Green Engineering of Dispersed Nanoparticles: Measuring and Modeling Nanoparticle Forces

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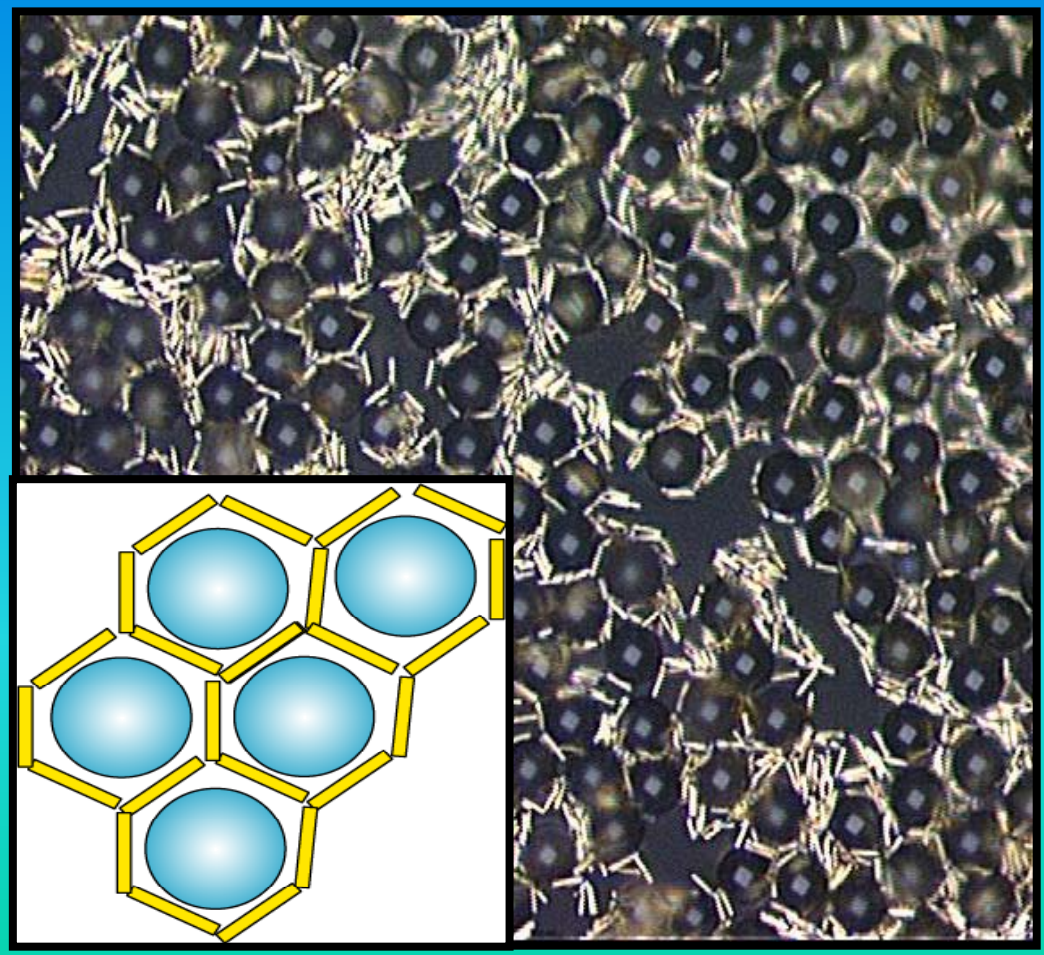
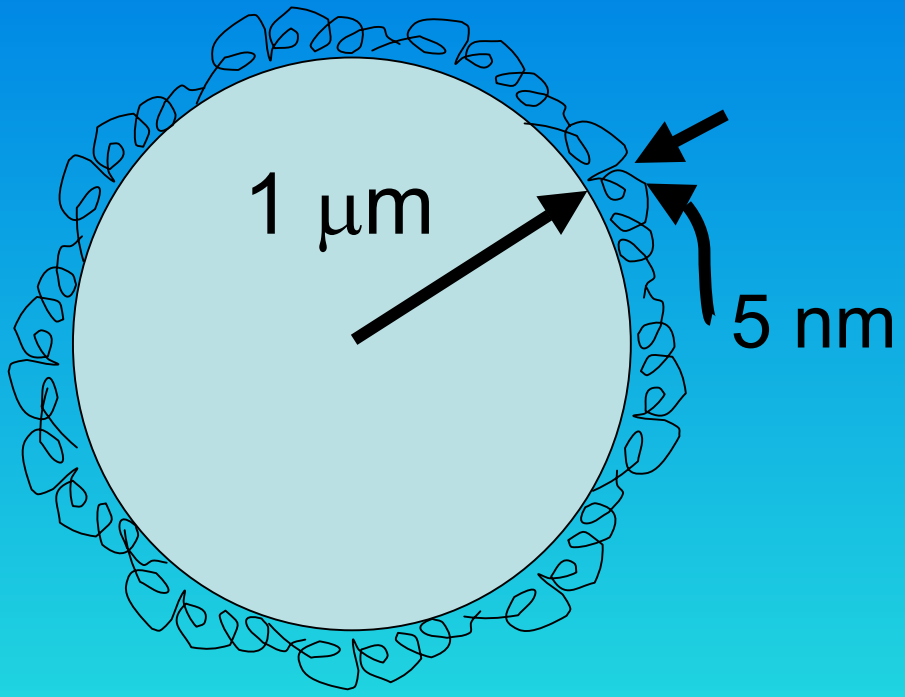
Nanoparticles: Potential Building Blocks For New and Existing Materials

