From raw data to differential scattering cross section

Alan Soper, ISIS Facility

UK

Total Scattering at ISIS

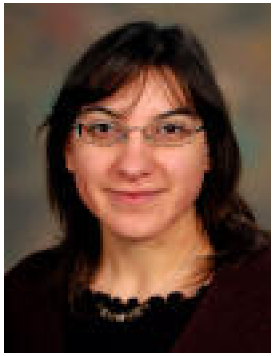
Daniel Bowron,

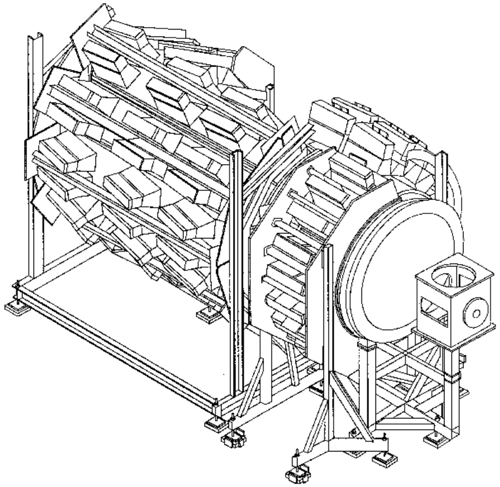
Group Leader

Disordered Materials

SANDALS

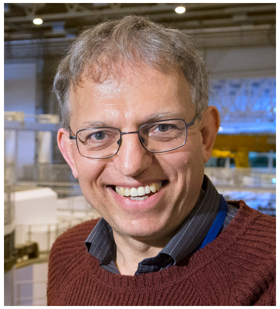
Sam Callear, Silvia Imberti



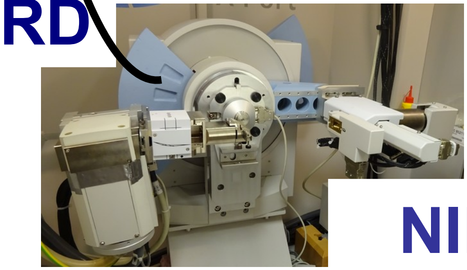


GEM

Alex Hannon
Dave Keen

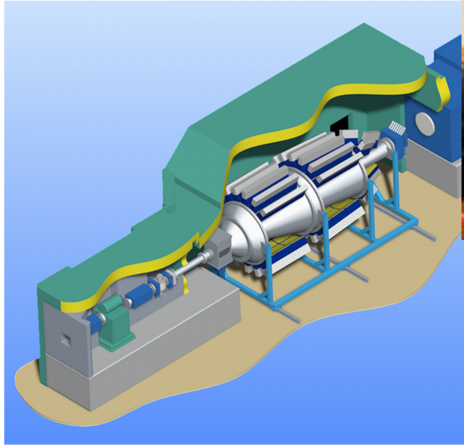


XRD

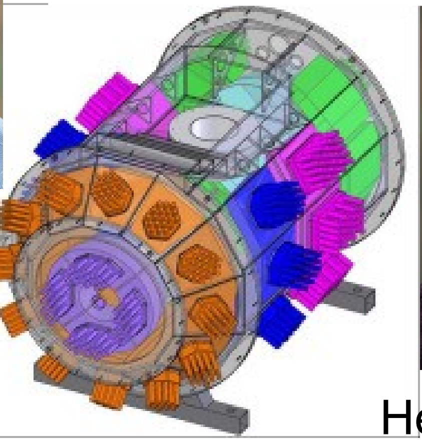


NIMROD

Tristan Youngs
Tom Headen

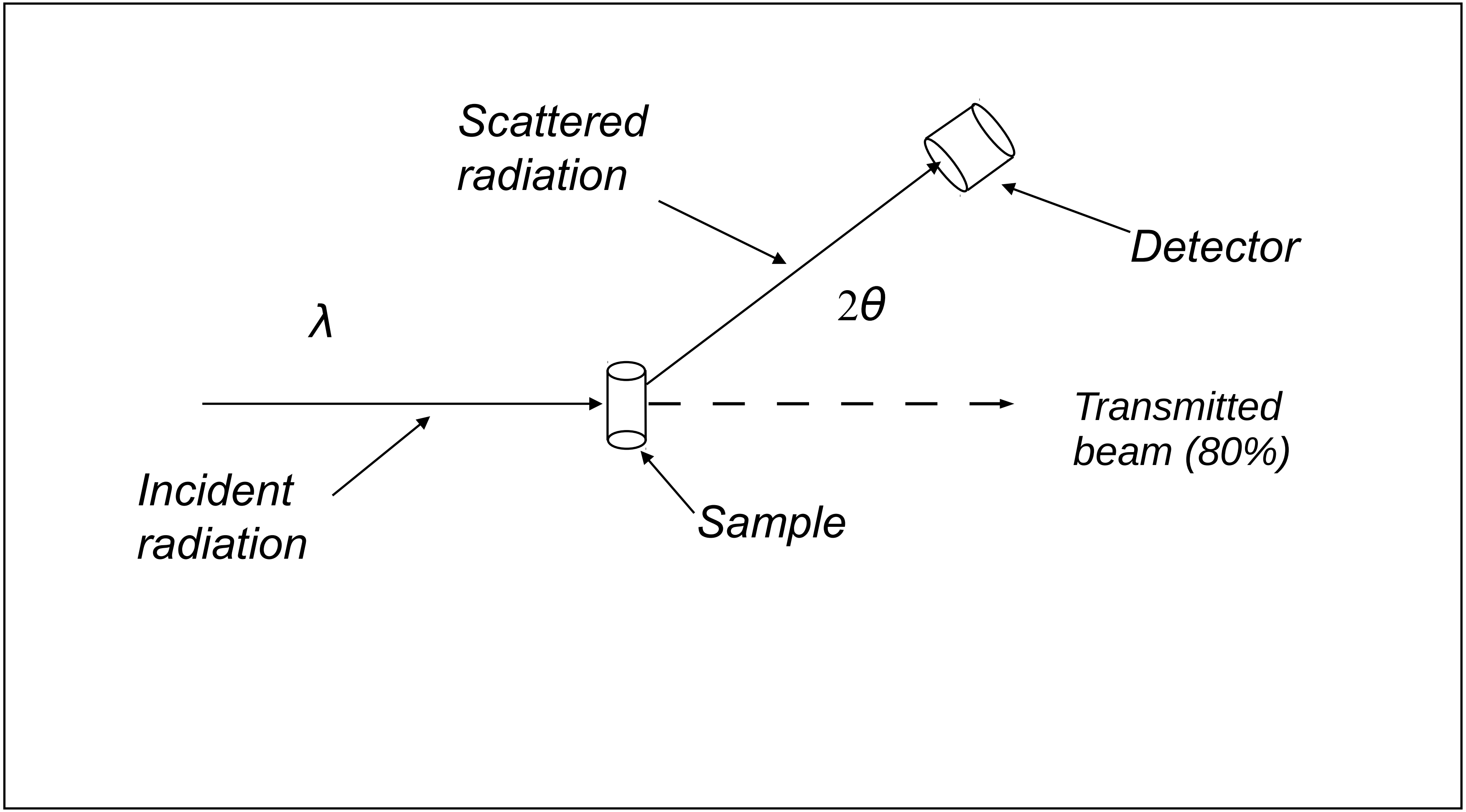


POLARIS



Helen Playford

Total scattering - a simple experiment "in principle"



The scattering cross section per atom (CS)

$$\sigma = \frac{No.\,of\ particles\ scattered\ per\ unit\ time \times Area\ of\ sample}{No.\,of\ particles\ incident\ per\ unit\ time \times No.\,of\ atoms}$$

This is a function of wavelength, λ:-

No. of particles scattered by sample per unit time

Area of sample

$$\sigma_S(\lambda) = \frac{I_S(\lambda)\,A}{N_S\,\Phi(\lambda)} = \frac{I_S(\lambda)\,A}{N_S\,\phi(\lambda)\,A} = \frac{I_S(\lambda)}{N_S\,\phi(\lambda)}$$

No. of scattering centres

No. of particles incident on sample per unit time

No. of particles incident on sample per unit area per unit time (= flux)

The differential scattering cross section (DCS)

$I_S(\lambda)$ is a function of scattering angle, 2θ.

