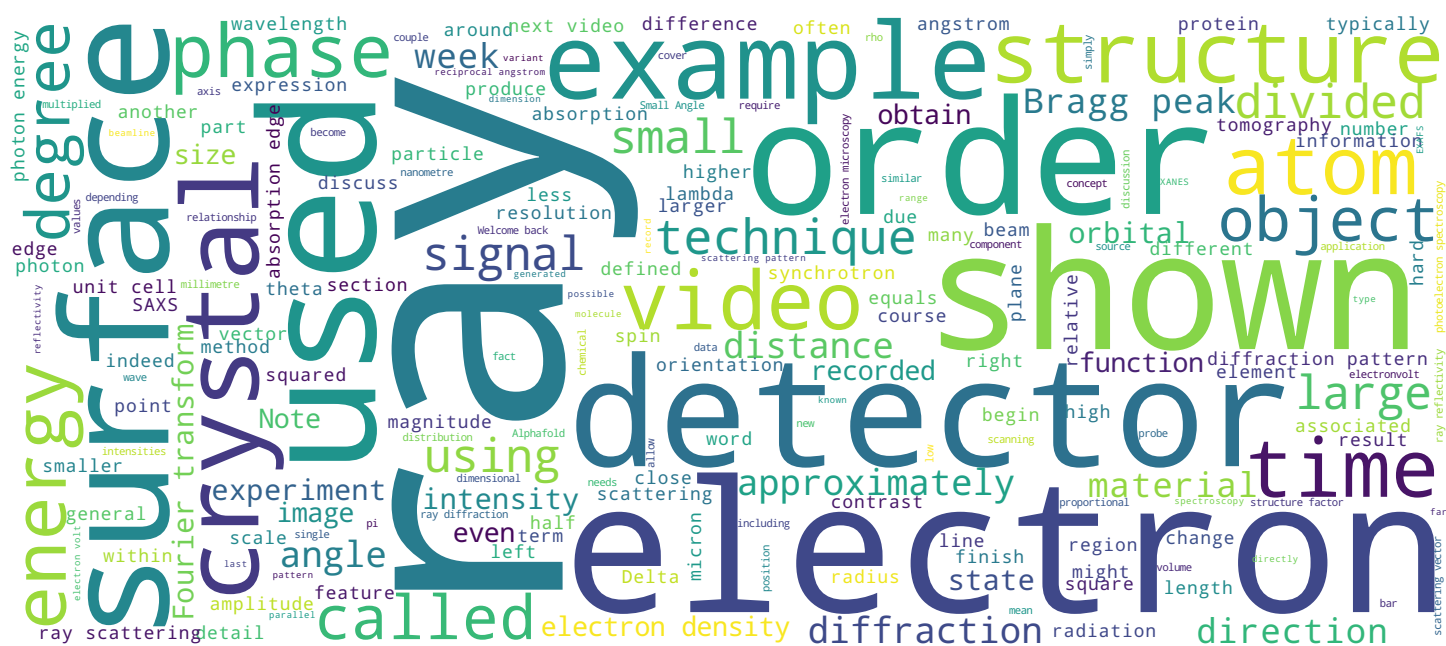


Synchrotrons and x-ray free-electron lasers

Techniques and applications

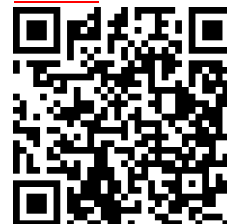
Prof. Philip Willmott



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Video



Contents and objectives of this video



- SAXS
 - Goals of SAXS
 - Fraunhofer condition
 - Typical experimental distances

Hello again. We're in the home straight now regarding week two. In this fourth and final section containing four videos, we will discuss Small-Angle X-ray Scattering and the related technique of X-ray reflectivity. In this first video, we consider the goals of SAXS and the geometrical condition that needs to be satisfied, namely the Fraunhofer condition. We will finish this short video with a brief comment on typical experimental distances.

