Outline QuasiElastic Neutron Scattering from an user point of view

Part II : what are the observables?

constraints on measurements, limitations

Models and theories

Sample environment : next challenges

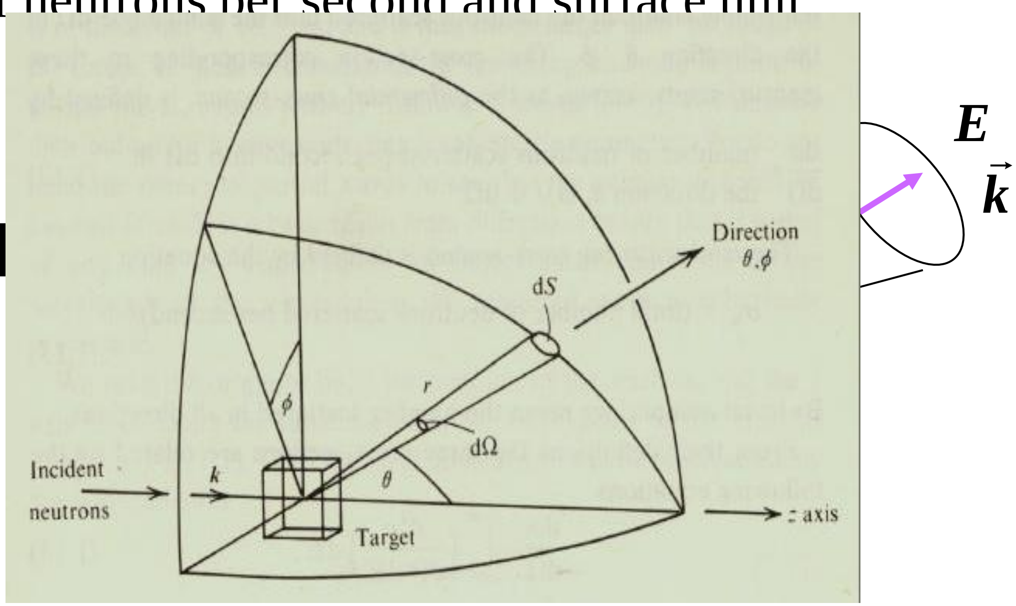
What do we measure ?

probability that a neutron (E_0, k_0) is scattered (E_0+ħω, k)

$$\boxed{\frac{d^2\sigma}{d\Omega\, dE} = \frac{1}{\Phi_0}\,\frac{\text{nb of neutrons scattered per second in } d\Omega \text{ and } dE}{d\Omega\, dE}}$$

Incident Neutron flux =
nbof neutrons per second and surface unit

in barns per stéradian and unit of energy



Momentum Transfert

$$\vec{\boldsymbol{Q}} = \vec{\boldsymbol{k}} - \vec{\boldsymbol{k}}_0$$

Energy Transfert

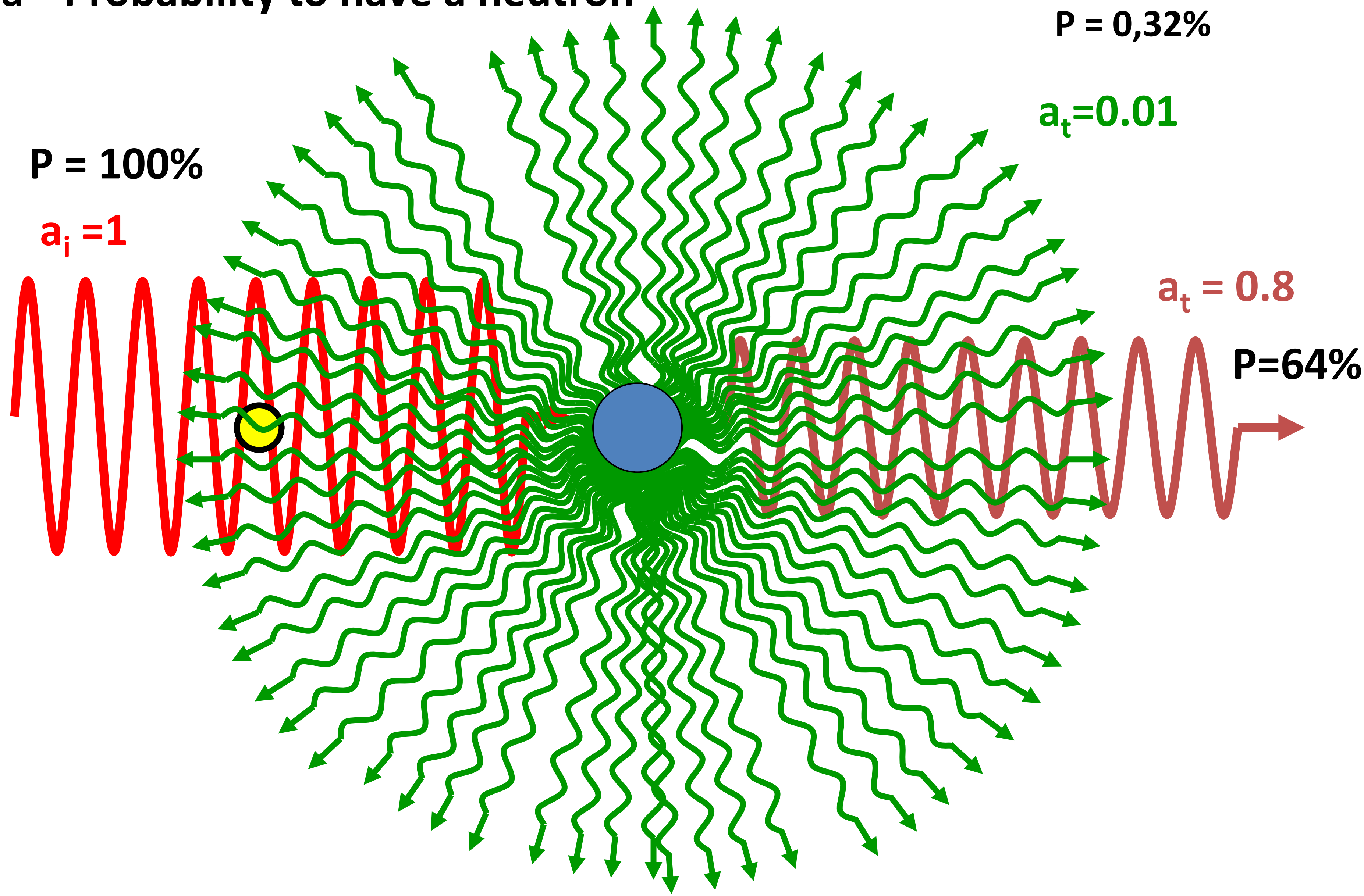
$$\hbar\boldsymbol{\omega} = \boldsymbol{E} - \boldsymbol{E}_0$$

Convention

ħω > 0 if the neutron gives energy to the system

a = amplitude of the wave

a^2=Probability to have a neutron



1

A part of the neutron flux is **transmitted** (the largest)

A part of the neutron flux is **absorbed**

A part of the neutron flux is scattered (the smallest)

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} \approx N * \sigma_{Scat} * S(\vec{Q},\omega)$$

2

If we have a multi atomic system :

many nuclear species with different scattering lengths,

Randomly distributed scattered waves

that could destroy the interference or enhance them if they are in phase.

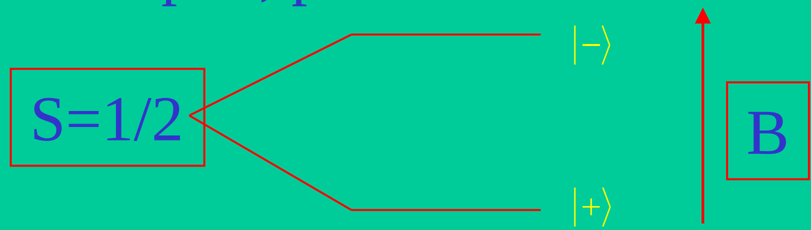
3

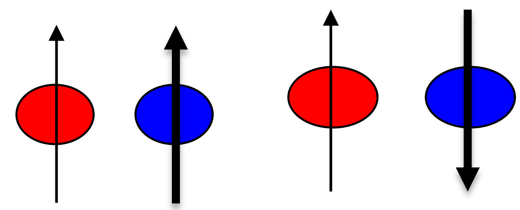
Depends on the **relative orientation**

of the spin of the neutron and the spin of the nucleus, b+ and b-

If the spins are **unpolarised** $\rightarrow$ this randomness detroys again part of the interference

Neutron spin , precession ...





Spin of **Neutron**+ **Nucleus** **I= nuclear spin**	$I+\frac{1}{2}$	$\left\lvert I-\frac{1}{2}\right\rvert$
Nb of states, fraction of each	$f_{+}=\dfrac{I+1}{2I+1}$	$f_{-}=\dfrac{I}{2I+1}$
diffusion lengths	b_{+}	b_{-}

Coherent and Incoherent scattering

$$\bar{b} = f_+ b_+ + f_- b_-$$

$$\overline{b^2} = f_+ b_+^2 + f_- b_-^2$$

$$\sigma_{coh} = 4\pi\left(\bar{b}\right)^2$$

$$\sigma_{inc} = 4\pi\left[\overline{b^2} - \left(\bar{b}\right)^2\right]$$

$$\sigma_S = \sigma_{coh} + \sigma_{inc}$$

	H	**D**
I	1/2	1
I+½	1	3/2
I-½	0	1/2
b_+ (10^{-12}cm)	1.085	0.953
b_- (10^{-12}cm)	-4.750	0.098
f_+	3/4	2/3
f_-	1/4	1/3
$b = \bar{b}$ (10^{-12}cm)	-0.374	0.668
$\overline{b^2}$ (barn)	6.523	0.609
σ_{coh} (barn)	1.758	5.607
σ_{inc} (barn)	79.81	2.04
σ_s (barn)	81.67	7.65

Scattered intensity can be split in 2 terms

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right) = \left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{coh} + \left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{inc}$$

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{coh} = \frac{1}{2\pi\hbar}\frac{k}{k_0}\frac{\sigma_c}{4\pi}\sum_{jj'}\int_{-\infty}^{+\infty}\left\langle e^{-i\vec{Q}\vec{R}_j(0)}\, e^{i\vec{Q}\vec{R}_{j'}(t)}\right\rangle e^{-i\omega t}\, dt \qquad j\neq j'$$

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{inc} = \frac{1}{2\pi\hbar}\frac{k}{k_0}\frac{\sigma_i}{4\pi}\sum_{j}\int_{-\infty}^{+\infty}\left\langle e^{-i\vec{Q}\vec{R}_j(0)}\, e^{i\vec{Q}\vec{R}_{j}(t)}\right\rangle e^{-i\omega t}\, dt$$

- Moyenne thermique $\langle\cdots\rangle$
- Moyenne sur le désordre $\overline{\cdots}$

where

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{coh} = \frac{k}{k_0}\frac{\sigma_c}{4\pi} N\, S(\vec{Q},\omega)$$

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{inc} = \frac{k}{k_0}\frac{\sigma_i}{4\pi} N\, S_{inc}(\vec{Q},\omega)$$

Roughly speaking

get the collective part dynamics from the coherent diffusion

and

the self part dynamics from the incoherent diffusion.

however

Experiments are specific coh/incoh ratio

The sample has also a specific coh/incoh ratio

Scattering functions

For a given number density of atoms at r $\rho(\vec{r},t) = \sum_j \delta\left(\vec{r} - \vec{R}_j(t)\right)$

pair correlation function

Probability to find a particule at $(\vec{r}, t)$
Knowing that there was one at $(0, 0)$

N scatterers

$$G(\vec{r},t) = \frac{1}{N} \int \langle \rho(\vec{r}',0)\, \rho(\vec{r}'+\vec{r},t) \rangle \, d\vec{r}'$$

$$= \frac{1}{N} \sum_{jj'} \int \left\langle \delta\left[\vec{r}' - \vec{R}_j(0)\right] \delta\left[\vec{r}' + \vec{r} - \vec{R}_{j'}(t)\right] \right\rangle d\vec{r}'$$

autocorrelation function (self)

$$G_s(\vec{r},t) = \frac{1}{N} \sum_j \int \left\langle \delta\left[\vec{r}' - \vec{R}_j(0)\right] \delta\left[\vec{r}' + \vec{r} - \vec{R}_j(t)\right] \right\rangle d\vec{r}'$$

dim : 1/volume

F(Q,t) no dimension.

