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Molecular Simulations of Complex Fluid Interactions with Clay Mineral Surfaces

Jeffery Greathouse
Geochemistry Department
Sandia National Laboratories
Albuquerque, New Mexico

jagreat@sandia.gov

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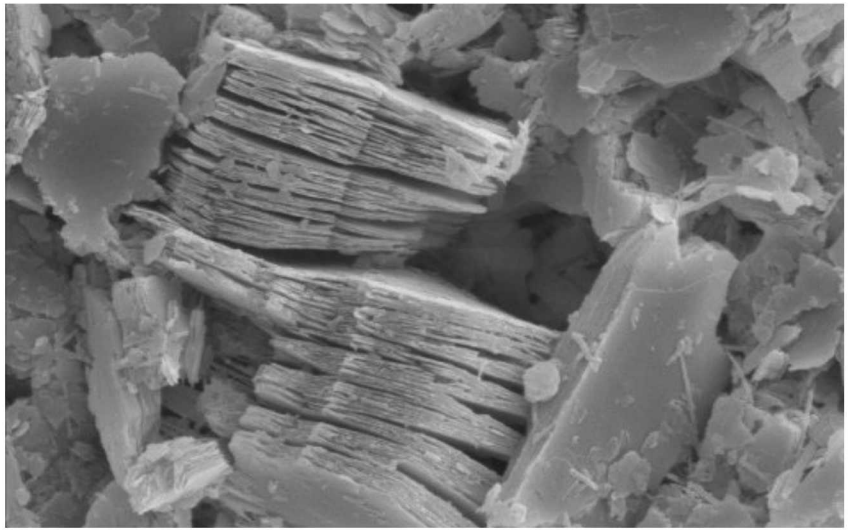
Notable UTSA Graduates

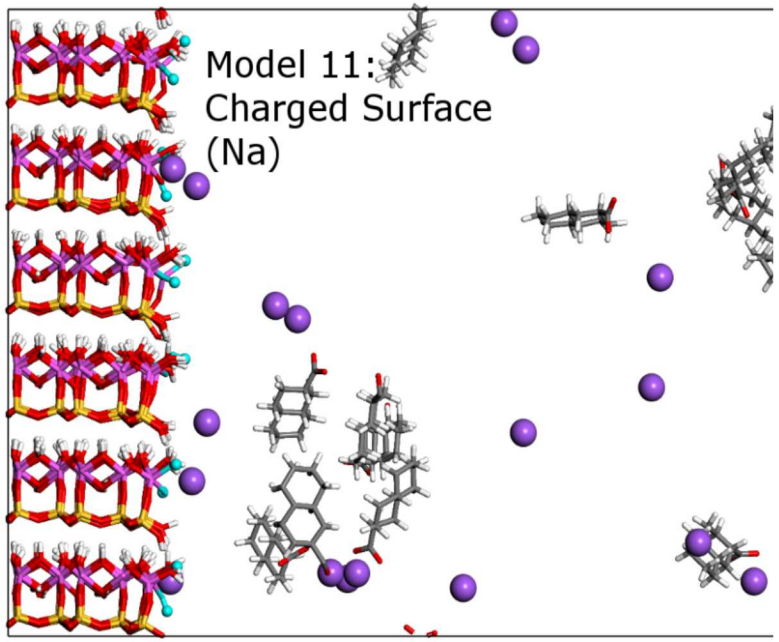
David Greathouse	UTSA	Biology / Kinesiology
Charlotte Greathouse	UTSA	Humanities
Jeffery Greathouse	Madison HS	

Outline

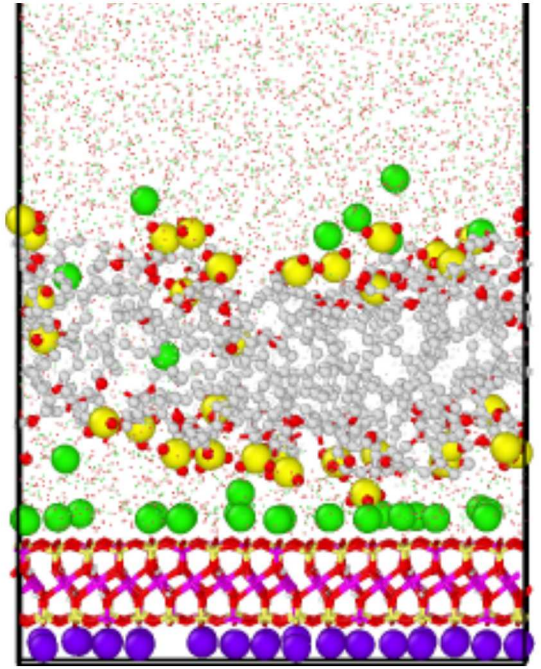
Molecular Simulation of Mineral-Fluid Interfaces: Techniques and Applications



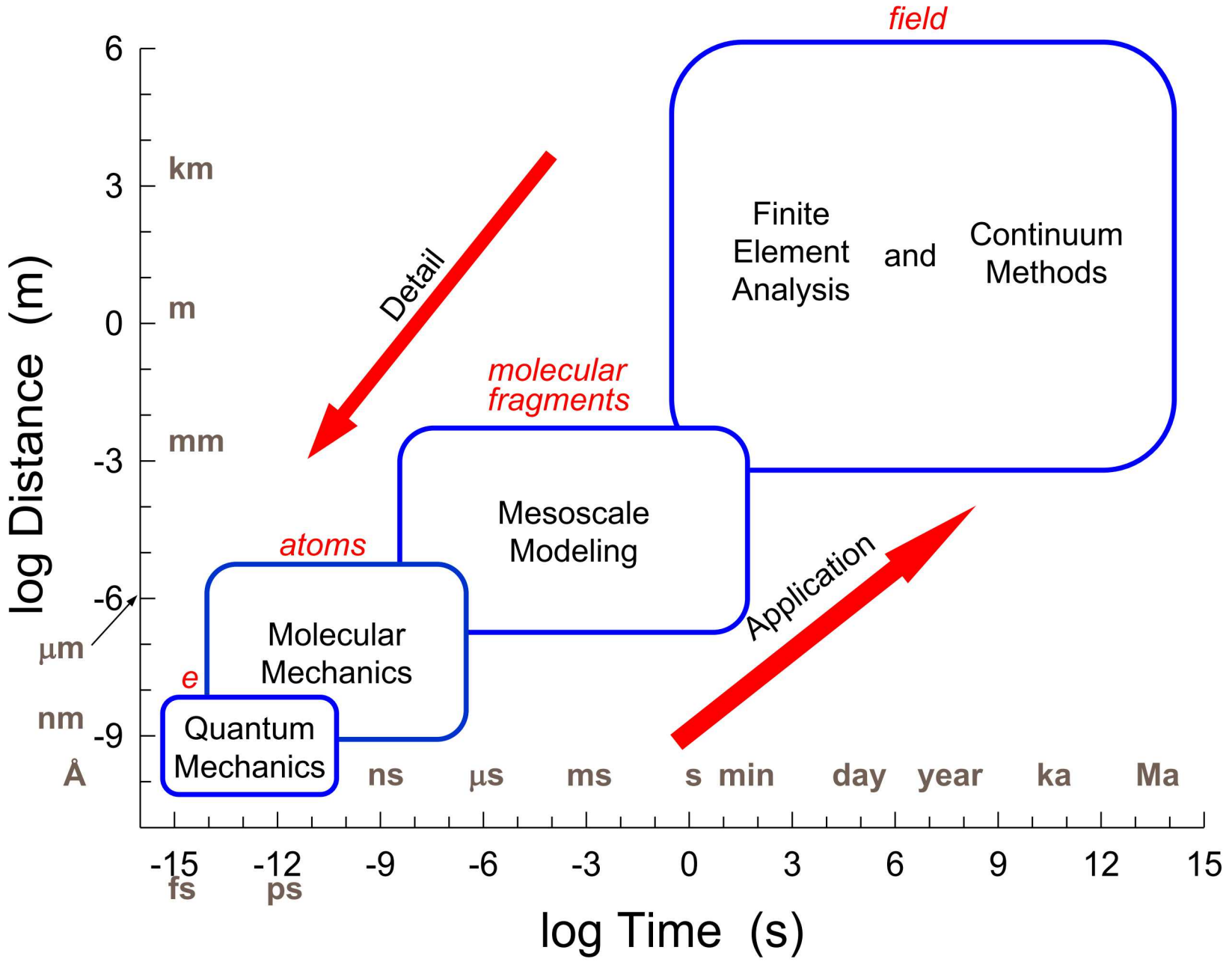
Adsorption of Crude Oil Molecules



Fluid Chemistry and Surfactant Behavior

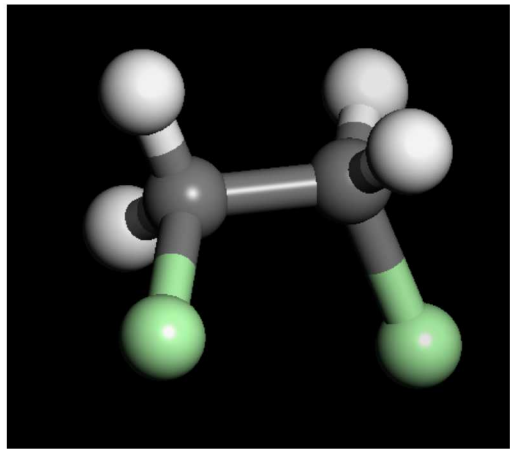


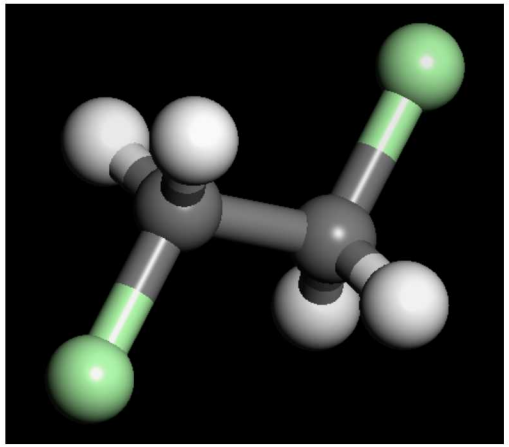
Simulations cover a wide range of length and time scales



Energy minimization of a molecule

Dichloroethane
$C_2H_4Cl_2$

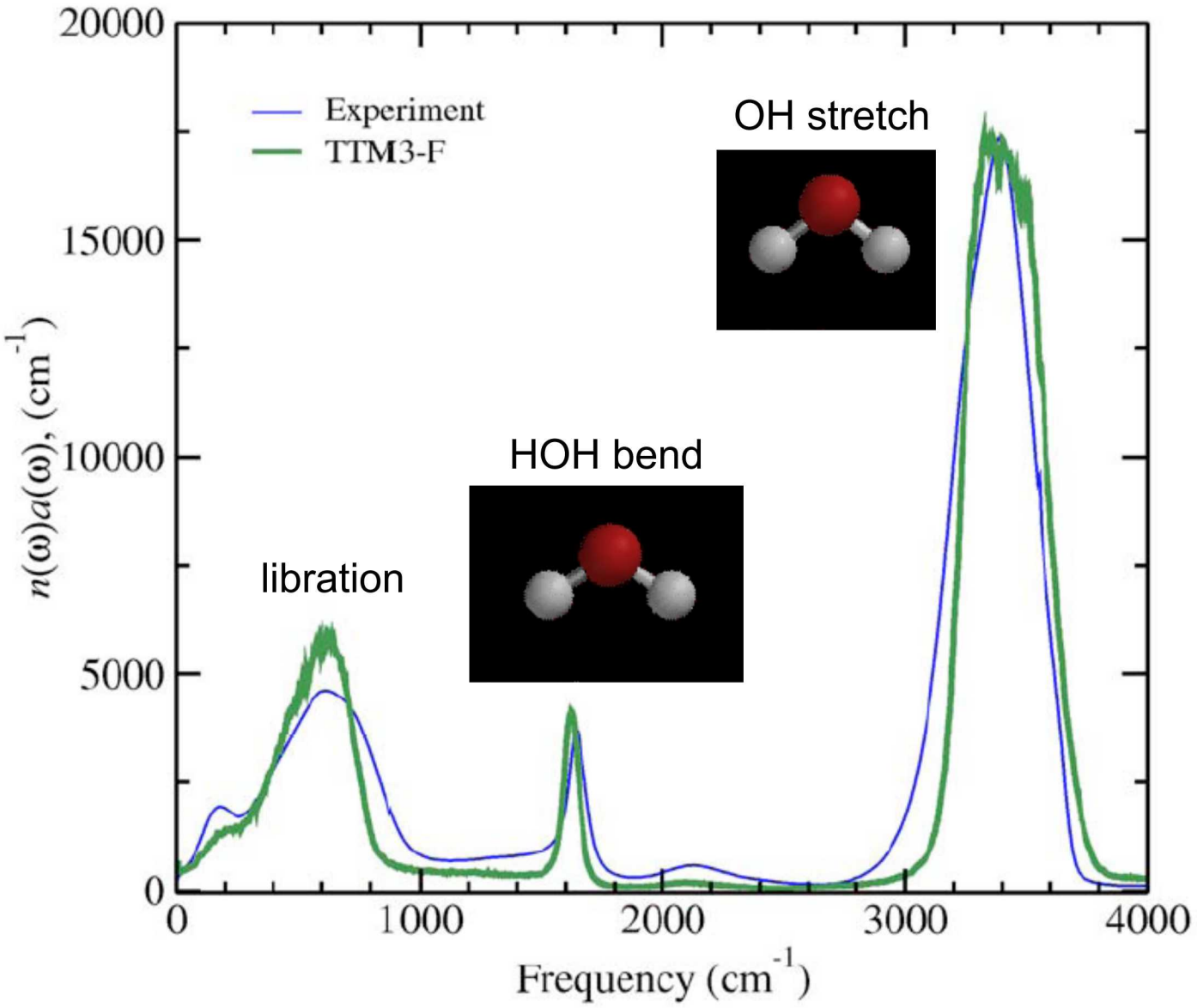




Intramolecular properties – vibrational spectrum

Vibrational spectrum of liquid water

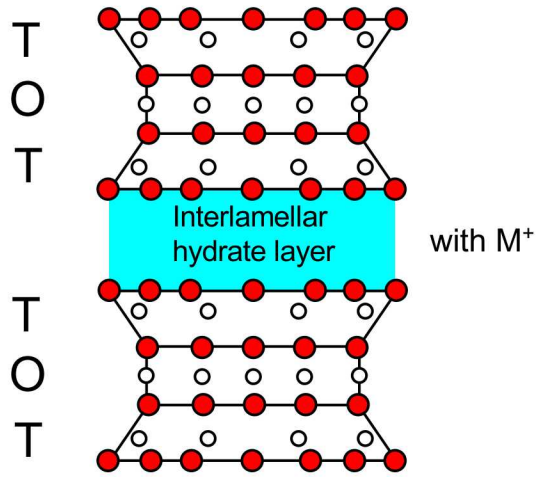
Fanourgakis and Xantheas, *J. Chem. Phys.* **2008**



Molecular simulation of clay minerals

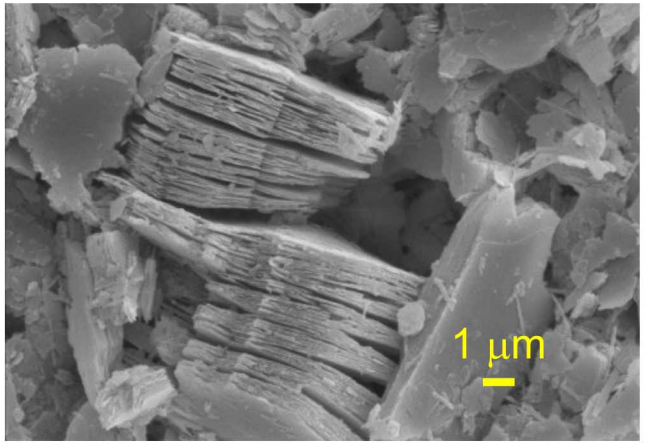
Crystal structure models of clay minerals are typically unknown

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

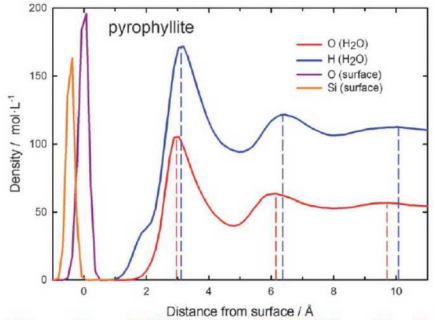


Atomistic simulations of clay minerals are non-trivial

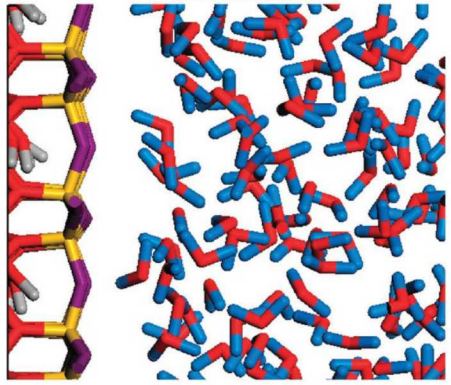
- Require accurate empirical energy forcefield; quantum methods are typically too costly
- Large unit cells or simulation supercells are required (100s to 10^6 atoms)
- Significant electrostatic fields associated with layer structure
- Validation of models is difficult



