# 1 Elements of Polymer Physics

1.1 Monomers

Polymers are macromolecules resulting from the polymerization of monomer units. If all units are identical, the polymer is named homopolymer, if the monomer units are different, the polymer is named heteropolymer. Polymers can form chains, rings, combs, ladders, stars, branched structures.

The (chemically) simplest polymer is composed by carbon and hydrogen (hydrocarbons) It is named **polyethylene**. The monomer is a CH_2 unit,

$$-CH_2-$$

repeated n times (where n, the degree of polymerization, can be very large ($n \sim 10^3 - 10^5$). The starting and final units of the polyethylene are CH_3 groups. Polyethylene is the material the very cheap plastic bags are made of. Also very common is **polypropilene**, in which one of the H atom of the ethylene is substituted with a CH_3 group

$$-CH(CH_3)-$$
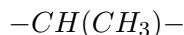
Another very much used polymer is **polystyrene**, in which the H atom is substituted with a benzene ring. This bulky moiety prevents crystallization of the polymer:

$$-CH(C_6H_5)-$$
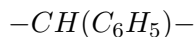
Other well known polymers are polyisopropene, polybutadiene, polyethilene oxide.

1.2 Proteins

Most proteins consist of linear polymers built from series of up to 20 different L-α-amino acids. All proteinogenic amino acids possess common structural features, including an α-carbon to which an amino group (NH), a carboxyl group, (CO) and a variable side chain are bonded. The side chains of the standard amino acids, detailed in the list of standard amino acids, have a great variety of chemical structures and properties; it is the combined effect of all of the amino acid side chains in a protein that ultimately determines its three-dimensional structure and its chemical reactivity. The amino acids in a polypeptide chain are linked by peptide bonds. Once linked in the protein chain, an individual amino acid is called a residue, and the linked series of carbon, nitrogen, and oxygen atoms are known as the main chain or protein backbone.

The C_α is a carbon atom connected to four different atom types (R,C,N,H). Hence it is chiral. Biological proteins are of the L forms (only rare exceptions are found). This means
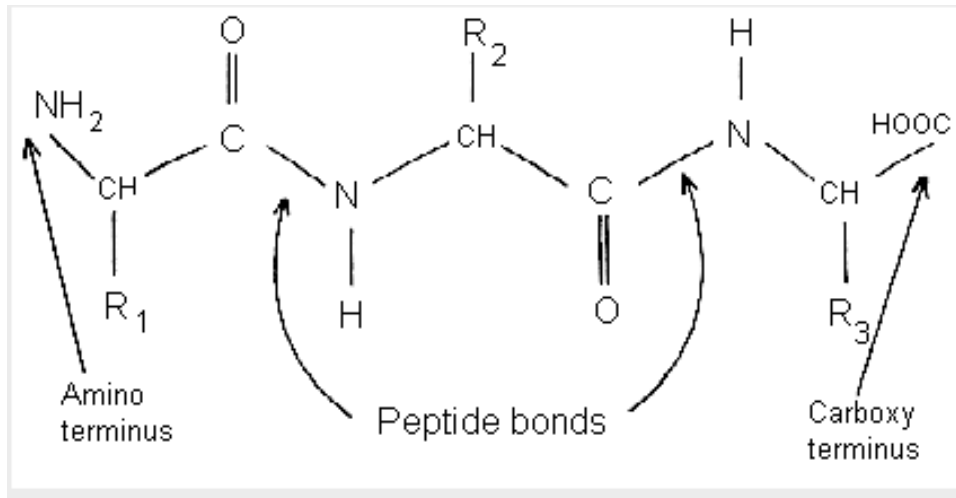
that if you look along the RC_α direction and put the N on the top, then the C connected to the O is always on the right (or left).

The peptide bond has two resonance forms that contribute some double-bond character and inhibit rotation around the axis connecting the N to the C attached to the O. As a result, the alpha carbons are roughly coplanar. The other two dihedral angles in the peptide bond determine the local shape assumed by the protein backbone. The possible distributions of values of the two dihedral angles (controlled essentially by the excluded volume interactions) are commonly described in the so-called Ramachandra steric maps.

The end with a free amino group is known as the N-terminus or amino terminus, whereas the end of the protein with a free carboxyl group is known as the C-terminus or carboxy terminus (the sequence of the protein is written from N-terminus to C-terminus, from left to right).

There are two relevant structures for proteins: $\alpha-$helix and β-sheet. These two structures are shown in the figure.

1.3 DNA

DNA is a long polymer made from repeating units called nucleotides. The structure of DNA is dynamic along its length, being capable of coiling into tight loops and other shapes. In all species it is composed of two helical chains, bound to each other by hydrogen bonds. Both chains are coiled around the same axis, and have the same pitch of 34 angstroms (3.4 nanometres). The pair of chains has a radius of 10 angstroms (1.0 nanometre). Although each individual nucleotide is very small, a DNA polymer can be very large and contain hundreds of millions, such as in chromosome 1. Chromosome 1 is the largest human chromosome with approximately 220 million base pairs, and would be 85 mm long if straightened.
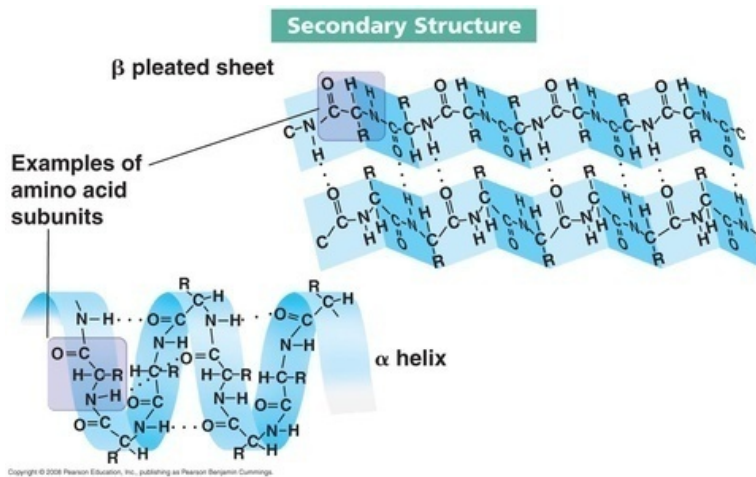
The backbone of the DNA strand is made from alternating phosphate and sugar residues. The sugar in DNA is 2-deoxyribose, which is a pentose (five-carbon) sugar. The sugars are joined together by phosphate groups that form phosphodiester bonds between the third and fifth carbon atoms of adjacent sugar rings. These are known as the 3'-end (three prime end), and 5'-end (five prime end) carbons, the prime symbol being used to distinguish these carbon atoms from those of the base to which the deoxyribose forms a glycosidic bond. When imagining DNA, each phosphoryl is normally considered to "belong" to the nucleotide whose 5' carbon forms a bond therewith. Any DNA strand therefore normally has one end at which there is a phosphoryl attached to the 5' carbon of a ribose (the 5' phosphoryl) and another end at which there is a free hydroxyl attached to the 3' carbon of a ribose (the 3' hydroxyl). The orientation of the 3' and 5' carbons along the sugar-phosphate backbone confers directionality (sometimes called polarity) to each DNA strand. In a nucleic acid double helix, the direction of the nucleotides in one strand is opposite to their direction in the other strand: the strands are antiparallel. The asymmetric ends of DNA strands are said to have a directionality of five prime end (5'), and three prime end (3'), with the 5' end having a terminal phosphate group and the 3' end a terminal hydroxyl group. One major difference between DNA and RNA is the sugar, with the 2-deoxyribose in DNA being replaced by the alternative pentose sugar ribose in RNA.

2 A first look at the structure of a polymer

In order to understand the multitude of conformations available for a polymer chain, consider an example of a polyethylene molecule. The distance between carbon atoms in the molecule is almost constant $l = 1.54\mathring{A}$. The fluctuations in the bond length (typically $\pm 0.05\mathring{A}$) do not affect chain conformations. The angle between neighbouring bonds $\theta = 68^o$
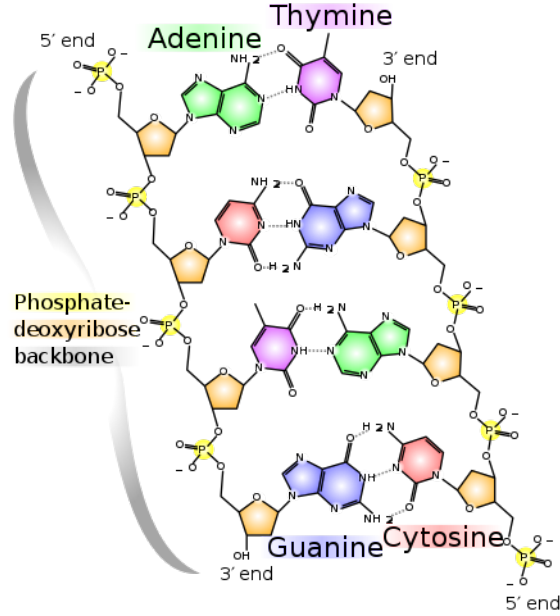
is also almost constant. The main source of polymer flexibility is the variation of torsion angles. In order to describe these variations, consider a plane defined by three neighbouring carbon atoms C_{i-2}, C_{i-1} and C_i. The bond vector $\vec{r}_i$ between atoms C_{i-1} and C_i defines the axis of rotation for the bond vector $\vec{r}_{i+1}$ between atoms C_i and C_{i+1} at constant bond angle θ_i. The zero value of the torsion angle ψ, corresponds to the bond vector $\vec{r}_{i+1}$ being colinear to the bond vector $\vec{r}_{i-1}$ (Note $i-1$) and is called the trans state (t) of the torsion angle. The trans state of the torsion angle ψ_i is the lowest energy conformation of the four consecutive CH_2 groups. The changes of the torsion angle ψ_i lead to the energy variations shown in Fig. 2.1(d). These energy variations are due to changes in distances and therefore interactions between carbon atoms and hydrogen atoms of this sequence of four CH_2 groups. The two secondary minima corresponding to torsion angles $\psi_i = \pm 120^o$ are called gauche-plus (g+) (see Fig. 1) and gauche-minus (g-). The energy difference between gauche and trans minima determines the relative probability of a torsion angle being in a gauche state in thermal equilibrium. In general, this probability is also influenced by the values of torsion angles of neighbouring monomers. The value of Δe for polyethylene at room temperature is $\Delta e = 0.8 k_B T$. The energy barrier between trans and gauche states determines the dynamics of conformational rearrangements. Any section of the chain with consecutive trans states of torsion angles is in a rod-like zig-zag conformation. If all torsion angles of the whole chain are in the trans state, the chain has the largest possible value of its end-to-end distance R_{max}. This largest end-to-end distance is determined by the product of the number of skeleton bonds n and their projected length $l \cos(\theta/2)$ along the

contour, and is referred to as the contour length of the chain:
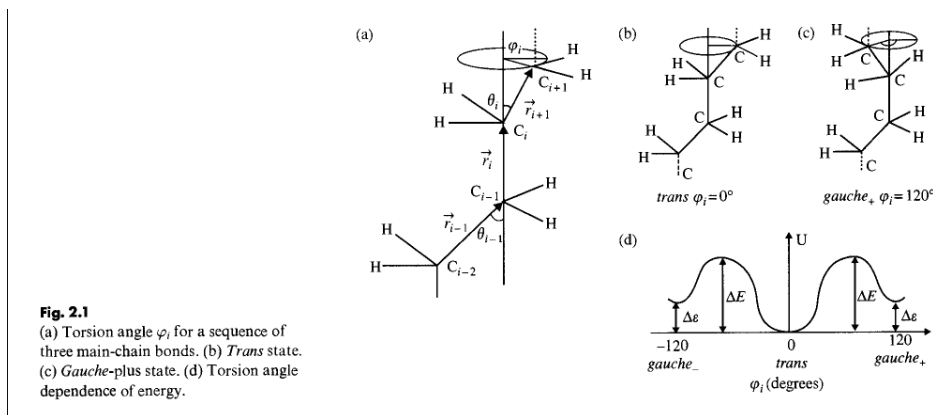
$$R_{max} = nl \cos \frac{\theta}{2}$$

Figure 1: Geometric properties of polyethylene

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

3   Conformations of a chain

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

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

$$\vec{R}_{ee} = \sum_{i=1}^{n} \vec{r}_i.$$

Different individual chains will have different bond vectors and hence different end-to-end vectors. The distribution of end-to-end vectors shall be discussed in Section 2.5. It is

useful to talk about average properties of this distribution. The average end-to-end vector of an isotropic collection of chains of n backbone atoms is zero:

$$< \vec{R}_{ee} >= 0$$

The ensemble average denotes an average over all possible states of the system (accessed either by considering many chains or many different conformations of the same chain). In this particular case the ensemble average corresponds to averaging over an ensemble of chains of n bonds with all possible bond orientations. Since there is no preferred direction in this ensemble, the average end-to-end vector is zero. The simplest non-zero average is the mean-square end-to-end distance:

$$< \vec{R}_{ee}^2 >=< \left(\sum_{i=1}^{n} \vec{r}_i \right) \cdot \left(\sum_{j=1}^{n} \vec{r}_j \right) >$$

If all bond vectors have the same length l, the scalar product can be represented in terms of the angle θ_{ij} between bond vectors $\vec{r}_i$ and $\vec{r}_j$

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

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

$$< \vec{R}_{ee}^2 >= l^2 \sum_i \sum_j < \cos \theta_{ij} >$$

3.1 Random Walk Model (freely jointed chain model)

One of the simplest models of an ideal polymer is the **freely jointed chain model** with a constant bond length l and no correlations between the directions of different bond vectors.