Notes

Summary



0m 05s

SAXS – Introduction



- Information obtained by SAXS
 - Characteristic size
 - Shapes (sphere, disc, rod, etc)
 - Surface-area/volume ratio
 - Special cases: ratio of two sizes (e.g., height/radius)

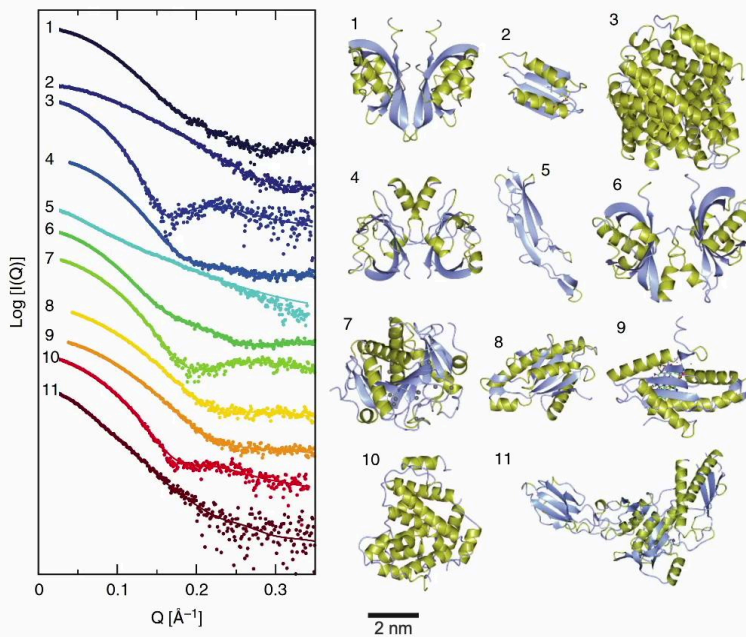
X-ray scattering from larger objects up to about a micron in size can also provide important structural and dimensional information. Typical information extracted from SAXS include characteristic shapes and sizes, surface-area-to-volume ratios, and in special cases, the relationship between two well-defined sizes, such as between the radius and thickness of a circular platelet.

Notes

Summary



SAXS – Introduction



See T.D. Grant *et al.*, *Biopolymers* DOI:10.1038/s41598-018-26182-1

- Technique to investigate the structure of mesoscopic objects
 - Crystallinity not required
- From Bragg's law for low θ ($\sin \theta \approx \theta$)
- Object, characteristic size d

$$\lambda = 2d\theta \Rightarrow \theta = \lambda/2d \ll 1$$
 - $Q = 2\pi/d$
 - $d \sim 10 - 1000 \text{ nm}$
- Applications
 - Colloidal science
 - Polymer science
 - Cell biology
 - Surface film structures
 - Systems without long-range structure – complementary to XRD

