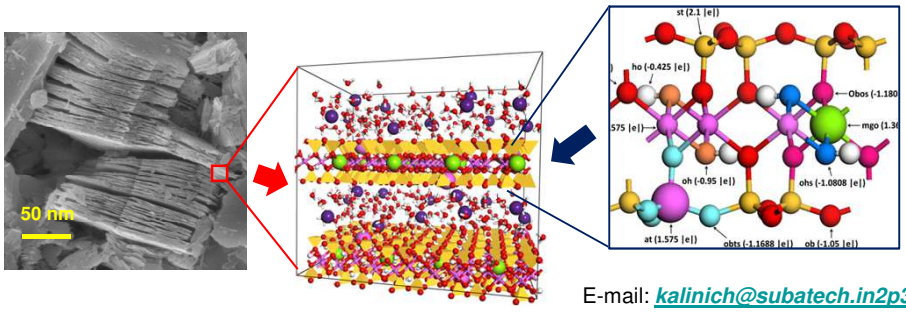
NE-M1-PRI12ENP – Integrated Nuclear Engineering Project

Molecular Modeling of Materials for Nuclear Waste Disposal Applications

Lecture 4 - Inorganic Interfaces

Andrey G. Kalinichev

Laboratoire SUBATECH (UMR 6457– IMT-Atlantique, Université de Nantes, CNRS/IN2P3), Nantes, France

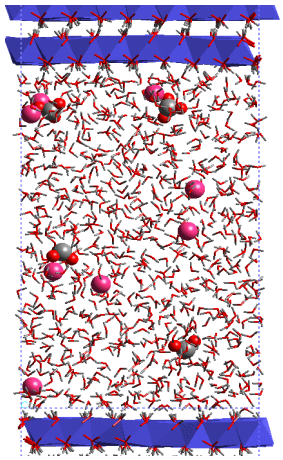


E-mail: *kalinich@subatech.in2p3.fr*

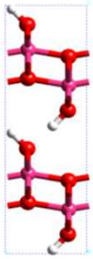
https://www.imt-atlantique.fr/en/person/andrey-kalinichev

Interfaces of Aqueous Solutions with Inorganic Substrates

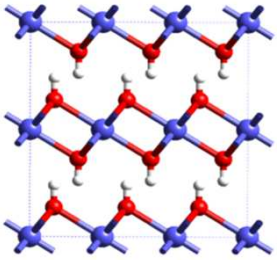
- Molecular models of aqueous interfaces with inorganic materials
- Rigid *vs* flexible substrate
- Structure, energetics, and dynamics of aqueous interfaces
- Hydrophobic and hydrophilic surfaces
- Local electrostatic fields and orientation of surface H_2O molecules



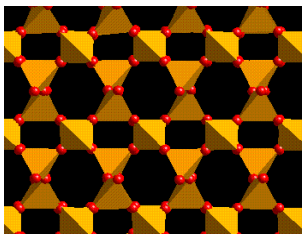
Atomistic Models of Simple (Hydr)Oxides



Boehmite γ-Al(OOH)



Portlandite $Ca(OH)_2$

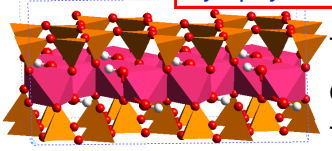


Quartz SiO_2

Structure and Composition of Complex Clays

$Si_4Al_2O_{10}(OH)_2$
No substitutions
Non-swelling

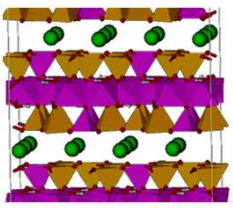
Pyrophyllite



T
O
T

Illite (muscovite)

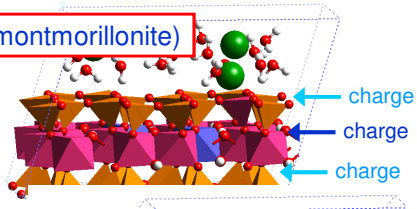
$K\ (Si_3Al)Al_2O_{10}(OH)_2$
Many substitutions
Many interlayer ions
1.0*e* charge per $O_{10}(OH)_2$
Non-swelling



Smectite (montmorillonite)

Dioctahedral Smectites

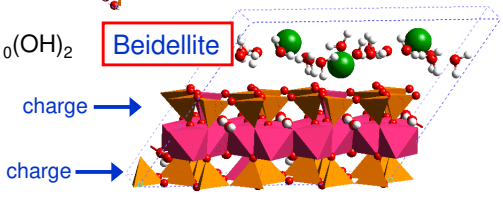
$Na_3(Si_{31}Al)(Al_{14}Mg_2)O_{80}(OH)_{16}\cdot nH_2O$
Some tetrahedral Al sub
Mostly octahedral Mg sub
Swelling



0.375*e* charge per $O_{10}(OH)_2$

Beidellite

$Na_3(Si_{29}Al_3)Al_{16}O_{80}(OH)_{16}\cdot nH_2O$
Mostly tetrahedral Al sub
Swelling

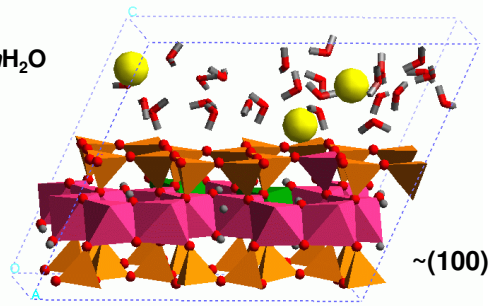


Simulation of Complex Clays

Wyoming Montmorillonite

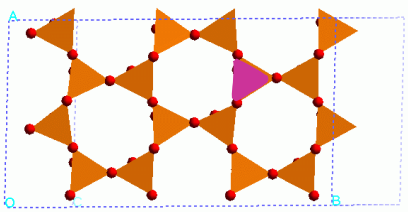
$Na_3(Si_{31}Al)(Al_{14}Mg_2)O_{80}(OH)_{16}\cdot nH_2O$

- No refined structures
- Cryptocrystalline
- Stacking disorder
- Complex compositions
- Site disorder



~(100) view

MD with *NPT*-ensemble
50 psec



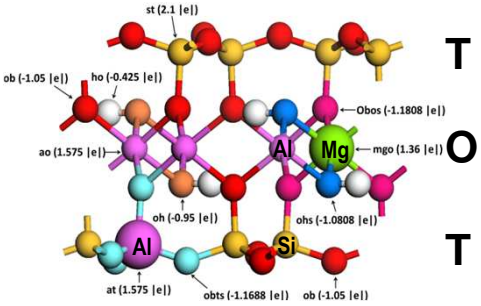
Basal view

Six-member rings
of SiO_4 tetrahedra

ClayFF Construction and Parametrization

1. **No explicit bonds – quasi-ionic**
2. **LJ parameters for all oxygen atoms are assumed to be equal to Ow for SPC water**

Both assumptions are great simplifications of reality, but they seem to work quite well



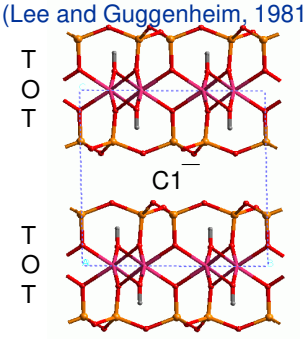
- Accurate determinations of partial charges are required to represent charge distributions of interlayer and external surfaces where electrostatic forces control sorption and transport processes
- Atomic charges derived from DFT calculations for cluster and periodic models of ***simple oxide and hydroxide phases*** (brucite, gibbsite, kaolinite, quartz…)
- Allows for ***charge delocalization*** among coordinating oxygens for substitutions

ClayFF: Cygan, Liang, Kalinichev, *J. Phys. Chem. B*, **108** 1255-1266 (2004)
Cygan, Greathouse, Kalinichev, *J. Phys. Chem. C*, **125** 17573-17589 (2021)

Modeling of Pyrophyllite

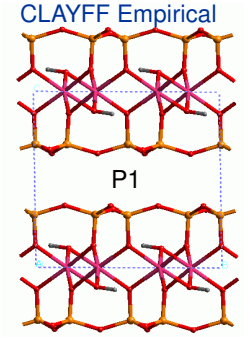
$Al_2Si_4O_{10}(OH)_2$ (100) views

Observed
(Lee and Guggenheim, 1981)



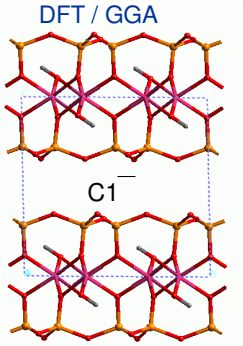
a = 5.16 Å
b = 8.97 Å
c = 9.35 Å

CLAYFF Empirical



a = 5.18 Å
b = 8.99 Å
c = 9.33 Å

DFT / GGA



a = 5.15 Å
b = 9.00 Å
c = 9.69 Å

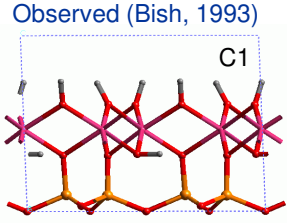
Unit cell parameters:	Δ < 0.5%	Δ < 3%
Bond lengths:	Δ < 4%	Δ < 2%

Modeling of a Simple Clay Crystal: Kaolinite

$Al_2Si_2O_5(OH)_4$ (100) views

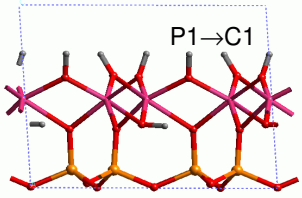
(Cygan et al., 2004)

Observed (Bish, 1993)



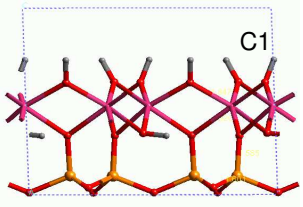
a = 5.15 Å
b = 8.94 Å
c = 7.39 Å

CLAYFF Empirical



a = 4.99 Å
b = 8.72 Å
c = 7.26 Å

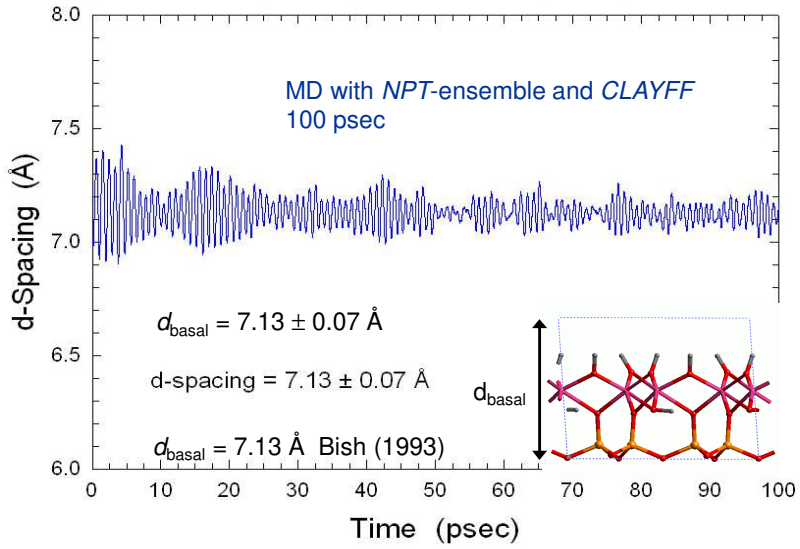
Quantum DFT/GGA



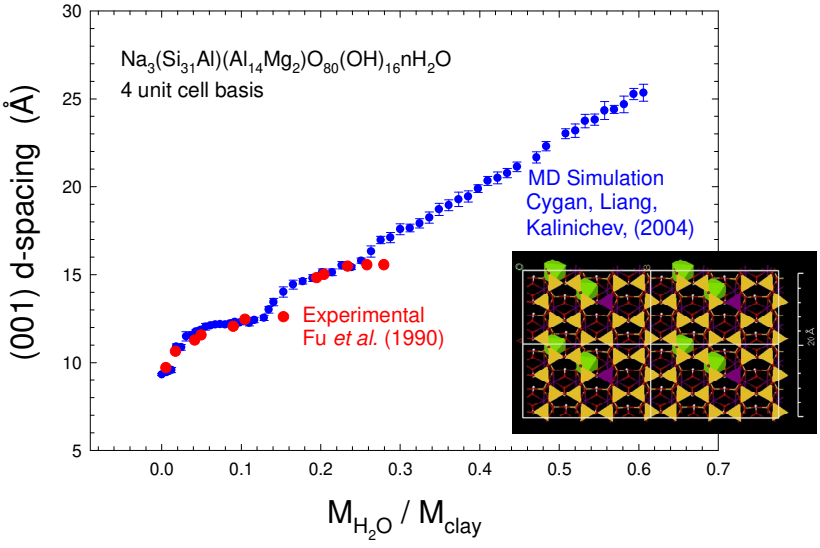
a = 5.15 Å
b = 8.96 Å
c = 7.52 Å

Unit cell parameters:	Δ < 3%	Δ < 2%
Bond lengths:	Δ < 4%	Δ < 3%

MD Simulation of Kaolinite Crystal

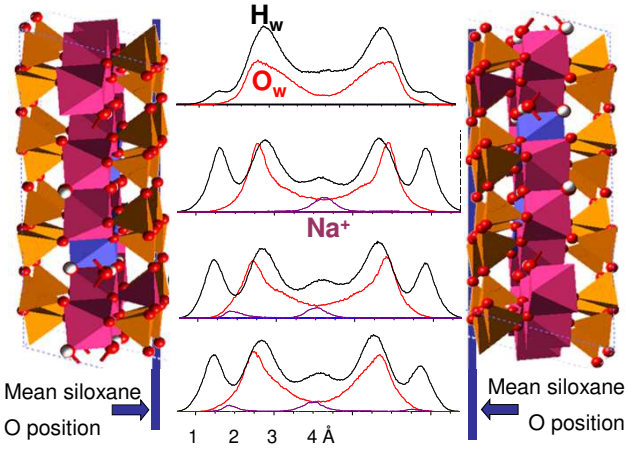


Swelling of Smectite (Montmorillonite)



