Diffusion studied by quasi-elastic neutron scattering and microscopic simulation: water in clays

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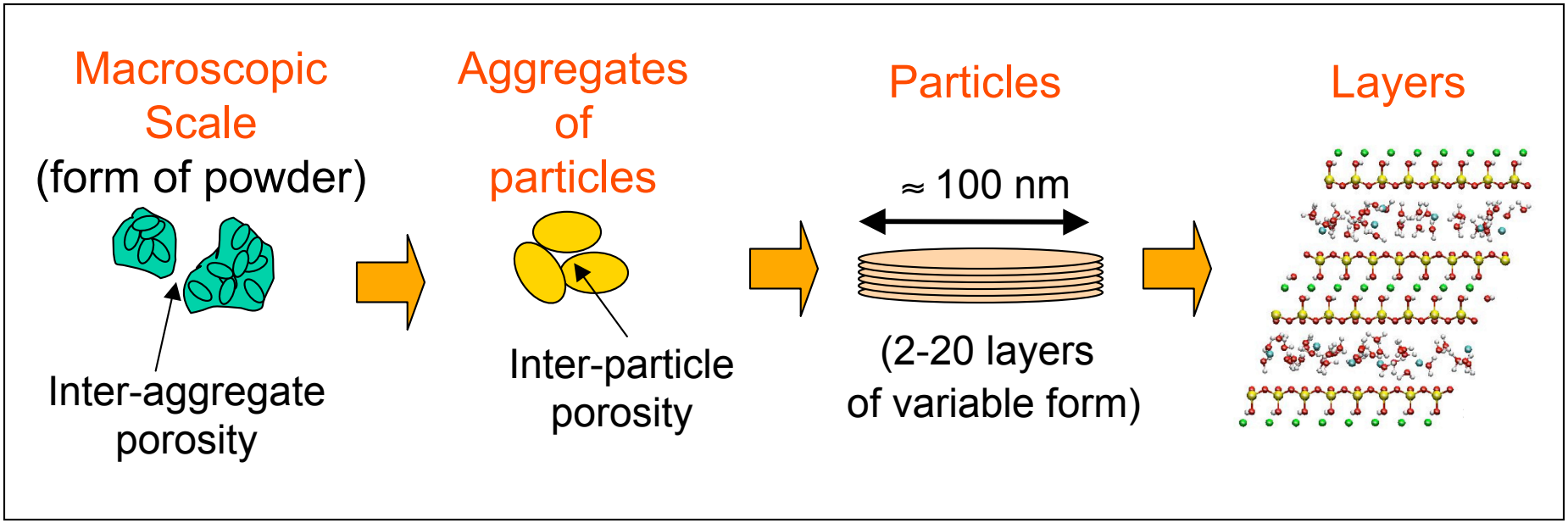
Clay system

Multiple porosity in clays

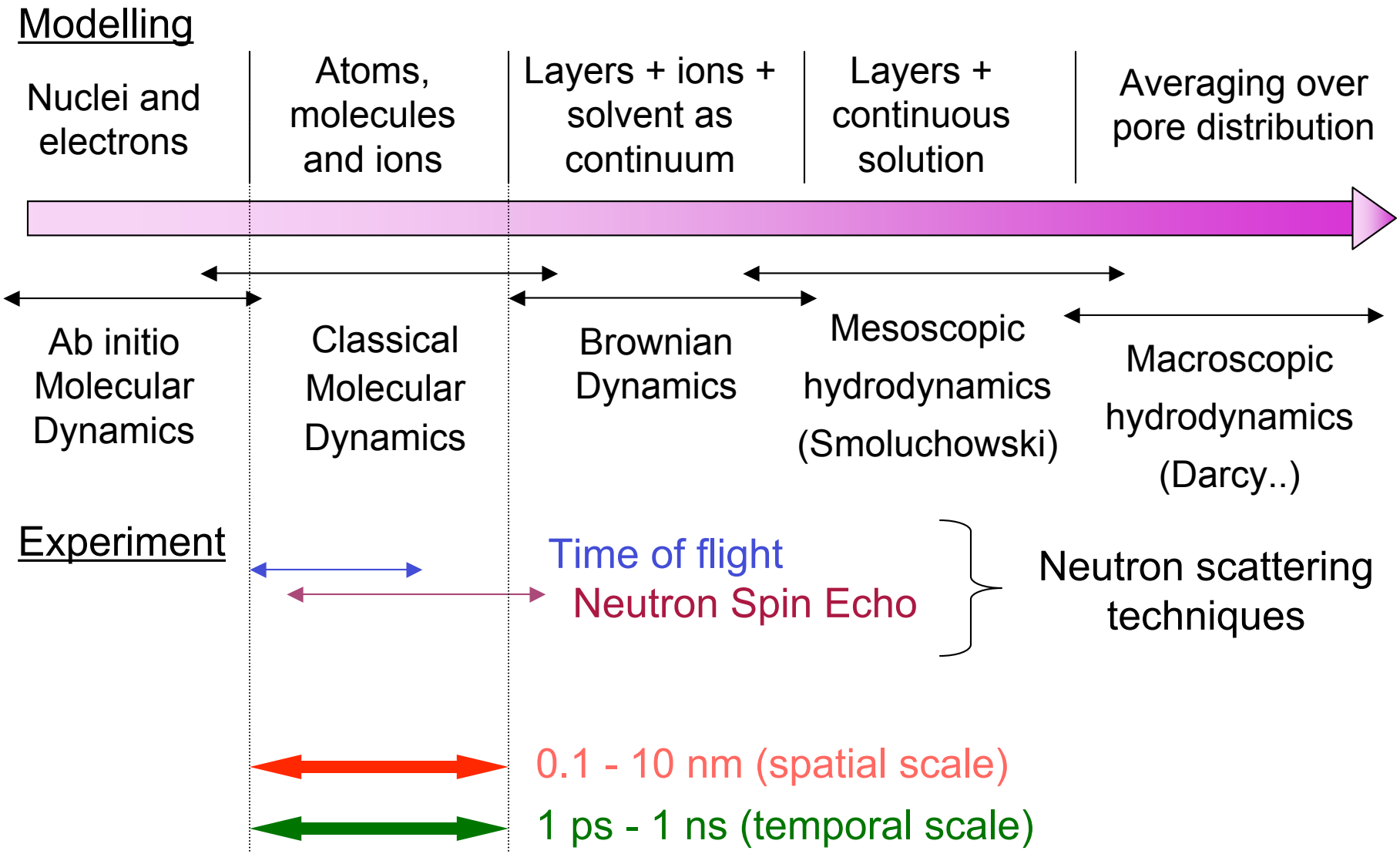
Mobile species - ions (Na^+, Ca^{2+}, Cl^-, Cs^+, I^- ...), water



Experimental techniques studying diffusion:

Tracer experiments, NMR, dielectric spectroscopy, neutron scattering

Simulation techniques



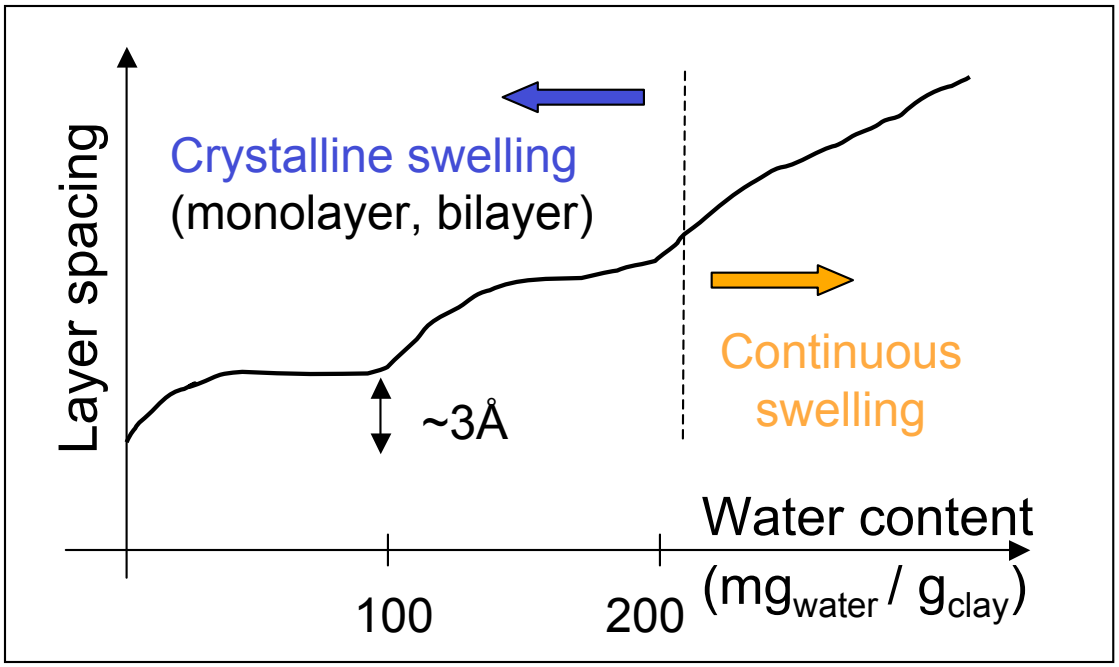
System and conditions of interest

CLAY : montmorillonite - naturally occuring clay, of abundance in the region of the French disposal site

IONS : Na^+ - natural ion
Cs^+ - potential radionuclide

ANDRA

HYDRATION STATE :
crystalline swelling region
Na^+ - mono- and bilayer
Cs^+ - monolayer
(bilayer does not exist)

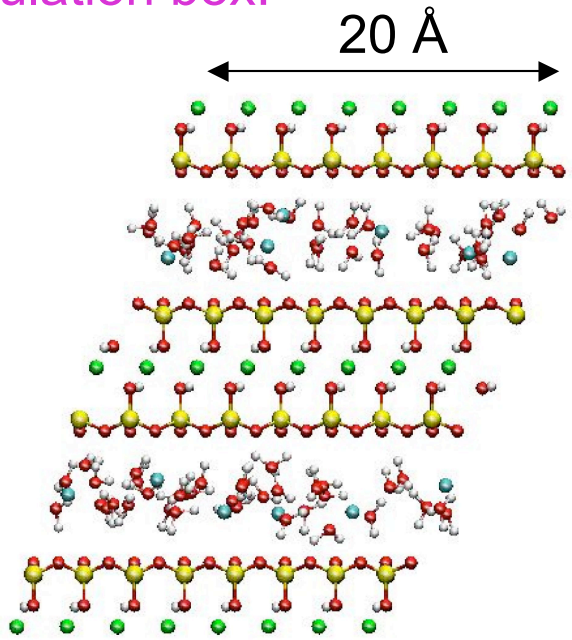


Construction of a model clay

ATOMIC DESCRIPTION of clay layers and interlayer species
(clay layers and water molecules taken as rigid)

Model clay unit cell: $[Si_8](Al_{3.25}Mg_{0.75})O_{20}(OH)_4Na_{0.75}$ (8 unit cells / clay layer)

Simulation box:



3D boundary conditions

Interlayer content:

- 6 counter-ions (Na^+ or Cs^+)
- 6 H_20 / cat and 12 H_2O / cat for mono- and bilayer systems respectively)

Marry , J Chem Phys 2002

Overall system size: 850 - 1050 atoms

Modelling - Classical microscopic simulations

Interaction two-body (pair) potentials *- Skipper, Smith*

Van der Waals and steric repulsion

$$V_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

Electrostatic Interactions

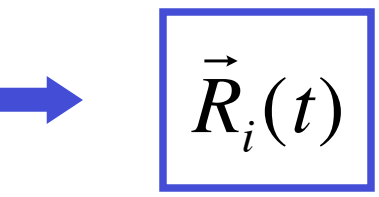
$$U_{ij} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

Each atom : charge (q), Lennard-Jones parameters (σ, ε)

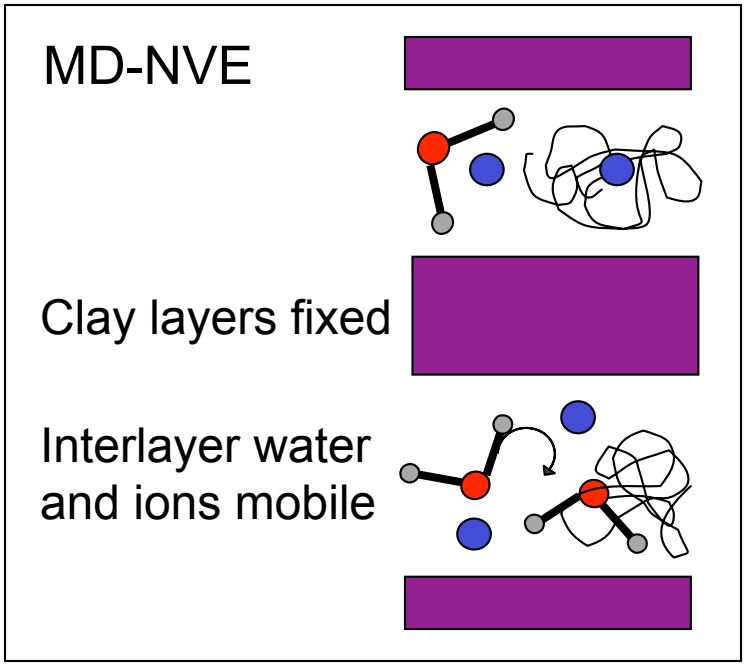
Monte Carlo: system equilibration
Molecular Dynamics (MD): dynamic properties (e.g. diffusive motion)

$$\vec{F}_i = -\vec{\nabla}\sum_j V_{ij}$$

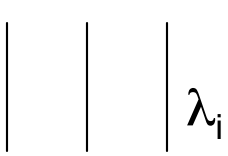
$$\vec{F}_i = m\vec{a}_i$$



$$\vec{R}_i(t)$$



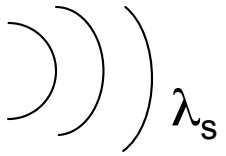
Neutron scattering - principles & techniques



Incident neutron

$E_i = h^2 / (2m\lambda_i^2)$

Atomic nucleus =
= scatterer



Scattered neutron

$E_s = h^2 / (2m\lambda_s^2)$

Information about <u>motion</u> of the scatterer is in $\Delta E\ (\Delta v, \Delta\lambda)$

1) Time-of-flight (TOF)

- ΔE - "time-of-flight" over a known distance
- measuring $S(Q,\omega)$, timescale

1-70/100 ps (λ = 9 Å)

- resolution not eliminated easily ("de-convolution" necessary)
- fast data acquisition (multiple Qs simultaneously)

