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Polymers and Neutron Scattering

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$$P(q) = 1 - \frac{q^2}{6z^2}\sum_{i=1}^{z}\sum_{j=1}^{z}\langle r_{ij}^2\rangle + \frac{q^4}{5!z^2}\sum_{i=1}^{z}\sum_{j=1}^{z}\langle r_{ij}^4\rangle - \frac{q^6}{7!z^2}\sum_{i=1}^{z}\sum_{j=1}^{z}\langle r_{ij}^6\rangle + \ldots . \tag{6.9}$$

6.2.2 The radius of gyration

One of the most important properties of small angle neutron scattering is that the second term of this expansion has a very simple geometrical meaning, independent of the scattering properties of the sample; it gives the radius of gyration (Guinier 1956). The square of the radius of gyration of a particle made of z identical elements, around its centre of gravity, is given by

$$\overline{R^2} = \frac{1}{z}\sum_{i=1}^{z}\langle r_i^2\rangle \tag{6.10}$$

where r_i is the vector joining the scattering point i to the centre of gravity. This quantity is also given by the formula

$$\overline{R^2} = \frac{1}{2z^2}\sum_{i=1}^{z}\sum_{j=1}^{z}\langle r_{ij}^2\rangle . \tag{6.11}$$

In order to show this result let us write $r_{ij} = r_i - r_j$ and introduce this quantity in expression (6.11); we obtain

$$\overline{R^2} = \frac{1}{2z^2}\sum_{i=1}^{z}\sum_{j=1}^{z}(\langle r_i^2\rangle + \langle r_j^2\rangle - 2\langle r_i \cdot r_j\rangle). \tag{6.12}$$

The two first terms are identical and equal to $z\Sigma\langle r_i^2\rangle$ and the last term is equal to zero since

$$\sum_{i=1}^{z}\sum_{j=1}^{z}\langle r_i \cdot r_j\rangle = \left\langle\sum_i r_i\right\rangle\left\langle\sum_j r_j\right\rangle = 0. \tag{6.13}$$

This last result is evident because of the properties of the centre of mass.

The preceding calculation proves, quite generally, that the form factor can always be written as

$$P(q) = 1 - \frac{1}{3}q^2\overline{R^2} + \ldots . \tag{6.14}$$

This relation is valid for rigid particles as well as for flexible molecules and gives a very elegant method for the determination of the size of the molecules. The initial slope of the curve $I(q)$ as function of q^2 is equal to

$(\overline{R^2})/3$. In fact this is a comparison of the size of the molecule to the factor q which depends on the wavelength and on the direction of observation. For practical purposes $q^2\overline{R^2}$ has to be neither too small, since the deviation from 1 would be difficult to detect, nor too large, because the influence of the remaining terms in the expansion can no longer be neglected. From an experimental point of view slow neutrons are perfect for molecules having a radius of gyration between a few to a few hundred angstroms. The upper and lower limits are difficult to establish rigorously since they depend on the contrast, on the wavelength of the neutrons, and on the quality of the instrument.

6.2.3 The radius of gyration for various geometrical shapes

This is a purely geometric calculation and we give only the results

$$\overline{R^2} = \frac{3}{5}r^2 \tag{6.15a}$$

for a sphere of radius r

$$\overline{R^2} = \frac{1}{5}(a^2 + b^2 + c^2) \tag{6.15b}$$

for an ellipsoid of half axes a,b,c; it reduces to a sphere if $a = b = c$

$$\overline{R^2} = \frac{L^2}{12} + \frac{b^2}{2} \tag{6.15c}$$

for a rod of length L and transverse radius b

$$\overline{R^2} = \frac{L^2}{12} \tag{6.15d}$$

for a rod of length L and negligible diameter

$$\overline{R^2} = \frac{b^2}{2} \tag{6.15e}$$

for a thin disc of radius b.

