Neutron Spectroscopy 2: high resolution spectrometers

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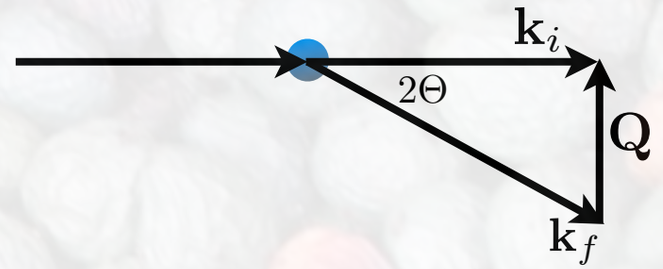
NEUTRONS FOR SCIENCE

content

- why do we need high energy resolution neutron spectroscopy?
  - low energy transitions and QENS at low energy
  - QENS: theory & models for confined and unconfined motion
- how to achieve the best energy resolution
  - in time-of-flight spectroscopy
  - in crystal spectroscopy
  - neutron spin echo (see C. Pappas)
- examples of applications
  - overview
  - low frequency inelastic examples
    - quantum tunnelling
  - quasielastic examples
    - energy materials, confined molecules, water dynamics

the scattering process neutron-sample



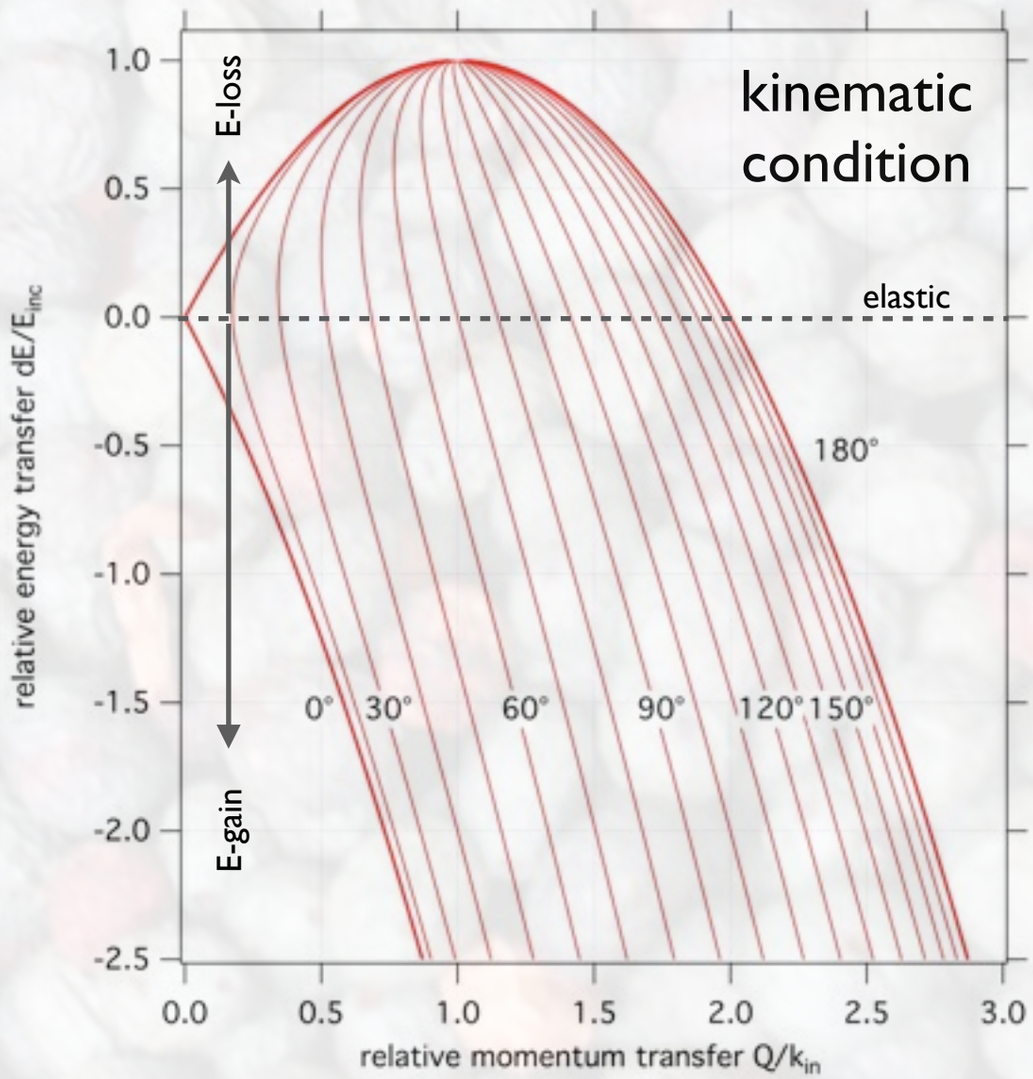
exchange of energy and momentum with the sample

$$\hbar\omega = E_1^S - E_0^S = E_i^n - E_f^n$$

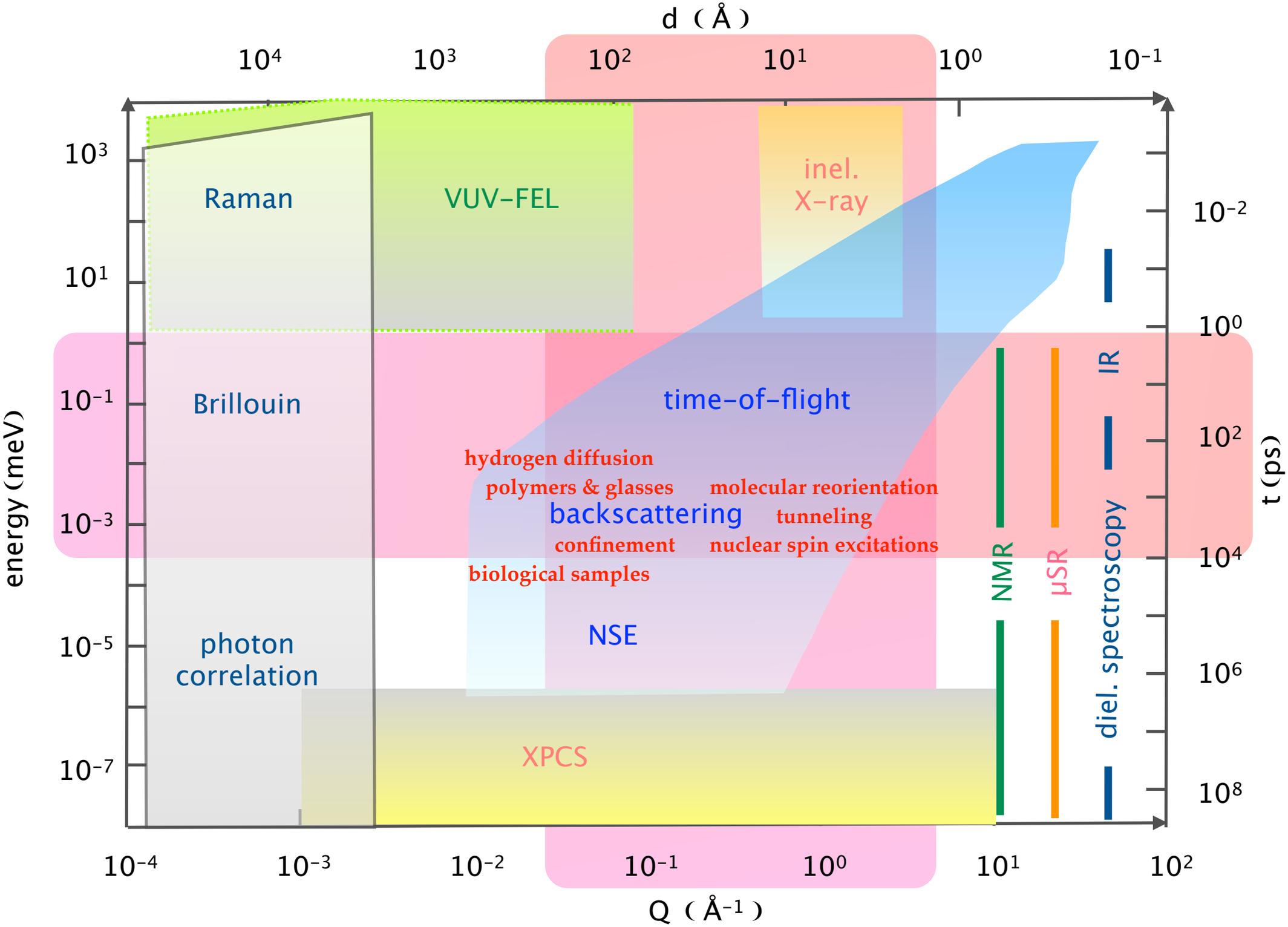
$$\hbar\mathbf{Q} = \hbar(\mathbf{k}_i - \mathbf{k}_f)$$

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

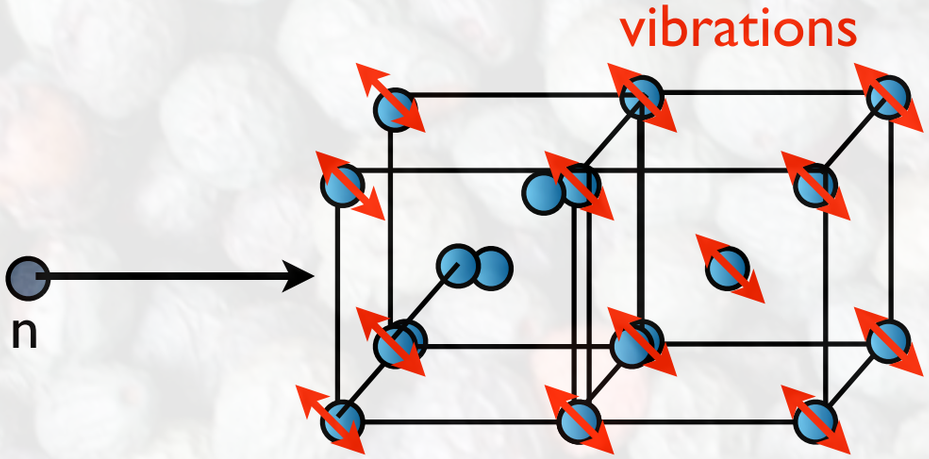
$$Q^2 = \frac{2m}{\hbar^2}(2E_i - \hbar\omega - 2E_i\sqrt{1 - \frac{\hbar\omega}{E_i}} \cdot cos(2\theta))$$



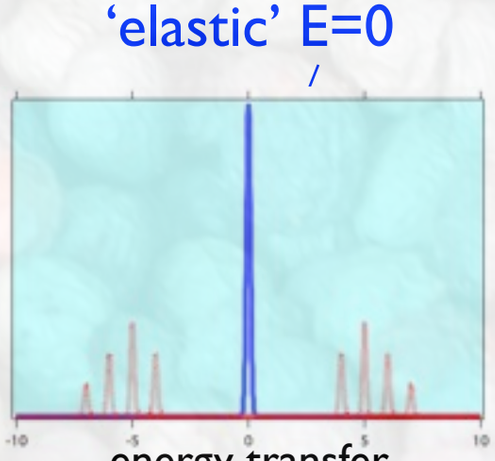
why do we need high E-resolution?



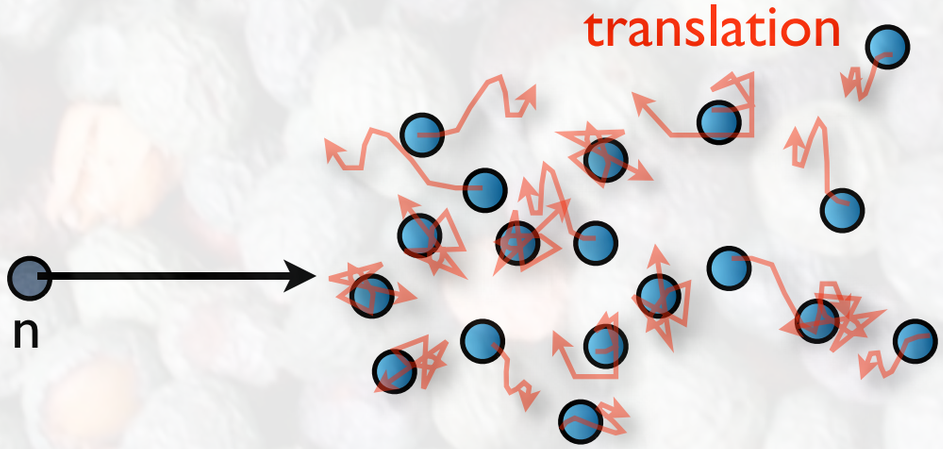
a simple definition of ‘quasielastic’



“rigid” crystal

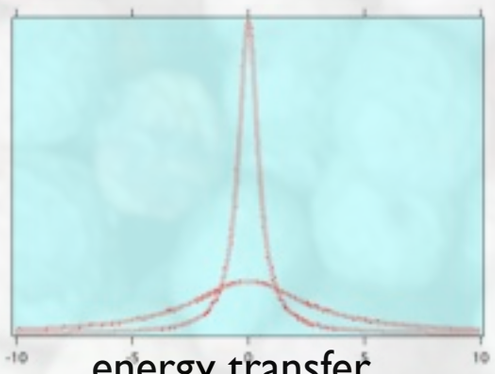


‘inelastic’ E=±dE



fast moving scatterers, e.g. liquid

~~elastic E=0~~



‘quasielastic’: centered at E=0

‘quasielastic scattering’ - an interpretation in terms of correlation functions

scattering function: $S(\mathbf{Q},\omega) = \frac{4\pi}{\sigma}\frac{1}{N}\frac{\mathbf{k}_i}{\mathbf{k}_f}\frac{\partial^2\sigma}{\partial\Omega\partial\omega}$

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

intermediate scattering functions:

$$I_d(\mathbf{Q},t) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle e^{-i\mathbf{Q}\mathbf{r}_i(0)}e^{i\mathbf{Q}\mathbf{r}_j(t)}\rangle$$

coherent

$$I_s(\mathbf{Q},t) = \frac{1}{N}\sum_{i=1}^{N}\langle e^{-i\mathbf{Q}\mathbf{r}_i(0)}e^{i\mathbf{Q}\mathbf{r}_i(t)}\rangle$$

incoherent

van Hove correlation functions:

$$G(\mathbf{r},t) = \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty} e^{-i(\mathbf{Q}\mathbf{r}-\omega t)} I_{coh}(\mathbf{Q},t)d\mathbf{Q}d\omega$$

$$G_s(\mathbf{r},t) = \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty} e^{-i(\mathbf{Q}\mathbf{r}-\omega t)} I_{inc}(\mathbf{Q},t)d\mathbf{Q}d\omega$$

correlation functions

density correlation functions - pair correlation function

e.g. T. Springer, 'Quasielastic Neutron Scattering for the Investigation of Diffusive Motions in Solids and Liquids', Springer Tracts in Modern Physics 64, 1972

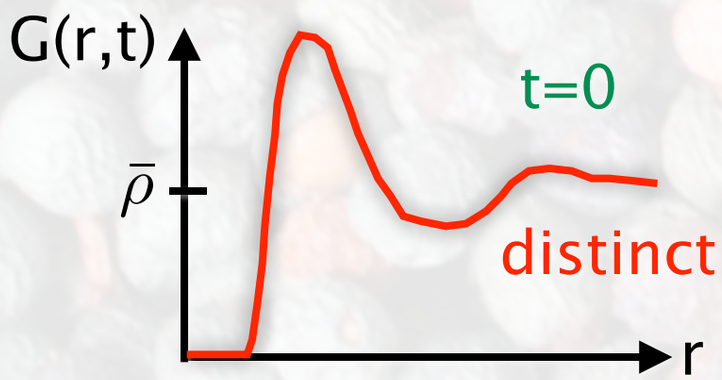
for a **classical** system formulated in terms of a microscopic particle density function: $\rho(\mathbf{r},t) = \sum_{i=1}^{N} \delta[\mathbf{r} - \mathbf{r}_i(t)]$

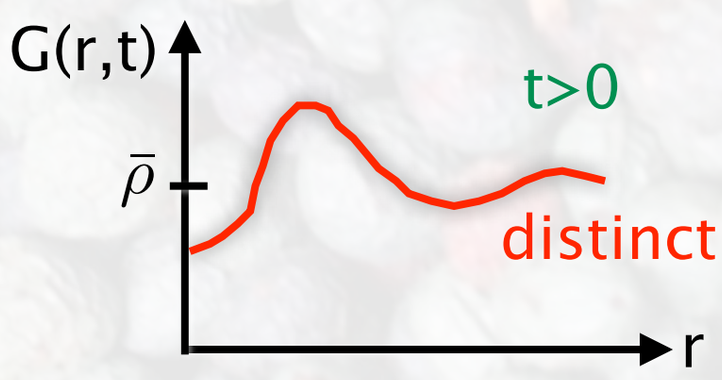
$$G(\mathbf{r},t) = \frac{1}{N}\int < \rho(\mathbf{r}^{'} - \mathbf{r},0)\rho(\mathbf{r}^{'},t) > d\mathbf{r}^{'}$$

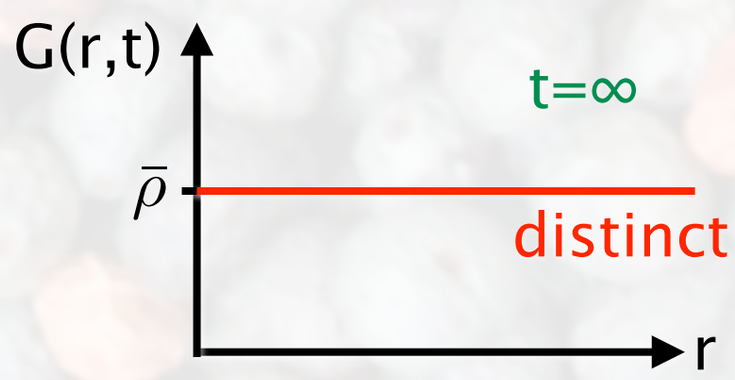
i.e. **auto-correlation function of the particle density**

asymptotic behaviour: $G^{\infty}(\mathbf{r}) = \lim_{\mathbf{r},t\to\infty} G(\mathbf{r},t) = \frac{1}{N}\int \bar{\rho}(\mathbf{r}^{'} - \mathbf{r})\bar{\rho}(\mathbf{r}^{'})d\mathbf{r}^{'}$

e.g. for liquid: $G^{\infty}(\mathbf{r}) = \bar{\rho} = \frac{N}{V}$







density correlation functions - self correlation function

for a **classical** system define average **probability per volume** to find particle i at r′: $p_i(\mathbf{r}') =< \delta[\mathbf{r}' - \mathbf{r}_i(t)] >$

asymptotic behaviour: $$G_s^{\infty}(\mathbf{r}) = \frac{1}{N}\sum_{i=1}^{N}\int p_i(\mathbf{r}' - \mathbf{r})p_i(\mathbf{r}')d\mathbf{r}'$$

liquid: $$\lim_{t\to\infty} G_s^{\infty}(\mathbf{r},t) = \frac{1}{V}$$

thus: $G_s^{\infty}(\mathbf{r}) \to 0$ for $V \to \infty$

but not if V is finite: EISF!

assume identical scattering particles (drop index i)

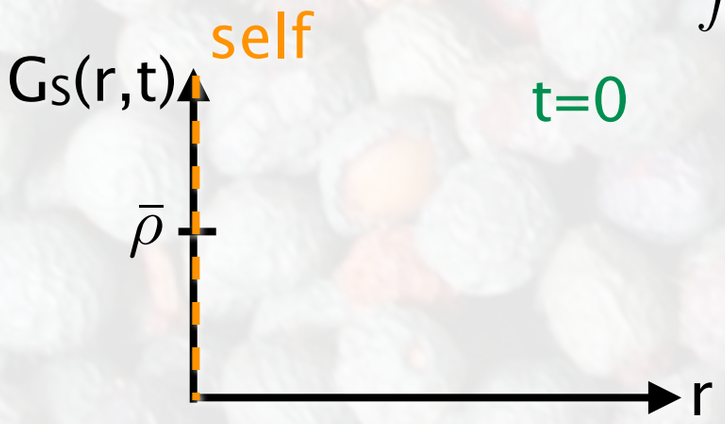
$$G_s^{\infty}(\mathbf{r}) = \int p(\mathbf{r}' - \mathbf{r})p_(\mathbf{r}')d\mathbf{r}'$$

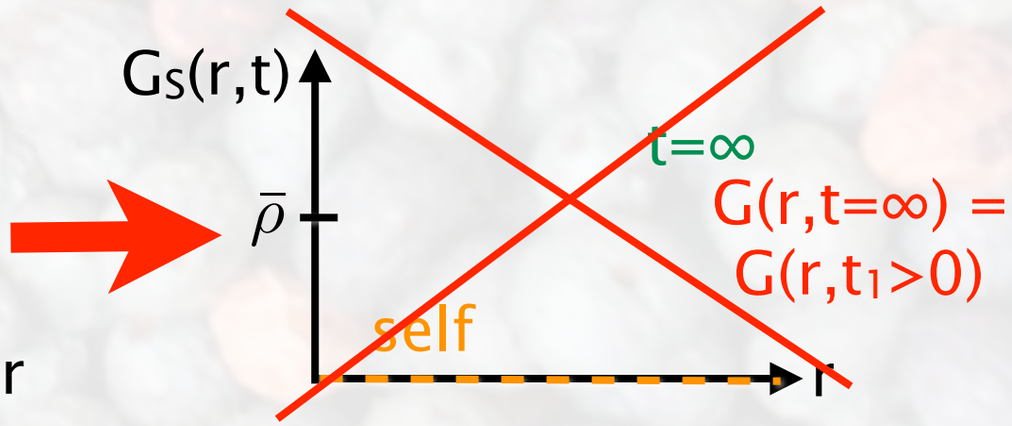
and separate $\mathbf{G_s}$ in decaying and stationary part:

$$G_s'(\mathbf{r},t) = \underline{G_s(\mathbf{r},t)} - \underline{G_s^{\infty}(\mathbf{r})}$$

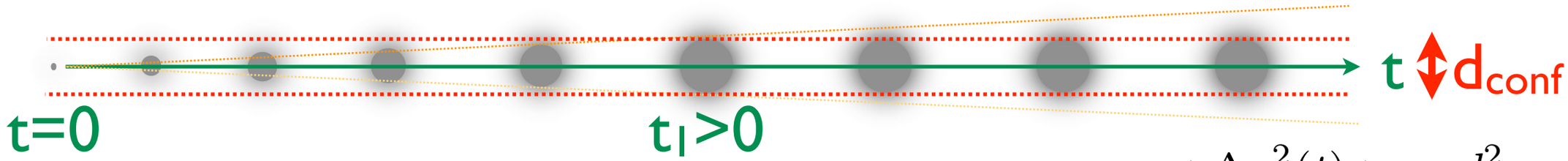
elastic incoherent structure factor (EISF):

$$S_{inc}^{el}(\mathbf{Q}) = \int \exp\{-i(\mathbf{Qr})\}G_s^{\infty}(\mathbf{r})d\mathbf{r} = |\int \exp\{-i(\mathbf{Qr})\}p(\mathbf{r})d\mathbf{r}|^2$$

