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Sandia National Laboratories

Molecular Origin of Gibbsite Particle Aggregation in Water

Louise J. Criscenti and Tuan Ho

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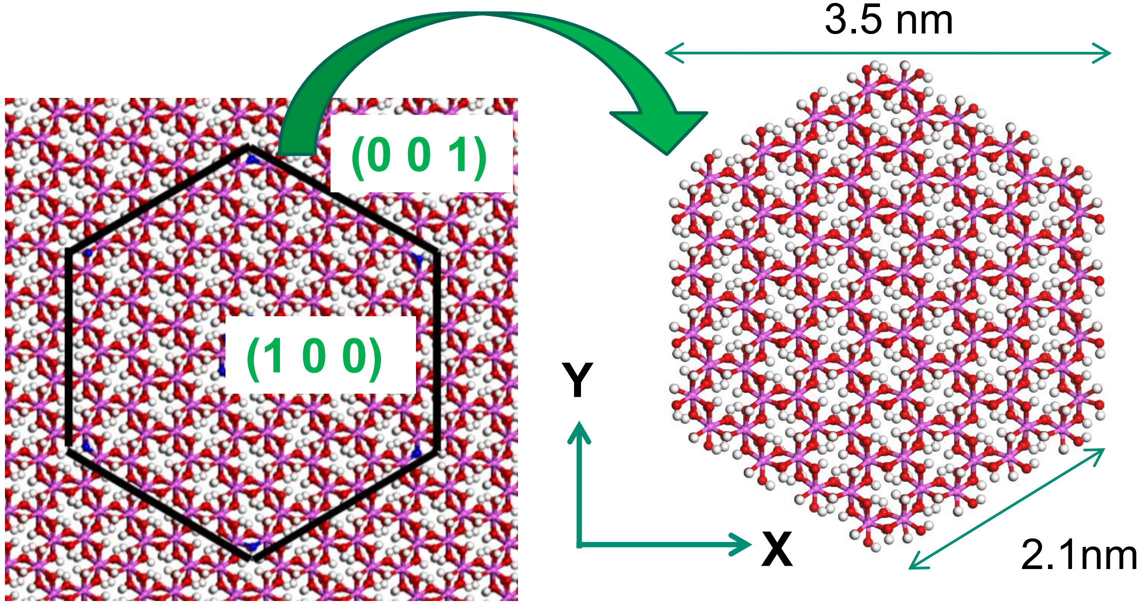
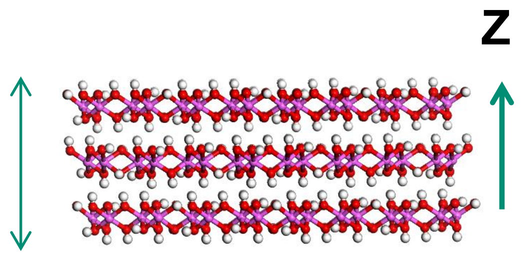
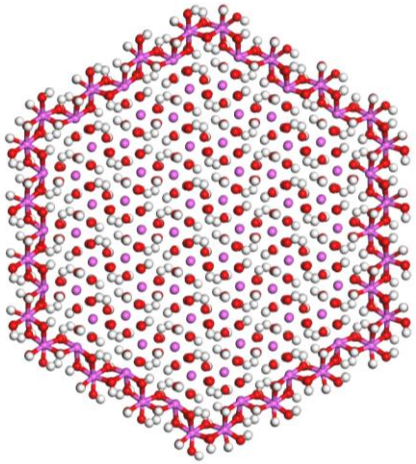
Gibbsite nanoparticle construction





