Nanoparticle Analysis: Dynamic Light Scattering for Particle Size Determination

Jeffrey Bodycomb, Ph.D.
HORIBA Scientific
www.horiba.com/us/particle
What is Dynamic Light Scattering?

- Dynamic light scattering refers to measurement and interpretation of light scattering data on a **microsecond** time scale.

- Dynamic light scattering can be used to determine
  - Particle/molecular size
  - Size distribution
  - Relaxations in complex fluids
Other Light Scattering Techniques

- **Static Light Scattering**: over a duration of ~1 second. Used for determining particle size (diameters greater than 10 nm), polymer molecular weight, 2nd virial coefficient, $R_g$.

- **Electrophoretic Light Scattering**: use Doppler shift in scattered light to probe motion of particles due to an applied electric field. Used for determining electrophoretic mobility, zeta potential.
Particle Diameter (μm)

0.001  0.01  0.1  1  10  100  1000

Sizes
Nano-Metric
Colloidal
Fine
Coarse

Apps
Macromolecules
Suspensions and Slurries
Powders

Methods
Electron Microscope
Acoustic Spectroscopy – DT-1201 and DT-300(Zeta)
Light Obscuration
Laser Diffraction – LA-950
Electrozone Sensing
DLS – SZ-100
Disc-Centrifuge (CPS)
Microscopy PSA300
Particles in suspension undergo Brownian motion due to solvent molecule bombardment in random thermal motion.

- Brownian Motion
  - Random
  - Related to size
  - Related to viscosity
  - Related to temperature
DLS Optics

Backscatter (173°) (High conc.)

Particles moving due to Brownian motion

Laser 532nm, 10mW

Attenuator

Particles

PD For T%

Zeta potential

Modulator

Attenuator
DLS signal

- Random motion of particles leads to random fluctuations in signal (due to changing constructive/destructive interference of scattered light.)
Random fluctuations are interpreted in terms of the autocorrelation function (ACF).

\[ C(\tau) = 1 + \beta \exp(-2\Gamma \tau) \]

\[ C(\tau) = \frac{\int_0^\tau I(t)I(t+\tau)dt}{\langle I(t)I(t) \rangle} \]
Gamma to Size

\[ \Gamma = D_m q^2 \]
\[ q = \frac{4\pi n}{\lambda} \sin(\theta/2) \]
\[ D_h = \frac{k_B T}{3\pi \eta(T) D_m} \]

\( \Gamma \) decay constant
\( D_m \) diffusion coefficient
\( q \) scattering vector
\( n \) refractive index
\( \lambda \) wavelength
\( \theta \) scattering angle
\( D_h \) hydrodynamic diameter
\( \eta \) viscosity
\( k_B \) Boltzmann’s constant

Note effect of temperature!
What is Hydrodynamic Size?

DLS gives the diameter of a sphere that moves (diffuses) the same way as your sample.
Hydrodynamic Size

- The instrument reports the size of sphere that moves (diffuses) like your particle.
- This size will include any stabilizers bound to the molecule (even if they are not seen by TEM).

Gold Colloids

<table>
<thead>
<tr>
<th>Technique</th>
<th>Size nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Force Microscopy</td>
<td>8.5 ± 0.3</td>
</tr>
<tr>
<td>Scanning Electron Microscopy</td>
<td>9.9 ± 0.1</td>
</tr>
<tr>
<td>Transmission Electron Microscopy</td>
<td>8.9 ± 0.1</td>
</tr>
<tr>
<td>Dynamic Light Scattering</td>
<td>13.5 ± 0.1</td>
</tr>
</tbody>
</table>

SEM (above) and TEM (below) images for RM 8011
Polystyrene Latex Sample
For a mixture of sizes, the autocorrelation function can be interpreted in terms of cumulants. This is the most robust method of analyzing DLS data.

\[ C(\tau) = 1 + \beta \exp\left[ 2\left(-\overline{\Gamma}\tau + \frac{\mu_2}{2!} - \Lambda\right)\right] \]

\[ \overline{\Gamma} = D_m q^2 \]

"z-average size"

\[ D_{z,h} = \frac{k_B T}{3\pi \eta(T) D_m} \]

\[ \text{Polydispersity} = \frac{\mu_2}{\overline{\Gamma}^2} \]
<table>
<thead>
<tr>
<th>Run</th>
<th>Z-average Diameter (nm)</th>
<th>Polydispersity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>473.2</td>
<td>0.127</td>
</tr>
<tr>
<td>2</td>
<td>479.5</td>
<td>0.066</td>
</tr>
<tr>
<td>3</td>
<td>478.8</td>
<td>0.077</td>
</tr>
<tr>
<td>4</td>
<td>487.7</td>
<td>0.039</td>
</tr>
<tr>
<td>Avg.</td>
<td>479.8</td>
<td>0.077</td>
</tr>
</tbody>
</table>
A more general relationship can be given between the autocorrelation function and the size distribution. Let each size have a relation constant $\Gamma$. The scattering from each population is then given by $S(\Gamma)$. Now we have an integral equation. Solving for $S(\Gamma)$ gives us size distribution.

$$C(\tau) = 1 + \beta \left| g^{(1)}(\tau) \right|^2$$

$$g^{(1)}(\tau) = \int S(\Gamma) \exp(-\Gamma \tau) d\Gamma$$
Bimodal Sample

- Nominal 20 nm and 500 nm latex run individually
Bimodal Sample

- Mixed sample (in black)
Dynamic Light Scattering
Practical Tips
Dust

- Dust: large, rare particles in the sample
- Generally not really part of the sample
- Since they are rare cannot get good statistics
Filtering

- Filter to remove dust. If particles are too large (D > 50 nm for 0.1 μm filter), at least filter diluent.
- Filters available in sizes 20nm to 2μm
- We can also centrifuge the sample and extract the supernatant.
Settling and DLS

<table>
<thead>
<tr>
<th>Particle Diameter (μm)</th>
<th>Movement due to Brownian Motion</th>
<th>Movement due to Gravitational Settling</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>2.36</td>
<td>&gt;&gt; 0.005</td>
</tr>
<tr>
<td>0.25</td>
<td>1.49</td>
<td>&gt; 0.0346</td>
</tr>
<tr>
<td>0.50</td>
<td>1.052</td>
<td>&gt; 0.1384</td>
</tr>
<tr>
<td>1.0</td>
<td>0.745</td>
<td>~ 0.554</td>
</tr>
<tr>
<td>2.5</td>
<td>0.334</td>
<td>&lt; 13.84</td>
</tr>
<tr>
<td>10.0</td>
<td>0.236</td>
<td>&lt;&lt; 55.4</td>
</tr>
</tbody>
</table>

The Natural limit for Dynamic Light Scattering: Gravitational Settling

Gravitational Settling occurs at about 1-3μm
Why DLS?

- Non-invasive measurement
- Requires only small quantities of sample
- Good for detecting trace amounts of aggregate
- Good technique for macro-molecular sizing
New Nanoparticle Analyzer

- Single compact unit that performs size, zeta potential, and molecular weight measurements.
Q&A

Ask a question at labinfo@horiba.com

Keep reading the monthly HORIBA Particle e-mail newsletter!

Visit the Download Center to find the video and slides from this webinar.

Jeff Bodycomb, Ph.D.
P: 866-562-4698
E: jeff.bodycomb@horiba.com

Thank-you