Nanoparticle Analysis: Dynamic Light Scattering for Particle Size Determination

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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

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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)

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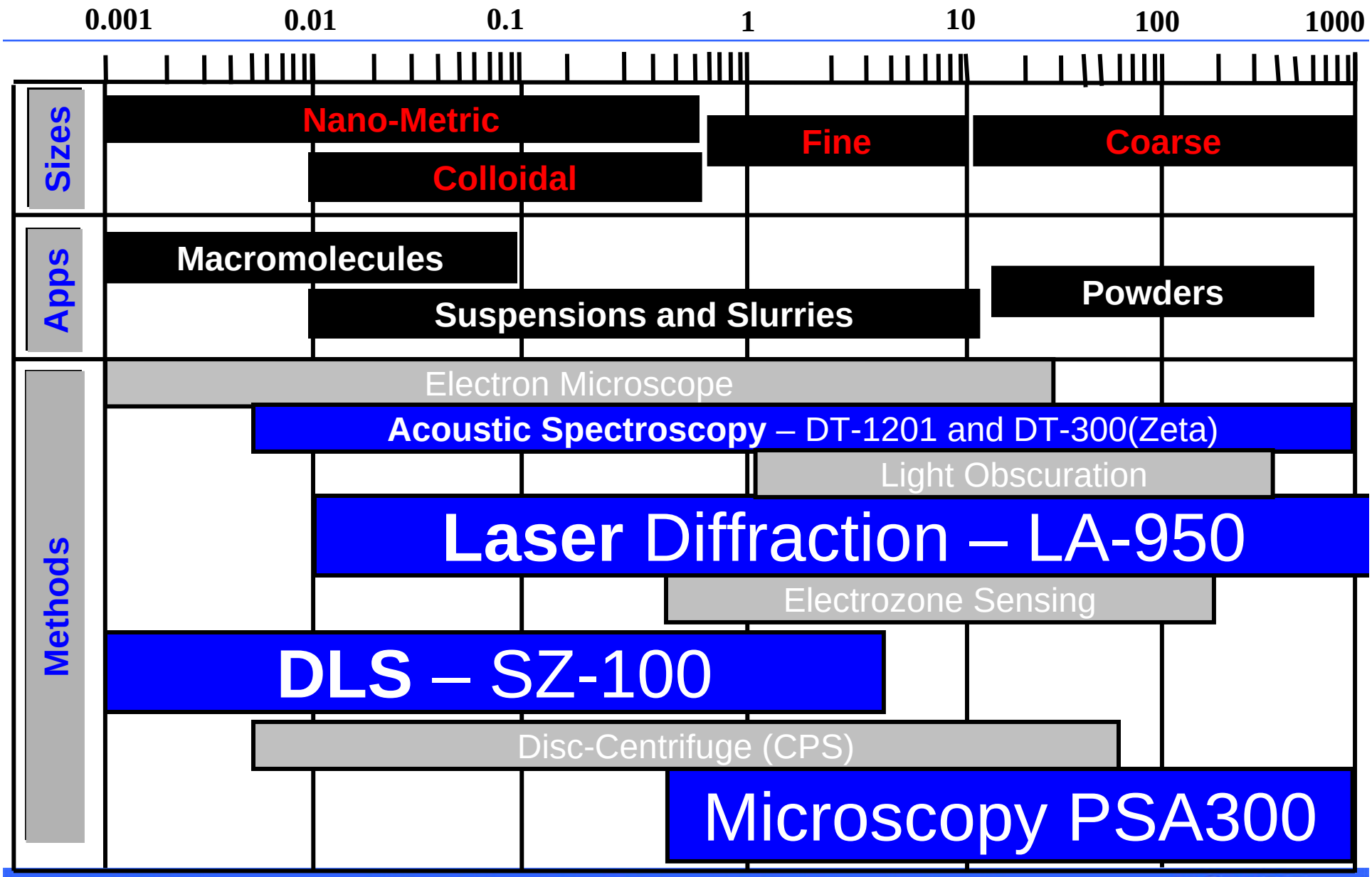
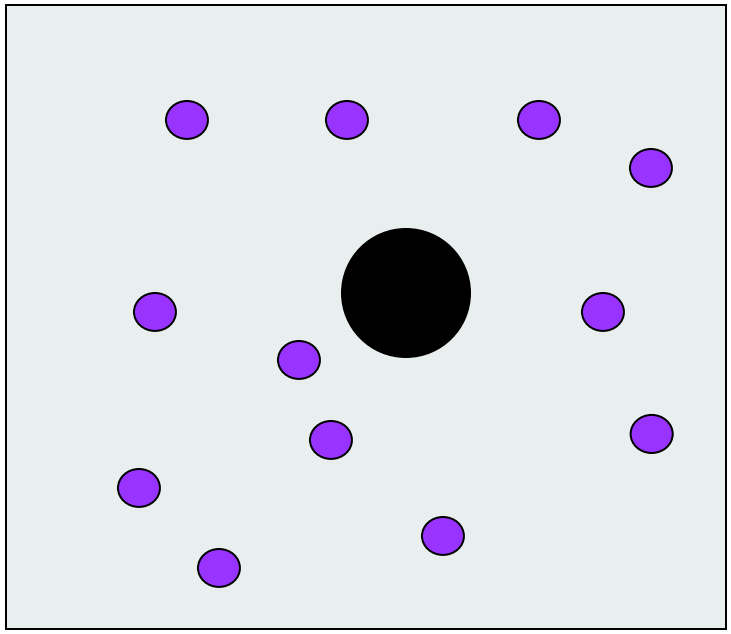


