Challenges of Simulating Nanoparticles Suspensions

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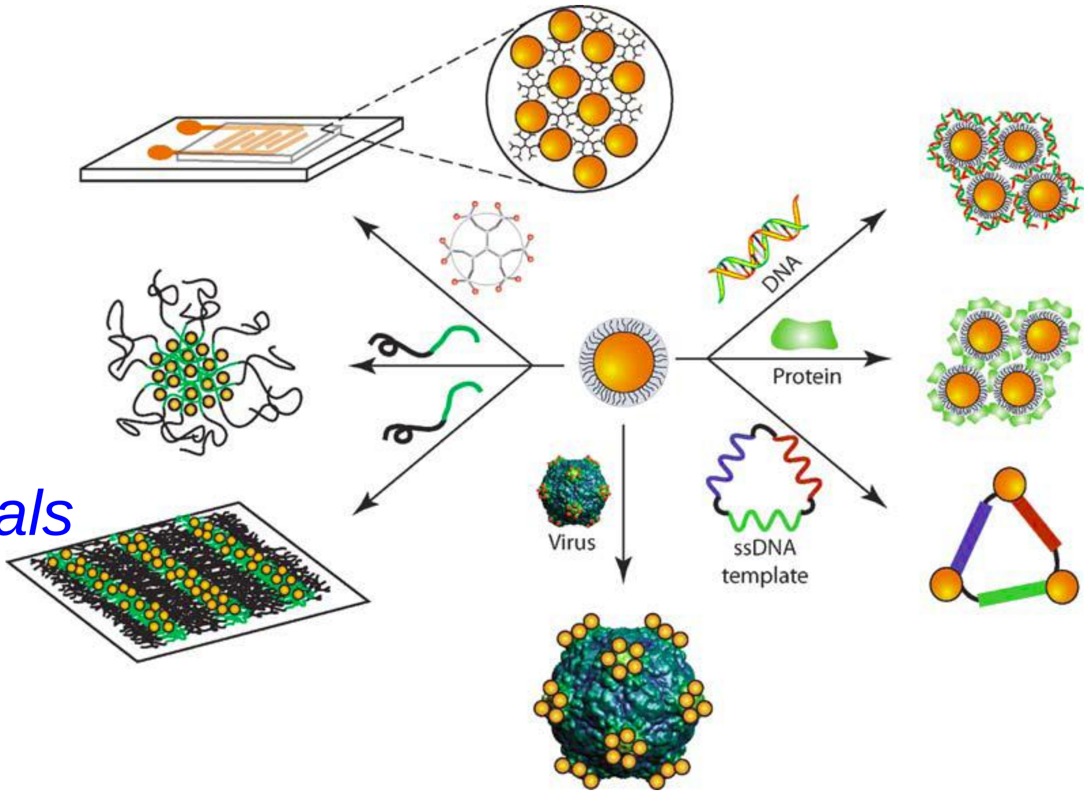
Polymer Nanoparticle Complexes

Controlled Designed Properties

- Mechanical, Thermal
- Optical
- Electronic
- Transport

High performance materials
Plasmonic devices
Sustainable energy

Protein Recognition
Drug and Gene Carriers



Polymer-mediated assembly of Au NP

Y. Ofir, B. Samanta and V. M. Rotello,
Chem. Soc. Rev. 37, 1814 (2008)

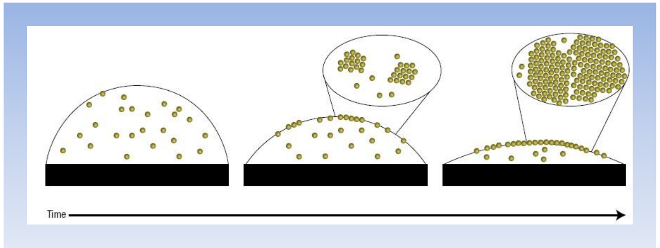
Nanoparticle Assembly Challenges

- Synthesis of nanoparticles
  well defined size,
  uniform, stable coating

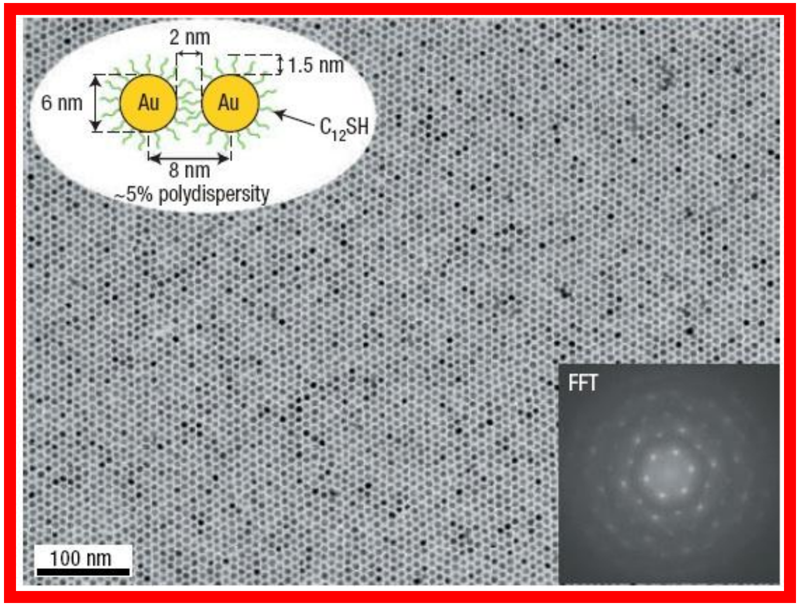
- Tailored properties
  optical, electrical, and
  magnetic

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

-long range order is possible, only some times desirable, but often not necessary

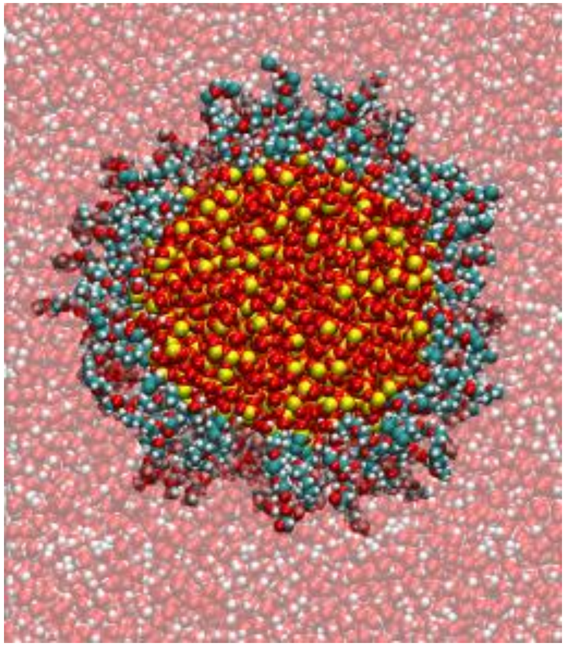


Slow evaporation of solvent



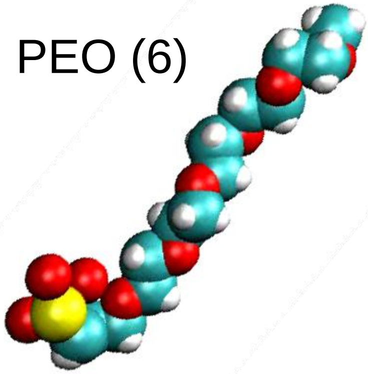
Bigioni *et al,* Nature Mat.5, 265 (2006)

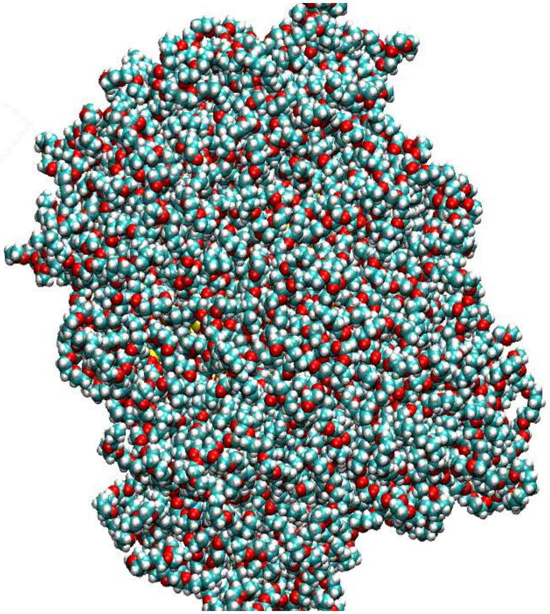
Organic Coated Nanoparticles



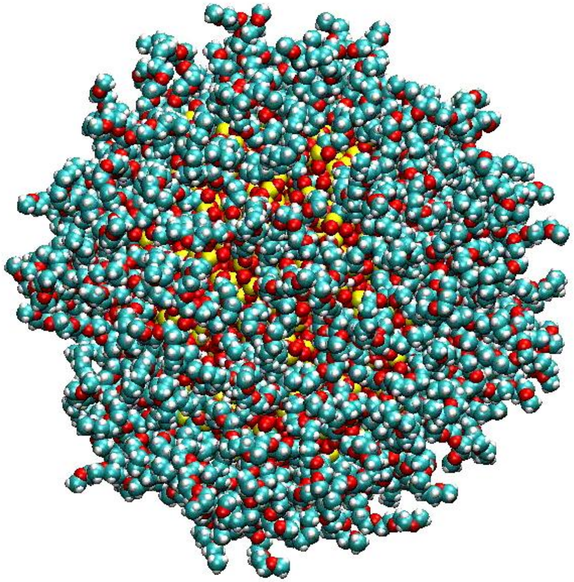
Polyethylene PEO(6) coated 5nm silica nanoparticle in water (3.1 chains/nm^2)

