Extracting Quantitative Nanoscale Information from Water-Mineral MD Simulations

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3rd NNIN/CNF Fall Workshop, Cornell Univ., Ithaca, NY, Nov. 12-13, 2007
Internet Resources

General
- http://www.ccl.net/ - Computational Chemistry Web-Site
- http://www.lsbu.ac.uk/water/ - Water Structure and Behavior

Free MC & MD Software
- http://www.cse.clrc.ac.uk/msi/software/DL_POLY/ - DL_POLY
- http://www.gromacs.org/ - GROMACS
- http://www.earth.ox.ac.uk/~keithr/moldy.html - MOLDY
- http://www.ks.uiuc.edu/Research/namd/ - NAMD
- http://www.emsl.pnl.gov/docs/nwchem/ - NWChem
- http://www.cpmd.org/ - CPMD
- http://www.ccp5.ac.uk/librar.shtml - A library of MC & MD software

Visualization
- http://www.ks.uiuc.edu/Research/vmd/ - Visual MD

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Methods of Molecular Computer Simulations: Molecular Dynamics (MD) and Monte Carlo (MC)

- **MD - time averages** over a dynamic trajectory in the phase space of the simulated system
- **MC - ensemble averages** over a computer-generated random Markov chain of molecular configurations
- Periodic boundary conditions (PBC)

\[
T = \frac{2}{3Nk_B} \left\langle \sum_{i=1}^{N} \frac{m_i v_i^2}{2} \right\rangle \\
D = \lim_{t \to \infty} \frac{1}{6Nt} \left\langle \left| \mathbf{r}(t) - \mathbf{r}(0) \right|^2 \right\rangle \\

P = \frac{Nk_B T}{V} - \left( \frac{1}{3V} \right) \left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle
\]

\[
H_{\text{conf}} = \langle U \rangle + P \langle V \rangle \\
V_m = \langle V \rangle \frac{N_A}{N}
\]

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Fluctuation Properties

\[ C_V = R \left( \frac{2}{3} - N \frac{\langle T^2 \rangle - \langle T \rangle^2}{\langle T \rangle^2} \right)^{-1} \]

Heat capacity

\[ C_P = \left( \frac{\langle H^2 \rangle - \langle H \rangle^2}{Nk_B T^2} \right) \]

\[ \kappa \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \left( \frac{\langle V^2 \rangle - \langle V \rangle^2}{Nk_B T^2 \langle V \rangle} \right) \]

Isothermal compressibility

\[ \alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \left( \frac{\langle H_{\text{conf}} V \rangle - \langle H_{\text{conf}} \rangle \langle V \rangle}{Nk_B T^2 \langle V \rangle} \right) \]

Thermal expansivity

\[ g_K = \frac{\langle \sum \mu_i \rangle^2 - \langle \sum \mu_i \rangle^2}{N\mu^2} \]

Kirkwood factor

\[ \varepsilon = 1 + \frac{4\pi \rho \mu^2 yg_K}{3k_B T} \]

Dielectric constant

Averages of fluctuation properties converge much slower than other thermodynamic averages.

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Possible Sources of Errors in Molecular Simulations

- System size, periodicity, correlation length
- Initial configuration: coordinates, velocities (MD), doubling temperature
- Equilibration
- MD: time scale, time step, numerical integration, total simulation time
- MC: acceptance rate, efficiency probing the configuration space
- Accumulation statistics, convergence, statistical errors
Statistical Distributions

MD simulation of 2.2m NaCl Aqueous Solution at 1 bar and 300 K

These distributions are due to the natural fluctuations of the thermodynamic properties, corresponding to an equilibrium state of the simulated system.
Statistical Errors

Method of block averages
If $\langle A \rangle_i$ is the mean value of the property $A$ computed over the block $i$, then the statistical error $\delta A$ of the mean value $\langle A \rangle$ over the whole trajectory (or chain of configurations) can be estimated as

$$(\delta A)^2 = \frac{1}{M(M-1)} \sum_{i=1}^{M} \left[ \langle A^2 \rangle_i - \langle A \rangle_i^2 \right]$$
Thermodynamic Properties of Water
MC Simulations with TIP4P potential


