Dynamics of water and ions in clays: combining experiment and simulation

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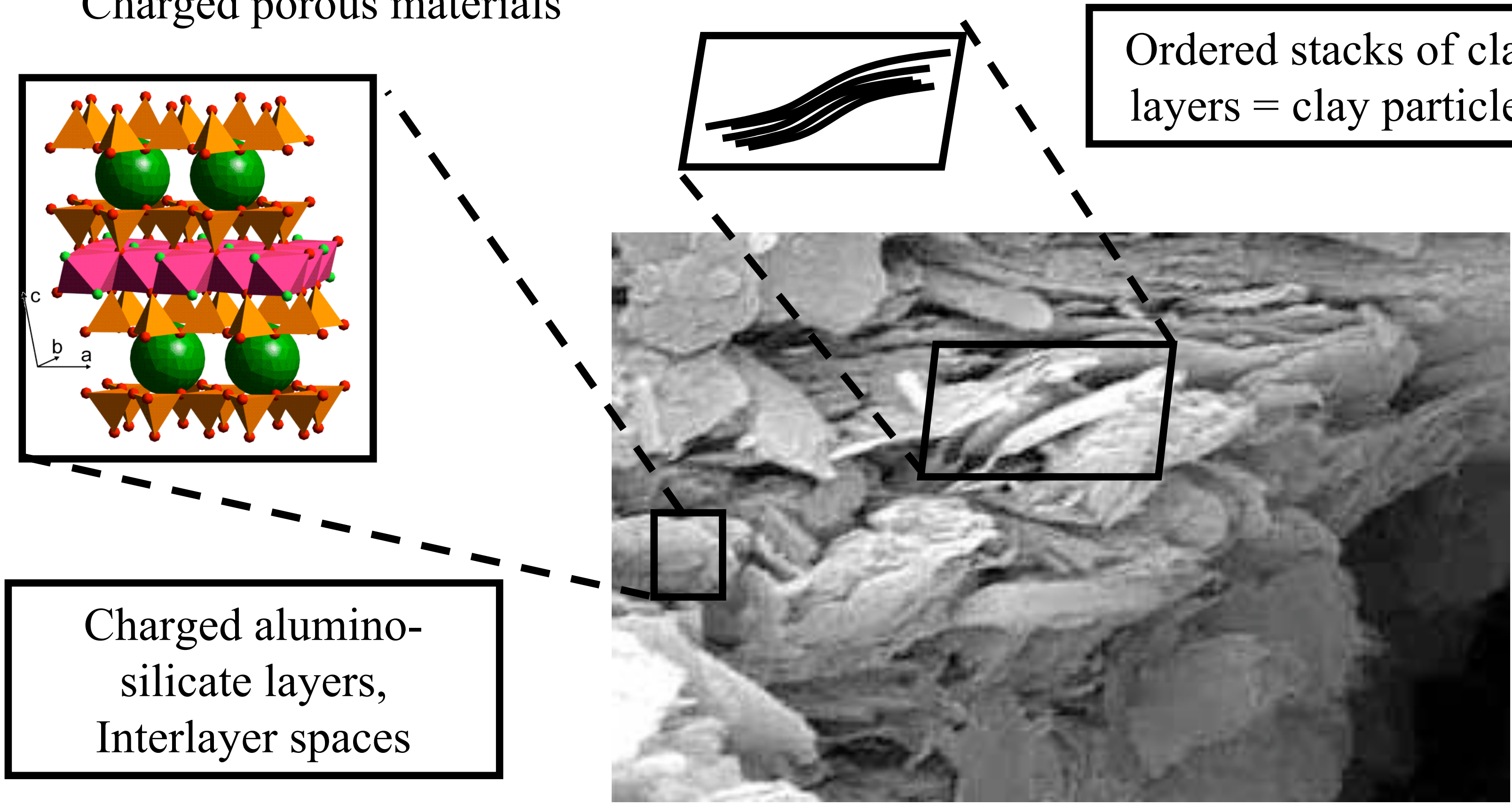
Clay structure

Charged porous materials



Porosity occupied by water and ions (e.g. Na^+, Ca^{2+}, Cl^-, Cs^+, I^-)