PEO (6)





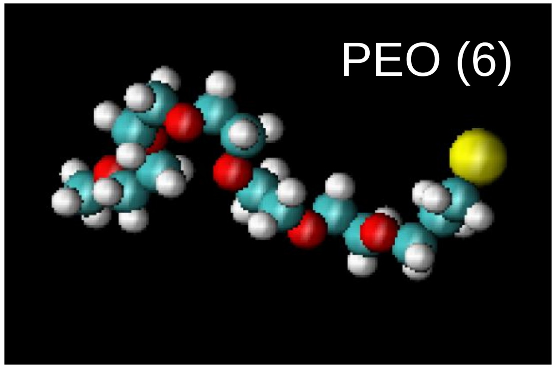
PEO(100)
0.5 chains/nm^2
Aspherical Shape



Lane et al, PRE 79, 050501 (2009); in prep (2011)

Molecular Dynamics Simulations

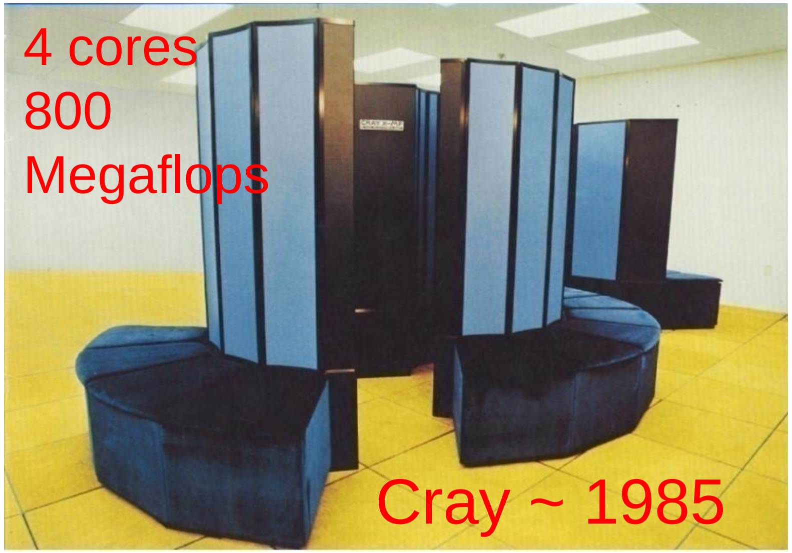
- 4×10^5 – 7.2×10^7 atoms
- van der Waal, bond, bending, torsional interactions
  - -*ab inito* quantum chemistry based
- Time step 1fs - runs 5 -100ns
- OPLS force fields
- TIP4P H_2O (fix shake for bonds/angles)

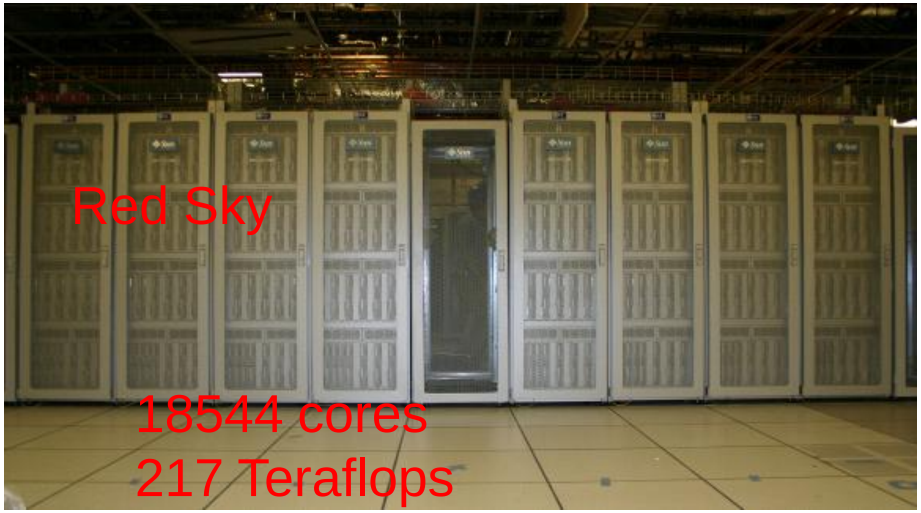


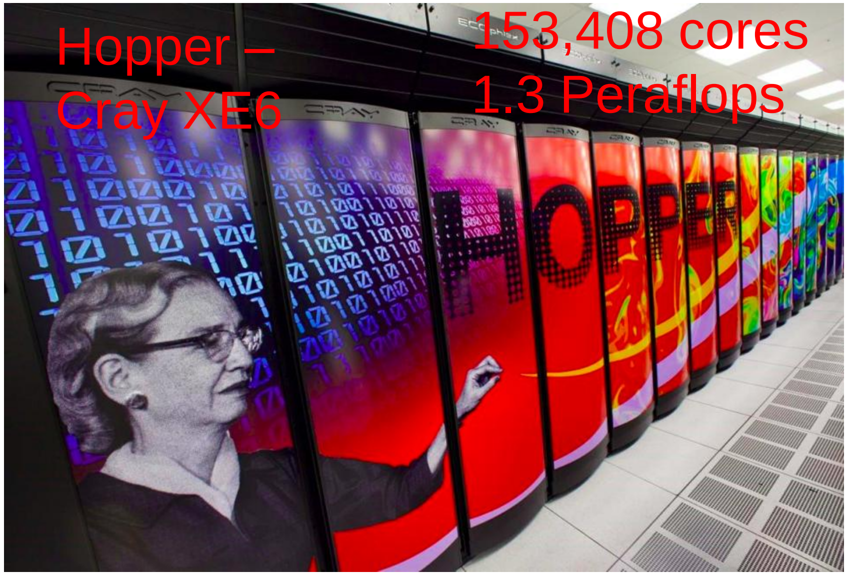
- Systems
  - – PEO coated Silica in H_2O
  - – Alkanethiol Au in H_2O and decane

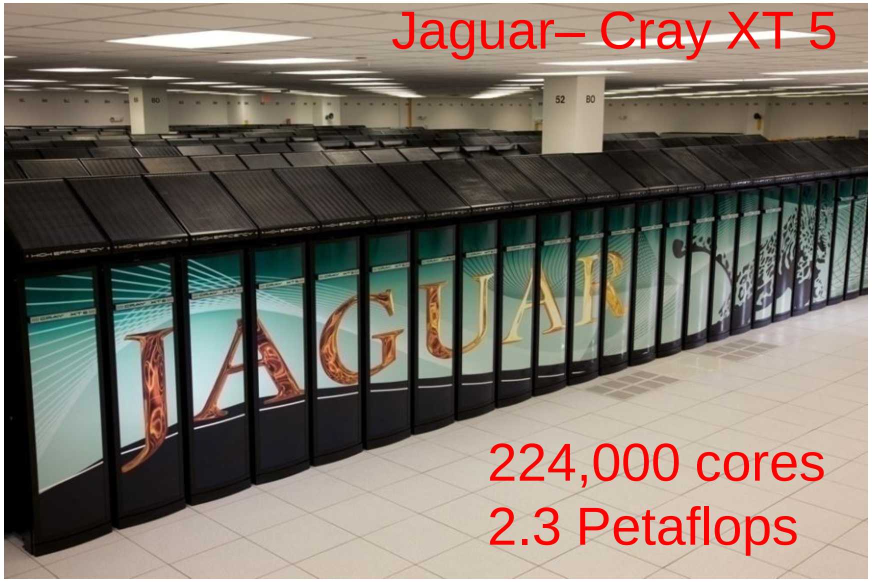
- LAMMPS Commands
  - –Nanoparticle core rigid (fix rigid/nve)
  - –Equilibrate Solvent – make hole (fix indent sphere)
  - –rRESPA (run_style respa)