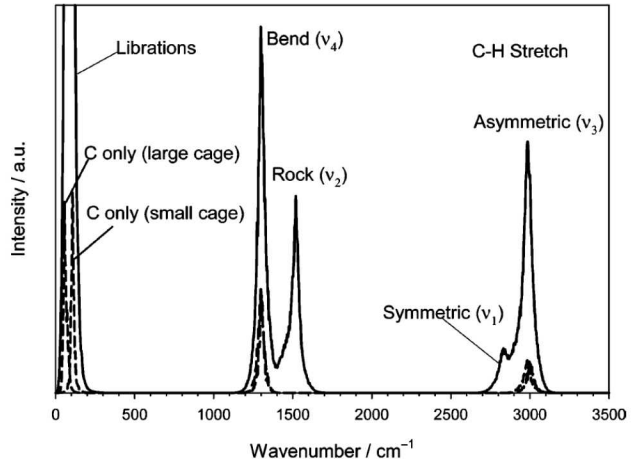
Molecular simulation of dynamical processes at mineral interfaces



Interfacial structure and dynamics

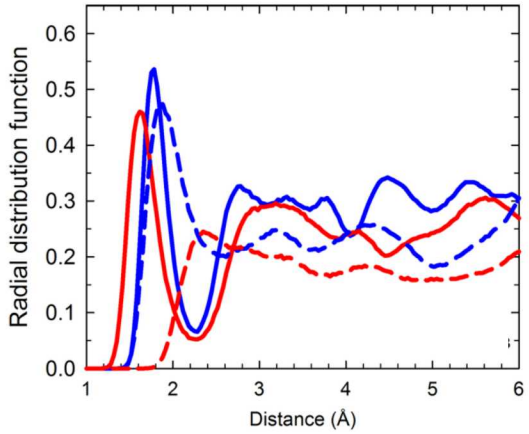


Vibrational motion



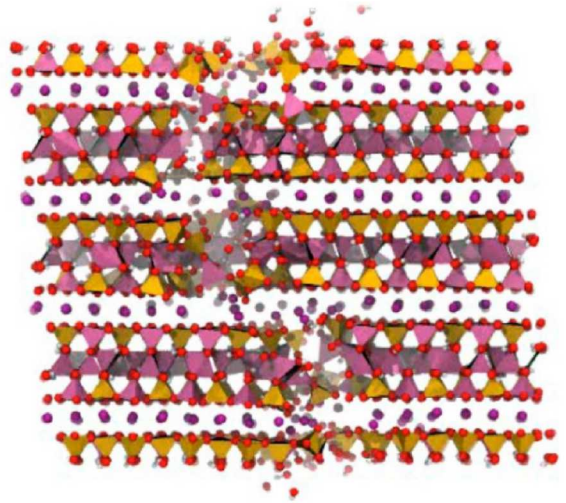
Clay Force Field energy expression

$$\text{ClayFF: } E = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{r_{ij}} + E_{\text{bonded}}$$



Local coordination

Mechanical properties



Clay hydration and swelling

Effect of interlayer cation
Teich-McGoldrick et al, *J. Phys. Chem. C* **2015**

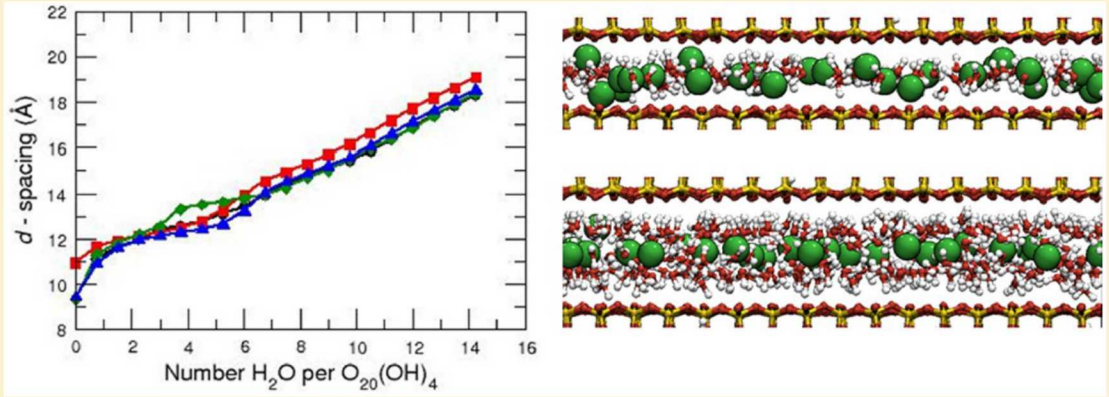
THE JOURNAL OF PHYSICAL CHEMISTRY C
Article
pubs.acs.org/JPCC

Swelling Properties of Montmorillonite and Beidellite Clay Minerals from Molecular Simulation: Comparison of Temperature, Interlayer Cation, and Charge Location Effects

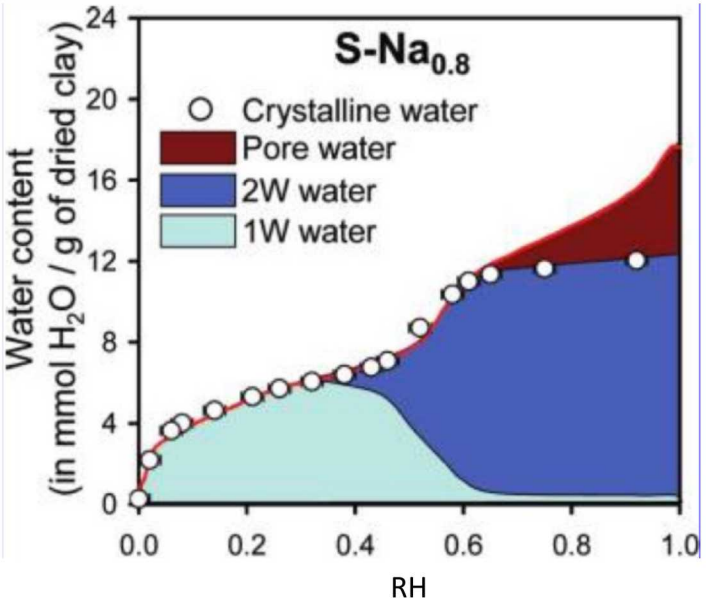
Stephanie L. Teich-McGoldrick,[†] Jeffery A. Greathouse,*[,†] Carlos F. Jové-Colón,[‡] and Randall T. Cygan[†]

[†]Geochemistry Department and [‡]Nuclear Waste Disposal Research and Analysis Department, Sandia National Laboratories, Albuquerque, New Mexico 87185, United States

Supporting Information



Interlayer vs pore water
Ferrage et al, *J. Phys. Chem. C* **2010**



Ion diffusion and electrical conductivity

THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

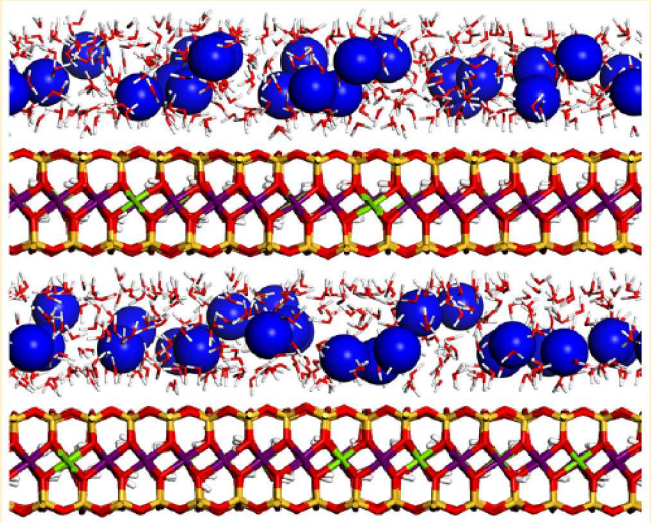
Molecular Dynamics Simulation of Diffusion and Electrical Conductivity in Montmorillonite Interlayers

J. A. Greathouse,*,† R. T. Cygan,† J. T. Fredrich,‡ and G. R. Jerauld‡

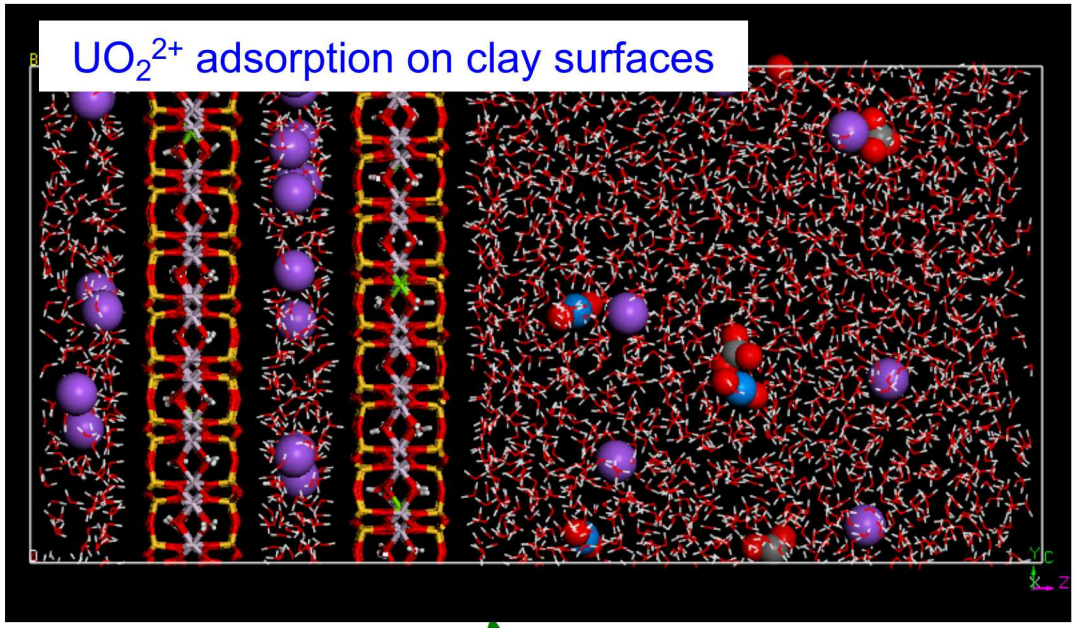
†Sandia National Laboratories, Albuquerque, New Mexico 87185-0754, United States

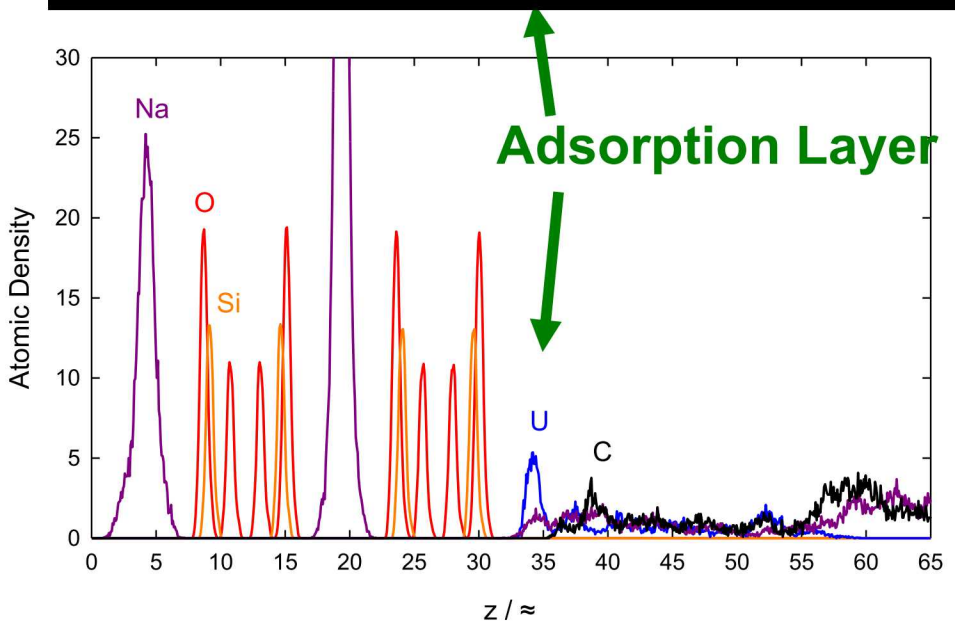
‡BP America, 501 Westlake Park Boulevard, Houston, Texas 77024, United States

ABSTRACT: The diffusion of water and ions in the interlayer region of smectite clay minerals represents a direct probe of the type and strength of clay–fluid interactions. Interlayer diffusion also represents an important link between molecular simulation and macroscopic experiments. Here we use molecular dynamics simulation to investigate trends in cation and water diffusion in montmorillonite interlayers, looking specifically at the effects of layer charge, interlayer cation and cation charge (sodium or calcium), water content, and temperature. For Na-montmorillonite, the largest increase in ion and water diffusion coefficients occurs between the one-layer and two-layer hydrates, corresponding to the transition from inner-sphere to outer-sphere surface complexes. Calculated activation energies for ion and water diffusion in Na-montmorillonite are similar to each other and to the water hydrogen bond energy, suggesting the breaking of water–water and water–clay hydrogen bonds as a likely