- Catalysts
- Optical Materials
- Structural Materials
- Electronic Materials

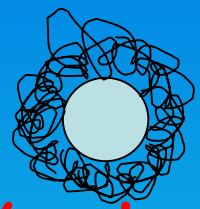
Nano-Electronics



Difficult to Disperse or Assemble "Bare" Nanoparticles



Conventional Colloids:
Dispersant: ~1% volume

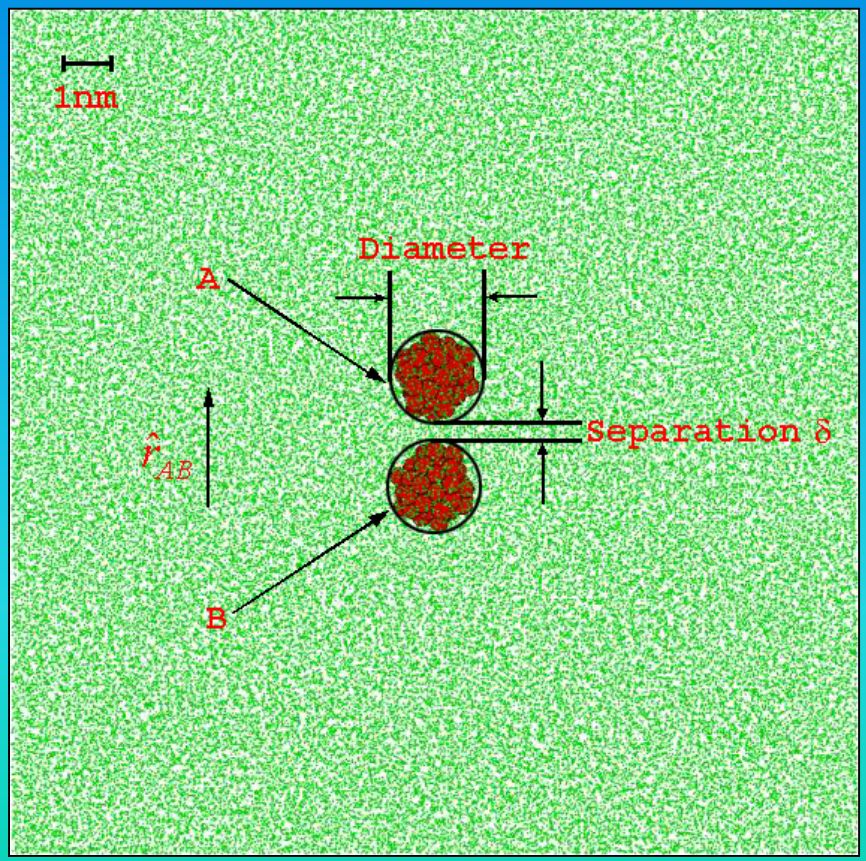


Nanoparticles:
Dispersant: ~ **90% volume**

A LOT OF WASTE !!!!!

Nanoparticle Forces are **POORLY UNDERSTOOD!**

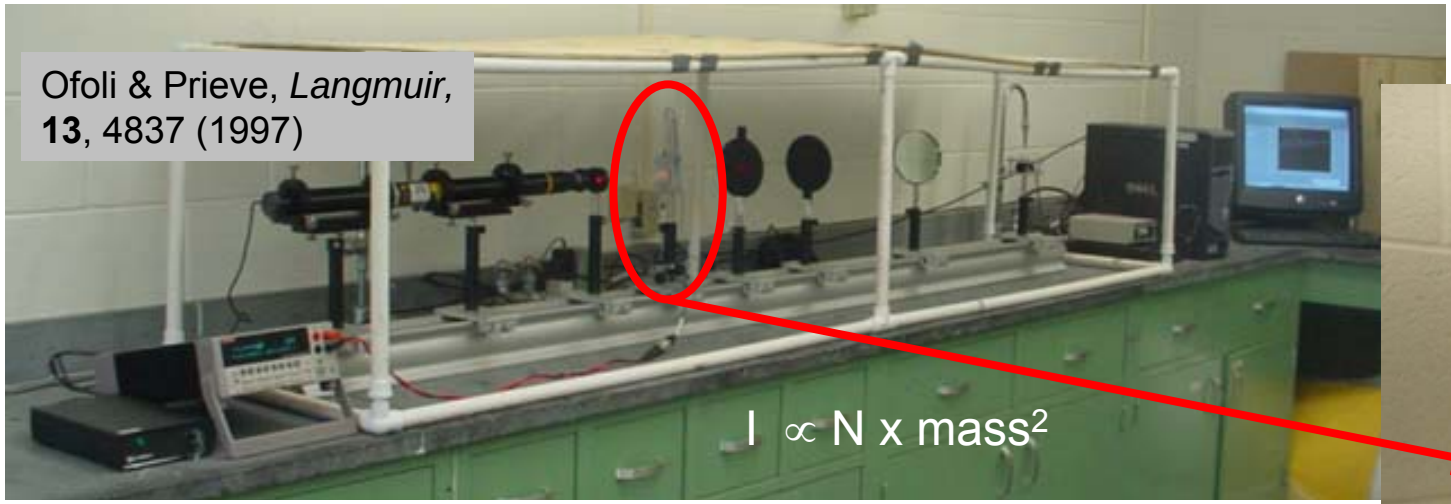
Colloidal Forces from Molecular Dynamics Simulations

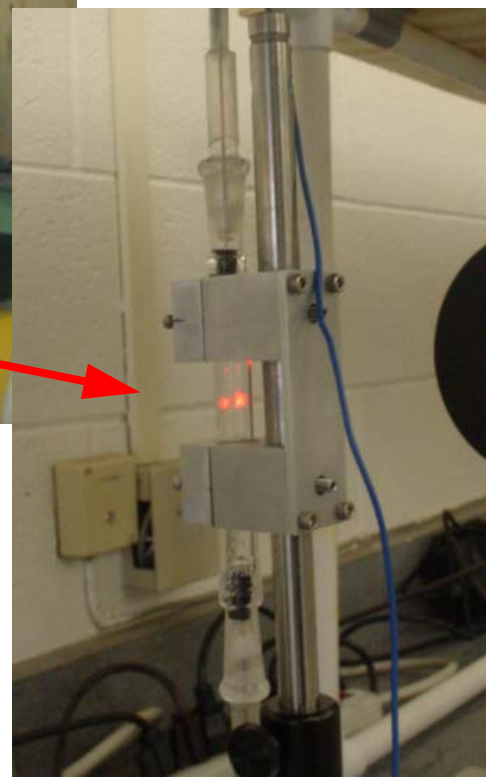


- van der Waals and Electrostatic Forces: DLVO theory
- Solvation Forces: Solvent Ordering
- Depletion Forces: Entropic

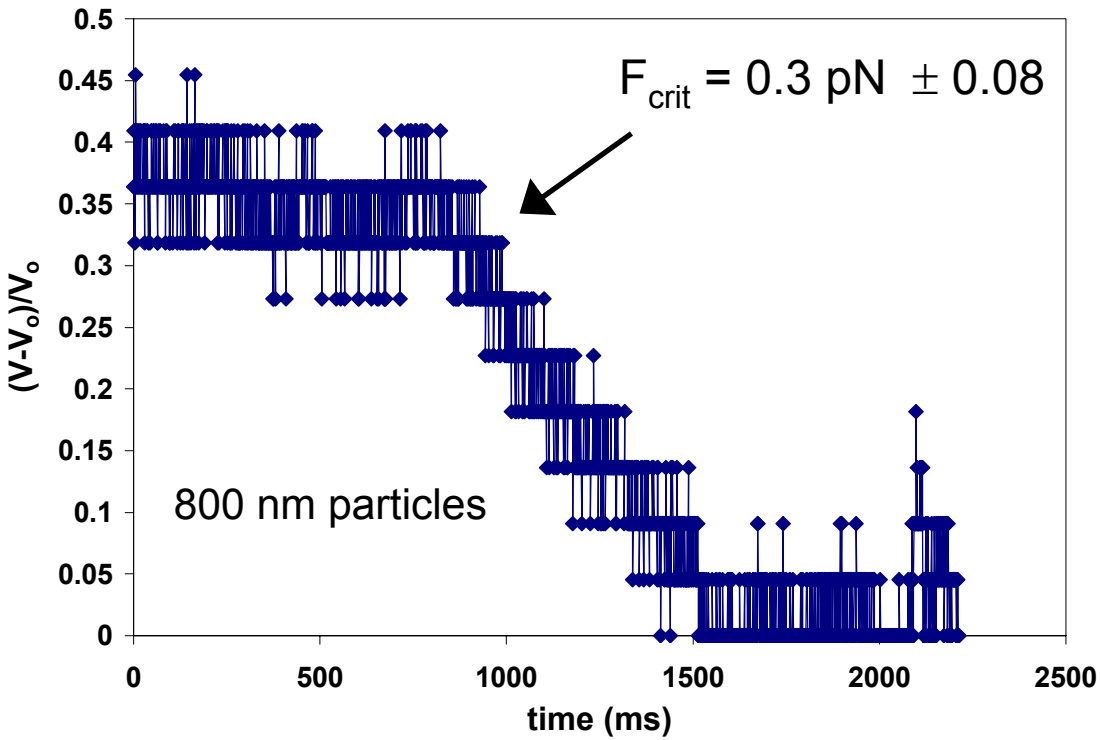
How Do These Work for Colloidal Nanoparticles?

