DLS

Dynamic Light Scattering

🇪🇸🇲🇽 ***Dispersión Dinámica de Luz***

Important Points for Discussion

- What is DLS?
  - Explain the basic principle
  - How light interacts with nanoparticles during DLS measurements?
- Describe how DLS is used for materials and nanomaterials characterization
- What are the range of size that DLS can measure?
- What does it means, of what does indicate a DLS measurement of particles?
- Can DLS measure non-spherical particles?
- What is Z-potential?
  - What is the relation between Z potential and stability of nanoparticle suspension?

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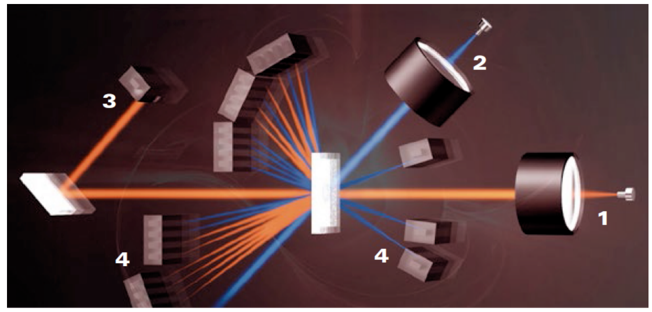
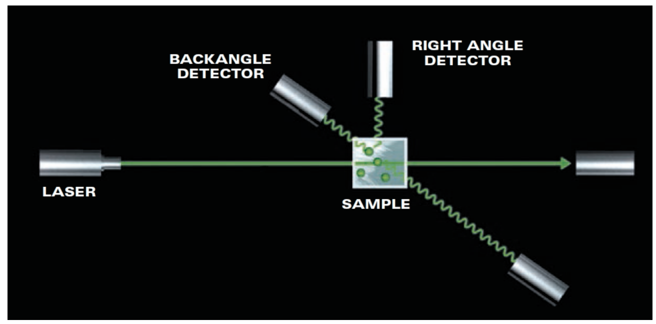
M5052 - Characterization of Materials & Nanomaterials

Light Scattering

- Static Light Scattering
  - Measure intensity (and polarization) of scattered light at different angles
    - MALS Multi-Angle Light Scattering
  - Laser light diffraction
- Dynamic Light Scattering
  - Measure variation of intensity with time at a fixed angle





Introduction to Dynamic Light Scattering

https://youtu.be/ET6S03GeMKE

Applications of Light Scattering in Nanomaterials

- Particle size and size distribution
  - Emulsions, latexes, sols, polymers, nanoparticles, powdered materials
- Growth kinetics
  - Changes in particle size due to aggregation, coalescence
  - Growth of polymer chains in emulsion polymerization
- MALS provides an *absolute measurement* of molar mass of macromolecules
  - Measurement is dependent on fundamental physical characteristics
  - Also provides information on size and shape of scattering particles
- Measurement of second virial coefficient
  - A key characteristic of the strength of attractive or repulsive interactions between particles
  - Obtained by measuring intensity of light scattering as function of concentration

Limitations of Light Scattering Techniques

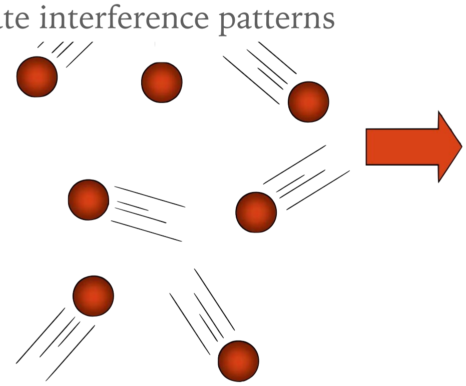
- DLS can only measure particles up to a few μm in size
- Lower size limit ~1 nm
- Static Light Scattering can not measure sizes below tens of nm
- Particles must be in a stable dispersion
- If liquid causes aggregation results will be inaccurate
- Inter-particle interactions can affect results
- DLS can not be used for solutions with large concentrations
- Variant of light scattering techniques can be used for dispersions where multiple scattering events will be a problem for DLS
  - E.g. Diffusion Wave Spectroscopy
- Size measurements by DLS are an average size, estimated for spherical particles
- In a mixture of particles with two sizes they have to be different by a factor of 3 to be distinguished by DLS (low resolution)

