QENS: from scattering profile to dynamical parameters

Neutron scattering for understanding energy materials

Imperial College London

13 June 2019

F Foglia

Neutrons: Why we care about

1) Magnetic Moment

- Magnetic structure / materials

2) Spin

- Polarized beams
- Coherent and incoherent scattering

3) No Charge

- Highly penetrating
- Nondestructive
- Probe Nuclei

the weak interaction with matter means that radiation damage is very low

- strength of the interaction = scattering length (b)
- b depends on : isotopes
  nuclear spin (if non zero)
- b 'defines' scattering cross section (σ)
- σ_{coh} = reflects the main scattering event

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

- σ_{inc} = reflects the variance of the distribution of scattering lengths

$$\sigma_{inc} = 4\pi \left[\langle b^2 \rangle - \langle b \rangle^2 \right]$$

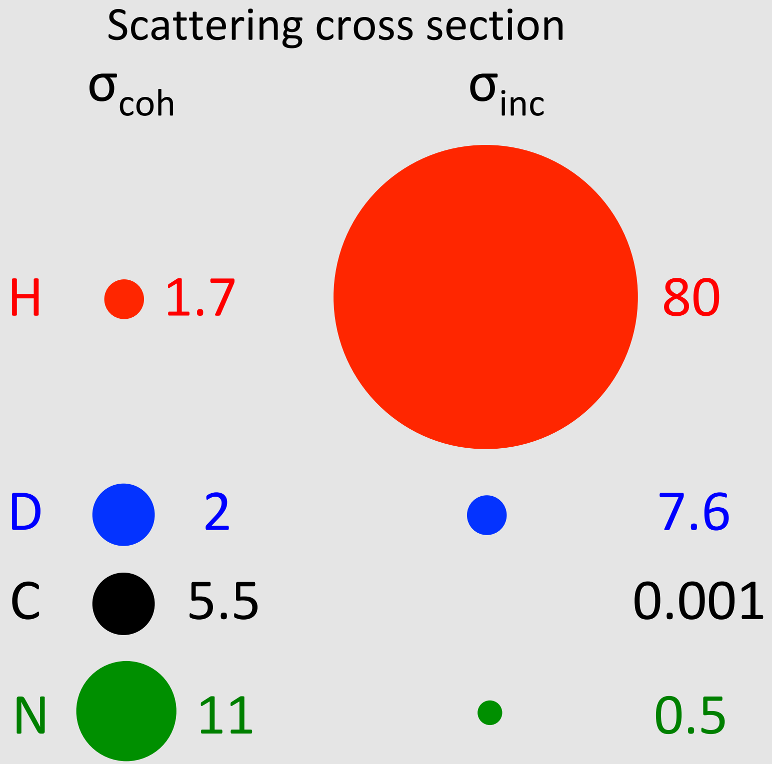
Neutrons: Why we care about

1) **Magnetic Moment**
- **Magnetic structure / materials**

2) **Spin**
- **Polarized beams**
- **Coherent and incoherent scattering**

3) **No Charge**
- **Highly penetrating**
- **Nondestructive**
- **Probe Nuclei**

Sensitive to Isotopic Substitution



Neutrons: Why we care about

UCL

1) Magnetic Moment

- Magnetic structure / materials

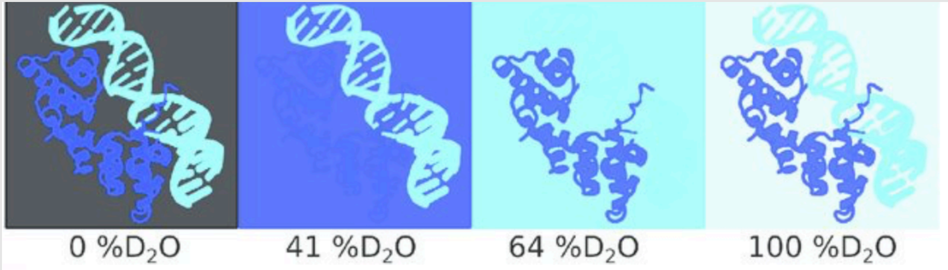
2) Spin

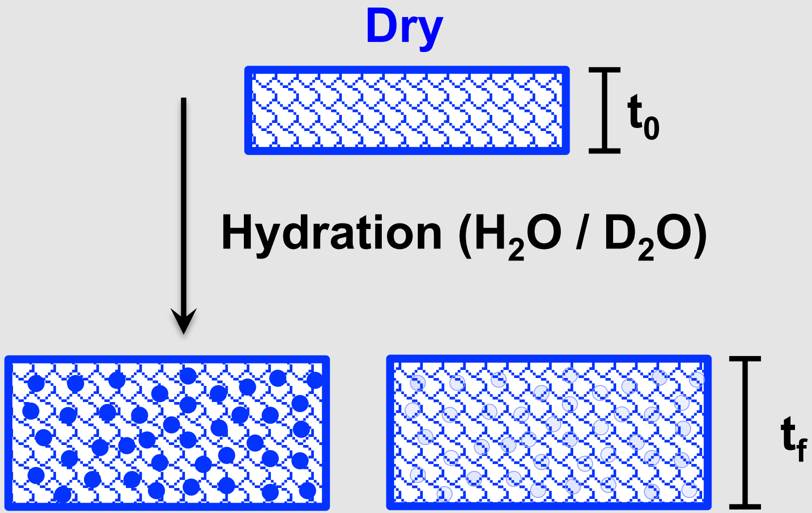
- Polarized beams
- Coherent and incoherent scattering

3) No Charge

- Highly penetrating
- Nondestructive
- Probe Nuclei

Sensitive to Isotopic Substitution





Neutrons: Why we care about

UCL

1) No Charge

- Highly penetrating
- Nondestructive

2) Magnetic Moment

- Magnetic structure / materials

3) Spin

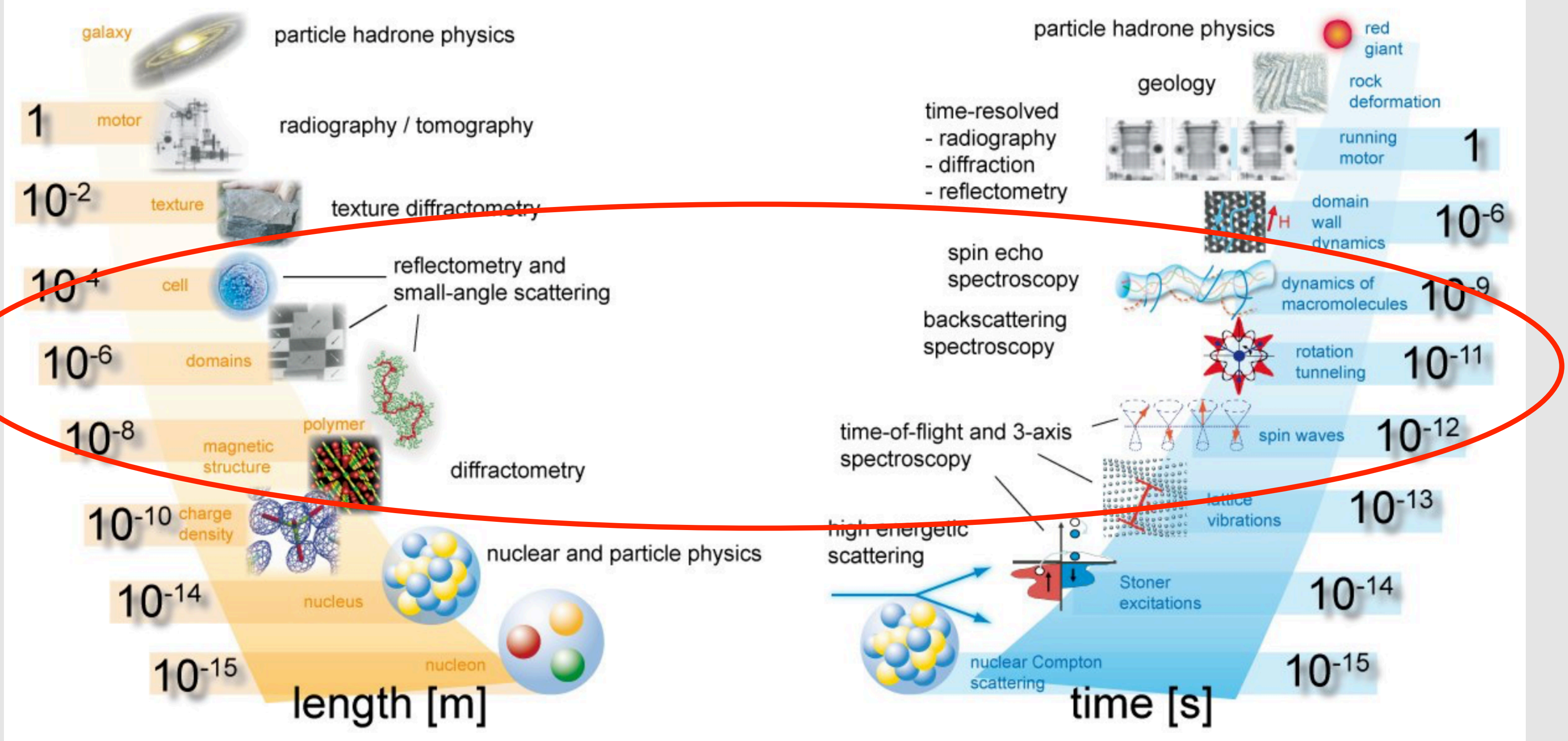
- Polarized beams
- Coherent and incoherent scattering