Adsorption of radionuclides

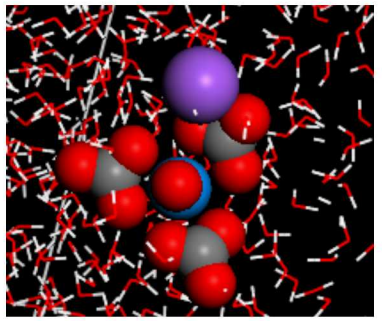


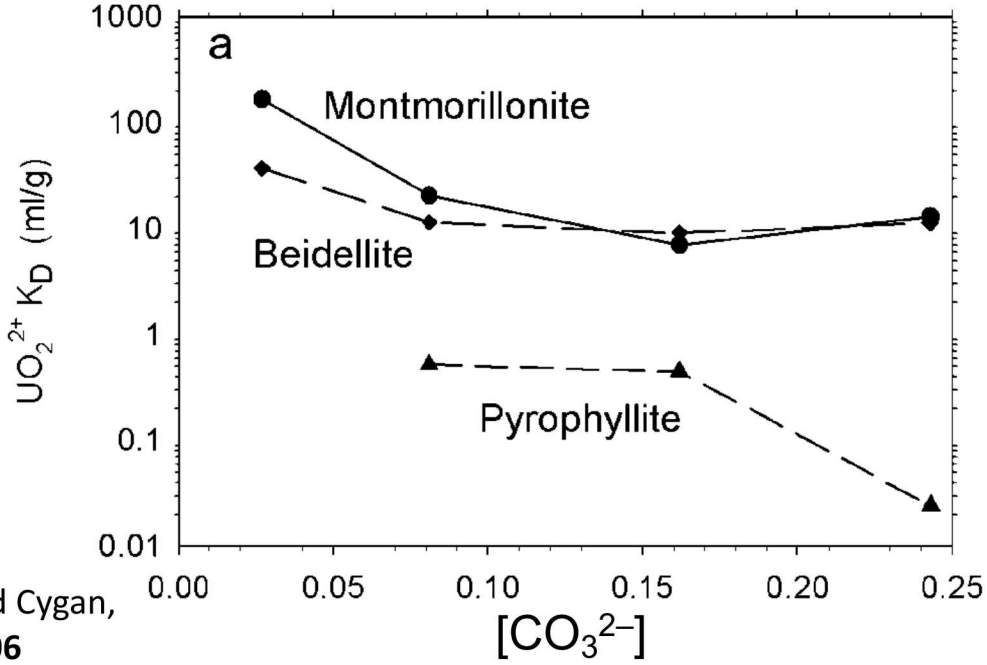


Greathouse and Cygan, *Phys. Chem. Chem. Phys.* **2005**

Solution concentration influences UO_2^{2+} adsorption

$[UO_2(CO_3)_3]^{4-}$

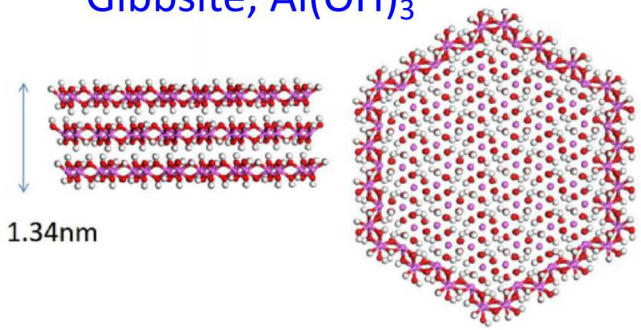


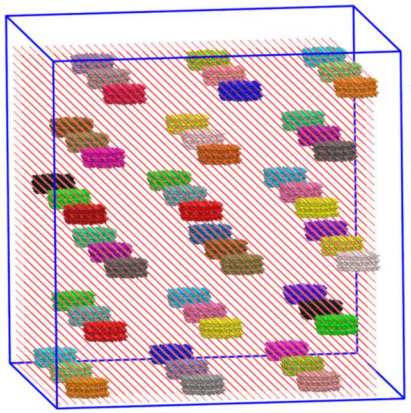


Greathouse and Cygan, *ES&T* **2006**

Gibbsite nanoparticle aggregation

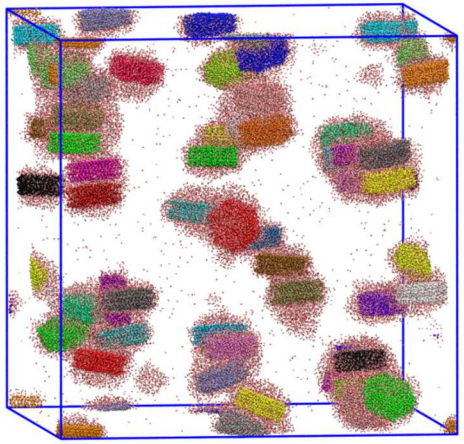
Gibbsite, $Al(OH)_3$



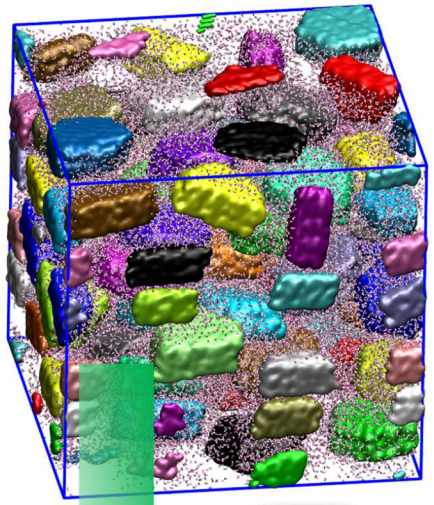


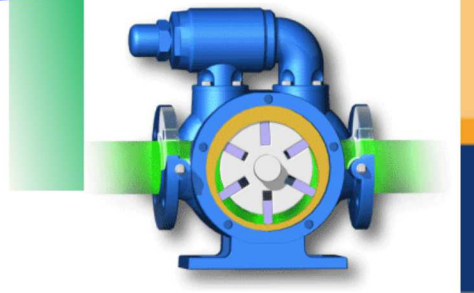
54 NPs, 55k H_2O
30 x 30 x 30 nm^3

NVT
0.3 ns
300 K

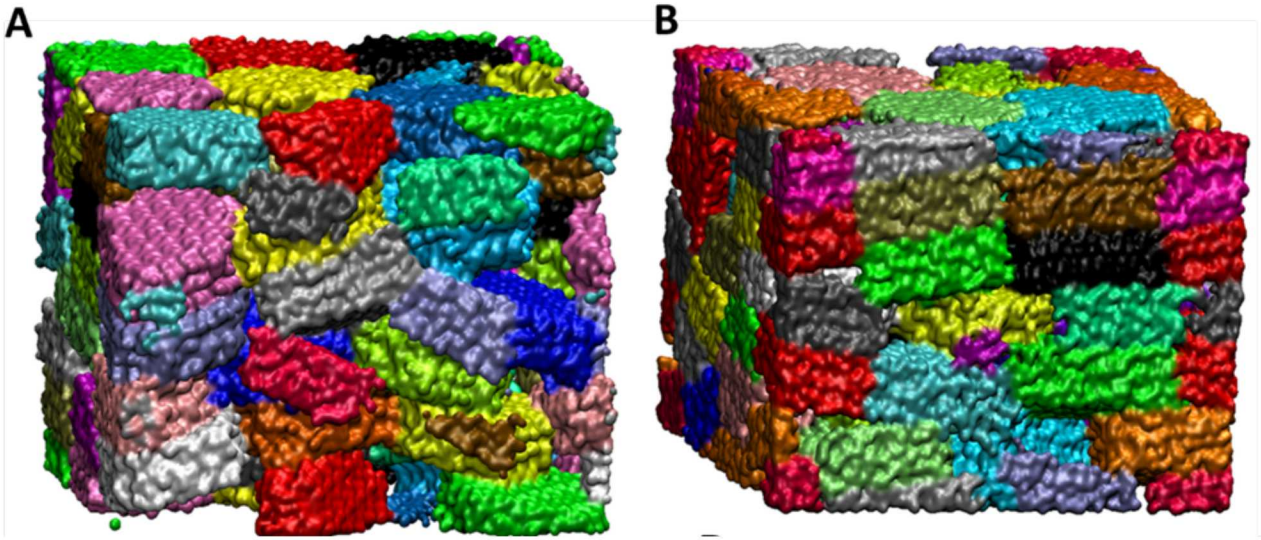


NPT
0.3 ns
300 K
100 MPa





'Virtual' pump removes waters from a pre-defined region.

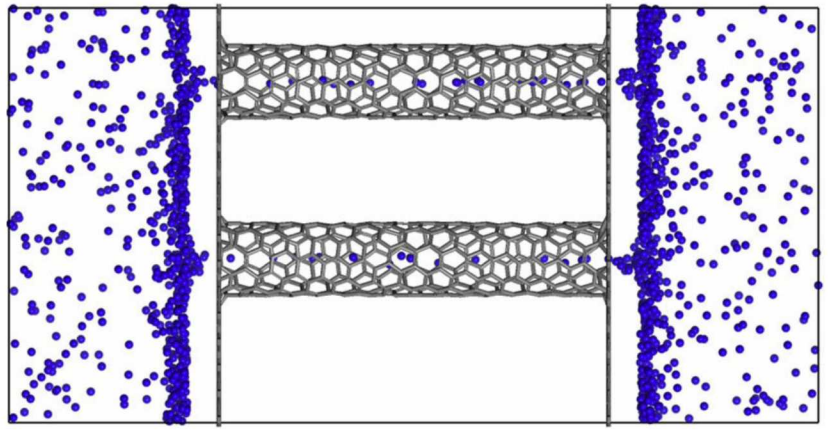


"Fast" dewatering

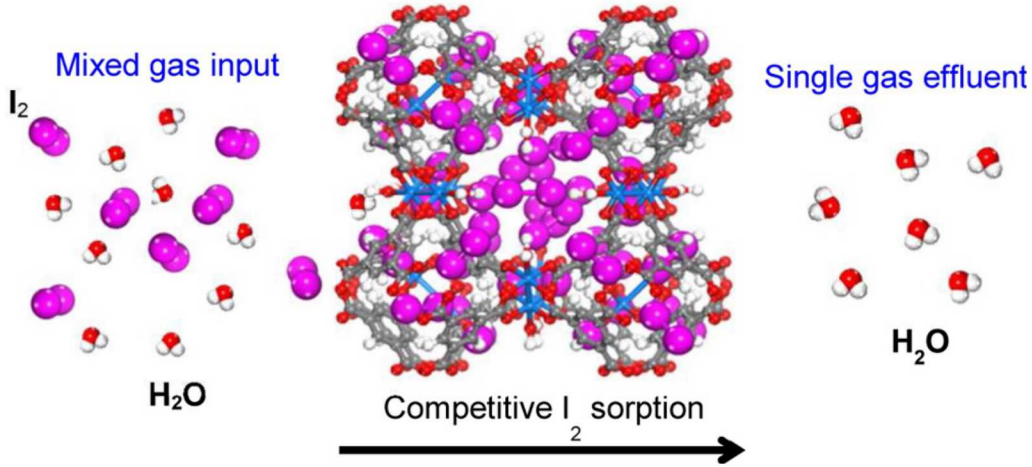
"Slow" dewatering

Ho et al, *Sci Rep.* **2017**

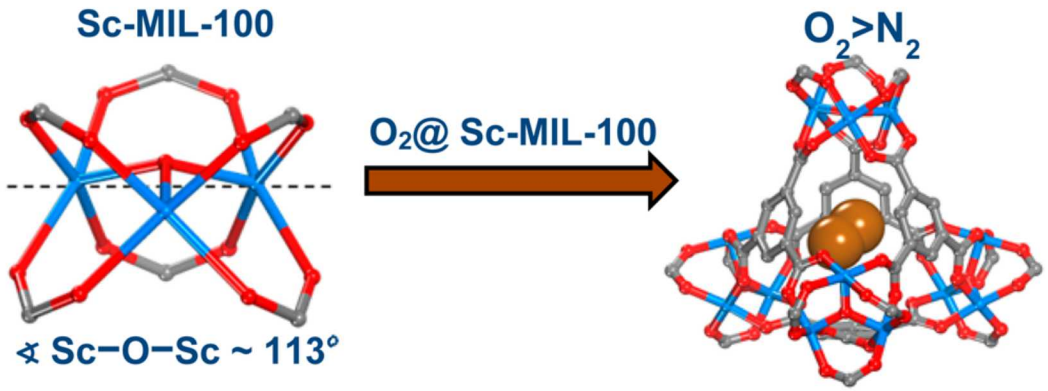
Materials for gas adsorption and separation



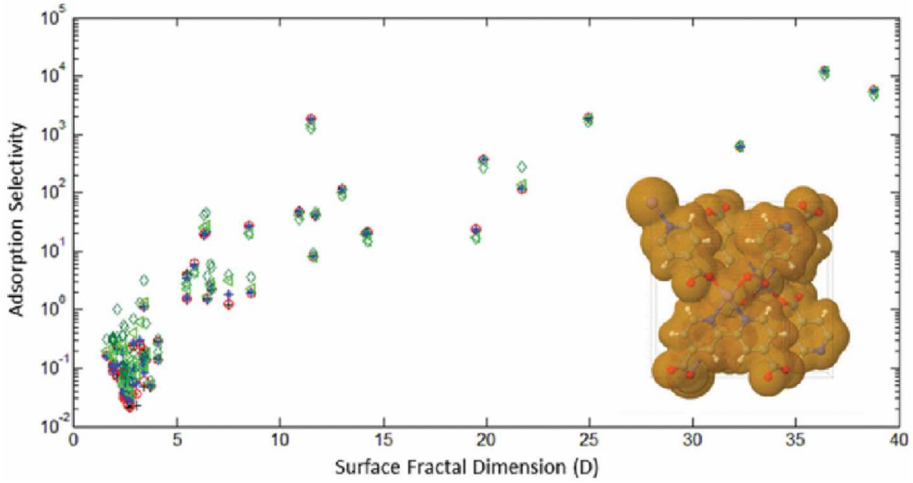
Gas diffusion in carbon nanotubes.
Greathouse et al, *Mol. Sim.* **2015**



Gas separation in MOFs.
Sava et al, *Chem. Mater.* **2013**



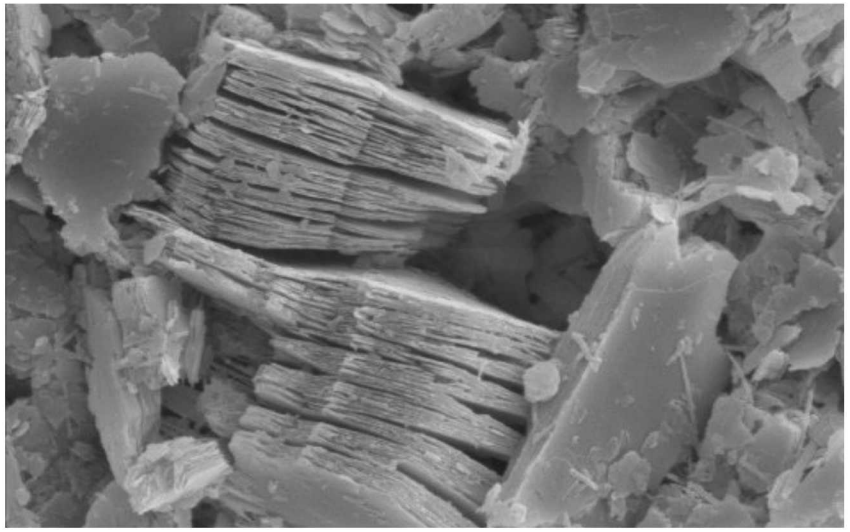
Selective gas adsorption in MOFs.
Sava et al, *Chem. Mater.* **2016**



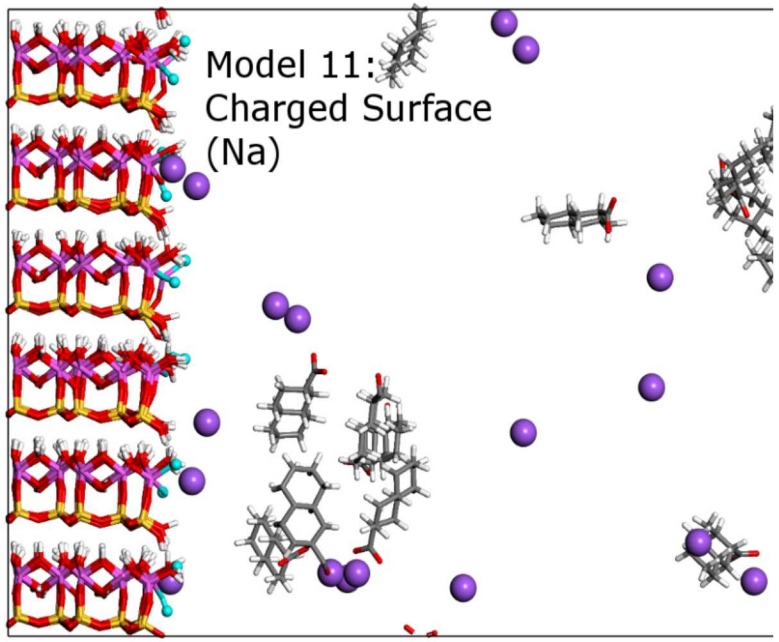
Computational screening of MOFs.
van Heest et al, *J. Phys. Chem. C* **2012**

Outline

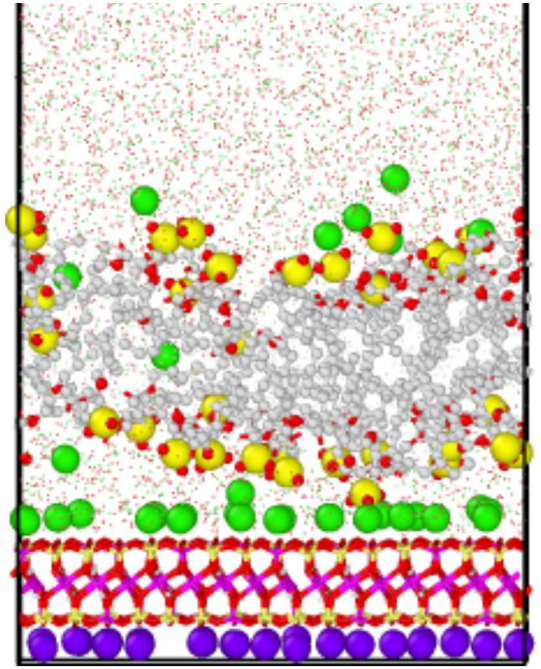
Molecular Simulation of Mineral-Fluid Interfaces: Techniques and Applications