Particle force light scattering (PFLS) for nanoparticle forces





custom differential electrophoresis cell

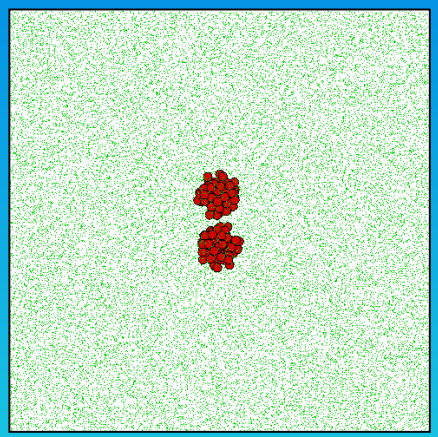


Large-Scale Parallel MD Simulation

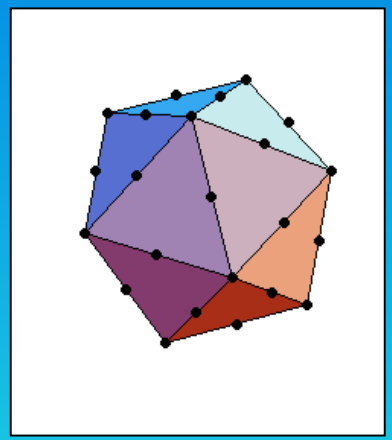
- Solvent: Lennard-Jones Liquid, n-Decane ($>10^5$ Atoms)
- Nanoparticles: Solid Clusters of Atoms
- Solvophilic Nanoparticles: ($\varepsilon_{sf} = 5.0\ \varepsilon_{ff}$)
- Solvophobic Nanoparticles: ($\varepsilon_{sf} = 0.2\ \varepsilon_{ff}$)

Beowulf Cluster: Cruncher

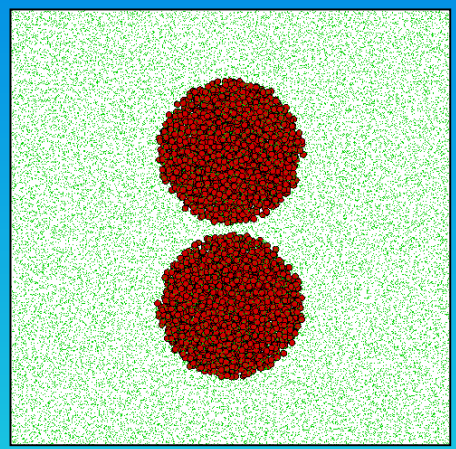
Model Nanoparticles



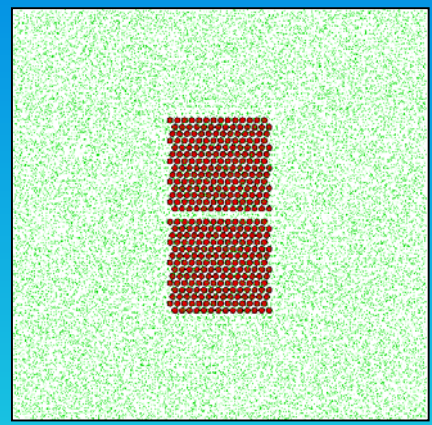
Small Sphere
d = 4.9 σ
64 atoms



Icosahedron
d = 4.0 σ
55 atoms



Large Sphere
d = 17.6 σ
2048 atoms



Cube
d = 13.2 σ
2744 atoms

Solvation Forces: Thermodynamic Integration

Free Energy Change

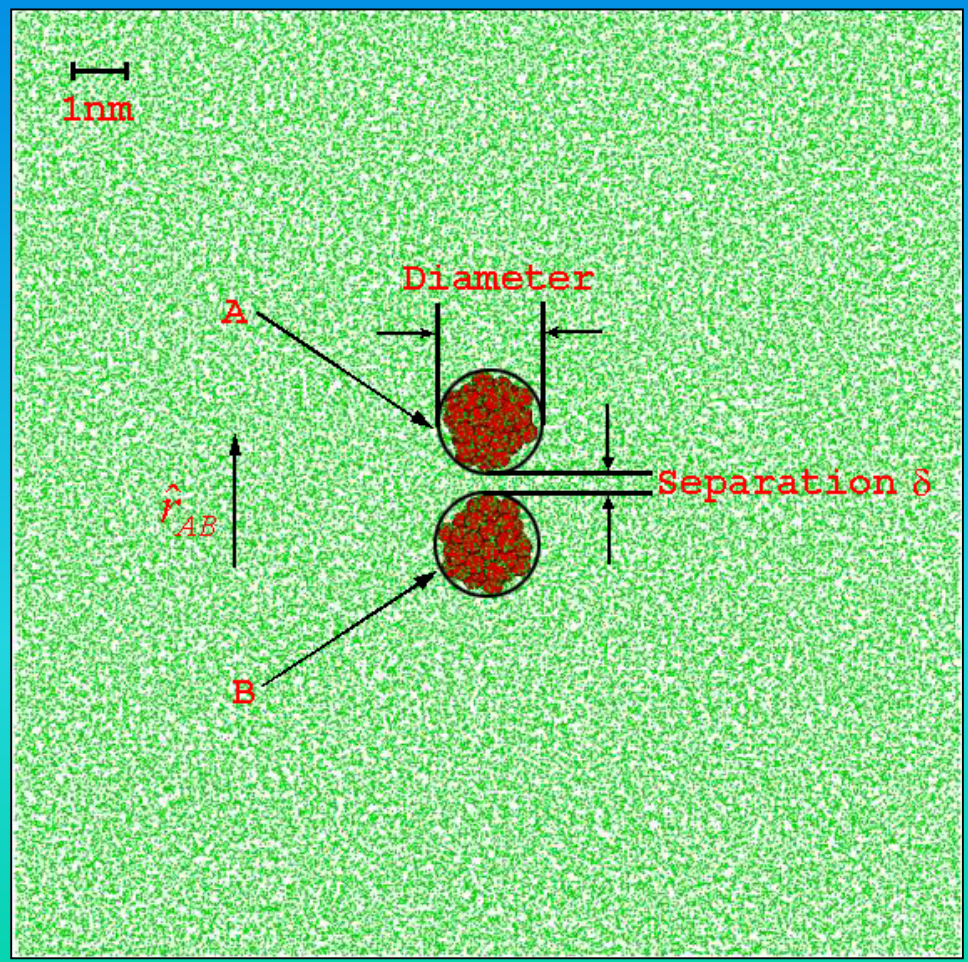
$$\Delta A_{ij} = \int_{\delta_i}^{\delta_j} d\delta \left\langle \frac{dU(\delta)}{d\delta} \right\rangle_{\delta}$$

Mezei and Beveridge,
Ann. N. Y. Acad. Sci. **482**, 1 (1986).

