Small Angle X-ray Scattering: Going Beyond the Bragg Peaks

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This article gives an introduction to the principles of small angle scattering. Some applications of this technique are also briefly discussed.

Introduction

Small angle X-ray scattering (SAXS) is a widely used technique to study large scale inhomogeneities in a medium, at length scales much larger than the wavelength of the X-rays. Such inhomogeneities arise, for example, when particles or macromolecules are dispersed in a solvent, and from clusters of defects or impurity atoms in a solid. Although SAXS studies began in the 1930s, in the early days it was limited to a few laboratories because of the specialized equipment required (*Box* 1). The advent of powerful synchrotron X-ray sources in recent decades has made this technique available to a much larger scientific community (*Box* 2). It has been put to a variety of uses, such as, measurement of sizes of particles dispersed in a solvent, investigation of the structure and conformational changes of biological macromolecules, determination of interaction parameters in fluids, and estimation of internal surface area of porous materials.

SAXS differs from conventional crystallography in the methods of analysis used and the kind of information sought. The diffraction pattern of a crystalline material consists of a set of sharp peaks, whose positions are given by the Bragg's law, and the objective is to obtain the structure of the material with atomic resolution. On the other hand, there are no sharp Bragg peaks in SAXS, and only an intensity profile smoothly varying with the scattering angle is obtained. The objective is typically

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Guinier law, Porod law, form factor, structure factor.

Box 1. The Kratky Camera

Specialized equipment is required to study SAXS, where the incident X-ray beam is very narrow and sharp. This results in very low X-ray intensities and hence data have to be collected over a long time, typically many hours with a laboratory source. The simplest setup consists of two or three sets of slits to collimate the X-ray beam. In the widely used Kratky camera the collimation is achieved with metal blocks, which results in a narrow beam with an asymmetric intensity profile. On one side the intensity drops down sharply and data can be collected at very small angles (of the order of 0.02°) close to the main beam.

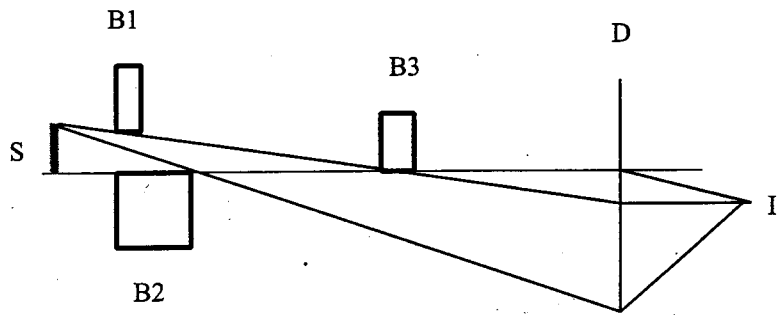

Figure A. Schematic of the Kratky camera. S is the source of X-rays, and B1, B2, B3 are the metal blocks. Note the asymmetric intensity profile of the beam (I) at the detector plane (D).

to get the size and shape of the inhomogeneities in the material at length scales much larger than the X-ray wavelength, and in some cases to determine their fluid-like organization.

In order to understand the origin of small angle scattering let us consider scattering from a particle of radius R. X-rays are scattered by the electrons in the particle. In the forward direction all of them scatter in phase, resulting in maximum intensity (*Figure* 1). As we move to larger scattering angles (2θ) there is some degree of

