SAND2011-4009C

Development of a Flexible Force Field for Carbon Dioxide in Subsurface Environments

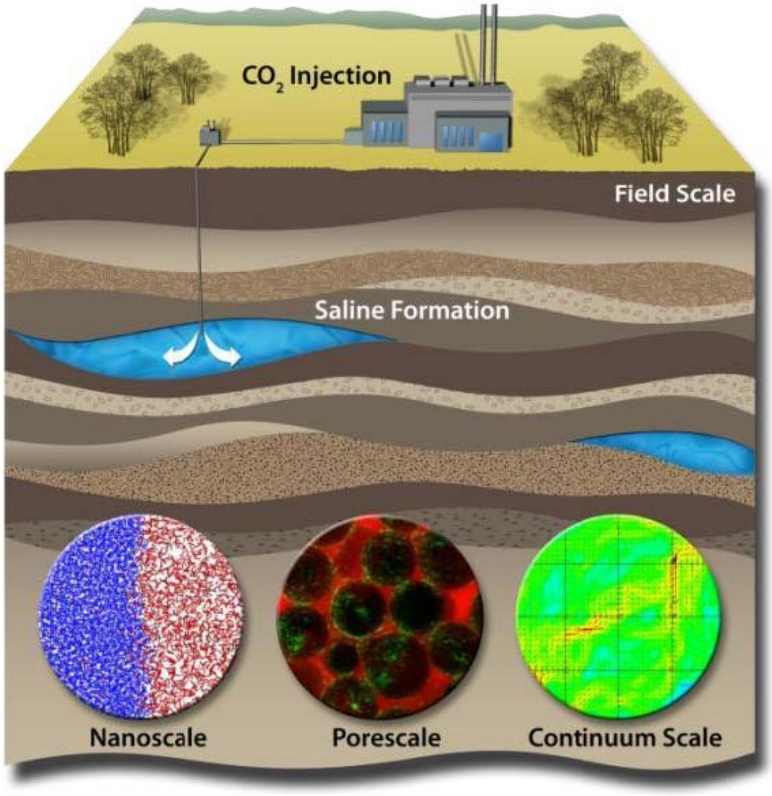
Craig M. Tenney, Louise J. Criscenti,
and Randall T. Cygan

Geochemistry Department
Sandia National Laboratories

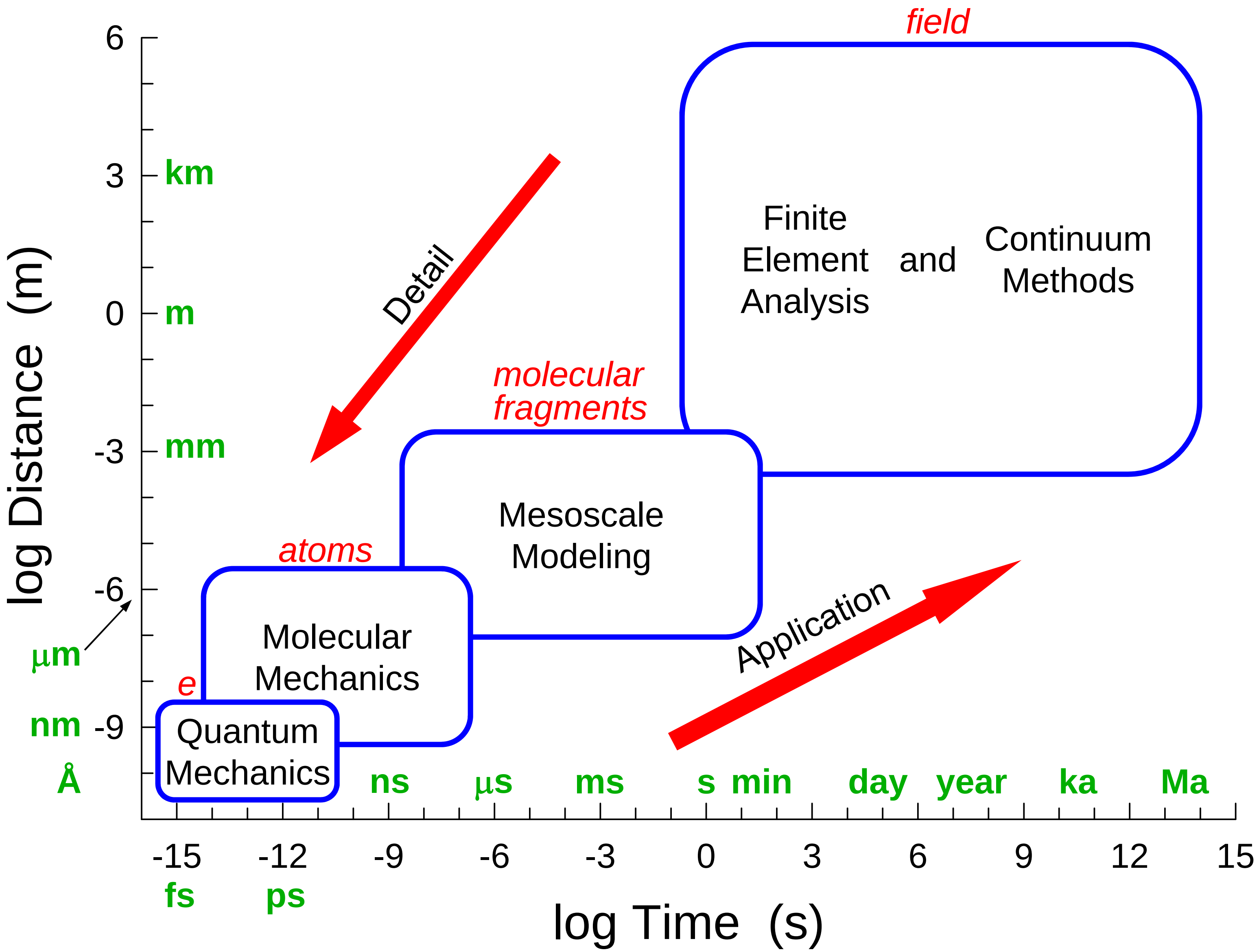
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation,
a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's
National Nuclear Security Administration under contract DE-AC04-94AL85000.

Objectives and Applications

- model the interaction of $scCO_2$ with resident fluids and minerals in subsurface reservoirs
  - Develop CO_2 forcefield
- three-phase interfaces – mineral-$scCO_2$-H_2O
  - contact angles on kaolinite surfaces
- $scCO_2$-brine interface
  - Examine solubility of CO_2 in H_2O
  - Compare cation solvation in H_2O and CO_2

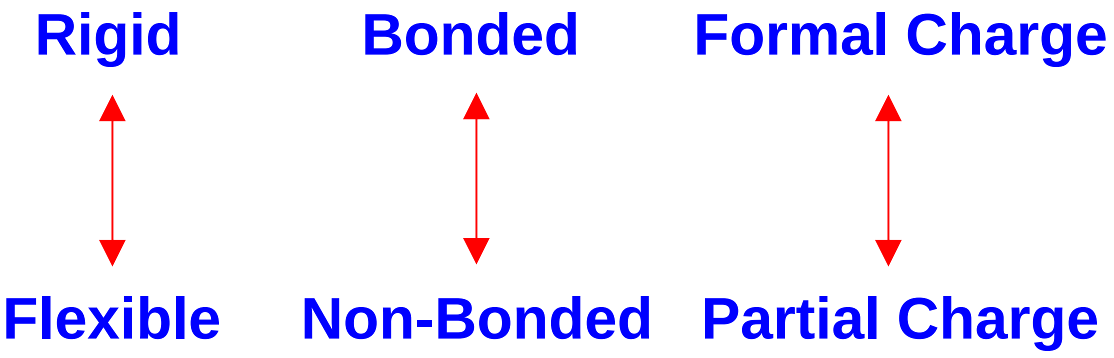


Multiscale Simulation

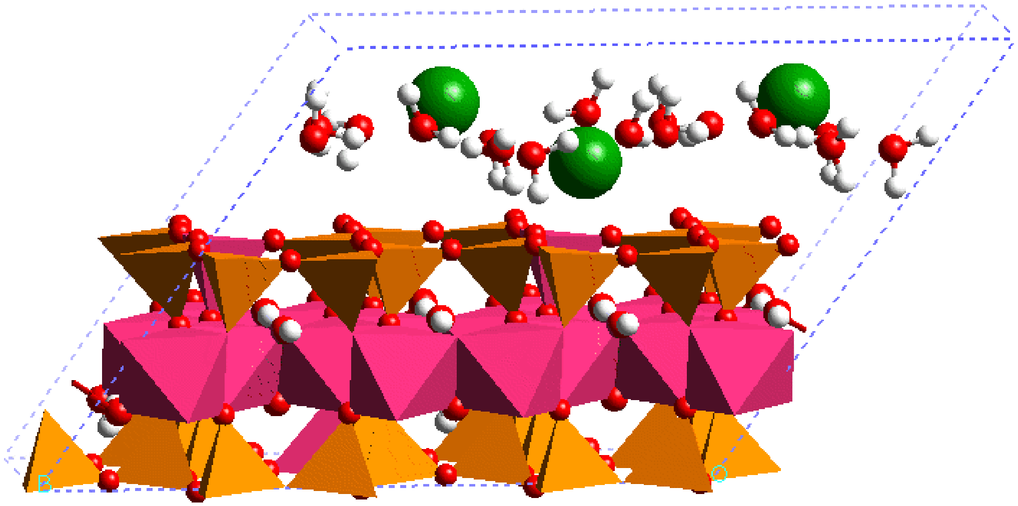


Forcefield Methods for the Simulation of Clay Phases

Skipper et al. (1989)
Teppen et al. (1997)
Sainz-Diaz et al. (2001)
Heinz et al. (2005)
Cygan et al. (2004)

