

Chapter 1

Random Walk Models for the Conformation

In this chapter we study simple statistical models for the entropic forces which are due to the large number of conformations characteristic for biopolymers like DNA or proteins (Fig. 1.1). First we discuss the freely jointed chain model. We evaluate the statistical distribution of end to end distances and discuss the force-extension relation. Then we study a two component model of a polymer chain which is composed of two types of units, which may interconvert. Interactions between the segments are included and explain the appearance of a very flat force-extension relationship, where a small force may lead to much larger changes in length than without interaction.

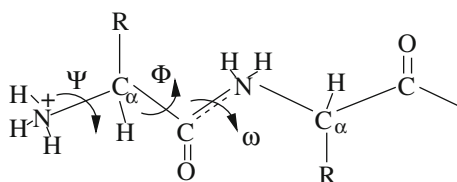


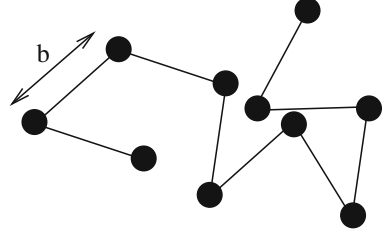
Fig. 1.1 Conformation of a protein. The relative orientation of two successive protein residues can be described by three angles (Ψ , Φ , ω). For a real protein the ranges of these angles are restricted by steric interactions, which are neglected in simple models

1.1 The Freely Jointed Chain

We consider a three-dimensional chain (Fig. 1.2) consisting of M units. The configuration can be described by a point in a $3(M+1)$ -dimensional space

$$(\mathbf{r}_0, \mathbf{r}_2 \dots \mathbf{r}_M). \quad (1.1)$$

Fig. 1.2 Freely jointed chain with constant bond length b



The M bond vectors

$$\mathbf{b}_i = \mathbf{r}_i - \mathbf{r}_{i-1} \quad (1.2)$$

have a fixed length $|\mathbf{b}_i| = b$ and are randomly oriented. This can be described by a distribution function

$$P(\mathbf{b}_i) = \frac{1}{4\pi b^2} \delta(|b_i| - b). \quad (1.3)$$

Since the different units are independent, the joint probability distribution factorizes

$$P(\mathbf{b}_1 \dots \mathbf{b}_M) = \prod_{i=1}^M P(\mathbf{b}_i). \quad (1.4)$$

There is no excluded volume interaction between any two monomers. Obviously the end-to-end distance

$$\mathbf{R} = \sum_{i=1}^N \mathbf{b}_i \quad (1.5)$$

has an average value of $\overline{\mathbf{R}} = 0$ since

$$\overline{\mathbf{R}} = \sum \overline{\mathbf{b}_i} = M \int \mathbf{b}_i P(\mathbf{b}_i) = 0. \quad (1.6)$$

The second moment is

$$\begin{aligned} \overline{R^2} &= \overline{\left(\sum_i \mathbf{b}_i \cdot \sum_j \mathbf{b}_j \right)} = \sum_{i,j} \overline{\mathbf{b}_i \cdot \mathbf{b}_j} \\ &= \sum_i \overline{b_i^2} + \sum_{i \neq j} \overline{\mathbf{b}_i \cdot \mathbf{b}_j} = Mb^2. \end{aligned} \quad (1.7)$$

1.1.1 Entropic Elasticity

The distribution of the end-to-end vector is

$$P(\mathbf{R}) = \int P(\mathbf{b}_1 \dots \mathbf{b}_M) \delta\left(\mathbf{R} - \sum \mathbf{b}_i\right) d^3b_1 \dots d^3b_M. \quad (1.8)$$

This integral can be evaluated by replacing the delta function by the Fourier integral

$$\delta(\mathbf{R}) = \frac{1}{(2\pi)^3} \int e^{-i\mathbf{k}\mathbf{R}} d^3k \quad (1.9)$$

which gives

$$P(\mathbf{R}) = \int d^3k e^{-i\mathbf{k}\mathbf{R}} \prod_{i=1}^M \left(\int \frac{1}{4\pi b^2} \delta(|\mathbf{b}_i| - b) e^{i\mathbf{k}\mathbf{b}_i} d^3b_i \right). \quad (1.10)$$

The inner integral can be evaluated in polar coordinates

$$\begin{aligned} & \int \frac{1}{4\pi b^2} \delta(|\mathbf{b}_i| - b) e^{i\mathbf{k}\mathbf{b}_i} d^3b_i \\ &= \int_0^{2\pi} d\phi \int_0^\infty b_i^2 db_i \frac{1}{4\pi b^2} \delta(|b_i| - b) \int_0^\pi \sin \theta d\theta e^{ikb_i \cos \theta}. \end{aligned} \quad (1.11)$$

The integral over θ gives

$$\int_0^\pi \sin \theta d\theta e^{ikb_i \cos \theta} = \frac{2 \sin kb_i}{kb_i} \quad (1.12)$$

and hence

$$\begin{aligned} \int \frac{1}{4\pi b^2} \delta(|\mathbf{b}_i| - b) e^{i\mathbf{k}\mathbf{b}_i} d^3b_i &= 2\pi \int_0^\infty db_i \frac{1}{4\pi b^2} \delta(b_i - b) b_i^2 \frac{2 \sin kb_i}{kb_i} \\ &= \frac{\sin kb}{kb} \end{aligned} \quad (1.13)$$

and finally we have

$$P(\mathbf{R}) = \frac{1}{(2\pi)^3} \int d^3k e^{-i\mathbf{k}\mathbf{R}} \left(\frac{\sin kb}{kb} \right)^M. \quad (1.14)$$

