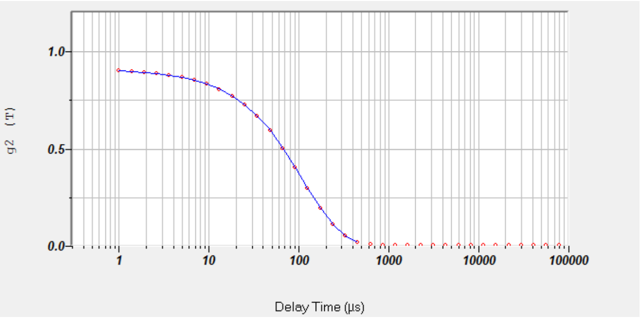
# Interpreting and Understanding Dynamic Light Scattering Data





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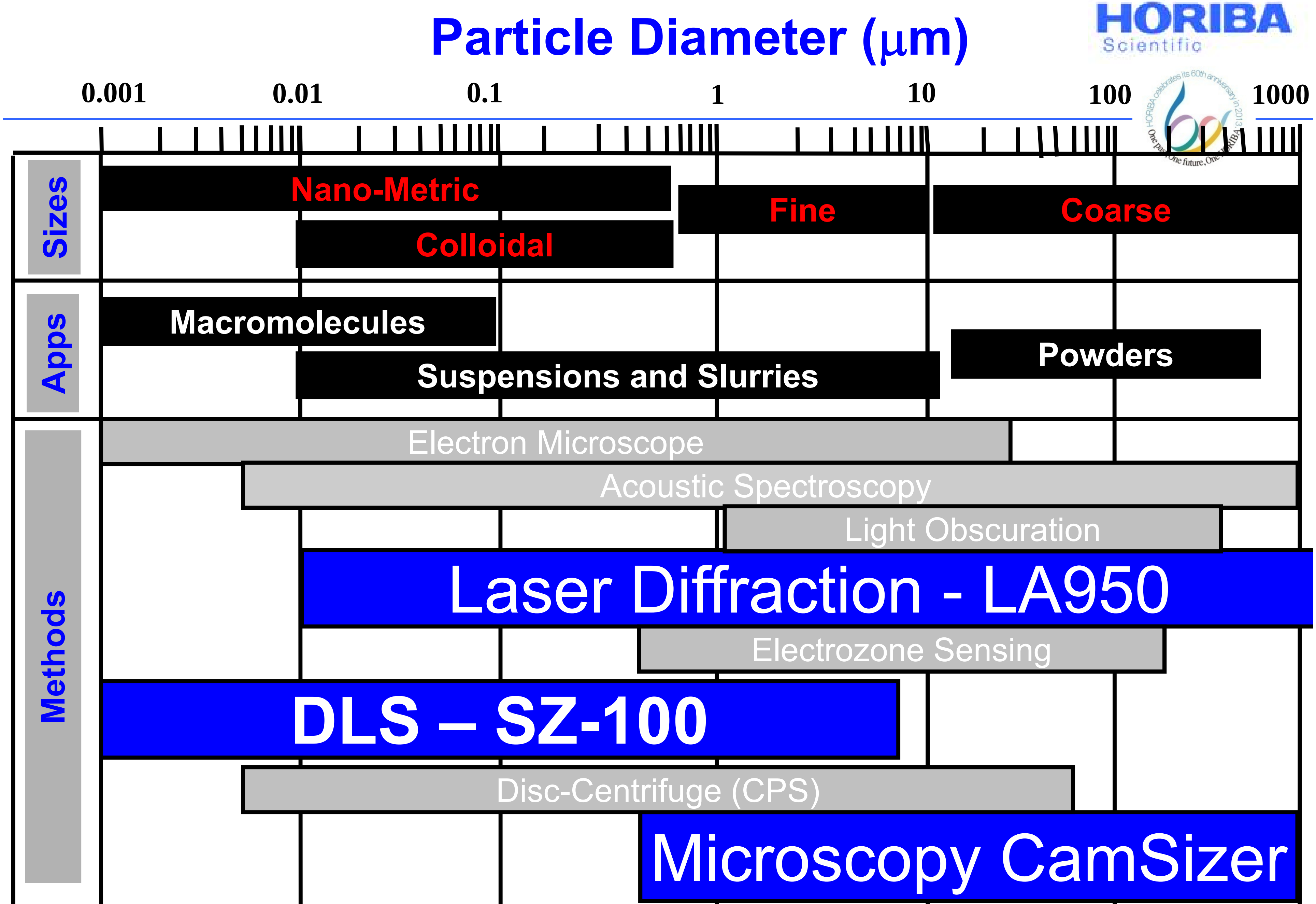
# Outline

"Kitchen sink" talk. I cover a range of topics with an emphasis on conclusions rather than derivations.

- Introduction
- Looking at the ACF
- Effect of temperature and what it means to you.
- The Z-average
- Effect of concentration
- Hydrodynamic size

# 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



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
Light Obscuration
Laser Diffraction - LA950
Electrozone Sensing
DLS – SZ-100
Disc-Centrifuge (CPS)
Microscopy CamSizer

# Use the Right Tool

- It is a struggle to use a micrometer with this steel block.


- It's easy with a steel rule (or calipers).