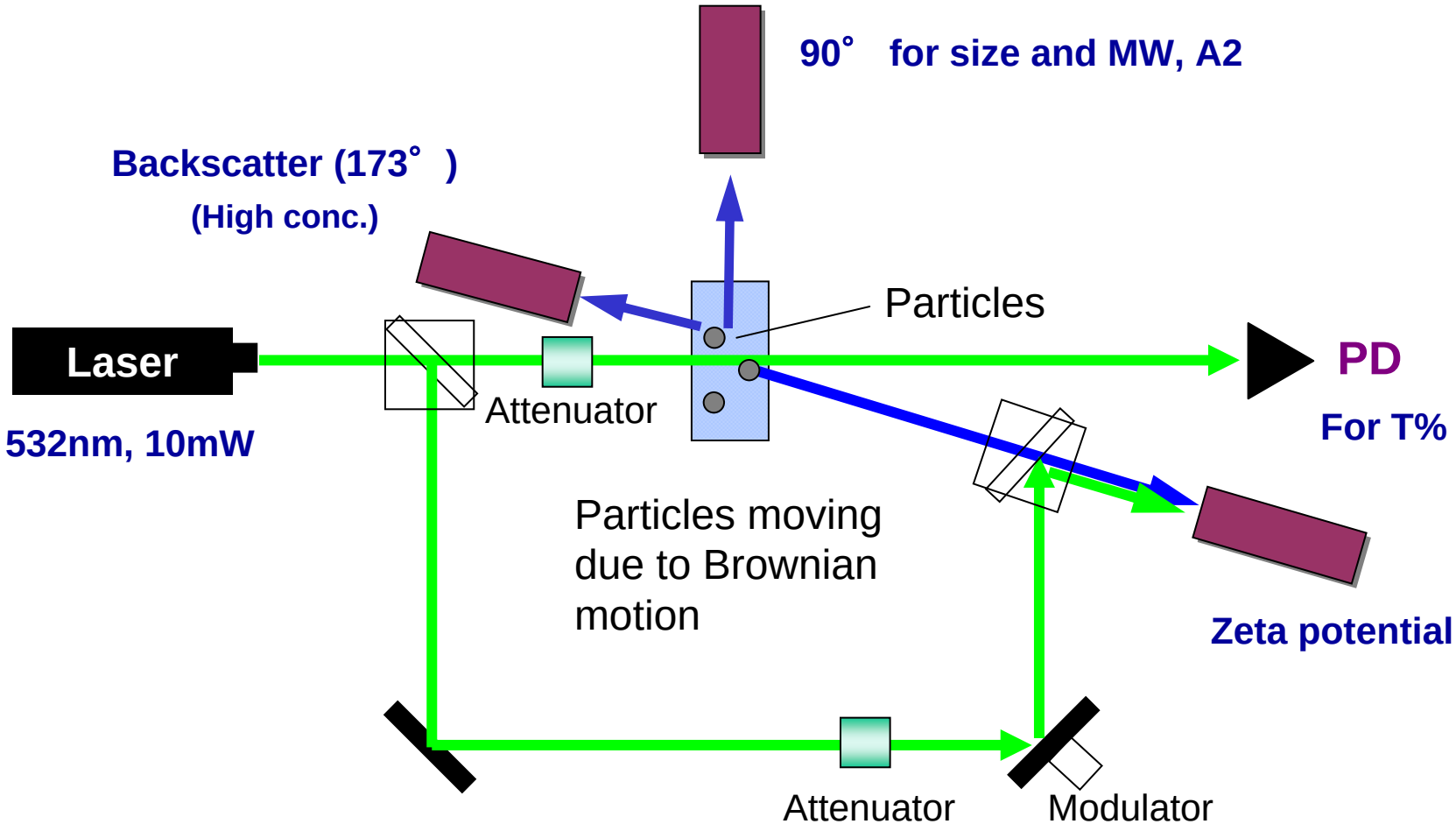
Brownian Motion

Particles in suspension undergo Brownian motion due to solvent molecule bombardment in random thermal motion.



