Modeling Nanoparticles in Solution

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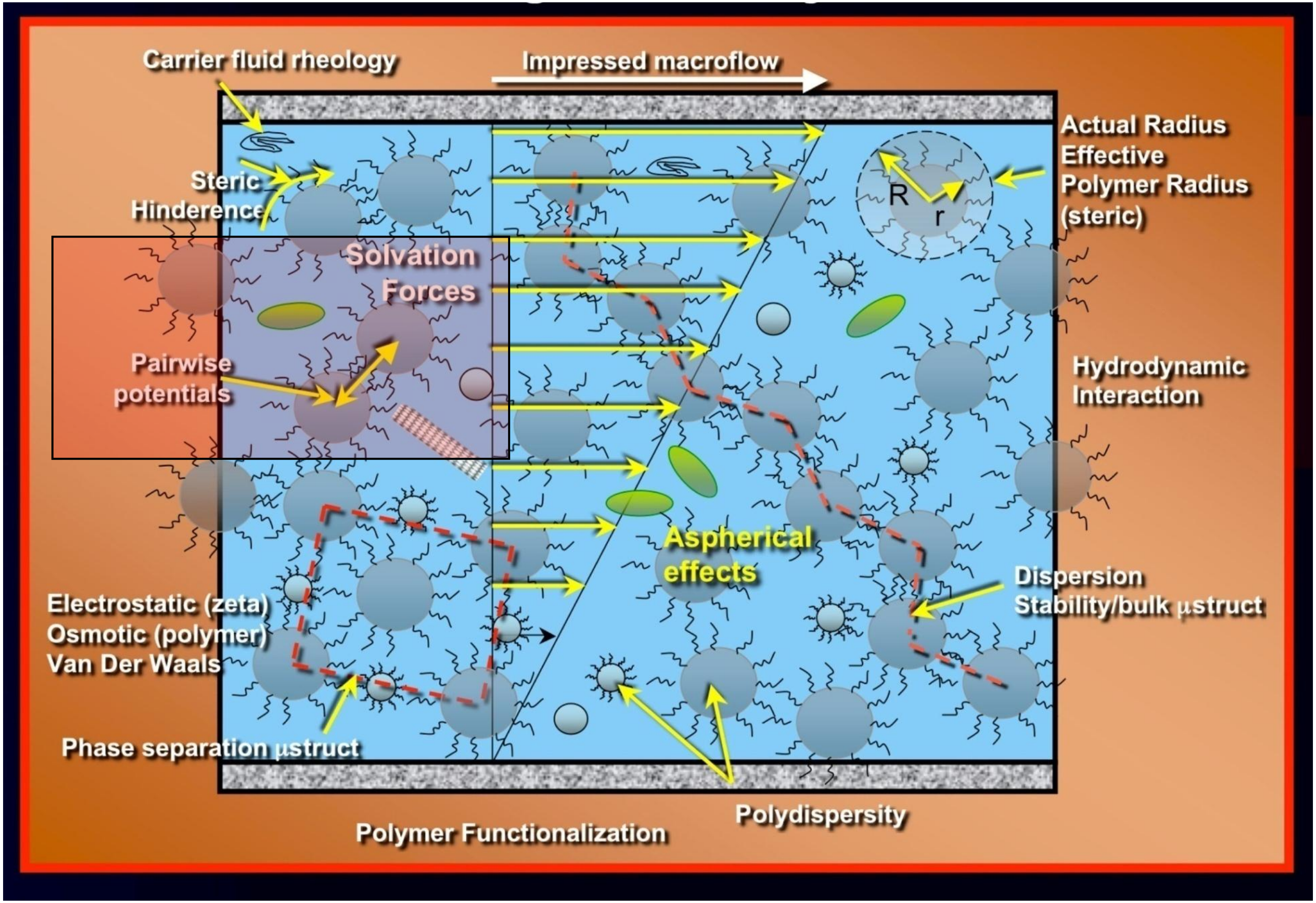
Rich Physical Phenomena



Courtesy of P. R. Schunk

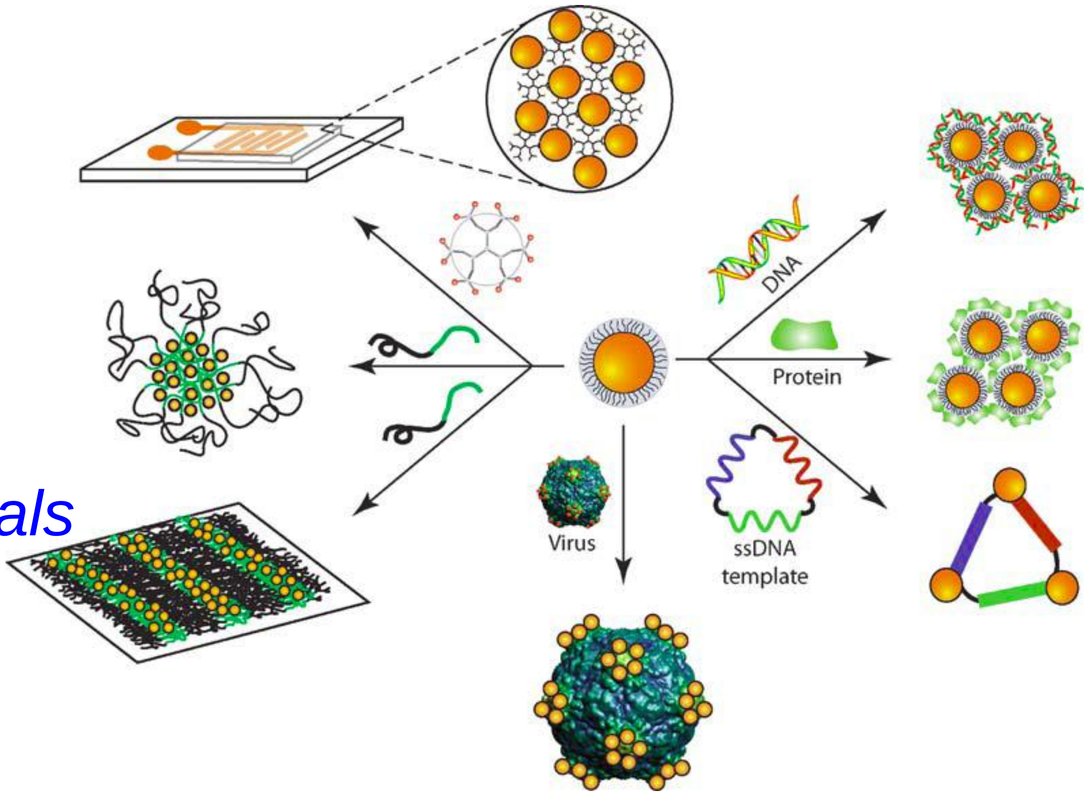
Polymer Nanoparticle Complexes

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)

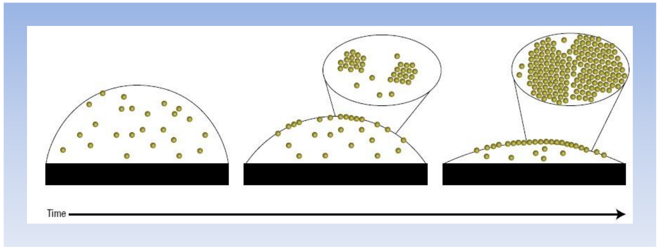
Nanoparticle Assembly Challenges

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

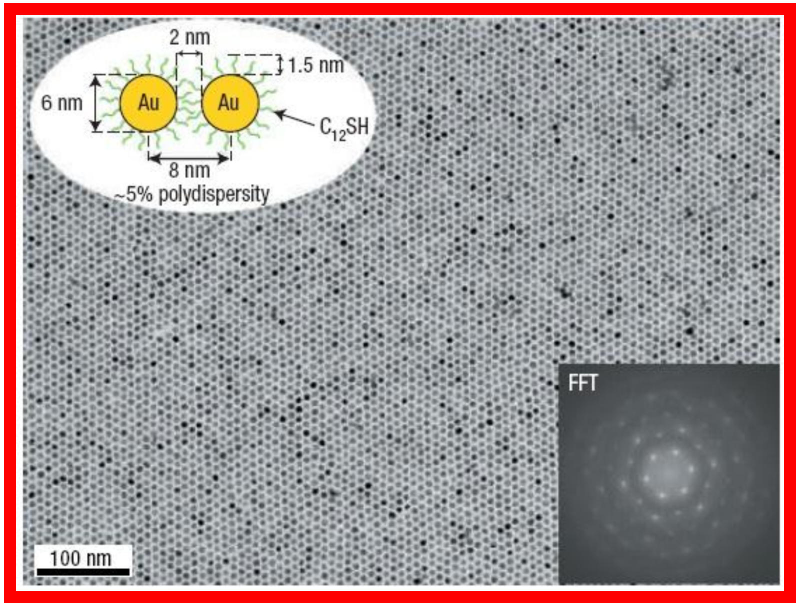
- Tailored properties
  optical, electrical, and
  magnetic

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

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

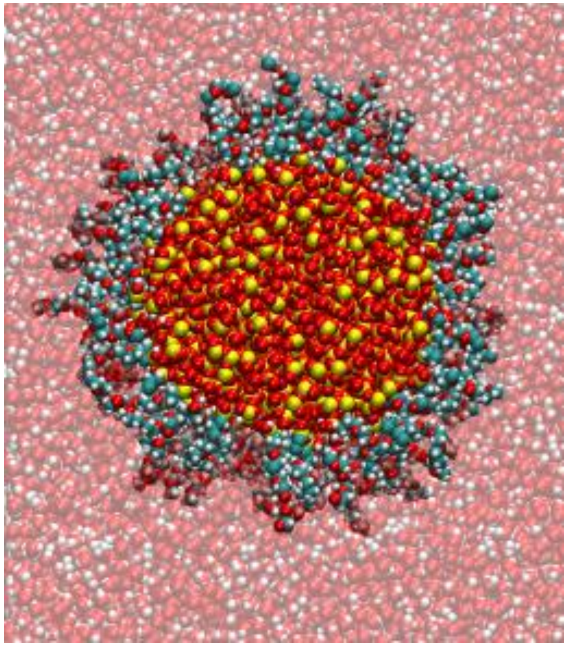


Slow evaporation of solvent



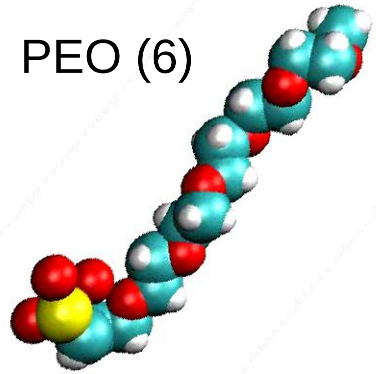
Bigioni *et al,* Nature Mat.5, 265 (2006)

