Chapter 27 – **SINGLE PARTICLE FORM FACTORS**

1. DEFINITION OF SCATTERING FACTORS

Consider a scattering object consisting of n scatterers occupying a volume V_P. The scattering density and its Fourier transform are defined as:

$$n(r) = \sum_{i=1}^{n} \delta(\vec{r} - \vec{r}_i) \qquad (1)$$

$$n(Q) = \sum_{i=1}^{n} \exp[-i\vec{Q}.\vec{r}_i] .$$

Note that these quantities vary randomly with position $\vec{r}$ and scattering vector $\vec{Q}$. The average density being constant ($<n(r)> = \bar{n} = n/V_p$), a fluctuating density and its Fourier transform are defined as:

$$\Delta n(r) = \sum_{i}^{n} \delta(\vec{r} - \vec{r}_i) - \bar{n} \qquad (2)$$

$$\Delta n(Q) = \sum_{i}^{n} \exp[-i\vec{Q}.\vec{r}_i] - (2\pi)^3 \bar{n} \delta(\vec{Q}) .$$

Here $\delta(\vec{Q})$ is the Dirac Delta function which does not contribute except at $\vec{Q} = \vec{0}$ (along the very forward scattering direction) which is experimentally irrelevant. The static form factor for the scattering "particles" is defined as the density-density correlation function summed up (or integrated) over the particle volume:

$$P(Q) = \frac{< n(-Q)n(Q) >}{n^2} = \frac{1}{n^2} \sum_{i,j}^{n} < \exp[i\vec{Q}.(\vec{r}_i - \vec{r}_j)] > \qquad (3)$$

$$= \int d\vec{r} \int d\vec{r}' \frac{< n(r)n(r') >}{n^2} \exp[i\vec{Q}.(\vec{r}' - \vec{r})] .$$

The form factor of various shape objects are worked out next (Guinier-Fournet, 1955; Glatter-Kratky, 1982; Higgins-Benoit, 1994; Hammouda, 1995; Roe, 2000).

2. FORM FACTOR FOR A UNIFORM SPHERE

Consider a sphere of radius R and uniform density (this could be a spherical domain in a microphase separated block copolymer or a latex particle in a colloidal suspension). The single particle form factor P(Q) involves integrations over the volume V_P of the sphere (in spherical coordinates):

$$P(Q) = \frac{<n(-Q)n(Q)>}{n^2} = \int d\vec{r} \int d\vec{r}' \frac{<n(r)n(r')>}{n^2} \exp[i\vec{Q}.(\vec{r}'-\vec{r})]. \qquad (4)$$

Since the scattering elements are not correlated, the average of the product <n(r)n(r')> is equal to the product of the averages <n(r)><n(r')> and therefore:

$$P(Q) = |F(Q)|^2. \qquad (5)$$

Here the amplitude of the form factor F(Q) has been defined as:

$$F(Q) = \int d\vec{r} \frac{<n(r)>}{n} \exp[-i\vec{Q}.\vec{r}]. \qquad (6)$$

For uniform density, the average over configurations <n(r)> becomes trivial:

$$<n(r)> = \frac{n}{V_P} = \bar{n} \qquad \text{if } r \leq R \qquad (7)$$

$$<n(r)> = 0. \qquad \text{if } r > R$$

Therefore:

$$F(Q) = \frac{3}{4\pi R^3} \int_0^R r^2 dr \int_{-1}^{1} d\mu \exp[-iQr\mu] \int_0^{2\pi} d\phi \qquad (8)$$

$$= \frac{3}{R^3} \int_0^R r^2 dr \frac{\sin(Qr)}{Qr} = \frac{3j_1(QR)}{QR}. \qquad (9)$$

Here the spherical Bessel function $j_1(x)$ has been defined as:

$$j_1(x) = \frac{\sin(x)}{x^2} - \frac{\cos(x)}{x} = \sqrt{\frac{\pi}{2x}} J_{3/2}(x). \qquad (10)$$

The spherical Bessel function $j_1(x)$ is related to the cylindrical Bessel function $J_{3/2}(x)$ as shown. It is also related to $j_0(x)$ as follows:

$$j_1(x) = -\frac{d}{dx}\left[j_0(x)\right] \text{ and } j_0(x) = \frac{\sin(x)}{x}. \qquad (11)$$

The form factor for the sphere is therefore:

$$P(Q) = \left[\frac{3j_1(QR)}{QR}\right]^2 = \left[\frac{3}{QR}\left(\frac{\sin(QR)}{(QR)^2} - \frac{\cos(QR)}{QR}\right)\right]^2. \qquad (12)$$

Note the following normalization $P(Q \to 0) = 1$ and recall the calculation of the radius of gyration squared for a uniform density sphere of radius R as $R_g^{\ 2} = 3R^2/5$.