Association of Metal Cations with Clay Surfaces

Two-Layer Clay Hydrates



Pyrophyllite
Zero

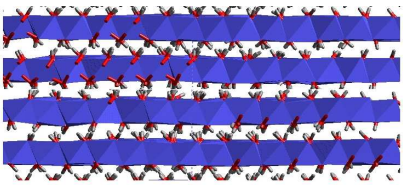
Montmorillonite
Oct

Wyoming
Montmorillonite
~Oct

Beidellite
Tet

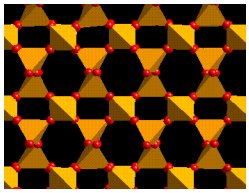
Location of substitution sites in the clay structure can strongly influence the distribution and mobility of adsorbed ions and H_2O molecules

Modeling Substrate-Water Interfaces (1)

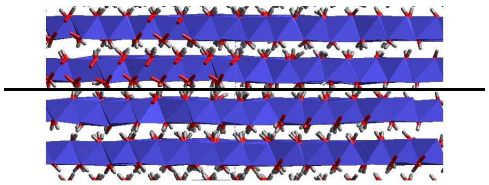


Building a mineral-solution interface model

- Build a model of bulk crystal

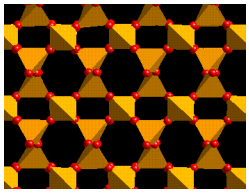


Modeling Substrate-Water Interfaces (2)

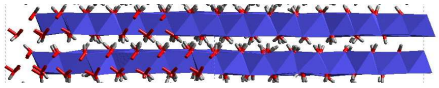


Building a mineral-solution interface model

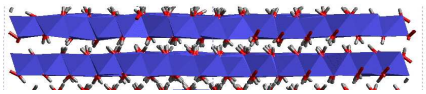
- Build a model of bulk crystal
- Define the cleavage plane



Modeling Substrate-Water Interfaces (3)



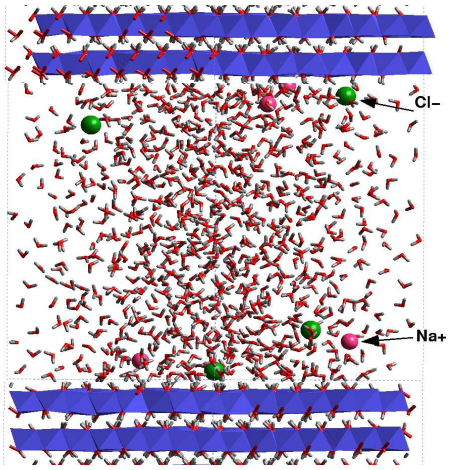
Most hydrated oxide surfaces are at least partially protonated (terminated by OH-groups) under normal pH



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)

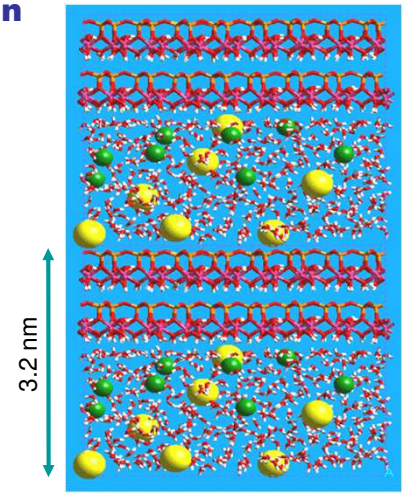


Building a mineral-solution interface model

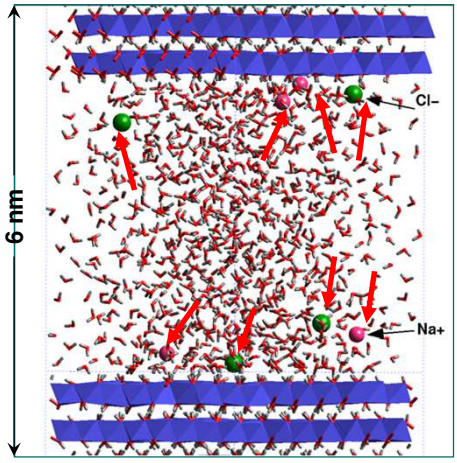
- Build a model of bulk crystal
- Define the cleavage plane
- Cleave the crystal to create a slit-like nano-pore
- Add pore solution from a preliminary bulk-solution simulation

1 *m* CsCl Aqueous Solution in Slit-Like Nanopores of Kaolinite

Layered model of interfaces in periodic boundary conditions



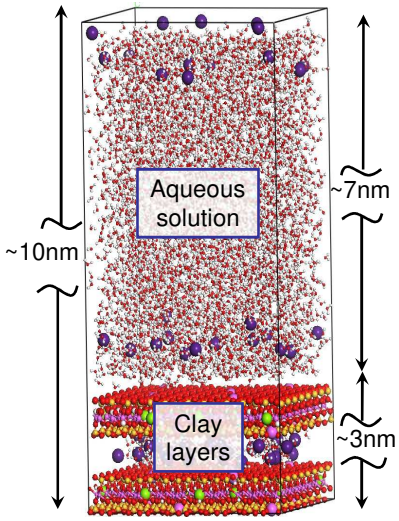
Ionic Sorption at the Interfaces



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)

MD Modeling of Clay-Solution Interfaces



Classical Newtonian dynamics

- N_{tot} ~ 3,000 – 10,000 atoms
- N_{H2O} ~ 0 – 1,000 molecules
- *ClayFF* force field (Cygan et al., 2004)
- $a \times b \times c$ ~ $3 \times 3 \times 10$ nm^3
- Periodic boundary conditions
- *NVT*- or *NPT*-ensemble T=300K; P =1 bar
- t ~ 200 - 1,000 ps
- Δt = 0.5-1.0 fs

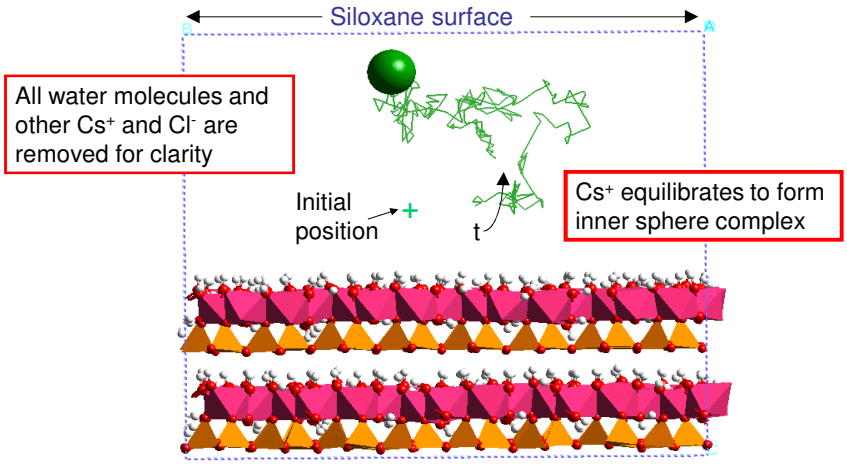
Solution structure:

- ✓ Atomic density profiles (⊥)
- ✓ Atomic density surface distributions (| |)
- ✓ Topology of the interfacial H-bond network

Dynamics:

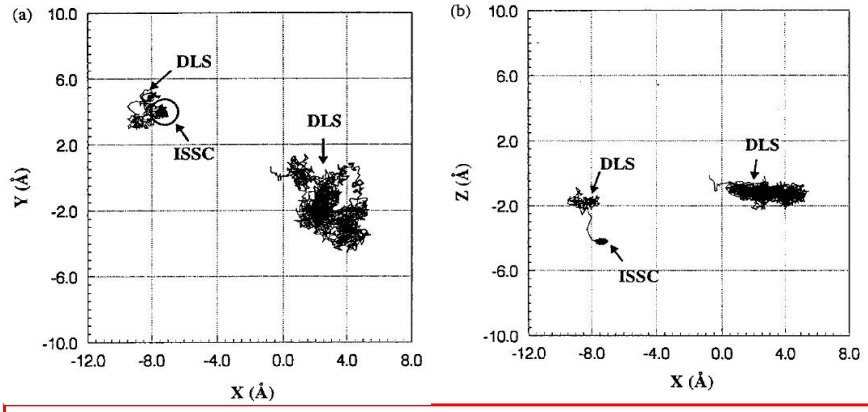
- ✓ Diffusion coefficients (longer time scale)
- ✓ Spectra of vibrational and rotational dynamics (shorter time scale)

Trajectory Path of Cesium Ion at the Interface of CsCl Aqueous Solution with Kaolinite



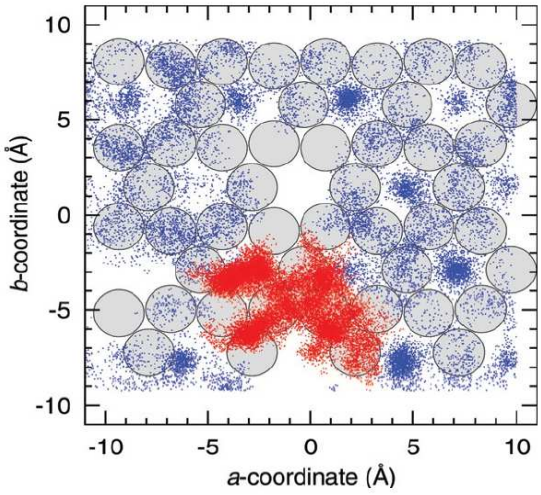
(001) surface

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. Chang et al., *Langmuir*, **13**, 2074-2082 (1997)

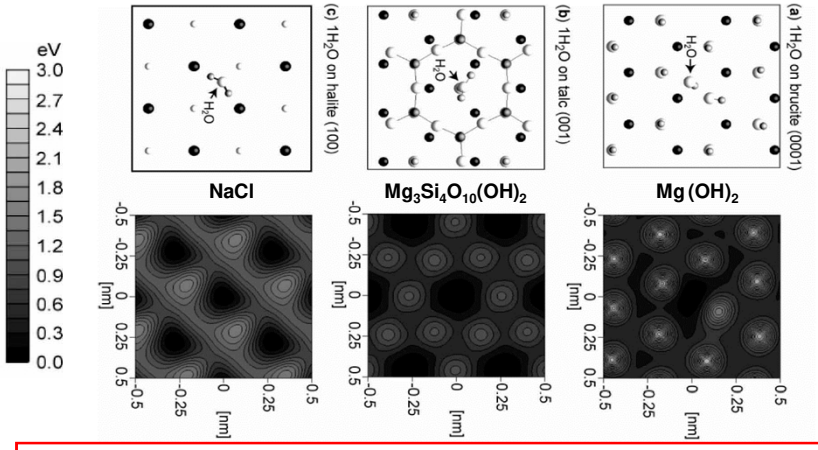
Analysis of Structure and Energetics of Aqueous Interfaces



Center-of-mass trajectory of a Zn^{2+}-"bound" H_2O molecule (red) and a "free " H_2O 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)

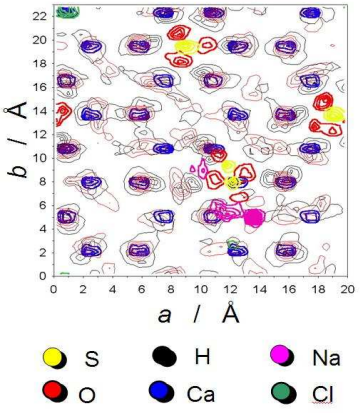
Analysis of Structure and Energetics of Aqueous Interfaces

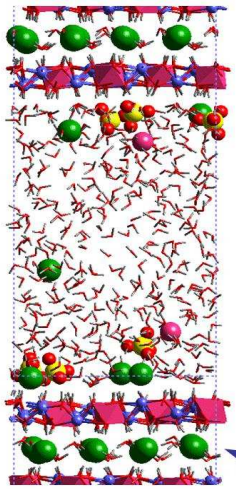


Most stable configuration (top) and contour maps of potential energy surface (bottom) for a water molecule on (**a**) brucite (0001), (**b**) talc (001), and (**c**) halite (100) surfaces.
Sakuma et al., *Molecular Simulations*, **30**, 861-871 (2004)

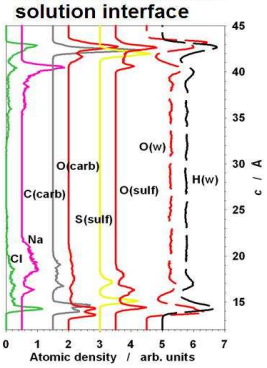
Modeling of Friedel's Salt $[Ca_2Al(OH)_6]Cl{\cdot}2H_2O$ Interfaces with Aqueous Na_2SO_4 solution

Atomic density map of the first surface layer ("inner-sphere" complexing)



