Ideal chains

2

In this chapter, we consider the conformations of chains with no interactions between monomers that are far apart along the chain, even if they approach each other in space. Such chains are called **ideal chains**. This situation is never completely realized for real chains, but there are several types of polymeric systems with nearly ideal chains. Real chains interact with both their solvent and themselves. The relative strength of these interactions determines whether the monomers effectively attract or repel one another. In Chapter 3, we will learn that real chains in a solvent at low temperatures can be found in a collapsed conformation due to a dominance of attractive over repulsive interactions between monomers. At high temperatures, chains swell due to dominance of repulsive interactions. At a special intermediate temperature, called the **θ-temperature**, chains are in nearly ideal conformations because the attractive and repulsive parts of monomer–monomer interactions cancel each other. This θ-temperature is analogous to the Boyle temperature of a gas, where the ideal gas law happens to work at low pressures. Even more importantly, linear polymer melts and concentrated solutions have practically ideal chain conformations because the interactions between monomers are almost completely screened by surrounding chains.

The conformation of an ideal chain, with no interactions between monomers, is the essential starting point of most models in polymer physics. In this sense, the role of the ideal chain is similar to the role of the harmonic oscillator or the hydrogen atom in other branches of physics.

2.1 Flexibility mechanisms

In order to understand the multitude of conformations available for a polymer chain, consider an example of a polyethylene molecule. The distance between carbon atoms in the molecule is almost constant $l = 1.54$ Å. The fluctuations in the bond length (typically ± 0.05 Å) do not affect chain conformations. The angle between neighbouring bonds, called the **tetrahedral angle** $\theta = 68°$ is also almost constant.

The main source of polymer flexibility is the variation of **torsion angles** [see Fig. 2.1(a)]. In order to describe these variations, consider a plane defined by three neighbouring carbon atoms C_{i-2}, C_{i-1}, and C_i. The bond

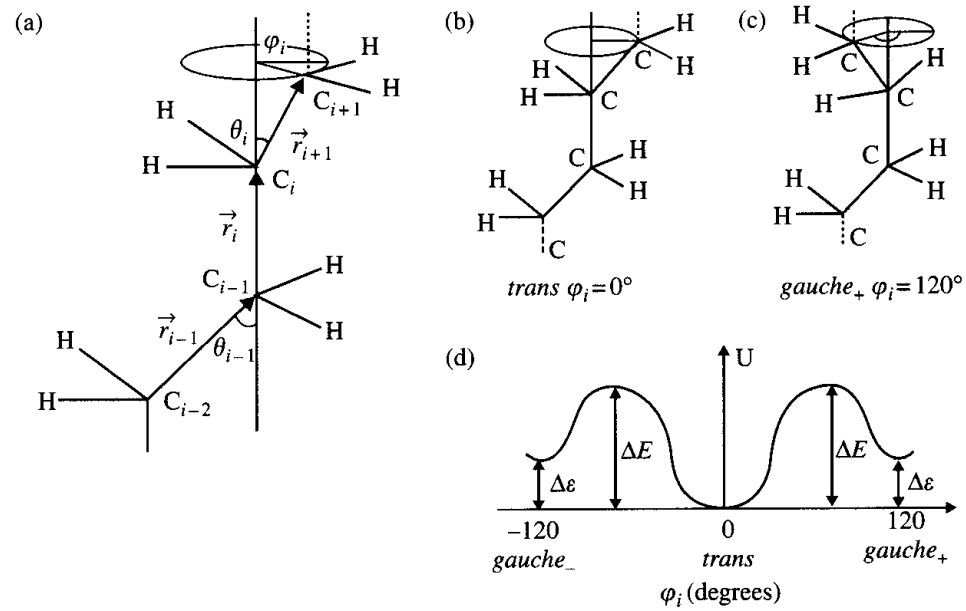

Fig. 2.1
(a) Torsion angle φ_i for a sequence of three main-chain bonds. (b) *Trans* state. (c) *Gauche*-plus state. (d) Torsion angle dependence of energy.

vector $\vec{r}_i$ between atoms C_{i-1} and C_i defines the axis of rotation for the bond vector $\vec{r}_{i+1}$ between atoms C_i and C_{i+1} at constant bond angle θ_i. The zero value of the torsion angle φ_i corresponds to the bond vector $\vec{r}_{i+1}$ being colinear to the bond vector $\vec{r}_{i-1}$ and is called the **trans** state (t) of the torsion angle φ_i [Fig. 2.1(b)].

The *trans* state of the torsion angle φ_i is the lowest energy conformation of the four consecutive CH_2 groups. The changes of the torsion angle φ_i lead to the energy variations shown in Fig. 2.1(d). These energy variations are due to changes in distances and therefore interactions between carbon atoms and hydrogen atoms of this sequence of four CH_2 groups. The two secondary minima corresponding to torsion angles $\varphi_i = \pm 120°$ are called **gauche-plus** ($g+$) [Fig. 2.1(c)] and **gauche-minus** ($g-$). The energy difference between *gauche* and *trans* minima $\Delta\varepsilon$ determines the relative probability of a torsion angle being in a *gauche* state in thermal equilibrium. In general, this probability is also influenced by the values of torsion angles of neighbouring monomers. These correlations are included in the rotational isomeric state model (Section 2.3.4). The value of $\Delta\varepsilon$ for polyethylene at room temperature is $\Delta\varepsilon \cong 0.8kT$. The energy barrier ΔE between *trans* and *gauche* states determines the dynamics of conformational rearrangements.

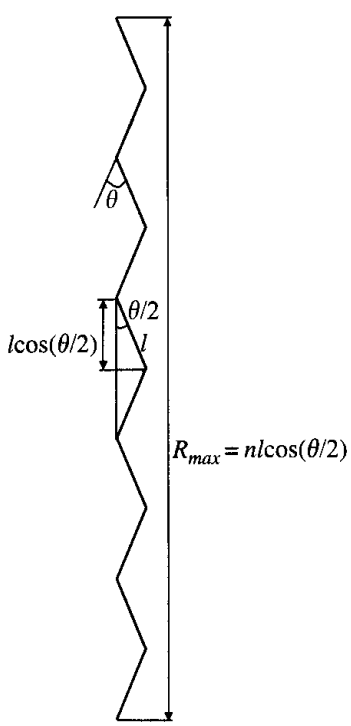

Fig. 2.2
All-*trans* (zig-zag) conformation of a short polymer with $n = 10$ main-chain bonds.

Any section of the chain with consecutive *trans* states of torsion angles is in a rod-like zig-zag conformation (see Fig. 2.2). If all torsion angles of the whole chain are in the *trans* state (Fig. 2.2), the chain has the largest possible value of its end-to-end distance $R_{\max}$. This largest end-to-end distance is determined by the product of the number of skeleton bonds n and their projected length $l\cos(\theta/2)$ along the contour, and is referred to as the **contour length** of the chain:

$$R_{\max} = nl \cos \frac{\theta}{2}. \tag{2.1}$$

Gauche states of torsion angles lead to flexibility in the chain conformation since each *gauche* state alters the conformation from the all-*trans* zig-zag of

Fig. 2.2. In general, there will be a variable number of consecutive torsion angles in the *trans* state. Each of these all-*trans* rod-like sections will be broken up by a *gauche*. The chain is rod-like on scales smaller than these all-*trans* sections, but is flexible on larger length scales. Typically, all-*trans* sections comprise fewer than ten main-chain bonds and most synthetic polymers are quite flexible.

A qualitatively different mechanism of flexibility of many polymers, such as double-helix DNA is uniform flexibility over the whole polymer length. These chains are well described by the worm-like chain model (see Section 2.3.2).

2.2 Conformations of an ideal chain

Consider a flexible polymer of $n+1$ backbone atoms A_i (with $0 \leq i \leq n$) as sketched in Fig. 2.3. The bond vector $\vec{r}_i$ goes from atom A_{i-1} to atom A_i The backbone atoms A_i may all be identical (such as polyethylene) or may be of two or more atoms [Si and O for poly(dimethyl siloxane)]. The polymer is in its ideal state if there are no net interactions between atoms A_i and A_j that are separated by a sufficient number of bonds along the chain so that $|i-j| \gg 1$.

The **end-to-end vector** is the sum of all n bond vectors in the chain:

$$\vec{R}_n = \sum_{i=1}^{n} \vec{r}_i. \tag{2.2}$$

Different individual chains will have different bond vectors and hence different end-to-end vectors. The distribution of end-to-end vectors shall be discussed in Section 2.5. It is useful to talk about average properties of this distribution. The average end-to-end vector of an isotropic collection of chains of n backbone atoms is zero:

$$\langle \vec{R}_n \rangle = 0. \tag{2.3}$$

The **ensemble average** $\langle\,\rangle$ denotes an average over all possible states of the system (accessed either by considering many chains or many

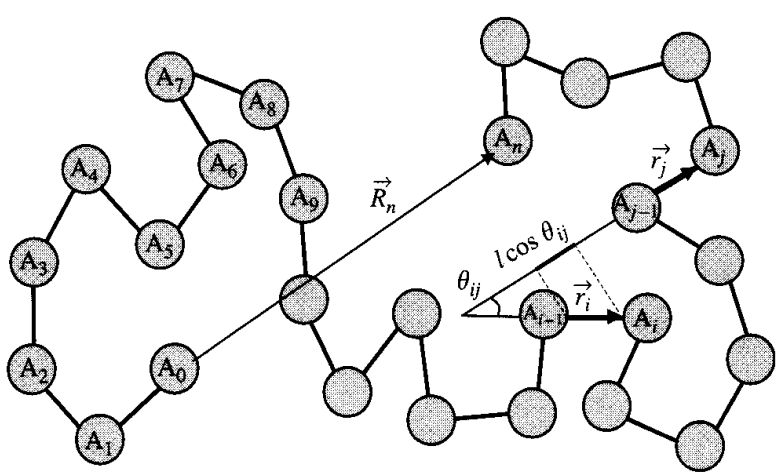

Fig. 2.3
One conformation of a flexible polymer.

different conformations of the same chain). In this particular case the ensemble average corresponds to averaging over an ensemble of chains of n bonds with all possible bond orientations. Since there is no preferred direction in this ensemble, the average end-to-end vector is zero [Eq. (2.3)]. The simplest non-zero average is the mean-square end-to-end distance:

$$\begin{aligned}\langle R^2\rangle \equiv \langle \vec{R}_n^2\rangle = \langle \vec{R}_n \cdot \vec{R}_n\rangle &= \left\langle \left(\sum_{i=1}^{n} \vec{r}_i\right) \cdot \left(\sum_{j=1}^{n} \vec{r}_j\right)\right\rangle \\ &= \sum_{i=1}^{n}\sum_{j=1}^{n}\langle \vec{r}_i \cdot \vec{r}_j\rangle. \end{aligned} \tag{2.4}$$

If all bond vectors have the same length $l = |\vec{r}_i|$, the scalar product can be represented in terms of the angle θ_{ij} between bond vectors $\vec{r}_i$ and $\vec{r}_j$ as shown in Fig. 2.3:

$$\vec{r}_i \cdot \vec{r}_j = l^2 \cos\theta_{ij}. \tag{2.5}$$

The mean-square end-to-end distance becomes a double sum of average cosines:

$$\langle R^2\rangle = \sum_{i=1}^{n}\sum_{j=1}^{n}\langle \vec{r}_i \cdot \vec{r}_j\rangle = l^2 \sum_{i=1}^{n}\sum_{j=1}^{n}\langle \cos\theta_{ij}\rangle. \tag{2.6}$$

One of the simplest models of an ideal polymer is the **freely jointed chain model** with a constant bond length $l = |\vec{r}_i|$ and no correlations between the directions of different bond vectors, $\langle \cos\theta_{ij}\rangle = 0$ for $i \neq j$. There are only n non-zero terms in the double sum ($\cos\theta_{ij} = 1$ for $i = j$). The mean-square end-to-end distance of a freely jointed chain is then quite simple:

$$\langle R^2\rangle = nl^2. \tag{2.7}$$

In a typical polymer chain, there are correlations between bond vectors (especially between neighbouring ones) and $\langle \cos\theta_{ij}\rangle \neq 0$. But in an ideal chain there is no interaction between monomers separated by a great distance along the chain contour. This implies that there are no correlations between the directions of distant bond vectors.

$$\lim_{|i-j|\to\infty} \langle \cos\theta_{ij}\rangle = 0. \tag{2.8}$$

It can be shown (see Section 2.3.1) that for any bond vector i, the sum over all other bond vectors j converges to a finite number, denoted by C_i':

$$C_i' \equiv \sum_{j=1}^{n}\langle \cos\theta_{ij}\rangle. \tag{2.9}$$

Therefore, Eq. (2.6) reduces to

$$\langle R^2 \rangle = l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \cos \theta_{ij} \rangle = l^2 \sum_{i=1}^{n} C_i' = C_n n l^2, \tag{2.10}$$

where the coefficient C_n, called Flory's **characteristic ratio**, is the average value of the constant C_i' over all main-chain bonds of the polymer:

$$C_n = \frac{1}{n} \sum_{i=1}^{n} C_i'. \tag{2.11}$$

The main property of ideal chains is that $\langle R^2 \rangle$ is proportional to the product of the number of bonds n and the square of the bond length l^2 [Eq. (2.10)].

An infinite chain has a C_i' value for all i given by C_∞. A real chain has a cutoff in the sum [Eq. (2.9)] at finite j that results in a smaller C_i'. This effect is more pronounced near chain ends.

The characteristic ratio is larger than unity ($C_n > 1$) for all polymers. The physical origins of these local correlations between bond vectors are restricted bond angles and steric hindrance. All models of ideal polymers ignore steric hindrance between monomers separated by many bonds and result in characteristic ratios saturating at a finite value C_∞ for large numbers of main-chain bonds ($n \to \infty$) (see Fig. 2.4). Thus, the mean-square end-to-end distance [Eq. (2.10)] can be approximated for long chains:

$$\langle R^2 \rangle \cong C_\infty n l^2. \tag{2.12}$$

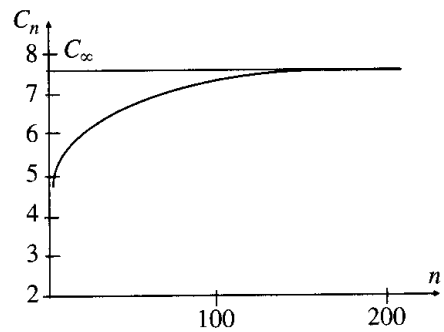

Fig. 2.4
Flory's characteristic ratio C_n saturates at C_∞ for long chains.

The numerical value of Flory's characteristic ratio depends on the local stiffness of the polymer chain with typical numbers of 7–9 for many flexible polymers. The values of the characteristic ratios of some common polymers are listed in Table 2.1. There is a tendency for polymers with bulkier side groups to have higher C_∞, owing to the side groups sterically hindering bond rotation (as in polystyrene), but there are many exceptions to this general tendency (such as polyethylene).

Flexible polymers have many universal properties that are independent of local chemical structure. A simple unified description of all ideal

Table 2.1 Characteristic ratios, Kuhn lengths, and molar masses of Kuhn monomers for common polymers

Polymer	Structure	C_∞	b (Å)	ρ (g cm^{-3})	M_0 (g mol^{-1})
1,4-Polyisoprene (PI)	$-(CH_2CH{=}CHCH(CH_3))-$	4.6	8.2	0.830	113
1,4-Polybutadiene (PB)	$-(CH_2CH{=}CHCH_2)-$	5.3	9.6	0.826	105
Polypropylene (PP)	$-(CH_2CH_2(CH_3))-$	5.9	11	0.791	180
Poly(ethylene oxide) (PEO)	$-(CH_2CH_2O)-$	6.7	11	1.064	137
Poly(dimethyl siloxane) (PDMS)	$-(OSi(CH_3)_2)-$	6.8	13	0.895	381
Polyethylene (PE)	$-(CH_2CH_2)-$	7.4	14	0.784	150
Poly(methyl methacrylate) (PMMA)	$-(CH_2C(CH_3)(COOCH_3))-$	9.0	17	1.13	655
Atactic polystyrene (PS)	$-(CH_2CHC_6H_5)-$	9.5	18	0.969	720

polymers is provided by an **equivalent freely jointed chain**. The equivalent chain has the same mean-square end-to-end distance $\langle R^2 \rangle$ and the same maximum end-to-end distance $R_{\max}$ as the actual polymer, but has N freely-jointed effective bonds of length b. This effective bond length b is called the **Kuhn length**. The contour length of this equivalent freely jointed chain is

$$Nb = R_{\max}, \tag{2.13}$$

and its mean-square end-to-end distance is

$$\langle R^2 \rangle = Nb^2 = bR_{\max} = C_\infty n l^2. \tag{2.14}$$

Therefore, the equivalent freely jointed chain has

$$N = \frac{R_{\max}^2}{C_\infty n l^2} \tag{2.15}$$

equivalent bonds (**Kuhn monomers**) of length

$$b = \frac{\langle R^2 \rangle}{R_{\max}} = \frac{C_\infty n l^2}{R_{\max}}. \tag{2.16}$$

Example: Calculate the Kuhn length b of a polyethylene chain with $C_\infty = 7.4$, main-chain bond length $l = 1.54$ Å, and bond angle $\theta = 68°$.

Substituting the maximum end-to-end distance from Eq. (2.1) into Eq. (2.16) determines the Kuhn length:

$$b = \frac{C_\infty l^2 n}{n l \cos(\theta/2)} = \frac{C_\infty l}{\cos(\theta/2)}. \tag{2.17}$$

For polyethylene $b \cong 1.54\,\text{Å} \times 7.4/0.83 \cong 14\,\text{Å}$.

The values of the Kuhn length b and corresponding molar mass of a Kuhn monomer M_0 for various polymers are listed in Table 2.1. Throughout this book, we will use the equivalent freely jointed chain to describe all flexible polymers and will call N the 'degree of polymerization' or number of 'monomers' (short for Kuhn monomers) and call b the monomer length (instead of the Kuhn monomer length) and

$$R_0 = \sqrt{\langle R^2 \rangle} = bN^{1/2}, \tag{2.18}$$

the root-mean-square end-to-end distance (the subscript 0 refers to the ideal state). This is not to be confused with the chemical definitions of the degree of polymerization and of monomer size. By renormalizing the monomer, Eq. (2.18) holds for *all* flexible linear polymers in the ideal state with $N \gg 1$, with all chemical-specific characteristics contained within that monomer size (Kuhn length).

2.3 Ideal chain models

Below we describe several models of ideal chains. Each model makes different assumptions about the allowed values of torsion and bond angles. However, every model ignores interactions between monomers separated

by large distance along the chain and is therefore a model of an ideal polymer. The chemical structure of polymers determines the populations of torsion and bond angles. Some polymers (like 1,4-polyisoprene) are very flexible chains while others (like double-stranded DNA) are locally very rigid, becoming random walks only on quite large length scales.