The low-Q Guinier expansion follows:

$$P(Q) \to \left[1 - \frac{(QR)^2}{10} + \frac{(QR)^4}{280}\right]^2 \cong 1 - \frac{Q^2R^2}{5} + \frac{3}{175}(QR)^4 \qquad (13)$$

$$= 1 - \frac{Q^2R_g^{\ 2}}{3} + \frac{Q^4R_g^{\ 4}}{21} \qquad \text{for } Q^2R_g^2 < 1$$

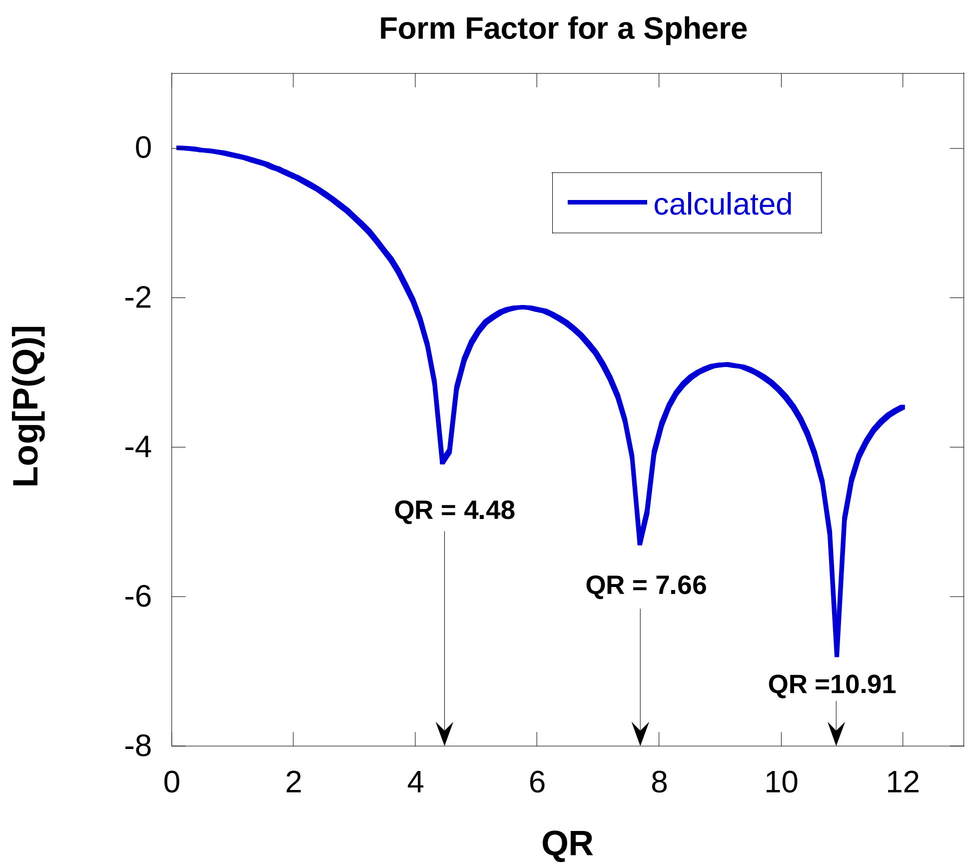

Figure 1: Plot of Log[P(Q)] *vs* QR for a uniform sphere showing many order oscillations.

3. SPHERICAL CORE-SHELL

Consider a sphere with an inner core and an outer shell. Three regions can be defined corresponding to the inner core, the outer shell and the solvent. Three cases are considered where (1) the shell is visible (with matched core and solvent scattering lengths), (2) the core and shell scattering length densities are matched and (3) the core is visible (with matched shell and solvent scattering length densities).

