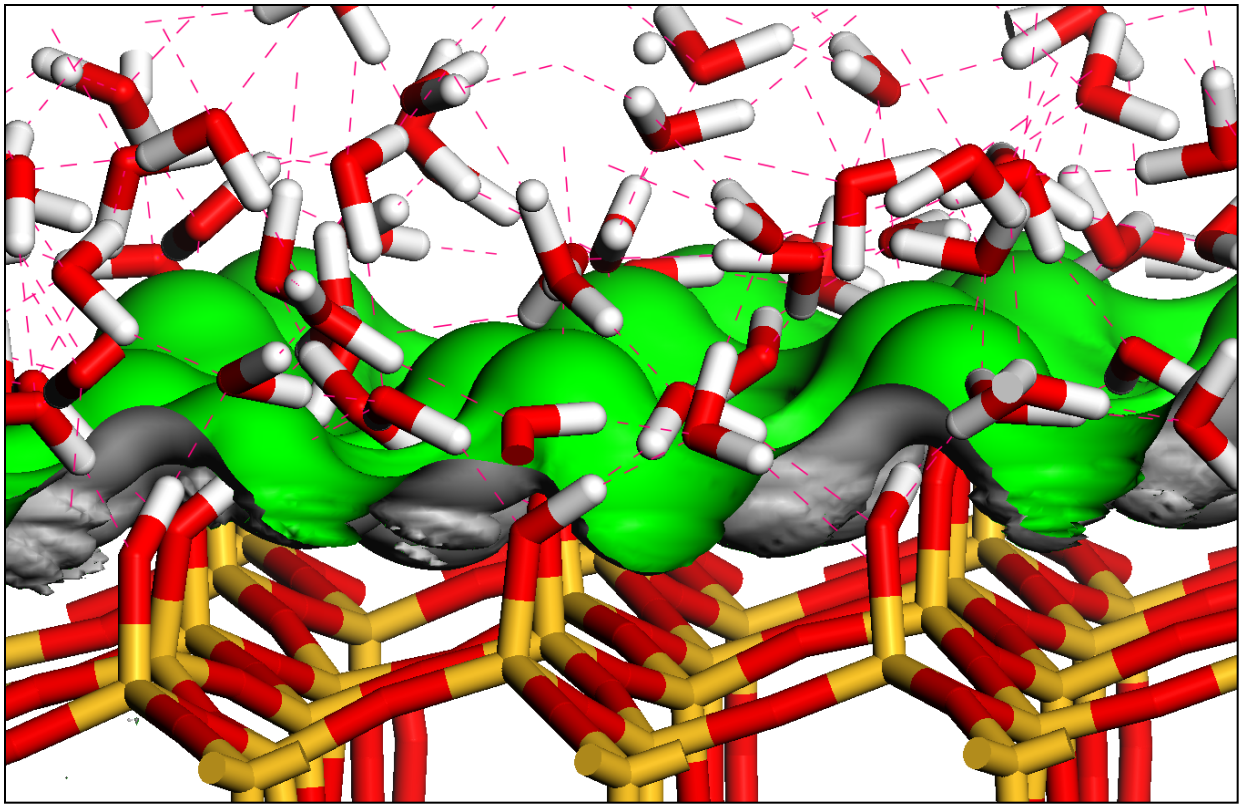
Effects of Thermodynamic Ensemble and Mineral Surface on Interfacial Water Structure

SAND2011-6740C



Todd R. Zeitler
Jeffery A. Greathouse
Randall T. Cygan

Geochemistry Department
Sandia National Laboratories

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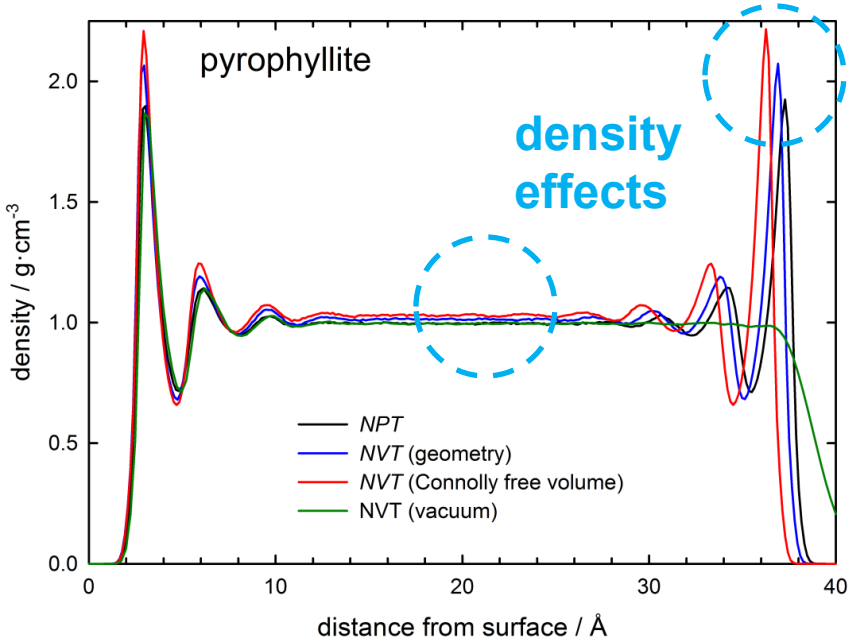
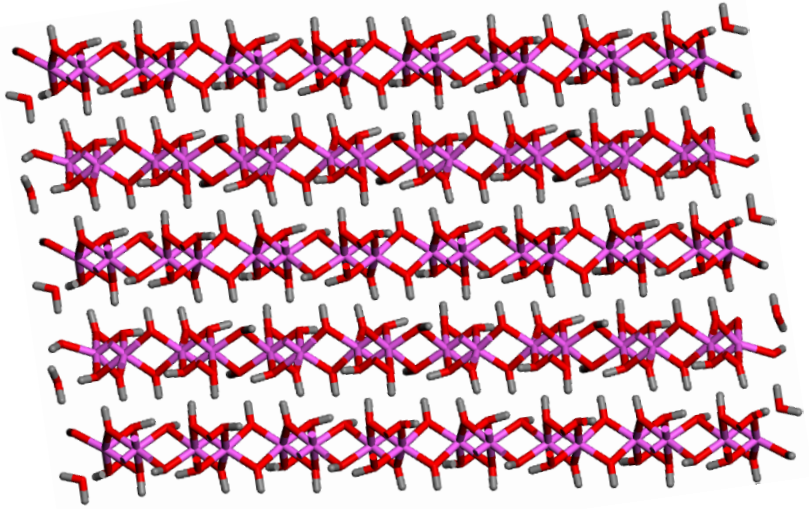
This presentation focuses on interfacial water structure and FF development



