SAND2017-3516C

253rd ACS National Meeting
Colloidal Nanoparticle Synthesis & Assembly Session
San Francisco, CA – 6 April 2017

Modeling nanoparticle assembly using polymer coatings, interfaces and pressure to build 1D, 2D and 3D nanostructures

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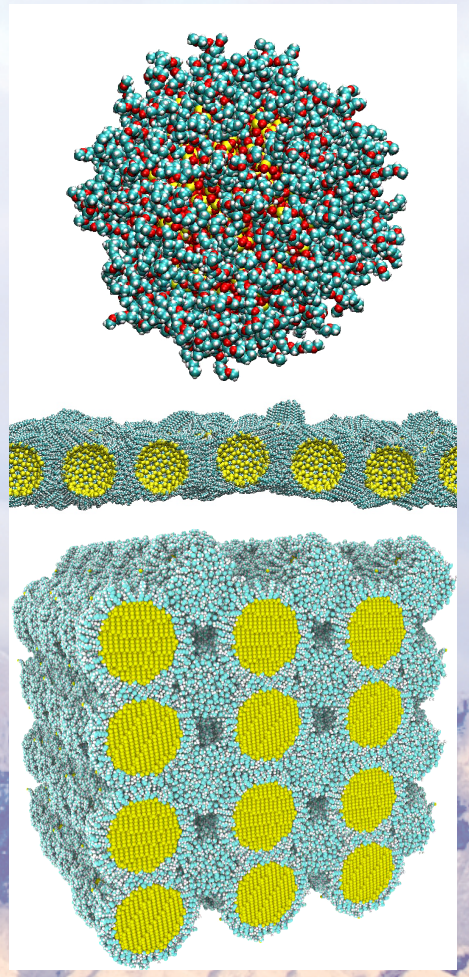

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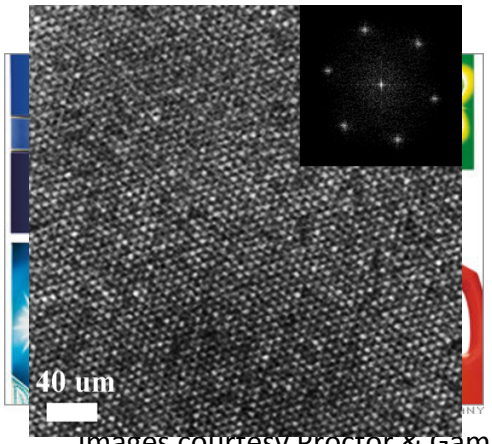
Acknowledgments:
Gary Grest, Steve Plimpton, Mike Salerno, Dan Bolintineanu, **Hongyou Fan**

Nanoparticle coating for stabilization and assembly

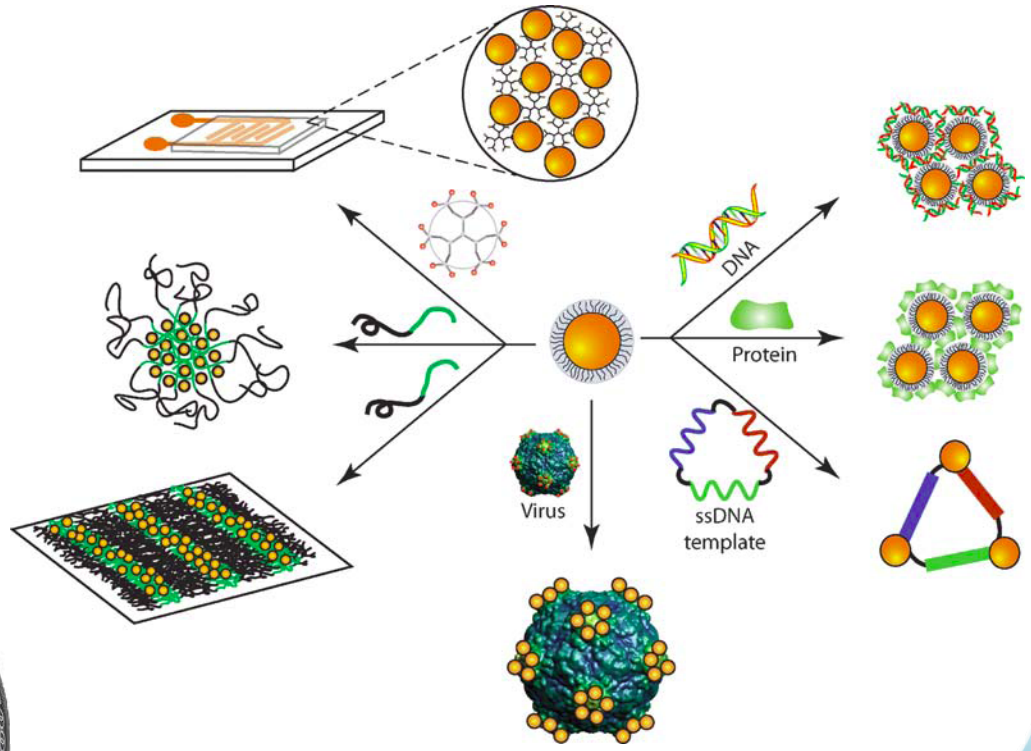
Nanoparticles are commonly coated to prevent aggregation in solution

- Efficient processing requires understanding the rheology of functionalized NP suspensions
- Controlled self-assembly of spherical NPs for "bottom-up" fabrication of materials



Images courtesy Proctor & Gamble and Goodyear websites

Wu et al., JACS, 132, 12826 (2010)



Polymer-mediated assembly of Au NP

Ofir, Samanta & Rotello, Chem. Soc. Rev. 37, 1814 (2008)

Courtesy Rotello group at UMass-Amherst

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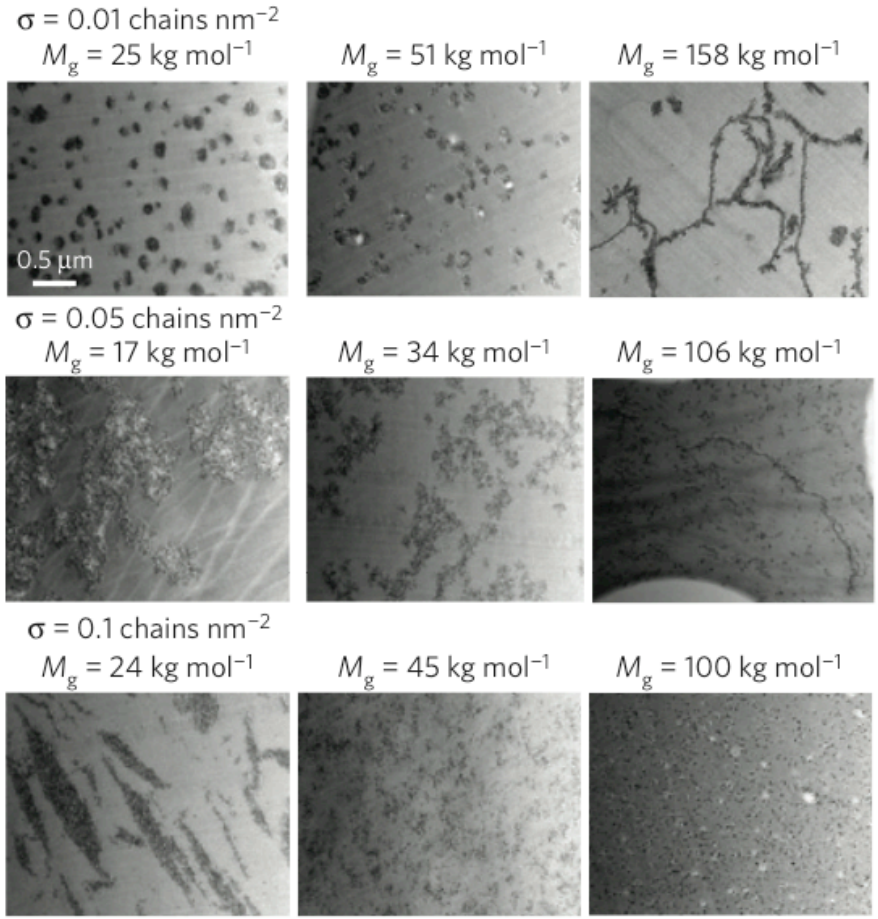
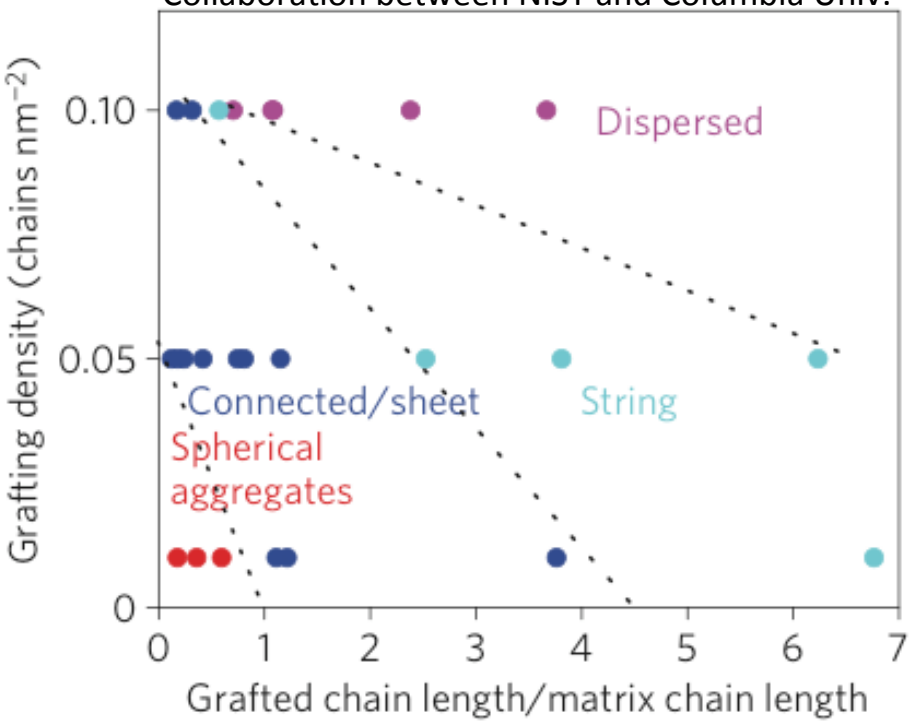
3D nanoparticle assembly experiments

- Controlled self-assembly of spherical NPs
  - Functionalized NPs provide opportunities to manufacture functionally tailored materials



Akcora, et al. Nature Mat. 8, 354 (2009)
Collaboration between NIST and Columbia Univ.

