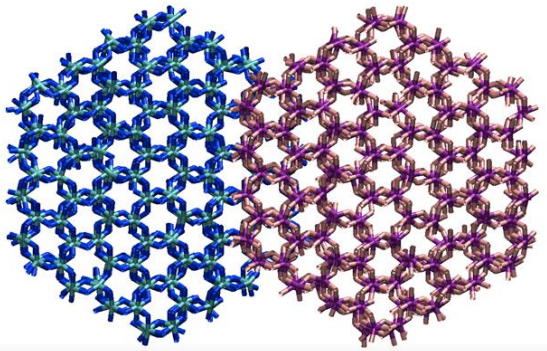
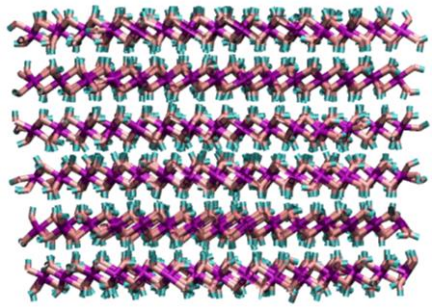
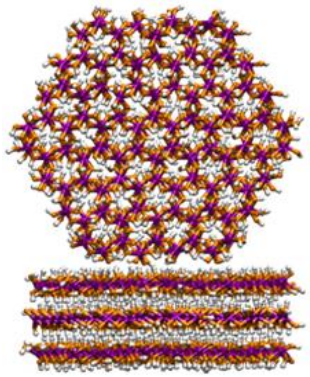
SAND2022-13555C

Sandia National Laboratories

Discoveries regarding gibbsite nanoparticle behavior using molecular simulation







Louise Criscenti, Tuan Ho, Tuan Vu; SNL

Kevin Rosso; PNNL

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U.S. DEPARTMENT OF ENERGY | NNSA National Nuclear Security Administration

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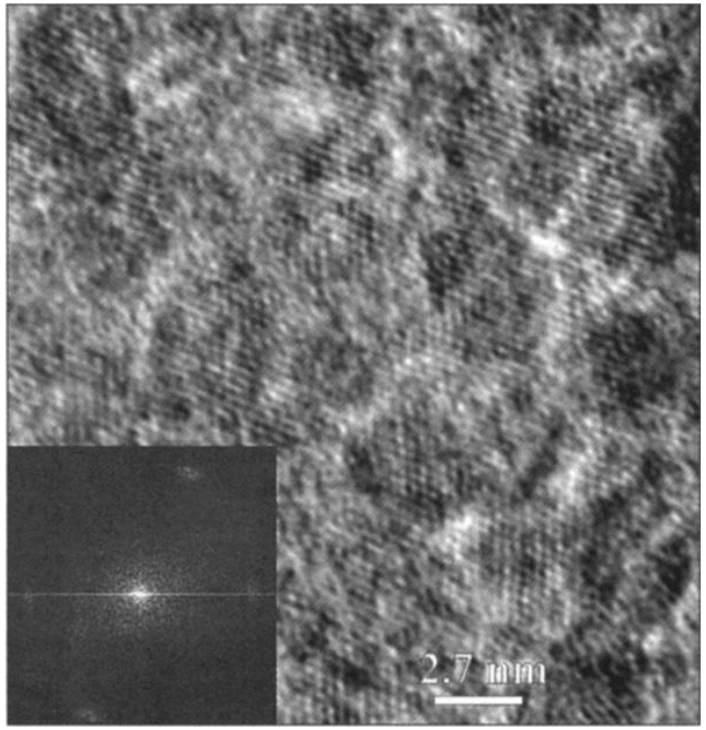
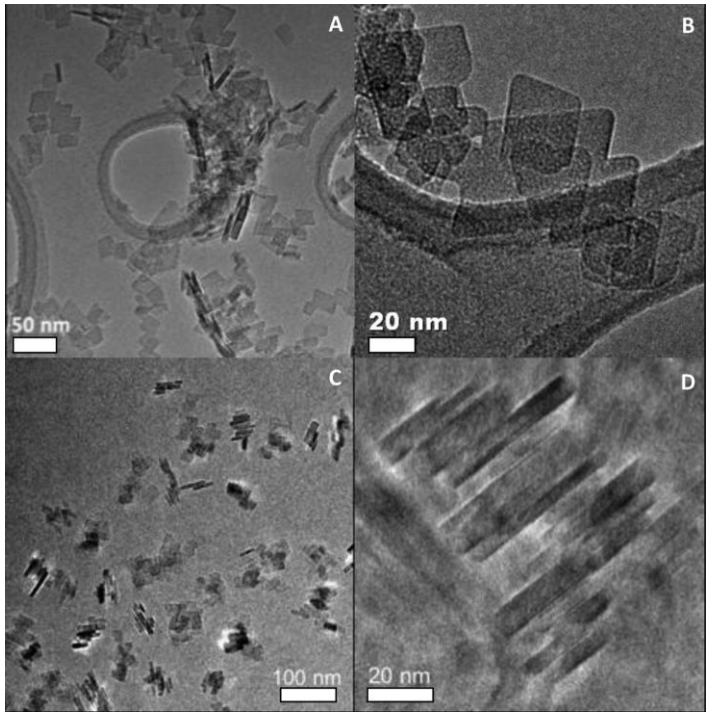
Particle aggregation and oriented attachment



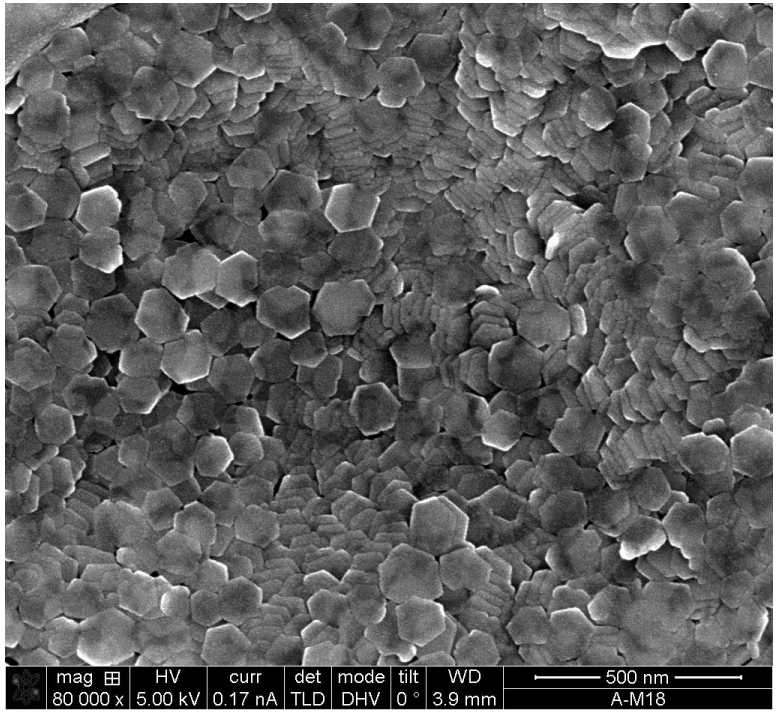
HRTEM image of aggregate of ferrihydrite nanocrystals; lattice fringe orientations demonstrate particles have assembled so they share a single crystallographic orientation.