Note that the "correlation hole" peak is enhanced in case 1 for which the shell is visible whereas the core is not (i.e., it is matched to the solvent). Polydispersity ($\sigma/R = 0.3$) has been included in order to damp higher order oscillations. This level of polydispersity was enough to damp oscillations for case 3 but not enough for case 2.

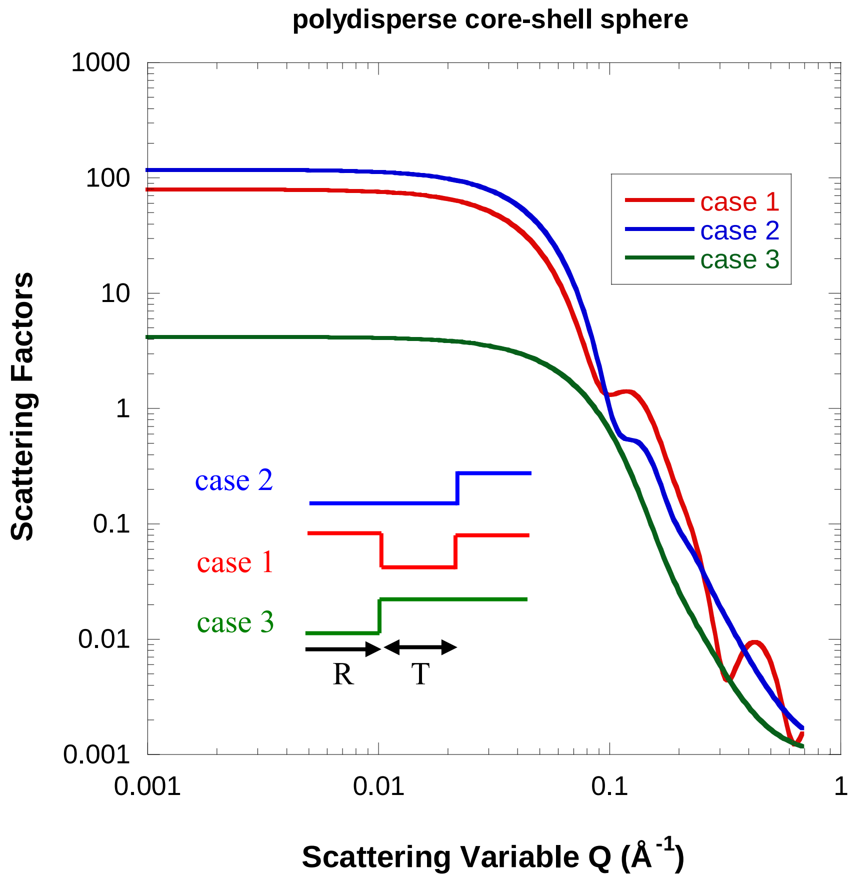

Figure 2: Scattering factors for a core-shell sphere of inner radius R = 20 Å and radial shell thickness T = 20 Å. Case 1 corresponds to the core scattering length density matched to the solvent. Case 2 corresponds to matched scattering length densities for the core and shell. Case 3 corresponds to the shell scattering length density matched to the solvent. The vertical scale is arbitrary and a constant background value of 0.001 has been added.

4. FORM FACTORS FOR OTHER SPHEROID SHAPES

Following the same procedure, the form factor for a spherical shell between radii R_1 and R_2 (and hollow for $r<R_1$) can be calculated as follows:

$$F(Q) = \frac{3}{4\pi(R_2^3 - R_1^3)} \int_{R_1}^{R_2} r^2 dr \int_{-1}^{+1} d\mu \exp[-iQr\mu] \int_0^{2\pi} d\phi \qquad (14)$$

$$= \frac{1}{(R_2^3 - R_1^3)} \left[\left(\frac{3j_1(QR_2)}{QR_2} \right) R_2^3 - \left(\frac{3j_1(QR_1)}{QR_1} \right) R_1^3 \right].$$