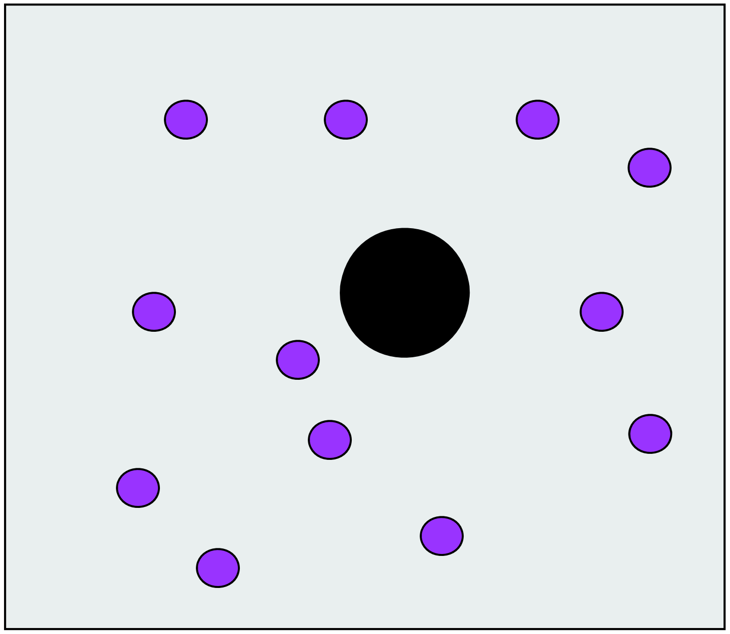

- The same applies for particles

# Particle Sizes over 1 micron

- Note that the upper limit of DLS is at 8 microns. This depends on particle density and other factors.
- Rule of thumb: If your particles are routinely bigger than 1 micron, consider laser diffraction.
- Particles that are too big often appear as 10~20 microns in DLS results. You will not be trapped by big particles that seem small.

# Brownian Motion

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



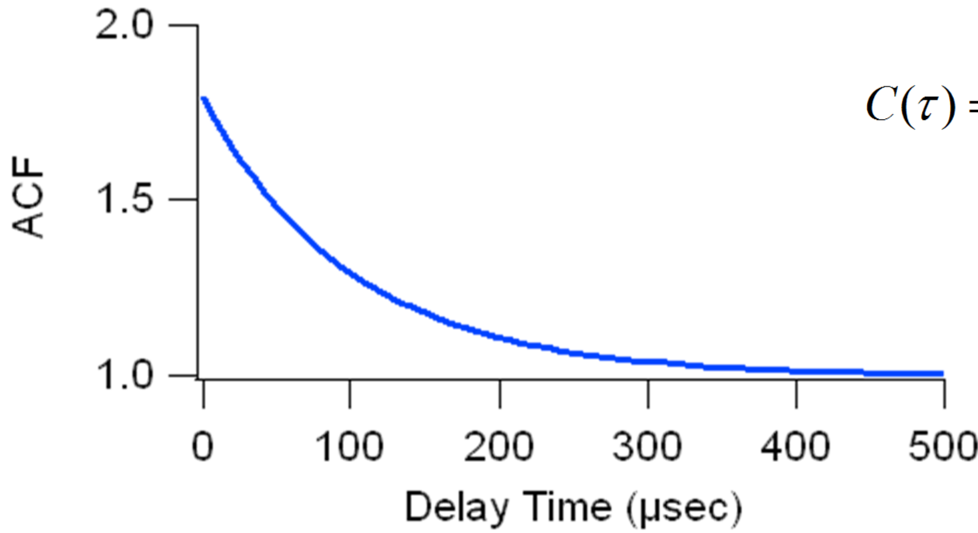
- Brownian Motion
  - Random
  - Related to Size
  - Related to viscosity
  - Related to temperature

# The SZ-100

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

# Correlation Function

- Random fluctuations are interpreted in terms of the autocorrelation function (ACF).

