Neutron Spectroscopies

Quasi-Elastic Neutron Scattering

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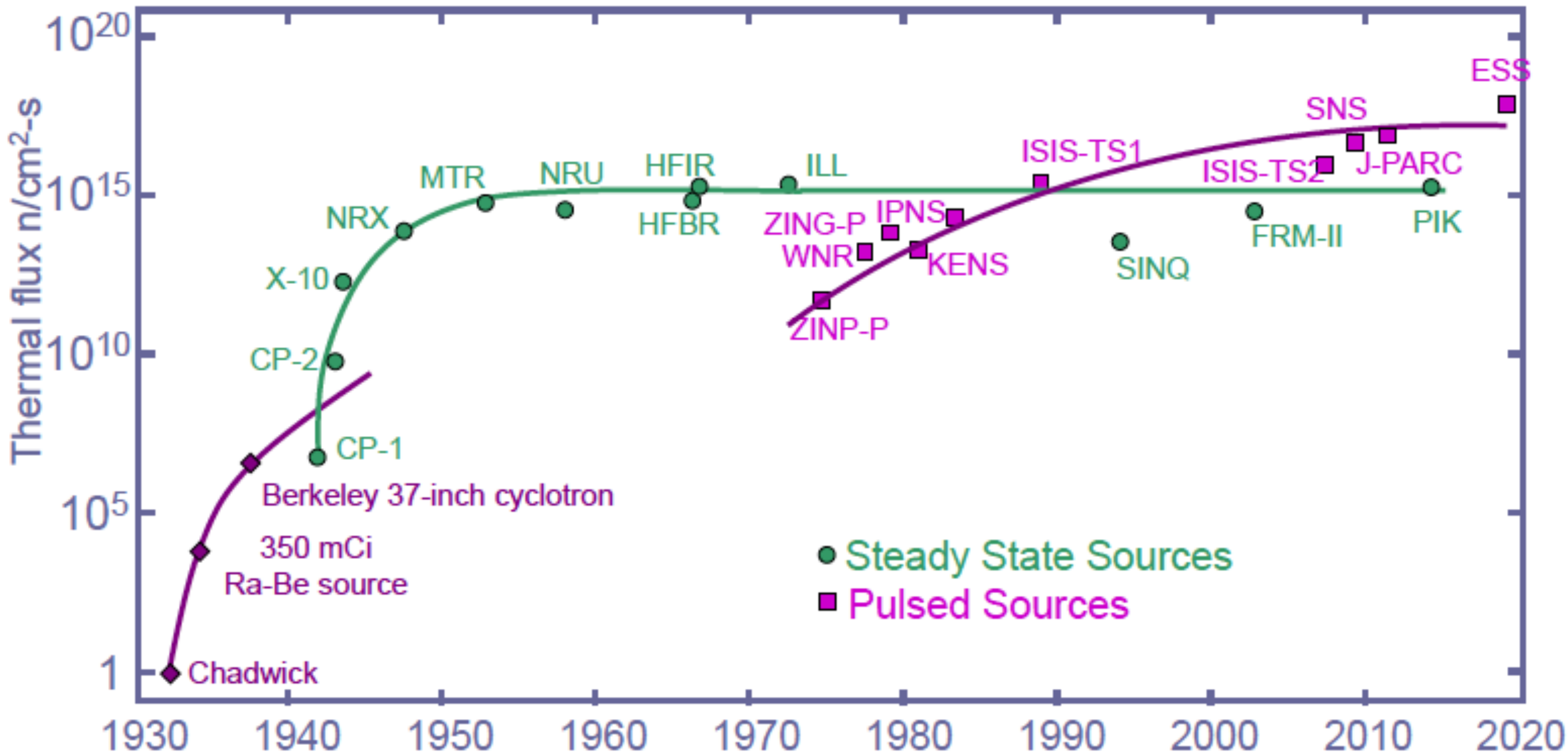
Production of neutron beams

Research reactors by nuclear fission, example HFIR, ORNL, FRM II, Munich, Institute Laue Langevin (ILL) Grenoble, France, www.ill.fr

Spallation sources by using linear proton accelerators (for example at ISIS at the Rutherford Appleton Lab. Oxford, Great Britain, see www.isis.rl.ac.uk or at the US Spallation Neutron Source (SNS) www.sns.gov), ESS-European Spallation Source.

Advances in the effective thermal flux for neutron



(Updated from *Neutron Scattering*, K. Skold and D. L. Price, eds., Academic Press, 1986)

Today's best sources typically 10^7-10^8 neutrons $cm^2 s^{-1}$ on the sample

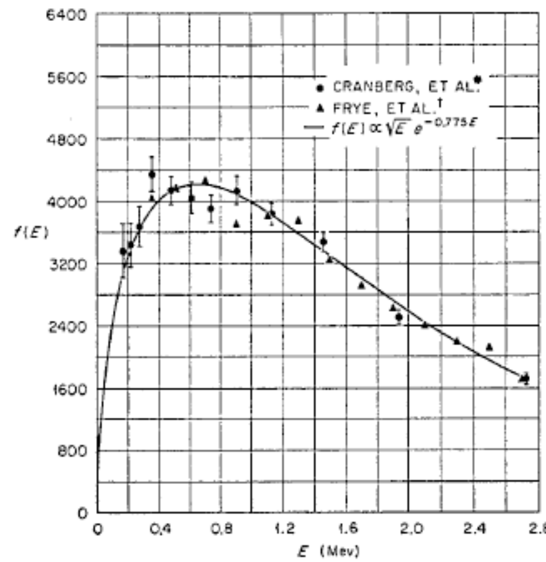
K. Anderson, Lectures

Energy Spectrum of neutrons

$$E = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$$

$$E(\text{meV}) = \frac{81.8042}{\left(\lambda(\text{Å})\right)^2}.$$

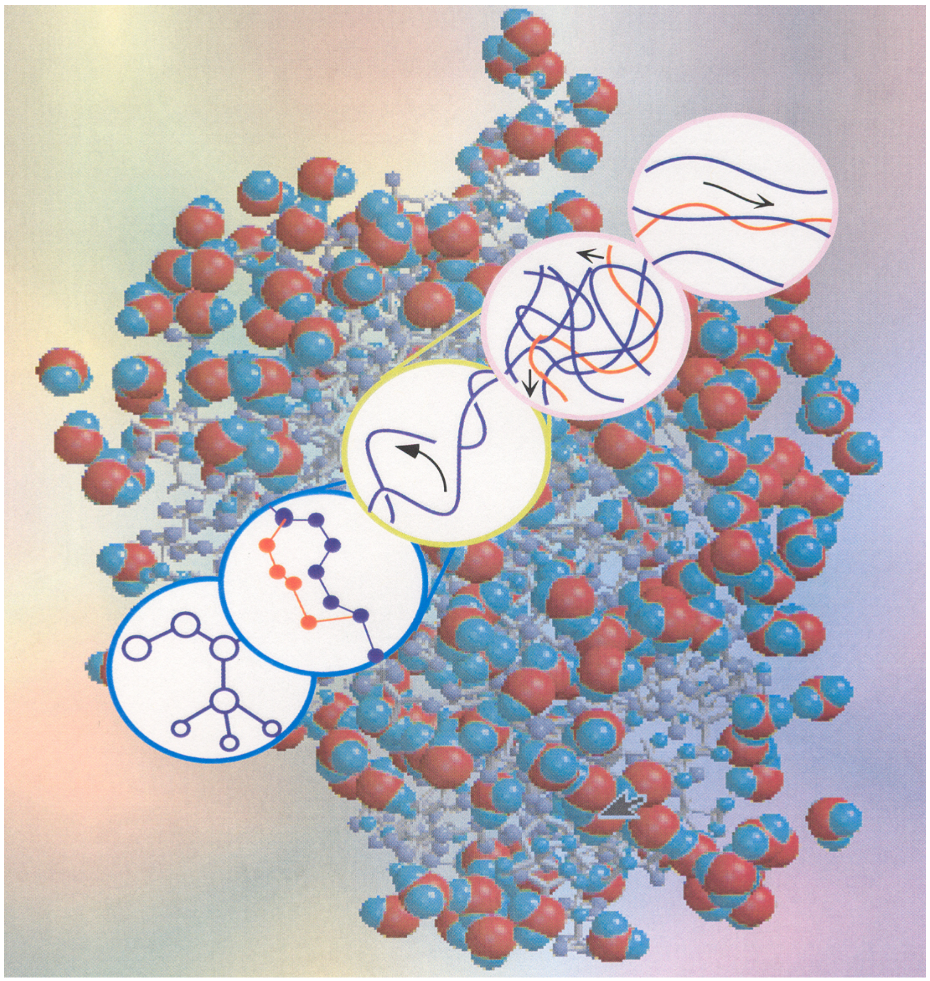
Energy distribution of prompt neutrons from a reactor