Define the **differential** scattering CS per atom per unit solid angle:

$$\frac{d\sigma_S}{d\Omega}(\lambda, 2\theta) = \frac{dI_S(\lambda, 2\theta)}{N_S \phi(\lambda) d\Omega}$$

This can be related directly to structure:-

The differential scattering cross section (DCS)

"Neutron scattering length" or
"electron form factor"

Scattering amplitude: $A(Q)=\sum_i b_i \exp(i\vec{Q}\cdot\vec{r}_i)$

Scattered intensity [per atom]:-

$$\frac{d\sigma}{d\Omega}(\lambda,2\theta) = \frac{|A(Q)A(Q)|}{N} = \frac{\sum_{i,j} b_i b_j \exp i\vec{Q}\cdot(\vec{r}_i-\vec{r}_j)}{N}$$

$$= \frac{\sum_i b_i^2}{N} + \frac{\sum_{i,j\neq i} b_i b_j \exp i\vec{Q}\cdot(\vec{r}_i-\vec{r}_j)}{N}$$

$$Q=\frac{4\pi\sin\theta}{\lambda}$$

"Single atom" or
"self" term

"Distinct" or
"interference" term

The differential scattering cross section:

Partial structure factors, $H_{\alpha\beta}(Q) = S_{\alpha\beta}(Q)-1$

Site-site radial distribution functions

$$\frac{d\sigma}{d\Omega}=\sum_{\alpha} c_{\alpha} b_{\alpha}^{2}+\sum_{\alpha,\,\beta\geq\alpha}\left(2-\delta_{\alpha\beta}\right) c_{\alpha} c_{\beta} b_{\alpha} b_{\beta}\left\{4\pi\rho\int_{0}^{\infty} r^{2}\left(g_{\alpha\beta}(r)-1\right)\frac{\sin Qr}{Qr}\,dr\right\}$$

"Single atom" or "self" term

Atomic fraction of component "α": $c_{\alpha}=\frac{N_{\alpha}}{N}$

Properties of the neutron differential cross section – effect of inelastic scattering

- According to van Hove (1954) the dynamic structure factor, $S(Q,\varepsilon)$, splits into two terms:
  - The self term, $S_s(Q,\varepsilon)$, corresponds to atoms correlating with themselves.
  - The distinct term, $S_d(Q,\varepsilon)$, corresponds to atoms correlating with other atoms.
- The total scattering cross section is related to:-

$$\frac{d^2\sigma}{d\Omega\, d\varepsilon} \sim \frac{k_f}{k_i}\left\{ \langle b^2\rangle S_s(Q,\varepsilon) + \langle b\rangle^2 S_d(Q,\varepsilon) \right\}$$

Properties of the neutron differential cross section – effect of inelastic scattering

- The self term, $S_s(Q,\varepsilon)$, corresponds to atoms correlating with themselves:

$$g_s(r,t)$$

  - Vibrational motions, quasi-elastic scattering, **not** energy dispersive.

- The distinct term, $S_d(Q,\varepsilon)$, corresponds to atoms correlating with other atoms:

$$g_d(r,t)$$

  - Propagating modes, phonons, magnons, collective motions, energy dispersive

Sum rules: the “static” structure factor

- For self scattering:-

$$\int_Q S_s(Q,\varepsilon)\, d\varepsilon = 1$$

Sum rules: the "static" structure factor

- For distinct scattering :-

$$\int_Q S_d(Q,\epsilon)\,d\epsilon = S(Q,\Delta t=0)-1=\frac{4\pi\rho}{Q}\int r\left(g(r,\Delta t=0)-1\right)\sin Qr\,dr$$

  - "Instantaneous structure" averaged over positions

- This must be carefully distinguished from the **elastic** structure factor from Bragg scattering

$$S_d(Q,\epsilon=0)\equiv\int S_d(Q,\Delta t)\,d\Delta t$$

  - "Time averaged structure"


ISIS TS2 1 Tue Jun 22 10:37:01 2004


ISIS TS2 1 Tue Jun 22 10:38:01 2004

ISIS TS2 1 Tue Jun 22 10:39:01 2004


ISIS TS2 1 Tue Jun 22 10:40:01 2004


ISIS TS2 1 Tue Jun 22 10:41:01 2004


ISIS TS2 1 Tue Jun 22 10:42:01 2004


ISIS TS2 1 Tue Jun 22 10:43:01 2004


ISIS TS2 1 Tue Jun 22 10:44:01 2004


ISIS TS2 1 Tue Jun 22 10:45:01 2004


ISIS TS2 1 Tue Jun 22 10:46:01 2004

Time averaged structure

Effect of energy transfer

- Kinematics of neutron scattering:-

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

$$\varepsilon = \frac{\hbar^2}{2m}\left(k_i^2 - k_f^2\right)$$

- In a diffraction experiment the neutron detector integrates *S(Q,ε)* at constant 2*θ*, NOT constant *Q*.

Effect of energy transfer

- For distinct scattering (Placzek, 1952):-

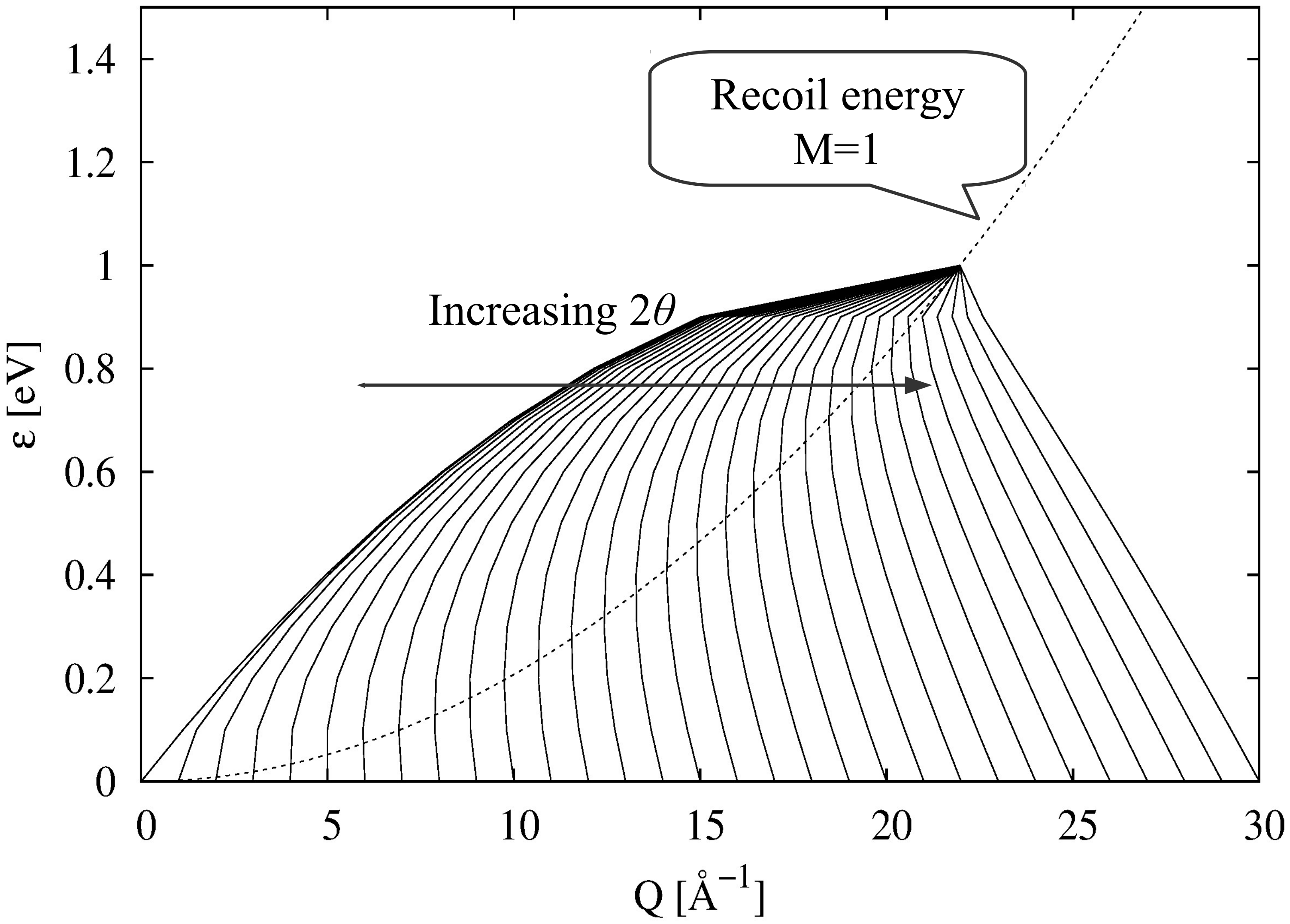
$$\int_Q \epsilon S_d(Q,\epsilon)\, d\epsilon = 0$$