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

Exploit the hexagonal symmetry of bulk gibbsite

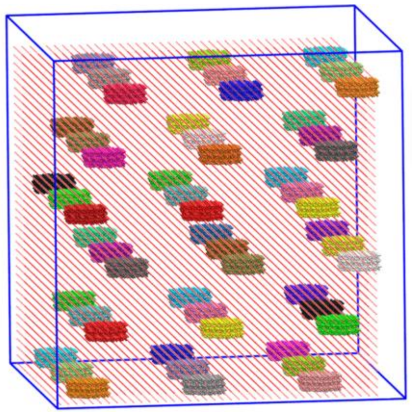


<u>Molecular dynamics</u>

- **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.**

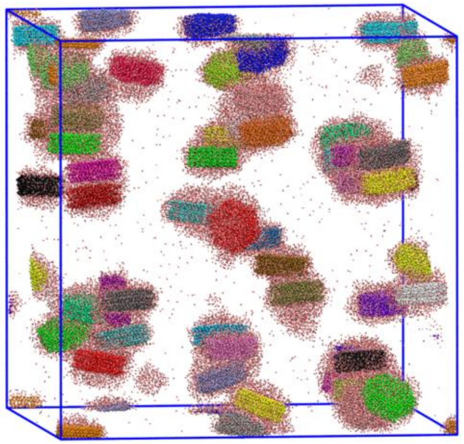
Ho, T.A. et al. (2017) Scientific Reports 7:15286

Gibbsite aggregation



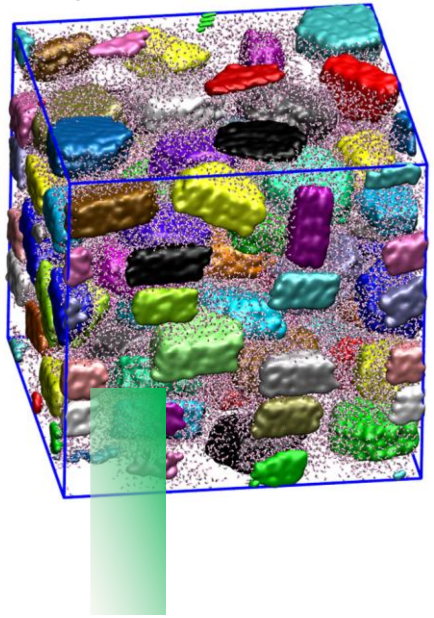
54 NPs, 55k H_2O
30 x 30 x 30 nm^3

NVT
0.3 ns
300 K



NPT
0.3 ns
300 K
100 MPa

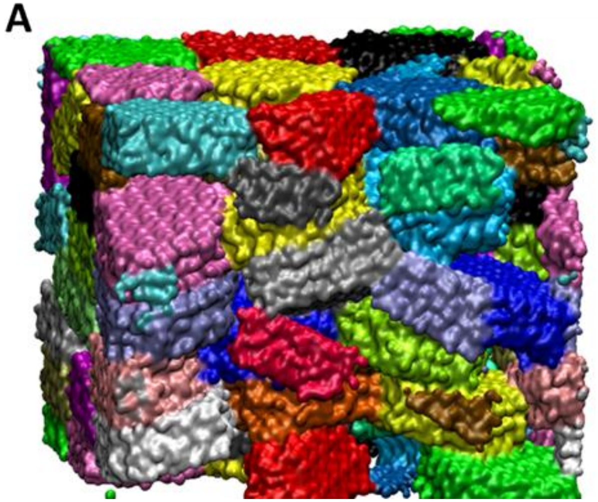
Hydrated aggregate
15 x 15 x 15 nm^3



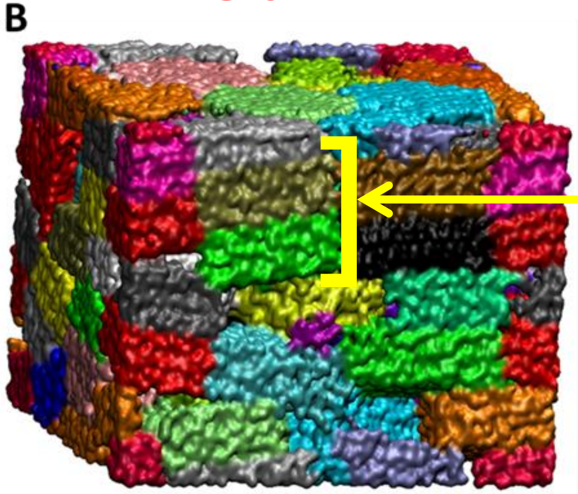
'Virtual' pump removes waters from a pre-defined region.

