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Coated Nanoparticles in Solution and at Interfaces

Gary S. Grest
Center for Nanotechnologies
Sandia National Laboratories
Albuquerque, NM

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Nanoparticle Properties and Promise

Mechanical, Thermal

- Super-light super-strong materials with polymer nanocomposites

Optical

- Sustainable energy with durable photovoltaic quantum dot arrays

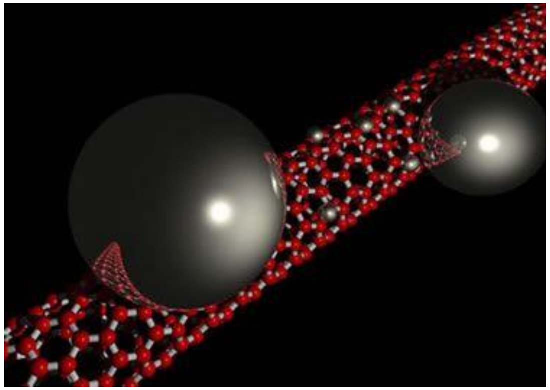
Electronic

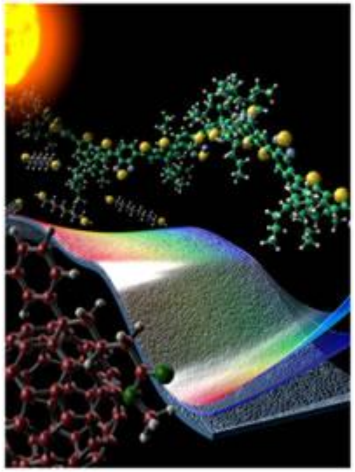
- Next-generation carbon-based electronics
- High energy density capacitors

Biomedical

- Protein recognition and bio-sensors
- Medical breakthrough for drug delivery

National Nanotechnology Initiative at Ten:
NANOTECHNOLOGY INNOVATION SUMMIT

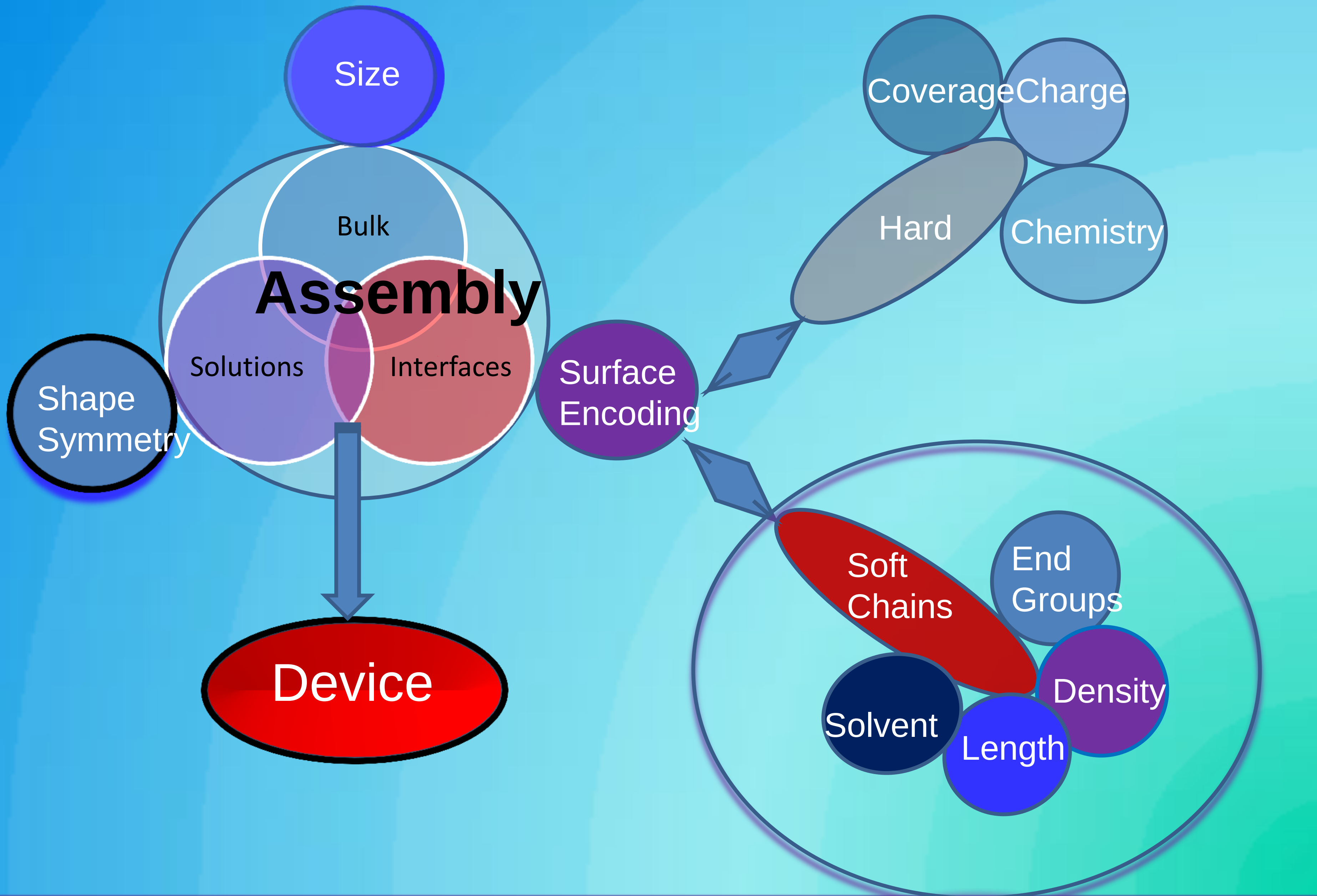




Images:www.nano.gov

Nano is an ‘enabling technology’

Challenges of Nanoparticle Assembly

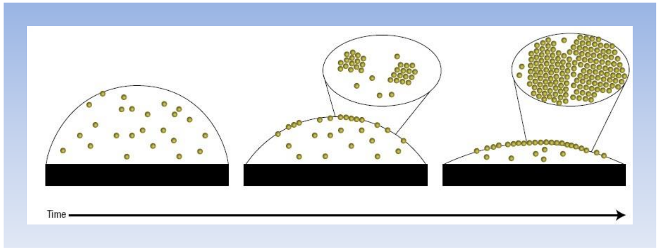


Assembly of 2D Nanoparticle Film

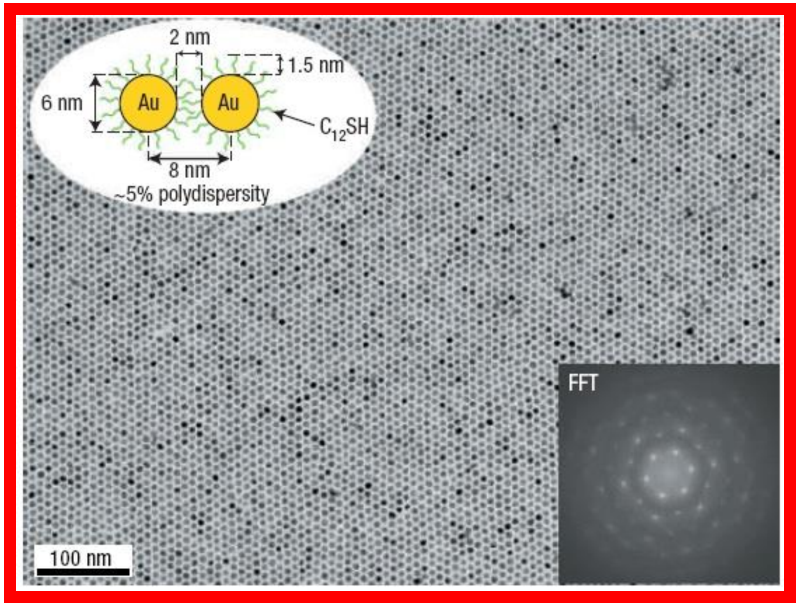
- Synthesis of nanoparticle monolayers, only nanometers thick with, well defined size, long-range order, stable coating

- Assemble nanoparticles retaining unique properties without acting like a bulk metal