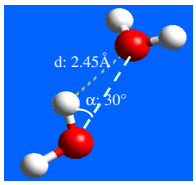


Atomic density profiles of aqueous species across the substrate-solution interface



anion-H_2O interlayers

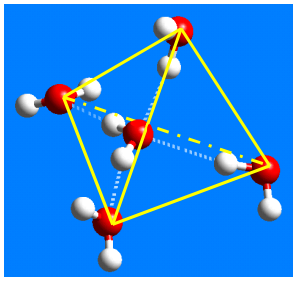
The name is Bond, H-Bond

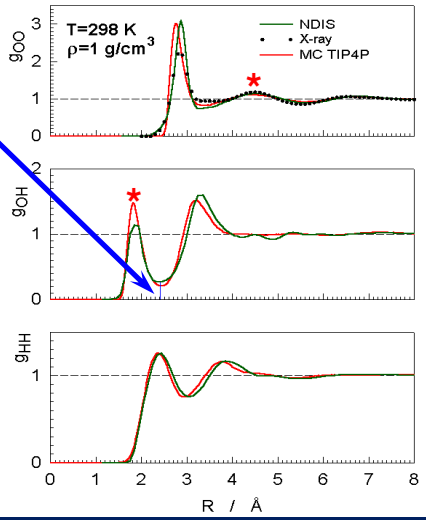


Hydrogen bonding is the most important phenomenon governing the properties of all aqueous systems

H --- O distance: < 2.45Å
H—O---O angle : < 30°

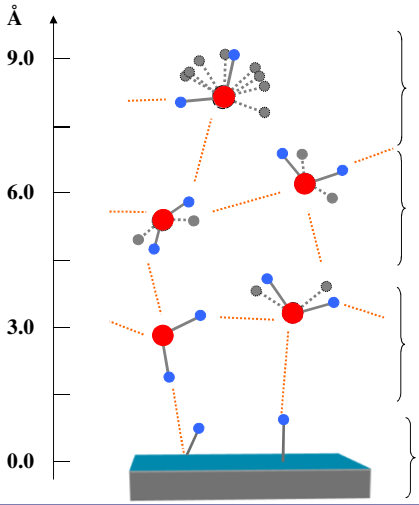
A.Luzar, *JCP*, **113**, 10663 (2000)





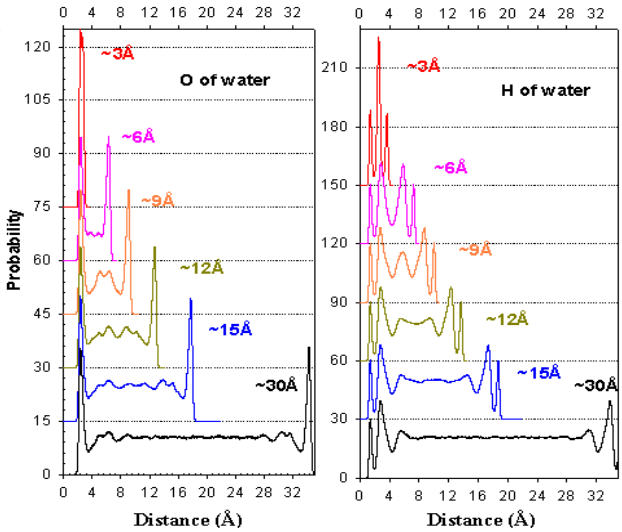
Ideally, each H_2O molecule in the H-bonding network can *donate* 2 H-bonds to its neighbors and *accept* 2 H-bonds from other neighbors

Water at a Hydroxylated Mineral Surface, e.g., $Mg(OH)_2$, $Ca(OH)_2$



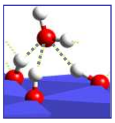
Kalinichev, Kirkpatrick, *Chemistry of Materials*, **14**, 3539-3549 (2002)
Wang, Kalinichev, Kirkpatrick, *Geochim. Cosmochim. Acta*, **68**, 3351-3365 (2004)

Density Profiles of Confined Water Between Brucite $Mg(OH)_2$ Layers

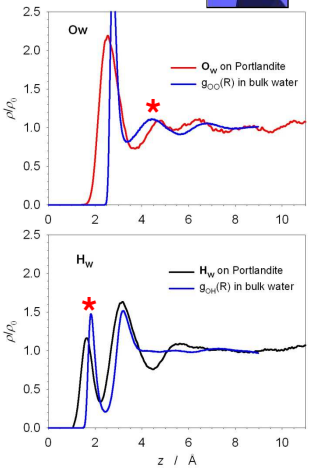


Wang, Kalinichev, Kirkpatrick, *Geochim. Cosmochim. Acta*, **68**, 3351-3365 (2004)
Kirkpatrick, Kalinichev, Wang, *Mineralogical Magazine*, **69**, 287-306 (2005)

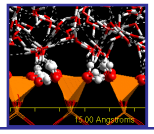
Water Structure at Neutral Hydroxylated Surfaces



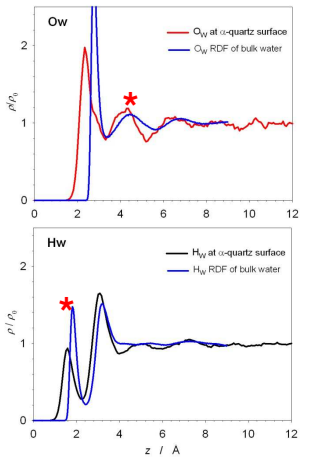
$Ca(OH)_2$



- Interfacial H_2O molecules can both ***donate and accept*** H-bonds to surface OH
- On average, local environment of individual H_2O molecules is ***very similar to bulk liquid water***
- Interfacial water structure is very similar between these two hydroxylated surfaces



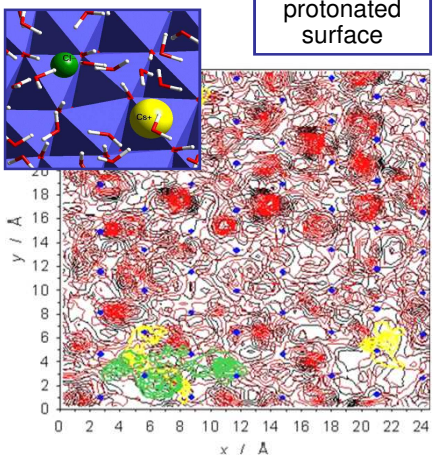
α-SiO_2 (hydroxylated quartz surface)

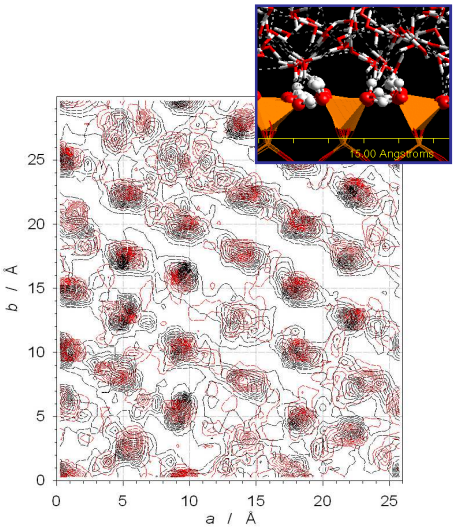


Comparison with a Protonated Surface of Ca-Hydroxide (Portlandite)

Ca ● O ● H ●

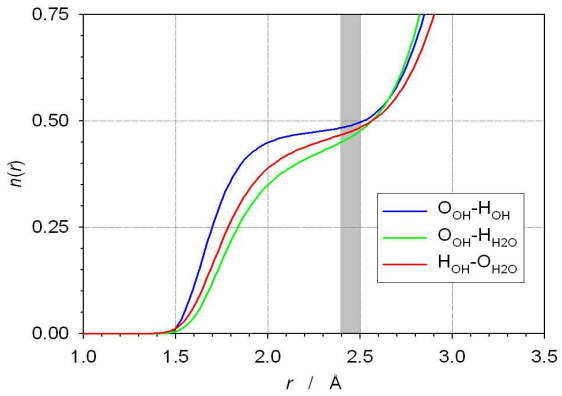
$Ca(OH)_2$ fully protonated surface





Running Coordination Numbers and the Degree of H_2O H-bonding at α-Quartz Surface

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

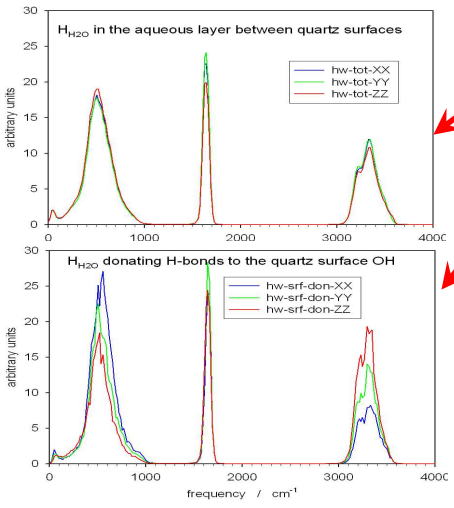


- At low pH (fully protonated quartz surface), about 50% of the surface OH groups are oriented parallel to the surface, form H-bonds to other surface OHs.
- Simultaneously, they accept H-bonds from interfacial H_2O molecules.
- The other 50% of the surface OH groups are oriented nearly perpen-dicular to the surface and donate H-bonds to interfacial H_2O.

Velocity Autocorrelation Functions and Vibrational Spectra of Surface H_2O

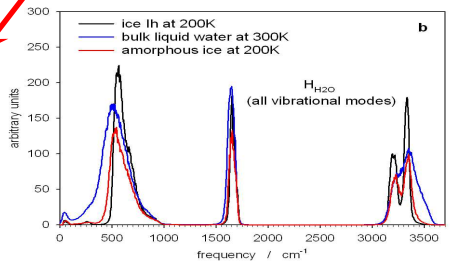
$$\mathrm{VACF} \equiv C_{vv}(t) = \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)^2\rangle} = \frac{1}{\langle \mathbf{v}(0)^2\rangle}\int \mathbf{v}(0)\cdot\mathbf{v}(t)\, d\Gamma$$

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

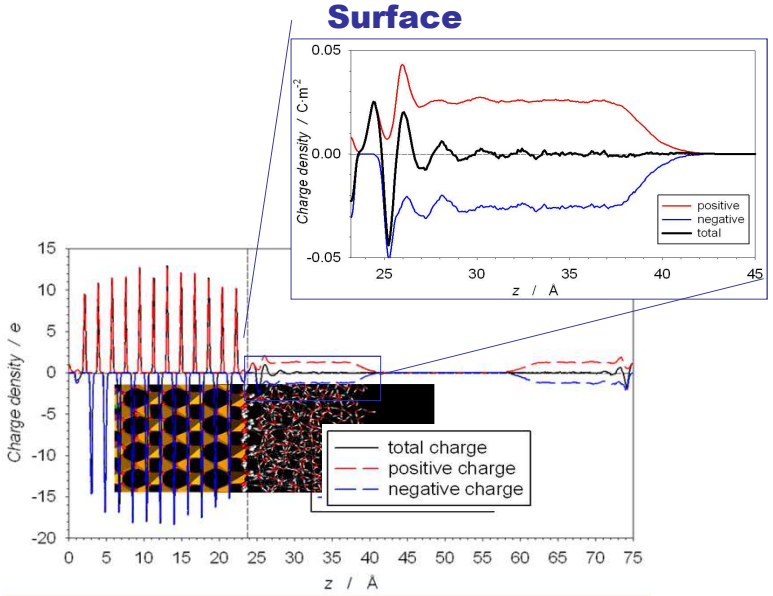


Total H_2O

Surface H_2O
- Narrower spectral bands
- More anisotropic
- Closer to 'ice-like"



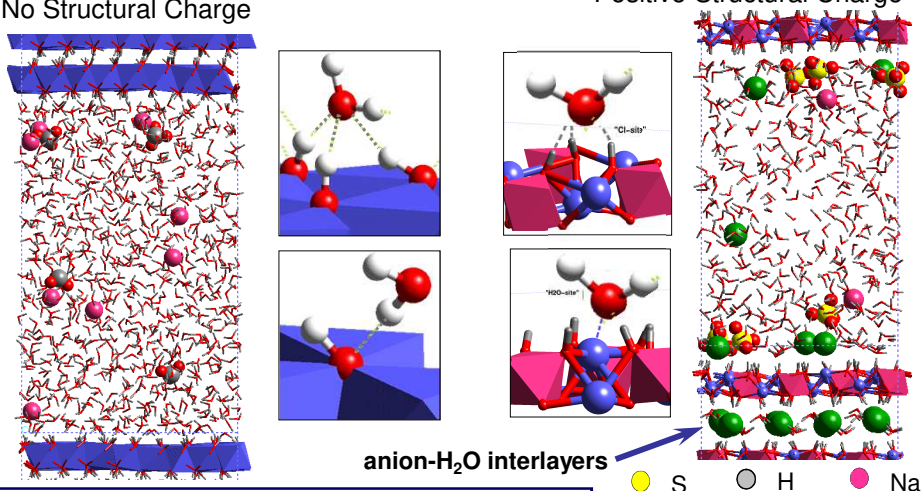
Charge Density Profiles at Hydroxylated Quartz Surface



