HORIBA Scientific

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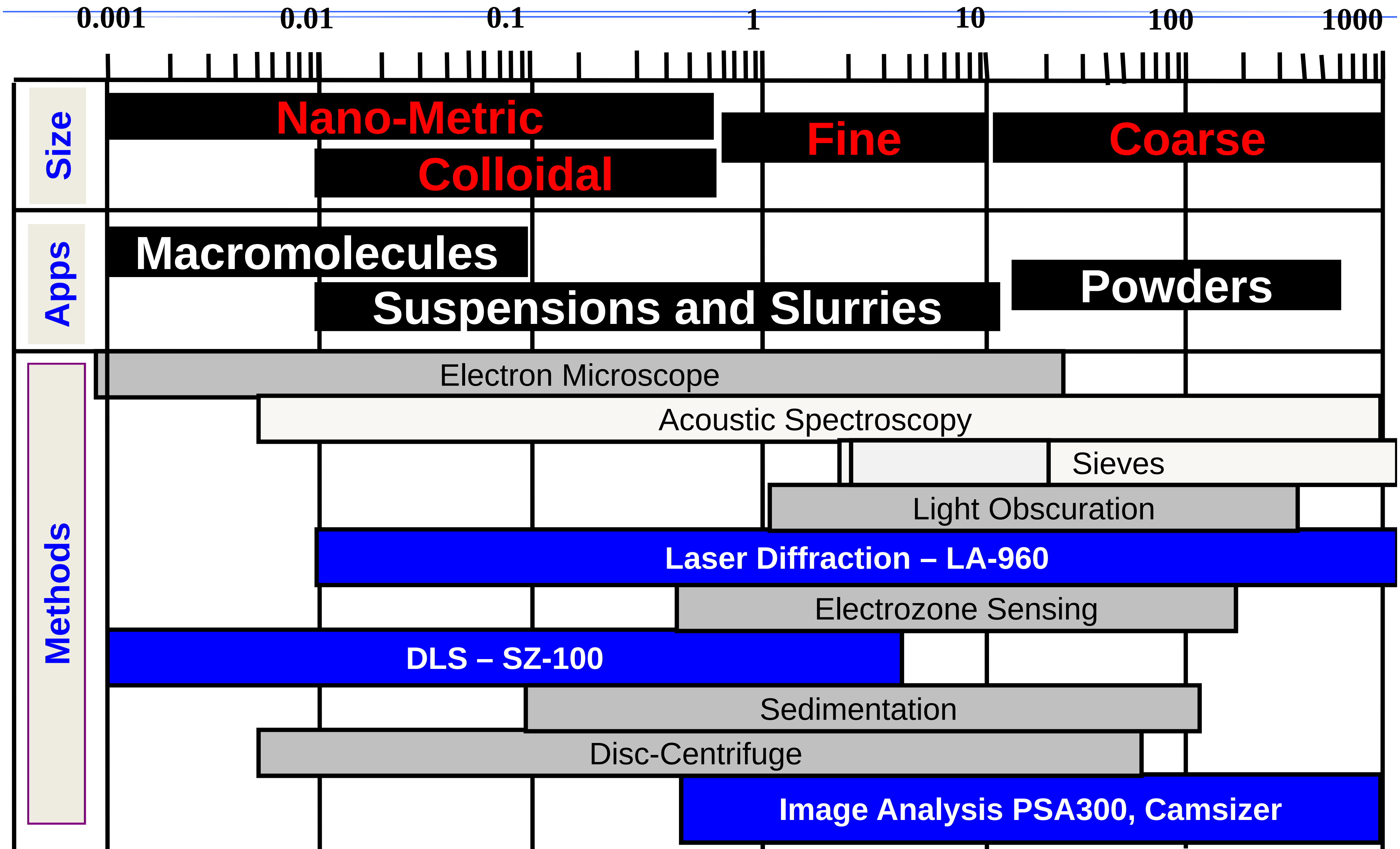
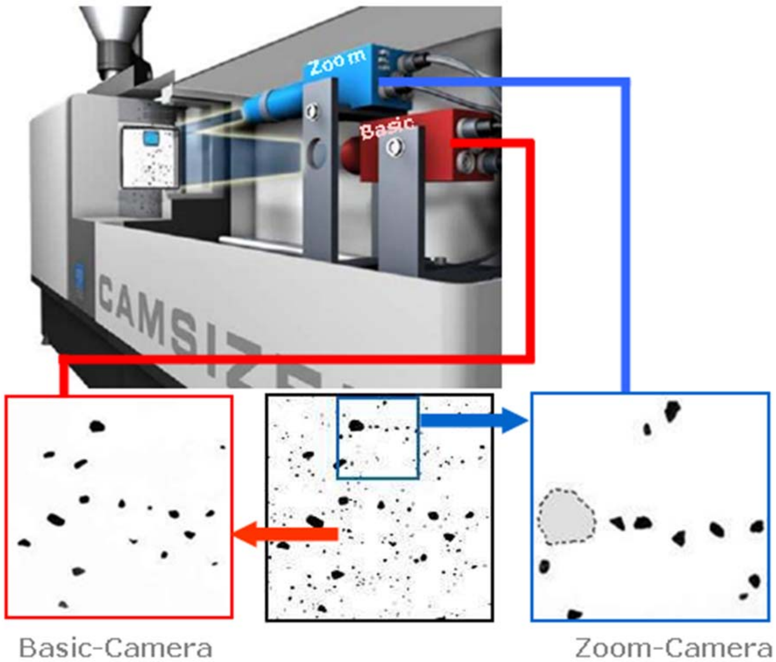
Introduction to Dynamic Light Scattering for Particle Size Determination

Sizing Techniques



Two Approaches to Image Analysis

Dynamic:
particles flow past camera

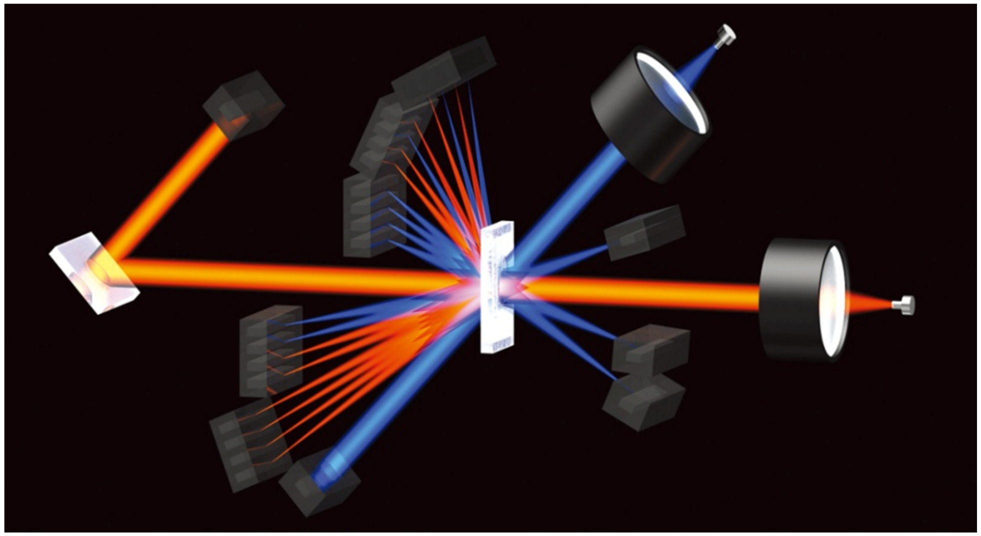


1 – 3000 um

Static:
particles fixed on slide,
stage moves slide

0.5 – 1000 um
2000 um w/1.25 objective

Laser Diffraction



Laser Diffraction

- Particle size 0.01 – 3000 µm
- Converts scattered light to particle size distribution
- Quick, repeatable
- Most common technique
- Suspensions & powders

