# Diffusion in solids and liquids

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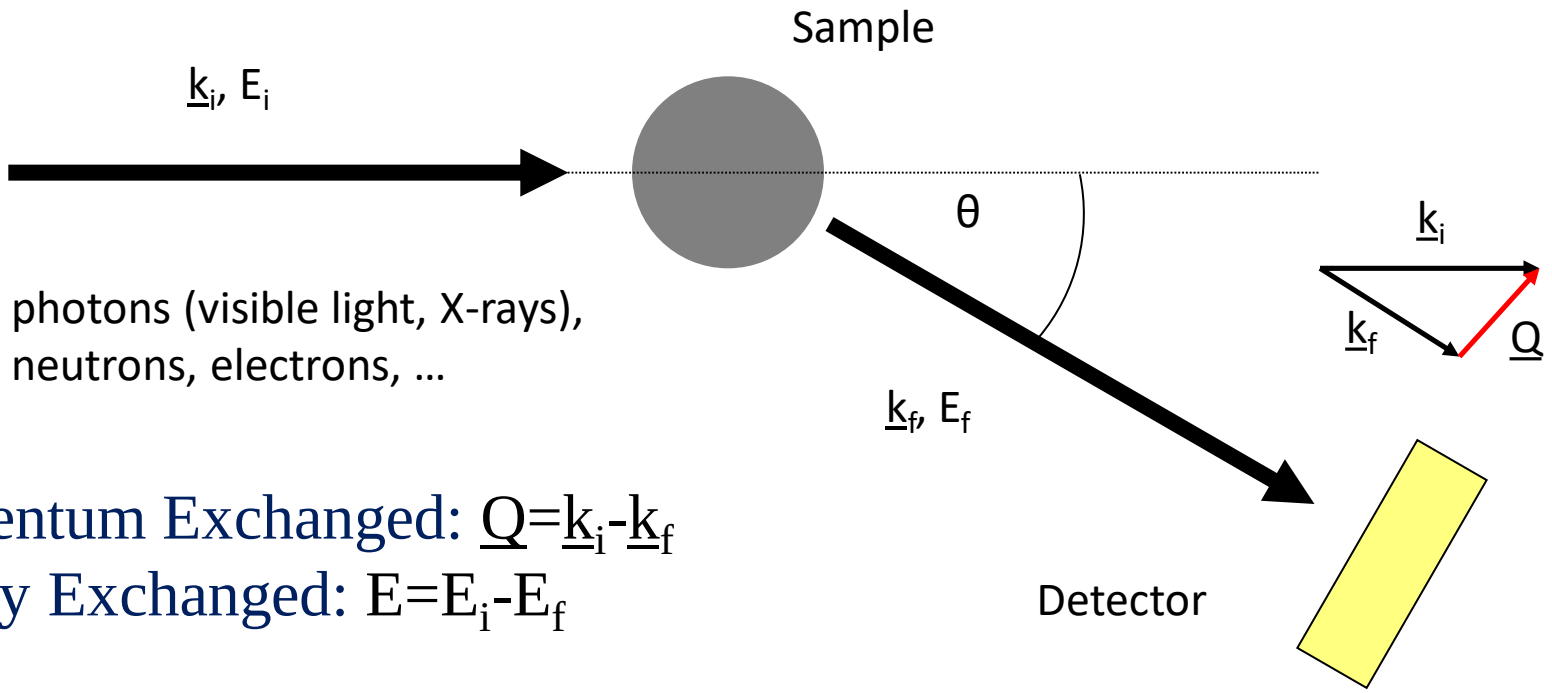
**NIST Center for Neutron research**

Oxford School on Neutron Scattering, 9/2-12/2019

# Outline

- Overview of (incoherent) Quasielastic Neutron Scattering
  - Origin of the quasielastic broadening
  - Overview of most common models
- Neutron Spin Spectroscopy
  - Principle of operation
- Examples of relevant applications
- Conclusion

# Static and Dynamic Scattering




Probe: photons (visible light, X-rays), neutrons, electrons, …

Momentum Exchanged: $\underline{Q}=\underline{k}_i-\underline{k}_f$

Energy Exchanged: $E=E_i-E_f$

Static Scattering: $\frac{d\sigma}{d\Omega} \approx S(Q)$

Dynamic Scattering: $\frac{d^2\sigma}{d\Omega dE} \approx S(Q,E)$

# Static and Dynamic Scattering

$$S(Q) = FT_S\left\{\left\langle \exp[-i\underline{Q}(\underline{r}_i - \underline{r}_j)]\right\rangle\right\}$$

Fourier Transform of the Space Correlation Function

$$S(Q,E) = FT_T\left\{\left\langle \exp[-i\underline{Q}(\underline{r}(t) - \underline{r}(0))]\right\rangle\right\} = FT_T\left\{I(Q,t)\right\} = FT_{ST}\left\{G(r,t)\right\}$$

Fourier Transform of the Space-Time Correlation Function

*I(Q,t)* Intermediate Scattering Function (ISF)

*G(r,t)* van Hove Correlation Function

# Dynamic Structure Factor

$$\frac{d^2\sigma}{d\Omega dE} = N_0 \frac{k_s}{k_0} S^{neutrons}(Q,E)$$

$$S(Q,E) = \frac{1}{N} FT\left\{\sum_{i,j}\left\langle b_i b_j \exp[-i\underline{Q}(\underline{r}_i(t) - \underline{r}_j(0))]\right\rangle\right\}$$

$$S_{coh}(Q,E) = \frac{1}{N} FT\left\{\sum_{i,j}\left\langle b_i\right\rangle\left\langle b_j\right\rangle\left\langle \exp[-i\underline{Q}(\underline{r}_i(t) - \underline{r}_j(0))]\right\rangle\right\}$$

$$S_{inc}(Q,E) = \frac{1}{N} FT\left\{\sum_{i}\left[\left\langle b_i^2\right\rangle - \left\langle b_i\right\rangle^2\right]\left\langle \exp[-i\underline{Q}(\underline{r}_i(t) - \underline{r}_i(0))]\right\rangle\right\}$$

**Coherent Scattering Cross Section**

$$\sigma_i^{coh} = 4\pi\left\langle b_i\right\rangle^2$$

**Incoherent Scattering Cross Section**

$$\sigma_i^{incoh} = 4\pi\left[\left\langle b_i^2\right\rangle - \left\langle b_i\right\rangle^2\right]$$

# Translational Dynamics

The goal is to derive an expression for the quantities measured by neutron spectroscopy (the dynamic structure factor, *S(Q,E)*, or the intermediate scattering function, *I(Q,t)*) in terms of macroscopic and/or microscopic quantities.

For simplicity and didactical purposes, let's consider Brownian dynamics.

We can take advantage of the established relation between neutron spectra and the van Hove correlation function, the probability of finding a particle at position **r** at time t.

$$G^s(\boldsymbol{r},t) = \frac{1}{(4\pi Dt)^{3/2}} e^{-\frac{r^2}{4Dt}}$$

*D* is the diffusion coefficient.

$G^s(r,t)$ obeys the Fick's law:

$$\frac{\partial G^s(\boldsymbol{r},t)}{\partial t} = D\frac{\partial^2 G^s(\boldsymbol{r},t)}{\partial r^2}$$

# Intermediate Scattering Function

The intermediate scattering function is the Fourier transform of the van Hove correlation function

$$I(Q,t) = \int G^s(\boldsymbol{r},t)exp(-i\boldsymbol{Q}\boldsymbol{r})d\boldsymbol{r} = exp(-DQ^2t) = exp(-\Gamma t)$$

# Dynamic Structure Factor

The dynamic structure factor is the Fourier transform of the intermediate scattering function.

$$S^T(Q,E) = \frac{1}{2\pi}\int I(Q,t)exp\left(-i\frac{Et}{\hbar}\right)dt = \frac{1}{\pi}\frac{DQ^2}{E^2 + (DQ^2)^2} =$$

$$= \frac{1}{\pi}\frac{\Gamma}{E^2 + \Gamma^2} \qquad \Gamma = HWHM = DQ^2$$

# Intermediate Scattering Function

The intermediate scattering function is the Fourier transform of the van Hove correlation function

*Exponential*

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# Dynamic Structure Factor

The dynamic structure factor is the Fourier transform of the intermediate scattering function.

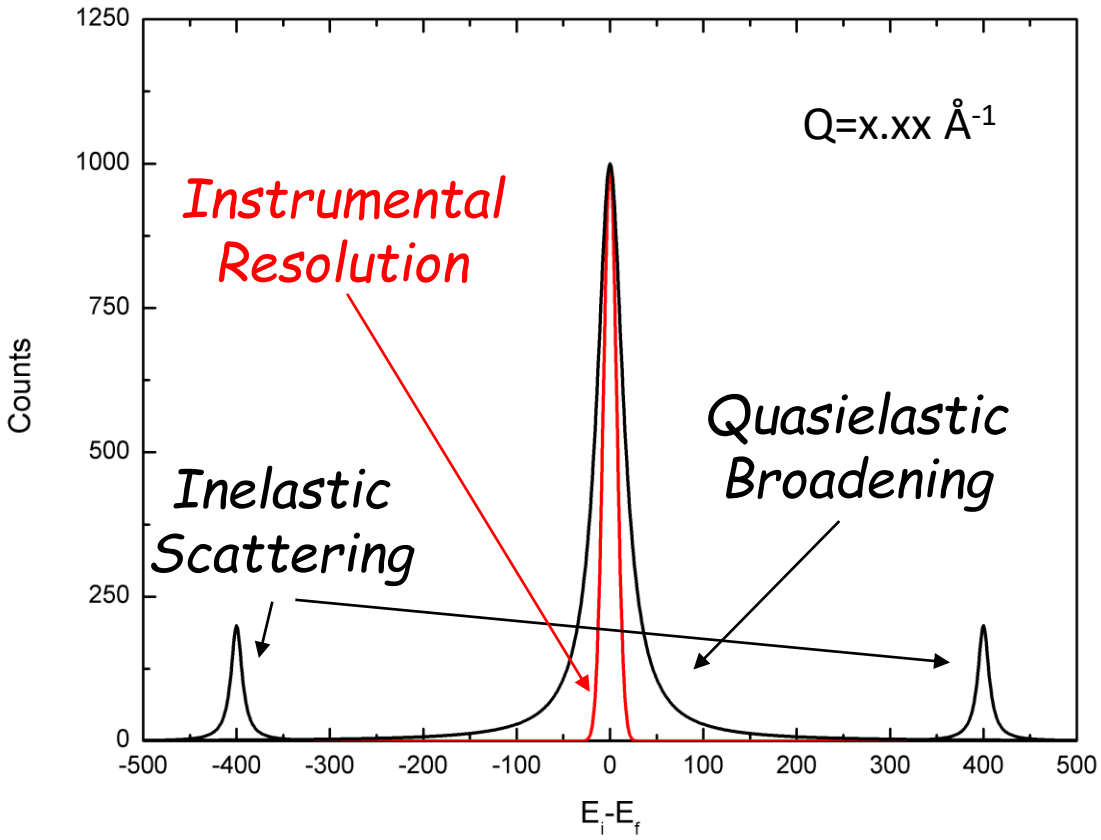
$$S^T(Q,E) = \frac{1}{2\pi}\int I(Q,t)exp\left(-i\frac{Et}{\hbar}\right)dt = \frac{1}{\pi}\frac{DQ^2}{E^2 + (DQ^2)^2} =$$

*Lorentzian centered at E=0*

$$= \frac{1}{\pi}\frac{\Gamma}{E^2 + \Gamma^2}$$

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

# S(Q,E)




**Thermally Activated Motions Take Place in the System.**

## Inelastic Scattering

**excitation:** neutrons exchange energy with an oscillatory motion which has a finite energy transfer

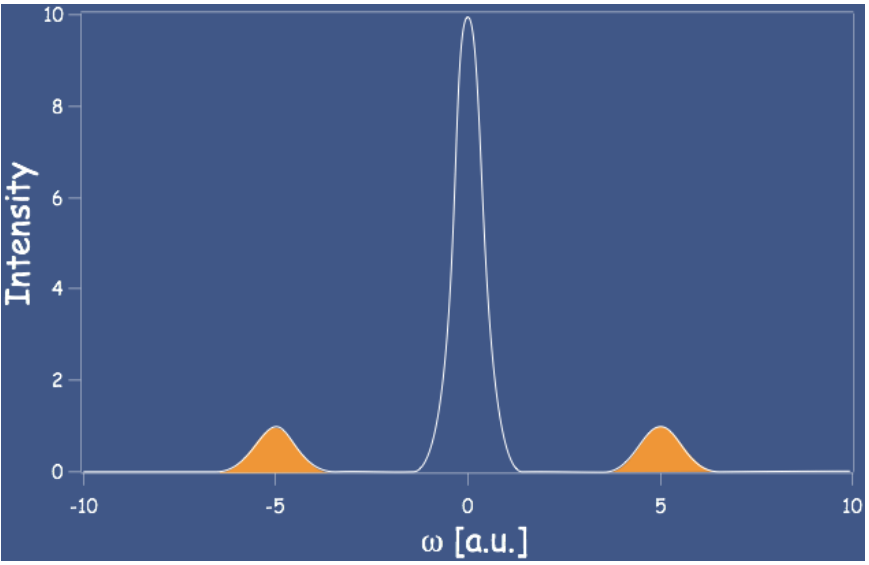
Ex: phonon, magnon, ...

## Quasielastic Scattering

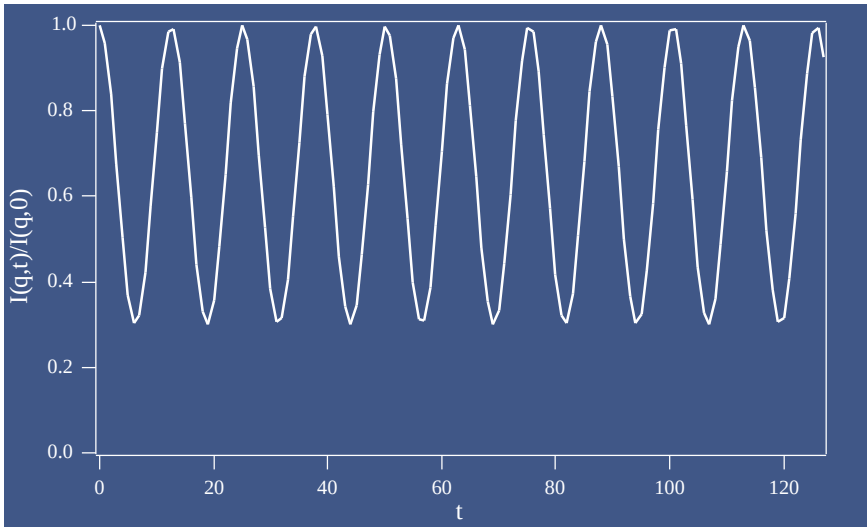
**relaxation:** neutrons exchange energy with random motion which makes another new equilibrium state (no typical finite energy transfer exists)

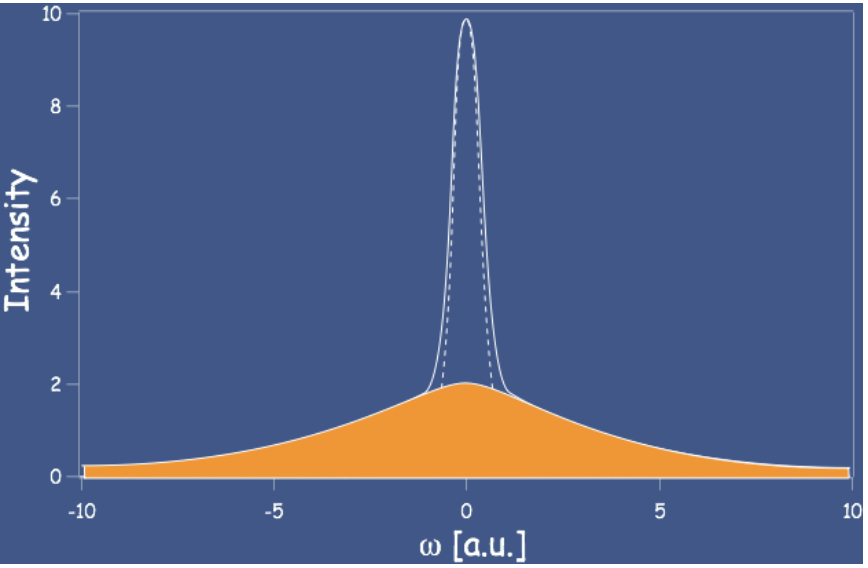
Ex.: rotation, vibration, diffusion…

# Energy and Time Domain

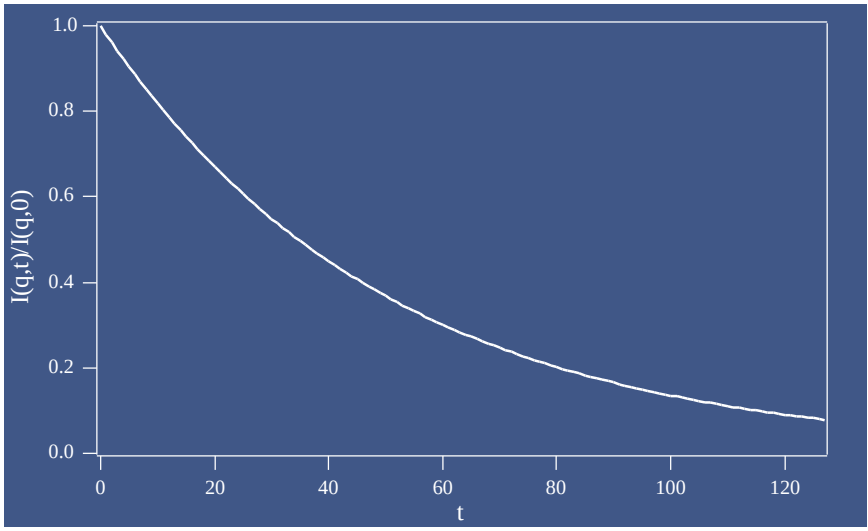



FT



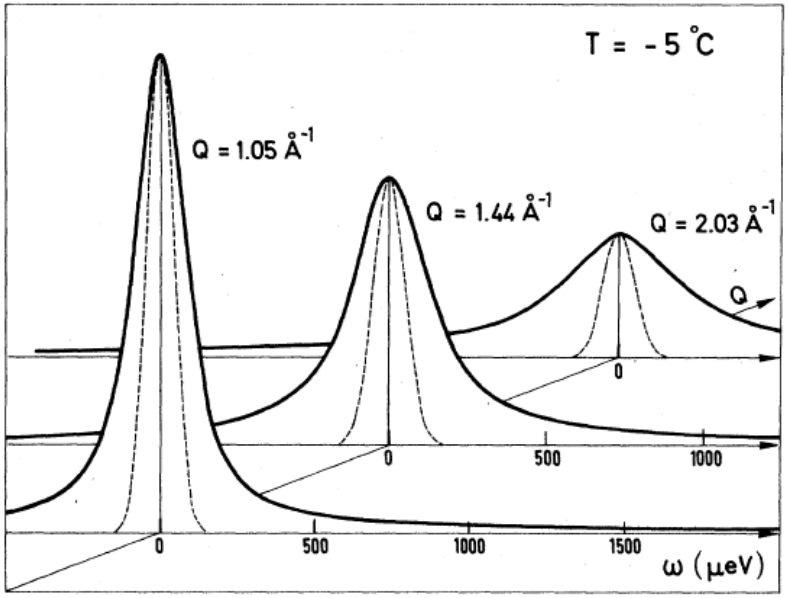




FT



# Q-dependence

The width of the quasielastic broadening (usually) increases with $Q$.
Shorter length scales $\rightarrow$ faster time scales.
The analysis of the Q-dependence provides information on the geometry of the motion.




J. Teixeira, et al., "Experimental determination of the nature of diffusive motions of water molecules at low temperatures" *PRA*, **31**, 1913 (1985)

# Isotropic Rotational Diffusion

Let's consider another relevant case: isotropic rotational diffusion on a sphere of radius b. The probability distribution function of the scatterer orientation, $G_{\Omega}^{S}$, obeys a an equation similar to the Fick's law:

$$\frac{\partial G^{s}(\Omega,\Omega_0,t)}{\partial t} = D_r \nabla_{\Omega}^{2} G^{s}(\Omega,\Omega_0,t)$$

Where $\Omega$ indicates the orientation and $D_r$ is the rotational diffusion coefficient. The solution of this equation is:

$$G^{s}(\Omega,\Omega_0,t) = 4\pi \sum_{l=0}^{\infty} exp[-D_r l(l+1)t] \sum_{m=-l}^{l} Y_m^l(\Omega) {Y_m^l}^{*}(\Omega_0)$$

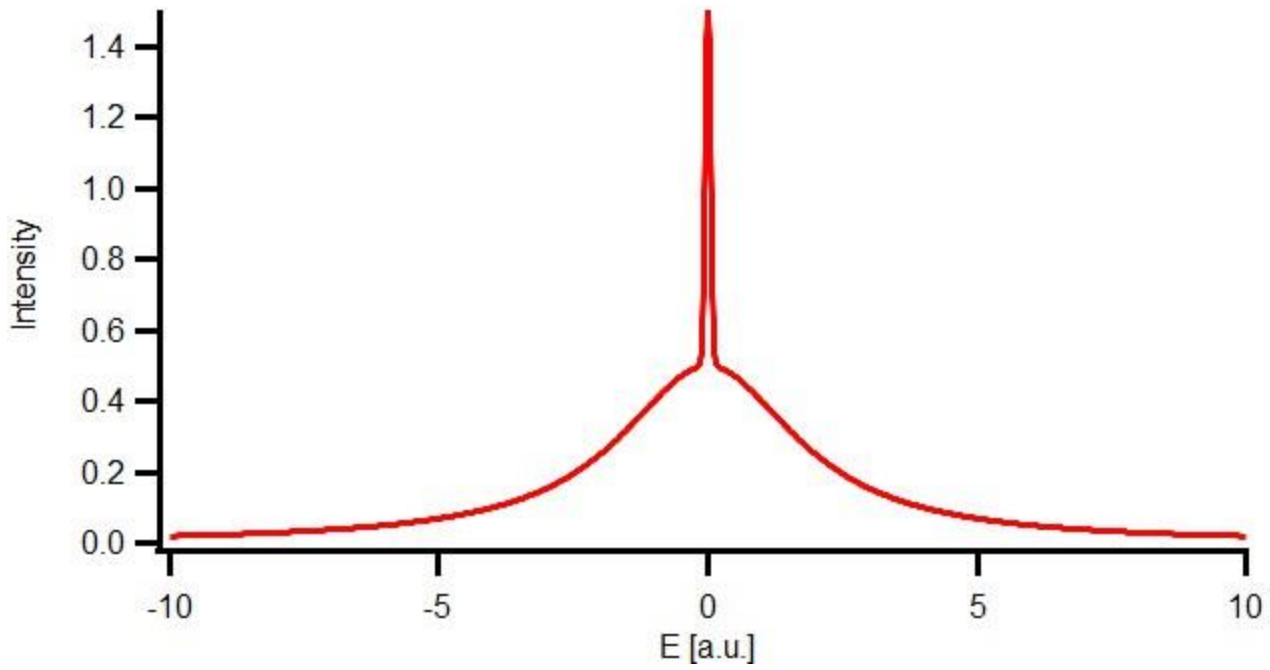
After Fourier transform:

$$I(Q,t) = FT\{G^{s}(\Omega,\Omega_0,t)\} = j_0^2(Qb) + \sum_{l=1}^{\infty}(2l+1) j_l^2(Qb) exp[-D_r l(l+1)t]$$

$$S^{R}(Q,E) = FT\{I(Q,t)\} = j_0^2(Qb)\delta(E) + \sum_{l=1}^{\infty}(2l+1) j_l^2(Qb) \frac{1}{\pi} \frac{D_r l(l+1)}{[D_r l(l+1)]^2 + E^2}$$

# Isotropic Rotational Diffusion

The spectra for isotropic rotational diffusion is composed by a sharp elastic peak superimposed on a broadened component.



