Polymer Simulations Companion: An Introduction to Brownian Dynamics

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Preface

This set of notes has been prepared to assist a novice graduate student in engineering to make a start in the simulation of polymer dynamics, using the Brownian Dynamics (BD) method. Most of the books known to the author, are quite daunting and do not help much in showing where to start and how to proceed. This requires serious study of the books and rigorous courses. These notes are intended to serve as a guideline that shows the important aspects, and how they are connected to the larger picture of polymer simulation, and will hopefully get a polymer simulation started in a few hours. The three corner stones for a successful simulation of polymer dynamics–Polymer Kinetic Theory, Stochastic Processes, and Brownian Dynamics Simulation—are covered in three separate chapters. The exercises, embedded along with the chapter contents, should help the learning by doing a short calculation or computer simulation.

As the title of the book implies it is only a companion, and helps to serve as a guide to polymer simulations. Authoritative books on polymer kinetic theory by Bird *et al.* (1987*b*) and on Brownian Dynamics by Öttinger (1996) must be consulted by serious researchers. References to these textbooks and other sources are made at appropriate places for proofs and details. Nevertheless, the material provided here is sufficient to carry out a simple polymer simulation without loss of continuity that requires to refer outside. Once this simple simulation (algorithm) is understood, it should be easier to study the advanced text books.

The updated version of these notes and related program codes are available for down-load from www.che.iitb.ac.in/online/faculty/p-sunthar

Chapter 1

Polymeric Liquids

Concepts You Must Know

- 1. What is the origin for the flexibility of polymer molecules?
- 2. Kuhn length is the fundamental length for polymer physics purposes.
- 3. Bead spring model is the coarsest representation of a polymer that captures the essential physics.
- 4. The Random Walk has an asymptotic Gaussian distribution for the distance travelled (for large number of steps).
- 5. Entropic spring force is physical model to capture the behaviour of two points on a freely jointed chain separated by a large number of Kuhn lengths.
- 6. The time scales of polymer motion are much large compared to that of the solvent molecules
- 7. Kinetic theory considers distribution function instead of individual particle position and velocities.
- 8. Given the distribution function, various properties can be obtained as its moments.

1.1 Polymeric Molecules

Polymers are substances formed by chemical reactions of simple molecules called monomers which result in multiple copies (usually $\gg O(100)$ in number) of one or more monomers. These super-assemblies of molecules result in the interesting physical properties of the bulk materials formed exclusively or in combination (such as blend or liquid solution) of these substances. The study of flow and processing of polymeric liquids is important for better control and predictability in various applications. This lecture notes set pertains to modelling only the flow related properties, such as viscosity of polymeric liquids.



Figure 1.1: A schematic diagram of a snapshot of linear polymer chain in one of the myriads of configurations. A small flexibility at the bod level is the reason for the macroscopic flexibility.

1.1.1 Structure and Rigidity of Polymers

The microscopic structure of polymers is not unique: It can be

- 1. Linear: the monomers form a single linear chain (monomer connected only to two other monomers)
- 2. Branched: At some points along the chain the monomer are connected to more than two monomers.
- 3. Ring: Linear chain with ends tied together.
- 4. Block co-polymers: more than one type of chemical species act as monomers.

Some schematic 3-D models of polymers can be seen in the book by Bird *et al.* (1987*b*). Owing to the large number of copies of the monomers, even a small flexibility (which is about 3% of the average) at the level of the bond angles between adjacent monomers propagates to a large variations in the bond angles of monomers that are separated by even 10 monomers. Figure 1.1 shows a snapshot of one of the several configurations adopted by a long chain polymer. The important thing is that this configuration is not static, and changes continuously, owing to a finite temperature of the surroundings. This is especially true of a polymer in a solution form where the surrounding solvent molecules are much smaller.

1.2 Models of Polymers

The flexibility of a long chain polymer is accurately quantified in terms of the correlations between bond angles. A small flexibility with two adjacent bond angles implies their directions are highly correlated. This correlation keeps decreasing as the angles are separated by more than one bond. When the distances (in bond lengths) reach a value where the bond angle correlation becomes negligible (compared to the adjacent case), the polymer is said to have attained a fully flexible state. This bond length is given a special name called as the *Kuhn length*. For polymer physics purposes the fundamental quantity of interest is the Kuhn length. At the level of the Kuhn length, the chemical nature of the substance can often be ignored. The degree of macroscopic flexibility of a polymer depends on the number of Kuhn lengths it has. The polymer with higher number of Kuhn lengths is more flexible.

Exercise 1.1 A chemical monomer T requires 10 monomers that lead to a Kuhn length, and another chemical species H requires 100 monomers for a Kuhn length. Which of the following polymers will be more flexible: (a) a polymer p-T made out of 3000 T monomers (b) a polymer p-H made out of 30000 H monomers?

The physical configuration of a polymer can be approximated by various models that reproduce the behaviour at various length scales (Bird *et al.*, 1987*b*). The adjacent bonds can be described by two angles in spherical coordinates: the zenith angle θ and the azimuth ϕ . The zenith angle represents the angle between adjacent bonds, and the azimuth represents the rotations about the zenith. Here we provide the major models of polymers in increasing order of coarseness in the length scales.

- **Rotational Isomeric (RIS) Model** In this model the bond angle with respect to the adjacent one is allowed to take distinct rotational positions (usually about three).
- **Freely Rotating Chain (FRC)** The rotational restriction is removed, and the azimuth can take any value, but the zenith angle is fixed.
- **Worm-Like Chain (WLC)** A continuous version of the freely rotating chain, with vanishing bond lengths.
- **Freely Jointed Chain (FJC)** A sequence of freely rotating chains looses its bond angle correlation after one Kuhn length. When the bond sequence is replaced by a sequence of Kuhn lengths, two adjacent Kuhn lengths have uncorrelated bond angles. They are like rods joined freely without any angular restrictions (both in ϕ and θ). In these models the rod represents a Kuhn length only in the distance. The rods are assumed to be of fixed length and mass less. The mass of the local collection of monomers (equivalent to one Kuhn length) is replaced by a spherical bead at the joints. This bead models the mass and the surface drag of the monomers motion in the surrounding solution. The model is also called as the **bead-rod model** or the **Random-walk model**. The name "random walk" has its origins in the path taken by a drunken person. Fully drunken that (s)he is, each step taken in a direction has no correlation to the previous steps! The FJC is a 3-dimensional random walk.
- Bead Spring Chain This is the most coarse grained version of a polymer model. Just as Kuhn length represents a collection of bonds, a collection of Kuhn lengths is represented by a spring. However, the spring is not a replacement of a fixed distance (like a Kuhn length or a "rod"), but represents a variable distance, with a *certain probability*. This concept fundamental to studying the dynamics of polymers, and will be explained in the following section.