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Micro-Thermodynamic Properties: Bonding Energy Distributions

\[ E_{b,i} = \sum_{j \neq i}^N U_{ij} \]
Micro-Thermodynamic Properties: Pair Energy Distributions
Fluid Structure
Radial Distribution Functions (RDFs)

- **Pair distribution function** or **radial distribution function** $g(r)$ — probability to find an atom $i$ at a certain distance $r$ from another atom $j$
- Normalized to a completely random distribution of atoms in space

$$g(r) = \rho^{-2} \left\langle \sum_i \sum_{j \neq i} \delta(r_i) \delta(r_j - r) \right\rangle = \frac{V}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \right\rangle$$

- Comparable to exp. data on X-ray or neutron diffraction
- In practice, $\delta(r-r_{ij})$ is replaced by a function which is non-zero in a very narrow range of $r$, and $g(r)$ is calculated as a histogram
- $g(r) = 1$ for ideal gas
Structure of Water: Atom-Atom Radial Distribution Functions (RDFs)

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Fluid Structure - Running Coordination Numbers

Average number of atoms \( i \) within a sphere of radius \( r \) from another atom \( j \):

\[
n_{ij}(r) = 4\pi \rho_i \int_0^r g_{ij}(r) r^2 dr = 4\pi \frac{N_i}{V} \int_0^r g_{ij}(r) r^2 dr
\]

RDFs and running coordination numbers for \( \text{Na}^+-\text{Cl}^- \) ion pairs in solution

- At \( T < 373 \text{ K} \) only water-separated \( \text{Na}^+-\text{H}_2\text{O}-\text{Cl}^- \) ion pairs can be found in the solution
- At \( 373 \text{ K} < T < 573 \text{ K} \) ~25% of ions participate in contact ion pairs
- At \( T > 673 \text{ K} \) the number of contact ion pairs increases very quickly involving the majority of ions
Radial Distribution Functions and Running Coordination Numbers

- Importance of $g(r)$ normalization
- Height of the $g(r)$ peaks is not necessarily an indication of high population
- Average density or concentration of species is equally important

$$g_{ij}(r) = \frac{1}{N_j \rho_i} \left\langle \sum_i \sum_j \delta(r - r_{ij}) \right\rangle$$

$$n_{ij}(r) = 4 \pi \rho_i \int_0^r g_{ij}(r) r^2 dr$$

3 Cs$^+$ ions in aqueous solution with humic acid (NOM anion)
Self-Diffusion Coefficients

Self-diffusion coefficient $D$ of a species is proportional to the mean-squared displacement of this species in the limit of large $t$:

$$D = \lim_{t \to \infty} \frac{1}{6Nt} \langle |r(t) - r(0)|^2 \rangle$$

 MSD

$D = \lim_{t \to \infty} \frac{1}{6Nt} \int_{0}^{t} \langle v(0) \cdot v(t') \rangle \, dt'$

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Dynamics of Individual Atoms: Velocity Autocorrelation Functions

\[ VACF \equiv C_{vv}(t) = \frac{\langle v(0) \cdot v(t) \rangle}{\langle v(0)^2 \rangle} = \frac{1}{\langle v(0)^2 \rangle} \int v(0) \cdot v(t) \, d\Gamma \]

Qualitatively, the VACF reflects the relative rate with which the system or its individual atoms “forget” the velocities they had at a particular moment in time, indicated here as \( t = 0 \).

\[ \langle v(0) \cdot v(t) \rangle = \frac{1}{N_\tau N} \sum_{i=1}^{N_\tau} \sum_{j=1}^{N} v_j(t_i) \cdot v_j(t_i + t) \]
Dynamics of Individual Atoms
VACFs and Power Spectra

\[
VACF \equiv C_{vv}(t) = \frac{\langle v(0) \cdot v(t) \rangle}{\langle v(0)^2 \rangle} = \frac{1}{\langle v(0)^2 \rangle} \int v(0) \cdot v(t) \, d\Gamma
\]

\[
P(\omega) = \int_{0}^{\infty} \frac{\langle v(0) \cdot v(t) \rangle}{\langle v(0)^2 \rangle} \cos(\omega t) \, dt
\]
Dynamics of Individual Atoms
VACFs and Power Spectra

Cl\(^-\) in LiAl\(_2\)(OH)\(_6\)Cl\(\cdot3\)H\(_2\)O

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Local Hydration Environment of Cl⁻ in the LDH Interlayers

H-bonding environment of Cl⁻ in the interlayers of LDH is very similar to bulk water.