# In general for rotations

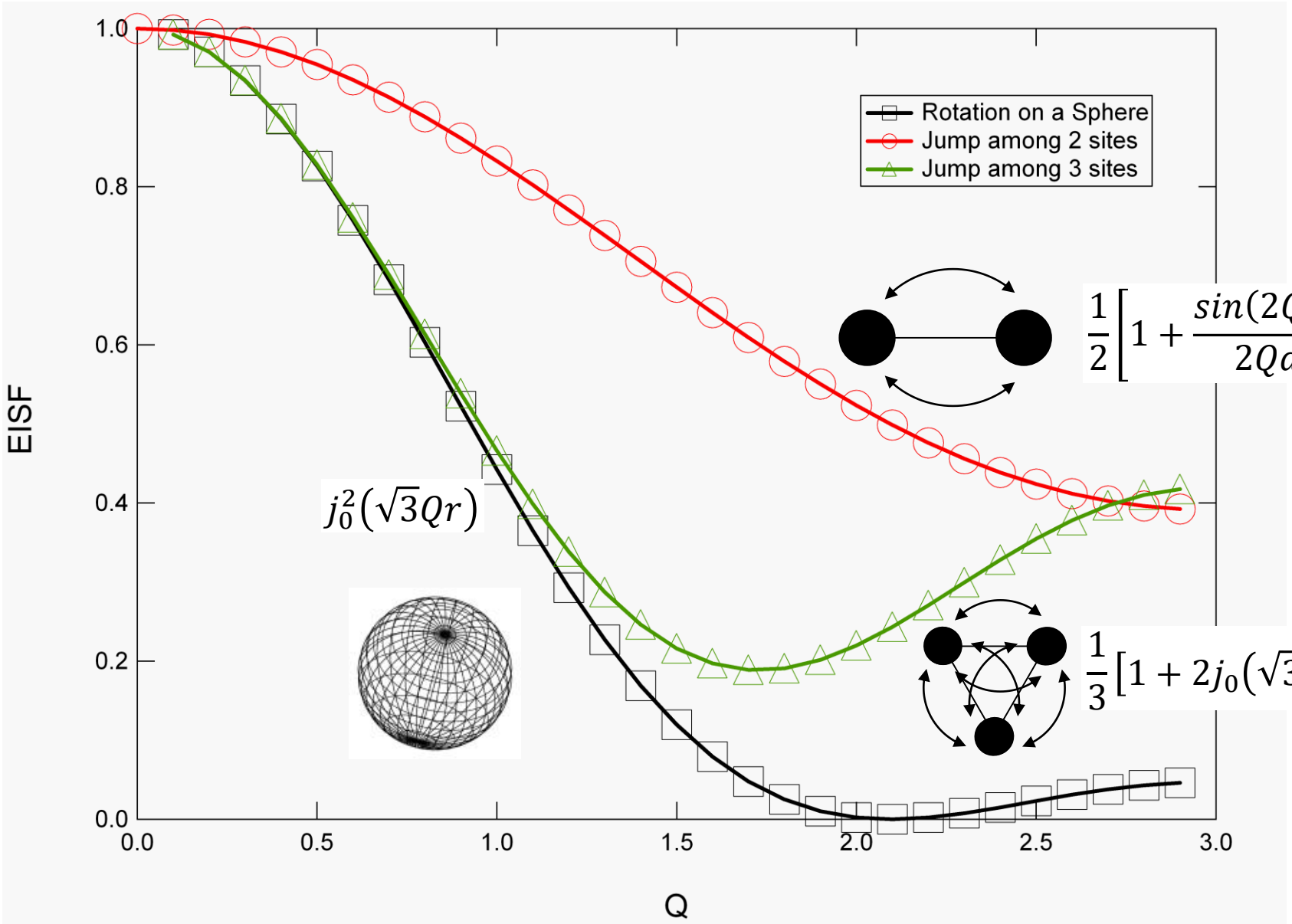
$$S^R(Q,t) = A_0(Q) + \sum_{l=1} A_l(Q) F_l(t)$$

$A_0$ is the Elastic Incoherent Structure Factor (EISF)

The EISF is the form factor corresponding to the area explored by the scatterer in the limit of the time corresponding to the instrumental resolution.

$$EISF = \frac{Elastic\ Intensity}{Total\ Intensity}$$

# EISFs


Rotation on a Sphere
Jump among 2 sites
Jump among 3 sites
EISF
Q
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
$j_0^2(\sqrt{3}Qr)$
$\frac{1}{2}\left[1+\frac{sin(2Qd)}{2Qd}\right]$
$\frac{1}{3}\left[1+2j_0(\sqrt{3}Qr)\right]$

# Diffusion Models

- Fickian diffusion:

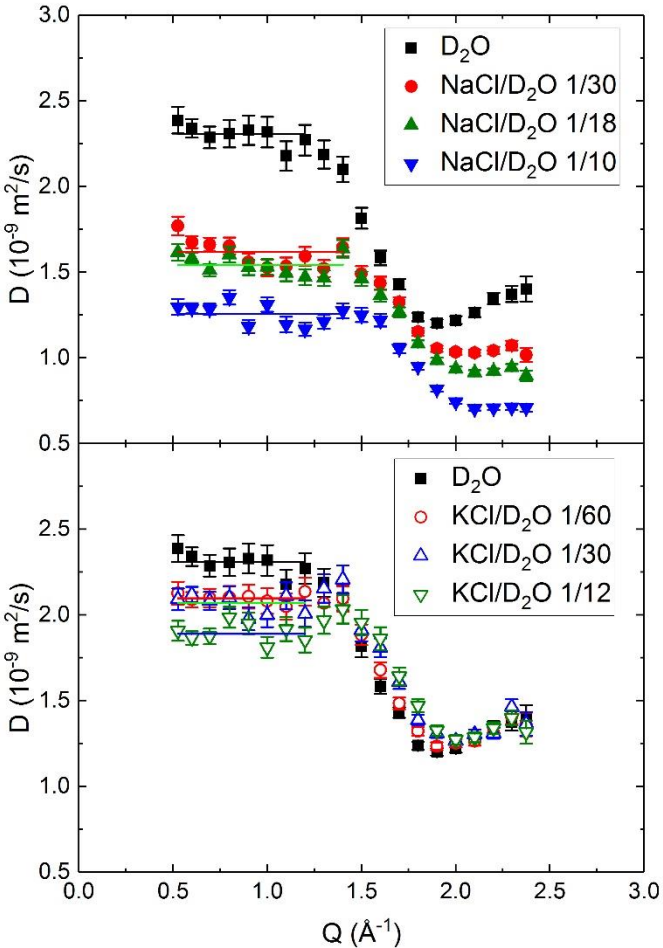
$$\Gamma = DQ^2$$

- Collective diffusion:

$$\Gamma = D(Q)Q^2$$

De Gennes narrowing: slowing down of the dynamics in correspondence of structural peaks

$$D(Q) \sim \frac{1}{S(Q)}$$



# Jump Diffusion Models

For a time interval the scatterer remains on a given site, vibrating about a center of equilibrium. After a residence time, τ, the atom moves rapidly to another site, in a negligible jump time. The length of the jump vector, l, is much larger than the vibration amplitude. Notice, $D=l^2/6\tau$.

Chudley-Elloitt (CE) – jumps on a lattice

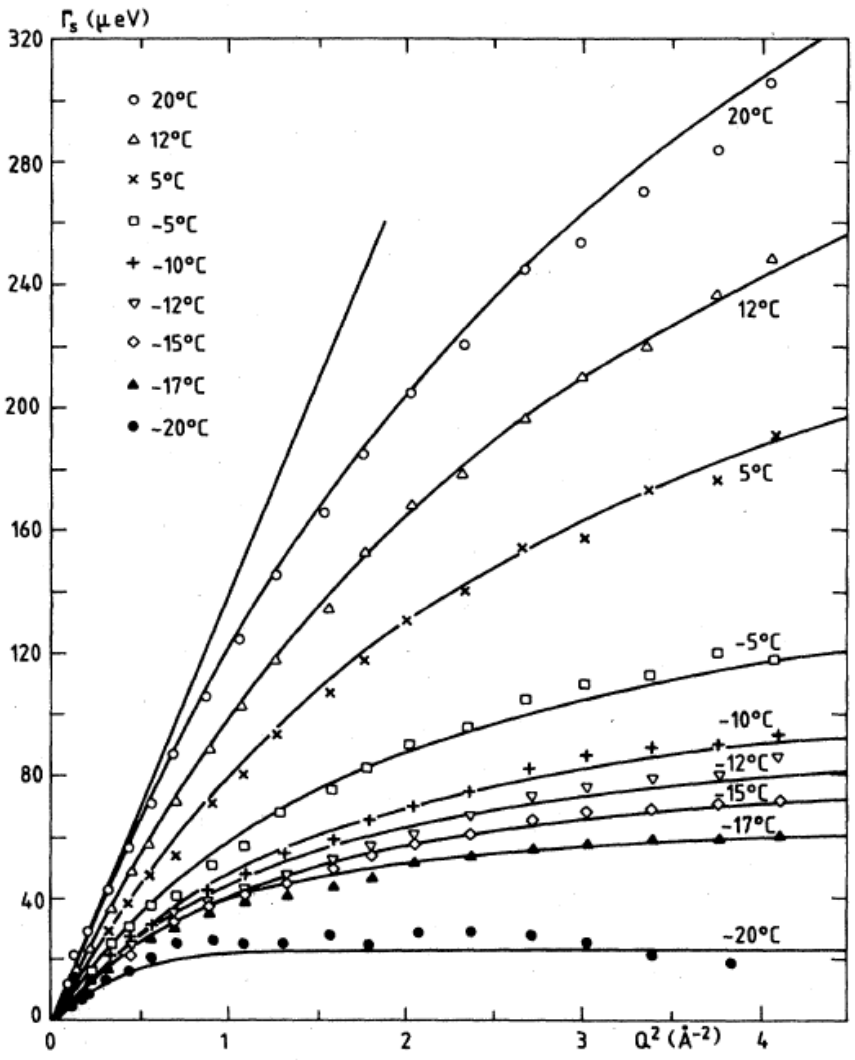
$$\Gamma(Q) = \frac{1}{\tau}\left[1 - \frac{sin(Ql)}{Ql}\right]$$

$$\Gamma(Q \to 0) = \frac{Q^2 l^2}{6\tau} = DQ^2$$

Singwi-Sjölander (SS) – random jump lengths

$$\Gamma(Q) = \frac{DQ^2}{1 + DQ^2\tau}$$

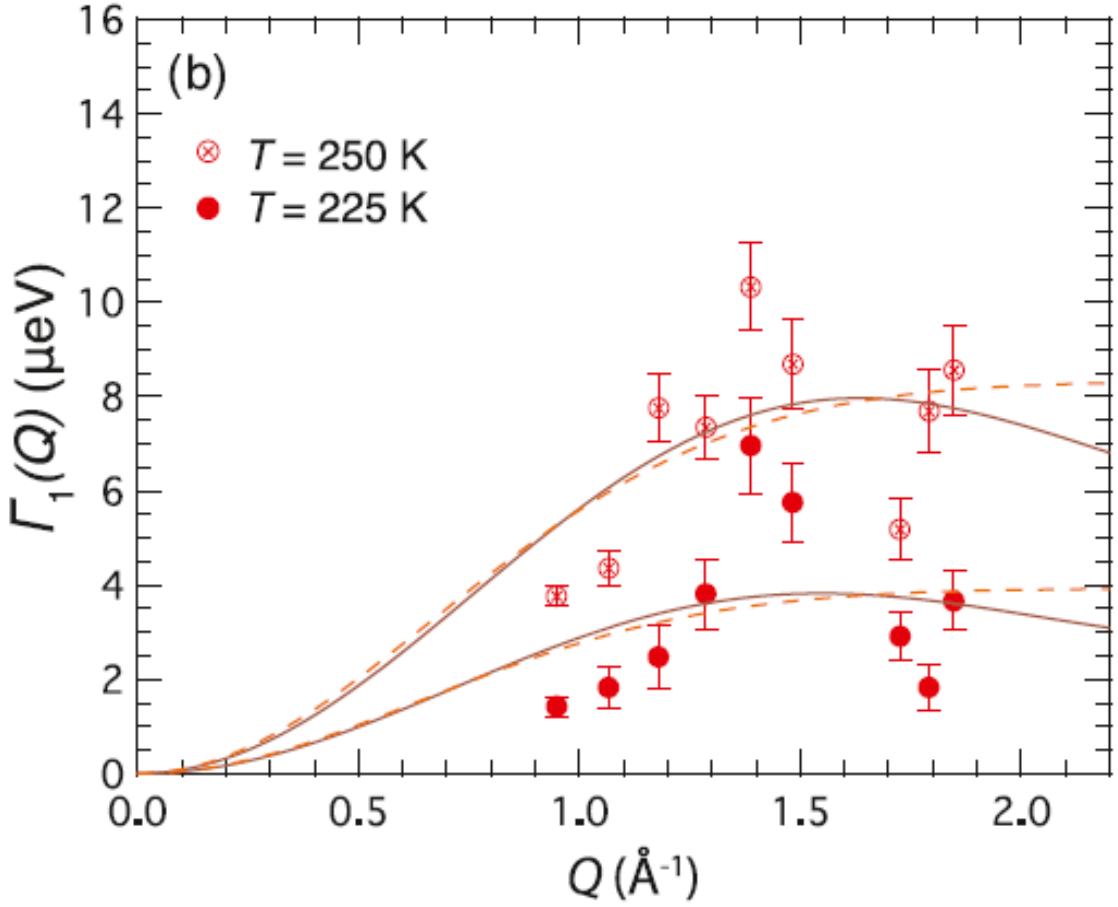
# Jump Diffusion Models




SS-RJD

J. Teixeira, et al., "Experimental determination of the nature of diffusive motions of water molecules at low temperatures" *PRA*, **31**, 1913 (1985)

# Jump Diffusion Models



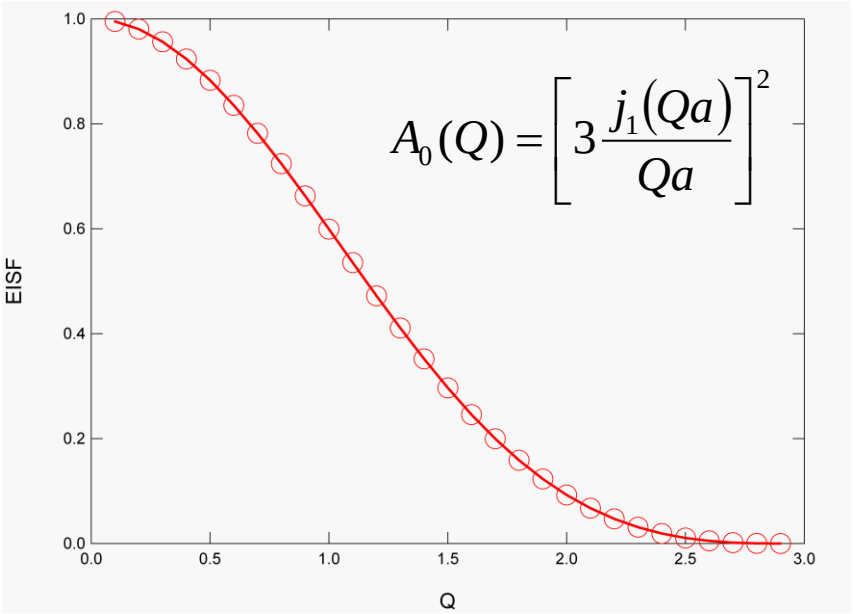

— CE-RJD
--- Gaussian distribution

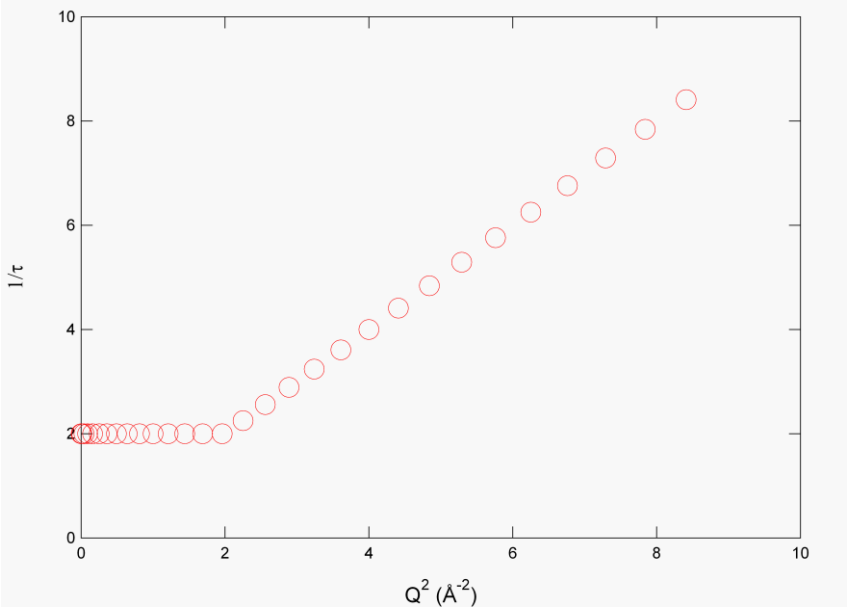
K. Eklöf-Österberg, et al., "Dynamics of Hydride Ions in Metal Hydride-Reduced BaTiO3 Samples Investigated with Quasielastic Neutron Scattering" *JPCC*, **123**, 2019 (2019)

# EISF for Translational Dynamics

- Dynamics in Confinement:

$$S^{CM}(Q,t) = A_0(Q) + \sum_{l=1} A_l(Q) F(Q,t)$$

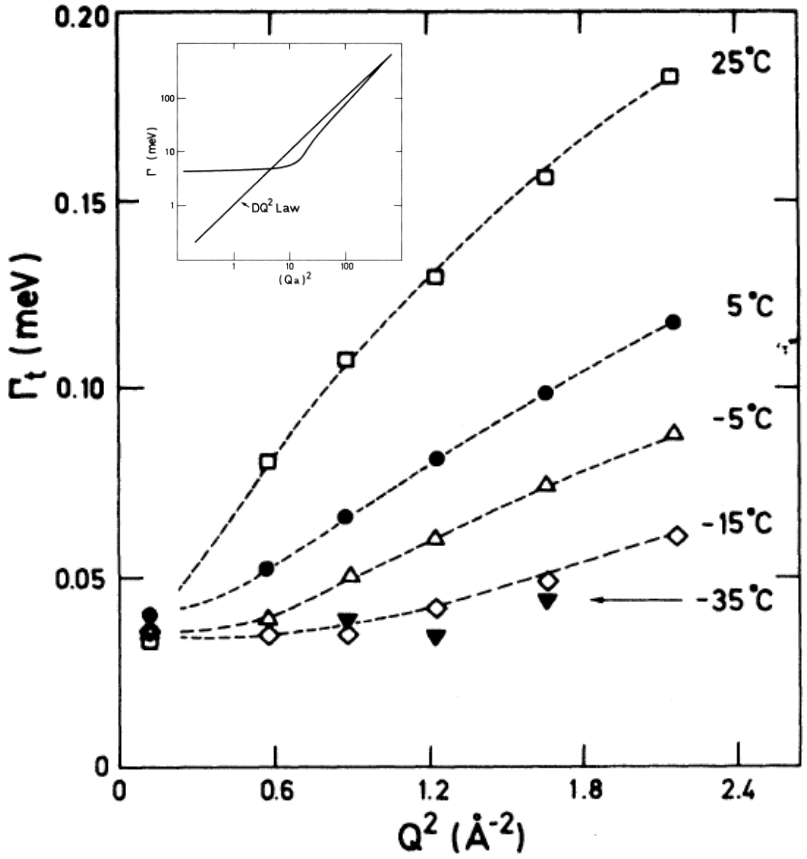


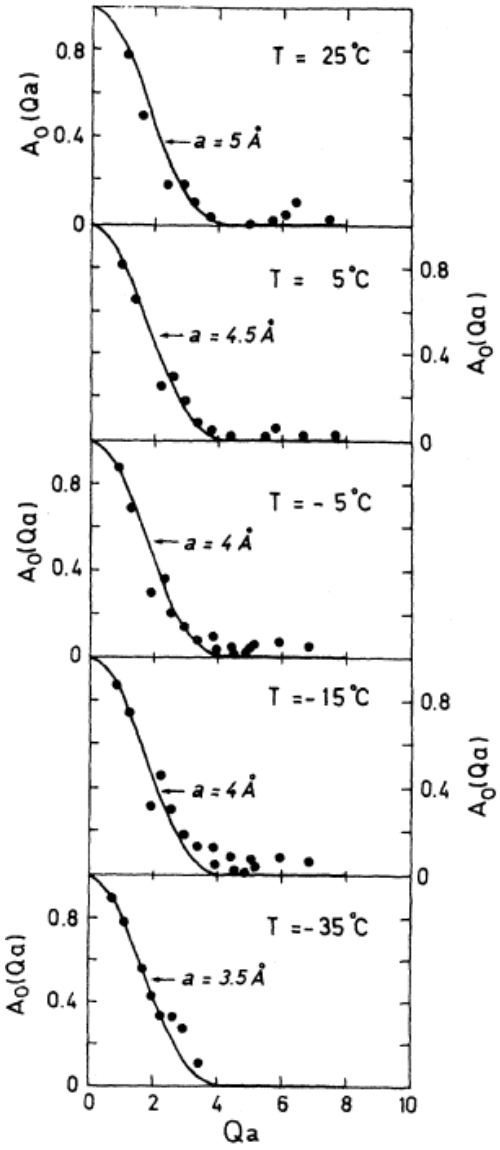




Volino F. and Dianoux A.J., *Mol. Phys.*, **41,** 271 (1980 ).