- Extremely strong but flexible, Young's modulus of several GPa



Slow evaporation of solvent



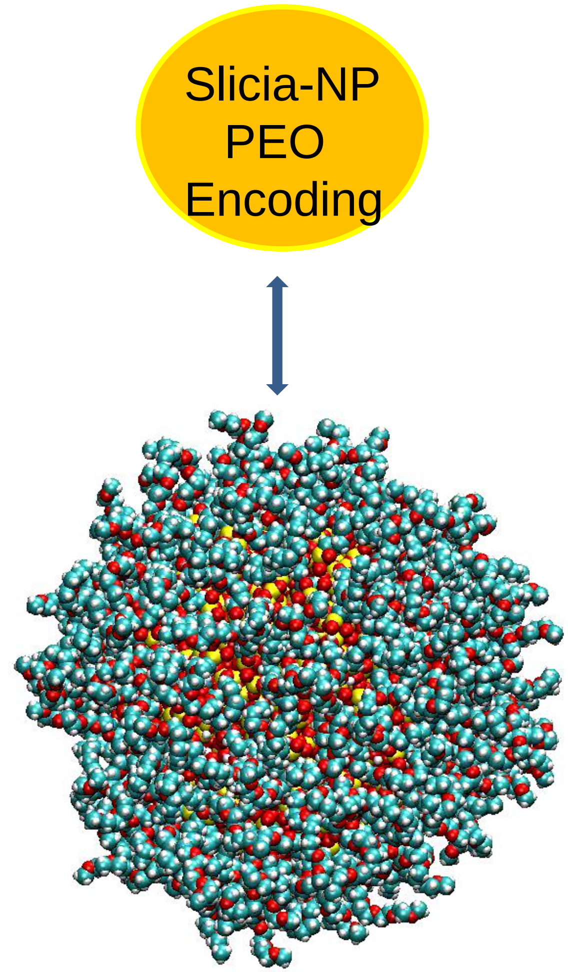
Bigioni *et al,* Nature Mat.5, 265 (2006)

Molecular Dynamics Simulations

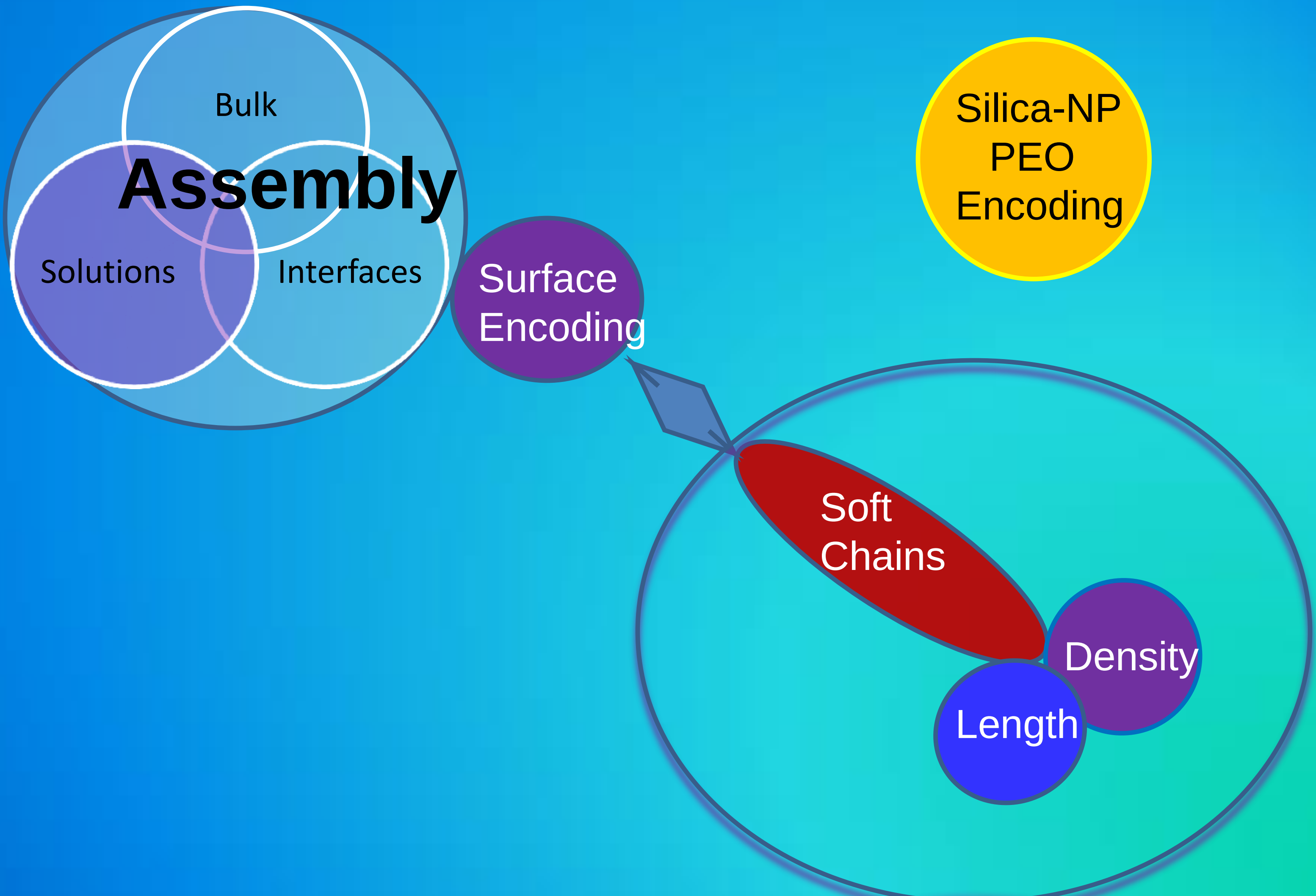
- $4x10^5$ – $1.2x10^6$ atoms
- van der Waal, bond, bending, torsional interactions
  - -*ab inito* quantum chemistry based

- Time step 1fs - runs 10 - 200ns
- OPLS force fields
- TIP4P H_2O

- Systems
  – d=5 nm PEO/Silica NPs
  – d=2-8 nm Alkanethiol Au NPs

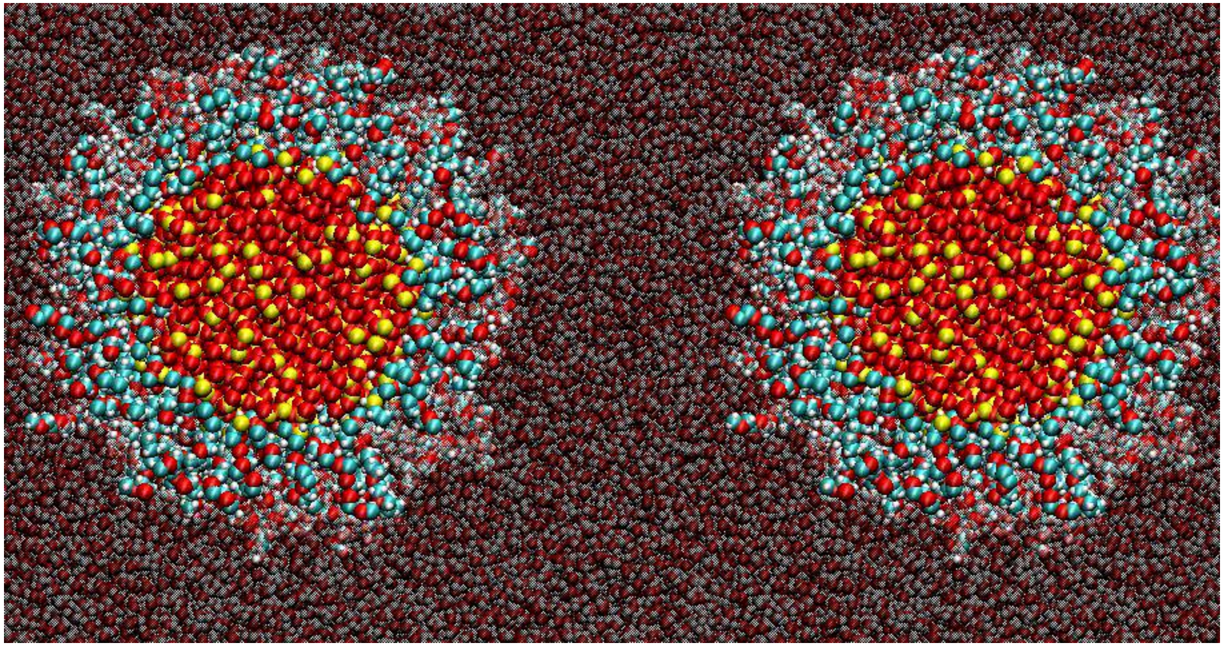


Challenges of Nanoparticle Assembly



Interactions Between Nanoparticles

- Determine velocity independent (solvation) and velocity dependent (lubrication) forces
  - -chain length, nanoparticle size/shape, coverage
- Integrate into coarse-grained model

