Iowa State University
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Ligand Structure and Free Energy of Nanoparticles on Substrates

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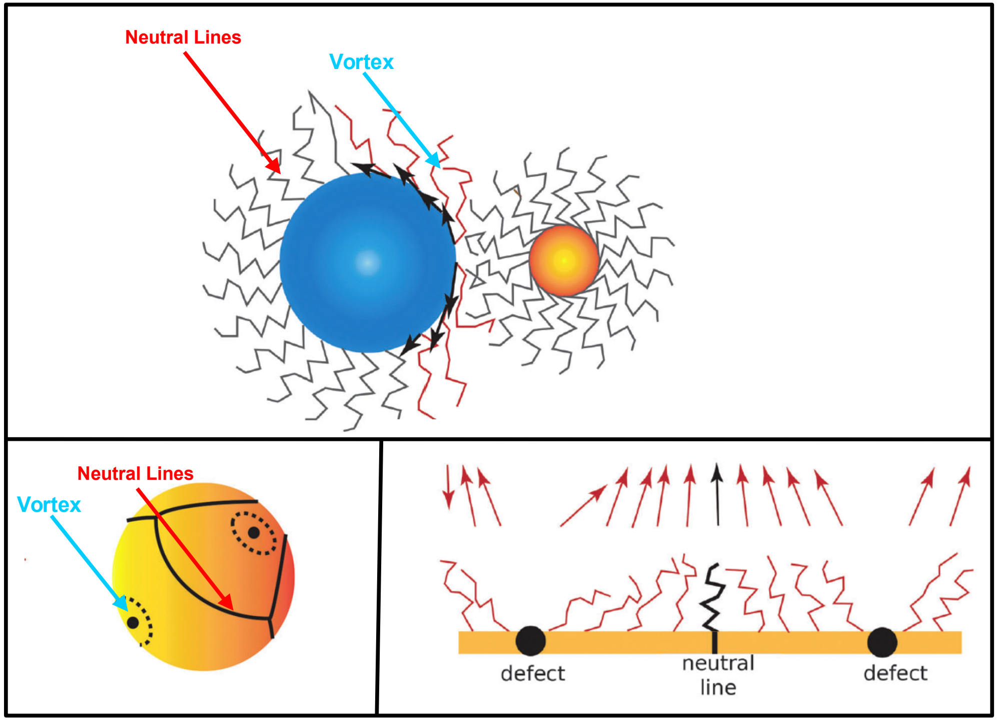
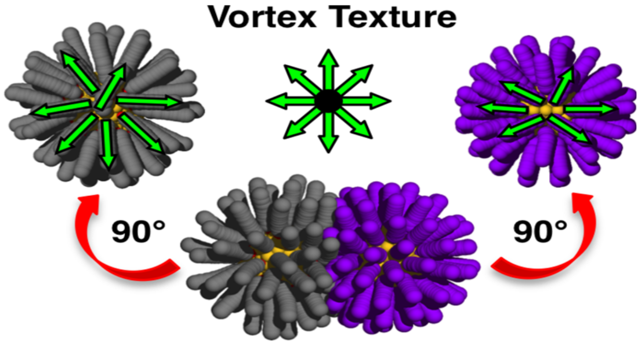
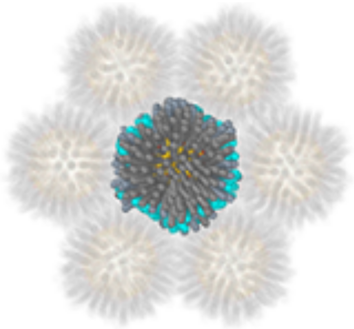
Motivation and Background: Ligand Vortices



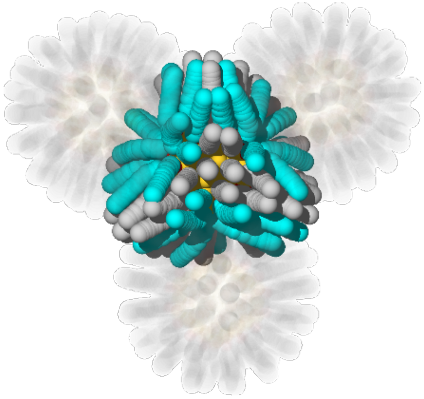
A. Travesset, Soft Matter (2017)



