

Chapter 3

Brownian motion

3.1 Friction and random forces on colloids

Consider a spherical colloidal particle of radius a (typically between a nanometer and a micrometer) and mass M moving through a solvent along a path $\mathbf{R}(t)$. The colloidal particle will continuously collide with the solvent molecules. Because on average the colloid will collide more often on the front side than on the back side, it will experience a systematic force proportional with its velocity \mathbf{V} , and directed opposite to its velocity. The colloid will also experience a random or stochastic force $\mathbf{F}(t)$. These forces are summarized in Fig. 3.1 The equations of motion then read¹

$$\frac{d\mathbf{R}}{dt} = \mathbf{V} \quad (3.1)$$

$$\frac{d\mathbf{V}}{dt} = -\xi\mathbf{V} + \mathbf{F}. \quad (3.2)$$

By solving Stokes' equations (2.30), with no-slip boundaries on the surface of the sphere, it can be shown that the friction constant ξ is given by

$$\xi = \zeta/M = 6\pi\eta_s a/M, \quad (3.3)$$

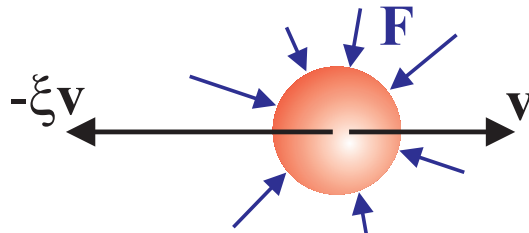
where η_s is the shear viscosity of the solvent.

Solving Eq. (3.2) yields

$$\mathbf{V}(t) = \mathbf{V}_0 e^{-\xi t} + \int_0^t d\tau e^{-\xi(t-\tau)} \mathbf{F}(\tau). \quad (3.4)$$

¹Note that we have divided all forces by the mass M of the colloid. Consequently, $\mathbf{F}(t)$ is an acceleration and the friction constant ξ is a frequency.

Figure 3.1: A colloid moving with velocity \mathbf{V} will experience a friction force $-\xi\mathbf{V}$ opposite to its velocity and random forces \mathbf{F} due to the continuous bombardment of solvent molecules.



where \mathbf{V}_0 is the initial velocity. We will now determine averages over all possible realizations of $\mathbf{F}(t)$, with the initial velocity as a condition. To this end we have to make some assumptions about the stochastic force. In view of its chaotic character, the following assumptions seem to be appropriate for its *average* properties:

$$\langle \mathbf{F}(t) \rangle = \mathbf{0} \quad (3.5)$$

$$\langle \mathbf{F}(t) \cdot \mathbf{F}(t') \rangle_{\mathbf{V}_0} = C_{\mathbf{V}_0} \delta(t - t') \quad (3.6)$$

where $C_{\mathbf{V}_0}$ may depend on the initial velocity. Using Eqs. (3.4) - (3.6), we find

$$\begin{aligned} \langle \mathbf{V}(t) \rangle_{\mathbf{V}_0} &= \mathbf{V}_0 e^{-\xi t} + \int_0^t d\tau e^{-\xi(t-\tau)} \langle \mathbf{F}(\tau) \rangle_{\mathbf{V}_0} \\ &= \mathbf{V}_0 e^{-\xi t} \end{aligned} \quad (3.7)$$

$$\begin{aligned} \langle \mathbf{V}(t) \cdot \mathbf{V}(t) \rangle_{\mathbf{V}_0} &= V_0^2 e^{-2\xi t} + 2 \int_0^t d\tau e^{-\xi(2t-\tau)} \mathbf{V}_0 \cdot \langle \mathbf{F}(\tau) \rangle_{\mathbf{V}_0} \\ &\quad + \int_0^t d\tau' \int_0^t d\tau e^{-\xi(2t-\tau-\tau')} \langle \mathbf{F}(\tau) \cdot \mathbf{F}(\tau') \rangle_{\mathbf{V}_0} \\ &= V_0^2 e^{-2\xi t} + \frac{C_{\mathbf{V}_0}}{2\xi} (1 - e^{-2\xi t}). \end{aligned} \quad (3.8)$$

The colloid is in thermal equilibrium with the solvent. According to the equipartition theorem, for large t , Eq. (3.8) should be equal to $3k_B T/M$, from which it follows that

$$\langle \mathbf{F}(t) \cdot \mathbf{F}(t') \rangle = 6 \frac{k_B T \xi}{M} \delta(t - t'). \quad (3.9)$$

This is one manifestation of the fluctuation-dissipation theorem, which states that the systematic part of the microscopic force appearing as the friction is actually determined by the correlation of the random force.

Integrating Eq. (3.4) we get

$$\mathbf{R}(t) = \mathbf{R}_0 + \frac{\mathbf{V}_0}{\xi} (1 - e^{-\xi t}) + \int_0^t d\tau \int_0^\tau d\tau' e^{-\xi(\tau-\tau')} \mathbf{F}(\tau'), \quad (3.10)$$

from which we calculate the mean square displacement

$$\langle (\mathbf{R}(t) - \mathbf{R}_0)^2 \rangle_{\mathbf{V}_0} = \frac{V_0^2}{\xi^2} (1 - e^{-\xi t})^2 + \frac{3k_B T}{M\xi^2} (2\xi t - 3 + 4e^{-\xi t} - e^{-2\xi t}). \quad (3.11)$$

For very large t this becomes

$$\langle (\mathbf{R}(t) - \mathbf{R}_0)^2 \rangle = \frac{6k_B T}{M\xi} t, \quad (3.12)$$

from which we get the Einstein equation for the self-diffusion coefficient

$$\boxed{D = \frac{k_B T}{\zeta}}, \quad (3.13)$$

where we have used $\langle (\mathbf{R}(t) - \mathbf{R}_0)^2 \rangle = 6Dt$ and $\zeta = M\xi = 6\pi\eta_s a$. Notice that the self-diffusion coefficient D is independent of the mass M of the colloid.