- For self scattering:-

$$\int_Q \epsilon S_s(Q,\epsilon)\, d\epsilon = \frac{\hbar^2 Q^2}{2\mathrm{M}}$$

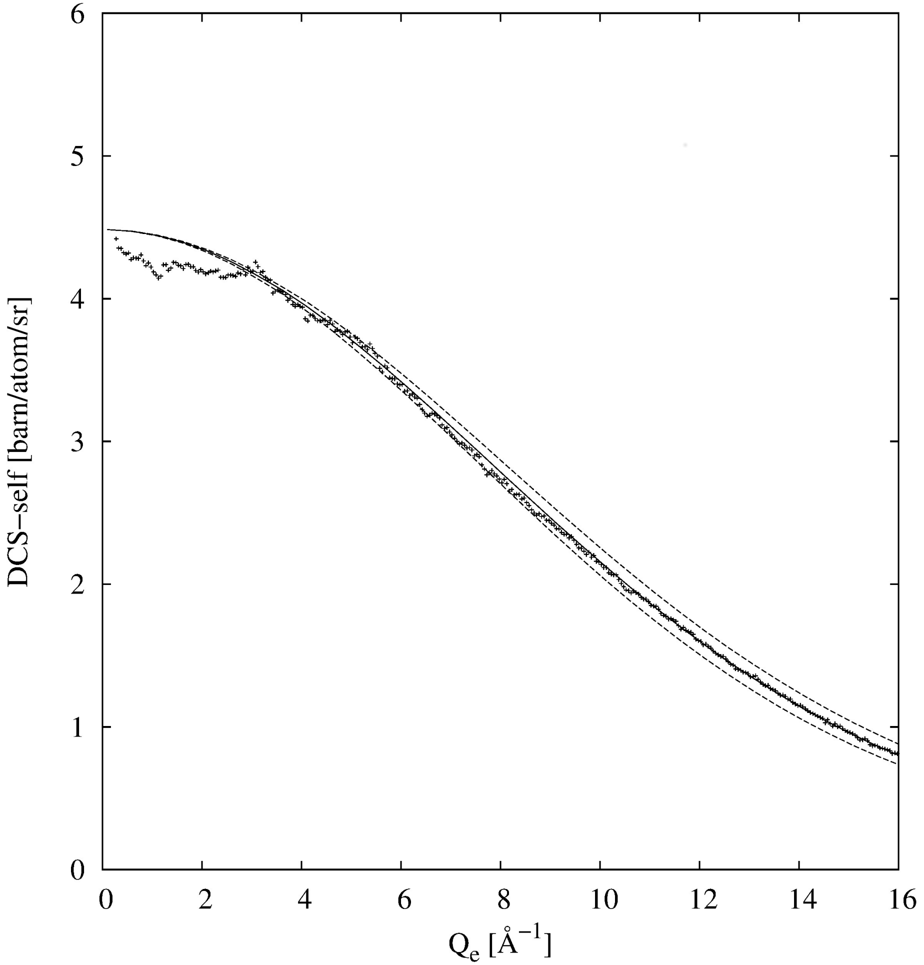
- $M_p \approx M_n$ means significant energy loss on scattering by protons.