3) Energies are similar to the energies of elementary excitations

4) Wavelengths of neutrons are similar to atomic spacing

Allow investigations and correlations of structure form Å- to nano-scale together with molecular motions on a nano- to pico-second time regimes.

Neutrons: Why we care about



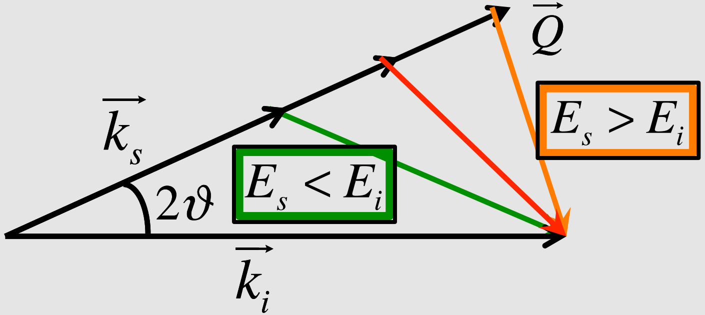
Neutrons: Why we care about

momentum transfer

$$\vec{Q} = \vec{k}_s - \vec{k}_i$$

energy transfer

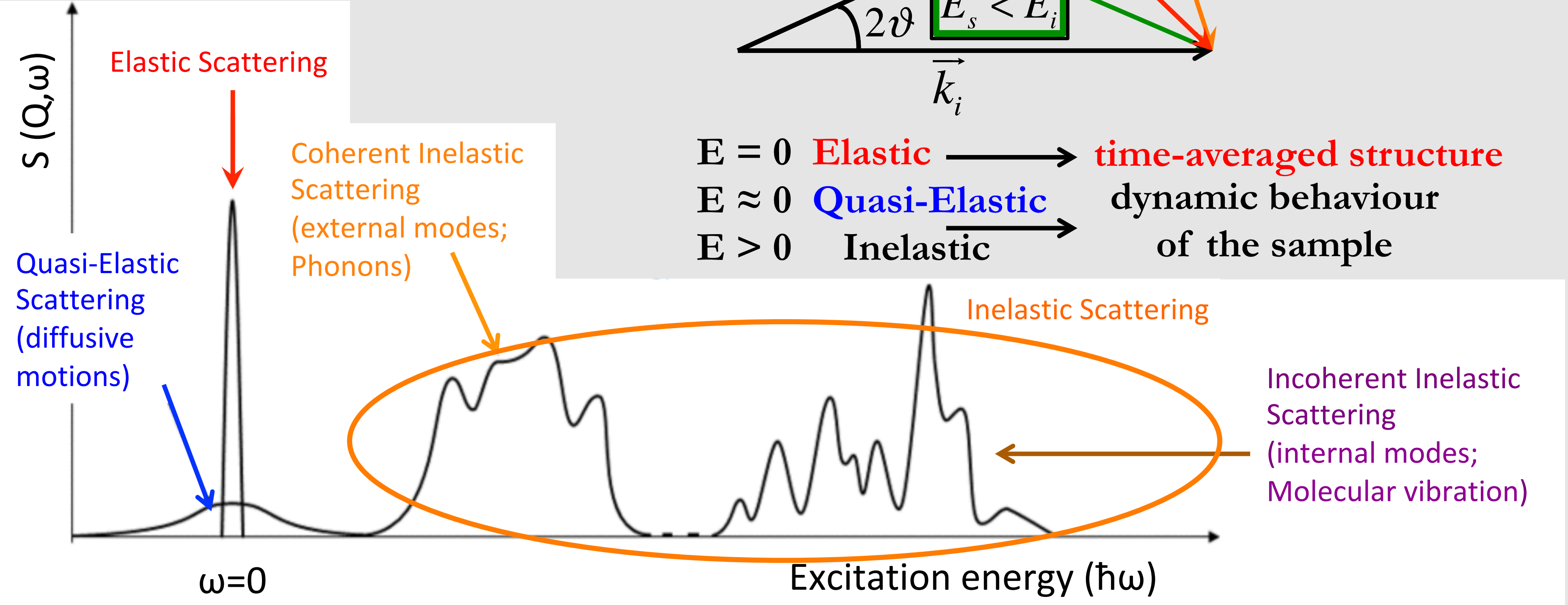
$$E = E_s - E_i$$



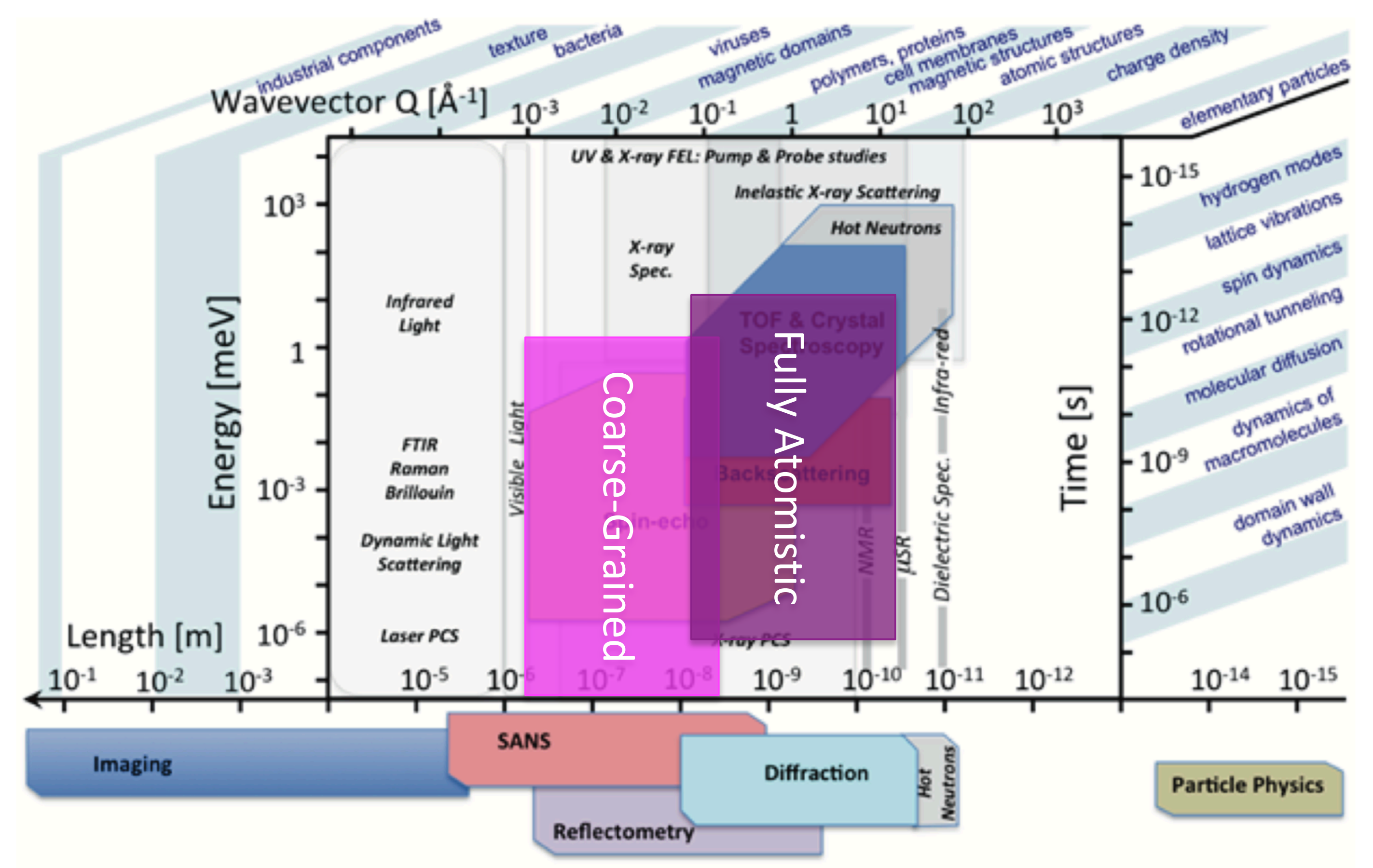
E = 0 **Elastic** → **time-averaged structure**