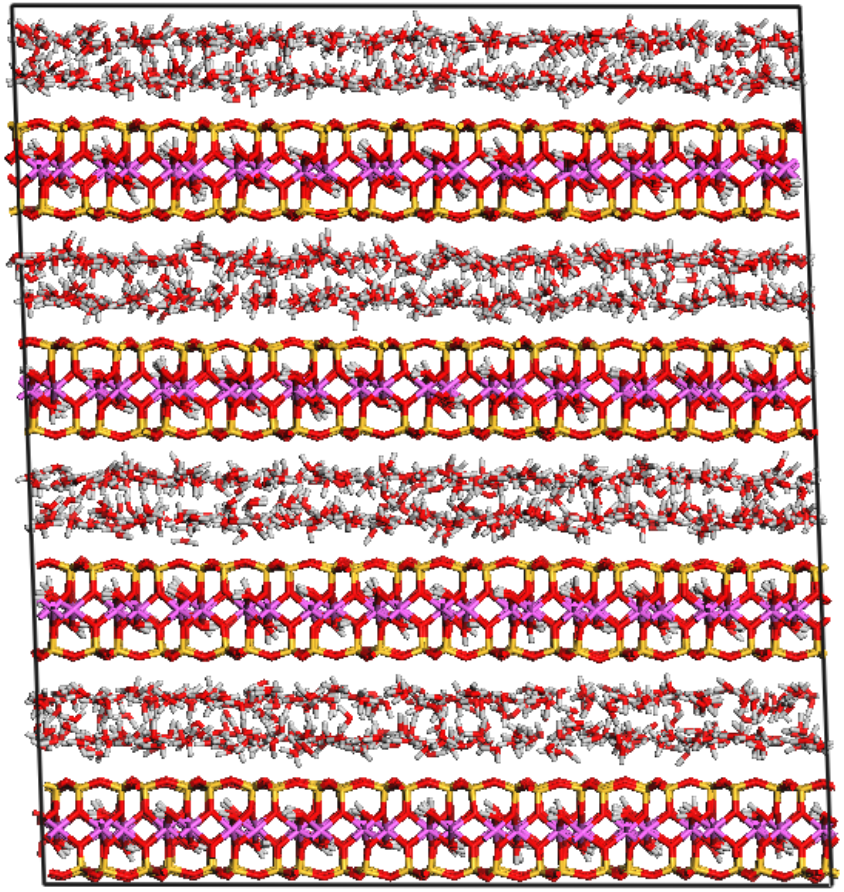
Accurate interfacial density

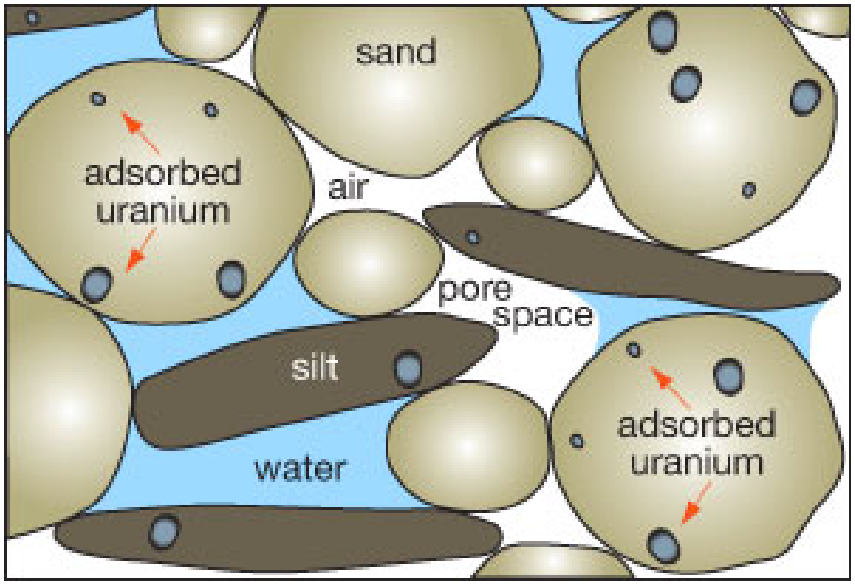


FF development for clay edge sites

Water-mineral interactions are interesting from many standpoints

swelling due to interlayer H_2O in clays



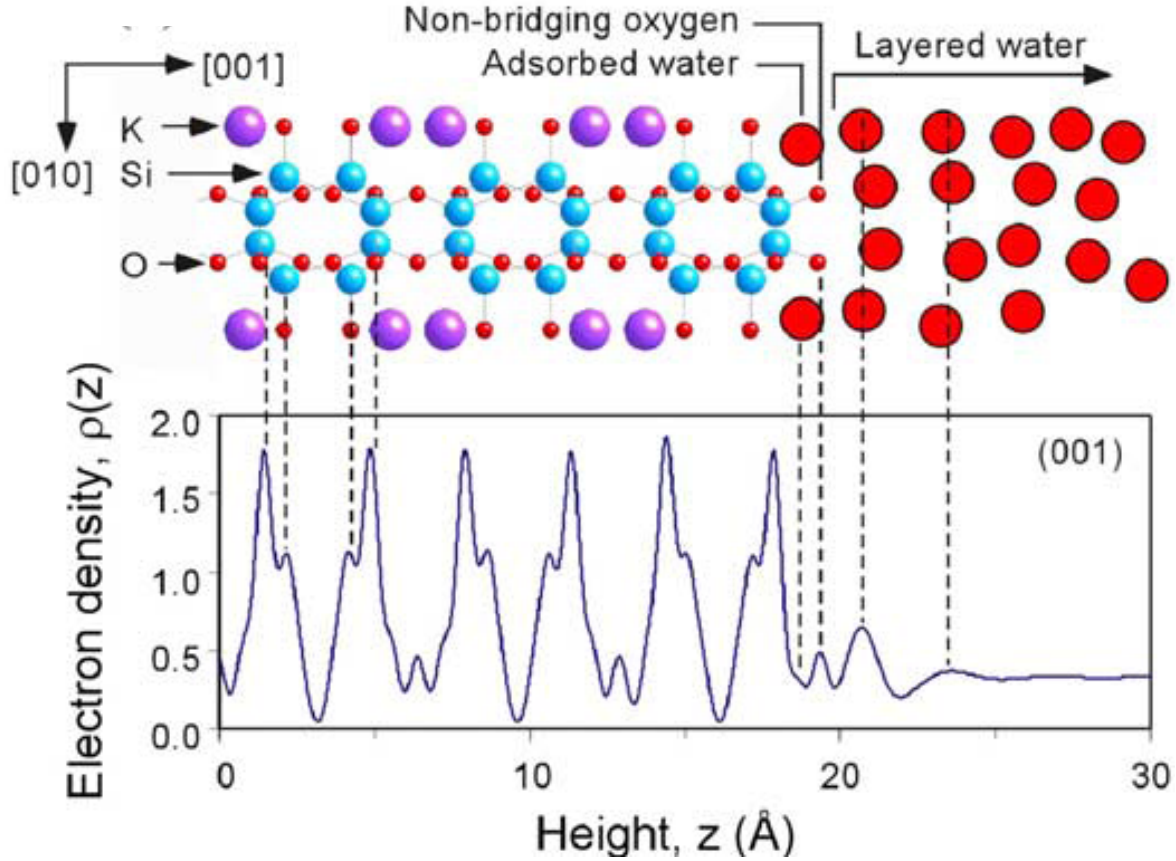


mobility of uranium in groundwater

http://www.kgs.ku.edu

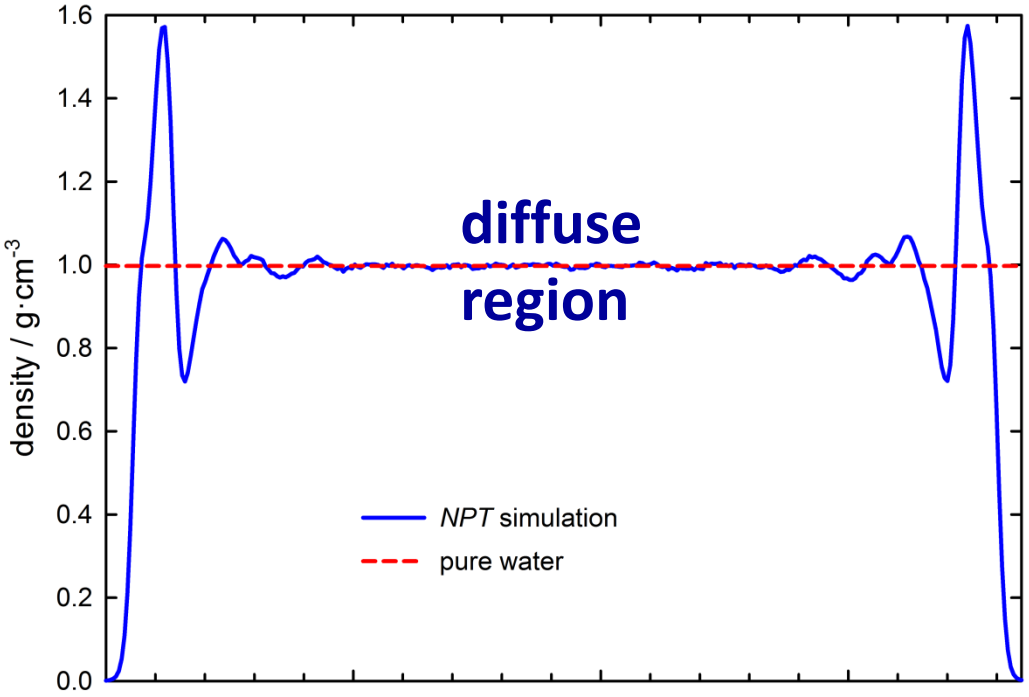
Kansas Geological Survey

Understanding water-mineral interface interactions from experimental methods alone is difficult



Fenter, P.; Cheng, L.; Park, C.; Zhang, Z.; Sturchio, N. C. *Geochim. Cosmochim. Acta 2003, 67, 4267-4275.*

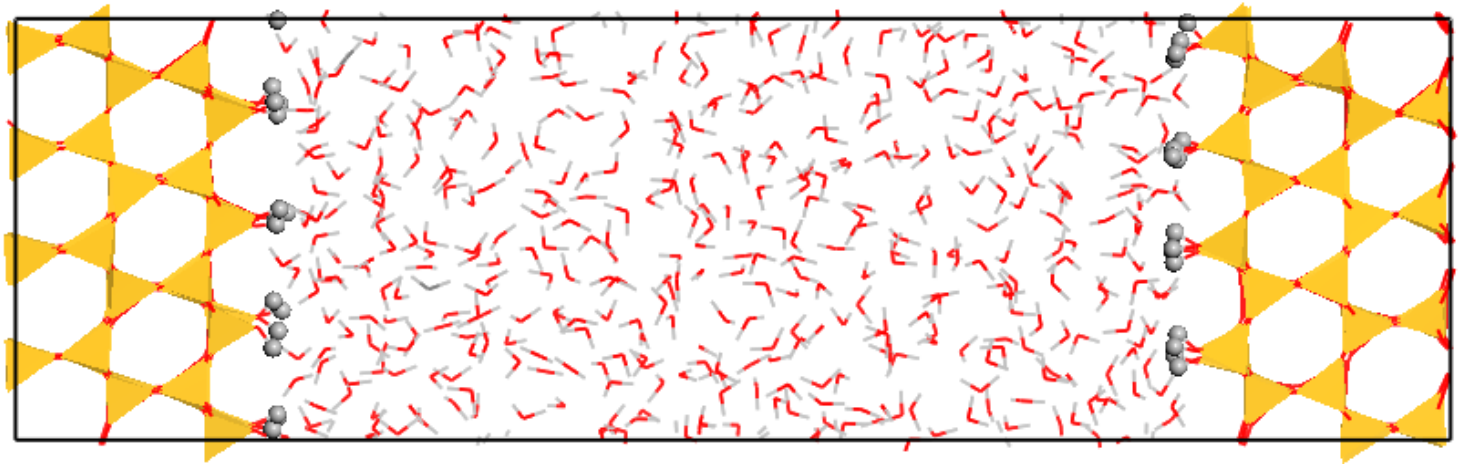
A good interface model reproduces bulk behavior