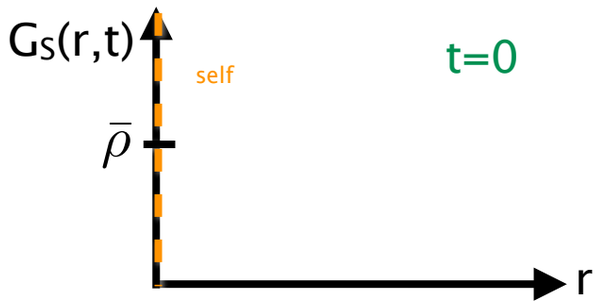


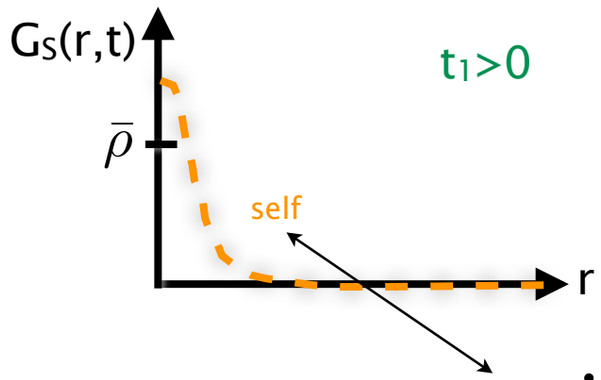


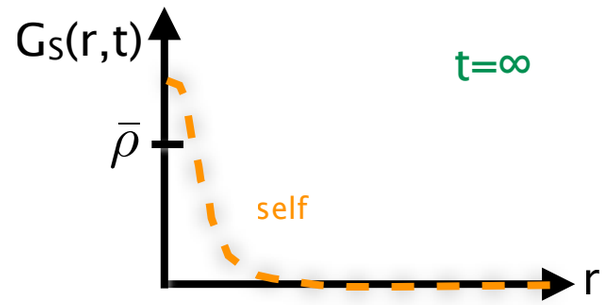
self correlation function - EISF



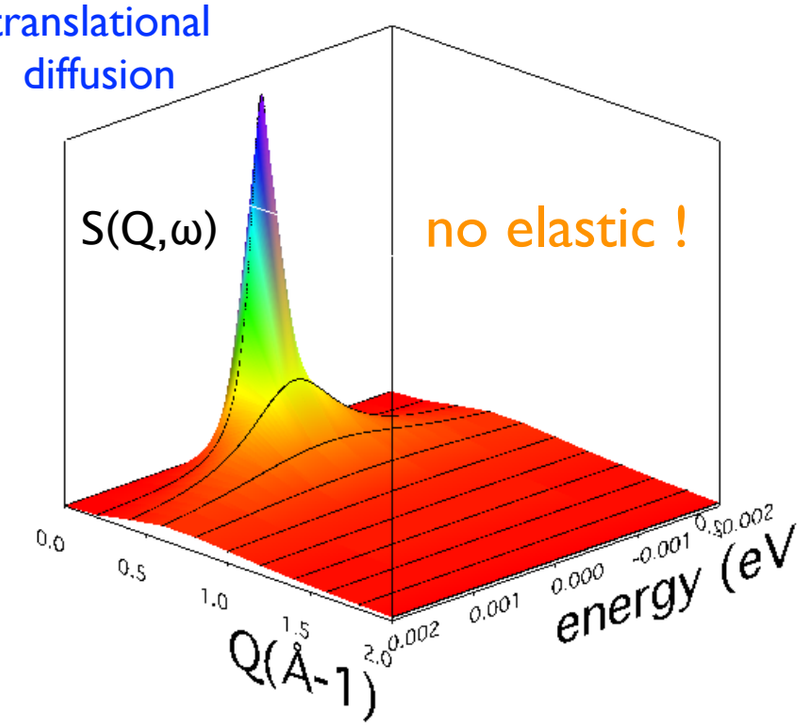
$$< \Delta r^2(t) > \rightarrow d^2_{conf}$$



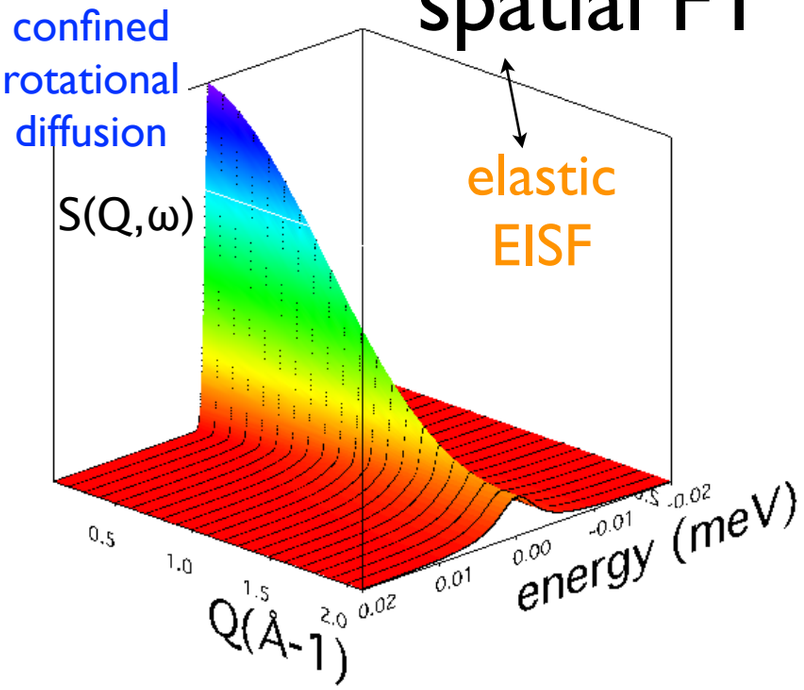


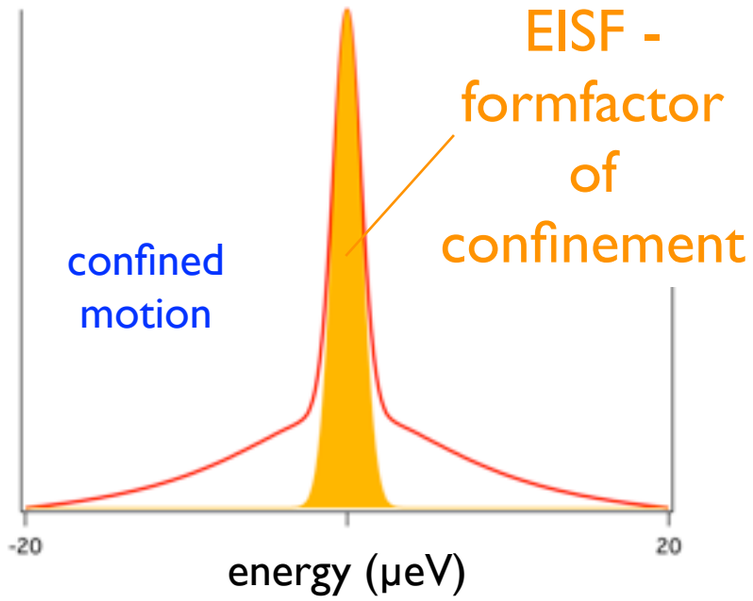


translational diffusion



confined rotational diffusion





typical incoherent scattering law

$$S_{inc}(\mathbf{Q},\omega) = A_0(\mathbf{Q})\delta(\omega) + (1 - A_0(\mathbf{Q}))\mathbf{L}(\mathbf{Q},\omega)$$

elastic, EISF
stationary part; sign of
confined motion

quasi-elastic
decaying part

for a given Q: $\int_{-\infty}^{\infty} S_{inc}(\mathbf{Q},\omega)d\omega = 1$

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

example for a simple incoherent scattering law

isotropic translational diffusion

no stationary part -> not confined -> no elastic scattering

time space

$$S_{inc}(\mathbf{Q},t) = \exp(-DQ^2t)$$

relaxation rate $|\tau| = 1/(DQ^2)$

energy space

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

Lorentzian with energy width

$HWHM = \Gamma/2 = \hbar DQ^2$

D=self diffusion constant [m^2/s]

$D \sim \exp(-E_a/kT)$

$$Q = 1\mathring{A}^{-1} : D = \frac{\Gamma\pi}{hQ^2} = \frac{\Gamma[\mu eV]\pi}{4.136[\mu eV ns]10^{16}[cm^2]} \approx \frac{3}{4}\Gamma[\mu eV]\cdot 10^{-7}\frac{cm^2}{s}$$

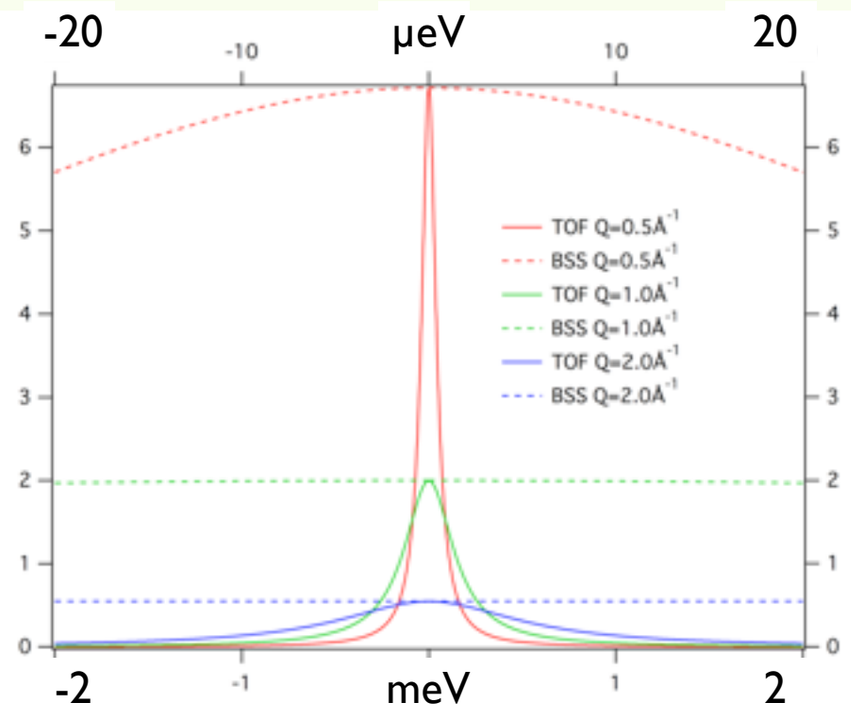
example:

D(H_2O @ RT) ~ 2 10^{-5}cm²/s

FWHM ~ 270 μeV @ 1Å^{-1}; τ=5ps

FWHM ~ 2.7 μeV @ 0.1Å^{-1}; τ=50ps

=> TOF dynamic range



other diffusion models

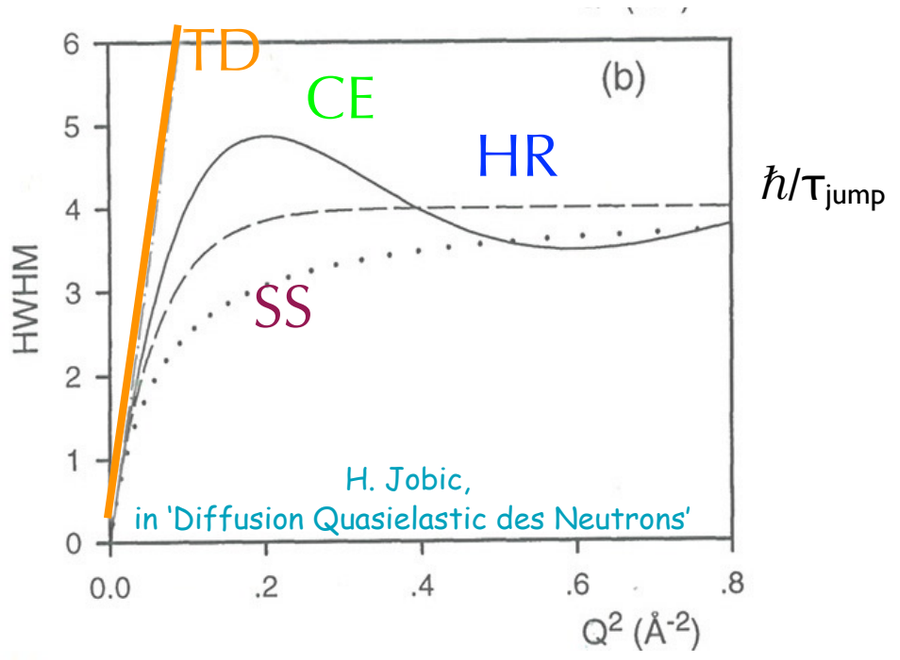
at high Q deviations from 'normal' low-Q translational diffusion (Fick's law)

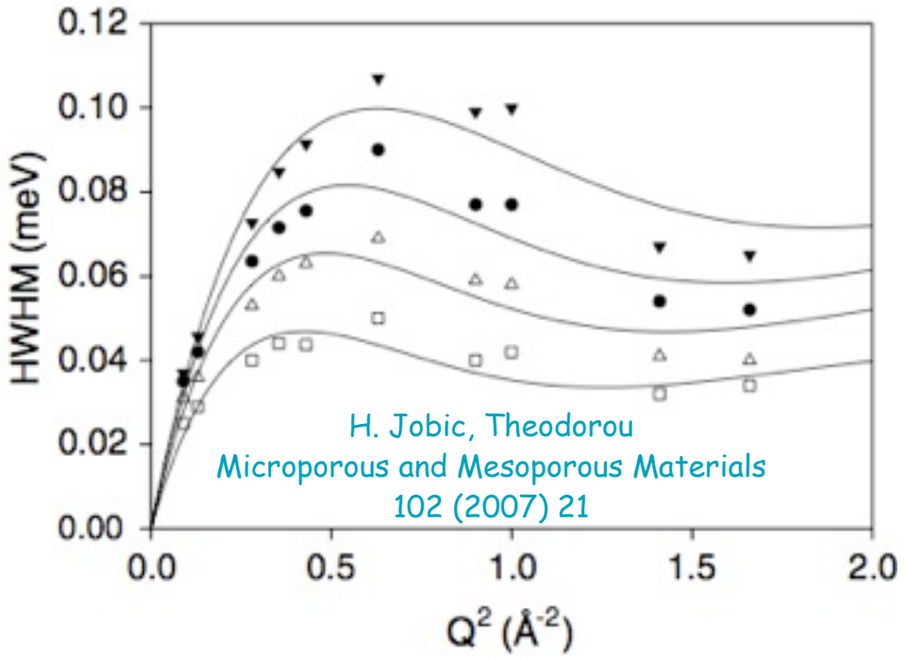
- continuous / translational diffusion

  ~ DQ^2 for all Q

- jump diffusion models (unconfined):
  - Chudley-Elliott
  - Singwi-Sjölander
  - Hall-Ross

~ DQ^2 at low Q
approaches $1/\tau_{jump}$ at high Q





- not shown:
  - anisotropic diffusion models
  - diffusion in lower dimensions

simple incoherent scattering law:

- locally confined jump models

see e.g.: - M. Bée, 'Quasielastic Neutron Scattering'

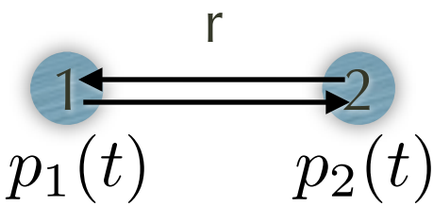
stationary & decaying part -> confined -> elastic scattering

local motions -> Q-independent linewidth & EISF

- jumps between 2,3,4,...n (non-)equivalent sites
  - rotational diffusion on a circle
  - diffusion on a sphere
- diffusion inside a sphere, cylinder,...

simple incoherent scattering law:

- two site jump among equivalent sites



stationary & decaying part -> confined -> elastic scattering

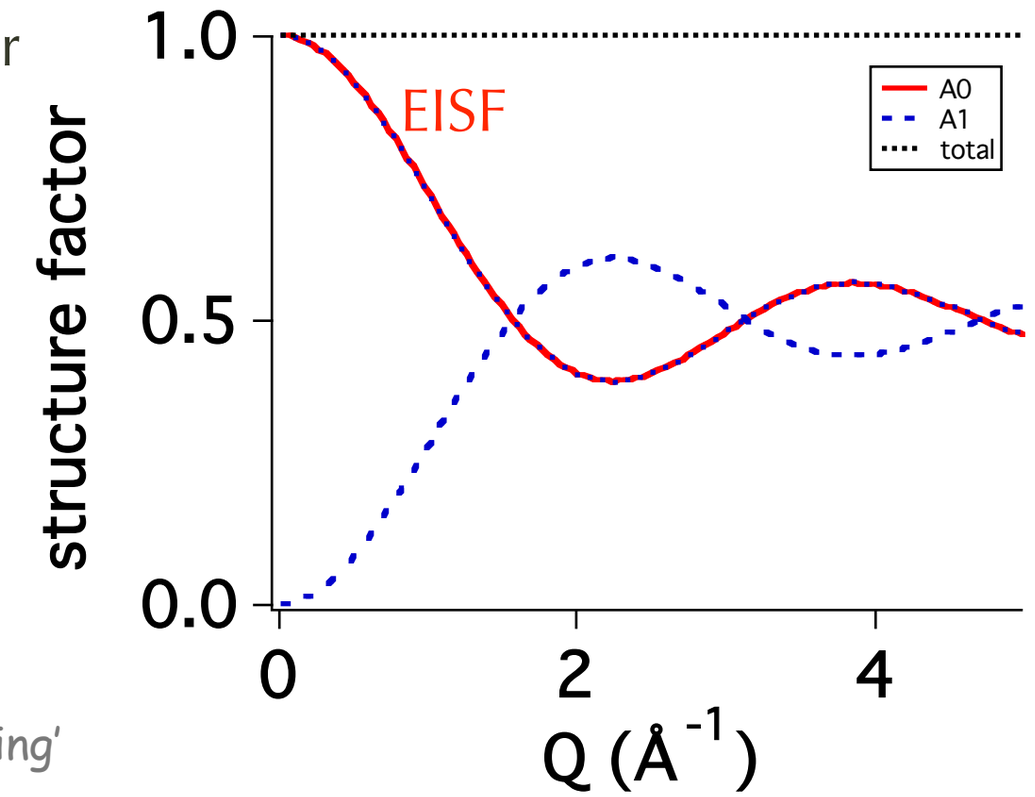
$$I(\mathbf{Q},t) = A_0(\mathbf{Q}) + A_1(\mathbf{Q}))exp(-\frac{2t}{\tau})$$

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

structure factors for a two-site jump over distance r; powder averaged:

EISF: $A_0(Q) = [1 + j_0(Qr)]/2$
$A_1(Q) = [1 - j_0(Qr)]/2$

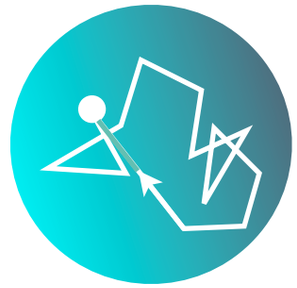
j_0 = 0-th order spherical Besselfct.



see e.g. M. Bée, 'Quasielastic Neutron Scattering'

simple incoherent scattering law:

- free diffusion inside a sphere



stationary & decaying part -> confined -> elastic scattering

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

$$A_0(Q) = \left(\frac{3j_1(Qa)}{Qa}\right)^2 \qquad \text{and} \qquad j_1(x) = \frac{sin(x)}{x^2} - \frac{cos(x)}{x}$$

spherical Besselfct. of 1st order

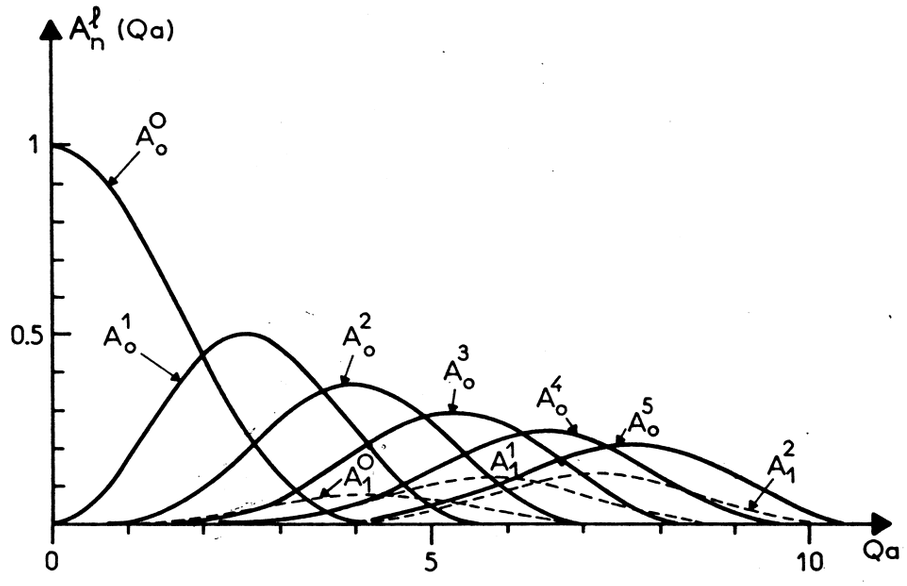


Figure 1. Variation of the first incoherent structure factors $A_n{}^l(Q)$ versus Qa (31–32) for diffusion inside an impermeable sphere of radius a. The elastic incoherent structure factor (EISF) is $A_0{}^0(Q)$.

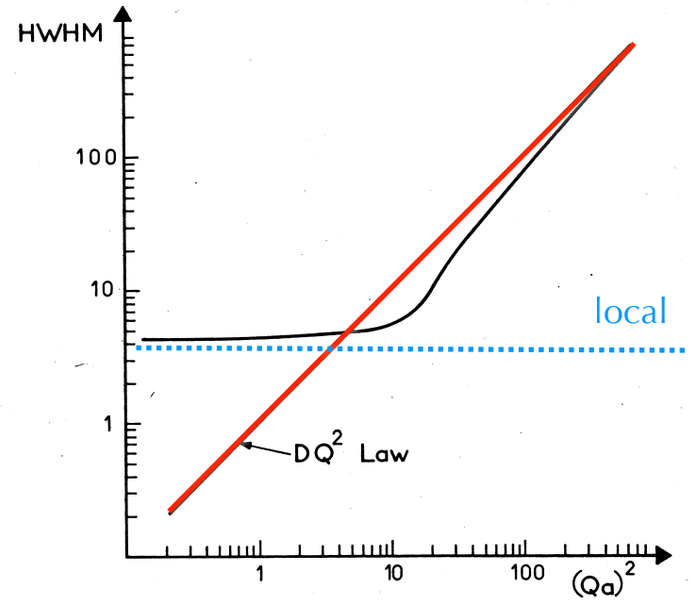


Figure 2. Variation of the half width at half maximum (HWHM) of the broadened component of the scattering law for diffusion inside a sphere of radius a, (33), expressed in D/a^2 energy units, versus $(Qa)^2$. The HWHM of the DQ^2 law is also represented. In the present units, its value is $(Qa)^2$.

Volino F., Dianoux A.J. , Mol. Phys. 41, 271-279 (1980)

more realistic scattering laws:

see e.g. M. Bée, 'Quasielastic Neutron Scattering Principles and Applications in Solid State Chemistry, Biology and Material Science', Adam Hilger, Bristol 1988

- take convolution with resolution fct. into account
- combination of scattering laws, e.g.:
  - whole molecule rotation
  - + part of molecule rotation (methyl group)
  - + c.o.m.-diffusion of whole molecule
  - + vibrations, phonons

why do we need high energy resolution neutron spectroscopy?

