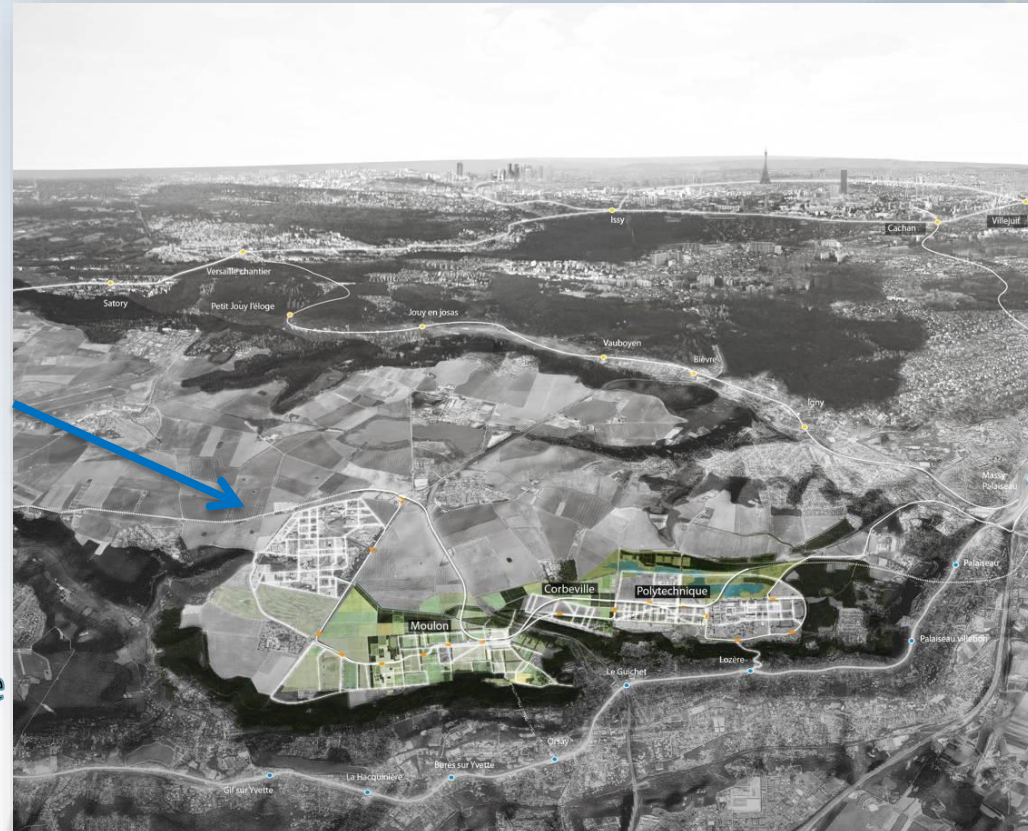


17th Oxford School on Neutron Scattering

DYNAMICS OF SOFT MATTER

C. Alba-Simionesco

Laboratoire Léon Brillouin (LLB)
Centre National de Diffusion Neutronique

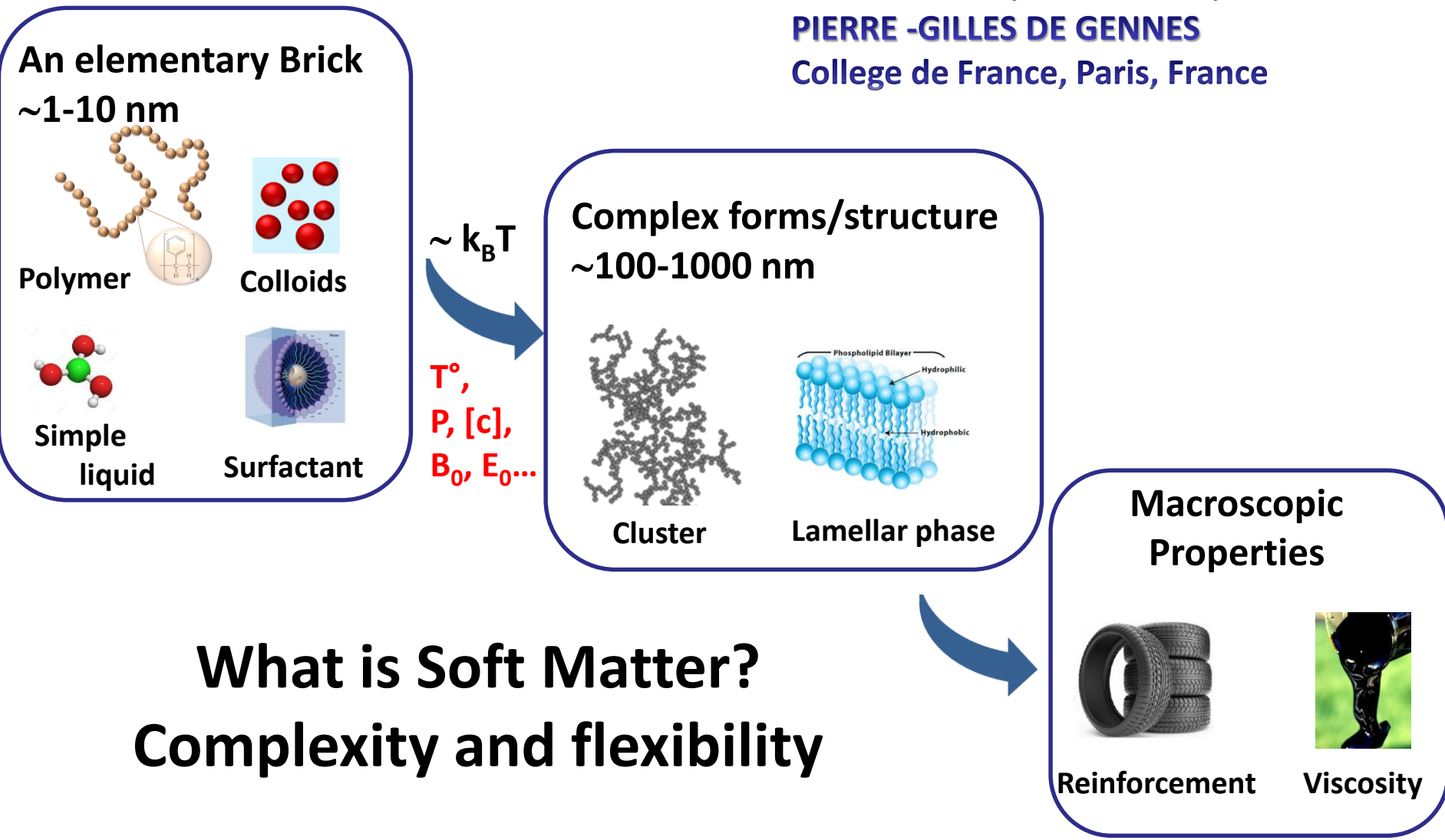


SOFT MATTER

Nobel Lecture, December 9, 1991

PIERRE -GILLES DE GENNES

College de France, Paris, France



What is Soft Matter?
Complexity and flexibility

Fundamental questions

Applications



Phenomena

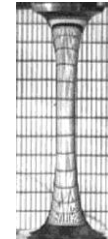
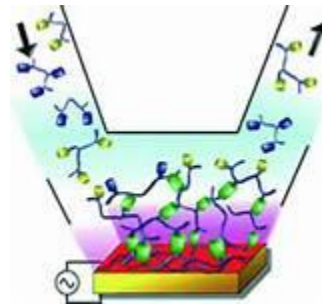
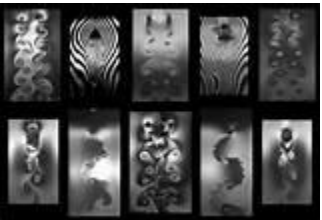
self-organisation, self-healing, interfacial dynamics, nucleation and growth of phases, solvation phenomena, enzymatic activity and **glass formation**

Control parameters and specific conditions

temperature, pressure, pH, ionic strength, light and electromagnetic fields, concentration confinement effects, functionalization, stretching

Scientific disciplines, applications

Chemistry, physics, chemical engineering, materials science, food science, mechanics, required the combination of methods, disciplines, expertises



PHYSICS TODAY

January 2016 • volume 69, number 1

A publication of the American Institute of Physics

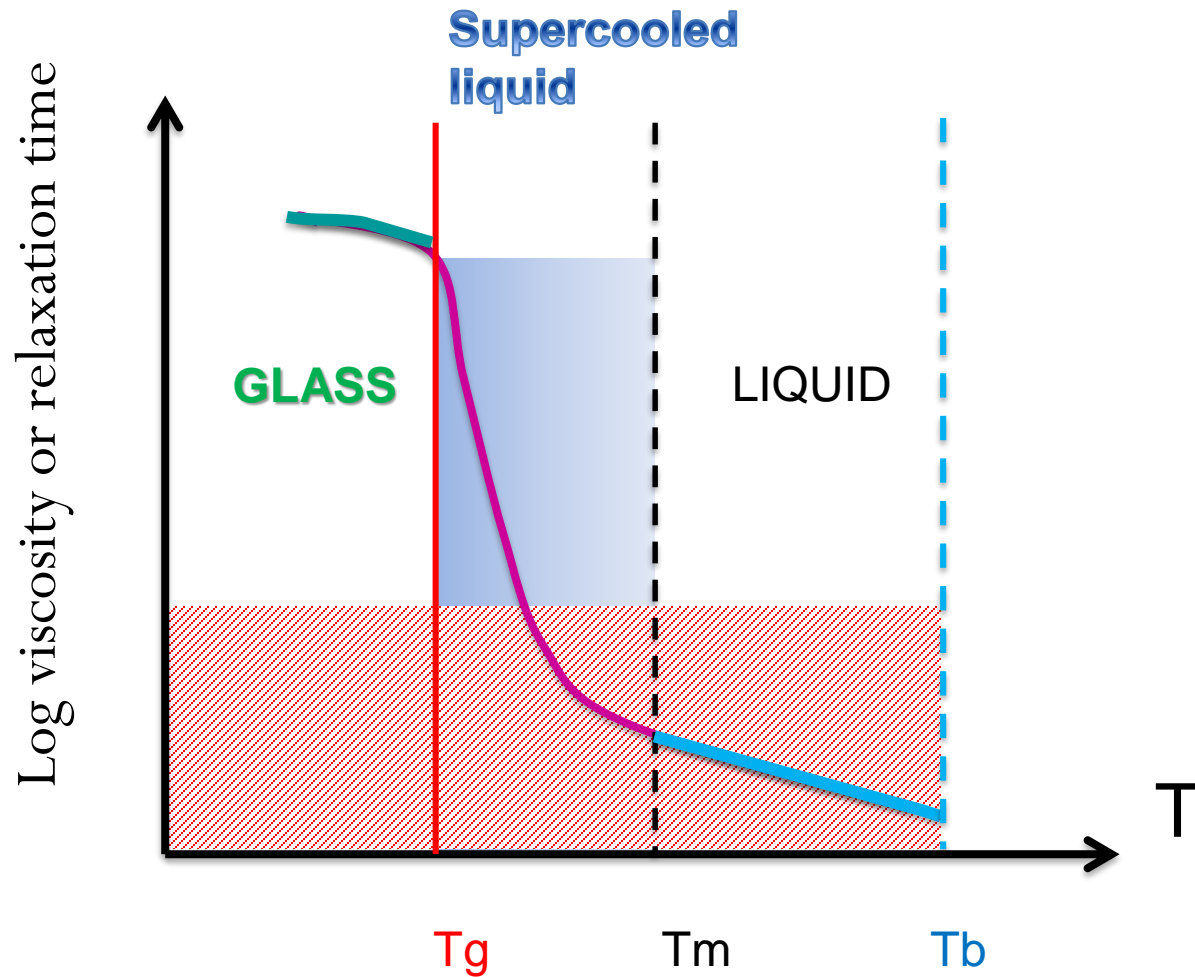
GLASS transitions

Shape-shifting
materials

Unspooky action
at a distance

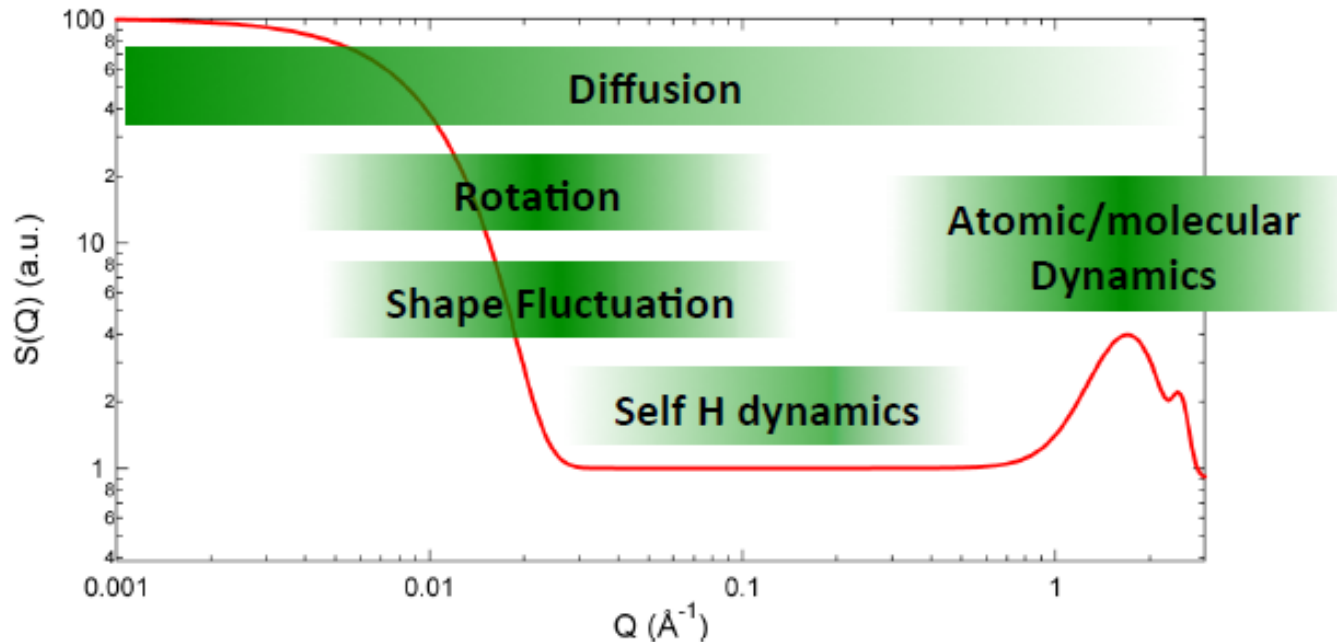


Phase transitions and rigidity by NS



Neutron scattering time window

Q range of the processes



At length scales larger than the macromolecular size: Diffusion.

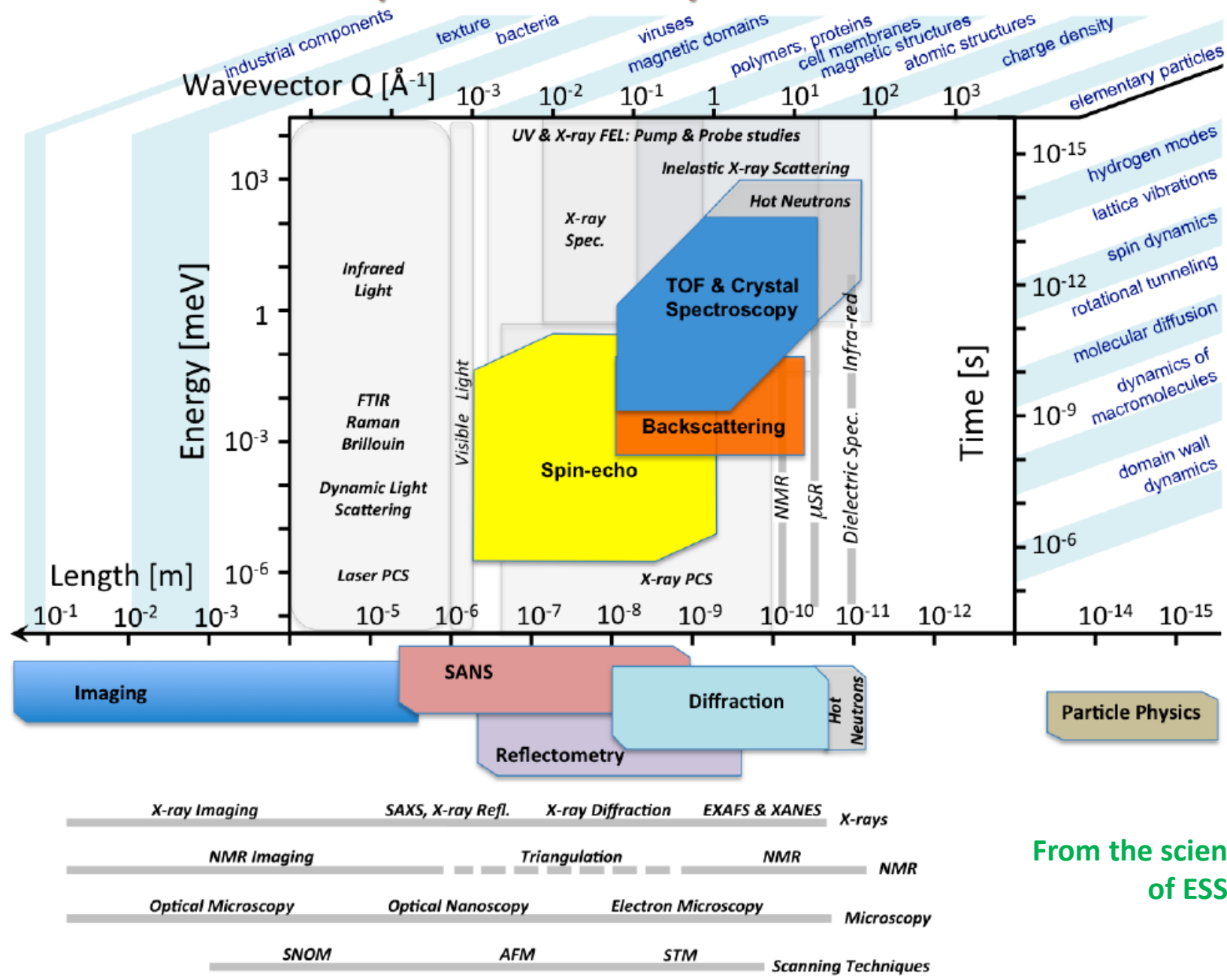
At length scales of the order the macromolecular size: Rotations and shape fluctuations.

