Coated nanoparticles in solvents and at interfaces

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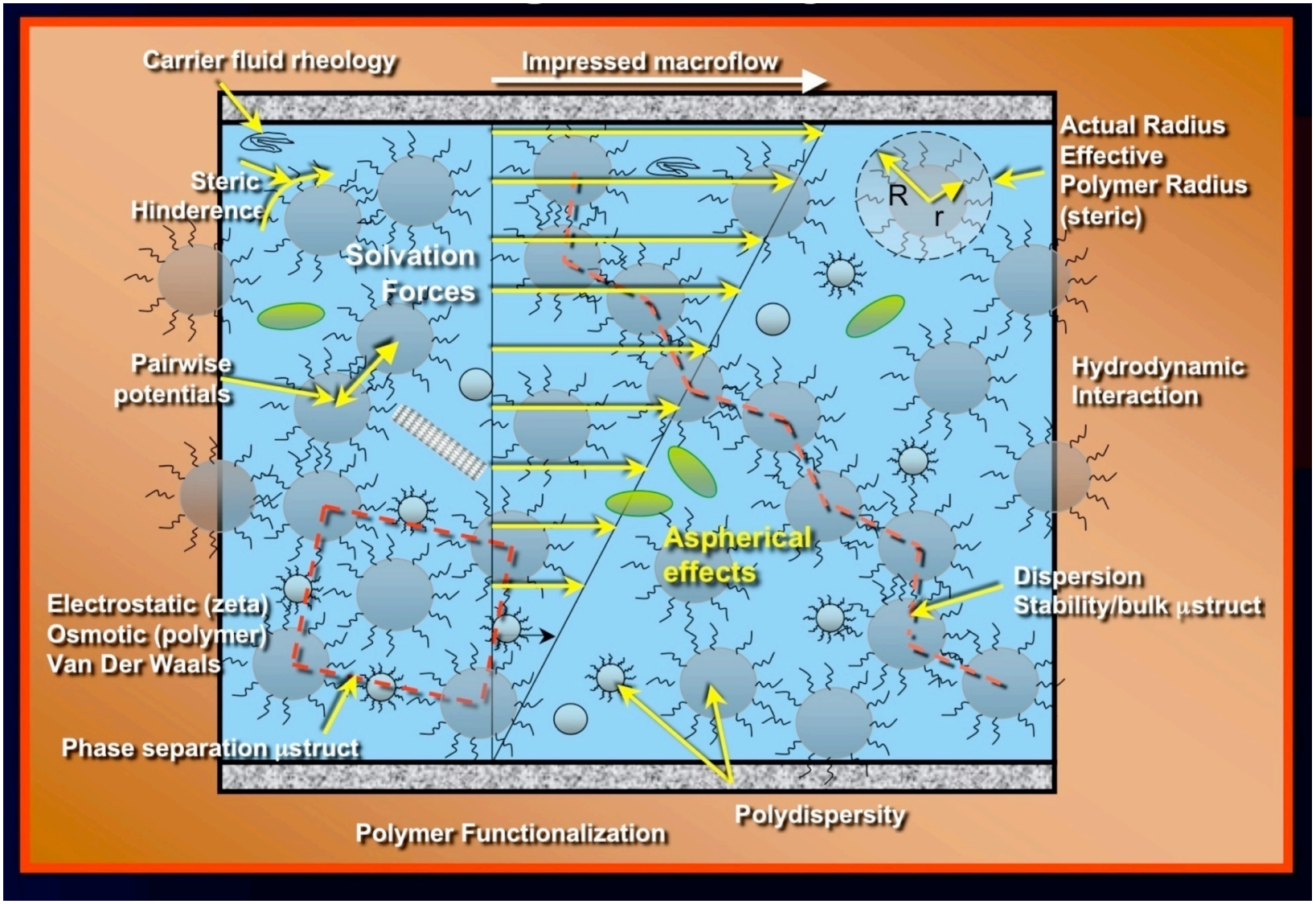
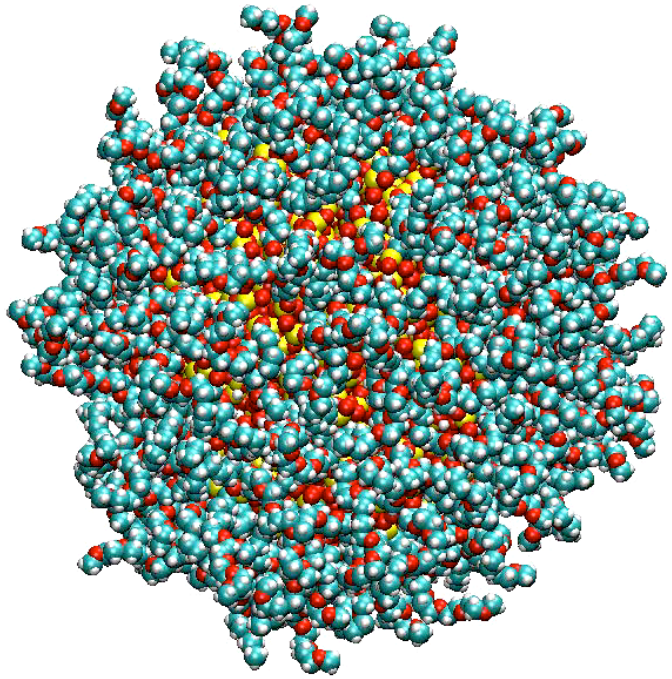
Problem description



Courtesy of P. R. Schunk

System details



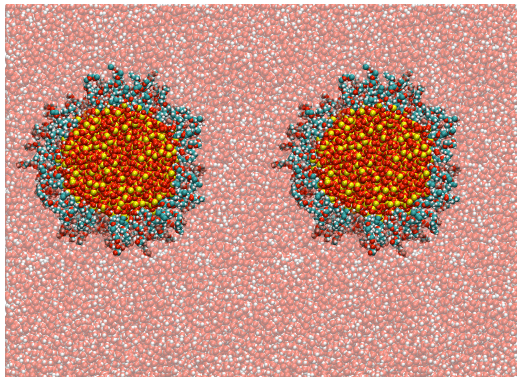
• Polyethylene oxide PEO(6) coated 5nm silica nanoparticle in water (3 chains/nm^2)