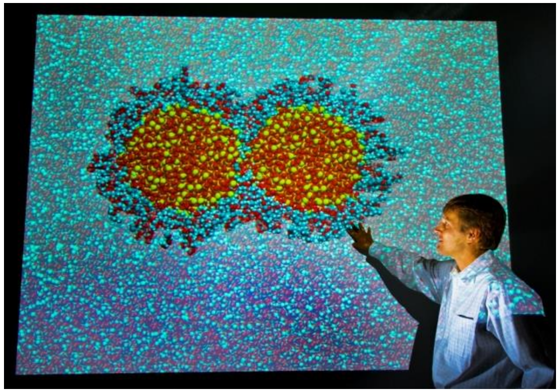


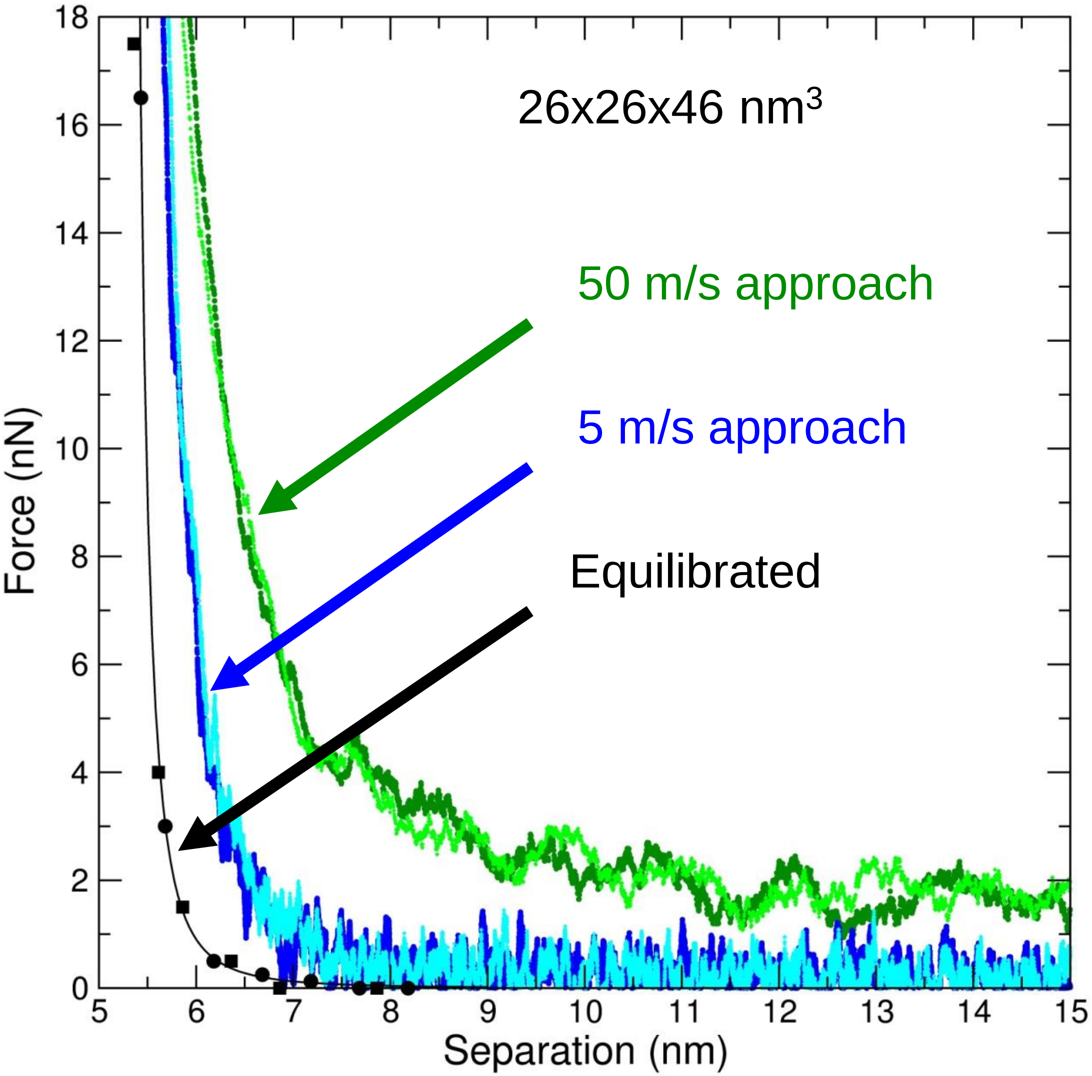
vel=50 m/s

Lane et al, Phys. Rev. E 79, 050501(R) (2009); Ismail, Lane, Grest, in prep.

Force Between Coated Nanoparticles

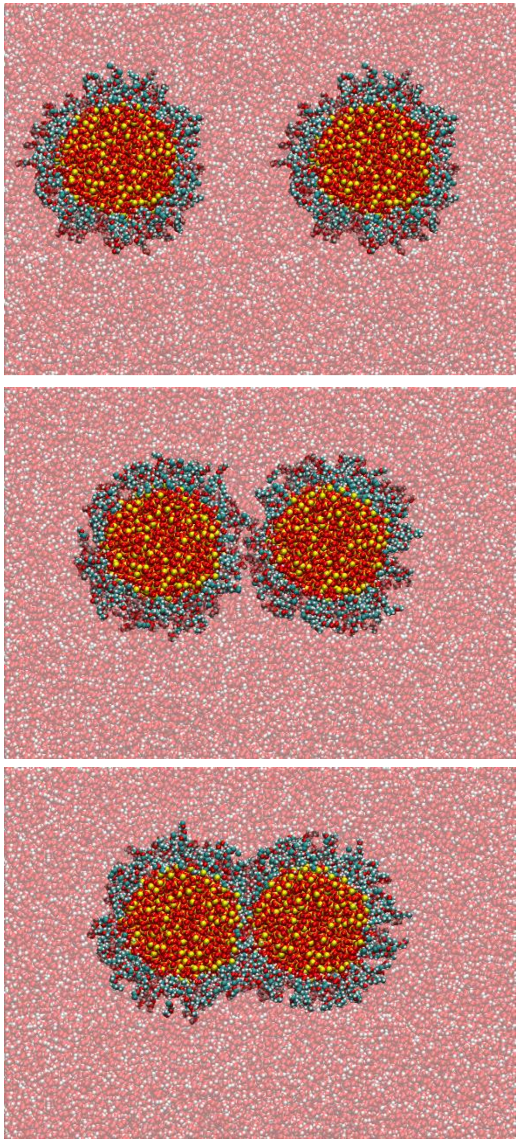
- Stokes drag at large separation with linear velocity scaling
- Complex mixed response in the separation range of interest (near contact)
- No oscillations in force due to layering