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

At the structural peaks: Atomic/Molecular Dynamics.

(slide from A. Faraone, NIST)

Complementarity of methods



From the scientific case of ESS

QUASI ELASTIC NEUTRON SCATTERING : QENS

Measure of scattering processes involving small amounts of energy exchange, classical approximation ($|\hbar\omega| \ll \frac{1}{2}k_B T$)
i.e. in the low energy region of inelastic spectra close to 0

Dynamical phenomena at 10^{-13} to 10^{-7} s

Motions explored in space on lengthscales comparable with λ of the neutrons

Vibrational displacements, librations, jump distances, diffusion paths, correlation lengths (**nano to micro**)

Observables : Dynamical structure factor, $S(Q,w)$ or intermediate scattering function, mean square-displacements, self diffusion coefficient, relaxation time, Reptation Rouse modes, friction coefficient, Rotational diffusion, EISF, VDOS, C_p

motions

{
0.1psec to 500nsec
.5meV à 20meV
1000Å à 1 Å
}

Several
instruments

Triple Spectrometer

Time of Flight Spectrometer (*based on energy transfer analysis*)

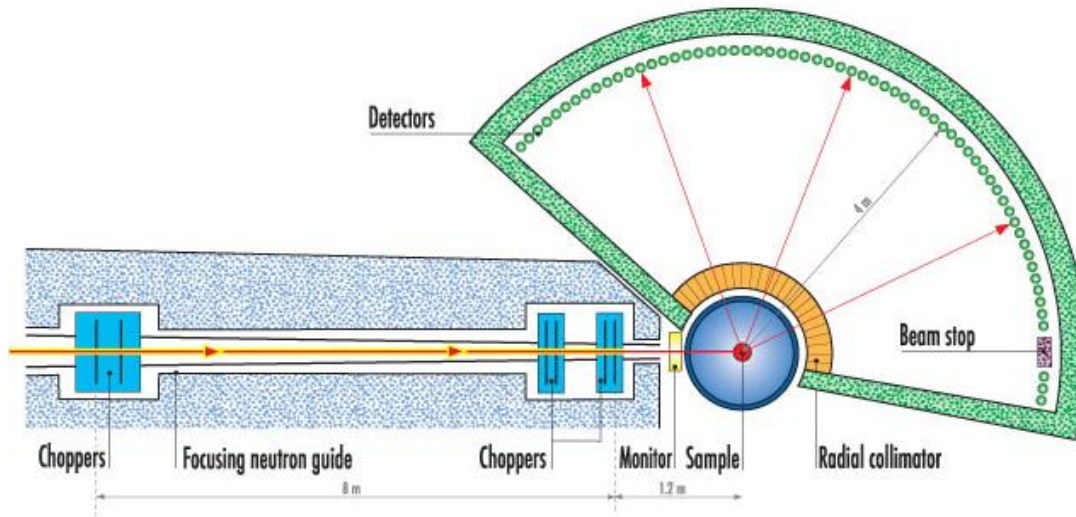
Backscattering Spectrometer

Neutron spin Echo Spectrometer (NSE and NRSE)

Based on the Fourier time analysis of the scattered intensity

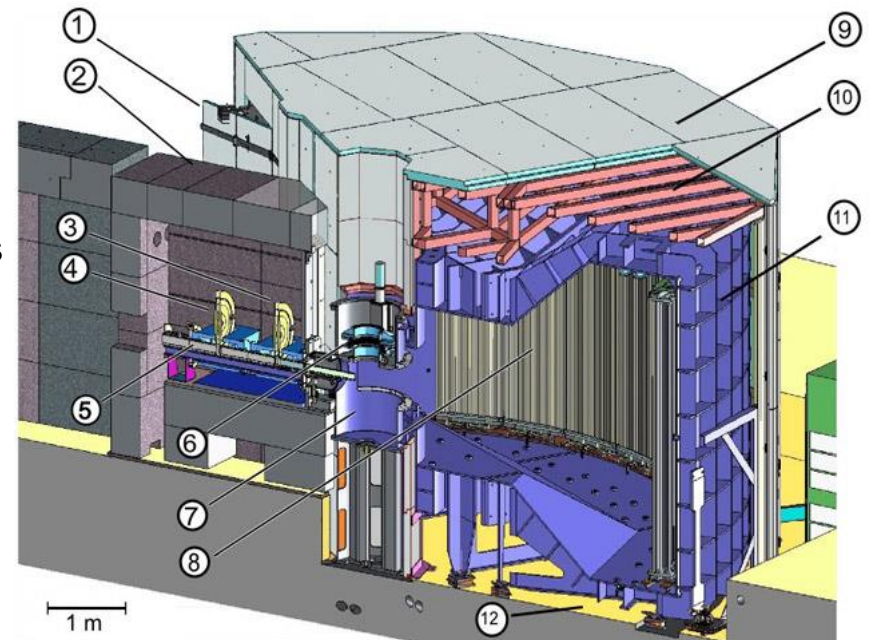
Disk chopper time-of-flight spectrometer IN5

<https://www.ill.eu/users/instruments/instruments-list/in5/description>



Monochromatisation	
6 counter-rotating choppers	
Chopper velocity V_0 (revolution per minute)	2000 rpm to 17000 rpm
Incident wavelength λ_0	1.8 Å to 20 Å
Sample	
elastic energy resolution at 5.0 Å, 8500rpm	~ 100 μ eV
max neutron energy loss	$E_{\max} \approx 0.6 \times E_0$ $E_{\min} \approx 0.4 \times E_0$ ($\lambda_{\max} = 1.5\lambda_0$)
max energy gain for the neutrons	$E_{\max} \rightarrow \infty \dots$
max momentum transfer Q_{\max}	11.48/Å Å ⁻¹
horizontal divergence (no collim.)	~ 0.1 × 2 × λ_0 [°]
vertical divergence (no collim.)	~ 0.1 × 3 × λ_0 [°]
Collimation before sample	- / 30' / 60'
beam size at the sample	~ 15 × 50 mm ²
flux at the sample at 5.0 Å	6.83 × 10 ⁵ [n/cm ² /s]

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

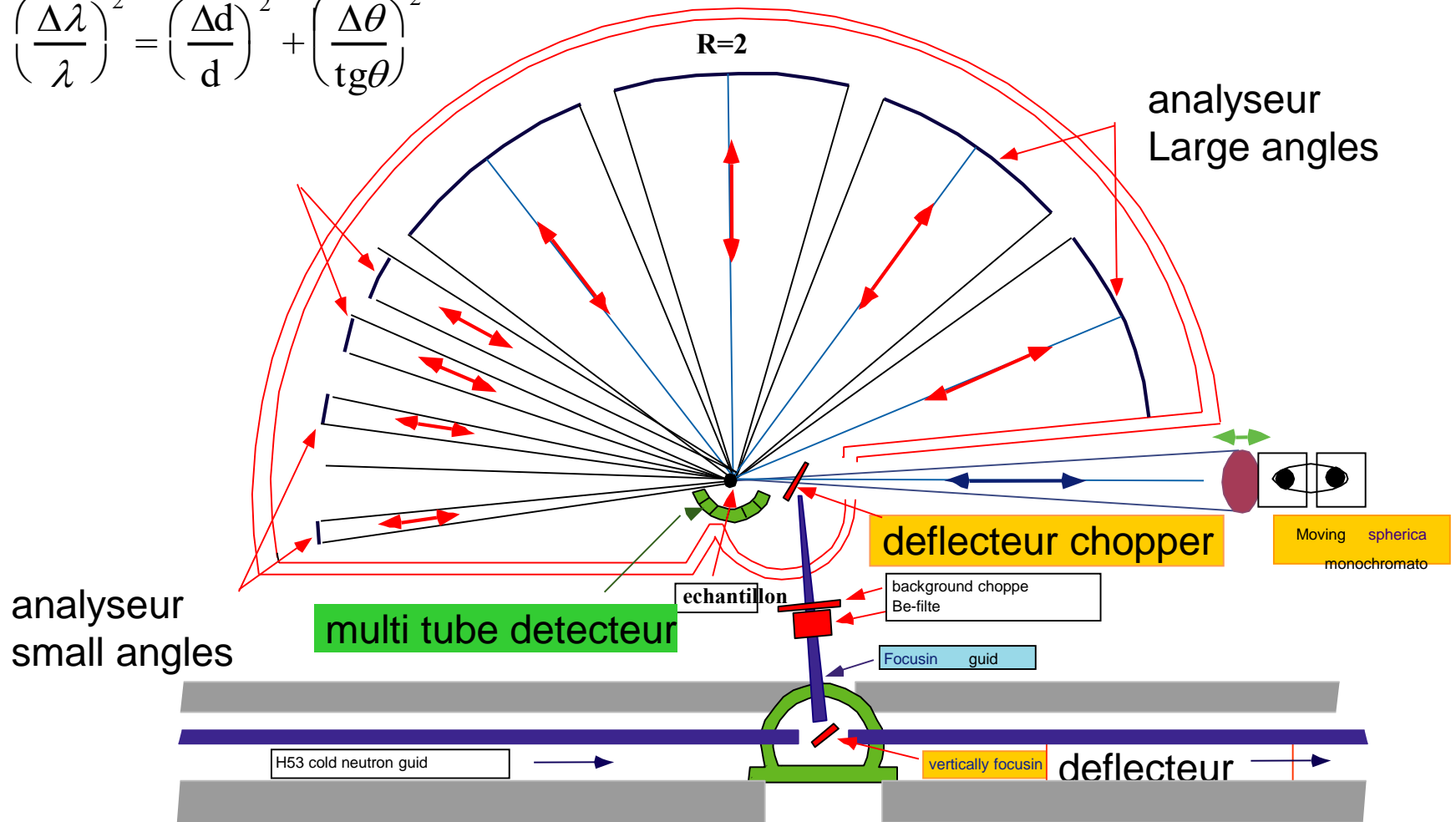


Backscattering Spectrometers

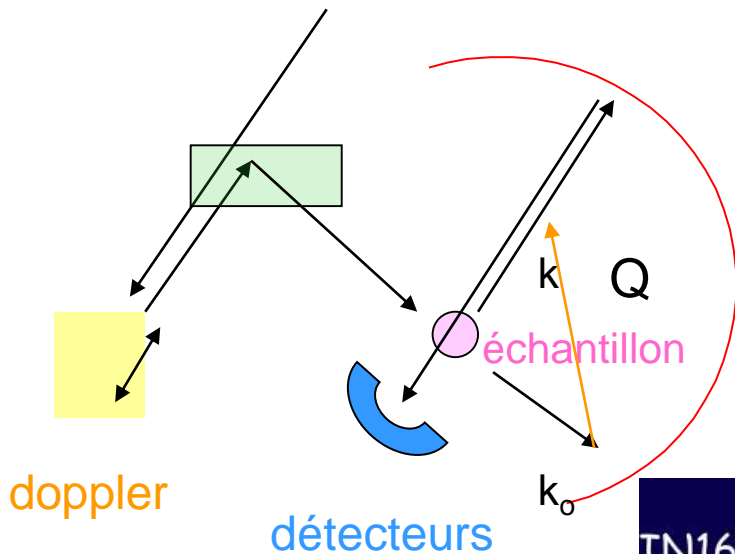
B. Frick, IN16, ILL

monochromator and analyseur : perfect crystals in backscattering ($2q=180^\circ$)
Bragg law differentiation

$$\left(\frac{\Delta\lambda}{\lambda}\right)^2 = \left(\frac{\Delta d}{d}\right)^2 + \left(\frac{\Delta\theta}{\text{tg}\theta}\right)^2$$



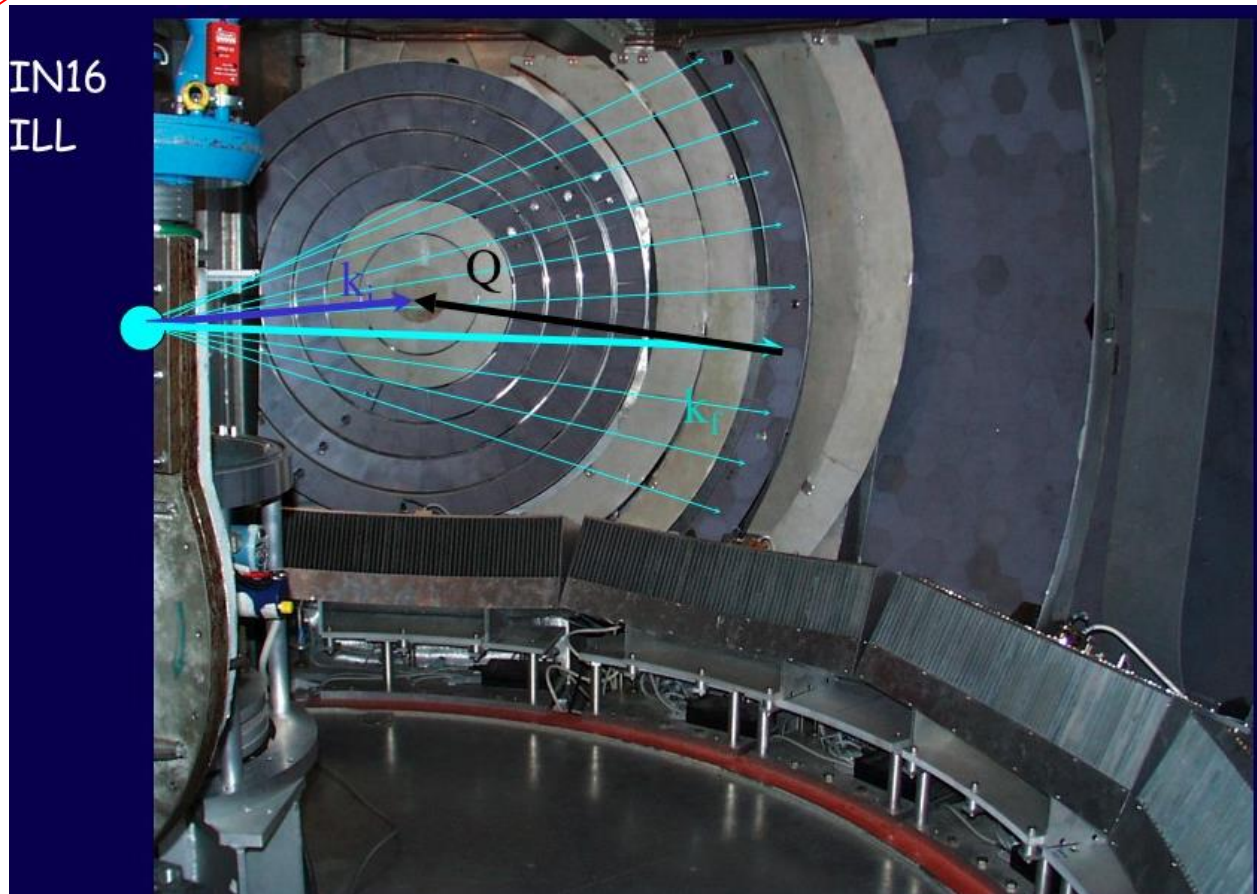
Backscattering Spectrometers



$Q=Q_{\text{élastique}}$

Résolution $< 1 \mu\text{eV}$
Gamme -15 à $+15 \mu\text{eV}$

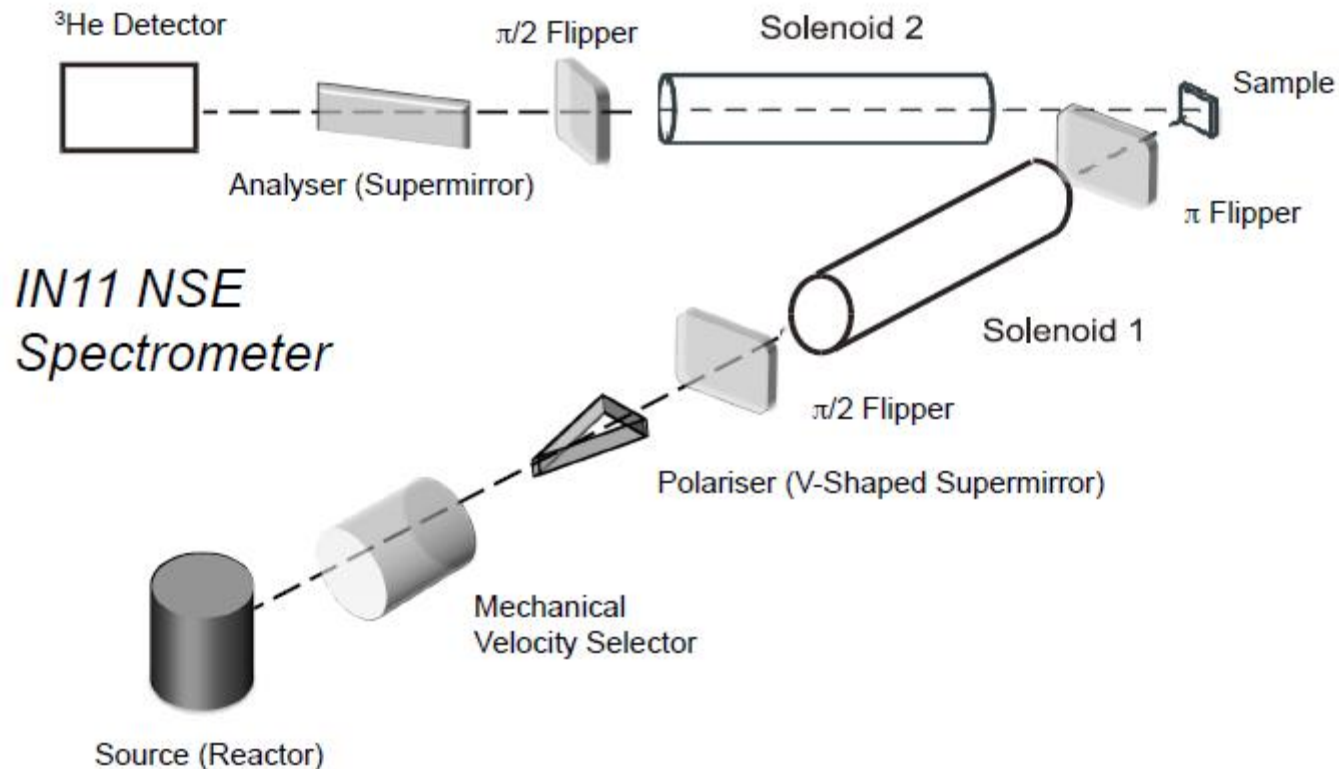
BASIS @SNS $\pm 300 \mu\text{eV}$



Spin Echo Spectrometers

Mezei 1972 NSE, Gähler 1987 NRSE

NSE measures the sample dynamics in the time domain, via the determination of the intermediate scattering functions $F(Q,t)$