Banfield J. F. et al. (2000). *Science* ***289, 751-754.***



TEM images of boehmite. TOP: Dry material after synthesis. BOTTOM: cryo-TEM images of boehmite in 10 mg boehmite/10 mL fluid, showing oriented attachment of boehmite nanoplatelets by stacking along the basal plane.

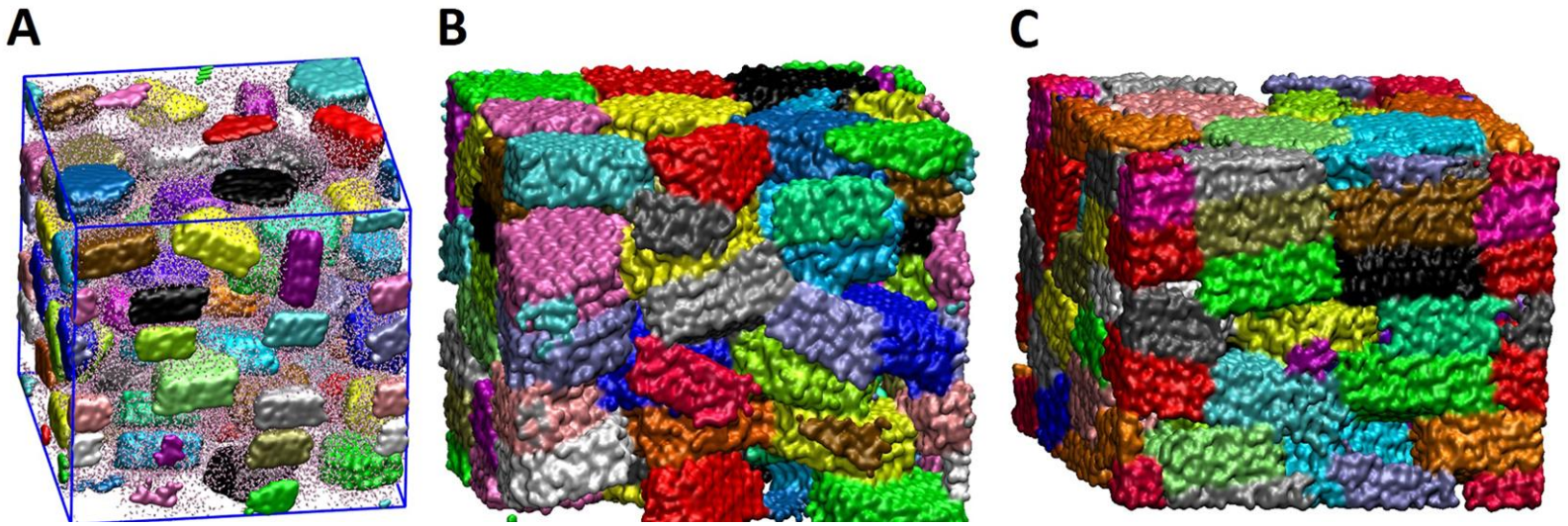
Anovitz L. M. et al.(2018) *Langmuir* ***34, 15839-15853.***



Gibbsite nanoparticle 90 day sedimentation on TEM grid; NaCl 50 mM.

From PNNL: Courtesy of X. Shen

Motivations



Initial Simulation Cell Fast water removal Slow water removal

Ho T. A. et al. (2017) *Scientific Reports* ***7.***

1. Dewatering and Compaction

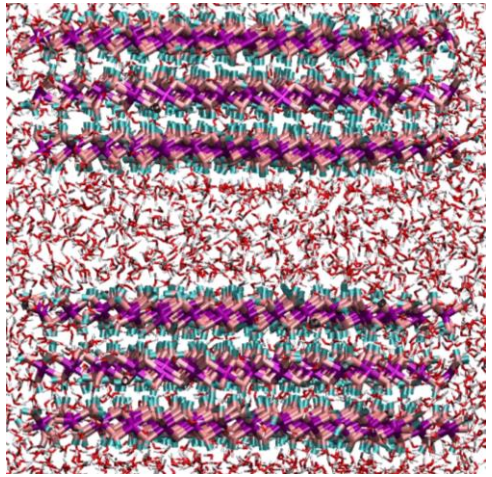
- Mineral colloids including gibbsite, aggregate, settle, and compact on the floor of the Hanford waste tanks.
- Aggregation affects rheology of the waste
- Dewatering of interparticle regions during sedimentation affects porosity, the more rapidly the platelets are deposited, the less time to remove water.

2. Oriented Attachment

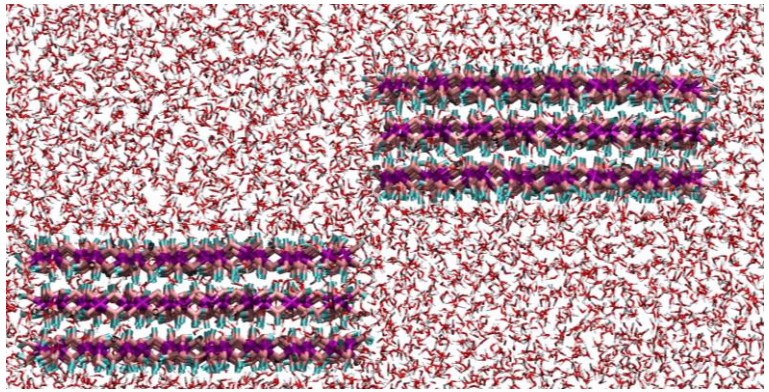
- Oriented attachment is a special case of particle aggregation and crystal growth.
- Crystalline particles assemble into a larger particle/crystal by attaching on specific crystal faces that are lattice-matched.