Toys for the Simulator

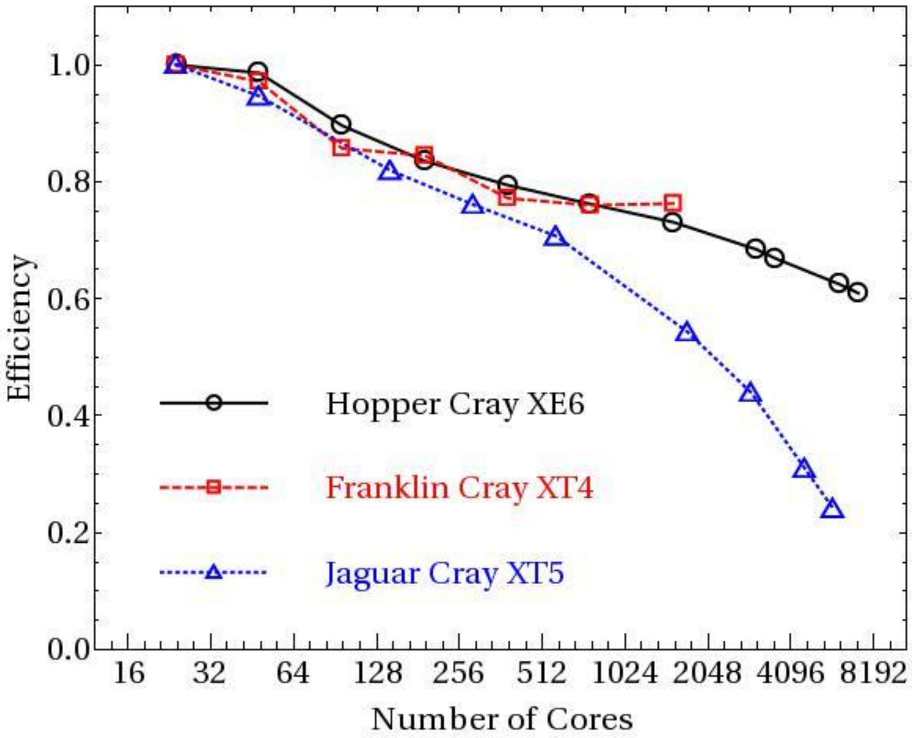








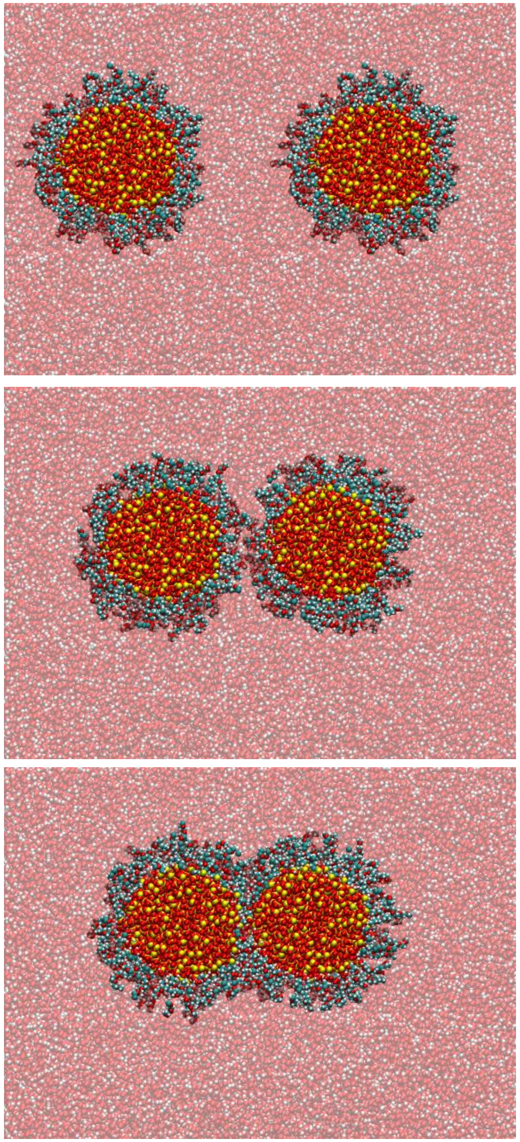
LAMMPS Benchmarks



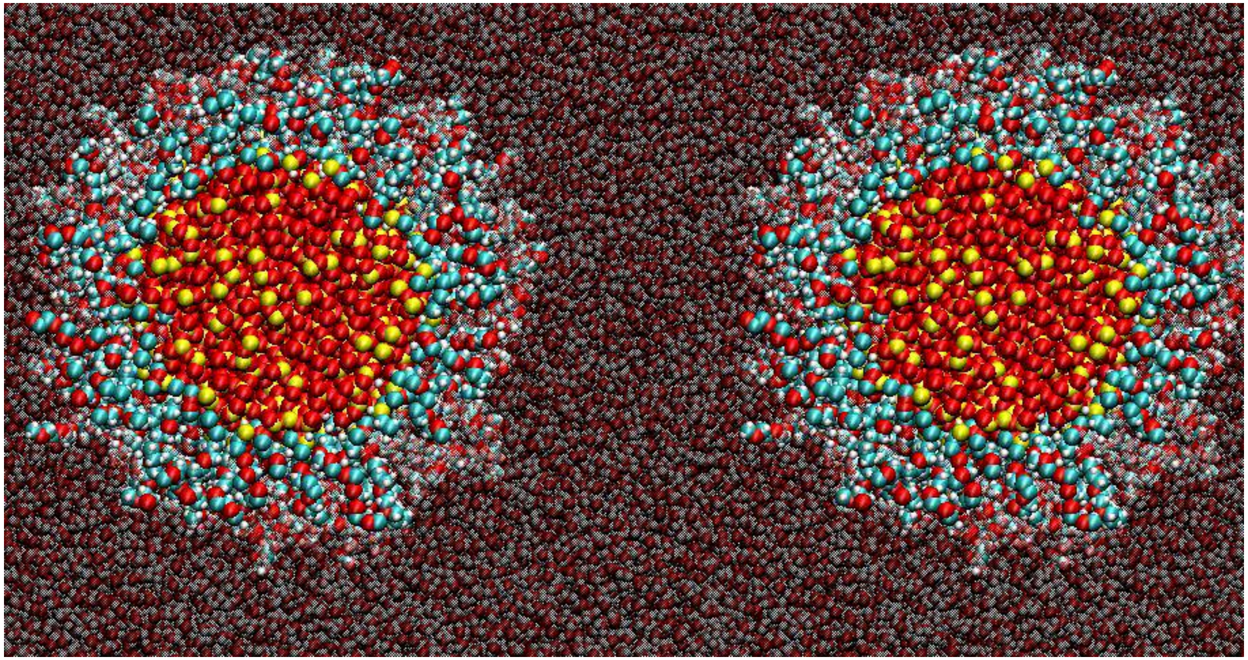
- Strong scaling for a 5.3 million all-atom simulation of 8 nanoparticles in water
- run_style respa –k-space every 4th step
  - Improved efficiency
  - 30-40% speedup over run_style verlet
- Sweet spot ~ 512-2048 cores
- More than 4096 cores scaling becomes very inefficient
  - XT5 – wall clock increases with increasing number of cores

- Scientific output limited - 0.5-0.7ns/day on 2048 cores with present implementation of PPPM
  - 1D FFT's limit total number of cores

Interactions between Nanoparticles



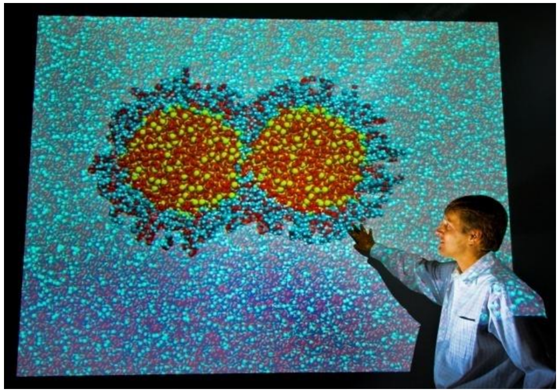
- Determine velocity independent (solvation) and velocity dependent (lubrication) forces
  - -chain length, nanoparticle size/shape, coverage
- Integrate into coarse-grained model