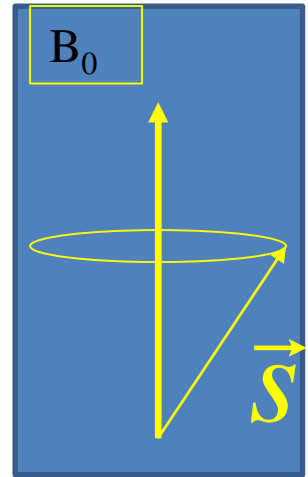
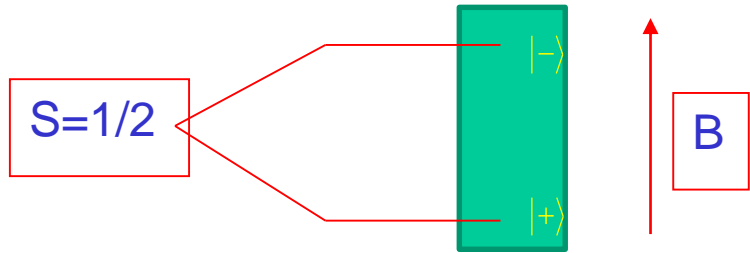


ILL, IN11A

Neutrons are polarised, π/E rotation, then under magnetic field

The measured quantity : the scattered beam polarisation...

Neutron spin , precession ...



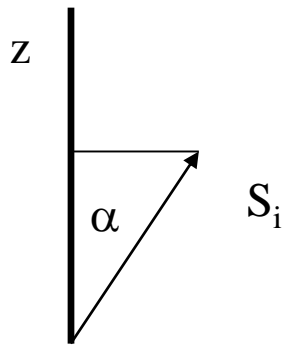
$$\frac{d\vec{s}}{dt} = \gamma\vec{s} \wedge \vec{B}_0$$

$$\omega = |\gamma_n|B_0$$

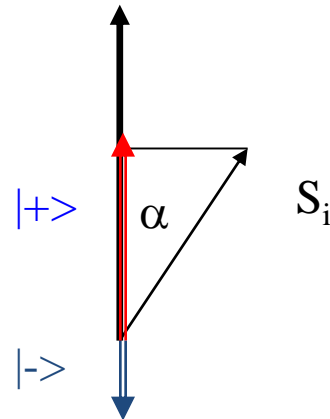
$$N = \gamma_n B_0 t / 2\pi$$

$$\gamma_n = -2913.2\pi \text{ (Gs)}^{-1}$$

$B_0=0$



B_0

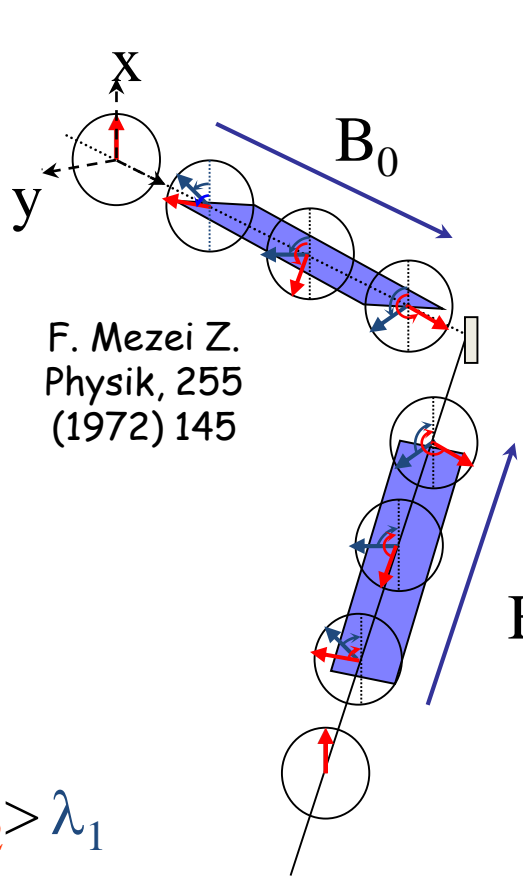


$$p_{|+\rangle} = \cos^2(\alpha/2)$$

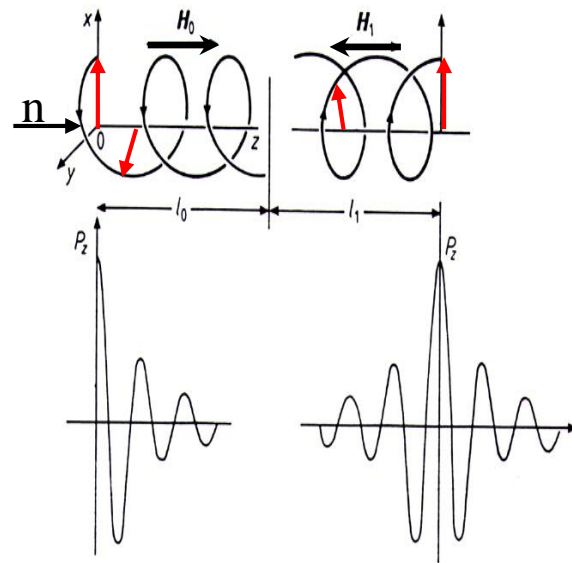
$$p_{|-\rangle} = \sin^2(\alpha/2)$$

$$\langle P \rangle = \frac{n_+ - n_-}{n_+ + n_-} = \langle p_{|+\rangle} \rangle - \langle p_{|-\rangle} \rangle = \left\langle \cos^2\left(\frac{\alpha}{2}\right) \right\rangle - \left\langle \sin^2\left(\frac{\alpha}{2}\right) \right\rangle = \langle \cos(\alpha) \rangle$$

to increase the energy resolution without drastic loss of intensity as in QENS-ToF energy transfer *is causing a phase shift of the neutron spin precession angle for each scattered neutron.*



F. Mezei Z. Physik, 255 (1972) 145



$$I(Q, t) \approx \langle P \rangle \approx \int_{-\infty}^{+\infty} S(Q, \omega) \cos(\omega \tau_{NSE}) d\omega$$

Polarisation

Probability of energy exchange

$$\lambda_2 > \lambda_1$$

$$\langle P \rangle = S_{coh}^{-1} / 3 S_{inc} \rightarrow H/D !!!$$

$$\tau_{NSE} = \frac{m^2 \gamma \int B dz}{2\pi h^2} (\lambda_0')^3$$

Comparaison TOF-BS et NSE

- **Frequency measurement**
- **Scan at fixed ω**
- **$S(Q, \omega) = S(Q, \omega) \otimes R(Q, \omega)$**
- **Self motions**
- **Shorter dynamical range**
- **Good Q resolution**
- **Excitations, vibrations**

- Time measurement
- Scan at fixed t
- $S(Q, t) = S(Q, t) \cdot R(Q, t)$
- Collective motions
- Large dynamical range (3 to 4 decades)
- $\Delta\lambda/\lambda \sim 15\% = \Delta Q/Q$
- Define R the flipping ratio

Current trend

Doing Neutron Scattering experiments

but

Combine **in situ** the measurement of another probe
With another method

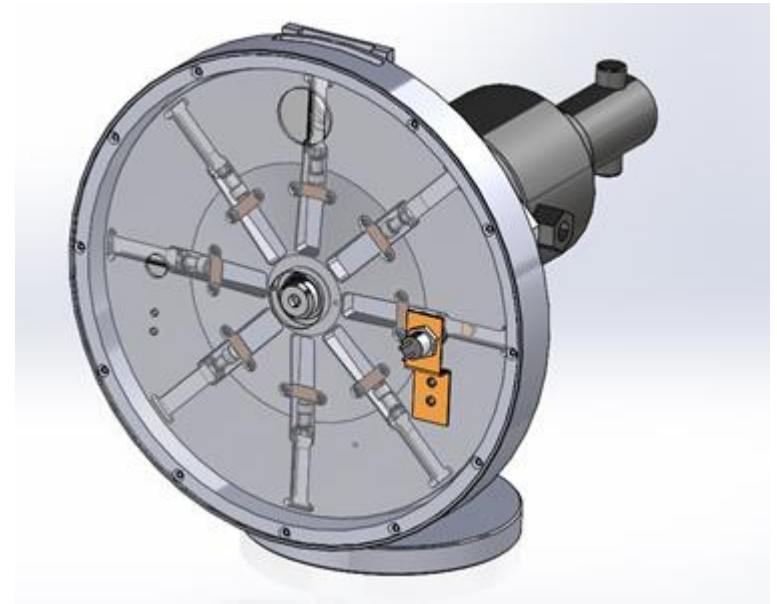
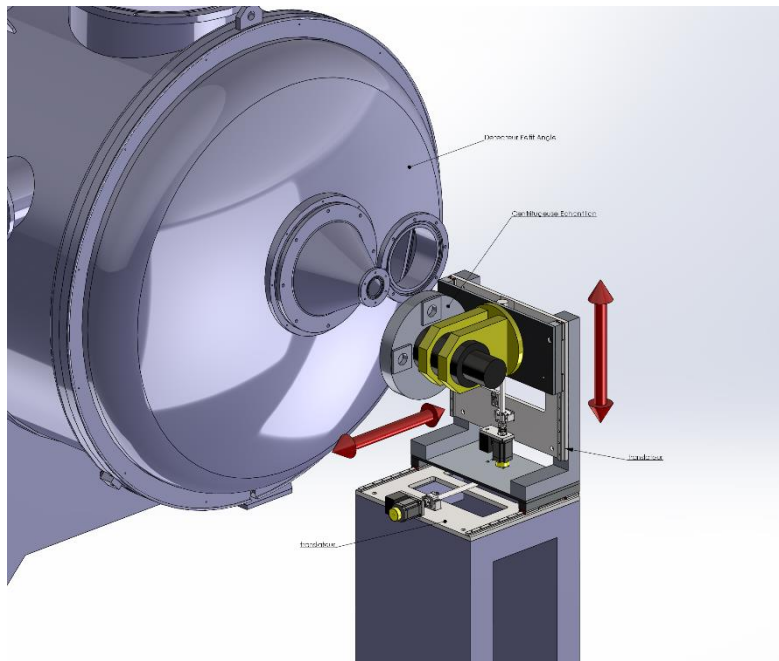
Especially useful with metastable samples

Ex : Calorimetry at LET

Sample environment NEW

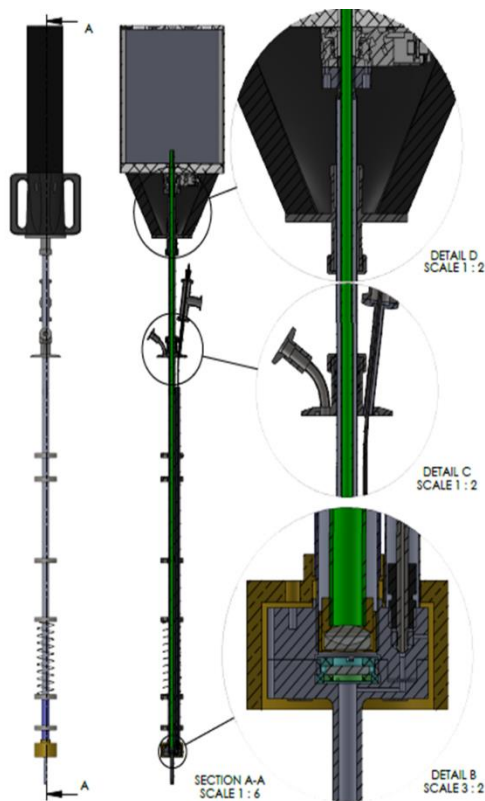
A new in situ centrifugation set-up for the separation of fluids by SANS and Diffraction

Up to >6000g (gravity)



Liquid extraction, phase separation, purification

simultaneous measurement of the structure and vibrational modes during the hydrate formation by elastic (and Quasielastic) Neutron Scattering and Raman Spectroscopy.

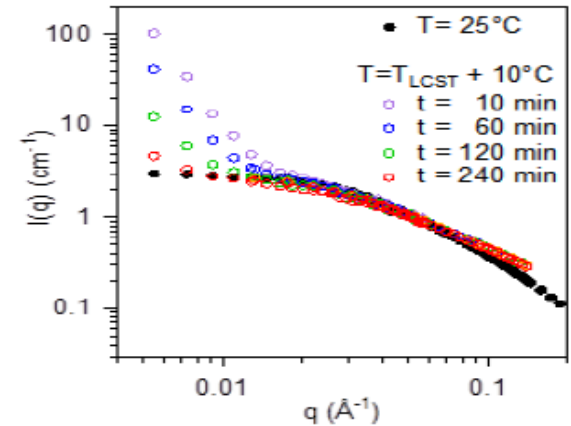
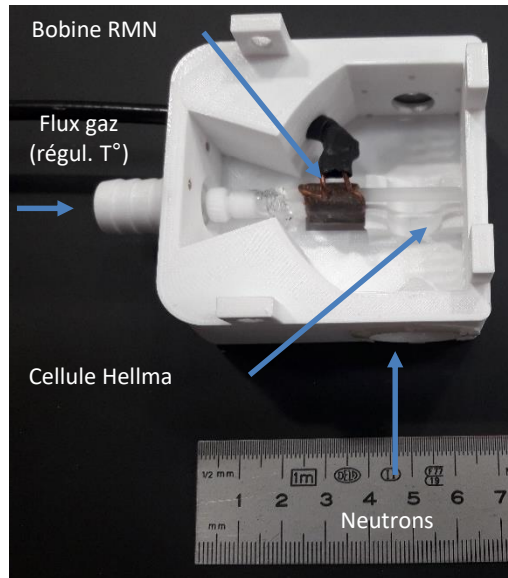


new equipment for coupled Raman/Neutron scattering experiments; left view of the neat sample can, sample cell and neutron beam (arrow A), middle focus on the equipped can, right zooms on the optical head for the laser beam injection and collection of the Raman signal (from A. Helary, LLB, coll A Desmedt and D. Morineau)

dedicated to the hydrate formation at Room Temperature with CO₂ and CH₄ gas

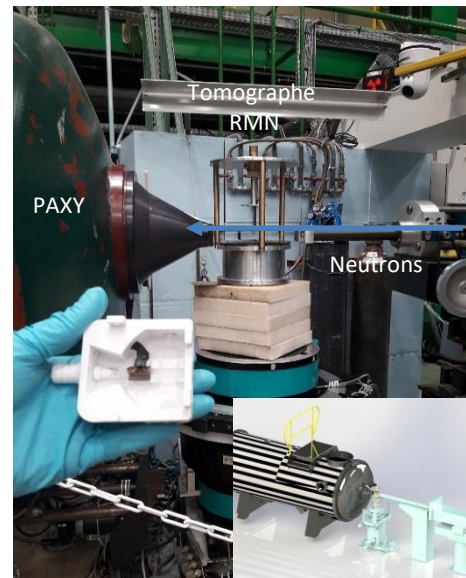
Coupling NMR and Neutron

Sol-gel, H⁺ and Li⁺ mobility



Signal SANS(neutrons)