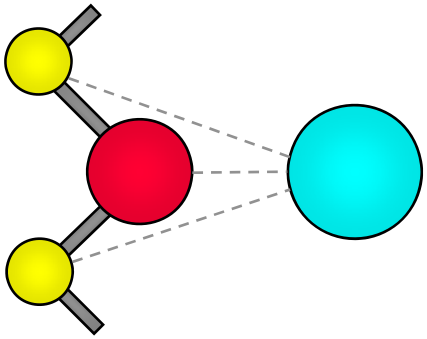


Rigid	Bonded	Formal Charge
Flexible	Non-Bonded	Partial Charge



Sandia
National
Laboratories

ClayFF for Modeling Clays and Hydrous Phases



Fully **flexible** model for exchange of momentum and energy among all species

$$E = \sum_i \sum_j \left(A_{ij}/r_{ij}^{12} - B_{ij}/r_{ij}^{6} + q_i q_j / \varepsilon\, r_{ij} \right)$$

Short-range repulsion Van der Waals Coulombic

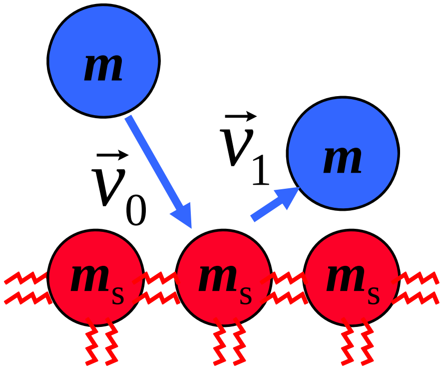
- SPC water model and quantum-derived partial charges
- LJ terms parameterized from observed mineral structures

Input structures: oxides, hydroxides, oxyhydroxides

quartz, corundum, diaspore, boehmite, gibbsite, brucite, goethite, lepidocrocite, portlandite, *etc.*

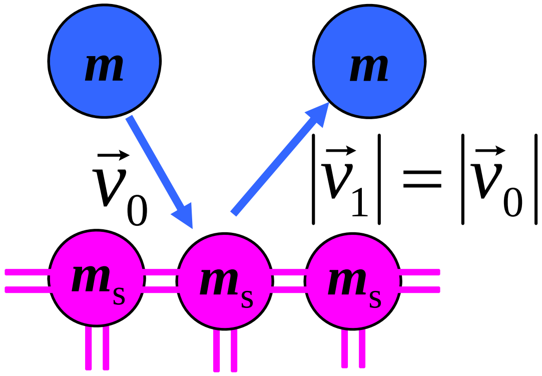
Sandia National Laboratories

ClayFF and the Importance of Flexibility



Mobile atoms

versus

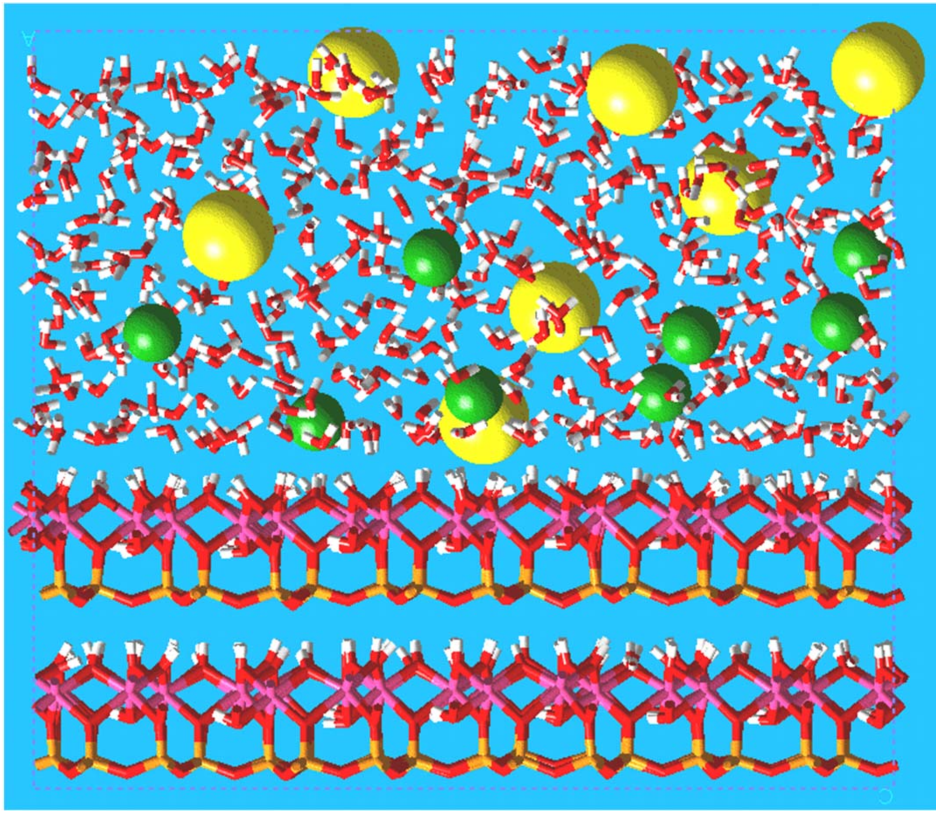


Restricted atoms

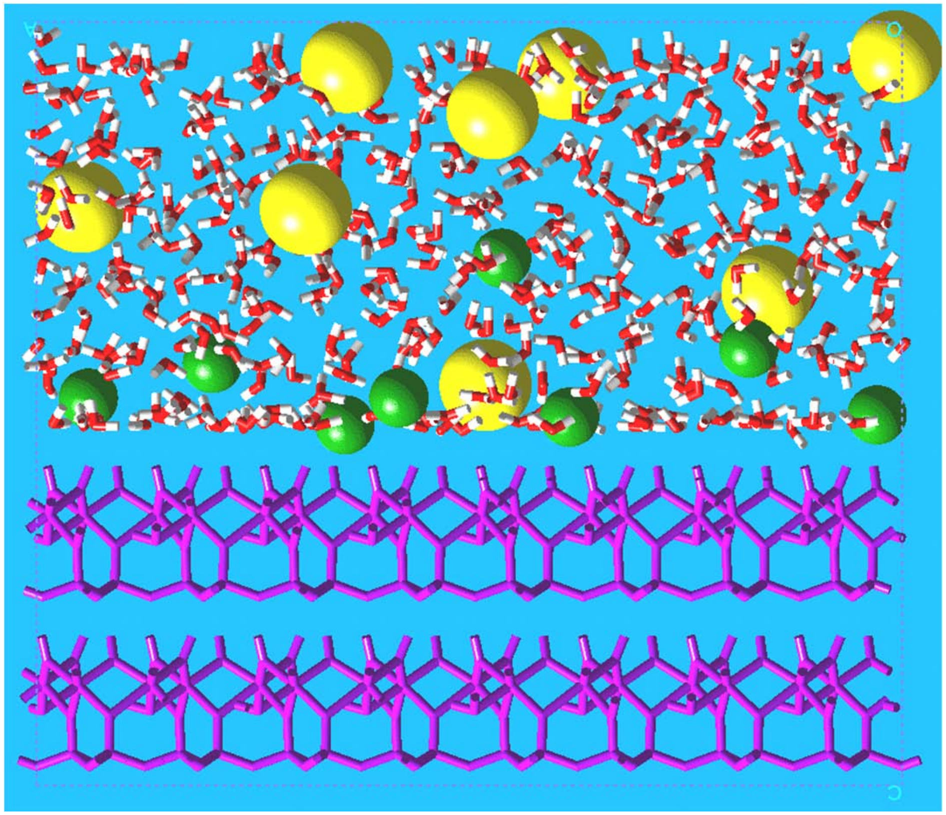
- Molecular structure of the aqueous interfaces
- Effective diffusion coefficients of surface-sorbed species
- Residence times of surface-sorbed species
- Translational, librational, and vibrational dynamics of surface-sorbed species

