The Nature of the Mineral-Water Interface: A Molecular Simulation and Spectroscopic Investigation

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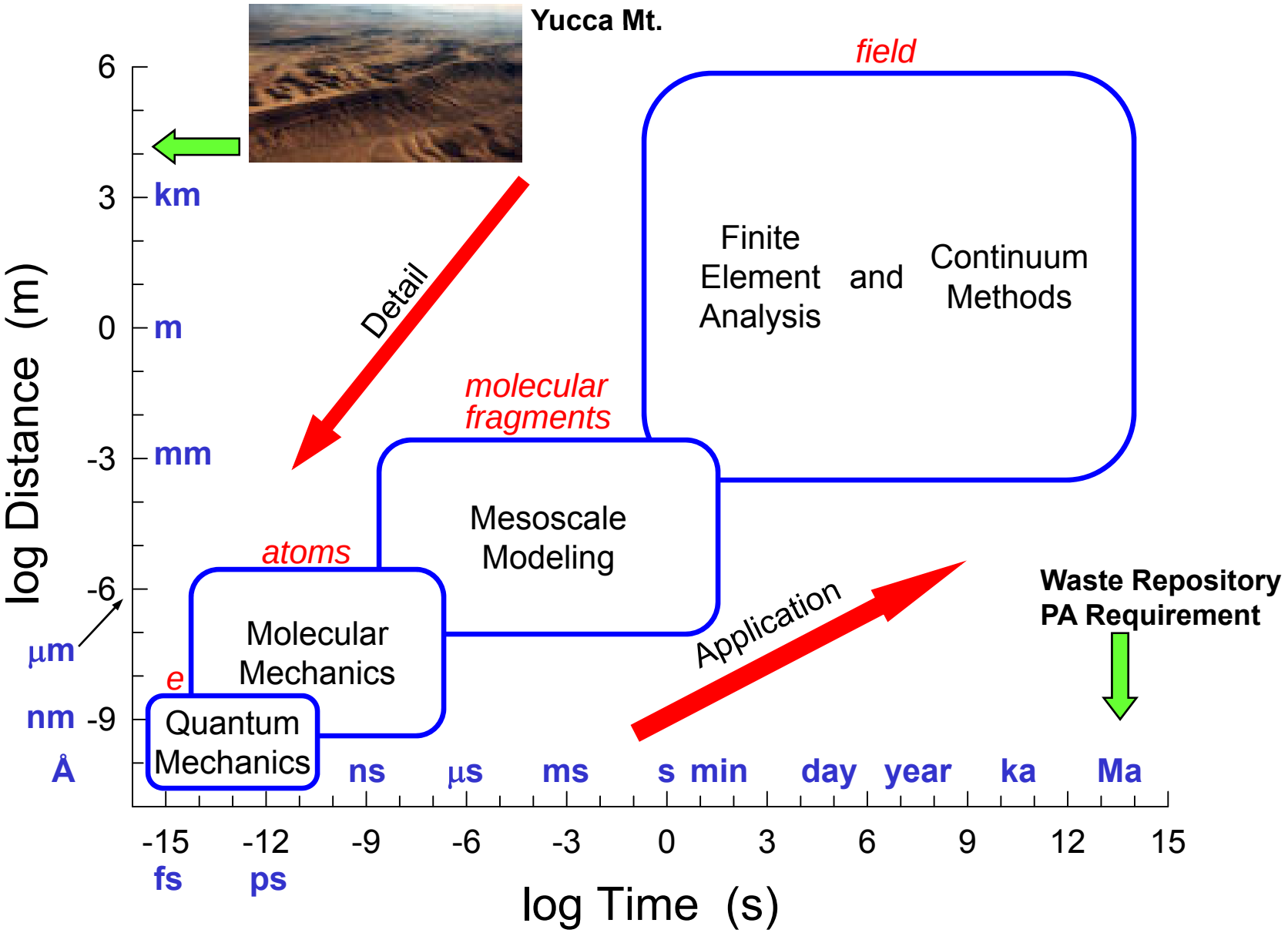
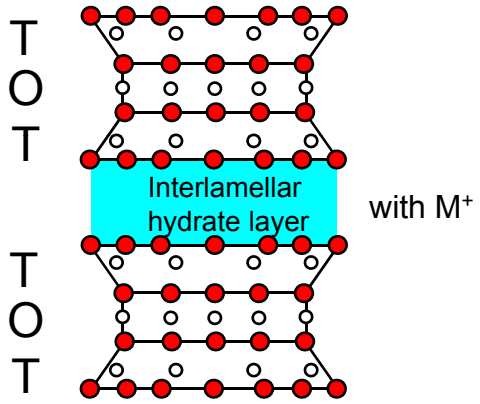
Multiscale Simulations



Atomistic Simulation of Clays and Clay Processes

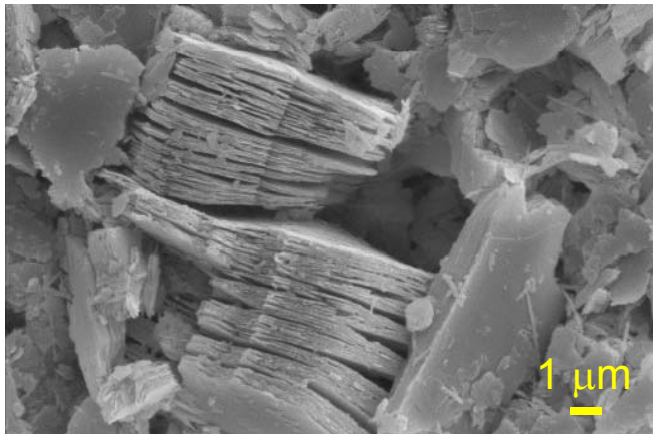
Crystal structure models of clay minerals are typically unknown

- Nanocrystalline (cryptocrystalline) materials (less than 1 μm grain size)
- No large single crystals for X-ray diffraction refinements
- Hydrogens positions are often unknown (require neutron diffraction analysis) and control sorption process
- Complex chemistry with multicomponent systems, cation disorder, and vacancies
- Low symmetry (monoclinic or triclinic)
- Stacking disorder complicates structural analysis



Atomistic simulations of clay minerals are non-trivial

- Require accurate empirical energy forcefield; quantum methods are too costly
- Large unit cells or simulation supercells are required (>100 atoms)
- Significant electrostatic fields associated with layer structure
- Validation of models is difficult



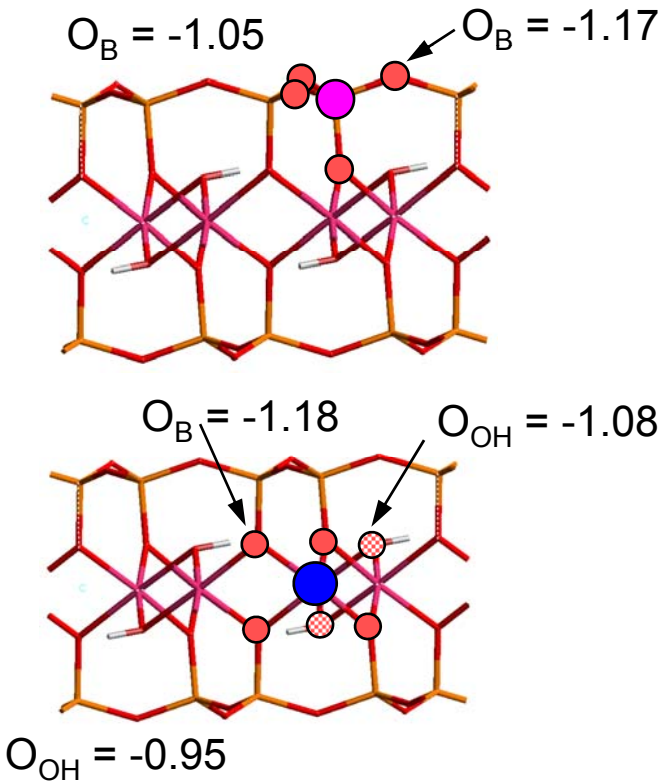
Forcefield for Modeling Clays and Hydrated Phases