![HORIBA Scientific]

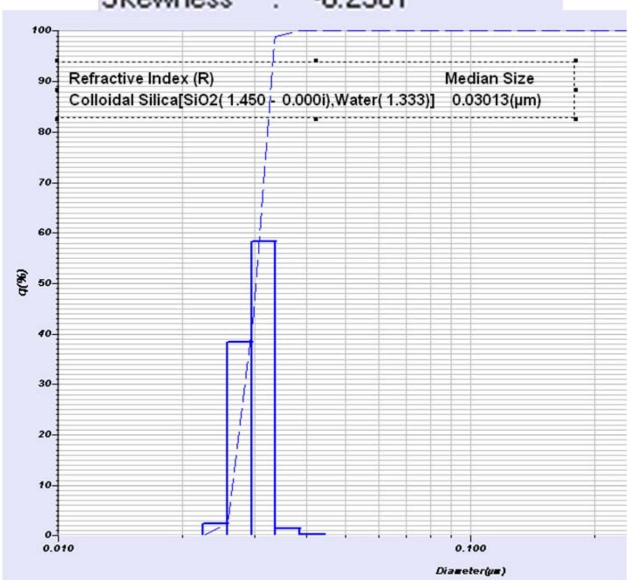
Laser Diffraction

Suspension

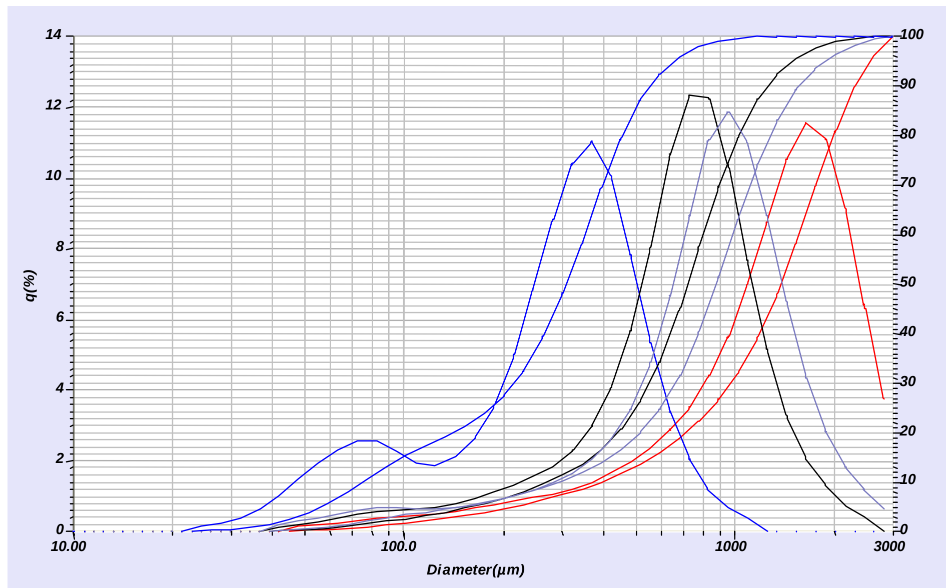
Powders

Silica
~ 30 nm

S.P.Area	:	2.0183E+6(cm²/cm³)
Mean Size	:	0.02990(μm)
Variance	:	5.0313E-6(μm²)
Median Size	:	0.03013(μm)
Mode Size	:	0.0302(μm)
Skewness	:	-0.2901



Coffee Results
0.3 – 1 mm



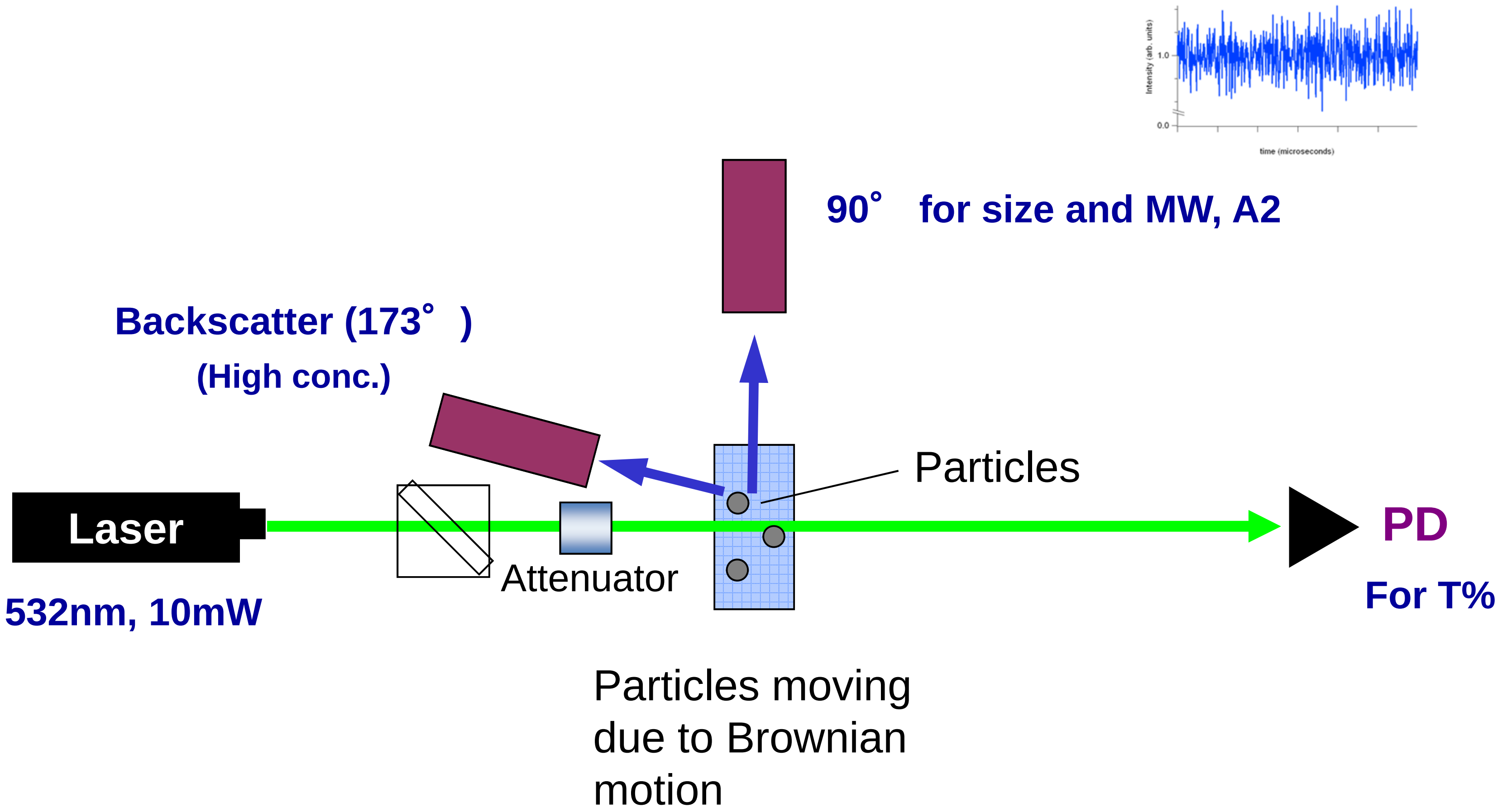
What is Dynamic Light Scattering?