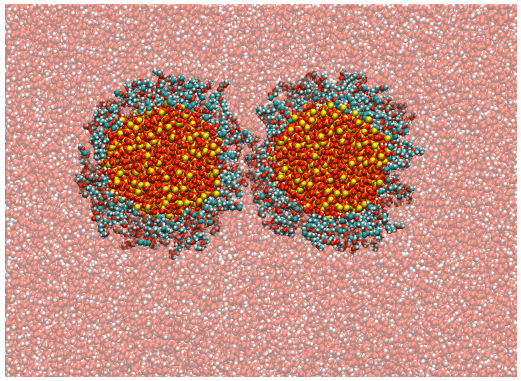
Lane et al, PRE 79, 050501 (2009)

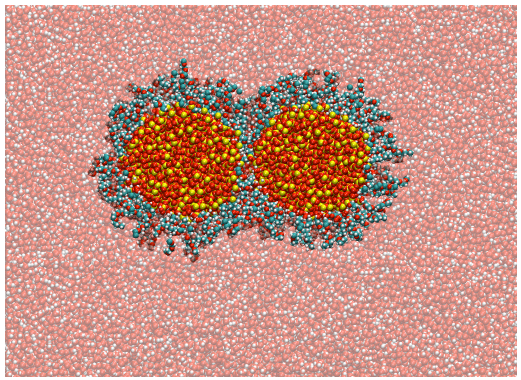
Amorphous silica particles
– 5 nm diameter
– Treated as rigid objects
PEO chains
– ca. 240 per 5 nm particle
– Attached at OH sites
Water solvent used with PEO

MD run details
– T = 300 K
– 10 Å cutoff on pair potentials
– 4x10^5 – 7.2x10^6 atoms
– Timestep 1fs – runs of 5-10ns