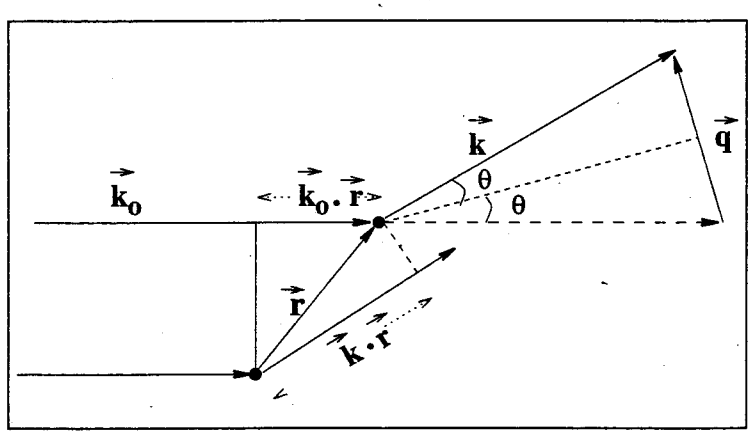

Figure 1. Scattering of a plane wave by a collection of point scatterers. $\vec{k}_0$ and $\vec{k}$ are the wavevectors of the incident and scattered waves, respectively.

Box 2. Synchrotron X-ray Sources

Early synchrotron sources were particle accelerators built by high energy physicists, where the synchrotron radiation was an unwanted byproduct. Later ones were constructed exclusively as sources of radiation. They are based on the principle that an accelerated charged particle, such as an electron, emits radiation. In a synchrotron, electrons or positrons are made to circulate at relativistic speeds in a storage ring, whose diameter is typically of the order of 100 m, by using a series of so-called bending magnets. This ring contains some straight segments where an insertion device, such as undulator, is placed. The undulator consists of an array of magnets, which forces the particles to execute small amplitude oscillations in the horizontal plane, which produces the intense beam of radiation. A monochromator is used to select radiation of a particular wavelength, which is then focused on the sample. Latest generation of synchrotrons produce very intense pulsed beams of X-rays, which are about 10^{12} times more brilliant than the ones obtained with laboratory sources.

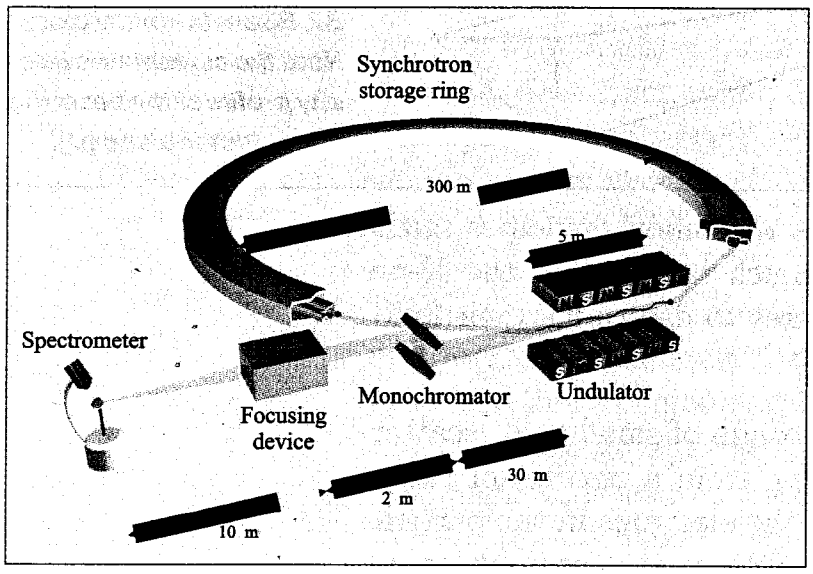

Figure B. Schematic of a third generation synchrotron X-ray source. Typical dimensions are indicated.

destructive interference between the waves scattered from different points in the particle and the intensity decreases. We would expect the intensity to be very small when the path difference between the waves scattered from the two extreme points in the particle is of the order of the wavelength λ. This would happen at an angle $2\theta \sim \lambda/R$. Therefore, it is clear that small angle scattering occurs for particles whose size is very much larger than the wavelength. However, if it is extremely large, the scattering is confined to exceedingly small angles and will not be accessible experimentally. Typical

length scales probed with SAXS are in the 1-100 nm range, using X-rays of wavelength of the order of 0.1 nm. From the above relation it would appear advantageous to use X-rays of very high wavelength, but their much higher absorption by matter makes them unsuitable.