**Design et fabrication
d'une cellule
« Sonde RMN+Cellule
Neutron+Régulation en
température ».
(LLB)**



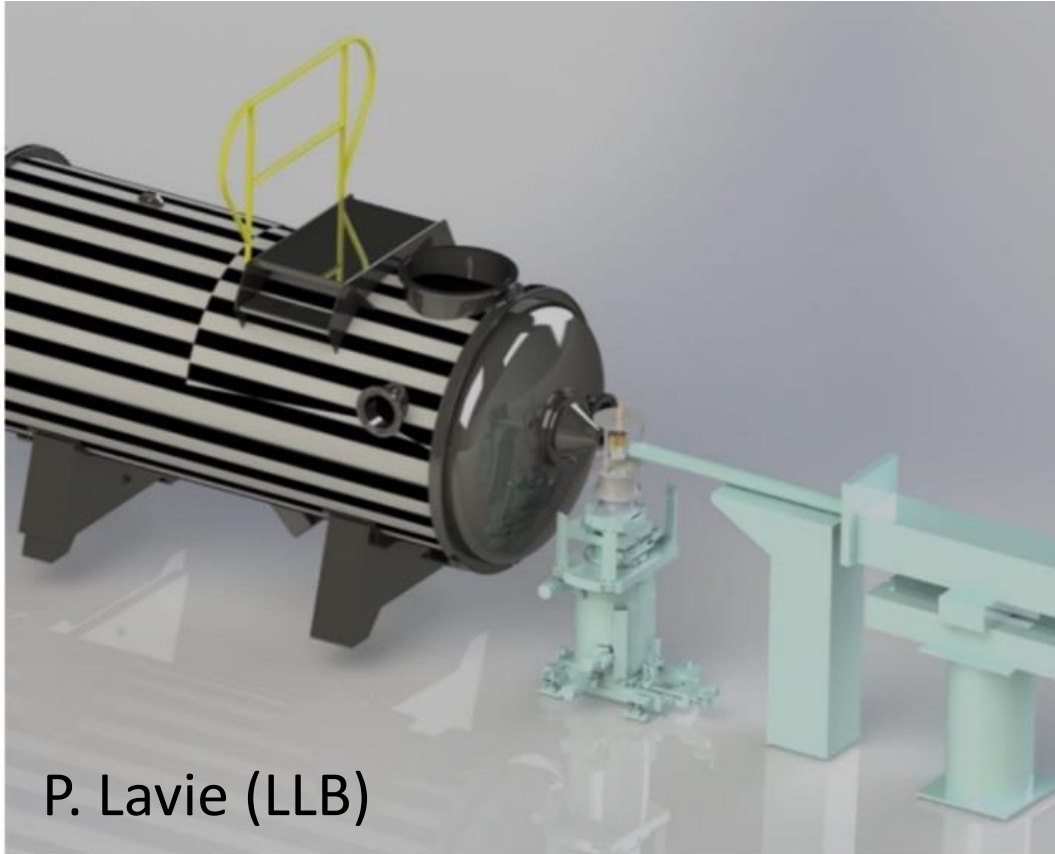
Tomography
NMR -Imagine
(LLB, NIMBE)

measuring simultaneously NMR and neutrons

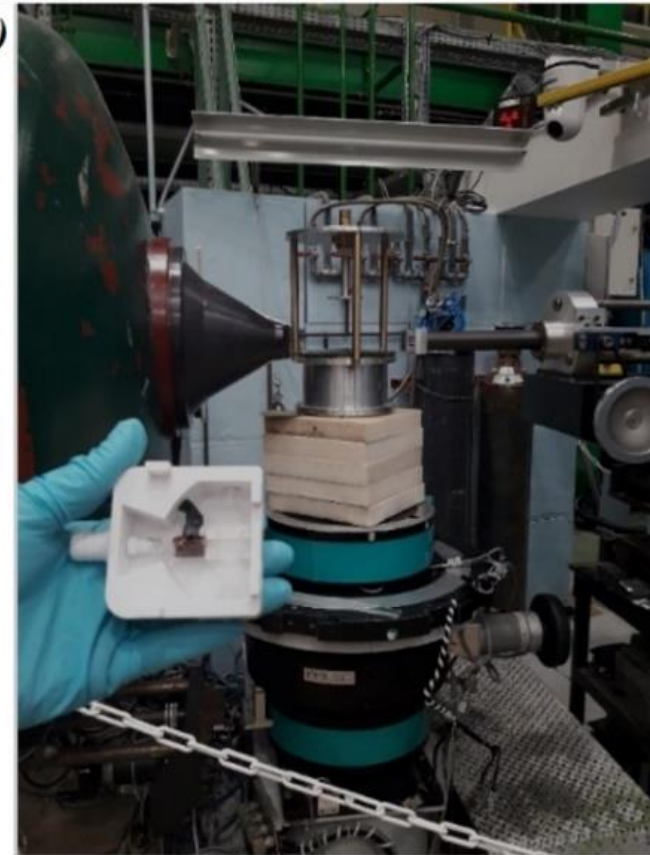
P Judeinstein, JM Zanotti

“another environment” to perform NMR experiments

a)



b)



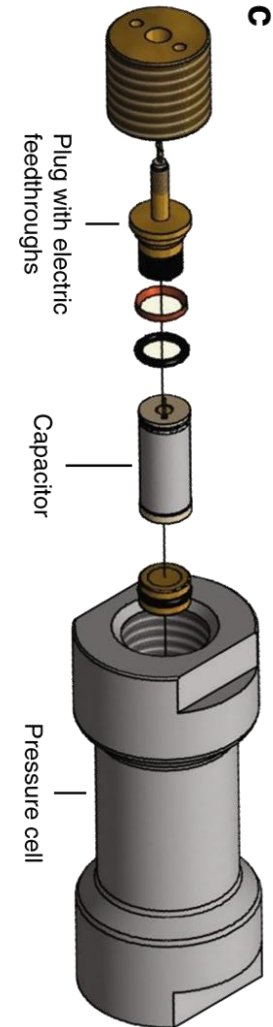
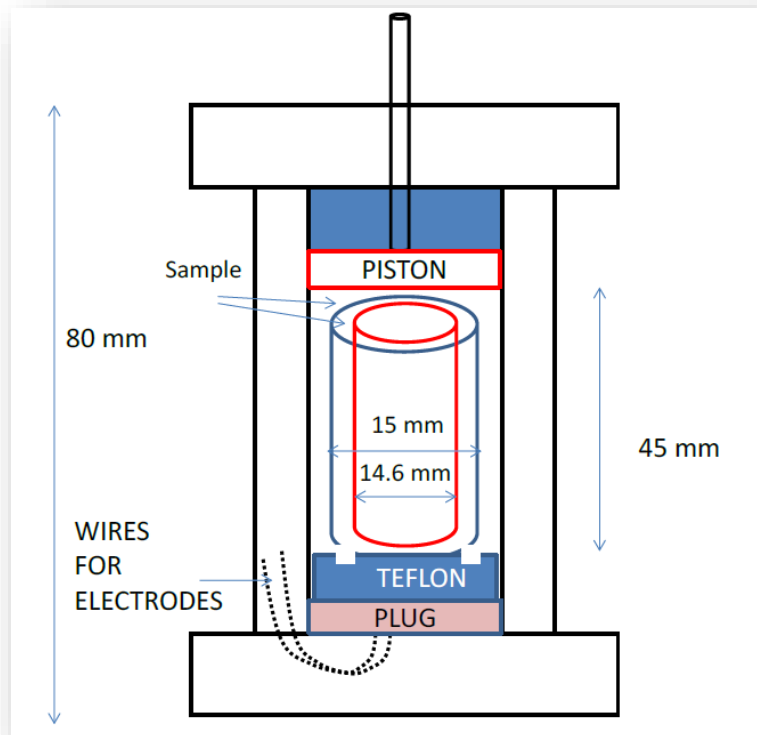
set-up adaptation (2 hours)

!! beware of metallic/magnetic parts in the surrounding

Simultaneous measurement of long time relaxation processes and quasi-elastic scattering

K. Niss, B. Frick, M. Appel, ILL

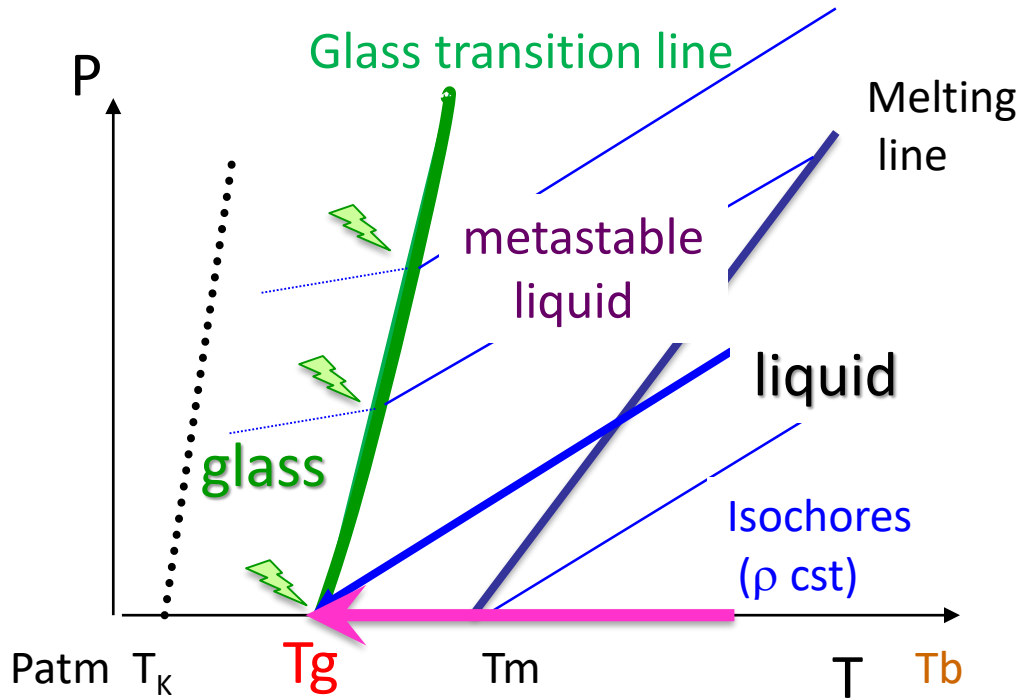
Select T and P according to the dynamics measured by dielectric spectroscopy



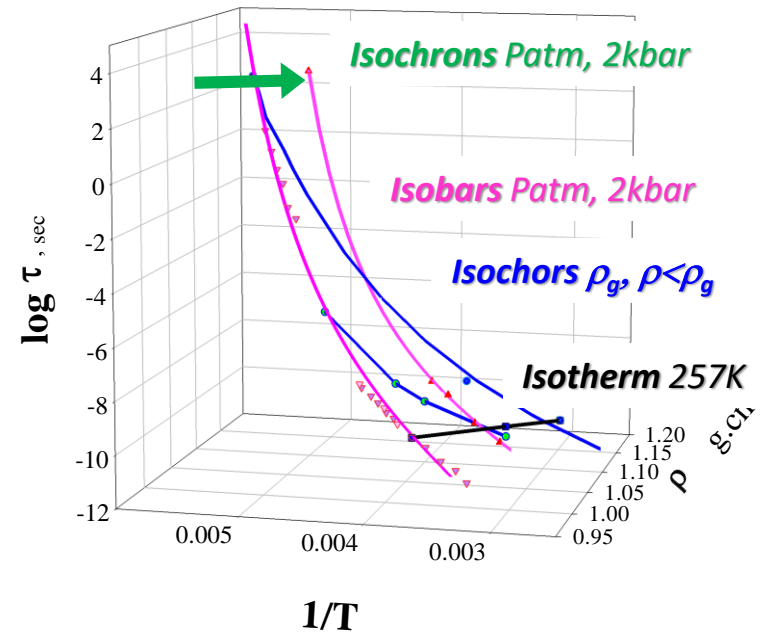
High-pressure cell for simultaneous dielectric and neutron spectroscopy, A. Sanz et al
Review of Scientific Instruments 89, 023904 (2018); <https://doi.org/10.1063/1.5007021>

Phase diagram and thermodynamic path

High pressure experiments



GLASS : the 4th state of matter



Liquid high pressure cell for inelastic neutron scattering

Alba-Simionesco, Paris-Sud / Melesi, ILL

Material: Niobium

- $P_{\max} \sim 400 \text{ MPa}$ $T \sim 2-450\text{K}$

outer cell diameter 23mm

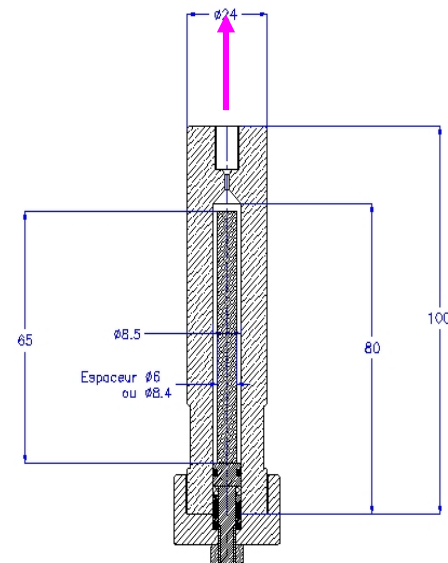
inner $\varnothing = 8.6\text{mm}$

- **inner piston** changeable for adjusting sample thickness

Sample geometry:

- **hollow cylinder** min.thickness $d_{\min} = 0.12\text{m}$ with an internal gauge
- calculations of attenuation factors

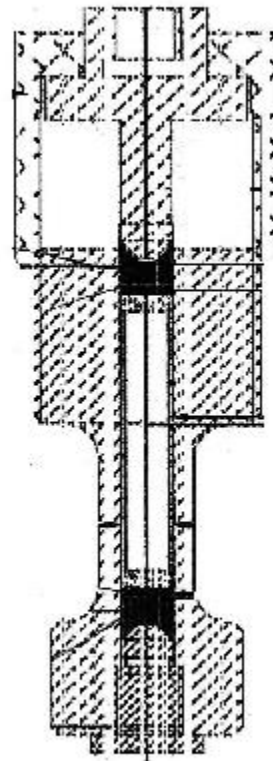
Compressor and external gauge



Boson peak under the highest pressure by inelastic neutron scattering



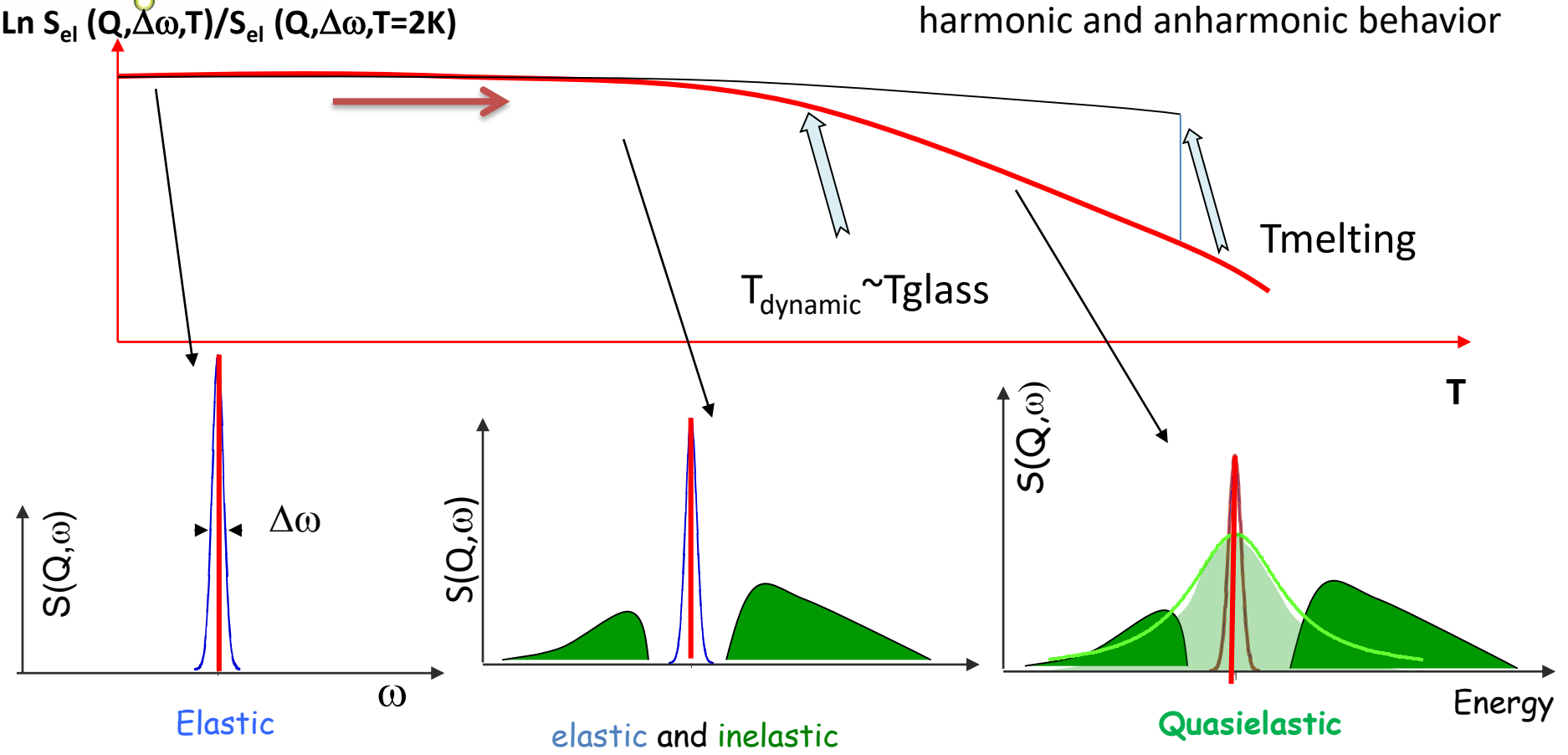
Neutron Time Of Flight and Backscattering spectrometers



Clamp pressure cell,
Pressure up to 1500 MPa

Sample :
PIB ($M_w=3580\text{g/mol}$)

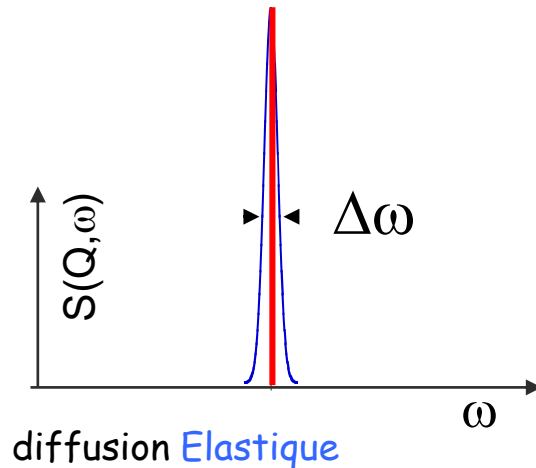
scenario of quasielastic scattering as T increases