The function

$$\left(\frac{\sin kb}{kb} \right)^M \quad (1.15)$$

has a very sharp maximum at $kb = 0$. For large M , it can be approximated quite accurately by a Gaussian

$$\left(\frac{\sin kb}{kb} \right)^M \approx e^{-M \frac{1}{6} k^2 b^2} \quad (1.16)$$

which gives

$$P(\mathbf{R}) \approx \frac{1}{(2\pi)^3} \int d^3k e^{-i\mathbf{k}\mathbf{R}} e^{-\frac{M}{6} k^2 b^2} = \left(\frac{3}{2\pi b^2 M} \right)^{3/2} e^{-3R^2/(2b^2 M)}. \quad (1.17)$$

We consider \mathbf{R} as a macroscopic variable. The free energy is (no internal degrees of freedom, $E = 0$)

$$F = -TS = -k_B T \ln P(\mathbf{R}) = \frac{3R^2}{2b^2 M} k_B T + \text{const.} \quad (1.18)$$

The quadratic dependence on L is very similar to a Hookean spring. For a potential energy

$$V = \frac{k_s}{2} x^2 \quad (1.19)$$

the probability distribution of the coordinate is

$$P(x) = \sqrt{\frac{k_s}{2\pi k_B T}} e^{-k_s x^2 / 2k_B T} \quad (1.20)$$

which gives a free energy of

$$F = -k_B T \ln P = \text{const} + \frac{k_s x^2}{2}. \quad (1.21)$$

By comparison, the apparent spring constant is

$$k_s = \frac{3k_B T}{Mb^2}. \quad (1.22)$$

1.1.2 Force–Extension Relation

We consider now a chain with one fixed end and an external force acting in x -direction at the other end (Fig. 1.3) [1].

Fig. 1.3 Freely jointed chain with external force

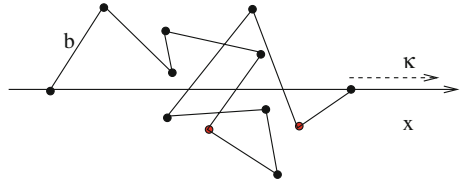
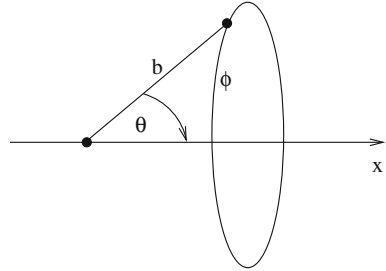


Fig. 1.4 Projection of the bond vector



The projection of the i -th segment onto the x -axis has a length of (Fig. 1.4)

$$b_i = -b \cos \theta \in [-b, b]. \quad (1.23)$$

We discretize the continuous range of b_j by dividing the interval $[-b, b]$ into n bins of width $\Delta b = \frac{2b}{n}$ corresponding to the discrete values l_i , $i = 1 \dots n$. The chain members are divided into n groups according to their bond projections b_j . The number of units in each group is denoted by M_i so that

$$\sum_{i=1}^n M_i = M \quad (1.24)$$

and the end-to-end length is

$$\sum_{i=1}^n l_i M_i = L. \quad (1.25)$$

The probability distribution is

$$P(\theta, \phi) d\theta d\phi = \frac{\sin(\theta) d\theta d\phi}{4\pi}. \quad (1.26)$$

Since we are only interested in the probability of the l_i , we integrate over ϕ

$$P(\theta) d\theta = \frac{\sin(\theta) d\theta}{2} \quad (1.27)$$

and transform variables to have

$$P(l)dl = P(-b \cos \theta)d(-b \cos \theta) = \frac{1}{2b}d(-b \cos \theta) = \frac{1}{2b}dl. \quad (1.28)$$

The canonical partition function is

$$Z(L, M, T) = \sum_{\{M_i\} \sum M_i l_i = L} \frac{M!}{\prod_j M_j!} \prod_i z_i^{M_i} = \sum_{\{M_i\}} M! \prod_i \frac{z_i^{M_i}}{M_i!}. \quad (1.29)$$

The $z_i = z$ are the independent partition functions of the single units which we assume as independent of i . The degeneracy factor $\frac{M!}{\prod M_i!}$ counts the number of microstates for a certain configuration $\{M_i\}$. The summation is only over configurations with a fixed end-to-end length. This makes the evaluation rather complicated. Instead, we introduce a new partition function by considering an ensemble with fixed force and fluctuating length

$$\Delta(\kappa, M, T) = \sum_L Z(L, M, T) e^{\kappa L / k_B T}. \quad (1.30)$$

Approximating the logarithm of the sum by the logarithm of the maximum term we see that