Small angle X-ray scatteering is produced by inhomogeneities in the electron density of a material at length scales much larger than the X-ray wavelength.

Since X-rays are scattered by the electrons in a material, the scattered intensity depends on its electron density $\rho(\vec{r})$, which gives the number of electrons per unit volume at each point in the material. $\rho(\vec{r})$ is a spatially varying function at length scales comparable to interatomic separations, reflecting the atomic structure of the material. However, in SAXS we are interested in much larger length scales and these short length scale fluctuations in $\rho(\vec{r})$ are irrelevant, and we can take it to be a smooth function of $\vec{r}$. The amplitude of the scattered wave is then proportional to the Fourier transform of $\rho(\vec{r})$ (see *Box* 3), i.e.,

Box 3. Scattering by a Collection of Particles

Consider a plane electromagnetic wave, $\phi_i = \phi_o\ exp(i\vec{k_o}\cdot\vec{r})$ incident on a point scatterer placed at the origin (*Figure* 1). The scattered radiation is spherically symmetric and its amplitude at the observation point R is given by $\phi_s = (\phi_o\ a/R)\ exp(ikR)$, where a is the scattering strength of the point scatterer. If the point is at a distance $\vec{r}$ from the origin a phase difference of $(\vec{k}-\vec{k_o})\cdot\vec{r}$ has to be introduced, and the amplitude of the scattered wave is $\phi_s = (\phi_o\ a/R)\ exp(ikR)exp(-i\vec{q}\cdot\vec{r})$, where $q = \vec{k}-\vec{k_o}$ is the scattering vector. If there are N scatterers at positions $\vec{r_i}$ (i=1,2,..N) the total scattered amplitude is

$$\phi_s = (\phi_o\ a/R)\ exp(ikR)\sum_{i=1}^{N} exp(-i\vec{q}\cdot\vec{r_i}). \qquad (1)$$

If we want to treat the scattering medium as a continuum, instead of a collection of distinct point scatterers, we can introduce the density function $\rho(\vec{r}) = \sum\delta(\vec{r}-\vec{r_i})$, which consists of delta functions at the positions of the scatterers. Then the scattered amplitude can be written as the Fourier transform of the density function

$$\phi_s = K\int_{-\infty}^{\infty}\rho(\vec{r})exp(-i\vec{q}\cdot\vec{r})d\vec{r}, \qquad (2)$$

where $K = (\phi_o\ a/R)exp(ikR)$.

$$A(\vec{q}) = K \int_{-\infty}^{\infty} \rho(\vec{r})\ exp(-i\vec{q}\cdot\vec{r})d\vec{r}, \qquad (1)$$

where the scattering vector $\vec{q} = \vec{k} - \vec{k_o}$, $\vec{k_o}$ and $\vec{k}$ being the wavevectors of the incident and scattered waves, respectively. K is a q-independent factor depending on the details of the experimental set-up. The scattering is elastic, so that $|\vec{k}| = |\vec{k_o}|$. In terms of the scattering angle 2θ (the angle between $\vec{k}$ and $\vec{k_0}$) the magnitude of $\vec{q}$ is given by $q = (4\pi/\lambda)sin\theta$. In principle, if we know $A(\vec{q})$, which is in general a complex function, we can obtain $\rho(\vec{r})$ by inverting the above relation, and thus get the structure of the material. However, the intensity of the scattered wave $I(\vec{q}) = |A(\vec{q})|^2$, and hence only the magnitude of A can be obtained from the experiment. Therefore, the phase information that is lost has to be restored in some way before the structure can be determined. In SAXS studies this problem is often circumvented by using a model for $\rho(\vec{r})$ with a few adjustable parameters that describe the unknown features of the system. The scattered intensity is calculated from the model using (1) and the values of the model parameters are adjusted to get the best fit with the observed intensity. If a good fit can be obtained the model can be taken to be a fairly accurate representation of the electron density of the material.