ClayFF and the Importance of Flexibility

MD simulation of kaolinite interface with CsCl aqueous solution



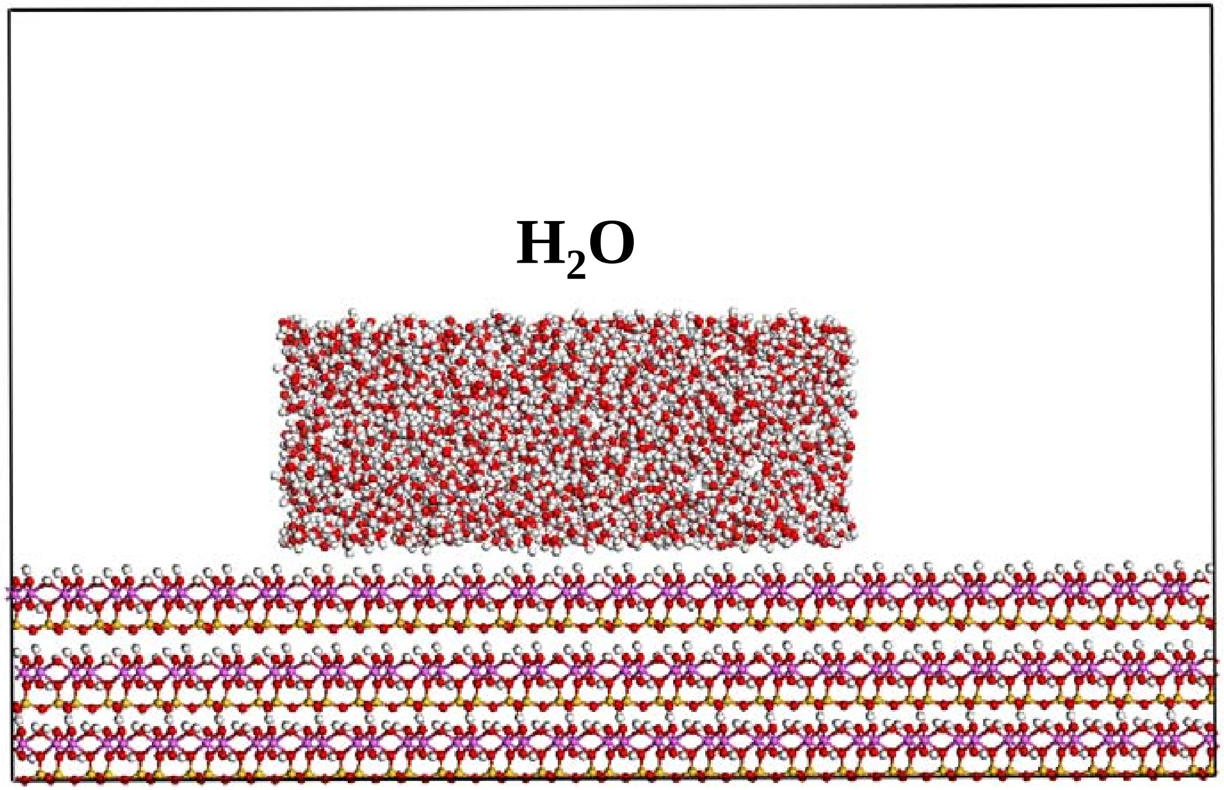
Fully flexible; no constraints

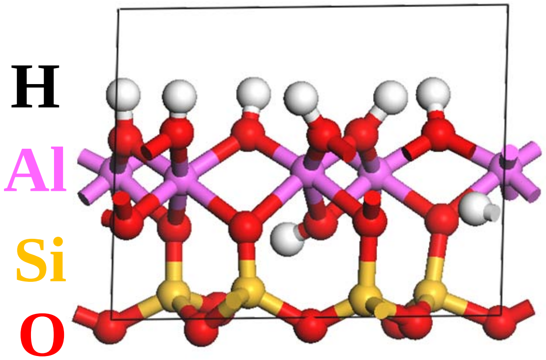


Fixed atoms in kaolinite substrate

Gas-Liquid-Solid Interfaces: Contact Angles

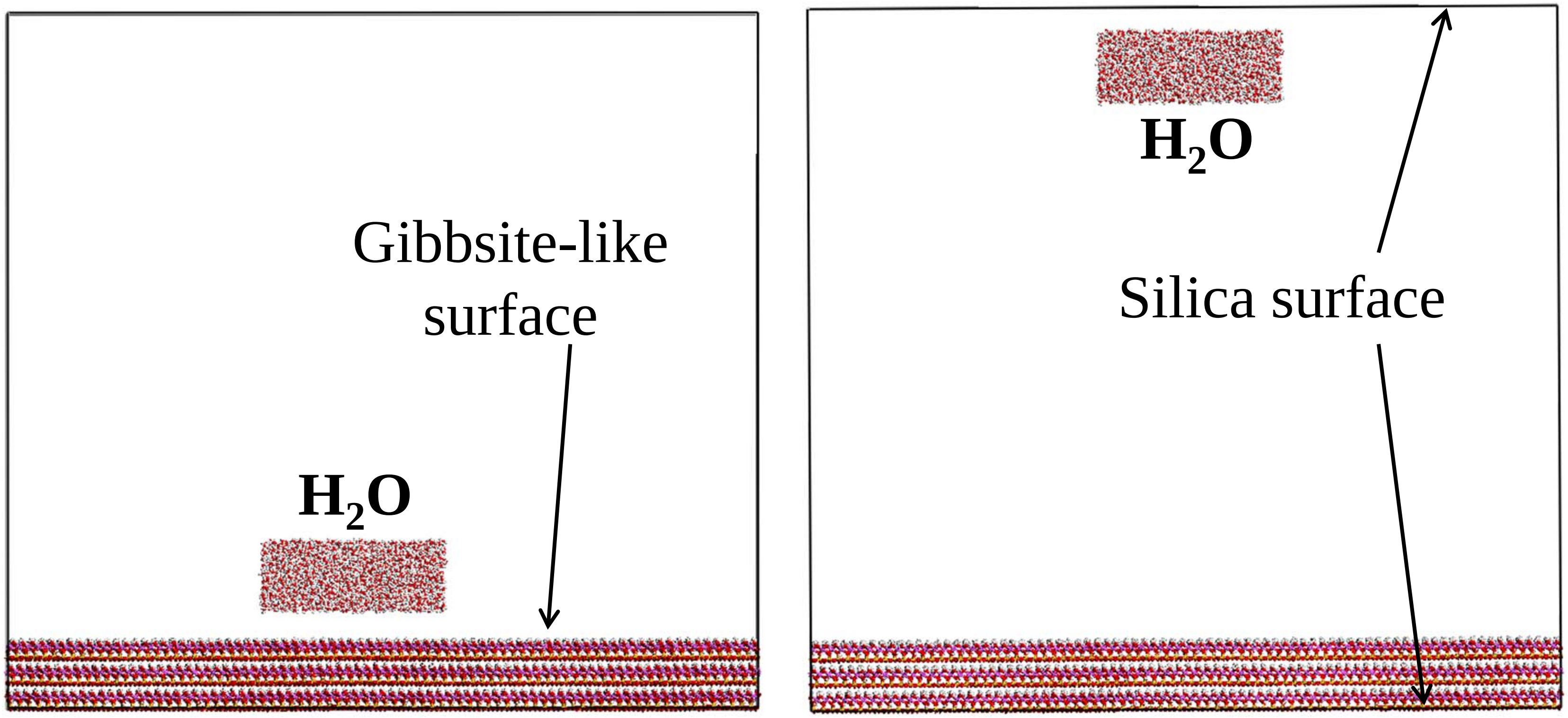
Initial configuration

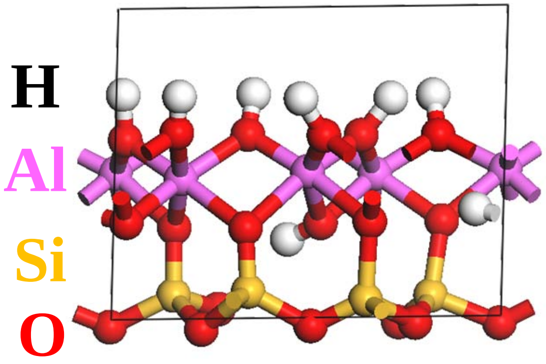




Kaolinite

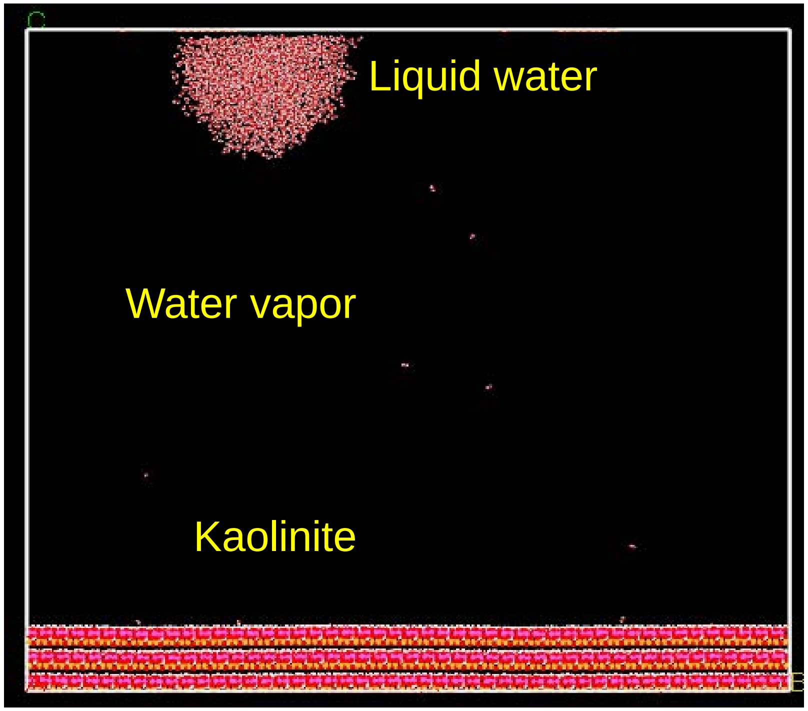
Gas-Liquid-Solid Interfaces: Contact Angles