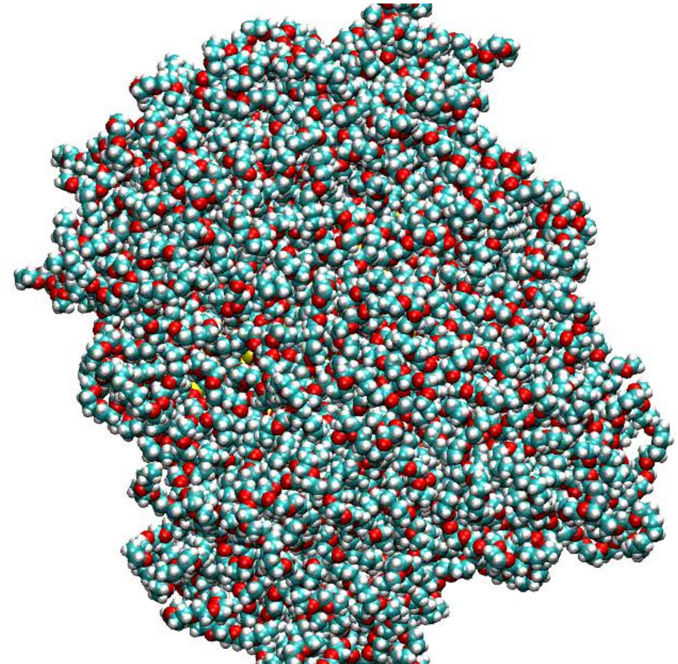
Coated Nanoparticles



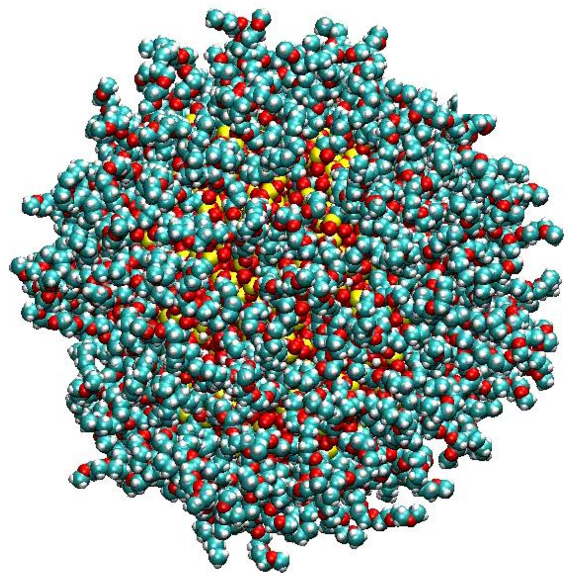
Polyethylene PEO(6) coated 5nm silica nanoparticle in water (3.1 chains/nm^2)

PEO (6)



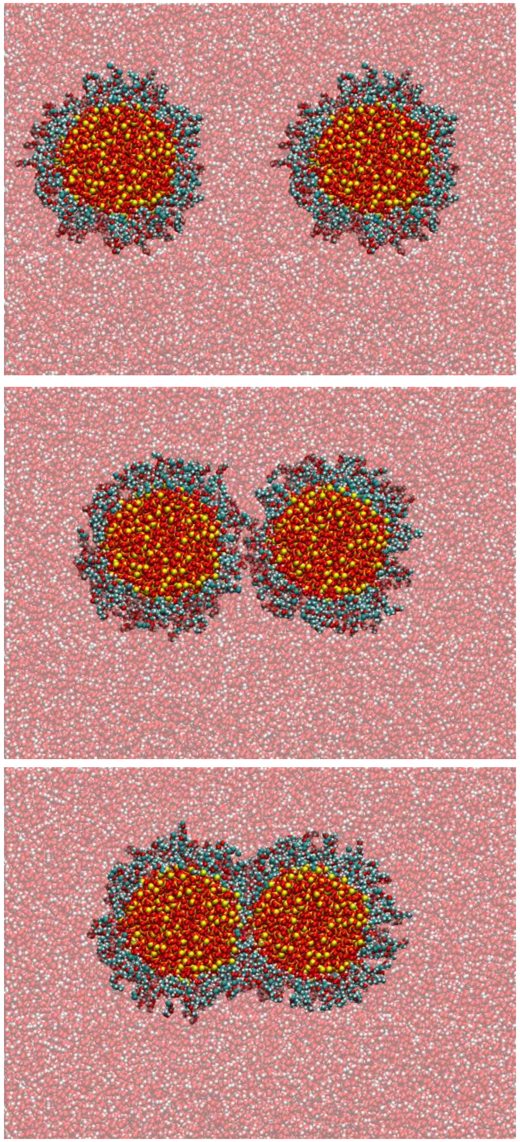


PEO(100)
0.5 chains/nm^2
Aspherical Shape

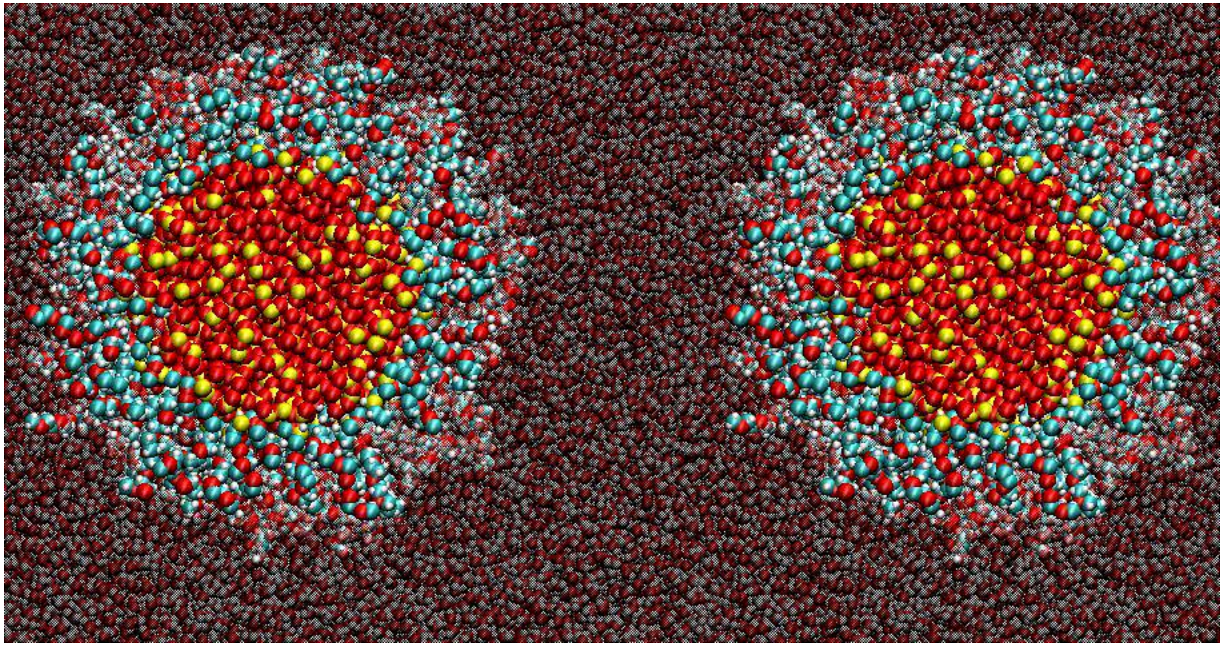


Lane et al, PRE 79, 050501 (2009); in prep (2012)

Interactions between Nanoparticles



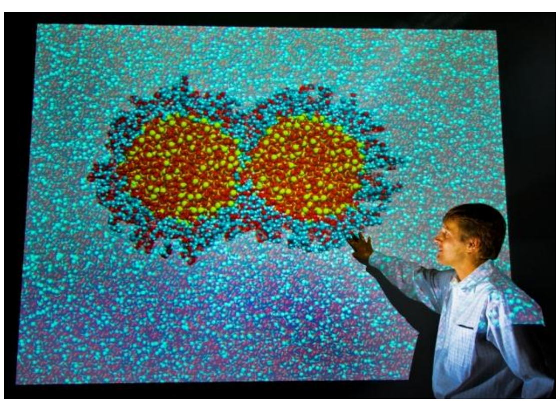
- Determine velocity independent (solvation) and velocity dependent (lubrication) forces
  - -chain length, nanoparticle size/shape, coverage
- Integrate into coarse-grained model

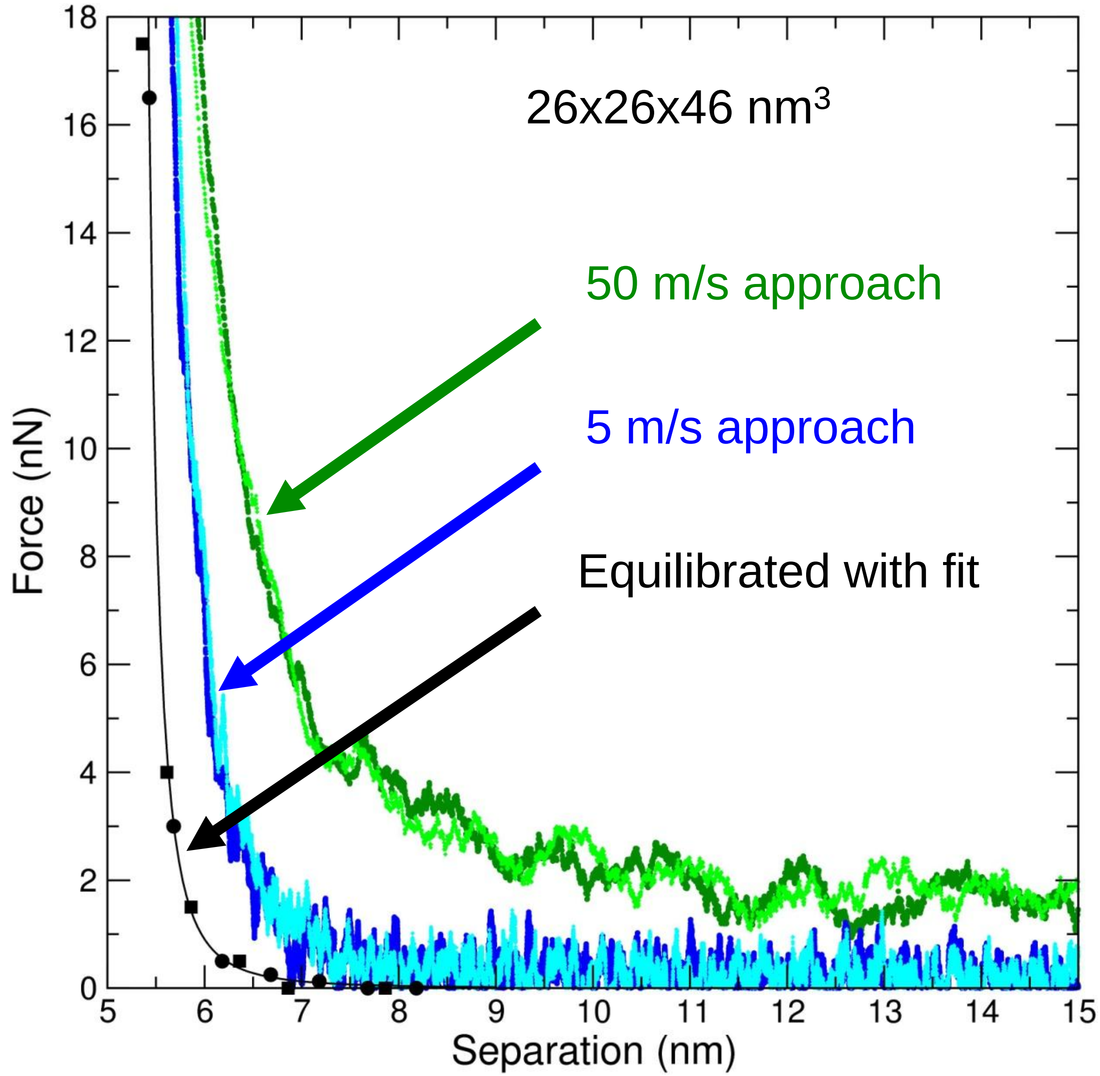


Lane et al, Phys. Rev. E 79, 050501(R) (2009); Ismail, Lane, Grest, in prep.