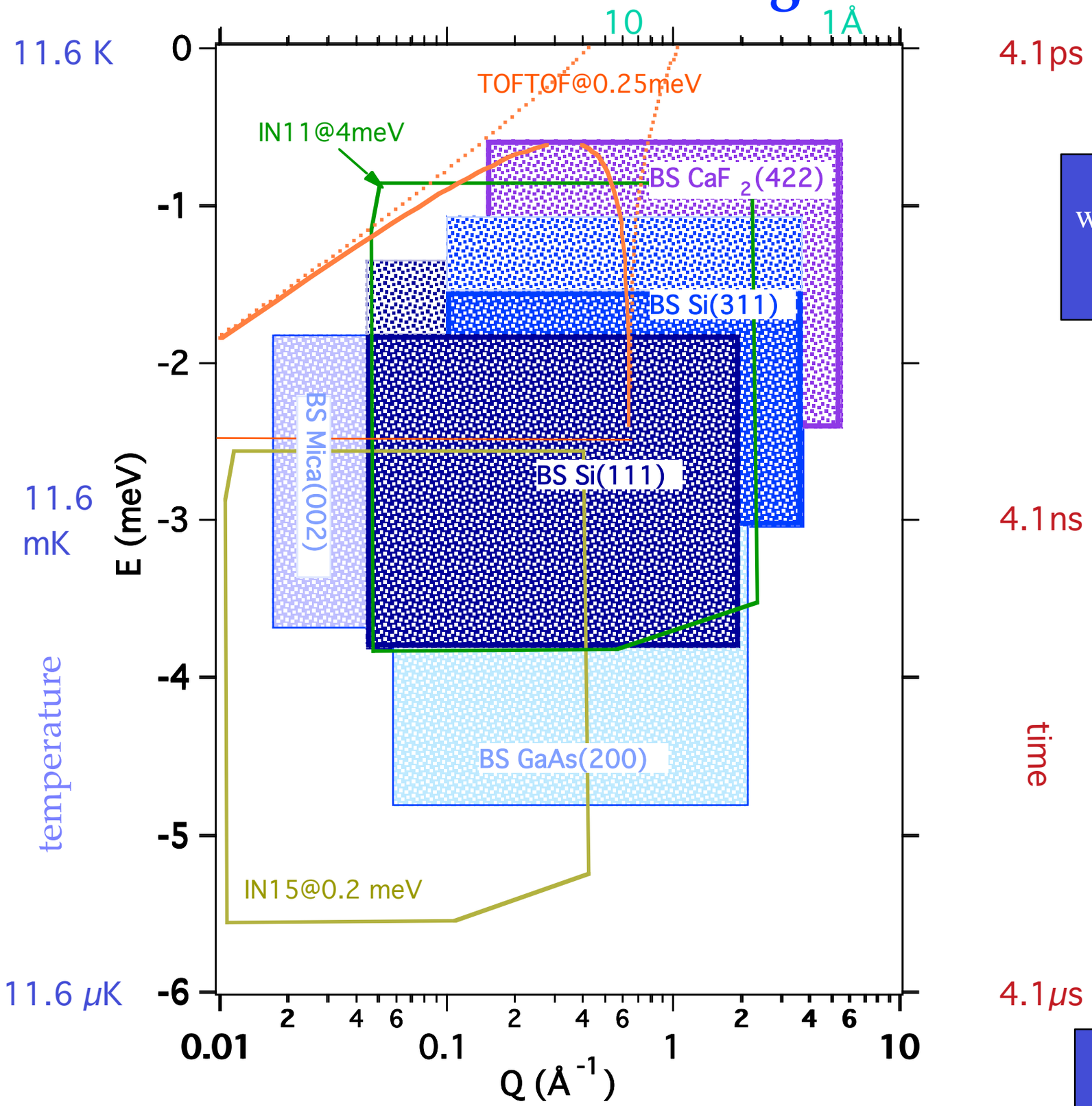
- because of its suitable time resolution for some dynamic phenomena at the proper length scale
- because it is either the unique method or complementary to other spectroscopic techniques (time & spatial probe)
- to investigate the character of diffusive versus confined motion

content

- why do we need high energy resolution neutron spectroscopy?
  - low energy transitions and QENS at low energy
  - QENS: theory & models for confined and unconfined motion
- how to achieve the best energy resolution
  - in time-of-flight spectroscopy
  - in crystal spectroscopy
  - neutron spin echo (see C. Pappas)
- examples of applications
  - overview
  - low frequency inelastic examples
    - quantum tunnelling
  - quasielastic examples
    - energy materials, confined molecules, water dynamics

Q-ω map for high resolution spectrometers

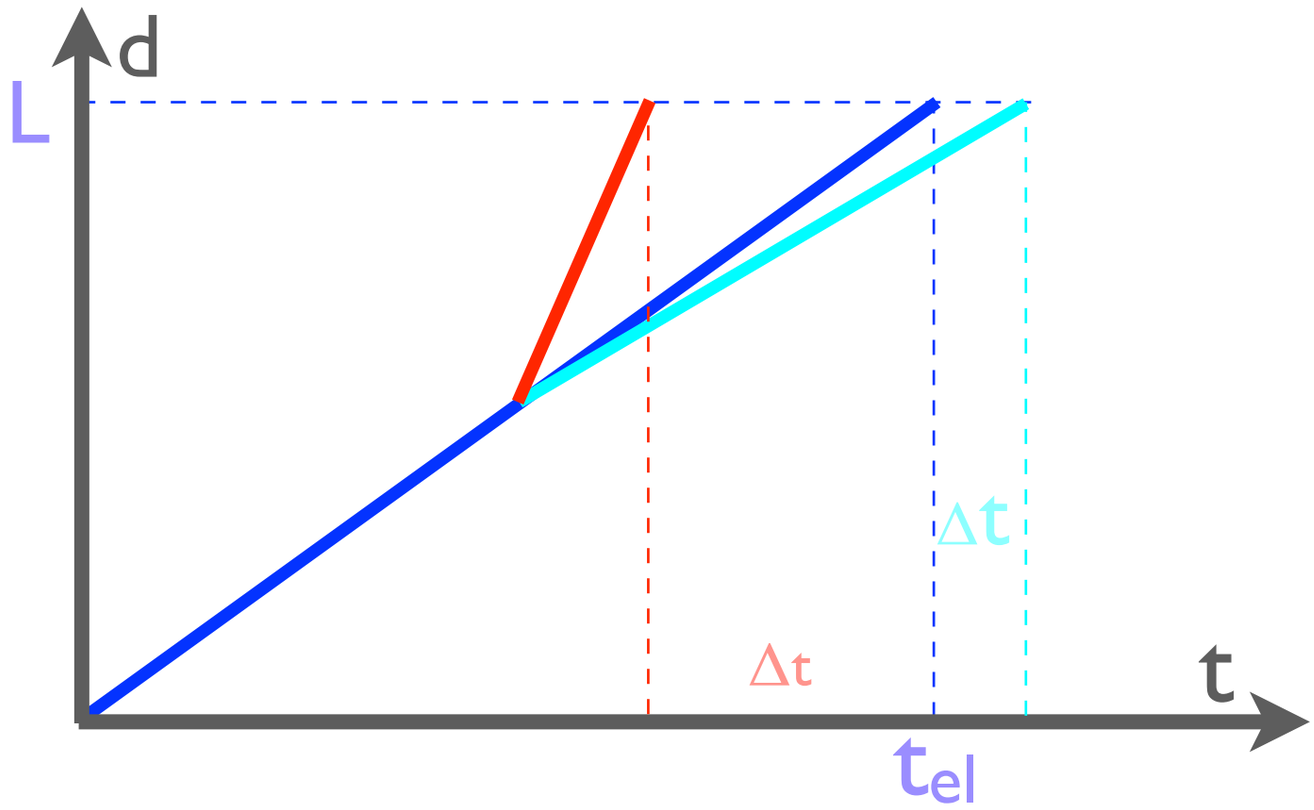
- TOF / - backscattering / NSE



E = hν
with: h=4.136 meVps
⇒1THz : 4.1meV
⇒ 1meV : 4.1ps

elastic scattering:
$Q=4\pi/\lambda\sin(\Theta)$

TOF-spectroscopy

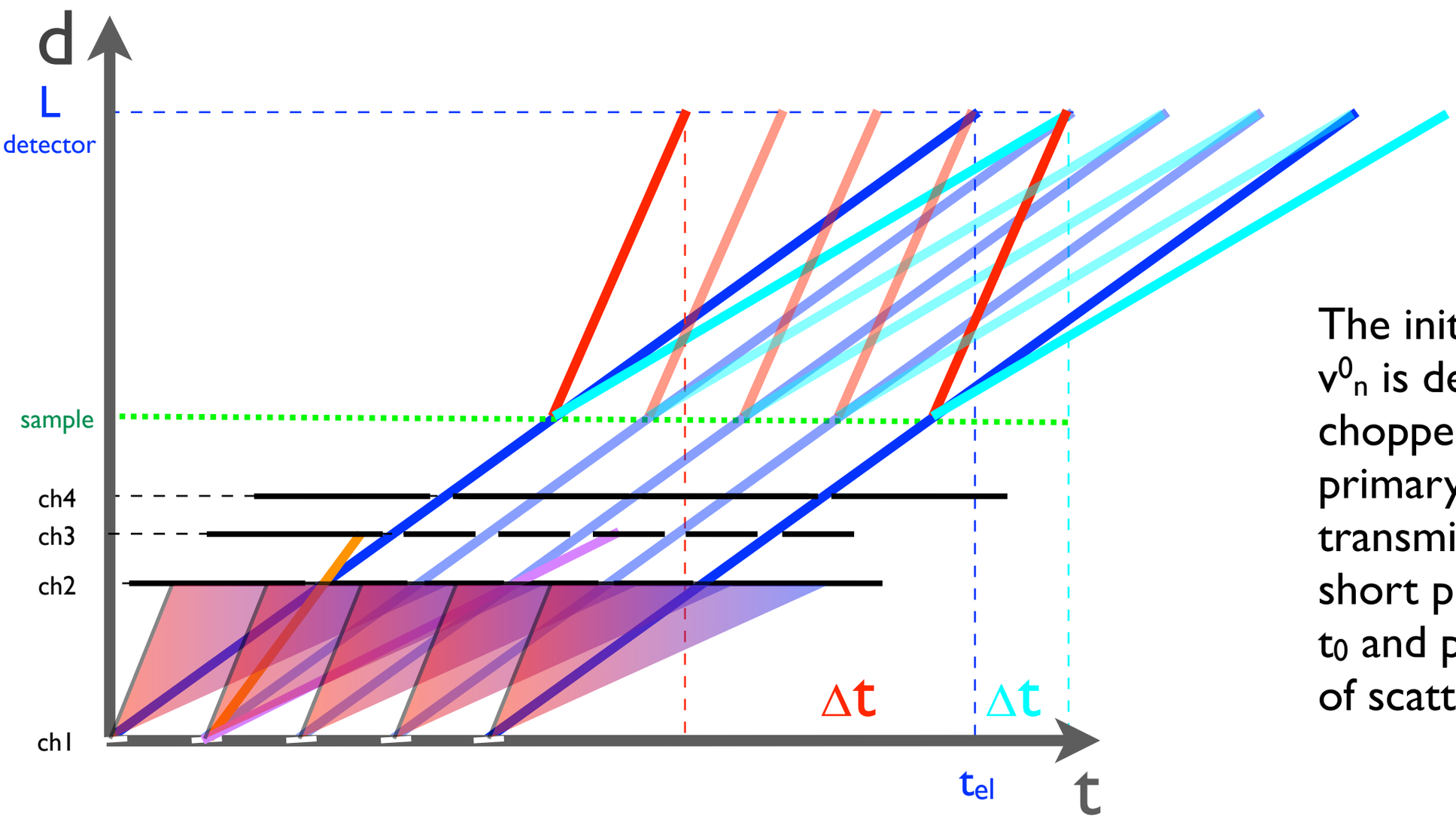


- TOF: we deduce the energy transfer from the flight time t over a distance L: $t = L/v_n$
  - therefore we have to know precisely L and v_n
- we count the neutrons at the detector as a function of their arrival time with respect to elastically scattered neutrons $\Delta t = t - t_{el}$

TOF-spectroscopy

- direct TOF - k_i fixed

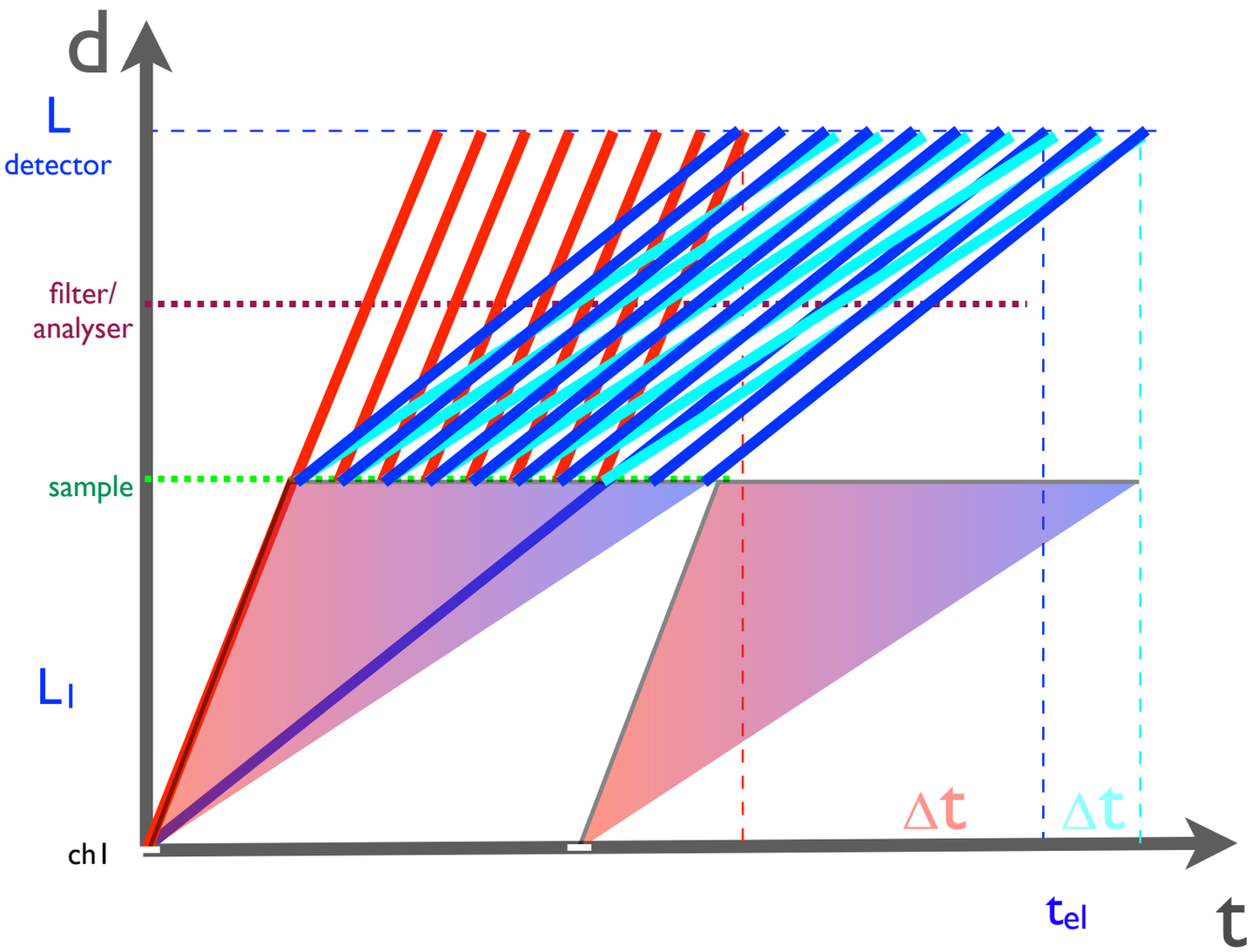
multi-chopper instrument



The initial neutron velocity v^0_n is determined by a multi-chopper system in the primary spectrometer, which transmits monochromatic short pulses with start time t_0 and prevents frame-overlap of scattered neutrons.

TOF-spectroscopy

- inverted TOF - k_f fixed



- neutrons with an initial velocity distribution $p(v^0_n)$ start at time t_0, defined by a pulse chopper. The final neutron velocity is known because a k_f-filter /-analyser allows only monochromatic neutrons to reach the detector.

TOF-resolution

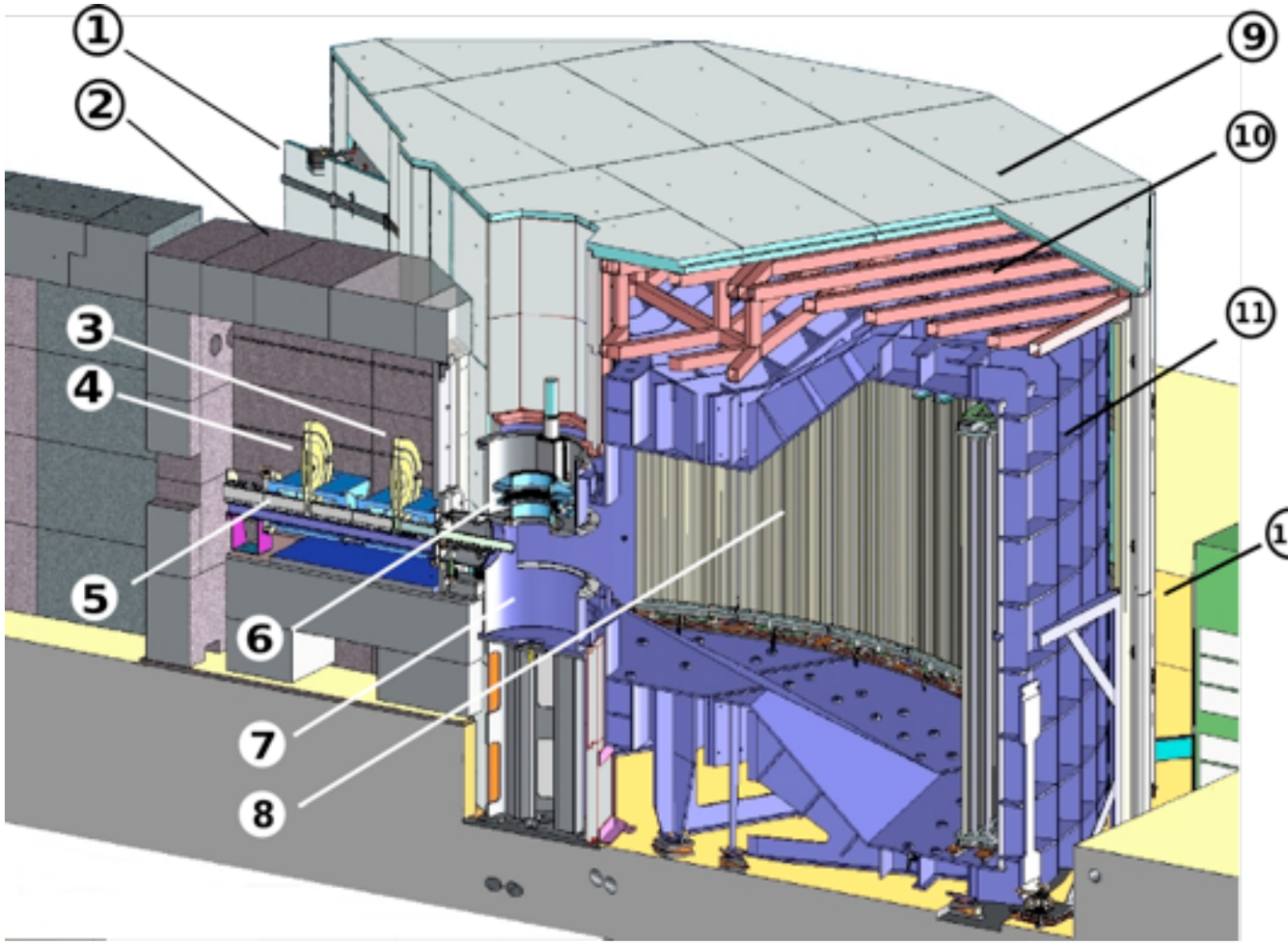
- some comments how to achieve high E-resolution

- precise knowledge of the start time of neutrons implies short pulses: (fast choppers with narrow slits; multi-choppers, counter rotating...)
- the art is to keep flight time uncertainties $\Delta t/t$ small
  - minimise path length in sample & detector, ...
  - choose long total flight path to reduce the relative weight of other unavoidable length uncertainties ($\Delta t/t \sim \Delta L/L$)
  - use long wavelength / slow neutrons - but this will limit the maximum Q ($Q_{elastic}=4\pi/\lambda \sin(\Theta)$)

IN5B - direct geometry TOF

Jacques Olivier

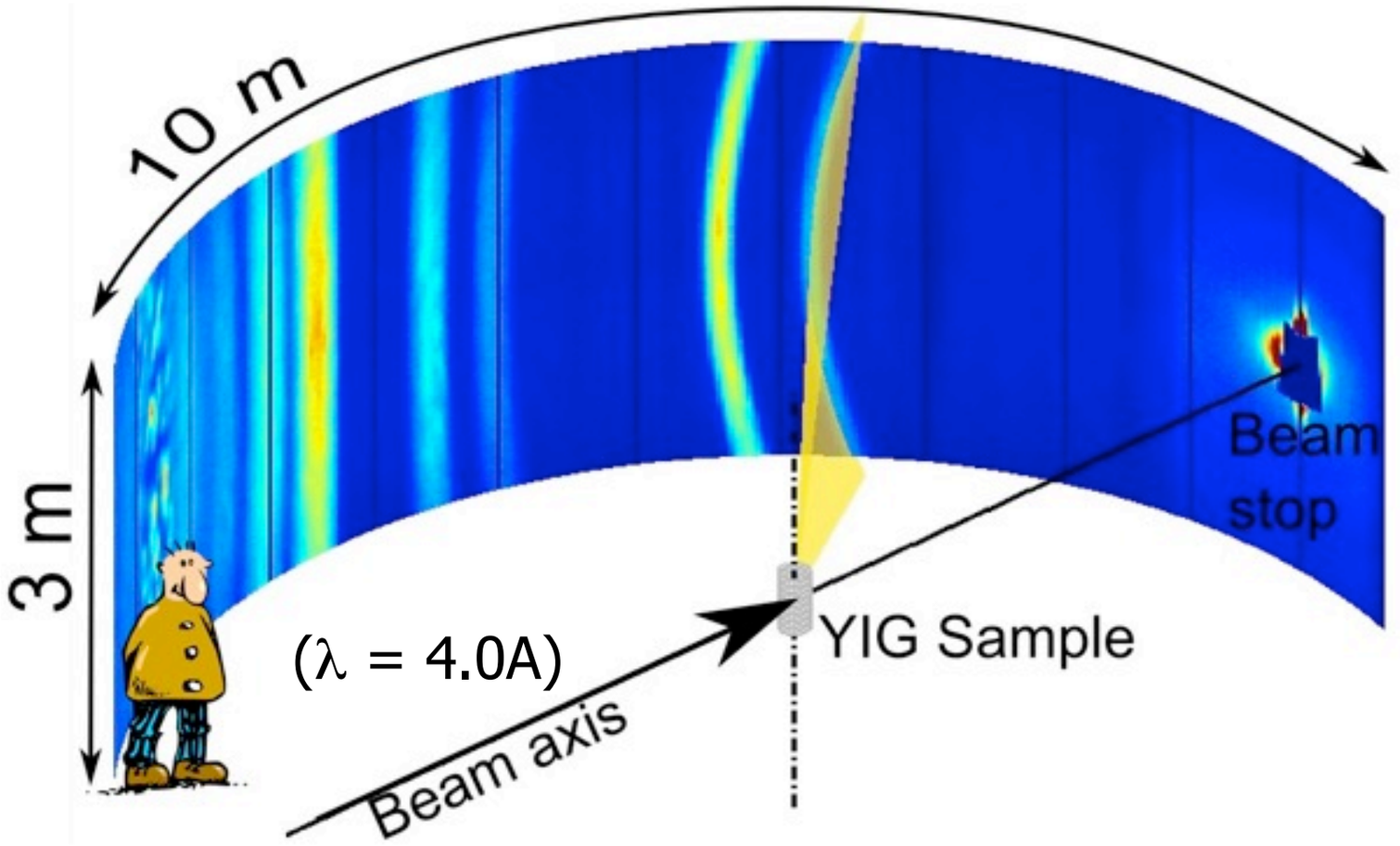
The new IN5 with Position Sensitive Detectors