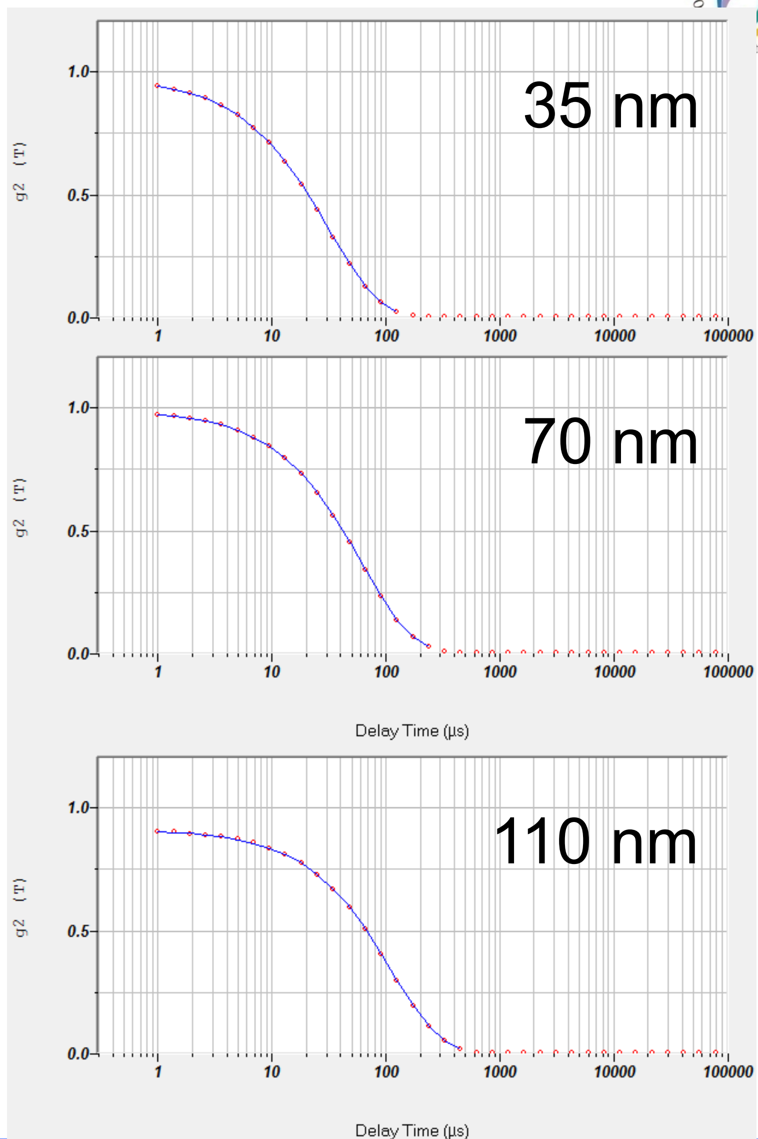



$$C(\tau) = \frac{\int_0^T I(t)I(t+\tau)dt}{\langle I(t)I(t)\rangle}$$

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

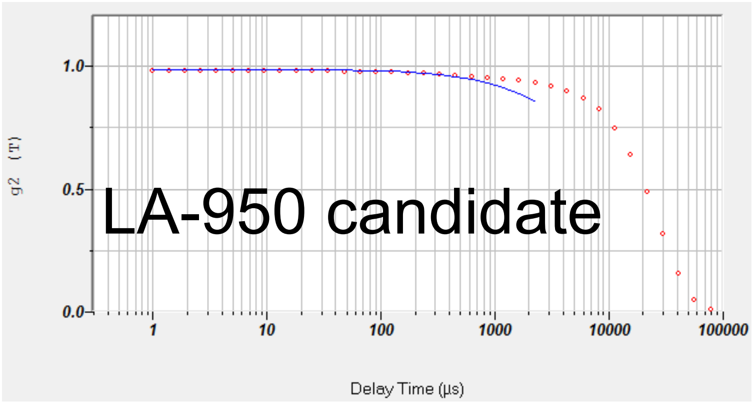
# Smooth Autocorrelation Function

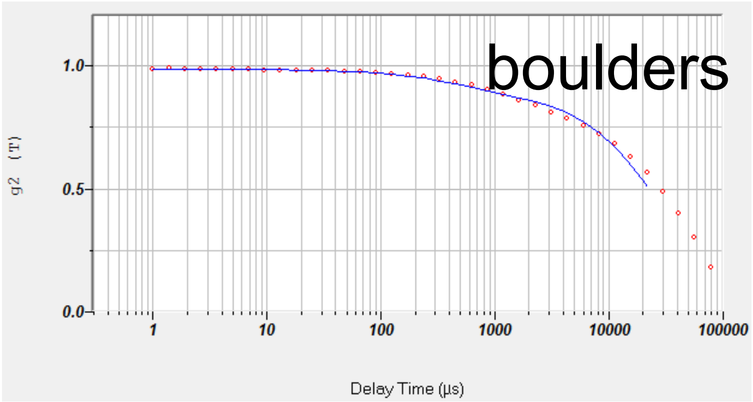
- These look good.
- As size increases, decay moves to longer times.
- Not enough data to decide if concentration is too high.



# Effect of Dust and Contamination

- These are examples of questionable data.
- Either the particle of interest is too large or there are too many large particle impurities.
- Filter samples or use software noise cut function.



# Gamma to Size

$$\Gamma = D_m q^2$$

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

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

Note effect of temperature!

$\Gamma$ decay constant
$D_t$ diffusion coefficient
q scattering vector
n refractive index
$\lambda$ wavelength
$\theta$ scattering angle
$D_h$ hydrodynamic diameter
$\eta$ viscosity
$k_B$ Boltzman's constant

