

# Theory of Polymer Dynamics

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# Preface

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The manuscript was typed by Pierre van Sinderen, who also did the calculations in chapter 2, together with Roelof de Vries. The final editing of the manuscript was done by Johan Padding, who also meticulously removed many errors, typing errors as well as insecurities from my side.

Some books and articles which have been very helpful in preparing these lectures are:

P.J. Flory, *Statistical Mechanics of Chain Molecules*, Hanser Publishers, Munich 1989.

M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics*, Clarendon Press, Oxford 1986.

D.M. McQuarrie, *Statistical Mechanics*, Harper & Row, New York 1976.

J.G. Curro and K.S. Schweizer, *J. Chem. Phys.*, **87**, 1842 (1987).

P. Strating, *J. Chem. Phys.*, **103**, 10226 (1995).

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# Chapter 1

## The Rotational Isomeric State model

### 1.1 The model

Polymers are huge molecules constructed out of many identical building blocks called monomers. Here we shall restrict ourselves to linear molecules in which every monomer has one successor and/or predecessor. The number of monomers per polymer may vary from a few hundreds to many thousands.

The simplest example of a polymer is drawn below.

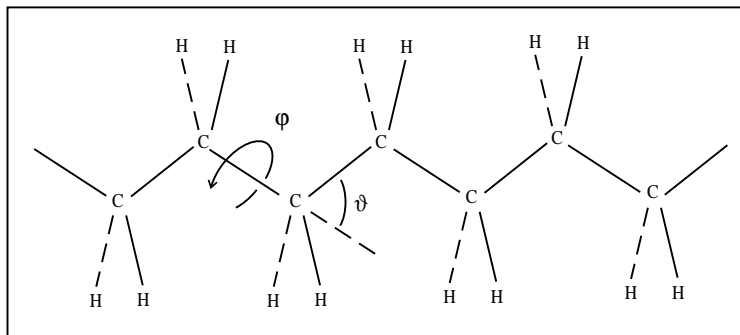


Figure 1.1: A simple polymer in the trans conformation.

The polymer is drawn here in the trans conformation. Many other conformations exist, and it is the aim of the RIS model to describe the statistics of these conformations.

We shall describe the conformation of the polymer by giving the position vectors of its backbone atoms, in this case the carbon atoms. The positions of the remaining atoms then usually follow by simple chemical rules. So, suppose we have  $N + 1$  monomers, then we have  $N + 1$  position vectors

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

We then have  $N$  bond vectors

$$\vec{r}_1 = \vec{R}_1 - \vec{R}_0, \vec{r}_2 = \vec{R}_2 - \vec{R}_1, \dots, \vec{r}_N = \vec{R}_N - \vec{R}_{N-1}.$$

Alternatively we may also use the  $N - 2$  dihedral angles

$$\varphi_2, \varphi_3, \dots, \varphi_{N-1}.$$

The dihedral angle  $\varphi_i$  is the angle between the plane of the vectors  $\vec{r}_{i-1}$  and  $\vec{r}_i$  and the plane of the vectors  $\vec{r}_i$  and  $\vec{r}_{i+1}$ . Further conventions will be given later on. In order to completely specify the conformation we should also give the  $N - 1$  angles  $\vartheta_i$  and the  $N$  bond lengths, but we shall consider them to be fixed in the rest of this chapter. This description leaves six variables to fix the centre of mass and the orientation of the molecule.

Now first consider the case of n-butane. We have but one dihedral, and the energy as a function of this angle is drawn below.

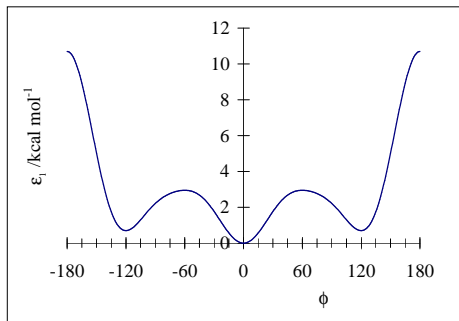


Figure 1.2: Dihedral angle energy of n-butane.

The conformation with  $\varphi = 0$  is called the trans conformation, the one with  $\varphi \approx 120^\circ$  is called gauche plus ( $g^+$ ), and the one with  $\varphi \approx -120^\circ$  is called gauche minus ( $g^-$ ). Notice that at room temperature only the three minima will be populated which makes it possible to restrict interest to three conformations called  $t$ ,  $g^+$  and  $g^-$ .

Now let us try to write down the energy of a polymer as a function of the angles  $\varphi_i$ . In order to do so we start with the molecule in its all trans conformation i.e.  $\varphi_i = t$  for all  $i$ . Next we successively bring the angles  $\varphi_2, \varphi_3, \dots, \varphi_{N-1}$  to their actual values. Every angle will then contribute to the total energy like in the case of butane i.e.

$$E = \sum_{i=2}^{N-1} \epsilon_1(\varphi_i). \quad (1.1)$$

In doing so we have neglected the fact that for example the sequence  $\varphi_i = g^+$ ,  $\varphi_{i+1} = g^-$  brings the monomers  $i - 2$  and  $i + 2$  virtually to the same position, which leads to a larger positive contribution to the energy. The same holds true for the sequence  $\varphi_i = g^-, \varphi_{i+1} = g^+$ . This phenomenon is called the "pentane" effect because pentane is the smallest molecule in which it may occur. In order to incorporate the pentane effect into our formalism we write

$$E = \sum_{i=2}^{N-1} \epsilon_1(\varphi_i) + \sum_{i=3}^{N-1} \epsilon_2(\varphi_{i-1}, \varphi_i). \quad (1.2)$$

It will be clear that the above is also only part of the story because we have neglected the possibility that monomers  $i$  and  $i + n$  ( $n > 4$ ) will occupy the same position. We may say that we have included the short range excluded volume



effect, but not the long range excluded volume. Short range and long range here refer to the distance along the chain. Inclusion of long range effects makes the problem virtually intractable, so we stop at the level of Eq. (1.2). We shall say a few qualitative things about the excluded volume effect later on.

## 1.2 The partition function

The RIS model can be treated in considerable detail. As a first step we calculate the partition function

$$Z = \sum_{\varphi_2 \in \{t, g^+, g^-\}} \cdots \sum_{\varphi_{N-1} \in \{t, g^+, g^-\}} \exp\{-\beta E(\varphi_2, \dots, \varphi_{N-1})\}. \quad (1.3)$$

Introducing the energy (1.2) and using a short hand notation for the summations we get

$$Z = \sum_{\varphi_2} \cdots \sum_{\varphi_{N-1}} e^{-\beta \epsilon_1(\varphi_2)} t(\varphi_2, \varphi_3) \cdots t(\varphi_{N-2}, \varphi_{N-1}) \quad (1.4)$$

$$t(\varphi_{i-1}, \varphi_i) = \exp\{-\beta \epsilon_1(\varphi_i) - \beta \epsilon_2(\varphi_{i-1}, \varphi_i)\}. \quad (1.5)$$

We recognize a sequence of matrix products in Eq. (1.4), which makes it possible to write

$$Z = \sum_{\varphi_2} \sum_{\varphi_{N-1}} e^{-\beta \epsilon_1(\varphi_2)} [T^{N-3}]_{\varphi_2, \varphi_{N-1}} \quad (1.6)$$

$T$  is a matrix with elements  $t(\varphi_{i-1}, \varphi_i)$ . In the case of polyethylene it is given by

$$T = \begin{matrix} & t & g^+ & g^- \\ \begin{matrix} t \\ g^+ \\ g^- \end{matrix} & \left( \begin{array}{ccc} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{array} \right) & \end{matrix}, \quad (1.7)$$

where  $\sigma = \exp\{-\beta \epsilon_1(g^+)\} = \exp\{-\beta \epsilon_1(g^-)\}$  and  $\epsilon_2(\varphi_{i-1}, \varphi_i) = 0$  except for  $\epsilon_2(g^+, g^-) = \epsilon_2(g^-, g^+) = \infty$ . The zero of energy has been chosen such that  $\epsilon_1(t) = 0$ .

Eq. (1.6) may also be written as

$$Z = (1 \ \sigma \ \sigma) T^{N-3} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}. \quad (1.8)$$

Moreover, using

$$(1 \ \sigma \ \sigma) = (1 \ 0 \ 0) T \quad (1.9)$$

we may write

$$Z = Y^T T^{N-2} X \quad (1.10)$$

with  $Y^T = (1 \ 0 \ 0)$  and  $X^T = (1 \ 1 \ 1)$ .

It is useful to decompose the matrix  $T$  in terms of its eigenvectors:

$$TA = A\Lambda \quad (1.11)$$

$$T = A\Lambda A^{-1} \equiv A\Lambda B \quad (1.12)$$

where  $\Lambda$  is the diagonal matrix containing the eigenvalues of  $T$ . For notational convenience we have introduced  $B = A^{-1}$ .

Eq. (1.12) may be written like

$$T = \sum_i \lambda_i A_i B_i^T \quad (1.13)$$

where the  $A_i$  are the columns of  $A$  and the  $B_i^T$  the rows of  $B$ . Then

$$\begin{aligned} T^N &= (A\Lambda A^{-1})(A\Lambda A^{-1}) \cdots (A\Lambda A^{-1}) = A\Lambda^N A^{-1} = A\Lambda^N B \\ T^N &= \sum_i \lambda_i^N A_i B_i^T. \end{aligned} \quad (1.14)$$

The partition function then reads

$$Z = \sum_i \lambda_i^{N-2} (Y^T A_i) (B_i^T X) = \sum_i c_i \lambda_i^{N-2}. \quad (1.15)$$

In practice we are usually interested in the free energy per monomer

$$\frac{1}{N} \ln Z = \frac{N-2}{N} \ln \lambda_{\max} + \frac{1}{N} \ln \left\{ \sum_i c_i \left( \frac{\lambda_i}{\lambda_{\max}} \right)^{N-2} \right\}, \quad (1.16)$$

where  $\lambda_{\max}$  is the largest eigenvalue of  $T$ . In the limit of  $N$  going to infinity the second term goes to zero

$$\lim_{N \rightarrow \infty} \frac{1}{N} \ln Z = \ln \lambda_{\max}. \quad (1.17)$$

In the case of matrix (1.7) one easily calculates the eigenvectors. From  $\det(T - \lambda I) = 0$  one gets

$$\begin{aligned} (\lambda^2 - \lambda(1 + \sigma) - \sigma)(\sigma - \lambda) &= 0 \\ \lambda_{\max} &= \frac{1}{2} \{ (1 + \sigma) + \sqrt{1 + 6\sigma + \sigma^2} \}. \end{aligned} \quad (1.18)$$

### 1.3 Some probabilities

It is instructive to calculate some probabilities occurring in the RIS model. An important probability for computer simulations is the conditional probability  $q_{\xi\eta}$  defined below. We shall always assume that the chain is infinitely long, and that end effects may be neglected. In this case  $\lambda_{\max}$  is the only eigenvalue we need.

We define the probability that a given bond is in state  $\eta$  by

$$p_\eta = \langle \delta_{\varphi_i, \eta} \rangle. \quad (1.19)$$

Explicitly introducing the averaging procedure yields

$$\begin{aligned} p_\eta &= \frac{1}{Z} \sum_{\varphi_2} \cdots \sum_{\varphi_{N-1}} e^{-\beta \epsilon_1(\varphi_2)} t(\varphi_2, \varphi_3) \cdots t(\varphi_{i-1}, \varphi_i) \times \\ &\quad \delta_{\varphi_i, \eta} t(\varphi_i, \varphi_{i+1}) \cdots t(\varphi_{N-2}, \varphi_{N-1}). \end{aligned} \quad (1.20)$$

Using the same method as in the previous section we find

$$\begin{aligned} p_\eta &= \frac{1}{Z} \sum_{\varphi_i} (Y^T T^{i-1})_{\varphi_i} \delta_{\varphi_i, \eta} (T^{N-1-i} X)_{\varphi_i} \\ &= \frac{1}{Z} (Y^T T^{i-1})_{\eta} (T^{N-1-i} X)_{\eta} \\ &= \frac{\{ \sum_k \lambda_k^{i-1} (Y^T A_k) (B_k^T)_{\eta} \} \{ \sum_l \lambda_l^{N-1-i} (A_l)_{\eta} (B_l^T X) \}}{\sum_k \lambda_k^{N-2} (Y^T A_k) (B_k^T X)}. \end{aligned} \quad (1.21)$$

Dividing numerator and denominator by  $\lambda_{\max}^{N-2}$ , and assuming  $N$ ,  $i$ , and  $N - i$  are large we get

$$p_\eta = (B_{\max}^T)_\eta (A_{\max})_\eta. \quad (1.22)$$

Because here and in the remaining part of the chapter we only need  $\lambda_{\max}$  and the corresponding vectors  $A_{\max}$  and  $B_{\max}^T$ , we shall omit the subscript "max" and write

$$p_\eta = B_\eta^T A_\eta. \quad (1.23)$$

Similarly one calculates

$$\begin{aligned} p_{\xi\eta} &= \langle \delta_{\varphi_{i-1,\xi}} \delta_{\varphi_{i,\eta}} \rangle \\ &= B_\xi^T \frac{t(\xi, \eta)}{\lambda} A_\eta. \end{aligned} \quad (1.24)$$

An important quantity is  $q_{\xi\eta}$ , the conditional probability to find bond  $i$  in state  $\eta$ , given that bond  $i - 1$  is in state  $\xi$

$$q_{\xi\eta} = \frac{p_{\xi\eta}}{p_\xi}. \quad (1.25)$$

Introducing Eqs. (1.23) and (1.24) we get

$$q_{\xi\eta} = \frac{t(\xi, \eta)}{\lambda} \frac{A_\eta}{A_\xi}. \quad (1.26)$$

This quantity may be used to generate chain conformations on a computer.

## 1.4 The mean square end-to-end vector

A rough measure of the average size of the polymer is given by the mean square end-to-end vector, which we shall calculate in this section. Related properties are the radius of gyration, and the persistence length. Both of them may be calculated using methods similar to the ones in this section.

The end-to-end vector is given by

$$\vec{R} = \vec{R}_N - \vec{R}_0 = \sum_{i=1}^N \vec{r}_i. \quad (1.27)$$

The mean square then reads

$$\begin{aligned} \langle R^2 \rangle &= \langle (\sum_i \vec{r}_i) \cdot (\sum_j \vec{r}_j) \rangle \\ &= \sum_i \sum_j \langle \vec{r}_i \cdot \vec{r}_j \rangle \\ &= \sum_i \langle \vec{r}_i \cdot \vec{r}_i \rangle + 2 \sum_{i < j} \langle \vec{r}_i \cdot \vec{r}_j \rangle. \end{aligned} \quad (1.28)$$

Again assuming the chain is infinitely long, we may put  $\langle \vec{r}_i \cdot \vec{r}_{i+n} \rangle$  independent on  $i$ . Then

$$\begin{aligned} \langle R^2 \rangle &= Nl^2 + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \langle \vec{r}_i \cdot \vec{r}_j \rangle \\ &= Nl^2 + 2 \sum_{n=1}^N (N-n) \langle \vec{r}_i \cdot \vec{r}_{i+n} \rangle \end{aligned} \quad (1.29)$$

where  $(N - n)$  is the number of times the distance  $n$  may occur along the chain.

We now set forth to calculate  $\langle \vec{r}_i \cdot \vec{r}_{i+n} \rangle$ . In order to do so we need to calculate the scalar product  $\vec{r}_i \cdot \vec{r}_{i+n}$  as a function of the angles  $\varphi_i, \dots, \varphi_{i+n-1}$ . To this end we associate with every monomer  $i$  a Cartesian coordinate system  $\hat{e}^\alpha(i)$ . Every vector  $\vec{v}$  may then be expanded like

$$\vec{v} = \sum_{\alpha} \hat{e}^\alpha(i) v^\alpha(i) \equiv \underline{\hat{e}}(i)^T \underline{v}(i). \quad (1.30)$$

The precise definition of the local coordinate system is given in Appendix A. Here we only mention that

$$\begin{aligned} \vec{r}_i &= l \hat{e}^3(i) \\ \underline{r}_i &= l(0, 0, 1)^T \equiv \underline{l}. \end{aligned} \quad (1.31)$$

A particular example of Eq. (1.30) is

$$\hat{e}^\alpha(i+1) = \sum_{\beta} \hat{e}^\beta(i) M_{\beta\alpha}(\varphi_i). \quad (1.32)$$

The matrix  $\underline{M}(\varphi)$  is calculated in Appendix B.

The scalar product  $\vec{r}_i \cdot \vec{r}_{i+1}$  now reads

$$\begin{aligned} \vec{r}_i \cdot \vec{r}_{i+1} &= \sum_{\alpha} \hat{e}^\alpha(i) r_i^\alpha(i) \cdot \sum_{\beta} \hat{e}^\beta(i+1) r_{i+1}^\beta(i+1) \\ &= \sum_{\alpha} \sum_{\beta} r_i^\alpha(i) M_{\alpha\beta}(\varphi_i) r_{i+1}^\beta(i+1) \\ &= \underline{l}^T \underline{M}(\varphi_i) \underline{l} \end{aligned} \quad (1.33)$$

and in general

$$\vec{r}_i \cdot \vec{r}_{i+n} = \underline{l}^T \underline{M}(\varphi_i) \cdots \underline{M}(\varphi_{i+n-1}) \underline{l} \quad (1.34)$$

from which we get

$$\langle R^2 \rangle = Nl^2 + 2 \sum_{n=1}^N (N-n) \underline{l}^T \langle \underline{M}(\varphi_1) \cdots \underline{M}(\varphi_n) \rangle \underline{l}. \quad (1.35)$$

We finally calculate the remaining average using the methods of the last section

$$\begin{aligned} \langle \underline{M}(\varphi_i) \cdots \underline{M}(\varphi_{i+n-1}) \rangle &= \\ &= \frac{1}{Z} \sum_{\varphi_i} \cdots \sum_{\varphi_{i+n}} (Y^T T^{i-1})_{\varphi_i} t(\varphi_i, \varphi_{i+1}) \underline{M}(\varphi_i) \cdots \\ &\quad t(\varphi_{i+n-1}, \varphi_{i+n}) \underline{M}(\varphi_{i+n-1}) (T^{N-n-i-2} X)_{\varphi_{i+n}} \\ &= \sum_{\varphi_i} \cdots \sum_{\varphi_{i+n}} (B^T)_{\varphi_i} \frac{t(\varphi_i, \varphi_{i+1})}{\lambda} \underline{M}(\varphi_i) \cdots \\ &\quad \frac{t(\varphi_{i+n-1}, \varphi_{i+n})}{\lambda} \underline{M}(\varphi_{i+n-1}) A_{\varphi_{i+n}} \end{aligned} \quad (1.36)$$

where again we have omitted the subscript "max". We may write this in a concise form like

$$\begin{aligned} \langle \underline{M}(\varphi_i) \cdots \underline{M}(\varphi_{i+n-1}) \rangle &= (B_t^T E_3 \ B_+^T E_3 \ B_-^T E_3) \times \\ &\lambda^{-n} \begin{pmatrix} t(t, t) \underline{M}(t) & t(t, +) \underline{M}(t) & t(t, -) \underline{M}(t) \\ t(+, t) \underline{M}(+) & t(+, +) \underline{M}(+) & t(+, -) \underline{M}(+) \\ t(-, t) \underline{M}(-) & t(-, +) \underline{M}(-) & t(-, -) \underline{M}(-) \end{pmatrix}^n \begin{pmatrix} A_t E_3 \\ A_+ E_3 \\ A_- E_3 \end{pmatrix} \end{aligned} \quad (1.37)$$

where  $E_3$  is the 3-d unit matrix. In terms of direct products of matrices this reads

$$\langle \underline{M}(\varphi_i) \cdots \underline{M}(\varphi_{i+n-1}) \rangle = (B^T \otimes E_3) S^n (A \otimes E_3) \quad (1.38)$$

$$\begin{aligned} S &= \lambda^{-1} \begin{pmatrix} t(t, t)\underline{M}(t) & t(t, +)\underline{M}(t) & t(t, -)\underline{M}(t) \\ t(+, t)\underline{M}(+) & t(+, +)\underline{M}(+) & t(+, -)\underline{M}(+) \\ t(-, t)\underline{M}(-) & t(-, +)\underline{M}(-) & t(-, -)\underline{M}(-) \end{pmatrix} \\ &= \lambda^{-1} \begin{pmatrix} t(t, t)E_3 & t(t, +)E_3 & t(t, -)E_3 \\ t(+, t)E_3 & t(+, +)E_3 & t(+, -)E_3 \\ t(-, t)E_3 & t(-, +)E_3 & t(-, -)E_3 \end{pmatrix} \begin{pmatrix} \underline{M}(t) & 0 & 0 \\ 0 & \underline{M}(+) & 0 \\ 0 & 0 & \underline{M}(-) \end{pmatrix} \\ &= \lambda^{-1} (T \otimes E_3) \|\underline{M}\|. \end{aligned} \quad (1.39)$$

Introducing everything into Eq. (1.35) we get

$$\langle R^2 \rangle = Nl^2 + 2l^T (B^T \otimes E_3) \left\{ \sum_{n=1}^N (N-n) S^n \right\} (A \otimes E_3) \underline{l}. \quad (1.40)$$

For infinitely long chains we can analytically sum, obtaining

$$\frac{\langle R^2 \rangle}{Nl^2} = 1 + \frac{2}{l^2} l^T (B^T \otimes E_3) \frac{S}{E_9 - S} (A \otimes E_3) \underline{l} \quad (1.41)$$

where  $E_9$  is the 9-d unit matrix. In this derivation of Eq. (1.41) we have made use of  $\sum_{n=1}^N (N-n)x^n = (N-x\frac{d}{dx}) \sum_{n=1}^N x^n = N\frac{x}{1-x} - x\frac{(1-x^N)}{(1-x)^2} \approx N\frac{x}{1-x}$  for large  $N$ .

Similar equations, but much more complicated, may be derived for  $\langle R^4 \rangle$ . For these and other equations we refer to P.J. Flory, *Statistical Mechanics of Chain Molecules*.

## 1.5 The radius of gyration

An alternative measure of the size of a polymer chain is provided by its radius of gyration, which may be measured by light scattering experiments. It is defined by

$$R_g^2 = \frac{1}{(N+1)} \sum_{i=0}^N \langle (\vec{R}_i - \vec{R}_G)^2 \rangle \quad (1.42)$$

$$\vec{R}_G = \frac{1}{(N+1)} \sum_{i=0}^N \vec{R}_i. \quad (1.43)$$

It measures the average squared distance to the centre of gravity  $\vec{R}_G$ .

A little manipulation yields

$$\begin{aligned} R_g^2 &= \frac{1}{(N+1)} \sum_{i=0}^N \langle R_i^2 - 2\vec{R}_i \cdot \vec{R}_G + R_G^2 \rangle \\ &= \frac{1}{(N+1)} \sum_{i=0}^N \langle R_i^2 \rangle - \frac{1}{(N+1)^2} \sum_{i=0}^N \sum_{j=0}^N \langle \vec{R}_i \cdot \vec{R}_j \rangle \\ &= \frac{1}{(N+1)^2} \sum_{i=0}^N \sum_{j=0}^N \langle R_i^2 - \vec{R}_i \cdot \vec{R}_j \rangle \\ &= \frac{1}{2(N+1)^2} \sum_{i=0}^N \sum_{j=0}^N \langle (\vec{R}_i - \vec{R}_j)^2 \rangle \\ &= \frac{1}{(N+1)^2} \sum_{i=0}^{N-1} \sum_{j=i+1}^N \langle (\vec{R}_i - \vec{R}_j)^2 \rangle. \end{aligned} \quad (1.44)$$

It is clear that expressions for  $R_g$  can easily be obtained using methods similar to the ones of the previous section.

## 1.6 Some results for polyethylene

Polyethylene was modelled with a RIS model:  $\vartheta = 112^\circ$ ,  $\varphi_+ = 120^\circ$ ,  $\varphi_t = 0^\circ$ ,  $\varphi_- = -120^\circ$ ,  $\epsilon_1(\varphi_+) = \epsilon_1(\varphi_-) = 500$  cal/mol and  $l = 1.54$  Å.

Using methods similar to those of section 4, the second and fourth moment of the end-to-end vector were calculated. For chains of length up to 17 monomers these quantities were calculated exactly by generating all configurations and averaging  $R^2$  respectively  $R^4$ . In Fig. (1.3) is plotted  $\langle R^4 \rangle / \langle R^2 \rangle^2$  as a function of the number of monomers in the chain. Notice that for large  $N$  the graph approaches a limit value of  $5/3$ :

$$\lim_{N \rightarrow \infty} \frac{\langle R^4 \rangle_N}{(\langle R^2 \rangle_N)^2} = \frac{5}{3}. \quad (1.45)$$

In Fig. (1.4) the radius of gyration is plotted as a function of  $N$ . For chains consisting of 1000 monomers or more the radius of gyration can be written like

$$R_g = bN^{1/2}. \quad (1.46)$$

Notice that this behaviour sets in at the same value of  $N$  at which  $\langle R^4 \rangle / \langle R^2 \rangle^2$  attains its plateau value  $5/3$ . Many more results may be found in the book of Flory.