Fixed incident energy plot
E_i = 1eV

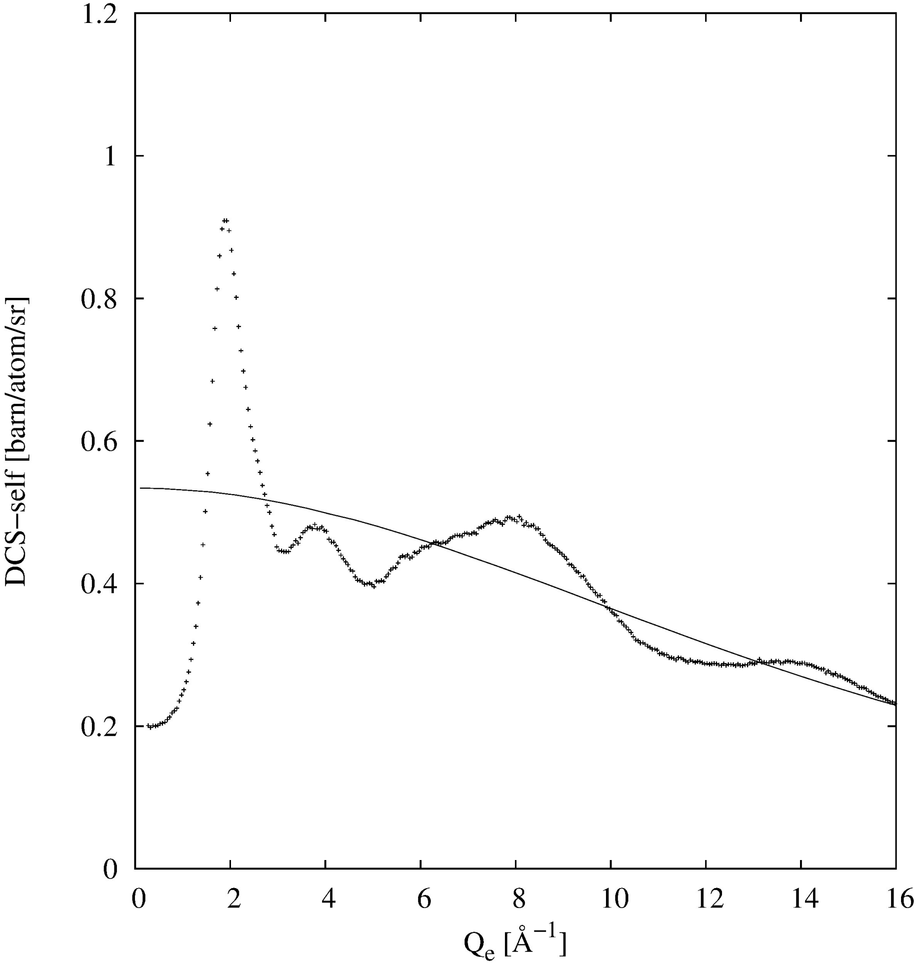


Fixed wavelength data

H_2O



D_2O



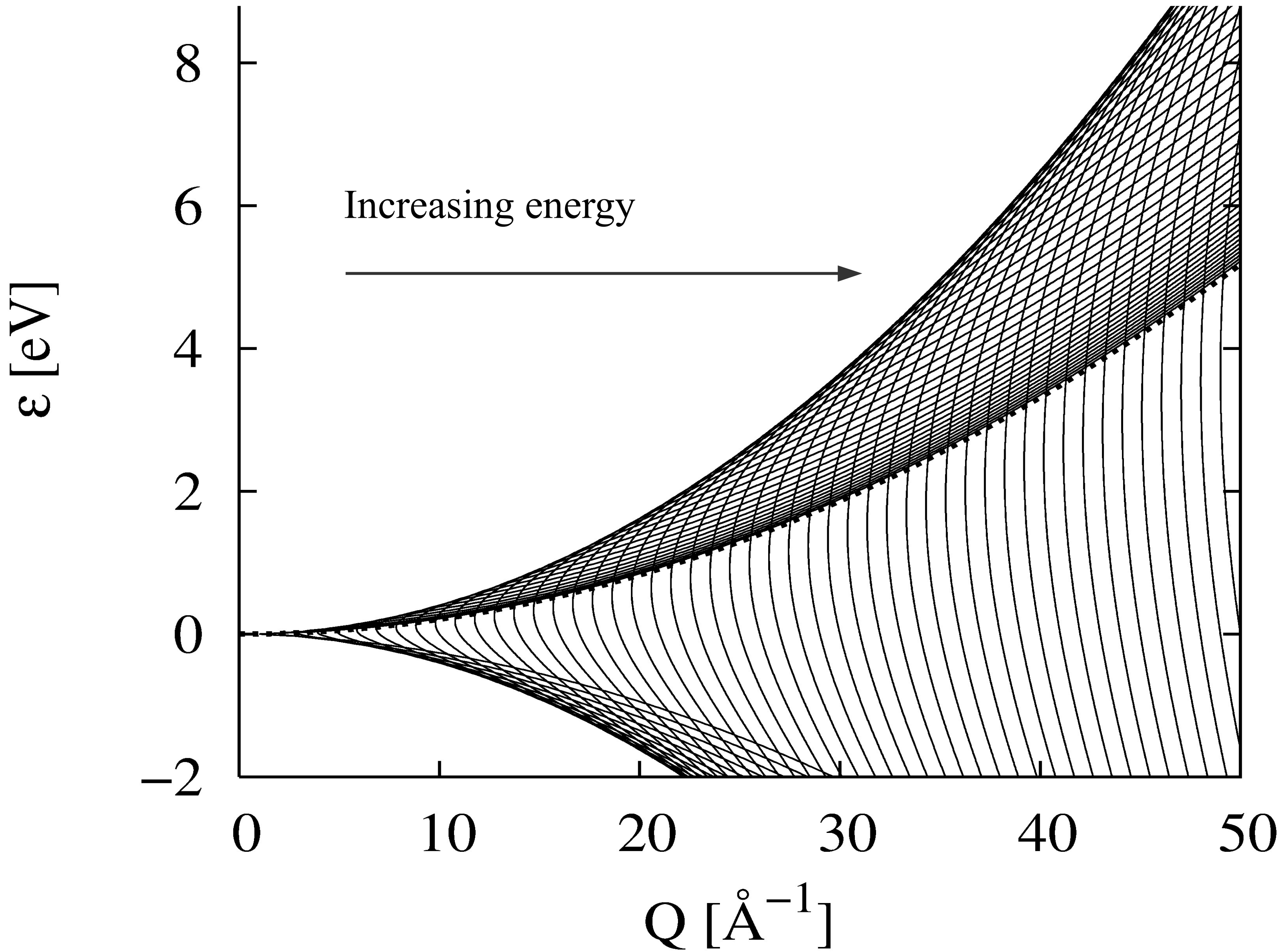
Time of Flight diffraction

- Energy dispersive.
- Detector at fixed scattering angle.
- Detector still integrates at constant angle, but *each* time of flight channel corresponds to a *range* of incident energies:

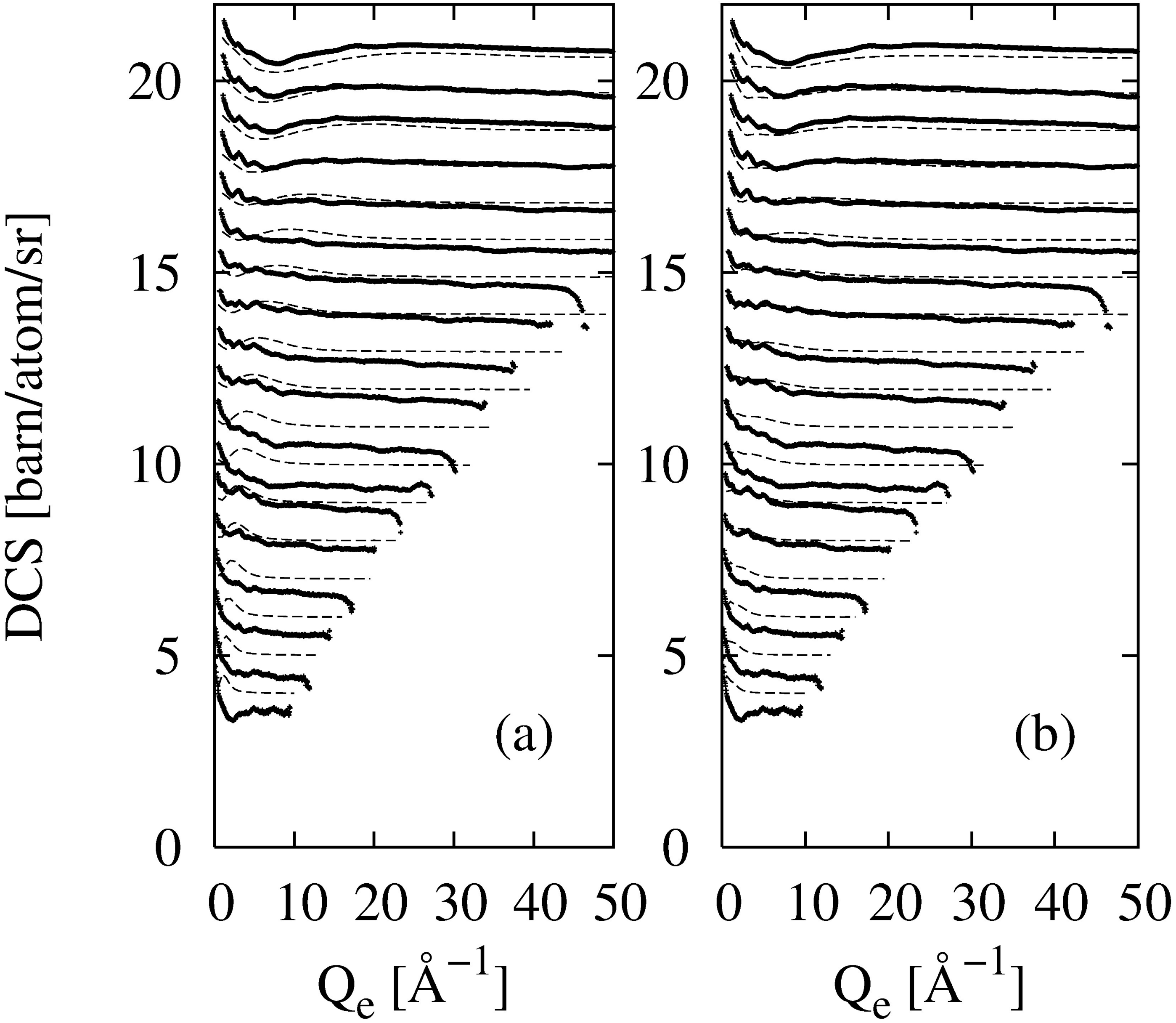
$$\frac{(1+R)}{k_e} = \frac{1}{k_i} + \frac{R}{k_f}, \quad k_e = \frac{Q_e}{2\sin\theta}$$

Constant time-of-flight plots:

Fixed 2θ = 30º



Pulsed Source Data



The known unknowns in data analysis...

- We don’t know incident flux;
- Our neutron or X-ray detector is not perfect – efficiency and solid angle known only approximately;
- Data will include “background”;
- Sample (+ containers) will self-attenuate radiation;
- Sample (+ containers) will multiply scatter radiation;
- Data need to be corrected for container scattering
- Radiation may lose or gain energy in the scattering process;
- (For x-rays) Sample may fluoresce;
- (For x-rays) White beam corrections;
- **Data need to be corrected for all of the above and put on an absolute scale of DCS**.

So why would you NOT do this?

- It's difficult – does not always work very well;
- It's tedious – accurate attenuation, multiple scattering and inelasticity corrections can be difficult to obtain;
    - Nobody wants to write the code!
    - Does not (immediately) lead to high impact publications!
- It might be slow, hence bad for multiple datasets through a transition;
- You do not need it (possibly?) if you are only interested in Rietveld refinement.

Billinge and Farrow, JPCM 2012

  - “We examine the equations to obtain atomic pair distribution functions (PDFs) from x-ray, neutron and electron powder diffraction data with a view to obtaining reliable and accurate PDFs from the raw data using a largely ad hoc correction process.”
  - “We find that this should be possible under certain circumstances that hold, to a reasonably good approximation, in many modern experiments.”
  - “We describe a variational approach that could be applied to find data correction parameters that is highly automatable and should require little in the way of user inputs yet results in quantitatively reliable PDFs, modulo unknown scale factors that are often not of scientific interest when profile fitting models ...”