C. Waltmann, N. Horst, A. Travesset, ACS Nano (2017)



X. Zha, A. Travesset, JACS (2018)



T. Waltmann, C. Waltmann, N. Horst, A. Travesset, JACS (2018)

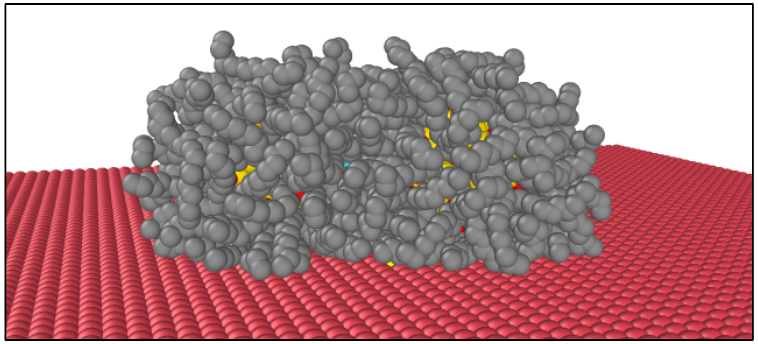
Analogy

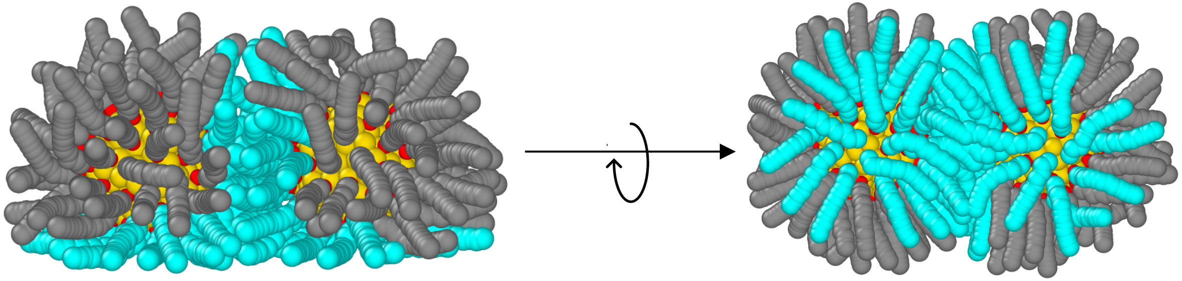
- **Atoms → Electron Orbitals**
- **Nanoparticles → "Ligand Orbitals"**

Many systems studied (pairs, tetrahedron, lattices,etc.), but all unsupported/free-standing

Motivation and Background: Solid Interfaces

- NP-Substrate interactions present in:
  - Transmission Electron Microscopy (TEM) Supports
  - Solvent Evaporation
  - Langmuir-Blodgett Films/Transfers



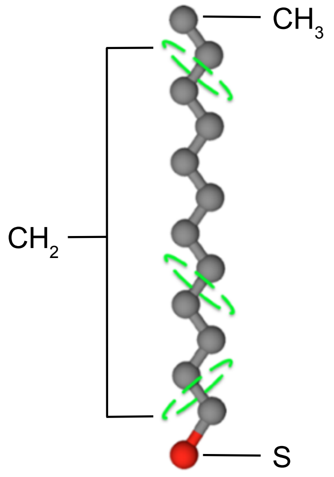


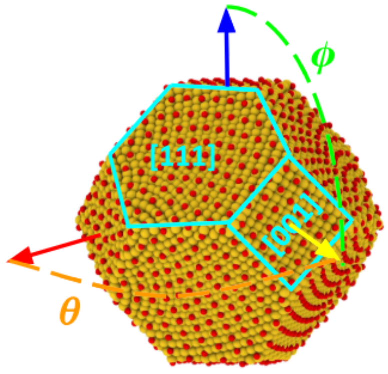
- NP-Substrate and NP-NP Interactions → Ligand Vortices
- NP-Substrate and NP-NP Vortex Coalescence

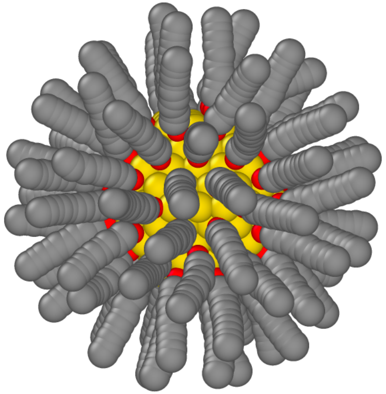
Simulation Model

- United Atom Model for CH_3 and CH_2
- Rigid Truncated Octahedron (TO) Gold Core
- Lennard-Jones Potential

$$V_{LJ} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \alpha\left(\frac{\sigma}{r}\right)^{6}\right]$$







Simulation Methods

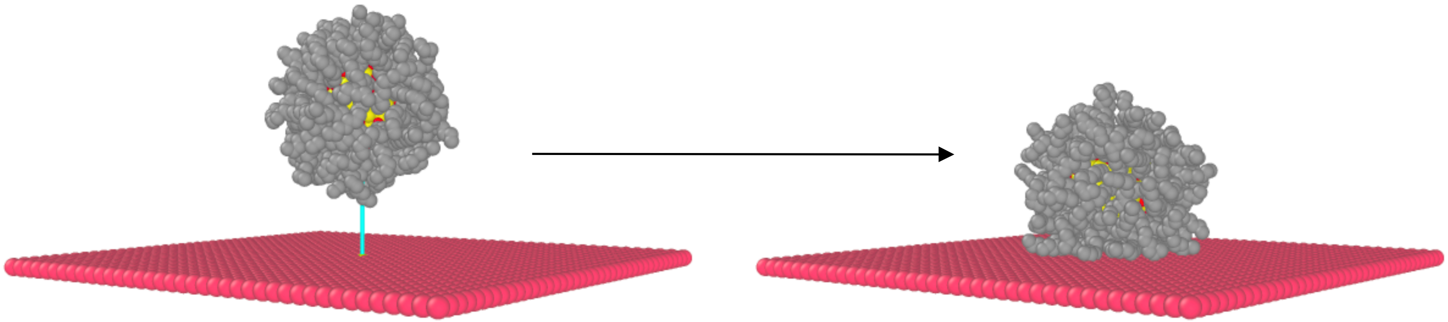
- Simulations setup and run using *HOODLT* and *HOOMD*
- NP orientation restricted to [001] or [111] face towards substrate
- Static gold substrate
- Umbrella Sampling and Weighted Histogram Analysis Method (WHAM)

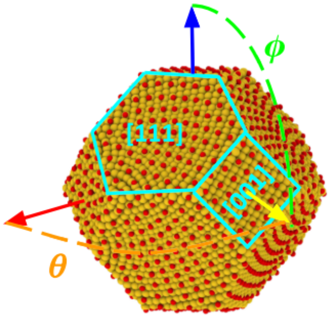
J. A. Anderson, C. D. Lorenz, A. Travesset, J of. Comput. Phys. (2008)

J. Glaser, T. D. Nguyen, J. A. Anderson, P. Lui, F. Spiga, J. A. Millan, D. C. Morse, S. C. Glotzer, Comput. Phys. Commun. (2015)