$$-k_B T \ln \Delta = -k_B T \ln Z - \kappa L \quad (1.31)$$

($-\kappa L$ corresponds to $+pV$) gives the Gibbs free enthalpy

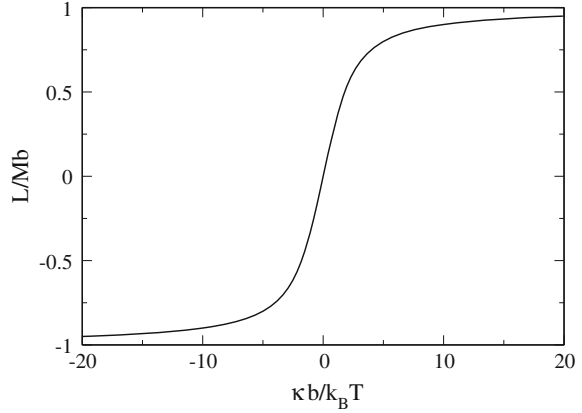
$$G(\kappa, M, T) = F - \kappa L. \quad (1.32)$$

In this new ensemble the summation over L simplifies the partition function

$$\begin{aligned} \Delta &= \sum_{\{M_i\}} e^{\kappa \sum M_i l_i / k_B T} M! \prod_i \frac{z_i^{M_i}}{M_i!} \\ &= \sum_{\{M_i\}} M! \prod_i \frac{(ze^{\kappa l_i / k_B T})^{M_i}}{M_i!} \\ &= \left(\sum_i ze^{\kappa l_i / k_B T} \right)^M = \xi(\kappa, T)^M. \end{aligned} \quad (1.33)$$

Now returning to a continuous distribution of $l_i = -b \cos \theta$ we have to evaluate

$$\xi = \int_{-b}^b P(l)dl \quad ze^{\kappa l / k_B T} = z \frac{\sinh t}{t} \quad (1.34)$$

Fig. 1.5 Force - extension relation

with

$$t = \frac{\kappa b}{k_B T}. \quad (1.35)$$

From

$$dG = -SdT - Ld\kappa \quad (1.36)$$

we find (Fig. 1.5)

$$\begin{aligned} L &= -\left. \frac{\partial G}{\partial \kappa} \right|_T \\ &= \frac{\partial}{\partial \kappa} \left(M k_B T \ln \left(\frac{z}{\frac{\kappa b}{k_B T}} \sinh \frac{\kappa b}{k_B T} \right) \right) \\ &= M k_B T \left(-\frac{1}{\kappa} + \frac{b}{k_B T} \coth \left(\frac{\kappa b}{k_B T} \right) \right) = M b \mathfrak{L} \left(\frac{\kappa b}{k_B T} \right) \end{aligned}$$

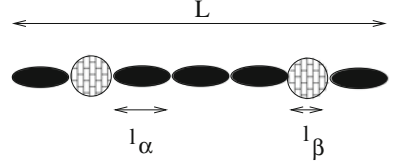
with the Langevin function

$$\mathfrak{L}(x) = \coth(x) - \frac{1}{x}. \quad (1.37)$$

1.2 Two Component Model

A one-dimensional random walk model can be applied to a polymer chain which is composed of two types of units (named α and β), which may interconvert (Fig. 1.6). This model is for instance applicable to the *dsDNA* \rightarrow *SDNA* transition or the

Fig. 1.6 Two component model



α -Helix \rightarrow random coil transition of proteins which show up as a plateau in the force-extension curve [1, 2].

We follow the treatment given in [1] which is based on an explicit evaluation of the partition function. Alternatively, the two component model can be mapped onto a one-dimensional Ising model, which can be solved by the transfer matrix method [3, 4]. We assume that of the overall M units M_α are in the α -configuration and $M - M_\alpha$ are in the β -configuration. The lengths of the two conformers are l_α and l_β , respectively.

1.2.1 Force-Extension Relation

The total length is given by

$$L = M_\alpha l_\alpha + (M - M_\alpha) l_\beta = M_\alpha (l_\alpha - l_\beta) + M l_\beta. \quad (1.38)$$

The number of configurations with length L is given by

$$\Omega(L) = \Omega\left(M_\alpha = \frac{L - M l_\beta}{l_\alpha - l_\beta}\right) = \frac{M!}{\left(\frac{L - M l_\beta}{l_\alpha - l_\beta}\right)! \left(\frac{M l_\alpha - L}{l_\alpha - l_\beta}\right)!}. \quad (1.39)$$

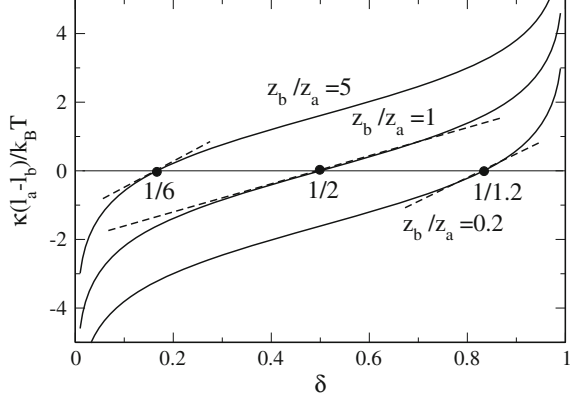
From the partition function

$$Z = z_\alpha^{M_\alpha} z_\beta^{M - M_\alpha} \Omega = z_\alpha^{\frac{L - M l_\beta}{l_\alpha - l_\beta}} z_\beta^{\frac{M l_\alpha - L}{l_\alpha - l_\beta}} \Omega \quad (1.40)$$

