Polymers and Neutron Scattering

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the numbering of the scattering elements. After normalization to unity at $q = 0$, we call $A(q)$, $A_0(q)$

$$A_0(q) = \frac{1}{z} \sum_{i=-z/2}^{+z/2} \exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_i). \tag{6.42}$$

The symmetry implies that the phase difference between the total scattered wave and the wave scattered by the centre of symmetry is zero; this makes $A(q)$ real since one can always associate the points $\boldsymbol{r}_i$ and $-\boldsymbol{r}_i$

$$\exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_i) + \exp(+\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_i) = 2\cos(\boldsymbol{q}\cdot\boldsymbol{r}_i). \tag{6.43}$$

The scattered intensity for a given orientation is

$$A_0^2(q) = \frac{1}{z^2}\left[\sum_{-z/2}^{+z/2} \cos(\boldsymbol{q}\cdot\boldsymbol{r}_i)\right]^2 \tag{6.44}$$

and the form factor $P(q)$ is obtained after averaging over all orientations

$$P(q) = \frac{1}{z^2}\left\langle\left[\sum \cos(\boldsymbol{q}\cdot\boldsymbol{r}_i)\right]^2\right\rangle_{\text{orientations}} \tag{6.45}$$

As an example of the use of this method we shall calculate the form factor of a sphere.

6.3.2 The sphere

This case is extremely simple since the scattering intensity does not depend on the orientation of the sphere. One evaluates the amplitude scattered by the sphere (eqn (6.42)) transformed from discrete to continuous notation and normalized to unity for $q = 0$

$$A_0(q) \approx \frac{1}{V}\iiint_V \exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r})r^2\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi\,\mathrm{d}r, \tag{6.46}$$

the factor V comes from the fact that our normalization condition $A^2(0) = 1$ has to be satisfied. Using the direction of q as the z axis ($qr = qr\cos\theta$) and as new variable $u = \cos\theta$, one obtains after integration over φ

$$A_0(q) \approx \frac{2\pi}{V}\int_{u=-1}^{+1}\int_{r=0}^{R} \exp(-\mathrm{i}qru)r^2\,\mathrm{d}u\,\mathrm{d}r. \tag{6.47}$$

Integrating first over u we recover the well-known result

$$A_0(q) \approx \frac{3}{R^3}\int_0^R \frac{\sin qr}{qr} r^2\,\mathrm{d}r. \tag{6.48}$$

The integration over r is made by parts leading (with $v = qR$) to the expression

$$A_0(q) = \frac{3}{v^3}(\sin v - v\cos v). \tag{6.49}$$

As expected this expression depends only on R and the form factor (Rayleigh 1914) is

$$P(q) = [A_0(q)]^2 = \frac{9}{v^6}(\sin v - v\cos v)^2. \tag{6.50}$$

In some texts this formula is given in an equivalent form as function of the Bessel function

$$J_{\frac{3}{2}}(v) = \sqrt{\frac{2}{\pi v}}\,\frac{\sin v - v\cos v}{v}.$$

Expanding around q (or v) $= 0$ we obtain

$$P(q) = 1 - \frac{v^2}{5} + \frac{3v^4}{175} - \frac{4v^6}{4725} + \frac{2v^8}{72765} + \ldots. \tag{6.51}$$

If one writes $P(q)$ as $1 - (q^2\overline{R^2}/3)$ the second term gives the correct value for the radius of gyration of a sphere (eqn (6.15a)). Figure 6.6(a) shows $P(q)$ as a function of $v = qR$.

Equation (6.50) shows that the scattering intensity becomes zero for all the values of v (except zero) satisfying the equation

$$v = tg\,v$$

or practically: $v = (2n+1)\pi/2$ (n being a positive integer) and goes through a maximum between two consecutive zeros. The main maximum at $q = 0$ is much more important that the secondary maxima (Fig. 6.6(b)). It is almost two orders of magnitude larger but it is quite possible to detect several maxima from well-defined systems. In order to see these minima and maxima more clearly Fig. 6.6(c) shows the logarithm of the form factor as function of $v = q^2R^2$.

6.3.3 Other objects with spherical symmetry (for example, shells)

The method we have just used can be applied to many other systems having spherical symmetry. If, instead of having an uniform density, the sphere has a density $\rho(r)$ of scattering elements which depends on the distance r to the centre, one can immediately write for the scattering amplitude, by generalization of eqn (6.48)