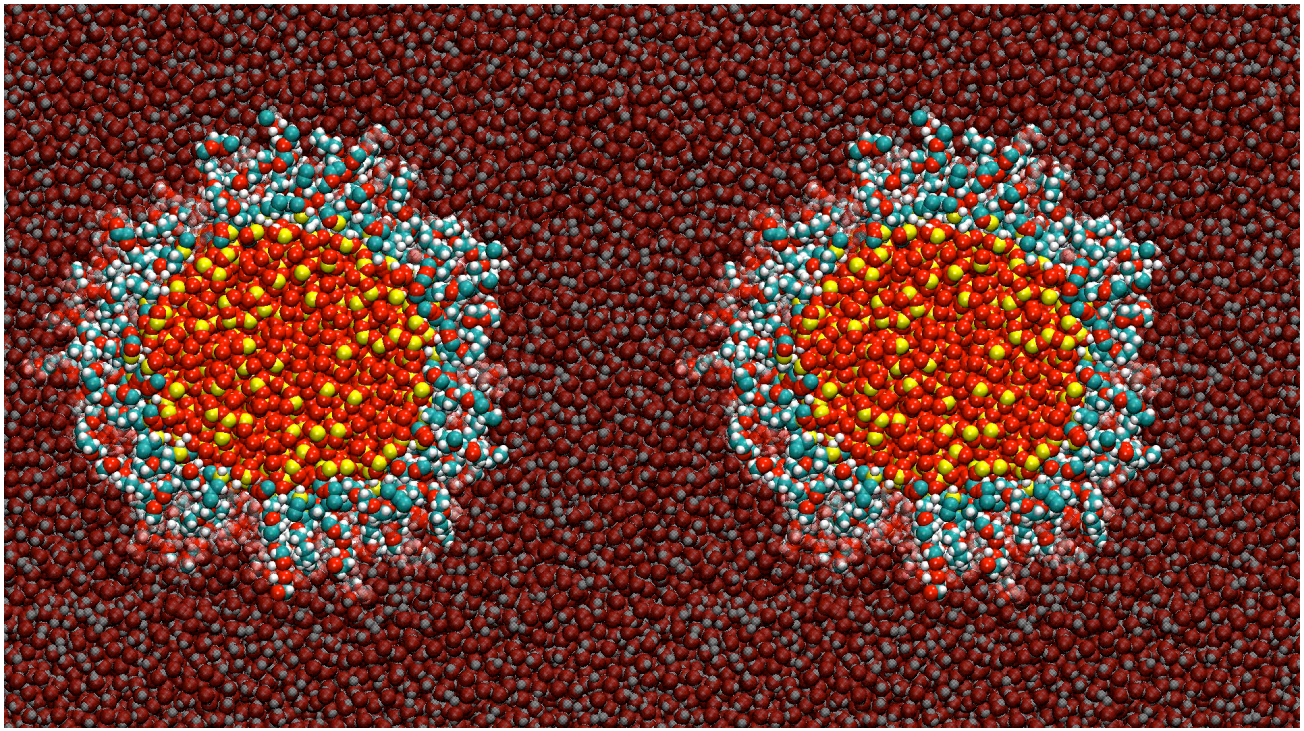
Interactions between nanoparticles



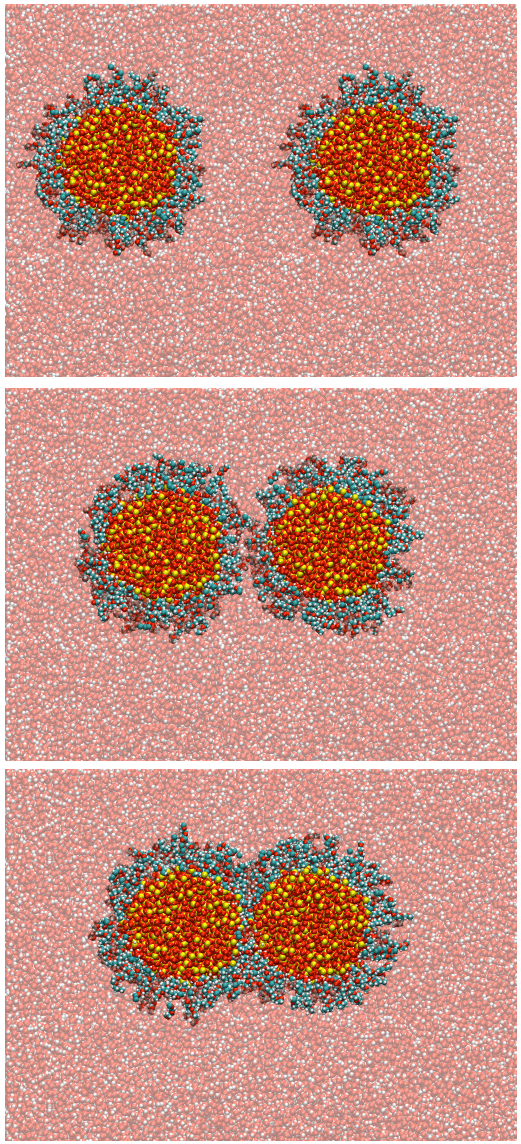


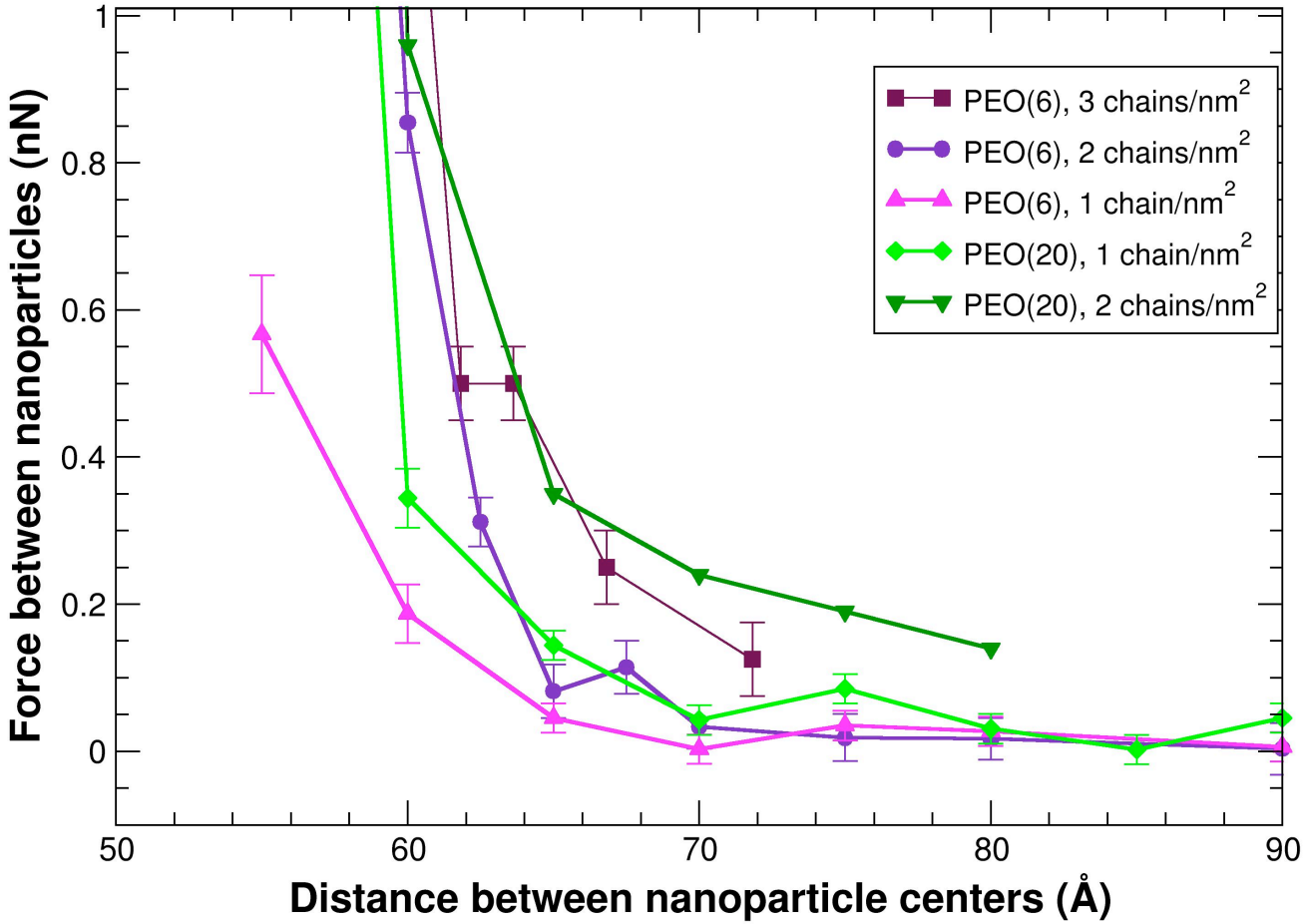


- Determine velocity independent (solvation) and velocity dependent (lubrication) forces
  - -chain length, nanoparticle size/shape, coverage
- Integrate into coarse-grained model