application of Stirling's approximation gives for the free energy

$$\begin{aligned} F &= -k_B T \ln Z \\ &= -k_B T \frac{L - M l_\beta}{l_\alpha - l_\beta} \ln z_\alpha - k_B T \frac{M l_\alpha - L}{l_\alpha - l_\beta} \ln z_\beta - k_B T (M \ln M - M) \\ &= -k_B T \left\{ -\left(\frac{L - M l_\beta}{l_\alpha - l_\beta}\right) \ln \left(\frac{L - M l_\beta}{l_\alpha - l_\beta}\right) + \left(\frac{L - M l_\beta}{l_\alpha - l_\beta}\right) \right. \\ &\quad \left. - \left(\frac{M l_\alpha - L}{l_\alpha - l_\beta}\right) \ln \left(\frac{M l_\alpha - L}{l_\alpha - l_\beta}\right) + \left(\frac{M l_\alpha - L}{l_\alpha - l_\beta}\right) \right\}. \end{aligned} \quad (1.41)$$

Fig. 1.7 Force - extension relation for the 2-component model



The derivative of the free energy gives the force-extension relation (Fig. 1.7)

$$\kappa = \frac{\partial F}{\partial L} = \frac{k_B T}{l_\alpha - l_\beta} \ln \left(\frac{M l_\beta - L}{L - M l_\alpha} \right) + \frac{k_B T}{l_\alpha - l_\beta} \ln \frac{z_\beta}{z_\alpha}. \quad (1.42)$$

This can be written as a function of the fraction of segments in the α -configuration

$$\delta = \frac{M_\alpha}{M} = \frac{L - M l_\beta}{M(l_\alpha - l_\beta)} \quad (1.43)$$

in the somewhat simpler form

$$\kappa \frac{l_\alpha - l_\beta}{k_B T} = \ln \frac{\delta}{1 - \delta} + \ln \frac{z_\beta}{z_\alpha}. \quad (1.44)$$

The mean extension for zero force is obtained by solving $\kappa(L) = 0$

$$\bar{L}_0 = M \left(\frac{z_\alpha l_\alpha + z_\beta l_\beta}{z_\alpha + z_\beta} \right) \quad (1.45)$$

$$\delta_0 = \frac{\bar{L}_0 - M l_\beta}{M(l_\alpha - l_\beta)} = \frac{z_\alpha}{z_\alpha + z_\beta}. \quad (1.46)$$

Taylor series expansion around \bar{L}_0 gives the linearized force-extension relation

$$\begin{aligned}
\kappa &= \frac{\partial F}{\partial L} \\
&= \frac{k_B T}{M(l_\alpha - l_\beta)^2} \frac{(z_\alpha + z_\beta)^2}{z_\alpha z_\beta} (L - \bar{L}_0) + \dots \\
&\approx \frac{k_B T}{l_\alpha - l_\beta} \frac{(z_\alpha + z_\beta)^2}{z_\alpha z_\beta} (\delta - \delta_0) \\
&= \frac{k_B T}{l_\alpha - l_\beta} \frac{1}{\delta_0(1 - \delta_0)} (\delta - \delta_0).
\end{aligned} \tag{1.47}$$

1.2.2 Two Component Model with Interactions

We now consider additional interaction between neighboring units. We introduce the interaction energies $w_{\alpha\alpha}$, $w_{\alpha\beta}$, $w_{\beta\beta}$ for the different pairs of neighbors and the numbers $N_{\alpha\alpha}$, $N_{\alpha\beta}$, $N_{\beta\beta}$ of such interaction terms. The total interaction energy is then

$$W = N_{\alpha\alpha}w_{\alpha\alpha} + N_{\alpha\beta}w_{\alpha\beta} + N_{\beta\beta}w_{\beta\beta}. \tag{1.48}$$

The numbers of pair interactions are not independent from the numbers of units M_α , M_β . Consider insertion of an additional α -segment into a chain. Figure 1.8 counts the possible changes in interaction terms. In any case, by insertion of an α -segments the expression $2N_{\alpha\alpha} + N_{\alpha\beta}$ increases by 2.

Similarly, insertion of an extra β -segment increases $2N_{\beta\beta} + N_{\alpha\beta}$ by 2 (Fig. 1.9).

Fig. 1.8 Insertion of an α -segment

α ↓	M_α	M_β	$N_{\alpha\alpha}$	$N_{\alpha\beta}$	$N_{\beta\beta}$	$2N_{\alpha\alpha} + N_{\alpha\beta}$
*** $\alpha\alpha$ ***	+1		+1			+2
*** $\alpha\beta$ ***	+1		+1			+2
*** $\beta\alpha$ ***	+1		+1			+2
*** $\beta\beta$ ***	+1			+2	-1	+2

Fig. 1.9 Insertion of a β -segment

β ↓	M_α	M_β	$N_{\alpha\alpha}$	$N_{\alpha\beta}$	$N_{\beta\beta}$	$2N_{\beta\beta} + N_{\alpha\beta}$
*** $\alpha\alpha$ ***		+1	-1	+2		+2
*** $\alpha\beta$ ***		+1			+1	+2
*** $\beta\alpha$ ***		+1			+1	+2
*** $\beta\beta$ ***		+1			+1	+2