3.2 Smoluchowski and Langevin equations

From Eq. (3.7) we see that the colloid loses its memory of its initial velocity after a time $\tau \approx 1/\xi$. Using equipartition its initial velocity may be put equal to $\sqrt{3k_B T/M}$. The distance l it travels, divided by its radius then is

$$\frac{l}{a} = \frac{\sqrt{3k_B T/M}}{a\xi} = \sqrt{\frac{\rho_m k_B T}{9\pi\eta_s^2 a}}, \quad (3.14)$$

where ρ_m is the mass density of the colloid. Typical values are $l/a \approx 10^{-2}$ for a nanometre sized colloid and $l/a \approx 10^{-4}$ for a micrometre sized colloid in water at room temperature. We see that the particles have hardly moved at the time possible velocity gradients have relaxed to equilibrium. When we are interested in timescales on which particle configurations change, we may restrict our attention to the space coordinates, and average over the velocities. The time development of the distribution of particles on these time scales is governed by the Smoluchowski equation.

The Smoluchowski equation describes the time evolution of the probability density $\Psi(\mathbf{R}, \mathbf{R}_0; t)$ to find a particle at a particular position \mathbf{R} at a particular time t , given it was at \mathbf{R}_0 at $t = 0$. It is assumed that at every instant of time the particle is in thermal equilibrium with respect to its velocity, i.e., the particle velocity is strongly damped on the Smoluchowski timescale. A flux will exist, given by

$$\mathbf{J}(\mathbf{R}, \mathbf{R}_0, t) = -D\nabla\Psi(\mathbf{R}, \mathbf{R}_0; t) - \frac{1}{\zeta}\Psi(\mathbf{R}, \mathbf{R}_0; t)\nabla\Phi(\mathbf{R}). \quad (3.15)$$

The first term in Eq. (3.15) is the flux due to diffusion of the particle. The second term is the flux in the ‘‘downhill’’ gradient direction of the external potential $\Phi(\mathbf{R})$, damped by the friction coefficient ζ . At equilibrium, the flux must be zero and the distribution must obey the Boltzmann distribution

$$\Psi_{\text{eq}}(\mathbf{R}) = C \exp[-\Phi(\mathbf{R})/(k_B T)], \quad (3.16)$$

where C is a normalization constant. Using this in Eq. (3.15) while setting $\mathbf{J} = \mathbf{0}$, leads to the Einstein equation (3.13). In general, we assume that no particles are generated or destroyed, so

$$\frac{\partial}{\partial t}\Psi(\mathbf{R}, \mathbf{R}_0; t) = -\nabla \cdot \mathbf{J}(\mathbf{R}, \mathbf{R}_0, t). \quad (3.17)$$

Combining Eq. (3.15) with the above equation of particle conservation we arrive at the Smoluchowski equation

$$\frac{\partial}{\partial t}\Psi(\mathbf{R}, \mathbf{R}_0; t) = \nabla \cdot \left[\frac{1}{\zeta}\Psi(\mathbf{R}, \mathbf{R}_0; t)\nabla\Phi(\mathbf{R}) \right] + \nabla \cdot [D\nabla\Psi(\mathbf{R}, \mathbf{R}_0; t)] \quad (3.18)$$

$$\lim_{t \rightarrow 0} \Psi(\mathbf{R}, \mathbf{R}_0; t) = \delta(\mathbf{R} - \mathbf{R}_0). \quad (3.19)$$

The Smoluchowski equation describes how particle distribution functions change in time and is fundamental to the non-equilibrium statistical mechanics of overdamped particles such as colloids and polymers.

It can be shown (though we will not do that here) that the explicit equations of motion for the particles, i.e. the Langevin equations, which lead to the Smoluchowski equation are

$$\frac{d\mathbf{R}}{dt} = -\frac{1}{\zeta}\nabla\Phi + \nabla D + \mathbf{f} \quad (3.20)$$

$$\langle \mathbf{f}(t) \rangle = \mathbf{0} \quad (3.21)$$

$$\langle \mathbf{f}(t)\mathbf{f}(t') \rangle = 2D\bar{\mathbf{I}}\delta(t-t'). \quad (3.22)$$

where $\bar{\mathbf{I}}$ denotes the 3-dimensional unit matrix $I_{\alpha\beta} = \delta_{\alpha\beta}$. We use these equations in the next chapter to derive the equations of motion for a polymer.

Problems

3-1. Derive the last step in Eq. (3.14). Calculate the relative distance l/a over which a typical colloidal particle with radius $a = 1$ micrometer forgets its initial velocity. Assume the density of the colloid is equal to that of the surrounding liquid (water), which has a density of 1000 kg/m^3 , a viscosity of $\eta_s = 10^{-3} \text{ Pa s}$, and a temperature of 300 K .