1.2.1 Bead Spring Chain Model

The bead spring chain model of a polymer is the simplest idealisation of a polymer molecule, that captures the essential physics required to simulate polymer dynamics. The simplest realisation of a bead spring model is to consider only one spring and two beads: The Dumbbell Model. We will start by explaining how the dumbbell model is obtained and then later see why more springs need to be introduced to make a chain of springs.

Consider a chain of freely jointed rods (the bead-rod model). This model was obtained by coarse graining several bonds that after a distance (equal to the Kuhn length) lost any correlation with the first bond. If we want to coarse grain the freely jointed rod model, we must ask the question at what distance could we replace a collection of Kuhn lengths by another equivalent length. However, no such single length exists. Owing to the flexibility of the FJC, it is a *continuous distribution of lengths* for a collection of N_k Kuhn lengths. For every N_k rods there is a different distribution. We can ask for the probability that the end to end distance is between **r** and **r** + d**r** for a given number of rods N_k , each of length *a*. This can be worked out for any N_k however, for very large $N_k \gg 1$ the probability has a asymptotic form (Bird *et al.*, 1987*b*)

$$P(\mathbf{r}) \approx \left(\frac{3}{2\pi N_{\rm k} a^2}\right)^{3/2} \,\mathrm{e}^{-3\,r^2/2N_{\rm k} a^2} \tag{1.1}$$

This is a *Gaussian distribution* of the end-to-end distance with zero mean and variance $N_k a^2$. That random-walks have a Gaussian distribution for the distance travelled is a theme that will repeatedly appear in these notes in other contexts as well. The Gaussian distribution of the distances has an important consequence for the mean square end-to-end distance (which is the variance of the distribution) is given by

$$\left\langle r^2 \right\rangle = N_{\rm k} \, a^2 \tag{1.2}$$

If N_k represents the Kuhn steps for the entire polymer, then $N_k \sim M$ where M is the molecular weight of the polymer, and the RMS end to end distance is given by:

$$\sqrt{\langle r^2 \rangle} = \sqrt{N_{\rm k}} \, a \sim \sqrt{M} \, a \tag{1.3}$$

In three dimensions this represents the radius of a sphere within which most of the molecules (in an ensemble) would be in. If the polymer solution is considered as a suspension of "spherical" particles the *radius of these spheres scales only as the* \sqrt{M} : The molecular weight has to be quadrupled to get double the effective radius of the spheres in the suspension.

The end-to-end distance has the maximum probability at r = 0 and decays as the end points are separated. The probability distribution can be seen from an alternate view point in terms of *configurational entropy*. The entropy is related to the logarithm of the possible number of microscopic states for a given macroscopic state. For fixed end points of a chain (fixed end-to-end distance), which is a "macroscopic state", the positions of the intermediate rods denote the "microscopic" states. This number is maximum when the end to end distance is zero. When the end to end distance is equal to the fully stretched length $N_k a$, the number of states is just one, or asymptotically negligible, for $N_k \gg 1$.

This entropic interpretation can be used to provide a further physical simplification. The probability is maximum at r = 0, but it costs some "energy" to move the points away. This

energy can be thought of an interaction energy between the end points. This potential is always attractive, and vanishes at r = 0. Associated with this energy is a force that is zero at r = 0 and increases as the points are separated. Note that this force has its origins in entropy (possible microstates) and is not related to any potential (like Lennard Jones) that has origins in electro-magnetic interactions. This force is specially qualified as *entropic spring force*, to mark this difference. The expression for the force for the Gaussian distribution can be worked out (Bird *et al.*, 1987*b*) to be

$$\mathbf{F}^{c}(\mathbf{Q}) = \frac{3k_{B}T}{N_{k}a^{2}}\mathbf{Q}; \qquad N_{k} \gg 1$$
(1.4)

where **Q** denotes the vector connecting the end-to-end points. This force is linear in the distance—like a force of the Hookean spring, and is often written in shortened form as

$$\mathbf{F}^{c}(\mathbf{Q}) = H \,\mathbf{Q}; \qquad H = \frac{3k_B T}{N_k a^2}$$
(1.5)

Therefore we arrive at an important simplification: *Any two points along the FJC with large* N_k *can therefore approximated as though they are connected by a Hookean spring*. Remember the rods were anyway mass less, so the spring will also be mass less. All the mass of the beads of the intermediate rods can be clubbed together to a larger bead at the end of the spring. A schematic replacement of the bead rod by chain of bead springs is shown in Figure 1.2. If the whole chain is replaced by a single spring we get the two bead one spring or the dumbbell model. The dumbbell model is a widely used model, or the first approximation model of a polymer chain, and captures the important physics: chain flexibility and drag due to solvent. The simple Hookean dumbbell model is not sufficient to capture certain details of polymer dynamics such as finite extension, shear thinning, bounded elongational viscosity, etc. (Doi & Edwards, 1986; Bird et al., 1987b). This requires inclusion of solvent mediated effects such as hydrodynamic interaction, finite extension of the springs, and multiple beads or a bead spring chain. The constitutive equation of solution of Hookean dumbbells (Bird *et al.*, 1987b) is identical to the Oldroyd-B fluid (Bird *et al.*, 1987a) obtained from phenomenological arguments.

So far we were concerned only with the description and modelling of static equilibrium configurations of polymeric molecules. What is of interest is however, how they behave when disturbed by a flow field. This requires a description of the dynamics of the motion of the beads as affected by the flow and other forces.

1.3 On Molecular Simulation of Polymers

The simulation of polymers can be carried out at various levels of coarse graining.

1. Molecular dynamics with actual polymer chain: At the finest level, a solution of polymers is simply modelled as a large molecule, with monomer-monomer, bond flexibility, and monomer-solvent interactions specified. Let us estimate the numbers that may be required. To simulate one polymer in solution with *N* monomers, we need to consider at least $O(N^3)$ molecules: Assuming the monomers and solvent molecules are



Figure 1.2: A schematic diagram of the replacement of sequence of rods by beads and springs.

of the same size, we need a box of edge length equivalent to at least O(N) molecules, to accommodate the fully stretched polymer. If periodic boundaries are to be used, then to minimise neighbour interactions the box polymer inside the simulation box must be well inside. This would lead to a box of edge O(10N) and a total simulation of $O(1000N^3)$. This leaves simulations possible only for very small number of monomers, say 10!

2. Molecular dynamics with coarse grained models. If we use one of the coarse grained models, we could realistically increase the monomer count, by considering O(10) beads (each bead may represent say 100 monomers). Such simulations have been done, but is severely restrictive in obtaining useful new predictions for polymer dynamics.