classical MD

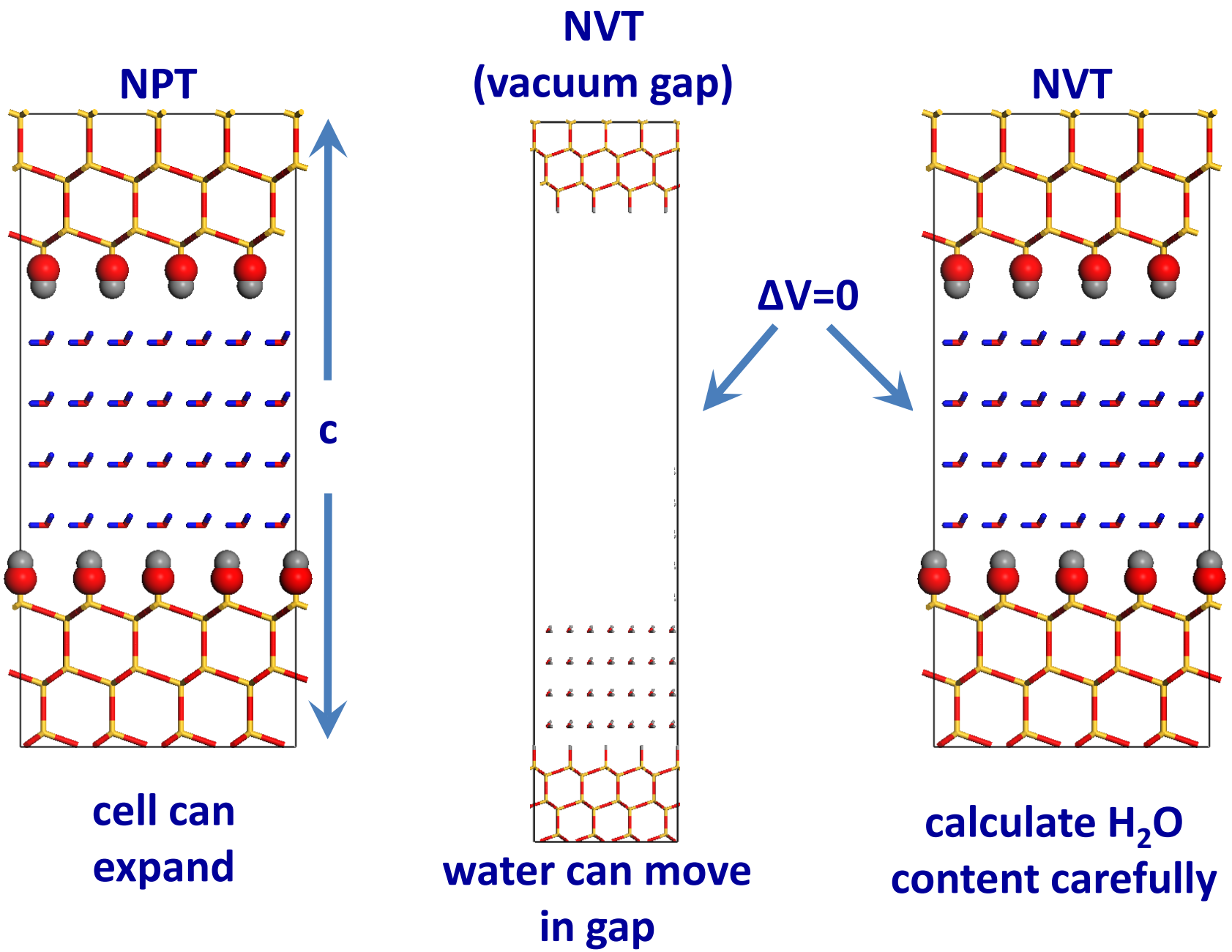
CLAYFF parameters

LAMMPS code

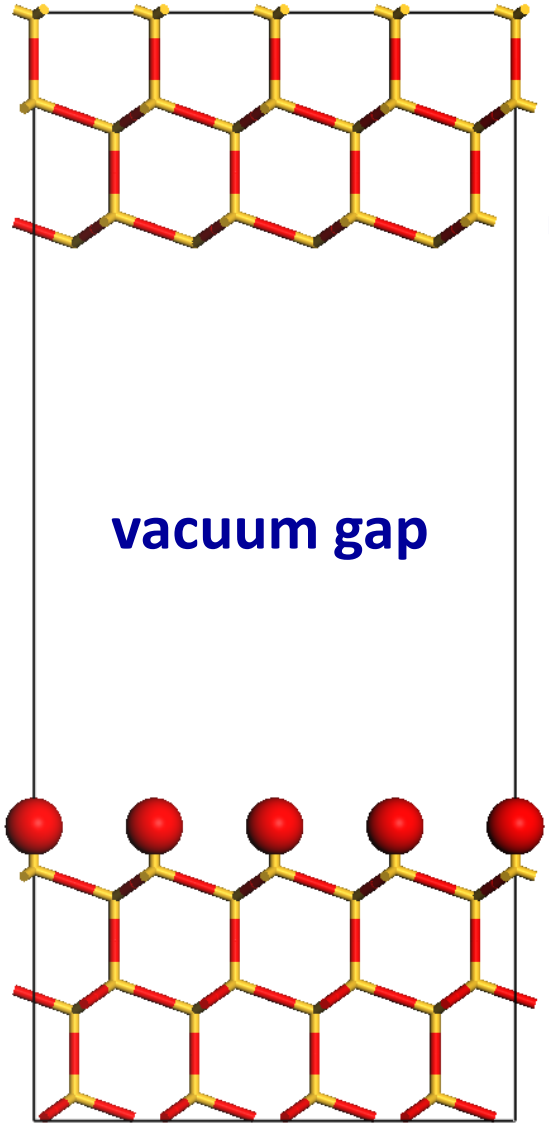


bulk water density is the link to reality

How do we get good bulk liquid properties?



Making a surface from a bulk structure introduces water-accessible volume in a complicated manner



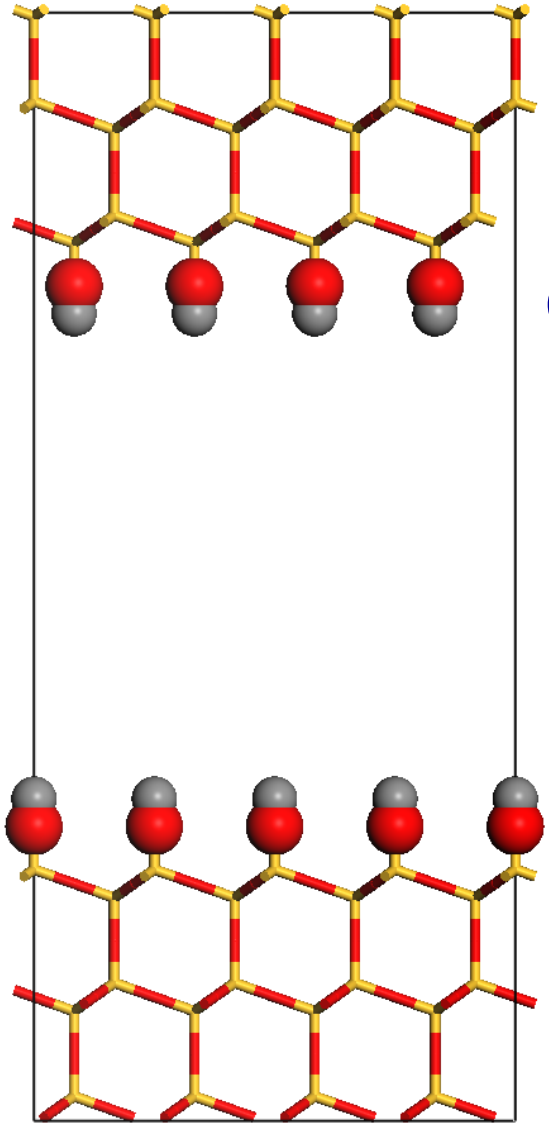
undercoordinated silicon

vacuum gap

nonbridging oxygen

cristobalite (111)

Making a surface from a bulk structure introduces water-accessible volume in a complicated manner

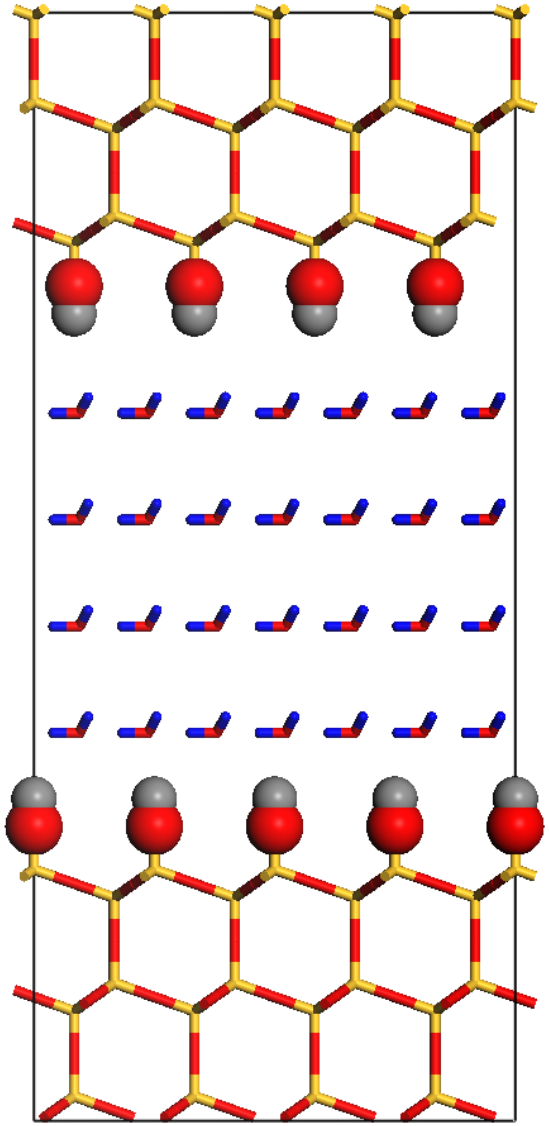


introduction of H_2O (OH + H) to hydroxylate surface

geometry of vacuum gap changes

cristobalite (111)

Making a surface from a bulk structure introduces water-accessible volume in a complicated manner