Adsorption of Crude Oil Molecules

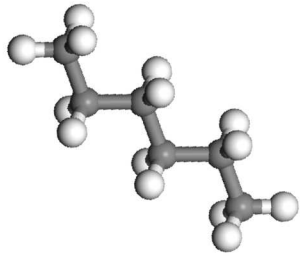


Fluid Chemistry and Surfactant Behavior

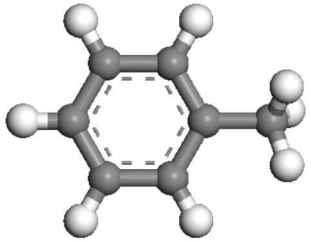


Adsorption of Crude Oil Molecules at Kaolinite Edges

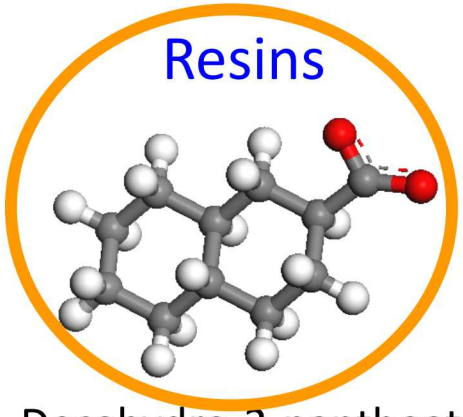
Saturates



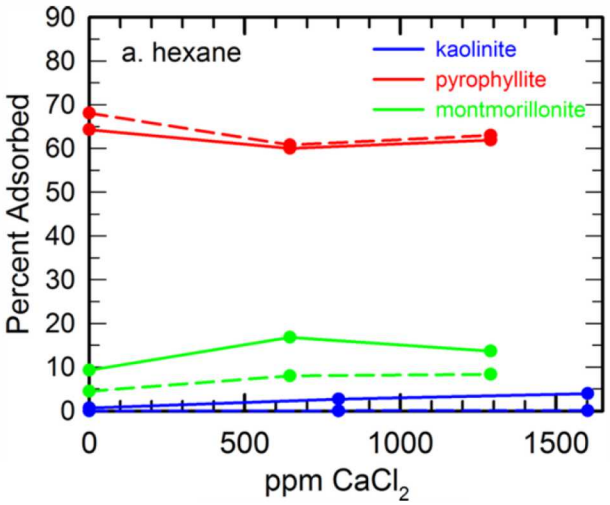
Aromatics

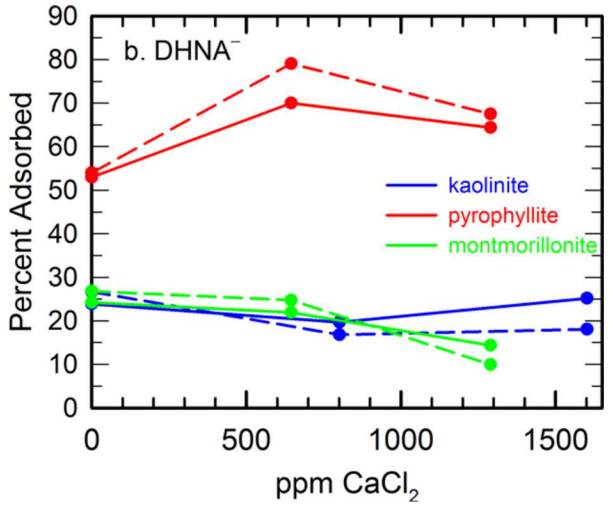


Resins



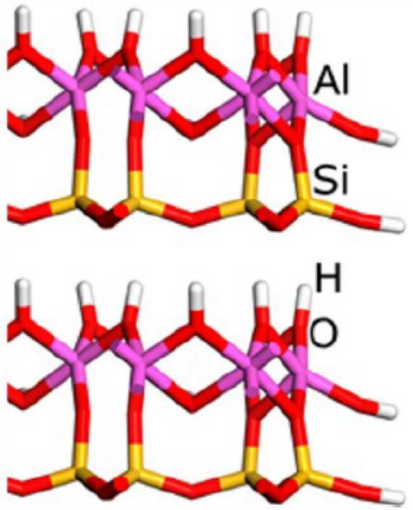
Decahydro-2-napthoate
($DHNA^-$)





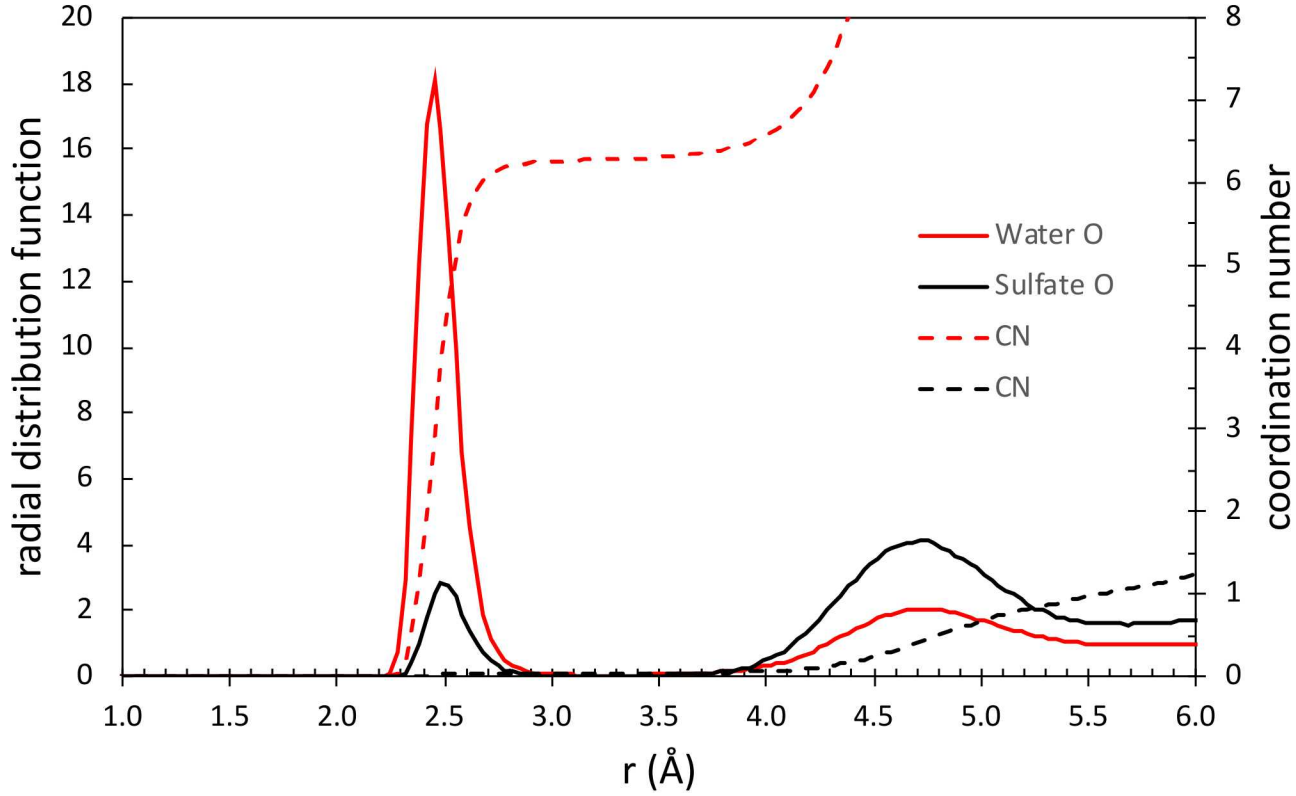
- Enhanced Oil Recovery (EOR): better understanding of the adsorption tendencies of crude oil components on mineral surfaces.
- Resins have polar groups:
  - Increased adsorption on hydrophilic surfaces.
  - Targeted in enhanced oil recovery efforts (e.g., low salinity waterflooding).
- Adsorption trends on clay basal surfaces have been modeled (no pH dependence).
  Greathouse et al, J. Phys. Chem. C **2017**, *121*, 22773
- Adsorption trends on pH-dependent edge surfaces is needed, particularly for resins.

MD Simulations of Resin Adsorption on Kaolinite Edges

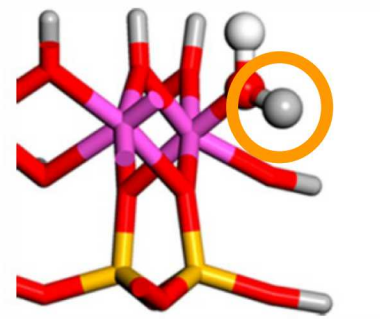


kaolinite (010) surfac

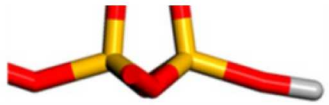
- (010) surface created from an 8 x 5 x 6 supercell.
  - Surface area 41.6 Å x 43.0 Å



nm².
Å thick.
rdinated but become
-H angle
/Ca²⁺ ions used
) initial
ch.



neutral

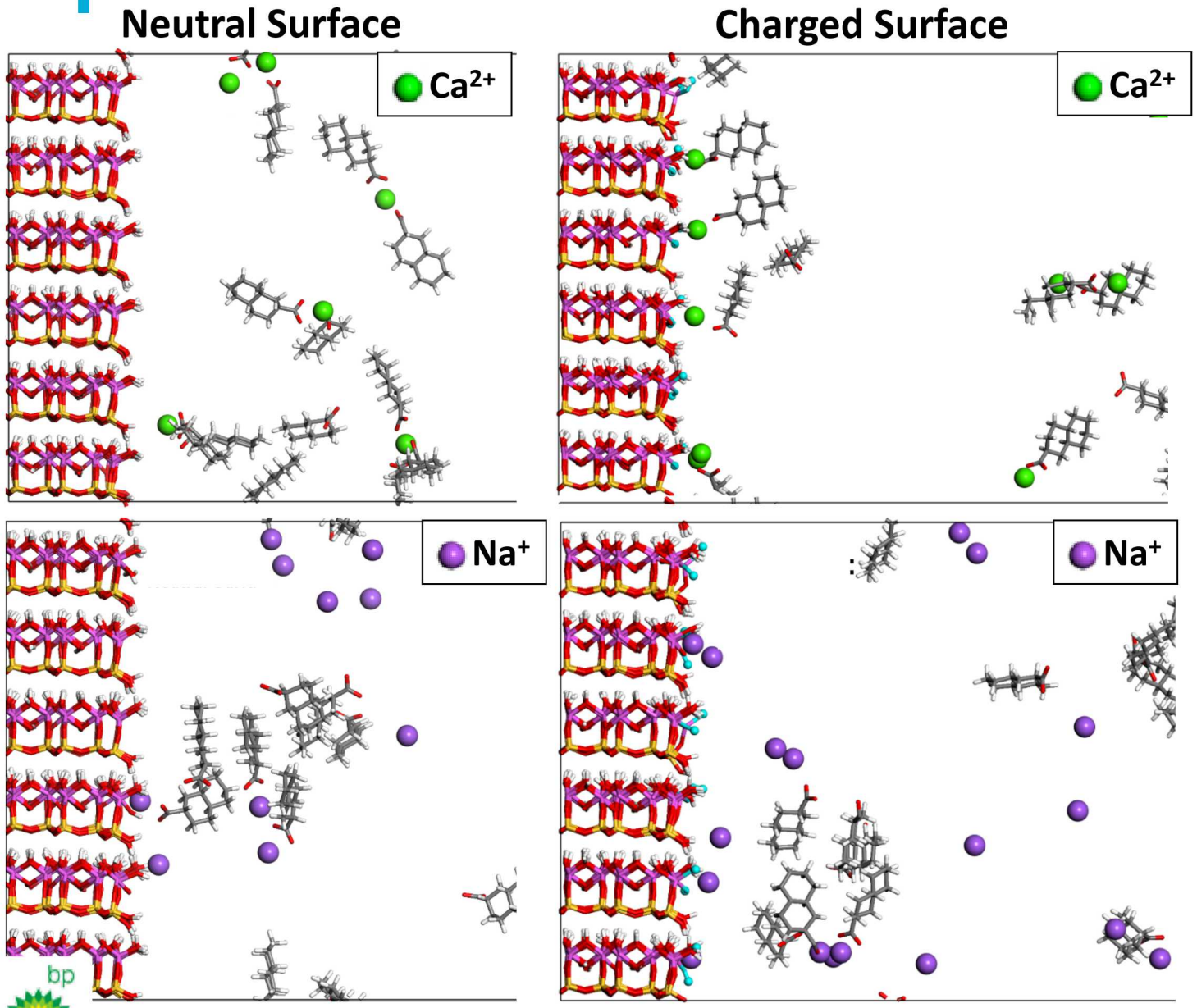


negative

- pH effects: negative surface charge created by removing a proton from adsorbed H_2O.

Zeitler et al, J. Phys. Chem. C **2017**, *121*, 22787

MD Snapshots Showing Adsorption Trends



Water molecules removed for clarity

Neutral Surface: $AlO_2(OH)_3(OH_2)$

- Very little interaction with edge sites (only Na^+).
- Strong ion pairing between resin and Ca^{2+} but not with Na^+.

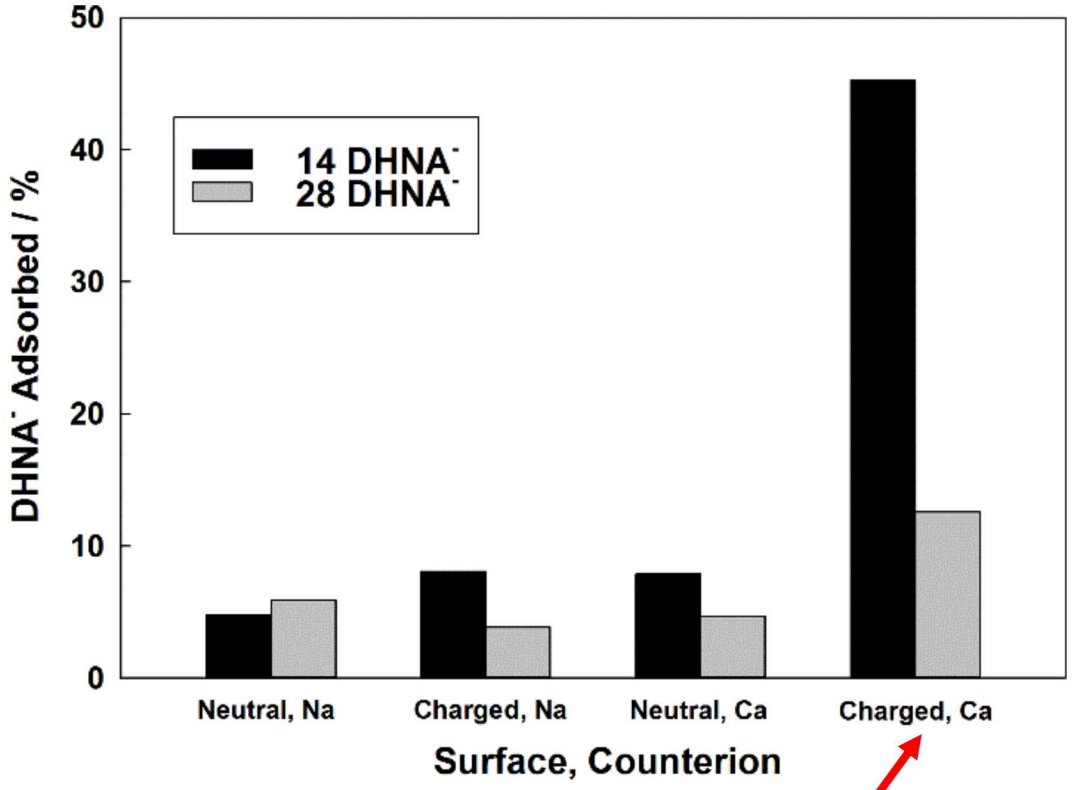
Charged Surface: $[AlO_2(OH)_4]^-$

- Increased cation adsorption.
- Significant adsorption of Ca-bridged resin species.

