What we studied

- Hard spheres vs soft spheres
- Monodisperse vs polydisperse
- High packing fraction


Goals

- Effect of polydispersity at high packing fraction
- Model system of bimodal spheres
  - Different ratios of radius
  - Different fraction of each radius
  - Soft spheres
Why Poly-NIPAM

- Thermosensitive gel
- Hard and soft
- Easy to prepare controlled radius particles
Applications

- Ceramics
- Glass
- Minerals
- Drug delivery vector

Microgel Particle Synthesis

- Monomer \( N \)-isopropylacrylamide (NIPAM), crosslinker \( N,N' \)-methylenbisacrylamide (BIS), initiator potassium persulfate (KPS) in degassed aqueous solution
- Heat solution to 70°C, add KPS, stir 4-6 hours
- Amount of BIS controls swelling
- Amount of KPS controls radius
Characterization of Microgel Particles

- Dynamic Light Scattering (DLS)
- Small Angle Neutron Scattering (SANS)
- Ultra Small Angle Neutron Scattering (USANS)

PNIPAM beads, magnification x40000

Dynamic Light Scattering

- Light passes through sample, fluctuations of intensity of scattered light are measured
- Yields diffusion coefficient
  - Stokes-Einstein equation, assuming spherical shape yields hydrodynamic radius
- Temperature scan
- Shows transition temperature (lower critical solution temperature, LCST)
Dynamic Light Scattering

- Transition temperature at 33°C
- Radius changes by a factor of 2
Small Angle Neutron Scattering

- 1 nm to 500 nm
- $Q = (4\pi/\lambda)\sin(\theta/2)$
- $D = 2\pi/Q$

USANS
- 100 nm to 1000 nm

SANS of Microgel vs Temperature

- Data at 40°C and 34°C are modeled using Schulz Spheres. Data at 33°C, 31.5°C, and 30°C are modeled using Fuzzy Spheres.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Radius (nm)</th>
<th>InterfaceThickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>134.6 ± 0.6</td>
<td>8.3 ± 0.3</td>
</tr>
<tr>
<td>31.5</td>
<td>126.2 ± 0.5</td>
<td>7.7 ± 0.1</td>
</tr>
<tr>
<td>33</td>
<td>104.1 ± 0.3</td>
<td>6.1 ± 0.1</td>
</tr>
<tr>
<td>34</td>
<td>96.0 ± 0.2</td>
<td>N/A</td>
</tr>
<tr>
<td>40</td>
<td>89.2 ± 0.2</td>
<td>N/A</td>
</tr>
</tbody>
</table>

- Confirms that particles are spherical
- Shows change of radius
Last week...

- 2 large batches of microgel
- 2 radii: 150 nm and 300 nm
- 3 mixtures: total \( \phi = 0.70 \)
  - 90/10 large/small
  - 70/30 large/small
  - 50/50 large/small
  - Individual components

- Random Packing of Hard Spheres: \( \phi = 0.63 \)
- Hexagonal Close Packing: \( \phi = 0.74 \)
Last week... con’t

- SANS and USANS
  - Below LCST
- Low-high-low temperature cycle
  - Crystallization
  - Shows no difference in SANS, only visually

![Graph showing q vs l(q) for different conditions](image-url)
Concentrated Bimodal Mixtures

Mixture 1: 90% large/10% small
By Volume: 63% large, 7% small

Mixture 2: 70% large/30% small
By Volume: 49% large, 21% small

Mixture 3: 50% large/50% small
By Volume: 35% large, 35% small
Conclusion

- More small particles give less organized order
- Small particles are easy to make, but need detail cleaning
- Large particles are more difficult
- Temperature cycling increases order

Future Plans

- Develop “cleaning” process to rid sample of low molecular weight contaminants
- Model individual particle and mixtures
- Synthesize larger particles
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