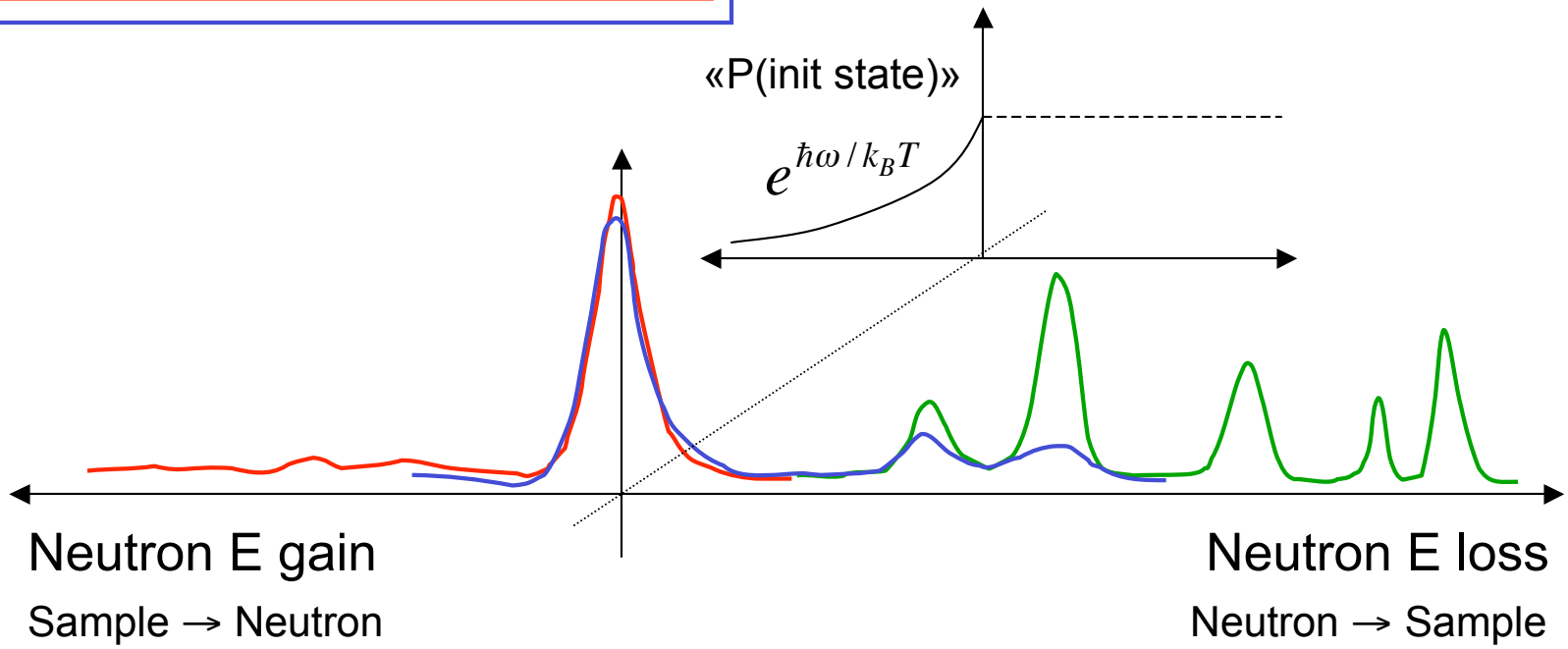
2) Neutron Spin Echo (NSE + NRSE)

- ΔE - change of neutron spin orientation
- measuring $S(Q,t)$, timescale
1-1000 ps (λ = 5 Å)
- resolution eliminated easily (division)
- slow data acquisition (weak incoherent signal, single Q detector)

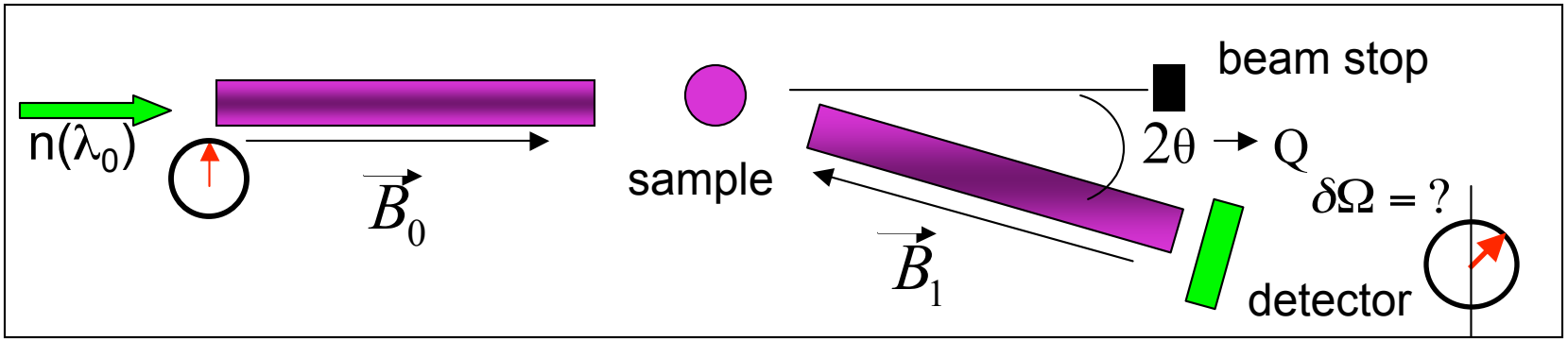
Neutron sources - complementarity

Small energy transfers (QENS): Both pulsed (IPNS) and continuous (LLB) neutron sources

Large energy transfers (INS): epithermal neutrons at pulsed neutron sources



Neutron Spin Echo - the technique



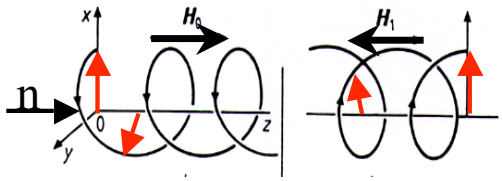
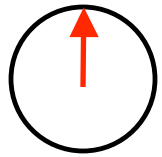


