ENAS 606 : Polymer Physics

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Scattering for Size and Mass Characterization

1 Introduction

Scattering of light and neutrons have long been used in the study of polymer structure and thermodynamics. Here, we will use the term *light scattering* to refer to the use of generally visible wavelengths of light (ca. 400-800 nm), x-ray scattering for the use of photons with wavelengths ranging from ca. 1-2 Å. In a scattering experiment, a coherent beam of light is directed onto the sample. The interaction of the light with the sample produces a scattering of the incident radiation, which is then detected at some distance away, and at some varying angles with respect to the direction of the incident beam. We will consider light and x-ray scattering here, and only elastic scattering, i.e. where there is no change in the energy of the photon due to the scattering event. Scattering of light and x-rays occurs due to index of refraction and electron density differences.

1.1 Units, Scattering Cross Section, Intensity

In a light/x-ray scattering experiment, we make some measure of the intensity of the scattered radiation as a function of the angle with respect to the incident beam direction. This intensity is related to the flux of radiation, J, which is proportional to the square of the amplitude of the oscillating field of the radiation, so $J = |A|^2 = AA^*$ where A^* is the complex conjugate of A. For a plane wave, the flux is related to the energy transmitted per unit area per unit time, and is independent of the distance from the source to the area over which the detection is made. For a spherical wave, in order to make the flux independent of the distance, it is measured as the energy transmitted per unit solid angle per unit time.

The sample is irradiated/illuminated with an incident beam of flux J_0 and the flux of scattered radiation J is recorded as a function of angle away from the incident direction. The ratio J_0/J has units of area per solid angle, and is formally known as the *differential scattering cross section*. Strictly speaking, the word intensity (absolute) refers to this ratio, although in the x-ray community, intensity (arbitrary) is used to refer to measurements of the flux J.

$$\frac{d\sigma}{d\Omega} \equiv \frac{J}{J_0}$$

The differential scattering cross section is the probability that a photon impinging on the sample is scattered into a unit solid angle in the given direction [1], that is, the number of particles scattered into a unit solid angle in a given direction per second divided by the flux of the incident beam. The integral of the differential scattering cross section provides the total scattering cross section, σ with dimensions of $[L^2]$ or area as

$$\sigma_{tot} = \int \left(\frac{d\sigma}{d\Omega}\right) \, d\Omega = \int_0^{2\pi} \, \int_0^{\pi} \, \frac{d\sigma}{d\Omega} \, \sin\Theta \, d\Theta \, d\Phi$$

where $\Theta \equiv 2\theta$.

2 The Interference Construction

Consider the interaction of a plane wave with two scatterers in a sample, Figure 1. The amplitude of the wave is represented conveniently in the complex notation (we need only the real part) as a function of time and space variables as

$$A(x,t) = \mathcal{A} e^{i2\pi(\nu t - x/\lambda)}$$

where ν is the frequency, λ the wavelength and \mathcal{A} is the modulus of absolute value of A(x, t).



Figure 1: Interference geometry

Scattering at locations j and k occur without a change of phase, producing an intensity at the detector due to the combination of the scattered waves. The phase difference between the beams scattered at the two points depends on the path length difference $\vec{ak} - \vec{jb}$. If the vector between the two points is denoted as \vec{r} , we see \vec{ak} is just $\vec{S_0} \cdot \vec{r}$ and \vec{jb} is $\vec{S} \cdot \vec{r}$ so that the phase difference is

$$\Delta \phi = \frac{2\pi}{\lambda} \left(\vec{S_0} \cdot \vec{r} - \vec{S} \cdot \vec{r} \right) = -2\pi \, \vec{s} \cdot \vec{r}$$

where $\vec{s} = (\vec{S} - \vec{S_0})/\lambda$ and is referred to as the scattering vector. The magnitude of the scattering vector is related to the scattering angle as