In this case, when $i \neq j$

$$< \cos \theta_{ij} >= \frac{\int_0^\pi \cos \theta \sin \theta d\theta d\phi}{\int_0^\pi \sin \theta d\theta d\phi} = \frac{-\cos \theta^2 |_0^\pi}{\int_0^\pi \sin \theta d\theta d\phi} = 0$$

When $i = j$, by definition $\theta_{ii} = 0$ and $\cos \theta_{ii} = 1$. There are only n non-zero terms in the double sum. The mean-square end-to-end distance of a freely jointed chain is then quite simple:

$$< \vec{R}_{ee}^2 >= nl^2$$

3.2 Random walk beyond the persistence length scale: ideal chain

In a typical polymer chain, there are correlations between bond vectors (especially between neighbouring ones) and $< \cos \theta_{ij} >\neq 0$. But in an ideal chain there is no interaction

between monomers separated by a great distance along the chain contour. This implies that there are no correlations between the directions of distant bond vectors for $|i-j| \gg 1$.

Let now assume that there exist an m-values such that for $j > i + m$, $< \cos \theta_{ij} >= 0$. Then the sum

$$C_\infty = \sum_{j=1}^{n} < \cos \theta_{ij} >= \sum_{j=1}^{m} < \cos \theta_{ij} >$$

Therefore,

$$< \vec{R}_{ee}^2 >= l^2 \sum_{i=1}^{n} C_\infty = C_\infty n l^2$$

where the coefficient C_∞ is called **Flory's characteristic ratio**. The main property of ideal chains is that $< \vec{R}_{ee}^2 >$ is proportional to the product of the number of bonds n and the square of the bond length l^2

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

$$< \vec{R}_{ee}^2 >\approx C_\infty n l^2$$

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

3.3   Equivalent freely jointed chain

Flexible polymers have many universal properties that are independent of local chemical structure. A simple unified description of all ideal polymers is provided by an **equivalent freely jointed chain**. The equivalent chain has the same mean-square end-to-end distance $< \vec{R}_{ee}^2 >$ and the same maximum end-to-end distance R_{max} (the maximum possible value of $\vec{R}_{ee}$) as the actual polymer, but has N freely-jointed effective bonds of length b. N and b are adjustable parameters, fixed to satisfy the equivalence with the contour length and the mean-square end-to-end distance. The effective bond length b is called the **Kuhn length**. The contour length of this equivalent freely jointed chain is

$$Nb = R_{max}$$

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

$$< \vec{R}_{ee}^2 >= Nb^2 = C_\infty n l^2 \quad \rightarrow \quad bR_{max} = C_\infty n l^2$$

Therefore, the equivalent freely jointed chain has equivalent bonds (Kuhn monomers) of length

$$b = \frac{< \vec{R}_{ee}^2 >}{R_{max}} \quad and \quad N = R_{max}/b$$

4   Ideal chain models

Below we describe several models of ideal chains. Each model makes different assumptions about the allowed values of torsion and bond angles. However, every model ignores interactions between monomers separated by large distance along the chain and is therefore a model of an ideal polymer. The chemical structure of polymers determines the populations of torsion and bond angles. Some polymers (like 1,4-polyisoprene) are very flexible chains while others (like double-stranded DNA) are locally very rigid, becoming random walks only on quite large length scales.

4.1   Freely rotating chain model

As the name suggests, this model ignores differences between the probabilities of different torsion angles and assumes all torsion angles $-\pi < \phi_i < \pi$ to be equally probable. Thus, the freely rotating chain model ignores the variations of the potential $U(\phi_i)$. This model assumes all bond lengths and bond angles are fixed (constant) and all torsion angles are equally likely and independent of each other. To calculate the mean-square end-to-end distance the correlation between bond vectors $\vec{r}_i$ and $\vec{r}_j$ must be determined. This correlation is passed along through the chain of bonds connecting bonds i and j. Let's start by considering the case $j = i+1$. For the freely rotating chain, the component of $\vec{r}_i$ normal to vector $\vec{r}_{i+1}$ averages out to zero due to free rotations of the torsion angle ϕ_i. The parallel part instead is correlated. Hence

$$< \vec{r}_i \cdot \vec{r}_{i+1} >= l^2 \cos \theta$$

where $\theta = \pi - \phi_i$. This expression can be generalized, by induction, for any $|i-j|$ considering that the only correlation between the bond vectors that is transmitted down the chain is the component of vector $\vec{r}_j$ along the bond vector $\vec{r}_{j-1}$. Indeed we can write

$$\vec{r}_{i+1} = \vec{r}_i \cos \theta + \vec{v}_{i+1}$$

where $\vec{v}_{i+1}$ is uniformly distributed over a circle. Analogously

$$\vec{r}_{i+2} = \vec{r}_{i+1} \cos \theta + \vec{v}_{i+2} = (\vec{r}_i \cos \theta + \vec{v}_{i+1}) \cos \theta + \vec{v}_{i+2} = \vec{r}_i \cos \theta^2 + \vec{v}_{i+1} \cos \theta + \vec{v}_{i+2}$$

$$\vec{r}_{i+3} = \vec{r}_{i+2}\cos\theta + \vec{v}_{i+3} = (\vec{r}_i\cos\theta^2 + \vec{v}_{i+1}\cos\theta + \vec{v}_{i+2})\cos\theta + \vec{v}_{i+3}$$

and so on. As a result

$$\vec{r}_{i+k} = \vec{r}_i\cos\theta^k + \vec{v}_{i+1}\cos\theta^{k-1} + \vec{v}_{i+2}\cos\theta^{k-2} + \ldots\ldots + \vec{v}_{i+k}$$

The vectors $\vec{v}_l$ are uniformly distributed on a circle, so that,

$$< \vec{r}_i \cdot \vec{v}_{i+k} >= 0$$

for all $k > 0$. As a result bond vector $\vec{r}_1$ passes this correlation down to vector $\vec{r}_2$, but only the component along $\vec{r}_2$ survives due to free rotations of torsion angle ϕ_i. The leftover memory of the vector $\vec{r}_j$ at this stage is $l\cos\theta^2$. The correlations from bond vector $\vec{r}_i$ at bond vector $\vec{r}_j$ are reduced by the factor $l\cos\theta^{|i-j|}$ due to independent free rotations of $|j-i|$ torsion angles between these two vectors. Therefore, the correlation between bond vectors $\vec{r}_i$ and $\vec{r}_j$ is

$$< \vec{r}_i \cdot \vec{r}_j >= l^2\cos\theta^{|i-j|}$$

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

$$< \vec{R}_{ee}^2 >=< \left(\sum_{i=1}^{n}\vec{r}_i\right) \cdot \left(\sum_{j=1}^{n}\vec{r}_j\right) >= \sum_{i=1}^{n}\left(\sum_{j=1}^{i-1} < \vec{r}_i \cdot \vec{r}_j > + < \vec{r}_i^2 > + \sum_{j=i+1}^{n} < \vec{r}_i \cdot \vec{r}_j >\right)$$

$$= \sum_{i=1}^{n} < \vec{r}_i^2 > + l^2\sum_{i=1}^{n}\left(\sum_{j=1}^{i-1}\cos\theta^{|i-j|} + \sum_{j=i+1}^{n}\cos\theta^{|j-i|}\right)$$

and changing variable $k = i - j$,

$$= nl^2 + l^2\sum_{i=1}^{n}\left(\sum_{k=1}^{i-1}\cos\theta^k + \sum_{k=1}^{n-i}\cos\theta^k\right)$$

Now... if $\cos\theta < 1$, and n is large then

$$\sum_{k=1}^{i-1}\cos\theta^k \approx \sum_{k=1}^{\infty}\cos\theta^k = \frac{\cos\theta}{1-\cos\theta}$$

and

$$< \vec{R}_{ee}^2 >= nl^2 + l^2 2n\frac{\cos\theta}{1-\cos\theta} = nl^2\frac{1+\cos\theta}{1-\cos\theta}$$

It is also useful to observe that the correlation can be also be written as

$$< \vec{r}_i \cdot \vec{r}_j >= l^2\cos\theta^{|i-j|} = l^2 e^{|i-j|\ln\cos\theta} = l^2 e^{-|i-j|l_\theta}$$

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where we have defined a persistence angle l_θ as

$$l_\theta = -\frac{1}{\ln \cos \theta}$$

Multiplying the persistence angle by l one obtains the persistence length $l_p = l l_\theta$.

4.2 Worm-like chain model

The worm-like chain model (sometimes called the **Kratky-Porod model**) is a special case of the freely rotating chain model for very small values of the bond angle. This is a good model for very stiff polymers, such as double- stranded DNA for which the flexibility is due to fluctuations of the contour of the chain from a straight line rather than to trans-gauche bond rotations. For small values of the bond angle

$$\cos \theta = 1 - \frac{\theta^2}{2}$$

and at the same time

$$\ln \cos \theta = -\frac{\theta^2}{2} \qquad l_\theta = \frac{2}{\theta^2}$$

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

$$C_\infty = \frac{1 + \cos \theta}{1 - \cos \theta} \approx \frac{4}{\theta^2}$$

The corresponding Kuhn length is twice the persistence length:

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

For example, the persistence length of a double-helical DNA $l_p \approx 50$ nm and the Kuhn length is $b \approx 100$nm. The combination of parameters l/θ^2 enters in the expressions of the persistence length l_p and the Kuhn length b. The worm-like chain is defined as the limit $l \to 0$ and $\theta \to 0$ at constant persistence length l_p and constant chain contour length $R_{max} = nl \cos(\theta/2) \approx nl$.

