Particle Characterization using Acoustics and Electro Acoustics

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Outline

- Introduce concepts of colloidal stability
- Acoustic theory/modeling
- Electro acoustic theory
- Hardware configurations
- Applications
A **colloid** is a type of mechanical mixture where one substance is dispersed evenly throughout another. Because of this dispersal, some colloids have the appearance of solutions. A colloidal system consists of two separate phases: a **dispersed phase** (or **internal phase**), and a **continuous phase** (or **dispersion medium**). A colloidal system may be solid, liquid, or gaseous. Size range 1 nm – 1 micron.

<table>
<thead>
<tr>
<th>Continuous Medium (solvent)</th>
<th>Dispersed Medium (particles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td><strong>NONE</strong> (all gases are mutually miscible)</td>
</tr>
<tr>
<td>Liquid</td>
<td>Foam (Examples: whipped cream)</td>
</tr>
<tr>
<td>Solid</td>
<td>Solid Foam (Examples: aerogel, styrofoam, pumice)</td>
</tr>
</tbody>
</table>

Colloid. — An entity phase dispersed to such a degree that the surface forces become an important factor in determining its properties.
Stability

- Want stable dispersion
- Either suspensions or emulsions
- Suspensions sediment & flocculate
- Emulsions phase separate, creaming or coalescence
Stabilization

- Steric stabilization: coat surface with polymers
  - Particles can’t touch so they don’t interact
- Electrostatic stabilization: alter surface chemistry to put charge on particle surface
  - Repel like magnets
Electrostatic Stabilization

No charge = collide & aggregate

Charged particles repel each other
Zeta Potential

- If surface has + charge, then - ions attracted to surface
- + ions attracted to – ions, builds electric double layer
- Slipping plane: distance from particle surface where ions move with particle
- ZP = potential (mV) at slipping plane
**Zeta Potential & Stability**

<table>
<thead>
<tr>
<th>Stability</th>
<th>Average Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extreme to very good stability</td>
<td>–100 to –60 mv</td>
</tr>
<tr>
<td>Reasonable stability</td>
<td>–60 to –40 mv</td>
</tr>
<tr>
<td>Moderate stability</td>
<td>–40 to –30 mv</td>
</tr>
<tr>
<td>Threshold of light dispersion</td>
<td>–30 to –15 mv</td>
</tr>
<tr>
<td>Threshold of agglomeration</td>
<td>–15 to –10 mv</td>
</tr>
<tr>
<td>Strong agglomeration &amp; precipitation</td>
<td>–5 to +5 mv</td>
</tr>
</tbody>
</table>

*Stability of Solution-Zeta Potential from "A Control of Colloidal Stability" by Thomas Riddick*
Size Measurement Hardware

- Sample
- Servomotor with transducer
- Dispersion chamber
- Detector

Frequency: 1-100 MHz
Variable gap: 0.15-20 mm
Acoustic Attenuation

\[ \alpha = \frac{10}{f[MHz]L[cm]} \log \frac{I_{in}}{I_{out}} \]

Sound speed \([cm/sec]\)

\[ V = \frac{L[cm]}{t[sec]} \]

Shifts right with decreasing size
Acoustic Attenuation

Adsorption – conversion to heat

Scattering - energy redirection

- 0.3 micron
- 0.5 micron
- 1 micron
- 5 micron
- 10 micron
1. **Measure** - the attenuation spectrum over a wide range of ultrasound frequencies

2. **Depict** - as a *model* colloid making assumptions & defining a recipe w/ name & amount of disperse phase and the suspending media.

3. **Define** - the *relevant physical properties* of these named materials

4. **Predict** - the *sound attenuation spectrum* considering all loss mechanisms for any size distribution and properties

5. **Search** - for particle size distribution that provides the best match between the predicted attenuation spectrum for the model colloid and the measured.
Loss Mechanisms

- Intrinsic: results from the energy dissipated in the flexing of its molecular structure as the sound wave passes through the material.

- Viscous: sound wave causes a relative motion between the particle and the surrounding fluid and some of the energy in the sound wave is converted to heat by virtue of the viscous drag.