➔ To cover a wide w range requires the combination of several instruments

$S(Q, \omega)$ and $\langle u^2 \rangle$ mean square displacement

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



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

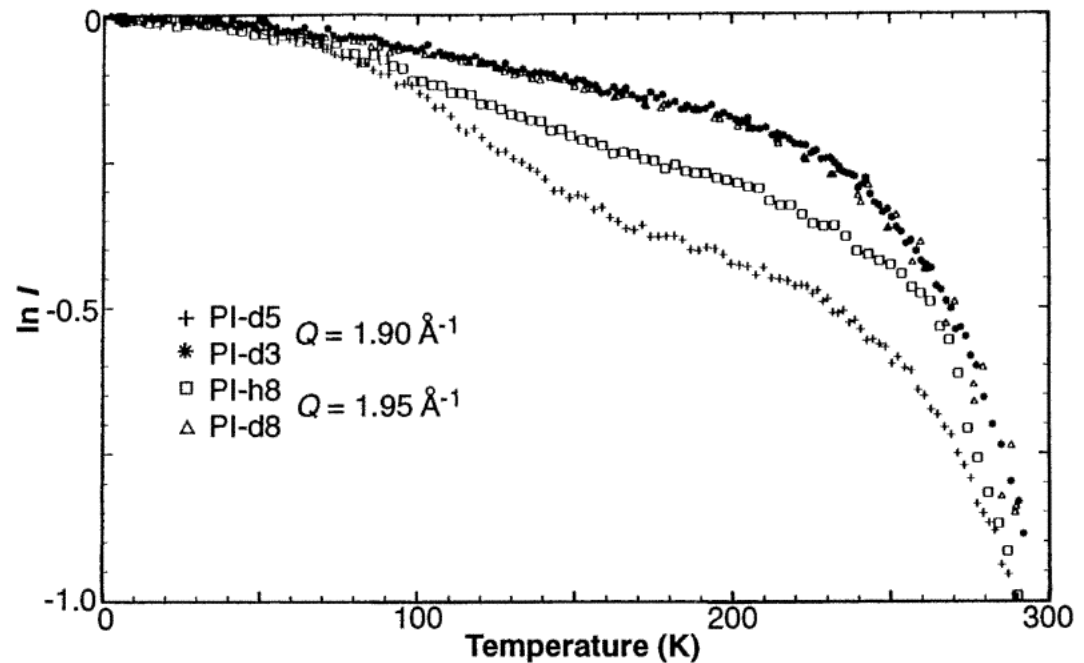
msd = measure of the atoms motions
fastest than the resolution fonction
 $\Delta\omega$

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

The Microscopic Basis of the Glass Transition in Polymers from Neutron Scattering Studies

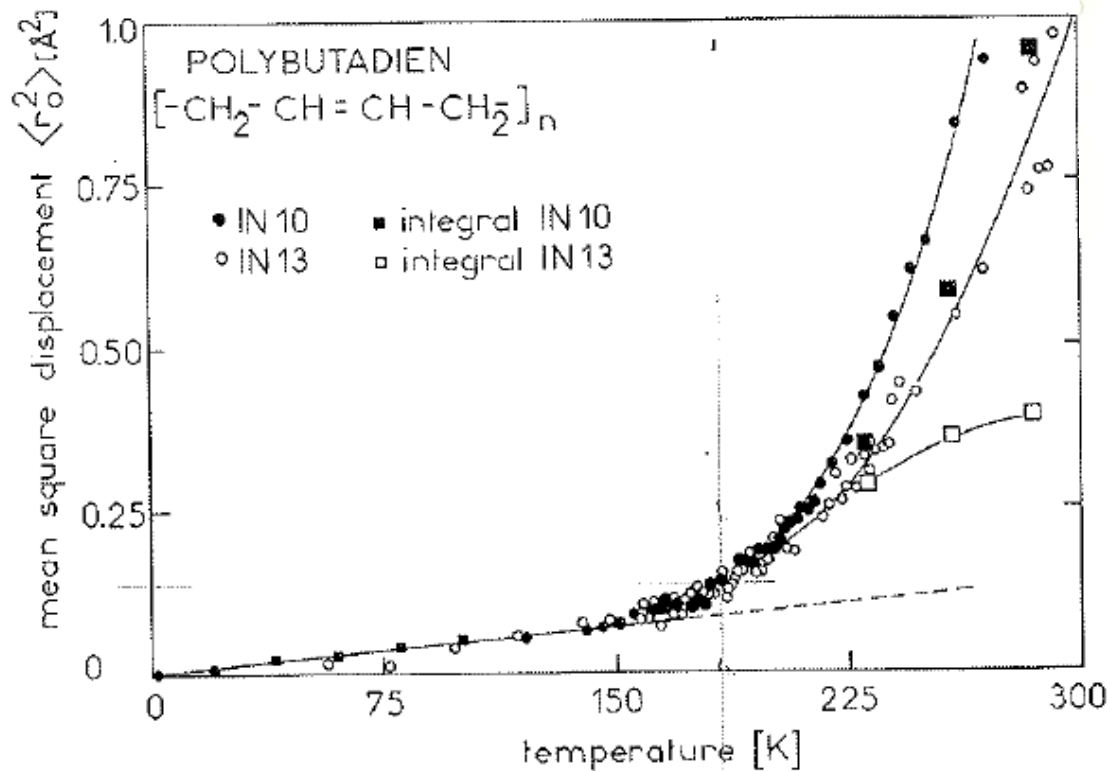
B. Frick* and D. Richter

Fig. 2. Elastic scattering of PI for different degrees of deuteration. The intensity decrease shows the onset of the dynamics on a time scale faster than picoseconds (12); the first step in the temperature dependence arises from the methyl-group dynamics, the second step from the glass transition. All samples have microstructures with about 93% 1,4-PI and 7% 3,4-PI (12). Intensity is normalized to the value at $T = 1.5$ K.



A major observable was defined msd from elastic intensity

76



Study of the Glass Transition Order Parameter in Amorphous Polybutadiene by Incoherent Neutron Scattering

B. Frick¹, D. Richter¹, W. Petry¹, and U. Buchenau²¹ Institut Laue – Langevin, Grenoble, France² Institut für Festkörperforschung, Kernforschungsanlage Jülich, Federal Republic of Germany

Received June 22; revised version August 25, 1987

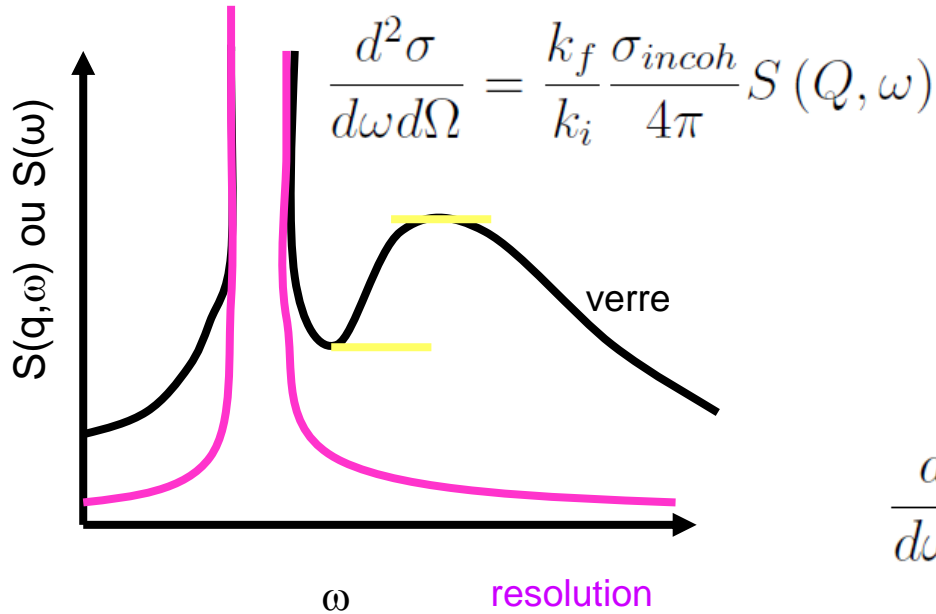
The temperature dependent elastic incoherent scattering from a glass forming polybutadiene was studied using high resolution neutron spectroscopy. This elastic scattering measures directly the non-ergodicity order parameter of the glass transition. We observed an anomalous decrease of this scattering setting in around 30 K below the thermodynamic glass transition, T_g , the temperature dependence of which is in agreement with the square root of T prediction of the mode coupling approach. The critical temperature of 220 K lies about 30 K above T_g . The missing elastic intensity reappears as inelastic scattering in the 1 meV range. Within the μeV resolution of the backscattering spectrometer no quasielastic scattering can be detected up to 20 K above T_g . The observed inelastic scattering may be interpreted as resulting from a continuous shift of the density of states towards low frequencies as a consequence of a general softening of the structure.

Fig. 3. Fit results for the mean-square-displacement $\langle r_0^2 \rangle$ as a function of temperature. The values are taken from the slope of straight lines fitted to the experimental data of IN 10 and IN 13, in the representation $\ln I_0$ vs Q^2 (see Fig. 2). The square points display the normalized scattering intensities integrated over the energy window of $\pm 14 \mu\text{eV}$ on IN 10 and $\pm 60 \mu\text{eV}$ on IN 13. The drawn lines are guide to the eyes. The dashed straight line extrapolates the linear low temperature behaviour

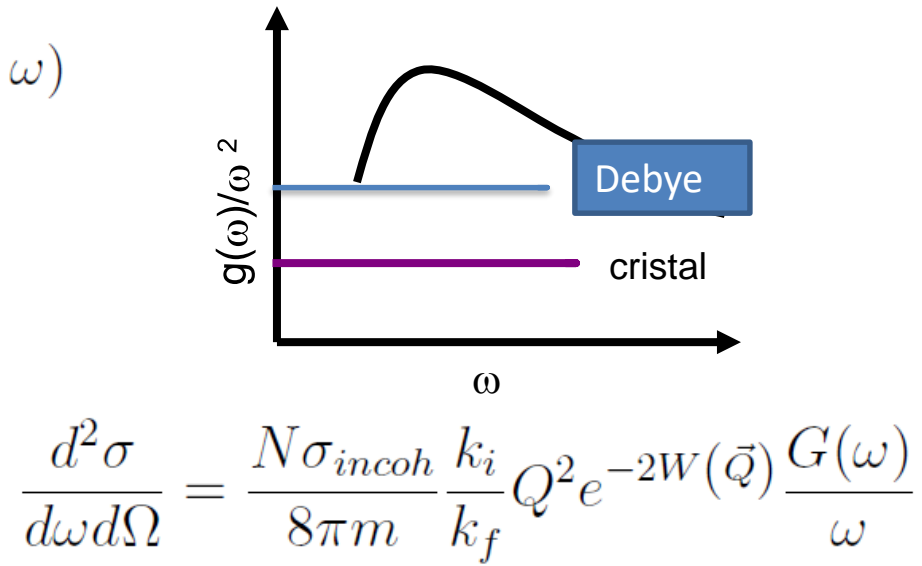
As soon as all motions are within the resolution : useful and fast

Due to disorder and stress, excess of vibrational modes

S(Q, ω)
0.1 meV < ω < 10 meV



VDOS g(ω)
0.1 meV < ω < 10 meV



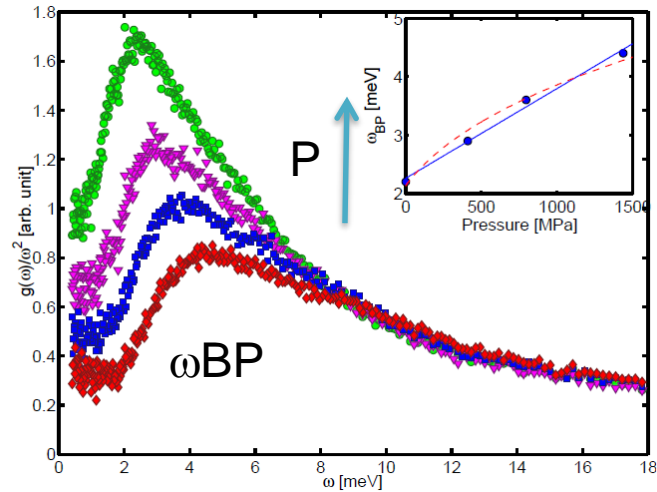
Specific Heat



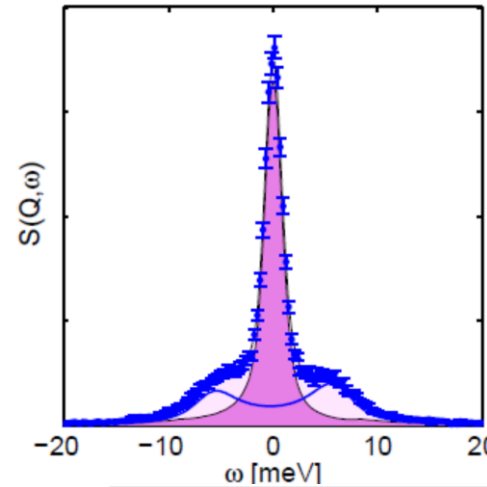
$$c_p(T) \simeq c_v(T) = N_{at} R \int d\omega g(\omega) \frac{(\beta/2)^2}{\sinh^2(\beta/2)}, \beta = \hbar\omega/k_B T$$

Combining IXS, DLS and INS

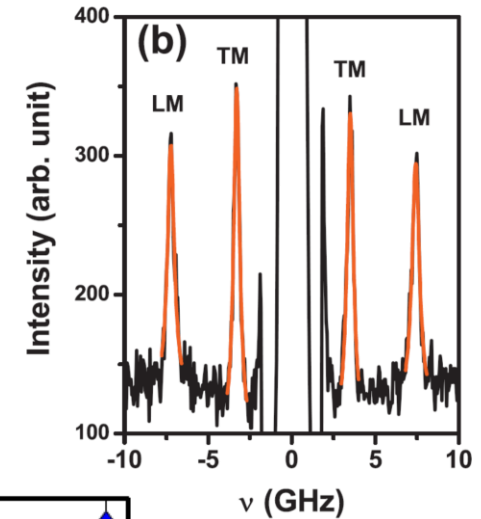
INS : Boson Peak (BP) changes
Here incoherent scattering



IXS : dispersion of longitudinal sound modes

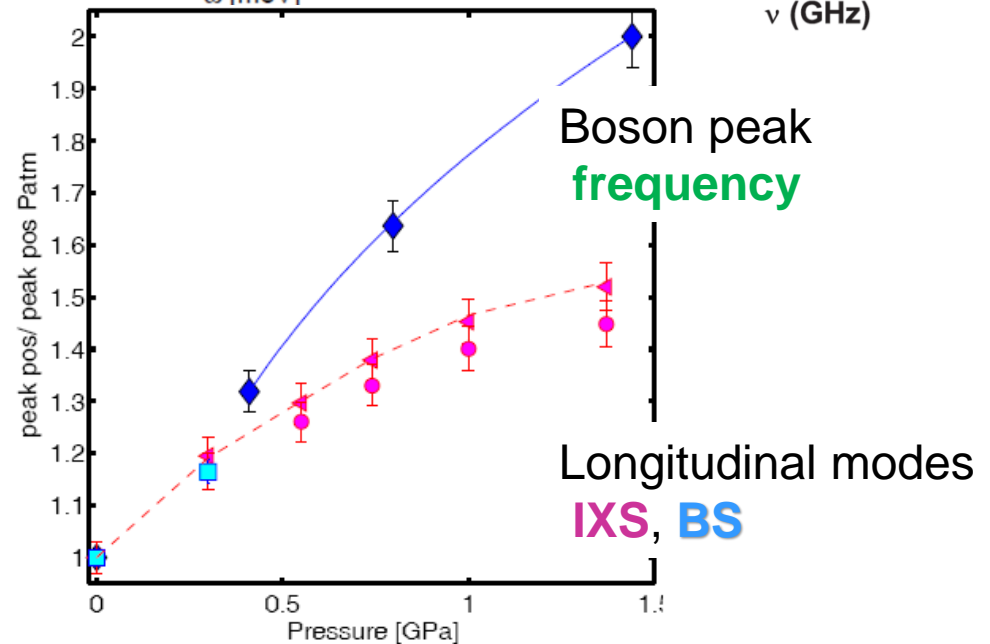
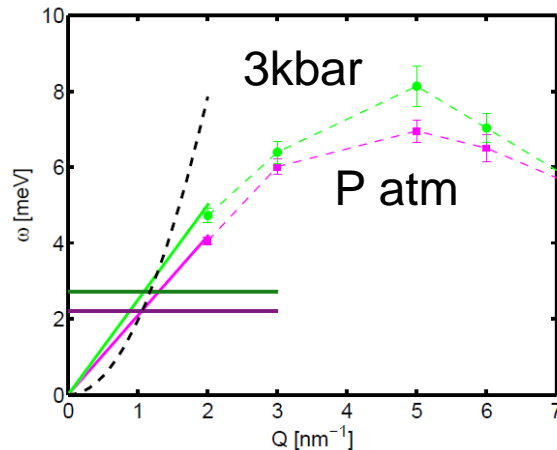


DLS
Brillouin scattering



$$S_{inc}(\omega, Q) \propto Q^2 \frac{g(\omega)}{\omega^2} n(\omega) \approx Q^2 \frac{g(\omega)}{\omega^2}$$