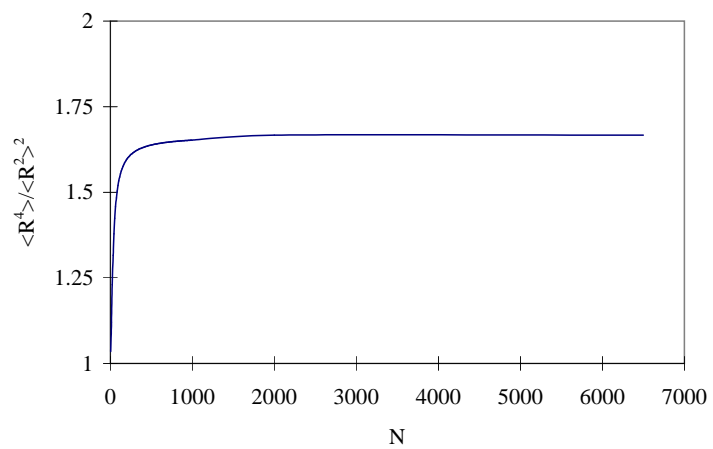


Figure 1.3:

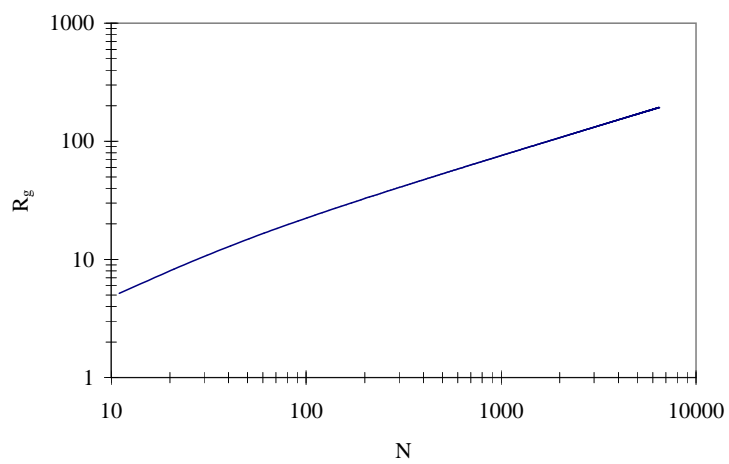


Figure 1.4:

## Appendix A

The choice of the local coordinate frames is given in Fig. (1.5). This figure also gives our conventions concerning the angles  $\vartheta_i$  and  $\varphi_i$ . The coordinate frame unit vectors are calculated according to

$$\hat{e}^x(i) = -\frac{1}{\sin\vartheta}\hat{r}_{i-1} + \frac{\cos\vartheta}{\sin\vartheta}\hat{r}_i \quad (1.47)$$

$$\hat{e}^y(i) = \frac{1}{\sin\vartheta}\hat{r}_{i-1} \times \hat{r}_i \quad (1.48)$$

$$\hat{e}^z(i) = \hat{r}_i \quad (1.49)$$

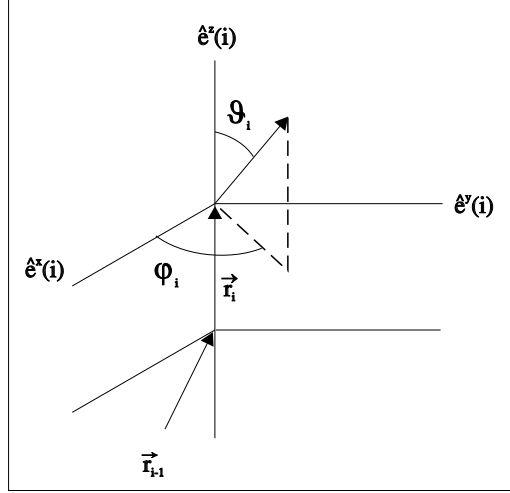


Figure 1.5: Local coordinate frames

## Appendix B

From Fig. (1.5) it follows that

$$\hat{r}_{i+1} = \sin\vartheta \cos\varphi_i \hat{e}^x(i) + \sin\vartheta \sin\varphi_i \hat{e}^y(i) + \cos\vartheta \hat{e}^z(i). \quad (1.50)$$

Using this in

$$\hat{e}^x(i+1) = -\frac{1}{\sin\vartheta}\hat{r}_i + \frac{\cos\vartheta}{\sin\vartheta}\hat{r}_{i+1} \quad (1.51)$$

$$\hat{e}^y(i+1) = \frac{1}{\sin\vartheta}\hat{r}_i \times \hat{r}_{i+1} \quad (1.52)$$

$$\hat{e}^z(i+1) = \hat{r}_{i+1} \quad (1.53)$$

one easily derives

$$\hat{e}^x(i+1) = \cos\vartheta \cos\varphi_i \hat{e}^x(i) + \cos\vartheta \sin\varphi_i \hat{e}^y(i) - \sin\vartheta \hat{e}^z(i) \quad (1.54)$$

$$\hat{e}^y(i+1) = -\sin\varphi_i \hat{e}^x(i) + \cos\varphi_i \hat{e}^y(i) \quad (1.55)$$

$$\hat{e}^z(i+1) = \sin\vartheta \cos\varphi_i \hat{e}^x(i) + \sin\vartheta \sin\varphi_i \hat{e}^y(i) + \cos\vartheta \hat{e}^z(i) \quad (1.56)$$

from which the matrix  $\underline{M}(\varphi_i)$  may be read off.



## Chapter 2

# Integral equations for polymer liquids

### 2.1 Flory's hypothesis

In the previous chapter we have treated a model which takes into account the short range excluded volume effect. The long range excluded volume effect however has not been taken into account, in concreto: two monomers whose indices along the chain differ by more than 4 units may happen to occupy the same position, something that in a real system is impossible. As we shall see in the next chapter Eq. (1.46) is a direct consequence of this fact. In fact numerous computer simulations have shown that in reality

$$R_g = bN^\nu, \quad (2.1)$$

$$\nu = 0.588. \quad (2.2)$$

One interesting point about  $\nu$  is that it is a universal coefficient, i.e. that it is independent of the details of the chain and depends only on very few parameters, like for example the dimension of the chain.

Calculation of the coefficient  $\nu$  is an extremely hard problem. In the case of a chain in vacuum like in Eq. (2.2) one may intuitively understand why  $\nu > 0.5$ . Consider building the chain by consecutively adding monomers. At every step there are on average more monomers in the back than in front of the last monomer. Therefore the chain can gain entropy by going out, and being larger than a chain in which the new monomer does not feel its predecessors.

For chains in a solvent the story may be different. In a good solvent the situation is like in vacuum. In a bad solvent however apart from the excluded volume, which is nothing but the short range van der Waals interaction, two monomers may feel an effective attraction at distances just outside the van der Waals radius. In case this attraction is strong enough it may cause the chain to shrink. Of course there is a whole range between good and bad solvents, and at some point both effects cancel and Eq. (1.46) holds true. A solvent having this property is called a  $\Theta$ -solvent.

Now we come to Flory's argument. In a polymer melt, every monomer is isotropically surrounded by other monomers, and there is no way to decide whether the surrounding monomers belong to the same chain as the monomer at hand or to a different one. Consequently there will be no preferred direction and the polymer melt will act as a  $\Theta$ -solvent.

Flory's hypothesis has gotten some credibility from experiments and computer simulations. Here we shall adopt the hypothesis and use it to calculate the in-

tramolecular distribution function defined below. Using the integral equation theory of simple liquids we shall then calculate the complete radial distribution function.

## 2.2 The radial distribution function

Consider a simple atomic liquid or colloidal suspension. The average density  $\rho(r)$  at a distance  $r$  of a given particle is defined to be  $\rho g(r)$ , i.e.

$$\rho(r) = \rho g(r). \quad (2.3)$$

Here  $\rho$  is the average density in the fluid. Notice that  $\rho(r)$  is a conditional density; it is the density at  $\vec{r}$ , given a particle is present in the origin. A qualitative picture of  $g(r)$  is given in Fig. (2.1); it is called the radial distribution function.

It is clear that  $g(r)$  should go to 1 for large  $r$ . At very short  $r$  the radial distribution function must be zero, because two particles cannot occupy the same space. Outside the van der Waals diameter, there is a peak because the remaining  $N - 1$  particles try to diffuse into the region occupied by the one at the origin. The surplus of particles in the first peak causes a lack of particles a little bit further on, explaining the minimum of  $g(r)$  around  $r = 2\sigma$ .

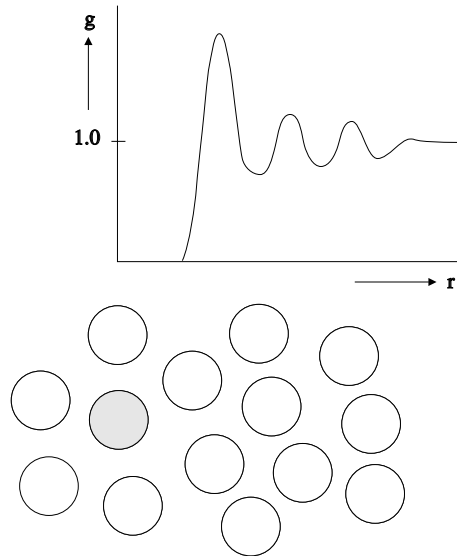


Figure 2.1: Radial distribution function.

Radial distribution functions may be measured by means of scattering experiments, for example by means of X-ray or neutron scattering in the case of atomic liquids, or by means of SAXS, SANS or light scattering in the case of colloidal suspensions. Generally the sample produces a scattering amplitude

$$F(\vec{k}) = \int d^3r B(\vec{r}) \exp\{i\vec{k} \cdot \vec{r}\} \quad (2.4)$$

at the detector. Here  $B(\vec{r})$  is the scattering power at position  $\vec{r}$ , and  $\vec{k}$  is defined by

$$\vec{k} = \vec{k}_{\text{out}} - \vec{k}_{\text{in}} \quad (2.5)$$

where  $\vec{k}_{\text{out}}$  and  $\vec{k}_{\text{in}}$  are the wavevectors of the outgoing and incoming wave respectively. The measured intensity is proportional to

$$\langle |F(\vec{k})|^2 \rangle = \langle \int d^3r \int d^3r' : B(\vec{r})B(\vec{r}') \exp\{i\vec{k} \cdot (\vec{r} - \vec{r}')\} \rangle. \quad (2.6)$$

Writing the scattering power like

$$B(\vec{r}) = \sum_j b(\vec{r} - \vec{r}_j) \quad (2.7)$$

we find after some algebra

$$\langle |F(\vec{k})|^2 \rangle = N |f(\vec{k})|^2 \langle \frac{1}{N} \sum_i \sum_j \exp\{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)\} \rangle \quad (2.8)$$

$$f(\vec{k}) = \int d^3x b(\vec{x}) \exp\{i\vec{k} \cdot \vec{x}\} \quad (2.9)$$

The important quantity for us is

$$\begin{aligned} & \langle \frac{1}{N} \sum_i \sum_j \exp\{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)\} \rangle \\ &= 1 + \frac{1}{N} \langle \sum_{i \neq j} \sum \exp\{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)\} \rangle \\ &= 1 + \int d^3r \rho g(r) \exp\{i\vec{k} \cdot \vec{r}\} \\ &= 1 + \int d^3r \rho \{g(r) - 1\} \exp\{i\vec{k} \cdot \vec{r}\} + (2\pi)^3 \rho \delta(\vec{k}). \end{aligned} \quad (2.10)$$

The  $\delta$ -function only gives a contribution at  $\vec{k} = \vec{0}$ , i.e. to the forward scattering. At all other  $k$ -values one measures the scattering factor

$$S(k) = 1 + \rho \int d^3r (g(r) - 1) \exp\{i\vec{k} \cdot \vec{r}\} \quad (2.11)$$

i.e. essentially the Fourier transform of the total correlation function  $h(r) = g(r) - 1$ .

Once we have determined the radial distribution function we may calculate several quantities of interest, like

$$U = \frac{3}{2} N k T + \frac{1}{2} N \int d^3r \rho g(r) \phi(r) \quad (2.12)$$

$$P = \frac{N k T}{V} - \frac{1}{6} \rho^2 \int d^3r g(r) r \frac{d\phi}{dr} \quad (2.13)$$

where  $\phi(r)$  is the interaction potential between two particles in the system, and  $U$  and  $P$  are the thermodynamic energy and pressure respectively. Another important relation is the compressibility equation

$$\rho k T \kappa_T = 1 + \rho \int d^3r (g(r) - 1) = S(k = 0). \quad (2.14)$$

For more information we refer to any book on liquid state theory, like for example J. -P. Hansen and I. R. McDonald, Theory of simple liquids.

### 2.3 The Ornstein-Zernike equation and integral equations

As we have stressed at the beginning of the previous section, the surplus of density  $\rho(r) - \rho = \rho h(r)$  may be regarded as being the convolution of a short range function and  $\rho h(r)$  itself. We formalize this by introducing the direct correlation function  $c(r)$  according to

$$h(r) = c(r) + \int d^3 r' c(r') \rho h(|\vec{r} - \vec{r}'|). \quad (2.15)$$

The total correlation at  $\vec{r}$  is the sum of a direct correlation plus an indirect contribution coming from all surrounding points: the surplus induced at  $\vec{r}'$  causes an effect at  $\vec{r}$  (see Fig. (2.2)). Notice that Eq. (2.15) is nothing more but a definition of the total correlation function.

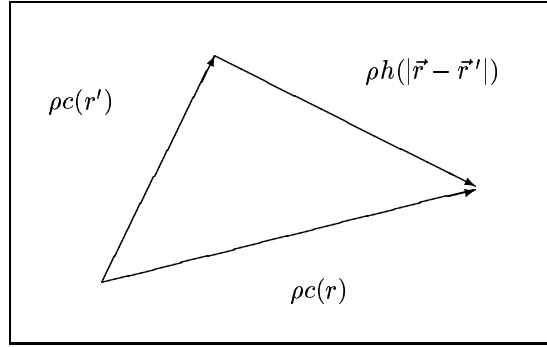


Figure 2.2: Contributions to the total correlation function.

A simple relation exists between  $S(k)$  and the Fourier transform  $\hat{c}(k)$  of  $c(r)$ . Fourier transforming Eq. (2.15) we get

$$\hat{h}(k) = \hat{c}(k) + \rho \hat{c}(k) \hat{h}(k) \quad (2.16)$$

$$S(k) = 1 + \rho \hat{h}(k) = \frac{1}{1 - \rho \hat{c}(k)}. \quad (2.17)$$

Fourier transforms are defined by

$$\hat{f}(\vec{k}) = \int d^3 r f(\vec{r}) \exp\{i\vec{k} \cdot \vec{r}\} \quad (2.18)$$

$$f(\vec{r}) = \frac{1}{(2\pi)^3} \int d^3 k \hat{f}(\vec{k}) \exp\{-i\vec{k} \cdot \vec{r}\} \quad (2.19)$$

We have introduced the direct correlation function such that it is a short range function. Writing

$$g(r) = \exp\{-\beta\phi(r)\} y(r) \quad (2.20)$$

we see that  $g(r)$  equals  $y(r)$  outside the range of the potential. In order to obtain a short ranged function to approximate  $c(r)$ , we try

$$c(r) = g(r) - y(r). \quad (2.21)$$

This equation is called the Percus-Yevick closure. Together with the Ornstein-Zernike equation it constitutes the Percus-Yevick equation.

For a first principles derivation of the Percus-Yevick equation we refer to the literature mentioned above. Using a slightly different approximation than the one producing the PY closure, one may also derive

$$y(r) = \exp\{h(r) - c(r)\}. \quad (2.22)$$

This result is called the hypernetted chain closure. Together with the OZ equation it gives the HNC equation.

Here we restrict ourselves to mentioning that both equations have been very successful in predicting correlation functions, the PY equation being the more successful one in the case of hard spheres, and the HNC being the more successful one in the case of Lennard-Jones atoms.

## 2.4 Molecular liquids

We shall now generalize the results of the previous section to molecular liquids. We view the liquid at first as being a mixture of atomic liquids, containing as many components as there are atoms in the molecule. Eq. (2.3) then simply generalizes to

$$\rho_{\alpha\beta}(r) = G_{\alpha\beta}(r)\rho_{\beta} \quad (2.23)$$

where  $\rho_{\alpha\beta}$  is the density of  $\beta$ -atoms at a distance  $r$  from a given  $\alpha$ -atom. We use capital  $G_{\alpha\beta}(r)$  here for reasons to become clear in a minute. Defining

$$H_{\alpha\beta}(r) = G_{\alpha\beta}(r) - 1 \quad (2.24)$$

the OZ equation becomes

$$H_{\alpha\beta}(r)\rho_{\beta} = C_{\alpha\beta}(r)\rho_{\beta} + \sum_{\gamma} \int d^3 r' C_{\alpha\gamma}(r')\rho_{\gamma} H_{\gamma\beta}(|\vec{r} - \vec{r}'|)\rho_{\beta}. \quad (2.25)$$

Dividing by  $\rho_{\beta}$  and Fourier transforming we get in matrix notation

$$\hat{H}(k) = \hat{C}(k) + \hat{C}(k)\rho\hat{H}(k). \quad (2.26)$$

Here  $\rho$  is the diagonal matrix with elements  $\rho_{\alpha\beta} = \delta_{\alpha\beta}\rho_{\alpha}$ . The transition to  $\vec{k}$ -space is only for reason of simpler notation.

We of course know that the correlations between the atoms are partly due to the fact that they form molecules. Therefore we write

$$\begin{aligned} \hat{H}(k)\rho &= [\hat{H}(k)\rho]_{\text{intra}} + [\hat{H}(k)\rho]_{\text{inter}} \\ &= [\hat{\Omega}(k) - 1] + \hat{h}(k)\rho \end{aligned} \quad (2.27)$$

where  $\hat{\Omega}(k) - 1$  stems from the intramolecular correlations and  $\hat{h}(k)\rho$  from the intermolecular correlations.

In the ideal gas limit we may approximate

$$\hat{H}(k)\rho = \hat{\Omega}(k) - 1 \quad (2.28)$$

which, when introduced into the OZ equation (2.26) yields

$$\hat{C}(k)\rho = 1 - \hat{\Omega}(k)^{-1}. \quad (2.29)$$

We therefore write in general

$$\hat{C}(k)\rho = 1 - \hat{\Omega}(k)^{-1} + \hat{c}(k)\rho \quad (2.30)$$

where  $\hat{c}(k)$  is called the intermolecular part of the direct correlation function matrix. Introducing Eqs. (2.27) and (2.30) into the OZ equation we get after some algebra

$$\hat{h}(k) = \hat{\Omega}(k)\hat{c}(k)\hat{\Omega}(k) + \hat{\Omega}(k)\hat{c}(k)\rho\hat{h}(k) \quad (2.31)$$

where we have used the fact that  $\rho$  and  $\hat{\Omega}(k)$  commute. For pure molecular liquids this follows from the fact that  $\rho$  is equal to the molecular density times the unit matrix. A proof for molecular mixtures is a little bit more involved. Once we know the intramolecular correlation  $\hat{\Omega}(k)$  we may calculate the intermolecular correlation from Eq. (2.31) by using one of the closure relations

$$c_{\alpha\beta}(r) = g_{\alpha\beta}(r) - y_{\alpha\beta}(r) \quad (\text{PY}) \quad (2.32)$$

$$y_{\alpha\beta}(r) = \exp\{h_{\alpha\beta}(r) - c_{\alpha\beta}(r)\} \quad (\text{HNC}) \quad (2.33)$$

which we simply try in analogy with similar calculations on simple liquids. Of course this may turn out to be a very crude approximation. Experience so far shows that it works well as long as one is interested in describing the local structure in the liquid. For very small values of the wavevector  $k$ , or equivalently at large values of  $r$  problems occur which make thermodynamic predictions unreliable.

We end this section with some remarks about the intramolecular correlation function. We Fouriertransform Eq. (2.27), and next add  $\rho_\beta$  to each of its elements, obtaining

$$G_{\alpha\beta}(r) = \frac{1}{\rho_\beta} \{\Omega_{\alpha\beta}(r) - \delta_{\alpha\beta}\delta(r)\} + g_{\alpha\beta}(r). \quad (2.34)$$

Here  $\rho_\beta G_{\alpha\beta}(r)$  is the density of  $\beta$ -atoms at a distance  $r$  from an  $\alpha$ -atom; when  $\alpha = \beta$  the atom at the origin does, by definition, not contribute to the density.  $\rho_\beta g_{\alpha\beta}(r)$  is defined in exactly the same way, with the proviso that the  $\beta$ -atom should be on another molecule than the  $\alpha$ -atom. Using these definitions we see that  $\Omega_{\alpha\beta}(r) - \delta_{\alpha\beta}\delta(r)$  is the density of  $\beta$ -atoms at a distance  $r$  from an  $\alpha$ -atom, where  $\alpha$  and  $\beta$  should be on the same molecule, and where, in the case  $\alpha = \beta$ , the atom at the origin does not contribute to the density. So finally we conclude that  $\Omega_{\alpha\beta}(r)$  is the density of  $\beta$ -atoms at a distance  $r$  from an  $\alpha$ -atom, with the  $\delta$ -peak included when  $\alpha = \beta$ . In the latter case  $\Omega_{\alpha\alpha} = \delta(r)$ , because the total number of  $\alpha$ -atoms in each molecule equals one.

## 2.5 Polymer RISM

We now apply the RISM formalism to polymeric liquids. For simplicity we restrict the presentation to polyethylene, each  $\text{CH}_2$  will be viewed as one "atom". It is clear that if boundary effects may be neglected, all monomers along the chain are equivalent, i.e. that  $G_{\alpha\beta}(r)$  and all other functions do not depend on  $\alpha$  or  $\beta$ . Remember that  $\alpha$  and  $\beta$  each run from 0 to  $N$ , where  $(N+1)$  is the number of monomers per chain. The monomer-monomer radial distribution function then is

$$G(r) = \frac{1}{\rho_m} \sum_{\beta} G_{\alpha\beta}(r)\rho_\beta = G_{\alpha\beta}(r) \quad (2.35)$$

where  $\rho_m = (N+1)\rho_\beta$  is the monomer density. Introducing Eq. (2.34) into Eq. (2.35) we get

$$G(r) = \frac{1}{\rho_m} \{\omega(r) - \delta(r)\} + g(r) \quad (2.36)$$

$$\omega(r) = \sum_{\beta} \Omega_{\alpha\beta}(r) \quad (2.37)$$

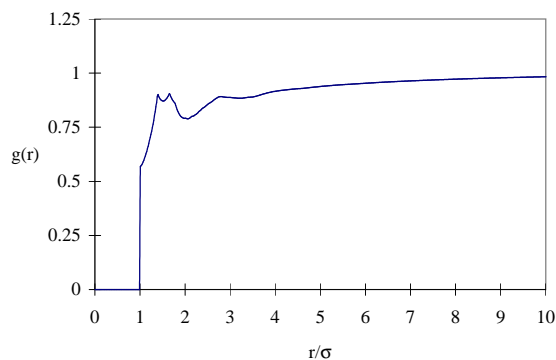


Figure 2.3: Intermolecular distribution function.

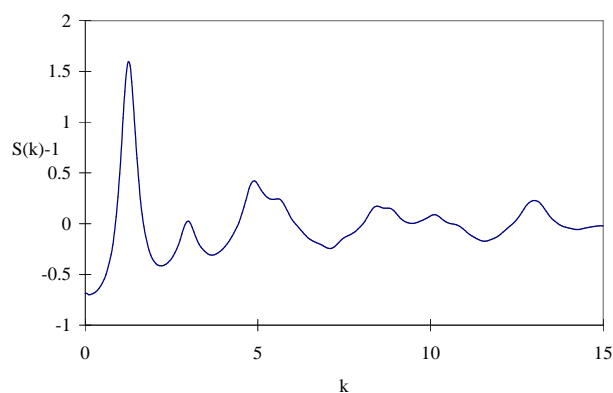


Figure 2.4: Scattering function.

where  $g(r) = g_{\alpha\beta}(r)$ . Using  $h(r) = h_{\alpha\beta}(r)$  and  $c(r) = c_{\alpha\beta}(r)$  in Eq. (2.31) we derive

$$\hat{h}(k) = \hat{\omega}(k)\hat{c}(k)\hat{\omega}(k) + \rho_m\hat{\omega}(k)\hat{c}(k)\hat{h}(k) \quad (2.38)$$

$\hat{\omega}(k)$  may be calculated using the methods of Chapter 1. Some details are given in Appendix A.

We now apply the method to polyethylene, which will be modelled by a RIS model with characteristics given in section 2.6. The interaction between two monomers on different chains is modelled by a hard sphere interaction with diameter  $\sigma = 3.9\text{\AA}$ . Moreover  $N = 6416$  and  $\rho_m = 33.58\text{nm}^{-3}$ . Calculations were done with PY closure.

In Fig. (2.3) is given the intermolecular distribution function. We clearly see what is called the "correlation hole" by de Gennes; the intermolecular distribution gradually rises to its limit value 1, with only little structure. The scattering function is given in Fig. (2.4), and is in perfect agreement with X-ray experiments, except at very small values of  $k$ .

We give two more results, from MD simulations this time. In Fig. (2.5) is given the intramolecular oxygen-oxygen correlation in PEO. The simulation was done with GROMOS united atom potentials. The box consisted of two chains of 800 monomers each;  $\rho_m = 14.45\text{nm}^{-3}$  and  $T = 400K$ . The corresponding intermolecular correlation function is given in Fig. (2.6).

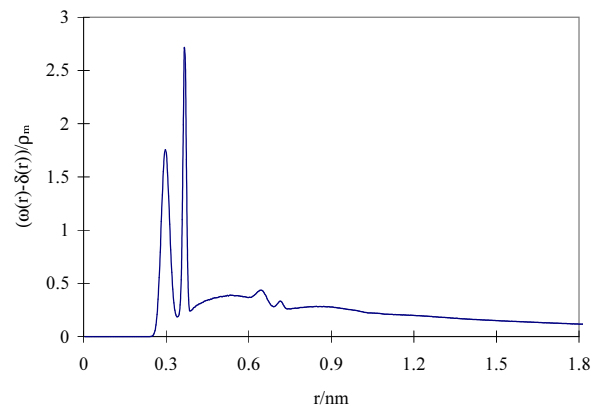


Figure 2.5: Intramolecular oxygen-oxygen correlation in polyethyleneoxide.

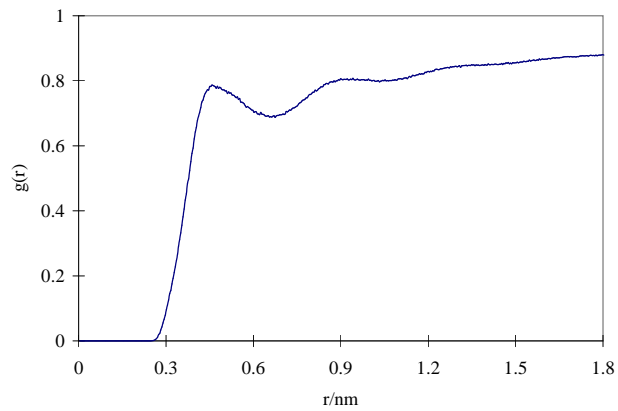


Figure 2.6: Intermolecular correlation function in polyethyleneoxide.



## Appendix A

According to Eq. (2.37)

$$\omega(r) = \frac{1}{N+1} \sum_{\alpha} \sum_{\beta} \Omega_{\alpha\beta}(r) \quad (2.39)$$

From the discussion at the end of section 2.4 it follows

$$\begin{aligned} \hat{\Omega}_{\alpha\beta}(k) &= \int d^3r e^{i\vec{k}\cdot\vec{r}} \Omega_{\alpha\beta}(r) \\ &= \delta_{\alpha\beta} + (1 - \delta_{\alpha\beta}) \int d^3r e^{i\vec{k}\cdot\vec{r}} \Omega_{\alpha\beta}(r) \\ &= \delta_{\alpha\beta} + (1 - \delta_{\alpha\beta}) 2\pi \int_0^{\infty} dr r^2 \Omega_{\alpha\beta}(r) \int_{-1}^1 d(\cos\theta) e^{ikr \cos\theta} \\ &= \delta_{\alpha\beta} + (1 - \delta_{\alpha\beta}) 4\pi \int_0^{\infty} dr r^2 \Omega_{\alpha\beta}(r) \frac{\sin kr}{kr} \\ \hat{\Omega}_{\alpha\beta}(k) &= \delta_{\alpha\beta} + (1 - \delta_{\alpha\beta}) \left\langle \frac{\sin kr_{\alpha\beta}}{kr_{\alpha\beta}} \right\rangle. \end{aligned} \quad (2.40)$$

The average may be calculated using the methods of Chapter 1. Usually it is a good approximation to describe  $\hat{\Omega}_{\alpha\beta}(k)$  with a damped sine function

$$\begin{aligned} \hat{\Omega}_{\alpha\beta}(k) &= \frac{\sin(B_{\alpha\beta}k)}{B_{\alpha\beta}k} \exp\{-A_{\alpha\beta}^2 k^2\} \\ A_{\alpha\beta}^2 &= \frac{1}{6} \langle r_{\alpha\beta}^2 \rangle (1 - C_{\alpha\beta}) \\ B_{\alpha\beta}^2 &= \langle r_{\alpha\beta}^2 \rangle C_{\alpha\beta} \\ C_{\alpha\beta}^2 &= \frac{1}{2} \left\{ 5 - 3 \frac{\langle r_{\alpha\beta}^4 \rangle}{\langle r_{\alpha\beta}^2 \rangle^2} \right\}. \end{aligned} \quad (2.41)$$

From Fig. (1.3) we conclude that  $c_{\alpha\beta} = 0$  for  $|\alpha - \beta| \geq 1000$ , in which case  $\hat{\Omega}_{\alpha\beta}(k)$  is a simple Gaussian.