- Problem is, particularly for energy dispersive scattering, corrections are both additive and multiplicative, and can be strongly energy dependent.

Why you should perform corrections...

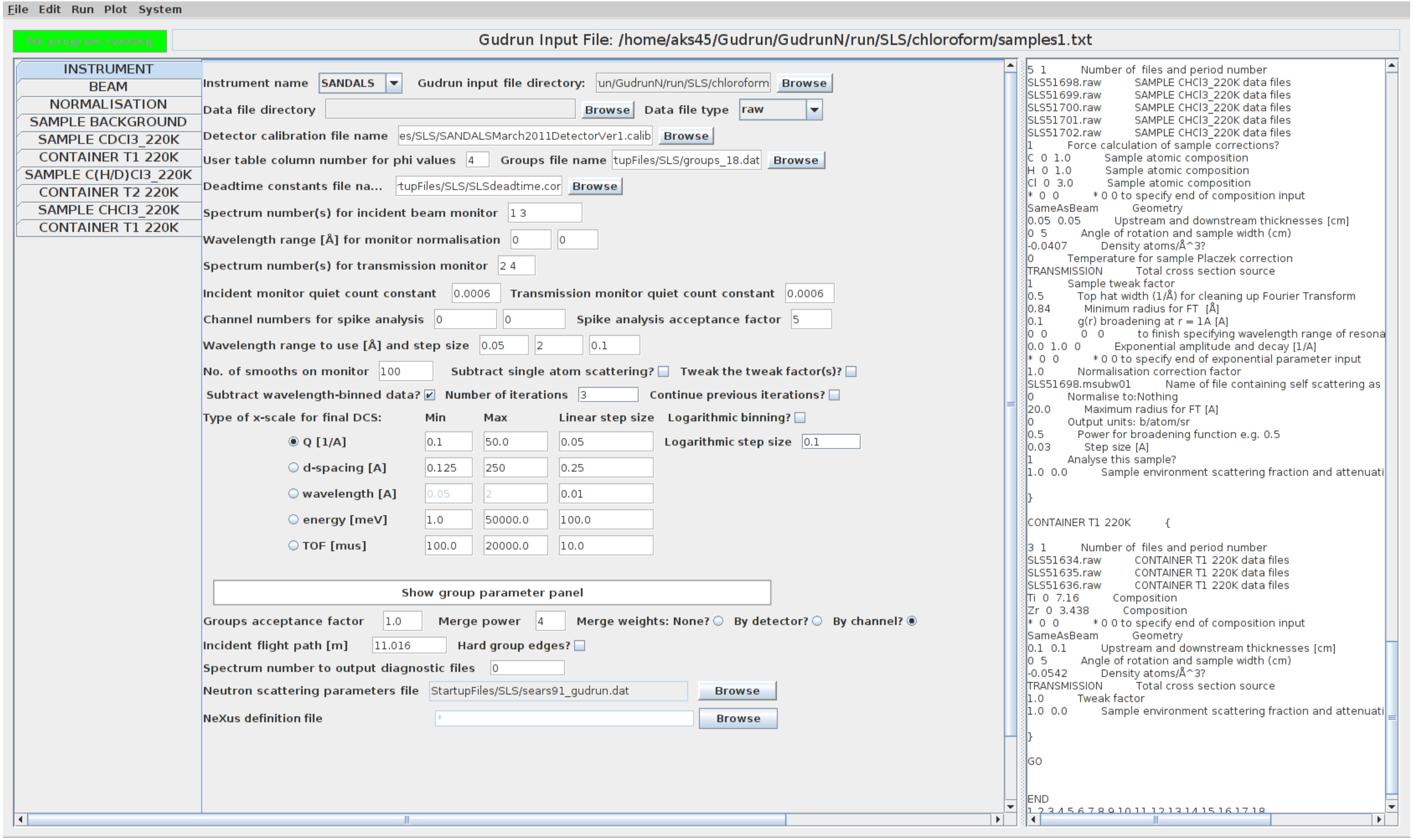
<u>Four</u> important reasons, particularly for disordered materials, but crystalline materials also:-

- Not all samples are what they seem!
  - If the DCS level comes out wrong at high Q, probably there is an error in the sample itself or the assumed sample composition and/or density.
  - This DOES happen, quite frequently!!
- Coordination numbers require absolute DCS data;
- Accurate computer modelling require absolute DCS data;
- Especially important to have an absolute scale if small angle scattering is present.

The steps in data analysis

1) Remove incident spectrum – divide by beam monitor;
2) Subtract the background;
3) Prepare the vanadium calibration data – this will be used to remove detector efficiency and solid angle effects;
4) Apply the vanadium calibration;
5) Remove multiple scattering;
6) Correct for attenuation and normalise to number of atoms in the beam. This includes removing any container scattering;
7) Remove any inelasticity effects;
8) Sum detectors on to a common Q or wavelength scale. Apply any final “tweaks”, e.g. packing fraction.

AT ISIS we use Gudrun to perform these steps



Gudrun Input File: /home/aks45/Gudrun/GudrunN/run/SLS/chloroform/samples1.txt

Instrument name: SANDALS
Gudrun input file directory: un/GudrunN/run/SLS/chloroform
Data file directory:
Data file type: raw
Detector calibration file name: es/SLS/SANDALSMarch2011DetectorVer1.calib
User table column number for phi values: 4
Groups file name: tupFiles/SLS/groups_18.dat
Deadtime constants file na...: tupFiles/SLS/SLSdeadtime.cor
Spectrum number(s) for incident beam monitor: 1 3
Wavelength range [Å] for monitor normalisation: 0 0
Spectrum number(s) for transmission monitor: 2 4
Incident monitor quiet count constant: 0.0006
Transmission monitor quiet count constant: 0.0006
Channel numbers for spike analysis: 0 0
Spike analysis acceptance factor: 5
Wavelength range to use [Å] and step size: 0.05 2 0.1
No. of smooths on monitor: 100
Subtract single atom scattering? ☐
Tweak the tweak factor(s)? ☐
Subtract wavelength-binned data? ☑
Number of iterations: 3
Continue previous iterations? ☐

Type of x-scale for final DCS:	Min	Max	Linear step size
● Q [1/A]	0.1	50.0	0.05
○ d-spacing [A]	0.125	250	0.25
○ wavelength [A]	0.05	2	0.01
○ energy [meV]	1.0	50000.0	100.0
○ TOF [mus]	100.0	20000.0	10.0

Logarithmic binning? ☐
Logarithmic step size: 0.1

Groups acceptance factor: 1.0
Merge power: 4
Merge weights: None? ○ By detector? ○ By channel? ●
Incident flight path [m]: 11.016
Hard group edges? ☐
Spectrum number to output diagnostic files: 0
Neutron scattering parameters file: StartupFiles/SLS/sears91_gudrun.dat
NeXus definition file: *

```
5  1          Number of  files and period number
SLS51698.raw          SAMPLE CHCl3_220K data files
SLS51699.raw          SAMPLE CHCl3_220K data files
SLS51700.raw          SAMPLE CHCl3_220K data files
SLS51701.raw          SAMPLE CHCl3_220K data files
SLS51702.raw          SAMPLE CHCl3_220K data files
1          Force calculation of sample corrections?
C  0  1.0          Sample atomic composition
H  0  1.0          Sample atomic composition
Cl  0  3.0          Sample atomic composition
*  0  0          * 0 0 to specify end of composition input
SameAsBeam          Geometry
0.05  0.05          Upstream and downstream thicknesses [cm]
0  5          Angle of rotation and sample width (cm)
-0.0407          Density atoms/Å^3?
0          Temperature for sample Placzek correction
TRANSMISSION          Total cross section source
1          Sample tweak factor
0.5          Top hat width (1/Å) for cleaning up Fourier Transform
0.84          Minimum radius for FT  [Å]
0.1          g(r) broadening at r = 1A [A]
0  0          0   0          to finish specifying wavelength range of resona
0.0  1.0  0          Exponential amplitude and decay [1/A]
*  0  0          * 0 0 to specify end of exponential parameter input
1.0          Normalisation correction factor
SLS51698.msubw01          Name of file containing self scattering as
0          Normalise to:Nothing
20.0          Maximum radius for FT [A]
0          Output units: b/atom/sr
0.5          Power for broadening function e.g. 0.5
0.03          Step size [A]
1          Analyse this sample?
1.0  0.0          Sample environment scattering fraction and attenuati

}

CONTAINER T1 220K          {

3  1          Number of  files and period number
SLS51634.raw          CONTAINER T1 220K data files
SLS51635.raw          CONTAINER T1 220K data files
SLS51636.raw          CONTAINER T1 220K data files
Ti  0  7.16          Composition
Zr  0  3.438          Composition
*  0  0          * 0 0 to specify end of composition input
SameAsBeam          Geometry
0.1  0.1          Upstream and downstream thicknesses [cm]
0  5          Angle of rotation and sample width (cm)
-0.0542          Density atoms/Å^3?
TRANSMISSION          Total cross section source
1.0          Tweak factor
1.0  0.0          Sample environment scattering fraction and attenuati

}

GO


END
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
```