6.2.4 The radius of gyration for a Gaussian chain

Since macromolecular chains are of particular interest, the value of th radius of gyration for Gaussian chains will be evaluated. We call freel jointed chain or Gaussian a chain made of z independent units attache sequentially and without correlation between the orientation of any pair c segments. (See Fig. 6.2.) It is shown in Appendix 1 that the average of th square of the end to end distance $\overline{L^2}$ is given by the relation

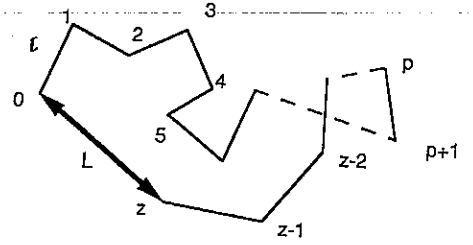

Fig. 6.2 Schematic diagram of a freely jointed chain starting at O and finishing at z.

$$\overline{L^2} = z\overline{l^2} \tag{6.16}$$

where $\overline{l^2}$ is the average of the square of the length of any of the elementary steps. This is true for any chain length

$$\langle r_{ij}^2 \rangle = |i-j|\,\overline{l^2} \tag{6.16'}$$

where the sign $|\ldots|$ indicates that one has to take the absolute value of $i-j$. Since r_{ij}^2 is always positive. Instead of replacing the summation in eqn (6.11) by an integration, assuming that z is large, we shall make the rigorous calculation, valid for any z using the following method. All the values of $\langle r_{ij}^2 \rangle / \overline{l^2}$ are placed in a square matrix having $z+1$ rows and columns since the chain has z segments (see Fig. 6.3). We consider as scattering

j \ i	0	1	...	p	...	z–1	z
0	0	1	...	p–	...	z–1	z
1	1	0	...	p–1	...	z–2	z–1
...	...	...	...	...	...	...	...
p	p	p–1	...	0	...	z–p–1	z–p
...	...	...	...	...	...	...	...
z–1	z–1	z–2	...	z–p	...	0	1
z	z	z–1	...	z–p	...	1	0

Fig. 6.3 A matrix for evaluating $\overline{R^2}$.

units the ends of the segments. One sees immediately that the major diagonal is a symmetry axis. Grouping the elements on lines parallel to the direction of this diagonal gives

$$\sum\sum \frac{\langle r_{ij}^2 \rangle}{\overline{l^2}} = \sum\sum |i-j| = 2[z + (z-1)2 + (z-2)3 + \ldots +$$

$$(z-p+1)p + \ldots + 2(z-1) + z] = 2S. \tag{6.17}$$

The evaluation of this sum is straightforward

$$S = z\sum_{p=1}^{z}(z+1-p)p = (z+1)\sum_{p=1}^{z} p - \sum_{p=1}^{z} p^2 \tag{6.18}$$

and, consulting tables of formulae, one finds

$$S = \frac{z(z+1)(z+2)}{6}. \tag{6.19}$$

Remembering that our chain is made of $z+1$ elements and applying eqn (6.11) we obtain for its radius of gyration (Debye 1946)

$$\overline{R^2} = \overline{l^2}\frac{z}{6}\frac{z+2}{z+1}. \tag{6.20}$$

As soon as z is large enough the second fraction in eqn (6.20) is unity and

$$\overline{R^2} \simeq \frac{1}{6}\overline{L^2} \tag{6.21}$$

where $\overline{L^2}$ is the average square of the end to end distance. This calculation, made for a simple example demonstrates a general property which we shall use later: if one writes a double sum or a double integral of the form

$$\sum_{i=0}^{N}\sum_{j=0}^{N} f(|i-j|)$$

it is possible to transform it into a simple sum or integral simply by writing: $|i-j| = p$. This gives the equality, valid only for N large

$$\sum_{i=0}^{N}\sum_{j=0}^{N} f(|i-j|) = 2\sum_{p=0}^{N}(N-p)f(p). \tag{6.22}$$

The relation has been proved for a simple example using our matrix demonstration but can be applied to any function $f(|i-j|)$.

6.2.5 The ring polymer

Physical chemists are interested in the properties of ring polymers, i.e. polymers having both ends linked together in order to make a loop without end. We shall first calculate the distance between two arbitrary units in a loop in order to be able to evaluate its radius of gyration. Let us assume that we have a ring, made of z elements; the initial element is arbitrary and they are numbered from 0 to $z-1$ (see Fig. 6.4). We should like to know the probability to go from 0 to p on the loop. This requires that we arrive at the point p either via the left side or via the right along a chain of p or of $z-p$ segments respectively. The left side is a random walk of p segments and the probability of arriving at r will be

$$w_p(r) = \left(\frac{3}{2\pi p\overline{l^2}}\right)^{\frac{3}{2}} \exp - \frac{3r^2}{2p\overline{l^2}}. \tag{6.23}$$

By the right path it is

$$w_{z-p}(r) = \left(\frac{3}{2\pi(z-p)\overline{l^2}}\right)^{\frac{3}{2}} \exp - \frac{3r^2}{2(z-p)\overline{l^2}}. \tag{6.24}$$