## Chapter 3

# The Gaussian chain

### 3.1 Simple models

When introducing new concepts, and developing a theory of dynamic processes in polymeric systems it is of great value to have available simple models which can be treated analytically. Of course these models should incorporate the essential aspects of what are polymers.

Several simple models have been proposed ever since the beginning of microscopic modelling of polymers, two of the more important ones being the freely rotating chain and the freely jointed chain. In both models bond lengths are constrained to a fixed value. In the freely rotating chain the angle  $\vartheta$  is also constrained, while the angle  $\varphi$  may randomly take any value. In the freely jointed chain both the angles  $\vartheta$  and  $\varphi$  are random. We shall say a few more things about these models in Appendix A and Appendix B.

In these lectures we shall make use of an even simpler model, the Gaussian chain.

### 3.2 The central limit theorem

We shall discuss here the central limit theorem as applied to the calculation of the distribution function of the end-to-end vector.

Consider a chain consisting of  $N$  independent bond vectors  $\vec{r}_i$ . By this we mean that the probability density in configuration space  $\Psi(\vec{r}^N)$  may be written as

$$\Psi(\vec{r}^N) = \prod_{i=1}^N \psi(\vec{r}_i). \quad (3.1)$$

Assume further that the bond vector probability density depends only on the length of the bond vector, and has zero mean. For the second moment we write

$$\langle r^2 \rangle = \int d^3 r r^2 \psi(r) = b^2. \quad (3.2)$$

The distribution of the end-to-end vector may be calculated according to

$$\Omega(\vec{R}) = \langle \delta(\vec{R} - \sum_{i=1}^N \vec{r}_i) \rangle. \quad (3.3)$$

The central limit theorem then states that

$$\Omega(\vec{R}) = \left\{ \frac{3}{2\pi N b^2} \right\}^{3/2} \exp \left\{ -\frac{3R^2}{2N b^2} \right\} \quad (3.4)$$

i.e. that the end-to-end vector has Gaussian distribution.

In order to prove Eq. (3.4) we write

$$\begin{aligned}
\Omega(\vec{R}) &= \frac{1}{(2\pi)^3} \int d^3 k \langle \exp\{i\vec{k} \cdot (\vec{R} - \sum_i \vec{r}_i)\} \rangle \\
&= \frac{1}{(2\pi)^3} \int d^3 k e^{i\vec{k} \cdot \vec{R}} \langle \exp\{-i\vec{k} \cdot \sum_i \vec{r}_i\} \rangle \\
&= \frac{1}{(2\pi)^3} \int d^3 k e^{i\vec{k} \cdot \vec{R}} \left\{ \int d^3 r e^{-i\vec{k} \cdot \vec{r}} \psi(r) \right\}^N. \tag{3.5}
\end{aligned}$$

For  $k = 0$ , the Fourier transform of  $\psi(r)$  will be equal to one. Because  $\psi(r)$  has zero mean and finite second moment, the Fourier transform of  $\psi(r)$  will have its maximum around  $k = 0$  and go to zero for large values of  $k$ . Raising such a function to the  $N$ 'th power leaves us with a function that differs from zero only very close to the origin, and which may be approximated by

$$\begin{aligned}
\left\{ \int d^3 r e^{-i\vec{k} \cdot \vec{r}} \psi(r) \right\}^N &\approx \left\{ 1 - \frac{1}{2} \langle (\vec{k} \cdot \vec{r})^2 \rangle \right\}^N \\
&\approx 1 - \frac{1}{2} N \langle (\vec{k} \cdot \vec{r})^2 \rangle \\
&= 1 - \frac{1}{6} N k^2 b^2 \tag{3.6}
\end{aligned}$$

for small values of  $k$ , and by zero for the values of  $k$  where  $1 - \frac{1}{6} N k^2 b^2$  is negative. This again may be approximated by  $\exp\{-\frac{1}{6} N k^2 b^2\}$  for all values of  $k$ . Then

$$\begin{aligned}
\Omega(\vec{R}) &= \frac{1}{(2\pi)^3} \int d^3 k \exp\{i\vec{k} \cdot \vec{R} - \frac{1}{6} N k^2 b^2\} \\
&= I(R_x) I(R_y) I(R_z) \tag{3.7}
\end{aligned}$$

$$\begin{aligned}
I(R_x) &= \frac{1}{2\pi} \int dk_x \exp\{iR_x k_x - \frac{1}{6} N b^2 k_x^2\} \\
&= \left\{ \frac{3}{2\pi N b^2} \right\}^{1/2} \exp\left\{ -\frac{3R_x^2}{2N b^2} \right\}. \tag{3.8}
\end{aligned}$$

Combining Eqs. (3.7) and (3.8) we get Eq. (3.4).

Now apply the above result to a general RIS chain. To this end we write

$$\vec{R} = \sum_{i=1}^N \vec{r}_i = \sum_{n=1}^{N/\lambda} \left( \sum_{i=1}^{\lambda} \vec{r}_{(n-1)\lambda+i} \right) = \sum_{n=1}^{N/\lambda} \vec{x}_n \tag{3.9}$$

i.e. we combine  $\lambda$  bond vectors into one new vector as in Fig. (3.1) where  $\lambda = 5$ . For  $\lambda$  large enough the distribution of these new vectors meets the conditions on  $\psi(\vec{r})$  used to derive the central limit theorem. Notice that this holds true because there are no long range excluded volume interactions in the RIS chain. Writing

$$\langle x^2 \rangle = \lambda b^2 \tag{3.10}$$

we find that the distribution of the end-to-end vector is again given by Eq. (3.4). We conclude that every model which does not incorporate the long range excluded volume effect will have a Gaussianly distributed end-to-end vector. It is an easy exercise to check that in this case Eq. (1.45) holds true.

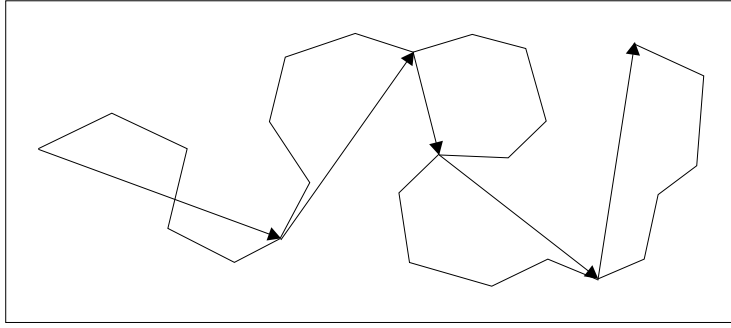


Figure 3.1: Five bonds combined into one new vector.

### 3.3 The Gaussian chain

The simplest model consistent with a Gaussian end-to-end vector distribution is one in which every bond vector itself is Gaussianly distributed. The probability distribution in configuration space then is

$$P(\vec{r}_1, \dots, \vec{r}_N) = \left\{ \frac{3}{2\pi b^2} \right\}^{\frac{3}{2}N} \exp \left\{ - \sum_{i=1}^N \frac{3}{2b^2} r_i^2 \right\}. \quad (3.11)$$

One may think of this model as a coarse grained model of a polymer, where like in the previous section, every vector  $\vec{r}_i$  actually is the sum of  $\lambda_i$  bond vectors, and where  $\lambda$  is large enough for  $\psi(\vec{r}_i)$  to be Gaussian. Usually the model is pictured as a chain of  $N$  beads connected by springs.

It is a useful exercise to calculate  $\Omega(\vec{R})$  from Eqs. (3.3) and (3.11).

### 3.4 Green's function method

In this section we shall investigate the Gaussian chain at a level where the distance between two consecutive beads may be considered to be small.

Suppose we study a Gaussian chain in an external field with potential  $\Phi(\vec{R})$ . The distribution in configuration space then reads

$$P(\vec{R}_0, \dots, \vec{R}_N) = \frac{1}{Z} \exp \left\{ - \sum_{i=1}^N \frac{3}{2b^2} (\vec{R}_i - \vec{R}_{i-1})^2 - \beta \sum_{i=0}^N \Phi(\vec{R}_i) \right\} \quad (3.12)$$

where  $Z$  is a normalizing constant. In many cases we are interested in properties depending on the position vectors of only a few beads along the chain. It will turn out to be useful then to introduce the Green's function

$$G(\vec{R}, \vec{R}'; N) = \left\{ \frac{3}{2\pi b^2} \right\}^{\frac{3}{2}N} \int d^3 R_1 \dots \int d^3 R_{N-1} \\ \times \exp \left\{ - \sum_{i=1}^N \frac{3}{2b^2} (\vec{R}_i - \vec{R}_{i-1})^2 - \beta \sum_{i=1}^N \Phi(\vec{R}_i) \right\} \quad (3.13)$$

where  $\vec{R}_0 = \vec{R}'$  and  $\vec{R}_N = \vec{R}$ . Notice that the Green's function is not normalized. One easily verifies however

$$G(\vec{R}, \vec{R}'; N+n) = \int d^3 R'' G(\vec{R}, \vec{R}''; n) G(\vec{R}'', \vec{R}'; N). \quad (3.14)$$

This equation is called the Chapman-Kolmogorov equation. For this equation to hold true, it is essential that the second summation in the exponent in Eq. (3.13) starts at  $i = 1$ , and not at  $i = 0$  as in Eq. (3.12).

Now we shall treat  $N$  like a continuous variable. In Appendix C we shall prove that  $G(\vec{R}, \vec{R}'; N)$  is the solution of

$$\left\{ \frac{\partial}{\partial N} - \frac{b^2}{6} \nabla_{\vec{R}}^2 + \beta \Phi(\vec{R}) \right\} G(\vec{R}, \vec{R}'; N) = 0 \quad (3.15)$$

$$\lim_{N \rightarrow 0} G(\vec{R}, \vec{R}'; N) = \delta(R - R'). \quad (3.16)$$

Accepting this for the moment we may immediately write down the formal solution

$$G(\vec{R}, \vec{R}'; N) = \sum_{n=1}^{\infty} e^{-E_n N} \Psi_n(\vec{R}) \Psi_n(\vec{R}') \quad (3.17)$$

$$\left\{ -\frac{b^2}{6} \nabla_{\vec{R}}^2 + \beta \Phi(\vec{R}) \right\} \Psi_n(\vec{R}) = E_n \Psi_n(\vec{R}). \quad (3.18)$$

One easily checks this by introducing Eq. (3.17) into Eq. (3.15) and using Eq. (3.18). Eq. (3.16) is nothing but the closure equation of the complete set of functions.

Knowing  $G(\vec{R}, \vec{R}'; N)$  makes it possible to calculate all kinds of averages:

$$Z = \left\{ \frac{3}{2\pi b^2} \right\}^{-\frac{3}{2}N} \int d^3 R \int d^3 R' G(\vec{R}, \vec{R}'; N) \exp\{-\beta \Phi(\vec{R}')\} \quad (3.19)$$

$$\langle A(\vec{R}_n) \rangle = \frac{1}{Z} \int d^3 R \int d^3 R' \int d^3 R_n G(\vec{R}, \vec{R}_n; N - n) A(\vec{R}_n) G(\vec{R}_n, \vec{R}'; n) \exp\{-\beta \Phi(\vec{R}')\} \quad (3.20)$$

etc.

### 3.5 One Gaussian chain in a box

As an example of the use of the Green's function method, we calculate the pressure exerted by a Gaussian chain on the walls of a confining box.

The potential is zero everywhere inside the box, and infinite everywhere outside the box. Then  $\Psi_n(\vec{R}) = 0$  at the walls of the box. Solving Eq. (3.18) yields

$$\Psi_{n_1, n_2, n_3}(\vec{R}) = \varphi_{n_1}^{(1)}(R_1) \varphi_{n_2}^{(2)}(R_2) \varphi_{n_3}^{(3)}(R_3) \quad (3.21)$$

$$E_{n_1, n_2, n_3} = \epsilon_{n_1}^{(1)} + \epsilon_{n_2}^{(2)} + \epsilon_{n_3}^{(3)} \quad (3.22)$$

where

$$\varphi_n^{(i)}(R) = \sqrt{2/L_i} \sin(\pi n R/L_i) \quad (3.23)$$

$$\epsilon_n^{(i)} = \frac{\pi^2 b^2}{6L_i^2} n^2. \quad (3.24)$$

The partition function then reads

$$Z = \left\{ \frac{3}{2\pi b^2} \right\}^{-\frac{3}{2}N} Z_1 Z_2 Z_3 \quad (3.25)$$

$$Z_i = \int dR_i \int dR'_i \sum_n \exp\{-\epsilon_n^{(i)} N\} \varphi_n^{(i)}(R_i) \varphi_n^{(i)}(R'_i) \quad (3.26)$$

Introducing the eigenfunctions and eigenvalues from Eqs. (3.23) and (3.24) we get

$$Z_i = \frac{8}{\pi^2} L_i \sum_{n=1}^{\infty} ' \frac{1}{n^2} \exp\left\{-\frac{\pi^2 b^2}{6L_i^2} n^2 N\right\} \quad (3.27)$$

where the prime at the summation sign indicates that only odd  $n$  should occur in the sum.

Now look at two limits

i.  $\sqrt{N}b \ll L_i$

The polymer is much smaller than the box

$$Z_i = \frac{8}{\pi^2} L_i \sum_{n=1}^{\infty} ' \frac{1}{n^2} = L_i \quad (3.28)$$

$$Z = \left\{ \frac{3}{2\pi b^2} \right\}^{-\frac{3}{2}N} L_1 L_2 L_3. \quad (3.29)$$

The pressure on wall one is

$$P_1 = -\frac{1}{L_2 L_3} \frac{\partial}{\partial L_1} A = \frac{kT}{L_2 L_3} \frac{\partial}{\partial L_1} \ln Z = \frac{kT}{V} \quad (3.30)$$

i.e. independent of the wall number, and equal to the ideal gas result.

ii.  $\sqrt{N}b \gg L_i$

The polymer is very much constrained by the box

$$Z_i \approx \frac{8}{\pi^2} L_i \exp\left\{-\frac{\pi^2 b^2}{6L_i^2} N\right\} \quad (3.31)$$

$$P_1 = \frac{kT}{L_2 L_3} \frac{\partial}{\partial L_1} \left\{ \ln L_1 - \frac{\pi^2 b^2}{6L_1^2} N \right\} \quad (3.32)$$

$$= \frac{kT}{L_1 L_2 L_3} \left\{ 1 + \frac{\pi^2 b^2}{3L_1^2} N \right\} \approx \frac{\pi^2 b^2}{3L_1^2} \frac{NkT}{V}. \quad (3.33)$$

In this case the pressure on the different walls depends on the size of the box orthogonal to the wall.

## Appendix A

In the case of a freely rotating chain it is rather easy to calculate the mean square end-to-end vector, the radius of gyration and the persistence length.

The freely rotating chain is defined by saying that the angles  $\vartheta_i$  are fixed and that all  $\varphi_i$  may randomly take a value in  $[0, 2\pi]$ . In order to treat this chain mathematically we introduce the probability density in configuration space  $P_N(\vec{r}_1, \dots, \vec{r}_N)$  and define

$$P_n(\vec{r}_1, \dots, \vec{r}_n) = \int d^3 r_{n+1} \dots \int d^3 r_N P_N(\vec{r}_1, \dots, \vec{r}_N) \quad (3.34)$$

$$P_n(\vec{r}_1, \dots, \vec{r}_n) = Q(\vec{r}_n; \vec{r}_1, \dots, \vec{r}_{n-1}) P_{n-1}(\vec{r}_1, \dots, \vec{r}_{n-1}). \quad (3.35)$$

So  $P_n(\vec{r}_1, \dots, \vec{r}_n)$  is the probability density to find the first  $n$  bond vectors in the configuration  $\vec{r}_1, \dots, \vec{r}_n$ , and  $Q(\vec{r}_n; \vec{r}_1, \dots, \vec{r}_{n-1})$  is the conditional probability density to find bond vector  $n$  in state  $\vec{r}_n$ , given that the preceding vectors are in

configuration  $\vec{r}_1, \dots, \vec{r}_{n-1}$ . Integrating Eq. (3.35) over  $\vec{r}_n$  and using Eq. (3.34) we obtain

$$\int d^3 r_n Q(\vec{r}_n; \vec{r}_1, \dots, \vec{r}_{n-1}) = 1. \quad (3.36)$$

In our case

$$Q(\vec{r}_n; \vec{r}_1, \dots, \vec{r}_{n-1}) = q(\vec{r}_n; \vec{r}_{n-1}) \quad (3.37)$$

i.e. the conditional probability to have vector  $n$  in state  $\vec{r}_n$  depends only on the state of vector  $n-1$ . In mathematics it is said that the chain has the Markov property. Using the definitions given so far we may write

$$P_n(\vec{r}_1, \dots, \vec{r}_n) = q(\vec{r}_n; \vec{r}_{n-1})q(\vec{r}_{n-1}; \vec{r}_{n-2}) \dots q(\vec{r}_2; \vec{r}_1)P_1(\vec{r}_1). \quad (3.38)$$

We may now easily calculate all quantities of interest.

We first notice, that in the present case

$$\int d^3 r_n \vec{r}_n q(\vec{r}_n; \vec{r}_{n-1}) = \cos \vartheta \vec{r}_{n-1}. \quad (3.39)$$

Repeatedly using this equation we calculate

$$\begin{aligned} \langle \vec{r}_i \cdot \vec{r}_{i+n} \rangle &= \int d^3 r_1 \dots \int d^3 r_{i+n} \vec{r}_i \cdot \vec{r}_{i+n} q(\vec{r}_{i+n}; \vec{r}_{i+n-1}) \dots q(\vec{r}_2; \vec{r}_1) P(\vec{r}_1) \\ &= l^2 (\cos \vartheta)^n. \end{aligned} \quad (3.40)$$

Using this in Eqs. (1.29) and (1.44) we get for large  $N$ :

$$\langle R^2 \rangle = Nl^2 \frac{1 + \cos \vartheta}{1 - \cos \vartheta} \quad (3.41)$$

$$R_g^2 = \frac{1}{6} Nl^2 \frac{1 + \cos \vartheta}{1 - \cos \vartheta}. \quad (3.42)$$

Another quantity characteristic of the chain is the persistence length. It is defined by

$$a = \sum_{i=1}^N \langle \vec{r}_i \cdot \hat{r}_1 \rangle = \left\langle \left( \sum_{i=1}^N \vec{r}_i \right) \cdot \hat{r}_1 \right\rangle \quad (3.43)$$

and it gives the average of the projection of the end-to-end vector on the direction of the first bond. For large  $N$  we may write Eq. (1.29) like  $\langle R^2 \rangle = Nl^2 + 2N(la - l^2)$  from which we get

$$a = \frac{1}{2} \left( l + \frac{\langle R^2 \rangle}{Nl} \right) = l \frac{1}{1 - \cos \vartheta}. \quad (3.44)$$

We see that for a rod the persistence length is infinite.

## Appendix B

In the case of the freely jointed chain both the angles  $\vartheta$  and  $\varphi$  are completely random. Then

$$\langle R^2 \rangle = Nl^2 \quad (3.45)$$

$$\begin{aligned} R_g^2 &= \frac{1}{(N+1)^2} \sum_{i=0}^{N-1} \sum_{j=i+1}^N (j-i)l^2 = \frac{1}{(N+1)^2} \sum_{i=0}^N \sum_{k=1}^{N-i} kl^2 \\ &= \frac{1}{(N+1)^2} \sum_{i=0}^{N-1} \frac{1}{2} (N-i)(N-i+1)l^2 = \frac{1}{(N+1)^2} \sum_{k=1}^N \frac{1}{2} k(k+1)l^2 \\ &= \frac{N+2}{N+1} \frac{1}{6} Nl^2. \end{aligned} \quad (3.46)$$



A simple trick exists to calculate all the moments of the chain. To this end, look at the Fourier transform

$$\begin{aligned}
\hat{\Omega}(\vec{k}) &= \int d^3 R e^{-i\vec{k}\cdot\vec{R}} \Omega(\vec{R}) \\
&= \sum_n \frac{1}{n!} \int d^3 R (-i\vec{k}\cdot\vec{R})^n \Omega(\vec{R}) \\
&= \sum_n \frac{(-ik)^n}{n!} \int d^3 R (\cos\vartheta)^n R^n \Omega(R) \\
&= \sum_n \frac{(-ik)^n}{n!} 2\pi \int_{-1}^1 d\cos\vartheta (\cos\vartheta)^n \int dR R^2 R^n \Omega(R) \\
&= \sum_n' \frac{(-ik)^n}{(n+1)!} 4\pi \int dR R^2 R^n \Omega(R) \\
&= \sum_n (-1)^n \frac{k^{2n}}{(2n+1)!} \langle R^{2n} \rangle
\end{aligned} \tag{3.47}$$

The prime at the summation sign in the last but one line indicates that only terms with even  $n$  should occur in the sum. Eq. (3.47) tells us that

$$\langle R^{2n} \rangle = (2n+1)(-1)^n \left. \frac{d^{2n} \hat{\Omega}}{dk^{2n}} \right|_{k=0} \tag{3.48}$$

In order to use this formula we need to know  $\hat{\Omega}(k)$ . Inverting Eq. (3.5) we get

$$\begin{aligned}
\hat{\Omega}(k) &= \langle e^{-i\vec{k}\cdot\vec{r}} \rangle^N \\
&= \left\{ \frac{\sin kl}{kl} \right\}^N.
\end{aligned} \tag{3.49}$$

Although the trick is nice, the task to evaluate the derivations is rather tedious.

## Appendix C

We shall first show that for small  $n$  we may write

$$G(\vec{R}, \vec{R}'; n) = \exp\{-n\beta\Phi(\vec{R})\} \left\{ \frac{3}{2\pi n b^2} \right\}^{\frac{3}{2}n} \exp\left\{-\frac{3}{2n b^2} (\vec{R} - \vec{R}')^2\right\}. \tag{3.50}$$

Taking the limit for  $n \rightarrow 0$  we then easily check Eq. (3.16). In order to prove Eq. (3.50) we first notice that  $n$  being small, all  $R_i$  in the exponent in Eq. (3.13) are approximately equal to  $\vec{R}$ , from which it follows that

$$\begin{aligned}
G(\vec{R}, \vec{R}'; n) &= \exp\{-n\beta\Phi(\vec{R})\} \left\{ \frac{3}{2\pi b^2} \right\}^{\frac{3}{2}n} \\
&\int d^3 R_1 \cdots \int d^3 R_{n-1} \exp\left\{-\sum_{i=1}^n \frac{3}{2b^2} (\vec{R}_i - \vec{R}_{i-1})^2\right\}.
\end{aligned} \tag{3.51}$$

It is now simply a matter of successively performing the integrals. The simplest way to do this is by induction.

$$\left\{ \frac{3}{2\pi b^2} \right\}^{\frac{3}{2}n} \int d^3 R_1 \cdots \int d^3 R_{n-1} \exp\left\{-\sum_{i=1}^n \frac{3}{2b^2} (\vec{R}_i - \vec{R}_{i-1})^2\right\}$$

$$\begin{aligned}
&= \left\{ \frac{3}{2\pi b^2} \right\}^{\frac{3}{2}} \left\{ \frac{3}{2\pi(n-1)b^2} \right\}^{\frac{3}{2}} \int d^3 R_{n-1} \\
&\exp \left\{ -\frac{3}{2(n-1)b^2} (\vec{R}_{n-1} - \vec{R}')^2 - \frac{3}{2b^2} (\vec{R}_{n-1} - \vec{R})^2 \right\} \\
&= \left\{ \frac{3}{2\pi n b^2} \right\}^{\frac{3}{2}} \exp \left\{ -\frac{3}{2n b^2} (\vec{R} - \vec{R}')^2 \right\}. \tag{3.52}
\end{aligned}$$

The first equals sign is the induction step, and the second one is the final proof.

Now look at the Chapman-Kolmogorov equation (3.14), and take  $n$  to be small. Then  $G(\vec{R}, \vec{R}''; n)$  differs from zero only if  $\vec{R}''$  is in the neighbourhood of  $\vec{R}$ . We therefore expand the second factor  $G(\vec{R}'', \vec{R}'; N)$  in Eq. (3.14) with respect to  $\vec{R}''$ .

$$\begin{aligned}
G(\vec{R}'', \vec{R}'; N) &= G(\vec{R}, \vec{R}'; N) \\
&+ \sum_{\alpha} (R_{\alpha}'' - R_{\alpha}) \frac{\partial}{\partial R_{\alpha}} G(\vec{R}, \vec{R}'; N) \\
&+ \frac{1}{2} \sum_{\alpha} \sum_{\beta} (R_{\alpha}'' - R_{\alpha})(R_{\beta}'' - R_{\beta}) \frac{\partial^2}{\partial R_{\alpha} \partial R_{\beta}} G(\vec{R}, \vec{R}'; N) \tag{3.53}
\end{aligned}$$

where  $R_{\alpha}$  denotes the  $\alpha$ 'th Cartesian component of  $\vec{R}$ . Introducing Eqs. (3.50) and (3.53) into (3.14) we get

$$G(\vec{R}, \vec{R}'; N+n) = \exp\{-n\beta\Phi(\vec{R})\} \left\{ 1 + \frac{1}{6} n b^2 \nabla_{\vec{R}}^2 \right\} G(\vec{R}, \vec{R}'; N) \tag{3.54}$$

where we have used

$$\begin{aligned}
&\left\{ \frac{3}{2\pi n b^2} \right\}^{\frac{3}{2}} \int d^3 R'' (R_{\alpha}'' - R_{\alpha})(R_{\beta}'' - R_{\beta}) \exp \left\{ -\frac{3}{2n b^2} (\vec{R} - \vec{R}'')^2 \right\} \\
&= \frac{1}{3} n b^2 \delta_{\alpha\beta} \tag{3.55}
\end{aligned}$$

For small  $n$ , we expand the exponent

$$G(\vec{R}, \vec{R}'; N+n) = \{1 - n\beta\Phi(\vec{R})\} \left\{ 1 + \frac{1}{6} n b^2 \nabla_{\vec{R}}^2 \right\} G(\vec{R}, \vec{R}'; N). \tag{3.56}$$

Collecting terms of order  $n$ , and using

$$\frac{\partial}{\partial N} G(\vec{R}, \vec{R}'; N) = \lim_{n \rightarrow 0} \frac{1}{n} \{G(\vec{R}, \vec{R}'; N+n) - G(\vec{R}, \vec{R}'; N)\} \tag{3.57}$$

we finally arrive at Eq. (3.15).

# Chapter 4

## Stochastic processes

### 4.1 The Langevin equation

In this chapter we shall study the basics of the theory of stochastic processes. This is most easily done in the language of colloidal suspensions.