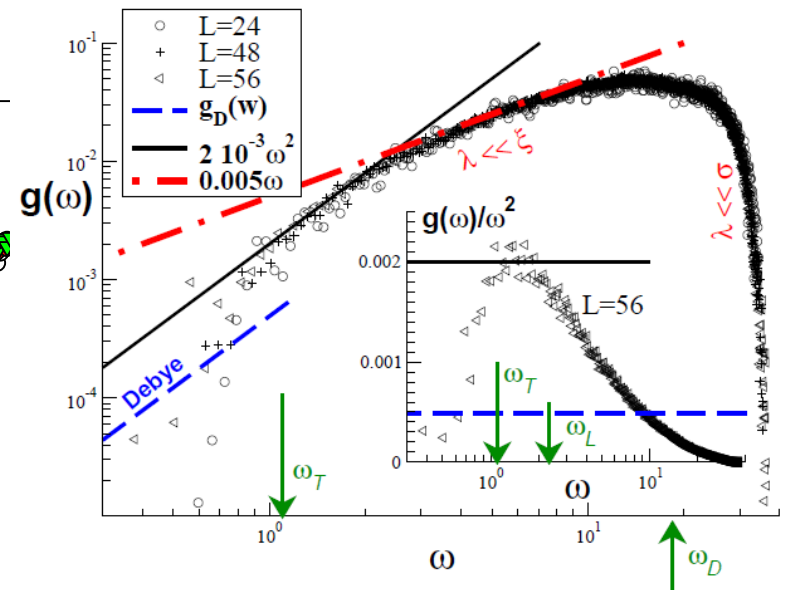
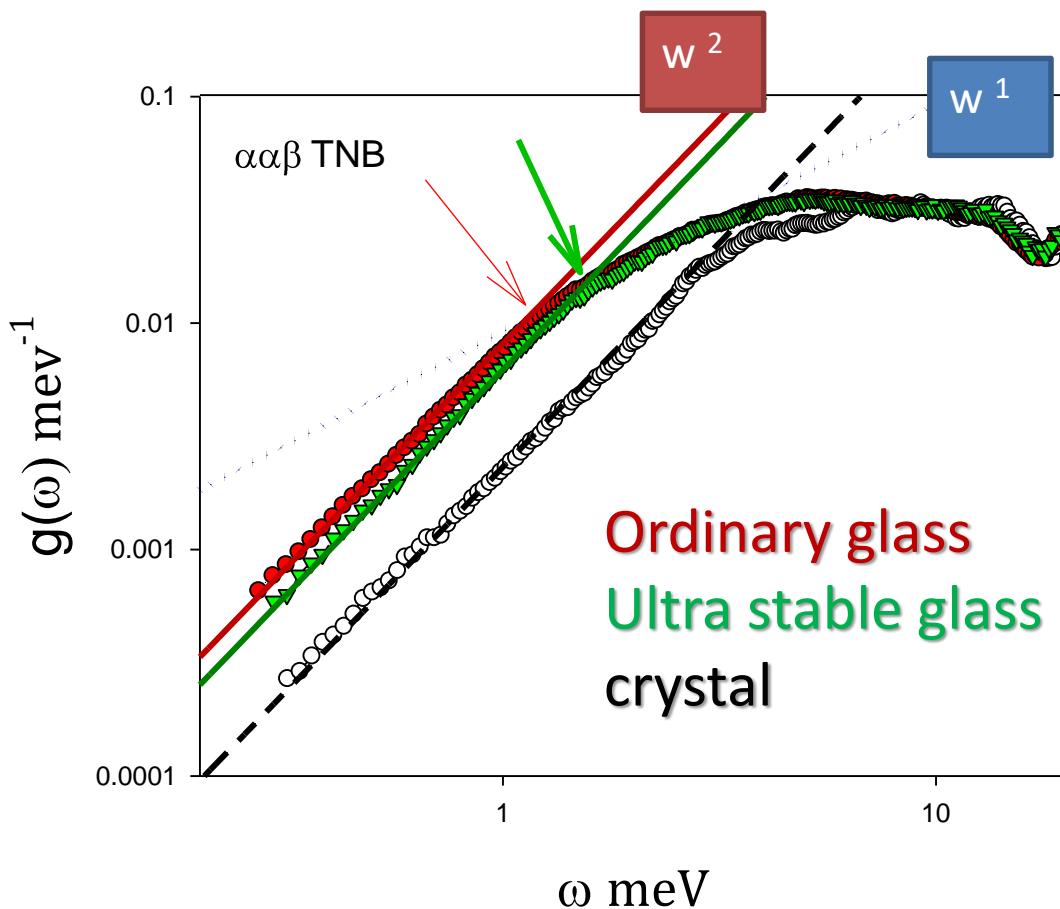
$$g_{Deb}(E) = \frac{3E^2}{E_{Deb}^3}; \text{ where } \frac{1}{E_{Deb}^3} = \frac{1}{18\pi^2 \hbar^3 N} \left(\frac{1}{V_{LA}^3} + \frac{2}{V_{TA}^3} \right)$$



VDOS analysis at low energies

Looking at the structural disorder and inhomogeneities
in amorphous systems

Deviation from the elastic medium theory (Debye)

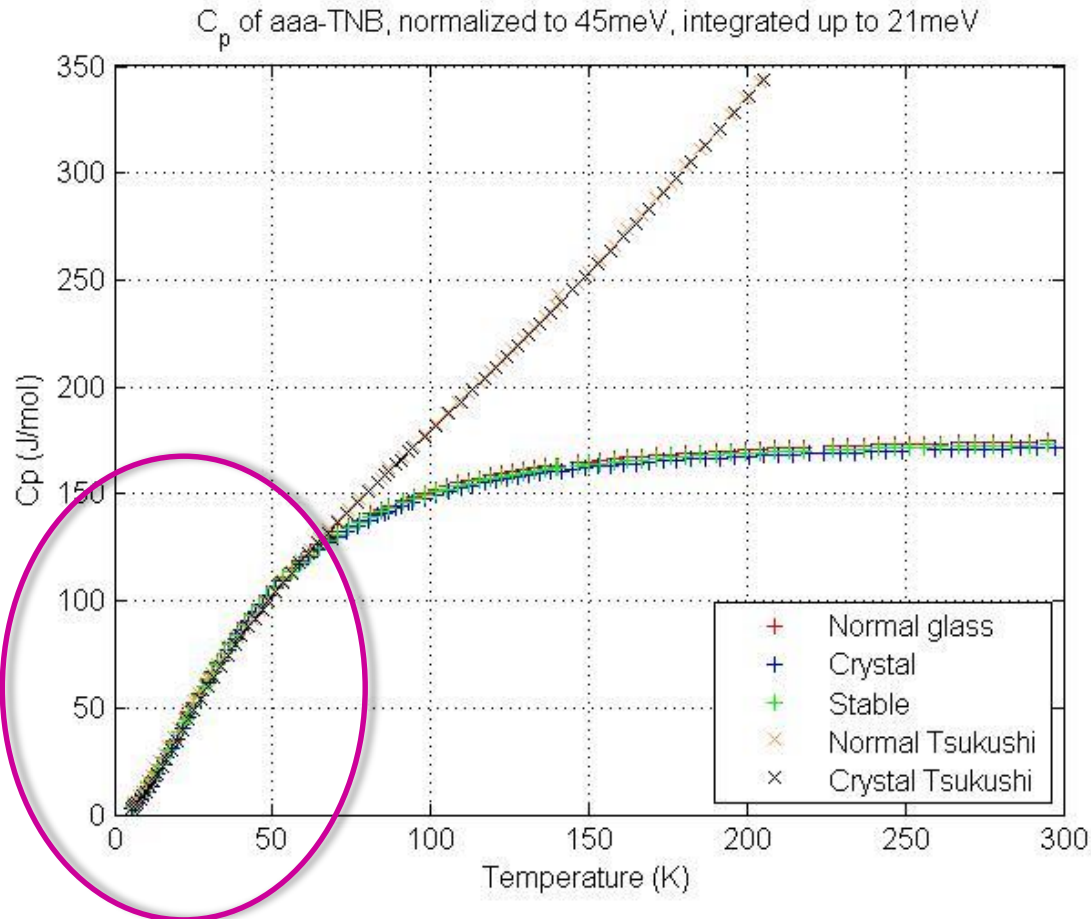


Léonforte et al PRE 2004, 2005

Ultra stable glass from M Ediger group
(Science 2007)

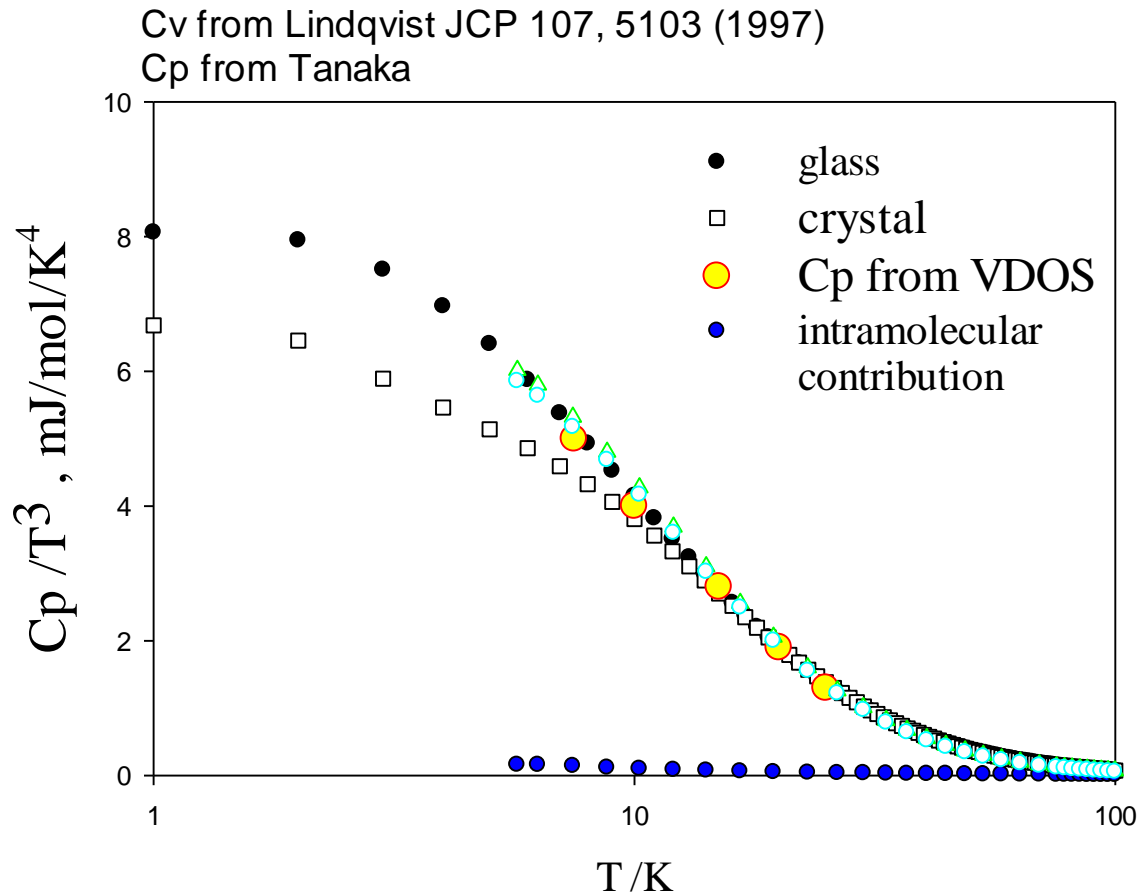
Heat capacity at low T

$$c_p(T) \simeq c_V(T) = N_{at} R \int d\omega g(\omega) \frac{(\beta/2)^2}{\sinh^2(\beta/2)}, \beta = \hbar\omega/k_B T$$



Where low frequency modes are active

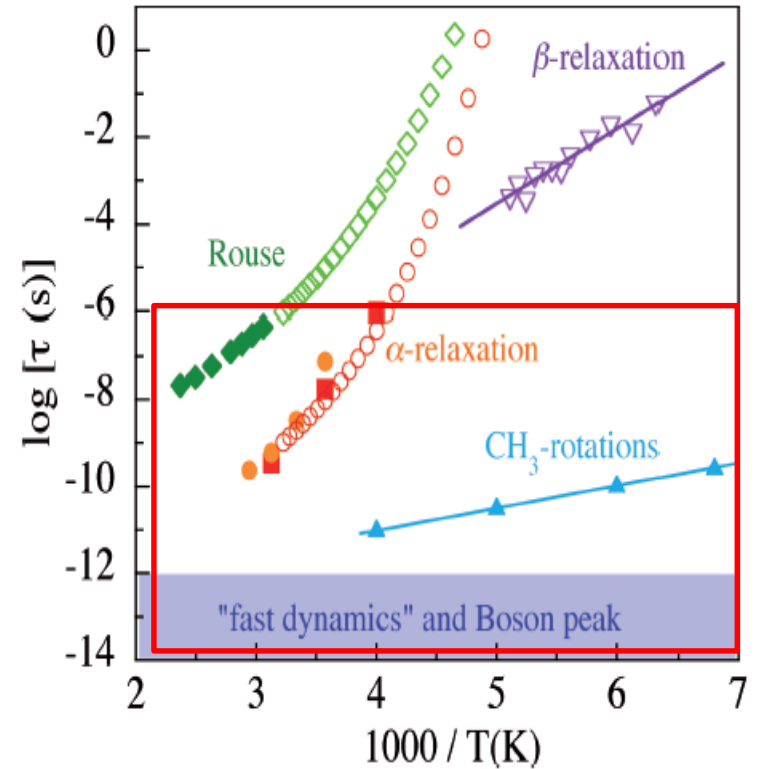
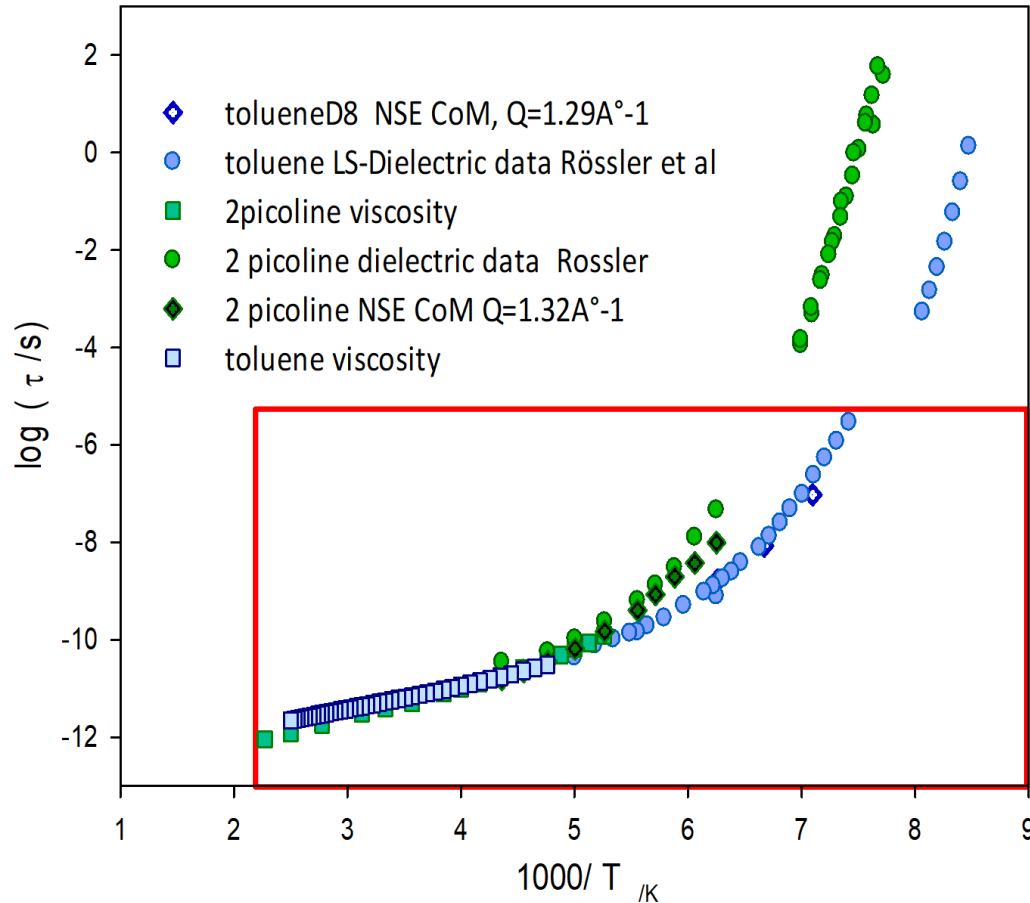
Low temperature properties by QENS in the glassy disordered state



The excess gives rise to a peak in the reduced density of vibrational states (rDOS) ($g(\omega)/\omega^2$) and the peak is seen directly in inelastic neutron spectra. The excess also gives rise to a peak in the reduced low temperature heat capacity $C_p(T)/T^3$.

