IX School of Neutron Scattering
"Francesco Paolo Ricci"

Application of Neutrons to Structural Determination in Soft Matter:
From Short and Medium Range Order to Wetting Processes

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Inelastic scattering effect in a diffraction experiment

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Scheme of the lecture

Short introduction to an idealized neutron diffraction experiment for a monatomic fluid
validity of the static approximation → no inelasticity effect

Description of a real neutron diffraction experiment focusing on the inelasticity effect

Presentation of possible methods used to correct the inelasticity effect:

First method:
Series expansion in power of m/M (Placzek, 1952)
for the measured differential scattering cross section
i) for a monatomic fluid on a stationary neutron source
ii) for a monatomic fluid on a pulsed neutron source
evidencing the sample and instrumental parameters that influence the inelasticity effect

Extension of the Placzek method to the molecular fluid

Second method:
Use of models or of experimental determination of the dynamics of the sample
(**model or measured S(Q, ω)**)
to calculate the differential scattering cross section

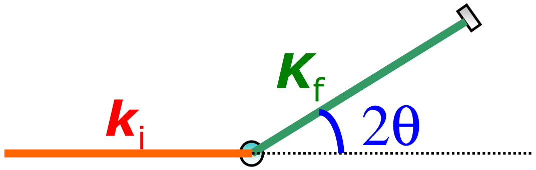
The physical quantity of interest to obtain information on the structure of a fluid is the static structure factor $S(Q)$:

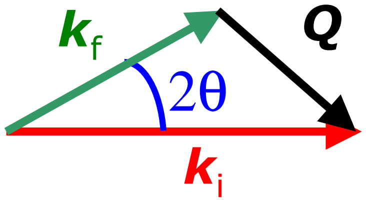
$$S(Q) = \int_{-\infty}^{+\infty} S(Q,\omega)\, d\omega$$

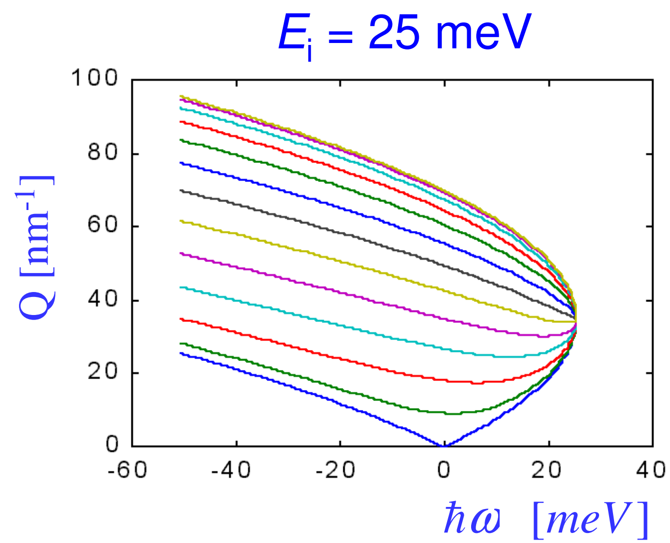
Kinematic conditions:

$$\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f \qquad Q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos(2\theta)$$

$$\hbar\omega = E_i - E_f \qquad (E_{i,f} = \frac{\hbar^2 k_{i,f}^2}{2m})$$







We consider an **idealized** neutron diffraction experiment on a reactor:
no container, very thin sample (negligible multiple scattering and attenuation),
"black" detectors (efficiency=1 for all energies).

The "measured" intensity I(θ) is simply related to the differential scattering cross section $\left.\frac{d\sigma}{d\Omega}\right|_{meas}$:

$$I(\theta) = N\Phi\Delta\Omega \left.\frac{d\sigma}{d\Omega}\right|_{meas} = N\Phi\Delta\Omega \underset{\text{constant } \theta}{\int_{-\infty}^{E_i/\hbar}} \frac{d^2\sigma}{d\omega d\Omega}(\theta)\, d\omega$$

The finite upper limit arises because the neutron cannot lose more than its incident energy to the sample

where (monatomic case)

$$\frac{d^2\sigma}{d\omega d\Omega} = \frac{\sigma_{coh}}{4\pi}\frac{k_f}{k_i}S(Q,\omega) + \frac{\sigma_{inc}}{4\pi}\frac{k_f}{k_i}S_{self}(Q,\omega)$$

If $k_f \approx k_i$ (***Static Approximation***) we have: $Q \approx Q_{el} = 2k_i \sin(\theta) \quad \hbar\omega << E_i$

θ=constant ⟷ Q=constant

$$\left.\frac{d\sigma}{d\Omega}\right|_{S.A.} = \underset{\theta\ \mathrm{constant}}{\int_{-\infty}^{E_i/\hbar}} \frac{d^2\sigma}{d\omega d\Omega} d\omega = \underset{Q\ \mathrm{constant}}{\int_{-\infty}^{+\infty}} \frac{d^2\sigma}{d\omega d\Omega} d\omega$$

$$\left.\frac{d\sigma}{d\Omega}\right|_{S.A.} = \underset{Q\ \mathrm{constant}}{\int_{-\infty}^{+\infty}} \cancel{\frac{k_f}{k_i}} \left[\frac{\sigma_{coh}}{4\pi} S(Q,\omega) + \frac{\sigma_{inc}}{4\pi} S_{self}(Q,\omega)\right] d\omega = \frac{\sigma_{coh}}{4\pi} S(Q) + \frac{\sigma_{inc}}{4\pi}$$

In the *Static Approximation*

the measured quantity $\frac{d\sigma}{d\Omega}$ **is simply related to the relevant physical quantity S(Q)**

Some comments on the Static Approximation …

Note that although the **Static Approximation** gives elastic scattering, the resulting cross section is not the same as the cross section for **true elastic scattering:**
the cross section for Static Approximation **includes scattering from all final states of the sample**,
the cross section for true elastic scattering **contains only terms with final state of the sample equals to initial state** (no change of energy in the sample)

In the **language of correlation functions,** we can say that **if the time, t_1, during which the neutron is in the interaction region is much shorter than the relaxation time, t_0,** then the **neutron has no time to feel the motions of the atoms of the system**.

It is as though an **instantaneous photograph** is taken of the positions of the atoms during the scattering. Hence the name, Static Approximation.

The **condition $t_1 << t_0$ is equivalent to $k_i \approx k_f$**.

Some comments on the Static Approximation ...(continued)

The Static Approximation assumes that the **scattering particles are rigidly bound**, so that **all exchange of energy between radiation and sample can be neglected**.

The condition for the **validity of the Static Approximation** is that the maximum energy that can be transferred to and from the scattering system, $\hbar\omega_{max}$, **is small compared to the energy of the incident neutron** E_i.

For **thermal neutron** the incident energy, E_i, **is comparable to** the excitation energy of the systems, $\hbar\omega$, and **departure from the Static Approximation** must be considered.

The **inelasticity correction** is simply the **difference between the quantity measured with** $\hbar\omega/E_i \neq 0$ **and the ideal result for** $\hbar\omega/E_i \to 0$

We consider now a **real** neutron diffraction experiment

We have to correct the measured intensity for:

- the **scattering of the environment** (container, furnace or cryostat)

- **attenuation**

- **multiple scattering**

- **other effects (normalization, resolution…)**

Here we suppose that all **these corrections have already been performed**

So, we deal with a **single scattering event**

BUT

the Static Approximation doesn't hold

(that is: the generic **scattering process is inelastic**)

First method

Series expansion in powers of m/M

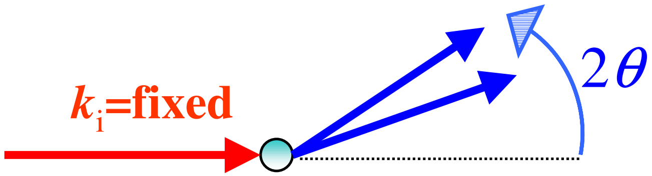
First case of first method:

inelasticity correction for

Monatomic systems on a Steady state source

Two axis diffractometer on a reactor (e.g. D4C at ILL):

The incoming neutron wavelength, $\lambda_i=2\pi/k_i$, is fixed and we measure the intensity as a function of the diffraction angle, 2θ, with no selection of the final energy, E_f.



$$Q_{el} = 2k_i \sin(\theta)$$

For simplicity, here we consider a **monatomic fluid**

Detector efficiency

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \int_{-\infty \atop \theta \text{ const}}^{E_i/\hbar} \frac{\varepsilon(k_f)}{\varepsilon(k_i)} \frac{k_f}{k_i} \left[\frac{\sigma_{coh}}{4\pi} S(Q,\omega) + \frac{\sigma_{inc}}{4\pi} S_{self}(Q,\omega)\right] d\omega$$

$$\neq \left.\frac{d\sigma}{d\Omega}\right|_{S.A.} = \frac{\sigma_{coh}}{4\pi} S(Q_{el}) + \frac{\sigma_{inc}}{4\pi}$$

First approach to estimate the inelasticity correction is due to Placzek in 1952

By the way: this is the reason why the inelasticity correction is also called Placzek correction

Method based on a power series expansion that can express the correction in terms of frequency moments of S(Q,ω)

PHYSICAL REVIEW VOLUME 86, NUMBER 3 MAY 1, 1952

The Scattering of Neutrons by Systems of Heavy Nuclei*†

G. PLACZEK
Institute for Advanced Study, Princeton, New Jersey

(Received December 20, 1951)

It is shown that the scattering of neutrons by a system of heavy nuclei may, for neutron energies that are large compared with the level separation of the system, be described in terms of averages of simple two-particle operators over the initial state. Expressions are derived for the total and differential cross sections and for the first few moments of the energy transfer. The expression for the cross section can be explicitly evaluated even for complicated scattering systems and leads to an accurate representation of the energy dependence of the nuclear scattering. The results are applied to the problem of the detection of small electronic contributions to the cross section.

See also: Yarnell et al. Phys. Rev. A **7**, 2130 (1973), Appendix A

Placzek gave a method of calculating the **correction to the static approximation**, valid when the mean value of ħω is small compared to the incident energy, E_i:

$$(\hbar\omega)_{mean} << E_i$$

Here, this method is developed for **atomic systems**
and with the atomic mass, M_a, heavy with respect to the neutron mass, m:

$$m/M_a << 1$$

Physically meaningful

For simplicity, Placzek considered the **detector efficiency** $\varepsilon(k_f)=1/k_f$, so that:

$$\varepsilon(k_f)/\varepsilon(k_i) * k_f / k_i = 1$$

He assumed that, **when ħω = E_i, S(Q,ω) is sufficiently small** for

the **upper limit of the integration in $(d\sigma/d\Omega)_{meas}$ to be extended to infinity**

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \int_{\substack{-\infty \\ \theta\ \text{const}}}^{E_i/\hbar} \frac{\varepsilon(k_f)}{\varepsilon(k_i)} \frac{k_f}{k_i} \left[\frac{\sigma_{coh}}{4\pi} S(Q,\omega) + \frac{\sigma_{inc}}{4\pi} S_{self}(Q,\omega)\right] d\omega =$$

$$= \int_{\substack{-\infty \\ \theta\ \text{const}}}^{+\infty} \left[\frac{\sigma_{coh}}{4\pi} S(Q,\omega) + \frac{\sigma_{inc}}{4\pi} S_{self}(Q,\omega)\right] d\omega$$

The method of Placzek consists of expanding the integrand in powers of $\boxed{x = \hbar\omega / E_i}$

The transformation of the integral is carried out in two steps:

First step

S(Q,ω), at a point on path II (θ=constant), **is obtained from a Taylor-series expansion of the dynamical structure factor about S(Q_{el},ω) with ω held constant,** where (Q_{el},ω) is a point on path I. **In this expansion S(Q,ω) is considered to be a function of Q^2.**

