Scattering . 4 Structure factors

4.1 The structure factor and Osmotic pressure

The theorems above related *g(r)* to the potential existing between particles but it is also very useful to relate this to macroscopic properties such as osmotic pressure. As *Q* tends to 0:

$$\left(\frac{\partial \Pi}{\partial N_p}\right) = \frac{kT}{S(Q \to 0)} \quad [4.1]$$

We can determine *S(0)* by extrapolating our scattering curves to zero *Q.* Π is the excess osmotic pressure in the system and is just due to the presence of the particles. For an ideal solution we can use the Vant Hoff equation for osmotic pressure in a non-interacting system:

$$: \Pi = cRT \quad [4.2]$$

where *c* is the molar concentration. For a system with strong interactions the excess osmotic pressure is reduced and in the limit of a very strong interaction is zero. Hence the behaviour of *S(Q) as Q* tends to zero is very sensitive to inter-particle interactions and the observation of the first maximum in *S(Q)* is often considered to be a reflection of strong interactions in the system.

4.2 X-ray and Neutrons

Both X-rays and neutrons can be used to determine structure of polymers, surfactants and micelles. The attainable *Q* range as we discussed earlier is rather similar but there are some other significant differences.

The basic scattering equation takes on a simpler form for both X-rays and Neutrons

$$I(Q) = (\rho_p - \rho_s)^2 \phi_p V_p P(Q) \qquad [4.3]$$

where ρ_p is the scattering length density of a particle (*p)* and solvent (*s*). ϕ_p is the volume fraction of particles and V_p is the volume of the particle, We can rewrite ϕ_p as N_pV_p where N_p is the number density of particles if you want to. One of the major differences between X-rays, neutrons and light is the value of the scattering length density (SLD).

We define $\rho = \frac{\rho_m N_A}{M}\sum_i n_i b_i$ [4.4]

where ρ_m is the mass density *M* is the molecular weight b_i is the scattering length of atom *i* and n_i is the number of atoms of type *i* and N_A is Avogadro's Number. . The scattering length density is calculated over the molecular volume, but for a polymer we take the volume of one monomer. ρ has units of Å^{-2}. In the table below we show values of the contrast factor between solute(polymer) and solvent $(\rho_p - \rho_s)$ for two different solvents for polystyrene

Table 1 Comparing Scattering length densities

Substance	Light / 10^{-6} Å^{-2}	X-ray / 10^{-6} Å^{-2}	Neutron /10^{-6} Å^{-2}
Polystyrene in Toluene(D)	O.0582	1.86	4.2
Polystyrene in Toluene(H)	0.0582	1.86	0.48

Notes:
[1] Light contrast is much smaller almost a factor 100x [light sources are much more intense!] values depend on the refractive indexes
[2] Neutron contrast depends on the nuclear structure and is isotope dependent
[3] X-ray contrast depends on the electronic structure and is not isotope dependent

Other important differences besides the Q range depend on the way the radiation is absorbed by the medium of interest. The absorption can be calculated using the Beer Lambert Law as in Lecture 1

$I_T = I_o \exp(-\mu\ell)$ [4.5]

where μ is an absorption coefficient.

X-rays:

X-rays are scattered by electrons and the coherent contrast factor depends on the number of electrons and the physical density. Typical values for the SLD for some common materials is given in Table 1.

For absorption of X-rays μ depends on both the atomic composition of a material and wavelength and if the wavelength is near an absorption edge. Typically samples for SAXS must be ~ 1mm in thickness.

X-rays can be produced in the laboratory quiet easily, but of high intensity is required the you need to visit a synchrotron.

For X-rays the scattering length density is given by a slight variation of [4.4] as the scattering is only due to electrons and they are all identical. The scattering length of an electron is given by $b_e = \frac{\mu_0}{4\pi}\frac{e^2}{m} = 2.85 \times 10^{-5}$ Å [4.6] Hence

$$\rho_X = \frac{b_e \rho_m N_A}{M}\sum_i n_i z_i \quad [4.8]$$

Table 2 Comparing neutrons and X-rays SLD

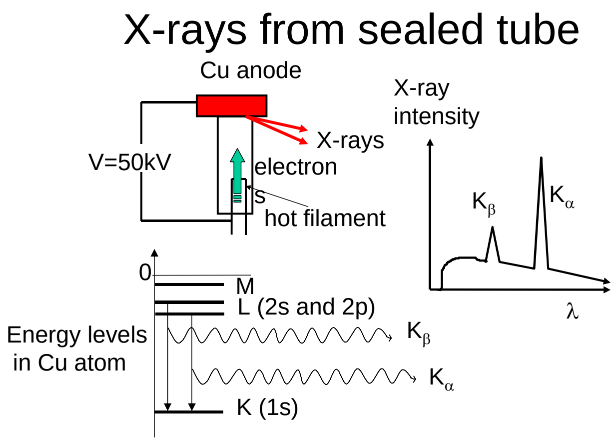
Material	ρ_N / 10^{-6} Å^{-2}	ρ_X / 10^{-6} Å^{-2}
H_2O	-0.5	9.4
D_2O	6.4	9.4
(CH_2)-	-0.6	6.5
$-(CD_2)_n$-	6.1	6.5

Absorption of X-rays is important and samples must be thin especially if high atomic number element are present .

Table 3 the absorption cross-sections ($=4\pi b_{ABS}{}^2$) for X-rays and neutrons.