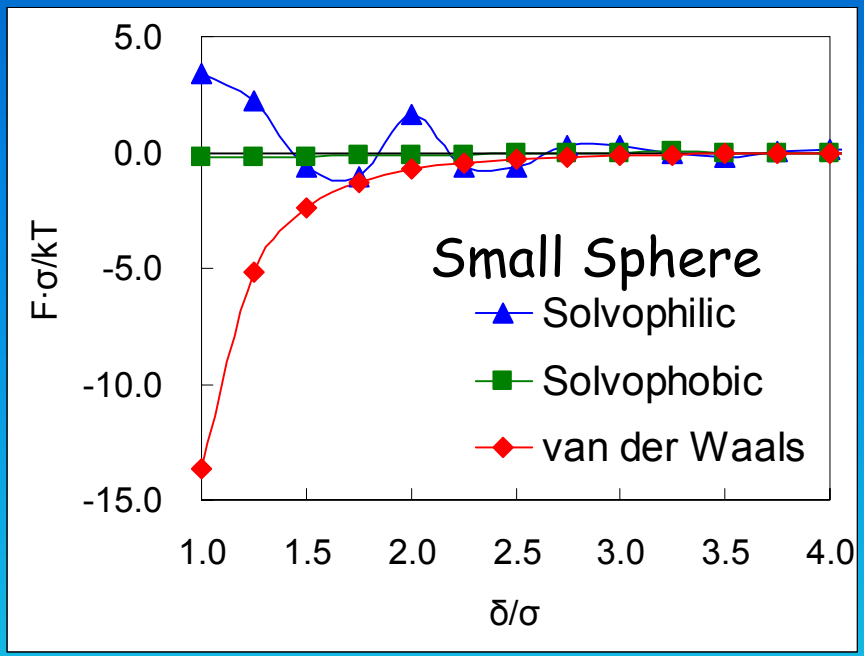
Solvation Force

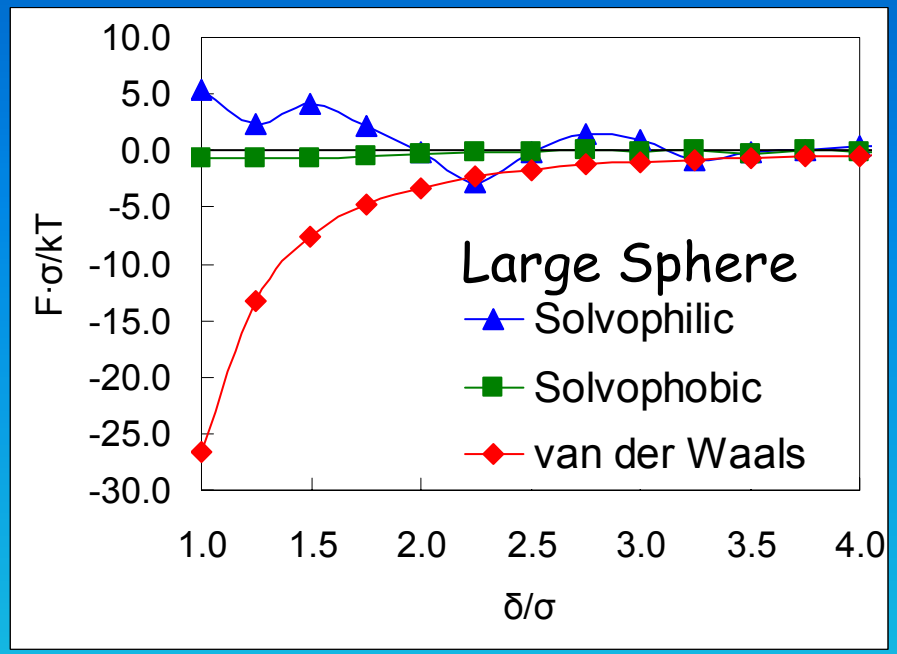
$$F^{solv}(\delta) = \left\langle -\frac{dU^{solv}(\delta)}{d\delta} \right\rangle_{\delta}$$

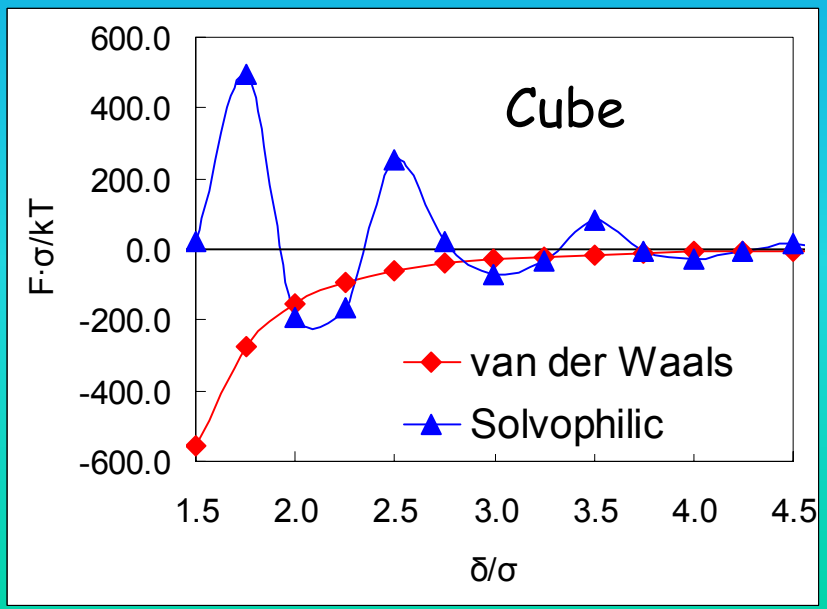
$$= \left\langle \hat{r}_{AB} \cdot (F_{AS} - F_{BS}) \right\rangle$$



