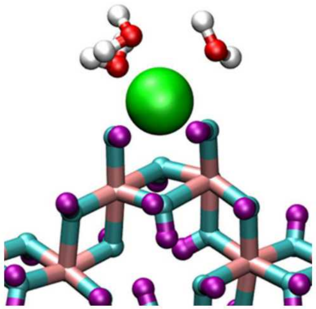
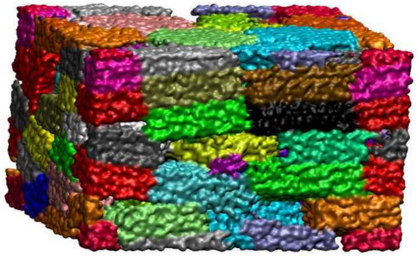
SAND2018-8788C





Molecular dynamics simulation of interaction of aqueous solution with mineral nanoparticle and nanoparticle aggregate

Tuan A. Ho, Louise J. Criscenti
Jeffery A. Greathouse , Yifeng Wang
Sandia National Laboratories

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Motivation 1

- **Availability and transport of ions depend on adsorption/desorption to/from mineral surfaces**
- **Experimental data are collected on mineral particles**
- **MD simulation studies interaction of one mineral surface with aqueous solution**

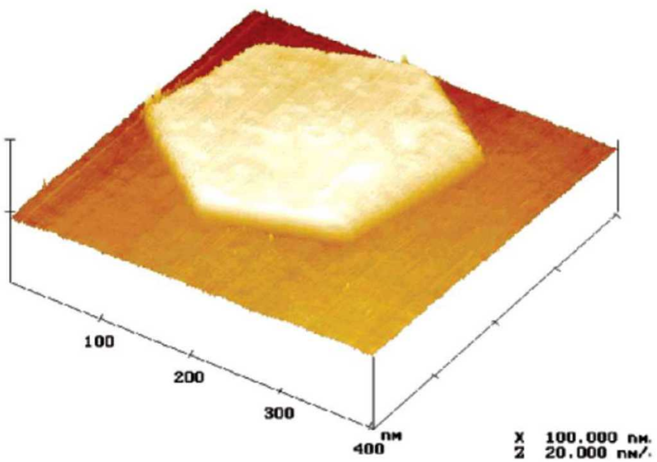
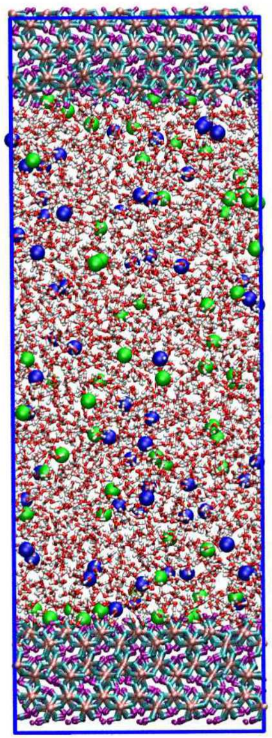


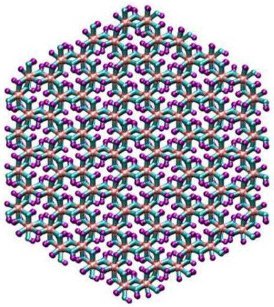
Figure 1. AFM image of a gibbsite particle.

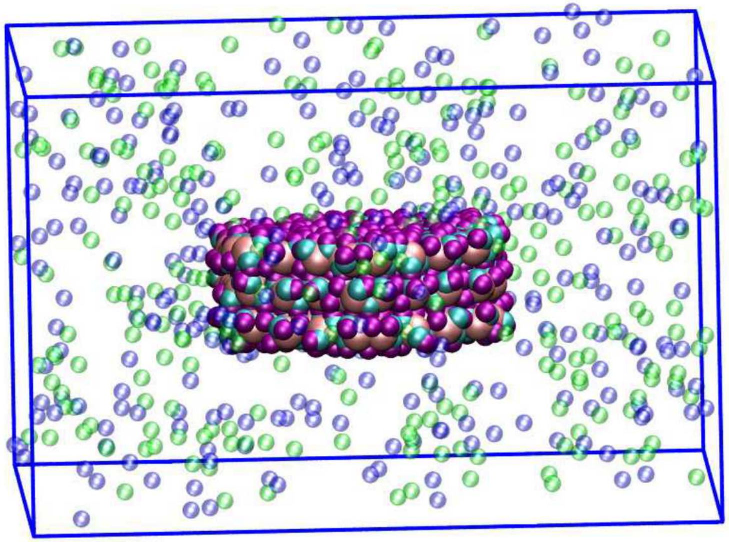
Langmuir 18, 4598 (2002)

Slit-pore model



Hexagonal nanoparticle





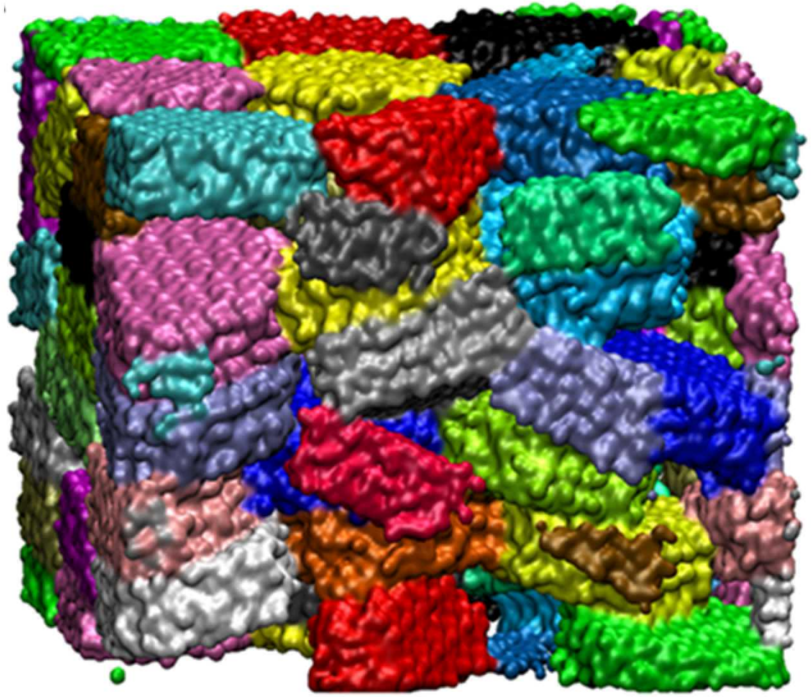
Motivation 2

- **Transport of ions, water and gas also depends on the structure of clay aggregates**

- **Pore spaces: interlayer pore and interparticle pores**

→ Create a molecular structure that includes interlayer and interparticle pores.