- Dynamic light scattering refers to measurement and interpretation of light scattering data on a <u>microsecond</u> time scale.
- Dynamic light scattering can be used to determine
  - Particle/molecular size
  - Size distribution
  - Relaxations in complex fluids

Other Light Scattering Techniques

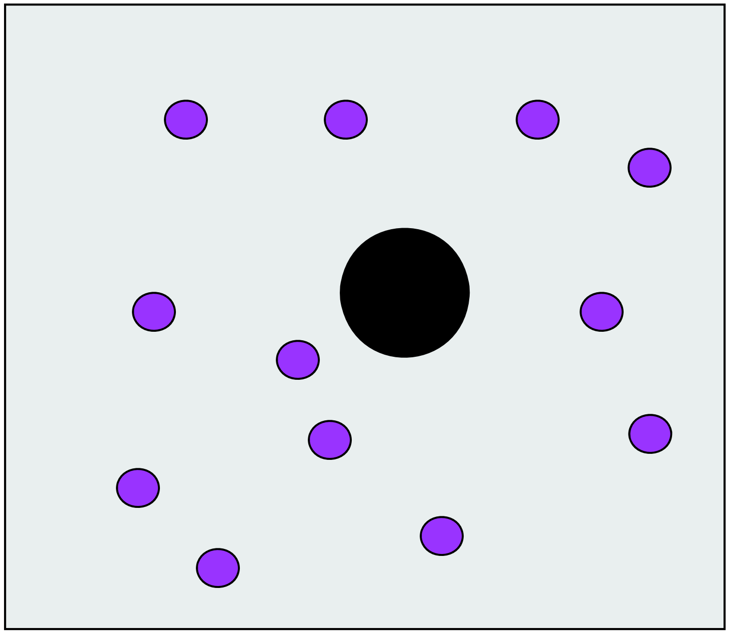
- Static Light Scattering: over a duration of ~1 second. Used for determining particle size (diameters greater than 10 nm), polymer molecular weight, 2nd virial coefficient, R_g.
- Electrophoretic Light Scattering: use Doppler shift in scattered light to probe motion of particles due to an applied electric field. Used for determining electrophoretic mobility, zeta potential.

DLS Optics


Intensity (arb. units)
1.0
0.0
time (microseconds)
90° for size and MW, A2
Backscatter (173°)
(High conc.)
Particles
Laser
Attenuator
PD
For T%
532nm, 10mW
Particles moving
due to Brownian
motion

Brownian Motion

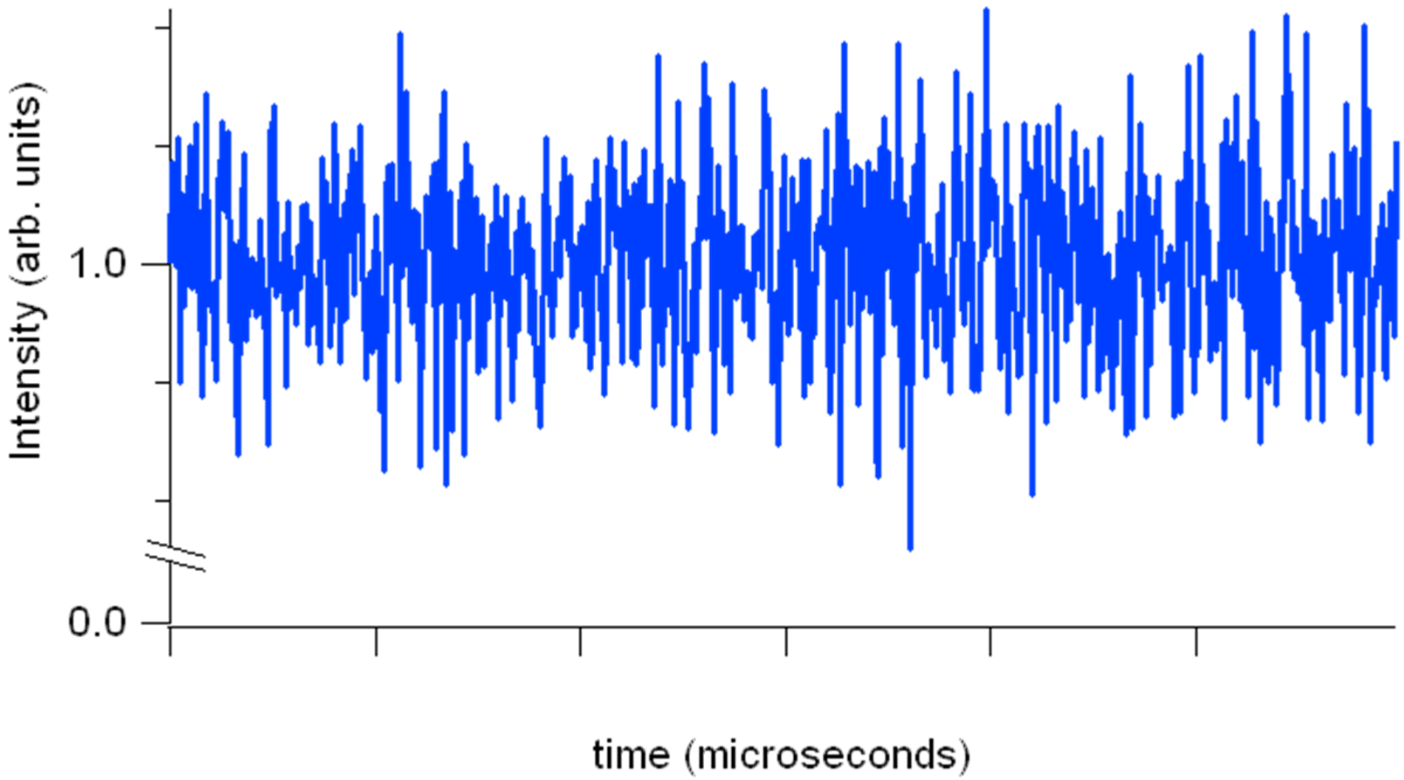
Particles in suspension undergo Brownian motion (random thermal motion.



