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Molecular Modeling of Nanoparticle-Water Interactions: Adsorption and Aggregation

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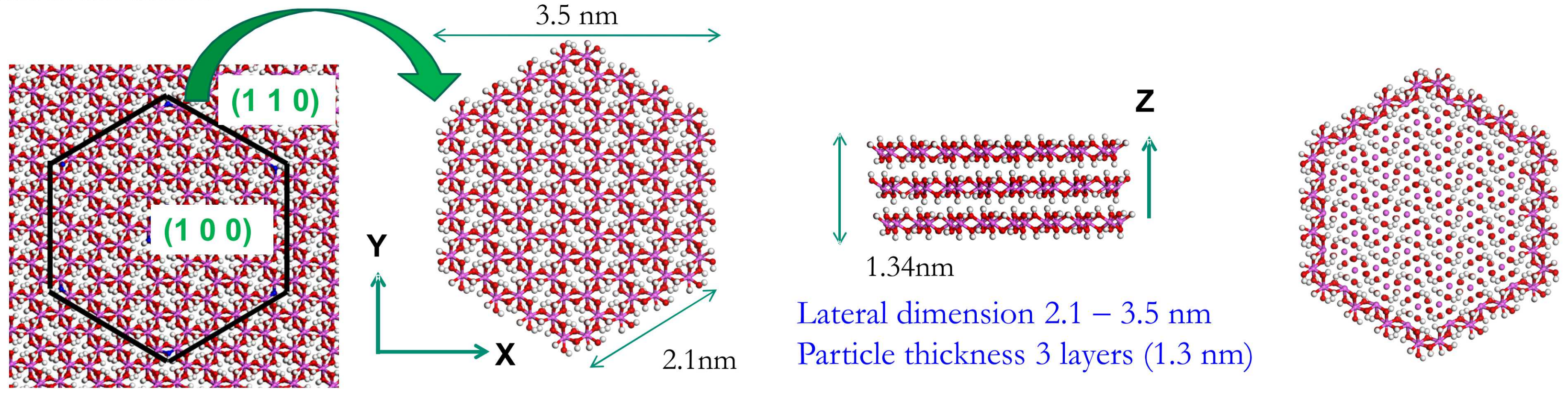
Introduction

- The objective is to use molecular simulation to investigate aqueous ion diffusion and adsorption to mineral surfaces in more complex systems more representative of compact soils and rocks.
- Gibbsite is used as a model mineral because it has properties similar to a clay mineral but does not include the additional complexity of an interlayer.
- Molecular simulations are performed for:
  - Water and ion adsorption to the basal (001) and edge (100) gibbsite surfaces
  - Water and ion adsorption to a gibbsite nanoparticle
  - Water adsorption to gibbsite nanoparticle aggregates that are created through de-watering and compaction

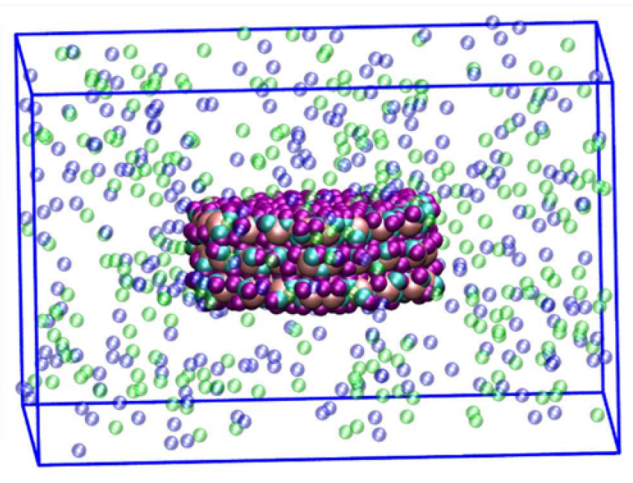
Adsorption to Gibbsite Nanoparticle

Construction:



Lateral dimension 2.1 – 3.5 nm
Particle thickness 3 layers (1.3 nm)

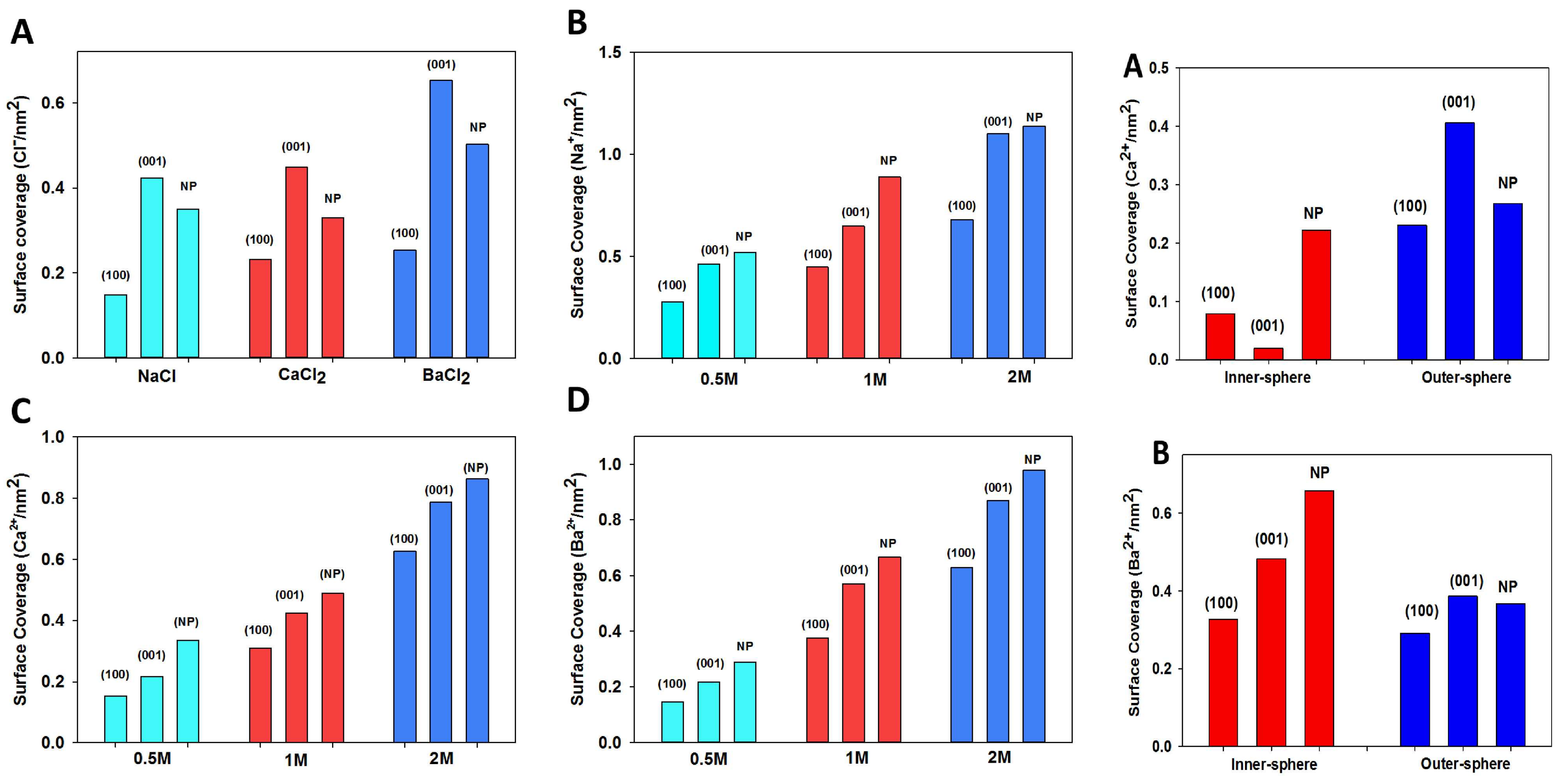
Exploit the hexagonal symmetry of bulk gibbsite