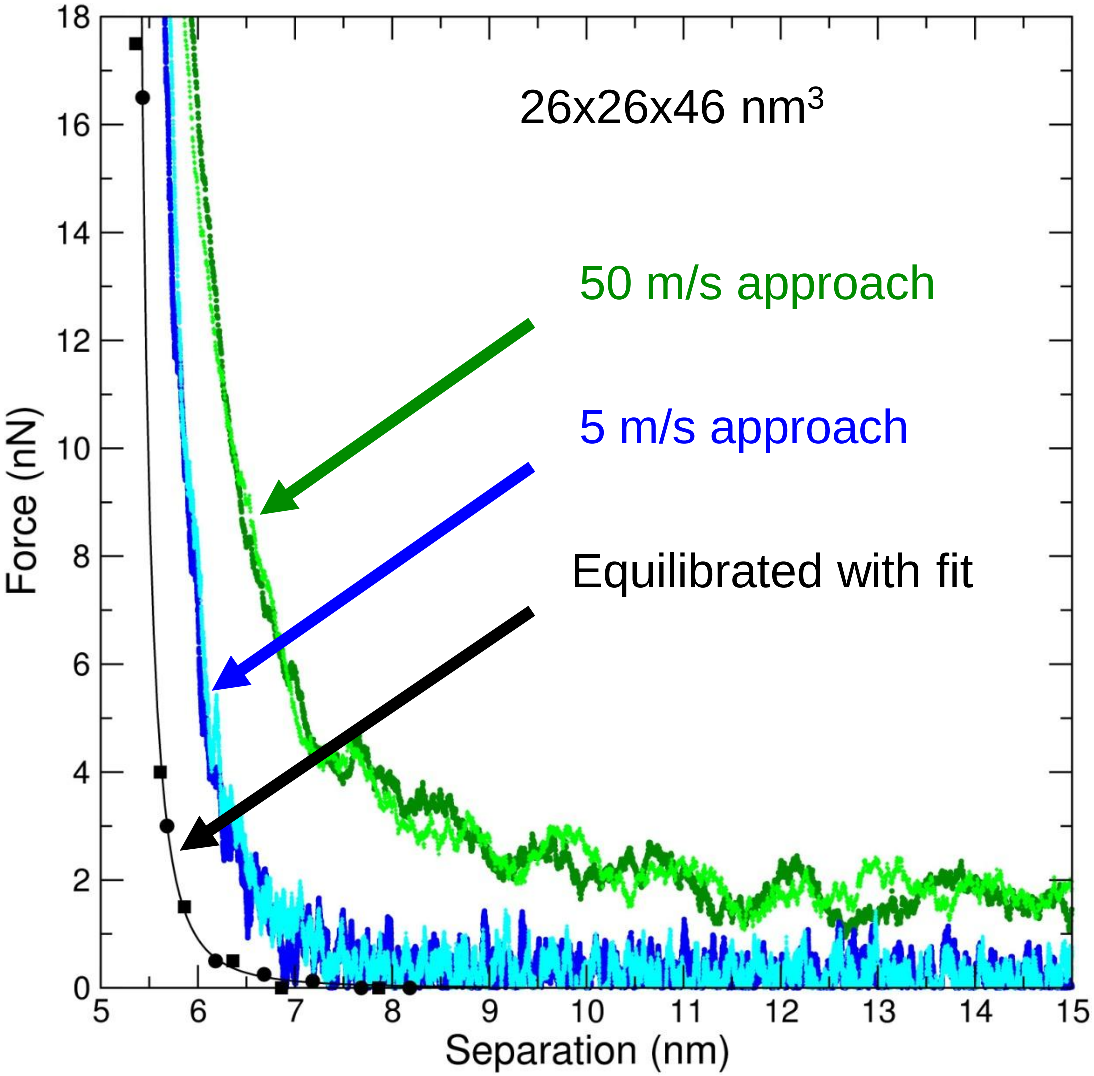


Lane et al, Phys. Rev. E 79, 050501(R) (2009); Ismail, Lane, Grest, in prep.

Force between Silica Nanoparticles

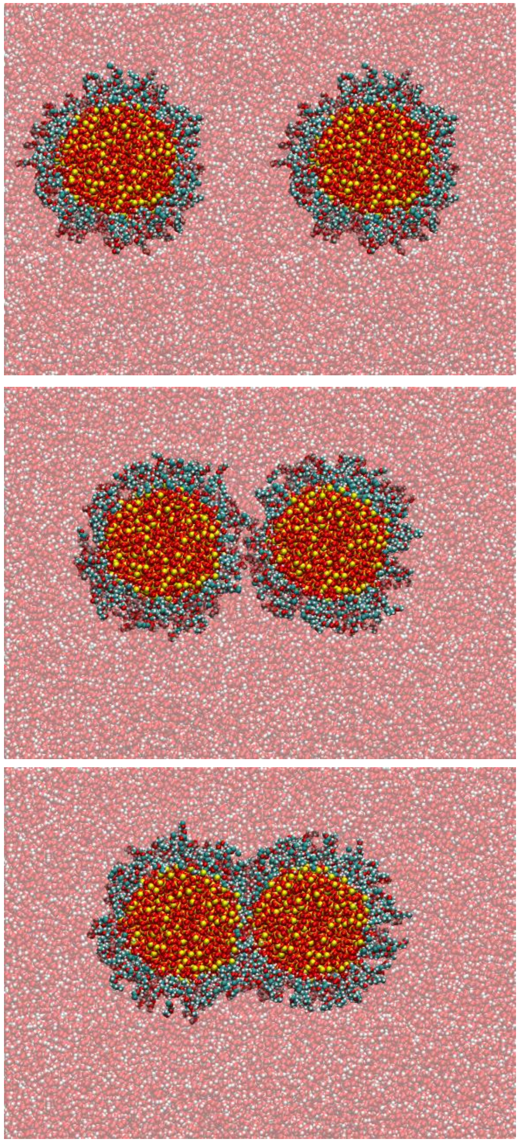
- Stokes drag at large separation with linear velocity scaling
- Complex mixed response in the separation range of interest (near contact)
- No oscillations in force