For an ellipsoid of half axes a, b, c oriented so that its axes make angles α, β, θ with the $\vec{Q}$ direction, an effective radius R_e is defined as:

$$R_e^2 = a^2 \cos^2(\alpha) + b^2 \cos^2(\beta) + c^2 \cos^2(\theta). \qquad (15)$$

The form factor amplitude is the same as the one for a sphere of radius R_e:

$$F(Q, \mu) = \frac{3j_1(QR_e)}{QR_e}. \qquad (16)$$

The form factor (for a randomly oriented sample) is an average over all possible orientations of the ellipsoid:

$$P(Q) = \frac{1}{2} \int_{-1}^{+1} d\mu \, | F(Q, \mu) |^2. \qquad (17)$$

$\mu = \cos(\theta)$ and θ is the angle between the major axis of the ellipsoid and the $\vec{Q}$ direction. It is straightforward to extend these results to an ellipsoidal shell.

5. FORM FACTORS FOR CYLINDRICAL SHAPES

The form factor amplitude F(Q) for a uniform cylinder (rod) of radius R and length L oriented at an angle θ from the $\vec{Q}$ direction is the product of a longitudinal (z along the rod) and a transverse ($\perp$ perpendicular to the rod) contributions in cylindrical coordinates:

$$F(Q, \mu) = F_z(Q, \mu) F_\perp(Q, \mu) \qquad (18)$$

$$F_z(Q, \mu) = \frac{1}{L} \int_{-L/2}^{L/2} dz \exp[-iQ\mu z] = \frac{\sin(Q\mu L/2)}{Q\mu L/2}$$

$$F_\perp(Q, \mu) = \frac{1}{\pi R^2} \int_0^R d\rho \rho \int_0^{2\pi} d\phi \exp[-iQ\sqrt{1-\mu^2} \cos(\phi)\rho].$$

Here $\mu = \cos(\theta)$ and θ is the inclination angle. The following definition of the cylindrical Bessel functions are used (Abromowitz-Stegun, 1972):

$$J_0(z) = \frac{1}{\pi}\int_0^{\pi} d\phi \exp[iz\cos(\phi)]. \tag{19}$$

$$J_1(z) = \frac{1}{i\pi}\int_0^{\pi} d\phi \exp[iz\cos(\phi)]\cos(\phi)$$

One obtains:

$$F_\perp(Q,\mu) = \frac{2}{R^2}\int_0^R d\rho \rho J_0(Q\sqrt{1-\mu^2}\rho). \tag{20}$$

An integration variable change to $t = \rho/R$ is made and the following integral is used:

$$\int_0^1 t dt J_0(at) = \frac{1}{a} J_1(a). \tag{21}$$

The following result is obtained:

$$F_\perp(Q,\mu) = \frac{2J_1(Q\sqrt{1-\mu^2}R)}{Q\sqrt{1-\mu^2}R}. \tag{22}$$

The final result for the form factor amplitude for an oriented rod is:

$$F(Q,\mu) = \left[\frac{\sin(Q\mu L/2)}{Q\mu L/2}\right]\left[\frac{2J_1(Q\sqrt{1-\mu^2}R)}{Q\sqrt{1-\mu^2}R}\right]. \tag{23}$$

The form factor for a randomly oriented rod is therefore given by the following orientation average:

$$P(Q) = \frac{1}{2}\int_{-1}^{1} d\mu \,|F(Q,\mu)|^2. \tag{24}$$

In order to model the scattering from very dilute solutions of rods, the last integral (over θ) is performed numerically.

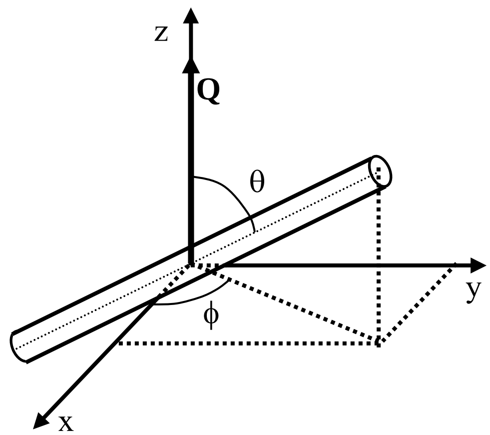

Figure 3: Geometry of the uniform rod.