The mean-square end-to-end distance of the worm-like chain can be evaluated using the exponential decay of correlations between tangent vectors along the chain

$$< \vec{R}_{ee}^2 > = < \left(\sum_{i=1}^{n} \vec{r}_i \right) \cdot \left(\sum_{j=1}^{n} \vec{r}_j \right) > = l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} < \cos \theta_{ij} > = l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} (\cos \theta)^{|j-i|}$$

$$= l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} e^{-\frac{|i-j|}{l_p} l}$$

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

$$l \sum_{i=1}^{n} \to \int_0^{R_{max}} du \qquad\qquad l \sum_{j=1}^{n} \to \int_0^{R_{max}} d\nu$$

so that

$$< \vec{R}_{ee}^2 > = \int_0^{R_{max}} du \left[\int_0^{R_{max}} d\nu\, e^{-\frac{|u-\nu|}{l_p}l} \right] = \int_0^{R_{max}} \left[e^{-\frac{u}{l_p}l} \int_0^{u} d\nu\, e^{\frac{\nu}{l_p}l} + e^{\frac{u}{l_p}l} \int_u^{R_{max}} d\nu\, e^{-\frac{\nu}{l_p}l} \right] du$$

$$= l_p \int_0^{R_{max}} \left[e^{-\frac{u}{l_p}} \left(e^{\frac{u}{l_p}} - 1 \right) + e^{\frac{u}{l_p}} \left(-e^{-\frac{R_{max}}{l_p}} + e^{-\frac{u}{l_p}} \right) \right] du =$$

$$= l_p \int_0^{R_{max}} \left[2 - e^{-\frac{u}{l_p}} - e^{-\frac{R_{max}}{l_p}} e^{\frac{u}{l_p}} \right] du = l_p \left[2R_{max} + l_p \left(e^{-\frac{R_{max}}{l_p}} - 1 \right) - l_p e^{-\frac{R_{max}}{l_p}} \left(e^{\frac{R_{max}}{l_p}} - 1 \right) \right]$$

$$= 2 l_p R_{max} - 2 l_p^2 \left(1 - e^{-\frac{R_{max}}{l_p}} \right) \tag{1}$$

There are two simple limits of this expression. The ideal chain limit is for worm-like chains much longer than their persistence length ($R_{max} \gg l_p$). Neglecting l_p^2 compared to $l_p R_{max}$

$$< \vec{R}_{ee}^2 > \approx 2 l_p R_{max} = b R_{max} \qquad \text{for} \qquad R_{max} \gg l_p$$

The rod-like limit is for worm-like chains much shorter than their persistence length ($R_{max} \ll l_p$). The exponential in Eq. 1 can be expanded in this limit:

$$e^{-\frac{R_{max}}{l_p}} \approx 1 - \frac{R_{max}}{l_p} + \frac{1}{2} \left(\frac{R_{max}}{l_p} \right)^2 - \frac{1}{6} \left(\frac{R_{max}}{l_p} \right)^3$$

such that

$$< \vec{R}_{ee}^2 > \approx R_{max}^2 - \frac{R_{max}^3}{3 l_p}$$

The mean-square end-to-end distance of the worm-like chain is a smooth crossover between these two simple limits. The important difference between freely jointed chains and worm-like chains is that **each bond of Kuhn length b of the freely jointed chain is assumed to be completely rigid**. Worm-like chains are also stiff on length scales shorter than the Kuhn length, but are not completely rigid and can fluctuate and bend. These bending modes lead to a qualitatively different dependence of extensional force on elongation near maximum extension, as will be discussed later on.

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4.3 Other models

The interested student may consider more realistic ideal models, accounting for the energy dependence of the torsional angle, usually named "Hindered rotation motion" and "Rotational isomeric state model".

5 Radius of Gyration

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

$$\vec{R}_g^2 \equiv \frac{1}{N} \sum_{i=1}^{N} (\vec{R}_i - \vec{R}_{cm})^2.$$

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

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

Substituting the definition of the position vector of the centre of mass gives an expression for the square radius of gyration as a double sum of squares over all inter-monomer distances:

$$\vec{R}_g^2 \equiv \frac{1}{N} \sum_{i=1}^{N} (\vec{R}_i^2 - 2\vec{R}_i\vec{R}_{cm} + \vec{R}_{cm}^2) = \frac{1}{N} \sum_{i=1}^{N} \left[\vec{R}_i^2 \frac{1}{N} \sum_{j=1}^{N} 1 - 2\vec{R}_i \frac{1}{N} \sum_{j=1}^{N} \vec{R}_j + \left(\frac{1}{N} \sum_{j=1}^{N} \vec{R}_j \right)^2 \right]$$

The last term can be rewritten as

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

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

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

This expression does not depend on the choice of summation indices and can be rewritten in a symmetric form (by duplicating the sum in two identical parts and then swapping the index in the second term)

$$\vec{R}_g^2 \equiv \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} (\vec{R}_i^2 - \vec{R}_i \vec{R}_j) = \frac{1}{2} \left[\sum_{i=1}^{N} \sum_{j=1}^{N} (\vec{R}_i^2 - \vec{R}_i \vec{R}_j) + \sum_{i=1}^{N} \sum_{j=1}^{N} (\vec{R}_j^2 - \vec{R}_i \vec{R}_j) \right]$$

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

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

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

The associated mean squared radius of gyration is then

$$< \vec{R}_g^2 > = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j>i}^{N} < (\vec{R}_i - \vec{R}_j)^2 >$$

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

5.1 Radius of gyration of an ideal linear chain

To illustrate how to calculate $\vec{R}_g^2$, we now calculate the mean-square radius of gyration for an ideal linear chain. For the linear chain, the summations over the monomers can be changed into integrations over the contour of the chain, by replacing monomer indices i and j with continuous coordinates u and v along the contour of the chain:

$$\sum_{i=1}^{n} \rightarrow \int_{0}^{N} du \qquad \sum_{j>i}^{n} \rightarrow \int_{u}^{N} d\nu$$

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

$$< \vec{R}_g^2 > = \frac{1}{N^2} \int_{0}^{N} du \int_{u}^{N} d\nu < (\vec{R}(u) - \vec{R}(\nu))^2 >$$

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

$$< (\vec{R}(u) - \vec{R}(\nu))^2 > = (\nu - u)b^2$$

The mean-square radius of gyration is then calculated by a simple integration using the change of variable $\nu' = \nu - u$

$$< \vec{R}_g^2 > = \frac{1}{N^2} \int_0^N du \int_u^N d\nu (\nu - u)b^2 = \frac{b^2}{N^2} \int_0^N \int_0^{N-u} \nu' d\nu' du$$

$$= \frac{b^2}{N^2} \int_0^N \frac{(N-u)^2}{2} du =$$

and now changing $u' = N - u$,

$$= \frac{b^2}{2N^2} \int_0^N (u')^2 du' = \frac{b^2}{2N^2} \frac{N^3}{3} = \frac{Nb^2}{6}$$

Comparing this result with the evaluation of R_{ee}, we obtain the classic Debye result relating the mean-square radius of gyration and the mean-square end-to-end distance of an ideal linear chain:

$$< \vec{R}_g^2 > = \frac{R_{ee}^2}{6}$$

5.2   Radius of gyration of a rod polymer

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

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

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

$$\left[\left(\vec{R}(u) - \vec{R}_{cm} \right)^2 \right] = \left[\left(u - \frac{N}{2} \right)^2 \right]$$

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

$$R_g^2 = \frac{b^2}{N} \int_0^N \left[\left(u - \frac{N}{2} \right)^2 \right] du = \frac{b^2}{N} \int_{-\frac{N}{2}}^{\frac{N}{2}} x^2 dx = \frac{N^2 b^2}{12}$$

where the change of variables $x = u - N/2$ has been used. Note that the relation between the end-to-end distance $R_{ee} = Nb$ and the radius of gyration for a rod polymer is different from that for an ideal linear chain

$$R_g^2 = \frac{N^2 b^2}{12} = \frac{R_{ee}^2}{12}$$

5.3 (Kramers theorem) A cute way to calculate R_g for loopless (ideal) polymers

Kramers theorem refers to an alternative way of expressing the gyration radius, particularly useful for branched polymers.

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

$$< \vec{R}_g^2 > = \frac{1}{N^2} \sum_{i=1}^N \sum_{j>i}^N < (\vec{R}_i - \vec{R}_j)^2 >$$

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

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

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

$$< \vec{r}_k \vec{r}_{k'} > = b^2 \delta_{k,k'}$$

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

$$< (\vec{R}_i - \vec{R}_j)^2 > = \sum_{k=i+1}^j \sum_{k'=i+1}^j < \vec{r}_k \vec{r}_{k'} > = \sum_{k=i+1}^j < \vec{r}_k^2 > = (j-1)b^2$$

and

$$< \vec{R}_g^2 > = \frac{1}{N^2} \sum_{i=1}^N \sum_{j>i}^N \sum_{k=i+1}^j < \vec{r}_k^2 >$$

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This way of writing offers an alternative way of looking at the problem. If we focus on one specific bond, k in the following, this bond will contribute to the double sum with a term b^2 for each of the path connecting any arbitrary selected i and j which passes through k. Since we assume that there are no loops, this means that the bond k breaks the polymer into two sub-polymers. For a path of the original polymer to pass by k, it has to originate from one of the pieces and end in the different piece. It means that the number of paths going through k is given by $N_1(N - N_1)$, where N_1 is the number of monomers composing one of the two split polymers and $N - N_1$ the other one. Then, the radius of gyration can be expressed as the sum over all N molecular bonds, of the product of the number of monomers of the two branches $N_1(k)$ and $N - N_1(k)$ that each bond k divides the molecule into

$$< \vec{R}_g^2 > = \frac{b^2}{N^2} \sum_{k=1}^{N} N_1(k)(N - N_1(k))$$

The Kramers theorem express the gyration radius in terms of average over all possible ways of dividing the molecule into two parts. It also of course applies to linear polymers. Indeed, for a linear polymer (remembering that

$$\sum_{k=1}^{N} k = \frac{1}{2} N(N + 1) \qquad \text{and} \qquad \sum_{k=1}^{N} k^2 = \frac{1}{6} N(N + 1)(2N + 1)$$

) we find

$$\frac{b^2}{N^2} \sum_{k=1}^{N} N_1(k)(N - N_1(k)) = \frac{b^2}{N^2} \sum_{k=1}^{N} k(N - k) = \frac{b^2}{N^2} \left(N \sum_{k=1}^{N} k - \sum_{k=1}^{N} k^2 \right) =$$

$$\frac{b^2}{N^2} \left(N \frac{1}{2} N(N + 1) - \frac{1}{6} N(N + 1)(2N + 1) \right)$$

and in the limit of large N

$$= Nb^2 \left(\frac{1}{2} - \frac{1}{3} \right) = \frac{Nb^2}{6}$$

6   Distribution of end-to-end distances in an ideal polymer

In one dimension, the end to end distance is

$$X_{ee} = b \sum_{i=1}^{N} \hat{x}_i$$

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dove $\hat{x}_i = \pm 1$ (randomly). Then the end to end distance is a random variable which, for large N, is a gaussian with mean equal to the sum of the mean of the x_i and with variance equal to the sum of the x_i N variances (times b^2).

$$< X_{ee} >= 0 \qquad \sigma^2_{X_{ee}} = Nb^2$$

Thus

$$P(X) = \frac{1}{\sqrt{2\pi Nb^2}} e^{-\frac{X^2}{2bN^2}}$$

The same can be obtained by starting from a binomial process. In the hypothesis of an ideal random walk in one dimension, the number of realization that start from the origin with N_r steps to the right (and correspondingly $N - N_r$ steps to the left) is given by the combinatorial term

$$\Omega(N_r) = \frac{N!}{(N - N_r)!N_r!}$$

The final position of the walker after the N steps is

$$N_w = N_r - (N - N_r) = 2N_r - N \quad \text{and hence} \quad N_r = \frac{N + N_w}{2} \quad \text{and} \quad N - N_r = \frac{N + N_w}{2}$$