Consider a colloidal particle suspended in a liquid. On its path through the liquid it will continuously collide with the liquid molecules. Because on average the particle will collide more often on the front side than on the back side, it will experience a systematic force proportional with its velocity, and directed opposite to its velocity. Besides this systematic force the particle will experience a stochastic force  $\vec{F}(t)$ . The equations of motion then read

$$\frac{d\vec{r}}{dt} = \vec{v} \quad (4.1)$$

$$\frac{d\vec{v}}{dt} = -\xi\vec{v} + \vec{F}. \quad (4.2)$$

From hydrodynamics we know that the friction constant  $\xi$  is given by

$$\xi = 6\pi\eta a/m \quad (4.3)$$

where  $\eta$  is the viscosity of the solvent and  $a$  is the radius of the particle. We shall derive this and some other results from hydrodynamics in the next chapter.

Solving Eq. (4.2) yields

$$\vec{v}(t) = \vec{v}_0 e^{-\xi t} + \int_0^t d\tau e^{-\xi(t-\tau)} \vec{F}(\tau). \quad (4.4)$$

If we want to get some useful information out of this, we have to average over all possible realizations of  $\vec{F}(t)$ , with the initial velocity as a condition. A useful quantity for example is

$$\begin{aligned} \langle \vec{v}(t) \cdot \vec{v}(t) \rangle_{\vec{v}_0} &= v_0^2 e^{-2\xi t} + 2 \int_0^t d\tau e^{-\xi(2t-\tau)} \vec{v}_0 \cdot \langle \vec{F}(\tau) \rangle_{\vec{v}_0} \\ &+ \int_0^t d\tau' \int_0^t d\tau e^{-\xi(2t-\tau-\tau')} \langle \vec{F}(\tau) \cdot \vec{F}(\tau') \rangle_{\vec{v}_0}. \end{aligned} \quad (4.5)$$

In order to continue we have to make some assumptions about the conditional averages of the stochastic forces. In view of the chaotic character of the stochastic forces the following assumptions seem to be appropriate

$$\langle \vec{F}(t) \rangle = 0 \quad (4.6)$$

$$\langle \vec{F}(t) \cdot \vec{F}(t') \rangle_{\vec{v}_0} = C_{\vec{v}_0} \delta(t - t'). \quad (4.7)$$

Here and elsewhere we omit the subscript  $\vec{v}_0$ , when the quantity of interest turns out to be independent of  $\vec{v}_0$ . Using Eqs. (4.6) and (4.7) in Eq. (4.5) we get

$$\langle \vec{v}(t) \cdot \vec{v}(t) \rangle_{\vec{v}_0} = v_0^2 e^{-2\xi t} + \frac{C_{\vec{v}_0}}{2\xi} (1 - e^{-2\xi t}). \quad (4.8)$$

For large  $t$  this should be equal to  $3kT/m$ , from which it follows that

$$\langle \vec{F}(t) \cdot \vec{F}(t') \rangle = 6 \frac{kT}{m} \xi \delta(t - t'). \quad (4.9)$$

This result is called the fluctuation-dissipation theorem.

Integrating Eq. (4.4) we get

$$\vec{r}(t) = \vec{r}_0 + \vec{v}_0 \frac{1}{\xi} (1 - e^{-\xi t}) + \int_0^t d\tau \int_0^\tau d\tau' e^{-\xi(\tau-\tau')} \vec{F}(\tau') \quad (4.10)$$

from which we calculate the mean square displacement

$$\langle (\vec{r}(t) - \vec{r}_0)^2 \rangle_{\vec{v}_0} = \frac{v_0^2}{\xi^2} (1 - e^{-\xi t})^2 + \frac{3kT}{m\xi^2} (2\xi t - 3 + 4e^{-\xi t} - e^{-2\xi t}). \quad (4.11)$$

For very large  $t$  this becomes

$$\langle (\vec{r}(t) - \vec{r}_0)^2 \rangle = \frac{6kT}{m\xi} t \quad (4.12)$$

from which we get the Einstein relation

$$D = \frac{kT}{m\xi} \quad (4.13)$$

where we have used  $\langle (\vec{r}(t) - \vec{r}_0)^2 \rangle = 6Dt$ .

## 4.2 The Fokker-Planck equation

An alternative way to study stochastic processes is by means of distribution functions. Let  $\mathcal{G}(\vec{r}, \vec{v}; \vec{r}_0, \vec{v}_0; t)$  be the probability density to find a particle at time  $t$  at position  $\vec{r}$  with velocity  $\vec{v}$ , given that at  $t = 0$  it was at position  $\vec{r}_0$  with velocity  $\vec{v}_0$ . We shall demonstrate in Appendix A that this function satisfies

$$\frac{\partial}{\partial t} \mathcal{G}(\vec{z}; \vec{z}_0; t) + \vec{v} \cdot \vec{\nabla}_{\vec{r}} \mathcal{G}(\vec{z}; \vec{z}_0; t) = \vec{\nabla}_{\vec{v}} \cdot \xi \vec{v} \mathcal{G}(\vec{z}; \vec{z}_0; t) + \vec{\nabla}_{\vec{v}}^2 \frac{\xi kT}{m} \mathcal{G}(\vec{z}; \vec{z}_0; t) \quad (4.14)$$

$$\lim_{t \rightarrow 0} \mathcal{G}(\vec{z}; \vec{z}_0; t) = \delta(\vec{r} - \vec{r}_0) \delta(\vec{v} - \vec{v}_0) \quad (4.15)$$

where  $\mathcal{G}(\vec{z}; \vec{z}_0; t)$  is short hand for  $\mathcal{G}(\vec{r}, \vec{v}; \vec{r}_0, \vec{v}_0; t)$ . Eq. (4.14) together with the initial value condition Eq. (4.15) is called the Fokker-Planck equation.

We shall not treat this equation any further here, except for one quick remark. The probability to find the particle at time  $t$  with velocity  $\vec{v}$ , at any position, given it was at  $t = 0$  at position  $\vec{r}_0$  with velocity  $\vec{v}_0$  is given by

$$\tilde{\mathcal{G}}(\vec{v}; \vec{v}_0; t) = \int d^3 r \mathcal{G}(\vec{v}, \vec{r}; \vec{v}_0, \vec{r}_0; t) \quad (4.16)$$

where we have assumed the system is translational invariant, i.e. both sides of Eq. (4.16) are independent of  $\vec{r}_0$ . Integrating Eq. (4.14) with respect to  $\vec{r}$  we get

$$\frac{\partial}{\partial t} \tilde{\mathcal{G}}(\vec{v}; \vec{v}_0; t) = \vec{\nabla}_{\vec{v}} \cdot \xi \vec{v} \tilde{\mathcal{G}}(\vec{v}; \vec{v}_0; t) + \nabla_{\vec{v}}^2 \frac{\xi kT}{m} \tilde{\mathcal{G}}(\vec{v}; \vec{v}_0; t) \quad (4.17)$$

$$\lim_{t \rightarrow 0} \tilde{\mathcal{G}}(\vec{v}; \vec{v}_0; t) = \delta(\vec{v} - \vec{v}_0) \quad (4.18)$$

We may easily obtain the solution to this equation by using the results of the previous section. To this end we notice that  $\vec{U}(t) = \vec{v}(t) - \vec{v}_0 e^{-\xi t}$  according to Eq. (4.4) is a sum of many random vectors. According to the central limit theorem therefore it must have a Gaussian distribution. The first and second moments are given by

$$\langle U_\alpha(t) \rangle = 0 \quad (4.19)$$

$$\langle U_\alpha(t) U_\beta(t) \rangle = \delta_{\alpha\beta} \frac{kT}{m} (1 - e^{-2\xi t}) \quad (4.20)$$

where we have used the fluctuation-dissipation theorem in the form

$$\langle F_\alpha(t) F_\beta(t') \rangle = \delta_{\alpha\beta} 2 \frac{kT}{m} \xi \delta(t - t'). \quad (4.21)$$

Using Eqs. (4.19) and (4.20) we may write

$$\tilde{\mathcal{G}}(\vec{v}; \vec{v}_0; t) = \left\{ \frac{m}{2\pi kT(1 - e^{-2\xi t})} \right\}^{\frac{3}{2}} \exp \left\{ -\frac{m(\vec{v} - \vec{v}_0 e^{-\xi t})^2}{2kT(1 - e^{-2\xi t})} \right\} \quad (4.22)$$

Although it is a tedious task, it is not difficult to check that this result indeed is the solution to Eqs. (4.17) and (4.18).

### 4.3 The Smoluchowski time scale

From Eq. (4.8) we see that the particle loses its memory of its initial velocity after a time span  $\tau \approx 1/\xi$ . Using equipartition its initial velocity may be put equal to  $\sqrt{3kT/m}$ . The distance it travels, divided by its diameter then is

$$\frac{1}{a} \frac{\sqrt{3kT/m}}{\xi} = \frac{\sqrt{3mkT}}{6\pi\eta a^2} \approx 10^{-5} \quad (4.23)$$

where the value  $10^{-5}$  refers to normal colloidal particles. 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, like in dynamic light scattering experiments, we may restrict our attention to the space coordinates, and average over the velocities.

A very crude way to arrive at the equations of motion is the following. On the timescale referred to above, and which is called the Smoluchowski time scale, the average velocity is zero, or constant in case we apply an external force. Eq. (4.2) then becomes

$$\vec{0} = -\xi \vec{v} - \frac{1}{m} \vec{\nabla} \Phi + \vec{F} \quad (4.24)$$

where  $\Phi(\vec{r})$  is the external potential. Rewriting this, and using the fluctuation-dissipation theorem we get

$$\frac{d\vec{r}}{dt} = -\frac{1}{\xi m} \vec{\nabla} \Phi + \vec{f} \quad (4.25)$$

$$\langle \vec{f}(t) \cdot \vec{f}(t') \rangle = 6 \frac{kT}{m\xi} \delta(t - t') = 6D\delta(t - t'). \quad (4.26)$$

These equations are correct when  $D$  is independent of the position of the particle. However it is clear that the random term now refers to a completely different timescale than in the original Langevin equation; nevertheless  $\vec{f}(t)$  is obtained here from  $\vec{F}(t)$  by dividing the latter by  $\xi$ , meaning that the "derivation" given here

must be wrong. The flaw occurs when the instantaneous acceleration is put equal to zero in Eq. (4.24). In fact it is the average acceleration which should be put equal to zero.

In the next section we shall derive the Smoluchowski equation, governing the time development of the distribution of particles on the Smoluchowski timescale. In Appendix C we shall then show that the correct Langevin equations which lead to the Smoluchowski equation are:

$$\frac{d\vec{r}}{dt} = -\frac{1}{m\xi}\vec{\nabla}\Phi + \vec{\nabla}D + \vec{f} \quad (4.27)$$

$$\langle \vec{f}(t) \cdot \vec{f}(t') \rangle = 6D\delta(t-t'). \quad (4.28)$$

In our treatment of the Rouse chain in Chapter 6 the diffusion constant will be independent of  $\vec{r}$ , in which case Eqs. (4.27) and (4.28) are equivalent to Eqs. (4.25) and (4.26).

## 4.4 The Smoluchowski equation

We shall now derive the equivalent of the Fokker-Planck equation, but this time applicable at the Smoluchowski timescale.

Suppose we are given a distribution  $G(\vec{r}; \vec{r}_0; t)$  of particles which were at position  $\vec{r}_0$  at time  $t = 0$ . We assume that the particles are at every instant of time in thermal equilibrium with respect to their velocities. A flux will exist, given by

$$\vec{j}(\vec{r}, \vec{r}_0, t) = -D\vec{\nabla}G(\vec{r}; \vec{r}_0; t) - \frac{1}{m\xi}G(\vec{r}; \vec{r}_0; t)\vec{\nabla}\Phi(\vec{r}) \quad (4.29)$$

where  $D$  is the diffusion constant, occurring in  $\langle (\vec{r}(t) - \vec{r}_0)^2 \rangle = 6Dt$ , and  $\xi$  is the friction coefficient on the Smoluchowski timescale. At equilibrium, the flux must be zero and the distribution be equal to

$$G_{\text{eq}}(\vec{r}) = C \exp\{-\beta\Phi(\vec{r})\}. \quad (4.30)$$

Using this in Eq. (4.29) while setting  $\vec{j}(\vec{r}, t) = 0$ , leads to the Einstein equation (4.13).

Introducing Eq. (4.29) into the equation of particle conservation

$$\frac{\partial}{\partial t}G(\vec{r}; \vec{r}_0; t) = -\vec{\nabla} \cdot \vec{j}(\vec{r}, \vec{r}_0, t) \quad (4.31)$$

we get the Smoluchowski equation

$$\frac{\partial}{\partial t}G(\vec{r}; \vec{r}_0; t) = \vec{\nabla} \cdot \frac{1}{m\xi}G(\vec{r}; \vec{r}_0; t)\vec{\nabla}\Phi(\vec{r}) + \vec{\nabla} \cdot D\vec{\nabla}G(\vec{r}; \vec{r}_0; t) \quad (4.32)$$

$$\lim_{t \rightarrow 0} G(\vec{r}; \vec{r}_0; t) = \delta(\vec{r} - \vec{r}_0) \quad (4.33)$$

In the remaining part of this section we shall substantiate the above derivation. First we define the particle distribution on the Smoluchowski timescale by

$$G(\vec{r}, \vec{r}_0; t) = \int d^3v \bar{G}(\vec{r}, \vec{v}, \vec{r}_0; t) \quad (4.34)$$

$$\bar{G}(\vec{r}, \vec{v}, \vec{r}_0; t) = \int d^3v_0 \left\{ \frac{m}{2\pi kT} \right\}^{\frac{3}{2}} \exp\left\{-\frac{1}{2}\beta m v_0^2\right\} \mathcal{G}(\vec{r}, \vec{v}, \vec{r}_0, \vec{v}_0; t). \quad (4.35)$$

Averaging the Fokker-Planck equation over the initial velocities and integrating over  $\vec{v}$ , we find the continuity equation Eq. (4.31), with

$$\begin{aligned} \vec{j}(\vec{r}, \vec{r}_0; t) &= \int d^3v \vec{v} \bar{G}(\vec{r}, \vec{v}, \vec{r}_0; t) \\ &= G(\vec{r}, \vec{r}_0; t) \vec{V}(\vec{r}, \vec{r}_0; t) \end{aligned} \quad (4.36)$$

where the second step serves to define the velocity  $\vec{V}(\vec{r}, \vec{r}_0; t)$  at time  $t$  at position  $\vec{r}$ , given that the particle was originally at  $\vec{r}_0$ .

We next derive an equation describing the time development of the velocity  $\vec{V}(\vec{r}, \vec{r}_0; t)$ . To this end we multiply the Fokker-Planck equation by  $\vec{v}$ , average over the initial velocities, and integrate over  $\vec{v}$ , obtaining

$$\frac{\partial}{\partial t} G \vec{V} = -\vec{\nabla} \cdot \int d^3v \vec{v} \bar{v} \bar{G} - \xi G \vec{V} - \frac{1}{m} G \vec{\nabla} \Phi. \quad (4.37)$$

Using the continuity equation and rearranging we find

$$m \left( \frac{\partial}{\partial t} + \vec{V} \cdot \vec{\nabla} \right) \vec{V} = -m \xi \vec{V} - \vec{\nabla} \Phi - \frac{m}{G} \vec{\nabla} \cdot \int d^3v (\vec{v} - \vec{V})(\vec{v} - \vec{V}) \bar{G}. \quad (4.38)$$

In a strongly damped system the integral on the right hand side yields the velocity fluctuation at position  $\vec{r}$ , multiplied by the probability to find the particle at position  $\vec{r}$ , which is  $GkT/m$ . On the left hand side we recognize the acceleration of the particle at  $\vec{r}$  (see section 5.1). Eq. (4.38) may then be written as

$$m \frac{D}{Dt} \vec{V} = -m \xi \vec{V} - \vec{\nabla} \Phi - kT \vec{\nabla} \ln G. \quad (4.39)$$

In a strongly damped system the average particle velocity is almost constant. We therefore put the left hand side of Eq. (4.39) equal to zero and solve for  $\vec{V}$ . Introducing the result into Eq. (4.36) we find the flux Eq. (4.29) and next the Smoluchowski equation. In Eq. (4.39)  $-kT \vec{\nabla} \ln G$  is called the Brownian force.

In appendix B we shall present an alternative derivation of the Smoluchowski equation. In appendix C we will demonstrate that the Langevin equations (4.27), (4.28) are equivalent to the Smoluchowski equation.

## Appendix A

We shall derive the Fokker-Planck equation by looking at  $\int d^6z F(\vec{z}) \mathcal{G}(\vec{z}; \vec{z}_0; t)$  for any function  $F(\vec{z})$ . Because we are always interested in averages like this, equations that may be derived using this object are all we need. (In mathematical terms  $\mathcal{G}(\vec{z}; \vec{z}_0; t)$  is a distribution or generalized function, not an ordinary function).

Our proof very much resembles the one in Appendix 3.C. Our starting point is again the Chapman-Kolmogorov equation

$$\mathcal{G}(\vec{z}; \vec{z}_0; t + \Delta t) = \int d^6z' \mathcal{G}(\vec{z}; \vec{z}'; \Delta t) \mathcal{G}(\vec{z}'; \vec{z}_0; t). \quad (4.40)$$

Multiplying by  $F(\vec{z})$  and integrating yields

$$\int d^6z F(\vec{z}) \mathcal{G}(\vec{z}; \vec{z}_0; t + \Delta t) = \int d^6z \int d^6z' F(\vec{z}) \mathcal{G}(\vec{z}; \vec{z}'; \Delta t) \mathcal{G}(\vec{z}'; \vec{z}_0; t). \quad (4.41)$$

Now we shall perform the integral with respect to  $z$  on the right hand side. Because  $\mathcal{G}(\vec{z}; \vec{z}'; \Delta t)$  differs from zero only when  $\vec{z}$  is in the neighbourhood of  $\vec{z}'$ , we expand

$F(\vec{z})$  around  $\vec{z}'$

$$\begin{aligned} F(\vec{z}) &= F(\vec{z}') + \sum_{\alpha} (z_{\alpha} - z'_{\alpha}) \frac{\partial}{\partial z'_{\alpha}} F(\vec{z}') \\ &\quad + \frac{1}{2} \sum_{\alpha} \sum_{\beta} (z_{\alpha} - z'_{\alpha})(z_{\beta} - z'_{\beta}) \frac{\partial^2}{\partial z'_{\alpha} \partial z'_{\beta}} F(\vec{z}'). \end{aligned} \quad (4.42)$$

Introducing this into Eq. (4.41) we get

$$\begin{aligned} &\int d^6 z F(\vec{z}) \mathcal{G}(\vec{z}; \vec{z}_0; t + \Delta t) \\ &= \int d^6 z' \left\{ \int d^6 z \mathcal{G}(\vec{z}; \vec{z}'; \Delta t) \right\} \mathcal{G}(\vec{z}'; \vec{z}_0; t) F(\vec{z}') \\ &\quad + \sum_{\alpha} \int d^6 z' \left\{ \int d^6 z (z_{\alpha} - z'_{\alpha}) \mathcal{G}(\vec{z}; \vec{z}'; \Delta t) \right\} \mathcal{G}(\vec{z}'; \vec{z}_0; t) \frac{\partial}{\partial z'_{\alpha}} F(\vec{z}') \\ &\quad + \frac{1}{2} \sum_{\alpha} \sum_{\beta} \int d^6 z' \left\{ \int d^6 z (z_{\alpha} - z'_{\alpha})(z_{\beta} - z'_{\beta}) \mathcal{G}(\vec{z}; \vec{z}'; \Delta t) \right\} \\ &\quad \times \mathcal{G}(\vec{z}'; \vec{z}_0; t) \frac{\partial^2}{\partial z'_{\alpha} \partial z'_{\beta}} F(\vec{z}'). \end{aligned} \quad (4.43)$$

Now we make use of

$$\int d^6 z \mathcal{G}(\vec{z}; \vec{z}'; \Delta t) = 1 \quad (4.44)$$

$$\int d^6 z (\vec{r} - \vec{r}') \mathcal{G}(\vec{z}; \vec{z}'; \Delta t) = \vec{v}' \Delta t \quad (4.45)$$

$$\int d^6 z (\vec{v} - \vec{v}') \mathcal{G}(\vec{z}; \vec{z}'; \Delta t) = -\xi \vec{v}' \Delta t \quad (4.46)$$

$$\int d^6 z (\vec{r} - \vec{r}') (\vec{r} - \vec{r}') \mathcal{G}(\vec{z}; \vec{z}'; \Delta t) = 0 \quad (4.47)$$

$$\int d^6 z (\vec{r} - \vec{r}') (\vec{v} - \vec{v}') \mathcal{G}(\vec{z}; \vec{z}'; \Delta t) = 0 \quad (4.48)$$

$$\int d^6 z (\vec{v} - \vec{v}') (\vec{v} - \vec{v}') \mathcal{G}(\vec{z}; \vec{z}'; \Delta t) = 2 \frac{kT}{m} \xi \mathbf{1} \Delta t \quad (4.49)$$

which hold true to the first order in  $\Delta t$ . The first three of these equations are obvious. The last three easily follow from the Langevin equation in section 4.1 together with the fluctuation-dissipation theorem Eq. (4.21).  $\mathbf{1}$  in Eq. (4.49) denotes the 3-dimensional unit matrix. Introducing everything into Eq. (4.43), dividing by  $\Delta t$  and taking the limit  $\Delta t \rightarrow 0$ , we get

$$\begin{aligned} &\int d^6 z F(\vec{z}) \frac{\partial}{\partial t} \mathcal{G}(\vec{z}; \vec{z}_0; t) \\ &= \int d^6 z' \vec{v}' \mathcal{G}(\vec{z}'; \vec{z}_0; t) \cdot \{ \vec{\nabla}_{\vec{r}'} - \xi \vec{\nabla}_{\vec{v}'} \} F(\vec{z}') \\ &\quad + \int d^6 z' \frac{kT}{m} \xi \mathcal{G}(\vec{z}'; \vec{z}_0; t) \nabla_{\vec{v}'}^2 F(\vec{z}'). \end{aligned} \quad (4.50)$$

Next we change the integration variable  $\vec{z}'$  into  $\vec{z}$  and perform some partial integrations, obtaining

$$\int d^6 z F(\vec{z}) \frac{\partial}{\partial t} \mathcal{G}(\vec{z}; \vec{z}_0; t)$$



$$\begin{aligned}
&= \int d^6 z F(\vec{z}) \{ \vec{\nabla}_{\vec{v}} \xi - \vec{\nabla}_{\vec{r}} \} \cdot (\vec{v} \mathcal{G}(\vec{z}; \vec{z}_0; t)) \\
&\quad + \int d^6 z F(\vec{z}) \nabla_{\vec{v}}^2 \frac{kT}{m} \xi \mathcal{G}(\vec{r}; \vec{r}_0; t).
\end{aligned} \tag{4.51}$$

Because this has to hold true for all possible  $F(\vec{z})$  we conclude that the Fokker-Planck equation (4.14) must hold true.

## Appendix B

In this appendix we derive the Smoluchowski equation directly from the Fokker-Planck equation. This appendix will be rather technical.

In a potential field the Fokker-Planck equation reads

$$\begin{aligned}
\frac{\partial \mathcal{G}}{\partial t} &= - \sum_{i=1}^3 v_i \frac{\partial}{\partial r_i} \mathcal{G} + \sum_{i=1}^3 \frac{1}{m} \frac{\partial \Phi}{\partial r_i} \frac{\partial}{\partial v_i} \mathcal{G} \\
&\quad + \xi \sum_{i=1}^3 \frac{\partial}{\partial v_i} (v_i \mathcal{G}) + \xi \frac{kT}{m} \sum_{i=1}^3 \frac{\partial^2}{\partial v_i^2} \mathcal{G}.
\end{aligned} \tag{4.52}$$

On the Smoluchowski timescale we are interested in

$$G(\vec{r}, \vec{r}_0; t) = \int d^3 v \bar{G}(\vec{r}, \vec{v}, \vec{r}_0; t) \tag{4.53}$$

$$\bar{G}(\vec{r}, \vec{v}, \vec{r}_0; t) = \int d^3 v_0 \left\{ \frac{m}{2\pi kT} \right\}^{\frac{3}{2}} \exp\left\{-\frac{1}{2}\beta m v_0^2\right\} \mathcal{G}(\vec{r}, \vec{v}; \vec{r}_0, \vec{v}_0; t) \tag{4.54}$$

We first notice that  $\bar{G}$  also satisfies Eq. (4.52), but with initial value condition

$$\lim_{t \rightarrow 0} \bar{G}(\vec{r}, \vec{v}, \vec{r}_0; t) = \delta(\vec{r} - \vec{r}_0) \left\{ \frac{m}{2\pi kT} \right\}^{\frac{3}{2}} \exp\left\{-\frac{1}{2}\beta m v^2\right\}. \tag{4.55}$$

For large values of  $\xi$  we expect that the velocities will continually be in thermal equilibrium, i.e. that the equilibration time of the velocities is small on the Brownian timescale. We therefore expect that

$$\bar{G}(\vec{r}, \vec{v}, \vec{r}_0; t) \approx \left\{ \frac{m}{2\pi kT} \right\}^{\frac{3}{2}} \exp\left\{-\frac{1}{2}\beta m v^2\right\} \int d^3 v \bar{G}(\vec{r}, \vec{v}, \vec{r}_0; t). \tag{4.56}$$

From Eq. (4.55) we see that this certainly holds true in the limit of  $t$  going to zero.

We now define the projection operator  $P$  by

$$PF(\vec{v}) = \left\{ \frac{m}{2\pi kT} \right\}^{\frac{3}{2}} \exp\left\{-\frac{1}{2}\beta m v^2\right\} \int d^3 v F(\vec{v}) \tag{4.57}$$

where  $F(\vec{v})$  may be any function of  $\vec{v}$ . We write the Fokker-Planck equation as

$$\frac{\partial \bar{G}}{\partial t} = \xi \mathcal{L}_1 \bar{G} + \mathcal{L}_2 \bar{G} \tag{4.58}$$

$$\mathcal{L}_1 = \sum_{i=1}^3 \frac{\partial}{\partial v_i} v_i + \frac{kT}{m} \sum_{i=1}^3 \frac{\partial^2}{\partial v_i^2} \tag{4.59}$$

$$\mathcal{L}_2 = - \sum_{i=1}^3 v_i \frac{\partial}{\partial r_i} + \sum_{i=1}^3 \frac{1}{m} \frac{\partial \Phi}{\partial r_i} \frac{\partial}{\partial v_i} \tag{4.60}$$

The projection can easily be shown to have the following properties

$$P^2 = P \quad (4.61)$$

$$\mathcal{L}_1 P = 0 \quad (4.62)$$

$$P \mathcal{L}_1 = 0 \quad (4.63)$$

$$P \mathcal{L}_2 P = 0 \quad (4.64)$$

We shall now derive the equation of motion of  $P\bar{G}$ . The Smoluchowski equation, i.e. the equation of motion of  $G(\bar{r}, \bar{r}_0; t)$  then follows at once from  $P\bar{G} = \{m/2\pi kT\}^{3/2} \times \exp\{-\frac{1}{2}\beta m v^2\} G$   
Defining

$$\mathcal{V} = P\bar{G} \quad (4.65)$$

$$\mathcal{W} = (1 - P)\bar{G} \quad (4.66)$$

we get from Eq. (4.58)

$$\frac{\partial \mathcal{V}}{\partial t} = P \mathcal{L}_2 \bar{G} = P \mathcal{L}_2 (1 - P) \bar{G} = P \mathcal{L}_2 \mathcal{W} \quad (4.67)$$

$$\begin{aligned} \frac{\partial \mathcal{W}}{\partial t} &= \xi(1 - P) \mathcal{L}_1 \bar{G} + (1 - P) \mathcal{L}_2 \bar{G} \\ &= \{\xi \mathcal{L}_1 + (1 - P) \mathcal{L}_2\} \mathcal{W} + \mathcal{L}_2 \mathcal{V}. \end{aligned} \quad (4.68)$$

We now solve Eq. (4.68) using  $\mathcal{W}(0) = 0$ , and introduce the result in Eq. (4.67):

$$\frac{\partial \mathcal{V}}{\partial t} = \int_0^t d\tau P \mathcal{L}_2 \exp\{\{\xi \mathcal{L}_1 + (1 - P) \mathcal{L}_2\}(t - \tau)\} \mathcal{L}_2 \mathcal{V}(\tau). \quad (4.69)$$

This result is exact, and therefore not very useful.