→ Study the effects of water content and dewatering on structure



Nanoparticle aggregate

Current MD approach and limitations

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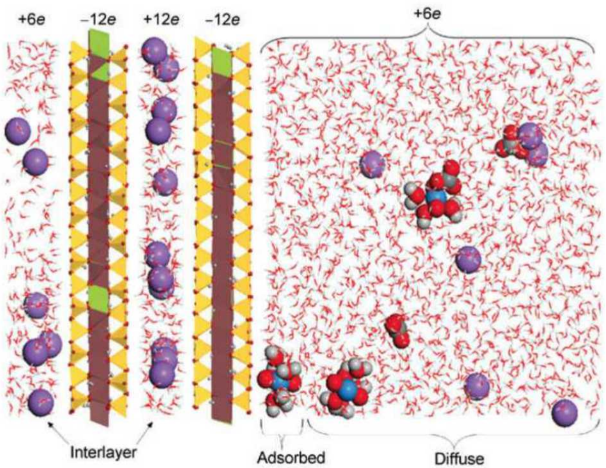
- **CLAYFF**: Fully flexible force field model allowing for realistic exchange of momentum and energy among all atoms-solid substrate and aqueous solution

$$U_{ij} = \Sigma\Sigma(A_{ij}/r_{ij}^{12} - B_{ij}/r_{ij}^{6} + q_i q_j / e_0 r_{ij}) + \Sigma \tfrac{1}{2} k_b (r_{ij} - r_0)^2 + \Sigma \tfrac{1}{2} k_q (q_{ij} - q_0)^2$$

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

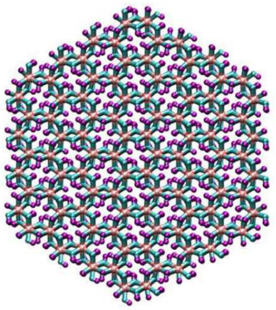
Cygan et al. (2004) JPCB 108, 1255



Adsorption of Uranyl on Montmorillonite

Greathouse and Cygan (2005) PCCP 7, 3580

- **CLAYFF usually fails when simulating mineral edges**



- **In general, structure of edge surface is not well known**

Force field for modeling clays

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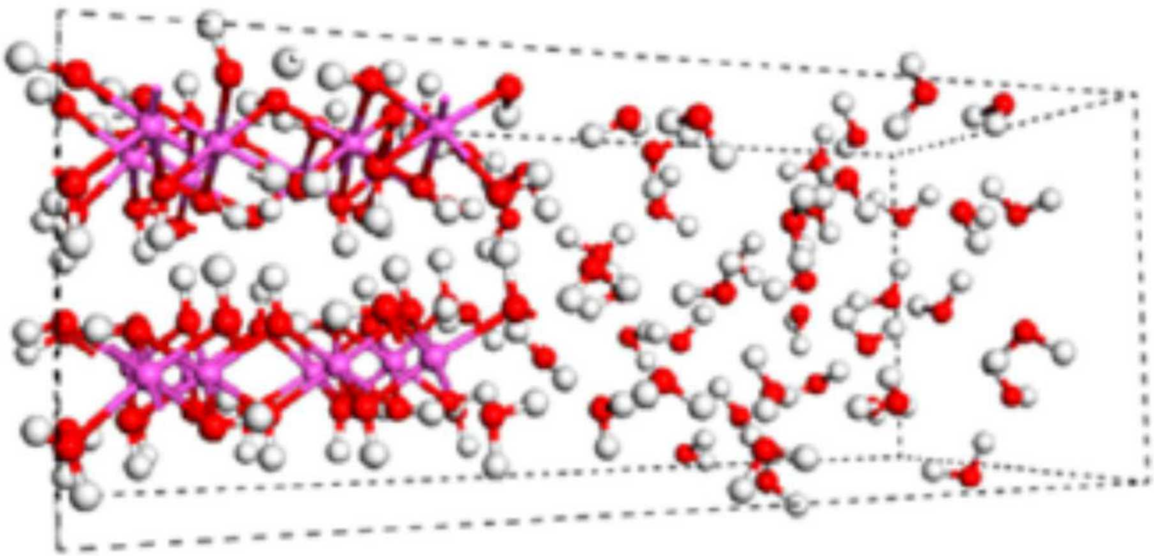
$$U_{ij} = \Sigma\Sigma(A_{ij}/r_{ij}^{12} - B_{ij}/r_{ij}^{6} + q_i q_j/e_0 r_{ij}) + \Sigma \tfrac{1}{2}k_b (r_{ij} - r_0)^2 + \Sigma\tfrac{1}{2}k_q (q_{ij} - q_0)^2$$

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

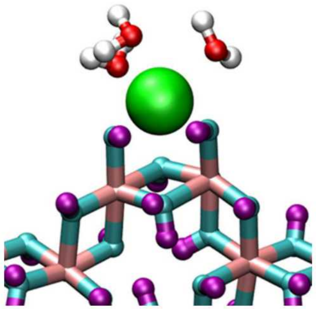


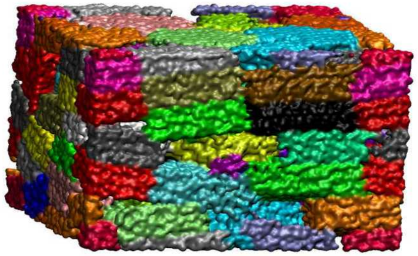
Edge gibbsite model

Add AlOH angle bending term

JPCC (2017), 121, 14757

Molecular dynamics simulation of interaction of aqueous solution with mineral nanoparticle and nanoparticle aggregate





Outline

- Interaction of aqueous solution with nanoparticle
- Structure of nanoparticle aggregate under compaction and dewatering

Hexagonal gibbsite nanoparticle

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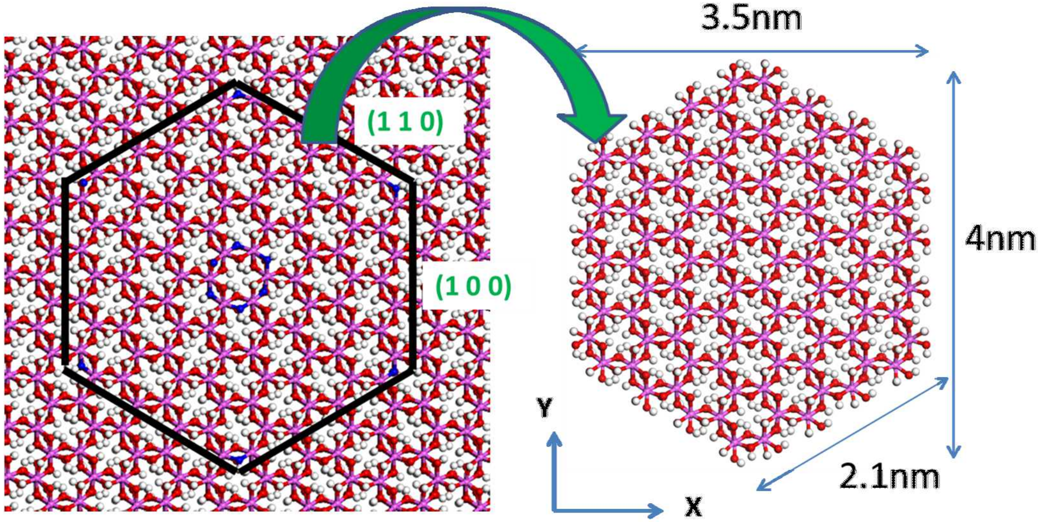


Additional term:

Al-O-H angle harmonic

110^{o} , k =15 Kcal.mol^{-1}.rad^{-2}

Al-O-Al angle harmonic

(edge surfaces)

100^{o}

k = 800Kcal.mol^{-1}.rad^{-2}

ClayFF force field:

Lennard-Jones:σ (Å), ϵ (Kcal/mol)

Al: 4.27132, 1.3297e-06

O:3.165, 0.1554

H: 0, 0

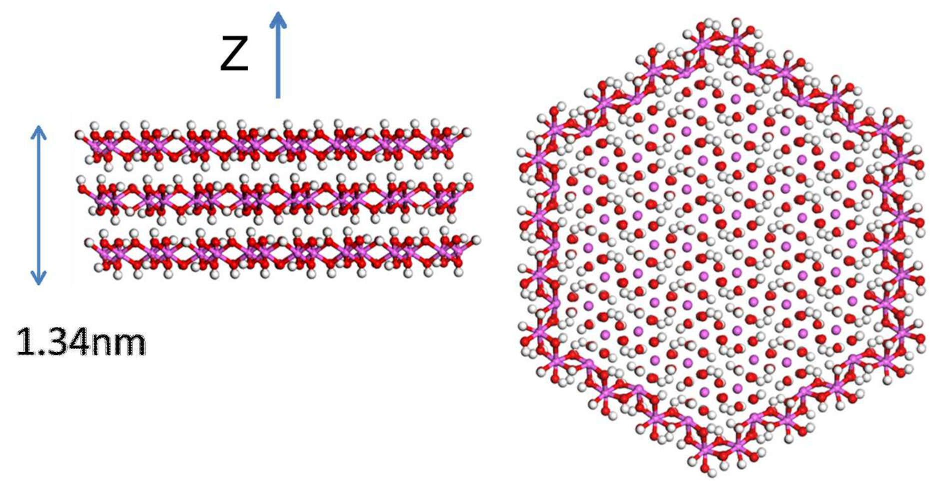
Charge

Al :1.575e

O : -0.95e

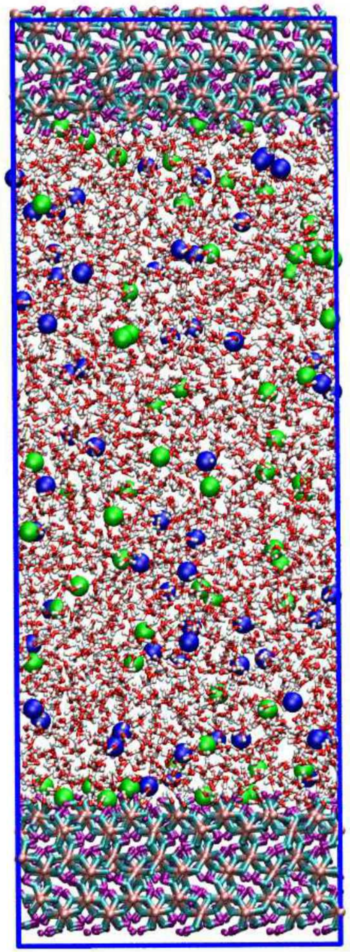
H : 0.425 e

Bond: OH harmonic

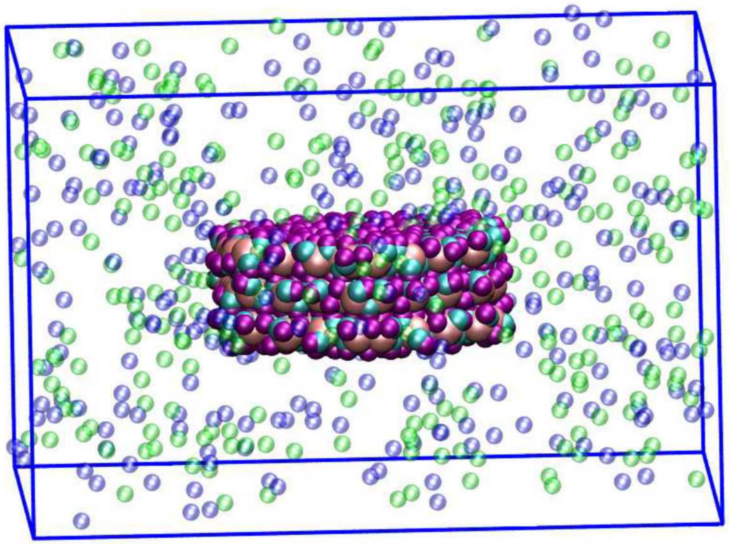


Enhanced ion adsorption on mineral nanoparticles

(Langmuir 34, 5926, 2018)



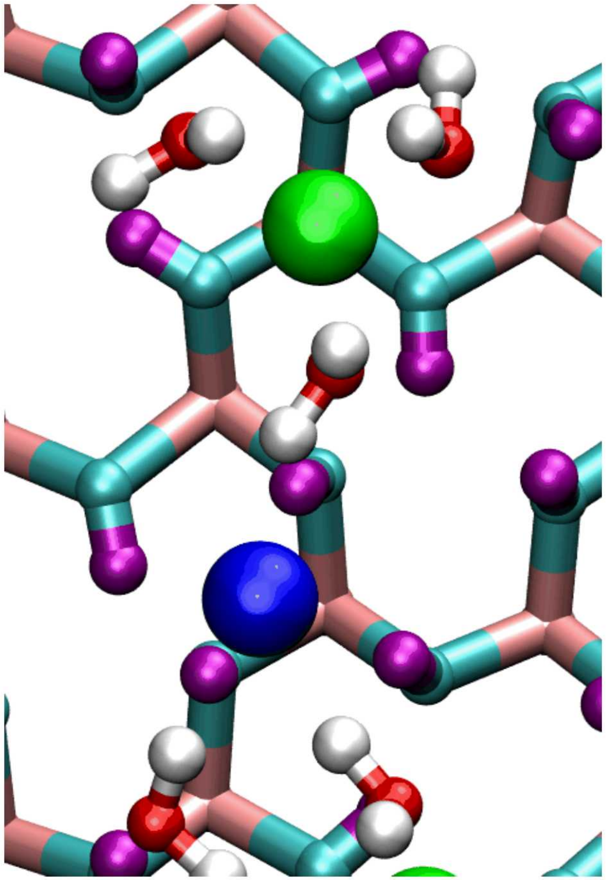
(1 0 0) or (0 0 1)