- Scatter: When the size of the particle becomes comparable to the wavelength of the sound wave, we experience a significant contribution from scattering.
Loss Mechanisms

- Thermal: additional energy loss if the thermal properties of the particles differ from the thermal properties of the medium.

  Droplet is more easily compressed than H2O as sound wave passes by. Increases temp, heat flows from particle to H2O.

- Structural: example; particles in polymer, the polymer establishes links between particles. As particles move polymer linkages are periodically stretched and relaxed causing some additional energy dissipation in the linkages.
Intrinsic Attenuation

Intrinsic loss of water at 25°C

Intrinsic loss of methanol at 25°C

Relative change in intrinsic loss for water vs. temperature

Intrinsic loss of corn oil
Viscous loss: 0.3 μm Alumina

0.3 micron 5 vol% alumina dispersion in water
Viscous loss: 0.1 mm Alumina

Shift in frequency changes with the square of particle size shift.

0.1 micron 5 vol% alumina dispersion in water.
Viscous loss: 0.03 \( \mu \)m Alumina

0.03 micron 5 vol% alumina dispersion in water
Viscous loss: 1.0 μm Alumina

Shifts to lower frequencies

1.0 micron 5 vol% alumina dispersion in water
Viscous loss: 3.0 μm Alumina

Off scale, scattering appears

3.0 micron 5 vol% alumina dispersion in water
Scatter loss: 10 μm Alumina

Viscous, scattering & intrinsic must all play role, must be understood

10 micron 5 vol% alumina dispersion in water
Scatter loss: 30 μm Alumina

30 micron 5 vol% alumina dispersion in water
Scatter loss: 100 μm Alumina

100 micron 5 vol% alumina dispersion in water
Thermal loss: 1.0 µm Droplet

1.0 micron droplets in 20 wt% corn oil in water emulsion
Thermal loss: 3.0 μm Droplet

3.0 micron droplets in 20 wt% corn oil in water emulsion
Thermal loss: 10 μm Droplet

Scattering more dominant

10 micron droplets in 20 wt% corn oil in water emulsion
Structural loss: no Links

0.3 micron particles without any structural links between particles
Structural loss: with Links

0.3 micron particles with structural links between particles
## Relevant Properties for Loss Mechanisms

<table>
<thead>
<tr>
<th>Loss Mechanism &gt; Relevant property</th>
<th>Intrinsic</th>
<th>Viscous</th>
<th>Scatter</th>
<th>Thermal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>For Particle</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td></td>
<td>Relevant</td>
<td></td>
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<tr>
<td>Micro viscosity</td>
<td></td>
<td></td>
<td>Relevant</td>
<td></td>
</tr>
<tr>
<td>Porosity/Fractal No</td>
<td></td>
<td></td>
<td>Relevant</td>
<td></td>
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<tr>
<td>Thermal conductivity</td>
<td></td>
<td></td>
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<td>Relevant</td>
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<tr>
<td>Heat capacity</td>
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<td>Relevant</td>
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<tr>
<td>Thermal expansion</td>
<td></td>
<td></td>
<td></td>
<td>Relevant</td>
</tr>
<tr>
<td>Sound speed</td>
<td></td>
<td></td>
<td>Relevant</td>
<td></td>
</tr>
<tr>
<td>Scatter factor</td>
<td></td>
<td></td>
<td></td>
<td>Relevant</td>
</tr>
<tr>
<td>Intrinsic</td>
<td>Relevant</td>
<td></td>
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<tr>
<td><strong>For Media</strong></td>
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<td></td>
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What do I Need to Know?