CLAYFF – specialized semi-empirical fully flexible force field model allowing for realistic exchange of momentum and energy among all atoms – solid substrate and aqueous solution

Cygan, Liang, and Kalinichev (2004) *J. Phys. Chem. B*, **108** 1255-1266

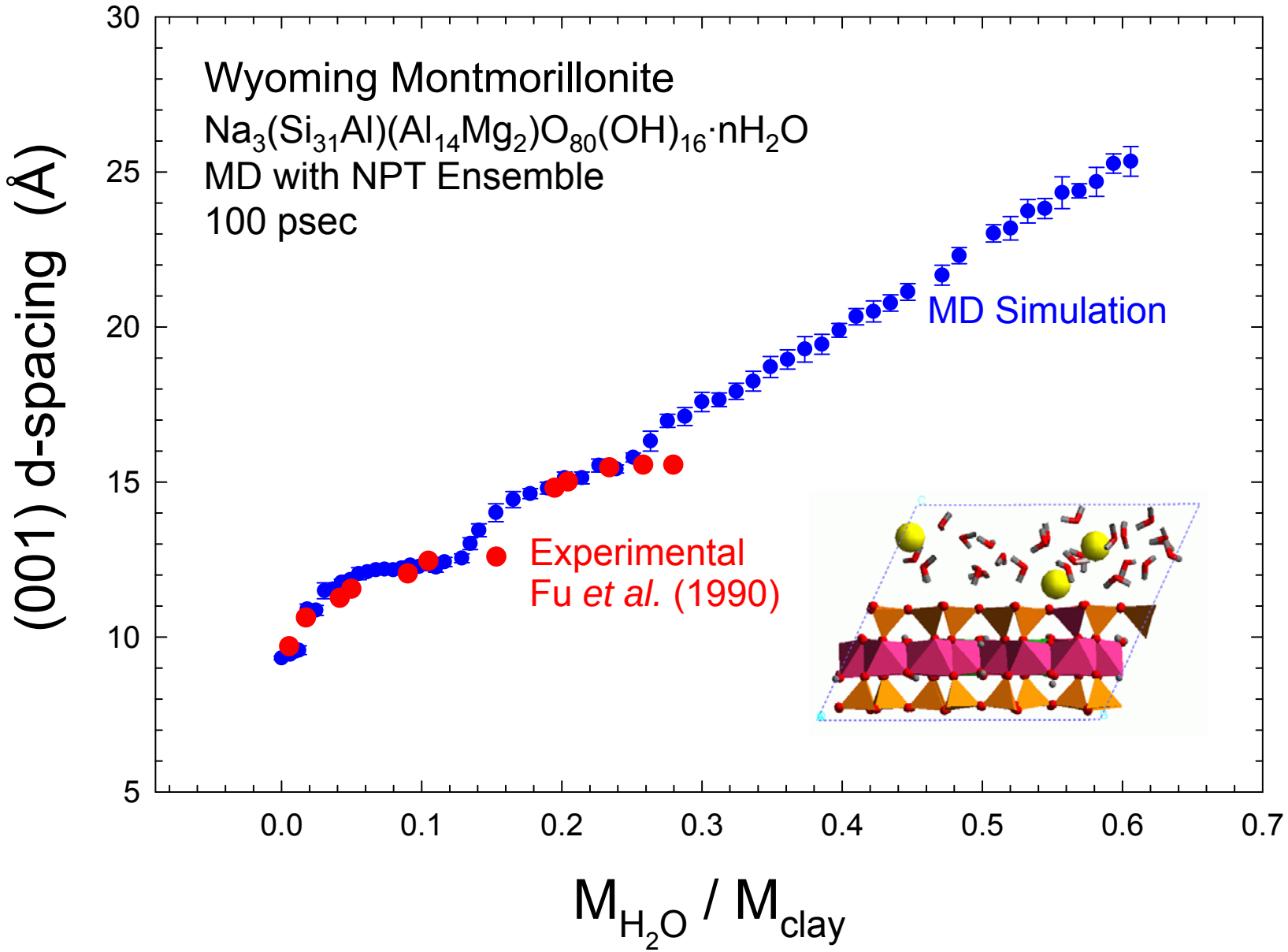
$$U_{ij} = \Sigma\Sigma(A_{ij}/r_{ij}^{12} - B_{ij}/r_{ij}^{6} + q_i q_j /e_0 r_{ij}) + \Sigma\, ½k_b\,(r_{ij} - r_0)^2 + \Sigma ½k_q\,(q_{ij} - q_0)^2$$

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

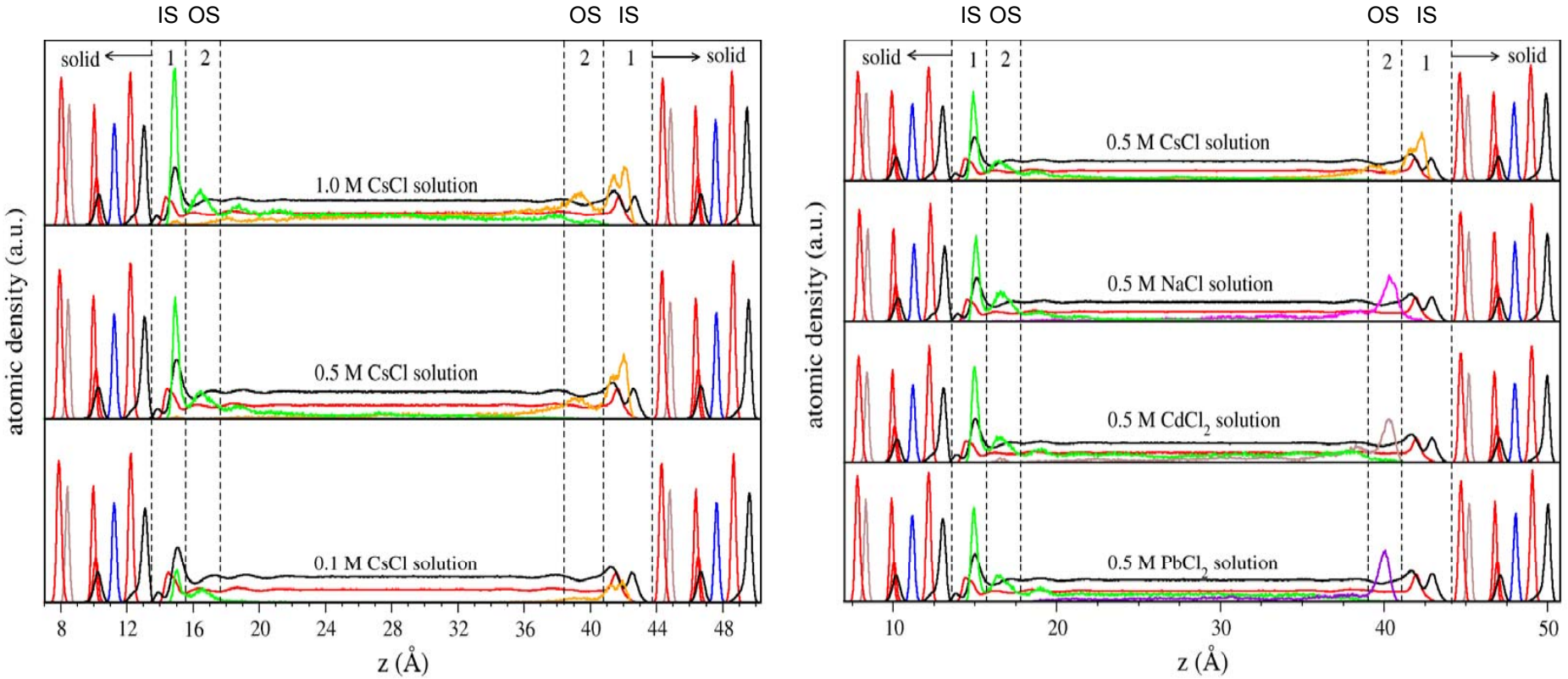


- Simple Point Charge (*SPC*) flexible model for H_2O
- Structural ions: Si, Ca, Al, Fe, Mg, O, OH with partial charges derived from quantum DFT calculations for a number of simple oxides and hydroxides
- Aqueous species: Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Cl^-, OH^-, SO_4^{2-}, CO_3^{2-}, NO_3^-
- Theoretical models of oxides, hydroxides, clays, and other hydrous materials
- Combination with *CVFF*, *AMBER* or *CHARMM* to model hybrid organic-inorganic systems