Dewatering Rate

"Fast"



"Slow"



Why do gibbsite particles prefer to stack basal-surface to basal-surface?

Ho, T.A. et al. (2017) Scientific Reports 7:15286

Objectives and Computational Methods

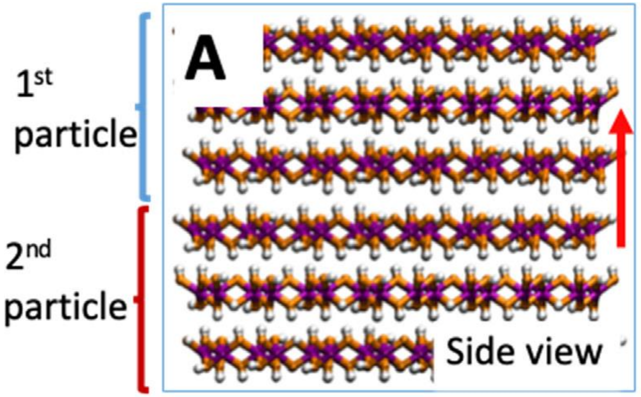
Objective: Evaluate the differences in energy associated with different particle-particle attachment orientations.

Methods:

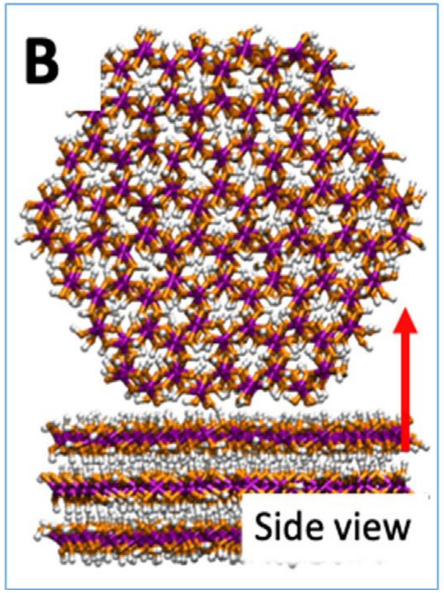
For the PMF calculations, the umbrella sampling method is applied with a separation between windows of 0.025A (3.0 ns per window, NPT) and a force constant of 5000Kcal/mol.A^2.

- Large force constant is needed to keep the two particles fluctuating around a specific reaction coordinate.
- Small window separation is required to obtain sufficient overlap among windows for the convergence of the PMF calculation.
- The COM of one particle is kept fixed by excluding 8 atoms from the integration of the equation of motion.
- The second particle is translated away from the first particle with a constant velocity 5 A/ns.
- The Weighted Histogram Analysis Method (WHAM) is applied to extract the PMF profile from the simulation trajectory.

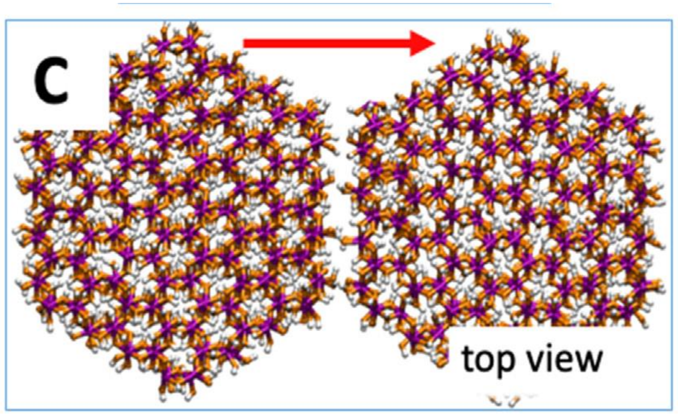
Free Energy Profiles for Particle-Particle Attachment in Different Orientations