Both the above method involving direct molecular dynamics are wrought with difficulties involving the simulation of a huge number of solvent molecules. This can be overcome by simplifying the problem. We first estimate the timescales of motion of the polymer and the solvent molecules. If the polymer can be considered as a suspension of spheres, then the radius of an average sphere is given by Equation (1.3) as $R \sim a \sqrt{\frac{M}{m}}$, where M is the molar mass of the polymer and m is the molar mass of the monomer (The factor \sqrt{m} appears in the denominator for dimensional consistency of $\sqrt{N_k}$). If we assume the monomer is roughly the same size as the solvent molecule then solvent molecule size $\sim a$ and weight $\sim m$. For a liquid (closely packed molecules), the time scales of motion can be taken to be the period to cover distances of the size of the molecule. The ratio of the time scales is therefore

$$\frac{T}{t} = \frac{R/V}{a/v} \tag{1.6}$$

where *V* and *v* are the characteristic velocities (one estimate is the RMS velocity which is related to the temperature). Since both the molecules are at the same temperature, the ratios

of the RMS velocities scales as

$$\frac{v}{V} \sim \sqrt{\frac{M}{m}} \tag{1.7}$$

since $mv^2 \sim k_B T$. Substituting this in Equation (1.6) we get

$$\frac{T}{t} = \frac{R}{a} \frac{v}{V} = \frac{M}{m}$$
(1.8)

Polymer molecular weights are typically 1000 times the monomer molecular weight, this results in the timescales also being of the same order. Such a wide variation in time scales usually need not be resolved.

An alternate method is to consider the simulation only of the polymer, and approximating the effects of solvent suitably. If the degrees of freedom of solvent motion are ignored, then their effect has to be considered in some probabilistic way. That is instead of studying positions and momentum of the individual molecules, a function is defined that gives the distribution of velocities around a given spatial point. This is the subject of kinetic theory. Just as we have kinetic theory of liquids and gases, we can derive a kinetic theory of polymeric liquids as well (Bird *et al.*, 1987*b*).

1.4 Kinetic Theory of Polymeric Fluids

Kinetic theory of polymeric liquids expresses the dynamics of a distribution function i.e., evolution of the distribution function, because of the action of forces. In kinetic theory, the distribution function is written as a product of configurational and velocity distribution functions. From the models of polymers we have seen that the positions of the beads (either of the FJC or a bead spring chain) represent the configuration of the polymer. The derivation of this equation is given in the book by Bird *et al.* (1987*a*) and Doi & Edwards (1986). We only provide some physical insights to interpretation of some of the terms.

The general equation for a polymer with a chain of beads tied together by springs is called as the Fokker-Planck equation or "diffusion equation" for the configuration distribution function ψ , which is defined so that $\psi d\mathbf{r}$ is the probability to find the position vector of the first bead within $d\mathbf{r}_1$ around \mathbf{r}_1 , second bead at $d\mathbf{r}_2$ around \mathbf{r}_2 , and so on.

$$\frac{\partial \psi}{\partial t} = -\sum_{\mu=1}^{N} \frac{\partial}{\partial \mathbf{r}_{\mu}} \cdot \left[\boldsymbol{\kappa} \cdot \mathbf{r}_{\mu} + \frac{1}{\zeta} \sum_{\nu=1}^{N} \boldsymbol{\Gamma}_{\mu\nu} \cdot \left(\mathbf{F}_{\nu}^{s} + \mathbf{F}_{\nu}^{int} \right) \right] \psi + \frac{k_{B} T}{\zeta} \sum_{\mu,\nu=1}^{N} \frac{\partial}{\partial \mathbf{r}_{\mu}} \cdot \boldsymbol{\Gamma}_{\mu\nu} \cdot \frac{\partial \psi}{\partial \mathbf{r}_{\nu}}.$$
 (1.9)

Here, κ is a time-dependent, homogeneous, velocity gradient tensor of the surrounding fluid motion, ζ is the hydrodynamic friction (drag) coefficient associated with the bead, $k_B T$ is thermal energy and $\Gamma_{\mu\nu}$ is the hydrodynamic interaction tensor, representing the effect of the motion of a bead μ on another bead ν through the disturbances carried by the surrounding fluid. \mathbf{F}_{ν}^{s} is the entropic spring force on bead ν due to adjacent beads, $\mathbf{F}_{\nu}^{s} = \mathbf{F}^{c}(\mathbf{Q}_{\nu}) - \mathbf{F}^{c}(\mathbf{Q}_{\nu-1})$, where $\mathbf{F}^{c}(\mathbf{Q}_{\nu-1})$ is the force between the beads $\nu - 1$ and ν , acting in the direction of the connector vector between the two beads $\mathbf{Q}_{\nu} = \mathbf{r}_{\nu} - \mathbf{r}_{\nu-1}$. The quantity \mathbf{F}_{μ}^{int} is the sum total of the remaining interaction forces on bead μ due to all other beads,

 $\mathbf{F}_{\mu}^{\text{int}} = \sum_{\nu=1}^{N} \mathbf{F}^{\text{e}}(\mathbf{r}_{\mu\nu})$, where \mathbf{F}^{e} is the binary force acting along the vector $\mathbf{r}_{\mu\nu} = \mathbf{r}_{\nu} - \mathbf{r}_{\mu}$ connecting beads μ and ν .

In Equation (1.9), the hydrodynamic interaction tensor $\Gamma_{\mu\nu}$ is written in general as

$$\Gamma_{\mu\nu} = \delta_{\mu\nu} \,\delta + \zeta \,\Omega_{\mu\nu},\tag{1.10}$$

where $\Omega_{\mu\nu}$, for $\mu \neq \nu$, represents the actual interaction matrix, and δ and $\delta_{\mu\nu}$ represent a unit tensor and a Kronecker delta, respectively. For theoretical analyses, it is usually convenient to use the Oseen-Burgers function for the tensor, $\Omega_{\mu\nu} = \Omega(\mathbf{r}_{\mu\nu})$, where the functional form is given by Öttinger (1996),

$$\Omega(\mathbf{r}) = \frac{1}{8\pi\eta_{s}r} \left(\delta + \frac{\mathbf{rr}}{r^{2}} \right), \tag{1.11}$$

where η_s is the solvent viscosity.

Some physical insights into the Fokker-Planck equation are in order: The LHS is the time rate of change of the distribution function and the RHS represents various effects that either increase or decrease it. The κ term represents the effect of relative solvent motion, any non-zero velocity gradient can modify the bead position. The second term in the square brackets is the change in the bead position due to external forces such as the entropic spring force, electro-magnetic interaction forces between the beads, and the hydrodynamic interaction force. The last term is called as the diffusion term, or the Brownian term, and represents the effect of ignored solvent degrees of freedom.