Swelling Behavior of Montmorillonite



Density Profiles for Kaolinite Simulations

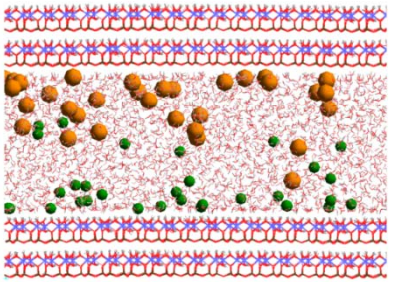


- Profiles calculated from 500 ps of accumulated dynamics after an equilibration period of 600 ps
- Regions named 1 and 2 define inner and outer adsorption shell distances
- Adsorption statistics are obtained by integrating the profiles under regions 1 and 2

Atoms: **Al**, **Si**, **O**, **H**, **Cl^-**, **Cs^+**, **Na^+**, **Cd^{2+}** and **Pb^{2+}**

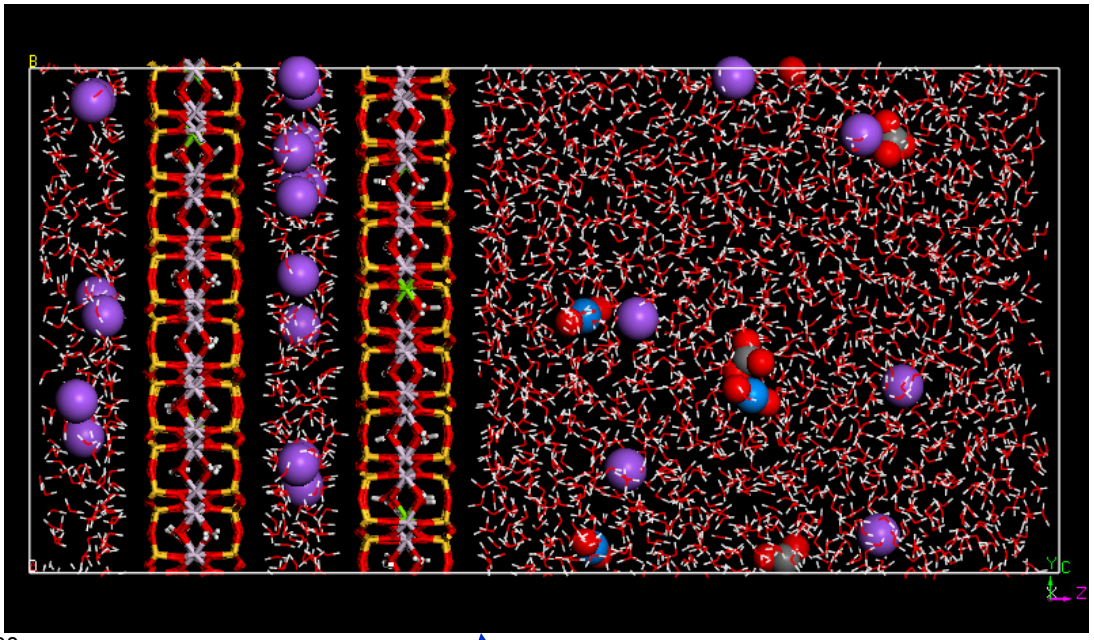
Derived adsorption statistics: X_{ads}, K_D, site density, etc.

20k atoms



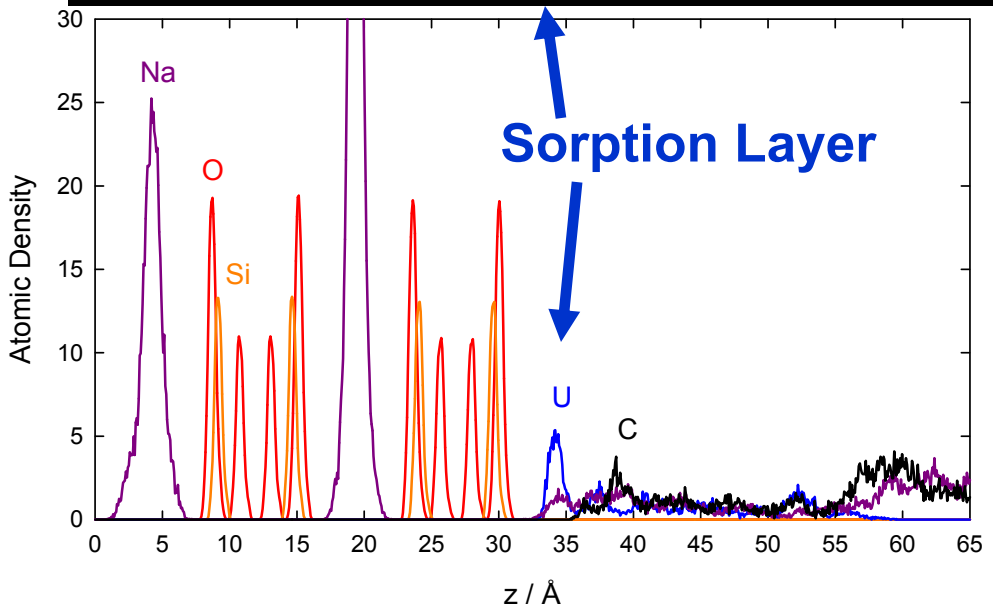
Vasconcelos et al. (2007) Journal of Physical Chemistry C

Adsorption of Uranyl on Montmorillonite



LAMMPS software
42 Å x 36 Å x 72 Å
10k atoms

y



"low charge" montorillonite
x = −0.375 *e* / unit cell

Density Profiles → % Adsorbed

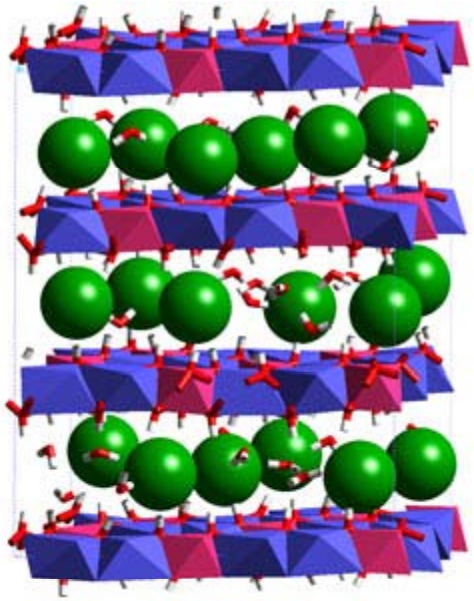
Percent Ion Adsorption

[Na]	[UO_2]	% UO_2	% Na
0.162	0.027	37.4	10.4
0.162	0.081	21.8	8.5
0.162	0.162	10.2	7.6
0.324	0.162	3.9	8.1