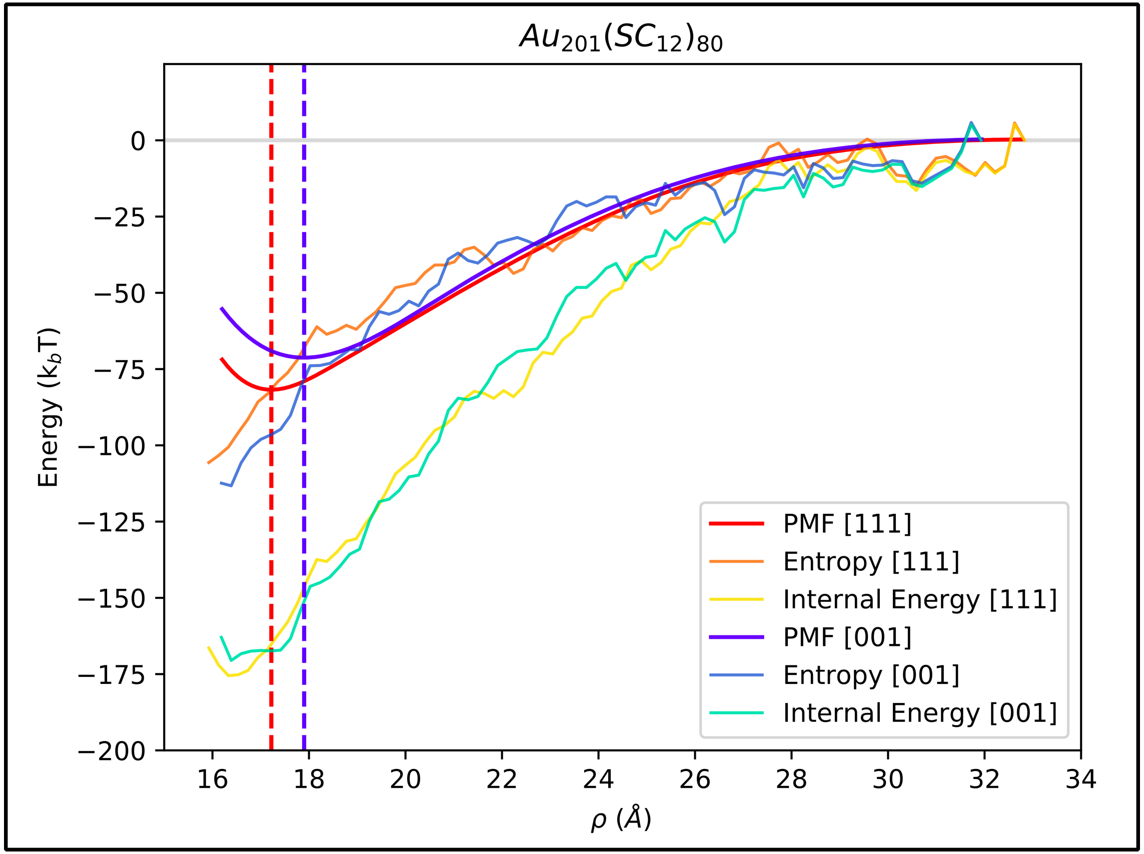
HOODLT

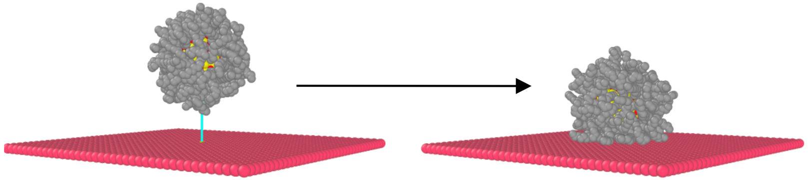
A. Travesset, J. of Phys. Chem (2014)

