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 ($\text{Na}^+$, $\text{Ca}^{2+}$, $\text{Cl}^-$, $\text{Cs}^+$, $\text{I}^-$ ...), water

<table>
<thead>
<tr>
<th>Macroscopic Scale</th>
<th>Aggregates of particles</th>
<th>Particles</th>
<th>Layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>(form of powder)</td>
<td>Inter-particle porosity</td>
<td>$\approx 100 \text{ nm}$</td>
<td>(2-20 layers of variable form)</td>
</tr>
</tbody>
</table>

Experimental techniques studying diffusion:

Tracer experiments, NMR, dielectric spectroscopy, neutron scattering
### Simulation techniques

<table>
<thead>
<tr>
<th>Modelling</th>
<th>Nuclei and electrons</th>
<th>Atoms, molecules and ions</th>
<th>Layers + ions + solvent as continuum</th>
<th>Layers + continuous solution</th>
<th>Averaging over pore distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ab initio Molecular Dynamics</td>
<td>Classical Molecular Dynamics</td>
<td>Brownian Dynamics</td>
<td>Mesoscopic hydrodynamics (Smoluchowski)</td>
<td>Macroscopic hydrodynamics (Darcy..)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Neutron Spin Echo</th>
<th>Time of flight</th>
<th>Neutron scattering techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.1 - 10 nm (spatial scale)</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>1 ps - 1 ns (temporal scale)</td>
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</tr>
</tbody>
</table>

0.1 - 10 nm (spatial scale)

1 ps - 1 ns (temporal scale)
CLAY: montmorillonite - naturally occurring clay, of abundance in the region of the French disposal site

IONS: Na\(^+\) - natural ion
       Cs\(^+\) - potential radionuclide

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

Water content (mg\(_{water}\)/g\(_{clay}\))

Layer spacing

Crystalline swelling (monolayer, bilayer)

Continuous swelling

~3Å
**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: \([\text{Si}_8\text{(Al}_{3.25}\text{Mg}_{0.75})\text{O}_{20}\text{(OH)}_4\text{Na}_{0.75}}\times 8\) (unit cells / clay layer)

Simulation box: 20 Å

Interlayer content:

- 6 counter-ions (Na\(^+\) or Cs\(^+\))
- 6 \(\text{H}_2\text{O} / \text{cat}\) and 12 \(\text{H}_2\text{O} / \text{cat}\) 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**

Van der Waals and steric repulsion

Electrostatic Interactions

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

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

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

**Monte Carlo**: system equilibration

**Molecular Dynamics (MD)**: dynamic properties (e.g. diffusive motion)

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

\[ \vec{F}_i = m\vec{a}_i \]

**MD-NVE**

Clay layers fixed

Interlayer water and ions mobile
**Neutron scattering - principles & techniques**

Incident neutron:
\[ E_i = \frac{\hbar^2}{2m\lambda_i^2} \]

Atomic nucleus = scatterer

Scattered neutron:
\[ E_s = \frac{\hbar^2}{2m\lambda_s^2} \]

Information about motion of the scatterer is in
\[ \Delta E (\Delta v, \Delta \lambda) \]

1) Time-of-flight (TOF)
- \( \Delta E \) - “time-of-flight” over a known distance
- measuring \( S(Q,\omega) \), timescale 1-70/100 ps (\( \lambda = 9 \text{ Å} \))
- resolution not eliminated easily ("de-convolution" necessary)
- fast data acquisition (multiple Qs simultaneously)

2) Neutron Spin Echo (NSE + NRSE)
- \( \Delta E \) - change of neutron spin orientation
- measuring \( S(Q,t) \), timescale 1-1000 ps (\( \lambda = 5 \text{ Å} \))
- 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

ELASTIC process

\[ \delta \lambda = 0 \rightarrow \delta \Omega = 0 \rightarrow P = 1 \]