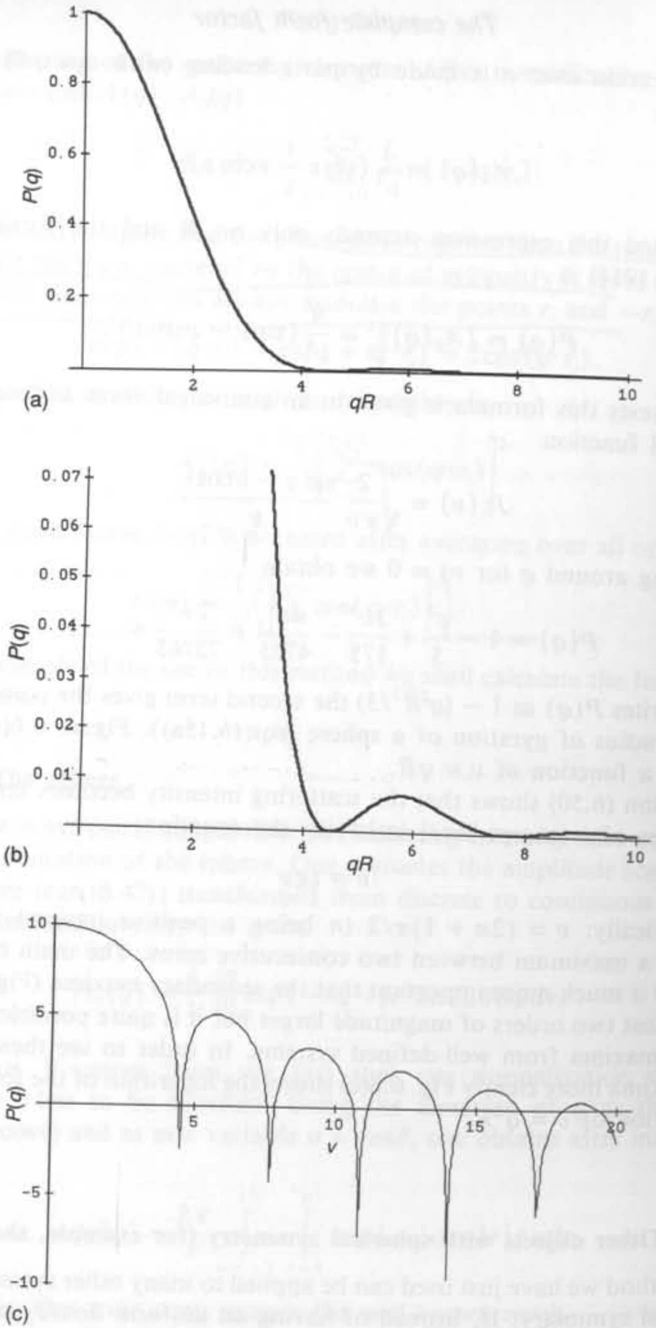

Fig. 6.6 (a) Form factor for a sphere of radius R as function of qR. (b) Enlarging the tail of the curve. (c) Plot of the form factor of a sphere $[\log(P(q))]$ as function of $v = q^2R^2$).

$$A_0(q) = \frac{1}{C}\int n(r)\,\frac{\sin qr}{qr}\,r^2\mathrm{d}r. \tag{6.52}$$

The constant C is defined by the normalization condition $A(0) = 1$

$$C = \int n(r)r^2\mathrm{d}r \tag{6.53}$$

and one obtains for the form factor

$$P(q) = \left[\frac{1}{C}\int n(r)\left(\frac{\sin qr}{qr}\right)r^2\mathrm{d}r\right]^2. \tag{6.54}$$

As an example let us assume that we want to evaluate the form factor of a hollow sphere where there are only scattering points between the radius R_{int} and the external radius R_{ext} (see Fig. 6.7). It suffices to take $n =$ constant for $R_{\text{int}} < r < R_{\text{ext}}$ and $n = 0$ everywhere else, obtaining

$$A_0(q) = \frac{1}{C'}\int_{R_{\text{int}}}^{R_{\text{ext}}} \frac{\sin qr}{qr}\,r^2\mathrm{d}r = \frac{3}{q^3R_{\text{int}}^3}\,(\sin qR_{\text{int}} - qR_{\text{int}}\cos qR_{\text{int}})$$

$$-\frac{3}{q^3R_{\text{ext}}^3}\,(\sin qR_{\text{ext}} - qR_{\text{ext}}\cos qR_{\text{ext}}). \tag{6.55}$$

The normalization constant C' is obtained by writing that for $q = 0$, $A_0(q)$ should be equal to 1. C' is equal to the volume of the shell divided by 4π

$$C' = \int_{R_{\text{int}}}^{R_{\text{ext}}} r^2\mathrm{d}r = \frac{1}{3}\,(R_{\text{ext}}^3 - R_{\text{int}}^3). \tag{6.56}$$

The form factor is evidently $(A_0(q))^2$. If the difference $R_{\text{ext}} - R_{\text{int}}$ is small compared to q

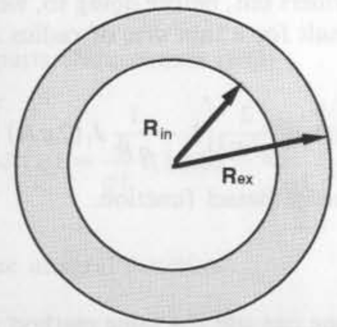

Fig. 6.7 Model for an empty sphere.

