

# 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,  $\sigma$  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  $\nu$  is the frequency,  $\lambda$  the wavelength and  $\mathcal{A}$  is the modulus of absolute value of  $A(x, t)$ .

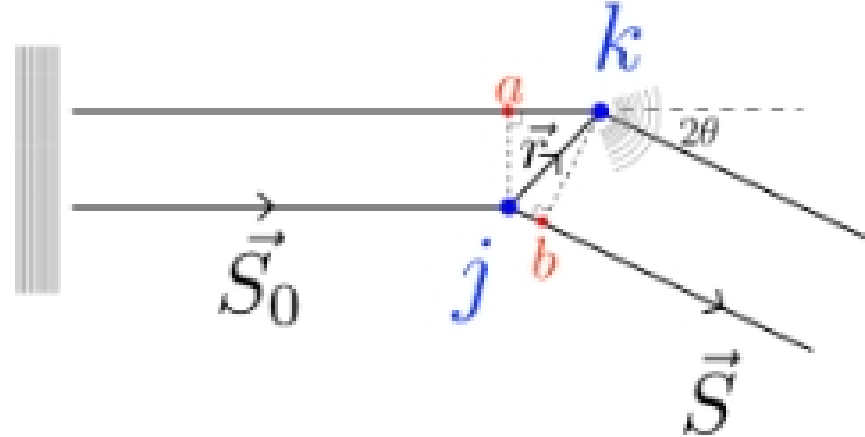


Figure 1: Interference geometry

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  $a\vec{k} - j\vec{b}$ . If the vector between the two points is denoted as  $\vec{r}$ , we see  $a\vec{k}$  is just  $\vec{S}_0 \cdot \vec{r}$  and  $j\vec{b}$  is  $\vec{S} \cdot \vec{r}$  so that the phase difference is

$$\Delta\phi = \frac{2\pi}{\lambda} (\vec{S}_0 \cdot \vec{r} - \vec{S} \cdot \vec{r}) = -2\pi \vec{s} \cdot \vec{r}$$

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  $A_j(x, t)$  and  $A_k(x, t)$  is

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

The flux is given by the square of the intensity so

$$\begin{aligned} J(\vec{s}) &= A_{jk}(x, t) A_{jk}^*(x, t) \\ &= A_0^2 b^2 (1 + e^{-i2\pi \vec{s} \cdot \vec{r}}) (1 + e^{i2\pi \vec{s} \cdot \vec{r}}) \end{aligned} \quad (1)$$

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  $j^{\text{th}}$  scatterer from an arbitrary origin.

$$\begin{aligned} A(s) &= A_0 b (1 + e^{-i2\pi\vec{s}\cdot\vec{r}}) \\ A(s) &= A_0 b \sum_{j=1}^N e^{-i2\pi\vec{s}\cdot\vec{r}_j} \\ A(s) &= A_0 b \int_V n(\vec{r}) e^{-i2\pi\vec{s}\cdot\vec{r}} d\vec{r} \end{aligned} \quad (2)$$

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 in 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

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

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

$$\hbar\mathbf{q} = \hbar\mathbf{s} = (h/\lambda)\mathbf{S} - (h/\lambda)\mathbf{S}_0$$

## 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  $A_0 b_e$  where  $b_e$  is the scattering length of a single electron, and is given by

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

For a spherically symmetric  $n(r)$ ,  $f(\mathbf{s})$  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

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

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  $m^{\text{th}}$  electron of the  $k$ -atom. From Equation 2 we can write the scattered amplitude as

$$A(\mathbf{s}) = A_0 b_e \sum_{k=1}^{N_{\text{atoms}}} \left( \sum_{m=1}^Z e^{-i2\pi\mathbf{s}\cdot\mathbf{r}_{k,m}} \right) e^{-i2\pi\mathbf{s}\cdot\mathbf{r}_k} \quad (4)$$