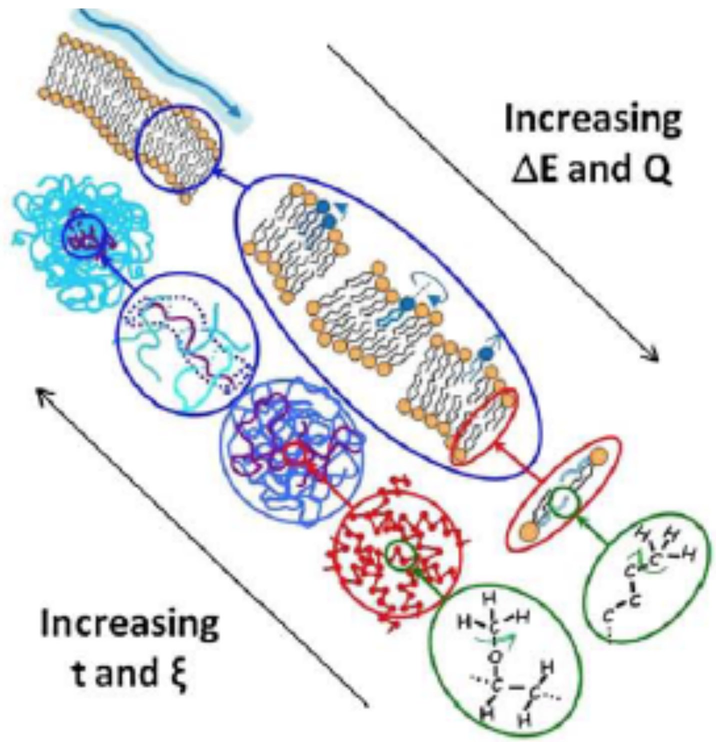
Typical neutron energies and corresponding wavelengths used in experiments

i.	"hot" neutrons	$E = 100 - 500$ meV	$\lambda = 0.5 - 1$ Å
ii.	"thermal" neutrons	$E = 10 - 100$ meV	$\lambda = 1 - 3$ Å
iii.	"cold" neutrons	$E = 0.1 - 10$ meV	$\lambda = 3 - 30$ Å

Going beyond the center of mass diffusion



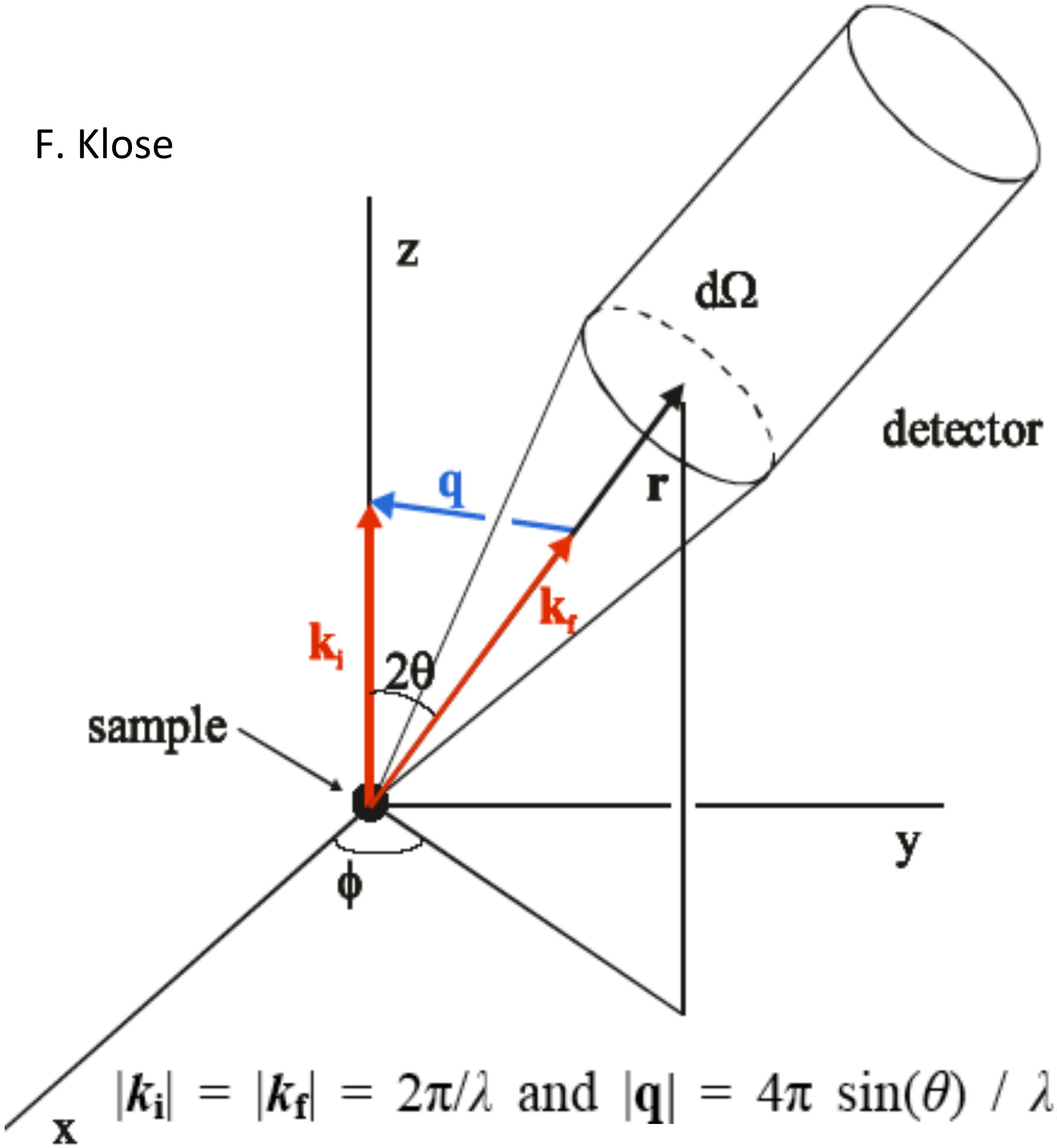
< 10^9 Hz slow motion
ΔE ~ μeV
lowest available E = 1-5meV neutrons
Thus, define neutron E 1 part in 10^3 or better



V. García Sakai, A. Arbe
Current Opinion in Colloid & Interface Science

Momentum Transfer q

F. Klose



$|k_i| = |k_f| = 2\pi/\lambda$ and $|\mathbf{q}| = 4\pi \sin(\theta) / \lambda$

cross section
number of neutrons/time/dΩ
with energy transfer in the
interval ($h\omega$, $h\omega+d\omega$)
normalized by incident flux

Incident neutron along z,
wave vector k_i and energy E_i
$|k_i| = \text{sqrt}(2mE_i)/h$

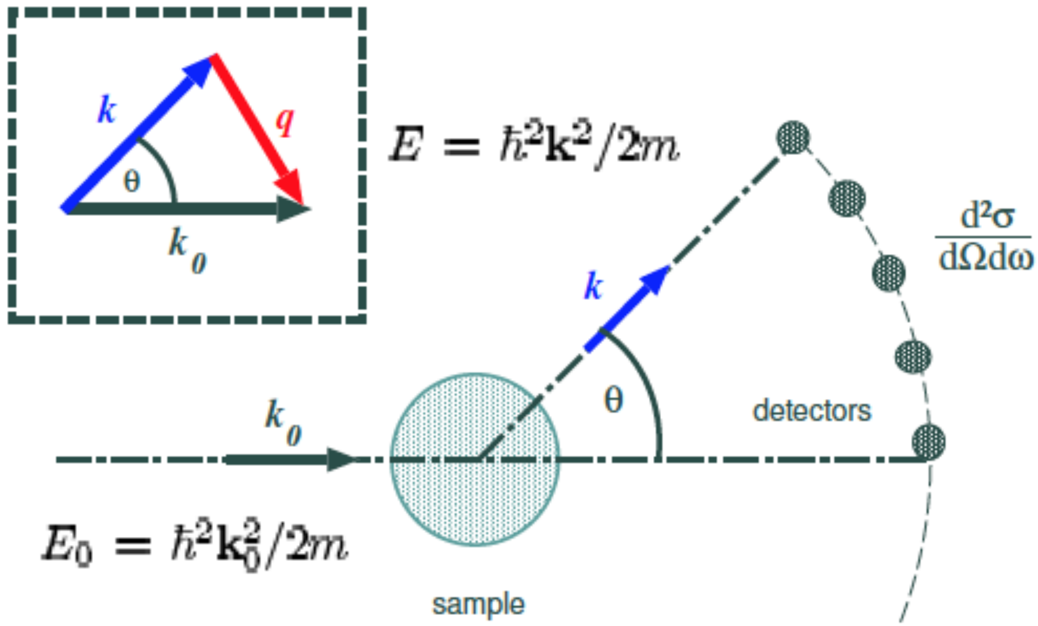
2θ and φ define the direction
of the scattered beam

$q = k_i - k_f$ wave vector
or momentum transfer
$\Delta p = hq/2\pi = h(k_i - k_f)/2\pi$