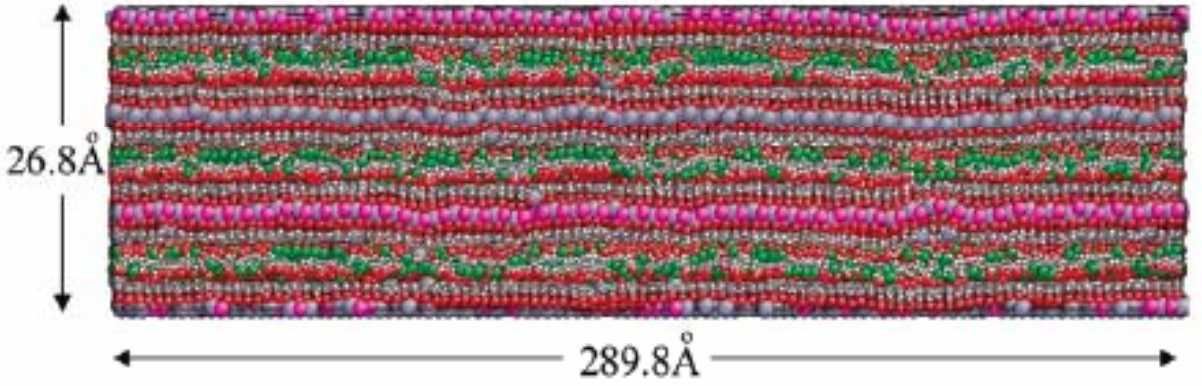
Greathouse and Cygan (2005)
Physical Chemistry Chemical Physics

Elastic Moduli

$[Mg_2Al(OH)_6]Cl{\bullet}2H_2O$

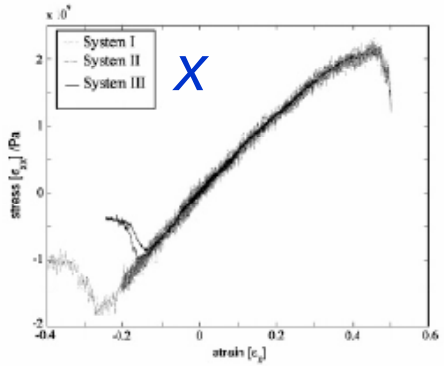


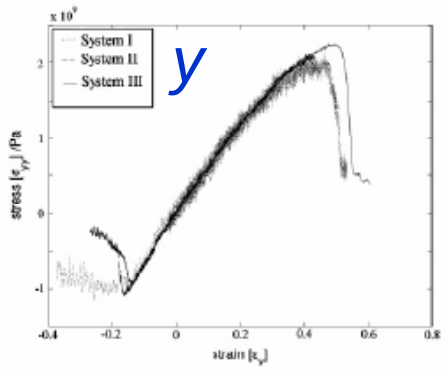
> 10^6 atoms



Stress-Strain

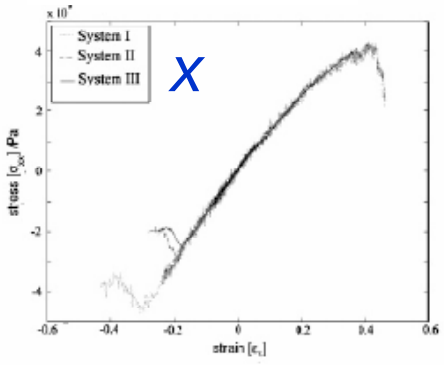
LDH sheet and interlayer

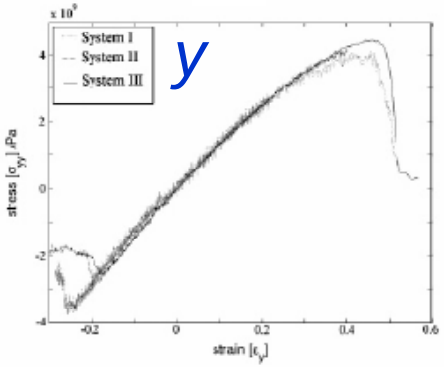




slope = Young's modulus

LDH sheet only





macroscopic stress

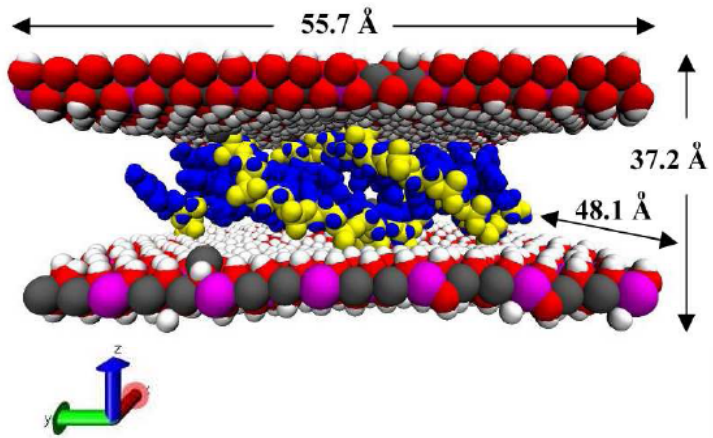
$$\sigma_{ij} = \frac{1}{V}\left(\frac{\partial E}{\partial \epsilon_{ij}}\right)_S$$

atomistic stress

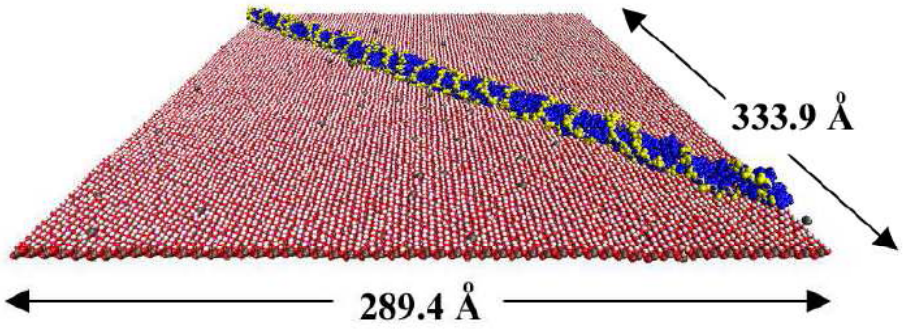
$$\sigma_{kl} = \frac{1}{V}\sum_{i=1}^{N}\left(\frac{m_i}{2}\mathbf{v}_i\mathbf{v}_i + \frac{1}{2}\sum_{j=1}^{N}\mathbf{F}_i\mathbf{r}_{ij}\right)_{kl}$$

Thyveetil et al. (2007) Chemistry of Materials

MD Models of DNA-Intercalated Clay Minerals

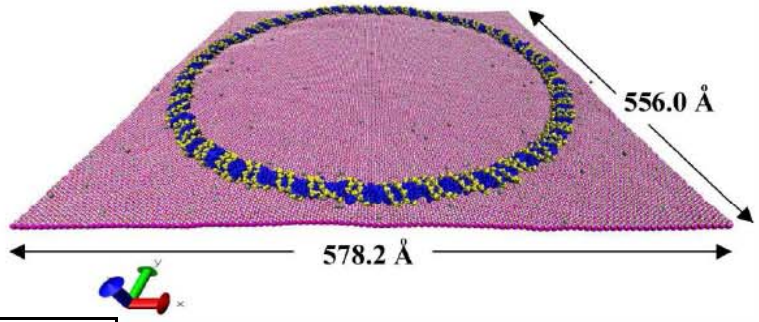


(a)



(b)

Layered Double Hydroxide



(c)