Then

$$\Omega(N_r) = \frac{N!}{(\frac{N - N_w}{2})!(\frac{N + N_w}{2})!}$$

Using Stirling approximation

$$\ln N! = N \ln N - N + \frac{1}{2}\ln(2\pi N)$$

$$\ln \Omega(N_r) = N \ln N - N + \frac{1}{2}\ln(2\pi N)$$
$$-\left(\frac{N - N_w}{2}\right)\ln\left(\frac{N - N_w}{2}\right) + \left(\frac{N - N_w}{2}\right) - \frac{1}{2}\ln\left(2\pi\left(\frac{N - N_w}{2}\right)\right)$$
$$-\left(\frac{N + N_w}{2}\right)\ln\left(\frac{N + N_w}{2}\right) + \left(\frac{N + N_w}{2}\right) - \frac{1}{2}\ln\left(2\pi\left(\frac{N + N_w}{2}\right)\right)$$

and defining $x = N_w/N$,

$$\ln \Omega(N_r) = N \ln N - \cancel{N} + \frac{1}{2}\ln(2\pi N)$$

$$-\frac{N}{2}(1-x)\ln\left[\frac{N}{2}(1-x)\right] + \frac{N}{2}\cancel{(1-x)} - \frac{1}{2}\ln\left[2\pi(\frac{N}{2}(1-x))\right]$$

$$-\frac{N}{2}(1+x)\ln\left[\frac{N}{2}(1+x)\right] + \frac{N}{2}\cancel{(1+x)} - \frac{1}{2}\ln\left[2\pi(\frac{N}{2}(1+x))\right]$$

$$\ln \Omega(N_r) = N \ln N$$

$$-\frac{N}{2}(1-x)\ln\left[\frac{N}{2}\right] - \frac{N}{2}(1-x)\ln\left[(1-x)\right] - \frac{N}{2}(1+x)\ln\left[\frac{N}{2}\right] - \frac{N}{2}(1+x)\ln\left[(1+x)\right]$$

$$+\cancel{\frac{1}{2}\ln(2\pi N)} - \cancel{\frac{1}{2}\ln(2\pi N)} - \frac{1}{2}\ln(2\pi N) + \frac{1}{2}\ln\left[\frac{1}{2}(1-x)\right] - \frac{1}{2}\ln\left[\frac{1}{2}(1+x)\right]$$

Expanding

$$\ln(1+x) = x - \frac{x^2}{2} \qquad \text{and} \qquad \ln(1-x) = -x - \frac{x^2}{2}$$

and neglecting $\ln\frac{1-x}{1+x}$ since it does not scale with N

$$\ln \Omega(N_r) = \cancel{N \ln N}$$

$$-\cancel{N\ln N} - N \ln 2 - \frac{N}{2}(1-x)\left[-x - \frac{x^2}{2}\right] - \frac{N}{2}(1+x)\left[x - \frac{x^2}{2}\right] - \frac{1}{2}\ln(2\pi N) + \frac{1}{2}\ln\cancel{\frac{1-x}{1+x}}$$

so that

$$\ln \Omega(N_r) = -N \ln 2 - \frac{N}{2}\left[-\cancel{x} - \frac{x^2}{2} + \cancel{x} - \frac{x^2}{2})\right] - \frac{N}{2}\left[x^2 + \cancel{\frac{x^3}{2}} + x^2 - \cancel{\frac{x^3}{2}}\right] - \frac{1}{2}\ln(2\pi N)$$

$$\ln \Omega(N_w) = -N \ln 2 - \frac{Nx^2}{2} - \frac{1}{2}\ln(2\pi N)$$

or

$$\Omega(N_w) = 2^N e^{-\frac{Nx^2}{2}}\frac{1}{\sqrt{2\pi N}} = 2^N \frac{1}{\sqrt{2\pi N}}e^{-\frac{N_w^2}{2N}} \qquad \text{for} \qquad N_w << N$$

or, by indicating with X the position of the walker, naming b the unit step and normalizing by the total number of possibilities 2^N,

$$P(X) = \frac{1}{\sqrt{2\pi N b^2}}e^{-\frac{X^2}{2Nb^2}}$$

Generalizing to three dimensions (and considering that there are $N/3$ steps in each direction)

$$P(\vec{R}, N) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} e^{-\frac{3(R_x^2 + R_y^2 + R_z^2)}{2N b^2}} = \left(\frac{3}{2\pi N b^2}\right)^{3/2} e^{-\frac{3R^2}{2N b^2}}$$

The Gaussian approximation is valid only for end-to-end vectors much shorter than the maximum extension of the chain. For $R > Nb$ the gaussian expression predicts finite (though exponentially small) probability, which is physically unreasonable.

7 Free energy of an ideal polymer

The entropy S is the product of the Boltzmann constant k_B and the logarithm of the number of states Ω. Denote $\Omega(N, \vec{R})$ as the number of conformations of a freely jointed chain of N monomers with end-to-end vector $\vec{R}$. The entropy is then a function of N and $\vec{R}$

$$S(N, \vec{R}) = k_B \ln \Omega(N, \vec{R})$$

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

$$S(N, \vec{R}) = -\frac{3}{2} k_B \frac{\vec{R}^2}{N b^2} + \frac{3}{2} k_B \ln \left(\frac{3}{2\pi N b^2}\right) + N k_B \ln 2$$

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

$$S(N, \vec{R}) = -\frac{3}{2} k_B \frac{R^2}{N b^2} + S(N, 0).$$

The Helmholtz free energy of the chain F is the energy U minus the product of absolute temperature T and entropy S: The energy of an ideal chain $U(N, R)$ is independent of the end-to-end vector $\vec{R}$, since the monomers of the ideal chain have no interaction energy. The free energy can be written as

$$F(N, \vec{R}) = \frac{3}{2} k_B T \frac{R^2}{N b^2} + F(N, 0).$$

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

opposite forces acting on the chain ends that are proportional to $\vec{R}$. For example, to separate the chain ends by distance R_x in x direction, requires force f_x

$$f_x = \frac{\partial F}{\partial R_x} = 3k_BT\frac{R_x}{Nb^2}$$

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

$$\vec{f} = 3k_BT\frac{\vec{R}}{Nb^2}$$

The coefficient of proportionality $3kT/(Nb^2)$ is the entropic spring constant of an ideal chain. It is easier to stretch polymers with larger numbers of monomers N, larger monomer size b, and at lower temperature T. The fact that the spring constant is proportional to temperature is a signature of entropic elasticity. The entropic nature of elasticity in polymers distinguishes them from other materials. Metals and ceramics become softer as temperature is raised because their deformation requires displacing atoms from their preferred positions (energetic instead of entropic elasticity). The force increases as the chain is stretched because there are fewer possible conformations for larger end-to-end distances. The linear entropic spring result for the stretching of an ideal chain [Eq. (2.96)] is extremely important for our subsequent discussions of rubber elasticity and polymer dynamics. This linear dependence (Hooke's law for an ideal chain), is due to the Gaussian approximation, valid only for $\vec{R} < R_{max} = Nb$. If the chain is stretched to the point where its end-to-end vector approaches the maximum chain extension, the dependence becomes strongly non-linear, with the force diverging at $\vec{R} = R_{max}$.

7.1 Scaling argument for chain stretching

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

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

$$\xi^2 \approx b^2g$$

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

$$R_x \approx \xi\frac{N}{g} \qquad \rightarrow \qquad g = \frac{\xi N}{R_x}$$

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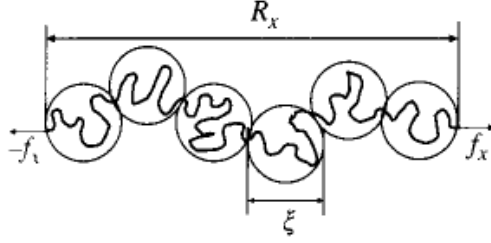
Fig. 2.13
An elongated chain is only stretched on
its largest length scales. Inside the
tension blob, the conformation of the
chain is essentially unperturbed by the
stretch.

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

$$\xi \approx \frac{Nb^2}{R_x} \qquad g \approx \frac{N^2 b^2}{R_x^2}$$

The number of monomers g and the size ξ of these sections were specially chosen so that the polymer conformation changes from that of a random walk on smaller size scales to that of an elongated chain on larger length scales. Such sections of stretched polymers are called tension blobs. Being extended on only its largest length scales allows the chain to maximize its conformational entropy. The physical meaning of a tension blob is the length scale ξ at which external tension changes the chain conformation from almost undeformed on length scales smaller than ξ to extended on length scales larger than ξ. The trajectory of the stretched chain (see figure) shows that each tension blob is forced to go in a particular direction along the x axis (rather than in a random direction as in an unperturbed chain). Therefore one degree of freedom is restricted per tension blob and the free energy of the chain increases by $k_B T$ per blob

$$F \approx k_B T \frac{N}{g} \approx k_B T \frac{R_x^2}{N^2 b^2}$$

The scaling method gets the correct result within a prefactor of order unity. This is the character of all scaling calculations: they provide a simple means to extract the essential physics but do not properly determine numerical coefficients. The previous equation is the first of many instances where the free energy stored in the chain is of the order of $k_B T$ per blob, because the blobs generally describe a length scale at which the conformation of the chain changes and is the elementary unit of deformation. In the case of stretching, the free

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energy is F/N per monomer. On length scales smaller than the tension blob, the thermal energy k_BT that randomizes the conformation is larger than the cumulative stretching energy, and the conformation is essentially unperturbed. On length scales larger than the tension blob, the cumulative stretching energy is larger than k_BT, and the ideal chain gets strongly stretched. Similar arguments apply to other problems involving conformational changes beyond a particular length scale, making the free energy of order k_BT per blob quite general.

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

$$f_x = \frac{\partial F}{\partial R_x} \approx k_B T \frac{R_x}{N^2 b^2} \approx \frac{k_B T}{\xi}$$

The tension blobs provide a simple framework for visualizing the chain stretching and provide simple relations for calculating the stretching force and free energy. They define the length scale at which elastic energy is of order k_BT. Since the force has dimensions of energy divided by length, a dimensional analysis shows that the length scale of tension blob ξ corresponding to k_BT of stored elastic energy.

8 Real Chains: Do we need to account for excluded volume interactions ?

Previously 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 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:

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

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

$$\phi^* \approx b^d \frac{N}{bN^{1/2}} \approx N^{1-d/2}$$

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

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

The volume fraction of the polymer can also be interpreted as the probability of overlap between a randomly selected monomer and the chain. In three-dimensional space the probability of a given monomer contacting another monomer on the same chain is then $\phi^* \sim N^{-1/2} \ll 1$.

If we now multiply the probability of overlap between a randomly selected monomer and the chain for the number of monomers in the chain we get an estimate of the number of monomer-monomer contacts between pairs of monomers that are far away from each other along the chain, but yet close together in space

$$N\phi^* \approx N^{2-d/2}$$

In spaces with dimension above 4, this number is small and monomer- monomer contacts are extremely 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 instead scales as $N^{1/2}$ since

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

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.

9 Second virial coefficient

Starting from the partition function (for a system of pairwise additive interactions, assuming $\lambda = 1$)

$$Z = \frac{1}{N!} \int e^{-\beta \sum_{ij} v(r_{ij})} d\mathbf{r}_1 ... \mathbf{r}_N = \frac{1}{N!} \int \prod_{ij} e^{-\beta v(r_{ij})} d\mathbf{r}_1 ... \mathbf{r}_N$$

and summing and subtracting one to $e^{-\beta v(r_{ij})}$

$$Z = \frac{1}{N!} \int \prod_{ij} \left(e^{-\beta v(r_{ij})} - 1 + 1 \right) d\mathbf{r}_1...\mathbf{r}_N = \frac{1}{N!} \int \prod_{ij} (f_{ij} + 1) \, d\mathbf{r}_1...\mathbf{r}_N$$

where we have defined the Mayer function $f_{ij} \equiv e^{-\beta v(r_{ij})} - 1$. The Mayer function vanishes beyond the interaction range and is equal to minus 1 when $v(r)$ diverges.