figure - M. Bée

$$\omega = |\gamma| B_o$$

ELASTIC process

$$\delta\lambda = 0 \rightarrow \delta\Omega = 0 \rightarrow P = 1$$

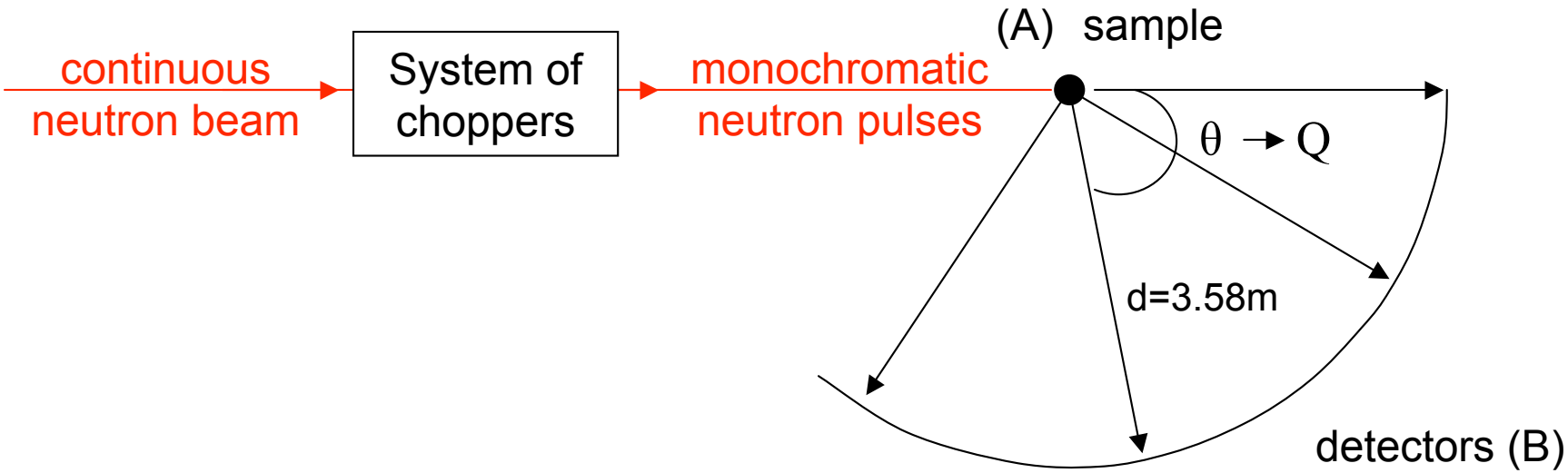


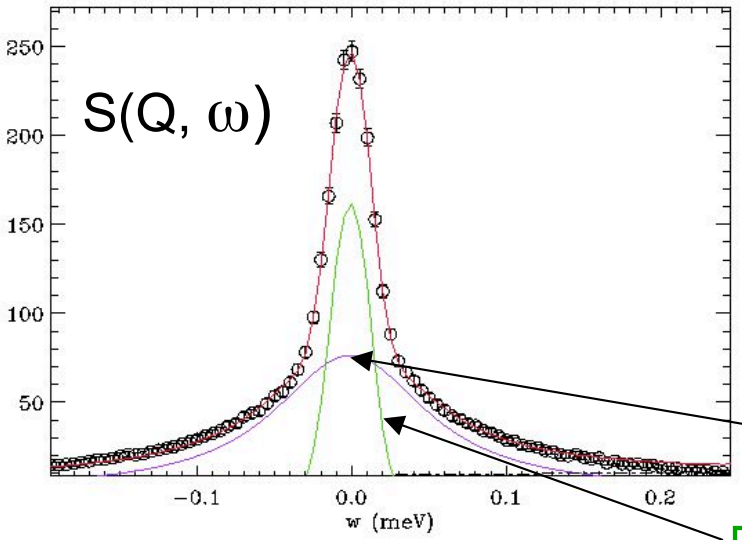
QUASIELASTIC process

$$\delta\lambda \neq 0 \rightarrow \delta\Omega \neq 0 \rightarrow P < 1$$

$$\langle \cos(\delta\Omega) \rangle = \frac{\int_{-\infty}^{+\infty} \cos(t_{NSE}\omega) S(Q,\omega) d\omega}{\int_{-\infty}^{+\infty} S(Q,\omega) d\omega} = \frac{I(Q,t_{NSE})}{I(Q,0)} = P(Q,t_{NSE})$$

Time of flight - the experiment (direct geometry)





1) Elastic signal

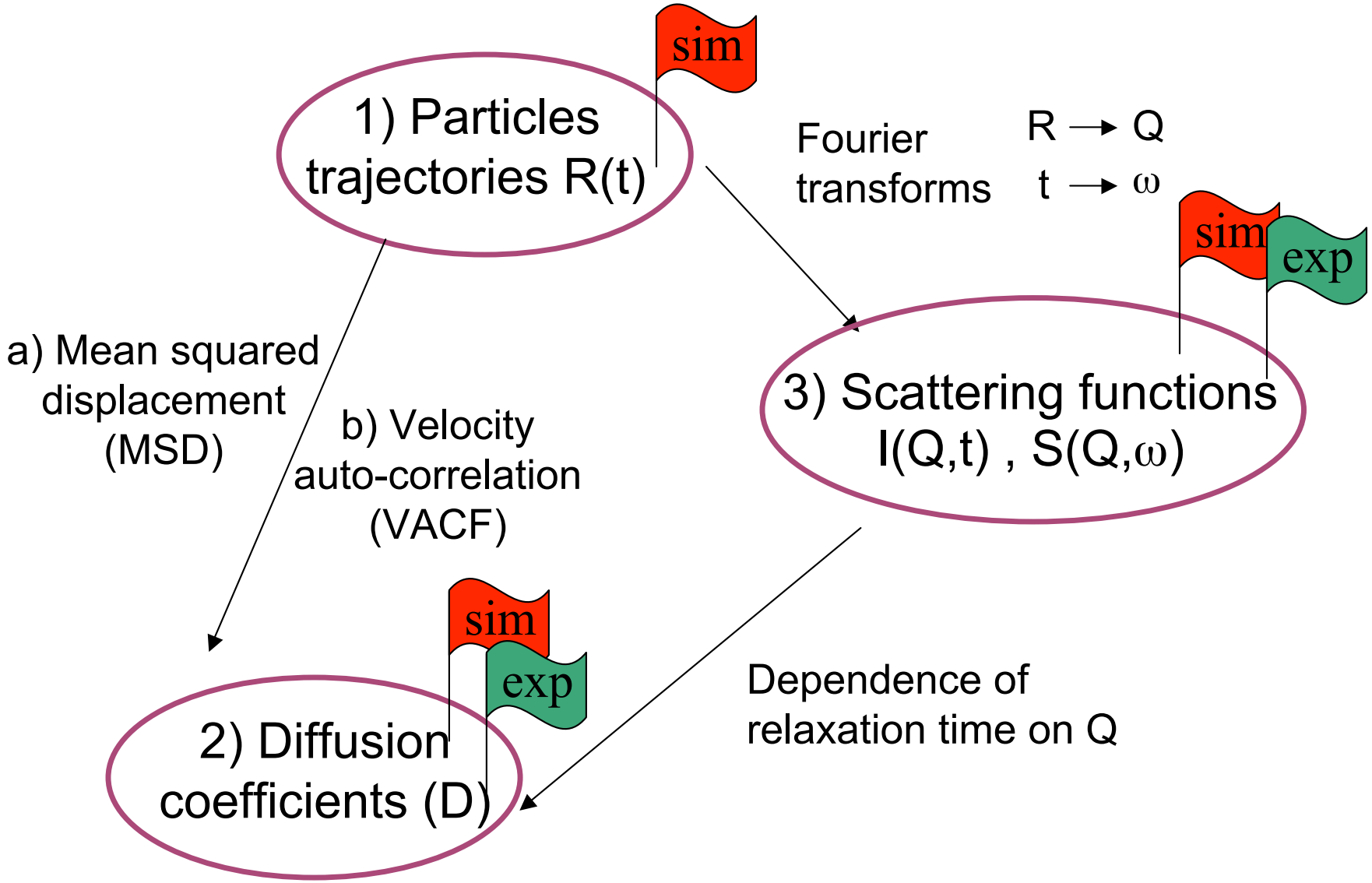
Vanadium sample, resolution - R(Q, ω)