QUASIELASTIC process

\[ \delta \lambda \neq 0 \rightarrow \delta \Omega \neq 0 \rightarrow P < 1 \]

\[ \omega = \gamma |B_0| \]

\[ \langle \cos(\delta \Omega) \rangle = \frac{\int_{-\infty}^{+\infty} \cos(t_{NSE} \omega) S(Q,\omega) d\omega}{\int_{-\infty}^{+\infty} S(Q,\omega) d\omega} = \frac{I(Q,t_{NSE})}{I(Q,0)} = P(Q,t_{NSE}) \]
**Time of flight - the experiment (direct geometry)**

- **Continuous neutron beam** → **System of choppers** → **Monochromatic neutron pulses**

(A) Sample

- \( \theta \rightarrow Q \)
- \( d = 3.58 \text{m} \)

Detectors (B)

1) Elastic signal
   - Vanadium sample, resolution - \( R(Q, \omega) \)

2) Quasi-elastic signal of sample
   - e.g. Lorentzian shape:
     \[
     \frac{(1/\tau)}{(1/\tau)^2 + \omega^2}
     \]

**Mathematical Expression:**

\[
S(Q, \omega) = A(Q)R(Q, \omega) + [1 - A(Q)][R(Q, \omega) \otimes \frac{(1/\tau)}{(1/\tau)^2 + \omega^2}]
\]
Dependence of relaxation time on Q

1) Particles trajectories \( R(t) \) 
   - Fourier transforms \( R(t) \rightarrow Q \) \( t \rightarrow \omega \) 
   - Scattering functions \( I(Q,t) , S(Q,\omega) \) 
   - Dynamic information: simulation & experiment

2) Diffusion coefficients \( D \) 
   - Mean squared displacement (MSD)
   - Velocity auto-correlation (VACF)

3) Scattering functions \( I(Q,t) , S(Q,\omega) \) 
   - Dependence of relaxation time on Q
Particle trajectories (effect of temperature)

Projections in XY plane

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

Gaussian approximation \((R,t)\)

- \(t=0\)
- \(t>0\)

Isotropic translational motion

In reality...
Here in both simulation and experiment

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

Exponential form

\[ t \rightarrow \omega \]

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

\( \beta < 1 \)

\[ \langle \tau \rangle = \frac{\tau}{\beta} \Gamma \left( \frac{1}{\beta} \right) \]

Lorentzian form
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**

\[
\frac{1}{\langle \tau \rangle} = D Q^2
\]

gradient of \(1/\langle \tau \rangle\) versus \(Q^2\) in the limit of \(Q^2 \to 0\): diffusion coefficient

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

\[D_{\text{water}} \times 10^{-10} \text{ m}^2\text{s}^{-1}, \ T=298 \text{ K}\]

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<tr>
<th></th>
<th>Simulation (MSD)</th>
<th>NSE</th>
<th>TOF</th>
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<tr>
<td>Na(^+), monolayer</td>
<td>2.5 (3.8)</td>
<td>2.5</td>
<td>8.0</td>
</tr>
<tr>
<td>Cs(^+), monolayer</td>
<td>1.5 (2.8)</td>
<td>1.5</td>
<td>11.0</td>
</tr>
<tr>
<td>Na(^+), bilayer</td>
<td>10.0 (8.1)</td>
<td>5.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

- Monolayers systems: Sim \leftrightarrow NSE - very good agreement
- Monolayer systems: Sim, NSE \leftrightarrow TOF - issue of TOF resolution
- Bilayer systems: agreement of all three techniques reasonable
Confinement and Elastic Incoherent Structure Factor

\[ \text{EISF}(Q) = \lim_{t \to \infty} I(Q,t) \]

\[ \text{EISF}(Q) = \frac{1}{N_H} \sum_{\forall H} \left\langle \exp\left[ -i\vec{Q} \cdot \vec{R}_H \right] \right\rangle^Q \]

\[ \text{EISF}(Q)_{\text{NSE}} = \lim_{t \to \text{large}} I(Q,t)_{\text{NSE}} \]

\[ \text{EISF}(Q) = \frac{I_{el}}{I_{el} + I_{qel}} \]

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

simulation only

Na bilayer - anisotropic analysis
**Confinement and EISF(Q)**

Confinement between two planes, separation $L$  
_{Hall & Ross 1978, 1981_}

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

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: $\tau$ 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

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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