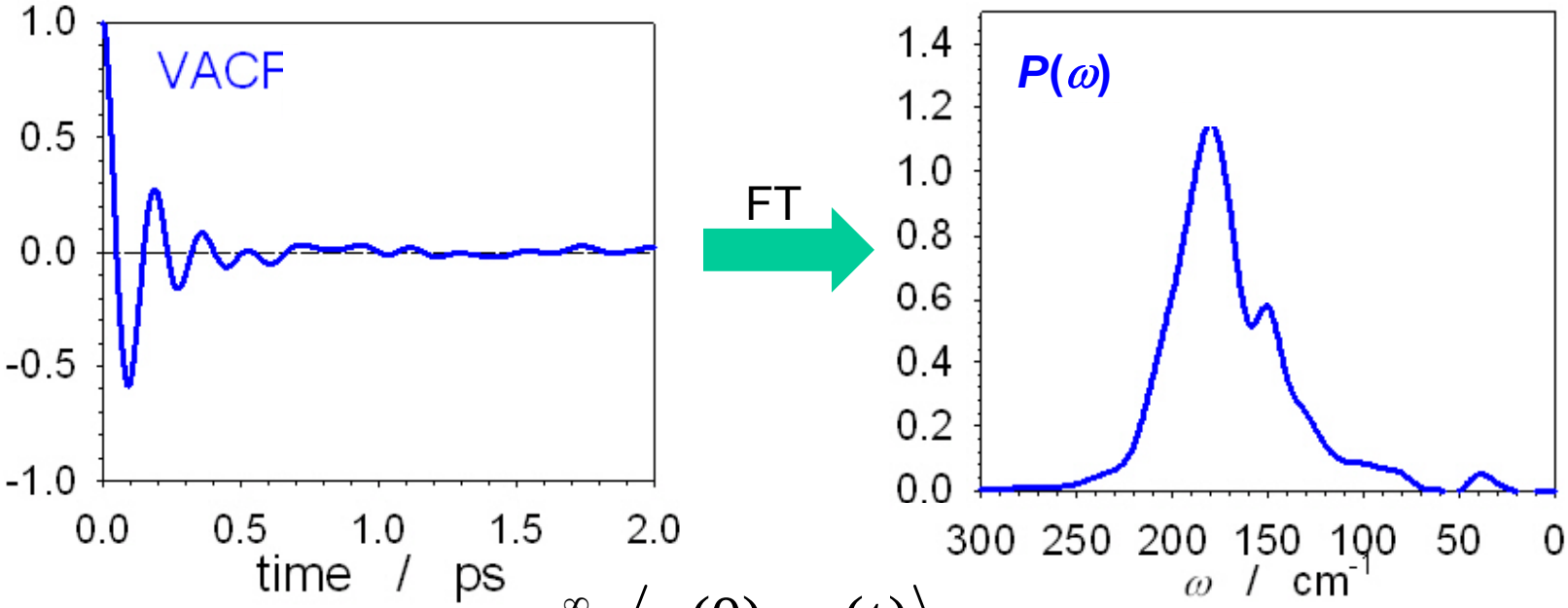
	Total Atoms	Water Molecules	DNA Base Pairs
(a)	10,142	1,406	12
(b)	256,608	23,328	108
(c)	1,026,432	93,312	480

AtomEye visualization

Thyveetil et al. (2008) Journal of the American Chemical Society

Dynamics of Individual Atoms
VACFs and Power Spectra

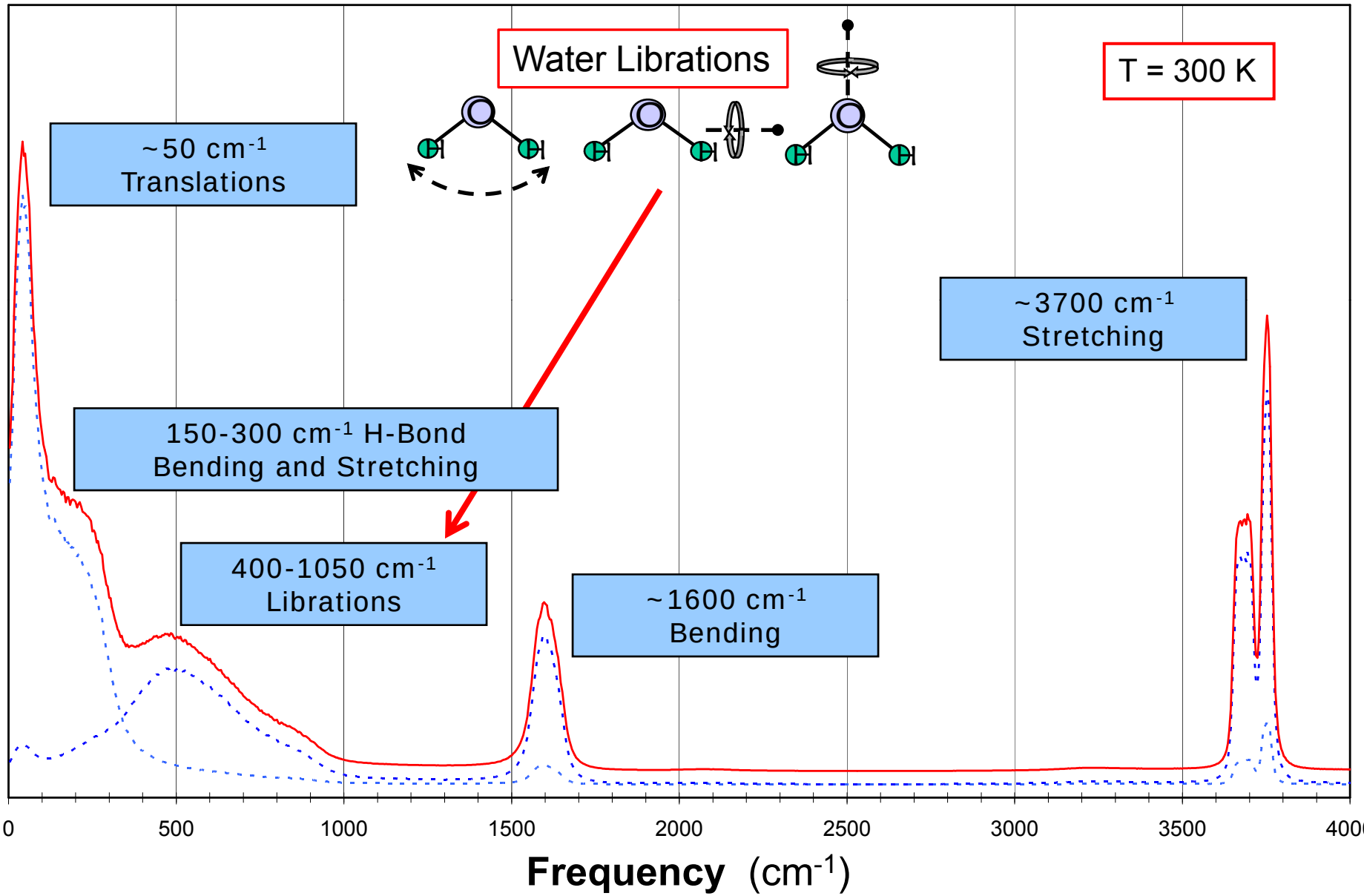
$$\mathrm{VACF} \equiv C_{vv}(t) = \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)^2\rangle} = \frac{1}{\langle \mathbf{v}(0)^2\rangle}\int \mathbf{v}(0)\cdot\mathbf{v}(\mathrm{t})\, d\Gamma$$



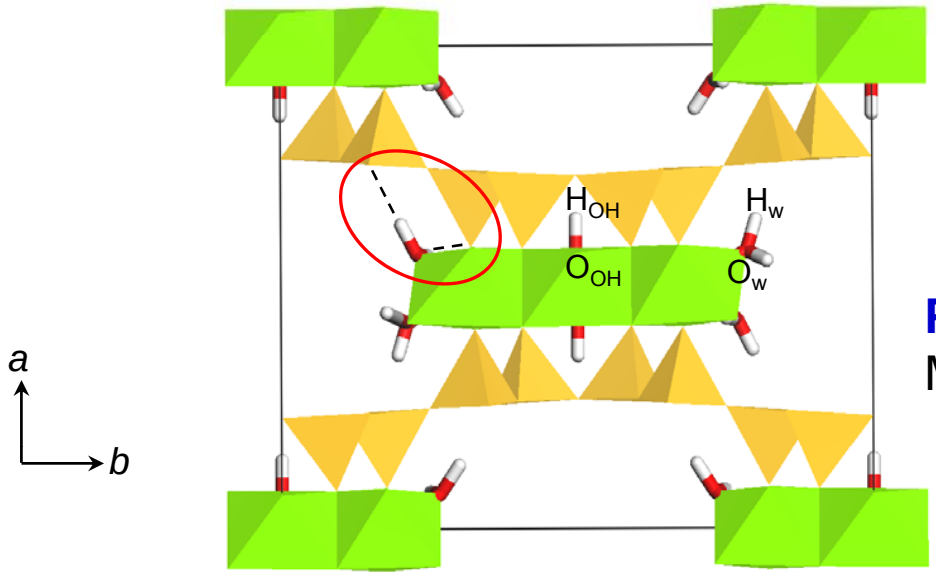
$$P(\omega) = \int_0^{\infty} \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)^2\rangle} \cos(\omega t)\, dt$$