System 1: Gibbsite particle-particle attachment

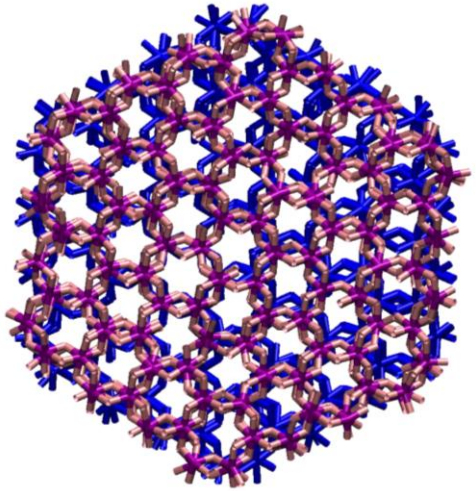
Approaching



Sliding



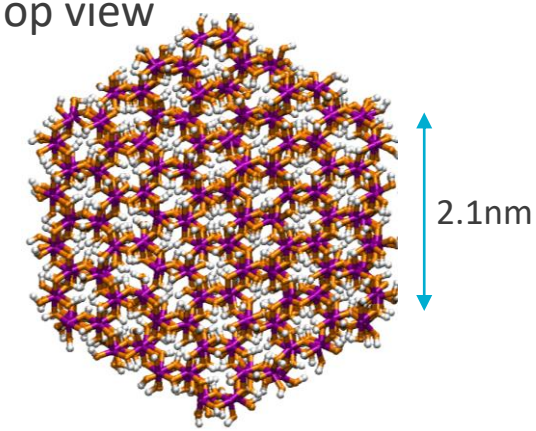
Rotating



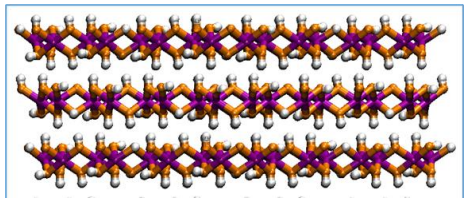
Gibbsite particle-particle attachment: Approaching motion