# Dynamics in confinement

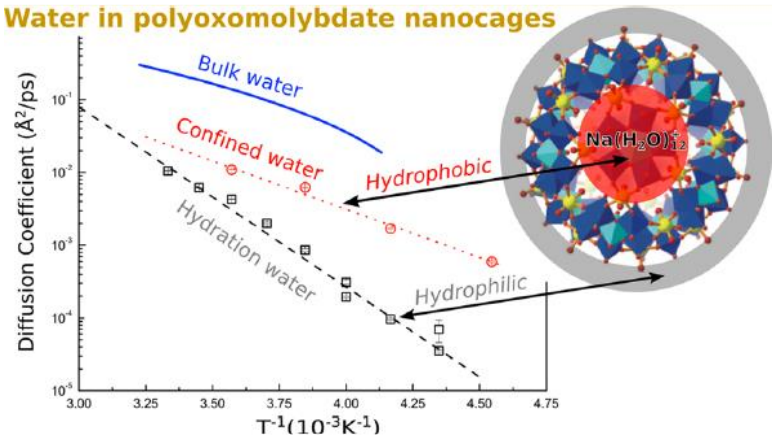
$$S_h(Q,\omega) = A\delta(\omega) + x\{B(Q)\delta(\omega) + [1-B(Q)]L_1(\omega,\Gamma_t)\} + \mathcal{B}$$

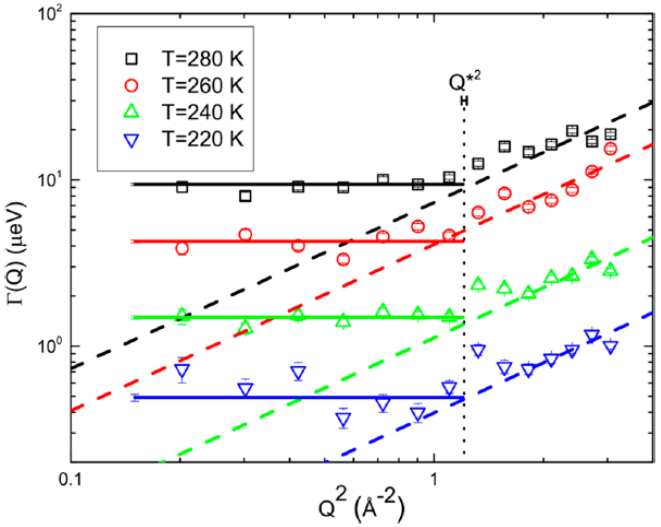



J.-M. Zanotti, et al., "Single-particle dynamics of water molecules in confined space" *PRE*, **51**, 4558 (1995)

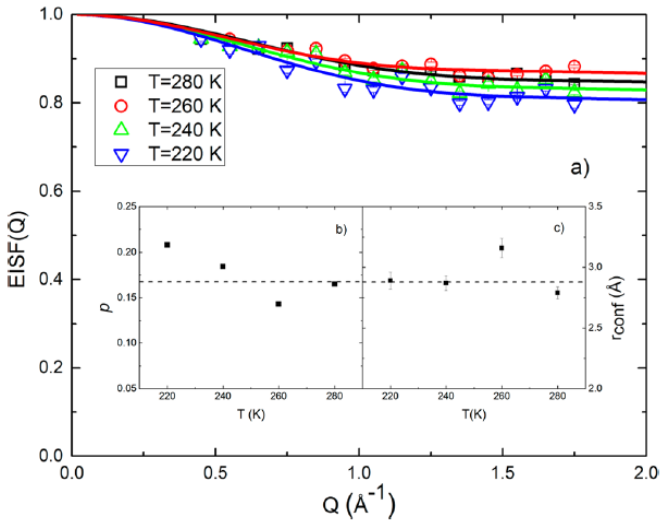
# Dynamics in confinement




Faraone, et al., "Incoherent Quasielastic Neutron Scattering Study of the Relaxation Dynamics in Molybdenum-Oxide Keplerate-Type Nanocages" *JPCC*, **118**, 13300 (2014)

$$\mathrm{EISF}(Q) = \frac{q\cdot\mathrm{EISF}_{\mathrm{CH_3}}(Q) + (1-q)[p\cdot\mathrm{EISF}_{\mathrm{VD}}(Q) + (1-p)]}{q\cdot\mathrm{EISF}_{\mathrm{CH_3}}(Q) + (1-q)}$$



# Vibrational Dynamics

It is very fast… too fast to be seen by QENS.

The only effect is a reduction of the QENS total intensity which is usually called the Debye-Waller factor.

$$S^V(Q,E) = exp(-Q^2\langle u^2\rangle)$$

Assuming that the scatterers behave as harmonic oscillators, connected by a spring we can obtain an effective force constant by measuring $\langle u^2\rangle$ as a function of temperature. This method has been applied, for example, initially to proteins.

$$\langle k'\rangle = 2k_B\left(\frac{d\langle u^2(T)\rangle}{dT}\right)^{-1}$$

# Stretched exponential

Simple relaxation processes can be described by an exponential decay. However, non-exponentiality can be observed in complex phenomena, such as the structural relaxation on approaching the glass transition, or because of the presence of inhomogeneities which introduce a distribution of relaxation processes.

The stretched exponential function, or Kohlrausch-Williams-Watts (KWW), is a common phenomenological approach to deal with these cases.

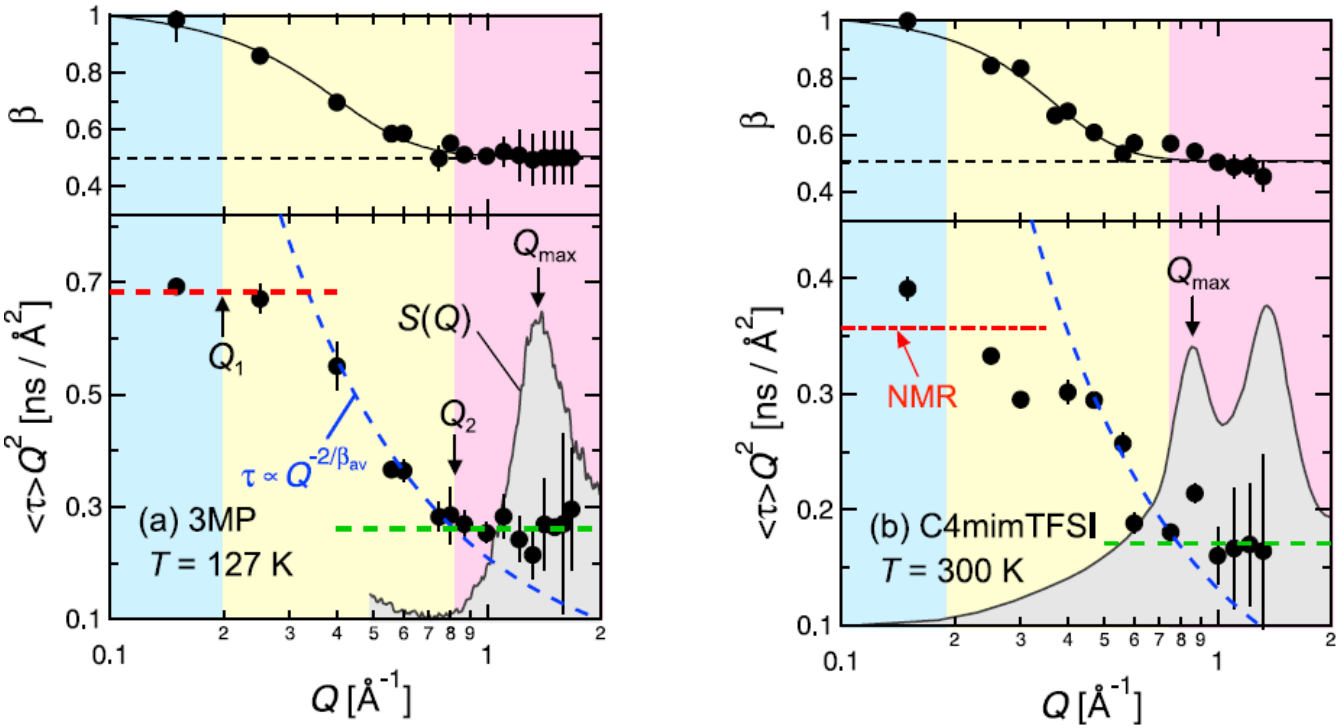
$$KWW(t) = exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \qquad \beta \leq 1$$

$$KWW(t) = exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] = \int G(\tau')exp\left(-\frac{t}{\tau'}\right)d\tau'$$

$$\langle\tau\rangle = \int exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]dt = \frac{\tau}{\beta}\Gamma\left(\frac{1}{\beta}\right)$$

# Homogeneous vs Heterogeneous

Not always the stretched exponential originates from a distribution of relaxation times. The relaxation process might inherently be non-exponential because of its complexity. The Q dependence of $\tau$ can provide some insight. For the translational dynamics the homogeneous versus heterogeneous scenario predict different Q dependence.

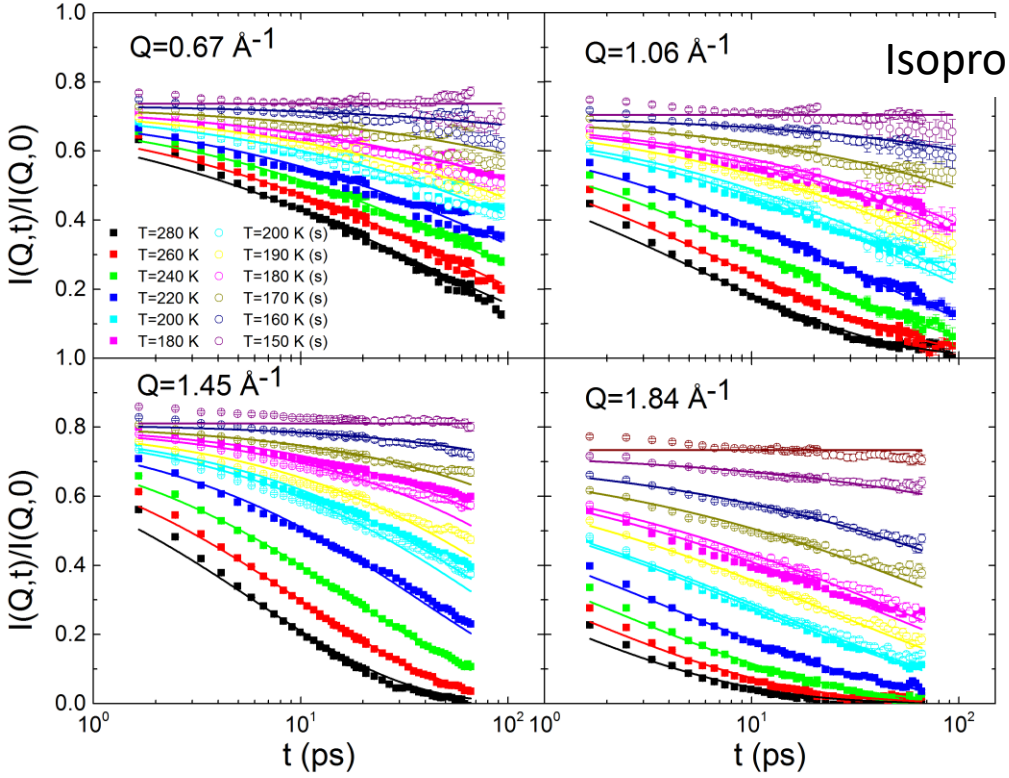



M. Kofu, et al., "Two inherent crossovers of the diffusion process in glass-forming liquids" *PRE*, **98**, 042601 (2018)

# Fourier Transform methods

There is no analytical Fourier transform of the stretched exponential function. A data fitting of QENS data has to rely on numerical methods to Fourier transform the fitting function.

Alternatively, the experimental data can be Fourier transformed to the time domain. This method is especially valuable if data with different resolutions are used in conjunction.



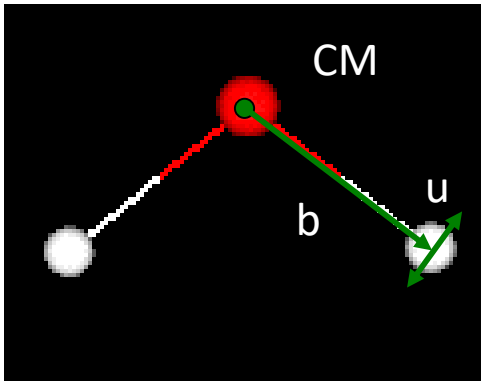

$$\frac{I(Q,t)}{I(Q,0)} = \mathrm{A}(Q)exp\left[-\left(\frac{t}{\tau(Q,T)}\right)^{\beta(Q)}\right]$$

# The Decoupling Approximation

Different types of motions might be present at the same time.

Let's consider, for example, the case of water:

$$S(Q,E) = S^{H}_{incoh}(Q,E) = FT\left\{\left\langle \exp\left[iQ\left[r_i(t) - r_i(0)\right]\right]\right\rangle\right\}$$



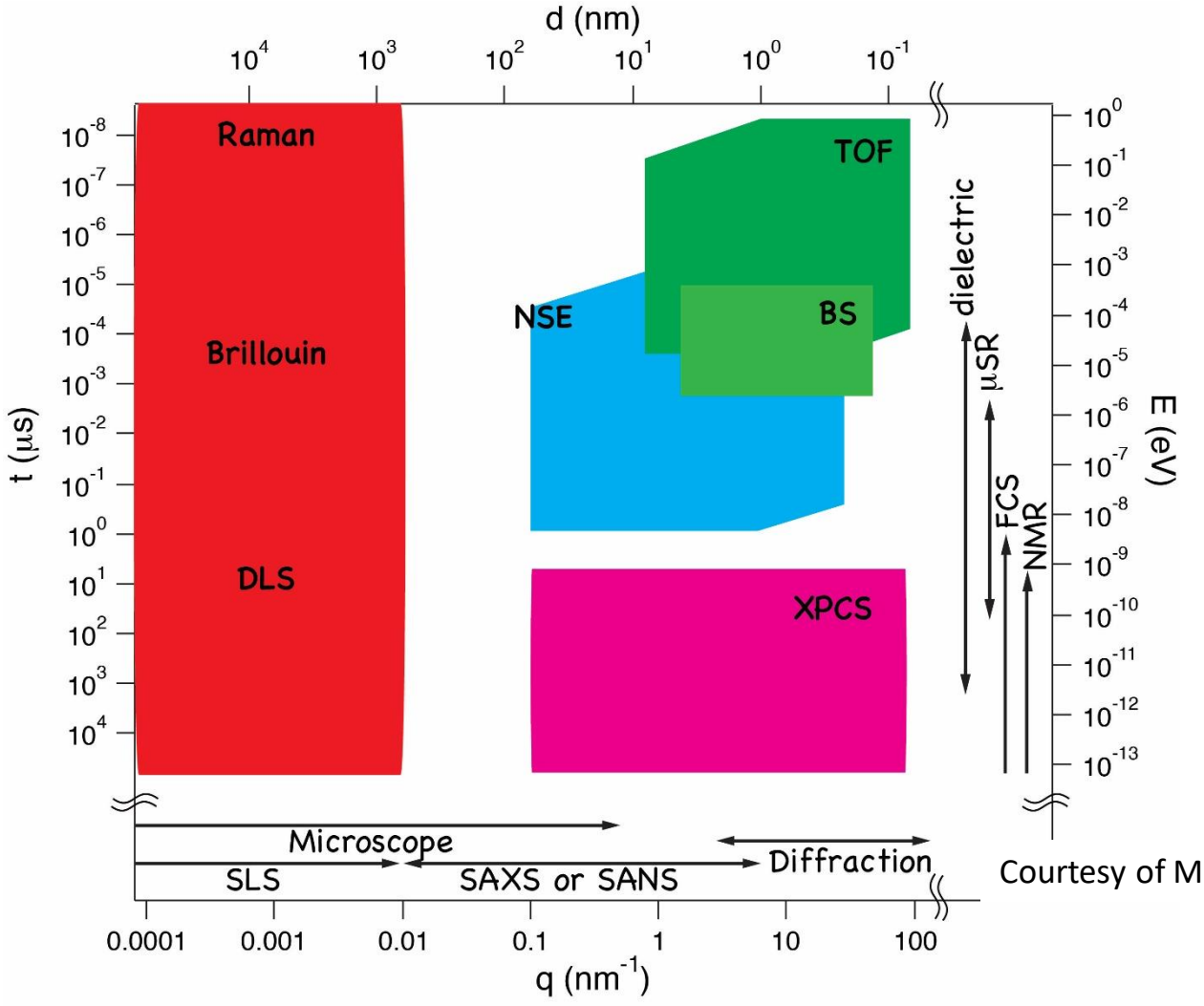

$$\underline{r} = \underline{r}_{CM} + \underline{b} + \underline{u}$$

Assuming statistical independence of the motions:

$$\begin{aligned} S^{H}_{incoh}(Q,E) &= FT\left\{\left\langle \exp\left[iQ\left[r_{CM\,i}(t) - r_{CM\,i}(0)\right]\right]\exp\left[i\underline{Q}\left[\underline{b}_i(t) - \underline{b}_i(0)\right]\right]\exp\left[iQ\left[u_i(t) - u_i(0)\right]\right]\right\rangle\right\} \\ &= FT\left\{\left\langle \exp\left[iQ\left[r_{CM\,i}(t) - r_{CM\,i}(0)\right]\right]\right\rangle\left\langle \exp\left[i\underline{Q}\left[\underline{b}_i(t) - \underline{b}_i(0)\right]\right]\right\rangle\left\langle \exp\left[iQ\left[u_i(t) - u_i(0)\right]\right]\right\rangle\right\} = \\ &= FT\left\{S^{CM}(Q,t)S^{R}(Q,t)S^{V}(Q,t)\right\} = S^{CM}(Q,E)\otimes S^{R}(Q,E)\otimes S^{V}(Q,E) \end{aligned}$$

# Instrumental Considerations

# Instrumentation and timescales




Courtesy of Michihiro Nagao

# Resolution

$$\frac{d^2\sigma}{d\Omega dE} = N_0 \frac{k_s}{k_0} S(Q,E) \otimes R(Q,E)$$

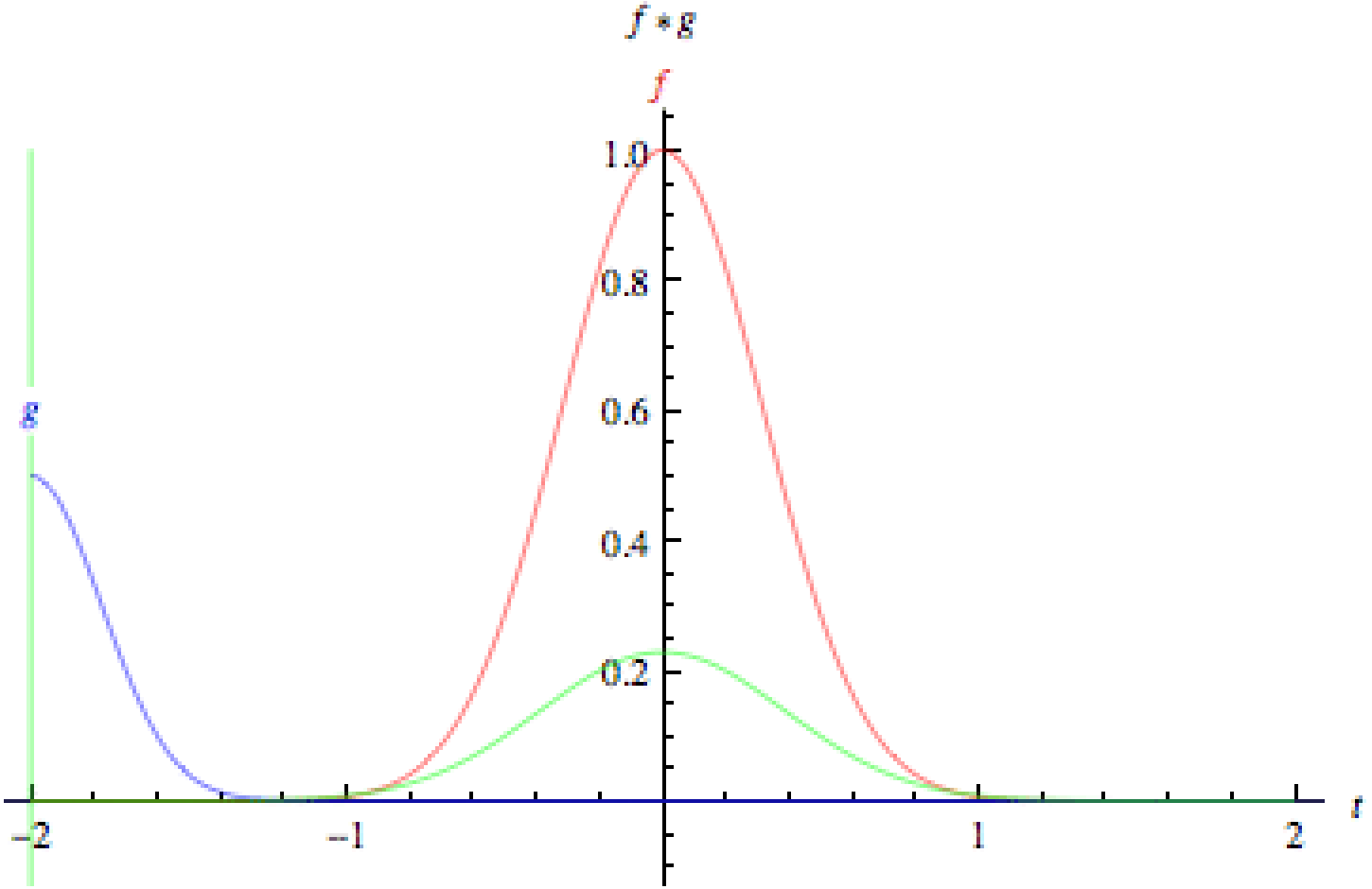
$$\frac{d^2\sigma}{d\Omega dE} = N_0 \frac{k_s}{k_0} \int_{-\infty}^{+\infty} S(Q,E-E') R(Q,E') dE'$$

The double differential scattering cross section at each energy value is given by the average of the ideal (what it would be obtained by a perfect instrument) dynamic structure factor around the energy value of interest, weighted by the resolution function.

The Convolution Product:

- Broadens Sharp Features.
- Smears Sudden Changes.