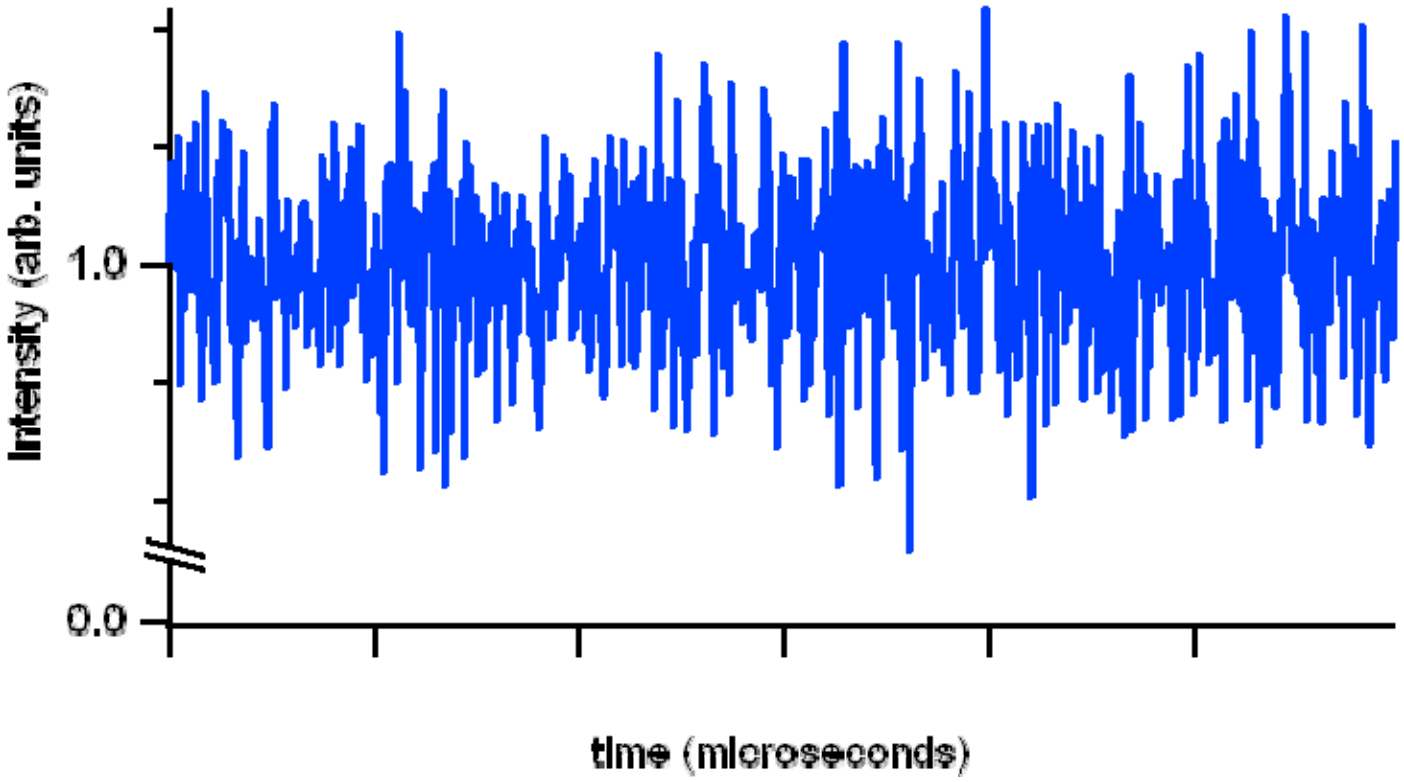
- Brownian Motion
  - Random
  - Related to Size
  - Related to viscosity
  - Related to temperature