$$|\vec{s}| = s = \frac{2\sin\theta}{\lambda}$$

The spherical wave produced by the point scatterer at j is represented by $A_j(x,t) = A_0 b e^{i2\pi(\nu t - x/\lambda)}$ where A_0 is the amplitude of the incident radiation and b is termed the scattering length - it expresses the efficiency or ability of the object to scatter the incident radiation, and has dimensions of length (think about the relationship between the intensity of a spherical wave as dependent on the square of the amplitude, and that of the intensity of a plane wave). The scattered wave at k can be expressed as a phase shift of the scattered wave from j (the two differ only in phase) so

$$A_k(x,t) = A_j(x,t)e^{i\Delta\phi}$$

The combination of the scattered waves $A_i(x,t)$ and $A_k(x,t)$ is

$$A_{jk}(x,t) = A_j(x,t) + A_k(x,t) = A_0 b \, e^{i2\pi(\nu t - x/\lambda)} \left(1 + e^{-i2\pi\vec{s}\cdot\vec{r}}\right)$$

The flux is given by the square of the intensity so

$$J(\vec{s}) = A_{jk}(x,t)A_{jk}^{*}(x,t) = A_{0}^{2}b^{2}\left(1 + e^{-i2\pi\vec{s}\cdot\vec{r}}\right)\left(1 + e^{i2\pi\vec{s}\cdot\vec{r}}\right)$$
(1)

We can ignore the x and t dependence and inspect only the scattering vector dependence. It is given in individual, discrete summation and continuous integral forms in Equation 2 where $n(\vec{r})$ is the number of scatterers within a volume element $d\vec{r}$ around \vec{r} and $\vec{r_j}$ is the vector to the jth scatterer from an arbitrary origin.

$$A(s) = A_0 b \left(1 + e^{-i2\pi \vec{s} \cdot \vec{r}} \right) A(s) = A_0 b \sum_{j=1}^N e^{-i2\pi \vec{s} \cdot \vec{r_j}} A(s) = A_0 b \int_V n(\vec{r}) e^{-i2\pi \vec{s} \cdot \vec{r_j}} d\vec{r}$$
(2)

From the integral form in Equation 2 we can recognize that the wave amplitude is proportional to the three-dimensional Fourier transform of the local number density $n(\vec{r})$ of scatterers.

A more common notation is much of the x-ray literature is the use of the scattering vector, \mathbf{q} given by $\mathbf{q} = 2\pi \mathbf{s}$. The quantity is also defined with respect to wave vectors as

$$\mathbf{q} \equiv \mathbf{k} - \mathbf{k}_0$$

q is also referred to sometimes as the momentum transfer vector since momentum, from the de Broglie equation is $p = h/\lambda = \hbar k$ and

$$\hbar \mathbf{q} = h \mathbf{s} = (h/\lambda) \mathbf{S} - (h/\lambda) \mathbf{S}_{\mathbf{0}}$$

2.1 Scattering from an Atom

We can consider the scattering from an atom as the independent contributions due to the scattering from the distribution of electrons around the nucleus. The atomic scattering factor is measured in units of A_0b_e where b_e is the scattering length of a single electron, and is given by

$$f(\mathbf{s}) = \int n(\mathbf{r}) \, e^{-i2\pi \mathbf{s}\mathbf{r}} d\mathbf{r}$$

For a spherically symmetric $n(\mathbf{r})$, f(mathbfs) is a function only of the magnitude of the scattering vector, s. The atomic scattering factor is given by a 3D Fourier transform [1] as

$$f(s) = \int_0^\infty 4\pi r^2 \, n(r) \frac{\sin(2\pi sr)}{2\pi sr} \, dr$$
(3)

At zero angle (s=0), all scattered waves are in phase and sum to give the atomic number of the atom. We shall see later on that in similar fashion, the zero angle scattered intensity in a light or x-ray scattering experiment is directly related to the molecular weight of the polymer under investigation.