VACF = velocity autocorrelation function

Power Spectra of Water



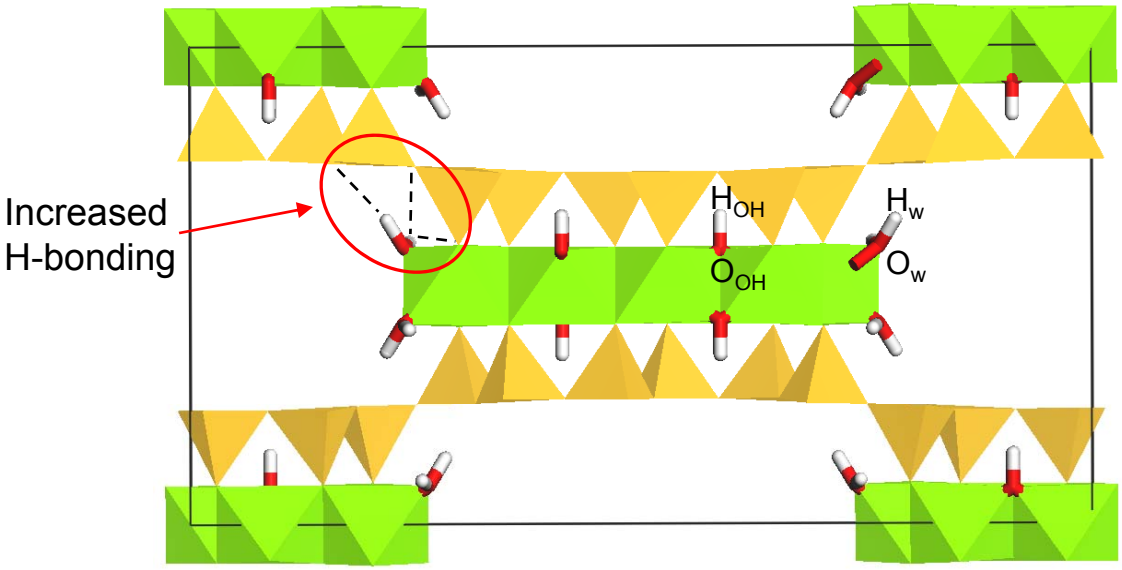
DFT Optimized Structures for Clay Phases