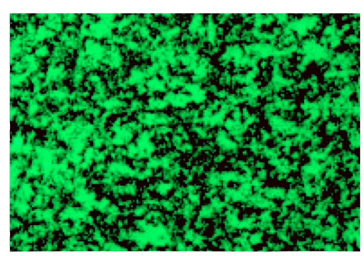
Dynamic Light Scattering

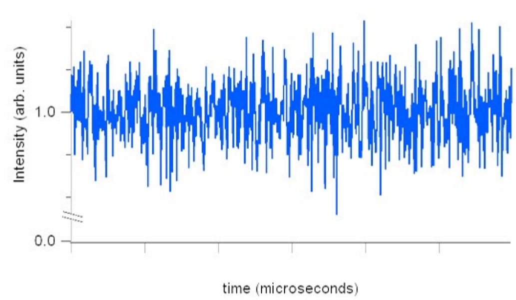
- **QELS=PCS=DLS**
- QELS: Quasi-Elastic Light Scattering
  - Differences in energies of incident and scattered photons are small
- PCS: Photon Correlation Spectroscopy
  - The instrument calculates an autocorrelation function from the variations in time intensity of light due to diffusion of particles moving due to Brownian motion
- **DLS: Dynamic Light Scattering**
  - The technique relies on the motion (dynamics) of the scattering particles
  - Particles in the path of the laser beam will scatter light
- Their position and size change the intensity of scattered light
  - Technically, each scattering particle experiences a slightly different electric field from the incident light and thus changes the phase of the scattered wavelets, the different distances between particle and detector also result in phase changes. The electric field at the detector is a superposition of the fields of all scattered wavelets. After a short time the particles have diffused and the electric field at the detector changes in response
- Particles are moving constantly due to Brownian motion
- Small particles diffuse rapidly: intensity fluctuations are faster
  - For larger particles and aggregates fluctuations are slower

DLS Measurement Principles

- Particles behave like diffraction slits, their different relative orientations generate interference patterns
- Interference generates a "speckle" pattern







- Various points have different intensities due to different interference
  - Measure intensity fluctuations vs. time for a specific spot
  - Rate of fluctuation is related to movement

Images modified from "Dynamic Light Scattering" Tutorial. Downloaded from: http://mmrc.caltech.edu/PD_Expert/Expert.html

DLS Measurement Principles

- Intensity of one speckle (a point in a detector) changes in time
  - Changes are in time frames of miliseconds
    - Times required for movement in the order of the wavelength of light due to Brownian motion

- Correlation Function of Intensity $\boldsymbol{G_2(\tau)}$
  - Due to nature of photodetection the product of number of photons at given times (intensity) is a measure of the correlation funtion

$$G_2(\tau) = \frac{1}{T}\int_o^T I(t)I(t+\tau)d\tau$$

- Correlation Function of Electric Field, $\boldsymbol{G_1(\tau)}$
  - Electric field decays as a function of time with a decay constant Γ

$$G_2(\tau) \approx \frac{1}{N}\sum_{i=1}^{N_{\text{large}}} I(t_i)I(t_i+\tau)$$

DLS Measurement Principles

- For Brownian motion the relationship of $\boldsymbol{G_1}$ and $\boldsymbol{\Gamma}$ is exponential

$$G_1(\tau) = \frac{1}{T}\int_o^T E(t)E(t+\tau)d\tau$$

- $\boldsymbol{\Gamma}$ is related to diffusivity, $\boldsymbol{D}$ (diffusion coefficient, D), and distance travelled by a particle, $\boldsymbol{q}$ (scattering vector)
  - $\boldsymbol{n}$, refractive index; $\boldsymbol{\lambda}$ wavelength of laser; $\boldsymbol{\theta}$ scattering angle

$$G_1(\tau) = e^{-\Gamma\tau} \qquad \Gamma = -Dq^2$$

- The Diffusivity is related to the radius of a particle, $\boldsymbol{r}$
  - $\boldsymbol{k_B}$, Boltzmann's constant; $\boldsymbol{T}$, temperature; $\boldsymbol{\mu}$, viscosity (also represented as η)

$$q = \frac{4\pi n}{\lambda}\sin\frac{\theta}{2} \qquad \boxed{D = \frac{k_B T}{6\pi\mu r}}$$