Expanding the product one can now write Z as

$$Z = \frac{1}{N!} \int d\mathbf{r}_1...\mathbf{r}_N [1 + (f_{12} + f_{13} + ...) + (f_{12}f_{13} + f_{12}f_{14} + ...) + ...]$$

If the density is small, then the probability that in the same region of space distinct Mayer functions are different from zero is negligible and one can stop the sum to the first term obtaining

$$Z = \frac{1}{N!} \int d\mathbf{r}_1...\mathbf{r}_N + \frac{N(N-1)}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 f_{12} \int d\mathbf{r}_3 .... \int d\mathbf{r}_N = \frac{1}{N!} \left[V^N + V^{N-2} \frac{N(N-1)}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 f_{12} \right] =$$

$$\frac{1}{N!} \left[V^N + V^{N-1} \frac{N(N-1)}{2} \int d\mathbf{r_{12}} f_{12}(r_{12}) \right] = \frac{V^N}{N!} \left(1 + \frac{N(N-1)}{2V} \int d\mathbf{r_{12}} f_{12}(r_{12}) \right)$$

Defining B_2, named second virial coefficient, as

$$B_2(T) = -\frac{1}{2} \int d\mathbf{r_{12}} f_{12}(r_{12}) = -\frac{4\pi}{2} \int r_{12}^2 dr_{12} f_{12}(r_{12}) = -2\pi \int r_{12}^2 dr_{12} f_{12}(r_{12}),$$

taking the log and expanding around one

$$\ln Z = N \ln V - N \ln N + N + \frac{N(N-1)}{V} B_2(T) \tag{2}$$

The free energy per particle becomes

$$\beta f(T) = -\frac{\ln Z}{N} = 1 - \ln \rho + \rho B_2(T) = \beta f_{ideal-gas} + \rho B_2(T)$$

so that $\rho B_2(T)$ provides the first correction to the free-energy over the ideal gas case. When $B_2(T)$ is negative, the free energy will favour states of higher density (attraction), while when $B_2(T)$ is positive, the gas phase is stabilized.

For the case of HS, the second virial coefficent can be easily calculated, considering that the Mayer function is -1 for $r < \sigma$ and 0 elsewhere. Then

$$B_2^{HS} = -2\pi \int r_{12}^2 dr_{12} f_{12}(r_{12}) = 2\pi \int_0^\sigma r^2 dr = 2\pi \frac{\sigma^3}{3}$$

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which coincides with the excluded volume assumed by van der Waals.

To evaluate the equation of state

$$\beta P = -\frac{\partial \beta F}{\partial V} = \frac{\partial \ln Z}{\partial V} = \frac{N}{V} - \frac{N(N-1)}{2V^2} \int d\mathbf{r_{12}} f_{12}(r_{12})$$

which for large N gives

$$\frac{\beta P}{\rho} = 1 + \rho B_2$$

One simple way to account for the monomer monomer interaction is to assume that the free energy of the polymer includes also a contribution coming from pair-wise interactions (virial expansion). In this case one can write for the interaction free-energy per unit volume (indicating with ρ_n the monomer number density)

$$\frac{F_{interaction}}{V} = k_B T \ \left(B_2(T)\rho_n^2 + B_3(T)\rho_n^3 + ... \right)$$

Since the interaction between the monomers is mediated also by the solvent quality, different possibilities exist for the value of $B_2(T)$. The polymer nomenclature includes (in order of decreasing $B_2(T)$, or equivalently going from repulsion to attraction)

- (A) Athermal solvents (hard-sphere like). In the high-temperature limit, $B_2(T)$ 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
$$B_2(T) \approx b^2 d$$
where we have assumed that the monomer is a cylinder with a diameter d and a length coincident with the Kuhn distance b. Note that the excluded volume between two cylinders is not the volume of a cylinder.

- (B) Good solvents (mostly repulsive). In the a-thermal 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 favour 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 a-thermal value. Still, the net effect is repulsive
$$0 < B_2(T) < b^2 d$$

- (C) Theta solvents (attraction compensates repulsion). At some special temperature, called the θ-temperature, the contribution to the excluded volume from the attractive

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well exactly cancels the contribution from the hard-core repulsion, resulting in a net zero excluded volume:
$$B_2(T) = 0$$

The chains have nearly ideal conformations at the θ-temperature because there is no net penalty for monomer-monomer contact. Polystyrene in cyclohexane at $T = 34.5$ ^oC is an example of a polymer-solvent pair at the θ-temperature.

- (D) Poor solvents (mostly attraction). 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:

$$-b^2 d < B_2(T) < 0$$

  Ethanol is a poor solvent for polystyrene.

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

$$B_2(T) < -b^2 d$$

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

9.1 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 $k_B T$ per exclusion or $k_B T B_2(T) N/R^3$ per monomer. For all N monomers in the chain, this energy is N times larger [see the first term in the virial expansion with $V \approx R^3$:

$$\frac{F_{int}}{V} \approx k_B T B_2(T) c_n^2 = k_B T B_2(T) \frac{N^2}{V^2} \quad \rightarrow \quad F_{int} \approx k_B T B_2(T) \frac{N^2}{R^3}$$

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

$$F_{ent} \approx k_B T \frac{R^2}{Nb^2}$$

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

$$F = F_{int} + F_{ent} \approx k_B T B_2(T) \frac{N^2}{R^3} + k_B T \frac{R^2}{Nb^2}$$

The minimum free energy of the chain (obtained by setting $dF/dR = 0$) gives the optimum size of the real chain in the Flory theory R_F

$$\frac{\partial F}{\partial R} = 0 = k_B T \left(-3 B_2(T) \frac{N^2}{R_F^4} + 2 \frac{R_F}{Nb^2} \right)$$

$$R_F^5 \approx B_2(T) b^2 N^3 \qquad R_F \approx B_2(T)^{1/5} b^{2/5} N^{3/5}$$

For positive $B_2(T)$, the size of long real chains is much larger than that of ideal chains with the same number of monomers, as reflected in the ratio between R_F and R_{ideal} (the swelling ratio)

$$\frac{R_F}{R_{ideal}} = \frac{R_F}{bN^{1/2}} \approx \frac{B_2(T)^{1/5} b^{2/5} N^{3/5}}{bN^{1/2}}$$

$$= \left(\frac{B_2(T)}{b^3} N^{1/2} \right)^{1/5}$$

When the argument is larger than 1, i.e. for $\frac{B_2(T)}{b^3} N^{1/2} > 1$ the chain sensibly swell.

If the total interaction energy of a chain in its ideal conformation $F_{int}(R_0)$ is less than $k_B T$, the chain will not swell. In this case, $\frac{B_2(T)}{b^3} N^{1/2} < 1$ and the chain's conformation remains nearly ideal. Thus, excluded volume interactions only swell the chain when the **chain interaction parameter**,

$$z \equiv \frac{B_2(T)}{b^3} N^{1/2} >> 1$$

In these conditions ($z >> 1$) the interaction free energy, evaluated in the ideal conformation, is significantly larger than the thermal energy

$$\frac{F_{int}(R_0)}{k_B T} >> 1$$

Indeed

$$\frac{F_{int}(R_{ideal})}{k_B T} \approx B_2(T) \frac{N^2}{R_{ideal}^3} \approx \frac{B_2(T)}{b^3} N^{1/2}$$

The Flory estimate for R_F is therefore only valid for chain interaction parameters that are larger than some number of order unity. 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 $b^3 N^2 / R^3 \approx N^{1/5}$. 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 overestimated 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. 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 realise that Flory theory leads to a universal power law dependence of polymer size R on the number of monomers N

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

(where now the symbol ν reflect the scaling exponent). The quality of solvent, reflected in the excluded volume ν, enters only in the prefactor, but does not change the value of the scaling exponent. 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 $\mathcal{D} = 2$, while for a swollen chain it is lower $\mathcal{D} = 5/3$. More sophisticated theories lead to a more accurate estimate of the scaling exponent of the swollen linear chain in three dimensions:

$$\nu = 0.588$$

While the ideal chain 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.

10   Just for fun: two regular fractals

As the first example of a self-similar object, consider a regular fractal, called a triadic Koch curve. We start from a section of straight line and divide it into three equal subsections (hence the name triadic). On the top of the middle subsection we draw an equilateral

(a)

(b)

(c)

(d)

(e)

(f)

r_2
r_1
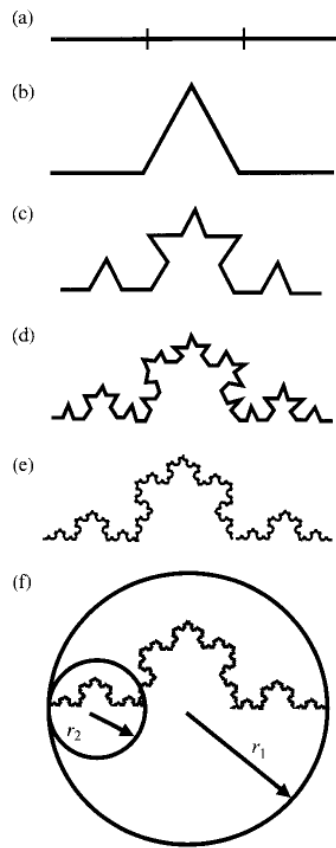
Fig. 1.12
Construction of a triadic Koch curve.

(a)

(b)

(c)

(d)

(e)

(f)
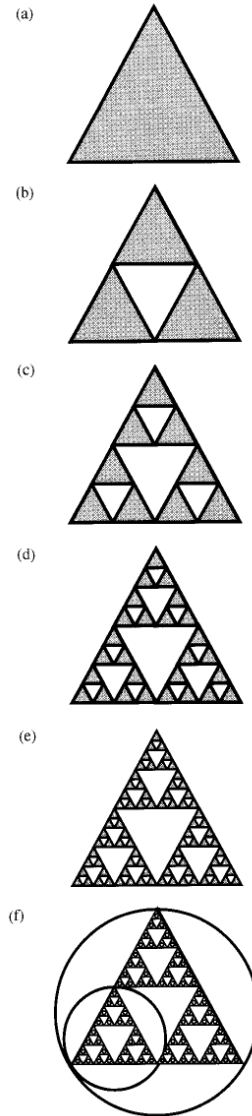
Fig. 1.13
Construction of a Sierpinski gasket.

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triangle and erase its bottom side (the original middle subsection of the line). Thus, we end up with four segments of equal length instead of the three original ones. We repeat the above procedure for each of these four segments?divide each of them into three equal subsections and replace the middle subsections with the two opposite sides of equilateral triangles. At the end of the second step, we obtain a line with each of the four sections consisting of four smaller subsections. This process can continue as long as your patience allows. It is usually limited by the resolution of the computer screen or of the printer. In order to calculate the dependence of the mass of the triadic Koch curve on the length scale, let us draw circles of diameter $2r$ equal to the lengths of the segments of two consecutive generations. As we compare circles drawn around the segments of the consecutive generations of the curve, the radius of the circles changes by the factor of 3, while the mass m of the section of the curve inside these circles changes by the factor of 4. We are looking for an exponent defined by the relation

$$M = A r^{d_f}$$

The exponent d_f is called the fractal dimension. The fractal dimension for a triadic Koch curve can be determined from the fact that we have two ways to calculate m in terms of r_2,

$$M_1 = A r_1^{d_f} \quad \text{and} \quad M_2 = A r_2^{d_f}$$

Since $r_2 = 3r_1$ and $M_2 = 4M_1$, then

$$\frac{M_2}{M_1} = \frac{r_2^{d_f}}{r_1^{d_f}} \qquad 4 = 3^{d_f}$$

or

$$d_f = \frac{\ln 4}{\ln 3} \approx 1.26$$

The self-similar nature of the Koch curve is clear from the fact that if a small piece of the curve is magnified, it looks exactly like the larger piece.

Another example of a regular fractal is a Sierpinski gasket. Start with a filled equilateral triangle, draw the three medians that divide it into four smaller equilateral triangles and cut out the middle one, In the second step, repeat the same procedure with each of the three remaining equilateral triangles, obtaining nine still smaller ones, and so on. The fractal dimension of this Sierpinski gasket is calculated by the same method as for the Koch curve above. As the radius of the circle around a section of the Sierpinski gasket doubles, the number of triangles (the mass of the gasket inside the circle) triples.