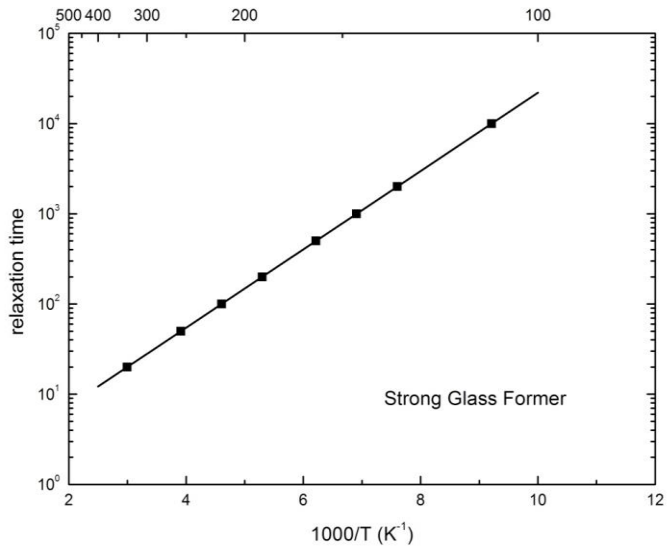
# Convolution



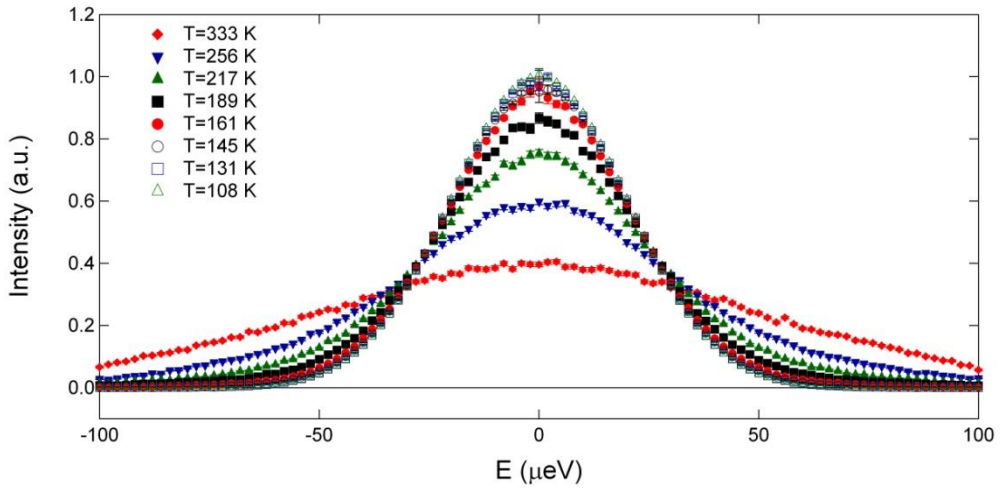

http://mathworld.wolfram.com/Convolution.html

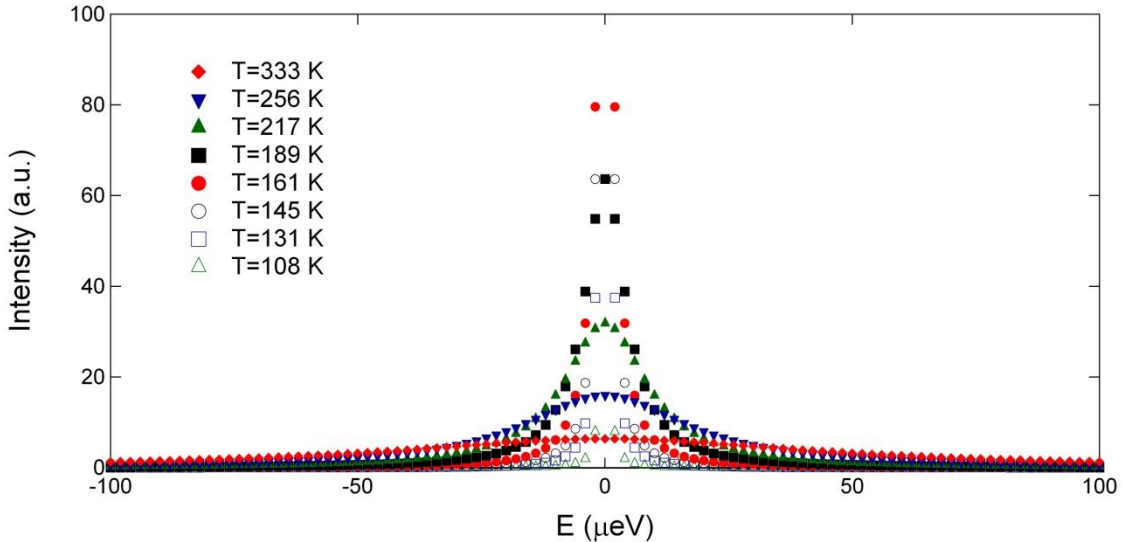
# Resolution

$$S^{Meas}(Q,E) = S(Q,E) \otimes R(Q,E)$$



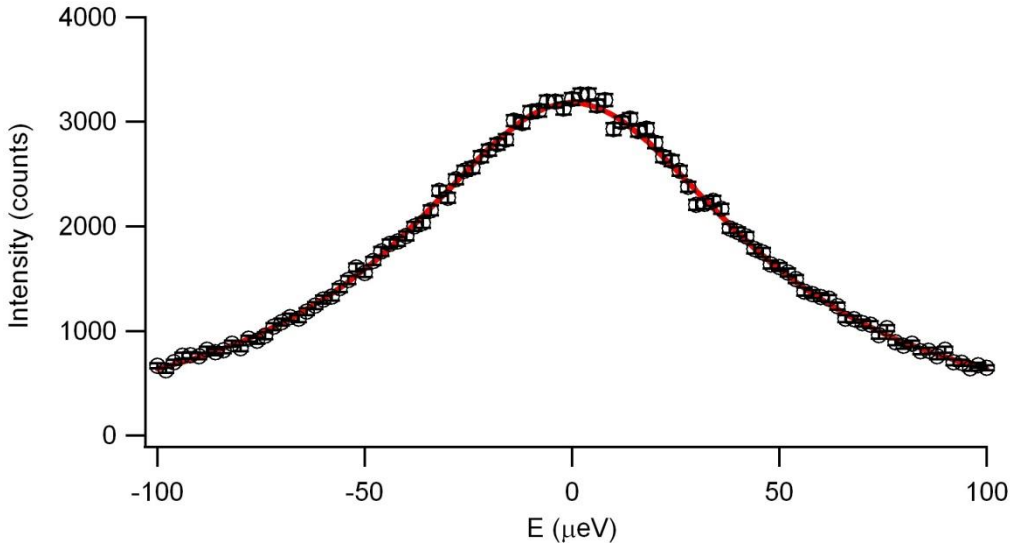

Experimental



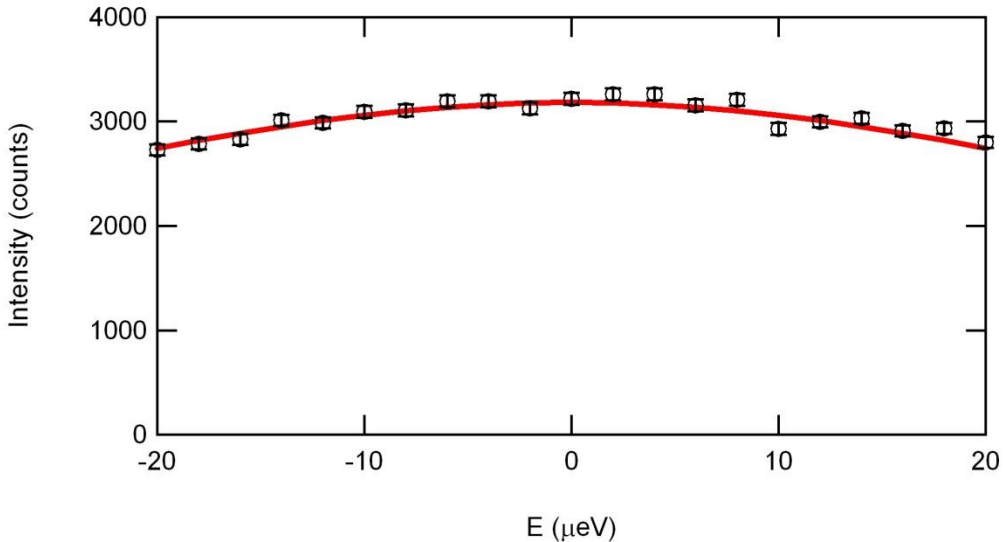




Ideal

# Dynamic Window




Large Dynamic Window

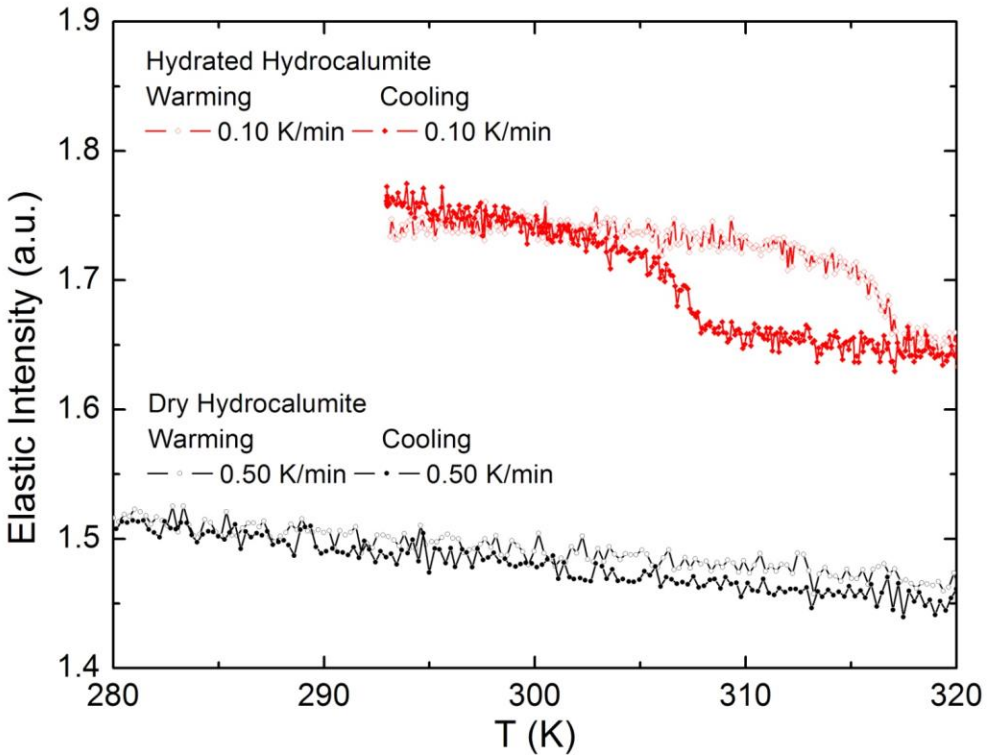



Small Dynamic Window

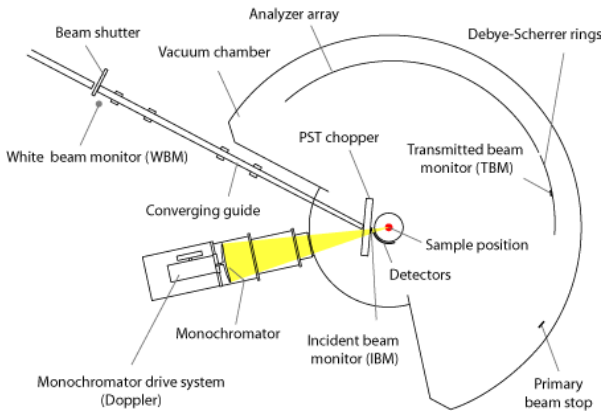
# Elastic Scattering S(Q,E≅0)

$$S^{Meas}(Q, E = 0) = \int S(Q,E)R(Q,E)dE$$

Measurement of the elastic intensity as a function of temperature is a common technique. It resembles a DSC scan and is very good for locating what temperatures do the dynamics enter the time window of the neutron spectrometer?

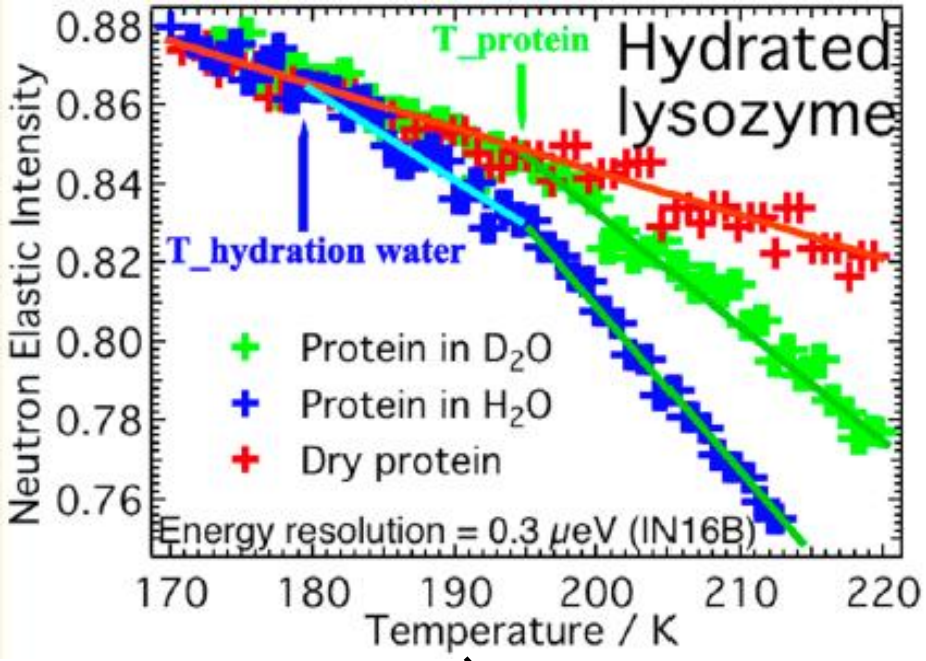


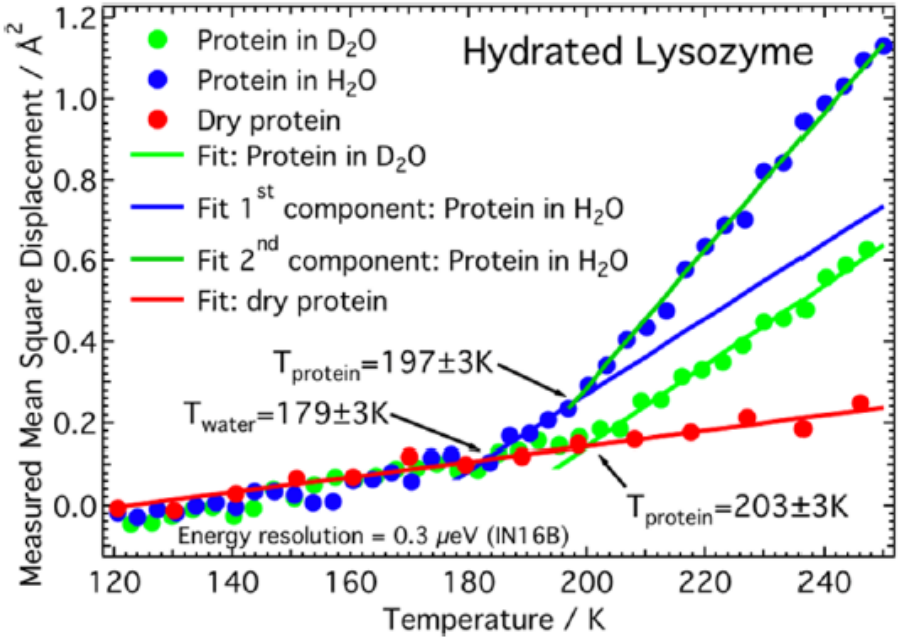

In the Elastic Scan Mode the monochromator does not move



# Elastic Scattering S(Q,E≅0)

Elastic scan measurements are commonly performed on biologically related samples




$$\langle r^2 \rangle = \frac{-6\ln[S(Q, E \approx 0)]}{Q^2}$$

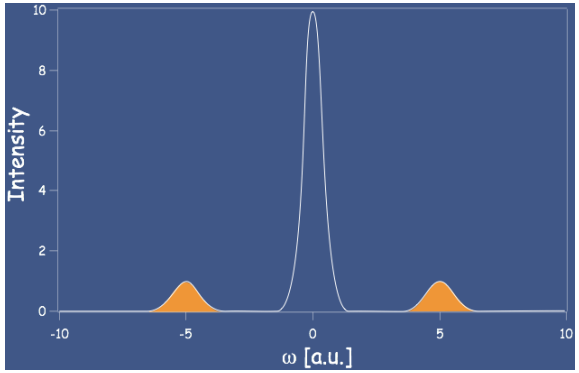
A. Benedetto, "Low-Temperature Decoupling of Water and Protein Dynamics Measured by Neutron Scattering" *JPCL*, **8**, 4883 (2017)

# Neutron Spin Echo Spectroscopy

# Energy and Time Domain

NSE works in the TIME domain

NSE measures the Normalized Intermediate Scattering Function: *I(Q,t)/I(Q,0)*

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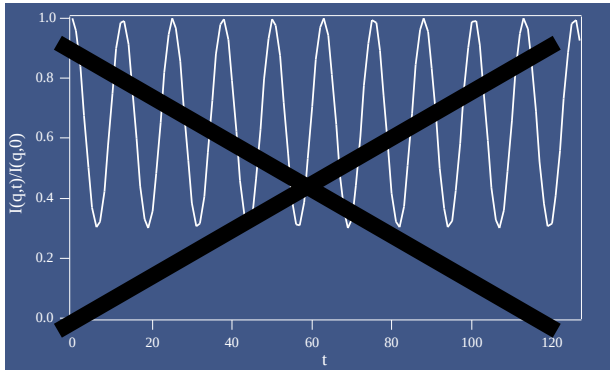


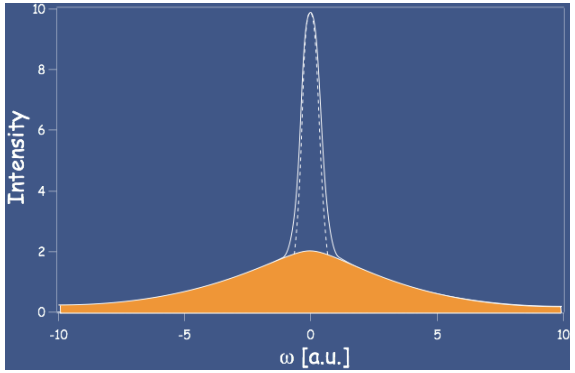


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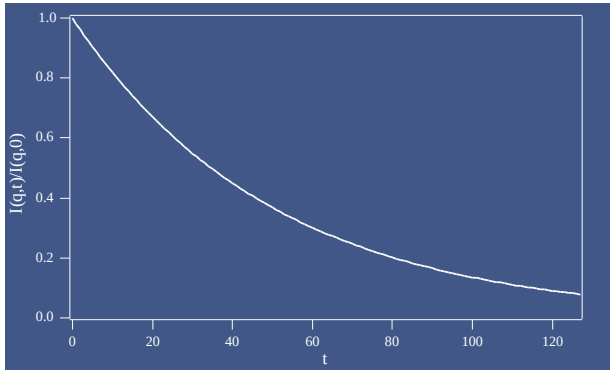
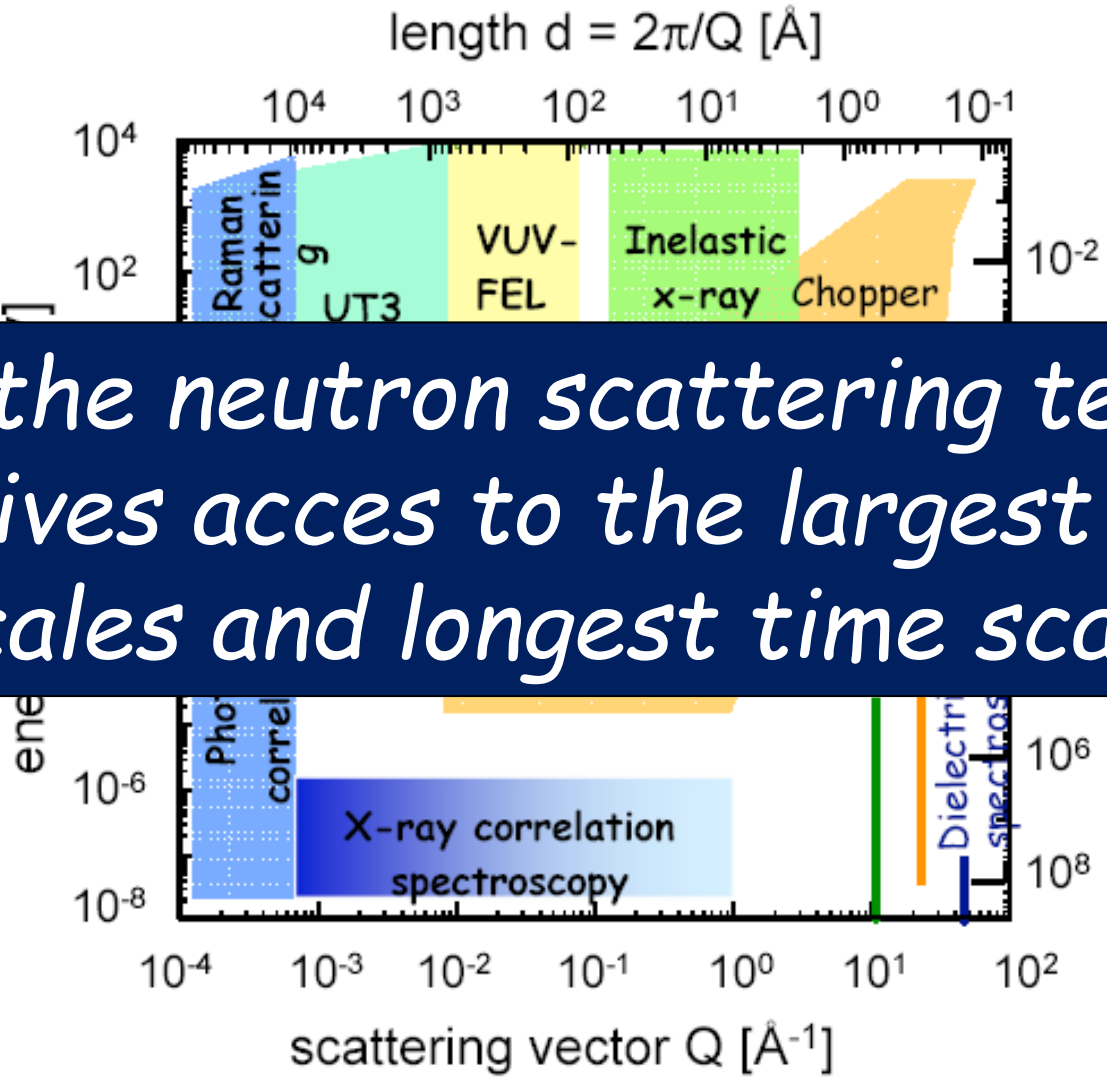



NSE Deals Almost Exclusively with Quasielastic Scattering

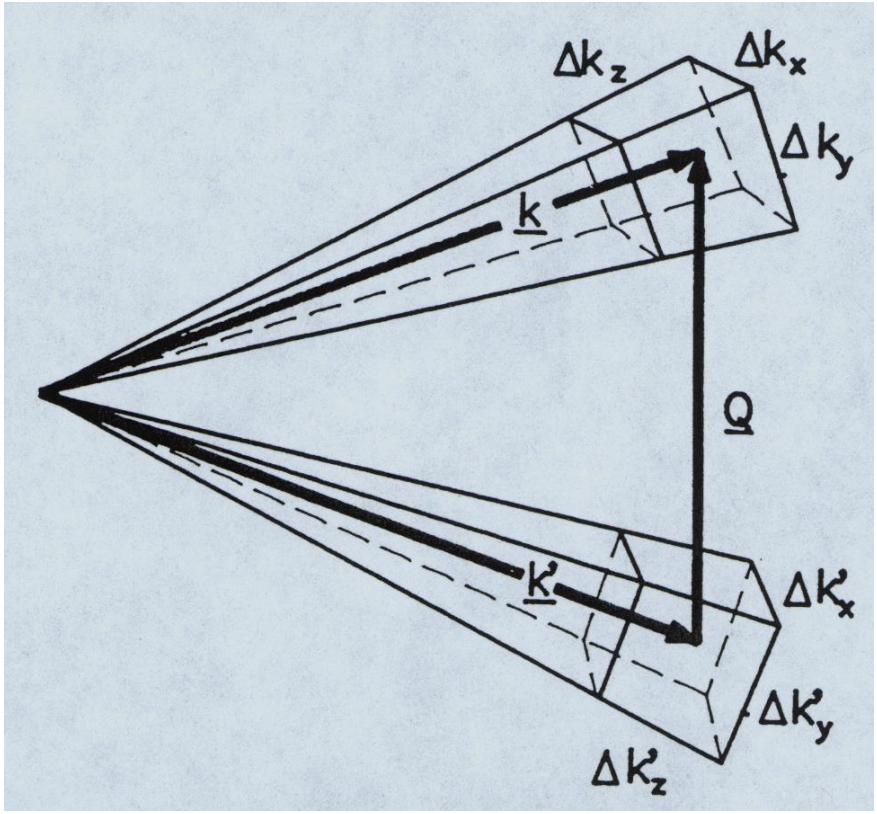
# Dynamic Neutron Scattering




NSE is the neutron scattering techniques that gives acces to the largest length-scales and longest time scales

# Instrumental Resolution

- Uncertainties in the neutron wavelength & direction of travel imply that *Q* and *E* can only be defined with a certain precision
- When the box-like resolution volumes in the figure are convolved, the overall resolution is Gaussian (central limit theorem) and has an elliptical shape in *(Q,E)* space
- The total signal in a scattering experiment is proportional to the phase space volume within the elliptical resolution volume




The better the resolution, the smaller the resolution volume and the lower the count rate

# The Idea of Neutron Spin Echo

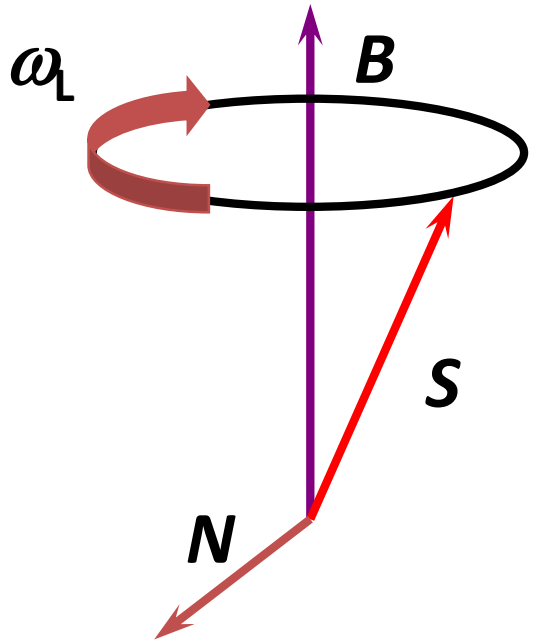
NSE Breaks the Relationship between Intensity & Resolution

