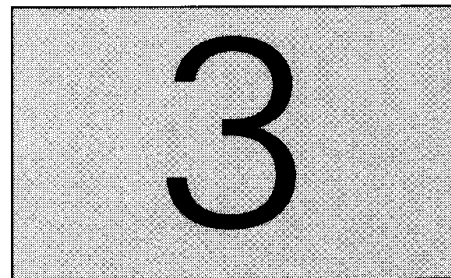# Real chains

In Chapter 2, we studied the conformations of an ideal chain that ignore interactions between monomers separated by many bonds along the chain. In this chapter we study the effect of these interactions on polymer conformations. To understand why these interactions are often important, we need to estimate the number of monomer–monomer contacts within a single coil. This number depends on the probability for a given monomer to encounter any other monomer that is separated from it by many bonds along the polymer.

A mean-field estimate of this probability can be made for the general case of an ideal chain in d-dimensional space by replacing a chain with an ideal gas of N monomers in the pervaded volume of a coil $\sim R^d$. The probability of a given monomer to contact any other monomer within this mean-field approximation is simply the overlap volume fraction ϕ^*, of a chain inside its pervaded volume, determined as the product of the monomer 'volume' b^d and the number density of monomers in the pervaded volume of the coil N/R^d:

$$\phi^* \approx b^d \frac{N}{R^d}. \tag{3.1}$$

Ideal chains obey Gaussian statistics in any dimension with $R = bN^{1/2}$, leading to the overlap volume fraction:

$$\phi^* \approx b^d \frac{N}{(bN^{1/2})^d} \approx N^{1-d/2}. \tag{3.2}$$

The overlap concentration of long ideal coils is very low in spaces with dimension d greater than 2:

$$\phi^* \approx N^{1-d/2} \ll 1 \quad \text{for } d > 2 \text{ and } N \gg 1. \tag{3.3}$$

In particular, in three-dimensional space the probability of a given monomer contacting another monomer on the same chain is $\phi^* \approx N^{-1/2} \ll 1$.

The number of monomer–monomer contacts between pairs of monomers that are far away from each other along the chain, but get close
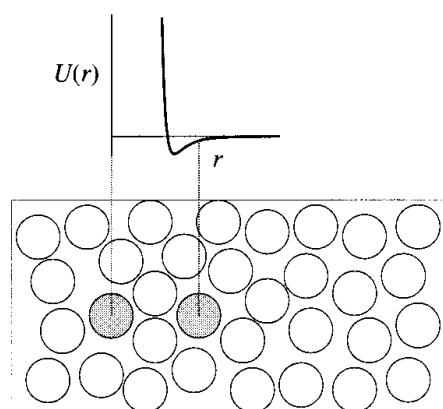
together in space, is the product of the number of monomers in the chain and the volume fraction of chains in the pervaded volume of the coil:
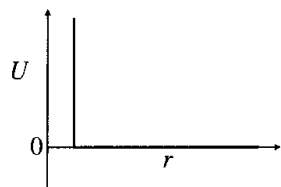
$$N\phi^* \approx N^{2-d/2}. \tag{3.4}$$

In spaces with dimension above 4, this number is small and monomer–monomer contacts are rare. Therefore, linear polymers are always ideal in spaces with dimension $d > 4$. In spaces with dimension less than 4 (in particular, in three-dimensional space relevant to most experiments), the number of monomer–monomer contacts for a long ideal chain is very large:

$$N\phi^* \approx N^{1/2} \gg 1 \quad \text{for } d = 3 \text{ and } N \gg 1. \tag{3.5}$$

It is important to understand how the energy arising from these numerous contacts affects the conformations of a real polymer chain. The effective interaction between a pair of monomers depends on the difference between a monomer's direct interaction with another monomer and with other surrounding molecules. An attractive effective interaction means that the direct monomer–monomer energy is lower and monomers would rather be near each other than in contact with surrounding molecules. In the opposite case of repulsive effective interactions, monomers 'do not like' to be near each other and prefer to be surrounded by other molecules. In the intermediate case, with zero net interaction, monomers 'do not care' whether they are in contact with other monomers or with surrounding molecules. In this case there is no energetic penalty for monomer–monomer contact and the chain conformation is nearly ideal. In the next section, this qualitative description of the monomer–monomer interaction is quantified.

3.1 Excluded volume and self-avoiding walks

3.1.1 Mayer f-function and excluded volume

Consider the energy cost $U(r)$ of bringing two monomers from ∞ to within distance r of each other in a solvent. A typical profile of this function is sketched in Fig. 3.1. It contains a repulsive hard-core barrier that corresponds to the energy cost of steric repulsion of two overlapping monomers. Typical monomers 'like' each other more than they 'like' solvent and therefore there is usually an attractive well corresponding to this energy difference. On the other hand, if monomers are chemically identical to the solvent and there is no energy difference between their interactions, the energy $U(r)$ will contain only the hard-core repulsion (see Fig. 3.2). For reasons that become clear later, in this case the solvent is called **athermal**. On the other hand, if monomers 'like' each other less than surrounding solvent (for example, similarly charged monomers) there is no attractive well in $U(r)$ but instead, extra repulsion.

The probability of finding two monomers separated by a distance r in a solvent at temperature T is proportional to the Boltzmann factor

Fig. 3.1
Effective interaction potential between two monomers in a solution of other molecules.

Fig. 3.2
The hard-core potential prevents monomers from overlapping.

exp $[-U(r)/(kT)]$ which is plotted in Fig. 3.3 for the potential of Fig. 3.1. The relative probability is zero at short distances, corresponding to the **hard-core repulsion** (it is impossible to find two overlapping monomers). The probability is large in the attractive well (it is energetically more favourable and therefore more likely to find the two monomers at these distances). The Boltzmann factor is equal to one at large distances if there are no long-range interactions.

The **Mayer f-function** is defined as the difference between the Boltzmann factor for two monomers at distance r and that for the case of no interaction (or at infinite distance):

$$f(r) = \exp\left[-U(r)/(kT)\right] - 1. \tag{3.6}$$

At short distances, the energy $U(r)$ is large because of the hard-core repulsion, making the Mayer f-function negative. The probability of finding monomers at these distances is significantly reduced relative to the non-interacting case (see Fig. 3.3). The Mayer f-function is positive in the attractive well and the probability of finding a second monomer there is enhanced compared to the non-interacting case.

The **excluded volume** v is defined as minus the integral of the Mayer f-function over the whole space:

$$v = -\int f(r)\, d^3r = \int \left(1 - \exp\left[-U(r)/(kT)\right]\right) d^3r. \tag{3.7}$$

This single parameter summarizes the *net* two-body interaction between monomers. As shown in Fig. 3.4, the hard-core repulsion ($r < 1$) makes a negative contribution to the integration of the Mayer f-function and a positive contribution to excluded volume. The example in Fig. 3.4 also has an effective attraction between monomers ($r > 1$) that makes a positive contribution to the integration of the Mayer f-function and a negative contribution to excluded volume. The attraction and repulsion largely offset each other for this example, making the net excluded volume quite small. A net attraction has a negative excluded volume $v < 0$ and a net repulsion has $v > 0$.

### 3.1.1.1 Non-spherical monomers

The simple calculation of excluded volume in Eq. (3.7) is only valid for spherical monomers. Particularly because of the 'monomer' being defined as a Kuhn monomer, the monomer is better described as a cylinder of length equal to the Kuhn length b, but smaller diameter d, as depicted in Fig. 3.5. Polymers without bulky side groups, such as polyethylene and poly(ethylene oxide), have effective diameter $d \cong 5\,\text{Å}$. Polystyrene has $d \cong 8\,\text{Å}$, and the diameter of the cylindrical Kuhn monomer steadily increases as side groups increase in size. Most flexible polymers have aspect ratio b/d in the range 2–3, but this ratio is larger for stiffer polymers.

Excluded volume describes the two-body (pairwise) monomer–monomer interaction in solution. At low polymer concentrations, the interaction
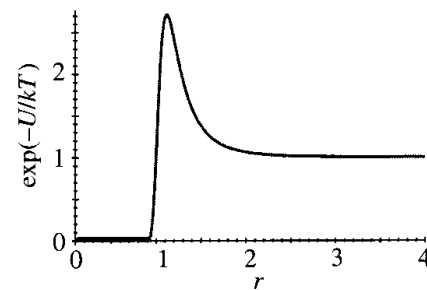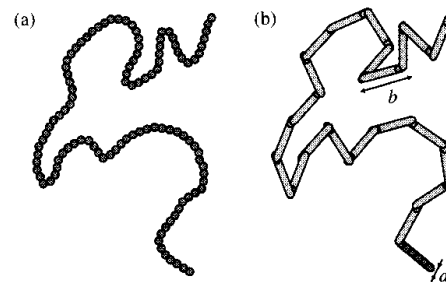
Fig. 3.3
The relative probability of finding a second monomer at distance r from a given monomer is given by the Boltzmann factor.
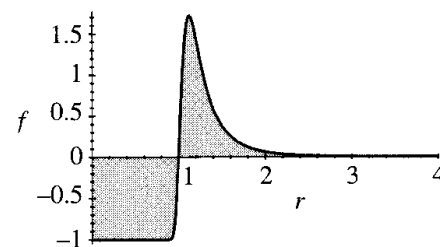
Fig. 3.4
The Mayer f-function and its integration (shaded regions) to determine excluded volume.

Fig. 3.5
(a) Chain with symmetric monomers. (b) Chain with strongly asymmetric cylindrical Kuhn segments of length b and diameter d.

part of the free energy density F_{int}/V can be written as a virial expansion in powers of the **monomer number density** c_n. The coefficient of the c_n^2 term is proportional to the excluded volume v and the coefficient of the c_n^3 term is related to the **three-body interaction coefficient** w:

$$\frac{F_{\text{int}}}{V} = \frac{kT}{2}(\text{v}c_n^2 + wc_n^3 + \cdots) \approx kT\left(\text{v}\frac{N^2}{R^6} + w\frac{N^3}{R^9} + \cdots\right). \qquad (3.8)$$

This virial expansion is analogous to that used for the osmotic pressure in Chapter 1 [Eq. (1.74)] and we will see in Section 3.3.4, how the excluded volume is related to the second virial coefficient.

For athermal spherical monomers of diameter d, $\text{v} \approx d^3$ and $w \approx d^6$. The interaction energy must not change if we redefine what is meant by a monomer. The chain in Fig. 3.5 can be thought of as a chain of n spheres of diameter d or a chain of $N = nd/b$ cylinders of length b and diameter d. Each term in the virial expansion must be unchanged by these choices, which requires:

$$\text{v}_s n^2 = \text{v}_c N^2 \quad w_s n^3 = w_c N^3. \qquad (3.9)$$

Using the renormalization of $N = nd/b$ and the spherical results $\text{v}_s \approx d^3$ and $w_s \approx d^6$, the cylindrical Kuhn monomer has

$$\text{v}_c \approx \text{v}_s\left(\frac{n}{N}\right)^2 \approx \text{v}_s\left(\frac{b}{d}\right)^2 \approx b^2 d, \qquad (3.10)$$

$$w_c \approx w_s\left(\frac{n}{N}\right)^3 \approx w_s\left(\frac{b}{d}\right)^3 \approx b^3 d^3 \qquad (3.11)$$

as coefficients in Eq. (3.8). The excluded volume of strongly asymmetric objects (long rods) $\text{v}_c \approx b^2 d$ is much larger than their occupied volume $\text{v}_0 \approx bd^2$, since $b \gg d$. The ratio of excluded volume and occupied volume is the aspect ratio $\text{v}_c/\text{v}_0 = b/d$. If the aspect ratio of the rod polymer is large enough, excluded volume creates nematic liquid crystalline ordering in solutions of rods, originally derived by Onsager. Once the excluded volumes of neighbouring rods overlap, these rods strongly interact and prefer to orient predominantly parallel to neighbouring rods. Similar nematic ordering is seen with polymers as well if the rigidity of the monomers is large enough (making the aspect ratio b/d large). Further discussion of strongly asymmetric monomers is beyond the scope of this book. Here, we focus on flexible polymers, which typically have aspect ratios in the range 2–3. For this reason, we write results below in terms of cylindrical monomers, which reduce to the results for a spherical monomer when $b \approx d$. The spherical monomer results are often used in the rest of this book, owing to the simplicity of a single length scale to describe the monomer. The excluded volume discussed in this book always refers to the excluded volume of a Kuhn monomer. The transformation rules of

Eq. (3.9) can be used to recast the excluded volume in terms of any part of the chain, including the chemical monomer.

(A) *Athermal solvents.* In the high-temperature limit, the Mayer f-function has a contribution only from hard-core repulsion. The excluded volume becomes independent of temperature at high temperatures, making the solvent athermal. An example is polystyrene in ethyl benzene (essentially polystyrene's repeat unit). The excluded volume in athermal solvent was derived in Eq. (3.10):

$$v \approx b^2 d. \tag{3.12}$$

(B) *Good solvents.* In the athermal limit, the monomer makes no energetic distinction between other monomers and solvent. In a typical solvent, the monomer–monomer attraction is slightly stronger than the monomer–solvent attraction because dispersion forces usually favor identical species. Benzene is an example of a good solvent for polystyrene. The net attraction creates a small attractive well $U(r) < 0$ that leads to a lower excluded volume than the athermal value:

$$0 < v < b^2 d. \tag{3.13}$$

As temperature is lowered, the Mayer f-function increases in the region of the attractive well, reducing the excluded volume.