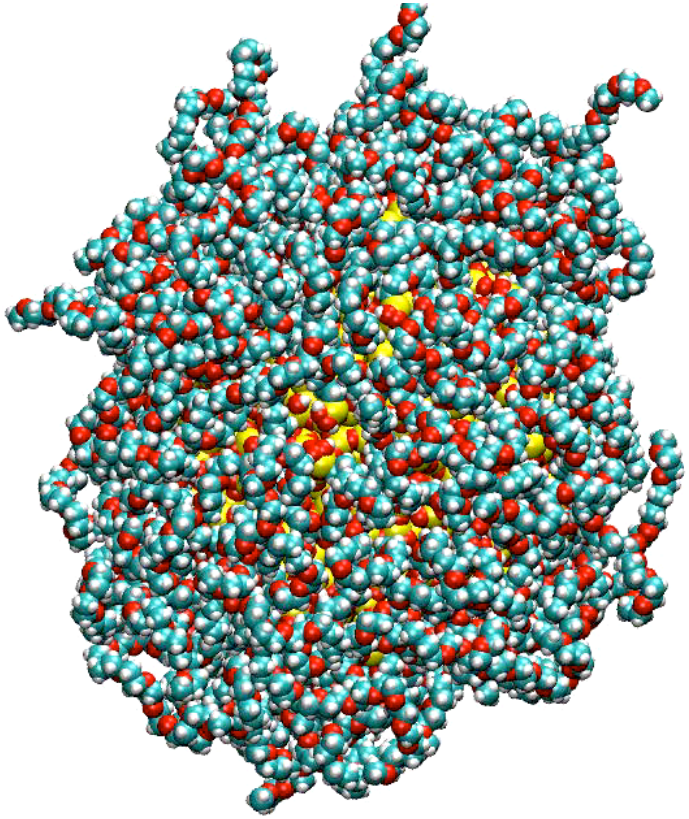


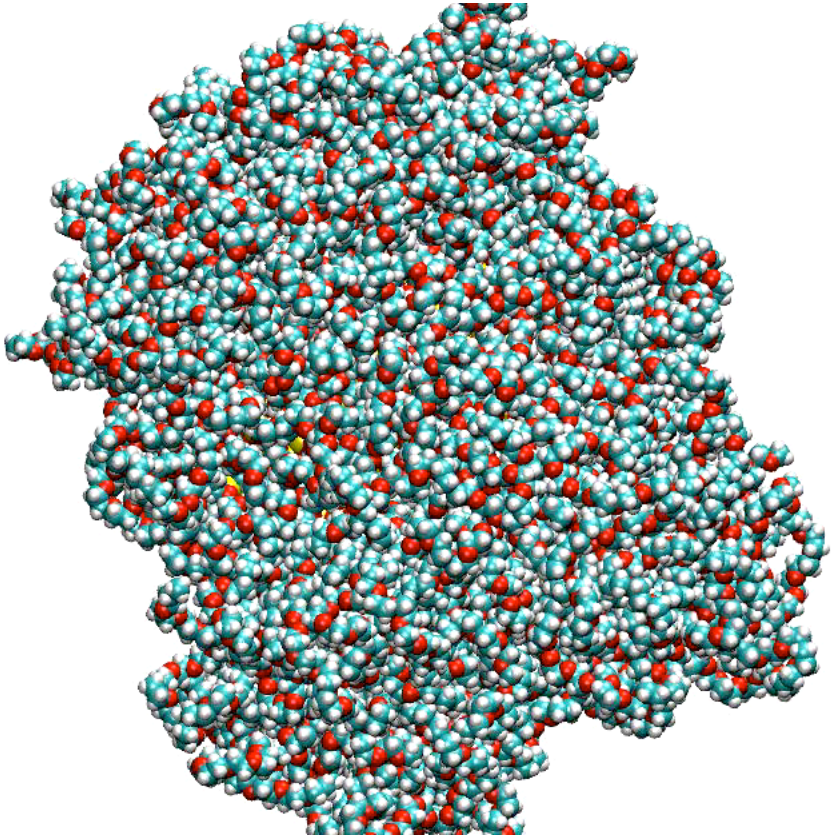
Interactions between nanoparticles





PEO-coated silica NP in water

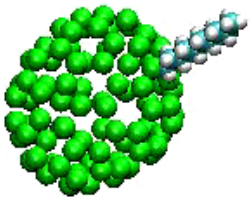


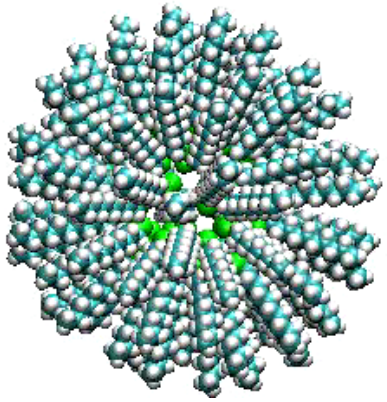


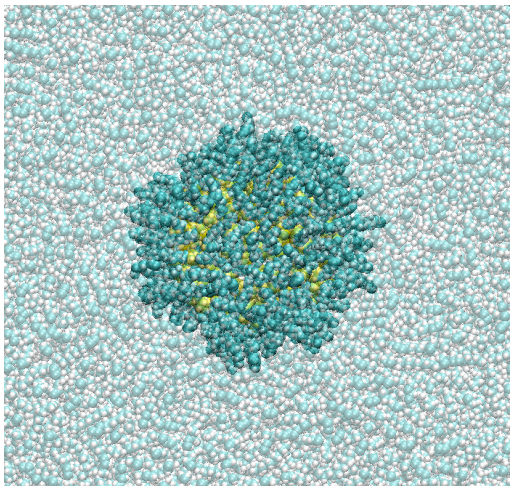
- PEO(20), 1.0 chains/nm^2
- PEO(100), 0.5 chains/nm^2

- Mitra et al, Langmuir 19, 8994 (2003) – exp. - PEO(100), 0.2chains/nm^2

Constructing model Au-thiol nanoparticles







Fact sheet:

2, 4, and 8 nm diameter core with Au implicit

S-$(CH_2)_9$-X and S-$(CH_2)_{17}$-X where X = CH_3 or COOH

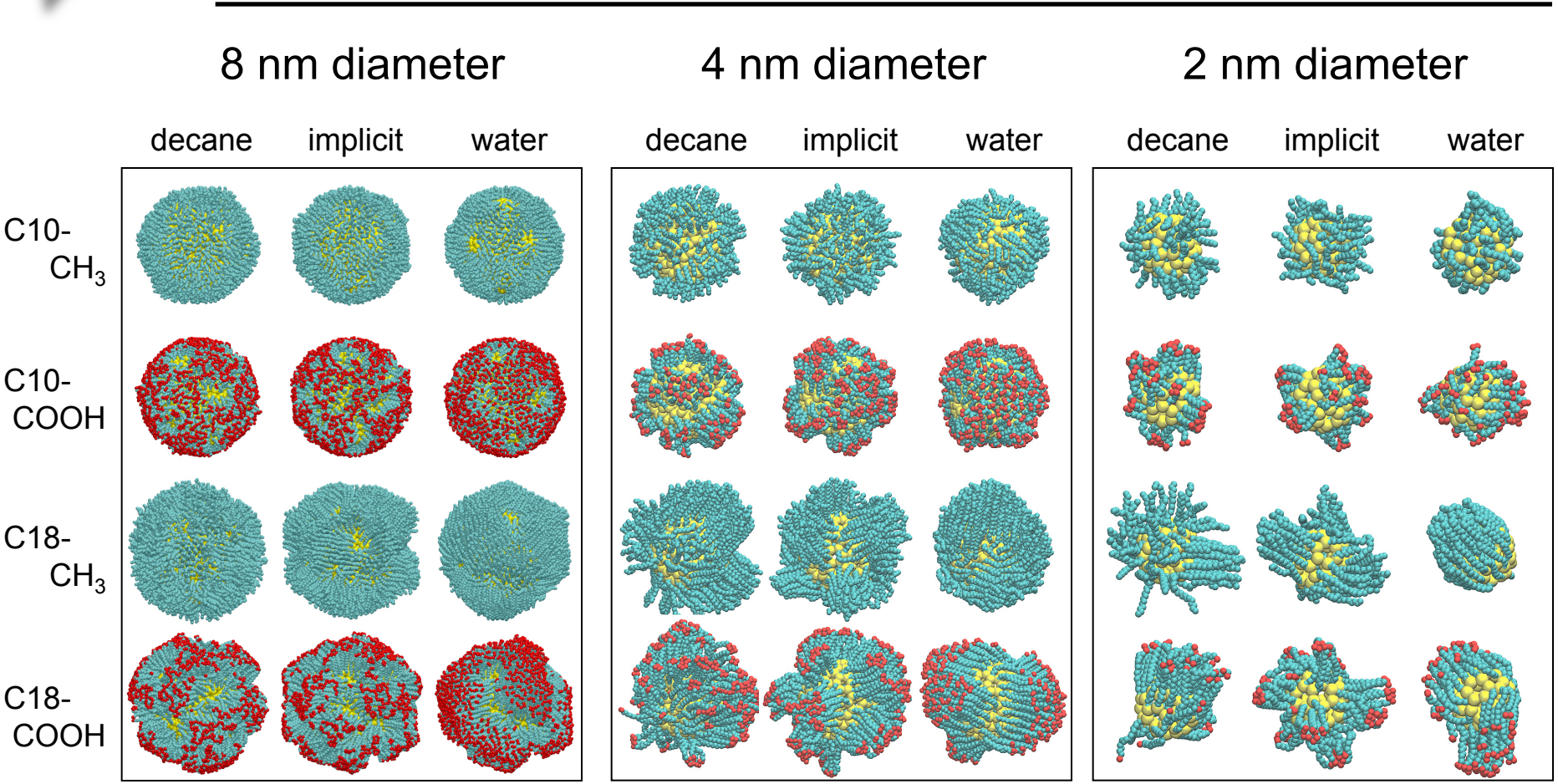
Simple structure of 60, 240 and 960 rigid grafting sites from fullerene structure

Constant coverage density of 21 $Å^2$ per chain

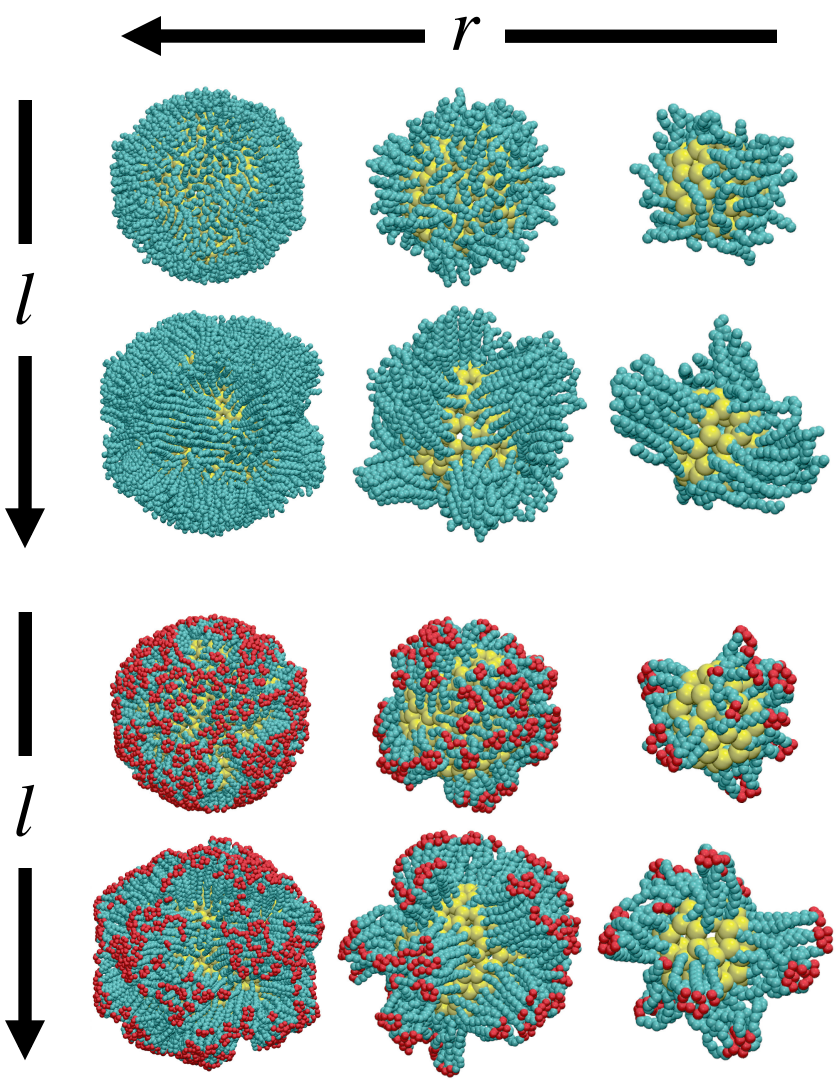
- **D. Dunphy, UNM/Sandia personal communication**