Intermédiate scattering function F(Q,t) - coherent

$$F(\vec{Q},t) = \int G(\vec{r},t)\, e^{i\vec{Q}.\vec{r}}\, d\vec{r}$$

j≠j'

$$= \frac{1}{N} \sum_{jj'} \left\langle e^{-i\vec{Q}.\vec{R}_j(0)}\, e^{i\vec{Q}.\vec{R}_{j'}(t)} \right\rangle$$

Intermédiate scattering function F(Q,t) - incoherent (self)

$$F_{S\,ou\,inc}(\vec{Q},t) = \int G_S(\vec{r},t)\, e^{i\vec{Q}.\vec{r}}\, d\vec{r}$$

$$= \frac{1}{N} \sum_{j} \left\langle e^{-i\vec{Q}.\vec{R}_j(0)}\, e^{i\vec{Q}.\vec{R}_j(t)} \right\rangle$$

F(Q,t)=I(Q,t)=S(Q,t)

Dynamic structure factor S(Q,ω)

dimension : energy^{-1}

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

$$= \frac{1}{2\pi\hbar N}\int_{-\infty}^{\infty}\sum_{jj'} \left\rangle e^{-i\vec{Q}.\vec{R}_j(0)}\, e^{i\vec{Q}.\vec{R}_{j'}(t)} \right\langle e^{-i\omega t}\, dt$$

incoherent Dynamic structure factor S_{inc} (Q,ω)

$$S_{inc}(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} F_S(\vec{Q},t)\, e^{-i\omega t}\, dt$$

$$= \frac{1}{2\pi\hbar N}\int_{-\infty}^{\infty}\sum_{j} \left\rangle e^{-i\vec{Q}.\vec{R}_j(0)}\, e^{i\vec{Q}.\vec{R}_{j}(t)} \right\langle e^{-i\omega t}\, dt$$

$$\int S(Q,\omega)\,d\omega = S(Q)$$

$$\int S_{inc}(Q,\omega)\,d\omega = 1$$

summary

Dynamical structure factor
S(q,w)

$$\frac{d^2\sigma}{d\Omega d\omega} \equiv \frac{b^2}{\hbar}\frac{k}{k_0}S(q,\omega)$$

Pair correlation function
time dependent
(Van Hove)

$$G(r,t)=\frac{1}{2\pi^2}\int_0^{\infty}F(q,t)\cdot\frac{\sin qr}{qr}\cdot q^2\cdot dq$$

Intermediate Scattering function

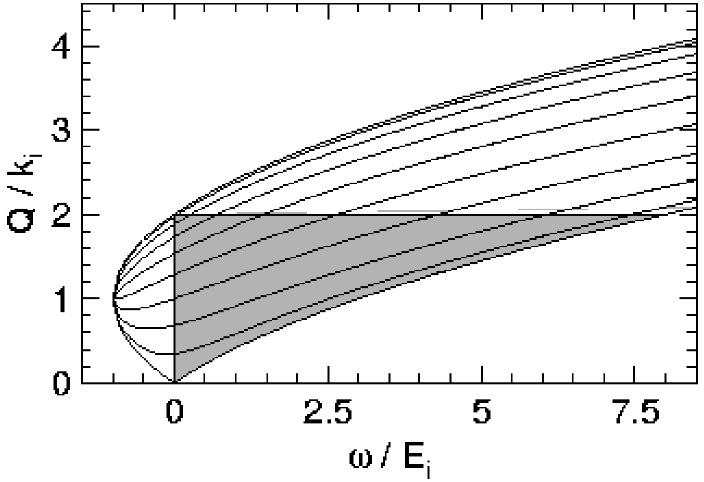
$$F(q,t)=\int_{-\infty}^{\infty}S(q,\omega)\cdot\cos\omega t\cdot d\omega$$

ToF : standard corrections

- Detector efficiency
- vanadium (or quartz) normalisation, **resolution** ;
  or sample at very low T
- Background, emplty cell , crystat, furnace
- Absorption for a given sample geometry
- Multiple scattering

- $2\theta \rightarrow Q$, interpolation

(only TOF, not for BS or NSE)



$$Q(\hbar\omega) = \left(\frac{2m_n}{\hbar^2}\left[2E_i - \hbar\omega - 2cos(2\theta)\sqrt{{E_i}^2 - \hbar\omega E_i}\right]\right)^{1/2}$$

Atome/molécule	σ_{inc}	%	σ_{coh}	%
H	80.27		1.76	
D	2.05		5.59	
C	0.00		5.55	
$C_6H_5CD_3$	407.50	86.3	64.42	13.7
$C_6D_5CD_3$	16.65	16.6	83.56	83.4
C_6H_5C	401.35	90.0	47.65	10.0
C_6D_5C	10.45	13.5	66.79	86.5

Combining ToF and NSE spectra, ToF-BS spectra ?

Different measurement

TOF, BS $S^{exp}(Q,\omega) = \sigma_{coh}\, S_{coh}(Q,\omega) + \sigma_{incoh}\, S_{incoh}(Q,\omega)$

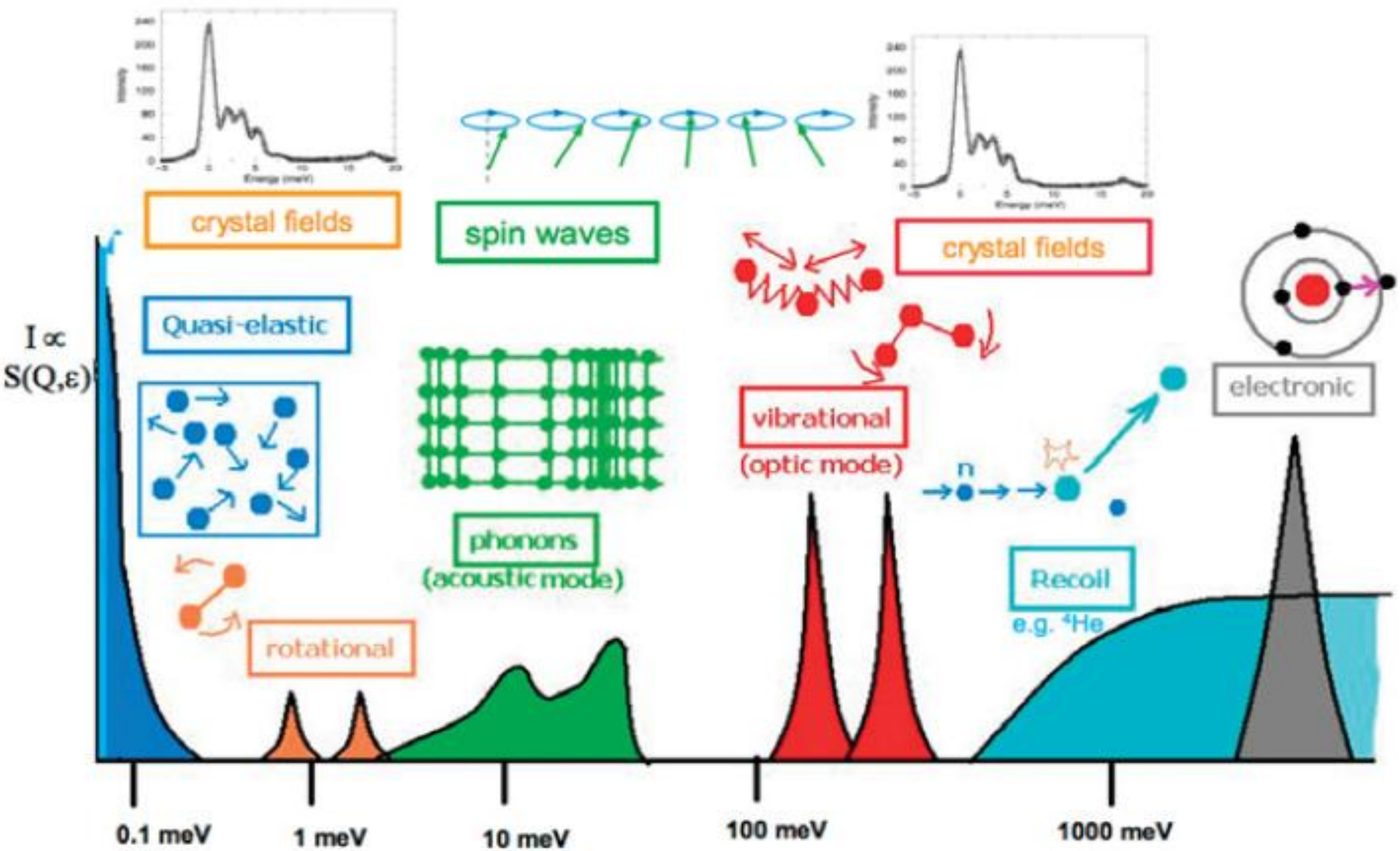
Polarisation NSE

$$\tilde{S}_{\mathrm{NSE}}(Q,t) = \frac{I_{\mathrm{coh}}\tilde{S}_{\mathrm{pair}}(Q,t) - \frac{1}{3}I_{\mathrm{inc}}\tilde{S}_{\mathrm{self}}(Q,t)}{I_{\mathrm{coh}} - \frac{1}{3}I_{\mathrm{inc}}}$$

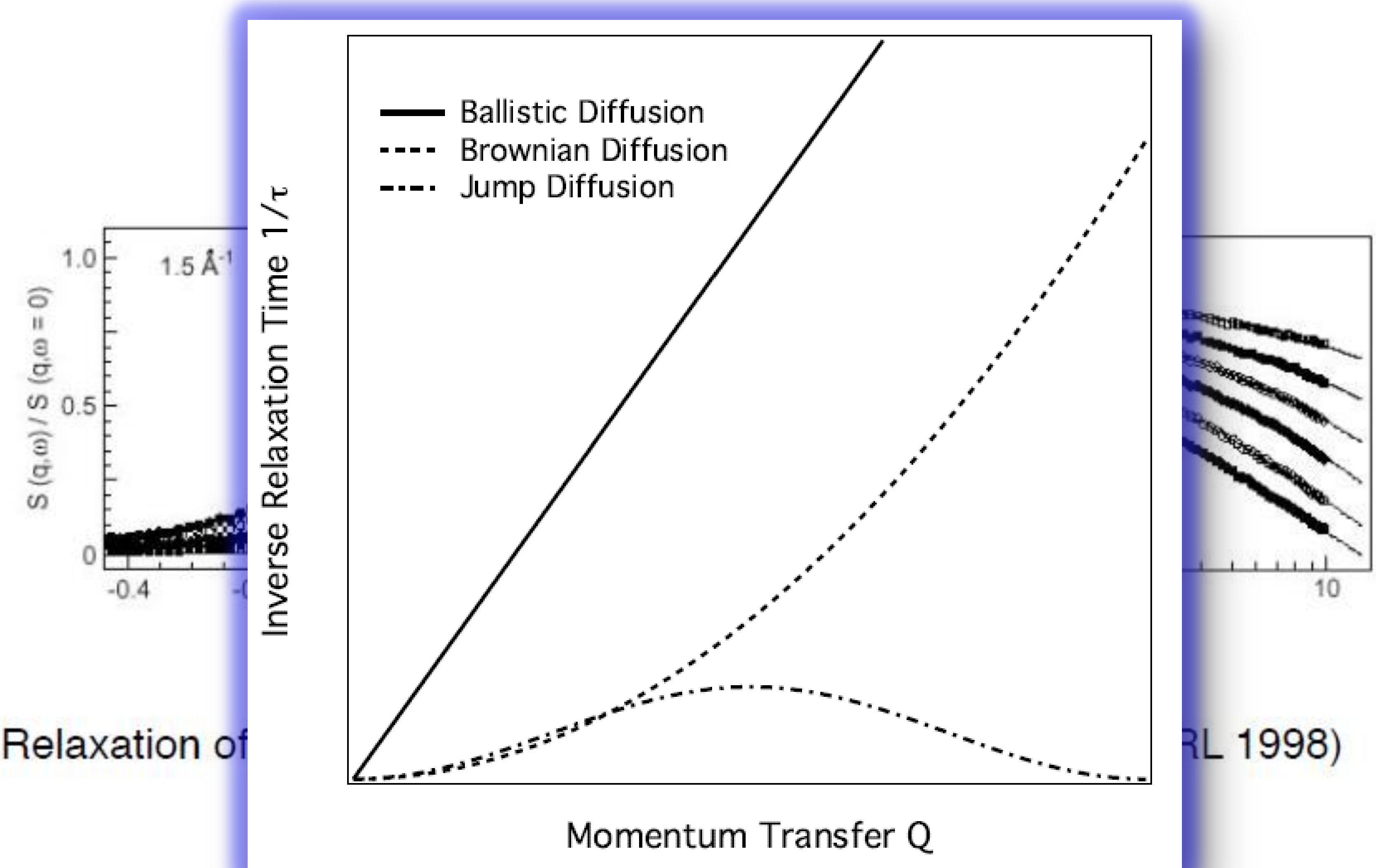
TOF pol, NSE $S^{\uparrow\uparrow}(Q,\omega) = \sigma_{coh}\, S_{coh}(Q,\omega) + 1/3\ \sigma_{incoh}\, S_{incoh}(Q,\omega)$