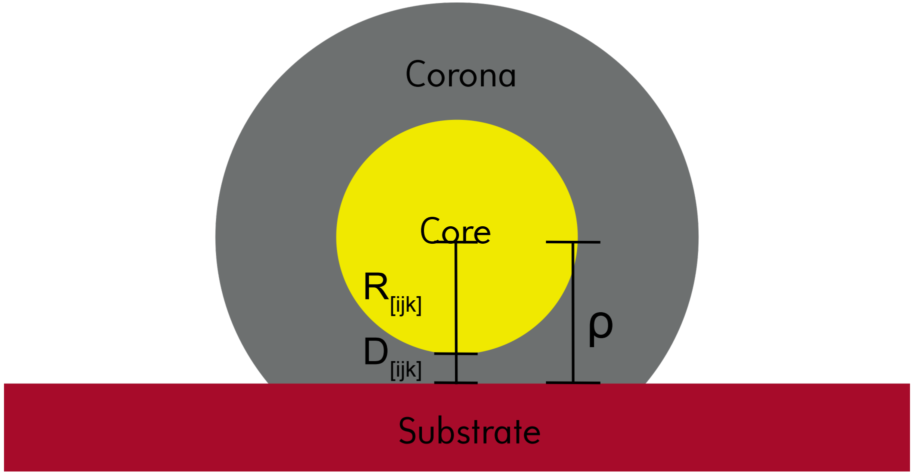




Potential of Mean Force





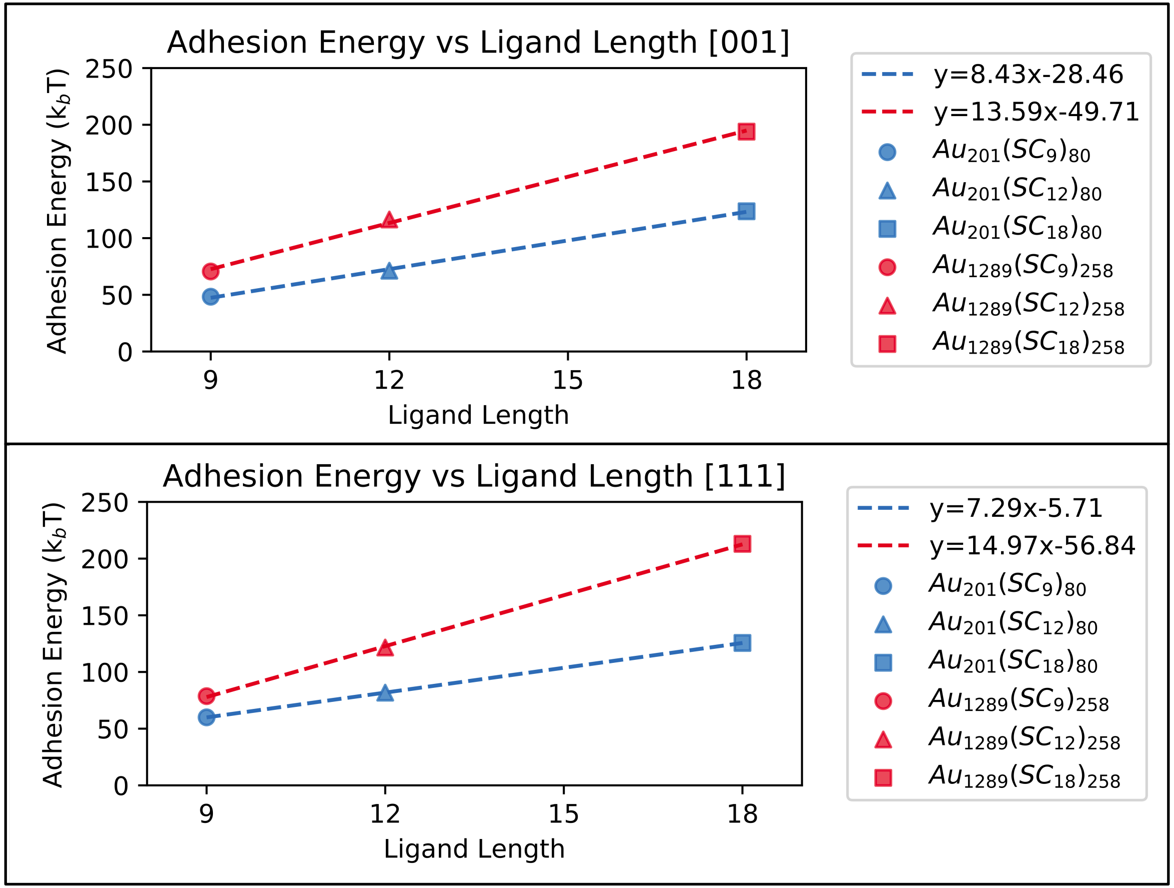


$R_{[001]}$ = 7.92 Å $\xrightarrow{D_{[ijk]} = \rho - R_{[ijk]}}$ $D_{[001]}$ = 9.98 Å

$R_{[111]}$ = 6.86 Å $D_{[111]}$ = 10.36 Å

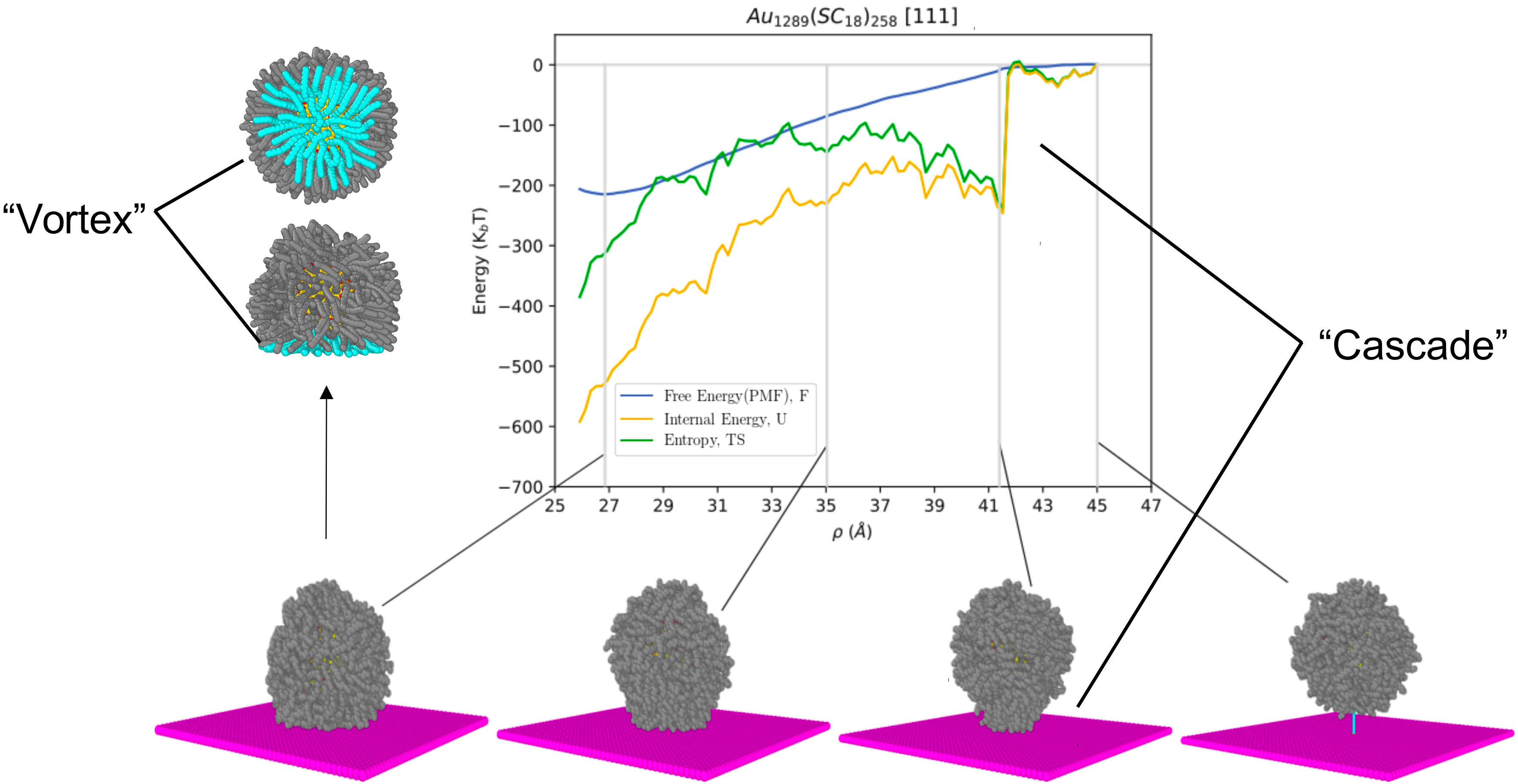
- Larger [111] face vs [001] face
- Similar face-substrate separation