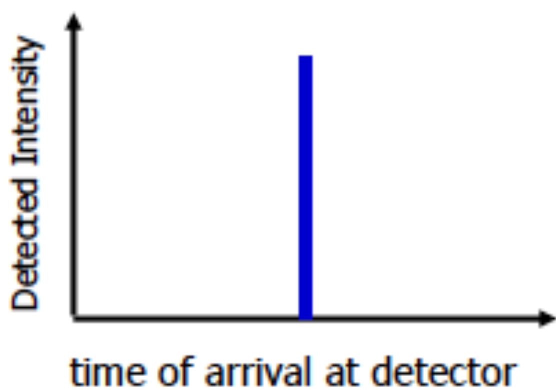
Energy transfer ΔE (TOF)

$$E = \frac{\mathbf{p}^2}{2m}$$

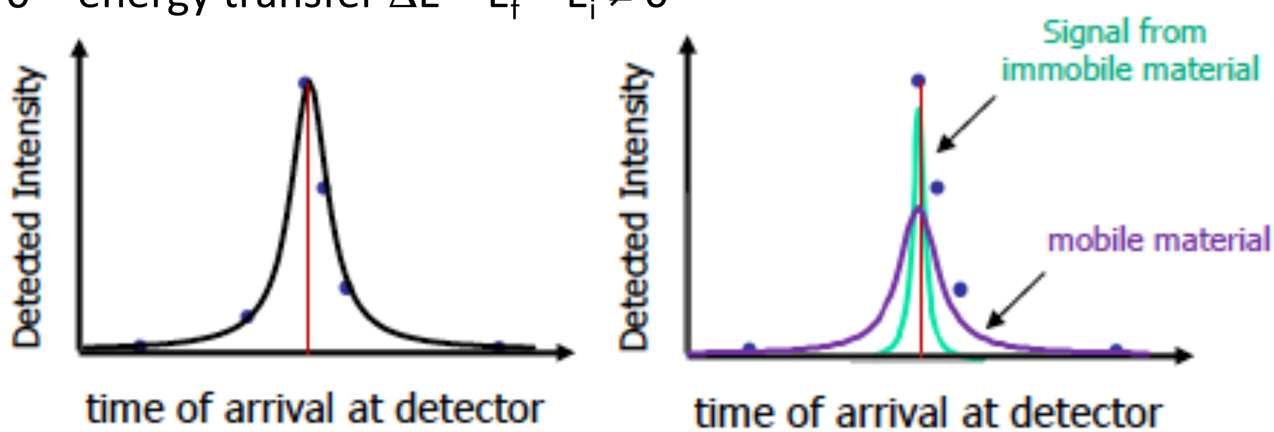
$$\mathbf{p} = \hbar\mathbf{k} = mv$$



energy transfer $\Delta E = E_f - E_i = 0$



energy transfer $\Delta E = E_f - E_i \neq 0$



Lecture M. Telling

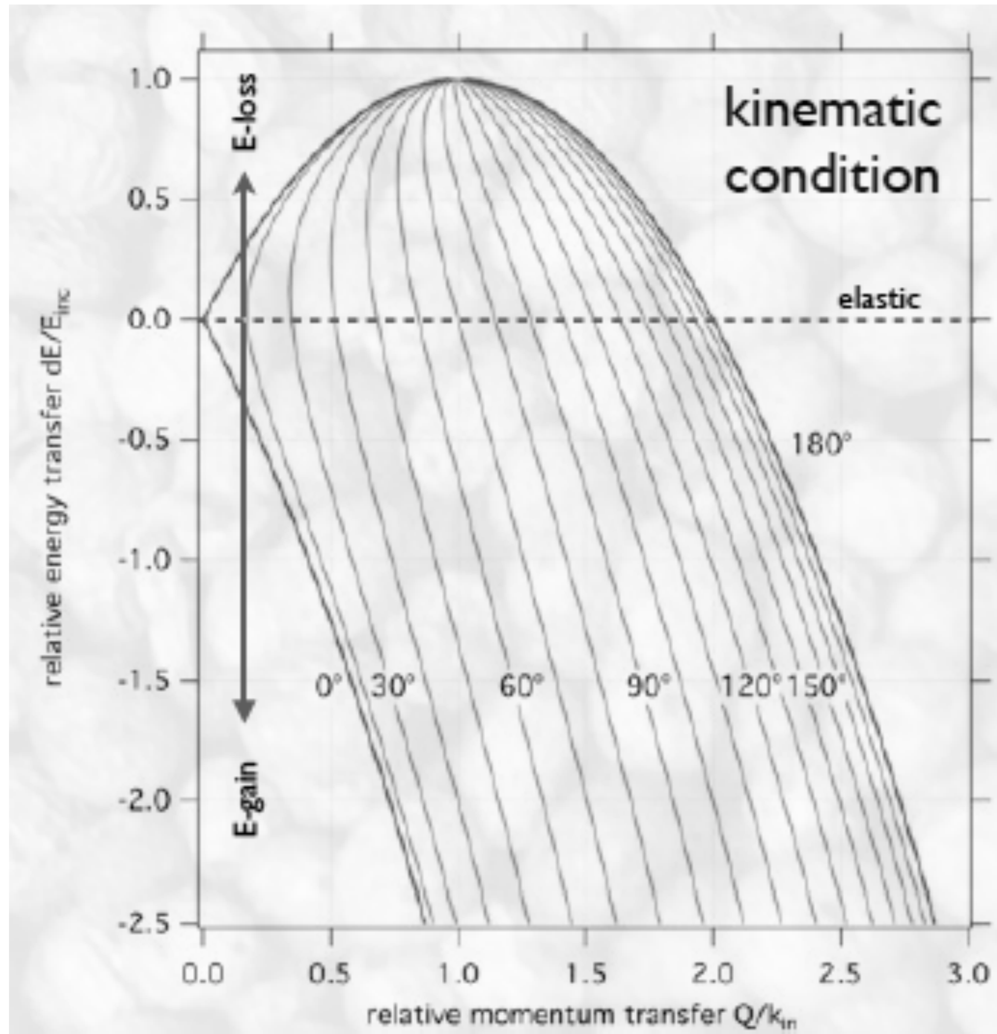
Exchange of energy and momentum with the sample

Scattering triangle
(cosine rule)

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

Kinematic condition

$$\frac{\hbar^2 Q^2}{2m} = E_i + E_f - 2\sqrt{E_i E_f}\,\cos 2\theta$$

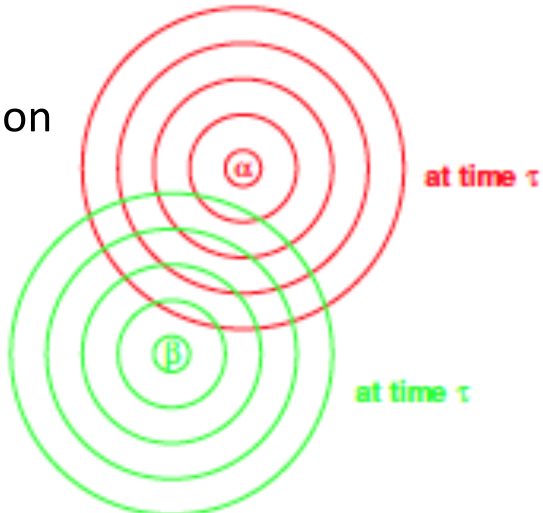


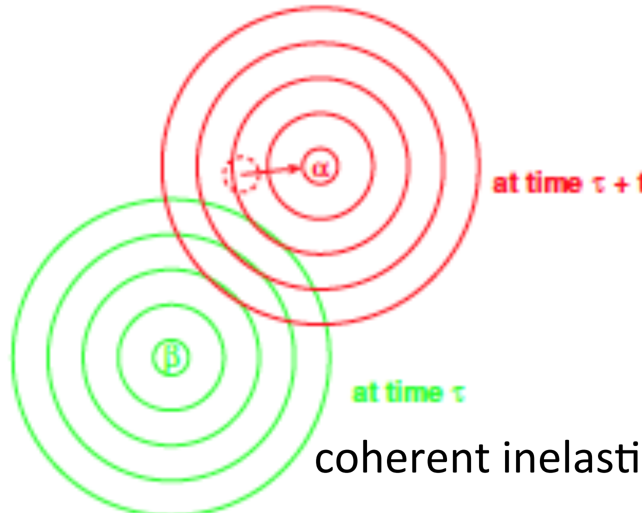
B. Frick

Coherent and Incoherent Scattering

Interference of neutron waves emitted from different atoms

Coherent elastic scattering=diffraction





coherent inelastic scattering

Interference of neutron waves emitted from same atom

incoherent inelastic scattering

Lecture: Gerald R. Kneller

Scattering Functions- Correlations

Remember that in the experiment we measure the total $S(\mathbf{Q},\omega)$ and that each term, coherent and incoherent is weighted by its respective cross-section σ

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

$$S_{\text{inc}}(\boldsymbol{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty}\sum_{i}\langle \exp(-i\boldsymbol{Q}\cdot\boldsymbol{R}_i(0))\exp(-i\boldsymbol{Q}\cdot\boldsymbol{R}_i(t))\rangle \exp(-iwt)\,dt$$

$$S_{\text{coh}}(\boldsymbol{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty}\sum_{i,j}\langle \exp(-i\boldsymbol{Q}\cdot\boldsymbol{R}_i(0))\exp(-i\boldsymbol{Q}\cdot\boldsymbol{R}_j(t))\rangle \exp(-iwt)\,dt$$

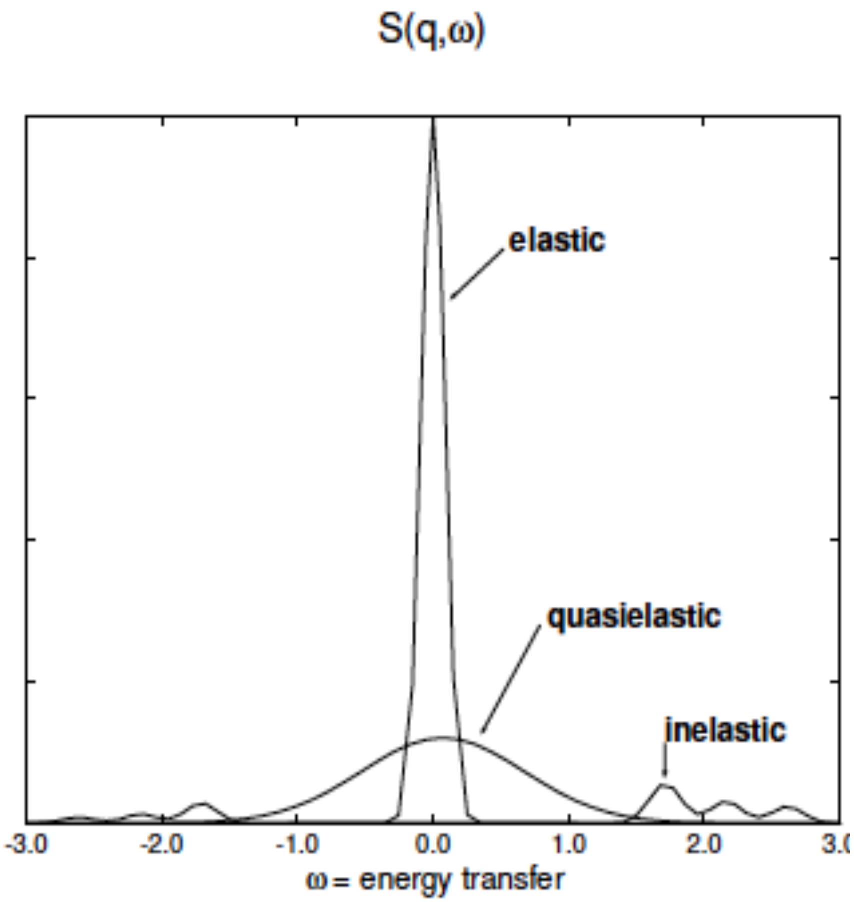
These expressions can also be re-written in terms of the self and collective **intermediate scattering functions, I(Q,t)**, such that:

$$S_{\text{inc}}(\boldsymbol{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} I_{\text{self}}(\boldsymbol{Q},t)\exp(-iwt)\,dt$$

$$S_{\text{coh}}(\boldsymbol{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} I_{\text{coll}}(\boldsymbol{Q},t)\exp(-iwt)\,dt$$

Lecture: V. García Sakai

Neutron Scattering Spectrum



$$S(Q,\omega) = \frac{1}{\pi} \frac{\Gamma}{\Gamma^2 + \omega^2}$$ "A Lorentzian"

Half Width at Half Maximum=HWHM=Γ = DQ^2

Elastic scattering – no energy exchange ħω=0. In an ideal world this should be a delta function. Of course, this is not the case giving rise to an instrumental resolution.

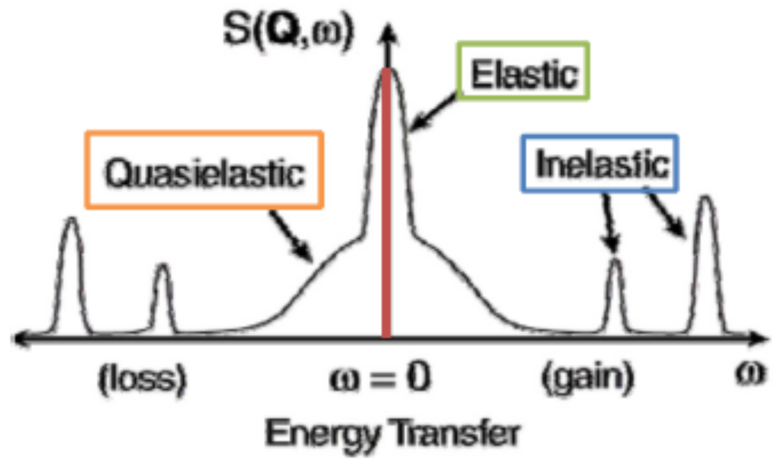
$$S(\boldsymbol{Q},\omega) = S^*(\boldsymbol{Q},\omega) \otimes R(\boldsymbol{Q},\omega)$$

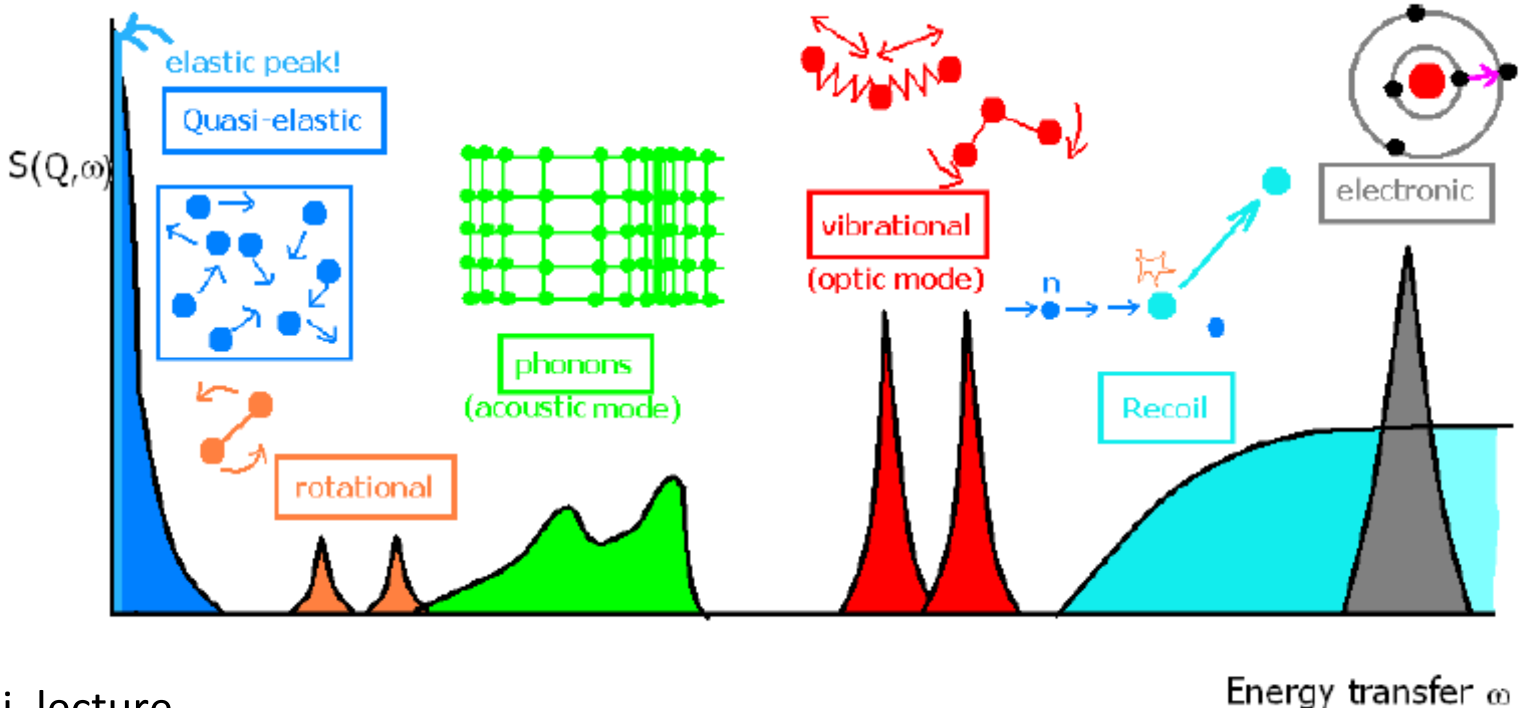
Inelastic scattering – there is energy exchange ħω≠0. Due to processes occurring discrete energy steps such as vibrational modes, stretching modes...

Quasi-elastic scattering (QENS)– there is small energy exchange ħω≠0≈neV or μeV . **High energy resolution**. Due to processes occurring with a distribution of energies (rotations, translations...).

V. G. Sakai, lecture

Map of the dynamical modes



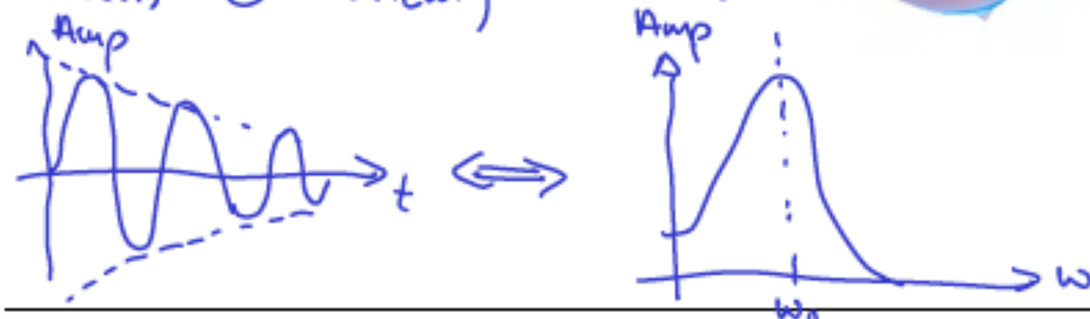


V. G. Sakai, lecture

Quasi- and Inelastic Neutron Scattering

$$m\cdot a = -kx - f\dot{x} \Rightarrow \ddot{x} + \underbrace{\frac{f}{m}}_{\lambda}\dot{x} + \underbrace{\frac{k}{m}}_{\omega_0^2}x = 0$$