Interactions for Spheres, Cubes

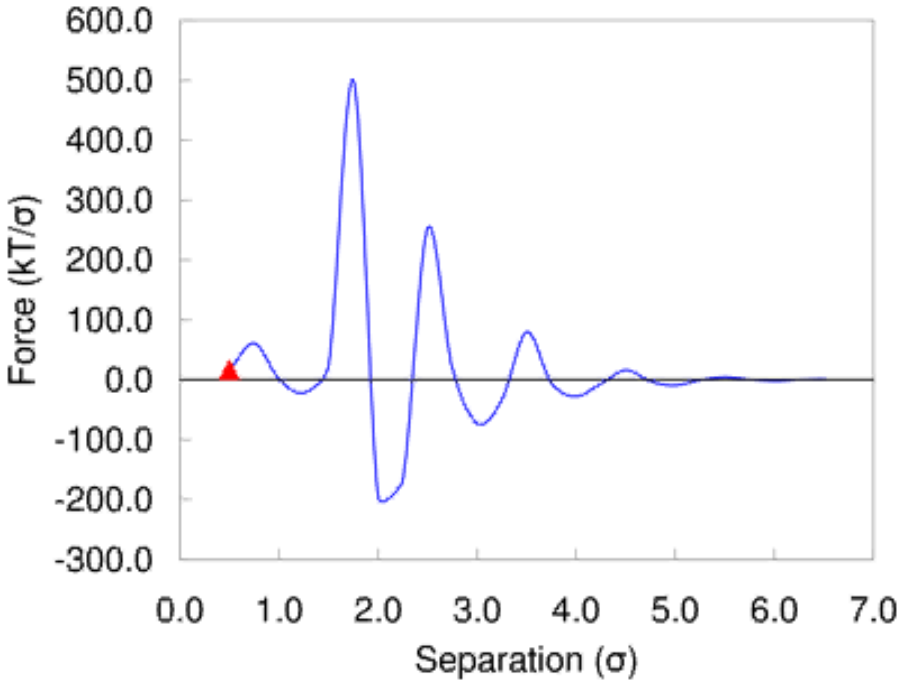


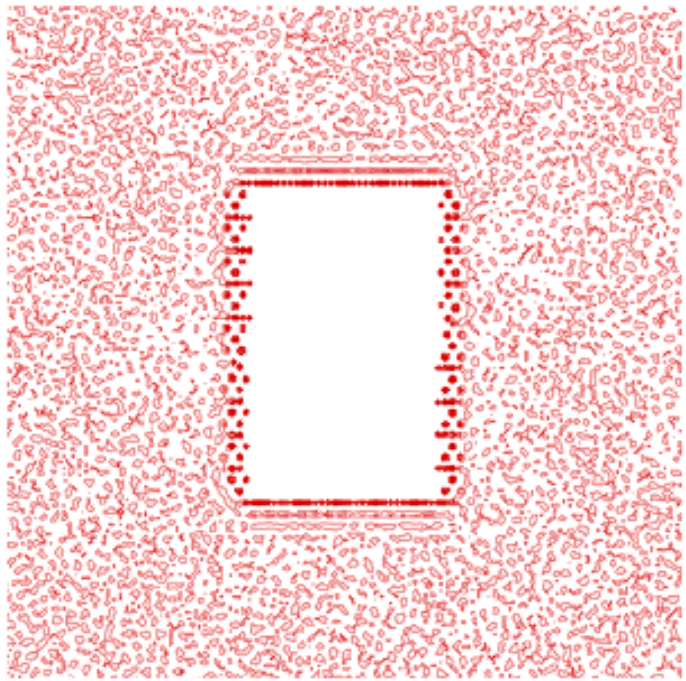




- Solvophilic solvation forces are oscillatory and comparable to van der Waals forces
- Solvophobic solvation forces are attractive

Fluid Ordering: Origin of Solvation Forces

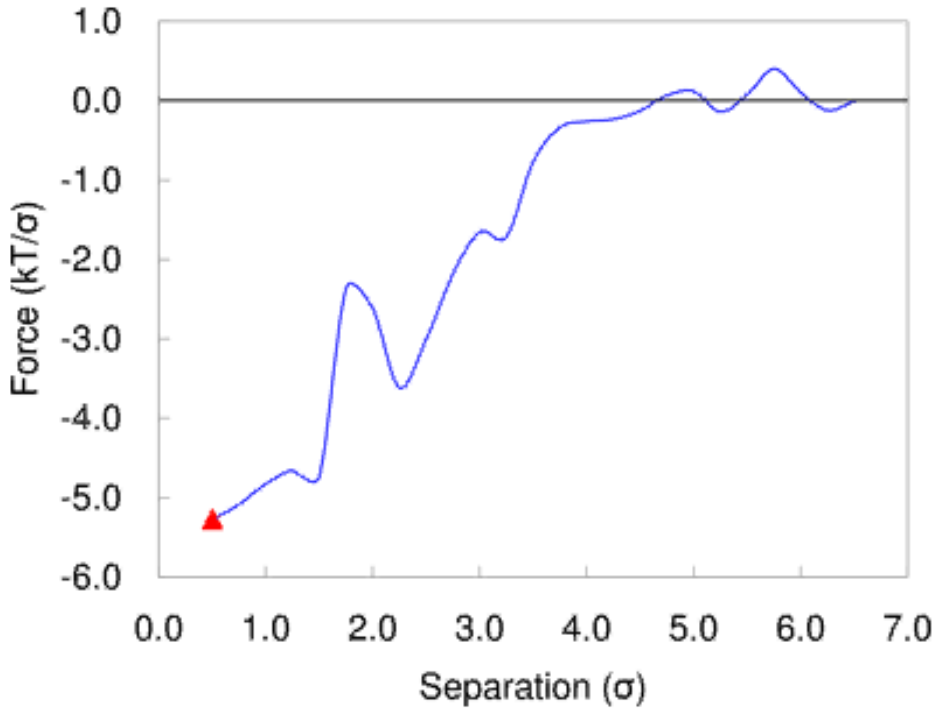


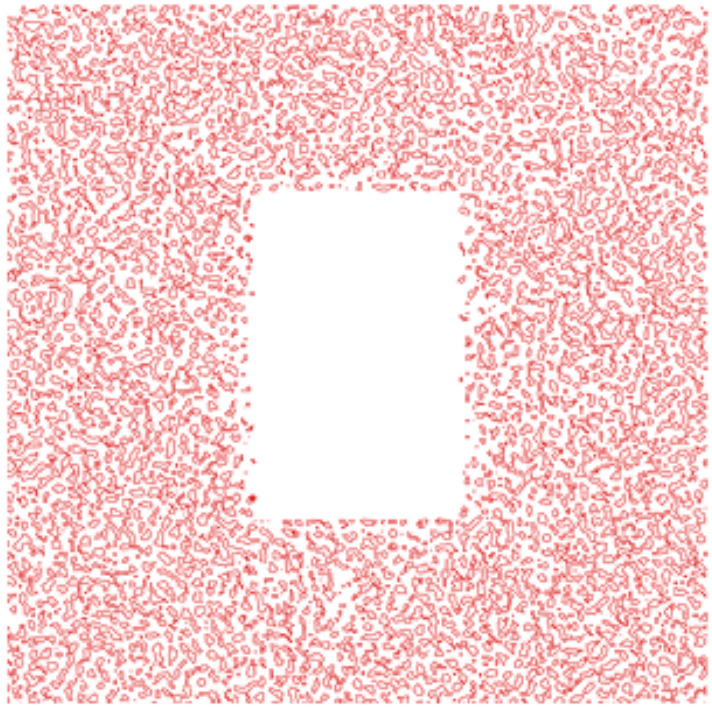


(Movie)

- Solvent ordering around nanoparticles can be observed in all solvophilic simulations