Model Gibbsite Particle

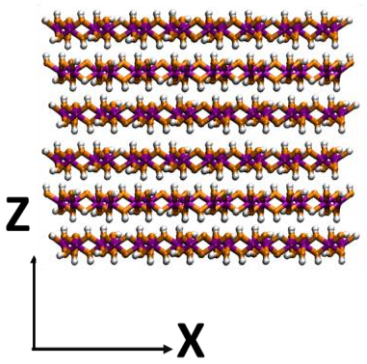
Top view

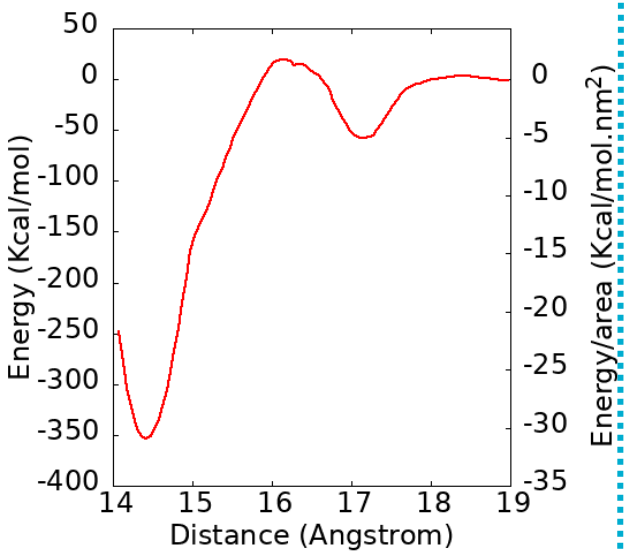


Side view

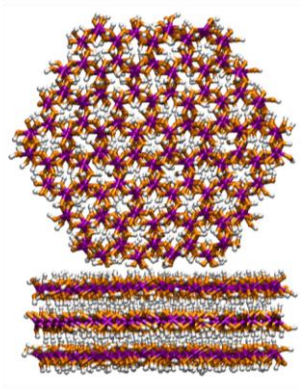


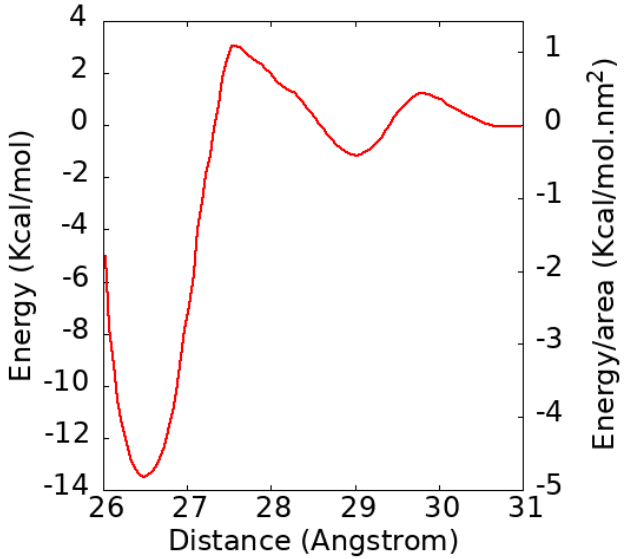
Basal-Basal



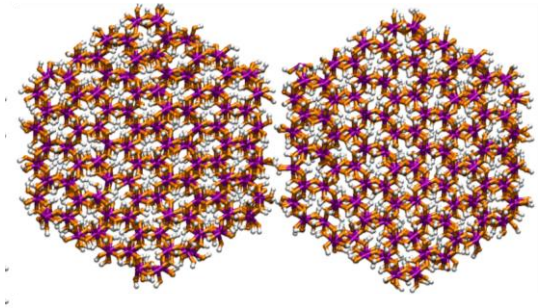


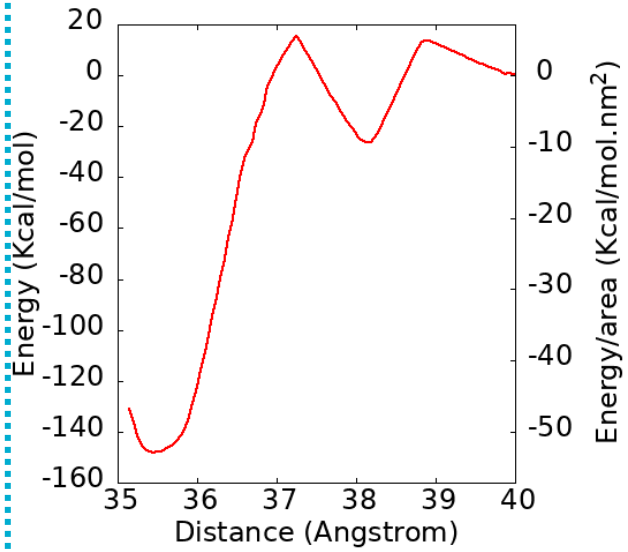
Basal-Edge





Edge-Edge



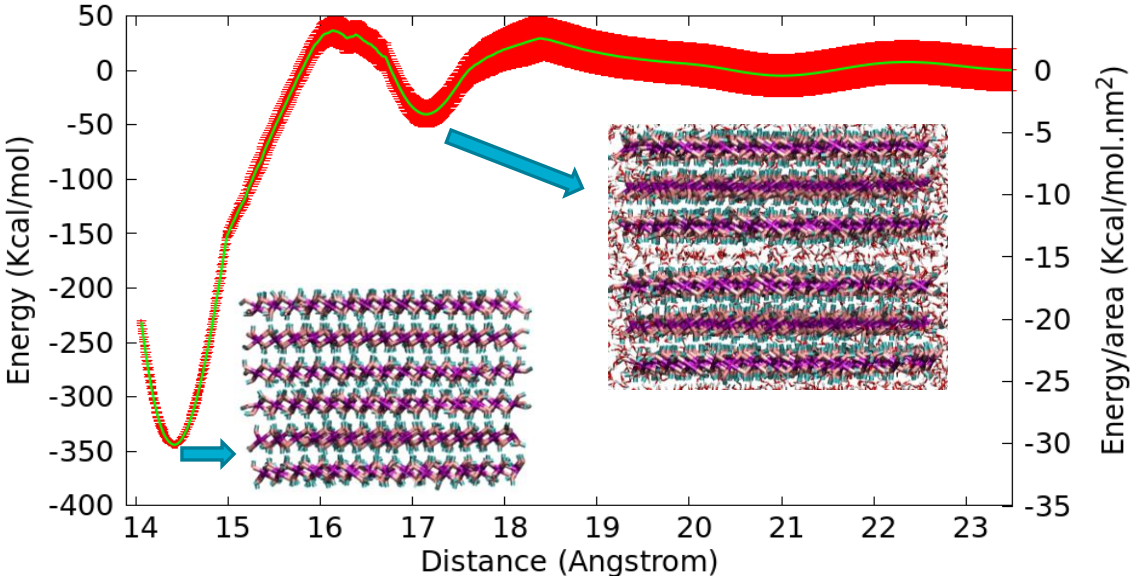


Per surface area: edge-edge attachment is more favorable
Large particle: basal-basal attachment is more favorable

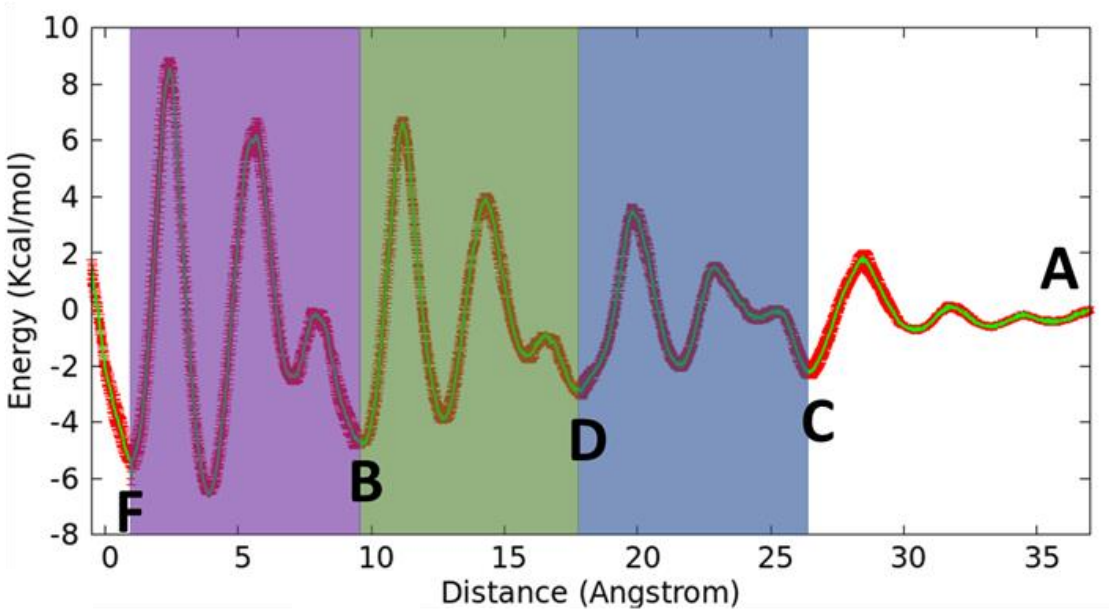
Ho and Criscenti, Journal of Colloid and Interface Science 600, 310-317