(C) *Theta solvents.* At some special temperature, called the θ-**temperature**, the contribution to the excluded volume from the attractive well exactly cancels the contribution from the hard-core repulsion, resulting in a net zero excluded volume:

$$v = 0. \tag{3.14}$$

The chains have nearly ideal conformations at the θ-temperature[1] because there is no net penalty for monomer–monomer contact. Polystyrene in cyclohexane at $\theta \cong 34.5\,°C$ is an example of a polymer–solvent pair at the θ-temperature.

(D) *Poor solvents.* At temperatures below θ, the attractive well dominates the interactions and it is more likely to find monomers close together. In such poor solvents the excluded volume is negative signifying an effective attraction:

$$-b^2 d < v < 0. \tag{3.15}$$

Ethanol is a poor solvent for polystyrene.

(E) *Non-solvents.* The limiting case of the poor solvent is called non-solvent:

$$v \approx -b^2 d. \tag{3.16}$$

In this limit of strong attraction, the polymer's strong preference for its own monomers compared to solvent nearly excludes all solvent from being

---

[1] There are actually logarithmic corrections at the θ-temperature that make the chain conformation not quite ideal.

within the coil. Water is a non-solvent for polystyrene, which is why styrofoam coffee cups are made from polystyrene.

In a typical case of the Mayer f-function with an attractive well, repulsion dominates at higher temperatures and attraction dominates at lower temperatures. In athermal solvents with no attractive well there is no temperature dependence of the excluded volume. It is possible to have monomer–solvent attraction stronger than the monomer–monomer attraction. In this case, there is a soft barrier in addition to the hard-core repulsion and the excluded volume $v > b^2 d$ decreases to the athermal value $v = b^2 d$ at high temperatures.

3.1.2 Flory theory of a polymer in a good solvent

The conformations of a real chain in an athermal or good solvent are determined by the balance of the effective repulsion energy between monomers that tends to swell the chain and the entropy loss due to such deformation. One of the most successful simple models that captures the essence of this balance is the **Flory theory**, which makes rough estimates of both the energetic and the entropic contributions to the free energy.

Consider a polymer with N monomers, swollen to size $R > R_0 = bN^{1/2}$. Flory theory assumes that monomers are uniformly distributed within the volume R^3 with no correlations between them. The probability of a second monomer being within the excluded volume v of a given monomer is the product of excluded volume v and the number density of monomers in the pervaded volume of the chain N/R^3. The energetic cost of being excluded from this volume (the energy of excluded volume interaction) is kT per exclusion or $kTvN/R^3$ per monomer. For all N monomers in the chain, this energy is N times larger [see the first term of Eq. (3.8) with $V \approx R^3$]:

$$F_{\text{int}} \approx kTv\frac{N^2}{R^3}. \qquad (3.17)$$

The Flory estimate of the entropic contribution to the free energy of a real chain is the energy required to stretch an ideal chain to end-to-end distance R [Eq. (2.101)]:

$$F_{\text{ent}} \approx kT\frac{R^2}{Nb^2}. \qquad (3.18)$$

The total free energy of a real chain in the Flory approximation is the sum of the energetic interaction and the entropic contributions:

$$F = F_{\text{int}} + F_{\text{ent}} \approx kT\left(v\frac{N^2}{R^3} + \frac{R^2}{Nb^2}\right). \qquad (3.19)$$

The minimum free energy of the chain (obtained by setting $\partial F/\partial R = 0$) gives the optimum size of the real chain in the Flory

theory, $R = R_F$:

$$\frac{\partial F}{\partial R} = 0 = kT\left(-3v\frac{N^2}{R_F^4} + 2\frac{R_F}{Nb^2}\right),$$

$$R_F^5 \approx vb^2N^3,$$

$$R_F \approx v^{1/5}b^{2/5}N^{3/5}. \tag{3.20}$$

The size of long real chains is much larger than that of ideal chains with the same number of monomers, as reflected in the swelling ratio:

$$\frac{R_F}{bN^{1/2}} \approx \left(\frac{v}{b^3}N^{1/2}\right)^{1/5} \quad \text{for} \quad \frac{v}{b^3}N^{1/2} > 1. \tag{3.21}$$

If the total interaction energy of a chain in its ideal conformation $F_{int}(R_0)$ [Eq. (3.17) for $R = R_0 = bN^{1/2}$] is less than kT, the chain will not swell. In this case, $N^{1/2}v/b^3 < 1$ and the chain's conformation remains nearly ideal. Excluded volume interactions only swell the chain when the **chain interaction parameter,**

$$z \equiv \left(\frac{3}{2\pi}\right)^{3/2}\frac{v}{b^3}N^{1/2} \approx \frac{F_{int}(R_0)}{kT} \approx v\frac{N^2}{R_0^3} \approx \frac{v}{b^3}N^{1/2}, \tag{3.22}$$

becomes sufficiently large. Equation (3.20) is therefore only valid for chain interaction parameters that are larger than some number of order unity. The precise value of this number is discussed in Section 3.3.4.

The predictions of the Flory theory are in good agreement with both experiments and with more sophisticated theories (renormalization group theory, exact enumerations and computer simulations). However, the success of the Flory theory is due to a fortuitous cancellation of errors. The repulsion energy is overestimated because the correlations between monomers along the chain are omitted. The number of contacts per chain is estimated to be $b^3N^2/R^3 \approx N^{1/5}$. Computer simulations of random walks with excluded volume show that the number of contacts between monomers that are far apart along the chain does not grow with N. Hence, Flory overestimated the interaction energy. The elastic energy is also over-estimated in the Flory theory because the ideal chain conformational entropy is assumed. The conformations of real chains are qualitatively different from the ideal chains as will be demonstrated in the remainder of this chapter. Simple modifications of the Flory theory that take into account only some of these effects usually fail. However, Flory theory is useful because it is simple and provides a reasonable answer. We will make calculations in a similar spirit throughout this book. Mean-field estimates of the energetic part of the free energy, ignoring correlations between monomers, are used with entropy estimates based on ideal chain statistics. We will refer to such simple calculations as 'Flory theory' and will hope that the errors will cancel again.

It is important to realize that Flory theory leads to a universal power law dependence of polymer size R on the number of monomers N:

$$R \sim N^\nu \tag{3.23}$$

Real chains
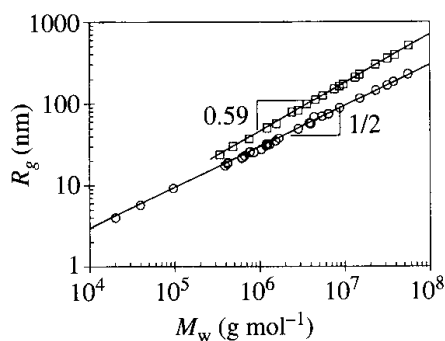
Fig. 3.6

Molar mass dependence of the radius of gyration from light scattering in dilute solutions for polystyrenes in a θ-solvent (cyclohexane at $\theta = 34.5\,^{\circ}$C, circles) and in a good solvent (benzene at $25\,^{\circ}$C, squares). Data are compiled in L. J. Fetters, *et al.*, *J. Phys. Chem. Ref. Data*, **23**, 619 (1994).
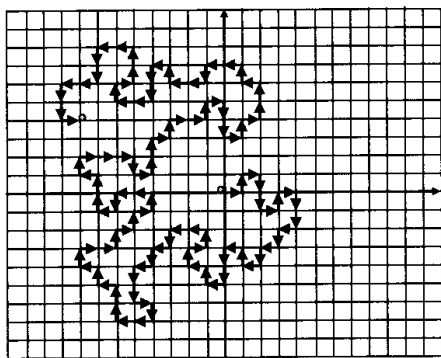
Fig. 3.7

A two-dimensional self-avoiding walk on a square lattice. The direction of each step is randomly chosen from four possible directions (up, down, right or left) with the requirement that previously visited sites cannot be visited again.

The quality of solvent, reflected in the excluded volume v, enters only in the prefactor, but does not change the value of the scaling exponent ν for any v > 0. The Flory approximation of the scaling exponent is $\nu = 3/5$ for a swollen linear polymer. For the ideal linear chain the exponent $\nu = 1/2$. In the language of fractal objects, the fractal dimension of an ideal polymer is $\mathcal{D} = 1/\nu = 2$, while for a swollen chain it is lower $\mathcal{D} = 1/\nu = 5/3$. More sophisticated theories lead to a more accurate estimate of the scaling exponent of the swollen linear chain in three dimensions:

$$\nu \cong 0.588. \tag{3.24}$$

Comparison of Eq. (3.23) with experimental data for polystyrenes in cyclohexane at the θ-temperature (a θ-solvent) and in toluene (a good solvent) is shown in Fig. 3.6. Both data sets obey Eq. (3.23), with $\nu = 1/2$ in θ-solvent and $\nu \cong 0.59$ in good solvent.

While the ideal chain discussed in Chapter 2 has a random walk conformation, the real chain has additional correlations because two monomers cannot occupy the same position in space. The real chain's conformation is similar to that of a **self-avoiding walk**, which is a random walk on a lattice that never visits the same site more than once. An example of a self-avoiding walk is shown in Fig. 3.7, on a two-dimensional square lattice.

3.2 Deforming real and ideal chains

3.2.1 Polymer under tension

In order to emphasize the difference between ideal and real chains, we compare their behaviour under tension. Consider a polymer containing N monomers of size b, under tension in two different solvents: a θ-solvent with nearly ideal chain statistics and an athermal solvent with excluded volume $v \approx b^3$. An ideal chain under tension was already discussed in Section 2.6.1 and is repeated for comparison with that of a swollen chain. The major difference between ideal and real chains is that in the latter there are excluded volume interactions between monomers that are far apart along the chain when they approach each other in space.

The end-to-end distances of the chains in the unperturbed state (with no applied external force) are given by Eqs (2.18) and (3.20) with $v \approx b^3$:
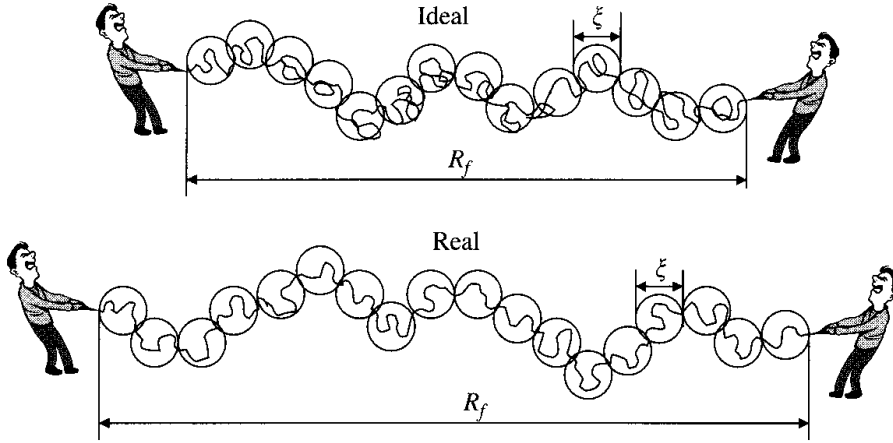
$$R_0 \approx bN^{1/2} \quad \text{ideal}, \tag{3.25}$$

$$R_F \approx bN^{3/5} \quad \text{real}. \tag{3.26}$$

Since both ideal and real chains are self-similar fractals, the same scaling applies to subsections of the chains of size r containing n monomers:

$$r \approx bn^{1/2} \quad \text{ideal}, \tag{3.27}$$

$$r \approx bn^{3/5} \quad \text{real}. \tag{3.28}$$

Fig. 3.8
Maxwell demons stretching ideal and real chains of the same contour length with the same force f.

Note that there are fewer monomers within the same distance r in the real chain case compared with the ideal chain because the real chain is swollen.

Let us now employ Maxwell demons to put both chains under tension with force of magnitude f applied at both ends of each chain, stretching them out as sketched in Fig. 3.8. As in Section 2.6.1, we subdivide each chain into tension blobs of size ξ containing g monomers each, such that on length scales smaller than these tension blobs the chain statistics are unperturbed,

$$\xi \approx bg^{1/2} \quad \text{ideal,} \tag{3.29}$$

$$\xi \approx bg^{3/5} \quad \text{real,} \tag{3.30}$$

while on larger length scales both chains are fully extended arrays of tension blobs.