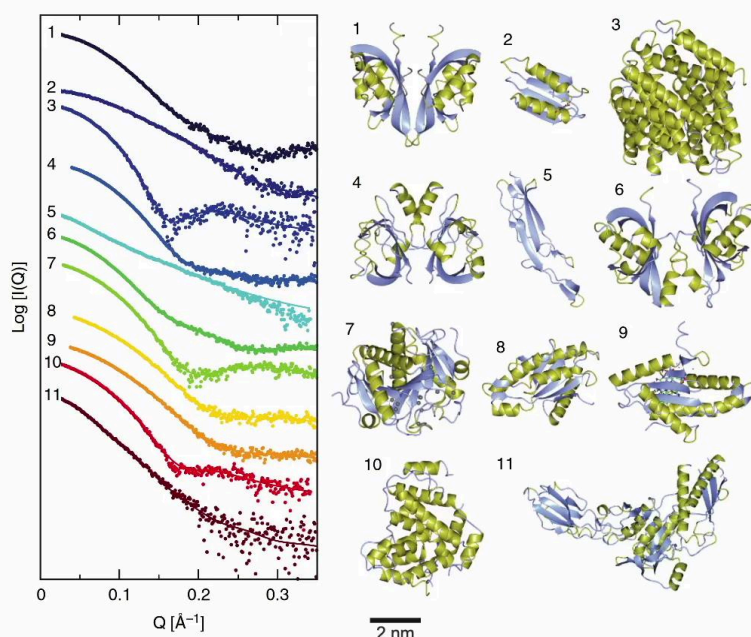
Importantly, the samples investigated using SAXS need not be crystalline, and actually, the large majority of experiments are indeed on non-crystalline samples. Scattering occurs just as it does in X-ray reflectivity through electron density variations $\Delta \rho$ and not from individual atoms, the case in diffraction. Consider an object with a characteristic length d . The ratio of this length to that of the X-ray wavelength being used can, depending on the system, be anything from about 20 to several thousands. Scattering is thus typically over on angles λ upon $2d$, which can thus be anything from a couple of a thousandths of a degree to a couple of degrees, while Q -vectors have magnitudes from about 0.05, to 0.0005 reciprocal angstroms. SAXS information can be extremely valuable in disciplines such as colloidal science, liquid crystal technology, biochemistry and cell biology, to name but a few. In particular, it allows one to study systems which lack long-range order, and is therefore complementary to X-ray diffraction. Indeed, because proteins and crystals are forced into a regular repeat configuration, SAXS provides important information on the overall envelope of the structure in close to native conditions.

Notes

Summary



SAXS – Introduction



See T.D. Grant *et al.*, Biopolymers DOI:10.1038/s41598-018-26182-1

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The scattering patterns in SAXS can, at first glance at least, appear to be comparatively nondescript and diffuse. Look at the images on the left. Nonetheless, gradients, oscillations, and intensities can all combine to deliver very valuable information. As hard X-rays can penetrate water to significant depths, SAXS is particularly interesting for in vivo and biological samples in ambient liquid environments or in embedded systems which are excluded to most other nanoscale imaging techniques, such as transmission electron microscopy and scanning electron microscopy.

Notes

Summary



SAXS – Introduction

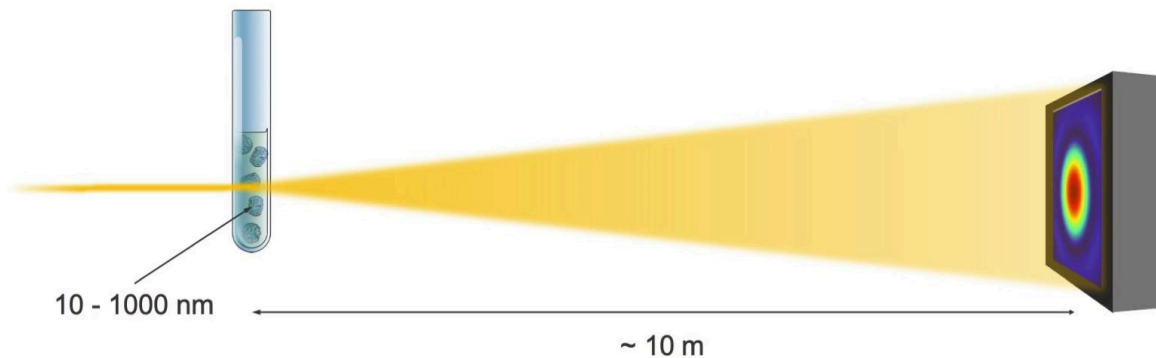
- Measures $\Delta\rho$, difference in electron density between object and its surroundings

- If $\Delta\rho = 0$, object appears to be transparent

- e.g., protein $\rho = 0.44 \text{ e}/\text{\AA}^3$, pure water $\rho = 0.33 \text{ e}/\text{\AA}^3$

- Intensity proportional to

- $(\Delta\rho)^2$
- N_p , number of scatterers



As I've just stated, unlike X-ray diffraction, SAXS is purely a contrast technique, whereby the scattering signal is generated by differences in the average electron density on scales which are significantly larger than that of atomic radii. There are similarities between XRD and SAXS however. Just as a scattering intensity in diffraction scales with the square of Z , the atomic number, SAXS signal increases with the square of $\Delta\rho$, the difference in electron density. In general, one assumes that the individual scatterers in an ensemble investigated with SAXS, are well enough separated, in other words, they have neighbour distances which are larger than the X-ray coherence lengths, and can be regarded as separate scattering entities in which case, the scattering intensity in total, increases linearly with N_p , the number of illuminated scatterers.

