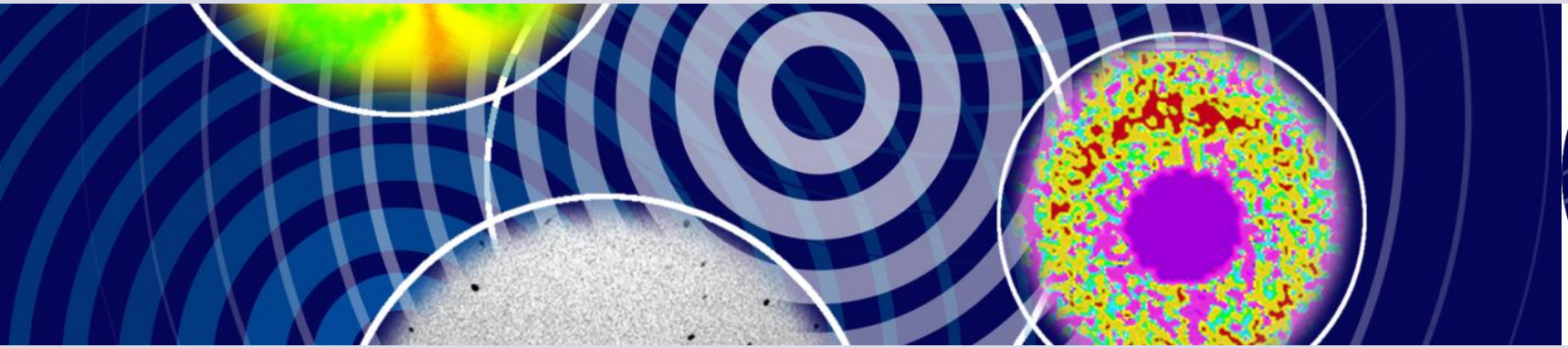
Formation Annuelle à la Neutronique (FAN) 2025

23 – 25 juin 2026, Institut Laue Langevin, Grenoble



Introduction to Quasi-Elastic Neutron Scattering

Marie Plazanet, LiPHY, Grenoble

2F DN
Fédération Française de Diffusion Neutronique

LiPhy
Laboratoire interdisciplinaire de Physique

Why studying molecular dynamics ?

-mechanical properties
-fluctuations timescale
-transport properties (electricity/charges, sound, heat, mass…)

Quasi-elastic neuron scattering measured by TOF/BS spectroscopy

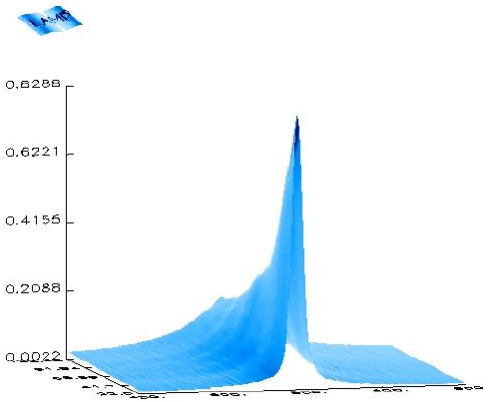
Short distances (high Q-values), thermal energies : probe motions at the atomic/molecular scale (not colloidal)

$2 < \lambda < 12$ Å
$0.05 < Q < 5$ Å^{-1}
$0.001 < E < 10$ meV
1 ns < t < 0.1 ps

Outline

- dynamical structure factor S(q,ω) and diffusive dynamics

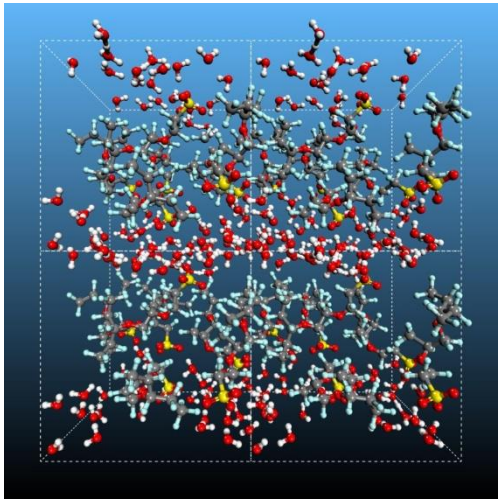
- basic QENS models



- examples:
  - *fixed window* scan: MSD in proteins
  - molecular dynamics in physical gels
  - coherent and incoherent dynamics in bulk water
  - molecular dynamics in nano-organized ternary mixtures
  - dynamics in ionic liquids
  - dynamics of proteins in solution

Pair correlation function, self and collective dynamics

The Pair Correlation Function G(**r**,t) describe the probability to find an atom i at the position $\mathbf{R_i(t)}$at the instant t if another one was at the position $\mathbf{R_i(0)}$ at the time t=0:



$$G(\mathbf{r},t) = \frac{1}{N}\sum_i \sum_j \int \left\langle \delta(\mathbf{r} - \mathbf{r}' + \mathbf{R}_i(0))\delta(\mathbf{r}' - \mathbf{R}_j(t)) \right\rangle dr$$

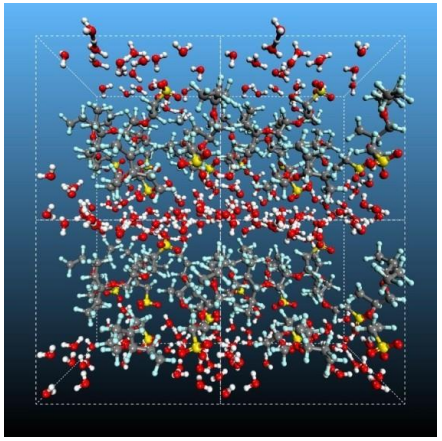
The intermediate scattering function is the spatial Fourier transform of the Pair correlation function:

$$I(\mathrm{Q},t) = \int_{-\infty}^{+\infty} G(r,t)\cdot e^{iQr}\,dr = \frac{1}{N}\sum_i \sum_j \left\langle e^{\left(iQ.R_i(0)\right)} e^{\left(iQ.R_j(t)\right)} \right\rangle$$

And the Dynamical Structure factor is the temporal Fourier transform of the intermediate function:

$$S(\mathrm{Q},\omega) = \int_{-\infty}^{+\infty} I(Q,t)\cdot e^{-i\omega t}\,dt$$

Pair correlation function, self and collective dynamics



Time-dependent pair correlation function...

$$G(\mathbf{r},t)=\frac{1}{N}\sum_i\sum_j\int\left\langle\delta(\mathbf{r}-\mathbf{r}'+\mathbf{R}_i(0))\delta(\mathbf{r}'-\mathbf{R}_j(t))\right\rangle dr$$

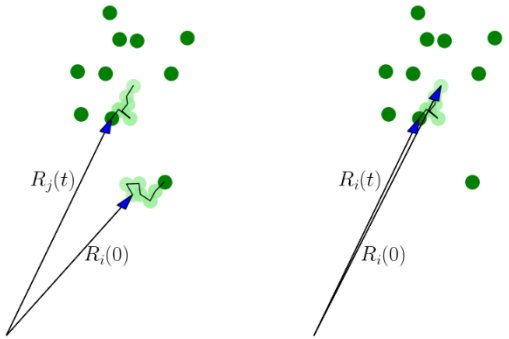
$$G(\boldsymbol{r},t)=G_d(\boldsymbol{r},t)+G_s(\boldsymbol{r},t)$$

distinct (i≠j) + self (i=j)

...and its Fourier transforms:

$$F(\boldsymbol{q},t)=\int G(\boldsymbol{r},t).e^{i\boldsymbol{q}.\boldsymbol{r}}dr=F_d(\boldsymbol{q},t)+F_s(\boldsymbol{q},t)$$

$$S(\boldsymbol{q},\omega)=\int F(\boldsymbol{q},t).e^{-i\omega t}dt=S_d(\boldsymbol{q},\omega)+S_s(\boldsymbol{q},\omega)$$

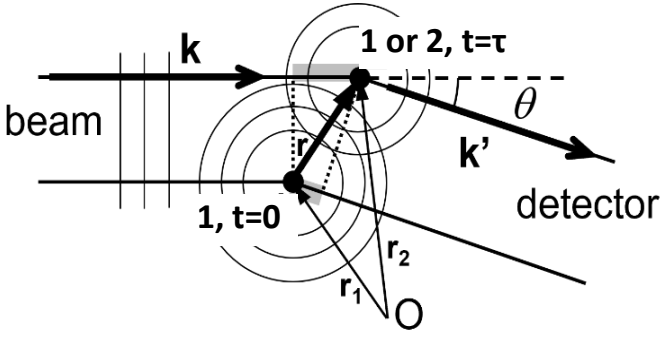


Space vs time interferences

Interferences from particle(s) at different times:

in space : r >> q, Fourier transform of the instantaneous spatial organisation

In time : t >> ω, Fourier transform of the trajectory



Plane wave : spatial and temporal periodic modulation

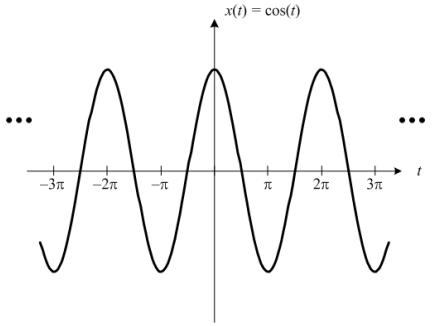
> Interferences in space or in time identified by their

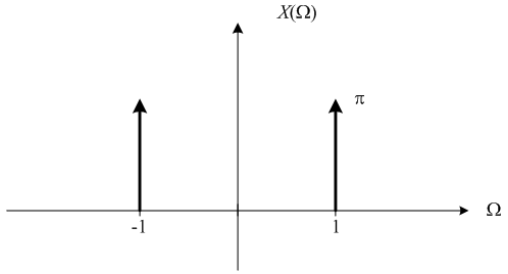
Fourier transformed form in variables q and ω

(frequencies dispersed with a monochromator)

Dynamics in a Fourier Transform

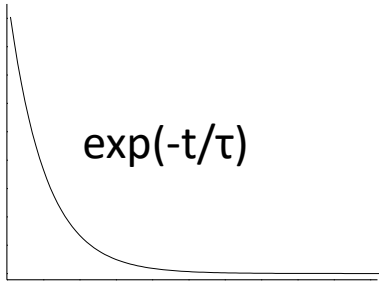
Vibrations: Underdamped, oscillatory

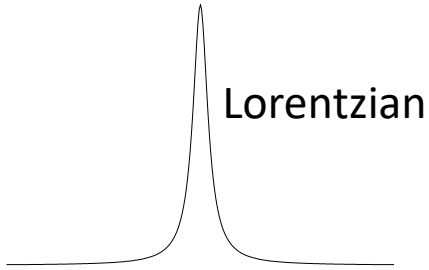




Fourier Transform

Diffusive dynamics: overdamped, characteristic time



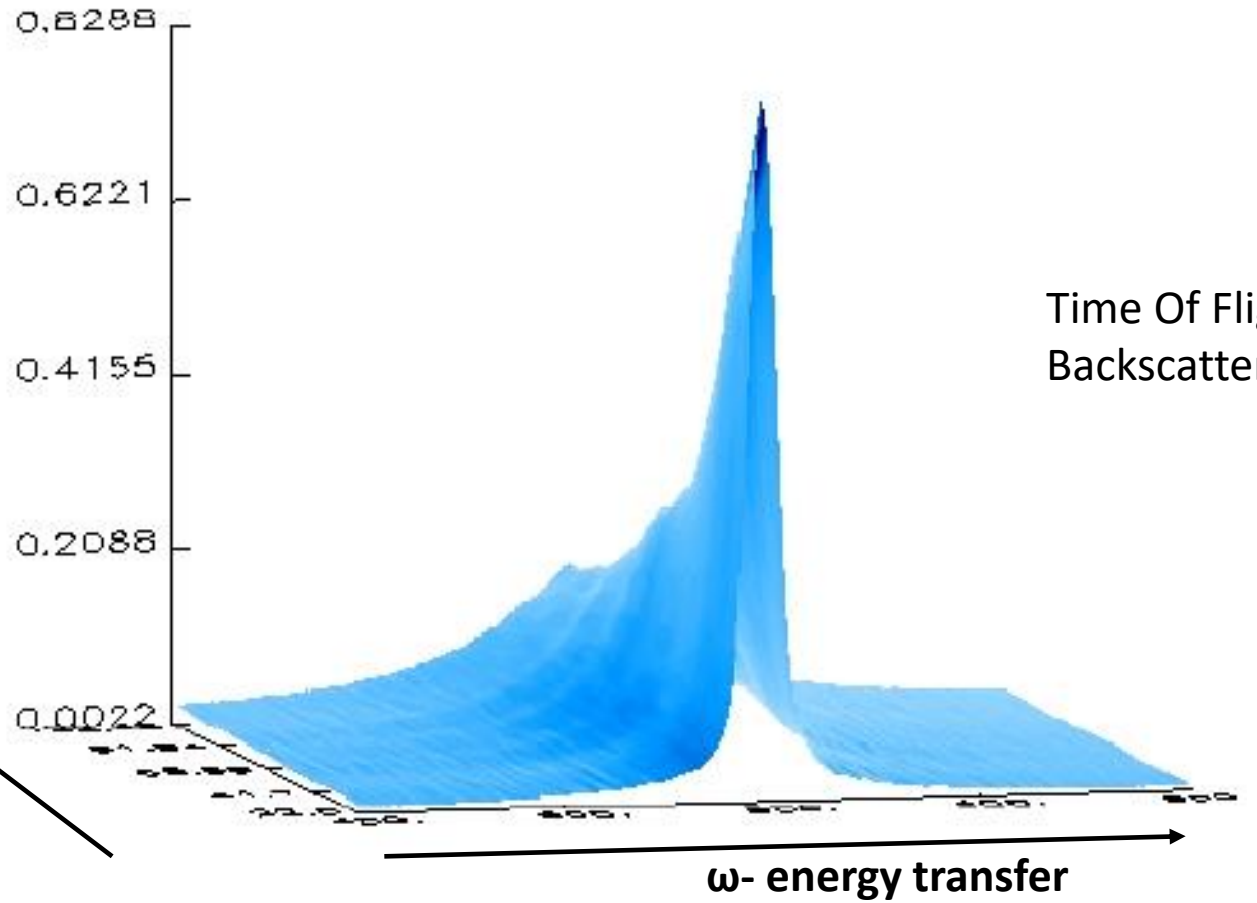


QENS gives a direct measure of S(q,ω), not the time correlation of S(q) such as DLS

What is measured is:

$$\frac{d\sigma(\mathbf{q},\omega)}{d\omega d\Omega} = \frac{k_f}{k_i} N\sigma \cdot S(\boldsymbol{q},\omega)$$

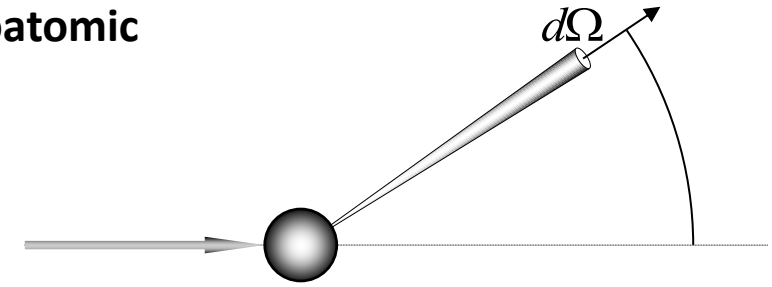
S(Q,ω)



Time Of Flight Backscattering

Quasi-elastic neutron scattering : Self/incoherent and collective/coherent dynamics

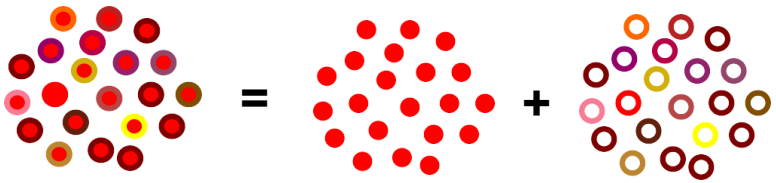
The experimentally measured quantity (for **a monoatomic system**) is the double differential cross section :



$$\frac{d\sigma(\mathrm{Q},\omega)}{d\omega d\Omega} = \frac{k_f}{k_i} N\sigma \cdot S(Q,\omega)$$

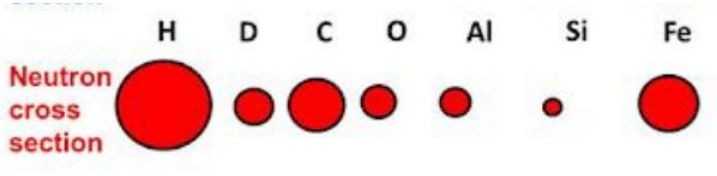
The cross section for neutron scattering can be separated as :

$$\overline{(\mathrm{b})^2} = \left(\overline{\mathrm{b}}\right)^2 + \overline{(\Delta \mathrm{b})^2}$$ or $\sigma_{tot} = \sigma_{coh} + \sigma_{inc}$, σ scattering cross section

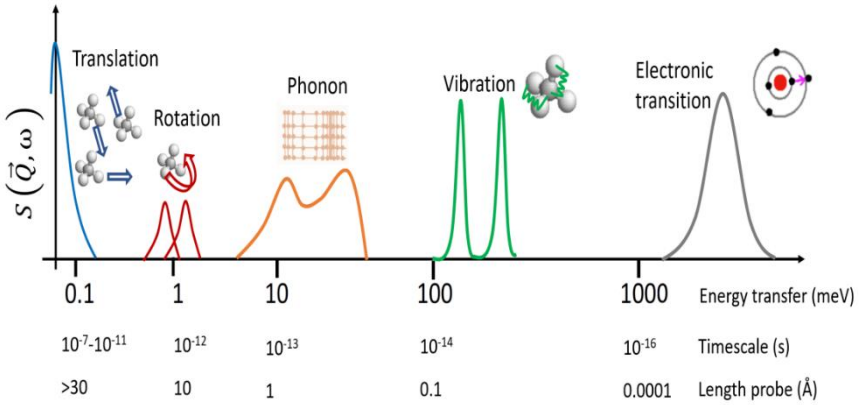


$$\frac{d\sigma(\mathbf{Q},\omega)}{d\omega d\Omega} = \frac{k_f}{k_i} N \left[\frac{\sigma_{coh}}{4\pi} \int\int G\,(\vec{r},t) e^{i(\vec{Q}\vec{r}-\omega t)} d\vec{r}dt + \frac{\sigma_{inc}}{4\pi} \int\int G_s(\vec{r},t) e^{i(\vec{Q}\vec{r}-\omega t)}\, d\vec{r}dt \right]$$

In the simplified case of incoherent scattering from a monoatomic system



Separation of motions: considering that vibrational, rotational and translational motions are uncoupled, or occur on separated timescales

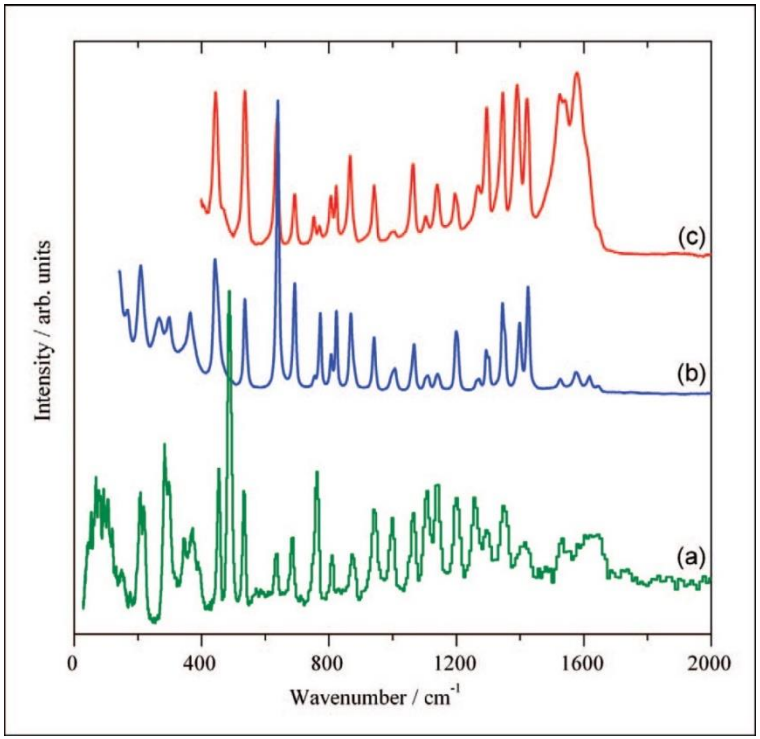


$$\mathbf{R}(t) = \mathbf{R}_0 + \mathbf{u}_{vib}(t) + \mathbf{u}_{rot}(t) + \mathbf{u}_{trans}(t)$$

$$I(\mathbf{Q},t) = \left\langle e^{-i\mathbf{Q}.[\mathbf{u}_{vib}(t)-\mathbf{u}_{vib}(0)]} \right\rangle \cdot \left\langle e^{-i\mathbf{Q}.[\mathbf{u}_{rot}(t)-\mathbf{u}_{rot}(0)]} \right\rangle \cdot \left\langle e^{-i\mathbf{Q}.[\mathbf{u}_{trans}(t)-\mathbf{u}_{trans}(0)]} \right\rangle$$
$$= I^{vib}(\mathbf{Q},t) \cdot I^{rot}(\mathbf{Q},t) \cdot I^{trans}(\mathbf{Q},t)$$

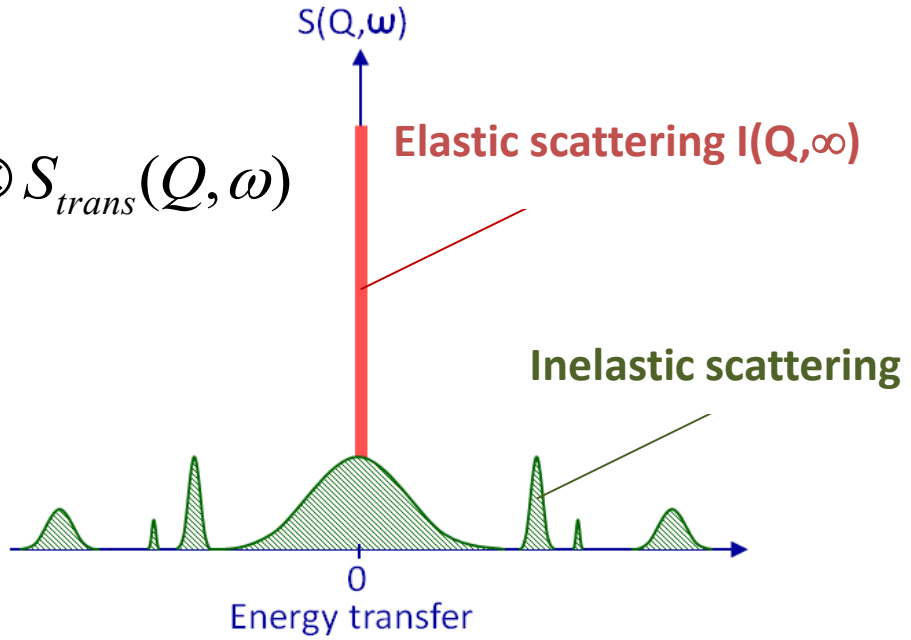
$$S(Q,\omega) = S_{vib}(Q,\omega) \otimes S_{rot}(Q,\omega) \otimes S_{trans}(Q,\omega)$$

Oscillating dynamics (Phonons, vibrations)



Vibrational spectra of L-cysteine. (a) INS spectrum measured with TOSCA, (b) Raman spectrum, and (c) infrared spectrum.
App. Spec. (2011) 1325.