Since we have to be on the ring the total probability to be at a distance r, $w_{0p}(r)$ is the product of these two probabilities and, writing for the moment the normalization constant as K, we obtain

$$w_{0p}(r) = w_p(r)w_{z-p}(r) = K \exp\left[-\frac{3r^2}{2\overline{l^2}}\left(\frac{1}{p}+\frac{1}{z-p}\right)\right]. \tag{6.25}$$

This expression shows that the probability is still Gaussian and, if we put it in the form $\exp -(3r^2/2\overline{L^2_{z,p}})$ we obtain, calling $\overline{L^2_{z,p}}$ the root mean square distance between 0 and p

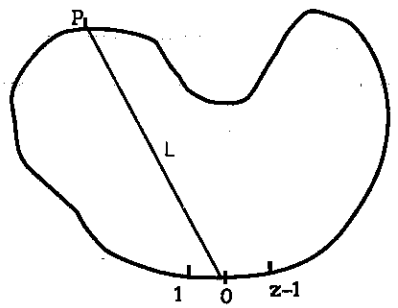

Fig. 6.4 Schematic diagram of a ring molecule.

$$\frac{1}{\overline{L^2_{z,p}}} = \frac{1}{\overline{l^2}}\left(\frac{1}{p}+\frac{1}{z-p}\right) \tag{6.26}$$

or:

$$\overline{L^2_{p,z}} = \overline{r^2_{i,i+p}} = \overline{l^2}P\left(1-\frac{p}{z}\right). \tag{6.27}$$

Applying eqn (6.11) to this result one obtains, for the radius of gyration of a ring

$$\overline{R^2} = \frac{z\overline{l^2}}{12}. \tag{6.28}$$

It is half the value obtained for a linear chain having the same number of segments.

6.2.6 The case of copolymers

We have seen (Chapter 5) that in the case of a copolymer, made of two different kinds of monomers A and B, one has to introduce three form factors S_{AA}, S_{BB}, and S_{AB}. These form factors are associated with three radii of gyration $\overline{R^2_{AA}}$, $\overline{R^2_{BB}}$, and $\overline{R^2_{AB}}$. It is important to understand the physical meaning of these quantities. If one looks at the part A of the copolymer the meaning of $\overline{R^2_{AA}}$ is clear and eqn (6.11) can be applied. The same is true for the part B. The question is less clear for the cross term but, by analogy, we define the 'cross radius of gyration' by a similar expression. We have therefore the three following expressions

$$\overline{R^2_A} = \frac{1}{2z_A^2}\sum_{i=0}^{z}\sum_{j=0}^{z}\overline{r^2_{i_Aj_A}} \tag{6.29}$$

$$\overline{R^2_B} = \frac{1}{2z_B^2}\sum_{i=0}^{z}\sum_{j=0}^{z}\overline{r^2_{i_Bj_B}} \tag{6.30}$$

$$\overline{R^2_{AB}} = \frac{1}{2z_Az_B}\sum_{i=0}^{z}\sum_{j=0}^{z}\overline{r^2_{i_Aj_B}}. \tag{6.31}$$

In order to clarify the physical meaning of $\overline{R^2_{AB}}$ we write

$$r_{i_Aj_B} = A_iG_A + G_AG_B + G_BB_j \tag{6.32}$$

replacing the direct route between the scattering points A_i and B_j by a detour through G_A and G_B, where G_A and G_B are the centre of mass of the

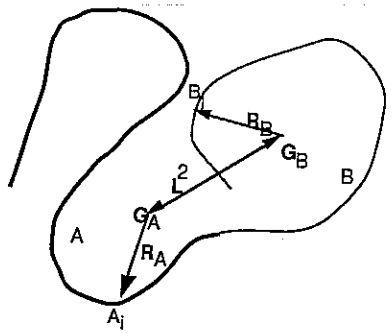

Fig. 6.5 Schematic diagram of a diblock copolymer and geometrical meaning of the quantity L.

two sequences. (See Fig. 6.5.) Squaring this last expression and making the double summation gives, for $\bar{R}^2_{AB}$, the following expression where all the cross terms disappear (Benoît and Wippler 1960)

$$2\overline{R^2_{AB}} = \overline{R^2_A} + \bar{R}^2_B + \overline{G_A G^2_B}. \tag{6.33}$$

