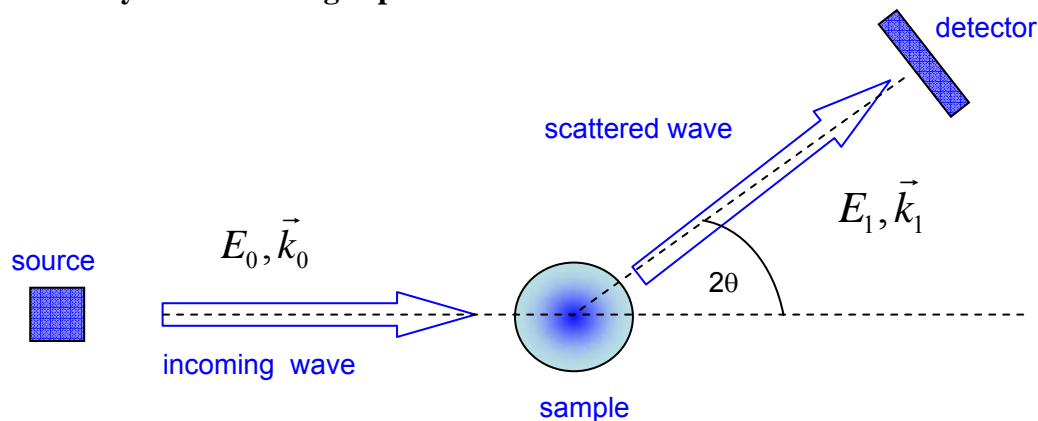


Chapter 5: SCATTERING METHODS

5.1 Static scattering

Scattering experiments with neutrons-, x-rays and visible light

Geometry of a scattering experiment



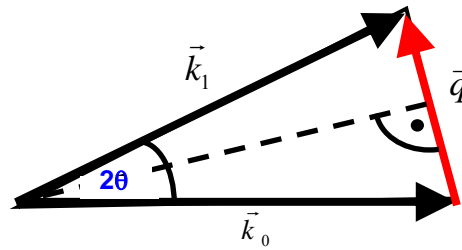
- (1) Incoming planar: electro-magnetic (visible, x-rays...) or particle (electrons, neutrons, ...).
- (2) After interaction with the sample the intensity of the scattered wave is detected as a function of the scattering angle.
- (3) Outgoing wave is spherical; each scattering center of the sample acts as origin of a spherical wave (Huygens principle).

Energy $E_i = \hbar\omega_i = h\nu_i$ with $\omega_i =$ angular frequency
 $i = 0,1$ $\nu_i =$ frequency
 $\hbar = h/2\pi =$ Dirac's constant
 $h =$ Planck's constant

Wave vector $\vec{k}_i = \vec{p}_i/\hbar$ with $p_i =$ momentum
 with norm $|\vec{k}_i| = 2\pi/\lambda_i$ $\lambda_i =$ wavelength

Conservation laws $\Delta E = \hbar\Delta\omega = \hbar(\omega_0 - \omega_1)$ for the energy
 $\Delta\vec{p} = \hbar\Delta\vec{q} = \hbar(\vec{k}_0 - \vec{k}_1)$ for the momentum

\vec{q} is the **scattering vector**



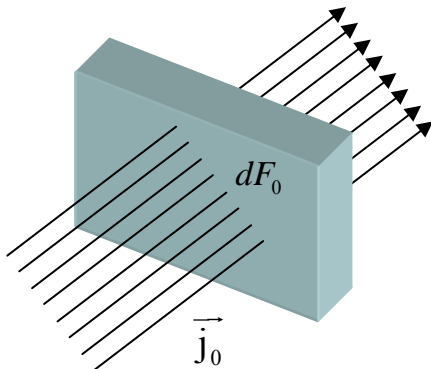
Here only elastic scattering is considered, i.e. incident and scattered wave have the same energy

$$\Rightarrow \Delta E = 0 \quad \text{and} \quad |\vec{k}_1| = |\vec{k}_0|$$

$$\Rightarrow |\vec{q}|^2 = |\vec{k}_1|^2 + |\vec{k}_0|^2 - 2|\vec{k}_1||\vec{k}_0|\cos(2\theta) = 2|\vec{k}_0|^2 [1 - \cos(2\theta)] = 4|\vec{k}_0|^2 \sin^2 \theta$$

$$\Rightarrow |\vec{q}| = 2|\vec{k}_0|\sin \theta = \frac{4\pi}{\lambda_0} \sin \theta$$

First some definitions



(1) Current density of the incoming beam $|\vec{j}_0|$

Planar wave

$$|\vec{j}_0| = \frac{\text{\#scattered particles}}{(\text{times interval}) \times (\text{unit area})} = \frac{dN_0}{dt dF_0}$$

(2) Current density of the scattered beam $|\vec{j}_1|$

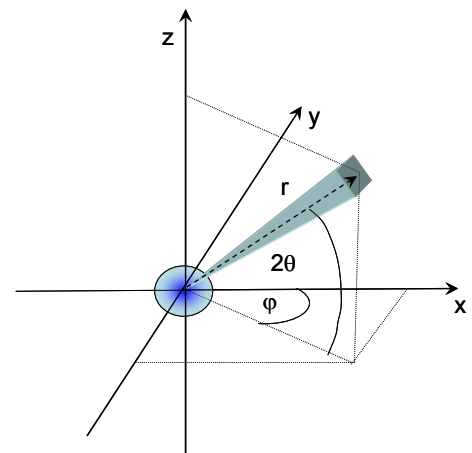
Spherical wave

in polar coordinates $\theta = \text{polar angle}$
 $\varphi = \text{azimuth angle}$

solid angle element $d\Omega = \sin \theta d\theta d\varphi$

area element $dF_1 = r^2 d\Omega$

$$\Rightarrow |\vec{j}_1| = \frac{dN_1}{dt dF_1} = r^{-2} \frac{dN_1}{d\Omega dt}$$



(3) Differential scattering cross section $\frac{d\sigma}{d\Omega}$

is the # of particles scattered per time interval into a solid angle interval normalized to the current density of the incoming beam.

$$\frac{d\sigma}{d\Omega} = \frac{1}{|\vec{j}_0|} \frac{dN_1}{d\Omega dt}$$

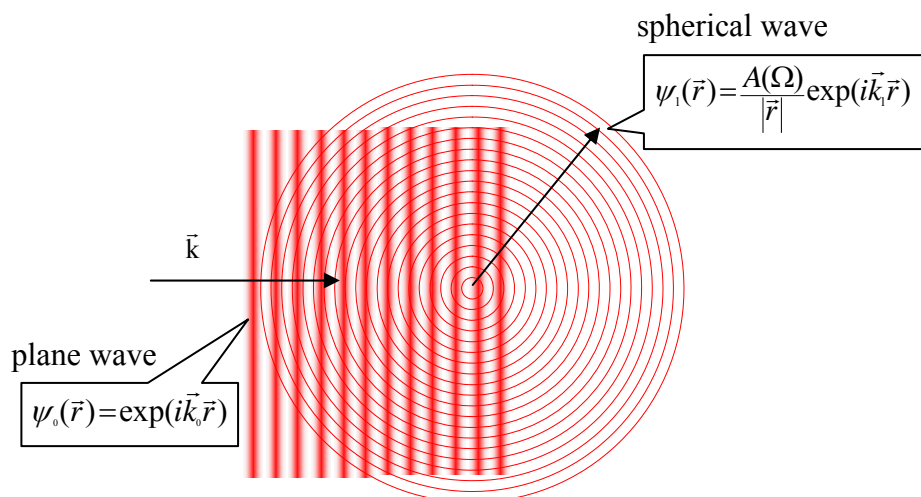
is a function of θ and φ but not of r !

with $\frac{dN_1}{d\Omega dt} = |\vec{j}_1| r^2 \Rightarrow \frac{d\sigma}{d\Omega} = r^2 \frac{|\vec{j}_1|}{|\vec{j}_0|}$ unit: $\left[\frac{d\sigma}{d\Omega} \right] = [\text{length}^2]$

(4) Total scattering cross section $\sigma = \int \frac{d\sigma}{d\Omega} d\Omega$

gives the # of all particles (that means in all direction of space) scattered per time interval normalized to the current density of the incoming beam.

In **quantum mechanics** the particle current is replaced by the probability current Ψ^2



The incoming planar wave $\psi_0(\vec{r}) = \exp(i\vec{k}_0 \vec{r})$ is scattered at an interaction potential $V(\vec{r})$.

At sufficient large distance the outgoing wave appears as spherical wave

$$\psi_1(\vec{r}) = \frac{A(\Omega)}{|\vec{r}|} \exp(i\vec{k}_1 \vec{r})$$

$$\Rightarrow \frac{d\sigma(\Omega)}{d\Omega} = r^2 \frac{|\vec{j}_1|}{|\vec{j}_0|} = \frac{\Psi_1^2}{\Psi_0^2} r^2 = |A(\Omega)|^2$$

where $A(\Omega)$ = scattering amplitude depends on the scattering angle

Experiment yields only information about intensities but not about amplitudes!

Scattering problem can be described by **Schroedinger equation**

(here probe particles with mass only)

$$\left[-\frac{\hbar^2}{2m} \Delta + \left(V(\vec{r}) - \frac{\hbar^2 \vec{k}_0^2}{2m} \right) \right] \Psi = 0 \quad \text{with} \quad \Delta = \sum_{k=1}^3 \frac{\partial^2}{\partial x_k^2} = \text{Laplace operator}$$

or equivalently $(\Delta + \vec{k}_0^2) \Psi = U(\vec{r}) \Psi$ with $U(\vec{r}) = \frac{2m}{\hbar^2} V(\vec{r})$

Solution of the differential equation:

- general solution of the homogenous system: $U(\vec{r}) = 0 \Rightarrow \Psi_h = \Psi_0$
- special solution of the inhomogenous system:

introduce: $G(\vec{r} - \vec{r}') = \frac{\exp(i\vec{k}_1(\vec{r} - \vec{r}'))}{|\vec{r} - \vec{r}'|}$

which is the solution of $(\Delta + \vec{k}_0^2)G(\vec{r} - \vec{r}') = -4\pi\delta(\vec{r} - \vec{r}')$

$$\int d\vec{r}' \underbrace{G(\vec{r} - \vec{r}') (\Delta + \vec{k}_0^2)}_{=-4\pi\delta(\vec{r} - \vec{r}')} \Psi(\vec{r}') = \int d\vec{r}' G(\vec{r} - \vec{r}') U(\vec{r}') \Psi(\vec{r}') = -\Psi_{\text{inh}}(\vec{r}) \cdot 4\pi$$

- general solution::

$$\begin{aligned} \Psi(\vec{r}) &= \Psi_h + \Psi_{\text{inh}} = \Psi_0 - \frac{1}{4\pi} \int d\vec{r}' G(\vec{r} - \vec{r}') U(\vec{r}') \Psi(\vec{r}') \\ \Rightarrow &= \underbrace{\Psi_0}_{\text{through-going beam}} - \underbrace{\frac{1}{4\pi} \int d\vec{r}' G U \Psi_0}_{\text{single scattered beam}} + \underbrace{\left(\frac{1}{4\pi} \right)^2 \int d\vec{r}' G U G U \Psi_0}_{\text{twice scattered beam}} \mp \dots \end{aligned}$$

Born approximation (single scattering)

$$\Psi(\vec{r}) = \Psi_0 - \frac{1}{4\pi} \int \underbrace{\frac{\exp(i\vec{k}_1(\vec{r} - \vec{r}'))}{|\vec{r} - \vec{r}'|}}_G \underbrace{\frac{2m}{\hbar^2} V(\vec{r}')}_{U} \underbrace{\frac{\psi_0(\vec{r}')}{\exp(i\vec{k}_0 \vec{r}')}}_{\text{incoming wave}} d\vec{r}'$$

$= \Psi_1(\vec{r})$ (scattered wave)

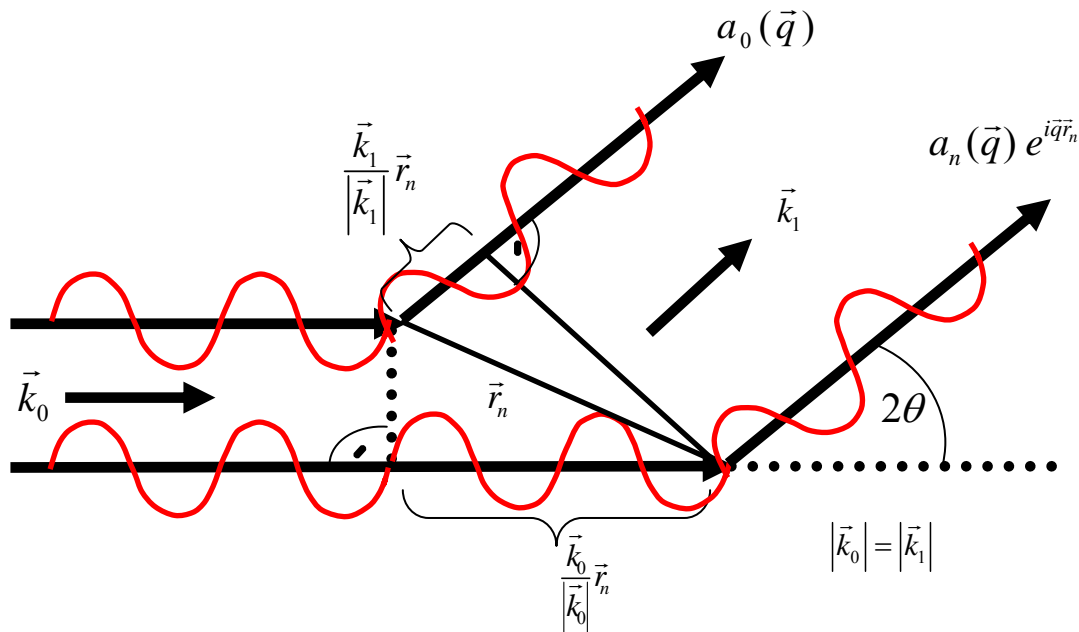
$$\Psi_1(\vec{r}) = \frac{1}{r} A(\Omega) \exp(i\vec{k}_1 \vec{r}) \Rightarrow A(\Omega) = r \Psi_1(\vec{r}) / \exp(i\vec{k}_1 \vec{r})$$

if $|\vec{r}'|$ (sample dimension) $\ll |\vec{r}|$ (distance from sample) $\Rightarrow |\vec{r} - \vec{r}'| \approx |\vec{r}|$

$$\Rightarrow |A(\Omega)|^2 = \left(\frac{m}{2\pi\hbar^2} \right)^2 \left| \int \exp(-i\vec{k}_1 \vec{r}') V(\vec{r}') \exp(i\vec{k}_0 \vec{r}') d\vec{r}' \right|^2 = \frac{d\sigma}{d\Omega}$$

The scattering amplitude is proportional to the matrix element for the transition from state $|k_0\rangle$ to $|k_1\rangle$ in the interaction potential $V(\vec{r})$. This conclusion is independent of the radiation but $V(\vec{r})$ and the proportionality constant are radiation dependent. Notice: here probe particles with mass only.

Classical picture



Contributions originating from different scattering centers have to be summed with correct phases

since $|\vec{k}_1| = |\vec{k}_0| \Rightarrow$ phase difference of the scattered waves $|\vec{k}_0| \cdot \Delta s = (\vec{k}_0 - \vec{k}_1) \cdot \vec{r}_n = \vec{q} \cdot \vec{r}_n$

where $\Delta s = \frac{\vec{k}_0}{|\vec{k}_0|} \cdot \vec{r}_n - \frac{\vec{k}_1}{|\vec{k}_1|} \cdot \vec{r}_n =$ differences in path length

\Rightarrow scattering amplitude of n scatters $A = \sum_n a_n(\vec{q}) \exp(i\vec{q} \cdot \vec{r}_n)$

where $a_n(\vec{q})$ is scattering amplitude of an individual scatterer and

$I = \langle AA^* \rangle$ is the scattering intensity

Distinguish two aspects of the scattering process

- (1) Characteristic interaction with the material – the scattering process itself. Plane waves strikes the object and any point of the object where a scattering process takes place is an origin of new wave (Huygens principle) $\rightarrow a_n(\vec{q})$
- (2) Interference of the resulting wave gives a characteristic pattern which contains structural information and allows reconstruction of the object.

Destructive interference yielding information about the structure are obtained for $\vec{q} \cdot \vec{r}_n \geq \pi$

$$q = \frac{4\pi}{\lambda} \sin \theta \Rightarrow \text{with } \theta_{\max} = 90^\circ \text{ (backscattering)} \Rightarrow q_{\max} = \frac{4\pi}{\lambda} \sin 90^\circ = \frac{4\pi}{\lambda}$$

\Rightarrow resolved length scales are $r \geq \pi/q_{\max} = \lambda/4$

Typical wave length

Neutrons, x-rays $\lambda = 0.1 - 1 \text{ nm}$ \Rightarrow resolution down to interatomic distances

assume $r \approx 50 \text{ nm}$ and $\lambda \approx 0.5 \text{ nm}$

$$q = \frac{4\pi}{\lambda} \sin \theta \geq \frac{\pi}{r} \Rightarrow \theta \geq \sin^{-1} \left(\frac{\lambda}{4r} \right) \approx 0.14^\circ \Rightarrow \text{scattering angle } 2\theta \approx 0.28^\circ$$

\Rightarrow small-angle scattering!

Light $\lambda = 500 \text{ nm}$ dimensions of polymers are typically of the order 1 to 100 nm

$$r \geq \frac{\lambda}{4} \sin \theta \Rightarrow \text{smallest length scale resolved from backscattering } \theta = 90^\circ \Rightarrow r_{\min} \geq \frac{\lambda}{4} \approx 125 \text{ nm}$$

Question: What are the atomic scattering cross sections for different types of radiation?

Neutrons

- are neutral particles which are not affected by the atomic electron shells.
- the neutron-core interaction is strong but short-ranged
- since the core radius $r_c = 10^{-12} \text{ m} \ll$ neutron wave length details of the core potential are irrelevant

single scatterer

$$\Rightarrow V_i(\mathbf{r}) = \left(\frac{2\pi\hbar^2}{m_n} \right) b_i \delta(\vec{r} - \vec{r}_i) \quad \text{with } m_n = \text{neutron mass}$$

$$\vec{r}_i = \text{core positions}$$

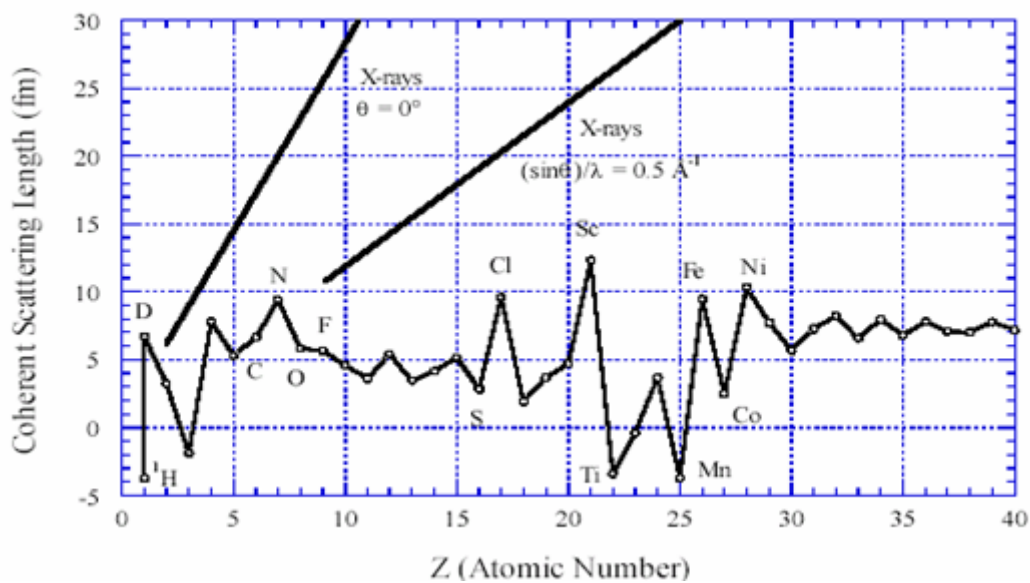
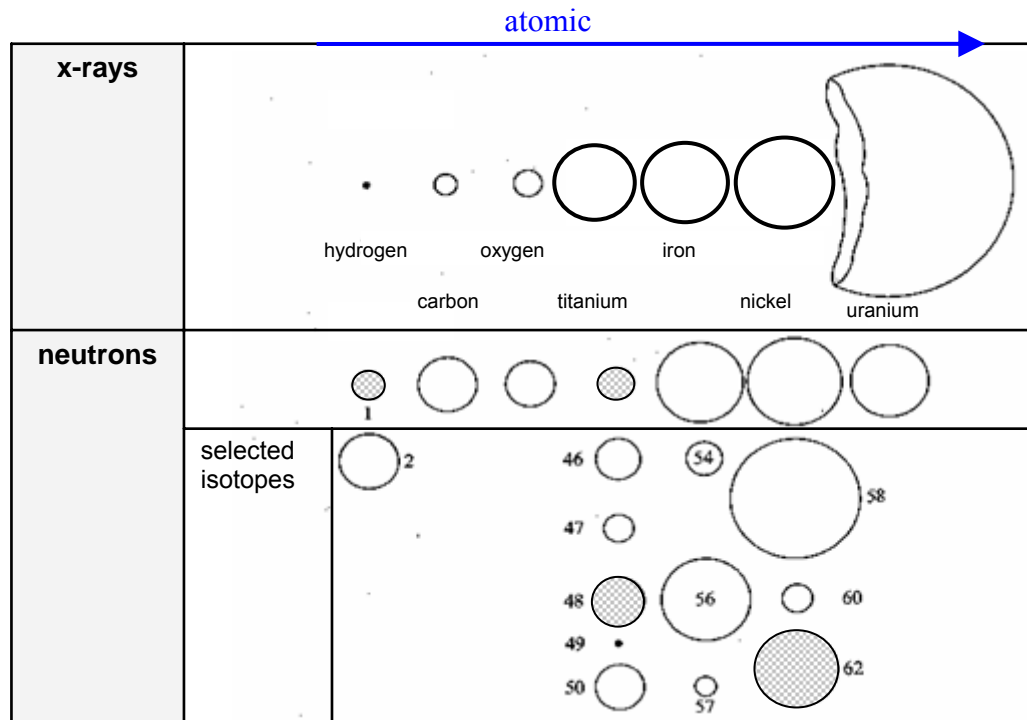
$$(a_i(\Omega))^2 = \frac{d\sigma}{d\Omega} = b_i^2 = \text{constant} \quad b_i = \text{scattering length}$$

$$V(\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} \sum_i b_i \delta(\vec{r} - \vec{r}_i)$$

b is independent of the scattering angle but

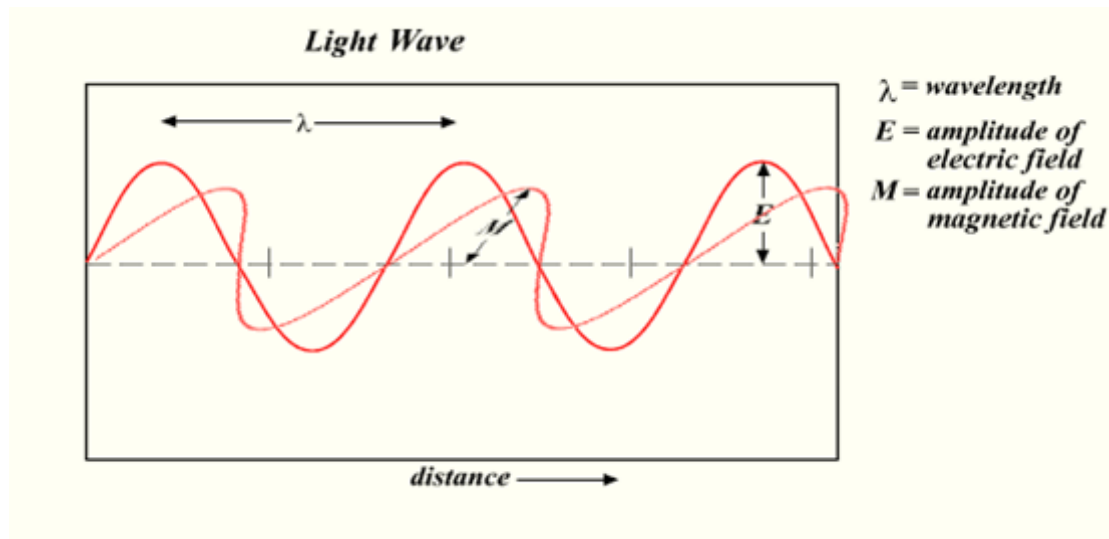
- a) varies unsystematically with the atomic weight
- b) depends on the neutron wave length
- c) depends on the spin direction of the core relative to the neutron spin direction (neutrons are spin 1/2 particles)
- d) is different for different isotopes \Rightarrow enables selective labeling by deuterium and proton exchange

Comparison between scattering lengths: x-rays versus neutrons



Electromagnetic Radiation

Electromagnetic wave = is a self propagating transverse oscillating wave of electric and magnetic field. \vec{E} and \vec{M} are perpendicular.