1.4.1 Simplified Equations

Equation (1.9) represents the complete diffusion equation. For an introductory course, we consider only a simple form of the equation, applicable for the so called Rouse Dumbbell. Rouse model of polymers is a model in which there is no hydrodynamic interactions. This implies $\Gamma_{\mu\nu} = \delta_{\mu\nu} \delta$. For a dumbbell model, the particle position vectors \mathbf{r}_1 and \mathbf{r}_2 . The set of two Fokker-Planck equations can be reduced to two equivalent equations for the variables $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$ for the centre of mass motion and $\mathbf{Q} = (\mathbf{r}_2 - \mathbf{r}_1)$ for the connector vector (Öttinger, 1996). The Fokker-Planck equation for the connector vector is

$$\frac{\partial \psi}{\partial t} = -\frac{\partial}{\partial \mathbf{Q}} (\boldsymbol{\kappa} \cdot \mathbf{Q} \,\psi) + \frac{2H}{\zeta} \frac{\partial \mathbf{Q} \,\psi}{\partial \mathbf{Q}} + \frac{2k_B T}{\zeta} \frac{\partial \psi}{\partial \mathbf{Q}^2} \tag{1.12}$$

and for the centre of mass is

$$\frac{\partial \psi}{\partial t} = -\frac{\partial}{\partial \mathbf{R}} (\boldsymbol{\kappa} \cdot \mathbf{R} \,\psi) + \frac{k_B T}{\zeta} \frac{\partial \psi}{\partial \mathbf{R}^2} \tag{1.13}$$

The centre of mass motion corresponds to the Brownian motion of the polymer (considered as a sphere). Here, the factor $k_B T/\zeta$ is called as the diffusivity and is denoted by $\mathcal{D} = k_B T/\zeta$.

Once the distribution function is known the all other average properties of the polymer can be evaluated by computing appropriate moments of the distribution function. One of the main object of interest is the stress tensor, which makes the connection to continuum fluid mechanics by providing an appropriate microscopic constitutive relationship.

1.5 Stresses in a Polymeric fluid

A simple calculation of the viscosity of a solution of polymers is to model the polymers as dumbbells, and compute the total stress tensor. The stress tensor has the usual components from the solvent. Apart from this there is an additional component from the polymers. The total stress tensor is given by two contributions from the solvent (s) and polymers (p)

$$\tau_{ij} = \tau_{ij}^{\rm s} + \tau_{ij}^{\rm p} \tag{1.14}$$

When the polymer intersects a surface (on which the stress has to be computed) it leads to a contribution to the surface stress, this contribution can be derived (Öttinger, 1996; Bird *et al.*, 1987*b*), and we use the Kramer's expression for the polymeric stress which is written as

$$\tau_{ij}^{\rm p} = n_{\rm p} k_B T \,\delta_{ij} + n_{\rm p} H \left\langle Q_i \, Q_j \right\rangle \tag{1.15}$$

where $\langle . \rangle$ denotes an ensemble average of the connector vectors, and n_p is the polymer number density (number per unit volume). The shear viscosity of the polymer solution is defined as

$$\eta_{\rm p} \equiv \frac{\tau^{\rm p}}{\dot{\gamma}} \tag{1.16}$$

where τ^{p} is the non-zero component stress tensor. For the planar shear flow given by Equation (3.8), the viscosity can be written from Equation (1.15) as

$$\eta_{\rm p} = \frac{\tau_{12}^{\rm p}}{\dot{\gamma}} = \frac{n_{\rm p} H}{\dot{\gamma}} \langle Q_1 Q_2 \rangle \tag{1.17}$$

Chapter 2

Stochastic Processes

Concepts You Must Know

- 1. There are two ways to solve stochastic problems:
 - (a) Fokker-Planck equation for probability density function ψ
 - (b) Equivalent stochastic differential equation (SDE) for the random variable
- 2. Evolution of Probability density is deterministic, whereas that for the random variable is stochastic.
- 3. Fokker-Planck equation and the SDE are inter-convertible.
- 4. Wiener process is a stochastic evolution caused by Gaussian (white noise) random variable.
- 5. Infinitesimal increments of a Wiener process are proportional to \sqrt{dt} .

In this chapter, as before, we will follow a top-to-down approach. The conventional mathematical way of introducing the topics would be to start with definitions, axioms and build theorems (readers who are convenient with this approach may refer Öttinger (1996) directly). Instead, we take an approach with an aim to solve the polymer suspension problem, and acquire only minimal knowledge step by step (often taking information "as given" in other references). This is like browsing an encyclopedia, and picking up only minimal relevant materials alongside. This may not provide the rigour, but is one way to solve a problem. The stress is more on the physical aspects of the problem and less on the mathematical rigour.

2.1 Diffusion Equation and SDE

One dimensional Brownian motion is governed by the diffusion equation for the probability density function ψ (which can be seen from Equation (1.13) by considering a stationary solvent)

$$\frac{\partial \psi}{\partial t} = \mathcal{D} \frac{\partial^2 \psi}{\partial x^2} \tag{2.1}$$

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where $\psi = \psi(x, t)$ is the **probability density** function, such that at a time t, $\psi(x) dx$ is the probability of finding a value in the interval x and x + dx. ψ has the units of 1/x (therefore called a density) so that the probability is dimensionless. The aim is to solve this equation for $\psi(x, t)$. As such this particular equation is directly solvable. However, in general the complete diffusion equation for polymer configurations is non-linear. There are numerical schemes to discretise the equation in ψ and solve it as a regular partial differential equation. However, here we will show an alternate method which converts the equation to an equivalent **stochastic differential equation**, (SDE) and solve it instead.

Stochastic differential equations do not yield the values of ψ directly. Instead a random variable is associated with ψ , and is computed by manipulations on other random variables generated from a known distribution function. To illustrate, the solution to the stochastic differential corresponding to the diffusion equation Equation (2.1) yields

$$X = N(0, 2\mathcal{D}t) \tag{2.2}$$

where *X* is the random variable which is associated with the distribution function ψ and *N* is a Gaussian distributed random variable with zero mean and variance equal to $2\mathcal{D}t$. Recall from basic statistics that associated with a random variable is a probability density function. Instead of solving for ψ , we solve for the random variable, *X*. Being random, one realisation will not yield a sufficient information about ψ , and several realisations of Equation (2.2) are required. Algorithmically speaking, several random numbers *N* will have to be generated, and the resultant *X* computed and "binned" over the possible range to obtain a discretised distribution function ψ .

Consider the simple diffusion equation Equation (2.1), for which there is a closed form solution

$$\psi(x,t) = \frac{1}{\sqrt{4\pi \mathcal{D}t}} e^{-\frac{x^2}{4\mathcal{D}t}}$$
(2.3)

which can be verified by substitution.

Exercise 2.1 Using a Gaussian random number generator with zero mean and unit variance, find *X* according to Equation (2.2), bin it in regular intervals and plot the function $\psi(x, t)$ for t = 1/4, 1, 4, and $\mathcal{D} = 1$.

[Hint: The Normal linear transform theorem should be used to transform between normally distributed random variables

$$\alpha + \beta N(m, \sigma^2) = N(\alpha + \beta m, \beta \sigma^2)$$
(2.4)

That is a linearly shifted and scaled normal variable (on the LHS) results in a normal variable with suitably transformed mean and variance (on the RHS) (Lemons, 2002)].