Species	$\sigma_N(abs)/10^{-8}$ Å^2	$\sigma_X(abs)/10^{-8}$ Å^2
H	0.28	0.73
D	0.0	0.73
C	0.003	92
O	0.0	306
Cd^{2+}	>103	9400

X-ray sources



Neutrons

Neutrons are scattered elastically or inelastically and coherently and incoherently. In SANS we are only concerned with the elastic component. Structural information is given by the coherent-elastic and some chemical non-structural information from the incoherent elastic scattering.

The wavelength, λ, of a neutron can be determined using the de Bröglie relation:

$\lambda = \frac{h}{p}$ [4.5] where h (= 6.626×10^{-34} J.s) is the Planck constant and p is the linear momentum (neutron mass = 1.674×10^{-27} kg).

The energy of a neutron is given by $E = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$ [4.6]

Hence a cold neutron with a wavelength of 4 Å (typical) has a velocity of ~100m s^{-1}.
Neutron Fluxes are typically 10^8 to 10^9 neutrons.cm^{-2}.s^{-1} .
The SLD of neutrons can be calculated as above with values of the coherent nuclear scattering lengths, b_{COH}. Some value are given in Table 2. Table 3 gives some typical values of the SLD.

Table 4 scattering lengths for neutrons

Nucleus	**$b_{CO\,H}/\ 10^{-5}$ Å**	**$b_{INC}\ /\ 10^{-5}$ Å**	**$b_{ABS}/\ 10^{-5}$ Å**

^{1}H	-3.741	25.3	1.5
^{2}D	6.671	4.1	0
^{11}B	5.304	5.3	78.1
^{12}C	6.646	6.7	0.0
^{16}O	5.803	5.8	0.0
Cd	5.130	4.5	141.6

Neutrons also scatter incoherently and this gives rise to a background. Hydrogen is the most notorious and it is best to minimise the amount of H in a given sample. i.e. measure an H polymer in a D solvent rather thane vice-versa. See Table 2

The absorption length of neutrons is also important and depends on the isotopic make up of the sample. Table 2 gives some values. of this and these can be used together with the other cross-sections to calculate the intensity of the scattered neutrons.

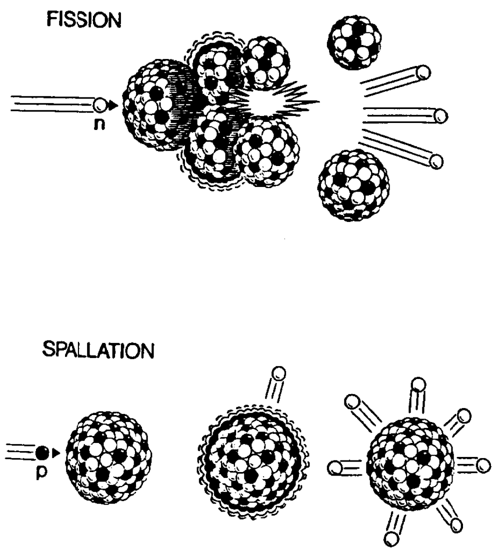
Example of a Transmission calculation for a 2 mm thickness sample.

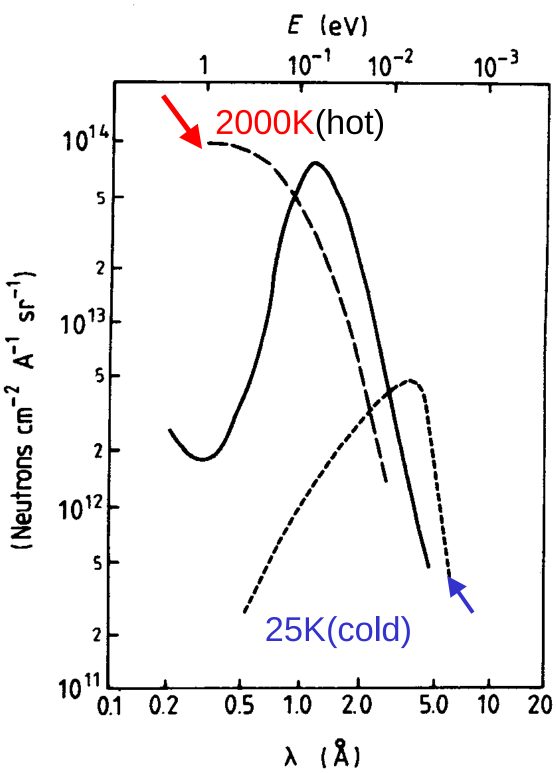
AT 12Å μ for H_2O is 9.519 cm^{-1} and for D_2O 0.691 cm^{-1}

Hence the transmissions are 0.0.149 and 0.87: so use D_2O!!

Neutron sources

Neutrons aren't readily available! You need to go to a reactor or a spallation source The neutrons coming out are far too hot and we need wavelength ~ 4-12Å so they need to be moderated.





.Some selected Characteristics pf radiation using in small-angle scattering

Parameter	Small-angle scattering		
	Neutrons	X-rays	Light
Radiation is scattered by	nuclei	electrons	electrons
Availability of radiation	large facility only	laboratory or large facility	laboratory
Relative brilliance of source	low	medium to high	medium to high
Typical counting time per sample	minutes to hours	seconds to minutes	minutes to hours
Typical wavelengths (nm)	0.15–2.5	0.15	400–700
Typical length scales probed (nm)	0.5–1000	0.1–2500	250[a]–25000
Typical sample volumes (cm^3)	0.05–3.5	0.0001–0.5	0.05–5
Study optically opaque samples	yes	yes	no
Use metallic sample containers	yes	no	no
Effect of isotopic substitution	generally large	generally small	none
Absolute intensity measurements	routine	possible	possible
Radiation/heat damage to sample	very unlikely	very likely	negligible

[a]Smaller length scales are accessible with dynamic light scattering.