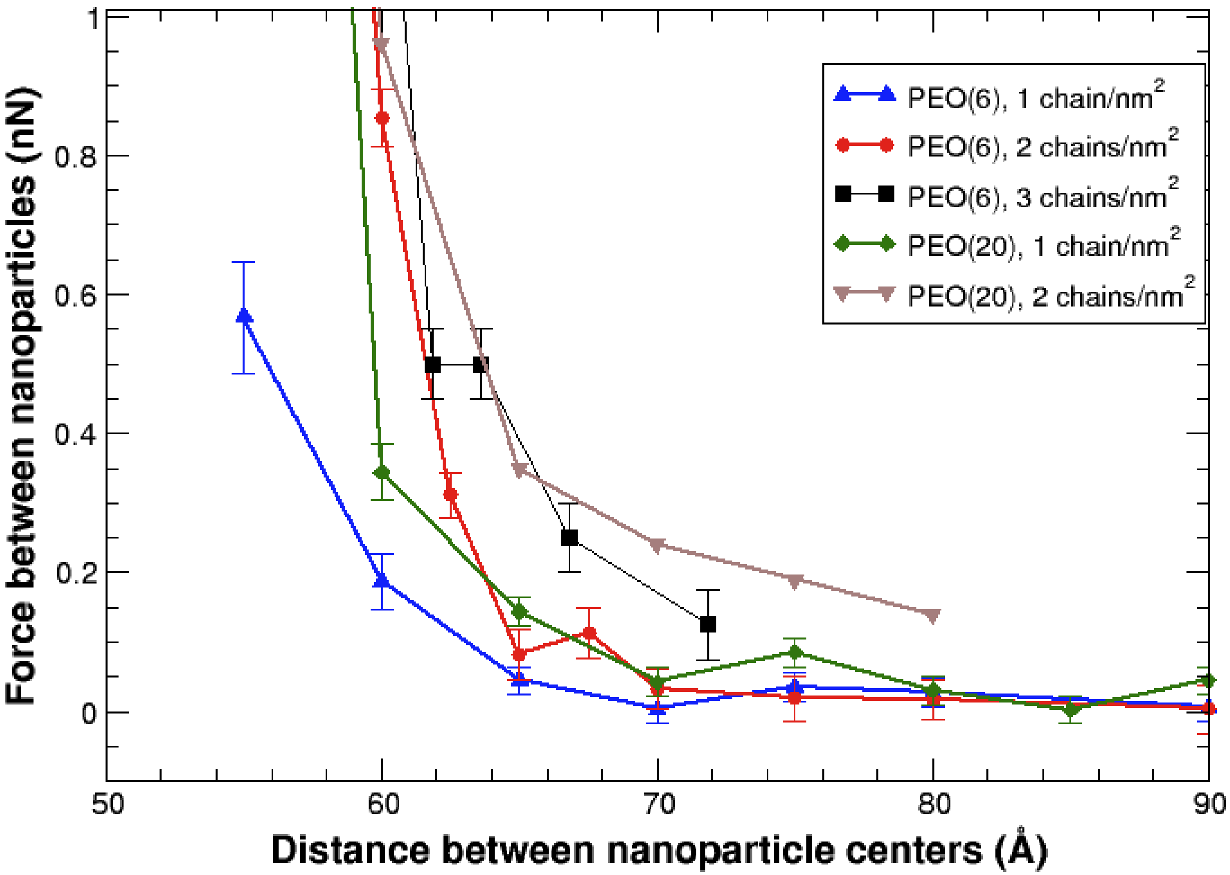




5 nm PEO(6) coated silica NP – 3 chains/nm^2

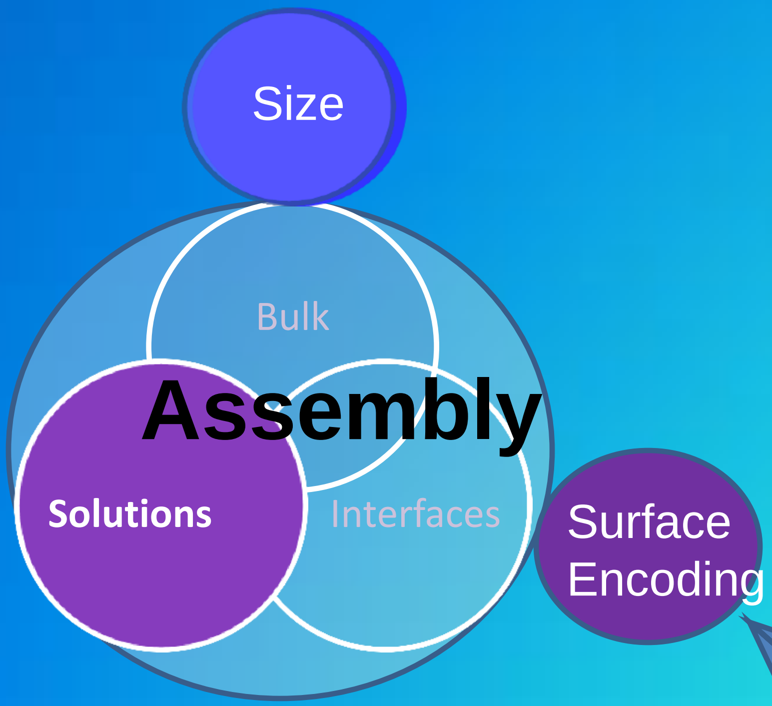
Interactions Between Nanoparticles



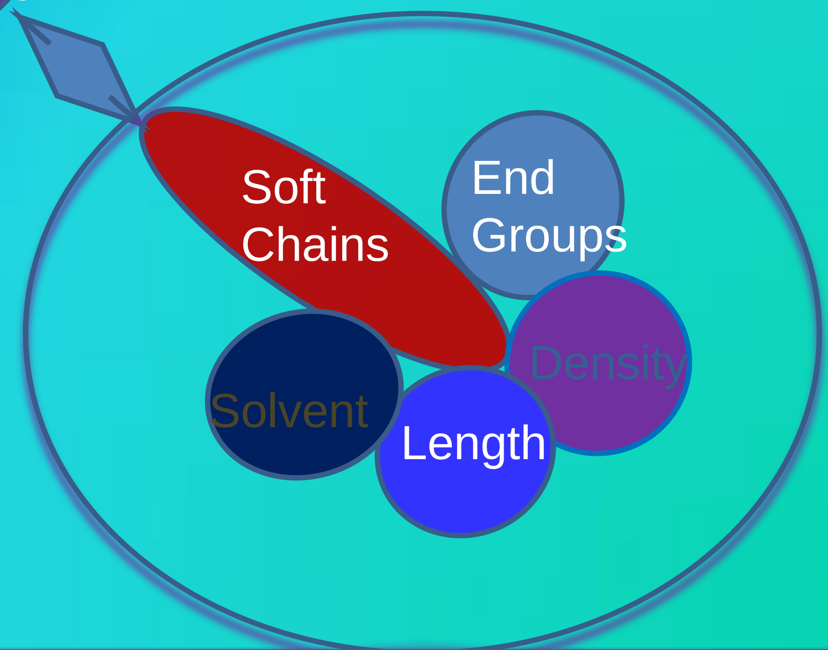


- 300K, thermal fluctuations corresponds to forces < 1 nN
- Difficult to equilibrate and extract accurate forces

Challenges of Nanoparticle Assembly

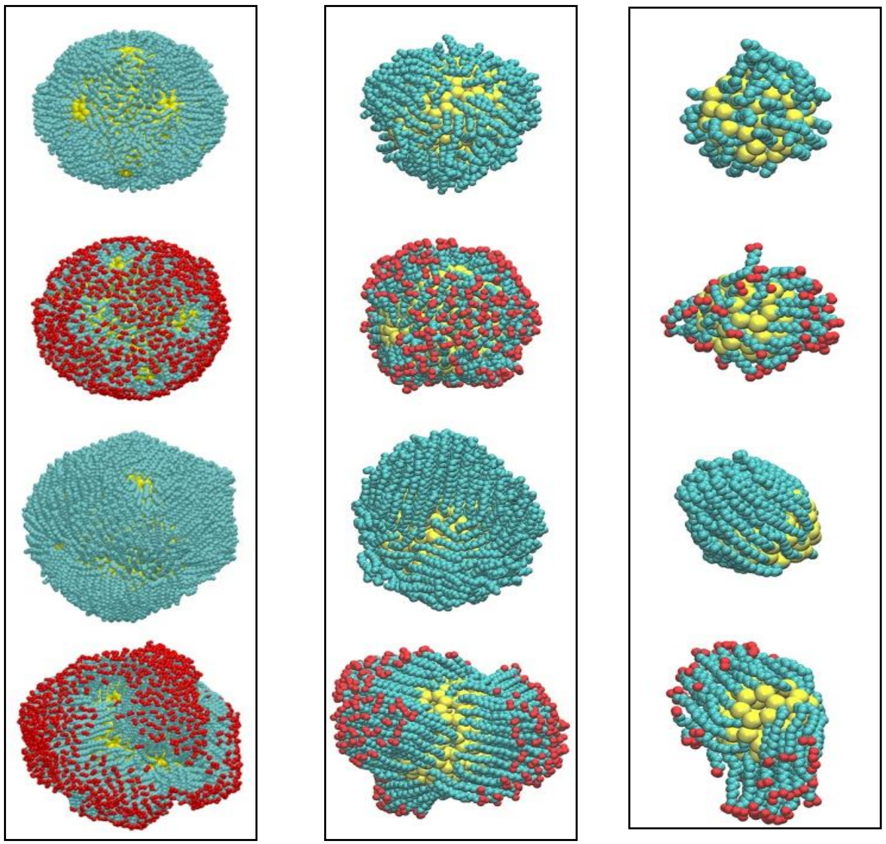


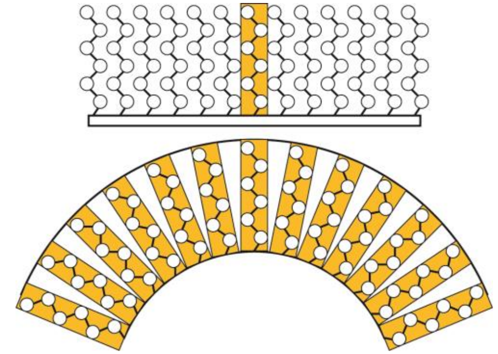
Forces Control Assembly



Symmetry and Size Effects Alkanethiol Coated Au Nanoparticles in Water

Symmetric Coating Leads to Asymmetric Shapes



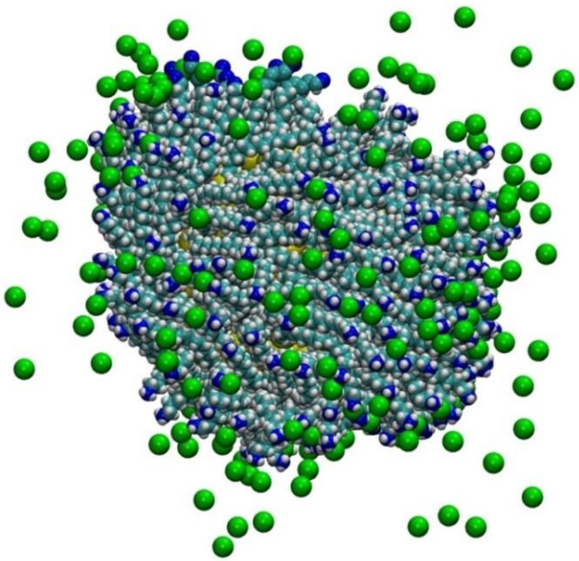


- Geometry is controlling parameter

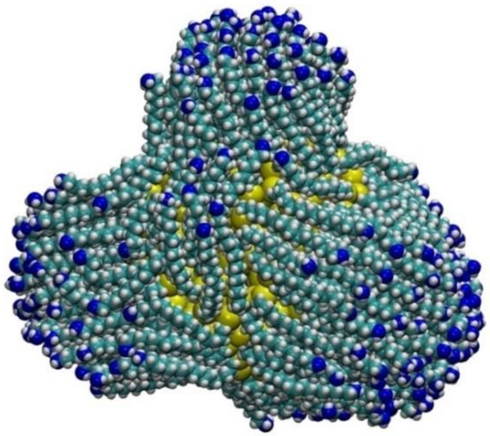
- Small changes affect structure → change potential activity/solubility