Exercise 2.2 Plot the analytical expression for $\psi(x, t)$ from Equation (2.3) along with the numerically determined function in Exercise 2.1.

In 1D-Brownian motion of a particle, *x* is a continuous variable that represents the position of the particle. As the particle is "pushed around" by the surrounding molecules, the

position *x* evolves continuously in time. (Note that in this problem both the spatial coordinate and time are continuous variables. There can be processes in which either one or both are discrete, eg: Number of people watching a particular annual event, average grade in an examination). Therefore there is a dynamics associated with it. Dynamics in physics are captured by differential equations, which describe the time variation of a quantity. Most of the problems we have been introduced in dynamics is that of a deterministic process, or "sure" processes, with Brownian motion, we need to deal with stochastic processes.

2.2 Deterministic and Stochastic Processes

A simple first order reaction has the dynamics for the concentration of a species

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -k\,C\tag{2.5}$$

This is a classical example of exponential decay in the dynamics. The concentration equation at any time can be written in a discrete manner as

$$C(t + dt) - C(t) = -k C(t) dt$$
(2.6)

It is *deterministic* since for a given initial condition, this equation will always yield identical variation in the evolution of the concentration C(t). The derivative exists and is unique and therefore the function is *smooth*. The process C(t) is also one without memory. That is the change in concentration is a function only of the instantaneous concentration at t, not the earlier times. Such processes are in general called as *Markov* processes, (after a Russian Mathematician by that name).

The evolution of a stochastic processes on the other hand are not predictable. There is always a probability associated with its evolution. At a time *t* we can only say with a certain probability that the process will evolve to another state. At first it might seem that stochastic processes are rare. But strictly speaking all processes are stochastic! To the extent we know, the time evolution of the quantum states of all matter are probabilistic (or stochastic). A differential equation expressing the evolution of a stochastic process is qualified by that name, and called SDE in short. With stochastic processes, are associated random variables and a corresponding probability density function. We denote random variables by a capital letter, eg., *X*. Stochastic processes, like the deterministic process is written in a different memory. The dynamical equation for a Markov stochastic process is written in a different manner

$$dX = X(t + dt) - X(t) = F[X(t), dt]$$
(2.7)

F[] is called as the Markov Propagator function that propagates the value of *X* from *X*(*t*) to X(t + dt). Note that in the RHS d*t* appears in the function *F*[], and does not simply multiply it linearly. This is a *special feature* of stochastic processes. There two main reasons for this: (1) For a stochastic process the derivative $\frac{dX}{dt}$ is not defined, so we cannot write d*t* below d*X*, (2) depending on the process, RHS can be a non-linear function of d*t*. We will see the physical interpretation of this soon.

The propagator function *F* contains all the physics. We can guess the SDE, i.e., *F* for a Brownian particle from the known solution to ψ from Equation (2.3). Consider a particle that is at the origin at *t* = 0. The probability that it takes a sure value *x* at a time d*t* is given by

$$\psi(x, \mathrm{d}t) = \frac{1}{\sqrt{4\pi \mathcal{D}\,\mathrm{d}t}} \mathrm{e}^{-\frac{x^2}{4\mathcal{D}\,\mathrm{d}t}} \tag{2.8}$$

therefore we can write X(dt) in terms of a random variable which is normally distributed (Gaussian) with zero mean and variance 2 D dt.

$$X(\mathrm{d}t) = \sqrt{2\,\mathcal{D}\,\mathrm{d}t}\,N(0,1) \tag{2.9}$$

where we have used Equation (2.1). More generally, if the initial position were not the origin, but a random variable itself, then the above jump at dt would be with respect to the initial position

$$X(dt) = X(0) + \sqrt{2}\mathcal{D} dt N(0, 1)$$
(2.10)

or we can write a stochastic differential equation for X(t) as

$$X(dt) - X(0) = \sqrt{2 \mathcal{D}} dt N(0, 1)$$
(2.11)

We wrote this equation from the known solution to ψ , but we find a \sqrt{dt} on the RHS. *Gaussian distributions always yield a* \sqrt{dt} *differential in the SDE*. With the definition

$$dW = \sqrt{dt} N(0, 1)$$
 (2.12)

Equation (2.11) is also written as

$$dX = \sqrt{2\mathcal{D}} \, \mathrm{d}W \tag{2.13}$$

where W(t) is a Gaussian random Markov process. This special stochastic process W(t) is *fundamental to all Brownian motion*, and is given a special name Wiener process. W(t) has the following properties

- 1. W(0) = 0
- 2. The increment W(t) W(s) is normally distributed with zero mean

$$W(t) - W(s) = \sqrt{t - s} N(0, 1)$$

3. *W*(*t*) is a Markov process. Finite increments at two different times are not correlated (i.e. they are independent).

Owing to the random nature the Wiener process is continuous but nowhere differentiable, i.e. the function is not smooth.

Exercise 2.3 Generate a discrete Wiener process W(t) in the interval t = 0, 1 with 500 increments. One such process is also called as a trajectory of W, as it is related to the trajectory of a Brownian particle. Plot five trajectories (with different random number sequences). Compute the average trajectory w(t) at a few points along t and the standard error about the mean, by considering 1000 trajectories.

A more general stochastic differential equation has the deterministic term included

$$dX = A(X) dt + B(X) dW$$
(2.14)

where *A* and *B* are random processes by virtue of being an arbitrary function of the random process *X*. The deterministic coefficient *A*(*X*) is also called as the *drift* term, and the stochastic coefficient is known as the *diffusion* term. We now provide some physical interpretations of this equation. Normally in differential calculus, we would not have terms in an equation that are different orders of magnitude in a small parameter. In this case the small parameter is *dt* and we have a $dW \sim O(\sqrt{dt})$ term appearing along with terms of *O*(*dt*). As noted before this is a special feature of stochastic differential equations. What it physically means is that the increments *dW* which are Gaussian distributed, could be smaller or larger than \sqrt{dt} , but in effect they all add up to provide a term of the same order as *dt* (Lemons, 2002).

2.3 Converting a General Diffusion Equation to an SDE

In the last section we used the known solution to the probability density function to arrive at the SDE for the random variable. Here we will sketch the steps to obtain the equivalent statements of deterministic dynamics of the probability density function and the stochastic differential equation. Consider the general dynamic equation Equation (2.14) for the stochastic process. We will derive the corresponding diffusion equation. This is required because we would like to develop a stochastic differential equation for the diffusion equation of the polymer bead positions.