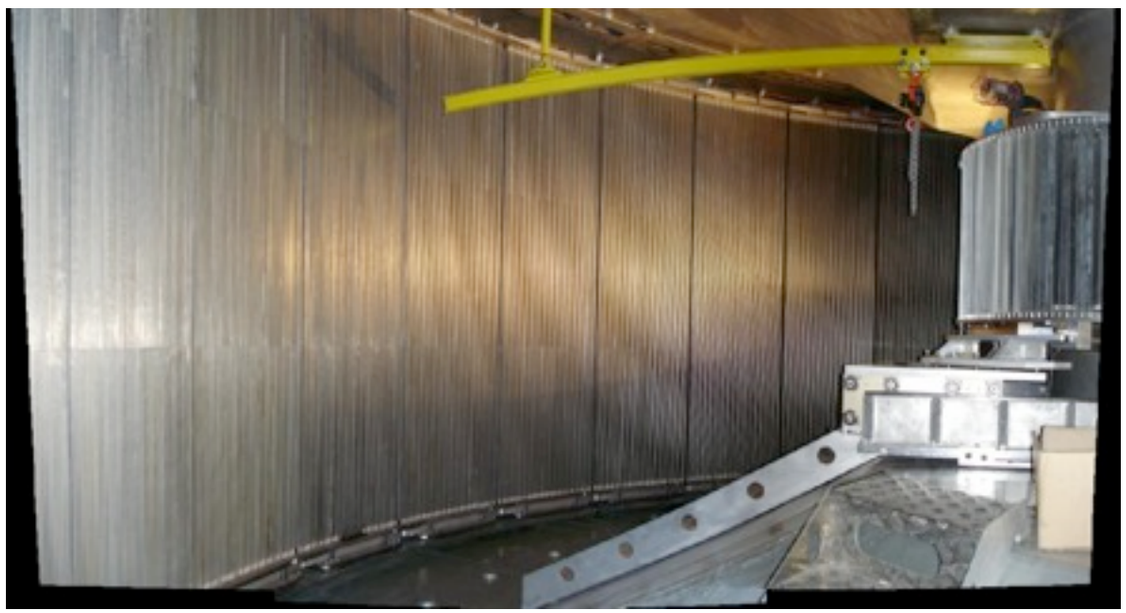


1) Main TOF chamber access gate
2) Radiological shielding
3) Monochromator choppers
4) Frame overlap & anti-contaminant order choppers
5) Focusing guide
6) Sample environment lift system
7) Sample chamber
8) Position sensitive detectors
9) Background shielding
10) Background shielding frame
11) Time-of-flight chamber
12) Instrument recess

IN5B - position sensitive detector array

Jacques Olivier

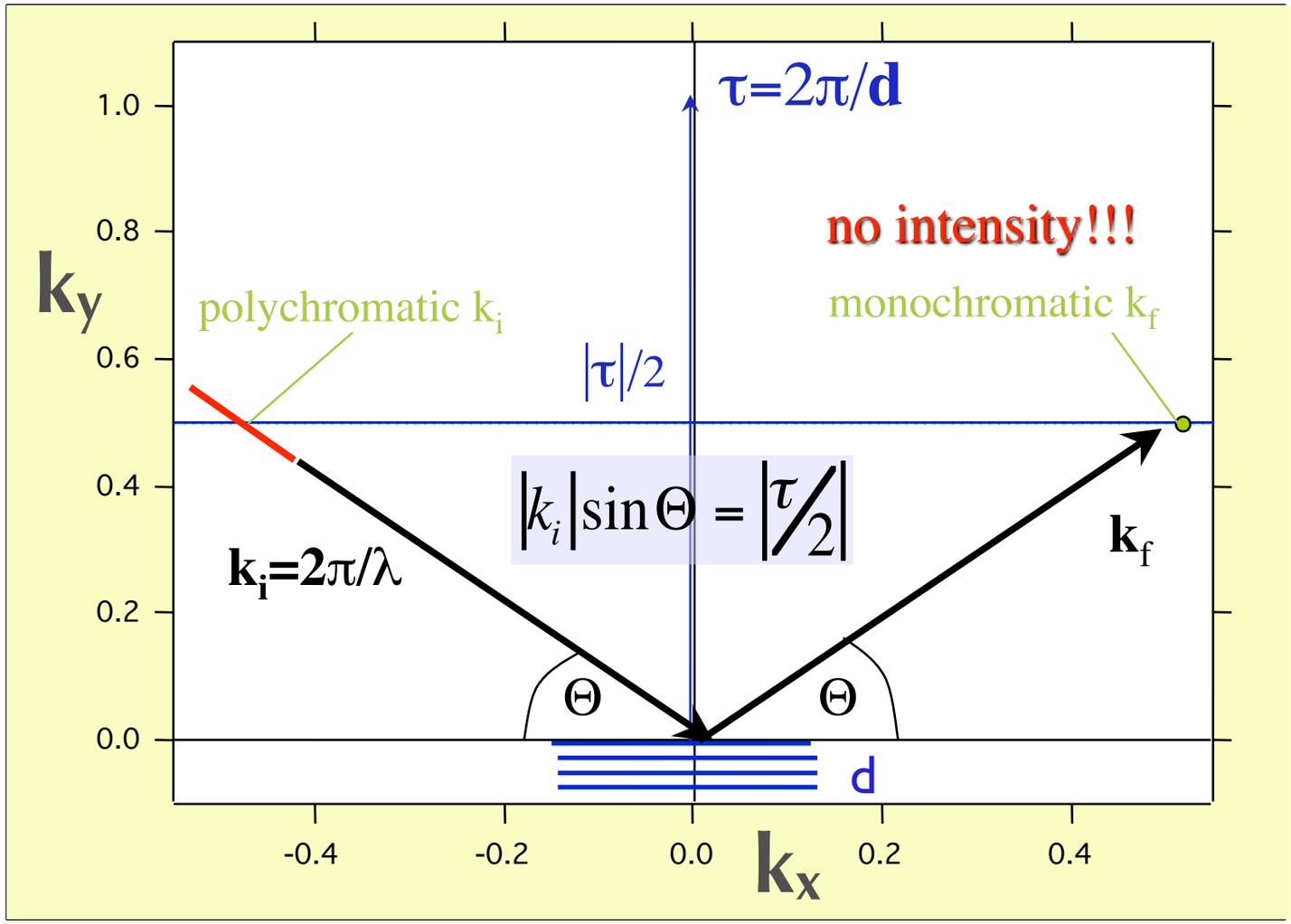




content

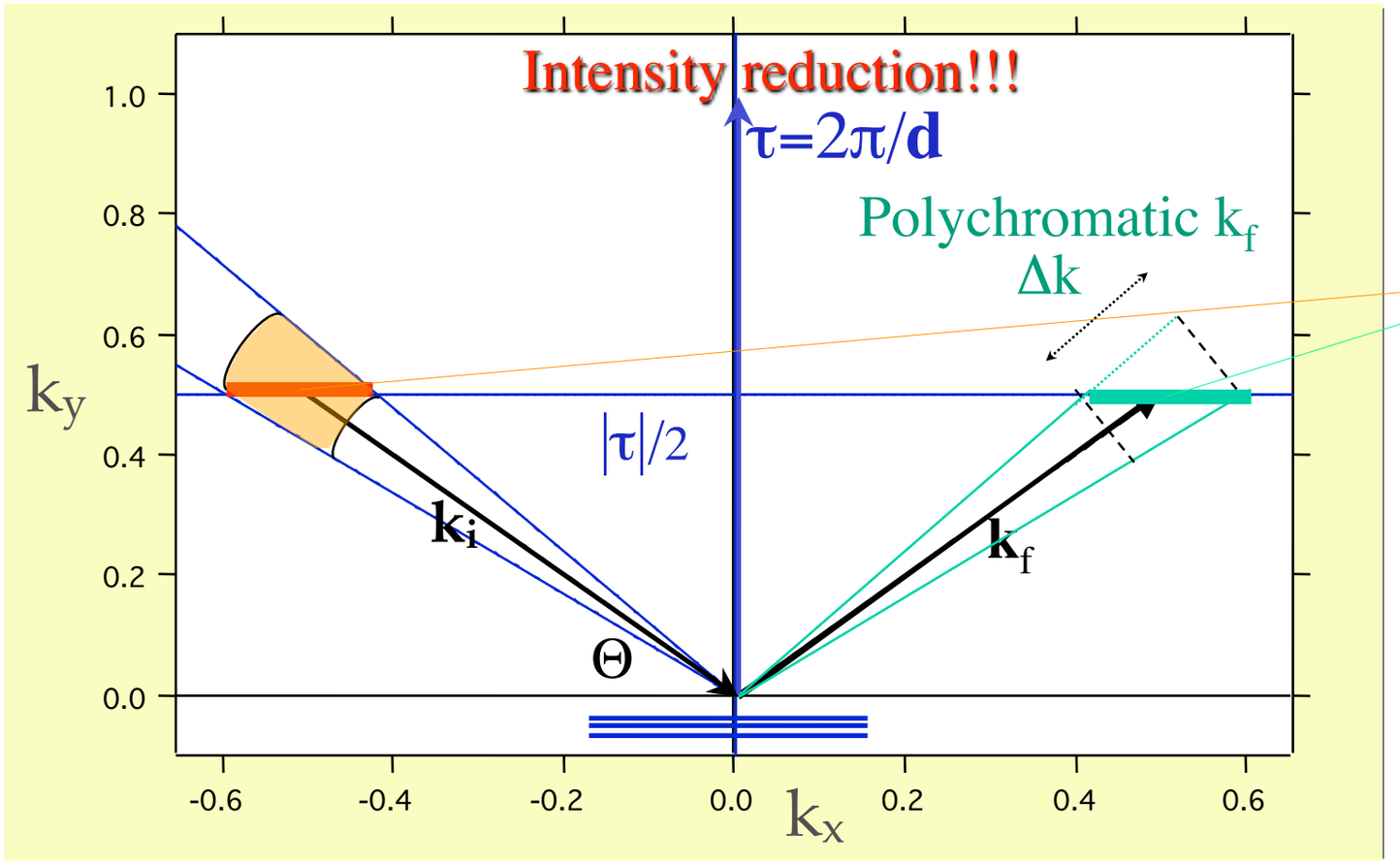
- ☑ why do we need high resolution neutron spectroscopy?
- how to achieve the best energy resolution
  - ☑ in time-of-flight spectroscopy (some comments only > K. Anderson)
  - in crystal spectroscopy
  - in neutron spin echo (C. Pappas)
- examples of applications
  - overview
  - low frequency inelastic examples
    - quantum tunnelling
  - quasielastic examples
    - energy materials, confined molecules, water dynamics

energy resolution from a perfect crystal



reciprocal space representation
***in:* perfectly collimated white beam**
***out:* perfectly monochromatic beam**

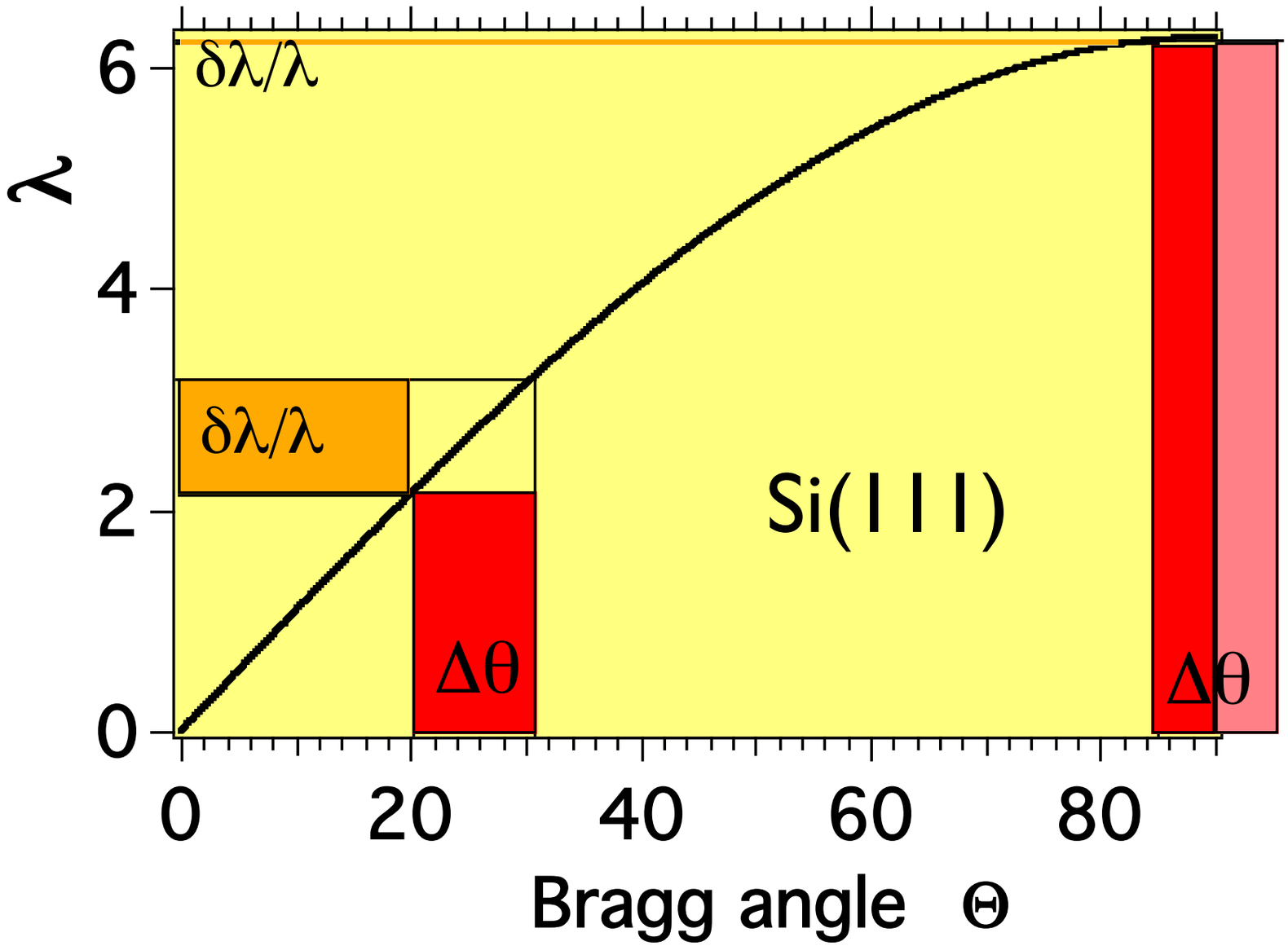
energy resolution from a perfect crystal



- intensity proportional phase space element. Thus the better the energy resolution, the lower the intensity
- energy resolution & divergence are coupled and depend on Θ

reciprocal space representation
***in:* wide collimation and white beam**
***out:* divergent and polychromatic beam**

energy resolution and divergence



Bragg's law:

$$2d \sin\Theta = n\lambda$$

differentiate:

$$2\Delta d \sin\theta + 2d\cos\theta\Delta\theta = \Delta\lambda$$

or:

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta d}{d} + \cot\theta\Delta\theta$$

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta k}{k} = \frac{\Delta E}{2E} \quad and \quad \frac{\Delta d}{d} = \frac{\Delta\tau}{\tau}$$

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta\tau}{\tau} + \frac{\Delta\theta^2}{8} + \frac{\Delta\varepsilon^2}{4}$$

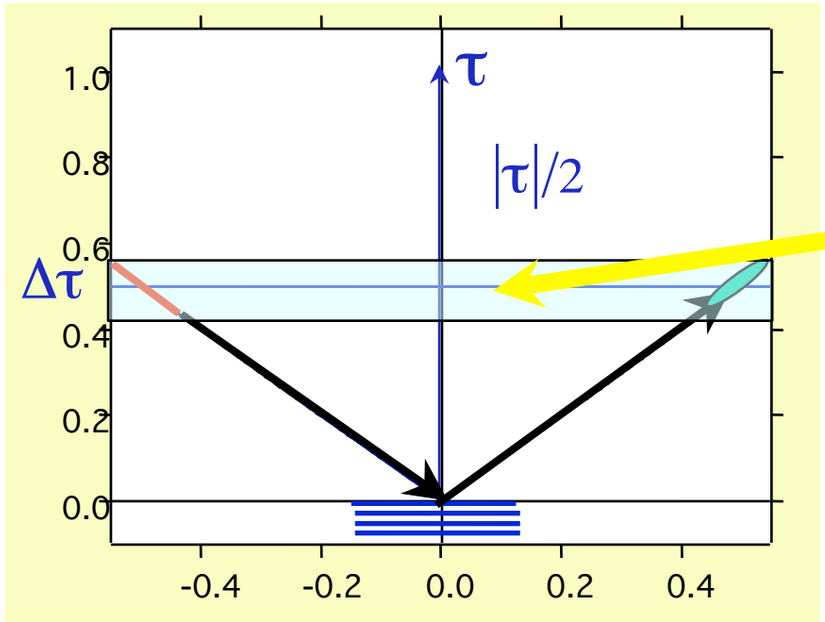
$\varepsilon = deviation\ from\ BS$

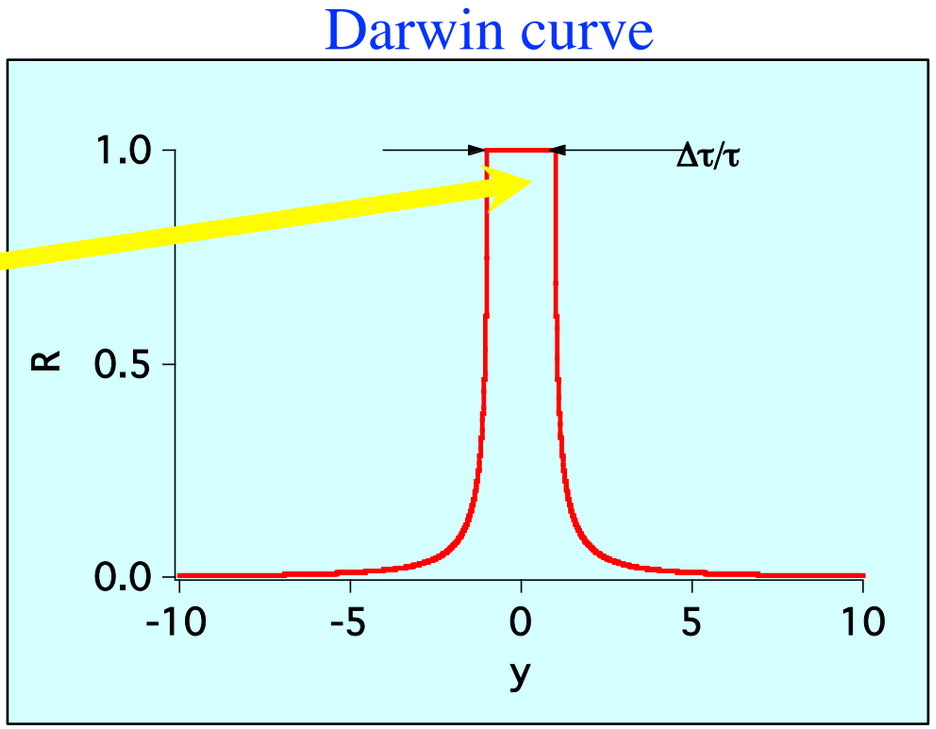
$\Delta\theta = beam\ divergence$

- **use perfect crystal**
- **stay in backscattering**

(at Θ=90° energy resolution and divergence decouple)

reflectivity of perfect crystals in dynamic scattering theory





- **primary extinction:** interaction and coherence effects between incoming and outgoing beam lead to finite resolution

$$R = \begin{cases} 1 & for\ |y| \le 1 \\ \left(|y| - \sqrt{y^2 - 1}\right)^2 & for\ |y| > 1 \end{cases}$$

Δτ is not zero - even for a perfect crystal

how large is the primary extinction of a perfect backscattering crystal?

$$\frac{\Delta\tau}{\tau} = \frac{16\pi F_\tau N}{\tau^2}$$

N=number density of unit cells

F= structure factor

$$F_\tau = \sum_{sites\ i\ in cell} b_{coh}^i \cdot DWF_i \cdot \exp(-i\vec{Q}\vec{R}_i)$$

for neutrons:

$$\Delta E = 2E\frac{\Delta\tau}{\tau}$$

$$\Delta E = 2\frac{\hbar^2\left(\frac{\tau}{2}\right)^2}{2m}\frac{16\pi F_\tau N}{\tau^2} = \frac{\hbar^2}{m}4\pi F_\tau N$$

Typical neutron backscattering monochromators:

crystal plane	$\Delta\tau/\tau$ (10^{-5})	ΔE_{ext} (μeV)	λ(Å) for Θ=90°
Si(111)	1.86	0.077	6.2708
Si(311)	0.51	0.077	3.2748
CaF_2(111)	1.52	0.063	6.307
CaF_2(422)	0.54	0.177	2. 23
GaAs(400)	0.75	0.153	2.8269
GaAs(200)	0.157	0.008	5.6537
Graphite(002)	12	0.44	6.70

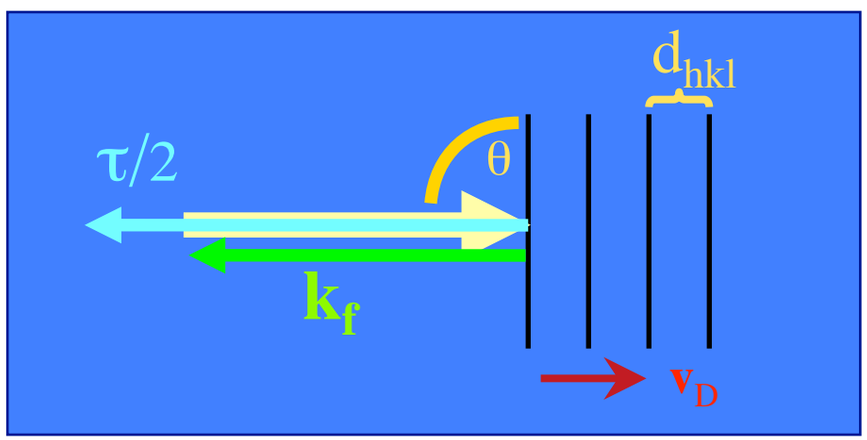
http://www.ill.eu/in16/bs-web-site/

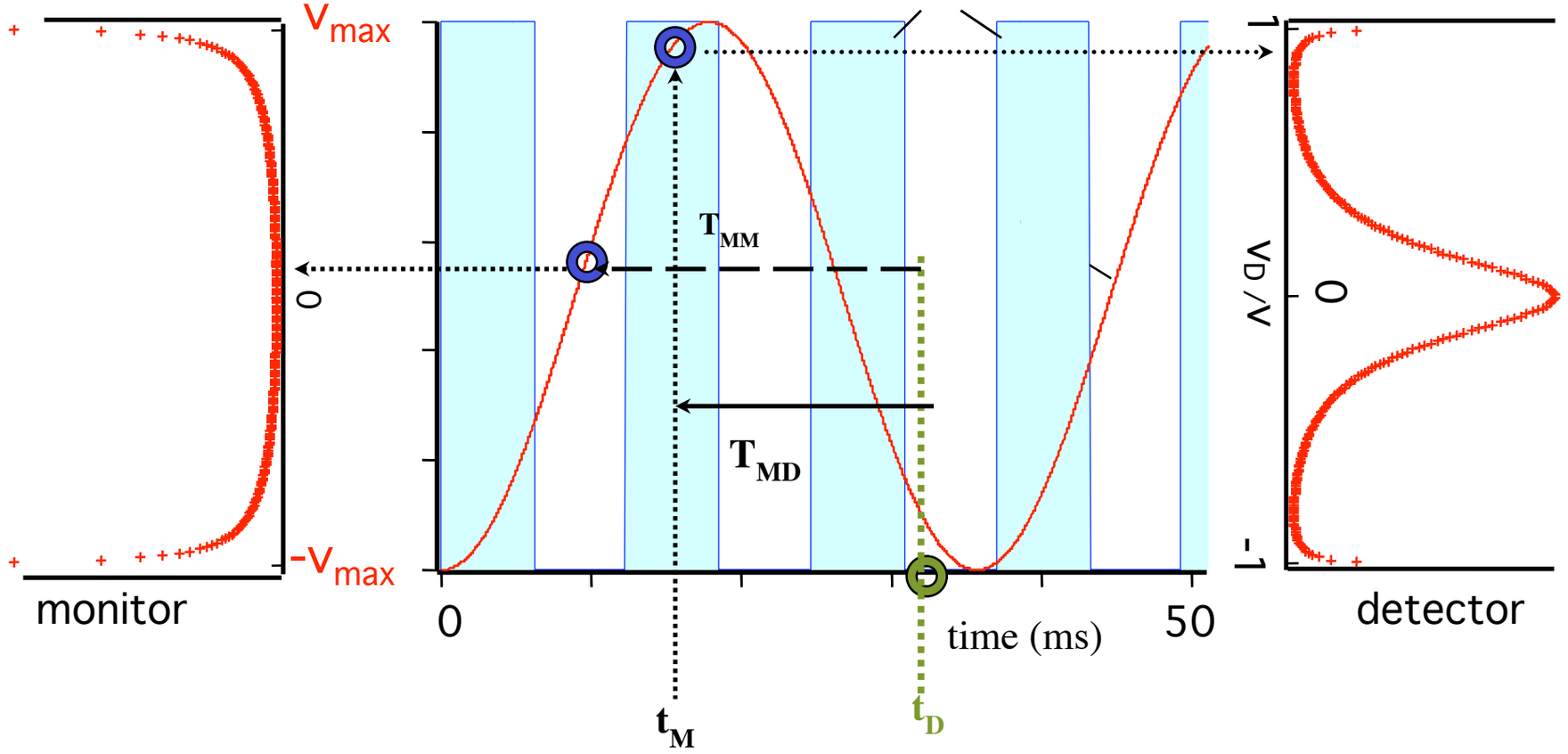
- energy resolution independent of order of reflection (for same F)
  - this is different for X-rays ($\Delta E \sim 1/\tau$)
- extremely small crystal contribution
  - other resolution contributions for TOF or 3X-spectrometers much larger)

how to scan the incident energy and remain in backscattering?