2.3.1 Freely rotating chain model

As the name suggests, this model ignores differences between the probabilities of different torsion angles and assumes all torsion angles $-\pi < \varphi_i \leq \pi$ to be equally probable. Thus, the **freely rotating chain model** ignores the variations of the potential $U(\varphi_i)$. This model assumes all bond lengths and bond angles are fixed (constant) and all torsion angles are equally likely and independent of each other.

To calculate the mean-square end-to-end distance [Eq. (2.4)]

$$\langle R^2 \rangle = \langle \vec{R}_n \cdot \vec{R}_n \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \vec{r}_i \cdot \vec{r}_j \rangle, \tag{2.19}$$

the correlation between bond vectors $\vec{r}_i$ and $\vec{r}_j$ must be determined. This correlation is passed along through the chain of bonds connecting bonds $\vec{r}_i$ and $\vec{r}_j$. For the freely rotating chain, the component of $\vec{r}_j$ normal to vector $\vec{r}_{j-1}$ averages out to zero due to free rotations of the torsion angle φ_j (see Fig. 2.5). The only correlation between the bond vectors that is transmitted down the chain is the component of vector $\vec{r}_j$ along the bond vector $\vec{r}_{j-1}$. The value of this component is $l \cos\theta$. Bond vector $\vec{r}_{j-1}$ passes this correlation down to vector $\vec{r}_{j-2}$, but again only the component along $\vec{r}_{j-2}$ survives due to free rotations of torsion angle φ_{j-1}. The leftover memory of the vector $\vec{r}_j$ at this stage is $l(\cos\theta)^2$. The correlations from bond vector $\vec{r}_j$ at bond vector $\vec{r}_i$ are reduced by the factor $(\cos\theta)^{|j-i|}$ due to independent free rotations of $|j-i|$ torsion angles between these two vectors. Therefore, the correlation between bond vectors $\vec{r}_i$ and $\vec{r}_j$ is

$$\langle \vec{r}_i \cdot \vec{r}_j \rangle = l^2 (\cos\theta)^{|j-i|}. \tag{2.20}$$

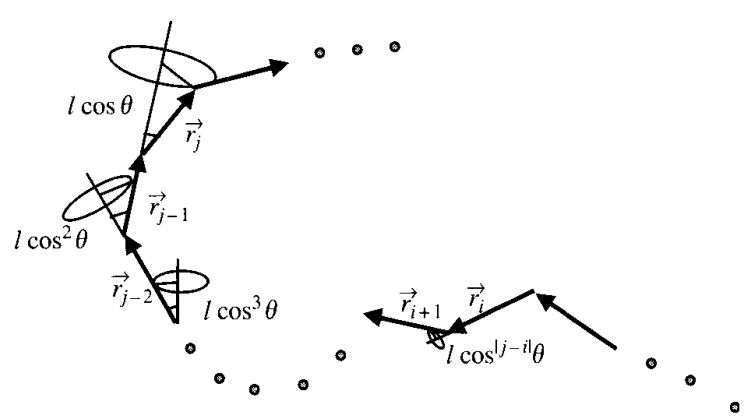

Fig. 2.5
All torison angles are equally likely in a freely rotating chain.

The mean-square end-to-end distance of the freely rotating chain can now be written in terms of cosines:

$$\begin{aligned}\langle R^2\rangle &= \sum_{i=1}^{n}\sum_{j=1}^{n}\langle \vec{r}_i\cdot\vec{r}_j\rangle = \sum_{i=1}^{n}\left(\sum_{j=1}^{i-1}\langle \vec{r}_i\cdot\vec{r}_j\rangle + \langle \vec{r}_i^{\,2}\rangle + \sum_{j=i+1}^{n}\langle \vec{r}_i\cdot\vec{r}_j\rangle\right)\\ &= \sum_{i=1}^{n}\langle \vec{r}_i^{\,2}\rangle + l^2\sum_{i=1}^{n}\left(\sum_{j=1}^{i-1}(\cos\theta)^{i-j} + \sum_{j=i+1}^{n}(\cos\theta)^{j-i}\right)\\ &= nl^2 + l^2\sum_{i=1}^{n}\left(\sum_{k=1}^{i-1}\cos^k\theta + \sum_{k=1}^{n-i}\cos^k\theta\right). \end{aligned} \tag{2.21}$$

Note that $(\cos\theta)^{|j-i|}$ decays rapidly as the number of bonds between bond vectors $\vec{r}_i$ and $\vec{r}_j$ is increased.

$$(\cos\theta)^{|j-i|} = \exp[|j-i|\ln(\cos\theta)] = \exp\left[-\frac{|j-i|}{s_\mathrm{p}}\right]. \tag{2.22}$$

The final relation defines s_p as the number of main-chain bonds in a persistence segment, which is the scale at which local correlations between bond vectors decay:

$$s_\mathrm{p} = -\frac{1}{\ln(\cos\theta)}. \tag{2.23}$$

Since the decay is so rapid, the summation in Eq. (2.21) can be replaced by an infinite series over k:

$$\begin{aligned}\sum_{i=1}^{n}\left(\sum_{k=1}^{i-1}\cos^k\theta + \sum_{k=1}^{n-i}\cos^k\theta\right) &\cong 2\sum_{i=1}^{n}\sum_{k=1}^{\infty}\cos^k\theta = 2n\sum_{k=1}^{\infty}\cos^k\theta\\ &= 2n\frac{\cos\theta}{1-\cos\theta}. \end{aligned} \tag{2.24}$$

The mean-square end-to-end distance of the freely rotating chain is a simple function of the number of bonds in the chain backbone n, the length of each backbone bond l and the bond angle θ:

$$\langle R^2\rangle = nl^2 + 2nl^2\frac{\cos\theta}{1-\cos\theta} = nl^2\frac{1+\cos\theta}{1-\cos\theta}. \tag{2.25}$$

Polymers with carbon single bonds making up their backbone have a bond angle of $\theta = 68°$.

$$C_\infty = \frac{1+\cos\theta}{1-\cos\theta} \cong 2 \quad \text{and} \quad s_\mathrm{p} \cong 1. \tag{2.26}$$

Polymer chains are never as flexible as the freely rotating chain model predicts, since the most flexible polymers with $\theta = 68°$ have $C_\infty > 4$

(see Table 2.1). This is because there is steric hindrance to bond rotation in all polymers.

2.3.2 Worm-like chain model

The **worm-like chain model** (sometimes called the Kratky–Porod model) is a special case of the freely rotating chain model for very small values of the bond angle. This is a good model for very stiff polymers, such as double-stranded DNA for which the flexibility is due to fluctuations of the contour of the chain from a straight line rather than to *trans–gauche* bond rotations. For small values of the bond angle ($\theta \ll 1$), the $\cos\theta$ in Eq. (2.23) can be expanded about its value of unity at $\theta = 0$:

$$\cos\theta \cong 1 - \frac{\theta^2}{2}. \tag{2.27}$$

For small x, $\ln(1-x) \cong -x$.

$$\ln(\cos\theta) \cong -\frac{\theta^2}{2}. \tag{2.28}$$

Since θ is small, the persistence segment of the chain [Eq. (2.23)] contains a large number of main-chain bonds.

$$s_p = -\frac{1}{\ln(\cos\theta)} \cong \frac{2}{\theta^2}. \tag{2.29}$$

The **persistence length** is the length of this persistence segment:

$$l_p \equiv s_p l = l\frac{2}{\theta^2}. \tag{2.30}$$

The Flory characteristic ratio of the worm-like chain is very large:

$$C_\infty = \frac{1+\cos\theta}{1-\cos\theta} \cong \frac{2-(\theta^2/2)}{(\theta^2/2)} \cong \frac{4}{\theta^2}. \tag{2.31}$$

The corresponding Kuhn length [see Eq. (2.16)] is twice the persistence length:

$$b = l\frac{C_\infty}{\cos(\theta/2)} \cong l\frac{4}{\theta^2} = 2l_p. \tag{2.32}$$

For example, the persistence length of a double-helical DNA $l_p \approx 50$ nm and the Kuhn length is $b \approx 100$ nm.

The combination of parameters l/θ^2 enters in the expressions of the persistence length l_p and the Kuhn length b. The worm-like chain is defined as the limit $l \to 0$ and $\theta \to 0$ at constant persistence length l_p (constant l/θ^2) and constant chain contour length $R_{max} = nl\cos(\theta/2) \cong nl$.

The mean-square end-to-end distance of the worm-like chain can be evaluated using the exponential decay of correlations between tangent vectors along the chain [Eq. (2.22)]:

$$\begin{aligned}\langle R^2\rangle &= l^2\sum_{i=1}^{n}\sum_{j=1}^{n}\langle\cos\theta_{ij}\rangle = l^2\sum_{i=1}^{n}\sum_{j=1}^{n}(\cos\theta)^{|j-i|}\\ &= l^2\sum_{i=1}^{n}\sum_{j=1}^{n}\exp\left(-\frac{|j-i|}{l_\mathrm{p}}l\right).\end{aligned} \tag{2.33}$$

The summation over bonds can be changed into integration over the contour of the worm-like chain:

$$l\sum_{i=1}^{n}\to\int_0^{R_\mathrm{max}}\mathrm{d}u \quad\text{and}\quad l\sum_{j=1}^{n}\to\int_0^{R_\mathrm{max}}\mathrm{d}v. \tag{2.34}$$

$$\begin{aligned}\langle R^2\rangle &= \int_0^{R_\mathrm{max}}\left[\int_0^{R_\mathrm{max}}\exp\left(-\frac{|u-v|}{l_\mathrm{p}}\right)\mathrm{d}v\right]\mathrm{d}u\\ &= \int_0^{R_\mathrm{max}}\left[\left(\exp\left(-\frac{u}{l_\mathrm{p}}\right)\int_0^{u}\exp\left(\frac{v}{l_\mathrm{p}}\right)\mathrm{d}v\right.\right.\\ &\qquad\left.\left.+\exp\left(\frac{u}{l_\mathrm{p}}\right)\int_u^{R_\mathrm{max}}\exp\left(-\frac{v}{l_\mathrm{p}}\right)\mathrm{d}v\right)\right]\mathrm{d}u\\ &= l_\mathrm{p}\int_0^{R_\mathrm{max}}\left[\exp\left(-\frac{u}{l_\mathrm{p}}\right)\left(\exp\left(\frac{u}{l_\mathrm{p}}\right)-1\right)\right.\\ &\qquad\left.+\exp\left(\frac{u}{l_\mathrm{p}}\right)\left(-\exp\left(-\frac{R_\mathrm{max}}{l_\mathrm{p}}\right)+\exp\left(-\frac{u}{l_\mathrm{p}}\right)\right)\right]\mathrm{d}u\\ &= l_\mathrm{p}\int_0^{R_\mathrm{max}}\left[2-\exp\left(-\frac{u}{l_\mathrm{p}}\right)-\exp\left(-\frac{R_\mathrm{max}}{l_\mathrm{p}}\right)\exp\left(\frac{u}{l_\mathrm{p}}\right)\right]\mathrm{d}u\\ &= l_\mathrm{p}\left[2R_\mathrm{max}+l_\mathrm{p}\left(\exp\left(-\frac{R_\mathrm{max}}{l_\mathrm{p}}\right)-1\right)\right.\\ &\qquad\left.-l_\mathrm{p}\exp\left(-\frac{R_\mathrm{max}}{l_\mathrm{p}}\right)\left(\exp\left(\frac{R_\mathrm{max}}{l_\mathrm{p}}\right)-1\right)\right]\\ &= 2l_\mathrm{p}R_\mathrm{max}-2l_\mathrm{p}^2\left(1-\exp\left(-\frac{R_\mathrm{max}}{l_\mathrm{p}}\right)\right).\end{aligned} \tag{2.35}$$

There are two simple limits of this expression. The ideal chain limit is for worm-like chains much longer than their persistence length.

$$\langle R^2\rangle \cong 2l_\mathrm{p}R_\mathrm{max} = bR_\mathrm{max} \quad\text{for } R_\mathrm{max}\gg l_\mathrm{p}. \tag{2.36}$$

The rod-like limit is for worm-like chains much shorter than their persistence length. The exponential in Eq. (2.35) can be expanded in this limit:

$$\exp\left(-\frac{R_\mathrm{max}}{l_\mathrm{p}}\right)\cong 1-\frac{R_\mathrm{max}}{l_\mathrm{p}}+\frac{1}{2}\left(\frac{R_\mathrm{max}}{l_\mathrm{p}}\right)^2+\cdots \quad\text{for } R_\mathrm{max}\ll l_\mathrm{p}, \tag{2.37}$$

$$\langle R^2 \rangle \cong R_{\max}^2 \quad \text{for } R_{\max} \ll l_p. \tag{2.38}$$

The mean-square end-to-end distance of the worm-like chain [Eq. (2.35)] is a smooth crossover between these two simple limits.

The important difference between freely jointed chains and worm-like chains is that each bond of Kuhn length b of the freely jointed chain is assumed to be completely rigid. Worm-like chains are also stiff on length scales shorter than the Kuhn length, but are not completely rigid and can fluctuate and bend. These bending modes lead to a qualitatively different dependence of extensional force on elongation near maximum extension, as will be discussed in Section 2.6.2.

2.3.3 Hindered rotation model

The **hindered rotation model** also assumes bond lengths and bond angles are constant and torsion angles are independent of each other. As its name suggests, the torsion angle rotation is taken to be hindered by a potential $U(\varphi_i)$ [see Fig. 2.1(d)]. The probability of any value of the torsion angle φ_i is taken to be proportional to the **Boltzmann factor** $\exp[-U(\varphi_i)/kT]$. Most of the torsion angles are in low energy states [near the minima in Fig. 2.1(d)] but for ordinary temperatures there are some torsion angles corresponding to high energy states as well. The Boltzmann factor ensures that states with higher energy are progressively less likely to be populated.

The hindered rotation model assumes independent but hindered rotations of torsion angles at constant bond lengths and bond angles with different potential profiles $U(\varphi_i)$ corresponding to different polymers. The hindered rotation model predicts the mean-square end-to-end distance

$$\langle R^2 \rangle = C_\infty l^2 n, \tag{2.39}$$

with the characteristic ratio (see problem 2.9)

$$C_\infty = \left(\frac{1+\cos\theta}{1-\cos\theta}\right)\left(\frac{1+\langle\cos\varphi\rangle}{1-\langle\cos\varphi\rangle}\right), \tag{2.40}$$

where $\langle\cos\varphi\rangle$ is the average value of the cosine of the torsion angle with probabilities determined by Boltzmann factors, $\exp[-U(\varphi_i)/kT]$:

$$\langle\cos\varphi\rangle = \frac{\int_0^{2\pi}\cos\varphi\exp(-U(\varphi)/kT)\,\mathrm{d}\varphi}{\int_0^{2\pi}\exp(-U(\varphi)/kT)\,\mathrm{d}\varphi}. \tag{2.41}$$

2.3.4 Rotational isomeric state model

This is the most successful ideal chain model used to calculate the details of conformations of different polymers. In this model, bond lengths l and bond angles θ are fixed (constant).

For a relatively high barrier between *trans* and *gauche* states $\Delta E \gg kT$ the values of the torsion angles φ_i are close to the minima (t, g_+, g_-) [see Fig. 2.1(d)]. In the **rotational isomeric state model** each molecule is assumed to exist only in discrete torsional states corresponding to the potential

energy minima. The fluctuations about these minima are ignored. A conformation of a chain with n main-chain bonds is thus represented by a sequence of $n-2$ torsion angles:

$$\cdots tg_- ttg_+ tg_+ ttg_- t \cdots. \tag{2.42}$$

Each of these $n-2$ torsion angles can be in one of three states (t, g_+, g_-) and therefore the whole chain has 3^{n-2} rotational isomeric states. For example, n-pentane, with $n=4$ main-chain bonds and $n-2=2$ torsion angles, has $3^2=9$ rotational isomeric states:[1]

$$tt,\ tg_+,\ tg_-,\ g_+t,\ g_-t,\ g_+g_+,\ g_+g_-,\ g_-g_+,\ g_-g_-. \tag{2.43}$$

In the rotational isomeric state model, these states are *not* equally probable. Correlations between neighbouring torsional states are included in the model. For example, a consecutive sequence of g_+ and g_- has high energy due to overlap between atoms and therefore is taken to have very low probability in the rotational isomeric state model. The relative probabilities of the states of neighboring torsional angles are used to calculate the mean-square end-to-end distance and C_∞ [Eq. (2.12)].

Table 2.2 summarizes the assumptions of the ideal chain models. The worm-like chain model is a special case of the freely rotating chain with a small value of the bond angle θ. Moving from left to right in Table 2.2, the models become progressively more specific (and more realistic). As more constraints are adopted, the chain becomes stiffer, reflected in larger C_∞.

Table 2.2 Assumptions and predictions of ideal chain models: FJC, freely jointed chain; FRC, freely rotating chain; HR, hindered rotation; RIS, rotational isomeric state

Models	FJC	FRC	HR	RIS
Bond length l	Fixed	Fixed	Fixed	Fixed
Bond angle θ	Free	Fixed	Fixed	Fixed
Torsion angle φ	Free	Free	Controlled by $U(\varphi)$	$t, g+, g-$
Next φ independent?	Yes	Yes	Yes	No
C_∞	1	$\frac{1+\cos\theta}{1-\cos\theta}$	$\left(\frac{1+\cos\theta}{1-\cos\theta}\right)\left(\frac{1+\langle\cos\theta\rangle}{1-\langle\cos\varphi\rangle}\right)$	Specific

2.4 Radius of gyration

The size of linear chains can be characterized by their mean-square end-to-end distance. However, for branched or ring polymers this quantity is not well defined, because they either have too many ends or no ends at all. Since all objects possess a radius of gyration, it can characterize the size of polymers of any architecture. Consider, for example, the branched polymer sketched in Fig. 2.6. The square **radius of gyration** is defined as the average square distance between monomers in a given conformation (position vector $\vec{R}_i$) and the polymer's centre of mass (position vector $\vec{R}_{\rm cm}$):

$$R_{\rm g}^2 \equiv \frac{1}{N}\sum_{i=1}^{N}(\vec{R}_i - \vec{R}_{\rm cm})^2. \tag{2.44}$$

[1] Six of the nine rotational isomers are distinguishable.