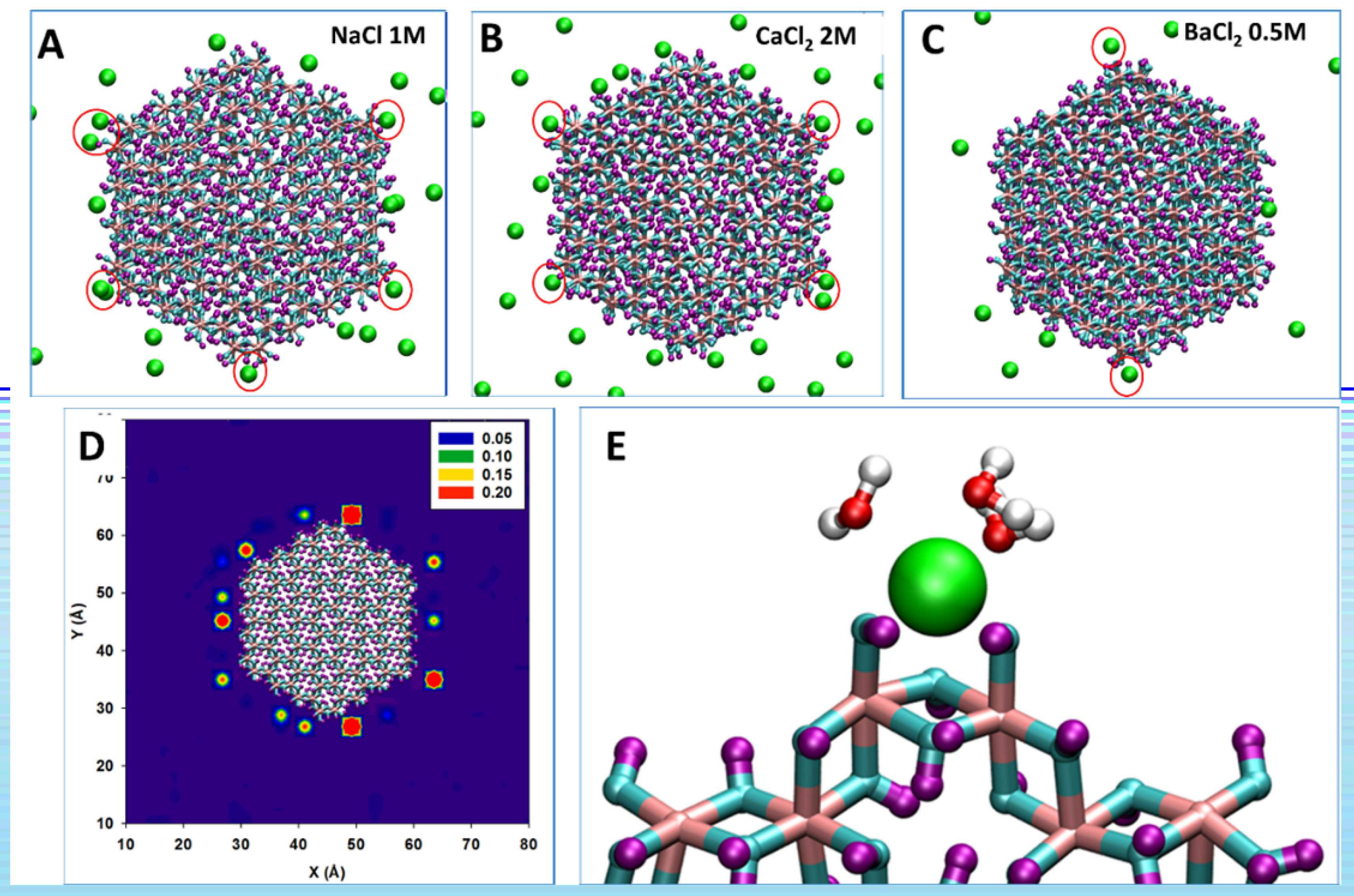
Molecular dynamics

- **LAMMPS code with ClayFF parameters.**
- **New Al-O-H angle bending term for stability of edge sites.**
- **Extra Al-O-Al term added for nanoparticle stability.**