From the definitions of the form factor of the whole polymer we have

$$(z_A + z_B)^2 P_T = z^2_A P_A + z^2_B P_B + 2z_A z_B P^2_{AB} \tag{6.34}$$

and for its radius of gyration

$$(z_A + z_B)^2 \overline{R^2_T} = z^2_A \overline{R^2_A} + z^2_B \overline{R^2_B} + 2z_A z_B \overline{R^2_{AB}}. \tag{6.35}$$

Introducing the value of $\overline{R^2_{AB}}$ obtained from eqn (6.33) into the definition of $\overline{R^2_T}$, calling x the fraction of monomer A in the molecule $x = z_A/(z_A + z_B)$ and $\overline{L^2} = \overline{G_A G^2_B}$ the mean square distance between the centres of mass of the part A and the part B of the molecule, we arrive at the formula

$$\overline{R^2_T} = x\overline{R^2_A} + (1 - x)\overline{R^2_B} + x(1 - x)\overline{L^2}. \tag{6.36}$$

This formula is quite general and valid for any type of molecule made of two parts; it is useful in the discussion of the scattering from copolymers when, by changing the contrast of the solvent, one looks for the changes in the scattering envelope as will be shown later.

As a simple example, we shall determine the value of $\overline{L^2}$ for a linear copolymer made of two monomers of the same size. For this purpose we

replace in eqn (6.36) $\overline{R^2_T}$, $\overline{R^2_A}$, $\overline{R^2_B}$ and x by their values as function of z_A, z_B, and $\overline{l^2}$ obtaining

$$\frac{z_A + z_B}{6}\overline{l^2} = \frac{z^2_A \overline{l^2}}{6(z_A + z_B)} + \frac{z^2_B \overline{l^2}}{6(z_A + z_B)} + \frac{z_A z_B}{(z_A + z_B)^2}\overline{L^2}. \tag{6.37}$$

After simplification this gives

$$\overline{L^2} = 2(\overline{R^2_A} + \overline{R^2_B}) = 2\overline{R^2_T}. \tag{6.38}$$

6.3 THE COMPLETE FORM FACTOR

6.3.1 The mathematical methods

In the first part of this chapter we have discussed the form factor for small q values. In this section we shall try to obtain a complete analytical expression valid for any value of q. Various methods are possible. The most classical starts from eqn (6.5)

$$P(q) = \frac{1}{z^2}\sum_{i=1}^{z}\sum_{j=1}^{z}\langle \exp - i\mathbf{q}\cdot\mathbf{r}_{ij}\rangle. \tag{6.39}$$

Since the molecules are randomly oriented one can average over all orientations obtaining

$$P(q) = \frac{1}{z^2}\sum_{i=1}^{z}\sum_{j=1}^{z}\left\langle \frac{\sin qr_{ij}}{qr_{ij}}\right\rangle. \tag{6.40}$$

This formula is very simple since it contains only distances and no imaginary numbers. Instead of making the summation over all pairs of scattering points one can count the number $n(r)$ of pairs being at the distance r and write

$$P(q) = \frac{1}{\int n(r)\mathrm{d}r}\int n(r)\left(\frac{\sin qr}{qr}\right)\mathrm{d}r. \tag{6.41}$$

This expression is used mainly for continuous bodies for which the sums are transformed into integrals. The function $n(r)$ has to be compared with the radial distribution function $g(r)$ introduced in Chapter 4; its definition is similar but in the present case we are dealing with one molecule and not a large number of small molecules. If the molecule has a centre of symmetry it is more convenient to use the following approach: first, the amplitude of the scattered wave $A(q)$ is calculated for a given orientation of the molecule using the centre of symmetry as the origin for the phases and for

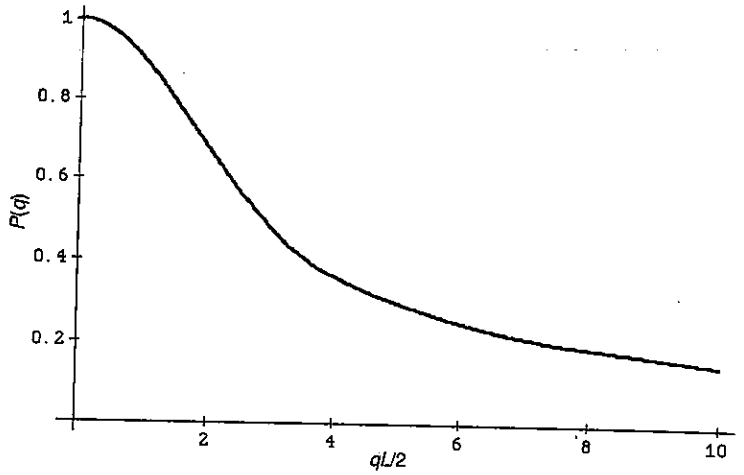

Fig. 6.10 $P(q)$ for a rod of length L as function of $qL/2$.