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



- Conservation of total scattering

- Factorisation of the vibrational part:

$$S_{vib}(\mathbf{Q},\omega) = \exp(-2W(\mathbf{Q}))\left[\delta(\omega) + S_{inel}(\mathbf{Q},\omega)\right]$$

with $2W(Q) \approx \langle u^2 \rangle Q^2$

Debye-Waller factor in the harmonic approximation
<u²>: mean square atomic displacements due to lattice and molecular vibrational modes.

Considered the sharp peaks of $S_{vib}(Q,\omega)$ arise at energy transfer much larger than the quasi-elastic region of interest, the expression becomes:

$$S(\mathbf{Q},\omega) = \exp\left(\frac{-Q^2 < u^2 >}{3}\right)\left[S_{rot}(\mathbf{Q},\omega) \otimes S_{trans}(\mathbf{Q},\omega) + S'_{inel}(\mathbf{Q},\omega)\right]$$

Debye-Waller factor :
decrease of intensity at high Q

$$F(Q) \approx e^{-\frac{1}{3}Q^2 . <u>^2}$$

Rotation and translations, diffusive dynamics

µeV to meV (tens of ps to ns)

Internal vibrations, oscillatory dynamics

few meV to 400 meV

Nb:
For isotropic system : **Q** -> Q

Diffusion

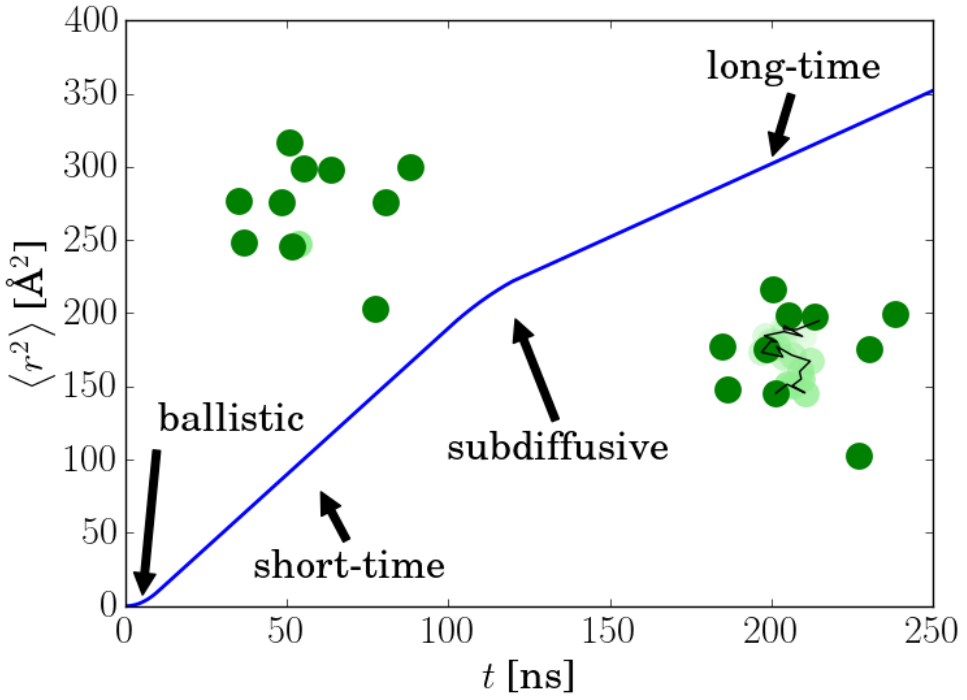
General form of the diffusion equation:

$$ {}^{C}_{\alpha}\mathcal{D}G(\mathbf{r},t) = D_\alpha \bigtriangledown^2 G(\mathbf{r},t), $$

with

$$ {}^{C}_{\alpha}\mathcal{D} = \frac{1}{\Gamma(1-\alpha)} \int_0^t \frac{G'(\xi)}{(t-\xi)^\alpha} d\xi $$

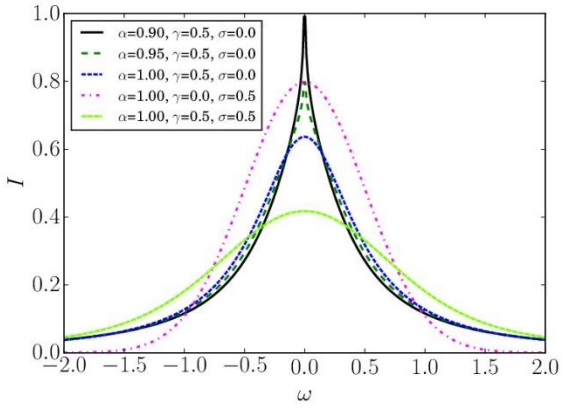
General solution: $E_{\alpha,\beta}(z) = \sum_{n=0}^{\infty} \frac{z^n}{\Gamma(\alpha n + \beta)}$



-short time regime dominated by hydrodynamic interactions
-long time regime dominated by collisions (Fickian regime)

Or its Fourier transform (for β=1):

$$ \mathcal{L}(\omega,\tau,\alpha) = \frac{1}{\pi} \frac{\tau \sin(\alpha\pi/2)}{|\omega\tau| \left(|\omega\tau|^\alpha + 2\cos(\alpha\pi/2) + |\omega\tau|^{-\alpha} \right)} $$



For α=1, the result is a stretched exponential

(Kohrausch-Williams-Watts)

Diffusion

Fick's second equation, for D constant in time and space:

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

$$G(r,t) = \frac{1}{\sqrt{4\pi Dt}} e^{\left(-\frac{r^2}{4Dt}\right)}$$

and its Fourier Transformed forms:

$$F(q,t) = e^{(-Dq^2 t)} \qquad S(q,\omega) = \frac{2Dq^2}{(Dq^2)^2 + \omega^2}$$

Relaxation time: $\tau(q) = \frac{1}{\gamma(q)} = 1/Dq^2$

Stokes-Einstein relation: $D = \frac{k_B T}{6\pi\eta R}$

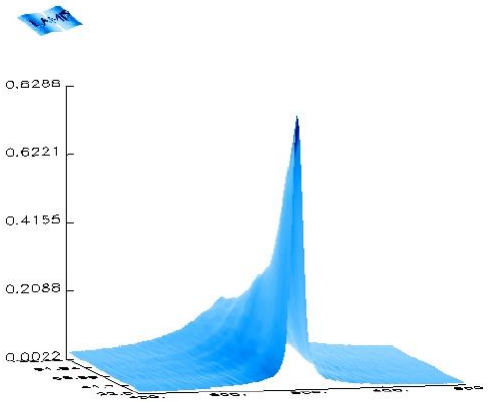
Mean square displacement: $\langle r^2(t)\rangle = 6Dt$

η viscosity, R radius

Outline

- dynamical structure factor S(q,ω) and diffusive dynamics

- **basic QENS models**



- examples:
  - *fixed window* scan: MSD in proteins
  - molecular dynamics in physical gels
  - coherent and incoherent dynamics in bulk water
  - molecular dynamics in nano-organized ternary mixtures
  - dynamics in ionic liquids
  - dynamics of proteins in solution

Translational diffusion

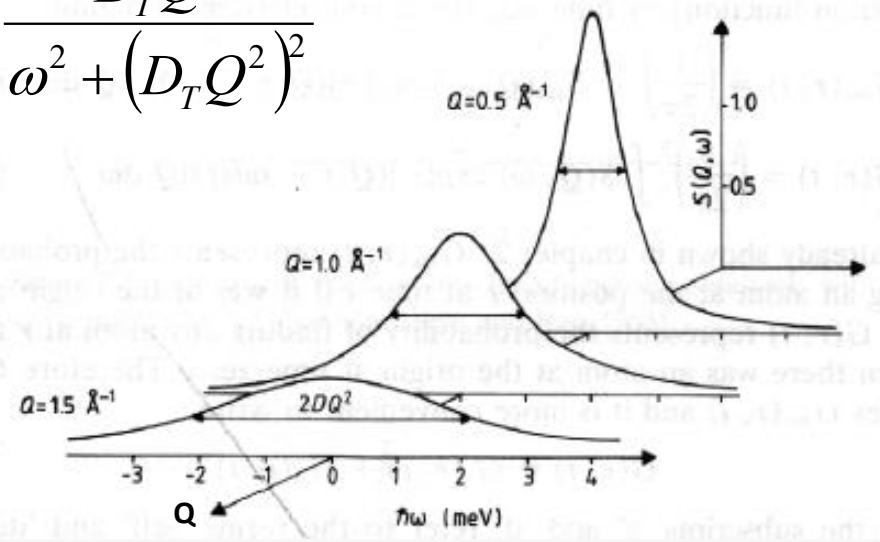
Long range diffusion process in a liquid that is considered as a macroscopic continuum is governed by the Fick's law, where D_T is the diffusion coefficient:

$$D_T \nabla^2 G(\vec{r},t) = \frac{\partial}{\partial t} G(\vec{r},t)$$

Solution : $$G(\vec{r},t) = \frac{1}{(4\pi D_T t)^{3/2}} \exp\left(-\frac{r^2}{4D_T t}\right)$$

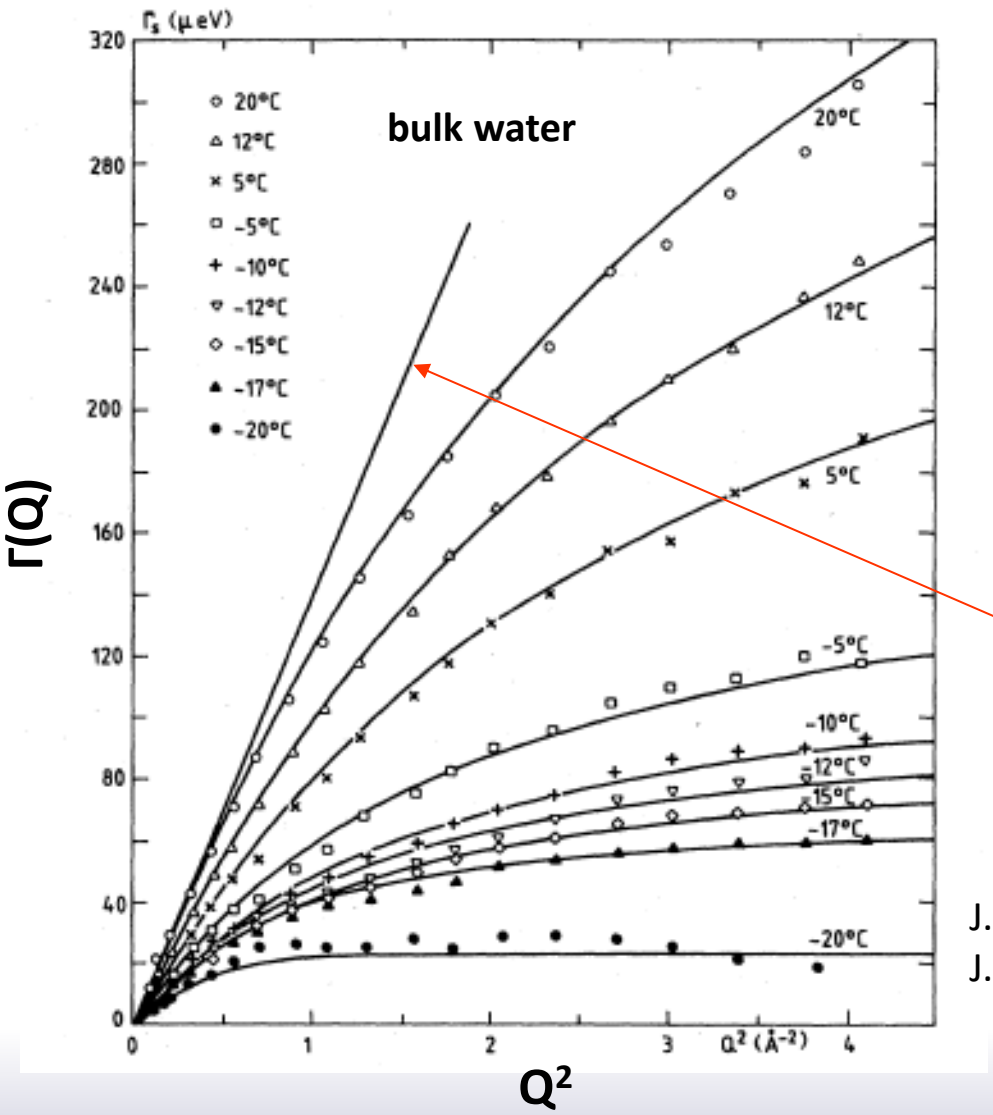
In the continuous model: $$S(Q,\omega) = \frac{1}{\pi} \frac{D_T Q^2}{\omega^2 + \left(D_T Q^2\right)^2}$$

- Single lorentzian of width $\Gamma(Q)=DQ^2$
- **intensity independent of Q**



Translational diffusion

At high Q, beyond the continuous model…



Random jump diffusion:

residence time is **τ** and a mean square jump length ***l***

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

$$D_T = \frac{< l^2 >}{6\tau}$$

The straight line indicates the Fick behaviour

J. Texeira, MC Bellissent Funel, S. H. Chen and A. J. Dianoux ,PRA, 31 (1985) p. 1913.

Translational diffusion

More models…

Chudley&Eliott model for isotropic jumps:

$$\Gamma(Q) = \frac{1}{\tau}\left(1 - \frac{\sin(Ql)}{Ql}\right) \qquad D_T = \frac{l^2}{6\tau}$$

Hall&Ross model (jump length distribution):

$$\Gamma(Q) = \frac{1}{\tau}\left(1 - \exp\left(-\frac{Q^2 l^2}{2}\right)\right)$$

Localised dynamics : rotational diffusion

$$D_R \cdot \nabla^2 P(\Omega,t) = \frac{\partial}{\partial t} P(\Omega,t)$$

P: orientational probability of the molecule

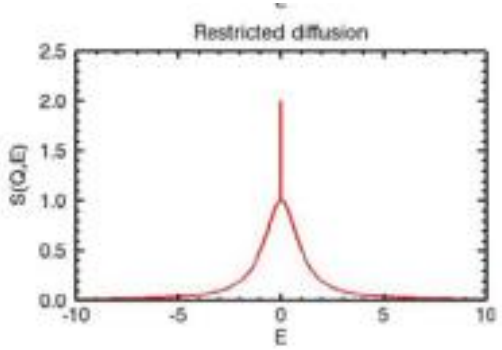
D_R : diffusional rotational constant

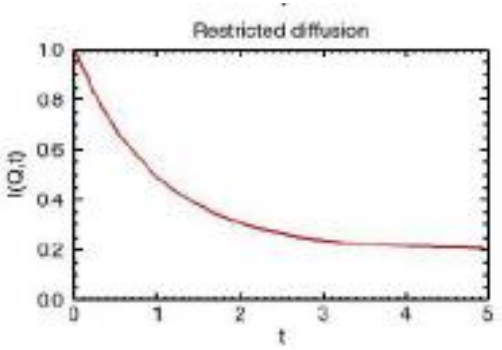
$$S(Q,\omega) = A_0(Q)\cdot\delta(\omega) + \sum_{j=1}^{\infty} A_j(Q)\cdot\frac{1}{\pi}\cdot\frac{\tau_j}{1+\omega^2\tau_j^2}$$

$$A_0(Q) = j_0^2(QR) = \left(\frac{\sin(QR)}{QR}\right)^2$$

$$A_j(Q) = (2j+1)j_j^2(QR) \qquad \tau_j = l(l+1)D_R$$

- HWHM independent of Q
- intensity factors A_j increases with Q

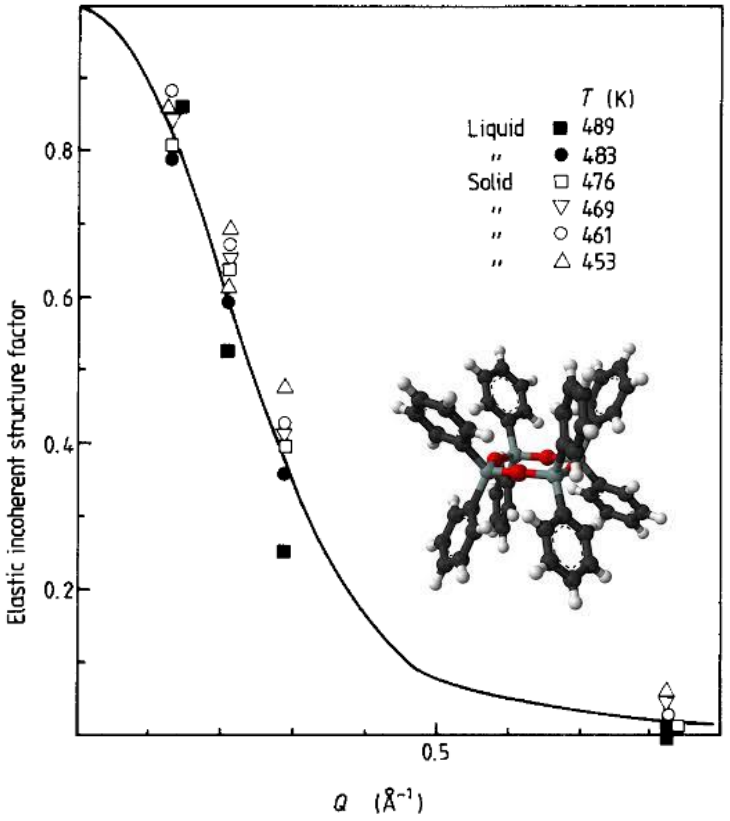




Localised dynamics : rotational diffusion

EISF of the OPCTS molecule measured on IN10 (ILL): rotational dynamics.

$$A_0(Q) = j_0^2(QR) = \left(\frac{\sin(QR)}{QR} \right)^2$$



Measure of the energy activation barrier thanks to the temperature dependence of D_R:

$$D_R = 0.86 \times 10^{13} \exp(-\Delta H_R / RT)$$

with D_R in s^{-1} and ΔH_R=33.8 kJ.mol^{-1}

Localised dynamics : jump between 2 sites

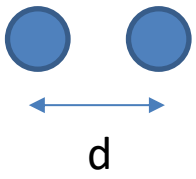
$p(r_1,t)$ and $p(r_2,t)$ denote the probability of finding the particle at the site r_1 and r_2 respectively, and τ^{-1} is the jump diffusion rate between the two sites, we can write the scattering function:

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

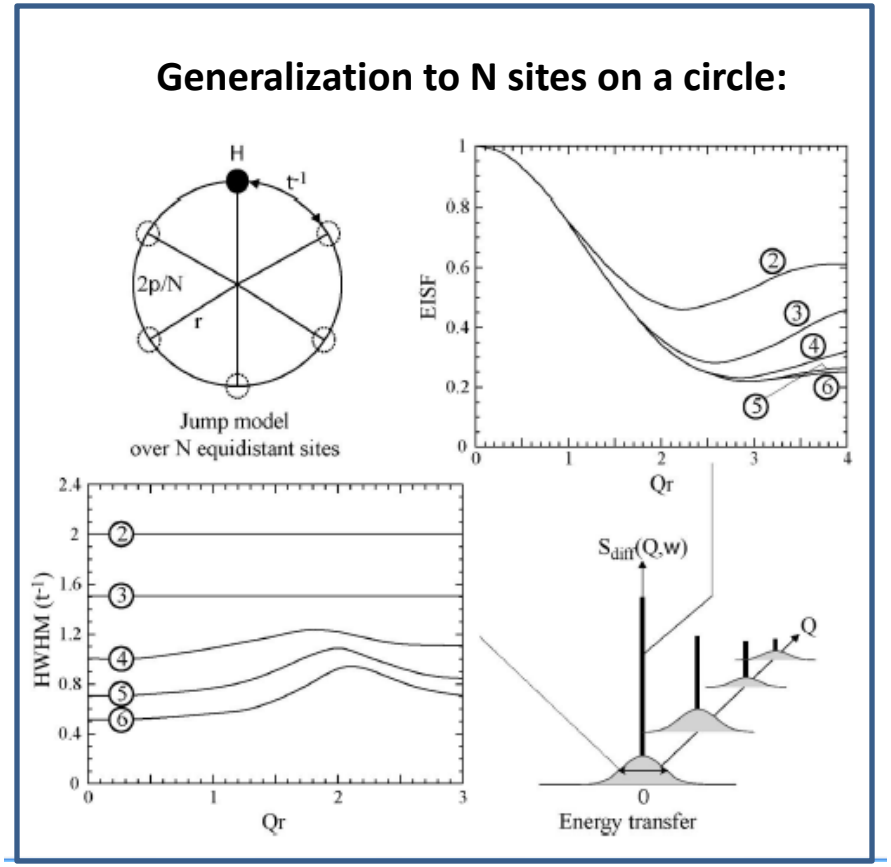
with $A_0(Q) + A_1(Q) = 1$

$$A_0(Q) = \frac{1}{2}\left[1 + j_0(Qd)\right],\ A_1(Q) = \frac{1}{2}\left[1 - j_0(Qd)\right]$$

Where $d=|r_1-r_2|$ is the jump distance between the two sites.