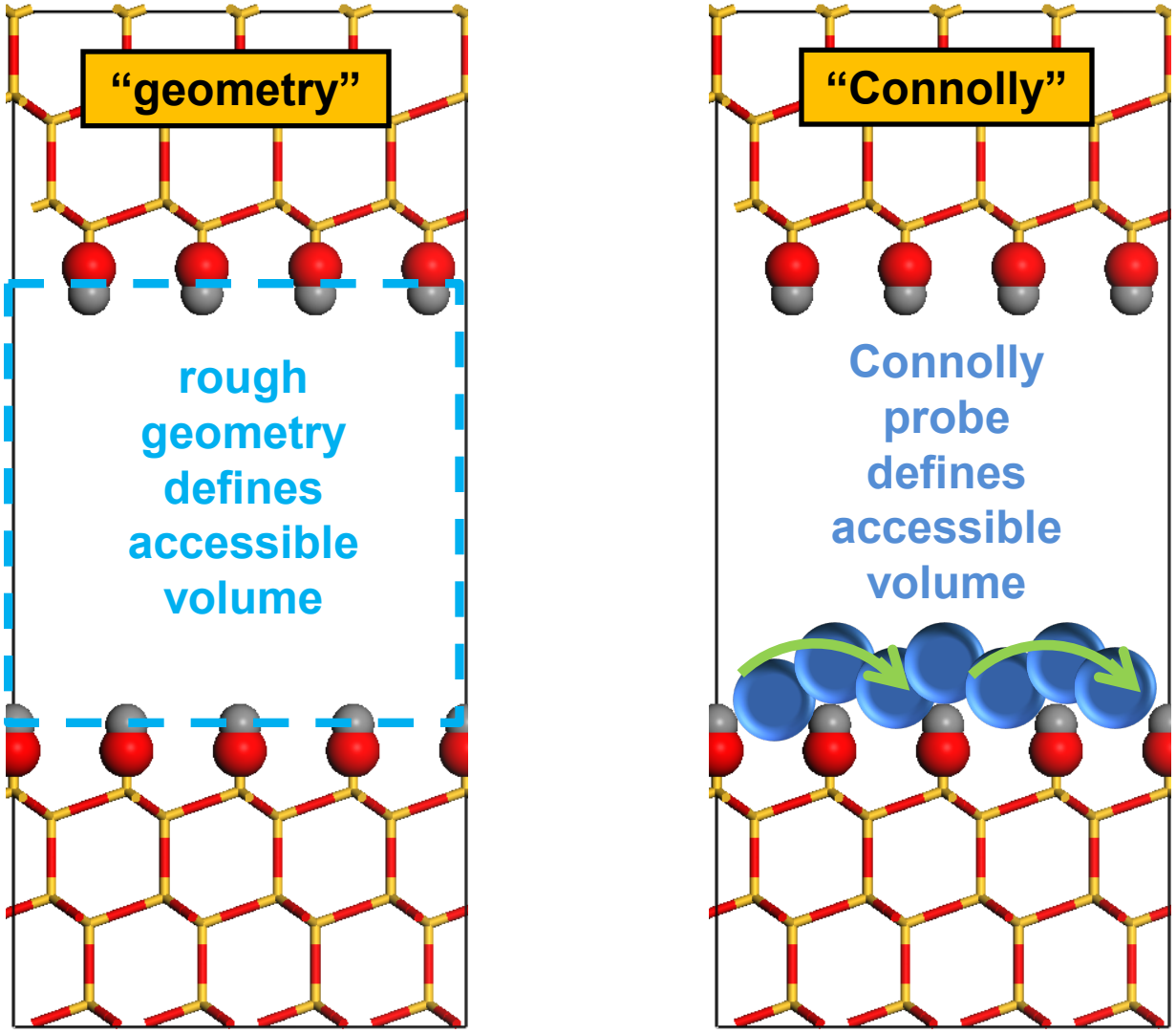


introduction of water into accessible volume

cristobalite (111)

How do we accurately calculate volume accessible to water for NVT simulations (and does it matter)?

traditional method



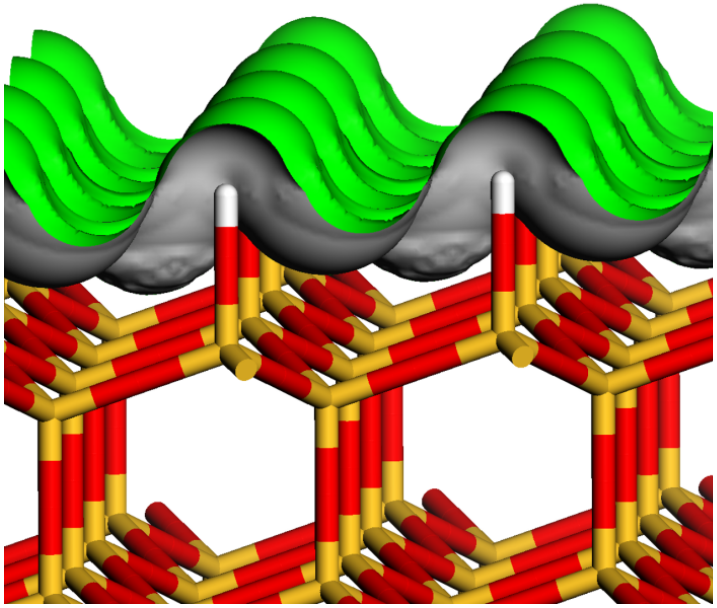
resulting bulk density plots will tell us if one method is better

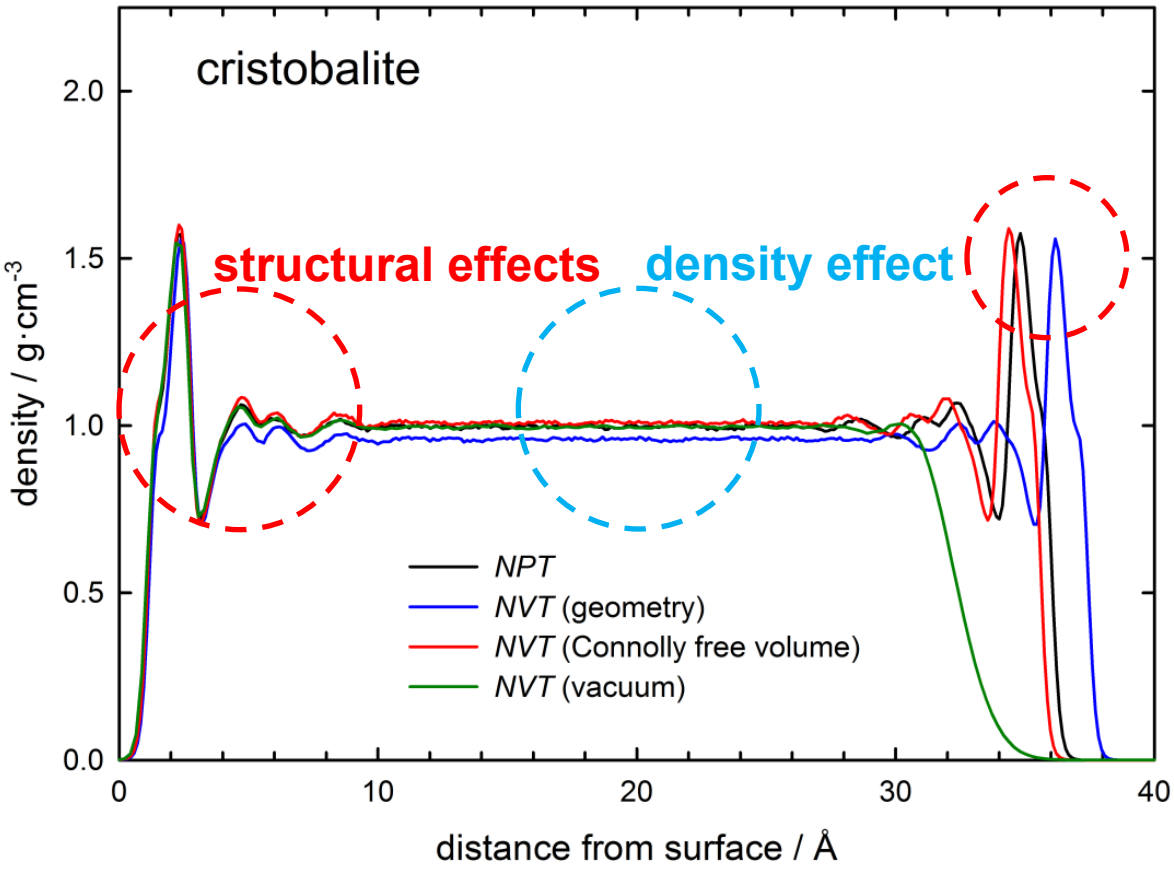
How we calculate accessible volume does matter!

NPT and NVT (vacuum) bulk density values are identical to pure H_2O simulation

SiO_2

cristobalite (111) (hydrophilic)