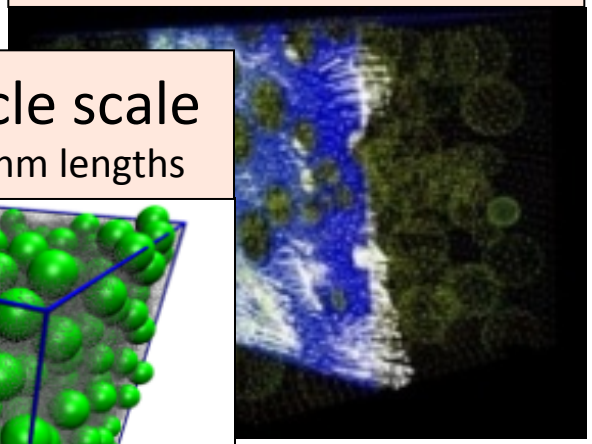


Role of MD simulation in bottom-up design

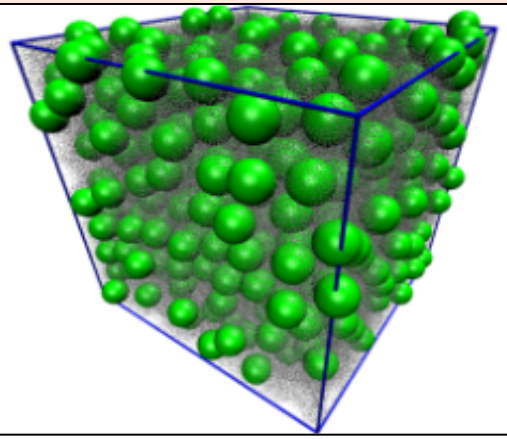
Bottom-up design:

- Understand the underlying building blocks & interactions
- Allow structural & dynamic complexity to develop as emergent phenomena

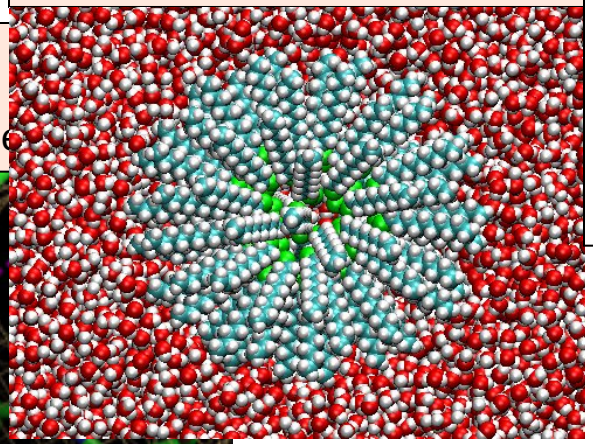
Mesoscale
µs times & µm lengths



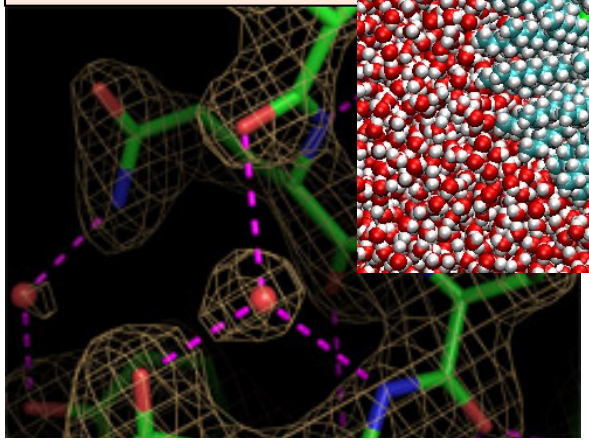
Meso/Particle scale
µs times & 100s nm lengths



Molecular scale
ns times & 10s nm lengths



Quantum
fs times & Å l



Advantages of molecular scale approach:
Well-defined interatomic potentials capture particle scale effective forces (i.e. solvation, lubrication & steric) as emergent phenomena

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Functionalized nanoparticle methods

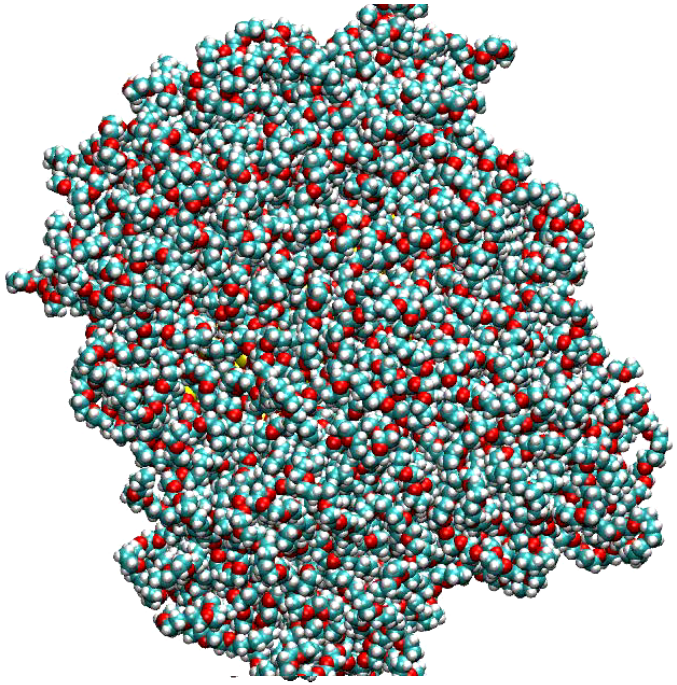

Image courtesy PNAS and Rotello Group

Coated Nanoparticle with Polyethylene oxide PEO(6) on 5nm core (3 chains/nm^2)

Mathematical Formulation

- Atoms are Point Masses: $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots\ldots \boldsymbol{r}_N$
- Positions, Velocities, Forces: $\boldsymbol{r}_i, \boldsymbol{v}_i, \boldsymbol{F}_i$
- Potential Energy Function = $V_i(\boldsymbol{r}^N)$

Lane et al, Phys. Rev. E, 79, 050501 (2009)

Molecular dynamics run details

- T = 300 K and 1 fs timestep
- 0.5 to 2.0 ns simulated per day
- fully-atomistic, including solvent

Atom potentials quantum chemistry

- TIP4P or TIP3P water, Jorgensen *et al.*
- OPLS potential for polymer & decane

Harmonic bond, angle, dihedral interactions
Charge and long-range coulomb interactions
van der Waals (Lennard-Jones) interaction

Polymer functional coatings:

PEO: $Si(OH)_3$-CH_2-$(CH_2CH_2O)_6$-CH_3
Alkanethiol: S-$(CH_2)_N$-X (X is CH_3 or COOH)

carbon sulfur hydrogen oxygen

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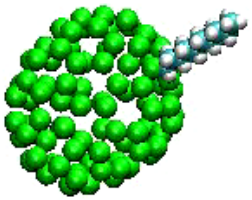
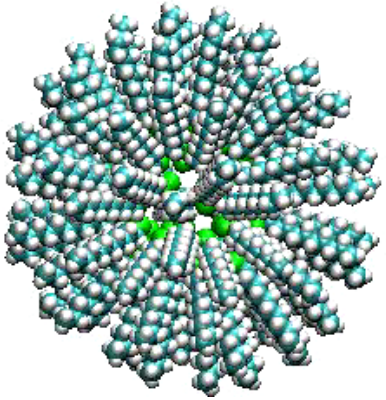
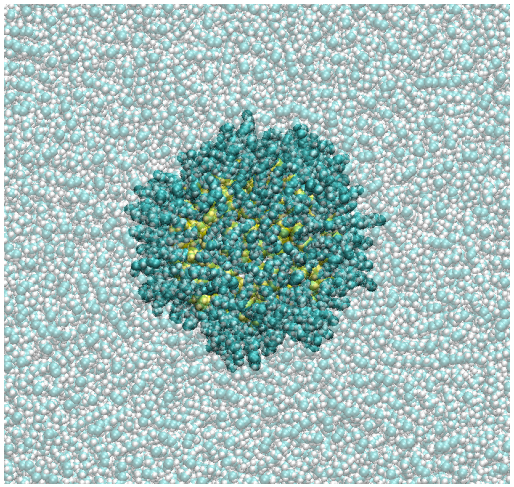
Building model Au-thiol nanoparticles







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 can be nonpolar (CH_3) or polar (COOH)

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

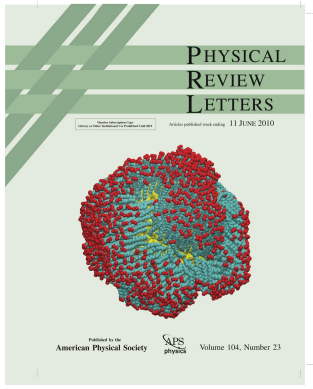
Constant coverage density of 4.8 chains per nm^2

Place each in nonpolar (decane), polar (water) and Brownian solvents.

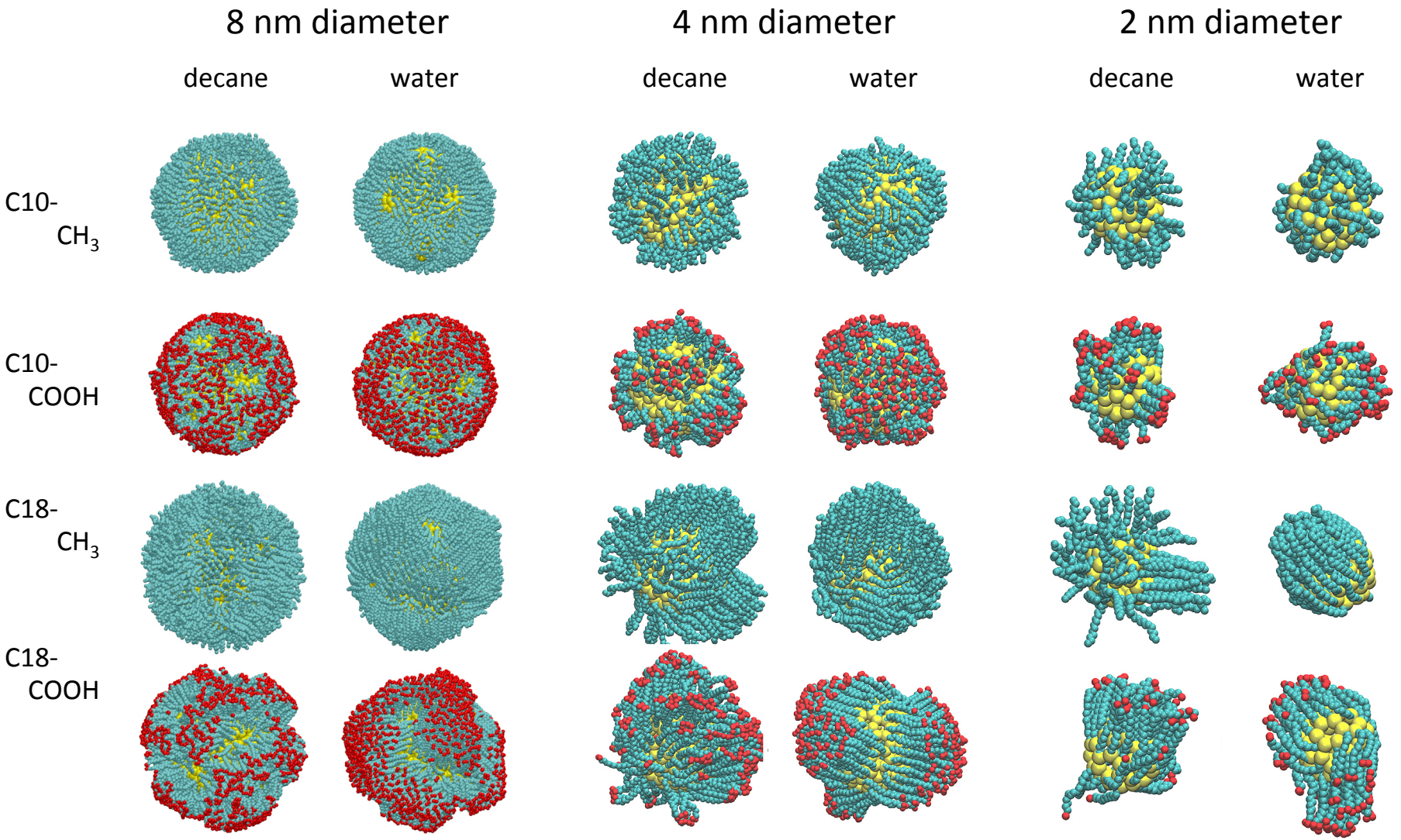
Standard atom potentials of quantum chemistry

- TIP4P and TIP3P water models of Jorgensen
- OPLS force field for polymers & decane