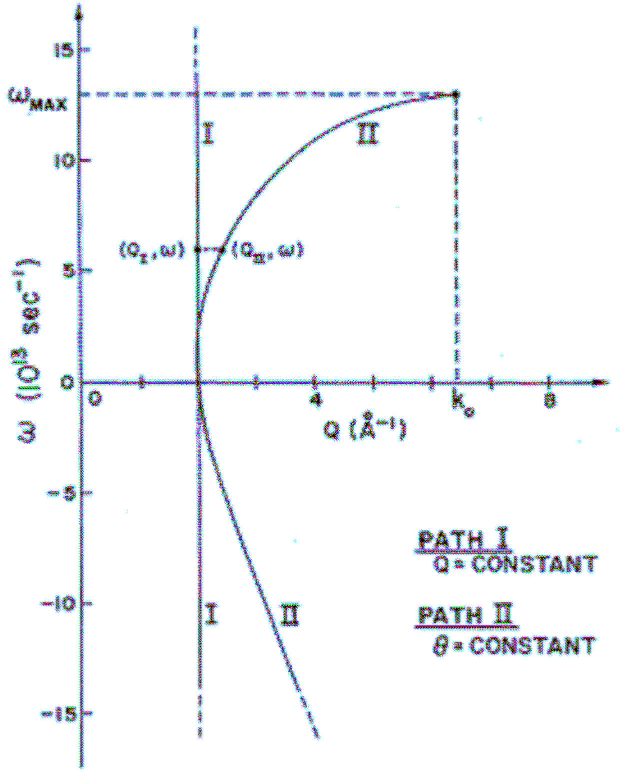


FIG. 8. Integration paths in Q-ω space. $S(Q)$ is defined by an integral along path I, whereas the experiment measures an integral along path II.

$$\boxed{S(Q,\omega) = S(Q_{el},\omega) + \left(\frac{\partial S(Q,\omega)}{\partial Q^2}\right)_{Q=Q_{el}} (Q^2 - Q_{el}^2) + \frac{1}{2!}\left(\frac{\partial^2 S(Q,\omega)}{\partial (Q^2)^2}\right)_{Q=Q_{el}} (Q^2 - Q_{el}^2)^2 + \ldots}$$

Same result holds for S$_{self}$(Q,ω)

Second step

Expansion of (Q^2- Q_{el}^2) in powers of x using the appropriate value of k_f for path II:

$$Q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos(2\theta)$$

Using $$Q_{el}^{\ 2} = 2k_i^2[1-\cos(2\theta)] \quad \Rightarrow \quad \boxed{\cos(2\theta) = \frac{2k_i^2 - Q_{el}^{\ 2}}{2k_i^2}}$$

$$x = \frac{E_i - E_f}{E_i} = \frac{k_i^2 - k_f^2}{k_i^2} \quad \Rightarrow \quad \boxed{k_f^2 = k_i^2(1-x)}$$

We have $$Q^2 - Q_{el}^{\ 2} = k_i^2 + \underline{k_i^2(1-x)} - 2k_i^2 \underline{\sqrt{(1-x)}}\, \underline{\frac{2k_i^2 - Q_{el}^{\ 2}}{2k_i^2}} - Q_{el}^{\ 2}$$

Expanding (1-x)$^{1/2}$ in series of x: $$\sqrt{(1-x)} = 1 - \frac{1}{2}x - \frac{1}{8}x^2 + \ldots$$

We arrive at the result of the second step

$$\boxed{Q^2 - Q_{el}^{\ 2} = -\frac{1}{2}Q_{el}^{\ 2}x + \frac{1}{8}(2k_i^2 - Q_{el}^{\ 2})x^2 + \ldots}$$

ENERGY CONSTRAINTS

$$\boxed{Q^2 - Q_{el}^{\ 2} = -\frac{1}{2} Q_{el}^{\ 2} x + \frac{1}{8}(2k_i^2 - Q_{el}^{\ 2}) x^2 + \ldots}$$

using $\boxed{Q_{el}^{\ 2} = 2k_i^2(1-\cos 2\theta)}$ **remembering** $x = \dfrac{\hbar\omega}{E_i}$

$$\boxed{\frac{Q^2}{Q_{el}^{\ 2}} = 1 - \frac{\hbar\omega}{2E_i} + \frac{1}{2}\left(\frac{\cos 2\theta}{1-\cos 2\theta}\right)\left(\frac{\hbar\omega}{2E_i}\right)^2 + \ldots}$$

$$\frac{|\hbar\omega|}{2E_i} << 1$$

Important constraint at high angles too

$$\left(\frac{\hbar\omega}{2E_i}\right)^2 << \frac{2(1-\cos 2\theta)}{\cos 2\theta}$$

Important constraint at low angles

Inserting :

- the Taylor-series **expansion of S(Q,ω)**

and

- the x-power **expansion of (Q^2-Q_{el}^2)**,

into the integral of the measured differential scattering cross section

we observe that:

the integrand now **contains** only S(Q,ω) **and its derivatives with respect to Q^2, evaluated at $Q=Q_{el}$ and multiplied by various powers of ω.**

When
the **integration is carried out term by term**
and
differentiations with respect to Q^2 are brought outside the integrals,
the **result** is
a **series** in the **frequency moments** of S(Q,ω) and $S_{self}(Q,\omega)$ **,** defined by:

$$\boxed{S_{coh}^{(n)}(Q) = \int_{-\infty}^{+\infty} \omega^n S(Q,\omega) d\omega \qquad S_{inc}^{(n)}(Q) = \int_{-\infty}^{+\infty} \omega^n S_{self}(Q,\omega) d\omega}$$

If terms up to the
second order in both the Taylor series and in the power series in *x* are retained,
the **following expression is obtained:**

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \frac{\sigma_{coh}}{4\pi}[S_{coh}^{(0)}(Q_{el}) - \frac{\hbar Q_{el}^2}{2E_i}S_{coh}^{(1)}{}'(Q_{el}) + \frac{\hbar^2}{8E_i^2}\left(2k_i^2 - Q_{el}^2\right)S_{coh}^{(2)}{}'(Q_{el}) + \frac{\hbar^2 Q_{el}^4}{8E_i^2}S_{coh}^{(2)}{}''(Q_{el})] +$$
$$+\frac{\sigma_{inc}}{4\pi}[S_{inc}^{(0)}(Q_{el}) - \frac{\hbar Q_{el}^2}{2E_i}S_{inc}^{(1)}{}'(Q_{el}) + \frac{\hbar^2}{8E_i^2}\left(2k_i^2 - Q_{el}^2\right)S_{inc}^{(2)}{}'(Q_{el}) + \frac{\hbar^2 Q_{el}^4}{8E_i^2}S_{inc}^{(2)}{}''(Q_{el})]$$

where $S^{(n)}{}'(Q_{el}) = \left(\frac{\partial S^{(n)}(Q)}{\partial Q^2}\right)_{Q=Q_{el}}$ $\qquad S^{(n)}{}''(Q_{el}) = \left(\frac{\partial^2 S^{(n)}(Q)}{\partial (Q^2)^2}\right)_{Q=Q_{el}}$

Remind on coherent and incoherent moments

$$S_{inc}^{(0)}(Q) = 1 \qquad S_{coh}^{(0)}(Q) = S(Q)$$

$$S_{inc}^{(1)}(Q) = \frac{\hbar Q^2}{2M} = \omega_{recoil} \qquad S_{coh}^{(1)}(Q) = \frac{\hbar Q^2}{2M}$$

$$S_{inc}^{(2)}(Q) = \cancel{\left(\frac{\hbar Q^2}{2M}\right)^2} + \frac{4}{3}\frac{Q^2}{2M}\langle E_{kin}\rangle \qquad S_{coh}^{(2)}(Q) = S_{inc}^{(2)}(Q) + \cancel{\left(\frac{\hbar Q^2}{2M}\right)^2 [1 - S(Q)]} + \cancel{\frac{Q^2}{2M^2}\sum_{i\neq j}\langle p_i p_j \cos(\mathbf{Q}\cdot\mathbf{r}_{ij})\rangle}$$

We limit the Placzek expansion to terms of the order of m/M

If the series is truncated at m/M, the term may be calculated without knowing the detailed dynamics.

$$\boxed{\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \left(\frac{\sigma_{coh}}{4\pi} S(Q_{el}) + \frac{\sigma_{inc}}{4\pi}\right) + \frac{\sigma_{coh} + \sigma_{inc}}{4\pi}\frac{m}{M}\left[\frac{\langle E_{kin}\rangle}{3E_i} - \frac{Q_{el}^2}{2k_i^2}\left(1 + \frac{\langle E_{kin}\rangle}{3E_i}\right)\right] + O\left(\frac{m^2}{M^2}\right)}$$

where $\langle E_{kin}\rangle$ **is the Mean Kinetic Energy of the system**

(Classically: $\langle E_{kin}\rangle = \frac{3}{2}k_B T$ **)**

Behavior of Placzek corrections with the instrumental (E_i and 2θ) and the physical (M, T) parameters

σ_{scat}

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \left(\frac{\sigma_{coh}}{4\pi}S(Q_{el}) + \frac{\sigma_{inc}}{4\pi}\right) + \frac{\sigma_{coh}+\sigma_{inc}}{4\pi}\frac{m}{M}\left[\frac{\langle E_{kin}\rangle}{3E_i} - \frac{Q_{el}^2}{2k_i^2}\left(1+\frac{\langle E_{kin}\rangle}{3E_i}\right)\right] + O\left(\frac{m^2}{M^2}\right)$$

$$\left.\frac{d\sigma}{d\Omega}\right|_{S.A.}$$

$$P(Q_{el}) = A - BQ_{el}^2$$

We rewrite the coherent and incoherent differential scattering cross section by means of the notation distinct and self:

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \left.\frac{d\sigma}{d\Omega}\right|_{meas}^{coh} + \left.\frac{d\sigma}{d\Omega}\right|_{meas}^{inc} = \left.\frac{d\sigma}{d\Omega}\right|_{meas}^{dist} + \left.\frac{d\sigma}{d\Omega}\right|_{meas}^{self}$$

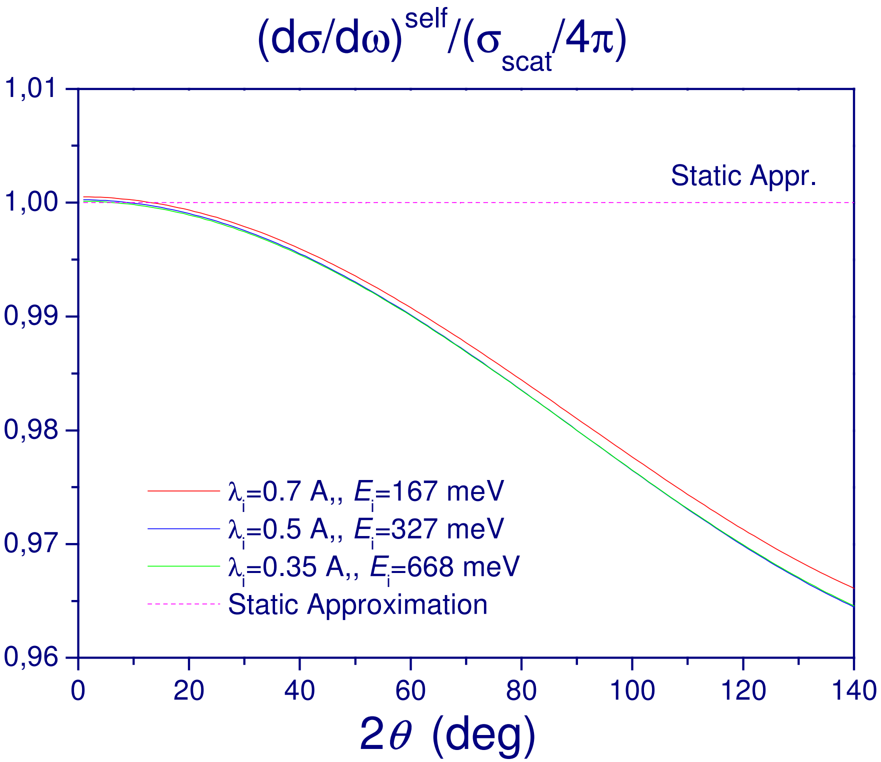
$$\frac{\sigma_{coh}}{4\pi}\sum i,j \qquad \frac{\sigma_{inc}}{4\pi}\sum i=j \qquad \frac{\sigma_{coh}}{4\pi}\sum i\neq j \qquad \frac{\sigma_{scat}}{4\pi}\sum i=j$$