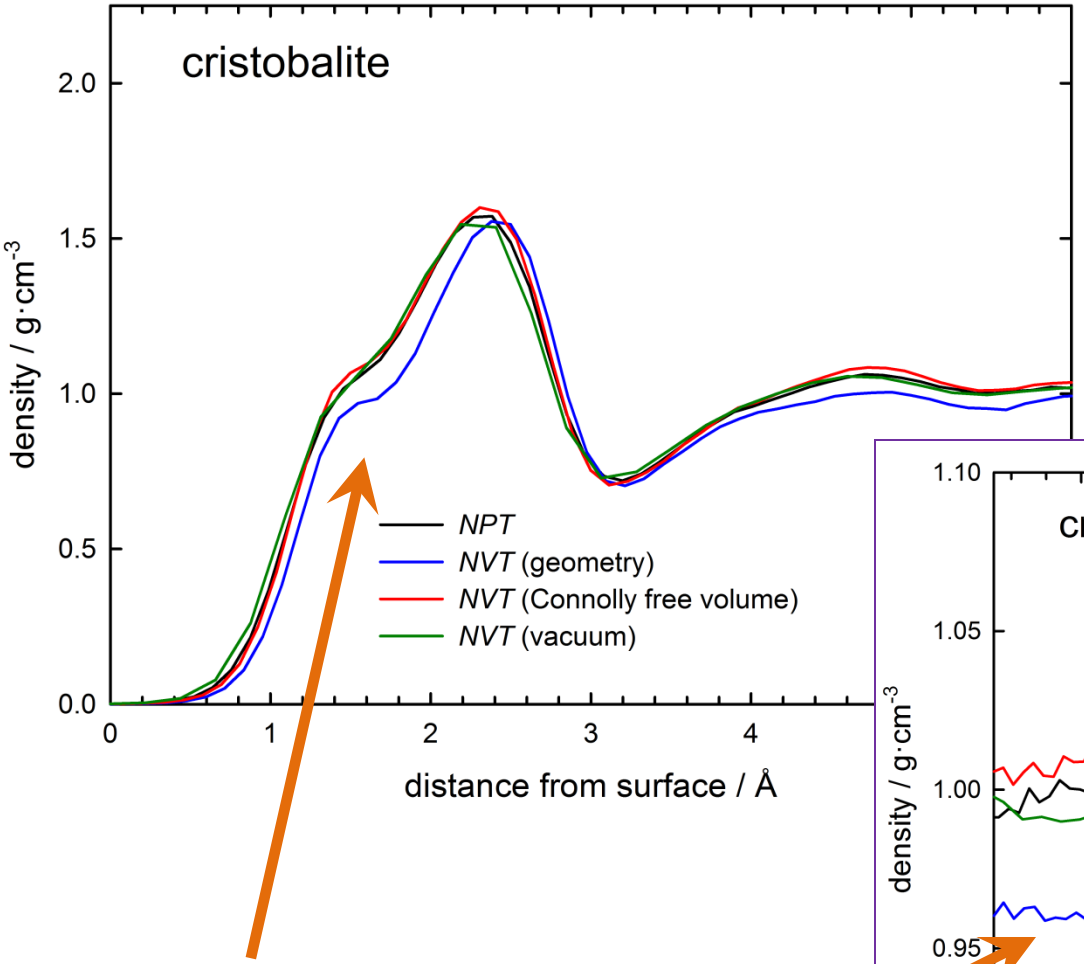


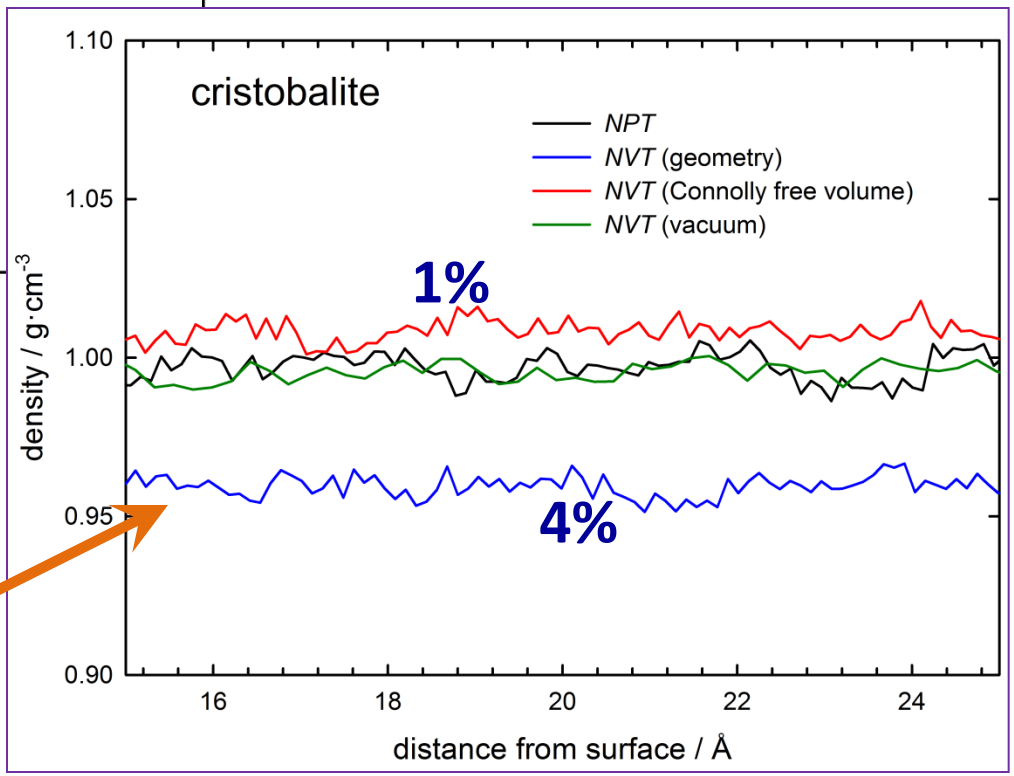


geometry method underestimates $V_{accessible}$ → lower bulk H_2O density

Connolly method overestimates $V_{accessible}$ → higher bulk H_2O density

Interfacial structural differences arise at interface depending on simulation ensemble and $V_{accessible}$



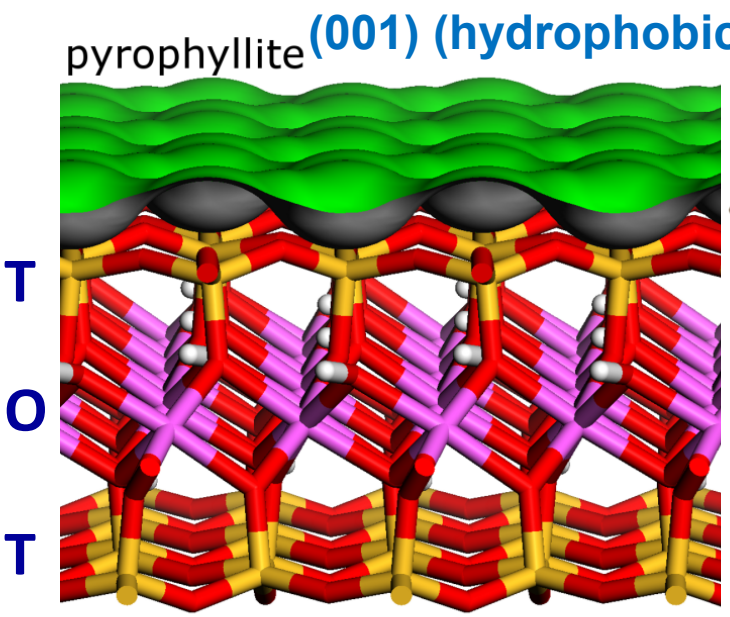


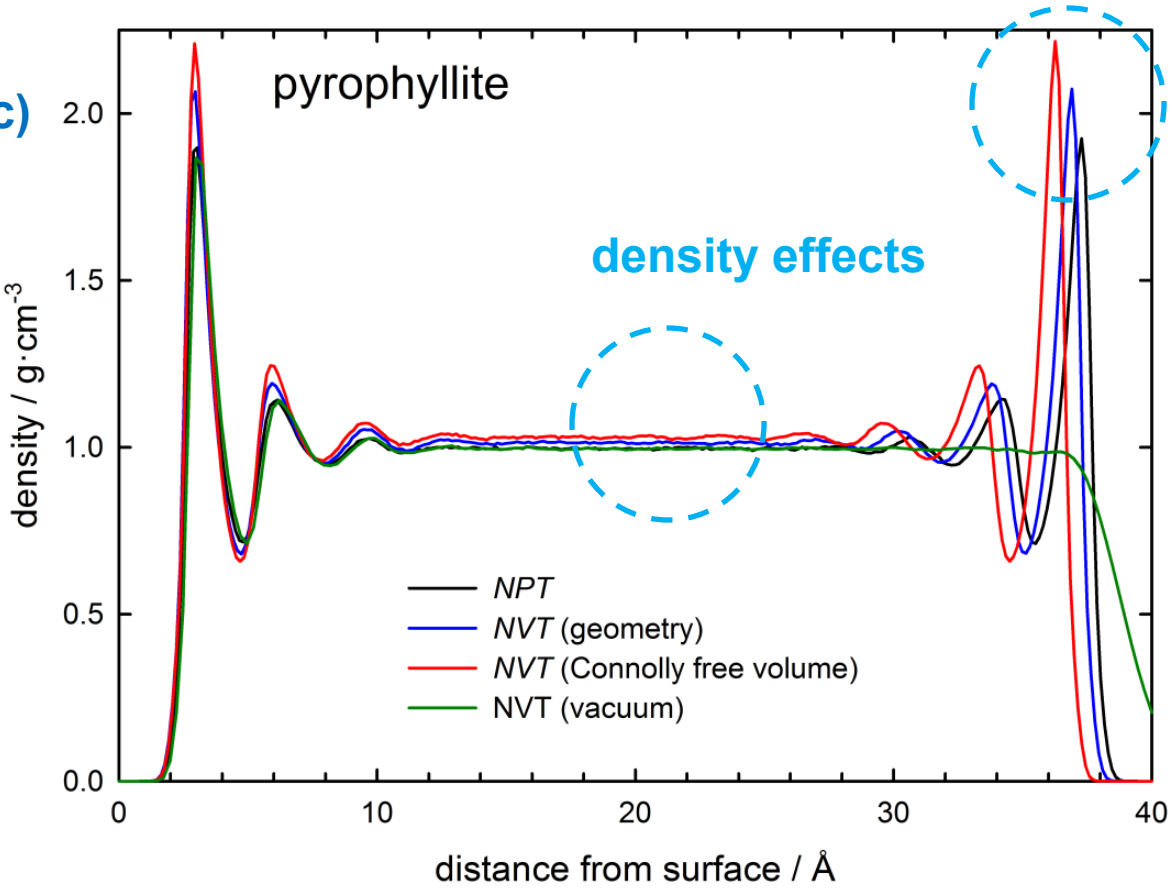
lower $V_{accessible}$ leads to lower density and peak shift

How we calculate accessible volume does matter!