Force between Silica Nanoparticles

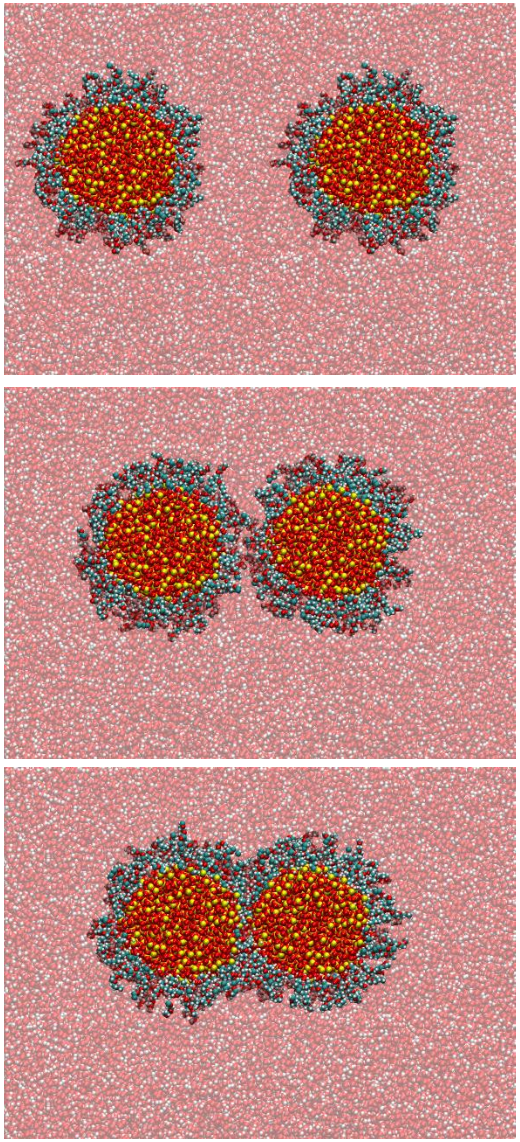
- Stokes drag at large separation with linear velocity scaling
- Complex mixed response in the separation range of interest (near contact)
- No oscillations in force

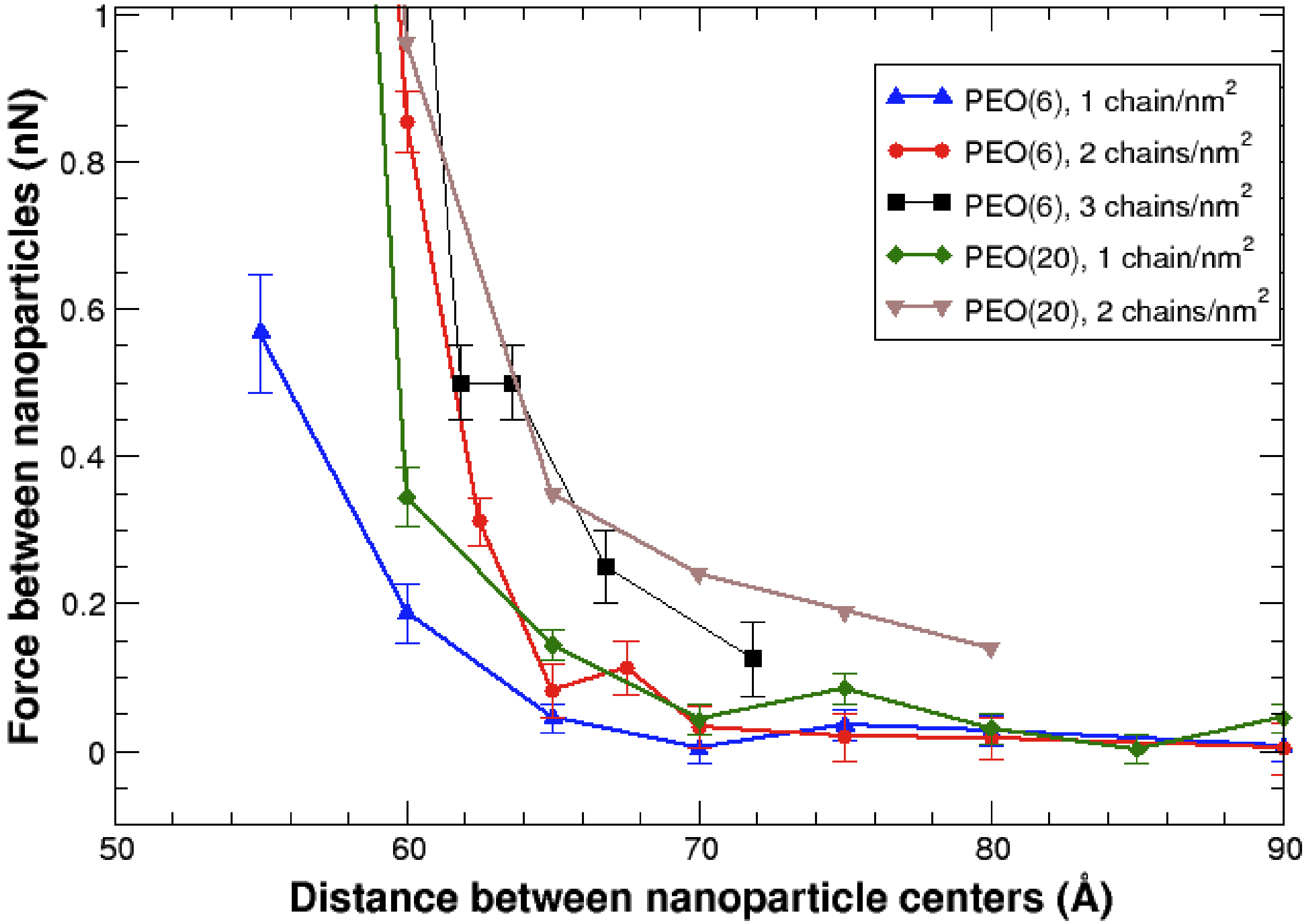




5 nm PEO(6) coated silica NP – 3 chains/nm^2

Interactions between Nanoparticles

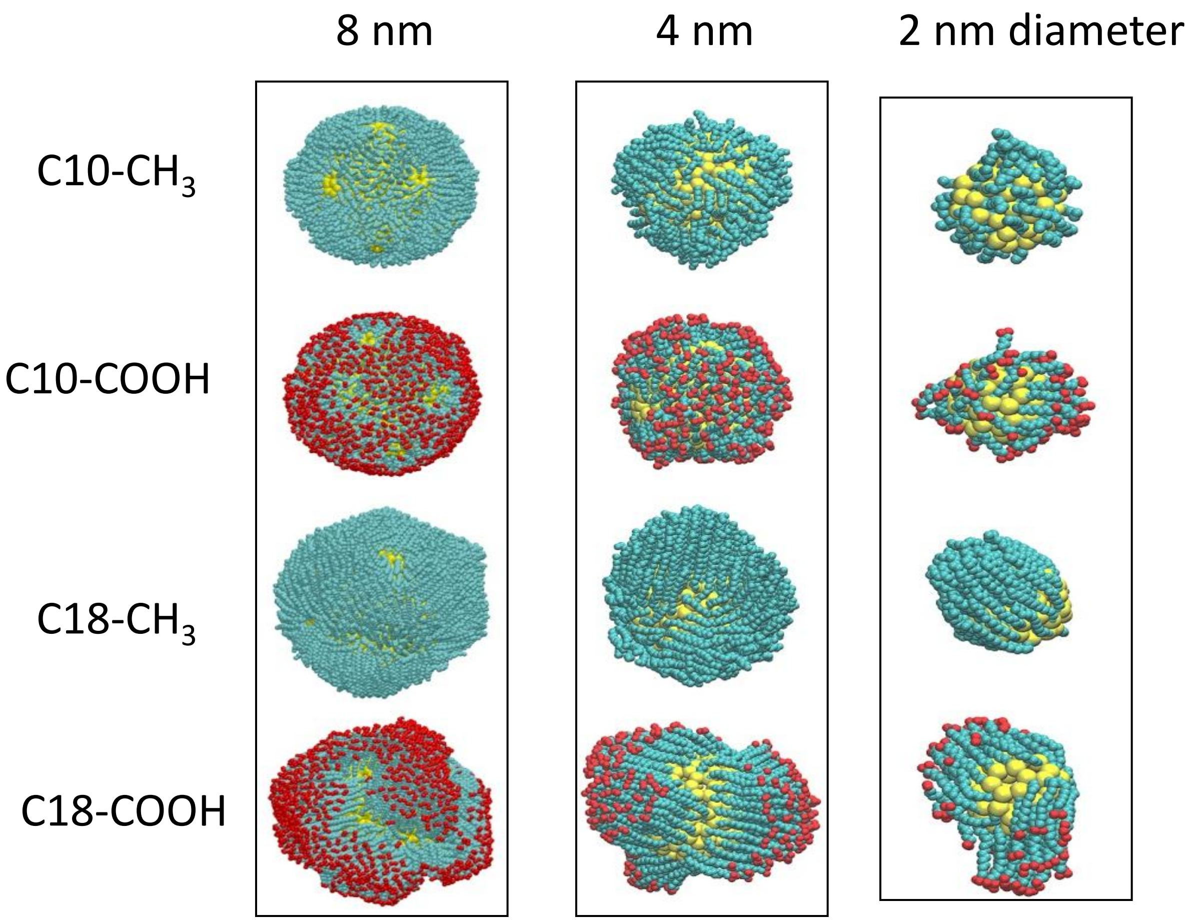


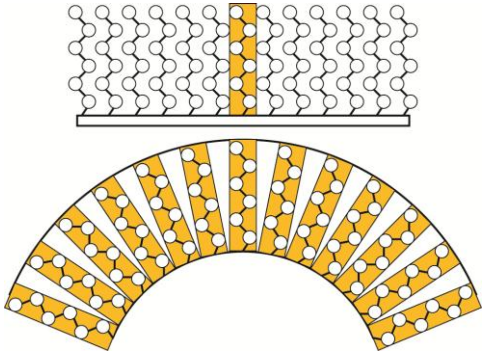


- 300K, thermal fluctuations corresponds to forces < 1 nN

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)