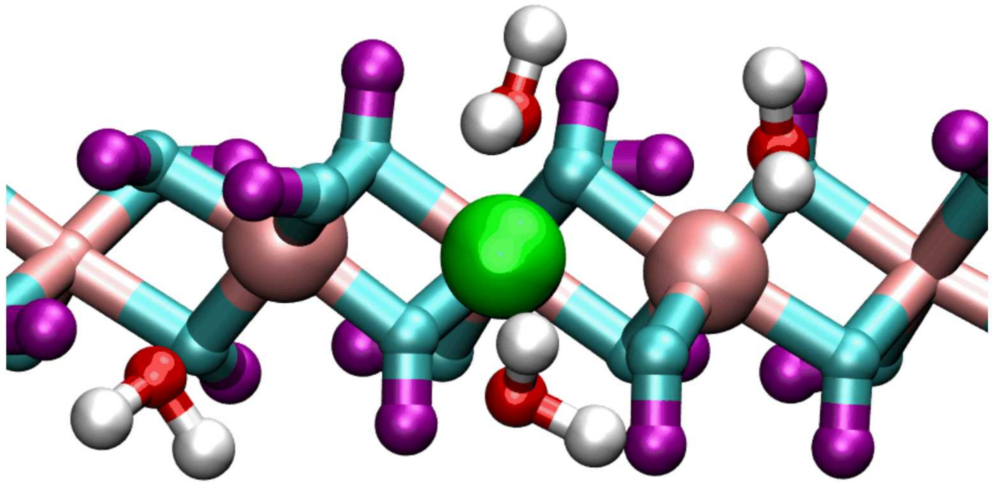
(1 0 0) and (0 0 1)

NaCl

Water and ion properties on (001) and (100) gibbsite surfaces



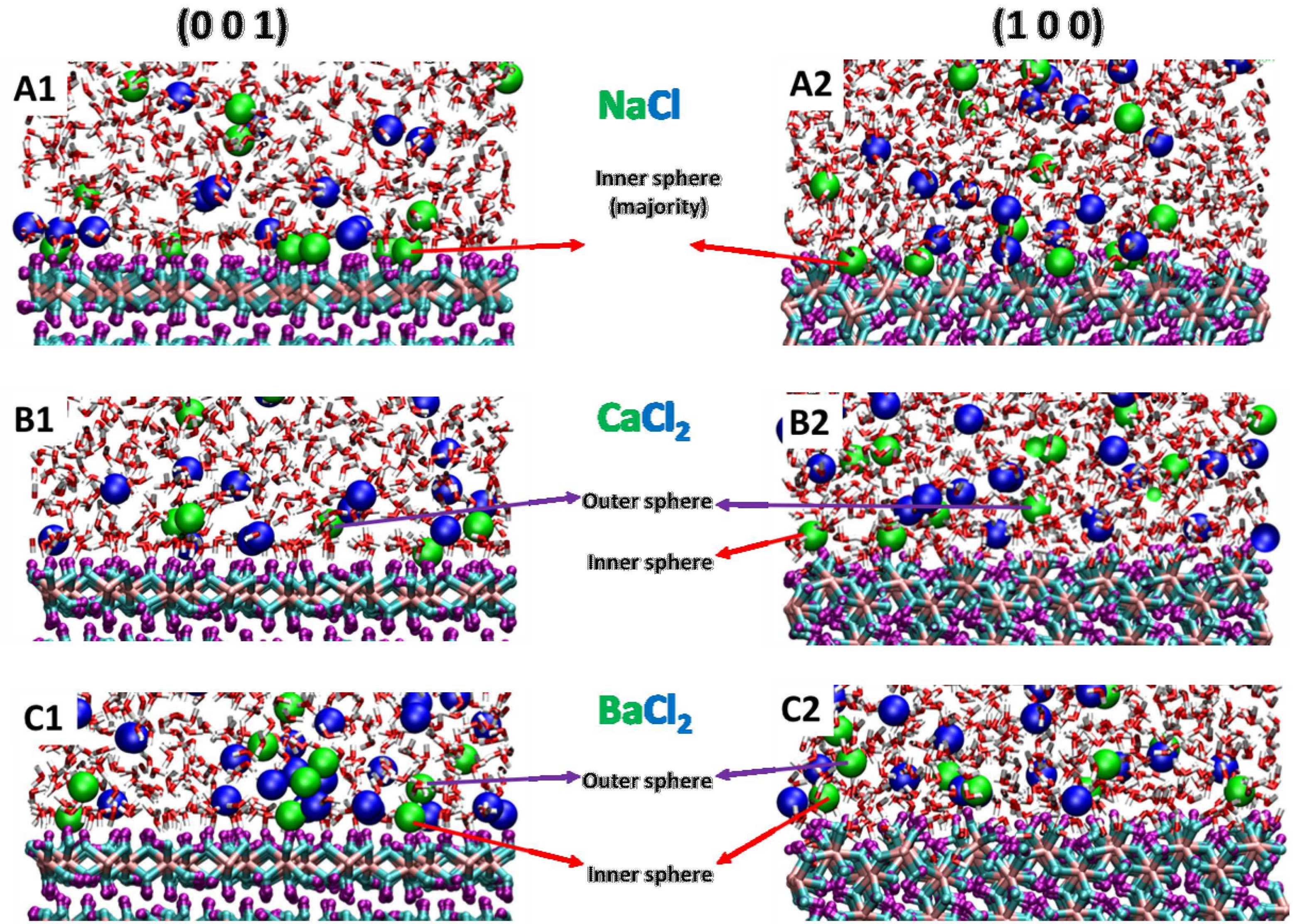
(0 0 1)



(1 0 0)