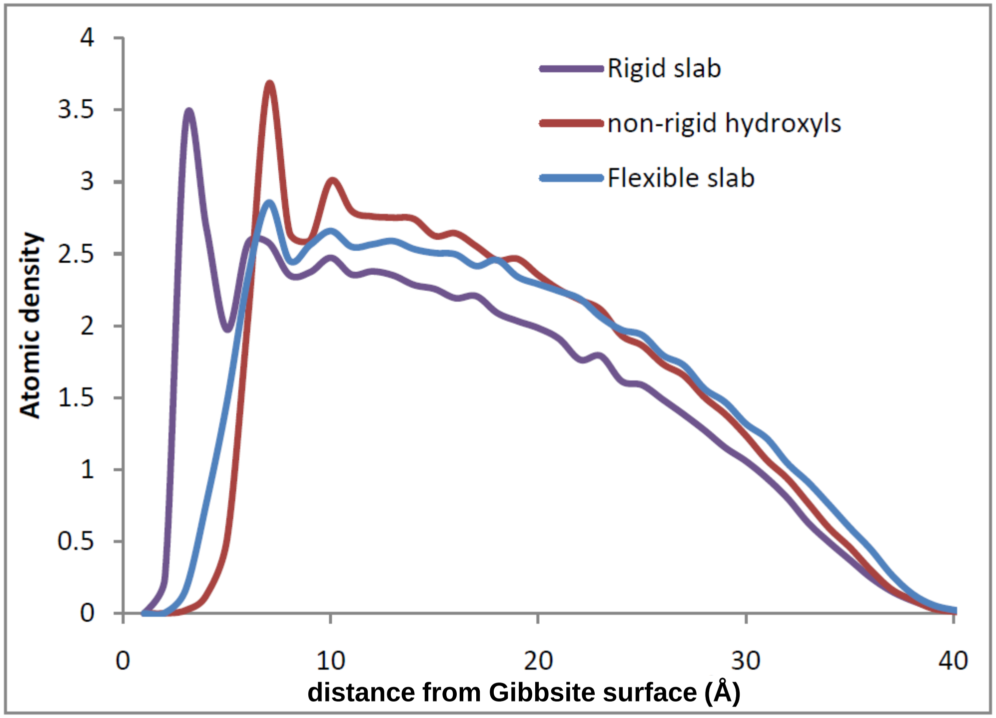




Kaolinite

Gas-Liquid-Solid Interfaces: Contact Angles and Flexibility





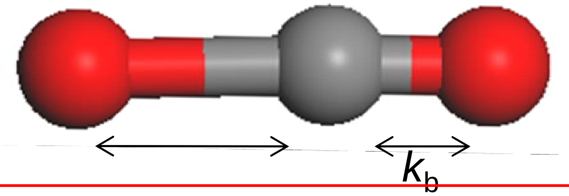
214 Å x 205 Å x 200 Å
180 Å vacuum gap

LAMMPS (Plimpton, 1995)
CLAYFF (Cygan et al., 2004)

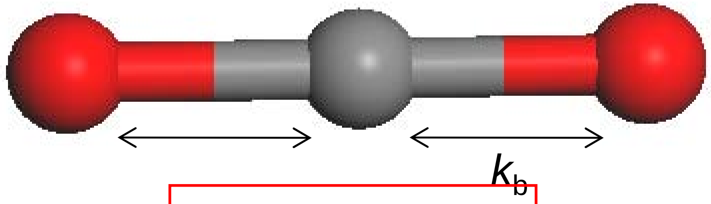
CO_2 Force Field Requirements

- Accurate liquid-vapor coexistence envelope and critical point
- Accurate vibrational spectra
- Realistic momentum and energy exchange among all atoms, *including solid substrates and aqueous solutions*
- Consistent with CLAYFF, a fully-flexible force field for mineral-water interfaces

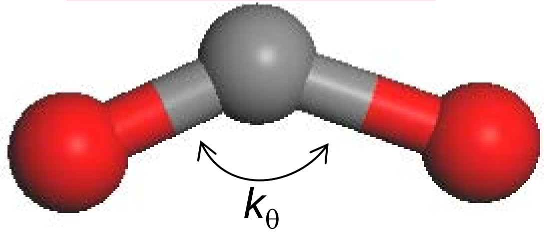
Asymmetric bond stretch



Symmetric bond stretch (IR inactive)



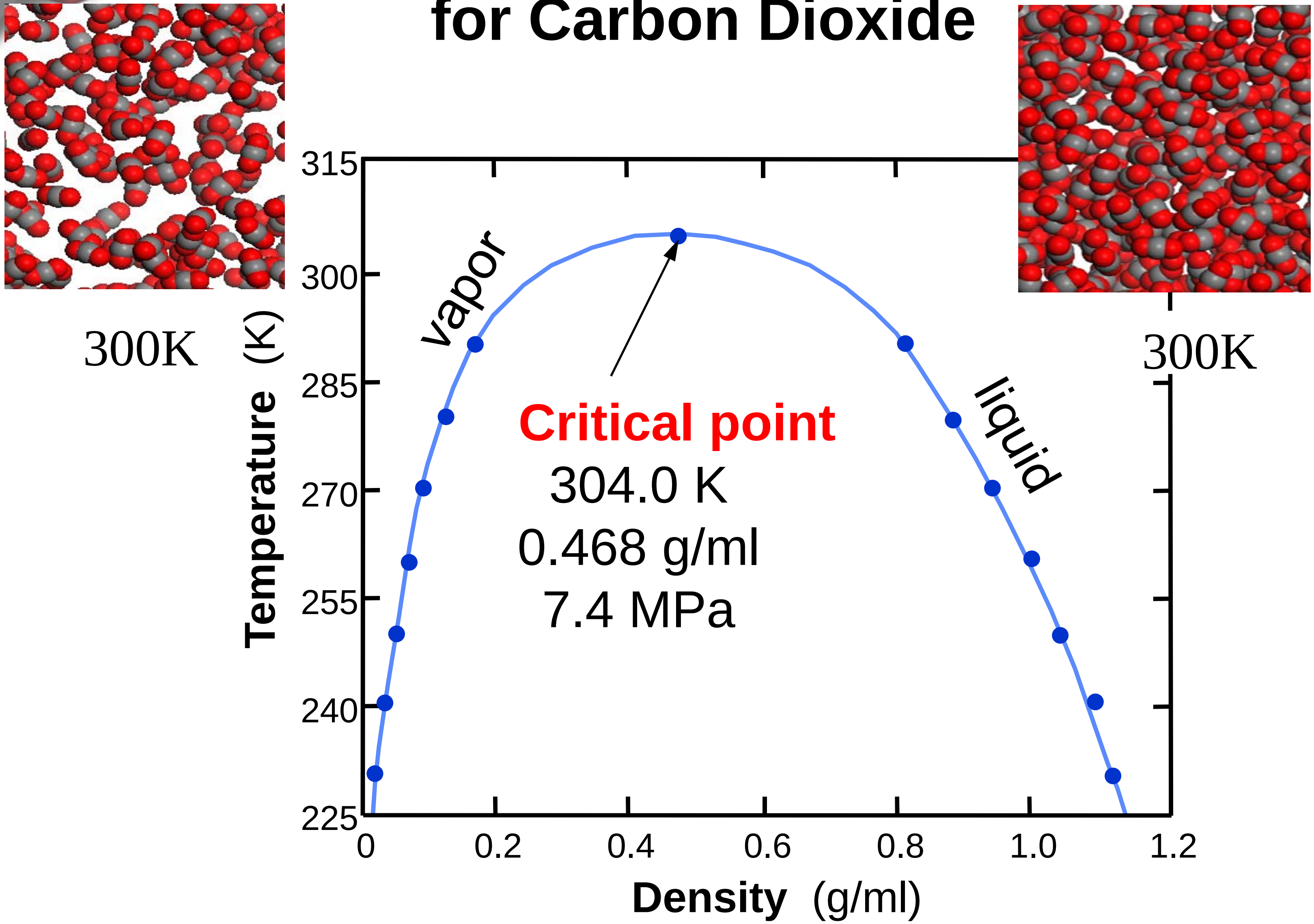
Angle bend



Liang and Lipscomb (1990)
Harris and Yung (1995)
Qin et al. (2008)
Zhu et al. (2009)