- Traditional Instruments – define *both* incident & scattered wavevectors in order to define $E$ and $\underline{Q}$ accurately
- Traditional Instruments – use collimators, monochromators, choppers etc to define both $\underline{k}_i$ and $\underline{k}_f$
- NSE – measure the *difference* between appropriate components of $\underline{k}_i$ and $\underline{k}_f$ (original use: measure $\underline{k}_i - \underline{k}_f$ i.e. energy change)
- NSE – use the neutron's spin polarization to encode the difference between components of $\underline{k}_i$ and $\underline{k}_f$
- NSE – can use large beam divergence &/or poor monochromatization to increase signal intensity, while maintaining very good resolution

# Neutron Precession

## Neutron Properties

- Mass, $m_n = 1.675\times10^{-27}$ kg
- Spin, $S = 1/2$ [in units of $h/(2\pi)$]
- Gyromagnetic ratio $\gamma = g_n\mu_n/[h/(2\pi)] = 1.832\times10^{8}\ s^{-1}T^{-1}$ (29.164 MHz $T^{-1}$)

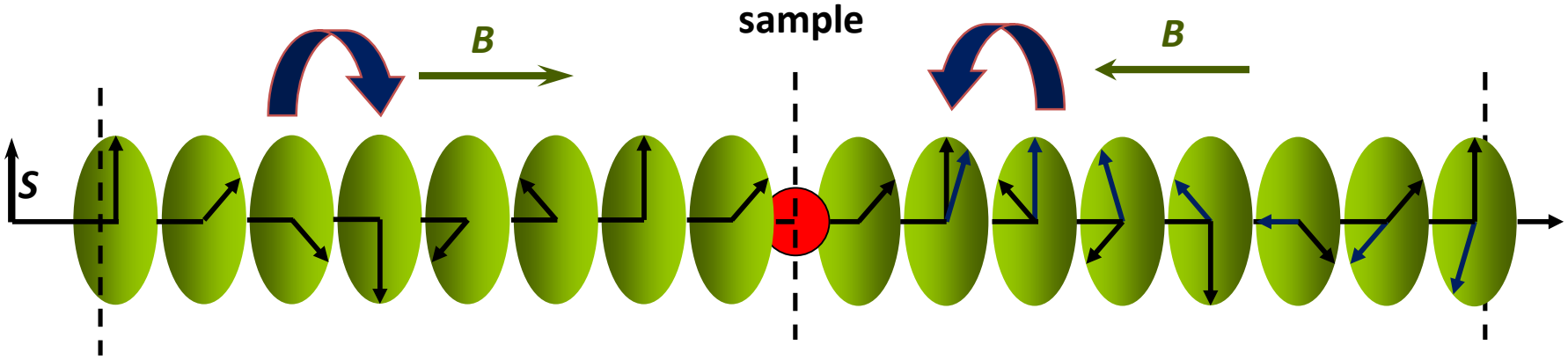



## In a Magnetic Field

- The neutron experiences a torque from a magnetic field $B$ perpendicular to its spin direction. ⟹ $N = S \times B$
- Precession with the Larmor frequency: ⟹ $\omega_L = \gamma B$

# Scattering Event: Single Neutron

- elastic scattering
- inelastic scattering



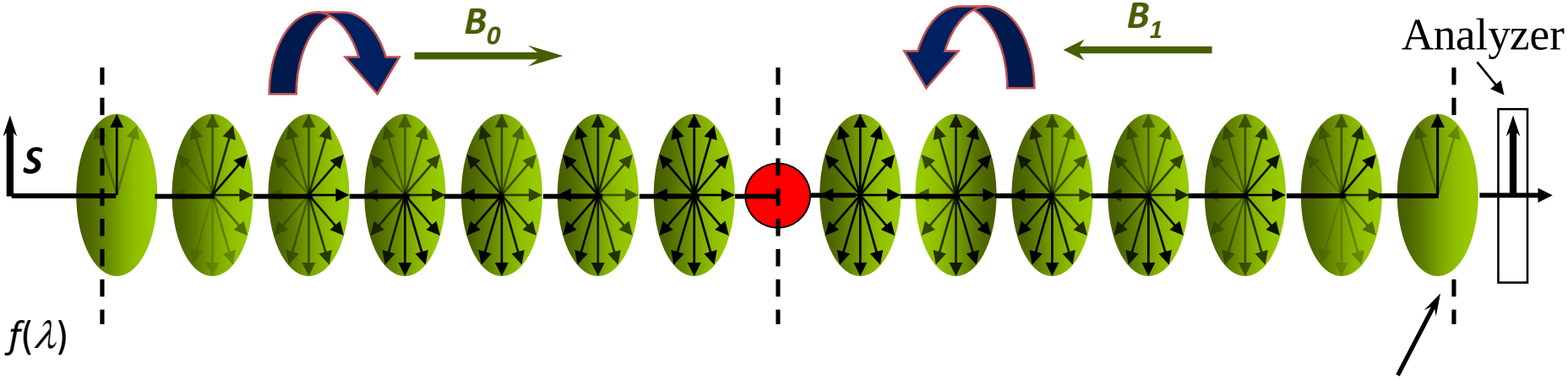

$$\varphi = \gamma \frac{\int Bdl}{v} \qquad \Delta\varphi = \gamma\left(\frac{1}{v} - \frac{1}{v'}\right)\int Bdl = \frac{\gamma\Delta v}{v^2}\int Bdl = \frac{m\lambda}{h}\frac{\gamma\Delta v}{v}\int Bdl$$

$$NT(\lambda) = \frac{1}{2\pi}\int \frac{\gamma Bm\lambda}{h} dl = \frac{\gamma m\lambda}{2\pi h}\int Bdl = 7370 \times J[T\cdot m]\times\lambda[\text{Å}]$$

$$J = \int Bdl$$

***J*** field integral. At NCNR: $J_{max}$ = 0.5 T.m
$NT$ ($\lambda$=8Å) ≈ $3\times10^5$

# Scattering Event: Neutron Beam




Elastic scattering

$$\bar{\varphi} = \left\langle \gamma \frac{\int B_0 dl}{v} - \gamma \frac{\int B_1 dl}{v} \right\rangle_{f(\lambda)}$$

$$P_x = 1 \qquad \bar{\varphi} = 0$$

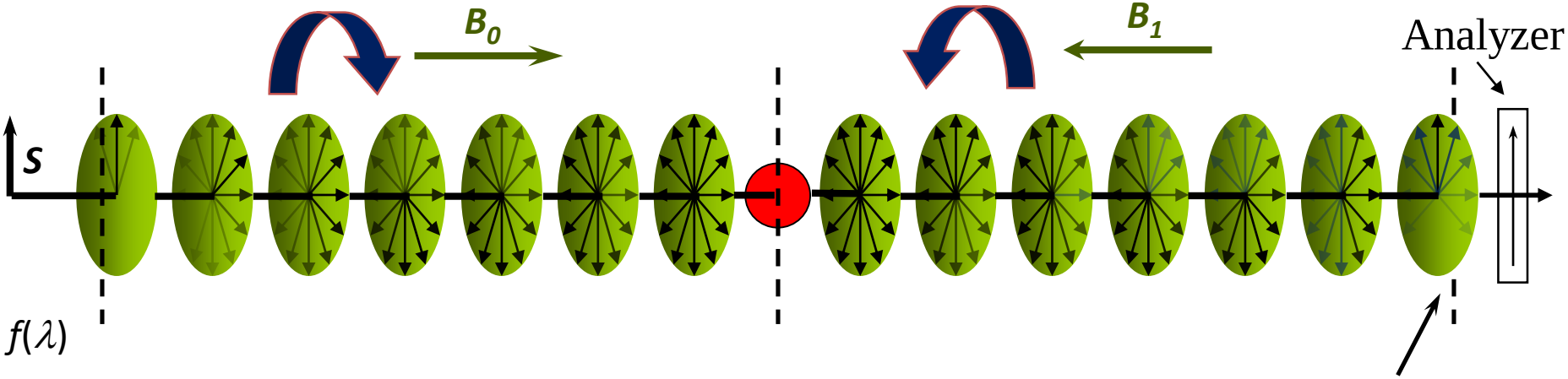
Again:
The measured quantity is the Polarization, i.e. the spin component along x: $P_x = \langle \cos\varphi(\lambda) \rangle$:

Echo Condition: $J_0 = J_1$

Note:

The requirement that φ=0 can be in some cases released. This treatment is valid for the most common case of Quasi-Elastic Scattering

# Scattering Event: Neutron Beam




Quasi-Elastic scattering

Again:
The measured quantity is the Polarization, i.e. the spin component along x: $P_x=\langle\cos\varphi(\lambda)\rangle$:

$$\varphi=\left\langle\gamma\frac{\int B_0 dl}{v(\lambda)}-\gamma\frac{\int B_1 dl}{v(\lambda)+\delta v}\right\rangle$$

Series Expansion in δλ and δJ

$$\varphi\approx\gamma\frac{m}{h}J_0\delta\lambda+\gamma\frac{m}{h}(J_0-J_1)\lambda$$

phase

$$\hbar\omega=\Delta E=\frac{h^2}{2m}\left[\frac{1}{\lambda^2}-\frac{1}{(\lambda+\delta\lambda)^2}\right]\approx\frac{h^2}{m}\frac{\delta\lambda}{\lambda^3}$$

$$\delta\lambda=\frac{\omega}{2\pi h}m\lambda^3$$

$$\varphi=\gamma\frac{m^2\lambda^3}{2\pi h^2}J_0\omega+\gamma\frac{m}{h}\cancel{(J_0-J_1)}\lambda$$

0 at the echo condition

# The Basic Equations of NSE

$$P_x = \langle \cos(\varphi) \rangle = \iint f(\lambda) S(Q,\omega) \cos\left[ \gamma \frac{m^2 \lambda^3}{2\pi\hbar^2} J_0 \omega + \gamma \frac{m}{h} (J_0 - J_1) \lambda \right] d\lambda d\omega$$

Even Function

$$P_x = \langle \cos(\varphi) \rangle = \int f(\lambda) \cos\left[ \gamma \frac{m}{h} (J_0 - J_1) \lambda \right] d\lambda \times \int S(Q,\omega) \cos\left[ \gamma \frac{m^2 \lambda^3}{2\pi\hbar^2} J_0 \omega \right] d\omega$$

FT of the wavelength distribution

Fourier time

$$t = \gamma \frac{m^2}{2\pi\hbar^2} J_0 \lambda^3$$

FT of the Dynamic Structure Factor

$$P_x\left(\Delta J^{ph_i}, Q, t\right) = P_s\left(\Delta J^{ph_i}\right) \int S(Q,\omega) \cos[\omega t] d\omega = P_s\left(\Delta J^{ph_i}\right) I(Q,t)$$

NSE measures the Fourier Transform of the Dynamic Structure Factor

# NSE principles: summary

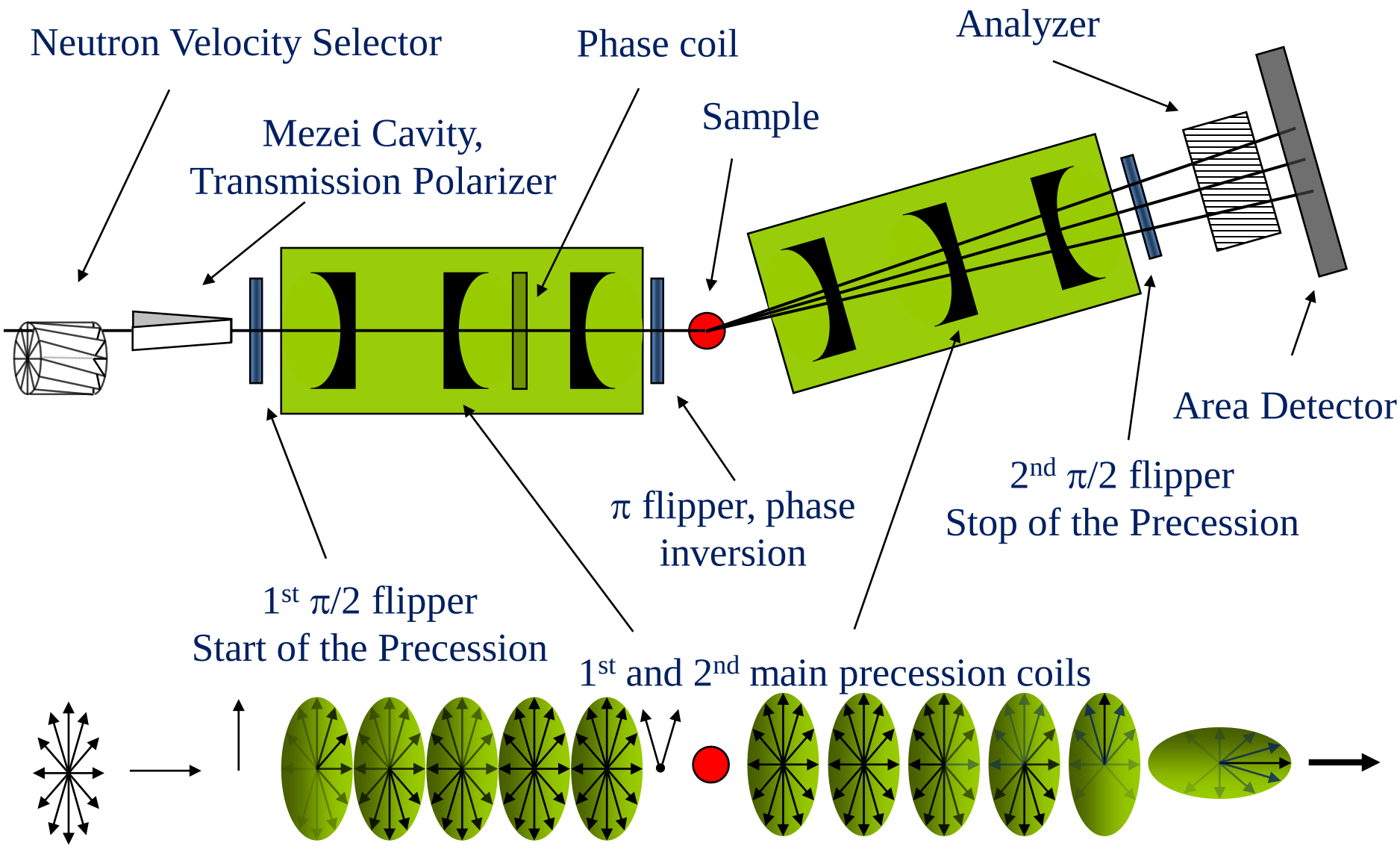
- Neutron Spin Echo Instruments are “machinery” which measure the Fourier transform of the Dynamic Structure Factor, $S(Q,\omega)$, i.e. the (normalized) Intermediate Scattering Function (ISF), $I(Q,t)/I(Q,0)$.
- The neutrons’ velocity is encoded into their spin state.

  - The neutron beam goes through two equals homogeneous magnetic field paths before and after the sample.

  - Within the magnetic fields each neutrons’ spin performs a precession at a speed determined by the field intensity.

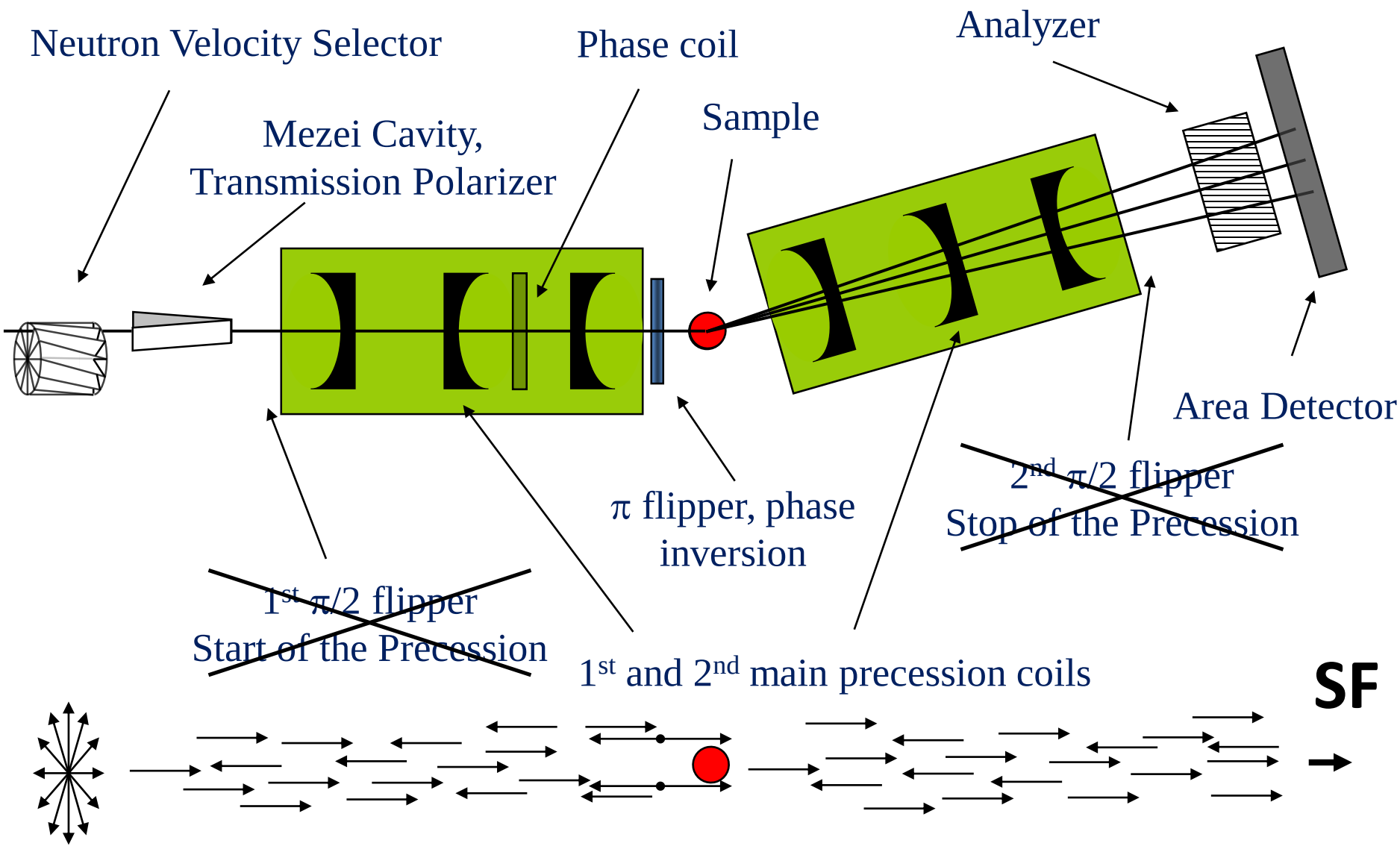
  - If the scattering event does not change the neutrons’ speed (elastic scattering), the initial polarization of the beam is recovered.
- The polarization of the scattered neutron beam is proportional to the ISF at a specific value of $t$ determined by the strength of the precession field (and by the incident neutron wavelength).

# NSE: Instrumental Setup

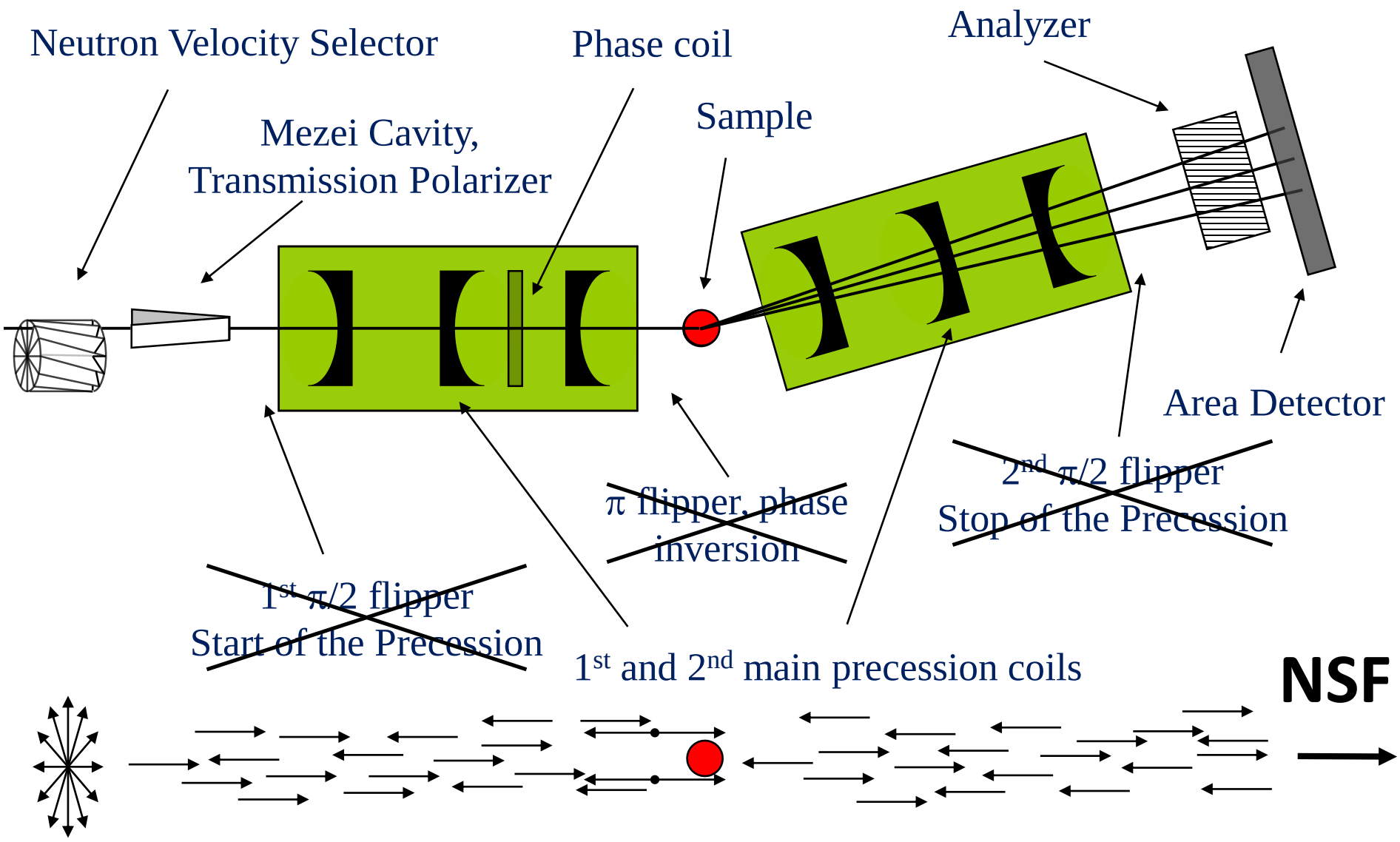


# NSE at NCNR

# Polarization Analysis



# Polarization Analysis



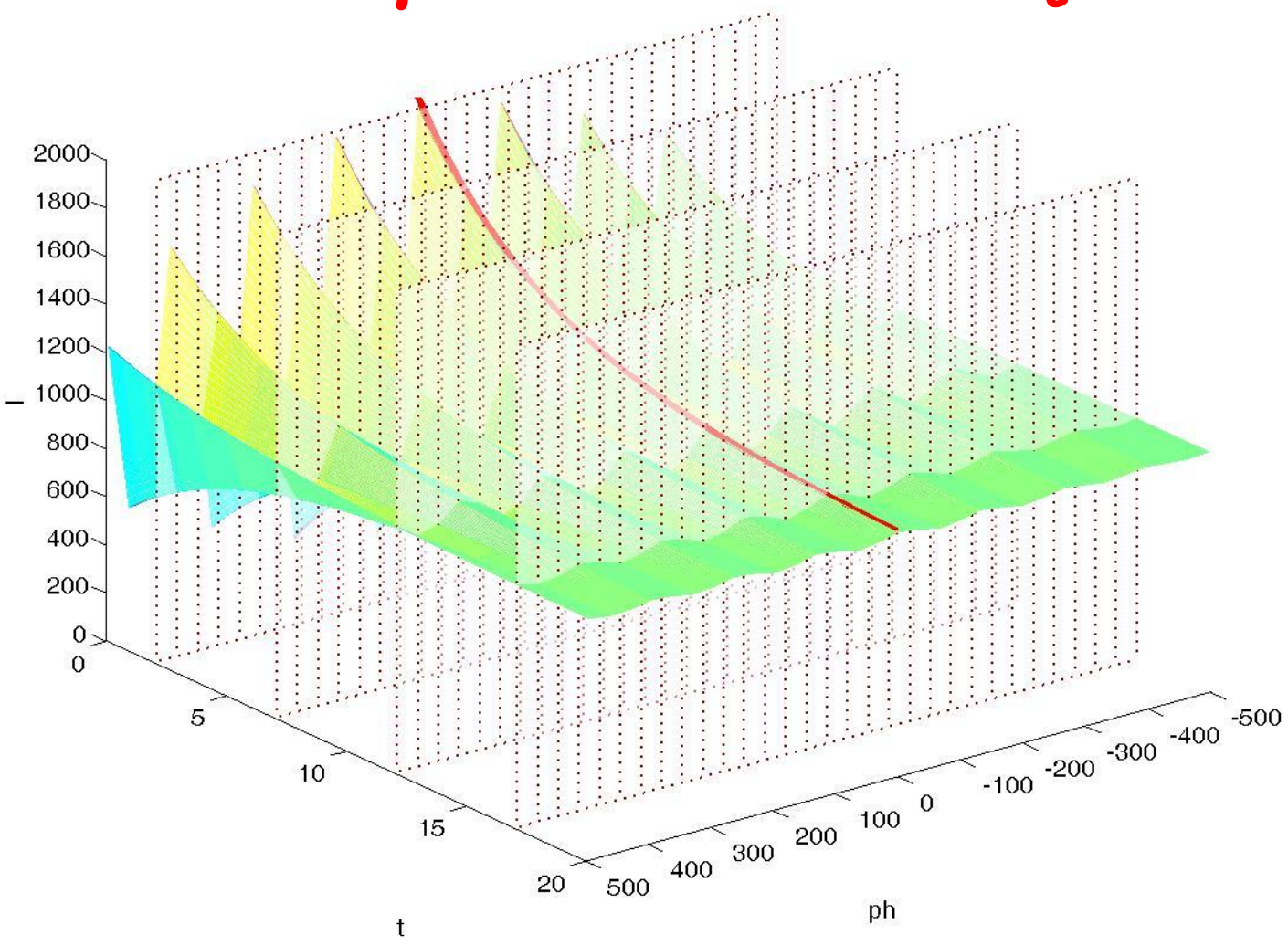
# The NSE Intermediate Scattering Function