- NOTE: these equations assume monodisperse spherical particles

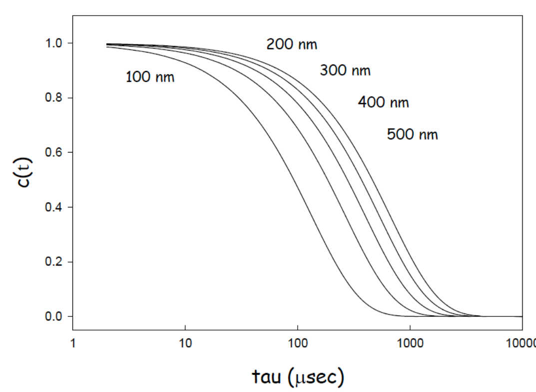
Dynamic Light Scattering

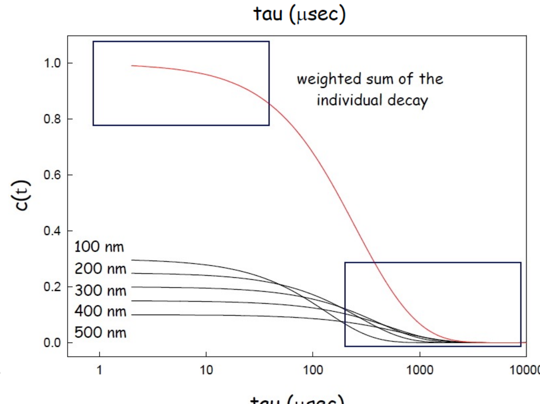
$$D_h = 2R_h^{app} = \frac{k_B T}{3\pi\eta D_t}$$

- Measures average particle size
  - Effective Hydrodynamic Diameter
  - Apparent Hydrodynamic Radius
    - k_B, Boltzmann's constant; T, temperature; η, viscosity; D_t, translational Diffusion coefficient
  - Hydrodynamic radius is not "real" size for non-spherical particles
  - Hydrodynamic Radius represents the size of a sphere that diffuses at the same rate as the actual particle
  - Relation between hydrodynamic radius and diffusion coefficient of spherical particles is given by the Stokes-Einstein equation
- Solution must be dilute
  - Solutes can increase viscosity which would reduce diffusivity and the apparent hydrodynamic radius
  - Single scattering assumption: each photon is scattered only by interaction with a single particle, multiple scattering events are not considered in the model
- Can provide distribution of particle sizes
  - Correlation function equations become more complicated when polydispersity is taken into account

Polydisperse Particles and Measured Correlation Functions

- Measured correlation function is an *intensity weighted* average of the individual particles
- Large particles (slower diffusion) have longer decay times
- Small particles (faster diffusion) have shorter decay times
- Consider an idealized case with specific fractions of specific particle sizes
  - 0.30 of 100 nm particles
  - 0.25 of 200 nm particles
  - 0.20 of 300 nm particles
  - 0.15 of 400 nm particles
  - 0.10 of 500 nm particles
- The actual measured correlation function shows the contributions of all fractions
  - At short times the correlation emphasizes the sum of all intensities
  - At long times the contribution of larger particles is emphasized





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Size Distributions from DLS

- Mathematical methods have been developed to extract size distributions from correlation functions
- Direct fit: a type of distribution is assumed and the actual correlation is compared to the one predicted from the assumed particle size distribution
- Cumulants method: calculates the moments (or cumulants) of the distribution by expanding the correlation function into an exponential series
  - Does not require a priori assumptions

$$C = \exp(-2\overline{\Gamma}\tau + \mu_2\tau^2 - \cdots)$$

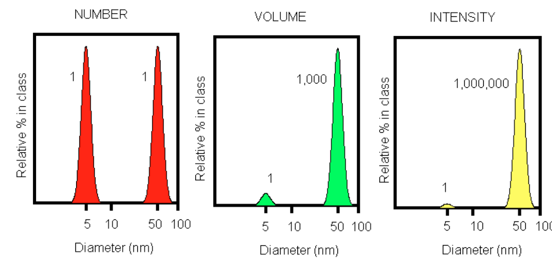
  - The second moment (μ_2) represents the standard deviation of the particle size
  - The size given by this method is the "z-average size"
    - It represents the intensity weighted harmonic mean size
- Regularization algorithms
  - CONTIN (constrained regularization program for inverting noisy linear algebraic and integral equations)
  - Non-Negative Least Squares (NNLS)
  - DLS equipment manufacturers may include proprietary algorithms in their software

Size Distributions from DLS

- Size distribution is an *intensity size-distribution*
- Plot of relative intensities of light scattered by particle of various size ranges
- It can be converted to a *volume size-distribution*
  - Distribution of sizes based on how much volume of each particle of a certain size contributes to the total volume occupied by all particles
  - Mie scattering theory is used to convert intensity distribution to volume distribution
    - Mie theory relates scattering angle, and particle size to scattering intensity

Size Distributions from DLS

- Consider equal *numbers* of 5 nm and 50 nm particles
  - Number size distribution is 1:1
- Volume (proportional to r^3): size distribution in a ratio 1:1000
- Intensity (proportional to r^6) shows a 1:1000000 ratio for those particles