We shall now simplify Eq. (4.69) by means of some approximations based on physical grounds. First, since we want to describe the Smoluchowski timescale, we let  $\xi$  be large, obtaining

$$\frac{\partial \mathcal{V}}{\partial t} = \int_0^t d\tau P \mathcal{L}_2 \exp\{\{\xi \mathcal{L}_1(t - \tau)\} \mathcal{L}_2 \mathcal{V}(\tau). \quad (4.70)$$

Next we invoke the Markov property; the coordinates develop slowly, meaning that the system quickly loses its memory of the past, and  $\partial \mathcal{V} / \partial t$  can only depend on the value of  $\mathcal{V}$  at time  $t$  and not on its values at earlier times

$$\frac{\partial \mathcal{V}}{\partial t} = \int_0^t d\tau P \mathcal{L}_2 \exp\{\{\xi \mathcal{L}_1(t - \tau)\} \mathcal{L}_2 \mathcal{V}(t). \quad (4.71)$$

It is a simple but rather tedious task to prove that

$$\mathcal{L}_1 \mathcal{L}_2 \mathcal{V} = -\mathcal{L}_2 \mathcal{V}. \quad (4.72)$$

Using this in Eq. (4.71) yields

$$\begin{aligned} \frac{\partial \mathcal{V}}{\partial t} &= \int_0^t d\tau P \mathcal{L}_2 \exp\{-\xi(t - \tau)\} \mathcal{L}_2 \mathcal{V}(t) \\ &= P \mathcal{L}_2 \frac{1}{\xi} (1 - e^{-\xi t}) \mathcal{L}_2 \mathcal{V}(t) \\ &= P \mathcal{L}_2 \frac{1}{\xi} \mathcal{L}_2 \mathcal{V}(t) \end{aligned} \quad (4.73)$$

where in the last step we have used the overdamped condition  $\xi t \gg 1$ . Introducing the definition of  $P$  and  $\mathcal{L}_2$ , and working through all derivations and integrals one obtains

$$\begin{aligned} \frac{\partial \mathcal{V}}{\partial t} &= \left\{ \frac{m}{2\pi kT} \right\}^{3/2} \exp\left\{-\frac{1}{2}\beta m v^2\right\} \\ &\quad \times \sum_i \frac{\partial}{\partial r_i} \left\{ D \frac{\partial}{\partial r_i} G + \frac{1}{m\xi} \frac{\partial \phi}{\partial r_i} G \right\} \end{aligned} \quad (4.74)$$

which is recognized as the Smoluchowski equation after using  $\mathcal{V} = P\bar{G} = \{m/2\pi kT\}^{3/2} \exp\{-\frac{1}{2}\beta m v^2\} G$ .

## Appendix C

In this appendix we shall derive the Smoluchowski equation, starting from the Langevin equation (4.27), (4.28).

Using exactly the same method as in appendix A, but now applied to  $G(\vec{r}; \vec{r}_0; t)$  we arrive at

$$\begin{aligned} \int d^3 r F(\vec{r}) G(\vec{r}; \vec{r}_0; t + \Delta t) &= \int d^3 r' \{ d^3 r G(\vec{r}; \vec{r}'; \Delta t) \} F(\vec{r}') \\ &\quad + \sum_{\alpha} \int d^3 r' \left\{ \int d^3 r (r_{\alpha} - r'_{\alpha}) G(\vec{r}; \vec{r}'; \Delta t) \right\} G(\vec{r}'; \vec{r}_0; t) \frac{\partial}{\partial r'_{\alpha}} F(\vec{r}') \\ &\quad + \frac{1}{2} \sum_{\alpha} \sum_{\beta} \int d^3 r' \left\{ \int d^3 r (r_{\alpha} - r'_{\alpha})(r_{\beta} - r'_{\beta}) G(\vec{r}; \vec{r}'; \Delta t) \right\} \\ &\quad \times G(\vec{r}'; \vec{r}_0; t) \frac{\partial^2}{\partial r'_{\alpha} \partial r'_{\beta}} F(\vec{r}'). \end{aligned} \quad (4.75)$$

Using

$$\int d^3 r G(\vec{r}; \vec{r}'; \Delta t) = 1 \quad (4.76)$$

$$\int d^3 r (\vec{r} - \vec{r}') G(\vec{r}; \vec{r}'; \Delta t) = -\frac{1}{\xi m} \vec{\nabla}' \Phi \Delta t + \vec{\nabla}' D \Delta t \quad (4.77)$$

$$\int d^3 r (\vec{r} - \vec{r}') (\vec{r} - \vec{r}') G(\vec{r}; \vec{r}'; \Delta t) = 2D \mathbf{1} \Delta t \quad (4.78)$$

which follow from Eqs. (4.27) and (4.28), and following the same strategy as in appendix A we arrive at

$$\begin{aligned} \frac{\partial}{\partial t} G(\vec{r}; \vec{r}_0; t) &= \vec{\nabla} \cdot \frac{1}{\xi m} G(\vec{r}; \vec{r}_0; t) \vec{\nabla} \Phi(\vec{r}) \\ &\quad - \vec{\nabla} \cdot G(\vec{r}; \vec{r}_0; t) \vec{\nabla} D + \nabla^2 D G(\vec{r}; \vec{r}_0; t) \end{aligned} \quad (4.79)$$

It is not difficult to show that the last two terms together yield  $\vec{\nabla} \cdot D \vec{\nabla} G(\vec{r}; \vec{r}_0; t)$ , which proves the equivalence of Eqs. (4.27), (4.28) and Eqs. (4.32), (4.33).



# Chapter 5

## Hydrodynamics

### 5.1 Introduction

Hydrodynamics describes the flow properties of viscoelastic materials. The basic quantities are the density  $\rho(\vec{r}, t)$  and velocity  $\vec{v}(\vec{r}, t)$ . Here  $\rho(\vec{r}, t)$  is the density of the material which at time  $t$  happens to be at position  $\vec{r}$ . Similarly  $\vec{v}(\vec{r}, t)$  is the velocity of the material which at time  $t$  is at position  $\vec{r}$ . A consequence of describing the flow field this way, is that for example  $\rho(\vec{r}, t_1)$  and  $\rho(\vec{r}, t_2)$  are the densities of two different amounts of material. If we want to know the change with time of the density of a given amount of material we shall write

$$\begin{aligned}\frac{D}{Dt}\rho(\vec{r}, t) &= \lim_{\tau \rightarrow 0} \frac{1}{\tau} \{ \rho(\vec{r} + \vec{v}(\vec{r}, t)\tau, t + \tau) - \rho(\vec{r}, t) \} \\ &= \left\{ \vec{v}(\vec{r}, t) \cdot \vec{\nabla} + \frac{\partial}{\partial t} \right\} \rho(\vec{r}, t)\end{aligned}\quad (5.1)$$

Similar expressions hold for other quantities.  $D/Dt$  is called the total derivative.

A second important concept in hydrodynamics is that of friction. Suppose we have a linear flow field like in Fig. (5.1), where the arrows indicate the velocities. The only nonzero velocity component is in the  $y$ -direction, and it only depends on  $z$ . Now look at a volume element at  $(x, y, z)$ . It has a velocity  $v_y(z)$  which is larger than the velocity  $v_y(z - dz)$  of the volume element just below it. As a result the element at  $(x, y, z)$  will be slowed down and the one at  $(x, y, z - dz)$  will be accelerated. Both forces will be proportional to  $\partial v_y(z)/\partial z$  and to the surface  $dx dy$ , with constant of proportionality  $\eta$ . Similarly the volume element at  $(x, y, z)$  will be accelerated by the one at  $(x, y, z + dz)$ . In total our volume element will feel a force in the  $y$ -direction given by

$$\begin{aligned}F_y &= \eta \left\{ \frac{\partial}{\partial z} v_y(z + dz) - \frac{\partial}{\partial z} v_y(z) \right\} dx dy \\ &= \eta \frac{\partial^2 v_y}{\partial z^2} dx dy dz.\end{aligned}\quad (5.2)$$

The constant  $\eta$  is called the viscosity. A second contribution to the force in the  $y$ -direction comes from the difference in pressure on the surfaces at  $(x, y, z)$  and  $(x, y + dy, z)$ :

$$\begin{aligned}F_y^P &= P(y) dx dz - P(y + dy) dx dz \\ &= -\frac{\partial P}{\partial y} dx dy dz\end{aligned}\quad (5.3)$$

These forces together will accelerate the mass in our volume element.

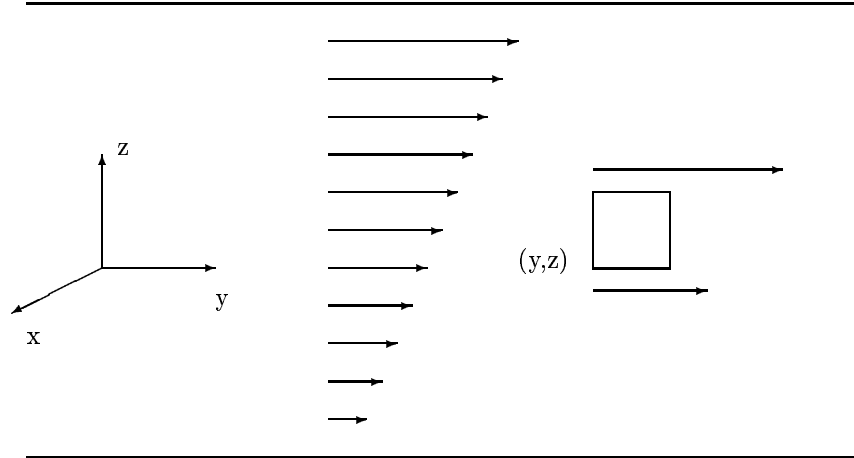


Figure 5.1:

## 5.2 Navier-Stokes equations

In this section we shall present two important equations governing the dynamics of fluid flow. First we obtain the equation describing the conservation of mass. Next we present the equation of motion. In order to do this we have to generalize the concept of viscosity as introduced in the previous section.

Consider a volume element with edges  $(dx, 0, 0)$ ,  $(0, dy, 0)$  and  $(0, 0, dz)$ . If we follow the mass in our volume element along the flow during a short time  $\tau$ , the line element  $(dx, 0, 0)$  will transform into

$$dx \left( 1 + \frac{\partial v_x}{\partial x} \tau, \frac{\partial v_y}{\partial x} \tau, \frac{\partial v_z}{\partial x} \tau \right). \quad (5.4)$$

Analogous equations hold for the other line elements. The volume after time  $\tau$  will be

$$\begin{aligned} & dx dy dz \left( 1 + \frac{\partial v_x}{\partial x} \tau, \frac{\partial v_y}{\partial x} \tau, \frac{\partial v_z}{\partial x} \tau \right) \cdot \left( \frac{\partial v_x}{\partial y} \tau, 1 + \frac{\partial v_y}{\partial y} \tau, \frac{\partial v_z}{\partial y} \tau \right) \times \\ & \quad \left( \frac{\partial v_x}{\partial z} \tau, \frac{\partial v_y}{\partial z} \tau, 1 + \frac{\partial v_z}{\partial z} \tau \right) \\ &= dx dy dz \left( 1 + \frac{\partial v_x}{\partial x} \tau, \frac{\partial v_y}{\partial x} \tau, \frac{\partial v_z}{\partial x} \tau \right) \cdot \left( 1 + \frac{\partial v_y}{\partial y} \tau + \frac{\partial v_z}{\partial z} \tau, -\frac{\partial v_x}{\partial y} \tau, -\frac{\partial v_x}{\partial z} \tau \right) \\ &= dx dy dz \left\{ 1 + \left( \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) \tau \right\} \end{aligned} \quad (5.5)$$

As a result we have

$$\frac{DV}{Dt} = V \vec{\nabla} \cdot \vec{v} \quad (5.6)$$

or using  $\rho = mN/V$

$$\frac{D\rho}{Dt} = -\rho \vec{\nabla} \cdot \vec{v}. \quad (5.7)$$

This equation describes the conservation of mass.

We shall now generalize the concept of viscosity as it was given in section 1. Consider a surface element of size  $dA$ , and normal  $\vec{t}$ . Let  $\vec{F}$  be the force exerted by

the fluid below the surface element on the fluid above the surface element. Then we define the stress tensor  $S$  by

$$F_i = - \sum_j S_{ij} t_j dA = -(\bar{S} \cdot \vec{t})_i dA \quad (5.8)$$

The total force in  $i$ -direction on a given volume element at  $(x, y, z)$  then is

$$\begin{aligned} F_i &= \{S_{ix}(x + dx, y, z) - S_{ix}(x, y, z)\} dydz \\ &\quad + \{S_{iy}(x, y + dy, z) - S_{iy}(x, y, z)\} dx dz \\ &\quad + \{S_{iz}(x, y, z + dz) - S_{iz}(x, y, z)\} dx dy \\ &= \sum_j \frac{\partial}{\partial x_j} S_{ij} dx dy dz \end{aligned} \quad (5.9)$$

where  $x_1 = x$ ,  $x_2 = y$  and  $x_3 = z$ . In vector notation

$$\vec{F} = V \vec{\nabla} \cdot \bar{S}. \quad (5.10)$$

Since  $S$  will turn out to be symmetric, there is no ambiguity in this notation. This force accelerates the mass in our volume element, which is  $\rho V$ . Newton's second law then reads

$$\frac{D}{Dt}(\rho V \vec{v}) = V \vec{\nabla} \cdot \bar{S} \quad (5.11)$$

Writing  $D/Dt(\rho V \vec{v}) = \rho V D/Dt(\vec{v})$ , because  $\rho V$  is constant along the flow, and dividing by  $V$  we get

$$\rho \frac{D}{Dt} \vec{v} = \vec{\nabla} \cdot \bar{S}. \quad (5.12)$$

This is the Navier-Stokes equation.

Many fluids may be described by assuming that the stress tensor  $S$  consists of a part, which is independent of the velocity, and a part which depends linearly on the derivatives  $\partial v_i / \partial x_j$ . In hydrodynamics it is shown that the most general stress tensor having these properties then reads

$$S_{ij} = \eta \left\{ \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right\} - \left\{ P + \left( \frac{2}{3} \eta - \kappa \right) \vec{\nabla} \cdot \vec{v} \right\} \delta_{ij}. \quad (5.13)$$

Here  $\eta$  is the shear viscosity,  $\kappa$  is the bulk viscosity, and  $P$  the pressure.

Many flow fields of interest may be described assuming that the fluid is incompressible, i.e. that the density along the flow is constant. In that case  $\vec{\nabla} \cdot \vec{v} = 0$ , as follows from Eq. (5.7). Assuming moreover that the velocities are small, and that the second order non-linear term  $\vec{v} \cdot \vec{\nabla} \vec{v}$  may be neglected we obtain Stokes equations for incompressible flow

$$\rho \frac{\partial \vec{v}}{\partial t} = \eta \nabla^2 \vec{v} - \vec{\nabla} P \quad (5.14)$$

$$\vec{\nabla} \cdot \vec{v} = 0. \quad (5.15)$$

These are the equations that we are going to use in the next two sections.

### 5.3 A moving sphere in a quiescent fluid

Consider a sphere of radius  $R$ , moving with velocity  $\vec{v}_0$  in a quiescent fluid. Referring all coordinates and velocities to a frame which moves with velocity  $\vec{v}_0$  relative to

the fluid transforms the problem into one of a resting sphere in a fluid which, at large distances from the sphere, moves with constant velocity  $-\vec{v}_0$ .

Our velocity field will be stationary. The Stokes equations then read

$$\eta \nabla^2 \vec{v} = \vec{\nabla} P \quad (5.16)$$

$$\vec{\nabla} \cdot \vec{v} = 0 \quad (5.17)$$

with boundary conditions

$$\vec{v}(R) = \vec{0} \quad (5.18)$$

$$\vec{v}(\infty) = -\vec{v}_0. \quad (5.19)$$

As a first step towards the solution, we take the divergence of Eq. (5.16). Making use of the incompressibility equation (5.17) we then get

$$\nabla^2 P = 0. \quad (5.20)$$

Now, notice that the flow field will be linear in  $\vec{v}_0$ . From Eq. (5.16) it follows that  $\vec{\nabla} P$  will then also be linear in  $\vec{v}_0$ . Moreover  $P(\vec{r})$  must be invariant under a rotation of both the coordinate frame and  $\vec{v}_0$ . Therefore we write

$$P(\vec{r}) = a + \vec{v}_0 \cdot \vec{r} f(r) \quad (5.21)$$

Introducing this into Eq. (5.20) we get

$$\begin{aligned} 2\vec{v}_0 \cdot \vec{\nabla} f + \vec{v}_0 \cdot \vec{r} \nabla^2 f &= 0 \\ \frac{\partial^2 f}{\partial r^2} + \frac{4}{r} \frac{\partial f}{\partial r} &= 0 \end{aligned} \quad (5.22)$$

Solving this under the condition  $f(\infty) = 0$ , we get  $f(r) = br^{-3}$ , and

$$P(\vec{r}) = a + b \frac{\vec{v}_0 \cdot \vec{r}}{r^3}. \quad (5.23)$$

Eq. (5.16) now reads

$$\eta \nabla^2 \vec{v} = \vec{v}_0 \frac{b}{r^3} - \vec{r} (\vec{v}_0 \cdot \vec{r}) \frac{3b}{r^5}. \quad (5.24)$$

Now again, we notice that  $\vec{v}(\vec{r})$  must be linear in  $\vec{v}_0$ . Moreover it must transform like  $\vec{v}_0$  and  $\vec{r}$  under a joint rotation of  $\vec{v}_0$  and the coordinate frame. Therefore

$$\vec{v}(\vec{r}) = \vec{v}_0 F_1(r) + \vec{r} (\vec{v}_0 \cdot \vec{r}) F_2(r). \quad (5.25)$$

Introducing this expression into Eq. (5.24), we get

$$\begin{aligned} &\vec{v}_0 \nabla^2 F_1 + 2\vec{\nabla} (\vec{v}_0 \cdot \vec{r} F_2) + \vec{r} \nabla^2 (\vec{v}_0 \cdot \vec{r} F_2) \\ &= \vec{v}_0 \{ \nabla^2 F_1 + 2F_2 \} + \vec{r} (\vec{v}_0 \cdot \vec{r}) \left\{ \frac{4}{r} \frac{\partial F_2}{\partial r} + \nabla^2 F_2 \right\} \\ &= \vec{v}_0 \frac{b/\eta}{r^3} - \vec{r} (\vec{v}_0 \cdot \vec{r}) \frac{3b/\eta}{r^5} \end{aligned} \quad (5.26)$$

from which

$$\nabla^2 F_1 + 2F_2 = \frac{b/\eta}{r^3} \quad (5.27)$$

$$\nabla^2 F_2 + \frac{4}{r} \frac{\partial F_2}{\partial r} = -\frac{3b/\eta}{r^5}. \quad (5.28)$$



The boundary conditions for these equations are

$$F_1(R) = 0, \quad F_1(\infty) = -1 \quad (5.29)$$

$$F_2(R) = 0, \quad F_2(\infty) = 0. \quad (5.30)$$

We first solve Eq. (5.28) under the condition Eq. (5.30). Solutions to the homogeneous equation are  $cr^{-5}$ ; a particular solution is  $(b/2\eta)r^{-3}$ . According to the boundary condition Eq. (5.30) we then get

$$F_2(r) = \frac{b}{2\eta} \frac{1}{r^3} \left( 1 - \frac{R^2}{r^2} \right). \quad (5.31)$$

Equation (5.27) now reads

$$\nabla^2 F_1 = \frac{bR^2}{\eta} \frac{1}{r^5}. \quad (5.32)$$

Solutions to the homogeneous equation are  $-1 + cr^{-1}$ ; a particular solution is  $(bR^2/6\eta)r^{-3}$ . The boundary conditions Eq. (5.29) then lead to

$$F_1(r) = \frac{bR^2}{6\eta} \frac{1}{r^3} + R \frac{1}{r} \left( 1 - \frac{b}{6\eta R} \right) - 1. \quad (5.33)$$

Finally we have to fulfill the incompressibility equation

$$\begin{aligned} \vec{\nabla} \cdot \vec{v} &= \vec{v}_0 \cdot \vec{\nabla} F_1 + 3(\vec{v}_0 \cdot \vec{r}) F_2 + \vec{r} \cdot \vec{\nabla} (\vec{v}_0 \cdot \vec{r} F_2) \\ &= (\vec{v}_0 \cdot \vec{r}) \left\{ \frac{1}{r} \frac{\partial F_1}{\partial r} + 4F_2 + r \frac{\partial F_2}{\partial r} \right\} = 0. \end{aligned} \quad (5.34)$$

Introducing  $F_1$  and  $F_2$  we find  $b = \frac{3}{2}\eta R$ .

We now introduce  $F_1$  and  $F_2$  from Eqs. (5.33) and (5.31), together with  $b = \frac{3}{2}\eta R$  into Eq. (5.25), and add  $\vec{v}_0$  to get the flow field around a sphere at the origin, moving with velocity  $\vec{v}_0$  in a quiescent fluid.

$$\vec{v}(\vec{r}) = \vec{v}_0 \frac{3R}{4r} \left( 1 + \frac{R^2}{3r^2} \right) + \vec{r} (\vec{v}_0 \cdot \vec{r}) \frac{3R}{4r^3} \left( 1 - \frac{R^2}{r^2} \right) \quad (5.35)$$

One easily checks the boundary conditions

$$\vec{v}(R) = \vec{v}_0 \quad (5.36)$$

$$\vec{v}(\infty) = \vec{0} \quad (5.37)$$

We shall now use this flow field to calculate the force exerted by the fluid on the particle.

According to Eq. (5.8) the force exerted by the fluid on the sphere is given by

$$\vec{F} = \int d\Omega R^2 S(\vec{R}) \cdot \frac{\vec{R}}{R} \quad (5.38)$$

where  $R^2 d\Omega$  is a surface element on the sphere. The stress tensor is given by Eq. (5.13), which in the case of an incompressible fluid reads

$$S_{ij} = \eta \left\{ \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right\} - P \delta_{ij}. \quad (5.39)$$

Using the flow field given in Eq. (5.35) and the pressure given in Eq. (5.23), where  $b = \frac{3}{2}\eta R$ , we calculate

$$\begin{aligned} \vec{S}(\vec{R}) \cdot \vec{R} &= -\frac{3}{2}\eta \vec{v}_0 + \left\{ \eta (\vec{v}_0 \cdot \vec{R}) \frac{3}{2R^2} - P(\vec{R}) \right\} \vec{R} \\ &= -\frac{3}{2}\eta \vec{v}_0 - a \vec{R}. \end{aligned} \quad (5.40)$$

Introducing this into Eq. (5.38) and performing the integral we obtain

$$\vec{F} = -6\pi\eta R\vec{v}_0 \quad (5.41)$$

$\vec{F}$  is known as the Stokes friction.

## 5.4 Hydrodynamic interaction in colloidal suspensions

Now consider a suspension of colloidal particles. The motion of a given particle induces a flow field in the solvent, which will be felt by all the other particles. As a result these particles experience a force which is said to result from hydrodynamic interaction with the original particle.

The hydrodynamic problem now is to find a flow field satisfying Eqs. (5.16) and (5.17) together with the boundary conditions

$$v(\vec{R}_i + \vec{R}) = \vec{v}_i \quad \forall i \quad (5.42)$$

where  $\vec{R}_i$  is the position vector of the  $i$ 'th particle, and  $\vec{R}$  is any vector of length  $R$ . If the particles are very far apart we may approximately consider any one of them to be alone in the fluid. The flow field is then just the sum of all flow fields emanating from the different particles

$$\vec{v}(\vec{r}) = \sum_i \vec{v}_i^{(0)}(\vec{r} - \vec{R}_i) \quad (5.43)$$

where according to the previous section (see Eq. (5.35))

$$\begin{aligned} \vec{v}_i^{(0)}(\vec{r} - \vec{R}_i) = & \vec{v}_i \frac{3R}{4|\vec{r} - \vec{R}_i|} \left\{ 1 + \frac{R^2}{3(\vec{r} - \vec{R}_i)^2} \right\} \\ & + (\vec{r} - \vec{R}_i)(\vec{v}_i \cdot (\vec{r} - \vec{R}_i)) \frac{3R}{4|\vec{r} - \vec{R}_i|^3} \left\{ 1 - \frac{R^2}{(\vec{r} - \vec{R}_i)^2} \right\}. \end{aligned} \quad (5.44)$$

We shall now calculate the correction to this flow field, which is of lowest order in the particles separation.

We shall first discuss the situation for only two particles in the solvent. In the neighbourhood of particle one the velocity field may be written as

$$\vec{v}(\vec{r}) = \vec{v}_1^{(0)}(\vec{r} - \vec{R}_1) + \frac{3R}{4|\vec{r} - \vec{R}_2|} \left\{ \vec{v}_2 + \frac{(\vec{r} - \vec{R}_2)(\vec{r} - \vec{R}_2)}{|\vec{r} - \vec{R}_2| |\vec{r} - \vec{R}_2|} \cdot \vec{v}_2 \right\} \quad (5.45)$$

where we have approximated  $\vec{v}_2^{(0)}(\vec{r} - \vec{R}_2)$  to terms of order  $R/|\vec{r} - \vec{R}_2|$ . On the surface of sphere one we approximate this further by

$$\vec{v}(\vec{R}_1 + \vec{R}) = \vec{v}_1^{(0)}(\vec{R}) + \frac{3R}{4R_{21}} \{ \vec{v}_2 + \hat{R}_{21} \hat{R}_{21} \cdot \vec{v}_2 \} \quad (5.46)$$

Because  $\vec{v}_1^{(0)}(\vec{R}) = \vec{v}_1$ , we notice that this result is not consistent with the boundary condition  $\vec{v}(\vec{R}_1 + \vec{R}) = \vec{v}_1$ . In order to satisfy this boundary condition we subtract from our result so far, a solution of Eqs. (5.16) and (5.17) which goes to zero at infinity, and which on the surface of particle one corrects for the second term in

Eq. (5.46). The flow field in the neighbourhood of particle one then reads

$$\begin{aligned} \vec{v}(\vec{r}) &= \vec{v}_1^{\text{corr}} \frac{3R}{4|\vec{r} - \vec{R}_1|} \left\{ 1 + \frac{R^2}{3(\vec{r} - \vec{R}_1)^2} \right\} \\ &+ (\vec{r} - \vec{R}_1)(\vec{r} - \vec{R}_1) \cdot \vec{v}_1^{\text{corr}} \frac{3R}{4|\vec{r} - \vec{R}_1|^3} \left\{ 1 - \frac{R^2}{(\vec{r} - \vec{R}_1)^2} \right\} \\ &+ \frac{3R}{4R_{21}} \{ \vec{v}_2 + \hat{R}_{21} \hat{R}_{21} \cdot \vec{v}_2 \} \end{aligned} \quad (5.47)$$

$$\vec{v}_1^{\text{corr}} = \vec{v}_1 - \frac{3R}{4R_{21}} \{ \vec{v}_2 + \hat{R}_{21} \hat{R}_{21} \cdot \vec{v}_2 \} \quad (5.48)$$

The flow field in the neighbourhood of particle two is treated similarly.