Effect of Surface Charge on Water Structure – Metal Hydroxide Interfaces

$Ca(OH)_2$
No Structural Charge

$Ca_2Al(OH)_6Cl{\cdot}2H_2O$ - LDH
Positive Structural Charge

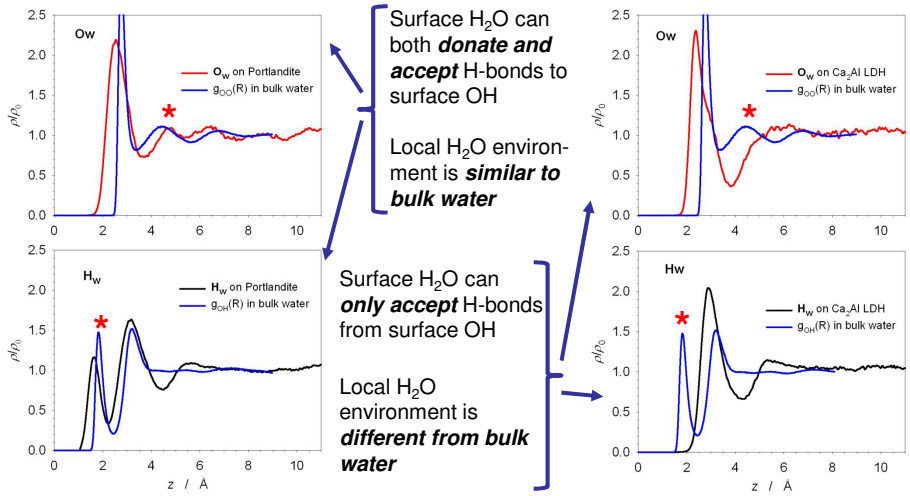


Kirkpatrick, Kalinichev, Wang, *Mineral. Magazine*, **69**, 287-306 (2005)

H_2O Density Profiles and H-Bond Network at Water-Hydroxide Interfaces

Ca-hydroxide

Ca_2Al LDH



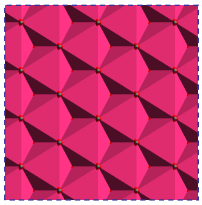
Surface H_2O can both ***donate and accept*** H-bonds to surface OH

Local H_2O environment is ***similar to bulk water***

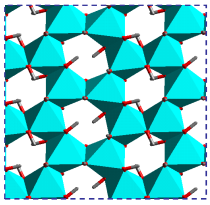
Surface H_2O can ***only accept*** H-bonds from surface OH

Local H_2O environment is ***different from bulk water***

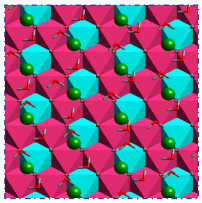
Diverse Mineral Substrate Phases Studied



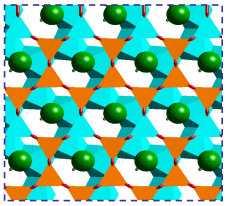
Brucite,$Mg(OH)_2$
Portlandite,$Ca(OH)_2$



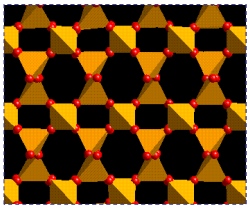
Gibbsite, $Al(OH)_3$
$LiAl_2(OH)_6Cl{\cdot}H_2O$



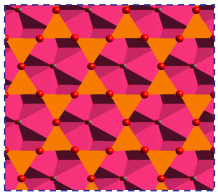
Hydrotalcite,
$Mg_2Al(OH)_6Cl{\cdot}nH_2O$
Hydrocalumite,
$Ca_2Al(OH)_6Cl{\cdot}2H_2O$



Muscovite,
$KAl_2(Si_3,Al)O_{10}(OH)_2$

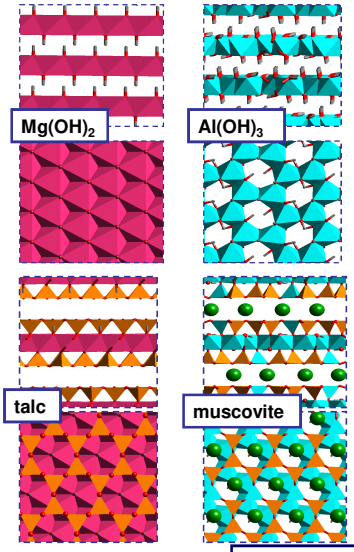


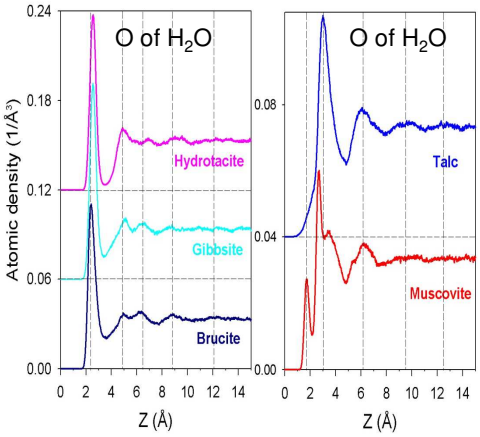
α-Quartz, SiO_2 (0001)
surface fully hydroxylated



Talc, $Mg_3Si_4O_{10}(OH)_2$

Hydrophilic and Hydrophobic Surfaces of Oxides and Hydroxides

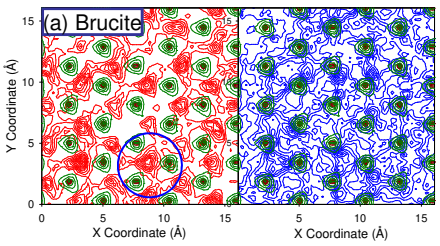


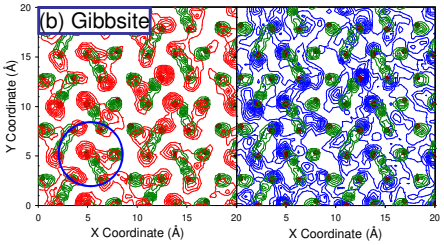


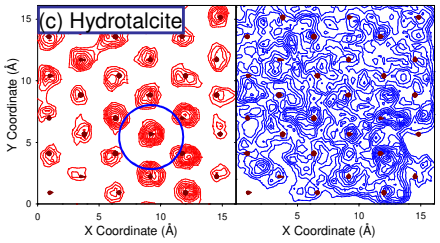
- The density profiles are very similar for hydroxides, but not for sheet silicates
- Unique and unambiguous interpretation is difficult with the profiles alone

Wang, Kalinichev, Kirkpatrick, *Geochim. Cosmochim. Acta*, **70**, 562-582 (2006)

Metal Hydroxide Surfaces



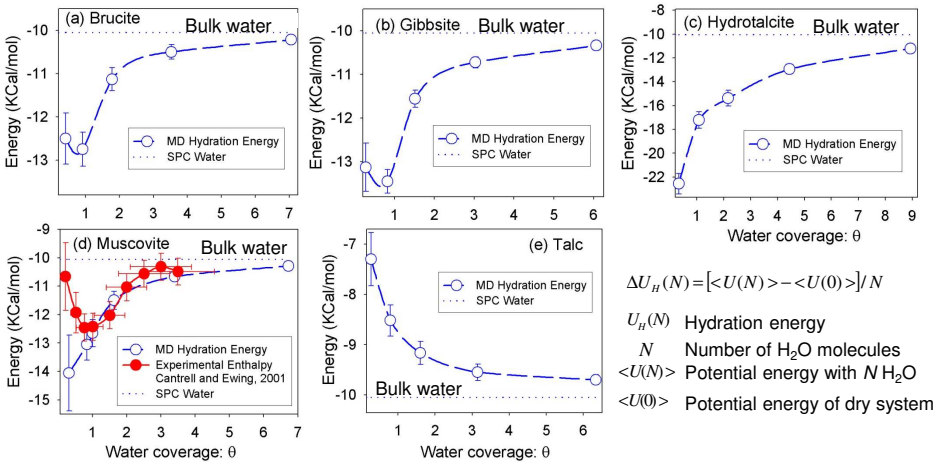




- The positions and orientations of first layer of H_2O molecules are well controlled by the substrate crystal structure, which facilitates the H-bonding with surface H_2O molecules
- Time-averaged positions of H_{H2O} (blue) are much more disordered than O_{H2O} (red)
- The second layer of water is much less ordered

Wang, Kalinichev, Kirkpatrick, *Geochim. Cosmochim. Acta*, **70**, 562-582 (2006)

Energetics of Surface Hydration



$$\Delta U_H(N) = \left[< U(N) > - < U(0) > \right] / N$$

$U_H(N)$ Hydration energy

N Number of H_2O molecules

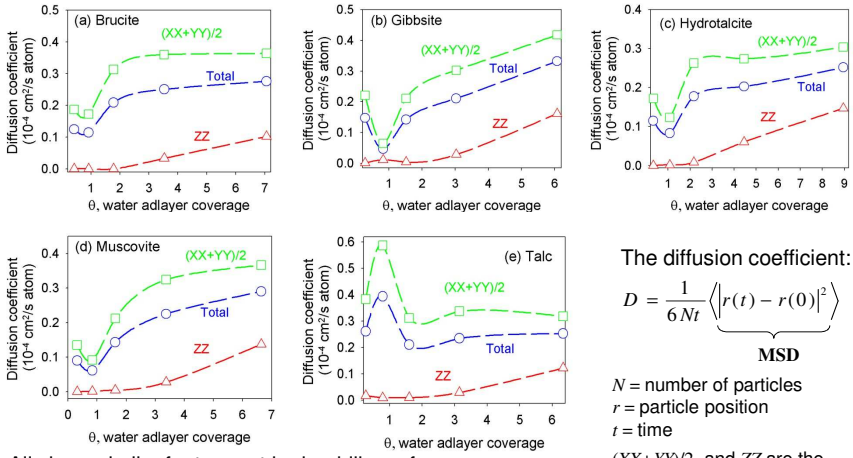
$<U(N)>$ Potential energy with N H_2O

$<U(0)>$ Potential energy of dry system

- For uncharged hydrophilic surfaces – the lowest hydration energy is at monolayer coverage
- For positively or negatively charged hydrophilic surfaces – the lowest hydration energy is at the lowest coverage
- For a hydrophobic surface (talc) – the lowest coverage has the highest hydration energy

Wang, Kalinichev, Kirkpatrick, *Geochim. Cosmochim. Acta*, **70**, 562-582 (2006)

Longer Time Scale Dynamics at the Interface: Diffusion Coefficients of Interfacial Water



The diffusion coefficient:

$$D = \frac{1}{6Nt} \underbrace{\left\langle \left| r(t) - r(0) \right|^2 \right\rangle}_{\text{MSD}}$$

N = number of particles
r = particle position
t = time

$(XX+YY)/2$, and ZZ are the components of diffusion

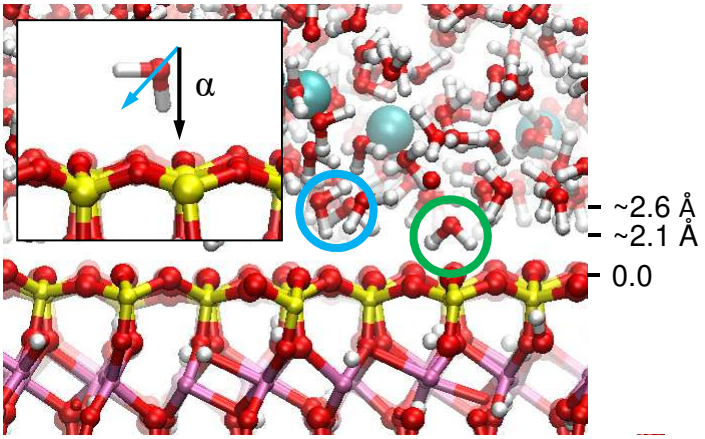
The error at each point ~10-15%

- All share similar features at hydrophilic surfaces
- A monolayer coverage stabilizes adsorbed molecules
- Hydrophobic surface: about 2 monolayer coverage stabilizes the water film

Wang, Kalinichev, Kirkpatrick, *Geochim. Cosmochim. Acta*, **70**, 562-582 (2006)

H_2O Orientation at the Clay-Water Interface

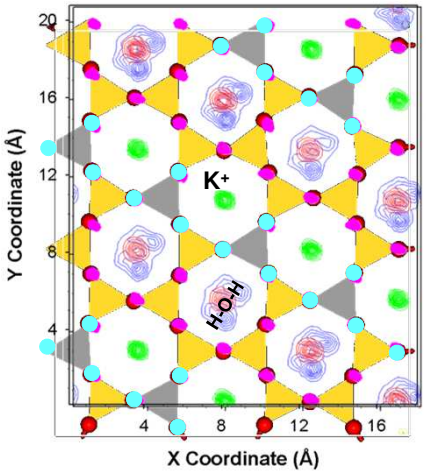
MD simulations show **two principal orientations of H_2O molecules** close to the clay surface : **monodentate** and **bidentate**:



Atomic Distributions at the Muscovite (001) Surface

Wang, Kalinichev, Kirkpatrick, Cygan, *J. Phys. Chem. B,* **109**, 15893-15905 (2005)
Wang, Kalinichev, Kirkpatrick, *Geochim. Cosmochim. Acta,* **70**, 562-582 (2006)