- Brownian Motion
  - Random
  - Related to Size
  - Related to viscosity
  - Related to temperature

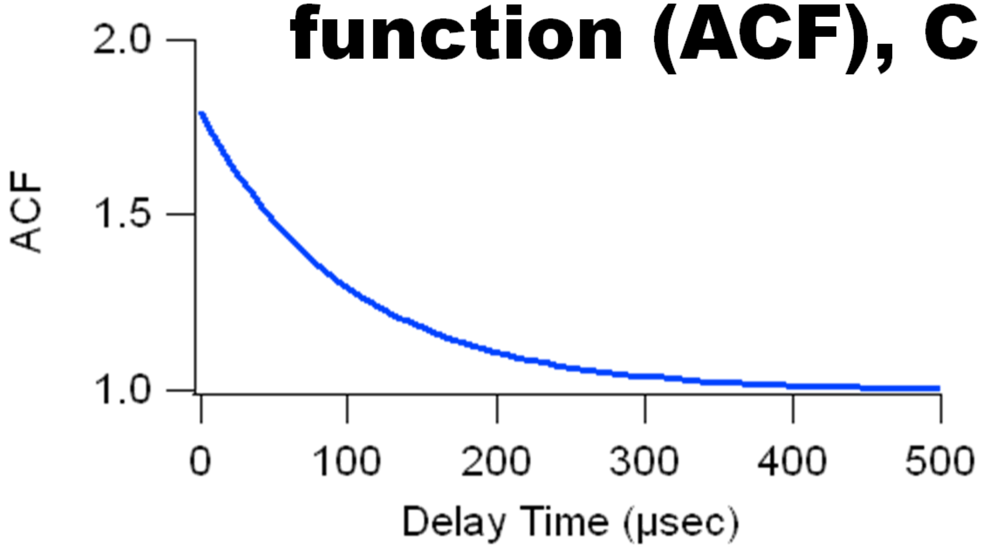
DLS signal

- Random motion of particles leads to random fluctuations in signal (due to changing constructive/destructive interference of scattered light.



Correlation Function

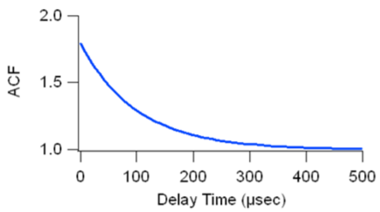
- Random fluctuations are interpreted in terms of the autocorrelation **function (ACF), C(**τ).



$$C(\tau) = \frac{\int_0^T I(t)I(t+\tau)dt}{\langle I(t)I(t)\rangle}$$

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

Gamma to Size



$$q = \frac{4\pi n}{\lambda}\sin\left(\theta/2\right)$$

$$\Gamma = D_m q^2$$

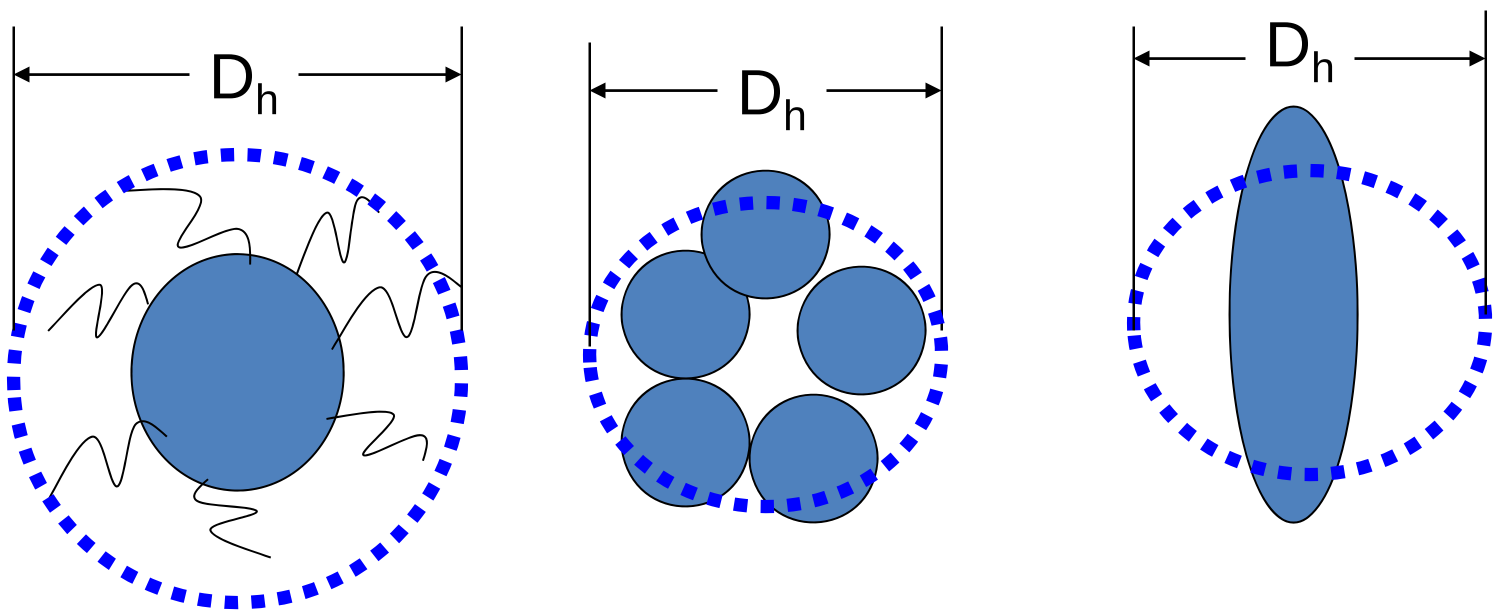
$$D_h = \frac{k_B T}{3\pi\eta(T) D_m}$$

Note effect of temperature!

Γ decay constant
D_m diffusion coefficient
q scattering vector
n refractive index
λ wavelength
θ scattering angle
D_h hydrodynamic diameter
η viscosity
k_B Boltzman's constant

What is Hydrodynamic Size?