3-2. Show that using the equilibrium distribution Eq. (3.16) in the flux equation Eq. (3.15) indeed leads to the Einstein equation (3.13).

Chapter 4

The dynamics of unentangled polymeric liquids

As an application of the theory presented in the previous chapters, we will study the dynamics of unentangled polymeric liquids. To this end we must first give a short introduction to their equilibrium properties.

4.1 Equilibrium properties of polymers

4.1.1 Global properties

Polymers are long linear macromolecules made up of a large number of chemical units or monomers, which are linked together through covalent bonds. The number of monomers per polymer may vary from a hundred to many thousands. We can describe the conformation of a polymer by giving the positions of its backbone atoms. The positions of the remaining atoms then usually follow by simple chemical rules. So, suppose we have $N + 1$ monomers, with $N + 1$ position vectors

$$\mathbf{R}_0, \mathbf{R}_1, \dots, \mathbf{R}_N.$$

We then have N bond vectors

$$\mathbf{r}_1 = \mathbf{R}_1 - \mathbf{R}_0, \dots, \mathbf{r}_N = \mathbf{R}_N - \mathbf{R}_{N-1}.$$

Much of the static and dynamic behavior of polymers can be explained by models which are surprisingly simple. This is possible because the global, large scale properties of polymers do not depend on the chemical details of the monomers, except for some species-dependent “effective” parameters. For example, one can measure the end-to-end vector, defined as

$$\mathbf{R} = \mathbf{R}_N - \mathbf{R}_0 = \sum_{i=1}^N \mathbf{r}_i. \quad (4.1)$$

If the end-to-end vector is measured for a large number of polymers in a melt, one will find that the distribution of end-to-end vectors is Gaussian and that the root mean squared end-to-end distance scales with the square root of the number of bonds, $\sqrt{\langle R^2 \rangle} \propto \sqrt{N}$, irrespective of the chemical details. This is a consequence of the central limit theorem.

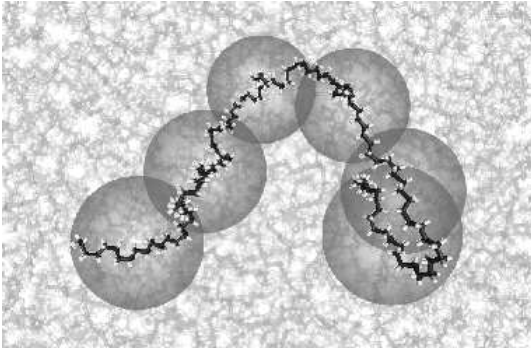


Figure 4.1: A polyethylene chain represented by segments of $\lambda = 20$ monomers. If enough consecutive monomers are combined into one segment, the vectors connecting these segments become independent of each other.

4.1.2 The central limit theorem and polymer elasticity

Consider a linear polymer chain. The bonds, angles and torsion angles between consecutive monomers are often fairly rigid. Therefore the vectors connecting consecutive *monomers* do not take up random orientations. However, if enough consecutive monomers are combined into one segment with center-of-mass position \mathbf{R}_i , the vectors connecting the segments ($\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_{i-1}$, $\mathbf{r}_{i+1} = \mathbf{R}_{i+1} - \mathbf{R}_i$, etcetera) do become independent of each other,¹ see Fig. 4.1.

Because the orientation and length of each segment-to-segment bond is independent of all others, the probability density in configuration space $\Psi(\mathbf{r}^N)$ may be written as

$$\Psi(\mathbf{r}^N) = \prod_{i=1}^N \psi(\mathbf{r}_i). \quad (4.2)$$

Assume further that the bond vector probability density $\psi(\mathbf{r}_i)$ depends only on the length of the bond vector and has zero mean, $\langle \mathbf{r}_i \rangle = \mathbf{0}$. For the second moment we write

$$\langle r^2 \rangle = \int d^3r r^2 \psi(r) \equiv b^2, \quad (4.3)$$

where we have defined the statistical segment (or Kuhn) length b . Let $\Omega(\mathbf{R}; N)$ be the probability distribution function for the end-to-end vector \mathbf{R} given that we have a chain of N bonds,

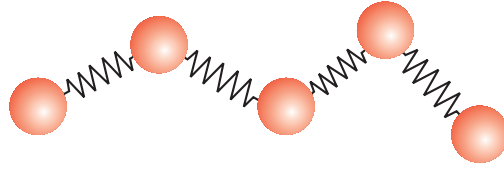
$$\Omega(\mathbf{R}; N) = \left\langle \delta \left(\mathbf{R} - \sum_{i=1}^N \mathbf{r}_i \right) \right\rangle, \quad (4.4)$$

where δ is the Dirac-delta function. The central limit theorem then states that for large enough N :

$$\Omega(\mathbf{R}; N) = \left\{ \frac{3}{2\pi N b^2} \right\}^{3/2} \exp \left\{ -\frac{3R^2}{2N b^2} \right\}. \quad (4.5)$$

¹For simplicity we ignore long range excluded volume interactions. This is allowed in a polymer melt or in a so-called Θ -solvent.

Figure 4.2: The gaussian chain can be represented by a collection of beads connected by harmonic springs of strength $3k_B T/b^2$.



So, irrespective of the precise form of the bond length distribution $\psi(r)$, the end-to-end vector will have a Gaussian distribution with zero mean and a variance given by N times the variance of a single bond:

$$\langle R^2 \rangle = Nb^2. \quad (4.6)$$

The local structure of the polymer appears only through the statistical segment length b .