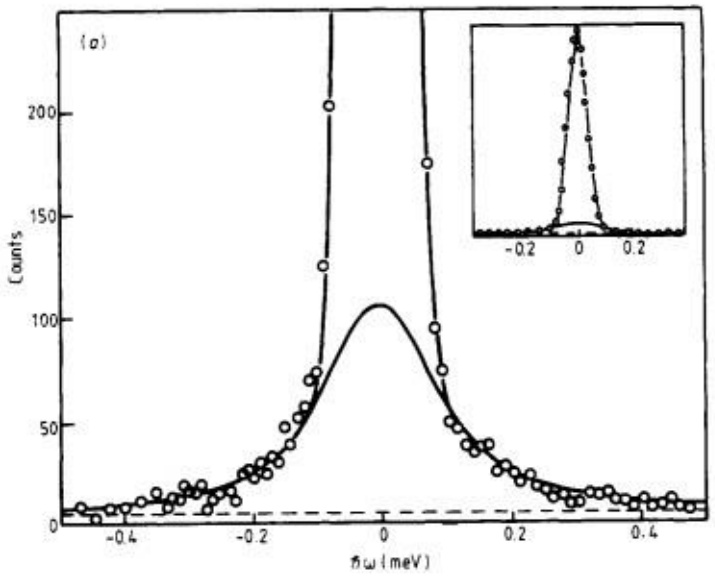


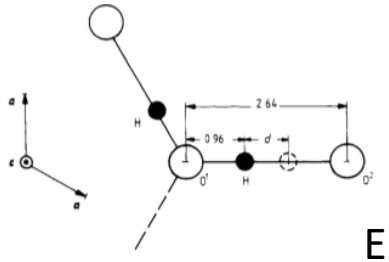
Generalization to N sites on a circle:

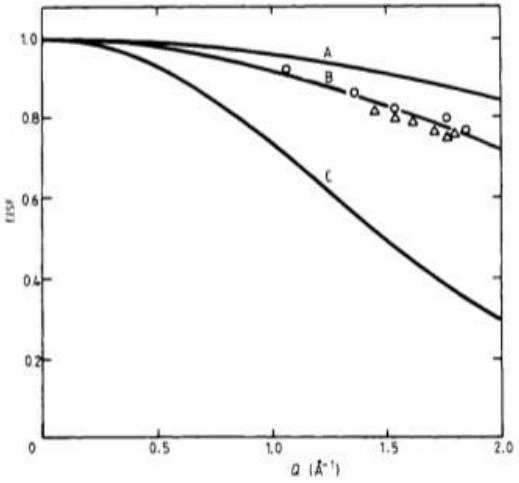


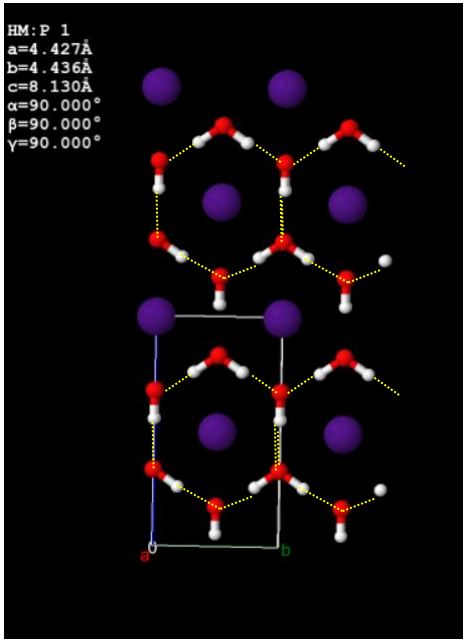
Localised dynamics : jump between 2 sites

Dynamics of the hydrogen bond in CsH_3O_2









EISF calculated for d=0.72 (A), 1.03 (B) and 1.66 Å (C).

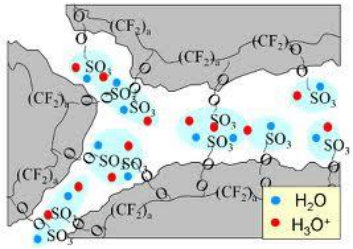
Localised dynamics : diffusion in a sphere

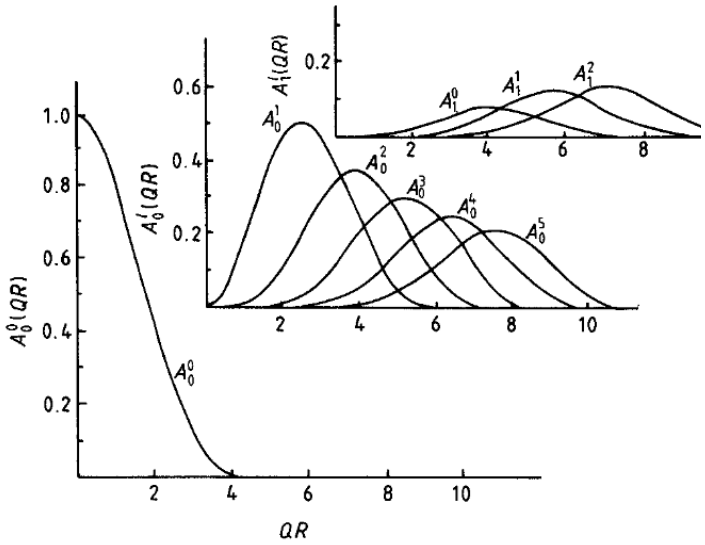
For a sphere of radius **R** with impermeable boundaries:

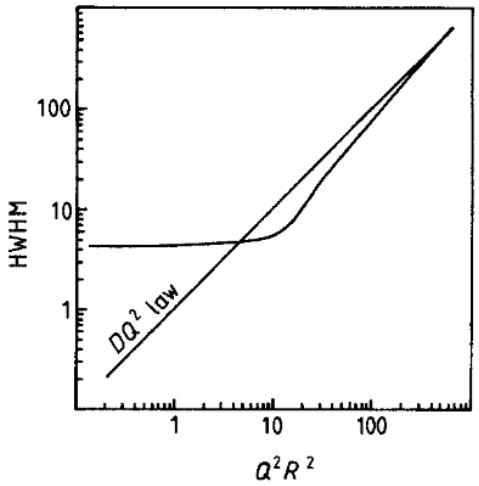
$$S(Q,\omega) = A_0^0(Q)\delta(\omega) + \sum_{l,n\neq 0,0} (2l+1) A_n^l(Q) \cdot \frac{1}{\pi} \frac{\lambda_n^l D}{\left(\lambda_n^l D\right)^2 + \omega^2}$$

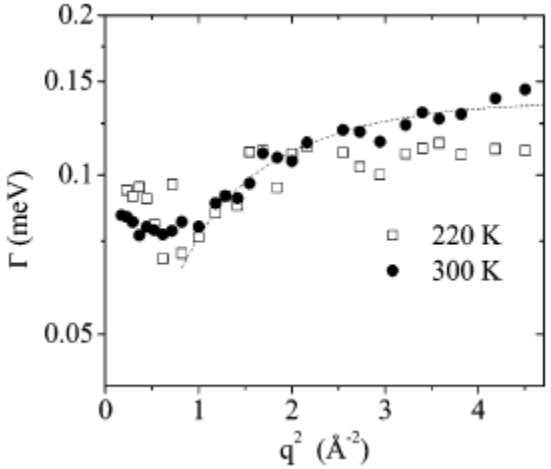
$$A_0^0(Q) = \left[\frac{3 j_1(QR)}{QR}\right]^2$$

The λ functions have to be calculated numerically.







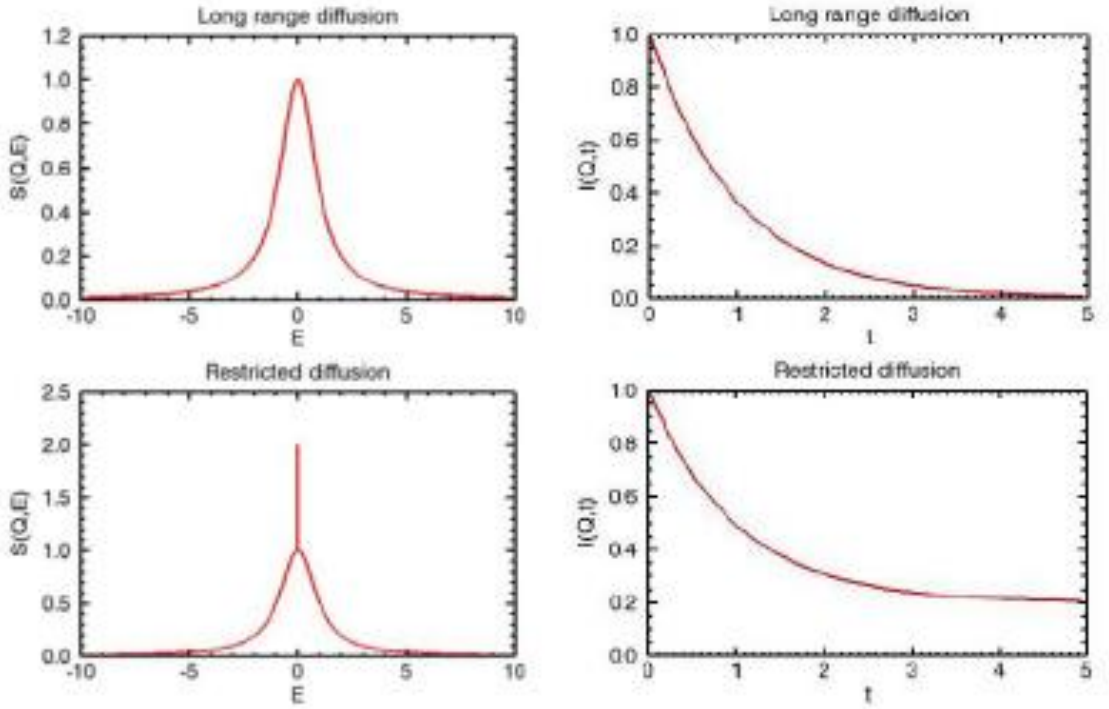


HWHM of water translational dynamics signal when confined in the Nafion membrane (Paciaroni et. al, JPCB(2006).

Long range diffusion or restricted dynamics

G(Q,∞)=I(Q, ∞)=S(Q,0)=0
No elastic peak in case of translational disorder (liquid)

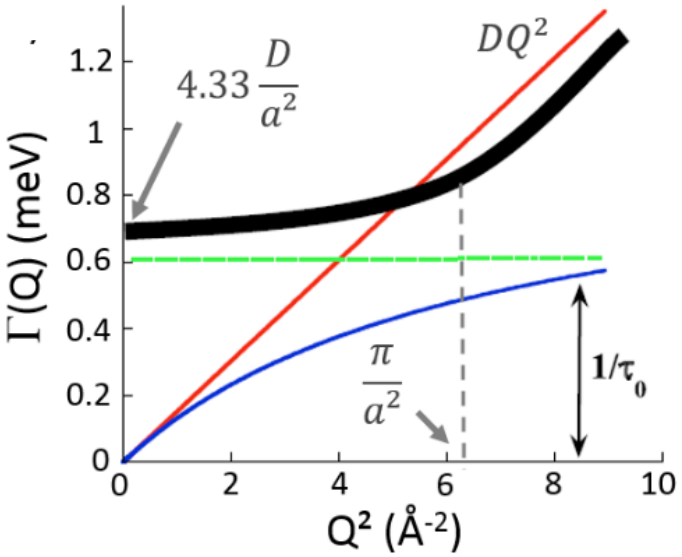
Restricted dynamics / « immobile » atoms: elastic component
EISF : Elastic Incoherent Structure Factor

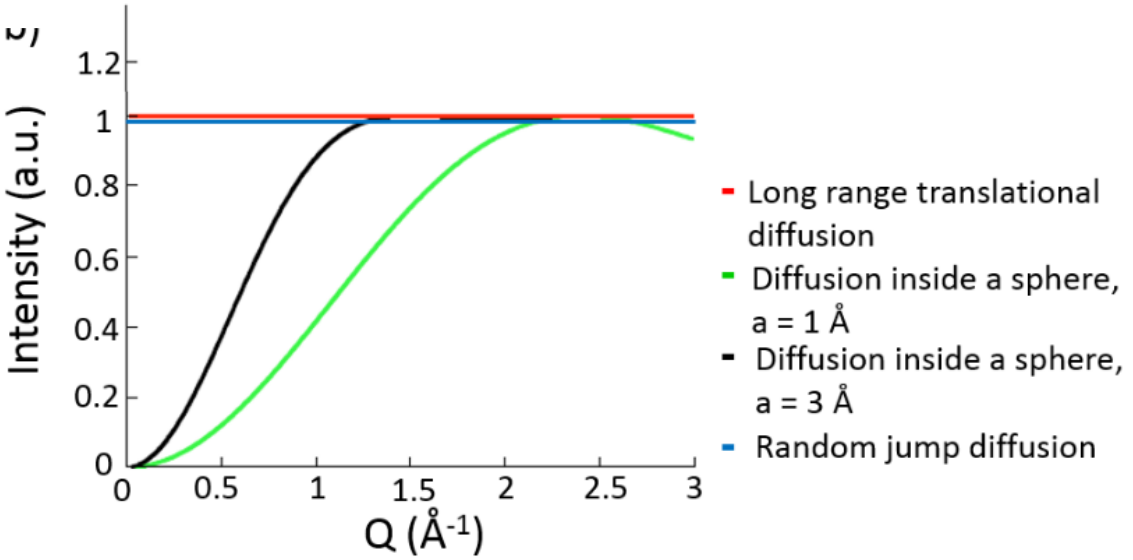


$$I(\mathrm{Q},t) = I(Q,0)\cdot e^{-t/\tau} + I(Q,\infty)$$

$$S(\mathrm{Q},\omega) = I(Q,\infty)\cdot\delta(\omega) + I(Q,0)\cdot\frac{1}{\pi}\frac{\tau}{1+\omega^2\tau^2}$$

In summary….

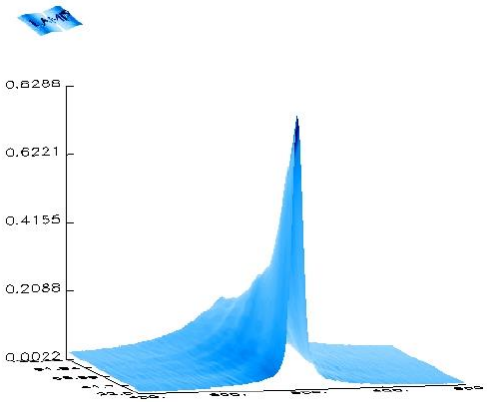




Berrod et al., EPJ 188, 05001 (2018)

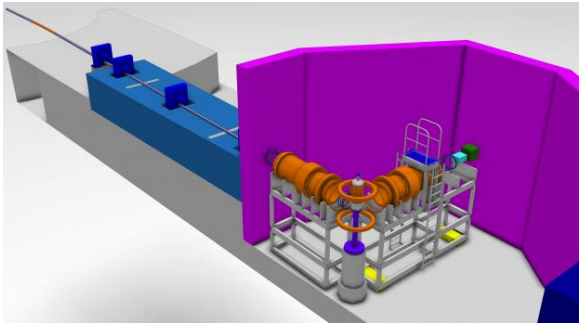
Outline

- dynamical structure factor S(q,ω) and diffusive dynamics
- basic QENS models
- **instruments and experiments**
- examples:
  - *fixed window* scan: MSD in proteins
  - molecular dynamics in physical gels
  - coherent and incoherent dynamics in bulk water
  - molecular dynamics in nano-organized ternary mixtures
  - dynamics in ionic liquids
  - dynamics of proteins in solution



In a real experiment

Neutron Spin Echo



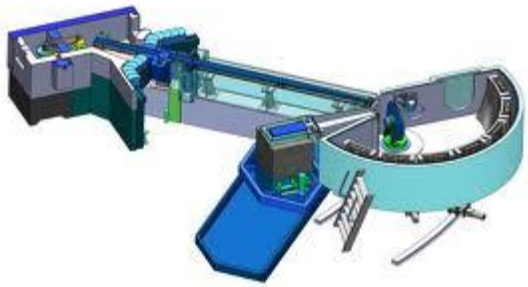
IN11, IN15 (ILL, Grenoble)

I(Q,t)

τ ~ 0.001 - 800ns
$\Delta\omega$ ~ neV

Q ~ 0.05 - 3.00Å^{-1}

Backscattering



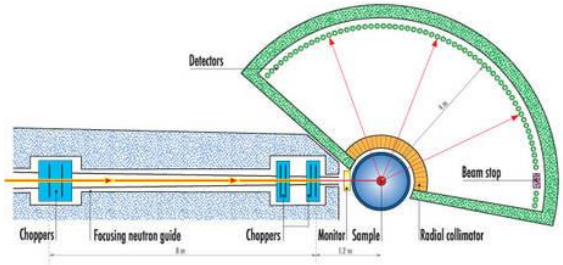
IN16B, IN10, IN13 (ILL, Grenoble)

S(Q,ω)

τ ~ 0.01 - 1ns
$\Delta\omega$ ~ 0.2 - 8 μeV

Q ~ 0.05 - 5.0Å^{-1}

Time of Flight



IN4, IN5, IN6 (ILL, Grenoble)