Zeitler et al, J. Phys. Chem. C **2017**, *121*, 22787

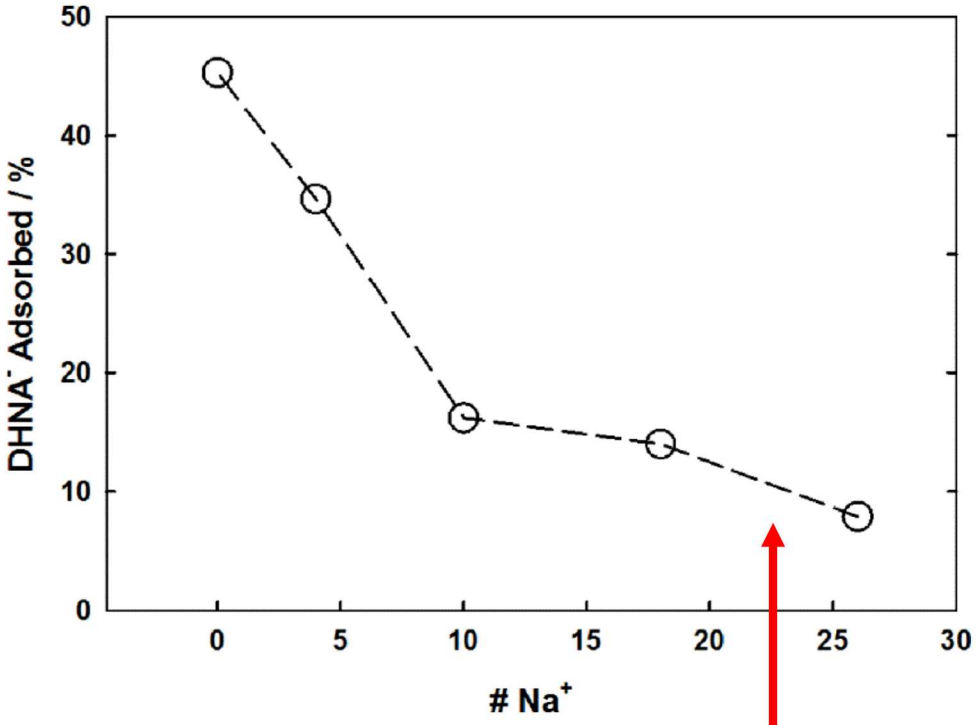
Trends in Resin Adsorption

Effect of surface charge



cation bridging
Divalent cation, charged surface

Effect of cation (monovalent/divalent)

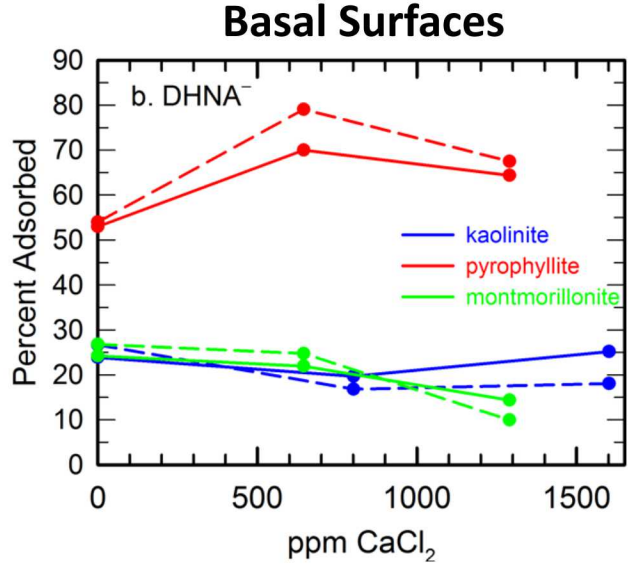


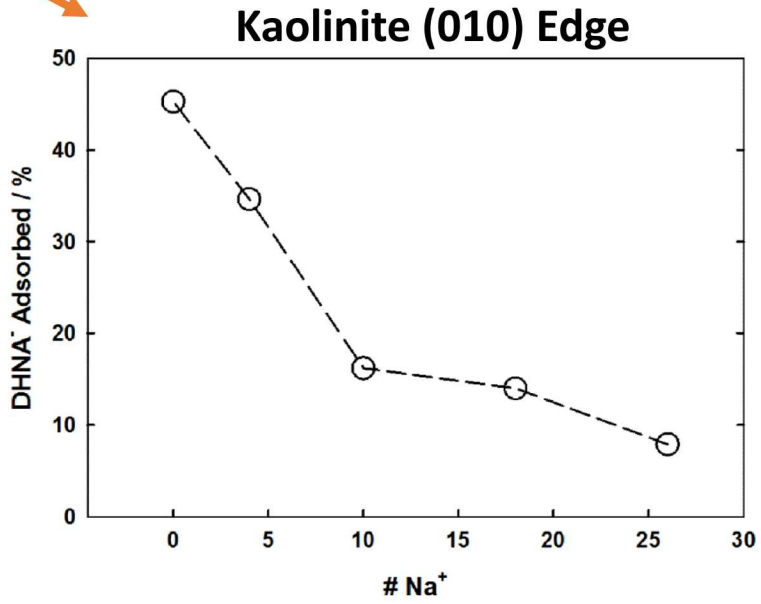
Reduced organic adsorption at higher Na^+/Ca^{2+} ratios (cation bridging)

Zeitler et al, J. Phys. Chem. C **2017**, *121*, 22787

Summary of Resin Adsorption on Kaolinite Edges

- The adsorption of a representative crude oil molecule (resin anion) on clay mineral surfaces depends significantly on:
  - Surface hydrophilicity.
  - Surface charge and type of bridging cation (pH-dependent edge surfaces).
- Adsorption trends on kaolinite edges:
  - Neutral surface (lower pH): weak adsorption.
  - Charged surface (higher pH): strong adsorption (Ca^{2+}).
    weak adsorption (Na^{+}).
- Divalent cations such as Ca^{2+} are able to efficiently bridge surface sites and organic anions.
- These results support ongoing EOR efforts based on low salinity waterflooding.





Funding

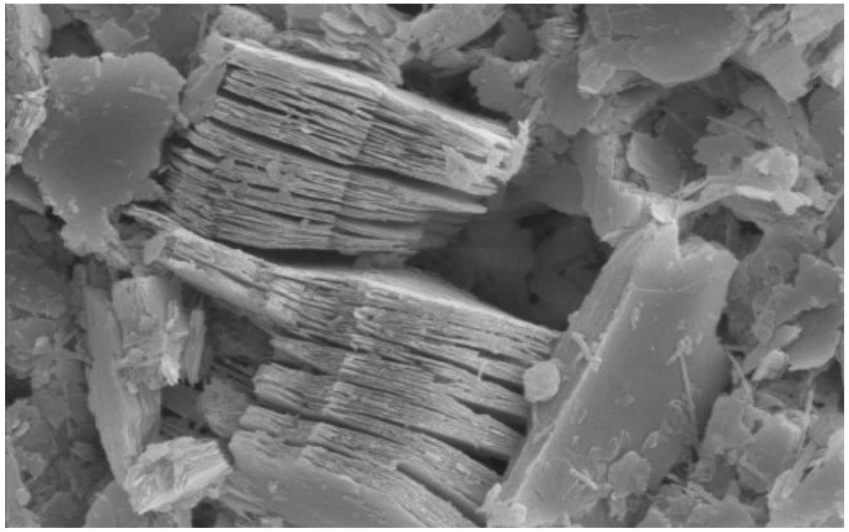
BP America

People

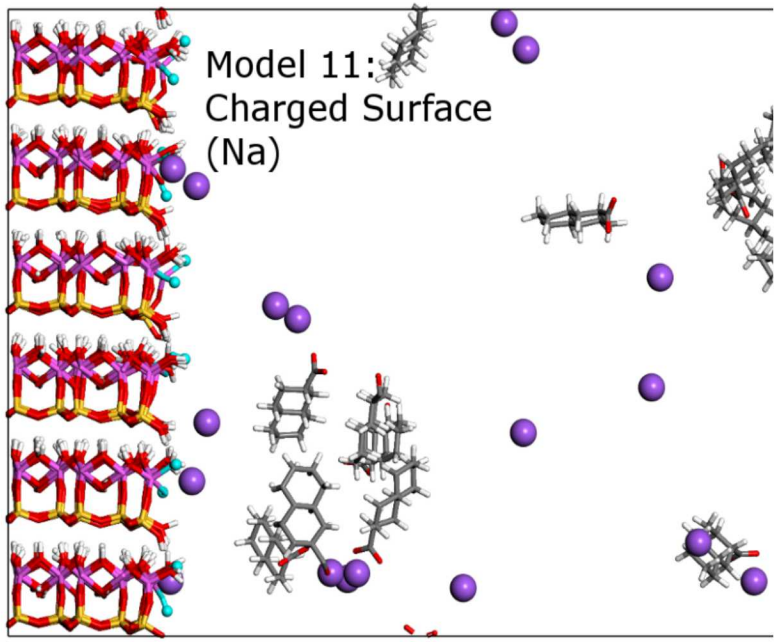
Todd Zeitler
Randy Cygan
Joanne Fredrich
Gary Jerauld

Outline

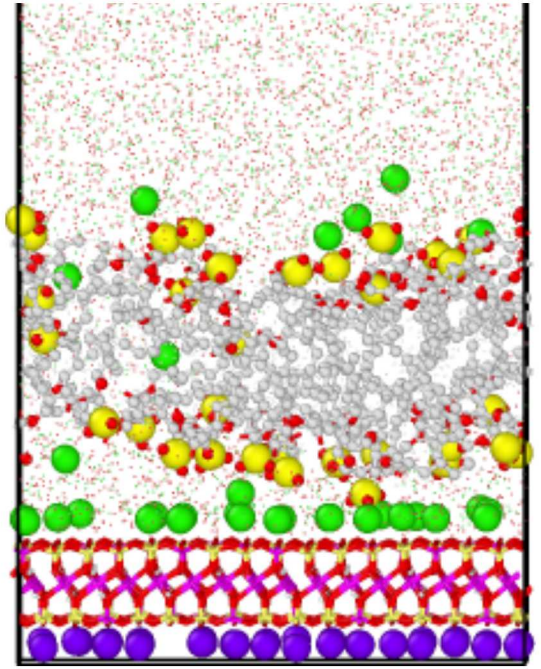
Molecular Simulation of Mineral-Fluid Interfaces: Techniques and Applications



Adsorption of Crude Oil Molecules

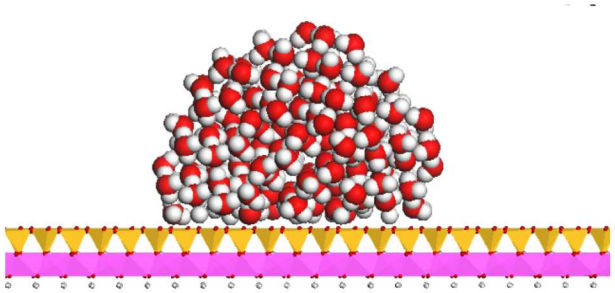


Fluid Chemistry and Surfactant Behavior

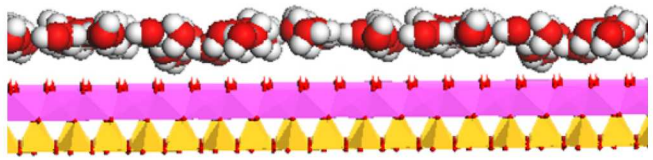


Surface Wettability

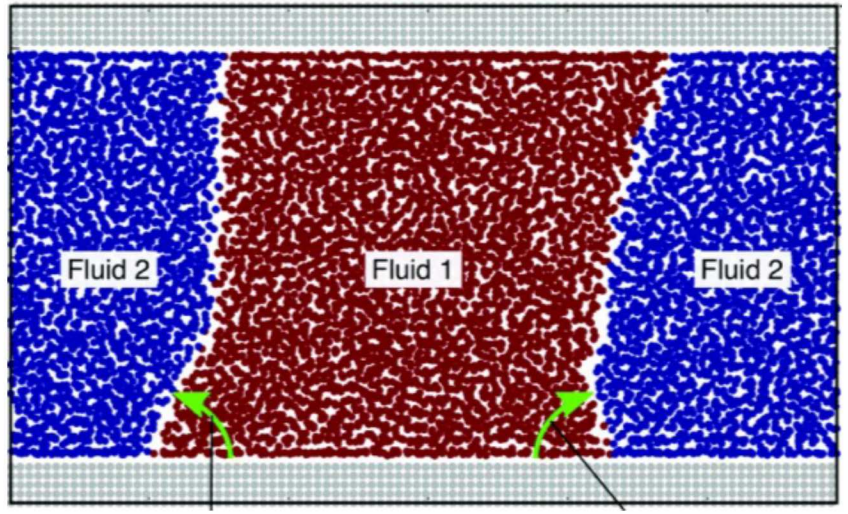
The partitioning of complex fluids at mineral interfaces depends greatly on chemical and physical properties of fluids and surfaces, particularly since intermolecular forces govern complex fluid interactions at interfaces.



non-wetting

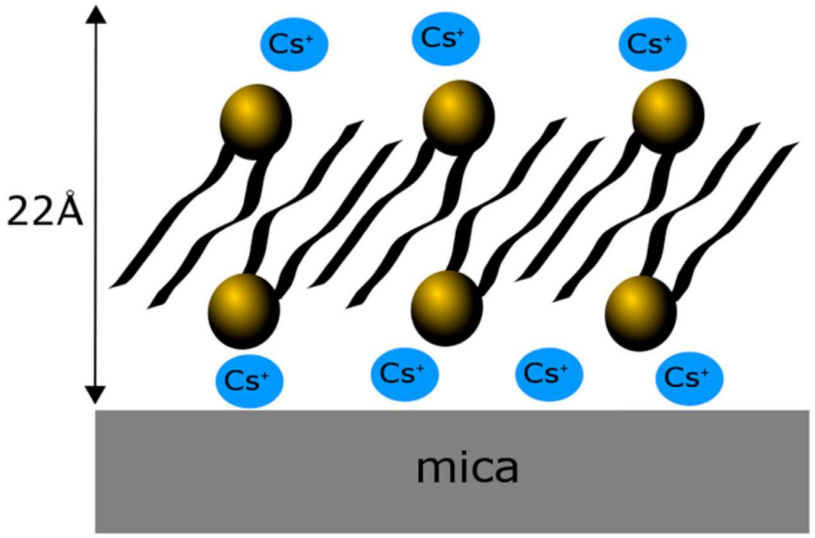


wetting



How does wettability vary with surface and fluid composition?

Omori et al., *Soft Matter* **2019**



Recent neutron reflectometry data suggest that an anionic surfactant (AOT) can bind to a negatively charged mica surface through cation bridging.

Allen et al., *Langmuir* **2017**

Surfactant-Mineral Interactions

Motivation

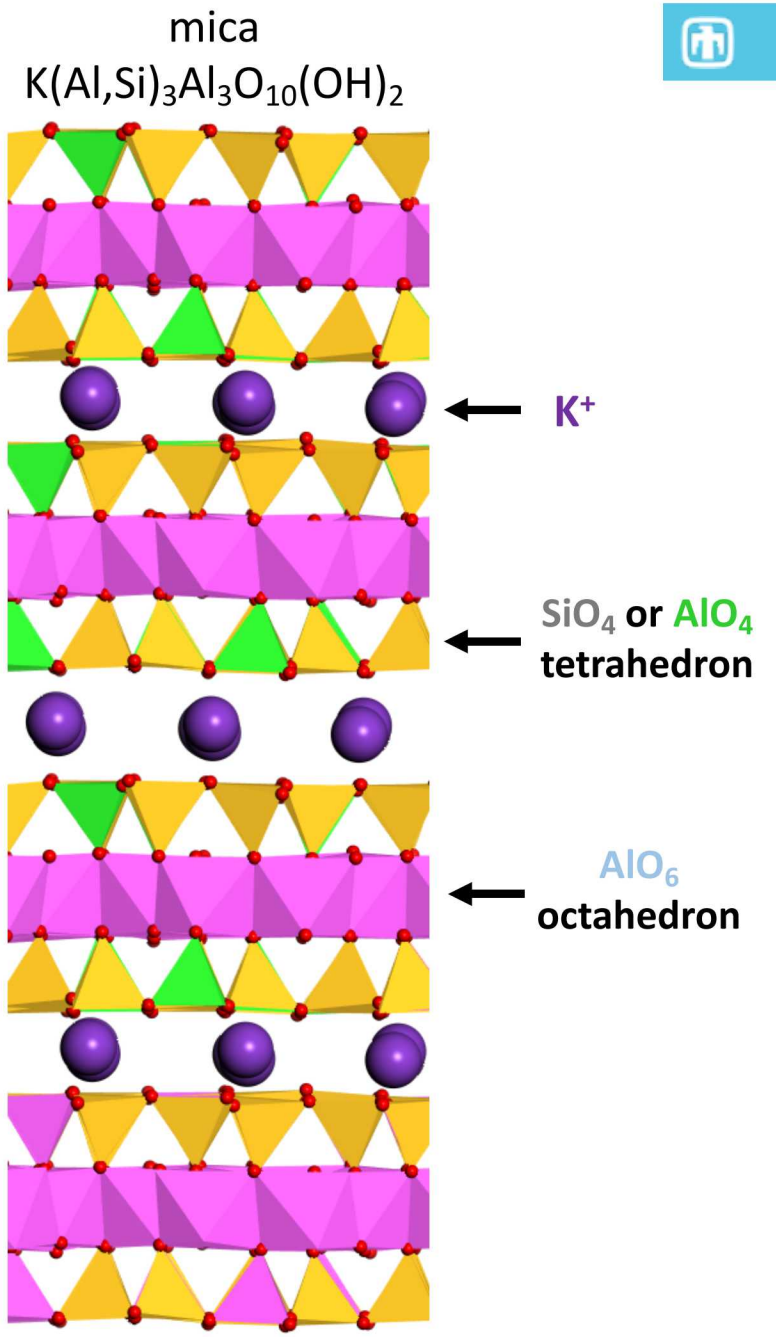
- Understand the behavior of complex fluids in the subsurface.
- Control the distribution of complex fluids by changing fluid chemistry, and to control rheological properties of complex fluids.

Relevance

Energy extraction, water treatment (produced water, energy generation)

Project goal

Quantify at the molecular scale the competing roles of fluid-fluid and fluid-surface interactions on fluid partitioning at a well-characterized mineral surface (**mica**).