Adsorption on Nanoparticle vs. Surfaces

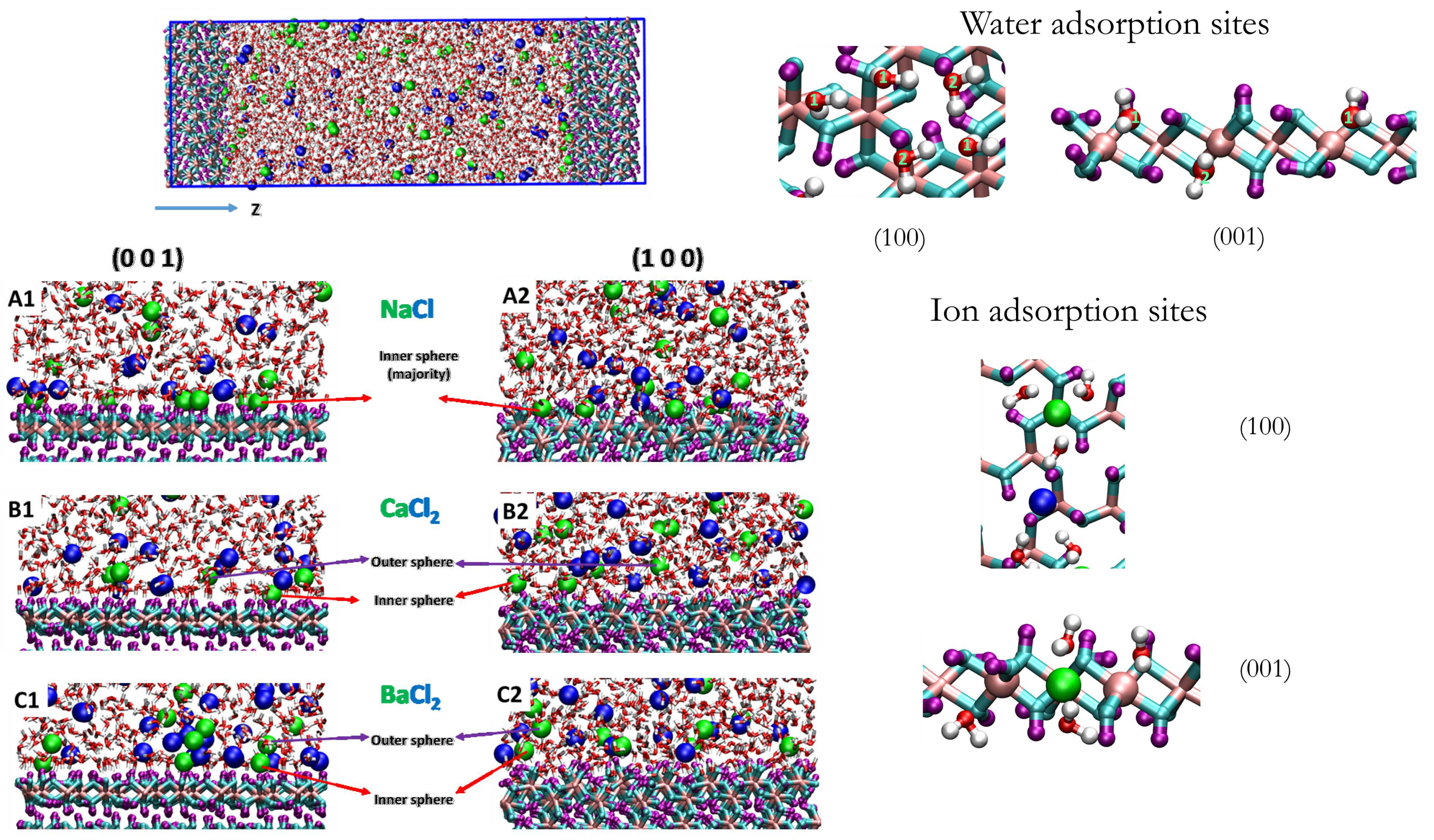


Adsorption at Nanoparticle Corners

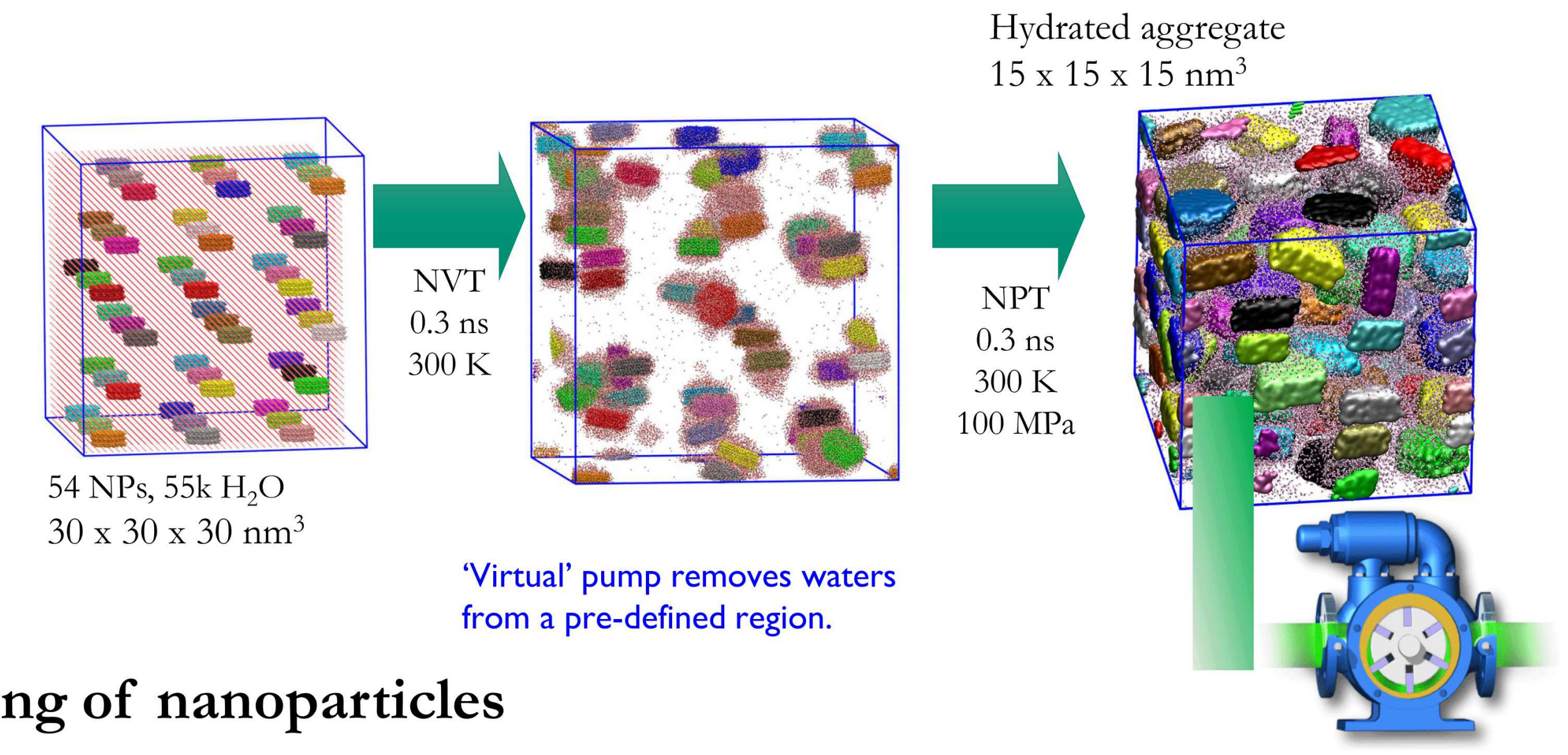


- Cl$^-$ adsorption is not enhanced on NP
- Na$^+$, Ca^{2+}, and Ba^{2+} adsorption are enhanced on NP
- NPs exhibit higher concentrations of IS complexes