Solvophobic Nanoparticles: The Drying Transition



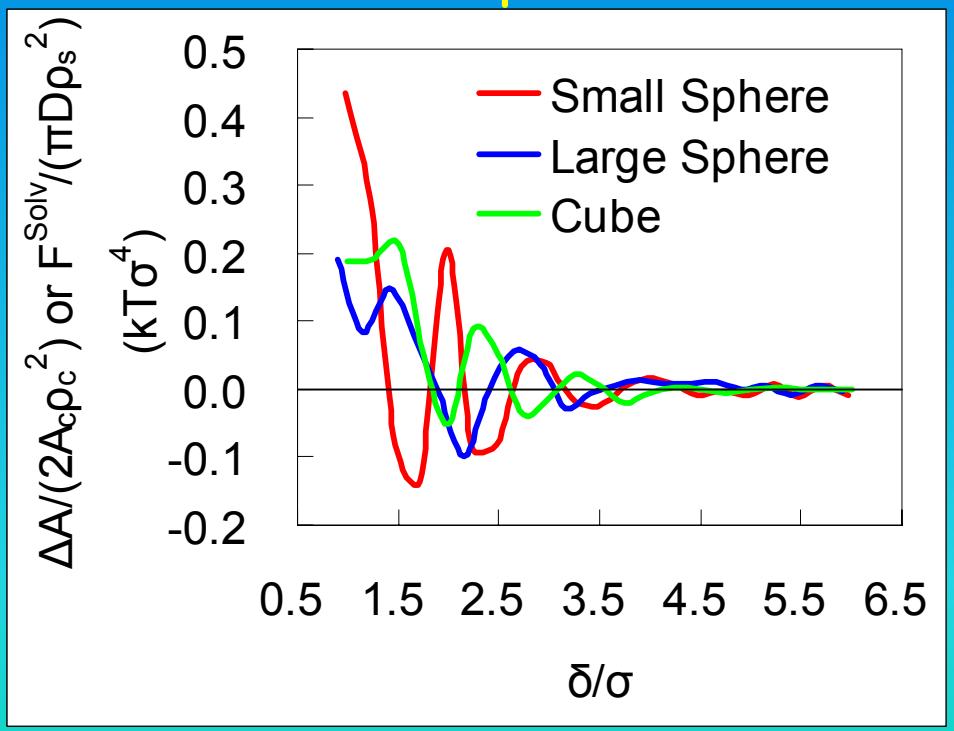


(Movie)

Derjaguin Approximation

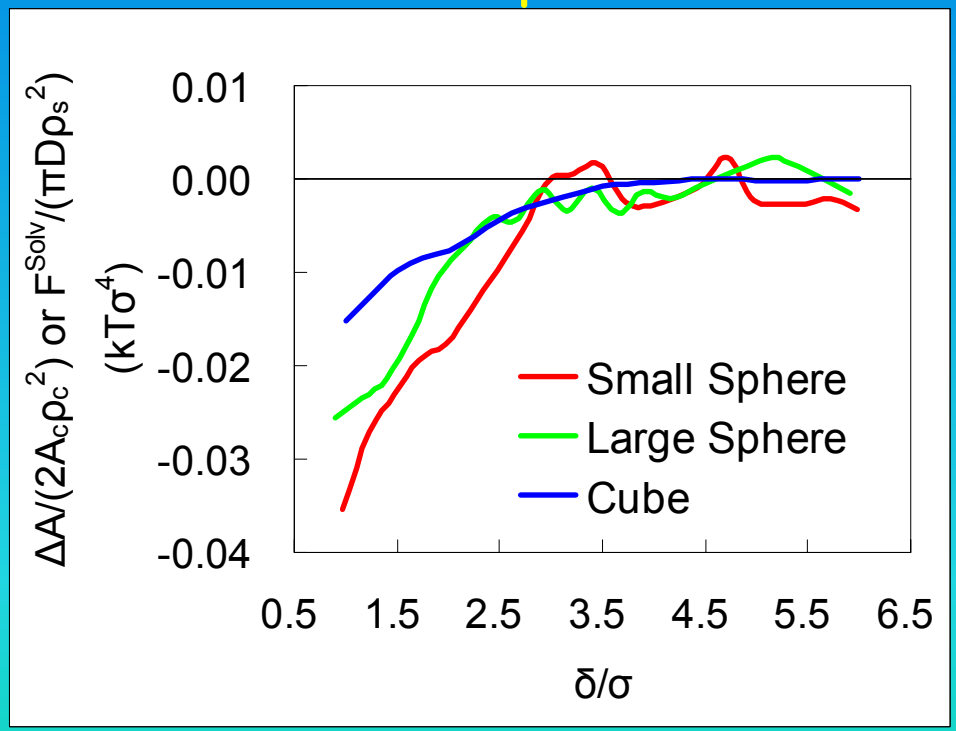
$$\frac{\Delta A(\delta)}{2A_C\rho_C^2} = \frac{F^{Solv}(\delta)}{\pi D\rho_S^2}$$

Solvophilic



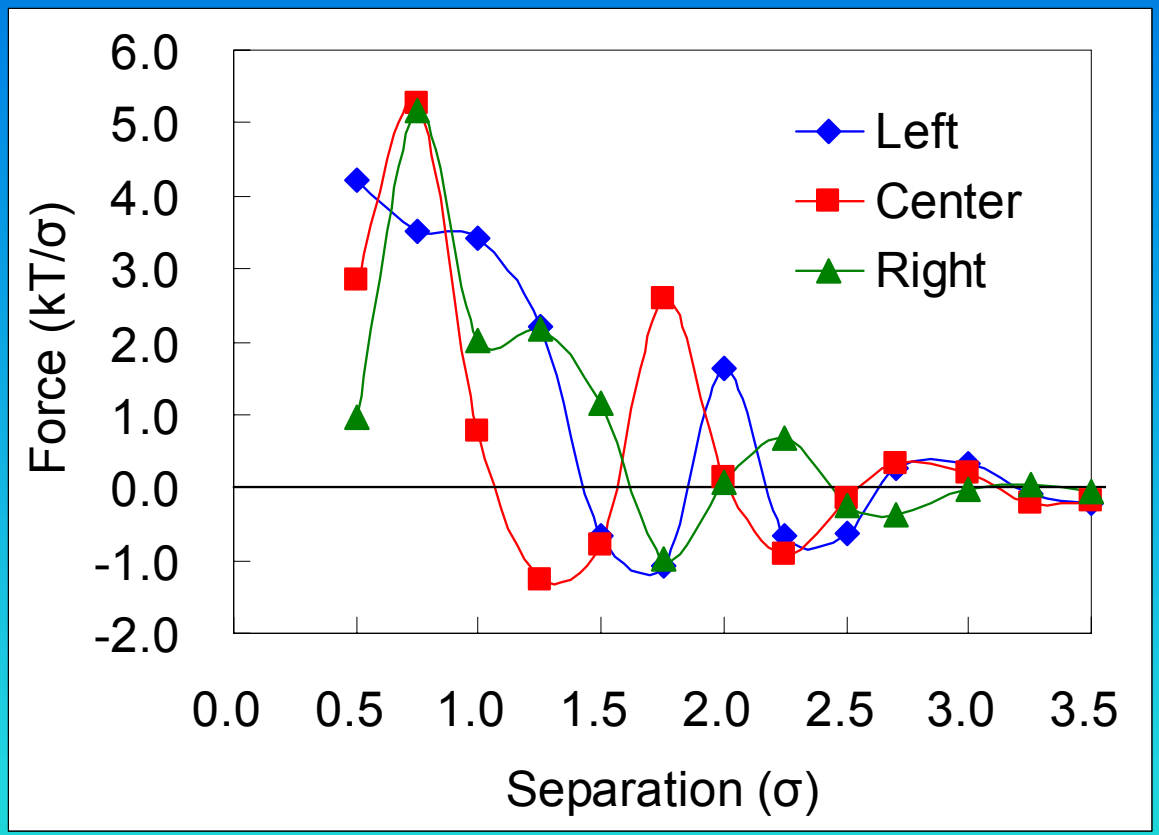
Derjaguin Approximation Describes the Envelope