1) Doppler motion of the monochromator:

$$\frac{\delta E_D}{E_i} \approx 2\frac{v_D}{v_i}$$

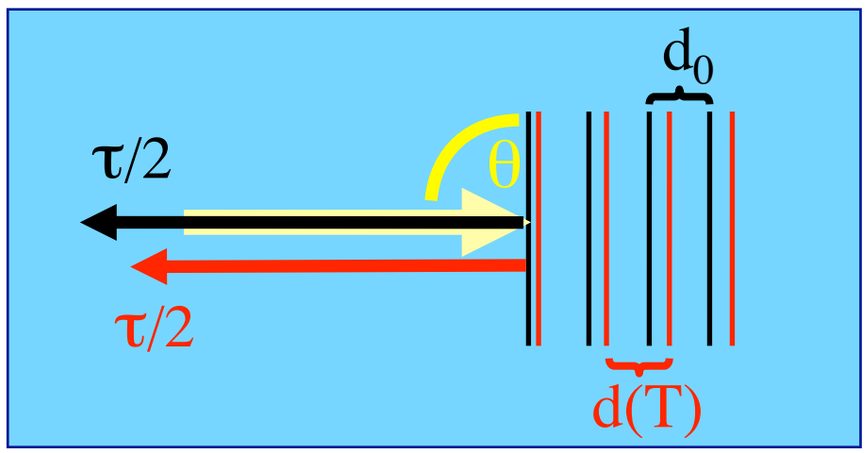


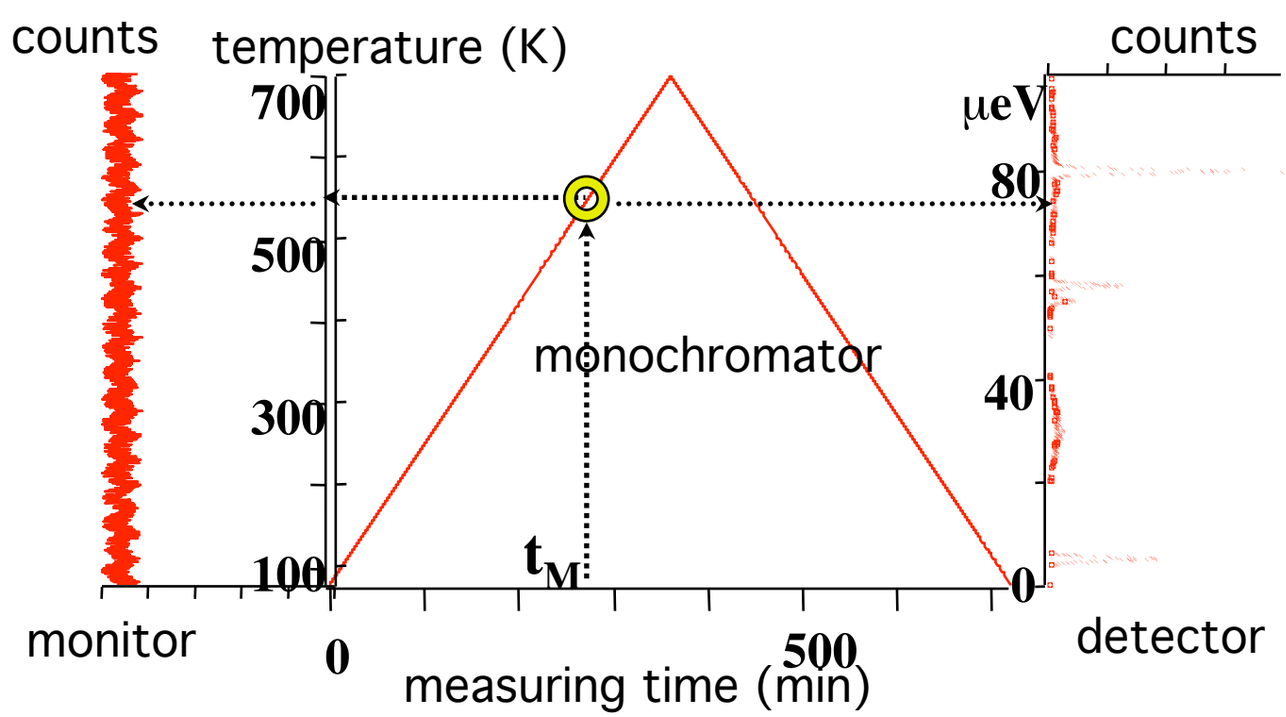


how to scan the incident energy and remain in backscattering?

2) Change of the monochromator temperature = change of lattice distance :

$$d(T) = d_0 (1 + \alpha T + O(2)\ldots). \qquad \frac{\delta E}{E_i} = \frac{\delta d(T)}{d_0}$$

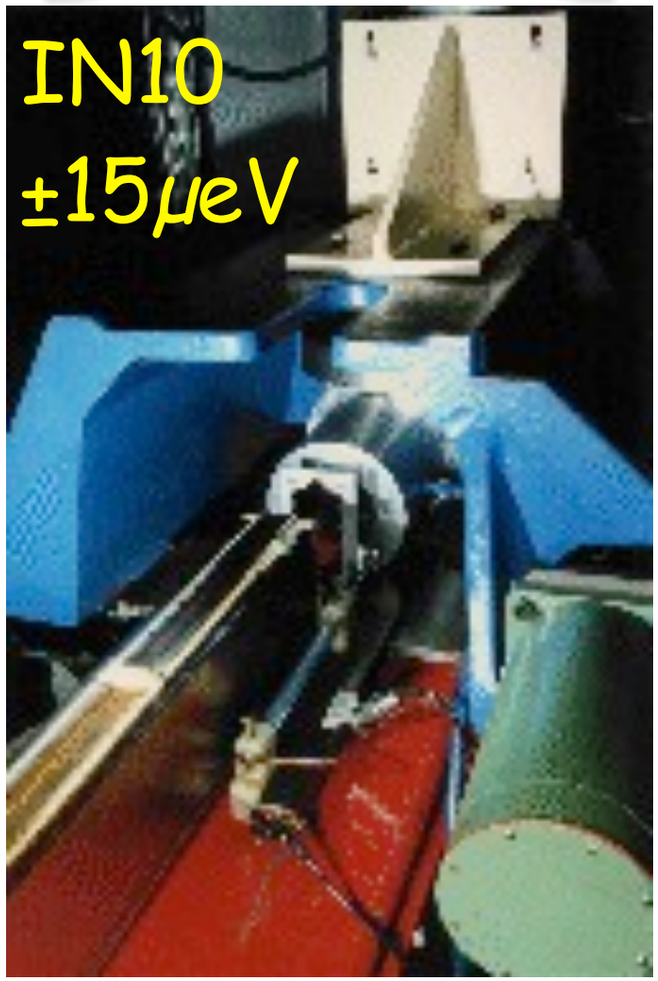




How to change k_i in backscattering

Doppler- and heated monochromators

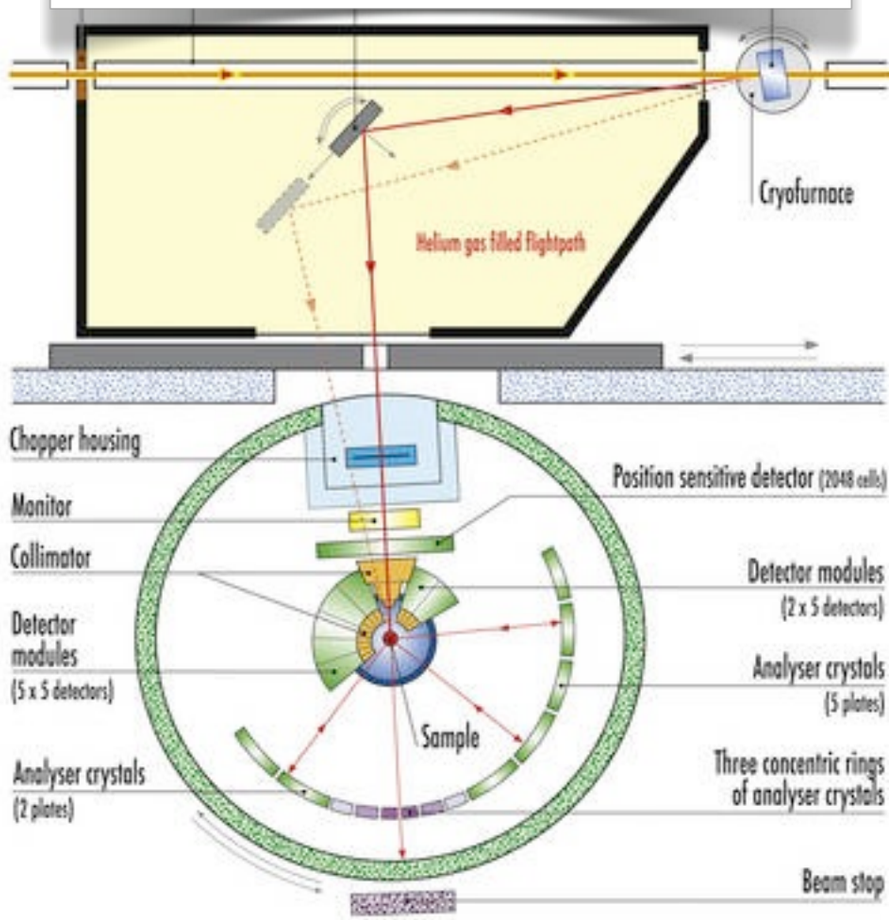
Doppler drives



AEROLAS

linear motor drive

heated monochromator IN13, IN10B



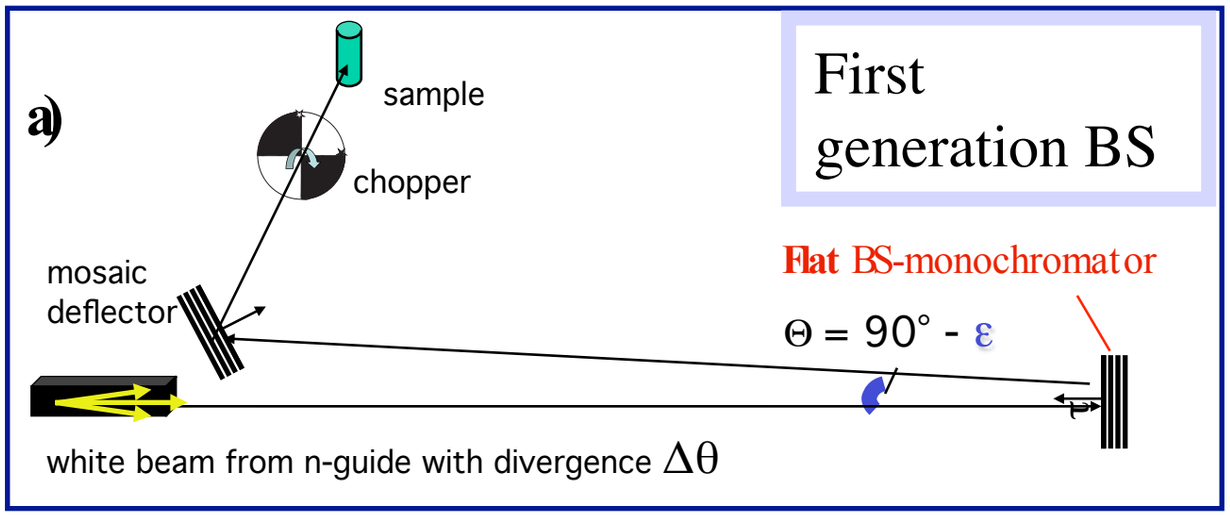
$$d(T) = d_0(1 + \alpha T + O(2)...).$$

α=thermal expansion

$$\frac{\delta E}{E_i} = \frac{\delta d(T)}{d_0}$$

reactor backscattering instruments

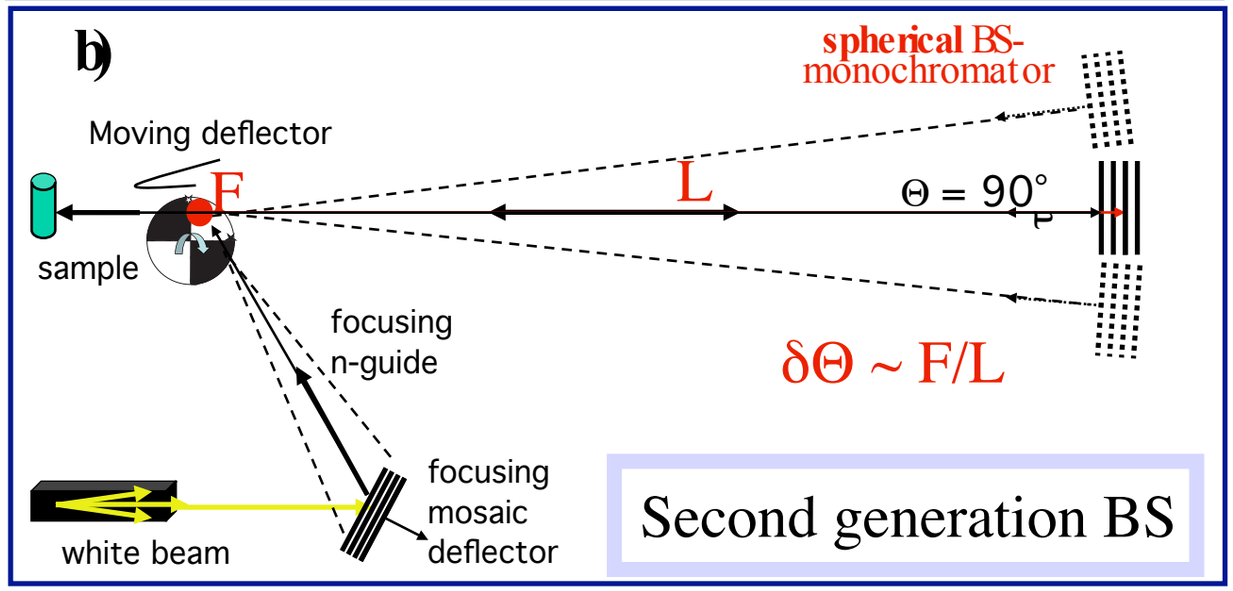
- generic primary spectrometer concepts



example
IN10:
$\varepsilon = 0.3°$
$\Delta\theta = 1.2°$

$\Delta E_{div} \sim 0.24\mu eV$
$\Delta E_{ext} \sim 0.08\mu eV$

divergence and extinction not matched,
But divergence and deviation from BS



IN16:
F~2.7cm
L=200cm

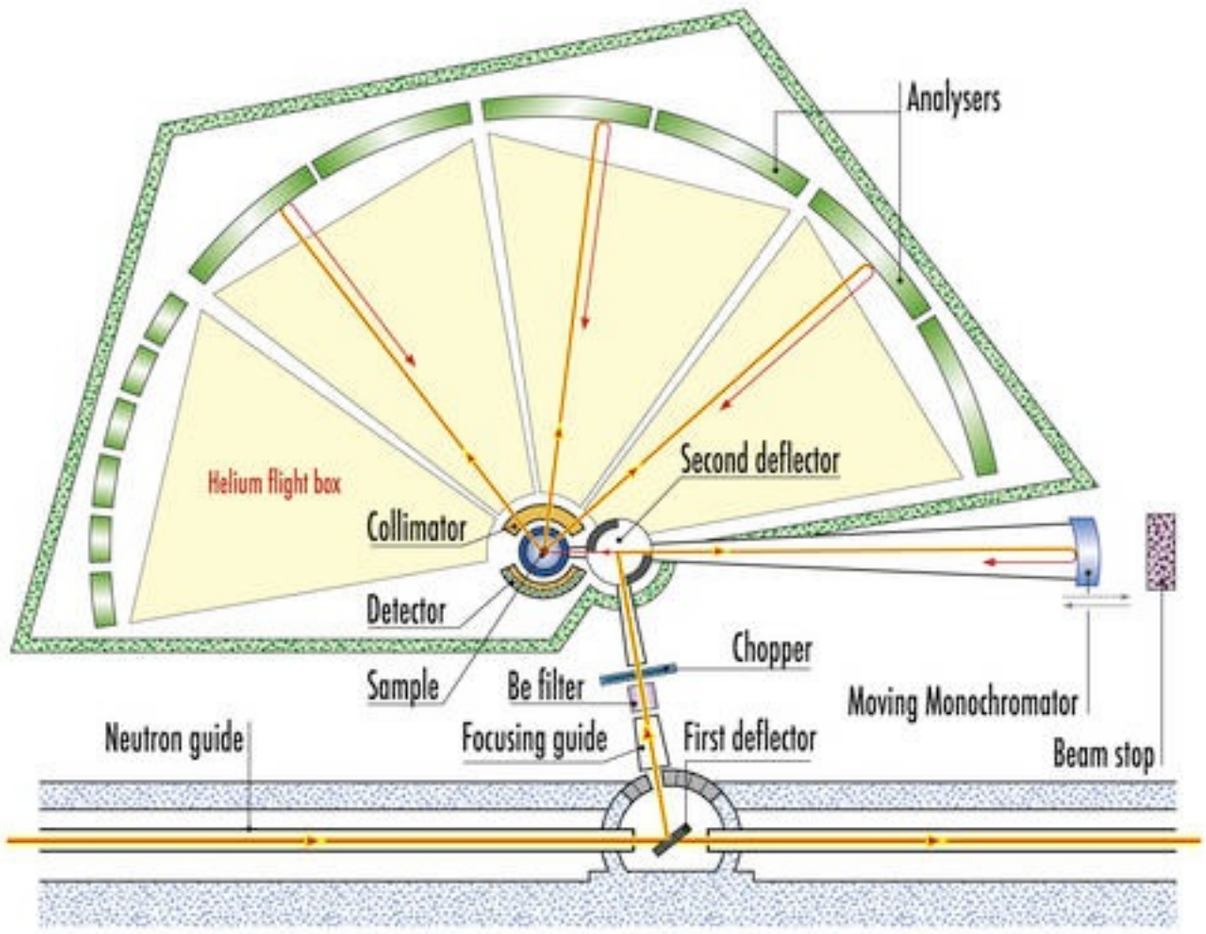
$\Delta E_{div} \sim 0.09\mu eV$
$\Delta E_{ext} \sim 0.08\mu eV$

resolution terms matched

backscattering instruments

- secondary spectrometers
are similar on reactors and spallation sources

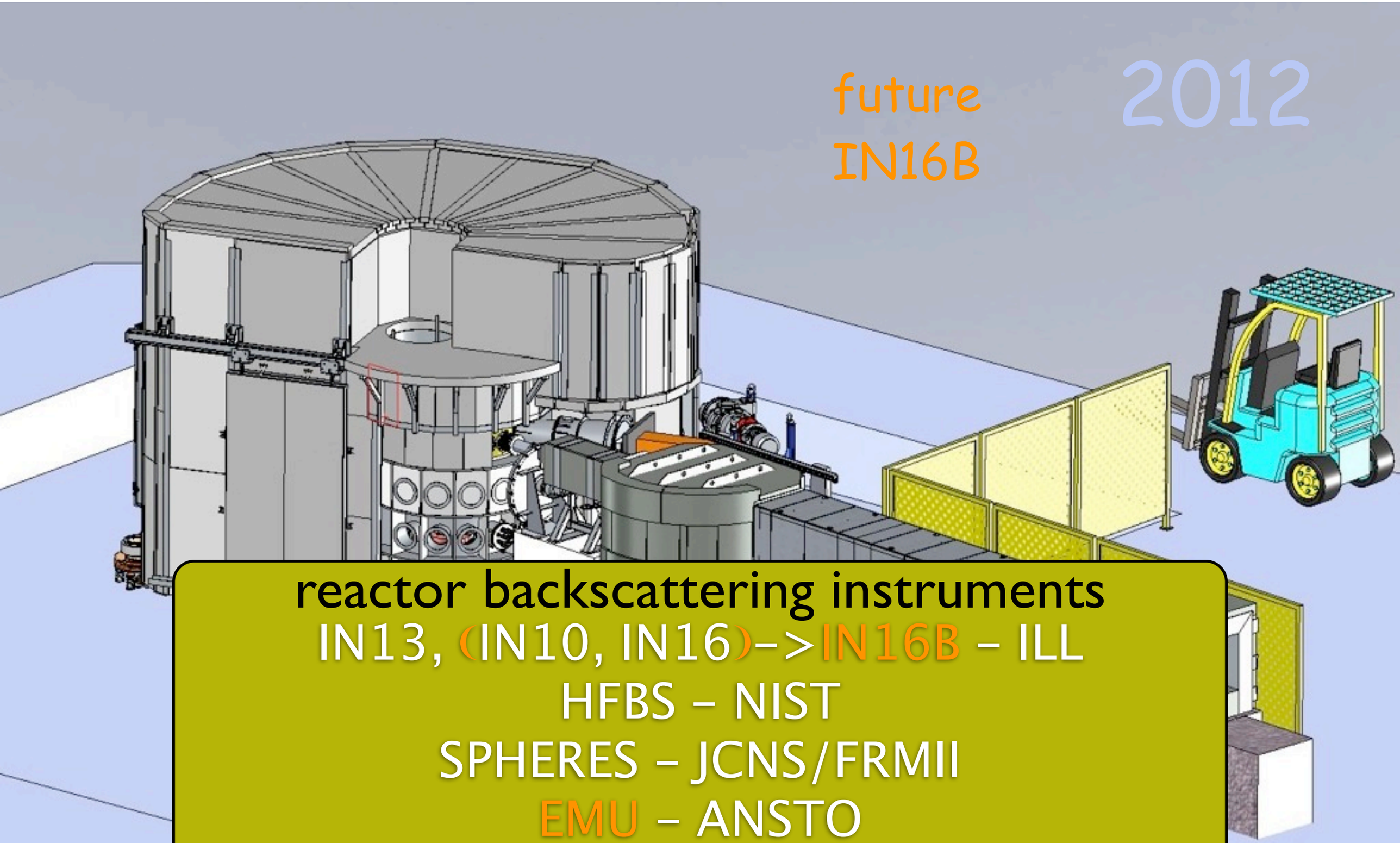
- k_i scanned (v_D or T_M)
- k_f fixed (static and T_A=T_M)
- gate detector to avoid counting neutrons scattered directly into the detector (several orders of magnitude stronger signal) -> introduce a 50%-chopper and count at arrival time of analyzed neutrons