Fig. 1.10 Determination of the constants

	N_α	N_β	$N_{\alpha\alpha}$	$N_{\alpha\beta}$	$N_{\beta\beta}$	$2N_{\alpha\alpha} + N_{\alpha\beta} - 2N_\alpha$	$2N_{\beta\beta} + N_{\alpha\beta} - 2N_\beta$
$\alpha \alpha$	2	0	1	0	0	-2	0
$\beta \beta$	0	2	0	0	1	0	-2
$\alpha \beta$	1	1	0	1	0	-1	-1
$\alpha \alpha$	2	0	2	0	0	0	0
$\beta \beta$	0	2	0	0	2	0	0
$\alpha \beta$	1	1	0	2	0	0	0

This shows that there are linear relationships of the form

$$\begin{aligned} 2N_{\alpha\alpha} + N_{\alpha\beta} &= 2M_\alpha + c_1 \\ 2N_{\beta\beta} + N_{\alpha\beta} &= 2M_\beta + c_2. \end{aligned} \quad (1.49)$$

The two constants depend on the boundary conditions as can be seen from an inspection of the shortest possible chains with 2 segments (Fig. 1.10). They are zero for periodic boundaries and will, therefore, be neglected in the following, since the numbers M_α , M_β are much larger.

We substitute

$$N_{\alpha\alpha} = M_\alpha - \frac{1}{2}N_{\alpha\beta} \quad (1.50)$$

$$N_{\beta\beta} = M_\beta - \frac{1}{2}N_{\alpha\beta} \quad (1.51)$$

$$w = w_{\alpha\alpha} + w_{\beta\beta} - 2w_{\alpha\beta} \quad (1.52)$$

to have the interaction energy

$$\begin{aligned} W &= w_{\alpha\alpha} \left(M_\alpha - \frac{1}{2}N_{\alpha\beta} \right) + w_{\beta\beta} \left(M_\beta - \frac{1}{2}N_{\alpha\beta} \right) + w_{\alpha\beta} N_{\alpha\beta} \\ &= w_{\alpha\alpha} M_\alpha + w_{\beta\beta} (M - M_\alpha) - \frac{w}{2} N_{\alpha\beta}. \end{aligned} \quad (1.53)$$

The canonical partition function is

Fig. 1.11 Degeneracy factor g .
The possible 8 configurations
are shown for $M = 4$, $M_\alpha = 3$,
 $M_\beta = 3$, $N_{\alpha\beta} = 3$

$\alpha\alpha$	$\beta\beta$	α	β
$\alpha\alpha$	β	α	$\beta\beta$
α	$\beta\beta$	$\alpha\alpha$	β
α	β	$\alpha\alpha$	$\beta\beta$

$\beta\beta$	$\alpha\alpha$	β	α
$\beta\beta$	α	β	$\alpha\alpha$
β	$\alpha\alpha$	$\beta\beta$	α
β	α	$\beta\beta$	$\alpha\alpha$

Fig. 1.12 Distribution of
three segments over three
blocks. This is equivalent to
the arrangement of three
segments and two border
lines

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$$\begin{aligned}
 Z(M_\alpha, T) &= z_\alpha^{M_\alpha} z_\beta^{M_\beta} \sum_{N_{\alpha\beta}} g(M_\alpha, N_{\alpha\beta}) e^{-W(N_{\alpha\beta})/k_B T} \\
 &= (z_\alpha e^{-w_{\alpha\alpha}/k_B T})^{M_\alpha} (z_\beta e^{-w_{\beta\beta}/k_B T})^{(M-M_\alpha)} \sum_{N_{\alpha\beta}} g(M_\alpha, N_{\alpha\beta}) e^{N_{\alpha\beta} w/2k_B T}.
 \end{aligned}
 \tag{1.54}$$

The degeneracy factor g will be evaluated in the following. Figure 1.11 shows an example.

The chain can be divided into blocks containing only α -segments (α -blocks) or only β -segments (β -blocks). The number of boundaries between α -blocks and β -blocks obviously is given by $N_{\alpha\beta}$. Let $N_{\alpha\beta}$ be an odd number. Then there are $(N_{\alpha\beta} + 1)/2$ blocks of each type (We assume that $N_{\alpha\beta}$, M_α , M_β are large numbers and neglect small differences of order 1 for even $N_{\alpha\beta}$). In each α -block there is at least one α -segment. The remaining $M_\alpha - (N_{\alpha\beta} + 1)/2$ α -segments have to be distributed over the $(N_{\alpha\beta} + 1)/2$ α -blocks (Fig. 1.12).