Adhesion Energies

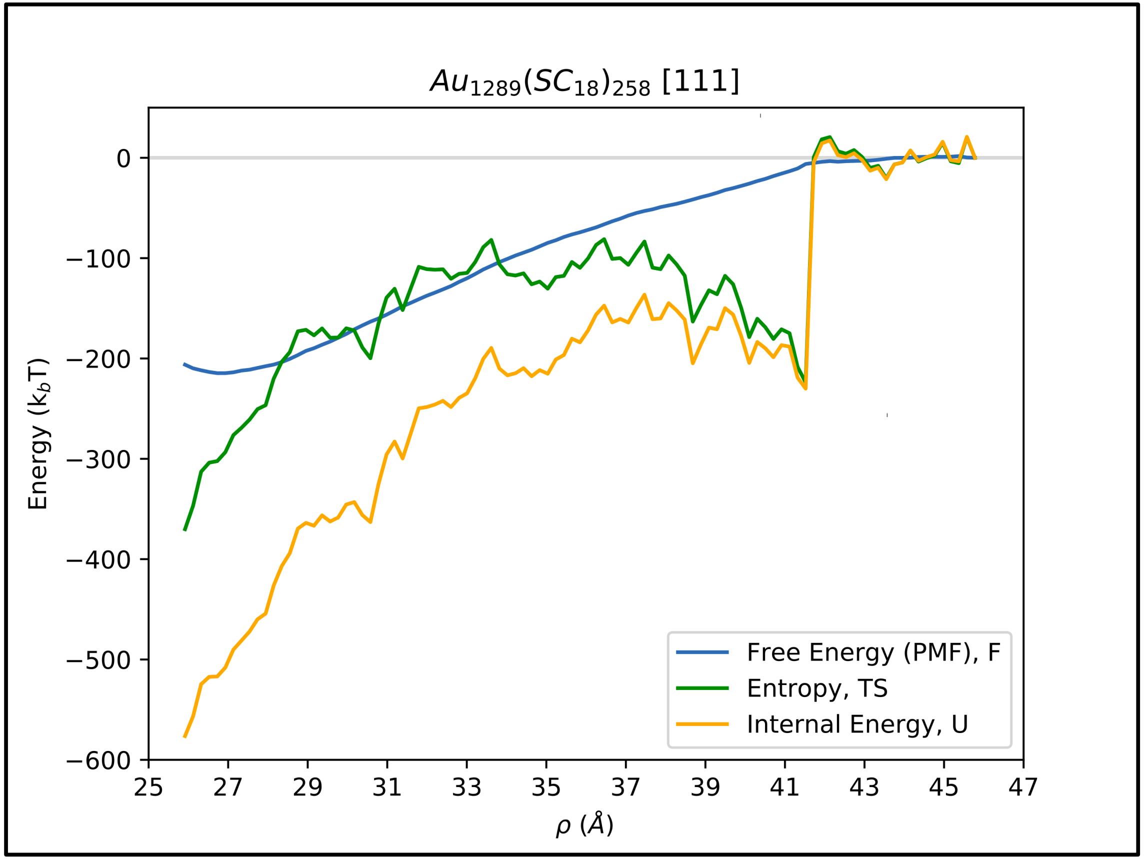


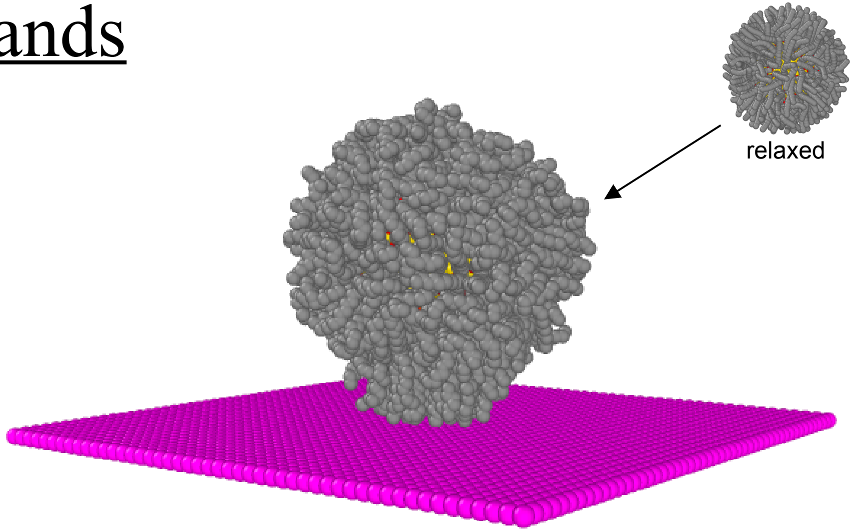
- Larger Core → More Vortex Ligands
- Non-spherical, TO Core → Orientation Dependent Number of Vortex Chains
- Longer ligands can allow side or top grafted chains to add to vortex