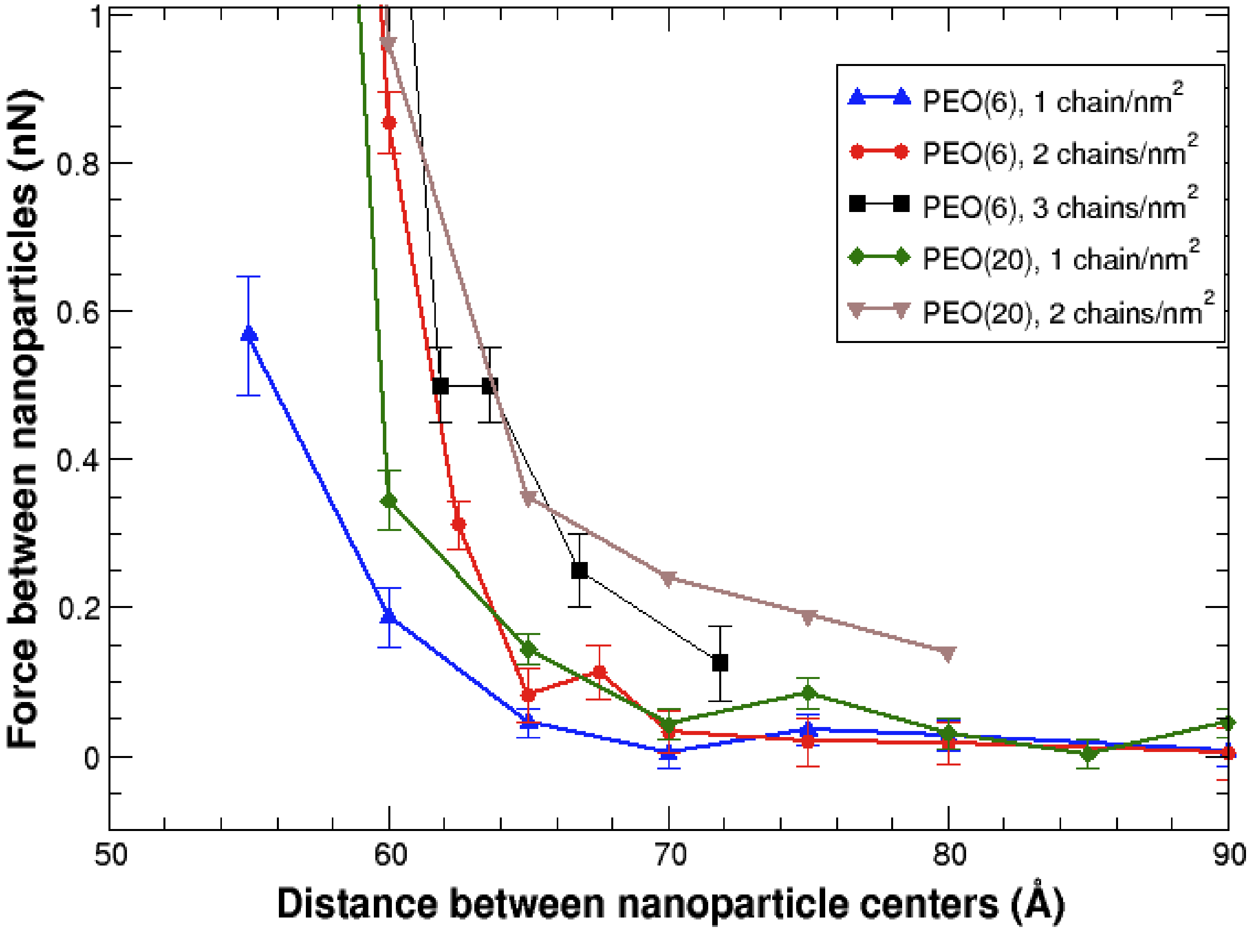




5 nm PEO(6) coated silica NP – 3 chains/nm^2

Interactions between Nanoparticles

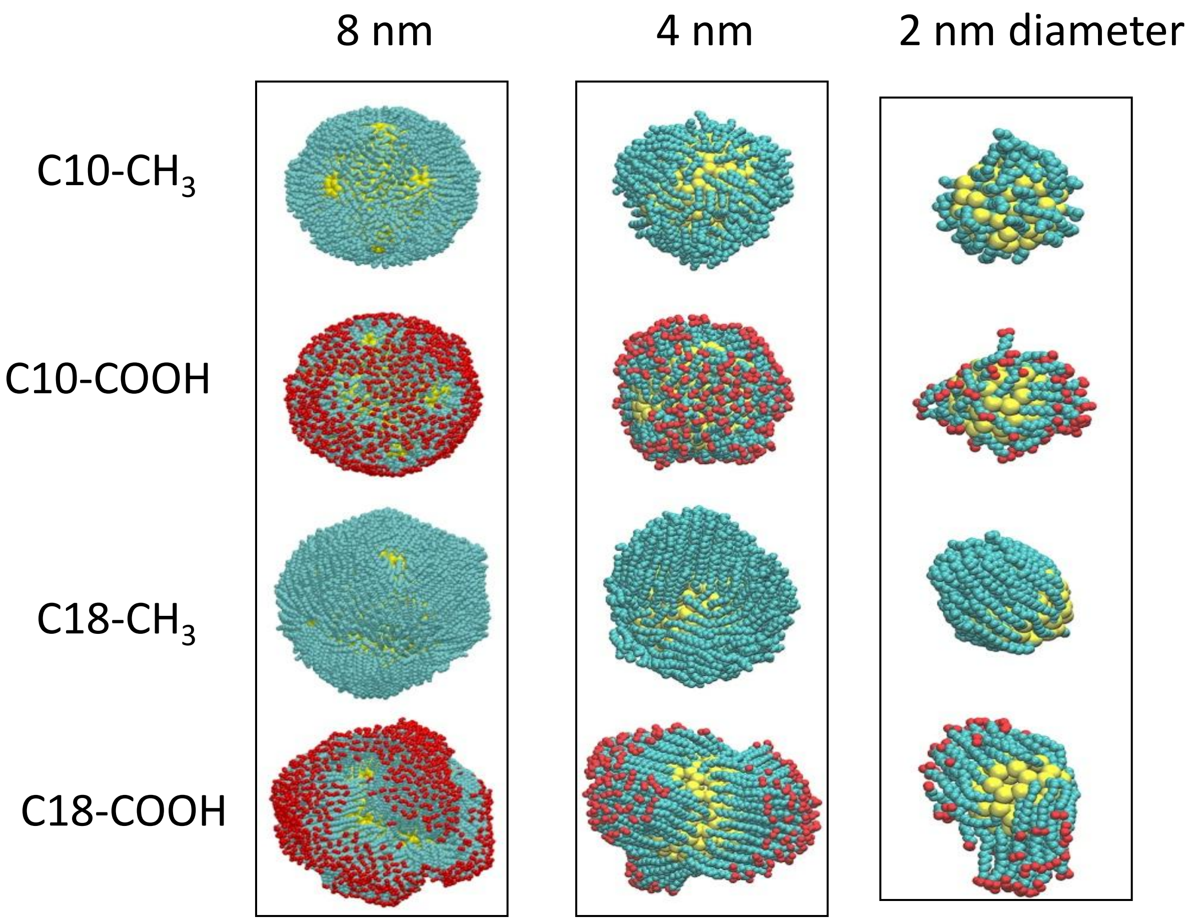


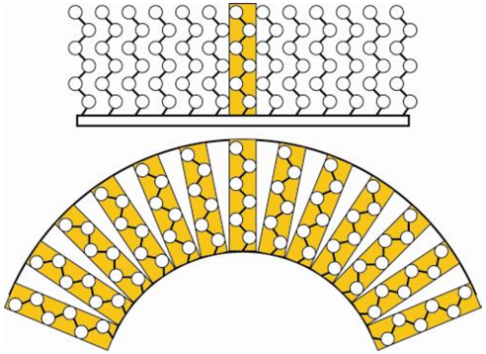


- 300K, thermal fluctuations corresponds to forces < 1 nN

Alkanethiol Coated Au Nanoparticles in Water

Symmetric Coating Leads to Asymmetric Shapes

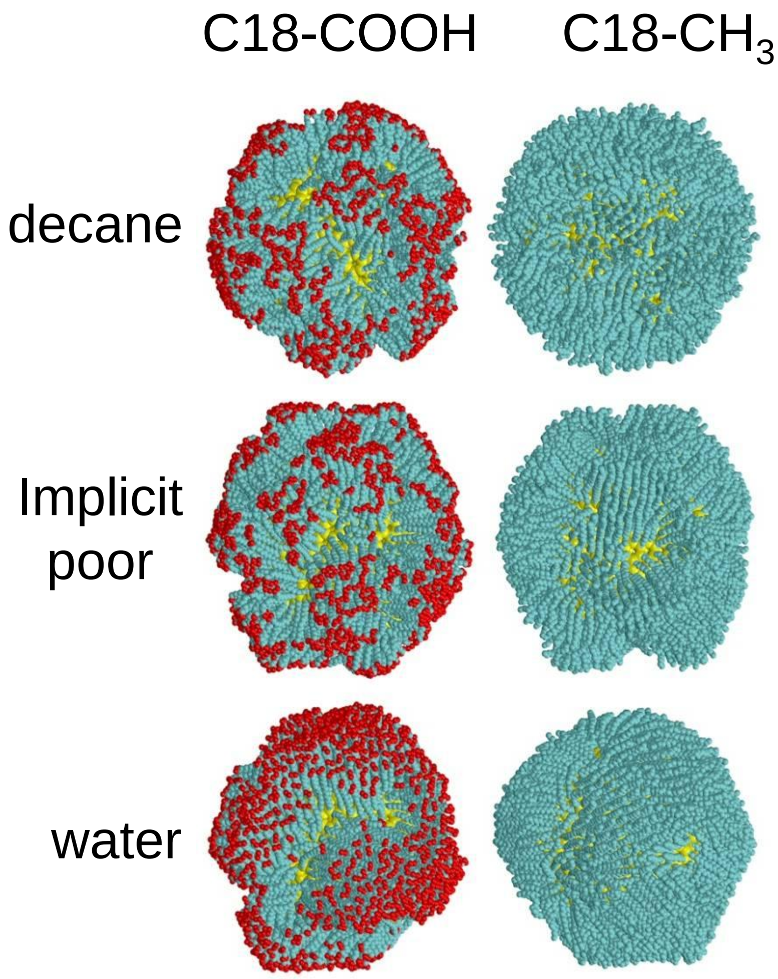




- Geometry is controlling parameter
- Symmetry Changes Change assembly
- Small changes affect structure →change potential activity

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

Different Solvents

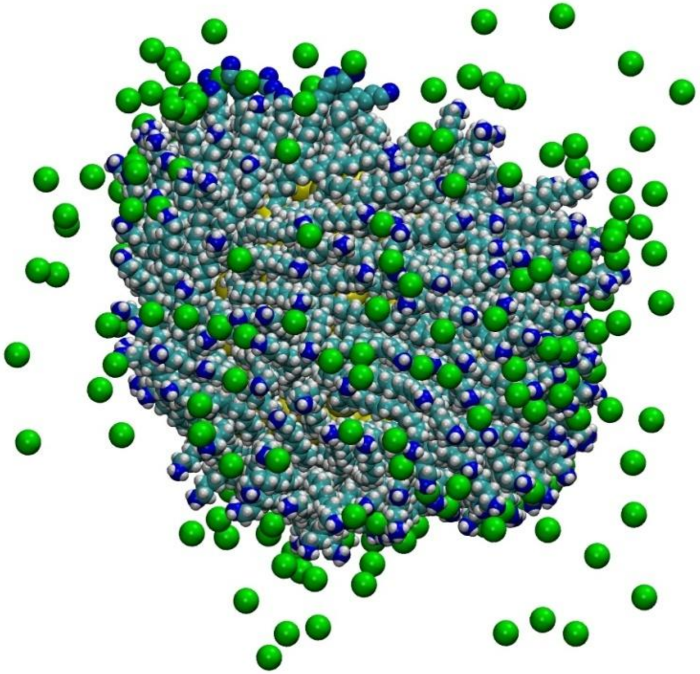


- CH_3 terminated chains behave largely as expected to solvent changes based on hydrophilic/phobic interactions

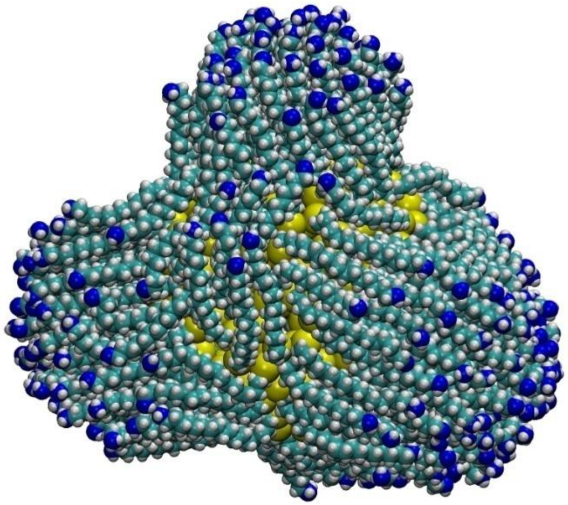
- COOH terminated chains form small tight bundles unless solvated