Since each chain is a stretched array of tension blobs, their end-to-end distance R_f in an extended state is the product of the tension blob size ξ and the number of these blobs N/g per chain:

$$R_f \approx \xi \frac{N}{g} \approx \frac{Nb^2}{\xi} \approx \frac{R_0^2}{\xi} \quad \text{ideal,} \tag{3.31}$$

$$R_f \approx \xi \frac{N}{g} \approx \frac{Nb^{5/3}}{\xi^{2/3}} \approx \frac{R_F^{5/3}}{\xi^{2/3}} \quad \text{real.} \tag{3.32}$$

These equations can be solved for the size of the tension blobs in terms of the normal size (R_0 or R_F) and stretched size (R_f) of the chains:

$$\xi \approx \frac{R_0^2}{R_f} \quad \text{ideal,} \tag{3.33}$$

$$\xi \approx \frac{R_F^{5/2}}{R_f^{3/2}} \quad \text{real.} \tag{3.34}$$

Real chains

As discussed in Section 2.6.1, the free energy cost for stretching the chains is of the order kT per tension blob (we are neglecting coefficients of order unity):

$$F(N, R_f) \approx kT\frac{N}{g} \approx kT\frac{R_f}{\xi} \approx kT\left(\frac{R_f}{R_0}\right)^2 \quad \text{ideal,} \tag{3.35}$$

$$F(N, R_f) \approx kT\frac{N}{g} \approx kT\frac{R_f}{\xi} \approx kT\left(\frac{R_f}{R_F}\right)^{5/2} \quad \text{real.} \tag{3.36}$$

The force necessary to stretch the chain to end-to-end distance R_f is of the order of the thermal energy kT per tension blob of size ξ:

$$f \approx \frac{kT}{\xi} \approx \frac{kT}{R_0^2}R_f \approx \frac{kT}{R_0}\frac{R_f}{R_0} \quad \text{ideal,} \tag{3.37}$$

$$f \approx \frac{kT}{\xi} \approx \frac{kT}{R_F^{5/2}}R_f^{3/2} \approx \frac{kT}{R_F}\left(\frac{R_f}{R_F}\right)^{3/2} \quad \text{real.} \tag{3.38}$$
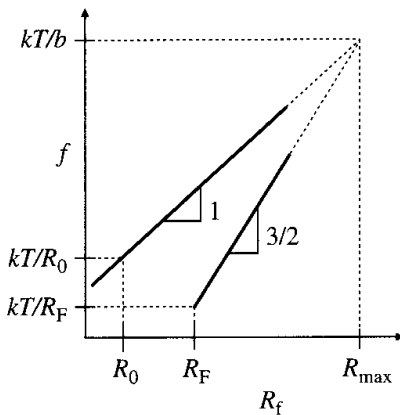
The same result (up to numerical prefactors of order unity) can be obtained by differentiation of the free energy with respect to end-to-end distance:

$$f = \frac{\partial F(N, R_f)}{\partial R_f}. \tag{3.39}$$

It is very important to notice the difference between the results for ideal and real chains under tension. Ideal chains satisfy Hooke's law with force f linearly proportional to elongation R_f. For real chains the dependence of force f on chain elongation R_f is non-linear with the exponent equal to $3/2$ for the Flory value of $\nu = 3/5$. This non-linear dependence of force on elongation for real chains was first derived by Pincus and tension blobs are often called **Pincus blobs**. The differences between real and ideal chains can be clearly seen when we consider the dimensionless stretching force:

$$\frac{fb}{kT} \approx \frac{R_f}{Nb} \quad \text{ideal} \quad \text{for } R_f < Nb, \tag{3.40}$$

$$\frac{fb}{kT} \approx \left(\frac{R_f}{Nb}\right)^{3/2} \quad \text{real} \quad \text{for } R_f < Nb. \tag{3.41}$$

The stretching energy is of order kT per monomer when either chain is nearly fully stretched ($R_f \approx Nb$) resulting in $f \approx kT/b$. The force required to stretch the real chain increases more rapidly with R_f, but is always *smaller* than the force required to stretch the ideal chain to the same end-to-end distance R_f, as shown in Fig. 3.9. Both chains have fewer possible conformations when they are stretched, but the real chain has fewer possible conformations to lose, resulting in a smaller stretching force.

Fig. 3.9

Extensional force f as a function of end-to-end distance R_f on logarithmic scales. Comparison between ideal chains (upper line) and real chains (lower line).

A similar scaling calculation can be carried out for stretching a linear chain with fractal dimension $1/\nu$. The free energy cost of stretching a chain from its original size bN^{ν} to end-to-end distance R is (derived in Problem 3.15)

$$F \approx kT \left(\frac{R}{bN^{\nu}}\right)^{1/(1-\nu)}. \tag{3.42}$$

The fractal dimension of an ideal chain is $1/\nu = 2$ and Eq. (3.42) reduces to free energy of stretching an ideal chain [Eq. (3.35)]. The Flory estimate of the fractal dimension of a real chain is $1/\nu = 5/3$ and Eq. (3.42) reduces to Eq. (3.36). A more accurate estimate of the fractal dimension of a real chain is $1/\nu \cong 1/0.588 \cong 1.7$ with corresponding free energy of stretching [Eq. (3.42)] $F \approx kT (R/R_{\text{F}})^{2.4}$.

The divergence of the force near maximal extension ($f \to \infty$ as $R_f \to R_{\text{max}}$) is not described by this scaling approach and is not shown in Fig. 3.9. This divergence is discussed in Section 2.6.2 for freely jointed and worm-like chain models.

3.2.2 Polymer under compression

Two simple examples comparing the properties of ideal and real chains are discussed in this section: uniaxial and biaxial compression. A related example of triaxial confinement shall be discussed in Section 3.3.2 for the case where polymers collapse into globules due to attraction between monomers.

3.2.2.1 Biaxial compression

We consider first biaxial compression corresponding to squeezing of a chain into a cylindrical pore of diameter D. The diameter of the pore defines a natural **compression blob** size. On length scales smaller than D, sections of the chain do not 'know' that it is compressed and their statistics are still the same as the statistics of an undeformed chain:

$$D \approx bg^{1/2} \quad \text{ideal,} \tag{3.43}$$

$$D \approx bg^{3/5} \quad \text{real.} \tag{3.44}$$

These equations can be solved for the number of monomers g in a compression blob of size D:

$$g \approx \left(\frac{D}{b}\right)^{2} \quad \text{ideal,} \tag{3.45}$$

$$g \approx \left(\frac{D}{b}\right)^{5/3} \quad \text{real.} \tag{3.46}$$

The above relations are identical to the corresponding equations for tension blobs (Section 3.2.1) because in both examples the conformational statistics are unperturbed on the shortest scales.

The length of a tube $R_\parallel$ occupied by an ideal chain can be estimated as a random walk of N/g compression blobs along the contour of the tube:

$$R_\parallel \approx D\left(\frac{N}{g}\right)^{1/2} \approx bN^{1/2} \quad \text{ideal.} \tag{3.47}$$

As expected, the size of the ideal chain along the contour of the tube is not affected by the confinement. This is an important property of an ideal chain. Deformation of the ideal chain in one direction does not affect its properties in the other directions because each coordinate's random walk is *independent*.

In the case of confinement of a real chain, the compression blobs repel each other and fill the pore in a sequential array. Therefore, the length of the tube $R_\parallel$ occupied by a real chain is the size of one compression blob D times the number N/g of these blobs:

$$R_\parallel \approx D\left(\frac{N}{g}\right) \approx \left(\frac{b}{D}\right)^{2/3} Nb \quad \text{real in a cylinder.} \tag{3.48}$$

Note that in the case of a real chain confined to a tube, the occupied length of the tube $R_\parallel$ is linearly proportional to the number of monomers N in the chain. The occupied length increases as the tube diameter D decreases. Ideal and real chains of the same length, confined in a cylinder of diameter D, are shown schematically in Fig. 3.10. There is no penalty to overlap the compression blobs of an ideal chain, whereas the compression blobs of the real chain have strong excluded volume interactions that prevent overlap.

The free energy of confinement is of the order of kT per compression blob for either chain:

$$F_{\text{conf}} \approx kT\frac{N}{g} \approx kTN\left(\frac{b}{D}\right)^2 \approx kT\left(\frac{R_0}{D}\right)^2 \quad \text{ideal,} \tag{3.49}$$

$$F_{\text{conf}} \approx kT\frac{N}{g} \approx kTN\left(\frac{b}{D}\right)^{5/3} \approx kT\left(\frac{R_F}{D}\right)^{5/3} \quad \text{real.} \tag{3.50}$$
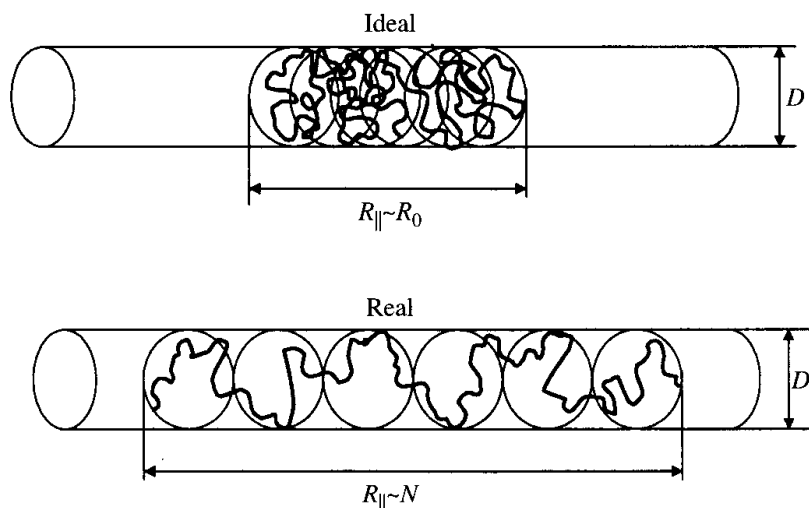
Fig. 3.10
Ideal and real chains of the same length, confined in a cylinder of diameter D.

R_0 and R_F are the end-to-end distances of unconfined ideal and real chains, respectively. These calculations can be generalized to confinement a polymer with fractal dimension $1/\nu$ from its original size bN^ν to a cylinder with diameter D. The confinement free energy in this case is (derived in Problem 3.16)

$$F_{conf} \approx kT\left(\frac{bN^\nu}{D}\right)^{1/\nu}, \tag{3.51}$$

with Eq. (3.49) corresponding to an ideal chain with $1/\nu = 2$ and Eq. (3.50) being the result for a real chain with the Flory estimate of fractal dimension $1/\nu = 5/3$. For a more accurate estimate of the fractal dimension of real chains $1/\nu = 1.70$ the confinement free energy is $F_{conf} \approx kT (R_F/D)^{1.70}$.

3.2.2.2 Uniaxial compression

The free energy of confinement of a chain between parallel plates in a slit of spacing D is the same as in the cylindrical pore (up to numerical prefactors of order unity [Eqs (3.49) and (3.50)]. The longitudinal size $R_\parallel$ of an ideal chain confined between parallel plates is still the same as for an unperturbed ideal chain [Eq. (3.47)] because the different x, y, z components of an ideal chain's random walk are not coupled. In the case of a real chain confined between parallel plates, the compression blobs repel each other, leading to a two-dimensional swollen conformation (see Fig. 3.11). The size of a two-dimensional swollen chain of compression blobs can be estimated from the Flory theory (Section 3.1.2). The 'excluded area' of each compression blob is $\approx D^2$, making the two-dimensional analogue of Eq. (3.17) for the repulsive interaction energy of the chain of N/g compression blobs $kTD^2(N/g)^2/R_\parallel^2$, where $R_\parallel^2$ is the area of the chain. The entropic part of the free energy that resists increasing the area of the chain of N/g compression blobs of size D is $kTR_\parallel^2/[(N/g)D^2]$ for a real chain confined between two parallel plates:

$$F \approx kT\left(D^2\frac{(N/g)^2}{R_\parallel^2} + \frac{R_\parallel^2}{(N/g)D^2}\right). \tag{3.52}$$

Minimizing this free energy with respect to $R_\parallel$ gives the size of a real chain between plates of spacing D:

$$R_\parallel \approx D\left(\frac{N}{g}\right)^{3/4} \approx N^{3/4}b\left(\frac{b}{D}\right)^{1/4} \quad \text{real between plates} \tag{3.53}$$

The size of the real chain confined between plates is again much larger than that of an ideal chain (where $R_\parallel \approx bN^{1/2}$) because the compression blobs of the real chain repel each other. The maximum confinement corresponds to thickness D of the order of the Kuhn monomer size b. In this case the chain becomes effectively two-dimensional with size

$$R_\parallel \approx N^{3/4}b \quad \text{real two-dimensional.} \tag{3.54}$$

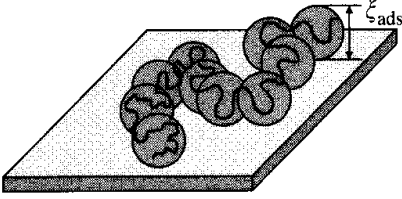The exponent $\nu = 3/4$ is universal for two-dimensional linear chains with excluded volume repulsion.
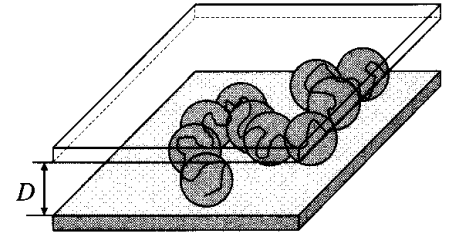
Fig. 3.11
Uniaxial compression—a real chain in a slit of spacing D between two parallel plates.

3.2.3 Adsorption of a single chain

For the final example comparing the properties of ideal and real chains, consider a polymer in dilute solution near a weakly adsorbing surface. Let the energy gain for a monomer in contact with the surface be $-\delta kT$, where we assume that $0 < \delta < 1$ (weak adsorption). The chain would like to increase the number of monomers in contact with the surface in order to gain adsorption energy. In order to do that, however, it would have to confine itself to a layer of thickness smaller than its unperturbed polymer size ($\xi_{ads} < R$), thereby losing conformational entropy.

3.2.3.1 Scaling calculation

The thickness ξ_{ads} of the adsorbed layer defines the **adsorption blob** size (see Fig. 3.12). This adsorption blob size is the length scale on which the cumulative interaction energy of a small section of the chain with the surface is of the order of the thermal energy kT. On smaller length scales, the interaction energy is weaker than the thermal energy and the chain remains in an unperturbed conformation, which is Gaussian for ideal chains [Eq. (3.45)] and swollen for real chains [Eq. (3.46)]. On scales larger than the adsorption blob, the interaction energy of the chain with the surface is larger than kT and the consecutive adsorption blobs are forced to be in contact with the surface. Therefore, the conformation of an adsorbed chain is a two-dimensional array of adsorption blobs and is similar to that for a chain confined between two parallel plates, discussed in the previous section.