Adsorption on Gibbsite basal (001) and edge (100) surfaces

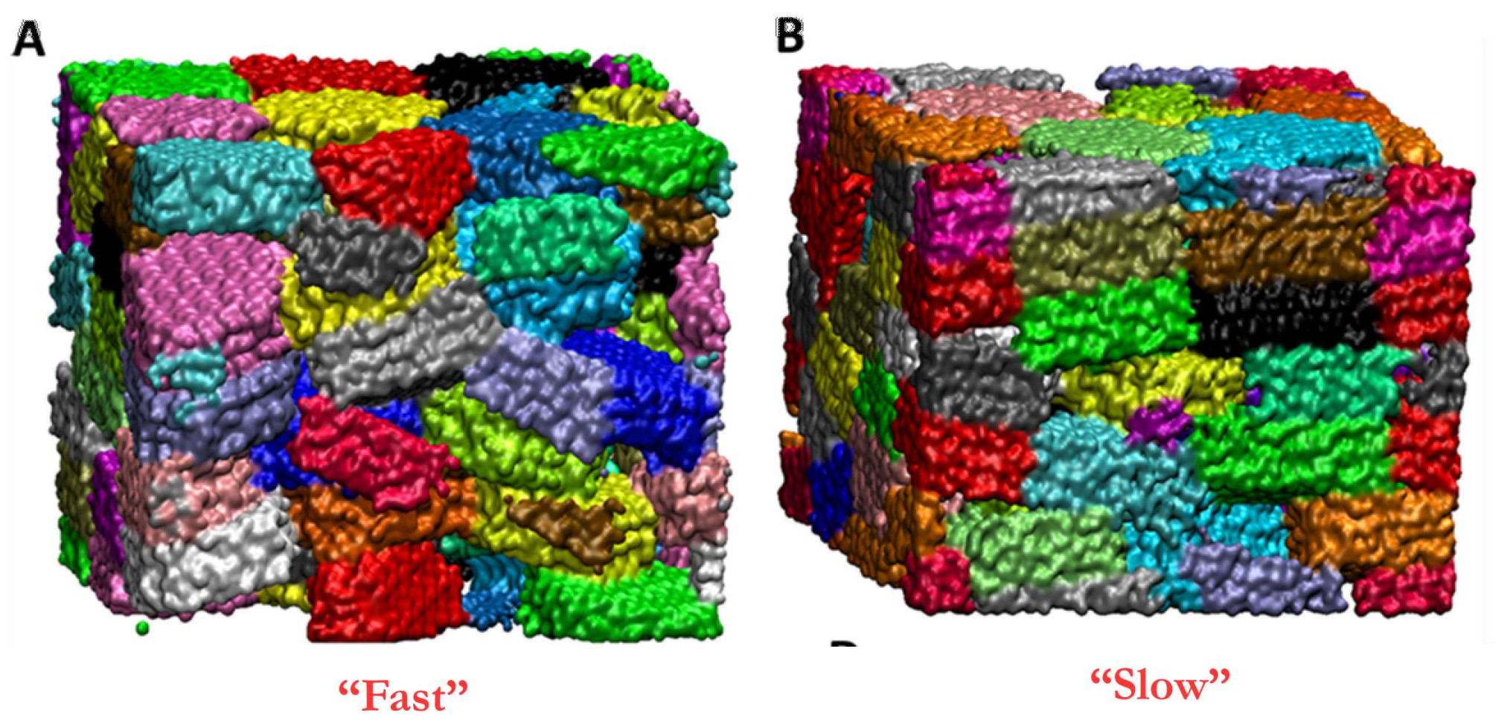


Particle Aggregation Model: Gibbsite



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