NSE measures a combination of coherent and incoherent scattering:

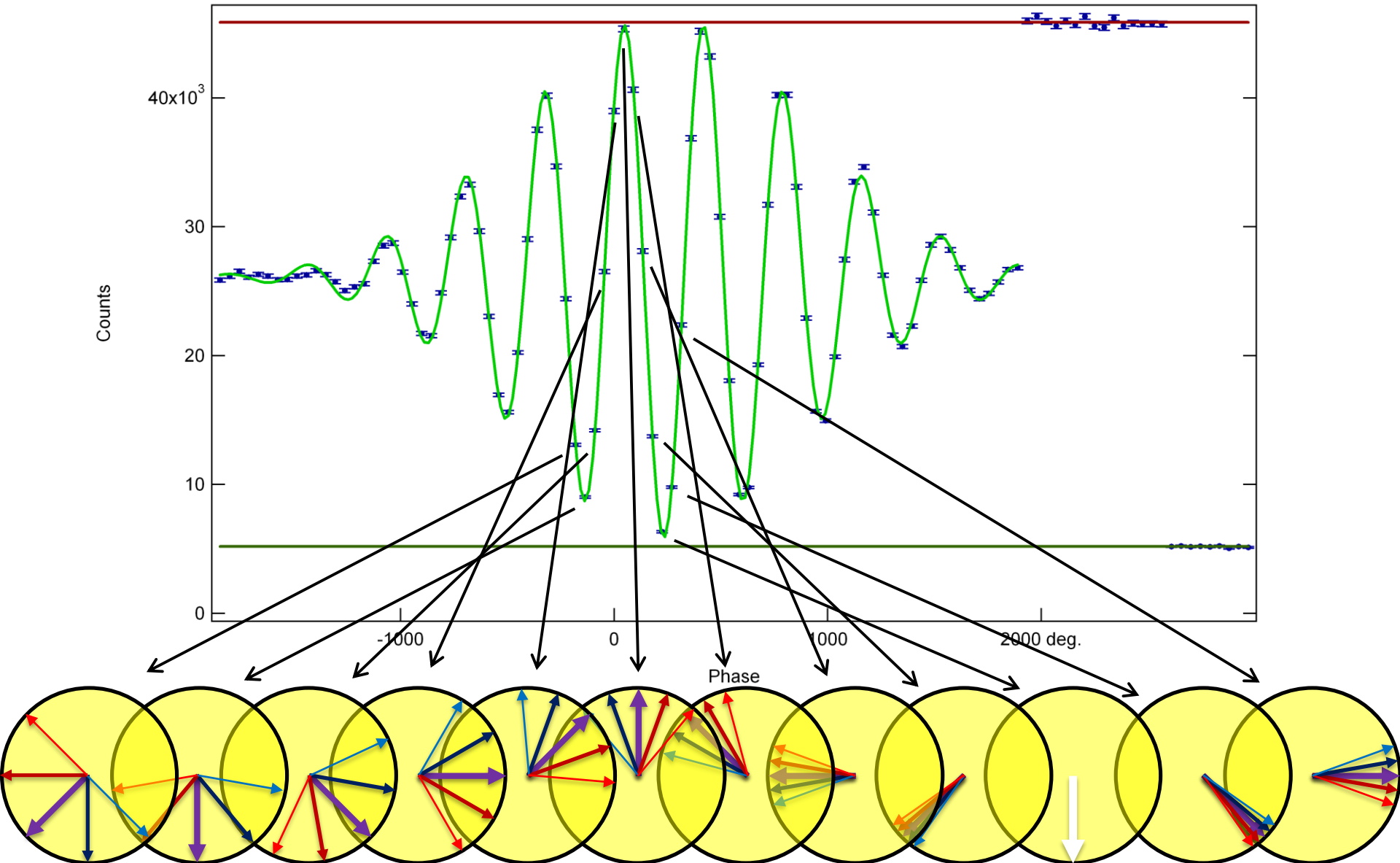
$$\frac{I^{NSE}(Q,t)}{I^{NSE}(Q,0)} = \frac{I^{coh}(Q,t) - \frac{1}{3} I^{inc}(Q,t)}{I^{coh}(Q,0) - \frac{1}{3} I^{inc}(Q,0)}$$

# NSE measurements

# Polarized Intensity vs phase and $F_t$



# Polarized Intensity vs phase



# Fitting the echo

$I_0$ Average Intensity

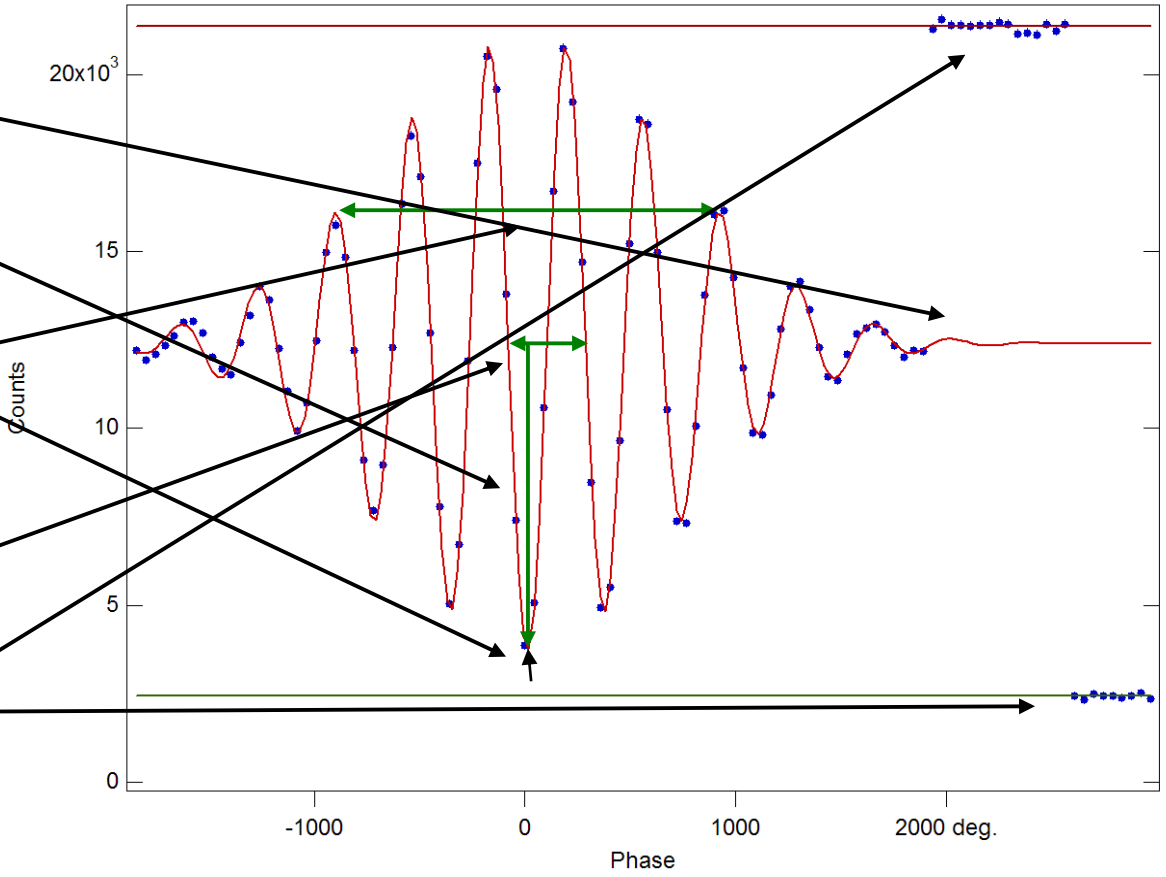
A Amplitude, related to I(Q,t)

$ph_0$ Echo point

σ Echo width, function of f(λ) width distribution

T Period, function of ⟨λ⟩

Static measurements (Up and Down) t=0 (J=0): ∫S(Q,ω)dω



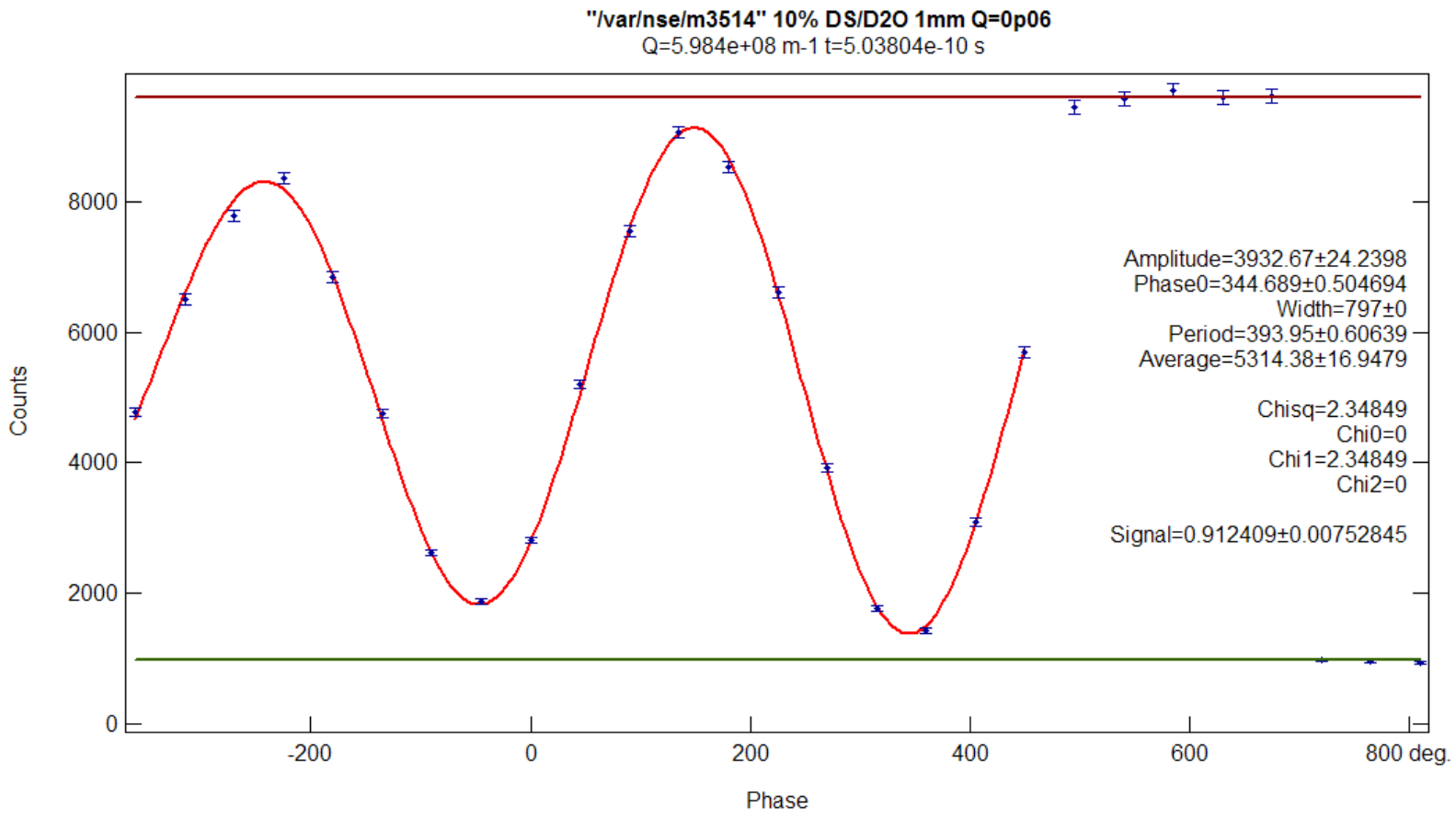

$$I^p = I_0 + A\exp\left[\frac{(ph-ph_0)^2}{2\sigma^2}\right]\cos\left[\frac{360}{T}(ph-ph_0)\right]$$

# The Physical Information is All in the Amplitude

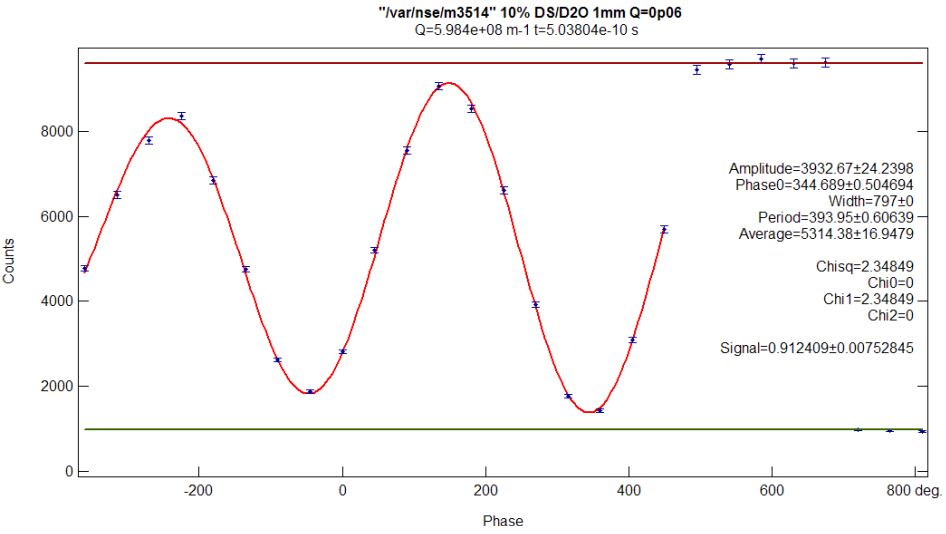
$$\frac{I(Q,t)}{I(Q)} \propto \frac{2A}{Up - Dwn}$$

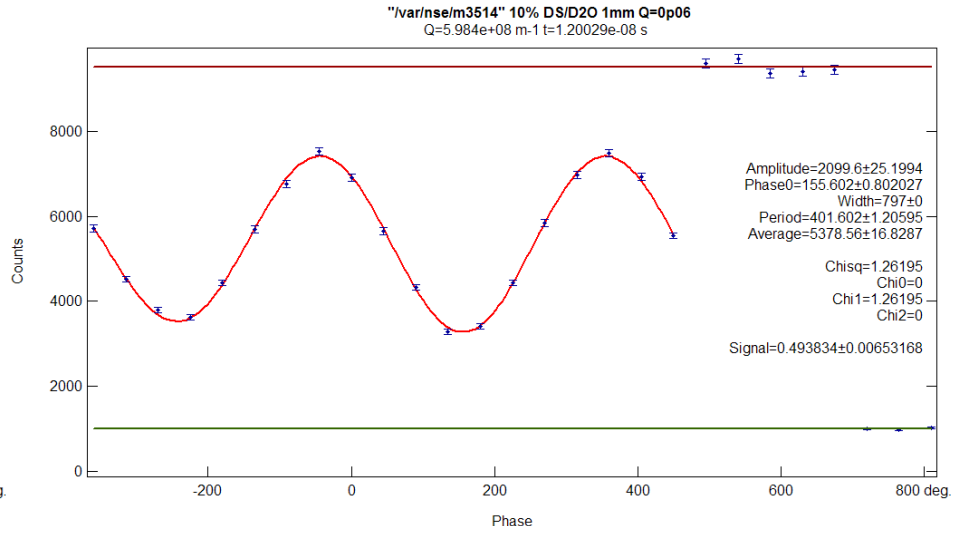
Incidentally, in this way, both polarization and detector efficiency effects are taken care off.

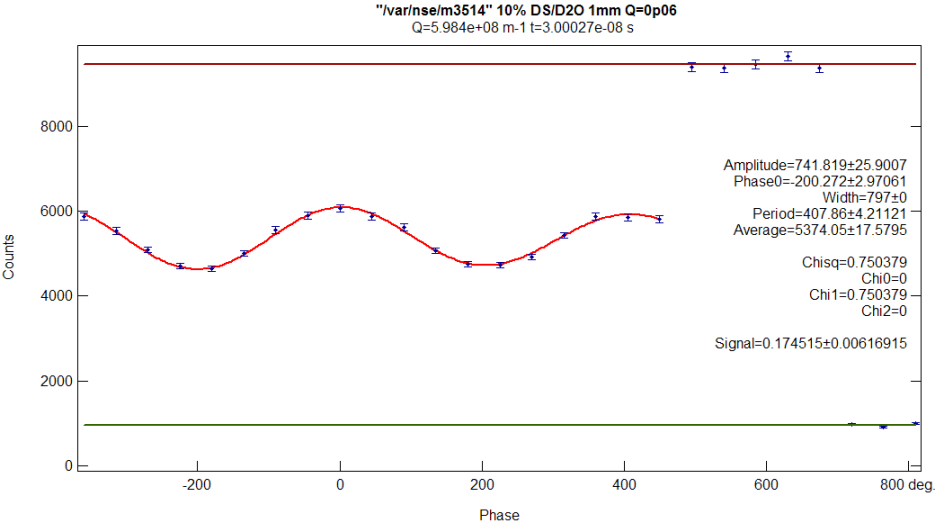
# A Small Portion of the Echo will do

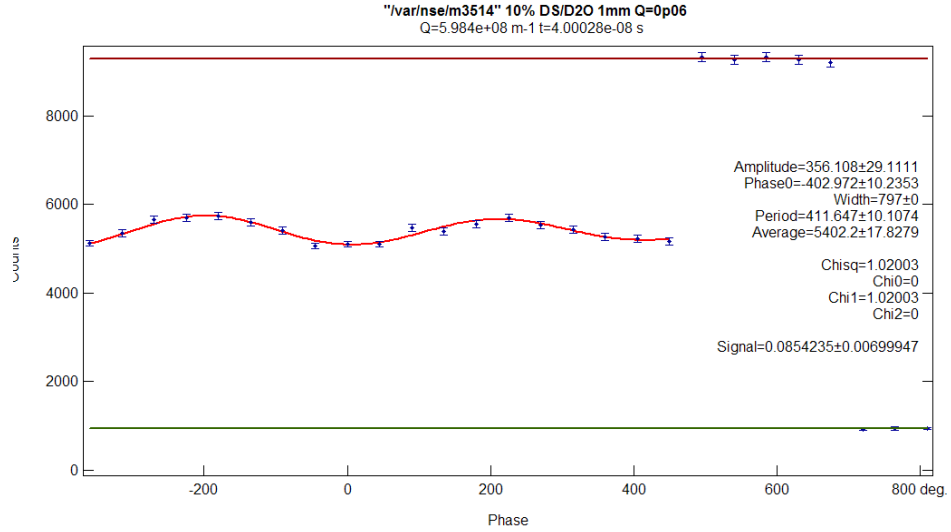


# Polarized Intensity vs $F_t$



# Resolution

Even for an elastic scatterer the echo signal will decrease with the increase of the Fourier time

- Inhomogeneities in the magnetic field will depolarize the beam.

Working in the time domain the Resolution can be divided out

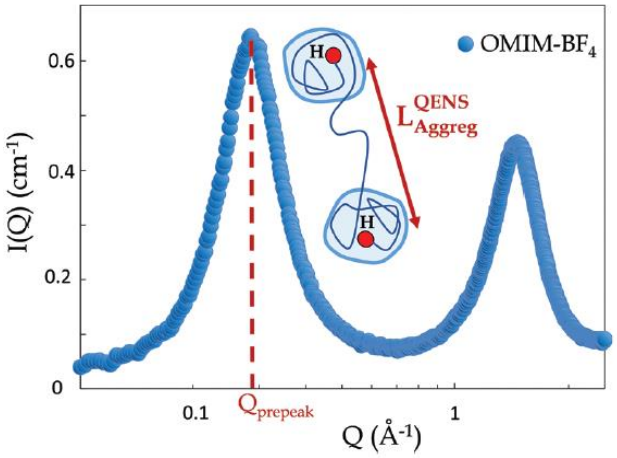
# Take home messages

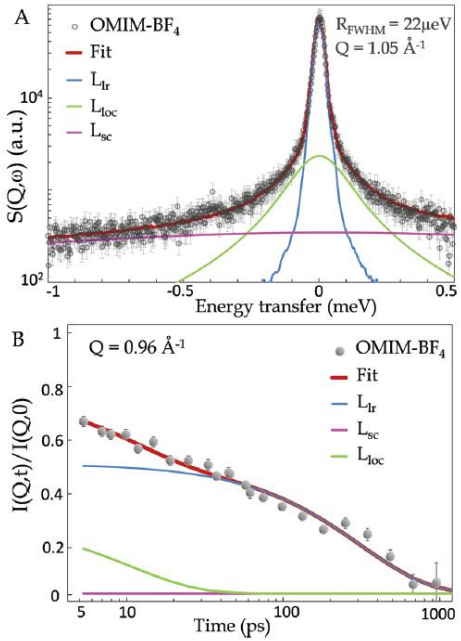
- NSE studies dynamics in the ps to ns time range, over lengthscales from tens of Ås to fractions of an Å. It covers the largest lengthscales and longest timescales of all neutron spectrometers.
- It is used most effectively to perform dynamic (quasielastic) neutron coherent scattering measurements (most notably density fluctuations corresponding to some SANS pattern)
- NSE works in the time domain. The instrumental resolution can be simply divided out.
- NSE works by encoding the neutron speed in its spin state. Do not depolarize the neutron beam.
- (iQENS/)NSE are counting intensive. Large samples and/or significant scattering intensities are required.
- Good knowledge of the sample, in particular of its structure, is needed for the preparation of (iQENS/)NSE experiments and the understanding of the results.