In order to calculate the size of the adsorption blob ξ_{ads}, we need to calculate the number of monomers in contact with the surface for a chain section of size ξ_{ads}. The average volume fraction in a chain section of size ξ_{ads} containing g_{ads} monomers is ϕ:

$$\phi \approx \frac{b^3 g_{ads}}{\xi_{ads}^3} \approx \frac{b}{\xi_{ads}} \quad \text{ideal,} \tag{3.55}$$

$$\phi \approx \frac{b^3 g_{ads}}{\xi_{ads}^3} \approx \left(\frac{b}{\xi_{ads}}\right)^{4/3} \quad \text{real.} \tag{3.56}$$

The number of monomers in each adsorption blob that are in direct contact with the surface (within a layer of thickness b from it) is estimated as the product of the mean-field number density of monomers in the blob ϕ/b^3 and the volume of this layer within distance b of the surface, $\xi_{ads}^2 b$:

$$\frac{\phi}{b^3} \xi_{ads}^2 b \approx \frac{\xi_{ads}}{b} \quad \text{ideal,} \tag{3.57}$$

$$\frac{\phi}{b^3} \xi_{ads}^2 b \approx \left(\frac{\xi_{ads}}{b}\right)^{2/3} \quad \text{real.} \tag{3.58}$$

Fig. 3.12
A chain adsorbed to a weakly attractive surface.

The energy gain per monomer in contact with the surface is δkT. Therefore, the energy gain per adsorption blob is

$$\delta kT \frac{\xi_{\text{ads}}}{b} \approx kT \quad \text{ideal,} \tag{3.59}$$

$$\delta kT \left(\frac{\xi_{\text{ads}}}{b}\right)^{2/3} \approx kT \quad \text{real,} \tag{3.60}$$

leading to the adsorption blob size:

$$\xi_{\text{ads}} \approx \frac{b}{\delta} \quad \text{ideal,} \tag{3.61}$$

$$\xi_{\text{ads}} \approx \frac{b}{\delta^{3/2}} \quad \text{real.} \tag{3.62}$$

The free energy of an adsorbed chain can be estimated as the thermal energy kT per adsorption blob:

$$F_{\text{ads}} \approx -kT \frac{N}{g_{\text{ads}}} \approx -kTN\delta^2 \quad \text{ideal,} \tag{3.63}$$

$$F_{\text{ads}} \approx -kT \frac{N}{g_{\text{ads}}} \approx -kTN\delta^{5/2} \quad \text{real.} \tag{3.64}$$

The adsorbed layer is thicker and bound less strongly for the real chain (since for weak adsorption $0 < \delta < 1$) because it pays a higher confinement penalty than the ideal chain. The excluded volume interaction of real chains make them more difficult to compress or adsorb than ideal chains. These scaling calculations can be generalized to adsorption of a polymer with general fractal dimension $1/\nu$:

$$F_{\text{ads}} \approx kTN\delta^{1/(1-\nu)}. \tag{3.65}$$

The same result can be obtained using the Flory theory, as demonstrated below.

3.2.3.2 Flory theory of an adsorbed chain

A mean-field estimate of the free energy of adsorption and the thickness of the adsorbed chain can be made by assuming the monomers are uniformly distributed at different distances from the surface up to thickness ξ_{ads}. Then the fraction of monomers in direct contact with the surface (within distance b from the surface) is b/ξ_{ads}. The number of adsorbed monomers Nb/ξ_{ads} is multiplied by the adsorption energy per monomer–surface contact $(-\delta kT)$ to calculate the energetic gain from the surface interaction:

$$F_{\text{int}} \approx -\delta kTN \frac{b}{\xi_{\text{ads}}}. \tag{3.66}$$

Real chains

In order to gain this energy, the chain must pay the entropic confinement free energy F_{conf}, derived in the example above [Eqs (3.49) and (3.50)]. Therefore, the total free energy of a weakly adsorbing chain is

$$F = F_{\text{conf}} + F_{\text{int}} \approx kTN\left(\frac{b}{\xi_{\text{ads}}}\right)^2 - kTN\delta\frac{b}{\xi_{\text{ads}}} \quad \text{ideal,} \tag{3.67}$$

$$F = F_{\text{conf}} + F_{\text{int}} \approx kTN\left(\frac{b}{\xi_{\text{ads}}}\right)^{5/3} - kTN\delta\frac{b}{\xi_{\text{ads}}} \quad \text{real.} \tag{3.68}$$

The minimum of the free energy corresponds to the optimal thickness of the adsorbed layer, determined from $\partial F/\partial\xi_{\text{ads}} = 0$:

$$\xi_{\text{ads}} \approx \frac{b}{\delta} \quad \text{ideal,} \tag{3.69}$$

$$\xi_{\text{ads}} \approx \frac{b}{\delta^{3/2}} \quad \text{real.} \tag{3.70}$$

These estimates are identical to the scaling results [Eqs (3.61) and (3.62)]. Substituting Eqs (3.69) and (3.70) into each individual term[2] in Eqs (3.67) and (3.68) shows that each term is actually of order the free energy of adsorption [Eqs (3.63) and (3.64)].

The adsorbed layer thickness for a polymer with general fractal dimension $1/\nu$ is derived in Problem 3.18:

$$\xi_{\text{ads}} \approx b\delta^{-\nu/(1-\nu)}. \tag{3.71}$$

Substituting this adsorbed layer thickness into the confinement free energy [Eq. (3.51)] or into the interaction free energy [Eq. (3.66)] gives the expected result for the free energy of adsorption [Eq. (3.65)].

3.2.3.3 Proximity effects

Both theories of single-chain adsorption, described above, ignore a very important effect—the loss of conformational entropy of a strand due to its proximity to the impenetrable surface. Each adsorption blob has $1/\delta$ contacts with the surface and each strand of the chain near these contacts loses conformational entropy due to the proximity effect. In order to overcome this entropic penalty, the chain must gain finite energy E_{cr} per contact between a monomer and the surface. This critical energy E_{cr} corresponds to the adsorption transition. For ideal chains $E_{\text{cr}} \approx kT$. The small additional free energy gain per contact $kT\delta$ should be considered in excess of the critical value E_{cr},

$$E = E_{\text{cr}} + \delta kT. \tag{3.72}$$

Polymer adsorption is, therefore, a sharp transition with chain thickness changing rapidly in the small interval δkT of monomer–surface interaction energy E above E_{cr} (Fig. 3.13). Strictly speaking, this correction [Eq. (3.72)]
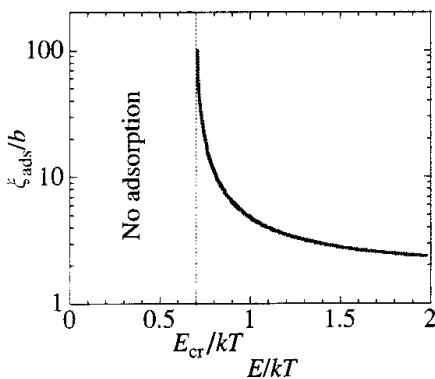
Fig. 3.13

The thickness ξ_{ads} of an adsorbed ideal chain decreases rapidly as the adsorption energy E is increased above the adsorption transition E_{cr}.

---

[2] Notice that if Eqs (3.69) and (3.70) are blindly substituted into Eqs (3.67) and (3.68), the conclusion would be that the adsorption free energy is zero for both ideal and real chains. This exemplifies the disadvantage of scaling calculations. There are unspecified prefactors of order unity in both terms of Eqs (3.67) and (3.68), which invalidates the blind substitution.

for the proximity effect is valid only for ideal chains. It is much harder to take into account the proximity effect for real chains due to strong correlation effects in these polymers. However, qualitatively there is still a threshold value of energy needed for the real chain to adsorb, as depicted in Fig. 3.13. For adsorption of real chains, the actual concentration inside each adsorption blob decays as a power law in distance from the surface. This power law decay modifies the exponent in Eqs (3.62) and (3.70) (see Problem 3.22).

3.3 Temperature effects on real chains

3.3.1 Scaling model of real chains

Several examples of scaling with different types of scaling blobs have already been introduced for tension, compression, and adsorption. The main idea in all scaling approaches is a separation of length scales. The blob in each case corresponds to the length scale at which the interaction energy is of the order of the thermal energy kT. On smaller scales the interaction is not important and smaller sections of the chain follow the unperturbed statistics (either ideal or swollen). On length scales larger than the blob size, the interaction energy is larger than kT and polymer conformations are controlled by interactions.

In this section, we will consider the excluded volume interaction following a similar scaling approach. The main idea is that of a thermal length scale (the **thermal blob**). On length scales smaller than the thermal blob size ξ_T, the excluded volume interactions are weaker than the thermal energy kT and the conformations of these small sections of the chain are nearly ideal. The thermal blob contains g_T monomers in a random walk conformation:

$$\xi_T \approx b g_T^{1/2} \tag{3.73}$$

The thermal blob size can be estimated by equating the Flory excluded volume interaction energy [Eq. (3.17)] for a single thermal blob and the thermal energy kT.

$$kT|v|\frac{g_T^2}{\xi_T^3} \approx kT. \tag{3.74}$$

In this section, we discuss both good ($v > 0$) and poor ($v < 0$) solvents and therefore, use $|v|$ in the definition of the thermal blob. The above two equations are combined to estimate the number of monomers in a thermal blob

$$g_T \approx \frac{b^6}{v^2}, \tag{3.75}$$

and the size of the thermal blob

$$\xi_T \approx \frac{b^4}{|v|}, \tag{3.76}$$

in terms of the monomer size b and the excluded volume v.

Real chains

The thermal blob size is the length scale at which excluded volume becomes important. For $v \approx b^3$, the thermal blob is the size of a monomer ($\xi_T \approx b$) and the chain is fully swollen in an athermal solvent [Eq. (3.12)]. For $v \approx -b^3$, the thermal blob is again the size of a monomer ($\xi_T \approx b$) and the chain is fully collapsed in a non-solvent [Eq. (3.16)]. For $|v| < b^3 N^{-1/2}$, the thermal blob is larger than the chain size ($\xi_T > R_0$) and the chain is nearly ideal. For $b^3 N^{-1/2} < |v| < b^3$ the thermal blob is between the monomer size and the chain size, with either intermediate swelling in a good solvent [$v > 0$, Eq. (3.13)] or intermediate collapse in a poor solvent [$v < 0$, Eq. (3.15)].
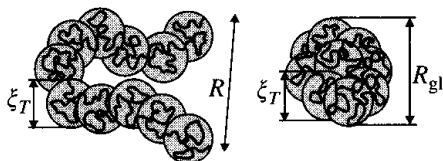
3.3.1.1 Excluded volume repulsion ($v > 0$)

On length scales larger than the thermal blob size ξ_T, in athermal and good solvents, the excluded volume repulsion energy is larger than the thermal energy kT and the polymer is a swollen chain of N/g_T thermal blobs (Fig. 3.14). The end-to-end distance of this chain is determined as a self-avoiding walk of thermal blobs with fractal dimension $D = 1/\nu \cong 1.7$:

$$R \approx \xi_T \left(\frac{N}{g_T}\right)^{\nu} \approx b \left(\frac{v}{b^3}\right)^{2\nu-1} N^{\nu}. \qquad (3.77)$$

For the swelling exponent $\nu \cong 0.588$ the expression for the chain size is $R \approx b \, (v/b^3)^{0.18} N^{0.588}$. Note that this scaling result reduces to the prediction of the Flory theory [Eq. (3.20)] for exponent $\nu = 3/5$.
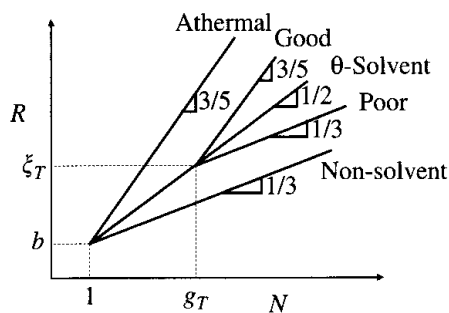
3.3.1.2 Excluded volume attraction ($v < 0$)

In poor solvents on length scales larger than the thermal blob size ξ_T, the excluded volume attraction energy is larger than the thermal energy kT. This causes the thermal blobs to adhere to each other, forming a dense globule (Fig. 3.14). The size of the globule is calculated by assuming a dense packing of thermal blobs:

$$R_{gl} \approx \xi_T \left(\frac{N}{g_T}\right)^{1/3} \approx \frac{b^2}{|v|^{1/3}} N^{1/3}. \qquad (3.78)$$

Thermal blobs in a poor solvent attract each other like molecules in a liquid droplet. The shape of the globule is roughly spherical to reduce the area of the unfavourable interface between it and the pure solvent. The volume fraction inside the globule is independent of the number of monomers N and is the same as inside a thermal blob:

$$\phi \approx \frac{Nb^3}{R_{gl}^3} \approx \frac{|v|}{b^3}. \qquad (3.79)$$

The dependence of the size R of the chain on the number of monomers N, for solvents of different quality, is sketched in Fig. 3.15. In athermal solvent ($v = b^3$), in θ-solvent ($v = 0$) and in non-solvent ($v = -b^3$) the dependence of size R on number of monomers N is a single power law $R \approx bN^{\nu}$ for $N \gg 1$. The scaling exponent ν adopts three values: $\nu \cong 3/5$ in an athermal solvent, $\nu = 1/2$ in a θ-solvent, and $\nu = 1/3$ in a non-solvent. In good and

Fig. 3.14
The conformation of a single chain in a good solvent (left side) is a self-avoiding walk of thermal blobs while the conformation in a poor solvent (right side) is a collapsed globule of thermal blobs.