Stacking of nanoparticles



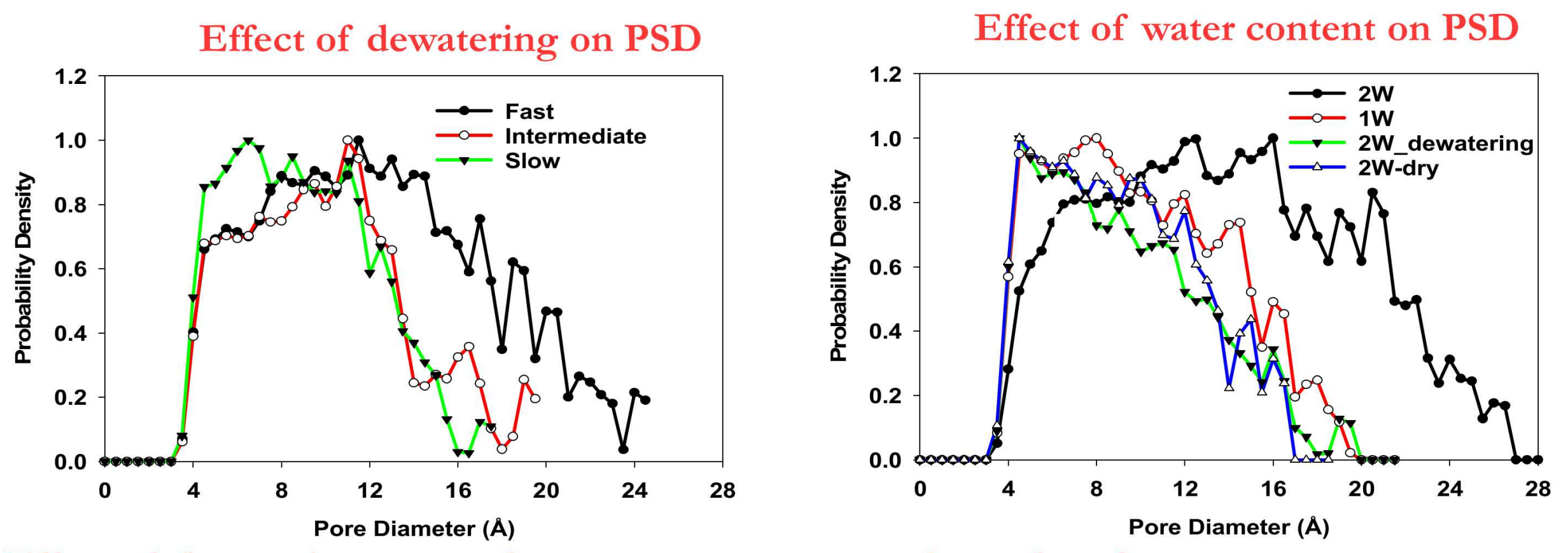
Effect of dewatering rate:

- Delete all water: "Fast"
- Delete 100 H2O/100 steps: "Intermediate"
- Delete 10 H2O/100 steps: "Slow"