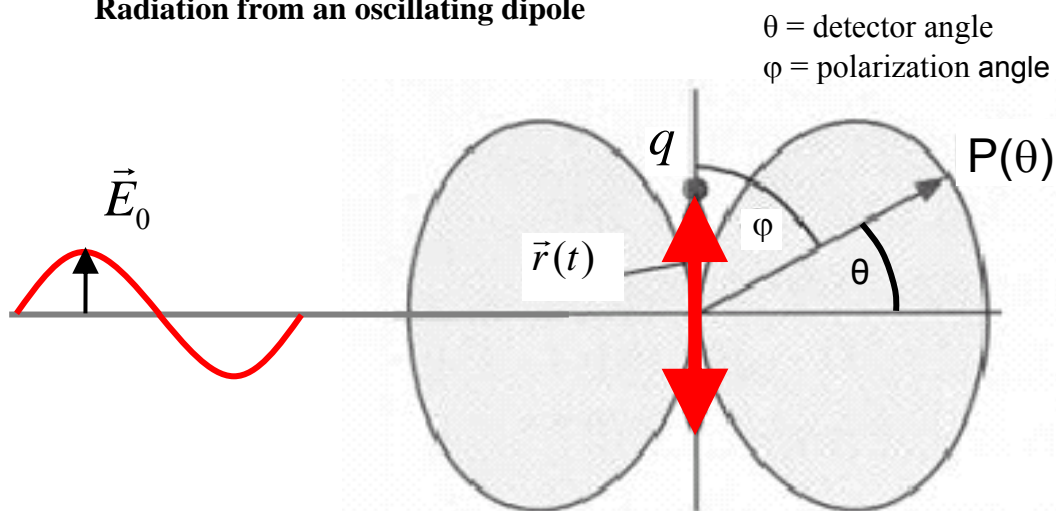


An alternating electromagnetic field deforms the electron shell \Rightarrow polarization

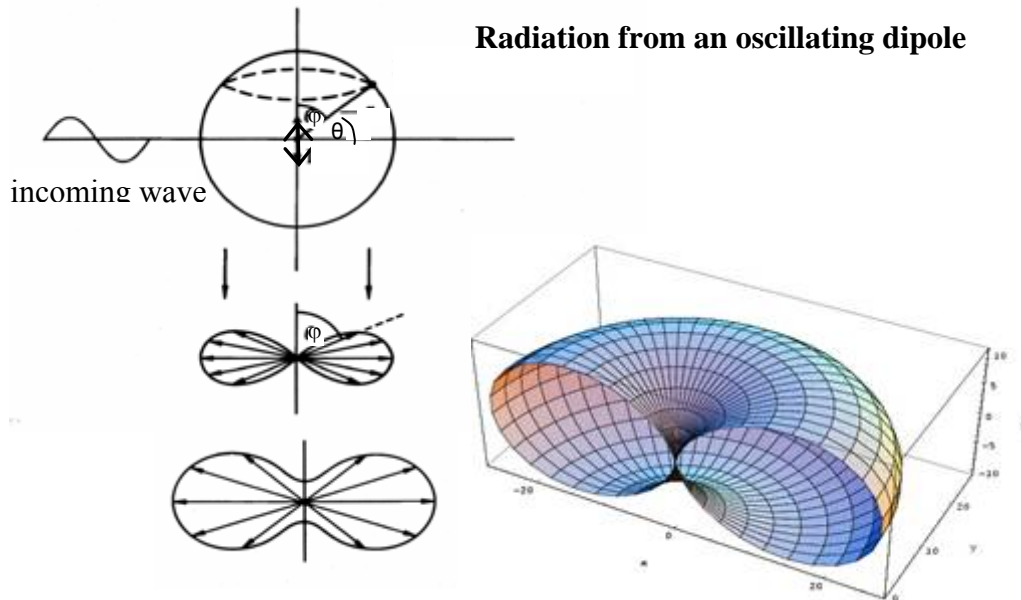
The consequence of such an excitation is an induced dipole oscillation which emits itself an electromagnetic wave

Dipole moment $\vec{p} = q \cdot \vec{r}(t) = q \cdot \vec{r}_0 \cos(\omega t + \alpha)$ with $q = \text{charge} = e^-$
 Emitted intensity $P(\varphi) = P_0 \sin^2 \varphi$

Radiation from an oscillating dipole



Radiation from an oscillating dipole



Depending on the polarization of the incident light

$$\sin^2 \varphi = \begin{cases} 1 & \text{horizontal polarized} \\ \cos^2 \theta & \text{vertical polarized} \\ \frac{(1 + \cos^2 \theta)}{2} & \text{unpolarized} \end{cases}$$

Depending on the frequency of the incident light

(1) $\omega \ll \omega_{\text{Resonance}}$ RAYLEIGH LIMIT $\vec{r}(t) = \vec{r}_0 \cos(\omega t)$

oscillator follows \vec{E} field of the incident wave in phase; strong slowing down of incident wave; refractive index $n = c/v > 1$.

\Rightarrow light scattering

(2) $\omega = \omega_{\text{Resonance}}$ $\vec{r}(t) = \vec{r}_0' \sin(\omega t) = -\vec{r}_0' \cos(\omega t + \pi/2)$

oscillator oscillates with large amplitude but out of phase with incident wave; wave loses energy to the oscillator.

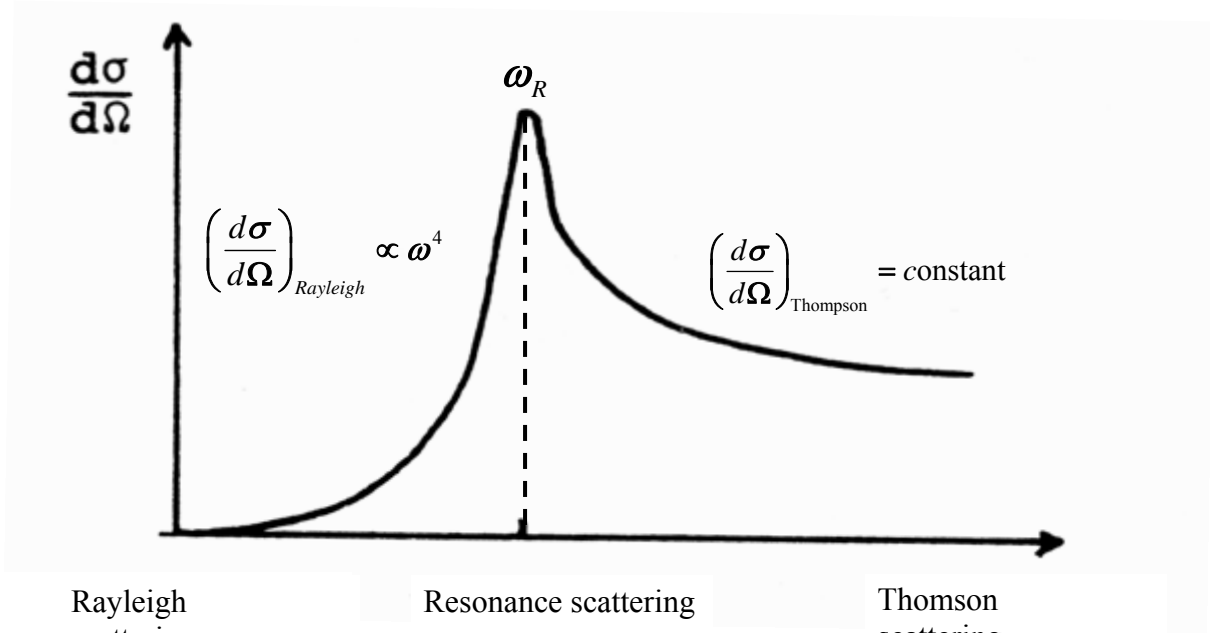
\Rightarrow absorption

(3) $\omega \gg \omega_{\text{Resonance}}$ THOMSON LIMIT $\vec{r}(t) = -\vec{r}_0'' \cos(\omega t) = \vec{r}_0'' \cos(\omega t + \pi)$

oscillator can barely follow \vec{E} field of incident wave in paraphase, no energy transfer between oscillator and wave; refractive index $n \approx 1$.

\Rightarrow x-ray scattering

Scattering of electromagnetic waves



visible light

x-rays

ω_R = resonance angular frequency of oscillator

(I) **x-rays** $\omega \gg \omega_R$

$$I_s = E_s E_s^* = E_0^2 r_e^2 \frac{\sin^2 \varphi}{r^2} \quad (\text{single dipole})$$

Scattering intensity is independent from incident wave length ω_0 !

with electron radius $r_e = \frac{1}{4\pi\epsilon_0} \frac{e^2}{m_e c_0^2} = 2.81 \cdot 10^{-15} \text{ m}$

$\omega \gg \omega_R \Rightarrow$ electrons can be assumed to be free / independent of each other

e = electron charge
 ϵ_0 = permittivity (free space)
 m_e = electron charge

$$\overset{\text{single}}{\Rightarrow} \left(\frac{d\sigma}{d\Omega}\right)_{\text{scatterer}} = |a(\Omega)|^2 = Z^2 r_e^2 \sin^2 \varphi$$

c_0 = speed of light in free space
 Z = # of electrons = atomic number

\Rightarrow heavy atoms are stronger scatterers!

(II) **visible light** $\omega \ll \omega_R$

$$I_s = E_s E_s^* = E_0^2 r_e^2 \frac{\sin^2 \varphi}{r^2} \left(\frac{\omega}{\omega_R}\right)^4 \quad (\text{single dipole})$$

$\omega = 2\pi c_0 / \lambda_0$ with λ_0 = speed of light in free space

Scattering intensity is higher for high frequencies i.e. short wave length!

$\omega \ll \omega_R \Rightarrow$ electrons are not independent of each other

$$\overset{\text{single}}{\Rightarrow} \left(\frac{d\sigma}{d\Omega} \right)_{\text{scatter}} = |a(\Omega)|^2 = \frac{\alpha^2 \omega^4}{\epsilon_0^2 c_0^4} \sin^2 \varphi = \frac{\alpha^2 16\pi^4}{\epsilon_0 \lambda_0^4} \sin^2 \varphi \quad \alpha = \text{polarizability of an atom}$$

for neutrons: incoherent and coherent scattering

scattering amplitude $A = \sum_n a_n(\vec{q}) \exp(i\vec{q}\vec{r}_n)$ where $a_n(\vec{q}) = b_n$

$$\left(\frac{\partial \sigma}{\partial \Omega} \right) = \langle AA^* \rangle = \left\langle \sum_{n=1}^N b_n(\vec{q}) \exp(i\vec{q}\vec{r}_n) \cdot \sum_{i=1}^N b_i(\vec{q}) \exp(-i\vec{q}\vec{r}_i) \right\rangle = \sum_{i=1}^N \sum_{n=1}^N \langle b_i b_n \exp[i\vec{q}(\vec{r}_n - \vec{r}_i)] \rangle$$

divide double sum into two parts: terms with $i=n$ and terms with $i \neq n$

$$\Rightarrow \left(\frac{\partial \sigma}{\partial \Omega} \right) = \underbrace{\sum_{n=1}^N \langle b_n^2 \rangle}_{(a)} + \underbrace{\sum_{i \neq n} \langle b_i b_n \exp[i\vec{q}(\vec{r}_n - \vec{r}_i)] \rangle}_{(b)}$$

$$(a) = N \langle b^2 \rangle$$

(b) $b_n b_i$ are independent and their values are not correlated with the positions of the atoms:

$$b_n b_i \text{ replaced by } \langle b_n \rangle \langle b_i \rangle = \langle b \rangle^2$$

$$\Rightarrow \left(\frac{\partial \sigma}{\partial \Omega} \right) = N \langle b^2 \rangle + \langle b \rangle^2 \sum_{i \neq n} \langle \exp(i\vec{q}(\vec{r}_n - \vec{r}_i)) \rangle$$

$$\text{define } \overline{\Delta b^2} = \langle (b - \langle b \rangle)^2 \rangle = \langle b^2 - 2b\langle b \rangle + \langle b \rangle^2 \rangle = \langle b^2 \rangle - \langle b \rangle^2$$

add and subtract $N \langle b \rangle^2$

$$\Rightarrow \left(\frac{\partial \sigma}{\partial \Omega} \right) = N \langle \Delta b^2 \rangle + \langle b \rangle^2 \sum_{i,n} \langle \exp(i\vec{q}(\vec{r}_n - \vec{r}_i)) \rangle$$

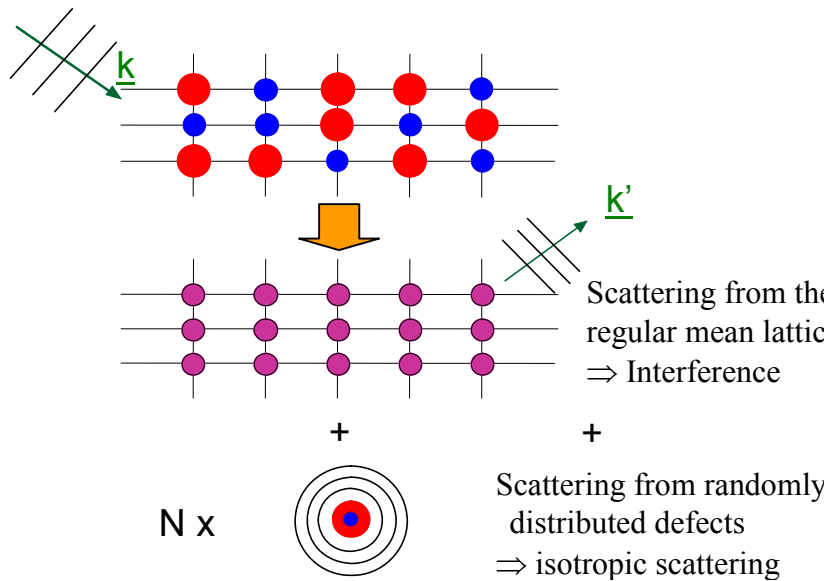
1st term: **incoherent scattering** (q-independent = isotropic in all directions)

Contains no structural information and originates from uncorrelated deviations of b from its average value $\langle b \rangle$.

2nd term: **coherent scattering** (q-dependent)

Contains structural information with scattering strength corresponding to the average value $\langle b \rangle$.

Coherent and incoherent scattering



Source for incoherent scattering

- (I) different isotopes
- (II) nuclear spin originates from random orientation of nuclear spin and neutron spin (neutrons are spin 1/2 particles)

define scattering cross section:

$$\sigma_{\text{coh}} = 4\pi \langle b \rangle^2 = 4\pi b_{\text{coh}}^2$$

$$\sigma_{\text{incoh}} = 4\pi \langle \Delta b \rangle^2 = 4\pi b_{\text{incoh}}^2$$

$b_{\text{incoh}}, b_{\text{coh}}$ = incoherent/coherent scattering length

E.g. proton H and deuterium D have very different scattering cross section

	H	D
$\sigma_{\text{coh}} [10^{-24} \text{ cm}^2]$	1.76	5.59
$\sigma_{\text{incoh}} [10^{-24} \text{ cm}^2]$	80.27	2.05
$b_{\text{incoh}} [10^{-15} \text{ m}]$	25.27	4.04
$b_{\text{coh}} [10^{-15} \text{ m}]$	-3.74	6.67

\Rightarrow very different $b_{\text{incoh}}, b_{\text{coh}}$ of H and D:

Advantage for scattering on polymers: selective labeling of the sample by exchange of protons with deuterium without changing the chemistry (significantly).

e.g. “single” polymer in the melt!

Relation between scattering intensity and density/ concentration fluctuations

Identical scatterers: $A(\vec{q}) = K \sum_n \exp[-i\vec{q}\vec{r}_n]$ with $K = \text{“scattering strength”}$

start point:

$$\left(\frac{d\sigma}{d\Omega} \right) (\vec{q}) = I(\vec{q}) = K^2 \langle A(\vec{q}) A^*(\vec{q}) \rangle = K^2 \left\langle \sum_n \exp[-i\vec{q}\vec{r}_n] \sum_j \exp[i\vec{q}\vec{r}_j] \right\rangle = K^2 \left\langle \sum_{n,j} \exp[-i\vec{q}(\vec{r}_n - \vec{r}_j)] \right\rangle$$

with the density $n(\vec{r}) = \sum_{j=1}^N \delta(\vec{r} - \vec{r}_j)$ and the identity $f(\vec{r}_k) = \int_V f(\vec{r}) \delta(\vec{r} - \vec{r}_k) d\vec{r}$

follows $\sum_j \exp[-i\vec{q}\vec{r}_j] = \int_V \sum_{j=1}^N \exp[-i\vec{q}\vec{r}_j] \delta(\vec{r} - \vec{r}_j) d\vec{r} = \int_V n(\vec{r}) \exp[-i\vec{q}\vec{r}] d\vec{r} \Rightarrow$

$$I(\vec{q}) = K^2 \left\langle \int_V n(\vec{r}) \exp[-i\vec{q}\vec{r}] d\vec{r} \int_{V'} n(\vec{r}') \exp[i\vec{q}\vec{r}'] d\vec{r}' \right\rangle = K^2 \int_V \int_{V'} \exp[-i\vec{q}(\vec{r} - \vec{r}')] \langle n(\vec{r}) n(\vec{r}') \rangle d\vec{r} d\vec{r}'$$

with $\Delta n(\vec{r}) = n(\vec{r}) - \bar{n}$ where $\bar{n} = \text{average density}$

$$\Rightarrow \langle n(\vec{r}) n(\vec{r}') \rangle = \langle (\Delta n(\vec{r}) + \bar{n})(\Delta n(\vec{r}') + \bar{n}) \rangle = \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle + \bar{n} \langle \Delta n(\vec{r}) + \Delta n(\vec{r}') + \bar{n} \rangle$$

since $\langle \Delta n(\vec{r}) \rangle = 0 \Rightarrow \langle n(\vec{r}) n(\vec{r}') \rangle = \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle + \bar{n}^2$

$$\Rightarrow I(\vec{q}) = K^2 \int_V \int_{V'} \exp[-i\vec{q}(\vec{r} - \vec{r}')] \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle d\vec{r} d\vec{r}' + K^2 \underbrace{\int_V \int_{V'} \bar{n}^2 \exp[-i\vec{q}(\vec{r} - \vec{r}')] d\vec{r} d\vec{r}'}_{(I)}$$

$$\text{with } \delta(\vec{q}) = \left(\frac{1}{2\pi} \right)^3 \int_{-\infty}^{\infty} \exp(\pm i\vec{q}\vec{r}) d\vec{r} \text{ (symmetric)} \Rightarrow (I) = (2\pi)^6 \delta^2(\vec{q}) K^2 \bar{n}^2$$

only contribution at $\vec{q} = 0$ (in the primary beam!)

Relation between scattering amplitude and density distribution

$A(\vec{q}) = K \int_V \Delta n(\vec{r}) \exp[-i\vec{q}\vec{r}] d\vec{r}$ is the Fourier transform of the (excess) density distribution

$$I(\vec{q}) = K^2 \langle A(\vec{q}) A^*(\vec{q}) \rangle = K^2 \int_V \int_{V'} \exp[-i\vec{q}(\vec{r} - \vec{r}')] \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle d\vec{r} d\vec{r}'$$

- \Rightarrow for an incompressible system of individual scatterers: no fluctuations in density.
- \Rightarrow no scattering

for incompressible system more than one component is needed to obtain scattering

\Rightarrow then concentration fluctuations are measured!