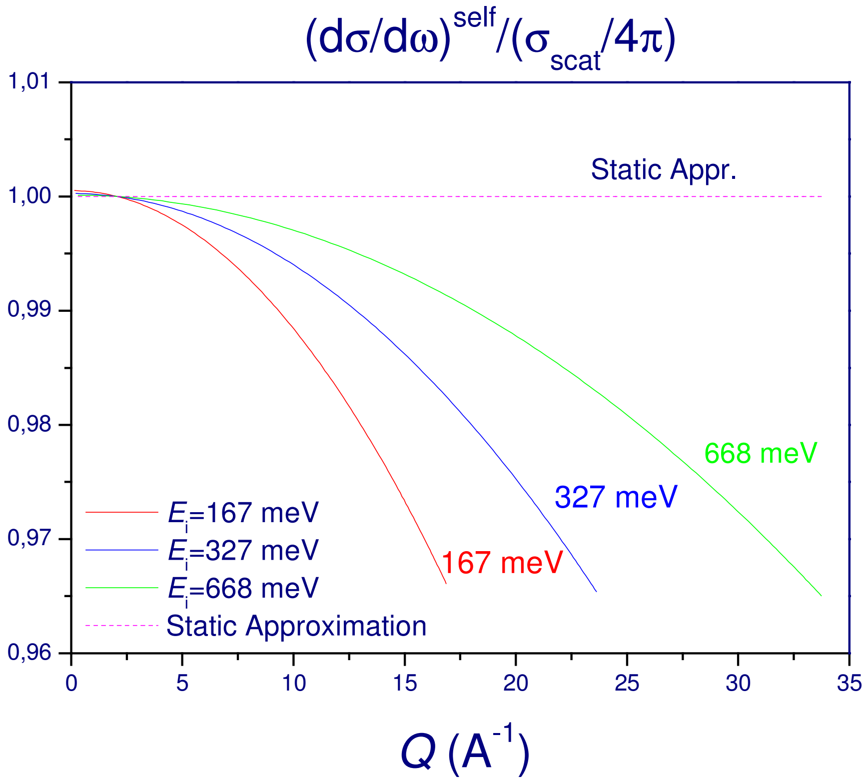
$$\left.\frac{d\sigma}{d\Omega}\right|_{meas}^{dist} = \frac{\sigma_{coh}}{4\pi}\left(S(Q_{el})-1\right)$$

$$\boxed{\left.\frac{d\sigma}{d\Omega}\right|_{meas}^{self} = \frac{\sigma_{scat}}{4\pi}\left(1+P(Q_{el})\right)}$$

Behavior of Placzek corrections with the instrumental (E_i and 2θ) and the physical (M, T) parameters

D4 @ ILL
***M/m*=50; *T*=100 K**





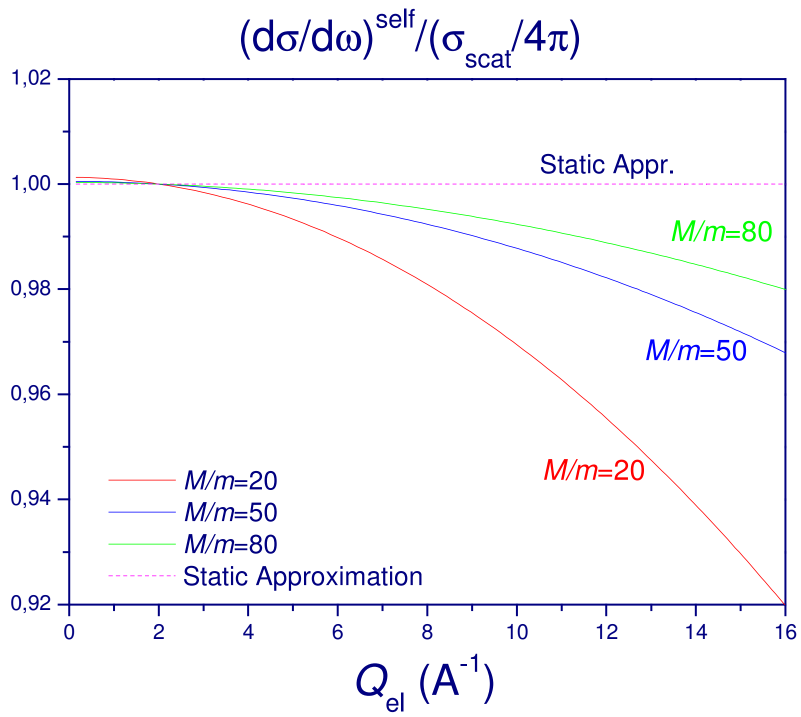
λ_i=0.35, 0.5, 0.7 Å

In some papers it is implied that large E_i are superior at all angles,
whereas the correct statement is:
at a given Q_{el} the inelasticity correction decreases as E_i is increased.

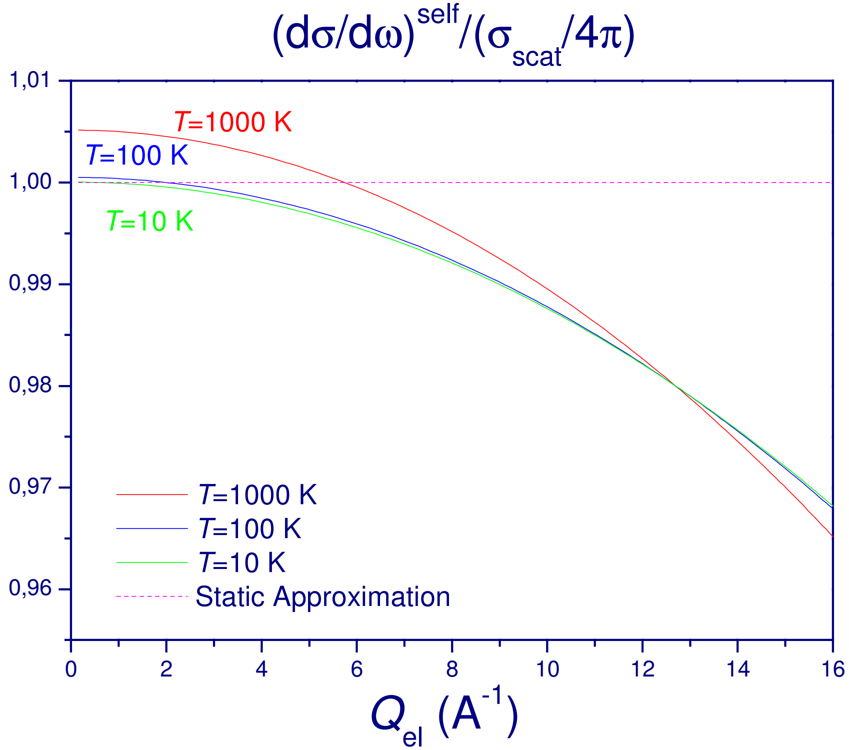
-for a given E_i, **the inelasticity correction increases with the scattering angle 2θ**

Behavior of Placzek corrections with the instrumental (E_i and 2θ) and the physical (M, T) parameters

D4 @ ILL
λ_i=0.7 Å



***M/m*=20, 50, 80**



***T*=10, 100, 1000 K**

The inelasticity correction decreases:

-for larger atomic mass, *M*, and **for smaller temperature, *T*,** (classically $\langle E_{kin}\rangle = \frac{3}{2}k_B T$)

Case of atomic systems on steady state source with a generic detector efficiency ε(k_f)

(Yarnell et al., Phys. Rev. A **7**, 2130 (1973))

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \int\limits_{\substack{-\infty \\ \theta\ \mathrm{const}}}^{+\infty} \frac{\varepsilon(k_f)}{\varepsilon(k_i)} \frac{k_f}{k_i} \left[\frac{\sigma_{coh}}{4\pi} S(Q,\omega) + \frac{\sigma_{inc}}{4\pi} S_{self}(Q,\omega)\right] d\omega$$

$$\frac{k_f}{k_i} = \sqrt{(1-x)} = 1 - \frac{1}{2}x - \frac{1}{8}x^2 + \ldots$$

$$\varepsilon(k_f) = \underbrace{\varepsilon(k_i)}_{\varepsilon_0} + \underbrace{\left(\frac{\partial \varepsilon(k_f)}{\partial k_f}\right)_{k_f = k_i}}_{\varepsilon_1} (k_f - k_i) + \frac{1}{2!} \underbrace{\left(\frac{\partial^2 \varepsilon(k_f)}{\partial {k_f}^2}\right)_{k_f = k_i}}_{\varepsilon_2} (k_f - k_i)^2 + \ldots$$

$$\varepsilon(k_f) = \varepsilon_0 - \varepsilon_1 k_i \frac{x}{2} + ({k_i}^2 \varepsilon_2 - k_i \varepsilon_1) \frac{x^2}{8} \ldots$$

Result for a
generic detector efficiency $\varepsilon(k_f)$

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \left(\frac{\sigma_{coh}}{4\pi} S(Q_{el}) + \frac{\sigma_{inc}}{4\pi}\right) + \frac{\sigma_{coh} + \sigma_{inc}}{4\pi} \cdot$$

$$\cdot \frac{m}{M}\left[\frac{\langle E_{kin}\rangle}{3E_i} - \frac{Q_{el}^2}{2k_i^2}[2 + \frac{k_i\varepsilon_1}{\varepsilon_0} - (\frac{3k_i\varepsilon_1}{\varepsilon_0} + \frac{k_i^2\varepsilon_2}{\varepsilon_0})\frac{\langle E_{kin}\rangle}{3E_i}]\right] + O(\frac{m^2}{M^2})$$

obviously for

$$\varepsilon(k_f) = \frac{1}{k_f} \quad \Longrightarrow \quad \varepsilon_1 = -\frac{1}{k_i^2} \qquad \varepsilon_2 = \frac{2}{k_i^3}$$

and we obtain the previous formula of Placzek

Second case of first method:

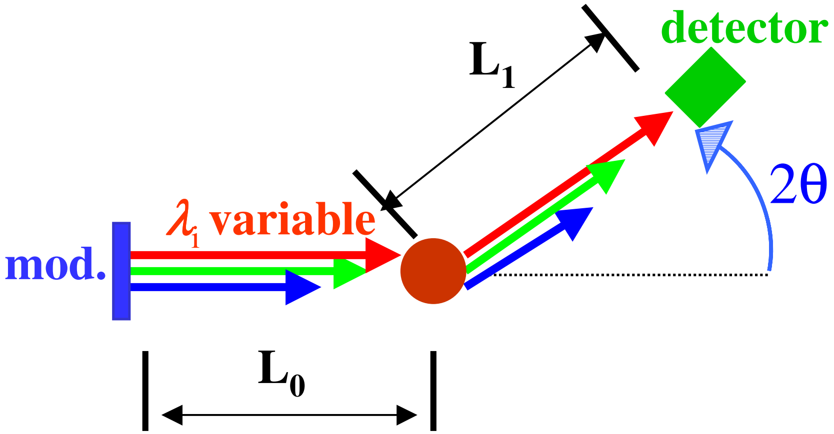
inelasticity correction for

Monatomic systems on a Pulsed source

Time of flight diffractometer on a pulsed source

(e.g. SANDALS at RAL):