Using $\Omega(\mathbf{R}; N)$, we can obtain an interesting insight in the thermodynamic behaviour of a polymer chain. The entropy of a chain in which the end-to-end vector \mathbf{R} is kept fixed, absorbing all constants into a reference entropy, is given by

$$S(\mathbf{R}; N) = k_B \ln \Omega(\mathbf{R}; N) = S_0 - \frac{3kR^2}{2Nb^2}. \quad (4.7)$$

The free energy is then

$$A = U - TS = A_0 + \frac{3k_B T R^2}{2Nb^2}. \quad (4.8)$$

We see that the free energy is related quadratically to the end-to-end distance, as if the chain is a harmonic (Hookean) spring with spring constant $3k_B T/Nb^2$. Unlike an ordinary spring, however, the strength of the spring *increases* with temperature! These springs are often referred to as entropic springs.

4.1.3 The Gaussian chain

Now we have established that global conformational properties of polymers are largely independent of the chemical details, we can start from the simplest model available, consistent with a Gaussian end-to-end distribution. This model is one in which every bond vector itself is Gaussian distributed,

$$\psi(\mathbf{r}) = \left\{ \frac{3}{2\pi b^2} \right\}^{3/2} \exp \left\{ -\frac{3}{2b^2} r^2 \right\}. \quad (4.9)$$

Such a Gaussian chain is often represented by a mechanical model of beads connected by harmonic springs, as in Fig. 4.2. The potential energy of such a chain is given by:

$$\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{2} k \sum_{i=1}^N r_i^2. \quad (4.10)$$

It is easy to see that if the spring constant is chosen equal to $k = 3k_B T/b^2$ the Boltzmann distribution of the bond vectors obeys Eqs. (4.2) and (4.9). The Gaussian chain is used as a starting point for the Rouse model.

4.2 Rouse dynamics of a polymer

4.2.1 From statics to dynamics

We will now adjust the static Gaussian chain model such that we can use it to calculate dynamical properties as well. A prerequisite is that the polymer chains are not very long, otherwise entanglements with surrounding chains will highly constrain the molecular motions.

When a polymer chain moves through a solvent every bead will continuously collide with the solvent molecules, leading to Brownian motion as described in the previous chapter. We will ignore hydrodynamic interactions between the beads.² This is allowed for polymer melts because the friction may be thought of as being caused by the motion of a chain relative to the rest of the material, which to a first approximation may be taken to be at rest; propagation of a velocity field like in a normal liquid is highly improbable, meaning there are no hydrodynamic interactions.

We will start with a Gaussian chain consisting of $N + 1$ beads connected by N springs. If we focus on one bead, while keeping all other beads fixed, we see that the external field Φ in which that bead moves is generated by connections to its predecessor and successor. We assume that each bead feels the same friction ζ , that its motion is overdamped, and that the diffusion coefficient $D = k_B T / \zeta$ is independent of the position \mathbf{R}_n of the bead. This model for a polymer is called the Rouse chain. According to Eqs. (3.20)-(3.22) the Langevin equations describing the motion of a Rouse chain are

$$\frac{d\mathbf{R}_0}{dt} = -\frac{3k_B T}{\zeta b^2} (\mathbf{R}_0 - \mathbf{R}_1) + \mathbf{f}_0 \quad (4.11)$$

$$\frac{d\mathbf{R}_n}{dt} = -\frac{3k_B T}{\zeta b^2} (2\mathbf{R}_n - \mathbf{R}_{n-1} - \mathbf{R}_{n+1}) + \mathbf{f}_n \quad (4.12)$$

$$\frac{d\mathbf{R}_N}{dt} = -\frac{3k_B T}{\zeta b^2} (\mathbf{R}_N - \mathbf{R}_{N-1}) + \mathbf{f}_N \quad (4.13)$$

$$\langle \mathbf{f}_n(t) \rangle = \mathbf{0} \quad (4.14)$$

$$\langle \mathbf{f}_n(t) \mathbf{f}_m(t') \rangle = 2D\bar{\mathbf{I}}\delta_{nm}\delta(t-t'). \quad (4.15)$$

4.2.2 Normal mode analysis

Equations (4.11) - (4.13) are $(3N + 3)$ coupled stochastic differential equations. In order to solve them, we will first ignore the stochastic forces \mathbf{f}_n and try specific solutions of the following form:

$$\mathbf{R}_n(t) = \mathbf{X}(t) \cos(an + c). \quad (4.16)$$

²When applied to dilute polymeric solutions, this model gives rather bad results, indicating the importance of hydrodynamic interactions. Hydrodynamic interactions are included in the so-called Zimm theory of polymer dynamics.