- Implicit solvent captures, some but not all features of explicit solvent

Effect of pH – Amine End Groups



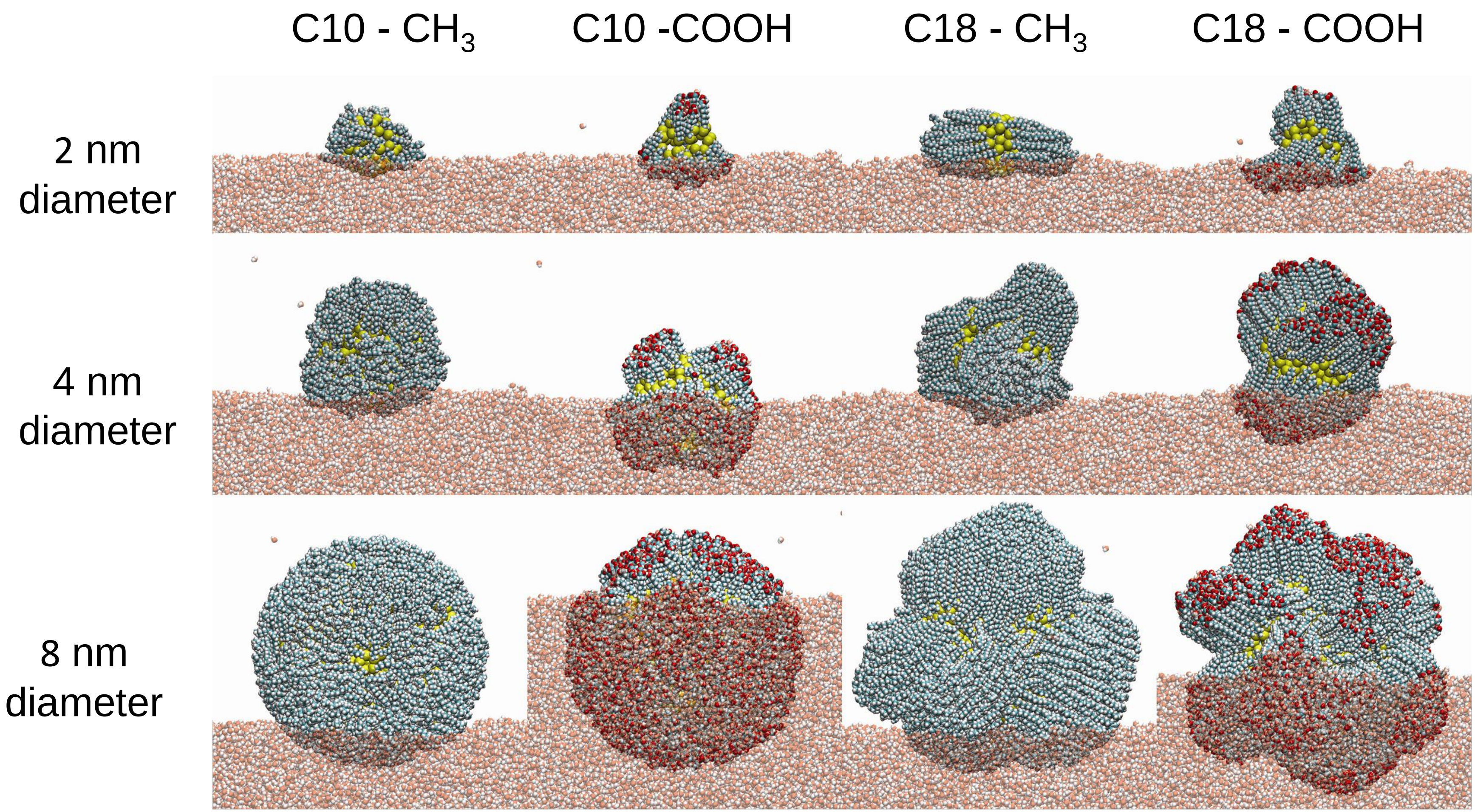
$C18\text{-}NH_3^+ + Cl^-$
Neutral pH



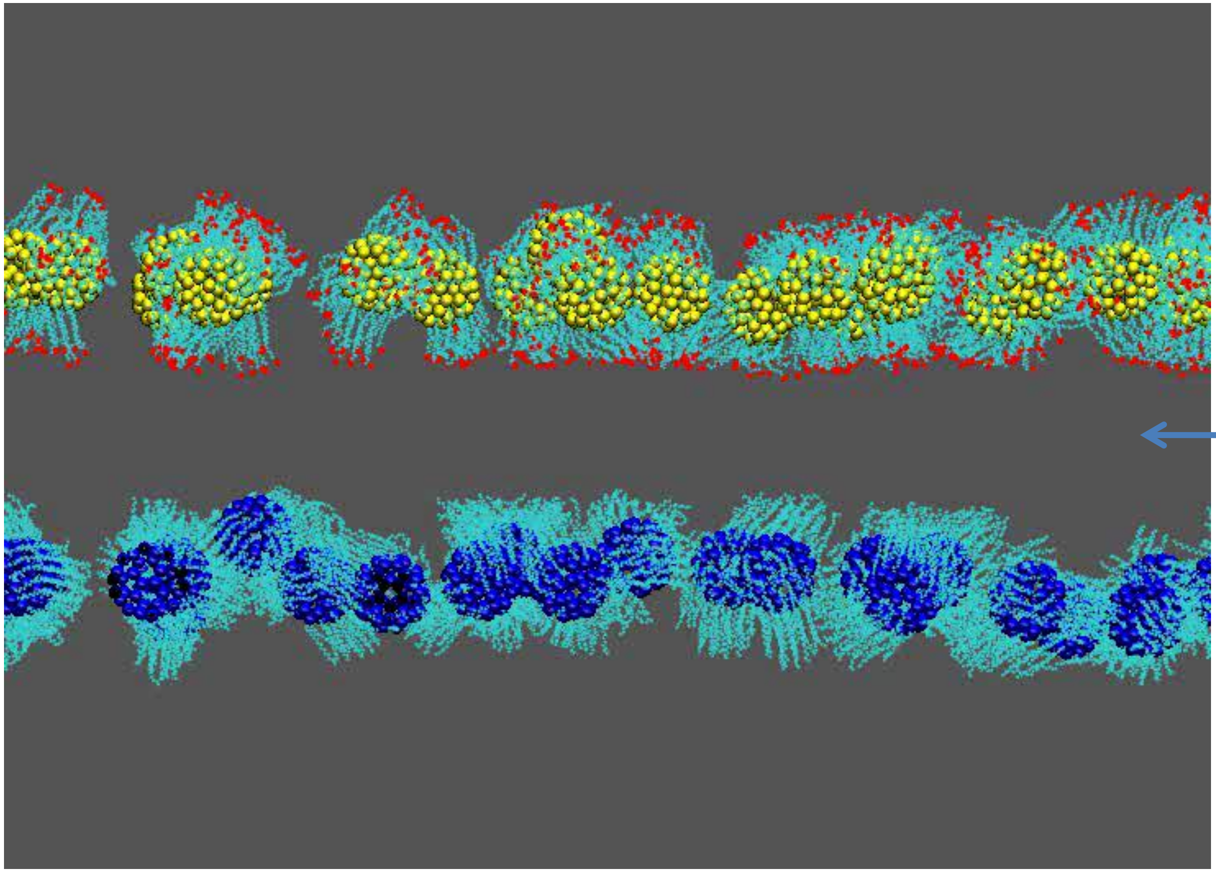
$C18\text{-}NH_2$
High pH

- High pH the nanoparticle is insoluble as NH_2 end group aggregate as found for COOH
- Neutral pH the ligand are dispersed – suggesting nanoparticle maybe soluble

Coated Nanoparticles at a Water/Vapor Interface



Surface Aggregation and Self-Assembly



Water (not shown)

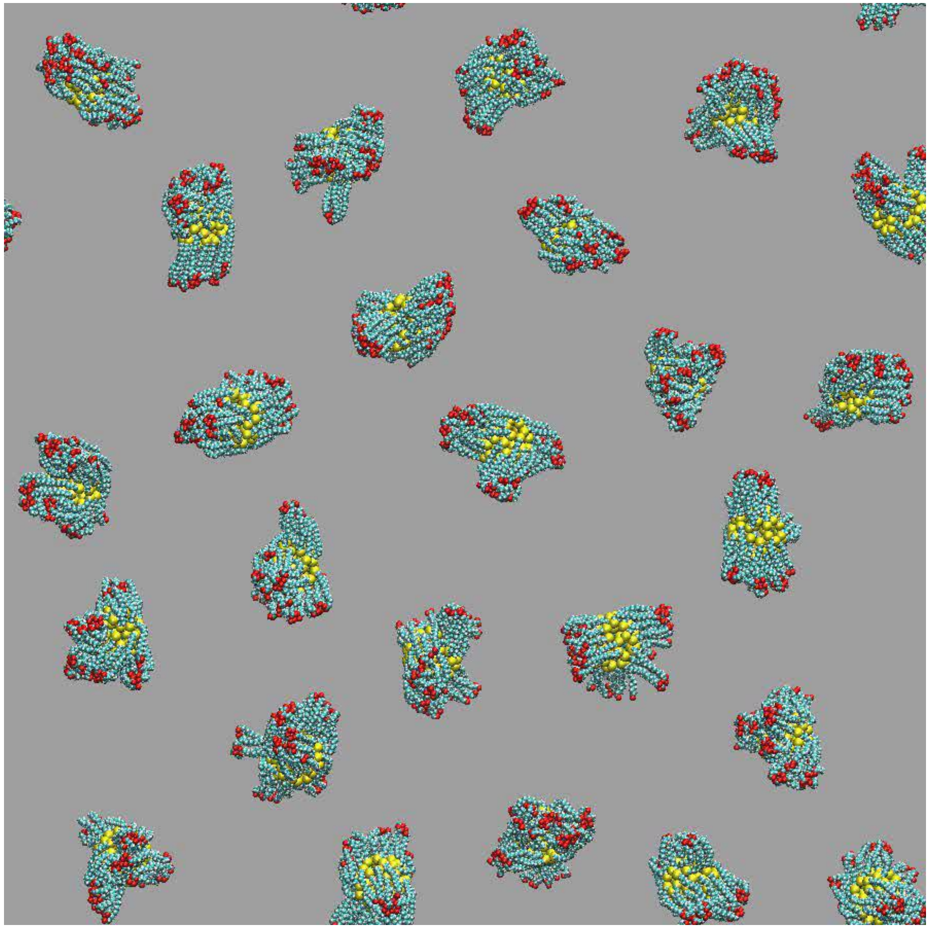
COOH terminal group

(top)