The diffraction angle, 2θ, is fixed and we measure the intensity as a function of the incoming neutron wavelength, $\lambda_i = 2\pi/k_i$, with no selection of the final energy, E_f.



$$v = \frac{p}{m} = \frac{\hbar k}{m} \qquad t = \frac{L}{v} = \frac{mL}{\hbar k}$$

$$k_i = \frac{mL_0}{\hbar t_i} \qquad k_f = \frac{mL_1}{\hbar t_f}$$

$$k_i = k_f \quad (t = t_i + t_f) \qquad k_{el} = \frac{m(L_0 + L_1)}{\hbar t}$$

$$Q_{el} = 2k_{el}\sin(\theta)$$

$$\boxed{\frac{L_0}{k_i} + \frac{L_1}{k_f} = \frac{L_0 + L_1}{k_{el}}} \qquad a = \frac{L_0}{L_1} \Rightarrow \boxed{\frac{a}{k_i} + \frac{1}{k_f} = \frac{a+1}{k_{el}}}$$

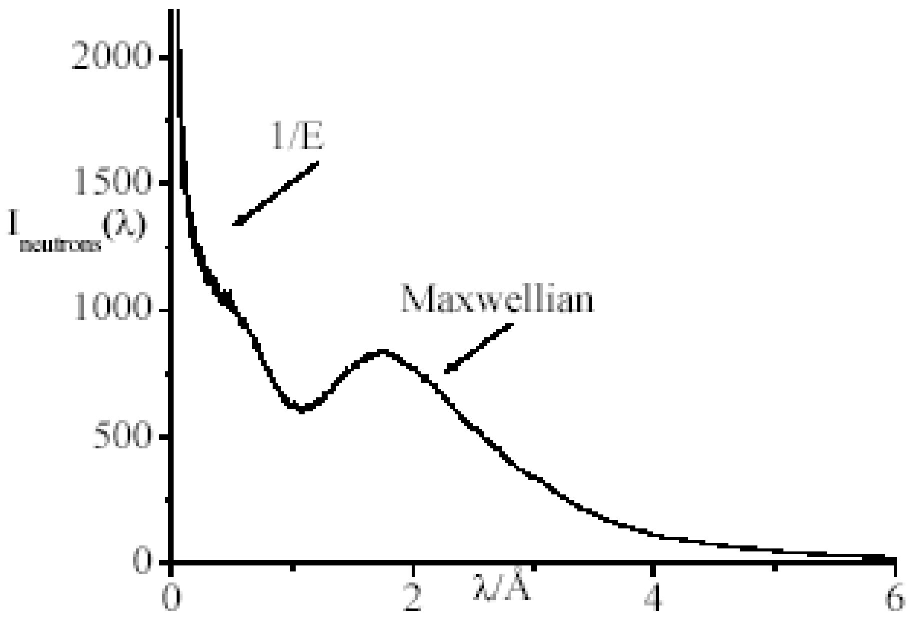
The differential scattering cross section for a time of flight diffractometer on a pulsed neutron source

Incident flux

Kinetic sampling factor

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \int_{\substack{-\infty \\ t\ \mathrm{const} \\ \theta\ \mathrm{const}}}^{+\infty} \frac{\phi(\lambda_i)}{\phi(\lambda_{el})} \left.\frac{\partial\lambda_i}{\partial\lambda_{el}}\right|_{\omega\ \mathrm{const}} \frac{\varepsilon(k_f)}{\varepsilon(k_{el})} \frac{k_f}{k_i} \left[\frac{\sigma_{coh}}{4\pi} S(Q,\omega) + \frac{\sigma_{inc}}{4\pi} S_{self}(Q,\omega)\right] d\omega$$

Incident flux



$$\phi(\lambda) = \phi_{\max}(\lambda) + \Delta(\lambda)\cdot\phi_{\mathrm{epi}}(\lambda)$$

Kinetic Sampling Factor

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \int_{-\infty}^{+\infty}\limits_{\substack{t\ \mathrm{const}\\ \theta\ \mathrm{const}}} \frac{\phi(\lambda_i)}{\phi(\lambda_{el})}\left.\frac{\partial\lambda_i}{\partial\lambda_{el}}\right|_{\omega\ \mathrm{const}} \frac{\varepsilon(k_f)}{\varepsilon(k_{el})}\frac{k_f}{k_i}\left[\frac{\sigma_{coh}}{4\pi}S(Q,\omega)+\frac{\sigma_{inc}}{4\pi}S_{self}(Q,\omega)\right]d\omega$$

using $\frac{a}{k_i}+\frac{1}{k_f}=\frac{a+1}{k_{el}}$ and $\hbar\omega=\frac{\hbar^2 k_i^2}{2m}-\frac{\hbar^2 k_f^2}{2m}$

Term accounting for the change of integration variable from λ_i to ω, it acts as a sampling factor in the integral (because it controls the way S(Q,ω) is sampled).

$$\left.\frac{\partial\lambda_i}{\partial\lambda_{el}}\right|_{\omega\ \mathrm{const}} = \frac{a+1}{a+\left(\frac{k_i}{k_f}\right)^3}$$

NOTE:

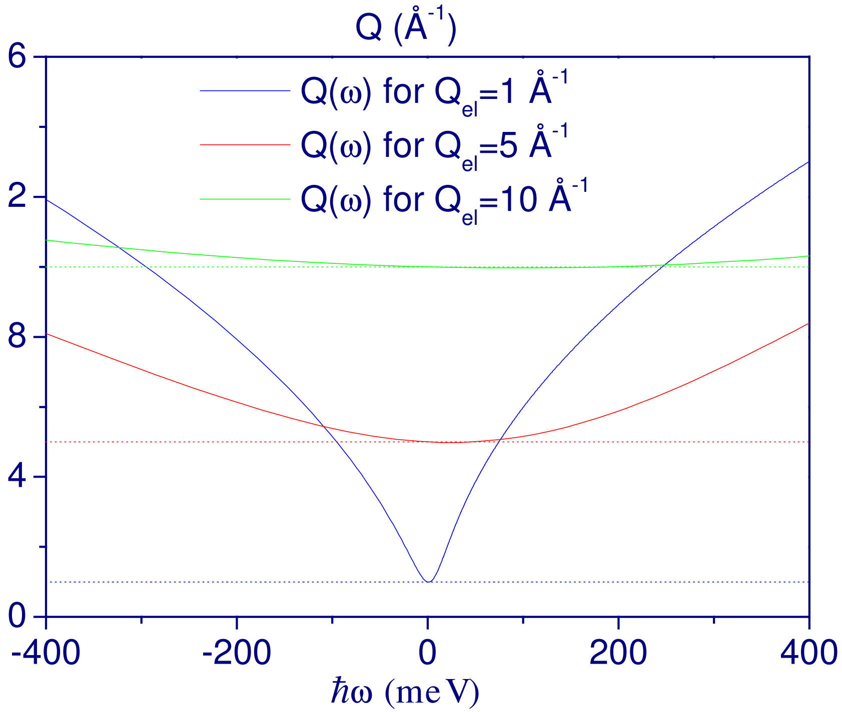
$$a=\frac{L_0}{L_1}\rightarrow\infty \quad\Rightarrow\quad k_i=k_{el};\ \left.\frac{\partial\lambda_i}{\partial\lambda_{el}}\right|_{\omega\ \mathrm{const}}=1 \quad \text{(steady source case)}$$

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \int_{-\infty}^{+\infty} \frac{\phi(\lambda_i)}{\phi(\lambda_{el})} \left.\frac{\partial \lambda_i}{\partial \lambda_{el}}\right|_{\omega\,\mathrm{const}} \frac{\varepsilon(k_f)}{\varepsilon(k_{el})} \frac{k_f}{k_i} [\frac{\sigma_{coh}}{4\pi} S(Q,\omega) + \frac{\sigma_{inc}}{4\pi} S_{self}(Q,\omega)] d\omega$$

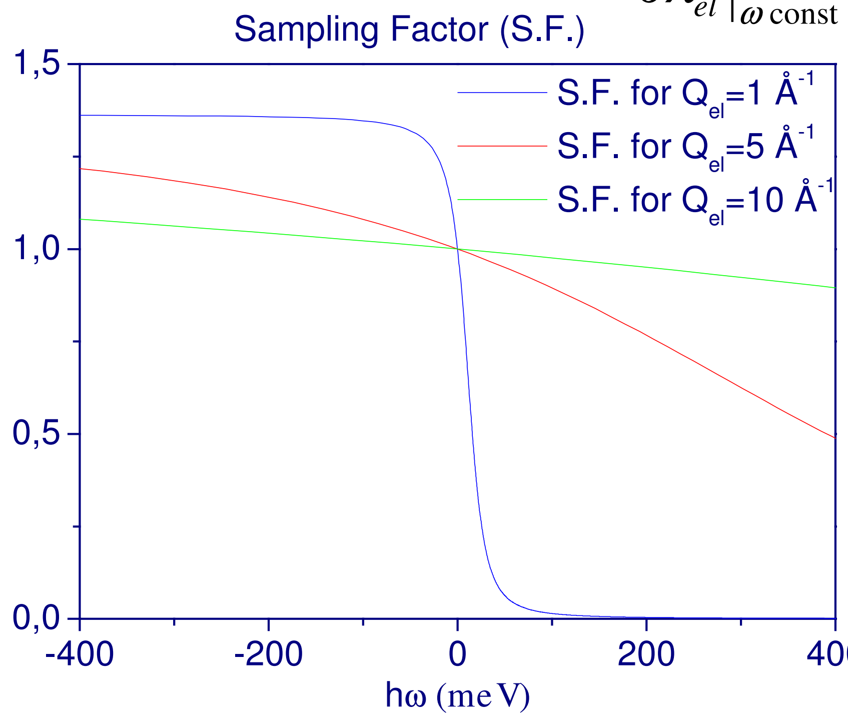
t const
θ const

SANDALS:
$L_0/L_1=11/4$
$2\theta=20^{\circ}$

Kinematic region $Q=Q(\omega)$



Sampling Factor $\left.\frac{\partial \lambda_i}{\partial \lambda_{el}}\right|_{\omega\,\mathrm{const}}$



Generalized Placzek correction to ToF
(method of the power series expansion)

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \int\limits_{\substack{-\infty \\ t\ \text{const} \\ \theta\ \text{const}}}^{+\infty} \frac{\phi(\lambda_i)}{\phi(\lambda_{el})} \left.\frac{\partial \lambda_i}{\partial \lambda_{el}}\right|_{\omega\ \text{const}} \frac{\varepsilon(k_f)}{\varepsilon(k_{el})} \frac{k_f}{k_i} \left[\frac{\sigma_{coh}}{4\pi} S(Q,\omega) + \frac{\sigma_{inc}}{4\pi} S_{self}(Q,\omega)\right] d\omega$$

$$\boxed{x = \hbar\omega / E_{el}}$$

$$\frac{k_f}{k_i} = 1 - \frac{x}{2} + \frac{(3-a)}{(a+1)} \frac{x^2}{8} + \dots$$

$$\left.\frac{\partial \lambda_i}{\partial \lambda_{el}}\right|_{\omega\ \text{const}} = 1 + \frac{1}{(a+1)} \frac{x}{2} - \frac{15a-7}{(a+1)^2} \frac{x^2}{8} + \dots$$