Green: Na^+
Blue : Cl^-
Purple: H
Cyan: O
Pink: Al

Water and ion properties on (001) and (100) gibbsite surfaces



Green: Na^+
Blue : Cl^-
Purple: H
Cyan: O
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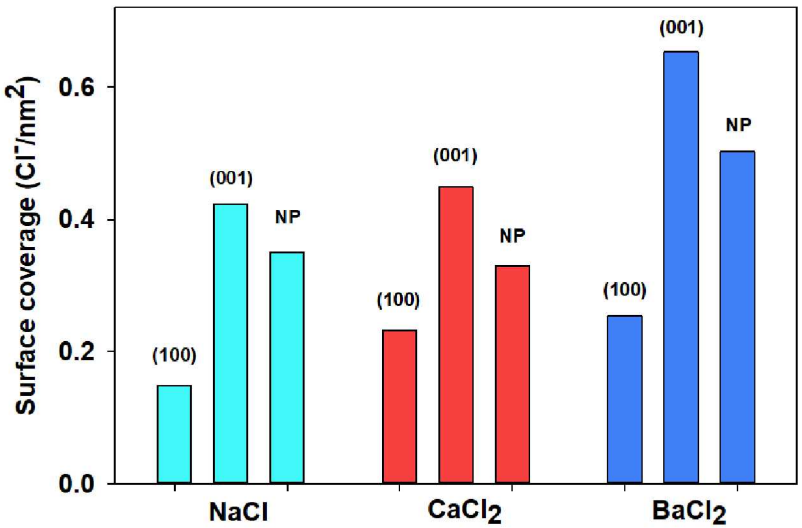
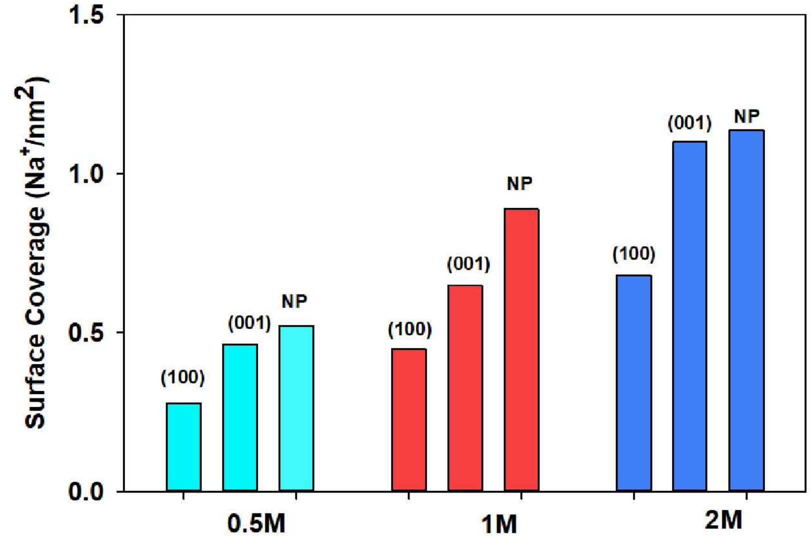
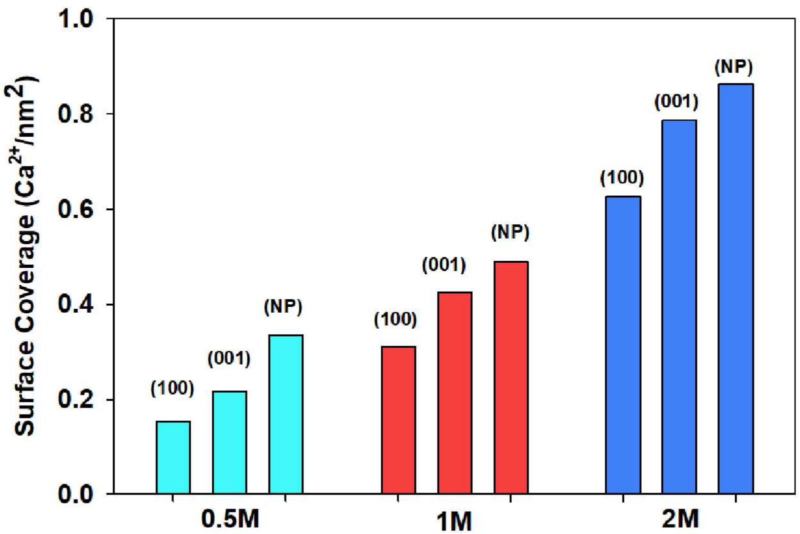
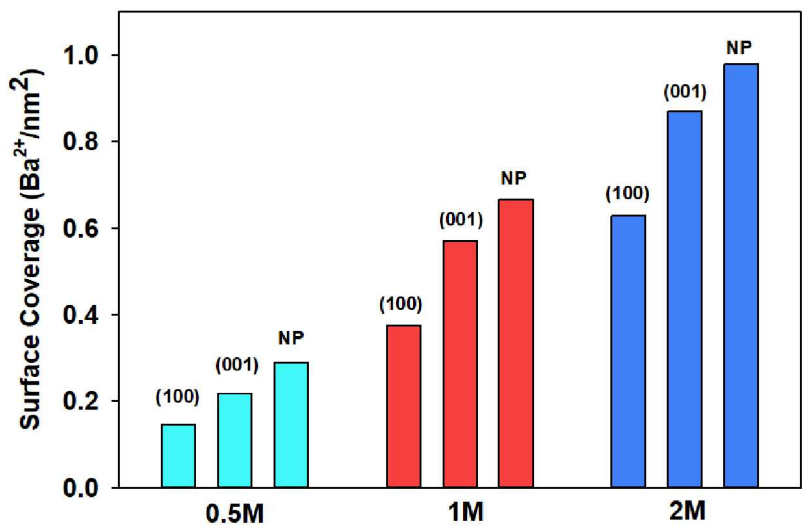
Ion surface coverage