Repeating the previous calculations, defining r_1 and $r_2 = 2r_1$ two successive iterations

$$M_1 = A r_1^{d_f} \quad M_2 = A r_2^{d_f} = A(2r_1)^{d_f} = 2^{d_f} M_1$$

and since $M_2 = 3M_1$

$$d_f = \frac{\ln 3}{\ln 2} \approx 1.58$$

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11 Thermodynamics of mixing

Mixtures are systems consisting of two or more different chemical species. Binary mixtures consist of only two different species. An example of a binary mixture is a blend of polystyrene and polybutadiene. Mixtures with three components are called ternary. An example of a ternary mixture is a solution of polystyrene and polybutadiene in toluene. If the mixture is uniform and all components of the mixture are intermixed on a molecular scale, the mixture is called homogeneous. An example of a homogeneous mixture is a polymer solution in a good solvent. If the mixture consists of several different phases (regions with different compositions), it is called heterogeneous. An example of a heterogeneous mixture is that of oil and water. Whether an equilibrium state of a given mixture is homogeneous or heterogeneous is determined by the composition dependence of the entropy and energy changes on mixing. Entropy always favours mixing, but energetic interactions between species can either promote or inhibit mixing.

11.1 Entropy of binary mixing - From Flory book

We calculate here the total configurational entropy of the polymer solution arising from the variety of ways of arranging the polymer and solvent molecules on a lattice. Hence the initial, or reference, states will be taken as the pure solvent and the pure, perfectly ordered polymer; i.e., the polymer chains will be taken to be initially in a perfect crystal-like arrangement.

The lattice contains n_0 cells, n_1 of them occupied by the solvent, and $n_2 L_2$ occupied by monomers. Here L_2 indicates the length of the polymer. Let z be the lattice coordination number or number of cells which are first neighbours to a given cell.

As done when evaluating the mixing entropy on a lattice, we need to evaluate first the total number Ω of arrangements, the number of ways in which each polymer chain may be inserted in the lattice will be estimated. Let's start our calculation by assuming an empty lattice and positioning the polymers in the lattice. At the end we will insert the solvent molecules.

Assume that i polymer molecules have been inserted previously at random. There remains a total of $n_0 - iL_2$ vacant cells in which to place the first segment of molecule $i + 1$. The second segment could be assigned to any of the z neighbors of the cell occupied by the first segment. To account for the fact that possibly some of the neighbouring sites are occupied, we will evaluate a (mean-field) estimate of the probability that a site is full. For the time being we call f_i the probability that a cell is occupied after the insertion of i polymers. Hence, $z f_i$ of the neighbour cells are occupied and then the second monomer can be put in $z(1 - f_i)$ cells. The expected number of cells available to the third segment will be $(z - 1)(1 - f_i)$ since one of the cells adjacent to the second segment is occupied by the first. For each succeeding segment the expected number of permissible alternative assignments can be taken also as $(z - 1)(1 - f_i)$, disregarding those comparatively infrequent instances

in which a segment other than the immediately preceding one of the same chain occupies one of the cells in question. Hence the expected number ν_{i+1} of sets of L_2 contiguous sites available to the molecule is

$$\nu_{i+1} = (n_0 - iL_2)z(z-1)^{L_2-2}(1-f_i)^{L_2-1}$$

If each of the n_2 polymer molecules to be added to the lattice were distinguishable from every other, the number of ways in which all of them could be arranged in the lattice would be given by the product of the ν_i for each molecule added consecutively to the lattice, i.e., by

$$\prod_{i=1}^{n_2} \nu_i$$

Arrangements in which the sets of L_2 contiguous lattice cells chosen for occupation by polymer molecules are identical but which differ only in the permutation of the polymer molecules over these sets would be counted as different in this enumeration scheme. Since the polymer molecules actually are identical, it is appropriate to eliminate this redundancy and write

$$\Omega = \frac{1}{n_2!} \prod_{i=1}^{n_2} \nu_i$$

To estimate f_i, we apply the standard mean-field rule that space-correlations are ignored. Thus we can write

$$f_i = \frac{iL_2}{n_0}$$

Substituting f_i and replacing the lone factor z with $z-1$, we obtain

$$\nu_{i+1} = (n_0 - iL_2)z(z-1)^{L_2-2}\left(\frac{n_0 - iL_2}{n_0}\right)^{L_2-1} = (n_0 - iL_2)^{L_2}\left(\frac{z-1}{n_0}\right)^{L_2-1}$$

which may be further approximated for convenience, and with an error which will be imperceptible, by

$$\nu_{i+1} = \frac{(n_0 - iL_2)!}{(n_0 - L_2(i+1))!}\left(\frac{z-1}{n_0}\right)^{L_2-1}$$

Indeed, consider the ratio between two factorials, when one (n^*) is large and the other one differ from the previous one for a small quantity (m). Then

$$\frac{n^*!}{(n^*-m)!} = \frac{n^*(n^*-1)(n^*-2)....1}{(n^*-m)(n^*-m-1)....1}$$

and simplifying

$$\frac{n^*!}{(n^*-m)!} = n^*(n^*-1)(n^*-2)...(n^*-m) \approx (n^*)^m$$

One can also obtain the same result looking at the log of the two expressions:

$$\ln(n_0 - iL_2)^{L_2} \qquad \text{and} \qquad \ln \frac{(n_0 - iL_2)!}{(n_0 - L_2(i+1))!}$$

The right expression can be transformed by Stirling

$$(n_0 - iL_2)\ln(n_0 - iL_2) - (n_0 - iL_2) - (n_0 - L_2(i+1))\ln(n_0 - L_2(i+1)) + (n_0 - L_2(i+1)) =$$

$$(n_0 - ix)\ln(n_0 - iL_2) - (n_0 - L_2(i+1))\ln(n_0 - L_2(i+1)) + L_2$$

$$\approx (n_0 - iL_2)\ln(n_0 - iL_2) - (n_0 - L_2(i+1))\ln(n_0 - iL_2) + L_2 \approx L_2\ln(n_0 - iL_2) + L_2 \approx L_2\ln(n_0 - iL_2) = \ln(n_0 - iL_2)^{L_2}$$

As a result

$$\Omega = \left(\frac{z-1}{n_0}\right)^{n_2(L_2-1)} \frac{1}{n_2!} \prod_{i=1}^{n_2} \frac{(n_0 - iL_2)!}{(n_0 - L_2(i+1))!}$$

and since

$$\prod_{i=1}^{n_2} \frac{(n_0 - iL_2)!}{(n_0 - L_2(i+1))!} = \frac{(n_0 - L_2)!(n_0 - 2L_2)!(n_0 - 3L_2)!....(n_0 - n_2L_2)!}{(n_0 - 2L_2))!(n_0 - 3L_2)!.....(n_0 - n_2L_2 - L_2))!} = \frac{(n_0 - L_2)!}{(n_0 - n_2L_2 - L_2))!}$$

where we have simplified the equal factorials in the numerator and denominator. If we now make use of the following approximate relation

$$n_0! \approx (n_0 - L_2)!(n_0 - L_2)^{L_2} \qquad (n_0 - n_2L_2)! \approx (n_0 - n_2L_2 - L_2)!(n_0 - n_2L_2)^{L_2}$$

and the further approximation

$$n_0! = (n_0 - L_2)!n_0^{L_2} \qquad (n_0 - n_2L_2)! = (n_0 - n_2L_2 - L_2)!n_0^{L_2}$$

$$\Omega = \left(\frac{z-1}{n_0}\right)^{n_2(L_2-1)} \frac{1}{n_2!}\frac{(n_0 - L_2)!}{(n_0 - n_2L_2 - L_2))!} \approx \frac{n_0!}{(n_0 - n_2L_2)!n_2!}\left(\frac{z-1}{n_0}\right)^{n_2(L_2-1)}$$

If each solvent molecule may occupy one of the remaining lattice sites, and in only one way, Ω represents also the total number of configurations for the solution, from which it follows that the configurational entropy of mixing the perfectly ordered pure polymer and the pure solvent is given by $S_c = k_B \ln \Omega$. Introduction of Stirling's approximations for the factorials occurring in Ω, one gets

$$\ln \Omega = n_0 \ln n_0 - n_0 - n_1 \ln n_1 + n_1 - n_2 \ln n_2 + n_2 + n_2(L_2 - 1)\ln(z-1) - n_2(L_2 - 1)\ln n_0$$

and rewriting $n_0 = n_1 + n_2 L_2 = n_1 + n_2 + n_2(L_2 - 1)$

$$= n_1 \ln n_0 + n_2 \ln n_0 + n_2(L_2-1)\ln n_0 - n_1 \ln n_1 - n_2 \ln n_2 + (n_1 + n_2 - n_0) + n_2(L_2-1)\ln(z-1) - n_2(L_2-1)\ln n_0$$

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$$\ln \Omega = -n_1 \ln \frac{n_1}{n_0} - n_2 \ln \frac{n_2}{n_0} - n_2(L_2 - 1) + n_2(L_2 - 1)\ln(z - 1)$$

and replacing n_0 with $n_1 + L_2 n_2$,

$$S_c = -k_B \left\{ n_1 \ln\left(\frac{n_1}{n_1 + L_2 n_2}\right) + n_2 \ln\left(\frac{n_2}{n_1 + L_2 n_2}\right) - n_2(L_2 - 1)\ln\left[\frac{z-1}{e}\right] \right\}$$

This configurational entropy includes both the mixing entropy and the entropy associated to the polymer disorder. To evaluate this last term we can estimate the value of S_c when there is no solvent, or equivalently evaluating S_c with $n_1 = 0$. This gives

$$\Delta S_{disorientation} = -k_B \left\{ n_2 \ln\left(\frac{1}{L_2}\right) - n_2(L_2 - 1)\ln\left[\frac{z-1}{e}\right] \right\}$$

Then, we can write, joining the $n_2 \ln\left(\frac{1}{L_2}\right)$ term with the previous one

$$\Delta S_{mix} = S_c - \Delta S_{disorientation} = -k_B \left\{ n_1 \ln\left(\frac{n_1}{n_1 + L_2 n_2}\right) + n_2 \ln\left(\frac{n_2 L_2}{n_1 + L_2 n_2}\right) \right\}$$

The result reduces, defining $\phi_1 = \frac{n_1}{n_1 + L_2 n_2}$ and $\phi_2 = \frac{n_2 L_2}{n_1 + L_2 n_2}$ (the volume fractions of solvent and solute)

$$\Delta S_{mix} = -k_B(n_1 \ln \phi_1 + n_2 \ln \phi_2)$$

The mixing entropy per lattice site can also be written as

$$\frac{\Delta S_{mix}}{n_1 + L_2 n_2} = -k_B \left(\phi_1 \ln \phi_1 + \frac{\phi_2}{L_2} \ln \phi_2 \right)$$

11.2   Considerations

A regular solution has $N_A = N_B = 1$ and a large entropy of mixing:

$$\Delta \tilde{S}_{mix} = -k_B(\phi_A \ln \phi_A + \phi_B \ln \phi_B)$$

A polymer solution has $N_A = N$ and $N_B = 1$:

$$\Delta \tilde{S}_{mix} = -k_B \left(\frac{\phi_A}{N} \ln \phi_A + \phi_B \ln \phi_B \right)$$

The previous equations predict enormous differences between the entropies of mixing for regular solutions, polymer solutions, and polymer blends.

Typically N is large, making the first term negligible compared to the second term. For solutions with $\phi_A = \phi_B = 0.5$, the entropy of mixing for the polymer solution is roughly half

of that for the regular solution. For polymer blends, both N_A and N_B are typically large, making the entropy of mixing very small. For this reason, polymers have *stymied entropy* (styme=ostacolare in italian). Connecting monomers into chains drastically reduces the number of possible states of the system. Despite the fact that the mixing entropy is small for polymer blends, it is always positive and hence promotes mixing. Mixtures with no difference in interaction energy between components are called ideal mixtures. Let us denote the volume fraction of component A by ϕ and the corresponding volume fraction of component B becomes $1 - \phi$. The free energy of mixing per site for ideal mixtures is purely entropic:

$$\Delta F_{mix} = -T\Delta \tilde{S}_{mix} = k_B T \left(\frac{\phi}{N_A} \ln \phi + \frac{1 - \phi}{N_B} \ln(1 - \phi) \right)$$

Ideal mixtures are always homogeneous (the concavity of ΔF_{mix} vs ϕ is always positive). The mixing entropy calculated above includes only the translational entropy that results from the many possible locations for the centre of mass of each component. The calculation assumes that the conformational entropy of a polymer is identical in the mixed and pure states. This assumption is very good for polymer blends, where each chain is nearly ideal in the mixed and pure states. However, many polymer solutions have excluded volume that changes the conformation of the polymer in solution, as discussed previously. Another important assumption in the entropy of mixing calculation is no volume change on mixing. Real polymer blends and solutions have very small, but measurable, volume changes when mixed.