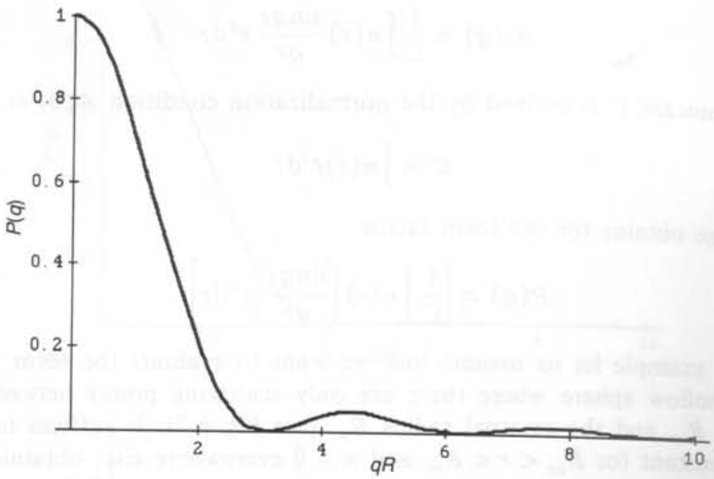

Fig. 6.8 Form factor of a hollow spherical shell of negligible thickness.

$$P(q) = \left[\frac{\sin qR}{qR}\right]^2 \qquad (6.57)$$

shell of infinitesimal thickness i.e. a step of sphere integral (2-d!)

with $R \approx R_{\text{int}} \approx R_{\text{ext}}$. (See Fig. 6.8.)

6.3.4 Other simple shapes – discs and rods

The disc

Until this point we have discussed the most simple case, the sphere. We could go on and discuss many other geometrical objects which can be used as models for molecular structure. This is purely a mathematical exercise and we shall discuss in detail only the linear molecules which are the most common model for polymers but, before doing so, we give here for the sake of completeness, the result for a thin disc of radius R (Kratky and Porod 1949*a*) (see Fig. 6.9).

$$P(q) = \frac{2}{q^2R^2}\left[1 - \frac{1}{qR}\,J_1(2qR)\right] \qquad (6.58)$$

where $J_1(x)$ is a first order Bessel function.

The rod

For a rod of length L one can use the same method and taking the centre of the rod as origin calculate the scattering amplitude. Using the classi-

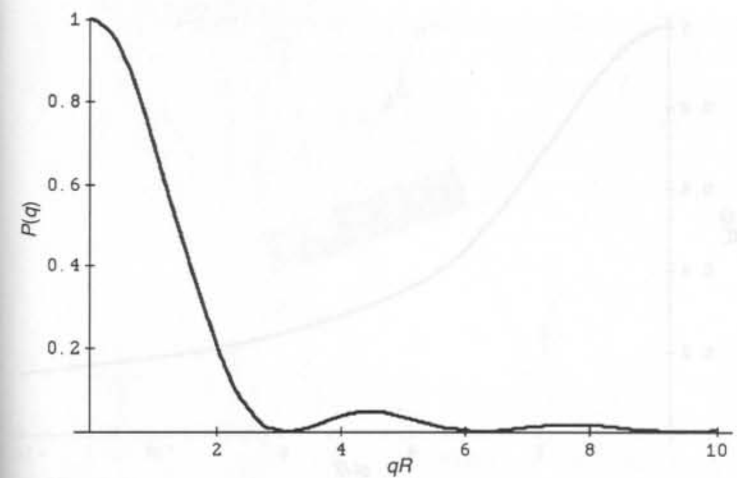

Fig. 6.9 Form factor for a thin disc of radius R as a function of qR.

al coordinate system with the z axis in the direction of the vector $(q \cdot r = qr\cos\theta)$ we immediately obtain

$$A_0(q) = \frac{1}{L}\int_{-\frac{L}{2}}^{\frac{L}{2}} \exp(-\mathrm{i}qr\cos\theta)\,\mathrm{d}r \qquad (6.59)$$

nd, after performing the integration

$$A_0(q) = \frac{2}{qL\cos\theta}\sin\left(\frac{qL\cos\theta}{2}\right). \qquad (6.60)$$

ow we take the square of this expression and integrate over all orientation

$$P(q) = \frac{1}{2}\int_{\theta=0}^{\pi} [A_0(q)]^2\sin\theta\,\mathrm{d}\theta.$$

fter integration by parts (Neugebauer 1943)

$$P(q) = \frac{2}{qL}\,S_i(qL) - \frac{\sin^2\dfrac{qL}{2}}{\left(\dfrac{qL}{2}\right)^2} \qquad (6.61)$$

here $S_i(x)$ is the sine integral function

$$S_i(x) = \int_0^x \frac{\sin u}{u}\,\mathrm{d}u. \qquad (6.62)$$