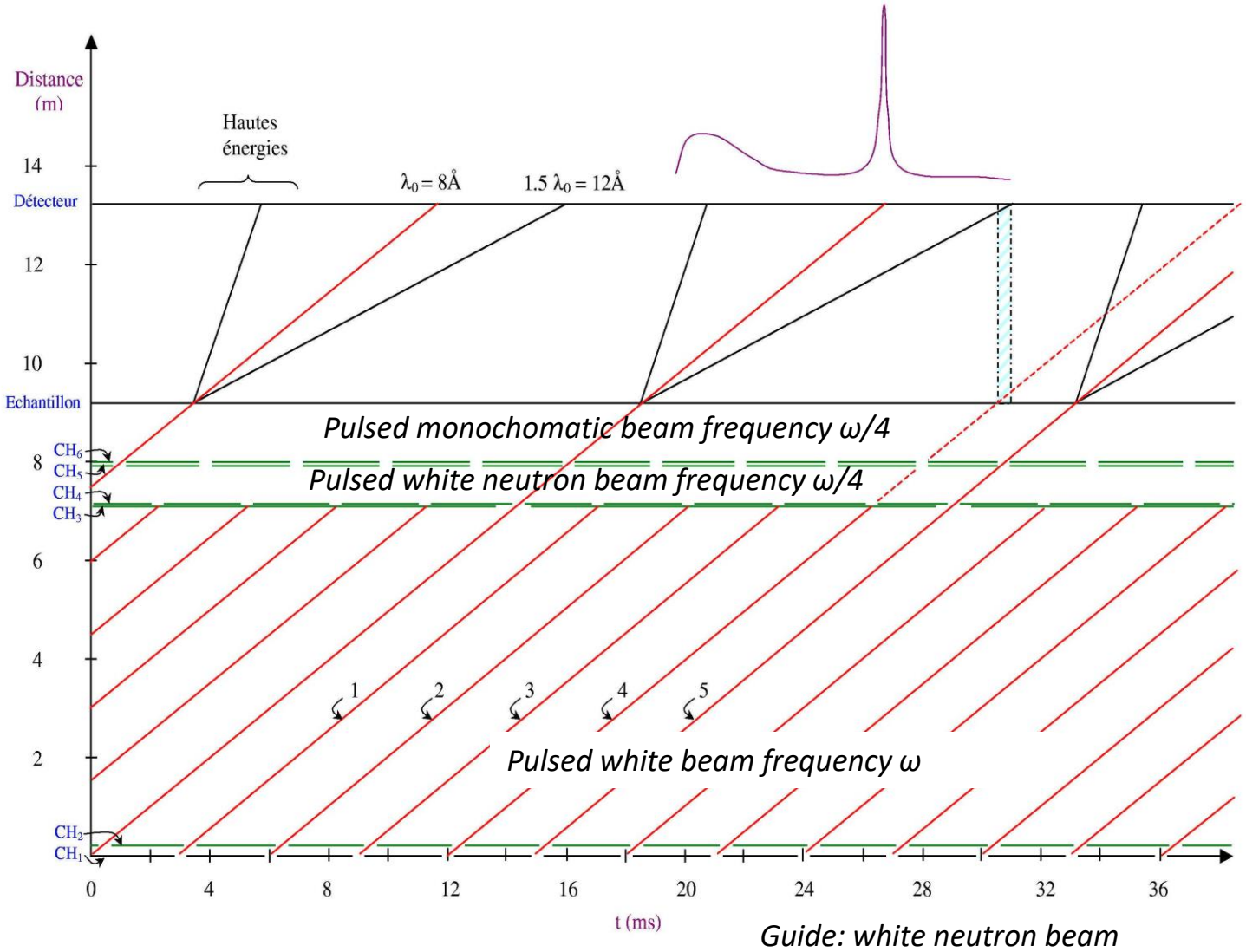
S(Q,ω)

τ ~ 0.1 - 100ps
$\Delta\omega$ ~ 0.01 – 6 meV

Q ~ 0.1 - 14.0 Å^{-1}

Long times (~1μs) → **Short times (~0.1ps)**

Time of Flight



Monochomatizing chppers

Contaminent orders and frame overlap chppers

Pulsing chppers

https://www.ill.eu/fileadmin/user_upload/ILL/3_Users/Instruments/Instruments_list/00_-_SPECTROSCOPY/00_-_TIME_OF_FLIGHT/IN5/html5/IN5B-principle/IN5.html

In a real experiment

- choose the instrument adapted to the dynamics you want to characterize : time scale (energy resolution, energy window), length scale (q-range)

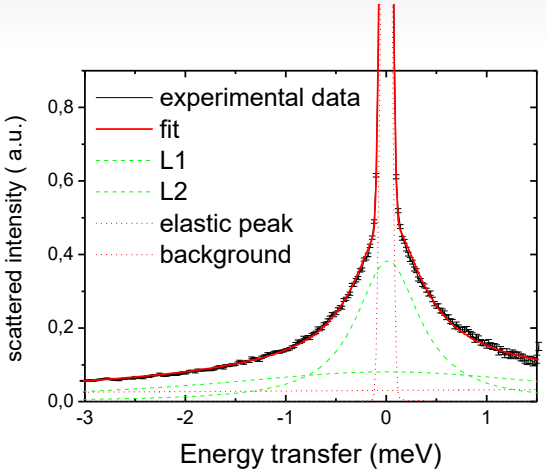
- measure all the components separately : background, empty cell…

- measure the response function of the instrument (resolution)

- adapt the counting time to reach the statistics you need to extract your parameters : following the Poisson' statistics, where N is the number of neutrons on the detector :

$$\sigma = \frac{1}{\sqrt{N}}$$

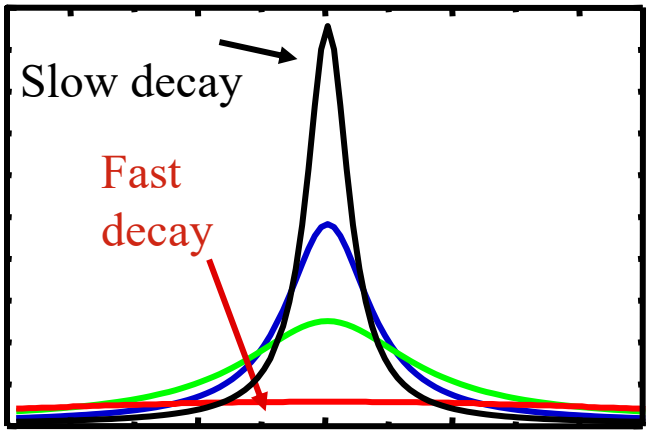
In a real experiment



Then choose/try the right model :

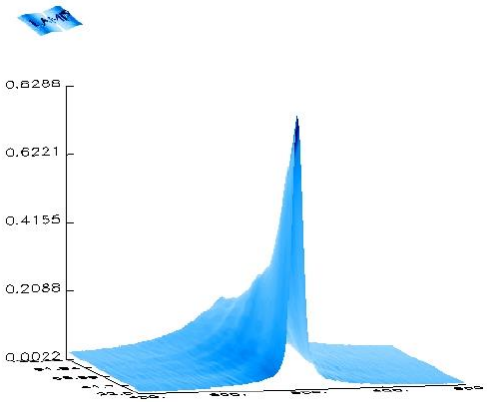
Convolution with instrumental function !

$$\left(\frac{d^2\sigma}{d\Omega dE}\right) \approx e^{(-2W(Q))} \cdot e^{\frac{-\hbar\omega}{kT}} \cdot \left(A_0(Q)\cdot\delta(\omega) + \sum_{i=1,n} A_i(Q)\cdot L(Q,\omega) \right) \otimes R(Q,\omega)$$

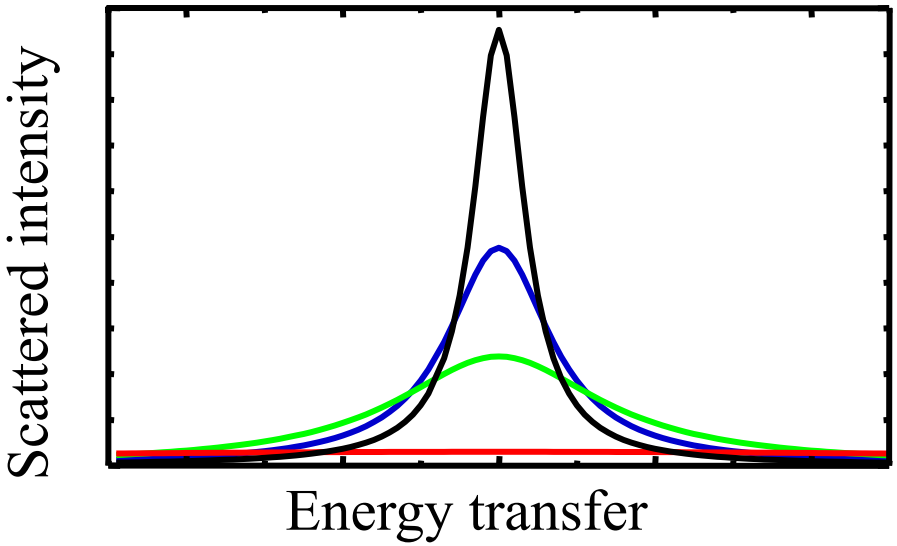


Outline

- dynamical structure factor S(q,ω) and diffusive dynamics
- basic QENS models
- **instruments and experiments**
- **examples:**
  - ***fixed window* scan: MSD in proteins**
  - molecular dynamics in physical gels
  - coherent and incoherent dynamics in bulk water
  - molecular dynamics in nano-organized ternary mixtures
  - dynamics in ionic liquids
  - dynamics of proteins in solution



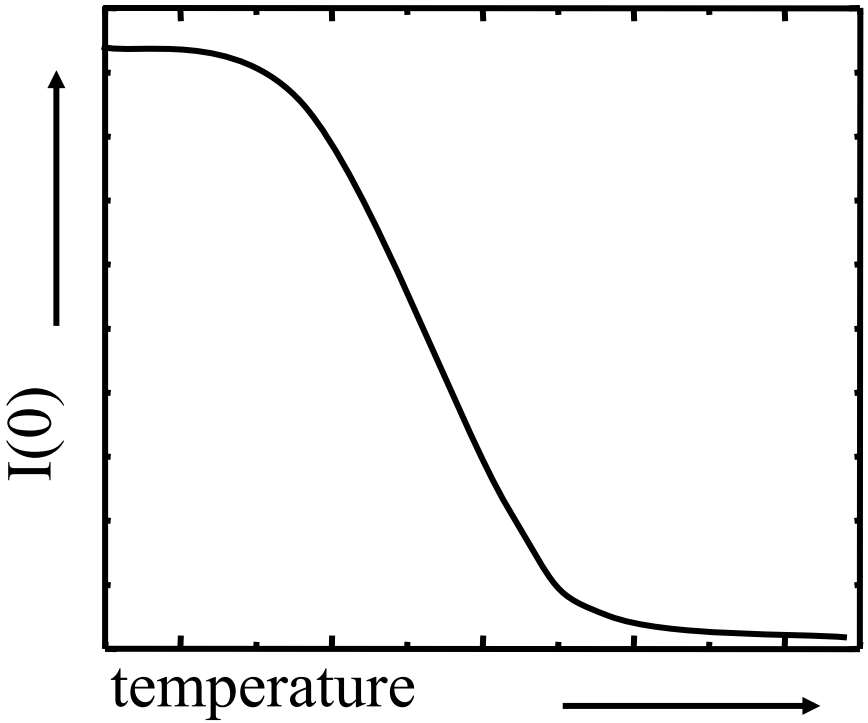
The Fixed window scan



Monitoring of the intensity at a given energy transfer (elastic or inelastic). The energy integration width is given by the instrumental resolution.

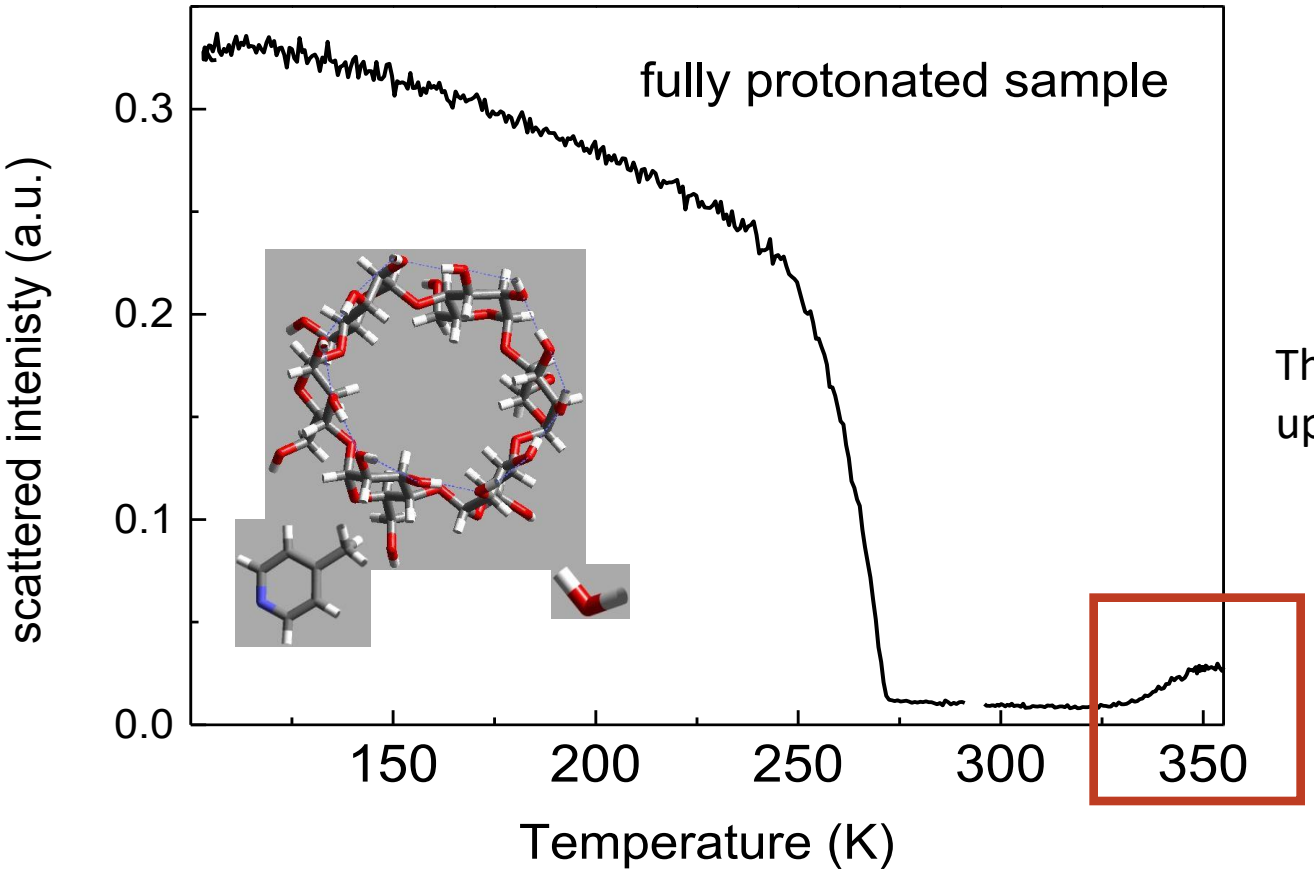
$$I(Q,0) = \int R(Q,0) * S(Q,\omega) d\omega$$

The most relevant elastic fixed-window scan.



The Fixed window scan : elastic intensity

Elastic scan measured on IN16 in a ternary mixture of 4 methyl pyridine, α-cyclodextrine and water.

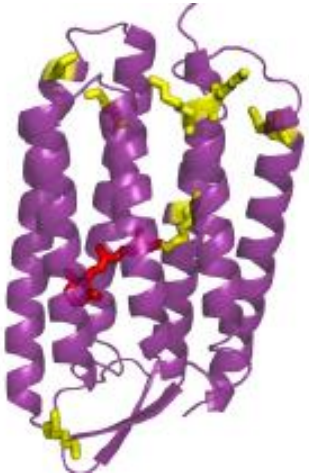


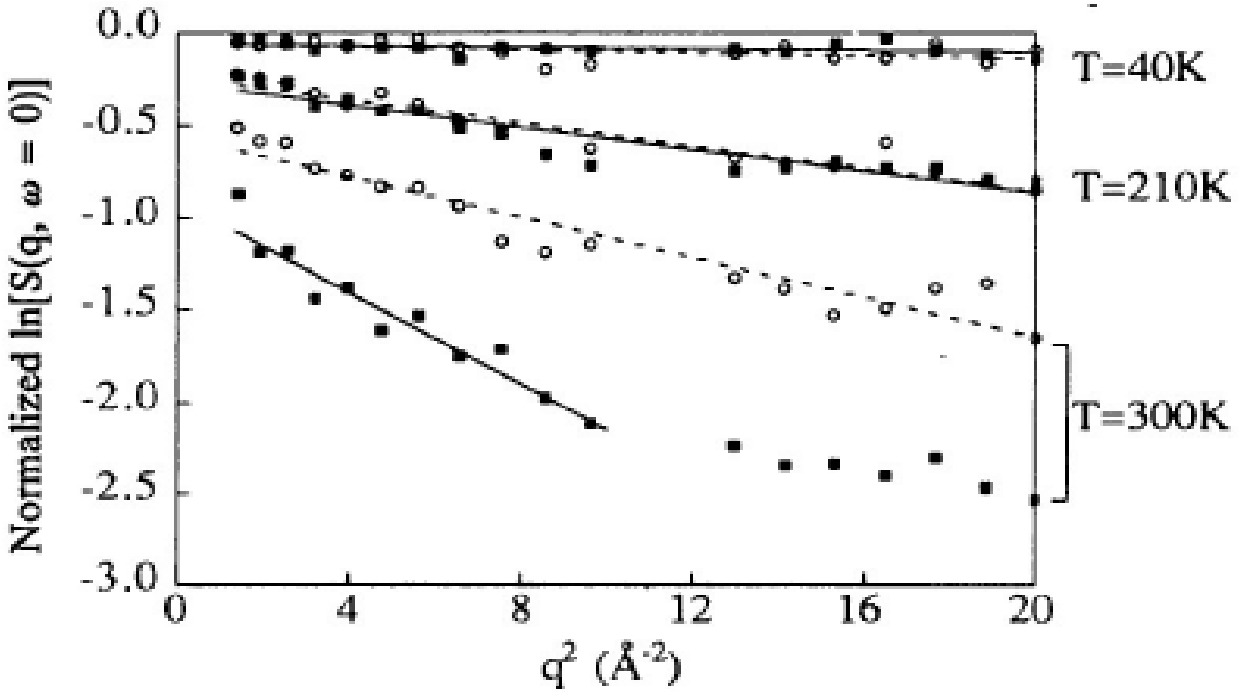
The sample solidifies upon heating.

Plazanet et al., J. Chem. Phys. 2006

The Fixed window scan : Q-dependence

Bacteriorhodopsin
D_2O-hydrated
powder



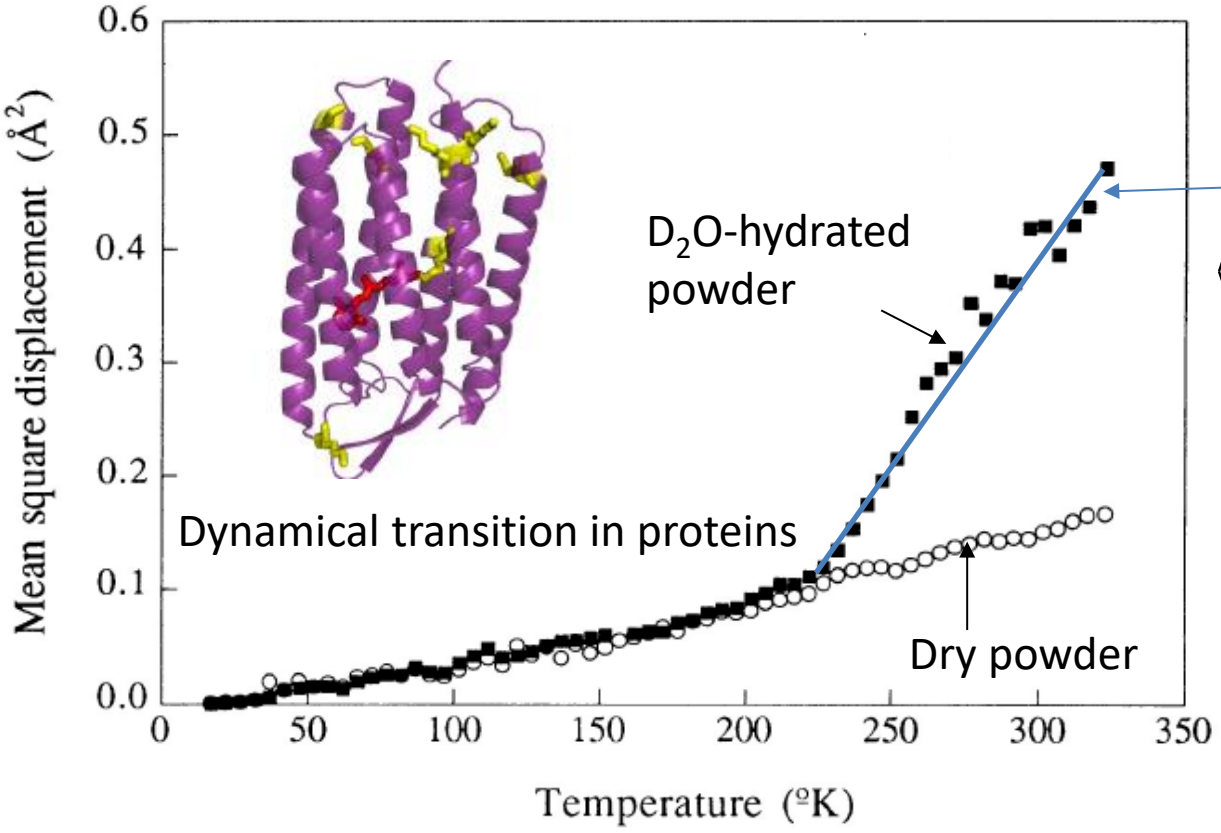


$$I(Q,\omega=0) \approx A_0 \exp\left(-\frac{<u(T)^2>Q^2}{3}\right)$$

<u(T)^2> : MSD in the Gaussian approximation

(Ferrand et al., PNAS 1993).

