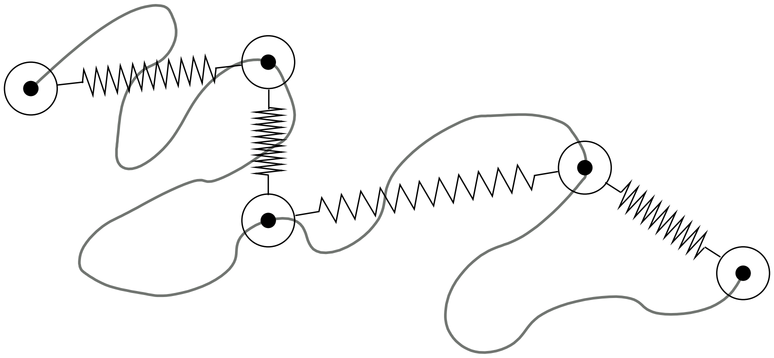
Öttinger, H. C., 1996. *Stochastic processes in polymeric fluids*. Springer-Verlag, New York.

Schroeder, C. M., Babcock, H. P., Shaqfeh, E. S. G. and Chu, S., 2003. Observation of polymer hysteresis in extensional flow. *Science* 3001, 1515.

Underhill, P. T. and Doyle, P. S., 2004. On the coarse-graining of polymers into bead-spring chains. *J. non-Newtonian Fluid Mech.* in press.

Yamakawa, H., 1997. *Helical Wormlike Chains in Polymer Solutions*. Springer, Berlin.

Patrick S. Doyle and Patrick T. Underhill
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts, USA
pdoyle@mit.edu; ptu@mit.edu



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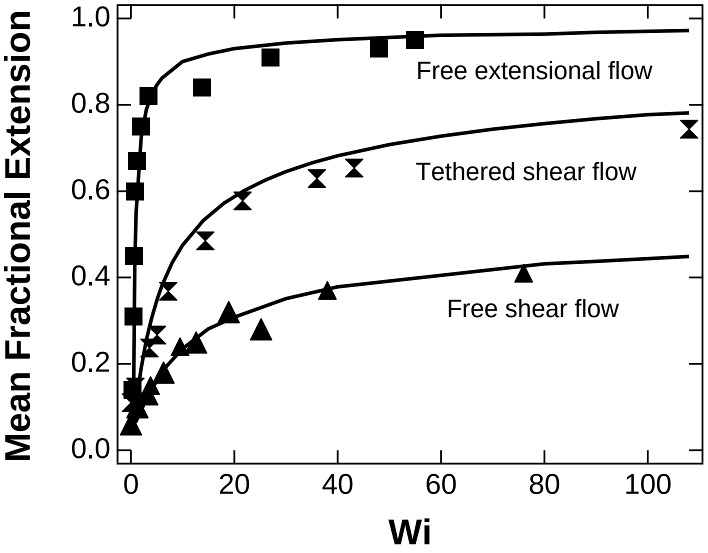

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