2) Quasi-elastic signal of sample

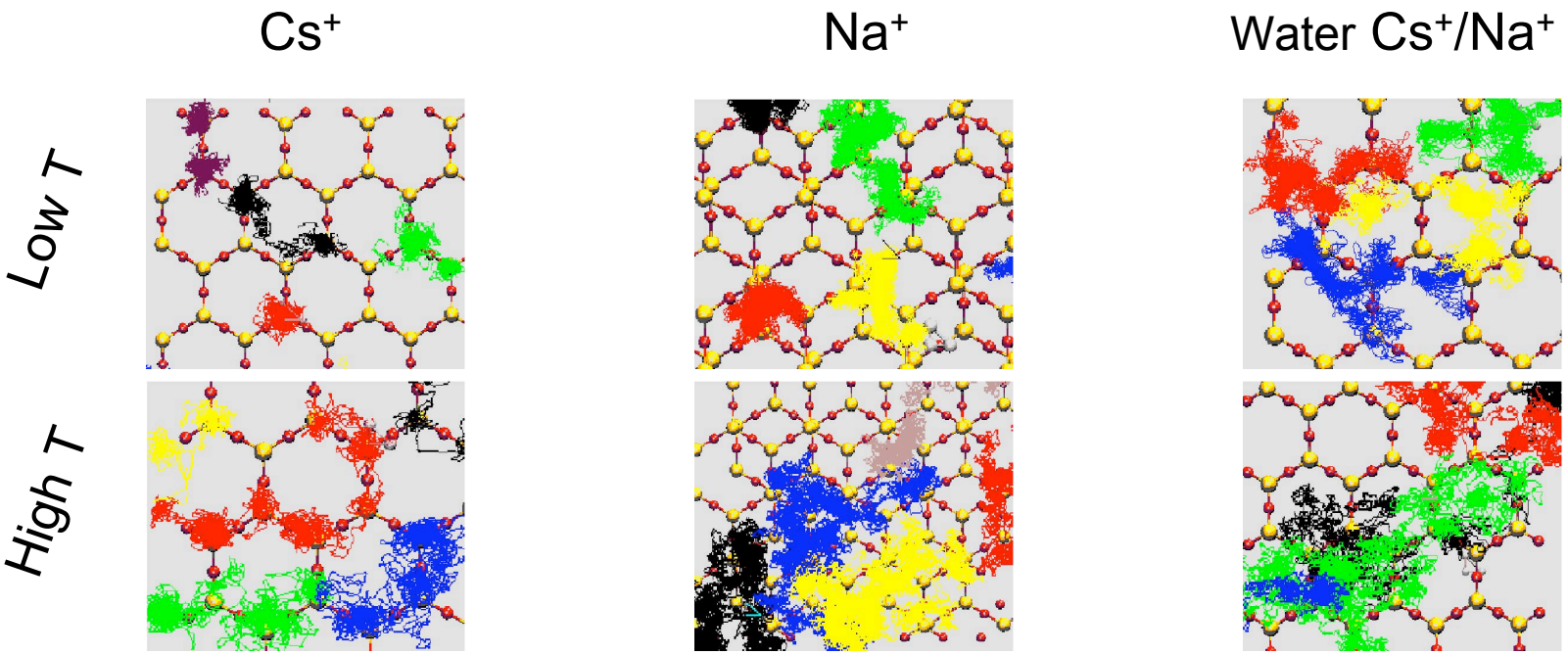
e.g. Lorentzian shape : $\dfrac{(1/\tau)}{(1/\tau)^2 + \omega^2}$

$$S(Q,\omega) = A(Q)R(Q,\omega) + [1 - A(Q)][R(Q,\omega) \otimes \frac{(1/\tau)}{(1/\tau)^2 + \omega^2}]$$

Dynamic information: simulation & experiment



Particle trajectories (effect of temperature)

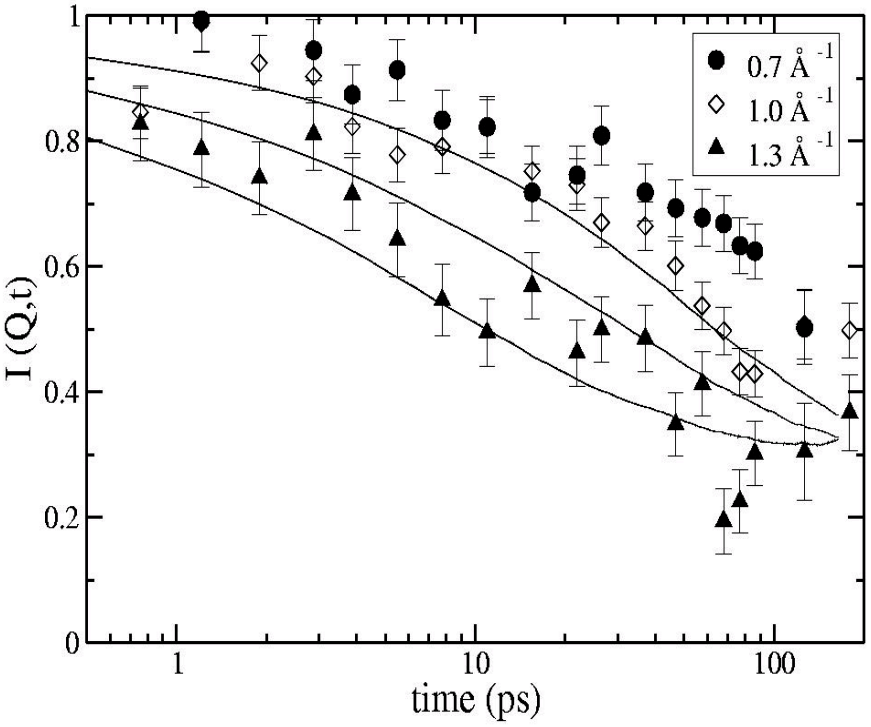


Projections in XY plane

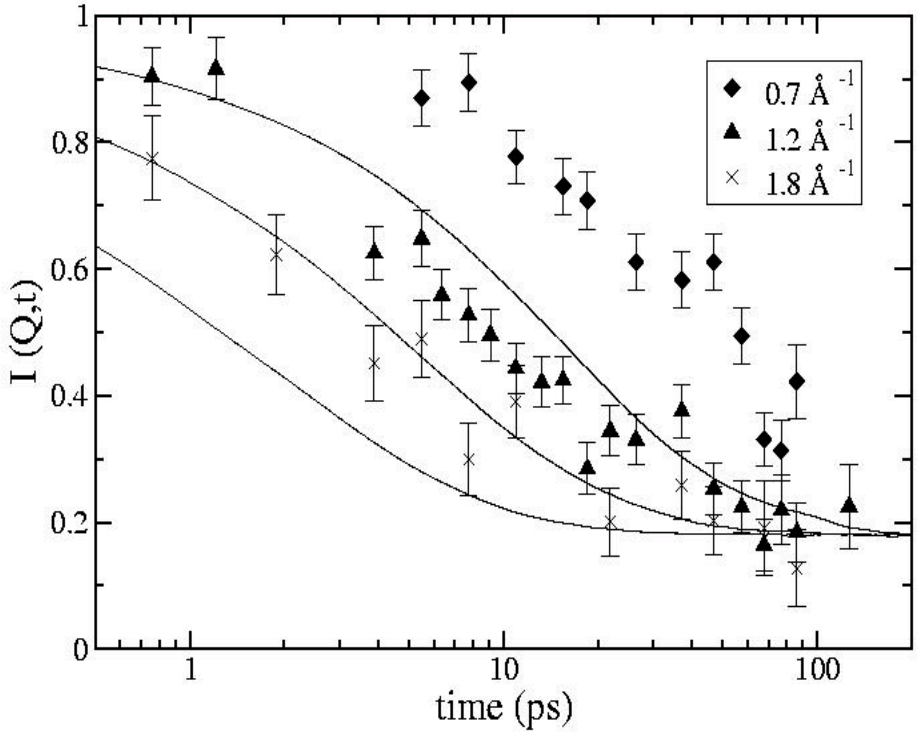
Malikova et al, 2004 Mol. Phys.