- Must know concentration wt% (>1-2%)
- What is the dispersed & continuous phase
- Relevant properties for loss mechanisms
- Many particles & liquids in software library
- Solid, sub micron particles need density
- Large solid particles determine scatter factor
- Emulsions, “soft particles” some thermal properties
Piezo crystal

Electrodes

Zeta Potential Probe

Colloid Vibration Current

\[ CVI = C \frac{(\rho_p - \rho_m) \varphi \mu_d \nabla P}{\rho_m} \]

Dynamic Mobility

\[ \mu_d = \frac{\varepsilon_m \varepsilon_0 \zeta (\rho_p - \rho_s) \rho_m K_s}{\eta (\rho_p - \rho_m) \rho_s K_m} \]
Hardware Configurations

- Size
- Zeta
- Conductivity
- Titration burettes
Hardware Configurations

External peristaltic pump

Separate size & zeta potential
Additional Sensors

- Temperature
- Conductivity
- Dielectric permittivity
- pH
pH vs. Zeta Potential Titrations

- Configure hardware: zeta potential probe can be in acoustic size chamber or simply placed in a beaker with the pH probe
- Fill chemical bottle 1 w/ 1N HCl & chemical bottle 2 w/ 1 N KOH
- Define material
- Double click on “Titration”, Under “Type” select pH ramp, define titration
- Click on “CVI – for zeta potential” and “Run”
Flow Through

Do basic lab characterizations first
Titania in Water pH = 4, 10

DT-1200, Attenuation Spectra

- 2009-10-29 08:57:42, 10% titania, CR828 in
- 2009-10-29 09:08:12, 10% titania, CR828 in
- 2009-10-29 09:19:15, 10% titania, CR828 in
- 2009-10-29 11:05:10, 10% titania, CR828 in
- 2009-10-29 11:14:10, 10% titania, CR828 in
- 2009-10-29 11:22:51, 10% titania, CR828 in
Titania, pH = 4
Titania, pH = 10
Titania in Water pH = 4, 10

DT-1200, Particle Size Distribution

- 2009-10-29 08:57:42, 10% titania, CR828 in water, pH
- 2009-10-29 09:08:12, 10% titania, CR828 in water
- 2009-10-29 09:19:15, 10% titania, CR828 in water
- 2009-10-29 11:22:51, 10% titania, CR828 in water, pH
Titania, pH = 3, in Corn Starch

First measure
Intrinsic attenuation
Of corn starch
pH Titration of Rutile 7%vl & Alumina 4%vl

Many application notes available on web site www.horibalab.com

Colloidal Stability

stable

unstable

stable
pH Titration of Rutile 7%vl & Alumina 4%vl

85 nm

300 nm

PSD unstable @ IEP
aggregates form
Chemical Mechanical Polishing fluid

<table>
<thead>
<tr>
<th>Manufacturer/Size Specification</th>
<th>Acoustics Size Determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ludox-TM 22 nm (area basis)</td>
<td>30 nm (weight basis)</td>
</tr>
<tr>
<td>Celtech 0.5 0.5 micron</td>
<td>0.65 micron</td>
</tr>
<tr>
<td>Celtech 1.5 1.5 micron</td>
<td>1.72 micron</td>
</tr>
<tr>
<td>Cabot 8812 N/A</td>
<td>53 nm</td>
</tr>
<tr>
<td>Cabot 8825 N/A</td>
<td>62 nm</td>
</tr>
</tbody>
</table>
CMP Size Data

Raw Data

Particle Size Distribution
CMP Addition Test: Raw Data

SS25 with various additions of silica Geltech 0.5
CMP Addition Test: Size Results

Proves ability to detect small amounts of second population
CVI & z-potential for silica CMP

200 continuous measurements

Precision of the z-potential characterization is about 0.2 mV with no special requirements for temperature control.
# Nanoparticles: Zinc Oxide