- VASP DFT code
- GGA with projector-augmented wave

Palygorskite

$Mg_5Si_8O_{20}(OH)_2 \cdot 8H_2O$



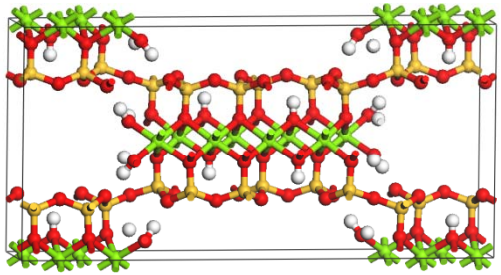
Sepiolite

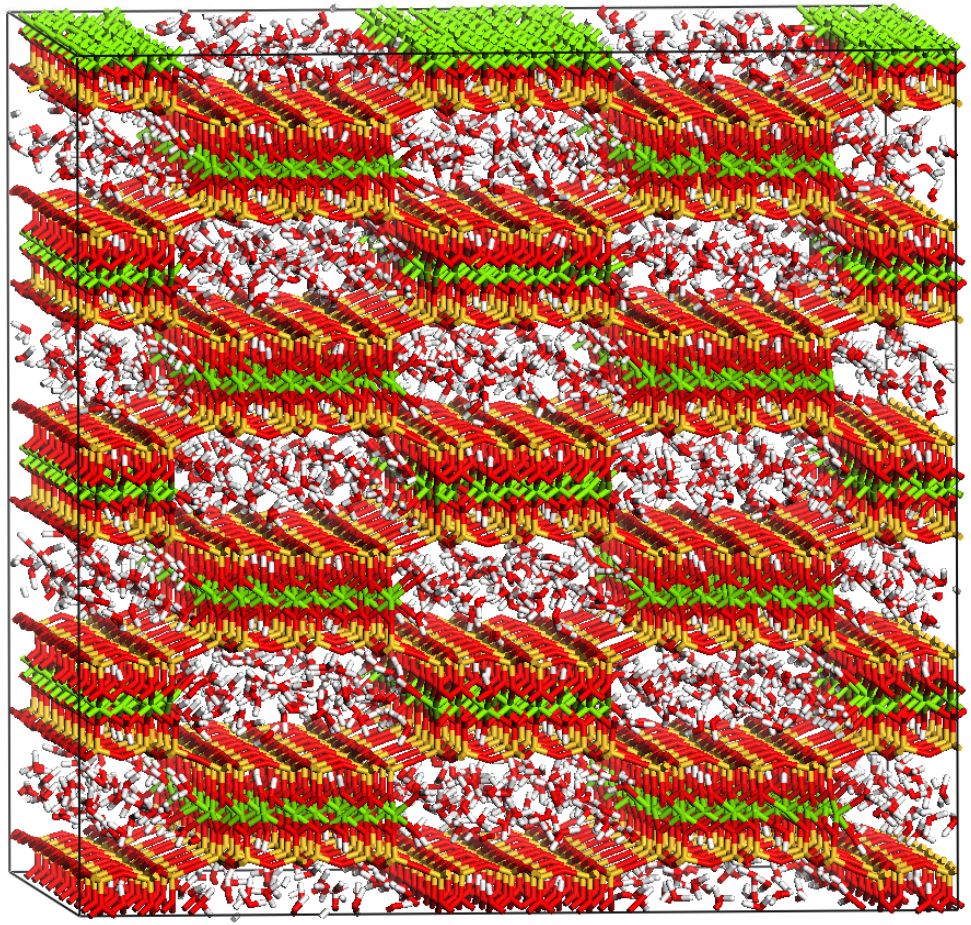
$Mg_8Si_{12}O_{30}(OH)_4 \cdot 12H_2O$

Ockwig et al. (2009)
Journal of the American Chemical Society

Classical and DFT Models for MD

Sepiolite Example





Classical MD — large scale

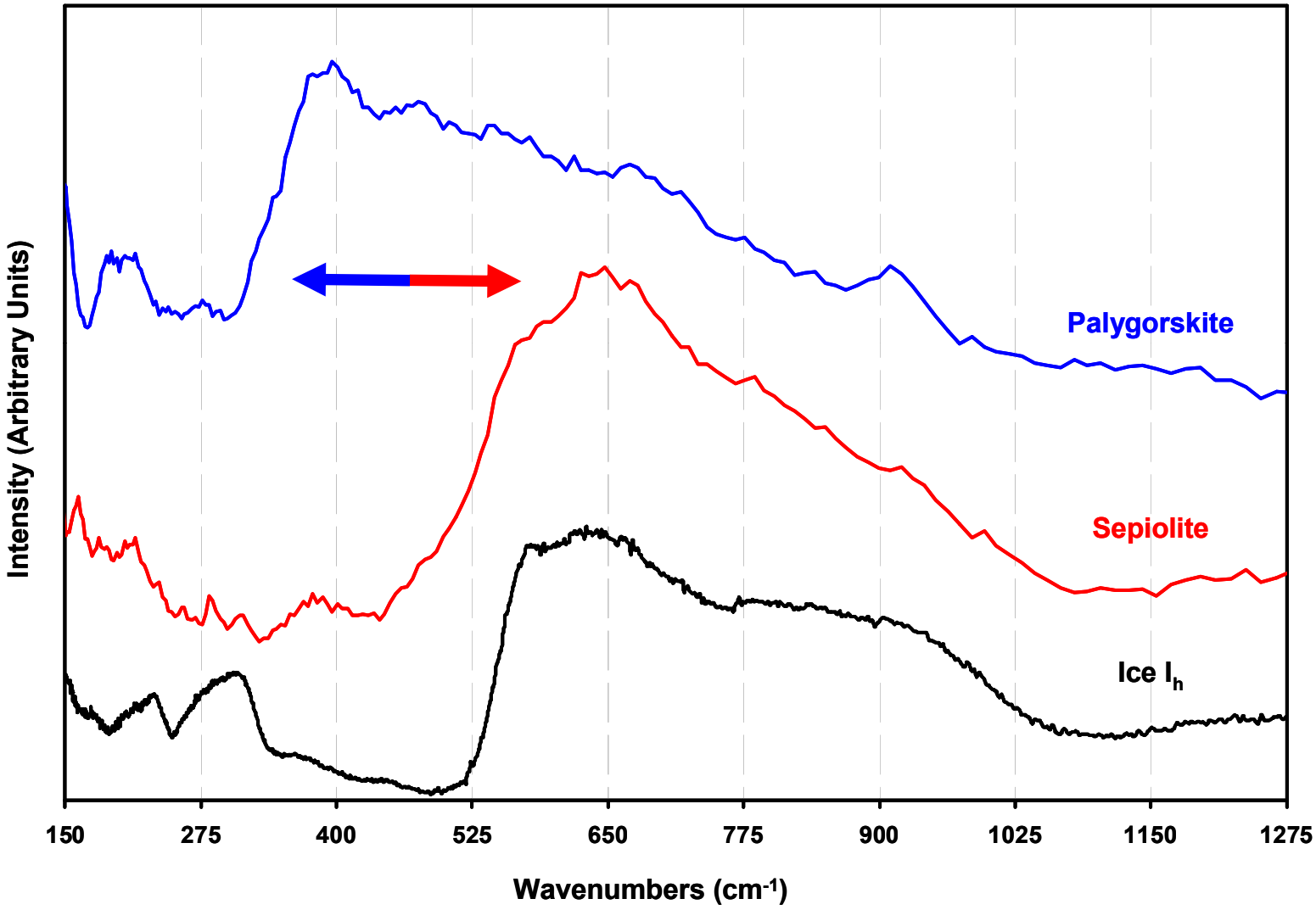
- LAMMPS classical code with CLAYFF
- 250 ps *NVT* and *NPT* MD to equilibrate then 1000 ps for production run
- 40 ps *NVT* MD for VACF calculations
- Structural and vibrational analysis using MD trajectory

Ab Initio MD — unit cell

- VASP DFT code
- GGA with projector-augmented wave
- AIMD for 62 ps *NVT*
- Structural and vibrational analysis using MD trajectory

Sepiolite: 15,040 atoms with 1920 waters
Palygorskite: 20,130 atoms with 2640 waters

INS Spectra for Clay Phases and Ice



Inelastic neutron scattering (INS) data of hydrated palygorskite, hydrated sepiolite, and ice Ih at 90 K

LAMMPS Software

Large-scale Atomic/Molecular Massively Parallel Simulator

LAMMPS is a classical molecular dynamics code that models an ensemble of particles in a liquid, solid, or gaseous state. It can model atomic, polymeric, biological, metallic, granular, and coarse-grained systems using a variety of force fields and boundary conditions. LAMMPS can efficiently model up to millions or billions of particles (atoms).

- Runs on a single processor or in parallel
- Distributed-memory message-passing parallelism (MPI)
- Spatial-decomposition of simulation domain for parallelism
- Open-source distribution
- Highly portable C++
- Optional libraries used: MPI and single-processor FFT
- Easy to extend with new features and functionality
- Runs from an input script
- Syntax for defining and using variables and formulas
- Syntax for looping over runs and breaking out of loops
- Run one or multiple simulations simultaneously (in parallel) from one script

Steve Plimpton, Sandia National Laboratories
lammps.sandia.gov

Computational Resources

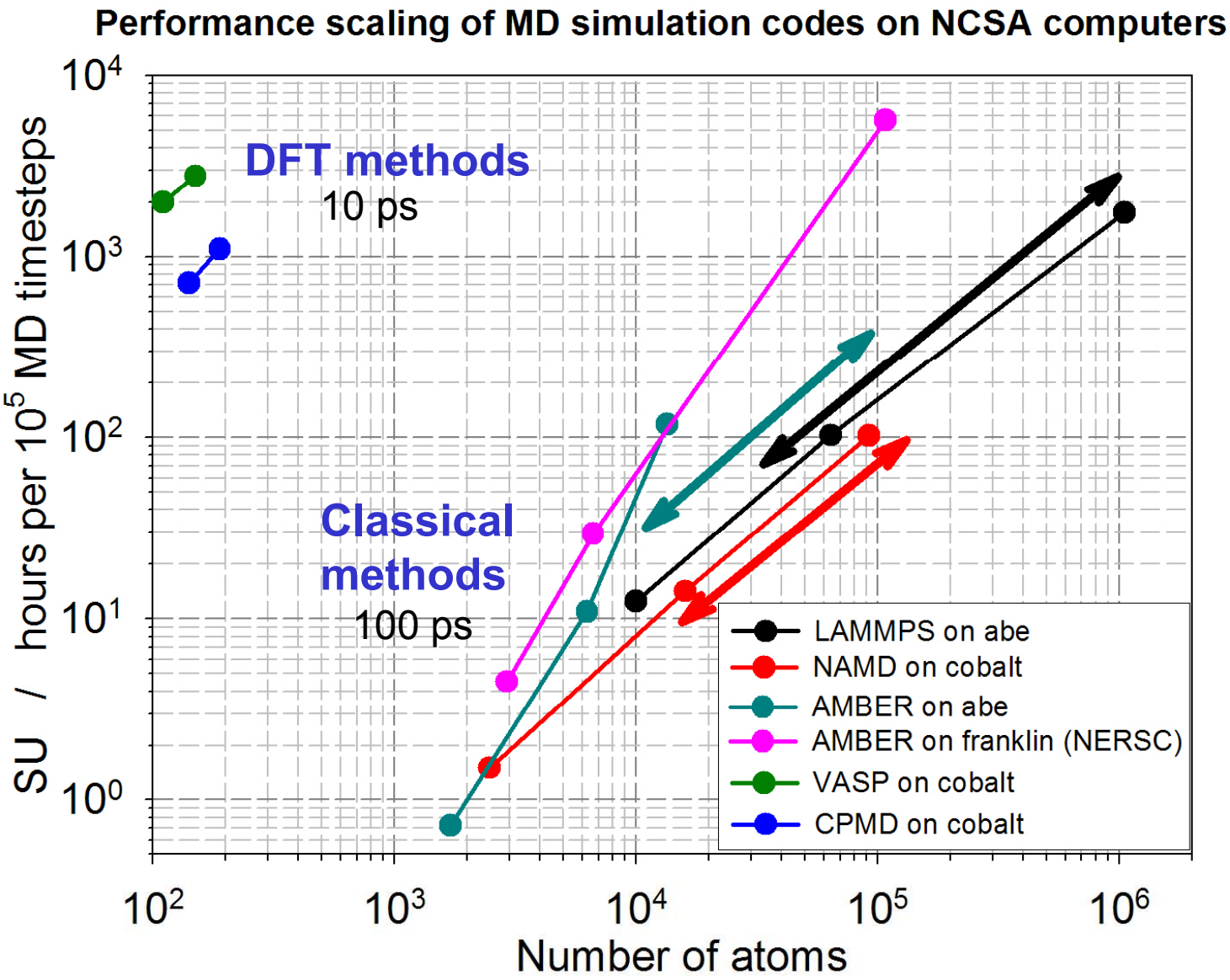
Sandia Geochemistry Facility
- 42-node AMD and Apple clusters with 100 processors

Sandia Thunderbird
- More than 53 Teraflops
- 4,480 compute nodes
- Soon to be decommissioned

Sandia Red Sky
- 169 Teraflops
- 960 node with 7,680 cores
- Scalable and extensible design
- On-line later this year

NM Encanto
- 172 Teraflops
- 1,792 nodes with 14,336 processors
- New Mexico Computing Alliance Center

Relative Performance



Courtesy of Andrey Kalinichev

What's Needed for Chemical Accuracy?