We now notice that the correction that we have applied to the flow field in order to satisfy the boundary conditions at the surface of particle one is of order  $R/R_{21}$ . Its strength in the neighbourhood of particle two is then of order  $(R/R_{21})^2$ , and need therefore not be taken into account when the flow field is adapted to the boundary conditions at particle two.

The flow field around particle one is now given by Eqs. (5.47) and (5.48). The last term in Eq. (5.47) does not contribute to the stress tensor. The force exerted by the fluid on particle one then equals  $-6\pi\eta R \vec{v}_1^{\text{corr}}$ . A similar result holds for particle two. In full we have

$$\vec{F}_1 = -6\pi\eta R \vec{v}_1 + 6\pi\eta R \frac{3R}{4R_{21}} (\mathbf{1} + \hat{R}_{21} \hat{R}_{21}) \cdot \vec{v}_2 \quad (5.49)$$

$$\vec{F}_2 = 6\pi\eta R \frac{3R}{4R_{21}} (\mathbf{1} + \hat{R}_{21} \hat{R}_{21}) \cdot \vec{v}_1 - 6\pi\eta R \vec{v}_1 \quad (5.50)$$

where  $\mathbf{1}$  is the 3-dim unit tensor. Inverting these equations, retaining only terms up to order  $R/R_{21}$  we get

$$\vec{v}_1 = -\frac{1}{6\pi\eta R} \vec{F}_1 - \frac{1}{8\pi\eta R_{21}} (\mathbf{1} + \hat{R}_{21} \hat{R}_{21}) \cdot \vec{F}_2 \quad (5.51)$$

$$\vec{v}_2 = -\frac{1}{8\pi\eta R_{21}} (\mathbf{1} + \hat{R}_{21} \hat{R}_{21}) \cdot \vec{F}_1 - \frac{1}{6\pi\eta R} \vec{F}_2 \quad (5.52)$$

When more than two particles are present in the fluid, corrections resulting from  $n$ -body interactions ( $n \geq 3$ ) are of order  $(R/R_{ij})^2$  or higher and need not be taken into account. The above treatment therefore generalizes to

$$\vec{F}_i = -\sum_{j=1}^N \bar{\xi}_{ij} \cdot \vec{v}_j \quad (5.53)$$

$$\vec{v}_i = -\sum_{j=1}^N \bar{\mu}_{ij} \cdot \vec{F}_j \quad (5.54)$$

with

$$\bar{\xi}_{ii} = 6\pi\eta R \mathbf{1}, \quad \bar{\xi}_{ij} = -6\pi\eta R \frac{3R}{4R_{ij}} (\mathbf{1} + \hat{R}_{ij} \hat{R}_{ij}) \quad (5.55)$$

$$\bar{\mu}_{ii} = \frac{1}{6\pi\eta R} \mathbf{1}, \quad \bar{\mu}_{ij} = \frac{1}{8\pi\eta R_{ij}} (\mathbf{1} + \hat{R}_{ij} \hat{R}_{ij}). \quad (5.56)$$

These results will be used in our treatment of the Zimm-chain.

## 5.5 The virial theorem, and the microscopic expressions for the stress tensor

### 5.5.1 A. General

We consider a small portion of fluid, small enough for all macroscopic gradients to be zero, and large enough to represent a homogeneous phase. Now consider the quantity

$$\dot{\bar{G}} = \left\langle \frac{1}{V} \frac{d}{dt} \sum_i m_i \vec{r}_i \vec{v}_i \right\rangle \quad (5.57)$$

where the average is an ensemble average, or a time average over a time span long enough to smooth out fluctuations, and short enough to assume that the macroscopic flow is stationary. The sum is over all particles in our control volume, i.e. particles leaving the control volume are from that moment on left out of the sum, and particles entering the control volume will from that moment on contribute to the sum. Since in this case  $\sum_i m_i \vec{r}_i \vec{v}_i$  is a bounded quantity, with a well defined average, the average of its time variation must be zero,  $\dot{\bar{G}} = \bar{0}$ .

Evaluating the derivative we obtain

$$\bar{0} = \left\langle \frac{1}{V} \sum_i m_i \vec{v}_i \vec{v}_i \right\rangle + \left\langle \frac{1}{V} \sum_i m_i \vec{r}_i \frac{d\vec{v}_i}{dt} \right\rangle. \quad (5.58)$$

Assuming for simplicity that no body forces are applied, we write

$$\frac{d\vec{v}_i}{dt} = \frac{d\vec{v}_i^{\text{int}}}{dt} + \frac{d\vec{v}_i^{\text{ext}}}{dt} \quad (5.59)$$

where the first term results from the presence of all particles, except  $i$ , in the control volume, and the second term results from the presence of all particles outside the control volume.

Since the control volume is assumed to be of macroscopic size, the second term may be assumed to be concentrated near the boundary of the volume. In terms of the stress tensor we have

$$\begin{aligned} & \left\langle \frac{1}{V} \sum_i m_i \left( \vec{r}_i \frac{d\vec{v}_i^{\text{ext}}}{dt} \right)_{\alpha\beta} \right\rangle \\ &= \frac{1}{V} \int \sum_{\gamma} r_{\alpha} \{ S_{\beta\gamma} - \rho v_{\beta} v_{\gamma} \} t_{\gamma} dA \\ &= \frac{1}{V} \int \sum_{\gamma} \frac{\partial}{\partial r_{\gamma}} r_{\alpha} \{ S_{\beta\gamma} - \rho v_{\beta} v_{\gamma} \} d^3r = S_{\beta\alpha} - \rho v_{\beta} v_{\alpha} \end{aligned} \quad (5.60)$$

where  $t_{\gamma}$  is a component of the outward normal  $\vec{t}$ , and  $\vec{v}$  is the average velocity. It has been assumed that gradients in  $\vec{S}$  and  $\vec{v}$  are negligible. Combining everything we get

$$\bar{S} = - \left\langle \frac{1}{V} \sum_i m_i (\vec{v}_i - \vec{v})(\vec{v}_i - \vec{v}) \right\rangle - \left\langle \frac{1}{V} \sum_i m_i \vec{r}_i \frac{d\vec{v}_i^{\text{int}}}{dt} \right\rangle. \quad (5.61)$$

This is the result we were after; it expresses the macroscopic stress tensor in terms of averages over microscopic quantities.

### 5.5.2 B. Suspensions

We now apply Eq. (5.61) to a volume containing solvent molecules and solute particles. The sum over  $i$  then runs over solvent molecules and solute particles. The

averaging may be performed by a conditional average given some particle configuration, followed by an average over all particle configurations.

We first perform the sum over solvent molecules. Dividing the space occupied by liquid into small cubes, large enough to be called a many body system, but small enough for gradients of cube properties to be small, we may write for the contribution of the solvent molecules

$$\begin{aligned}\bar{S}^{\text{solv}} &= \frac{1}{V} \langle \int_{\text{liq}} d^3r \bar{\sigma}(\vec{r}) \rangle_c - \frac{1}{V} \langle \int_{\text{liq}} d^3r \rho(\vec{r})(\vec{v}(\vec{r}) - \vec{v})(\vec{v}(\vec{r}) - \vec{v}) \rangle_c \\ &\quad + \langle \frac{1}{V} \sum_i \int \vec{r} \bar{\sigma}(\vec{r}) \cdot d\vec{A}_i \rangle_c.\end{aligned}\quad (5.62)$$

The averages are over particle configurations. The integrals in the first two terms are over the space occupied by liquid. The sum in the last term is over solute particles, and  $d\vec{A}_i$  is a vectorial surface element of particle  $i$ .  $\bar{\sigma}$  is the stress tensor in the solvent phase. The last term is a contribution from the forces exerted by the solute particles on the solvent.

We now calculate the contribution from the solute particles. Averaging over the solvent configurations turns  $m_i dv_i/dt$  into  $m_i DV_i/Dt$  given in Eq. (4.39). The contribution to the stress tensor by the solute particles then reads

$$\begin{aligned}\bar{S}^{\text{part}} &= - \langle \frac{1}{V} \sum_i m_i (\vec{V}_i - \vec{v})(\vec{V}_i - \vec{v}) \rangle_c - \langle \frac{1}{V} \sum_i \int \vec{R}_i \bar{\sigma}(\vec{r}) \cdot d\vec{A}_i \rangle_c \\ &\quad + \langle \frac{1}{V} \sum_i \vec{R}_i \vec{\nabla}_i \Phi \rangle_c + kT \langle \frac{1}{V} \sum_i \vec{R}_i \vec{\nabla}_i \ln \Psi \rangle_c\end{aligned}\quad (5.63)$$

where  $\Psi(\vec{R}_0, \dots, \vec{R}_N)$  is the joint probability function for the solute particles to be at positions  $\vec{R}_0, \dots, \vec{R}_N$ . Combining the results we find

$$\begin{aligned}\bar{S} &= \frac{1}{V} \langle \int_{\text{liq}} d^3r \bar{\sigma}(\vec{r}) \rangle_c + \langle \frac{1}{V} \sum_i \int (\vec{r} - \vec{R}_i) \bar{\sigma}(\vec{r}) \cdot d\vec{A}_i \rangle_c \\ &\quad + \langle \frac{1}{V} \sum_i \vec{R}_i \vec{\nabla}_i \Phi \rangle_c + kT \langle \frac{1}{V} \sum_i \vec{R}_i \nabla_i \ln \Psi \rangle_c.\end{aligned}\quad (5.64)$$

The sum of the second term in Eq. (5.62) and the first term in Eq. (5.63) is equal to the total mass weighed velocity fluctuation divided by the volume, and has been put equal to zero, which is reasonable for macroscopic volumes of fluid.

The first term in Eq. (5.64) reads

$$\begin{aligned}\frac{1}{V} \langle \int_{\text{liq}} d^3r \bar{\sigma}(\vec{r}) \rangle_c &= \frac{1}{V} \langle \int_{\text{liq}} d^3r \eta_s \{ \vec{\nabla} \vec{v}(\vec{r}) + \vec{\nabla} \vec{v}(\vec{r})^T \} \rangle_c - \frac{1}{V} \langle \int_{\text{liq}} d^3r P(\vec{r}) \rangle_c \mathbf{1} \\ &= \frac{1}{V} \langle \int d^3r \eta_s \{ \vec{\nabla} \vec{v}(\vec{r}) + \vec{\nabla} \vec{v}(\vec{r})^T \} \rangle_c - \frac{1}{V} \langle \int_{\text{liq}} d^3r P(\vec{r}) \rangle_c \mathbf{1} \\ &= \eta_s \{ \vec{\nabla} \vec{v} + \vec{\nabla} \vec{v}^T \} - \frac{1}{V} \langle \int_{\text{liq}} d^3r P(\vec{r}) \rangle_c \mathbf{1}\end{aligned}\quad (5.65)$$

In the second step we have used the fact that within the solute particle velocity gradients are zero. In the third step we have used  $\partial/\partial r_\alpha \int d^3r f(\vec{r}) = \int f(\vec{r}) t_\alpha dA = \int d^3r \partial/\partial r_\alpha f(\vec{r})$ , for any function  $f(\vec{r})$ .



# Chapter 6

## The Rouse chain

### 6.1 Introduction

We now need a model that we can use to calculate dynamical properties of polymeric systems. In order to be able to concentrate on concepts, and not on mathematical problems, we need a model which is as simple as possible. We therefore adjust the Gaussian chain such that it serves our purposes.

When a polymer chain moves through a liquid every bead, whether it represents a monomer or a larger part of the chain, will feel a certain friction together with random forces. Of course the motion of a bead through the liquid will, like in the previous chapter, induce a velocity field in the liquid which will be felt by all the other beads. To first order we might however neglect this effect and consider the solvent as being some kind of indifferent ether, only producing the friction. The model defined in this way is the Rouse model. When applied to dilute polymeric solutions it gives rather bad results, indicating the importance of the hydrodynamic interactions. When applied to polymeric melts we expect the model to be much more appropriate, because in polymeric melts the friction may be thought of as being caused by the motion of the 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 that there is no hydrodynamic interaction. It will turn out in Chapter 8 that the Rouse model is a very useful model to describe polymeric melts.

### 6.2 The Rouse chain

We now concentrate on one bead, say bead no.  $n$ , while keeping all the other beads fixed. Its equilibrium distribution is given by

$$G_{\text{eq}}(\vec{R}_n) = C \exp\left\{-\beta \frac{3k_B T}{2b^2} (\vec{R}_n - \vec{R}_{n-1})^2 - \beta \frac{3k_B T}{2b^2} (\vec{R}_{n+1} - \vec{R}_n)^2\right\}. \quad (6.1)$$

According to Eq. (4.30) and Eq. (4.27) the Langevin equation describing the motion of the bead then is, with  $\gamma = m\xi$

$$\frac{d\vec{R}_n}{dt} = -\frac{3k_B T}{\gamma b^2} (2\vec{R}_n - \vec{R}_{n-1} - \vec{R}_{n+1}) + \vec{f}_n \quad (6.2)$$

where we have assumed that  $D = kT/\gamma$  is independent on  $\vec{R}_n$ . The same reasoning may be applied to all other beads, leaving us with the equations of motion

$$\frac{d\vec{R}_0}{dt} = -\frac{3k_B T}{\gamma b^2} (\vec{R}_0 - \vec{R}_1) + \vec{f}_0 \quad (6.3)$$

$$\frac{d\vec{R}_n}{dt} = -\frac{3k_B T}{\gamma b^2}(2\vec{R}_n - \vec{R}_{n-1} - \vec{R}_{n+1}) + \vec{f}_n \quad (6.4)$$

$$\frac{d\vec{R}_N}{dt} = -\frac{3k_B T}{\gamma b^2}(\vec{R}_N - \vec{R}_{N-1}) + \vec{f}_N \quad (6.5)$$

$$\langle \vec{f}_n(t) \cdot \vec{f}_m(t') \rangle = 6D\delta_{n,m}\delta(t-t') \quad (6.6)$$

Eq. (6.4) applies when  $n = 1, \dots, N-1$ .

Before starting to analyse these equations in the next section, let us derive one simple result:

$$\frac{d\vec{R}_G}{dt} = \frac{1}{N+1} \sum_{n=0}^N \vec{f}_n \quad (6.7)$$

$$\vec{R}_G(t) = \vec{R}_G(0) + \int_0^t d\tau \frac{1}{N+1} \sum_n \vec{f}_n(\tau) \quad (6.8)$$

$$\begin{aligned} \langle (\vec{R}_G(t) - \vec{R}_G(0))^2 \rangle &= \\ \langle \int_0^t d\tau \int_0^t d\tau' \left( \frac{1}{N+1} \sum_n \vec{f}_n(\tau) \right) \cdot \left( \frac{1}{N+1} \sum_m \vec{f}_m(\tau') \right) \rangle &= \\ = \frac{6D}{N+1} t = 6D_G t \end{aligned} \quad (6.9)$$

So  $D_G = D/N = k_B T/N\gamma$ , which is perfectly understandable.

### 6.3 Normal mode analysis

We shall now solve the equations (6.3) to (6.6). We first solve them leaving out the fluctuating forces. The equations of motion then form a linear set of  $(3N+3)$  first order differential equations, whose general solutions are sums of  $(3N+3)$  independent specific solutions.

As a specific solution we try

$$\vec{R}_n(t) = \vec{X}(t) \cos(an + b). \quad (6.10)$$

The equations of motion then read

$$\frac{d\vec{X}}{dt} \cos b = -\frac{3kT}{\gamma b^2} \{ \cos b - \cos(a+b) \} \vec{X} \quad (6.11)$$

$$\frac{d\vec{X}}{dt} \cos(na + b) = -\frac{3kT}{\gamma b^2} 4 \sin^2 \left( \frac{1}{2}a \right) \cos(na + b) \vec{X} \quad (6.12)$$

$$\frac{d\vec{X}}{dt} \cos(Na + b) = -\frac{3kT}{\gamma b^2} \{ \cos(Na + b) - \cos((N-1)a + b) \} \vec{X} \quad (6.13)$$

where we have used

$$\begin{aligned} &2 \cos(na + b) - \cos((n-1)a + b) - \cos((n+1)a + b) \\ &= \cos(na + b) \{ 2 - 2 \cos a \} = \cos(na + b) 4 \sin^2 \left( \frac{1}{2}a \right). \end{aligned} \quad (6.14)$$

In order for equations (6.11) to (6.13) to be consistent we need

$$\cos b - \cos(a + b) = 4 \sin^2 \left( \frac{1}{2}a \right) \cos b \quad (6.15)$$

$$\cos(Na + b) - \cos((N-1)a + b) = 4 \sin^2 \left( \frac{1}{2}a \right) \cos(Na + b) \quad (6.16)$$



This may be rewritten as

$$\cos(a - b) = \cos b \quad (6.17)$$

$$\cos((N + 1)a + b) = \cos(Na + b). \quad (6.18)$$

We find independent solutions from

$$a - b = b \quad (6.19)$$

$$(N + 1)a + b = k2\pi - Na - b. \quad (6.20)$$

So, finally

$$a = \frac{k\pi}{N + 1}, \quad b = \frac{1}{2}a = \frac{k\pi}{2(N + 1)}. \quad (6.21)$$

The specific solution Eq. (6.10), with  $a$  and  $b$  from Eq. (6.21) decouple the set of differential equations.

In the following we shall frequently make use of

$$\frac{1}{N + 1} \sum_{n=0}^N \cos\left(\frac{k\pi}{N + 1}\left(n + \frac{1}{2}\right)\right) = \delta_{k,0} \quad 0 \leq k < 2(N + 1). \quad (6.22)$$

This is evident when  $k = 0$  or  $k = N + 1$ . In the remaining cases the sum may be evaluated by using  $\cos(na + b) = \frac{1}{2}(e^{ib}e^{ina} + e^{-ib}e^{-ina})$ . The result then is

$$\frac{1}{N + 1} \sum_{n=0}^N \cos\left(\frac{k\pi}{N + 1}\left(n + \frac{1}{2}\right)\right) = \frac{1}{N + 1} \frac{\sin(k\pi)}{\sin\left(\frac{k\pi}{N + 1}\right)} \quad (6.23)$$

which is consistent with Eq. (6.22).

We now turn to the solution of Eqs. (6.3) to (6.6). To this end we write

$$\vec{R}_n = \vec{X}_0 + 2 \sum_{k=1}^N \vec{X}_k \cos\left(\frac{k\pi}{N + 1}\left(n + \frac{1}{2}\right)\right). \quad (6.24)$$

The factor of two in front of the summation is only for reasons of convenience. Using Eq. (6.22) we may invert this to

$$\vec{X}_k = \frac{1}{N + 1} \sum_{n=0}^N \vec{R}_n \cos\left(\frac{k\pi}{N + 1}\left(n + \frac{1}{2}\right)\right). \quad (6.25)$$

The equations of motion then read

$$\frac{d\vec{X}_k}{dt} = -\frac{3k_B T}{\gamma b^2} 4 \sin^2\left(\frac{k\pi}{2(N + 1)}\right) \vec{X}_k + \vec{F}_k \quad (6.26)$$

$$\langle \vec{F}_0(t) \cdot \vec{F}_0(t') \rangle = \frac{6D}{N + 1} \delta(t - t') \quad (6.27)$$

$$\langle \vec{F}_k(t) \cdot \vec{F}_{k'}(t') \rangle = \frac{3D}{N + 1} \delta_{k,k'} \delta(t - t') \quad k \neq 0 \quad (6.28)$$

Eqs. (6.27) and (6.28) were obtained from Eq. (6.6) and Eq. (6.22) by using

$$\vec{F}_k = \frac{1}{N + 1} \sum_{n=0}^N \vec{f}_n \cos\left(\frac{k\pi}{N + 1}\left(n + \frac{1}{2}\right)\right). \quad (6.29)$$

We have finally arrived at a decoupled set of  $3(N + 1)$  stochastic differential equations. In fact all of them are similar to our first stochastic differential equation

(4.2). They only differ in their friction coefficients, and in the characteristics of the random forces.

Using Eq. (6.22) we easily see that  $\vec{R}_G = \vec{X}_0$ . Eqs. (6.26) and (6.27) for  $k = 0$  read

$$\frac{d\vec{X}_0}{dt} = \vec{F}_0 \quad (6.30)$$

$$\langle \vec{F}_0(t) \cdot \vec{F}_0(t') \rangle = 6 \frac{D}{N+1} \delta(t-t') \quad (6.31)$$

from which we get again the diffusion coefficient of the centre of mass as given in Eq. (6.9).

The specific solutions that we have found are called the normal modes of the chain.  $\vec{X}_0$  describes the motion of the centre of gravity. The other modes describe vibrations of the chain leaving the centre of mass unchanged.

In the applications ahead of us, our results will always be expressed as sums over normal modes, which sums will always be dominated by the contributions from the modes with small  $k$ , i.e. those with large wavelength. We therefore approximate Eq. (6.26) by

$$\frac{d\vec{X}_k}{dt} = -\frac{1}{\tau_k} \vec{X}_k + \vec{F}_k \quad (6.32)$$

$$\langle \vec{F}_k(t) \cdot \vec{F}_k(t') \rangle = \frac{3D}{N+1} \delta_{kk'} \delta(t-t'). \quad (6.33)$$

These equations apply when  $k \neq 0$ . The characteristic time  $\tau_k$  is given by

$$\tau_k = \frac{\gamma b^2 (N+1)^2}{3\pi^2 k_B T} \frac{1}{k^2} = \frac{b^2 (N+1)^2}{3\pi^2 D} \frac{1}{k^2}. \quad (6.34)$$

## 6.4 Correlation of the end-to-end vector

As an example of a dynamic characteristic of the Rouse chain we calculate  $\langle \vec{R}(t) \cdot \vec{R}(0) \rangle$ , i.e. the time correlation function of the end-to-end vector. First we notice that

$$\vec{R} = \vec{R}_N - \vec{R}_0 = 2 \sum_{k=1}^N \vec{X}_k \{(-1)^k - 1\} \cos\left(\frac{k\pi}{2(N+1)}\right). \quad (6.35)$$

Our result will be dominated by  $k$  values which are extremely small compared to  $N$ . We therefore write

$$\vec{R} = -4 \sum_{k=1}^N ' \vec{X}_k \quad (6.36)$$

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

$$\langle \vec{R}(t) \cdot \vec{R}(0) \rangle = 16 \sum_{k=1}^N ' \langle \vec{X}_k(t) \cdot \vec{X}_k(0) \rangle \quad (6.37)$$

where we have used the fact that different modes are uncorrelated.

From Eqs. (6.32) to (6.33) we get

$$\vec{X}_k(t) = \vec{X}_k(0) e^{-t/\tau_k} + \int_0^t d\tau e^{-(t-\tau)/\tau_k} \vec{F}_k(\tau) \quad (6.38)$$

$$\langle \vec{X}_k(t) \cdot \vec{X}_k(0) \rangle = \langle \vec{X}_k(0)^2 \rangle e^{-t/\tau_k} \quad (6.39)$$

In Appendix A of this chapter it is shown that

$$\langle \vec{X}_k(0) \cdot \vec{X}_k(0) \rangle = \frac{3D}{N+1} \frac{\tau_k}{2} \quad k \neq 0. \quad (6.40)$$

Introducing everything into Eq. (6.37) we get

$$\langle \vec{R}(t) \cdot \vec{R}(0) \rangle = \frac{8b^2}{\pi^2} (N+1) \sum_{k=1}^N \frac{1}{k^2} e^{-t/\tau_k}. \quad (6.41)$$

The characteristic decay time at large  $t$  is  $\tau_1$ , which is proportional to  $N^2$ .

Notice that in this derivation we have averaged over all initial values. We might also have calculated  $\langle \vec{R}(t) \cdot \vec{R}(t') \rangle_{\vec{X}_k(0)}$ , i.e. the time correlation function of  $\vec{R}(t)$ , given some initial configurations of the chain. For very large  $t$  and  $t'$  the result should be independent of  $\vec{X}_k(0)$ . Indeed using Eq. (6.38) twice, it is not difficult to find

$$\begin{aligned} \langle \vec{X}_k(t) \cdot \vec{X}_k(t') \rangle_{\vec{X}_k(0)} = \\ \vec{X}_k(0)^2 e^{-(t+t')/\tau_k} + \frac{3D}{N+1} \frac{\tau_k}{2} \left( e^{-|t'-t|/\tau_k} - e^{-(t+t')/\tau_k} \right). \end{aligned} \quad (6.42)$$

which for very large  $t$  and  $t'$  leads to the desired result.

## 6.5 Monomer motion

In this section we study the mean square displacements of the individual monomers. Using Eq. (6.24) and the fact that different modes are not correlated, we get

$$\begin{aligned} \langle (\vec{R}_n(t) - \vec{R}_n(0))^2 \rangle = \langle (\vec{X}_0(t) - \vec{X}_0(0))^2 \rangle \\ + 4 \sum_{k=1}^N \langle (\vec{X}_k(t) - \vec{X}_k(0))^2 \rangle \cos^2 \left( \frac{k\pi}{N+1} \left( n + \frac{1}{2} \right) \right) \end{aligned} \quad (6.43)$$

Introducing Eq. (6.38) we get

$$\begin{aligned} \langle (\vec{R}_n(t) - \vec{R}_n(0))^2 \rangle = 6D_G t \\ + \frac{4b^2}{\pi^2} (N+1) \sum_{k=1}^N \frac{1}{k^2} (1 - e^{-tk^2/\tau_1}) \cos^2 \left( \frac{k\pi}{N+1} \left( n + \frac{1}{2} \right) \right) \end{aligned} \quad (6.44)$$

where we have used Eqs. (6.30) and (6.31) to calculate the first term, and Eqs. (6.39) and (6.40) for the second term.