Consider any function g(x) which is continuous and smooth (Note we have used small x to denote a sure variable). Using this function, we transform the stochastic process X to another stochastic process Y = g(X) (Refer Theorem 3.16, Itô's Formula in Öttinger, 1996, for details). Then we have the following identity (see Appendix B in Lemons, 2002)

$$\left\langle \frac{\mathrm{d}Y}{\mathrm{d}t} \right\rangle = \int \mathrm{d}x \ g \ \frac{\partial\psi}{\partial t} \tag{2.15}$$

We need to evaluate the expression in LHS in terms of the stochastic differential dX. When there is a transformation from one random variable X to another random variable Y = g(X), the usual chain rules of deterministic calculus do not apply. The stochastic differential dYneeds special treatment. A simplistic way to arrive at the differential is to start with the usual chain rule of deterministic calculus

$$dY = \frac{\partial g}{\partial x} dX + \frac{1}{2} \frac{\partial^2 g}{\partial x^2} dX^2$$
(2.16)

where we retain terms up to dX^2 . Substituting Equation (2.14) we get for dX^2

$$dX^{2} = A^{2} dt^{2} + B^{2} dW^{2} + 2A B dt dW$$
(2.17)

In stochastic differentials (following the Itô calculus) we use the following identities (see Gardiner, 1985, Section 4.2.5)

$$\mathrm{d}W^2 = \mathrm{d}t \tag{2.18}$$

$$dW^{2+n} = 0; \quad n > 0 \tag{2.19}$$

The first of these equations can be seen in an average sense from Equation (2.12): $\langle dW^2 \rangle = dt$. With these identities we can write Equation (2.20) discarding terms smaller than dt as

$$dY = \left(A\frac{\partial g}{\partial x} + \frac{B^2}{2}\frac{\partial^2 g}{\partial x^2}\right)dt + B\frac{\partial g}{\partial x}dW$$
(2.20)

Exercise 2.4 Consider the SDE for the stochastic process *X* given by

$$\mathrm{d}X = (\alpha - X)\,\mathrm{d}t + \beta\,\sqrt{X}\,\mathrm{d}W$$

Verify the chain rule for $Y = \sqrt{X}$ from Equation (2.20) by plotting the function $Y = \sqrt{|X|}$ along side the stochastic process obtained from Equation (2.20) (Higham, 2001).

Note that as in Equation (2.14), the term with $dW \sim \sqrt{dt}$ is retained. Equation (2.20) is the stochastic differential equation for a transformed variable Y = g(x, t) with modified chain rule, in Itô calculus. Substituting Equation (2.20) in the LHS of Equation (2.21) we get

$$\left\langle \frac{\mathrm{d}Y}{\mathrm{d}t} \right\rangle = \left\langle A \frac{\partial g}{\partial x} + \frac{B^2}{2} \frac{\partial^2 g}{\partial x^2} \right\rangle + \left\langle B \frac{\partial g}{\partial x} \frac{1}{\sqrt{\mathrm{d}t}} N(0,1) \right\rangle \tag{2.21}$$

The last term is zero on average since $\langle BN \rangle = \langle B \rangle \langle N \rangle = 0$ (Lemons, 2002). Each of the other terms can be written by integration by parts as

$$\left\langle A \frac{\partial g}{\partial x} \right\rangle = \int dx \,\psi \, A \frac{\partial g}{\partial x}$$

$$= A \psi \, g \Big|_{-\infty}^{\infty} - \int dx \, \frac{\partial A \psi}{\partial x} \, g$$

$$= -\int dx \, g \, \frac{\partial A \psi}{\partial x}$$

$$(2.22)$$

where we have assumed that the probability density function ψ vanishes at the boundaries, and

$$\left\langle B^2 \frac{\partial^2 g}{\partial x^2} \right\rangle = \int dx \,\psi \, B^2 \frac{\partial^2 g}{\partial x^2}$$

$$= \int dx \,g \, \frac{\partial^2 B^2 \psi}{\partial x^2}$$
(2.23)

where we have assumed that in addition to ψ the first derivative $\frac{\partial \psi}{\partial x} \rightarrow 0$ at the boundaries. Substituting these results in Equation (2.21) and in turn in Equation (2.15), we get

$$\int dx \ g\left(-\frac{\partial A\psi}{\partial x} + \frac{1}{2}\frac{\partial^2 B^2\psi}{\partial x^2}\right) = \int dx \ g \ \frac{\partial \psi}{\partial t}$$
(2.24)

If this equation is to be valid for any function g(x) then the rest of the integrands must be equal, which gives

$$\frac{\partial \psi}{\partial t} = -\frac{\partial A \psi}{\partial x} + \frac{1}{2} \frac{\partial^2 B^2 \psi}{\partial x^2}$$
(2.25)

or

$$\frac{\partial\psi}{\partial t} + \frac{\partial A\psi}{\partial x} = \frac{1}{2} \frac{\partial^2 B^2 \psi}{\partial x^2}$$
(2.26)

These equations are the generalised diffusion equations, which are equivalent to the stochastic differential equation Equation (2.14) of the Itô form. They are also called by different names in different literature: *Fokker-Planck* equation or *Smoluchowski* equation. Given either of Equation (2.14) or Equation (2.26) the other form can now be easily written. In the case of polymer dynamics, the general diffusion equation for a dumbbell configuration in 1-D follows Equation (2.26). Equation (2.14) is not unique, it represents the formula in the so called *Itô calculus*. An alternative is the *Stratonovich calculus* formula (Higham, 2001; Gardiner, 1985; Öttinger, 1996).

Exercise 2.5 A strongly damped Brownian particle moving in a constant gravitational field has the following Fokker-Planck equation

$$\frac{\partial \psi}{\partial t} = \frac{\partial g \psi}{\partial x} + \frac{D}{2} \frac{\partial^2 \psi}{\partial x^2}$$

Find the equivalent SDE for the random variable *X*.

Exercise 2.6 Ornstein-Uhlenbeck process represents the evolution of the velocity of an Brownian particle and is given by the Langevin equation

$$\mathrm{d}V = -\gamma \, V \, \mathrm{d}t + \sqrt{D} \, \mathrm{d}W$$

Find the equivalent Fokker-Planck equation for the probability density function $\psi(v)$.