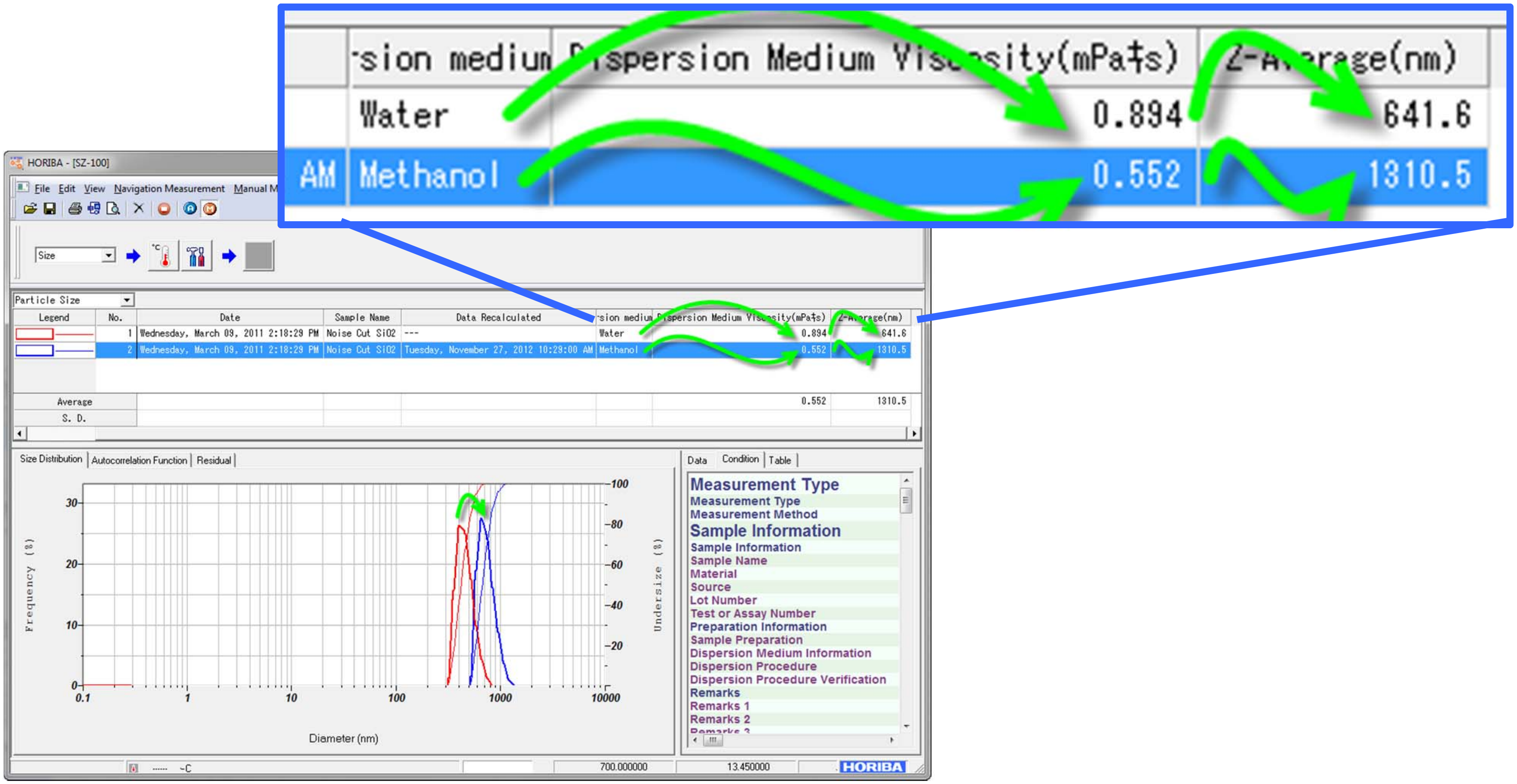
# Effect of Temperature (and trends)

| on(Sec | Z-Average(nm) | PI | Peak1 Size ( |
|---|---|---|---|
| 30 | 94.3 | 0.132 | |
| 30 | 102.5 | 0.054 | |
| 30 | 110.9 | 0.043 | |
| 30 | 109.7 | 0.014 | |
| 30 | 108.7 | 0.056 | |
| 30 | 105.2 | 0.060 | |
| 0 | 6.9 | 0.044 | |

- Look at Z-average size. Data is OK.
- Is there a trend?
- Probably sample is not to temperature and viscosity value used in calculation is incorrect.
- In this case, I set up measurement conditions to force this event.

# Viscosity

- Get your viscosity correct.
- Choose the right liquid.
- Use viscosity at temperature of measurement.



# Why Z-average?

- Numerically stable
  - Result is not overly sensitive to noise in the data.
  - Important for QC work
- Described in detail in ISO standards
  - ISO-22412:2008 as $\overline{d_{DLS}}$
  - ISO-13321:2004 as $x_{PCS}$
- It is a useful measure of size since as average size increases, so does Z-average.

# Huh? What is the Z-average?

Determined by a mathematical method known as cumulants.

# The equations

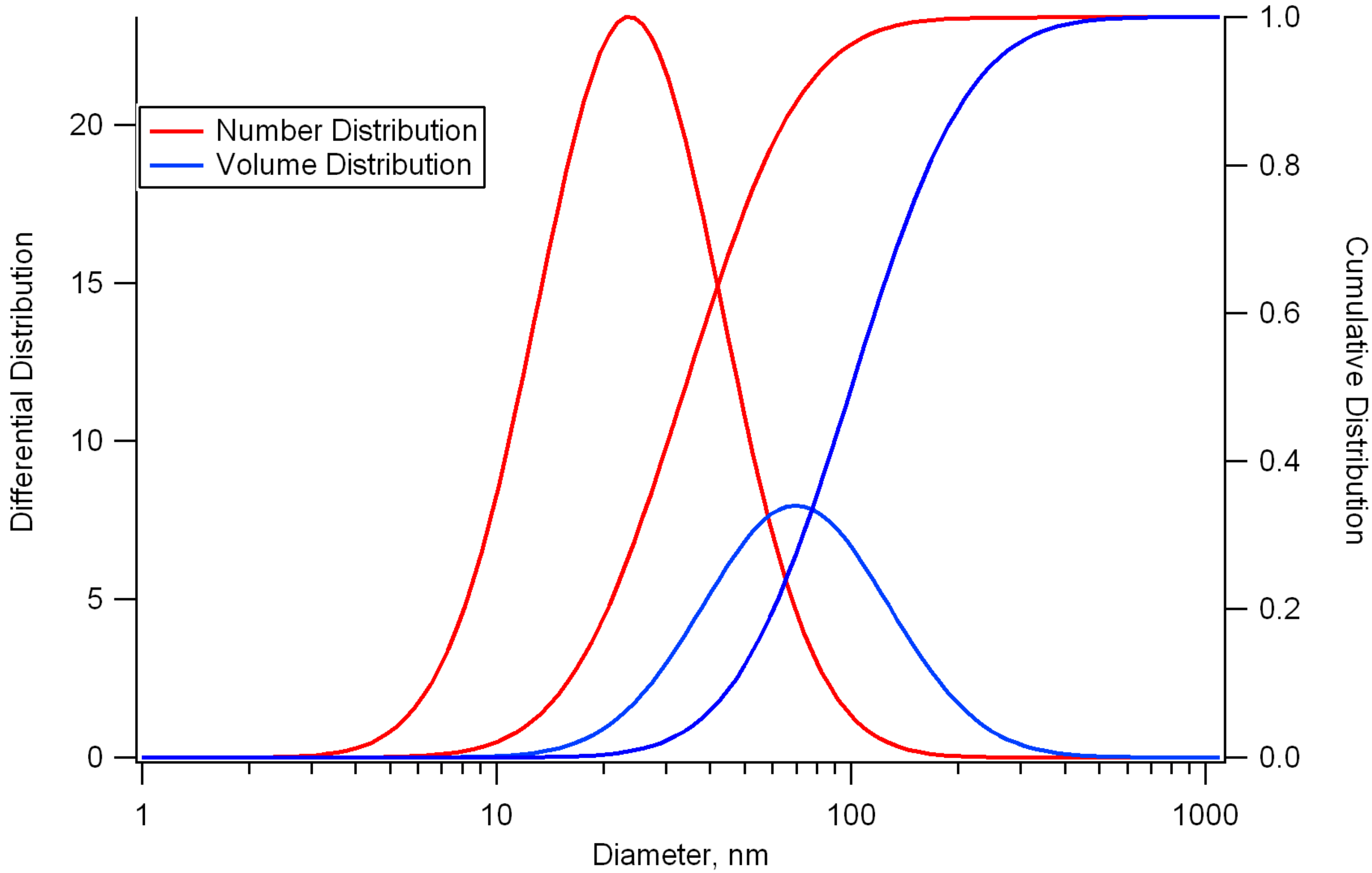
$$\frac{1}{D_z} = \frac{\sum f_i D_i^6 P(\theta) D_i^{-1}}{\sum f_i D_i^6 P(\theta)}$$