Relation between scattering intensity and pair correlation function

$$\begin{aligned}
 I(\vec{q}) &= K^2 \int_{\mathcal{V}} \int_{\mathcal{V}'} \exp[-i\vec{q}(\vec{r} - \vec{r}')] \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle d\vec{r} d\vec{r}' \quad \text{with} \quad \vec{r}'' = -(\vec{r} - \vec{r}') = \vec{r}' - \vec{r} \quad \text{and} \quad \frac{d\vec{r}''}{d\vec{r}'} = 1 \\
 &= K^2 \int_{\mathcal{V}} \int_{\mathcal{V}''} \exp[i\vec{q}(\vec{r}'')] \langle \Delta n(\vec{r}) \Delta n(\vec{r}'' + \vec{r}) \rangle d\vec{r} d\vec{r}'' \\
 &= K^2 \int_{\mathcal{V}''} \exp[i\vec{q}(\vec{r}'')] d\vec{r}'' \int_{\mathcal{V}} \langle \Delta n(\vec{r}) \Delta n(\vec{r}'' + \vec{r}) \rangle d\vec{r}
 \end{aligned}$$

replace $\vec{r}'' \rightarrow \vec{r}$ and $\vec{r} \rightarrow \vec{r}'$

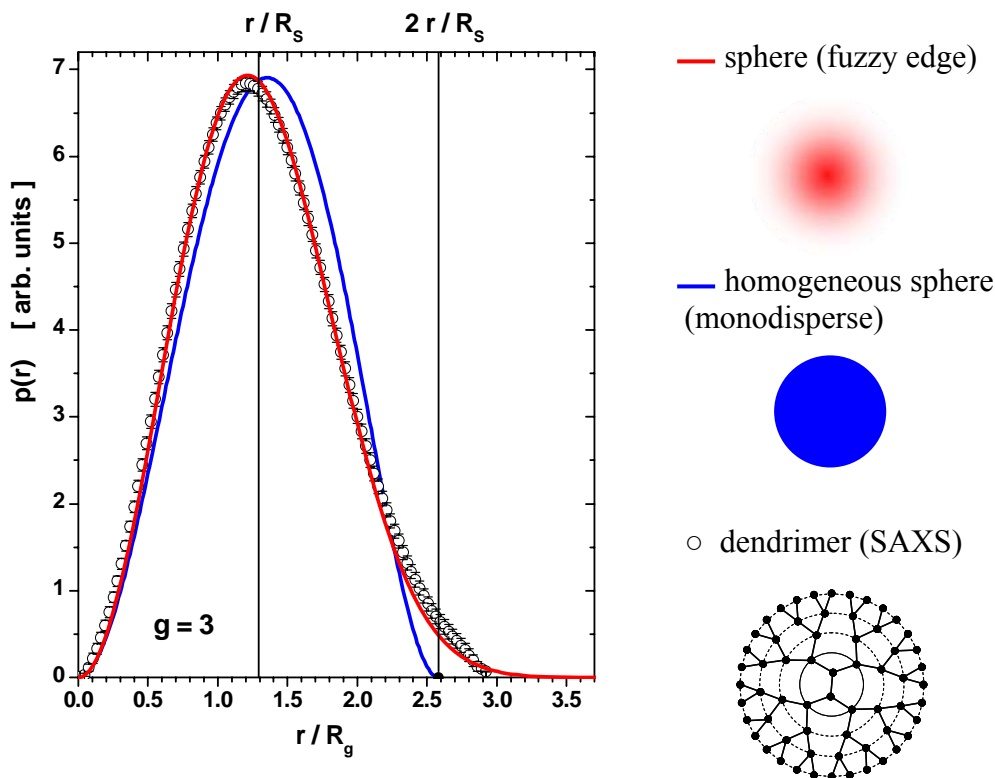
$$\Rightarrow \quad I(\vec{q}) = K^2 \underbrace{\int_{\mathcal{V}'} \langle \Delta n(\vec{r}) \Delta n(\vec{r} + \vec{r}') \rangle d\vec{r}}_{\gamma(\vec{r}) = \langle \Delta n(\vec{r}') \otimes \Delta n(\vec{r} + \vec{r}') \rangle} \int_{\mathcal{V}} \exp[-i\vec{q}(\vec{r})] d\vec{r} = \int_{\mathcal{V}} \exp[-i\vec{q}(\vec{r})] \gamma(\vec{r}) d\vec{r}$$

Pair correlation function $\gamma(r)$ is the convolution of $n(\vec{r})$

in isotropic case: $I(\vec{q}) = 4\pi \int_{\mathcal{V}} p(r) \frac{\sin(qr)}{qr} dr$ where

$\gamma(r) = r^{\dim-1} p(r)$ with $\dim = \text{dimension} \Rightarrow$ in 3 dim.: $\gamma(r) = r^2 p(r)$

$p(r)$ = pair distance distribution function which gives the probability to find two scattering units at a distance r to each other.

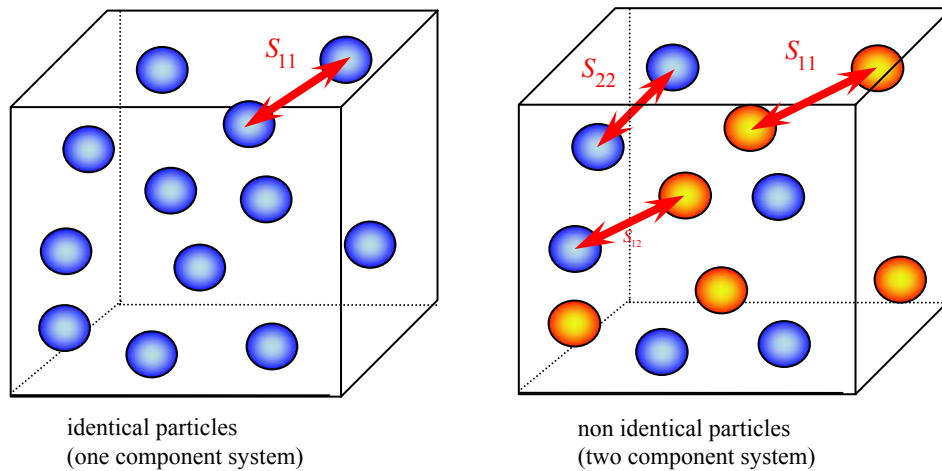


Partial structure factors

$$I(q) = K^2 \int_V \int_{V'} \exp[-i\vec{q}(\vec{r} - \vec{r}')] \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle d\vec{r} d\vec{r}'$$

- Deviations/fluctuations from average density: $I(0)$ measures the compressibility
- For an incompressible system of identical scatters no fluctuations in density \Rightarrow no scattering!

Now assume more than one component (e.g. two component system)



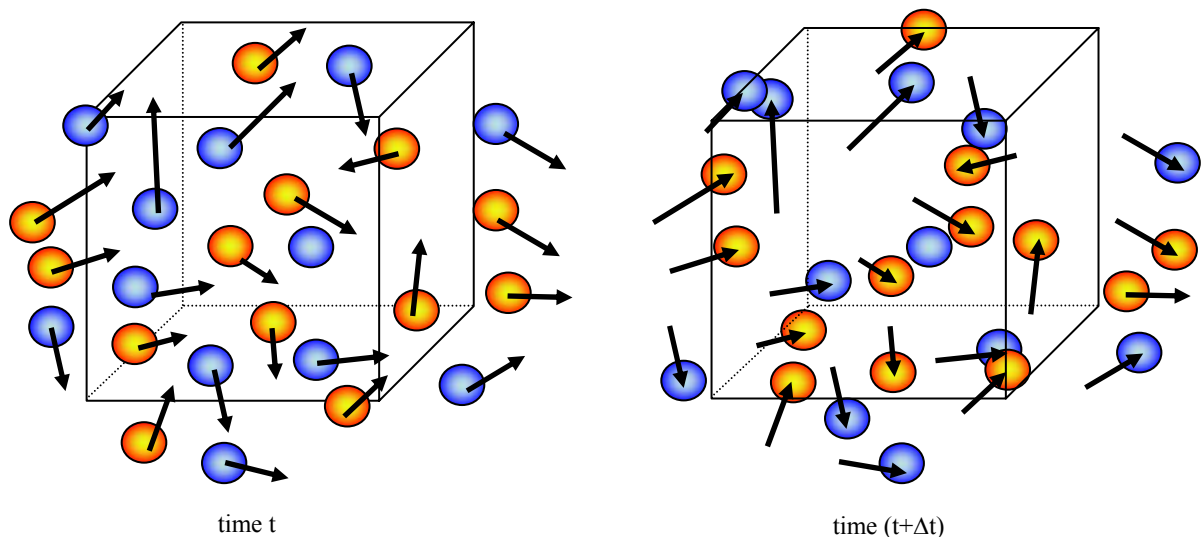
$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ (inter particle distances)

$$I(q) = K_1^2 \underbrace{\sum_i \sum_j \langle \exp[-i\vec{q}\vec{r}_{ij}] \rangle}_{S_{11} \ (1\leftrightarrow 1)} + 2K_1K_2 \underbrace{\sum_i \sum_j \langle \exp[-i\vec{q}\vec{r}_{ij}] \rangle}_{S_{12} \ (1\leftrightarrow 2)} + K_2^2 \underbrace{\sum_i \sum_j \langle \exp[-i\vec{q}\vec{r}_{ij}] \rangle}_{S_{22} \ (2\leftrightarrow 2)}$$

$$= K_1^2 S_{11} + 2K_1K_2 S_{12} + K_2^2 S_{22}$$

$S_{ij} = K^2 \int_V \int_{V'} \exp[-i\vec{q}(\vec{r} - \vec{r}')] \langle \Delta n_i(\vec{r}) \Delta n_j(\vec{r}') \rangle d\vec{r} d\vec{r}'$ are so called partial structure factors

Concentration fluctuations



- The total average particle density is constant for an incompressible system.
- Δn_i are deviations of the local density from the average density n_i of the two components.

⇒ concentration fluctuations/ deviations are measured.

In polymer solutions: $I(0)$ measures the osmotic pressure.

For incompressible system

$N_1 = \#$ particles of component 1; $N_2 = \#$ particles of component 2 with identical volume v

⇒ total volume $V = (N_1 + N_2)v$ (*)

⇒ volume fraction (= # fraction) of the two components: $\phi_1 = \frac{N_1}{N_1 + N_2}$, $\phi_2 = \frac{N_2}{N_1 + N_2}$

due to incompressibility of the system: $n_1(\vec{r}) + n_2(\vec{r}) = n = \frac{N_1 + N_2}{V} \stackrel{(*)}{=} \frac{1}{v}$ ⇒ variations away from

mean density: $\boxed{\Delta n_1(\vec{r}) + \Delta n_2(\vec{r}) = 0}$ (**)

multiplying (**) with $\Delta n_1(\vec{r}') \exp[-i\vec{q}(\vec{r} - \vec{r}')]$ and taking averages:

$$\int_V \int_{V'} \exp[-i\vec{q}(\vec{r} - \vec{r}')] \langle \Delta n_1(\vec{r}) \Delta n_1(\vec{r}') \rangle d\vec{r} d\vec{r}' + \int_V \int_{V'} \exp[-i\vec{q}(\vec{r} - \vec{r}')] \langle \Delta n_2(\vec{r}) \Delta n_1(\vec{r}') \rangle d\vec{r} d\vec{r}' = 0$$

⇒ in terms of partial structure factors $S_{11}(q) + S_{12}(q) = 0$ (***)

multiplying (**) with $\Delta n_2(\vec{r}') \exp[-i\vec{q}(\vec{r} - \vec{r}')]$ and taking averages:

\Rightarrow in term of partial structure factors $S_{12}(\mathbf{q}) + S_{22}(\mathbf{q}) = 0$ (****)

(***) + (****) $\Rightarrow S_{11}(\mathbf{q}) = S_{22}(\mathbf{q}) = -S_{12}(\mathbf{q})$

$\Rightarrow I(\mathbf{q}) = K_1^2 S_{11} + 2K_1 K_2 S_{12} + K_2^2 S_{22} = (K_1 - K_2)^2 S_{11}(\mathbf{q}) = (K_1 - K_2)^2 S_{22}(\mathbf{q}) = -(K_1 - K_2)^2 S_{12}(\mathbf{q})$

\Rightarrow scattering of an incompressible system depends only on one component.

\Rightarrow norm of the difference in scattering strength of the two components determines the contrast.

Babinet principle

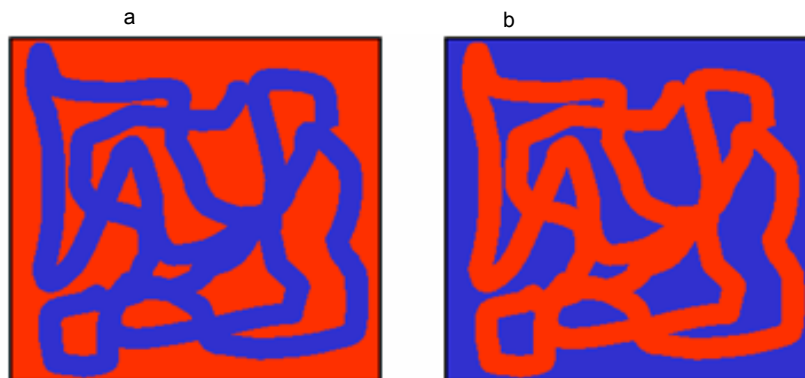


Diagram (a) is the negative of diagram (b) \Rightarrow both figures yield the same scattering pattern.

Contrast $\Delta K^2 = (K_1 - K_2)^2$

Neutrons $\Delta K^2 = (b_1 - b_2)^2$ difference in scattering length of the two components

x-rays $\Delta K^2 = r_e^2 (\Delta Z)^2 \sin^2 \varphi$ $r_e =$ classical electron radius
 $\Delta Z =$ difference in atomic number
 $=$ # electrons of component 1 & 2

visible light $\Delta K^2 = \frac{\Delta \alpha^2 \omega^4}{\epsilon_0^2 c_0^4} \sin^2 \varphi = \frac{\Delta \alpha^2 16\pi^4}{\epsilon_0^2 \lambda_0^4} \sin^2 \varphi$ $\omega = 2\pi c_0 / \lambda_0$

$\Delta \alpha =$ difference between polarizability of a monomer and the total polarizability of all displaced solvent molecules which together occupy an equal volume.

dilute solutions $c_p \Delta \alpha = \epsilon_0 (n^2 - n_s^2)$ $c_p =$ # monomer concentration

n = refractive index of solution
 n_s = refractive index of pure solvent

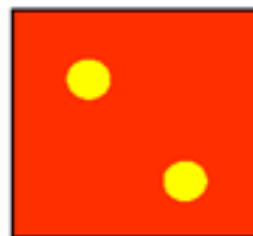
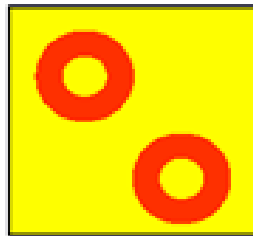
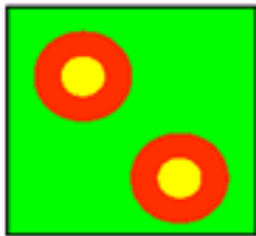
$$\Rightarrow \Delta K^2 = \frac{16\pi^4 (n^2 - n_s^2)^2}{\lambda_0^4 c_p^2}$$

$$\text{with } n^2 - n_s^2 \approx \frac{dn^2}{dc_p} c_p = 2n_s \frac{dn}{dc_p} c_p$$

$$\Rightarrow \Delta K^2 = \frac{64\pi^4}{\lambda_0^4} n_s^2 \left(\frac{dn}{dc_p} \right)^2$$

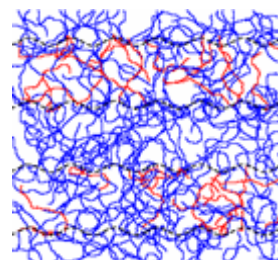
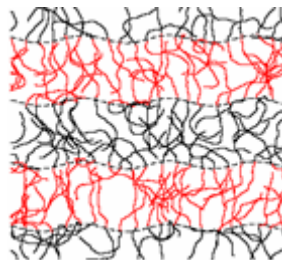
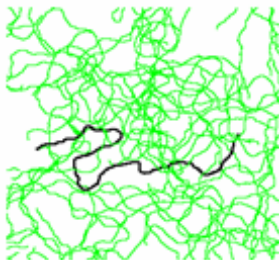
$\frac{dn}{dc_p}$ = refractive index increment

Contrast variation



$b_{\text{solvent}} = b_{\text{core}}$
 (shell)

$b_{\text{solvent}} = b_{\text{shell}}$
 (core)

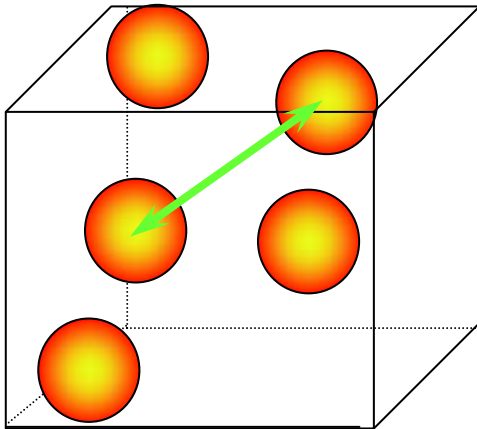


Three component system:

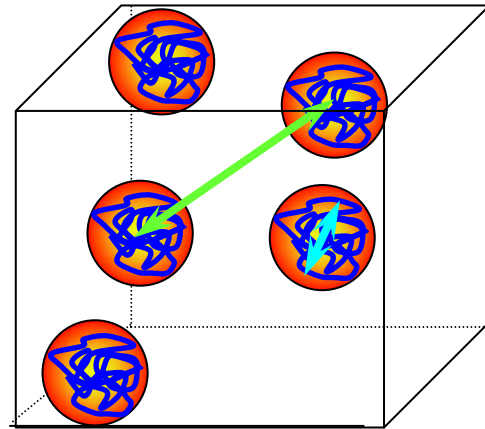
one component can be chosen to match one of the other two components; e.g. mixture of protonated and deuterated solvent to match either the core or shell of a core-shell particle.

\Rightarrow only certain parts of the sample are “visible”

Distinguish inter-molecular and intra-molecular contributions to the scattering



N particles



n particles (polymers) with
N monomeric units

so far:
$$I(q) = K^2 \sum_{i=1}^N \sum_{j=1}^N \langle \exp(-i\vec{q}(\vec{r}_i - \vec{r}_j)) \rangle$$

N= # of particles

now:
$$I(q) = K^2 \sum_{k=1}^n \sum_{m=1}^n \sum_{i=1}^N \sum_{j=1}^N \langle \exp(-i\vec{q}(\vec{r}_{i,k} - \vec{r}_{j,m})) \rangle$$

N= degree of polymerization

n= # of polymers

Distinguish contributions stemming from summations within a single molecule ($k = m$) between different molecules ($k \neq m$):

n intra-molecular contributions to the sum

$n(n-1) \approx n^2$ inter-molecular contributions to the sum

$$I(q) = K^2 \left\{ n \sum_{i=1}^N \sum_{j=1}^N \langle \exp(-i\vec{q}(\vec{r}_{i,k} - \vec{r}_{j,k})) \rangle + n^2 \sum_{i=1}^N \sum_{j=1}^N \langle \exp(-i\vec{q}(\vec{r}_{i,k} - \vec{r}_{j,m})) \rangle \right\}$$

$$= K^2 \left\{ \underbrace{nN^2 P(q)}_{\text{"intra-molecular interferences"}} + \underbrace{n^2 N^2 Q(q)}_{\text{"inter-molecular interferences"}} \right\}$$

“intra-molecular interferences”

$P(q)$ is the so called **form factor** defined so that $P(q) \rightarrow 1$ for $q \rightarrow 0$.

$$P(q) = \frac{1}{N^2} \sum_{i=1}^N \sum_{j=1}^N \langle \exp(-i\vec{q}(\vec{r}_{i,k} - \vec{r}_{j,k})) \rangle$$

carries information about structure/ shape of a single polymer; intra molecular monomer distribution.

“inter-molecular interferences”

carries information about inter-molecular distances/ structure; relative arrangement of the polymers; interaction potential.

if the distances between polymers are large compared to the polymer dimensions i.e. low concentrations: $\bar{q}(\bar{r}_{i,k} - \bar{r}_{j,m}) \gg 1$: $Q(q) \rightarrow 0 \Rightarrow$ on length scales \leq polymer dimension only the form factor is measured.

$Q(q)$ is not the structure factor.

Special case: deuterated and protonated polymer in the melt with same degree of polymerization

n = # of macromolecules ; ϕ = volume fraction protonated component = # fraction

ϕn = # protonated molecules with scattering length b_H

$(1 - \phi)n$ = # deuterated molecules with scattering length b_D

protonated and deuterated molecule have same volume

$$\Rightarrow I(q) = (b_D - b_H)^2 S_{DD}(q) = (b_D - b_H)^2 S_{HH}(q) = -(b_D - b_H)^2 S_{DH}(q) \quad (*)$$

now expressed in terms of $P(q)$ and $Q(q)$:

$$P_H(q) = P_D(q) = P(q) \text{ and } Q_{DH}(q) = Q_{DD}(q) = Q_{HH}(q) = Q(q)$$

$$S_{DD} = (1 - \phi)nN^2P(q) + (1 - \phi)^2 n^2 N^2 Q(q)$$

=

$$S_{HH} = \phi nN^2P(q) + \phi^2 n^2 N^2 Q(q)$$

=

$$-S_{DH} = -\phi(1 - \phi)n^2 N^2 Q(q) \quad (**) \quad (\text{only inter-molecular})$$

$$nN^2P(q) + n^2 N^2 Q(q) = 0 \Rightarrow nQ(q) = -P(q)$$

$$\Rightarrow (**) \text{ into } (*): \boxed{I(q) = -(b_D - b_H)^2 S_{DH} = (b_D - b_H)^2 \phi(1 - \phi)nN^2P(q)}$$

The form factor is measured!

