



**Malvern
Panalytical**

Zetasizer Nano User Training

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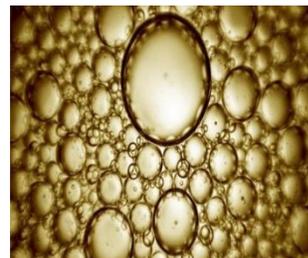
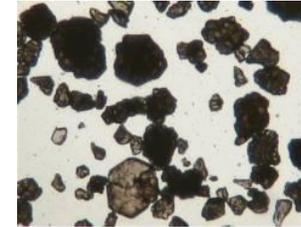




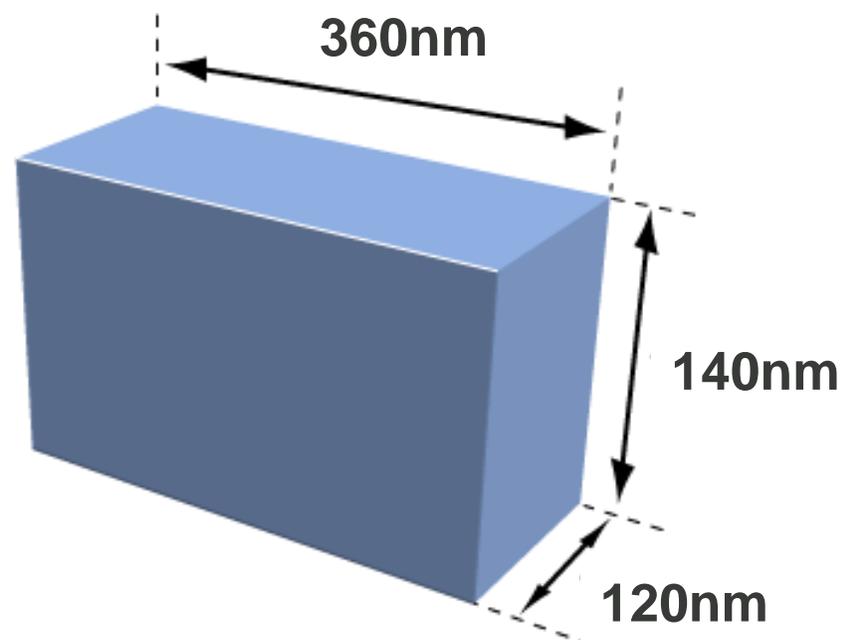
Basic concepts and theory of DLS

Particle

- A very general definition of a “**particle**” ...
“Any condensed-phase tri-dimensional discontinuity in a dispersed system may generally be considered a particle...”
(NIST, US Department of Commerce, Special Publication 960-3)
- This covers:
 - Solids in air or a liquid medium
 - Droplets in air or in a liquid medium
 - Gas bubbles in a liquid medium