DLS Optics



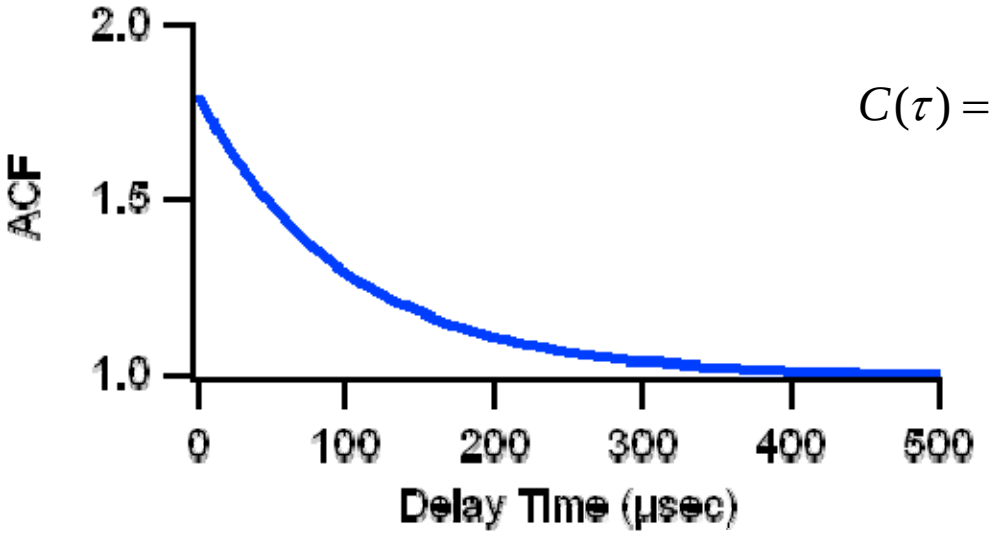
DLS signal

- 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).