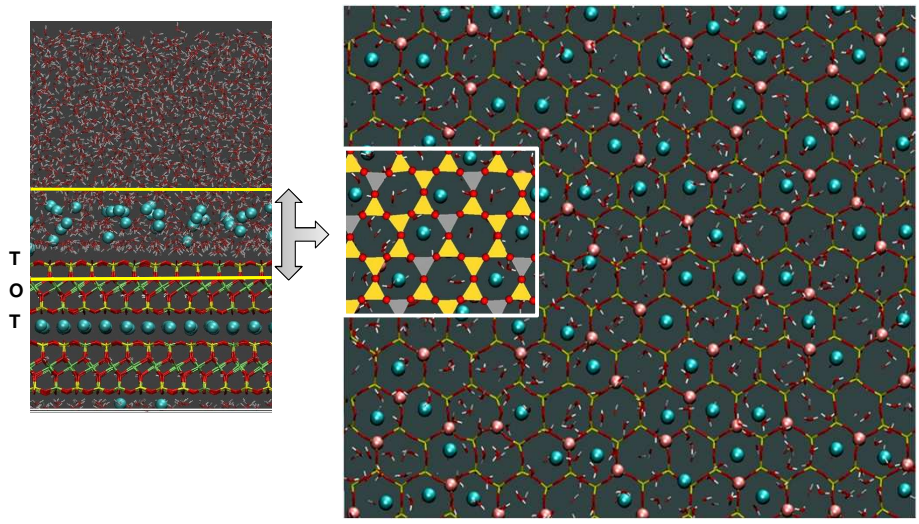
1-st molecular layer of surface species



- **Si** tetrahedron of surface layer
- Surface bridging oxygen atoms O_b
- **Al** tetrahedral substitution
- Surface bridging oxygen atoms O_{bts}
- Surface **K**+ ion
- O_w of adsorbed H_2O
- H_w of adsorbed H_2O

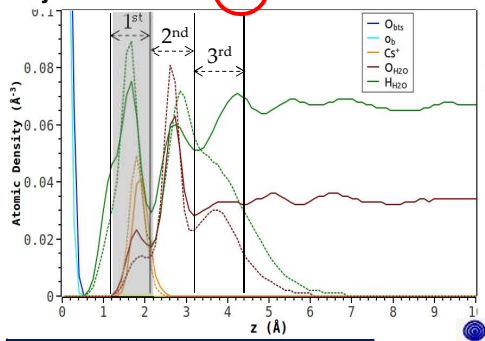
- Tetrahedral **Si**/**Al** substitutions are **ordered** in earlier models
- Hence, surface **K**+ ions and H_2O molecules are also forced to be ordered
- 50% of six-member rings are Si_4Al_2, the other 50% are Si_5Al_1.
- **K**+ ions occupy all the Si_4Al_2 rings

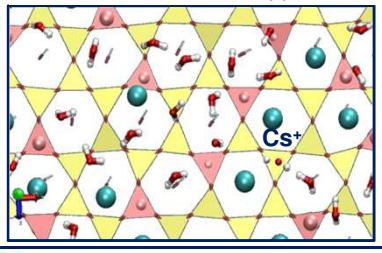
Disorder of Al/Si Tetrahedral Sites in Muscovite

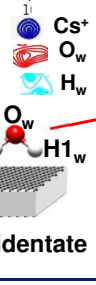


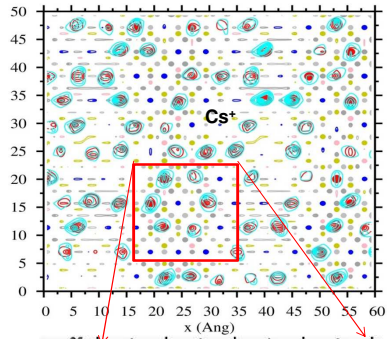
Surface Atomic Density Maps

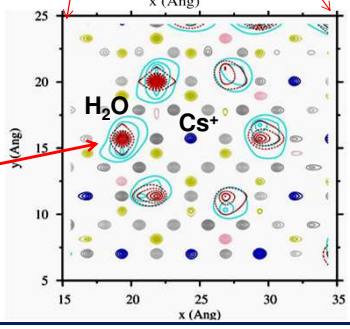
1-st layer of water on Cs^+-muscovite





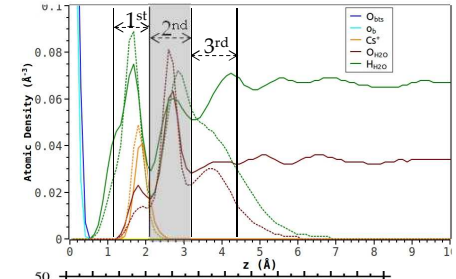


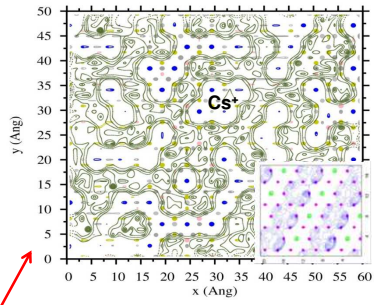


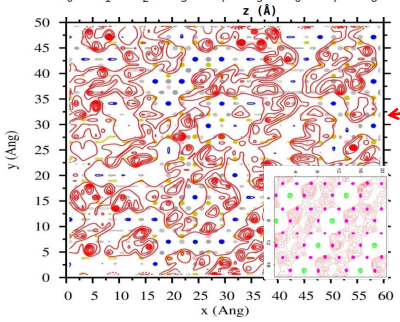


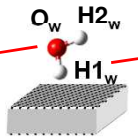
Surface Atomic Density Maps

2-nd layer of water on Cs⁺-muscovite

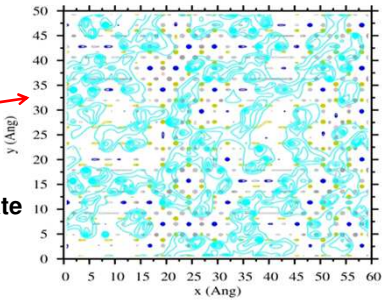






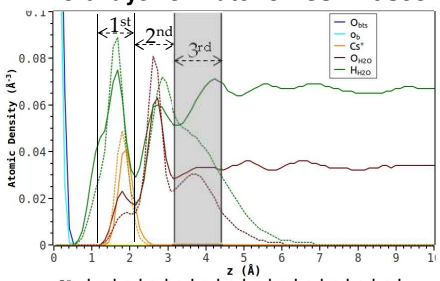


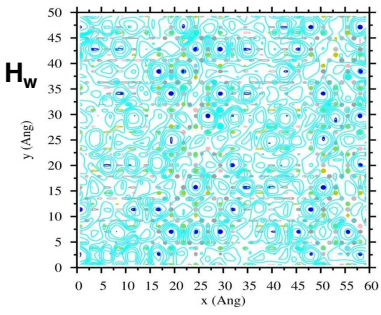
monodentate

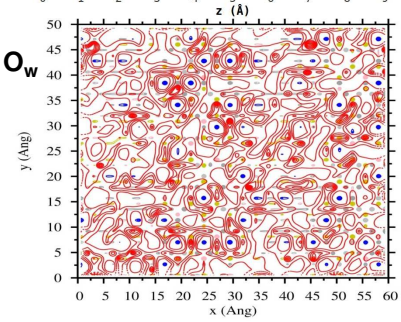


Surface Atomic Density Maps

3-d layer of water on Cs⁺-muscovite







Summary

- In-plane H_2O ordering induced by the surface
- Out-of-plane H_2O ordering induced by Cs^+ ions
- Consistent with the recent experimental data by S.Pintea and R.Felici, ESRF, Grenoble *(private communication)*

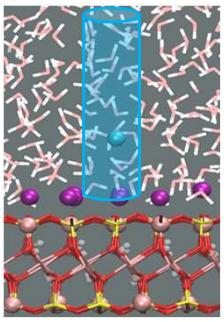
N. Loganathan, A.G.Kalinichev, in prep, 2024

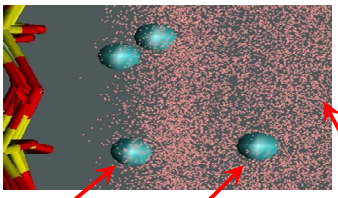
Free Energy of Ion Surface Adsorption

Potential of Mean Force:

$$W(z) = -k_B T \ln(\rho(z)) + const$$

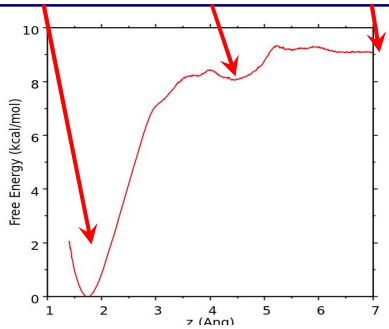
z - distance from the surface





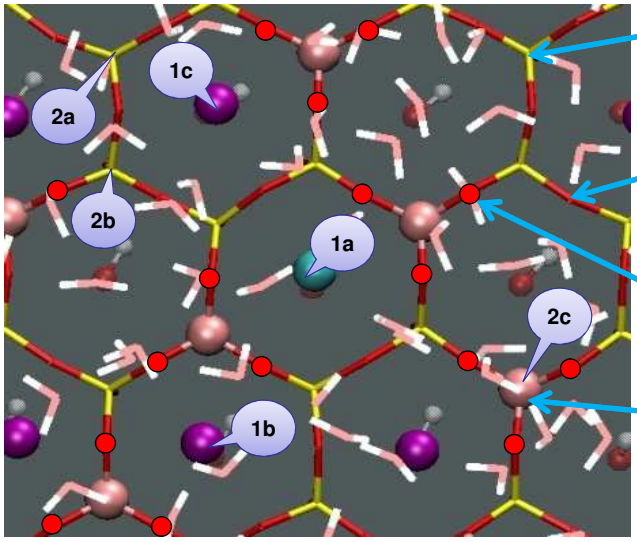
$$S{\cdot}I \Leftrightarrow S \cdot I(H_2O)_n \Leftrightarrow S + I$$

ISSC OSSC desorbed ions



$$K_{eq} = \frac{4\pi \int \exp(-W_{ISSC}/k_B T)\, r^2 dr}{4\pi \int \exp(-W_{OSSC}/k_B T)\, r^2 dr}$$

Different Adsorption Sites on Muscovite Surface

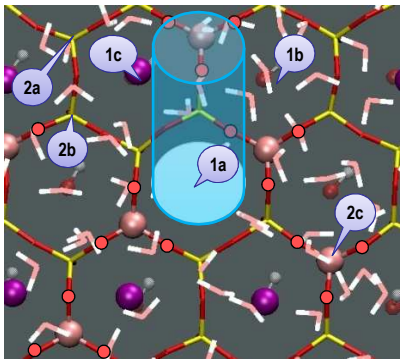


Surface Sites and Adsorption Free Energy Profiles of Cs^+ and K^+ on Muscovite

Potential of Mean Force:

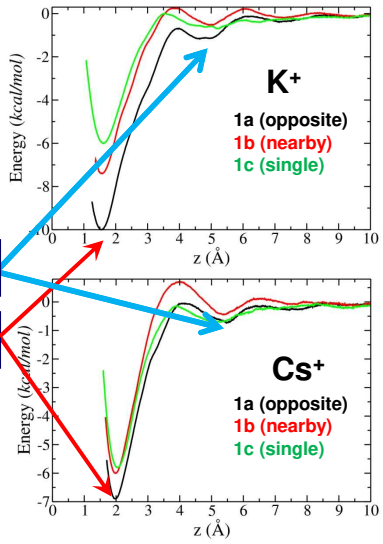
$$\text{PMF} \equiv W(z) = -k_B T \ln\left(\rho(z)\right) + const$$

z - distance from the surface



outer-sphere

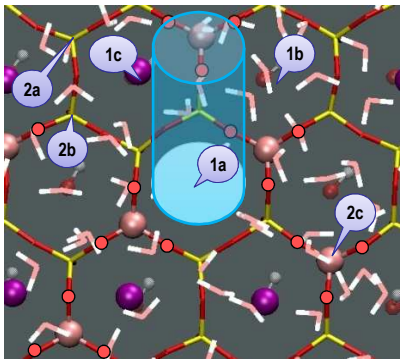
inner-sphere

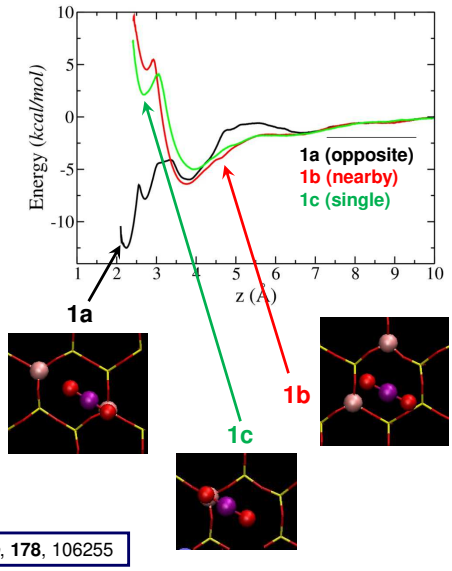


N. Loganathan, A.G.Kalinichev (2017) *J. Phys. Chem. C*, **121**, 7829–7836

$K^+_{surf} + Cs^+_{aq} \Leftrightarrow K^+_{aq} + Cs^+_{surf}$

Surface Sites and Adsorption Free Energy Profiles of UO_2^{2+} on Muscovite

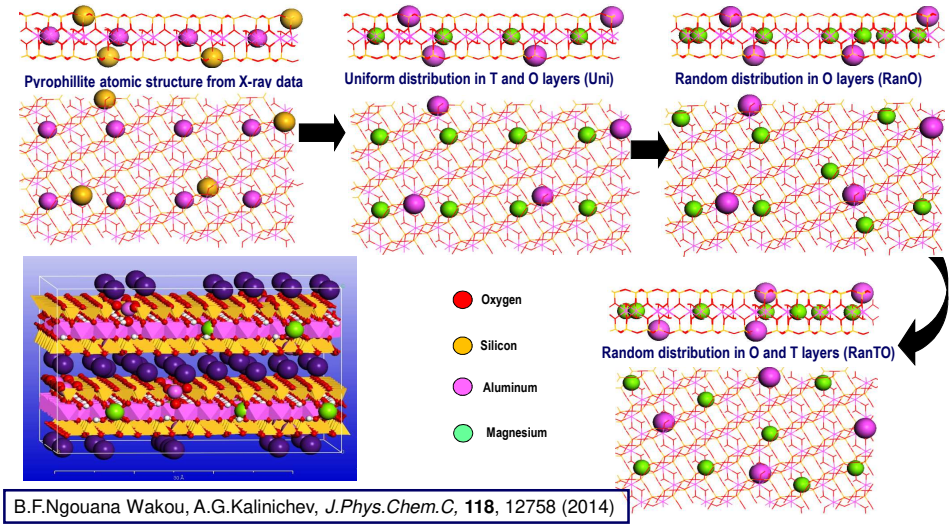




$$K_{eq} = \frac{4\pi \int \exp(-W_{ISSC}/k_B T)\, r^2 dr}{4\pi \int \exp(-W_{OSSC}/k_B T)\, r^2 dr}$$