Particle size

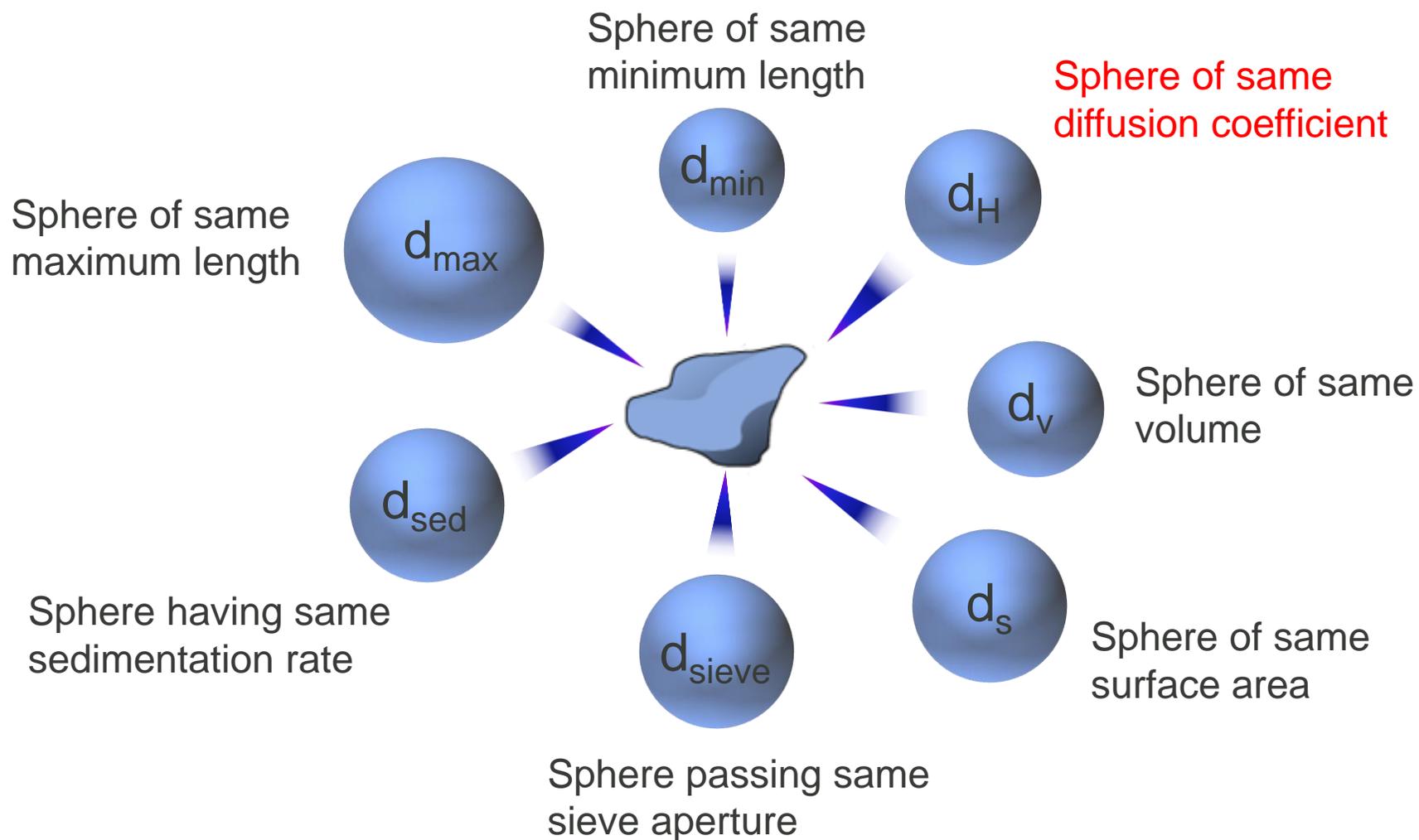


You may reply: “360x140x120nm”

Which might be correct *but it is not one number.*

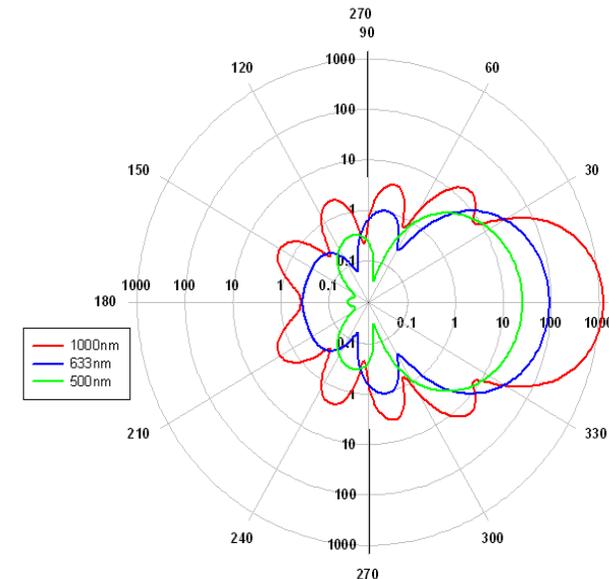
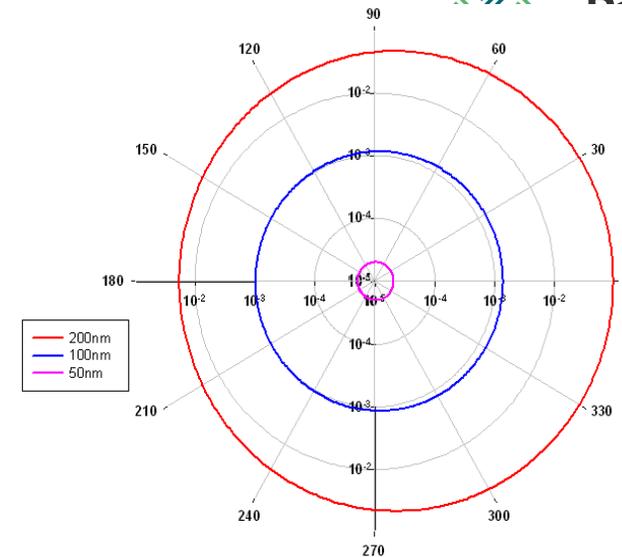
It is not possible to describe the 3-dimensional object with a single number