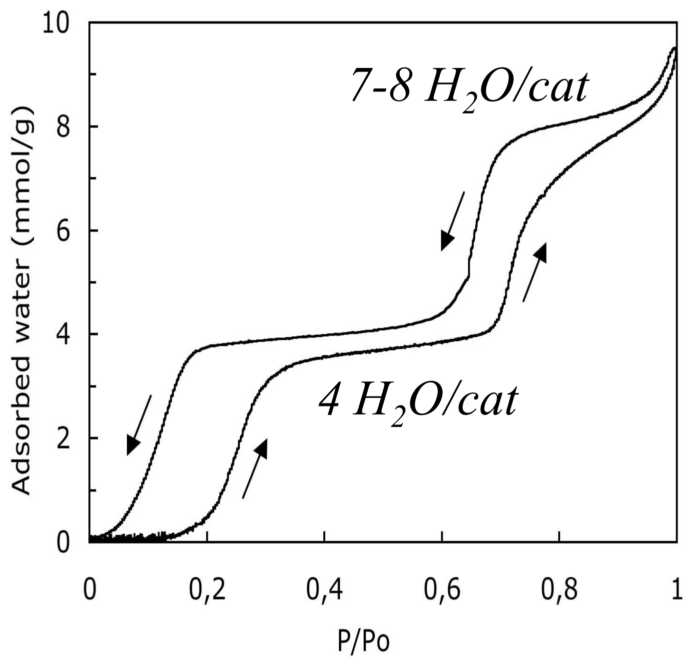
Clay hydration / swelling

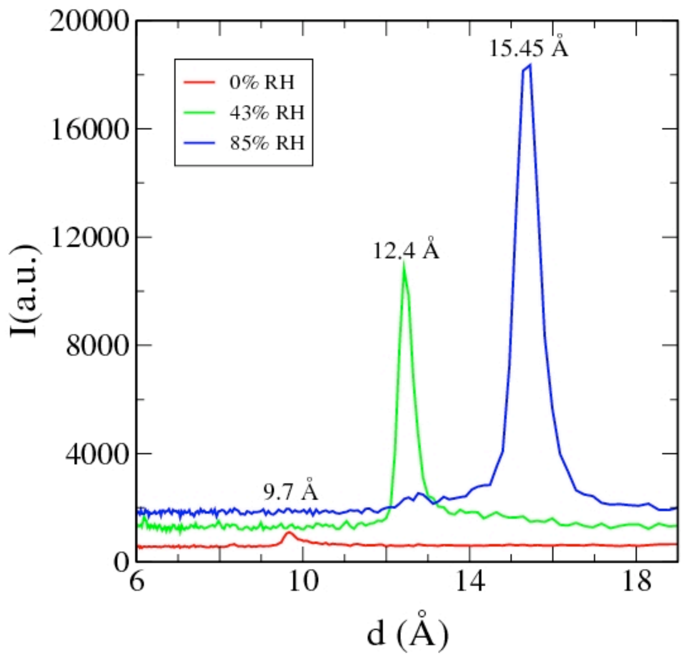
Discrete water layers in the clay interlayer