Therefore we need the number of possible ways to arrange $M_\alpha - (N_{\alpha\beta} + 1)/2$ segments and $(N_{\alpha\beta} - 1)/2$ walls which is given by the number of ways to distribute the $(N_{\alpha\beta} - 1)/2$ walls over the total of $M_\alpha - 1$ objects which is given by

$$\frac{(M_\alpha - 1)!}{\left(\frac{N_{\alpha\beta}-1}{2}\right)!(M_\alpha - \frac{N_{\alpha\beta}+1}{2})!} \approx \frac{M_\alpha!}{\left(\frac{N_{\alpha\beta}}{2}\right)!(M_\alpha - \frac{N_{\alpha\beta}}{2})!}. \quad (1.55)$$

The same consideration for the β -segments gives another factor of

$$\frac{(M - M_\alpha)!}{\left(\frac{N_{\alpha\beta}}{2}\right)!(M - M_\alpha - \frac{N_{\alpha\beta}}{2})!}. \quad (1.56)$$

Finally, there is an additional factor of 2 because the first block can be of either type. Hence for large numbers we find

$$g(M_\alpha, N_{\alpha\beta}) = 2 \frac{(M_\alpha)!}{\left(\frac{N_{\alpha\beta}}{2}\right)!(M_\alpha - \frac{N_{\alpha\beta}}{2})!} \frac{(M - M_\alpha)!}{\left(\frac{N_{\alpha\beta}}{2}\right)!(M - M_\alpha - \frac{N_{\alpha\beta}}{2})!}. \quad (1.57)$$

We look for the maximum summand of Z as a function of $N_{\alpha\beta}$. The corresponding number will be denoted as $N_{\alpha\beta}^*$ and is determined from the condition

$$0 = \frac{\partial}{\partial N_{\alpha\beta}} \ln \left(g(M_\alpha, N_{\alpha\beta}) e^{\frac{w N_{\alpha\beta}}{2k_B T}} \right) = \frac{w}{2k_B T} + \frac{\partial}{\partial N_{\alpha\beta}} \ln g(M_\alpha, N_{\alpha\beta}). \quad (1.58)$$

Stirling's approximation gives

$$0 = \frac{w}{2k_B T} + \frac{1}{2} \ln \left(M_\alpha - \frac{N_{\alpha\beta}^*}{2} \right) + \frac{1}{2} \ln \left(M - M_\alpha - \frac{N_{\alpha\beta}^*}{2} \right) - \ln \left(\frac{N_{\alpha\beta}^*}{2} \right) \quad (1.59)$$

or

$$0 = \frac{w}{k_B T} + \ln \left(\frac{(M_\alpha - \frac{N_{\alpha\beta}^*}{2})(M - M_\alpha - \frac{N_{\alpha\beta}^*}{2})}{(\frac{N_{\alpha\beta}^*}{2})^2} \right). \quad (1.60)$$

Taking the exponential gives

$$\left(M_\alpha - \frac{N_{\alpha\beta}^*}{2} \right) \left(M - M_\alpha - \frac{N_{\alpha\beta}^*}{2} \right) = e^{-w/k_B T} \left(\frac{N_{\alpha\beta}^*}{2} \right)^2. \quad (1.61)$$

Introducing the relative quantities

$$\delta = \frac{M_\alpha}{M} \quad \gamma = \frac{N_{\alpha\beta}^*}{2M} \quad (1.62)$$

we have to solve the quadratic equation

$$(\delta - \gamma)(1 - \delta - \gamma) = \gamma^2 e^{-\frac{w}{k_B T}}. \quad (1.63)$$

The solutions are

$$\gamma = \frac{-1 \pm \sqrt{(1-2\delta)^2 + 4e^{-w/k_B T} \delta(1-\delta)}}{2(e^{-w/k_B T} - 1)}. \quad (1.64)$$

Series expansion in $w/k_B T$ gives

$$\begin{aligned} \gamma &= \frac{k_B T}{2w} + \frac{1}{4} + \frac{w}{24k_B T} + \dots \\ &\dots \pm \left(-\frac{k_B T}{2w} + \delta(1-\delta) - \frac{1}{4} + \left((\delta - \delta^2)^2 - \frac{1}{24} \right) \frac{w}{k_B T} \right) + \dots \end{aligned} \quad (1.65)$$

The - alternative diverges for $w \rightarrow 0$ whereas the + alternative

$$\gamma = \delta(1-\delta) + (\delta - \delta^2)^2 \frac{w}{k_B T} - \delta^2 \left(\frac{1}{2}(1-\delta)^2 + 2\delta(\delta-1)^3 \right) \frac{w}{k_B T} \dots \quad (1.66)$$

approaches the value

$$\gamma_0 = \delta - \delta^2 \quad (1.67)$$

which is the only solution of the interactionless case

$$(\delta - \gamma_0)(1 - \delta - \gamma_0) = \gamma_0^2 \rightarrow \delta(1 - \delta) - \gamma = 0. \quad (1.68)$$

For $N_{\alpha\beta}^*$ we obtain approximately

$$N_{\alpha\beta}^* = 2M \left(\delta(1-\delta) + (\delta - \delta^2)^2 \frac{w}{k_B T} + \dots \right). \quad (1.69)$$