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



Polymer-coated Au nanoparticles in solution



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

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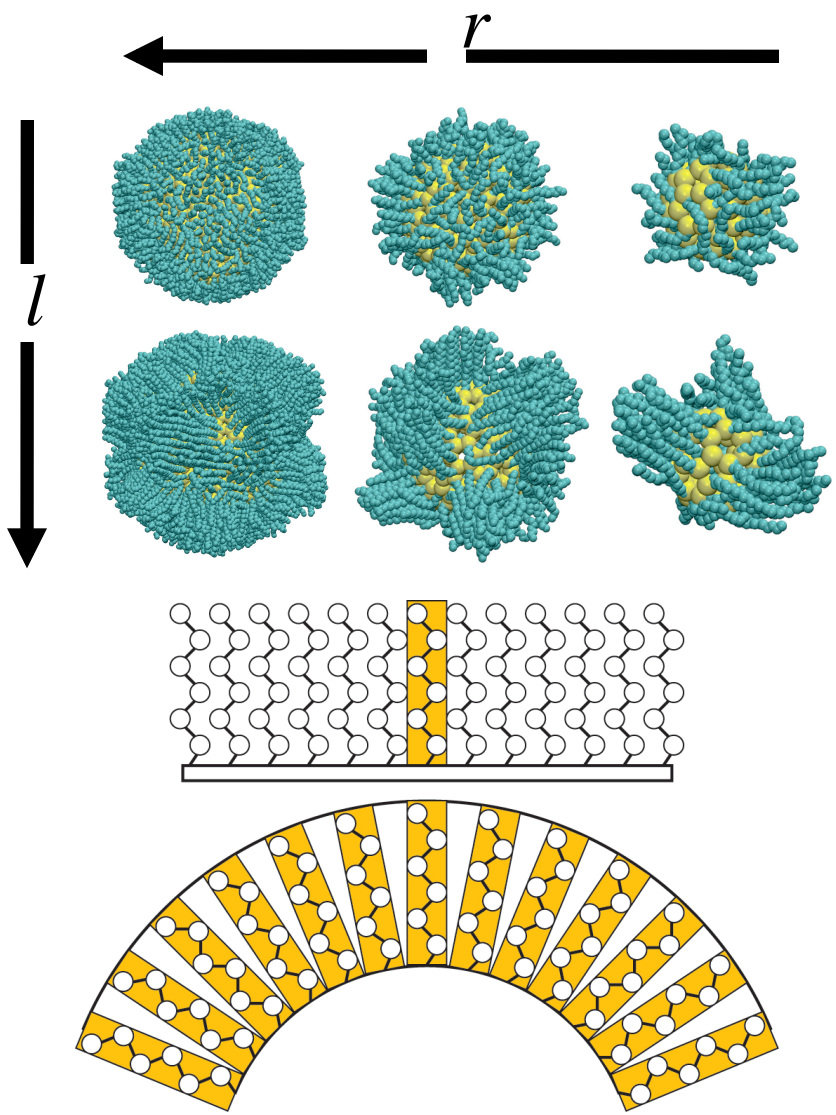
Particle geometry/curvature as a control parameter



Asymmetry depends on combination of:

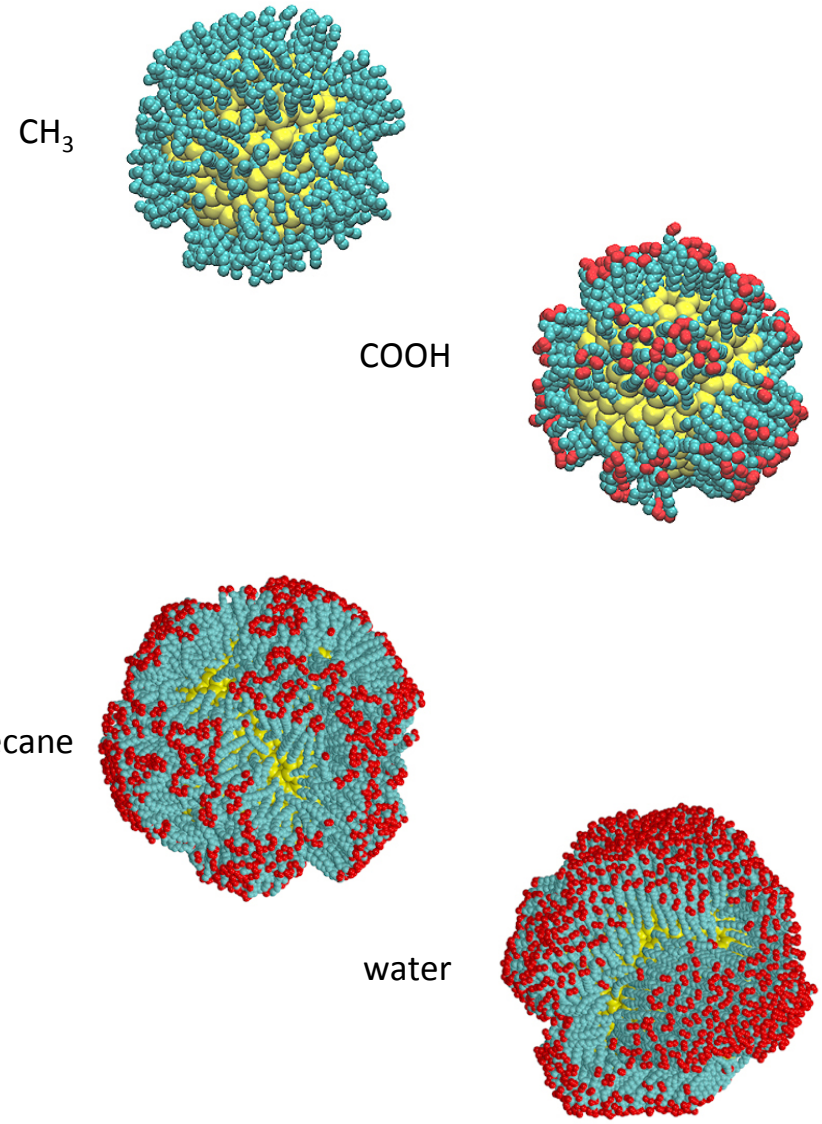
Particle size, r

Chain length, l

Change in free volume per chain:

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

Secondary effects: Termination and solvent quality



Chain termination is an key secondary variable

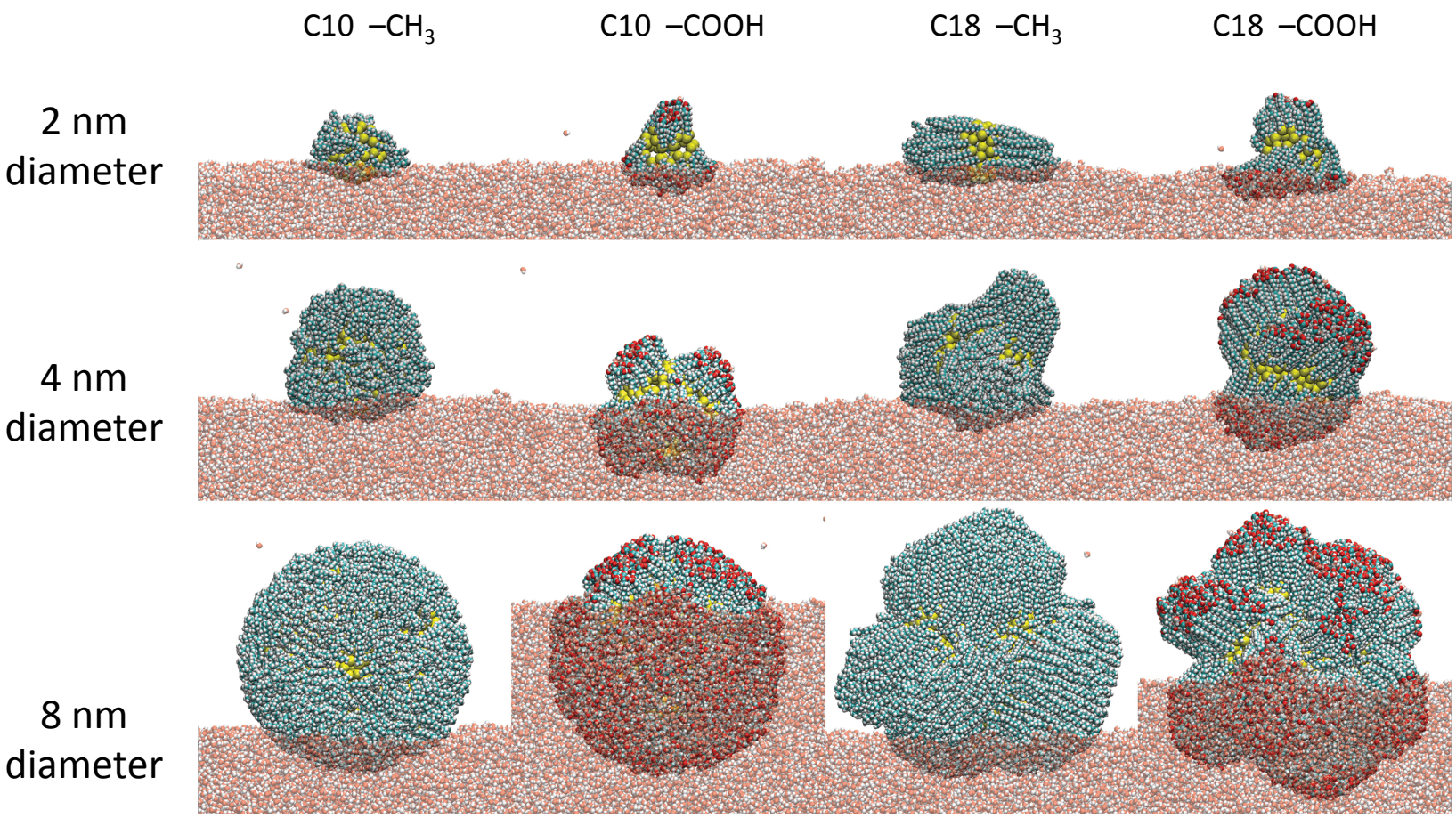
Polar (COOH) terminated chains bundled forming less uniform coating surfaces

Solvent quality is also an important variable

Nonpolar (CH_3) terminated chains behaved largely as expected to solvent changes based on hydrophilic/phobic interactions

Polar (COOH) terminated chains showed decreased uniformity in the coating surface as chains tended toward small tight bundles unless solvated

Coated particles at a water/vapor interface



NPs tend to stay at the water liquid/vapor interface and orient their asymmetry

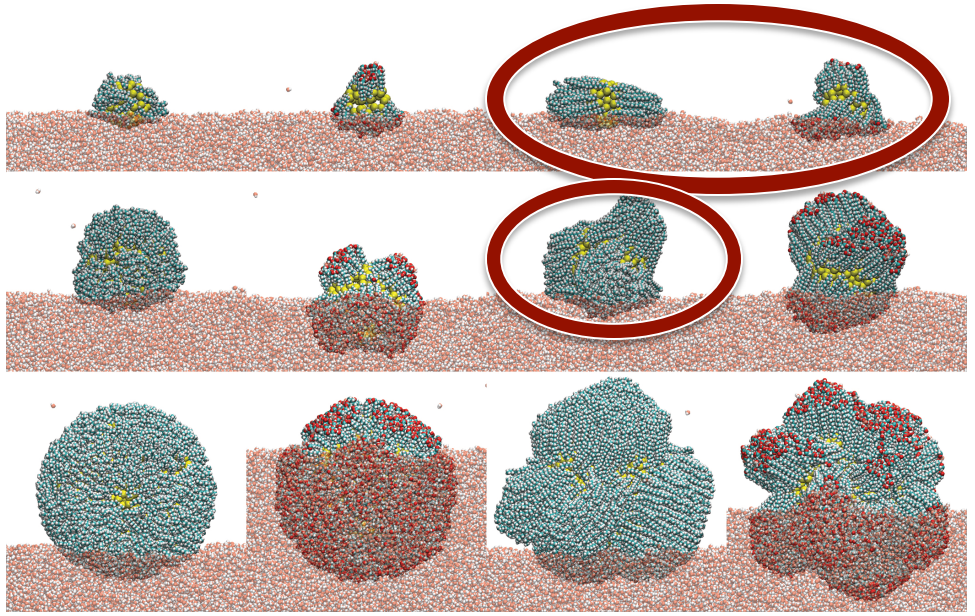
Lane, Grest, Phys. Rev. Lett. 104, 235501 (2010)

Assembly/aggregation at a water/vapor interface

Three coated particles were selected for further assembly/aggregation studies

For responsive asymmetric coatings:
2 nm diameter C18 COOH terminated
2 nm diameter C18 CH_3 terminated

For close match to experiment:
4 nm diameter C18 CH_3 terminated



Large-scale fully-atomistic multi-nanoparticle assembly simulations were conducted

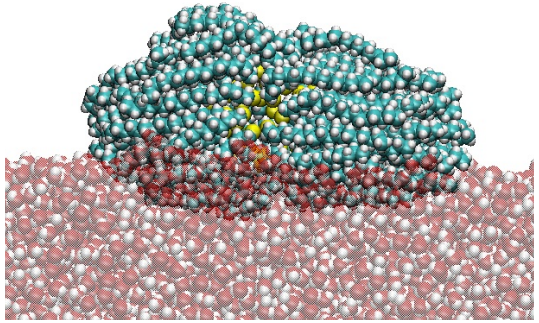
25 2-nm nanoparticle spaced in random orientations
36 4-nm nanoparticles in a 2D triangular lattice (to be deformed by compression, etc.)