Sandia National Laboratories

MD Simulations of Coexistence Envelope for Carbon Dioxide

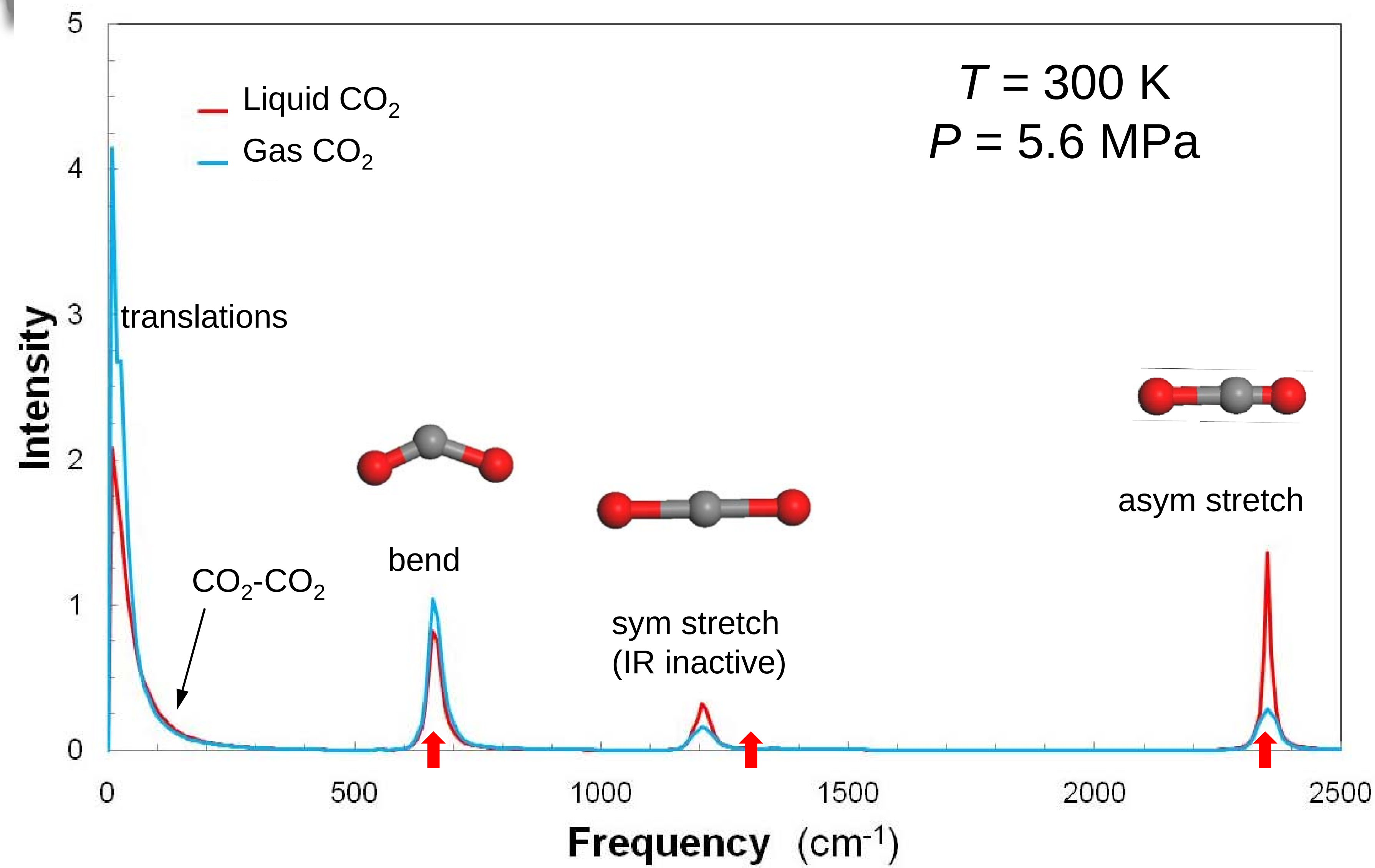


Critical point
304.0 K
0.468 g/ml
7.4 MPa

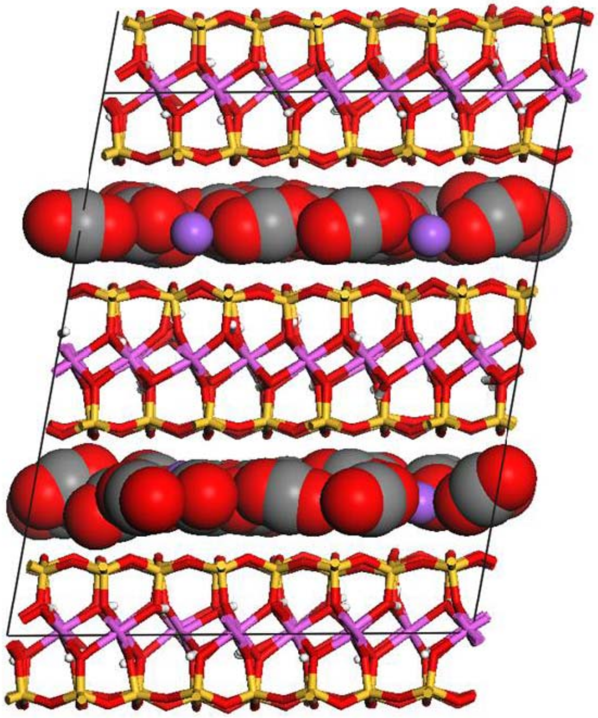
Zhu et al. (2009)
NIST thermodynamic database