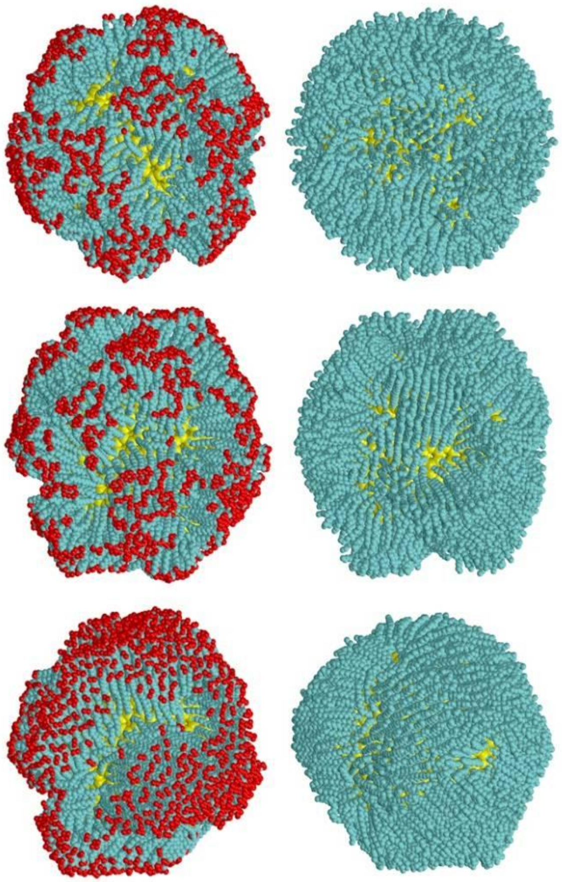
Different Solvents

C18-COOH　　C18-CH_3

decane

Implicit poor

water



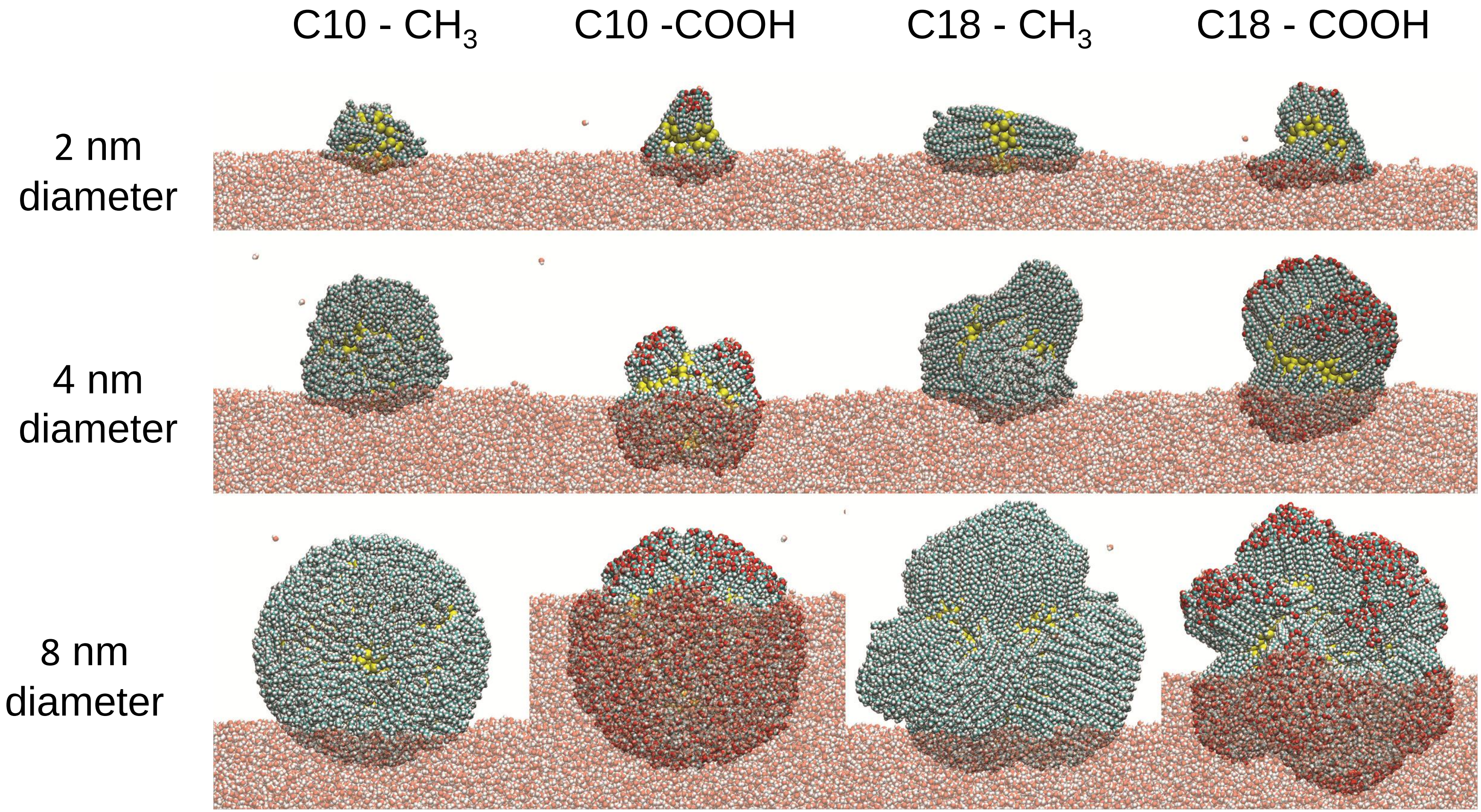
8 nm diameter

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

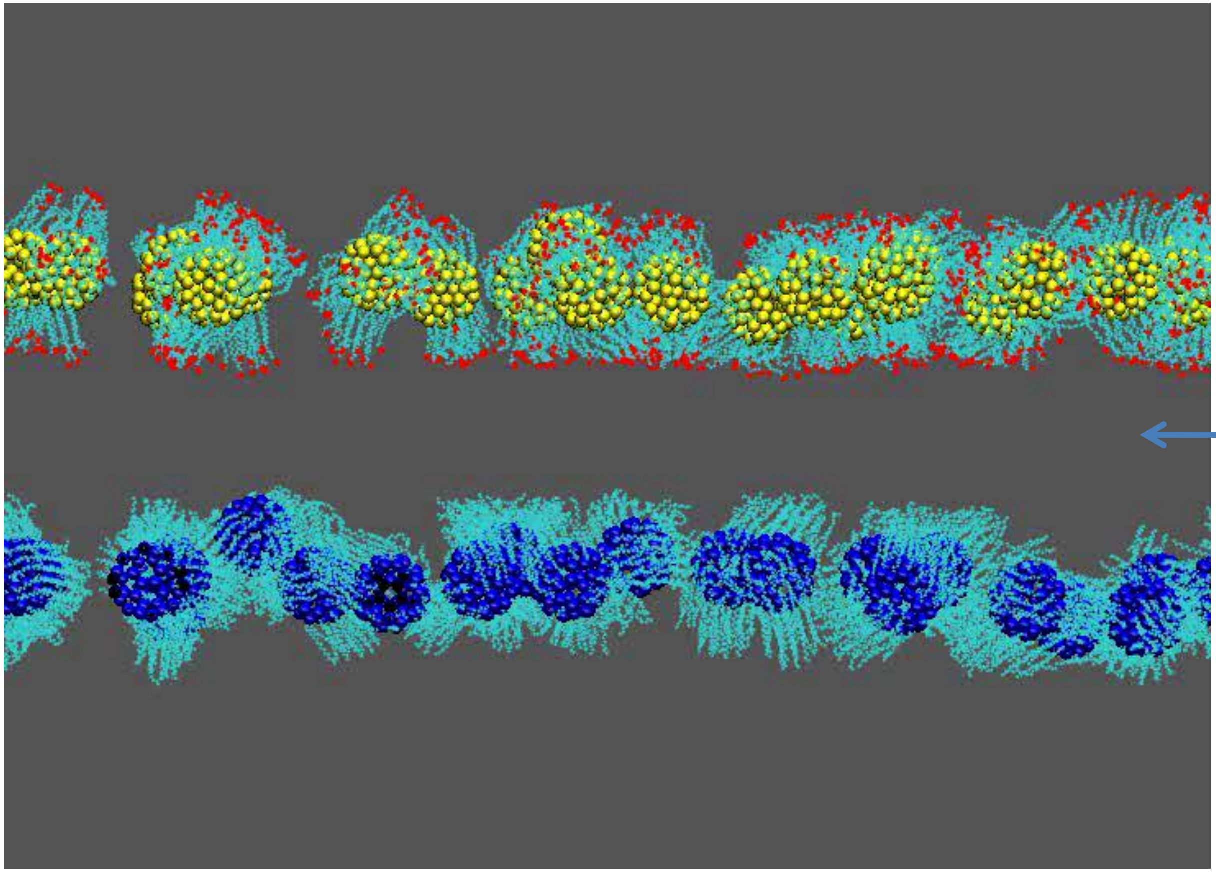
- COOH terminated chains form small tight bundles unless solvated

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

Coated Nanoparticles at a Water/Vapor Interface



Surface Aggregation and Self-Assembly

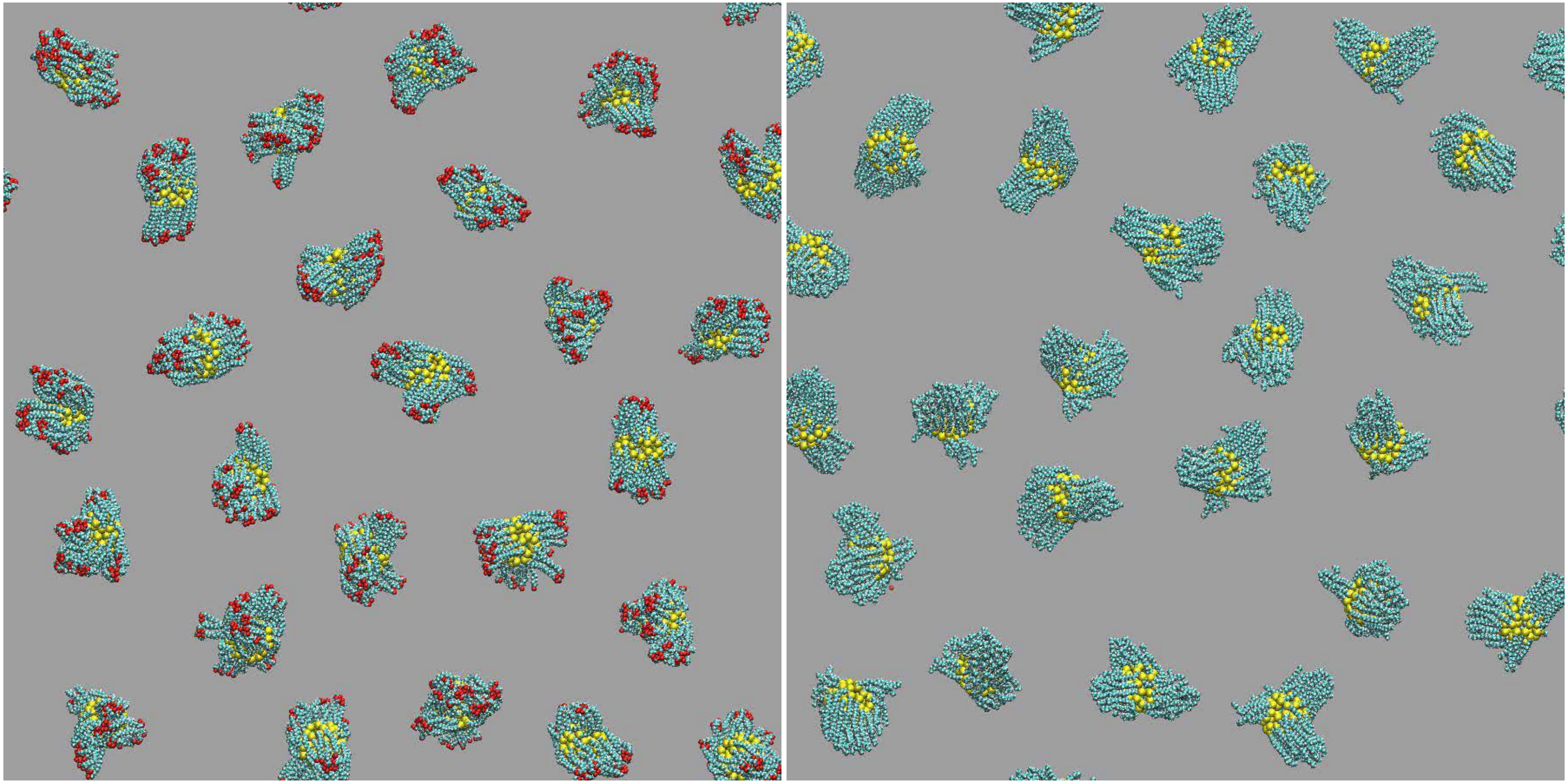


Water (not shown)