Ligand Structures: Vortices and Cascades



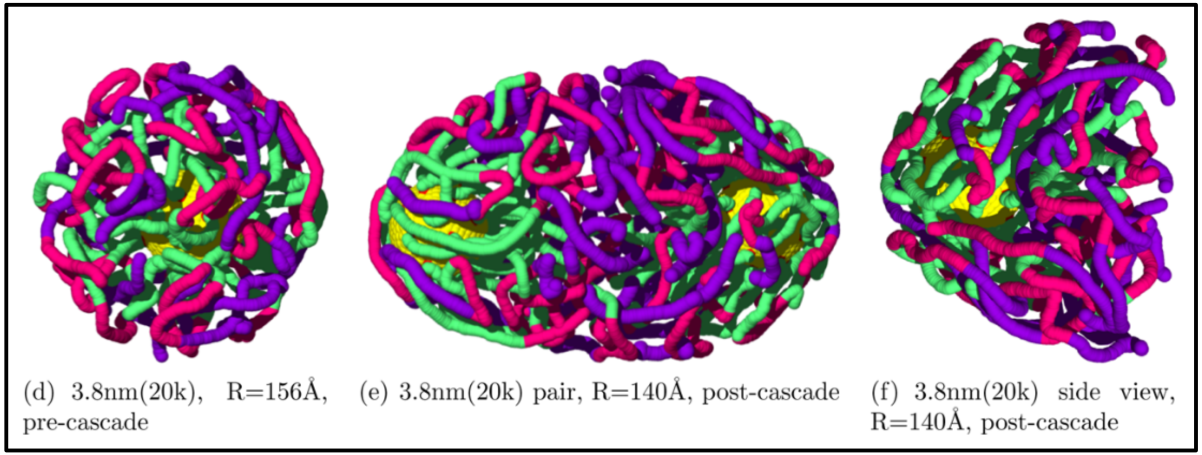
Cascaded Ligands



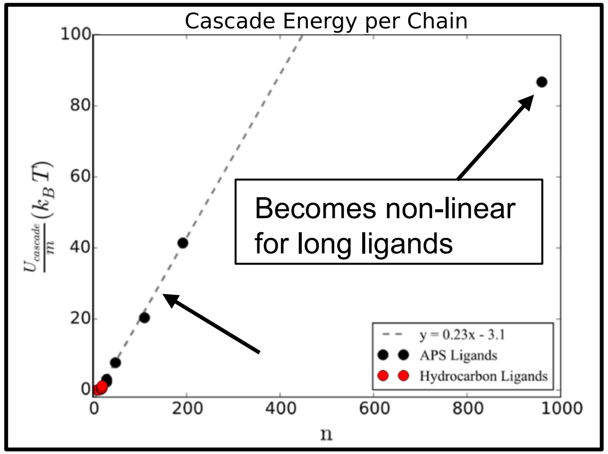


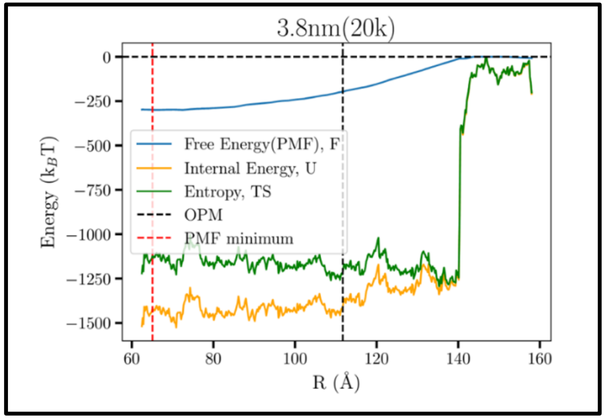
- Initial “anchoring” tugs NP towards substrate and restricts ligands into extended conformation
- Umbrella sampling holds NP in place during simulation, but without restriction along ρ, NP will descend towards substrate
- General phenomena beyond just NP-Substrate system ...

Cascaded Ligands



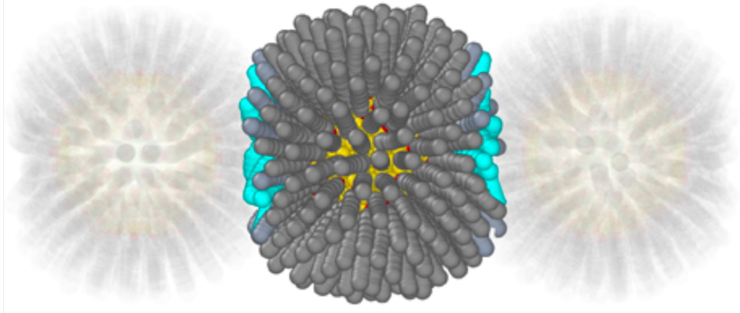
"Superlattices of Nanocrystals with Polystyrene Ligands: From the Colloidal to Polymer Limit"
J. Xia, N. Horst, H. Guo, A. Travesset, Macromolecules (2019)



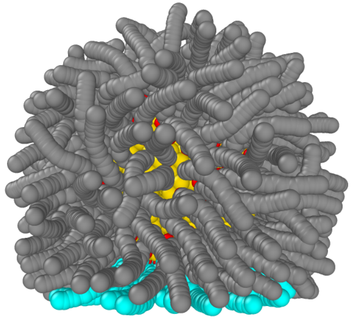


- Cascade effect is more prominent for NPs grafted with long ligands (ex: polymers)
- Long ligands enable back/side grafted chains to "droop" into vortex/cascade formation
- Cascade → Corona Deformation
- More investigation needed...