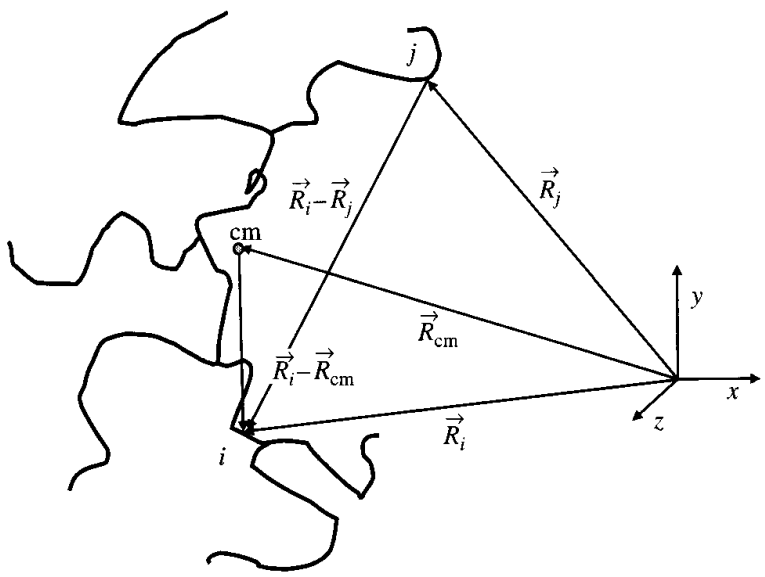

Fig. 2.6
One conformation of a randomly branched polymer and its centre of mass, denoted by cm.

The position vector of the centre of mass of the polymer is the number-average of all monomer position vectors:[2]

$$\vec{R}_{cm} \equiv \frac{1}{N}\sum_{j=1}^{N} \vec{R}_j. \tag{2.45}$$

Substituting the definition of the position vector of the centre of mass [Eq. (2.45)] into Eq. (2.44) gives an expression for the square radius of gyration as a double sum of squares over all inter-monomer distances:

$$\begin{aligned} R_g^2 &= \frac{1}{N}\sum_{i=1}^{N}(\vec{R}_i^2 - 2\vec{R}_i\vec{R}_{cm} + \vec{R}_{cm}^2) \\ &= \frac{1}{N}\sum_{i=1}^{N}\left[\vec{R}_i^2\frac{1}{N}\sum_{j=1}^{N}1 - 2\vec{R}_i\frac{1}{N}\sum_{j=1}^{N}\vec{R}_j + \left(\frac{1}{N}\sum_{j=1}^{N}\vec{R}_j\right)^2\right]. \end{aligned} \tag{2.46}$$

The last term in the sum can be rewritten as

$$\begin{aligned} \frac{1}{N}\sum_{i=1}^{N}\left(\frac{1}{N}\sum_{j=1}^{N}\vec{R}_j\right)^2 &= \left(\frac{1}{N}\sum_{j=1}^{N}\vec{R}_j\right)^2 = \left(\frac{1}{N}\sum_{i=1}^{N}\vec{R}_i\right)\left(\frac{1}{N}\sum_{j=1}^{N}\vec{R}_j\right) \\ &= \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\vec{R}_i\vec{R}_j. \end{aligned}$$

Therefore, the expression for the square radius of gyration takes the form

$$R_g^2 = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}(\vec{R}_i^2 - 2\vec{R}_i\vec{R}_j + \vec{R}_i\vec{R}_j) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}(\vec{R}_i^2 - \vec{R}_i\vec{R}_j).$$

[2] In general, the mass of the monomers M_j should be included in the definitions of the radius of gyration and of the centre of mass. For example, the proper centre of mass definition is

$$\vec{R}_{cm} \equiv \frac{\sum_{j=1}^{N} M_j\vec{R}_j}{\sum_{j=1}^{N} M_j}.$$

We assume that all the monomers have the same mass $M_j = M_0$ for all j.

This expression does not depend on the choice of summation indices and can be rewritten in a symmetric form:

$$\begin{aligned} R_g^2 &= \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}(\vec{R}_i^2 - \vec{R}_i\vec{R}_j) \\ &= \frac{1}{2}\left[\frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}(\vec{R}_i^2 - \vec{R}_i\vec{R}_j) + \frac{1}{N^2}\sum_{j=1}^{N}\sum_{i=1}^{N}(\vec{R}_j^2 - \vec{R}_j\vec{R}_i)\right] \\ &= \frac{1}{2N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}(\vec{R}_i^2 - 2\vec{R}_i\vec{R}_j + \vec{R}_j^2) \\ &= \frac{1}{2N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}(\vec{R}_i - \vec{R}_j)^2. \end{aligned} \tag{2.47}$$

Each pair of monomers enters twice in the double sum of Eq. (2.47). Alternatively, this expression for the square radius of gyration can be written with each pair of monomers entering only once in the double sum:

$$R_g^2 = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=i}^{N}(\vec{R}_i - \vec{R}_j)^2. \tag{2.48}$$

For polymers and other fluctuating objects, the square radius of gyration is usually averaged over the ensemble of allowed conformations giving the mean-square radius of gyration:

$$\langle R_g^2\rangle = \frac{1}{N}\sum_{i=1}^{N}\langle(\vec{R}_i - \vec{R}_{cm})^2\rangle = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=i}^{N}\langle(\vec{R}_i - \vec{R}_j)^2\rangle. \tag{2.49}$$

For non-fluctuating (solid) objects such averaging is unnecessary. The expression with the centre of mass is useful only if the position of the centre of mass $\vec{R}_{cm}$ of the object is known or is easy to evaluate. Otherwise the expression for the radius of gyration in terms of the average square distances between all pairs of monomers is used.

2.4.1 Radius of gyration of an ideal linear chain

To illustrate the use of Eq. (2.48), we now calculate the mean-square radius of gyration for an ideal linear chain. For the linear chain, the summations over the monomers can be changed into integrations over the contour of the chain, by replacing monomer indices i and j with continuous coordinates u and v along the contour of the chain:

$$\sum_{i=1}^{N} \to \int_0^N \mathrm{d}u \quad \text{and} \quad \sum_{j=i}^{N} \to \int_u^N \mathrm{d}v. \tag{2.50}$$

This transformation results in the integral form for the mean-square radius of gyration

$$\langle R_g^2 \rangle = \frac{1}{N^2} \int_0^N \int_u^N \langle (\vec{R}(u) - \vec{R}(\mathrm{v}))^2 \rangle \, \mathrm{d}\mathrm{v} \, \mathrm{d}u, \tag{2.51}$$

where $\vec{R}(u)$ is the position vector corresponding to the contour coordinate u. The mean-square distance between points u and v along the contour of the chain can be obtained by treating each section of $\mathrm{v} - u$ monomers as a shorter ideal chain. The outer sections of u and of $N - \mathrm{v}$ monomers do not affect the conformations of this inner section. The mean-square end-to-end distance for an ideal chain of $\mathrm{v} - u$ monomers is given by Eq. (2.18):

$$\langle (\vec{R}(u) - \vec{R}(\mathrm{v}))^2 \rangle = (\mathrm{v} - u) b^2. \tag{2.52}$$

The mean-square radius of gyration is then calculated by a simple integration using the change of variables $\mathrm{v}' \equiv \mathrm{v} - u$ and $u' \equiv N - u$:

$$\begin{aligned} \langle R_g^2 \rangle &= \frac{b^2}{N^2} \int_0^N \int_u^N (\mathrm{v} - u) \, \mathrm{d}\mathrm{v} \, \mathrm{d}u = \frac{b^2}{N^2} \int_0^N \int_0^{N-u} \mathrm{v}' \, \mathrm{d}\mathrm{v}' \, \mathrm{d}u \\ &= \frac{b^2}{N^2} \int_0^N \frac{(N-u)^2}{2} \, \mathrm{d}u = \frac{b^2}{2N^2} \int_0^N (u')^2 \, \mathrm{d}u' = \frac{b^2}{2N^2} \frac{N^3}{3} = \frac{Nb^2}{6} \end{aligned} \tag{2.53}$$

Comparing this result with Eq. (2.18), we obtain the classic Debye result relating the mean-square radius of gyration and the mean-square end-to-end distance of an ideal linear chain:

$$\langle R_g^2 \rangle = \frac{b^2 N}{6} = \frac{\langle R^2 \rangle}{6}. \tag{2.54}$$

The radius of gyration of other shapes of flexible ideal chains can be calculated in a similar way and examples of the results are given in Table 2.3.

Table 2.3 Mean-square radii of gyration of ideal polymers with N Kuhn monomers of length b: linear chain, ring, f-arm star with each arm containing N/f Kuhn monomers, and H-polymer with all linear sections containing $N/5$ Kuhn monomers

Ideal chains	Linear	Ring	f-arm star	H-polymer
$\langle R_g^2 \rangle$	$Nb^2/6$	$Nb^2/12$	$[(N/f)b^2/6]\,(3 - 2/f)$	$(Nb^2/6)\ 89/625$

2.4.2 Radius of gyration of a rod polymer

Consider a rod polymer of N monomers of length b, with end-to-end distance $L = Nb$. It is convenient to calculate the radius of gyration of a rod polymer using the original definition, Eq. (2.44), written in integral form:

$$R_g^2 \equiv \frac{1}{N} \int_0^N \left[(\vec{R}(u) - \vec{R}_{\mathrm{cm}})^2 \right] \mathrm{d}u. \tag{2.55}$$

A rigid rod polymer has only one conformation with the distance between coordinate u along the chain and its centre of mass (coordinate $N/2$):

$$|\vec{R}(u) - \vec{R}_{\mathrm{cm}}| = \left|u - \frac{N}{2}\right| b. \tag{2.56}$$

Therefore, no averaging is needed for calculation of the radius of gyration of a rod. The square radius of gyration of the rod polymer is calculated by a simple integration

$$R_{\mathrm{g}}^2 \equiv \frac{b^2}{N}\int_0^N \left(u - \frac{N}{2}\right)^2 \mathrm{d}u = \frac{b^2}{N}\int_{-N/2}^{N/2} x^2\,\mathrm{d}x = \frac{N^2 b^2}{12}, \tag{2.57}$$

where the change of variables $x = u - N/2$ has been used. Note that the relation between the end-to-end distance and the radius of gyration for a rod polymer is different from that for an ideal linear chain [Eq. (2.54)]:

$$R_{\mathrm{g}}^2 = \frac{N^2 b^2}{12} = \frac{L^2}{12}. \tag{2.58}$$

Examples of the radii of gyration of other rigid objects are listed in Table 2.4.

Table 2.4 Square radii of gyration of rigid objects: uniform thin disc of radius R, uniform sphere of radius R, thin rod of length L, and uniform right cylinder of radius R and length L

Rigid objects	Disk	Sphere	Rod	Cylinder
R_{g}^2	$R^2/2$	$3R^2/5$	$L^2/12$	$(R^2/2)+(L^2/12)$

2.4.3 Radius of gyration of an ideal branched polymer (Kramers theorem)

Consider an ideal molecule that contains an arbitrary number of branches, but no loops. This molecule consists of N freely jointed segments (Kuhn monomers) of length b. The mean-square radius of gyration of this molecule is calculated using Eq. (2.48):

$$\langle R_{\mathrm{g}}^2\rangle = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=i}^{N}\langle(\vec{R}_j - \vec{R}_i)^2\rangle. \tag{2.59}$$

The vector $\vec{R}_j - \vec{R}_i$ between monomers i and j can be represented by the sum over the bond vectors $\vec{r}_k$ of a linear strand connecting these two monomers:

$$\vec{R}_j - \vec{R}_i = \sum_{k=i+1}^{j} \vec{r}_k. \tag{2.60}$$

Since we have assumed freely jointed chain statistics with no correlations between different segments,

$$\langle \vec{r}_k \vec{r}_{k'}\rangle = 0 \quad \text{if } k \neq k', \tag{2.61}$$

the mean-square distance between monomers i and j can be rewritten:

$$\langle(\vec{R}_j - \vec{R}_i)^2\rangle = \sum_{k=i+1}^{j}\sum_{k'=i+1}^{j}\langle\vec{r}_k\vec{r}_{k'}\rangle = \sum_{k=i+1}^{j}(\vec{r}_k)^2. \tag{2.62}$$

Each segment of a linear strand connecting monomers i and j contributes $(\vec{r}_k)^2 = b^2$ to the double sum in Eq. (2.59). There is only one such strand connecting each pair of monomers because the molecule is assumed to have no loops. Therefore, the contribution of each segment of the molecule to the double sum in Eq. (2.59) is equal to b^2 times the number of strands between different monomers i and j that pass through this segment. Consider, for example, segment k in Fig. 2.7. It divides the molecule into two tree-like parts. The lower part contains N_1 monomers and the upper part contains $N - N_1$ monomers. Monomer i could be any one of $N - N_1$ monomers of the upper part, while monomer j could be any one of N_1 monomers of the lower part of the molecule. Therefore, there are $N_1(N - N_1)$ different strands between all pairs of monomers i and j passing through segment k. Thus, the segment k contributes $N_1(k)[N - N_1(k)]b^2$ to the double sum in Eq. (2.59).

The radius of gyration can be expressed as the sum over all N molecular bonds, of the product of the number of monomers of the two branches $N_1(k)$ and $N - N_1(k)$ that each bond k divides the molecule into:

$$\langle R_g^2\rangle = \frac{b^2}{N^2}\sum_{k=1}^{N} N_1(k)[N - N_1(k)]. \tag{2.63}$$

The average value of this product is:

$$\langle N_1(N - N_1)\rangle = \frac{1}{N}\sum_{k=1}^{N} N_1(k)[N - N_1(k)]. \tag{2.64}$$

The **Kramers theorem** is expressed in terms of this average over all possible ways of dividing the molecule into two parts:

$$\langle R_g^2\rangle = \frac{b^2}{N}\langle N_1(N - N_1)\rangle. \tag{2.65}$$

This expression is valid for a linear polymer with the average evaluated by integration.

$$\begin{aligned}\langle N_1(N - N_1)\rangle &= \frac{1}{N}\int_0^N N_1(N - N_1)\,\mathrm{d}N_1 \\ &= \int_0^N N_1\,\mathrm{d}N_1 - \frac{1}{N}\int_0^N N_1^2\,\mathrm{d}N_1 \\ &= \frac{N^2}{2} - \frac{N^2}{3} = \frac{N^2}{6}.\end{aligned} \tag{2.66}$$

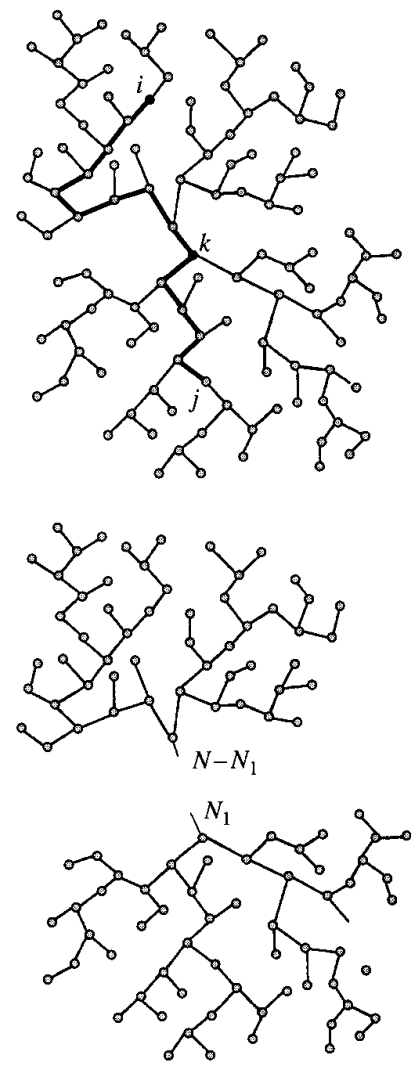

Fig. 2.7
The Kramers theorem effectively cuts a randomly branched polymer with N monomers into two parts, with N_1 and $N - N_1$ monomers.

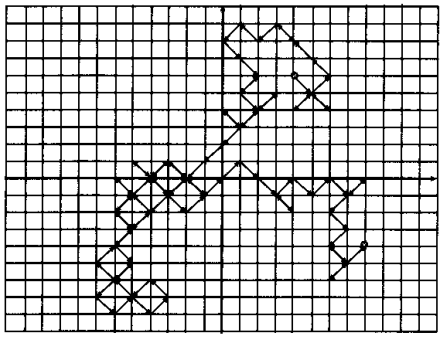

Fig. 2.8
A two-dimensional random walk on a square lattice. The direction of each step is randomly chosen from four possible diagonals.

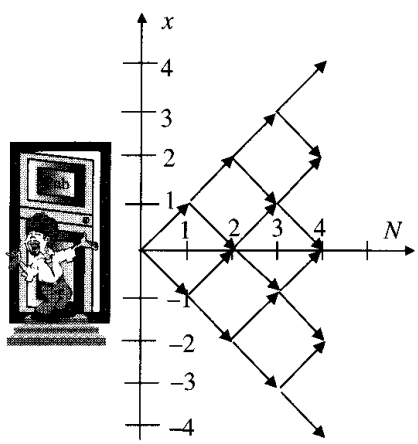

Fig. 2.9
A one-dimensional random walk of a drunk in an alley, showing all possible trajectories up to $N=4$ steps.

Table 2.5 The number of trajectories $W(N,x)$ for one-dimensional random walks of N steps that start at the origin and end at position x

	$N=1$	$N=2$	$N=3$	$N=4$
$x=-4$	0	0	0	1
$x=-3$	0	0	1	0
$x=-2$	0	1	0	4
$x=-1$	1	0	3	0
$x=0$	0	2	0	6
$x=1$	1	0	3	0
$x=2$	0	1	0	4
$x=3$	0	0	1	0
$x=4$	0	0	0	1

Substituting this average [Eq. (2.66)] into the Kramers theorem [Eq. (2.65)] recovers the classical result for the radius of gyration of an ideal linear chain [Eq. (2.54)]. In Section 6.4.6, we apply the Kramers theorem [Eq. (2.65)] to ideal randomly branched polymers. In this case the average is not only over different ways of dividing a molecule into two parts, but also over different branched molecules with the same degree of polymerization N.

2.5 Distribution of end-to-end vectors

A polydisperse collection of polymers can be described by an average molar mass (such as the number-average or weight-average discussed in Chapter 1). Much more information is contained in the whole molar mass distribution than in any of its moments or averages. Similarly, the average polymer conformation can be described by the mean-square end-to-end distance (or mean-square radius of gyration). Much more information is contained in the distribution of end-to-end vectors than in the mean-square end-to-end vector. In this section, we derive the distribution of end-to-end vectors for an ideal chain.

Every possible conformation of an ideal chain can be mapped onto a **random walk**. A particle making random steps defines a random walk. If the length of each step is constant and the direction of each step is independent of all previous steps, the trajectory of this random walk is one conformation of a freely jointed chain. Hence, random walk statistics and ideal chain statistics are similar.