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

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

Gamma to Size

$$\Gamma = D_m q^2$$

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

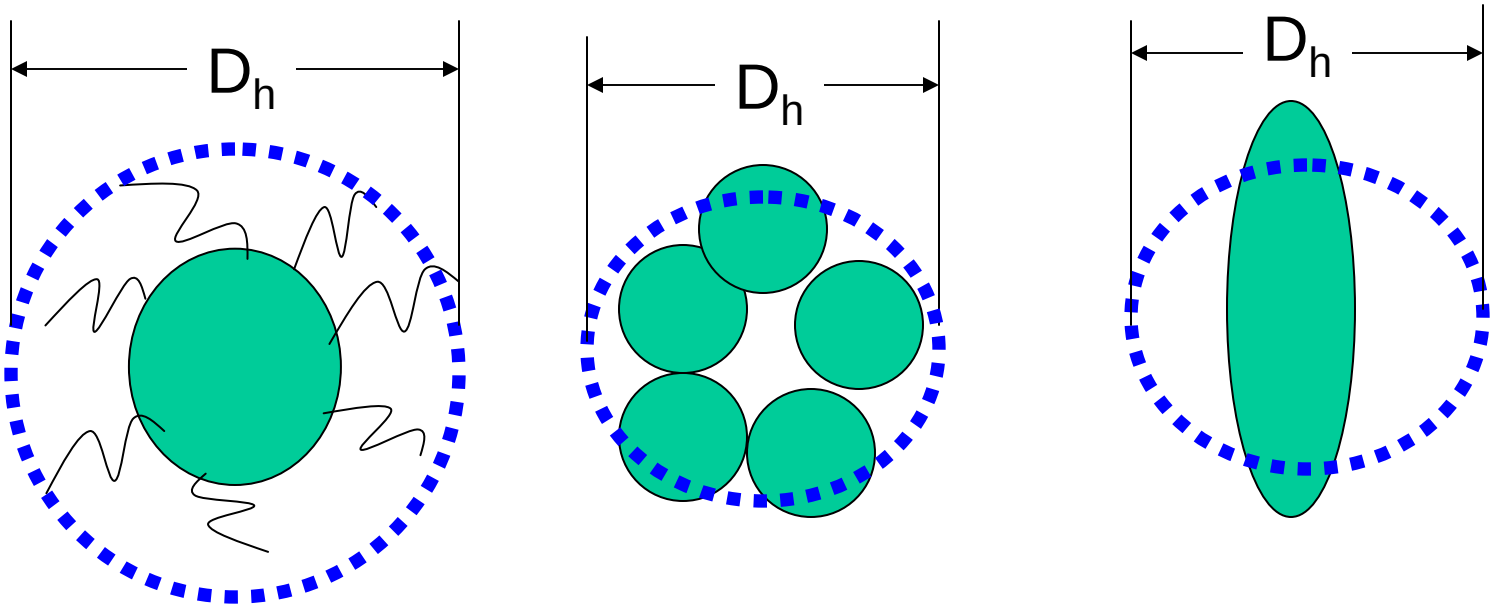
$$D_h = \frac{k_B T}{3\pi\eta(T) D_m}$$

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.

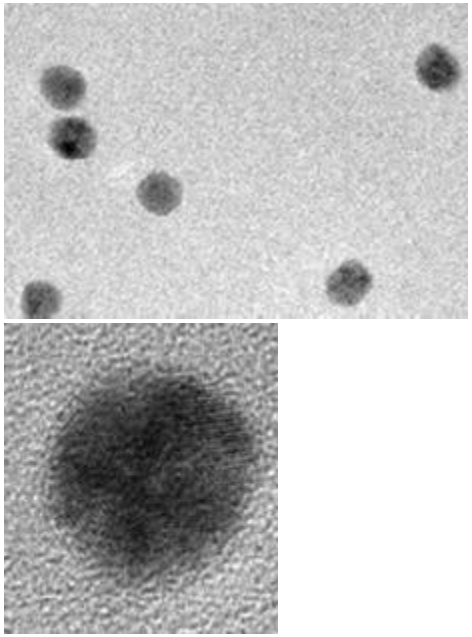


Hydrodynamic Size

- 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).