Step 1: Remove incident spectrum

- Every beam line will have an incident beam monitor.
- Use this to measure the incident spectrum:

$$I_M(\lambda)=\phi(\lambda)E_M(\lambda)$$

$$NORMMON_S(\lambda,2\theta)=\frac{\Delta I_S(\lambda,2\theta)}{I_M(\lambda)}=\frac{N_S\frac{d\sigma_S}{d\Omega}(\lambda,2\theta)E_{(d)}(\lambda)\Delta\Omega}{E_M(\lambda)}$$

Step 2: Subtract the background

- Every detector has an intrinsic quiet count.
- In addition there may be neutrons arriving not directly from the sample.

$$SUBBAK_S(\lambda, 2\theta) = NORMMON_S(\lambda, 2\theta) - NORMMON_B(\lambda, 2\theta)$$

$$= N_S \frac{d\sigma_S}{d\Omega}(\lambda, 2\theta) \frac{E_d(\lambda)}{E_M(\lambda)} \Delta\Omega$$

(B = Background)

Step 3: Set up the calibration

- Number of detected neutrons depends on:
  - Detector efficiency
  - Detector solid angle
- Measure a known sample to get these.
- Vanadium is ideal because it scatters (almost) isotropically:

First subtract vanadium background...

$$SUBBAK_V(\lambda,2\theta)=NORMMON_V(\lambda,2\theta)-NORMMON_B(\lambda,2\theta)$$

$$=N_V\frac{d\sigma_V}{d\Omega}(\lambda,2\theta)\frac{E_d(\lambda)}{E_M(\lambda)}\Delta\Omega$$

- (V = Vanadium = Calibration, since we can calculate

$$N_V\frac{d\sigma_V}{d\Omega}(\lambda,2\theta)$$

Then form calibration for each detector

Measured

$$VANCOR_V(\lambda,2\theta)=\frac{SUBBAK_V(\lambda,2\theta)}{N_V\frac{d\sigma_V}{d\Omega}(\lambda,2\theta)}=\frac{E_d(\lambda)\Delta\Omega}{E_M(\lambda)}$$

Calculated

- This can be smoothed if required.

$$SMOVAN_V(\lambda,2\theta)=\frac{E_d(\lambda)\Delta\Omega}{E_M(\lambda)}$$

Step 4: Apply calibration to sample data

- For every detector and every λ, form the ratio:

$$NORMVAN_S(\lambda, 2\theta) = \frac{SUBBAK_S(\lambda, 2\theta)}{SMOVAN_V(\lambda, 2\theta)}$$

$$= \frac{N_S \frac{d\sigma_S}{d\Omega}(\lambda, 2\theta) \frac{E_d(\lambda)}{E_M(\lambda)} \Delta\Omega}{\frac{E_d(\lambda)}{E_M(\lambda)} \Delta\Omega}$$

$$= N_S \frac{d\sigma_S}{d\Omega}(\lambda, 2\theta)$$

Step 5: Correct for multiple scattering

- Multiple scattering occurs in virtually all neutron scattering experiments.
- Cannot measure it – rely on computer estimates: $M_S(\lambda, 2\theta)$

$$
\begin{aligned}
MULCOR_S(\lambda, 2\theta) = {} & NORMVAN_S(\lambda, 2\theta) \\
& -M_S(\lambda, 2\theta)
\end{aligned}
$$

Step 6: Correct for attenuation and normalise to number of atoms in beam

- As with multiple scattering, attenuation occurs in virtually all neutron scattering experiments.

$$A_S(\lambda, 2\theta)$$

- Estimate correction:

$$ABSCOR_S(\lambda, 2\theta) = \frac{MULCOR_S(\lambda, 2\theta)}{T_S N_S A_S(\lambda, 2\theta)}$$

Further correction for packing fraction, calibration errors, etc.

Step 7: Remove inelasticity effects

- Inelastic scattering occurs in virtually all neutron scattering experiments
- For heavier elements, approximate estimate is good enough.
- For H and D impossible to calculate accurately enough.
- Sometimes called “Placzek” corrections, $P_S(\lambda, 2\theta)$

$$PLACOR_S(\lambda, 2\theta) = ABSCOR_S(\lambda, 2\theta) - P_S(\lambda, 2\theta)$$

Step 8: Finally sum detectors on to a common *Q* scale (if needed)

- Various ways of doing this.

Addendum: what to do about containers?

- Most samples are held in a container;
- Container will scatter, just like the sample;
- Therefore need a separate measure of the empty container.
- This is processed as far as step 5, exactly the same as for the sample: $MULCOR_C(\lambda, 2\theta)$

(C = Container)

At this point the two intensities are given by:

- (See Paalman and Pings)

$$MULCOR_{S+C}(\lambda, 2\theta) = A_{S,S+C} N_S \frac{d\sigma_S}{d\Omega}(\lambda, 2\theta) + A_{C,S+C} N_C \frac{d\sigma_C}{d\Omega}(\lambda, 2\theta)$$

$$MULCOR_C(\lambda, 2\theta) = A_{C,C} N_C \frac{d\sigma_C}{d\Omega}(\lambda, 2\theta)$$

Then step 6 becomes:

$$ABSCOR_S(\lambda, 2\theta) = \frac{MULCOR_{S+C}(\lambda, 2\theta) - \frac{A_{C,S+C}}{A_{C,C}} MULCOR_C(\lambda, 2\theta)}{T_S N_S A_{S,S+C}}$$