Consider a particular random walk on a lattice with each step having independent Cartesian coordinates of either $+1$ or -1. The projection of this three-dimensional random walk onto each of the Cartesian coordinate axes is an independent one-dimensional random walk of unit step length (see Fig. 2.8 for an example of a two-dimensional projection). The fact that the one-dimensional components are independent of each other is an important property of any random walk (as well as any ideal polymer chain).

An example of a one-dimensional random walk is a drunk in a dark narrow alley. Let the drunk start at the doors of the pub at the origin of the one-dimensional coordinate system and make unit steps randomly up and down the alley. Figure 2.9 represents random wandering of the drunk up and down the alley as a function of the number of steps taken. Let $W(N,x)$ be the number of different possible trajectories for a drunk to get from the pub to the position x in N steps. For example, after the first step he could have reached either position $x=+1$ or $x=-1$, making $W(1,1)=W(1,-1)=1$. The numbers of different trajectories $W(N,x)$ for the first four steps of the drunk are shown in Table 2.5.

A general expression for $W(N,x)$ can be obtained in the following way. Any trajectory of our drunk consists of N_+ steps up the alley and N_- steps down the alley. The total number of steps made by the drunk is $N=N_++N_-$ and his final position is $x=N_+-N_-$. The numbers of steps up N_+ and down N_- the alley uniquely specify both the total number of steps N and the final position x. Therefore, the total number of trajectories $W(N,x)$ is

equal to the number of combinations of N_+ steps up and N_- steps down, that reach x in a total of N steps, which is a binomial coefficient:

$$W(N,x) = \frac{(N_+ + N_-)!}{N_+!N_-!} = \frac{N!}{[(N+x)/2]![(N-x)/2]!}. \tag{2.67}$$

The factorial is defined as $N! = 1 \cdot 2 \cdot 3 \cdot 4 \cdots N$.

The total number of N-step walks is 2^N because on each step the drunk has two possibilities, which are independent from step to step. All of these 2^N walks are equally likely (if there is no wind or stairway in the alley) and therefore, the probability to find the drunk at position x after N steps is $W(N,x)$ divided by 2^N:

$$\frac{W(N,x)}{2^N} = \frac{1}{2^N}\frac{N!}{[(N+x)/2]![(N-x)/2]!}. \tag{2.68}$$

This is an exact probability distribution for a one-dimensional random walk. However, it is not convenient to use for large N because of the difficulty of calculating factorials for large N (try your calculator for $N = 100$). For any N, the probability of finding the drunk is highest at the pub (at $x = 0$ for even N and at $x = \pm 1$ for odd N). This probability falls off very fast for large $|x|$ and it is therefore convenient to use the Gaussian approximation of the distribution function, valid for $x \ll N$, derived next.

First, take the natural logarithm of the distribution function:

$$\ln\left(\frac{W(N,x)}{2^N}\right) = -N \ln 2 + \ln(N!) - \ln\left(\frac{N+x}{2}\right)! - \ln\left(\frac{N-x}{2}\right)!. \tag{2.69}$$

Each of the last two terms can be rewritten using the definition of the factorial function:

$$\begin{aligned}\ln\left(\frac{N+x}{2}\right)! &= \ln\left[\left(\frac{N}{2}\right)!\left(\frac{N}{2}+1\right)\left(\frac{N}{2}+2\right)\cdots\left(\frac{N}{2}+\frac{x}{2}\right)\right] \\ &= \ln\left(\frac{N}{2}\right)! + \sum_{s=1}^{x/2} \ln\left(\frac{N}{2}+s\right),\end{aligned} \tag{2.70}$$

$$\ln\left(\frac{N-x}{2}\right)! = \ln\left(\frac{N}{2}\right)! - \sum_{s=1}^{x/2} \ln\left(\frac{N}{2}+1-s\right). \tag{2.71}$$

The logarithm of the probability distribution can now be rewritten as

$$\begin{aligned}\ln\left(\frac{W(N,x)}{2^N}\right) &= -N \ln 2 + \ln(N!) - \ln\left(\frac{N}{2}\right)! - \sum_{s=1}^{x/2} \ln\left(\frac{N}{2}+s\right) \\ &\quad - \ln\left(\frac{N}{2}\right)! + \sum_{s=1}^{x/2} \ln\left(\frac{N}{2}+1-s\right) \\ &= -N \ln 2 + \ln(N!) - 2\ln\left(\frac{N}{2}\right)! - \sum_{s=1}^{x/2} \ln\left(\frac{(N/2)+s}{(N/2)+1-s}\right).\end{aligned}$$

The logarithm in the last term can be expanded for $s \ll N/2$ up to a linear term ($\ln(1+y) \cong y$ for $|y| \ll 1$). This expansion is the essence of the Gaussian approximation.

$$\begin{aligned}\ln\left(\frac{(N/2)+s}{(N/2)+1-s}\right) &= \ln\left(\frac{1+(2s/N)}{1-(2s/N)+(2/N)}\right)\\ &= \ln\left(1+\frac{2s}{N}\right) - \ln\left(1-\frac{2s}{N}+\frac{2}{N}\right)\\ &\cong \frac{4s}{N} - \frac{2}{N}. \end{aligned} \tag{2.72}$$

The logarithm of the probability distribution can be simplified using this approximation.

$$\begin{aligned}\ln\left(\frac{W(N,x)}{2^N}\right) &\cong -N\ln 2 + \ln(N!) - 2\ln\left(\frac{N}{2}\right)! - \sum_{s=1}^{x/2}\left(\frac{4s}{N}-\frac{2}{N}\right)\\ &\cong -N\ln 2 + \ln(N!) - 2\ln\left(\frac{N}{2}\right)! - \frac{4}{N}\sum_{s=1}^{x/2} s + \frac{2}{N}\sum_{s=1}^{x/2} 1\\ &\cong -N\ln 2 + \ln(N!) - 2\ln\left(\frac{N}{2}\right)! - \frac{4}{N}\frac{(x/2)(x/2+1)}{2} + \frac{x}{N}\\ &\cong -N\ln 2 + \ln(N!) - 2\ln\left(\frac{N}{2}\right)! - \frac{x^2}{2N}. \end{aligned} \tag{2.73}$$

This gives the Gaussian approximation of the probability distribution:

$$\frac{W(N,x)}{2^N} \cong \frac{1}{2^N}\frac{N!}{(N/2)!(N/2)!}\exp\left(-\frac{x^2}{2N}\right). \tag{2.74}$$

Using Stirling's approximation of $N!$ for large N

$$N! \cong \sqrt{2\pi N}\left(\frac{N}{\mathrm{e}}\right)^N, \tag{2.75}$$

the coefficient in front of the exponential can be rewritten:

$$\frac{1}{2^N}\frac{N!}{(N/2)!(N/2)!} \cong \frac{1}{2^N}\frac{\sqrt{2\pi N}N^N\exp(-N)}{\left(\sqrt{\pi N}(N/2)^{N/2}\exp(-N/2)\right)^2} = \sqrt{\frac{2}{\pi N}}. \tag{2.76}$$

The final expression for the Gaussian approximation of the probability distribution is quite simple:

$$\frac{W(N,x)}{2^N} \cong \sqrt{\frac{2}{\pi N}}\exp\left(-\frac{x^2}{2N}\right). \tag{2.77}$$

Recall from Table 2.5 that $W(N,x)$ is non-zero only either for even or odd x (depending on whether N is even or odd). Therefore, the spacing between non-zero values of $W(N,x)$ is equal to 2 along the x axis. The **probability**

distribution function $P_{1d}(N, x)$ is defined as the probability $P(N, x)\,dx$ that the drunk will be found in the interval dx along the x axis. Thus, the probability distribution function differs from Eq. (2.77) by a factor of 2:

$$P_{1d}(N, x) = \frac{1}{\sqrt{2\pi N}} \exp\left(-\frac{x^2}{2N}\right). \tag{2.78}$$

The square of the typical distance of the drunk from the pub after N steps is determined from the mean-square displacement averaged over all the walks the drunk makes day after day:

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P_{1d}(N, x)\,dx = \frac{1}{\sqrt{2\pi N}} \int_{-\infty}^{\infty} x^2 \exp\left(-\frac{x^2}{2N}\right) dx = N. \tag{2.79}$$

Therefore, the probability distribution function can be rewritten in terms of this mean-square displacement:

$$P_{1d}(N, x) = \frac{1}{\sqrt{2\pi \langle x^2 \rangle}} \exp\left(-\frac{x^2}{2\langle x^2 \rangle}\right). \tag{2.80}$$

This function has a maximum at $x = 0$ and decays fast for distances larger than the root-mean-square displacement $x > \sqrt{\langle x^2 \rangle}$ as can be seen from Fig. 2.10.

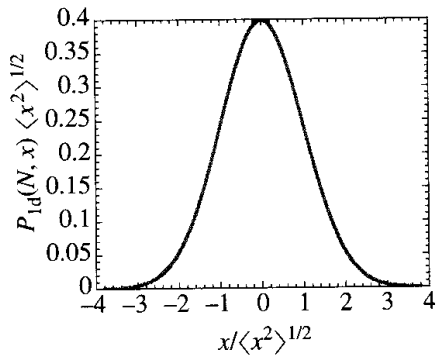

Fig. 2.10
Normalized one-dimensional Gaussian probability distribution function for occupying position x after random N steps from the origin ($x = 0$).

This probability distribution function for the displacement of a one-dimensional random walk can be easily generalized to three-dimensional random walks. The probability of a walk, starting at the origin of the coordinate system, to end after N steps, each of size b, within a volume $dR_x\,dR_y\,dR_z$ of the point with displacement vector $\vec{R}$ is $P_{3d}(N, \vec{R})\,dR_x\,dR_y\,dR_z$ (see Fig. 2.11). Since the three components of a three-dimensional random walk along the three Cartesian coordinates are independent of each other, the three-dimensional probability distribution function is a product of the three one-dimensional distribution functions:

$$P_{3d}(N, \vec{R})\,dR_x\,dR_y\,dR_z = P_{1d}(N, R_x)\,dR_x P_{1d}(N, R_y)\,dR_y P_{1d}(N, R_z)\,dR_z. \tag{2.81}$$

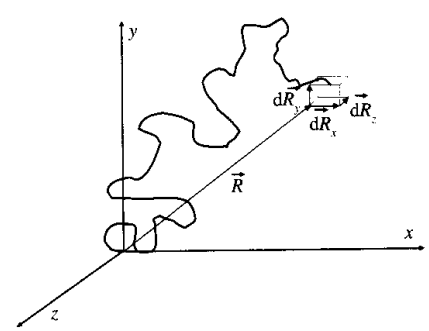

Fig. 2.11
One conformation of an ideal chain with one end at the origin and the other end within volume $dR_x\,dR_y\,dR_z$ of position $\vec{R}$.

The mean-square displacement of a random walk from the origin is equal to the mean-square end-to-end vector of a freely jointed chain with the number of monomers N equal to the number of steps of the walk and the monomer length b equal to the step size $\langle \vec{R}^2 \rangle = Nb^2$. This mean-square displacement is composed of three mean-square displacements of the three independent one-dimensional walks:

$$\langle \vec{R}^2 \rangle = \langle R_x^2 \rangle + \langle R_y^2 \rangle + \langle R_z^2 \rangle = Nb^2. \tag{2.82}$$

Since each of the three Cartesian axes are equivalent, the mean-square displacement along each of them must be one-third of the total:

$$\langle R_x^2 \rangle = \langle R_y^2 \rangle = \langle R_z^2 \rangle = \frac{Nb^2}{3}. \tag{2.83}$$

The one-dimensional probability distribution function for the components of a random walk along each of these three axes can be obtained by substituting these mean-square displacements into Eq. (2.80)

$$P_{1d}(N, R_x) = \frac{1}{\sqrt{2\pi\langle R_x^2\rangle}} \exp\left(-\frac{R_x^2}{2\langle R_x^2\rangle}\right)$$
$$= \sqrt{\frac{3}{2\pi N b^2}} \exp\left(-\frac{3R_x^2}{2Nb^2}\right). \tag{2.84}$$

The probability distribution function for the end-to-end vector $\vec{R}$ of an ideal linear chain of N monomers is the product of the three independent distribution functions [Eq. (2.81)]:

$$P_{3d}(N, \vec{R}) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} \exp\left(-\frac{3(R_x^2 + R_y^2 + R_z^2)}{2Nb^2}\right)$$
$$= \left(\frac{3}{2\pi N b^2}\right)^{3/2} \exp\left(-\frac{3\vec{R}^2}{2Nb^2}\right). \tag{2.85}$$

As a function of each Cartesian component R_i of the end-to-end vector $\vec{R}$, this probability distribution function looks the same as sketched in Fig. 2.10. The average of each component is $\langle R_i\rangle = 0$. As a function of the end-to-end distance $R = |\vec{R}|$ this probability distribution can be rewritten in the spherical coordinate system:

$$P_{3d}(N, R) 4\pi R^2 \, dR = 4\pi \left(\frac{3}{2\pi N b^2}\right)^{3/2} \exp\left(-\frac{3R^2}{2Nb^2}\right) R^2 \, dR. \tag{2.86}$$

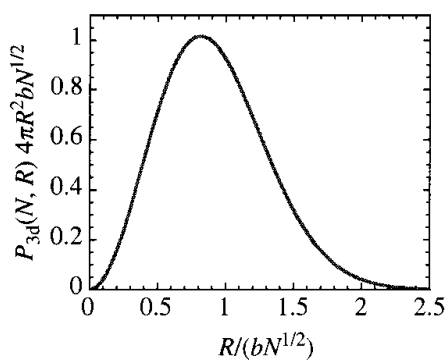

Fig. 2.12
Normalized distribution function of end-to-end distances for an ideal linear chain.

The probability distribution for the end-to-end distance R is the probability for the end-to-end vector $\vec{R}$ to be in the spherical shell with radius between R and $R + dR$. This probability of the end-to-end distance [Eq. (2.86)] is shown in Fig. 2.12. The Gaussian approximation is valid only for end-to-end vectors much shorter than the maximum extension of the chain (for $|\vec{R}| \ll R_{max} = Nb$). For $|\vec{R}| > Nb$, Eq. (2.85) predicts finite (though exponentially small) probability, which is physically unreasonable. For real chains $P_{3d}(N, R) \equiv 0$ for $R > Nb$ and this strong stretching is treated properly in Section 2.6.2.

2.6 Free energy of an ideal chain

The **entropy** S is the product of the Boltzmann constant k and the logarithm of the number of states Ω:

$$S = k \ln \Omega. \tag{2.87}$$

Denote $\Omega(N, \vec{R})$ as the number of conformations of a freely jointed chain of N monomers with end-to-end vector $\vec{R}$. The entropy is then a function

of N and $\vec{R}$:

$$S\left(N, \vec{R}\right) = k \ln \Omega\left(N, \vec{R}\right). \tag{2.88}$$

The probability distribution function is the fraction of all conformations that actually have an end-to-end vector $\vec{R}$ between $\vec{R}$ and $\vec{R} + \mathrm{d}\vec{R}$:

$$P_{3\mathrm{d}}\left(N, \vec{R}\right) = \frac{\Omega\left(N, \vec{R}\right)}{\int \Omega\left(N, \vec{R}\right) \mathrm{d}\vec{R}}. \tag{2.89}$$

The entropy of an ideal chain with N monomers and end-to-end vector $\vec{R}$ is thus related to the probability distribution function:

$$S\left(N, \vec{R}\right) = k \ln P_{3\mathrm{d}}\left(N, \vec{R}\right) + k \ln\left[\int \Omega\left(N, \vec{R}\right) \mathrm{d}\vec{R}\right]. \tag{2.90}$$

Equation (2.85) for the probability distribution function determines the entropy:

$$S\left(N, \vec{R}\right) = -\frac{3}{2} k \frac{\vec{R}^2}{Nb^2} + \frac{3}{2} k \ln\left(\frac{3}{2\pi N b^2}\right) + k \ln\left[\int \Omega\left(N, \vec{R}\right) \mathrm{d}\vec{R}\right]. \tag{2.91}$$

The last two terms of Eq. (2.91) depend only on the number of monomers N, but not on the end-to-end vector $\vec{R}$ and can be denoted by $S(N, 0)$:

$$S\left(N, \vec{R}\right) = -\frac{3}{2} k \frac{\vec{R}^2}{Nb^2} + S(N, 0). \tag{2.92}$$

The **Helmholtz free energy** of the chain F is the energy U minus the product of absolute temperature T and entropy S:

$$F\left(N, \vec{R}\right) = U\left(N, \vec{R}\right) - TS\left(N, \vec{R}\right). \tag{2.93}$$

The energy of an ideal chain $U(N, \vec{R})$ is independent of the end-to-end vector $\vec{R}$, since the monomers of the ideal chain have no interaction energy.[3] The free energy can be written as

$$F\left(N, \vec{R}\right) = \frac{3}{2} kT \frac{\vec{R}^2}{Nb^2} + F(N, 0), \tag{2.94}$$

where $F(N, 0) = U(N, 0) - TS(N, 0)$ is the free energy of the chain with both ends at the same point. As was demonstrated above, the largest number of chain conformations correspond to zero end-to-end vector. The number of conformations decreases with increasing end-to-end vector, leading to the decrease of polymer entropy and increase of its free energy. The free energy of an ideal chain $F(N, \vec{R})$ increases quadratically with the magnitude of the end-to-end vector $\vec{R}$. This implies that the entropic elasticity of an ideal

[3] The ideal chain never has long-range interactions, but short-range interactions are possible, and their consequences are discussed in problem 7.19.

chain satisfies Hooke's law. To hold the chain at a fixed end-to-end vector $\vec{R}$, would require equal and opposite forces acting on the chain ends that are proportional to $\vec{R}$. For example, to separate the chain ends by distance R_x in x direction, requires force f_x:

$$f_x = \frac{\partial F\left(N, \vec{R}\right)}{\partial R_x} = \frac{3kT}{Nb^2} R_x. \tag{2.95}$$

The force to hold chain ends separated by a general vector $\vec{R}$ is linear in $\vec{R}$, like a simple elastic spring:

$$\vec{f} = \frac{3kT}{Nb^2} \vec{R}. \tag{2.96}$$

The coefficient of proportionality $3kT/(Nb^2)$ is the **entropic spring constant** of an ideal chain. It is easier to stretch polymers with larger numbers of monomers N, larger monomer size b, and at *lower* temperature T. The fact that the spring constant is proportional to temperature is a signature of entropic elasticity. The entropic nature of elasticity in polymers distinguishes them from other materials. Metals and ceramics become softer as temperature is raised because their deformation requires displacing atoms from their preferred positions (energetic instead of entropic elasticity).