The equations of motion then read

$$\frac{d\mathbf{X}}{dt} \cos c = -\frac{3k_B T}{\zeta b^2} \{\cos c - \cos(a+c)\} \mathbf{X} \quad (4.17)$$

$$\frac{d\mathbf{X}}{dt} \cos(na+c) = -\frac{3k_B T}{\zeta b^2} 4 \sin^2(a/2) \cos(na+c) \mathbf{X} \quad (4.18)$$

$$\frac{d\mathbf{X}}{dt} \cos(Na+c) = -\frac{3k_B T}{\zeta b^2} \{\cos(Na+c) - \cos((N-1)a+c)\} \mathbf{X}, \quad (4.19)$$

where we have used

$$\begin{aligned} 2 \cos(na+c) - \cos((n-1)a+c) - \cos((n+1)a+c) \\ = \cos(na+c) \{2 - 2 \cos a\} = \cos(na+c) 4 \sin^2(a/2). \end{aligned} \quad (4.20)$$

The boundaries of the chain, Eqs. (4.17) and (4.19), are consistent with Eq. (4.18) if we choose

$$\cos c - \cos(a+c) = 4 \sin^2(a/2) \cos c \quad (4.21)$$

$$\cos(Na+c) - \cos((N-1)a+c) = 4 \sin^2(a/2) \cos(Na+c), \quad (4.22)$$

which is equivalent to

$$\cos(a-c) = \cos c \quad (4.23)$$

$$\cos((N+1)a+c) = \cos(Na+c). \quad (4.24)$$

We find independent solutions from

$$a - c = c \quad (4.25)$$

$$(N+1)a + c = p2\pi - Na - c, \quad (4.26)$$

where p is an integer. So finally

$$a = \frac{p\pi}{N+1}, \quad c = a/2 = \frac{p\pi}{2(N+1)}. \quad (4.27)$$

Eq. (4.16), with a and c from Eq. (4.27), decouples the set of differential equations. To find the general solution to Eqs. (4.11) to (4.15) we form a linear combination of all *independent* solutions:

$$\mathbf{R}_n = \mathbf{X}_0 + 2 \sum_{p=1}^N \mathbf{X}_p \cos \left[\frac{p\pi}{N+1} \left(n + \frac{1}{2} \right) \right]. \quad (4.28)$$

The factor 2 in front of the summation is only for reasons of convenience. Making use of

$$\frac{1}{N+1} \sum_{n=0}^N \cos \left[\frac{p\pi}{N+1} \left(n + \frac{1}{2} \right) \right] = \delta_{p0} \quad (0 \leq p < 2(N+1)), \quad (4.29)$$

we may invert this to

$$\boxed{\mathbf{X}_p = \frac{1}{N+1} \sum_{n=0}^N \mathbf{R}_n \cos \left[\frac{p\pi}{N+1} \left(n + \frac{1}{2} \right) \right]}. \quad (4.30)$$

The equations of motion then read

$$\frac{d\mathbf{X}_p}{dt} = -\frac{3k_B T}{\zeta b^2} 4 \sin^2 \left(\frac{p\pi}{2(N+1)} \right) \mathbf{X}_p + \mathbf{F}_p \quad (4.31)$$

$$\langle \mathbf{F}_p(t) \rangle = \mathbf{0} \quad (4.32)$$

$$\langle \mathbf{F}_0(t) \mathbf{F}_0(t') \rangle = \frac{2D}{N+1} \bar{\mathbf{I}} \delta(t-t') \quad (4.33)$$

$$\langle \mathbf{F}_p(t) \mathbf{F}_q(t') \rangle = \frac{D}{N+1} \bar{\mathbf{I}} \delta_{pq} \delta(t-t') \quad (p+q > 0) \quad (4.34)$$

where $p, q = 0, \dots, N$. \mathbf{F}_p is a weighted average of the stochastic forces \mathbf{f}_n ,

$$\mathbf{F}_p = \frac{1}{N+1} \sum_{n=0}^N \mathbf{f}_n \cos \left[\frac{p\pi}{N+1} \left(n + \frac{1}{2} \right) \right], \quad (4.35)$$

and is therefore itself a stochastic variable, characterised by its first and second moments, Eqs. (4.32) - (4.34).

4.2.3 Rouse relaxation times and amplitudes

Eqs. (4.31) - (4.34) form a decoupled set of $3(N+1)$ stochastic differential equations, each of which describes the fluctuations and relaxations of a normal mode (a Rouse mode) of the Rouse chain.

It is easy to see that \mathbf{X}_0 is the position of the polymer centre-of-mass $\mathbf{R}_G = \sum_n \mathbf{R}_n / (N+1)$. The mean square displacement of the centre-of-mass, $g_{\text{cm}}(t)$ can easily be calculated:

$$\mathbf{X}_0(t) = \mathbf{X}_0(0) + \int_0^t d\tau \mathbf{F}_0(\tau) \quad (4.36)$$

$$\begin{aligned} g_{\text{cm}}(t) &= \langle (\mathbf{X}_0(t) - \mathbf{X}_0(0))^2 \rangle = \left\langle \int_0^t d\tau \int_0^t d\tau' \mathbf{F}_0(\tau) \cdot \mathbf{F}_0(\tau') \right\rangle \\ &= \frac{6D}{N+1} t \equiv 6D_G t. \end{aligned} \quad (4.37)$$

So the diffusion coefficient D_G of the centre-of-mass of the polymer scales inversely proportional to the weight of the polymer chain.