Assume small angle compared to size so P(θ)=1

$$D_z = \frac{\sum f_i D_i^6}{\sum f_i D_i^5}$$

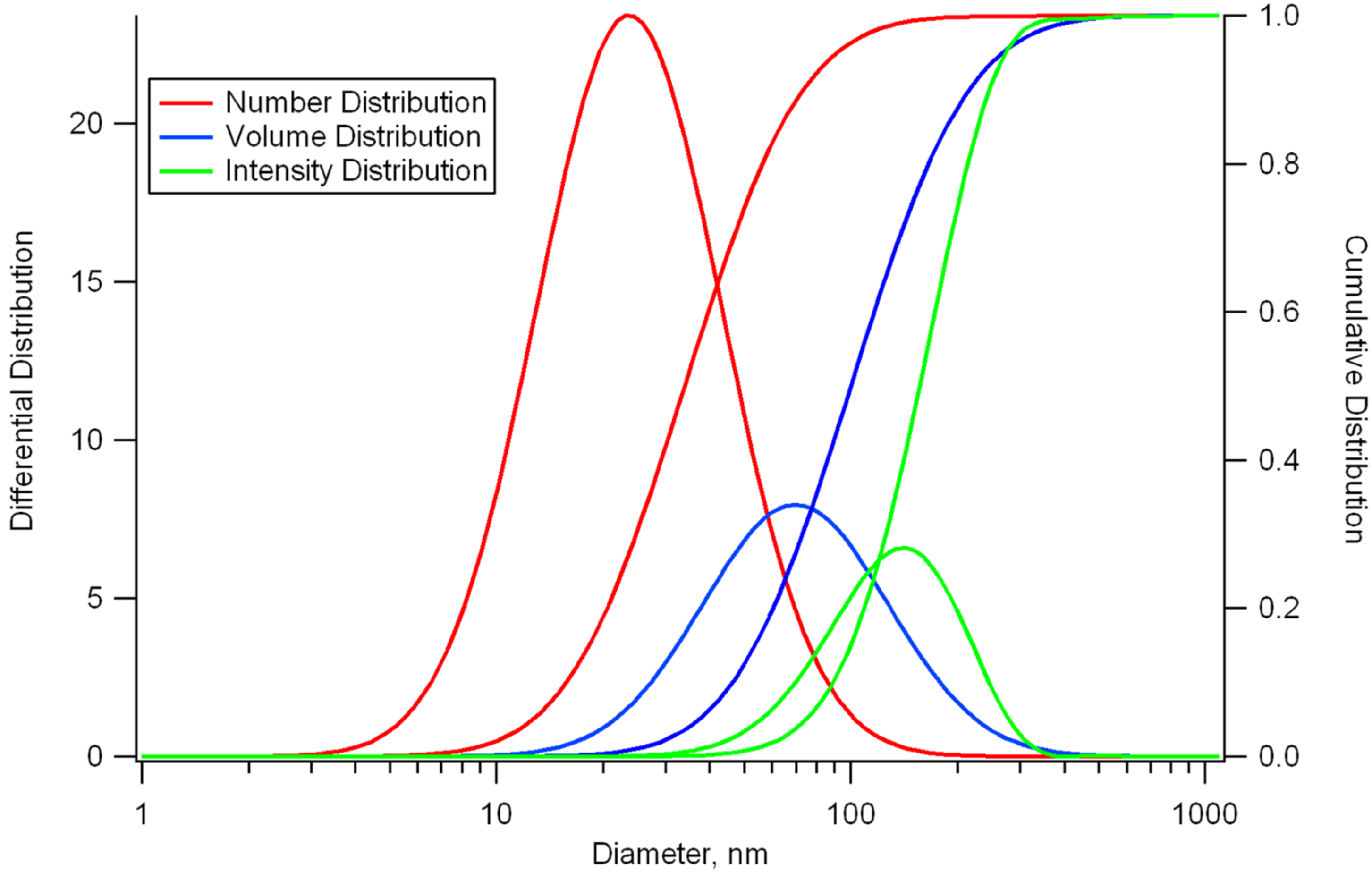
# Particle Size Distributions

- Particle size distributions can be plotted in several ways.
- Most often you see volume (mass) and number distributions