There are two different limits to Eq. (6.44). First, when  $t$  is very large, i.e.  $t \gg \tau_1$ , the first term will dominate, yielding

$$\langle (\vec{R}_n(t) - \vec{R}_n(0))^2 \rangle = 6D_G t \quad t \gg \tau_1. \quad (6.45)$$

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

Secondly, suppose  $t \ll \tau_1$ . Then the sum in Eq. (6.44) will dominate. Averaging over all monomers, and replacing the sum over  $k$  by an integral we get

$$\frac{1}{N+1} \sum_{n=0}^N \langle (\vec{R}_n(t) - \vec{R}_n(0))^2 \rangle = \frac{2b^2}{\pi^2} (N+1) \int_0^\infty dk \frac{1}{k^2} (1 - e^{-tk^2/\tau_1})$$

$$\begin{aligned}
&= \frac{2b^2}{\pi^2} (N+1) \int_0^\infty dk \frac{1}{\tau_1} \int_0^t dt' e^{-t'k^2/\tau_1} \\
&= \frac{2b^2}{\pi^2} \frac{(N+1)}{\tau_1} \frac{1}{2} \sqrt{\pi\tau_1} \int_0^t dt' \frac{1}{\sqrt{t'}}.
\end{aligned} \tag{6.46}$$

Performing the final integral we get

$$\langle (\vec{R}_n(t) - \vec{R}_n(0))^2 \rangle = \left( \frac{4k_B T b^2}{3\pi\gamma} \right)^{\frac{1}{2}} t^{\frac{1}{2}} \quad t \ll \tau_1. \tag{6.47}$$

So, at short times the mean square displacement of a typical monomer goes like the square root of  $t$ .

## 6.6 Viscosity of a dilute polymer solution and a polymer melt

### 6.6.1 A. Shear flow

In this final section we calculate the viscosity of a dilute polymer solution. Shear flows, for which the velocity components are given by

$$v_\alpha(\vec{r}, t) = \sum_\beta \kappa_{\alpha\beta}(t) r_\beta \tag{6.48}$$

are commonly used for studying viscoelastic properties. If the shear rates  $\kappa_{\alpha\beta}(t)$  are small enough, the stress tensor depends linearly on  $\bar{\kappa}(t)$  and can be written as

$$S_{\alpha\beta}(t) = \int_{-\infty}^t d\tau G(t-\tau) \kappa_{\alpha\beta}(\tau) \tag{6.49}$$

where  $G(t)$  is called the shear relaxation modulus.

An important special case is a stepwise shear flow, which is switched on at  $t = 0$ :

$$v_x(t) = \Theta(t) \dot{\gamma} r_y \tag{6.50}$$

$$v_y(t) = 0 \tag{6.51}$$

$$v_z(t) = 0 \tag{6.52}$$

where  $\dot{\gamma}$  is called the shear rate and  $\Theta$  is the Heaviside function ( $\Theta(t) = 0$  for  $t < 0$ ,  $\Theta(t) = 1$  for  $t \geq 0$ ). From Eqs. (5.13) and (6.49) we see that

$$\eta = \lim_{t \rightarrow \infty} \frac{S_{xy}(t)}{\dot{\gamma}} = \lim_{t \rightarrow \infty} \int_0^t d\tau G(t-\tau) = \int_0^\infty d\tau G(\tau). \tag{6.53}$$

The limit  $t \rightarrow \infty$  must be taken because during the early stages elastic stresses are built up.

The calculation now consists of two steps. First we shall bring Eq. (5.64) into a form applicable to the present case. In the second step we shall formulate the Langevin approach of section 6.3 in the case when the system is under shear, and calculate the stress tensor.

### 6.6.2 B. The stress tensor in normal coordinates

The beads in our polymer are assumed to be point particles. The second term in Eq. (5.64) is proportional to the volume fraction of beads, and therefore equals zero. The element  $S_{xy}(t)$  of the stress tensor then reads

$$S_{xy}(t) = \eta_s \dot{\gamma} + \frac{c}{N+1} \left\langle \sum_{i=0}^N R_{ix} \frac{\partial}{\partial R_{iy}} (\Phi + k_B T \ln \Psi) \right\rangle_c \quad (6.54)$$

where  $c$  is the monomer concentration. The  $\ln \Psi$  term yields

$$k_B T \frac{c}{N+1} \sum_{i=0}^N \int d^3 R_0 \dots \int d^3 R_N R_{ix} \frac{\partial \Psi}{\partial R_{iy}} = 0. \quad (6.55)$$

So, we are left with

$$S_{xy}(t) = \eta_s \dot{\gamma} + \frac{c}{N+1} \frac{3k_B T}{b^2} \sum_{i=0}^N \langle R_{ix}(t)(2R_{iy}(t) - R_{i-1,y}(t) - R_{i+1,y}(t)) \rangle_c. \quad (6.56)$$

We next introduce the normal mode expansion Eq. (6.24), and go through the usual analysis; finding

$$S_{xy}(t) = \eta_s \dot{\gamma} + \frac{c}{(N+1)^2} \frac{6\pi^2 k_B T}{b^2} \sum_{k=1}^N k^2 \langle X_{kx}(t) X_{ky}(t) \rangle \quad (6.57)$$

From now on we omit the subscript  $c$  at the averaging brackets, because it serves no purpose anymore.

### 6.6.3 C. Calculation of the stress tensor

We now must calculate  $\langle X_{kx}(t) X_{ky}(t) \rangle$  under the conditions given in Eqs. (6.50), (6.51) and (6.52). Let us write the flow like  $\vec{v}(t) = \Theta(t) \dot{\gamma} \cdot \vec{r}$ . It is not difficult to understand that under these conditions, the equations of motion read

$$\frac{d\vec{R}_0}{dt} = -\frac{3k_B T}{\gamma b^2} (\vec{R}_0 - \vec{R}_1) + \dot{\gamma} \cdot \vec{R}_0 + \vec{f}_0 \quad (6.58)$$

$$\frac{d\vec{R}_n}{dt} = -\frac{3k_B T}{\gamma b^2} (2\vec{R}_n - \vec{R}_{n-1} - \vec{R}_{n+1}) + \dot{\gamma} \cdot \vec{R}_n + \vec{f}_n \quad (6.59)$$

$$\frac{d\vec{R}_N}{dt} = -\frac{3k_B T}{\gamma b^2} (\vec{R}_N - \vec{R}_{N-1}) + \dot{\gamma} \cdot \vec{R}_N + \vec{f}_N \quad (6.60)$$

$$\langle \vec{f}_n(t) \cdot \vec{f}_m(t') \rangle = 6D \delta_{n,m} \delta(t - t') \quad (6.61)$$

Each bead simply gets an extra velocity equal to the average velocity at its instantaneous position.

The reader who wishes to explicitly check the above equations, may start with Eq. (4.2) and replace the particles velocity  $\vec{v}$  in the friction force by its velocity relative to the average velocity, i.e. replace  $-\xi \vec{v}$  by  $-\xi(\vec{v} - \dot{\gamma} \cdot \vec{r})$ . Going all the way to Eq. (4.39) he/she will find that also there  $-\xi \vec{V}$  is replaced by  $-\xi(\vec{V} - \dot{\gamma} \cdot \vec{r})$ . Next, putting  $D\vec{V}/Dt$  equal to zero, and solving for  $\vec{V}$ , he/she will find an extra term  $\dot{\gamma} \cdot \vec{r}$ . This finally will lead to an extra term in the Smoluchowski equation, which can only be obtained from the Langevin equation Eq. (4.27) if it is augmented with a term  $\dot{\gamma} \cdot \vec{r}$  on the right hand side.

We now continue our calculation of the stress tensor. To this end, we transform to normal coordinates

$$\frac{d\vec{X}_k}{dt} = -\frac{1}{\tau_k}\vec{X}_k + \bar{\gamma} \cdot \vec{X}_k + \vec{F}_k \quad (6.62)$$

$$\langle \vec{F}_{k\alpha}(t)\vec{F}_{k\beta}(t') \rangle = \frac{D}{N+1}\delta_{\alpha\beta}\delta_{kk'}\delta(t-t') \quad (6.63)$$

Using these equations of motion for the shear rate defined by Eqs. (6.50) to (6.52) we derive

$$\begin{aligned} \frac{d}{dt}\langle X_{kx}(t)X_{ky}(t) \rangle &= \left\langle \frac{dX_{kx}}{dt}(t)X_{ky}(t) \right\rangle + \langle X_{kx}(t)\frac{dX_{ky}}{dt}(t) \rangle \\ &= -\frac{2}{\tau_k}\langle X_{kx}(t)X_{ky}(t) \rangle + \dot{\gamma}\langle X_{ky}(t)X_{ky}(t) \rangle \\ &\quad + \langle F_{kx}(t)X_{ky}(t) \rangle + \langle X_{kx}(t)F_{ky}(t) \rangle \end{aligned} \quad (6.64)$$

At the end of this section we shall argue that the last two terms vanish. Moreover, for small values of  $\dot{\gamma}$  we shall approximate  $\langle X_{ky}(t)X_{ky}(t) \rangle$  by its equilibrium value  $\frac{1}{2}D\tau_k/(N+1)$ . Using  $\langle X_{kx}(0)X_{ky}(0) \rangle = 0$ , we find from Eq. (6.64)

$$\langle X_{kx}(t)X_{ky}(t) \rangle = \int_0^t d\tau \dot{\gamma} \frac{1}{2} \frac{D\tau_k}{N+1} \exp(-2(t-\tau)/\tau_k) \quad (6.65)$$

$$= \frac{D\tau_k^2}{4(N+1)}(1 - e^{-2t/\tau_k})\dot{\gamma} \quad (6.66)$$

Combining Eqs. (6.49), (6.57) and (6.65) we find an integral expression for the stress tensor:

$$S_{xy}(t) = \eta_s \dot{\gamma} + \frac{c}{N+1} k_B T \int_0^t d\tau \dot{\gamma} \left[ \sum_{k=1}^N \exp(-2(t-\tau)/\tau_k) \right] \quad (6.67)$$

In polymer melts, we must neglect the solvent contribution  $\eta_s \dot{\gamma}$ . We recognize that the contribution of the Rouse chains to the shear relaxation modulus is given by

$$G(t) = \frac{c}{N+1} k_B T \sum_{k=1}^N \exp(-2t/\tau_k) \quad (6.68)$$

So the viscosity of a Rouse melt, at constant monomer concentration  $c$ , is proportional to  $N$ :

$$\begin{aligned} \eta &= \int_0^\infty dt G(t) \approx \frac{c}{N+1} k_B T \frac{\tau_1}{2} \sum_{k=1}^N \frac{1}{k^2} \\ &\approx \frac{c}{N+1} k_B T \frac{\tau_1}{2} \frac{\pi^2}{6} = \frac{c\gamma b^2}{36} (N+1) \end{aligned} \quad (6.69)$$

This has been confirmed for polymer melts with low molecular weight. Polymer melts of high molecular weight give different results, stressing the importance of so-called entanglements. We will deal with this in chapter 8.

In dilute solutions, we do not neglect the solvent contribution  $\eta_s \dot{\gamma}$ . We combine Eqs. (6.53), (6.57) and (6.66) to obtain an expression for the intrinsic viscosity,

$$\begin{aligned} [\eta] &= \lim_{\rho \rightarrow 0} \frac{\eta - \eta_s}{\rho \eta_s} \\ &= \frac{N_{A_v}}{M} \frac{1}{\eta_s} \frac{\gamma b^2 (N+1)^2}{6\pi^2} \sum_{k=1}^N \frac{1}{k^2} \approx \frac{N_{A_v}}{M} \frac{1}{\eta_s} \frac{\gamma b^2}{36} (N+1)^2 \end{aligned} \quad (6.70)$$

Here,  $\rho = cM/(N_{A_v}(N+1))$  is the polymer concentration;  $M$  is the mol mass of the polymer, and  $N_{A_v}$  is Avogadro's number.

We finish this section by calculating  $\langle X_{k\alpha}(t)F_{k\beta}(t) \rangle$ . Integrating Eq. (6.62) we find

$$\vec{X}_k(t) = \vec{X}_k(0)e^{-t/\tau_k} + \int_0^t d\tau e^{-(t-\tau)/\tau_k} (\dot{\vec{\gamma}} \cdot \vec{X}_k(\tau) + \vec{F}_k(\tau)) \quad (6.71)$$

Because of causality  $\langle X_{k\alpha}(\tau)F_{k\beta}(t) \rangle = 0$  for  $\tau < t$ . Then

$$\begin{aligned} \langle X_{k\alpha}(t)F_{k\beta}(t) \rangle &= \int_0^t d\tau e^{-(t-\tau)/\tau_k} \langle F_{k\alpha}(\tau)F_{k\beta}(t) \rangle \\ &= \frac{1}{2} \int_0^\infty d\tau e^{-|t-\tau|/\tau_k} \langle F_{k\alpha}(\tau)F_{k\beta}(t) \rangle \\ &= \frac{D}{2(N+1)} \delta_{\alpha\beta} \end{aligned} \quad (6.72)$$

i.e.  $\langle X_{kx}(t)F_{ky}(t) \rangle = \langle X_{ky}(t)F_{kx}(t) \rangle = 0$ .

## 6.7 Summary

We have found the following results

$$D \sim \frac{1}{N} \quad (6.73)$$

$$\tau \sim N^2 \quad (6.74)$$

$$\eta \sim N \quad (\text{melt}) \quad (6.75)$$

$$[\eta] \sim N^2 \quad (\text{dilute}) \quad (6.76)$$

All of these are at variance with experimental results. In the next chapter we shall treat a different model, the model of Zimm, which is a generalization of the Rouse chain, and gives results which are in good agreement with experiments. The Rouse chain will be used again in Chapter 8.

## Appendix A

In this appendix we calculate the equilibrium expectation value of  $X_k^2$ . In Cartesian coordinates the statistical weight of some configuration  $\vec{R}_0, \vec{R}_1, \dots, \vec{R}_N$  is given by

$$P(\vec{R}_0, \dots, \vec{R}_N) = \frac{1}{Z} \exp\left\{-\sum_{n=1}^N \frac{3}{2b^2} (\vec{R}_n - \vec{R}_{n-1})^2\right\} \quad (6.77)$$

Since the transformation to normal coordinates is a linear transformation from one set of orthogonal coordinates to another, the corresponding Jacobian is simply a constant. The argument of the exponential may be written as

$$\begin{aligned} &\sum_{n=1}^N (\vec{R}_n - \vec{R}_{n-1})^2 \\ &= \vec{R}_0 \cdot (\vec{R}_0 - \vec{R}_1) + \sum_{n=1}^{N-1} \vec{R}_n \cdot (2\vec{R}_n - \vec{R}_{n-1} - \vec{R}_{n+1}) \\ &\quad + \vec{R}_N \cdot (\vec{R}_N - \vec{R}_{N-1}) \end{aligned}$$

$$\begin{aligned}
&= 4 \sum_{k_1=1}^N \sum_{k_2=1}^N \vec{X}_{k_1} \cdot \vec{X}_{k_2} 4 \sin^2 \left( \frac{k_2 \pi}{2(N+1)} \right) \\
&\quad \sum_{n=0}^N \cos \left( \frac{k_1 \pi}{N+1} \left( n + \frac{1}{2} \right) \right) \cos \left( \frac{k_2 \pi}{N+1} \left( n + \frac{1}{2} \right) \right) \\
&= 8(N+1) \sum_{k=1}^N \vec{X}_k \cdot \vec{X}_k \sin^2 \left( \frac{k\pi}{2(N+1)} \right). \tag{6.78}
\end{aligned}$$

The statistical weight therefore reads

$$P(\vec{X}_0, \dots, \vec{X}_N) = \frac{1}{Z} \exp \left\{ -\frac{12}{b^2} (N+1) \sum_{k=1}^N \vec{X}_k \cdot \vec{X}_k \sin^2 \left( \frac{k\pi}{2(N+1)} \right) \right\} \tag{6.79}$$

Since this is a simple product of independent Gaussians, all kinds of expectation values may easily be calculated, like for example

$$\langle \vec{X}_k \cdot \vec{X}_k \rangle = \frac{b^2}{8(N+1)} \frac{1}{\sin^2 \left( \frac{k\pi}{2(N+1)} \right)} \tag{6.80}$$



# Chapter 7

## The Zimm chain

### 7.1 Definition and equations of motion

One obvious way to improve on the Rouse chain, is by introducing hydrodynamic interactions between the beads. The chain so defined is called the Zimm chain. The equations describing hydrodynamic interactions have been obtained in section 5.4.

Let us now derive the equations of motion of the beads in a Zimm chain. Let  $\Psi = \Psi(\vec{R}_0, \dots, \vec{R}_N; t)$  be the probability density of finding particles  $0, \dots, N$  near  $\vec{R}_0, \dots, \vec{R}_N$  at time  $t$ . The time development of  $\Psi$  obeys

$$\frac{\partial \Psi}{\partial t} = - \sum_{j=0}^N \vec{\nabla}_j \cdot \vec{\mathcal{J}}_j \quad (7.1)$$

where  $\vec{\mathcal{J}}_j$  is the flux of particles  $j$ . This flux may be written as

$$\vec{\mathcal{J}}_j = - \sum_k \bar{\mu}_{jk} \cdot (\vec{\nabla}_k \Phi) \Psi - \sum_k \bar{D}_{jk} \cdot \vec{\nabla}_k \Psi \quad (7.2)$$

The first term results from the forces  $-\vec{\nabla}_k \Phi$  felt by all the beads. On the Smoluchowski time scale, these forces make the beads move with constant velocities  $\vec{v}_k$ . This amounts to saying that the forces  $-\vec{\nabla}_k \Phi$  are exactly balanced by the hydrodynamic forces acting on the beads  $k$ , i.e. the forces exerted by the fluid on the beads  $k$  are equal to  $\vec{\nabla}_k \Phi$ . Introducing these forces into Eq. (5.54), we find the systematic part of the velocity of bead  $j$ :

$$\vec{v}_j = - \sum_k \bar{\mu}_{jk} \cdot (\vec{\nabla}_k \Phi) \quad (7.3)$$

Multiplying this velocity by  $\Psi$ , we obtain the systematic part of the flux of particle  $j$ . The second term in Eq. (7.2) stems from the random displacements of all beads, which result in a flux along the negative gradient of the probability density.

Combining Eqs. (7.1) and (7.2) we find

$$\frac{\partial \Psi}{\partial t} = \sum_j \sum_k \vec{\nabla}_j \cdot \bar{D}_{jk} \cdot \{ \bar{D}_{jk}^{-1} \cdot \bar{\mu}_{jk} \cdot \vec{\nabla}_k \Phi + \vec{\nabla}_k \ln \Psi \} \Psi \quad (7.4)$$

where  $\bar{D}_{jk}^{-1}$  is the inverse of  $\bar{D}_{jk}$ . In the stationary state the right hand side must be zero, and  $\Psi = c \exp\{-\beta\Phi\}$ . From this it follows that

$$\bar{D}_{jk} = k_B T \bar{\mu}_{jk} \quad (7.5)$$

which is a generalization of the Einstein equation.

The equation of motion of the probability density, i.e. the Smoluchowski equation, now reads

$$\frac{\partial \Psi}{\partial t} = \sum_j \sum_k \vec{\nabla}_j \cdot \bar{\mu}_{jk} \cdot \{ \vec{\nabla}_k \Phi + k_B T \vec{\nabla}_k \ln \Psi \} \Psi \quad (7.6)$$

The Langevin equations corresponding to this Smoluchowski equation are

$$\frac{d\vec{R}_j}{dt} = - \sum_k \bar{\mu}_{jk} \cdot \vec{\nabla}_k \Phi + k_B T \sum_k \vec{\nabla}_k \cdot \bar{\mu}_{jk} + \vec{f}_j \quad (7.7)$$

$$\langle \vec{f}_j(t) \vec{f}_k(t') \rangle = 2k_B T \bar{\mu}_{jk} \delta(t - t') \quad (7.8)$$

The reader can easily check that these reduce to the equations of motion of the Rouse chain when hydrodynamic interactions are neglected.

Let us note at this point that for the approximation of the mobility tensor we make use of

$$\vec{\nabla}_k \cdot \bar{\mu}_{jk} = 0, \quad (7.9)$$

which greatly simplifies Eq. (7.7).

## 7.2 Normal coordinates and the spectrum

If we introduce the mobility tensors Eq. (5.56) into Eq. (7.7), we are left with a completely intractable set of equations. One way out of this is by noting that in equilibrium, on average, the mobility tensors will be proportional to the unit tensor. We therefore assume that  $\Psi$  will never differ much from  $\Psi_{\text{eq}}$ , and that we may replace the mobility tensor in Eq. (7.7) by

$$\langle \bar{\mu}_{jk} \rangle_{\text{eq}} = \int d^3 R_0 \dots \int d^3 R_N \bar{\mu}_{jk}(\vec{R}_j, \vec{R}_k) \Psi_{\text{eq}}(\vec{R}_0, \dots, \vec{R}_N) \quad (7.10)$$

where  $\Psi_{\text{eq}}$  is the Gaussian equilibrium distribution. A simple calculation yields

$$\begin{aligned} \langle \bar{\mu}_{jk} \rangle_{\text{eq}} &= \frac{1}{8\pi\eta} \langle \frac{1}{R_{jk}} \rangle_{\text{eq}} (1 + \langle \hat{R}_{jk} \hat{R}_{jk} \rangle_{\text{eq}}) \\ &= \frac{1}{6\pi\eta} \langle \frac{1}{R_{jk}} \rangle_{\text{eq}} \mathbf{1} \\ &= \frac{1}{6\pi\eta b} \left\{ \frac{6}{\pi |j - k|} \right\}^{1/2} \mathbf{1} \end{aligned} \quad (7.11)$$

The next step is to write down the equations of motion of the normal coordinates Eq. (6.26):

$$\frac{d\vec{X}_k}{dt} = - \sum_{p=0}^N \mu_{kp} \frac{3k_B T}{b^2} 4 \sin^2 \left( \frac{p\pi}{2(N+1)} \right) \vec{X}_p + \vec{F}_k \quad (7.12)$$

$$\langle \vec{F}_k(t) \cdot \vec{F}_{k'}(t') \rangle = 3k_B T \frac{\mu_{kk'}}{N+1} \delta(t - t'), \quad (7.13)$$

where

$$\begin{aligned} \mu_{kp} &= \frac{2}{N+1} \sum_{n=0}^N \sum_{m=0}^N \frac{1}{6\pi\eta b} \left\{ \frac{6}{\pi |n - m|} \right\}^{\frac{1}{2}} \\ &\quad \times \cos \left( \frac{k\pi}{N+1} \left( n + \frac{1}{2} \right) \right) \cos \left( \frac{p\pi}{N+1} \left( m + \frac{1}{2} \right) \right) \end{aligned} \quad (7.14)$$

Equation (7.12) still is not tractable. It turns out however (see Appendix), that for large  $N$  approximately

$$\mu_{kp} = \left\{ \frac{N+1}{3\pi^3 p} \right\}^{\frac{1}{2}} \frac{1}{\eta b} \delta_{kp} \quad (7.15)$$

Introducing this result in Eq. (7.12), we see that the normal modes, just like with the Rouse chain, constitute a set of decoupled coordinates.

For small values of  $k$  we find

$$\frac{d\vec{X}_k}{dt} = -\frac{1}{\tau_k} \vec{X}_k + \vec{F}_k \quad (7.16)$$

$$\langle \vec{F}_k(t) \cdot \vec{F}_{k'}(t) \rangle = 3k_B T \frac{\mu_{kk}}{N+1} \delta_{kk'} \delta(t-t') \quad (7.17)$$

where the first term on the right hand side of Eq. (7.16) equals zero when  $k = 0$ , and otherwise

$$\tau_k = \frac{3\pi\eta b^3}{k_B T} \left( \frac{N+1}{3\pi k} \right)^{\frac{3}{2}} \quad (7.18)$$

We are now in a position to calculate the diffusion coefficient  $D_G$  of a Zimm chain, and the viscosity of a dilute solution of Zimm chains.

### 7.3 Diffusion coefficient and viscosity

The diffusion coefficient of a Zimm chain can be easily calculated from Eqs. (7.16) and (7.17). The result is

$$D_G = \frac{kT}{2} \frac{\mu_{00}}{N+1} = \frac{kT}{6\pi\eta b} \sqrt{\frac{6}{\pi}} \frac{1}{(N+1)^2} \sum_{n=0}^N \sum_{m=0}^N \frac{1}{|n-m|^{1/2}} \quad (7.19)$$

$$\approx \frac{kT}{6\pi\eta b} \sqrt{\frac{6}{\pi}} \frac{1}{N^2} \int_0^N dn \int_0^N dm \frac{1}{|n-m|^{1/2}} \quad (7.20)$$

$$= \frac{8}{3} \frac{kT}{6\pi\eta b} \sqrt{\frac{6}{\pi N}} \quad (7.21)$$

The diffusion coefficient now scales with  $N^{-1/2}$ , in agreement with experiments.

In order to calculate the intrinsic viscosity of a dilute solution of Zimm chains we go back to Eq. (6.64):

$$\frac{d}{dt} \langle X_{kx}(t) X_{ky}(t) \rangle = -\frac{2}{\tau_k} \langle X_{kx}(t) X_{ky}(t) \rangle + \dot{\gamma} \langle X_{ky}(t) X_{ky}(t) \rangle \quad (7.22)$$

Again we shall approximate  $\langle X_{ky}(t) X_{ky}(t) \rangle$  by its equilibrium value. At the end of this section we shall show that

$$\langle X_{ky} X_{ky} \rangle_{\text{eq}} = kT \frac{\mu_{kk}}{N+1} \frac{\tau_k}{2} \quad (7.23)$$

The solution of Eq. (7.22) with this approximation is

$$\langle X_{kx}(t) X_{ky}(t) \rangle = kT \frac{\mu_{kk}}{N+1} \left( \frac{\tau_k}{2} \right)^2 (1 - e^{-2t/\tau_k}) \dot{\gamma} \quad (7.24)$$

Eqs. (6.53), (6.57) and (7.24) then yield

$$[\eta] = \frac{N_{Av}}{M} 12\pi \left\{ \frac{(N+1)b^2}{12\pi} \right\}^{3/2} \sum_{k=1}^N \frac{1}{k^{\frac{3}{2}}} \quad (7.25)$$

The intrinsic viscosity scales with  $N^{3/2}$ , in agreement with experiments.

We finish this section by proving Eq. (7.23). At equilibrium we have

$$0 = \frac{d}{dt} \langle X_{ky}(t) \bar{X}_{ky}(t) \rangle_{\text{eq}} \quad (7.26)$$

$$= -\frac{2}{\tau_k} \langle X_{ky}(t) X_{ky}(t) \rangle_{\text{eq}} + 2 \langle F_{ky}(t) X_{ky}(t) \rangle_{\text{eq}} \quad (7.27)$$

The last term here can be calculated according to

$$\langle F_{ky}(t) X_{ky}(t) \rangle = \int_0^t d\tau e^{-(t-\tau)/\tau_k} \langle F_{ky}(t) F_{ky}(\tau) \rangle \quad (7.28)$$

$$= \frac{1}{2} \int_{-\infty}^{\infty} d\tau e^{-|t-\tau|/\tau_k} \langle F_{ky}(t) F_{ky}(\tau) \rangle \quad (7.29)$$

Eq. (7.27), (7.29) and (7.17) yield Eq. (7.23).