Figure 6.10 shows $P(q)$ for rods of length L as function of $qL/2$.

Expanding eqn (6.61) as a function of $x = qL/2$, around q or $x = 0$, we obtain

$$P(q) = 1 - \frac{1}{9}x^2 + \frac{2}{225}x^4 - \frac{6}{2205}x^6 + \frac{2}{127\,575}x^8 \ldots . \qquad (6.63)$$

Remembering from Section 6.2 that the x^2 term is $1/3\ q^2\overline{R^2}$ we recover for the radius of gyration of a rod, $\overline{L^2}/12$.

6.3.5 Gaussian chains

The simplest method for evaluating the form factor of Gaussian chains is to start from the definition of the form factor given by eqn (6.5)

$$P(q) = \frac{1}{z^2}\sum_{i=0}^{z}\sum_{j=0}^{z}\langle \exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{ij})\rangle \qquad (6.64)$$

where the average has to be taken not only over the orientations but also over the distances since in a Gaussian chain these distances depend on the conformation of the chain. The first step is to take the average value of one term and then to sum these values in order to obtain $P(q)$. From the definition of an average value we can write

$$\langle \exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{ij})\rangle = \iiint w(r_{ij})\exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{ij})\mathrm{d}^3\boldsymbol{r}_{ij} \qquad (6.65)$$

where $w(r_{ij})$ is the probability for the segments i and j to be at the distance r_{ij}. This expression is nothing but the Fourier transform of $w(r_{ij})$. If the chain is made of z elements without any orientation correlations we have shown in Appendix 1 that one can calculate $w(r_{ij})$ knowing the probability of the elementary step $w_0(r_{i,i+1})$. More precisely if $\omega_0(q)$ is the Fourier transform of w_0, the Fourier transform of $w(r_{ij})$, $\omega_{ij}(q)$, is given by

$$\omega_{ij}(q) = \omega_0(q)^{|i-j|} \qquad (6.66)$$

$P(q)$ then has the form

$$P(q) = \frac{1}{z^2}\sum_{i=0}^{z}\sum_{j=0}^{z}\omega_0(q)^{|i-j|}. \qquad (6.67)$$

In these expressions q is a number and not a vector since it has been demonstrated (see Appendix 1) that if the probability w depends only on the distances and not on the orientations, w and ω depend only on r and q. One could replace the summation by an integration but, in order to have an expression valid even for small z, we shall perform the exact calculation. We write, as has been done for the radius of gyration, the ωs as a square matrix, $z^2P(q)$ being the sum of all the terms of this matrix (see Fig. 6.11). The index i runs from 1 to z along the rows and the index j down the columns. $\omega_0(q)^{|i-j|}$ is written as ω^p. The main diagonal of this matrix is a symmetry axis. Since on this diagonal $i = j$, we have $\omega^0 = 1$ and the

1	ω	ω^2	ω^3	...	ω^p	...	ω^z
ω	1	ω	ω^2	...	ω^{p-1}	...	ω^{z-1}
ω^2	ω	1	ω	...	...	...	ω^{z-2}
ω^3	ω^2	ω	1	...	...		ω^{z-3}
...	...	...	...	...	...	...	...
ω^p	ω^{p-1}	$\omega^{\pi-2}$	...	...	...	...	ω^{z-p}
...	...	...	...	...	...	...	...
ω^z	ω^{z-1}	ω^{z-2}	...	...	...	ω	1

Fig. 6.11 Matrix explaining the calculation of the form factor of a Gaussian chain.

sum of these terms is z. Let us call $2T$ the sum of all the other terms. T can be evaluated by grouping the terms of one-half of the matrix by lines. We write therefore

$$z^2P(q) = z + 2T$$

$$T = \omega[(1+\omega+\omega^2+\omega^3+\ldots\ldots+\omega^{z-2})+(1+\omega+\omega^2+\omega^3+\ldots+\omega^{z-3}) + (1+\omega+\omega^2+\ldots+\omega^{z-4})+\ldots+(1+\omega)+(1)]. \quad (6.68)$$