The Fixed window scan : Q-dependence



$$\Delta U = \frac{1}{2} k x^2$$

$$\langle x^2 \rangle \approx \frac{1}{\frac{d\langle 3x^2 \rangle}{dT}}$$

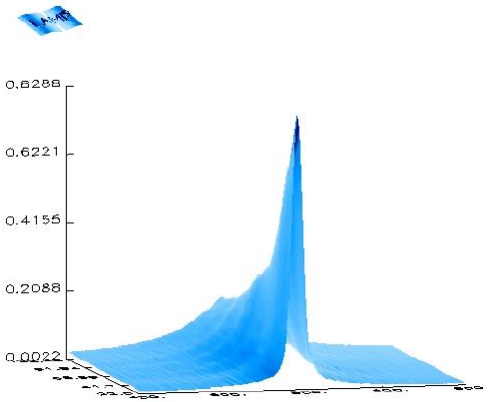
(Zaccai, Science, 2000)

Measured on the IN13 backscattering spectrometer at the ILL, energy resolution ~ 10 µeV, $1 < Q^2 < 8$ Å^{-2}.

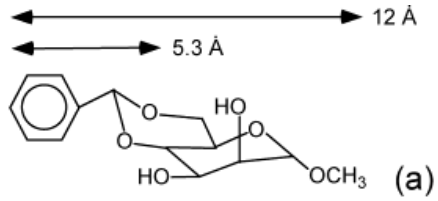
NB. Expression valid if the QENS contribution to the elastic intensity can be neglected.
This quantity is assimilated to a pseudo Debye-Waller factor.

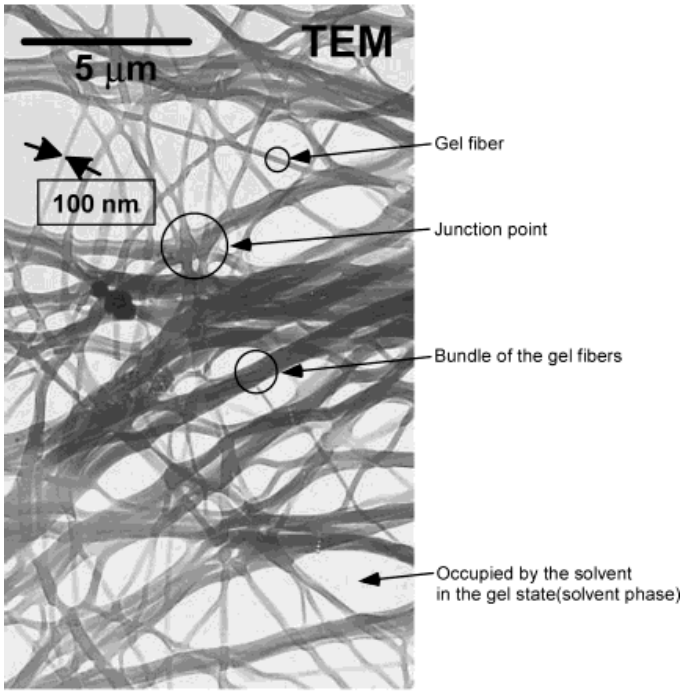
Outline

- dynamical structure factor S(q,ω) and diffusive dynamics
- basic QENS models
- **instruments and experiments**
- **examples:**
  - *fixed window* scan: MSD in proteins
  - **molecular dynamics in physical gels**
  - coherent and incoherent dynamics in bulk water
  - molecular dynamics in nano-organized ternary mixtures
  - dynamics in ionic liquids
  - dynamics of proteins in solution



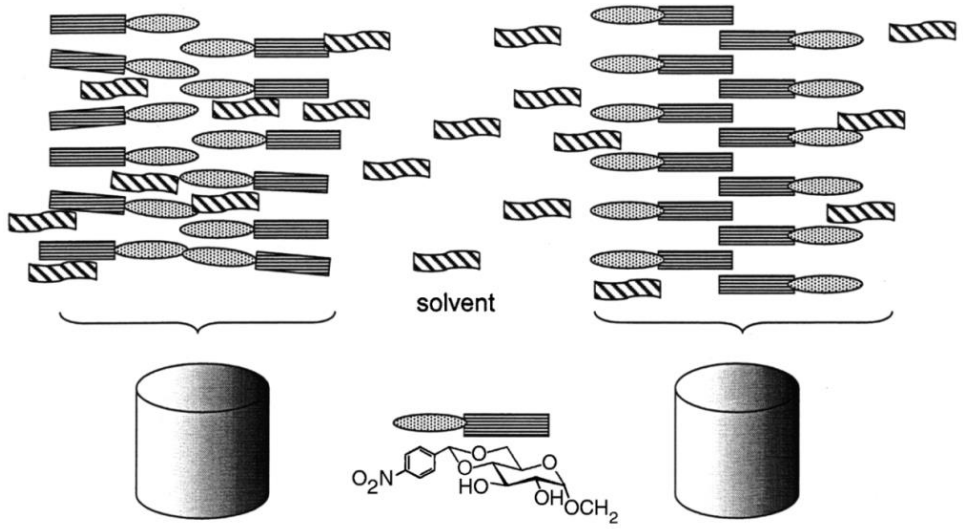
Example: physical gel





Sakurai et al., Langmuir 2003

methyl-4,6-O-benzylidene-α-D mannopyranoside in water and organic solvent



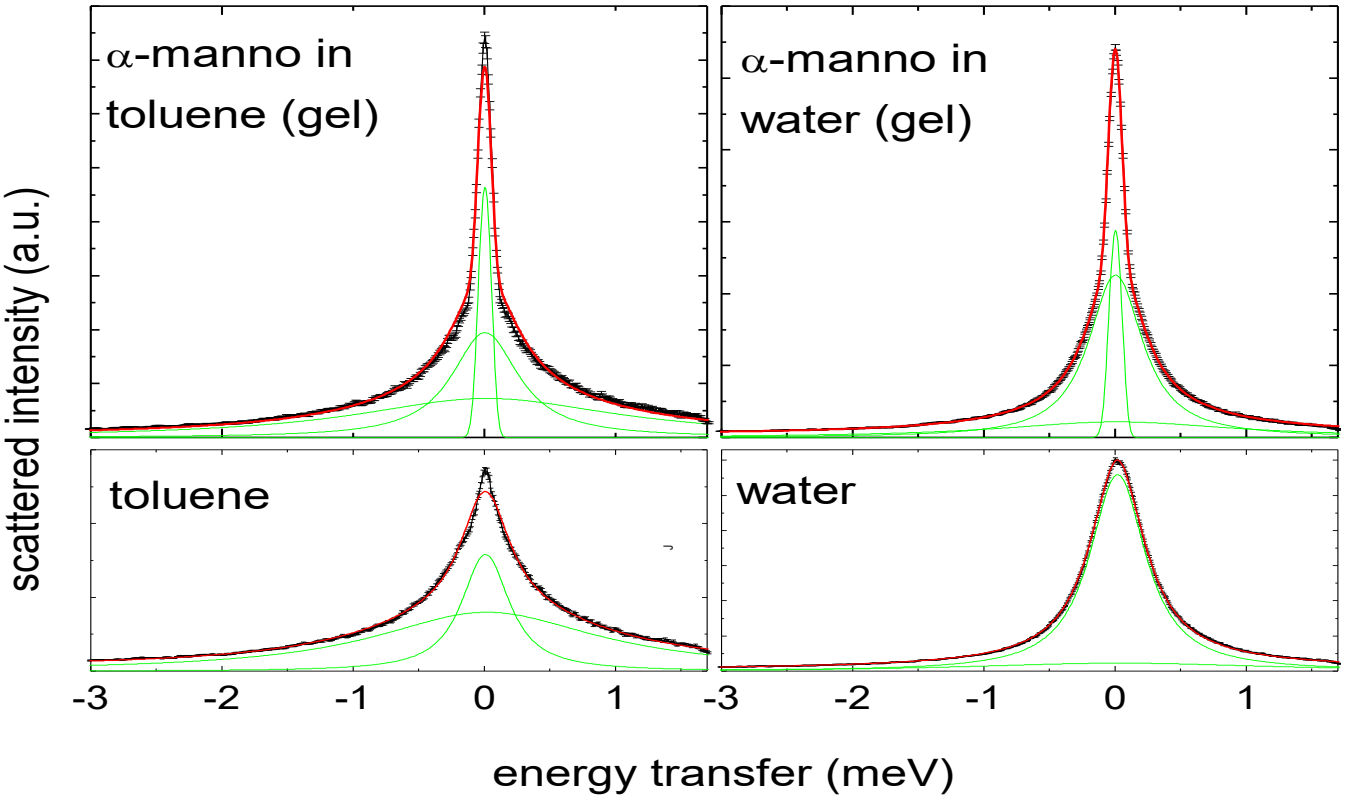
Hydrophobic interactions operating in polar solvents

in water

Hydrogen-bonding interactions operating in nonpolar solvents

in toluene

Example: physical gel

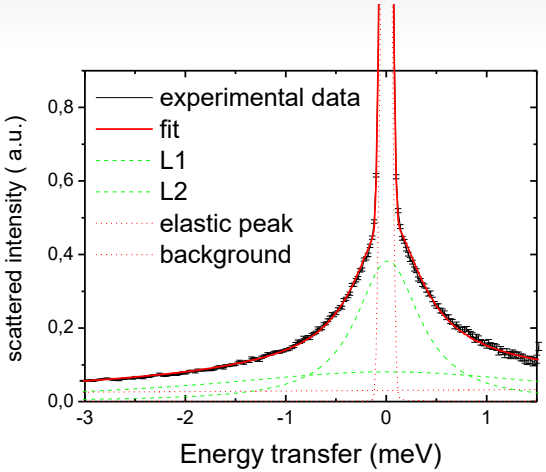


QENS measured on IN5 (ILL) and analyzed with
- an elastic contribution
- two lorentzian components.

$$S(Q,\omega) = \alpha S_{solid}(Q) + (1-\alpha) S_{solvent}(Q,\omega)$$

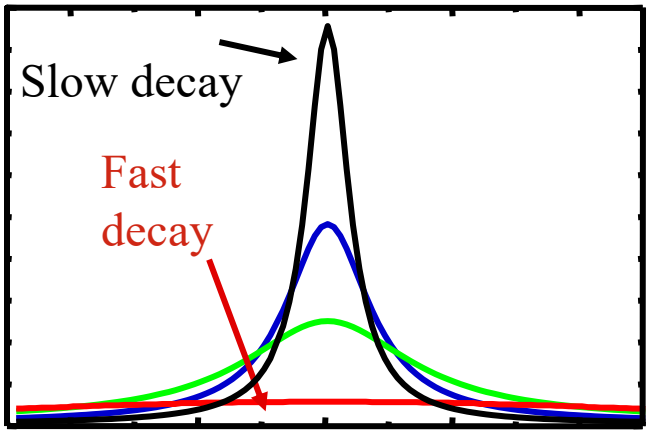
Elastic component on top of the quasielastic solvent contribution due to the presence of the network

Example: physical gel



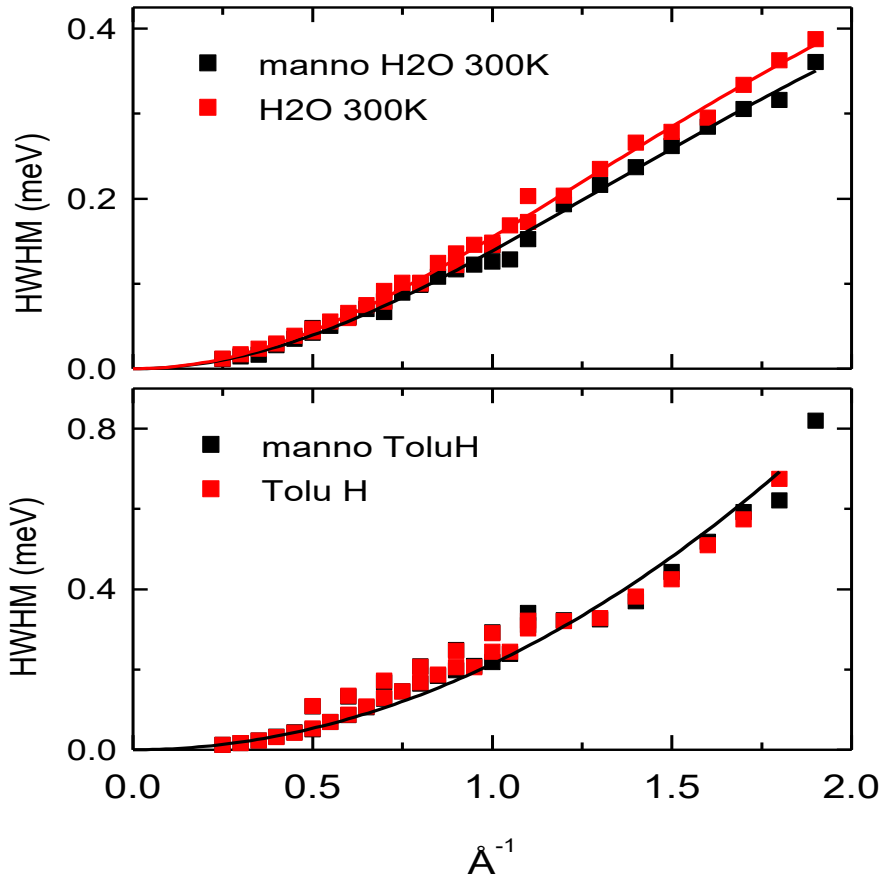
Phenomenological description : sum of Lorenzian function representative of the (uncoupled) different dynamics of the sample

$$\left(\frac{d^2\sigma}{d\Omega dE}\right) \approx e^{(-2W(Q))} \cdot e^{\frac{-\hbar\omega}{kT}} \cdot \left(A_0(Q)\cdot\delta(\omega) + \sum_{i=1,n} A_i(Q)\cdot L(Q,\omega) \right) \otimes R(Q,\omega)$$



Example: physical gel

Lorentzian with translational character:



Water: jump diffusion dynamics

Diffusion coefficient:
Water: $D = (2.8 \pm 0.1) \times 10^{-5}$ cm^2/s
Hydrogel: $D = (2.5 \pm 0.1) \times 10^{-5}$ cm^2/s

Residence time:
Water: $\tau = 0.75 \pm 0.03$ ps
Hydrogel: $\tau = 0.77 \pm 0.04$ ps

In toluene: Fickian diffusion

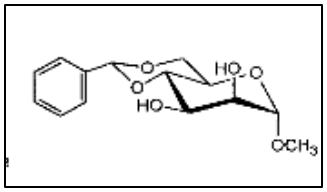
D= 3.2 × cm^2/s in pure solvent and organogel.

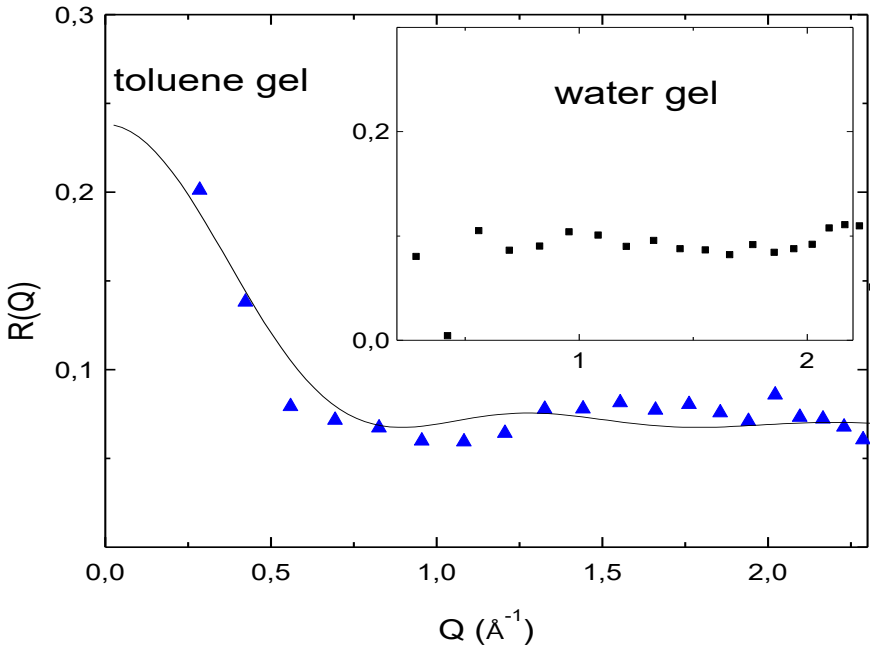
Example: physical gel

Elastic contribution

$$R(Q) = \frac{I_{el,solid}}{I_{el,solid} + I_{qens,solvent}}$$

$$R(0) = \frac{\sigma_{\alpha-manno} + n_{solvent,immo} \cdot \sigma_{solvent}}{\sigma_{\alpha-manno} + n_{solvent,total} \cdot \sigma_{solvent}}$$

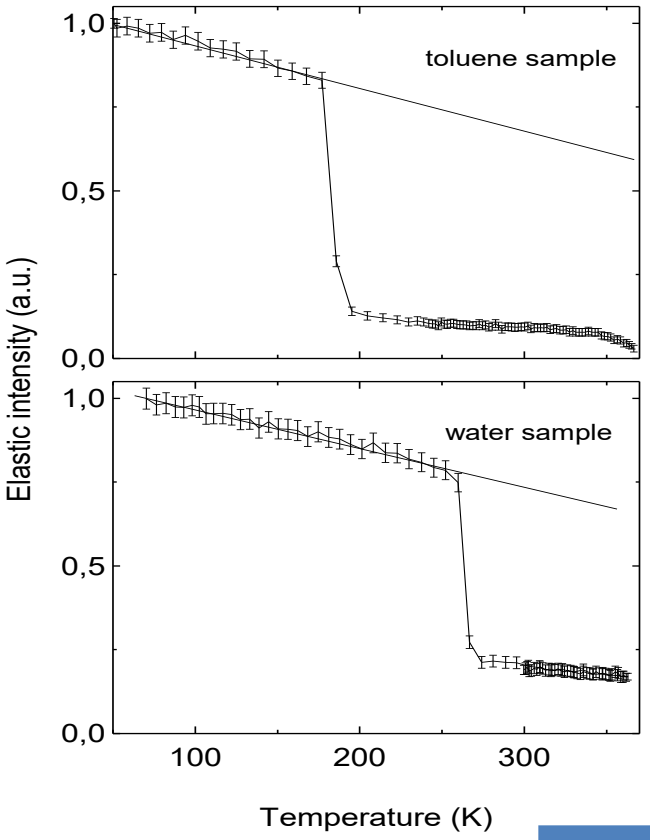




Sample	Solvent/gelator	R(0)	Solvent immobilised
Toluene	32.1	0.24	6.2 ± 2.1
water	180.2	0.1	10 ± 3

Rotation radius ~3.8Å
-> aromatic parts

Example: physical gel



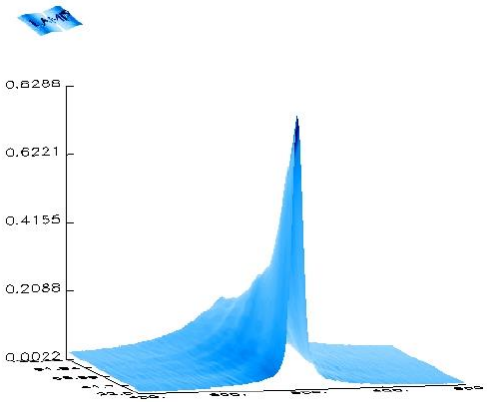
Elastic scan measured on IN16

$$\frac{I_{exp}}{I_{DW}} = \frac{\sigma_{\alpha-manno} + n_{solvent,immo} \cdot \sigma_{solvent}}{\sigma_{\alpha-manno} + n_{solvent} \cdot \sigma_{solvent}}$$

Sample	solvent/gelator	I_{exp}	I_{DW}	solvent immobilized
Toluene	22	1.25	8.6	1.23 ± 0.5
water	75.2	2.6	9.6	14 ± 2

Outline

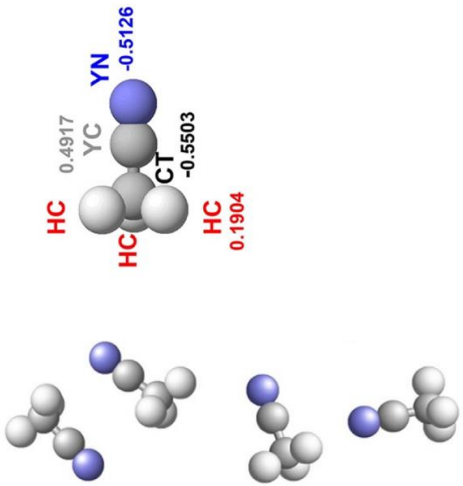
- dynamical structure factor S(q,ω) and diffusive dynamics
- basic QENS models
- **instruments and experiments**
- **examples:**
  - *fixed window* scan: MSD in proteins
  - molecular dynamics in physical gels
  - **coherent and incoherent dynamics in bulk water**
  - molecular dynamics in nano-organized ternary mixtures
  - dynamics in ionic liquids
  - dynamics of proteins in solution