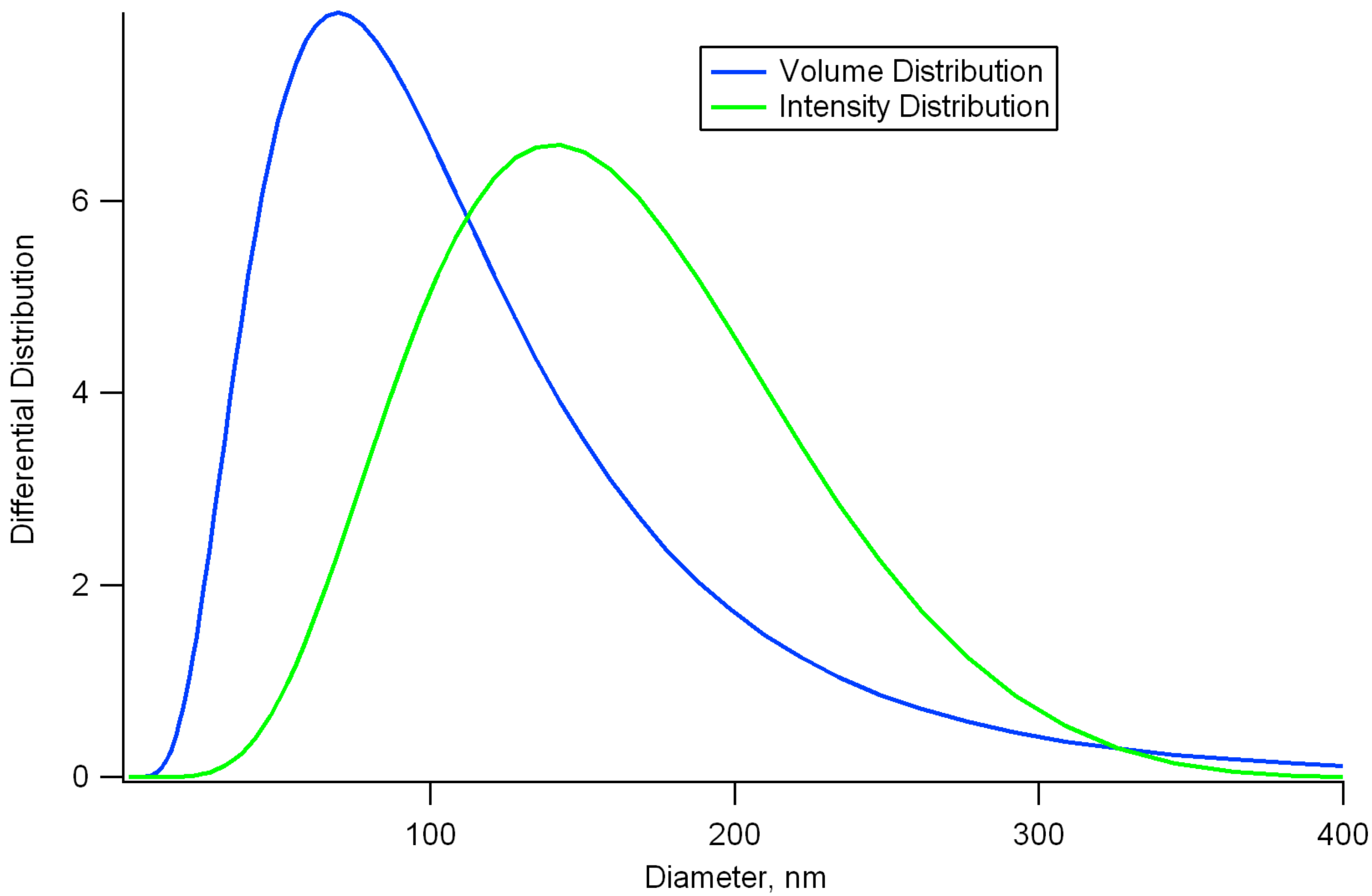
# A new distribution: Intensity

- Scattering goes by ~ $d^6$
- The exponent works for small particles. We do the full calculations.



