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

Nanoparticle Forces are POORLY UNDERSTOOD!

A LOT OF WASTE !!!!
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

**F_{\text{crit}} = 0.3 \ \text{pN} \pm 0.08**

I \propto N \times \text{mass}^2

800 nm particles

F_{\text{crit}} = 0.3 \ \text{pN} \pm 0.08

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
\[ d = 4.9 \sigma \]
64 atoms

Icosahedron
\[ d = 4.0 \sigma \]
55 atoms

Large Sphere
\[ d = 17.6 \sigma \]
2048 atoms

Cube
\[ d = 13.2 \sigma \]
2744 atoms
Solvation Forces: Thermodynamic Integration

Free Energy Change

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


Solvation Force

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

$$= \left\langle \vec{r}_{AB} \cdot (F_{AS} - F_{BS}) \right\rangle$$
Interactions for Spheres, Cubes

- Solvophilic solvation forces are oscillatory and comparable to van der Waals forces
- Solvophobic solvation forces are attractive
Solvent ordering around nanoparticles can be observed in all solvophilic simulations.
Solvophobic Nanoparticles: The Drying Transition

(Movie)
Derjaguin Approximation

\[
\frac{\Delta A(\delta)}{2A_C \rho_C^2} = \frac{F_{Solv}(\delta)}{\pi D \rho_S^2}
\]

\[\Delta A(\delta) = \frac{F_{Solv}(\delta)}{\pi D \rho_S^2}\]

\[\frac{\Delta A/(2A_c \rho_c^2)}{F_{Solv}/(\pi D \rho_s^2)}\]

\[\frac{\Delta A}{2A_c \rho_c^2} = \frac{F_{Solv}}{\pi D \rho_s^2}\]

Solvophilic

Solvophobic

Derjaguin Approximation Describes the Envelope

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

Solvophilic
- Green: fixed
- Red: rotation

Solvophobic
- Green: fixed
- Red: rotation
Nanocrystals Have Preferred Orientations
The Influence of Solvent Structure: n-Decane – Small Spheres

Weak Solvophilic Forces

Solvophilic
Solvophobic
van der Waals

n-Decane Length Comparable to Nanoparticle Diameter

Step-Like Solvophobic Forces
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......