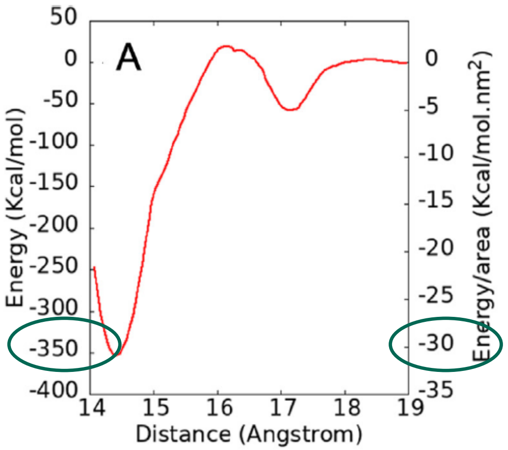
Basal-Basal

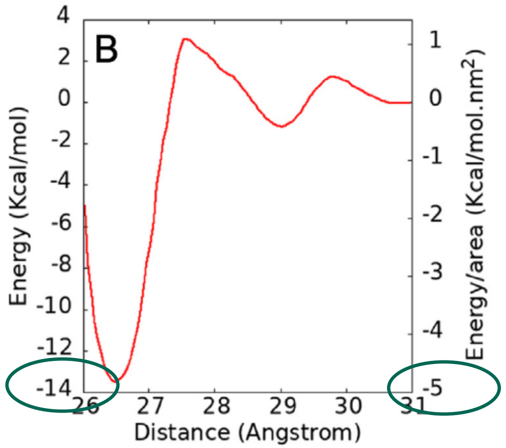


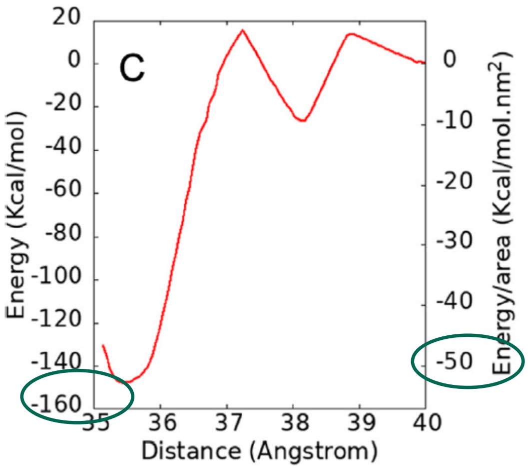
Basal-Edge



Edge-Edge