Place each in decane, water and Brownian solvents.

2 to 8 nm coated nanoparticle cores



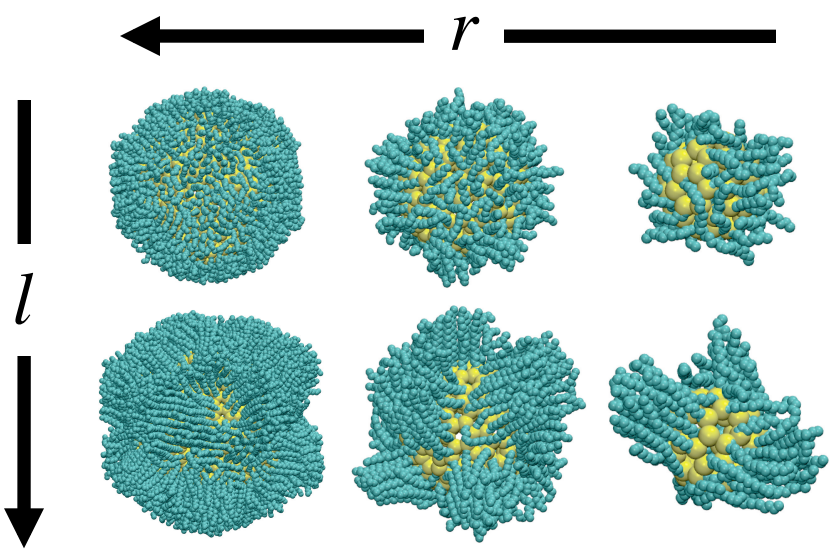
Geometry as a control parameter



- Particle size, r
- Chain length, l

- Change in free volume per chain

Geometry as a control parameter

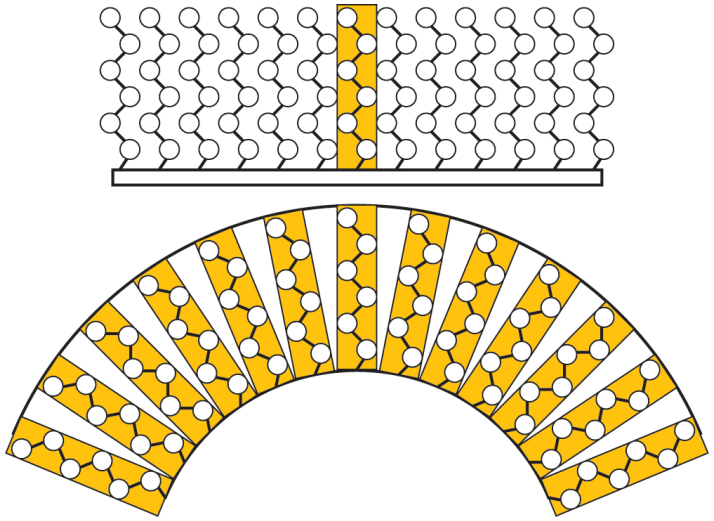


- Particle size, r
- Chain length, l

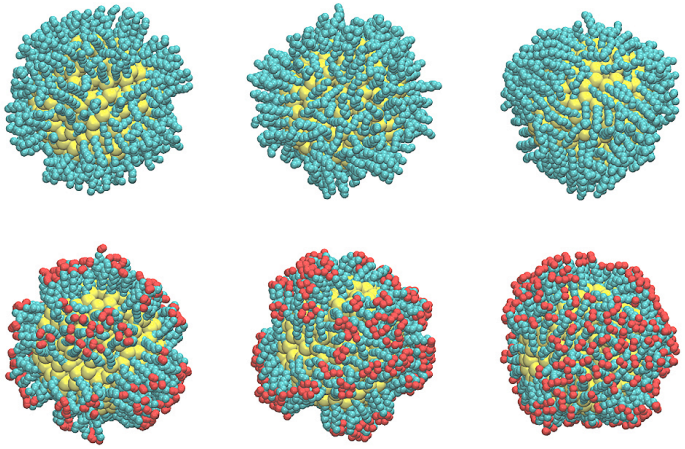
- Change in free volume per chain

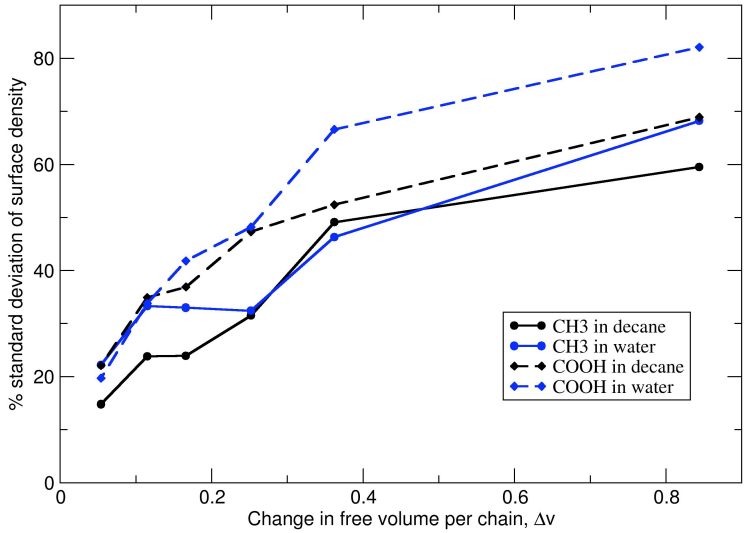
$$\Delta v = \frac{V_{\text{sphere}} - V_{\text{flat}}}{\#\text{ of chains}} = \frac{1}{3\sigma}\left[\frac{l^3}{r^2} + 3\frac{l^2}{r}\right]$$