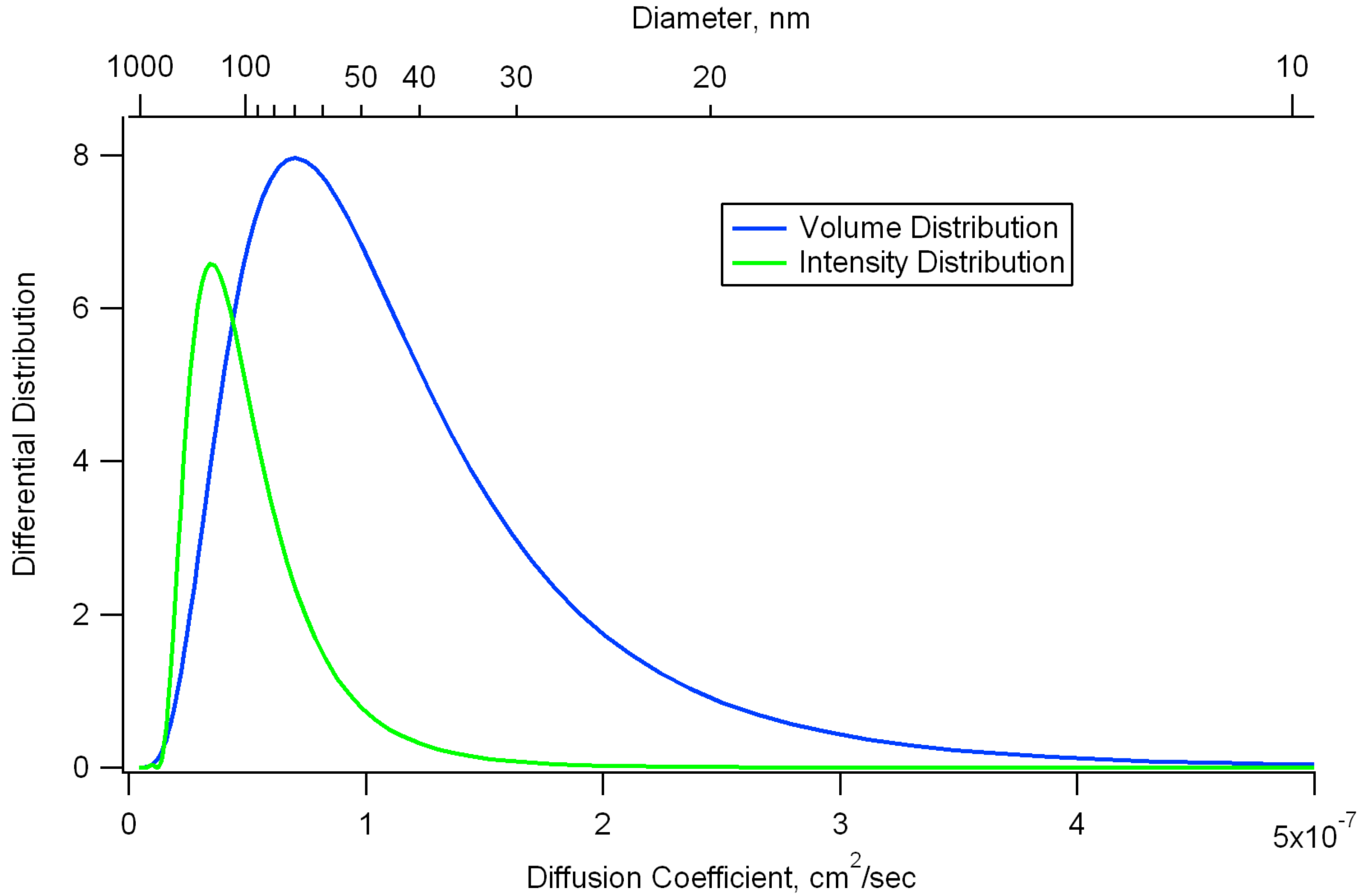
# Look at a linear scale

- These are lognormal distributions, so asymmetric.



# Need to use Diffusion Coefficient

- These are lognormal distributions, so asymmetric.



# Z-average

- As average size increases, so does Z-average.
- Tends to weight larger particles more than smaller (due to the physics of the measurement).

# Reproducibility

- PSL standards: you can get results better than 1%
- Don't expect this all the time.
- Expect 3~5%

- This is for Z-average.
  - Other average values (e.g., volume weighted mean) tend to vary more.
  - PI varies more.