The force increases as the chain is stretched because there are fewer possible conformations for larger end-to-end distances. The linear entropic spring result for the stretching of an ideal chain [Eq. (2.96)] is extremely important for our subsequent discussions of rubber elasticity and polymer dynamics. This linear dependence [Hooke's law for an ideal chain, Eq. (2.96)] is due to the Gaussian approximation, valid only for $|\vec{R}| \ll R_{\max} = Nb$. If the chain is stretched to the point where its end-to-end vector approaches the maximum chain extension $|\vec{R}| \leq R_{\max}$, the dependence becomes strongly non-linear, with the force diverging at $|\vec{R}| = R_{\max}$, as will be discussed in Section 2.6.2.

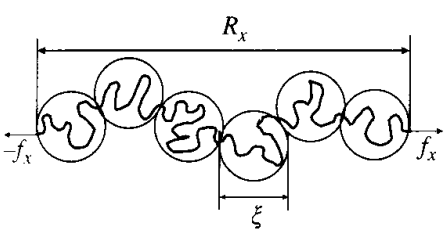

Fig. 2.13
An elongated chain is only stretched on its largest length scales. Inside the tension blob, the conformation of the chain is essentially unperturbed by the stretch.

2.6.1 Scaling argument for chain stretching

The linear relation between force and end-to-end distance can also be obtained by a very simple scaling argument. The key to understanding the scaling description is to recognize that most of the conformational entropy of the chain arises from local conformational freedom on the smallest length scales. For this reason, the random walks that happen to have end-to-end distance $R > bN^{1/2}$ can be visualized as a sequential array of smaller sections of size ξ that are essentially unperturbed by the stretch, as shown in Fig. 2.13.

The stretched polymer is subdivided into sections of g monomers each. We assume that these sections are almost undeformed so that the mean-square projection of the end-to-end vector of these sections of g monomers onto any of the coordinate axes obeys ideal chain statistics [Eq. (2.83)]:

$$\xi^2 \approx b^2 g. \tag{2.97}$$

There are N/g such sections and in the direction of elongation they are assumed to be arranged sequentially:

$$R_x \approx \xi \frac{N}{g} \approx \frac{Nb^2}{\xi}. \tag{2.98}$$

This can be solved for the size ξ of the unperturbed sections and the number of monomers g in each section:

$$\xi \approx \frac{Nb^2}{R_x}, \tag{2.99}$$

$$g \approx \frac{N^2 b^2}{R_x^2}. \tag{2.100}$$

The number of monomers g and the size ξ of these sections were specially chosen so that the polymer conformation changes from that of a random walk on smaller size scales to that of an elongated chain on larger length scales. Such sections of stretched polymers are called **tension blobs**. Being extended on only its largest length scales allows the chain to maximize its conformational entropy.

The physical meaning of a tension blob is the length scale ξ at which external tension changes the chain conformation from almost undeformed on length scales smaller than ξ to extended on length scales larger than ξ. The trajectory of the stretched chain (Fig. 2.13) shows that each tension blob is forced to go in a particular direction along the x axis (rather than in a random direction as in an unperturbed chain). Therefore one degree of freedom is restricted per tension blob and the free energy of the chain increases by kT per blob:[4]

$$F \approx kT \frac{N}{g} \approx kT \frac{R_x^2}{Nb^2}. \tag{2.101}$$

In comparing Eqs (2.94) and (2.101), we see that the scaling method gets the correct result within a prefactor of order unity. This is the character of all scaling calculations: they provide a simple means to extract the essential physics but do not properly determine numerical coefficients.

Equation (2.101) is the first of many instances where the free energy stored in the chain is of the order of kT per blob, because the blobs generally describe a length scale at which the conformation of the chain changes and is the elementary unit of deformation. In the case of stretching, the free energy is F/N per monomer. On length scales smaller than the tension blob, the thermal energy kT that randomizes the conformation is larger than the cumulative stretching energy, and the conformation is essentially unperturbed. On length scales larger than the tension blob, the cumulative stretching energy is larger than kT, and the ideal chain gets strongly stretched (see Fig. 2.13). Similar arguments apply to other problems involving conformational changes beyond a particular length scale, making the free energy of order kT per blob quite general.

[4] This is the consequence of the equipartition theorem.

The force needed to stretch the chain is given by the derivative of the free energy:

$$f_x = \frac{\partial F}{\partial R_x} \approx kT\frac{R_x}{Nb^2} \approx \frac{kT}{\xi}. \tag{2.102}$$

The tension blobs provide a simple framework for visualizing the chain stretching (Fig. 2.13) and provide simple relations for calculating the stretching force and free energy. They define the length scale at which elastic energy is of order kT. Since the force has dimensions of energy divided by length, Eq. (2.102) immediately follows from a dimensional analysis with length scale of tension blob ξ corresponding to kT of stored elastic energy.

The stretching along the x axis, shown in Fig. 2.13, makes the stretched conformation of an ideal chain a **directed random walk** of tension blobs. This conformation is sequential in the x direction, but the y and z directions have the usual random walk statistics that are unaffected by the stretching. The mean-square components of the end-to-end vector orthogonal to the stretching direction are obtained from one-dimensional random walks of N/g sections of step length ξ:

$$\langle R_y^2\rangle = \langle R_z^2\rangle \approx \xi^2\frac{N}{g} \approx Nb^2. \tag{2.103}$$

The linear relation between force f_x and end-to-end distance R_x (Hooke's law) is valid as long as there are many Kuhn monomers in each tension blob. As the end-to-end distance R_x approaches a significant fraction of its maximal value $R_{\max}$, a deviation from Hooke's law is expected. Note that the Gaussian approximation assumes $R_x \ll R_{\max}$ and always leads to Hooke's Law. Below we derive the non-linear relation between force and elongation for strongly stretched chains. The limit of the linear regime corresponds to a force of the order of

$$\frac{kT}{b} \cong \frac{1.38\times 10^{-23}\,\mathrm{J\,K^{-1}} \times 295\,\mathrm{K}}{1\times 10^{-9}\,\mathrm{m}} \cong 4\times 10^{-12}\,\mathrm{N} \tag{2.104}$$

for a chain with Kuhn length $b = 1$ nm at room temperature. Stiffer chains with larger Kuhn length get nearly fully stretched at weaker extension forces. For double-helical DNA with Kuhn length $b \cong 100$ nm (persistence length $l_p \cong 50$ nm) the force corresponding to the linear response limit is 100 times smaller (4×10^{-14} N).

2.6.2 Langevin dependence of elongation on force

Consider a freely jointed chain of N bonds subject to a constant elongational force f applied to its ends along the z axis. An example could be a chain with two opposite charges $+q$ and $-q$ at its ends in a constant electric field $\vec{E}$ applied along the z axis as sketched in Fig. 2.14. If the direct

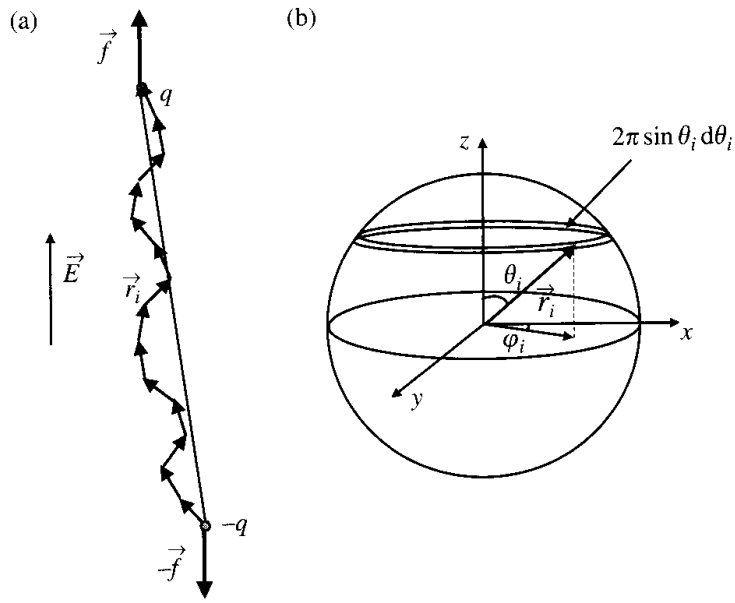

Fig. 2.14
(a) Freely jointed chain elongated by a pair of forces applied to its ends. (b) Spherical coordinate system for orientation of a bond.

Coulomb interaction between the charges is ignored, there is a constant force $\vec{f} = q\vec{E}$ acting along the z axis on the positive charge and an opposite force $-\vec{f}$ acting on the negative charge. Different chain conformations are no longer equally likely, because they correspond to different energy of the chain in the external electric field. The energy of the chain is proportional to the projection of the end-to-end vector on the direction of the field:

$$U = -q\vec{E} \cdot \vec{R} = -\vec{f} \cdot \vec{R} = -fR_z. \tag{2.105}$$

This energy is equal to the work done by the chain upon separation of the charges by vector $\vec{R}$ in an external electric field $\vec{E}$. The direction of the end-to-end vector $\vec{R}$ of the chain is chosen from the negative to the positive charge at its ends. Displacement of the positive charge down the field with respect to the negative charge, lowers the electrostatic energy of the chain and corresponds to a more favorable conformation. Thus, different chain conformations have different statistical Boltzmann factors $\exp(-U/kT)$ that depend on their corresponding energy U [Eq. (2.105)].

The sum of the Boltzmann factors over all possible conformations of the chain is called the **partition function**:

$$Z = \sum_{\text{states}} \exp\left(-\frac{U}{kT}\right) = \sum_{\text{states}} \exp\left(\frac{fR_z}{kT}\right). \tag{2.106}$$

The partition function is useful because we will calculate the free energy from it in Eq. (2.111). States with higher energy make a smaller contribution to the partition function because their Boltzmann factor determines that those states are less likely.

Different conformations in the freely jointed chain model correspond to different sets of orientations of bond vectors $\vec{r}_i$ in space [see Fig. 2.14(a)]. The orientation of each bond vector $\vec{r}_i$ can be defined by the two angles of the spherical coordinate system θ_i and φ_i [Fig. 2.14(b)]. Therefore, the sum

over all possible conformations of a freely jointed chain corresponds to the integral over all possible orientations of all bond vectors of the chain:

$$Z = \sum_{\text{states}} \exp\left(\frac{fR_z}{kT}\right) = \int \exp\left(\frac{fR_z}{kT}\right) \prod_{i=1}^{N} \sin\theta_i \, \mathrm{d}\theta_i \, \mathrm{d}\varphi_i. \tag{2.107}$$

The notation $\prod_{i=1}^{N}$ denotes the product of N terms. The z component of the end-to-end vector can be represented as the sum of the projections of all bond vectors onto the z axis:

$$R_z = \sum_{i=1}^{N} b \cos\theta_i. \tag{2.108}$$

Therefore, the partition function [Eq. (2.107)] becomes a product of N identical integrals:

$$\begin{aligned} Z(T,f,N) &= \int \exp\left(\frac{fb}{kT}\sum_{i=1}^{N}\cos\theta_i\right) \prod_{i=1}^{N} \sin\theta_i \, \mathrm{d}\theta_i \, \mathrm{d}\varphi_i \\ &= \left[\int_0^{\pi} 2\pi \sin\theta_i \exp\left(\frac{fb}{kT}\cos\theta_i\right) \mathrm{d}\theta_i\right]^N \\ &= \left[\frac{2\pi}{fb/(kT)}\left[\exp\left(\frac{fb}{kT}\right) - \exp\left(-\frac{fb}{kT}\right)\right]\right]^N \qquad (2.109) \\ &= \left[\frac{4\pi \sinh(fb/(kT))}{fb/(kT)}\right]^N. \qquad (2.110) \end{aligned}$$

The Gibbs free energy G can be directly calculated from the partition function:[5]

$$\begin{aligned} G(T,f,N) &= -kT \ln Z(T,f,N) \\ &= -kTN\left[\ln\left(4\pi \sinh\left(\frac{fb}{kT}\right)\right) - \ln\left(\frac{fb}{kT}\right)\right]. \end{aligned} \tag{2.111}$$

The average end-to-end distance corresponding to a given force can be obtained as the derivative of the free energy:

$$\langle R\rangle = -\frac{\partial G}{\partial f} = bN\left[\coth\left(\frac{fb}{kT}\right) - \frac{1}{fb/(kT)}\right]. \tag{2.112}$$

The expression in the square brackets of Eq. (2.112) is called the **Langevin function**:

$$\mathcal{L}(\beta) = \coth(\beta) - \frac{1}{\beta}. \tag{2.113}$$

The Langevin function relates average chain elongation $\langle R\rangle/R_{\max}$ and normalized extensional force $\beta = fb/(kT)$ for a freely jointed chain, as sketched in Fig. 2.15.

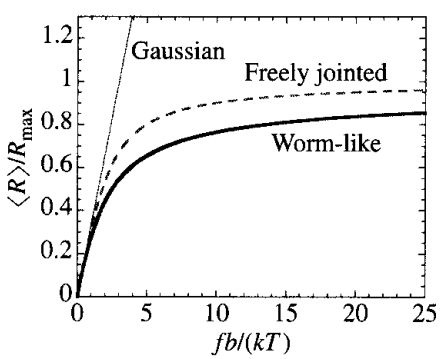

Fig. 2.15
Average end-to-end distance as a function of stretching force for a Gaussian chain [Eq. (2.95), thin line], a freely jointed chain [Langevin function, Eq. (2.112), dashed line], and a worm-like chain [Eq. (2.119), thick line].

[5] The Gibbs free energy is used here because the ensemble of chains corresponds to constant force f, not constant end-to-end distance R (analogous to the isothermal–isobaric ensemble, which has constant pressure instead of constant volume).

For small relative elongations ($\langle R\rangle \ll R_{\max} = bN$) the dependence is approximately linear,

$$\mathcal{L}(\beta) \cong \frac{\beta}{3} \quad \text{for } \beta \ll 1, \tag{2.114}$$

and follows Hooke's law derived above [Eq. (2.96)] $\langle R\rangle/(bN) = fb/(3kT)$. For larger relative elongations, the Langevin function significantly deviates from linear dependence and saturates at unity (see Fig. 2.15). For large extensional force $f \gg kT/b$, the Langevin function has another simple limit:

$$\mathcal{L}(\beta) \cong 1 - \frac{1}{\beta} \quad \text{for } \beta \gg 1. \tag{2.115}$$

This means that the extension for strong stretching has a simple form

$$\frac{\langle R\rangle}{R_{\max}} \cong 1 - \frac{kT}{fb},$$

where $R_{\max} = Nb$. The extensional force of the equivalent freely jointed chain diverges reciprocally proportional to $R_{\max} - \langle R\rangle$:

$$\frac{fb}{kT} \cong \frac{R_{\max}}{R_{\max} - \langle R\rangle} \quad \text{for } 1 - \frac{\langle R\rangle}{R_{\max}} \ll 1. \tag{2.116}$$

In the case of the worm-like chain model (Section 2.3.2), the extensional force diverges reciprocally proportional to the square of $R_{\max} - \langle R\rangle$:

$$\frac{fb}{kT} \cong \frac{1}{2}\left(\frac{R_{\max}}{R_{\max} - \langle R\rangle}\right)^2 \quad \text{for } 1 - \frac{\langle R\rangle}{R_{\max}} \ll 1. \tag{2.117}$$

The differences between divergences of force near maximum extension [Eqs (2.116) and (2.117)] are due to bending modes on length scales shorter than Kuhn length b. These modes do not exist in freely jointed chains because sections of length b are assumed to be absolutely rigid. In the worm-like chain model these bending modes with wavelength $\xi \ll b$ lead to much stronger divergence of the force [Eq. (2.117)].

At small relative extensions ($\langle R\rangle \ll R_{\max}$) worm-like chains behave as Hookean springs:

$$\frac{fb}{kT} \cong \frac{3\langle R\rangle}{R_{\max}} \quad \text{for } \langle R\rangle \ll R_{\max}. \tag{2.118}$$

There is no simple analytical solution for the worm-like chain model at all extensions, but there is an approximate expression valid both for small and for large relative extensions:[6]

$$\frac{fb}{kT} \cong \frac{2\langle R\rangle}{R_{\max}} + \frac{1}{2}\left(\frac{R_{\max}}{R_{\max} - \langle R\rangle}\right)^2 - \frac{1}{2}. \tag{2.119}$$

[6] J. F. Marko and E. D. Siggia, *Macromolecules* **28**, 8759 (1995).

Strong deviations from linear elasticity have been measured in polymer networks at large elongation (see Chapter 7). Optical tweezers and atomic force microscopy have been used to measure the dependence of the force applied to the ends of isolated chains on their elongation. In the optical tweezer experiments, beads were attached to the ends of long DNA segments. DNA is a biopolymer that exists as a double-stranded helix. Such stiff chains are best described by the worm-like chain model. The chain length of DNA is typically described in terms of the number of base pairs along the helix. The positions of the beads at the ends of DNA chains were manipulated by a focused laser beam (hence the name 'optical tweezers'). The force exerted on the chain ends was measured by the calibrated relative displacement of the beads with respect to the optical traps. In another type of nano-manipulation experiment a 97 kilobase λ-DNA dimer was chemically attached by one of its ends to a glass slide and by the other end to a small (3 μm) magnetic bead. The DNA was stretched by applying a known magnetic and hydrodynamic force to the bead. The stretching was measured by observing the position of the bead in an optical microscope. The extension of DNA as a function of applied force is compared with predictions of freely jointed and worm-like chain models in Fig. 2.16. The worm-like chain model is in excellent agreement with the experimental data.

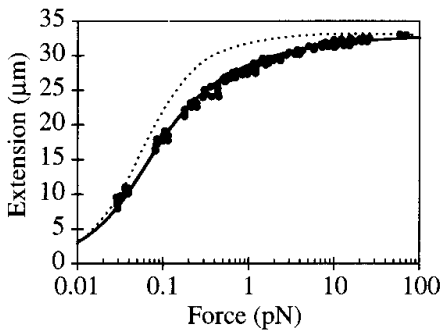

Fig. 2.16
Comparison of experimental force for 97 kilobase λ-DNA dimers with the worm-like chain model [solid curve is Eq. (2.119) with $R_{max} = 33$ μm and $b = 100$ nm]. The dotted curve corresponds to the Langevin function of the freely jointed chain model [Eq. (2.112)]. Data are from R. H. Austin *et al.*, *Phys. Today*, Feb. 1997, p. 32.

2.7 Pair correlations of an ideal chain

Consider a monomer of an ideal polymer trying to reach fellow monomers of the same chain via a CB radio (see Fig. 2.17). The number of monomers it can call depends on the range r of its transmitter. It can contact any monomer within the sphere of radius r of itself. The number of monomers m that can be reached via a CB radio with range r is given by random walk statistics:

$$m \approx \left(\frac{r}{b}\right)^2. \tag{2.120}$$

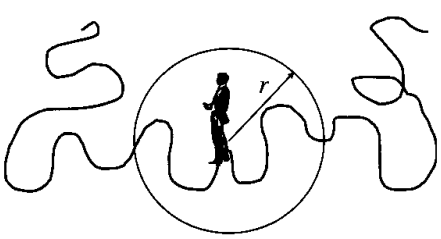

Fig. 2.17
A monomer can only reach other monomers with its CB radio if they are within the range of the radio.