$S^{\uparrow\downarrow}(Q,\omega) = 2/3\ \sigma_{incoh}\, S_{incoh}(Q,\omega)$

EXPLORING VARIOUS TYPES OF MOTIONS



An exemple on metallic liquids



diffusion processes (self) in quasi-elastic spectra :
broadening or inverse relaxation times versus momentum transfer

diffusion : translational dynamics
jumps or continous

Fick' s Law 1855

$$\boxed{\frac{\partial c(r,t)}{\partial t} = D\nabla^2 c(r,t)}$$

D = diffusion coefficeint
macroscopic quantity

N = total nbof atoms

$$G_S(r,t) = c(r,t)/N$$

$$G_S(r,t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(\frac{-r^2}{4Dt}\right)$$

microscopic
of neutrons
With Gs(r,0)=δr and Gs(r, t=∞)=0

$$F(Q,t) = \exp\left(-DQ^2 t\right)$$

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

At lage Q → jump **diffusion**

Case of liquid water

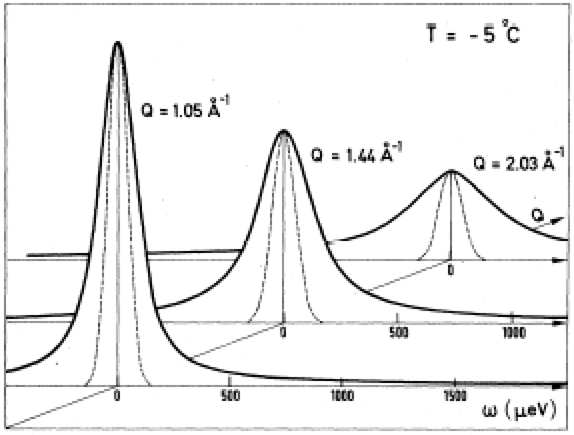
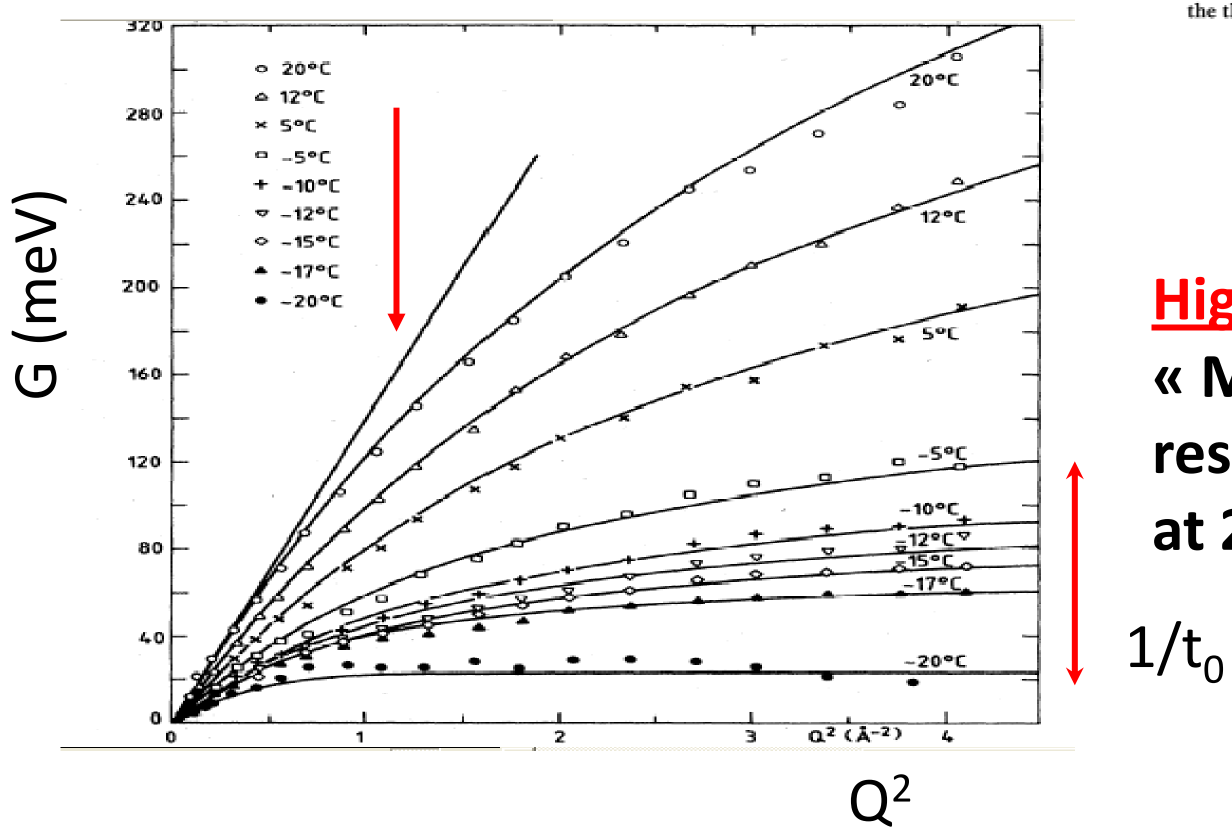


FIG. 1. Quasi-elastic incoherent neutron spectra from water at −5 °C for three different values of Q. ——: best fit. – – –: resolution function. Experimental points are within the thickness of the solid line.

Small Q:

« Macroscopic » → Fick's Law

Self Diffusion coef. D=2.5 10^{-5} cm^2/s at 298 K



High Q:

« Microscopic » →

residence time: t_0=1 ps at 298 K

At each Q:

Data fitting by a Lorenzian

Teixeira, Bellissent-Funel & Dianoux, Phys.Rev. A, 31,1915,(1985)

Jump Diffusion at large Q (M.Bée book)

τ_0 residence time in a given site

$$S_{inc}(Q,\omega) = \frac{1}{\pi}\frac{f(Q)}{\left(f(Q)\right)^2+\omega^2} \quad \text{with} \quad f(Q) = \frac{DQ^2}{DQ^2\tau_0+1}$$

Elastic Incoherent Structure Factor

Rotational Diffusion

Uni dimensional Diffusion

molecules in channels, membranes

$$\boldsymbol{S_{1D}(Q,\omega) = \tfrac{1}{2\pi}\int_0^{\pi} \frac{DQ^2\cos^2\theta\sin\theta}{\left(DQ^2\cos^2\theta\right)^2+\omega^2}d\theta}$$

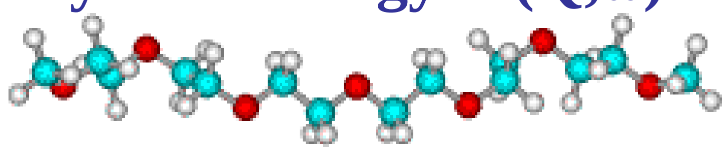
For d~σ, single file diffusion

<u>Incoherent</u> Quasi-Elastic Neutron Scattering:
Probe polymer self-correlation via H atoms
Local scale (0.3 à 3 $Å^{-1}$) / Short times (tens of ps)

(1) Analysis of the elastic intensity: $S(Q,\omega=0)$
Mean-Square displacement : $\langle u^2 \rangle$.

$$S(Q,\omega=0)=\exp(-Q^2\langle u^2\rangle).\delta(\omega)$$

(2) Analysis in energy: $S(Q,\omega)$

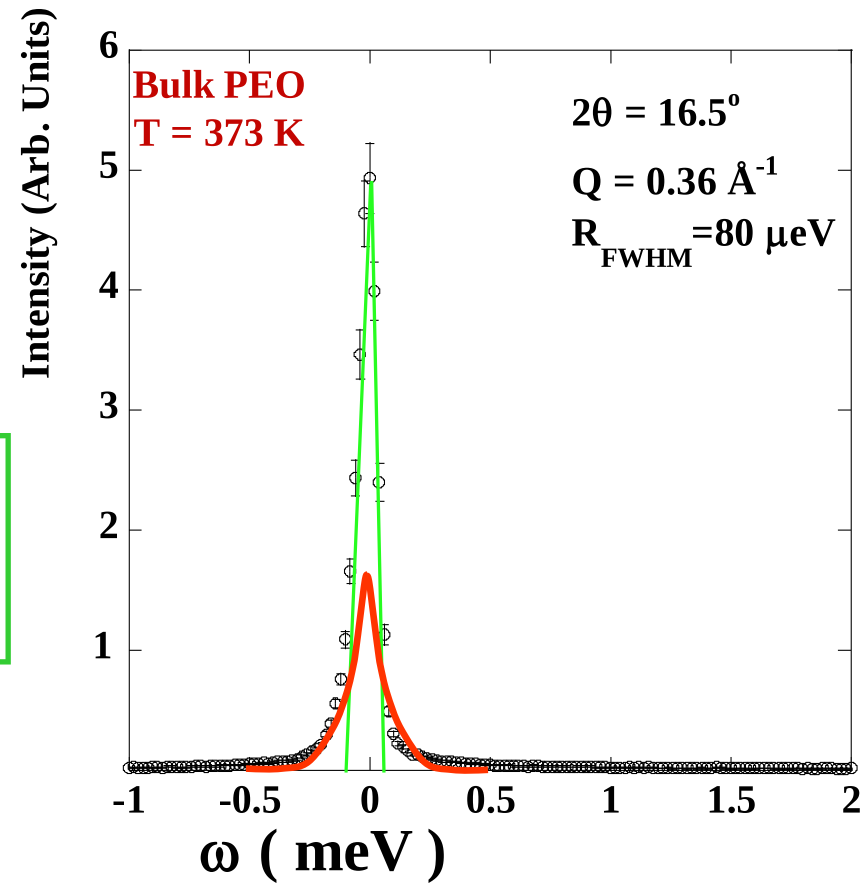


EISF: $A_0(Q)$ → Geometry

Conformational Change

Spatial Localization of a diffusive process

$$S(Q,\omega)=A_0(Q).\delta(\omega)+[1-A_0(Q)].L(Q,\omega)$$



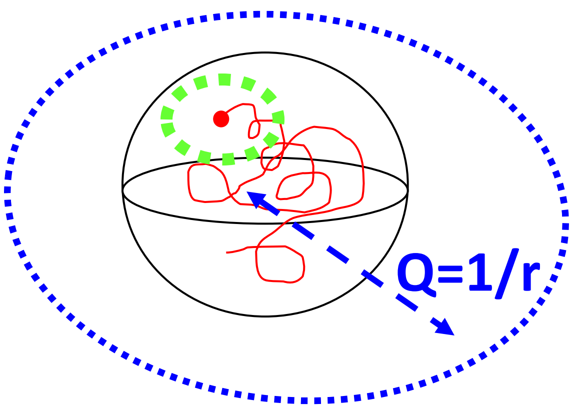
Diffusion in restricted geometry

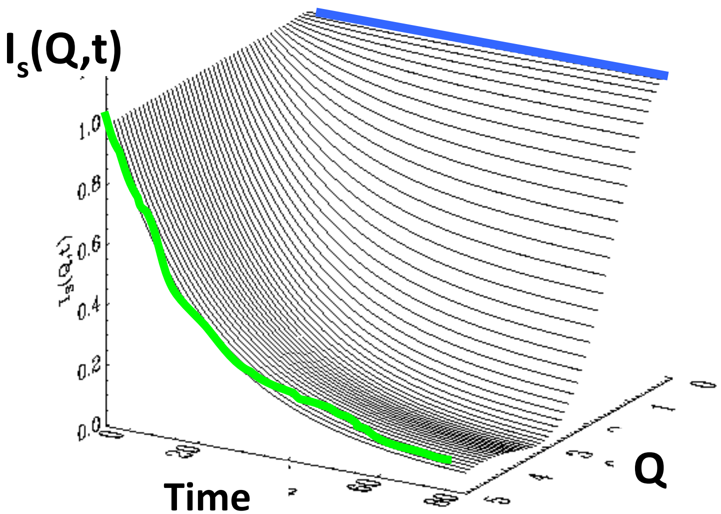
The **E**lastic **I**ncoherent **S**tructure **F**actor

Incoherent scatterer : Scattered intensity related to ***autocorrelation*** function of the particle **$G_s(r,t)$**

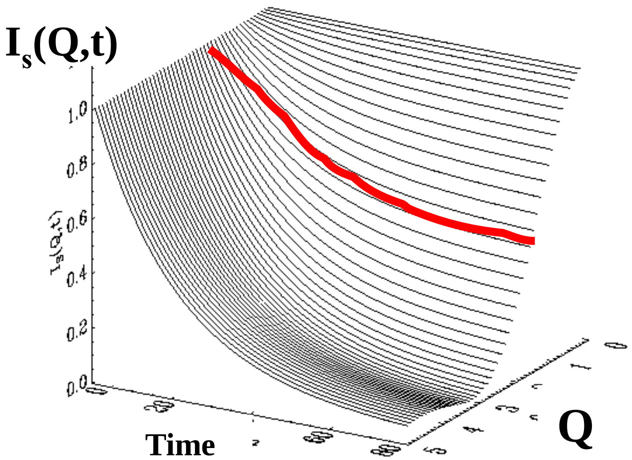
$G_s(r,t)$ probability to find the particle at r at time t provided it was at r=0 at time t=0.