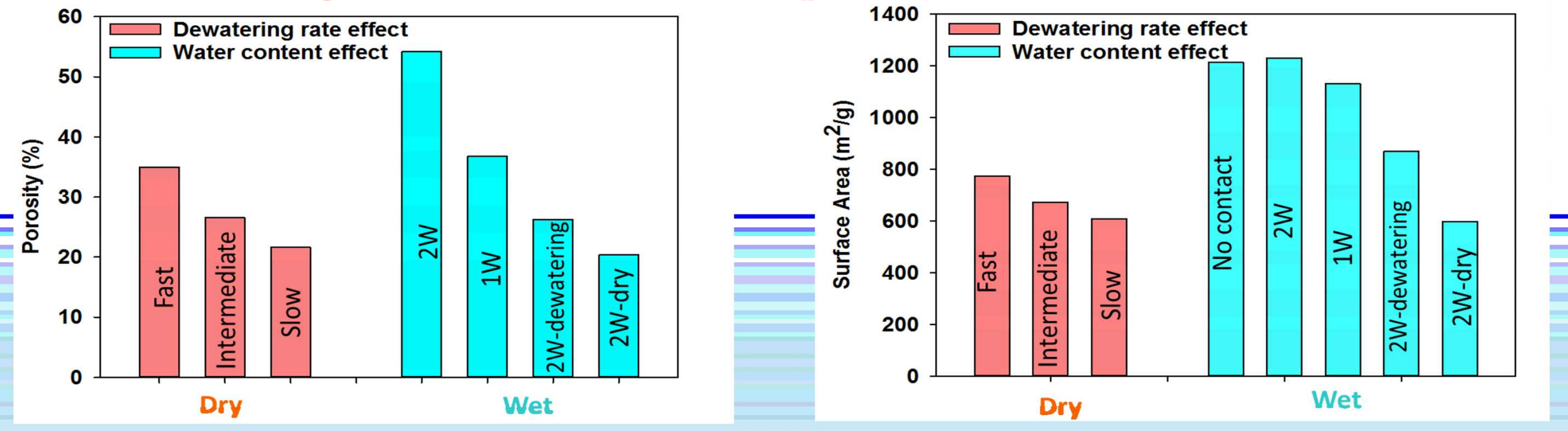
Effect of water content:

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

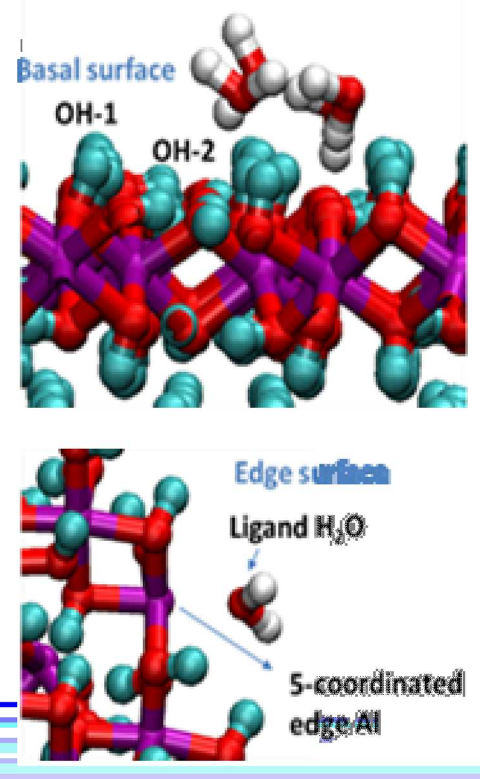
Pore Size Distribution and Porosity



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



Water structure



Conclusions

- The percent cation adsorption as inner-sphere complexes depends on the gibbsite surface.
- For all cations, surface coverages are higher on the basal surface than the edge surface.
- For the nanoparticles, cation surface coverages are enhanced, due to the significant number of inner-sphere cations found at nanoparticle corners.
- For the nanoparticle aggregates, slow dewatering creates more compact aggregates that fast dewatering.
- For the aggregates, the amount of water present strongly affects the particle-particle interactions and the aggregate structure

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