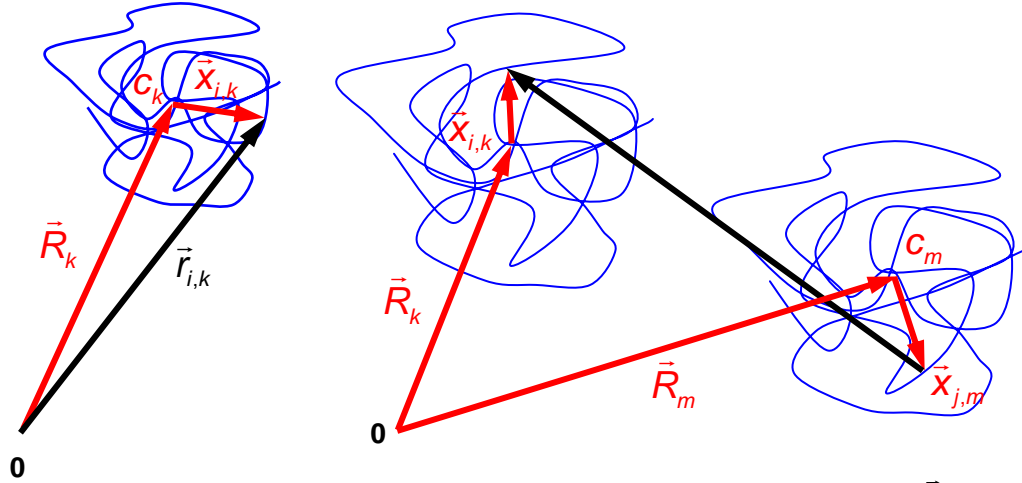
Contrast maximal for $\phi = 0.5$

0 for $\phi = 0$ or 1 as expected for incompressible system!

Decomposition into form- and structure factor for identical scatterers

$$I(q) = K^2 \left\{ nN^2 P(q) + n^2 \sum_{i=1}^N \sum_{j=1}^N \langle \exp(-i\vec{q}(\vec{r}_{i,k} - \vec{r}_{j,m})) \rangle \right\} \quad (*)$$

$$\vec{r}_{i,k} - \vec{r}_{j,m} = \vec{x}_{i,k} + \vec{R}_k - (\vec{x}_{j,m} + \vec{R}_m) = \vec{x}_{i,k} - \vec{x}_{j,m} + (\vec{R}_k - \vec{R}_m)$$



decomposition of monomer position vectors into center-of-mass coordinates \vec{R} and position coordinates \vec{x} relative to the center-of-mass positions

if now the vector \vec{x} and \vec{R} are independent to each other:

$$\langle \exp(-i\vec{q}(\vec{r}_{i,k} - \vec{r}_{j,m})) \rangle = \underbrace{\langle \exp(-i\vec{q}\vec{x}_{i,k}) \rangle}_{\text{Term I}} \underbrace{\langle \exp(i\vec{q}\vec{x}_{j,m}) \rangle}_{\text{Term II}} \langle \exp(-i\vec{q}(\vec{R}_k - \vec{R}_m)) \rangle$$

Term I and Term II give the scattering amplitudes in terms of the density distributions around the center-of-masses c_k and $c_m \Rightarrow P(q)$

$$\begin{aligned} I(q) &= K^2 N^2 P(q) \left[n + n^2 \langle \exp(-i\vec{q}(\vec{R}_k - \vec{R}_m)) \rangle \right] \\ &= K^2 n N^2 P(q) \underbrace{\left[1 + n \langle \exp(-i\vec{q}(\vec{R}_k - \vec{R}_m)) \rangle \right]}_{\text{so called structure factor } S(\vec{q})} \end{aligned}$$

In case $\vec{q}(\vec{R}_k - \vec{R}_m) \gg 1$ (large inter-particle distances compared to probed length scales)
 $\Rightarrow S(\vec{q}) \rightarrow 1$

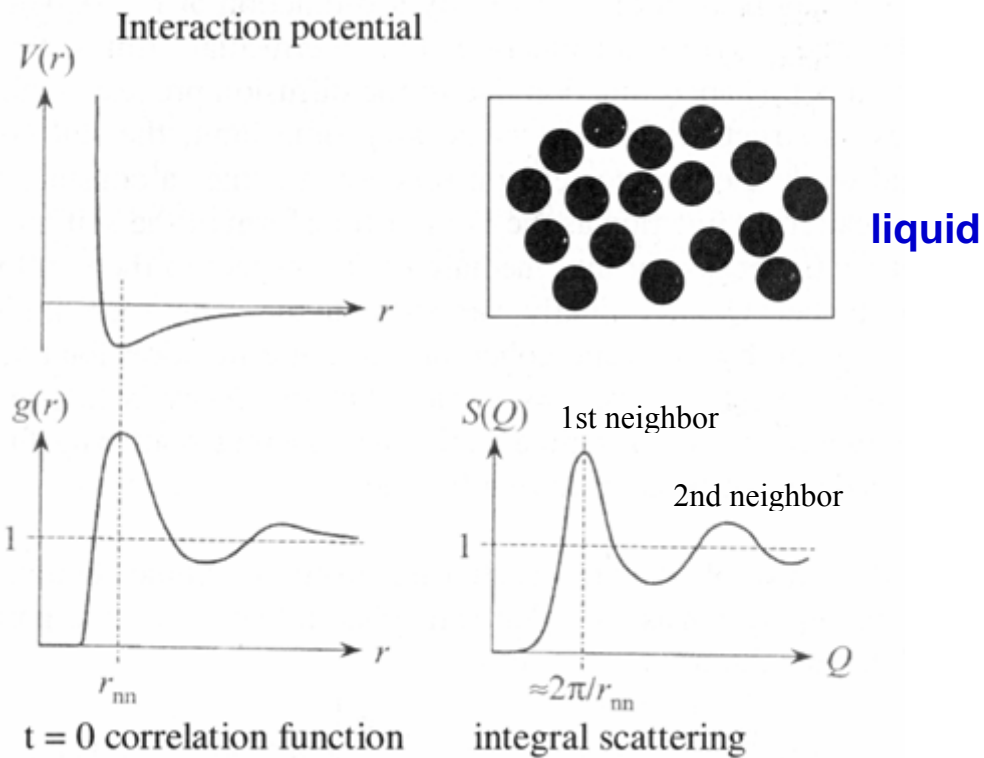
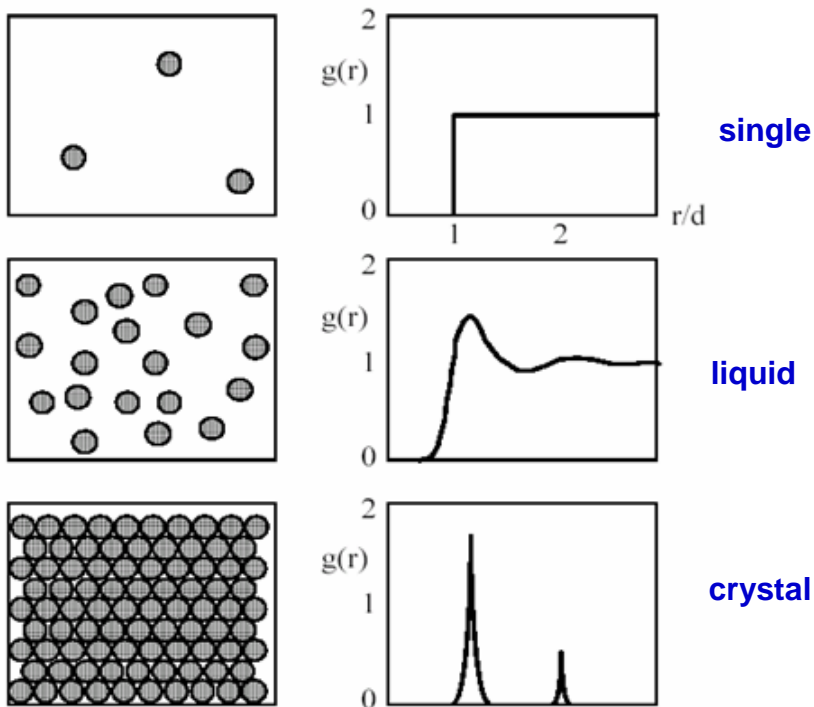
If intra-molecular distances are much smaller than inter-molecular distances then:

$P(q)$ can be resolved in a q -range where $S(q) \approx 1$, e.g. low concentrations

The **structure factor** $S(q)$ yields information about the distribution of the center-of-masses relative to each other (\Rightarrow interaction potentials). Similar to $P(q)$ a pair distance distribution function can be defined for $S(q)$.

(Inter-particle) pair-correlation function

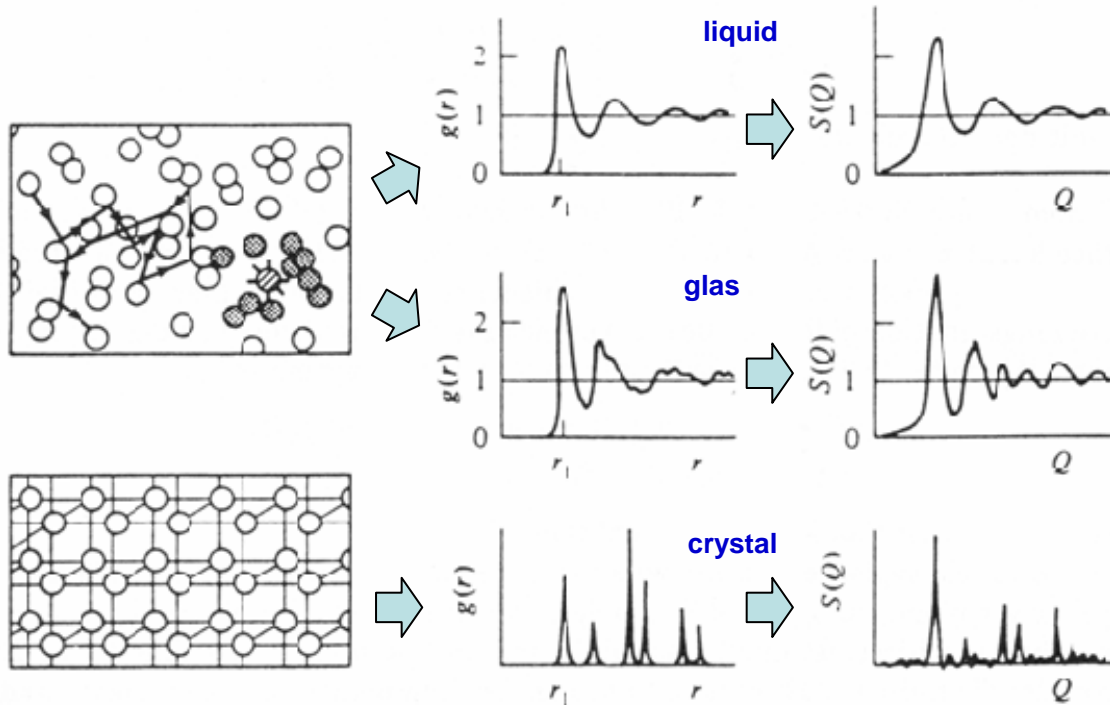
$$S(\vec{q}) = 1 + \bar{n} \int_V d\vec{r} g(\vec{r}) \exp(i\vec{q}\vec{r}) \text{ where } g(\vec{r}) = \text{(inter-particle) pair-correlation function}$$



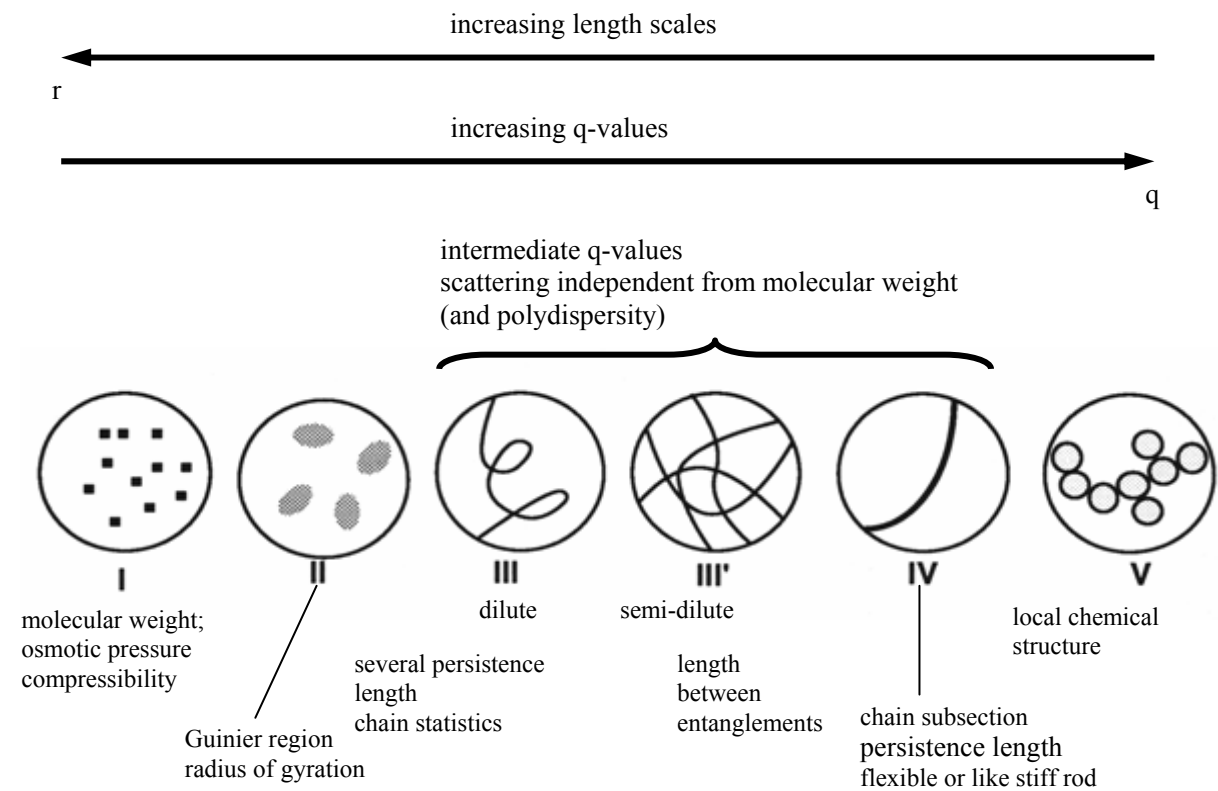
liquid: due to thermal motion spatial correlations are strongly smeared \Rightarrow broad peaks in structure factor.

glas: frozen liquid (amorphous solid); short distance correlations are strong \Rightarrow higher ordering on short distances

crystal: well defined structure; long distance correlations \Rightarrow Bragg peaks



With increasing q/ decreasing length scales different structures are resolved



scattering spectra contain different information in different q ranges

Forward scattering / Zero angle scattering

$$I(q) = \Delta K^2 N^2 n P(q) \text{ for } q \rightarrow 0 \Rightarrow P(q) \rightarrow 1$$

$$\Rightarrow I(q=0) = \Delta K^2 N^2 n$$

K = contrast factor (radiation dependent)
 n = # of macromolecules (known from preparation)
 m_p = monomer mass
 N = degree of polymerization

for a polydisperse system contributions to scattering of fractions having degree of polymerization N_i : $I_i(q) = \Delta K^2 N_i^2 n_i$

Summation of different contributions: $I(q) = \Delta K^2 \sum_i n_i N_i^2$ (total intensity)

with the definition of the weight-average of the degree of polymerization:

$$\langle N \rangle_w = \frac{\sum_i n_i N_i^2}{\sum_i n_i N_i} \Rightarrow I(q) = \Delta K^2 \langle N \rangle_w \sum_i n_i N_i = n_s c \Delta K^2 \langle N \rangle_w = V m_p^{-1} c' \Delta K^2 \langle N \rangle_w$$

Remember Chap. 2: number-average $\langle N \rangle_n = \frac{\sum_i n_i N_i}{\sum_i n_i}$ and z-average $\langle N \rangle_z = \frac{\sum_i n_i N_i^3}{\sum_i n_i N_i^2}$

with $c = \frac{\sum_i n_i N_i}{n_s + \sum_i n_i N_i} \approx \frac{\sum_i n_i N_i}{n_s}$ for low concentrations $n_s \gg \sum_i n_i N_i$

and $c' = V^{-1} m_p \sum_i n_i N_i$ often given in [g/l] ($n_s = \#$ of solvent molecules, $V =$ sample volume)

\Rightarrow forward scattering measures the weight-averaged molecular weight!

Relation between $I(0)$ and compressibility and osmotic pressure

start point: $I(0) = K^2 \int \int_{V V'} \exp[-i\vec{q}(\vec{r} - \vec{r}')] \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle d\vec{r} d\vec{r}'$

with $\Delta n(\vec{r}) = n(\vec{r}) - \bar{n}$ and $\Delta n(\vec{r}') = n(\vec{r}') - \bar{n}$ where $\bar{n} = \frac{n}{V}$ is the average density of

scattering center and $n(\vec{r})$ is the local density for $q=0 \Rightarrow I(0) = K^2 \int \int_{V V'} \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle d\vec{r} d\vec{r}'$

define $\overline{\Delta N^2}$ as the average of the square of the fluctuations in particle # in volume

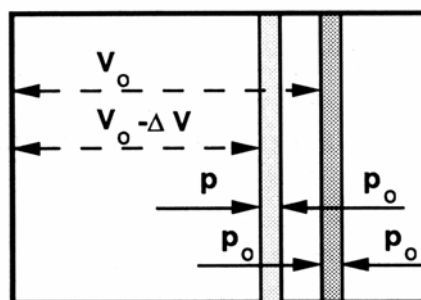
$$\Rightarrow \overline{\Delta N^2} = \left\langle \left[\int_V \Delta n(\vec{r}) d\vec{r} \right]^2 \right\rangle = \left\langle \int_V \Delta n(\vec{r}) d\vec{r} \int_{V'} \Delta n(\vec{r}') d\vec{r}' \right\rangle = I(0) = \int \int_{V V'} \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle d\vec{r} d\vec{r}'$$

$$\Rightarrow \boxed{I(0) = K^2 \overline{\Delta N^2}}$$

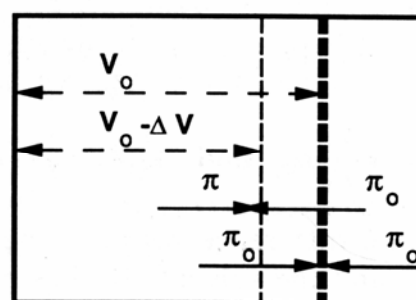
Goal: express $\overline{\Delta N^2}$ in terms of compressibility / osmotic pressure

Compressible one component system

enclose system into cylinder with piston allowing change of volume in one dimension



compressible system



incompressible system
(polymer solution)

$\bar{n} = \frac{N}{V}$ (average particle density) is constant in a first approximation

Brownian motion of particles will lead to fluctuation in the volume / position of the piston

$$\Rightarrow \text{1. approximation: } \frac{\Delta N}{N} = -\frac{\Delta V}{V} \Rightarrow \overline{\Delta V^2} = \frac{\overline{\Delta N^2}}{\bar{n}^2} \quad (*)$$

- piston fluctuates

work done by piston: $w = \int_{V_0}^{V_0 - \Delta V} (p - p_0) dV$ in linear approximation $p = p_0 + \left(\frac{dp}{dV}\right)_{T,N} dV$

replace V by $v = V_0 - V = \Delta V \Rightarrow dv = -dV$

$$\begin{aligned} w &= \int_0^{-\Delta V} (p - p_0)(-dv) = \int_0^{\Delta V} (p - p_0) dv = \int_0^{\Delta V} \left(\frac{dp}{dV}\right)_{T,N} dV dv = -\int_0^{\Delta V} \left(\frac{dp}{dV}\right)_{T,N} d^2v \\ &= -\int_0^{\Delta V} \left(\frac{dp}{dV}\right)_{T,N} v dv = -\frac{1}{2} \left(\frac{dp}{dV}\right)_{T,N} \Delta V^2 \end{aligned}$$

- piston has one degree of freedom

$$\Rightarrow \text{energy according equipartition of energy on average } \bar{w} = \frac{1}{2} k_B T$$

$$\Rightarrow \text{on average } \frac{1}{2} k_B T = \bar{w} = -\frac{1}{2} \left(\frac{dp}{dV}\right)_{T,N} \overline{\Delta V^2} \Rightarrow \overline{\Delta V^2} = -k_B T \left(\frac{dV}{dp}\right)_{T,N} \quad (**)$$

compressibility (isothermal) $\beta = -\frac{1}{V} \left(\frac{dV}{dp}\right)_T$

$$\Rightarrow I(0) = K^2 \overline{\Delta N^2} = K^2 \bar{n}^2 \overline{\Delta V^2} = -K^2 k_B T \bar{n}^2 \left(\frac{dV}{dp}\right)_T$$

$$\Rightarrow \boxed{I(0) = K^2 k_B T \bar{n}^2 V \beta \propto \beta}$$

Incompressible polymer solution

Replace piston by semipermeable membrane:

Exchange of solvent is due to difference in chemical potential $\mu_s - \mu_s^0 = -\Pi v_s$

μ_s = chem. potential solvent in pure solvent; μ_s^0 = chem. potential solvent in solvent/polymer mixture; v_s = partial molar volume solvent; Π = osmotic pressure

As above: $\frac{\Delta N}{N} = -\frac{\Delta V}{V} \Rightarrow \overline{\Delta V^2} = \frac{\overline{\Delta N^2}}{\bar{n}^2}$ but here: $\Delta N = \Delta N_s$!!!

replace p by Π in equation (**):

$$\Rightarrow \overline{\Delta V^2} = -k_B T \left(\frac{dV}{d\Pi}\right)_T = -k_B T \left(\frac{d\Pi}{dV}\right)_T^{-1} \Rightarrow I(0) = \Delta K^2 \overline{\Delta N^2} = \Delta K^2 \bar{n}^2 \overline{\Delta V^2} = -\Delta K^2 k_B T \bar{n}^2 \left(\frac{d\Pi}{dV}\right)_T^{-1}$$

Express in terms of polymer volume fraction $\phi_p = \bar{n}_p V_p = \frac{N_p V_p}{V}$ with

\bar{n}_p = average polymer density; V_p = volume of one polymer

$$\frac{d\Pi}{dV} = \frac{d\Pi}{d\phi_p} \frac{d\phi_p}{dV} = \left(\frac{d\Pi}{d\phi_p} \right)_T \left(-\frac{1}{V^2} N_p V_p \right) = \left(\frac{d\Pi}{d\phi_p} \right)_T \left(-\frac{1}{V} \bar{n}_p V_p \right)$$

$$\Rightarrow \boxed{I(0) = \Delta K^2 k_B T \frac{1}{\bar{n}_p} \frac{V}{V_p} \left(\frac{d\Pi}{d\phi_p} \right)_T^{-1} \propto \left(\frac{d\Pi}{d\phi_p} \right)_T^{-1}}$$