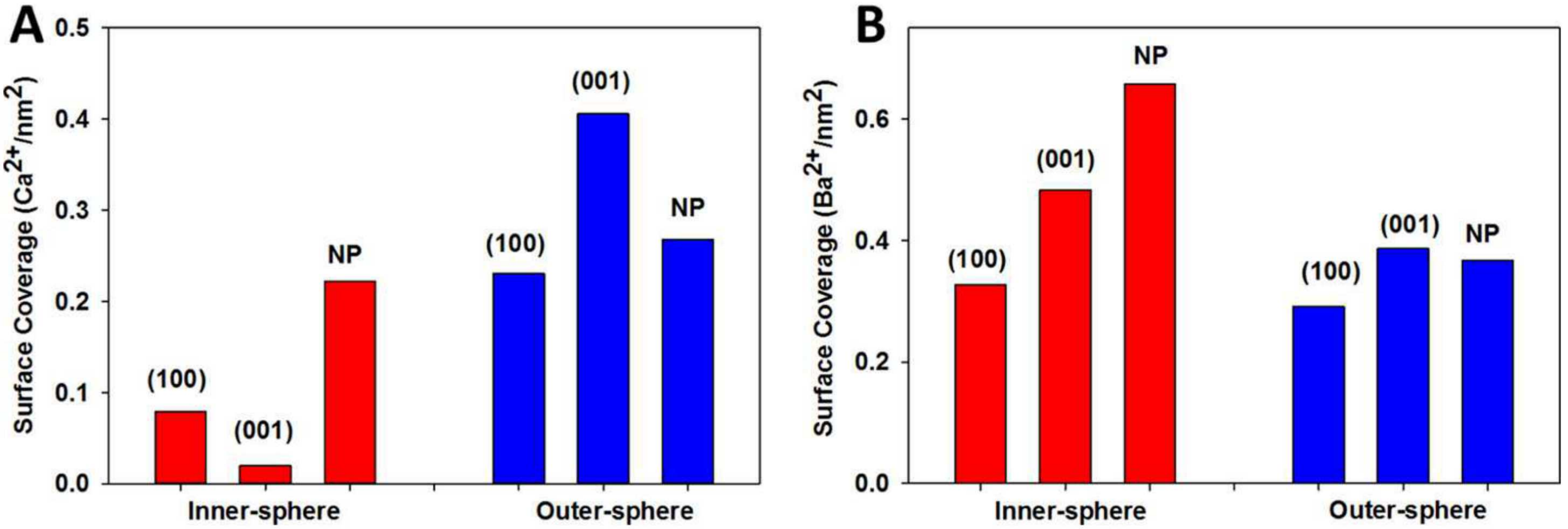




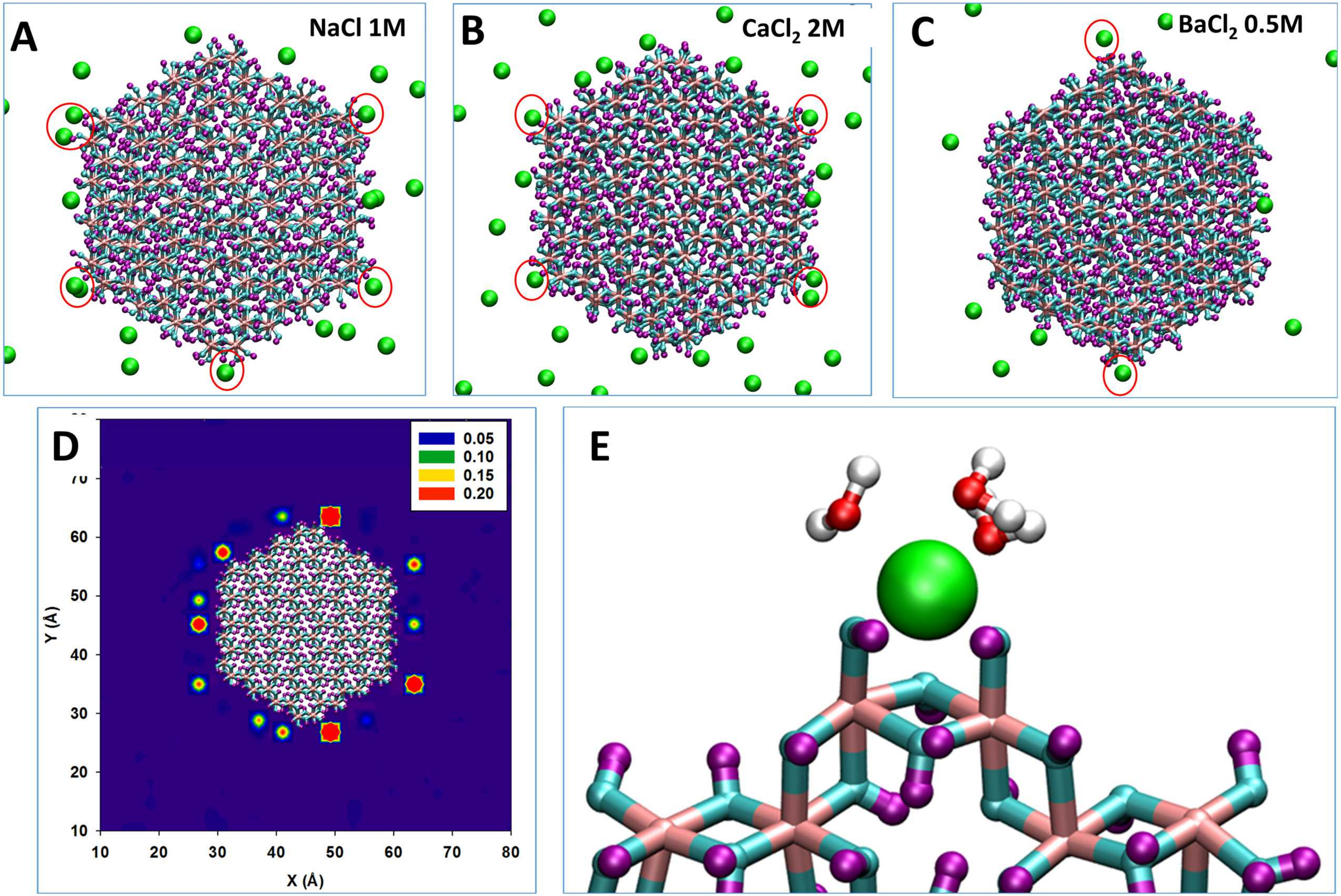




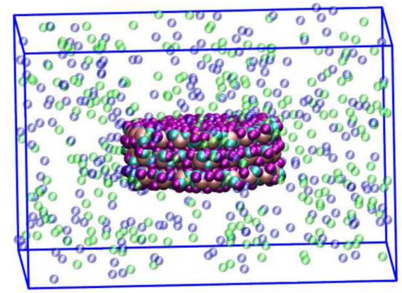
Ion surface coverage

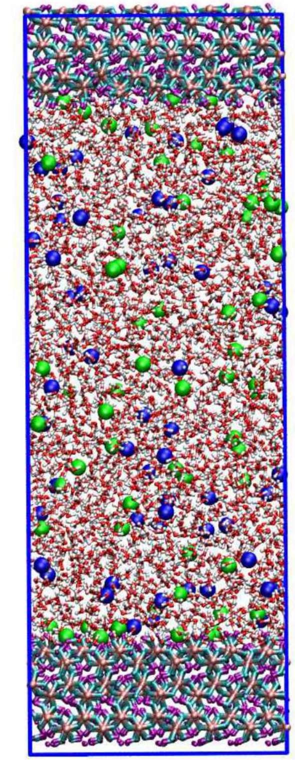


Conner effects on ion adsorption



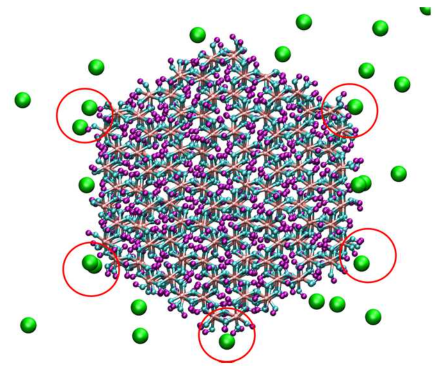
Conclusion 1





Scientific Achievement

► **Enhanced adsorption on nanoparticles**



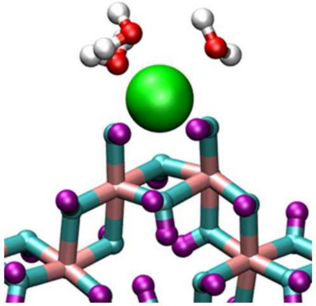
► **Corner effect**

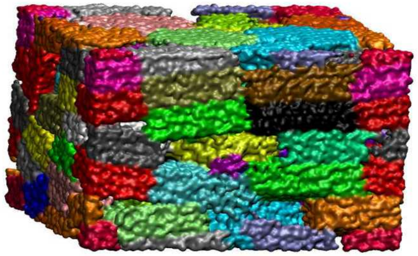
Significance and Impact

► Comparison of simulated ion adsorption trends with experiment will be improved when more realistic mineral models containing nanoparticles or nonideal binding sites are included.

► This work demonstrates that ion adsorption constants used in thermodynamic models should include adsorption at nonideal sites (edges, corners, defects) in addition to idealized surfaces.

Molecular dynamics simulation of interaction of aqueous solution with mineral nanoparticle and nanoparticle aggregate





Outline

- Interaction of aqueous solution with nanoparticle
- Structure of nanoparticle aggregate under compaction and dewatering