Simulation, NSE data in the (Q,t) domain

Na monolayer



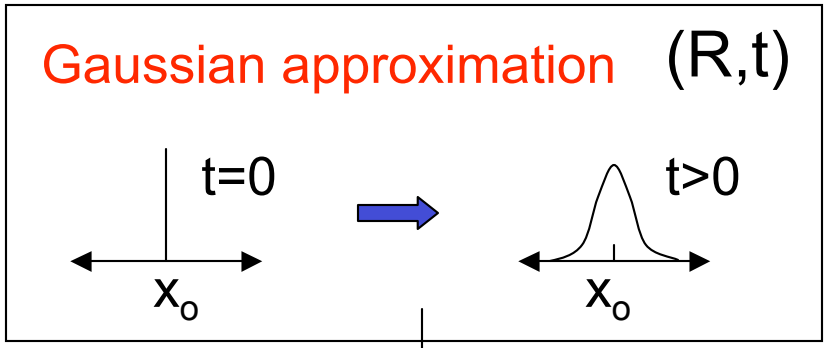
Na bilayer



Experimental and simulated water content and distribution:

1) Mixture of hydration states (interstratification) ? *(Cases, Bérend, Ferrage)*
2) Variation of water content for a given spacing ?
3) Water in mesoscopic (macroscopic) porosity ?

Data interpretation - model of atomic motion



$R \rightarrow Q$

$$I(Q,t) \propto e^{-DQ^2 t}$$

Exponential form

$t \rightarrow \omega$

$$S(Q,\omega) \propto \frac{DQ^2}{(DQ^2)^2 + \omega^2}$$

Lorentzian form

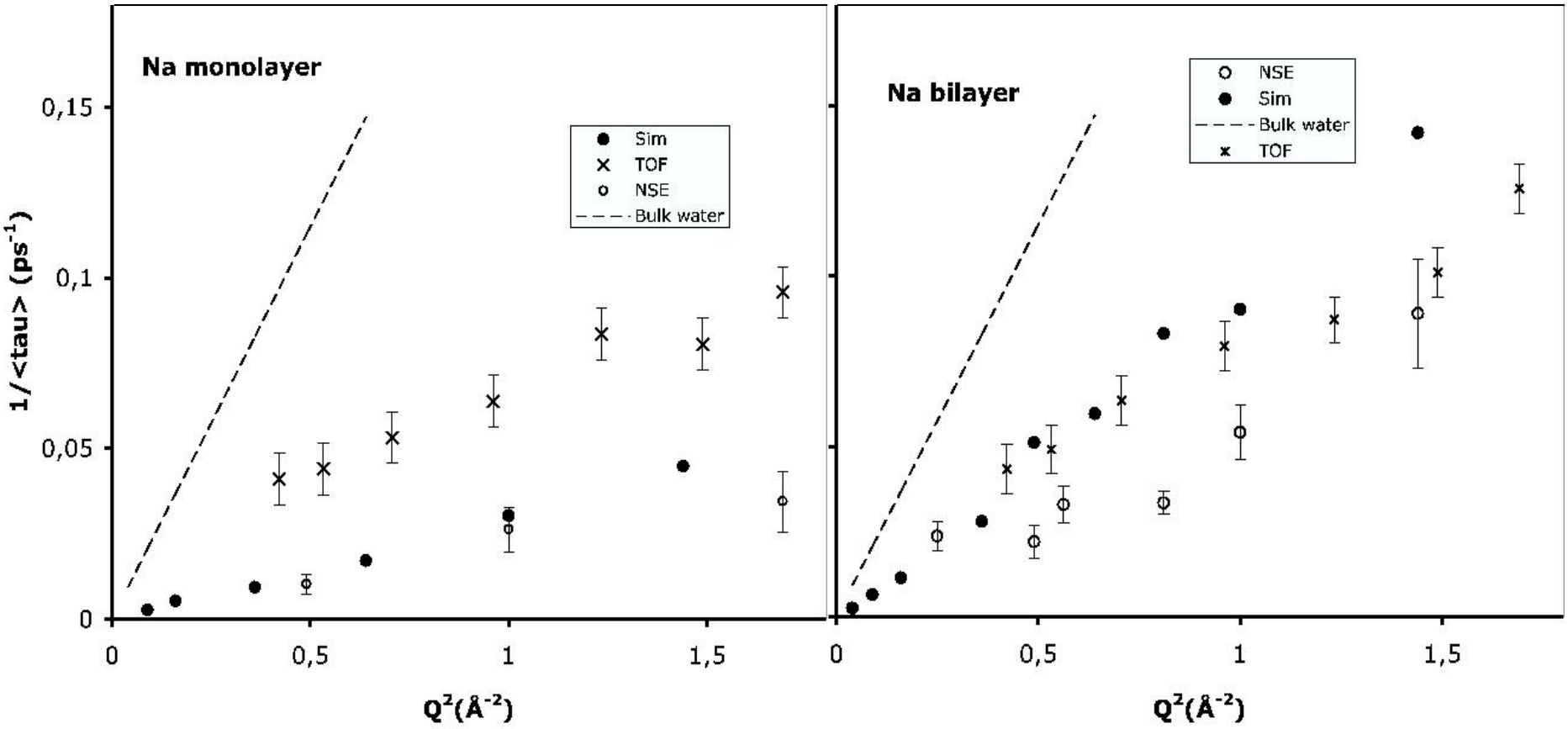
Isotropic translational motion

In reality…
Here in both simulation and experiment

$$e^{-(t/\tau_{relax})^{\beta}}$$

$$\beta < 1 \Rightarrow \langle \tau \rangle = \frac{\tau}{\beta} \Gamma\left(\frac{1}{\beta}\right)$$

NSE, TOF, simulation - relaxation times



Limitations: Non-exponential (non-Lorentzian) behaviour seen

- distribution of relaxation times
- breakdown of the isotropic diffusion model
  (present data cannot differentiate powder averaged 2D and 3D diffusion)
- translational-rotational coupling

NSE, TOF, simulation - diffusion coefficients

$$1/\langle\tau\rangle = DQ^2$$

gradient of $1/\langle\tau\rangle$ versus Q^2 in the limit of $Q^2 \rightarrow 0$: *diffusion coefficient*

$D_{bulk\ water}$ = $23 \times 10^{-10}\ m^2s^{-1}$

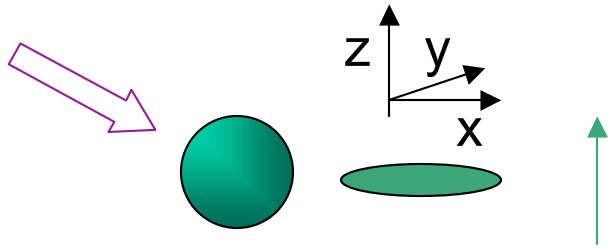
D_{water} ($\times 10^{-10}\ m^2s^{-1}$), T=298 K	Simulation (MSD)	NSE	TOF
Na^+, monolayer	2.5 (3.8)	2.5	8.0
Cs^+, monolayer	1.5 (2.8)	1.5	11.0
Na^+, bilayer	10.0 (8.1)	5.0	10.0