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Comparison of Observed and Computed Spectra for other LDH Phases

[LiAl₂(OH)₆] Cl · H₂O

[Ca₂Al(OH)₆] Cl · 2H₂O

[Li₂Al₄(OH)₁₂] SO₄ · 3H₂O

[Mg₃Al(OH)₆] Cl · 3H₂O

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Dynamics of Individual Atoms
VACFs and Power Spectra

\[ \omega \sim 4000 \text{ [cm}^{-1}] \]

\[ \lambda = 1 / \omega = 1 / 4000 \text{ [cm]} = 2.5 \cdot 10^{-6} \text{ [m]} \]

\[ c = \lambda \nu = \lambda / \tau \]

\[ \tau \sim \lambda / \chi = 2.5 \cdot 10^{-6} \text{ [m]} / 3 \cdot 10^8 \text{ [m/s]} \sim 10^{-14} \text{ [s]} \]

⇒ Time step \sim \tau / 10 \sim 10^{-15} \text{ [s]} = 1 \text{ [fs]}
SPC: Intramolecular Stretching Vibrations of H$_2$O Molecules in NaCl Solutions as a Function of Temperature

$$P(\omega) = \int_0^\infty \frac{\langle v(0) \cdot v(t) \rangle}{\langle v(0)^2 \rangle} \cos(\omega t) \, dt$$

Symmetric stretch

Asymmetric stretch

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SPC: Intramolecular Bending Vibrations of H$_2$O Molecules in NaCl Solutions as a Function of Temperature

\[
P(\omega) = \int_{0}^{\infty} \frac{\langle v(0) \cdot v(t) \rangle}{\langle v(0)^2 \rangle} \cos(\omega t) \, dt
\]

The bending spectrum is largely unaffected by the changes of temperature and density.

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The broad frequency band of H$_2$O librations (hindered rotations) in the H-bonding network is centered around ~500 cm$^{-1}$ and gradually decreases with increasing temperature and decreasing density.

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Dynamics of Individual Species
Power Spectra of Molecular Motions

\[ P(\omega) = \int_{0}^{\infty} \frac{\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle}{\langle \mathbf{v}(0)^2 \rangle} \cos(\omega t) \, dt \]

The two broad bands of the translational spectra at ~50 cm\(^{-1}\) and ~200 cm\(^{-1}\) are usually assigned to H-bond \(\text{O} \cdots \text{O} \cdots \text{O}\) bending and stretching, respectively.

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Dynamics of Individual Species
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The two broad bands of the translational spectra at \(~50\, \text{cm}^{-1}\) and \(~200\, \text{cm}^{-1}\) are usually assigned to H-bond \(\text{O} \cdots \text{O} \cdots \text{O}\) bending and stretching, respectively.
Hydrogen Velocity Decomposition to Calculate the Librational and Vibrational Modes of H₂O Molecules

\[ Q_1 = b_1 + b_2 \]
\[ Q_2 = p_1 + p_2 \]
\[ Q_3 = b_1 - b_2 \]

\[ R_\xi = p_1 - p_2 \]
\[ R_\eta = u_1^\perp + u_2^\perp \]
\[ R_\tau = u_1^\perp - u_2^\perp \]
BJH: VACFs and Power Spectra for Bending and Stretching Intramolecular Modes of H$_2$O Vibrations

771 K, 1.284 g/cm$^3$

673 K, 0.166 g/cm$^3$

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H-bond Dynamics in Water

Two definitions possible:

1) Autocorrelations for molecular pairs bonded continuously, i.e., without interruptions over the entire interval from 0 to $t$ (continuous HB correlation function).

2) Autocorrelations for molecular pairs irrespective of intervening interruptions, i.e., of possible prior H-bond breaking and reforming events (intermittent HB correlation function).

Exponential fit to estimate the H-bond relaxation time, $\tau$:

$$C_{\text{HB,c}}(t) = \exp(-t/\tau_{\text{HB}})$$

H-bond Dynamics in Water

\[ C_{HB}(t) = \frac{\sum_{ij} s_{ij}(t_0)s_{ij}(t_0 + t)}{\sum_{ij} s_{ij}(t_0)} \]

Exponential fit to estimate the H-bond relaxation time, \( \tau \):

\[ C_{HB,c}(t) = \exp\left(-\frac{t}{\tau_{HB}}\right) \]

Survival probabilities for a newly generated bond, \( s(t) \) (solid lines) and for an average bond, \( C_{HB,c}(t) \) (dashed lines), for stricter HB definition (thin lines) and for less strict HB definition (thick lines).