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

comparison Toluene and 2-Picoline



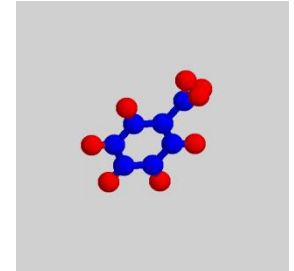
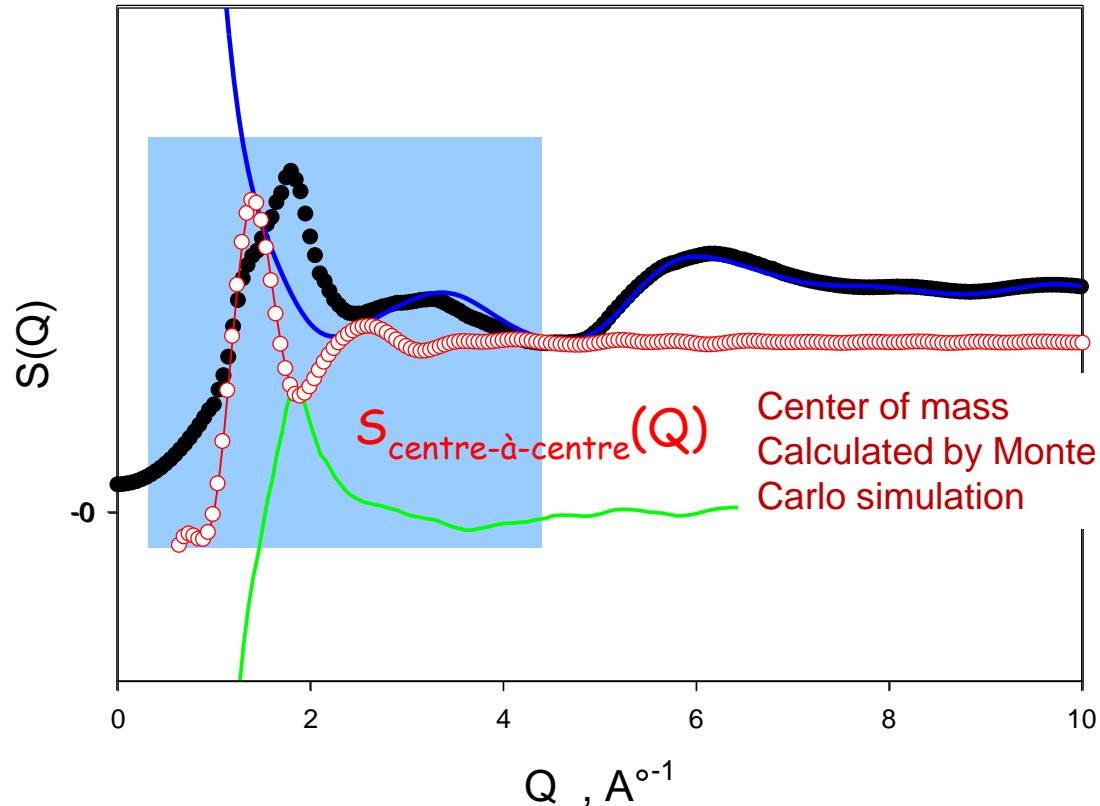
Relaxation map of polyisoprene.
Full symbols correspond to neutron scattering. Colmenero/Arbe 2012

Molecular Liquid : Q range for QENS experiments

Toluene Patm and T=193K

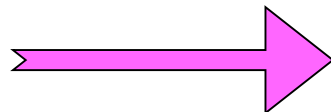
$$S_m(Q) = D_m(Q) + F_m(Q)$$

Inter and intra



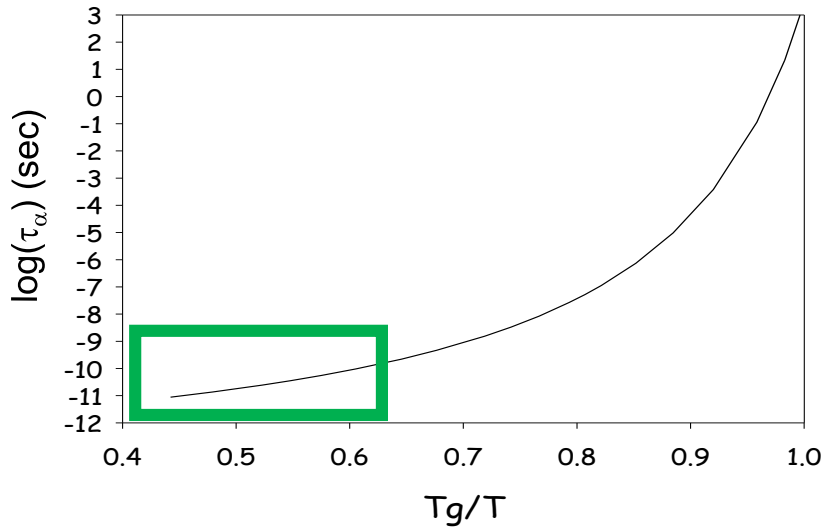
ToF, backscattering, NSE

$6 \cdot 10^0 \text{\AA}^{-1}$ (IN13)



10^{-2}\AA^{-1} (IN15)

Looking at relaxation time of a molecular liquid



Dynamics at pico-nano sec.

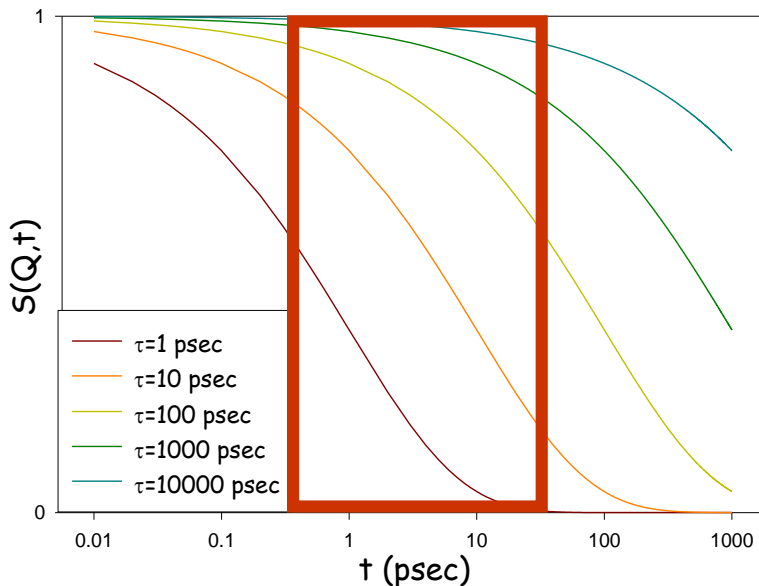
Many diffusional and relaxation processes are characterised by a Lorentzian dynamical correlation function:

$$S(\mathbf{Q}, \omega) \propto \frac{1}{\Gamma^2 + (\omega - \omega_0)^2}$$

Fourier transform:

$$F(Q, t) = a * \exp\left(-\frac{t}{\tau}\right)$$

Leading to an exponential decay with time



However, another function is commonly used
Stretched exponential

$$S(Q, t) = \exp\left(-\left(\frac{t}{\tau_\alpha}\right)^{\beta_{KWW}}\right)$$



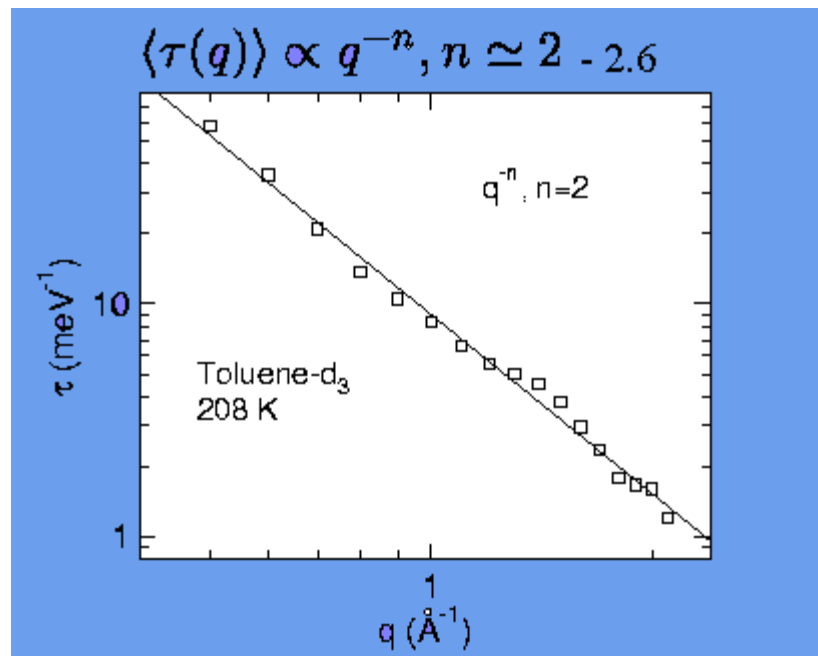
$$\tau_\alpha(Q), \beta_{KWW}(Q)$$

Experimental time window

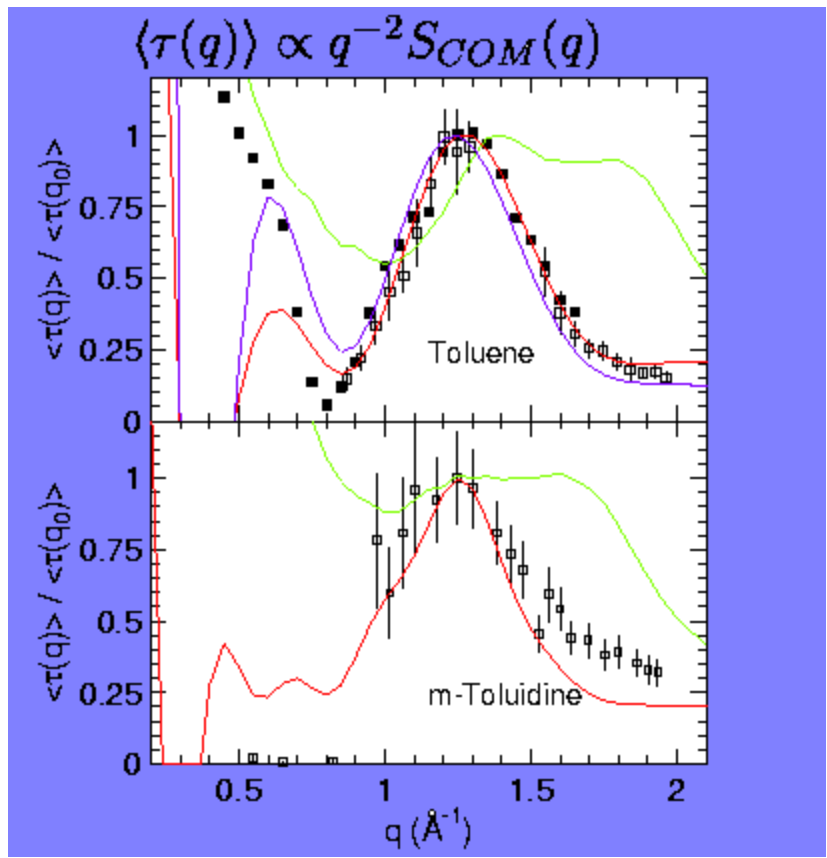
Q-dependence of the relaxation time $\tau(q)$ in the liquid state

diffusion **coherent fully deuterated** $C_6D_5CD_3$

diffusion **Incoherent** of $C_6H_5CD_3$

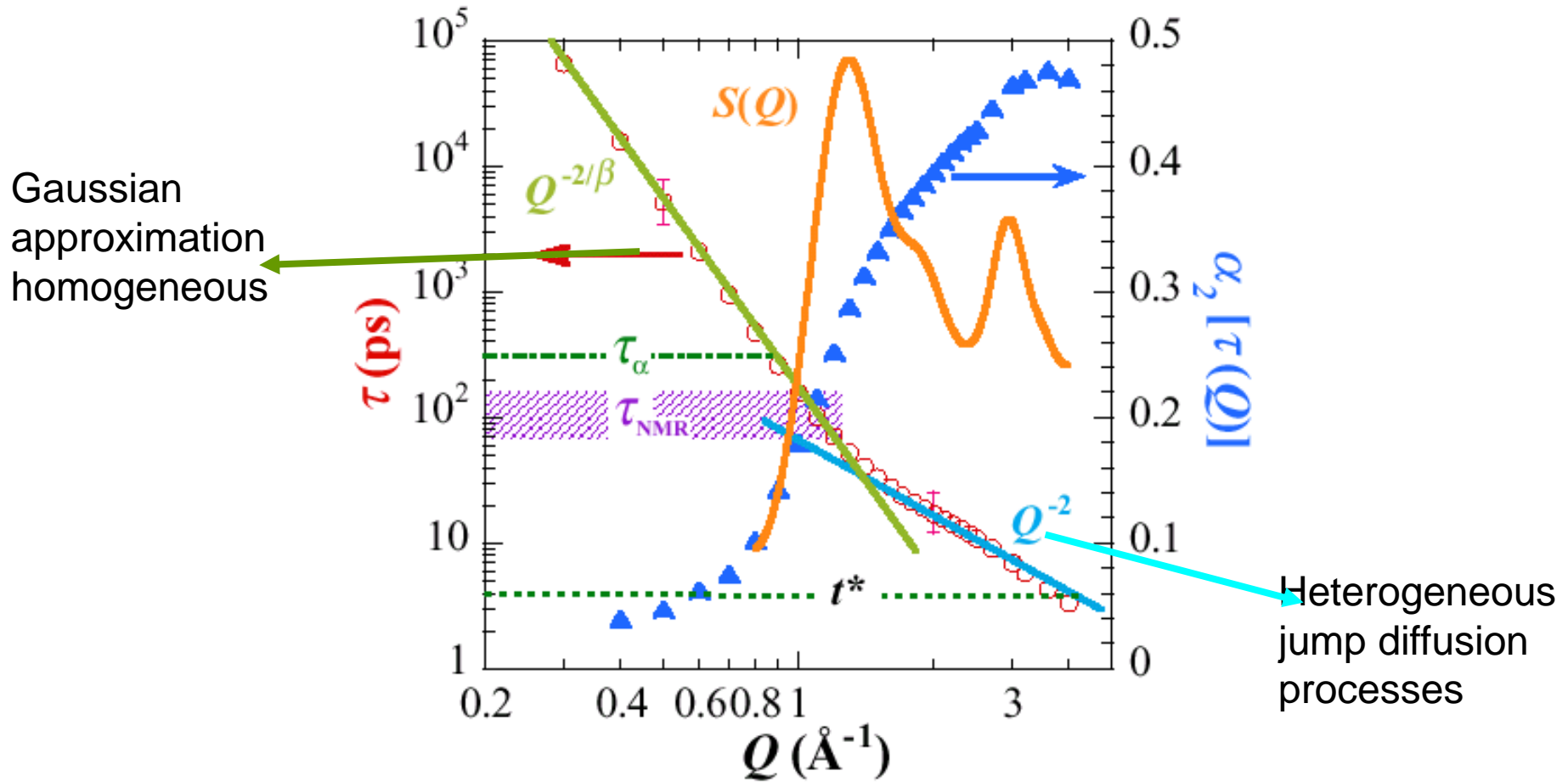


Diffusion



Q dependence
related to the de Gennes narrowing

Linear polymer chain : polyisoprene



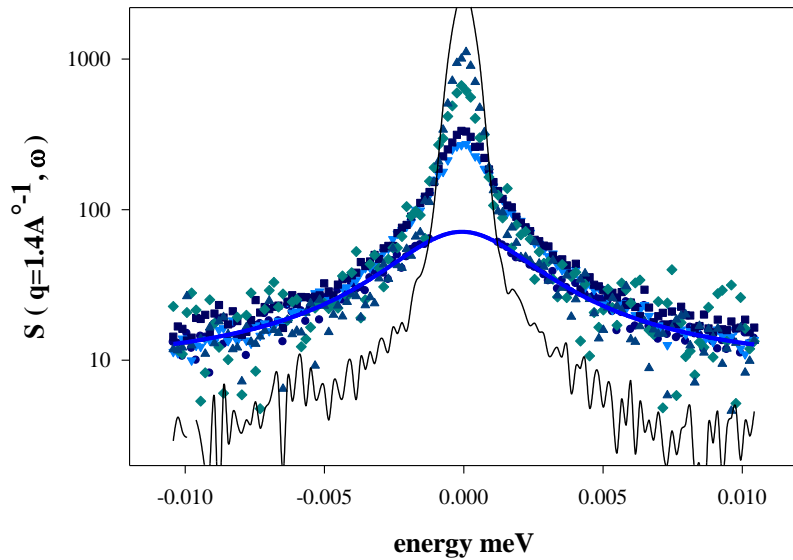
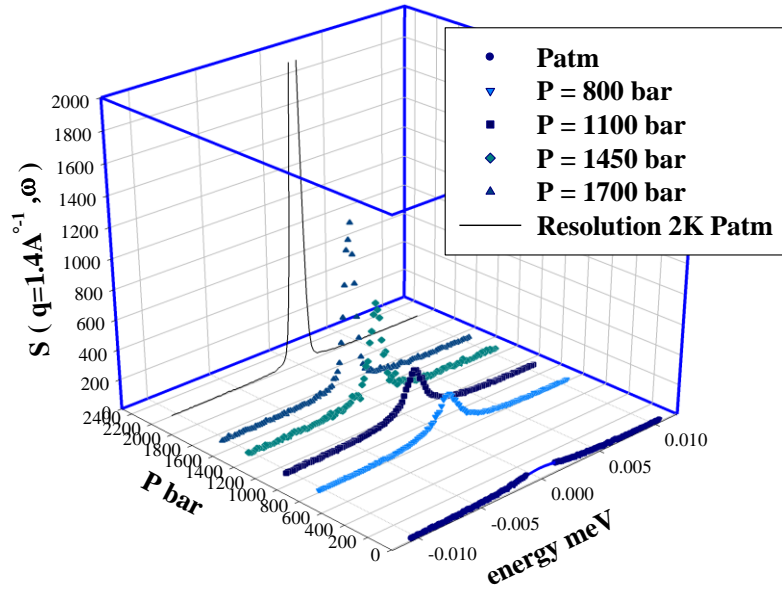
J. Colmenero, F. Alvarez and A. Arbe

“Self-motion and the α -Relaxation in a Simulated Glass-Forming Polymer:...”