COOH terminal group (top)

CH_3 terminal group (bottom)

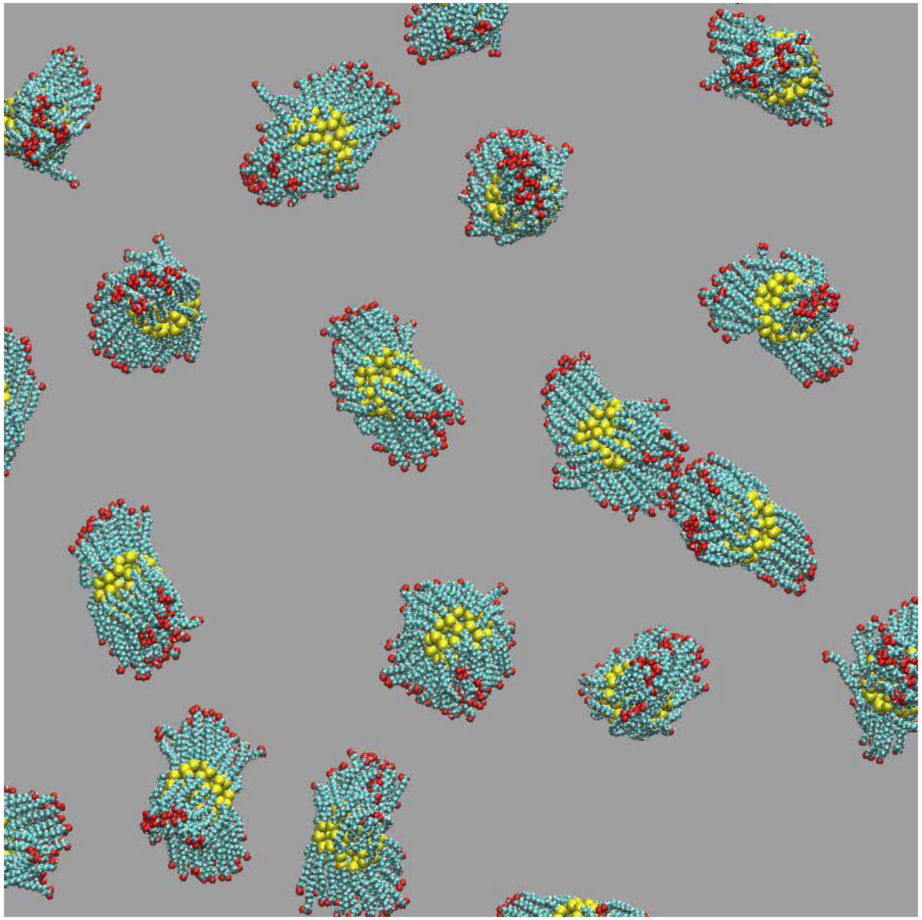
Surface Aggregation and Self-Assembly

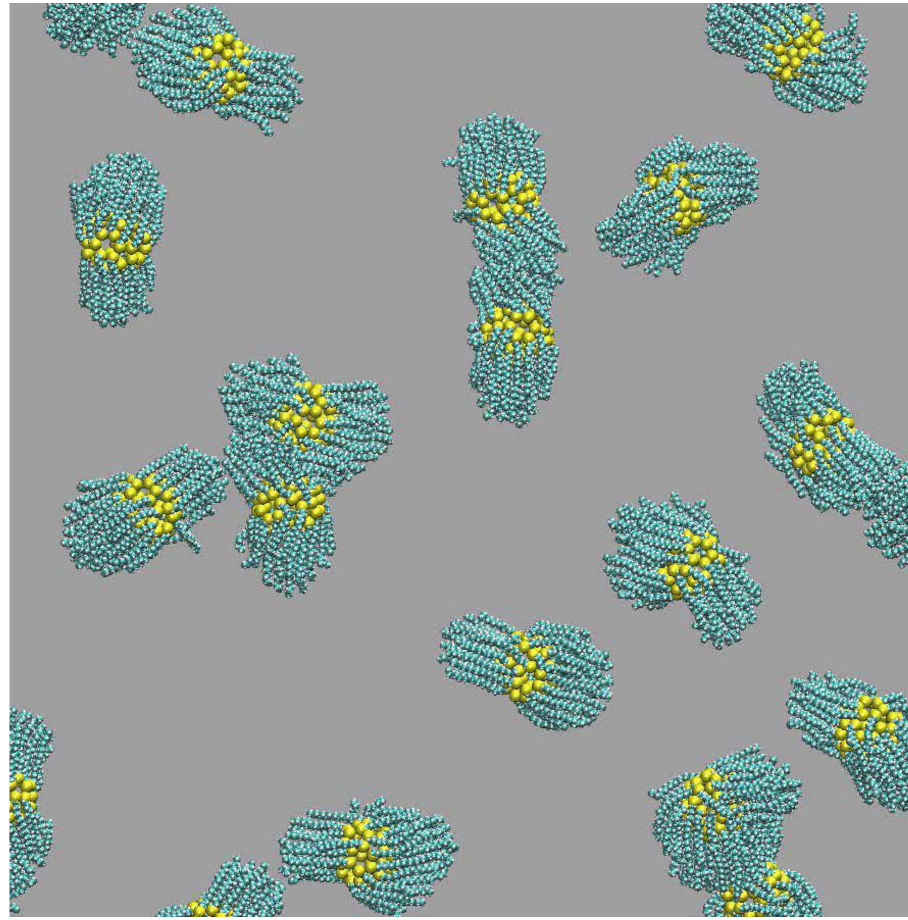


COOH terminal group   *CH_3 terminal group*

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

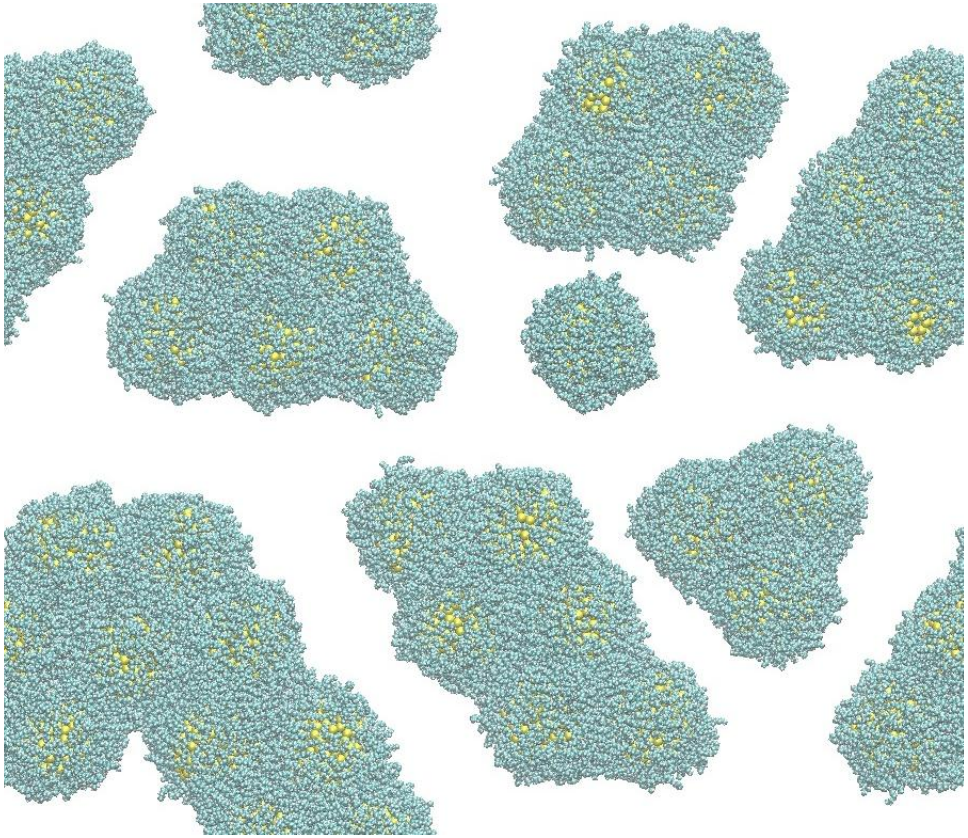




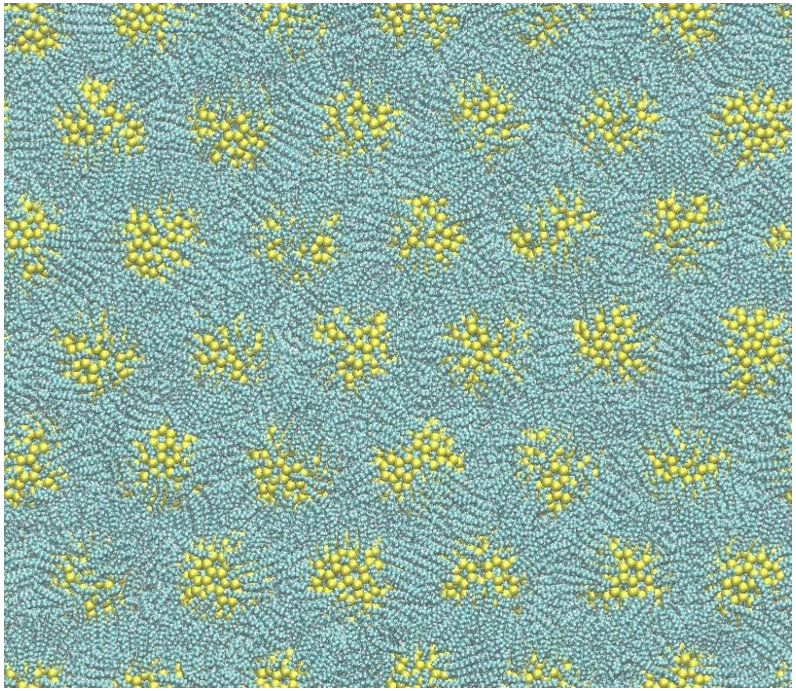
COOH terminal group 90 ns *CH_3 terminal group*