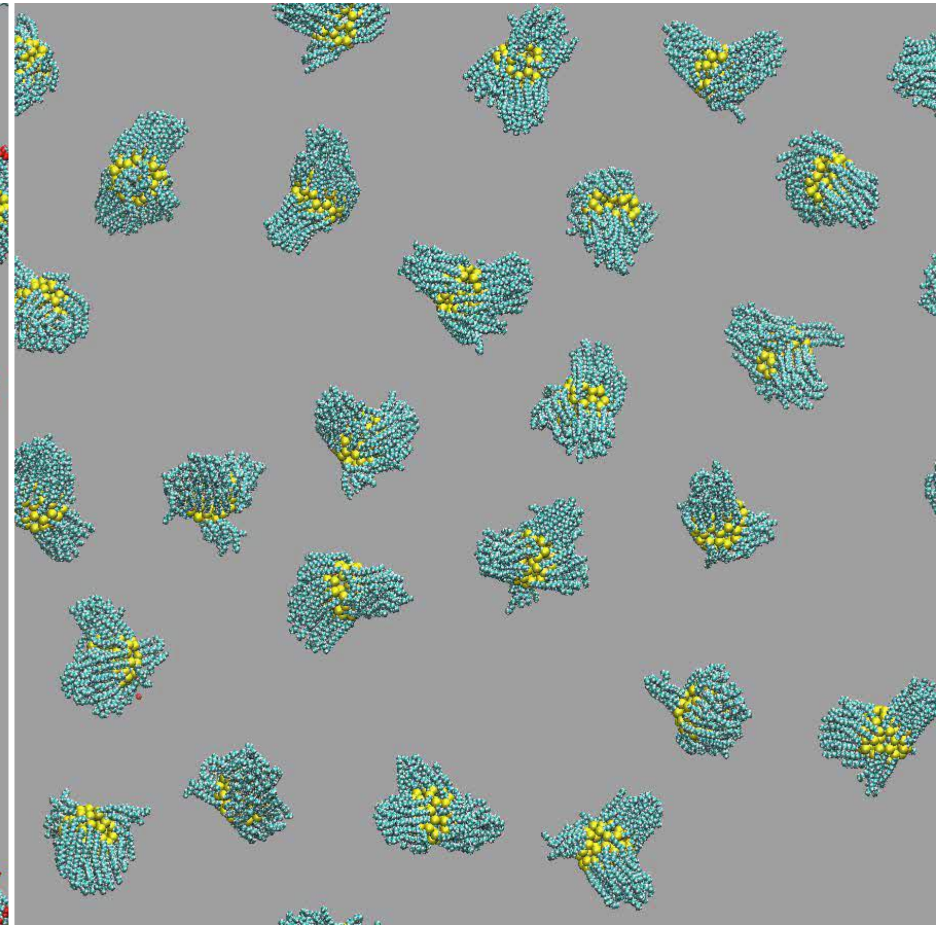
CH_3 terminal group

(bottom)

Surface Aggregation and Self-Assembly



COOH terminal group

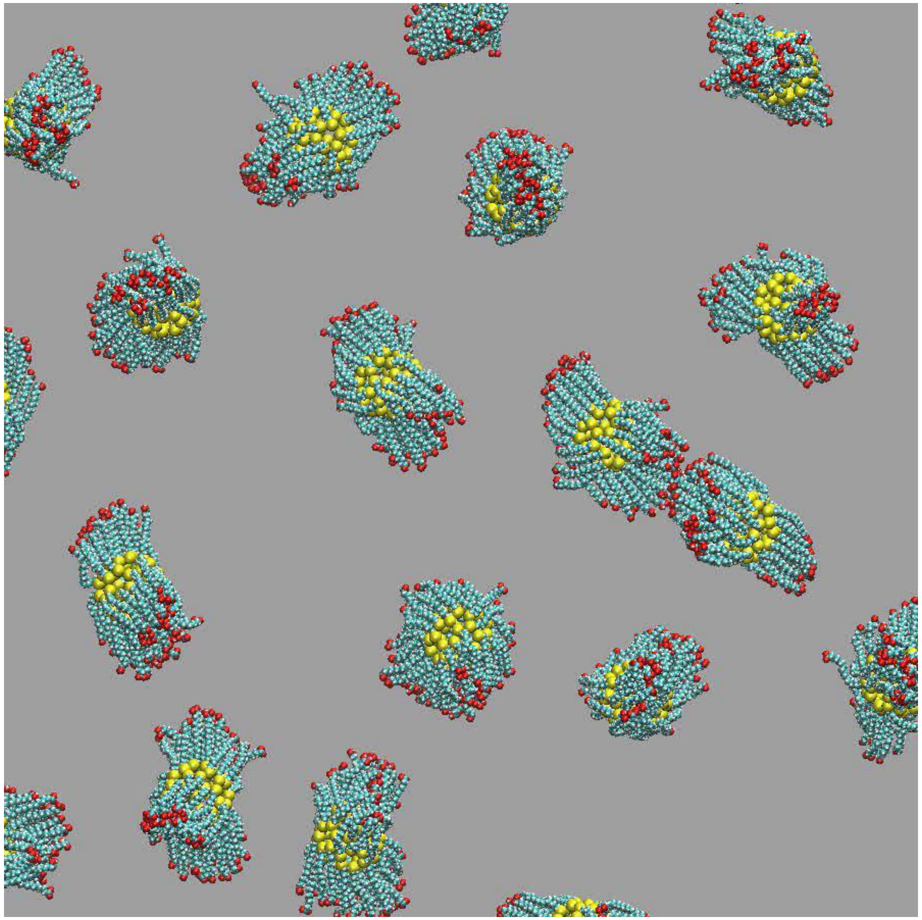


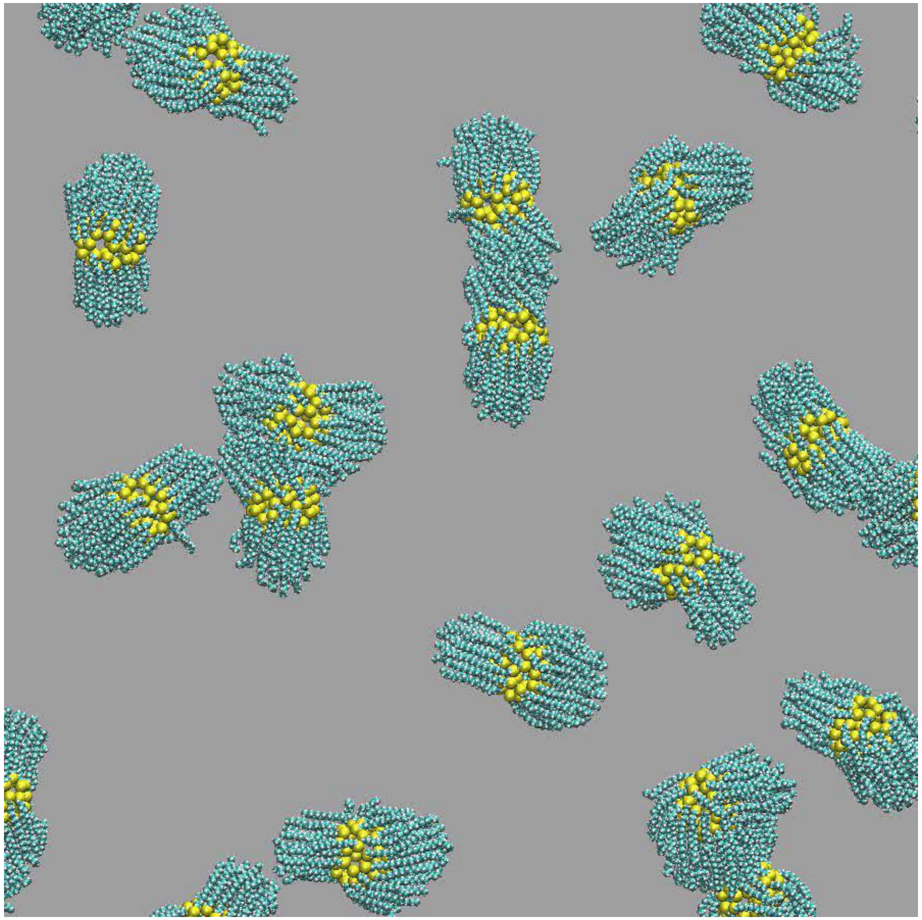
CH_3 terminal group

1,200,000 atoms, ~ 1.1 ns/day on 1152 cores (Red Sky)