Fig. 3.15
End-to-end distance of dilute polymers in various types of solvents, sketched on logarithmic scales. In a θ-solvent the thermal blob size is infinite. For athermal solvent and non-solvent the thermal blob is the size of a single monomer. Good and poor solvents have intermediate thermal blob size (shown here for the specific example of equivalent thermal blobs in good and poor solvent.

poor solvents the dependence follows the ideal chain scaling for polymers (or sections of polymers) smaller than the thermal blob ξ_T. On larger scales, the chain follows the corresponding limiting scaling, with good solvent exponent $\nu \cong 3/5$ for v > 0 and with collapsed globule exponent $\nu = 1/3$ for v < 0. Fig. 3.15 shows that finite length chains have essentially ideal conformations for small values of the excluded volume. Chains have approximately ideal conformations as long as $N < g_T \approx b^6/v^2$ because the net excluded volume interaction in the whole chain is still of smaller magnitude than the thermal energy. Note that Fig. 3.15 suggests the crossover at the thermal blob size is abrupt, while in reality the crossover will be smooth with intermediate effective slopes observed over limited ranges of data.

3.3.2 Flory theory of a polymer in a poor solvent

The scaling result for a polymer in a poor solvent can also be found using Flory theory. The Flory free energy for a polymer chain is given by Eq. 3.19:

$$F \approx kT\left(\frac{R^2}{Nb^2} + v\frac{N^2}{R^3}\right). \tag{3.80}$$

In poor solvent, the excluded volume is negative, indicating a net attraction and the minimum of the free energy of Eq. (3.80) corresponds to $R = 0$. Both entropic and energetic contributions decrease with decreasing R. Such strong collapse of a polymer into a point is unphysical and we need to add a stabilizing term to this free energy.

3.3.2.1 Entropy of confinement

Earlier in this chapter, we have discussed the entropic cost due to confinement of an ideal chain into a cylindrical tube or in a slit between two parallel walls. A similar entropic penalty has to be paid if a chain is confined within a spherical cavity of size $R < bN^{1/2}$. Each compression blob corresponds to a random walk that fills the cavity. Thus, the number of monomers in each compression blob is determined by ideal chain statistics within the blob:

$$g \approx \left(\frac{R}{b}\right)^2. \tag{3.81}$$

The N/g compression blobs of the ideal chain fully overlap for a chain confined in a spherical pore. The free energy cost of confinement within the spherical cavity is of the order of the thermal energy kT per compression blob:

$$F_{\text{conf}} \approx kT\frac{N}{g} \approx kT\frac{Nb^2}{R^2}. \tag{3.82}$$

The entropic part of the free energy, that includes both the penalty for stretching and one for confinement, and is valid for both $R > bN^{1/2}$ and for

$R < bN^{1/2}$, is a simple sum of the stretching and confinement terms:

$$F_{\text{ent}} \approx kT\left(\frac{R^2}{Nb^2} + \frac{Nb^2}{R^2}\right). \tag{3.83}$$

Note that this entropic free energy alone has a minimum at $R = Nb^2$, which is the conformation of an ideal chain.

Adding the excluded volume interaction term, we obtain a total free energy of the chain with three terms:

$$F \approx kT\left(\frac{R^2}{Nb^2} + \frac{Nb^2}{R^2} + v\frac{N^2}{R^3}\right). \tag{3.84}$$

This free energy still has a minimum at $R = 0$. The confinement entropy term is not strong enough to stabilize the collapse of the chain due to excluded volume attraction because $Nb^2/R^2 \ll |v|N^2/R^3$ for $R \to 0$.

3.3.2.2 Three-body repulsion

The stabilization of the collapsing coil comes from other terms of the interaction part of the free energy. The interaction energy per unit volume is an intrinsic property of any mixture, that is often expressed as a virial expansion in powers of the number density of monomers c_n [Eq. (3.8)]. The relevant volume of interest here is the pervaded coil volume R^3. The excluded volume term is the first term in the virial series and counts two-body interactions as vc_n^2. The next term in the expansion counts three-body interactions as wc_n^3, where w is the three-body interaction coefficient:

$$\frac{F_{\text{int}}}{R^3} \approx kT(vc_n^2 + wc_n^3 + \cdots). \tag{3.85}$$

At low concentration, the two-body term dominates the interaction. The three-body term becomes important at higher concentrations and can stabilize the collapse of the globule (since $w > 0$). The interaction free energy within the coil is estimated using the monomer concentration inside the coil $c_n = N/R^3$:

$$F_{\text{int}} \approx kT\left(v\frac{N^2}{R^3} + w\frac{N^3}{R^6}\right). \tag{3.86}$$

The total free energy of the chain is dominated by the interaction terms at higher densities (smaller chain sizes R):

$$F \approx kT\left(\frac{R^2}{Nb^2} + \frac{Nb^2}{R^2} + v\frac{N^2}{R^3} + w\frac{N^3}{R^6}\right)$$

$$\approx kT\left(v\frac{N^2}{R^3} + w\frac{N^3}{R^6}\right) \text{ for } R \ll R_0. \tag{3.87}$$

The globule seeks to minimize this free energy, by balancing the two-body attraction ($v < 0$) and three-body repulsion ($w > 0$) terms:

$$R_{\text{gl}} \approx \left(\frac{wN}{|v|}\right)^{1/3}. \tag{3.88}$$

A typical value of the three-body interaction coefficient for almost symmetric monomers is $w \approx b^6$ leading to the prediction of the globule size identical to that of the scaling approach [Eq. (3.78)]. For the cylindrical Kuhn monomer of length b and diameter d, Eq. (3.11) gives $w \approx (bd)^3$, making the globule size

$$R_{gl} \approx bd \left(\frac{N}{|v|}\right)^{1/3},$$

$$(3.89)$$

and the volume fraction within this globule is proportional to the magnitude of the excluded volume:

$$\phi \approx \frac{Nbd^2}{R_{gl}^3} \approx \frac{|v|}{b^2 d}.$$

$$(3.90)$$

In a non-solvent, $v \approx -b^2 d$ [Eq. (3.16)] and the globule is fully collapsed with volume fraction $\phi \approx 1$ and size $R_{gl} \approx (bd^2 N)^{1/3}$. This state is the result of a dense packing of N monomers, since the volume of the cylindrical Kuhn monomer is bd^2.

3.3.3 Temperature dependence of the chain size

All results for chain size are now written in terms of the excluded volume. To understand how the chain size changes with temperature, we simply need the temperature dependence of the excluded volume. There are two important parts of the Mayer f-function, from which the excluded volume is calculated [Eq. (3.7)]. The first part is the hard-core repulsion, encountered when two monomers try to overlap each other (monomer separation $r < b$). In the hard-core repulsion, the interaction energy is enormous compared to the thermal energy, so the Mayer f-function for $r < b$ is -1:

$$f(r) = \exp\left[-\frac{U(r)}{kT}\right] - 1 \cong -1 \quad \text{for } r < b, \text{ where } U(r) \gg kT. \quad (3.91)$$

The second part is for monomer separations larger than their size $(r > b)$, where the magnitude of the interaction potential is small compared to the thermal energy. In this regime, the exponential can be expanded and the Mayer f-function is approximated by the ratio of the interaction energy and the thermal energy:

$$f(r) = \exp\left[-\frac{U(r)}{kT}\right] - 1 \cong -\frac{U(r)}{kT} \quad \text{for } r > b, \text{ where } |U(r)| < kT. \quad (3.92)$$

The excluded volume v can be estimated using Eq. (3.7) with these two parts of the Mayer f-function:

$$v = -4\pi \int_0^\infty f(r) r^2 \, dr \approx 4\pi \int_0^b r^2 \, dr + \frac{4\pi}{kT} \int_b^\infty U(r) r^2 \, dr$$

$$\approx \left(1 - \frac{\theta}{T}\right) b^3.$$

$$(3.93)$$

Real chains

The first term is the contribution of the hard-core repulsion, and is of the order of the monomer volume b^3. The second term contains the temperature dependence, and the coefficient of $1/T$ defines an effective temperature called the θ-temperature:

$$\theta \approx -\frac{1}{b^3 k} \int_b^\infty U(r) r^2 \, dr. \tag{3.94}$$

Since $U(r) < 0$ in the attractive well, the θ-temperature is positive. This results in a very simple approximate temperature dependence of the excluded volume [Eq. (3.93)]:

$$v \approx \frac{T - \theta}{T} b^3. \tag{3.95}$$

For $T < \theta$ the excluded volume is negative, indicating a net attraction between monomers (poor solvent). For temperatures far below θ, the chain collapses into a dry globule that excludes nearly all solvent (with $v \approx -b^3$) at $\theta - T \approx T$ and Eq. (3.95) does not apply below this temperature. For $T = \theta$ the net excluded volume is zero and the chain adopts a nearly ideal conformation (θ-solvent). $T > \theta$ has a positive excluded volume, resulting in swelling of the coil (good solvent). For $T \gg \theta$, excluded volume becomes independent of temperature ($v \approx b^3$) and such solvents are termed athermal.

The temperature dependence of the radius of gyration, reduced by the radius of gyration at the θ-temperature $R_\theta = b N^{1/2}$, is shown in Fig. 3.16 for both experimental data and Monte-Carlo simulations of chains made of N freely jointed monomers interacting via a **Lennard–Jones potential**:

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \tag{3.96}$$

The abscissa of Fig. 3.16 is proportional to the chain interaction parameter [Eq. (3.22)]:

$$z \approx \frac{v}{b^3} N^{1/2} \approx \frac{T - \theta}{T} N^{1/2}. \tag{3.97}$$

Note that the square of the chain interaction parameter z is equal to the number of thermal blobs in a chain $z^2 \approx N/g_T$.

$$g_T \approx \frac{N}{z^2} \approx \left(\frac{T}{T - \theta}\right)^2. \tag{3.98}$$

The data reduction for R_g/R_θ as a function of chain interaction parameter z in Fig. 3.16 is remarkable for both simulation and experiment. Notice in Fig. 3.16 that the θ-temperature is a *compensation point* where the excluded volume happens to be zero. Below the θ-temperature, the chains are collapsed in poor solvent ($v < 0$), while above the θ-temperature, the coils are swollen in good solvent ($v > 0$).

The relative contraction of chains in poor solvents can be expressed in terms of the chain interaction parameter z [Eqs. (3.78) and (3.97)]:

$$\frac{R}{bN^{1/2}} \approx \frac{b}{|v|^{1/3} N^{1/6}} \approx |z|^{-1/3} \quad \text{for } T < \theta. \tag{3.99}$$
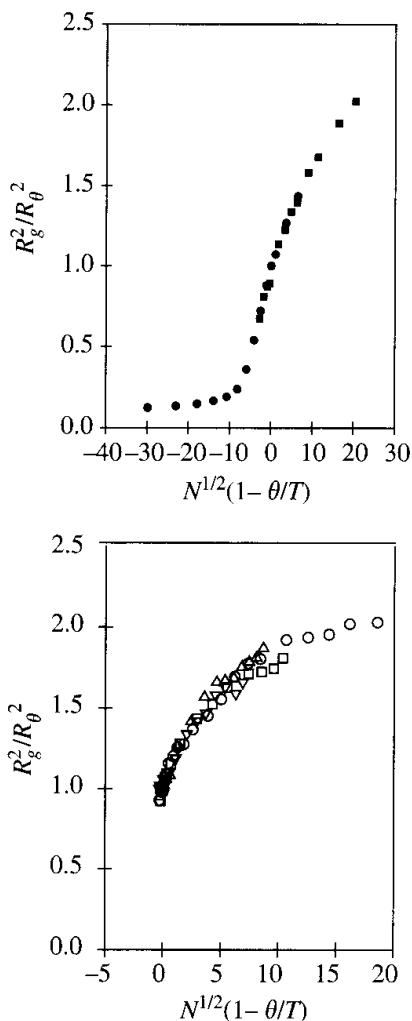
Fig. 3.16

Temperature dependence of radius of gyration in universal form. Upper plot shows Monte-Carlo simulation data on Lennard-Jones chains, with the filled squares from W. W. Graessley *et al.*, *Macromolecules* **32**, 3510 (1999) and the filled circles are courtesy of I. Withers. Lower plot shows experimental data on polystyrene in decalin: open circles have $M_z = 4\,400\,000$ g mol^{-1}, open squares have $M_w = 1\,560\,000$ g mol^{-1}, open triangles have $M_w = 1\,050\,000$ g mol^{-1} and open upside-down triangles have $M_z = 622\,000$ g mol^{-1}, from G. C. Berry, *J. Chem. Phys.* **44**, 4550 (1966).

The relative swelling in good solvents can also be written as a function of the chain interaction parameter z [Eq. (3.21)].

$$\frac{R}{bN^{1/2}} \approx z^{2\nu-1} \quad \text{for } T > \theta. \tag{3.100}$$

The relative swelling is proportional to $z^{0.18}$ for $\nu \cong 0.588$.

3.3.4 Second virial coefficient

The second virial coefficient A_2 is determined from the concentration dependence of osmotic pressure [Eq. (1.76)] or scattered light intensity [Eq. (1.91)] from dilute polymer solutions. A_2 is a direct measure of excluded volume interactions between pairs of chains.