N. Loganathan, A.G.Kalinichev (2025) *Applied Clay Science*, **178**, 106255

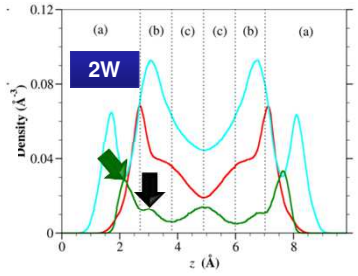
Effects of the Charge Localization on the Adsorption and Transport of Ions in $3M^{+}(Si_{31}Al)(Al_{14}Mg_2)O_{80}(OH)_{16}\cdot nH_2O$ (M^{+} = Li^{+}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}, ½Ca^{2+}, ½Sr^{2+}, ½Ba^{2+}, ½Ni^{2+})

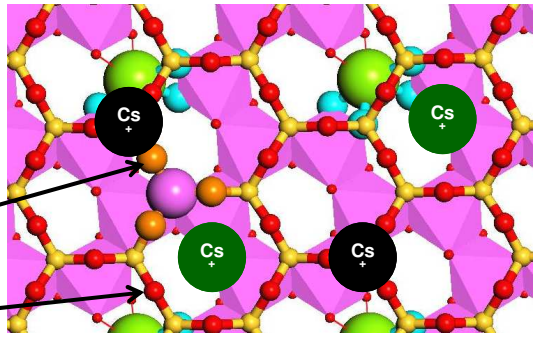


B.F.Ngouana Wakou, A.G.Kalinichev, *J.Phys.Chem.C,* **118**, 12758 (2014)

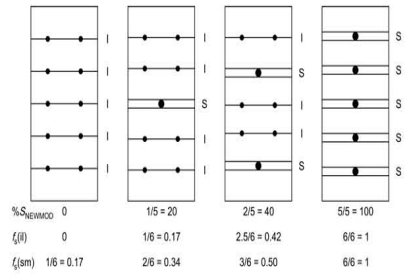
Interlayer and Surface Adsorption Sites on (001) of Cs^{+}-Montmorillonite Smectite

B.F. Ngouana Wakou, A.G.Kalinichev
J. Phys. Chem. C, **118**, 12758-12773 (2014)

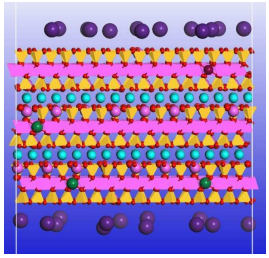


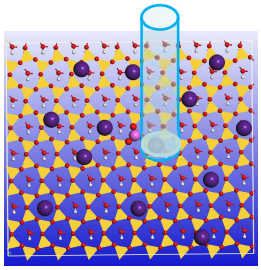


Interstratified Illite-Smectite Structural Model and Adsorption Sites on COx Clay Particles



J.Srodon et al., *Clays and Clay Minerals*, **57**, 649-671 (2009)



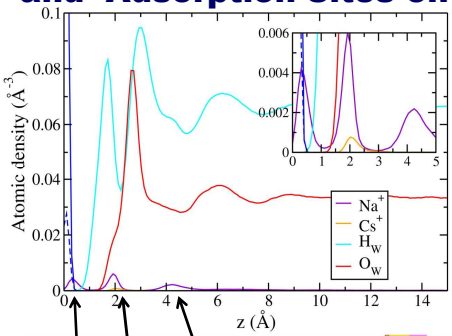


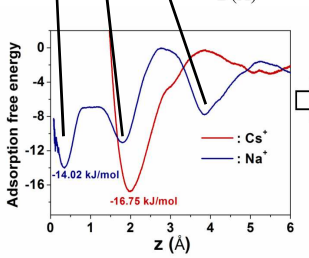
ISCz-1 model of COx used in experiments and simulations

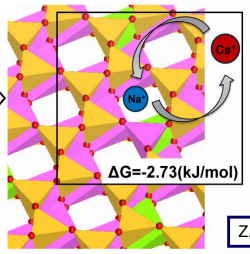
$Ca_{0.09}K_{0.48}Si_{3.52}Al_{0.48}(Al_{1.70}Fe_{0.08}Mg_{0.24})O_{10}(OH)\cdot nH_2O$

Noticeable effect not only of the distribution of charges in the nearest tetrahedral layer, but also in the lower octahedral and tetrahedral layers

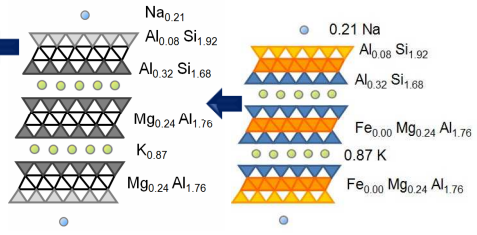
Interstratified Illite-Smectite Structural Model and Adsorption Sites on COx Clay Particles







ISCz-1 model of COx used in experiments and simulations



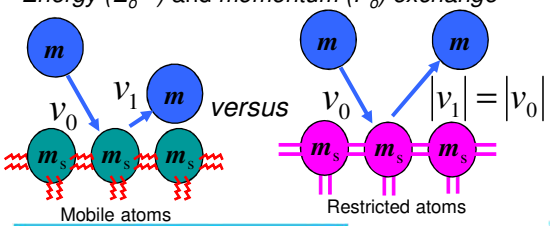
J.Srodon et al., *Clays and Clay Minerals*, **57**, 649-671 (2009)

Cs⁺ / Na⁺ exchange on the basal surface of interstratified illite-smectite

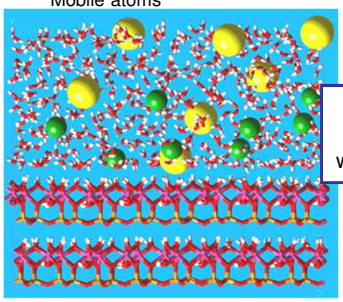
Z.Chen et al., 2025, *Env. Sci. Technol.*, in revision

ClayFF and Importance of the Substrate Mobility

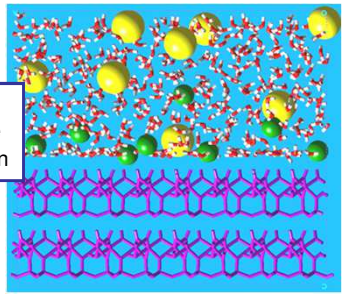
Energy (E_o^{kin}) and momentum (P_o) exchange



- Molecular structure of the aqueous interfaces
- Effective diffusion of surface-sorbed species
- Residence times of surface-sorbed species
- Translational, librational, and vibrational dynamics of surface-sorbed species



MD simulation of kaolinite interface with CsCl aq. solution

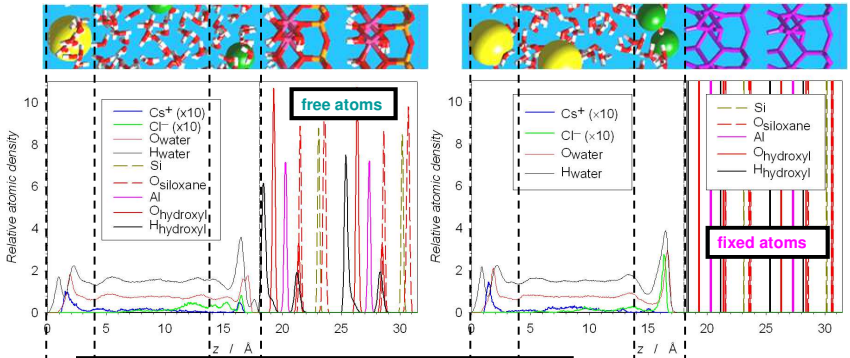


Fully flexible; no constraints

Fixed atoms in kaolinite substrate

Atomic Density Profiles and Surface Diffusion Rates

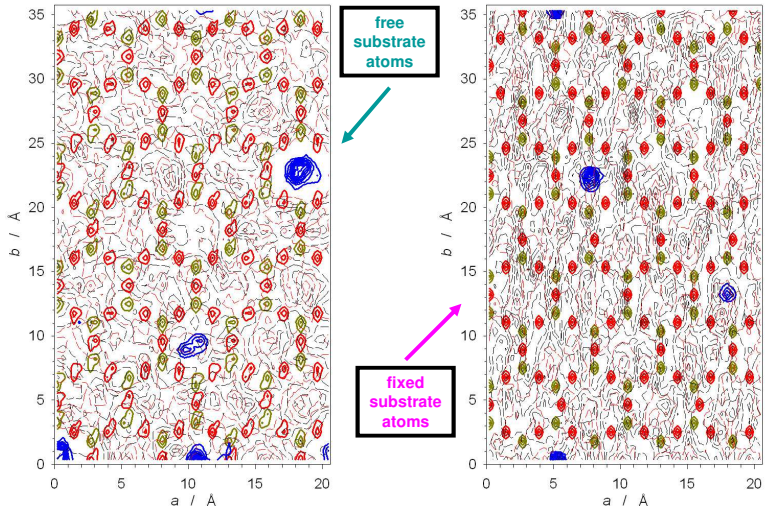
Interface of kaolinite with 1m CsCl aqueous solution



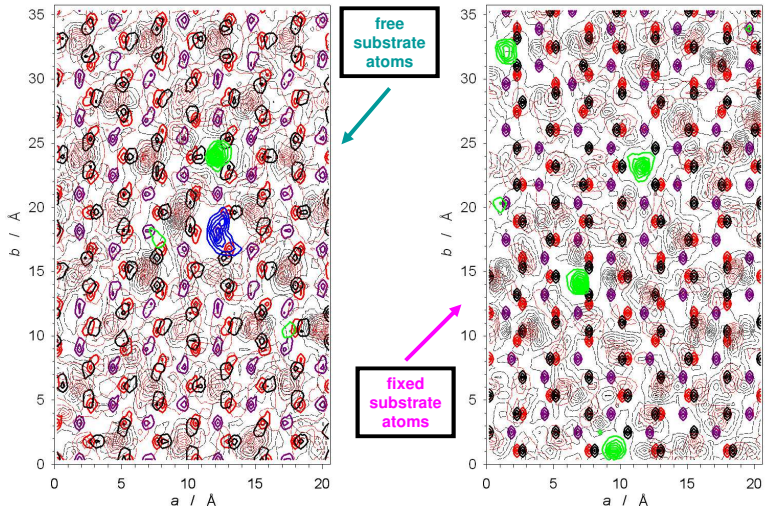
Diffusion coefficients of solution species (10^{-5} cm^2/s)

	"siloxane" interface		"gibbsite" interface		"siloxane" interface		"gibbsite" interface	
Cs^+	0.46	1.30	0.23		0.19	1.40	0.62	Cs^+
Cl^-	–	1.20	0.52		–	2.10	0.17	Cl^-
H_2O	2.25	1.80	0.80		2.00	1.80	0.39	H_2O

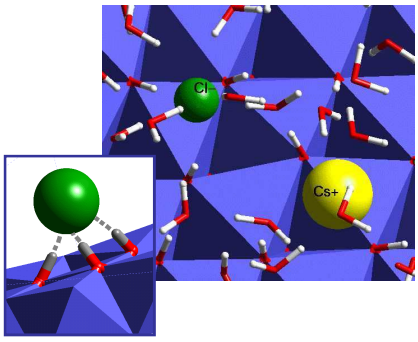
Contour Maps of Atomic Densities within the Inner-Sphere “Siloxane” Interface of Kaolinite



Contour Maps of Atomic Densities within the Inner-Sphere “Gibbsite” Interface of Kaolinite



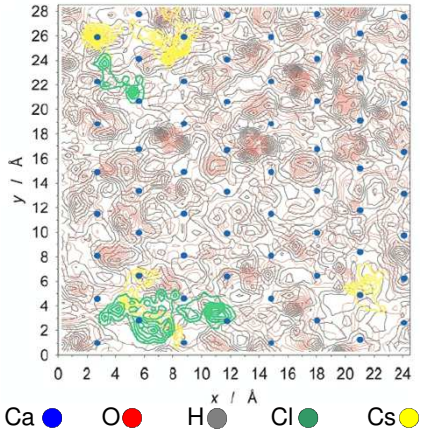
Adsorption of Cs^+ and Cl^- Ions at the Surface of Portlandite, $Ca(OH)_2$