Large systems that ran for extremely long times >100 ns
Systems ran on 1154 processors nearly continuously for more than a year

Greater than 10,000,000 processor-hours total

Early-time low-density assembly/aggregation

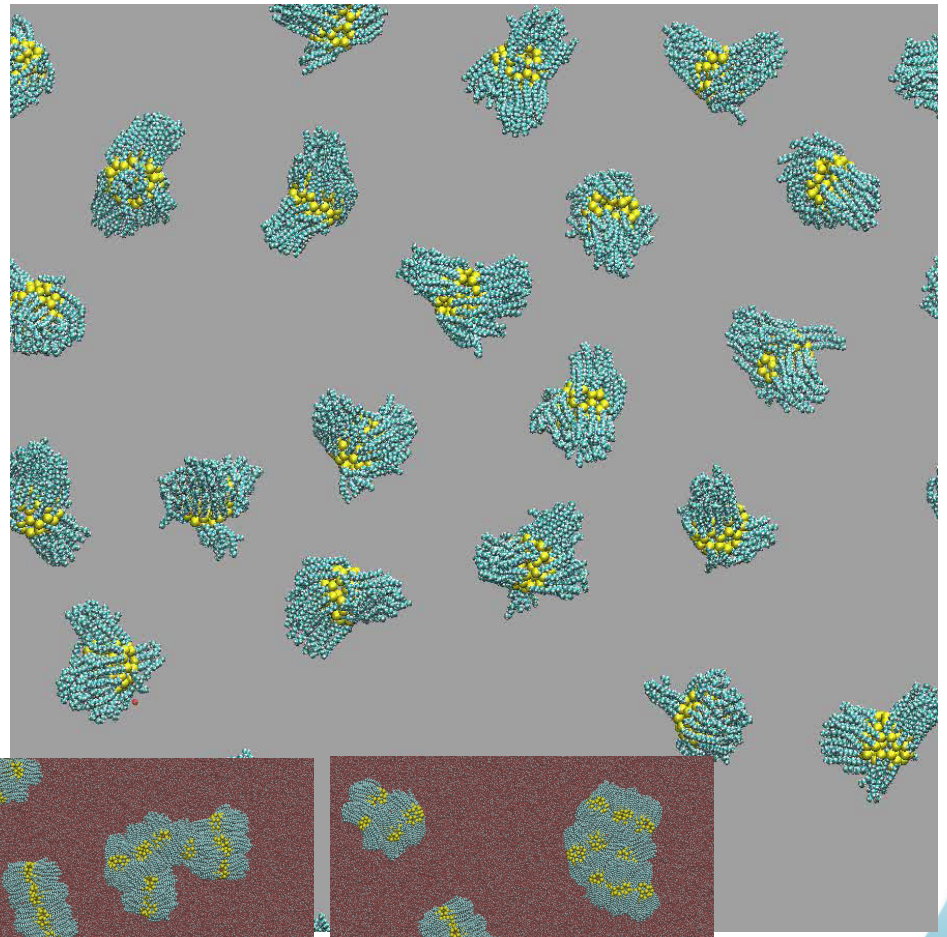
2 nm diam. CH_3 terminated case on H_2O

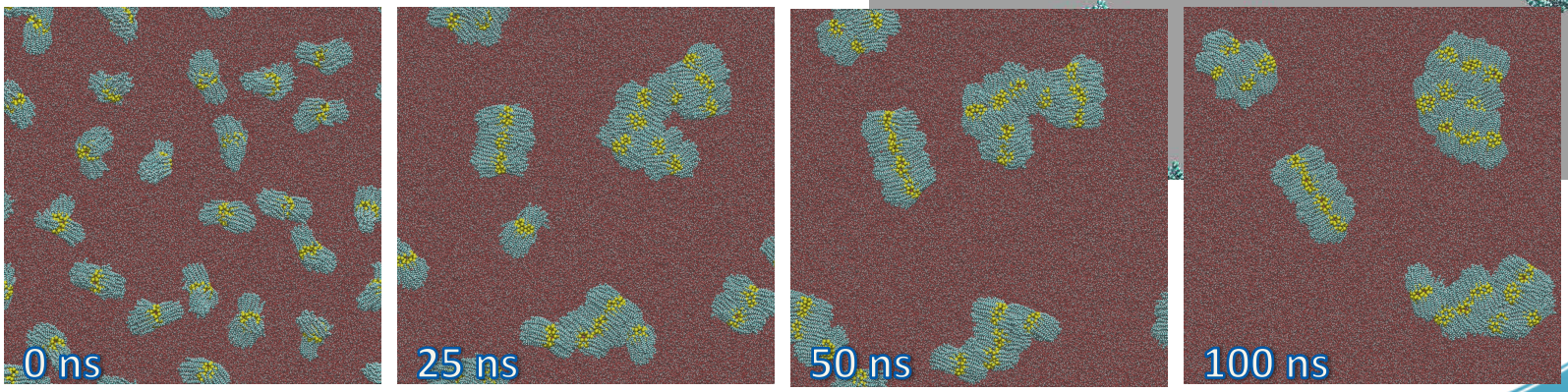


Purely attractive interaction and quick aggregation, then structure relaxation

Well-defined aggregation geometry prefers aligned linear arrangements

Lane, Grest, Nanoscale, 6, 4945 (2014)





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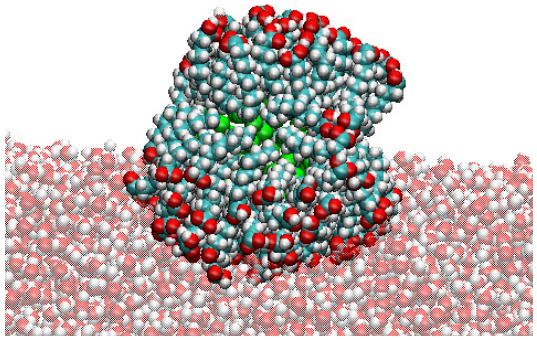
Early-time low-density assembly/aggregation

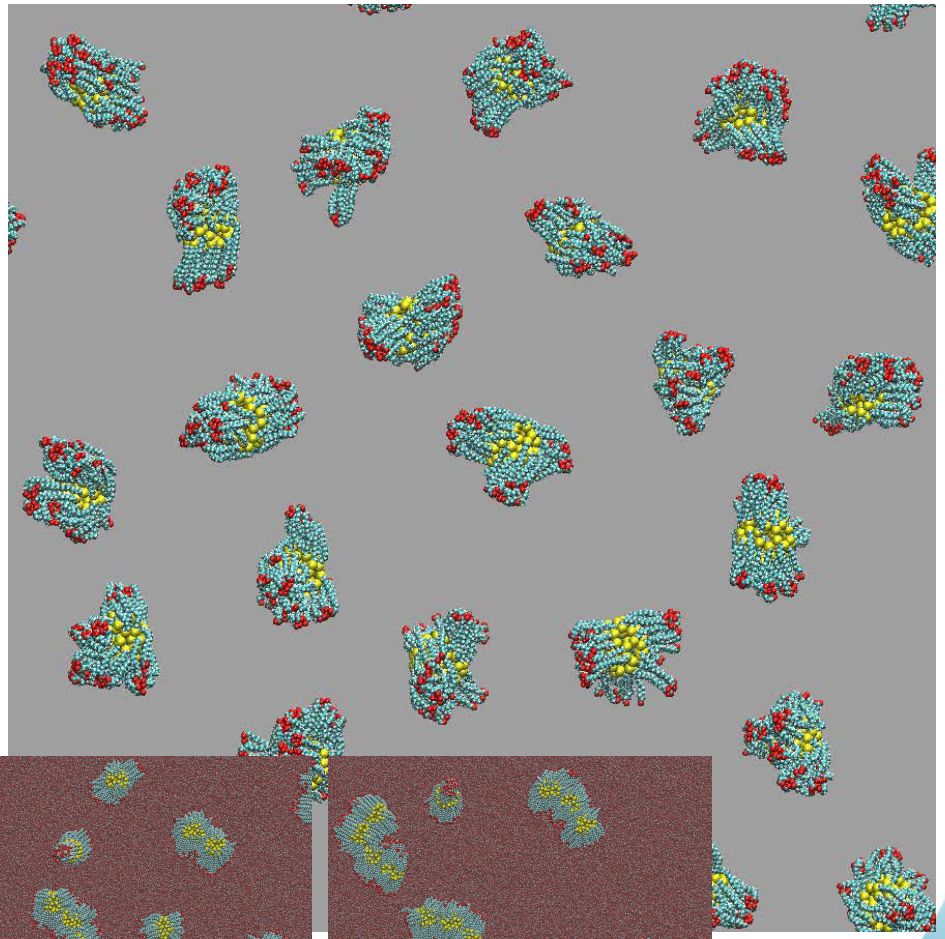
2 nm diam. COOH terminated case on H_2O

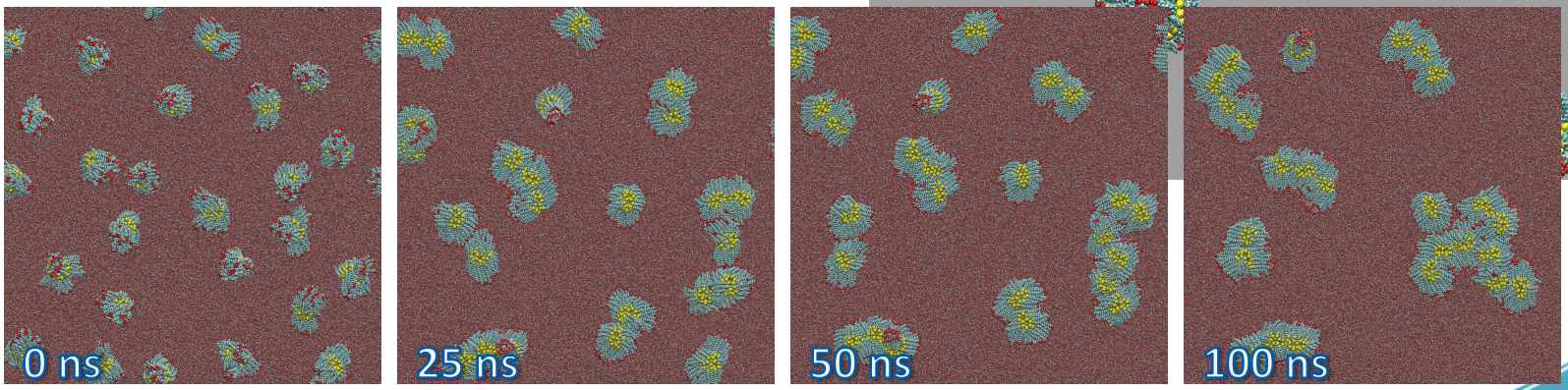


Repulsive/Attractive interaction leads to slow aggregation, and bimodal g(r)

No well defined aggregation geometry produces unordered clumps

Lane, Grest, Nanoscale, 6, 4945 (2014)





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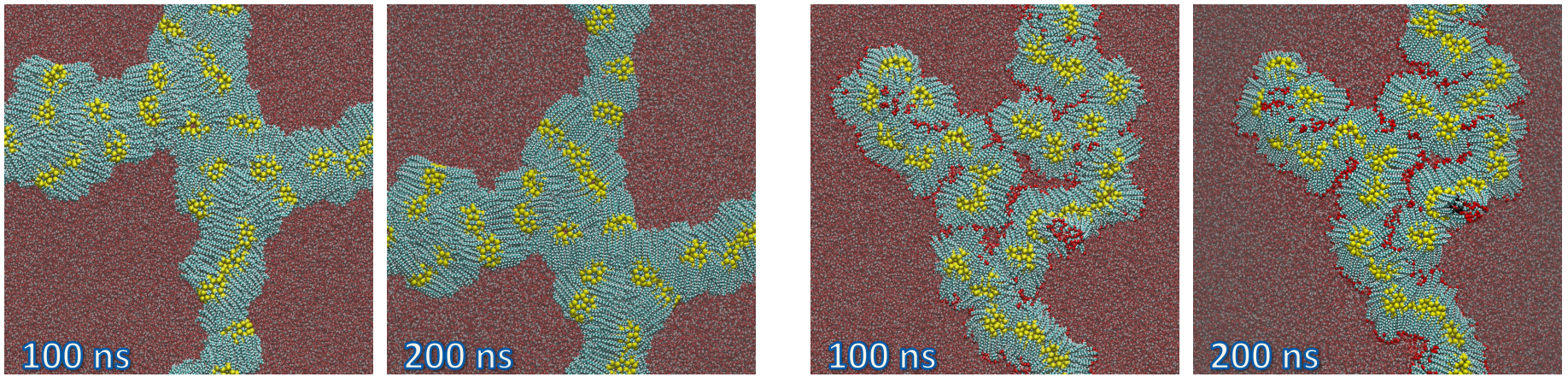
Higher-density assembly/aggregation for 2nm NPs