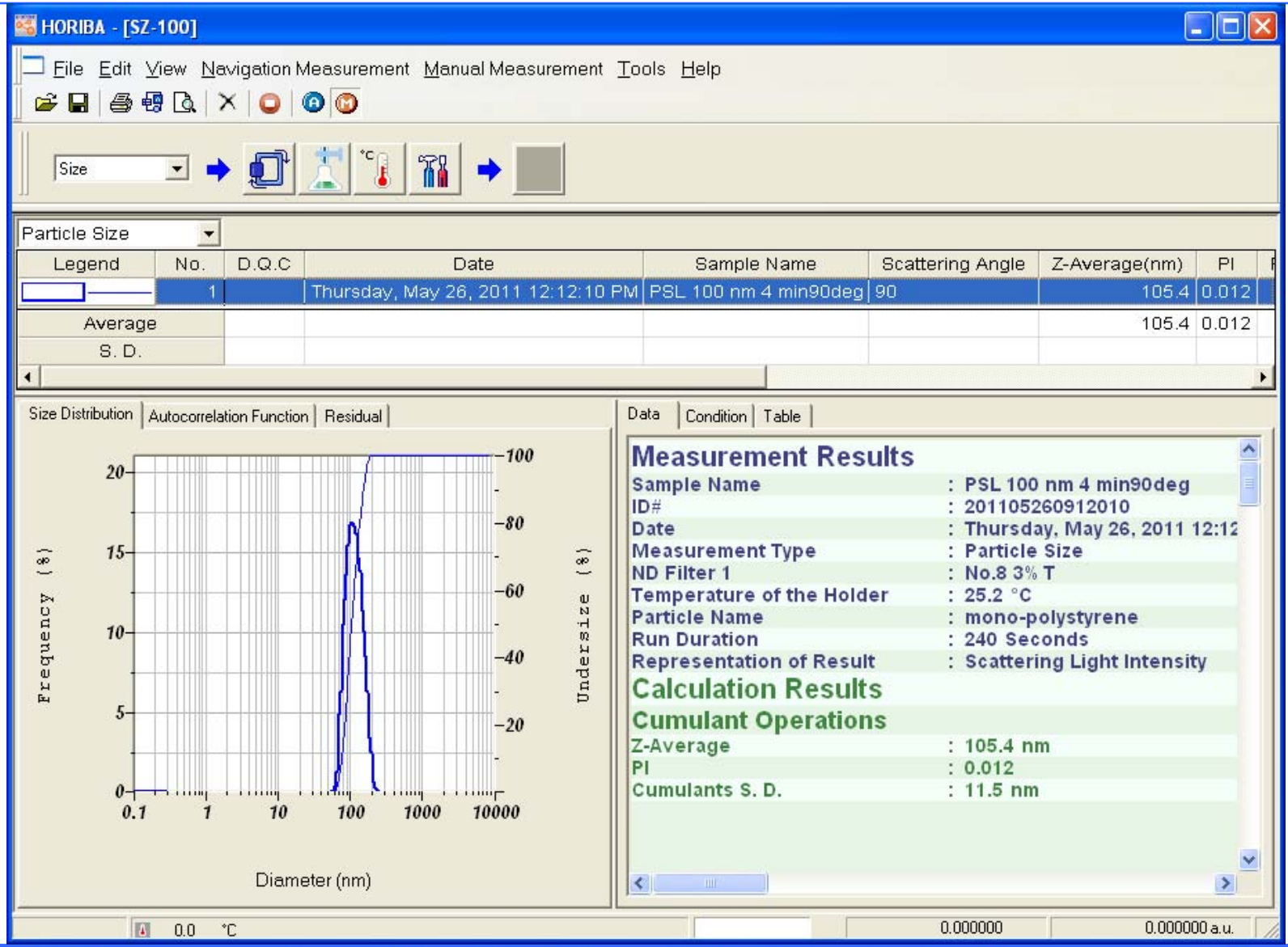
Gold Colloids

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

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.

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

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

"z-average size"

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

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

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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

Polydisperse Sample (ILT)