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

4 nm Diameter Alkanethiol Nanoparticles



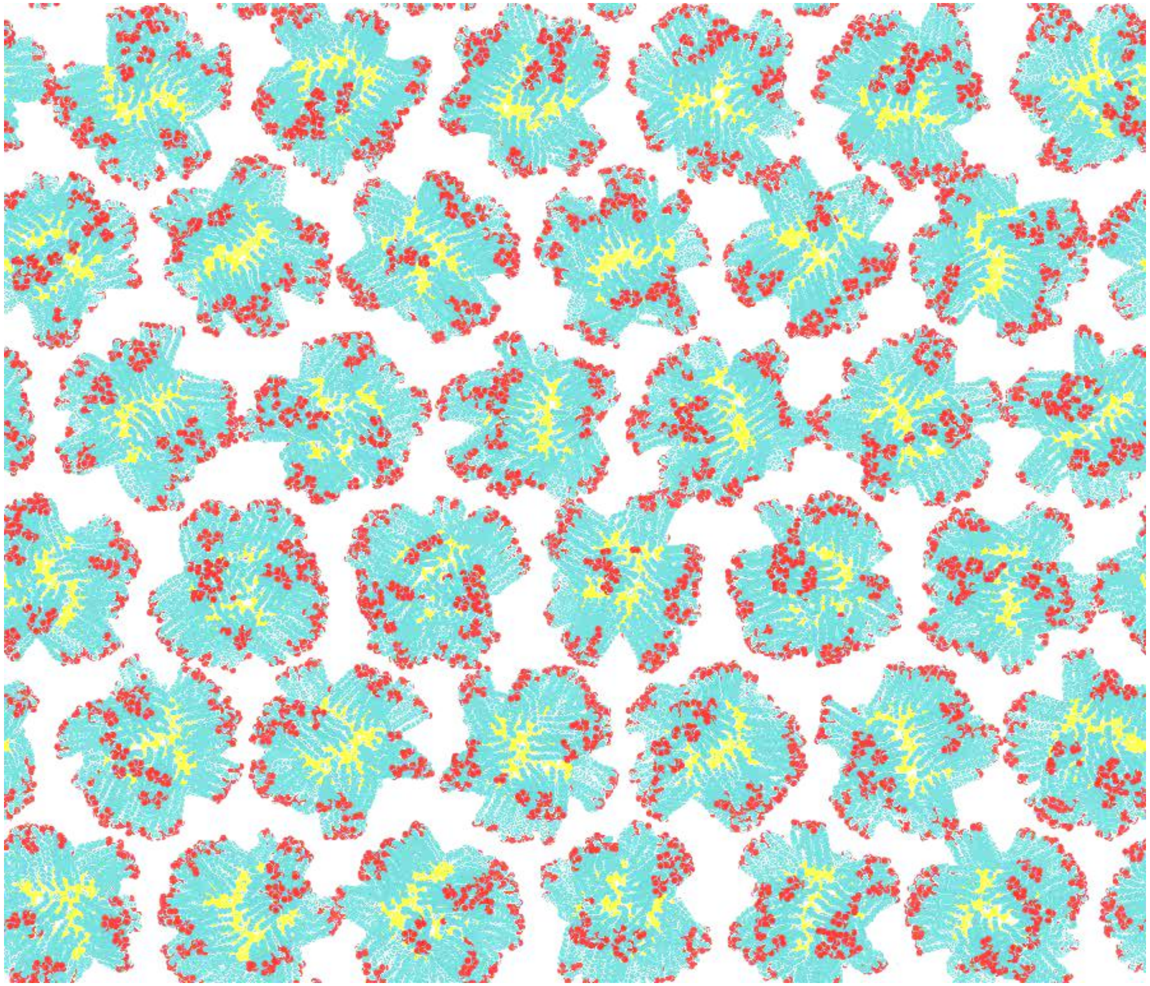
36 Nanoparticles – Hexagonal Lattice
4 ns – initial lattice spacing 80Å



Equilibrium 65 Å

CH_3 terminal group

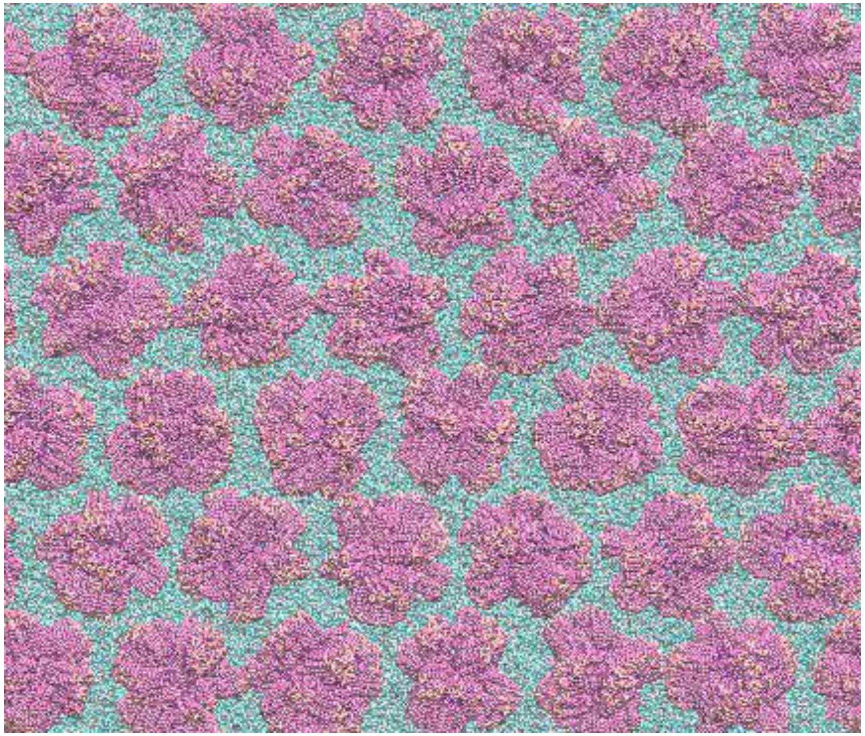
4 nm Diameter Alkanethiol Nanoparticles

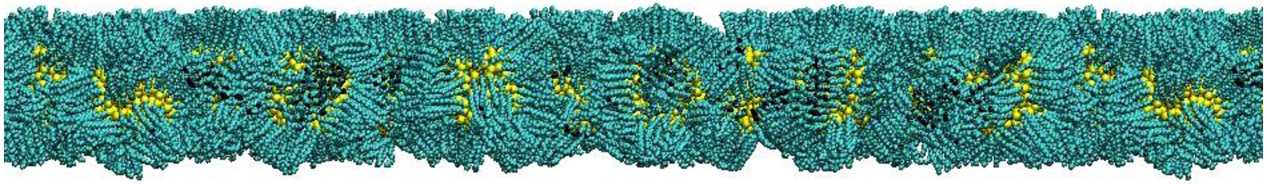


COOH terminal group

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

4 nm Diameter Alkanethiol Nanoparticles





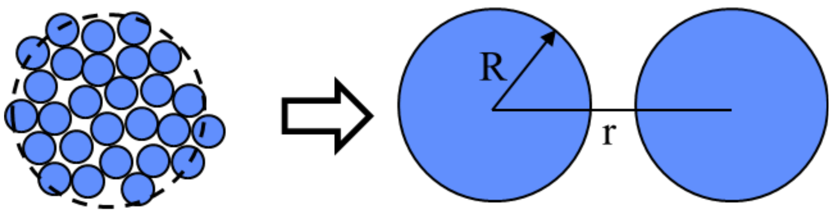
COOH terminal group

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

Coarse Graining - Nanoparticle Solutions

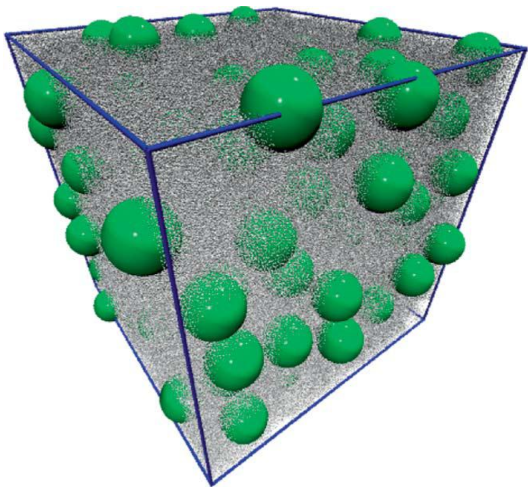
- Natural length scale of solvent is comparable to size of NP

- Effective Potential
  - Integrated NP potential
  - Potential of Mean Force



- Solvent representation
  - Implicit - easy/ignores hydrodynamics
  - Explicit - number increases as volume of nanoparticle
    NP diameter 20-25 x solvent diameter
  - Dissipative Particle Dynamics (DPD)
  - Stokesian Dynamics
  - Lattice Boltzmann
  - Multi-Particle Collision Dynamics

Minimal Model for NP in Suspension

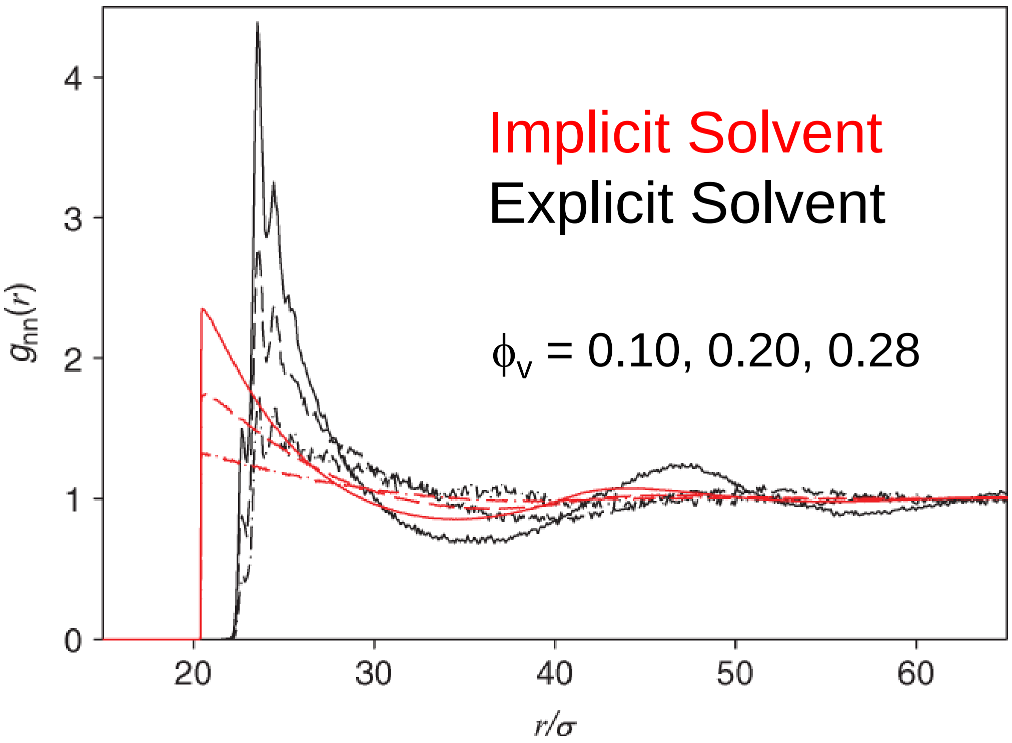


- 167 NP of diameter 20σ in 1.8 million LJ monomers
- Integrated interaction between NP

- Most models treat large colloidal particles as hard spheres
  - not suitable for modeling NPs in an explicit solvent
  - hard spheres strongly phase separate even for relatively small differences in size
- To solvate NPs in an explicit solvent critical to include attractive component of the interaction between NP and solvent
- Solvent layer surrounding NP forms increases the effective radii of NP

Grest et al, JCP 134, 144902 (2011)