2.3.1 Motion of a Polymer Chain

The diffusion equation for a bead spring chain model of a polymer can be written in indicial notation (we adopt this here as it is easier to code and the manipulations of the indices in the computer program are clear) with the following conversions

Greek indices: μ , ν ,... = index for beads Roman indices: i, j,... = index for Cartesian coordinates Repeated indices \Rightarrow Sum over all possible values with a contraction (dot product) Free indices \Rightarrow number denotes order of the tensor $\mathbf{r}_{\mu} = r_{\mu i}$ $\mathbf{F}_{\mu} = F_{\mu i}$ $\mathbf{\kappa} = \kappa_{i j}$

$$\kappa = \kappa_{ij}$$

$$\Gamma_{\mu\nu} = \Gamma_{\mu i\nu j}$$
(2.27)

The bead spring model from Equation (1.9) in bold face notation with $\mathbf{F} = \mathbf{F}^{s} + \mathbf{F}^{int}$,

$$\frac{\partial \psi}{\partial t} = -\sum_{\mu=1}^{N} \frac{\partial}{\partial \mathbf{r}_{\mu}} \cdot \left[\boldsymbol{\kappa} \cdot \mathbf{r}_{\mu} + \frac{1}{\zeta} \sum_{\nu=1}^{N} \boldsymbol{\Gamma}_{\mu\nu} \cdot \mathbf{F}_{\nu} \right] \psi + \frac{k_{B} T}{\zeta} \sum_{\mu,\nu=1}^{N} \frac{\partial}{\partial \mathbf{r}_{\mu}} \cdot \boldsymbol{\Gamma}_{\mu\nu} \cdot \frac{\partial \psi}{\partial \mathbf{r}_{\nu}}.$$
 (1.9)

is written with the indicial notation with the help of Equations (2.27)

$$\frac{\partial \psi}{\partial t} = -\frac{\partial}{\partial r_{\mu i}} \left[\kappa_{ij} r_{\mu j} + \frac{1}{\zeta} \Gamma_{\mu i \nu j} F_{\nu j} \right] \psi + \frac{k_B T}{\zeta} \frac{\partial}{\partial r_{\mu i}} \Gamma_{\mu i \nu j} \frac{\partial \psi}{\partial r_{\nu j}}.$$
(2.28)

The SDE equivalent to the above Fokker-Plack equation can be written with the help of Equations (2.14) and (2.26) for the position of each of the beads in 3-D as

$$dr_{\mu i} = \left[\kappa_{ij} r_{\mu j} + \frac{1}{\zeta} \Gamma_{\mu i \nu j} F_{\nu j} - \frac{k_B T}{\zeta} \frac{\partial \Gamma_{\mu i \nu j}}{\partial r_{\nu j}}\right] dt + \sqrt{\frac{2k_B T}{\zeta}} B_{\mu i \pi k} dW_{\pi k}$$
(2.29)

where the diffusion term coefficient is given by (Öttinger, 1996, Sections 3.3.3 and 4.2.1)

$$B_{\mu i \pi k} B_{\nu j \pi k} = \Gamma_{\mu i \nu j} \tag{2.30}$$

which is equivalent of the one dimensional single particle (bead) case of $B^2 = \Gamma$. In bold face notation $B_{\mu i \pi k} B_{\nu j \pi k} \Rightarrow \sum_{\pi} \mathbf{B}_{\mu \pi} \cdot \mathbf{B}_{\nu \pi}^{T}$. The term $\partial \Gamma_{\mu i \nu j} / \partial r_{\nu j}$ appears in Equation (2.28) because of the place where Γ appears in Equation (1.9) (in between two partial derivatives $\partial/\partial r$), and requires suitable manipulation to render it in the form of Equation (2.25). In the case of incompressible solvent this is usually zero, resulting in the SDE for the bead spring chain as

$$dr_{\mu i} = \left[\kappa_{ij} r_{\mu j} + \frac{1}{\zeta} \Gamma_{\mu i \nu j} F_{\nu j}\right] dt + \sqrt{\frac{2k_B T}{\zeta}} B_{\mu i \pi k} dW_{\pi k}$$
(2.31)

The numerical algorithm to solve this equation will be discussed in the next chapter.

Chapter 3

Brownian Dynamics Simulation

Concepts You Must Know

1. Euler-Maruyama method for and SDE is like the Euler method for an ODE.

2. Time step convergence is essential in first order methods.

In this chapter we are concerned with the solution of the stochastic differential equation. The SDE that concerns most of polymer dynamics is very much like a linear first order ordinary differential equation, except for the stochastic term. In this course we will only consider the simplest numerical solution, which is like the Euler method for ODEs.

3.1 Euler-Maruyama Integration

The SDE in Equation (2.14)

$$dX = A(X) dt + B(X) dW$$
(2.14)

is very much like a first order ODE. If B = 0, this reduces to

$$\frac{\mathrm{d}X}{\mathrm{d}t} = A(X) \tag{3.1}$$

The simplest method to solve this as an initial value problem given X(0), is to use the Euler method

$$X_{t+\Delta t} = X_t + A(X_t) \,\Delta t \tag{3.2}$$

A similar numerical algorithm for Equation (2.14) is called as the Euler-Maruyama method:

$$X_{t+\Delta t} = X_t + A(X_t)\,\Delta t + B(X_t)\,\Delta W \tag{3.3}$$

where the increments ΔW are not constant linear increments, but is a random variable of the Wiener process, as in Equation (2.12)

$$\Delta W = \sqrt{\Delta t} N(0, 1) \tag{3.4}$$

A simple example for which the analytical solution to the SDE is known (Gardiner, 1985, see Multiplicative noise solution in) is shown in the following exercise

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Exercise 3.1 Integrate the SDE

 $dX = \lambda X dt + \mu X dW$

from t = 0 to t = 1, with X(0) = 0, $\lambda = 2$, and $\mu = 1$. and validate it against the analytical result (Higham, 2001)

$$X(t) = X(0) \exp\left[\left(\lambda - \frac{1}{2}\mu^2\right)t + \mu W(t)\right]$$

3.2 Convergence of Euler-Maruyama Method

In all numerical methods involving discretisation, the solution is sensitive to the discretisation length or step. In the present case it is the discrete time step Δt . The desired numerical result has to be obtained as far as possible for small Δt . Often it is difficult to carry out simulations for small Δt owing to computational restrictions. Accurate solutions can however obtained by carrying out simulations at some plausible values Δt , that are easily realisable. The results at these "large" Δt are extrapolated to the limit $\Delta t \rightarrow 0$ to obtain a solution that is independent of Δt . This is often guaranteed in a numerical method as the errors behave as

$$\epsilon \equiv \frac{X - X_{\text{true}}}{X_{\text{true}}} = O\left(\Delta t^n\right) \tag{3.5}$$

which implies

$$\lim_{\Delta t \to 0} \frac{\epsilon}{\Delta t^n} = C \quad \text{a constant } O(1) \tag{3.6}$$

This implies the errors ϵ behaves as a simple polynomial for small Δt (close to zero). But what is the value of a small Δt and what is large is not known before hand. Only a trial and error and plotting the errors as a function Δt will show.