Water adsorption gravimetry

Neutron (X-ray) diffraction

⇒ interlayer spacing



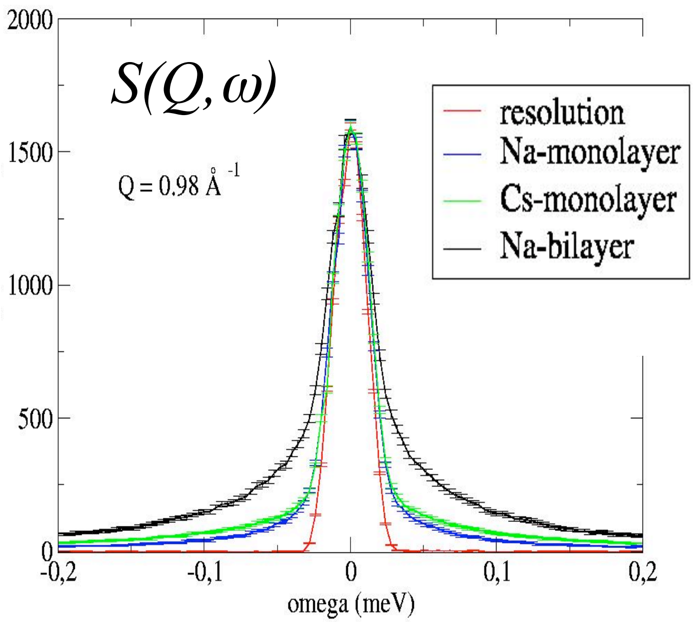


Data for synthetic hectorite clay

Water dynamics by quasi-elastic neutron scattering

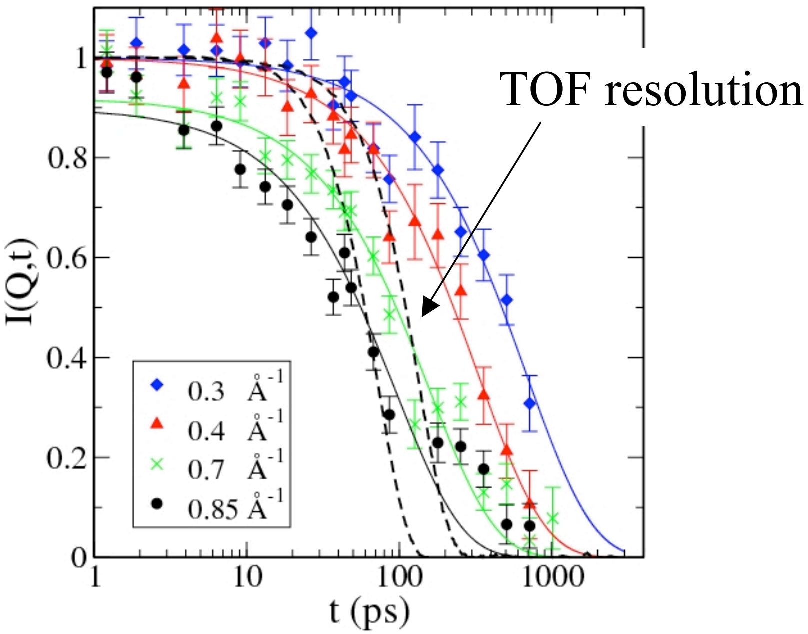
Measuring <u>incoherent</u> signal: self-diffusion of <u>H atoms</u> (scale of ps and Å)

Montmorillonite (TOF)



Resolution: 30 μeV (FWHM)

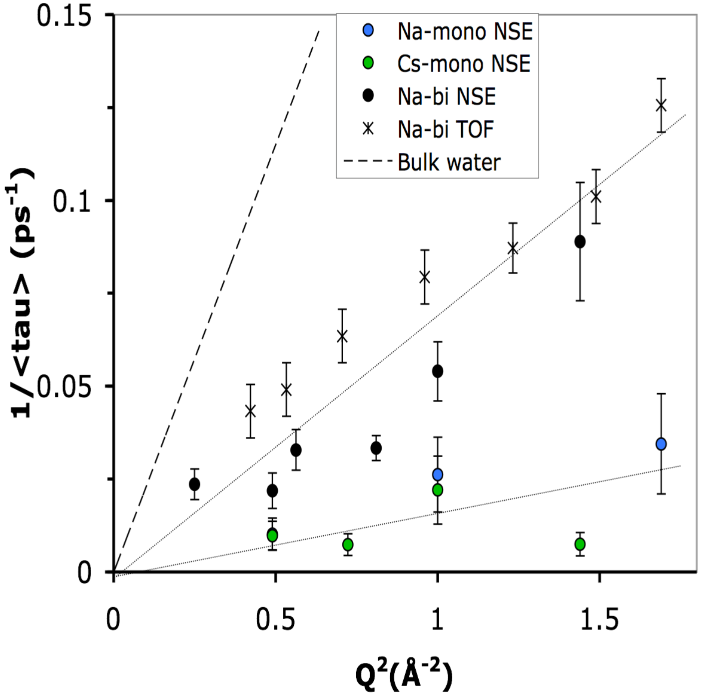
Hectorite monolayer (NSE)