Higher density assemblies were created by homogeneous compression of the initial systems to reduce the film's surface area to 65%



These clusters appear to be less ordered, perhaps due to kinetically driven structures which relax, if at all, only on long timescales compared to MD times

COOH and CH3 terminations both give largely equivalent large scale disorder, while maintaining distinct short-range order

Some very subtle evidence of structure relaxation over 100s of nanoseconds

2D nanoparticle film assembly

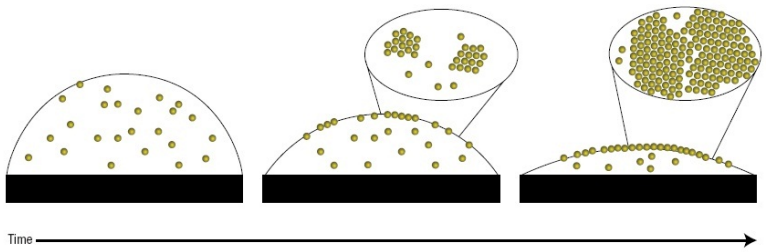
Xiao-Min Lin (ANL) & Jaeger (U. Chicago)

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

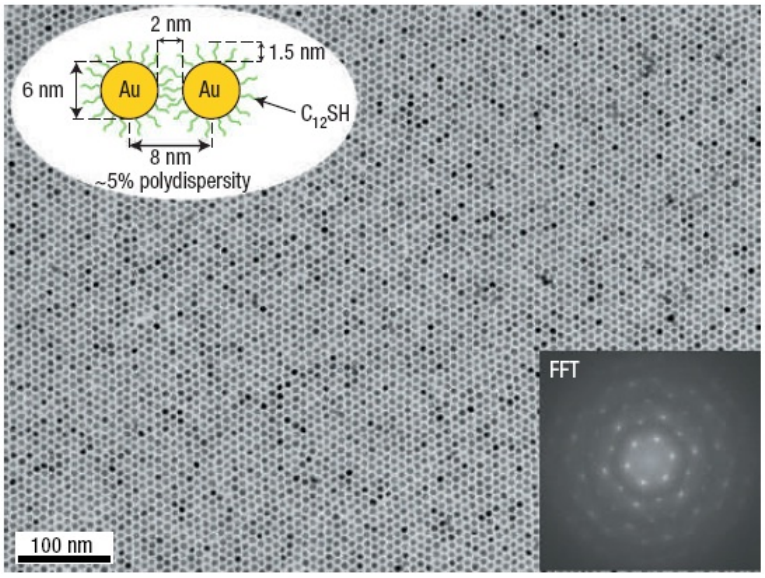
• Extremely strong but flexible, Young's modulus of several GPa

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

•First applications are mechanical, for filtration membranes



Slow evaporation of solvent



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

Courtesy Jaeger group at U. Chicago & Lin group at Argonne

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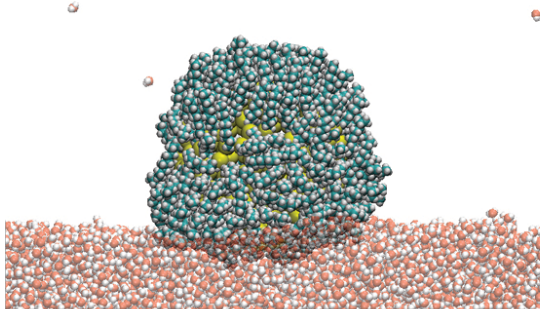
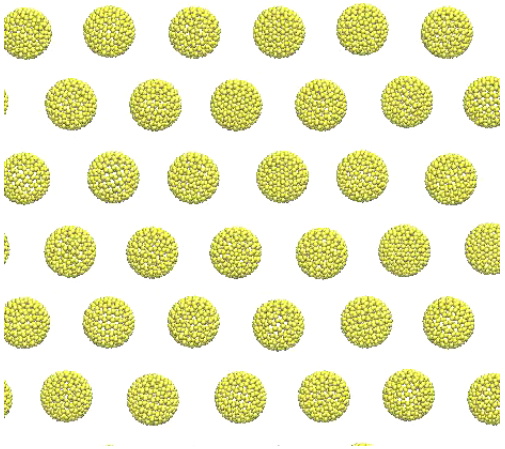
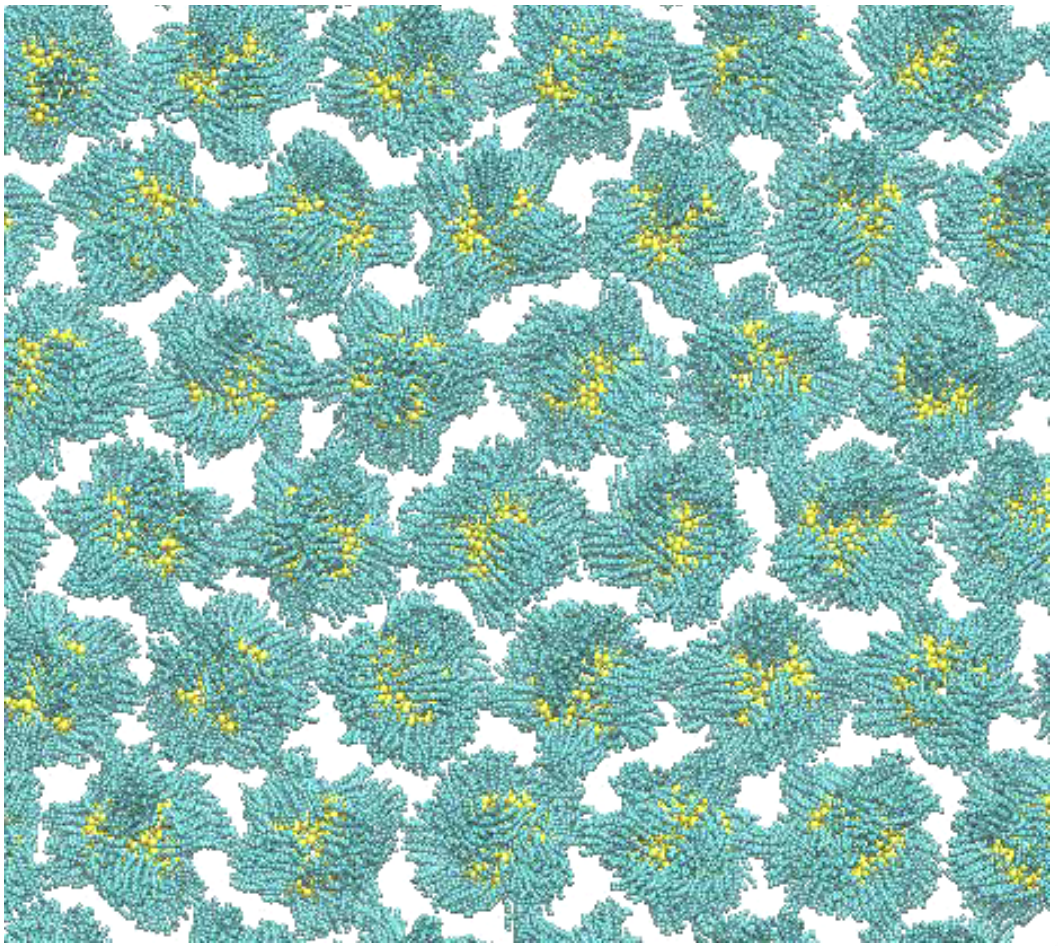
Pre-ordered assembly of 4 nm diameter NPs

4 nm diam. C18 CH_3 terminated





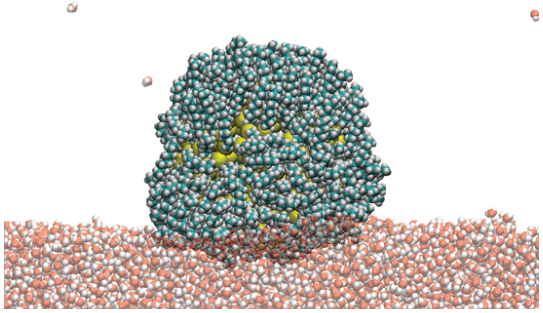


36 nanoparticles start an a triangular lattice with center-center spacing of 8.0 nm

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

Pre-ordered assembly of 4 nm diameter NPs

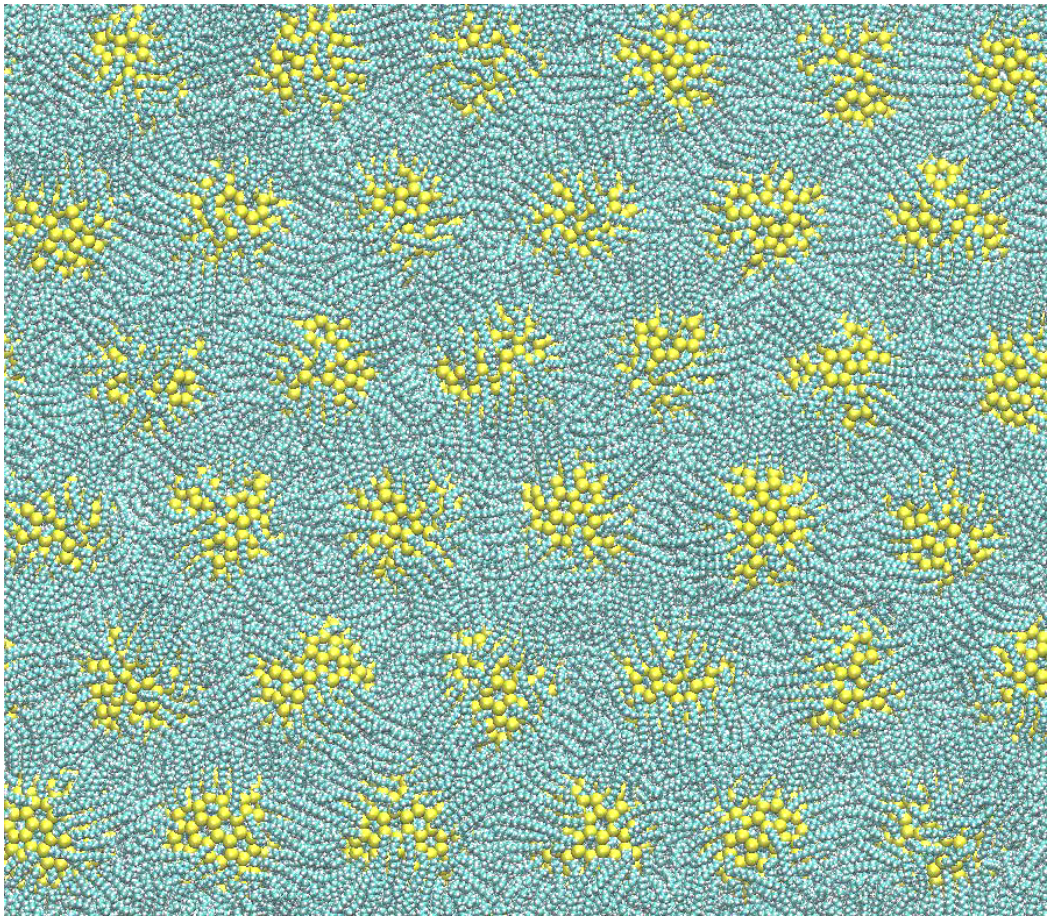
4 nm diam. C18 CH_3 terminated

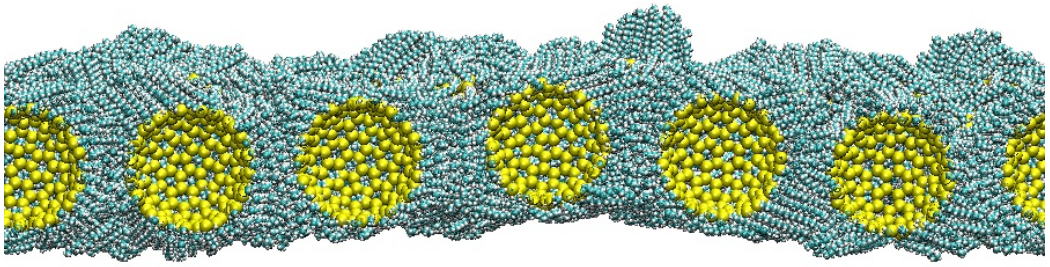


Properly spaced 36 nanoparticles in a stable triangular lattice with center-center spacing of 6.5 nm

Once stable films of nanoparticles are produced, water can be removed and the film becomes rigid and freestanding.