D	Chain	Δv (nm^3)	Decane s.d.	Implicit s.d.	Water s.d.
2	S-$(CH_2)_{17}$-CH_3	0.844	59.5%	75.3%	68.2%
4	S-$(CH_2)_{17}$-CH_3	0.362	49.1%	52.5%	46.3%
2	S-$(CH_2)_9$-CH_3	0.252	31.5%	36.1%	32.4%
8	S-$(CH_2)_{17}$-CH_3	0.166	23.9%	38.7%	33.0%
4	S-$(CH_2)_9$-CH_3	0.115	23.8%	25.2%	33.3%
8	S-$(CH_2)_9$-CH_3	0.054	14.8%	17.4%	22.2%
2	S-$(CH_2)_{17}$-COOH	0.844	68.9%	55.1%	82.1%
4	S-$(CH_2)_{17}$-COOH	0.362	52.4%	59.6%	66.6%
2	S-$(CH_2)_9$-COOH	0.252	47.3%	50.6%	48.2%
8	S-$(CH_2)_{17}$-COOH	0.166	36.9%	42.3%	41.8%
4	S-$(CH_2)_9$-COOH	0.115	34.9%	41.6%	33.8%
8	S-$(CH_2)_9$-COOH	0.054	22.1%	27.6%	19.7%



Effect of mixed-chain termination



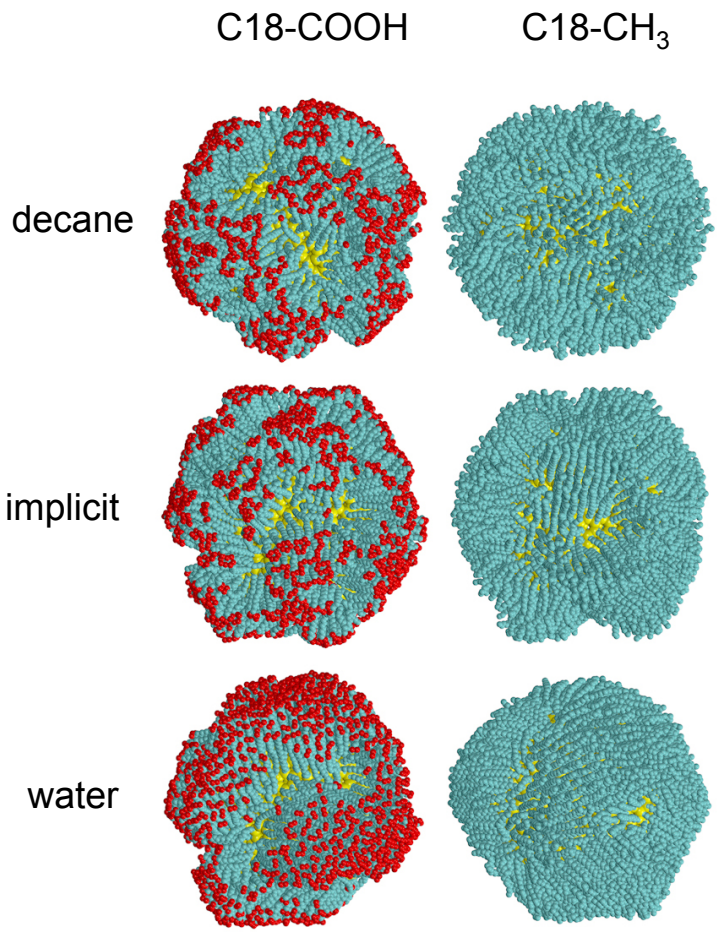


Coating termination is an important secondary variable

Bundling:

- Mixed-chains decreased uniformity in the coating surface
- Mixed chains tended toward small tight bundles unless solvated

Effect of solvent and backbone



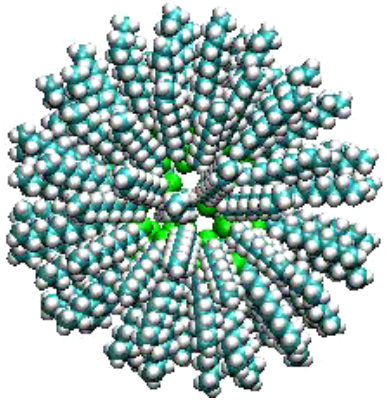
Solvent quality is another important secondary variable

Homogeneous chains behaved largely as expected to solvent changes based on hydrophilic/ phobic interactions