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

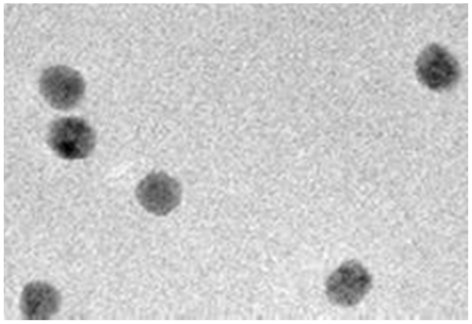


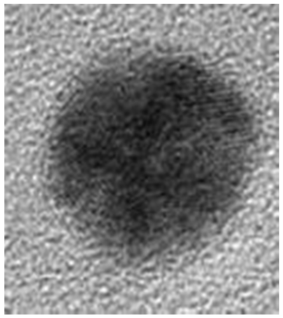
Hydrodynamic Size

- 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

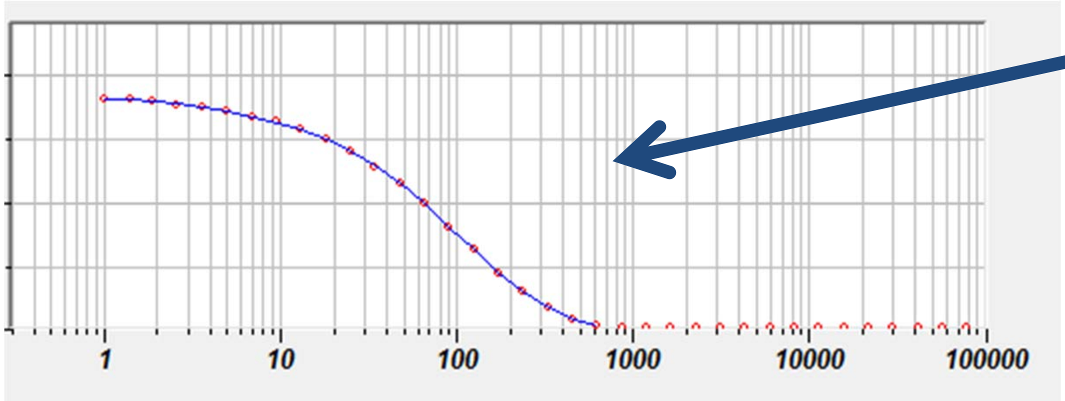
Technique	Size nm
Atomic Force Microscopy	8.5 ± 0.3
Scanning Electron Microscopy	9.9 ± 0.1
Transmission Electron Microscopy	8.9 ± 0.1
Dynamic Light Scattering	13.5 ± 0.1





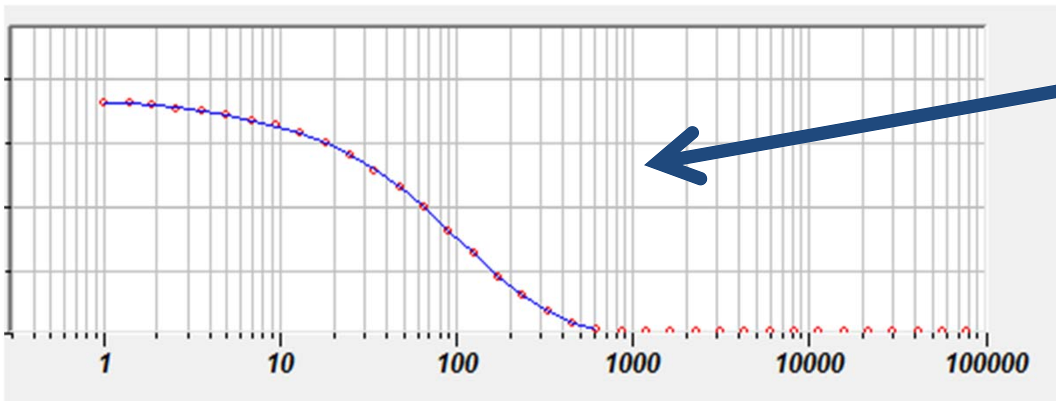
SEM (above) and TEM (below) images for RM 8011

Nanogold Data

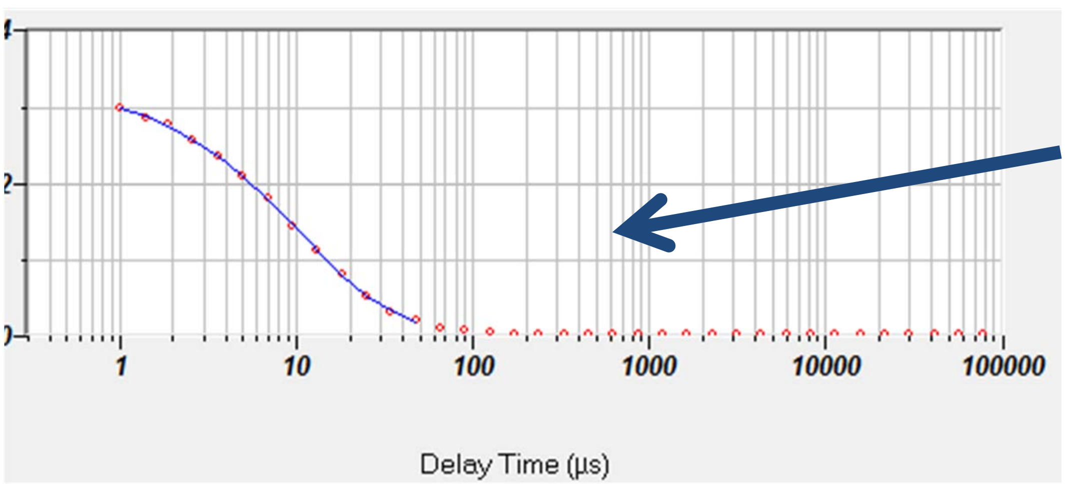


	Z-avg. Diameter, nm
Run 1	50.5
Run 2	51.1
Run 3	49.2
Run 4	51.5
Run 5	49.7
Run 6	50.9
Avg.	50.5
St. Dev.	0.9
COV	1.7 %

Nanogold Data



	Z-avg. Diameter, nm
Avg.	50.5
St. Dev.	0.9
COV	1.7 %



	Z-avg. Diameter, nm
Run 1	10.5
Run 2	10.6
Run 3	10.2
Run 4	10.5
Run 5	10.3
Avg.	10.4
St. Dev.	0.2
COV	1.9 %