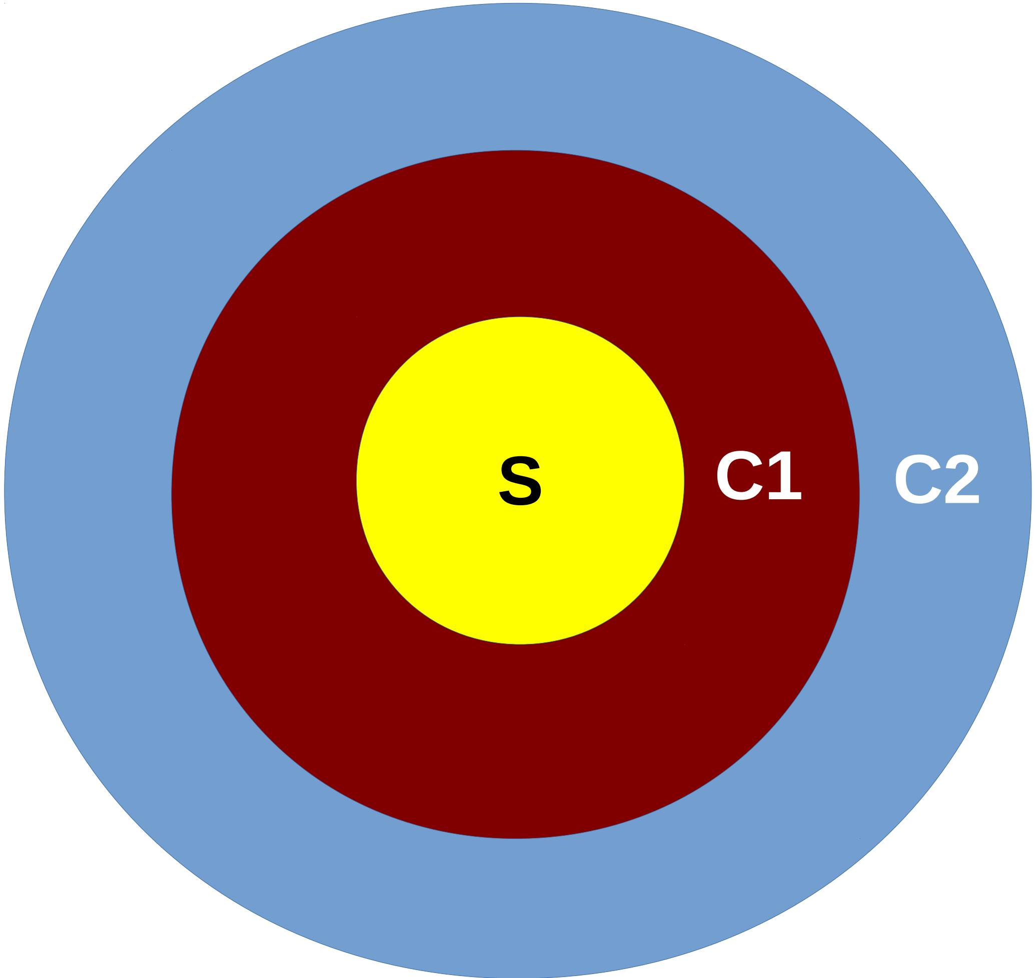
If there is more than one container

- Procedure is exactly analogous.
- Note that order of containers is important:
- We must measure:

$$I_{S+C1+C2}(\lambda, 2\theta)$$

$$I_{C1+C2}(\lambda, 2\theta)$$

$$I_{C2}(\lambda, 2\theta)$$

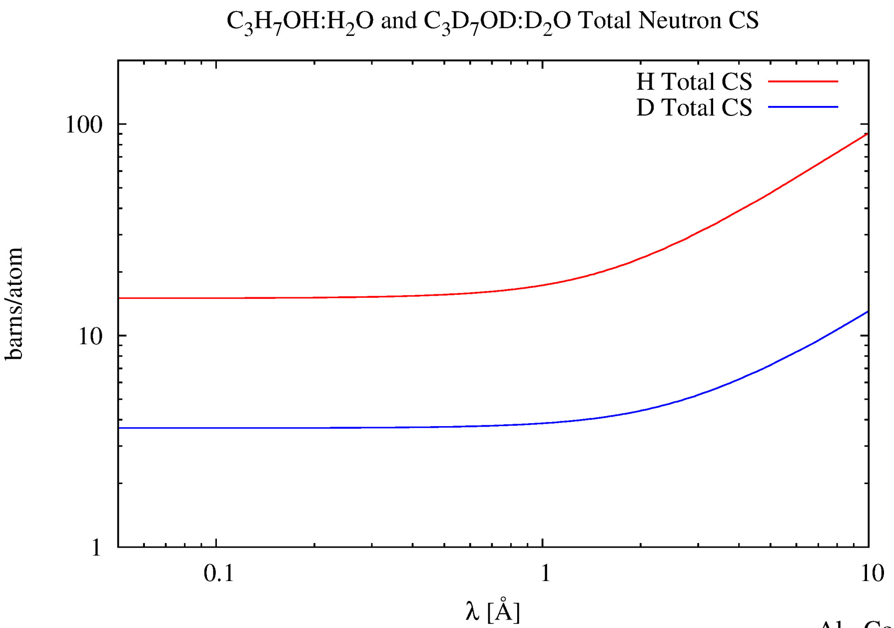


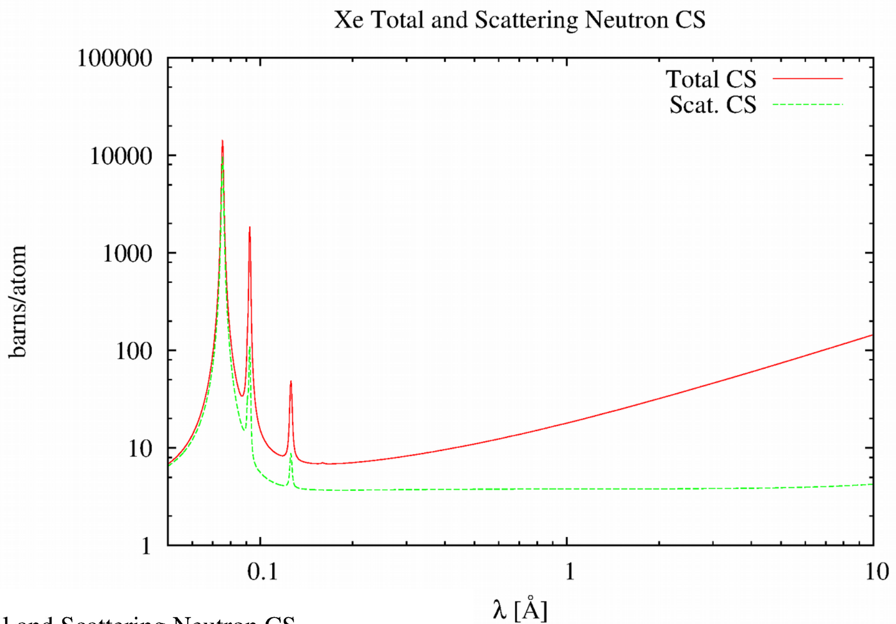
Neutron cross sections

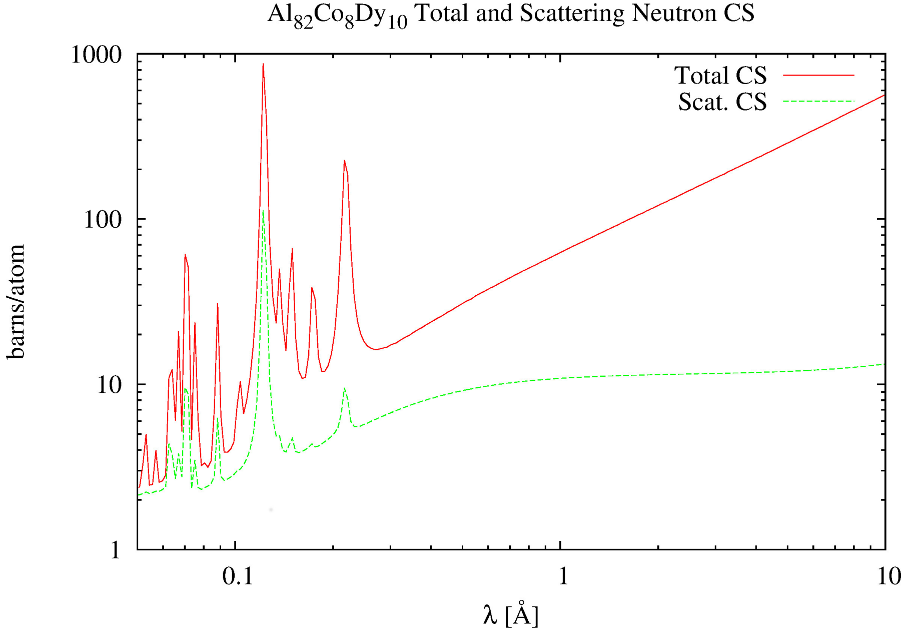
- You can use Sears table – good for many common materials.
- Or you can use a transmission monitor
  - Necessary for materials containing H and D and perhaps other light atoms, due to strong energy dependence of cross section
  - May be necessary if there are strong Bragg reflections
- Or you can supply your own values in a file. ENDF/B (NIST) libraries can also be used.

Caveat: Avoid strongly scattering or strongly absorbing samples. Avoid nuclear resonances!