E ≈ 0 **Quasi-Elastic** → **dynamic behaviour of the sample**

E > 0 **Inelastic**

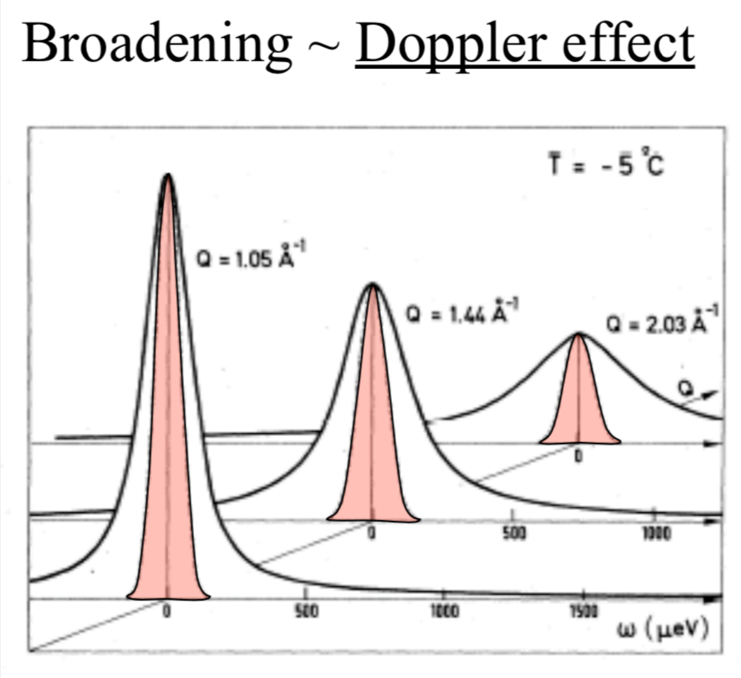


Neutrons: Why we care about



QENS: What it is

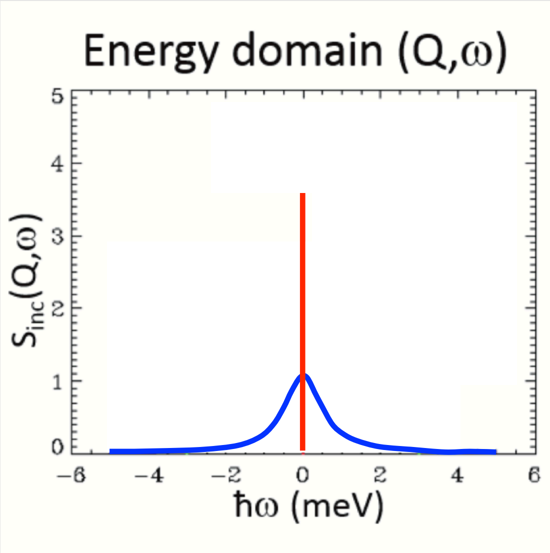
QENS is a broadening (**Doppler effect**) in the energy transfer function as consequence of local motions and/or diffusional events.



Teixeira J et al (1985) Phys Rev A 31;1913

QENS: What it is

QENS is a broadening (**Doppler effect**) in the energy transfer function as consequence of local motions and/or diffusional events.

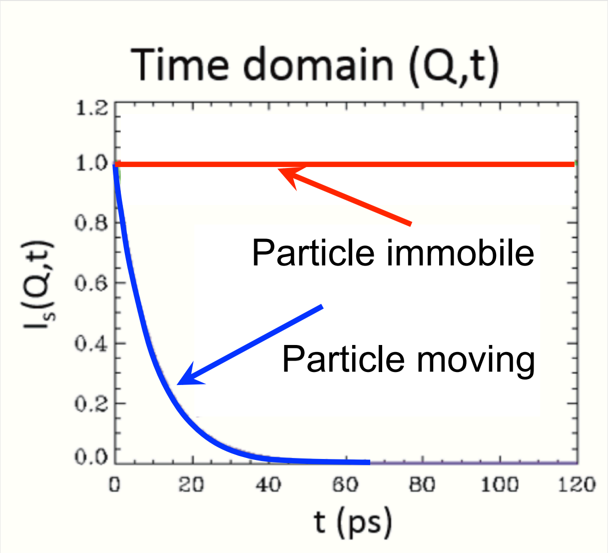


Fourier Transform

$$S(Q,\omega) = \frac{1}{2\pi}\int_{+\infty}^{-\infty} I(Q,t)e^{-i\omega t}\,dt$$

$$I(Q,t) = \frac{1}{2\pi}\int G(r,t)e^{i(Qr)}\,dr$$

Autocorrelation function



Intermediate scattering function

Berrod Q et al (2018) Web of Conferences 188, 05001

QENS: What it is

QENS is a broadening (**Doppler effect**) in the energy transfer function as consequence of local motions and/or diffusional events.
In these regards the scattering function (**S(Q,ω)**) contains information about the **static and dynamic correlations** of distinct nuclei (**S_{coh}**)
and the **spatio-temporal correlation** between identical nuclei (**S_{inc}**)

S_{coh} = How do atoms behave in relation to other?

Relative motion

S_{inc} = How do individual atoms behave independent of other atoms?

Self motion

$$S(Q,\omega) = S_{coh}(Q,\omega) + S_{inc}(Q,\omega)$$

$$S_{inc}(Q,\omega) = S_{vib}(Q,\omega) \otimes S_{rot}(Q,\omega) \otimes S_{trans}(Q,\omega)$$

QENS: 'Vibrational contribution'

Assuming that vibrations are **harmonic** and **isotropic**:

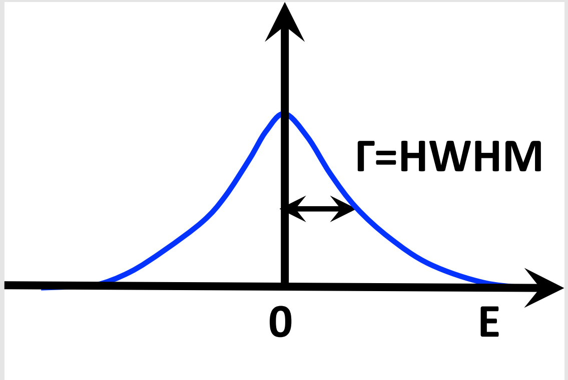
$$S_{vib}(Q,\omega) = e^{-\frac{1}{3}Q^2\langle u^2 \rangle}$$

Mean Square Displacement (Debye-Waller factor)

The rotational and translational terms are generally assumed to be independent (the motion is decoupled) and described by Lorentzian functions, whose linewidths are respectively Q-dependent or Q-independent.

$$S_{inc}(Q,\omega) = S_{vib}(Q,\omega) \otimes S_{trans}(Q,\omega) \otimes S_{rot}(Q,\omega)$$

$$S_{inc}(Q,\omega) = e^{-\frac{1}{3}Q^2\langle u^2 \rangle}\left(S_{trans}(Q,\omega) \otimes S_{rot}(Q,\omega)\right)$$