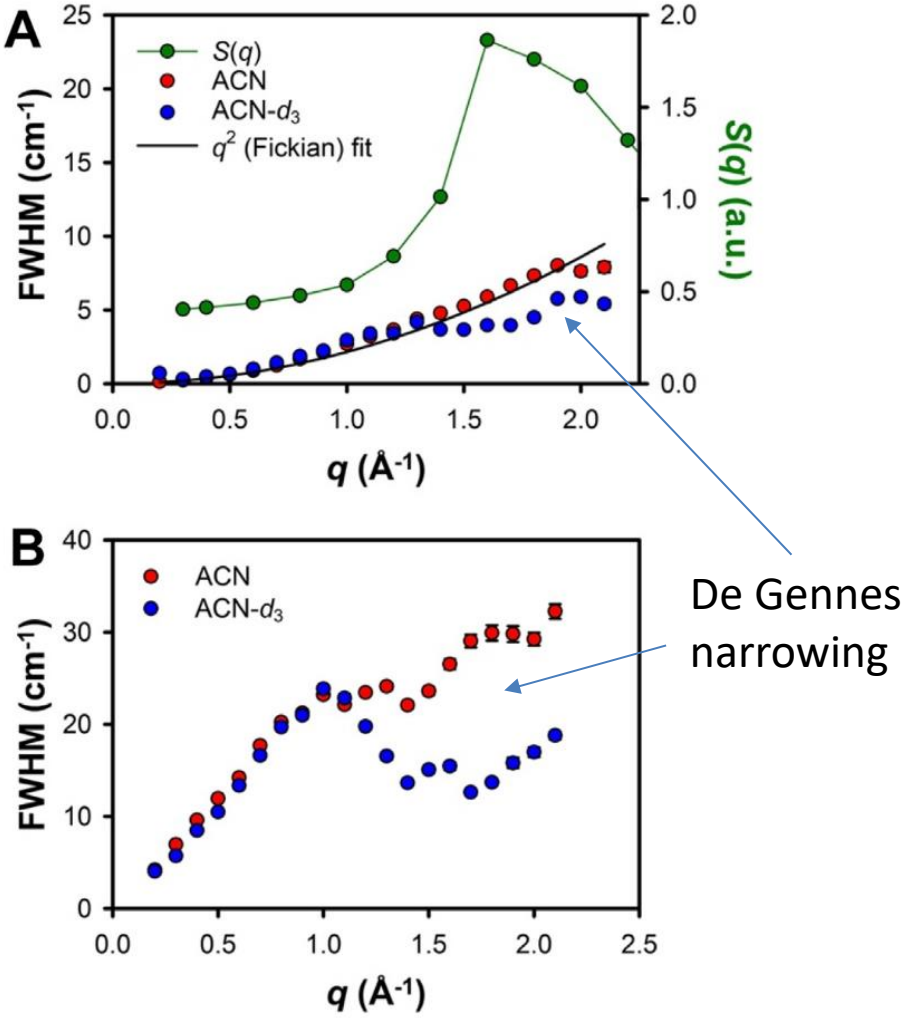


Coherent quasi-elastic scattering: translational dynamics

Acetonitrile

Coherent vs incoherent cross section:
Self vs collective dynamics





Coherent scattering :

$$HWHM(Q) \approx \frac{D_0 Q^2}{S(Q)}$$

Cohen et al., J. Mol. Liquids (2022)

Coherent quasi-elastic scattering: translational dynamics

Coherent diffusion in liquid germanium (Hugouvieux PRE2007)

De Gennes narrowing : slow down of the dynamics at the maximum of the structure factor.

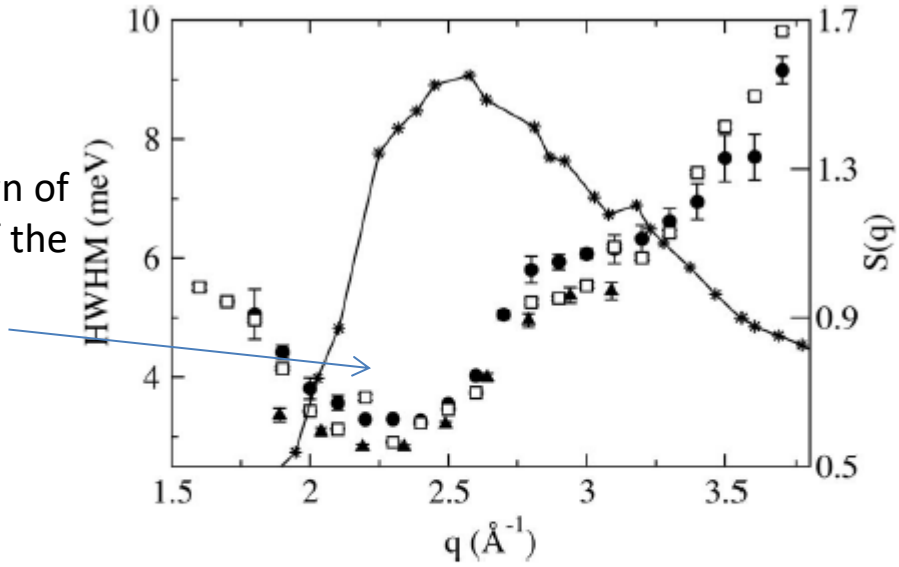
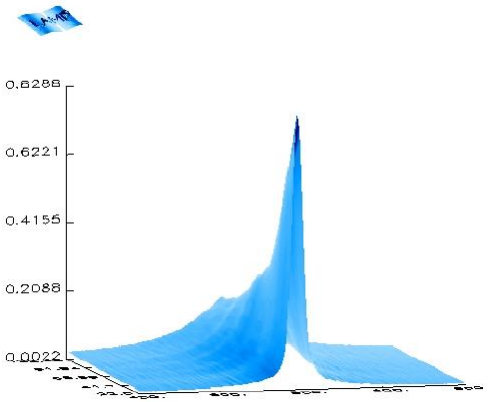


FIG. 13. Half-width at half-maximum of $S(q,\omega)$ as a function of q together with the static structure factor. Circles, triple-axis measurements (4F1); triangles, time-of-flight measurements (Focus); squares, simulation; stars and straight line, simulated $S(q)$ at 1390 K.

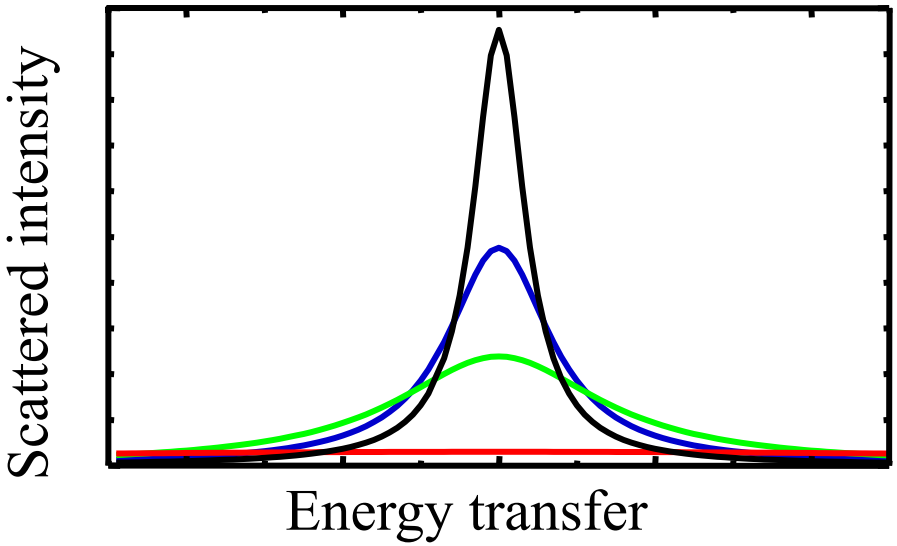
Outline

- dynamical structure factor S(q,ω) and diffusive dynamics
- basic QENS models



- **examples**:
  - ***fixed window* scan: MSD in proteins**
  - molecular dynamics in physical gels
  - coherent and incoherent dynamics in bulk water
  - molecular dynamics in nano-organized ternary mixtures
  - dynamics in ionic liquids
  - dynamics of proteins in solution

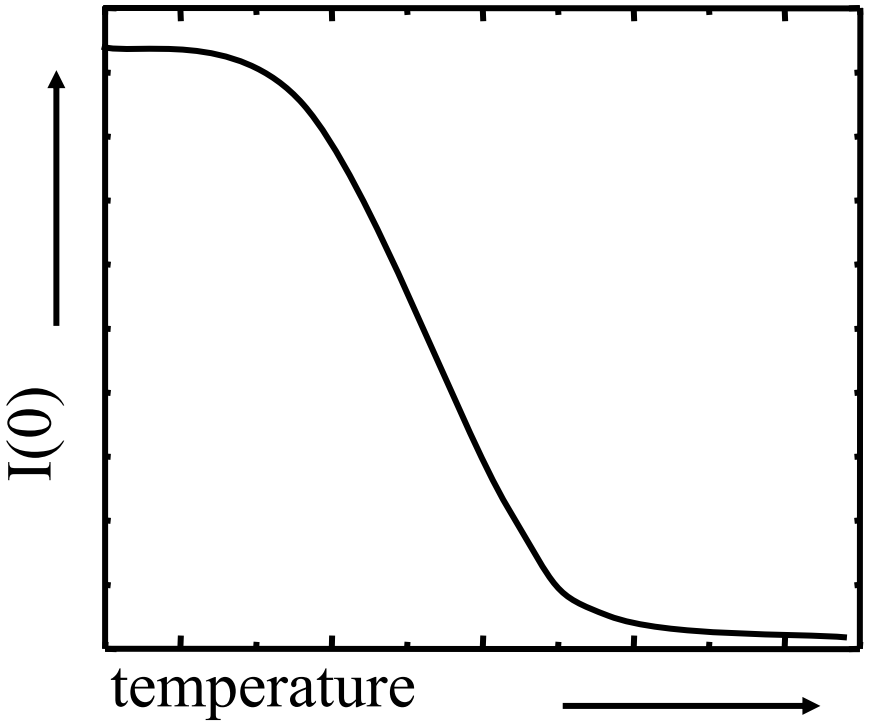
The Fixed window scan



Monitoring of the intensity at a given energy transfer (elastic or inelastic). The energy integration width is given by the instrumental resolution.

$$I(Q,0) = \int R(Q,0) * S(Q,\omega) d\omega$$

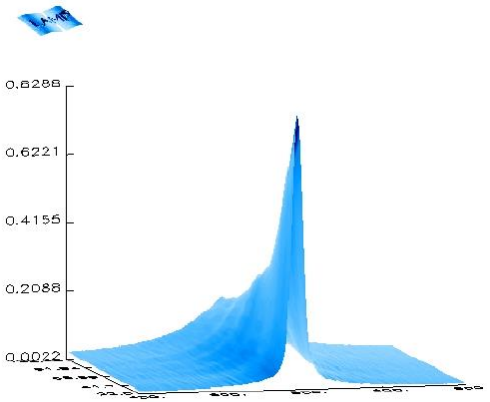
The most relevant elastic fixed-window scan.



Outline

- dynamical structure factor S(q,ω) and diffusive dynamics

- basic QENS models



- **examples**:
  - *fixed window* scan: MSD in proteins
  - molecular dynamics in physical gels
  - **coherent and incoherent dynamics in bulk water**
  - molecular dynamics in nano-organized ternary mixtures
  - dynamics in ionic liquids
  - dynamics of proteins in solution

Self and collective dynamics in D_2O

- different values of σ_{inc} and σ_{coh} for a same element
- different response to spin polarisation
- **$I_{SF}=2/3\ I_{inc}$; $I_{NSF} = I_{coh}+1/3\ I_{inc}$**

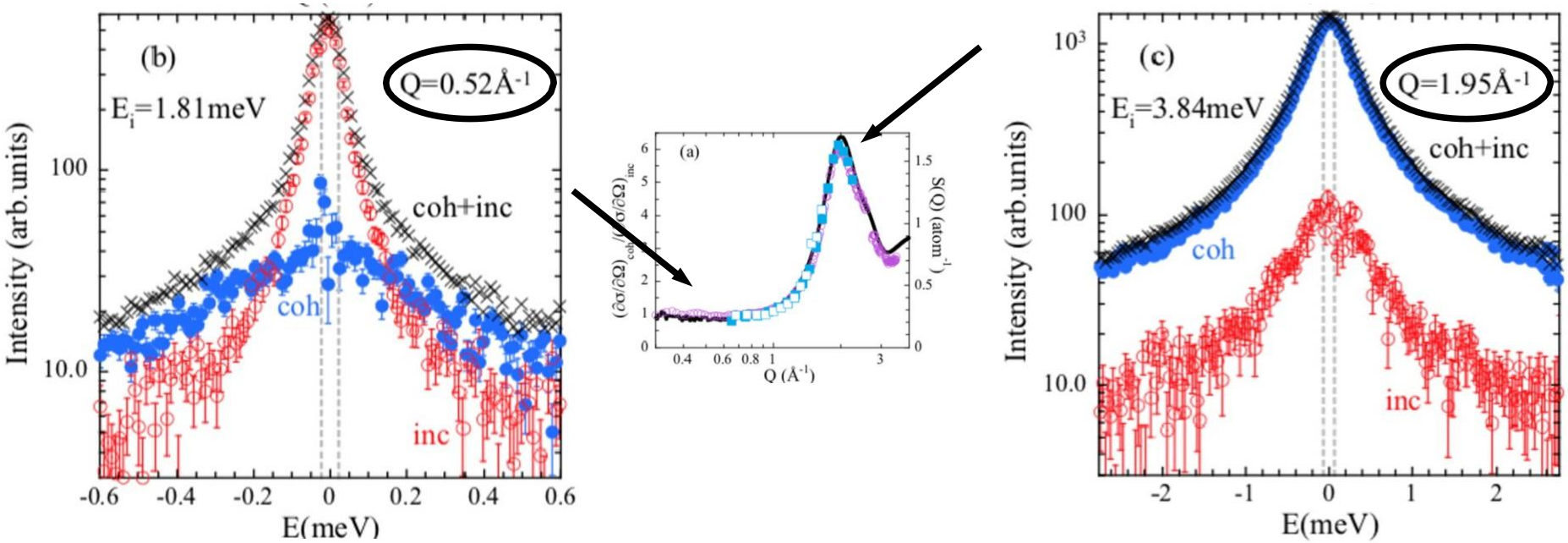
H: $\sigma_{inc}=80.3$, $\sigma_{coh}=1.76$

D: $\sigma_{inc}=2.05$, $\sigma_{coh}=5.6$

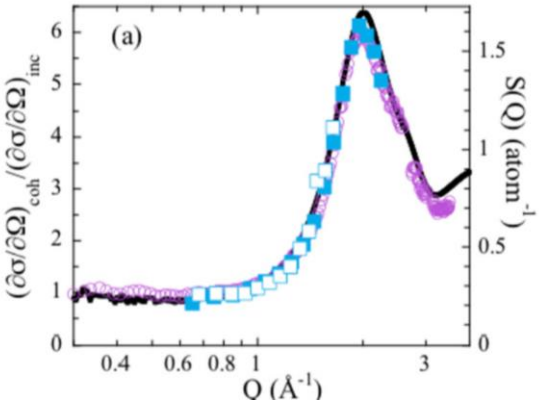
O: $\sigma_{inc}= 0.008$, $\sigma_{coh} =4.2$

A. Arbe et al., Physical Review Research 2, 022015(R) (2020)

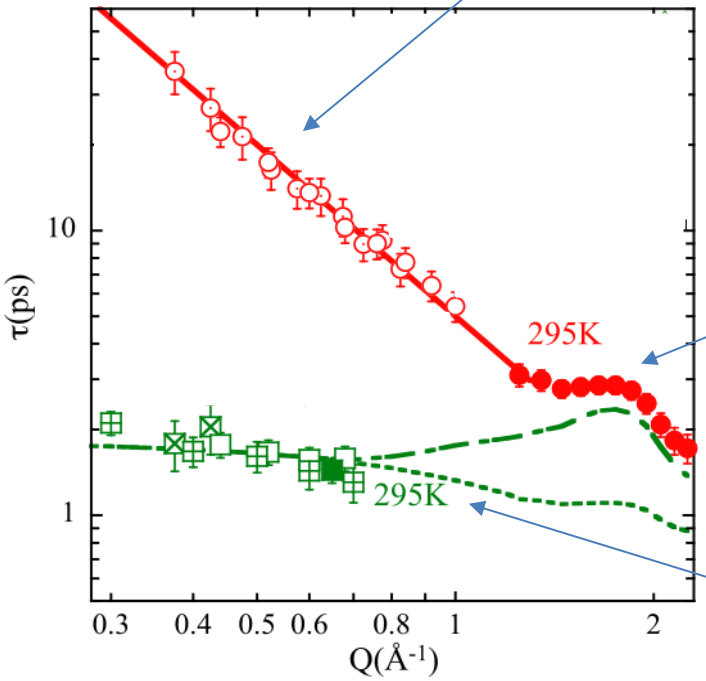
Measurements on P-LET (ISIS, UK) : TOF + polarization analysis



Self and collective dynamics in D_2O



D_s~D_c: self diffusion dynamics ~ q^2



De-Gennes narrowing:

$$D_0 \approx \frac{D_s q^2}{S(q)}$$

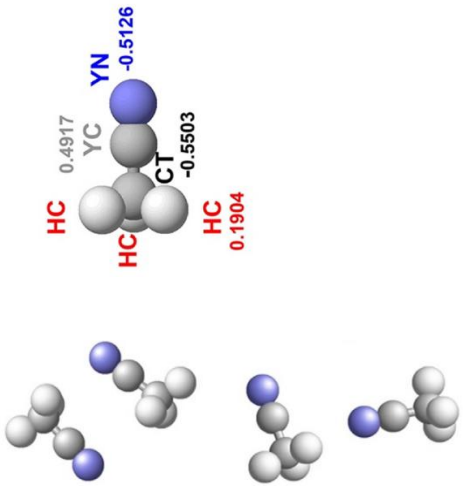
q-independent collective mode – diffusion at mesoscale

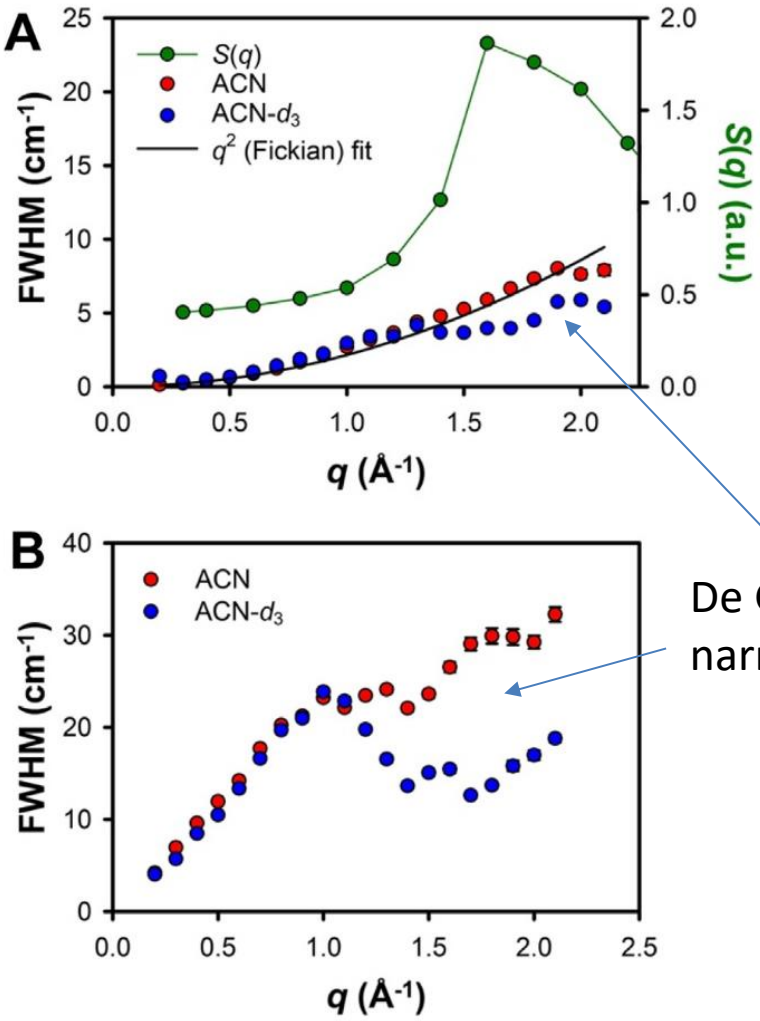
A. Arbe et al., Physical Review Research 2, 022015(R) (2020)

Coherent quasi-elastic scattering: translational dynamics

Acetonitrile

Coherent vs incoherent cross section:
Self vs collective dynamics





De Gennes narrowing

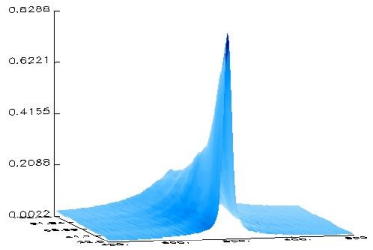
Coherent scattering :

$$HWHM(Q) \approx \frac{D_0 Q^2}{S(Q)}$$

Cohen et al., J. Mol. Liquids (2022)