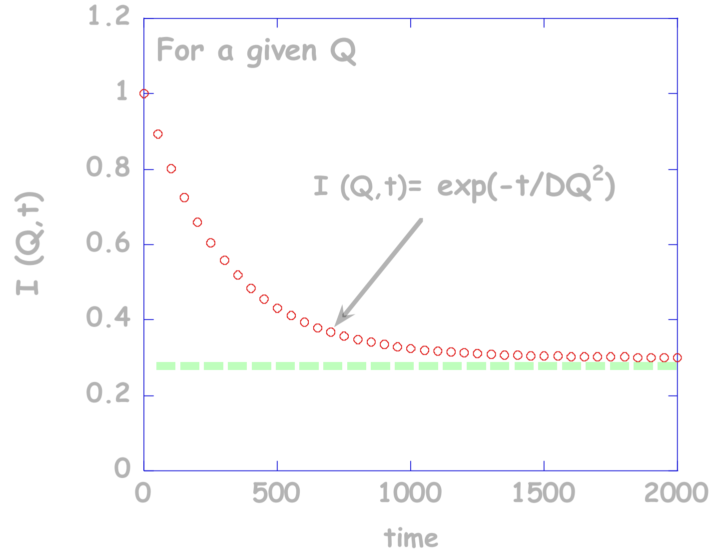
$G_s(r,t)$ ← FT over r → $I_s(Q,t)$ ← FT over t → $S_{inc}(Q,w)$



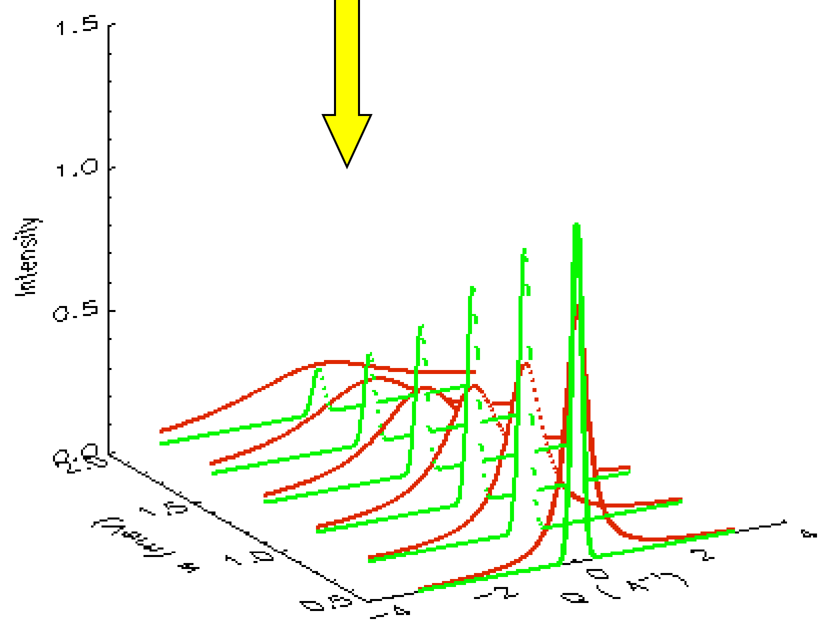


The Q dependence of the long-time tail (plateau) of the intermediate scattering function, $I_s(Q,t=\infty)$, is the form factor of the confining volume: the EISF.





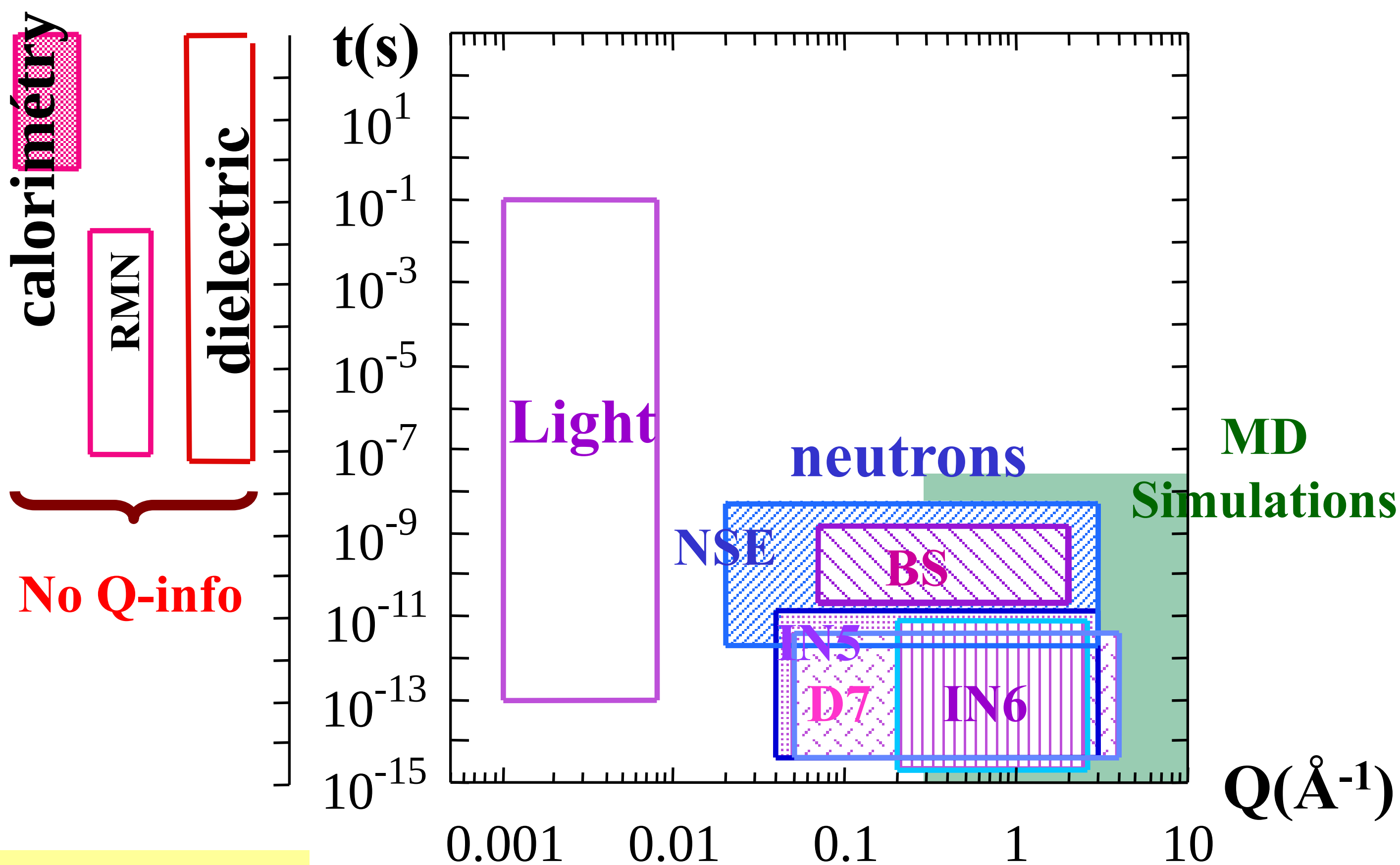
$I_s(Q,t)$ ← FT over t → $S_{inc}(Q,w)$

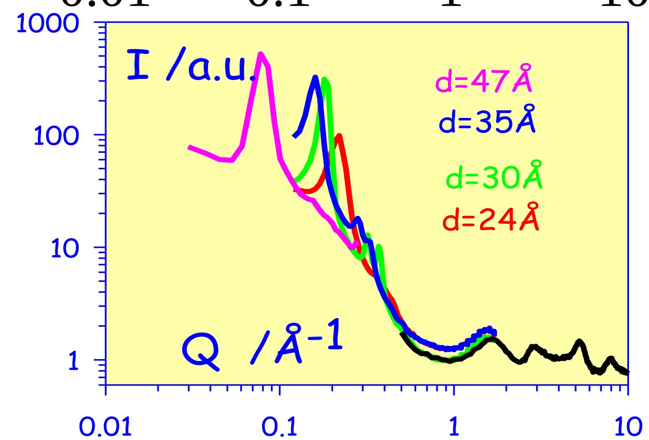


The Q dependence of the fraction of elastic scattering is the form factor of the confining volume: the EISF.

$$EISF(Q) = \frac{I_{El}(Q)}{I_{El}(Q) + I_{Quasi}(Q)}$$

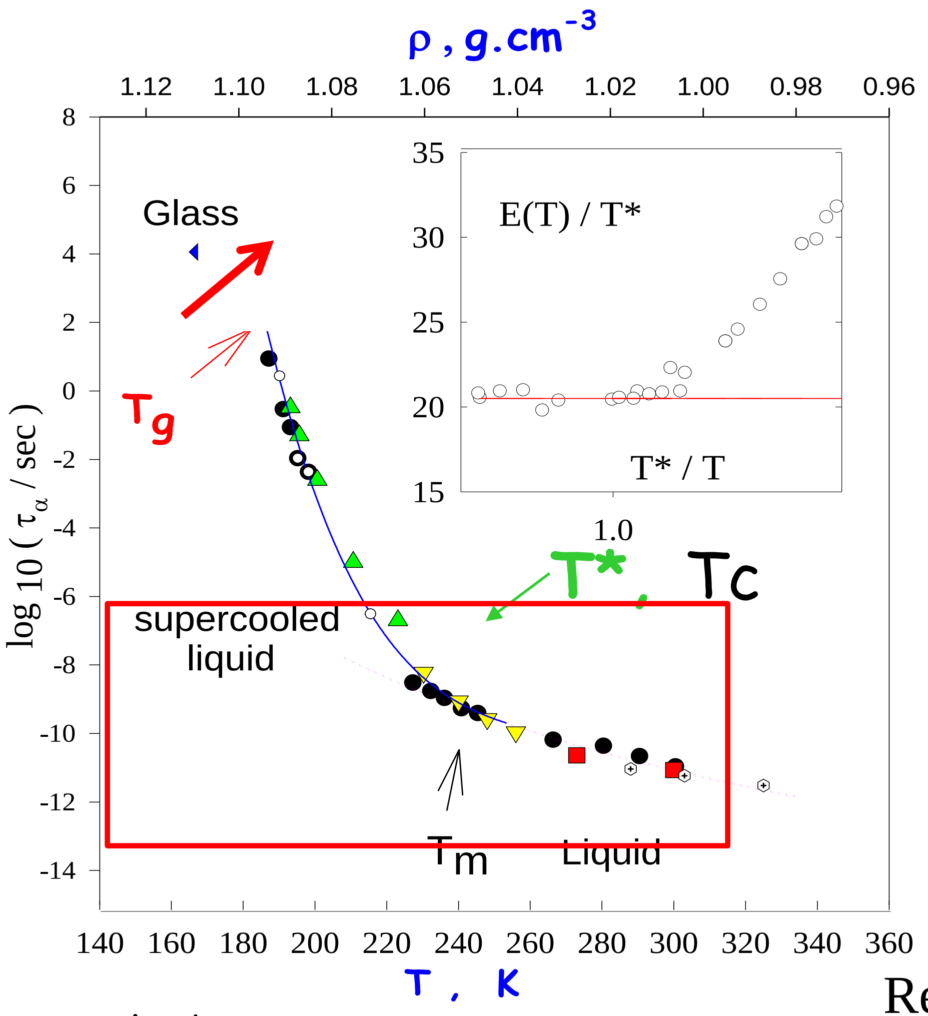
Spectroscopic Techniques ↔ Scattering Techniques