Mobility of surface OH groups is important for realistic modeling of **H-bonding** at the sorption sites

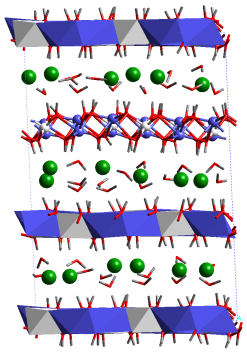
Kalinichev and Kirkpatrick, *Chem. Materials*, **14**, 3539-3549 (2002)

Atomic density maps of the adsorbed surface species ("inner sphere" complexing)



Structure and Dynamics of Water and Ions in Layered Double Hydroxides (Anionic Clays)

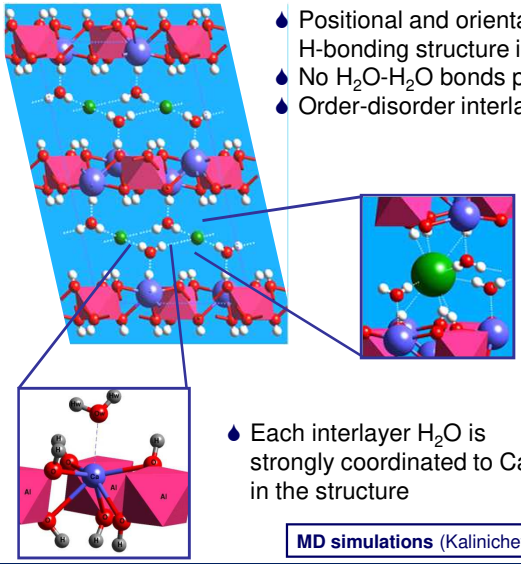
$M1(II)_{(1-x)}\,M2(III)_x(OH)_2 \cdot A^{n-}_{x/n} \cdot mH_2O$



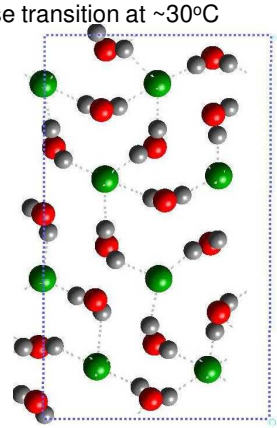
- **Layered double hydroxides** (LDHs), also called **anionic clays**
- Permanent anion exchange capacity due to isomorphic substitution of **M2(III)** for **M1(II)**
- Important applications:
  - Catalysts and catalyst supports
  - Potential repository materials
  - Drug delivery, gene therapy
  - Significant phases in cement systems
  - Origin of life
- Occur naturally, and can be easily synthesized

- **Good test example of nano-confined aqueous species**
- Hydrocalumite – $Ca_2Al(OH)_6Cl{\cdot}2H_2O$ – one of the best structurally defined LDH

Interlayer Structure of Hydrocalumite, Friedel's Salt, $[Ca_2Al(OH)_6]Cl\cdot 2H_2O$



- Positional and orientational ordering of the H_2O - Cl^- H-bonding structure in the interlayer
- No H_2O-H_2O bonds present
- Order-disorder interlayer phase transition at ~30°C

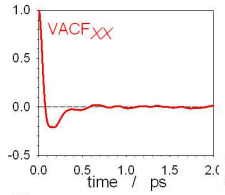


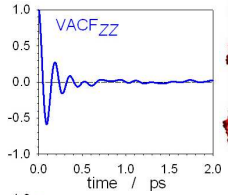
- Each interlayer H_2O is strongly coordinated to Ca in the structure

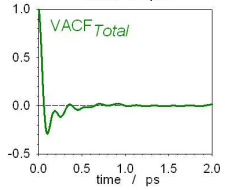
MD simulations (Kalinichev et al., 2000, 2002, 2005, 2010, 2017, 2023)

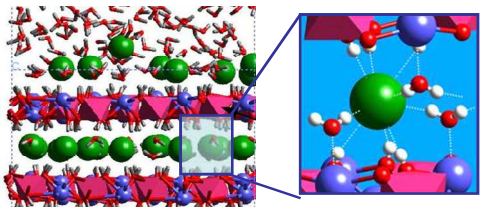
Shorter Time Scale: Dynamics of Individual Atoms - VACFs and Vibrational Density of States

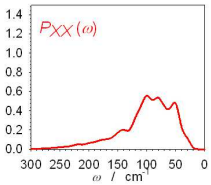
Cl^- in hydrocalumite - $[Ca_2Al(OH)_6]Cl\cdot 2H_2O$ - AFm Phase

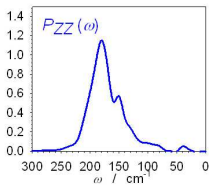


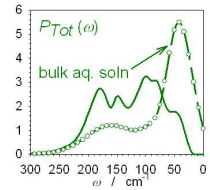












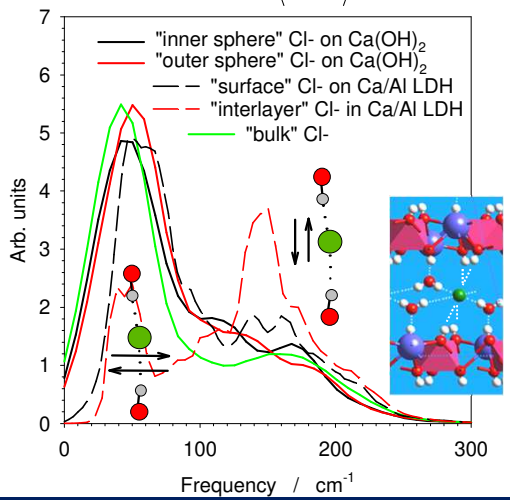
$$\mathrm{VACF} = \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)^2\rangle} = \frac{1}{\langle \mathbf{v}(0)^2\rangle}\int \mathbf{v}(0)\cdot\mathbf{v}(t)\,d\Gamma$$

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

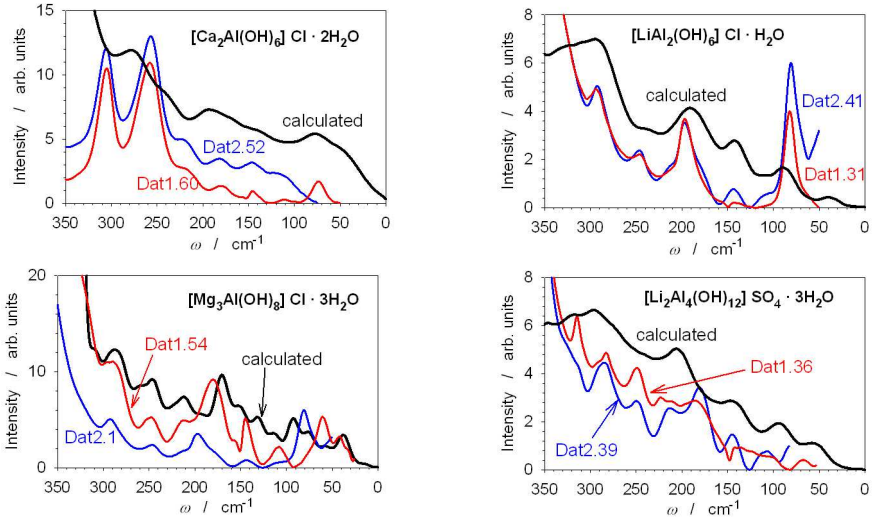
Power Spectra of Cl^- Ion Dynamics in $Ca(OH)_2$ and Ca_2Al-Cl AFm phase

$$\mathrm{VACF} \equiv C_{vv}(t) = \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)^2\rangle} = \frac{1}{\langle \mathbf{v}(0)^2\rangle}\int \mathbf{v}(0)\cdot\mathbf{v}(t)\,d\Gamma \qquad P(\omega) = \int_0^\infty \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)^2\rangle}\cos(\omega t)\,dt$$

- Dynamics of Cl^- in the AFm interlayers is different from that on the AFm surface
- Dynamics of Cl^- on the AFm surface is different from that on the $Ca(OH)_2$ surface
- Dynamics of "outer-sphere" Cl^- on the $Ca(OH)_2$ surface is similar to that in the bulk aqueous solution



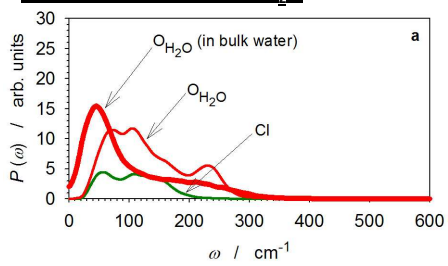
Comparison of Observed and Computed FIR Spectra for LDH Phases



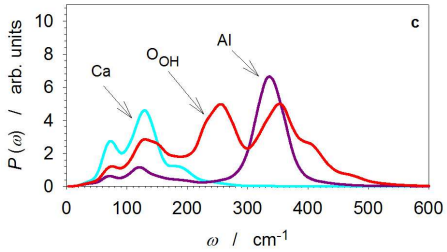
Kirkpatrick, Kalinichev, Wang et al. (2005) *Clay Minerals Society Workshop Lecture Series*, **13**, 239-285.

Low-Frequency Vibrations of Hydrocalumite

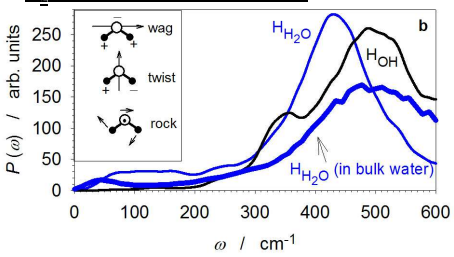
Interlayer species – Cl^-, H_2O



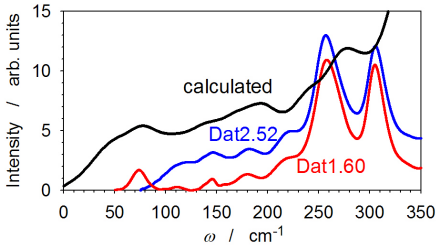
Lattice vibrations



H_2O & OH librational modes

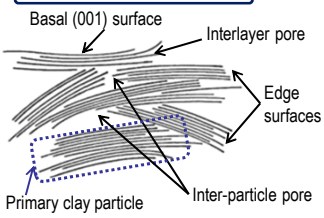


Comparison with FIR measurements



Particle Edges: Quantum (Ab Initio) Molecular Dynamics to Address the Chemical Reactivity

Aggregate of clay particles



- Basal (001) surfaces and interlayers are extensively studied; their properties are reasonably well known
- Clay edges have received much less attention yet
- Ab initio (quantum) MD is a direct answer, but it is very expensive computationally
- AIMD ⇒ ~n×100 atoms; ~15×15×15 Å^3; t ~10-50 ps

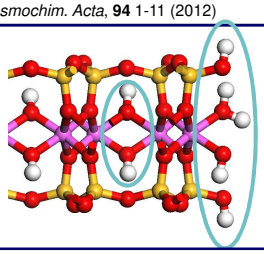
S.V.Churakov, *Geochim. Cosmochim. Acta*, **71**, 1130-1144 (2007)
X. Liu et al., *Geochim. Cosmochim. Acta* (2012, 2013, 2014, 2015)
S. Tazi et al., *Geochim. Cosmochim. Acta*, **94** 1-11 (2012)

ClayFF Parametrization for Clay Edges

New special ClayFF bending terms for Mg-O-H, Al-O-H, and Si-O-H

$$U_{\text{ClayFF-MOH}} = U_{\text{ClayFF-orig}} + U_{\text{M-O-H}} = U_{\text{ClayFF-orig}} + k(\theta - \theta_0)^2$$

k and θ_0 have to minimize the differences between DFT and ClayFF-MOH results

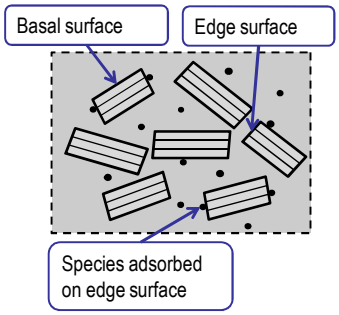


M.Pouvreau, PhD Thesis, Dec. 2016

Pouvreau, Greathouse, Cygan, Kalinichev, *J.Phys.Chem.C*, 2017, **121**, 14757-14771; 2019, **123**, 11628–11638

ClayFF Parametrization for Clay Particle Edges

M.Pouvreau, PhD Thesis, Dec. 2016

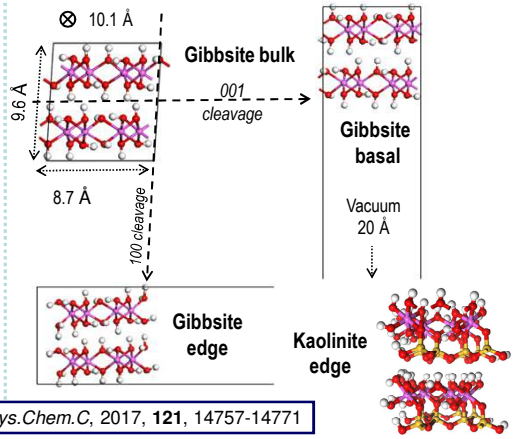


New special ClayFF M-O-H bending terms

$U_{ClayFF\text{-}MOH} = U_{ClayFF\text{-}orig} + U_{M\text{-}O\text{-}H} =$
$= U_{ClayFF\text{-}orig} + k(\theta - \theta_0)^2$

k and θ_0 have to minimize the differences between DFT and ClayFF-MOH results

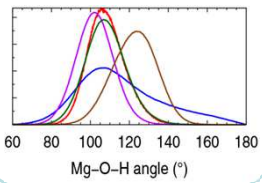
- ***Brucite, gibbsite, kaolinite*** edges
- 3D periodic boundary conditions
- Cells size:
  - ✓ N_{atoms} ~100 for DFT+parametrization;
  - ✓ N_{atoms} ~ 2500 for classical MD