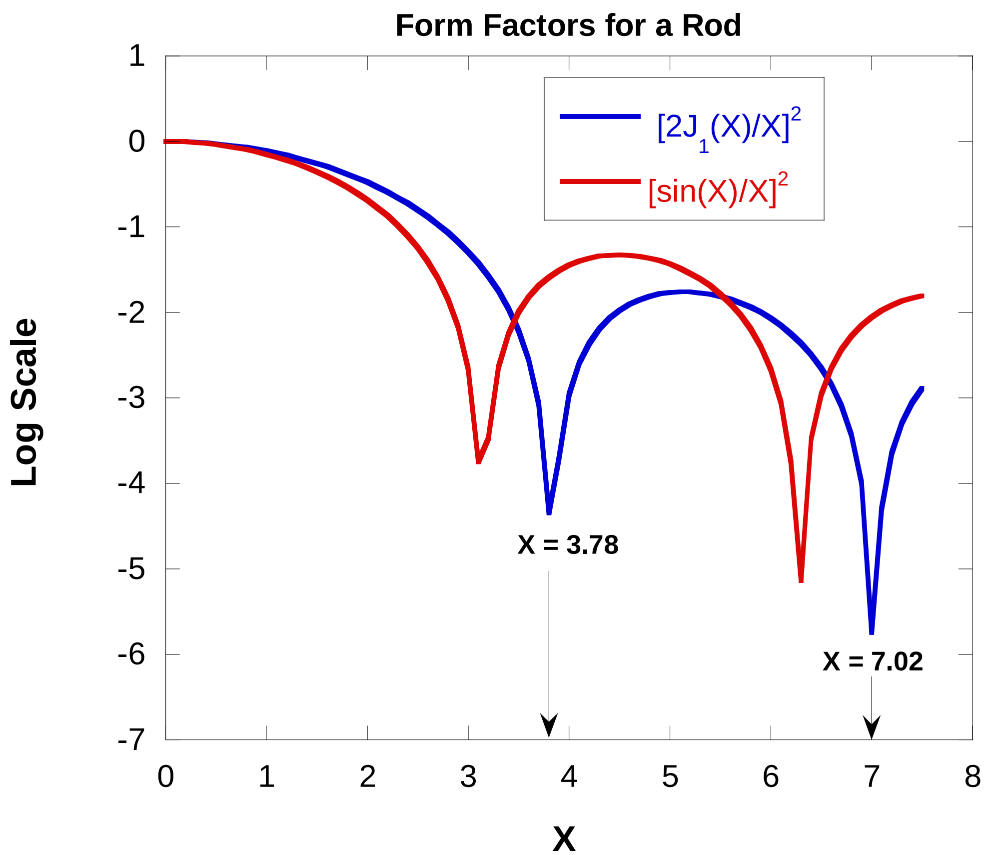

Figure 4: Plots of the two functions $[2J_1(X)/X]^2$ and $[\sin(X)/X]^2$ that give the variations of the form factor perpendicular and parallel to the rod axis respectively.