11.3   Energy of binary mixing

Interactions between species can be either attractive or repulsive. In most experimental situations, mixing occurs at constant pressure and the enthalpic interactions between species must be analysed to find a minimum of the Gibbs free energy of mixing. In the simplified lattice model (**Flory-Huggins theory**) discussed in the present chapter, components are mixed at constant volume and therefore we will be studying the energy of interactions between components and the change in the Helmholtz free energy of mixing. The energy of mixing can be either negative (promoting mixing) or positive (opposing mixing). Regular solution theory allows for both possibilities, using the lattice model. To estimate the energy of mixing this theory places species into lattice sites randomly, ignoring any correlations. Thus, for all mixtures, favourable or unfavourable interactions between monomers are assumed to be small enough that they do not affect the random placement. Worse still, the regular solution approach effectively cuts the polymer chain into pieces that are the size of the solvent molecules (the lattice size) and distributes these pieces randomly. Such a mean-field approach ignores the correlations between monomers along the chain (the chain connectivity). Here, for simplicity, it is assumed that in polymer blends the monomer volumes of species A and B are identical. Regular solution theory writes the en-

ergy of mixing in terms of three pairwise interaction energies (u_{AA}, u_{AB}, and u_{BB}) between adjacent lattice sites occupied by the two species. A mean field is used to determine the average **pairwise** interaction U_A of a monomer of species A occupying one lattice site with a neighbouring monomer on one of the adjacent sites. The probability of this neighbour being a monomer of species A is assumed to be the volume fraction ϕ_A of these molecules (ignoring the effect of interactions on this probability). The probability of this neighbour being a monomer of species B is $\phi_B = 1 - \phi_A$. The average pairwise interaction of an A-monomer with one of its neighbouring monomers is a volume fraction weighted sum of interaction energies:

$$U_A = u_{AA}\phi_A + u_{AB}\phi_B$$

The corresponding energy of a B-monomer with one of its neighbours is similar:

$$U_B = u_{AB}\phi_A + u_{BB}\phi_B$$

Each lattice site of a regular lattice has z nearest neighbours, where z is the coordination number of the lattice. For example, $z = 4$ for a square lattice and $z = 6$ for a cubic lattice. Therefore, the average interaction energy of an A monomer with all of its z neighbours is zU_A. The average energy per monomer is half of this energy ($zU_A/2$) due to the fact that every pairwise interaction is counted twice (once for the monomer in question and once for its neighbour). The corresponding energy per site occupied by species B is zU_B. The number of sites occupied by species A (the number of monomers of species A) is $n\phi_A$, where n is the total number of sites in the combined system. The number of sites occupied by monomers of species B is $n\phi_B$. Summing all the interactions gives the total interaction energy of the mixture:

$$U = \frac{zn}{2}[U_A\phi_A + U_B\phi_B]$$

Denoting the volume fraction of species A by ϕ the total interaction energy of a binary mixture with n lattice sites is expressed as

$$U = \frac{zn}{2}[(u_{AA}\phi_A + u_{AB}\phi_B)\phi_A + (u_{AB}\phi_A + u_{BB}\phi_B)\phi_B]$$

$$= \frac{zn}{2}[u_{AA}\phi^2 + u_{BB}(1 - \phi)^2 + 2u_{AB}\phi(1 - \phi)]$$

The interaction energy per site in a pure A component before mixing is $zu_{AA}/2$, because each monomer of species A before mixing is only surrounded by species A. We ignore the boundary effects because of the very small surface-to-volume ratio for most macroscopic systems. The total number of monomers of species A is $n\phi_A$ and therefore the total energy of species A before mixing is

$$\frac{zn}{2}u_{AA}\phi$$

and the total energy of species B before mixing is

$$\frac{zn}{2}u_{BB}(1 - \phi)$$

The total energy of both species before mixing is the sum of the energies of the two pure components:

$$U - U_0 = \frac{zn}{2}[u_{AA}\phi^2 + u_{BB}(1-\phi)^2 + 2u_{AB}\phi(1-\phi) - u_{AA}\phi u_{BB}(1-\phi) = \frac{zn}{2}[\phi(1-\phi)(2u_{AB} - u_{AA} - u_{BB}]$$

It is convenient to study the intensive property, which is the energy change on mixing per site:

$$\Delta\tilde{U}_{mix} = \frac{U - U_0}{n} = \frac{z}{2}\phi(1-\phi)(2u_{AB} - u_{AA} - u_{BB})$$

The Flory interaction parameter χ is defined to characterize the difference of interaction energies in the mixture:

$$\chi \equiv \frac{z}{2}\frac{2u_{AB} - u_{AA} - u_{BB}}{k_B T}$$

Defined in this fashion, χ is a dimensionless measure of the differences in the strength of pairwise interaction energies between species in a mixture (compared with the same species in their pure component states). Using this definition, we write the energy of mixing per lattice site as

$$\Delta\tilde{U}_{mix} = \chi\phi(1-\phi)k_B T$$

This energy equation is a mean-field description of all binary regular mixtures: regular solutions, polymer solutions, and polymer blends.

Combining with the expression for the entropy of mixing, we arrive at the Helmholtz free energy of mixing per lattice site:

$$\Delta\tilde{F}_{mix} = \Delta\tilde{U}_{mix} - T\Delta\tilde{S}_{mix} = k_B T\left[\frac{\phi}{N_A}\ln\phi + \frac{1-\phi}{N_B}\ln(1-\phi) + \chi\phi(1-\phi)\right]$$

The free energy of mixing per unit volume is $\Delta\tilde{F}_{mix}/v_0$. This equation was first calculated by Huggins and later independently derived by Flory, and is commonly referred to as the Flory-Huggins equation. For non-polymeric mixtures with $N_A = N_B = 1$, this equation was developed earlier by Hildebrand and is called regular solution theory:

$$\Delta\tilde{F}_{mix}^{regular} = [\phi\ln\phi + 1 - \phi\ln(1-\phi) + \chi\phi(1-\phi)]$$

For polymer solutions, $N_A = N$ and $N_B = 1$, reducing to the Flory-Huggins equation for polymer solutions:

$$\Delta\tilde{F}_{mix} = \Delta\tilde{U}_{mix} - T\Delta\tilde{S}_{mix} = k_B T\left[\frac{\phi}{N}\ln\phi + (1-\phi)\ln\phi + \chi\phi(1-\phi)\right]$$

The first two terms in the free energy of mixing have entropic origin and always act to promote mixing, although with blends of long- chain polymers these terms are quite small.

The last term has energetic origin, and can be positive (opposing mixing), zero [ideal mixture], or negative (promoting mixing) depending on the sign of the interaction parameter χ. If there is a net attraction between species (i.e. they like each other better than they like themselves), $\chi < 0$ and a single-phase mixture is favourable for all compositions. More often there is a net repulsion between species (they like themselves more than each other) and the Flory interaction parameter is positive $\chi > 0$. We will show that in this case the equilibrium state of the mixture depends not on the sign of the free energy of mixing at the particular composition of interest, but on the functional dependence of this free energy on the composition ϕ for the whole range of compositions. This functional dependence $\Delta \tilde{F}_{mix}$ depends on the value of the Flory interaction parameter χ as well as on the degrees of polymerization of both molecules N_A and N_B. It is very important to know the value of the Flory interaction parameter χ for a given mixture. Tables of χ parameters are listed in many reference books.

One of the major assumptions of the Flory-Huggins theory is that there is no volume change on mixing and that monomers of both species can fit on the sites of the same lattice. In most real polymer blends, the volume per monomer changes upon mixing. Some monomers may pack together better with certain other monomers. The volume change on mixing and local packing effects lead to a temperature-independent additive constant in the expression of the Flory interaction parameter. In practice, these effects are not fully understood and all deviations from the lattice model are lumped into the interaction parameterχ, which can display non-trivial dependences on composition, chain length, and temperature. Empirically, the temperature dependence of the Flory interaction parameter is often written as the sum of two terms:

$$\chi = A + \frac{B}{T}$$

The temperature-independent term A is referred to as the 'entropic part' of χ while B/T is called the 'enthalpic part'. The parameters A and B have been tabulated for many polymer blends.

12   Stability of polymer solutions

Ideal mixtures with $\Delta \tilde{U}_{mix} = 0$ have their free energy of mixing convex over the entire composition range. To understand why it is convex, we differentiate the entropy of mixing expression with respect to composition

$$\frac{\partial \Delta \tilde{F}_{mix}}{\partial \phi} = -T \frac{\partial \Delta \tilde{S}_{mix}}{\partial \phi} = k_B T \left[\frac{\ln \phi}{N_A} + \frac{1}{N_A} - \frac{\ln(1 - \phi)}{N_B} - \frac{1}{N_B} \right]$$

Notice that this purely entropic contribution diverges at both extremes of composition. This divergence means that a small amount of either species will always dissolve even

if there are strong unfavourable energetic interactions. Differentiating the free energy of mixing a second time determines the stability of the mixed state for ideal mixtures

$$\frac{\partial^2 \Delta \tilde{F}_{mix}}{\partial \phi^2} = -T \frac{\partial^2 \Delta \tilde{S}_{mix}}{\partial \phi^2} = k_B T \left[\frac{1}{N_A \phi} + \frac{1}{(1-\phi)N_B} \right] > 0$$

Homogeneous ideal mixtures are stable for all compositions because entropy always acts to promote mixing, and the ideal mixture does not have any energetic contribution to its free energy. The opposite case where the energy dominates is found at $T = 0$ K because the entropic contribution vanishes. The free energy only has an energetic part. Differentiating the free energy at $T = 0$ K twice with respect to composition determines whether the blend is locally stable at 0 K

$$\frac{\partial^2 \Delta \tilde{F}_{mix}}{\partial \phi^2} = \frac{\partial^2 \Delta \tilde{U}_{mix}}{\partial \phi^2} = -2\chi k_B T = -2B k_B - 3A k_B T$$

where in the last step we have written $\chi = A + B/T$. At $T = 0$ K

$$\frac{\partial^2 \Delta \tilde{F}_{mix}}{\partial \phi^2} = -2B k_B$$

If the components of the mixture like themselves more than each other

$$u_{AB} > \frac{u_{AA} + u_{BB}}{2} \quad \text{or} \quad B > 0$$

the free energy of mixing is concave and homogeneous mixtures are unstable for all compositions at $T = 0K$ because the second derivative of the free energy of mixing is negative. Any mixture phase separates into the two pure components at $T = 0K$ since entropy makes no contribution at this special T. This case corresponds to positive Flory interaction parameter χ. If the components like each other better than themselves

$$u_{AB} < \frac{u_{AA} + u_{BB}}{2} \quad \text{or} \quad B < 0$$

the free energy of mixing is convex and homogeneous mixtures of any composition are stable at $T = 0$ K. This case corresponds to negative Flory interaction parameter χ.