The number density of these monomers within the volume r^3 is m/r^3. The probability of finding a monomer in a unit volume at a distance r from a given monomer is called the **pair correlation function** $g(r)$. It can be approximated by the average number density within the volume r^3:

$$g(r) \approx \frac{m}{r^3} \approx \frac{1}{rb^2}. \tag{2.121}$$

The exact calculation of the pair correlation function of an ideal chain leads to an additional factor $3/\pi$:

$$g(r) = \frac{3}{\pi r b^2}. \tag{2.122}$$

Note that the pair correlation function decreases with increasing distance r. It is less likely to find a monomer belonging to the chain further away from

a given monomer because the average number density of monomers within the sphere of radius r decreases. Large polymer coils are almost empty.

To illustrate this concept, divide the cube of size R, containing an ideal polymer with N monomers of size b and end-to-end distance $R = bN^{1/2}$, into smaller cubes of size r (Fig. 2.18). There will be $(R/r)^3$ such smaller cubes. But only $(R/r)^2$ of these smaller cubes contain monomers of the chain. The average number of monomers in each of these occupied smaller cubes is $m \approx (r/b)^2$. The remaining $(R/r)^3 - (R/r)^2$ smaller cubes are empty. The local density of monomers strongly fluctuates from cell to cell. There are holes of all sizes inside a polymer chain.

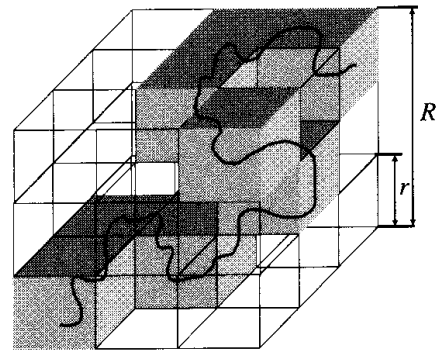

Fig. 2.18
Fractal nature of an ideal chain.

This description is a manifestation of the self-similarity (fractal nature) of polymers, discussed in Section 1.4. The fractal nature of ideal chains leads to the power law dependence of the pair correlation function $g(r)$ on distance r. This treatment for the ideal chain can be easily generalized to a linear chain with any fractal dimension $\mathcal{D}$. The number of monomers within range r is $m \sim r^{\mathcal{D}}$. We use the proportionality sign '$\sim$' if the dimensional coefficient (in the particular case above $\approx 1/b^{\mathcal{D}}$) is dropped from the relation. The pair correlation function is still proportional to the ratio of m and r^3:

$$g(r) \approx \frac{m}{r^3} \sim r^{\mathcal{D}-3}. \tag{2.123}$$

Hence, Eq. (2.121) is a special case of this result, with $\mathcal{D} = 2$ for an ideal chain. The fractal dimension of a rod polymer is $\mathcal{D} = 1$ and the pair correlation function is $g(r) \sim r^{-2}$.

2.8 Measurement of size by scattering

Polymer conformations are studied by various scattering experiments (light, small-angle X-ray and neutron scattering). These techniques are based on the contrast between the polymer and the surrounding media (solvent in the case of polymer solutions and other polymers in the case of polymer melts or blends). The contrast in light scattering arises from differences in refractive index between polymer and solvent, and the scattered intensity is proportional to the square of the refractive index increment $\mathrm{d}n/\mathrm{d}c$ [see Eq. (1.86)].

While neutron sources are not available in most laboratories, small-angle neutron scattering (SANS) has become a routine characterization method for polymer research using large-scale national and multinational facilities. To obtain the contrast needed for neutron scattering, some of the chains in a polymer melt have their hydrogen atoms replaced by deuterium. In a polymer solution, the solvent is often deuterated. This deuterium labelling appears to not alter the conformations of polymers.

2.8.1 Scattering wavevector

Consider an incident laser beam with wavelength λ illuminating a polymer sample, represented by the large circle in Fig. 2.19, along the direction with

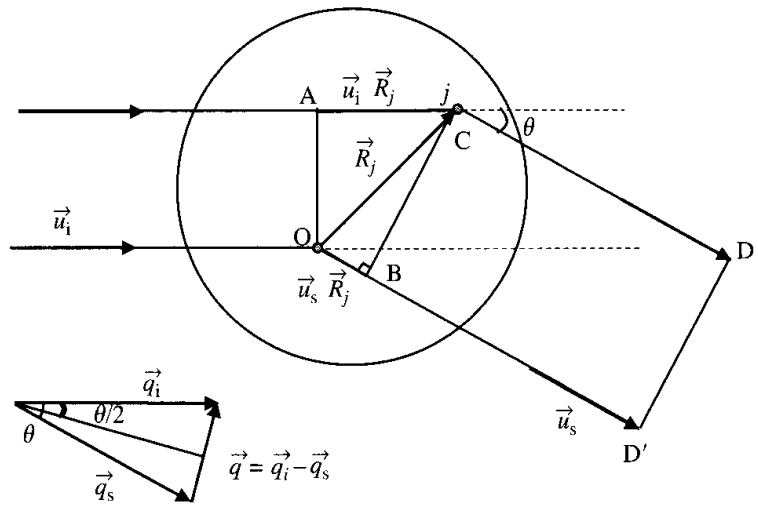

Fig. 2.19
Radiation scattered through angle θ from two distinct parts of the sample.

unit vector $\vec{u}_i$. This incident beam can be characterized by the **incident wavevector**:

$$\vec{q}_i \equiv \frac{2\pi n}{\lambda}\vec{u}_i, \tag{2.124}$$

where n is the refractive index of the solution. The incident light is scattered through angle θ and leaves the sample along the direction with unit vector $\vec{u}_s$. The scattered beam is characterized by the **scattered wavevector**:

$$\vec{q}_s \equiv \frac{2\pi n}{\lambda}\vec{u}_s. \tag{2.125}$$

The incident beam is coherent, meaning that all photons are in-phase. When the incident beam enters the sample, monomers absorb the radiation and re-emit it in all directions. The difference in optical paths between the light scattered by different monomers makes the scattered beam incoherent, meaning that the scattered photons are no longer in-phase.[7] In the example sketched in Fig. 2.19, the difference in optical paths of the radiation scattered by the monomer j at position $\vec{R}_j$ (at point C) and by the monomer at the origin O is easily calculated:

$$\mathrm{AC} + \mathrm{CD} - \mathrm{OD}' = \mathrm{AC} - \mathrm{OB}. \tag{2.126}$$

The section AC is the projection of the vector $\vec{R}_j$ onto the incident direction and has length $\vec{u}_i \cdot \vec{R}_j$. The section OB is the projection of the vector $\vec{R}_j$ onto the scattered direction and has length $\vec{u}_s \cdot \vec{R}_j$. Thus, the difference in the optical paths can be written in terms of these vectors:

$$\mathrm{AC} - \mathrm{OB} = \vec{u}_i \cdot \vec{R}_j - \vec{u}_s \cdot \vec{R}_j = (\vec{u}_i - \vec{u}_s) \cdot \vec{R}_j. \tag{2.127}$$

This difference in optical paths results in the phase difference φ_j, which is $2\pi n/\lambda$ times the optical path difference [see Eq. (1.77) with λ replaced by the wavelength in the dielectric medium λ/n].

$$\varphi_j = \frac{2\pi n}{\lambda}(\vec{u}_i - \vec{u}_s) \cdot \vec{R}_j = (\vec{q}_i - \vec{q}_s) \cdot \vec{R}_j = \vec{q} \cdot \vec{R}_j. \tag{2.128}$$

[7] It is assumed that there is no multiple scattering, although this is not always a valid assumption.

The **scattering wavevector** $\vec{q}$ is defined as the difference of the incident and scattered wavevectors:

$$\vec{q} \equiv \vec{q}_{\mathrm{i}} - \vec{q}_{\mathrm{s}}. \tag{2.129}$$

From their definitions in Eqs (2.124) and (2.125), the magnitudes of the incident and scattered wavevectors are the same:

$$|\vec{q}_{\mathrm{i}}| = |\vec{q}_{\mathrm{s}}| = \frac{2\pi n}{\lambda}. \tag{2.130}$$

The isosceles triangle of wavevectors in Fig. 2.19 shows that half of the magnitude of the scattering wavevector is equal to the magnitude of wavevectors $\vec{q}_{\mathrm{i}}$ or $\vec{q}_{\mathrm{s}}$ times the sine of half the angle θ between them:

$$q \equiv |\vec{q}| = 2|\vec{q}_{\mathrm{i}}| \sin\left(\frac{\theta}{2}\right) = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right). \tag{2.131}$$

2.8.2 Form factor

We concentrate here on light scattering, but similar results are valid for small-angle X-ray and neutron scattering. We describe scattering from a single molecule, assuming that the solution is dilute, which is the relevant regime for determining the size and shape of individual coils.

The electric field of light scattered by the jth segment is

$$E_j = E_{\mathrm{i}} A \cos(2\pi\nu t - \varphi_j), \tag{2.132}$$

where φ_j is the phase difference [(Eq. (2.128)], ν is the frequency, E_{i} is the amplitude of the incident electric field [Eq. (1.77)] and the coefficient A contains the factors such as polarizability α, the distance r to the detector, the wavelength of light λ, etc. [see Eq. (1.81)]. Summing over the N monomers gives the electric field scattered by an isolated polymer coil:

$$E_{\mathrm{s}} = E_{\mathrm{i}} \sum_{j=1}^{N} A \cos(2\pi\nu t - \varphi_j). \tag{2.133}$$

The intensity of scattered light is the energy of radiation that falls onto a unit area per unit time. It is proportional to the square of the electric field averaged over one oscillation period $1/\nu$:

$$\begin{aligned} I_{\mathrm{s}} &= 2I_{\mathrm{i}}A^2\nu \int_0^{1/\nu} \left[\sum_{j=1}^{N} \cos(2\pi\nu t - \varphi_j)\right]^2 \mathrm{d}t \\ &= 2I_{\mathrm{i}}A^2\nu \int_0^{1/\nu} \left[\sum_{j=1}^{N}\sum_{k=1}^{N} \cos(2\pi\nu t - \varphi_j)\cos(2\pi\nu t - \varphi_k)\right] \mathrm{d}t \\ &= I_{\mathrm{i}}A^2\nu \int_0^{1/\nu} \left[\sum_{j=1}^{N}\sum_{k=1}^{N} (\cos(4\pi\nu t - \varphi_j - \varphi_k) + \cos(\varphi_k - \varphi_j))\right] \mathrm{d}t. \end{aligned} \tag{2.134}$$

The final result used the equation for the product of cosines:

$$\cos\alpha\,\cos\beta = \frac{\cos(\alpha+\beta)+\cos(\alpha-\beta)}{2}. \tag{2.135}$$

The first term in Eq. (2.134) oscillates exactly two full periods (4π) and its integral over the time interval $0 \le t \le 1/\nu$ is thus equal to zero. The second term (cosine of the phase difference) is time independent and determines the intensity of light scattered by the molecule

$$I_s = I_i A^2 \sum_{k=1}^{N}\sum_{j=1}^{N} \cos(\varphi_k - \varphi_j), \tag{2.136}$$

where the phases φ_j are determined by the positions $\vec{R}_j$ of the corresponding monomers and the scattering wavevector $\vec{q}$ [Eq. (2.128)].

The dependence of the scattered intensity on the size and the shape of the polymer is usually described by the **form factor** defined as the ratio of intensity scattered at angle θ (scattering wavevector $\vec{q}$) to that extrapolated to zero angle ($\theta \to 0$) and therefore, zero scattering wavevector ($|\vec{q}| \to 0$):

$$P(\vec{q}) \equiv \frac{I_s(\vec{q})}{I_s(0)}. \tag{2.137}$$

All optical paths are the same at zero scattering angle ($q=0$) and there is no phase shift ($\varphi_j = 0$ for all j) because the scattering wavevector $q=0$ [Eq. (2.131)]. The intensity of light scattered by the molecule at zero angle,

$$I_s(0) = I_i A^2 \sum_{k=1}^{N}\sum_{j=1}^{N} 1 = I_i A^2 N^2, \tag{2.138}$$

leads directly to the form factor, defined by Eq. (2.137):

$$\begin{aligned} P(\vec{q}) &= \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N} \cos(\varphi_i - \varphi_j) \\ &= \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N} \cos[\vec{q}\cdot(\vec{R}_i - \vec{R}_j)]. \end{aligned} \tag{2.139}$$

It is important to stress that only the relative position of monomers

$$\vec{R}_{ij} \equiv \vec{R}_i - \vec{R}_j \tag{2.140}$$

enters into the form factor.

The form factor in Eq. (2.139) is defined for a specific orientation of the molecule with respect to the scattering wavevector $\vec{q}$. Often (but not always!), the system is isotropic with equal probabilities of all molecular

orientations in space. In this case, Eq. (2.139) can be averaged over all these orientations. This averaging can be carried out in the spherical coordinate system with the z axis along the scattering wavevector $\vec{q}$ and the angle between $\vec{q}$ and $\vec{R}_{ij}$ denoted by α. The polar angle in this spherical coordinate system is denoted by β. The scalar product of wavevector $\vec{q}$ and the relative vector between monomers i and j is

$$\vec{q} \cdot \left(\vec{R}_i - \vec{R}_j\right) = qR_{ij} \cos\alpha, \tag{2.141}$$

where R_{ij} is the distance between monomers i and j. Averaging the cosine of this scalar product over all orientations of the molecule leads to

$$\begin{aligned}\langle \cos[\vec{q} \cdot (\vec{R}_i - \vec{R}_j)] \rangle &= \frac{1}{4\pi} \int_0^{2\pi} \left[\int_0^{\pi} \cos(qR_{ij} \cos\alpha) \sin\alpha \, \mathrm{d}\alpha \right] \mathrm{d}\beta \\ &= \frac{1}{2} \int_{-1}^{1} \cos(qR_{ij}x) \, \mathrm{d}x = \frac{\sin(qR_{ij})}{qR_{ij}},\end{aligned} \tag{2.142}$$

where the integral was taken by the change of variables $x = \cos\alpha$. Thus, the form factor for any isotropic system is quite simple:

$$P(q) = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\sin(qR_{ij})}{qR_{ij}}. \tag{2.143}$$

2.8.3 Measuring R_g^2 by scattering at small angles

One important property of the form factor in dilute solutions is that at low scattering angle ($qR_g < 1$) it becomes independent of any assumption about the shape of the molecule. Using the Taylor series expansion,

$$\frac{\sin x}{x} = 1 - \frac{x^2}{3!} + \frac{x^4}{5!} - \cdots \tag{2.144}$$

the form factor at low angles can be rewritten, as

$$\begin{aligned}P(q) &= \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left[1 - \frac{(qR_{ij})^2}{3!} + \cdots \right] \\ &= 1 - \frac{q^2}{6N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} R_{ij}^2 + \cdots \quad \text{for } qR_g < 1,\end{aligned} \tag{2.145}$$

$$P(q) = 1 - \frac{1}{3} q^2 \langle R_g^2 \rangle + \cdots \quad \text{for } qR_g < 1. \tag{2.146}$$

In the final relation, Eq. (2.47) was used for R_g^2 and the average $\langle \cdots \rangle$ is over different polymer conformations contributing to scattering.

Substituting the relation (2.131) between scattering wavevector q and scattering angle θ provides the low-angle expression of the form factor in light scattering:

$$P(q) = 1 - \frac{16\pi^2 n^2}{3\lambda^2} \langle R_g^2 \rangle \sin^2\left(\frac{\theta}{2}\right) + \cdots \tag{2.147}$$

Recall from Chapter 1 that it is convenient to plot the reciprocal Rayleigh ratio times concentration and optical constant K [Eq. (1.96)] to determine the weight-average molar mass from the zero concentration limit. In Chapter 1, we considered the Rayleigh ratio in the zero wavevector limit, and since the Rayleigh ratio is a normalized intensity [Eq. (1.87)] it has the same q dependence as the form factor [see Eq. (2.137)].

$$\left(\frac{Kc}{R_\theta}\right)_{c\to 0} = \frac{1}{M_\mathrm{w}P(q)} = \frac{1}{M_\mathrm{w}}\left[1 + \frac{16\pi^2 n^2}{3\lambda^2}\left\langle R_\mathrm{g}^2\right\rangle \sin^2\left(\frac{\theta}{2}\right) + \cdots\right]. \quad (2.148)$$

Note that the plus sign in front of the $\langle R_\mathrm{g}^2\rangle$ term arises because $(1-x)^{-1} \cong 1 + x$ for small values of x. Thus, extrapolation of the ratio Kc/R_θ to zero concentration plotted as a function of $\sin^2(\theta/2)$ allows determination of the radius of gyration of the polymer (or any other scattering object) from the slope for low scattering angles ($qR_\mathrm{g} < 1$) and the mass of the object from the y-intercept. For polydisperse samples, this method leads to the weight-average molar mass M_w and the z-average square radius of gyration $\langle R_\mathrm{g}^2\rangle_z$. In order to understand this, we write the Rayleigh ratio for a mixture of different species with molar mass M_N, mean-square radius of gyration $\langle R_N^2\rangle$, and concentration c_N:

$$\begin{aligned} R_\theta &= K\left[\sum_N c_N M_N - \frac{q^2}{3}\sum_N c_N M_N \langle R_N^2\rangle + \cdots\right] \\ &= K\sum_N c_N \frac{\sum_N c_N M_N}{\sum_N c_N}\left[1 - \frac{q^2}{3}\frac{\sum_N c_N M_N \langle R_N^2\rangle}{\sum_N c_N M_N} + \cdots\right] \\ &= KcM_\mathrm{w}\left[1 - \frac{q^2}{3}\langle R_\mathrm{g}^2\rangle_z + \cdots\right]. \end{aligned} \quad (2.149)$$

The z-average mean-square radius of gyration is defined as

$$\langle R_\mathrm{g}^2\rangle_z \equiv \frac{\sum_N c_N M_N \langle R_N^2\rangle}{\sum_N c_N M_N}, \quad (2.150)$$

and the low-concentration limit of the scattering expansion for a polydisperse solution takes a form similar to Eq. (2.148):

$$\left(\frac{Kc}{R_\theta}\right)_{c\to 0} = \frac{1}{M_\mathrm{w}}\left[1 + \frac{16\pi^2 n^2}{3\lambda^2}\langle R_\mathrm{g}^2\rangle_z \sin^2\left(\frac{\theta}{2}\right) + \cdots\right]. \quad (2.151)$$

An expansion similar to Eq. (2.151) for non-zero concentrations is the basis for the Zimm plot (see Problem 2.47).