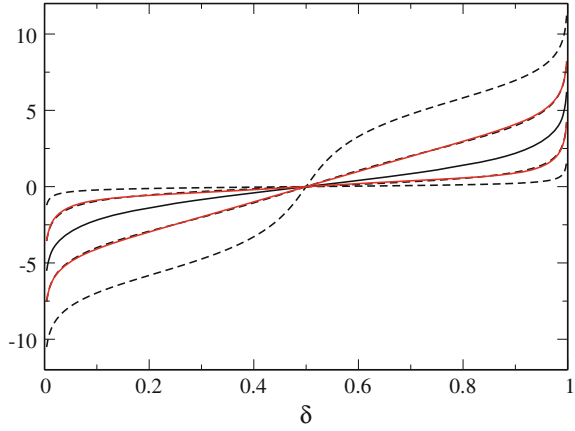
Let us now apply the maximum term method, which approximates the logarithm of a sum by the logarithm of the maximum summand

$$\begin{aligned} F &= -k_B T \ln Z(M_\alpha, T) \\ &\approx -k_B T M_\alpha \ln z_\alpha - k_B T (M - M_\alpha) \ln z_\beta + M_\alpha w_{\alpha\alpha} + (M - M_\alpha) w_{\beta\beta} \\ &\quad - k_B T \ln g(M_\alpha, N_{\alpha\beta}^*) - \frac{w N_{\alpha\beta}^*}{2}. \end{aligned} \quad (1.70)$$

The force-length relation (Fig. 1.13) is now obtained from

$$\begin{aligned} \kappa &= \frac{\partial F}{\partial L} = \frac{\partial F}{\partial M_\alpha} \frac{\partial \left(\frac{L - M l_\beta}{l_\alpha - l_\beta} \right)}{\partial L} = \frac{1}{l_\alpha - l_\beta} \frac{\partial F}{\partial M_\alpha} \\ &= \frac{1}{l_\alpha - l_\beta} \left(-k_B T \ln z_\alpha + k_B T \ln z_\beta + w_{\alpha\alpha} - w_{\beta\beta} - k_B T \frac{\partial}{\partial M_\alpha} \ln g \right) \\ &\quad + \frac{1}{l_\alpha - l_\beta} \frac{\partial N_{\alpha\beta}^*}{\partial M_\alpha} \frac{\partial}{\partial N_{\alpha\beta}^*} \left(-k_B T \ln g - \frac{w N_{\alpha\beta}^*}{2} \right). \end{aligned} \quad (1.71)$$

Fig. 1.13 Force - length relation for the interacting two-component model.
Dashed curves: exact results for $w/k_B T = 0, \pm 2, \pm 5$.
Solid curves: series expansion (1.73) which gives a good approximation for $|w/k_B T| < 2$



The last part vanishes due to the definition of $N_{\alpha\beta}^*$. Now using Stirling's formula we find

$$\frac{\partial}{\partial M_\alpha} \ln g = \ln \frac{M_\alpha}{M - M_\alpha} + \ln \frac{M - M_\alpha - \frac{N_{\alpha\beta}^*}{2}}{M_\alpha - \frac{N_{\alpha\beta}^*}{2}} = \ln \frac{\delta}{1 - \delta} + \ln \frac{1 - \delta - \gamma}{\delta - \gamma} \quad (1.72)$$

and substituting γ we have finally

$$\begin{aligned} \kappa \frac{(l_\alpha - l_\beta)}{k_B T} &= \ln \frac{z_\beta e^{-w_{\beta\beta}/k_B T}}{z_\alpha e^{-w_{\alpha\alpha}/k_B T}} - \ln \frac{(1 - \delta)}{\delta} \\ &\quad + \left(2\delta - 1\right) \frac{w}{k_B T} + \delta \left(3\delta - 2\delta^2 - 1\right) \left(\frac{w}{k_B T}\right)^2. \end{aligned} \quad (1.73)$$

Linearization now gives

$$\begin{aligned} \delta_0 &= \frac{z_\alpha e^{-w_{\alpha\alpha}/k_B T}}{z_\alpha e^{-w_{\alpha\alpha}/k_B T} + z_\beta e^{-w_{\beta\beta}/k_B T}} \\ \kappa &= \frac{k_B T}{l_\alpha - l_\beta} \frac{1}{\delta_0(1 - \delta_0)} (\delta - \delta_0) \\ &\quad + \frac{w}{k_B T} \left(2\delta_0 - 1\right) + \left(\frac{w}{k_B T}\right)^2 (3\delta_0^2 - \delta_0 - 2\delta_0^3) \\ &\quad + \left(2\frac{w}{k_B T} + \left(\frac{w}{k_B T}\right)^2 (6\delta_0 - 6\delta_0^2 - 1)\right) (\delta - \delta_0). \end{aligned} \quad (1.74)$$

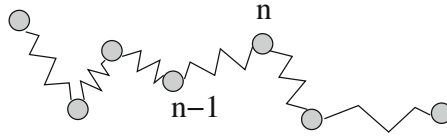
For negative w , a small force may lead to much larger changes in length than with no interaction. This explains, for example, how in proteins huge channels may open

although the acting forces are quite small. In the case of Myoglobin, this is how the penetration of oxygen in the protein becomes possible.

Problems

1.1 Gaussian Polymer Model

The simplest description of a polymer is the Gaussian polymer model which considers a polymer to be a series of particles joined by Hookean springs



(a) The vector connecting monomers $n-1$ and n obeys a Gaussian distribution with average zero and variance

$$\langle (\mathbf{r}_n - \mathbf{r}_{n-1})^2 \rangle = b^2.$$

Determine the distribution function $P(\mathbf{r}_n - \mathbf{r}_{n-1})$ explicitly.

(b) Assume that the distance vectors $\mathbf{r}_n - \mathbf{r}_{n-1}$ are independent and calculate the distribution of end-to-end vectors $P(\mathbf{r}_N - \mathbf{r}_0)$.