Energy barriers

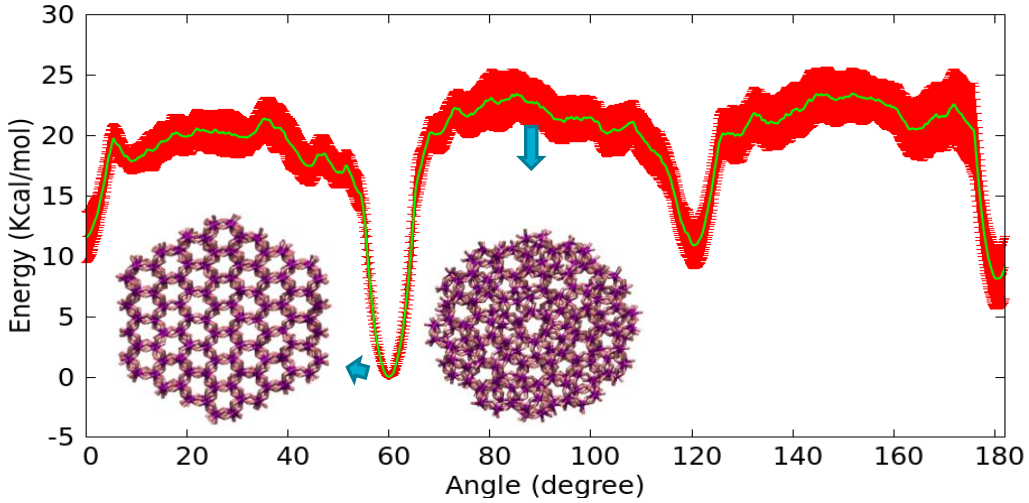
Approaching motion



Sliding motion



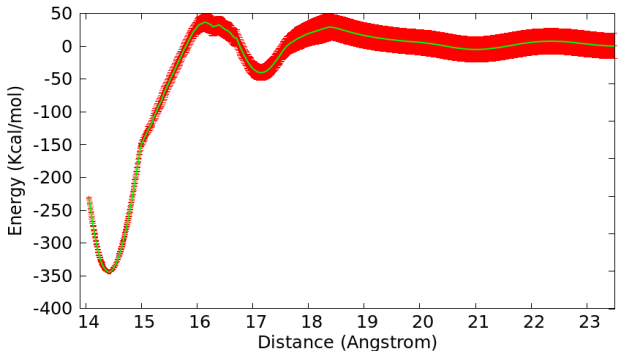
Rotating motion



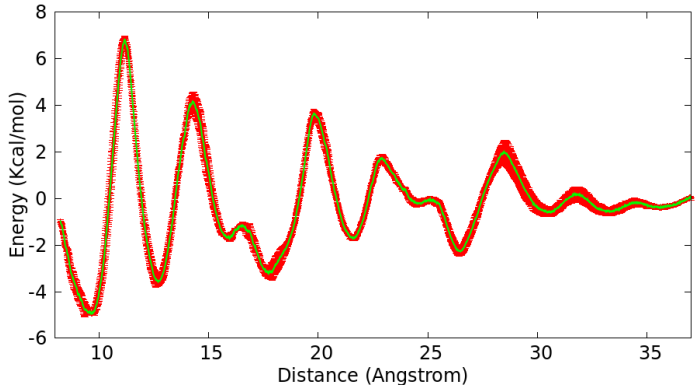
- Approaching motion encounters the highest energy barrier