Low angle scattering

Guinier approximation

form factor: $P(q) = \frac{1}{N^2} \sum_{ij} \langle \exp(-i\vec{q}\vec{r}_{ij}) \rangle$ average taken over all conformations & orientations

take only average over all orientations:

assume conformation probability distribution $\phi(\vec{r}_{ij}) = \phi(r_{ij})$ (isotropic system)

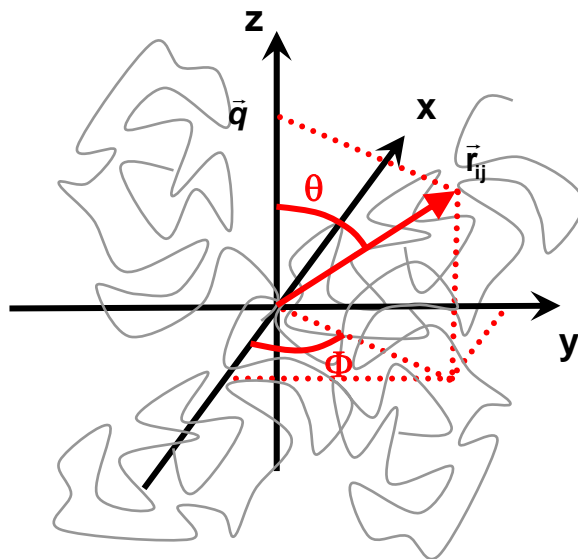
orientation average (in polar coordinates): $\langle f(\theta, \phi) \rangle = \frac{1}{4\pi} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} f(\theta, \phi) \sin\theta d\theta d\phi$

$$\vec{q} \cdot \vec{r}_{ij} = qr_{ij} \cos\theta = qr_{ij} u \quad \text{with } u = \cos\theta \Rightarrow du = -\sin\theta d\theta$$

the “-“ in du disappears by reverting integration boundaries for u from [1,-1] to [-1,1]:

$$\Rightarrow \langle \exp(-i\vec{q}\vec{r}_{ij}) \rangle_{\text{orientations}} = \frac{1}{4\pi} \int_{u=-1}^1 \int_{\phi=0}^{2\pi} \exp(-iqr_{ij}u) du d\phi = \frac{1}{2} \frac{\exp(iqr_{ij}) - \exp(-iqr_{ij})}{iqr_{ij}} = \frac{\sin(qr_{ij})}{qr_{ij}}$$

$$\Rightarrow P(q) = \frac{1}{N^2} \sum_{ij} \left\langle \frac{\sin(qr_{ij})}{qr_{ij}} \right\rangle_{\text{conformations}}$$



series expansion: $\frac{\sin(qr_{ij})}{qr_{ij}} = 1 - \frac{1}{3!}(qr_{ij})^2 + \frac{1}{5!}(qr_{ij})^4 - \frac{1}{7!}(qr_{ij})^6 + \dots$

\Rightarrow low q: $P(q) \approx \frac{1}{N^2} \sum_{ij} \left\langle 1 - \frac{1}{3!}(qr_{ij})^2 \right\rangle = 1 - \frac{1}{6}q^2 \frac{1}{N^2} \sum_{ij} \langle r_{ij}^2 \rangle$

with the definition of the radius of gyration: $\langle R_g^2 \rangle = \frac{1}{2} \frac{1}{N^2} \sum_{ij} \langle r_{ij}^2 \rangle$

\Rightarrow by comparison: $P(q) \approx 1 - \frac{1}{3}q^2 \langle R_g^2 \rangle + O(q^4) \approx \exp\left(-q^2 \frac{\langle R_g^2 \rangle}{3}\right)$

Guinier Plot $\ln\left(\frac{I(q)}{I(q=0)}\right) = -q^2 \frac{\langle R_g^2 \rangle}{3}$ plot versus q^2 slope is $-\frac{\langle R_g^2 \rangle}{3}$

Polydispersity

$I(q) = \Delta K^2 n N^2 P(q)$ $\Delta K =$ contrast factor depending on radiation
 $n =$ # of macromolecules
 $N =$ degree of polymerization

Contribution to scattering of a fraction of the sample having a degree of polymerization N_i and mean square radius of Gyration $\langle R_g^2 \rangle_i$

$I_i(q) = \Delta K^2 n_i N_i^2 P(q) = \Delta K^2 n_i N_i^2 \left(1 - \frac{q^2}{3} \langle R_g^2 \rangle_i + \dots\right)$

sum of single contributions yields total intensity

$I(q) = \sum I_i(q) = \Delta K^2 \left(\sum n_i N_i^2 - \frac{q^2}{3} \sum n_i N_i^2 \langle R_g^2 \rangle_i \right)$ with $I(q=0) = \Delta K^2 \sum n_i N_i^2$

$\Rightarrow \frac{I(q)}{I(q=0)} = 1 - \frac{q^2}{3} \frac{\sum n_i N_i^2 \langle R_g^2 \rangle_i}{\sum n_i N_i^2} = 1 - \frac{q^2}{3} \langle\langle R_g^2 \rangle\rangle_z$

\Rightarrow scattering measures the z-average of the square of the radius of gyration!

Zimm plot

Start from the relation between forward scattering and osmotic pressure

$\frac{I(q=0)}{V} = \Delta K^2 k_B T \phi_p \left(\frac{\partial \Pi}{\partial \phi_p} \right)^{-1}$ (*) $\Delta K =$ contrast factor (radiation dependent)
 $\phi_p =$ volume fraction polymer

$V =$ sample volume $\approx V_s$ solvent volume

$\Pi V_s^M = RT \left[\frac{c_p}{N} + \left(\frac{1}{2} - \chi \right) c_p^2 + \dots \right]$ $v_s^M =$ molar volume solvent
 $c_p =$ molar fraction polymer

(result for osmotic pressure from Chap. 4)

conversion molar fraction \leftrightarrow volume fraction \leftrightarrow concentration c

for low concentrations ($V_s \gg V_p$; $n_s \gg n_p$)

$$\boxed{\phi_p \approx \frac{N n_p V_p^0}{n_s V_s^0}} \wedge \boxed{c_p \approx \frac{N n_p}{n_s}} \wedge \boxed{c \approx \frac{N n_p m_p^0}{n_s V_s^0}} \quad \left[\begin{array}{l} \text{weight} \\ \text{volume} \end{array} \right]$$

$n_{s,p}$ = # of molecules / polymers;

N = degree of polymerization;

$V_{s,p}^0$ = Volume of molecules/monomers;

m_p^0 = monomer mass

$$\boxed{\phi_p = \frac{V_p^0}{m_p^0} c} \wedge c_p = \frac{V_s^0}{m_p^0} c \wedge \boxed{\phi_p = \frac{V_p^0}{V_s^0} c_p} \quad \boxed{R = N_A k_B}$$

$$(**) \Rightarrow \Pi = \frac{k_B T}{V_s^0} \left[\frac{1}{N} \frac{V_s^0}{V_p^0} \phi_p + \left(\frac{1}{2} - \chi \right) \left(\frac{V_s^0}{V_p^0} \right)^2 \phi_p^2 + \dots \right] = \frac{k_B T}{V_p^0} \left[\frac{1}{N} \phi_p + \left(\frac{1}{2} - \chi \right) \left(\frac{V_s^0}{V_p^0} \right) \phi_p^2 + \dots \right]$$

$$\Rightarrow \frac{\partial \Pi}{\partial \phi_p} = \frac{k_B T}{V_p^0} \left[\frac{1}{N} + \left(\frac{1}{2} - \chi \right) 2 \left(\frac{V_s^0}{V_p^0} \right) \phi_p + \dots \right]$$

$$(*) \Rightarrow \frac{V \Delta K^2}{I(q=0)} = \frac{\partial \Pi}{\partial \phi_p} \frac{1}{\phi_p} \frac{1}{k_B T} = \frac{1}{\phi_p} \frac{1}{V_p^0} \left[\frac{1}{N} + \left(\frac{1}{2} - \chi \right) 2 \left(\frac{V_s^0}{V_p^0} \right) \phi_p + \dots \right]$$

now express ϕ_p by c : $\Rightarrow \frac{V \Delta K^2}{I(q=0)} = \frac{m_p^0}{V_p^0 c} \frac{1}{V_p^0} \left[\frac{1}{N} + \left(\frac{1}{2} - \chi \right) 2 \left(\frac{V_s^0}{V_p^0} \right) \frac{V_p^0}{m_p^0} c + \dots \right]$

and $V_p^0 = \frac{m_p^0}{\rho_p}$ ρ_p = polymer density

$$\Rightarrow \frac{V \Delta K^2}{I(q=0)} = \frac{\rho_p^2}{m_p^0 c} \left[\frac{1}{N} + \left(\frac{1}{2} - \chi \right) 2 \left(\frac{V_s^0}{m_p^0} \right) c + \dots \right] = \frac{\rho_p^2}{c} \left[\frac{1}{M_p} + \left(\frac{1}{2} - \chi \right) 2 \frac{V_s^0}{m_p^0} c + \dots \right]$$

M_p = total mass single polymer = $N n_p^0$

$$\Rightarrow \frac{V \Delta K^2 c}{I(q=0) \rho_p^2} = \frac{1}{M_p} + \underbrace{2 \left(\frac{1}{2} - \chi \right) \frac{V_s^0}{m_p^0} c}_{\text{2. virial coefficient}} + \dots = \frac{1}{M_p} + 2 A_2 c + \dots$$

Generalization to final q-values

$$\frac{V\Delta K^2 c}{I(q)\rho_p^2} = \frac{1}{M_p P(q)} + 2A_2 c + \dots$$

take form factor in Guinier approximation $P(q) \approx \exp\left(-q^2 \frac{\langle R_g^2 \rangle}{3}\right)$

series expansion of $P^{-1}(q) = 1 + \frac{1}{3}q^2 \langle R_g^2 \rangle + O(q^4)$

$$\Rightarrow \boxed{\frac{V\Delta K^2 c}{I(q)\rho_p^2} = \left(\frac{1}{M_p} - 2A_2 c\right) + \frac{1}{3}q^2 \langle R_g^2 \rangle + \dots}$$

limits: (1) $(q \rightarrow 0) \wedge (c \rightarrow 0) \Rightarrow M_p$

(2) $(q \rightarrow 0) \Rightarrow$ slope when plotted versus $c = 2A_2$

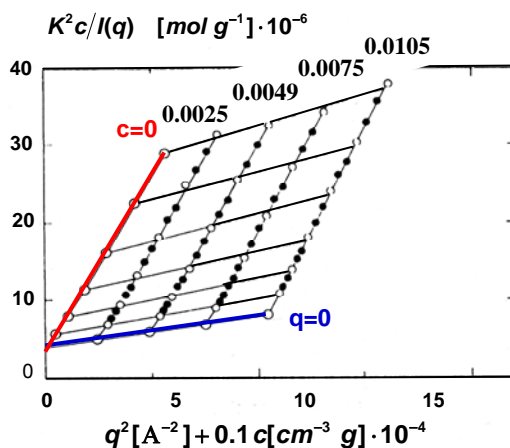
(3) $(c \rightarrow 0) \Rightarrow$ slope when plotted versus $q^2 = \frac{1}{3} \frac{\langle R_g^2 \rangle}{M_p}$

Zimm plot

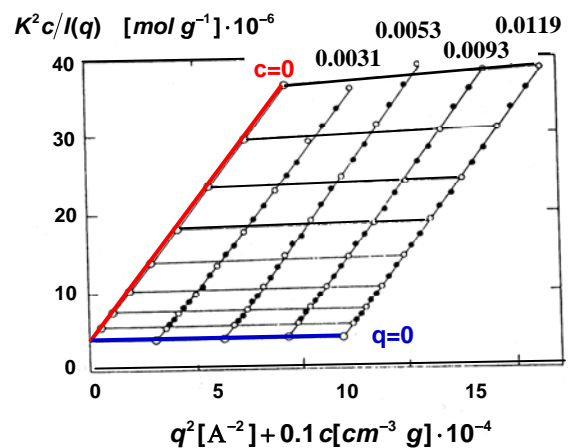
determination of molecular weight, radius of gyration and 2nd virial coefficient

plot $\frac{K^2 c}{I(q)} = \frac{1}{M_p} + \frac{1}{3} \frac{\langle R_g^2 \rangle}{M_p} (q^2 + \alpha c)$ with $K^2 = \frac{K^2}{\rho_p^2 V}$ and $\alpha = \alpha^* 6A_2 \frac{M_p}{\langle R_g^2 \rangle}$

α^* properly chosen so that data obtained for different concentrations are well separated.



h-PMMA in d-acetone



h-PMMA in d-PMMA

extrapolate at each q-value to c=0 \Rightarrow slope of straight line = $\frac{1}{3} \frac{\langle R_g^2 \rangle}{M_p}$

extrapolate at each concentration to q=0 \Rightarrow slope of straight line = $\frac{1}{3} \frac{\langle R_g^2 \rangle}{M_p} \alpha = 2A_2 \alpha^*$

both lines for c=0 \wedge q=0 intersection with y-axis = $\frac{1}{M_p}$

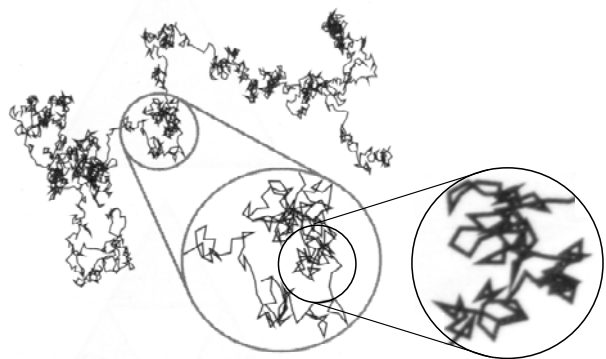
\Rightarrow 3 equation + 3 unknown variables \Rightarrow determination of M_p, A_2 and $\langle R_g^2 \rangle$!!!

For mixture of deuterated and protonated PMMA $q \rightarrow 0$ (almost) horizontal line $\Rightarrow A_2 \approx 0!$

Intermediate and high q range

Scattering from fractal structures

Fractal structures are self-similar structures independent from the length scale of observation. In the case of polymers the length scale range of similarity is limited:



lower limit: length of a segment l

upper limit: overall polymer dimension R_g

only, if $R_g \gg l$ the length scale range is large enough to consider fractality.

In most models q is associated with characteristic length scale of the model: $qR_g =$ dimensionless

$$\text{with } I(q) = nN^2 P(qR_g) = \frac{V}{v} \phi_p N P(qR_g)$$

$n = \#$ polymers

$N =$ degree of polymerization

$V =$ sample volume; $v =$ monomer volume

$\phi_p =$ volume fraction polymer

Series expansion of $P(qR_g)$ for large q with leading term $(qR_g)^{-\alpha} \Rightarrow I(q) \propto N(qR_g)^{-\alpha}$

for mass fractal:

mass M within a sphere with radius R around any arbitrary point of the structure yields

$$M(R) \propto R^D \quad D = \text{fractal dimension}$$

$$\Rightarrow N \text{ replaced by Mass } M: I(q) \propto M(qR_g)^{-\alpha} \propto M(qM^{1/D})^{-\alpha} = q^{-\alpha} M^{(1-\alpha/D)}$$

\Rightarrow at large q -values scattering should not depend on the mass of the polymer $\Rightarrow \alpha = D$

$\Rightarrow \boxed{S(q) \propto q^{-D}}$ with $1 \leq D \leq 3$ for mass fractals

$R^2 = N^{2\nu} l^2$ with ν = Flory exponent (see Chap. 3)

ideal chain		$\nu=1/2$	$D=2$	$P(q) \propto q^{-2}$ (see Gaussian chain)
with excluded volume interaction	3-dim	$\nu=3/5$	$D=5/3$	$\propto q^{-5/3}$
	2-dim	$\nu=3/4$	$D=4/3$	$\propto q^{-4/3}$
	1-dim	$\nu=1$	$D=1$	$\propto q^{-1}$

for surface fractal area $S \propto R^{D_s}$ with D_s = fractal dimension of surface

surface with fractal structure or surface deposited with material having fractal properties

for a smooth surface $S \propto R^2$ ($D_s=2$)

must be <3 , the dimension of a three dimensional compact object

$$I(q) \propto nM^2(qR)^{-\alpha} = \underbrace{nS}_{\text{total surface}} f(q)$$

replace $M \propto R^3$ and $S \propto R^{D_s}$

$$\Rightarrow I(q) \propto nR^{6-\alpha} q^{-\alpha} \propto nR^{D_s} f(q)$$

$$\Rightarrow D_s = 6 - \alpha \Leftrightarrow \alpha = 6 - D_s$$

$$\Rightarrow I(q) \propto q^{-(6-D_s)}$$

for a smooth surface $D_s = 2 \Rightarrow \boxed{I(q) \propto q^{-4}}$ (see sphere form factor)

scattering from surface only



The full form factor

Gaussian chain

In gernal:
$$P(q) = \frac{1}{N^2} \sum_{ij} \langle \exp(-i\vec{q}\vec{r}_{ij}) \rangle$$

average has to be taken over all conformations and orientations

distribution of \vec{r}_{ij} Gaussian:

$$\Phi(\vec{r}_{ij}) = \left(\frac{3}{2\pi|i-j|l^2} \right)^{3/2} \exp\left(-\frac{3}{2} \frac{r_{ij}^2}{|i-j|l^2} \right) = \Phi(r_{ij}) \quad (*)$$

$$\begin{aligned} \langle \exp(-i\vec{q}\vec{r}_{ij}) \rangle &= \int \Phi(\vec{r}_{ij}) \exp(-i\vec{q}\vec{r}_{ij}) d\vec{r}_{ij} \\ \Rightarrow &= \int_{r_{ij}=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \Phi(r_{ij}) \exp(-i\vec{q}\vec{r}_{ij}) r_{ij}^2 dr_{ij} \sin\theta d\phi d\theta \end{aligned}$$

integration over ϕ & θ :

$$\text{substitute } u = \cos\theta \Rightarrow \vec{q} \cdot \vec{r}_{ij} = qr_{ij} \cos\theta = qr_{ij}u \Rightarrow du = -\sin\theta d\theta$$

the negative sign in du disappears by reverting integration boundaries

$$\Rightarrow \langle \exp(-i\vec{q}\vec{r}_{ij}) \rangle = 2\pi \int_{u=-1}^1 \int_{r_{ij}=0}^{\infty} \Phi(r_{ij}) \exp(-iqr_{ij}u) r_{ij}^2 dr_{ij} du$$

integration over u :

$$\begin{aligned} \langle \exp(-i\vec{q}\vec{r}_{ij}) \rangle &= 2\pi \int_{r_{ij}=0}^{\infty} \Phi(r_{ij}) \left[\frac{1}{iqr_{ij}} \{ -\exp(-iqr_{ij}) + \exp(-iqr_{ij}) \} \right] r_{ij}^2 dr_{ij} \\ \Rightarrow &= 4\pi \int_{r_{ij}=0}^{\infty} \Phi(r_{ij}) \frac{\sin(qr_{ij})}{qr_{ij}} r_{ij}^2 dr_{ij} = \exp\left(-\frac{1}{6} q^2 |i-j|l^2 \right) \end{aligned}$$

$$\Rightarrow P(q) = \frac{1}{N^2} \sum_{ij} \exp\left(-\frac{1}{6} q^2 |i-j|l^2 \right) \quad \textbf{Gaussian chain}$$

for large N summations can be replaced by integrations

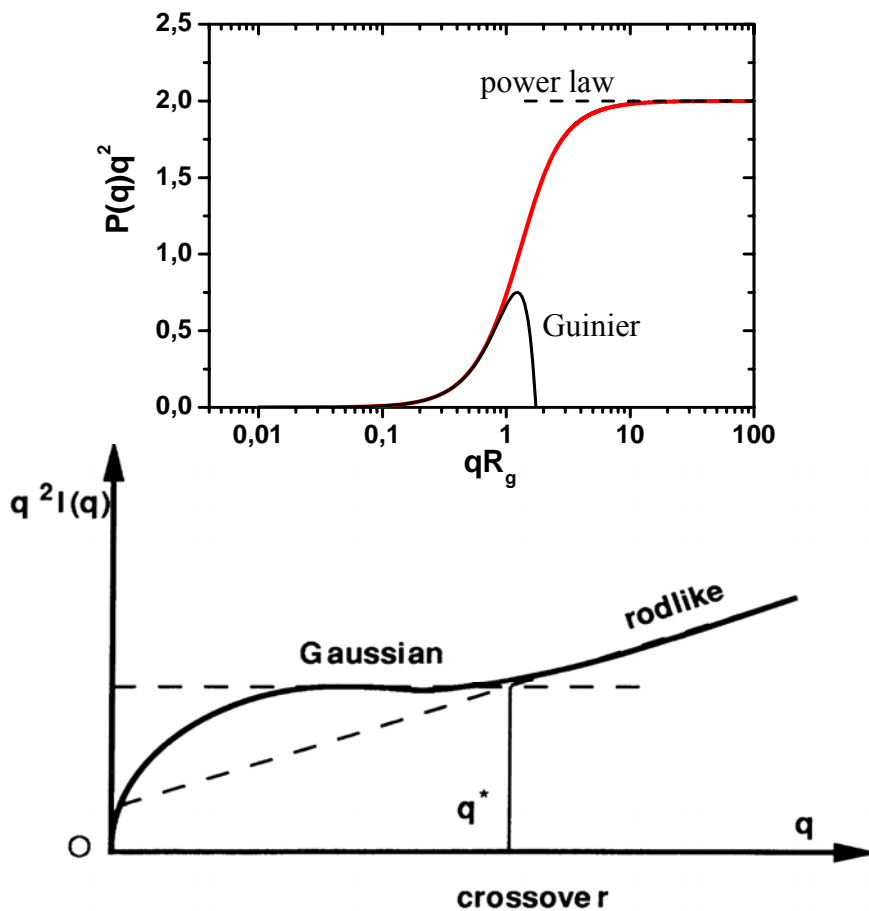
$$\Rightarrow P(q) = \frac{1}{N^2} \int_0^N \int_0^N \exp\left(-\frac{1}{6} q^2 |i-j|l^2 \right) di dj$$

$$\Rightarrow \boxed{P(q) = \frac{2}{x^2} (x - 1 + e^{-x})} \quad \textbf{Debye-function}$$

$$\text{with } x = \frac{1}{6} q^2 N l^2 = (qR_g)^2$$

$$\Rightarrow \boxed{P = P(qR_g)}$$

Gaussian polymer



rod: $I(q) \sim q^{-1}$

on length scales smaller than persistence length

$$q \gtrsim 2\pi/l_p$$

transition to rod-like behavior

asymptotic behaviour of $P(q) = \frac{2}{x^2}(x - 1 + e^{-x})$:

$$(I) \quad x = (qR_g)^2 \ll 1 \Leftrightarrow x \rightarrow 0$$

$$\text{series expansion: } \exp(-x) = 1 - x + \frac{1}{2}x^2 - \frac{1}{6}x^3 + O(x^4)$$

$$\Rightarrow P(q) = \frac{2}{x^2} \left(\cancel{x-1+1-x} + \frac{1}{2}x^2 - \frac{1}{6}x^2 + O(x^4) \right) = 1 - \frac{1}{3}x + O(x^2)$$