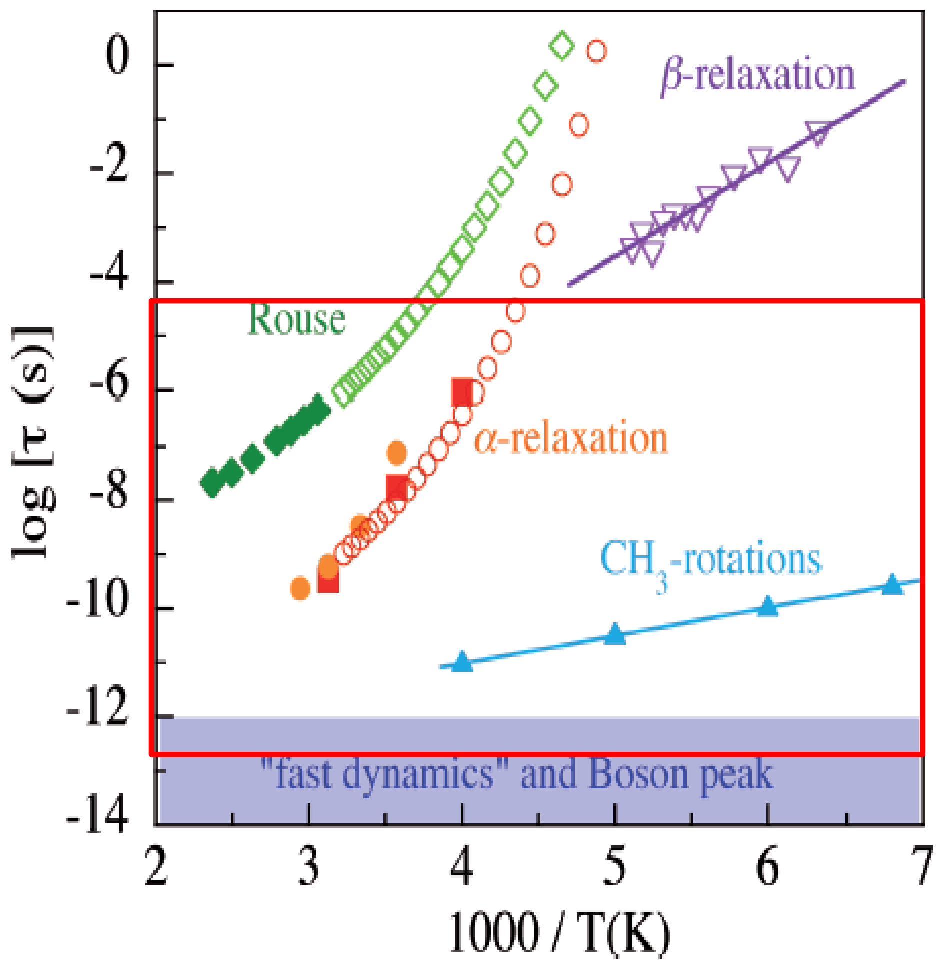


Processes observed at a given Q range

Dynamical processes observed in a given spectral window case of molecular liquids and polymers at normal pressure



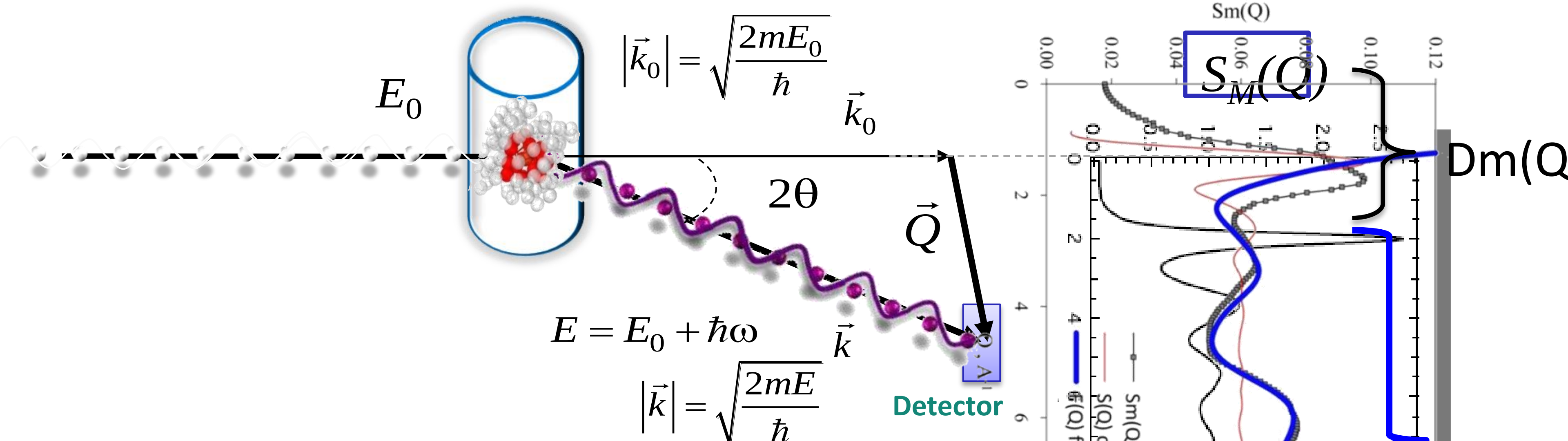
m-toluidine

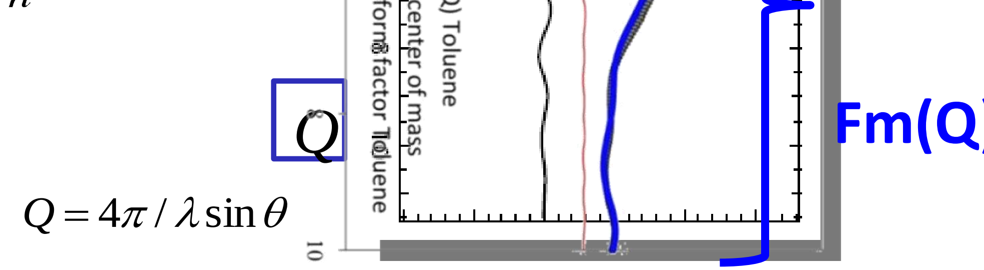


Relaxation map of polyisoprene. **Full symbols correspond to neutron scattering Colmenero/Arbe 2012**

Schematic of a diffraction experiment
Exploring the Q range

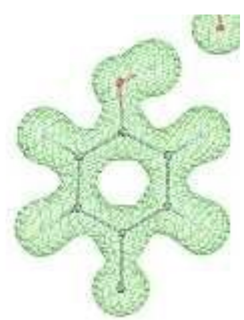
$$S_M(Q) = f_1(Q) + \frac{4\pi}{Q}\rho_M \int (g_L(r)-1)\, r \sin(Qr)\, dr$$





see by X Rays and neutron Scattering

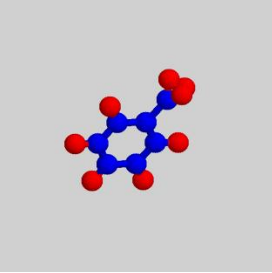
X-ray (H)



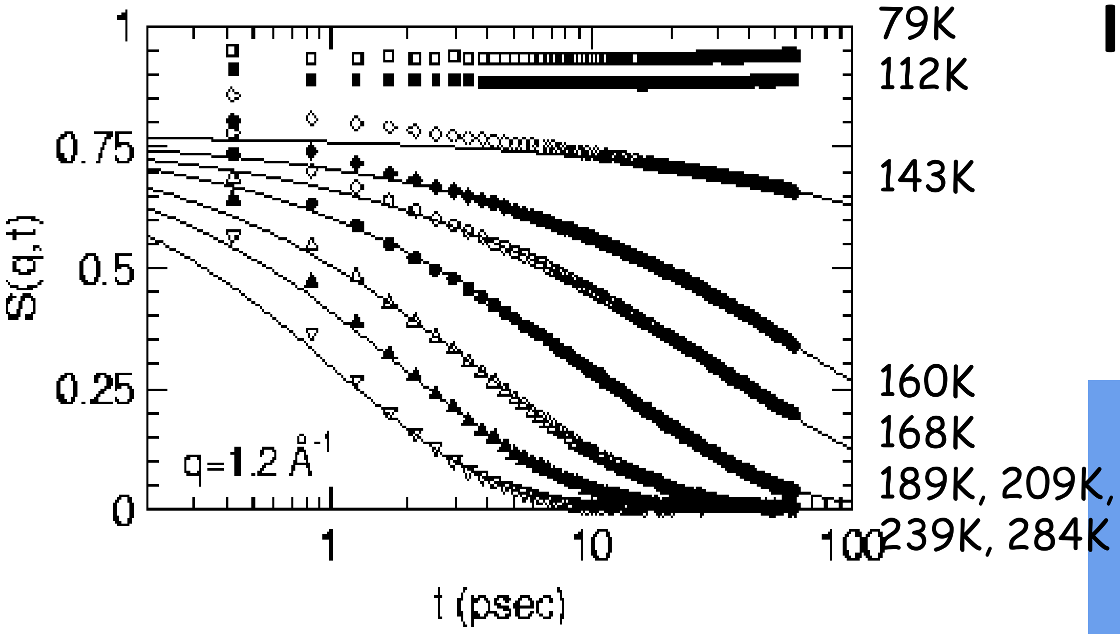
Neutron(D)

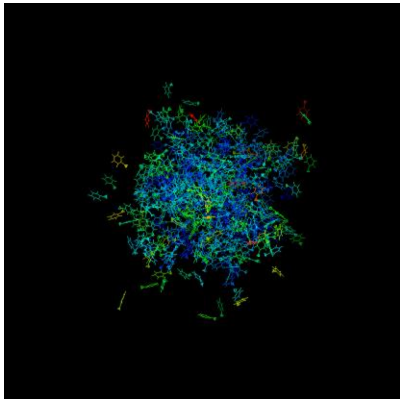
S(Q)= Dm(Q) + fm(Q)

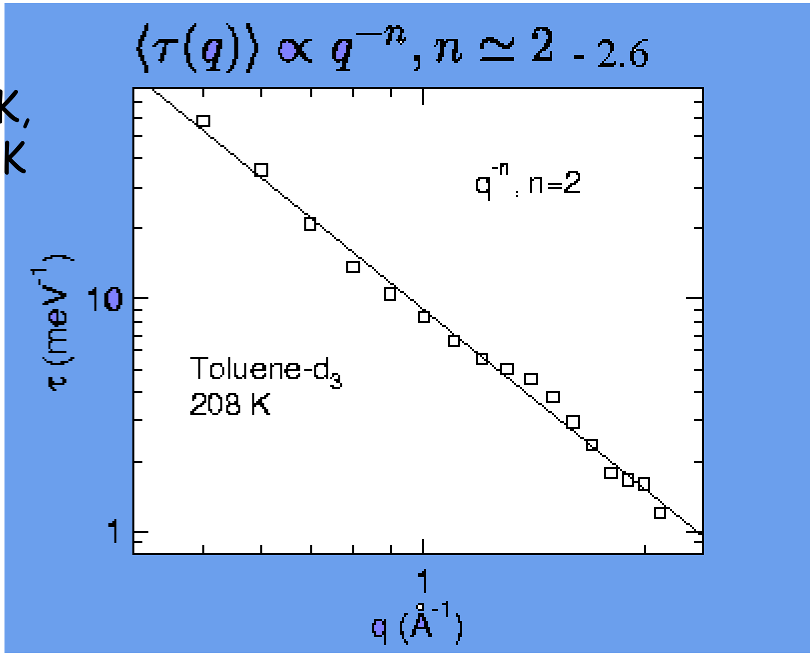
Q-dependence of the relaxation time τ(T, Q)



Incoherent scattering of liquid Toluene $C_6H_5CD_3$



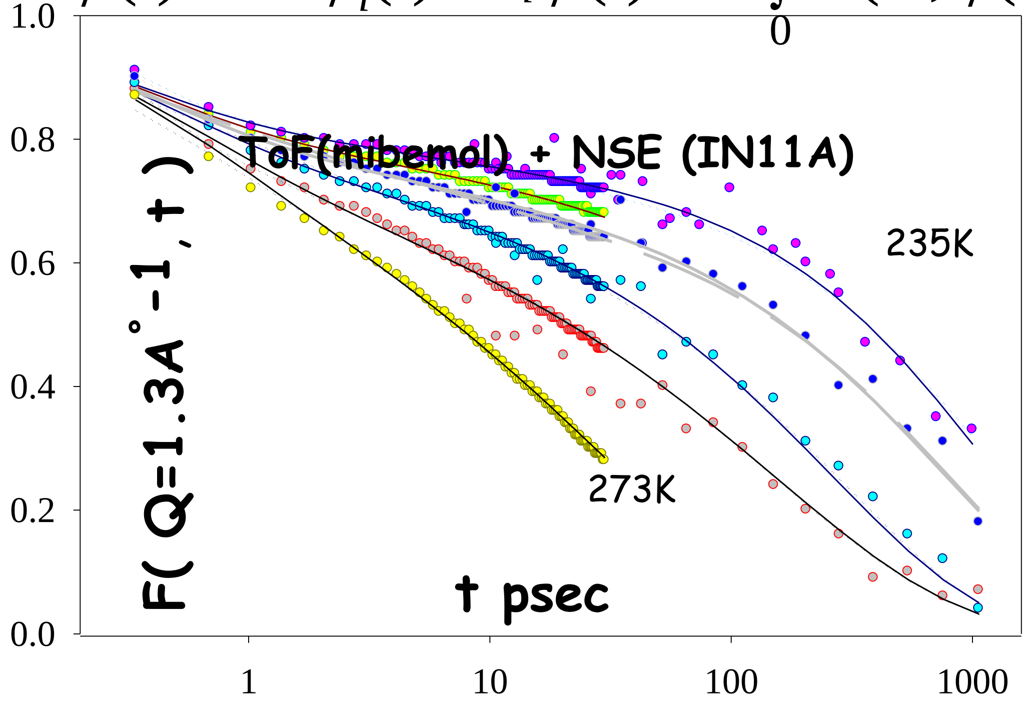




Combining ToF and NSE experiments to cover a larger dynamical range

Fitting the generalized Langevin equations (on the basis on the Mode Coupling Theory)

$$\ddot{\phi}_i(t)+\Gamma_i\Omega_i\dot{\phi}_i(t)+\Omega_i^2\phi_i(t)+\Omega_i^2\int_0^t m_i(\mathrm{V};\phi(t-t'))\dot{\phi}_i(t')dt'=0$$