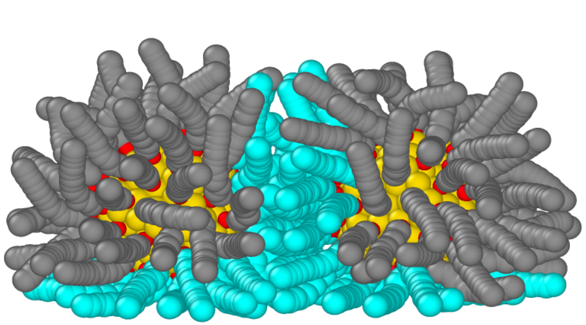
Ligand Vortices



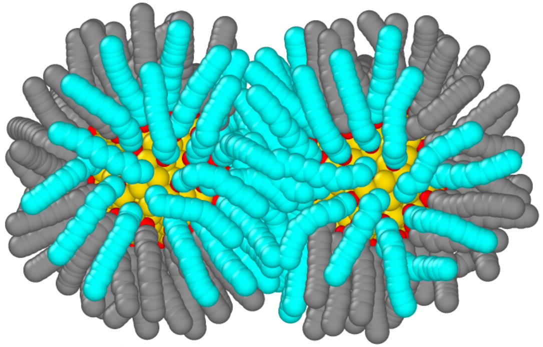
NP-NP Vortex



NP-Substrate Vortex



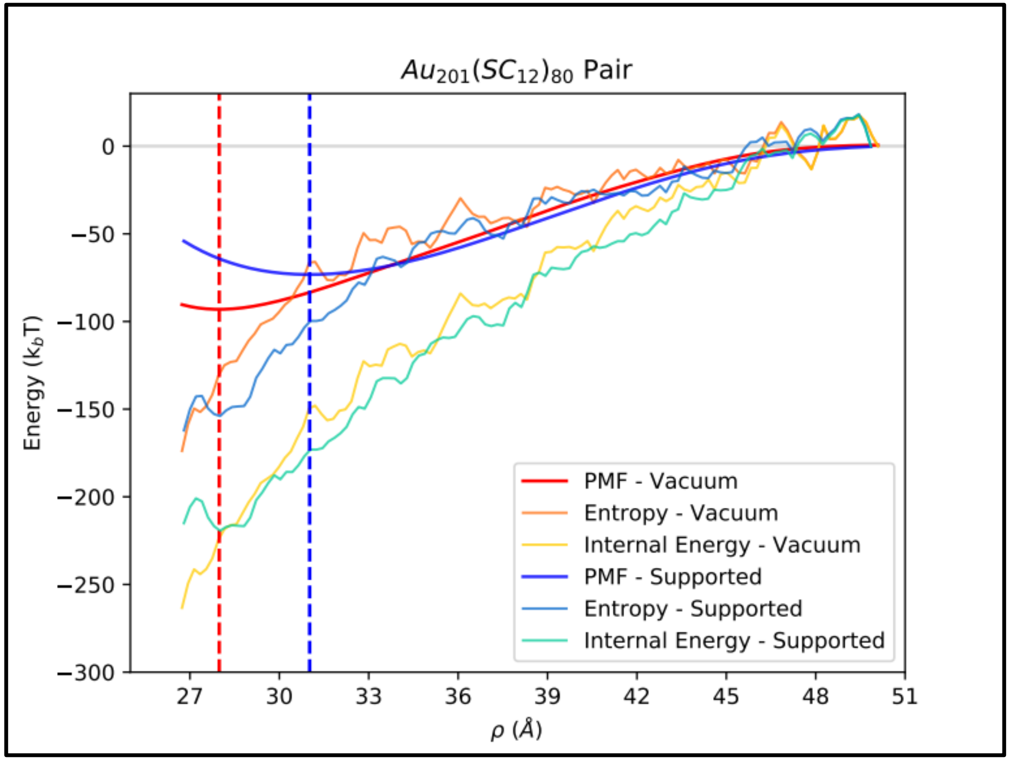
Coalesced Vortices

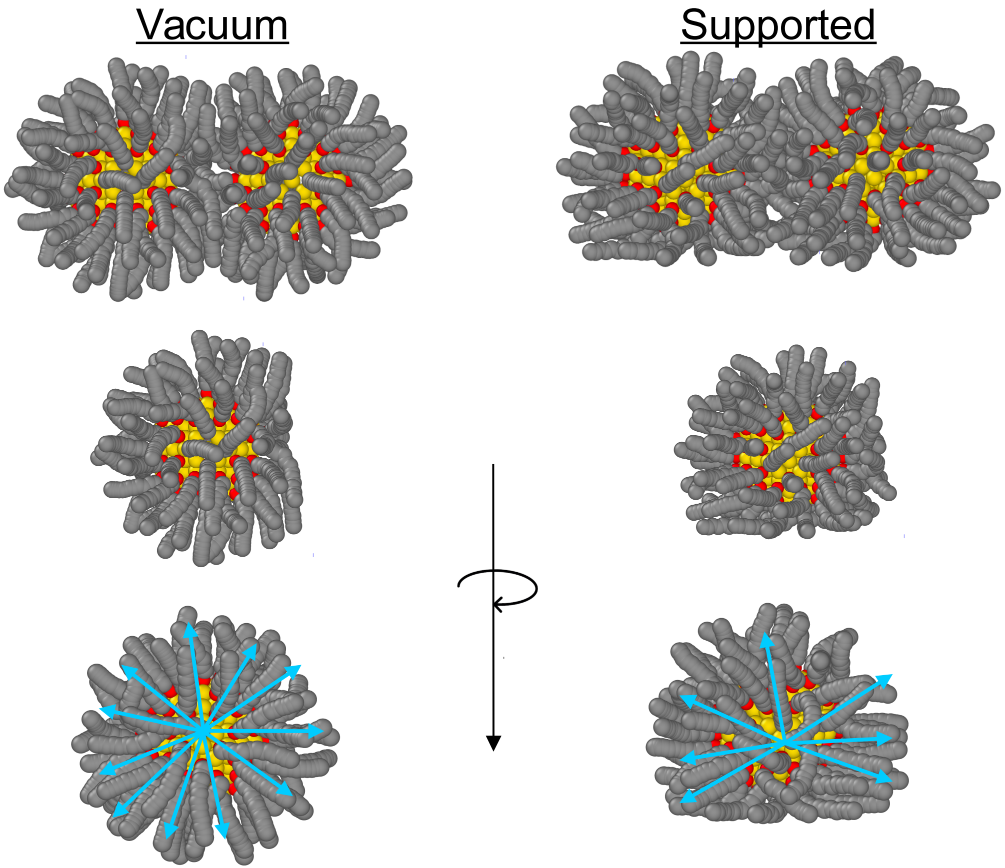


Coalesced Vortices

- “Harder” NP-Substrate vortex prevents formation of ideal NP-NP vortex
- NP-Substrate vortex shifts ligands into interstitial space between NPs
- Increased ligand density in interstitial space increases separation

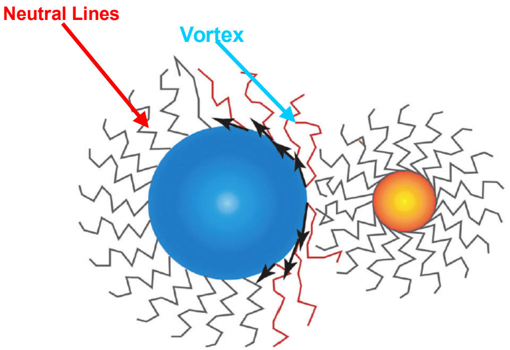
Ligand Vortices

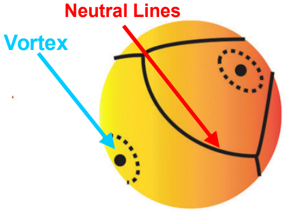




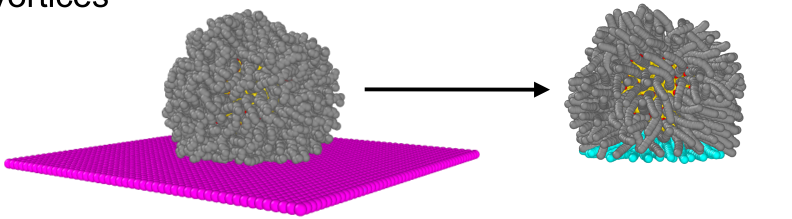
- Non-ideal NP-NP vortex in presence of NP-Substrate vortex
- Increased ligand density in interstitial space

Summary

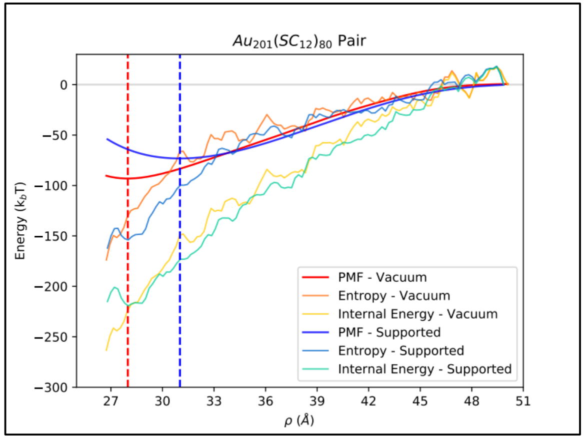


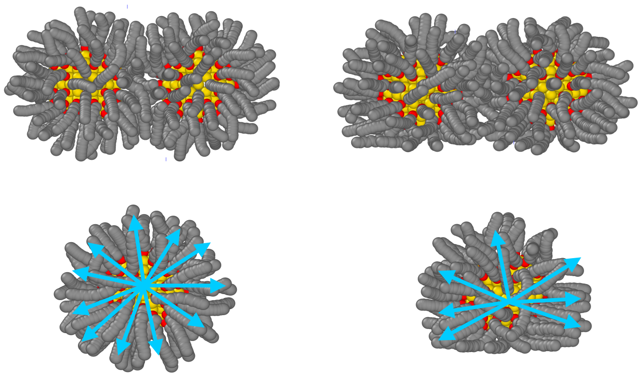