1ps < t <1 ns

Water dynamics: diffusion coefficients

Natural Montmorillonite



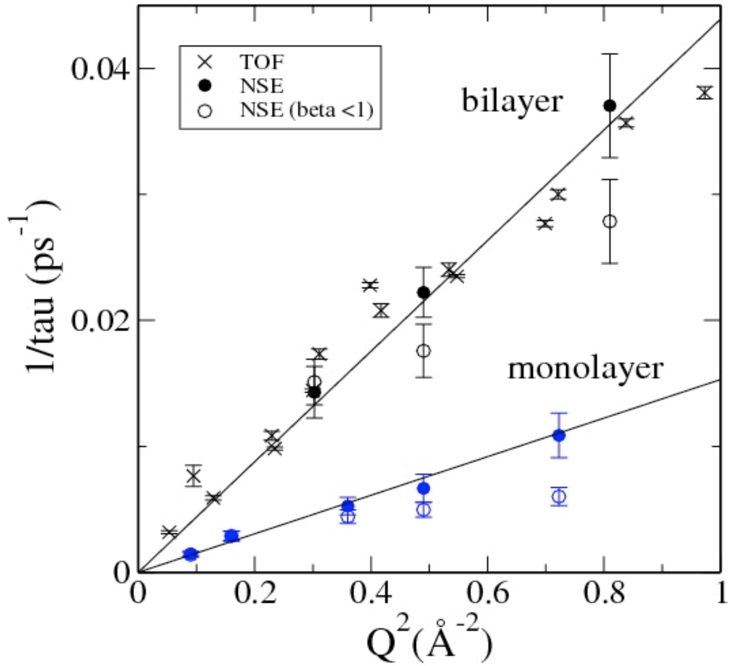
D_{water} ($\times$ 10^{-10} m^2s^{-1}), T=298 K

Bulk water	23
Bilayer	5.0-(10.0)
Monolayer	1.5-2.5

Isotropic translational model

$$1/\tau = D_t Q^2$$

Synthetic Na-Hectorite

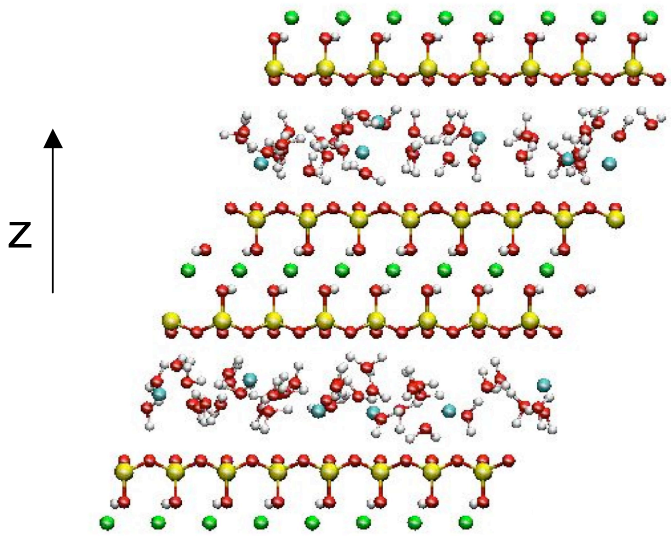


Malikova et al, J.Phys.Chem. C 2007

Classical molecular dynamics

Model montmorillonite

- Atomic detail, rigid clay and SPC/E water model
- pairwise Lennard-Jones and Coulombic potentials



Berendsen 1987 (SPC/E water)

Skipper 1989, 91, 95, Smith 1998

Koneshan 1998

Molecular Dynamics (NVT, NVE)

Particle trajectories, **R**(t)