NPT and NVT (vacuum) bulk density values are identical to pure H_2O simulation

$Al_2Si_4O_{10}(OH)_2$





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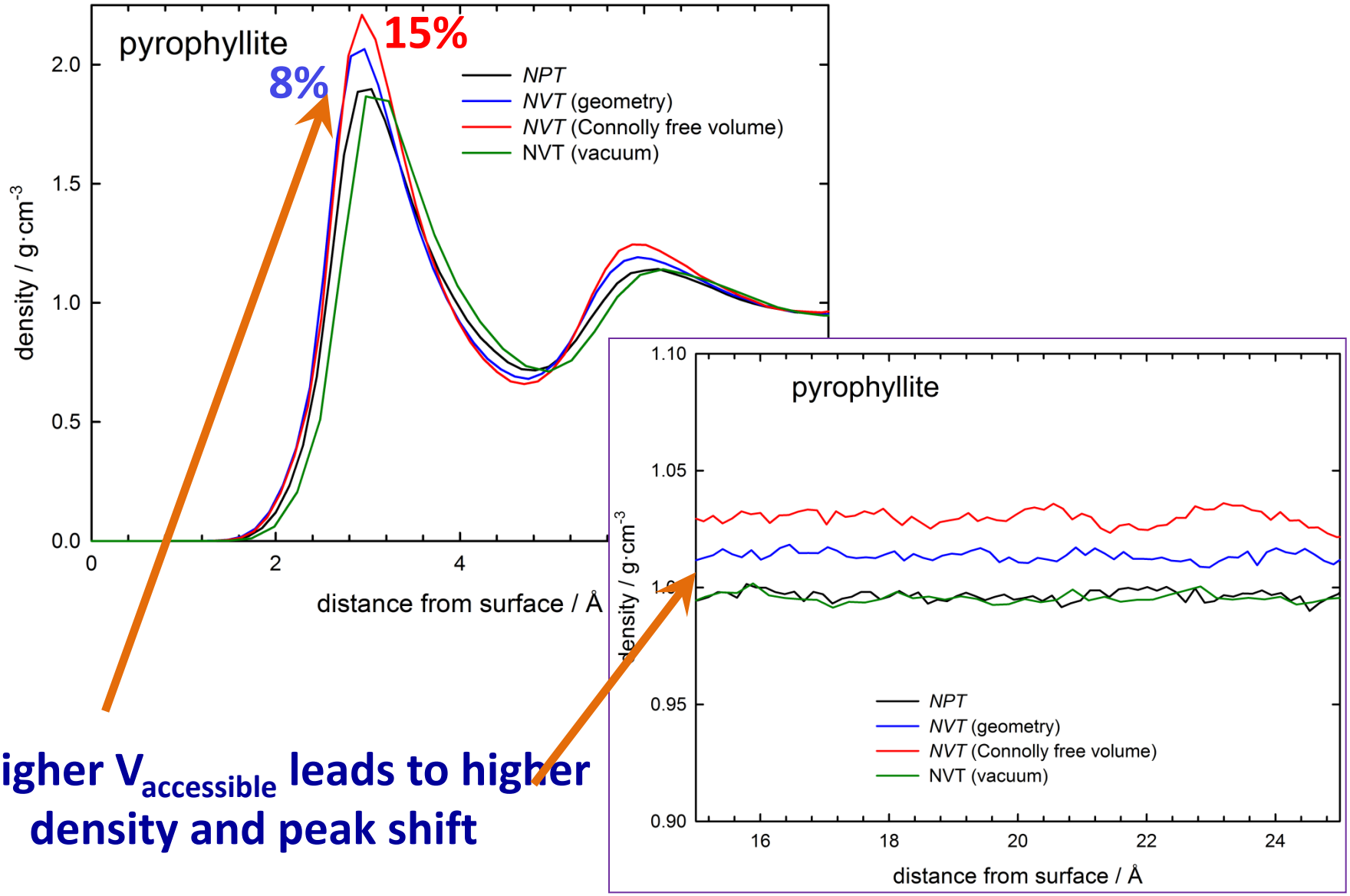
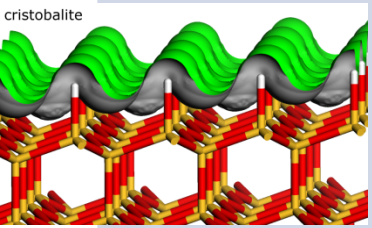
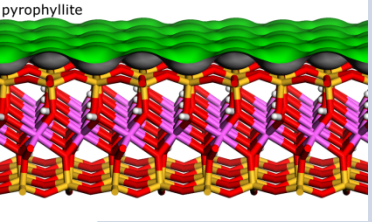
Interfacial structural differences arise at interface depending on simulation ensemble and $V_{accessible}$



higher $V_{accessible}$ leads to higher density and peak shift

How we calculate accessible volume does matter!

material	method	ρ_c ($g \cdot cm^{-3}$)	std. dev. ρ_c ($g \cdot cm^{-3}$)	% diff. ρ_c
cristobalite	***NPT***	**0.997**	0.004	-
	*NVT* (geometry)	0.959	0.004	-3.8
	NVT (Connolly)	1.008	0.003	1.1
	NVT (vacuum)	**0.996**	0.003	-0.1
pyrophyllite	***NPT***	**0.996**	0.002	-
	*NVT* (geometry)	1.013	0.002	1.7
	NVT (Connolly)	1.030	0.003	3.4
	NVT (vacuum)	**0.996**	0.003	-0.1
H_2O (model)	*NPT*	0.997	0.003	-

underestimate $V_{accessible}$ due to corrugated surface

NPT and NVT (vacuum) reproduce model H_2O density

How we calculate accessible volume does matter!

material	method	ρ_c ($g \cdot cm^{-3}$)	std. dev. ρ_c ($g \cdot cm^{-3}$)	% diff. ρ_c
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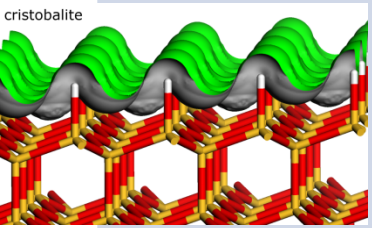	*NVT* (geometry)	0.959	0.004	-3.8
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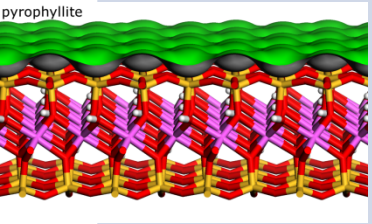	*NVT* (geometry)	1.013	0.002	1.7
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	NVT (vacuum)	**0.996**	0.003	-0.1
H_2O (model)	***NPT***	**0.997**	**0.003**	**-**

underestimate $V_{accessible}$ due to corrugated surface

overestimate $V_{accessible}$ due to excluded volume (hydrophobicity)

NPT and NVT (vacuum) reproduce model H_2O density

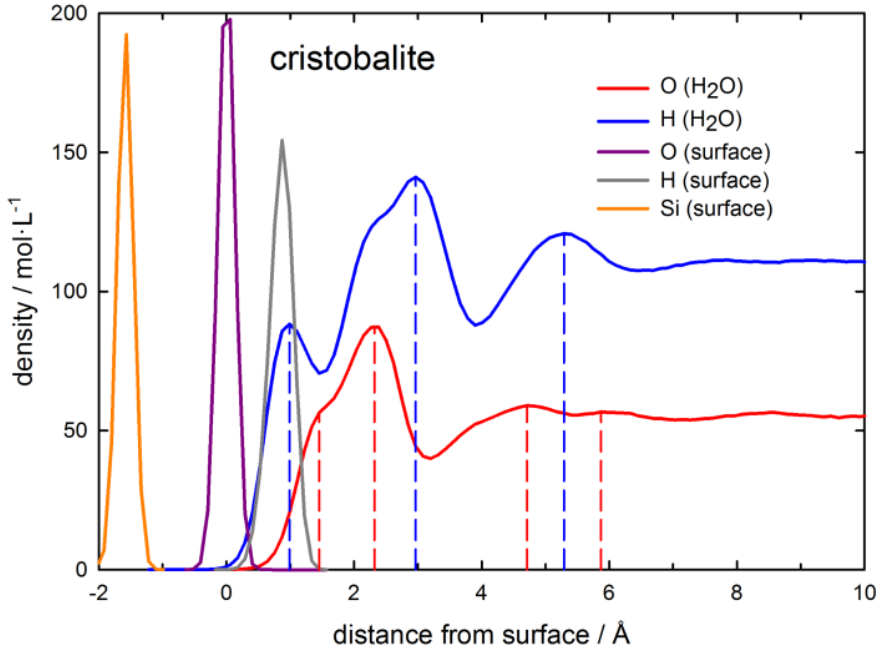
Interfacial structure is related to hydrophobicity