Gibbsite aggregate *(Scientific Reports, 7, 15286, 2017)*

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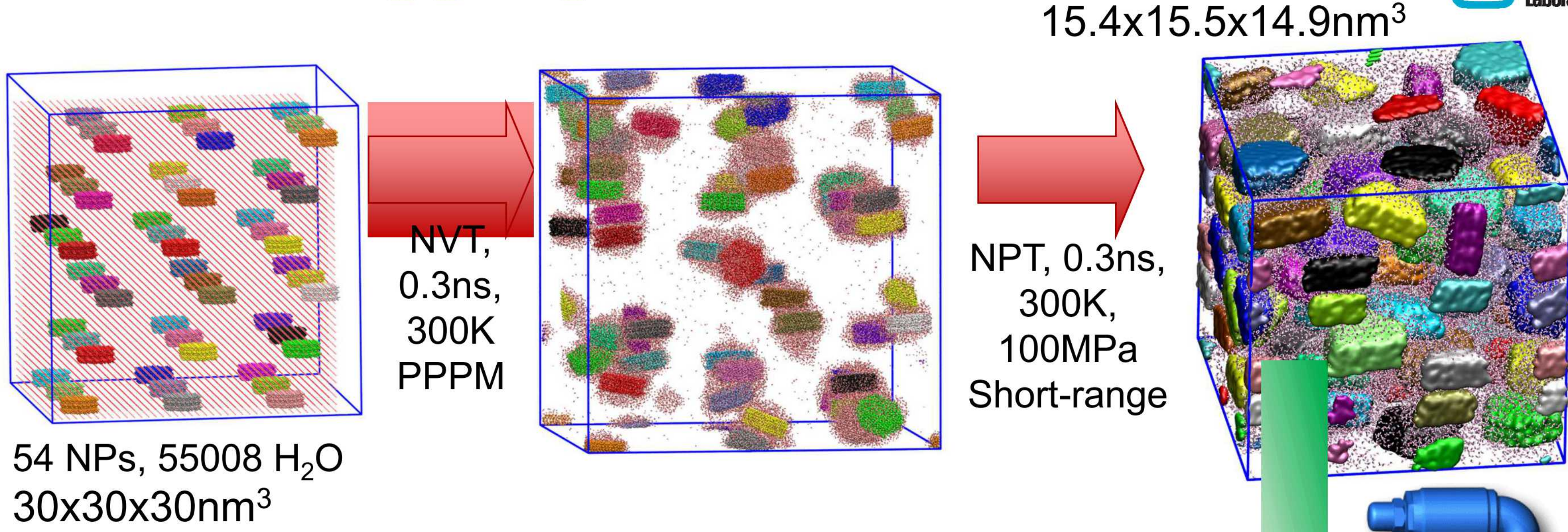
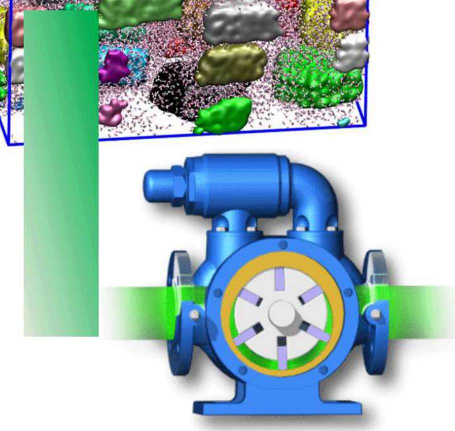




Effect of dewatering rate:

- Delete all water: "Fast"
- Delete 100 H_2O/100 steps: "Intermediate"
- Delete 10 H_2O/100 steps: "Slow"

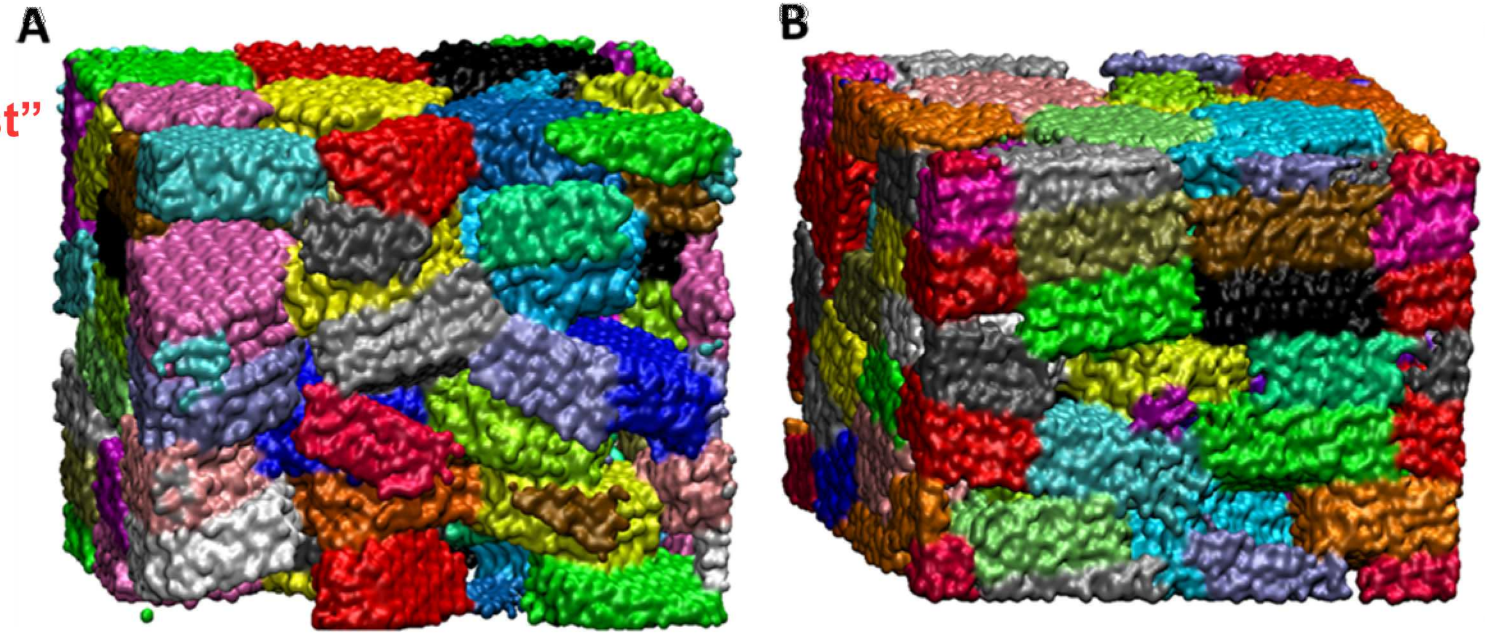
Effect of water content:

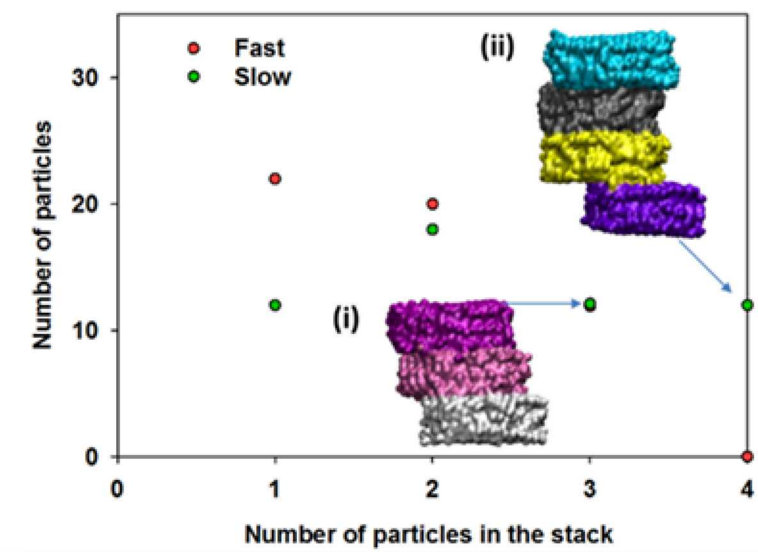
- 1 water layer around each particle: 1W (22.5wt%)
- 2 water layers around each particle: 2W (37.2wt%)
- Additional withdraw water from 2W: 2W_dewatering (6wt%)
- Dry: 2W_dry