Roles of water

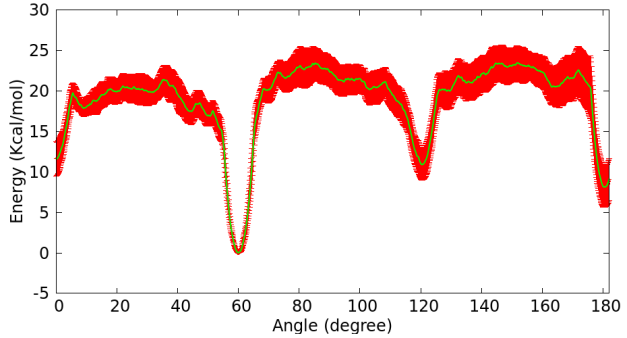
Interaction in water



Approaching motion

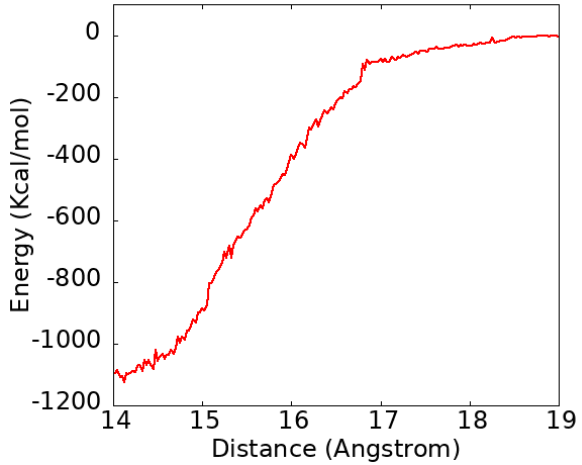


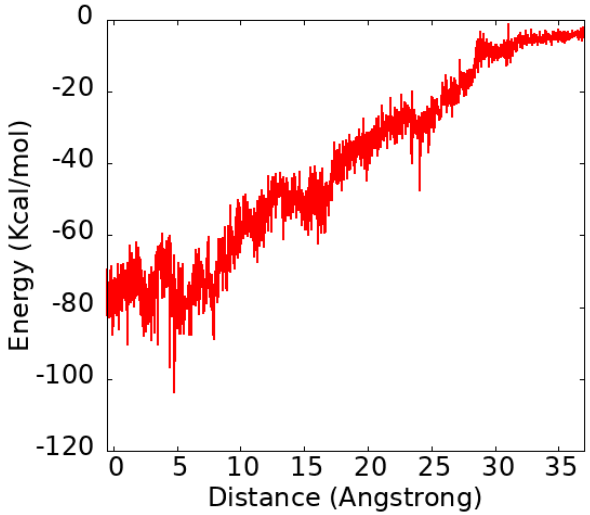
Sliding motion

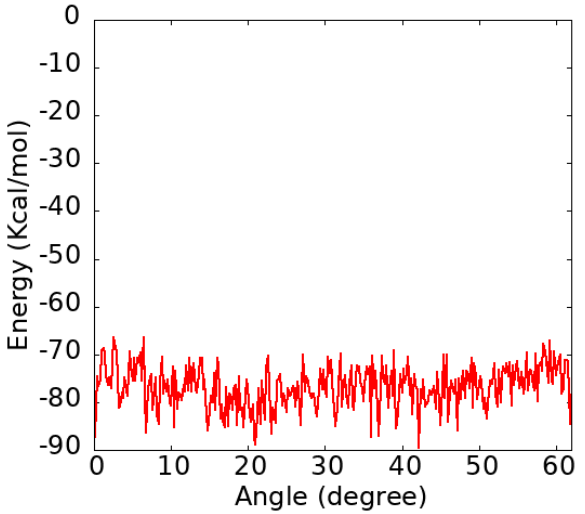


Rotating motion

Interaction in vacuum



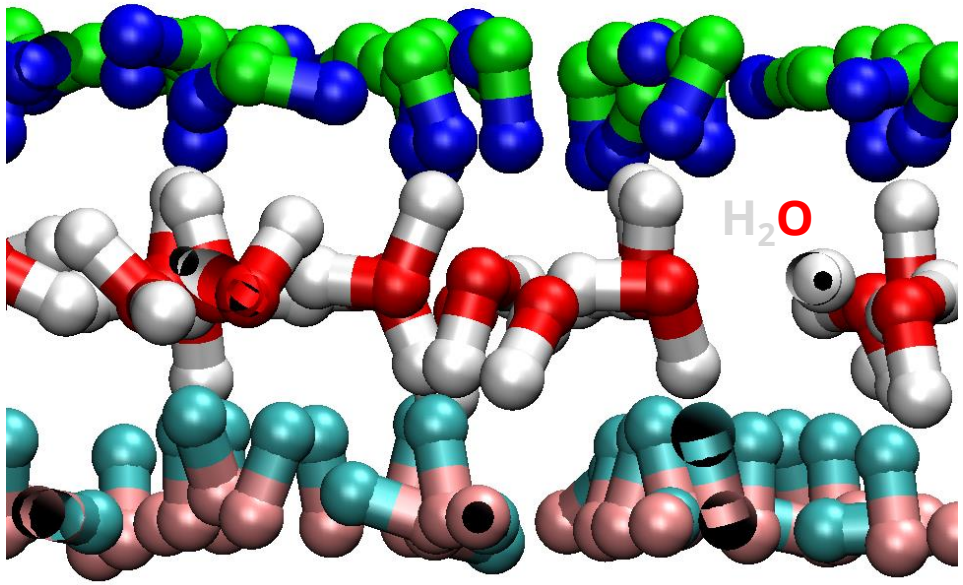




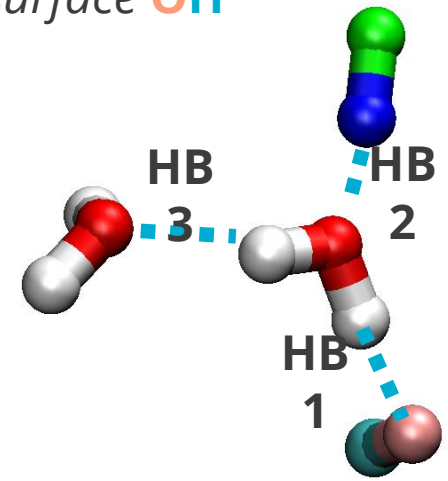
- Water controls the fluctuations in the PMF profiles for all three motions studied
- Water reduces the interaction between two particles
- However, particles still “feel” each other in water.

Water structure and H-bond Network

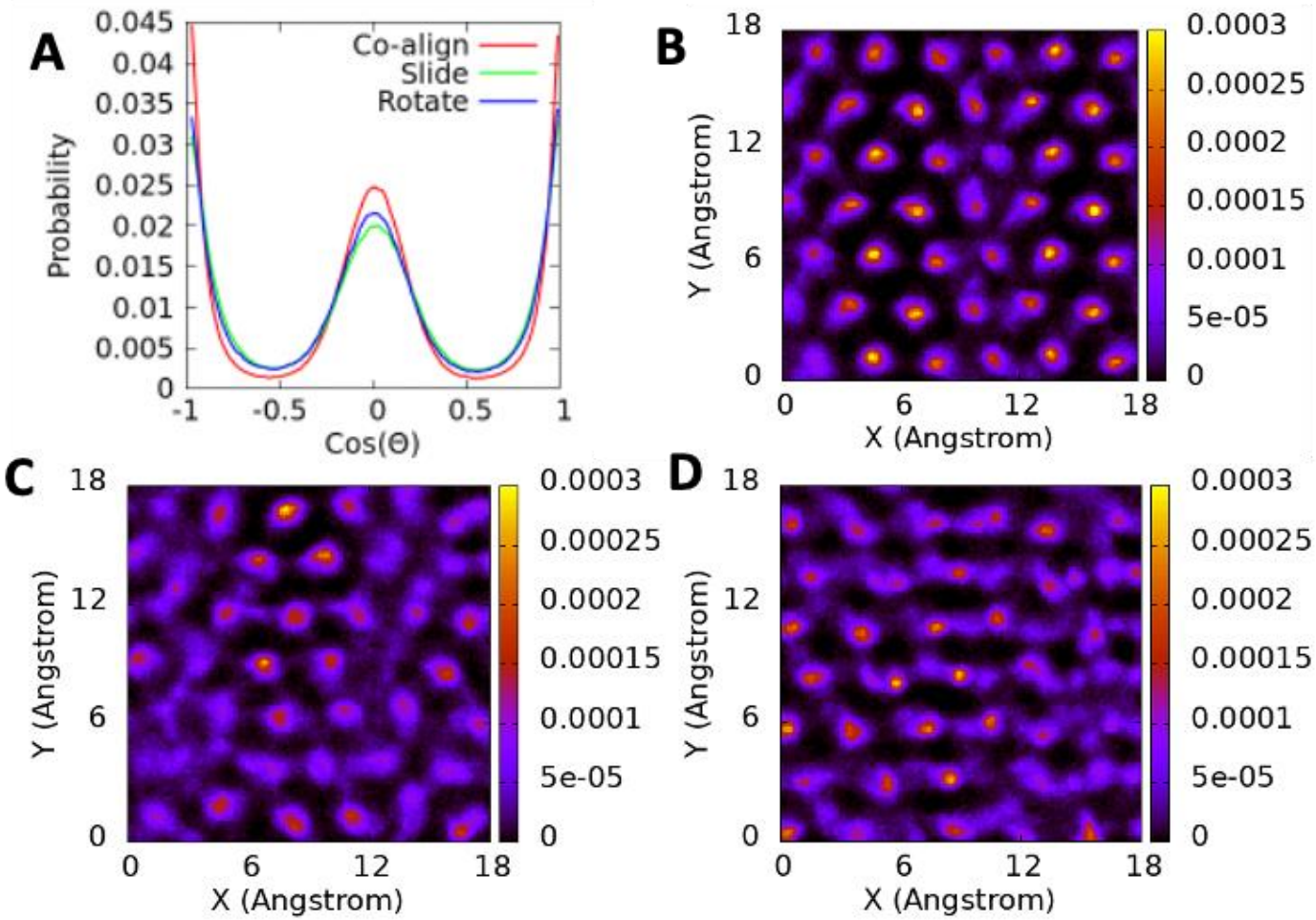
surface **OH**



surface **OH**



Perfect alignment



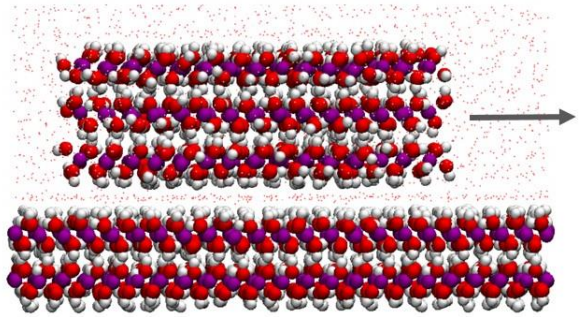
Misalignment (rotating)