Particle size - Equivalent spheres



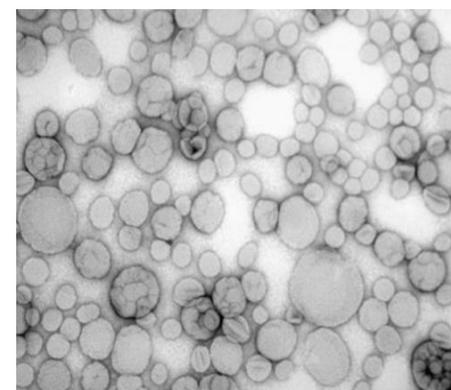
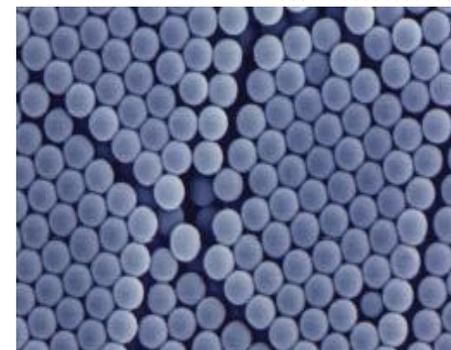
Light scattering - Rayleigh & Mie theory

- Rayleigh theory
 - small particles ($1/10^{\text{th}}$ of λ)
 - isotropic (equal in all directions)
 - intensity is proportional to d^6
- Mie theory
 - spherical particles of all sizes & optical properties
 - larger than $1/10^{\text{th}}$
 - : isotropic to a distortion in the forward
 - equivalent to or greater than λ
 - : complex function with angle
 - convert intensity PSD into vol. & num. PSD



DLS technique

- Very sensitive to the presence of aggregates, contaminants, or any other large species
- Minimal sample preparation
- Fast measurements - a few sec. to min.
- Suitable samples for DLS
 - Ideal : spherical mono-disperse (<100nm)
 - Excellent : colloidal metal particles, fine emulsions, proteins, etc
 - Good : any non-sedimenting particle under a few microns with a Pdl <0.5
- Technique limitations
 - large particles : filtration or centrifugation needed
 - particle shape : non-spherical particles (e.g. CNT)



ISO standards

INTERNATIONAL
STANDARD

**ISO
13321**

First edition
1996-07-01

**Particle size analysis Photon correlation
spectroscopy**

- **ISO 13321**

- a few nm to about $1\ \mu\text{m}$,
or onset of sedimentation
- dilute dispersions