Scattering by a Particle

Let us now discuss SAXS by taking a simple example of a colloidal particle of uniform electron density ρ_o, suspended in a solvent of electron density ρ_s. For a spherical particle of radius R the electron density can be written as

$$\begin{aligned} \rho(r) &= \rho_o, \quad r < R \\ &= 0, \quad r > R. \end{aligned} \qquad (2)$$

The internal structure of the particles leads to diffraction peaks (sharp or broad, depending on whether it is

crystalline or amorphous, respectively) at large angles, since the typical interatomic distances are comparable to the wavelength of X-rays. For the scattering at small angles $\rho(\vec{r})$ in (1) has to be replaced by $\rho(\vec{r}) - \rho_s$, as only the contrast between the particle and the solvent can lead to a non-zero scattered intensity. In a dilute solution different particles scatter independently and the total scattered intensity is just the sum of those scattered by each particle, i.e.,

$$I(\vec{q}) = nK^2P(\vec{q})$$

$$= nK^2\left[\int_0^\infty \{\rho(r) - \rho_s\}\ exp(-i.\vec{q}\cdot\vec{r})d\vec{r}\right]^2, \qquad (3)$$

where n is the number density of particles and the form factor $P(q)$ represents the scattering from one particle.

As mentioned earlier, $\rho(\vec{r})$ can be obtained from a detailed analysis of the observed intensity $I(\vec{q})$. However, certain features of the particles can be obtained directly from the scattering data. Some of these are discussed below.

Mass of the Particle: In the limit of $q \to 0$, (3) reduces to $I(0) = nK^2[v(\rho_o - \rho_s)]^2$, where v is the volume of the particle. In terms of the mass m of the particle and the mass concentration c of the solution, the above relation can be written as, $I(0) = K^2\ [u(\rho_o - \rho_s)]^2 mcV$, where u is its volume per unit mass and V the volume of the solution. The factor K can be determined using a standard scatterer. Hence if the electron density of the particles is known, their mass can be estimated.

Radius of Gyration: The radius of gyration R_g of a particle is defined as

$$R_g^2 = \frac{\int_v \rho(r)r^2dv}{\int_v \rho(r)dv}, \qquad (4)$$

where v is the volume of the particle. It can be shown that at very small q, $I(q) \propto exp(-R_g\ q^2/3)$. This relation is known as the Guinier law and is, in general,

The decay in the scattered intensity in the low-q limit is described by the Guinier law.

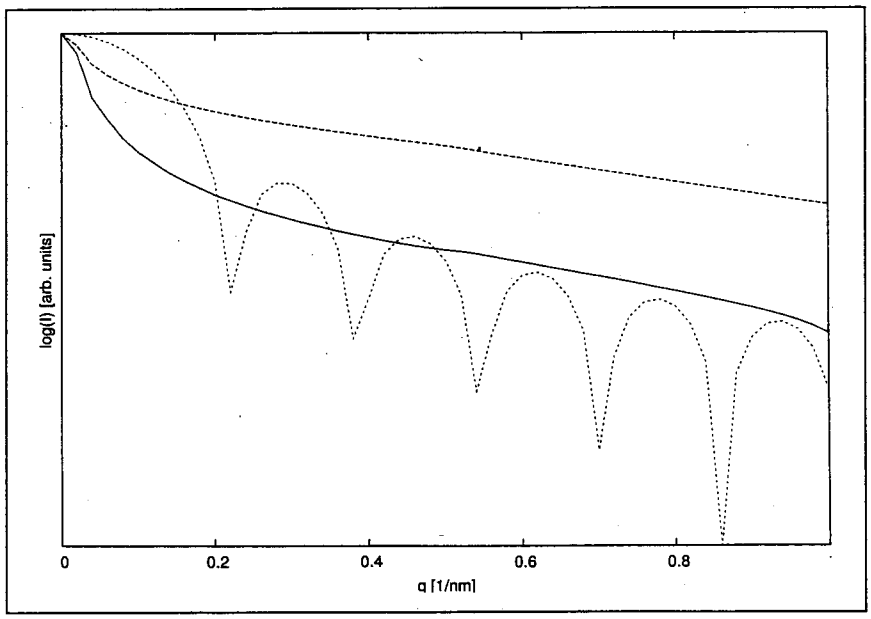

Figure 2. Calculated scattered intensity from a sphere of 20 nm radius (dotted line), a cylinder of length 100 nm and radius 2 nm (dashed line), and from a disc of radius 100 nm and thickness 1 nm (solid line). Note the quadratic decay of log(I) at small q in all the three cases, as predicted by the Guinier law.