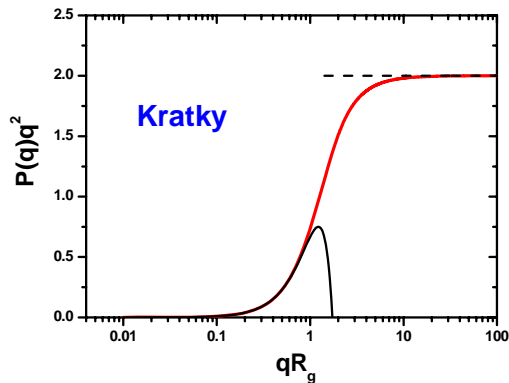
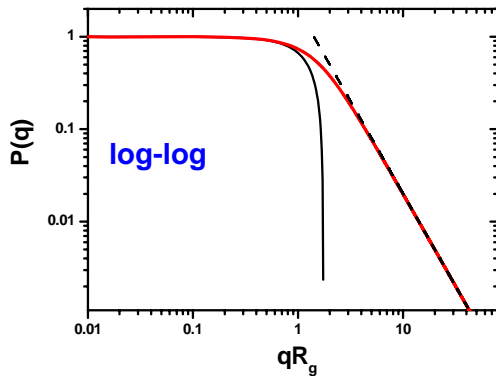
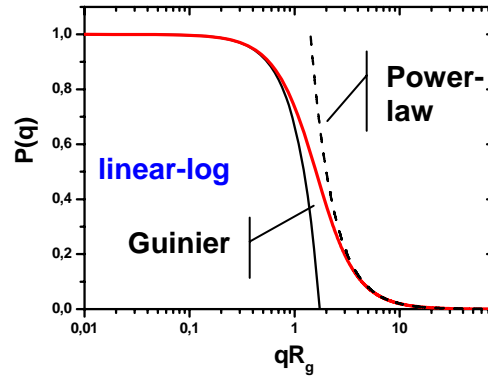
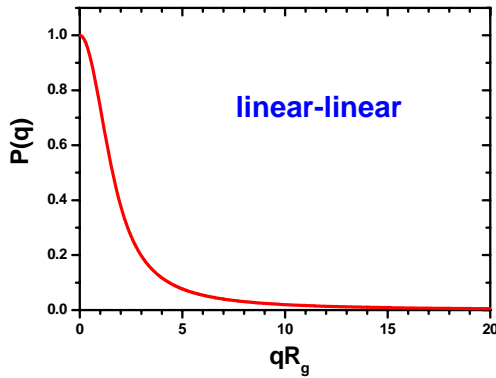
$$\Rightarrow P(q) \approx 1 - \frac{1}{3}(qR_g)^2 \quad \text{Guinier law}$$

$$(II) \quad x = (qR_g)^2 \gg 1 \Leftrightarrow \text{large } q$$

$$P(q) \approx \frac{2}{x} = \frac{2}{(qR_g)^2} \propto q^{-2} \quad \Rightarrow \quad \text{fractal dimension } D=2$$

[Different derivation of Debye function in B" S.Hoffmann "Conformations of Polymer Chains", 33 IFF-Ferienkurs 2002]

Representation of P(q) - example: Debye-function



Sphere form factor

scattering amplitude

$$A(\vec{q}) = \frac{4\pi}{c} \int_0^\infty \Delta\rho^2(r) \exp(-i\vec{q}\vec{r}) d\vec{r}$$

with normalization $c = 4\pi \int_0^\infty \Delta\rho^2(r) r^2 dr$

so that $P(q) \rightarrow 1$ for $q \rightarrow 0$

$\Delta\rho(r)$ = excess scattering length density

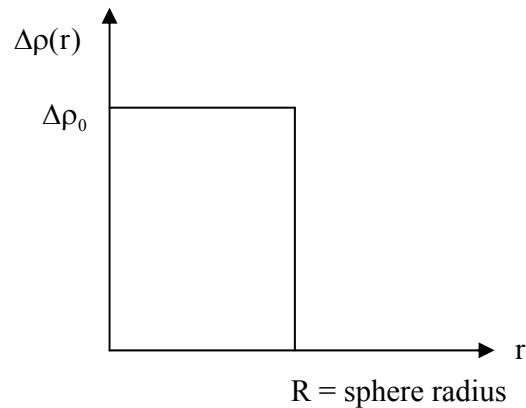
$$\Delta\rho^2(r) = V(K_1/v_1 - K_2/v_2)^2$$

with K_i =scattering strength and v_i = volume of scattering unit of component i

same calculation for orientation average as for Gaussian chain

$$A(q) = \frac{4\pi}{c} \int_0^R \Delta\rho_0^2 \frac{\sin(qr)}{qr} r^2 dr = \frac{\Delta\rho_0^2}{c} \frac{4\pi}{q^3} [\sin(qR) - (qR) \cos(qR)]$$

$$\text{with } c = 4\pi \Delta\rho_0^2 \int_0^R r^2 dr = \frac{4}{3} \pi R^3 \Delta\rho_0^2$$



$$\Rightarrow A(q) = \frac{3}{q_s^3} [\sin(q_s) - q_s \cos(q_s)] \quad \text{with } q_s = qR$$

$$\Rightarrow \boxed{P(q) = [A(q)]^2 = \frac{9}{q_s^6} [\sin(q_s) - q_s \cos(q_s)]^2} \quad \Rightarrow \quad \boxed{P = P(qR)}$$

the sphere form factor can also be expressed in terms of the

Bessel-function $J_{3/2}(x) = \sqrt{\frac{2}{\pi x}} \frac{\sin(x) - x \cos(x)}{x}$

$$\Rightarrow P(q) = \frac{9\pi}{2} \frac{J_{3/2}^2}{q_s^3} \quad \text{zeros of } P(q) \text{ are } q_{s,i}^0 = q_i^0 R = \frac{\pi}{2}(2i+1) \text{ with } 0 < i \in I$$

zeros are sensitive to the sphere radius!

asymptotic behavior

(I) $q_s = qR_g \ll 1 \Leftrightarrow q_s \rightarrow 0$

$$\Rightarrow \text{series expansion } P(q) = 1 - \frac{1}{5}q_s^2 + \frac{3}{175}q_s^4 - \frac{4}{4725}q_s^6 + O(q_s^8)$$

comparison with Guinier formula $P(q_s) \approx 1 - \frac{1}{3}(qR_g)^2$

$$\Rightarrow \frac{1}{3}(qR_g)^2 = \frac{1}{5}q_s^2 = \frac{1}{5}(qR)^2 \quad \Rightarrow \text{sphere radius} \quad \boxed{R^2 = \frac{5}{3}R_g^2}$$

(II) $q_s = qR_g \gg 1 \Leftrightarrow \text{large } q_s$

$$P(q) = \frac{9}{q_s^6} \left[\underbrace{\sin^2(q_s)}_{(i)} - 2 \underbrace{\sin(q_s)q_s \cos(q_s)}_{(ii)} + q_s^2 \underbrace{\cos^2(q_s)}_{(iii)} \right]$$

(i) fast oscillation between $[0...1] \rightarrow \frac{1}{2}$

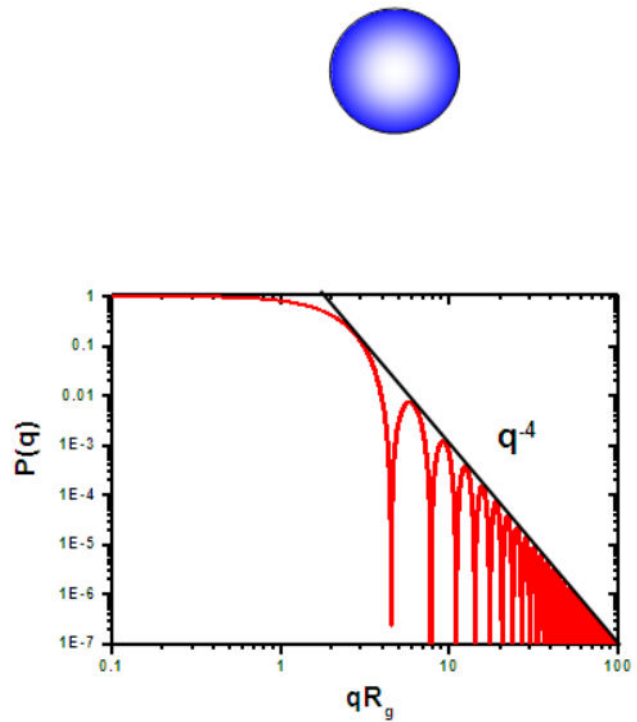
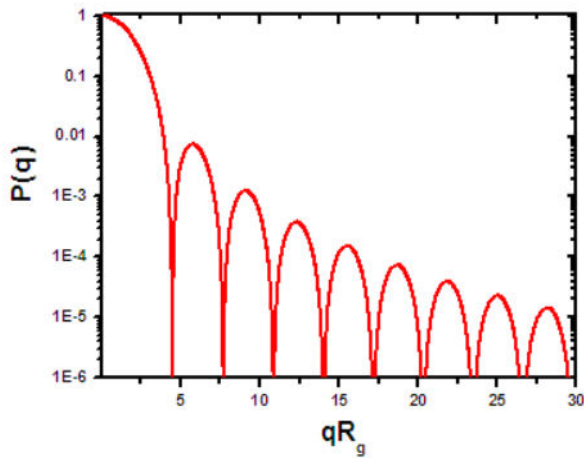
(ii) $= 2q_s \sin(2qR)$ fast oscillation between $[-1...1] \rightarrow 0$

(iii) fast oscillation between $[0...1] \rightarrow \frac{1}{2}$

$$\Rightarrow P(q) \approx \frac{9}{q_s^6} \left[\frac{1}{2} + \frac{1}{2}q_s^2 \right] = \frac{9}{2} \left[\frac{1}{(qR)^4} + \frac{1}{(qR)^6} \right]$$

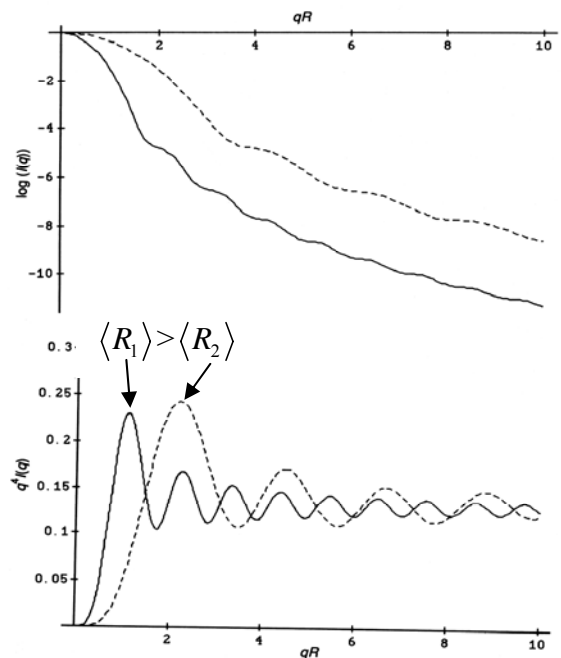
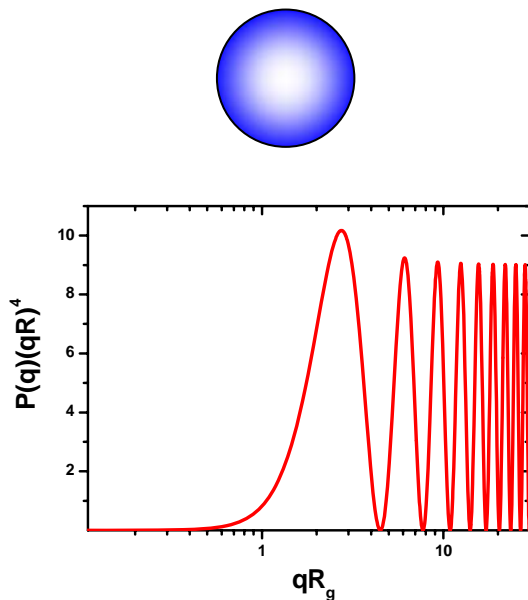
leading power in the decay of the form factor for large q : $P(q) \propto q^{-4}$

\Rightarrow fractal dimension $D_s=2$ (surface fractal)



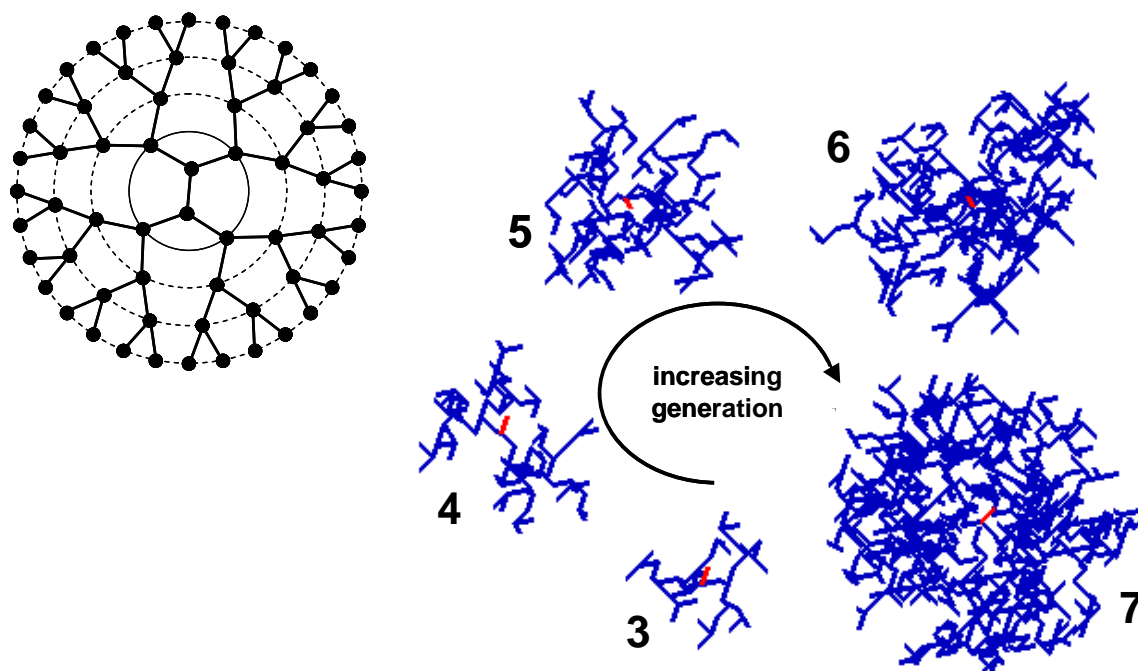
Impact of polydispersity on sphere form factor

Polydispersity leads to smearing out of the minima and the asymptotic power-law decay of $P(q)$ appears faster.



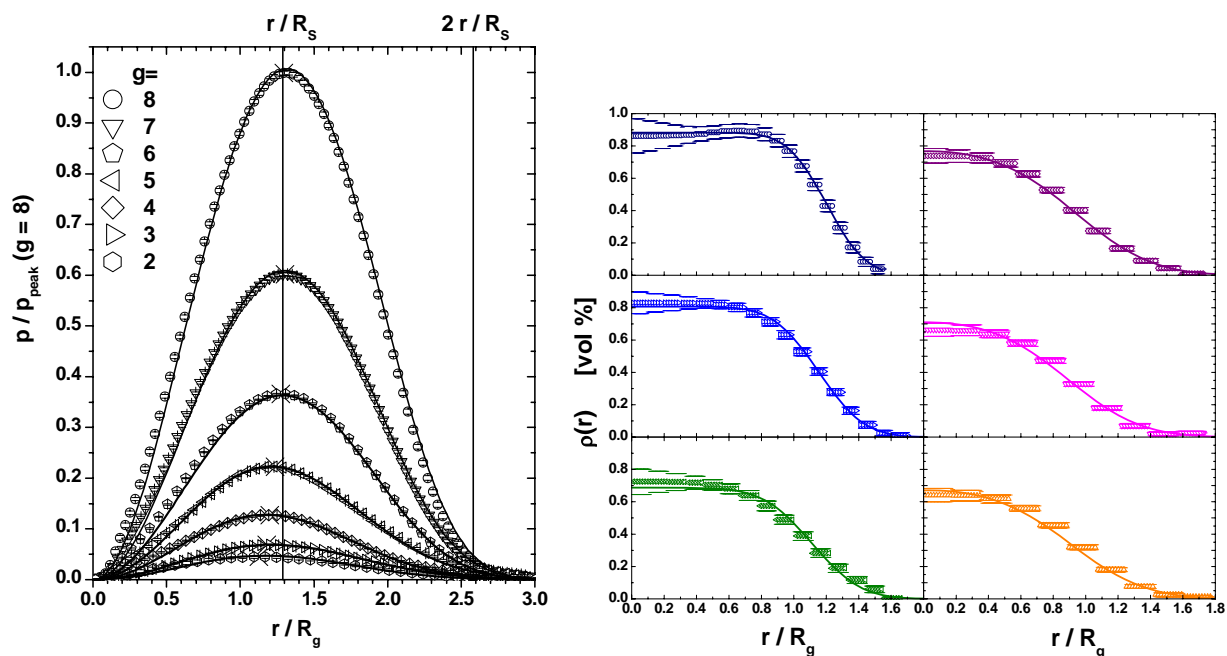
Note: average radii $\langle R_i \rangle$ also different

Compact polymers: dendrimers



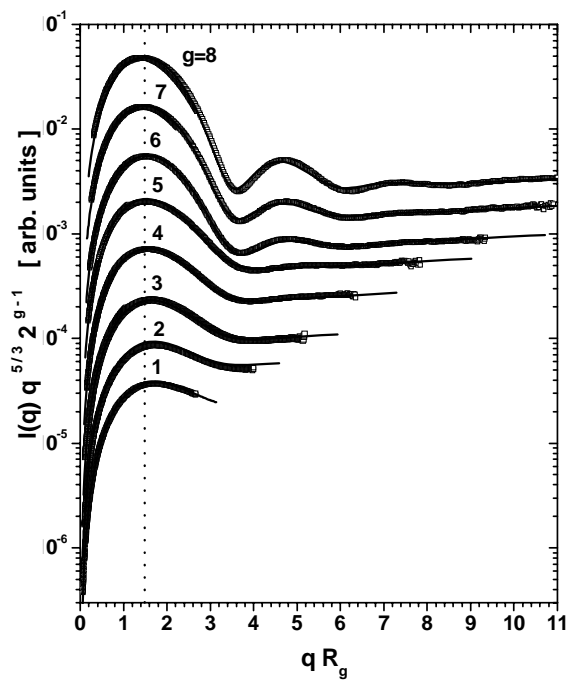
Density profiles and pair distance distribution functions

obtained from the SAXS spectra by inverse Fourier transformation and square-root deconvolution

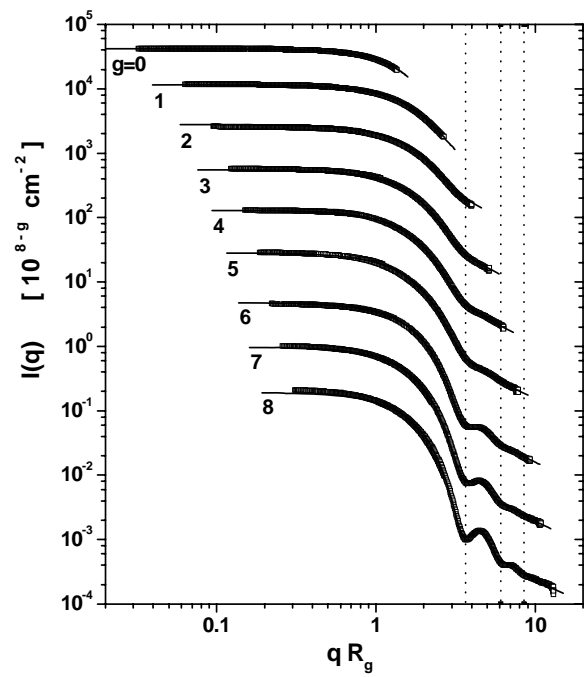


SAXS spectra

generalized Kratky presentation
(for good solvent conditions)



double logarithmic presentation



5.2 Dynamic scattering

During the collision the particles can loose or gain energy to the atom resulting in a change of the state of energy of the atom.

⇒ change of neutron energy \Leftrightarrow change of velocity

energy conservation $\Delta E = E_0 - E_1 = \hbar(\omega_0 - \omega_1) = \hbar\omega = \frac{\hbar^2}{2m_n}(k_0^2 - k_1^2)$

where m_n = neutron mass

momentum conservation $\Delta \vec{p} = \hbar \vec{q} = \hbar(\vec{k}_0 - \vec{k}_1)$

Experiments measure the fractions of neutrons scattered into a solid angle $d\Omega$ at a chosen scattering angle θ , and in a certain energy range dE relative to their initial intensity and energy.