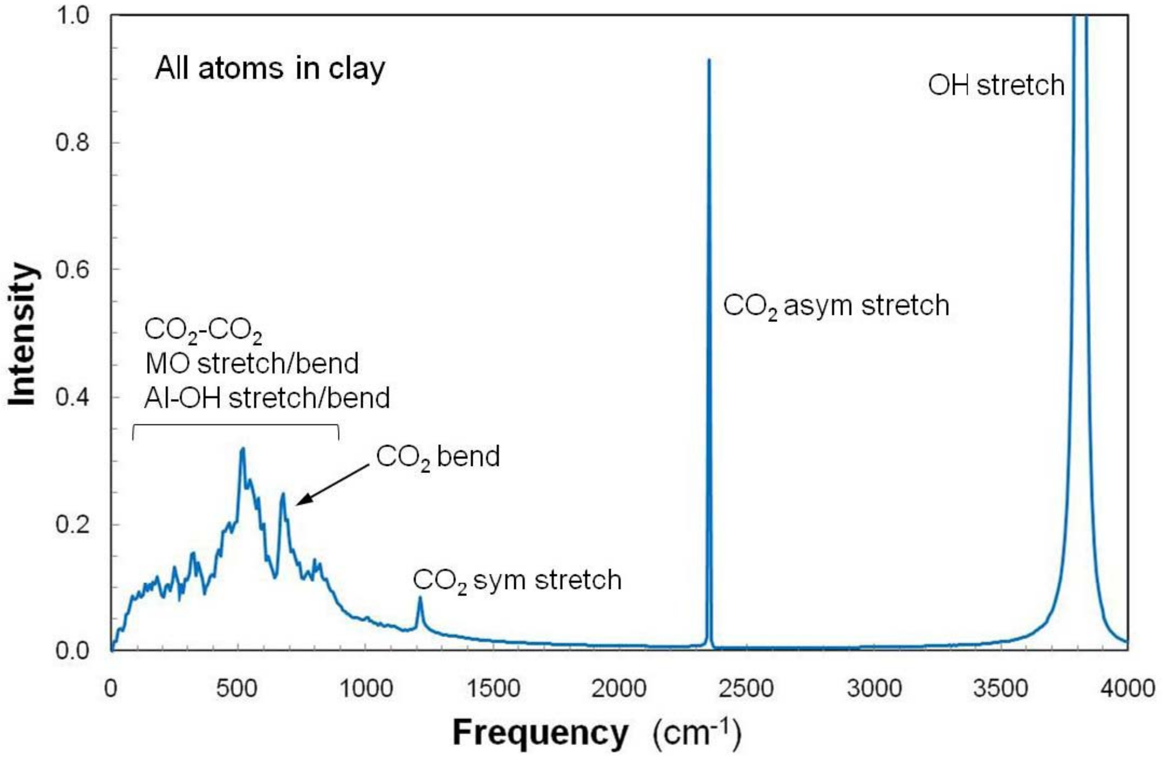
Sandia National Laboratories

Power Spectra of Carbon Dioxide



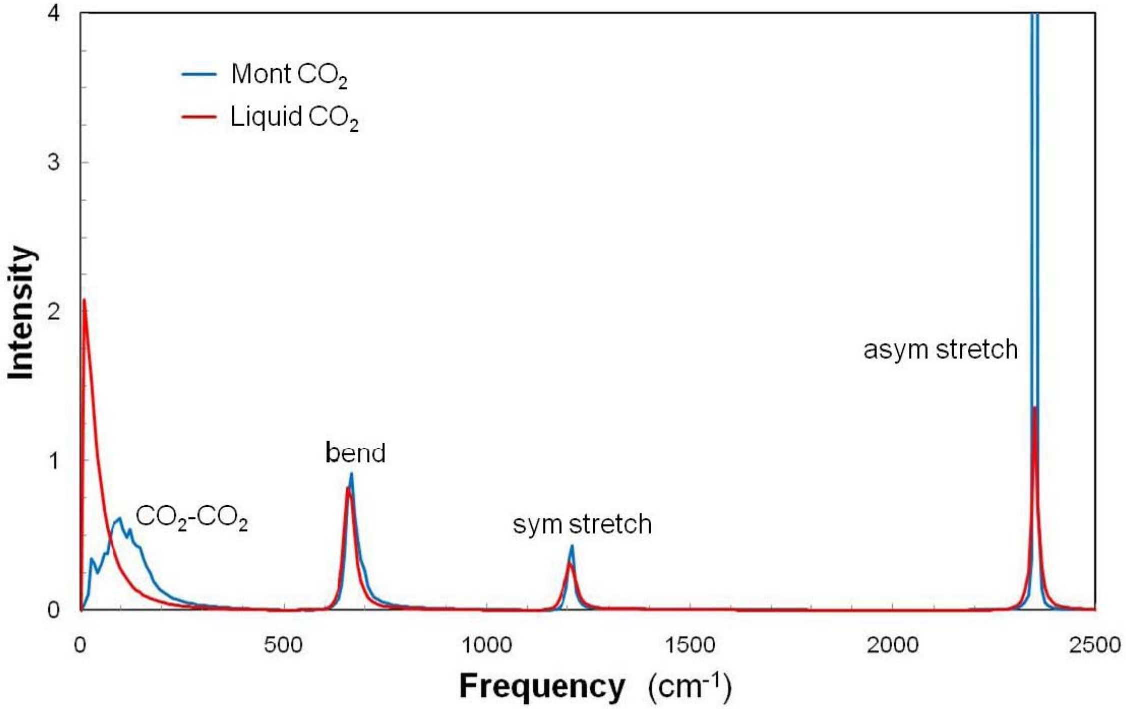
Power Spectra of CO_2-montmorillonite

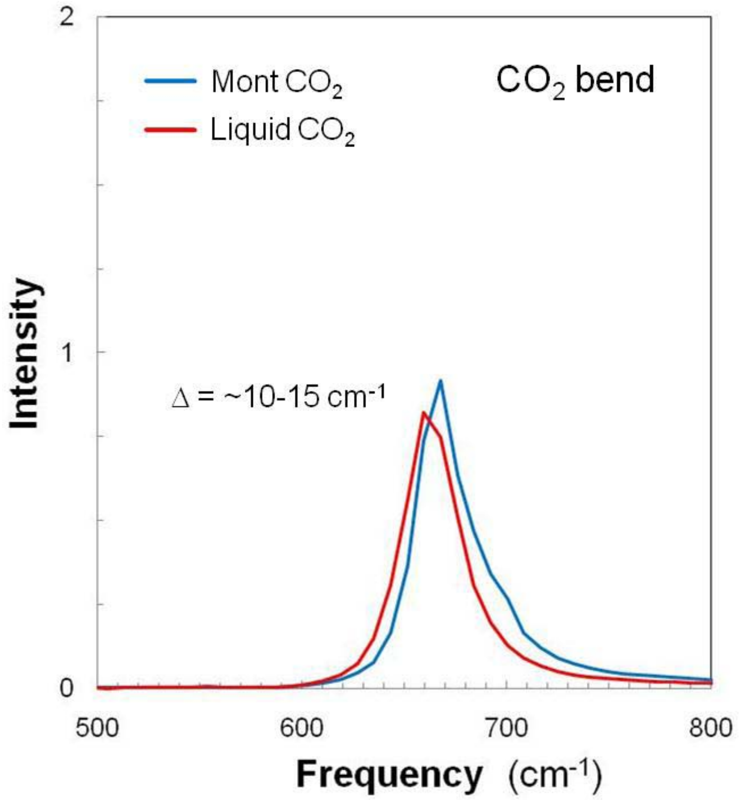




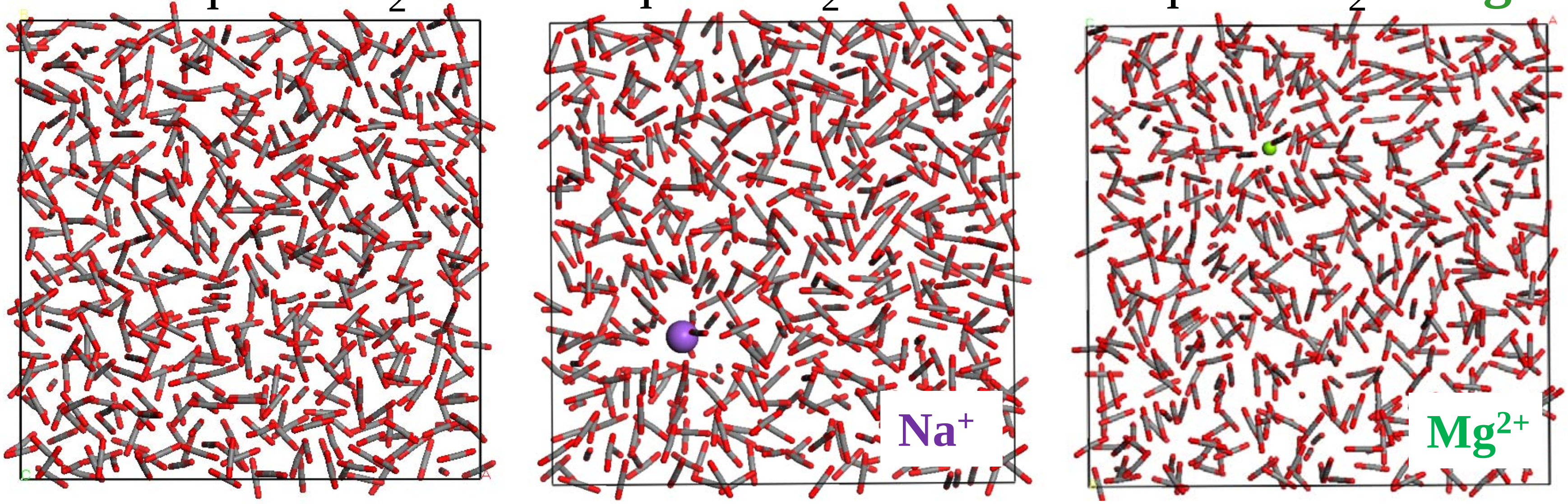
Sandia
National
Laboratories

Power Spectra of CO_2-montmorillonite





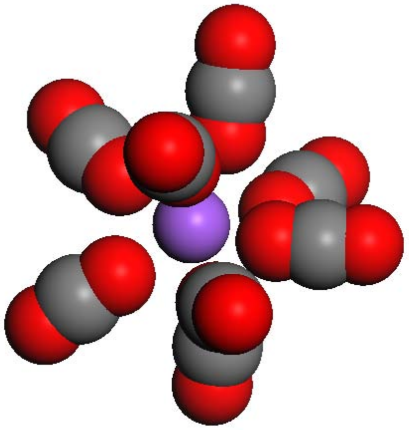
Cation Solvation by Liquid Carbon Dioxide



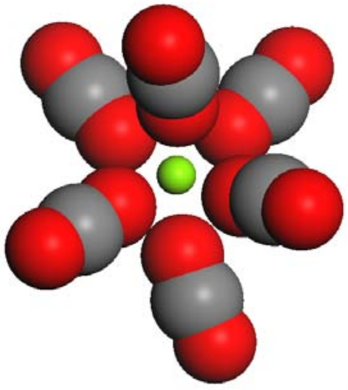
Liquid CO_2 | Liquid CO_2 + **Na^+** | Liquid CO_2 + **Mg^{2+}**

Molecular Dynamics
NVT ensemble
512 CO_2 molecules
1 ns at 300K

$CN_{Na+} = 8$



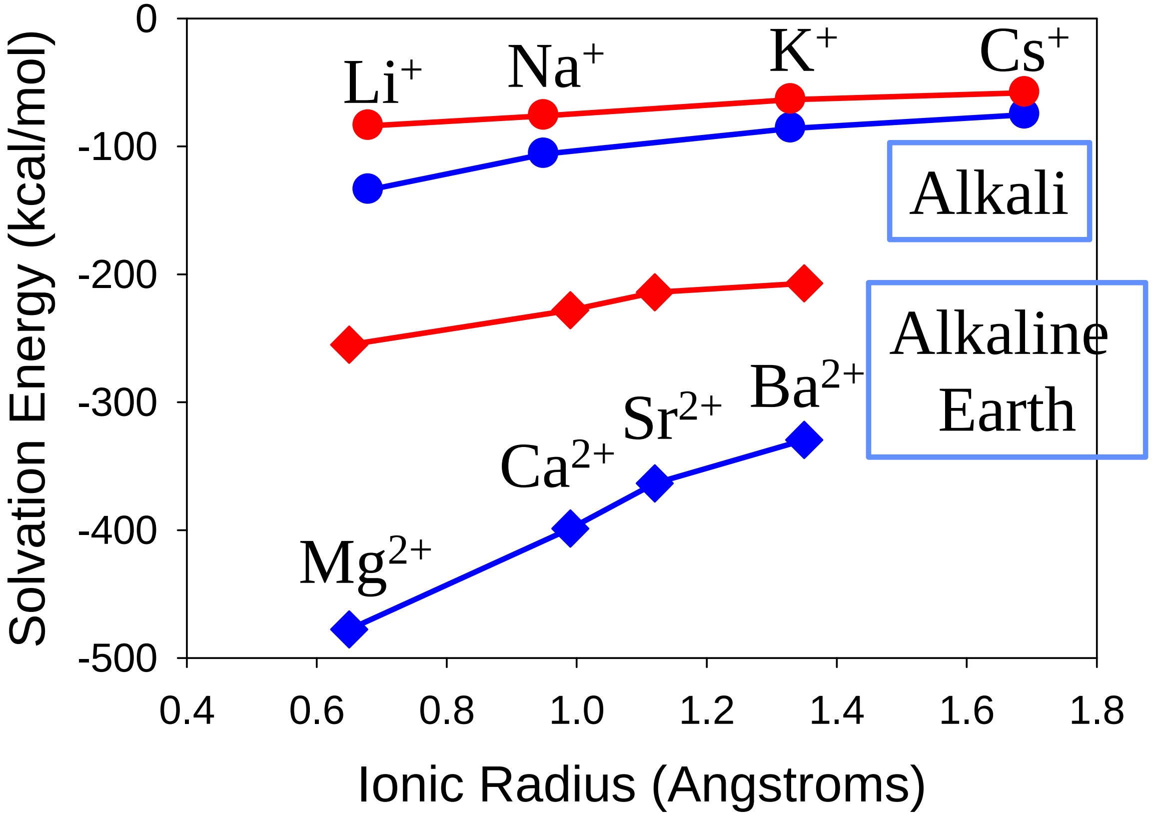
$CN_{Mg2+} = 6$



Cation Solvation by Liquid Carbon Dioxide

Solvation Energy =
PE(CO_2 + cation) – PE(CO_2 cell)

Cation Solvation Energies in Liquid **CO_2** and **H_2O**

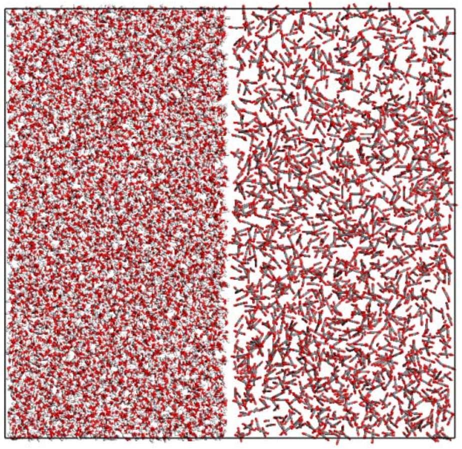


- Larger solvation energies suggest cations prefer to be in H_2O.
- Alkali (+1) cations will distribute almost equally between CO_2(*l*) and H_2O(*l*).
- Partitioning of ions into CO_2 will increase with ion size.