Lab to Lab comparison

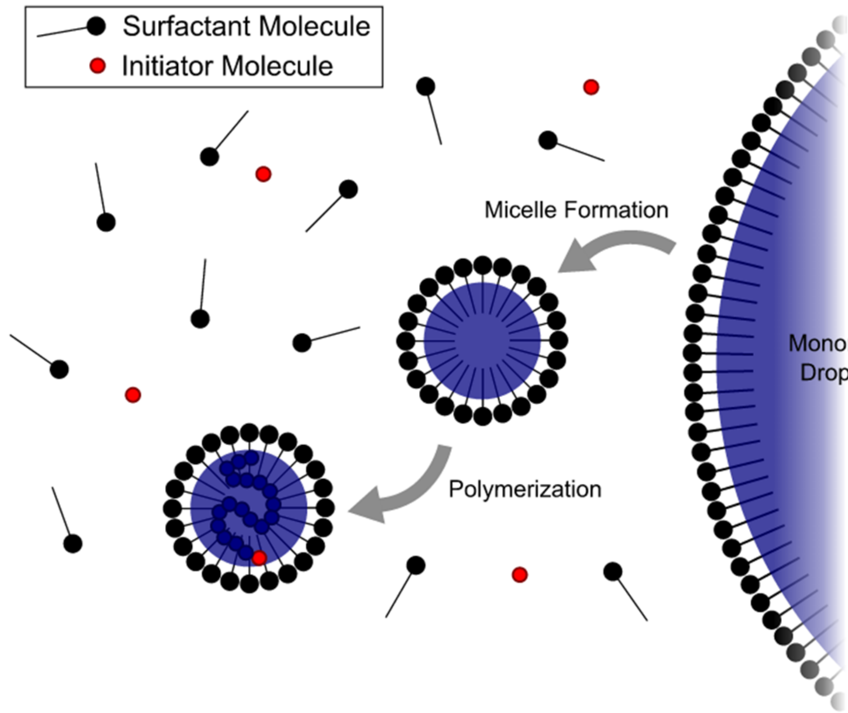
Colloidal Silica

	Mean determined Z-average size (nm)	COV (%)
Dynamic Light Scattering with SZ-100, laboratory 1	34.4	0.7
Dynamic Light Scattering with SZ-100, laboratory 2	34.6	0.3

Emulsion Polymers

IUPAC definition
Emulsion polymerization:

Polymerization whereby monomer(s), initiator, dispersion medium, and possibly colloid stabilizer constitute initially an inhomogeneous system resulting in particles of colloidal dimensions containing the formed polymer.



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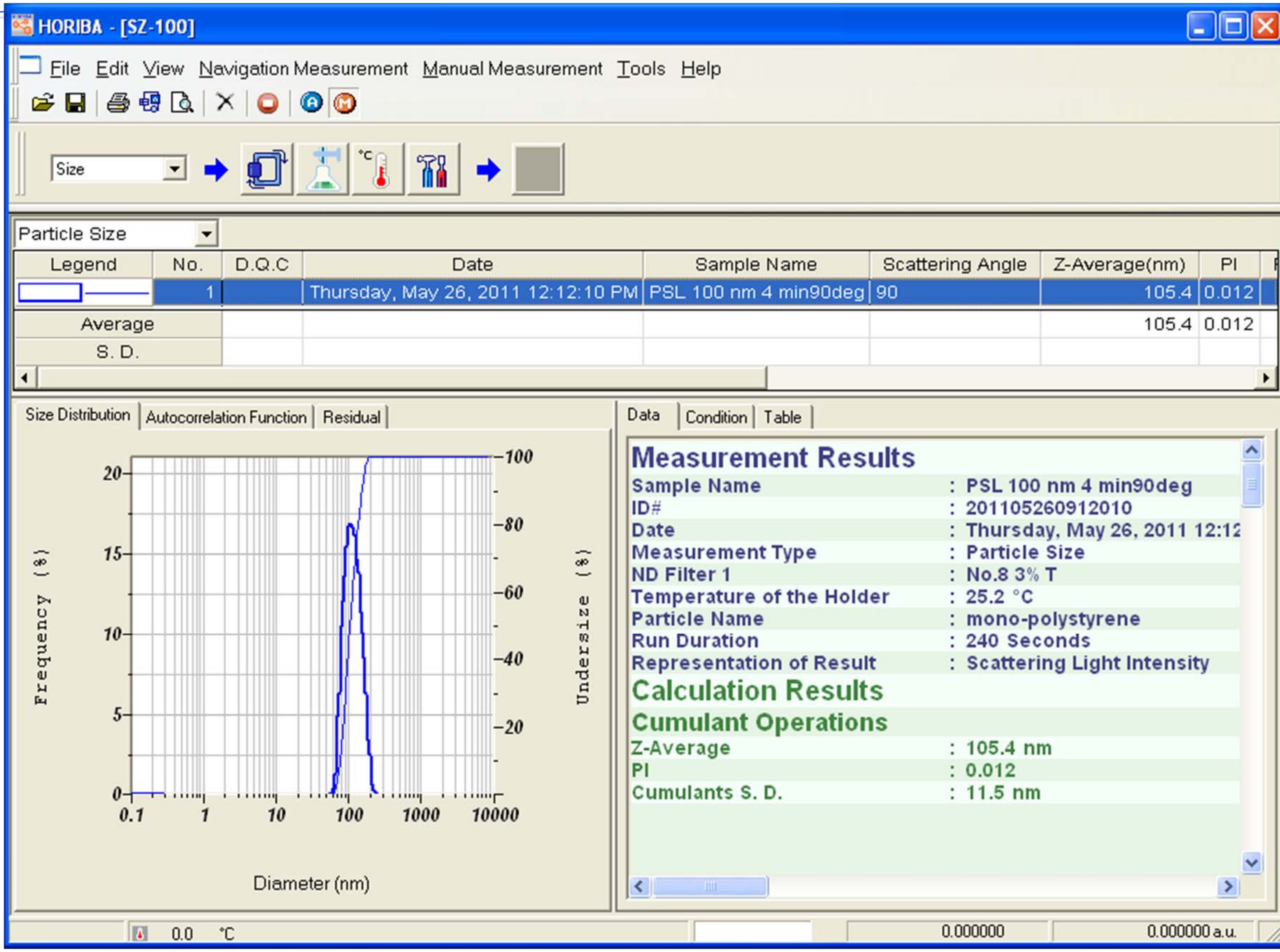
Polystyrene Latex Sample



Polydisperse Sample Cumulants

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.