In solvents near the θ-temperature, the thermal blob is larger than the chain ($g_T > N$ meaning $|z| < 1$ or $|T - \theta|/T < N^{-1/2}$) and the excluded volume interactions are weak. The interaction energy of two overlapping chains is less than the thermal energy kT, so chains can easily interpenetrate each other. In this limit, monomers interact directly and A_2 *is proportional to the excluded volume* v of a Kuhn monomer. The second virial coefficient of Eqs (1.76) and (1.91) has units of $m^3 \, mol \, kg^{-2}$, making the relation

$$v = \frac{2M_0^2}{\mathcal{N}_{Av}} A_2 \quad \text{for } \left|\frac{T-\theta}{T}\right| < N^{-1/2}, \tag{3.101}$$

as will be derived in Chapter 4 [see Eq. (4.72)]. Using Eq. (3.97), A_2 can be written in terms of the chain interaction parameter z:

$$A_2 \approx \frac{\mathcal{N}_{Av} v}{M_0^2} \approx \frac{\mathcal{N}_{Av} b^3}{M_0^{3/2}} \frac{z}{M^{1/2}} \quad \text{for } |z| < 1. \tag{3.102}$$

For good solvents ($z > 1$), chains repel each other strongly and do not interpenetrate. The volume excluded by a chain is of the order of its pervaded volume R^3 and the molar mass of the chain is M:

$$\frac{A_2 M^2}{\mathcal{N}_{Av}} \approx R^3 \quad \text{for } \frac{T-\theta}{T} > N^{-1/2}. \tag{3.103}$$

Using Eq. (3.100) for the chain size R allows the second virial coefficient in good solvent to be determined:

$$A_2 \approx \frac{\mathcal{N}_{Av}}{M^2} R^3 \approx \frac{\mathcal{N}_{Av} b^3}{M_0^{3/2}} \frac{z^{6\nu-3}}{M^{1/2}} \quad \text{for } z > 1. \tag{3.104}$$

The second virial coefficient is proportional to $z^{0.53}$ for exponent $\nu \cong 0.588$. Combining Eqs (3.102) and (3.104), we see that both θ-solvent and good solvent should have $A_2 M^{1/2}$ a function of chain interaction parameter z alone:

$$\frac{A_2 M^{1/2} M_0^{3/2}}{\mathcal{N}_{Av} b^3} = f(z) \approx \left\{ \begin{array}{ll} z & |z| < 1 \\ z^{6\nu-3} & z > 1 \end{array} \right\}. \tag{3.105}$$

The success of this functional form is demonstrated in Fig. 3.17 for polystyrene of various molar masses in decalin from slightly below θ to

Real chains
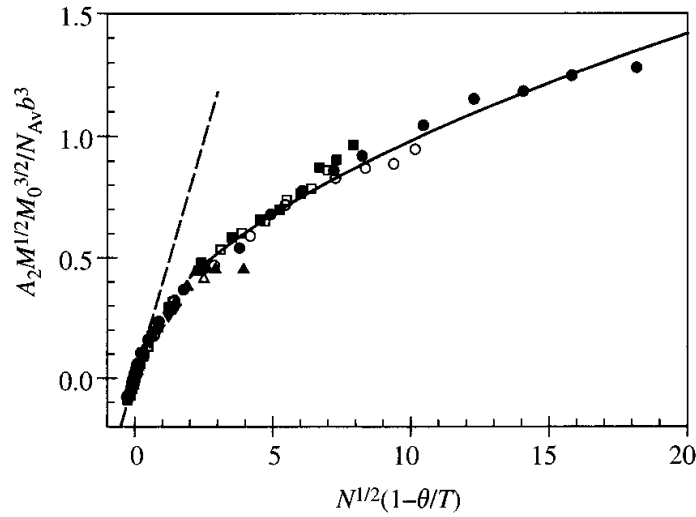
Fig. 3.17
Universal plot of second virial coefficient for linear polystyrenes in decalin (filled circles have
$M_w = 4\,400\,000$ g mol^{-1}, open circles have $M_w = 1\,560\,000$ g mol^{-1}, filled squares have
$M_w = 1\,050\,000$ g mol^{-1}, open squares have $M_w = 622\,000$ g mol^{-1}, filled triangles have
$M_w = 186\,000$ g mol^{-1}, open triangles have $M_w = 125\,000$ g mol^{-1} and filled inverted triangles
have $M_w = 48\,200$ g mol^{-1}. Data from G. C. Berry, *J. Chem. Phys.* **44**, 4550 (1966).

$\theta + 100\,K$. The collapse of the data is superb. The solid curve is the large
z branch of Eq. (3.105), $0.29\,[N^{1/2}(1 - \theta/T)]^{6\nu - 3}$. The slope of the dashed
line drawn in Fig. 3.17 is 0.39. The crossover between these two branches
occurs when there is a single thermal blob per chain $(N = g_T)$. Using
Eq. (3.98) allows the second virial coefficient to be written in terms of the
number of thermal blobs per chain N/g_T.

$$\frac{A_2 M^{1/2} M_0^{3/2}}{\mathcal{N}_{Av} b^3} \cong 0.20 \begin{Bmatrix} (N/g_T)^{1/2} & N < g_T \\ (N/g_T)^{0.264} & N > g_T \end{Bmatrix}. \tag{3.106}$$

This identifies the prefactors in Eq. (3.98)

$$g_T \cong 0.25 \left(\frac{T}{T - \theta}\right)^2, \tag{3.107}$$

and in Eq. (3.95)

$$\frac{v}{b^3} \cong 0.78 \frac{T - \theta}{T} \cong \frac{0.39}{\sqrt{g_T}}. \tag{3.108}$$

Examples of excluded volume and numbers of Kuhn monomers per
thermal blob are given in Table 3.1.

Indeed, data on the temperature dependence of second virial coefficient
for a variety of polymer–solvent combinations and from computer simul-
ation show that Eq. (3.106) can be written as a simple crossover function:

$$\frac{A_2 M^{1/2} M_0^{3/2}}{\mathcal{N}_{Av} b^3} = 0.20 \left[\left(\frac{g_T}{N}\right)^{1.32} + \left(\frac{g_T}{N}\right)^{0.70}\right]^{-0.38}. \tag{3.109}$$

Table 3.1 Number of Kuhn monomers per thermal blob and excluded volume of a Kuhn monomer for polystyrene in various solvents

Polymer/solvent	T (°C)	$T - \theta$ (K)	g_T	v/b^3	v (Å^3)
Polystyrene/cyclohexane	50	15	120	0.036	210
Polystyrene/cyclohexane	70	35	24	0.079	460
Polystyrene/decalin	115	100	4	0.21	1200
Polystyrene/benzene	25	$\sim 200^a$	0.6	0.5	3000

^{a} For benzene (and most other good solvents) the θ-temperature is far below all measurement temperatures and use of Eq. (3.107) to extrapolate to the θ-temperature has considerable error.

Measurement of the temperature dependence of second virial coefficient A_2 for polymers with known molar mass M and Kuhn length b allows estimation of the number of thermal blobs per chain N/g_T using Eq. (3.109).

3.4 Distribution of end-to-end distances

We have seen numerous examples of the qualitative difference in properties between ideal and real chains with excluded volume interactions. It is therefore not surprising that the distribution of end-to-end vectors of real chains is significantly different from the Gaussian distribution function of ideal chains [Eq. (2.86)].

Relative probabilities to find chain ends at distances much larger than the average end-to-end distance are related to the free energy penalty due to chain elongation [see Problem 3.15 and Eq. (3.42):

$$F \approx kT \left(\frac{R}{\sqrt{\langle R^2 \rangle}} \right)^\delta, \tag{3.110}$$

where the exponent $\delta = 1/(1 - \nu)$ is related to the exponent ν of the root-mean-square end-to-end distance of the chain:

$$\sqrt{\langle R^2 \rangle} \approx bN^\nu. \tag{3.111}$$

For ideal chains, $\nu = 1/2$ and $\delta = 2$ [see Eq. (3.35)], while for real chains in a good solvent $\nu \cong 0.588$ and $\delta \cong 2.43$ [see Eq. (3.36)]. The tail of the probability distribution function for end-to-end distances is determined by the Boltzmann factor arising from this free energy penalty [Eq. (3.110)]

$$P(N, R) \sim \exp\left(-\frac{F}{kT} \right) \sim \exp\left[-\alpha \left(\frac{R}{\sqrt{\langle R^2 \rangle}} \right)^\delta \right] \quad \text{for } R > \sqrt{\langle R^2 \rangle}, \tag{3.112}$$

where α is a numerical coefficient of order unity. For ideal chains ($\delta = 2$) this leads to the Gaussian distribution function [Eq. (2.86)]. For real chains, a faster decay of the distribution function is expected due to the higher power $\delta \cong 2.43$ in the exponential:

$$P(N, R) \sim \exp\left[-\alpha \left(\frac{R}{\sqrt{\langle R^2 \rangle}} \right)^{2.43} \right] \quad \text{for } R > \sqrt{\langle R^2 \rangle}. \tag{3.113}$$

Real chains

Another major difference between ideal and real chains is the reduced probability of two ends of a real chain to be near each other due to excluded volume repulsion of these and neighboring monomers. Recall from Section 2.5 that the probability of finding one end of an ideal chain within a small spherical shell of volume $4\pi R^2\,dR$ around the other end is proportional to the volume of this shell [see Eq. (2.86) for $R \ll bN^{1/2}$]. This probability is significantly reduced for real chains by an additional factor

$$P(N, R) \sim \left(\frac{R}{\sqrt{\langle R^2 \rangle}}\right)^g \quad \text{for } R \ll \sqrt{\langle R^2 \rangle}, \qquad (3.114)$$

due to excluded volume repulsion between sections of the polymer, as they approach each other. The exponent $g = 0$ for ideal chains because there is no reduction of probabilities for small end-to-end distances. For real chains, the exponent $g \cong 0.28$ in three dimensions and $g = 11/24$ in two dimensions.

By combining the two limits [Eqs. (3.113) and (3.114)], the distribution function of normalized end-to-end distances can be constructed:

$$P(x) \sim x^g \exp\left(-\alpha x^\delta\right), \qquad (3.115)$$

where

$$x = \frac{R}{\sqrt{\langle R^2 \rangle}}. \qquad (3.116)$$

An approximate expression for the three-dimensional distribution function for real chains results:

$$P(x) \cong 0.278 x^{0.28} \exp\left(-1.206 x^{2.43}\right) \quad \text{real.} \qquad (3.117)$$

For ideal chains, the corresponding function is Gaussian:

$$P(x) = \left(\frac{3}{2\pi}\right)^{3/2} \exp\left(-1.5 x^2\right) \quad \text{ideal.} \qquad (3.118)$$

The two functions are compared in Fig. 3.18. Note the dramatic difference between them. Real chains in an athermal solvent rarely have ends in close proximity. The probability to find chain ends within relative distance dx of x is $4\pi x^2 P(x)\,dx$. The coefficients of the distributions of end-to-end distances are chosen so that they are normalized:

$$\int P(x)\,d^3x = \int_0^\infty P(x) 4\pi x^2\,dx = 1. \qquad (3.119)$$
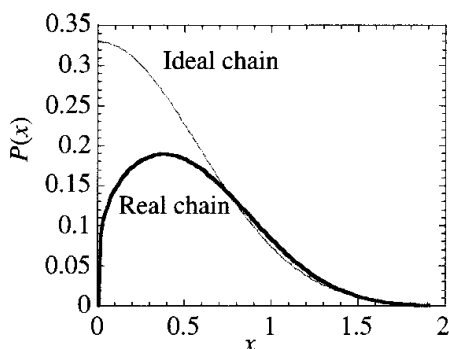
Their second moment is also equal to unity

$$\int x^2 P(x)\,d^3x = \int_0^\infty x^2 P(x) 4\pi x^2\,dx = 1, \qquad (3.120)$$

due to the definition of the relative distance x [Eq. (3.116)].

Fig. 3.18

Distribution function $P(x)$ of normalized end-to-end distances $x = R/\sqrt{\langle R^2 \rangle}$. Thin curve, ideal chain; thick curve, real chain.
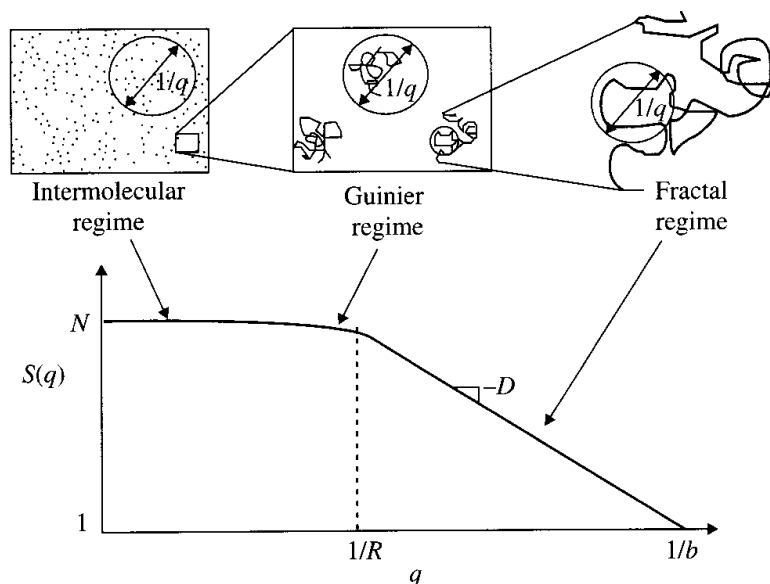
3.5 Scattering from dilute solutions

The size and shape of a polymer chain in dilute solution is best studied using scattering methods. Each monomer absorbs the incident radiation

and re-emits it in all directions. If there is contrast between monomers and solvent they can be distinguished. The scattered intensity at a given scattering wavevector is determined by this contrast and by the coherence of the re-emitted radiation from pairs of monomers. The **scattering function** $S(\vec{q})$ is defined as a sum over all pairs of n monomers in the scattering volume,

$$S(\vec{q}) = \frac{1}{n}\sum_{j=1}^{n}\sum_{k=1}^{n}\langle\exp[-i\vec{q}\cdot(\vec{r}_j - \vec{r}_k)]\rangle, \qquad (3.121)$$

where $\vec{q}$ is the scattering wavevector [Eq. (2.131)] and $\vec{r}_j$ is the position vector of jth monomer. This scattering function is simply a dimensionless version of the ratio of scattering intensity at wavevector $\vec{q}$ and concentration. The isotropic scattering function from dilute solution is sketched in Fig. 3.19. At large wavevectors $q \gg 1/R$ for each monomer j the sum over k has contribution of order unity from each of the n_q monomers within distance $1/q$ from monomer j since for $\vec{q}\cdot(\vec{r}_j - \vec{r}_k) < 1$ the exponential is close to one. On the other hand, the contribution from monomers further away from monomer j averages to zero. The scattering function at large wavevectors is

$$S(q) \approx \frac{1}{n}\sum_{j=1}^{n}n_q = n_q \quad \text{for } q \gg 1/R \qquad (3.122)$$

where n_q is the number of monomers in the volume $1/q^3$. The number of monomers n_q is related to the size of the chain segment $1/q$ through the fractal dimension of the chain $\mathcal{D}$:

$$S(q) \approx n_q \approx (qb)^{-\mathcal{D}} \quad \text{for } 1/R < q < 1/b. \qquad (3.123)$$

This power law extends from the monomer size b to the size of the chain R, provided that the entire chain has the same fractal dimension $\mathcal{D}$. Scattering on such small scales is dominated by **intra-molecular scattering** from

monomers inside individual coils and is related to the pair correlation function within the coil [Eq. (2.123)]:

$$g(r) \approx \frac{m}{r^3} \sim r^{\mathcal{D}-3}. \qquad (3.124)$$

For real chains in an athermal solvent, $\mathcal{D} = 1/\nu \cong 1.7$, so $S(q) \sim q^{-1.7}$ and $g(r) \sim r^{-1.3}$ within the coil.