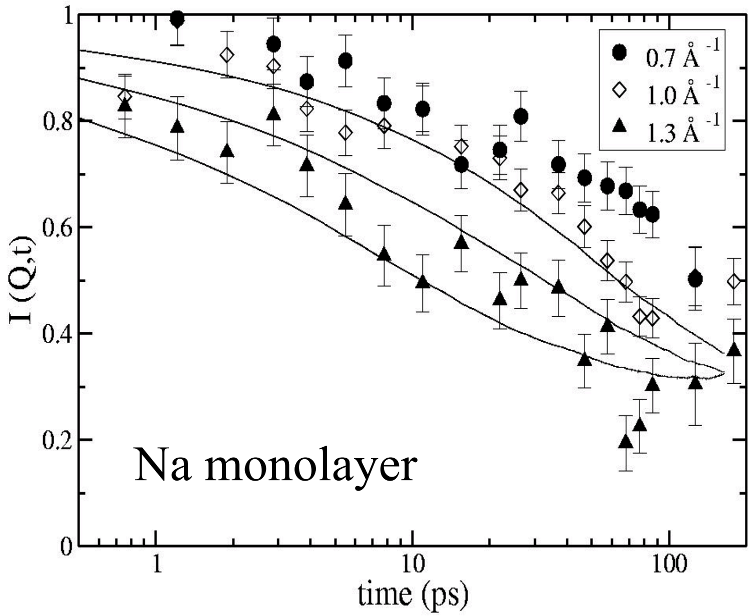
⇩

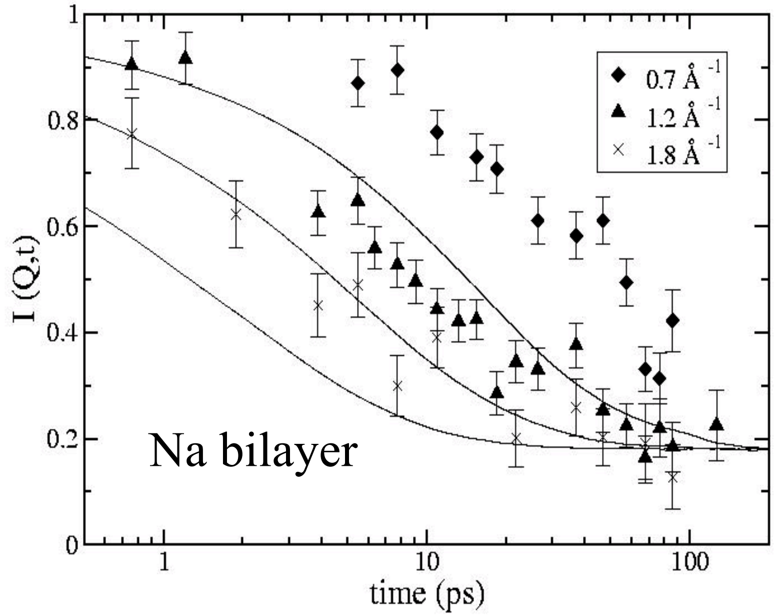
- dynamics of water and IONS
- details of motion, time correlation functions

- effect of temperature
- signature of confinement
- interlayer/micropore exchange

Assessment of the model: simulated / experimental $I_H(Q,t)$

Montmorillonite





Are experimental and simulated water content and distribution similar ?

Interest in modelling synthetic hectorite: no interstratification

Cases, Bérend, Ferrage

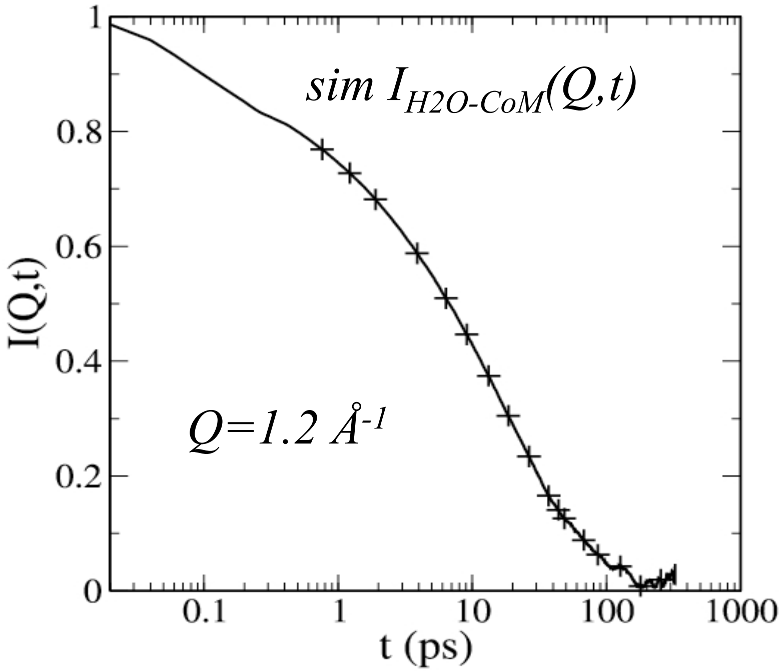
Note that departure from pure mono-exponential behaviour seen in both experiment and simulation

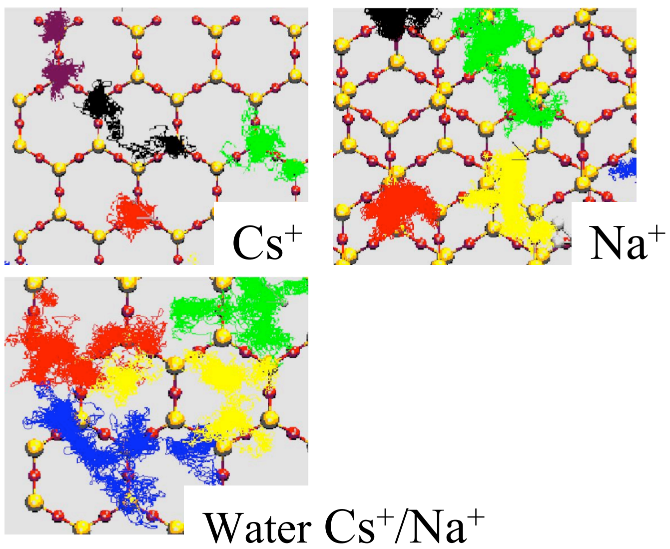
Malikova et al, J.Phys.Chem. B 2006

Exploiting Molecular Dynamics (1)