Aggregate structure

“Fast”

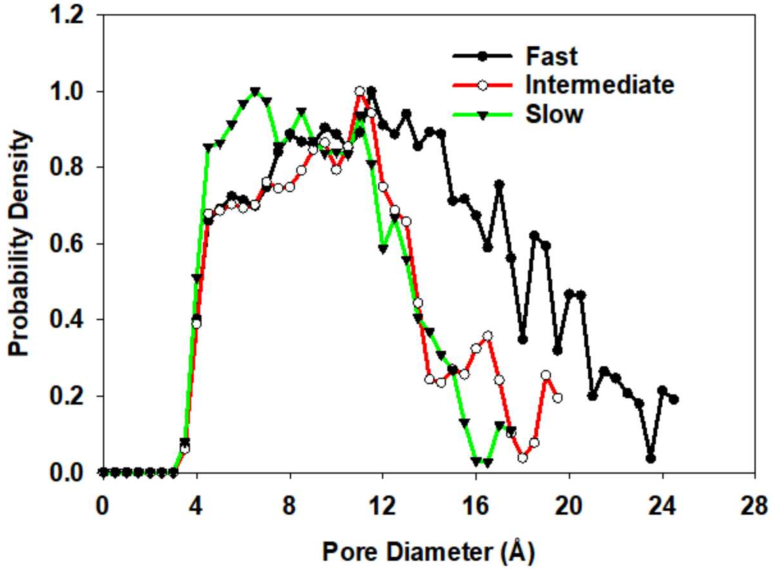
“Slow”



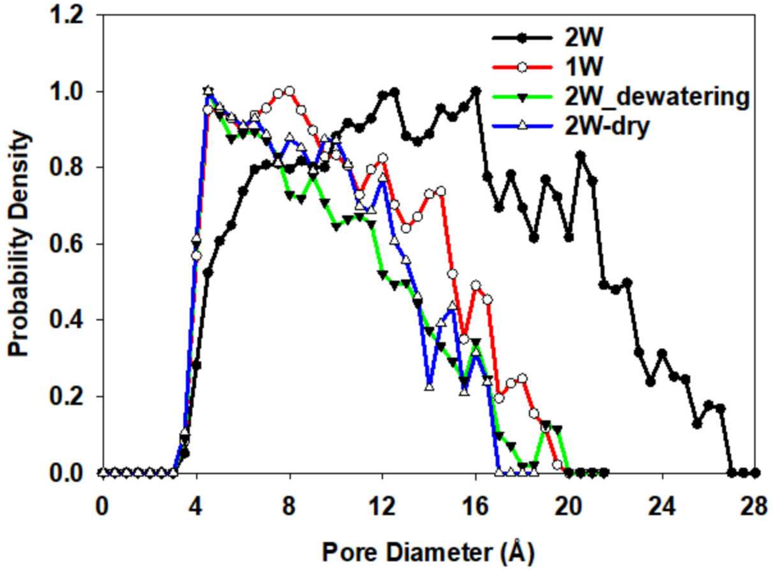


Results

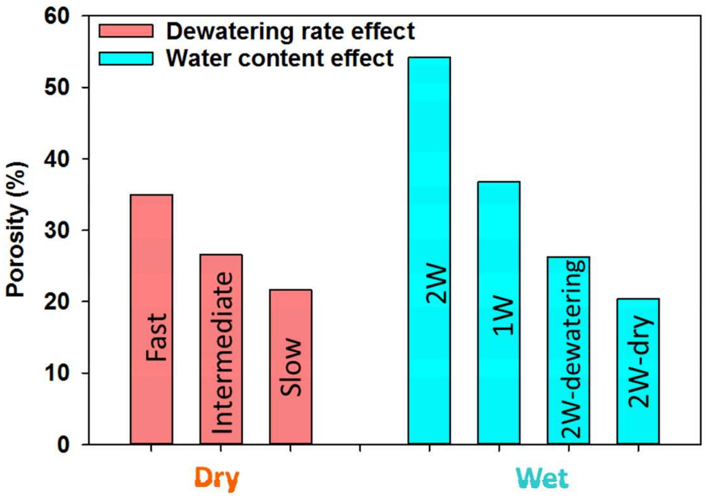
Effect of dewatering on PSD

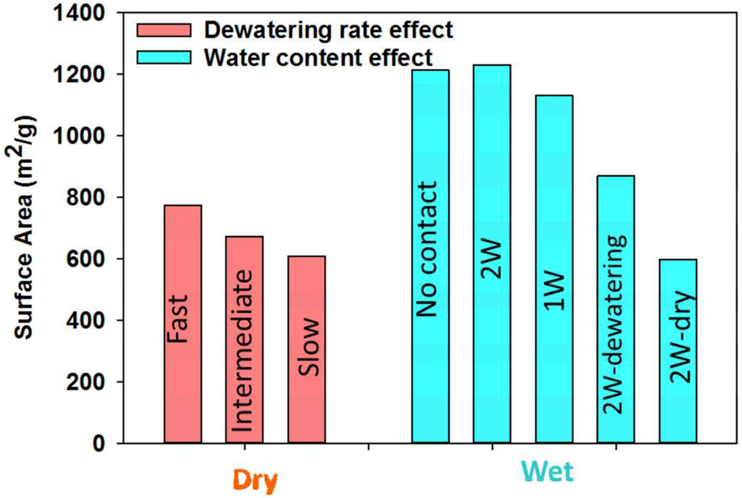


Effect of water content on PSD



Effect of dewatering rate and water content on porosity and surface area





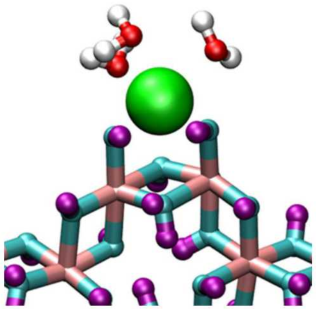
Conclusion 2

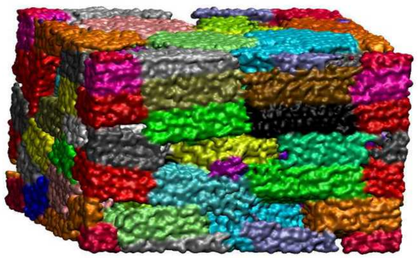
Scientific Achievement

- **We have developed a method for creating complex and realistic clay-like nanoparticle aggregates with interparticle pores and grain boundaries.**
- **Varying the water content and dewatering rate significantly affects**
(1) micro-porosity of the compacted aggregates and
(2) particle alignment and stacking.

Significance and Impact

- **To our knowledge, this method is the first of its kind for generating atomistic models of mineral nanopores beyond the standard geometries (planar, cylindrical, slit pore).**
- **Models of nanoparticle aggregates can be used to simulate fluid properties in a wide range of pore sizes and geometries.**





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Funding: BES
NETL

Thank you!