Water-Supercritical CO_2 Interface

Initial Simulation Cell

H_2O SC CO_2

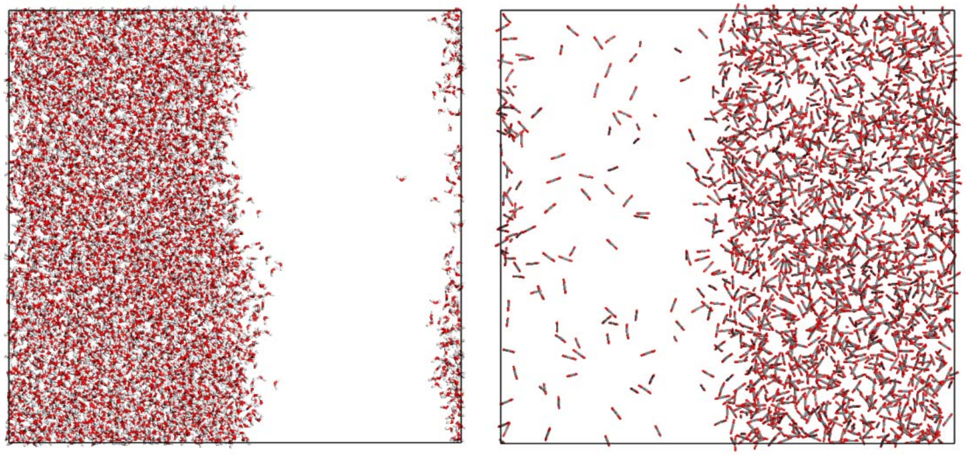


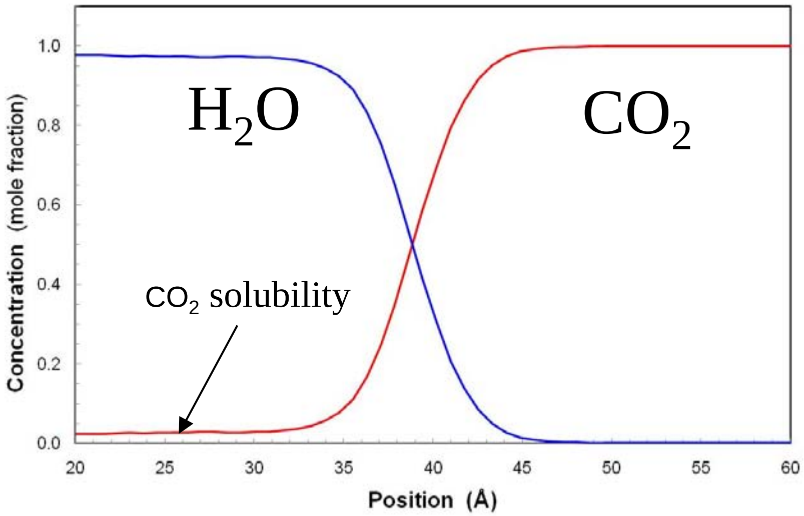
78 Å x 78 Å x 78 Å

NVT ensemble
6,912 H_2O molecules
2,048 CO_2 molecules
Densities at 20 MPa
(800 m depth)

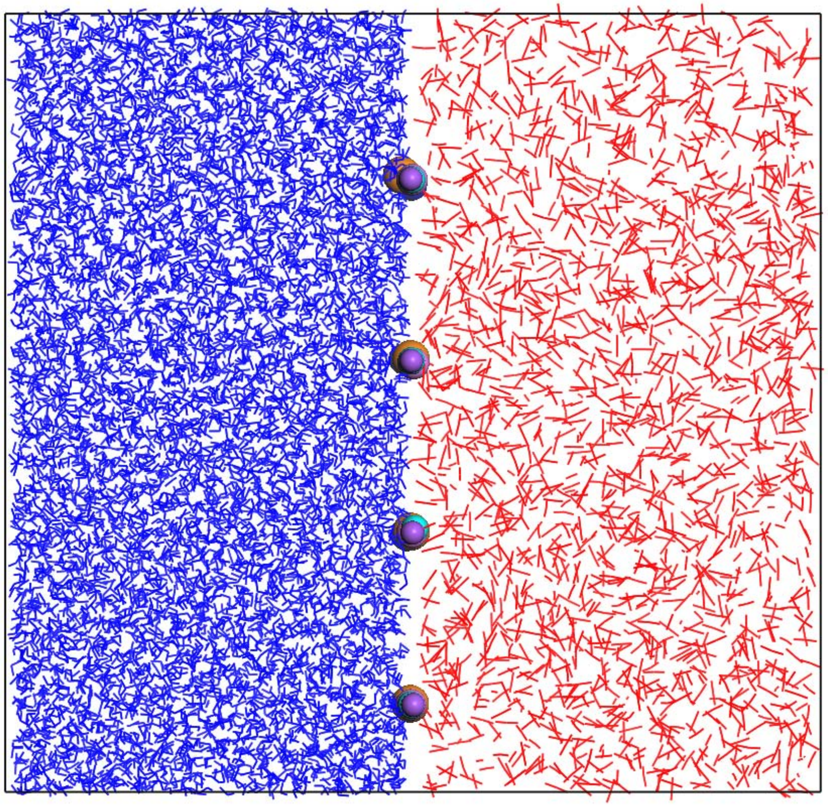
After 0.5 ns at 350K

H_2O only SC CO_2 only

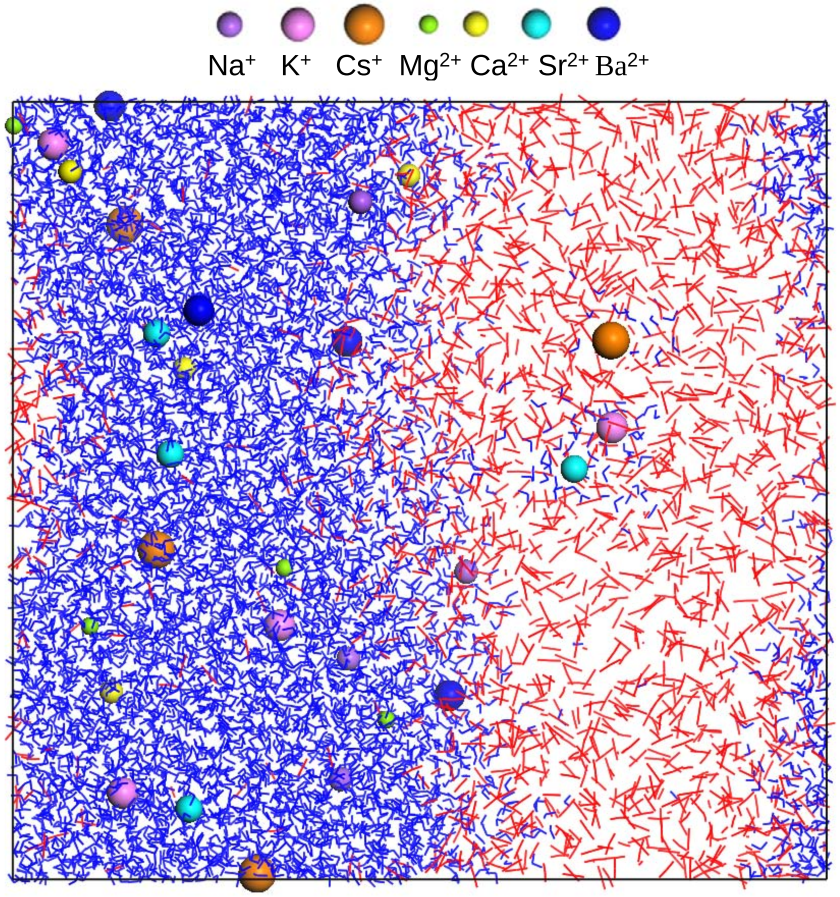




Cation Solvation in Water/Supercritical CO_2

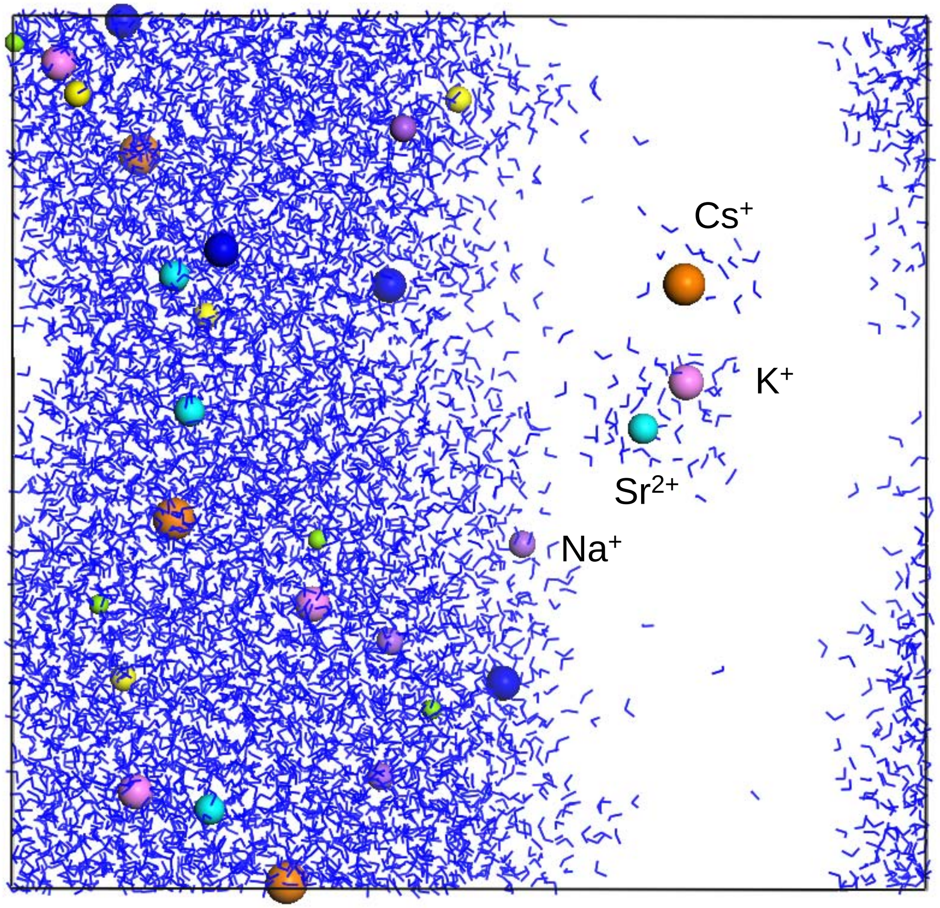


Initial interface
Four of each cation evenly distributed at interface
Neutral background screening



NVT MD
350 K for 0.5 ns

Cation Solvation in Water/Supercritical CO_2



- Cs^+, K^+, and Na^+ are partially hydrated in CO_2 phase
- Sr^{2+} is fully hydrated in CO_2 phase
- Other cations remain in aqueous phase

NVT MD
350 K for 0.5 ns

CO_2 removed

Conclusions and Future Work

- A flexible and accurate force field for CO_2 has been developed to calculate interfacial thermodynamics and properties.
- Alkali metal (+1) cations will be distributed almost equally between liquid CO_2 and liquid H_2O at 300K. Alkaline earth metal (+2) cations will partition preferentially into H_2O.
- Solubility of scCO_2 in H_2O is successfully predicted by the new CO_2 force field.
- A method to calculate contact angles (Solid-Liquid-Gas) has been demonstrated to be successful for hydrophobic and hydrophilic kaolinite surfaces.