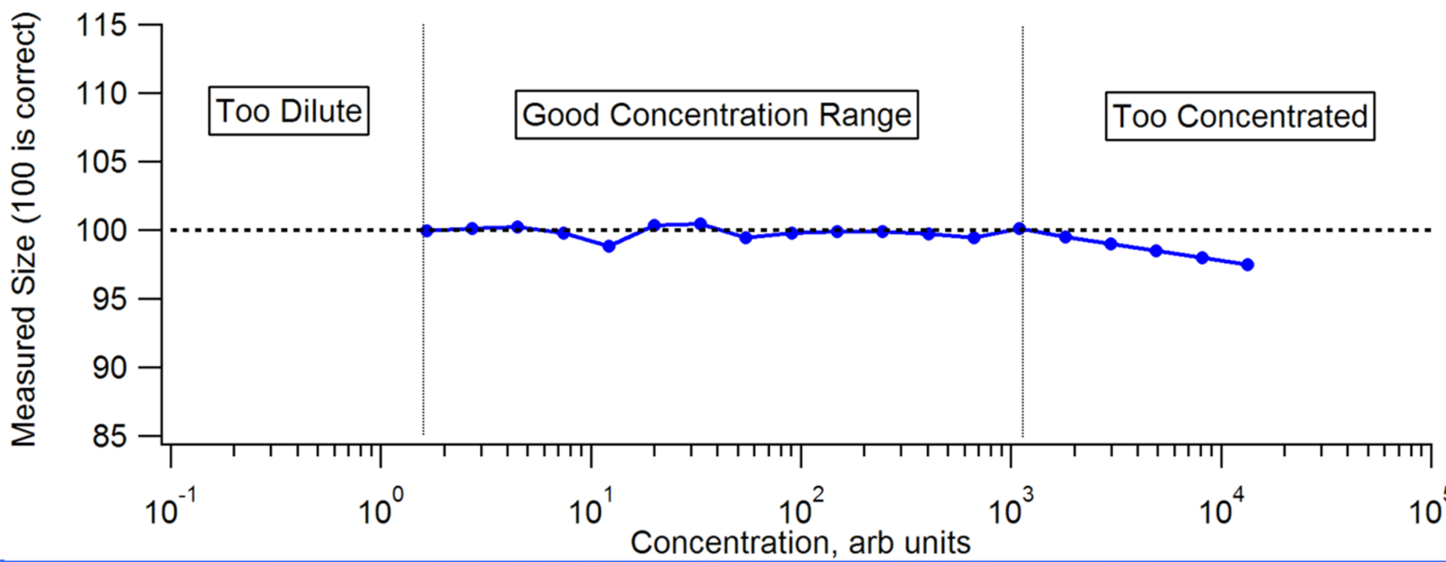
# Comparing Techniques

- Always a good idea to check your results.
- Don't expect an exact match.
- Differences of 10~20% between laser diffraction (LD) and DLS are to be expected.

| | D50 (vol. basis), nm LD | D50 (vol. basis), nm DLS | % diff in D50 (DLS/LD-1) | Z-avg. Diameter, nm DLS | % diff in size (DLS Z-avg./LD-1) |
|---|---|---|---|---|---|
| 100 nm PSL | 101 | 102.1 | 1.1 | 103.2 | 2.2 |
| 1 micron PSL | 1059 | 1039.5 | 1.8 | 1112.7 | 5.1 |
| E-1 | 129.8 | 146.6 | 12.9 | 118.3 | -8.9 |
| E-2 | 149.8 | 170.5 | 13.8 | 138.7 | -7.4 |
| E-3 | 110.0 | 100.2 | -8.9 | 112.7 | 2.5 |
| E-4 | 49.4 | 45.5 | -7.9 | 32.4 | -34.4 |
| Ludox + 0.01 M KCl | 36 | 21.2 | -41.1 | 31.8 | -11.7 |
| Coffee Creamer wet | 354 | 215.8 | -39.1 | 336.9 | -4.8 |

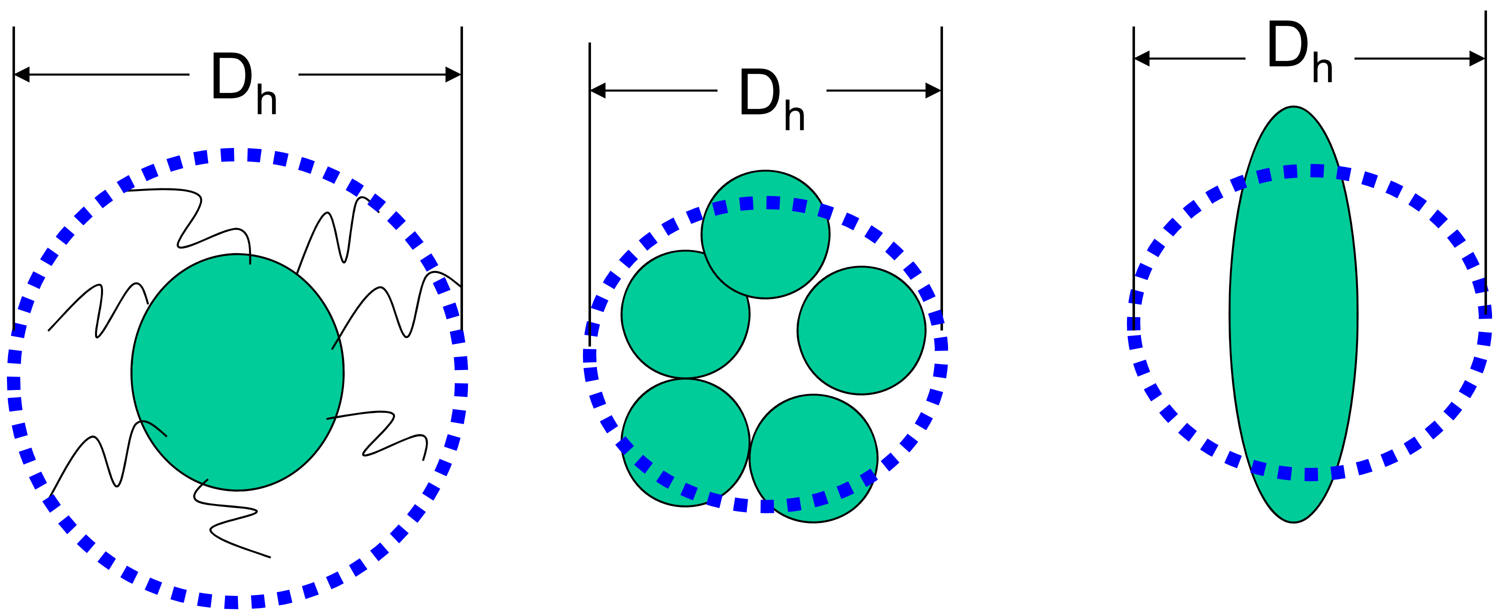
# Effect of Concentration

- Best is to make a study of measured size vs. concentration
- Note range of concentrations for which data is independent of concentration.
- Example below is “fake” data.



# What is Hydrodynamic Size?

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



# Why DLS?

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

The SZ-100 from HORIBA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# Thank you

ありがとうございました

Cảm ơn

ขอบคุณครับ

谢谢

اشكر

Gracias

Grazie

Σας ευχαριστούμε

धन्यवाद

நன்றி

Tacka dig

Danke

Merci

Obrigado

감사합니다

Большое спасибо

おもしろおかしく

Omoshiro Okashiku