valid for $q << R_g^{-1}$. R_g can be related to the geometric parameters of the particle. For example, for a spherical particle of radius R, $R_g^2 = (3/5)R^2$. Therefore, by measuring the decay of $I(q)$ at small q, the particle size can be estimated.

Shapes of Particles: For a spherical particle of radius R, the integral in (3) can be carried out analytically to give

$$I(q) = K^2[3(\rho_o - \rho_s)\ \{sin(qR) - qR\ cos(qR)\}/(qR)^3]^2. \quad (5)$$

$I(q)$ goes to zero at specific values of qR. For example, the first two zeros occur at $qR = 4.49$ and 7.73 (*Figure* 2). Therefore, from the minima in $I(q)$ the radius of the sphere can be estimated.

Certain other shapes can also be deduced from the behaviour of $I(q)$ at intermediate values of q. For example, for cylindrical particles it can be shown that $I(q) \sim q^{-1}$ in a range of q between $q_1 \sim 1/L$ and $q_2 \sim 1/R_c$, where L and R_c are the length and radius of the cylinder, respectively. In the case of a long flexible cylinder, L has to be replaced by the persistence length L_p, which is the length scale over which the cylinder can be taken to be

a stiff rod. In the case of disc-like objects, $I(q) \sim q^{-2}$ in a range between $q_1 \sim 1/D$ and $q_2 \sim 1/t$, where D and t are the diameter and thickness of the disc, respectively. Again, in the case of a flexible sheet, D has to be replaced by the persistence length D_p, over which it can be taken as stiff. Thus from the limits of the q-range over which the characteristic variation of $I(q)$ is observed, the geometric parameters of the particles can be estimated. The q^{-1} dependence of the intensity is unique to rods, whereas the q^{-2} dependence is also seen in some other systems, such as random coils. Therefore, some care has to be taken in using this procedure.

The behaviour of the scattered intensity in the high-q limit is described by the Porod law.

The Surface Area: In the high q limit of the small angle region, $I(q) \sim (\rho_o - \rho_s)^2 s q^{-4}$, where s is the surface area of a particle. This is known as the Porod law and holds good whenever the interface between the particle and the solvent is sharp. This expression has to be slightly modified when the variation of the electron density across the interface is smooth. This relation can also be used to determine the internal surface area of porous materials (*Figure* 3).