(c) Consider now a polymer under the action of a constant force κ in x -direction. The potential energy of a conformation is given by

$$V = \sum_{n=1}^N \frac{f}{2} (\mathbf{r}_n - \mathbf{r}_{n-1})^2 - \kappa(x_N - x_0)$$

and the probability of this conformation is

$$P \sim e^{-V/k_B T}.$$

Determine the effective spring constant f .

(d) Find the most probable configuration by searching for the minimum of the energy

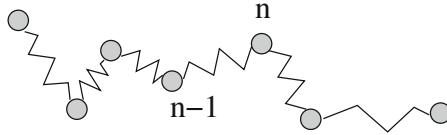
$$\frac{\partial V}{\partial x_n} = \frac{\partial V}{\partial y_n} = \frac{\partial V}{\partial z_n} = 0.$$

Calculate the length of the polymer for the most probable configuration (according to the maximum term method the average value coincides with the most probable value in the thermodynamic limit).

1.2 Three-Dimensional Polymer Model

Consider a model of a polymer in three-dimensional space consisting of N links of length b . The connection of the links i and $i + 1$ is characterized by the two angles ϕ_i and θ_i . The vector \mathbf{r}_i can be obtained from the vector \mathbf{r}_1 through application of a series of rotation matrices¹

$$\mathbf{r}_i = R_1 R_2 \dots R_{i-1} \mathbf{r}_1$$



with

$$\mathbf{r}_1 = \begin{pmatrix} 0 \\ 0 \\ b \end{pmatrix} \quad R_i = R_z(\phi_i) R_y(\theta_i) = \begin{pmatrix} \cos \phi_i & \sin \phi_i & 0 \\ -\sin \phi_i & \cos \phi_i & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos \theta_i & 0 & -\sin \theta_i \\ 0 & 1 & 0 \\ \sin \theta_i & 0 & \cos \theta_i \end{pmatrix}.$$

Calculate the mean square of the end-to-end distance $\left\langle \left(\sum_{i=1}^N \mathbf{r}_i \right)^2 \right\rangle$

for the following cases:

- The averaging $\langle \dots \rangle$ includes averaging over all angles ϕ_i and θ_i .
- The averaging $\langle \dots \rangle$ includes averaging over all angles ϕ_i while the angles θ_i are held fixed at a common value θ .
- The averaging $\langle \dots \rangle$ includes averaging over all angles ϕ_i while the angles θ_i are held fixed at either $\theta_{2i+1} = \theta_a$ or $\theta_{2i} = \theta_b$ depending on whether the number of the link is odd or even.
- How large must N be, so that it is a good approximation to keep only terms which are proportional to N ?
- What happens in the second case if θ is chosen as very small (wormlike chain)?

Hint: Show first that after averaging over the ϕ_i the only terms of the matrix which have to be taken into account are the elements $(R_i)_{33}$. The appearing summations can be expressed as geometric series.

¹The rotation matrices act in the laboratory fixed system (xyz). Transformation into the coordinate system of the segment (x'y'z') changes the order of the matrices. For instance $\mathbf{r}_2 = R(y, \theta_1) R(z, \phi_1) \mathbf{r}_1 = R(z, \phi_1) R(y', \theta_1) R^{-1}(z, \phi_1) R(z, \phi_1) \mathbf{r}_1 = R(z, \phi_1) R(y', \theta_1) \mathbf{r}_1$ (This is sometimes discussed in terms of active and passive rotations).

1.3 Two-Component Model

We consider the two-component model of a polymer chain which consists of M segments of two different types α, β (internal degrees of freedom are neglected). The number of configurations with length L is given by the Binomial distribution

$$\Omega(L, M, T) = \frac{M!}{M_\alpha!(M - M_\alpha)!} \quad L = M_\alpha l_\alpha + (M - M_\alpha) l_\beta.$$

(a) Make use of the asymptotic expansion² of the logarithm of the Gamma function

$$\ln(\Gamma(z + 1)) = (\ln z - 1)z + \ln(\sqrt{2\pi}) + \frac{1}{2} \ln z + \frac{1}{12z} + O(z^{-3})$$

$$N! = \Gamma(N + 1)$$

to calculate the leading terms of the force-extension relation which is obtained from

$$\kappa = \frac{\partial}{\partial L} \left(-k_B T \ln \Omega(L, M, T) \right).$$

Discuss the error of Stirling's approximation for $M = 1000$ and $l_\beta/l_\alpha = 2$.

(b) Now switch to an ensemble with constant force κ . The corresponding partition function is

$$Z(\kappa, M, T) = \sum_L e^{\kappa L/k_B T} \Omega(L, M, T).$$

Calculate the first two moments of the length

$$\bar{L} = -\frac{\partial}{\partial \kappa} (-k_B T \ln Z) = Z^{-1} k_B T \frac{\partial}{\partial \kappa} Z$$

$$\overline{L^2} = Z^{-1} (k_B T)^2 \frac{\partial^2}{\partial \kappa^2} Z$$

and discuss the relative uncertainty $\sigma = \frac{\sqrt{\overline{L^2} - \bar{L}^2}}{\bar{L}}$. Determine the maximum of σ .

²Several asymptotic expansions can be found in [5].

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