- Future work will include extending the use of the new CO_2 FF and contact angle methods to study scCO_2-brine interfaces and calculate interfacial tensions, contact angles and geometries between scCO_2, H_2O and different minerals.

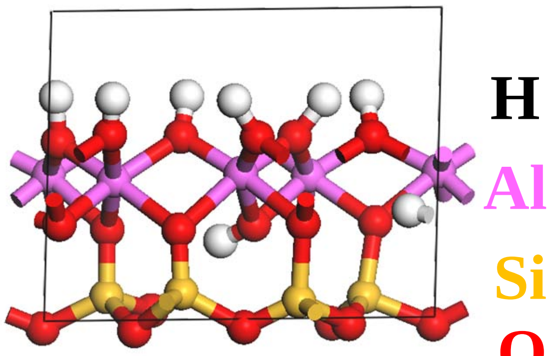
Acknowledgments

- This research has been sponsored by
  - the US Department of Energy, Office of Basic Energy Sciences as part of an Energy Frontier Research Center (CFSES - Center for Frontiers of Subsurface Energy Security)
  - Sandia National Laboratories LDRD Program.
- S. Altman, T. Dewers, and J. Heath for scientific discussions and D. Hart for computer support.

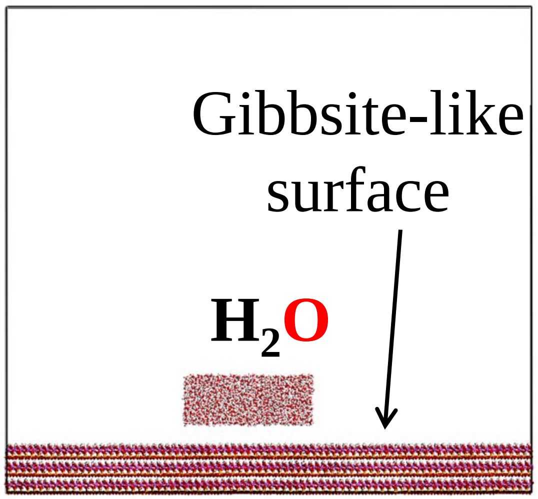
Appendix

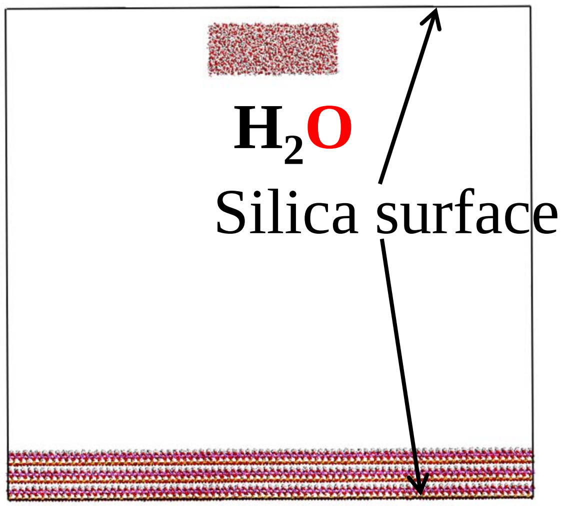
- **Sundry info slides follow**

Gas-Liquid-Solid Interfaces: Contact Angle Calculation



Kaolinite

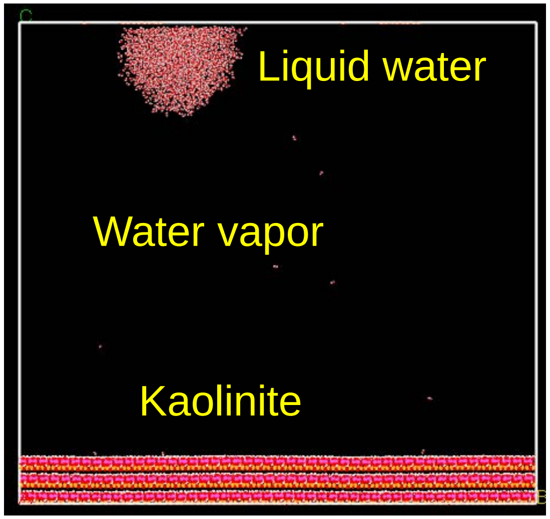




Water Drop
- 1700 H_2O molecules
- 200 ps NVT 1 g/cm^3 at 300K

Kaolinite + Water Drop
- 100 ps equilibration run NVE
- 5 ns NVT production run, 300K
- 2 ns data used for contact angle

214 Å x 205 Å x 200 Å
180 Å vacuum gap



LAMMPS (Plimpton, 1995)
CLAYFF (Cygan et al., 2004)

Sandia National Laboratories

Gas-Liquid-Solid Interfaces: Contact Angle

Young's Equation

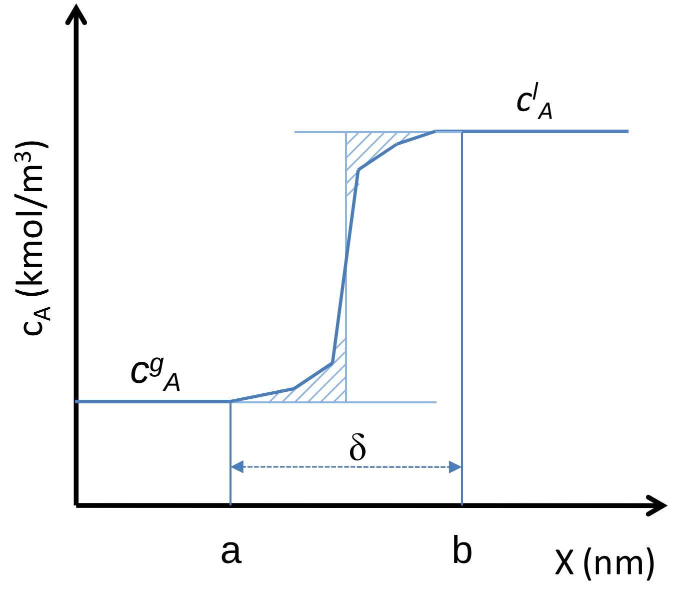
$$\gamma_{12} + \gamma_2 \cos\theta_0 = \gamma_1$$

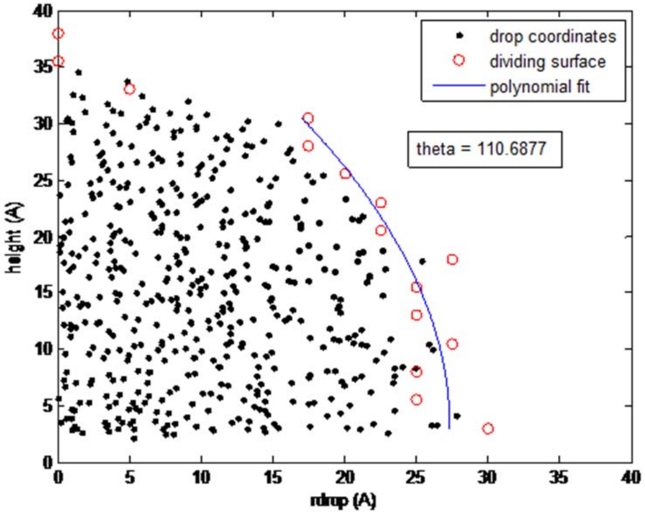
θ_0 = contact angle

γ_{12} = interfacial tension

γ_1, γ_2 = free energy changes with increased surface areas of 1 or 2

Equimolar Dividing Surface





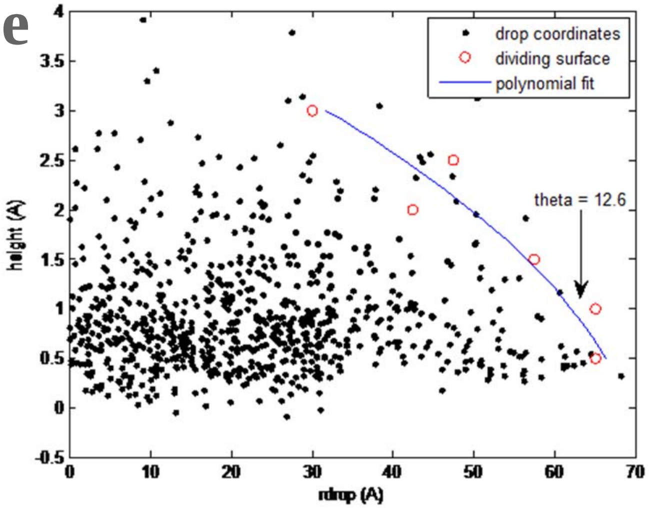
Silica Surface

Hydrophobic

Contact angle of 110^o

Similar to other calculations

(Chai, et al. 2009)



Gibbsite-like Surface

Hydrophilic

Contact angle of 12.6^o

Experimental values ~17-20^o

(*Shang, et al. 2008*)

Giovambattista et al. (2007)