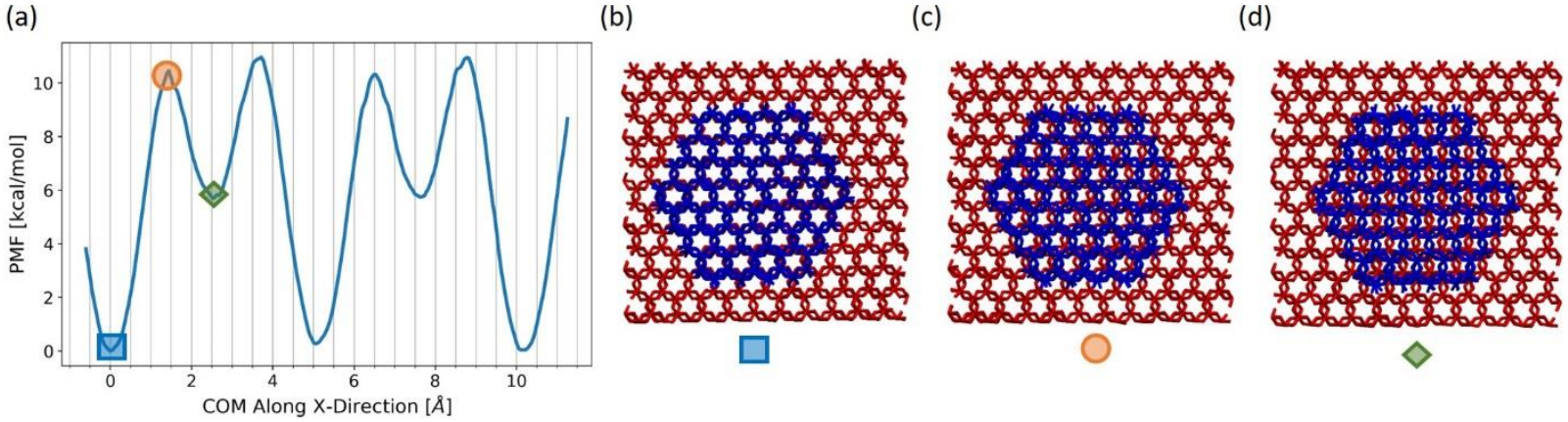
Misalignment (sliding)

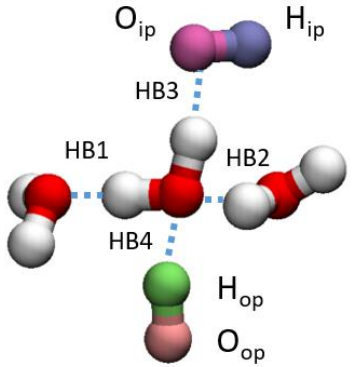
Perfect Alignment: # HB 3 =1.86
Misalignment: # HB 3 = 1.75

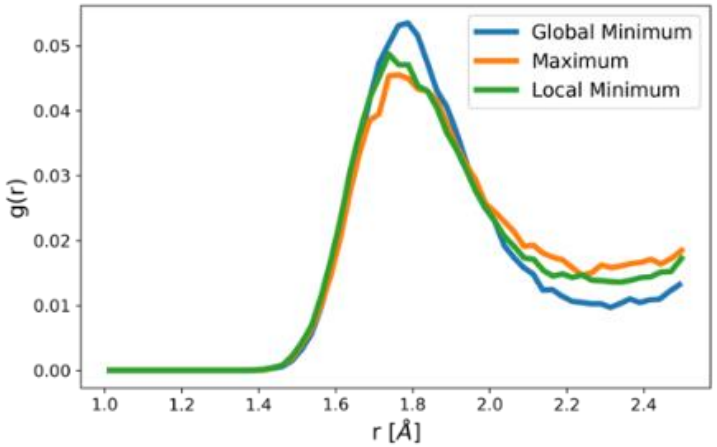
System 2: Gibbsite slab-gibbsite particle alignment: 1W + translation