2.2 Scattering from a Collection of Atoms

If we now have a collection of atoms, we can describe the location of all electrons in the system with respect to the atom to which they belong as $\mathbf{r_j} = \mathbf{r_k} + \mathbf{r_{k,m}}$ where k denotes the atom number, and $\mathbf{r_{k,m}}$ denotes the mth electron of the k-atom. From Equation 2 we can write the scattered amplitude as

$$A(\mathbf{s}) = A_0 b_e \sum_{k=1}^{Natoms} \left(\sum_{m=1}^{Z} e^{-i2\pi \mathbf{sr_k}} \right) e^{-i2\pi \mathbf{sr_k}}$$
(4)

$$A(\mathbf{s}) = A_o b_e \sum_{k=1}^{Natoms} f_k(s) e^{-i2\pi \mathbf{s} \mathbf{r}_k}$$
(5)

$$A(\mathbf{s}) = A_0 b_e f(s) \int n_{atoms}(\mathbf{r}) e^{-i2\pi \mathbf{s}\mathbf{r}} d\mathbf{r}$$
(6)

Here, we see that the scattered amplitude has a component that depends on the scattered amplitude from one atom, and a component that depends on the distribution of atoms. So called contributions from *form* and *structure* factors are ubiquitous in the treatment of scattering from discrete objects such as polymer coils or colloidal particles in solution.

2.2.1 Scattering and the Autocorrelation Function

We can rewrite Equation 2 as

$$A(\mathbf{q}) = \int_{V} \rho(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}$$
(7)

where $\rho(\mathbf{r}) = b_e n(\mathbf{r})$ is the scattering length density distribution. This says that the scattered amplitude is related to the Fourier transform of $\rho(\mathbf{r})$. Likewise, it can be shown [1] that the intensity, $I(\mathbf{q}) = |A(\mathbf{q})|^2$ is given by

$$I(\mathbf{q}) = \int \Gamma_{\rho}(\mathbf{r}) \, e^{-i\mathbf{q}\mathbf{r}} \, d\mathbf{r}$$

where

$$\Gamma_{
ho}(\mathbf{r}) = \int \rho(\mathbf{u}) \rho(\mathbf{u} + \mathbf{r}) \, d\mathbf{u}$$

is the autocorrelation function of the scattering length density distribution. So the scattered intensity is related to the Fourier transform of this autocorrelation function where

$$\langle \rho(\mathbf{u})\rho(\mathbf{u}')\rangle = \frac{\int \rho(\mathbf{u})\rho(\mathbf{u}+\mathbf{r})\,d\mathbf{u}}{\int d\mathbf{u}} = \frac{\Gamma_{\rho}(\mathbf{r})}{V}$$

At $\mathbf{r} = 0$

$$\Gamma_{\rho}(0) = \langle \rho^2 \rangle V$$

and at $\mathbf{r} \to \infty$

$$\Gamma_{\rho}(\mathbf{r} \to \infty) = \langle \rho \rangle^2 V$$

3 Small Angle Scattering of Polymers and Colloids

Here we will consider scattering at small angles where the length scale probed is generally 10Å and greater $(\sin \theta = \lambda/2d)$ where d is the length scale. We restrict our coverage to dilute particulate systems, whether of polymer coils in solution, or of colloidal objects of various shapes. Since we have the basic equation for the scattered amplitude as a function of the location of the scatterers, we can develop exact expressions for the expected dependence of the scattered amplitude(intensity) on scattering vector. For the polymer coil, we use a Gaussian distribution of scatterers, for instance.