Real mixtures have both energetic and entropic contributions to their free energy of mixing. The local stability of the mixture is determined by the sign of the second derivative of the free energy with respect to composition:

$$\frac{\partial^2 \Delta \tilde{F}_{mix}}{\partial \phi^2} = \frac{\partial^2 \Delta \tilde{U}_{mix}}{\partial \phi^2} - T \frac{\partial^2 \Delta \tilde{S}_{mix}}{\partial \phi^2} = k_B T \left[\frac{1}{N_A \phi} + \frac{1}{(1-\phi)N_B} \right] - 2\chi k_B T$$

At finite temperatures, $\Delta \tilde{F}_{mix}$ is convex at both ends of the composition range because its second derivative is positive due to the diverging slope of the entropy of mixing $\Delta \tilde{S}_{mix}$.

For example, consider a polymer blend with $N_A = 200$ and $N_B = 100$, for which $\chi T = 5K$. At high temperatures the entropic term of the mixing free energy dominates, and all blend compositions are stable (Draw figure). As temperature is lowered the entropic term diminishes, allowing the repulsive energetic term to start to be important at intermediate compositions. Entropy always dominates the extremes of composition (due to the divergent first derivative) making those extremes stable. Below some critical temperature T_c (defined in detail later on), a composition range with concave free energy appears, which makes intermediate compositions unstable. Below T_c there is a range of compositions for which there are phase separated states with lower free energy than the homogeneous state. Many demixed states have lower free energy than the homogeneous state, but the lowest free energy state defines the equilibrium state. Straight lines connecting the two phase compositions determine the free energy of the phase separated state. In order to minimize the free energy, the system chooses the compositions that have the lowest possible straightjine, which is a common tangent. The phases present are thus determined by the common tangent rule. This common tangent minimization of the free energy of mixing effectively requires that the chemical potential of each species in both phases are balanced at equilibrium. The two equilibrium compositions ϕ_I and ϕ_{II} correspond to a common tangent line. For any overall composition in the miscibility gap between ϕ_I and ϕ_{II}, the system can minimize its free energy by phase separating into two phases of composition ϕ_I and ϕ_{II}. The amounts of each phase are determined by the lever rule outlined above. The composition ranges $0 < \phi < \phi_I$ or $\phi_{II} < \phi < 1$ are outside the miscibility gap and the homogeneously mixed state is the stable equilibrium state for these blend compositions. Within the miscibility gap there are unstable and metastable regions, separated by inflection points at which the second derivative of the free energy is zero. Between the inflection points, the second derivative of the free energy is negative and the homogeneously mixed state is unstable. Even the smallest fluctuations in composition lower the free energy, leading to spontaneous phase separation (called spinodal decomposition). Between the infection points and the equilibrium phase separated compositions, there are two regions that have positive second derivative of the free energy of mixing. Even though the free energy of the homogeneous state is larger than that of the phase-separated state (on the common tangent line) the mixed state is locally stable to small composition fluctuations. Such states are metastable because large fluctuations are required for the system to reach thermodynamic equilibrium. Phase separation in this metastable regime occurs by nucleation and growth. The nuclei of the more stable phase must be larger than some critical size in order to grow in the metastable region because of the surface tension between phases. The new phase can grow only when a sufficiently large fluctuation creates a domain larger than the critical size.

13 Phase diagrams

By considering the temperature dependence of the free energy of mixing, a phase diagram can be constructed to summarize the phase behaviour of the mixture, showing regions of stability, instability, and metastability. Recall the free energy of mixing for a polymer blend

$$\Delta \tilde{F}_{mix} = k_B T \left[\frac{\phi}{N_A} \ln \phi + \frac{1 - \phi}{N_B} \ln(1 - \phi) + \chi \phi (1 - \phi) \right]$$

The phase boundary is determined by the common tangent of the free energy at the compositions ϕ_I and ϕ_{II} corresponding to the two equilibrium phases

$$\left(\frac{\partial \Delta \tilde{F}_{mix}}{\partial \phi} \right)_{\phi = \phi_I} = \left(\frac{\partial \Delta \tilde{F}_{mix}}{\partial \phi} \right)_{\phi = \phi_{II}}$$

This derivative of the free energy of mixing per site with respect to volume fraction of component A is

$$\left(\frac{\partial \Delta \tilde{F}_{mix}}{\partial \phi} \right) = k_B T \left[\frac{\ln \phi}{N_A} + \frac{1}{N_A} - \frac{\ln(1 - \phi)}{N_B} - \frac{1}{N_B} + \chi(1 - 2\phi) \right]$$

13.1 Symmetric polymer blend

For the simple example of a symmetric polymer blend with $N_A = N_B = N$ it is particularly easy to evaluate the coexistence curve, since the common tangent line is horizontal

$$\left(\frac{\partial \Delta \tilde{F}_{mix}}{\partial \phi} \right)_{\phi = \phi_I} = \left(\frac{\partial \Delta \tilde{F}_{mix}}{\partial \phi} \right)_{\phi = \phi_{II}} = k_B T \left[\frac{\ln \phi}{N} - \frac{\ln(1 - \phi)}{N} + \chi(1 - 2\phi) \right] = 0$$

The above equation can be solved for the interaction parameter corresponding to the phase boundary — the binodal of a symmetric blend:

$$\chi_{binodal} = \frac{1}{2\phi - 1} \left[\frac{\ln \phi}{N} - \frac{\ln(1 - \phi)}{N} \right]$$

Since the model is by construction symmetric, the critical packing fraction is $\phi = 0.5$. This allows us to evaluate the critical χ. Expanding around $\phi = 0.5$ one finds

$$\chi_{critical} = \frac{1}{N} \frac{1}{2\phi - 1} \ln\left(\frac{\phi}{1 - \phi} - 1 + 1\right) = \frac{1}{N} \frac{1}{2\phi - 1} \frac{\phi}{1 - \phi} - 1 = \frac{1}{N} \frac{1}{2\phi - 1} \frac{\phi - 1 + \phi}{1 - \phi} = \frac{1}{N} \frac{1}{1 - \phi} = \frac{2}{N}$$

which suggests that binary mixture of polymers of similar length always phase separate (since $\chi_{critical} \approx 0$).

Using the phenomenological temperature dependence of the interaction parameter ($\chi = A + B/T$), this relation can be transformed to the binodal of the phase diagram in the space of temperature and composition.

The binodal for binary mixtures coincides with the coexistence curve, since for a given temperature (or $N\chi$) with overall composition in the two-phase region, the two compositions that coexist at equilibrium can be read off the binodal. Any overall composition at temperature T within the miscibility gap defined by the binodal has its minimum free energy in a phase-separated state with the compositions given by the two coexistence curve compositions ϕ_I and ϕ_{II}.

13.2 A-Symmetric polymer blend

Returning to the general case of an asymmetric blend, the inflection points can be found by equating the second derivative of the free energy to zero:

$$\frac{\partial^2 \Delta \tilde{F}_{mix}}{\partial \phi^2} = k_B T \left[\frac{1}{N_A \phi} + \frac{1}{(1-\phi)N_B} \right] - 2\chi k_B T = 0$$

The curve corresponding to the inflection point is the boundary between unstable and metastable regions and it is called the spinodal

$$\chi_{spinodal} = \frac{1}{2} \left[\frac{1}{N_A \phi} + \frac{1}{(1-\phi)N_B} \right]$$

This spinodal can also be transformed to a phase diagram in the temperature-composition plane by using the experimentally determined $\chi(T)$.

In a binary blend the extreme point on the spinodal curve corresponds to the critical point:

$$\frac{\partial \chi_{spinodal}}{\partial \phi} = \frac{1}{2} \left[-\frac{1}{N_A \phi^2} + \frac{1}{(1-\phi)^2 N_B} \right] = 0$$

The solution of this equation gives the critical composition:

$$\phi_c = \frac{\sqrt{N_B}}{\sqrt{N_A} + \sqrt{N_B}}$$

Substituting this critical composition back into the equation of the spinodal determines the critical interaction parameter:

$$\chi_c = \frac{1}{2} \frac{(\sqrt{N_A} + \sqrt{N_B})^2}{N_A N_B} = \frac{1}{2} \left(\frac{1}{\sqrt{N_A}} + \frac{1}{\sqrt{N_B}} \right)^2$$

13.3 Symmetric blends again - they do not like to stay homogeneous

For a symmetric polymer blend ($N_A = N_B = N$), the whole phase diagram is symmetric with the critical composition

$$\phi_c = \frac{1}{2}$$

and very small critical interaction parameter

$$\chi_c = \frac{2}{N}$$

Since this critical interaction parameter is very small for blends of long chains, most polymer blends have $\chi > \chi_c$ and thus are phase separated over some composition range (within the miscibility gap). Only blends with either very weak repulsion ($0 < \chi < \chi_c$), or a net attraction between components of the mixture ($\chi < 0$) form homogeneous (single-phase) blends over the whole composition range.

### 13.4 Polymer solutions - the critical packing density goes to zero !

In polymer solutions ($N_A = N$ and $N_B = 1$), the phase diagram is strongly asymmetric with low critical composition

$$\phi_c = \frac{1}{\sqrt{N} + 1} \approx \frac{1}{\sqrt{N}}$$

and critical interaction parameter close to $1/2$

$$\chi_c = \frac{1}{2} + \frac{1}{\sqrt{N}} + \frac{1}{2N}$$

Note that the spinodal and binodal for any binary mixture meet at the critical point. For interaction parameters χ below the critical one (for $\chi < \chi_c$ the homogeneous mixture is stable at any composition For higher values of the interaction parameter (for $\chi > \chi_c$) there is a miscibility gap between the two branches of the binodal. For any composition in a miscibility gap, the equilibrium state corresponds to two phases with compositions ϕ_I and ϕ_{II} located on the two branches of the coexistence curve at the same value of χ.
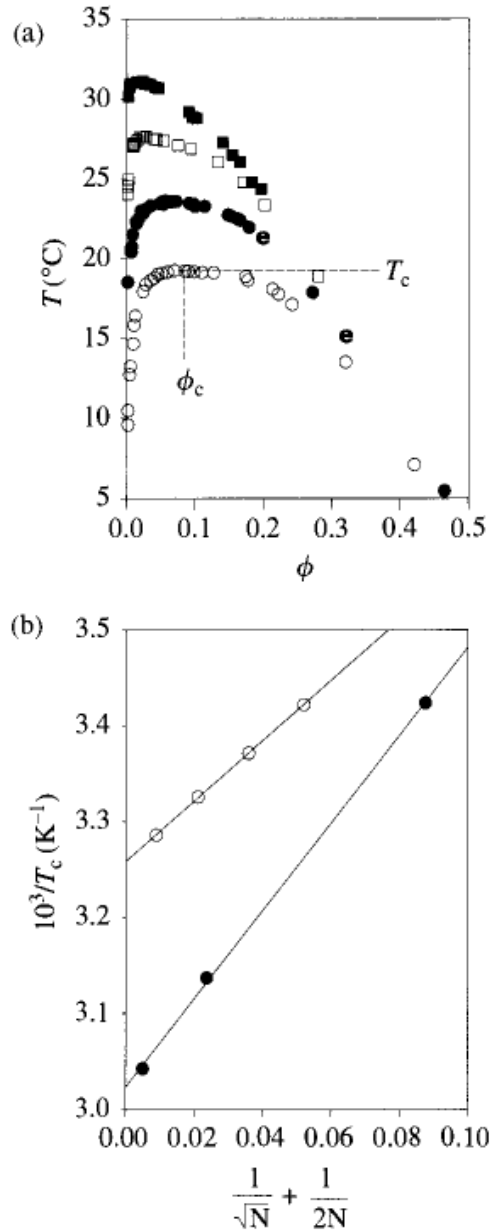
Fig. 5.2
(a) Phase diagrams for polystyrenes in cyclohexane, $M = 43\,600$ g mol^{-1} (open circles), $M = 89\,000$ g mol^{-1} (filled circles), $M = 250\,000$ g mol^{-1} (open squares), $M = 1\,270\,000$ g mol^{-1} (filled squares). (b) Chain length dependence of the critical temperature for polystyrene in cyclohexane (open circles) from part (a) and for polyisobutylene in diisobutyl ketone (filled circles). All data from A. R. Shultz and P. J. Flory, *J. Am. Chem. Soc.* **74**, 4760 (1952).