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**ISO
22412**

First edition
2008-05-01

**Particle size analysis — Dynamic light
scattering (DLS)**

- › **ISO 22412**

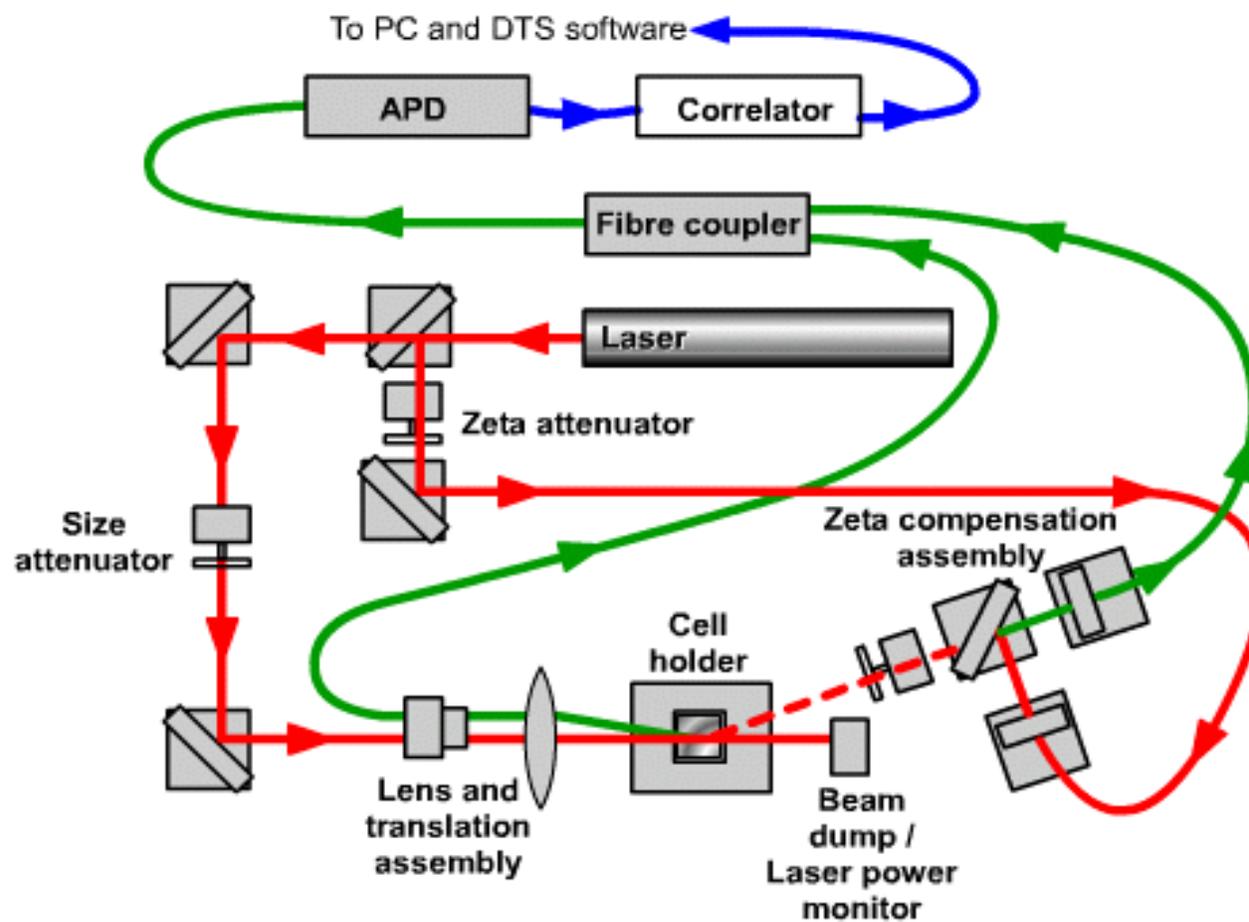
- sub μm particles or emulsions
- dilute & conc. suspensions

Zetasizer Nano, Pro and Ultra



- Particle Size
 - Dynamic Light Scattering
- Concentration
 - Multi angle Dynamic Light Scattering
- Zeta Potential
 - Electrophoresis
- Absolute Molecular Weight
 - Static Light Scattering
- Microrheology
 - DLS & MSD