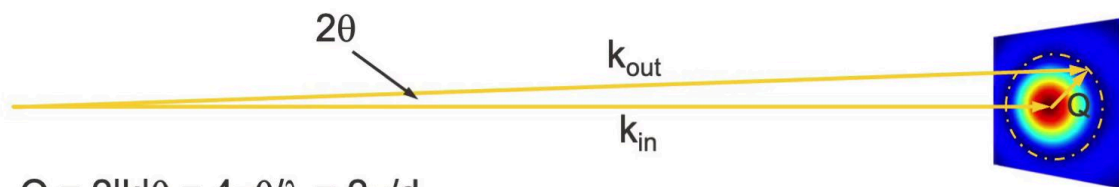
Notes

Summary



3m 20s

SAXS scattering vector magnitudes



$$Q = 2|k|\theta = 4\pi\theta/\lambda = 2\pi/d$$

$$I(Q) = \langle \mathbf{I}(\mathbf{Q}) \rangle_{\Omega} = \langle \mathbf{A}(\mathbf{Q}) \mathbf{A}^*(\mathbf{Q}) \rangle_{\Omega}$$

$$A(\mathbf{Q}) = \mathcal{FT} [\rho(\mathbf{r})] = \int \Delta\rho(\mathbf{r}) \exp(i\mathbf{Q}\mathbf{r}) d\mathbf{r}$$

Because scattering angles are small, we can approximate sine theta as being equal to theta if expressed in radians. Hence the scattering vector is simply $2k\theta$ which is equal to $4\pi\theta/\lambda$, which is equal to $2\pi/d$. The intensity at a radius Q from the direct beam is the absolute square of the amplitude, and, as is ever the case, equal to the Fourier transform of the electron density variation of the illuminated particle. As d might be as small as 10 nanometers, or as large as a micron, the Q -range of SAXS can lie somewhere roughly between 0.005 and 0.05 reciprocal angstroms, as we've already said actually.