Lane, Grest, Phys. Rev. Lett. 104, 235501(2010)

Effect of Ionic Charge: a Gateway to Biocompatibility



$C18\text{-}NH_3^+Cl^-$
Neutral pH=7



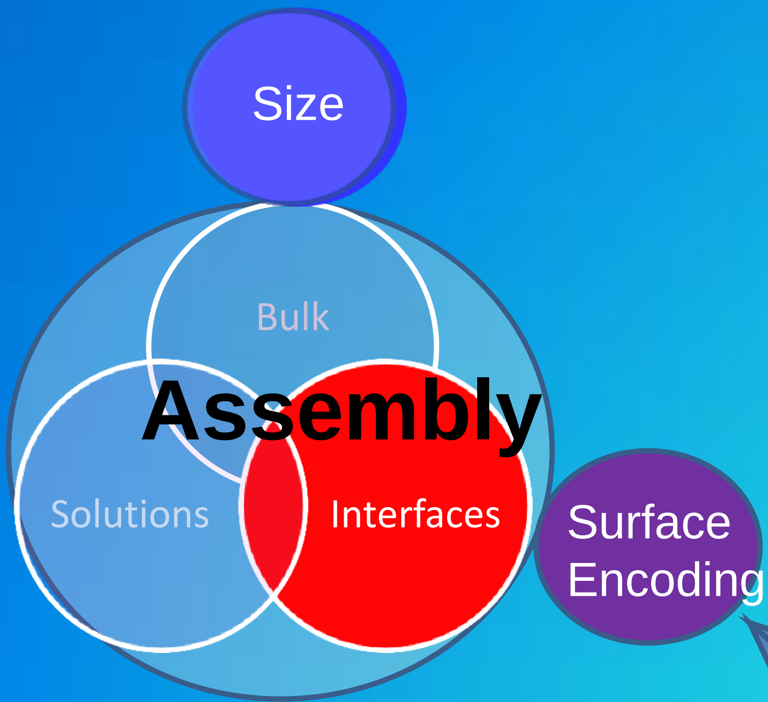
$C18\text{-}NH_2$
High pH>>7

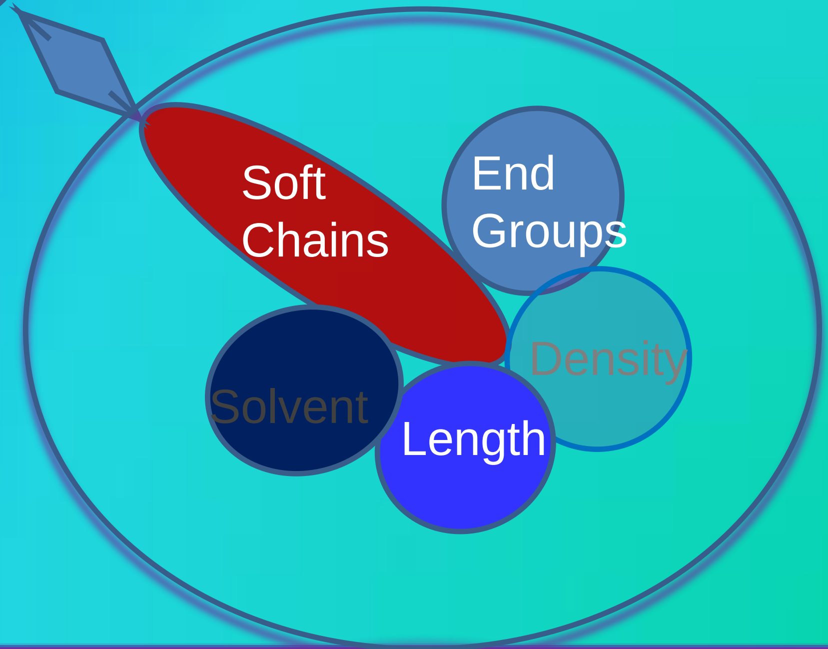
- Uncharged chains cluster => the NP is insoluble in water
- Charged end groups, chains are dispersed=> NP is water soluble

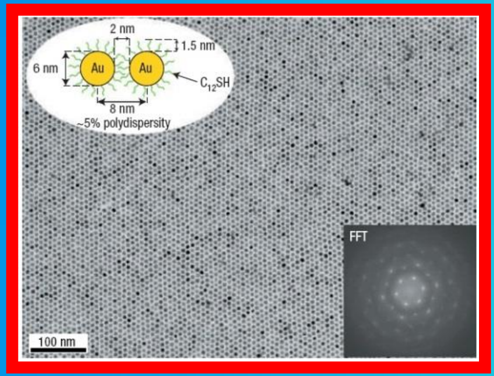
D. S. Bolintineanu, J. M. D. Lane, GSG (F32.00004)