Each line is a geometrical series which can be easily summed

$$T = \omega\sum_{1}^{z-1}\frac{1-\omega^p}{1-\omega}. \quad (6.69)$$

This simple sum can also be evaluated giving

$$P(q) = \frac{1}{z^2}\left\{z\frac{1+\omega}{1-\omega} - 2\omega\frac{1-\omega^z}{(1-\omega)^2}\right\}. \quad (6.70)$$

This formula allows $P(q)$ to be evaluated for any value of z; it is rigorous, even for $z = 1$. When z is large one can simplify $P(q)$, replacing $\omega_0(q)$ by the two first terms of its expansion

$$\omega_0(q) = 1 - \frac{q^2\overline{l^2}}{6} \quad (6.71)$$

which is equivalent to the assumption that $\omega_0(q)$ (or $w_0(r)$) obeys a Gaussian law

$$\omega_0(q) = \exp\left(-\frac{q^2\overline{l^2}}{6}\right). \quad (6.72)$$

With this approximation, neglecting the higher order terms in eqn (6.70) and assuming also that $q^2\overline{l^2}/6$ *is small* compared to unity gives the well known Debye (1946) formula

$$P(q) = \frac{2}{x^2}[x - 1 + \exp(-x)] \quad (6.73)$$

with $x = \dfrac{q^2z\overline{l^2}}{6} = q^2\overline{R^2}$.

An easier method for obtaining this result is to start from eqn (6.67) and to use the Gaussian approximation for $\omega_0(q)$, obtaining

$$P(q) = \frac{1}{z^2}\sum_{i=0}^{z}\sum_{j=0}^{z}\exp\left(-|i-j|\frac{q^2\overline{l^2}}{6}\right). \quad (6.74)$$

6.67 $P(q) = \frac{1}{z^2}\sum_{i=0}^{z}\sum_{j=0}^{z}\omega_0(q)^{|i-j|}$

We can transform the double sum into a simple sum using eqn (6.22)

$$P(q) = \frac{2}{z^2}\sum_{p=0}^{z}(z-p)\exp\left(-p\frac{q^2\overline{l^2}}{6}\right). \quad (6.75)$$

(Neglecting the term z^{-1} which is negligible when z is large.) Transforming the sum into an integral and using the variable $u = p/z$ one obtains

$$P(q) = 2\int_0^1(1-u)\exp\left(-\frac{uzq^2\overline{l^2}}{6}\right)du \quad (6.76)$$

and by integration by parts eqn (6.73) is recovered.

6.3.6 Chains of different architecture

$\sum_{i}^{N}\sum_{j}^{N} f(|i-j|) = 2\sum_{p=0}^{N}$ (6.22)

In this section we would like to show that it is relatively easy to extend these calculations of form factors to chains made of Gaussian segments but having different geometries. For this purpose we will study two cases. The first one will be the case of what is called by the polymer community 'stars'. These polymers, in the simplest case, are made of m identical chains joined together by a universal joint at one of their extremities. This model is idealized since it is impossible if m is large, to achieve junctions which have a negligible volume and allow for all the relative orientations of the chains. Nevertheless stars are the object of intense study mainly for their rheological and thermodynamic properties and it is important to be able to interpret their form factors. We shall also discuss the case of the 'ring polymers'. These polymers are made of one linear chain where both extremities are chemically attached. They make chains without end. They are also of rheological interest because it is difficult to apply to them the concept of reptation (de Gennes 1971).

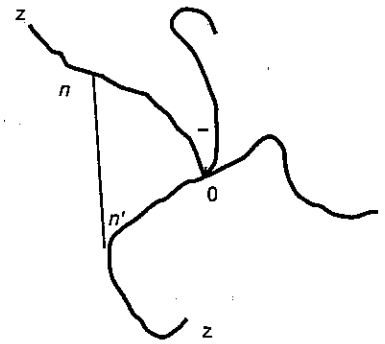

Fig. 6.12 Model for a star polymer.