$$\Rightarrow x(t) = e^{-\lambda\cdot t}\cdot\sin(\omega t)$$



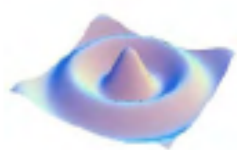
Propagating, Oscillating Mode

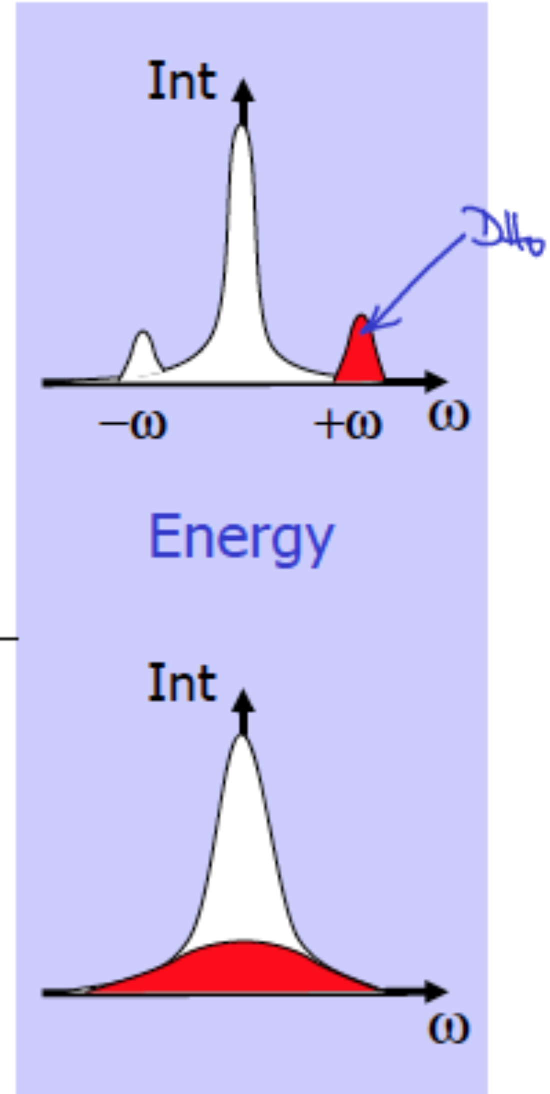
Relaxator

$$m\ddot{x} + f\dot{x} = 0$$

$$\Rightarrow x(t) = e^{-\lambda t}$$

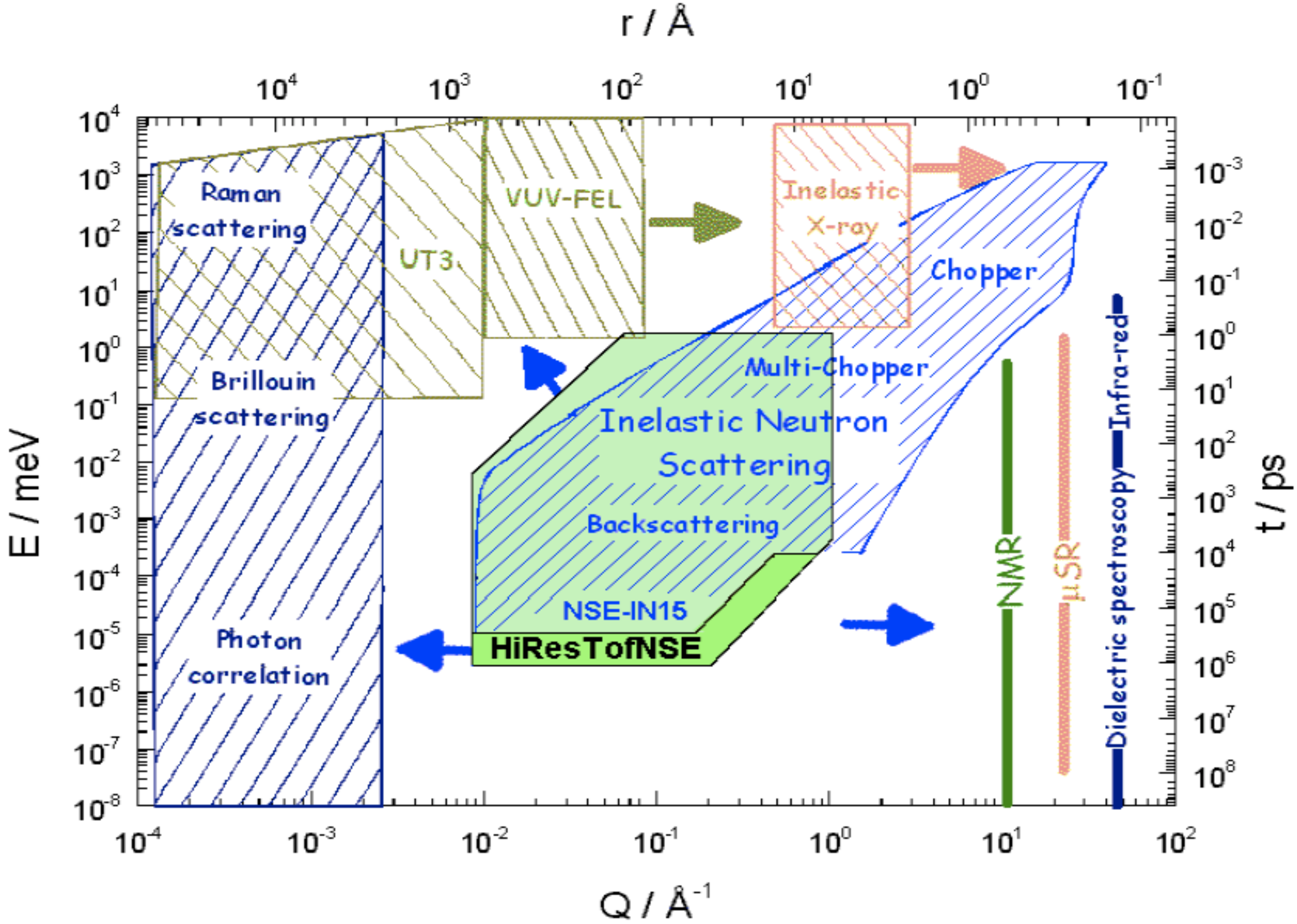
Relaxating (overdamped) Mode





Lecture notes: Maikel C. Rheinstädter

Exploring the dynamic phase space

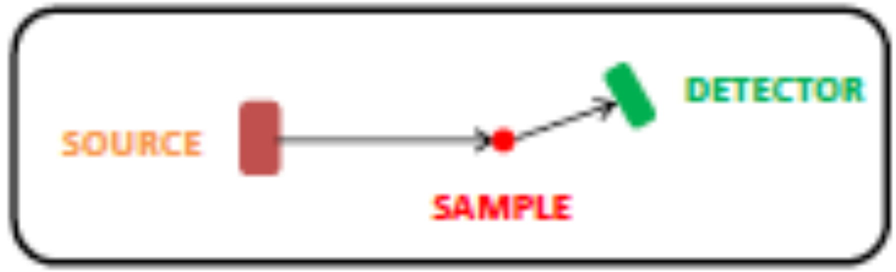


Instrumentation : direct geometry

To determine ΔE we need to define either E_i or E_f : Two methods

Measure : $S(Q,\omega)$

Define E_i

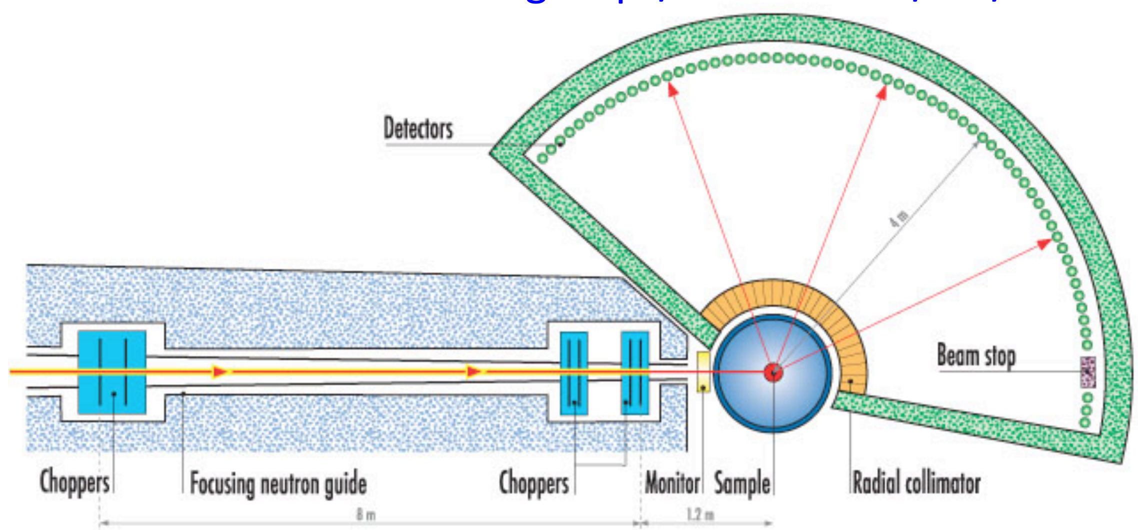


Send neutrons of known fixed E_i (v_i) –neutron can loose as much energy as it has but can gain any (defines energy window)

http://www.ill.eu/instruments-support/instruments-groups/instruments/in5/

Source-sample and sample-detector distances known

Time at which neutron is sent, known

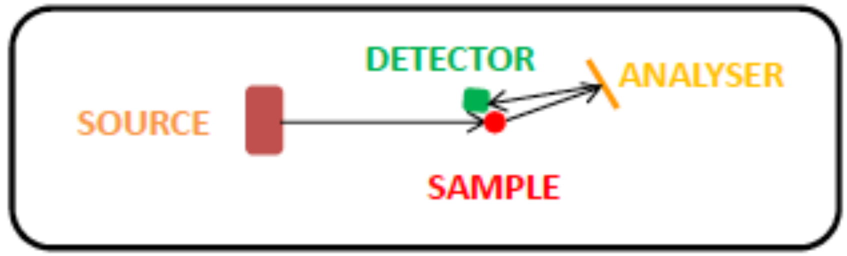


Time at which neutron is detected tells us E_f; thus we know ΔE

V. G. Sakai, lecture

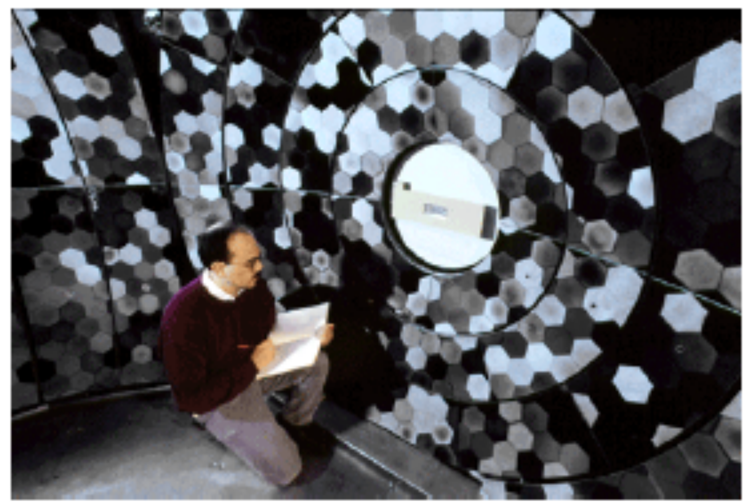
Instrumentation : indirect geometry

Measure : $S(Q,\omega)$
Define E_f



Send neutrons of a known band of wavelengths or E_i (v_i)s (defines your energy window)