Challenges of Nanoparticle Assembly

- Symmetry changes assembly

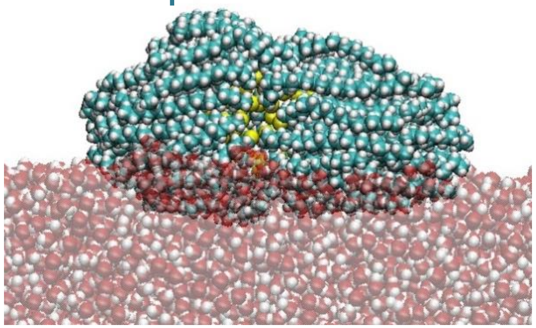




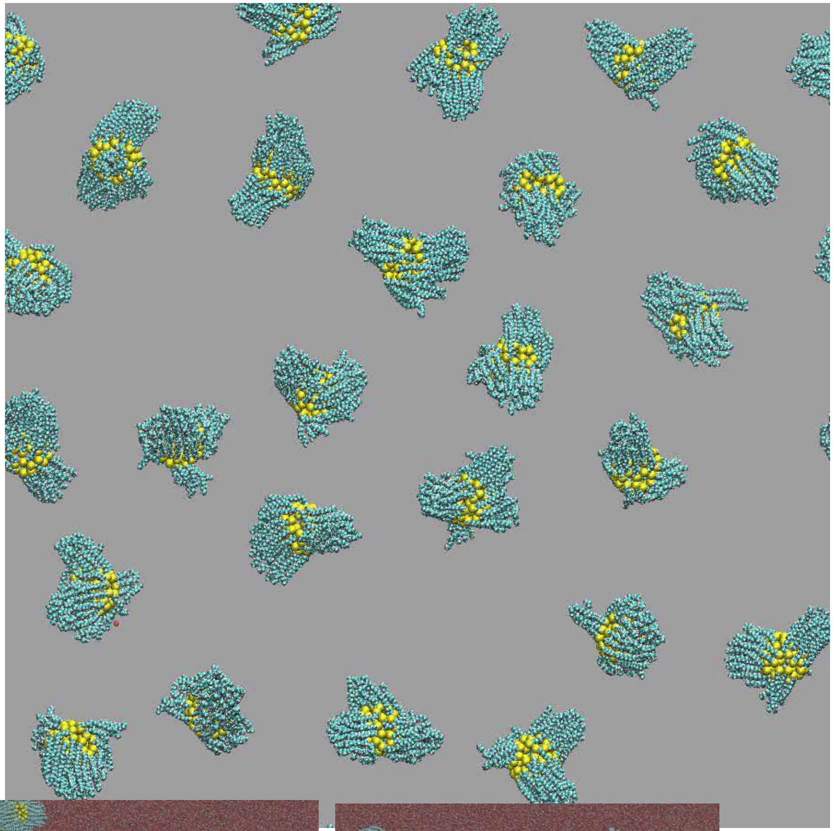


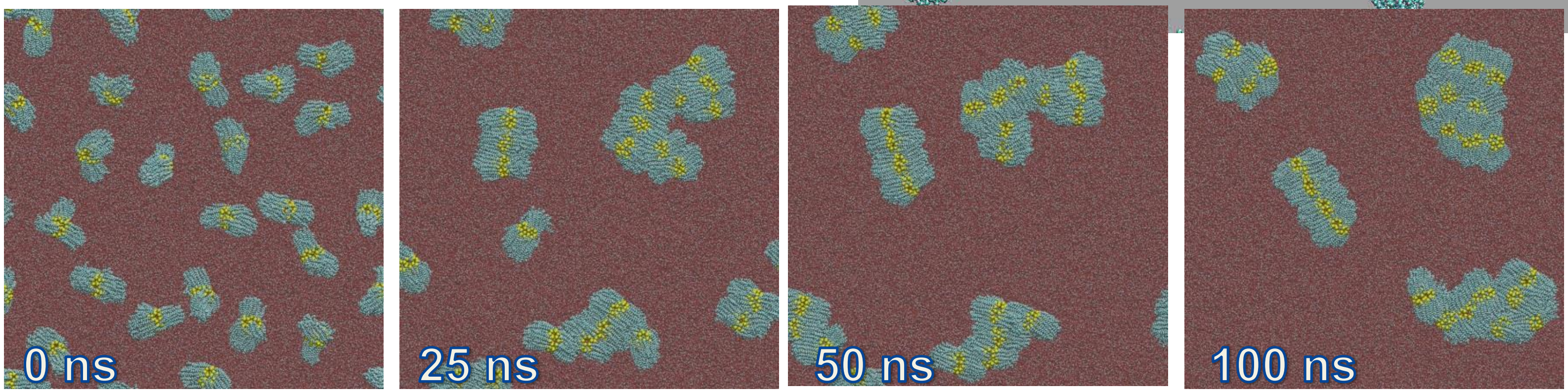
Low-density Assembly/Aggregation

- 2 nm diameter
- $-CH_3$ terminated
- water/vapor interface



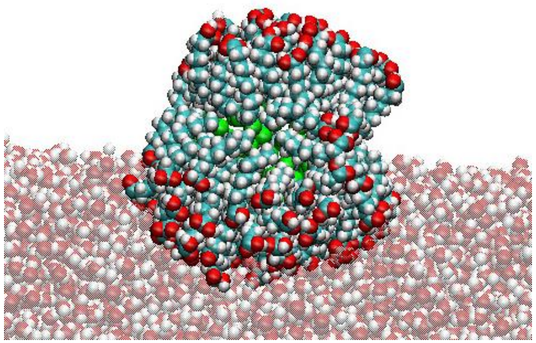
- Well-defined cylindrical aggregates
- Preferred alignment along the long axes of the aggregates.



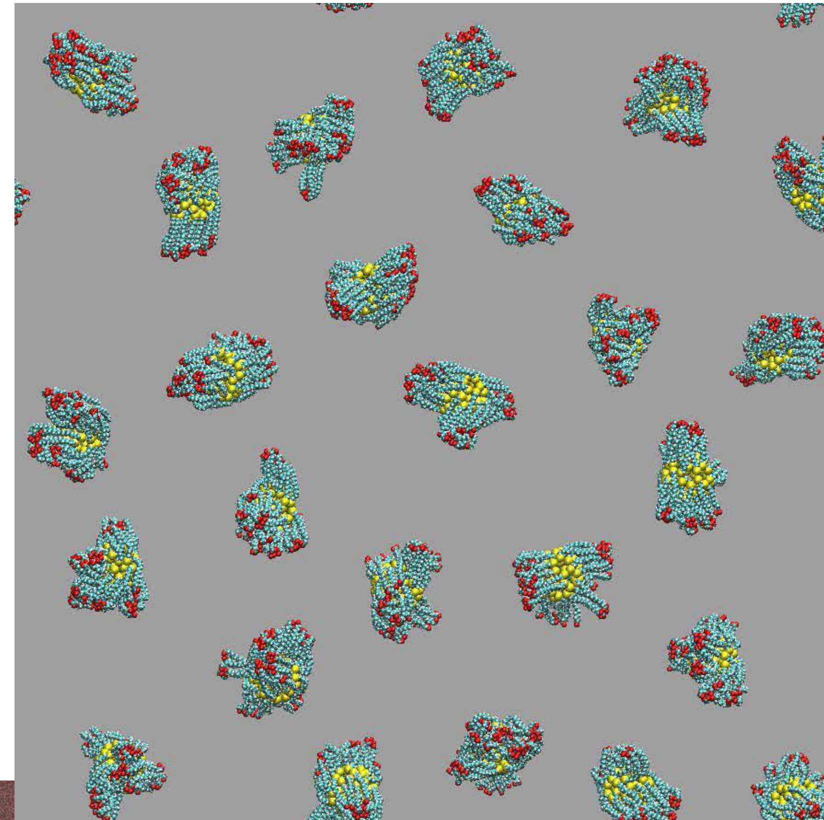


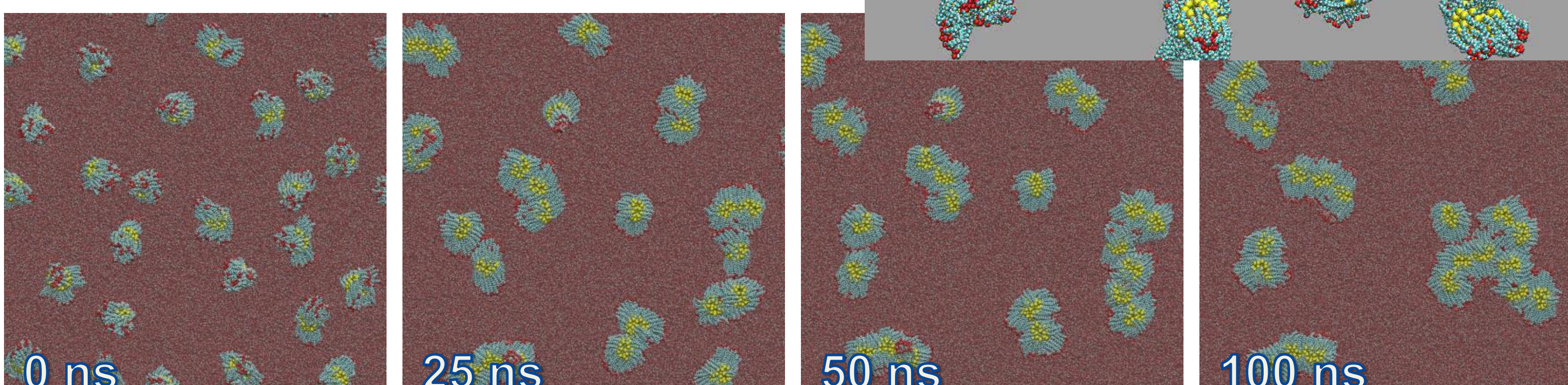
Low-density Assembly/Aggregation

- 2 nm diameter
- -COOH terminated
- water/vapor interface



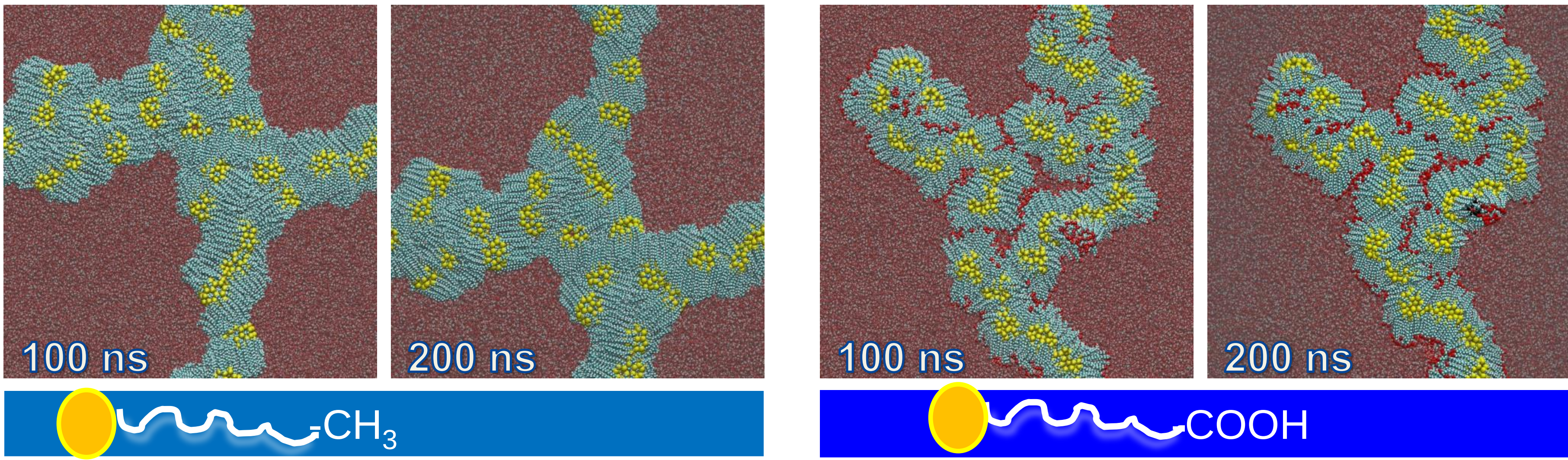
- Crew cut symmetry of NPs
- Aggregation rotates the main symmetry axis of the NP