1) Details of water motion

• short-time dynamics (<0.5ps)
• for H atom dynamics - rotation on a sphere does not apply (contrary to bulk SPC/E water)





2) Preferential sites on clay surfaces

• Na^+ and Cs^+ differ only by size
• uncharged Cs does not prefer these sites

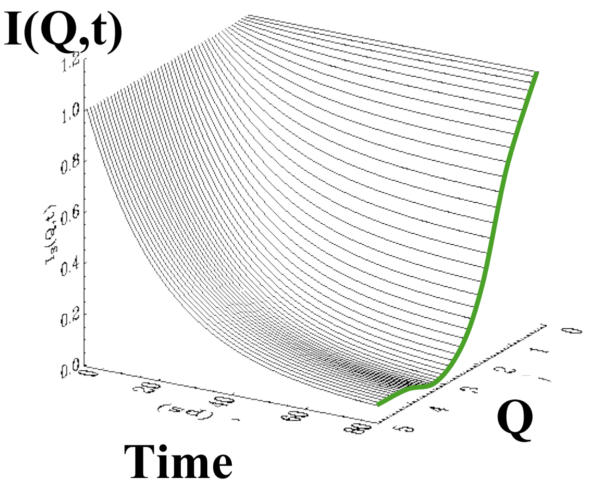
Malikova et al, Mol. Phys. 2004

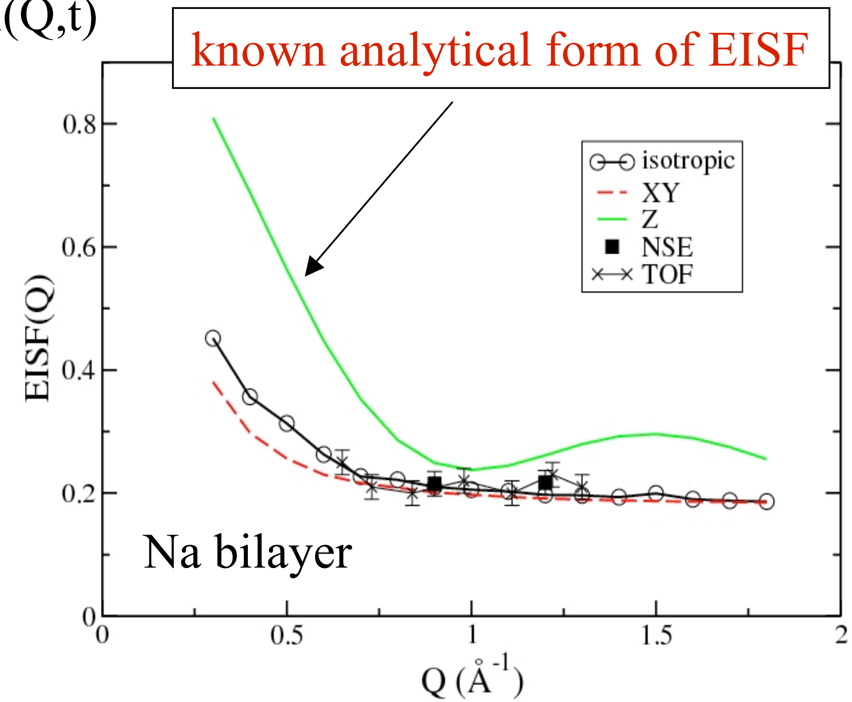
Exploiting Molecular Dynamics (2)

3) Signature of confinement

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

Hall & Ross 1978,1981





1) Powder samples (isotropic): characterisation of confinement impossible

→ oriented samples

2) Simulation: correlation time necessary to observe EISF is at least 400 ps or 2 μeV

Conclusions

• model hectorite clay *versus* natural montmorillonite clay in low hydrated states
• water diffusion by quasi-elastic neutron scattering: D_{diff} 10 and 4 times lower than bulk water (for one and two confined layers of water respectively)
• microscopic simulation -
  • assessment of model (exp/simulation comparison for water)
  • ion dynamics, temperature activation
  • signature of confinement

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