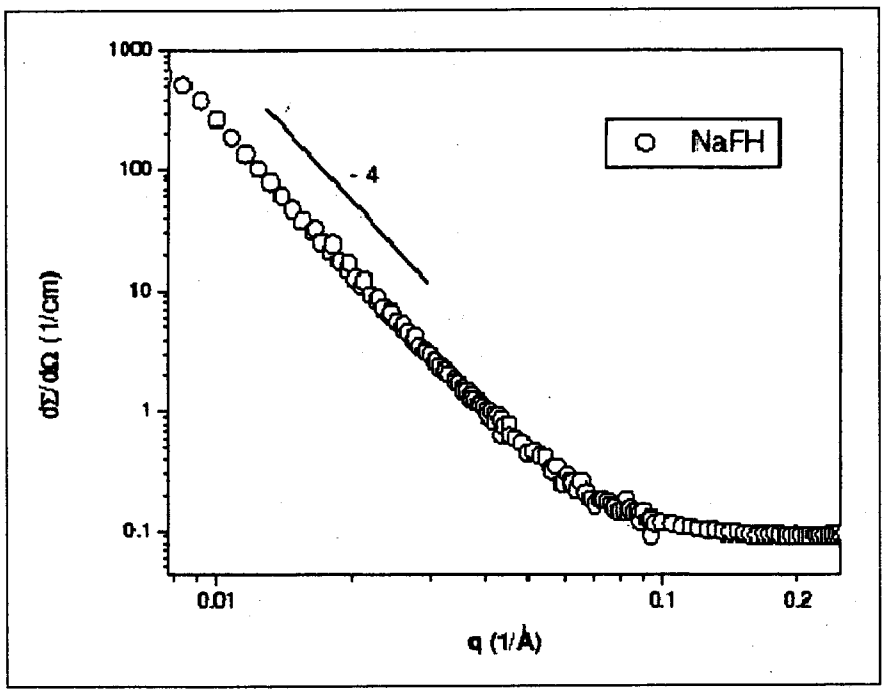

Figure 3. Scattering from a porous material showing the q^{-4} dependence predicted by the Porod law.

The scattered intensity from a concentrated colloidal suspension can be expressed as the product of a form factor $P(\vec{q})$ and a structure factor $S(\vec{q})$.

Scattering at Higher Concentrations

The above discussion has been restricted to very low density of scattering particles, such that they could be treated as scattering independently with no interference between the waves scattered by different particles. However, at higher concentrations this approximation is not valid and the interparticle interference effects have to be taken into account. In such a situation the scattered intensity can be written as

$$I(\vec{q}) = nK^2\ S(\vec{q})\ P(\vec{q}), \qquad (6)$$

where the structure factor $S(\vec{q})$ describes the interparticle interference, $P(\vec{q})$ is the particle form factor mentioned earlier. In systems such as colloidal dispersions, where the size and shape of particles do not change with concentration, $P(\vec{q})$ can be determined from very dilute solutions, and $S(\vec{q})$ can be extracted from the scattering data at higher concentrations (*Figure* 4). $S(\vec{q})$ is related to the pair correlation function $g(\vec{r})$, which gives the probability of finding a particle at a distance $\vec{r}$ from another, by

$$S(\vec{q}) = 1 + n \int_V g(\vec{r}) exp(-i\vec{q} \cdot \vec{r}) d\vec{r}, \qquad (7)$$

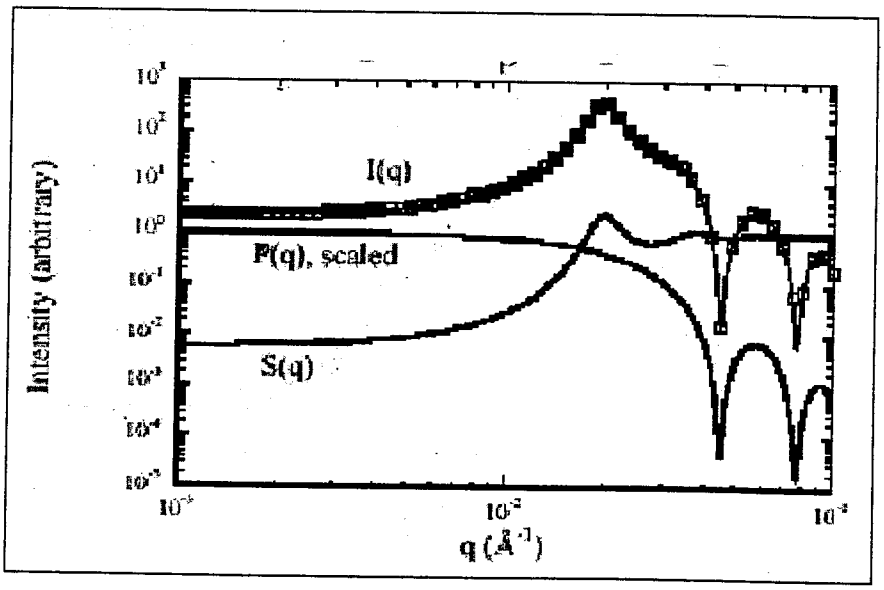

Figure 4. Decomposition of the scattered intensity I(q) from a dispersion of charged spheres into a form factor P(q) and a structure factor S(q). The broad peaks in S(q) are from the liquid-like short-range order in the system.

where n is the number density of the particles and V the volume of the solution. All the structural information about the fluid is contained in $g(r)$, and the interparticle interactions can, in principle, be deduced from it. In other systems, where the aggregate size depends on the concentration, it is often difficult to separate the intraparticle and interparticle interference effects unambiguously.