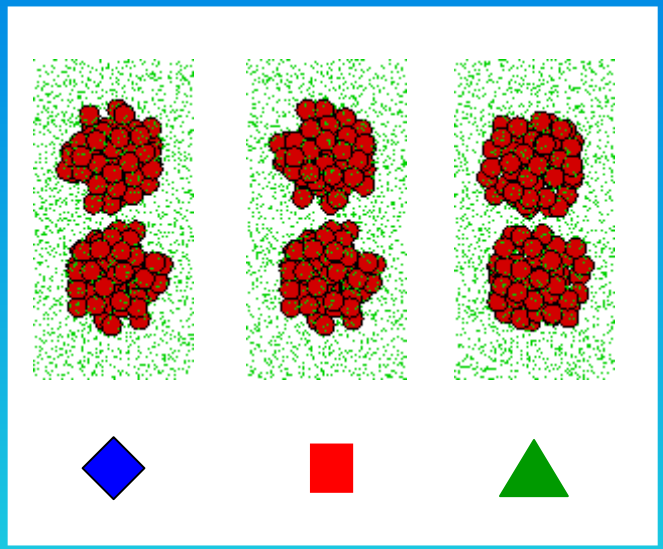
Solvophobic



Derjaguin Approximation Works

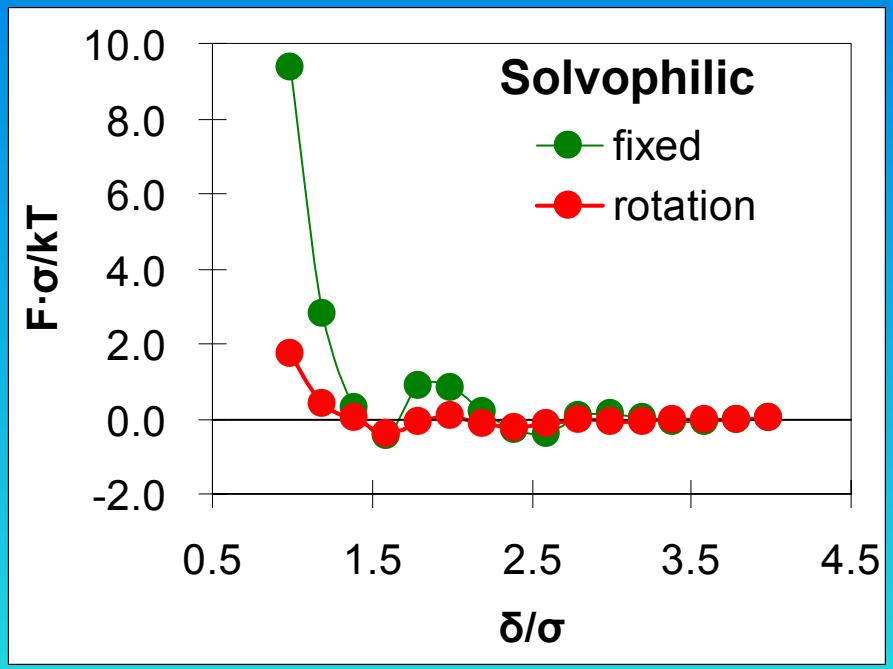
Influence of Surface Roughness on Solvation Forces

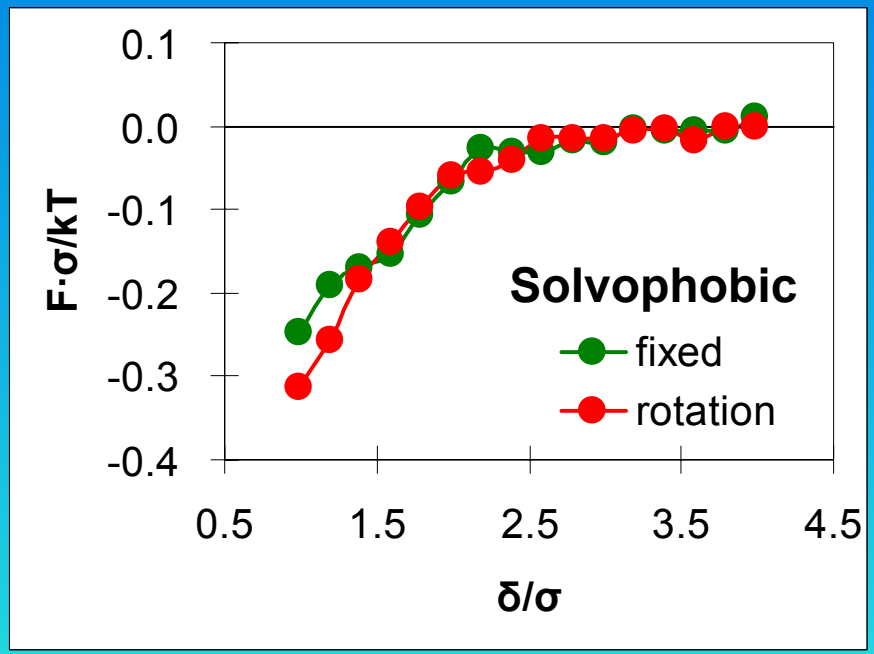




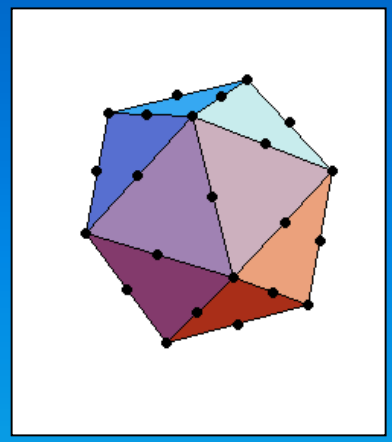
Particle orientation significantly affects the force profile: Particles will Rotate in Solution