High-NP Concentration Assembly

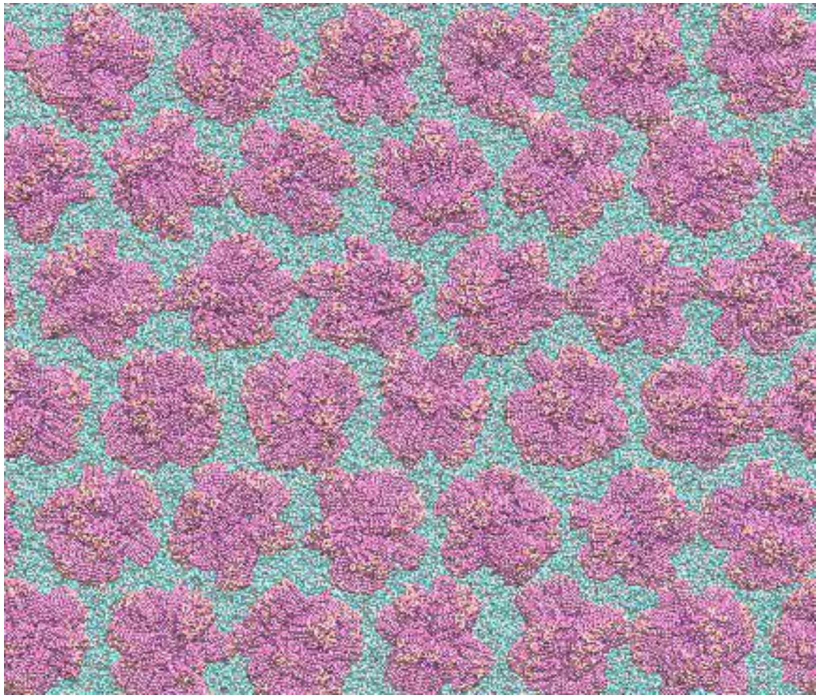
==> homogeneous compression of the initial systems to reduce the film's surface area

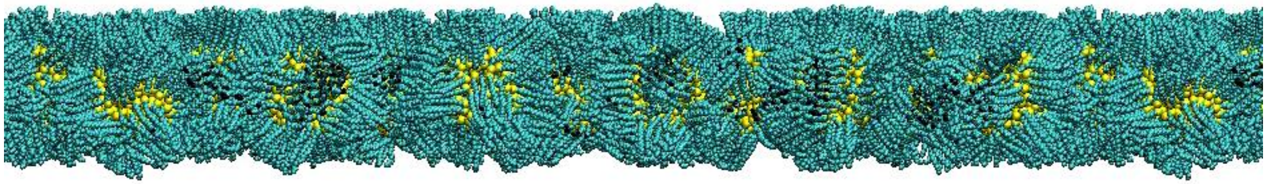


- Clusters are less ordered: can be attributed to kinetic effects
- Assemblies of NP encodes with chains terminated by -COOH and -CH_3 have equivalent large scale disorder
- Distinct short-range order within the assemblies
- Slow structural relaxation after 100 ns

Increasing Nanoparticles Size

4 nm diameter
COOH terminated
alkanes



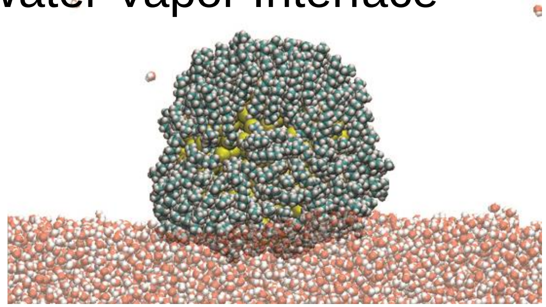


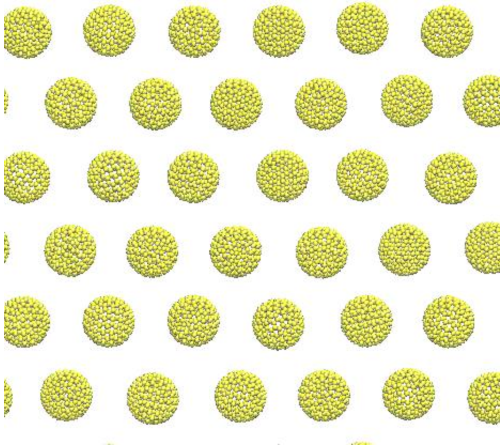
36 Nanoparticles – Hexagonal Lattice
12 ns – initial lattice spacing 90Å

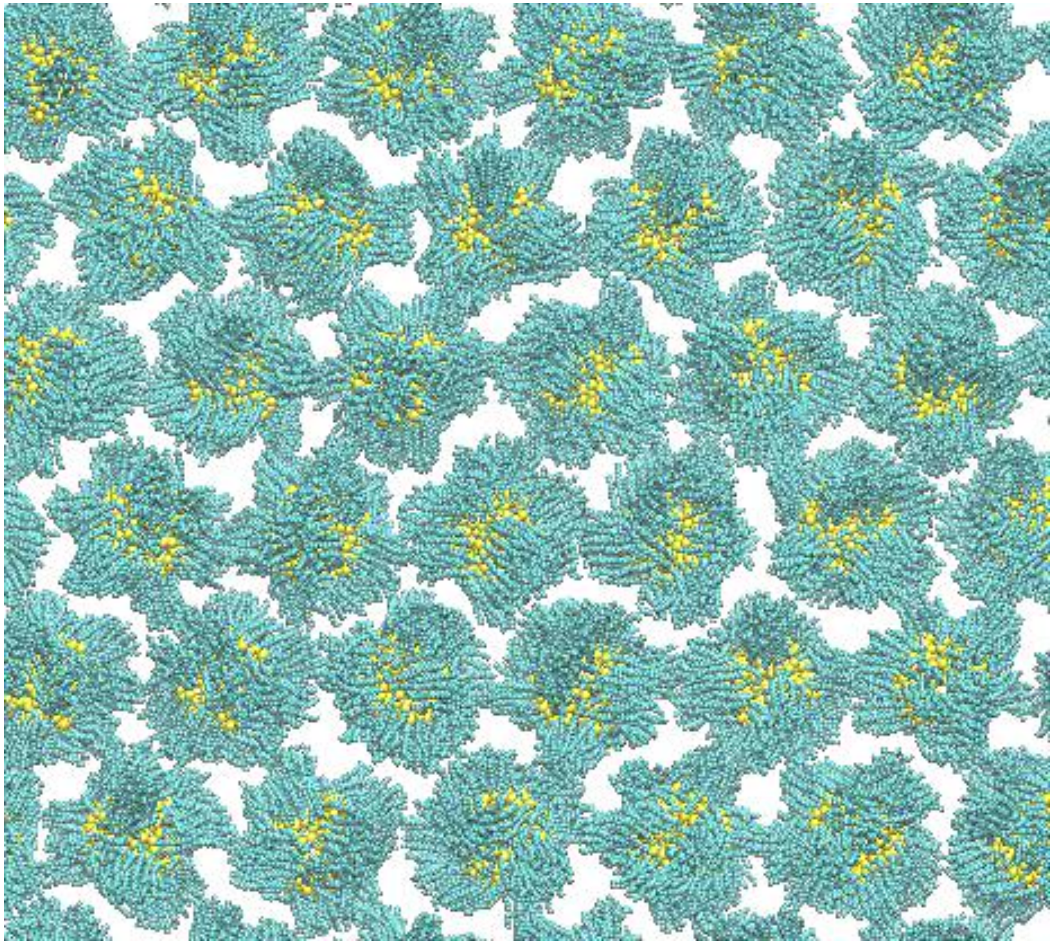
Film thickness matters

Assembly of 4 nm NPs

- 4 nm -CH3 terminated
- Water Vapor Interface





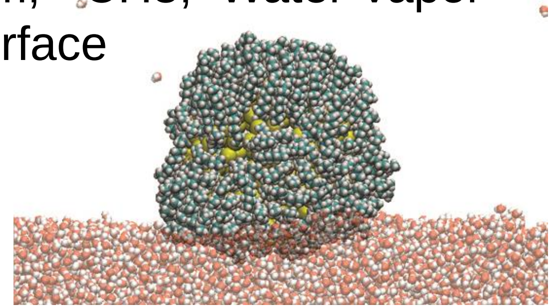


36 nanoparticles start an a triangular lattice with center-center spacing of 8.0 nm