The star polymers

Let us assume that we have a 'star' polymer made of m linear chains attached together at one end (see Fig. 6.12). Each chain has z segments; the total degree of polymerization is $Z = mz$. One scattering element is characterized by the double index i_n; n designates the chain and i the position on the chain. The is $(0 \leq i \leq z-1)$ are arranged in order to have the index zero at the junction point. We consider the quadruple sum

$$\sum_{n=1}^{m} \sum_{p=1}^{m} \sum_{i_n}^{z} \sum_{j_p}^{z} \exp\left[-(i_n + j_p)\frac{q^2\overline{l^2}}{6}\right] \tag{6.77}$$

(if $n = p$, one has to replace $i_n + j_n$ by $i_n - j_n$ in the exponential). This sum corresponds to the scattering by a pair of points having a Gaussian probability and a mean square distance $(i_n + j_p)\overline{l^2}$ or $(i_n - j_n)\overline{l^2}$ and can be split, by summation over i and j into m^2 units each having z^2 terms. One has m units for which $n = p$ called nn and $m(m-1)$ units for which $n \neq p$ called np. All the units called nn are identical; moreover they are equal to z^2 times the form factor of a linear Gaussian chain of z segments which will be called $z^2 P_{11}(q)$. The units np are also equal; they correspond to the interferences between two points on different chains and they will be called $z^2 P_{12}(q)$. Grouping all these terms in a square matrix (Fig. 6.13) gives

$$Z^2 P^*(q) = m^2 z^2 P^*(q) = mz^2 P_{11}(q) + m(m-1)z^2 P_{12}(q) \tag{6.78}$$

or

$$m^2 P^*(q) = mP_{11}(q) + m(m-1)P_{12}(q).$$

In order to evaluate the term $P_{12}(q)$ consider the four first cells of the matrix. They give the form factor of a two-branch star, i.e. a linear polymer of length $2z$. Its form factor is easy to evaluate and will be called $P_{22}(q)$. It follows that

$$4z^2 P_{22} = 2z^2 P_{11}(q) + 2z^2 P_{12}(q). \tag{6.79}$$

11	12	...	1n	...	1m
21	22	...	2n	...	2m
...	...	...	...	...	...
n1	n2	...	nn	...	nm
...	...	...	...	...	...
m1	m2	...	mn	...	mm

Fig. 6.13 Table explaining the calculation of the form factor of a star.

Eliminating $P_{12}(q)$ between eqns (6.78) and (6.79) leads to the result

$$P^*(q) = 2\left(1 - \frac{1}{m}\right)P_{22}(q) - \left(1 - \frac{2}{m}\right)P_{11}(q). \tag{6.80}$$

This relationship shows that the form factor of one star can be expressed by knowing the structure factor of one branch and of the linear polymer made of two branches.

Remark: if one wants to evaluate $P^*(q)$ for more complicated cases one cannot say that a two-branch star is identical to a double size linear polymer (consider for instance the case of a star with rod-like arms). Instead of using this short cut to evaluate $P_{12}(q)$ one can evaluate it directly (Benoît 1953). Keeping in mind that the root mean square distance between i and j on different branches is, in the case of a universal joint at the junction point

$$\overline{r_{ij}^2} = \overline{r_{i0}^2} + \overline{r_{0j}^2} = \overline{l^2}(i_n + j_n) \tag{6.81}$$

one obtains immediately

$$P_{12}(q) = \frac{1}{z^2}\sum_{n}^{z}\sum_{n'}^{z}\exp\left[-\frac{1}{6}q^2\overline{l^2}(n+n')\right]. \tag{6.82}$$

Replacing the sums by two integrations leads to

$$P_{12}(q) = \left[\frac{1 - \exp -\left(\frac{1}{6}q^2\overline{l^2}z\right)}{\frac{1}{6}q^2\overline{l^2}z}\right]. \tag{6.83}$$

We can easily verify that this expression is equal to $2P_{2z} - P_{1z}$. This method can also be used to evaluate the cross form factor $P_{AB}(q)$ in the case of Gaussian copolymers. Expanding $P^*(q)$ as function of q in the small q range, following eqn (6.14), allows us to evaluate the radius of gyration. Applying this method to eqn (6.80) gives

$$\overline{R^2} = 2\left(1 - \frac{1}{m}\right)\overline{R_{2z}^2} + \left(\frac{2}{m} - 1\right)\overline{R_z^2} \tag{6.84}$$

or, since we have assumed that the chain is Gaussian

$$\overline{R^2} = \left(3 - \frac{2}{m}\right)\frac{\overline{l^2}}{6}z. \tag{6.85}$$

For $m = 1$ and 2 we recover the classical results. Also, as in the case of $P^*(q)$ when m becomes large these expressions reach, as we could have guessed, a limiting value independent of m.