- Monolayers systems: Sim ↔ NSE - very good agreement
- Monolayer systems: Sim, NSE ↔ TOF - issue of TOF resolution
- Bilayer systems: agreement of all three techniques reasonable

Confinement and Elastic Incoherent Structure Factor

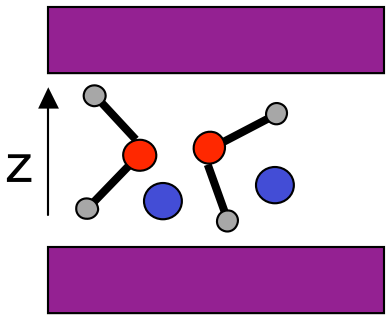
$$EISF(Q) = lim_{t\to\infty} I(Q,t)$$

$$EISF(Q) = \frac{1}{N_H}\sum_{\forall H}\overline{\left\langle \left|\exp\left[-i\vec{Q}\bullet\vec{R}_H\right]\right|^2\right\rangle}^{Q}$$

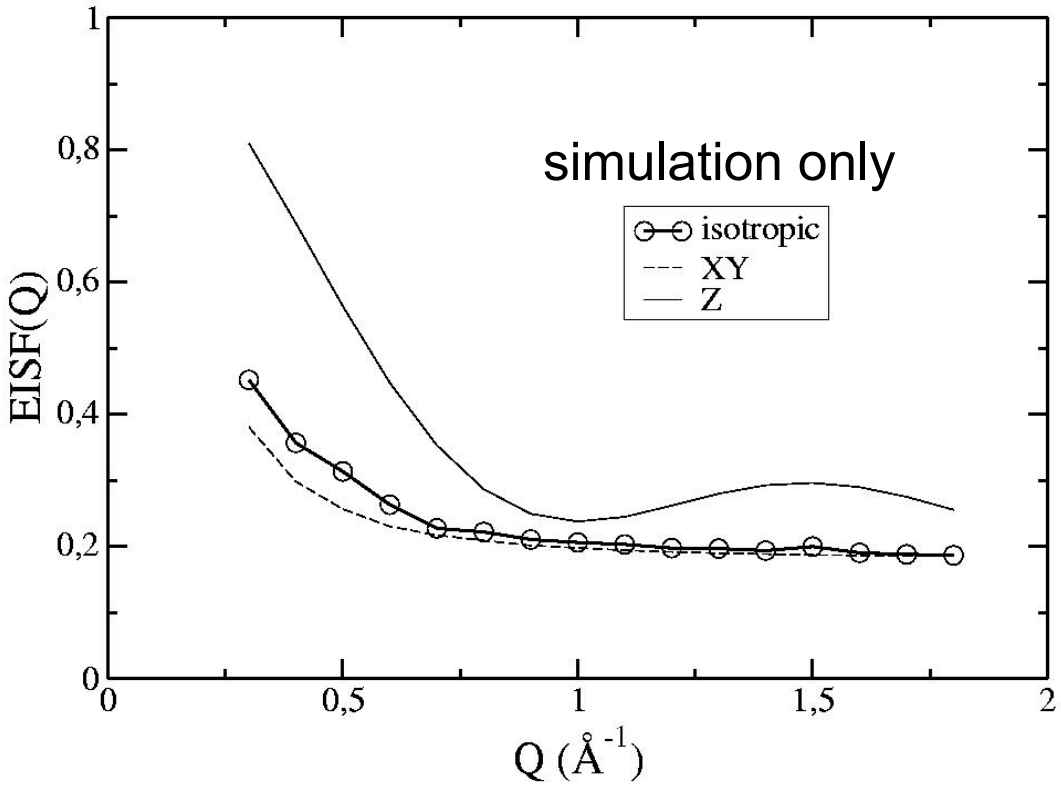


$$EISF(Q)_{NSE} = \lim_{t\ large} I(Q,t)_{NSE}$$

$$EISF(Q) = \frac{I_{el}}{I_{el} + I_{qel}}$$



Na bilayer - anisotropic analysis

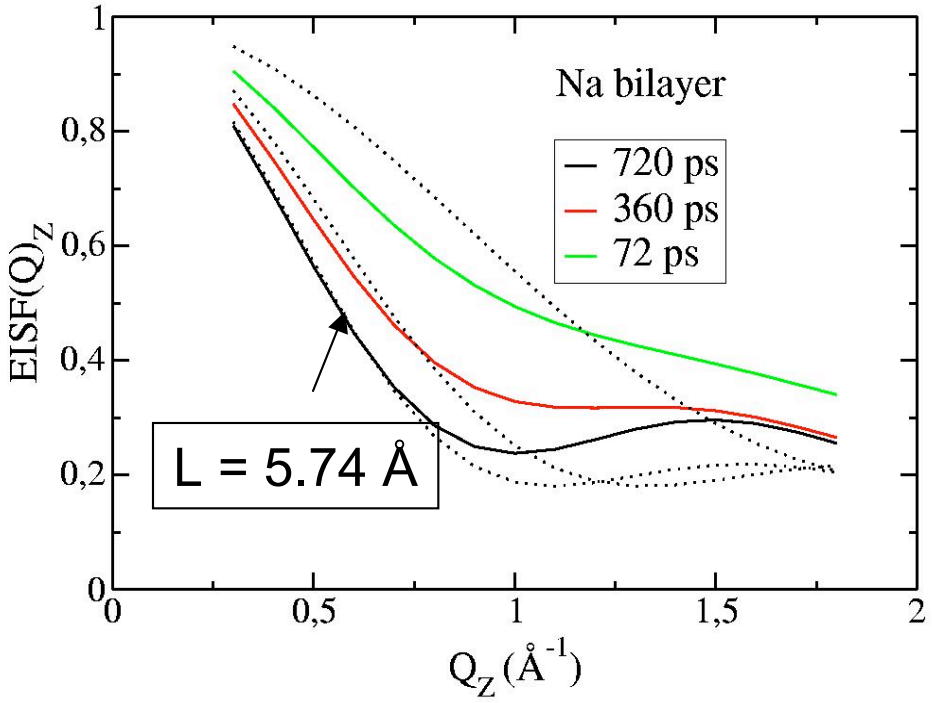


Confinement and EISF(Q)