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

$$C(\tau) = 1 + \beta \exp\left[2\left(-\overline{\Gamma}\tau + \left(\mu_2 / 2!\right)\tau^2 - \cdots\right)\right]$$

$$\overline{\Gamma} = \overline{D_m} q^2$$

"z-average size"

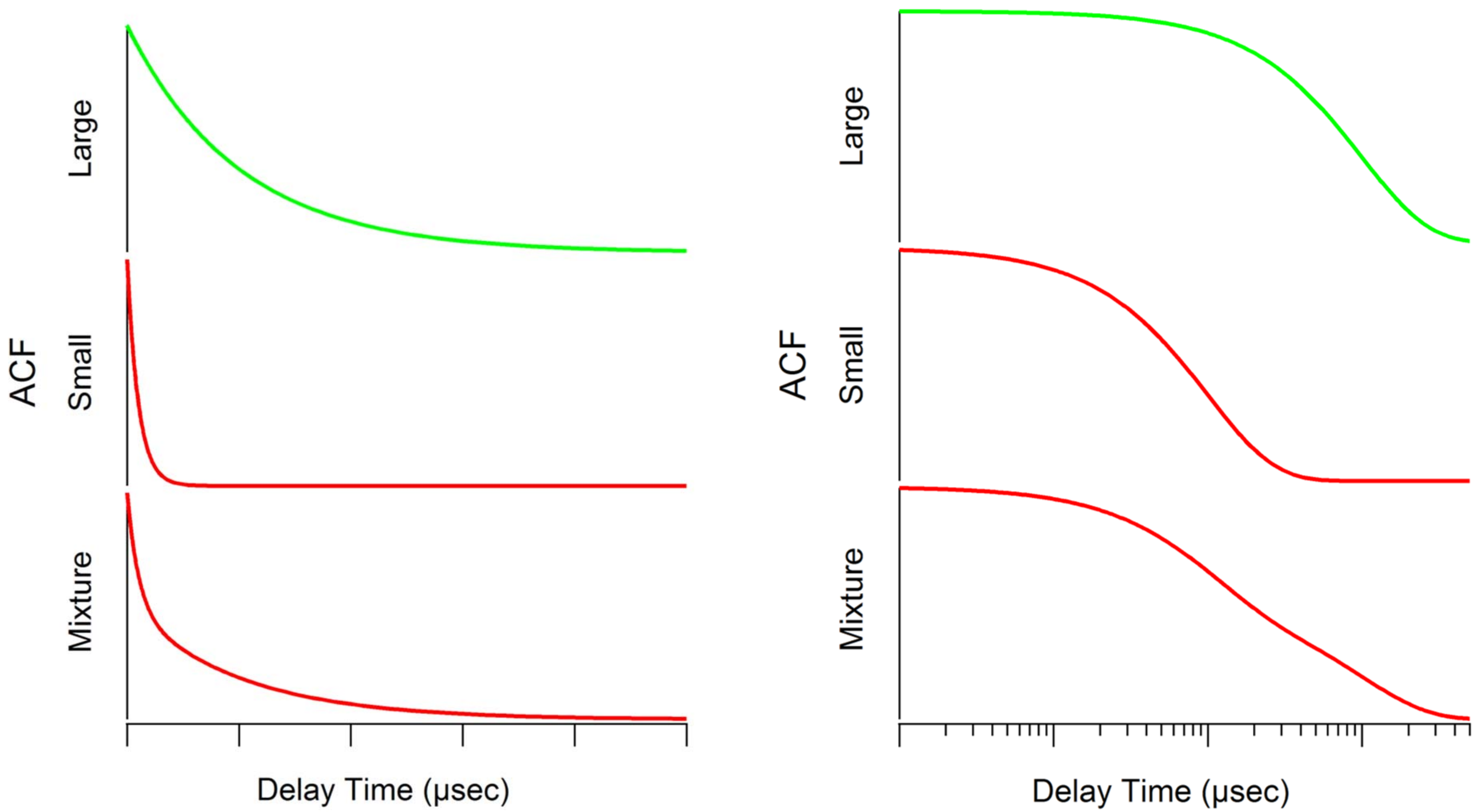
$$D_{z,h} = \frac{k_B T}{3\pi\eta(T)\overline{D_m}}$$

$$Polydispersity = \mu_2 / \overline{\Gamma}^2$$

SiO_2

Run	Z-average Diameter (nm)	Polydispersity Index
1	473.2	0.127
2	479.5	0.066
3	478.8	0.077
4	487.7	0.039
Avg.	479.8	0.077

Mixtures of Particles



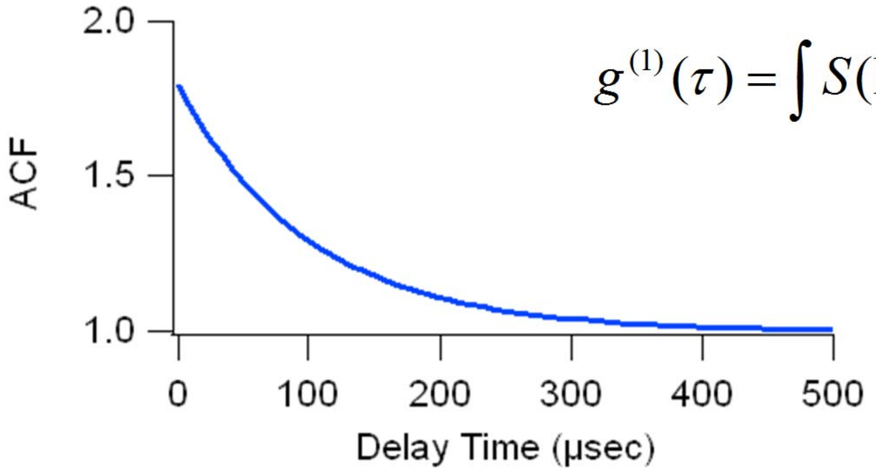
Sum the autocorrelation functions

Polydisperse Sample (ILT)

A more general relationship can be given between the autocorrelation function and the size distribution. Let each size have a relation constant Γ. 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.