⇒ double differential scattering cross section $\frac{d^2\sigma}{d\Omega dE} = \frac{dN}{d\Omega dt dE} \frac{1}{j_0}$

of particles scattered in a certain time interval dt in a certain solid angle element $d\Omega$ which experienced a certain energy change dE normalized to the flux of the incident beam.

in terms of the angular frequency change: $\frac{d^2\sigma}{d\Omega d\omega} = \hbar \frac{d^2\sigma}{d\Omega dE} = \frac{k_1}{k_0} \Delta K^2 S(q, \omega)$

$S(q, \omega)$ = dynamic structure factor contains information about the sample properties

Quasielastic scattering

$\frac{k_1}{k_0} \approx 1$, i.e. the energy transfer is small compared to energy of incident radiation

in terms of the time-dependent position vectors of the scattering units:

Fourier transform from time to frequency domain

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_1}{k_0} \Delta K^2 \frac{1}{2\pi} \sum_{ij} \int_{-\infty}^{\infty} \exp(-i\omega t) \left\langle \exp[-i\vec{q}(\vec{r}_i(0) - \vec{r}_j(t))] \right\rangle dt$$

for comparison static scattering: $\frac{d\sigma}{d\Omega} = \Delta K^2 \sum_{ij} \left\langle \exp[-i\vec{q}(\vec{r}_i - \vec{r}_j)] \right\rangle$

no experimental energy resolution \Leftrightarrow integration over all energies

Neutrons

split into incoherent and coherent dynamic scattering

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_1}{k_0} (\Delta b)^2 \underbrace{\frac{1}{2\pi} \sum_i \int_{-\infty}^{\infty} \exp(-i\omega t) \langle \exp[-i\vec{q}(\vec{r}_i(0) - \vec{r}_i(t))] \rangle dt}_{\text{Term II} = \underline{S}_{\text{inc}}(\mathbf{q}, \omega)}$$

$$+ \frac{k_1}{k_0} \langle b \rangle^2 \underbrace{\frac{1}{2\pi} \sum_{ij} \int_{-\infty}^{\infty} \exp(-i\omega t) \langle \exp[-i\vec{q}(\vec{r}_i(0) - \vec{r}_j(t))] \rangle dt}_{\text{Term I} = \underline{S}_{\text{coh}}(\mathbf{q}, \omega)}$$

Term I incoherent scattering
contains information about dynamics of an individual scattering unit.

Term II coherent scattering
contains information about relative motions of different scattering units located at positions \vec{r}_i and \vec{r}_j ($i \neq j$) but it also contains the self-correlation terms ($i=j$) containing information about dynamics of an individual scattering unit.

Intermediate structure factor denotes the dynamic structure factor as a function of time

$$S_{\text{inc}}(\mathbf{q}, t) = \sum_i \langle \exp[-i\vec{q}(\vec{r}_i(0) - \vec{r}_i(t))] \rangle dt$$

$$S_{\text{coh}}(\mathbf{q}, t) = \sum_{ij} \langle \exp[-i\vec{q}(\vec{r}_i(0) - \vec{r}_j(t))] \rangle dt$$

van Hove correlation function (in analogy to pair correlation of static scattering!)

$$\text{time dependent local density } n_j(\vec{r}', t) = \sum_{j=1}^N \delta(\vec{r}' - \vec{r}_j(t)) \text{ and } n_i(\vec{r}' - \vec{r}, t) = \sum_{i=1}^N \delta(\vec{r}' - \vec{r} - \vec{r}_i(t))$$

$$G_{ij}(\vec{r}', \vec{r}, t) = \langle n_i(\vec{r}' - \vec{r}, 0) n_j(\vec{r}', t) \rangle = \sum_{i,j=1}^N \langle \delta(\vec{r}' - \vec{r} - \vec{r}_i(0)) \delta(\vec{r}' - \vec{r}_j(t)) \rangle$$

convolution integral \Rightarrow **van Hove pair-correlation function** (*)

$$G_{ij}(\vec{r}, t) = \int_{-\infty}^{\infty} d\vec{r}' G_{ij}(\vec{r}', \vec{r}, t) = \int_{-\infty}^{\infty} d\vec{r}' \langle n_i(\vec{r}' - \vec{r}, 0) n_j(\vec{r}', t) \rangle = \sum_{i,j=1}^N \int_{-\infty}^{\infty} d\vec{r}' \langle \delta(\vec{r}' - \vec{r} - \vec{r}_i(0)) \delta(\vec{r}' - \vec{r}_j(t)) \rangle$$

with the definition of the delta-function

$$\delta(\vec{r}' - \vec{r} - \vec{r}_i(0)) = \int_{-\infty}^{\infty} \frac{d\vec{q}'}{(2\pi)^3} \exp[-i\vec{q}'(\vec{r}' - \vec{r} - \vec{r}_i(0))]$$

$$\delta(\vec{r}' - \vec{r}_j(t)) = \int_{-\infty}^{\infty} \frac{d\vec{q}}{(2\pi)^3} \exp[-i\vec{q}(\vec{r}' - \vec{r}_j(t))]$$

integral over \vec{r} can be executed:

$$\begin{aligned}
 G_{ij}(\vec{r}, t) &= \sum_{i,j=1}^N \int \frac{d\vec{q}'}{(2\pi)^3} \int \frac{d\vec{q}}{(2\pi)^3} \left\langle \exp[i\vec{q}'(\vec{r} + \vec{r}_i(0))] \exp[i\vec{q}\vec{r}_j(t)] \right\rangle \underbrace{\int d\vec{r}' \exp[-i(\vec{q} + \vec{q}')\vec{r}']}_{(2\pi)^3 \delta(\vec{q} + \vec{q}')} \\
 &= \sum_{i,j=1}^N \frac{1}{(2\pi)^3} \int d\vec{q}' \int d\vec{q} \delta(\vec{q} + \vec{q}') \exp[i\vec{q}'\vec{r}] \left\langle \exp[i\vec{q}'\vec{r}_i(0)] \exp[i\vec{q}\vec{r}_j(t)] \right\rangle \\
 &= \int \frac{d\vec{q}}{(2\pi)^3} \exp[-i\vec{q}\vec{r}] \underbrace{\sum_{i,j=1}^N \left\langle \exp[-i\vec{q}(\vec{r}_i(0) - \vec{r}_j(t))] \right\rangle}_{S_{\text{coh}}(\vec{q}, t)}
 \end{aligned}$$

$$\Rightarrow G_{ij}(\vec{r}, t) = \int \frac{d\vec{q}}{(2\pi)^3} \exp[-i\vec{q}\vec{r}] S_{\text{coh}}(\vec{q}, t)$$

$$\Rightarrow S_{\text{coh}}(\vec{q}, t) = \int \frac{d\vec{r}}{2\pi} \exp[i\vec{q}\vec{r}] G_{ij}(\vec{r}, t)$$

$$\Rightarrow S_{\text{coh}}(\vec{q}, \omega) = \int \frac{d\vec{r}}{2\pi} \int dt \exp[i(\vec{q}\vec{r} - \omega t)] G_{ij}(\vec{r}, t)$$

$S_{\text{coh}}(\vec{q}, t)$ is the Fourier transform ($\vec{r} \rightarrow \vec{q}$) and $S_{\text{coh}}(\vec{q}, \omega)$ the double Fourier transform ($\vec{r} \rightarrow \vec{q}, t \rightarrow \omega$) of the van Hove pair-correlation function

in an analogous manner the **van Hove self-correlation function** can be defined

$$\begin{aligned}
 G_{ii}(\vec{r}', \vec{r}, t) &= \sum_{i=1}^N \int d\vec{r}' \left\langle \delta(\vec{r}' - \vec{r} - \vec{r}_i(0)) \delta(\vec{r}' - \vec{r}_i(t)) \right\rangle \\
 \Rightarrow S_{\text{inc}}(\vec{q}, t) &= \int \frac{d\vec{r}}{2\pi} \exp[i\vec{q}\vec{r}] G_{ii}(\vec{r}, t) \\
 \Rightarrow S_{\text{inc}}(\vec{q}, \omega) &= \int \frac{d\vec{r}}{2\pi} \int dt \exp[i(\vec{q}\vec{r} - \omega t)] G_{ii}(\vec{r}, t)
 \end{aligned}$$

from the definition of the correlation functions a descriptive meaning can be derived:

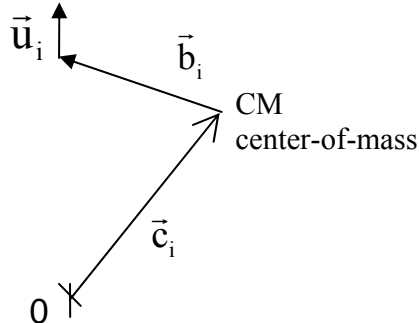
$$G_{ij}(\vec{r}, t) = \int d\vec{r}' \left\langle n_i(\vec{r}' - \vec{r}, 0) n_j(\vec{r}', t) \right\rangle$$

- (I) The self-correlation function G_{ii} gives the probability to find a scattering unit in the volume element $d\vec{r}$ at location \vec{r} at time t if the same scattering unit was at position $\vec{r}=0$ at time $t=0 \Rightarrow S_{\text{inc}}$ yields information about the motion of a single scattering unit.
- (II) The pair-correlation function G_{ij} gives the probability to find a scattering unit in the volume element $d\vec{r}$ at location \vec{r} at time t if another or the same scattering unit was at time $t=0$ at position $\vec{r}=0$. G_{ii} contains also the self-correlation $i=j \Rightarrow S_{\text{coh}}$ yields information about relative motions of the scattering units but also about the self-correlation.

Inelastic scattering: translation, rotation, vibration

$$S(\mathbf{q}, t) = \sum_{ij} \left\langle \exp \left[-i\mathbf{q}(\vec{r}_i(0) - \vec{r}_j(t)) \right] \right\rangle$$

time dependent position vectors: $\vec{r}_i(t) = \vec{b}_i(t) + \vec{c}_i(t) + \vec{u}_i(t)$



$\vec{c}_i(t)$ = center-of-mass (CM) coordinate
 $\vec{b}_i(t)$ = rotations around the CM
 $\vec{u}_i(t)$ = distance from its average position

$$\Rightarrow S(\mathbf{q}, t) = \sum_{ij} \left\langle \exp \left[-i\mathbf{q}(\vec{c}_i(0) - \vec{c}_j(t)) \right] \exp \left[-i\mathbf{q}(\vec{b}_i(0) - \vec{b}_j(t)) \right] \exp \left[-i\mathbf{q}(\vec{u}_i(0) - \vec{u}_j(t)) \right] \right\rangle$$

Assumption: the three vectors are independent
 (time domains are well separated, approximation for rotation and vibration)

$$S(\mathbf{q}, t) = \sum_{ij} \left\langle \exp \left[-i\mathbf{q}(\vec{c}_i(0) - \vec{c}_j(t)) \right] \right\rangle \cdot \left\langle \exp \left[-i\mathbf{q}(\vec{b}_i(0) - \vec{b}_j(t)) \right] \right\rangle \cdot \left\langle \exp \left[-i\mathbf{q}(\vec{u}_i(0) - \vec{u}_j(t)) \right] \right\rangle$$

$$S(\mathbf{q}, t) = \sum_{ij} \underbrace{S_{ij}^{\text{trans}}(\vec{q}, t)}_{\text{translation}} \cdot \underbrace{S_{ij}^{\text{rot}}(\vec{q}, t)}_{\text{rotation}} \cdot \underbrace{S_{ij}^{\text{vib}}(\vec{q}, t)}_{\text{vibration}}$$

For example:

If the rotational or vibrational motions are absent, $\vec{b}_i(t)$ or $\vec{u}_i(t)$ is zero and S_{ij}^{rot} or S_{ij}^{vib} equal to unity. For incoherent scattering $i=j \Rightarrow$ the double sum reduces to a simple summation.

Translational motion - free diffusion

Assumption: no vibrational or rotational motion $S_{ij}^{\text{rot}} = S_{ij}^{\text{vib}} = 1$

For example:

gas of rigid particles or large Brownian particles diffusing in a structureless solvent

random walk: $\left\langle [c_i(t) - c_i(0)]^2 \right\rangle = 6Dt$ (Einstein relation)

where D = translational CM diffusion coefficient

Incoherent scattering - intermediate structure factor

In the time domain

$$S_{\text{inc}}^{\text{trans}}(\mathbf{q}, t) = \sum_i \left\langle \exp[-i\mathbf{q}(\bar{c}_i(0) - \bar{c}_i(t))] \right\rangle = \sum_i \int_V \exp[-i\mathbf{q}\Delta\bar{c}_i(t)] \cdot \Phi(\Delta\bar{c}_i(t)) d\Delta\bar{c}_i(t)$$

where $\Delta\bar{c}_i(t) = \bar{c}_i(0) - \bar{c}_i(t)$

Brownian motion is in analogy to the Gaussian chain a random walk

⇒ Gaussian probability distribution for $\Delta\bar{c}_i(t)$

$$\Phi(c_i(t) - c_i(0)) = \left(\frac{3}{2\pi \langle \Delta\bar{c}_i(t)^2 \rangle} \right)^{3/2} \exp\left(-\frac{3}{2} \frac{\Delta\bar{c}_i(t)^2}{\langle \Delta\bar{c}_i(t)^2 \rangle} \right)$$

$S_{\text{inc}}^{\text{trans}}(\mathbf{q}, t)$ is sum of Fourier transforms of Gaussian functions

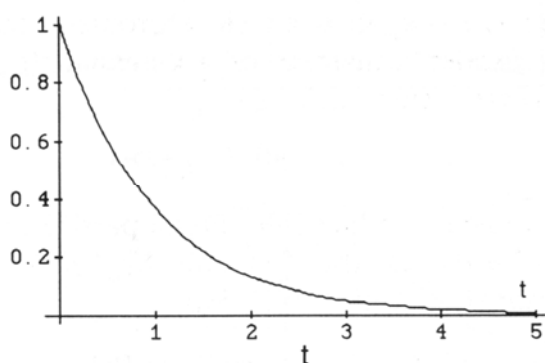
$$S_{\text{inc}}^{\text{trans}}(\mathbf{q}, t) = \sum_i \exp\left[-\langle \Delta\bar{c}_i(t)^2 \rangle \frac{q^2}{6} \right] = n \exp(-q^2 Dt)$$

$$\frac{S_{\text{inc}}^{\text{trans}}(\mathbf{q}, t)}{S_{\text{inc}}^{\text{trans}}(\mathbf{q}, t=0)} = \exp(-q^2 Dt) = \exp(-\Gamma t)$$

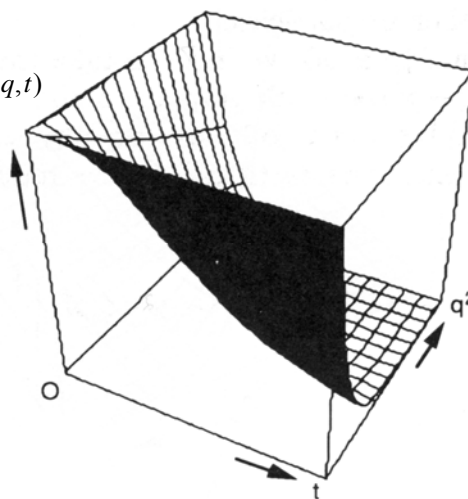
exponential decay

with $\Gamma = q^2 D = \tau^{-1}$ is the relaxation rate with unit [1/time] and $\tau = \Gamma^{-1}$ is the relaxation time ⇒ decay becomes faster with increasing q (decreasing length scale)

$$\frac{S_{\text{inc}}^{\text{trans}}(q, t)}{S_{\text{inc}}^{\text{trans}}(q, 0)}$$



$$S_{\text{inc}}^{\text{trans}}(q, t)$$



In order to obtain sufficient decay of $S_{\text{inc}}^{\text{trans}}$ in the time and q range of the experiment $\Gamma t = q^2 Dt$ should be in the order of 1

The relaxation time Γ^{-1} can be obtained by plotting $\ln \left[\frac{S_{\text{inc}}^{\text{trans}}(q, t)}{S_{\text{inc}}^{\text{trans}}(q, t=0)} \right]$ versus t

⇒ the slope is equal to $-\Gamma$

In the frequency domain

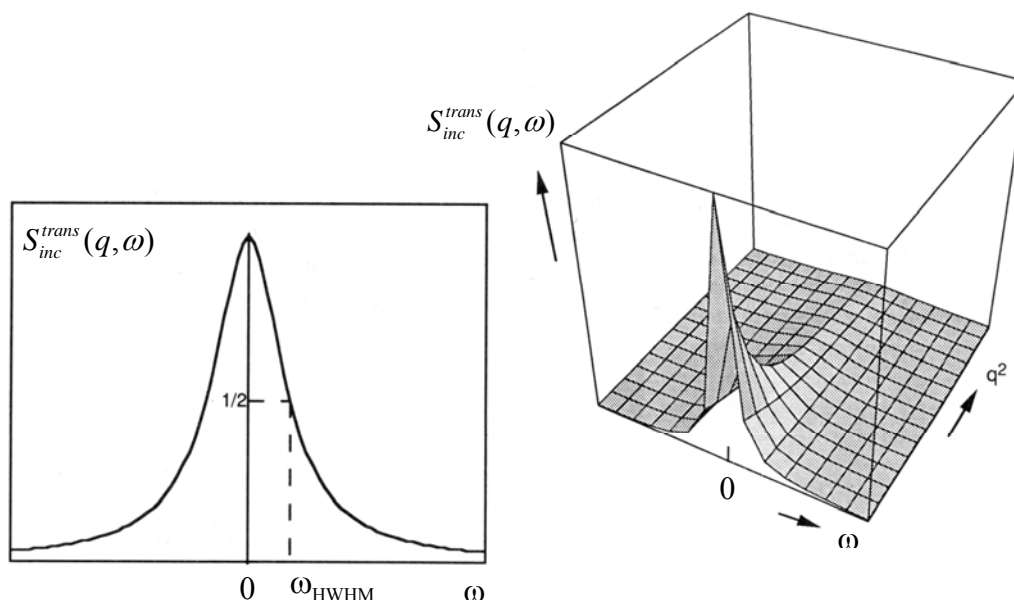
$S_{inc}^{trans}(q, \omega)$ is obtained from $S_{inc}^{trans}(q, t)$ by Fourier transform with respect to the variable t
 replace by $|t|$

$$S_{inc}^{trans}(q, \omega) = n \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp[-i\omega t] \exp[-\Gamma|t|] dt = n \operatorname{Re} \left\{ \frac{1}{\pi} \int_0^{\infty} \exp[-(i\omega + \Gamma)t] dt \right\}$$

$$S_{inc}^{trans}(q, \omega) = n \operatorname{Re} \left\{ \frac{1}{\pi} \frac{1}{\Gamma - i\omega} \right\} = \left\{ \frac{n}{\pi} \frac{\Gamma}{\Gamma^2 + \omega^2} \right\} = \left\{ \frac{n}{\pi} \frac{q^2 D}{(q^2 D)^2 + \omega^2} \right\} \quad \text{Lorentzian}$$

$S(q, \omega)$ is a delta function for $q \rightarrow 0$ and $\omega \rightarrow 0$

$$\text{else: } S(q, \omega = 0) = \frac{n}{\pi} \Gamma^{-1} = \frac{n}{\pi} q^{-2} D^{-1}$$



The curve is a Lorentzian with half-width-of-half maximum $\omega_{\text{HWHM}} = \Gamma$

$$S_{inc}^{trans}(q, \omega_{\text{HWHM}}) = \frac{1}{2} S_{inc}^{trans}(q, 0)$$

Coherent scattering

In dilute solutions inter-particle interferences can be neglected \Rightarrow structure factor goes to 1 and scattering reduces to n times contribution of one molecule.

If one neglects rotations/ vibrations/relaxations: each point of the molecule ($0 \leq k \leq N$) which has been at time $t=0$ at $\vec{c}_k(0)$ will be at time $t>0$ at $\vec{c}_k(t) = \vec{c}_k(0) + \Delta\vec{c}(t)$ where $\Delta\vec{c}$ is the CM displacement during this time of the whole molecule.

$$S_{\text{coh}}^{\text{trans}}(\mathbf{q}, t) = n \sum_k \sum_l \exp[-i\mathbf{q}(\bar{\mathbf{c}}_k(0) - \bar{\mathbf{c}}_l(t))] = n \sum_k \sum_l \exp[-i\mathbf{q}(\bar{\mathbf{c}}_k(0) - \bar{\mathbf{c}}_l(0) - \Delta\bar{\mathbf{c}}(t))] \\ = n \exp(-i\mathbf{q}\Delta\bar{\mathbf{c}}(t)) \sum_k \sum_l \exp[-i\mathbf{q}(\bar{\mathbf{c}}_k(0) - \bar{\mathbf{c}}_l(0))]$$

taking averages:

$$S_{\text{coh}}^{\text{trans}}(\mathbf{q}, t) = N^2 P(\mathbf{q}) \underbrace{\langle \exp(-i\mathbf{q}\Delta\bar{\mathbf{c}}(t)) \rangle}_{\text{for random walk}} \underbrace{\left\langle \sum_k \sum_l \exp[-i\mathbf{q}(\bar{\mathbf{c}}_k(0) - \bar{\mathbf{c}}_l(0))] \right\rangle}_{= N^2 P(\mathbf{q})} = n N^2 P(\mathbf{q}) \exp(-q^2 Dt) \\ = \exp\left(-\frac{1}{6} \bar{q}^2 \langle \Delta\bar{\mathbf{c}}(t)^2 \rangle\right)$$

True only for rigid objects. For polymers conformational changes as a function of time have to be considered (internal relaxations)

However, the formula shows that dynamic coherent scattering can only be measured in a q -range where there is sufficient coherent signal in a static experiment.