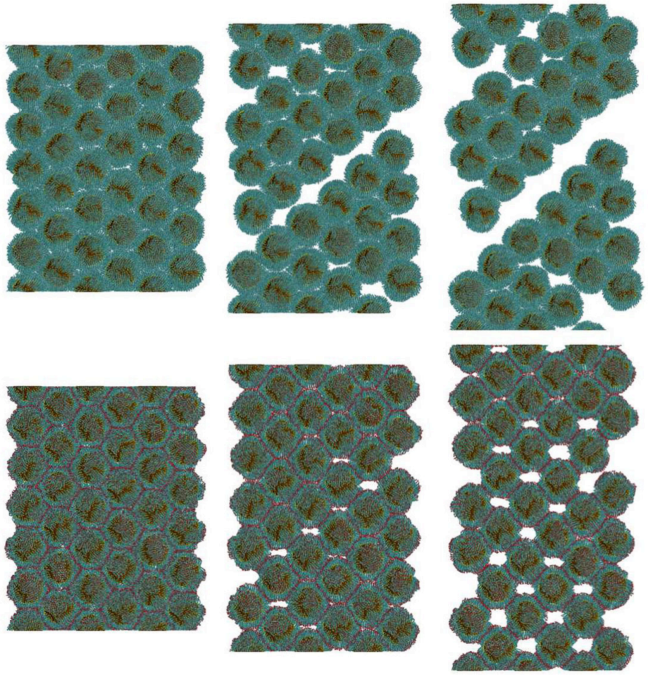
Good qualitative comparison is seen with experiment density profiles.





Comparison with 2D membrane experiment

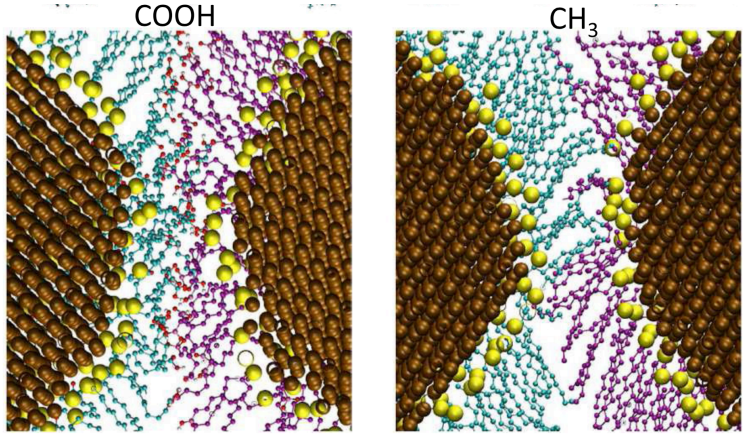
- 6x6 array of 6nm diameter full gold cores
- 4.7 chain/nm^2 surface grafted
- initiated at 10 nm separation, relaxed to 7.53 nm

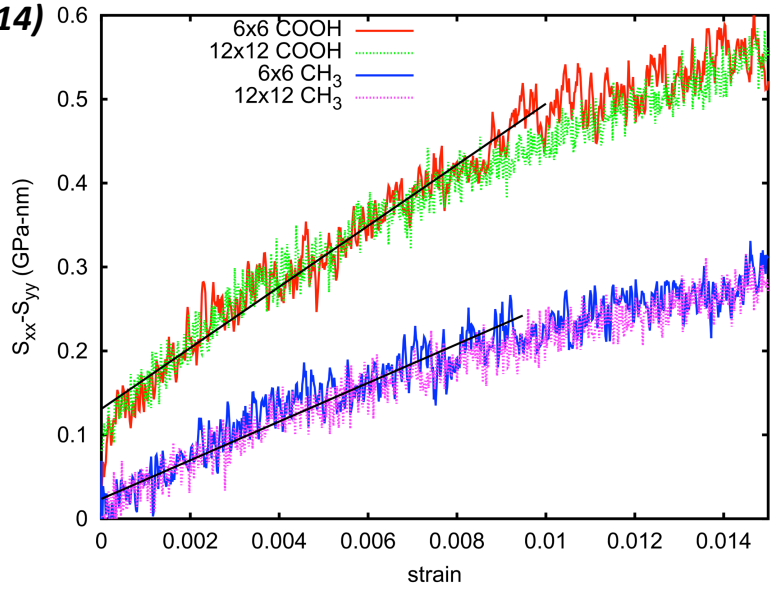


Atomistic simulations measured Young moduli of ~4 GPa for CH3 terminated coatings, comparable to the values measured in experiment. ***He, et al. Small, 6, 1449, (2010)***

Interdigitation is not pervasive, and is not the source of the material's high modulus and strength

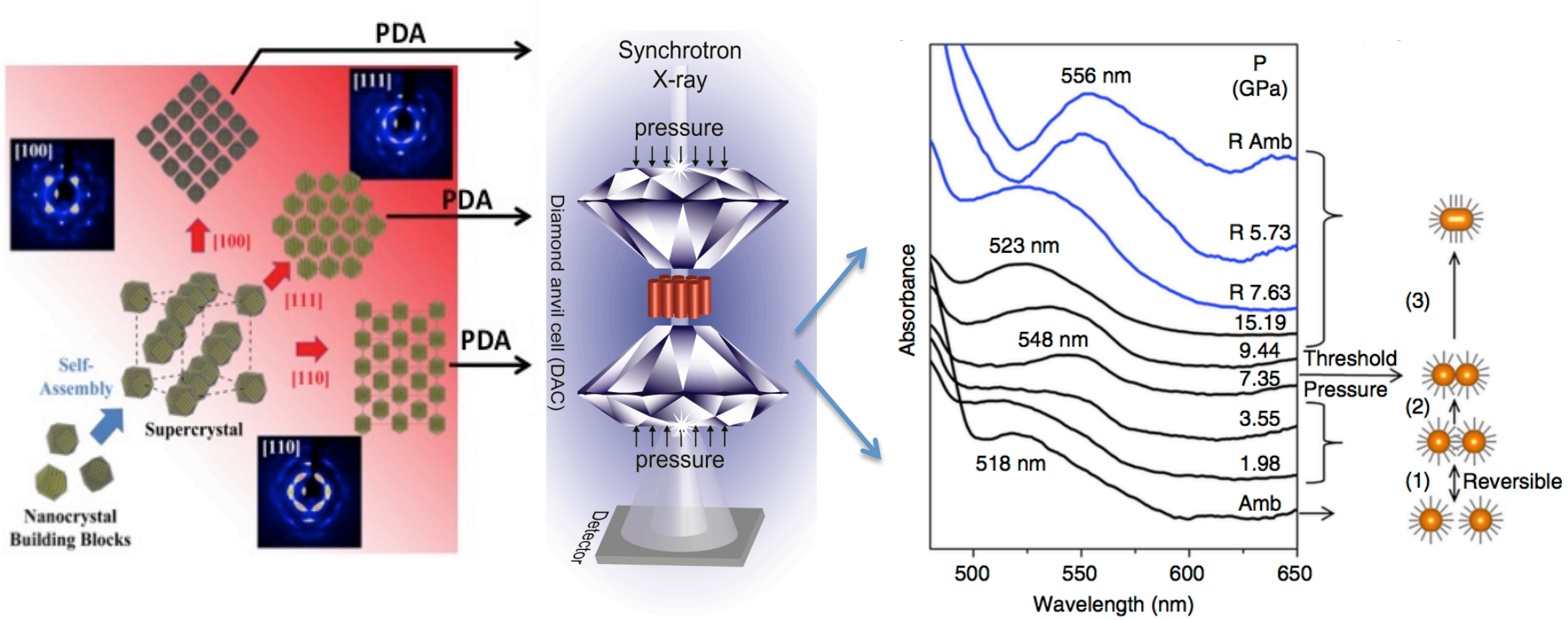
Salerno, Bolintineanu, Lane, Grest, Phys. Rev. Lett., 113, 258301 (2014)





Static pressure-driven assembly

Diamond anvil cells have been used to compress superlattice arrays of ligand coated gold nanoparticles

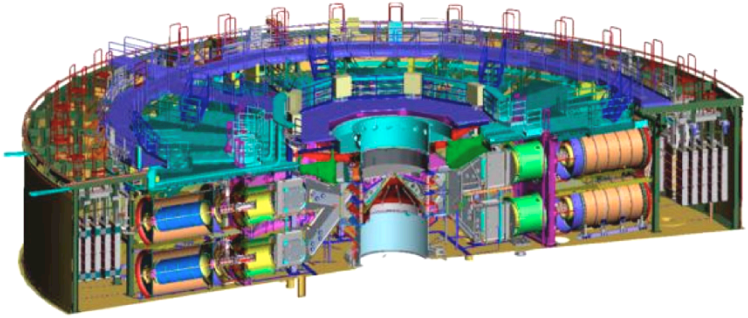


Li et al., Nature Comm, 5, 4179 (2014)
Wu et al., JACS, 132, 12826 (2010)

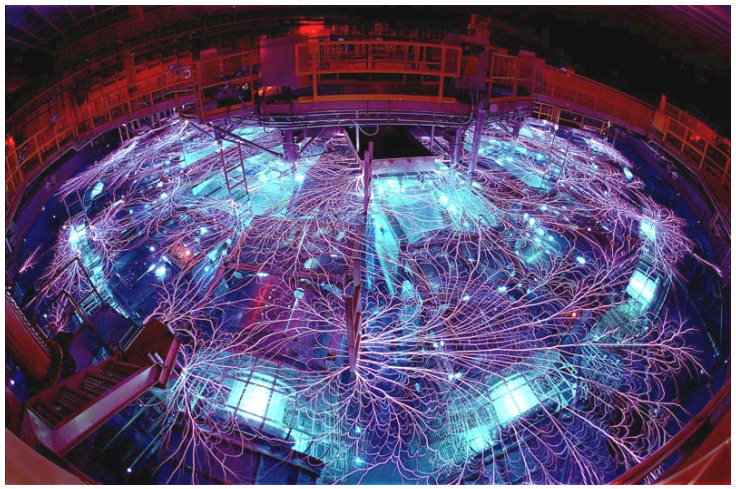
Above threshold pressure of approximately 8 GPa, nanoparticles consolidate into 1D and 3D (e.g., nanorods, nanowires, matrix, etc.)