Inset represents the short time behavior of all functions on a semi-log plot.

H-bond Dynamics in Water at High Temperature

\[ C_{\text{HB}}(t) = \frac{\sum_{(i,j)} s_{ij}(t_0)s_{ij}(t_0 + t)}{\sum_{(i,j)} s_{ij}(t_0)} \]

Exponential fit to estimate the H-bond relaxation time, \( \tau \):

\[ C_{\text{HB},c}(t) = \exp\left(-\frac{t}{\tau_{\text{HB}}}\right) \]

Modeling Substrate-Water Interfaces (1)

Building a mineral-solution interface model

- Build a model of bulk crystal
Modeling Substrate-Water Interfaces (2)

Building a mineral-solution interface model

- Build a model of bulk crystal
- Define the cleavage plane
Modeling Substrate-Water Interfaces (3)

Most hydrated oxide surfaces are at least partially protonated (terminated by OH-groups) under normal pH.

Building a mineral-solution interface model:
- Build a model of bulk crystal
- Define the cleavage plane
- Cleave the crystal to create a slit-like nano-pore
Modeling Substrate-Water Interfaces (4)

Building a mineral-solution interface model

- Build a model of bulk crystal
- Define the cleavage plane
- Cleave the crystal to create a slit-like nano-pore
- Add pore solution from a preliminary bulk-solution simulation
1m CsCl Aqueous Solution in Slit-Like Nanopores of Kaolinite

Layered model of interfaces in periodic boundary conditions

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Ionic Sorption at the Interfaces

3 types of surface species:

- **Inner-sphere** surface complexes (i.e., located directly on the solid-phase surface)
- **Outer-sphere** surface complexes (i.e., separated from the solid surface by one molecular layer of water)
- Ions in the **diffuse layer** or in the **bulk** solution (which still can feel the presence of the surface, but are separated from it by more than one molecular layer of water)
Trajectory Path of Cesium Ion at the Interface of CsCl Aqueous Solution with Kaolinite

All water molecules and other Cs\(^+\) and Cl\(^-\) are removed for clarity.

Cs\(^+\) equilibrates to form inner sphere complex.

(001) surface
Analysis of Structure and Energetics of Aqueous Interfaces

MD trajectory plots for Li+ counterions in the three layer montmorillonite hydrate (a) XY plane; (b) XZ plane. ISSC - inner-sphere surface complex; DLS - diffuse-layer species.

Analysis of Structure and Energetics of Aqueous Interfaces

Center-of-mass trajectory of a Zn\(^{2+}\)-“bound” \(\text{H}_2\text{O}\) molecule (red) and a “free” \(\text{H}_2\text{O}\) molecule (blue) in the \(ab\) crystallographic plane in the 2.4 ns MD run of a hydrated Zn-vermiculite. The large grey circles denote oxygen atoms of the clay surface.

Arab et al., *PCCP*, 6, 2446-2453 (2004)
Analysis of Structure and Energetics of Aqueous Interfaces

Most stable configuration (top) and contour maps of potential energy surface (bottom) for a water molecule on (a) brucite (0001), (b) talc (001), and (c) halite (100) surfaces.

Modeling of Friedel’s Salt [Ca$_2$Al(OH)$_6$]Cl $\cdot$ 2H$_2$O Interfaces with Aqueous Na$_2$SO$_4$ solution

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Rigid Substrate Approximation

\[ \mathbf{F}_i = m \mathbf{a}_i = - \frac{\partial U(r_1, r_2, \ldots, r_N)}{\partial r_i} ; \quad i = 1, 2, \ldots, N \]

\[ U = \sum \sum U_{ij} \]

\[ U_{ij} = \sum \sum \left( \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} + \frac{q_i q_j}{\varepsilon_0 r_{ij}} \right) + \frac{1}{2} k_b (r_{ij} - r_0) + \frac{1}{2} k_\theta (\theta_{ij} - \theta_0) \]