$\lambda_{sch}^{critique} < \lambda_{fit}$ lois asymp

$T_{sch}c$ précis mais ~Tc± 10K

Coherent Diffusion
Of a molecular liquid

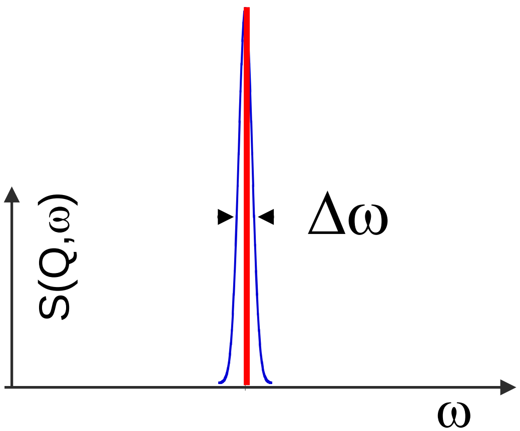
Lines = schematic mode coupling theory analysis

Elastic scan or fixed window method; following th elastic condistions

S(Q,ω) and <u²> mean square displacement

$$S_{el}(q,\Delta\omega,T)/S_{el}(q,\Delta\omega,T=0)=\exp[-2W(q,\Delta\omega,T)]=\exp[-<u^2(T)>q^2/3]$$

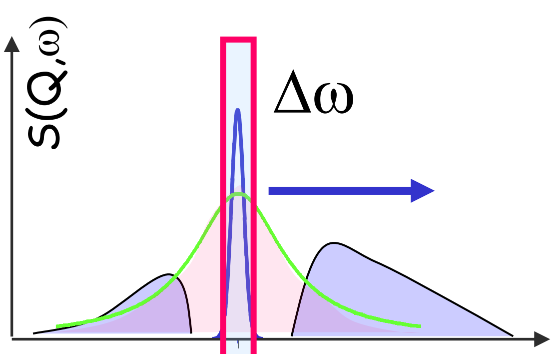
$$\left\langle u^2 \right\rangle_{eff} \propto k_B T \int_0^{\omega_m} \frac{1}{\omega^2} g(\omega)\, d\omega \propto T$$



diffusion Elastique

$$\boxed{g(\omega) = \text{VDOS}}$$

msd =measure of the atoms motions fastest than the resolution fonction Δω



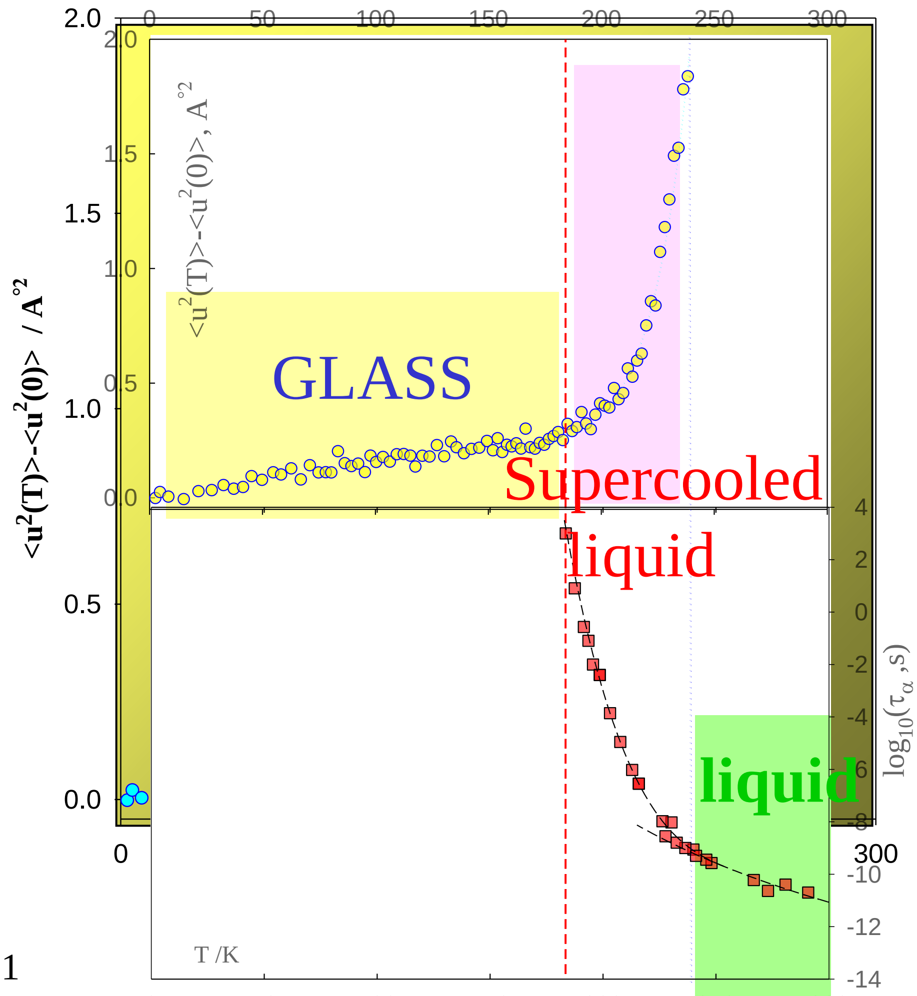
Elastic intensity at ω=0 sensitive to any contribuion arrising at high energy

Provides a good qualitative information

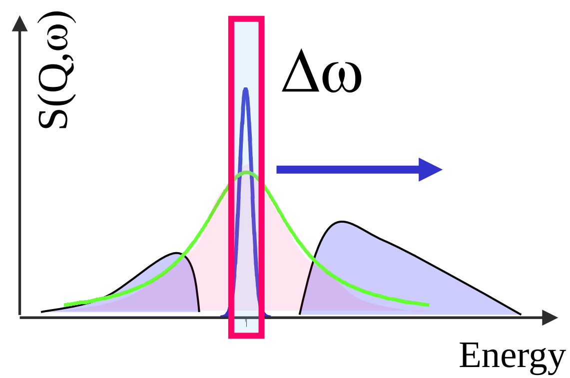
$$S_{inc}(Q,\omega) = DWF\left[A(Q)\delta(\omega) + (1 - A(Q))\sum_i L_i(Q,\omega)\right]$$

hidden connection between
the **flow process on a time scale of seconds** and
the **processes seen in a pico-nano time scale** experiment,
more than ten decades faster

$$S_{el}(q,\Delta\omega,T)/S_{el}(q,\Delta\omega,T=0)=\exp[-2W(q,\Delta\omega,T)]=\exp[-<u^2(T)>q^2/3]$$



Mean Square Displacement
sensitive to all motions faster tha
the resolution



the larger msd , the shorter τ_α

Local vibrations and phonons

VDOS vibrationnal density of states

$$\left(\frac{d^2\sigma}{dE_f d\Omega}\right)_{\mathrm{inc}} = \frac{N\sigma_{\mathrm{i}}}{8\pi m}\frac{k_f}{k_i}Q^2 e^{-2W(\vec{Q})}\frac{G(\omega)}{\omega}(n(\omega)+1)$$

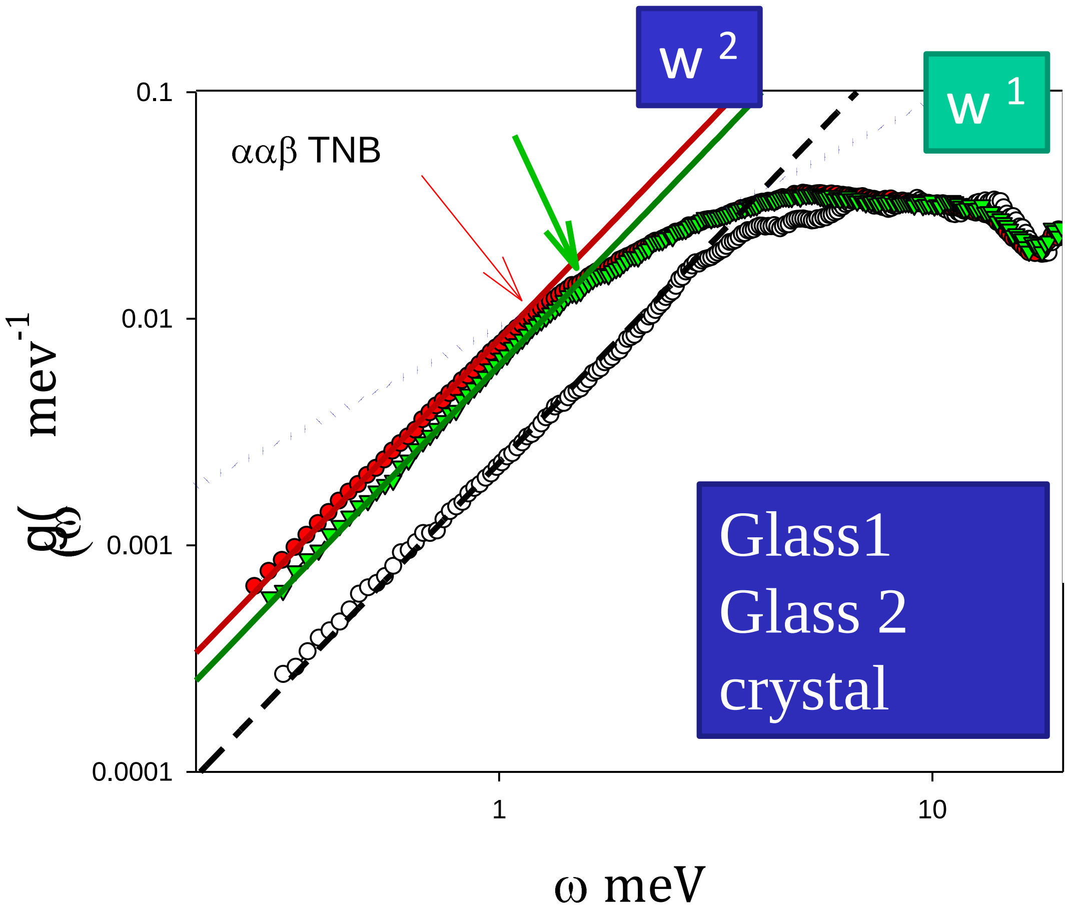
$$\int_{Q_{\min}}^{Q_{\max}}\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}(\hbar\omega)\mathrm{d}\Omega}\right)_{\mathrm{coh}} Q\mathrm{d}Q \approx \int_{Q_{\min}}^{Q_{\max}}\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}(\hbar\omega)\mathrm{d}\Omega}\right)_{\mathrm{inc}} Q\mathrm{d}Q$$

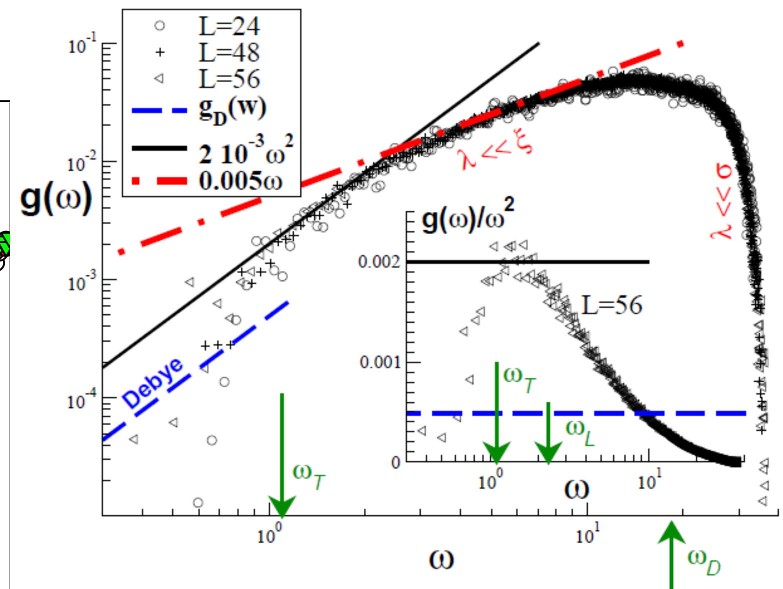
Incoherent approximation

VDOS analysis at low energies

Looking at the structural disorder and inhomogeneities in amorphous systems

Deviation from the elastic medium theory (Debye)