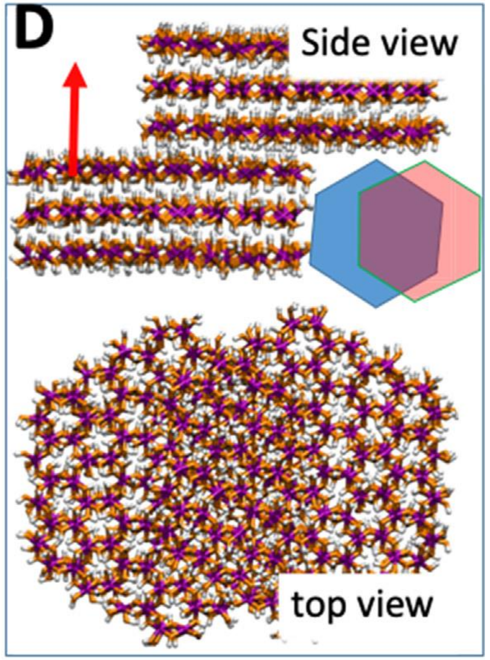


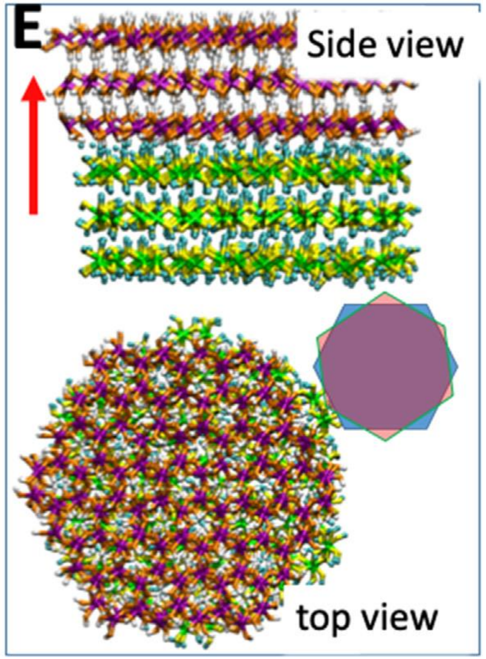


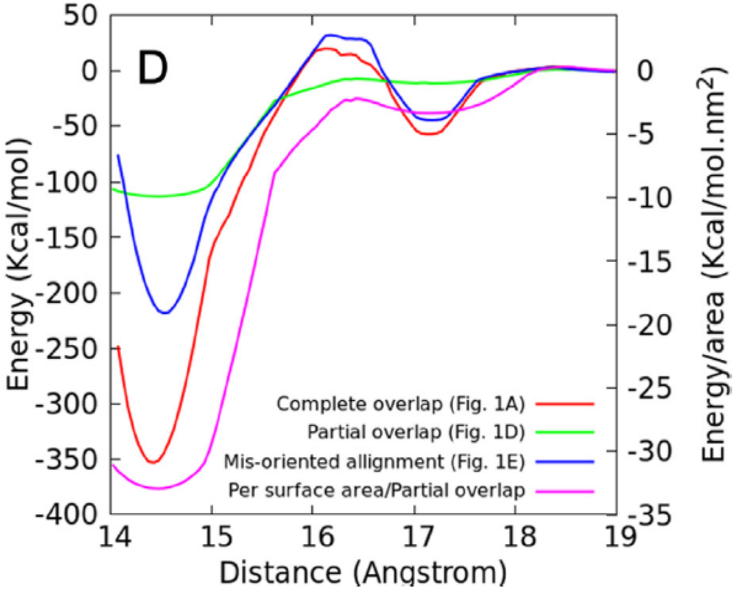


Ho and Criscenti, 2021, JCIS, 310-317.