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \int_{\substack{-\infty \\ t\text{ const} \\ \theta\text{ const}}}^{+\infty} \frac{\phi(\lambda_i)}{\phi(\lambda_{el})} \left.\frac{\partial\lambda_i}{\partial\lambda_{el}}\right|_{\omega\text{ const}} \frac{\varepsilon(k_f)}{\varepsilon(k_{el})} \frac{k_f}{k_i} [\frac{\sigma_{coh}}{4\pi} S(Q,\omega) + \frac{\sigma_{inc}}{4\pi} S_{self}(Q,\omega)]d\omega$$

$$\varepsilon(k_f) = \varepsilon_0 - \frac{a\varepsilon_1 k_{el}}{(a+1)}\frac{x}{2} + \left(\frac{a^2\varepsilon_2 k_{el}^2}{(a+1)^2} - \frac{a\varepsilon_1 k_{el}}{(a+1)}\right)\frac{x^2}{8} + \ldots$$

$$\varepsilon_0 = \varepsilon(k_{el}) \qquad \varepsilon_1 = \left.\frac{\partial\varepsilon(k_f)}{\partial(k_f)}\right|_{k_f = k_{el}} \qquad \varepsilon_2 = \left.\frac{\partial^2\varepsilon(k_f)}{\partial(k_f)^2}\right|_{k_f = k_{el}}$$

$$\phi(k_i) = \phi_0 - \frac{\phi_1\lambda_{el}}{(a+1)}\frac{x}{2} + \left(\frac{\phi_2\lambda_{el}^2}{(a+1)^2} - 3\frac{(a-1)}{(a+1)^2}\phi_1\lambda_{el}\right)\frac{x^2}{8} + \ldots$$

$$\phi_0 = \phi(\lambda_{el}) \qquad \phi_1 = \left.\frac{\partial\phi(\lambda_i)}{\partial(\lambda_i)}\right|_{\lambda_i = \lambda_{el}} \qquad \phi_2 = \left.\frac{\partial^2\phi(\lambda_i)}{\partial(\lambda_i)^2}\right|_{\lambda_i = \lambda_{el}}$$

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \int\limits_{\substack{-\infty \\ t\ \text{const} \\ \theta\ \text{const}}}^{+\infty} \frac{\phi(\lambda_i)}{\phi(\lambda_{el})} \left.\frac{\partial \lambda_i}{\partial \lambda_{el}}\right|_{\omega\ \text{const}} \frac{\varepsilon(k_f)}{\varepsilon(k_{el})} \frac{k_f}{k_i} \left[\frac{\sigma_{coh}}{4\pi} S(Q,\omega) + \frac{\sigma_{inc}}{4\pi} S_{self}(Q,\omega)\right] d\omega$$

$$S(Q,\omega) = S(Q_{el},\omega) + \left.\frac{\partial S(Q,\omega)}{\partial Q^2}\right|_{Q=Q_{el}} (Q^2 - Q_{el}^2) + \frac{1}{2!} \left.\frac{\partial^2 S(Q,\omega)}{\partial (Q^2)^2}\right|_{Q=Q_{el}} (Q^2 - Q_{el}^2)^2 + \ldots$$

$$Q^2 - Q_{el}^2 = Q_{el}^2 \frac{(1-a)}{(1+a)} \frac{x}{2} + \left(2k_{el}^2 - Q_{el}^2 \frac{(a^2 - 4a + 1)}{(a+1)^2}\right) \frac{x^2}{8} + \ldots$$

$$\boxed{S(Q,\omega) = S(Q_{el},\omega) + Q_{el}^2 \frac{(1-a)}{(1+a)} S' \frac{x}{2} + \left[\left(2k_{el}^2 - Q_{el}^2 \frac{(a^2 - 4a + 1)}{(a+1)^2}\right) S' + Q_{el}^2 \frac{(1-a)^2}{(1+a)^2} S''\right] \frac{x^2}{8} \ldots}$$

$$S' = \left.\frac{\partial S(Q,\omega)}{\partial (Q^2)}\right|_{Q=Q_{el}} \qquad S'' = \left.\frac{\partial^2 S(Q,\omega)}{\partial (Q^2)^2}\right|_{Q=Q_{el}}$$

Finally

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \frac{\sigma_{coh}}{4\pi}(S(Q_{el})-1) + \frac{\sigma_{scat}}{4\pi}(1+P(Q_{el}))$$

$$P(Q_{el}) = \frac{m}{M}\left[-\frac{1}{a+1}\frac{\phi_1\lambda_{el}}{\phi_0} - \frac{a}{a+1}\frac{\varepsilon_1 k_{el}}{\varepsilon_0} - \frac{2a+3}{a+1}\right]\frac{Q_{el}^2}{2k_{el}^2}$$

$$+\frac{m}{M}\frac{\langle E_{kin}\rangle}{3E_{el}}[1+\frac{Q_{el}^2}{2k_{el}^2}[\frac{a+9}{(a+1)^2}\frac{\phi_1\lambda_{el}}{\phi_0} + \frac{3a(a+3)}{(a+1)^2}\frac{k_{el}\varepsilon_1}{\varepsilon_0} +$$

$$\frac{2a}{(a+1)^2}\frac{\phi_1\lambda_{el}}{\phi_0}\frac{k_{el}\varepsilon_1}{\varepsilon_0} + \frac{1}{(a+1)^2}\frac{\phi_2\lambda_{el}^2}{\phi_0} + \frac{a^2}{(a+1)^2}\frac{\varepsilon_2 k_{el}^2}{\varepsilon_0} +$$

$$3\frac{a+5}{(a+2)^2}]] + O(\frac{m^2}{M^2})$$

$$P(Q_{el}) = A - B\frac{Q_{el}^2}{k_{el}^2} = A - \tilde{B}\sin^2(\theta)$$

Simplified case:
Epithermal flux ($\phi=\phi_0/E_i$) and detector efficiency $\varepsilon(k_f) = 1/k_f$

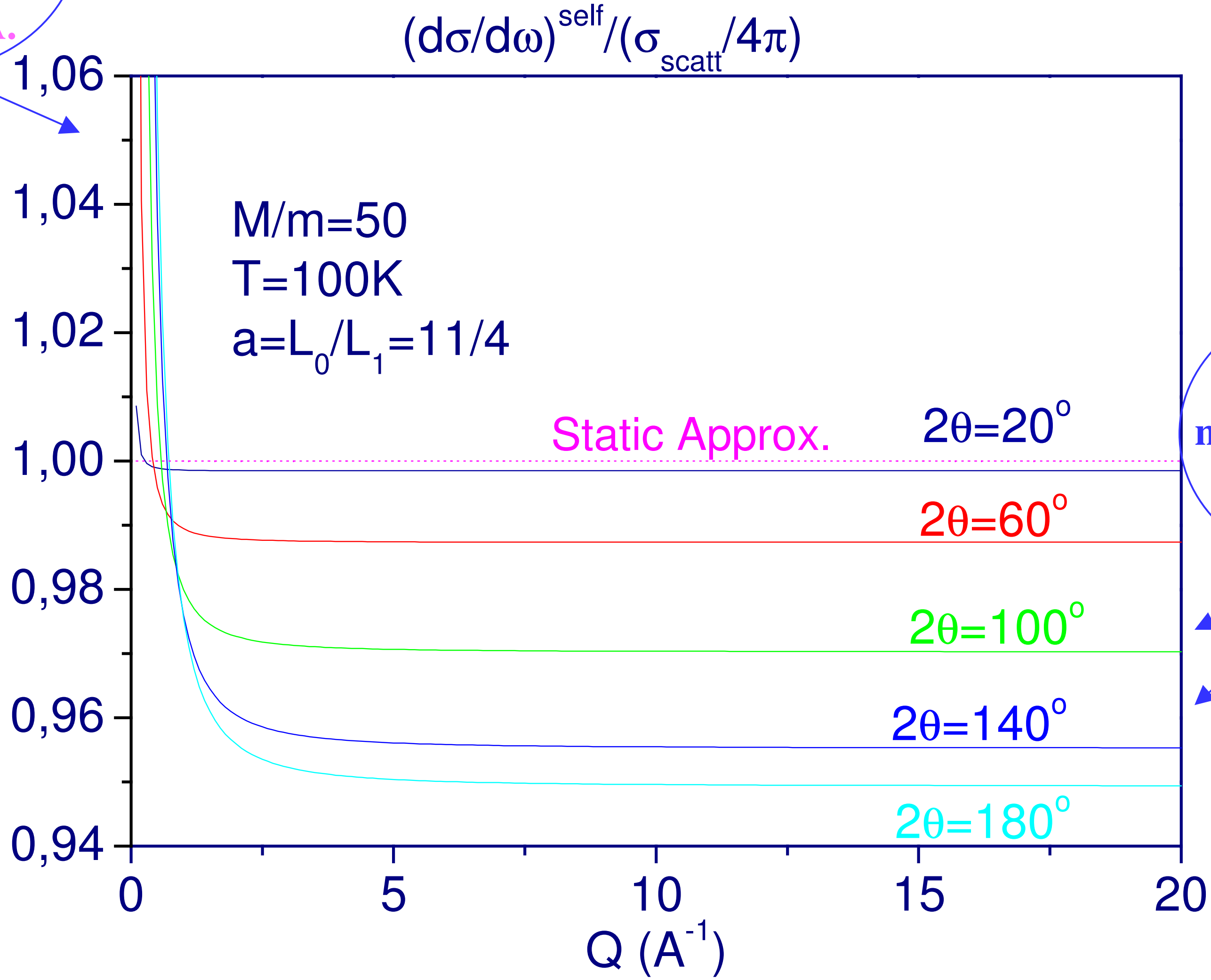
$$P(Q_{el}) = \frac{m}{M}\left[-\frac{a+2}{a+1}\frac{Q_{el}^2}{2k_{el}^2} + \frac{\langle E_{kin}\rangle}{3E_{el}}\left(1-\frac{Q_{el}^2}{2k_{el}^2}\frac{(a^2-25a-2)}{(a+1)^2}\right)\right] + O(\frac{m^2}{M^2})$$

$$\frac{Q_{el}^2}{4k_{el}^2} = \sin^2(\theta)$$

Behavior of Placzek correction
with the instrumental (E_i , 2θ, and L_0/L_1)
and the physical (M, T) parameters
on a pulsed source

Dependence on scattering angle 2θ

low Q_{el}: measured signal rises markedly above S.A.