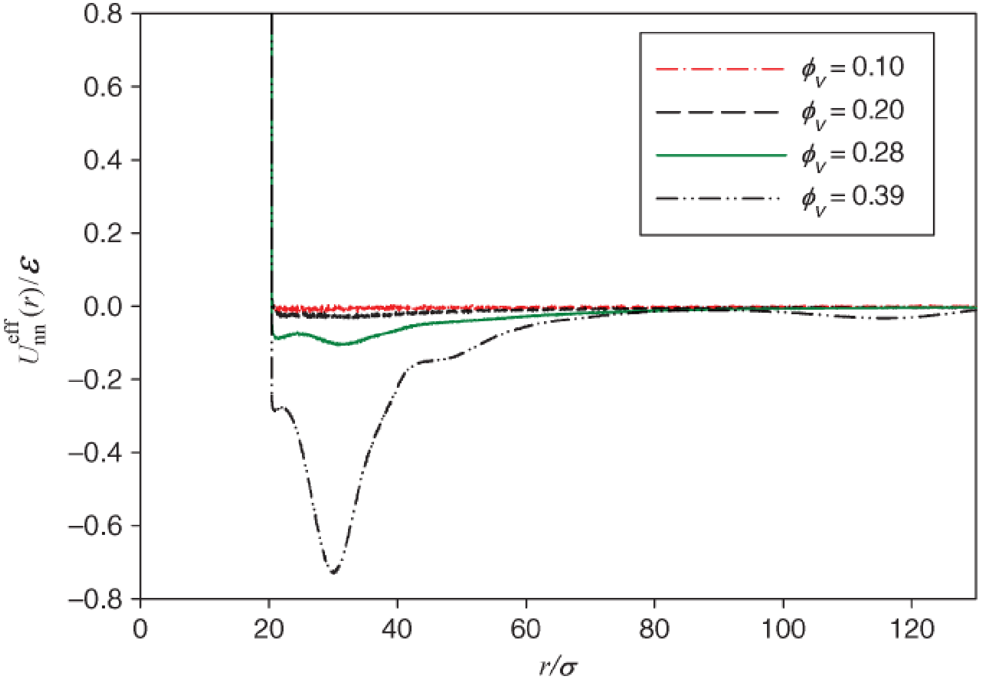
NP/NP Pair Correlation Function



- First peak is higher and shifted to larger separations for the explicit solvent
- Solvent forms a layer near NP
  - two NPs cannot approach as closely as for implicit solvent

Effective Potential between Nanoparticles

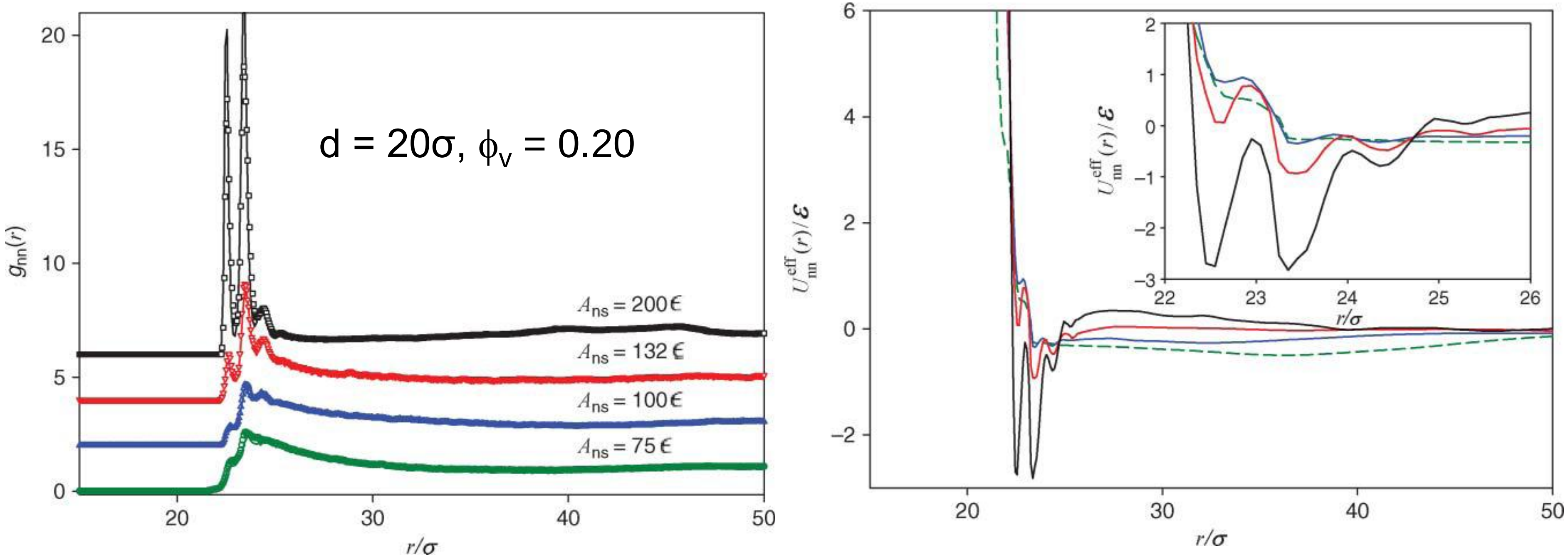
- Ornstein–Zernike equation with the Percus–Yevick closure approximation*
- Pure repulsive NP potential in implicit solvent recovered only for $\phi_v < 0.30$



*Behrens and Grier, PRE 64, 050401 (2001); Rajagopalan and Rao, PRE 55, 4423 (1997); Wang et al, PRE 81, 061204 (2010)

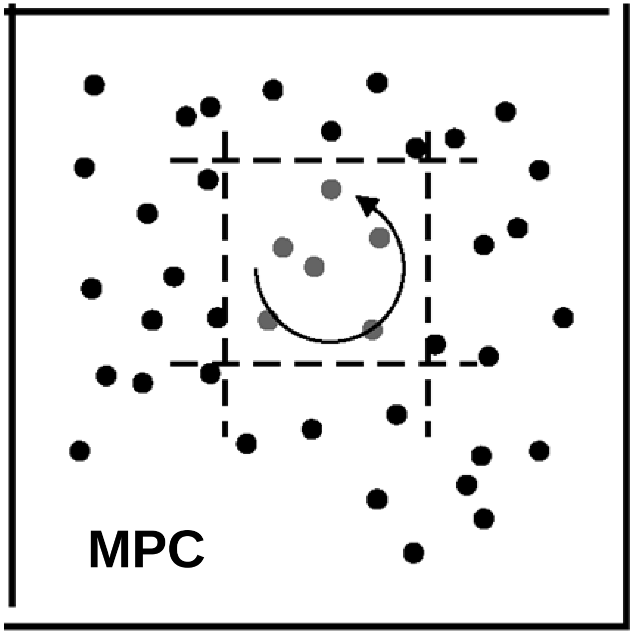
Effective Potential between Nanoparticles

- Effective Potential between NPs for varying strength of NP/solvent interaction



Multi-Particle Collision Dynamics

- Point particle based fluid
  - fluid interacts through collision operations
- Conserves linear momentum
- Produces fluctuating hydrodynamic behavior
- Computational efficient
  - No pair wise potential
  - Rotation does not limit time step
- Density/viscosity can be mapped to LJ fluid, water, …*

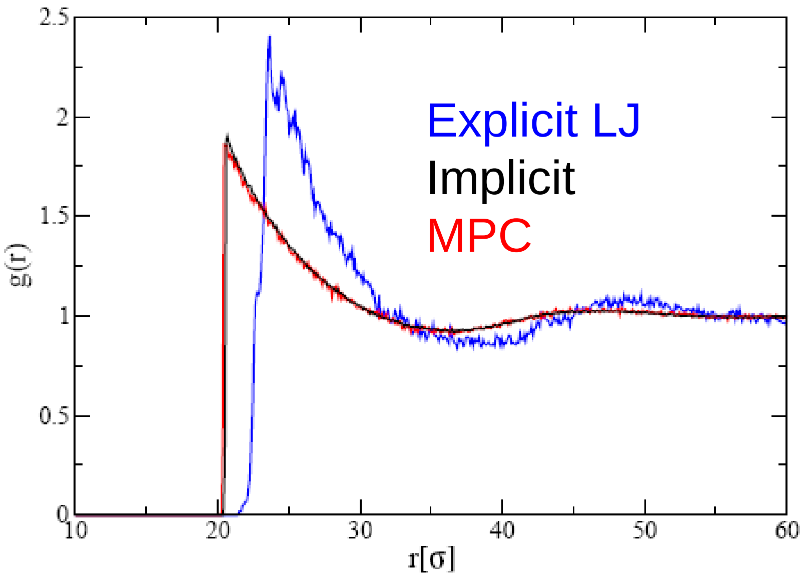


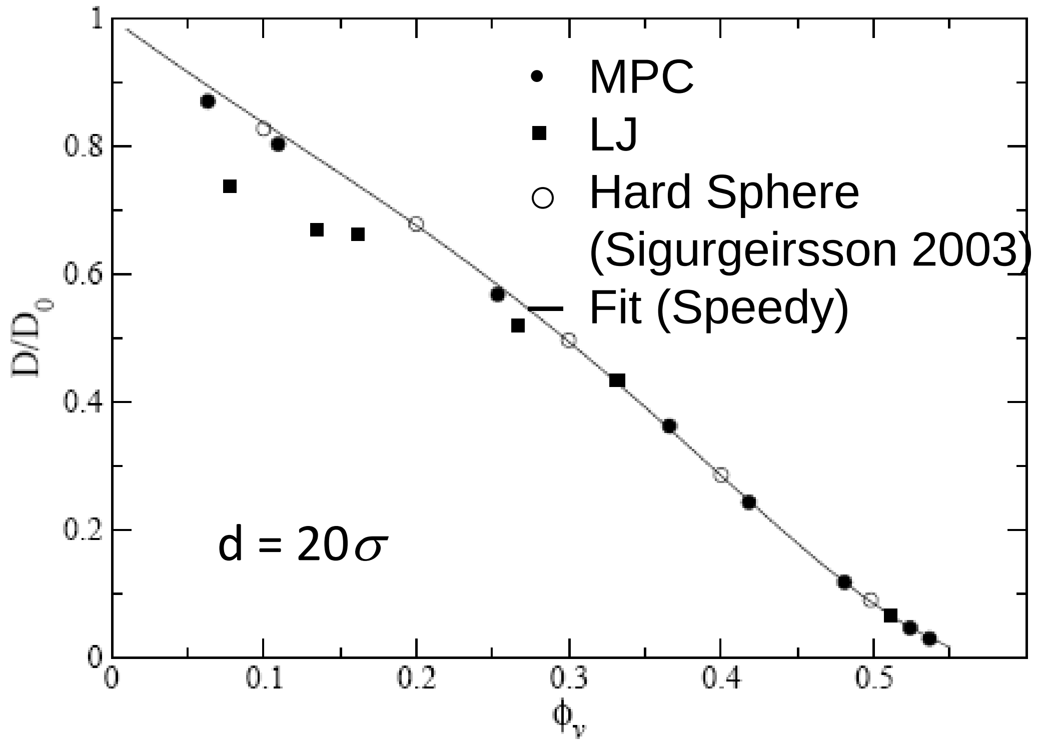
Malevanets and Kapral, J. Phys. Chem. 110, 8605 (1999).
Gompper et al, Adv. Polym. Sci. 221, 1 (2009)

*Petersen, JCP 132, 174106 (2010).