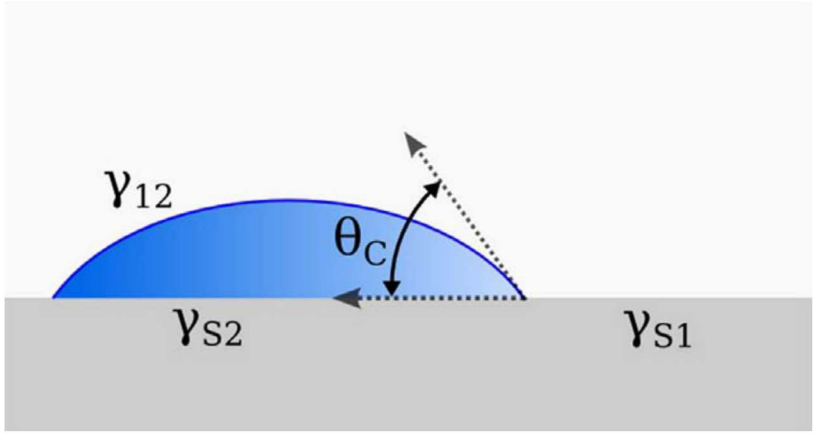
Research Plan

Experimental measurements + molecular modeling

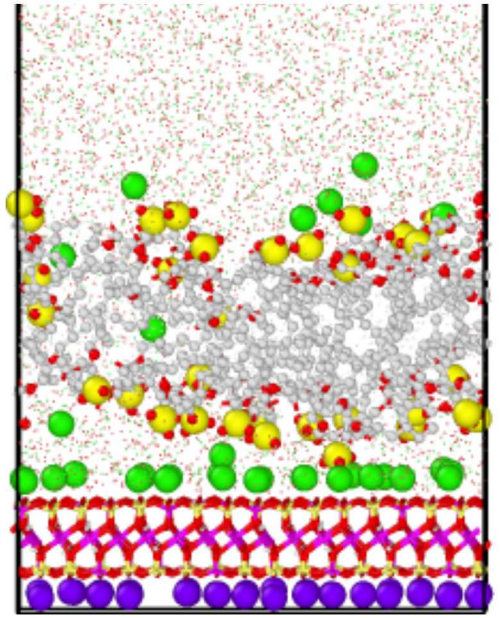
→ Trends in wetting properties of a complex fluids on mineral surfaces.

Complex fluid components: **water, aqueous cations**, nonpolar liquids, and **polar surfactant molecules**.

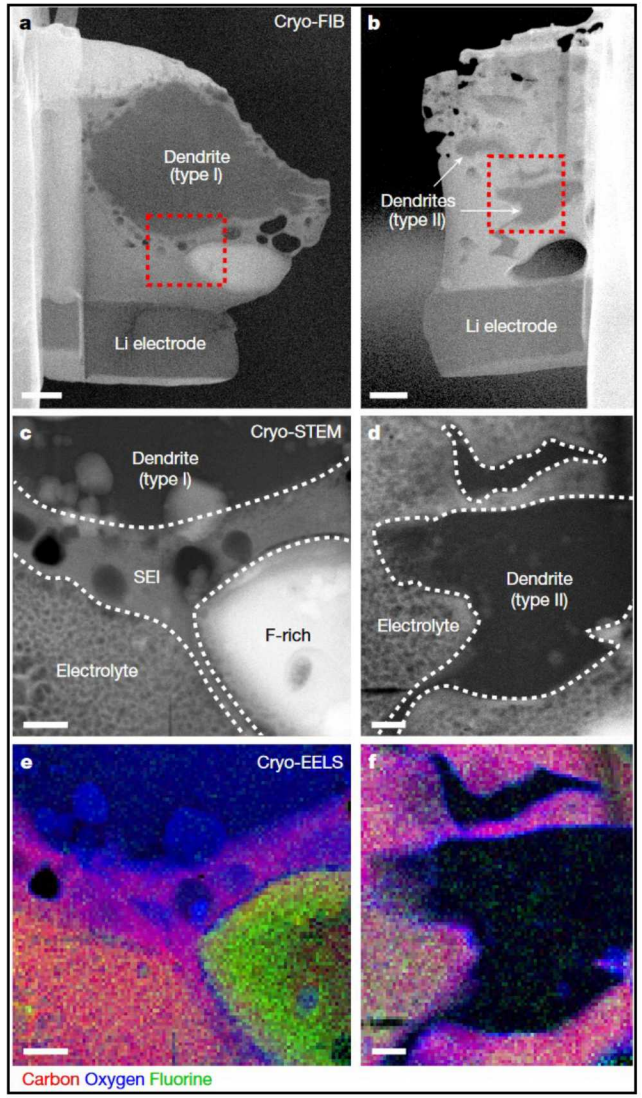
Determine how the adsorption properties change with cation composition.



Contact angle measurements

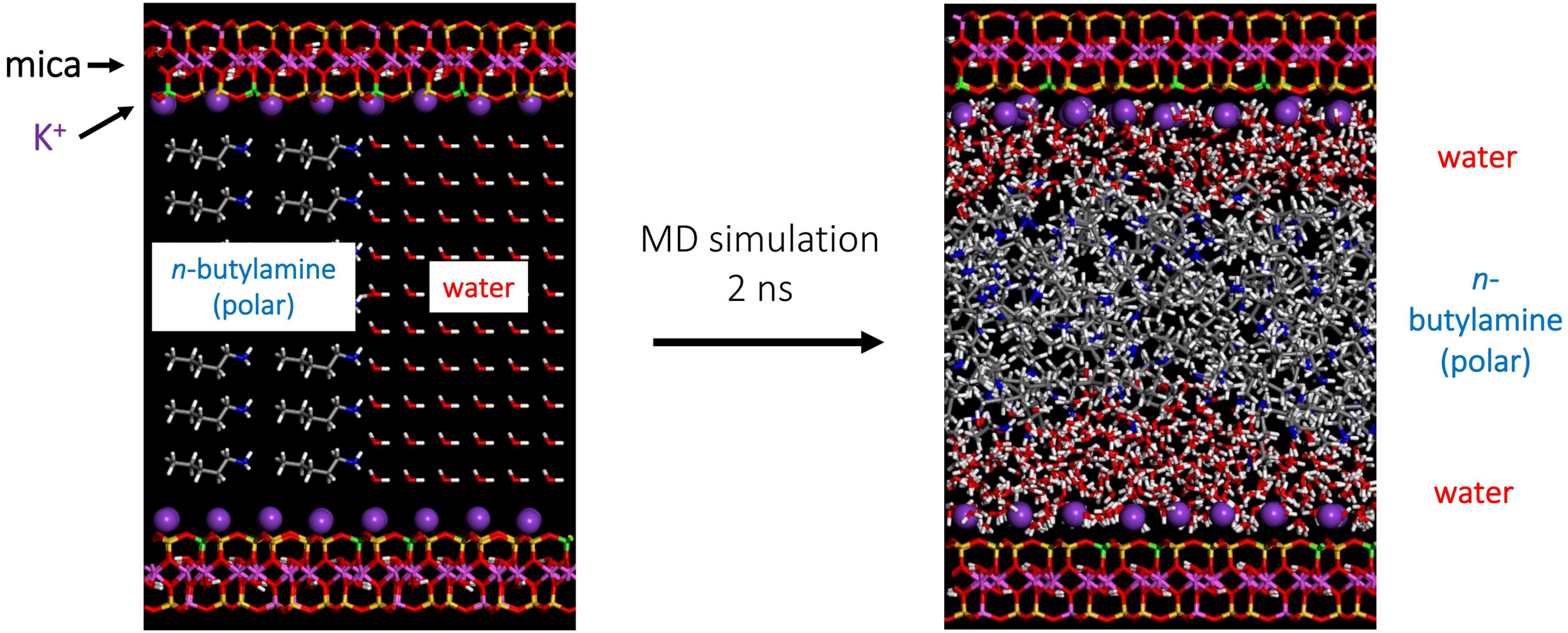


MD simulation



Cryo electron microscopy

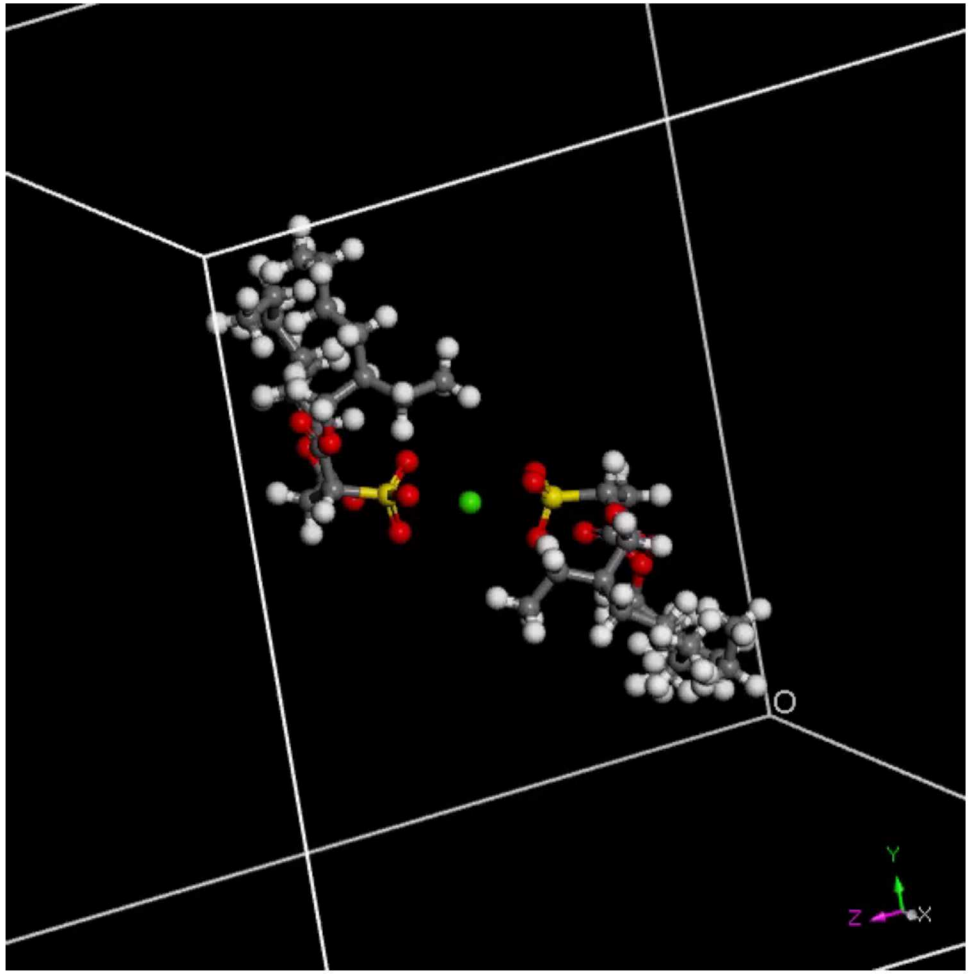
Preliminary Study: 2-Component Fluid

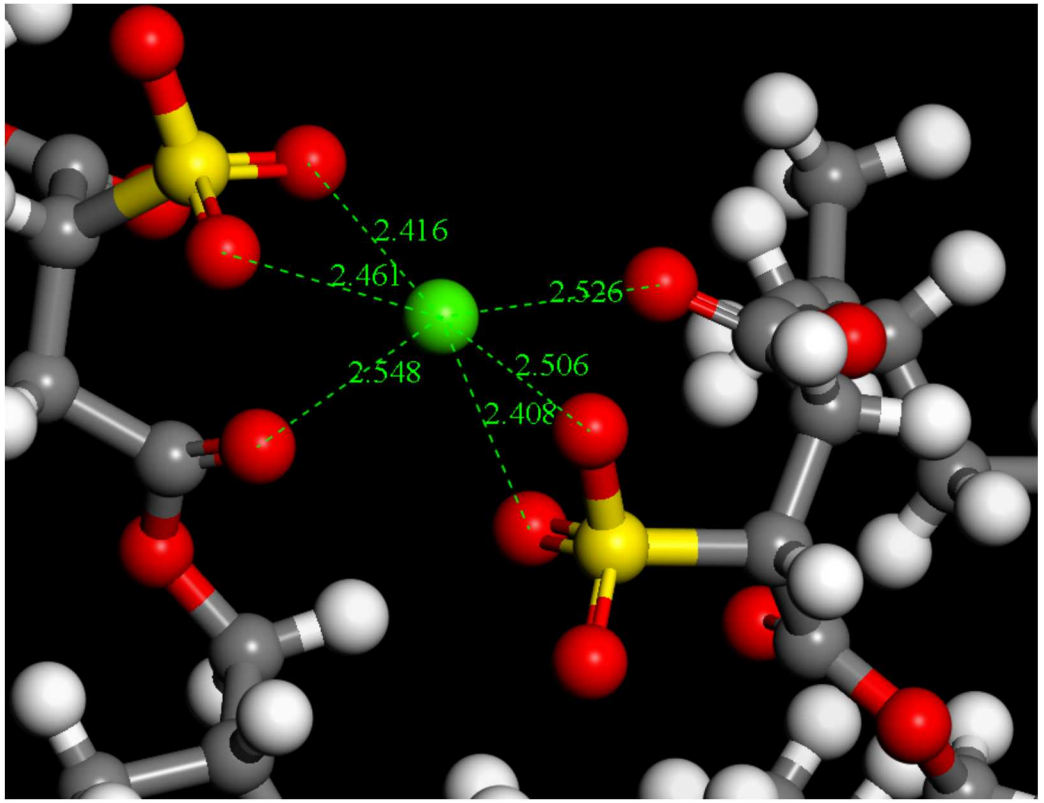


Driving forces for observed interfacial structure:
K^+ adsorption on the mica surface, K^+ hydration

AOT Surfactant

- Dioctyl calcium sulfosuccinate (Aerosol-OT, AOT)
- Neutron data suggests bilayer formation on mica.



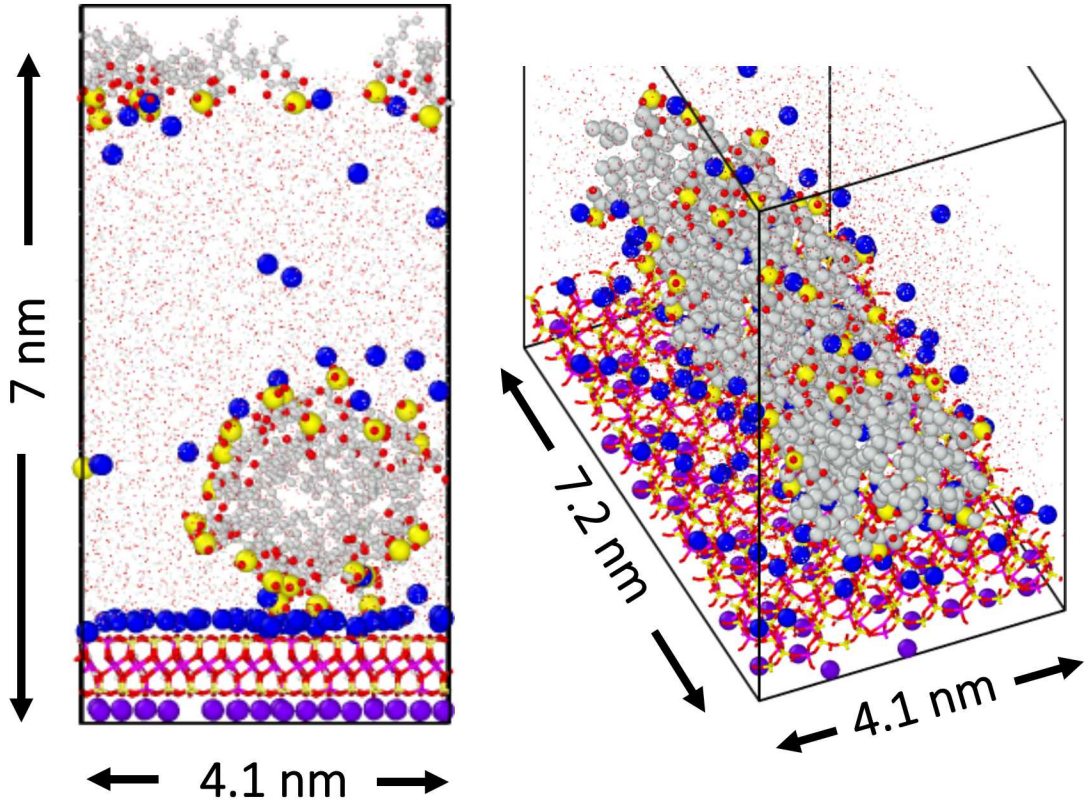


- 2 AOT monomers bridged by Ca^{2+}.
- Formation of polar and nonpolar regions.