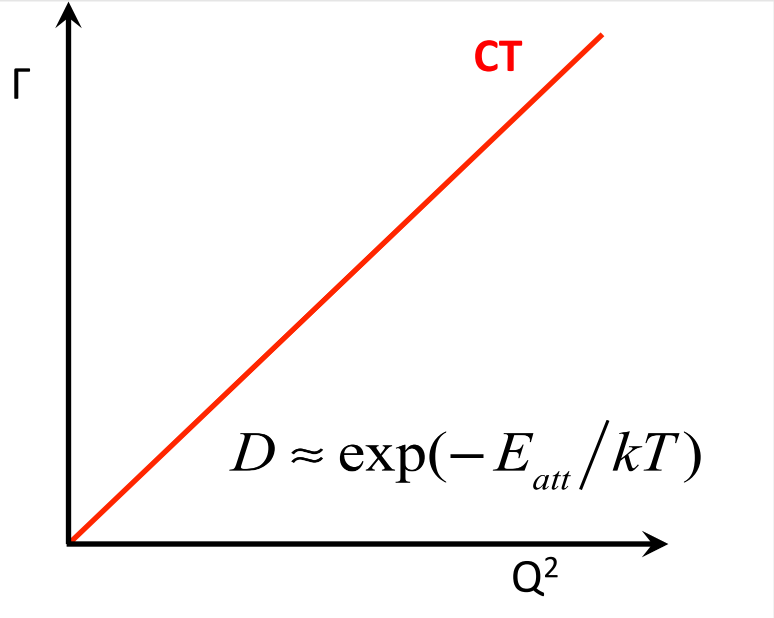


QENS: 'Translational Contribution'

Continuous diffusion (e.g. Fickian diffusion):

$$S_{inc}(Q,\omega) = \frac{1}{\pi}\frac{\Gamma}{\Gamma^2 + \omega^2}$$

$$\Gamma = DQ^2$$



Macroscopic Diffusion **Valid for $Q^{-1} >> a$**

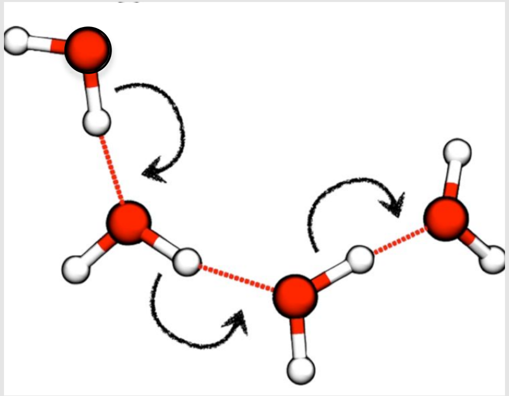
(a = mean distance between neighboring atoms in the liquid)

QENS: ‘Translational Contribution’

Deviation from Fickian diffusion: **$Q^{-1} \approx a$**

(neutrons can see microscopic details of the diffusion process)

Jump Diffusion



i. Center of mass diffusion

ii. τ_0 (time in each position -‘oscillations’- before moving)

iii. τ_1 (time to actually move to the next position)

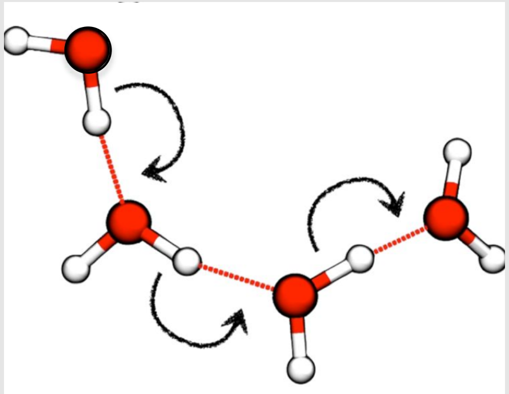
iv. Length of the jump

QENS: ‘Translational Contribution’

Deviation from Fickian diffusion: **$Q^{-1} \approx a$**

(neutrons can see <u>microscopic details of the diffusion process</u>)

Jump Diffusion



i. Center of mass diffusion

A. $\tau_1 >> \tau_0$ = **Continuous diffusion**

A. $\tau_0 >> \tau_1$ = **Singwi-Sjölander**

iv. Length of the jump

QENS: 'Translational Contribution'

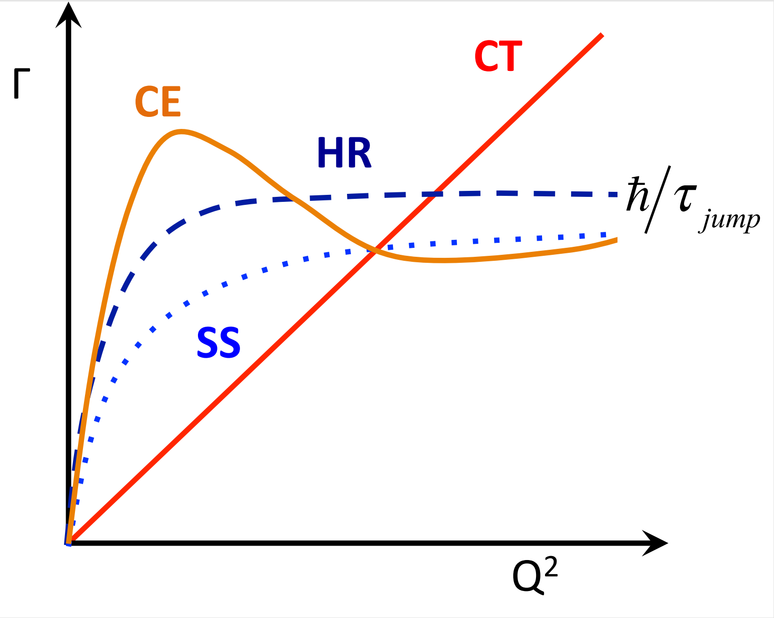
Jump Diffusion

i) Alternation between oscillatory motion and direct motions (**Singwi-Sjölander**)
ii) Jump diffusion with a Gaussian distribution of jump lengths (**Hall-Ross**)
iii) Jumps on a lattice -fixed jump length- (**Chudley-Elloitt**)

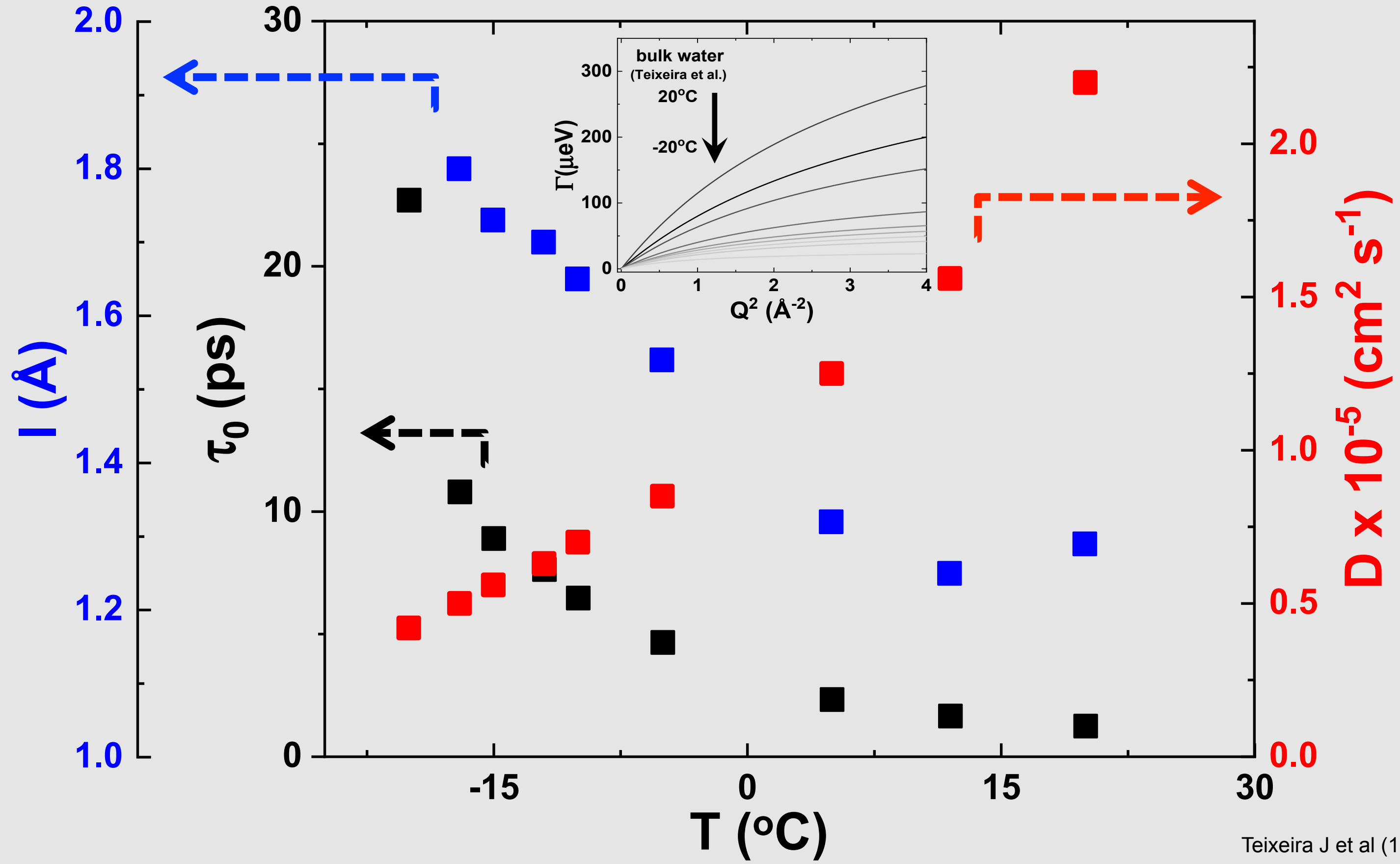
$$\Gamma(Q) = DQ^2 \Big/ (1 + DQ^2\tau_0)$$