Polydispersity smears out features in the scattered intensity characteristic of the shape of the particles.

Polydispersity

Another complication that arises in practice is from the fact that all particles are not of the same size. In the case of a dilute solution of such polydisperse particles, the scattered intensity is just the sum of those from the individual particles. As a result, many characteristic features of the particle form factor get smeared out (*Figure* 5), and it is very often difficult to distinguish between the scattering from a polydisperse distribution of particles of one shape and that from a monodisperse dispersion of another shape. For example, the same scattering curve can be fitted to polydisperse spheres as well as monodisperse ellipsoids. Under these circumstances additional information from other experimental techniques is required to remove the ambiguity.

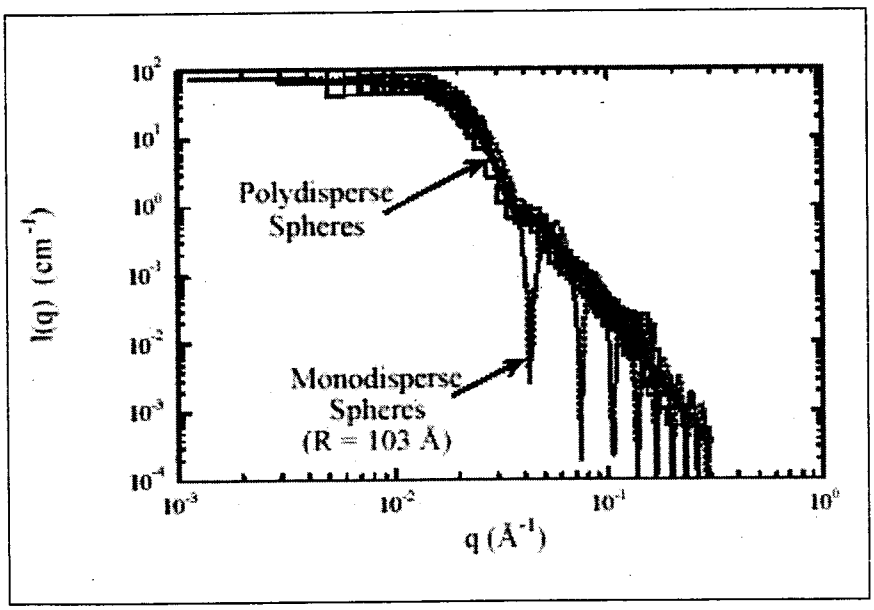

Figure 5. Scattering from polydisperse spheres. Note the smearing of the features in the scattered intensity due to the polydispersity.

As described by (3), the scattered intensity is proportional to the difference in the electron density of the particle and the solvent. Therefore, it is advantageous to maximize this contrast. It is not very easy to do this in the case of SAXS, since the electron densities can be changed only by changing the chemical nature of the substance. On the other hand, the contrast can be very easily changed if neutrons are used, instead of X-rays.

Neutrons are scattered by the nuclei of the atoms, and the scattering power of isotopes of the same element can be very different. For example, the difference in the scattering powers of hydrogen (^1H) and deuterium (^2H) is very large, and this difference is made use of in small angle neutron scattering (SANS) studies to enhance the contrast.

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Suggested Reading

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The most beautiful experience we can have is the mysterious. It is the fundamental emotion which stands at the cradle of true art and true science. Whoever does not know it and can no longer wonder, no longer marvel, is as good as dead, and his eyes are dimmed.

– Albert Einstein