In reactor source, use a Doppler drive; in a spallation source, use choppers

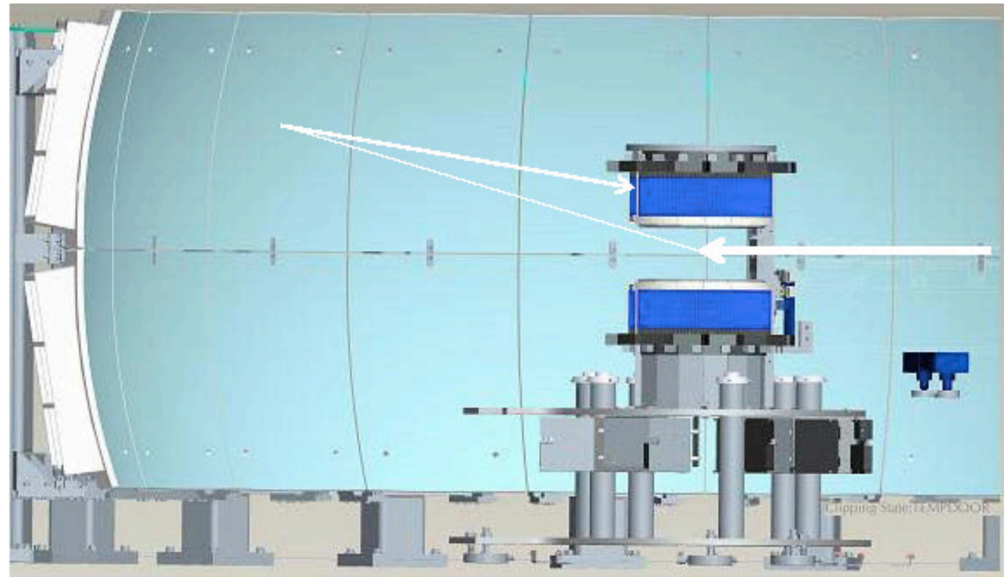


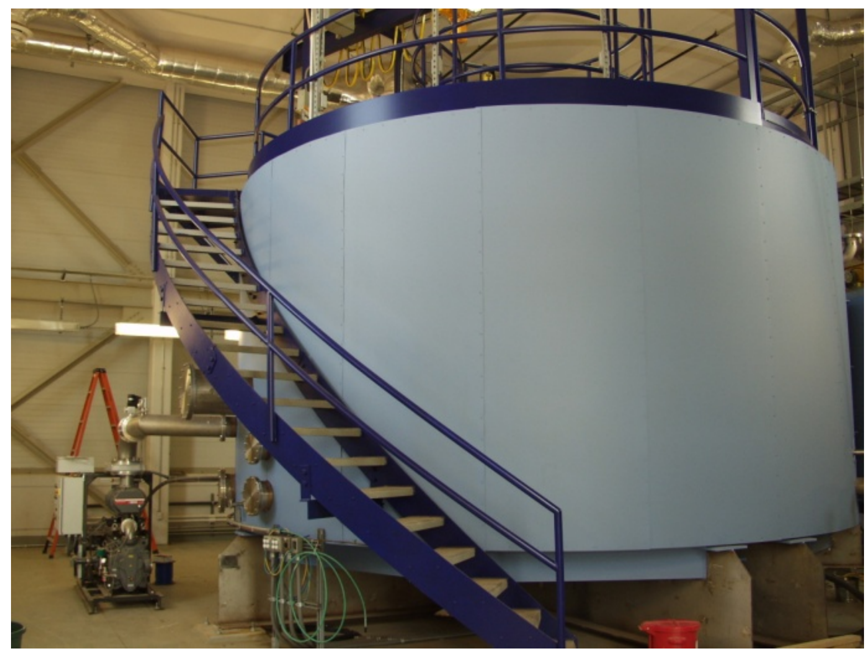
Analyser crystals reflect back only a fixed E_f (Bragg's Law)

Times & distances known, so detected neutron gives us ΔE

V. G. Sakai, lecture

Backscattering Spectrometer BASIS at SNS





QENS Spectrometers – Which one?

Direct geometry:

Poor resolution, higher energies, wider E transfer window, small Q range.

Indirect geometry:

@ reactor, highest resolution with good intensity but limited E transfer range

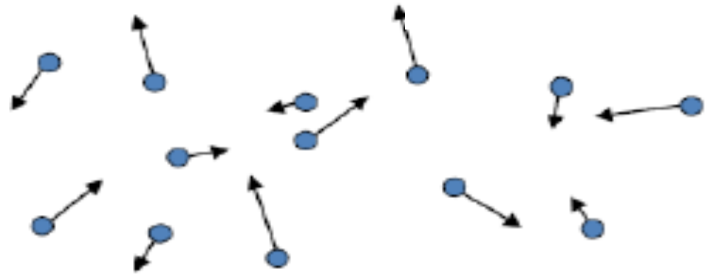
@ spallation, medium resolution, high flux, wider E transfer range

V. G. Sakai, lecture

QENS scattering function

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

- Incoherent scattering
- Contains no information about structure
- Describes the dynamics of individual particles



- Coherent scattering
- Contaminates elastic signal arising from structure
- Describes correlations between nuclei
- Describes the collective dynamics of nuclei

V. G. Sakai, lecture

H/D difference

	σ_{coh} (b)	σ_{incoh} (b)	σ_{abs} (b)
Hydrogen	1.76	**80.2**	0.33
Deuterium	5.59	2.05	0.00
Carbon	5.56	0.00	0.00
Nitrogen	11.0	0.50	1.90
Oxygen	4.23	0.00	0.00
Phosphorus	3.31	0.01	0.17
Aluminium	1.50	0.01	0.23
Silicon	2.17	0.00	0.17

Scattering can be coherent – remembering spatial arrangement of molecules
Incoherent – sensitive only to energy changes induced by molecular motion in the sample

Quasi-Elastic Scattering

Probes diffusion at a molecular scale

Is able to differentiate diffusion from confined dynamics

Analytical functions used to describe motions

Can be used as a systematic tool for comparisons

Time and spatial scale are directly comparable to results from Molecular Dynamics simulations

Complementarities with other experimental techniques

Unique view of motions (eg. contrast)

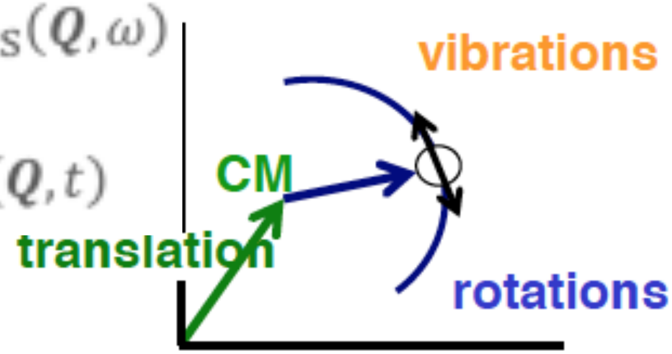
V. G. Sakai, lecture

Single-particle dynamics (incoherent)

For uncoupled motions

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

$$I_{self}(\boldsymbol{Q},t) = I_{vib}(\boldsymbol{Q},t) \times I_{rot}(\boldsymbol{Q},t) \times I_{trans}(\boldsymbol{Q},t)$$



motion decomposition

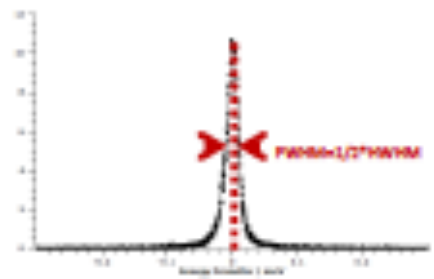
$$I_{self}(Q,t) = \frac{1}{N}\sum_i \left\langle e^{iQ\bullet[V(t)-V(0)]}\right\rangle \left\langle e^{iQ\bullet[T(t)-T(0)]}\right\rangle \left\langle e^{iQ\bullet[R(t)-R(0)]}\right\rangle$$

Vibrations: Debye-Waller factor

$$DWF = \langle \exp(i\boldsymbol{Q}\cdot\boldsymbol{u})\rangle = \exp(-\langle(\boldsymbol{Q}\cdot\boldsymbol{u})^2\rangle) = \frac{1}{3}\exp(Q^2\langle u^2(T)\rangle)$$