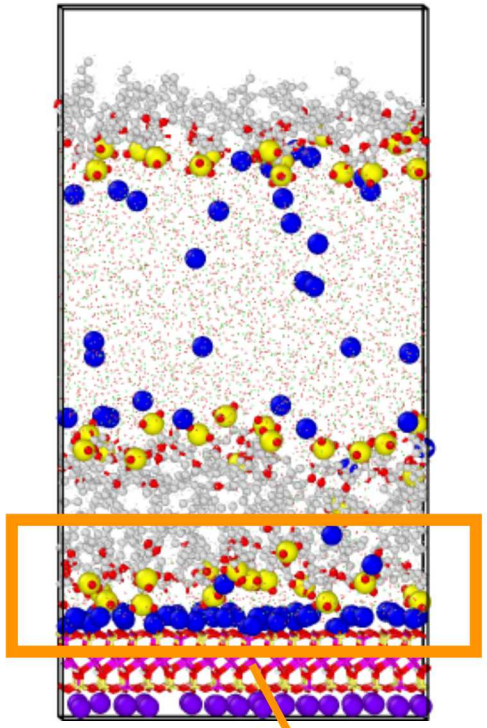
- Bidentate coordination with each sulfate.
- Coordination with carbonyl oxygens.

Effect of Surfactant Concentration on Interfacial Structure

32 Na-AOT
1 AOT per binding site
Adsorbed micelle (cylinder)

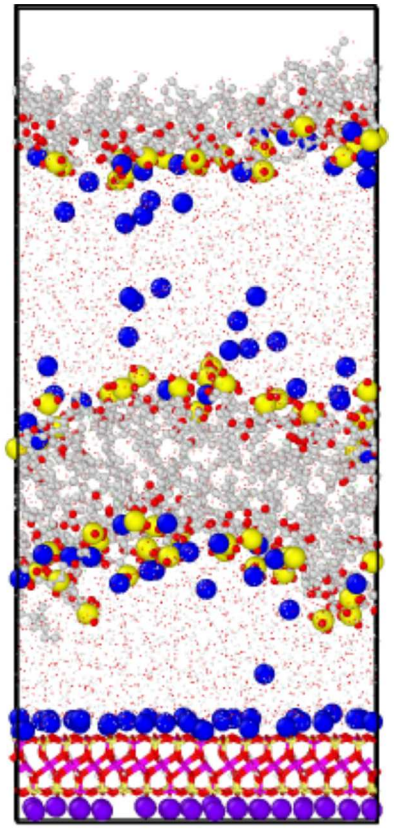


48 Na-AOT
1.5 AOT per binding site
Adsorbed bilayer



Surface density of AOT
0.9 AOT/nm^2 (Mg^{2+})
1.3 AOT/nm^2 (K^+)

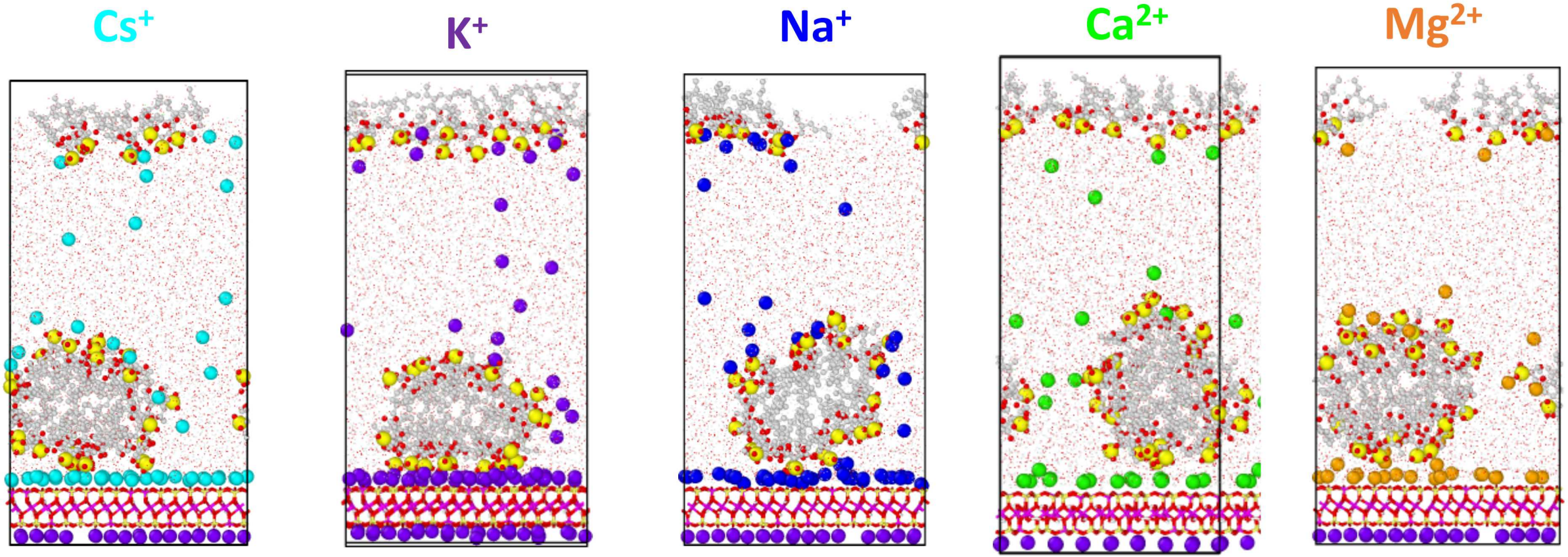
64 Na-AOT
2 AOT per binding site
Desorbed bilayer



Mica surface charge
2.2 *e*/nm^2

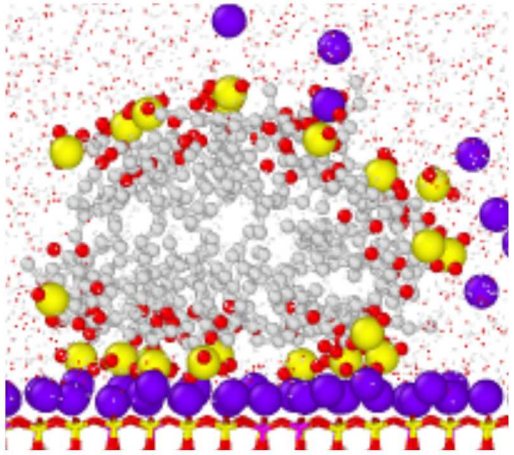
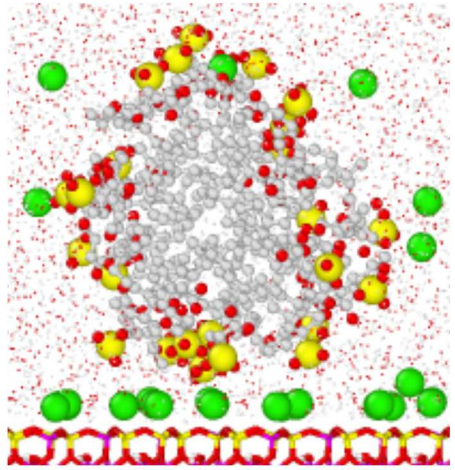
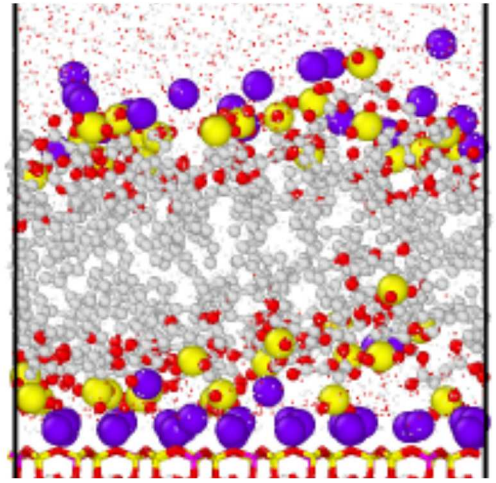
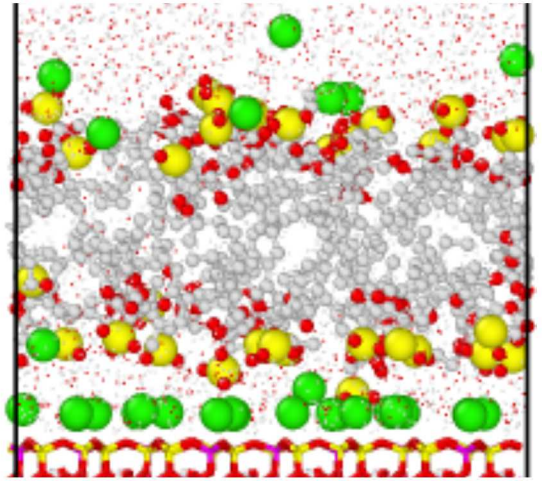
Cation Dependence on Interfacial Structure

Cation hydration energy



Equilibrium structures with 32 AOT after ~100 ns of MD simulation

Surfactant Structure – Layer Thickness

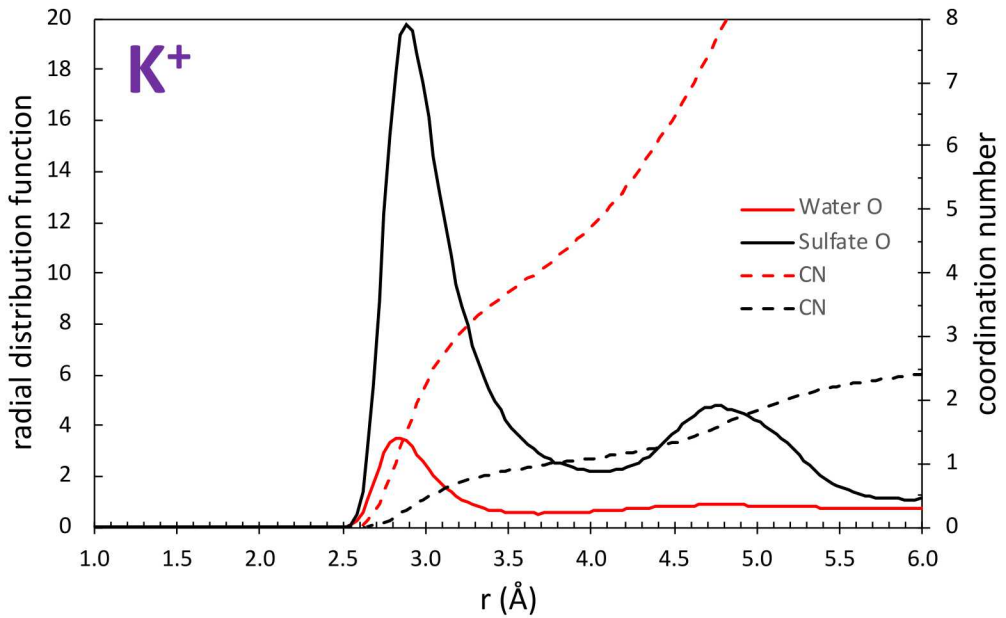
	K^+	Ca^{2+}
Micelle	2.3 nm 	3.0 nm 
Bilayer	2.0 nm 	2.3 nm 

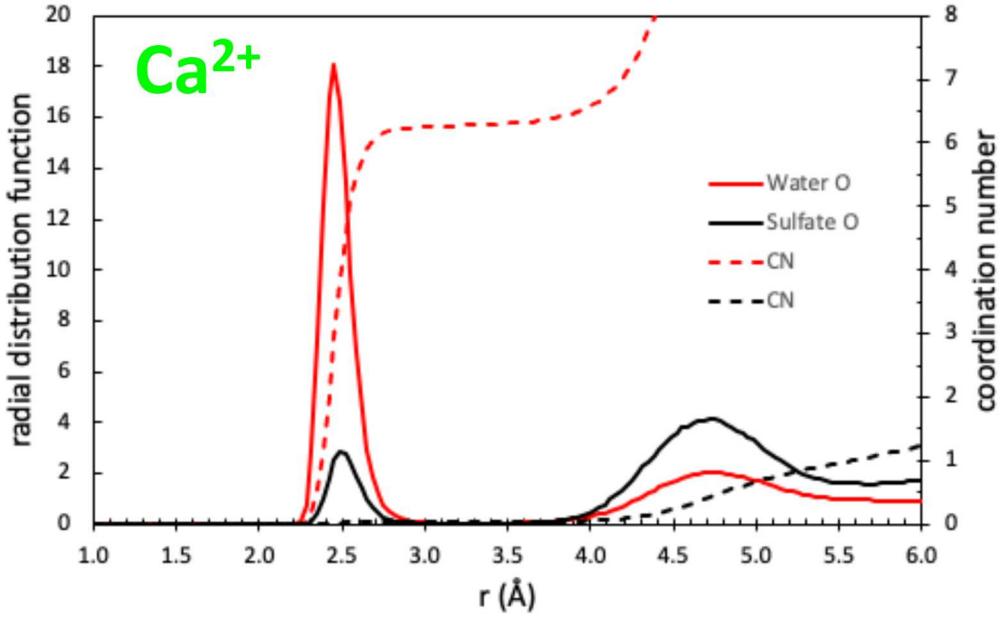
Ideal thickness of a single AOT chain 1.8 nm

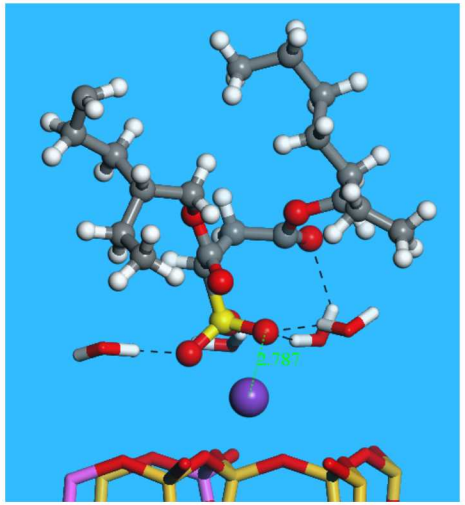
Bilayer thickness from neutron reflectometry 2.2 nm

Surfactant Binding Mechanisms

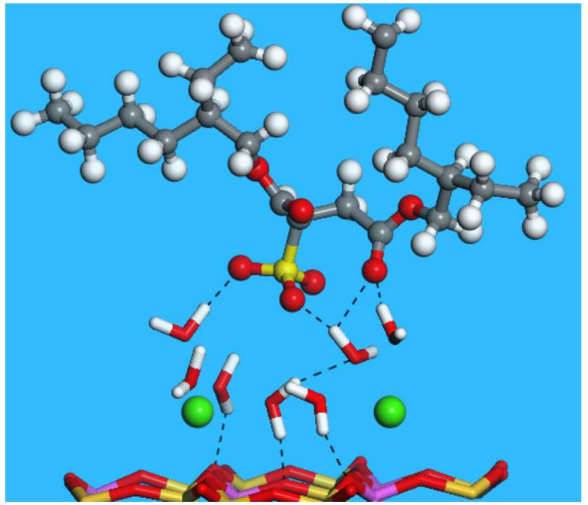
Cation-oxygen distances from radial distribution functions (RDFs)





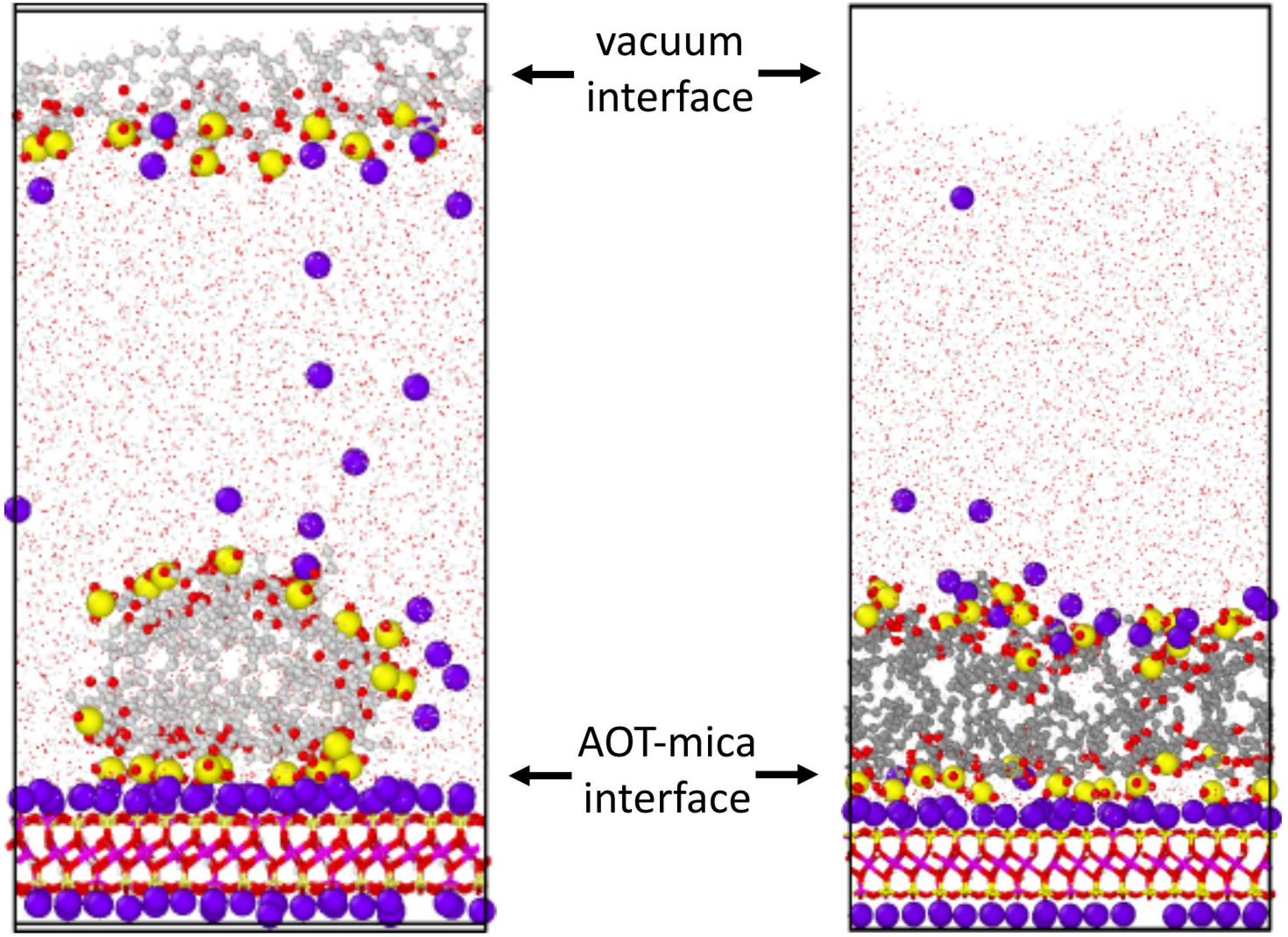


- Weakly hydrating cations (K^+) bind sulfate O atoms directly (inner-sphere coordination).
- Strongly hydrating cations (Ca^{2+}) retain water hydration shells, which in turn form H-bonds with sulfate O atoms (outer-sphere coordination).