Physical Review E (2002)

Isotherm : P or density changes at constant T

m-toluidine



1,4- Polybutadiene

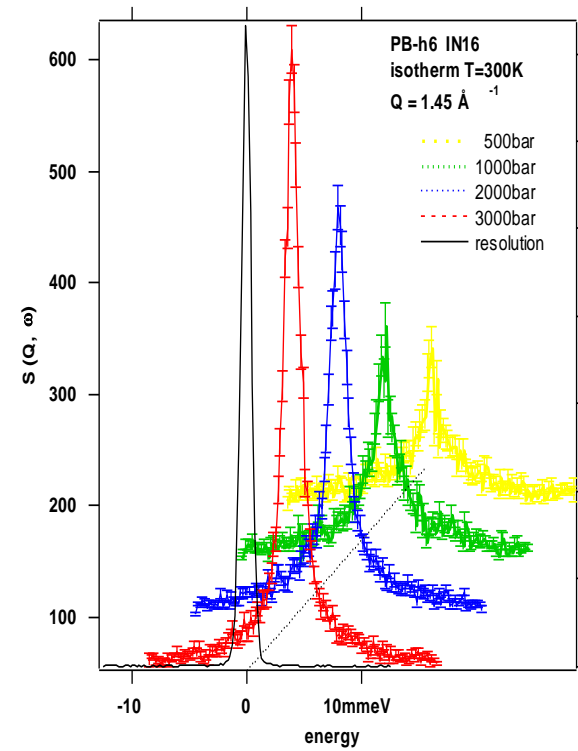


Figure n°6 Incoherent dynamical structure factor of m -TOLUIDINE at constant temperature ($T=257K$) and several pressures experiments performed on IN16

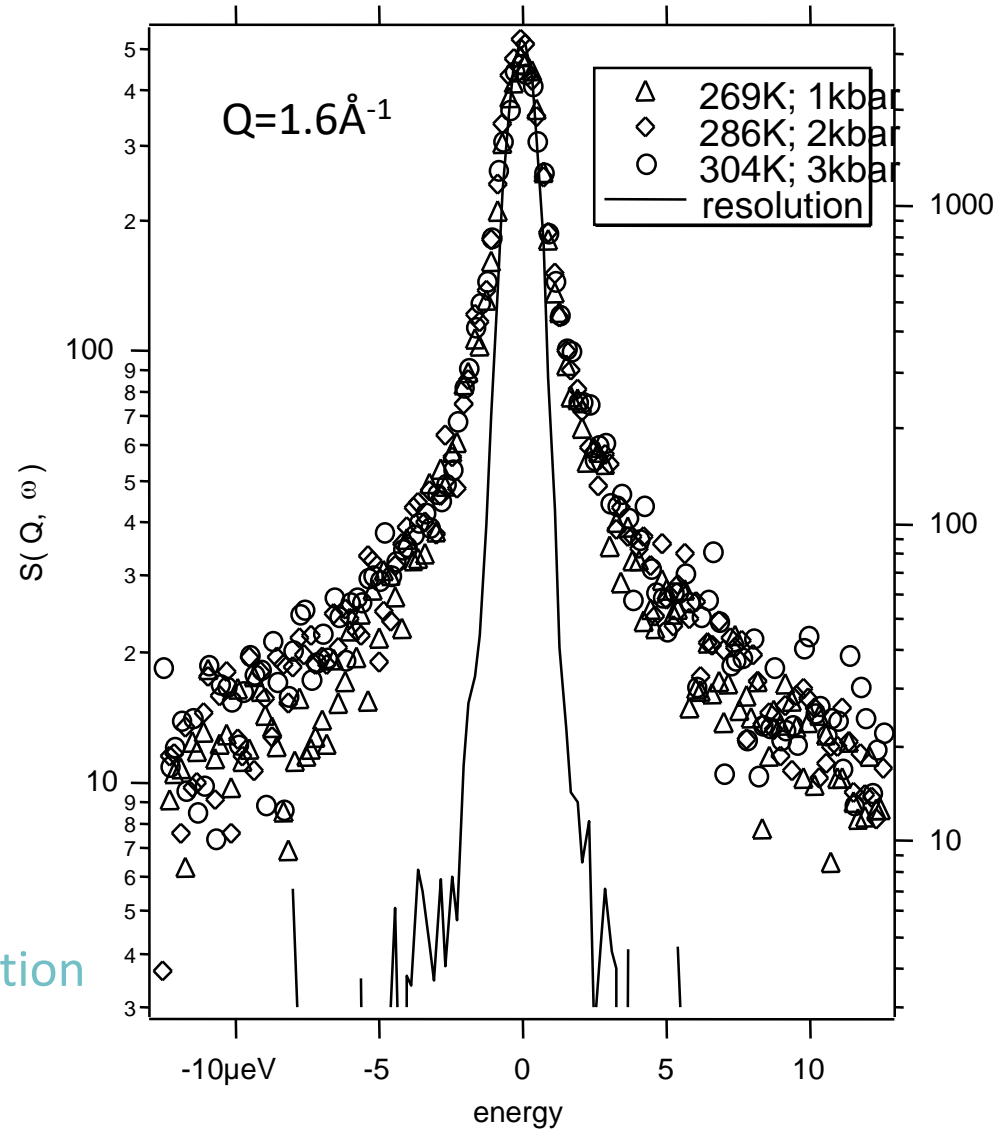
neutron backscattering experiments on α -relaxation; 1,4 polybutadien under high pressure

Isochrone at 0.4 nsec
17K/kbar

5% change in density over 40K

- Same relaxation time
- Same stretching of the relaxation function
- Same Q dependence

Confirmed latter by dielectric spectroscopy



How to get the structural relaxation function?

Ratio **signal/noise** and **shape of resolution** of the spectrometer $R(\omega)$

$$S^{\text{exp}}(Q, \omega) = S^{\text{theo}}(Q, \omega) \otimes R(\omega)$$

When convolution is controlled

$$\text{or } T.F.[S^{\text{exp}}(Q, \omega)] = S^{\text{theo}}(Q, t) \bullet R(t)$$

Model independent

Good when close to the resolution

What is measured on which instrument ?

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

polarisation

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

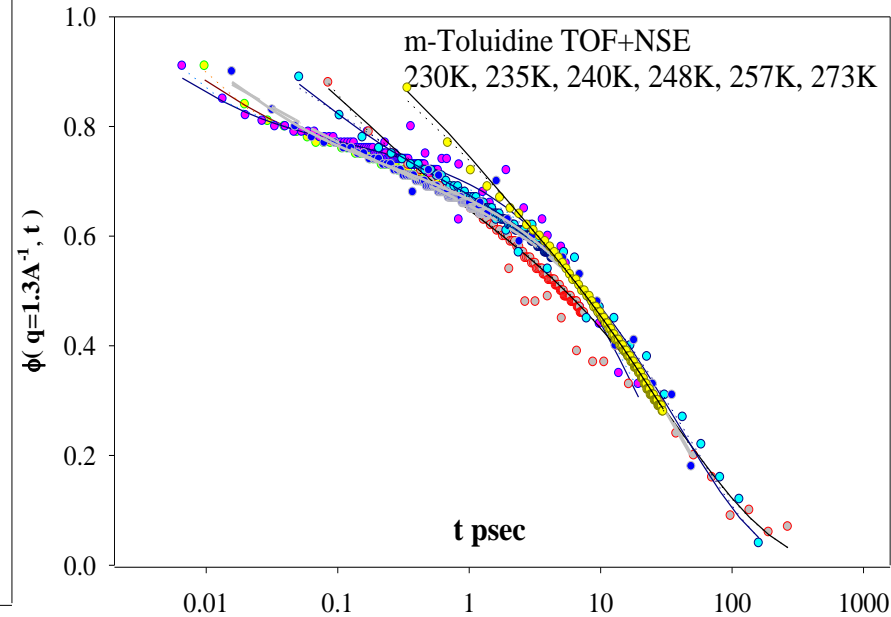
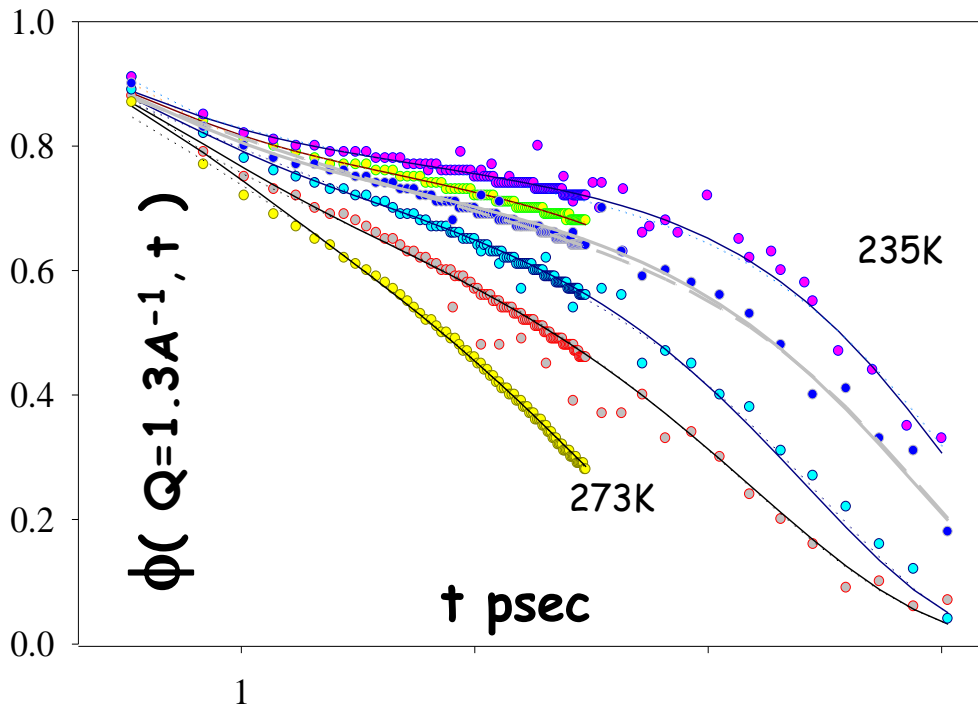
$$S^{\uparrow\downarrow}(Q, \omega) = 2/3 \sigma_{\text{incoh}} S_{\text{incoh}}(Q, \omega)$$

Incoherent scattering is reduced to 1/3;
coh and incoh might cancel each other at low Q 's

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

Combining different instrument to cover a large time domain ToF+ NSE

Data from TOF (Mibemol, LLB), NSE (IN11, ILL) deuterated sample



m-toluidine
 $T_g=183\text{K}$
 $T_m=241\text{K}$
 $T_c\sim 228\text{K}$

Lines are fits

$$\ddot{\phi}_i(t) + \Gamma_i \Omega_i \dot{\phi}_i(t) + \Omega_i^2 \phi_i(t) + \Omega_i^2 \int_0^t m_i(t-\tau) \dot{\phi}_i(\tau) d\tau = 0, \quad i = 0, 1$$

$$m_0(t) = v_1 \phi_0(t) + v_2 \phi_0(t)^2,$$

$$m_1(t) = r m_0(t),$$

Mode Coupling Schematic analysis

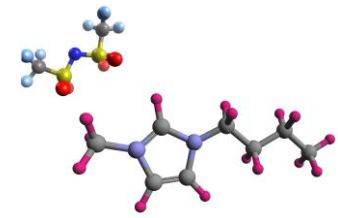
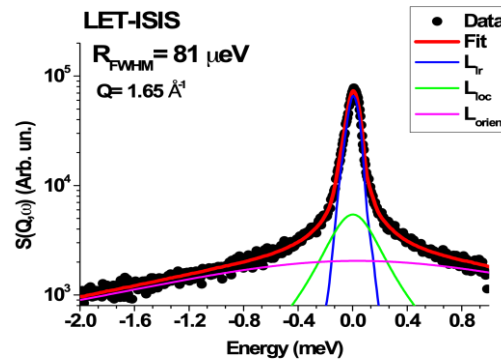
multiscale scale analysis of transport properties

multiscale analysis : QENS + NSE + PFG NMR (BMIMTFSI)

limited to the study of cation (incoherent neutron, ^1H NMR)

Quasi Elastic Neutron Scattering :

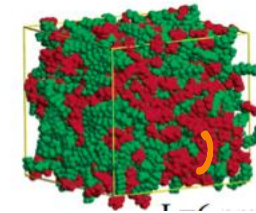
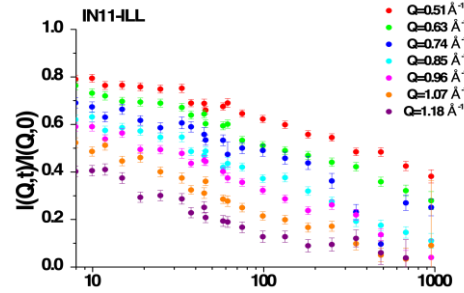
1-100 ps / 1-20 Å



$$D_{loc} = 4.8 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$$

Neutron Spin Echo :

50ps-1ns / 1-50 Å

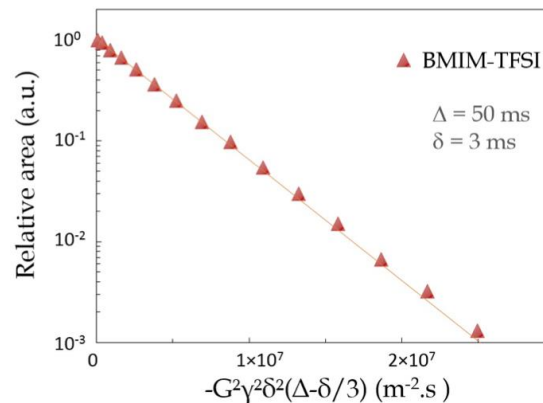


$$D_{lr} = 0.16 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$$

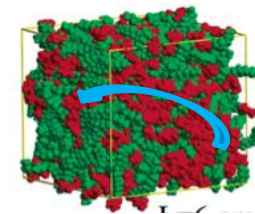
Pulsed Field Gradient-NMR :

1ms-1000ms / 0.5-10 μm

Other complementary techniques :
 fluorescence, EPR, 2D-IR ...

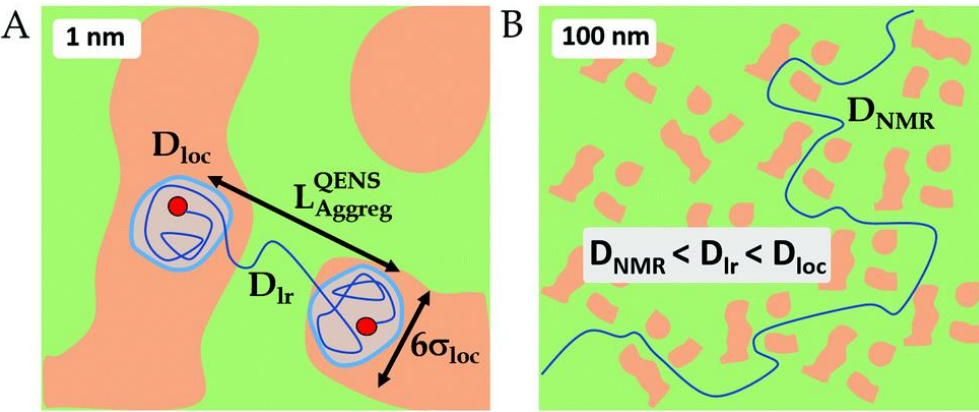


$$D_{sd} = 0.022 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$$



structure / dynamics synergy

Nanostructuring of ionic liquids: impact on the cation mobility.

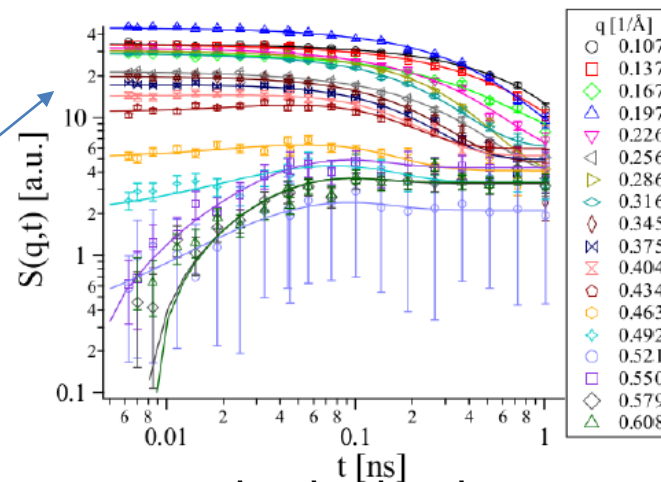
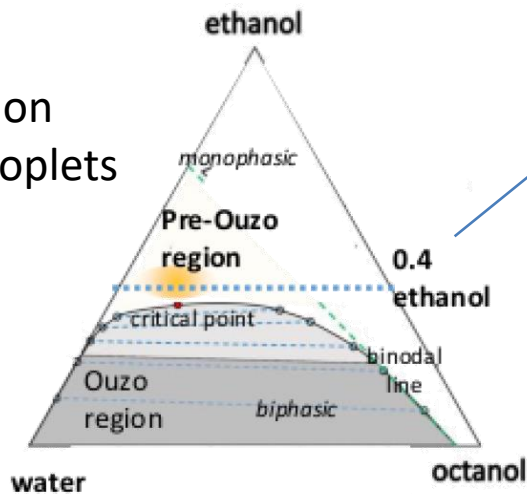


parameters	BMIM,TFSI	OMIM,BF4
$Q_{\text{prepeak}} (\text{\AA}^{-1})$	0.5	0.29
$\text{FWHM}_{\text{prepeak}} (\text{\AA}^{-1})$	0.4	0.1
$d = 2\pi/Q_{\text{prepeak}} (\text{\AA})$	12.6	21.6
$L_{\text{aggregate/QENS}} (\text{\AA})$	20 ± 5	22 ± 5
$6\sigma_{\text{loc}} (\text{\AA})$	11.4 ± 2	11.4 ± 2
$D_{\text{loc}} (* 10^{-9} \text{ m}^2\text{s}^{-1})$	4.8	2.9
$D_{\text{lr}} (* 10^{-9} \text{ m}^2\text{s}^{-1})$	0.16	0.04
$D_{\text{NMR}} (* 10^{-9} \text{ m}^2\text{s}^{-1})$	0.022	0.0028
$D_{\text{lr}} / D_{\text{NMR}}$	7.3	14.2
nano-organization	low	strong

F. Ferdeghini, et al, *Nanoscale*, (9), 2017, 1901-1908.

Nanostructuring in surfactant free microemulsions

Pre-Ouzo
structuration
nm size droplets



NSE data and fit for octanol – H in D ethanol mixture at the different values of Q. (IN11 at the ILL).

Plazanet et al submitted

Conclusion

Select the frequency-time range of interest

Look at the most suitable instrument , its wave length and resolution.

Check how coherent and incoherent contribution affect the spectra
prepare your sample accordingly.

Always put your results in a broad context

Compare (and if possibly complete) to other techniques.

Read literature, but feel free to improve a model or develop a new approach of an old question.