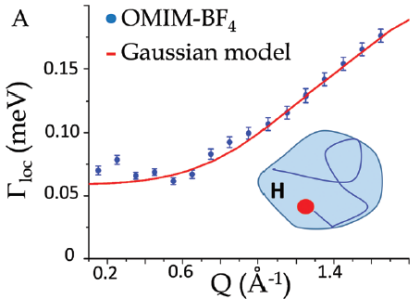
# Some Examples of Scientific Applications

# Translational Dynamics of IL

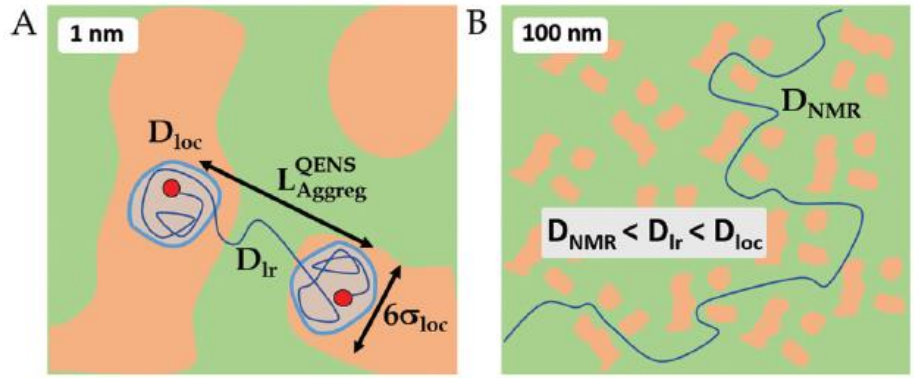
Ionic Liquids are room temperature molten salts with possible applications as solvents and for energy storage.



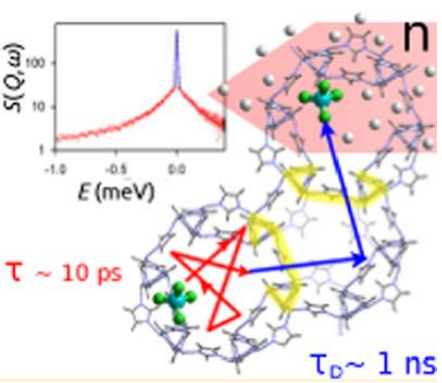




$$S(Q,E) = I_1(Q)L_{tr}(Q,E) + I_2(Q)L_{loc}(Q,E) + I_3(Q)L_{sc}(Q,E)$$



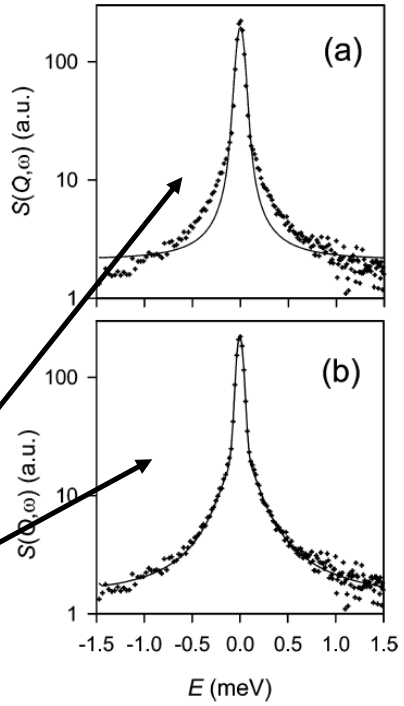

F. Federghini, et al., "Nanostructuration of ionic liquids: impact on the cation mobility. A multi-scale study" *Nanoscale*, **9**, 1911 (2017)

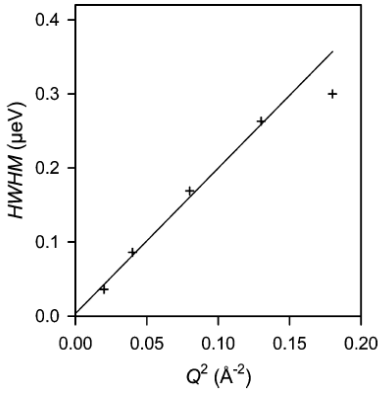
# Diffusion in Confinement

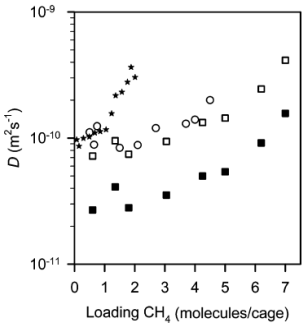



Rotational Diffusion

Jumps within a cage

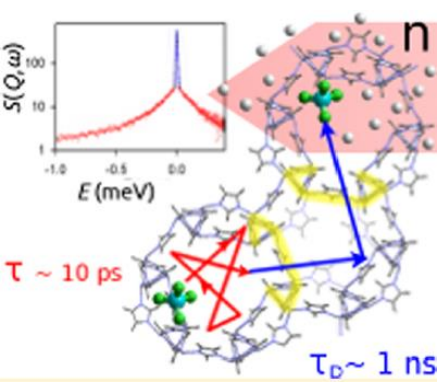


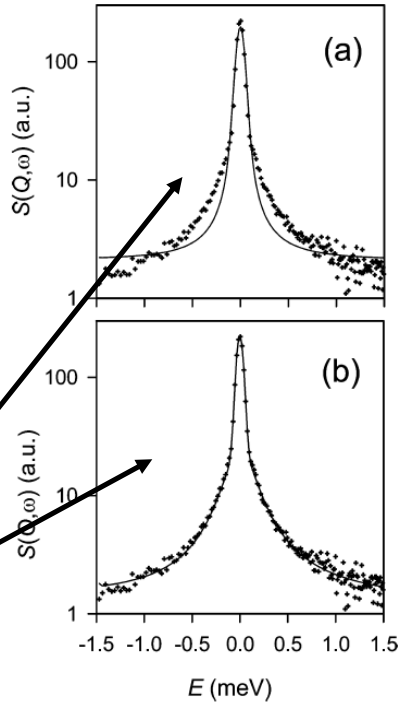



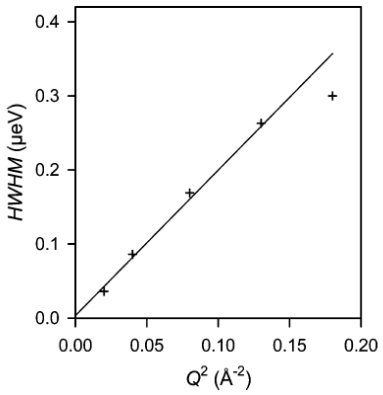

H. Jobic, et al., "Diffusion of $CH_4$ in ZIF-8 Studied by Quasi-Elastic Neutron Scattering" *JPCC*, **119**, 16115 (2018)

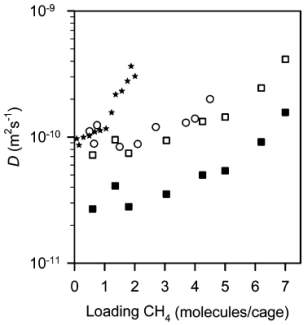
# Diffusion in Confinement



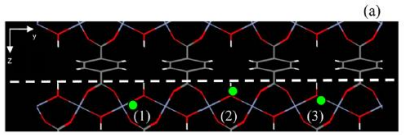

Rotational Diffusion
Jumps within a cage

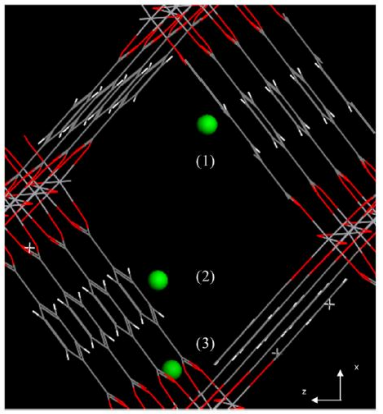


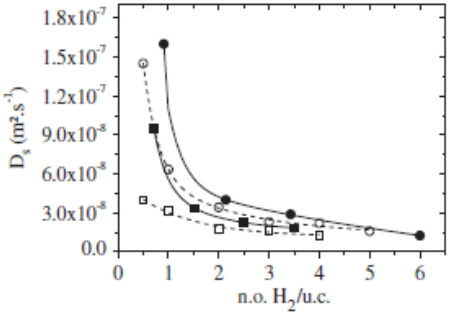



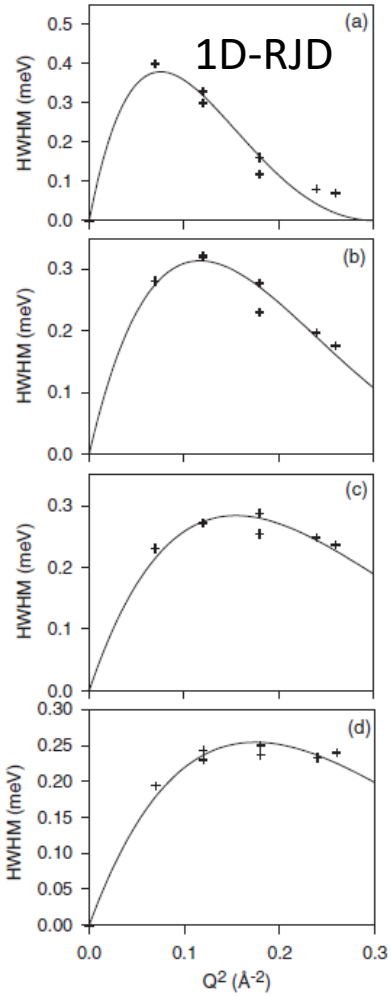




H. Jobic, et al., "Diffusion of $CH_4$ in ZIF-8 Studied by Quasi-Elastic Neutron Scattering" *JPCC*, **119**, 16115 (2018)



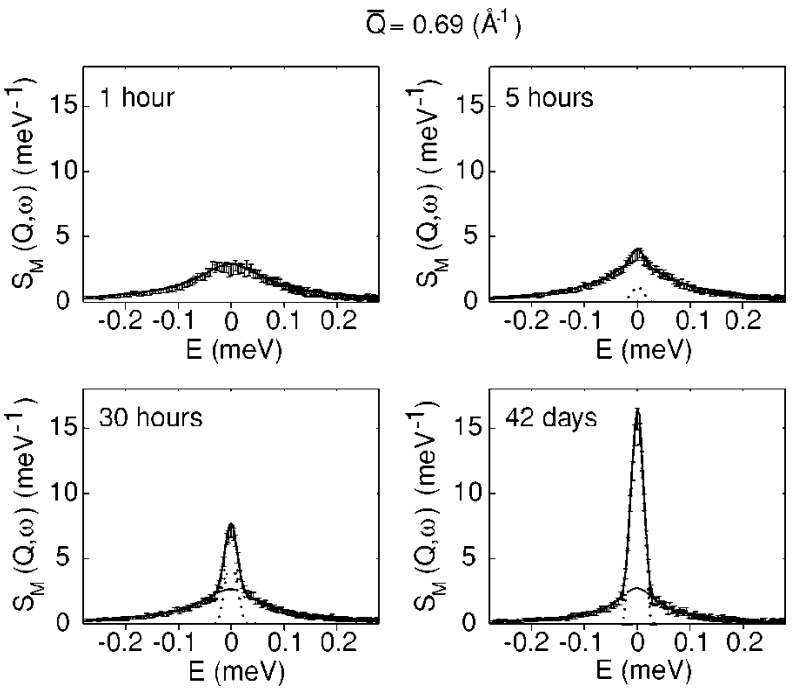



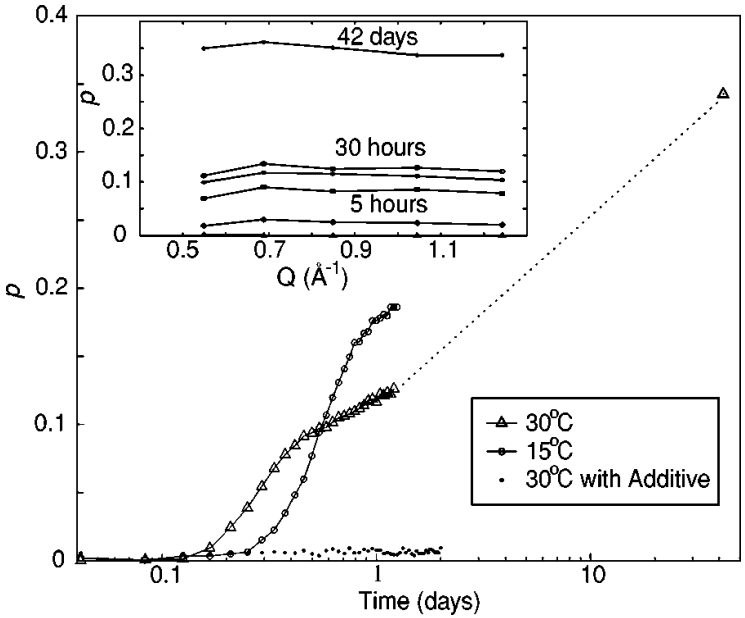



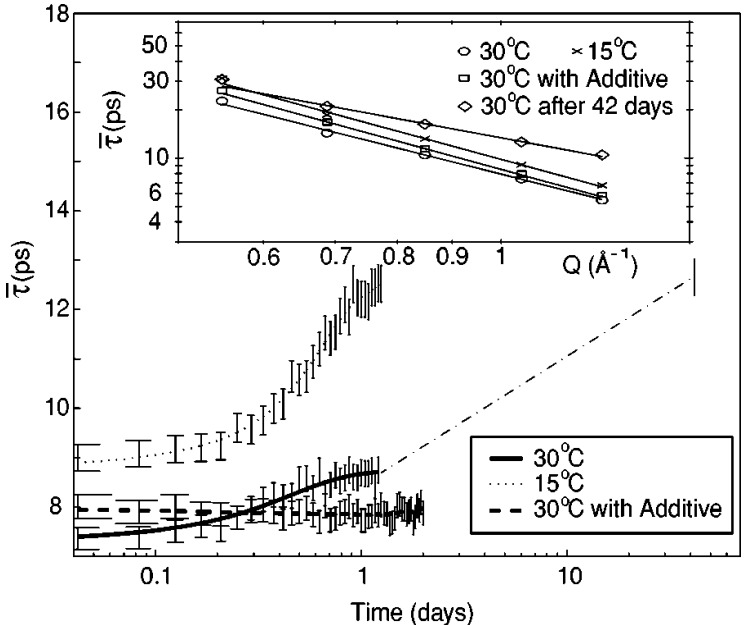




F. Salles, et al., "Experimental Evidence Supported by Simulations of a Very High $H_2$ Diffusion in Metal Organic Framework Materials" *PRL*, **100**, 245901 (2008)

# Water in Cement



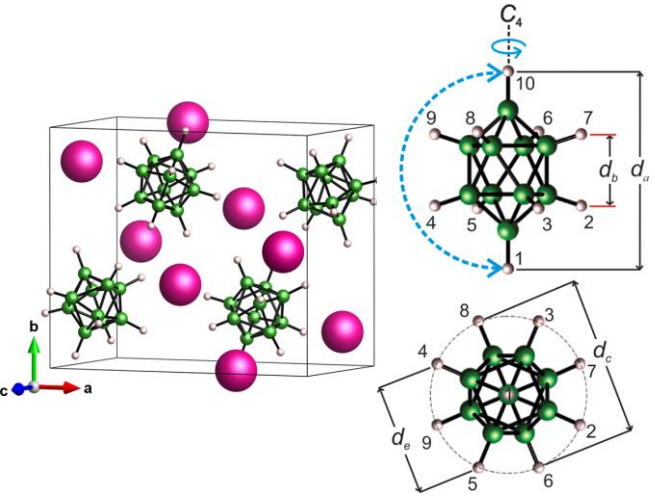



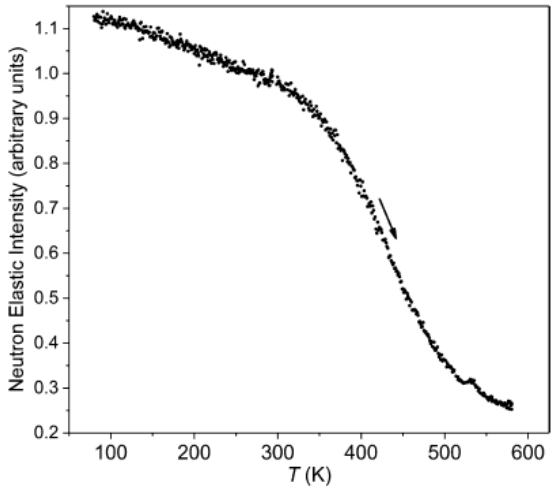



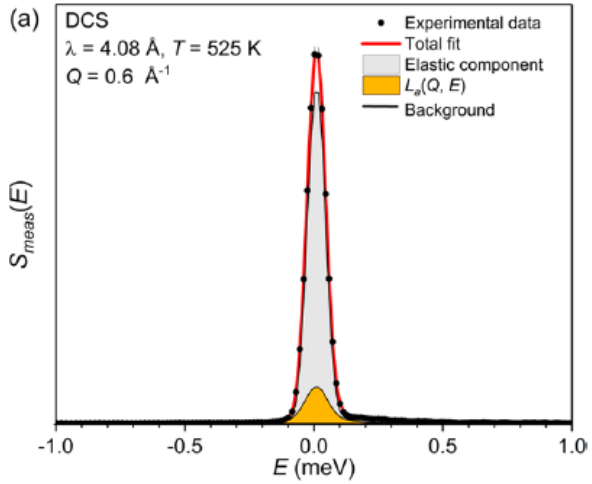

F. Fratini, et al., "Age-dependent dynamics of water in hydrated cement paste" *PRE*, **64**, 020201 (2001)

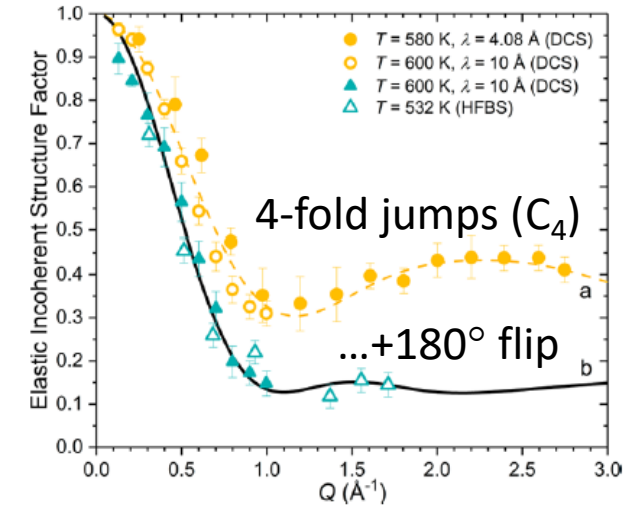
# Solid Ionic Conducting Salts

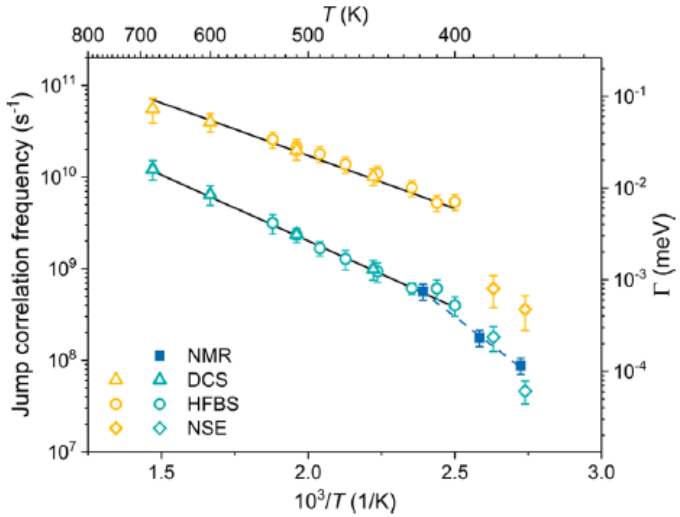
Orientational mobilities of the anions can facilitate cation conductivity.

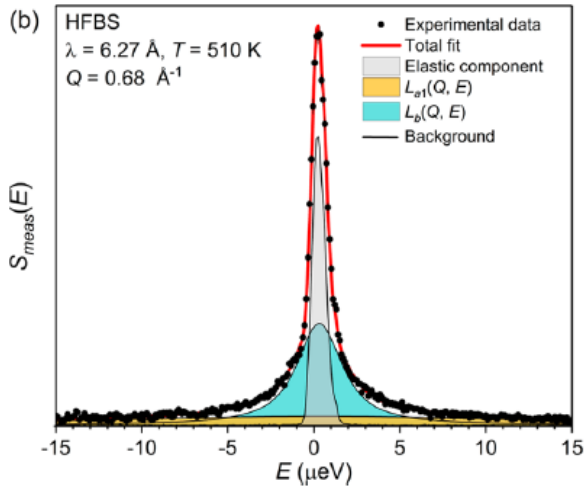


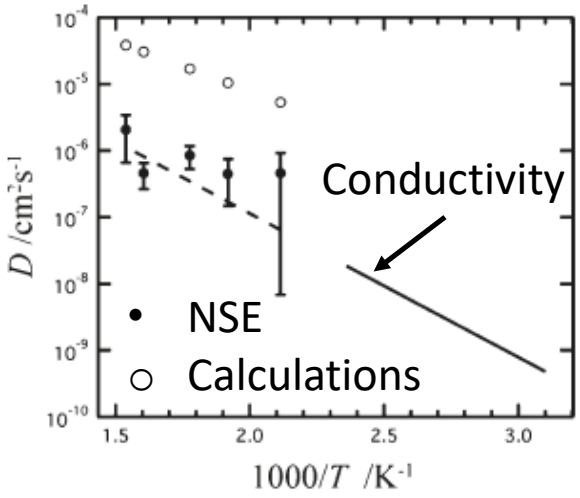



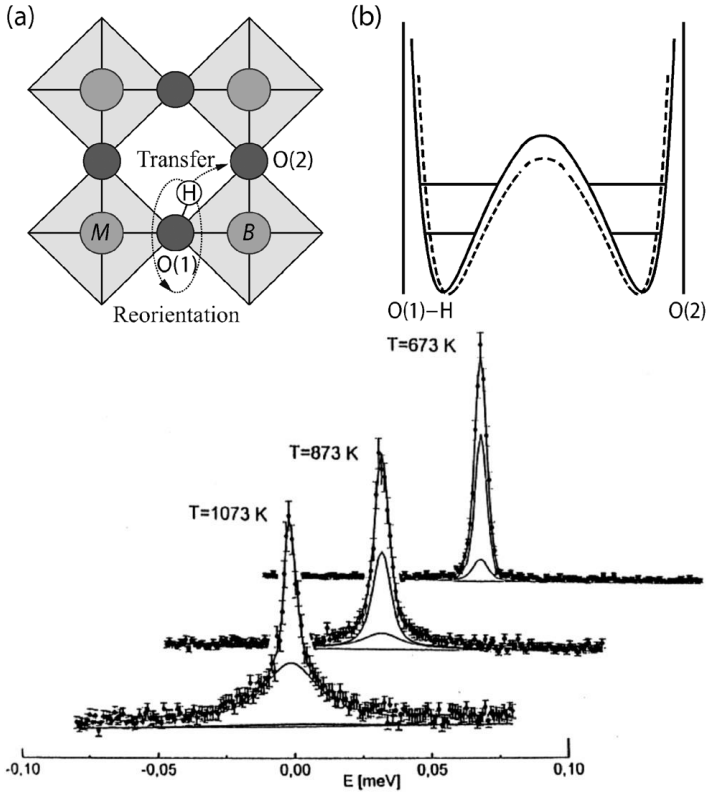

M. Dimitrievska, et al., "Nature of Decahydro-closo-decaborate Anion Reorientations in an Ordered Alkali-Metal Salt: $Rb_2B_{10}H_{10}$" *JPCC*, **122**, 15198 (2018)

# Proton Conductors

Many hydrated ABO3-type perovskites are found to be fast proton conductors in the intermediate temperature range ≈ 200 °C to 500 °C, and therefore have potential applications in solid oxide fuel cell technology.