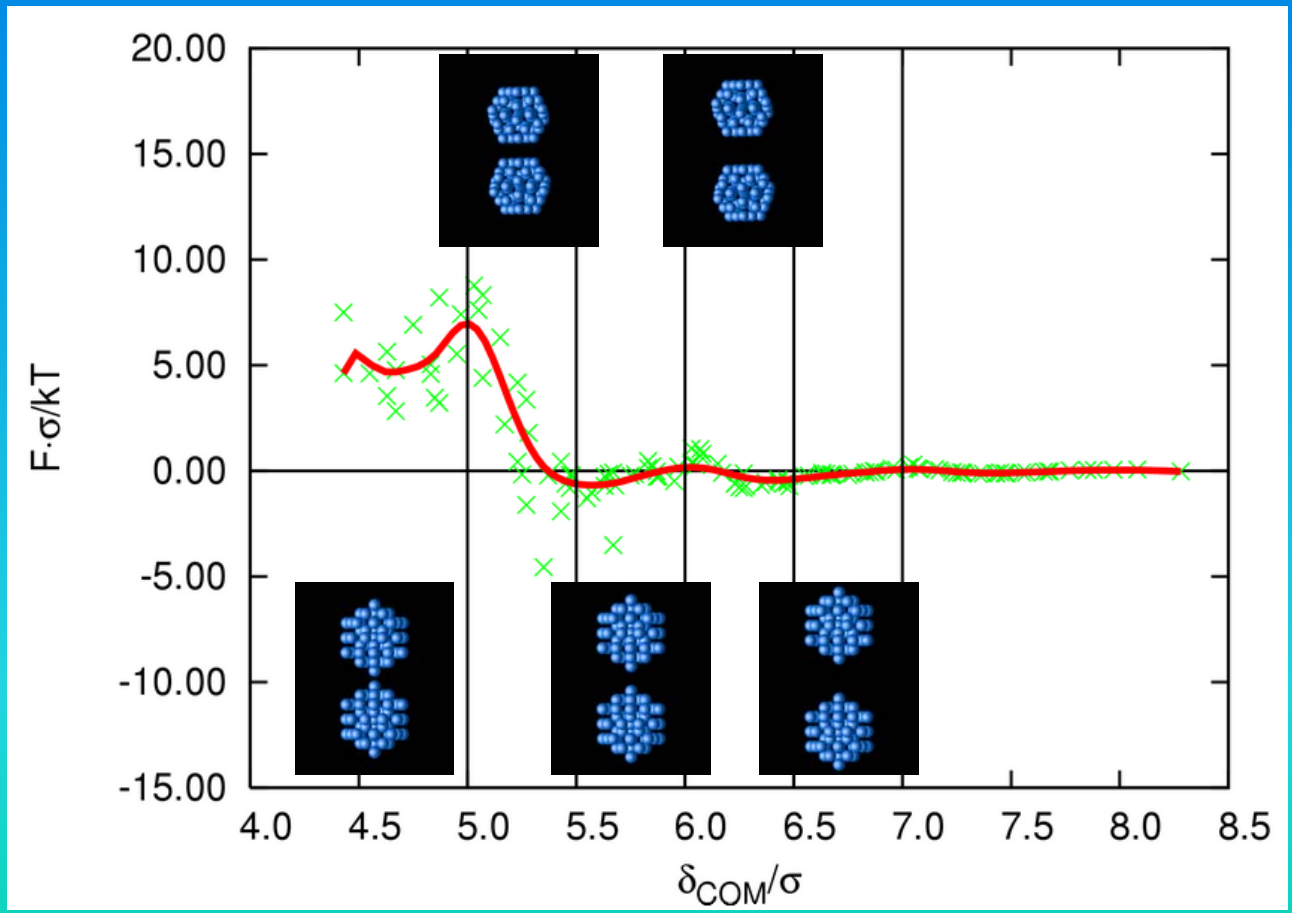
Rotation Reduces Solvophilic Solvation Forces



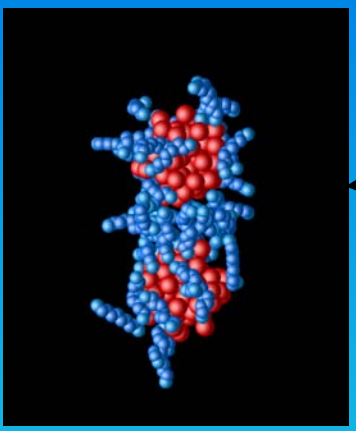


Nanocrystals Have Preferred Orientations

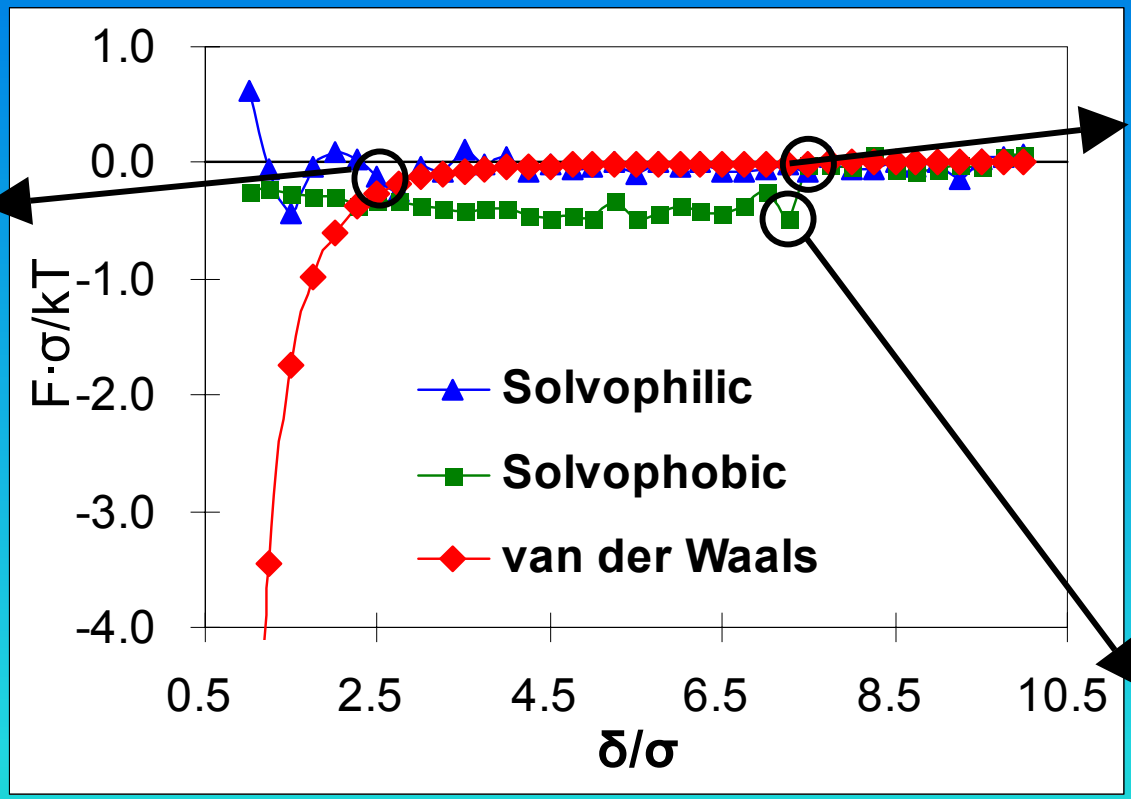


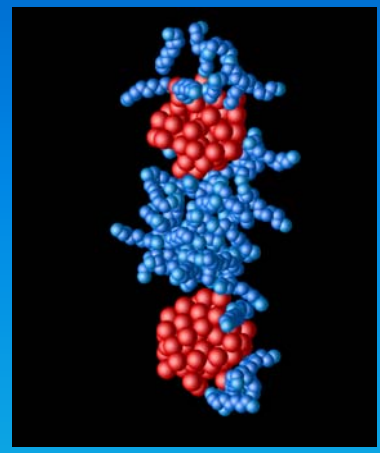


The Influence of Solvent Structure: n-Decane – Small Spheres

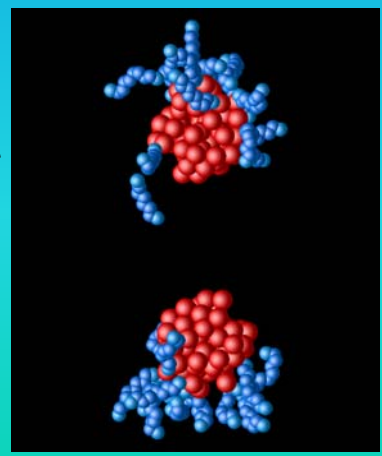


Weak Solvophilic Forces





Step-Like Solvophobic Forces



n-Decane Length Comparable to Nanoparticle Diameter

Conclusions

- Current theories do not accurately describe forces for small nanoparticles
- Solvation forces can be important for colloidal nanoparticles
- Solvation forces are strongly dependent on particle size, shape, surface roughness, particle-solvent interactions, and solvent structure
- Solvent-nanoparticle suspensions can be engineered for stability, assembly, environmental impact……