Equilibrium: Nanoparticle Diffusion

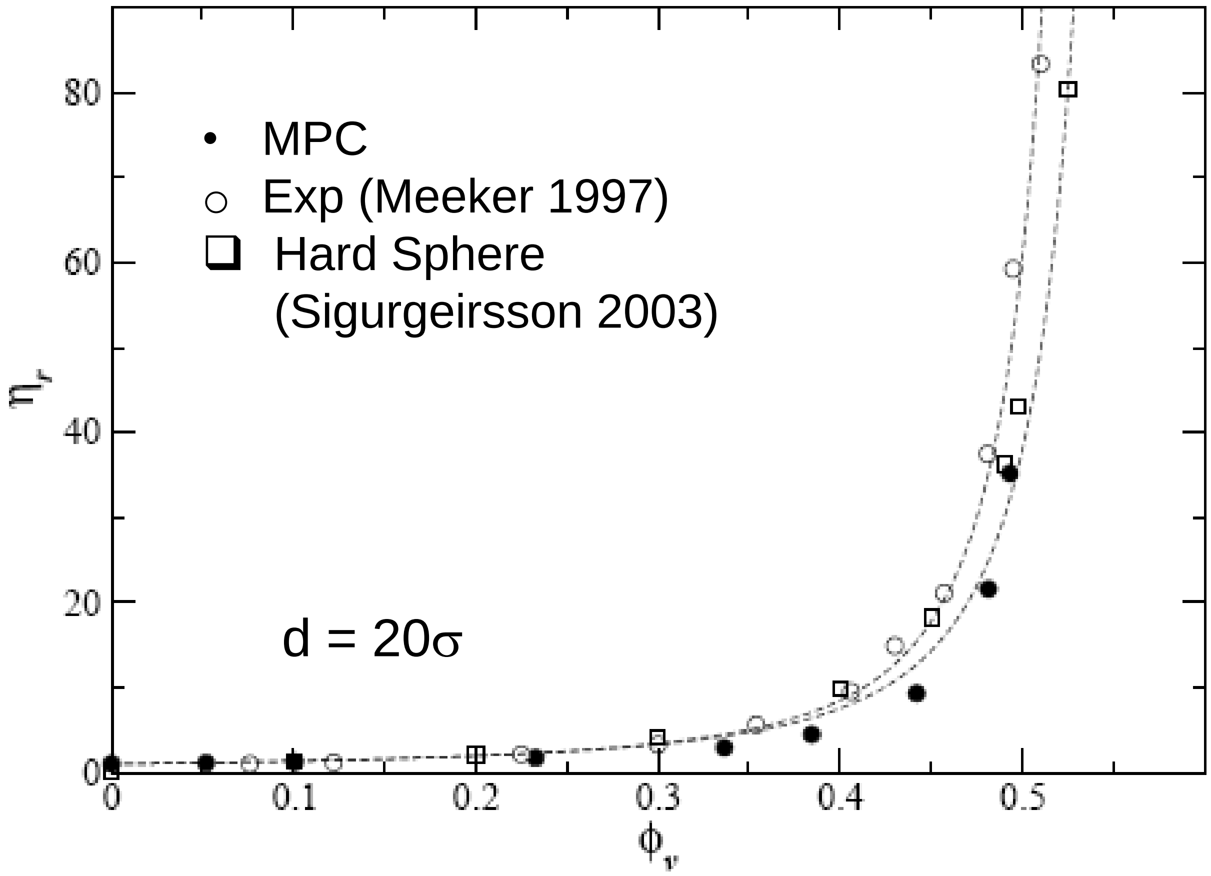
- Select MPC parameters to map to LJ viscosity and density
  - – MPC have ideal gas pressure
- Implicit/MPC give identical g(r)





- MPC results agree with hard sphere experiments on micron size colloids
- Deviations for low ϕ_v for LJ solvent due to solvation shell around NP

Zero Shear-Rate Viscosity



- MPC results in good agreement with hard sphere simulations and experiment

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
- Mapping to Coarse Grained Models captures some but not all the important details of Nanoparticles in Solution

Acknowledgements

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- Ahmed Ismail (Universität Aachen)
- Christian Lorenz (King's College)
- Qifei Wang, David J. Keffer (University of Tennessee

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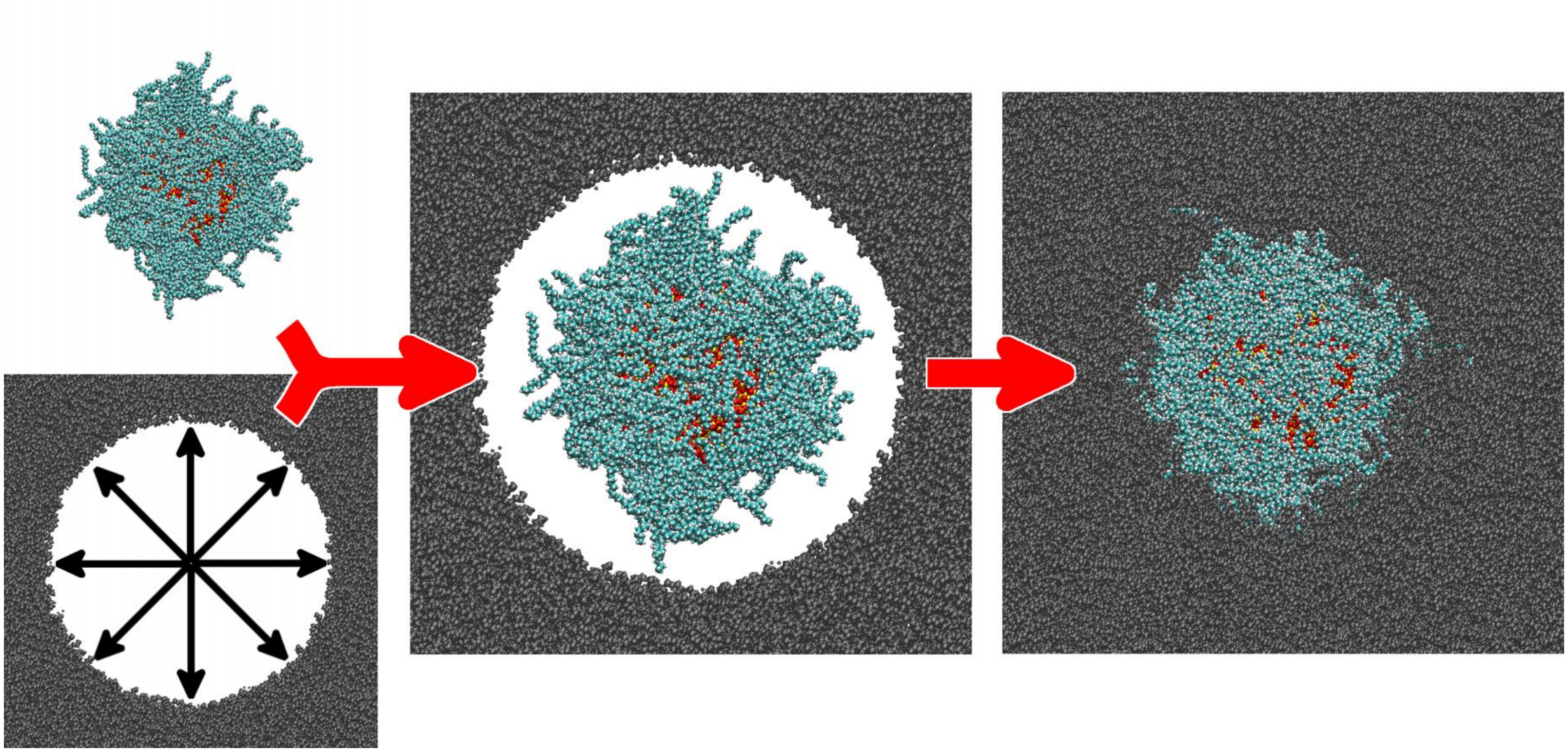
- Center for Integrated Nanotechnology (CINT)
- DOE – ALCC grant 40 million core hours on NERSC/ORNL

Computers:

- Sandia's Red Sky/Red Mesa
- NERSC Hopper XE6
- ORNL Jaguar Cray XE6

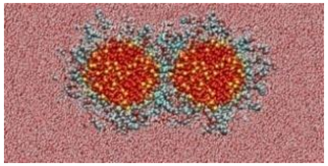
How Systems are Build



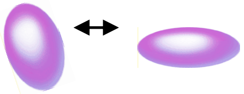
- Ligands attached to nanoparticle, equilibrated in implicit solvent
- Spherical cavity is grown in melt – NPT
- Nanoparticle inserted into melt, equilibrated - NPT
- System run for 2-10 ns - NVT

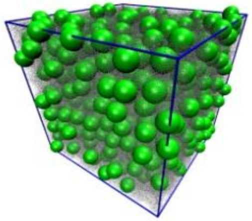
Integrated Hierarchical Approach

Molecular Dynamics — **Molecular scale** — *nsecs* *0.1 to 10 nm*



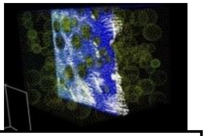
Effective potentials — **Particle Scale** — *μsecs* *10 to100 nm*





Coupled particle-fluid Interactions:
LB, SRD, DPD, SD

"Mesoscale" — *msecs* *100 nm-10 μm*



Integrating Tools Across Scales

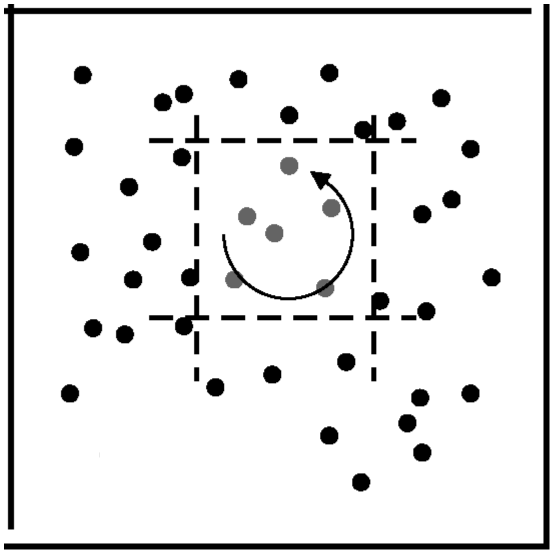
Constitutive Relations **Micro-structure**

Experimental Validation

Engineering Scale — *seconds* *mm*

Multi-Particle Collision Dynamics

- Simulation cell divided up into cubic cells of side
  - On average, M SRD particles with mass m_f are placed in each cell of volume a^3
- Two simulations steps
  - Particle streaming
    - particles move according to Forward Euler $v_i t$
  - Velocity update (coarse-grained collision)
    - Apply rotation about randomly chosen axis to fluctuating part of the velocity



$$\mathbf{v}_i(t+\tau) = \mathbf{u}(\xi_i(t+\tau)) + \omega(\xi_i(t+\tau))(\mathbf{v}_i(t) - \mathbf{u}(\xi_i(t+\tau)))$$

- Or can have $U(r_{coll}\text{-}r_{SRD})$

$$m_f \frac{d\mathbf{v}_i}{dt} = \mathbf{f}_i$$

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i$$

Coupling to Colloids

- MPC particles collide with colloids
  - Solvent coarse-grained so assume no-slip via stochastic rule
  - SRD particle receives a new random velocity magnitude

$$P(v_n) \propto v_n \exp(-\beta v_n^2)$$

$$P(v_t) \propto \exp(-\beta v_t^2)$$

  - Difference in new and old velocity is momentum transferred to colloid
- Generalized slip conditions or pair-interaction, $U(r_{coll}-r_{SRD})$ possible