$$\Gamma(Q) = \frac{1}{\tau_0}\left(1 - \exp\left(-Q^2 l^2/6\right)\right)$$

$$\Gamma(Q) = \frac{1}{\tau_0}\left(1 - \sin(Ql)/Ql\right)$$



QENS: ‘Translational Contribution’



Teixeira J et al (1985) Phys Rev A 31;1913

QEENS: 'Rotational Contributions'

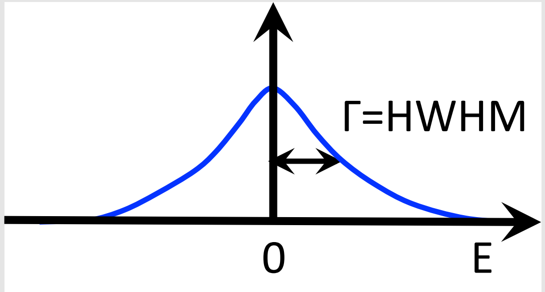
Assuming that our motions are **Localised** (e.g. rotation):

Stationary part (**EISF**) + Decay part (**Q-independent** contribution)

$$S_{inc}(Q,\omega) = e^{-\frac{1}{3}Q^2\langle u^2\rangle}\left[A_0(Q)\delta(\omega) + (1 - A_0(Q))L(Q,\omega)\right]$$

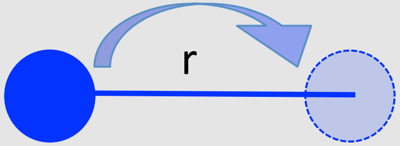
Geometry of motion

$$EISF = \frac{S_{inc}^{elastic}(Q)}{S_{inc}^{elastic}(Q) + S_{inc}^{quasi-elastic}(Q)}$$



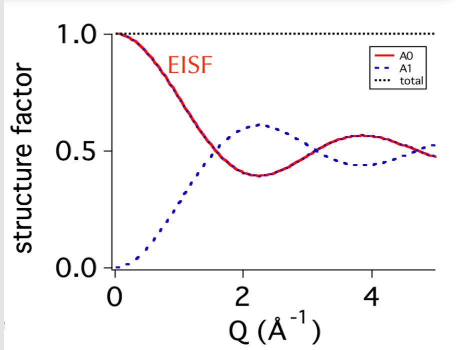
QENS: EISF

i) Jump between 2 equivalent sites

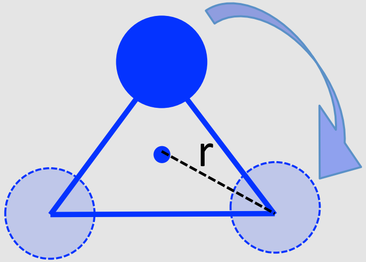


$$A_0(Q) = \frac{1}{2}\left(1 + j_0(Qr)\right)$$

$$S(Q,\omega) = A_0(A)\delta(\omega) + A_1(Q)\frac{1}{\pi}\frac{2\tau}{4+\omega^2\tau^2}$$

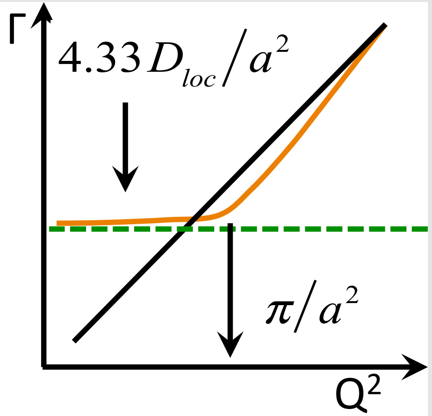


ii) Jump between 3 equivalent sites



$$A_0(Q) = \frac{1}{3}\left(1 + 2j_0(Qr\sqrt{3})\right)$$

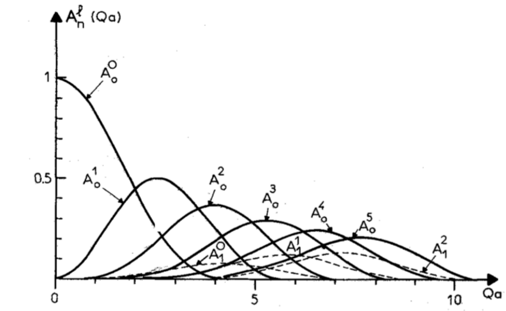
$$S(Q,\omega) = A_0(Q)\delta(\omega) + A_1(Q)\frac{1}{\pi}\frac{3\tau}{9+\omega^2\tau^2}$$



ii) Free-diffusion inside a sphere

$$A_0 = \left(3j_1(Qa)\right)^2$$

$$S(Q,\omega) = A_0^0(Q)\delta(\omega) + \frac{1}{\pi}\sum_{l,n}(2l+1)A_n^l(Q)\frac{(x_n^l)^2\,D/a^2}{\left[(x_n^l)^2\,D/a^2\right]^2+\omega^2}$$



Bée M (1988) Adam Hilger, Bristol
Volino F, Dianoux A (1980) Mol Phys 41;271

QENS: Preparing an experiment

1) $\lambda_{incident}$ (Å; monochromatic TOF)

2) Q-range (Å^{-1})

3) Dynamical Range (meV)

5) Instrumental Resolution (meV)

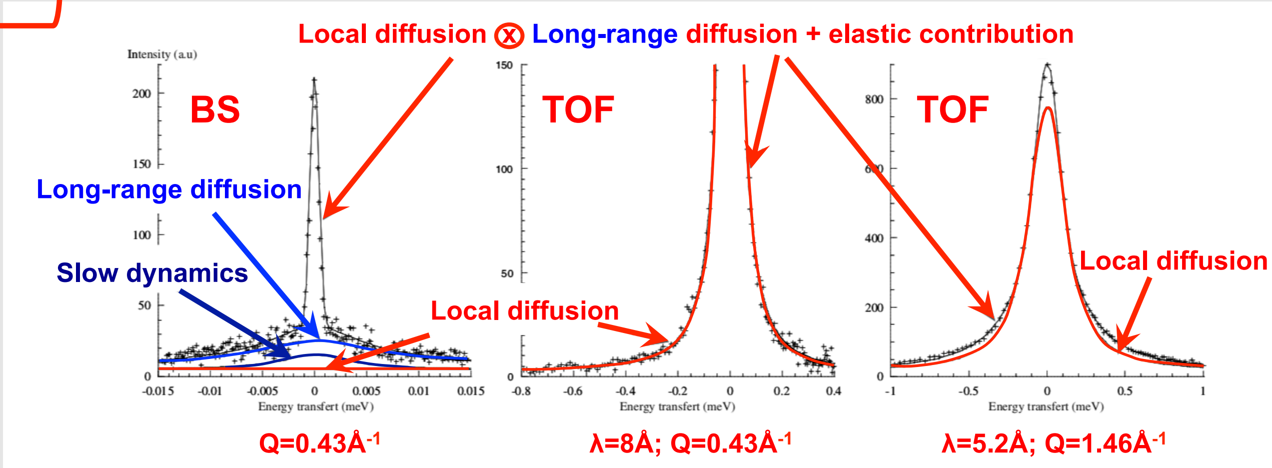
'slower protons' appears as immobile ($\delta(\omega)$)