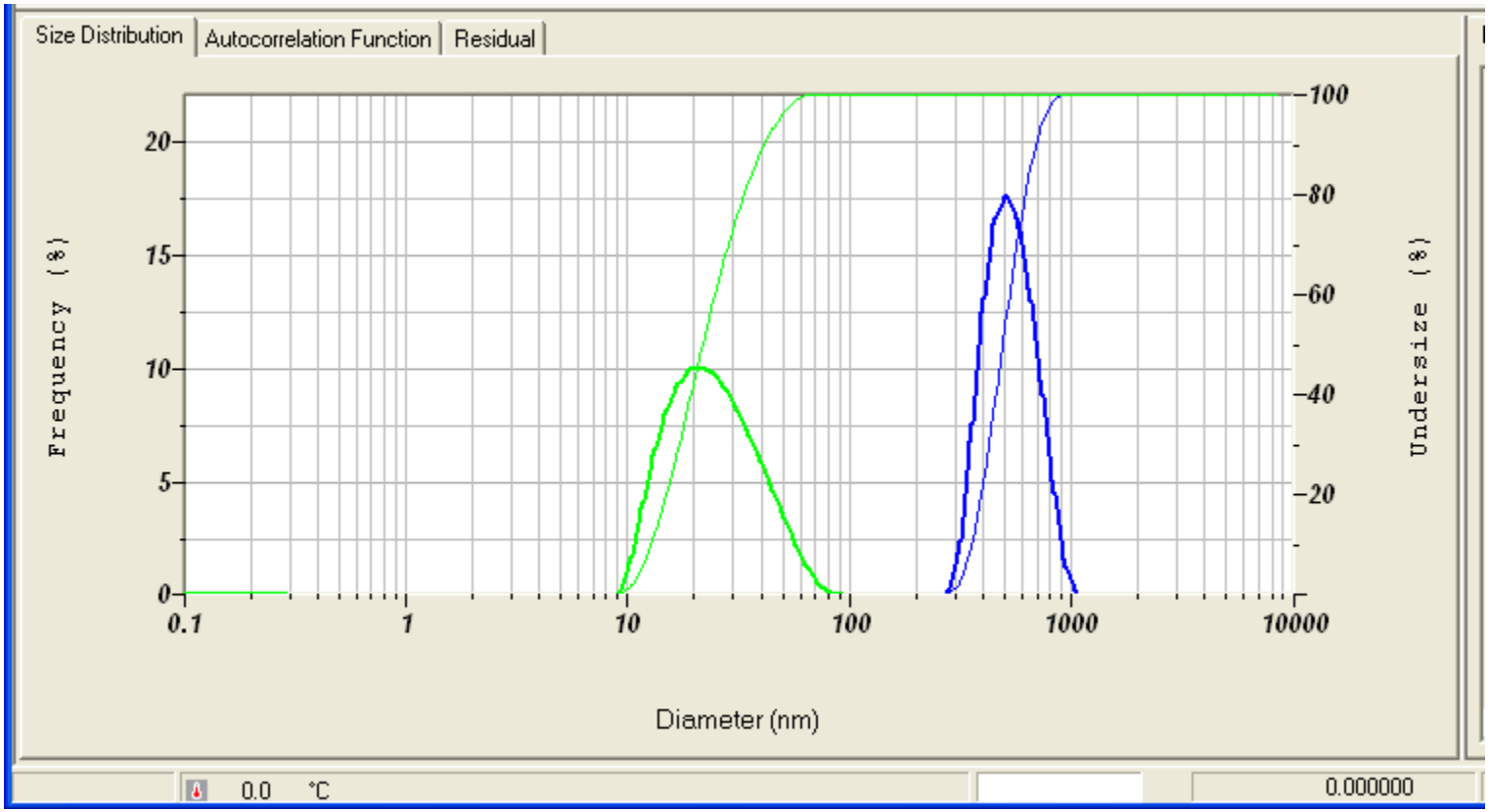
- A more general relationship can be given between the autocorrelation function and the size distribution. Let each size have a relation constant Γ. The scattering from each population is then given by $S(\Gamma)$. Now we have an integral equation. Solving for $S(\Gamma)$ gives us size distribution.