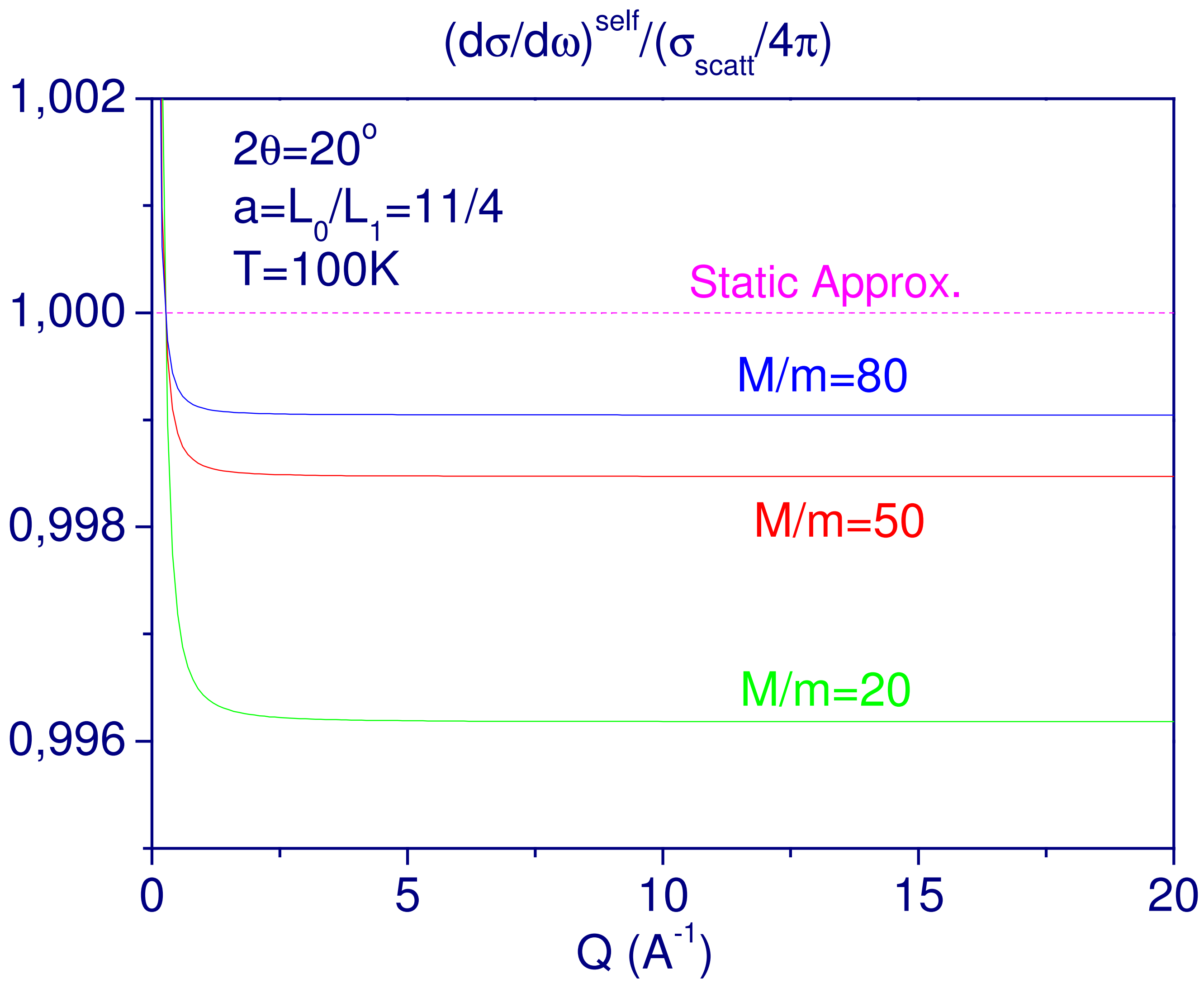


High Q_{el}: measured signal is below S.A.

The inelastic correction increases with scattering angle

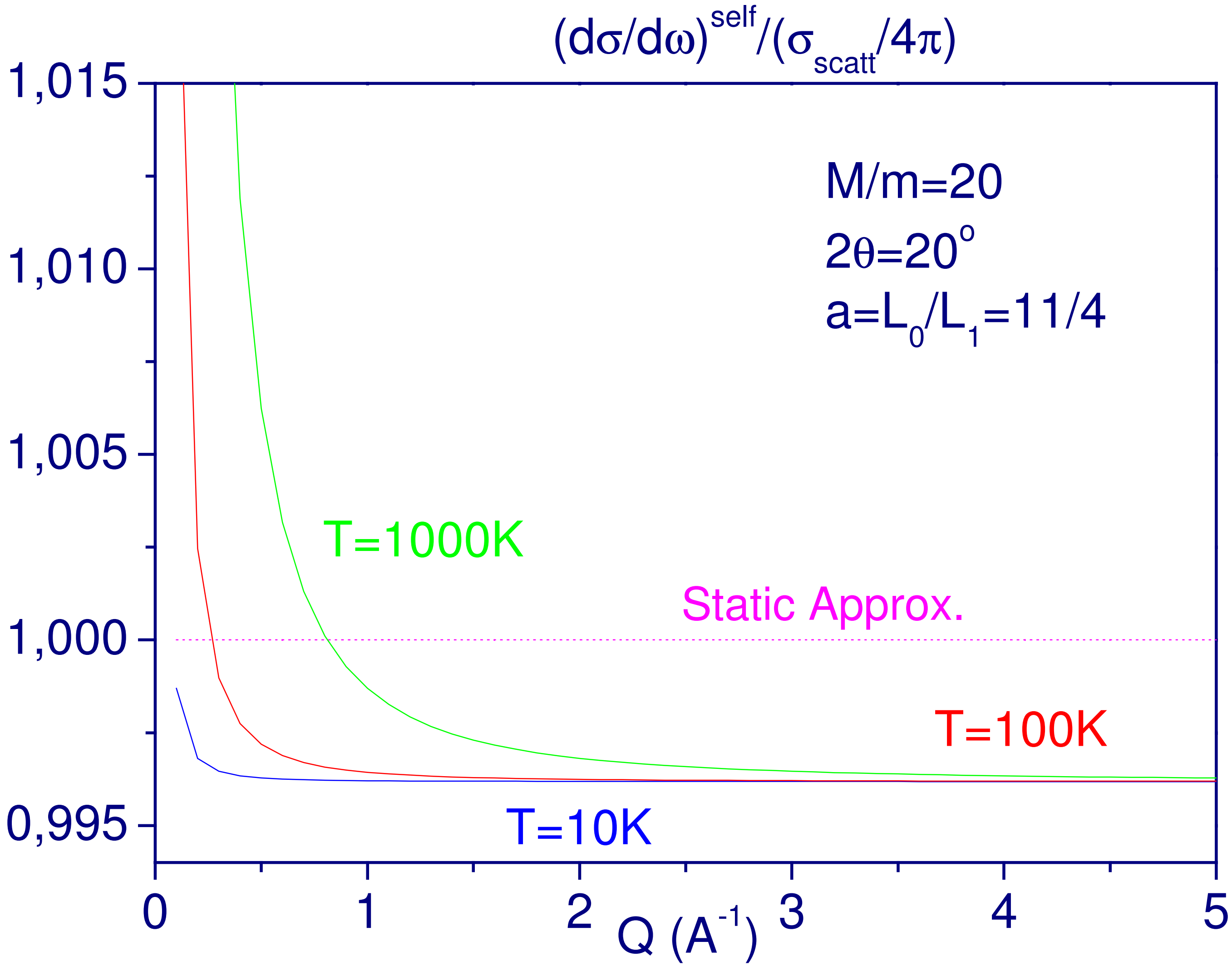
The dependence upon angle of the I.C. has the consequence that spectra at different angles must be analyzed separately until the I.C. has been performed

Dependence on atomic mass M



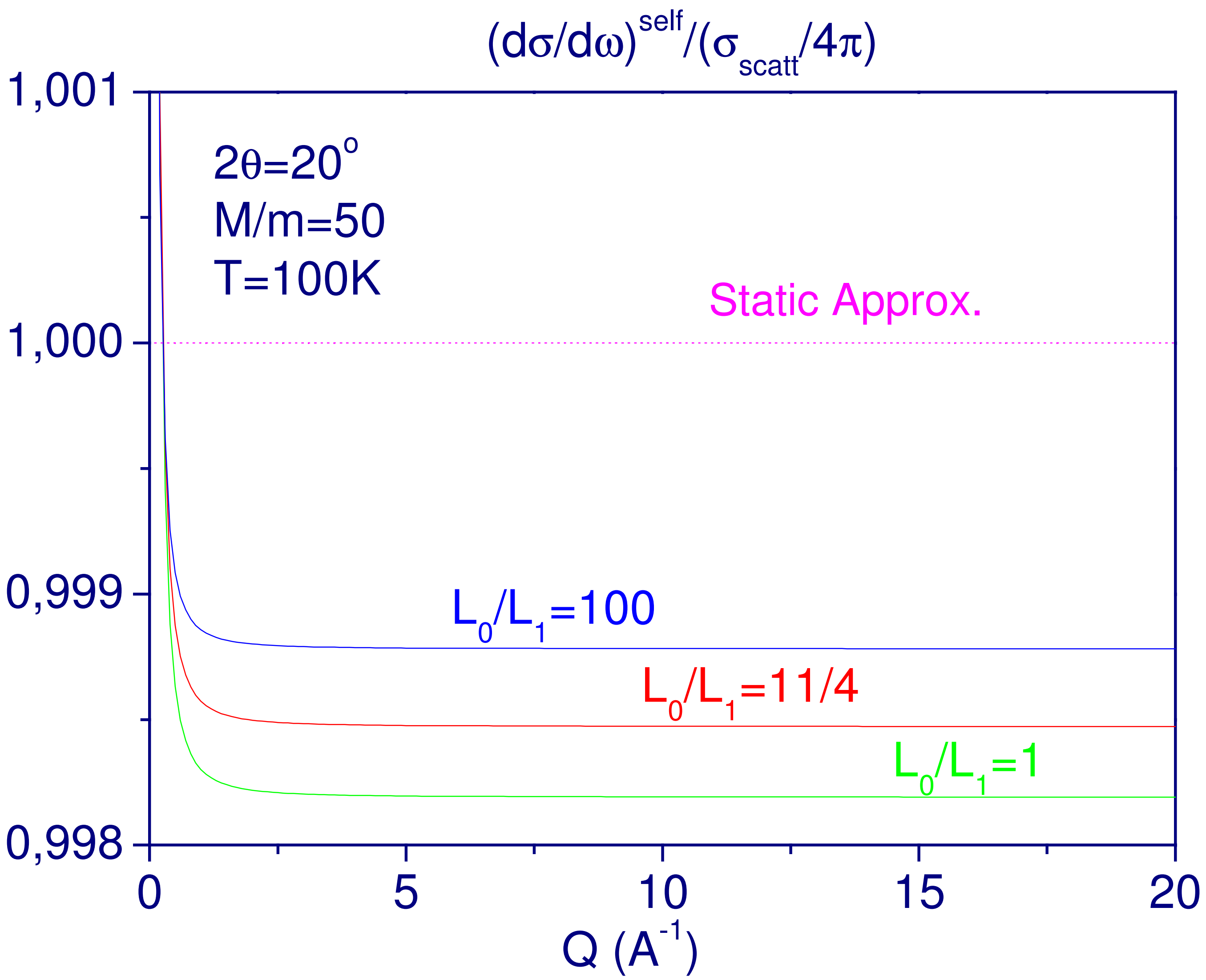
The inelastic correction increases with decreasing the mass

Dependence on temperature T



The inelastic correction increases with temperature

Dependence on the ratio of incident and scattering paths



The inelastic correction increases decreasing the ratio L_0/L_1

Comparison of the inelasticity effect
on a reactor source (RS) and on a pulsed neutron source (PNS)

For neutron diffraction measurements at RS,

the self scattering falls off with increasing scattering angle, 2*θ*,
i.e. with increasing *Q* (polynomial expansion in powers of Q^2).

Note that for hydrogen and for other very light atoms, there is no suitable polynomial in Q^2 that can be used to correct the data for inelasticity effects

For neutron diffraction measurements at PNS,

the inelasticity effect is generally weaker with respect to RS due to the higher incident energies, provided the diffraction patterns are measured at small scattering angles,

and occurs principally at low Q-values in the diffractogram,
while at high Q-values is a negative constant contribution
(high Q-range: very useful for molecular light systems)

BUT… the Inelasticity effect on PNS is more difficult to parametrize than on RS.

NOTE:

The program **GUDRUN**,
used at RAL for the data analysis,
contains the routine PLATOM that performs the inelasticity correction.

The output of this routine is a calculation of the
self scattering cross section for each detector bank.

The **effect of inelasticity P(Q) is included**
by use of the general expression given before
(see also Howe et. al, J. Phys. Cond. Matter 1, 3433 (1989))
using a fitted function for the incident flux shape
and the appropriate detector efficiency.