Sandia's magnetically-driven dynamic ramp compression experiments

Z-machine at Sandia National Labs



33 m in diameter, 3 stories high



22 MJ stored energy

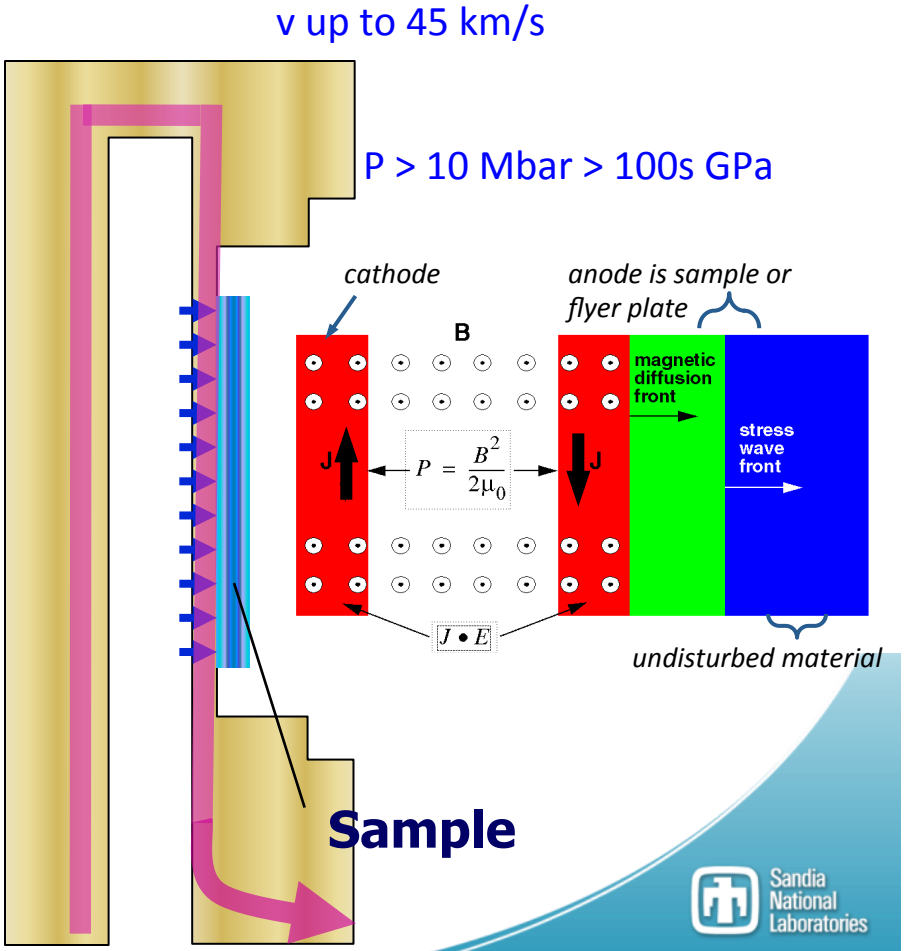
25 MA peak current

100-600 ns rise time

25 MA is the max current load of 160,000 homes

Z-machine experiments allow:

- Extremely high-pressure shock-less studies
- Inertial confinement fusion (ICF) research



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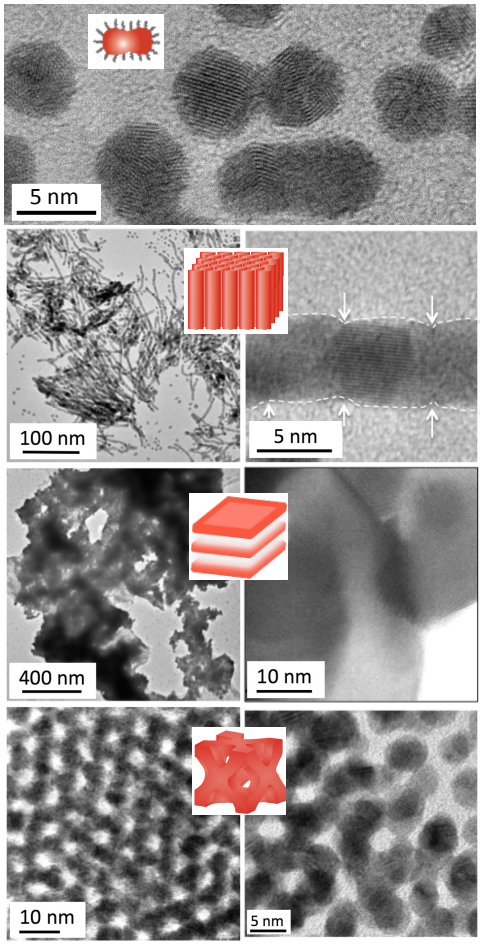
Dynamic isentropic compression experiments

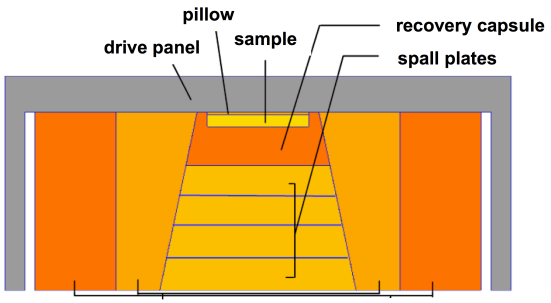
Nanosecond pressure-driven assembly (PDA) has been demonstrated using Magnetically-driven Dynamic Ramp Compression to produce nanostructures of several geometries.

- The Veloce driver was used to drive pressures to 12 GPa, producing several assembled mesostructures from dynamic uniaxial ramp waves.
- Veloce was fitted with a capture capsule to allow soft recovery of gold samples.

Chantrenne et al., AIP Conf. Proc 1195, 695 (2010)

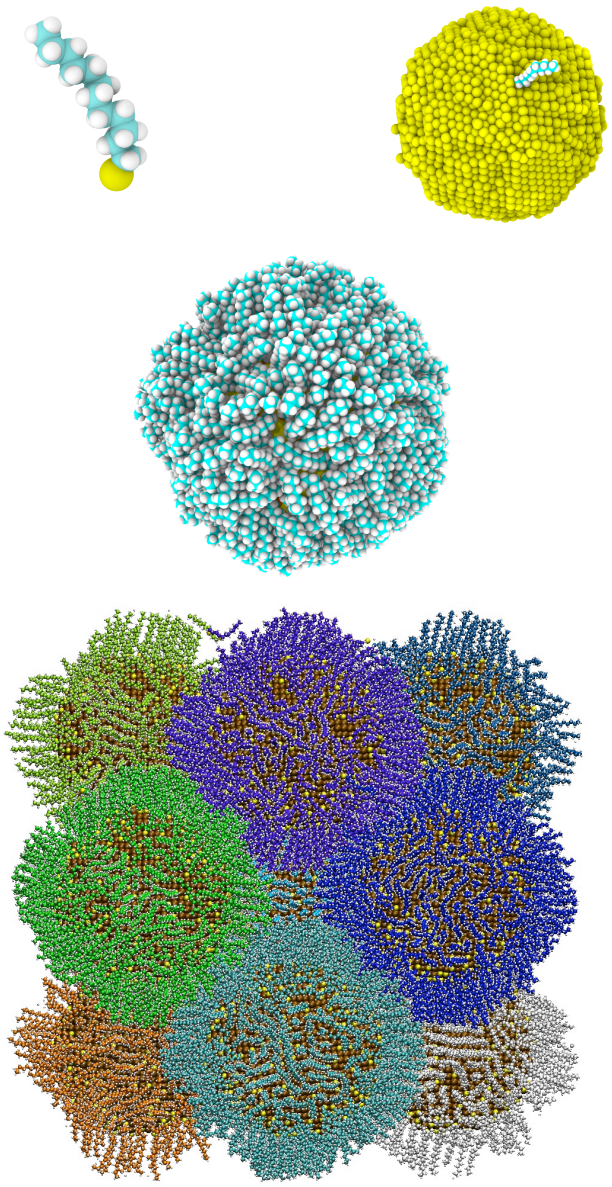
The success of this dynamic compression experiment in producing a variety of gold nanostructures, without initial hydrostatic loading, and at nanosecond timescales challenged some assumptions. But, opened the door to using molecular simulations to better understand the link between loading, and particle/coating properties on the final structures.





Li, Bian, Lane, Salerno, Grest, Ao, Hickman, Wise and Fan, Nature Comm., 8, 14778 (2017)

MD approach: nanoparticle superlattice



Hierarchical complexity

Coated Nanoparticle

- 5.9 nm diameter solid gold core
- Attach 515 hydrocarbon ligands $S\text{-}(CH_2)_{11}CH_3$
  - Full coverage at 4.7 chains per nm^2
  - Mobile ligands w/ 10 kcal/mol binding strength

Nanoparticle superlattice

- 96 nanoparticles in fcc lattice with 2.5 million atoms
- Core-core center separation of 7.6 nm

Heterogeneous hard/soft sample

Analogies to atomic systems

Complex NP-NP interactions mediated by soft material

Interatomic potentials vetted for high pressure

- Embedded atom method (EAM) for gold cores,
  Foiles et al, Phys Rev B, 33, 7983 (1986)
- Exp-6 modified OPLS for hydrocarbons
  - bonds, angles, dihedrals and electrostatics
    Jorgensen et al., J. Am. Chem. Soc. 118, 11225 (1996).
    Siu et al., J. Chem. Theory Comput. 8, 1459 (2012).
- Morse interactions for sulfur-gold surface

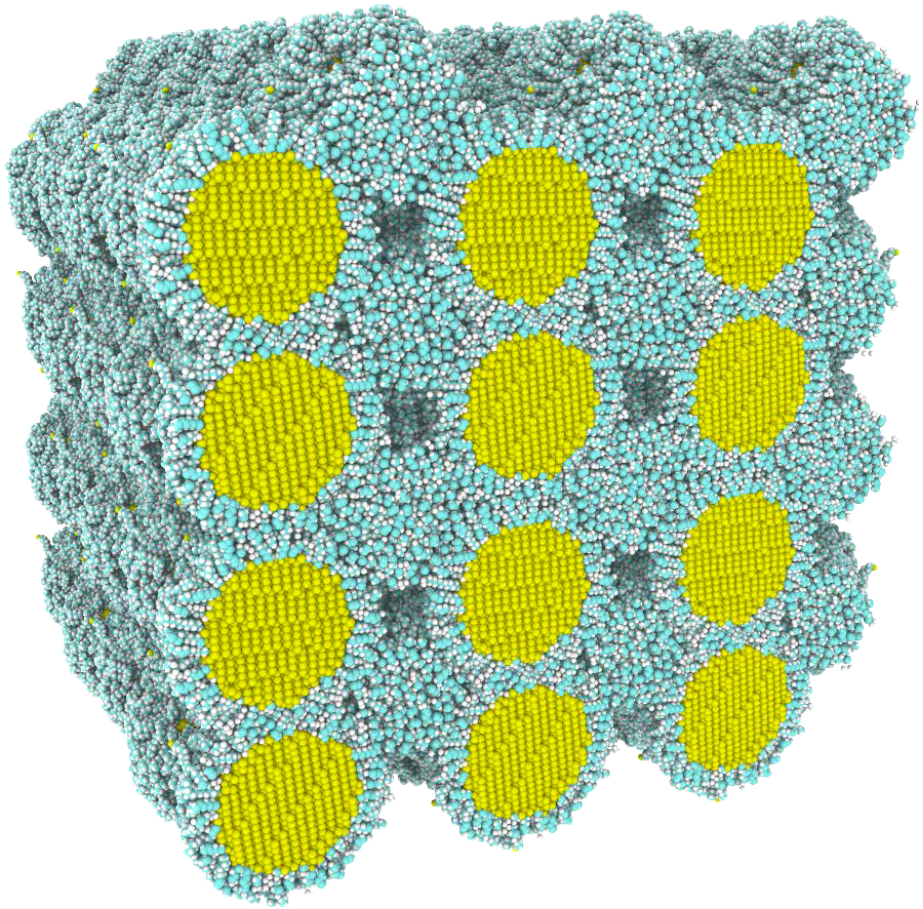
MD approach: Dynamic loading

We load the superlattices uniaxially along three different orientation [100], [110] and [111]