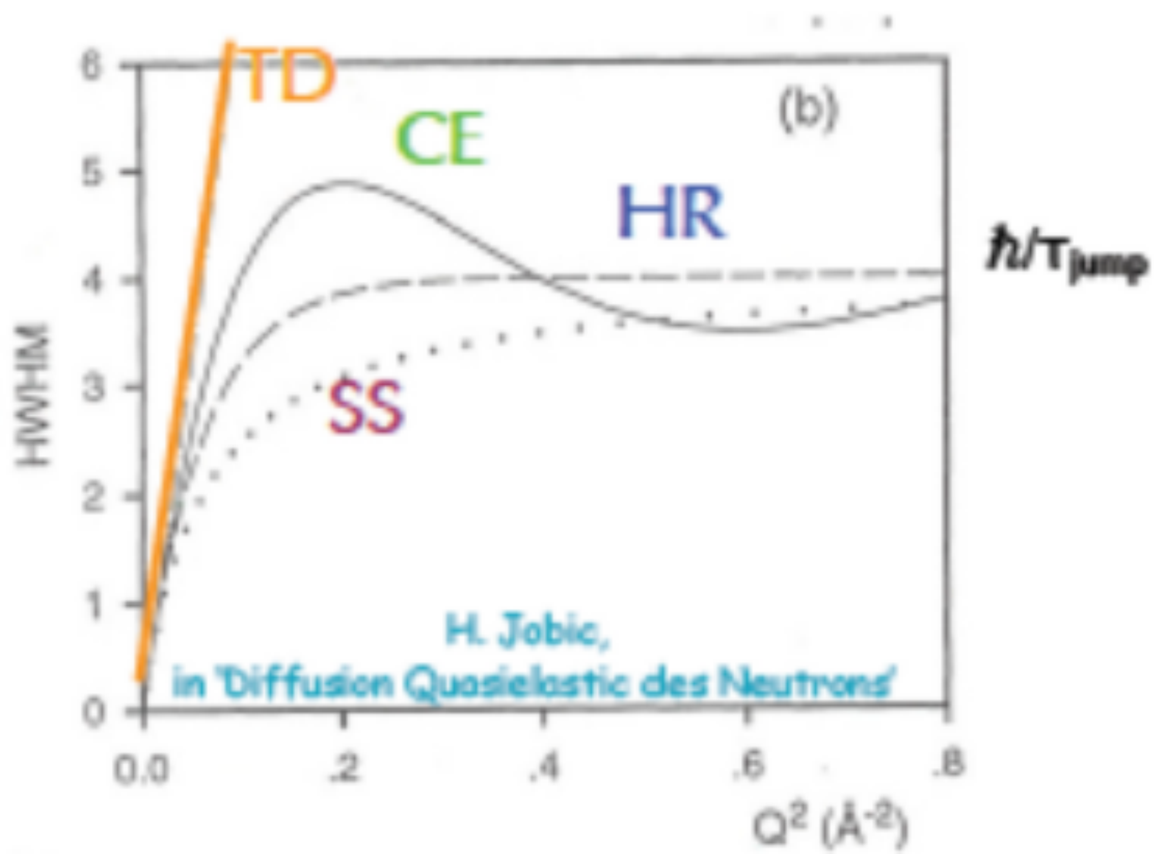
Simple Translational Diffusion

$$I(Q,t) = \exp(-Q^2Dt) \qquad relaxation\ rate\ |\tau| = 1/(DQ^2)$$



$$S_{trans}(\boldsymbol{Q},\omega) = \frac{1}{\pi}\frac{\Gamma}{\Gamma^2+\omega^2}$$ ie. a Lorentzian

Models of translation diffusion-restricted diffusion



V. G. Sakai, lecture

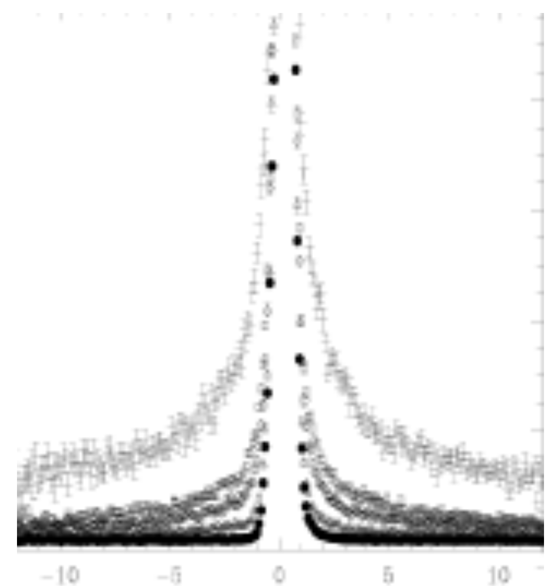
More models including rotations

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

Elastic stationary part, EISF

Quasi-elastic decaying part

$$EISF = \frac{S_{inc}^{el}(\boldsymbol{Q})}{S_{inc}^{el}(\boldsymbol{Q}) + S_{inc}^{qel}(\boldsymbol{Q})}$$



The EISF is the area of the elastic curve divided by the total area, i.e. The fraction of elastic contribution.

For any given Q

$$\int_{-\infty}^{+\infty} S_{\text{inc}}(\boldsymbol{Q},\omega)\,d\omega = 1$$

V. G. Sakai, lecture

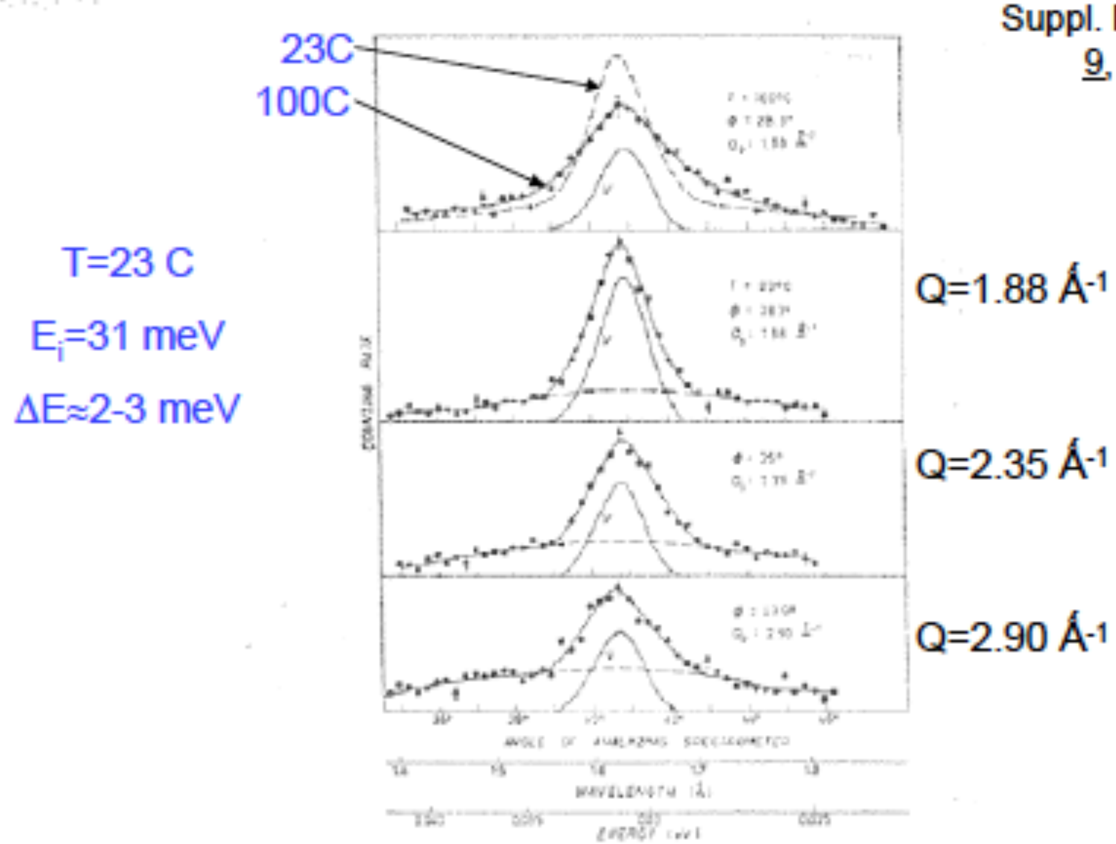
Structural dynamics of water by neutron spectrometry

Unambiguous statements to be made about the dynamical nature of liquids in ; general and of water in particular.