3.1 Spheres, Rods, Disks

Using Equation 7, we can determine the scattered intensity for a solid sphere of radius R with a uniform density ρ_0 for $r \leq R$.

$$A(q) = \int_{0}^{\infty} \rho(r) 4\pi r^{2} \frac{\sin(qr)}{qr} dr$$

$$A(q) = \frac{\rho_{0}}{q} \int_{0}^{R} 4\pi r \sin(qr) dr$$

$$A(q) = \rho_{0} v \frac{3 (\sin(qR) - qR \cos(qR))}{(qR)^{3}}$$

$$I(q) = \rho_{0}^{2} v^{2} \frac{9 (\sin(qR) - qR \cos(qR))^{2}}{(qR)^{6}}$$
(8)

Zeros of the function occur where $qR = \tan(qR)$ as shown in Figure 2



Figure 2: Scattering from an individual solid spherical particle of radius R

For a rod, the expression is given by

$$I(q) = \rho_0^2 v^2 \frac{2}{qL} \left[\operatorname{Si}(qL) - \frac{1 - \cos(qL)}{qL} \right]$$
(9)

where

$$Si(x) \equiv \int_0^x \frac{\sin(u)}{u} du$$

For a thin circular disk, the scattered intensity is given in Equation 10 where J_1 is the first order Bessel function.

$$I(q) = \rho_0^2 v^2 \frac{2}{q^2 R^2} \left[1 - \frac{J_1(2qR)}{qR} \right]$$
(10)



Figure 3: Scattering from individual particles of different shape, as a function of the dimensionless product qR_q .

3.1.1 Scaling at high q

At high q, the intensity scales as $I(q) \sim q^{-\alpha}$ where $\alpha = 4$ for spheres, 2 for thin disks and 1 for rods. At small q, the intensities are independent of the shape of the particles, if plotted as a function of qR_g , which provides the basis for the Guinier law.

3.2 Scattering from a Gaussian Chain

The scattering from an independent polymer chain following Gaussian statistics was solved by Debye [7]. The derivation is based on an evaluation of the intensity as a double sum resulting from the square of the expression for the amplitude of the scattered wave.

$$A(\mathbf{q}) = \rho_0 v_u \sum_{j=0}^{N+1} e^{-i\mathbf{q}\mathbf{r}_j}$$

$$I(\mathbf{q}) = \rho_0^2 v_u^2 \sum_{j=0}^{N+1} \sum_{k=0}^{N+1} e^{-i\mathbf{q}\mathbf{r}_{jk}}$$

$$I(\mathbf{q}) = \rho_0^2 v_u^2 \int P(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}$$
(11)

where v_u is the volume of a monomer, the polymer is made up of N+1 such monomers, and $P(\mathbf{r})$ represents the number of monomer pairs that are separated by 4. It is via this last term that the Gaussian distribution enters, as $P(\mathbf{r})$ is a function of the distribution in the square brackets below

$$P(r) = 2\sum_{K=0}^{N} (N+1-K) \left[\left(\frac{3}{2\pi K l^2} \right)^{3/2} \exp\left(-\frac{3r^2}{2K l^2} \right) \right]$$

where there are (N + 1 - K) pairs of monomers separated by K bonds, and the bond length is l. The solution is

$$I(q) = \rho_o^2 v_u^2 D(x)$$

$$D(x) = \frac{2(e^{-x} + x - 1)}{x^2}; \quad x = q^2 R_g^2$$
(12)

At small q, it can be approximated as

$$D(x) \cong 1 - \frac{q^2 R_g^2}{3}$$

3.2.1 Length Scales

The Gaussian distribution contains no inherent length scale - Gaussian (ideal) chains obey the statistics down to and out to aphysical dimensions. In reality, we understand that there is a length scale below which the polymer chain appears locally stiff due to the persistence of bond orientation for a finite monomer sequence. We should thus expect a crossover from rod-like scattering to Gaussian like scattering at a particular scattering vector, corresponding to the persistence length. This is in fact the case. At small q, the scattering is shape independent and scales as $\exp(-q^2)$. At slightly larger q, we observe the $1/q^2$ dependence of the Debye formulation, and at even larger q, a q^{-1} dependence of intensity, characteristic of rod-like scattering. This is well illustrated on a Kratky plot of $I(q).q^2$ vs q [1].