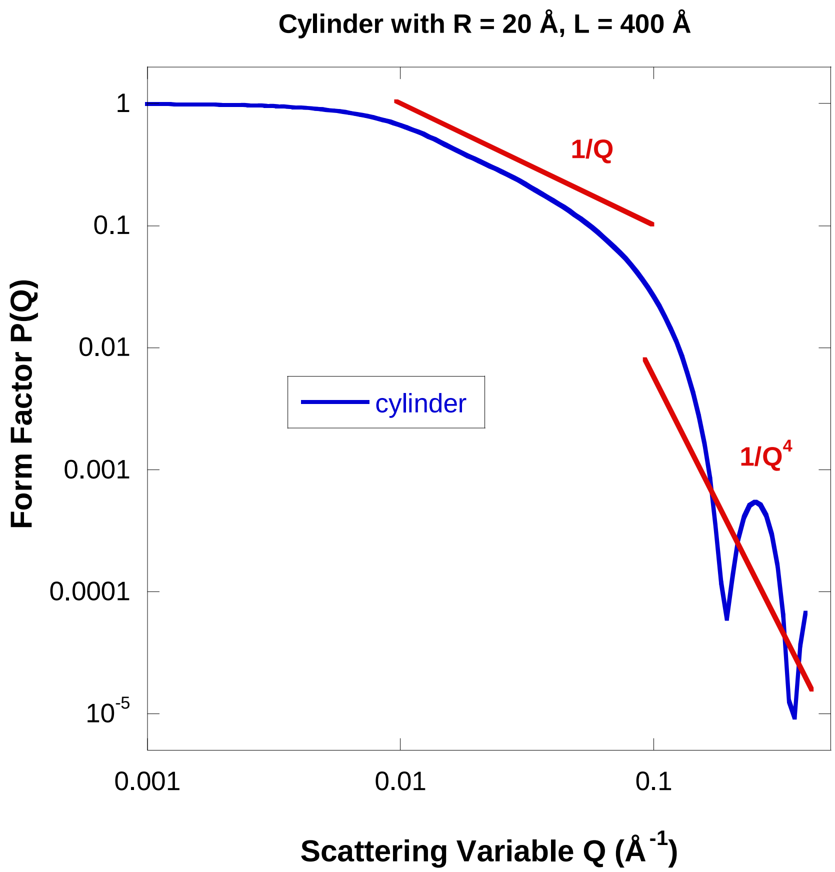

Figure 5: Form factor P(Q) for a cylinder with radius R = 20 Å and length L = 400 Å.

Note that the result for a rod of length L applies also to a disk of thickness L.

For a disk of radius R and negligible thickness, the $L \to 0$ limit in the general result is taken so that:

$$F_{\perp}(Q,\mu) = \frac{1}{\pi R^2}\int_0^R d\rho\rho\int_0^{2\pi} d\phi \exp[-iQ\sqrt{1-\mu^2}\cos(\phi)\rho] \tag{25}$$

$$= \frac{2J_1(Q\sqrt{1-\mu^2}R)}{Q\sqrt{1-\mu^2}R}.$$

Averaging over orientations is performed as follows:

$$P(Q) = \frac{1}{2}\int_{-1}^{1} d\mu \left[\frac{2J_1(Q\sqrt{1-\mu^2}R)}{Q\sqrt{1-\mu^2}R}\right]^2 \tag{26}$$

$$= \frac{2}{(QR)^2}\left[1 - \frac{J_1(2QR)}{QR}\right].$$

To obtain the form factor for an infinitely thin rod of length L, we take the $R \to 0$ limit instead, and obtain:

$$P(Q) = \frac{1}{2}\int_{-1}^{1} d\mu \left[\frac{\sin(Q\mu L/2)}{Q\mu L/2}\right]^2 . \tag{27}$$

Integrate by part once to obtain:

$$P(Q) = \frac{1}{2}\left\{\left[-\frac{\sin^2(QL\mu/2)}{(QL/2)^2 \mu}\right]_{\mu=-1}^{\mu=1} + \int_{-1}^{+1} d\mu \frac{2\sin(QL\mu/2)\cos(QL\mu/2)}{(QL\mu/2)}\right\} \tag{28}$$

$$= \left(\frac{2}{QL}\right)\mathrm{Si}(QL) - \frac{\sin^2(QL/2)}{(QL/2)^2}.$$

Si(x) is the sine integral function defined as:

$$\mathrm{Si}(x) = \int_0^x du \frac{\sin(u)}{u} . \tag{29}$$

6. FORM FACTOR FOR A PARALLELEPIPED

Consider a uniform density rectangular parallelepiped of sides a, b, c. In Cartesian coordinates, the form factor amplitude can be split into the product of three parts that depend on the three coordinates respectively:

$$F(Q) = \frac{1}{abc}\left[\int_{-a/2}^{a/2} dx \exp[-iQ_x x)\right]\left[\int_{-b/2}^{b/2} dy \exp[-iQ_y y)\right]\left[\int_{-c/2}^{c/2} dz \exp[-iQ_z z)\right] \tag{30}$$

$$= \left[\frac{\sin(Q_x a/2)}{(Q_x a/2)}\right]\left[\frac{\sin(Q_y b/2)}{(Q_y b/2)}\right]\left[\frac{\sin(Q_z c/2)}{(Q_z c/2)}\right].$$

The form factor is, here also, an average over orientations:

$$P(Q) = \frac{1}{2}\int_{-1}^{1} d\mu \,|\, F(Q,\mu)\,|^2 . \tag{31}$$

$\mu = \cos(\theta)$ and θ is the orientation angle between $\vec{Q}$ and one of the symmetry axes of the parallelepiped.