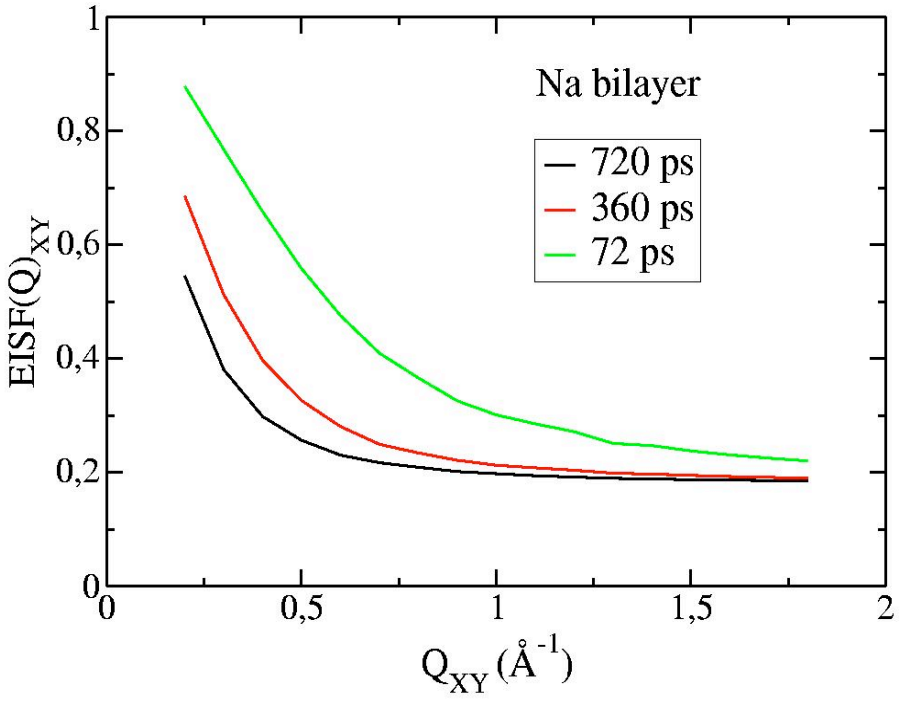
Confinement between two planes, separation L *Hall & Ross 1978,1981*

Analytical form of EISF: $$EISF(Q_z L) = \frac{2}{(Q_z L)^2}(1 - \cos(Q_z L))$$

Along Z: Spatial confinement



In XY plane: Temporal confinement



In experiment (isotropic analysis) : both forms combined !

Conclusion

- Non-exponential (non-Lorentzian) behaviour, experiment and simulation, (range of relaxation times, breakdown of the isotropic diffusion model etc.)

- Simulation and NSE in (Q,t) - monolayer: very good agreement, bilayer: τ differ by up to a factor of 3 (real / simulated water contents)

- NSE and TOF - underestimation of relaxation times by TOF in monolayers (resolution), agreement better for bilayer

- Diffusion coefficients: water dynamics slowed down by a factor of up to 10 and 2 / 3 with respect to bulk water (mono- and bilayer systems resp.)

  i.e. Rapid approach to bulk dynamics in bilayer

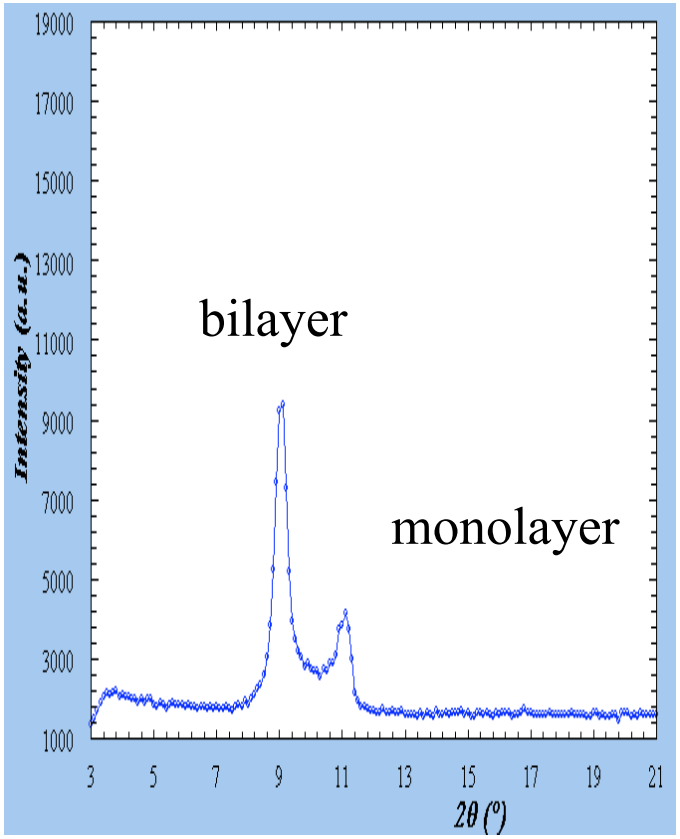
- Experimental data not suitable for analysis of anisotropy in H motion

Malikova et al, 2006 J. Phys. Chem. B

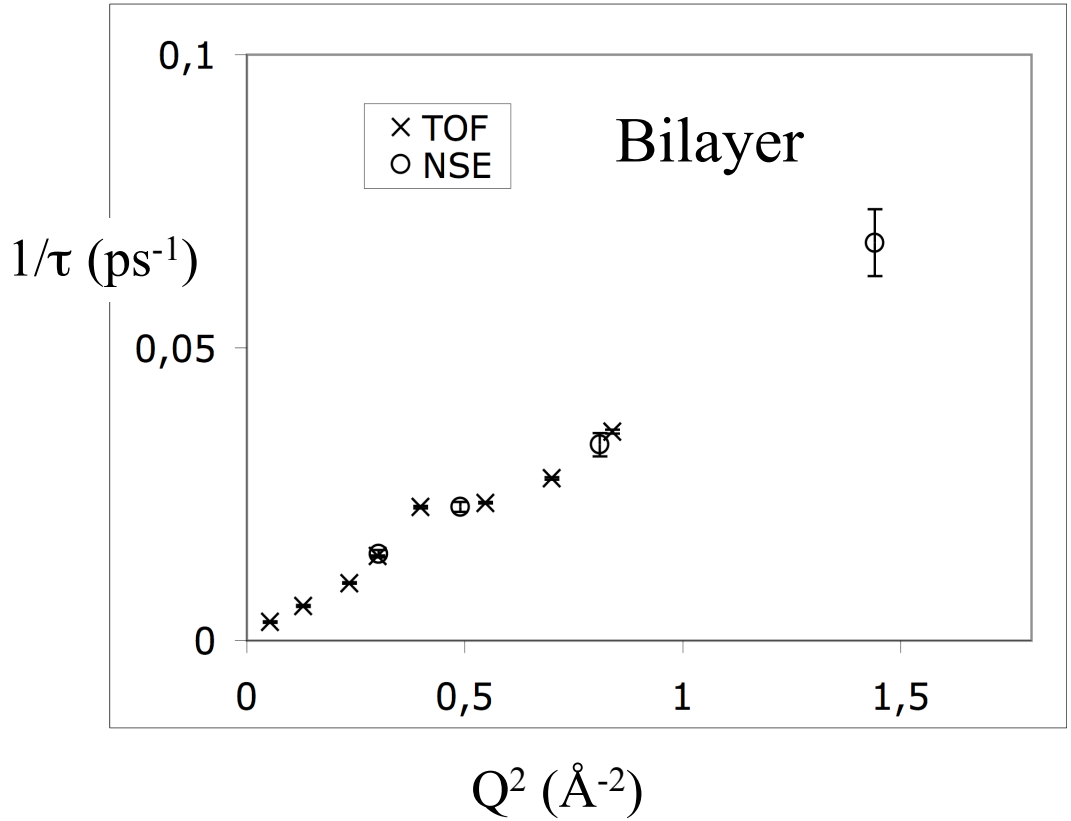
http://www.li2c.upmc.fr/perso/Malikova_PhD.pdf

Going further - synthetic fluro-hectorite

Better control of hydration level



Very good agreement NSE-TOF



simulations in progress, decoupling translational and rotational motion (V. Marry)

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