Bimodal distribution examples taken from: "Dynamic Light Scattering: An Introduction in 30 Minutes" Technical Note MRK656-01, ©Malvern Instruments Ltd.. Downloaded April 2013 from http://www.malvern.com/labeng/technology/dynamic_light_scattering/dynamic_light_scattering.htm
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Bean examples in next page taken from "A Guidebook to Particle Size Analysis", Horiba Instruments Inc. ©2012, . Downloaded April 2013 from:
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Number, Volume and Intensity – Size Distributions

- *NOTE: Number size distribution* is not as useful in particle size characterization
  - Distribution of sizes based on how many particles of a certain size there are, as fraction of the total number of particles

- Equal number (13) of beans of three sizes…

- Equal volumes of the same beans of three sizes…

… occupy very different volumes

… correspond to very different numbers of beans

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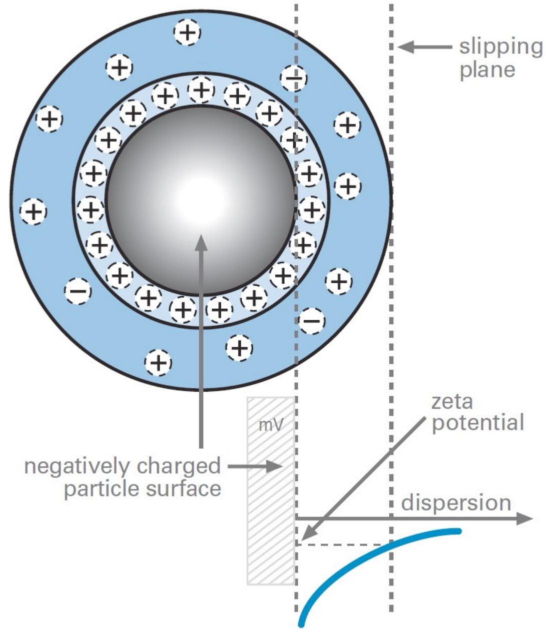
ZETA POTENTIAL

- Zeta-potential (ζ) measures surface charge for particles in a specific liquid medium
  - Charged particles are surrounded by an ionic double layer (nearer ion layer attached to particle; a diffuse layer away from surface)
  - Slipping plane: boundary between electric double layer and ions in equilibrium in the solution
  - Zeta potential is the potential (mV) at the slipping plane
    - Particle suspensions are usually stable if $|\zeta| >$ 25-30 mV
    - Isoelectric Point: when zeta potential is zero (usually colloidal suspensions at this point are the least stable)



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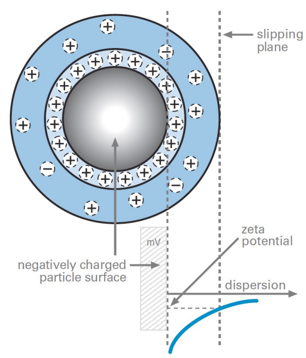
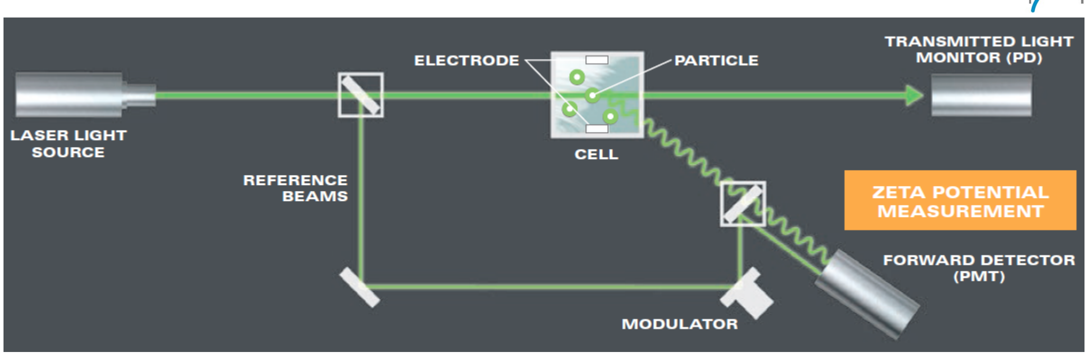
MEASURING ZETA POTENTIAL

- Zeta-potential (ζ) can be measured in a DLS if an electric field is applied to the sample
  - Direction of motion depends on type of charge
  - Speed of particles depends on magnitude of charge
- Measured by using reference beam to measure frequency shift of scattered light
  - Doppler Velocimetry





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Z Potential

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