## Monitoring Nano-Particles in the Presence of Large Particles Using Acoustics

<table>
<thead>
<tr>
<th>POWDER Name, Manufacturer</th>
<th>Median size, microns</th>
<th>Cum % of nanoparticles &lt;100 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc oxide, 99.5+% by Acros Organics</td>
<td>0.273±0.01</td>
<td>11.0±1.4</td>
</tr>
<tr>
<td>Zinc oxide, reagent ACS by Acros Organics</td>
<td>0.430±0.02</td>
<td>7.0±0.5</td>
</tr>
<tr>
<td>Z50-500 USP powder</td>
<td>0.561±0.017</td>
<td>2.7±0.39</td>
</tr>
<tr>
<td>Z52-500 USP powder</td>
<td>0.660±0.037</td>
<td>1.9±0.4</td>
</tr>
<tr>
<td>S80249 by Fisher Scientific</td>
<td>0.398±0.001</td>
<td>6.1±0.2</td>
</tr>
<tr>
<td>Zinc oxide ACS reagent grade by MO Biomedicals, LLC</td>
<td>0.349±0.017</td>
<td>8.2±2.1</td>
</tr>
<tr>
<td>Zinc oxide Polystormor by Mallinckrodt Chemicals</td>
<td>0.223±0.009</td>
<td>19.6±1.8</td>
</tr>
<tr>
<td>Zinc oxide Nanopowder by American Elements</td>
<td>0.631±0.1</td>
<td>4.7±2.5</td>
</tr>
</tbody>
</table>

**Base**

**Dopant**
Nanoparticles: Zinc Oxide

- Zinc oxide A in solvent
- Zinc oxide B in water
- Zinc oxide A and B in < 100nm range

PSD, weight basis
Nanoparticles

- Zinc oxide, reagent ACS by Acros Organics
- Zinc oxide, 99.5+%  Acros Organics
- Z50-500 USP
- Z52-500 USP
- S80249 by Fisher Scientific
- Zinc oxide 99.99% by Alfa Aesar
- Zinc oxide ACS MO Biomedicals, LLC
- PolystormorTM by Mallinckrodt Chemicals
- Nanopowder America Elements
Nanoparticles Detection

Add 223 nm ZnO (dope) to 660 nm ZnO (base)

Plot estimated (x) vs. measured (y) % nanoparticles (<100nm)

Observed deviation ~ 1%

Conclusion: acoustics can detect small amount of nanoparticles, even as smaller second population
Milling: Simple QC Measurement

20 wt% Alumina
Starting size >20 microns
Zeta Potential of Proteins

Zeta Potential of Bovine Serum Albumin (BSA) Protein

<table>
<thead>
<tr>
<th>pH</th>
<th>CVI</th>
<th>Zeta</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>157,701</td>
<td>8.2</td>
<td>0.17</td>
</tr>
<tr>
<td>3.5</td>
<td>365,881</td>
<td>19.1</td>
<td>0.24</td>
</tr>
<tr>
<td>3.8</td>
<td>415,370</td>
<td>21.6</td>
<td>0.26</td>
</tr>
<tr>
<td>4.1</td>
<td>363,881</td>
<td>19</td>
<td>0.08</td>
</tr>
<tr>
<td>4.4</td>
<td>218,582</td>
<td>11.4</td>
<td>0.07</td>
</tr>
<tr>
<td>4.9</td>
<td>72,347</td>
<td>3.8</td>
<td>0.62</td>
</tr>
<tr>
<td>5.3</td>
<td>104,411</td>
<td>-5.4</td>
<td>0.06</td>
</tr>
<tr>
<td>6.7</td>
<td>329,171</td>
<td>-17.6</td>
<td>0.11</td>
</tr>
<tr>
<td>7.9</td>
<td>453,600</td>
<td>-24.2</td>
<td>0.15</td>
</tr>
<tr>
<td>9.2</td>
<td>526,892</td>
<td>-28.2</td>
<td>0.15</td>
</tr>
<tr>
<td>10</td>
<td>593,132</td>
<td>-31.7</td>
<td>0.29</td>
</tr>
<tr>
<td>10.7</td>
<td>634,293</td>
<td>-33.9</td>
<td>0.4</td>
</tr>
<tr>
<td>11.2</td>
<td>541,855</td>
<td>-28.9</td>
<td>0.2</td>
</tr>
</tbody>
</table>

![Zeta Potential vs pH: BSA](image)
Conclusions

- Particle size without dilution for concentrated (> 1wt %) dispersions
- Zeta potential without dilution for concentrated (> 1wt %) dispersions
- Automatic titration of pH, surfactant conc., etc.
- Micro rheology
- Colloids, nanoparticles, emulsions, dispersion stability