All other modes $1 \leq p \leq N$ describe independent vibrations of the chain leaving the centre-of-mass unchanged; Rouse mode \mathbf{X}_p describes vibrations of a wavelength corresponding to a subchain of N/p segments. In the applications ahead of us, we will frequently need the time correlation functions of these Rouse modes. From Eq. (4.31) we get

$$\mathbf{X}_p(t) = \mathbf{X}_p(0) e^{-t/\tau_p} + \int_0^t d\tau e^{-(t-\tau)/\tau_p} \mathbf{F}_p(\tau), \quad (4.38)$$

where the characteristic relaxation time τ_p is given by

$$\tau_p = \frac{\zeta b^2}{3k_B T} \left[4 \sin^2 \left(\frac{p\pi}{2(N+1)} \right) \right]^{-1} \approx \frac{\zeta b^2 (N+1)^2}{3\pi^2 k_B T} \frac{1}{p^2}. \quad (4.39)$$

The last approximation is valid for large wavelengths, in which case $p \ll N$. Multiplying Eq. (4.38) by $\mathbf{X}_p(0)$ and taking the average over all possible realisations of the random force, we find

$$\langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle = \langle X_p^2 \rangle \exp(-t/\tau_p). \quad (4.40)$$

From these equations it is clear that the lower Rouse modes, which represent motions with larger wavelengths, are also slower modes. The relaxation time of the slowest mode, $p = 1$, is often referred to as the Rouse time τ_R . It scales with the square of the molecular weight of the polymer:

$$\tau_R = \frac{\zeta b^2 (N+1)^2}{3\pi^2 k_B T}. \quad (4.41)$$

This has been confirmed for concentrated polymers of low molecular weight.

We now calculate the equilibrium expectation values of X_p^2 , i.e., the amplitudes of the normal modes. To this end, first consider the statistical weight of a configuration $\mathbf{R}_0, \dots, \mathbf{R}_N$ in Cartesian coordinates,

$$P(\mathbf{R}_0, \dots, \mathbf{R}_N) = \frac{1}{Z} \exp \left[-\frac{3}{2b^2} \sum_{n=1}^N (\mathbf{R}_n - \mathbf{R}_{n-1})^2 \right]. \quad (4.42)$$

We can use Eq. (4.28) to find the statistical weight of a configuration in Rouse coordinates. Since the transformation to the Rouse coordinates is a linear transformation from one set of orthogonal coordinates to another, the corresponding Jacobian is simply a constant. The probability therefore reads

$$P(\mathbf{X}_0, \dots, \mathbf{X}_N) = \frac{1}{Z} \exp \left[-\frac{12}{b^2} (N+1) \sum_{p=1}^N \mathbf{X}_p \cdot \mathbf{X}_p \sin^2 \left(\frac{p\pi}{2(N+1)} \right) \right]. \quad (4.43)$$

Since this is a simple product of independent Gaussians, the amplitudes of the Rouse modes can easily be calculated:

$$\langle X_p^2 \rangle = \frac{b^2}{8(N+1) \sin^2 \left(\frac{p\pi}{2(N+1)} \right)} \approx \frac{(N+1)b^2}{2\pi^2} \frac{1}{p^2}. \quad (4.44)$$

Again, the last approximation is valid when $p \ll N$.

We now have the ingredients to calculate all kinds of dynamic quantities of the Rouse chain.

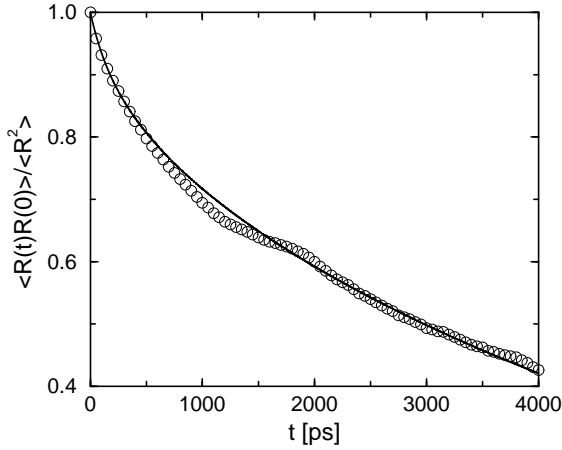


Figure 4.3: Molecular dynamics simulation results for the orientational correlation function of the end-to-end vector of a $C_{120}H_{242}$ polyethylene chain under melt conditions (symbols), compared with the Rouse model prediction (solid line). J.T. Padding and W.J. Briels, *J. Chem. Phys.* **114**, 8685 (2001).

4.2.4 Correlation of the end-to-end vector

The first dynamic quantity we are interested in is the time correlation function of the end-to-end vector \mathbf{R} . Notice that

$$\mathbf{R} = \mathbf{R}_N - \mathbf{R}_0 = 2 \sum_{p=1}^N \mathbf{X}_p \{(-1)^p - 1\} \cos \left[\frac{p\pi}{2(N+1)} \right]. \quad (4.45)$$

Because the Rouse mode amplitudes decay as p^{-2} , our results will be dominated by p values which are extremely small compared to N . We therefore write

$$\mathbf{R} = -4 \sum_{p=1}'^N \mathbf{X}_p, \quad (4.46)$$

where the prime at the summation sign indicates that only terms with odd p should occur in the sum. Then

$$\langle \mathbf{R}(t) \cdot \mathbf{R}(0) \rangle = 16 \sum_{p=1}'^N \langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle = \frac{8b^2}{\pi^2} (N+1) \sum_{p=1}'^N \frac{1}{p^2} e^{-t/\tau_p}. \quad (4.47)$$

The characteristic decay time at large t is τ_1 , which is proportional to $(N+1)^2$.