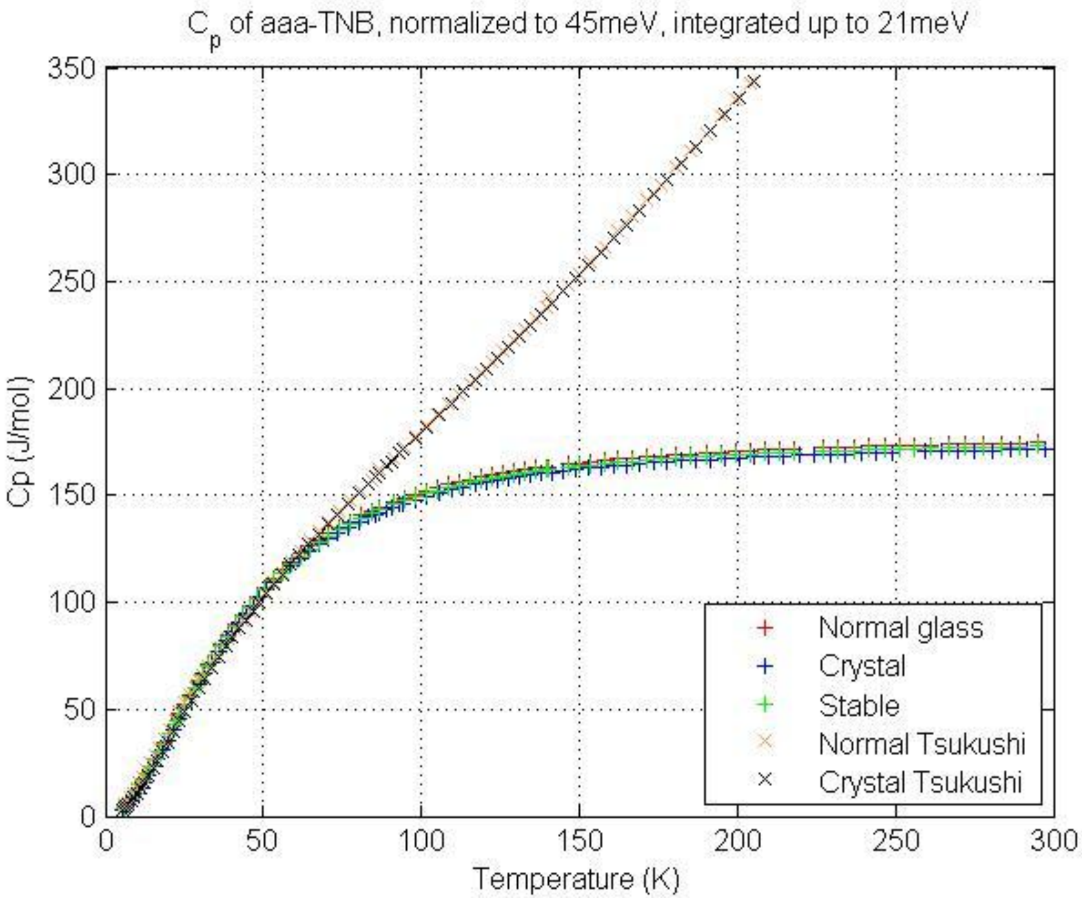




Léonforte et al PRE 2004, 2005

Heat capacity at low Tà basses T

$$c_{\mathrm{p}}(T) \simeq c_{\mathrm{V}}(T) = N_{at} R \int d\omega g(\omega) \frac{(\beta/2)^2}{\sinh^2(\beta/2)}, \beta = \hbar\omega/k_{\mathrm{B}}T$$



Where low frequency modes are active

Another important concept Susceptibility

$$S(\vec{Q},\omega) = \frac{1}{\pi}\{1 + n(\omega)\}\chi''[\omega]$$

Get rid of T effects

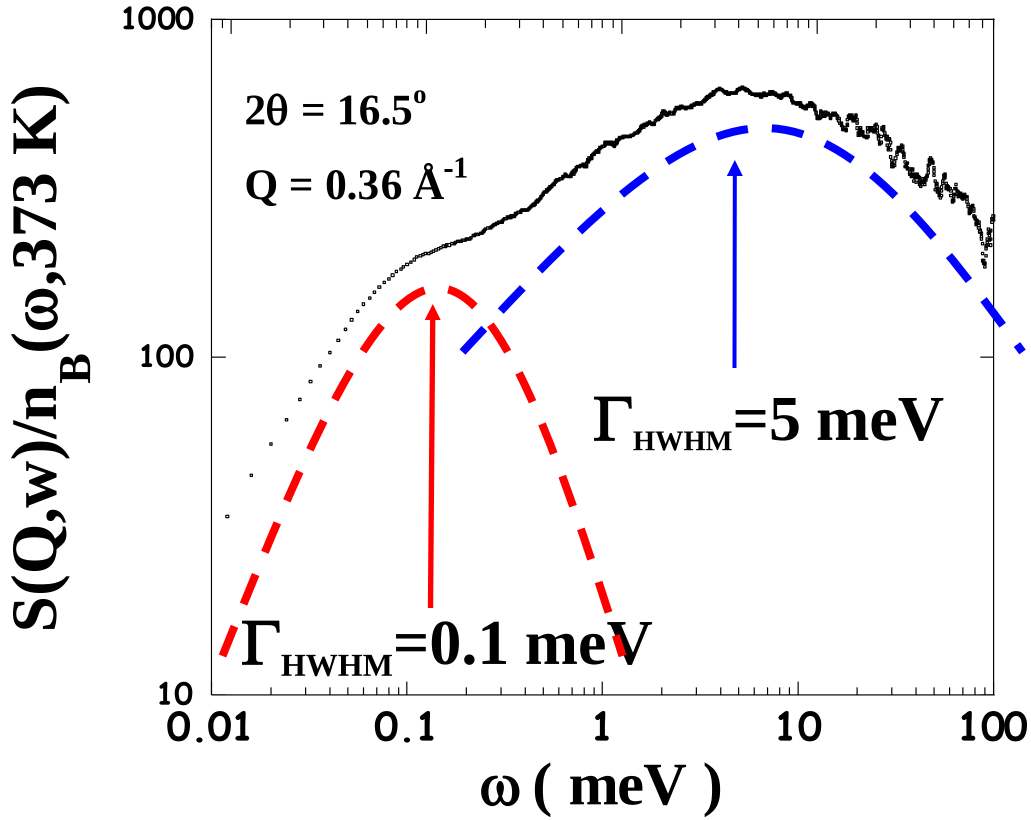
For an harmonic oscillator

$$\chi''[\omega] = \frac{\pi}{2\omega_0}\delta(\omega - \omega_0) - \delta(\omega + \omega_0)$$

Dynamical Susceptibility : bulk PEO

$$\chi(Q,\omega) = S(Q,\omega) \,/\, n_{Bose}(\omega,T)$$

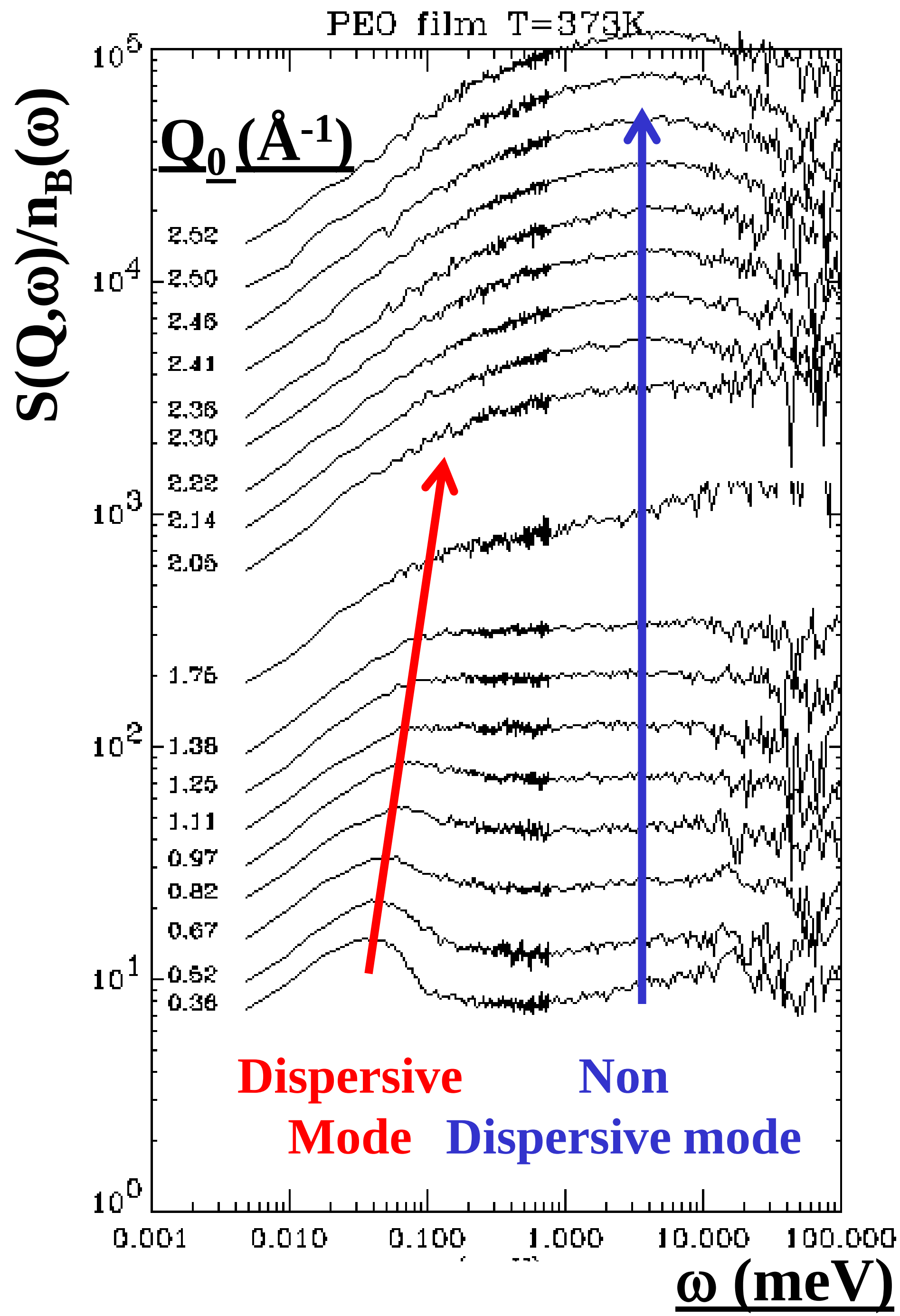
A Lorentzian CENTERED at $\omega = 0$ and HWHM= Γ in $S(Q,\omega)$ <u>appears</u> as a band centered at Γ in $\chi(Q,\omega)$ representation



PEO Dynamical Susceptibility
2 dynamical contributions

Quasi-elastic non dispersive mode :
↳ **Localized Dynamics**

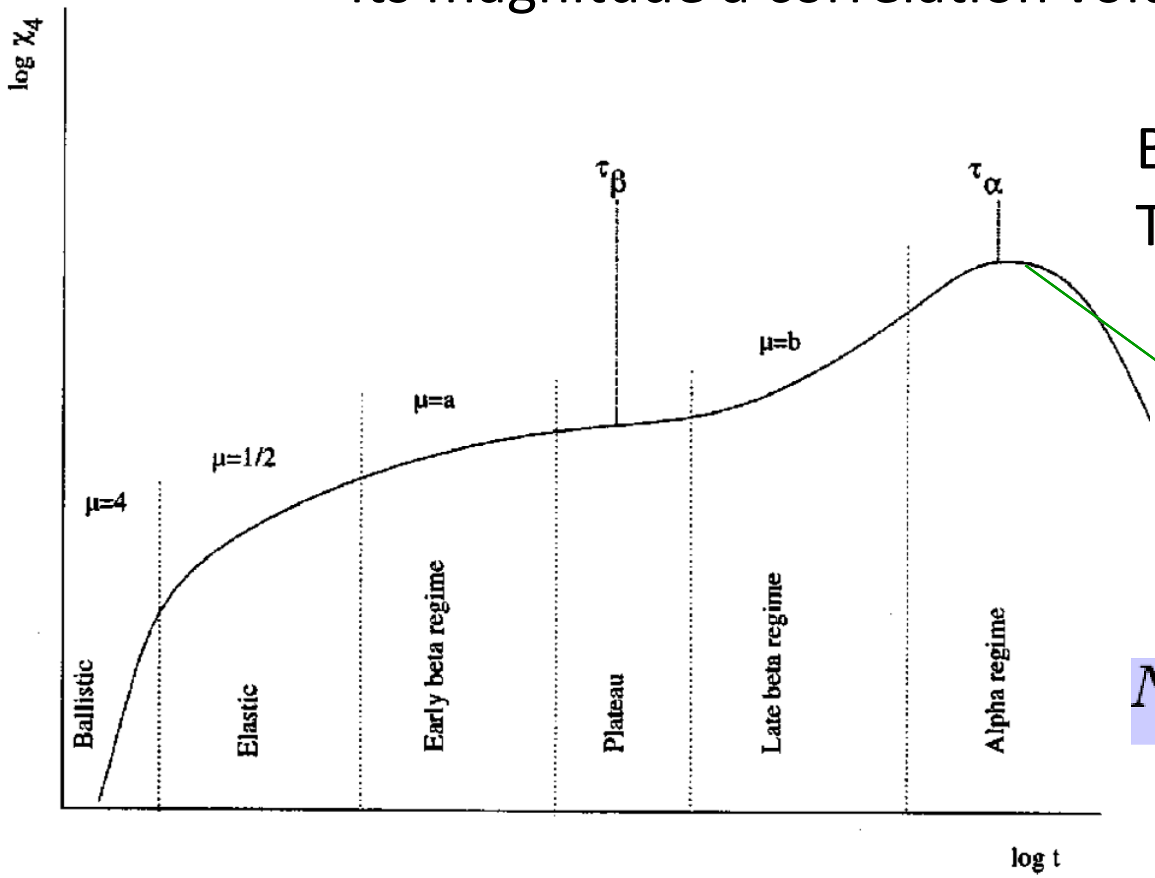
Quasi-elastic dispersive mode :
↳ **Translational Dynamics**



Zanotti, Smith, Price, Saboungi,
J.Phys. Cond. Matt.,18, 2391 (2006)

the **four-point correlation function** characterizes nontrivial **cooperative dynamics** in glassy systems within several models of glasses.