3.2.2 Guinier's Law

Guinier's law results from an expansion of the exponential dependence of the scattering intensity in Equation 7

$$A(\mathbf{q}) = \int \rho(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}$$

$$A(\mathbf{q}) = \int \rho(\mathbf{r}) d\mathbf{r} - i \int \mathbf{q}\mathbf{r} \,\rho(\mathbf{r}) d\mathbf{r} - \frac{1}{2!} \int (\mathbf{q}\mathbf{r})^2 \rho(\mathbf{r}) d\mathbf{r} + \dots$$
(13)

Given that $(\mathbf{qr})^2 = (q_x x + q_y y + q_z z)^2$, the expression ultimately yields

$$I(q) = \rho_0^2 v^2 \left(1 - \frac{1}{3} q^2 R_g^2 + ... \right)$$

$$I(q) \cong \rho_0^2 v^2 \exp\left(-\frac{q^2 R_g^2}{3} \right)$$
(14)

A plot of $\ln I(q)$ vs. q^2 has a slope of $-R_g^2/3$. Guinier's law is applicable in the regime where $qR_g \leq 1.3$ and can only be applied in dilute solution scattering where there are no positional correlations between individual polymer chains. The radius of gyration is shape independent. An extrapolation of the scattered intensity in absolute units back to q = 0 makes it possible to determine the value of $(\rho_0 v)^2$ if the concentration of particles is known, since I(q) is the scattered intensity per particle. Knowledge of the volume per particle and the radius of gyration gives some information about the shape of the particle (polymer chain). Additionally, molecular weight can be determined, as will be discussed in a later section.

3.3 Fractal Scattering

Here we consider the functional form of the scattering from mass and surface fractals.

The mass of a fractal object of dimension d scales as $M(r) \sim r^d$. For a surface fractal, the surface area scales as $S(r) \sim r^{2-d_s}$ where d_s is between 2 and 3 for a surface fractal in three-dimensional space. It is equal to 2 for a perfectly smooth surface, and approaches 3 for a highly folded/convoluted surface.

3.3.1 Mass Fractal

Scattering from a mass fractal is considered from the 3D Fourier transform of the scattering length distribution function, which now scales as

$$I(q) \sim \frac{1}{q} \int_0^\infty r^{d-2} \sin(qr) \, dr$$

This yield a scaling of

$$I(q) \sim q^{-d}$$

The slope of a log-log plot of intensity vs wave vector thus yields the fractal dimension of the object under study at a particular length scale. At very high q, we get a scaling of q^{-4} which is characteristic of sharp interfaces, as described by Porod's law [1].

3.3.2 Surface Fractal

The scattered intensity due to surface fractal scattering scales as

$$I(q) \sim q^{-(6-d_s)}$$

3.3.3 Polymer Chains at Different Length Scales

If we examine the scattering of a polymer chain across a wide q-range, we can see that at very low q, as discussed prior, we are in a regime where we are probing correlations between polymer chains. In a dilute solution, there are no correlations and so the scattered intensity is constant, independent of q and proportional to the concentration of the system. At higher q, we start to probe scattering due to correlations of monomers on a single polymer chain, yielding information about the radius of gyration. At slightly higher q, $> 1/R_g$, we become sensitive to the fractal nature of the polymer and the intensity here scales as q^{-d} where the fractal dimension is related to the polymer scaling exponent ν in $R \sim bN^{\nu}$ encountered earlier. For ideal (Gaussian) chains, $\nu = 1/2$ and so d = 2, the Debye result. At very high q, we start to probe scattering from individual monomers, which, since they are presumed to have sharp smooth interfaces, produce the Porod scaling of q^{-4} . Figure 4 schematically illustrates the transition among length scales in typical SAXS data [3].



Figure 4: Schematic illustration of the transition from inter-chain to intra-chain and finally monomeric scattering

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