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

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

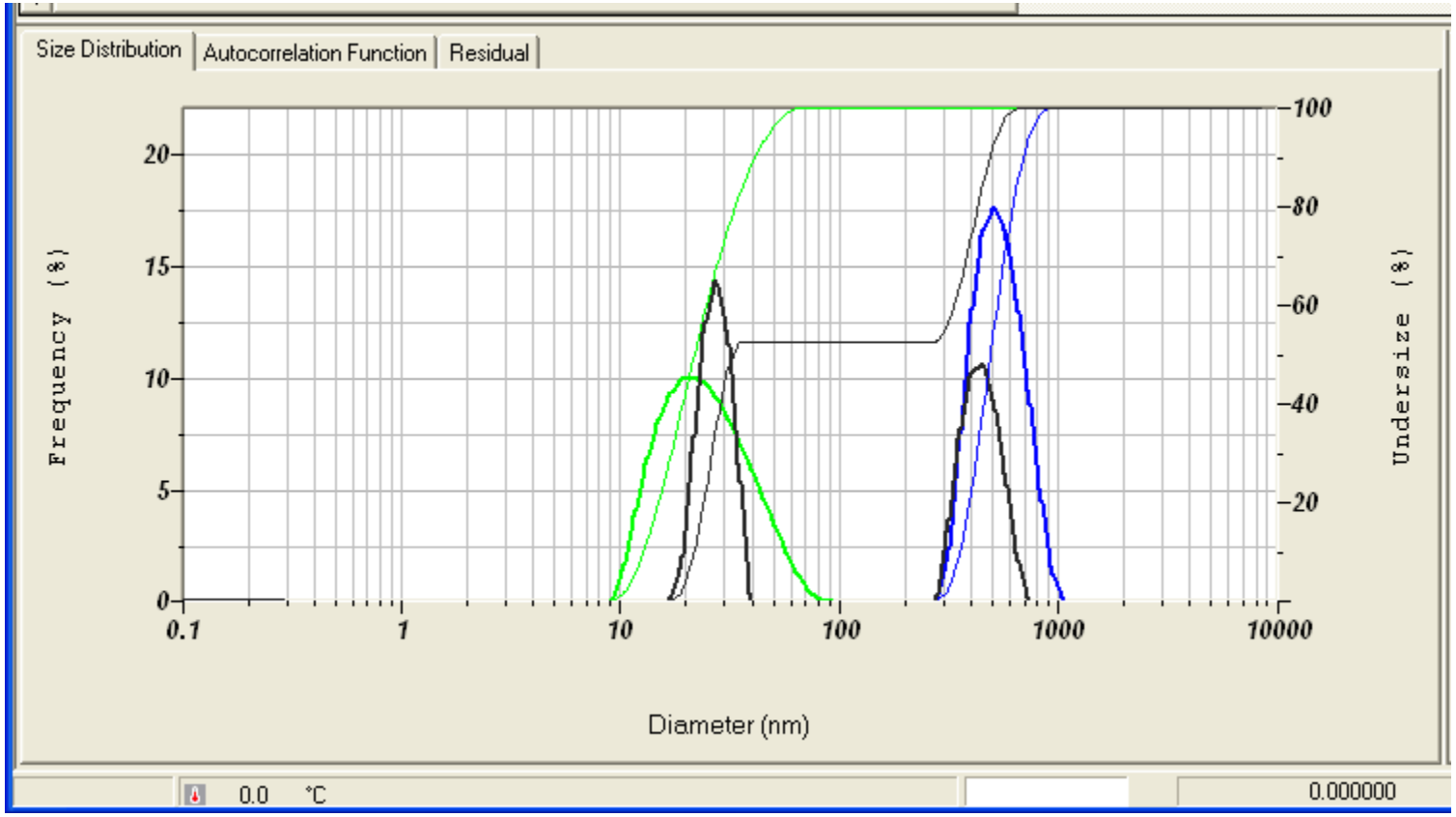
Bimodal Sample

- Nominal 20 nm and 500 nm latex run individually

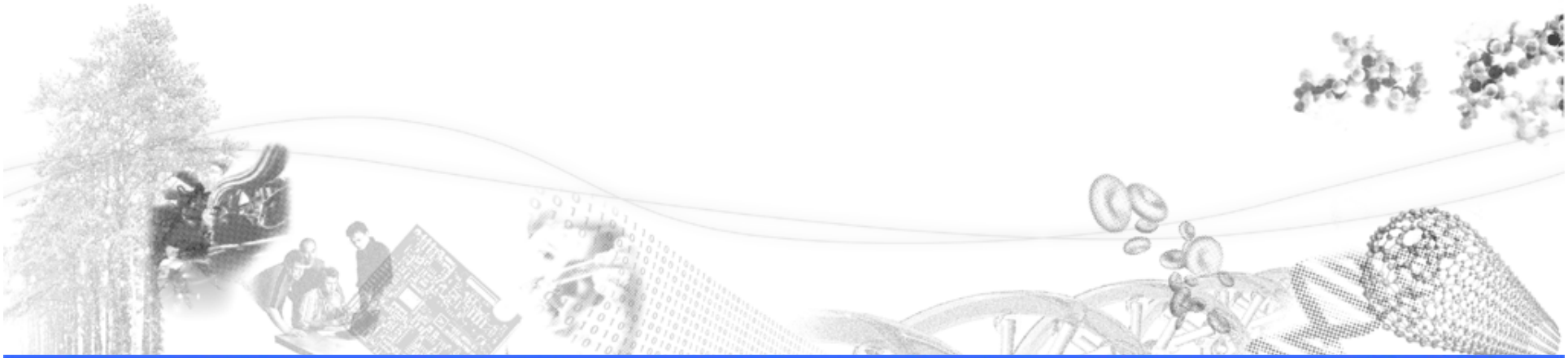


Bimodal Sample

- Mixed sample (in black)



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

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

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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

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Thank-you