Ring macromolecules

In a ring macromolecule the distances between two points i and j are Gaussian and we can rewrite eqn (6.74)

$$P(q) = \frac{1}{z^2} \sum_{i=0}^{z-1} \sum_{j=0}^{z-1} \exp\left(-\overline{L_{ij}^2} \frac{q^2}{6}\right) \tag{6.86}$$

(we have z scattering points numbered from 0 to $z-1$) where $\overline{L_{ij}^2}$ is the root mean square distance between the scattering points i and j. If we draw the same square as in the study of linear molecules we realize that all lines contain exactly the same sum of terms; we can therefore write

$$P(q) = \frac{1}{z} \sum_{p=0}^{z-1} \exp - \left(\frac{q^2 \overline{L_p^2}}{6}\right). \tag{6.87}$$

From eqn (6.27) we can replace $\overline{L_p^2}$ by its value: $\overline{l^2} p(1 - p/z)$. Writing $\lambda = (q^2 \overline{l^2} z/6)$, transforming the sum into an integral and using as variable $u = p/z$ we obtain the simple expression

$$P(q) = \int_0^1 \exp\{-\lambda u(1-u)\} \mathrm{d}u. \tag{6.88}$$

This expression cannot be integrated to give classical functions. It is usually transformed to a new integral by completing the square of the expression in the exponential and writing $v = \sqrt{\lambda}\,(u - 1/2)$ (Cassasa 1965)

$$P(q) = \frac{2}{\sqrt{\lambda}} \exp - \frac{\lambda}{4} \int_0^{\frac{\sqrt{\lambda}}{2}} \exp(v^2) \mathrm{d}v. \tag{6.89}$$

Figure 6.14 shows the result of the numerical integration.

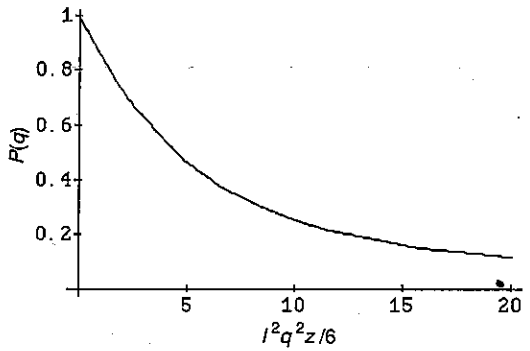

Fig. 6.14 Form factor for a ring as function of $(\overline{l^2} q^2 Z/6)$.

6.4 THE INTERMEDIATE AND HIGH q RANGE

6.4.1 Qualitative interpretation of the different q domains

Up to now we have discussed the methods for the calculation of the radius of gyration and the form factor $P(q)$ but we have not considered how it might be possible to compare experimental data to the curves evaluated for models. At first sight this seems to be very difficult since, forgetting the relatively small oscillations which are very frequently erased by polydispersity, all these curves look very similar. In Fig. 6.15 we have collected the curves calculated for rods, Gaussian chains, and spheres having the same radius of gyration; they look very similar except for the fact that, at large angles, they decrease more or less rapidly. It is this behaviour, at large q that we would like to discuss but, before doing so, it is interesting to see qualitatively what one can expect from neutron scattering in different q domains.

It is evident that, since the scattering intensity as a function of q is the Fourier transform of the pair distribution of scattering centres in the sample, one can say that q space and r space are conjugated, or in other words that small q corresponds to large values of r and vice versa. Looking at a scattering diagram as function of q is just like looking at it with a magnifying glass of changing power. When the power increases the field decreases and is of the order of q^{-1}. In this discussion we shall assume that we are studying a dilute solution or a system in which the scattering

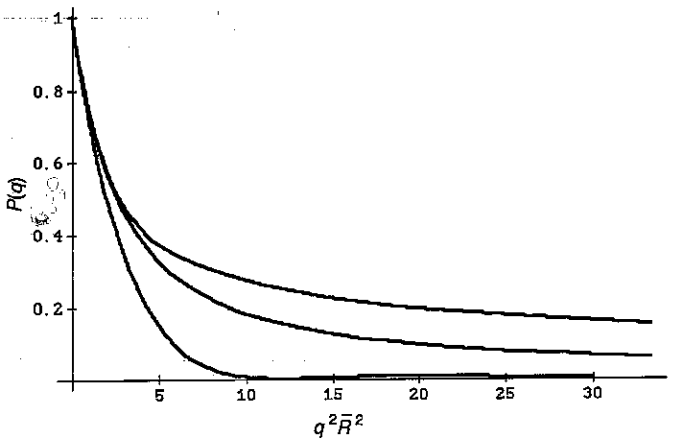

Fig. 6.15 $P(q)$ for, in decreasing order, a rod, a Gaussian chain, and a sphere as function of $q^2 R^2$.