## Appendix A

In order to derive Eq. (7.15) we write

$$\begin{aligned} \mu_{kp} &= \frac{2}{N+1} \frac{1}{6\pi\eta b} \sqrt{\frac{6}{\pi}} \sum_{n=0}^N \cos\left(\frac{k\pi}{N+1}\left(n+\frac{1}{2}\right)\right) \\ &\quad \times \sum_{m=n-N}^n \cos\left(\frac{p\pi}{N+1}\left(n-m+\frac{1}{2}\right)\right) \frac{1}{\sqrt{|m|}} \\ &= \frac{2}{N+1} \frac{1}{6\pi\eta b} \sqrt{\frac{6}{\pi}} \sum_{n=0}^N \cos\left(\frac{k\pi}{N+1}\left(n+\frac{1}{2}\right)\right) \cos\left(\frac{p\pi}{N+1}\left(n+\frac{1}{2}\right)\right) \\ &\quad \times \sum_{m=n-N}^n \cos\left(\frac{p\pi m}{N+1}\right) \frac{1}{\sqrt{|m|}} + \frac{2}{N+1} \frac{1}{6\pi\eta b} \sqrt{\frac{6}{\pi}} \sum_{n=0}^N \cos\left(\frac{k\pi}{N+1}\left(n+\frac{1}{2}\right)\right) \\ &\quad \times \sin\left(\frac{p\pi}{N+1}\left(n+\frac{1}{2}\right)\right) \sum_{m=n-N}^n \sin\left(\frac{p\pi m}{N+1}\right) \frac{1}{\sqrt{|m|}} \end{aligned} \quad (7.30)$$

We now approximate

$$\begin{aligned} \sum_{m=n-N}^n \cos\left(\frac{p\pi m}{N+1}\right) \frac{1}{\sqrt{|m|}} \\ \approx \int_{-\infty}^{\infty} dm \cos\left(\frac{p\pi m}{N+1}\right) \frac{1}{\sqrt{|m|}} = \sqrt{\frac{2(N+1)}{p}} \end{aligned} \quad (7.31)$$

$$\begin{aligned} \sum_{m=n-N}^n \sin\left(\frac{p\pi m}{N+1}\right) \frac{1}{\sqrt{|m|}} \\ \approx \int_{-\infty}^{\infty} dm \sin\left(\frac{p\pi m}{N+1}\right) \frac{1}{\sqrt{|m|}} = 0 \end{aligned} \quad (7.32)$$

Introducing these results into Eq. (7.30) one finds Eq. (7.15). As a technical detail we notice that in principle diagonal terms in Eq. (7.14) should have been treated separately, which is clear from Eq. (5.56). Since the contributions of all other terms is proportional to  $N^{1/2}$ , we omit the diagonal terms.

## Chapter 8

# Dynamics of dense polymer systems: reptation

### 8.1 The tube model

The movement of a chain in a dense polymeric system is highly constrained. Due to entanglements with other chains lateral motions of the chain at many points are highly improbable.

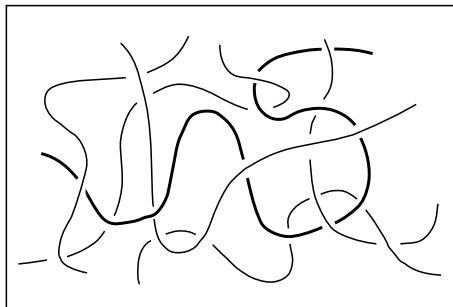


Figure 8.1: An entangled chain.

Qualitatively we may imagine that the chain has available a tube in which it may move with some freedom. In order to move over large distances the chain has to leave the tube by means of longitudinal motions.

The concept of tube introduced above, clearly has only a statistical meaning. The tube can change by two mechanisms. First by means of the motion of the central chain itself, by which the chain leaves parts of its original tube, and generates new parts. Secondly the tube will fluctuate because of the motions of the chains which built up the tube.

Situations where the second cause of tube fluctuations are reduced to a minimum, are those of a long chain in a melt of chains which are even much longer, and a chain in a gel. Also in the case of a chain in its own melt, tube fluctuations due to the motions of the environmental chains may be assumed to be negligible. This clearly amounts to a mean field treatment, which will not be able to describe certain collective motions of the system.

Let us now look at the mechanism which allows the chain to move along the tube axis, which is also called the primitive chain.

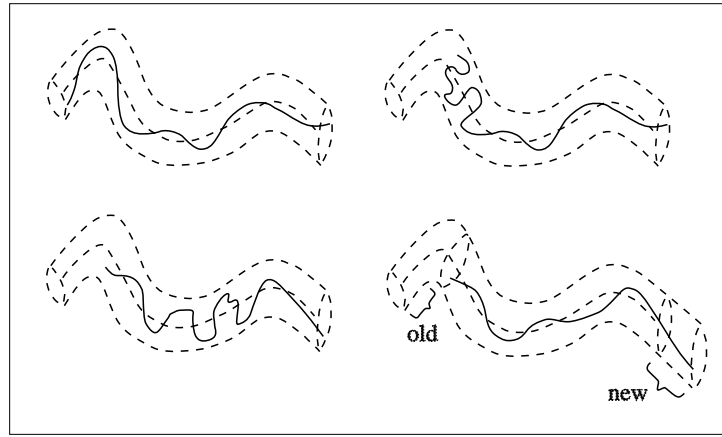


Figure 8.2: Reptation.

The chain fluctuates around the primitive chain. By some fluctuation it may store some excess mass in part of the chain. This mass may diffuse along the primitive chain and finally leave the tube. The chain thus creates a new piece of tube and at the same time destroys part of the tube on the other side. This kind of motion is called reptation.

It is clear from the above picture that the reptative motion will determine the long time motion of the chain. The main concept of the model is the primitive chain. The details of the polymer itself are to a high extent irrelevant. We may therefore choose a convenient polymer as we wish. In this chapter our polymer will be a Gaussian chain. Its motion will be governed by the Langevin equations at the Smoluchowski time scale. Our basic chain therefore is a Rouse chain.

## 8.2 Mathematical definition of the model

Our model consists of two parts. First we have the basic chain, and secondly we have the tube and its motion. So:

- Basic chain  
Rouse chain with parameters  $N$ ,  $b$  and  $\gamma$ .
- Primitive chain
  - i ) The primitive chain has contour length  $L$ . The position along the chain is indicated by  $s \in [0, L]$ . The configurations of the chain are Gaussian; by this we mean that

$$\langle (\vec{R}(s) - \vec{R}(s'))^2 \rangle = a|s - s'| \quad (8.1)$$

where  $a$  is a new parameter having the dimensions of length.

- ii ) The primitive chain diffuses along the tube axis with diffusion constant

$$D_G = \frac{kT}{(N+1)\gamma} \quad (8.2)$$

i.e. with the Rouse diffusion constant.

The Gaussian character of the distribution of primitive chain conformations is consistent with the reptation pictured in Fig. (8.2). The chain continuously creates new pieces of tube, which may be chosen in random directions with step length  $a$ . Then  $\vec{R}(s) - \vec{R}(s')$  is a Gaussian vector.

Apparently we have introduced two new parameters, the contour length  $L$  and the step length  $a$ . Only one of them however is independent, because they are related by  $Nb^2 = \langle R^2 \rangle = aL$ , where the first equality stems from the fact that we are dealing with a Rouse chain, and the second equality follows from an application of Eq. (8.1).

### 8.3 Monomer motion

We shall now demonstrate that according to our model the mean quadratic displacement of a typical monomer behaves like in Fig. (8.3). This behaviour has been qualitatively verified by computer simulations for times up to somewhere in the third regime. Of course the final regime should be simple diffusive motion. The important prediction is the dependence of the diffusion constant on  $N$ .

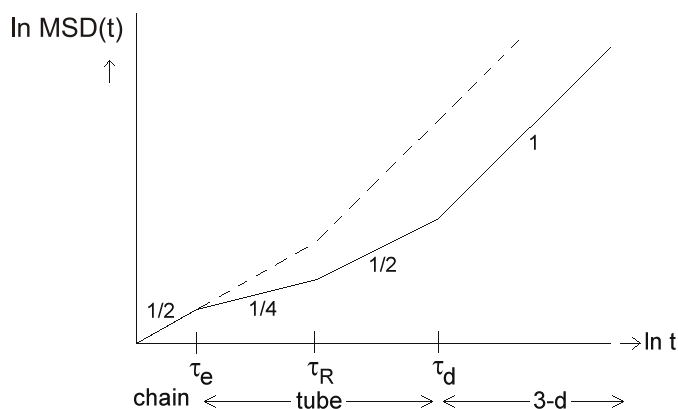


Figure 8.3: Double-logarithmic plot of the mean square displacement,  $\langle (\vec{R}_n(t) - \vec{R}_n(0))^2 \rangle$ , in case of the reptation model (solid line) and the Rouse model (dashed).

In Fig. (8.3)  $\tau_R$  is the Rouse time which is equal to  $\tau_1$  in chapter 6. The meaning of  $\tau_e$  and  $\tau_d$  will become clear in the remaining part of this section.

We shall now treat the different regimes in Fig. (8.3) one after another.

i)  $t \leq \tau_e$ .

At short times a Rouse bead doesn't know about any tube constraints. According to section 6.5 then

$$\langle (\vec{R}_n(t) - \vec{R}_n(0))^2 \rangle = \left( \frac{4kTb^2}{3\pi\gamma} \right)^{\frac{1}{2}} \sqrt{t}. \quad (8.3)$$

Consistent with the Gaussian character of the primitive chain we may suppose that the diameter of the tube is equal to  $a$ . Once the segment has moved a distance  $a$ , it will feel the constraints of the tube, and a new regime will set in. The time at which this happens is given by

$$\tau_e = \frac{3}{4} \pi a^4 \frac{\gamma}{kTb^2} \quad (8.4)$$

Notice that this is independent of  $N$ .

ii)  $\tau_e < t \leq \tau_R$ .

On the time and distance scale we are looking now, the bead performs random motions, still constrained by the fact that the monomer is a part of a chain because  $t \leq \tau_R$ . Orthogonally to the primitive chain these motions do not lead to any displacement, because of the constraints implied by the tube. Only along the primitive chain the bead may diffuse free of any other constraint than the one implied by the fact that it belongs to a chain. The diffusion therefore is given by the 1-dim. analog of Eq. (6.47) or Eq. (8.3).

$$\langle (s_n(t) - s_n(0))^2 \rangle = \frac{1}{3} \left( \frac{4kTb^2}{3\pi\gamma} \right)^{\frac{1}{2}} \sqrt{t} \quad (8.5)$$

where  $s_n(t)$  is the position of bead  $n$  along the primitive chain at time  $t$ . It is assumed here that for times  $t \leq \tau_R$  the chain as a whole does not move, i.e. that the primitive chain does not change. Using Eq. (8.1) then

$$\langle (\vec{R}_n(t) - \vec{R}_n(0))^2 \rangle = \left( \frac{4}{27\pi} \right)^{1/4} a b^{1/2} \left( \frac{kT}{\gamma} \right)^{1/4} t^{1/4} \quad (8.6)$$

where we have assumed  $\langle |s_n(t) - s_n(0)| \rangle \approx \langle (s_n(t) - s_n(0))^2 \rangle^{1/2}$ .

iii)  $\tau_R < t \leq \tau_d$ .

The bead still moves along the tube diameter. Now however  $t > \tau_R$ , which means that we should use the 1-dim. analog of Eq. (6.45).

$$\langle (s_n(t) - s_n(0))^2 \rangle = 2D_G t \quad (8.7)$$

Again assuming that the tube doesn't change appreciably during time  $t$ , we get

$$\langle (\vec{R}_n(t) - \vec{R}_n(0))^2 \rangle = \left( \frac{2kT}{\gamma} \right)^{1/2} a \frac{1}{\sqrt{N+1}} \sqrt{t}. \quad (8.8)$$

From our treatment it is clear that  $\tau_d$  is the time it takes for the chain to create a tube which is uncorrelated to the old one. We will calculate  $\tau_d$  in the next paragraph.

iv)  $\tau_d < t$ .

This is the regime in which reptation dominates. On this time and space scale we may attribute to every bead a definite value of  $s$ . We then want to calculate

$$\varphi(s, t) = \langle (\vec{R}(s, t) - \vec{R}(s, 0))^2 \rangle \quad (8.9)$$

where  $\vec{R}(s, t)$  is the position of bead  $s$  at time  $t$ .

In order to calculate  $\varphi(s, t)$  it is useful to introduce

$$\varphi(s, s'; t) = \langle (\vec{R}(s, t) - \vec{R}(s', 0))^2 \rangle \quad (8.10)$$

i.e. the mean square distance between bead  $s$  at time  $t$  and bead  $s'$  at time zero. According to Fig. (8.4), for all  $s$ , except  $s = a$  and  $s = L$ , we have

$$\varphi(s, s'; t + \Delta t) = \langle \varphi(s + \Delta\xi, s'; t) \rangle \quad (8.11)$$

where  $\Delta\xi$  according to the definition of the primitive chain in section 2 is a stochastic variable. The average on the right hand side has to be taken over the distribution of  $\Delta\xi$ . Expanding the right hand side of Eq. (8.11) we get

$$\begin{aligned} & \langle \varphi(s + \Delta\xi, s'; t) \rangle \\ & \approx \varphi(s, s'; t) + \langle \Delta\xi \rangle \frac{\partial}{\partial s} \varphi(s, s'; t) + \frac{1}{2} \langle (\Delta\xi)^2 \rangle \frac{\partial^2}{\partial s^2} \varphi(s, s'; t) \\ & \approx \varphi(s, s'; t) + D_G \Delta t \frac{\partial^2}{\partial s^2} \varphi(s, s'; t). \end{aligned} \quad (8.12)$$



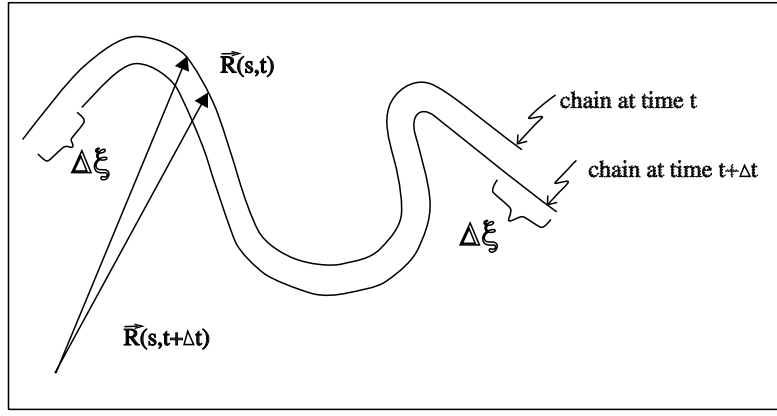


Figure 8.4: Motion of the primitive chain along its contour.

Introducing this into Eq. (8.11) and taking the limit for  $\Delta t$  going to zero, we get

$$\frac{\partial}{\partial t}\varphi(s, s'; t) = D_G \frac{\partial^2}{\partial s^2}\varphi(s, s'; t). \quad (8.13)$$

In order to complete our description of reptation we have to find the boundary conditions going with this diffusion equation. We will demonstrate that these are given by

$$\varphi(s, s'; t)|_{t=0} = a|s - s'| \quad (8.14)$$

$$\frac{\partial}{\partial s}\varphi(s, s'; t)|_{s=L} = a \quad (8.15)$$

$$\frac{\partial}{\partial s}\varphi(s, s'; t)|_{s=0} = -a. \quad (8.16)$$

The first of these is obvious. The second follows from

$$\begin{aligned} & \frac{\partial}{\partial s}\varphi(s, s'; t)|_{s=L} \\ &= 2\left\langle \frac{\partial \vec{R}(s, t)}{\partial s} \Big|_{s=L} \cdot (\vec{R}(L, t) - \vec{R}(s', 0)) \right\rangle \\ &= 2\left\langle \frac{\partial \vec{R}(s, t)}{\partial s} \Big|_{s=L} \cdot (\vec{R}(L, t) - \vec{R}(s', t)) \right\rangle + \\ & \quad 2\left\langle \frac{\partial \vec{R}(s, t)}{\partial s} \Big|_{s=L} \cdot (\vec{R}(s', t) - \vec{R}(s', 0)) \right\rangle \\ &= 2\left\langle \frac{\partial \vec{R}(s, t)}{\partial s} \Big|_{s=L} \cdot (\vec{R}(L, t) - \vec{R}(s', t)) \right\rangle \\ &= \frac{\partial}{\partial s} \langle (\vec{R}(s, t) - \vec{R}(s', t))^2 \rangle \Big|_{s=L} \\ &= \frac{\partial}{\partial s} a|s - s'|_{s=L} \end{aligned} \quad (8.17)$$

Condition Eq. (8.16) follows from a similar reasoning.

We now solve Eqs. (8.13)–(8.16), obtaining

$$\begin{aligned} \varphi(s, s'; t) &= |s - s'|a + 2D_G \frac{a}{L} t \\ &+ 4 \frac{La}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} (1 - e^{-tk^2/\tau_a}) \cos\left(\frac{k\pi s}{L}\right) \cos\left(\frac{k\pi s'}{L}\right) \end{aligned} \quad (8.18)$$

$$\tau_d = \frac{1}{\pi^2} \frac{b^4}{a^2} \frac{\gamma}{k_B T} N^3. \quad (8.19)$$

We shall not derive this here. One may check that Eq. (8.18) indeed is the solution to Eq. (8.13) satisfying (8.14)-(8.16).

Now taking the limit  $s \rightarrow s'$  we get

$$\begin{aligned} \langle (\vec{R}(s, t) - \vec{R}(s, 0))^2 \rangle &= 2D_G \frac{a}{L} t + \\ &4 \frac{La}{\pi^2} \sum_{k=1}^{\infty} \cos^2 \left( \frac{k\pi s}{L} \right) (1 - e^{-tk^2/\tau_d}) \frac{1}{k^2}. \end{aligned} \quad (8.20)$$

For  $t > \tau_d$  we get diffusive behaviour with diffusion constant

$$D = \frac{1}{3} D_G \frac{a}{L} = \frac{1}{3} \frac{a^2}{b^2} \frac{k_B T}{\gamma} \frac{1}{N^2}. \quad (8.21)$$

Notice that this is proportional to  $N^{-2}$ , whereas the diffusion coefficient of the Rouse model was proportional to  $N^{-1}$ . The reptation result,  $N^{-2}$ , is confirmed by experiments which measured the diffusion coefficients of polymer melts as a function of their molecular weight.

## 8.4 Viscoelastic behavior

Experimentally the shear relaxation modulus  $G(t)$  of a polymer melt turns out to be like in Fig. 8.5.

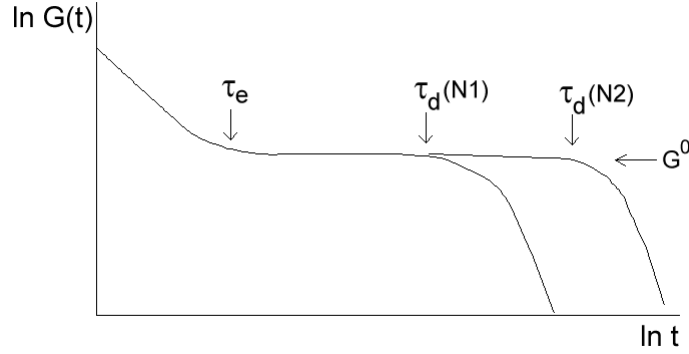


Figure 8.5: Logarithmic plot of the time behavior of the shear relaxation modulus  $G(t)$  of a polymer melt;  $N_1 < N_2$ .

We distinguish two regimes.

i)  $t < \tau_e$

At short times the chain behaves like a 3-dimensional Rouse chain. Using Eq. 6.68 we find

$$\begin{aligned} G(t) &= \frac{c}{N+1} k_B T \sum_{k=1}^N \exp(-2t/\tau_k) \\ &\approx \frac{c}{N+1} k_B T \int_0^{\infty} dk \exp(-2k^2 t/\tau_R) \\ &= \frac{c}{N+1} k_B T \sqrt{\frac{\pi}{8}} \left( \frac{\tau_R}{t} \right)^{1/2} \end{aligned} \quad (8.22)$$

which decays as  $t^{-1/2}$ .<sup>1</sup> At  $t = \tau_e$  this possibility to relax ends. The only way for the chain to relax any further is by breaking out of the tube.

ii)  $t > \tau_e$

The stress that remains in the system is caused by the fact that the chains are trapped in twisted tubes. By means of reptation the chain can break out of its tube. The newly generated tube contains no stress. So, it is plausible to assume that the stress at any time  $t$  is proportional to the fraction of the original tube that is still part of the tube at time  $t$ . We'll call this fraction  $\Psi(t)$ . So,

$$G(t) = G^0 \Psi(t). \quad (8.23)$$

On the reptation time scale,  $\tau_e$  is practically zero, so we can set  $\Psi(\tau_e) = \Psi(0) = 1$ . To make a smooth transition from the Rouse regime to the reptation regime, we match Eq. (8.22) with Eq. (8.23) at  $t = \tau_e$ , yielding

$$\begin{aligned} G^0 &= \frac{c}{N+1} k_B T \sqrt{\frac{\pi}{8}} \left( \frac{\tau_R}{\tau_e} \right)^{1/2} \\ &= \frac{c}{3\sqrt{2}\pi} k_B T \frac{b^2}{a^2} \end{aligned} \quad (8.24)$$

We will now calculate  $\Psi(t)$ . Take a look at

$$\langle \vec{u}(s', t) \cdot \vec{u}(s, 0) \rangle \equiv \left\langle \frac{\partial \vec{R}(s', t)}{\partial s'} \cdot \frac{\partial \vec{R}(s, 0)}{\partial s} \right\rangle \quad (8.25)$$

The vector  $\vec{u}(s', t)$  is the tangent to the primitive chain, at segment  $s'$  at time  $t$ . Because the primitive chain has been parametrized with the contour length, we have from Eq.(8.1)  $\langle \vec{u} \cdot \vec{u} \rangle = \langle \Delta \vec{R} \cdot \Delta \vec{R} \rangle / (\Delta s)^2 = a/\Delta s$ ; the non-existence of the limit of  $\Delta s$  going to zero is a peculiarity of a Gaussian process. Using Eq. 8.10 we calculate,

$$\begin{aligned} &\langle \vec{u}(s', t) \cdot \vec{u}(s, 0) \rangle \\ &= -\frac{1}{2} \frac{\partial^2}{\partial s \partial s'} \varphi(s', s; t) \\ &= a\delta(s - s') - \frac{2a}{L} \sum_{k=1}^{\infty} (1 - e^{-tk^2/\tau_a}) \sin\left(\frac{k\pi s}{L}\right) \sin\left(\frac{k\pi s'}{L}\right) \\ &= \frac{2a}{L} \sum_{k=1}^{\infty} e^{-tk^2/\tau_a} \sin\left(\frac{k\pi s}{L}\right) \sin\left(\frac{k\pi s'}{L}\right) \end{aligned} \quad (8.26)$$

$$= \frac{2a}{L} \sum_{k=1}^{\infty} e^{-tk^2/\tau_a} \sin\left(\frac{k\pi s}{L}\right) \sin\left(\frac{k\pi s'}{L}\right) \quad (8.27)$$

where we have used

$$\frac{2}{L} \sum_{k=1}^{\infty} \sin\left(\frac{k\pi s}{L}\right) \sin\left(\frac{k\pi s'}{L}\right) = \delta(s - s') \quad (8.28)$$

Using this last equation, we also find

$$\langle \vec{u}(s', 0) \cdot \vec{u}(s, 0) \rangle = a\delta(s - s') \quad (8.29)$$

This equation states that there is no correlation between the tangents to the primitive chain at a segment  $s$ , and at another segment  $s'$ . If we consider  $\langle \vec{u}(s', t) \cdot \vec{u}(s, 0) \rangle$

<sup>1</sup>Actually, at extremely short times we observe a transition from a plateau to  $t^{-1/2}$ . Also, the longer the chain, the longer this  $t^{-1/2}$ -behavior is sustained. In the integral approximation we have assumed that  $N$  is very large.

as a function of  $s'$ , at time  $t$ , we see that the original delta function has broadened and lowered. However, the tangent  $\vec{u}(s', t)$  can only be correlated to  $\vec{u}(s, 0)$  by means of diffusion of segment  $s'$ , during the time interval  $[0, t]$ , to the place where  $s$  was at time  $t = 0$ , and still lies in the original tube. So,  $\frac{1}{a} \langle \vec{u}(s', t) \cdot \vec{u}(s, 0) \rangle$  is the probability density that, at time  $t$ , segment  $s'$  lies within the original tube at the place where  $s$  was initially. Integrating over  $s'$  gives us the probability  $\Psi(s, t)$  that at time  $t$  *any* segment lies within the original tube at the place where segment  $s$  was initially. In other words, the chance that the original tube segment  $s$  is still up-to-date, is

$$\begin{aligned} \Psi(s, t) &= \frac{1}{a} \int_0^L ds' \langle \vec{u}(s', t) \cdot \vec{u}(s, 0) \rangle \\ &= \frac{4}{\pi} \sum_{k=1}^{\infty} \frac{1}{k} \sin\left(\frac{k\pi s}{L}\right) e^{-tk^2/\tau_d} \end{aligned} \quad (8.30)$$

We have plotted this in Fig. 8.6.

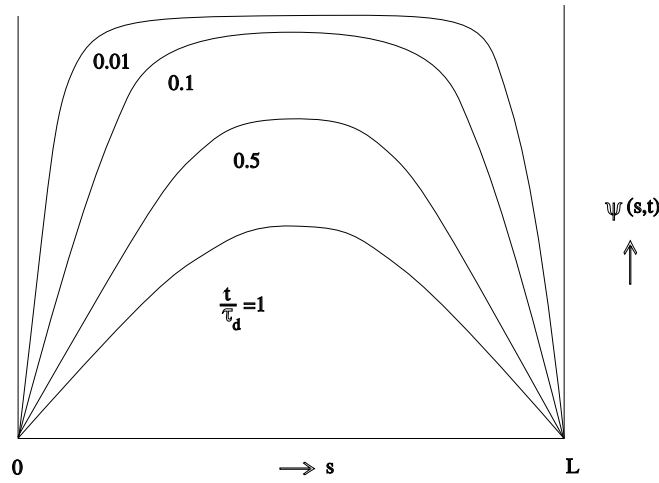


Figure 8.6: Development of  $\Psi(s, t)$  in time.

The fraction of the original tube that is still intact at time  $t$ , is therefore given by

$$\begin{aligned} \Psi(t) &= \frac{1}{L} \int_0^L ds \Psi(s, t) \\ &= \frac{8}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} e^{-tk^2/\tau_d} \end{aligned} \quad (8.31)$$

where the prime at the summation sign indicates that only terms with odd  $k$  should occur in the sum. This formula shows why  $\tau_d$  is the time needed by the chain to reptate out of its tube; for  $t > \tau_d$ ,  $\Psi(t)$  is falling to zero quickly.

In conclusion we have found results that are in good agreement with Fig. 8.5. We see an initial drop proportional to  $t^{-1/2}$ ; after that a plateau value  $G^0$  independent of  $N$ ; and finally a maximum relaxation time  $\tau_d$  proportional to  $N^3$ .

Finally, we are able to calculate the viscosity that is associated with the reptation model. Using Eq. 6.53 we find

$$\eta = \int_0^{\infty} G(t) dt = G^0 \frac{8}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} \int_0^{\infty} dt e^{-tk^2/\tau_d}$$

$$\begin{aligned} &= G^0 \frac{8}{\pi^2} \tau_d \sum_{k=1}^{\infty} \frac{1}{k^2} \int_0^{\infty} d\tau e^{-\tau k^2} \\ &= H \frac{b^6}{a^4} \zeta N^3 \end{aligned} \tag{8.32}$$

where  $H$  is a constant. We see that the viscosity is proportional to  $N^3$ . This is close to the experimentally verified  $N^{3.4}$  behavior of polymer melts with high molecular weight.

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