Extension to a multicomponent system
(excluding molecular system)

In a monatomic system all the N atoms are chemically identical:

$$\frac{d\sigma}{d\Omega} = \bar{b}^2 (S(Q) - 1) + \overline{b^2} \qquad (\bar{b}^2 = \frac{\sigma_{coh}}{4\pi} \qquad \overline{b^2} = \frac{\sigma_{scat}}{4\pi})$$

$$S(Q) = 1 + \frac{1}{N} \left\langle \sum_{i,j\neq i}^{N} \frac{\sin(Qr_{ij})}{(Qr_{ij})} \right\rangle$$

In a multicomponent system we have n different chemical species α, each species with concentration $c_\alpha = N_\alpha / N$

$$\frac{d\sigma}{d\Omega} = \sum_{\alpha,\beta}^{n} c_\alpha c_\beta \bar{b}_\alpha \bar{b}_\beta (S_{\alpha\beta}(Q) - 1) + \sum_{\alpha}^{n} c_\alpha \overline{b_\alpha^2} \qquad (\sum_{\alpha}^{n} c_\alpha = 1)$$

Faber-Ziman partial structure factor

$$S_{\alpha\beta}(Q) = 1 + \frac{1}{c_\alpha c_\beta N} \left\langle \sum_{\substack{i\in\alpha,\, j\in\beta \\ j\neq i}}^{N_\alpha N_\beta} \frac{\sin(Qr_{ij})}{(Qr_{ij})} \right\rangle$$

Extension to a multicomponent system (continued)

(excluding molecular system)

I.C. for monatomic case:

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \bar{b}^2 (S(Q)-1) + \overline{b^2}(1+P(Q))$$

I.C. for polyatomic case:

$$\frac{d\sigma}{d\Omega} = \sum_{\alpha,\beta}^{n} c_\alpha c_\beta \bar{b}_\alpha \bar{b}_\beta (S_{\alpha\beta}(Q)-1) + \sum_{\alpha}^{n} c_\alpha \overline{b_\alpha^2}(1+P_\alpha(Q))$$

Note: GUDRUN calculates the inelasticity correction for a multicomponent system, (provided the atomic masses M_α and the concentrations c_α are given)

Extension to a molecular fluid

Simplified case: **homonuclear diatomic molecule**

Possible separation:

i,j: indices of the atoms

$$\frac{d\sigma}{d\Omega} = \left.\frac{d\sigma}{d\Omega}\right|^{\text{dist}} + \left.\frac{d\sigma}{d\Omega}\right|^{\text{self}}$$

$$\frac{\sigma_{coh}}{4\pi}\sum i \neq j \qquad \frac{\sigma_{scat}}{4\pi}\sum i = j$$

More useful separation:

k,l: indices of the molecules

This is the **single molecular contribution** that **should be subtracted** from the total intensity to extract the interesting structural information about the fluid

$$\frac{d\sigma}{d\Omega} = \left.\frac{d\sigma}{d\Omega}\right|^{\text{intermol}} + \left.\frac{d\sigma}{d\Omega}\right|^{\text{self}} + \left.\frac{d\sigma}{d\Omega}\right|^{\text{interf}}$$

$$\frac{\sigma_{coh}}{4\pi}\sum k \neq l \qquad \frac{\sigma_{scat}}{4\pi}\sum i = j \qquad \frac{\sigma_{coh}}{4\pi}\sum (k = l \text{ but } i \neq j)$$

Is it possible to use Placzek expansion for molecular fluids?

First: analysis of the SELF term

(note that also for molecular systems **the self term is a constant in the static approx.**)

We would like to use the Placzek expansion, derived for atomic systems, $P(Q_{el})=(m_n/M_{at})(A+BQ_{el}^2)+\dots$ with the minimum possible modification

In a molecule, the **effective mass** of the recoiling atom struck by the neutron (I.C.) depends on the value of the neutron incident energy, E_i, with respect to the typical energies of the molecular motion, E_{rot} and E_{vib}, and of the temperature, T, of the system.

That is: we can sketch the molecule, for example, as a "ball", a rigid rotor, a harmonically vibrating oscillator, an ensemble of free atoms… depending on the value of the various energies involved in the process

More in details, even if still in a crude schematization… we can subdivide the energy range in different regimes

Regime I

$$E_i < E_{rot} \;\; and \;\; k_B T < E_{rot} \;\; \Rightarrow$$

No excitation of any internal motion of the molecule: "ball" of mass equal to the molecular mass

$$M_{eff} \cong M_{mol}$$

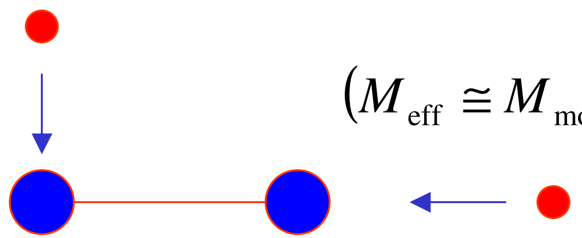
Regime II

$$E_{rot} < E_i < E_{vib} \;\; and \;\; k_B T < E_{vib} \;\; \Rightarrow$$

No excitation of vibrational modes: rigid rotating molecule
(neglecting the zero point vibrational energy)

$$M_{eff} \cong M_{Sachs\text{-}Teller} = \frac{6}{5} M_{at}$$

$(M_{eff} \cong M_{at})$



$$M^{-1}_{Sachs-Teller} = \frac{1}{3}\left(M^{-1}_{mol} + 2M^{-1}_{at}\right)$$

Regime III

$$E_{\mathrm{i}} >> E_{\mathrm{vib}} \Rightarrow$$

Excitation of all the internal modes:
Almost free atom

$$\Downarrow$$

$$M_{\mathrm{eff}} \cong M_{\mathrm{at}}$$

Other Regimes…

examples:

$$E_{\mathrm{i}} \geq E_{\mathrm{vib}}$$

$$or \qquad \Rightarrow$$

$$k_{\mathrm{B}} T \geq E_{\mathrm{vib}}$$

Some or all the vibrational modes are excited
Complicated expression for M_{eff}, function of E_{vib} and T

Note that in the pulsed neutron source
a lot of values of the incident energy are involved all together… M_{eff}=???

For a quantitative (and more rigorous) presentation of this topic see:
Powles: references [5]-[11]
Egelstaff and Soper: references [12]-[13] and references therein

Is it possible to use Placzek expansion for molecular fluids?

continued..

Second: analysis of the INTERF term

note that **the interf term** presents **oscillations** (related to the internal structure of the molecule) even **in the Static Approx.**

Hyp: rigid homonuclear diatomic molecule
(d=internuclear distance)

$$\left.\frac{d\sigma}{d\Omega}\right|_{S.A.}^{\text{interf}} = 2\frac{\sigma_{\text{coh}}}{4\pi}\frac{\sin(Qd)}{(Qd)}$$

Note that the Sachs-Teller mass tensor is not usable here because this model is valid only for a single nucleus while the interf term involves two masses.

However, extending the idea of effective mass to the interf. term, its effective mass tends to be of the order of the sum of the two masses

In a very intuitive way, we can say that
if the I.C. for the self term (involving only one mass) is small,
the I.C. for the interf term (involving TWO mass) is even smaller…
So…if the self term is very small, the interf term is calculated
in Static Approx. (neglecting I.C., but... with a good model for the molecule)

For a quantitative (and more rigorous) presentation of this topic see:
Powles: references [5]-[11]
Egelstaff and Soper: references [12]-[13] and references therein

Second method

Calculation of the inelasticity correction using models or measured S(Q,ω)

Very simplified model…
to understand the method!

Monatomic fluid measured on a steady source

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i}[\frac{\sigma_{coh}}{4\pi} S(Q,\omega) + \frac{\sigma_{inc}}{4\pi} S_{self}(Q,\omega)] =$$

$$= \frac{k_f}{k_i}[\frac{\sigma_{coh}}{4\pi} S_{dist}(Q,\omega) + \frac{\sigma_{scat}}{4\pi} S_{self}(Q,\omega)]$$

Ideal gas model

$$S(Q,\omega) = S_{self}(Q,\omega) = S^{i.g.}(Q,\omega) = \sqrt{\frac{M}{2\pi k_B T Q^2}} \exp\left[-\frac{M}{2k_B T Q^2}\left(\omega - \frac{\hbar Q^2}{2M}\right)^2\right]$$

$$S_{dist}(Q,\omega) = 0$$

$$\left.\frac{d\sigma}{d\Omega}\right|_{S.A.} = \int_{\substack{-\infty \\ Q\,\text{constant}}}^{+\infty} \frac{d^2\sigma}{d\omega\, d\Omega} d\omega = \frac{\sigma_{scat}}{4\pi}$$

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas}^{i.g.} = \frac{\sigma_{scat}}{4\pi} \int_{\substack{-\infty \\ \theta\,\text{constant}}}^{E_i/\hbar} \frac{\varepsilon(k_f)}{\varepsilon(k_i)} \frac{k_f}{k_i} S^{i.g.}(Q(\omega),\omega) d\omega$$

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas}^{i.g.} = \left.\frac{d\sigma}{d\Omega}\right|_{S.A.} + \frac{\sigma_{scat}}{4\pi} P(Q_{el}) = \frac{\sigma_{scat}}{4\pi}(1 + P(Q_{el}))$$

Calculation of the inelasticity contribution using ideal gas model

Detectors efficiency:

$\varepsilon(k)=1/k$

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas}^{i.g.} = \frac{\sigma_{scat}}{4\pi} \int_{-\infty}^{E_i/\hbar} S^{i.g.}(Q(\omega),\omega)\,d\omega$$

θ constant

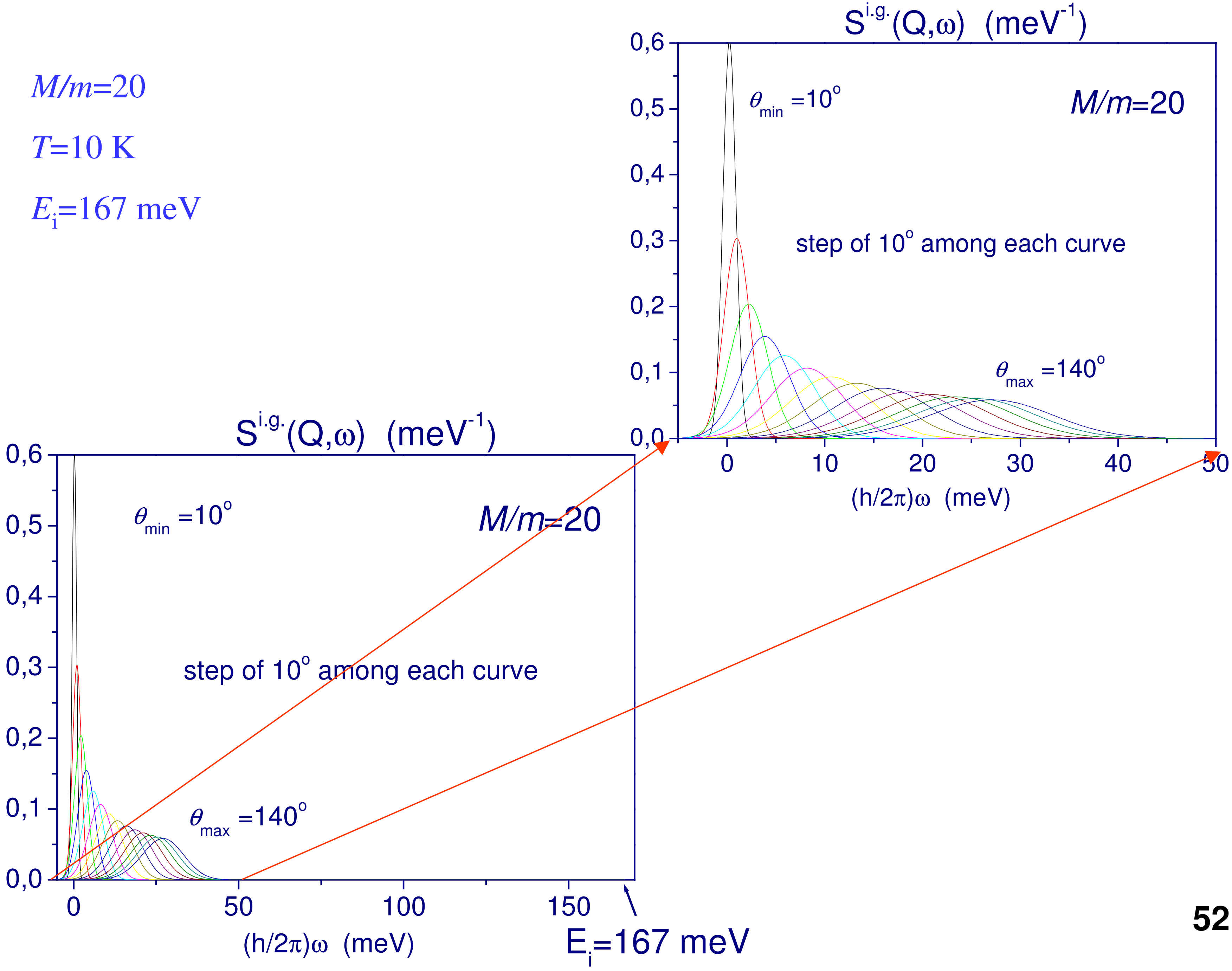
$$S^{i.g.}(Q(\omega),\omega) = \sqrt{\frac{M}{2\pi k_B T Q(\omega)^2}} \exp\left[-\frac{M}{2k_B T Q(\omega)^2}\left(\omega - \frac{\hbar Q(\omega)^2}{2M}\right)^2\right]$$

$$Q(\omega) = \frac{\sqrt{2m}}{\hbar}\sqrt{2E_i - \hbar\omega - 2\sqrt{E_i(E_i - \hbar\omega)}\cos(2\theta)}$$