Rotational motion

simple example: scattering unit can take two positions $\bar{\mathbf{r}}_1$ and $\bar{\mathbf{r}}_2$ jumping through energy barrier from $1 \rightarrow 2$ and from $2 \rightarrow 1$

$p(\bar{\mathbf{r}}, t)$ = probability of finding scattering unit at time t in one of the possible positions

$$p(\bar{\mathbf{r}}_1, t) + p(\bar{\mathbf{r}}_2, t) = 1 \quad (*)$$

rate equations:

$$\frac{d}{dt} [p(\bar{\mathbf{r}}_1, t)] = -\frac{1}{\tau} p(\bar{\mathbf{r}}_1, t) + \frac{1}{\tau} p(\bar{\mathbf{r}}_2, t) \\ \frac{d}{dt} [p(\bar{\mathbf{r}}_2, t)] = -\frac{1}{\tau} p(\bar{\mathbf{r}}_2, t) + \frac{1}{\tau} p(\bar{\mathbf{r}}_1, t)$$

rate constant $1/\tau$ is the same for jump $2 \rightarrow 1$ and $1 \rightarrow 2$

$$\text{with } (*) \Rightarrow \frac{d}{dt} [p(\bar{\mathbf{r}}_1, t)] = \frac{1}{\tau} [1 - 2p(\bar{\mathbf{r}}_1, t)]$$

solution for differential equation with initial condition $p(\bar{\mathbf{r}}_1, t=0) = 1$ and $p(\bar{\mathbf{r}}_2, t=0) = 0$

$$\Rightarrow p(\bar{\mathbf{r}}_1, t) = \frac{1}{2} \left[1 + \exp\left(-2\frac{t}{\tau}\right) \right] \\ p(\bar{\mathbf{r}}_2, t) = \frac{1}{2} \left[1 - \exp\left(-2\frac{t}{\tau}\right) \right]$$

for $t \rightarrow \infty$ the probability for finding the scattering unit in 1 or 2 identical ($p = 1/2$)

in this simple example no correlation between different scattering units

$$\Rightarrow \text{incoherent scattering } S_{\text{inc}}^{\text{rot}}(\mathbf{q}, t) = n \sum_i \langle \exp(-i\mathbf{q}(\bar{\mathbf{r}}_i(0) - \bar{\mathbf{r}}_i(t))) \rangle \quad (**)$$

$$p(\bar{\mathbf{r}}_1, t, \bar{\mathbf{r}}_1, 0) = \frac{1}{2} \left[1 + \exp\left(-2\frac{t}{\tau}\right) \right] \quad (\text{I})$$

$$p(\bar{\mathbf{r}}_2, t, \bar{\mathbf{r}}_1, 0) = \frac{1}{2} \left[1 - \exp\left(-2\frac{t}{\tau}\right) \right] \quad (\text{II})$$

four possible states:

$$p(\bar{\mathbf{r}}_2, t, \bar{\mathbf{r}}_2, 0) = \frac{1}{2} \left[1 + \exp\left(-2\frac{t}{\tau}\right) \right] \quad (\text{III})$$

$$p(\bar{\mathbf{r}}_1, t, \bar{\mathbf{r}}_2, 0) = \frac{1}{2} \left[1 - \exp\left(-2\frac{t}{\tau}\right) \right] \quad (\text{IV})$$

multiplying in (**) the contribution of each state to the sum by its probability and performing the averages yields

$$\Rightarrow n^{-1} S_{\text{inc}}^{\text{rot}}(\mathbf{q}, t) = \overbrace{\frac{1}{2} \left[1 + \exp\left(-2\frac{t}{\tau}\right) \right]}^{\text{I } 1-1} + \overbrace{\langle \exp[-i\mathbf{q}(\bar{\mathbf{r}}_1(0) - \bar{\mathbf{r}}_2(t))] \rangle \left[1 - \exp\left(-2\frac{t}{\tau}\right) \right]}^{\text{II } 1-2} \\ + \overbrace{\frac{1}{2} \left[1 + \exp\left(-2\frac{t}{\tau}\right) \right]}^{\text{III } 2-2} + \overbrace{\langle \exp[-i\mathbf{q}(\bar{\mathbf{r}}_2(0) - \bar{\mathbf{r}}_1(t))] \rangle \left[1 - \exp\left(-2\frac{t}{\tau}\right) \right]}^{\text{IV } 2-1}$$

$$n^{-1} S_{\text{inc}}^{\text{rot}}(\mathbf{q}, t) = A_0(\bar{q}) + A_1(\bar{q}) \exp(-2t/\tau)$$

$$\text{with } A_0(\bar{q}) = \frac{1}{2} \left[1 + \cos[\bar{q}(\bar{\mathbf{r}}_1 - \bar{\mathbf{r}}_2)] \right] \quad \bar{\mathbf{r}}_1(0) - \bar{\mathbf{r}}_2(0) = \bar{\mathbf{r}}_1(t) - \bar{\mathbf{r}}_2(t)$$

$$\text{and } A_1(\bar{q}) = \frac{1}{2} \left[1 - \cos[\bar{q}(\bar{\mathbf{r}}_1 - \bar{\mathbf{r}}_2)] \right]$$

for an isotropic sample take average over all orientations

$$\Rightarrow A_0(\bar{q}) = A_0(q) = \frac{1}{2} \left[1 + \frac{\sin(qd)}{qd} \right] = \frac{1}{2} [1 + J_0(qd)]$$

$$A_1(\bar{q}) = A_1(q) = \frac{1}{2} \left[1 - \frac{\sin(qd)}{qd} \right] = \frac{1}{2} [1 - J_0(qd)]$$

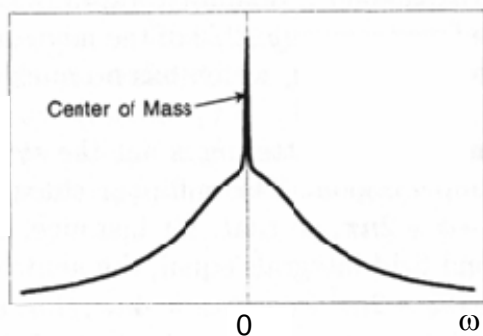
where $d = |\bar{\mathbf{r}}_1 - \bar{\mathbf{r}}_2|$, J_0 =zeroth order Bessel function

Fourier transform in respect to t

$$\Rightarrow n^{-1} S_{\text{inc}}^{\text{rot}}(\mathbf{q}, \omega) = \text{Re} \left\{ \frac{1}{\pi} \int_0^{\infty} \exp(-i\omega t) S(\mathbf{q}, |t|) dt \right\} = A_0(q) \delta(\omega) + A_1(q) \frac{1}{\pi} \underbrace{\frac{2\tau}{4 + \omega^2 \tau^2}}_{\text{Lorentzian}}$$

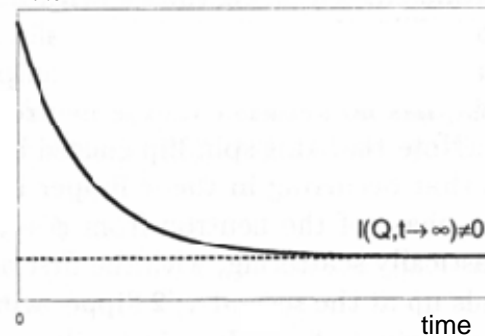
Rotational motion

$$S_{inc}^{rot}(q, \omega)$$



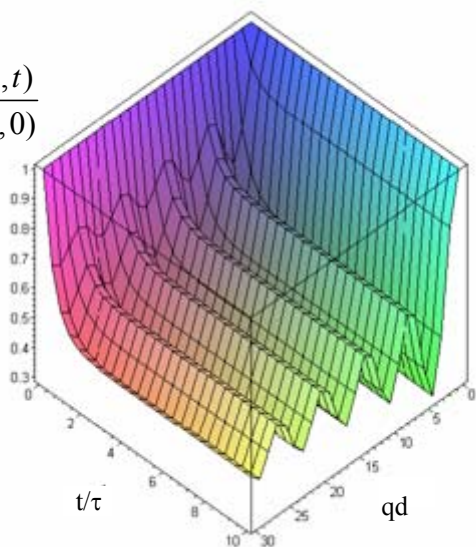
time domain

$$S_{inc}^{rot}(q, t)$$

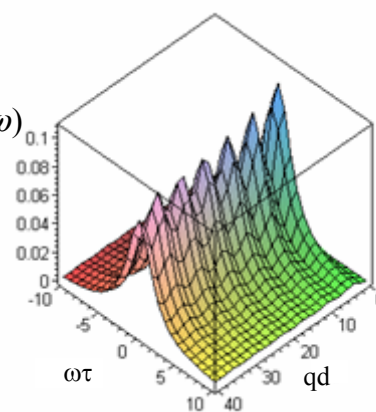


frequency domain

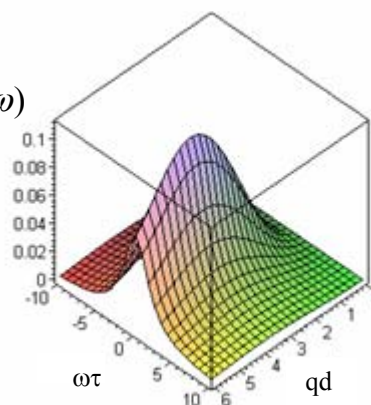
$$\frac{S_{inc}^{rot}(q, t)}{S_{inc}^{rot}(q, 0)}$$



$$S_{inc}^{rot}(q, \omega)$$



$$S_{inc}^{rot}(q, \omega)$$



scattered intensity is composed of two terms:

1. Elastic peak (delta-function) due to absence of center-of-mass diffusion \Rightarrow broadening as result of the imperfections of the instrumentation (limited resolution) and results of the translational motion
2. Lorentzian as contribution from rotation. The intensity of the rotational contribution depends on q . For $q \rightarrow 0$ only elastic peak remains but for $q \geq 1$ the second peak gives significant contribution. For the half-width-of-half maximum $\omega_{\text{HWHM}} = 2/\tau$ is obtained.

$$(S_{\text{inc}}^{\text{rot}}(q, \omega_{\text{HWHM}})) = \frac{1}{2} S_{\text{inc}}^{\text{rot}}(q, 0)$$

Vibrational motion

$$S^{\text{vib}}(q, t) = \sum_{ij} \left\langle \exp \left[-i\vec{q} \left[\vec{u}_i(0) - \vec{u}_j(t) \right] \right] \right\rangle = \sum_{ij} S_{ij}^{\text{vib}}(q, t)$$

series expansion of the exponential function

$$S_{ij}^{\text{vib}}(q, t) = \left\langle \exp \left[-i\vec{q} \left[\vec{u}_i(0) - \vec{u}_j(t) \right] \right] \right\rangle = 1 - i \left\langle \vec{q} \left[\vec{u}_i(0) - \vec{u}_j(t) \right] \right\rangle - \frac{1}{2} \left\langle \left[\vec{q} \left[\vec{u}_i(0) - \vec{u}_j(t) \right] \right]^2 \right\rangle \dots$$

linear term \vec{q} vanishes since the orientations of \vec{u} and \vec{q} are not correlated

$$\begin{aligned} S_{ij}^{\text{vib}} &= 1 - \frac{1}{2} \left\langle (\vec{q}\vec{u}_i(0))^2 + (\vec{q}\vec{u}_j(t))^2 - 2\vec{q}\vec{u}_i(0)\vec{q}\vec{u}_j(t) \right\rangle \\ &= 1 - \frac{1}{2} \left\langle (\vec{q}\vec{u}_i(0))^2 \right\rangle + \frac{1}{2} \left\langle (\vec{q}\vec{u}_j(t))^2 \right\rangle - \left\langle \vec{q}\vec{u}_i(0)\vec{q}\vec{u}_j(t) \right\rangle \\ &= 1 - \left\langle (\vec{q}\vec{u}_i)^2 \right\rangle + \left\langle \vec{q}\vec{u}_i(0)\vec{q}\vec{u}_j(t) \right\rangle \\ &\approx \exp \left[-\left\langle (\vec{q}\vec{u}_i)^2 \right\rangle + \left\langle \vec{q}\vec{u}_i(0)\vec{q}\vec{u}_j(t) \right\rangle \right] \end{aligned}$$

$$\Rightarrow S^{\text{vib}}(q, t) = \sum_{ij} \underbrace{\exp \left[-\left\langle (\vec{q}\vec{u}_i)^2 \right\rangle \right]}_{\text{Debye-Waller effect}} \exp \left[\underbrace{\left\langle \vec{q}\vec{u}_i(0)\vec{q}\vec{u}_j(t) \right\rangle}_{\text{true inelastic term}} \right]$$

Debye-Waller effect

Vibrations decrease the amplitude of the static peaks even at $T=0$ there is a residual quantum energy

If all scattering units have the same vibration amplitude, then

$$S_{ij}^{\text{vib}}(\mathbf{q}, t) = \underbrace{\exp\left[-\langle(\bar{q}\bar{u}_i)^2\rangle\right]}_{(a)} \sum_{ij} \exp\left[\langle\bar{q}\bar{u}_i(0)\bar{q}\bar{u}_j(t)\rangle\right] = \exp(-2W) \sum_{ij} \exp\left[\langle\bar{q}\bar{u}_i(0)\bar{q}\bar{u}_j(t)\rangle\right]$$

(a) in isotropic case = $\exp\left(-q^2\langle\bar{u}^2\rangle/3\right)$ since $\langle\cos^2\theta\rangle = 1/3$ in 3 dimensions

W = Debye-Waller factor where the factor 2 comes from the fact that in general $\langle u_i^2 \rangle \neq \langle u_j^2 \rangle$

$$\Rightarrow S_{ij}^{\text{vib}}(\mathbf{q}, t) = \sum_{ij} \exp\left(-\left(W_i + W_j\right)\right) \exp\left[\langle\bar{q}\bar{u}_i(0)\bar{q}\bar{u}_j(t)\rangle\right]$$

significant decrease of the static peaks if $q^2\langle u^2 \rangle \geq 1$

- since in most problems concerning polymers one works at rather small q values \Rightarrow Debye-Waller corrections are negligible

- in the frame work of the classical harmonic oscillator in 3 dim $E = \frac{3}{2}k_B T = \frac{m\langle v^2 \rangle}{2}$
 $\langle v^2 \rangle =$ averaged square of the oscillator velocity

relation between velocity and amplitude with $\omega =$ angular frequency of oscillator

$$\langle u^2 \rangle = \langle v^2 \rangle / \omega^2 \Rightarrow W = \frac{k_B T q^2}{2m\omega^2}$$

Inelastic scattering

$$S^{\text{vib}}(\mathbf{q}, t) = \exp(-2w) \underbrace{\sum_{ij} \exp\left[\langle\bar{q}\bar{u}_i(0)\bar{q}\bar{u}_j(t)\rangle\right]}_{(I)} \quad (I) \approx 1 + \langle\bar{q}\bar{u}_i(0)\bar{q}\bar{u}_j(t)\rangle \quad (\text{first order})$$

independent scattering units: $\bar{u}_i(0)$ and $\bar{u}_j(t)$ are not correlated unless $i=j$

\Rightarrow incoherent scattering!

$$\Rightarrow S_{\text{inc}}^{\text{vib}}(\mathbf{q}, t) = \exp(-2w) \sum_i \left(1 + \langle\bar{q}\bar{u}_i(0)\bar{q}\bar{u}_i(t)\rangle\right) \approx n \exp(-2w) \left[1 + q^2\langle u^2 \rangle \cos(\omega_v t)\right],$$

where ω_v is the circular frequency fo the oscillator

\Rightarrow to calculate $S_{\text{inc}}^{\text{vib}}(q\omega)$ do inverse Fourier transform (FT) of t into ω and write

$$\cos(\omega_v t) = \frac{1}{2} \left[\exp(i\omega_v t) + \exp(-i\omega_v t) \right]$$

$$S_{\text{inc}}^{\text{vib}}(\mathbf{q}, \omega) = n \exp(-2W) \underbrace{\frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(i\omega t) \left[1 + \frac{q^2 \langle u^2 \rangle}{2} [\exp(i\omega_v t) + \exp(-i\omega_v t)] \right] dt}_{\text{FT}}$$

⇒ with definition of the delta-function

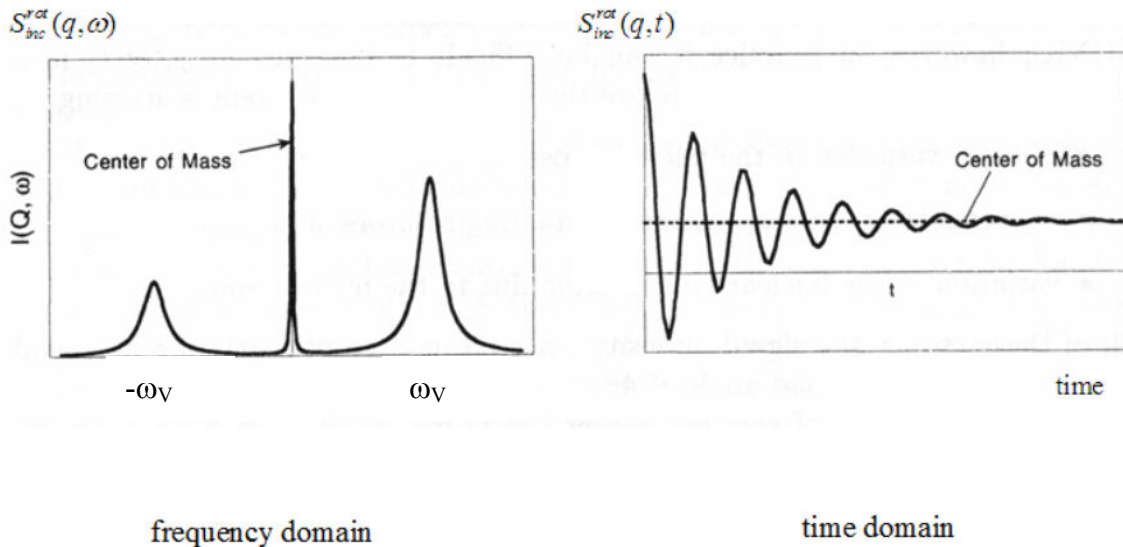
$$\text{FT} = \delta(\omega) + \frac{q^2 \langle u^2 \rangle}{2} [\delta(\omega + \omega_v) + \delta(\omega - \omega_v)]$$

$$S_{\text{inc}}^{\text{vib}}(\mathbf{q}, \omega) = n \exp(-2W) \left[\underbrace{\delta(\omega)}_{\text{(i)}} + \frac{q^2 \langle u^2 \rangle}{2} \left[\underbrace{\delta(\omega + \omega_v)}_{\text{(ii)}} + \underbrace{\delta(\omega - \omega_v)}_{\text{(iii)}} \right] \right]$$

- (i) elastic scattering
- (ii) scattering probe absorbs a phonon
- (iii) scattering probe creates a phonon

peaks are broadened by (1) experimental resolution
(2) other inelastic processes such as translational motion or rotations

Vibrational motion



Peaks for vibration creation and annihilation are asymmetric in respect to the peak height. Vibration creation has an higher probability than vibration annihilation.

e.g. at T=0 initial state before scattering: no vibration ⇒ only vibration creation possible

initial states are distributed according to their thermal weights

$$p_i(T) = \frac{\exp\left(-E_i/k_B T\right)}{\sum_k \exp\left(-E_k/k_B T\right)}$$

according to Bose-Einstein statistics (detailed equilibrium)

$$\Rightarrow S(\mathbf{q}, \omega) = \exp\left(\hbar\omega/k_B T\right) S(-\mathbf{q}, -\omega)$$

Coherent scattering

correlated vibrational motions

\Rightarrow phonons propagating through crystalline materials

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E}\right)_{\text{coh}} = \frac{k_1}{k_0} \sum_{ij} k_i k_j \exp[-i\vec{q}(\vec{c}_i - \vec{c}_j)] \exp[-\omega_i - \omega_j] \int_{-\infty}^{\infty} dt \exp(-i\omega t) [1 + \langle \vec{q}\vec{u}_i(0) \cdot \vec{q}\vec{u}(t) \rangle]$$

(I) Center-of-mass term is not equal to 1 \Rightarrow pattern of Bragg diffraction spots where each spot corresponds to $\vec{q} = \vec{\sigma}$ with $\vec{\sigma}$ = reciprocal lattice vector; $\sigma = 2\pi/a$ where a = lattice plane spacing along a certain symmetric direction.

(II) Phonon passes through the crystal \Rightarrow atoms are displaced from rest position and sequential planes are displaced by varying amounts corresponding to the phase of the propagating phonon.

\Rightarrow some intensity of the Bragg spots is shifted by \vec{k} being the wave vector of the phonon with frequency $\omega(\vec{k})$

\Rightarrow result:

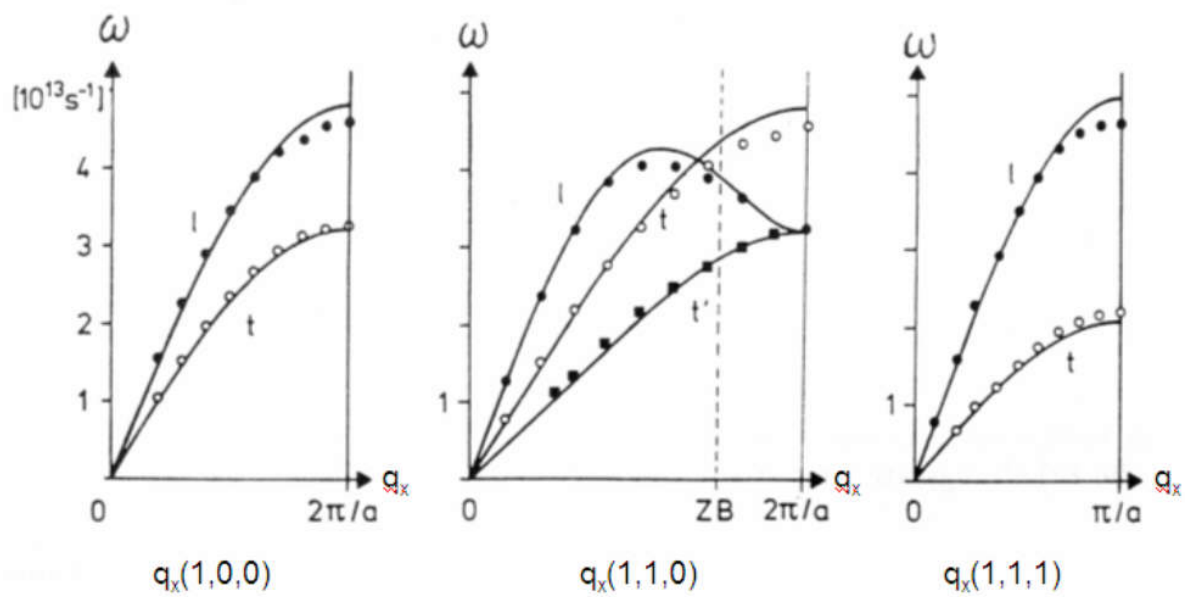
each delta-function $\delta(\omega - \omega_v)$ and $\delta(\omega + \omega_v)$ has to be multiplied by a second delta function to ensure momentum conservation

$$\delta(\vec{q} + \vec{k} - \sigma) \text{ or } \delta(\vec{q} - \vec{k} - \sigma) \text{ (similar to Ewald construction)}$$

$$\text{Energy conservation} \quad E_0 - E_1 = \hbar\omega(\vec{k})$$

$$\text{Momentum conservation} \quad \vec{q} = \vec{k}_0 - \vec{k}_1 = \vec{\sigma} \pm \vec{k}$$

Phonon dispersion



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