System selects the lattice spacing 6.5 nm through film relaxation within 10 ns

Assembly of 4 nm NPs

4 nm; -CH3; Water Vapor Interface



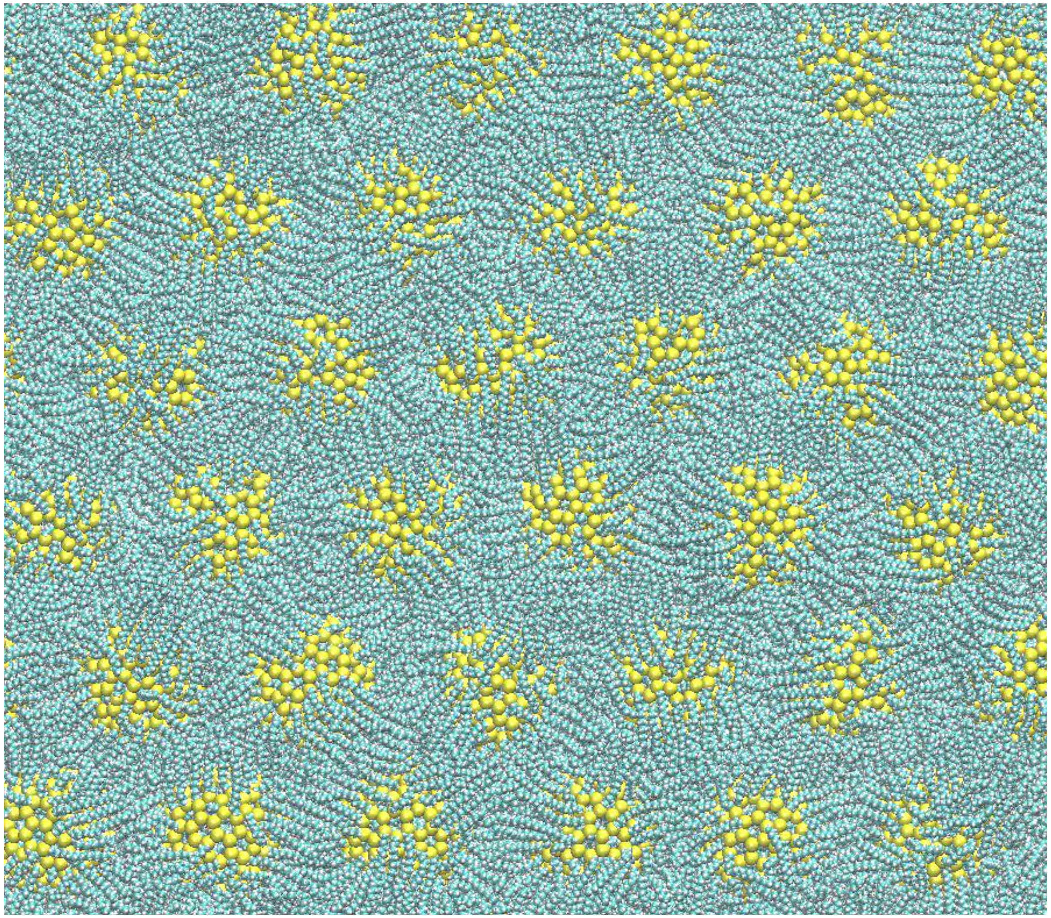
- Nanoparticles in a stable triangular lattice with center-center spacing of 6.5 nm

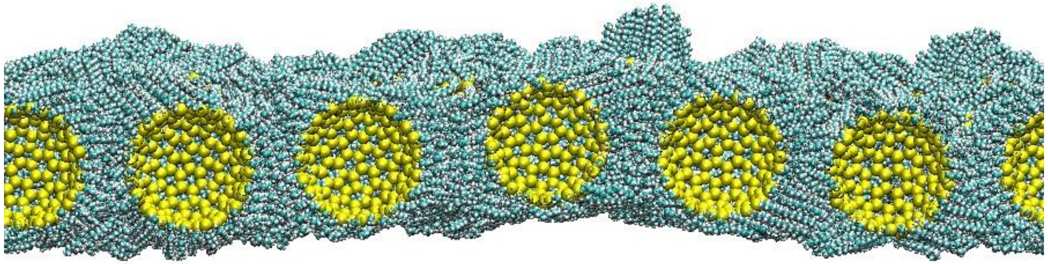
- Once stable films of nanoparticles are produced, water was removed.

- NP remains on the lattice in dry films

- Dry films are stable

- Asymmetry in density of the soft chains at the air and liquids interfaces: in agreement with experimental observations.





What's Next?

- Correlate assembly symmetries
with mechanical properties.

- Predictive guidelines for asymmetry

- Self-Assembly in 3d

- Extend biologically relevant ligands
  - single stranded DNA

Summary

- Asymmetric coatings are prevelant even for uniform grafting
  - higher the curvature of the NP, the more asymmetric the soft encodes hybrid is
  - chain end group play an important role in determining the properties of NP surface symmetry

- The symmetry of the soft encoding at interfaces differs significantly from that in solution.

- Asymmetric and oriented coatings have dramatic effects on the interactions between NPs
  - strong influence self-assembly at surfaces

Acknowledgements

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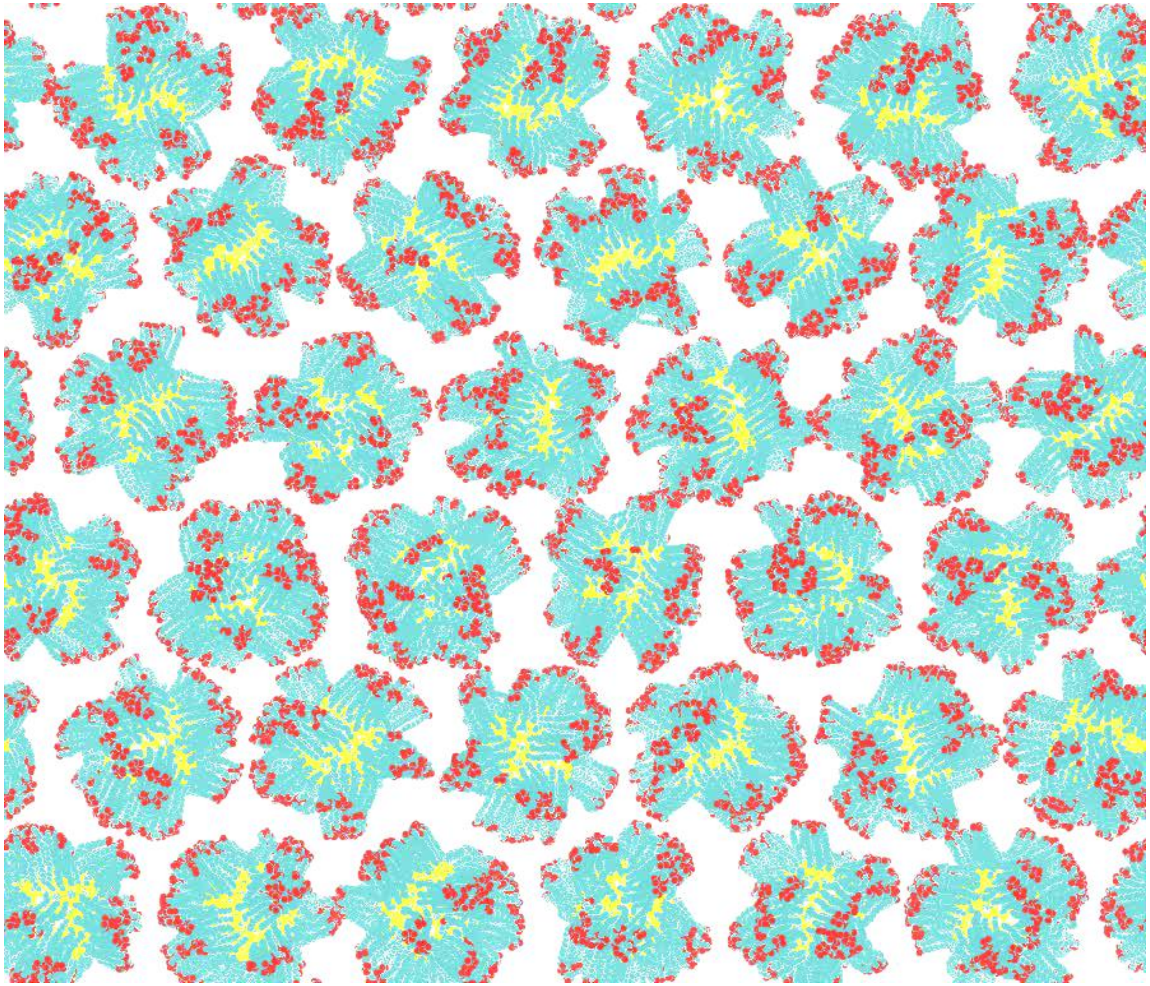
- Center for Integrated Nanotechnology (CINT)
- DOE – ALCC grant

Computers:
- Sandia’s Red Sky/Red Mesa
- NERSC Hopper XE6

4 nm Diameter Alkanethiol Nanoparticles



COOH terminal group

36 Nanoparticles – Hexagonal Lattice
6.2 ns – initial lattice spacing 90Å

Challenges

Nanoparticles are commonly coated to prevent aggregation in solution

Effects, chem., length, shape, coverage, matrix

Forces, symmetry

Interface or bulk

Np size, shape, surface encoding, coverage,

Length, chemistry, end group, counterion