http://www.ill.eu/in16/

IN16 - cold neutron backscattering instrument at ILL

backscattering spectrometers



reactor backscattering instruments

IN13, (IN10, IN16)->IN16B – ILL

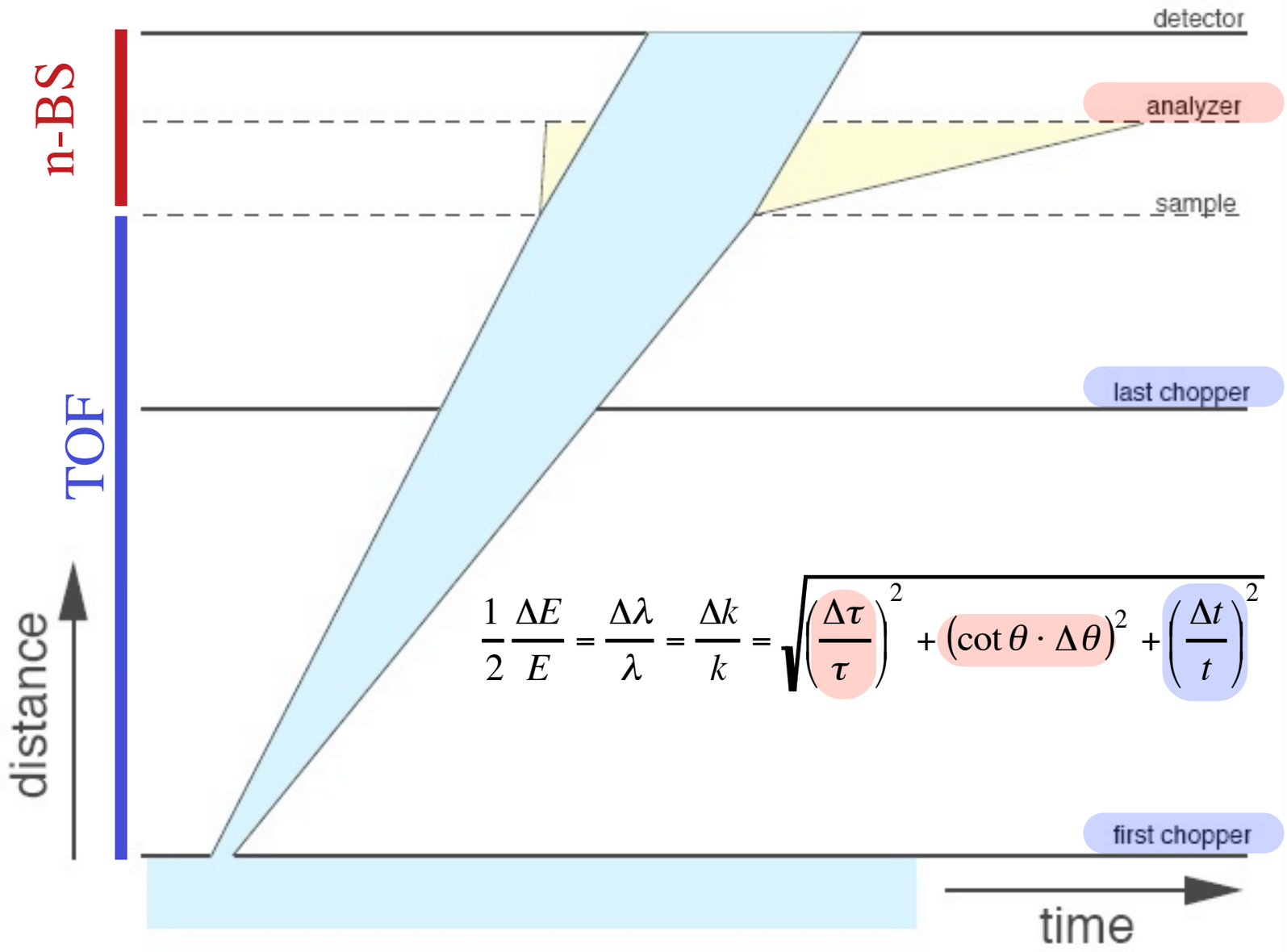
HFBS – NIST

SPHERES – JCNS/FRMII

EMU – ANSTO

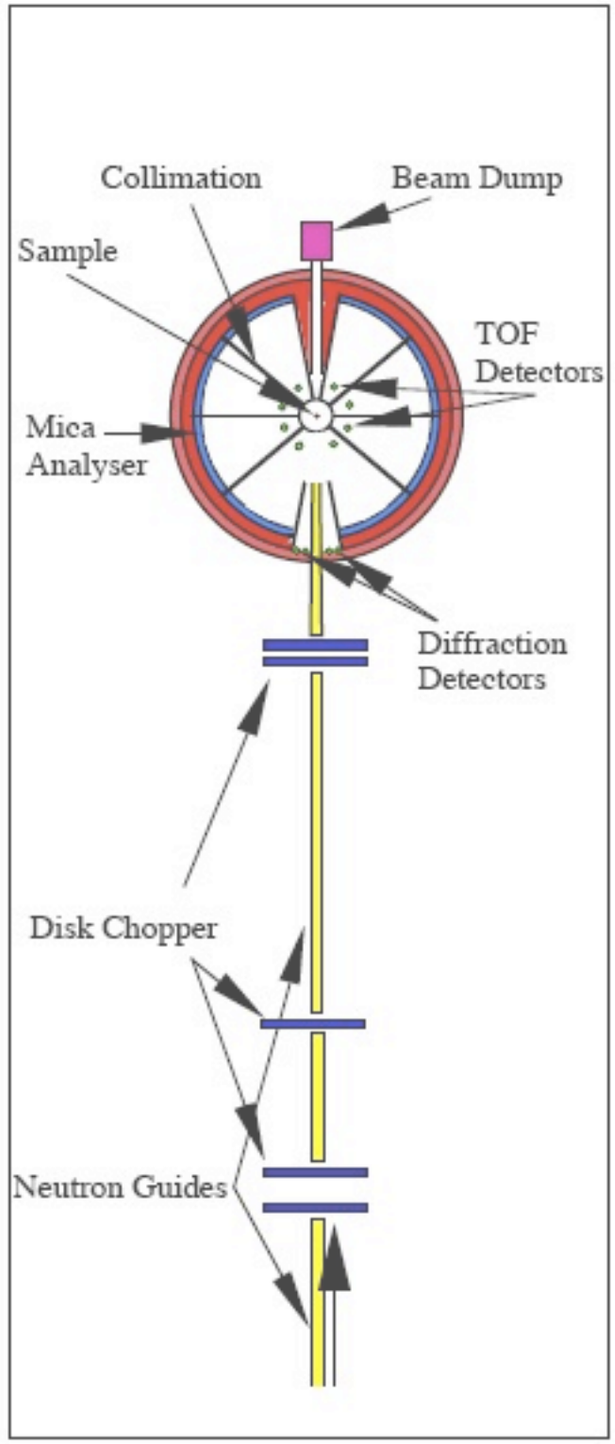
Backscattering spectrometers at spallation sources

combine TOF and backscattering



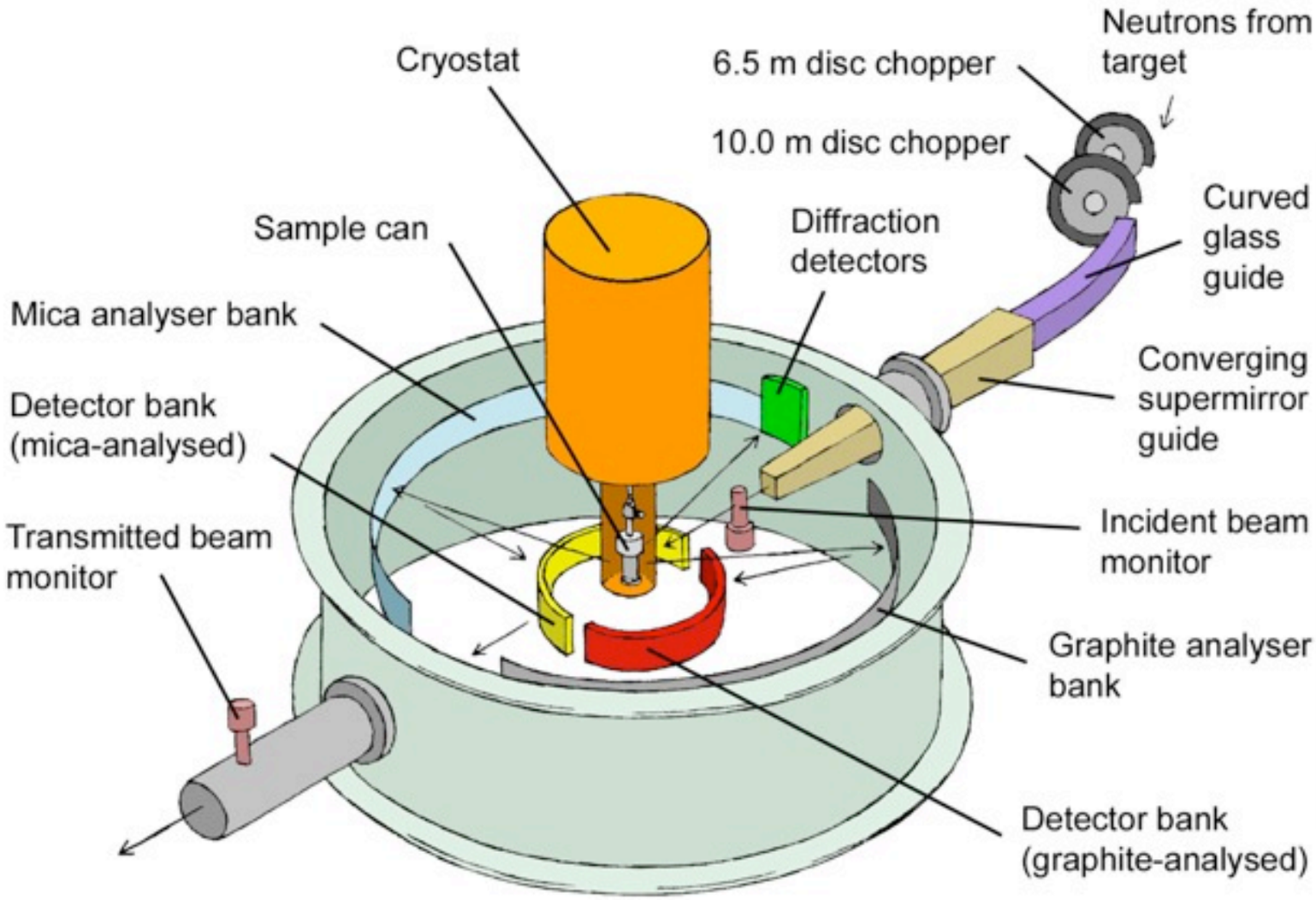
$$\frac{1}{2}\frac{\Delta E}{E} = \frac{\Delta\lambda}{\lambda} = \frac{\Delta k}{k} = \sqrt{\left(\frac{\Delta\tau}{\tau}\right)^2 + \left(\cot\theta\cdot\Delta\theta\right)^2 + \left(\frac{\Delta t}{t}\right)^2}$$

from Allenspach, PSI; modified BF



examples: IRIS-IRIS, MARS-PSI, BASIS-SNS, DNS-JPARC

IRIS at ISIS,RAL,GB
the "mother" of spallation source backscattering

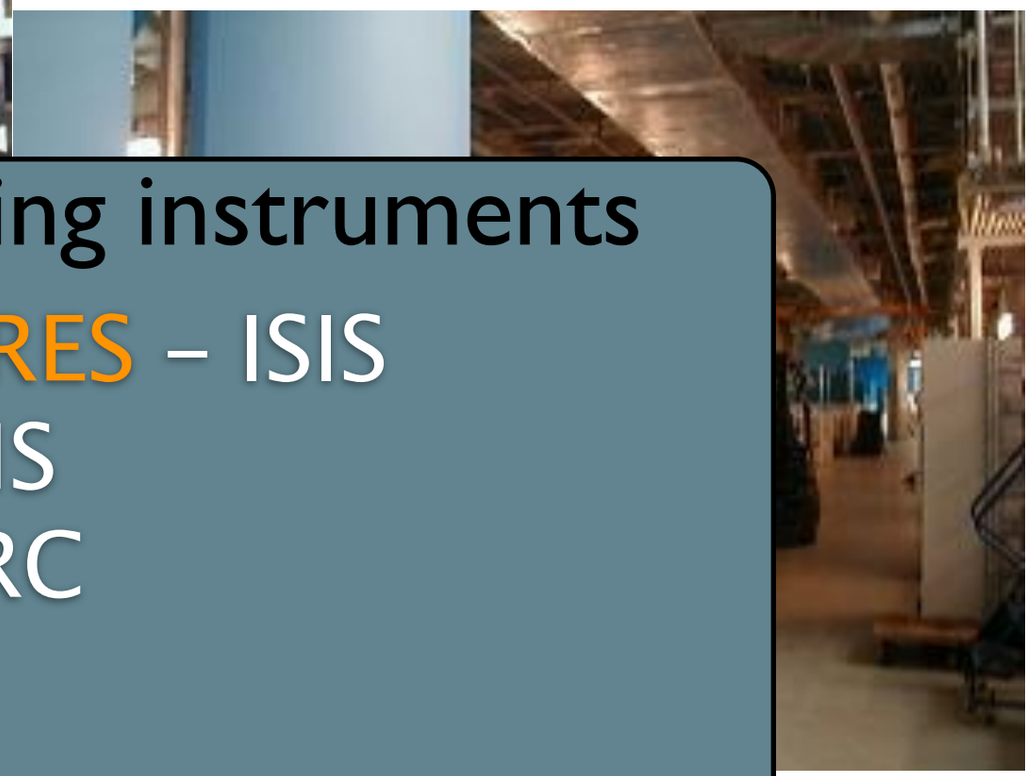


Technical Specifications

	PG (002)	PG (004)	Mica (002)	Mica (004)	Mica (006)
Analysing energy (meV)	1.84	7.38	0.207	0.826	1.86
Dynamic range (meV)	-0.4 to +0.4	-3.5 to +4.0	0.02 to +0.02	-0.15 to +0.15	-0.4 to +0.4
Resolution μeV	17.5	54.5	1.0	4.5	11.0
Scattering angle (deg)	20 - 160	20 - 160	25 - 155	25 - 155	25 - 155
Q range ($Å^{-1}$)	0.3 - 1.8	0.5 - 3.7	0.1 - 0.6	0.2 - 1.2	0.3 - 1.8
Spectroscopy detectors	51 ZnS scintillators				
Diffraction detectors	8 He^3 tubes at $2\theta \approx 170°$; $\Delta d/d = 2.5 \times 10^{-3}$; d-range (Å) = 1 - 12				

http://www.isis.rl.ac.uk/molecularspectroscopy/iris/

BASIS-SNS backscattering spectrometer: the youngest



Moderator

Beam line
Source-sample
Sample-analyzer cr
Analyzer crystal-det

decoupled poisoned
supercritical hydrogen

Elastic energy
Band width
Resolution (elas
Q-range (elastic
Solid angle

spallation backscattering instruments

OSIRIS, (IRIS)–>FIRES – ISIS

BASIS – SNS

DNA – JPARC

content

- ☑ why do we need high resolution neutron spectroscopy?
- ☑ how to achieve the best energy resolution
  - ☑ in time-of-flight spectroscopy (some comments only > K. Anderson)
  - ☑ in crystal spectroscopy
  - in neutron spin echo (C. Pappas)

examples of applications

- overview
- low frequency inelastic examples
  - quantum tunnelling
- quasielastic examples
  - energy materials, confined molecules, water dynamics

scientific fields for high resolution spectroscopy

- low frequency inelastic spectroscopy
  - tunneling spectroscopy (CH3, NH4, ...)
  - hyperfine interaction
  - low frequency vibrations: aerogels & fractons
  - ^{4}He excitation spectrum (roton)
  - magnetic excitations (i.e. molecular magnets)

scientific fields for high resolution spectroscopy

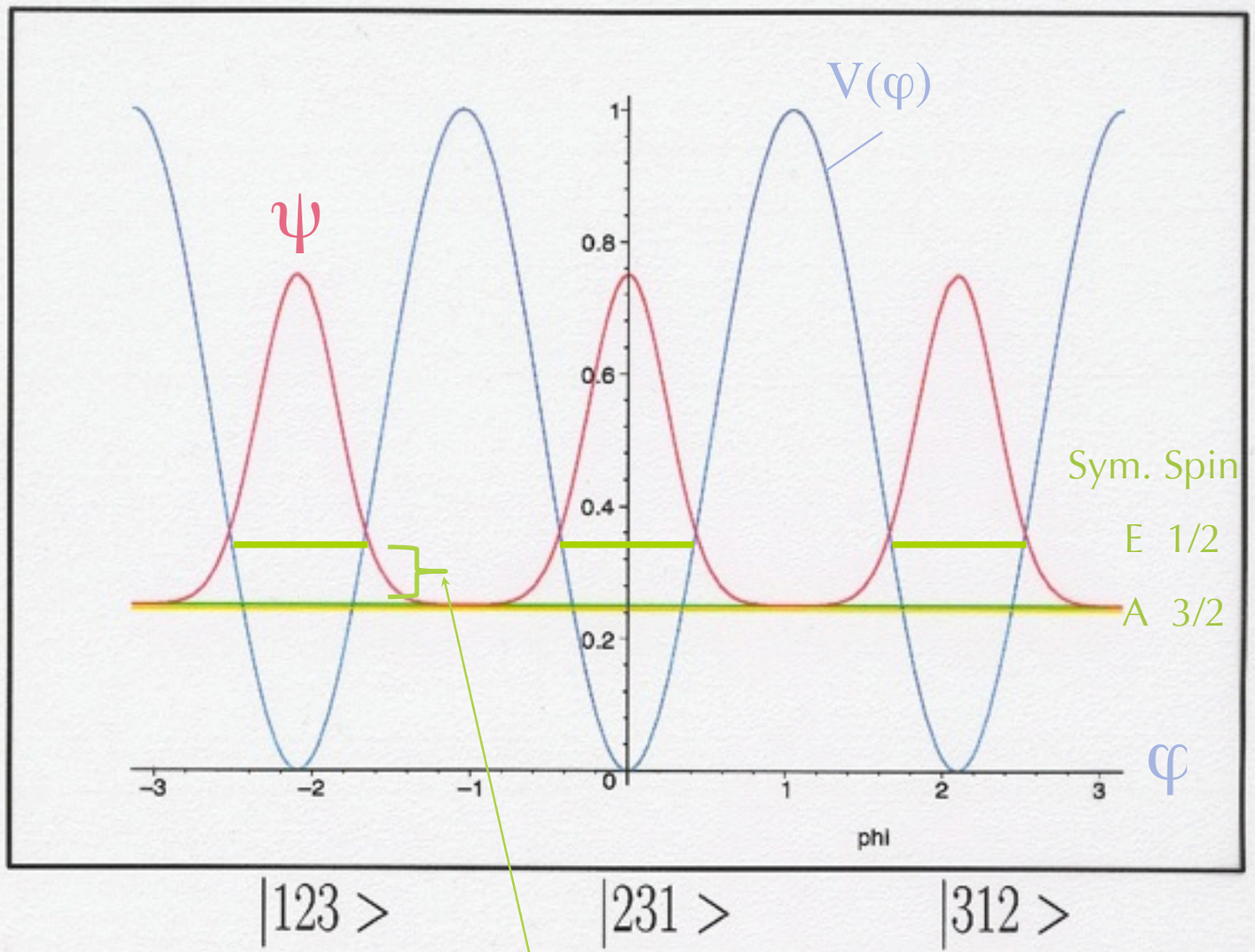
- quasielastic
  - Diffusion and self-diffusion in metals, alloys, intercalation compounds
  - Diffusion of hydrogen
    - in metals or alloys (e.g. for H-storage materials)
    - fuel cells (understanding of basic transport in membranes)
    - materials for fuel cell electrodes
  - Diffusion of molecules in catalytic materials
  - Dynamics in polymers
    - local motions of main chain and side chains
    - polyelectrolytes
    - dendrimers
    - changes of dynamics under stretching (orientation dependent studies)
    - effect of fillers in polymers (carbon black, silica, C_{60},..)
    - thin polymer films
    - polymer blends
    - nanocomposites

- quasielastic spectroscopy (cont.)
  - more soft matter
    - microemulsion freezing phenomena
  - Dynamics of biological or bio-related molecules
    - dynamical transition (glass like transition?)
    - relation between local mobility and function / stability
    - role of water in bio-materials: hydration water / confined water
    - biological membranes
    - natural materials (spider silk, ...)
  - pharmaceutical systems
    - potential drug delivery systems
    - functional molecules
    - relation of local mobility to storage and stability
  - Dynamics near the glass transition and in undercooled liquids
    - mode coupling theory
    - P, T dependence of local dynamics near Tg
    - supercooled water, strong-to-fragile transition
  - Dynamics of orientational glasses
  - Atomic and molecular motion on surfaces

- quasielastic spectroscopy (cont.)
  - Dynamics in confinement (nano-confinement in porous materials, nanotubes,...)
    - small molecules in confinement (clathrates,...)
    - water, aqueous ionic solutions, mixtures in confinement
    - water in geological materials, concrete, clays
    - surface water
    - glass forming liquids in confinement
    - liquid crystals in confinement
  - Dynamics of liquids
    - highly viscous liquids (oils,..)
    - ionic liquids, ionomers
    - liquids under shear
  - Dynamics of liquid crystals
  - Dynamics of hydrogen bonds
  - Rotations of large or hindered molecules
  - Dynamics of the phase transition, critical scattering
  - Magnetism
    - spin glasses and frustrated magnets
    - spin ice

rotational tunnelling

Single particle model: environment=potential $V(\varphi)$



Extreme sensitivity: $\hbar\omega_t \sim e^{-\alpha V(\varphi)}$

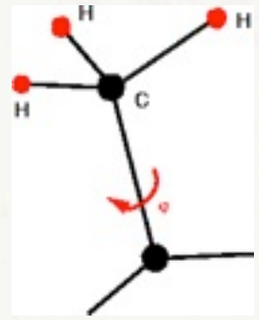
Courtsey: M. Prager

Rotational Tunneling and Neutron Spectroscopy: A Compilation

M. Prager
Institut für Festkörperforschung des Forschungszentrums Jülich, D-52425 Jülich, FRG

A. Heidemann
Institut Laue-Langevin, B.P. 156, F-38042 Grenoble, France

1d rotor: e.g. **CH_3**
1 tunnel transition
doublet ground-state (A,E)



3d rotors: e.g. **CH_4, NH_4**
more complex tunneling spectra
5 sub-states (A,3T,E)

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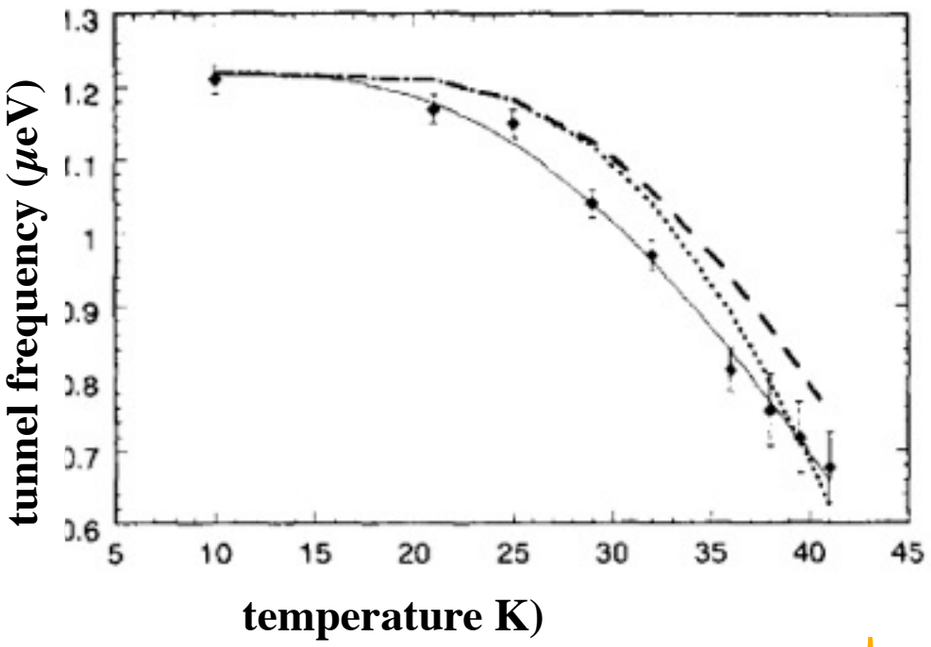
Volume 97, Number 8, Pages 2933–2966