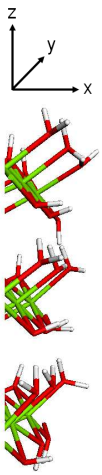


Pouvreau, Greathouse, Cygan, Kalinichev, *J.Phys.Chem.C*, 2017, **121**, 14757-14771

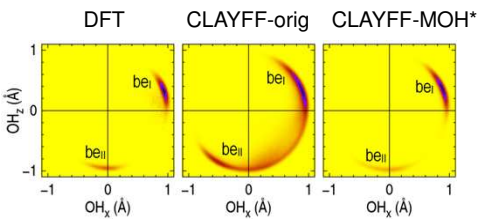
Brucite edge: ∠Mg-O-H and $\overrightarrow{OH}$

∠Mg-O-H distribution





$\overrightarrow{OH}$ distribution in *xz* plane



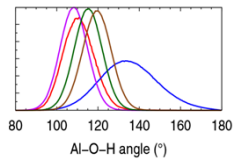
*θ_0 = 110°; k_{MgOH} = 6 kcal·mol⁻¹·rad⁻²

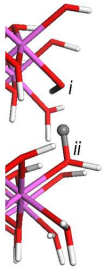
- Narrowing of ∠Mg-O-H and $\overrightarrow{OH}$ distributions

M.Pouvreau, J.A.Greathouse, R.T.Cygan, A.G.Kalinichev, *J.Phys.Chem.C*, 2017, **121**, 14757-14771

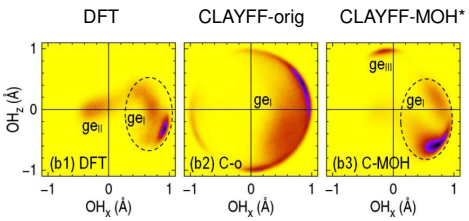
Gibbsite Edge: ∠Al-O-H and $\overrightarrow{OH}$

∠Al-O-H distribution





$\overrightarrow{OH}$ distribution of OH groups in *xz* plane



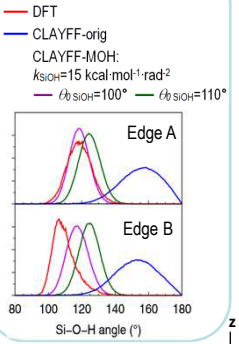
* θ_0 = 110°; k_{MgOH} ~ 15 kcal·mol^{-1}·rad^{-2}

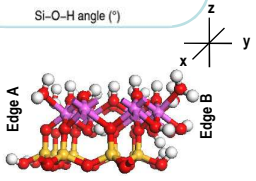
- Narrowing of ∠Al-O-H and $\overrightarrow{OH}$ distributions
- ∠Al-O-H: both θ_0=100° and θ_0=110° are close enough to DFT results
- DFT MD: observed proton transfers between OH and OH_2 groups

M.Pouvreau, J.A.Greathouse, R.T.Cygan, A.G.Kalinichev, *J.Phys.Chem.C*, 2017, **121**, 14757-14771

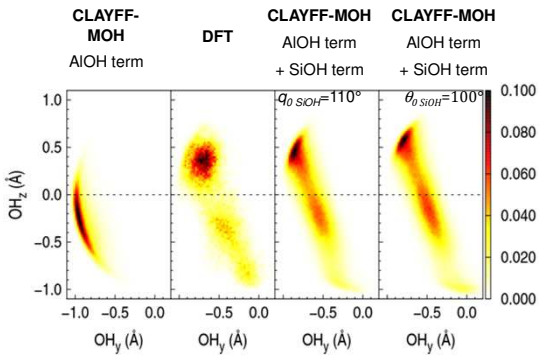
Kaolinite Edge: ∠Si-O-H and $\overrightarrow{OH}$

∠Si-O-H distribution





$\overrightarrow{OH}$ distribution of OH groups in *yz* plane for edge A



- $\theta_{0\ AlOH}$= 110°; k_{AlOH} =k_{SiOH} = 15 kcal·mol^{-1}·rad^{-2}
- $\theta_{0\ SiOH}$= 100° better than $\theta_{0\ SiOH}$= 110° on both edges
- $\overrightarrow{OH}$ distribution not affected with both values of θ_0

M.Pouvreau et al., *J.Phys.Chem.C*, 2019, **123**, 11628–11638

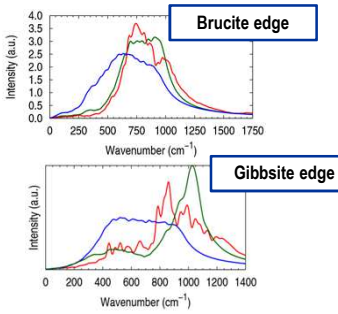
O-H Librational (M-O-H Bending) Spectra

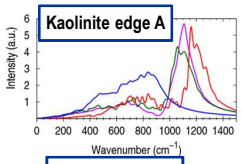
— DFT
— CLAYFF-orig
CLAYFF-MOH:
k_{MgOH} = 6 kcal·mol^{-1}·rad^{-2}
k_{AlOH} = k_{SiOH} 15 kcal·mol^{-1}·rad^{-2}
— $\theta_{0\,MOH}$ = 100°
— $\theta_{0\,MOH}$ = 110°

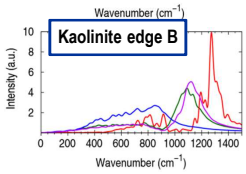
- Fourier Transform of the velocity autocorrelation function:

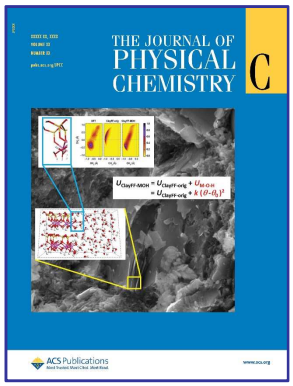
$$P(\nu) = \int \langle \dot{\boldsymbol{r}}(\tau) \cdot \dot{\boldsymbol{r}}(t+\tau) \rangle_\tau \, e^{-i\omega t} dt$$

- We consider the velocity of the H atoms of O-H groups
  → $\bar{\nu}$ < 1500 cm^{-1}: O-H libration





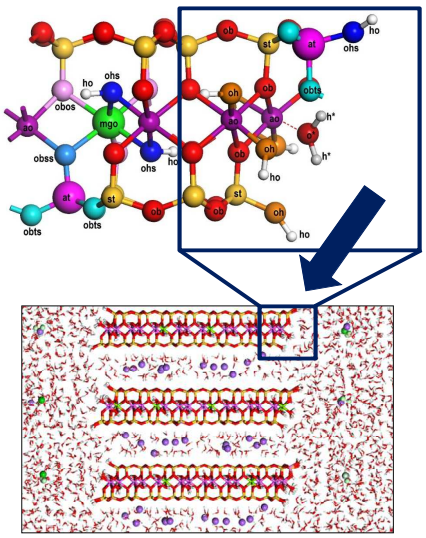


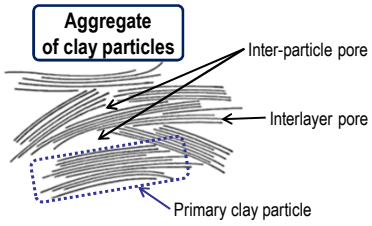


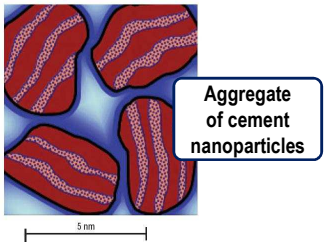
- Spectra shifted of 250 to 600 cm^{-1} and narrowed
- Kaolinite: as expected not much difference between q_0=100° and q_0=110°

M.Pouvreau et al., *J.Phys.Chem.C*, 2019, **123**, 11628–11638

Next: Adsorption at the Particle Edges and Mesoscale Modeling of Nanoparticle Aggregates

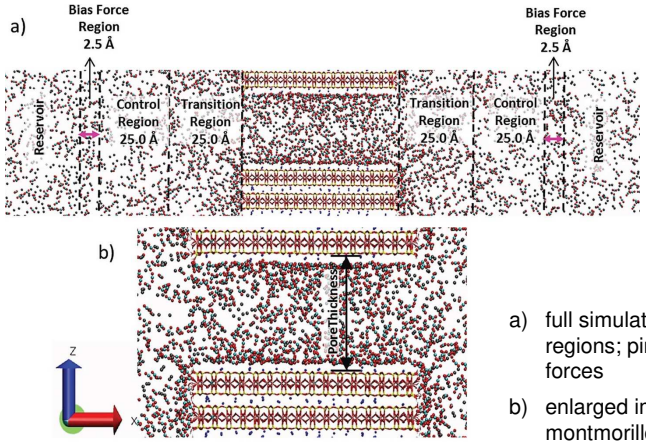






CH_4/CO_2 Partitioning in Clay Nano- and Meso-Pores: Molecular Dynamics Modeling with Constant Reservoir Composition (I)

N.Loganathan, G.M.Bowers, B.F.Ngouana-Wakou, A.G.Kalinichev, R.j.Kirkpatrick, O.Yazaydin. (2019) *Physical Chemistry - Chemical Physics*, **21**, 6917-6924



Scheme of the simulation cells used in the constant reservoir composition molecular dynamics, CRC-MD calculations of CO_2/CH_4 partitioning into pores bounded by montmorillonite basal surfaces

a) full simulation cell showing the different regions; pink arrows represent bias forces

b) enlarged image of the silt-like pore and montmorillonite T-O-T layers

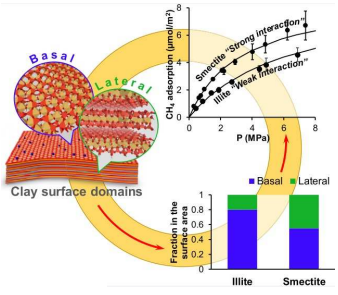
CH_4/CO_2 Partitioning in Clay Nano- and Meso-Pores: Molecular Dynamics Modeling with Constant Reservoir Composition (II)

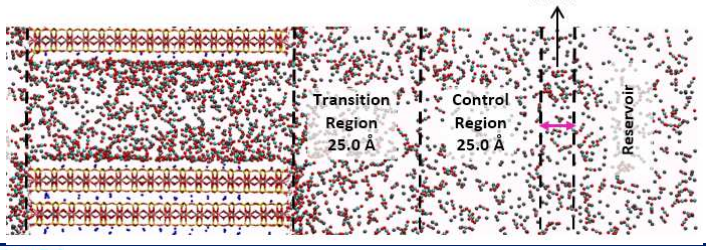
N.Loganathan, G.M.Bowers, B.F.Ngouana-Wakou, A.G.Kalinichev, R.J.Kirkpatrick, O.Yazaydin (2019) *Phys.Chem.-Chem.Phys*, **21**, 6917-6924

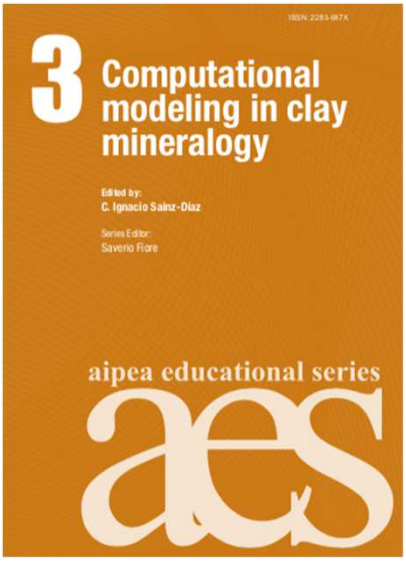
N.Loganathan, A.O.Yazaydin, G.M.Bowers, B.F.Ngouana-Wakou, A.G.Kalinichev, R.J.Kirkpatrick (2020) *J.Phys.Chem. C,* **124**, 2490−2500

D.I.Grekov, T.Suzuki-Muresan, A.G.Kalinichev, P.Pré, B.Grambow (2020) *Phys.Chem.-Chem.Phys*, **22**, 16727-16733

D.I.Grekov, T.Suzuki-Muresan, A.G.Kalinichev, P.Pré, B.Grambow (2021) *J.Phys.Chem. C,* **125**, 11499−11507







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Questions for the final paper / report on one of the 21 topics, e.g., 1 – clays; 2 – cement; 3 – TiO_2 surfaces; 4 – corrosion; 5 – organics, etc.
(Please use only as a guidance)

- What molecular modeling method was used and why?
- Was it a fully atomistic simulations, or some simplified models were used?
- What other approximations were used in the modeling?
- What was the number of particles in the simulations? Was it big enough for the specific problem? Was it small enough to make the simulations computationally efficient?
- How long-range electrostatic interactions were handled in the simulations? Was it important for the given problem?
- What kind of boundary conditions were applied to the simulation box? Why?
- What properties of the system were calculated from the molecular simulation?
- Make a qualitative assessment of the accuracy for the calculated properties given the number of atoms in the simulated system and the duration of the simulation.
- What other properties would you additionally calculate from the same simulations for the same system?
- Formulate 2 or 3 strong points of the given molecular simulation paper and 2 or 3 weak points of the paper.