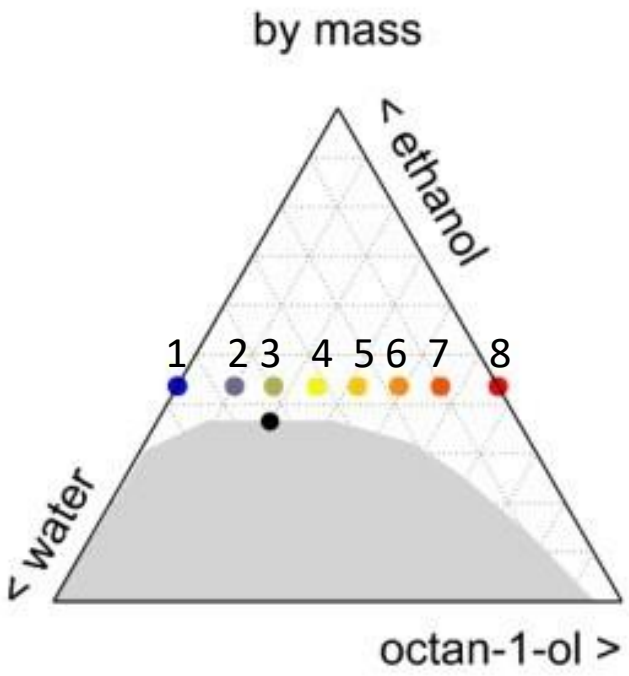
Outline

- dynamical structure factor S(q,ω) and diffusive dynamics
- basic QENS models
- data analysis
- **examples:**
  - molecular dynamics in physical gels
  - *fixed window* scan: MSD in proteins
  - coherent and incoherent dynamics in bulk water
  - molecular dynamics in nano-organized ternary mixtures
  - **dynamics in ionic liquids**
  - dynamics of proteins in solution

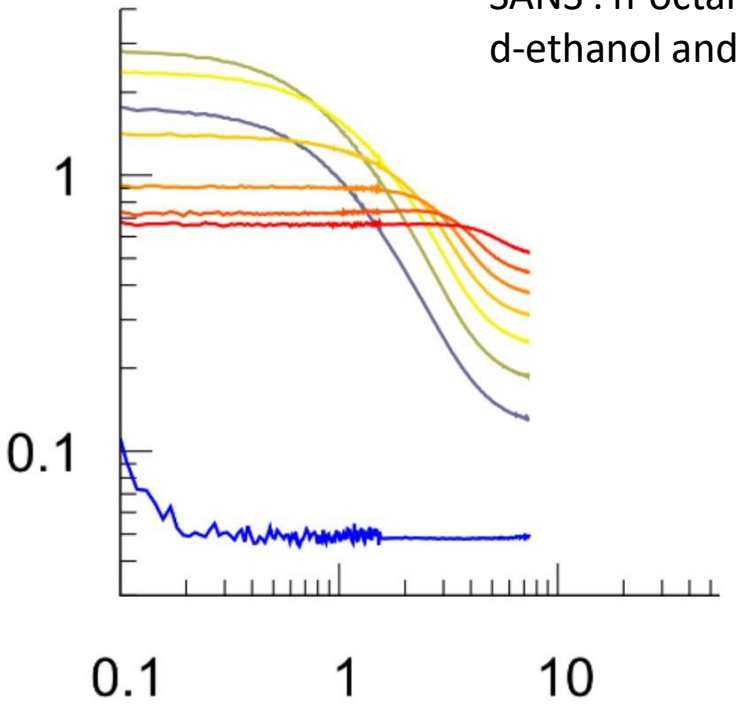


Water – ethanol – octanol phase diagram

1-8 horizontal line : ~40 wt.% ethanol



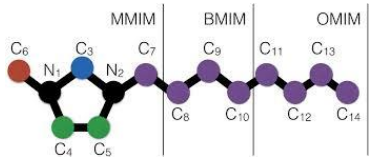
SANS : h-octanol in d-ethanol and D_2O



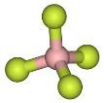
Schottle et al., J. Coll. Int. Sci. (2019)

Ionic liquids

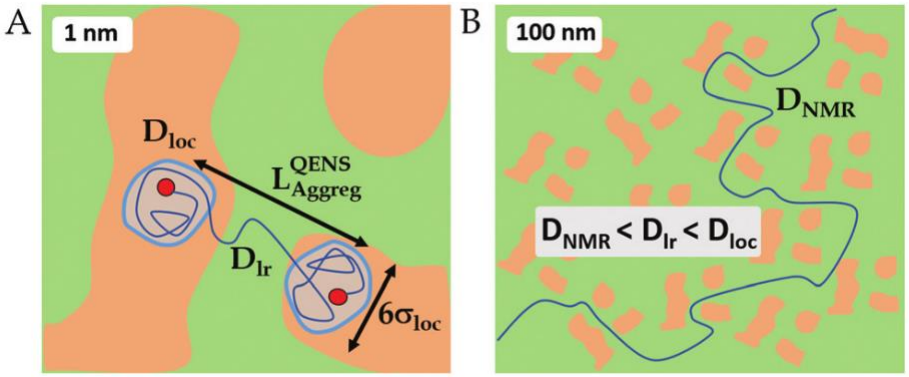
CMIM-, OMIM- BF_4



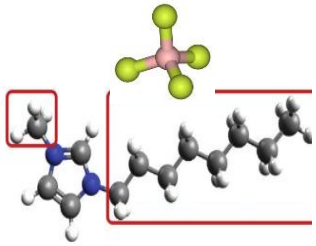
methyl imidazolium (MIM)

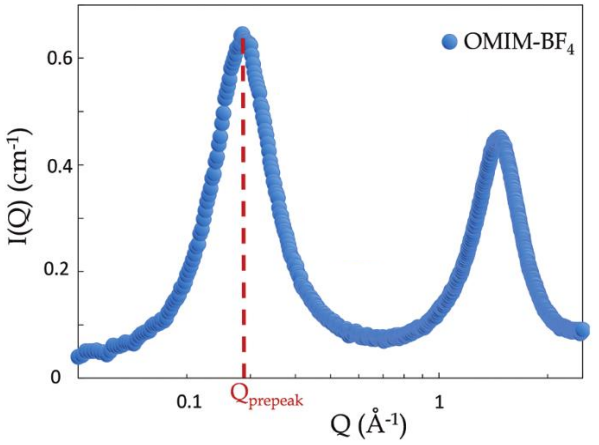


Tetrafluoroborate
BF_4



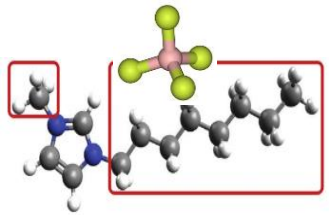
Dynamics depends
on the lengthscale



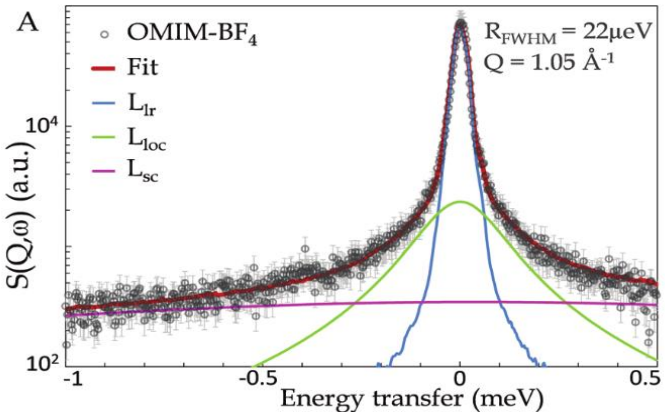


Ionic liquids: OMIM cation dynamics

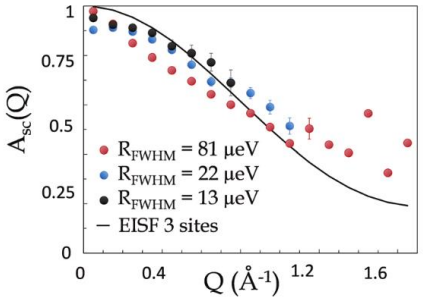
$$I(q,\omega) \sim I_1(q) L_{long\ range}(q,\omega) + I_2(q) L_{loc}(q,\omega) + I_3(q) L_{side\ chains}(q,\omega)$$



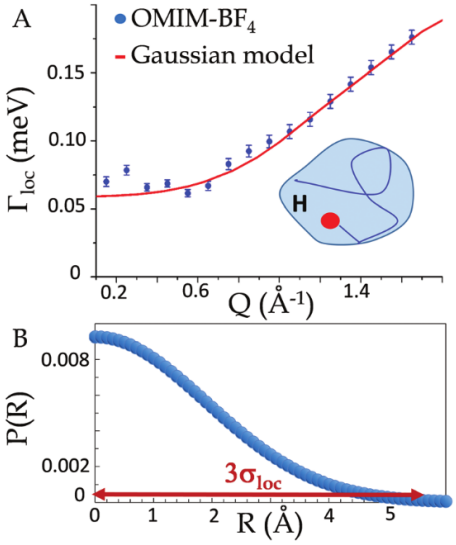
2 protons populations : from side chains and from imidazolium cations



EISF from side chains motions (jump between 3 sites, radius=1.5Å)



Confined diffusion (simplified Volino's model)



Berrod et al., Nanoscale (2017)

HWHM of the QENS (L_{loc}) signal -> D_{loc}=2.9 10^{-5} cm^2/s

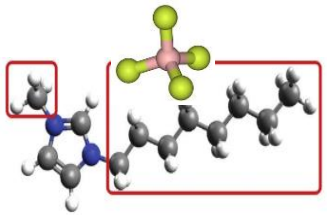
FT of the QENS intensity:

$$F(q) \sim e^{(-\sigma^2 q^2)}$$

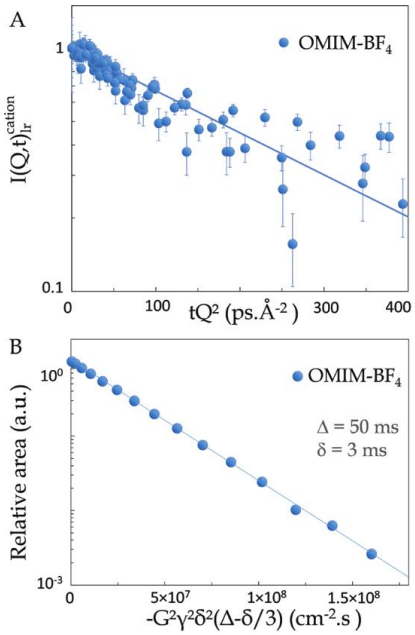
Radius of confinement σ~11Å, in good agreement with prepeak position

Ionic liquids: OMIM cation dynamics

$$I(q,\omega) \sim I_1(q) L_{long\ range}(q,\omega) + I_2(q) L_{loc}(q,\omega) + I_3(q) L_{side\ chains}(q,\omega)$$



2 protons populations: from side chains and from imidazolium cations



Long range diffusion (NSE) :
D_{loc}=4.0 10^{-7} cm^2/s

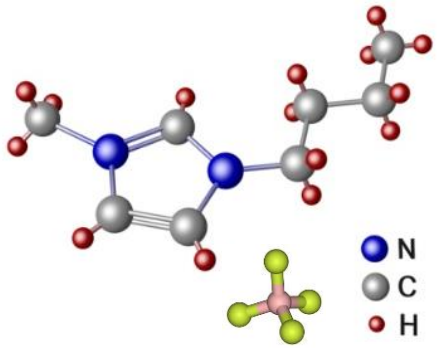
Long range diffusion (NMR :
D_{loc}=2.8 10^{-8} cm^2/s

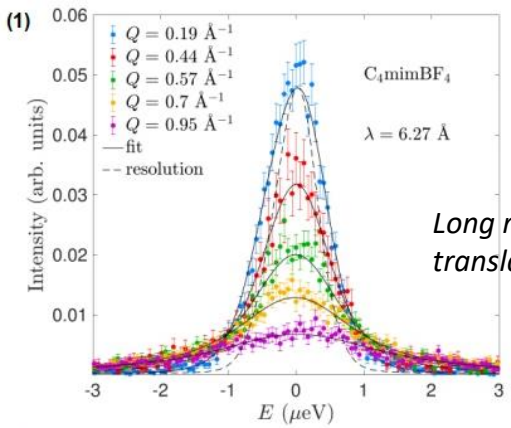
Diffusion coefficient depends on the scale at which it is probed when a supramolecular organization is present.

Ionic liquids: probing the BF_4 anion dynamics

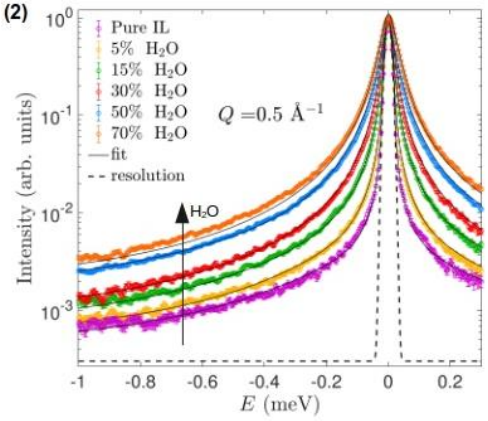
$$S(q,\omega) = S(q,\omega)_{BMIM} + p_f S(q,\omega)_{free\ water} + p_b S(q,\omega)_{bound\ water}$$

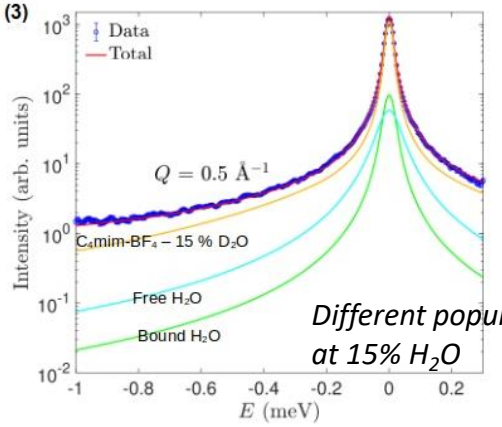
- Dynamics at different water contents, using H_2O and D_2O with adequate subtraction enables to extract the cation dynamics.
- Then , the water is split into two populations : one straightly bound to the anion, the other as 'free' water.
- The 'bound' water therefore gives a characterisation of the anion, and further on the type of electrolyte of the whole solution (weak or strong).





Long range translation



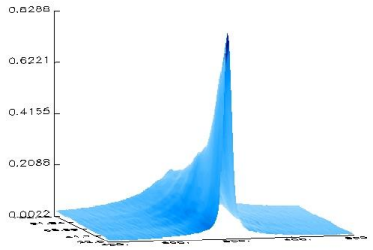


Different populations at 15% H_2O

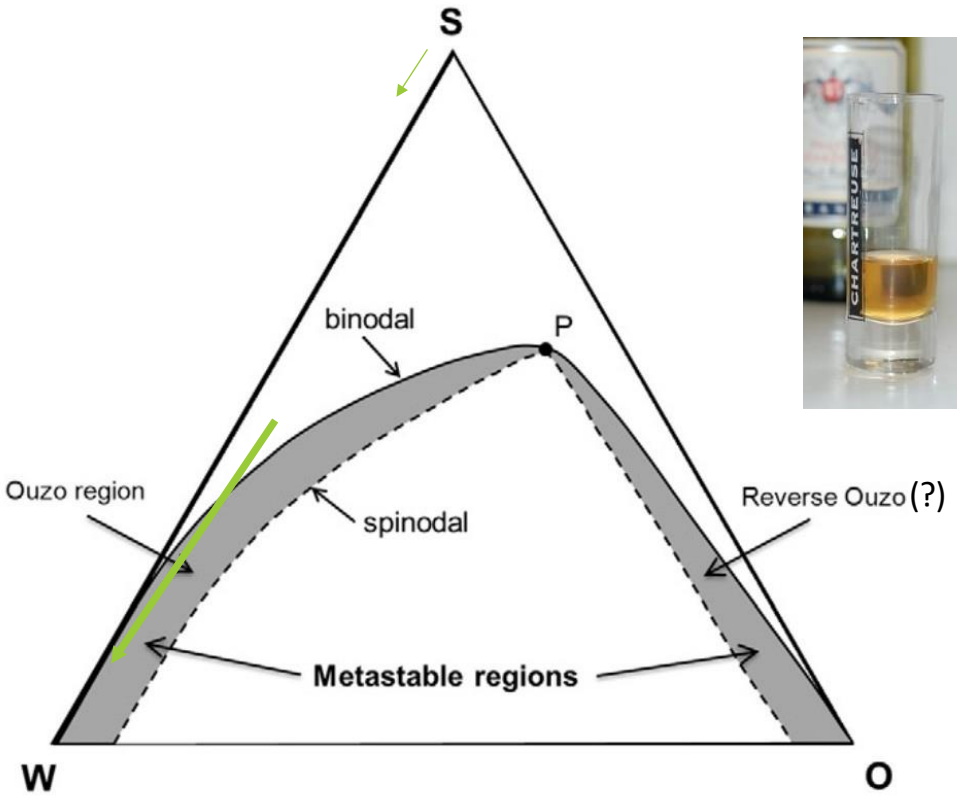
Ruiz Martin et al., J. Chem. Phys. (2022)

Outline

- dynamical structure factor S(q,ω) and diffusive dynamics
- basic QENS models
- data analysis
- **examples:**
  - molecular dynamics in physical gels
  - *fixed window* scan: MSD in proteins
  - coherent and incoherent dynamics in bulk water
  - **molecular dynamics in nano-organized ternary mixtures**
  - dynamics in ionic liquids
  - dynamics of proteins in solution