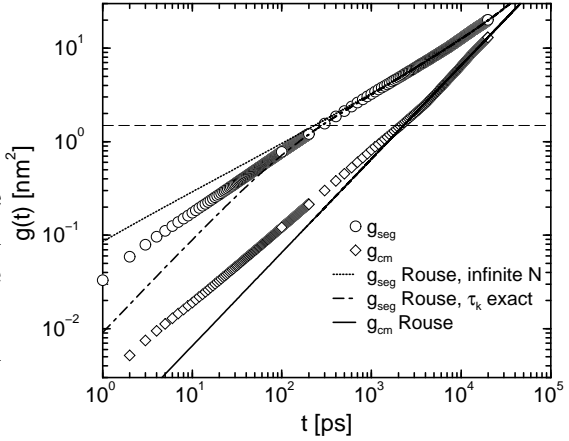
Figure 4.3 shows that Eq. (4.47) gives a good description of the time correlation function of the end-to-end vector of a real polymer chain in a melt (provided the polymer is not much longer than the entanglement length).

4.2.5 Segmental motion

In this section we will calculate the mean square displacements $g_{\text{seg}}(t)$ of the individual segments. Using Eq. (4.28) and the fact that different modes are not correlated, we get for segment n

$$\begin{aligned} \langle (\mathbf{R}_n(t) - \mathbf{R}_n(0))^2 \rangle &= \langle (\mathbf{X}_0(t) - \mathbf{X}_0(0))^2 \rangle \\ &+ 4 \sum_{p=1}^N \langle (\mathbf{X}_p(t) - \mathbf{X}_p(0))^2 \rangle \cos^2 \left[\frac{p\pi}{N+1} \left(n + \frac{1}{2} \right) \right]. \end{aligned} \quad (4.48)$$

Figure 4.4: Molecular dynamics simulation results for the mean square displacements of a $C_{120}H_{242}$ polyethylene chain under melt conditions (symbols). The dotted and dot-dashed lines are Rouse predictions for a chain with an infinite number of modes and for a finite Rouse chain, respectively. The horizontal line is the statistical segment length b^2 . J.T. Padding and W.J. Briels, *J. Chem. Phys.* **114**, 8685 (2001).



Averaging over all segments, and introducing Eqs. (4.37) and (4.40), the mean square displacement of a typical segment in the Rouse model is

$$\begin{aligned} g_{\text{seg}}(t) &= \frac{1}{N+1} \sum_{n=0}^N \langle (\mathbf{R}_n(t) - \mathbf{R}_n(0))^2 \rangle \\ &= 6D_G t + 4 \sum_{p=1}^N \langle X_p^2 \rangle (1 - e^{-t/\tau_p}). \end{aligned} \quad (4.49)$$

Two limits may be distinguished. First, when t is very large, $t \gg \tau_1$, the first term in Eq. (4.49) will dominate, yielding

$$g_{\text{seg}}(t) \approx 6D_G t \quad (t \gg \tau_1). \quad (4.50)$$

This is consistent with the fact that the polymer as a whole diffuses with diffusion coefficient D_G .

Secondly, when $t \ll \tau_1$ the sum over p in Eq. (4.49) dominates. If $N \gg 1$ the relaxation times can be approximated by the right hand side of Eq. (4.39), the Rouse mode amplitudes can be approximated by the right hand side of Eq. (4.44), and the sum can be replaced by an integral,

$$\begin{aligned} g_{\text{seg}}(t) &= \frac{2b^2}{\pi^2} (N+1) \int_0^\infty dp \frac{1}{p^2} (1 - e^{-tp^2/\tau_1}) \\ &= \frac{2b^2}{\pi^2} (N+1) \int_0^\infty dp \frac{1}{\tau_1} \int_0^t dt' e^{-t'p^2/\tau_1} \\ &= \frac{2b^2}{\pi^2} \frac{(N+1)}{\tau_1} \frac{1}{2} \sqrt{\pi\tau_1} \int_0^t dt' \frac{1}{\sqrt{t'}} \\ &= \left(\frac{12k_B T b^2}{\pi \zeta} \right)^{1/2} t^{1/2} \quad (\tau_N \ll t \ll \tau_1, N \gg 1). \end{aligned} \quad (4.51)$$

At short times the mean square displacement of a typical segment is subdiffusive and independent of the number of segments N in the chain.

Figure 4.4 shows the mean square displacement of monomers (circles) and centre-of-mass (squares) of an unentangled polyethylene chain in its melt. Observe that the chain motion is in agreement with the Rouse model prediction, but only for displacements larger than the square statistical segment length b^2 .

4.2.6 Polymer stress and viscosity

We will finally calculate the viscosity of a melt of Rouse chains, using the Green-Kubo relation Eq. (2.41). Generalizing Eq. (2.42), the (equilibrium) microscopic stress tensor $\boldsymbol{\sigma}$ can be expressed as

$$\boldsymbol{\sigma} = -\frac{1}{V} \left(\sum_{i=1}^{N_{\text{tot}}} M_i \mathbf{V}_i \mathbf{V}_i + \sum_{i=1}^{N_{\text{tot}}-1} \sum_{j=i+1}^{N_{\text{tot}}} (\mathbf{R}_i - \mathbf{R}_j) \mathbf{F}_{ij} \right), \quad (4.52)$$

where M_i is the mass of particle i and \mathbf{F}_{ij} is the force that particle j is exerting on particle i .