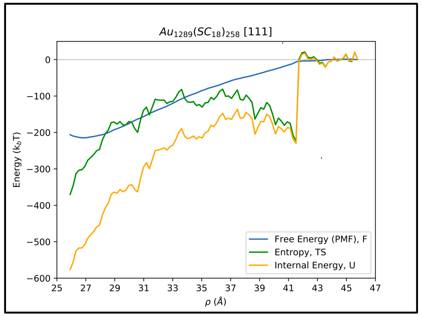
- “Ligand Orbitals” overlap forming vortices, but NP adsorption onto substrate also forms vortices

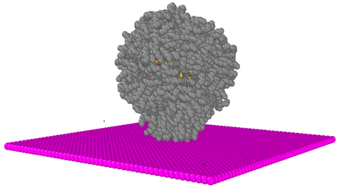


- “Harder” NP-Substrate vortex prevents ideal NP-NP vortex, and increased ligand density in interstitial space pushes NPs apart.









- Cascaded ligands at initial “anchoring” of NP to substrate become fully extended
- Cascade effect more prominent for longer ligands due to greater corona deformation

Acknowledgments

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- NSF Grant DMR-CMMT 1606336 CDS&E: Design Principles for Ordering Nanoparticles into Super-crystals
- XSEDE Allocation TG-MCB140071: Bonding Rules and Structure Prediction in Nanocrystal Clusters and Superlattices

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