M/m=20

T=10 K

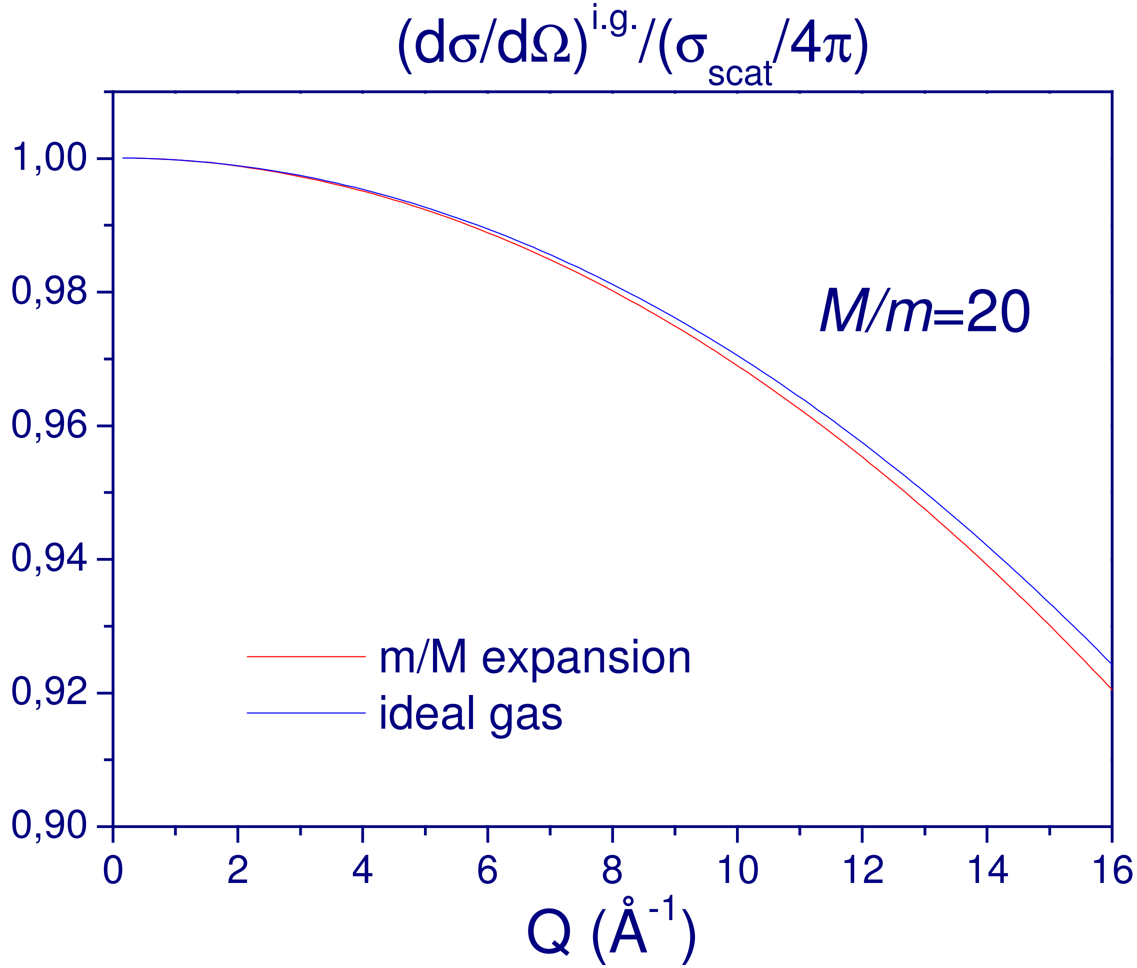
E_i=167 meV



M/m=20

T=10 K

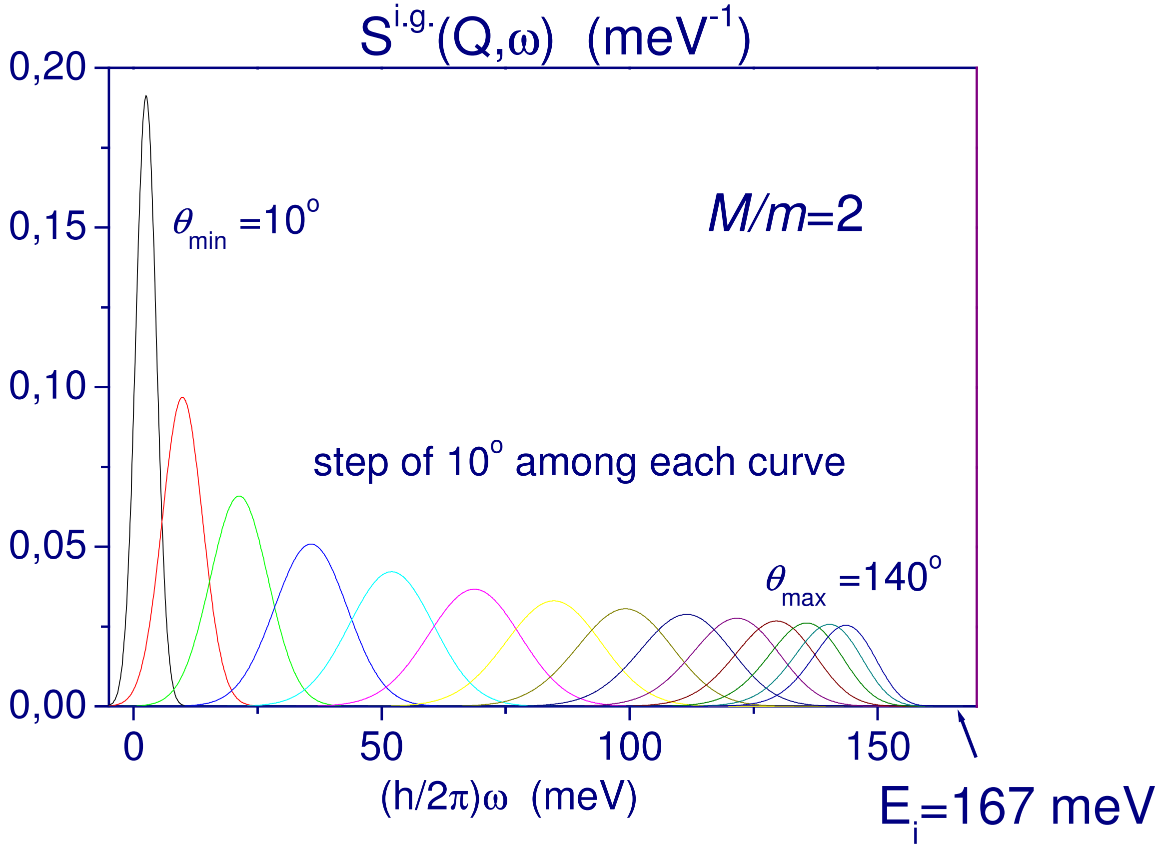
E_i=167 meV



***M/m*=2**

T=10 K

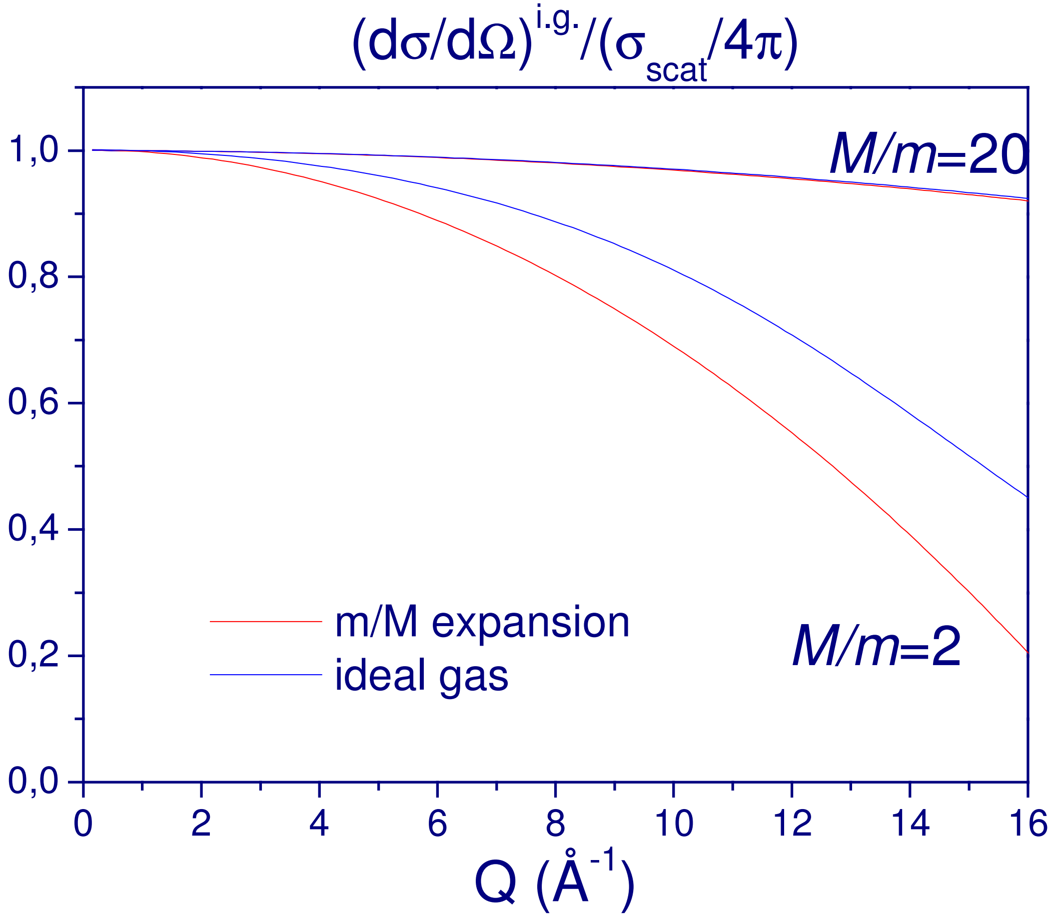
E_i=167 meV



M/m=2 **and *M/m*=2**

T=10 K

E_i=167 meV



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