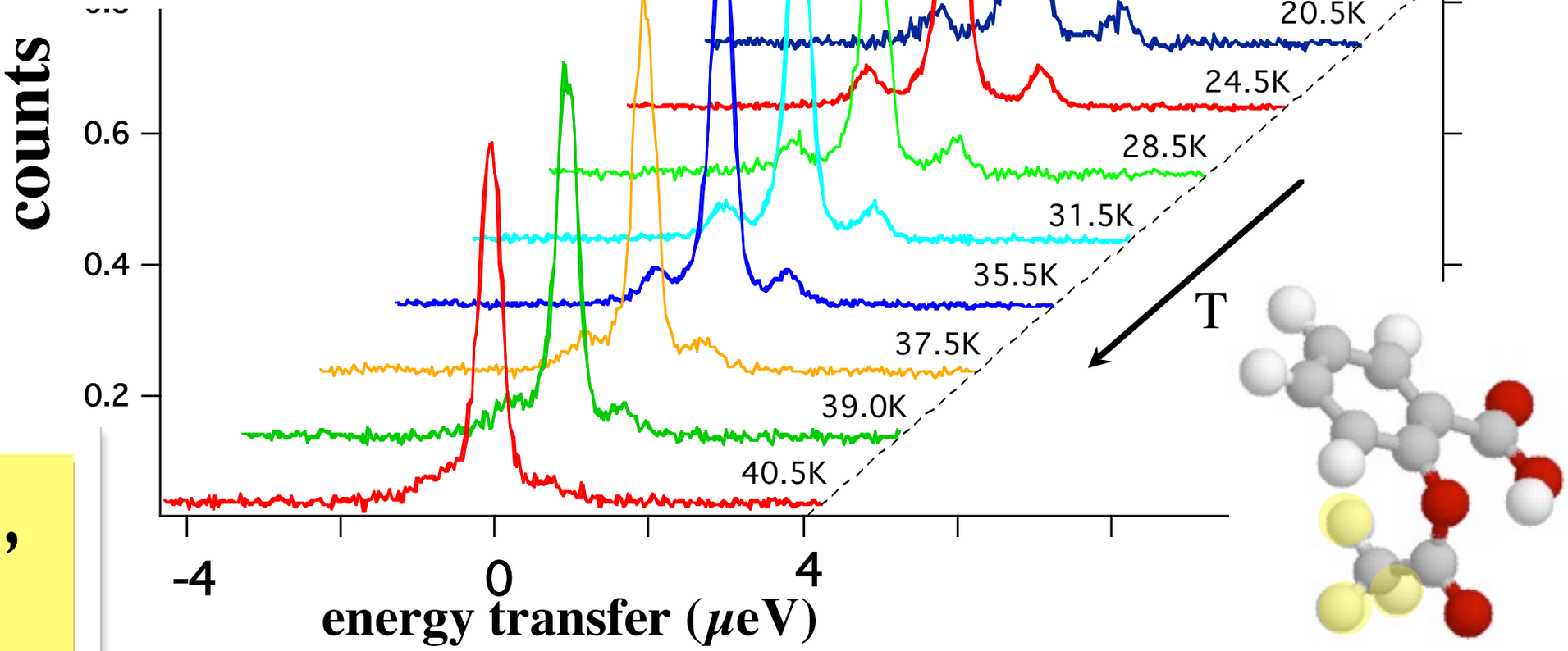
methyl group tunneling

- example for high energy resolution on IN16 (FWHM~0.3μeV)



aspirin

acetyl salicylic acid



IN16, ILL

back

M. Johnson, B. Frick, and H.P. Trommsdorff, Chemical Physics Letters **258**, 187 (1996).

a motivation example
e.g. **hydrogen economy**

important fundamental science questions to solve:

- sustainable hydrogen production

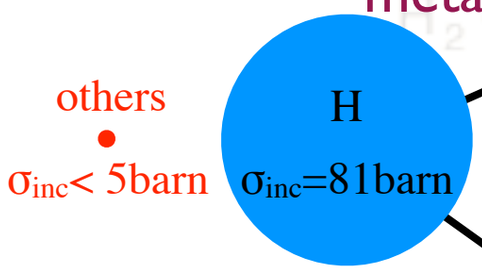
dynamics of new materials

- new hydrogen storage materials

aim storage: >9% by weight; reversible absorption

metal hydrates ($LaNi_5$,Mg_2Ni,MgH_2); BH_3NH_3, $LiBH_4$, $Mg(BH_4)_2$, $Ca(BH_4)_2$

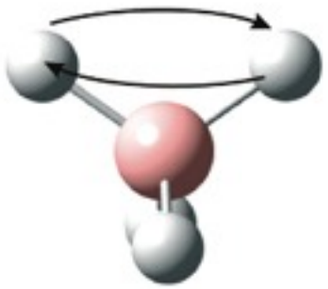
understand diffusion



- more efficient fuel cells

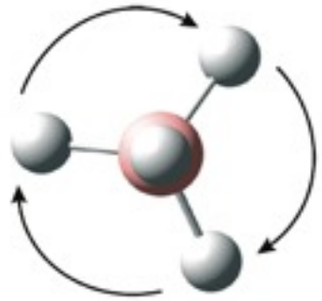
better Proton Exchange Membranes (H, methanol, formic acid, phosphoric acid)

understand diffusion of H or H-containing chem.units



Light Weight Hydrogen Storage Materials

- e.g.: TOF and Backscattering on Alkaline-TetraHydroBorates



Verdal et al. Reorientational Dynamics of NaBH4 and KBH4. J. Phys. Chem. C , 114 (2010) 10027-10033

Verdal et al. Reorientational Dynamics of the Dodecahydro-closo-dodecaborate Anion in Cs2B12H12. J Phys Chem A, 115 (2011) 2933-2938

Remhof et al. Rotational Diffusion in NaBH4. J Phys Chem C, 113 (2009) 16834-16837

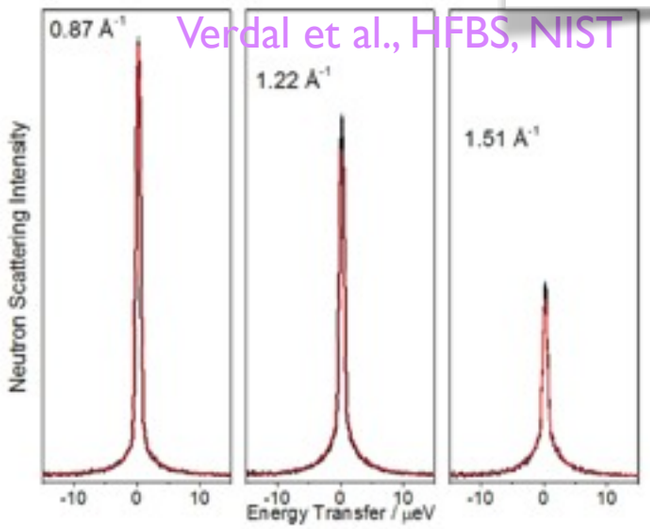
Remhof et al. Rotational motion of BH4 units in MBH4 (M=Li,Na,K) from quasielastic neutron scattering and density functional calculations. Physical Review B, 81 (2010) 214304

Martelli et al. Rotational Motion in LiBH4/LiI Solid Solutions. J Phys Chem A, 115 (2011) 5329-5334

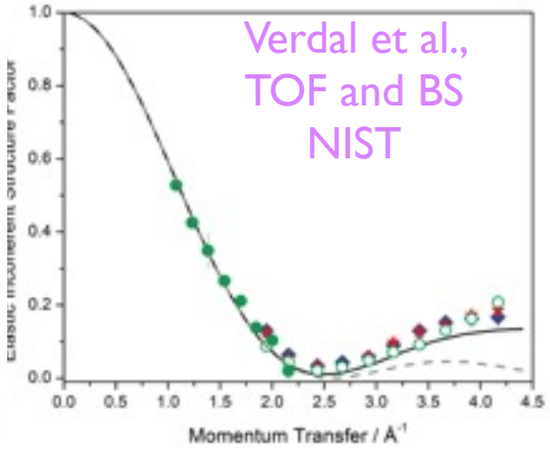
- determine rotational dynamics of hydrogen at low temperature: geometry, time scale and activation energy
  - modeling of EISF up to high Q could discriminated between models (Verdal et al.)
- determine H-jump dynamics of hydrogen at high temperature:
  - combination with DensityFunctionalTheory-calculations (Remhof et al.

DCS & HFBS, NIST

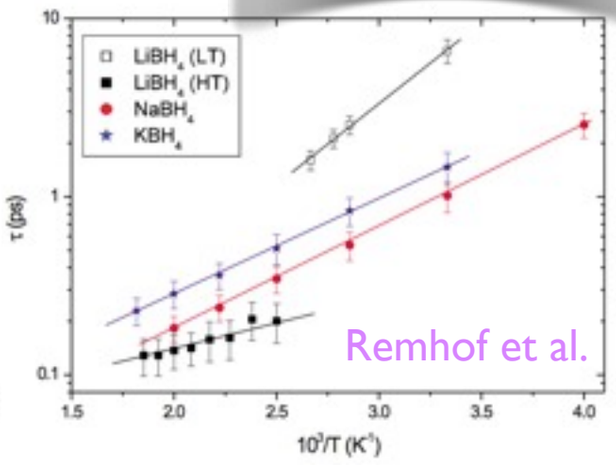
FOCUS, PSI



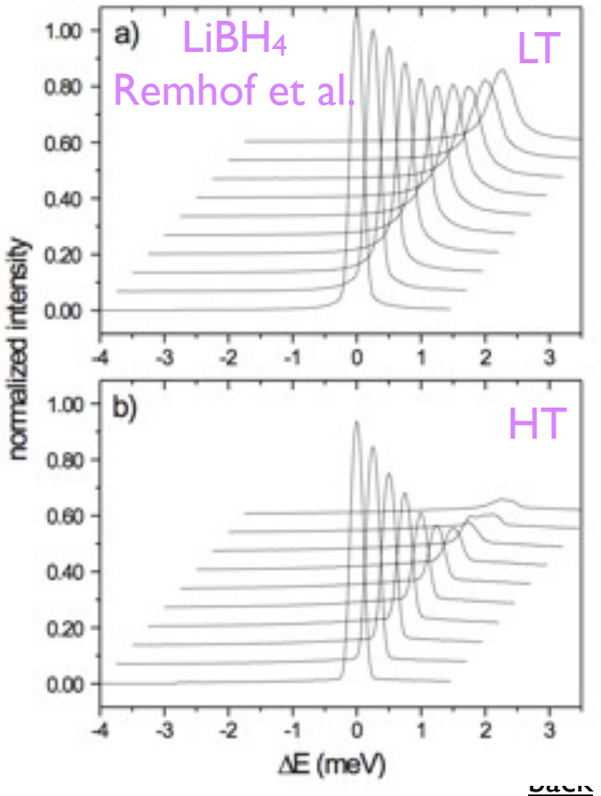
Verdal et al., HFBS, NIST



Verdal et al., TOF and BS NIST



Remhof et al.

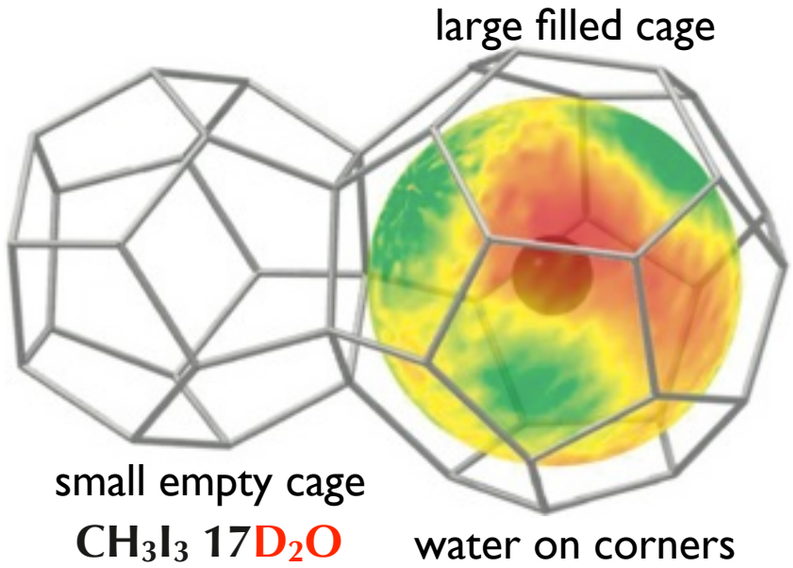


Remhof et al.

Dynamics of Methyl Iodide Clathrate Hydrate
- QENS experiment and MD simulation

A. Desmedt, J.C. Soetens, M. Prager, M. Russina, and J. Ollivier, J. Phys. Chem. C, 115 (2011)

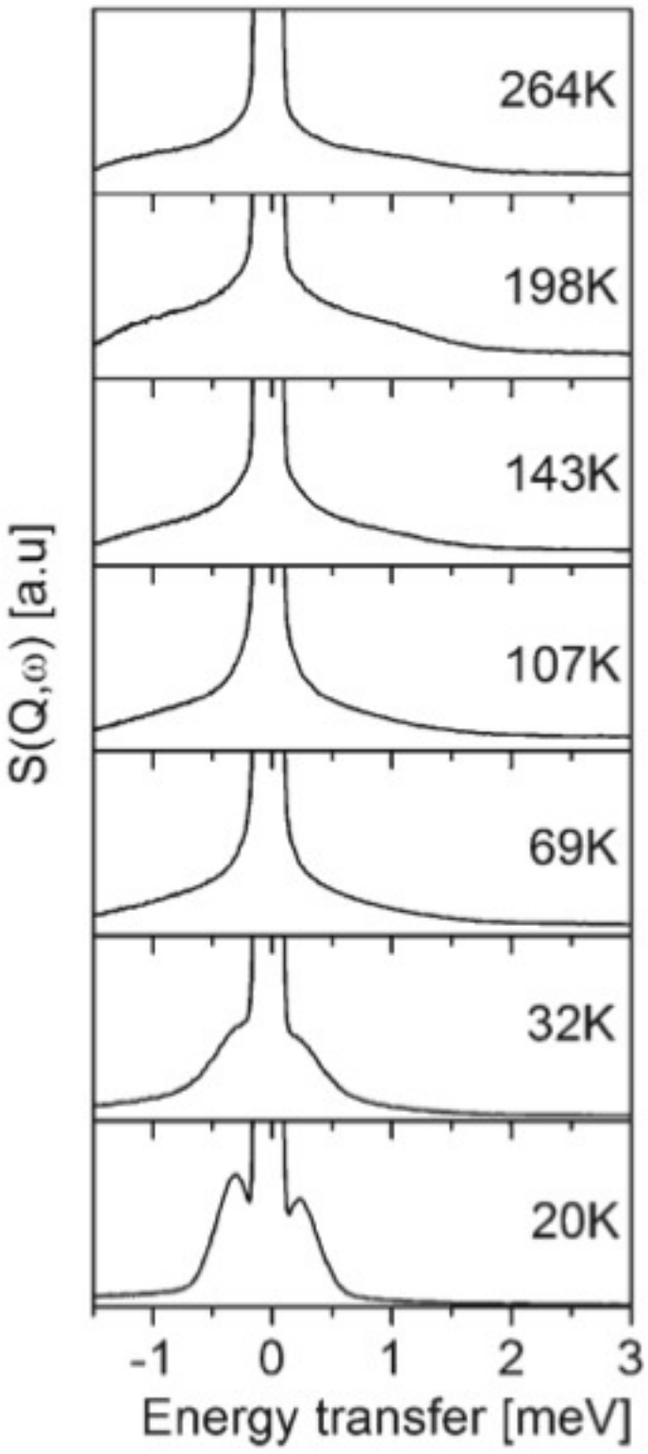
- complex dynamics extending over wide time range:
  - water / cage dynamics
  - methyl group rotation / tunneling
  - translation & rattling in the cage
  - whole molecule rotation in the cage
- deuterated water to increase contrast for confined molecules and reduce cage scattering
- qualitative evaluation with simple model
- detailed comparison of MD trajectories with experiment



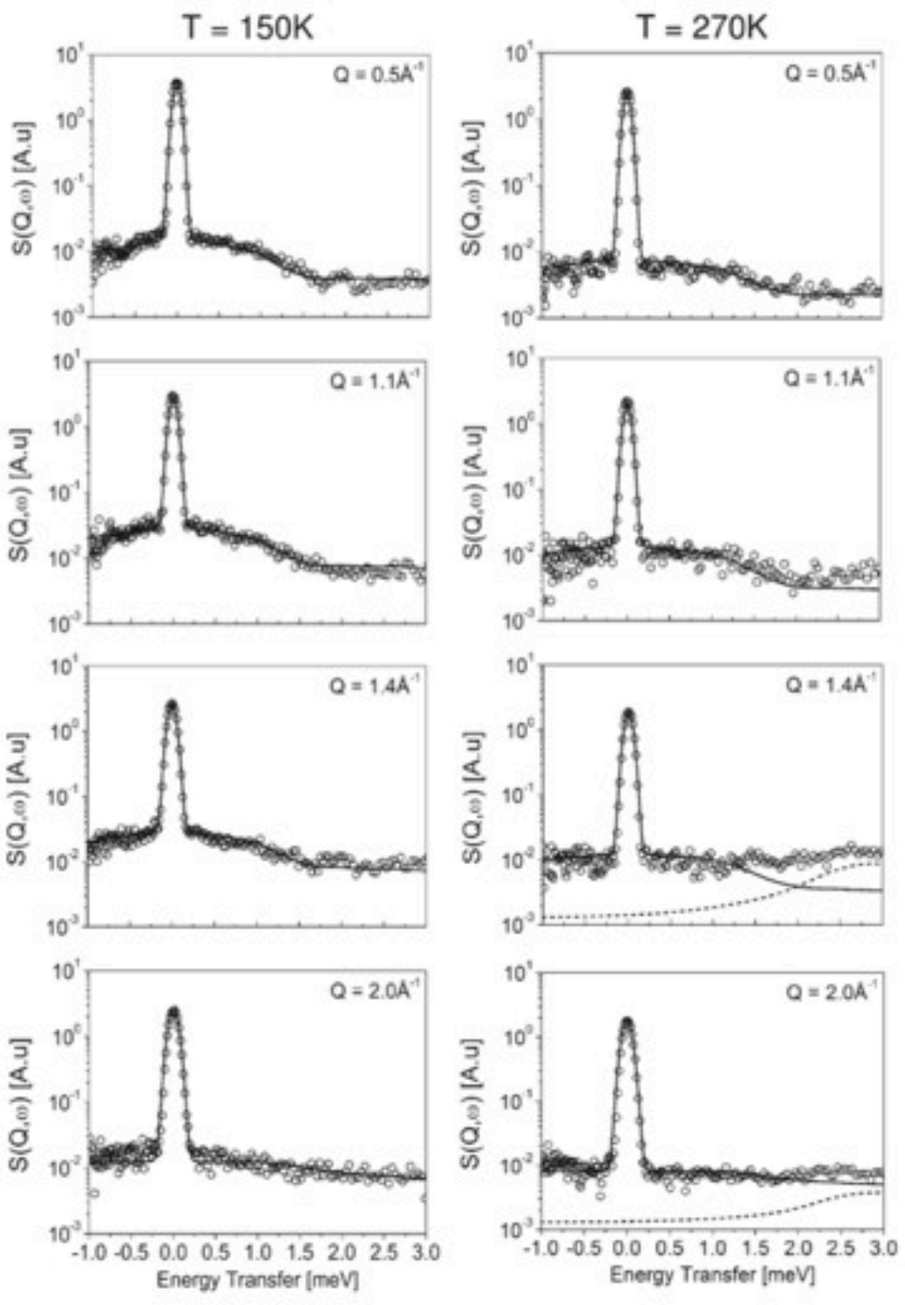
Dynamics of Methyl Iodide Clathrate Hydrate

- QENS experiment and MD simulation

A. Desmedt, J.C. Soetens, M. Prager, M. Russina, and J. Ollivier, J. Phys. Chem. C, 115 (2011)

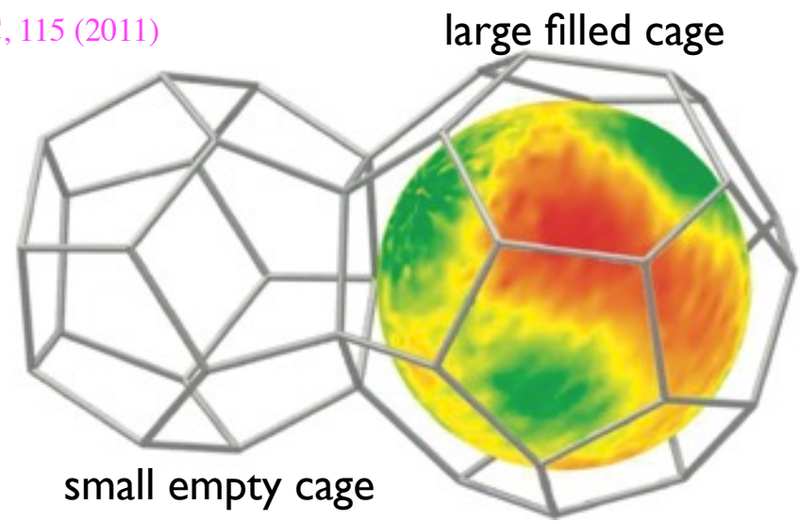


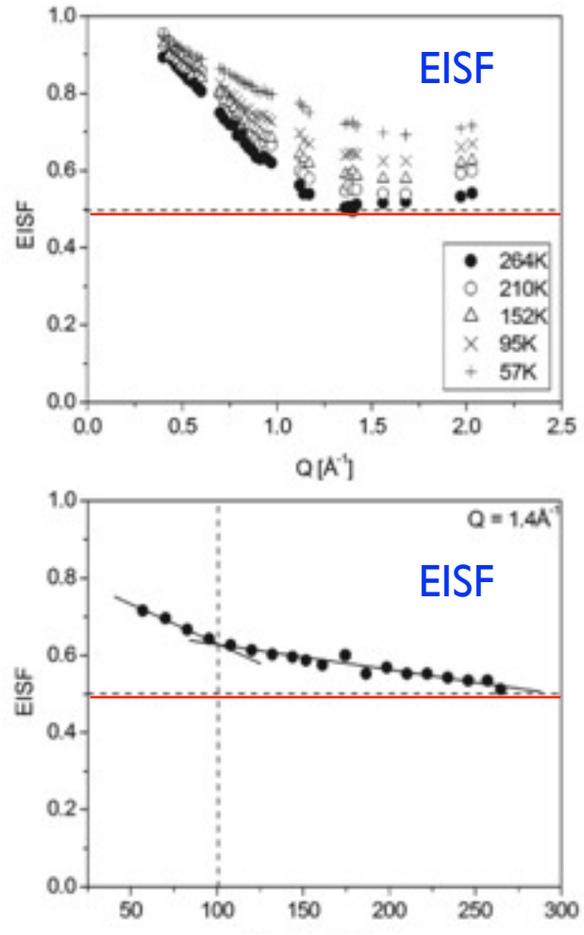
TOF on IN5B -
Q-averaged; 10min/temperature



n of the experimental QENS spectra (opened circles) with the MD-derived scattering laws (continuous line) a
ıd, T = 150 K; right-hand, T = 270 K). The dashed lines represent the phenomenological background due t
st cages (text for details).