The coil size of chains in dilute solution is typically measured by light scattering, using a laser. Visible light has a wavelength of order $\lambda \approx 500$ nm, which is much longer than the wavelength of neutrons ($\lambda \approx 0.3$ nm). This means that much smaller scattering wavevectors q are realized in light scattering than in neutron scattering. The limit $qR_\mathrm{g} < 1$, required for the expansion of the form factor in Eq. (2.146), is satisfied for all but the

highest molar mass chains in small-angle light scattering. At low scattering angles (for $qR_g < 1$), the form factor can also be approximated by an exponential:

$$P(q) \cong \exp\left(-\frac{q^2 R_g^2}{3}\right) \quad \text{for } qR_g < 1. \tag{2.152}$$

This last result is known as the **Guinier function** and is the basis for determining the radius of gyration from small-angle scattering experiments for objects with unknown form factor.

2.8.4 Debye function

Debye first calculated the form factor for scattering from an ideal chain in 1947. This form factor will be useful in interpretation of a wide variety of scattering experiments on polymers. The form factor for an ideal linear chain is obtained by averaging the form factor of isotropic scatterers [Eq. (2.143)] over the probability distribution for distances R_{ij} between monomers i and j on the ideal chain:

$$P(q) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\int_0^\infty \frac{\sin(qR_{ij})}{qR_{ij}} P_{3d}(|i-j|, R_{ij})\, 4\pi R_{ij}^2\, \mathrm{d}R_{ij}. \tag{2.153}$$

The probability distribution function $P_{3d}(|i-j|, R_{ij})$ is given by Eq. (2.86):

$$P_{3d}(|i-j|, R_{ij}) 4\pi R_{ij}^2\, \mathrm{d}R_{ij} = 4\pi\left(\frac{3}{2\pi|i-j|b^2}\right)^{3/2} \exp\left(-\frac{3R_{ij}^2}{2|i-j|b^2}\right) R_{ij}^2\, \mathrm{d}R_{ij}. \tag{2.154}$$

The integral over R_{ij} can be evaluated by converting it into a Gaussian integral (by writing the complex representation of sine and completing the square in the exponent):

$$\int_0^\infty R_{ij} \sin(qR_{ij}) \exp\left(-\frac{R_{ij}^2}{x}\right) \mathrm{d}R_{ij} = \frac{\pi^{1/2} q x^{3/2}}{4} \exp\left(-\frac{q^2 x}{4}\right). \tag{2.155}$$

The variable

$$x = \frac{2|i-j|b^2}{3} \tag{2.156}$$

was defined for convenience and the form factor for an ideal linear chain becomes a double sum of exponentials:

$$P(q) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N} \exp\left(-\frac{q^2 b^2 |i-j|}{6}\right). \tag{2.157}$$

Replacing the summations over monomer indices by integrations provides the integral form of the form factor of an ideal chain:

$$P(q) = \frac{1}{N^2}\int_0^N \left[\int_0^N \exp\left(-\frac{q^2b^2}{6}|u-\mathrm{v}|\right)\mathrm{d}u\right]\mathrm{d}\mathrm{v}. \tag{2.158}$$

Next, we change the variables of integration $s \equiv u/N$ and $t \equiv \mathrm{v}/N$ and denote the coefficient in the exponent by $Q \equiv q^2b^2N/6 = q^2\langle R_\mathrm{g}^2\rangle$ [we have used Eq. (2.54) for the radius of gyration of an ideal linear chain].

$$\begin{aligned}
P(q) &= \int_0^1 \left[\int_0^1 \exp(-Q|s-t|)\,\mathrm{d}s\right]\mathrm{d}t \\
&= \int_0^1 \left[\int_0^t \exp[-Q\,(t-s)]\,\mathrm{d}s + \int_t^1 \exp[-Q\,(s-t)]\,\mathrm{d}s\right]\mathrm{d}t \\
&= \int_0^1 \left[\exp(-Qt)\int_0^t \exp(Qs)\,\mathrm{d}s + \exp(Qt)\int_t^1 \exp(-Qs)\,\mathrm{d}s\right]\mathrm{d}t \\
&= \frac{1}{Q}\int_0^1 [\exp(-Qt)\,(\exp(Qt)-1) - \exp(Qt)\,(\exp(-Q)-\exp(-Qt))]\,\mathrm{d}t \\
&= \frac{1}{Q}\int_0^1 [2-\exp(-Qt)-\exp(-Q)\,\exp(Qt)]\,\mathrm{d}t \\
&= \frac{1}{Q}\left[2+\frac{\exp(-Q)-1}{Q} - \exp(-Q)\,\frac{\exp(Q)-1}{Q}\right] \\
&= \frac{2}{Q^2}\,[\exp(-Q)-1+Q].
\end{aligned} \tag{2.159}$$

This form factor of an ideal linear polymer is called the **Debye function** and can be rewritten in terms of the product of the square of scattering wavevector q^2 and the mean-square radius of gyration of the chain $\langle R_\mathrm{g}^2\rangle$:

$$P(q) = \frac{2}{(q^2\langle R_\mathrm{g}^2\rangle)^2}\,[\exp(-q^2\langle R_\mathrm{g}^2\rangle) - 1 + q^2\langle R_\mathrm{g}^2\rangle]. \tag{2.160}$$

The Debye function is plotted in Fig. 2.20.

In the limit of small scattering angles, where $qR_\mathrm{g} < 1$, the exponential can be expanded to simplify the Debye function:

$$\begin{aligned}
P(q) &\cong \frac{2}{(q^2\langle R_\mathrm{g}^2\rangle)^2} \\
&\quad\times\left[1 - q^2\langle R_\mathrm{g}^2\rangle + \frac{(q^2\langle R_\mathrm{g}^2\rangle)^2}{2} - \frac{(q^2\langle R_\mathrm{g}^2\rangle)^3}{6} + \cdots - 1 + q^2\langle R_\mathrm{g}^2\rangle\right] \\
&\cong \left(1 - \frac{q^2\langle R_\mathrm{g}^2\rangle}{3} + \cdots\right) \quad \text{for } q\sqrt{\langle R_\mathrm{g}^2\rangle} < 1.
\end{aligned} \tag{2.161}$$

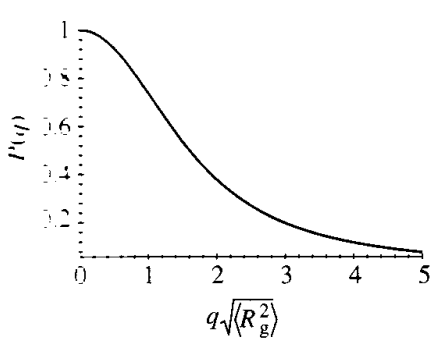

Fig. 2.20
The Debye function is the form factor of an ideal linear chain.

Note that we recover Eq. (2.146) for a general form factor for small values of $q\sqrt{\langle R_g^2\rangle}$.

At large scattering angles, the form factor describes the conformations of smaller sections of the chain on length scales $1/q < \sqrt{\langle R_g^2\rangle}$:

$$P(q) = \frac{2}{\left(q^2\langle R_g^2\rangle\right)^2}\left[\exp\left(-q^2\langle R_g^2\rangle\right) - 1 + q^2\langle R_g^2\rangle\right]$$
$$\cong \frac{2}{q^2\langle R_g^2\rangle} \quad \text{for } q\sqrt{\langle R_g^2\rangle} > 1. \tag{2.162}$$

This power law character of the form factor is related to the power law decay of the pair correlation function of an ideal chain [Eq. (2.121)]. Quite generally, the form factor is related to the Fourier transform of the intramolecular pair correlation function $g(r)$:

$$P(\vec{q}) = \frac{1}{N}\left[1 + \int g(\vec{r})\exp(\mathrm{i}\vec{q}\cdot\vec{r})\,\mathrm{d}^3r\right] \tag{2.163}$$

Equation (2.162) is a special case for a form factor of a fractal (with fractal dimension $\mathcal{D} = 2$). For any fractal, the wavevector dependence of the form factor gives a direct measure of the fractal dimension $\mathcal{D}$:

$$P(q) \sim \left(q\sqrt{\langle R_g^2\rangle}\right)^{-\mathcal{D}} \quad \text{for } q\sqrt{\langle R_g^2\rangle} > 1. \tag{2.164}$$

The reciprocal form factor $1/P(q)$ for a ideal linear chain [Eq. (2.160)] is shown in Fig. 2.21 as a function of $q^2\langle R_g^2\rangle$ (medium line) and is compared with the reciprocal form factors for a rigid rod (thin line) and for a solid sphere (thick line). The form factors of a rod,

$$P(q) = \frac{1}{\sqrt{3}qR_g}\int_0^{\sqrt{12}qR_g}\frac{\sin t}{t}\,\mathrm{d}t - \left(\frac{\sin(\sqrt{3}qR_g)}{\sqrt{3}qR_g}\right)^2, \tag{2.165}$$

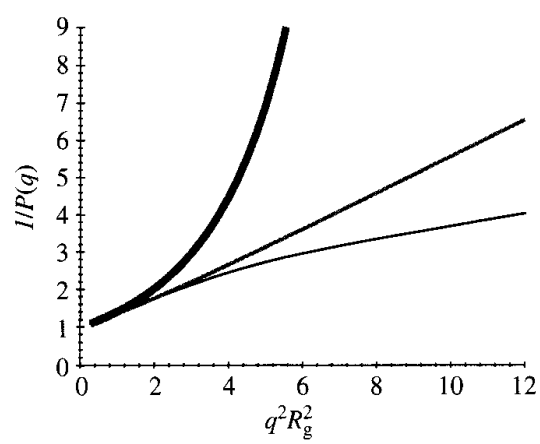

Fig. 2.21
Reciprocal form factors for simple objects: a solid sphere [Eq. (2.166), thick curve], an ideal linear chain [reciprocal Debye function, Eq. (2.160), medium line], and a rigid rod [Eq. (2.165), thin curve].

and a sphere,

$$P(q)=\left(\frac{3}{(\sqrt{5/3}qR_g)^3}[\sin(\sqrt{5/3}qR_g)-(\sqrt{5/3}qR_g)\cos(\sqrt{5/3}qR_g)]\right)^2, \tag{2.166}$$

are derived in Problems 2.44 and 2.45. Since all curves are plotted in Fig. 2.21 as functions of $q^2\langle R_g^2\rangle$, the initial slope of all of them is the same and is equal to 1/3 [see Eq. (2.146)].

The Debye function describes the q dependence of scattering data from dilute solutions of ideal chains. Such dilute solutions can either be obtained in a θ-solvent or by having a dilute solution of ordinary chains in a melt of perdeuterated chains. Small-angle neutron scattering data for four dilute concentrations of poly(methyl methacrylate) (PMMA with M_w= 250 000 g/mol^{-1}) in perdeuterated PMMA are shown to be fit by the Debye function in Fig. 2.22. Two parameters are used in the fits, $R_g = 13.3$ nm and a multiplicative intensity scale factor.

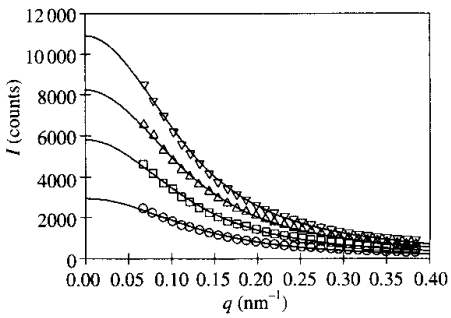

Fig. 2.22
Small-angle neutron scattering data fit to the Debye function multiplied by a zero wavevector scattering. Data are for 0.31% (circles), 0.63% (squares), 0.93% (triangles), and 1.19% (upside down triangles) PMMA with $M_w = 250\,000$ g mol^{-1} in a melt of perdeuterated PMMA, from R. Kirste *et al.*, *Polymer* **16**, 120 (1975).

2.9 Summary of ideal chains

Polymers with no interactions between monomers separated by many bonds along the chain are called ideal chains. Chains are nearly ideal in polymer solutions at a special compensation temperature (the θ-temperature) as well as in polymer melts.

The mean-square end-to-end distance for an ideal chain with n main-chain bonds of length l is $\langle R^2\rangle = C_n n l^2$, where C_n is called Flory's characteristic ratio. For long chains, this characteristic ratio converges to C_∞, leading to a simple expression for the mean-square end-to-end distance of any long ideal linear chain:

$$\langle R^2\rangle \cong C_\infty n l^2. \tag{2.167}$$

It is convenient to define the Kuhn monomer of length b and the number of Kuhn monomers N such that the mean-square end-to-end distance of an ideal linear chain is a freely jointed chain of Kuhn monomers:

$$\langle R^2\rangle = Nb^2. \tag{2.168}$$

The mean-square radius of gyration is defined as the averaged square distance from all monomers to the center of mass of the polymer [Eq. (2.44)] and is related to the averaged square distance between all pairs of monomers [Eq. (2.48)]. The mean-square radius of gyration of an ideal linear polymer is one-sixth of its mean-square end-to-end distance:

$$\langle R_g^2\rangle = Nb^2/6. \tag{2.169}$$

The radius of gyration of ideal branched polymers can be calculated using the Kramers theorem [Eq. (2.65)].

The probability distribution of the end-to-end vector of an ideal chain is well described by the Gaussian function:

$$P_{3d}(N, \vec{R}) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} \exp\left(-\frac{3\vec{R}^2}{2Nb^2}\right) \quad \text{for } |\vec{R}| \ll R_{max} = Nb. \tag{2.170}$$

The free energy of an ideal chain is purely entropic and changes quadratically with the end-to-end vector:

$$F = \frac{3}{2} kT \frac{\vec{R}^2}{Nb^2} \quad \text{for } |\vec{R}| \ll Nb. \tag{2.171}$$

The quadratic form of the free energy implies a linear relationship between force and the end-to-end vector, that is valid for small extensions:

$$\vec{f} = \frac{3kT}{Nb^2} \vec{R} \quad \text{for } |\vec{R}| \ll Nb. \tag{2.172}$$

Thus, the ideal chain can be thought of as an entropic spring and obeys Hooke's law for elongations much smaller than the maximum elongation ($|\vec{R}| \ll R_{max} = bN$). For stronger deformations, the Langevin function [Eq. (2.112)] for freely jointed chains or Eq. (2.119) for worm-like chains can be used to describe the non-linear relation between force and elongation.

The probability to find a monomer within a distance r of a given monomer is called the pair correlation function $g(r)$. For ideal linear chains, $g(r)$ is reciprocally proportional to the distance r:

$$g(r) = \frac{3}{\pi r b^2}. \tag{2.173}$$

The radius of gyration of any polymer can be determined from the wavevector q dependence of the scattering intensity at low angles ($qR_g < 1$) in the limit of zero concentration:

$$P(q) = 1 - \frac{1}{3} q^2 \langle R_g^2 \rangle + \cdots \quad \text{for } q\sqrt{\langle R_g^2 \rangle} < 1. \tag{2.174}$$

Distributions of monomers and correlations between them inside the chain can be determined from the angular dependence of scattering intensity in the range of higher wavevectors $q\sqrt{\langle R_g^2 \rangle} > 1$:

$$P(q) \sim \left(q\sqrt{\langle R_g^2 \rangle}\right)^{-\mathcal{D}} \quad \text{for } q\sqrt{\langle R_g^2 \rangle} > 1, \tag{2.175}$$

where $\mathcal{D}$ is the fractal dimension of the polymer ($\mathcal{D} = 2$ for ideal chains). The Debye function is the form factor for scattering from an ideal linear chain:

$$P(q) = \frac{2}{(q^2 \langle R_g^2 \rangle)^2} [\exp(-q^2 \langle R_g^2 \rangle) - 1 + q^2 \langle R_g^2 \rangle]. \tag{2.176}$$

Problems

Section 2.2

2.1 Prove that $\langle \cos\theta_{ij} \rangle = 0$ for the angle θ_{ij} between two bonds i and j if there are no correlations between bond vectors (see Fig. 2.3).

2.2 Calculate the mean-square end-to-end distance of atactic polystyrene with degree of polymerization 100 assuming that it is an ideal chain with characteristic ratio $C_\infty = 9.5$. (Note that the characteristic ratio is defined in terms of the main-chain bonds of length $l = 1.54$ Å rather than monomers.)

2.3 Calculate the root-mean-square end-to-end distance for polyethylene with $M = 10^7\,\mathrm{g\,mol^{-1}}$ in an ideal conformation with $C_\infty = 7.4$. Compare the end-to-end distance with the contour length of this polymer.

Section 2.3

2.4 Calculate Flory's characteristic ratio C_n for a freely rotating chain consisting of n bonds of length l with bond angle θ. Plot C_n/C_∞ as a function of n for bond angles $\theta = 68°$ and $10°$.

2.5 Calculate the Kuhn monomer length b and number of Kuhn monomers N of a freely rotating chain consisting of n bonds of length l with angle θ.

2.6 Consider a restricted random walk on a square lattice. Let us assume that a walker is not allowed to step back (but can go forward, turn right, or turn left with equal probability). Calculate the mean-square end-to-end distance for such a restricted n-step random walk. What is the characteristic ratio C_∞ for this walk? The lattice constant is equal to l.

2.7 Consider a restricted random walk on a 3D cubic lattice. Let us assume that a walker is not allowed step back (but can go forward, turn up, down, right, or left with equal probability). The lattice constant is equal to l.

(i) Calculate the mean-square end-to-end distance for such a restricted n-step random walk.
(ii) What is the C_∞ for this walk?

Hint: Recall for a freely rotating chain $C_\infty = (1 + \cos\theta)/(1 - \cos\theta)$.

2.8* Demonstrate that the mean-square end-to-end distance of a worm-like chain with contour length $R_{\max}$ and persistence length l_p is

$$\langle R^2 \rangle = 2R_{\max} l_p - 2l_p^2\left(1 - \exp\left(-\frac{R_{\max}}{l_p}\right)\right), \tag{2.177}$$

and the mean-fourth end-to-end distance is

$$\begin{aligned}\langle R^4 \rangle = {} & \frac{20}{3} R_{\max}^2 l_p^2 - \frac{208}{9} R_{\max} l_p^3 - \frac{8}{27} l_p^4\left(1 - \exp\left(-\frac{3R_{\max}}{l_p}\right)\right) \\ & + 32 l_p^4\left(1 - \exp\left(-\frac{R_{\max}}{l_p}\right)\right) - 8R_{\max} l_p^3 \exp\left(-\frac{R_{\max}}{l_p}\right).\end{aligned} \tag{2.178}$$

2.9* Derive the characteristic ratio of the hindered rotation model [Eq. (2.40)].