1W

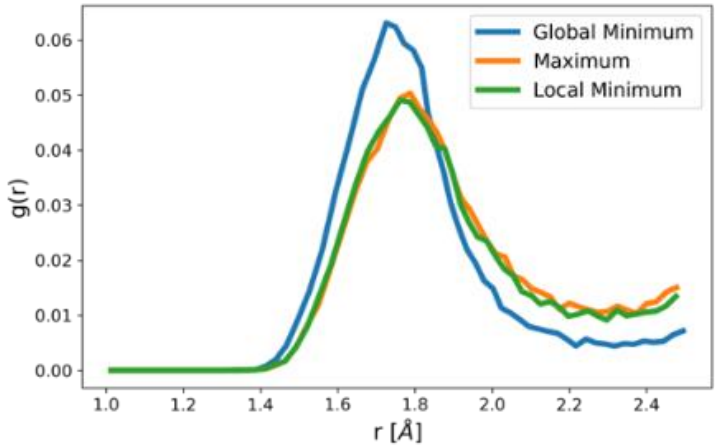






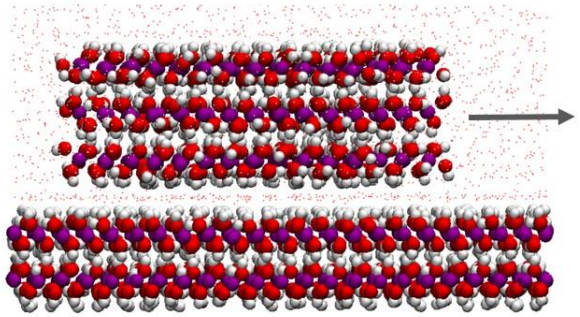


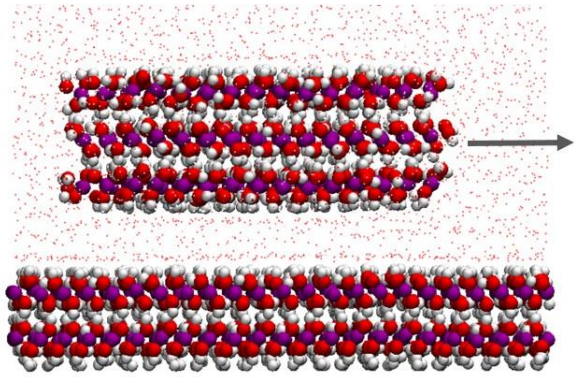
HB3

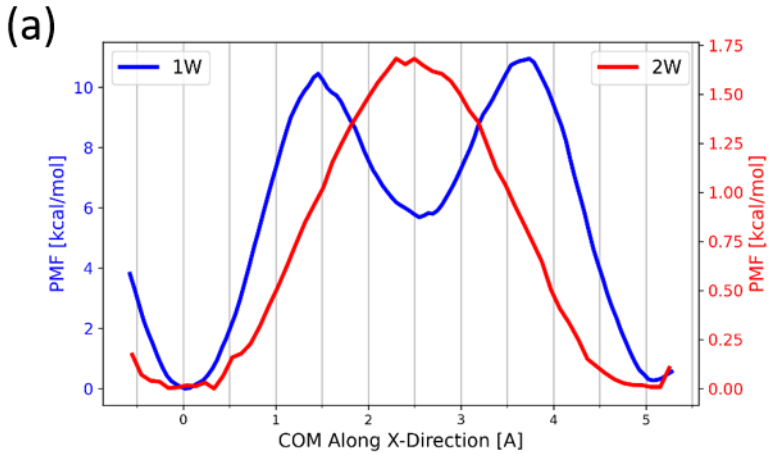


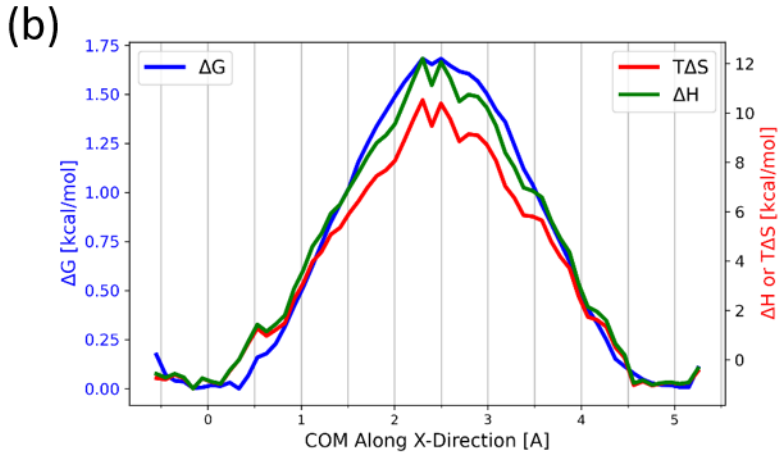
HB4

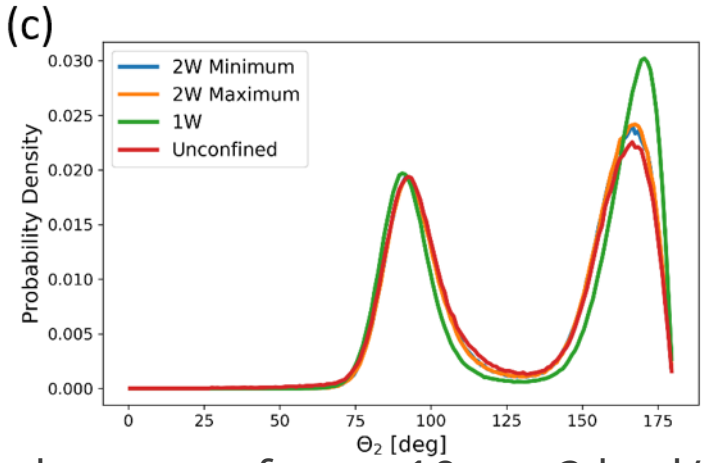
Gibbsite slab-particle alignment: 1W compared to 2W

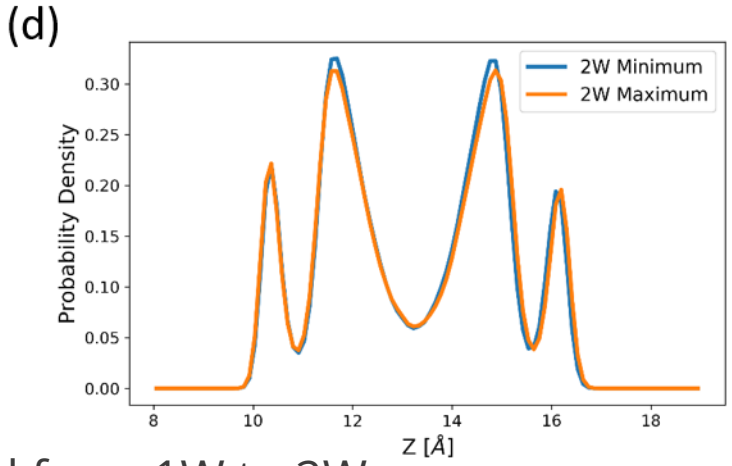












Magnitude of energy barrier decreases from >10 to <2 kcal/mol from 1W to 2W

Complete mismatch is most unfavorable at 2.5 A for 2W; H-bonding more important in 1W case. C shows o

Conclusion

- We have observed that in an aggregate of particles oriented attachment is a function of rate of water removal but is energetically preferred.
- We have studied the energy-structure relationships during two gibbsite particles in close proximity approaching, sliding, and rotating to achieve oriented attachment and found that the “jump to contact” that occurs once the particles are crystallographically aligned is the highest energy barrier to oriented attachment.
- The translation of the particle over a slab at 1W exhibits a more symmetric PMF that particle-particle PMF because the surface area of the interaction remains constant.
- The H-bonds that form between the gibbsite surfaces and interlayer water play a key role in the energetics of surface alignment.

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