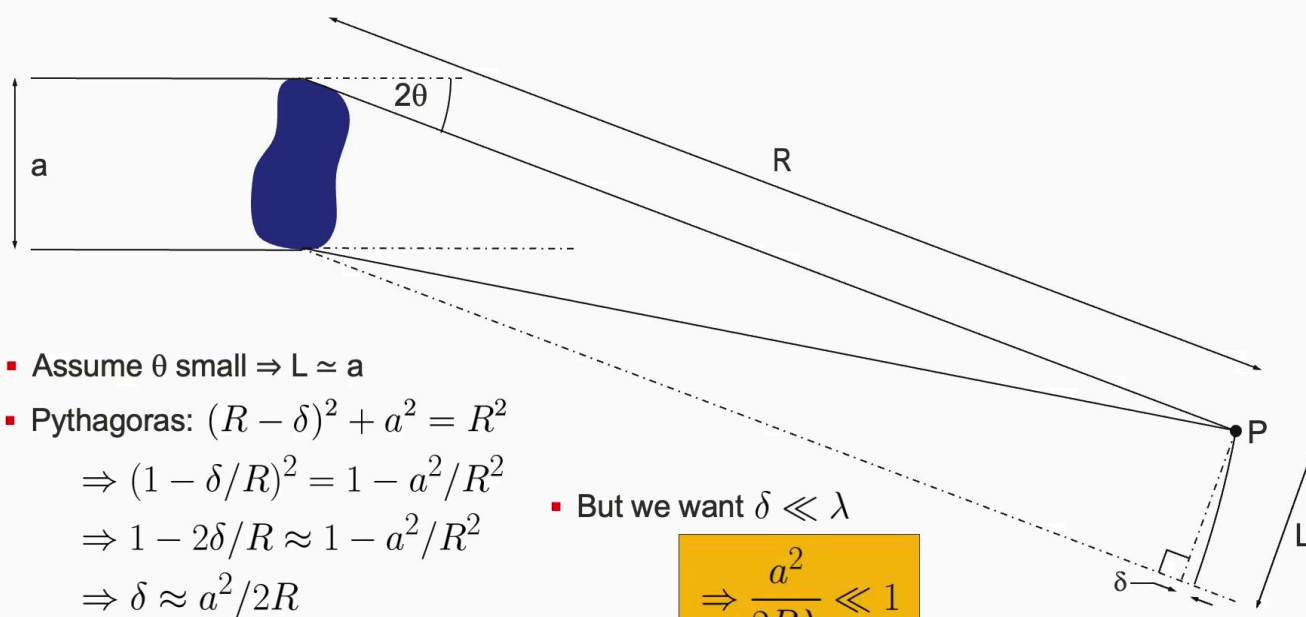
Notes

Summary



4m 25s

The Fraunhofer condition



▪ Assume θ small $\Rightarrow L \approx a$

▪ Pythagoras: $(R - \delta)^2 + a^2 = R^2$

$$\Rightarrow (1 - \delta/R)^2 = 1 - a^2/R^2$$

$$\Rightarrow 1 - 2\delta/R \approx 1 - a^2/R^2$$

$$\Rightarrow \delta \approx a^2/2R$$

▪ But we want $\delta \ll \lambda$

$$\Rightarrow \frac{a^2}{2R\lambda} \ll 1$$

How far must the detector be away from the object in order that the true square of the Fourier transform is recorded? In the so-called Fraunhofer, or far-field regime, the difference Δ in the optical path difference between two rays emanating from opposite sides of the object, converging on the detector at a point P , at a distance R , and angle 2θ from the illuminated object, and that between two parallel waves propagating in the same direction, should be much less than the wavelength of light being used. First, we have assumed that θ is small, which is a reasonable approximation, seeing as we're dealing with Small Angle X-ray scattering. In this case, the distance L is approximately equal to a . We then use Pythagoras to obtain the relationship that $R - \Delta^2 + a^2$ is equal to R^2 . From which we obtain $1 - \Delta/R^2$ is equal to $1 - a^2/R^2$. But we know that Δ/R is small, so we can make the approximation on the left hand side as being equal to $1 - 2\Delta/R$. From which we directly see that Δ is approximately equal to $a^2/2R$. But remember that we want Δ to be much smaller than λ , from which we finally get the inequality that $a^2/2R\lambda$ should be much smaller than unity.