At first sight, it would be a tremendous task to calculate the viscosity analytically because the sums in Eq. (4.52) must be taken over all N_{tot} particles, i.e. over all segments of all polymer chains in the system. This is why in real polymer systems the stress tensor is a collective property. In the Rouse model, however, there is no correlation between the dynamics of one chain and the other, so one may just as well analyze the stress relaxation of a single chain and make an ensemble average over all initial configurations. Moreover, because the velocities of the polymer segments are usually overdamped, the polymer stress is dominated by the interactions between the segments. The first (kinetic) part of Eq. (4.52) may then be neglected.

Using Eqs. (4.28) and (4.52), the microscopic stress tensor of a Rouse chain in a specific configuration, neglecting kinetic contributions, is equal to

$$\begin{aligned} \boldsymbol{\sigma} &= \frac{1}{V} \frac{3k_B T}{b^2} \sum_{n=1}^N (\mathbf{R}_{n-1} - \mathbf{R}_n) (\mathbf{R}_{n-1} - \mathbf{R}_n) \\ &= \frac{1}{V} \frac{48k_B T}{b^2} \sum_{n=1}^N \sum_{p=1}^N \sum_{q=1}^N \mathbf{X}_p \mathbf{X}_q \sin\left(\frac{p\pi n}{N+1}\right) \sin\left(\frac{q\pi n}{N+1}\right) \times \\ &\quad \sin\left(\frac{p\pi n}{N+1}\right) \sin\left(\frac{q\pi n}{N+1}\right) \\ &= \frac{1}{V} \frac{24k_B T}{b^2} N \sum_{p=1}^N \mathbf{X}_p \mathbf{X}_p \sin^2\left(\frac{p\pi}{2(N+1)}\right). \end{aligned} \quad (4.53)$$

Combining this with the expression for the equilibrium Rouse mode amplitudes, Eq. (4.44), this can be written more concisely as

$$\boldsymbol{\sigma} = \frac{3k_B T}{V} \sum_{p=1}^N \frac{\mathbf{X}_p \mathbf{X}_p}{\langle X_p^2 \rangle}. \quad (4.54)$$

The product of the xy -component of the microscopic stress tensor at $t = 0$ and the one at $t = t$ is therefore

$$\sigma_{xy}(t) \sigma_{xy}(0) = \left(\frac{3k_B T}{V} \right)^2 \sum_{p=1}^N \sum_{q=1}^N \frac{X_{px}(t) X_{py}(t) X_{qx}(0) X_{qy}(0)}{\langle X_p^2 \rangle \langle X_q^2 \rangle}. \quad (4.55)$$

To obtain the shear viscosity the ensemble average must be taken over all possible configurations at $t = 0$. Now, since the Rouse modes are Gaussian variables, all the

ensemble averages of products of an odd number of X_p 's are zero and the ensemble averages of products of an even number of X_p 's can be written as a sum of products of averages of only two X_p 's. For the even term in Eq. (4.55) we find:

$$\begin{aligned} \langle X_{px}(t) X_{py}(t) X_{qx}(0) X_{qy}(0) \rangle &= \langle X_{px}(t) X_{py}(t) \rangle \langle X_{qx}(0) X_{qy}(0) \rangle \\ &+ \langle X_{px}(t) X_{qy}(0) \rangle \langle X_{py}(t) X_{qx}(0) \rangle \\ &+ \langle X_{px}(t) X_{qx}(0) \rangle \langle X_{py}(t) X_{qy}(0) \rangle. \end{aligned} \quad (4.56)$$

The first four ensemble averages equal zero because, for a Rouse chain in equilibrium, there is no correlation between different cartesian components. The last two ensemble averages are nonzero only when $p = q$, since the Rouse modes are mutually orthogonal. Using the fact that all cartesian components are equivalent, and Eq. (4.40), the shear relaxation modulus of a melt of Rouse chains can be expressed as

$$G(t) = \frac{k_B T}{V} \sum_{p=1}^N \left[\frac{\langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle}{\langle X_p^2 \rangle} \right]^2 = \frac{ck_B T}{N+1} \sum_{p=1}^N \exp(-2t/\tau_p), \quad (4.57)$$

where $c = N/V$ is the number density of beads.

The Rouse model predicts a viscosity, at constant monomer concentration c and segmental friction ζ , proportional to N :

$$\eta = \int_0^\infty dt G(t) \approx \frac{ck_B T}{N+1} \frac{\tau_1}{2} \sum_{p=1}^N \frac{1}{p^2} \approx \frac{ck_B T}{N+1} \frac{\tau_1}{2} \frac{\pi^2}{6} = \frac{c\zeta b^2}{36} (N+1). \quad (4.58)$$

This has been confirmed for concentrated polymers with low molecular weight.³ Concentrated polymers of high molecular weight give different results, stressing the importance of entanglements.

Problems

4-1. Why is it obvious that the expression for the end-to-end vector \mathbf{R} , Eq. (4.46), should only contain Rouse modes of odd mode number p ?

4-2. Show that the shear relaxation modulus $G(t)$ of a Rouse chain at short, but not too short, times decays like $t^{-1/2}$ and is given by

$$G(t) = \frac{ck_B T}{N+1} \sqrt{\frac{\pi \tau_1}{8t}} \quad (\tau_N \ll t \ll \tau_1).$$

We know that $G(t)$ must be finite at $t = 0$. Explain how the stress relaxes at very short times. Make a sketch of $G(t)$ on a double logarithmic scale.

³A somewhat stronger N dependence is often observed because the density and, more important, the segmental friction coefficient increase with increasing N .

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