'faster protons' appears as background

dynamic window = (movement detectable)

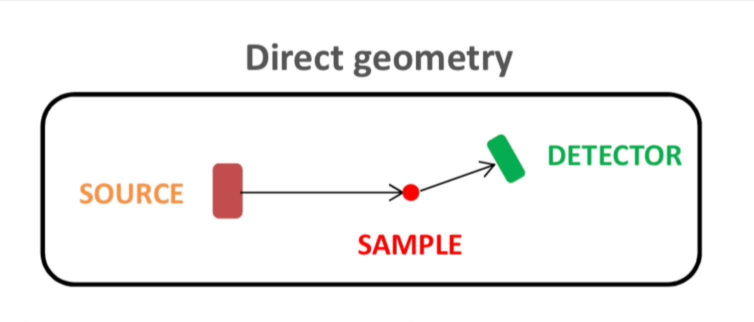
↓

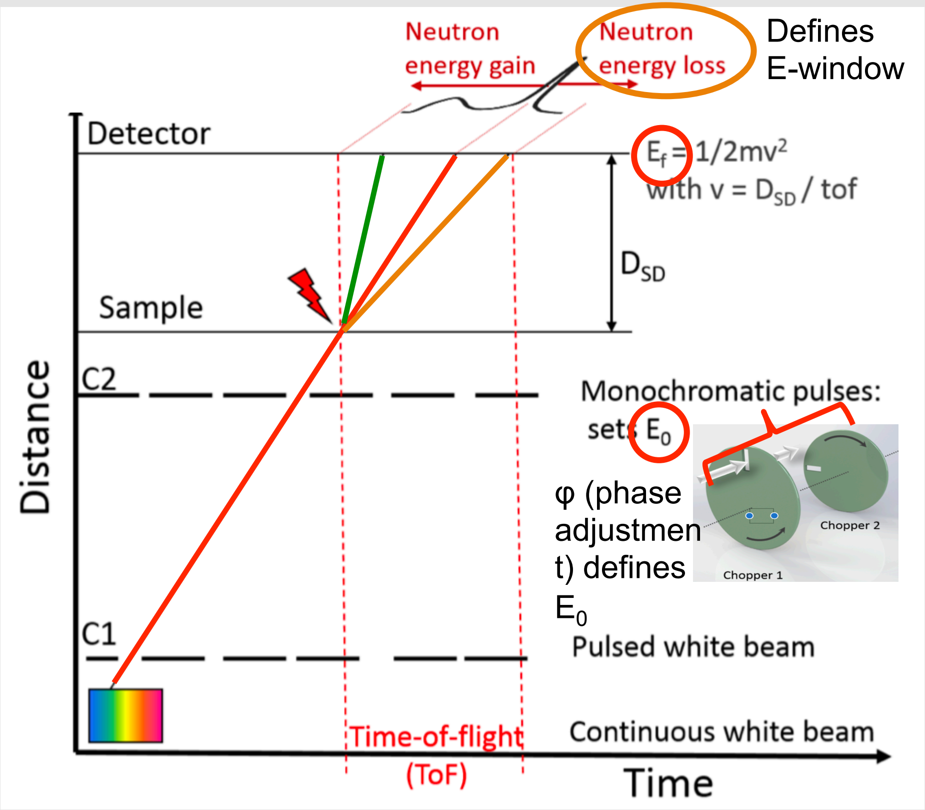
Instrument



Perrin JC et al (2007) Eur. Phys. J. Special Topics 141, 57

QENS: Preparing an experiment

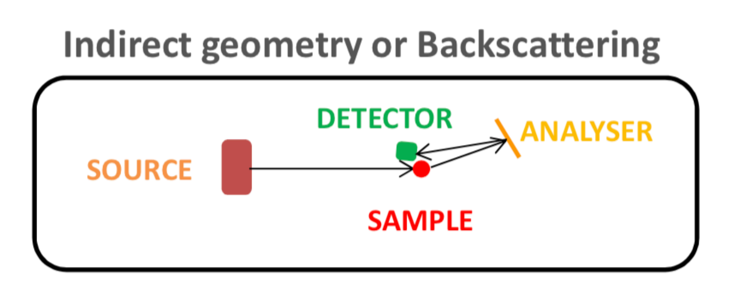


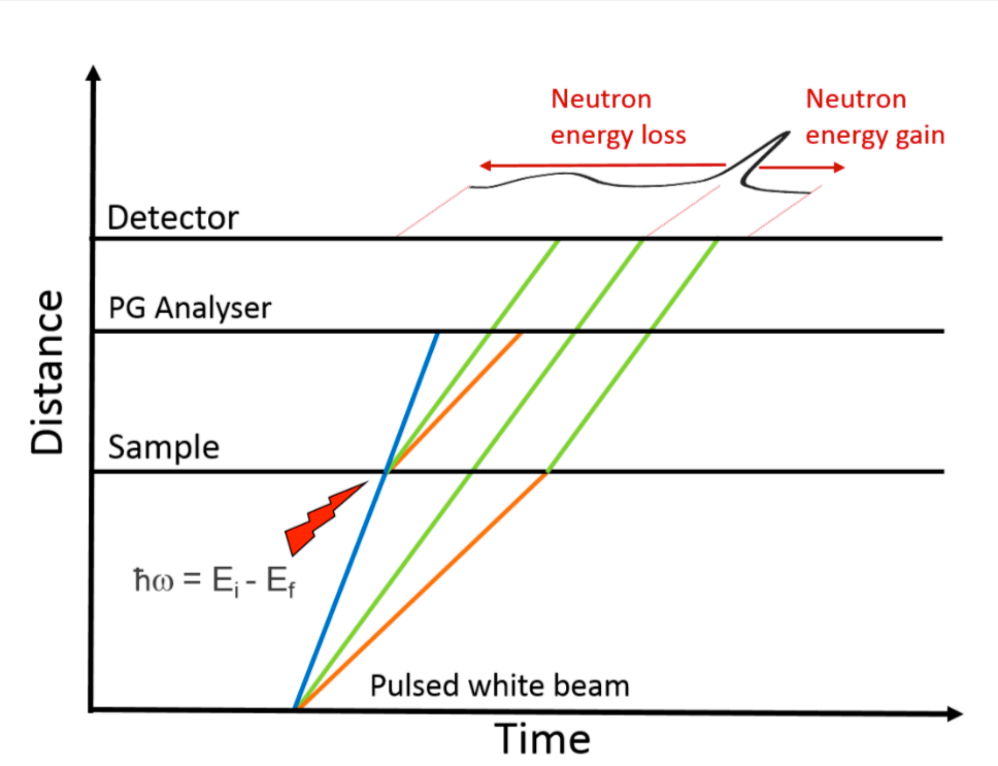


The incident energy is defined before the sample by a chopper system and the final energy is determined by time-of-flight between the sample and the detectors.

Berrod Q et al (2018) Web of Conferences 188, 05001

QENS: Preparing an experiment





Berrod Q et al (2018) Web of Conferences 188, 05001

The sample is illuminated by a white incident beam, the incident energy is determined at the sample position by the measurement of the time-of-flight, and the final energy is measured by a monocrystal.