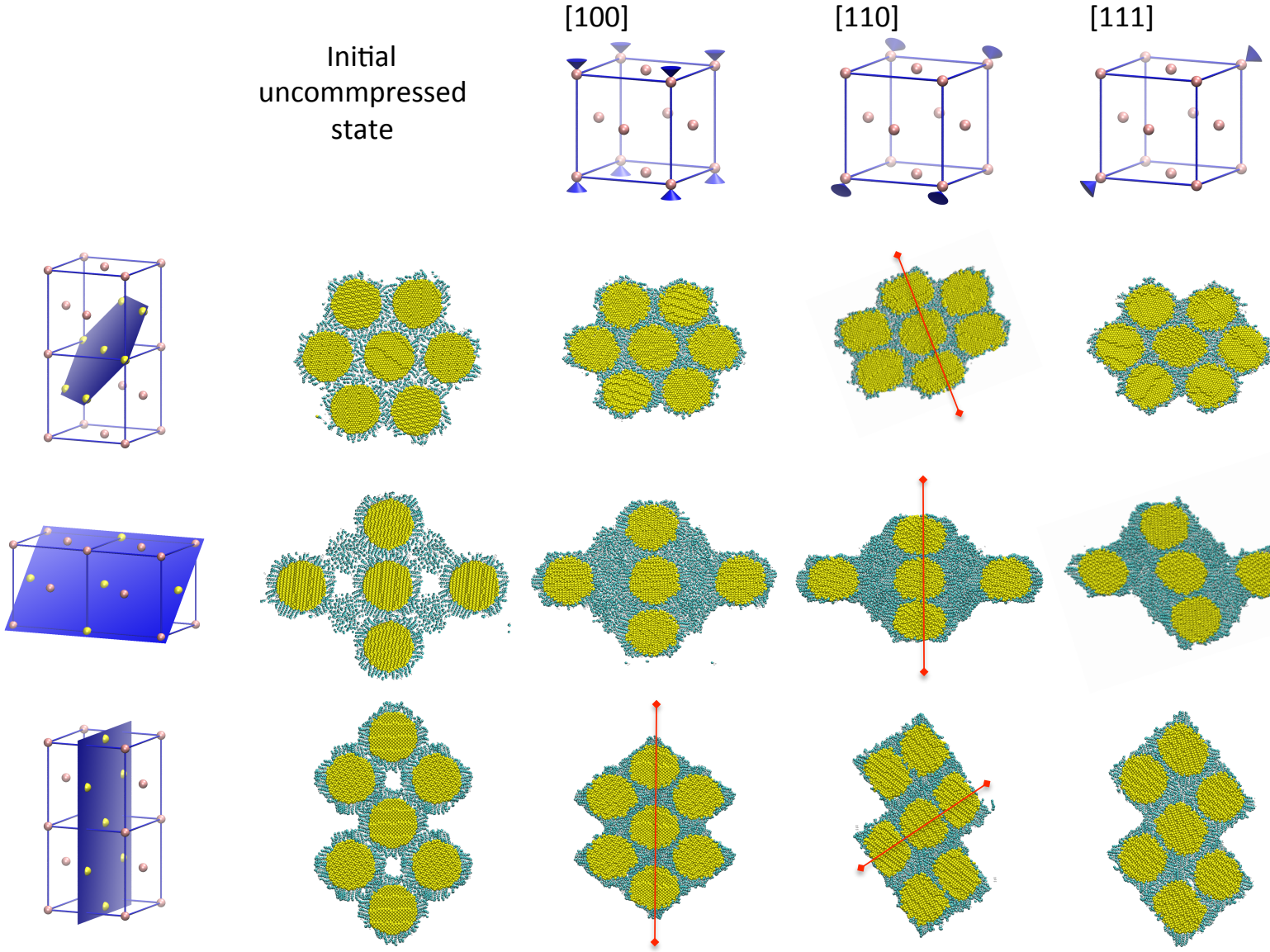
We initially used a Hugoniostat method, but then confirmed the results with isothermal ramp compression

Like hard spheres initial structures are not fully dense. As the loading progresses the ligands deform to fill space as pressure increases.

Ultimately, the gold cores contact and sinter to form continuous gold structures in 1D, 2D and 3D depending on compression orientation.



Orientation dependent response



Nearest Neighbor analysis

Initial fcc = 12

[100] -> 8

[110] -> 2

[111] -> 6

Li, Bian, Lane, Salerno, Grest, Ao, Hickman, Wise and Fan, Nature Comm., 8, 14778 (2017)

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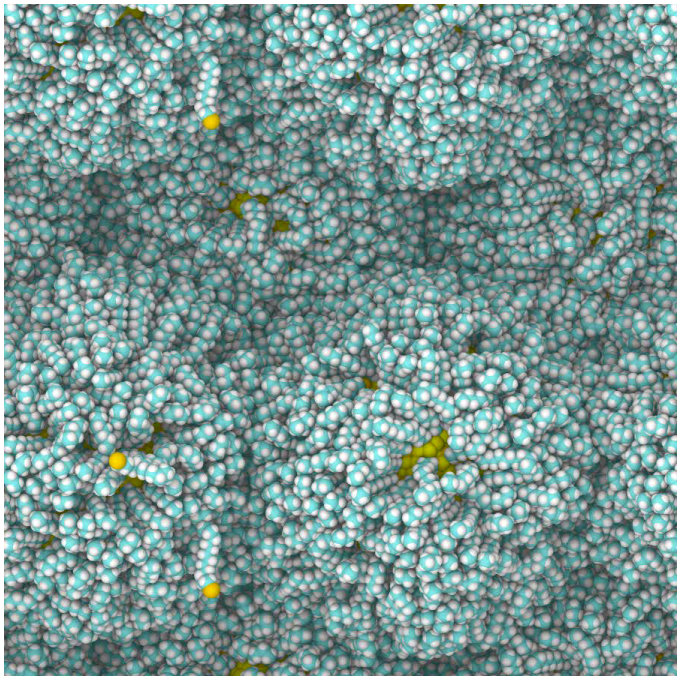
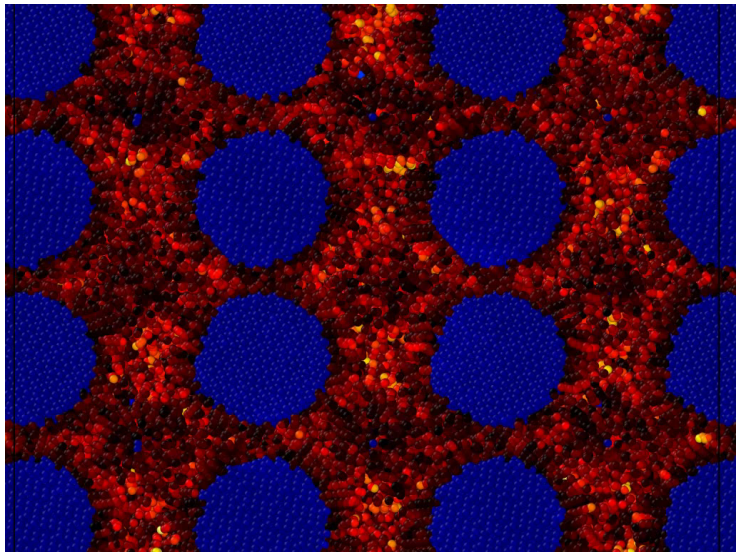
What coating/nanoparticle properties can be used to control final nanostructures?

What controls do we have on the symmetry and dimensionality of our final structures?

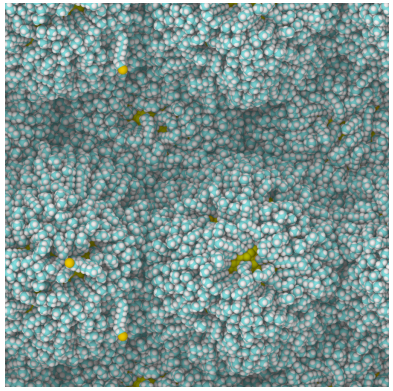
- Orientation of superlattice, loading direction, and perhaps even gold lattice
- Ligand density, length, and grafting strength
- Pressure thresholds and need for hydrostatic vs. uniaxial compression

Ligand migration at contact points

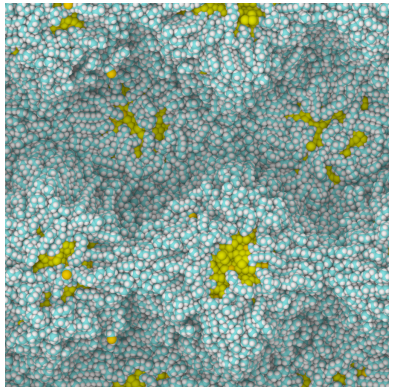




0 GPa



7.5 GPa

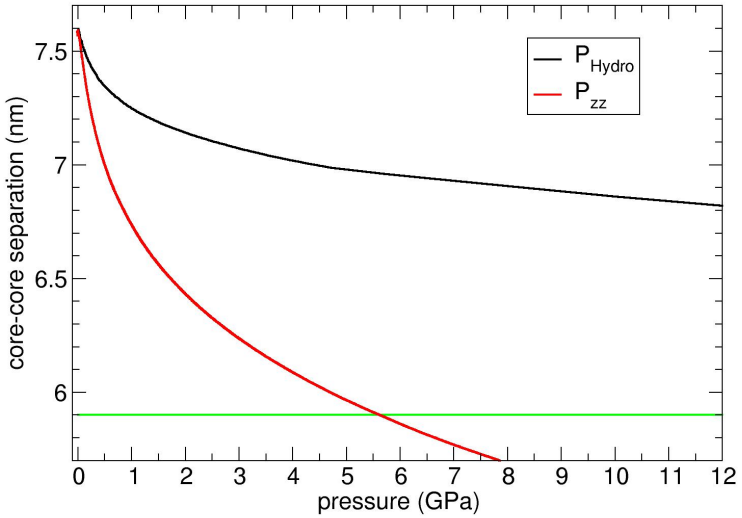


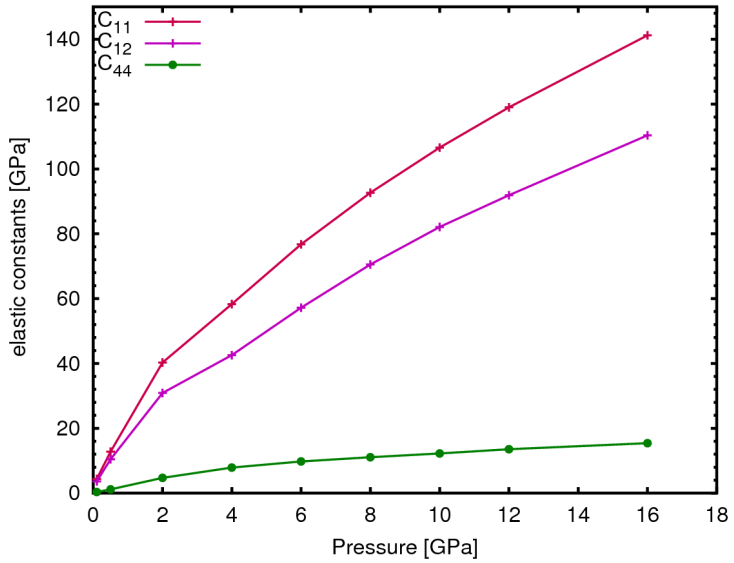
Ligands are pushed laterally from between the gold cores, but not pulled from the gold surface

Some crystalline alignment is observed

At the highest pressures, the gold cores are also deformed, laterally

Uniaxial vs hydrostatic deformation





Ju Li et al. had previously shown that sintering requires a deviatoric stress component. We agree that sintering can't result from hydrostatic compression.

Li et al., Nano Letters, 14, 4951 (2014)

Hydrostatic pressures up to >15 Gpa, are reversible and do not lead to sintered nanostructures in simulations.

The elastic constants increase with applied hydrostatic pressure, which can stabilize the superlattice.

At our rates, we do not observe a need to overcoming a critical hydrostatic pressure before linear nanowires can be formed. However, this may be a result of our loading rates.

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Dynamic compression induced assembly

Our simulations reproduce the the various sintered structures from experiments (1D, 2D and 3D) and unambiguously tie each structure to the initial orientations between loading and lattice.

Significant deformation is seen in the ligand coatings in order to fill space. These vary significantly with loading direction.

Significant surface mobility at contact points, but ligand chains are not pulled from the nanoparticle surfaces on these timescales.

Uniaxial compression is key to sintering, while initial hydrostatic compression is not.

- Future Work
  - Investigate the role of ligand length, grafting density, core orientation and core size
  - Investigate other initial superlattices (bcc, hcp)
  - Investigate pressure-sensitive cores

Conclusions

Atomistic modeling can be an effective tool in investigating the relationship between structure and dynamics in nanoparticle assembly

Simple coatings can be used in conjunction with geometry/ curvature and dynamic pressure to influence and control assembly

- For small (~2 nm diameter) nanoparticles, coatings can be spontaneously asymmetric, which when combined with surfaces strongly influence the short-range order in aggregations
- Larger (>4nm diameter) nanoparticles form hexagonal 2D lattices with properties in good agreement with experiments. Atomistic simulations offers clues to explain the unusual properties of these nanoparticle monolayers
- Dynamic pressure experiments can be used to sinter nanostructured materials on nanosecond timescales, allowing new structures to be achieved