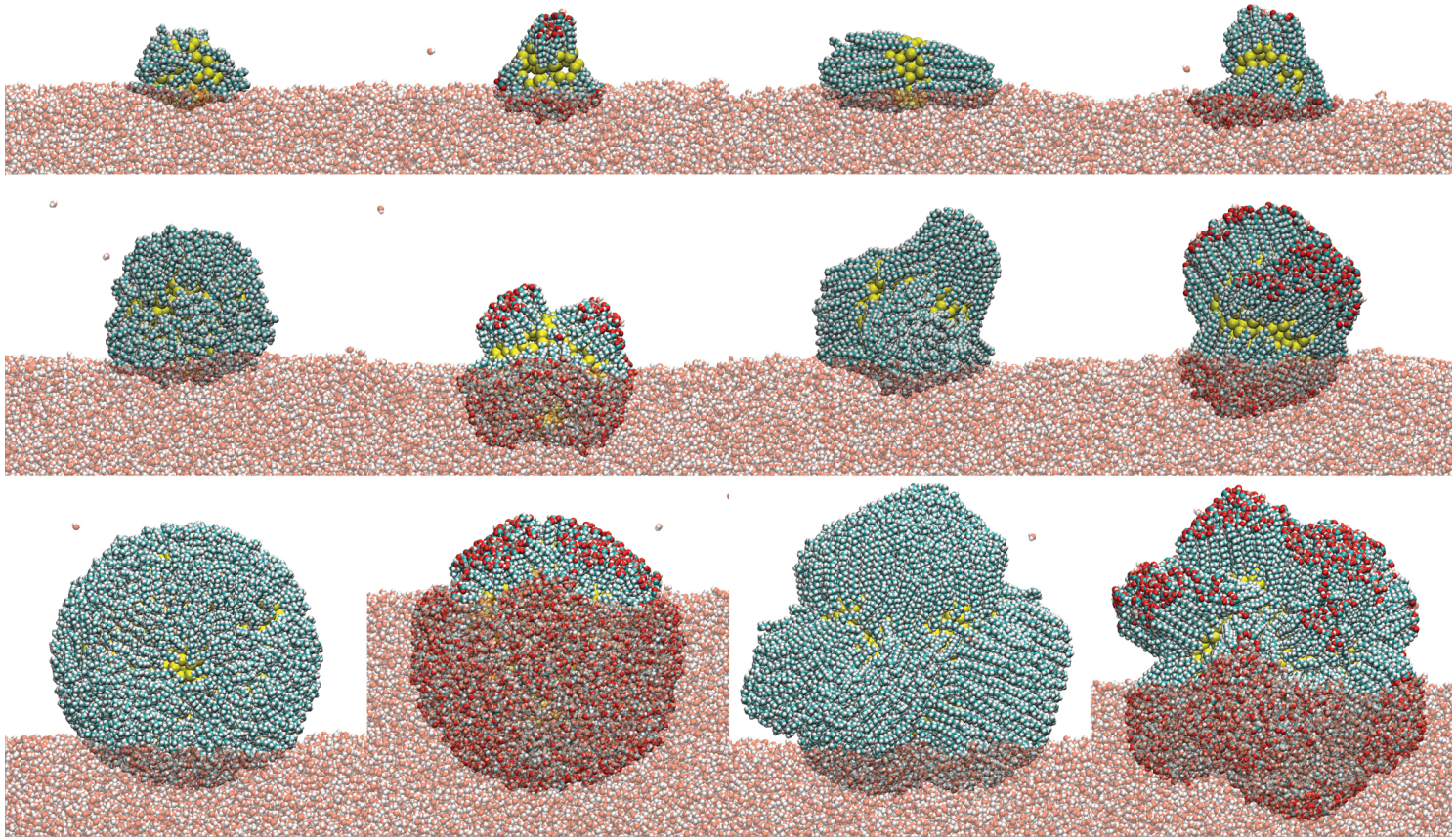
Mixed-chains deceased uniformity in the coating surface as chains tended toward small tight bundles unless solvated

Surface initial conditions

- NPs placed at liquid/ vapor interface of water
- All 12 particle type were began equilibrated in implicit solvent
- Simulation continued until vertical motion ceased



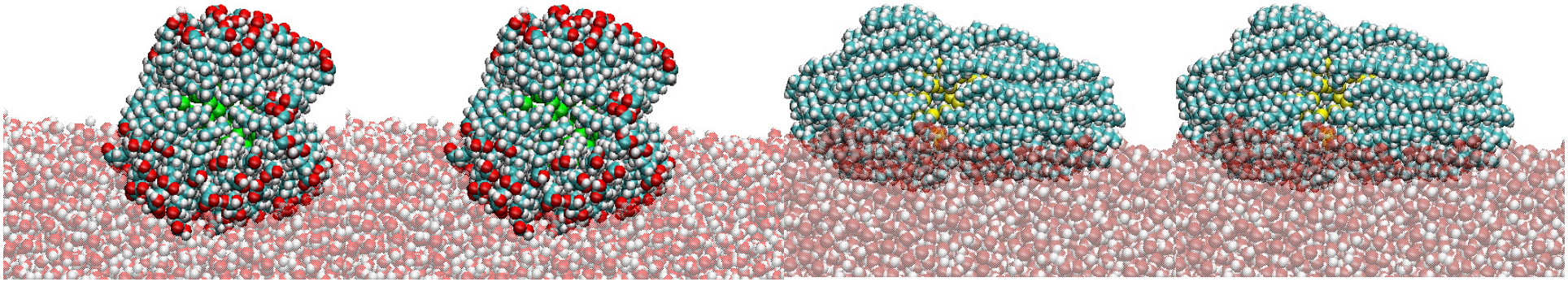
Coated particles at a water surface



Future direction: Surface interaction

- How will collections of particles behave at the surface?

- Can we preselect drivers of self-assembly by altering the particle coatings?



COOH terminal group

CH_3 terminal group

Summary and conclusions

- Nanoscale forces between functionalized NPs can be found from fully-atomistic simulations
  - Contact forces between NPs are velocity & separation dependent
  - Coatings remove features of bare NPs – make more like macroscopic
  - The important regime for NP interactions in solution is F < 1nN making accurate force extraction difficult
  - Coarse-grained NPs will allow study of longer time and length scales

- Coating quality can be dramatically affected by geometry and secondarily by coating and solvent interactions

- "Poor" coatings could be exploited at surfaces and in the bulk to select structures during self-assembly

- Resources now available to make significant inroads in understanding nanoparticle suspensions

Collaborators

• Sandia:	Gary Grest, Ahmed Ismail, Michael Chandross, Jeremy Lechman, Steve Plimpton
•Sandia/UNM:	P. Randal Schunk, Tim Boyle
• Univ of Utah:	Matt Petersen
• King's College:	Christian Lorenz