QENS: Preparing an experiment

6) **Sample composition**

7) **Sample mass/thickness**

8) **Can thickness**

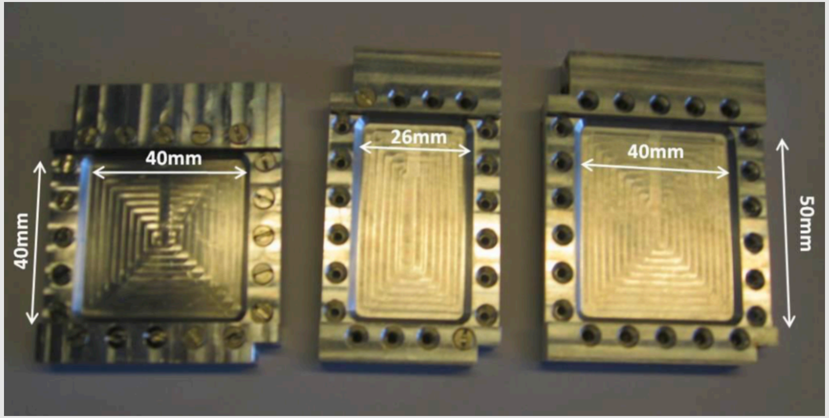
90% transmission

↓

Reduced multiple scattering

‘Common’ Sample can

- Aluminum
- ~0.1 / 0.05 mm internal thickness



QENS: Preparing an experiment

6) **Sample composition**

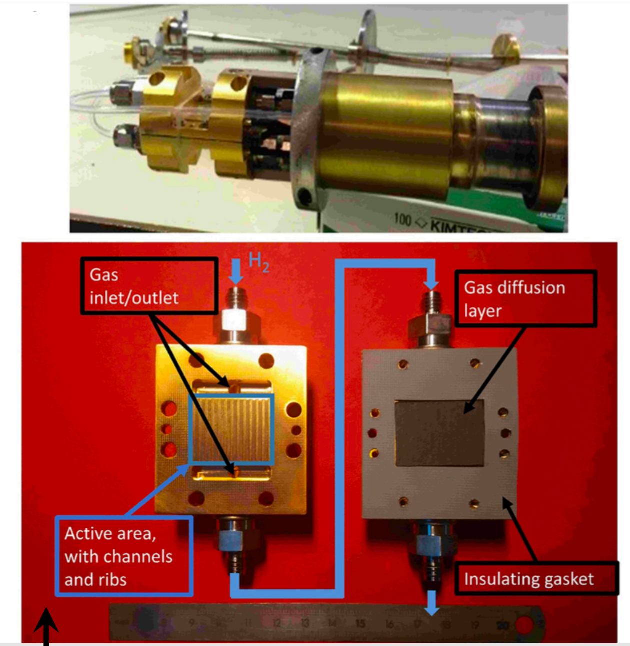
7) **Sample mass/thickness**

8) **Can thickness**

90% transmission

↓

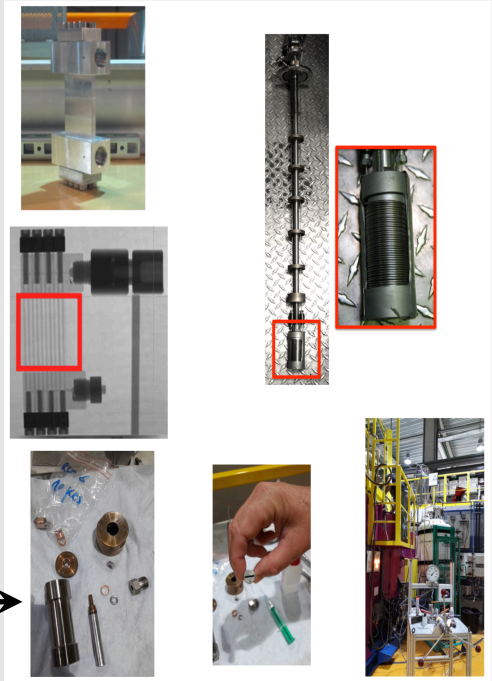
Reduced multiple scattering



Fuel Cell (in operando studies)

High-Pressure Cells →

'More exotic' Sample can



Maritnez N et al (2017) J. Phys. Chem. C 2018, 122, 1103
Foglia F et al (2019) Sci rep , in press

QENS: Reducing data

UCL

1) **MANTID**

MANTID

https://www.mantidproject.org/Main_Page

Partners

Oxfordshire, UK
ISIS at Rutherford Appleton Laboratory
ISIS

OAK RIDGE National Laboratory
Tennessee, USA
SNS & HFIR at Oak Ridge National Laboratory

Scandinavia
European Spallation Source
ess EUROPEAN SPALLATION SOURCE

ill NEUTRONS FOR SCIENCE
Grenoble , France
Institut Laue-Langevin

Contributors

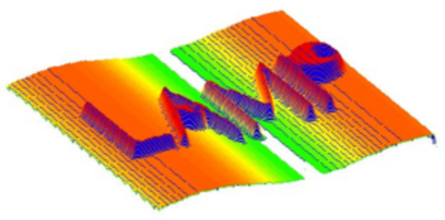
Oxford, UK
Tessella, Technology & Consulting
Tessella .ALTRAN GROUP

ansto
Sydney, Australia
ANSTO

Villigen, Switzerland
SINQ at Paul Scherrer Institute
PAUL SCHERRER INSTITUT PSI

Copenhagen, Denmark
Neutron scattering simulation
McStas

2) **LAMP**



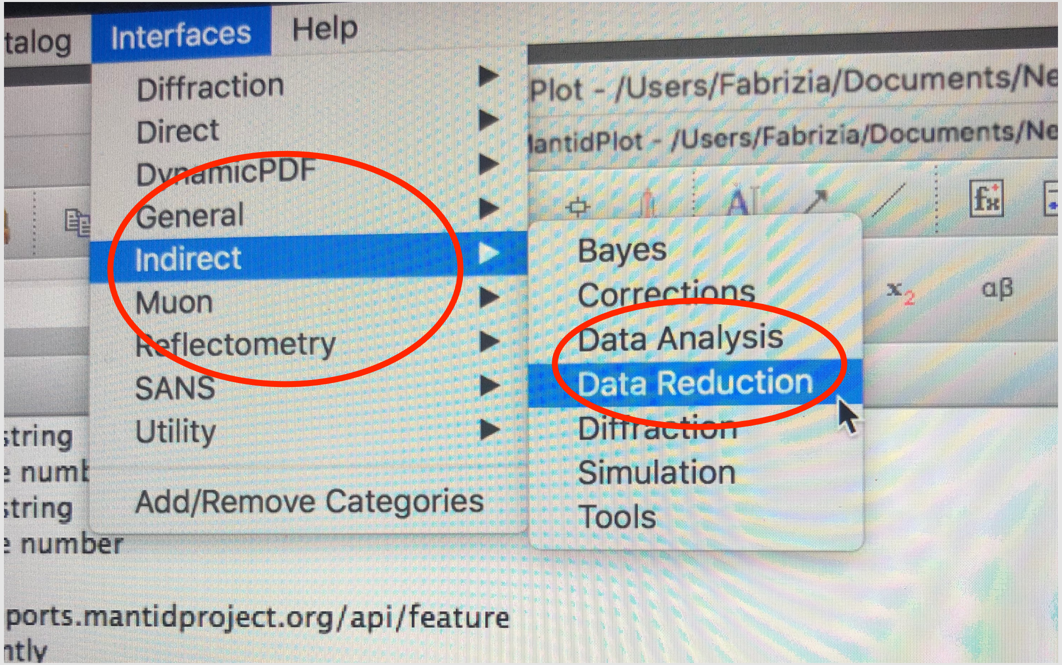
Primary ILL, but also FRMII

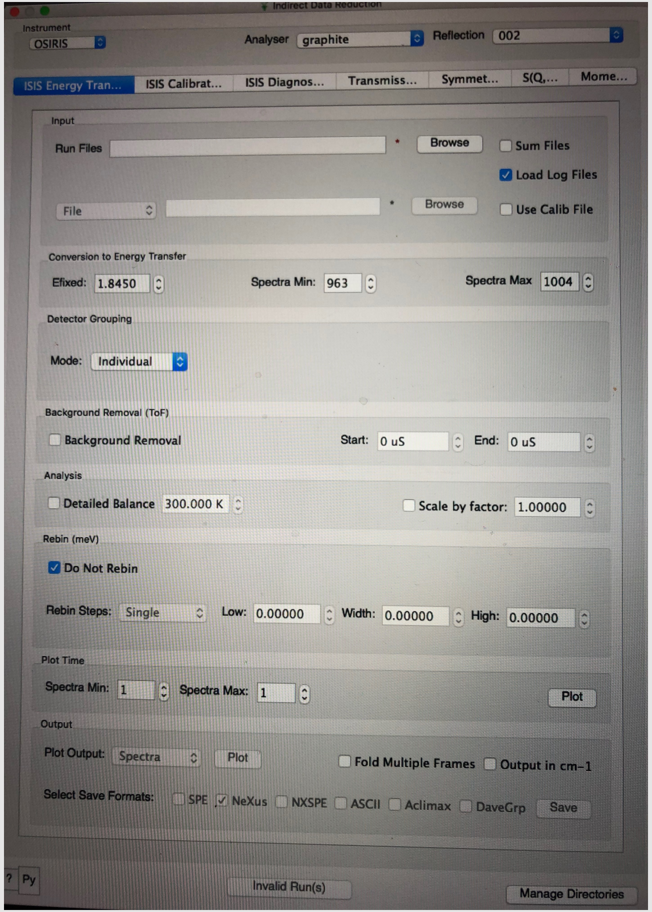
https://www.ill.eu/users/support-labs-infrastructure/software-scientific-tools/lamp/download-links/