B. N. BROCKHOUSE

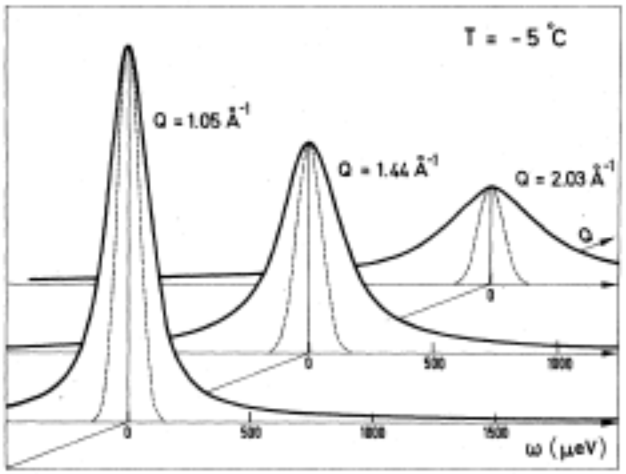
General Physics Branch, Atomic Energy of Canada Limited - Chalk River, Ontario

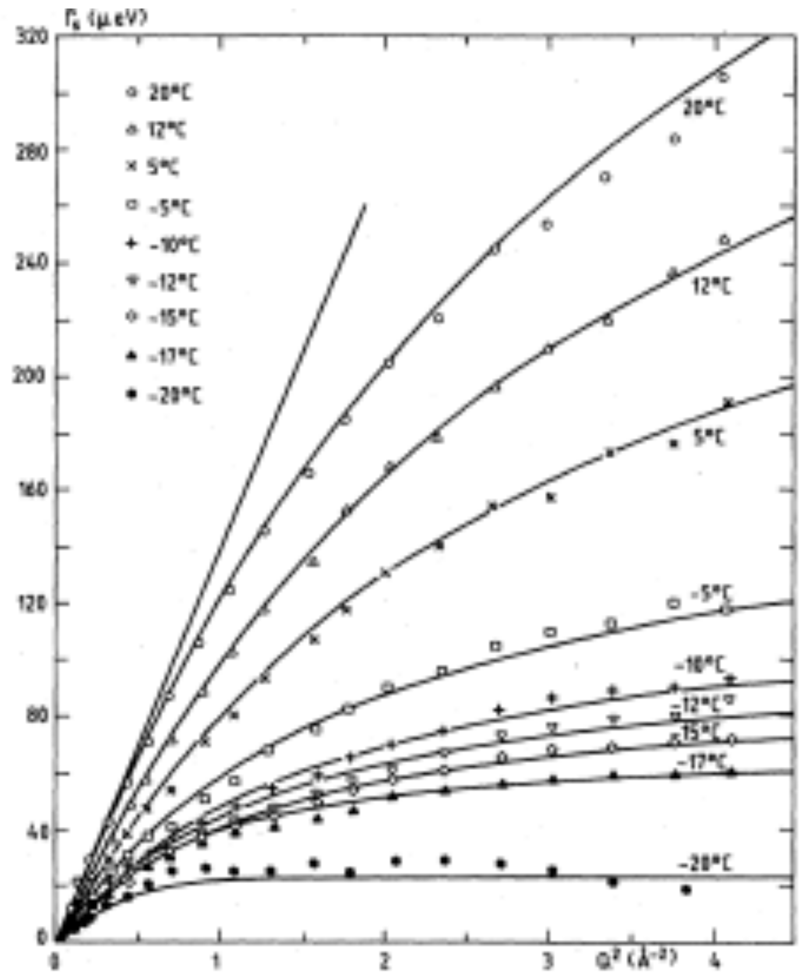
Suppl. Nuovo Cimento
9, 45 (1958)



J. Copley, NIST

Improved measurements IN6, ILL





$$\Gamma_{(Q)} = \frac{DQ^2}{1 + DQ^2\tau_0}$$

$$D = \frac{\langle l^2 \rangle_{av}}{6\tau_0}$$

Random jump diffusion model

Teixeira et al Phys. Rev. A 1985

Why investigate dynamics?

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Chemical Physics 292 (2003) 283–287
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Quasielastic neutron scattering for the investigatior
of liquids under shear ☆

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Water, Solute, and Segmental Dynamics in Polysaccharide Hydrogels

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Restricted dynamics in polymer-filler systems

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Dynamics of fresh and freeze-dried strawberry and red onion by quasielastic neutron scattering.
J Phys Chem B. 2006; 110(28):13786-92 (ISSN: 1520-6106)

Jansson H; Howells WS; Swenson J
Department of Applied Physics, Chalmers University of Technology,
SE-412 96 Göteborg, Sweden.

Letters to Nature
Nature 337, 754 - 756 (23 February 1989);

Dynamical transition of myoglobin revealed by inelastic neutron scattering

Wolfgang Doster*, Stephen Cusack† & Winfried Petry‡

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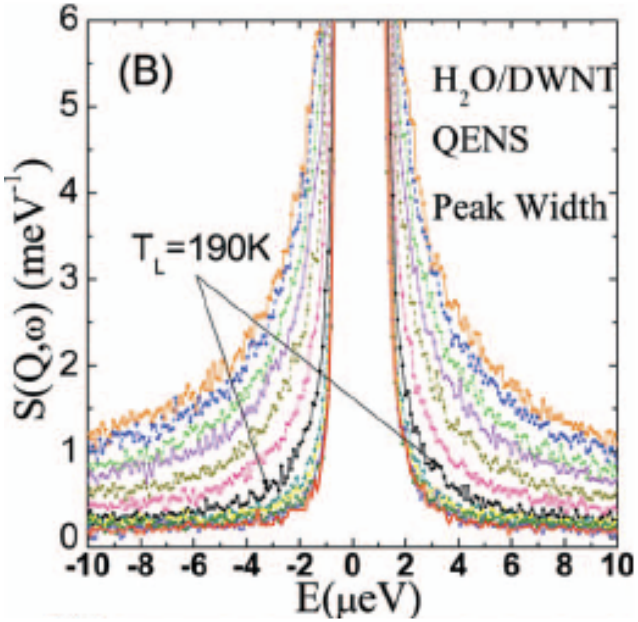
By understanding microscopic dynamics tune a materials bulk properties

Lecture M. Telling

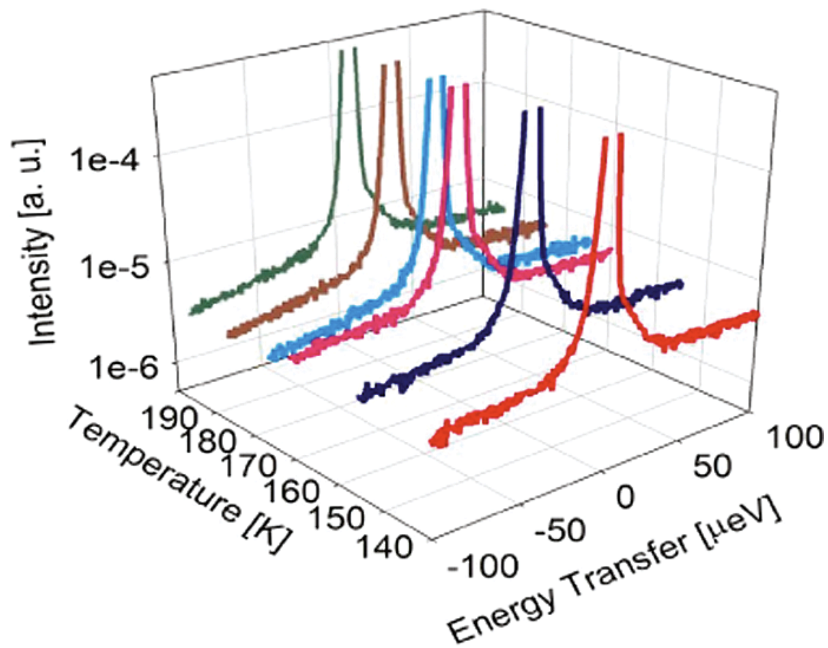
Quasi-elastic neutron Scattering measures S(q,ω) (BASIS at SNS)



The line width of S(q,ω) is related to diffusion of small molecules like water in confined nanometer channels (PHYSICAL REVIEW E 76, 021505 2007)

$$\frac{S(q,\omega)}{S(q)} = \frac{\Delta\omega}{\Delta\omega^2 + \omega^2}$$

http://neutrons.ornl.gov/research/highlights/BASIS/



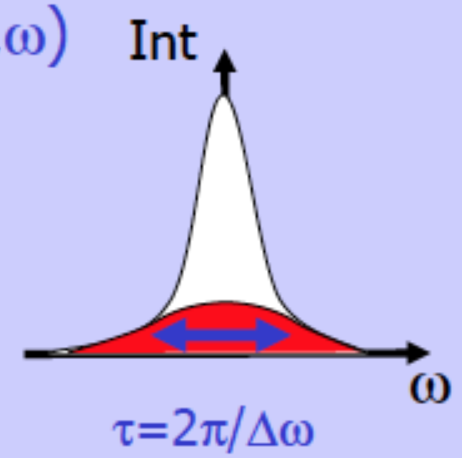
Fast Proton Hopping Detection in Ice Ih by Quasi-Elastic Neutron Scattering

I. Presiado, JL et al. *J. Phys. Chem. C.* **2011**

Energy-Time domains

Maikel C. Rheinstädter

S(q,ω)

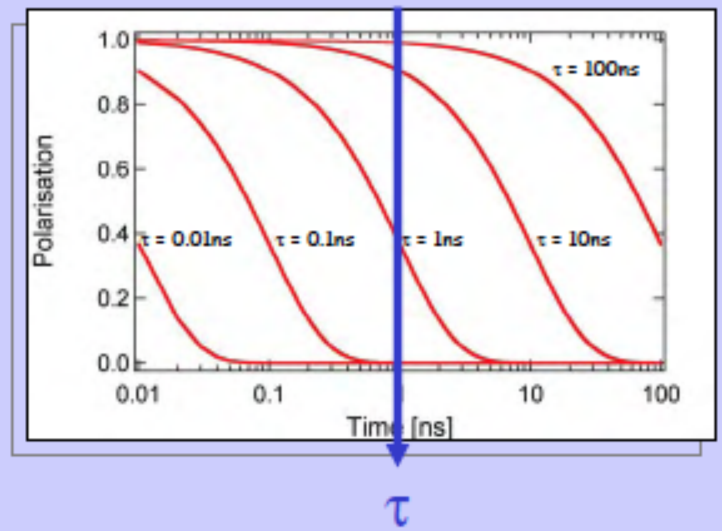


Lorentzian

$$E = \frac{h}{et}$$

Line shape

S(q,t)



Exponential decay
Debye relaxation

$$1ps = \frac{4.14}{1meV} \qquad 1ns = \frac{4.14}{1\mu eV} \qquad 1\mu s = \frac{4.14}{1neV}$$