~ 2.2 million core hours for 90 ns

Surface Aggregation and Self-Assembly

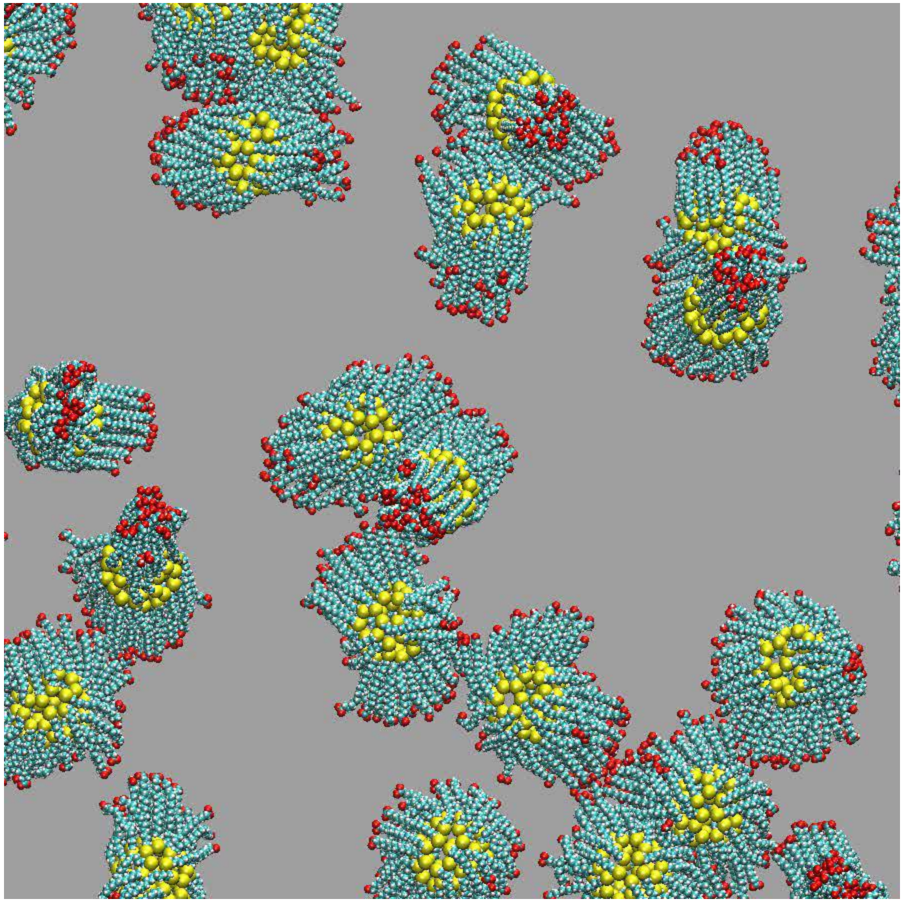


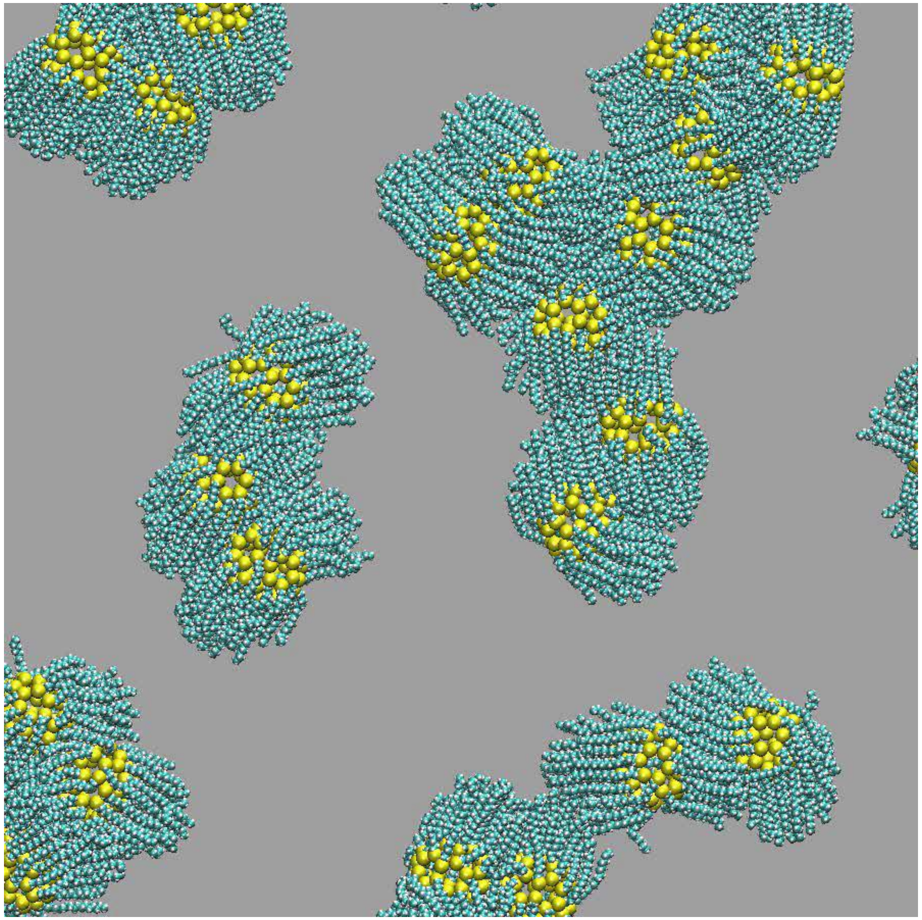


COOH terminal group　　90 ns　　*CH_3 terminal group*

0.8 ns/day on 1920 cores Cray XE6 (Hopper), 1.1 ns/day on 1152 cores Red Sky

Surface Aggregation and Self-Assembly





COOH terminal group

45 ns

CH_3 terminal group

Summary and Conclusions

- For small particles asymmetric coatings are the norm even for perfectly uniform grafting at full coverage
  - –Geometric properties dictate when a coatings' spherical symmetry will be unstable
  - – Chain end group and the solvent play a secondary role in determining the properties of surface patterns

- Water/vapor interface significantly distorts and orients the particle coatings

- Asymmetric and oriented coatings are expected to have dramatic effects on the interactions between NPs and strongly influence self-assembly at surfaces

Acknowledgements

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– Christian Lorenz (King's College)

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– DOE – ALCC grant 40 million core hours on NERSC/ORNL

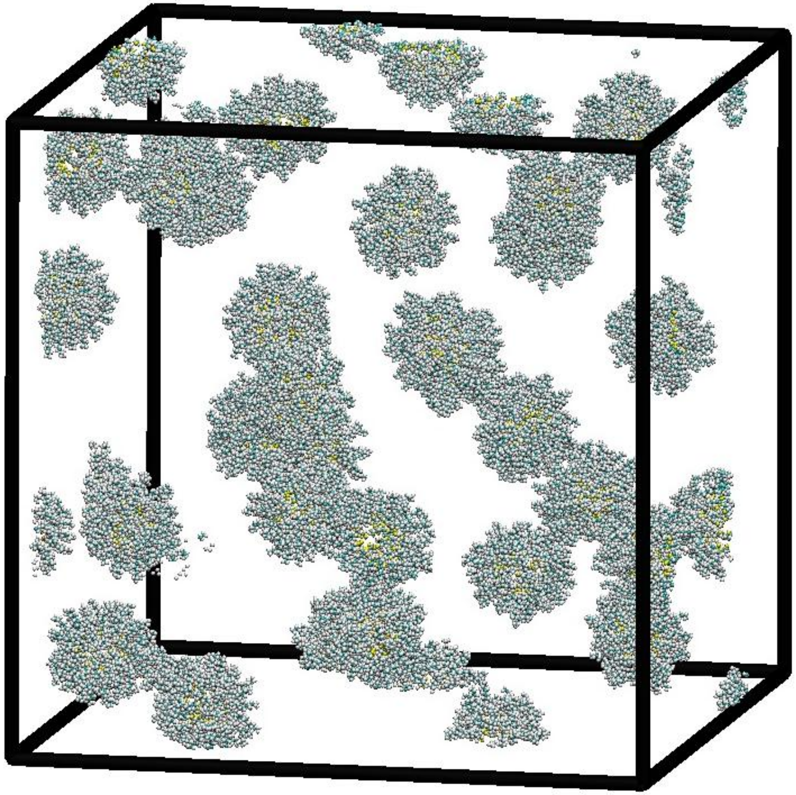
Computers:

– New Mexico Computing Applications Center
– Sandia's Red Sky
– NERSC Hopper XE 6
– ORNL Jaguar Cray XT 5

Alkanethiol Au Nanoparticles in Solution

From a Single Particle to a System:

32 coated
nano particles in
decane (not shown)



100 ns – 40 days on 512 processors