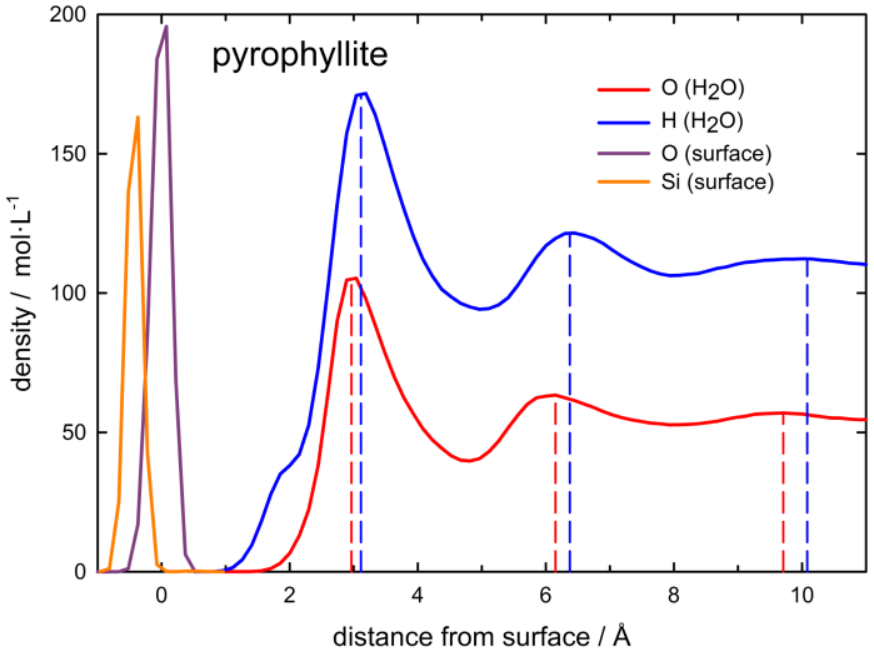
hydrophilic

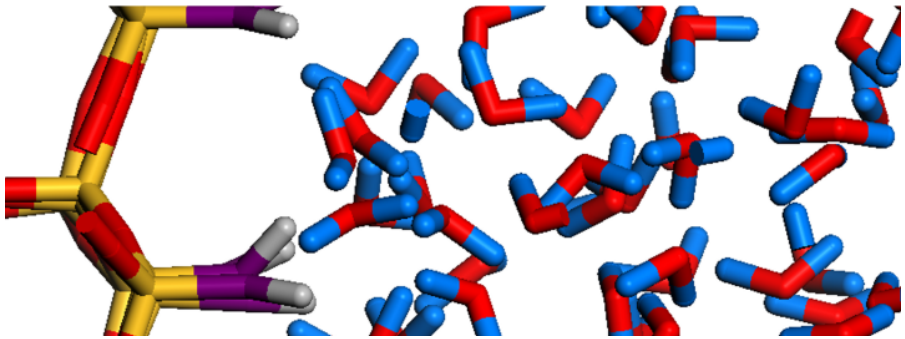
water-surface structuring

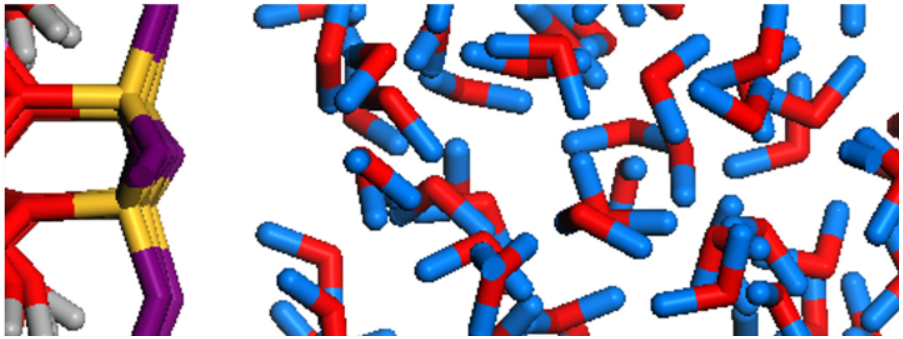
hydrophobic

water layers

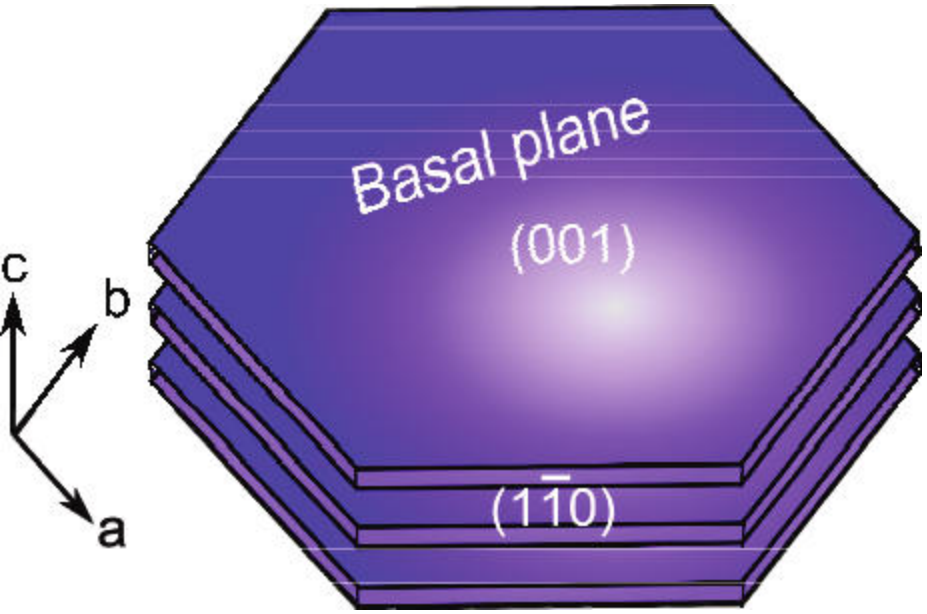




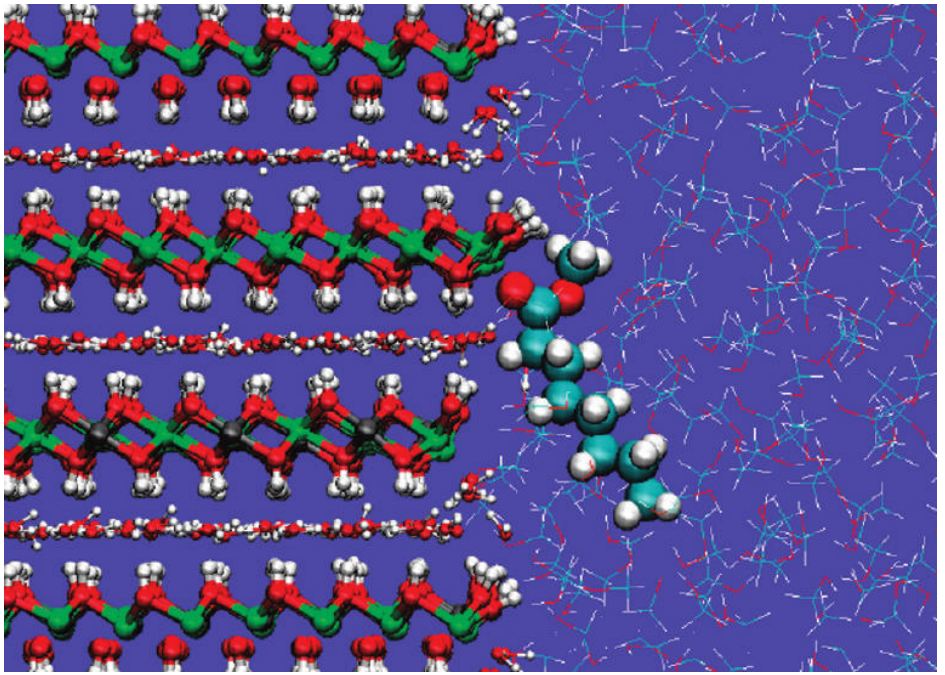




The chemistry of clay edge sites is of ever-increasing interest



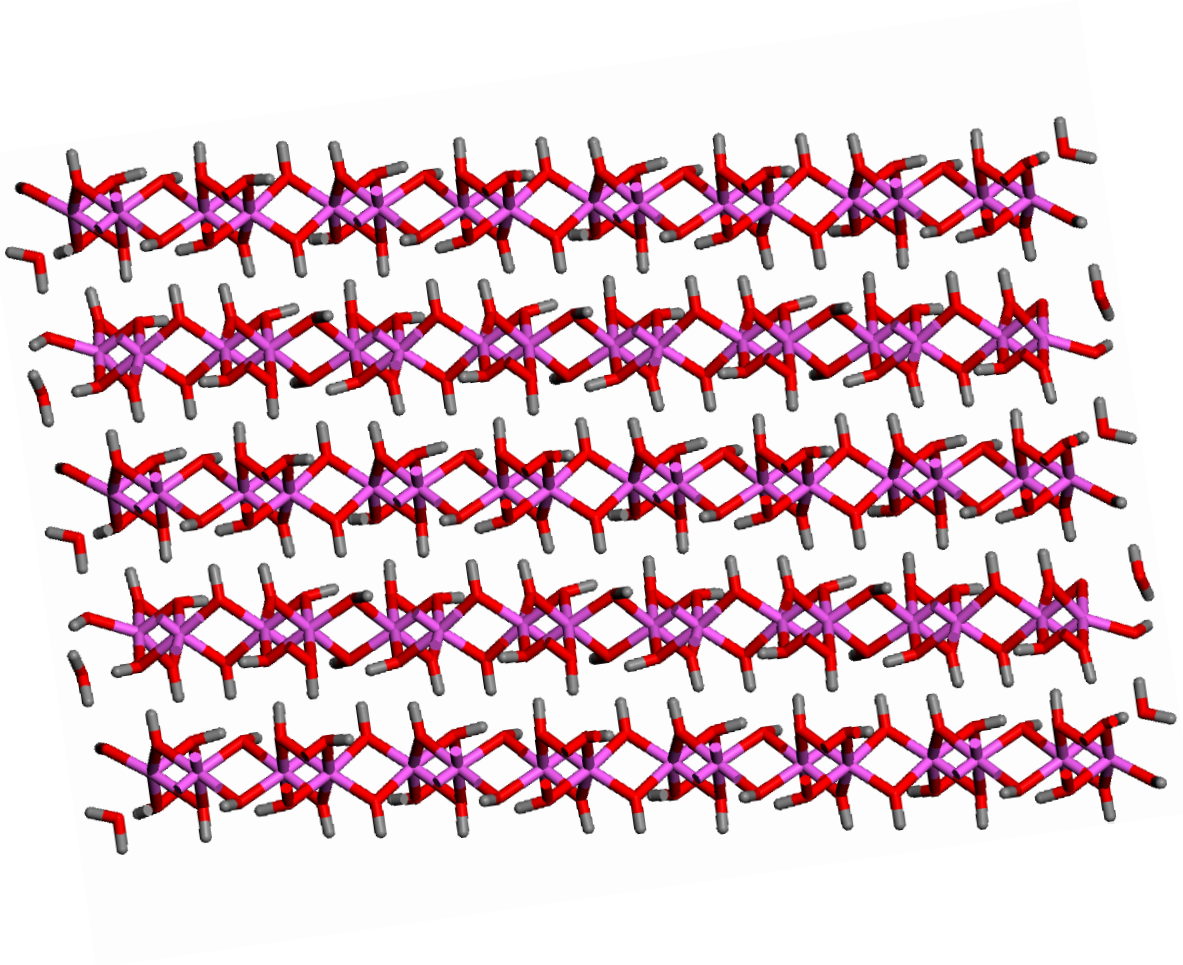
hydrotalcite (1-10)



Yu, K.; Schmidt, J. R. *J. Phys. Chem. C* 2011, **115**, 1887-1898.