Micelle vs Bilayer

32 K-AOT (1 AOT per binding site)



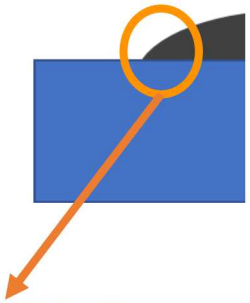
Initial Configuration

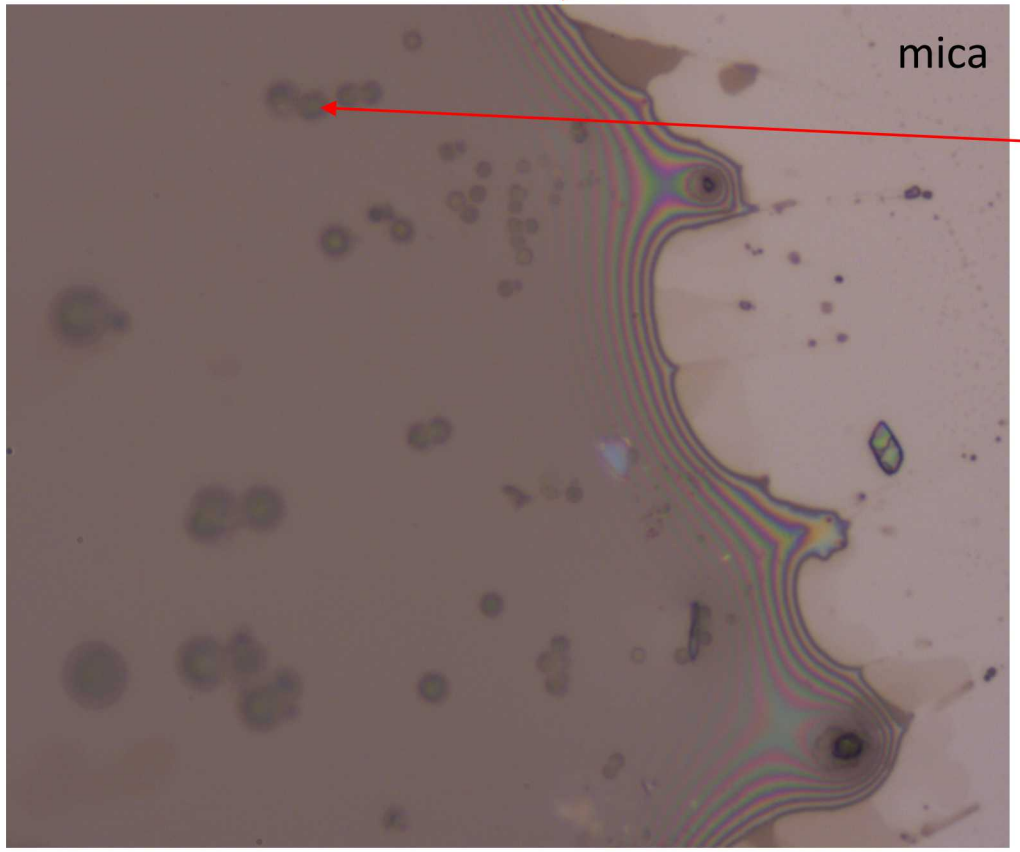
Random fluid

Adsorbed bilayer

Initial fluid configuration affects surfactant structure but not surfactant-surface structure

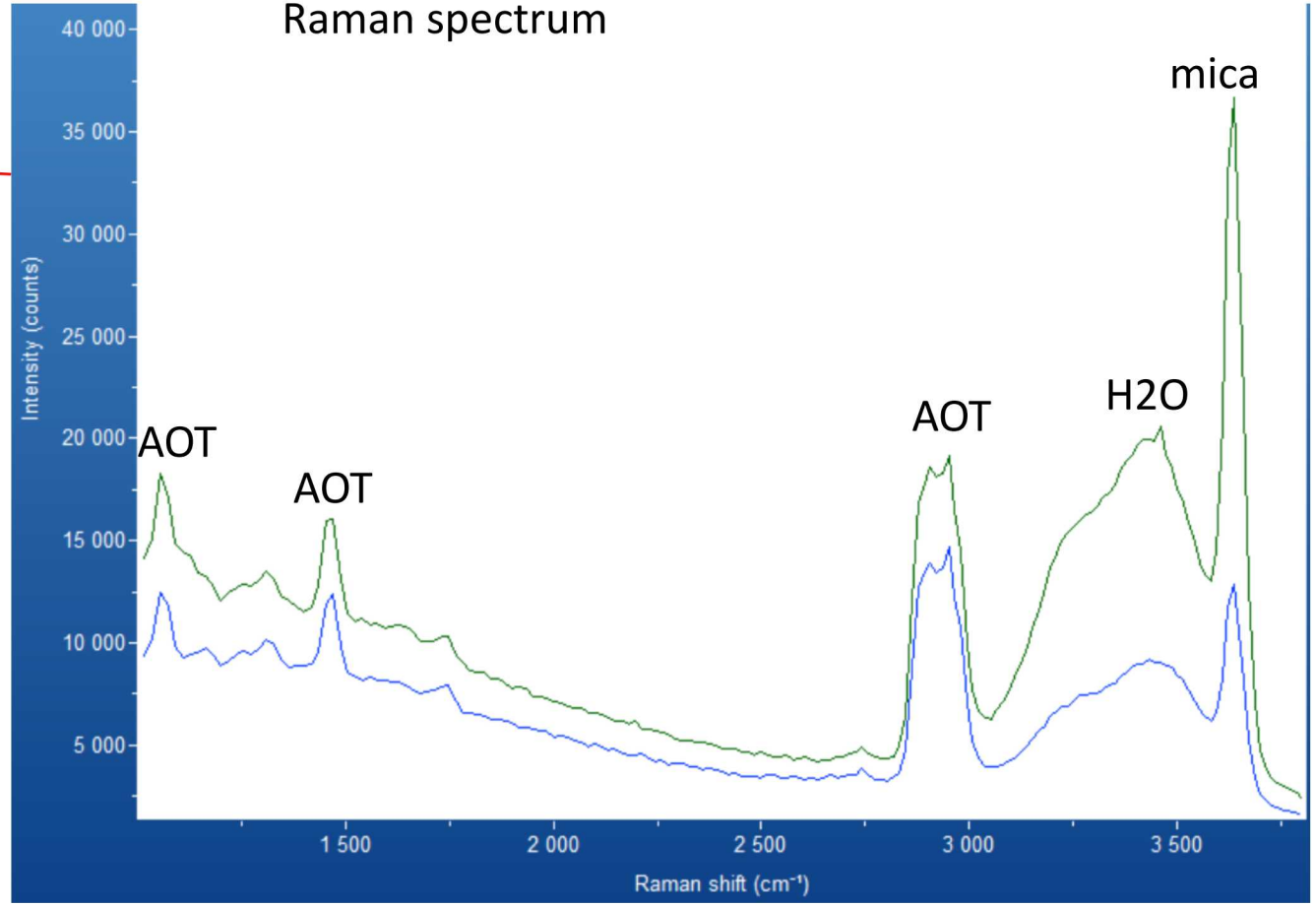
Raman Microscope





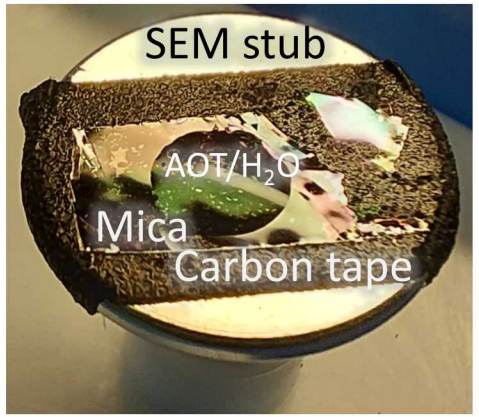
50x

Raman spectrum



Cryo-EM Workflow For Mica/AOT System

1 Sample Setup



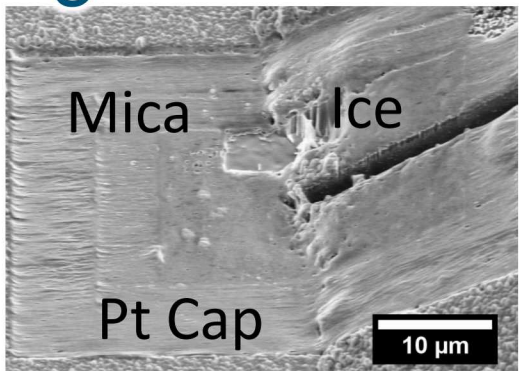
2 Vitrification

3 Load, Coat, Transfer

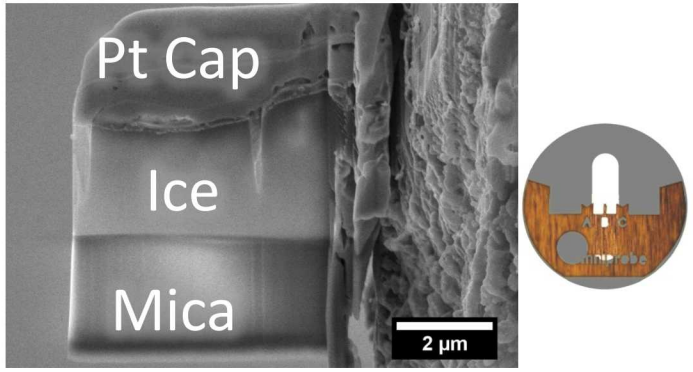
4 Scios FIB/SEM

5 Identify Region on Interest

6 Pt deposition, FIB Milling



7 Liftout, Thinning and Transfer

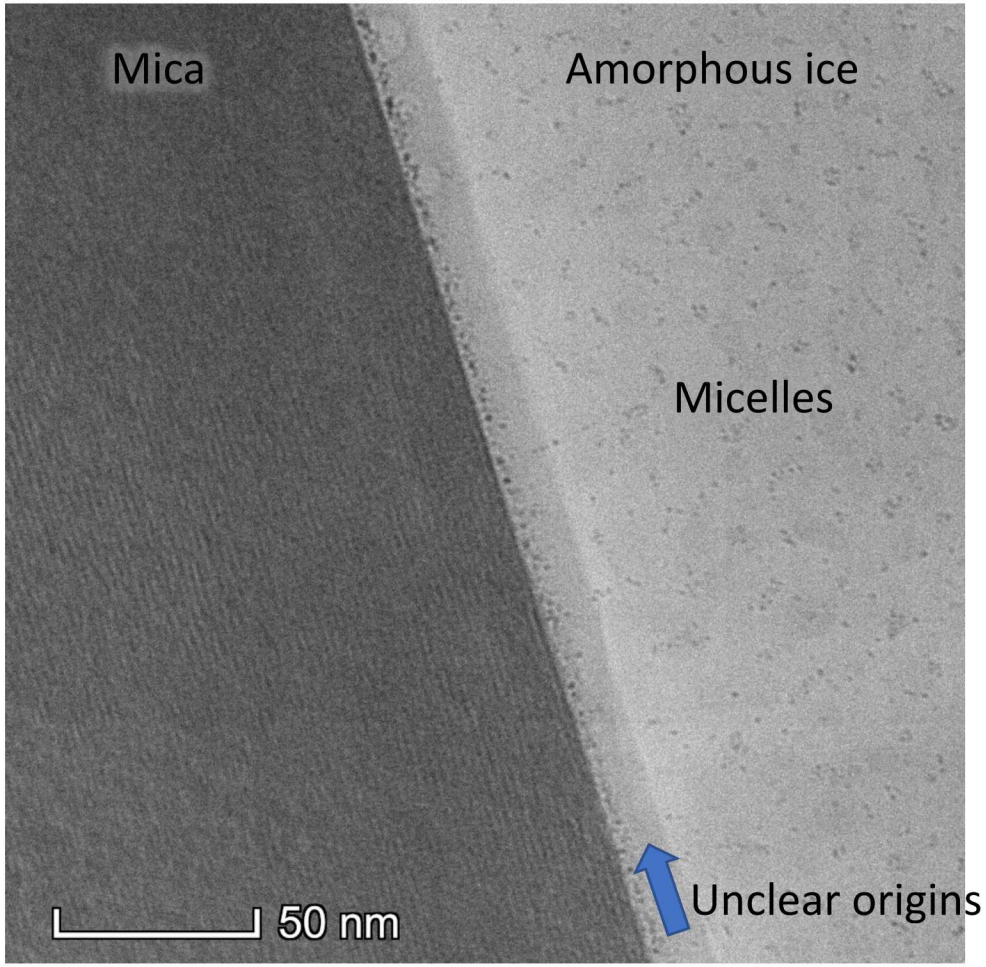


8 Talos L120C Cryo-TEM

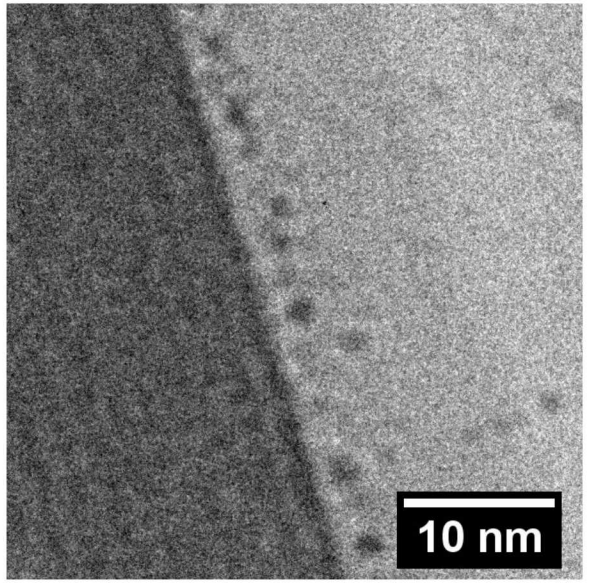
Preliminary Cryo-EM Results

2.3 mM NaAOT on Mica
Imaging – Talos 120 kV

- Organized layer near interface
- Interfacial micelle layer is not continuous(no bilayer)
- Micelles in amorphous-ice bulk tend to cluster
- Thicker ~10 nm interfacial layer is not always visible, possible artifact
- Mica tilted towards [100] zone to show basal planes



- Micelles ~ 2 nm
- Interfacial layer thickness 2-3 nm



Summary of Surfactant Interactions with Mica Surfaces

- MD simulations of an anionic surfactant (AOT) are consistent with observations from published neutron reflectometry:
  - AOT binds to the negatively-charged mica surface via cation bridging.
  - Surfactant thickness is consistent with a bilayer (or micelle).
- Cation hydration properties govern the presence of water layers at the mineral-surfactant interface.
- AOT bilayers form at the mica surface at surface concentration of ~ 1 AOT/nm^2. In experiments, the critical micelle concentration (CMC) of the cation-AOT pair must also be considered.
- The combination of nano-scale characterization (spectroscopy, cryo-EM) and molecular modeling will provide the molecular-level insight to drive innovation to control complex fluid behavior in the subsurface.

Funding

Sandia Laboratory Directed Research and Development (LDRD) Program

LDRD
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

People

Katie Jungjohann
Dan Long
Guangping Xu
Hongkyu Yoon