MD-simulation compared to QENS





back

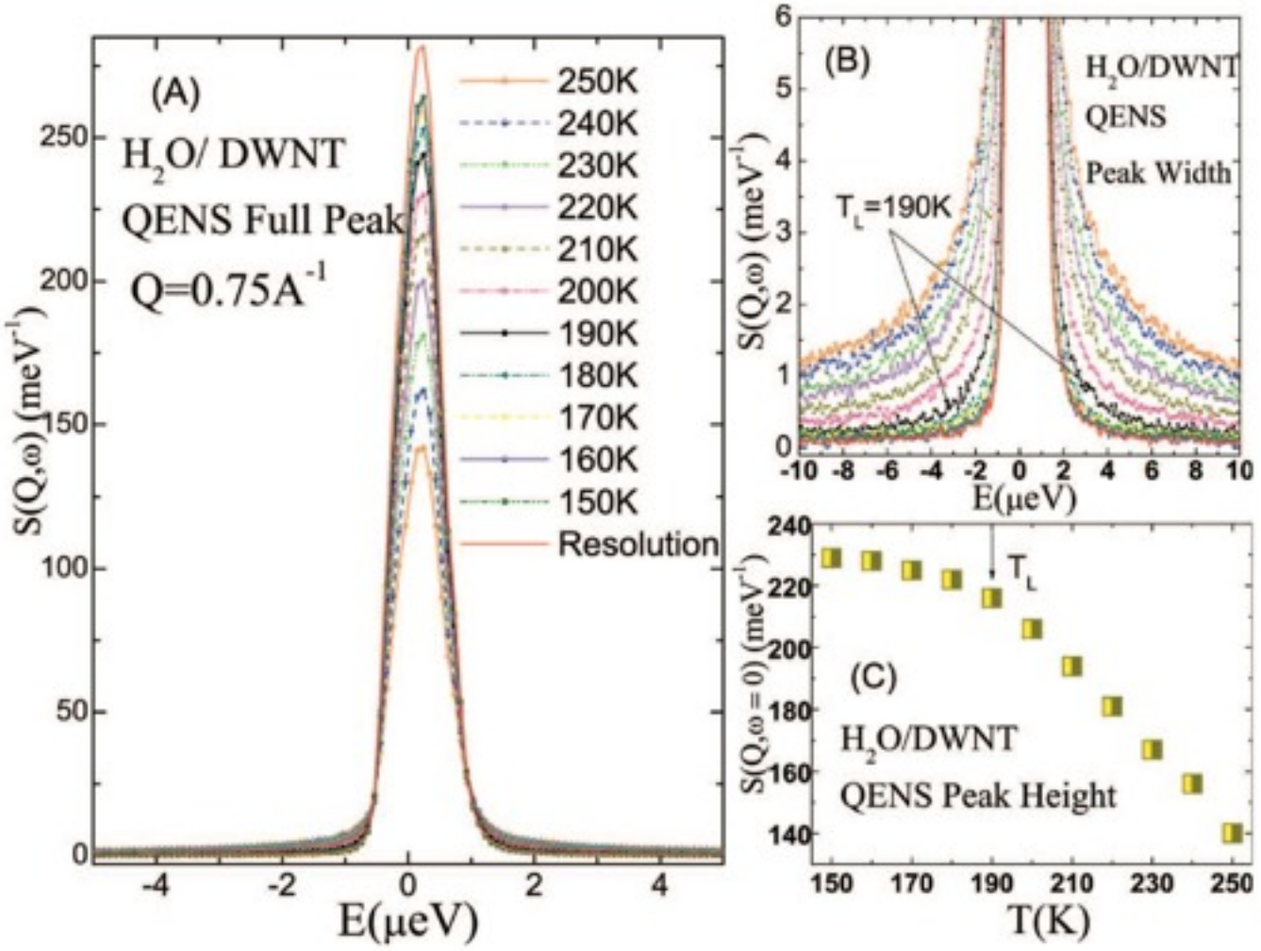
Dynamics of Water - is there a dynamic crossover?
- a controversial discussion in water research

example of exp. result:

Chu X.-Q., Kolesnikov A.I., Moravsky A.P., Garcia-Sakai V. and Chen S.H.,
Observation of a dynamic crossover in water confined in double-wall carbon nanotubes. Phys Rev E (2007) vol. 76 (2) pp. 021505

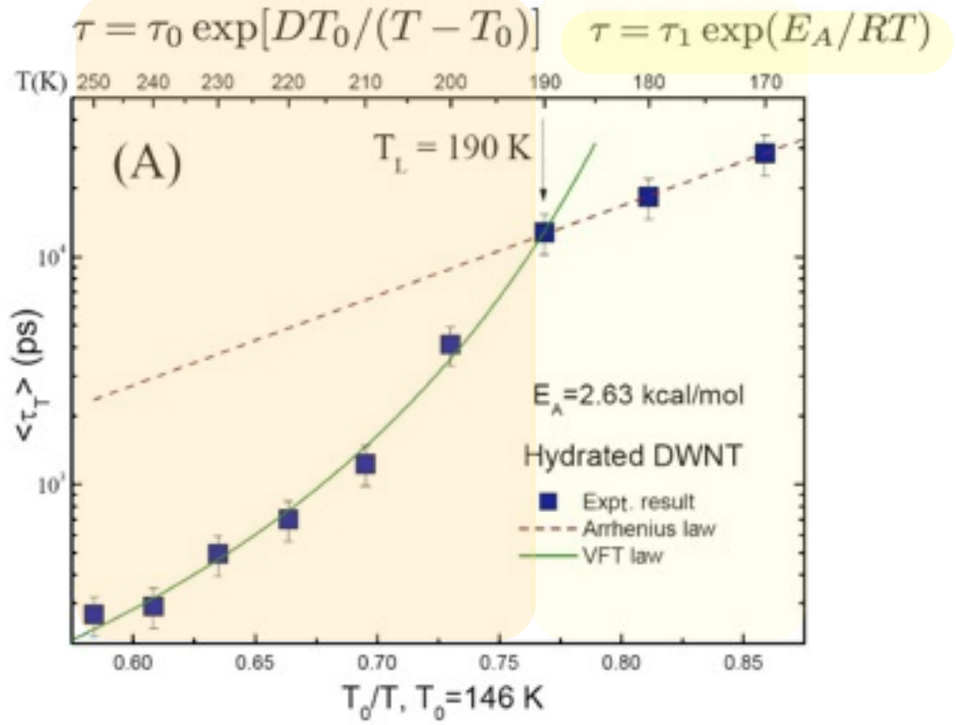
HFBS, NIST

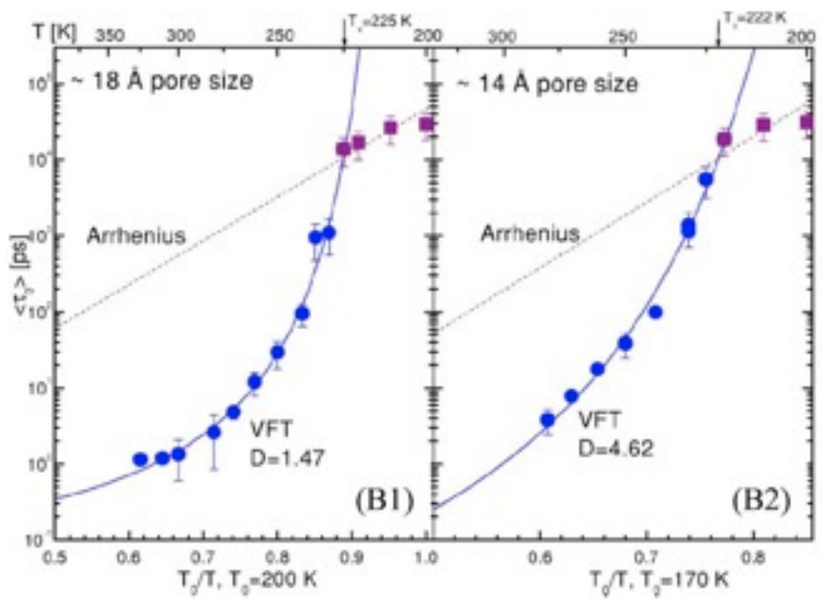
water confined in double walled Carbon nanotubes



fit with a stretched exponential function

$$F_H(Q,t) = F^S(Q,t)\exp[-(t/\tau_T(Q))^\beta]$$

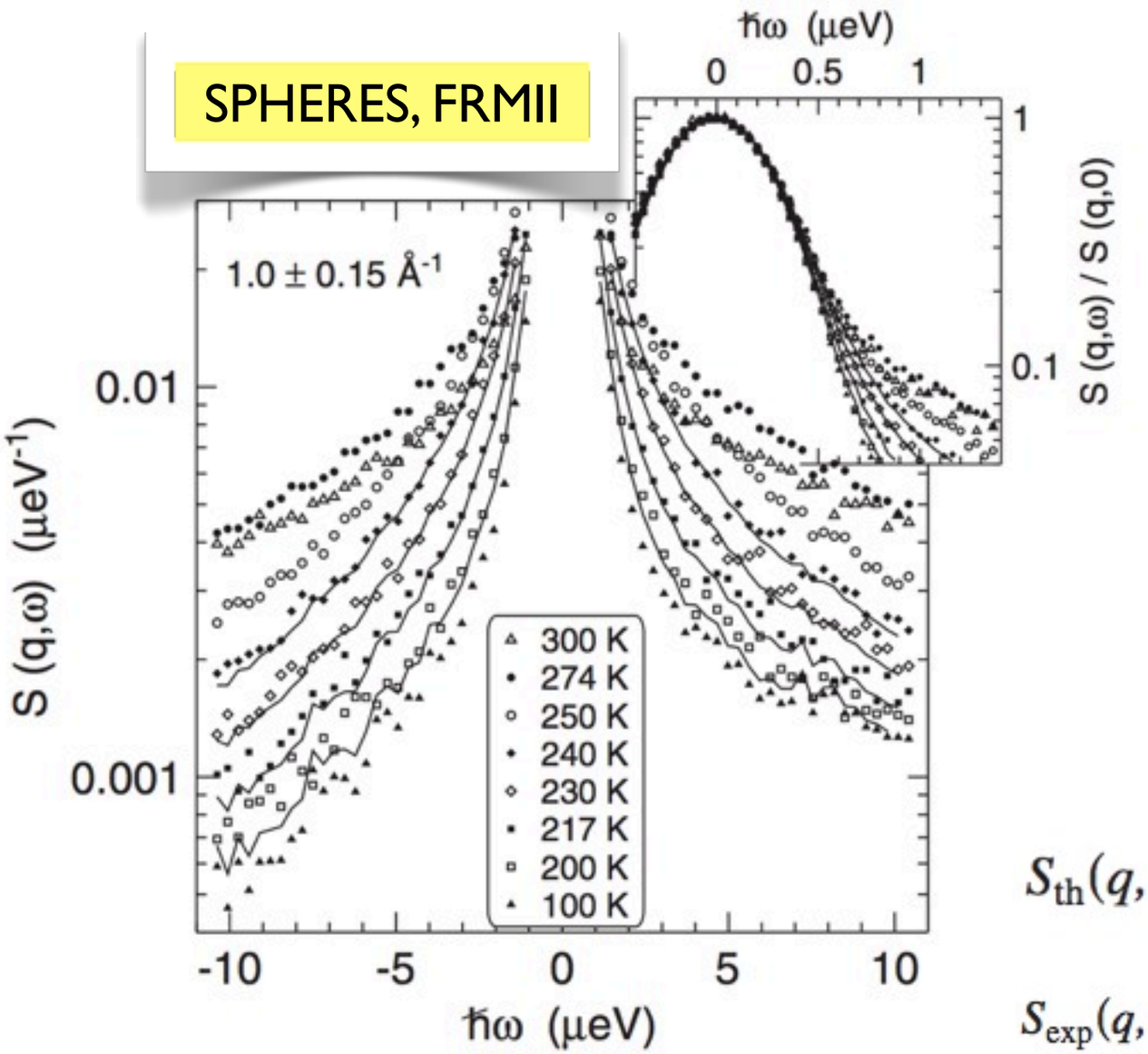


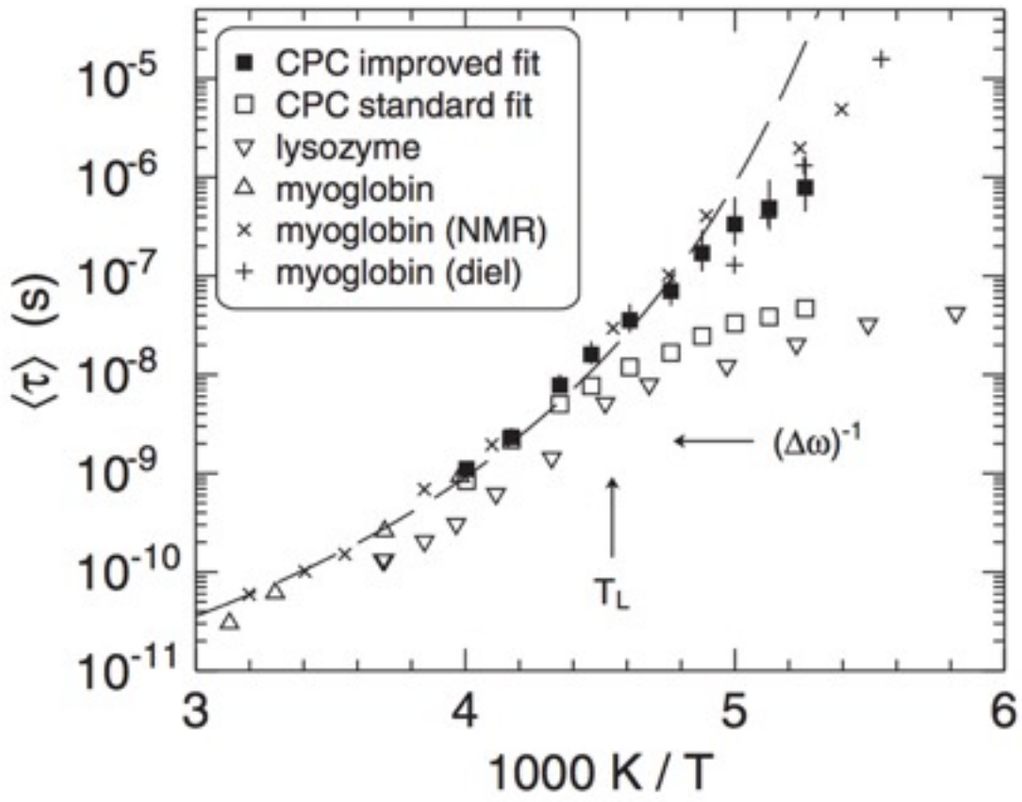


postulate: crossover from Vogel-Fulcher at high temperature to Arrhenius at low temperature

Dynamics of Water - is there a dynamic crossover?
- a controversial discussion in water research

recent example: Doster et al. Dynamical Transition of Protein-Hydration Water. Physical Review Letters (2010) vol. 104 (9) pp. 098101





$$S_{\mathrm{th}}(q,\omega) = f_q\left\{a_1\,\delta(\omega) + a_2\int_{-\infty}^{\infty}\frac{dt}{2\pi}\,e^{i\omega t-(|t|/\tau)^{\beta}}\right\}$$

$$S_{\mathrm{exp}}(q,0) = \int d\omega S_{\mathrm{th}}(q,\omega)R_q(-\omega)$$

$$= f_q\left\{a_1 R_q(0) + (1-a_1)\int_0^{\infty}\frac{dt}{\pi}\,e^{-(t/\tau)^{\beta}}\tilde{R}_q(t)\right\}$$

postulate: **no anomaly; fit-procedure may explain cross-over;**

Dynamics of Water - is there a dynamic crossover?
- a controversial discussion in water research

most recent example: S. M. Chathoth, E. Mamontov, A. I. Kolesnikov, Y. Gogotsi and D. J. Wesolowski Eur. Phys. Lett. 95 (2011) 56001

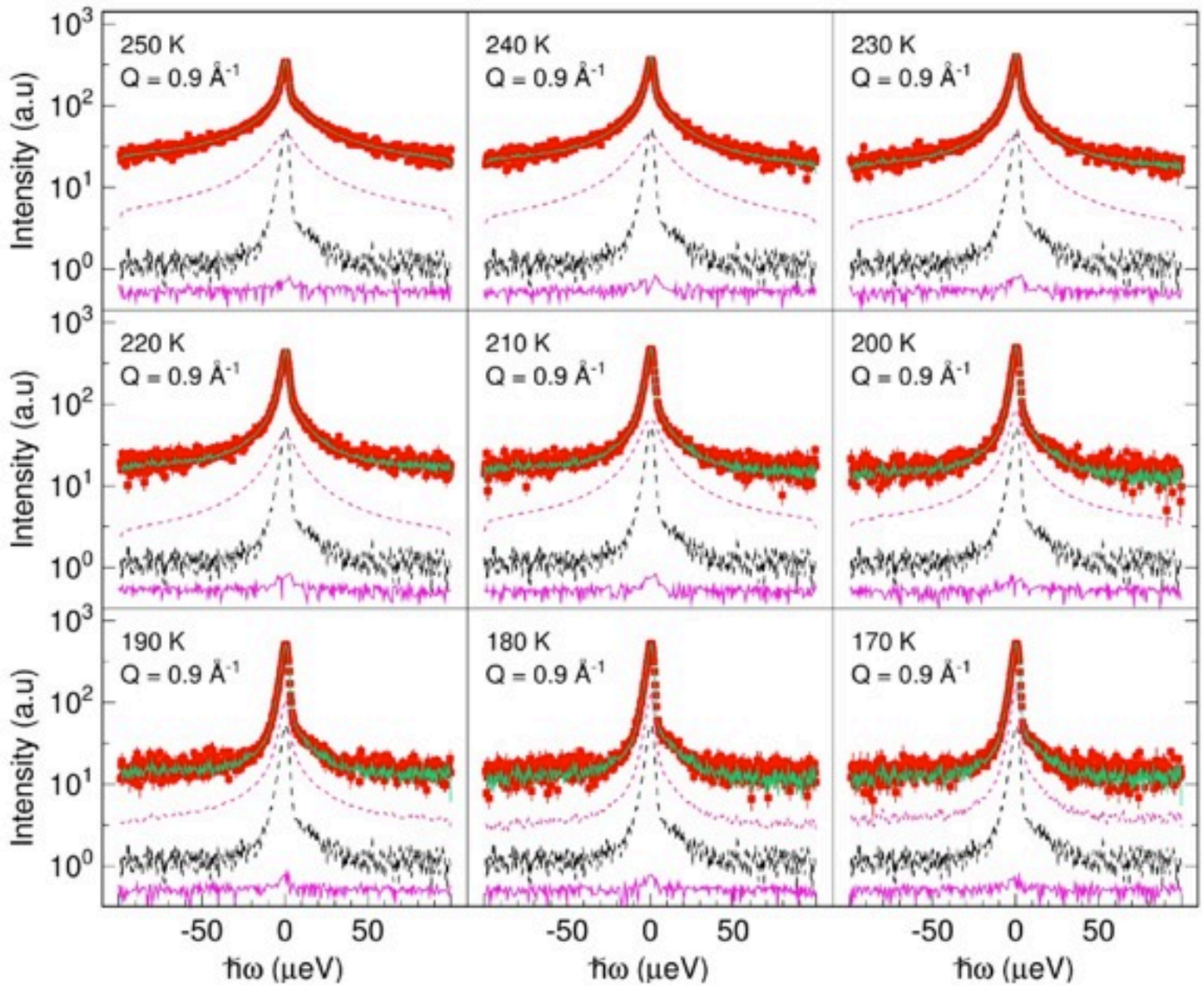
water confined in nanoporous Carbon

BASIS, SNS

fit with a stretched exponential function

$$S_{\mathrm{QENS}}(E) = A \int_0^{\infty} \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \exp\left(i\frac{E}{\hbar}t\right) \mathrm{d}t$$

convoluted with the resolution function



Dynamics of Water - is there a dynamic crossover?

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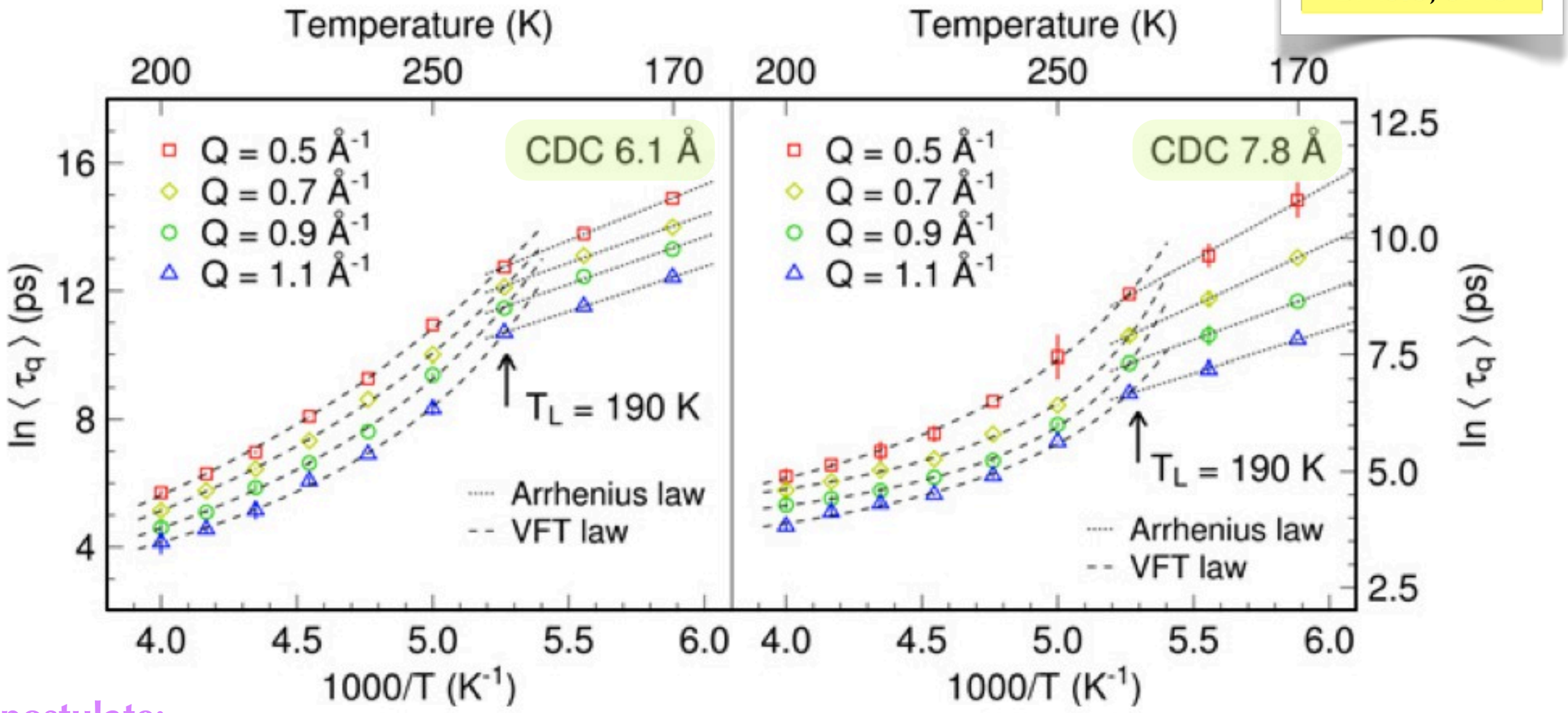
most recent example:

S. M. Chathoth1(a), E. Mamontov1, A. I. Kolesnikov1, Y. Gogotsi2 and D. J. Wesolowski Eur. Phys. Lett. 95 (2011) 56001

BASIS, SNS



postulate:

crossover from Vogel-Fulcher at high temperature to Arrhenius at low temperature

$$\tau = \tau_0 \exp[DT_0/(T - T_0)] \qquad \tau = \tau_1 \exp(E_A/RT)$$

back

some literature:

books on QENS:

T. Springer, 'Quasielastic Neutron Scattering for the Investigation of Diffusive Motions in Solids and Liquids', Springer Tracts in Modern Physics 64, 197, Springer-Verlag 1972

M. Bée, 'Quasielastic Neutron Scattering Principles and Applications in Solid State Chemistry, Biology and Material Science', Adam Hilger, Bristol 1988

R. Hempelmann, 'Quasielastic Neutron Scattering and Solid State Diffusion', Oxford Series on Neutron Scattering in Condensed Matter 13, Claredon Press, Oxford 2000

general books on n-scattering:

G.L. Squires, 'Thermal Neutron Scattering', Cambridge University Press 1978

S.W. Lovesey, 'Theory of Neutron Scattering from Condensed Matter', Claredon Press, Oxford 1987

references on QENS scattering techniques:

BSS: The Backscattering Web-site: A. Heidemann, B.F., http://www.ill.eu/other_sites/BS-review/index.htm; B.Frick, "Neutron Backscattering"in 'Neutron and X-Ray Spectroscopy, Springer, 2006

General n-Instrumentation: e.g. H. Schober. Neutron Scattering Instrumentation. Neutron Applications in Earth, Energy and Environmental Sciences (2009) pp. 37-104

references on special topics:

diffusion in zeolites: H. Jobic, Theodorou, Microporous and Mesoporous Materials 102 (2007) 212

confinement studies: e.g. 'Int. Workshop on Dynamics in Confinement', Eur. Phys. J. - ST 141 (2007) & 189 (2010)

Thank You for Attention