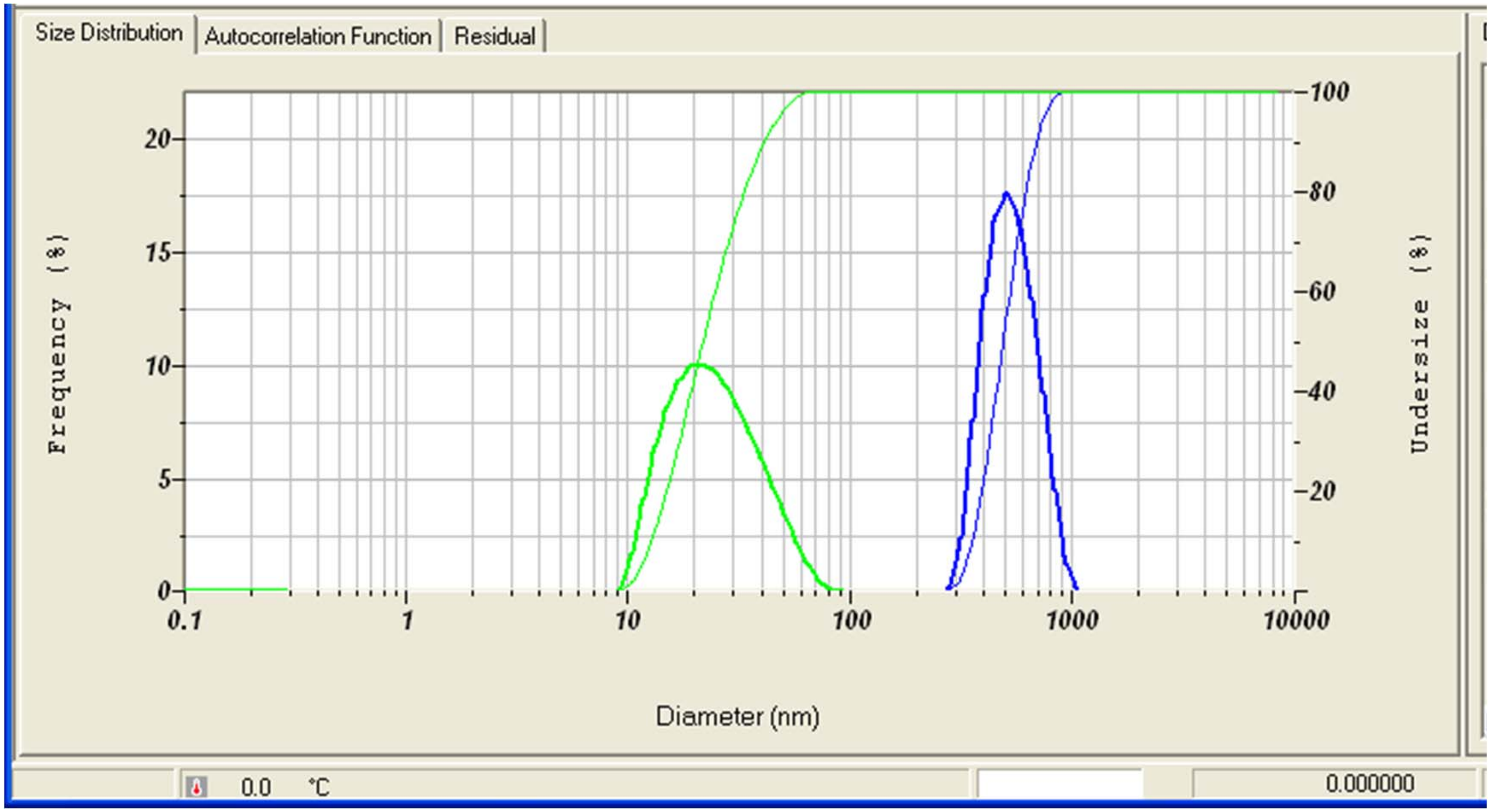
$$C(\tau) = 1 + \beta \left| g^{(1)}(\tau) \right|^2$$

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



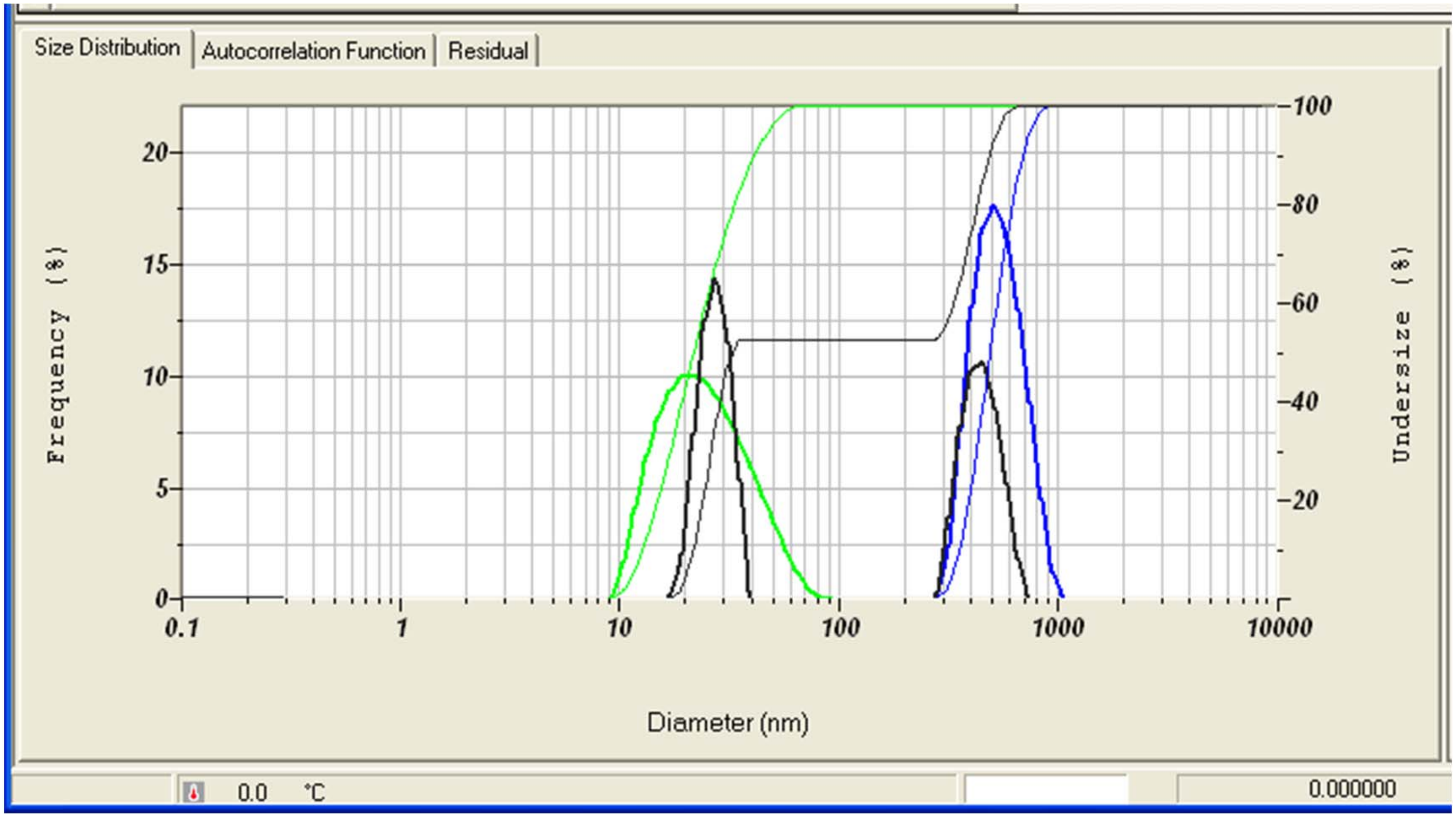
Bimodal Sample

- Nominal 20 nm and 500 nm latex run individually



Bimodal Sample

- Mixed sample (in black)



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

Particle Diameter (μm)	Movement due to Brownian Motion		Movement due to Gravitational Settling
0.01	2.36	>>	0.005
0.25	1.49	>	0.0346
0.50	1.052	>	0.1384
1.0	0.745	~	0.554
2.5	0.334	<	13.84
10.0	0.236	<<	55.4

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

Nanoparticle Analyzer

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

Q&A

Ask a question at labinfo@horiba.com

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Thank-you