For smaller wavevectors $q < 1/R$, the number of monomers n_q within distance $1/q$ from monomer j saturates at the number of monomers in the chain N. The exact form of the scattering function in this Guinier regime enables calculation of the radius of gyration R_g [Eq. (2.152)]. In both the Guinier and fractal regimes, the scattering comes from pairs of monomers on the same chain and the scattering function is proportional to the form factor:

$$S(q) = NP(q) \quad \text{for } q > \left(\frac{c_n}{N}\right)^{1/3}. \qquad (3.125)$$

The **inter-molecular scattering** dominates the scattering function at wavevectors q smaller than the reciprocal distance between chains $(c_n/N)^{1/3}$, where c_n is the number density of monomers in solution. The inter-molecular regime is controlled by concentration fluctuations arising from the difference in the number of chains in volumes $1/q^3$. Assuming there are no interactions between chains (strictly valid only in very dilute solutions), the mean-square fluctuation in the number of chains in the volume $1/q^3$ is of the order of the average number $n_q/N \approx c_n/(Nq^3)$. The fluctuation in the number of monomers in volumes of size $1/q^3$ is $\sqrt{\langle(\delta n_q)^2\rangle} = N\sqrt{c_n/(Nq^3)}$. The scattering function is the mean-square fluctuation in the number of monomers in the volume $1/q^3$ normalized by the number of monomers n_q in this volume:

$$S(q) = \frac{\langle(\delta n_q)^2\rangle}{n_q} = \frac{N^2 c_n/(Nq^3)}{Nc_n/(Nq^3)} = N \quad \text{for } q \ll \left(\frac{c_n}{N}\right)^{1/3}. \qquad (3.126)$$

Note that this value matches the low-q end of the fractal regime. It is hardly surprising that the scattering function contains information about the chain length, since in Chapter 1 we demonstrated how light scattering can be used to determine molar mass from the low concentration limit of $R_\theta/(Kc)$, where R_θ is Rayleigh ratio [Eq. (1.87)], K is the optical constant [Eq. (1.89)], and c is mass concentration. The scattering function for light scattering is related to the Rayleigh ratio as

$$S(q) = \frac{R_\theta}{KcM_0}, \qquad (3.127)$$

where M_0 is the molar mass of a monomer. We give this relation for light scattering for completeness, but scattering inside the polymer coils is usually measured using neutrons and X-rays, which extend the range of wavevectors to 1 nm^{-1}. The scattering function from all of these scattering experiments is the same, with the prefactor relating the scattering function to scattered intensity being specific to the type of radiation used.

3.6 Summary of real chains

Real chains have interactions between monomers. If the attraction between monomers just balances the effect of the hard core repulsion, the net excluded volume is zero ($v = 0$) and the chain will adopt a nearly ideal conformation (see Chapter 2):

$$R_0 = bN^{1/2} \quad \text{for } \theta\text{-solvent.} \tag{3.128}$$

Such a situation with zero net excluded volume is called the θ-condition, corresponding to a particular θ-temperature for a given solvent.

If the attraction between monomers is weaker than the hard-core repulsion, the excluded volume is positive and the chain swells. This corresponds to a good solvent at a temperature above the θ-temperature, and the coil size is larger than the ideal size:

$$R_F \approx b\left(\frac{v}{b^3}\right)^{2\nu-1} N^{\nu} \approx b\left(\frac{v}{b^3}\right)^{0.18} N^{0.588} \quad \text{for good solvent.} \tag{3.129}$$

The chain conformation is a self-avoiding walk of thermal blobs, whose size decreases as temperature is raised.

In an athermal solvent, the monomer–solvent energetic interaction is identical to the monomer–monomer interaction. This makes the net interaction between monomers zero, leaving only the hard core repulsion between monomers. The excluded volume is independent of temperature ($v \approx b^3$), and the chain is a self-avoiding walk of monomers:

$$R \approx bN^{\nu} \approx bN^{0.588} \quad \text{for athermal solvent.} \tag{3.130}$$

If the attraction between monomers is stronger than the hard-core repulsion, the excluded volume is negative and the chain collapses. This occurs below the θ-temperature, and corresponds to a poor solvent. In a poor solvent, the polymer is in a collapsed globular conformation corresponding to a dense packing of thermal blobs. The size of a globule is smaller than the ideal size:

$$R_{gl} \approx |v|^{-1/3} b^2 N^{1/3} \quad \text{for poor solvent.} \tag{3.131}$$

A chain in a poor solvent collapses into a globule with significant amounts of solvent inside. Most chains agglomerate with other chains and precipitate from solution. Only a very small number of polymers remain in the solvent-rich phase of a poor solvent in a globular conformation described by Eq. (3.131). Far below the θ-temperature, the attraction dominates completely and the excluded volume $v \approx -b^3$. This limit is called a non-solvent, and an individual chain in that solvent would have a fully collapsed conformation:

$$R \approx bN^{1/3} \quad \text{for non-solvent.} \tag{3.132}$$

In this case, most chains precipitate from solution into a melt excluding nearly all solvent, and the chains then adopt ideal conformations to maximize their entropy.

The good solvent and poor solvent results only apply to chains that are sufficiently long. Short chains with degree of polymerization less than the number of monomers in a thermal blob remain ideal, as depicted in Fig. 3.15.

Several examples were given of scaling models that utilize blobs to separate regimes of chain conformation. The common idea in these scaling models is that, on the smallest length scales (inside the blobs), there is not enough cumulative interaction to alter the chain conformation. On length scales larger than the blob size, the cumulative interactions become larger than the thermal energy, and can then modify the conformation of the chain of blobs. Since the cumulative interaction energy of each blob is roughly the thermal energy kT, the total interaction energy can be conveniently estimated as kT per blob.

The free energy of stretching a real linear chain in a good solvent has a stronger dependence on size R than the quadratic dependence of the ideal chain:

$$F \approx kT \left(\frac{R}{R_F} \right)^{1/(1-\nu)} \approx kT \left(\frac{R}{R_F} \right)^{2.43}. \tag{3.133}$$

The stretching force for a real chain increases non-linearly with elongation:

$$\frac{fb}{kT} = \frac{b}{kT} \frac{\partial F}{\partial R} \approx \left(\frac{R}{Nb} \right)^{\nu/(1-\nu)} \approx \left(\frac{R}{Nb} \right)^{1.43}. \tag{3.134}$$

The free energy of confining a real linear chain in a good solvent either into a slit of spacing D or to a cylindrical pore of diameter D is larger than for an ideal chain because the real chain has repulsive interactions:

$$F \approx kT \left(\frac{R_F}{D} \right)^{1/\nu} \approx kT \left(\frac{R_F}{D} \right)^{1.7}. \tag{3.135}$$

Excluded volume changes with temperature in the vicinity of the θ-temperature:

$$v \approx b^3 \left(\frac{T - \theta}{T} \right). \tag{3.136}$$

Good solvents typically have $T \gg \theta$, and their θ-temperature is not accessible because the solvent crystallizes at much higher temperatures. Similarly, θ-solvents cannot usually be heated far enough above the θ-temperature to reach the athermal limit because the solvent will boil at a lower temperature.

Problems

Section 3.1

3.1 (i) Taking the volume of a cylindrical Kuhn monomer to be bd^2, derive an expression for the cylindrical monomer diameter d in terms of the characteristic ratio, molar mass per backbone bond, melt density, Kuhn length b and bond angle θ.

(ii) Using the melt density of polyethylene $\rho = 0.784$ g cm^{-3} and the melt density of polystyrene $\rho = 0.784$ g cm^{-3}, along with the data of Table 2.1 for C_∞ and b, calculate the diameter of the Kuhn cylindrical monomer for these two polymers.

3.2 Consider the excluded volume interaction between hard spheres of radius R.

(i) What is the shortest possible distance between their centres?

(ii) What is the interaction potential between these spheres?

(iii) Demonstrate that the excluded volume of hard spheres is eight times larger than the volume v_0 a sphere:

$$v = \frac{32\pi}{3} R^3 = 8v_0.$$

3.3 Consider the excluded volume interaction between spherical particles with effective pairwise interaction potential

$$U(r) = \left\{ \begin{array}{ll} \infty & \text{for } r \leq 2R \\ -kT_0(2 - r/(2R)) & \text{for } 2R \leq r \leq 4R \\ 0 & \text{for } r > 4R \end{array} \right\},$$

where kT_0 is the strength of the attractive potential with $T_0 = 100$ K.

(i) Calculate the excluded volume of these particles.

(ii) Plot the dimensionless excluded volume v/R^3 as a function of temperature and determine the θ-temperature of these particles.

3.4 Consider two cylindrical rods of length b and diameter d with $b \gg d$. Fix the centre of one of the rods at the origin of the coordinate system, pointing in the x direction.

(i) Estimate the volume excluded for the second rod if it is fixed to always point in the y direction (perpendicular rods).

(ii) Estimate the volume excluded for the second rod if it is fixed to always point in the x direction (parallel rods).

(iii) How do you expect the excluded volume to change at different fixed angles between the two rods?

3.5 Consider a linear polymer chain with N monomers of length b, restricted to the air–water interface (two-dimensional conformations). Repeat the Flory theory calculation and demonstrate that the size R of the chain as a function of the 'excluded area' a per monomer (two-dimensional analogue of excluded volume v) is

$$R = a^{1/4}b^{1/2}N^{3/4}. \tag{3.137}$$

Compare the size of this chain at the interface to that in the bulk for parameters $N = 1000$, $b = 3$ Å, $a = 7.2$ Å^2, $v = 21.6$ Å^3.

3.6 Consider a randomly branched polymer in a dilute solution. Let us assume that the radius of gyration for this polymer in an ideal state (in the absence of

excluded volume interactions) is

$$R_0 = bN^{1/4},$$

where b is the Kuhn monomer size and N is the number of Kuhn monomers. Use a Flory theory to determine the size R of this randomly branched polymer in a good solvent with excluded volume v. What is the size R of a randomly branched polymer with $N = 1000$, $b = 3$ Å, $v = 21.6$ Å^3? Compare this size to the size of a linear chain with the same degree of polymerization in the same good solvent and in θ-solvent.

3.7 Using the results of Problem 3.6, calculate the overlap volume fraction for the three cases:

(i) randomly branched monodisperse polymer in good solvent.
(ii) linear chain in good solvent.
(iii) linear chain in θ-solvent.

3.8 Consider a randomly branched polymer with N monomers of length b. The polymer is restricted to the air–water interface and thus assumes a two-dimensional conformation. The ideal size of this polymer R_0 in the absence of excluded volume interactions is

$$R_0 = bN^{1/4}.$$

(i) Repeat the Flory theory calculation to determine the size R of the branched polymer at the interface as a function of the 'excluded area' a per monomer (two-dimensional analogue of the excluded volume v). degree of polymerization N and monomer length b.
(ii) Calculate the size of the branched polymer with $N = 1000$, $b = 3$ Å, $a = 7.2$ Å^2 at the air–water interface.
(iii) Calculate the surface coverage (number of monomers per square Angstrom) at overlap for this randomly branched polymer at the air–water interface in good solvent.
(iv) How much higher is the surface coverage at the overlap of randomly branched chains with $N = 100$, $b = 3$ Å, $a = 7.2$ Å^2 at the air–water interface, compared with $N = 1000$?

3.9 Consider a linear polymer chain with $N = 400$ Kuhn monomers of Kuhn length $b = 4$ Å in a solvent with θ-temperature of $27\,^\circ$C. The mean-field approximation of the interaction part of the free energy for a chain of size R is

$$F_{\text{int}} \approx kTR^3 \left[v\left(\frac{N}{R^3}\right)^2 + w\left(\frac{N}{R^3}\right)^3 + \cdots \right],$$

where the excluded volume of a monomer is

$$v \approx \left(1 - \frac{\theta}{T}\right) b^3,$$

and $w \approx b^6$ is the three-body interaction coefficient.