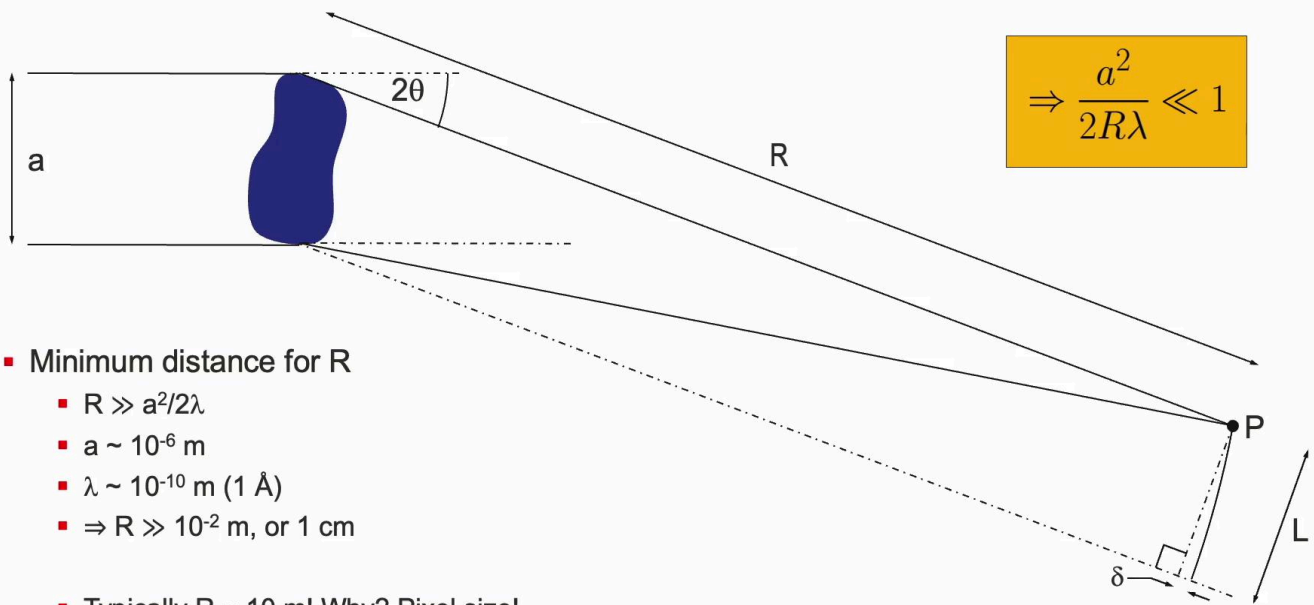
Notes

Summary



5m 11s

The Fraunhofer condition



- Minimum distance for R
 - $R \gg a^2/2\lambda$
 - $a \sim 10^{-6} \text{ m}$
 - $\lambda \sim 10^{-10} \text{ m}$ (1 Å)
 - $\Rightarrow R \gg 10^{-2} \text{ m}$, or 1 cm
- Typically $R \sim 10 \text{ m}$! Why? Pixel size!

If we plug in typical values for a and λ , we see that in fact R need only be greater than a couple of centimetres, even for particles as large as a micron. Typically, however, R is of the order of 10 metres. Why is that so? Well the prosaic reason for this is that the spatial profile needs to be accurately recorded, and the pixel sizes are perhaps a 20th of a millimetre, thus requiring these larger separations to really resolve the signal in detail.

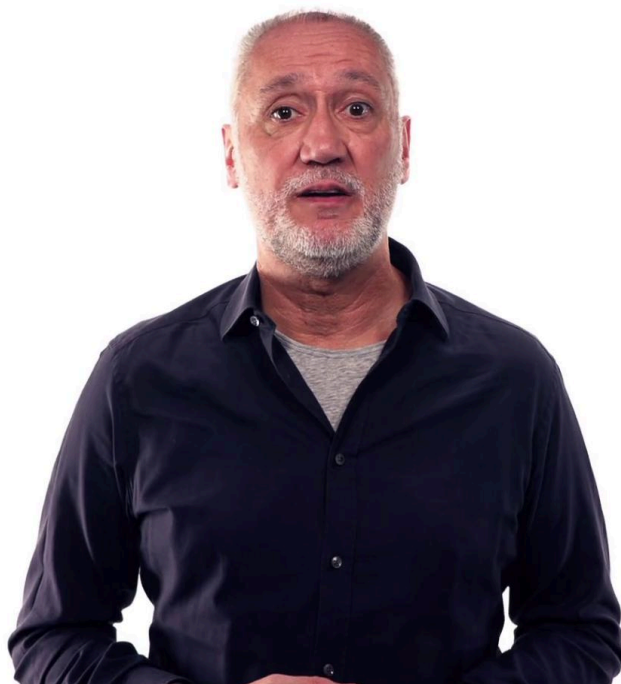
Notes

Summary



6m 59s

In the next video...



In the next video, we will discuss in detail what information can be extracted by SAXS, and how we set about doing this.

Notes

Summary



7m 32s