2.10 What are the common features of all models for ideal linear chains?

Section 2.4

2.11 The radius of gyration of a polystyrene molecule ($M_w = 3\times 10^7\,\mathrm{g\,mol^{-1}}$) was found to be $R_g = 1010$ Å. Estimate the overlap concentration c^* in $\mathrm{g\,cm^{-3}}$, assuming that the pervaded volume of the chain is a sphere of radius R_g.

2.12 Consider a polymer containing N Kuhn monomers (of length b) in a dilute solution at the θ-temperature, where ideal chain statistics apply.

Answer questions (i)–(vi) symbolically before substituting numerical values.

(i) What is the mean-square end-to-end distance R_0^2 of the polymer?
(ii) What is its fully extended length R_{max}?
(iii) What is the mean-square radius of gyration R_g^2 of this polymer?

The molar mass of the polymer is M

(iv) Estimate the overlap concentration c^* for this polymer, assuming that the pervaded volume of the chain is a sphere of radius R_g. (*Hint*: It is of the order of the concentration inside the coil.)
(v) How does this overlap concentration depend on the degree of polymerization?
(vi) What is the ratio of its fully extended length to the average (root-mean-square) end-to-end distance R_{max}/R_0?
(vii) Consider an example of a polymer with molar mass $M = 10^4\,\mathrm{g\,mol^{-1}}$ consisting of $N = 100$ Kuhn monomers (of length $b = 10\,\text{Å}$) and determine R_0, R_g, R_{max}, c^* and R_{max}/R_0.

2.13 One property of an ideal chain is that its subsections are also ideal. Derive the general relation between the end-to-end distance of the chain R, the end-to-end distance of the section ξ, the number of monomers in the chain N and the number of monomers in the section g.

2.14 The previous problem showed that the equivalent freely jointed chain follows random walk statistics even if the effective monomer is renormalized to be larger than b. What is the smallest effective monomer size for which this renormalization works?

2.15 Calculate the radius of gyration of a rod polymer with N monomers of length b using Eq. (2.51).

2.16 Calculate the radius of gyration of a uniform disc of radius R and negligible thickness.

2.17 Calculate the radius of gyration of a uniform sphere of radius R.

2.18 Calculate the radius of gyration of a uniform right cylinder of radius R and length L.

2.19 Consider a fractal line with fractal dimension $\mathcal{D}$. The mean-square distance between monomers u and v along this line is

$$\langle(\vec{R}(u) - \vec{R}(\mathrm{v}))^2\rangle = b^2(\mathrm{v} - u)^{2/\mathcal{D}}. \tag{2.179}$$

Calculate the mean-square end-to-end distance R^2 and radius of gyration R_g^2 for this fractal line. Determine the ratio R^2/R_g^2 symbolically and then calculate this ratio for fractal dimensions $\mathcal{D} = 1$, 1.7 and 2.

2.20 Show that the mean-square radius of gyration of a worm-like chain is

$$\langle R_g^2\rangle = \frac{1}{3}R_{max}l_p - l_p^2 + \frac{2l_p^3}{R_{max}} - \frac{2l_p^4}{R_{max}^2}\left(1 - \exp\left(-\frac{R_{max}}{l_p}\right)\right). \tag{2.180}$$

Verify that in the two simple limits (ideal chains $R_{max} \gg l_p$ and rigid rods $R_{max} \ll l_p$) the correct limiting expressions for the radius of gyration are recovered.

2.21 Calculate the radius of gyration of an ideal symmetric f-arm star polymer with N monomers of length b. *Hint*: Each arm of a symmetric star polymer can be treated as an ideal chain of N/f monomers.

2.22 Calculate the radius of gyration of an ideal H-polymer with all five sections containing equal number ($N/5$) of Kuhn monomers with length b.

2.23
(i) Calculate the radius of gyration of an asymmetric three arm star polymer with a short arm consisting of $n = N/4$ Kuhn monomers of length b and two equal long arms containing $3N/8$ Kuhn monomers each.

(ii) Evaluate R_g of this asymmetric star for $N = 1000$, $n = 250$, and $b = 3$ Å.
(iii) What length of the asymmetric arm n corresponds to the largest and smallest radii of gyration of a star polymer for constant N and b?

2.24 Consider an ideal f-arm star with n_j Kuhn monomers in the jth arm ($j = 1,2,\ldots,f$) and with Kuhn length b. The total number of Kuhn monomers in a molecule is $N = \sum_{j=1}^{f} n_j$. Show that the mean-square radius of gyration of this star is

$$\langle R_g^2 \rangle = Nb^2 \left(\frac{1}{2N^2} \sum_{j=1}^{f} n_j^2 - \frac{1}{3N^3} \sum_{j=1}^{f} n_j^3 \right). \tag{2.181}$$

2.25* Consider a tree polymer consisting of f branches (but no loops). Each of these branches contains N/f Kuhn monomers with Kuhn length b. Let v_{ij} be the number of branches along the linear chain connecting branch i and branch j. Demonstrate that the mean-square radius of gyration of this polymer is

$$\langle R_g^2 \rangle = Nb^2 \left(\frac{1}{2f} - \frac{1}{3f^2} + \frac{1}{f^3} \sum_{i=1}^{f} \sum_{j=i+1}^{f} v_{ij} \right). \tag{2.182}$$

2.26* Calculate the radius of gyration of an ideal ring polymer with N Kuhn monomers of length b, and compare it to the radius of gyration of a linear chain with the same number of monomers.

2.27 The radius of gyration of a spherical globule containing a single polymer and some solvent is 450 Å. Calculate the polymer density inside this globule if the molar mass of the polymer is $M = 2.6 \times 10^7\,\mathrm{g\,mol^{-1}}$.

Section 2.5

2.28 Derive Stirling's approximation for large N:

$$N! \cong \sqrt{2\pi N} N^N \exp(-N). \tag{2.183}$$

2.29 Demonstrate that the Gaussian probability distribution function of a one-dimensional random walk is normalized to unity:

$$\int_{-\infty}^{\infty} P_{1d}(N,x)\,dx = \frac{1}{\sqrt{2\pi N}} \int_{-\infty}^{\infty} \exp\left(\frac{-x^2}{2N}\right) dx = 1. \tag{2.184}$$

2.30 Show that the mean-square displacement of a one-dimensional random walker is

$$\int_{-\infty}^{\infty} x^2 P_{1d}(N,x)\,dx = \frac{1}{\sqrt{2\pi N}} \int_{-\infty}^{\infty} x^2 \exp\left(-\frac{x^2}{2N}\right) dx = N. \tag{2.185}$$

2.31 Suppose a person walks from the origin in one dimension forward or backward. The probability for a step in each direction is 1/2. What is the probability of finding the person five steps ($x = 5$) forward from the origin after $N = 25$ steps.

2.32 Calculate the location of the maximum of the distribution of end-to-end distances (Fig. 2.12) of an ideal chain with N Kuhn monomers of length b.

2.33 Calculate the average end-to-end distance of an ideal linear chain with N Kuhn monomers of length b.

2.34* Demonstrate that the higher moments of the end-to-end vector of an ideal chain with N Kuhn monomers of length b is

$$\langle \vec{R}^{2p} \rangle = \frac{(2p+1)!}{6^p p!} (Nb^2)^p \tag{2.186}$$

within the Gaussian approximation [with probability distribution Eq. (2.85)].

2.35* Show that the mean-square distance of the jth monomer from the centre of mass of an ideal chain with N Kuhn monomers of length b is

$$\langle(\vec{R}_j - \vec{R}_{\mathrm{cm}})^2\rangle = \frac{Nb^2}{3}\left[1 - \frac{3j(N-j)}{N^2}\right] \tag{2.187}$$

within the Gaussian approximation. What are the maximum and minimum values of this mean-square distance?

2.36* The mean-square radius of gyration is the second moment of the distribution of monomers around the centre of mass of the chain [Eq. (2.44)]. The mean-square radius of gyration of an ideal linear chain with N Kuhn monomers of length b is related to its mean-square end-to-end vector [Eq. (2.54)]:

$$\langle R_{\mathrm{g}}^2\rangle = \frac{1}{N}\sum_{i=1}^{N}\langle(\vec{R}_i - \vec{R}_{\mathrm{cm}})^2\rangle = \frac{1}{6}\langle\vec{R}^2\rangle. \tag{2.188}$$

(i) Show that higher moments of the distribution of monomers around the centre of mass are related to the corresponding higher moments of the end-to-end vector:

$$\frac{1}{N}\sum_{i=1}^{N}\langle(\vec{R}_i - \vec{R}_{\mathrm{cm}})^4\rangle = \frac{1}{18}(Nb^2)^2 = \frac{1}{30}\langle\vec{R}^4\rangle, \tag{2.189}$$

$$\frac{1}{N}\sum_{i=1}^{N}\langle(\vec{R}_i - \vec{R}_{\mathrm{cm}})^6\rangle = \frac{29}{972}(Nb^2)^3 = \frac{29}{3780}\langle\vec{R}^6\rangle. \tag{2.190}$$

(ii) Demonstrate that higher moments of the radius of gyration are

$$\left\langle\left[\frac{1}{N}\sum_{i=1}^{N}\left(\vec{R}_i - \vec{R}_{\mathrm{cm}}\right)^2\right]^2\right\rangle = \frac{19}{540}(Nb^2)^2 = \frac{19}{15}\langle R_{\mathrm{g}}^2\rangle^2, \tag{2.191}$$

$$\left\langle\left[\frac{1}{N}\sum_{i=1}^{N}\left(\vec{R}_i - \vec{R}_{\mathrm{cm}}\right)^2\right]^3\right\rangle = \frac{631}{68040}(Nb^2)^3 = \frac{631}{315}\langle R_{\mathrm{g}}^2\rangle^3. \tag{2.192}$$

2.37* Consider an ideal linear chain with N Kuhn monomers of length b and fixed end-to-end vector $\vec{R}$ directed along the x axis. Demonstrate that the mean-square projection of the radius of gyration onto the direction of its end-to-end vector is

$$\frac{1}{N}\sum_{i=1}^{N}\langle(\vec{R}_i - \vec{R}_{\mathrm{cm}})_x^2\rangle = \frac{1}{36}Nb^2\left(1 + \frac{3\vec{R}^2}{Nb^2}\right), \tag{2.193}$$

while the mean-square projection of the radius of gyration onto the perpendicular direction is independent of the magnitude of the end-to-end vector

$$\frac{1}{N}\sum_{i=1}^{N}\langle(\vec{R}_i - \vec{R}_{\mathrm{cm}})_y^2\rangle = \frac{1}{N}\sum_{i=1}^{N}\langle(\vec{R}_i - \vec{R}_{\mathrm{cm}})_z^2\rangle = \frac{1}{36}Nb^2. \tag{2.194}$$

Note that for $|\vec{R}| = 0$ the mean-square radius of gyration of a ring polymer $\langle R_{\mathrm{g}}^2\rangle = Nb^2/12$ is recovered, for $|\vec{R}| = bN^{1/2}$ the mean-square

radius of gyration of an ideal linear chain $\langle R_g^2 \rangle = Nb^2/6$ is recovered, and for $|\vec{R}| = bN$ the mean-square radius of gyration of a rod $\langle R_g^2 \rangle \cong (Nb)^2/12$ is recovered. It is interesting to point out that the asymmetry of the ideal linear chain,

$$\left(1 + \frac{3\vec{R}^2}{Nb^2}\right),$$

is quite large and a typical shape is better represented by an elongated ellipsoid than by a sphere.

2.38* Show that the one-dimensional probability of finding a monomer of an ideal chain whose ends are fixed at positions X_1 and X_2 is the following Gaussian function.

$$P_{1d}(s, x) = \sqrt{\frac{3}{2\pi K_s b^2}} \exp\left(-\frac{3(x - x_s)^2}{2K_s b^2}\right). \tag{2.195}$$

Written in this way, the position of the monomer that is s monomers from the end of the chain at X_1 is described as though that monomer was the end monomer of a single 'effective chain' of

$$K_s = \frac{1}{1/s + 1/(N - s)} = \frac{s(N - s)}{N} \tag{2.196}$$

monomers, whose other end is at position

$$x_s = X_1 \frac{N - s}{N} + X_2 \frac{s}{N}. \tag{2.197}$$

2.39 Consider a linear chain consisting of $m + N$ monomers. The ends of this chain are fixed in space. The x coordinates of the ends are X_1' and X_2', while the junction point fluctuates with x coordinate R'. What is the mean-square x coordinate of the end-to-end vector of the section containing N monomers $\langle (R' - X_2')^2 \rangle$?

Section 2.6

2.40 Consider an ideal chain with N Kuhn monomers of length b. The chain is carrying a positive charge $+e$ at one end and a negative charge $-e$ at the other end. What will be its average end-to-end distance R_x in an electric field $E = 10^4$ V cm^{-1} acting along the x axis at room temperature, if $N = 10^4$ and $b = 6$ Å? What is the ratio of this average distance R_x and root-mean-square projection R_{x0} of the end-to-end vector along the x axis in the absence of the field? Ignore the direct Coulomb interaction between the charges.

2.41 Consider an ideal chain with N Kuhn monomers of length b. The chain has two multivalent positive charges $+Ze$ at both of its ends (it is called a telechelic polymer). These two charges repel each other and stretch the polymer.

(i) What is the expression for the average distance R between the chain ends in a polar solvent with dielectric constant ϵ at temperature T (in terms of Z, e, N, b, T, ϵ, etc.)?

(ii) What is the ratio of this average distance R and the root-mean-square projection of the end-to-end vector along the x axis R_{x0} in the absence of Coulomb interaction for the chain with $N = 100$ Kuhn monomers

of length $b = 3$ Å in water (dielectric constant $\epsilon = 80$) at room temperature (20 °C) for charges of valency $Z = 10$?

Hint: The Coulomb force between two charges $+Ze$ separated by distance R in a solution with dielectric constant ϵ is $(Ze)^2/(\epsilon R^2)$.

In order to avoid complicated conversions of units note that a combination of variables, called the Bjerrum length, is $l_B = e^2/(\epsilon kT) \cong 7$ Å in water at room temperature.

2.42* Demonstrate that the probability distribution function of the end-to-end distance R of a freely jointed chain can be expressed in terms of the inverse Langevin function $\mathcal{L}^{-1}(x)$ of the ratio $x = R/R_{max}$ of the end-to-end distance R to its maximum value $R_{max} = Nb$:

$$P(R) = \frac{[\mathcal{L}^{-1}(x)]^2}{(2\pi Nb^2)^{3/2} x\{1 - [\mathcal{L}^{-1}(x)\operatorname{csch}\mathcal{L}^{-1}(x)]^2\}^{1/2}} \times \left\{\frac{\sinh \mathcal{L}^{-1}(x)}{\mathcal{L}^{-1}(x)\exp[x\mathcal{L}^{-1}(x)]}\right\}^N . \tag{2.198}$$

Compare this distribution function with the Gaussian approximation [Eq. (2.85)].

2.43 What is the difference between the probability distribution function and the pair correlation function?

Section 2.8

2.44 Calculate the form factor of a uniform sphere of radius R.

2.45 Calculate the form factor of a long thin rod of length L.

2.46 (i) Use the tabulated small-angle neutron scattering data[5] for a 1% solution of $M = 254\,000$ g mol^{-1} deuterium-labelled polystyrene in $M = 110\,000$ g mol^{-1} ordinary polystyrene to determine the radius of gyration by fitting the data to the Debye function [Eq. (2.160)].

(ii) Why is the Guinier limit [Eq. (2.146) or (2.152)] not useful for determining R_g for these data?

(iii) If Eq. (2.146) were used to estimate R_g from the five lowest q data points, is R_g overestimated or underestimated? Why?

q (1/Å)	0.00980	0.0128	0.0158	0.0188	0.0218	0.0248	0.0278
$I(q)$	4.43	3.37	2.55	2.05	1.58	1.23	0.966
q (1/Å)	0.0308	0.0338	0.0368	0.0399	0.0429	0.0459	0.0504
$I(q)$	0.804	0.758	0.592	0.509	0.445	0.370	0.275
q (1/Å)	0.0564	0.0624	0.0684	0.0744	0.0804	0.0864	0.0940
$I(q)$	0.246	0.197	0.175	0.139	0.128	0.107	0.081
q (1/Å)	0.1060						
$I(q)$	0.077						

[5] Data from M. R. Landry.

2.47 In Chapter 1, we learned how to determine weight-average molar mass M_w and second viral coefficient A_2 from the concentration dependence of light scattered at a very small angle from a polymer solution. In this chapter, we learned that the angular dependence of light scattering gives information about the radius of gyration R_g of the polymer coil. In practice, these analyses are often combined to obtain M_w, A_2, and R_g using a **Zimm plot**. The following equation is the basis of the Zimm plot and was obtained by combining the concentration expansion of Eq. (1.96) with the angular expansion of Eq. (2.147):

$$\frac{Kc}{R_\theta} = \left[\frac{1}{M_w} + 2A_2c + \cdots\right]\left[1 + \frac{16\pi^2 n^2}{3\lambda^2} R_g^2 \sin^2\left(\frac{\theta}{2}\right) + \cdots\right]. \tag{2.199}$$

Use the following table of data for Kc/R_θ of a polystyrene in benzene at four concentrations and five angles, to construct a Zimm plot by plotting Kc/R_θ against $100c + \sin^2(\theta/2)$ with c in $\mathrm{g\,mL^{-1}}$ and extrapolating to $c \to 0$ and $\theta \to 0$ to determine M_w, A_2, and R_g.

Table of $10^6 Kc/R_\theta$ (in $\mathrm{mol\,g^{-1}}$) for a polystyrene in benzene:

c ($\mathrm{mg\,mL^{-1}}$)	$\theta = 30°$	$\theta = 45°$	$\theta = 60°$	$\theta = 75°$	$\theta = 90°$
0.5	1.92	1.98	2.16	2.33	2.51
1.0	2.29	2.37	2.53	2.66	2.85
1.5	2.73	2.81	2.94	3.08	3.27
2.0	3.18	3.25	3.45	3.56	3.72

For the laser used, $\lambda = 546\,\mathrm{nm}$ and the refractive index for light of this wavelength travelling though benzene is $n = 1.5014$. After plotting the 20 data points, the data at each angle must be extrapolated to zero concentration, making a $c = 0$ line of five points (corresponding to the five angles) whose slope determines R_g. The data at each concentration must be extrapolated to zero angle, making a $\theta = 0$ line of four points (corresponding to the four concentrations) whose slope determines A_2. Both the $c = 0$ line and the $\theta = 0$ line should have the same intercept, which is the weight-average molar mass M_w.

2.48 Calculate the radius of gyration and the mean-square end-to-end distance of an ideal linear diblock copolymer consisting of N_1 Kuhn monomers of length b_1 connected at one end to N_2 Kuhn monomers of length b_2.

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