Short-range repulsion  v-d-Waals  Coulombic  bond stretching  bond bending

All atoms can move

Fixed atoms in the kaolinite structure

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Mechanics of Surface-Fluid Interaction

Mobile substrate atoms $\Rightarrow$ exchange of energy and momentum is possible

$p_0 = m v_0$

$E_0^{\text{kin}} = \frac{m v_0^2}{2}$

$E_1^{\text{kin}} = \frac{m v_1^2}{2}$

$p_1 = m v_1$

Fixed (immobile) substrate atoms $\Rightarrow$ exchange of energy and momentum is restricted

$p_0 = m v_0$

$E_0^{\text{kin}} = \frac{m v_0^2}{2}$

$E_1^{\text{kin}} = \frac{m v_1^2}{2}$

$|p_1| = m |v_0|$

$|v_1| = |v_0|$

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Test of Rigid vs Flexible Substrate Models

*Interface of kaolinite with 1m CsCl solution*

- **Size** 3.57 x 2.07 x 3.15 nm
- **Water layer** ~1.8 nm
- **Two different surfaces:**
  - hydrophobic “siloxane”
  - hydrophilic “gibbsite”
- $N_{\text{kaol}} = 1088$
- $N_{\text{H}_2\text{O}} = 420 \times 3 = 1260$ / $N_{\text{Cs}} = N_{\text{Cl}} = 8$
- **Time step** $\Delta t = 0.5$ fs
- **Total simulation length** 200 ps (incl. 100 ps preequilibration)
- **Dynamic trajectories sampled every** 0.004 ps
- 250,000 equilibrium frames

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Atomic Density Profiles and Surface Diffusion Rates

Interface of kaolinite with 1m CsCl aqueous solution

Diffusion coefficients of solution species (10^{-5} cm^2/s)

<table>
<thead>
<tr>
<th>Species</th>
<th>“siloxane” interface</th>
<th>“gibbsite” interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs^+</td>
<td>0.46</td>
<td>0.23</td>
</tr>
<tr>
<td>Cl^-</td>
<td>-</td>
<td>0.52</td>
</tr>
<tr>
<td>H_2O</td>
<td>2.25</td>
<td>0.80</td>
</tr>
</tbody>
</table>

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Contour maps of atomic densities at the hydrophobic “siloxane” interface of kaolinite
Contour maps of atomic densities at the hydrophilic “gibbsite” interface of kaolinite

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Power spectra of surface species
Hydrophobic “siloxane” interface of kaolinite

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Power spectra of surface species
Hydrophilic “gibbsite” interface of kaolinite
Swelling of Montmorillonite

\[ \text{Na}_3(\text{Si}_{31}\text{Al})(\text{Al}_{14}\text{Mg}_2)\text{O}_{80}(\text{OH})_{16}n\text{H}_2\text{O} \]

4 unit cell basis

\( (001) \text{ d-spacing (Å)} \)

\( \text{M}_\text{H}_2\text{O} / \text{M}_\text{clay} \)

Experimental
Fu et al. (1990)

MD Simulation
Comparison of Clay-Water Interlayers with Different Surface Charge Distribution

Two-Layer Hydrate

Pyrophyllite

Montmorillonite

Wy Montmorillonite

Beidellite

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Angular Distribution of H$_2$O Dipole Moment Orientation within ~1.5 nm Aqueous Interlayers

Clay minerals with different surface charge density and distribution

montmorillonite
tetraedric

pyrophyllite
tetraedric

beidellite
tetraedric

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Charge Density Profiles at the Fully Protonated Quartz Interface

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Effects of Scale:
Non-swelling amine-clay composites

The 1-D atomic density profile for the 350K atom model is much more diffuse.

“Increased sampling phase space” is a plausible explanation.

However, when the 350K atom model was visualized it became apparent that something else is happening.

(Greewell and Coveney, 2006)
Effects of Scale: Sheet Undulations in Non-swelling Amine-Clay Composites

- Using very large simulation super-cells (350,840 atoms; 28×50×3nm) the clay sheets had been able to flex, resulting in a much broader distribution of atom density.

- This distortion may be more evident at even larger super cell sizes, or using 2-dimensional boundary conditions.

- Small models suffer from unphysical finite size effects.

(Greewell and Coveney, 2006)