(i) Use Flory theory to estimate the size of the chain swollen at the θ-temperature due to three-body repulsion.
(ii) For what values of the excluded volume v does the two-body repulsion dominate over the three-body repulsion? Is the chain almost ideal or swollen if the two interactions are of the same order of magnitude?
(iii) For what values of temperature T does the two-body repulsion dominate over the three-body repulsion?

(iv) Use Flory theory to estimate the size of the chain swollen at 60 °C due to excluded volume repulsion (ignore the three-body repulsion).

(v) Estimate the overlap volume fraction ϕ^* of the chain at 60 °C.

(vi) What is the number of Kuhn monomers in the largest chain that stays ideal at 60 °C?

3.10 Consider an oligomer with $N = 3$ bonds occupying four lattice sites on a two-dimensional square lattice with lattice constant b. One end of the oligomer is fixed at the origin of the lattice.

(i) How many different conformations would such an oligomer have if it *can* occupy the same lattice site many times (simple random walk)?

(ii) How many different conformations would such an oligomer have if it *cannot* occupy the same lattice site (self-avoiding walk)?

(iii) Find the root-mean-square end-to-end distance of the oligomer for the first case.

(iv) Find the root-mean-square end-to-end distance of the oligomer for the second case.

3.11 Why is there no temperature dependence of the excluded volume in an athermal solvent?

3.12 If the monomer–solvent interaction potential is identical to the monomer–monomer interaction potential, the solvent is called:

(i) good,

(ii) θ,

(iii) athermal.

Explain your answer.

3.13 (i) Construct a Flory theory for the free energy of a polyelectrolyte chain consisting of N monomers of length b and net charge of the chain $Q = efN$, where f is the fraction of Kuhn monomers bearing a charge.

Hint: The electrostatic energy of the chain is $Q^2/(\epsilon R)$, where ϵ is the dielectric constant of the solvent and R is the size of the chain.

(ii) Show that the size of the chain at temperature T is

$$R \approx Nbf^{2/3}\left(\frac{l_B}{b}\right)^{1/3},$$

where the Bjerrum length is defined as $l_B \equiv e^2/(\epsilon kT)$.

3.14 (i) What is the relation of the fourth virial coefficients of spherical ($v_{4,s}$) and cylindrical ($v_{4,c}$) monomers if there are b/d spheres per cylinder?

(ii) What is the relation of the kth virial coefficients of spherical ($v_{k,s}$) and cylindrical ($v_{k,c}$) monomers?

Section 3.2

3.15 Calculate the free energy $F(N, R_f)$ and the force f for stretching a chain with an arbitrary scaling exponent ν in the dependence of the end-to-end distance on the number of monomers $R = bN^{\nu}$.

3.16 Calculate the free energy for compressing a real chain into a cylindrical tube with diameter D. Assume an arbitrary scaling exponent ν in the dependence of end-to-end distance of the chain on the number of monomers $R = bN^{\nu}$.

Real chains

3.17 Calculate the free energy for squeezing a real chain between parallel plates into a slit of width D. Assume an arbitrary scaling exponent ν in the dependence of the end-to-end distance of the chain on the number of monomers $R = bN^{\nu}$.

3.18 Calculate the thickness ξ_{ads} of the adsorbed layer for a polymer with N monomers of size b. The interaction energy of a monomer in contact with the (planar) surface is $-\delta KT$. Assume an arbitrary scaling exponent ν in the dependence of end-to-end distance of the chain on the number of monomers $R = bN^{\nu}$.

3.19 Scaling theory of two-dimensional adsorption.
Consider a linear chain confined to an air–water interface. The attraction of each monomer at the contact line between the edge of the interface and the walls of the container is $-\delta kT$.

   (i) Estimate the thickness and length of the ideal adsorbed chain of N Kuhn monomers with Kuhn length b.

   (ii) Calculate the energy of adsorption of the ideal polymer of part (i) to the contact line.

   (iii) Estimate the thickness and length of the real adsorbed chain of N Kuhn monomers with Kuhn length b. Recall that the unperturbed size of the real chain confined to the air–water interface in good solvent is $R \approx bN^{3/4}$ [Eq. (3.54)].

   (iv) Calculate the energy of adsorption of the real polymer of part (iii) to the contact line.

3.20 Flory theory of adsorption from a two-dimensional interface onto a one-dimensional line.

Consider a real linear chain confined to an air–water interface. The attraction of a monomer at the contact line between the edge of the interface and the walls of the container is $-\delta kT$.

Calculate the thickness ξ_{ads} of the adsorbed real chain and the energy of adsorption using Flory theory. Recall that the unperturbed size of the real chain confined to the air–water interface in good solvent is given by Eq. (3.54).

3.21 Consider a polymer chain consisting of N Kuhn monomers of length b, adsorbed from a good solvent onto a solid substrate. A monomer in contact with the surface has interaction energy $-\delta kT$.

   (i) What is the thickness ξ_{ads} of the adsorbed chain?

   (ii) What is the size of the adsorption blob if $N = 1000$, $b = 3\,\text{Å}$, and $\delta = 0.4$?

Suppose that one of the ends of the adsorbed chain is attached to the tip of an atomic force microscope and is pulled away from the surface (still in a good solvent) with force f.

   (iii) What is the minimal force f required to pull the chain away from the surface at room temperature?

   (iv) What would be the minimal force f required to pull the chain away from the surface if the tip of the atomic force microscope were attached to a middle monomer rather than to the end monomer?

   (v) Would the minimal force required to pull the chain away from the surface in a θ-solvent be smaller or larger (as compared to a good solvent) for the same attractive energy $-\delta kT$? Explain your answer.

3.22 Consider a real chain adsorbed at a surface with an excess free energy gain per monomer δkT. Assume that the monomer concentration decreases as a power law of the distance z from the surface

$$c(z) = c(0)\left(\frac{b}{z}\right)^{a} \quad \text{for } 0 < z < \xi_{ads},$$

where exponent $0 < a < 1$ and ξ_{ads} is the thickness of the adsorbed chain.

(i) Calculate the fraction of monomers within distance b of the surface. These are the monomers that lower their energy by favourable contacts with the surface.

(ii) Construct a modified Flory theory for the adsorption of a real chain and estimate the thickness ξ_{ads} of the adsorbed chain as a function of the excess free energy gain per monomer $\delta k T$. Ignore the effects of the density profile $c(z)$ on the confinement free energy penalty.

3.23 The effective interaction between each monomer and an adsorbing surface is

$$W(z) = -kT \frac{b^3}{z^3} A,$$

where A is the **Hamaker constant** of the polymer–surface interaction. Consider an ideal chain adsorbed at the surface. Find the relation between the free energy gain per contact $- \delta k T$ and the effective Hamaker constant A.

Section 3.3

3.24 Calculate the force needed to stretch a chain, of $N = 1000$ Kuhn monomers with Kuhn length $b = 5 \text{Å}$ in a good solvent with excluded volume $v = 37.5 \text{Å}^3$, by a factor of 4 from its unperturbed root-mean-square end-to-end distance at room temperature.

3.25 Consider a chain of N Kuhn monomers with Kuhn length b in a good solvent with excluded volume v confined between parallel plates in a slit of width D.

(i) What is the size of a thermal blob and the number of monomers in a thermal blob?

(ii) What is the size of a compression blob?

(iii) What is the number of monomers in a compression blob? Note: Be careful with respect to relative sizes of compression and thermal blobs.

(iv) What is the free energy of confinement of the chain in a slit?

(v) At what thickness of the slit D does the free energy change form between real and ideal chain expressions?

(vi) Estimate the value of this crossover thickness D for a chain with $N = 1000$ Kuhn monomers with Kuhn length $b = 5 \text{Å}$ in a good solvent with excluded volume $v = 20 \text{Å}^3$.

3.26 Consider a randomly branched polymer in a dilute solution. The ideal size of this polymer, R_0, in the absence of excluded volume interactions is

$$R_0 = bN^{1/4},$$

where b is the monomer size and N is the degree of polymerization.

(i) Use the scaling theory to determine the size R of this randomly branched polymer in a good solvent with excluded volume v.

(ii) What is the number of monomers in a thermal blob for this randomly branched polymer as a function of excluded volume v and monomer size b. How does it compare to the similar expression for the number of monomers in a thermal blob in linear polymers?

(iii) What is the size, ξ_T, of a thermal blob for a randomly branched polymer? How does it compare to the similar expression for the size of the thermal blob in linear polymers.

Hint: Recall that the cumulative energy of all excluded volume interactions inside a thermal blob is equal to kT.

(iv) What is the size of a randomly branched polymer with $N = 1000$, $b = 3\,\text{Å}$, in a good solvent with $v = 2.7\,\text{Å}^3$?

(v) What is the size of a linear chain for the same set of parameters?

(vi) What are the size and the number of monomers in the largest randomly branched polymer that stays ideal for monomer length $b = 3\,\text{Å}$, and excluded volume $v = 2.7\,\text{Å}^3$? (*Hint*: Thermal blob.)

(vii) What are the size and the number of monomers in the largest linear polymer that stays ideal for monomer length $b = 3\,\text{Å}$, and excluded volume $v = 2.7\,\text{Å}^3$? (*Hint*: Thermal blob.)

3.27 Assume the simple approximation for a temperature dependence of the excluded volume:

$$v = \left(1 - \frac{\theta}{T}\right) b^3.$$

Consider a chain with degree of polymerization $N = 1000$ and monomer size $b = 3\,\text{Å}$ in a solvent with θ-temperature of $30\,°C$.

(i) What would be the chain size at temperatures: $T = 10$, 30, and $60\,°C$?

(ii) Sketch the temperature dependence of the size of this polymer.

(iii) What is the degree of polymerization of the largest chain that stays ideal at $T = 60\,°C$ (*Hint*: Thermal blob)?

(iv) Estimate the degree of polymerization of the largest chain that dissolves in the solvent at $T = 10\,°C$ (*Hint*: Thermal blob)?

3.28 Use the following light scattering data for the temperature dependence of the second virial coefficient of a linear poly(methyl methacrylate) with $M_w = 2\,380\,000\,\text{g mol}^{-1}$ in a water/t-butyl alcohol mixture to determine the temperature dependence of excluded volume, assuming the Kuhn length of PMMA is $17\,\text{Å}$:

T (°C)	37.0	38.0	40.0	43.8	50.0	55.8
$10^5\,A_2$ (cm^3 mol g^{-2})	−6.4	−3.4	−0.4	0.5	3.5	4.1

(i) Estimate the excluded volume at each of the six temperatures.

(ii) Estimate the θ-temperature from these data.

(iii) To measure the excluded volume of this polymer/solvent system at lower temperature, should a higher or lower molar mass sample be studied?

Data from M. Nakata, *Phys. Rev. E* **51**, 5770 (1995).

3.29 Derive an equation for the second virial coefficient in a solution of collapsed globules below their θ-temperature, in terms of the number of Kuhn monomers per chain N, the Kuhn monomer size b and the reduced temperature $(\theta - T)/T$. Can this second virial coefficient be related to the chain interaction parameter of Eq. (3.97)?

3.30 Determine the relation between the chain interaction parameter z [defined in Eq. (3.22)] and the number of thermal blobs per chain N/g_T.

Section 3.4

3.31 Polymerization of ring polymers.

Ring polymers are synthesized by linking two reactive ends of linear polymers in dilute solution. The cyclization probability can be defined as the

probability of two ends of a chain being found within monomeric distance b of each other.

(i) What are the cyclization probabilities of N-mers in θ-solvent and in good solvent? What is the ratio of these probabilities for $N = 100$?

(ii) Are the resulting ring polymers obtained by cyclization in θ-solvent and good solvent statistically equivalent? In other words will these rings have the same size if they are placed in the same solvent? If they are different, which one is larger? Explain your answer.

Section 3.5

3.32 A pair correlation function $g(\vec{r})$ was defined in Section 2.7 as the probability of finding a monomer in a unit volume at distance $\vec{r}$ away from a given monomer (labeled by $j = 1$). Note that $j = 1$ is not necessarily the end monomer of any chain. The pair correlation function $g(\vec{r})$ can be written in terms of the delta function summed over all monomers except for the one at $\vec{r}_1$

$$g(\vec{r}) = \left\langle \sum_{j \neq 1} \delta(\vec{r} - (\vec{r}_j - \vec{r}_1)) \right\rangle \tag{3.138}$$

(i) Show that the Fourier transform of the pair correlation function is

$$g(\vec{q}) = \int g(\vec{r}) \exp(-i\vec{q} \bullet \vec{r}) d^3 r = \sum_{j=1}^{n} \langle \exp[-i\vec{q} \bullet (\vec{r}_j - \vec{r}_1)] \rangle - 1 \tag{3.139}$$

(ii) Recognize that the choice of the $j = 1$ monomer was arbitrary and use the definition of the scattering function (Eq. 3.121) to show that

$$S(\vec{q}) = 1 + g(\vec{q}) = 1 + \int g(\vec{r}) \exp(-i\vec{q} \bullet \vec{r}) d^3 r \tag{3.140}$$

Bibliography

des Cloizeaux, J. and Jannink, G. *Polymers in Solution: Their Modelling and Structure* (Clarendon Press, Oxford, 1990).

Eisenriegler, E. *Polymers near Surfaces* (World Scientific, Singapore, 1993).

Flory, P. J. *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, NY, 1953).

Freed, K. *Renormalization Group Theory of Macromolecules* (Wiley, New York, 1987).

de Gennes, P. G. *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).

Grosberg, A. Yu. and Khokhlov, A. R. *Statistical Physics of Macro-molecules* (AIP Press, Woodbury, NY, 1994).

McQuarrie, D. A. *Statistical Mechanics* (University Science, 2000).

Yamakawa, H. *Modern Theory of Polymer Solutions* (Harper & Row, New York, 1971).