Coated nanoparticles in solvents and at interfaces

J. Matthew Lane
Sandia National Laboratories
Albuquerque, NM

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Problem description

Courtesy of P. R. Schunk
• Polyethylene oxide PEO(6) coated 5nm silica nanoparticle in water (3 chains/nm²)

Lane et al, PRE 79, 050501 (2009)

System details

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
- $4 \times 10^5 - 7.2 \times 10^6$ 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

![Graph showing force between nanoparticles vs. distance between centers](image)

- Force between nanoparticles (nN) vs. Distance between nanoparticle centers (Å)
- Different curves represent different polymer densities and chain lengths.

- PEO(6), 3 chains/nm²
- PEO(6), 2 chains/nm²
- PEO(6), 1 chain/nm²
- PEO(20), 1 chain/nm²
- PEO(20), 2 chains/nm²
• PEO(20), 1.0 chains/nm²

• PEO(100), 0.5 chains/nm²

• Mitra et al, Langmuir 19, 8994 (2003) – exp. - PEO(100), 0.2chains/nm²
Constructing model Au-thiol nanoparticles

Fact sheet:
2, 4, and 8 nm diameter core with Au implicit

S-(CH₂)₉-X and S-(CH₂)₁₇-X where X = CH₃ or COOH

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

Constant coverage density of 21 Å² per chain

• D. Dunphy, UNM/Sandia personal communication

Place each in decane, water and Brownian solvents.
2 to 8 nm coated nanoparticle cores

<table>
<thead>
<tr>
<th>Decane</th>
<th>Implicit</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10-CH$_3$</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>C10-COOH</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>C18-CH$_3$</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>C18-COOH</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
</tbody>
</table>
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

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

<table>
<thead>
<tr>
<th>Chain</th>
<th>$\Delta v$ (nm$^3$)</th>
<th>Decane s.d.</th>
<th>Implicit s.d.</th>
<th>Water s.d.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-(CH$<em>2$)$</em>{17}$-CH$_3$</td>
<td>0.844</td>
<td>59.5%</td>
<td>75.3%</td>
<td>68.2%</td>
</tr>
<tr>
<td>S-(CH$<em>2$)$</em>{17}$-CH$_3$</td>
<td>0.362</td>
<td>49.1%</td>
<td>52.5%</td>
<td>46.3%</td>
</tr>
<tr>
<td>S-(CH$_2$)$_9$-CH$_3$</td>
<td>0.252</td>
<td>31.5%</td>
<td>36.1%</td>
<td>32.4%</td>
</tr>
<tr>
<td>S-(CH$<em>2$)$</em>{17}$-CH$_3$</td>
<td>0.166</td>
<td>23.9%</td>
<td>38.7%</td>
<td>33.0%</td>
</tr>
<tr>
<td>S-(CH$_2$)$_9$-CH$_3$</td>
<td>0.115</td>
<td>23.8%</td>
<td>25.2%</td>
<td>33.3%</td>
</tr>
<tr>
<td>S-(CH$_2$)$_9$-CH$_3$</td>
<td>0.054</td>
<td>14.8%</td>
<td>17.4%</td>
<td>22.2%</td>
</tr>
<tr>
<td>S-(CH$<em>2$)$</em>{17}$-COOH</td>
<td>0.844</td>
<td>68.9%</td>
<td>55.1%</td>
<td>82.1%</td>
</tr>
<tr>
<td>S-(CH$<em>2$)$</em>{17}$-COOH</td>
<td>0.362</td>
<td>52.4%</td>
<td>59.6%</td>
<td>66.6%</td>
</tr>
<tr>
<td>S-(CH$_2$)$_9$-COOH</td>
<td>0.252</td>
<td>47.3%</td>
<td>50.6%</td>
<td>48.2%</td>
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<tr>
<td>S-(CH$<em>2$)$</em>{17}$-COOH</td>
<td>0.166</td>
<td>36.9%</td>
<td>42.3%</td>
<td>41.8%</td>
</tr>
<tr>
<td>S-(CH$_2$)$_9$-COOH</td>
<td>0.115</td>
<td>34.9%</td>
<td>41.6%</td>
<td>33.8%</td>
</tr>
<tr>
<td>S-(CH$_2$)$_9$-COOH</td>
<td>0.054</td>
<td>22.1%</td>
<td>27.6%</td>
<td>19.7%</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Diameter</th>
<th>C10 with CH₃</th>
<th>C10 with COOH</th>
<th>C18 with CH₃</th>
<th>C18 with COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 nm</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
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?

**Future direction: Surface interaction**

- 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