7. TWISTED RIBBON FORM FACTOR

The parametrization of the twisted ribbon was described in an earlier section when calculating the radius of gyration. Consider a helically twisted ribbon aligned along the vertical z axis with a helical radius R, height L, width W and ribbon thickness T. Define the helix pitch p and the azimuthal angle ϕ in the horizontal plane. Define also the polar coordinate variable in the horizontal plane ρ and the vertical variable z. The parametric position along the ribbon is given by:

$$r(\phi, z, \rho) = \sqrt{\rho^2 + \left(\frac{p\phi}{2\pi} + z\right)^2} . \qquad (32)$$

The single twisted ribbon form factor amplitude is given by:

$$F(Q, \mu) = \frac{\int d\phi \int dz \int \rho d\rho \left[\frac{\sin[Qr(\phi, z, \rho)\mu]}{Qr(\phi, z, \rho)\mu}\right]}{\int d\phi \int dz \int \rho d\rho} . \qquad (33)$$

All three integrations can be performed numerically using the following limits: $-\pi L/p \le \phi \le \pi L/p$, $-W/2 \le z \le W/2$ and $R-T/2 \le \rho \le R+T/2$.

Here also, the form factor is given by an average over orientations:

$$P(Q) = \frac{1}{2}\int_{-1}^{1} d\mu \, | F(Q, \mu) |^2 . \qquad (34)$$

$\mu = \cos(\theta)$ and θ is the orientation angle between $\vec{Q}$ and the vertical axis of the ribbon.

8. PAIR CORRELATION FUNCTIONS

The form factor P(Q) is the Fourier transform of the probability distribution function $P(\vec{r})$:

$$P(Q) = \int d^3r \exp(-i\vec{Q}.\vec{r}) P(\vec{r}) . \qquad (35)$$

Given an infinitesimal scattering volume chosen randomly inside the considered "particle", $P(\vec{r})$ represents the probability of finding another scatterer within the particle a distance $\vec{r}$ away. Usually, a one-dimensional probability distribution p(r) (also referred to as "distance distribution function") is defined instead:

$$P(Q) = \frac{1}{R}\int_0^R dr \frac{\sin(Qr)}{Qr} p(r). \tag{36}$$

p(r) is available for some of the common shape objects. For a sphere of radius R:

$$p(r) = 12\left(\frac{r}{2R}\right)^2\left(1-\frac{r}{2R}\right)^2\left(2+\frac{r}{2R}\right) \tag{37}$$

$$= 3\left(\frac{r}{R}\right)^2\left(1-\frac{3}{4}\frac{r}{R}+\frac{1}{16}\left(\frac{r}{R}\right)^3\right).$$

Note the other definition $p(r) = 3(r/R)^2\gamma(r)$ where γ(r) is the radial pair correlation function given by $\gamma(r) = \left(1-\frac{3}{4}\frac{r}{R}+\frac{1}{16}\left(\frac{r}{R}\right)^3\right)$.

For a disk of radius R, the distance distribution function is given by:

$$p(r) = \frac{8}{\pi}\frac{r}{R}\left[\arccos\left(\frac{r}{2R}\right) - \frac{r}{2R}\sqrt{1-\left(\frac{r}{2R}\right)^2}\right]. \tag{38}$$

For an infinitely thin rod of length L, the integration is performed from 0 to L and the normalization constant is 1/L so that:

$$p(r) = 2\left(1-\frac{r}{L}\right). \tag{39}$$

Note that the probability distribution function $P(\vec{r})$ is better known when defined for the "inter-particle" structure factor $S_I(Q)$ and is often referred to as pair correlation function $g(\vec{r})=VP(\vec{r})$ (where V is the sample volume):

$$S_I(Q) = \frac{1}{V}\int d\vec{r} \exp\left(-i\vec{Q}.\vec{r}\right)\left[g(\vec{r})-1\right]. \tag{40}$$

Here the following constant term:

$$\int d\vec{r} \exp\left(-i\vec{Q}.\vec{r}\right) = (2\pi)^3\delta\left(\vec{Q}\right) \tag{41}$$

has been subtracted from $g(\vec{r})$. This term has no contribution except in the (experimentally irrelevant) forward scattering direction (for which $\vec{Q} = \vec{0}$).