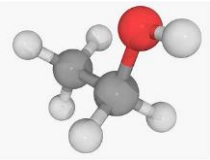


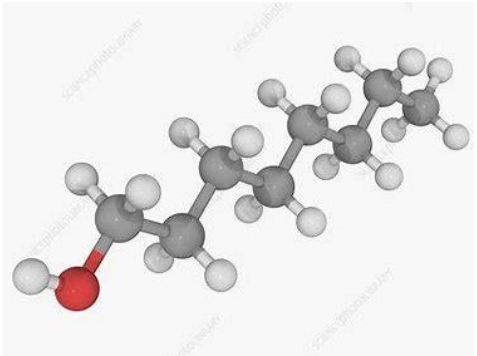
The Ouzo effect

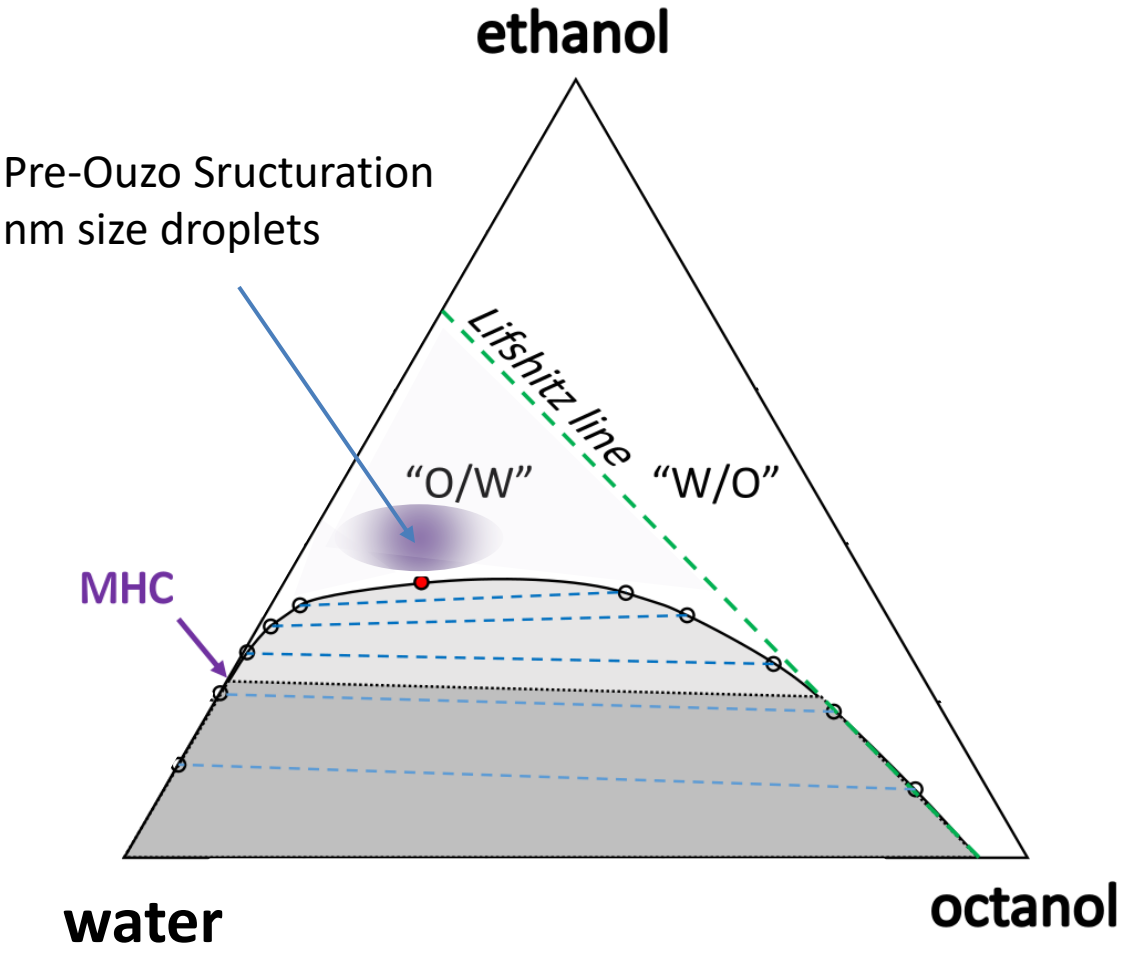


C. Solans et al. / Current Opinion in Colloid & Interface Science 22 (2016) 88–93

Water – ethanol – octanol phase diagram



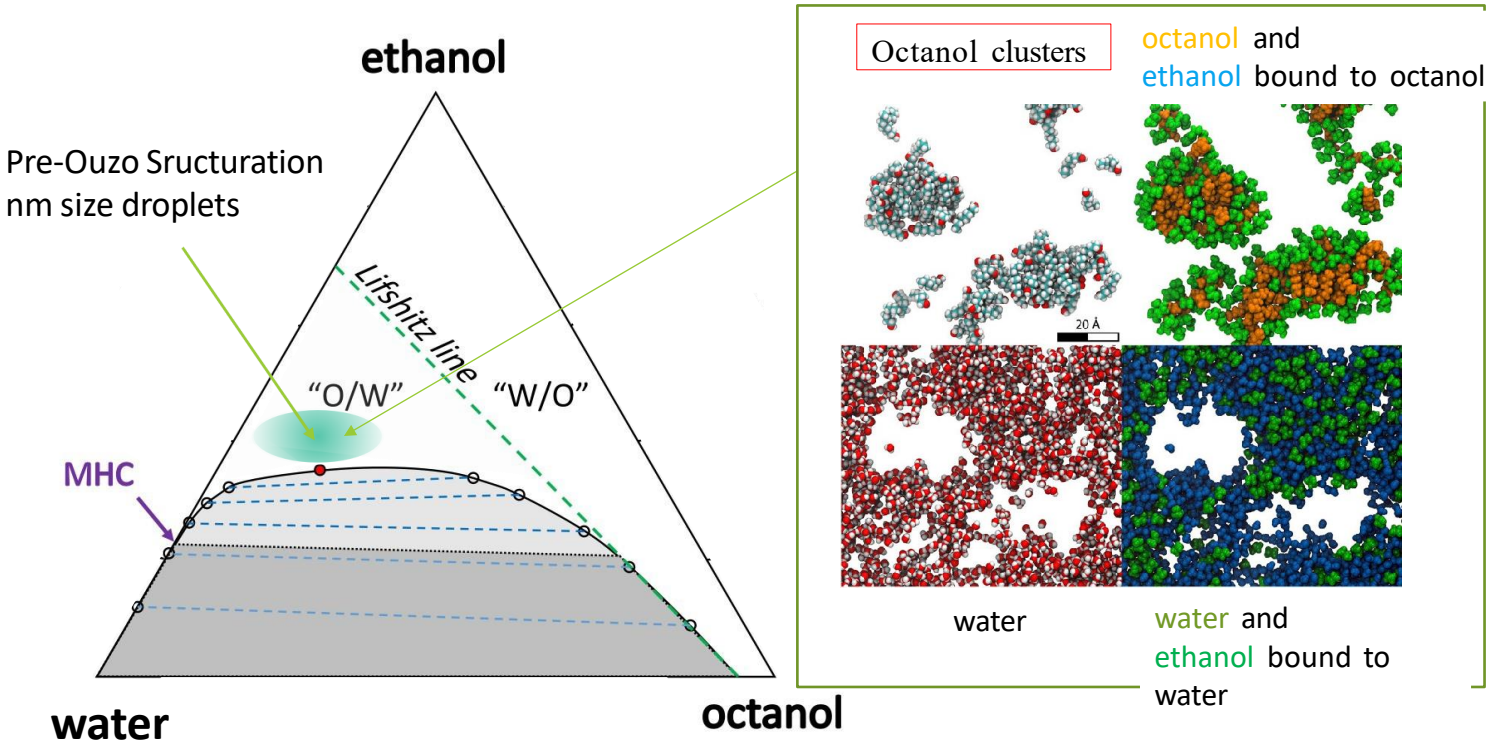




How is the molecular dynamics affected by the pre-Ouzo region ?

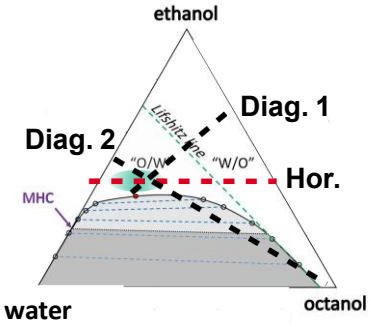
Prévost et al., Langmuir (2021)

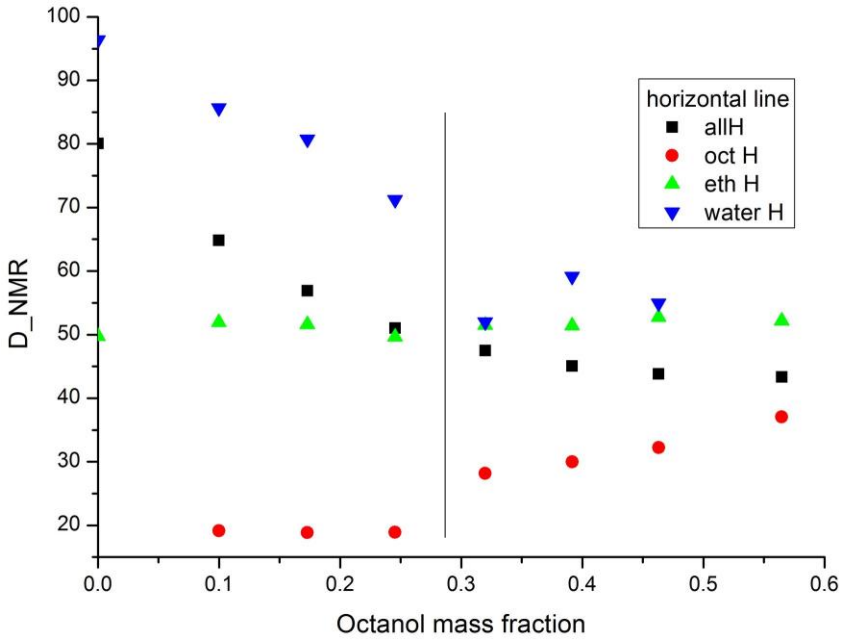
Water – ethanol – octanol phase diagram



Zemb et al., PNAS (2016)
Prévost et al., Langmuir (2021)

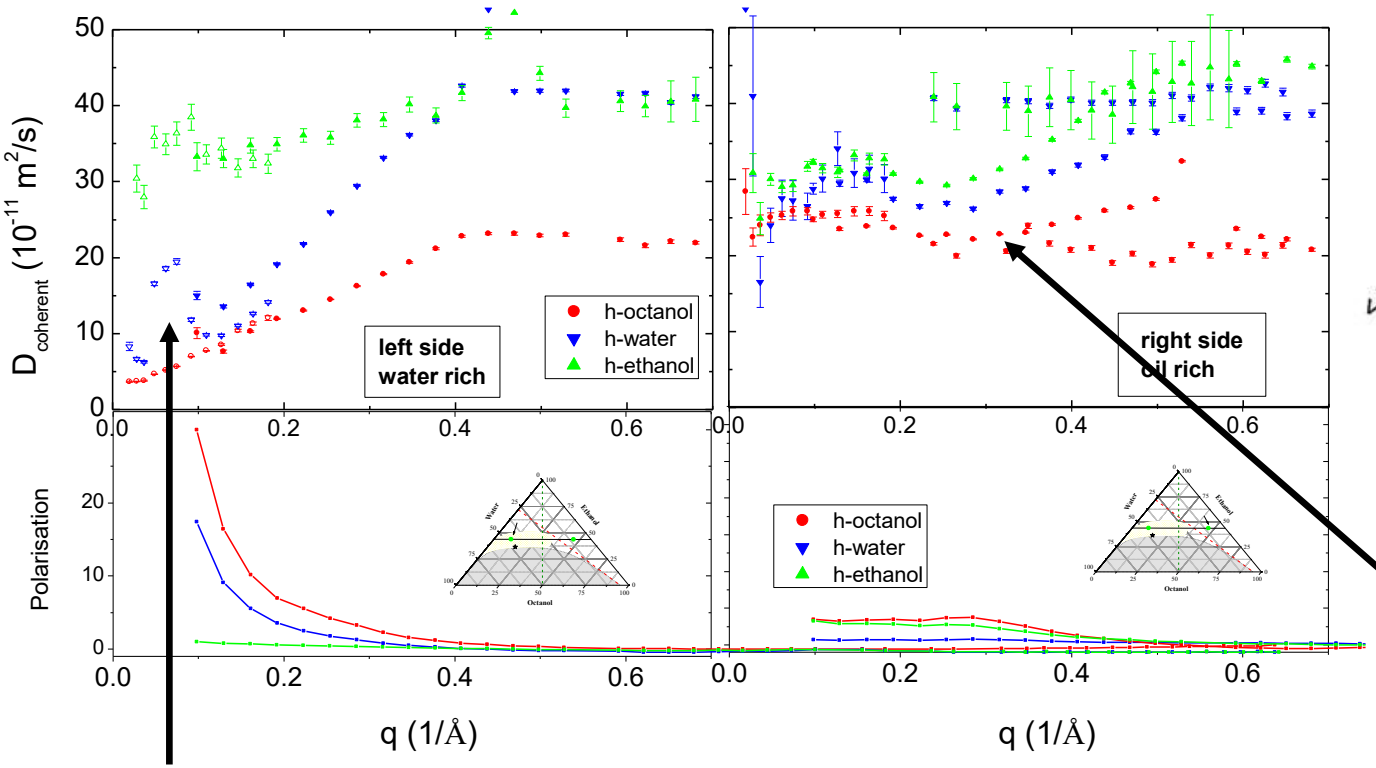
Dynamics in the ternary mixture across the phase diagram
Individual dynamics from NMR

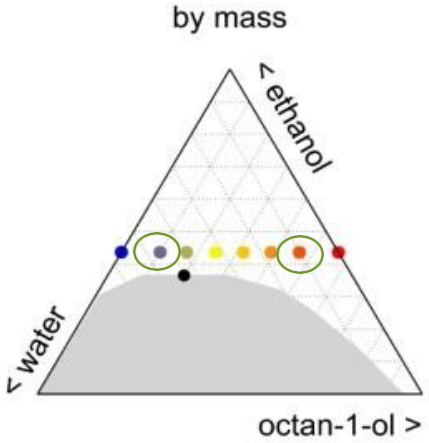




Dynamics in the ternary mixture across the phase diagram: collective effects

Collective dynamics : from homogeneous to nanostructured solution

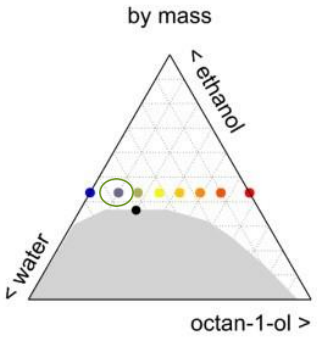




'pre-peak' organisation of alcohol mixture, i.e. De Gennes narrowing.

variation in D_c caused by the droplet organization, as observed in the structure factor

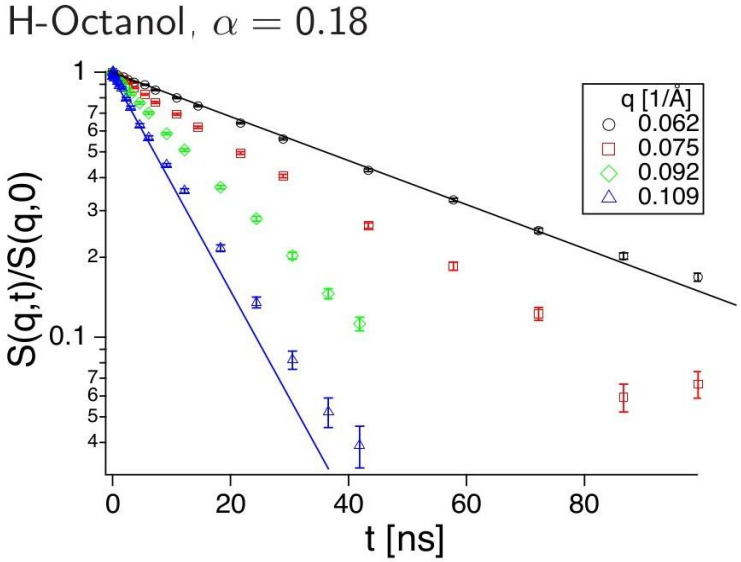
Dynamics in the ternary mixture across the phase diagram: collective effects



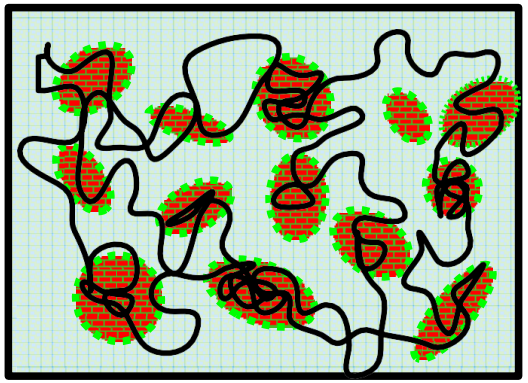
-structural measurements show Ornstein-Zerniche component > polydisperse aggregates

-signal from long lives aggregates : multi-exp. $\sum_i x_i e^{(-D_i q^2 t)}$

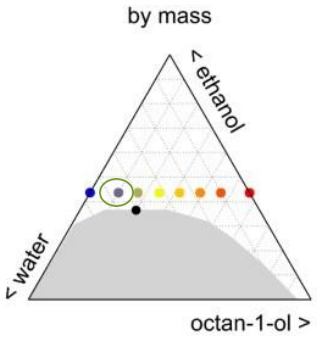
-signal from short-live time aggregates : single exp. $e^{\left(-\left(\sum_i x_i D_i q^2 t\right)\right)}$



Roosen-Runge et al., J. Chem. Phys (2016) 144:204109.



Dynamics in the ternary mixture across the phase diagram: collective effects

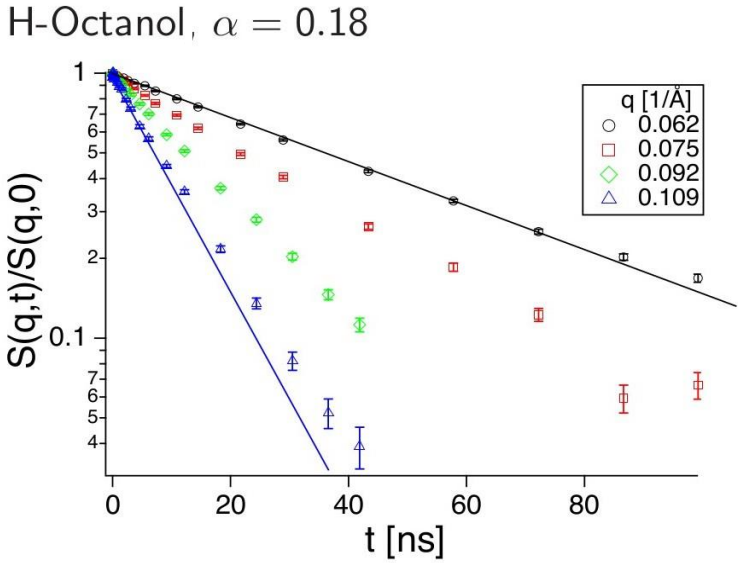


-structural measurements show Ornstein-Zerniche component > polydisperse aggregates

-signal from long lives aggregates : multi-exp. $\sum_i x_i \exp(-D_i q^2 t)$

-signal from short-live time aggregates : single exp. $\exp(-(\sum_i x_i D_i q^2)t)$

Roosen-Runge et al., J. Chem. Phys (2016) 144:204109.



-on a long lengthscale (small q), signal is exponential : we see « short life time aggregates ».

τ_I < τ~30 ns

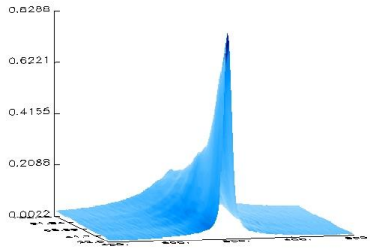
-on a short lengthscale (high q), signal is not exponential anymore, we see long life time aggregates.

τ_I > τ~10 ns

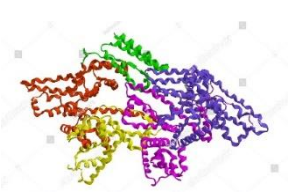
Life time of the aggregates ~ 20 ns

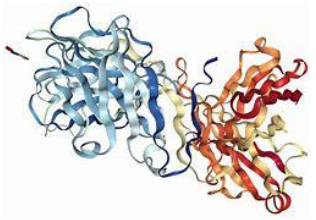
Outline

- dynamical structure factor S(q,ω) and diffusive dynamics
- basic QENS models
- data analysis
- **examples:**
  - molecular dynamics in physical gels
  - *fixed window* scan: MSD in proteins
  - coherent and incoherent dynamics in bulk water
  - molecular dynamics in nano-organized ternary mixtures
  - dynamics in ionic liquids
  - **dynamics of proteins in solution**



Protein dynamics

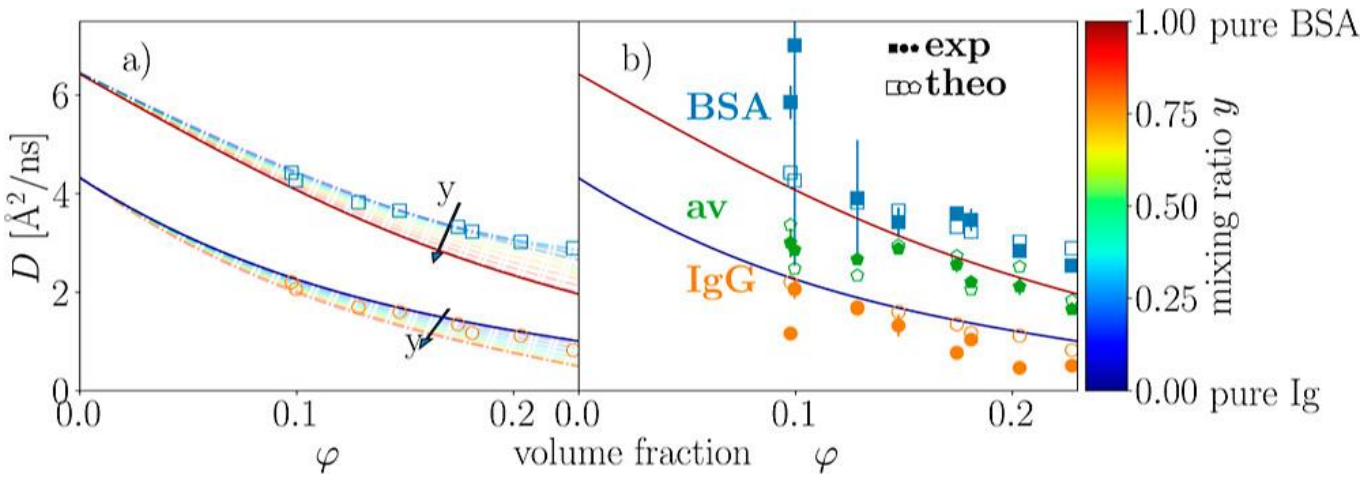




Proteins seen as ‘patchy’ colloids (because of charges at the surface)

Ex. Bovine Serum Albumin (BSA, diameter ~7 nm) in dilute conditions has D=3 Å^2/ns: over a timescale of 4 ns (ΔE= 1 µeV), the protein travels a fraction of its radius: we probe the hydrodynamic / short time regime.

How is modified the diffusion in crowding solutions ? And in bi-dispersed solution ? Mixture of BSA and IgG (~10 nm).



Beck et al., J. Phys. Chem. B (2022)

- Solid lines: pure protein solutions, hard-sphere behaviour.
- Right: symbols for fit of one averaged D or two different D (prefered)
- Left: HS calculation for bi-dispersed solution: smaller particles diffuse faster than expected in a monodisperse solution at the same φ, while larger diffuse more slowly.

Bibliography :

-G. L. Squires : Introduction to the theory of thermal neutron scattering Cambridge University Press, 2012

-Marc Bée , Quasielastic Neutron Scattering, Taylor & Francis, 1988

-SPECTROSCOPY IN BIOLOGY AND CHEMISTRY: NEUTRON, X-RAY LASER, Ed. Sow-Hsin Chen & Sidney Yip, Academic press, 1974.

-collection “SFN” :
http://www.sfn-asso.fr/ecoles-thematiques/

or

http://www.neutron-sciences.org/index.php?option=com_issues&task=proceedings&Itemid=282&lang=fr_FR.utf8%2C+fr_FR.UT

Thank you for your attention !