Free Energy Profiles for Imperfect Attachment Between Basal Surfaces



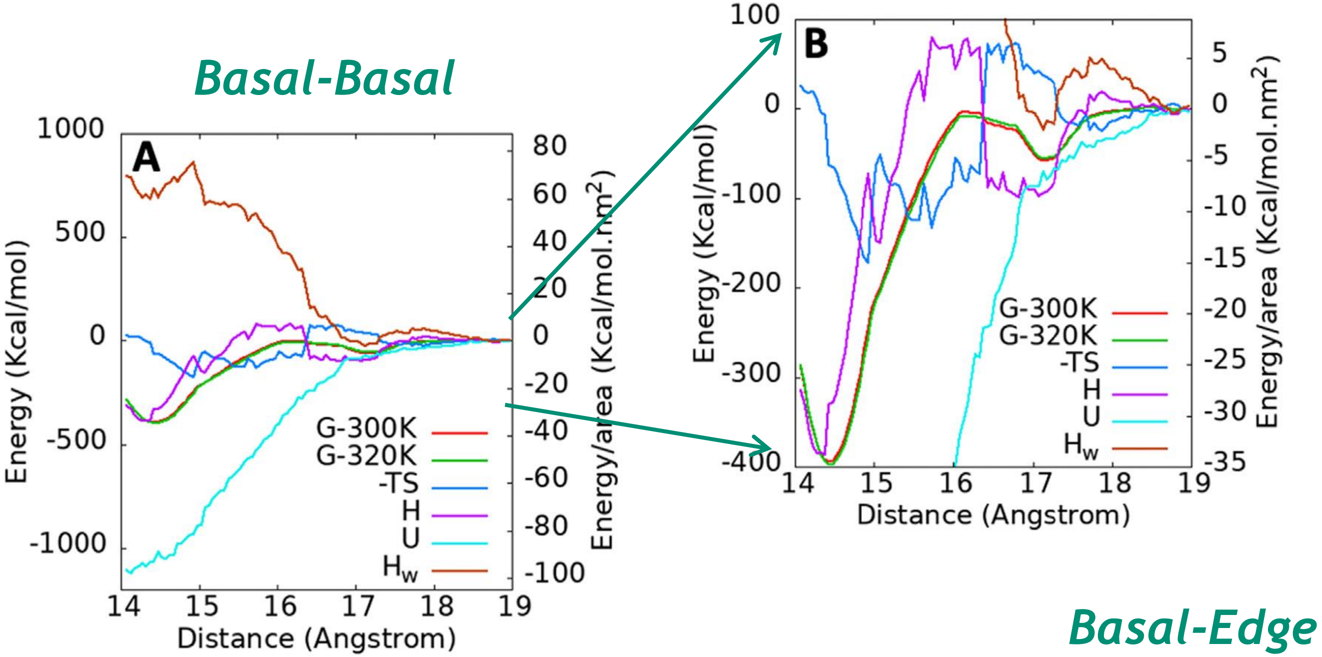




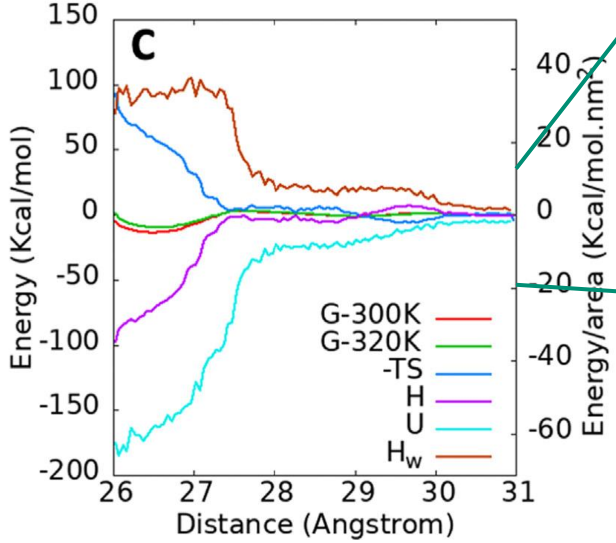
Left Axis
Red
Green
Blue
Right Axis
Red
Blue
Pink

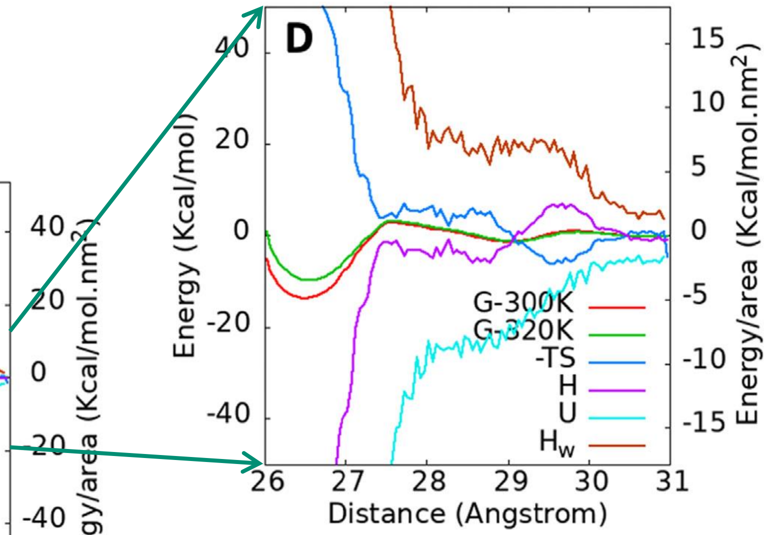
Enthalpic and Entropic Contributions to Particle Aggregation