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QUESTIONS

1. What is the relationship between the form factor P(Q) and its amplitude F(Q) for the case of a uniform sphere? How about the case of a Gaussian polymer coil?
2. What is the form factor for a uniform sphere of radius R?
3. What is the form factor for a disk of radius R with its axis of rotation oriented parallel to the $\vec{Q}$ direction?
4. What is the form factor for a disklike lamella of thickness L with its normal axis oriented parallel to the $\vec{Q}$ direction?
5. What is the form factor for a cylinder of radius R and length L oriented perpendicular to the $\vec{Q}$ direction?
6. How is the averaging over random orientations performed for the calculation of the form factor?
7. Write down the radial pair correlation function γ(r) for a uniform sphere of radius R. γ(r) is defined through the following 1D Fourier transform:

$$P(Q) = \frac{1}{V_P} \int_0^R dr 4\pi r^2 \frac{\sin(Qr)}{Qr} \gamma(r).$$

8. What are the various parts that are used to calculate the SANS macroscopic scattering cross section for a solution of compact scatterers?
9. What is the Porod exponent for an infinitely thin rod of length L?

10. Define the spherical Bessel function of first order $j_1(x)$. What is $J_1(x)$?

ANSWERS

1. For a uniform sphere $P(Q) = |F(Q)|^2$. For a Gaussian coil, there is no uniform density and the form factor amplitude cannot be defined.
2. The form factor for a uniform sphere is given as $P(Q) = [3j_1(QR)/QR]^2$ where $j_1(QR)$ is the spherical Bessel function.
3. The form factor for a disk of radius R with its axis of rotation oriented parallel to the $\vec{Q}$ direction is given by $P(Q) = [\sin(QR)/QR]^2$.
4. The form factor for a disklike lamella of thickness L with its normal axis oriented parallel to the $\vec{Q}$ direction is given by $P(Q) = [2J_1(QL/QL]^2$ where $J_1(QL)$ is the cylindrical Bessel function.
5. The form factor for a cylinder of radius R and length L oriented perpendicular to the $\vec{Q}$ direction is given by $P(Q) = [2J_1(QR)/QR]^2$.
6. The form factor for a randomly oriented object with its symmetry axis along the z-direction is calculated as $P(Q) = (1/2)\int_{-1}^{1} d\mu P(Q,\mu)$ where $P(Q,\mu)$ is the form factor for the object oriented at an angle θ from the $\vec{Q}$ direction ($\mu = \cos(\theta)$).
7. The radial pair correlation function for a uniform sphere of radius R is given as $\gamma(r) = \left(1 - \frac{3}{4}\frac{r}{R} + \frac{1}{16}\left(\frac{r}{R}\right)^3\right)$. Note that $\gamma(r=2R) = 0$.
8. The SANS macroscopic scattering cross section for a solution of compact scatterers is the product of (1) the contrast factor, (2) the number density of scatterers, (3) the scatterer's volume squared, (4) the form factor and (4) the structure factor.
9. Since P(Q) for an infinitely thin rod of length L is given by
$P(Q) = \frac{1}{2}\int_{-1}^{1} d\mu \left[\frac{2J_1(Q\sqrt{1-\mu^2}R)}{Q\sqrt{1-\mu^2}R}\right]^2$, one would think that the Porod law gives $P(Q) \to 1/Q^2$. However after orientational averaging, one obtains the following $P(Q) = \left(\frac{2}{QL}\right)Si(QL) - \frac{\sin^2(QL/2)}{(QL/2)^2}$, so that $P(Q) \to 1/Q$. The Porod exponent for an infinitely thin rod is 1.
10. The spherical Bessel function of first order is given by $j_1(x) = \frac{\sin(x)}{x^2} - \frac{\cos(x)}{x}$. $J_1(x)$ is the cylindrical Bessel function.