Its magnitude a correlation volume



Biroli Bouchaud EPL 2004
Toninelli et al PRE2005

Number of dynamically correlated molecules

$$N_{\mathrm{corr},4}(T) = \max_t \{\chi_4(t,T)\}$$

A QUEST FOR A GROWING LENGTH SCALE IN SUPERCOOLED LIQUIDS

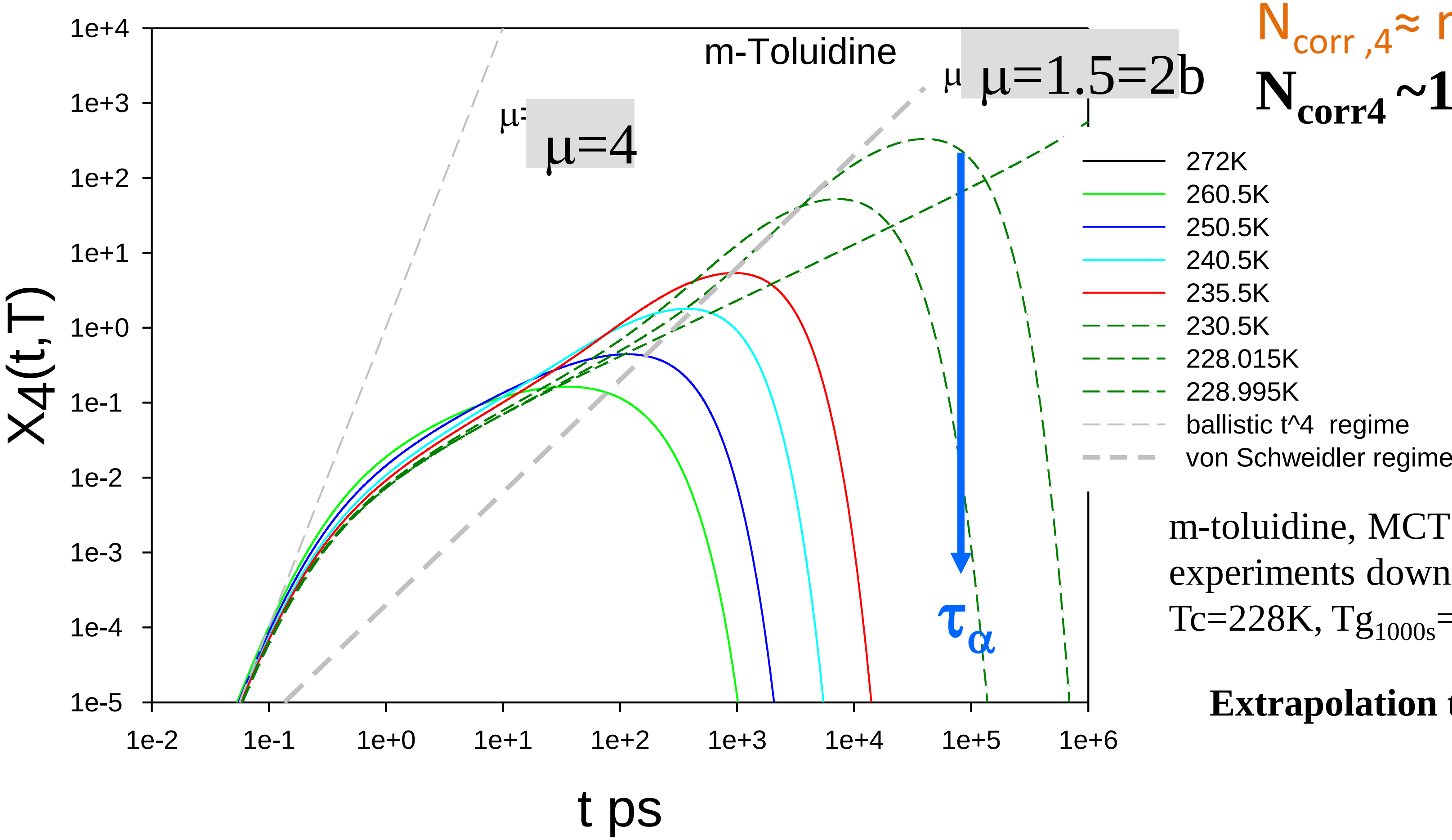
$\chi_4(t,T) \cong k_B/Cp(T_g) * T^2 * (d\phi_q(t)/dT)^2$

MCT makes prediction

-on the average dynamics, and On spatial correlation embodied in **multiple point correlation function**

$N_{corr,4} \approx \max\{\chi_4(\tau_\alpha)\}$

$\mathbf{N_{corr4} \sim 1/(Tc-T)^2}$



m-toluidine, MCT analysis experiments down to 230K, Tc=228K, Tg_{1000s}=183K

Extrapolation to Tc

By using a Fluctuation-dissipation relation + Cauchy-Schwartz inequality, they relate the χ_4 (t) to an easy accessible response function

$$N_{\mathrm{corr},4}(T) \gtrsim \frac{k_B T^2}{\Delta c_p} \chi_T(\tau, T)^2$$

where $$\chi_T(t,T) = \frac{\partial C(t,T)}{\partial T}$$ is the response of the dynamics to temperature changes

Accessible in experiments !

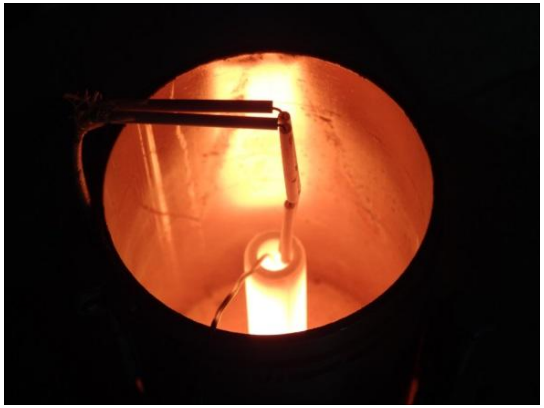
Example : derivative of the intermediate scattering function, or dielectric susceptibility

Changing the sample conditions

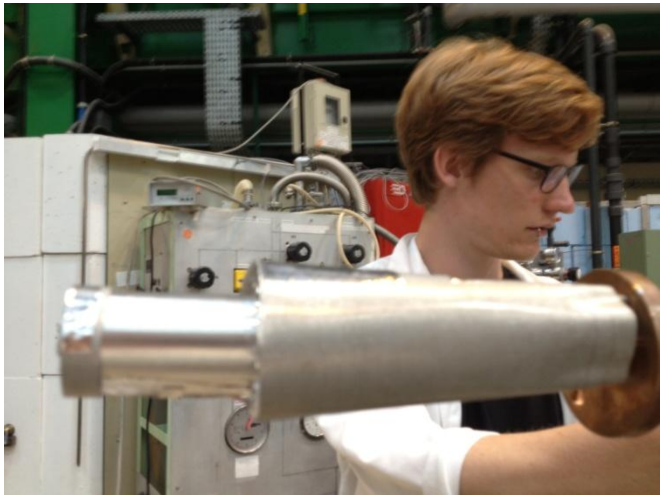
Introducing multiple control parameters

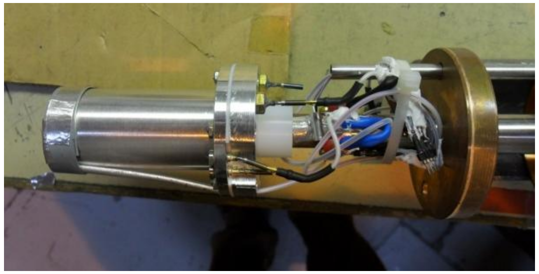
Combining probes and observables

furnace 1100°C for 5C2
(under air, inert gas or vacuum)



SAMPLE ENVIRONNEMENT





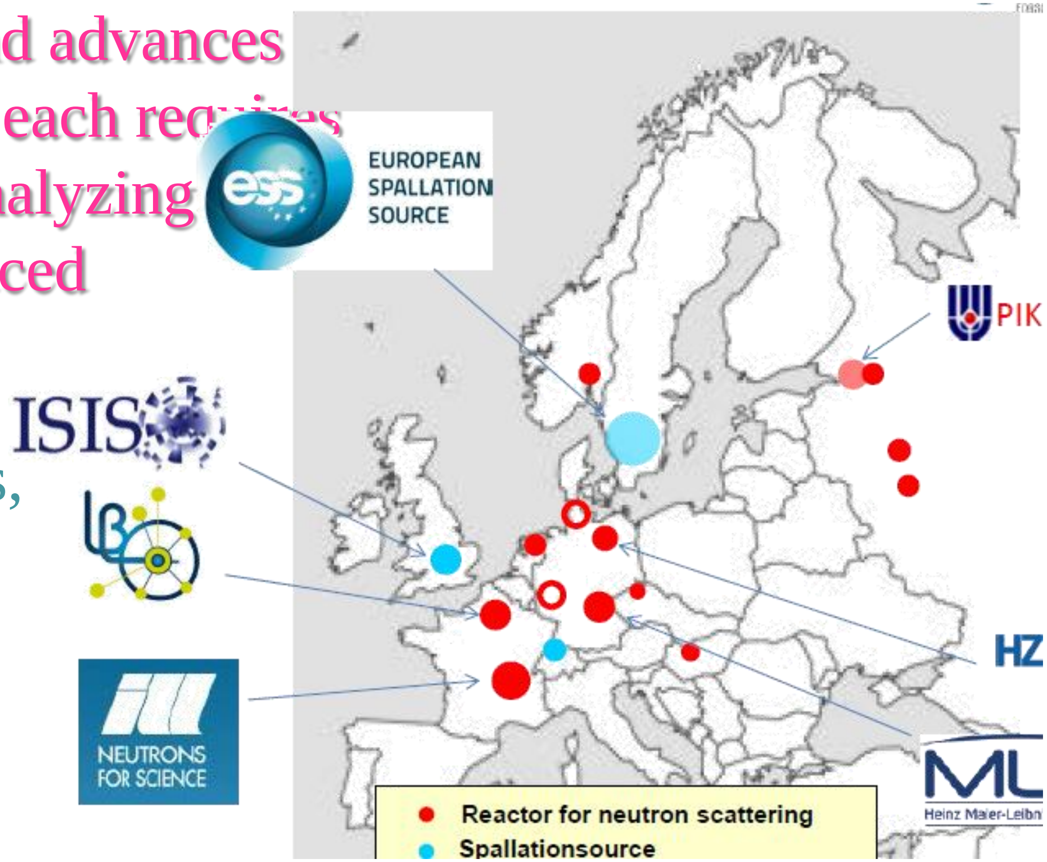
Device for dielectric measurements

Measuring slow relaxations processes by dielectric spectroscopy
Simultaneously with the structural changes

Huge questions for a huge variety of materials

from atomic scale to very large samples (few cm, m)
by increasing the levels of organizations
by increasing the properties of interest or mixing them

each step produces novelty and advances (sometimes unexpected) but each requires a new way of thinking and analyzing
new concepts must be introduced



The continued overlapping of Length scales and Time scales, Multiplicity of Observables

More Is Different

P. W. Anderson

Science, New Series, Vol. 177, No. 4047 (Aug. 4, 1972), 393-396.