Example cross sections

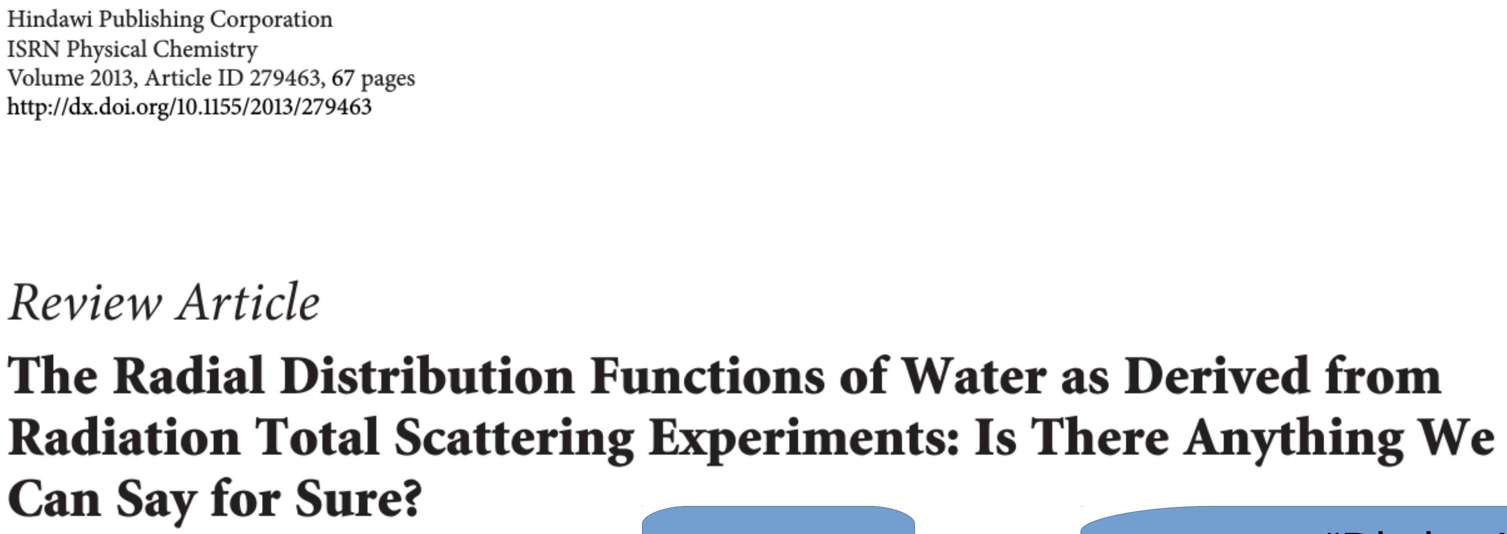

$C_3H_7OH{:}H_2O$ and $C_3D_7OD{:}D_2O$ Total Neutron CS


Xe Total and Scattering Neutron CS


$Al_{82}Co_8Dy_{10}$ Total and Scattering Neutron CS

Removing inelasticity effects for samples containing H

- Iterative scheme proposed in:-



Hindawi Publishing Corporation
ISRN Physical Chemistry
Volume 2013, Article ID 279463, 67 pages
http://dx.doi.org/10.1155/2013/279463

Review Article

The Radial Distribution Functions of Water as Derived from Radiation Total Scattering Experiments: Is There Anything We Can Say for Sure?

“Self” term

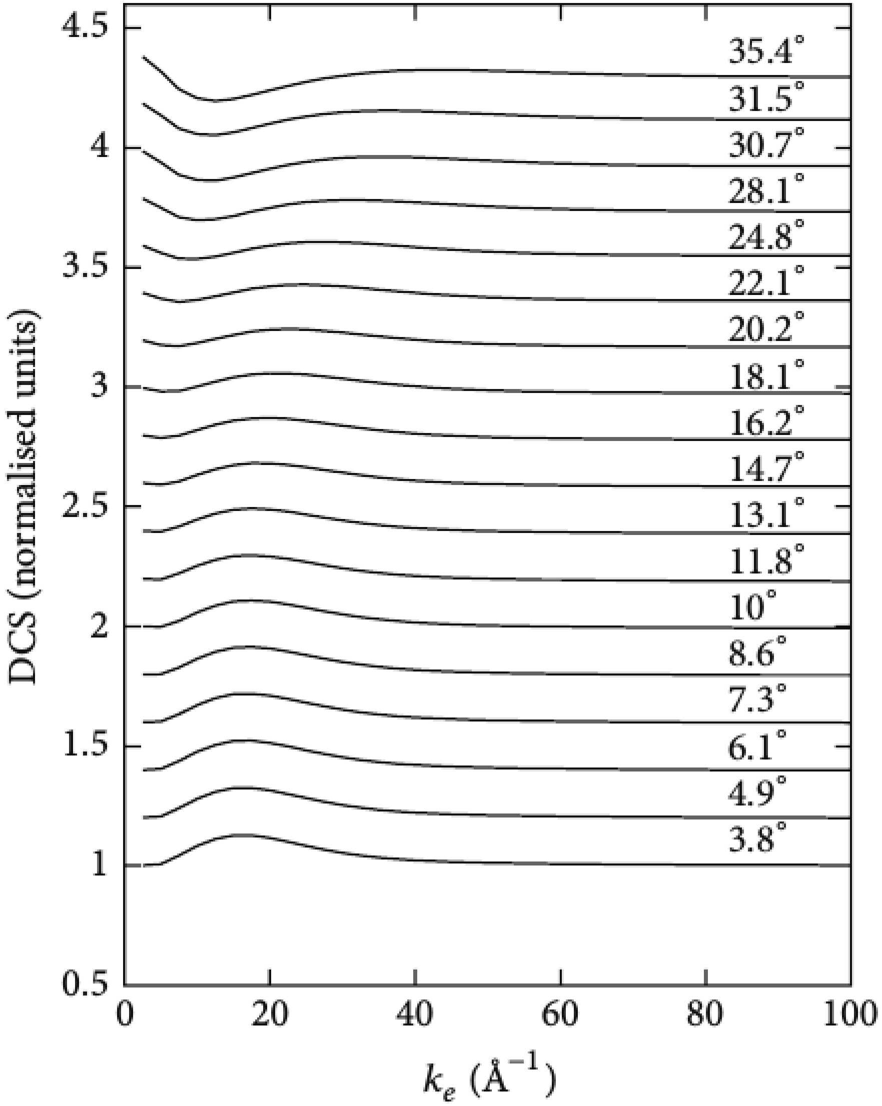
“Distinct” term
– assumed dependent ONLY on Q_e

Idea: $$J\left(k_e, 2\theta\right) = J_{\text{self}}\left(k_e, 2\theta\right) + D\left(Q_e\right).$$

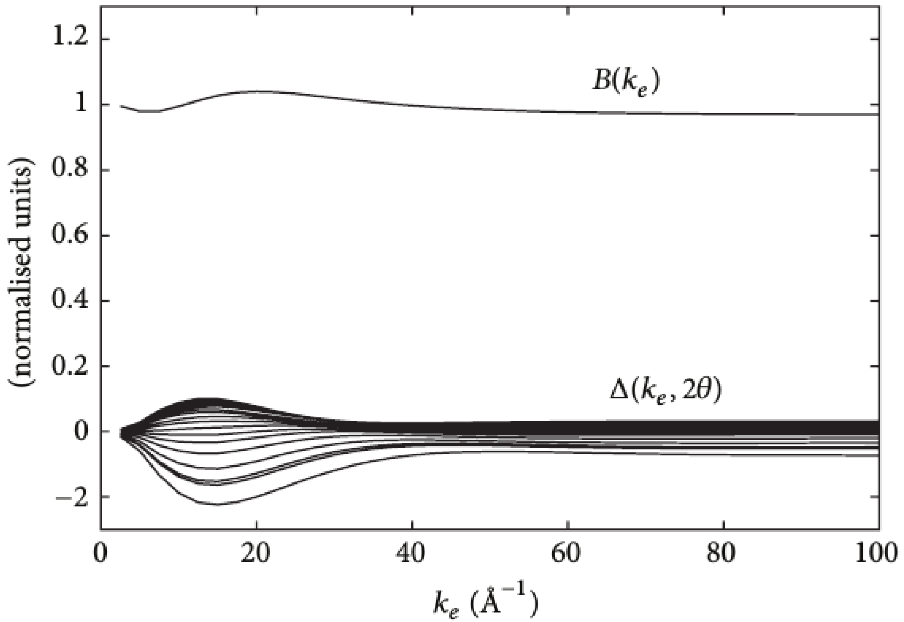
$$\left(Q_e = 2k_e \sin\theta\right)$$

Removing inelasticity effects for samples containing H

Single atom scattering for H



Add detectors at constant energy



Add detectors at constant Q_e