adsorption on edges can be fundamentally different from that on basal surfaces

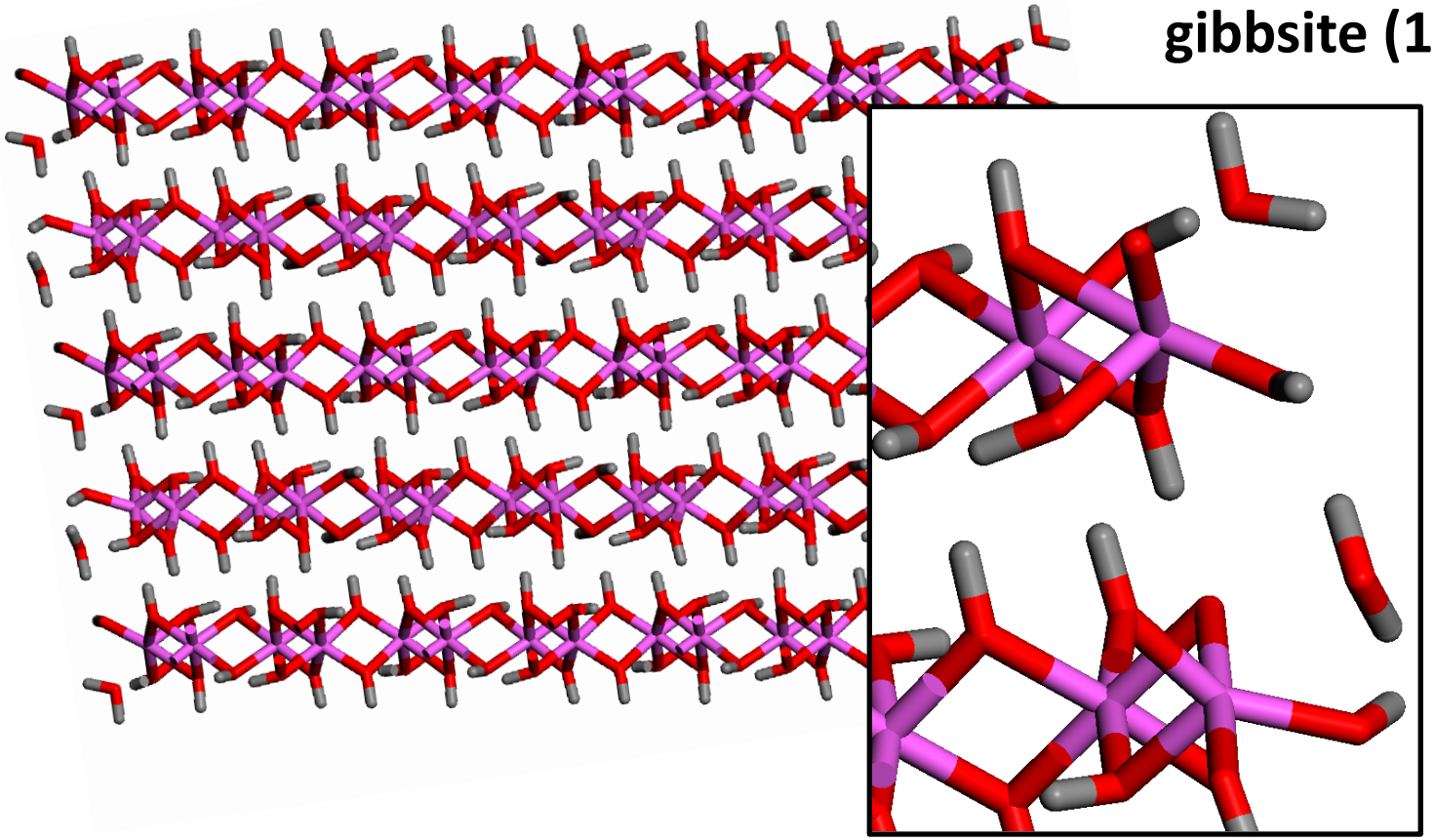
Force field development for clay edge sites is underway for CLAYFF



gibbsite (100)

our FF development will initially focus on simple minerals (brucite, gibbsite, cristobalite)

Force field development for clay edge sites is underway for CLAYFF



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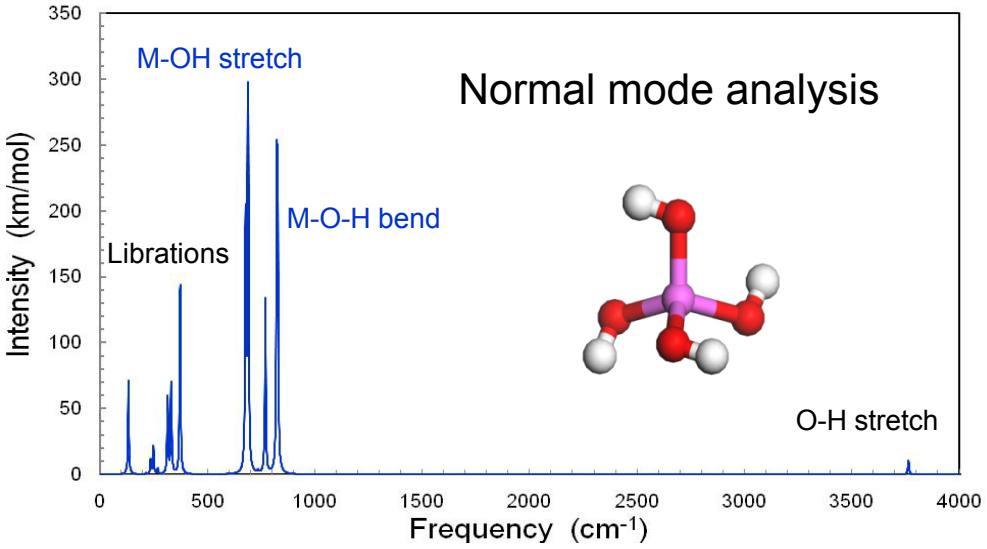
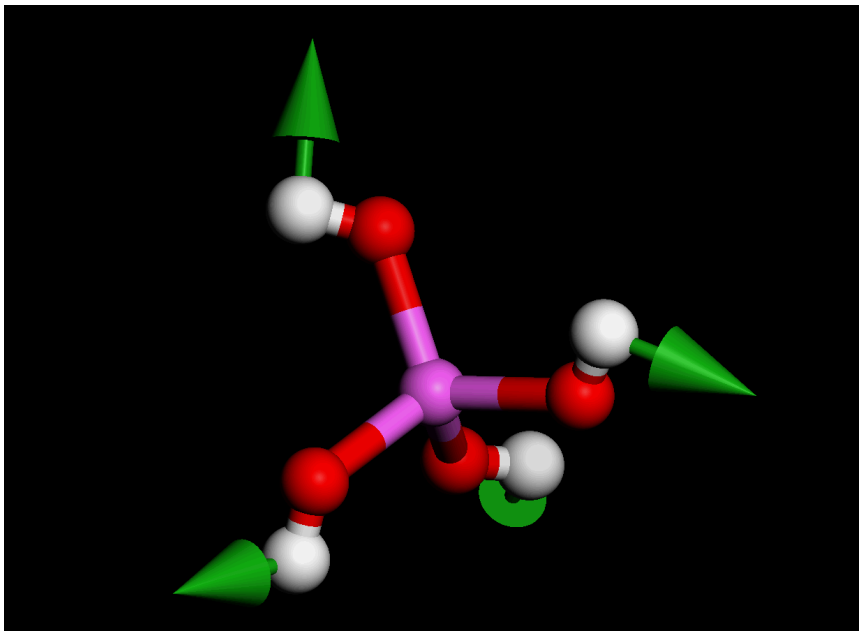
our FF development will initially focus on simple minerals (brucite, gibbsite, cristobalite)

Force field parameterization involves matching normal modes from DFT and classical calculations





M = Al, Si, Mg

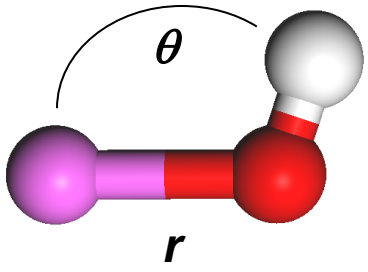
Al-O-H symmetric bend

$$E_{stretch} = \tfrac{1}{2}\, k_r (r - r_o)^2$$

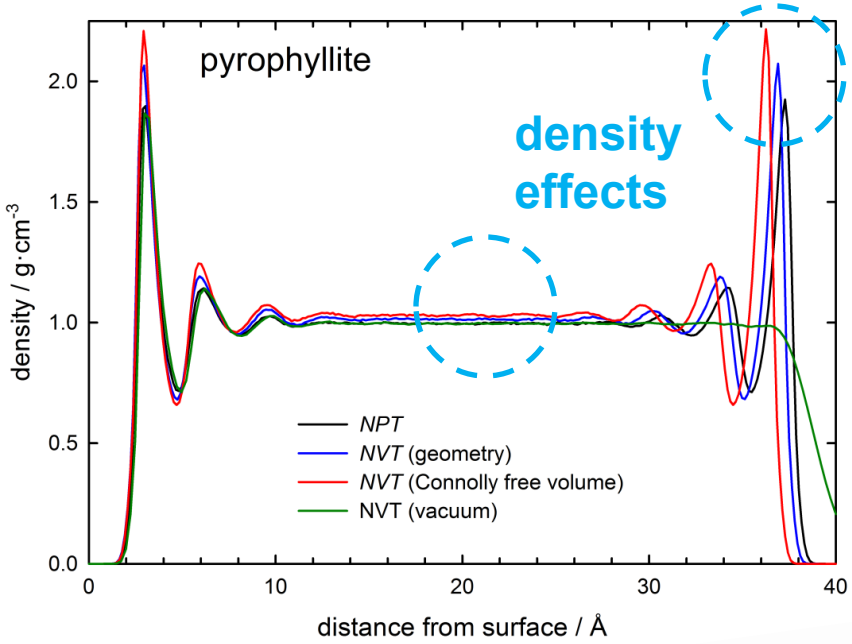
$$E_{bend} = \tfrac{1}{2}\, k_\theta (\theta - \theta_o)^2$$

r_o, θ_o from DFT-optimized geometry

k_r, k_θ from normal mode analysis

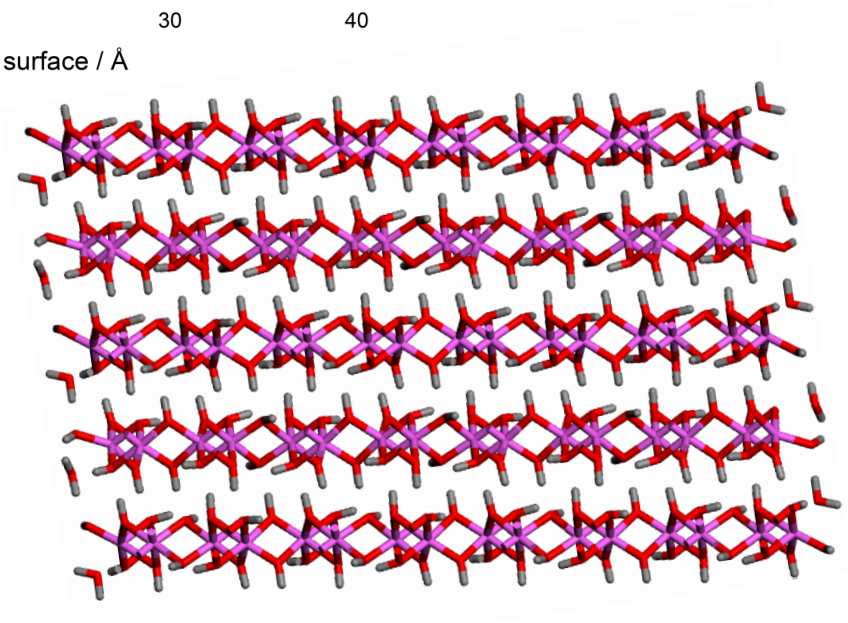


Summary



NPT or NVT(vac): accurate density

NVT: be careful with H_2O content
surface definition
hydrophobicity



FF development for clay edge sites