$BaZr_{0.90}Y_{0.10}O_{2.95}$ (10Y:BZO)



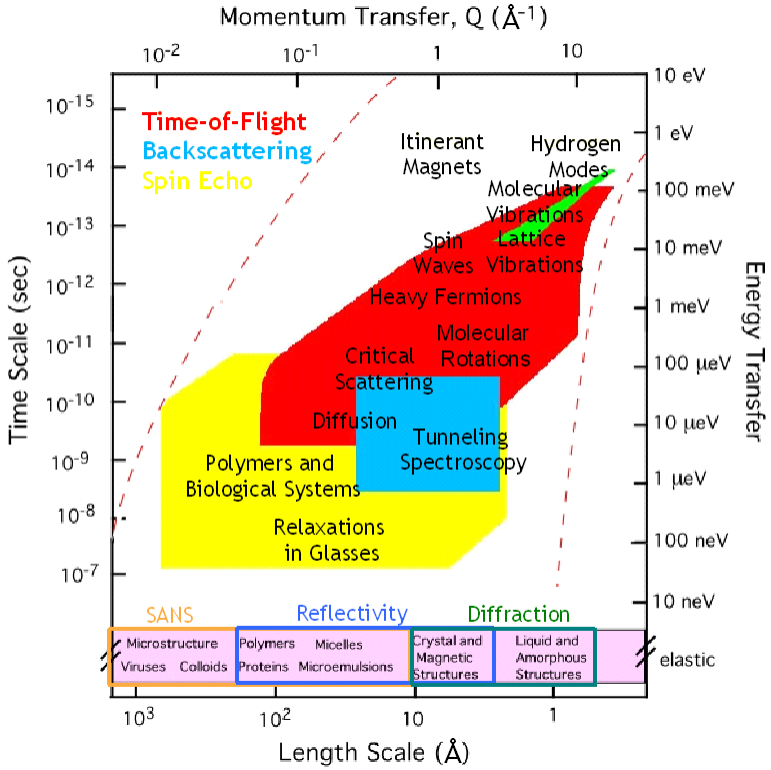




M. Karlsson, et al., "Using Neutron Spin-Echo To Investigate Proton Dynamics in Proton-Conducting Perovskites" *Chem. Mater.*, **22**, 740 (2010); M. Karlsson "Proton dynamics in oxides: insight into the mechanics of proton conduction from quasielastic neutron scattering" *PCCP*, **17**, 26 (2015).

# Conclusion

## Applications

- Materials science: hydrogen storage, surface science, fuel cells
- Physical Chemistry: ionic liquids, clays, porous media, complex fluids
- Soft Matter: polymer melts, eloctrolytes, nanocomposites, and blends
- Biology: hydration water, proteins transport and dynamics, phospholipid membranes



# Conclusion

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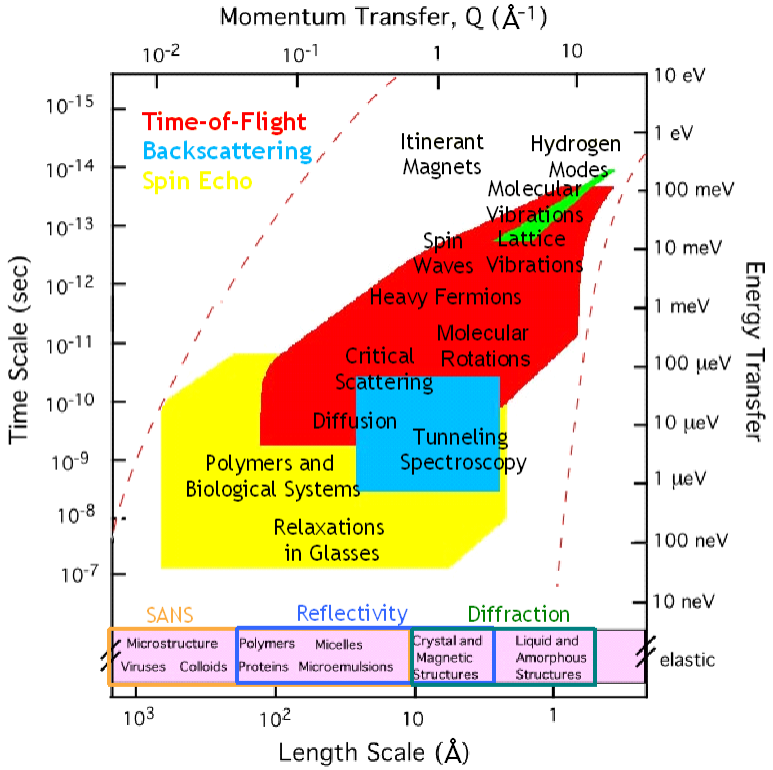
- Biology: hydration water, proteins transport and dynamics, phospholipid membranes

## Characteristics

- Nanoscopic length and time scale
- Hydrogen sensitivity
- Penetrating
- Isotope sensitive
- Matches well with MD

## Limitations:

- Intensity
- Dynamic range



# Few Additional Considerations

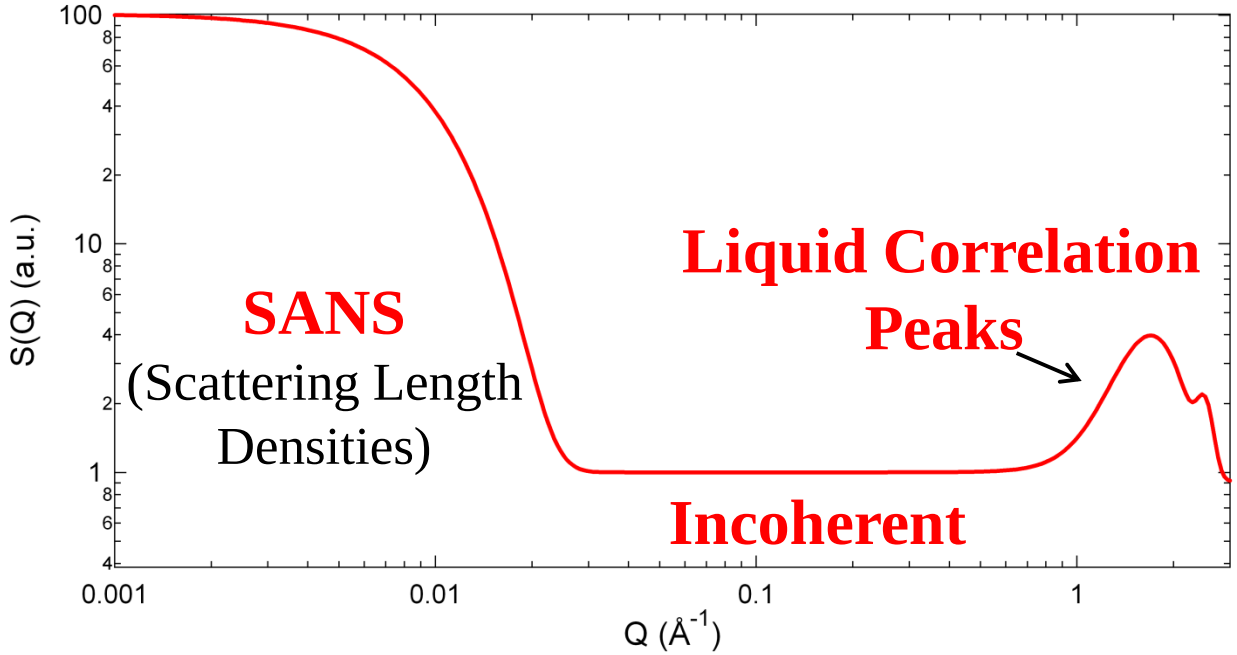
Successful iQENS/NSE studies

- Exploit the time and length scales accessible to iQENS/NSE (only).
- Take advantage of deuteration techniques.
- Require a good knowledge of the sample, in particular its structure. Coupling with other experimental techniques is often necessary.
- Require a significant effort in the analysis and modeling. Coupling with simulation techniques is often very helpful.
- Are time intensive/consuming.

# Relevance of the Lengthscale

# Structure Factor

The Structure Factor, *S(Q)*, is the most relevant information for the preparation and, later, interpretation of a NSE experiment.



# The Coherent Intermediate Scattering Function

$$\frac{I^{NSE}(Q,t)}{I^{NSE}(Q,0)} = \frac{I^{coh}(Q,t) - \frac{1}{3} I^{inc}(Q,t)}{I^{coh}(Q,0) - \frac{1}{3} I^{inc}(Q,0)}$$

When the coherent scattering dominates, NSE measures the time decay of the structures defining *S(Q)*:

$$\frac{I^{NSE}(Q,t)}{I^{NSE}(Q,0)} = \frac{I^{coh}(Q,t)}{I^{coh}(Q,0)} = \frac{\left\langle \exp\left\{-iQ\left[r_i(t) - r_j(0)\right]\right\}\right\rangle}{\left\langle \exp\left\{-iQ\left[r_i(0) - r_j(0)\right]\right\}\right\rangle}$$

# The Incoherent Intermediate Scattering Function

$$\frac{I^{NSE}(Q,t)}{I^{NSE}(Q,0)} = \frac{I^{coh}(Q,t) - \frac{1}{3} I^{inc}(Q,t)}{I^{coh}(Q,0) - \frac{1}{3} I^{inc}(Q,0)}$$

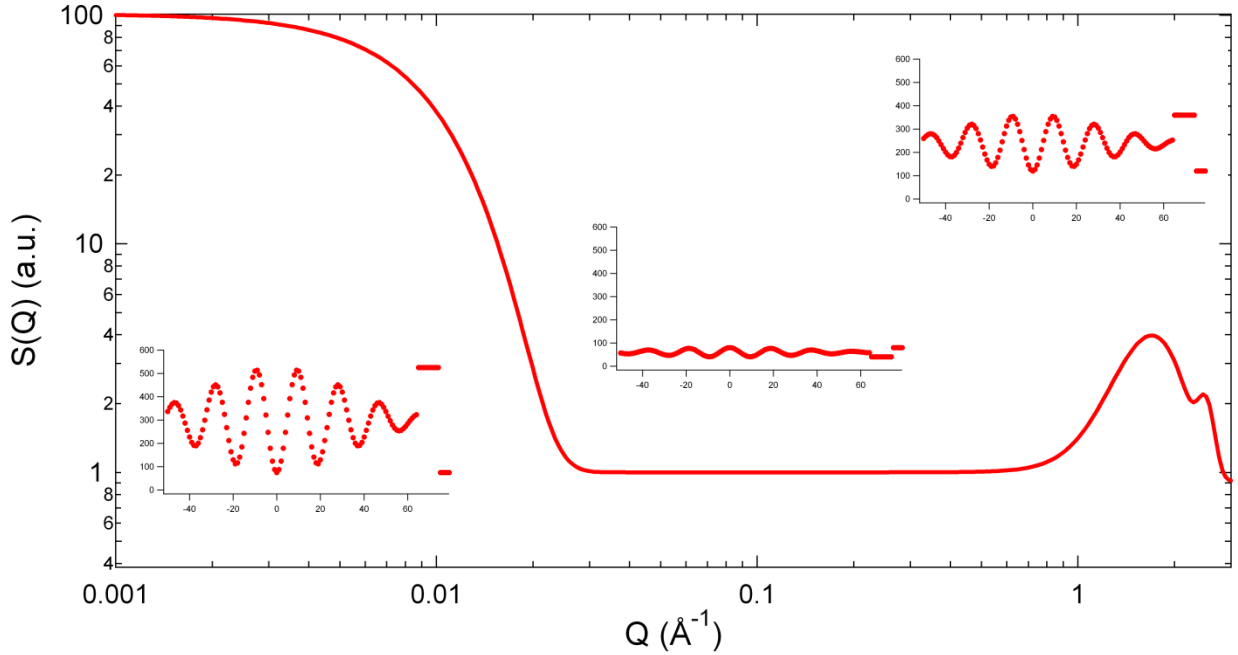
When the incoherent scattering dominates NSE measures the single particle dynamics:

$$\frac{I^{NSE}(Q,t)}{I^{NSE}(Q,0)} = \frac{I^{inc}(Q,t)}{I^{inc}(Q,0)} = \frac{\left\langle \exp\left\{-iQ\left[r_i(t) - r_i(0)\right]\right\}\right\rangle}{\left\langle \exp\left\{-iQ\left[r_i(0) - r_i(0)\right]\right\}\right\rangle}$$

# NSE: Coherent vs Incoherent

NSE is known for the investigation of the coherent dynamics.

Incoherent scattering intensity is reduced to -1/3 in NSE. The best achievable flipping ratio is 0.5.




However, the main limitation to the study of incoherent scattering by NSE is the *Q* coverage of the instrument.

Recent advancements in NSE instrumentation aim to overcome this limitation (IN-11C, the WASP project).

# NSE: Coherent vs Incoherent

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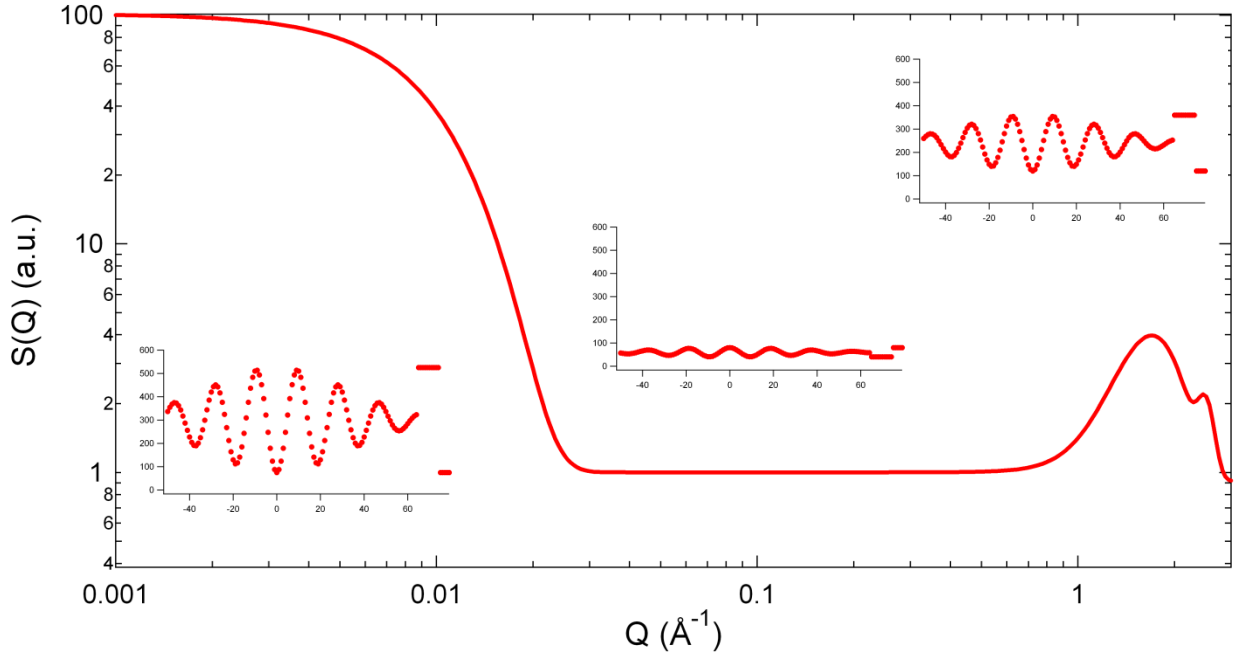
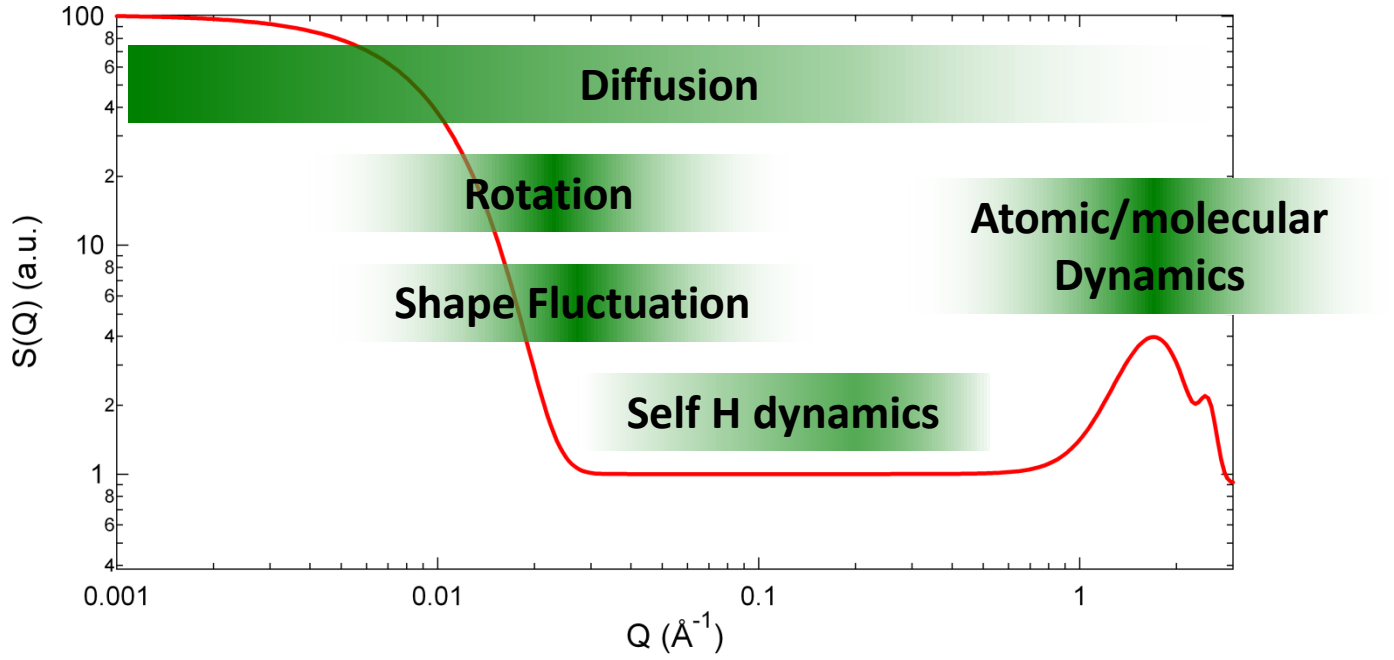



However, the main limitation to the study of incoherent scattering by NSE is the *Q* coverage of the instrument.

Most important is to avoid *Q* areas where coherent and incoherent intensity cancel each other.

# Types of Dynamics



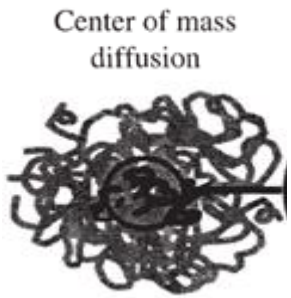

At length scales larger than the macromolecular size: Diffusion.

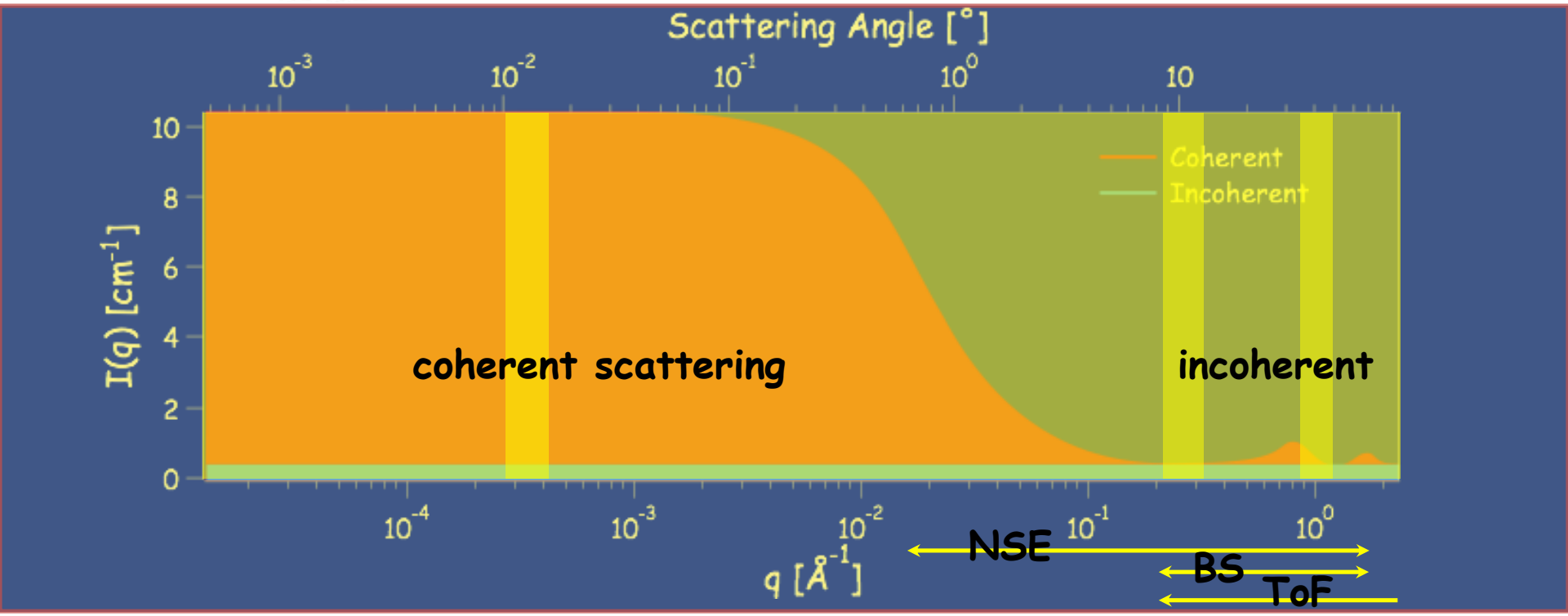
At length scales of the order the macromolecular size: Rotations and shape fluctuations.

Where the incoherent signal is dominant: Self H dynamics (translations, rotations, vibrations,…)

At the structural peaks: Atomic/Molecular Dynamics.

# Lengthscales of Polymer Dynamics




**larger scale objects: slower dynamics**

**coherent dynamics at low Q and at Q corresponding to relevant length scales**
**incoherent dynamics at high Q**

D. Richter, et al., *Adv. in polym. Sci.*, **174**, 1 (2005).