… many others

QENS: Reducing data

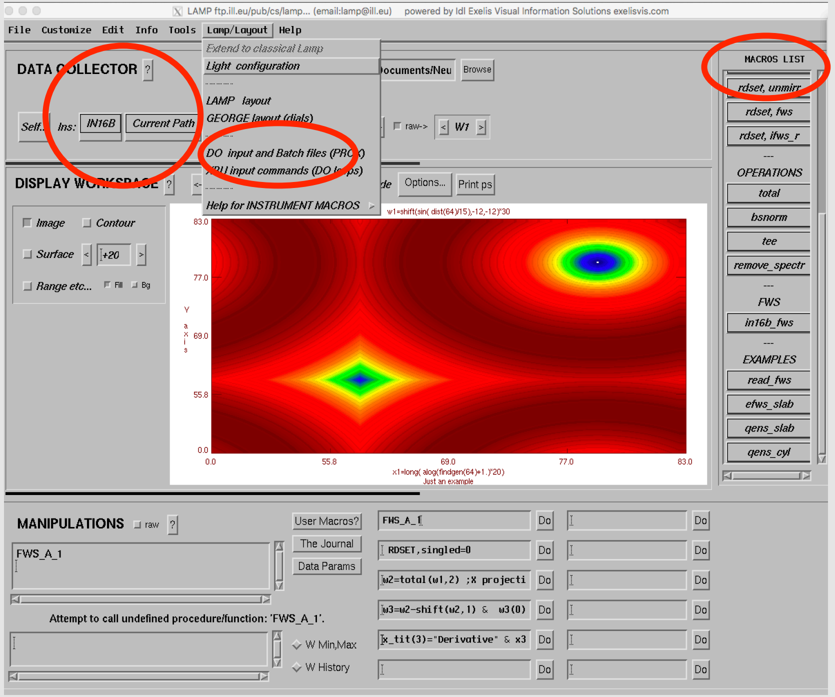
1) **MANTID**

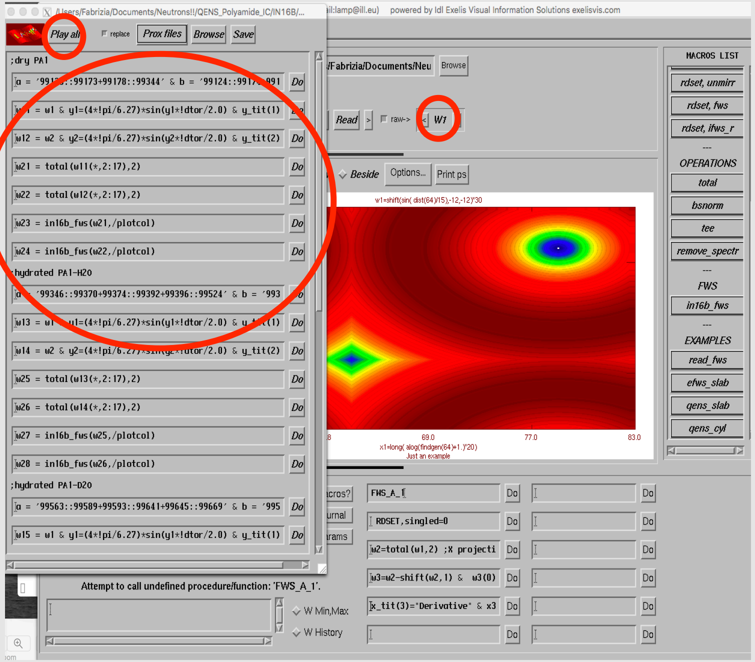




QENS: Reducing data

2) LAMP





QENS: Reducing data

Regardless the facility (spallation source and/or reactor) and the program (/platform) you are using to reduce you data the 1st thing to do is:

MONITOR NORMALISATION

↓

Neutron flux 'can change' over the time, therefore the flux has to be normalised by counting the total number of neutrons before hinting the sample

↓

A beam monitor is placed before the sample so that the total flux of neutron impacting the sample and the total counts of the monitor are normalised with the detector efficiency

QENS: Reducing data

Regardless the facility (spallation source and/or reactor) and the program (/platform) you are using to reduce you data the 1st thing to do is:

MONITOR NORMALISATION

EMPTY CAN

↓

which usually contributes 'massively' to the elastic scattering

QENS: Reducing data

Regardless the facility (spallation source and/or reactor) and the program (/platform) you are using to reduce you data the 1st thing to do is:

MONITOR NORMALISATION

EMPTY CAN

VANADIUM

↓

~purely incoherent scatterer; provides an absolute cross-section calibration and serves to determine the ENERGY RESOLUTION.

↓

'slower protons' appears as immobile (ELASTIC contribution; ħω=0)

↓

$$S_{measured}(Q,\omega) = S_{theoretical}(Q,\omega) \otimes Resolution$$

SAMPLE AT LOW T (~2K)

(FWS)

↓

The T-dependence of the mean-square displacement (msd) of hydrogen (H) atoms can be computed assuming that oscillations are harmonic and isotropic. This condition holds only at sufficiently low T (≤100K).

QENS: Acquiring data

1) **Fixed Window Scan**

- it resembles a DSC scan and is useful for locating transitions
- T at which the dynamics enter the time window of the spectrometer

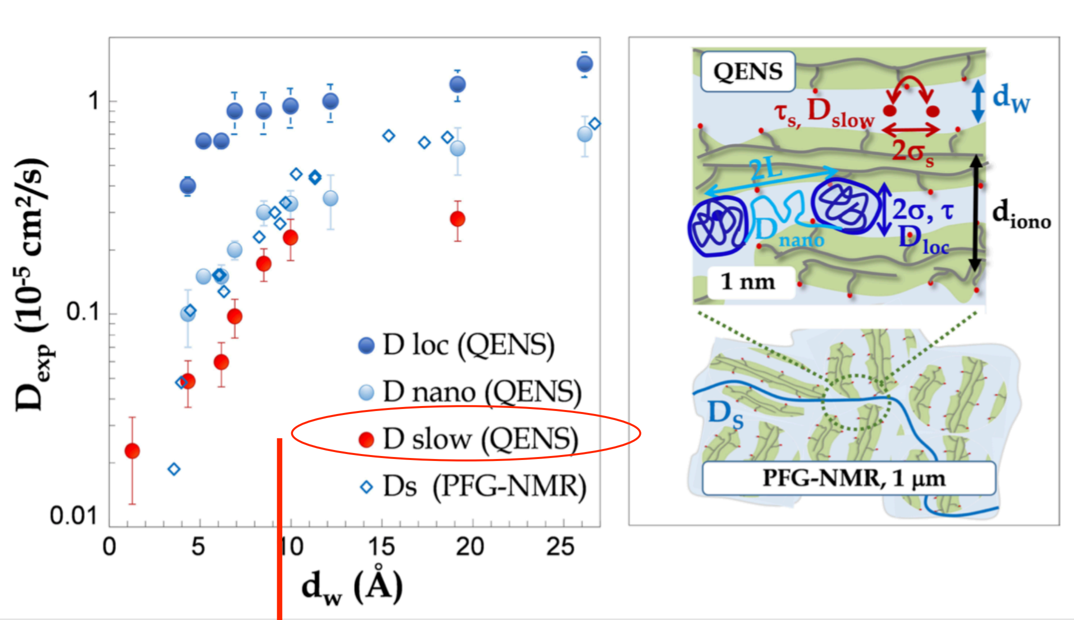
Elastic (mean square displacement & 'n. of proton moving')

Inelastic (diffusional or rotational? And E_{att})

QENS: Acquiring data

2) **QENS**

- dynamical properties of system under analysis
- T chosen form FWS



Proton hopping

Berrod Q et al (2017) Sci Rep 7:8326

Acknowledgment

Prof. PF McMillan

Dr V Garcia Sakai, Dr F Demmel, Dr M Skoda

Dr B Frick, Dr S Lyonnard, Dr J-M Zanotti and Dr Q Berrod

Dr G Watson and M-RHEX consortium

YOU ALL!!