GOAL: Develop computational approaches that are highly accurate for the right system. Get the right answer for the right reason.

Predict equilibrium chemistry: ***Selectivity***

Change in K_{eq} @ 298 K

$K_{eq} = 1$	50:50	$\Delta G =$ 0 kcal/mol
$K_{eq} = 10$	90:10	$\Delta G =$ 1.4 kcal/mol
$K_{eq} = 100$	99:1	$\Delta G =$ 2.8 kcal/mol

Predict accurate rates: ***Reactivity***

Absolute rates @ 298 K

Factor of 10 in rate @ 25°C is a change in E_a of 1.4 kcal/mol

Do this in a complex system where the model represents the system accurately under the relevant conditions

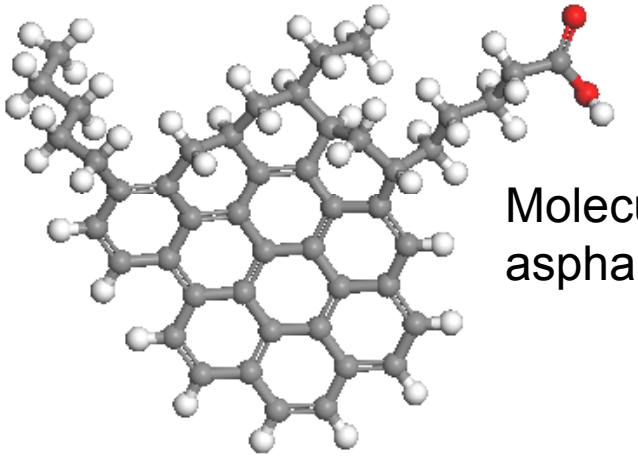
Complexity examples for system size:

- 100x100x100 nm box of water molecules would have 4 x 10^5 H_2O molecules
- Neutral pH requires 10^7 H_2O molecules per H^+/OH^- pair
- Minimum number of atoms in a molecular dynamics trajectory study will be 10^5 to 10^6 atoms for microseconds (10^{-6} s) with femtosecond (10^{-15} s) time steps.

Courtesy of David Dixon

Computational Challenges

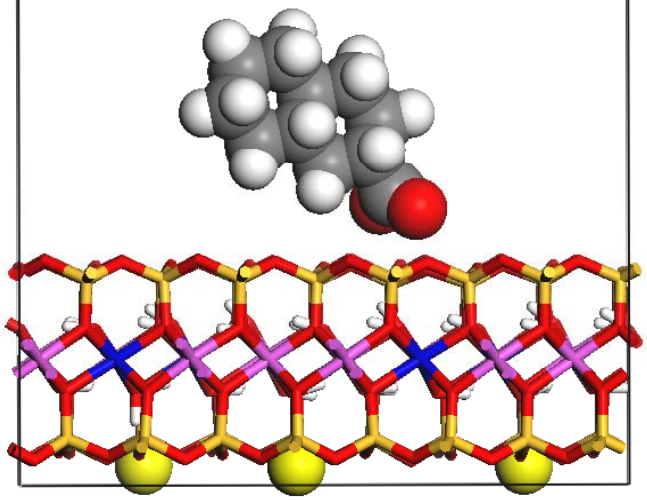
- Enhanced oil recovery
- Carbon sequestration
- Environmental contamination

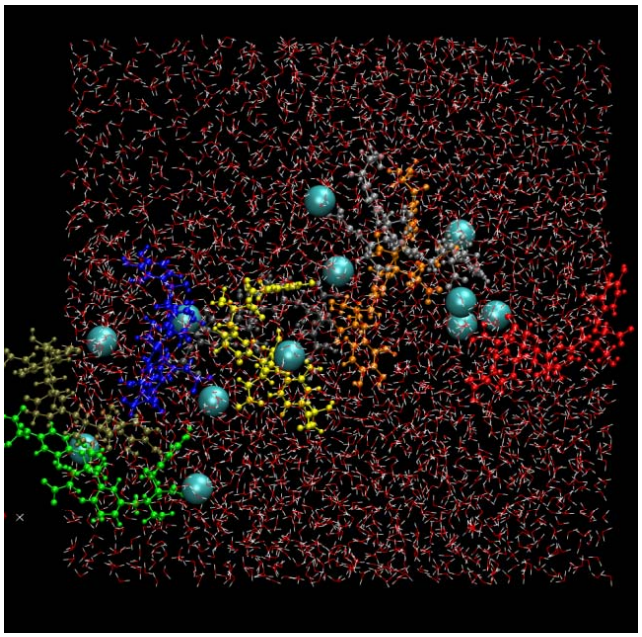


Molecular abstract for an asphaltene (only ~10%)

VASP optimization
Napthoic acid adsorption
montmorillonite

~600 atoms

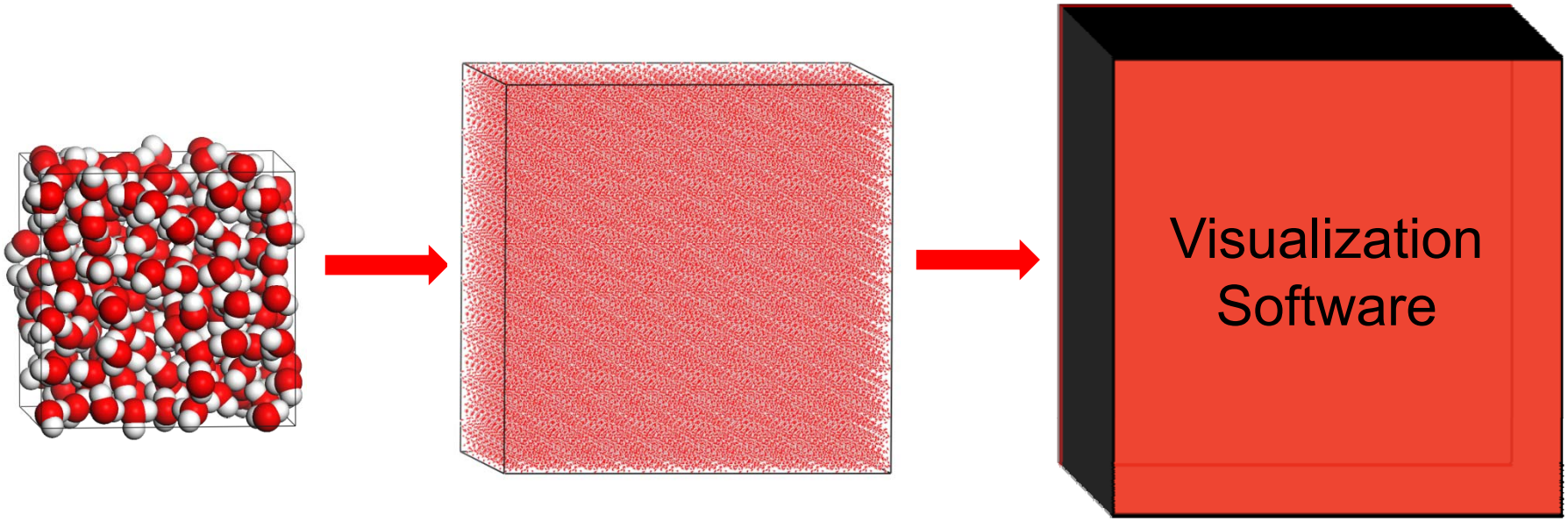




Natural organic matter
M^+ complex formation
Surface adsorption
Aggregation

t = 10 ns

The Future



216 water molecules
19 Å periodic box

110,000 water molecules
150 Å periodic box

10^6 water molecules
450 Å periodic box

Classical MD	100 ns to 1 μs 10^7 to10^8 atoms	Gigascale to Terascale
Ab Initio MD	100 ps to 1 ns 10^3 to10^4 atoms	Petascale to Exascale