3.3 Rouse Polymer Dumbbell

Before we take up the simulation of polymers, we derive the basic equations (SDE and analysis tools) for polymers. We will study only a simple case, reducing the problem to bare minimum in polymeric flows. As in Chapter 1 we will make the following simplifications

- 1. Two bead and a spring model
- 2. Hookean (linear) force spring
- 3. No interactions between the beads (hydrodynamic, excluded volume, or electro-magnetic)

This simplifies the problem leaving the bare minimum physical description: an extensible configuration (spring) that is subjected to the drag force of the solvent flow (through the beads). The stochastic differential equation for the bead positions can be simplified to two equivalent equations: one for the centre of mass (sum of the equations of the beads) and one for the vector connecting the two bead centres (difference of the two bead equations). The

centre of mass motion is simply a simple Brownian motion, a Wiener process. The SDE for the connector vector can be obtained from Equation (1.12)

$$dQ_i = \left[\kappa_{ij} Q_j - \frac{2H}{\zeta} Q_i\right] dt + \sqrt{\frac{4k_B T}{\zeta}} dW_i$$
(3.7)

Here, $Q_i = r_{2i} - r_{1i}$ is the connector vector, H is the Hookean spring constant, ζ friction (drag) coefficient of the bead with $\zeta = 6\pi \eta_s a$ for a bead of radius a, $\kappa_{ij} = \partial_j u_i$ is the solvent mean velocity gradient tensor (which contains the information of the mean velocity field surrounding a bead). For planar shear flow $u_x = \dot{\gamma} y$; $u_y = u_z = 0$. this gives

$$\kappa_{ij} = \frac{\partial u_i}{\partial x_j} = \dot{\gamma} \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$
(3.8)

It is often convenient to simulate the dimensionless SDE, leaving all dimensional calculations post-simulations. We adopt the standard scales for length and time as given in Bird *et al.* (1987*b*), which comes out naturally from Equation (3.7). Let $l_{\rm H}$ be the length scale and $\lambda_{\rm H}$ be the time scale, then the terms in Equation (3.7) scale as (see the term below curly brackets)

$$\underbrace{\mathrm{d}Q_{i}}_{l_{\mathrm{H}}} = \left[\underbrace{\kappa_{ij}Q_{j}}_{l_{\mathrm{H}}/\lambda_{\mathrm{H}}} - \frac{2H}{\zeta}Q_{i}}_{(2H/\zeta)l_{\mathrm{H}}}\right]\underbrace{\mathrm{d}t}_{\lambda_{\mathrm{H}}} + \underbrace{\sqrt{\frac{4k_{B}T}{\zeta}}\,\mathrm{d}W_{i}}_{(4k_{B}T/\zeta)\sqrt{\lambda_{\mathrm{H}}}}$$
(3.7)

Taking $l_{\rm H} = \sqrt{k_B T/H}$ and $\lambda_{\rm H} = \zeta/4H$, we get the dimensionless form of the stochastic differential equation for the Rouse dumbbell

$$dQ_{i}^{*} = \left[\kappa_{ij}^{*}Q_{j}^{*} - \frac{Q_{i}^{*}}{2}\right]dt^{*} + dW_{i}^{*}$$
(3.9)

where for planar shear flow $\kappa_{12}^* = \dot{\gamma}^*$. One of the common quantities of interest of calculation is the viscosity of the polymer solution. The expression for viscosity can be written from Equation (1.17) in terms of dimensionless variables as

$$\eta_{\rm p} = \frac{n_{\rm p} H}{1/\lambda_{\rm H}} l_{\rm H}^2 \frac{\langle Q_1^* Q_2^* \rangle}{\dot{\gamma}^*}$$

$$= n_{\rm p} k_B T \lambda_{\rm H} \frac{\langle Q_1^* Q_2^* \rangle}{\dot{\gamma}^*}$$
(3.10)

Therefore the appropriate dimensional scale for the polymer viscosity is $n_p k_B T \lambda_H$, which gives the dimensionless polymer viscosity as

$$\eta_{\rm p}^* \equiv \frac{\eta_{\rm p}}{n_{\rm p} k_B T \lambda_{\rm H}} = \frac{\left\langle Q_1^* Q_2^* \right\rangle}{\dot{\gamma}^*} \tag{3.11}$$

The brackets $\langle . \rangle$ denote an ensemble average, which in case of polymer simulations is achieved by simulating several trajectories.

3.4 Brownian Dynamics Simulation Algorithm

The simulation of a polymer using Brownian Dynamics involves the following broad steps.

- 1. The Euler **time integration step** Δt is chosen.
- 2. A Wiener process is started (one trajectory)
- 3. **Initialise** the positions of the beads. The centre of the beads in a chain form a Random walk, therefore represent a Wiener process in space. Three dimensional connector vectors are generated from a Gaussian distribution, and added one by one to form the 3-D random walk chain.
- 4. The position vectors are advanced according to the SDE for the bead positions (or connector vectors) using the Euler-Maruyama method. This step is similar to the Euler step in Molecular Dynamics (force calculation and position advancement).
- 5. Sampling is done at regular intervals, and data is saved to disk.
- 6. Above steps from Step 2 are repeated for several trajectories.
- 7. **Averages and Errors** of mean are estimated for the trajectories, to get an average time evolution of a property.
- 8. Above steps from Step 1 are repeated for several integration time steps Δt .
- 9. Results for various Δt are extrapolated to $\Delta t \rightarrow 0$.

Exercise 3.2 Develop a BD code to simulate the viscosity of a polymer solution containing Rouse dumbbells. Calculate the evolution of viscosity for a start up of planar shear flow (Öttinger, 1996, Exercise 4.11).

3.5 Other Aspects

3.5.1 Random Number Generation

So far we have dealt only with the Gaussian random number generator (RNG). This is obtained by a transformation of the uniform random variable. For large polymer simulations, the computational cost of these transformations is significant. Since we are adopting a numerical procedure, which is an approximation in discrete time steps Δt , it is possible to approximate the Wiener process increments itself. What is required, within the order of the numerical approximation, is that the moments of the stochastic process have a particular behaviour. This lets us use an uniform random number generator with appropriate computationally less costing transformations that yields a random number with the correct moments. The simulation codes given in Öttinger (1996) use these transformations, see Section 3.4.3 in Öttinger (1996) for details.

Large polymer simulations also require random number generators whose periodicity is large (so as to avoid any sequential correlations). Öttinger (1996) in Excercise 4.8 also provides a RNG that has a periodicity of $\approx 3 \times 10^{18}$.

3.5.2 Interaction between Beads

In the above example we considered only a simple case of no interaction between the beads of the model other than a linear spring force between adjacent beads. In general, there could be non-linear springs, hydrodynamic interactions (HI), excluded volume (EV) interactions, and electro-magnetic (EM) interactions between the beads, depending on the nature of the polymer and the solvent. HI is always present, and it is necessary to include this interaction for all polymer solutions. It can be neglected in melt simulations. EV interactions are absent in theta solvents, but are present in good solvents. EM interactions are present in poor solvents and polyelectrolytes. The BD simulation algorithm for these kind of systems have been discussed in Fixman (1986); Öttinger (1996); Jendrejack *et al.* (2000); Prabhakar & Prakash (2004); Sunthar & Prakash (2005). The inclusion of interactions makes the simulations computationally intensive. Higher order approximation schemes are required for numerical integration to make the simulation manageable. A predictor-corrector, and semi-implicit predictor-corrector are some of the methods suggested in Öttinger (1996); Jendrejack *et al.* (2000); Prabhakar & Prakash (2004).

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