Basal-Basal



Basal-Edge





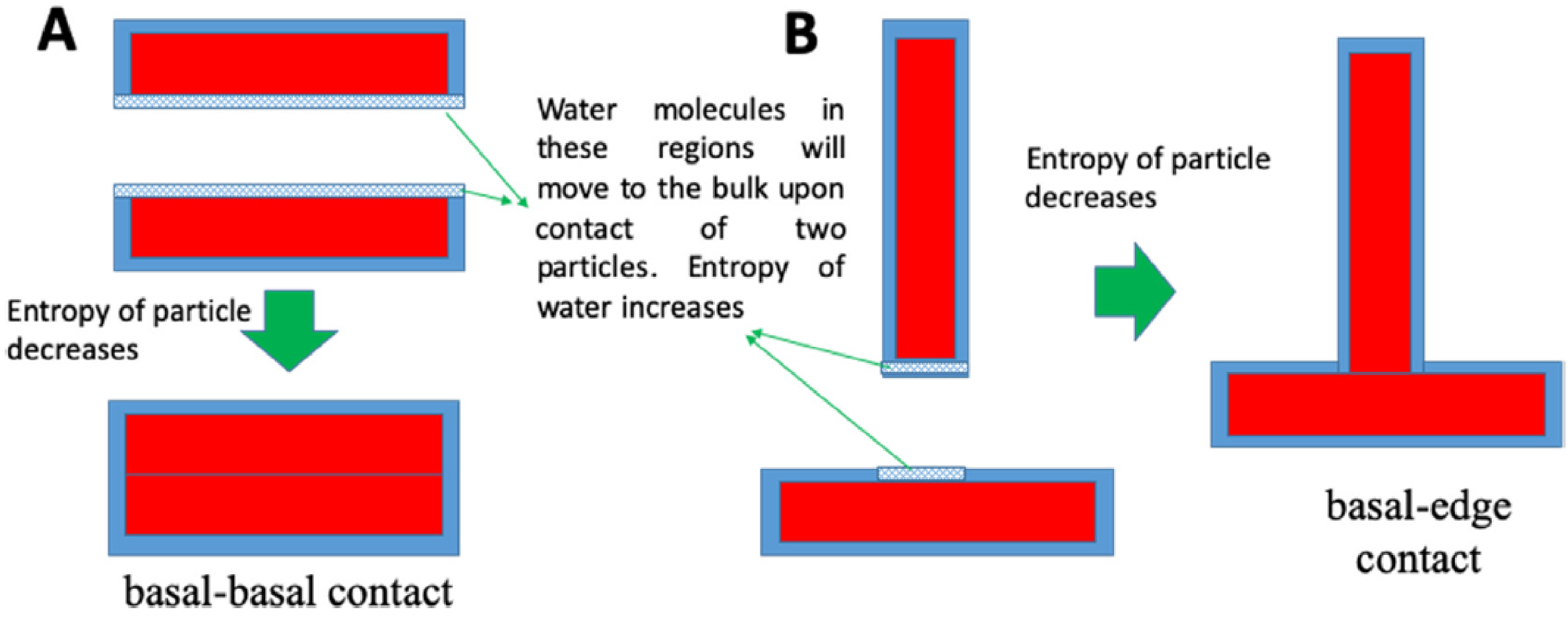
$-S(r) = G(r, T+\Delta T) - G(r, T)/\Delta T$

$H(r) = G(r) + TS(r)$

$Hw(r) = H(r) - U(r)$

r = interparticle separation
T = 300K, ΔT = 20K
Hw(r) = solvent contribution to enthalpy
U(r) = direct potential between particles

Conceptual Model Used to Explain Entropic Changes with Attachment



Summary and Next Steps

- MD Simulations show that the most stable attachments between gibbsite nanoparticles are those with no Interlayers of water.

- For the same contact surface area (SA), edge-edge attachment is the most favorable. However, the high (basal SA)/(edge SA) typical of gibbsite particles leads to a lower free energy for basal-basal attachment.

- Enthalpy is the driving force for gibbsite coalescence and is dominated by short-range electrostatic interactions including H-bonds.

- The enthalpy of the basal-edge attachment is offset by entropy leading to a higher free energy than for the basal-basal attachment.

- Future research includes
  (1) energetics of imperfect attachment and
  (2) effects of solution composition on gibbsite aggregation.

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