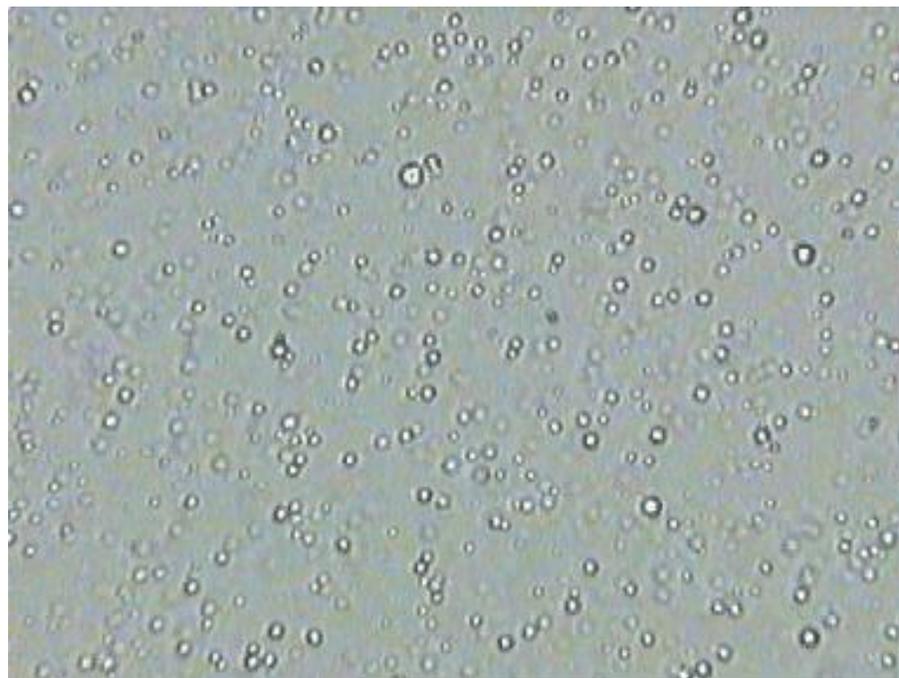
Optical configuration : Nano Pro&ultra



DLS & Brownian motion



- **D**ynamic **L**ight **S**cattering or **P**hoton **C**orrelation **S**pectroscopy measures **B**rownian motion and relates it to size
- **B**rownian motion : random movement of particles due to the bombardment by the solvent molecules that surround them



Brownian motion



- Temperature must be accurately known because we need to know the viscosity
- The larger the particle the more slowly the Brownian motion will be
- Higher the temperature the more rapid the Brownian motion will be
- Velocity of the Brownian motion is defined by the translational diffusion coefficient (D)

$$D(h) = \frac{kT}{3 \pi \eta D}$$

where

D(h) = hydrodynamic diameter

k = Boltzmann's constant

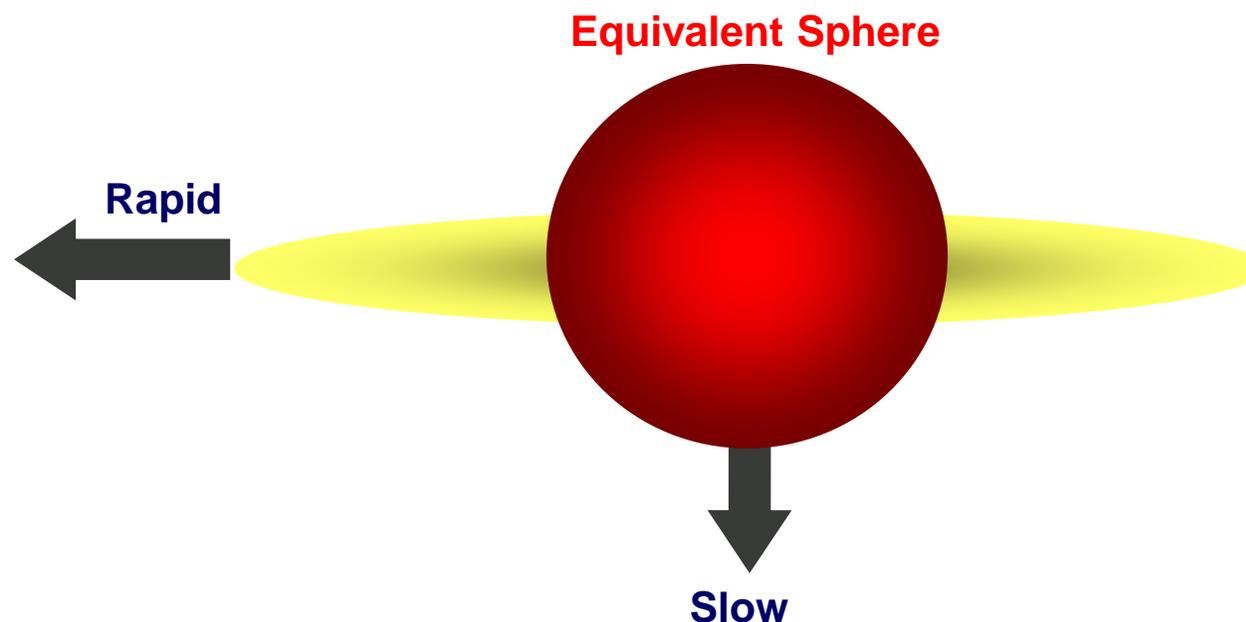
T = absolute temperature

η = viscosity

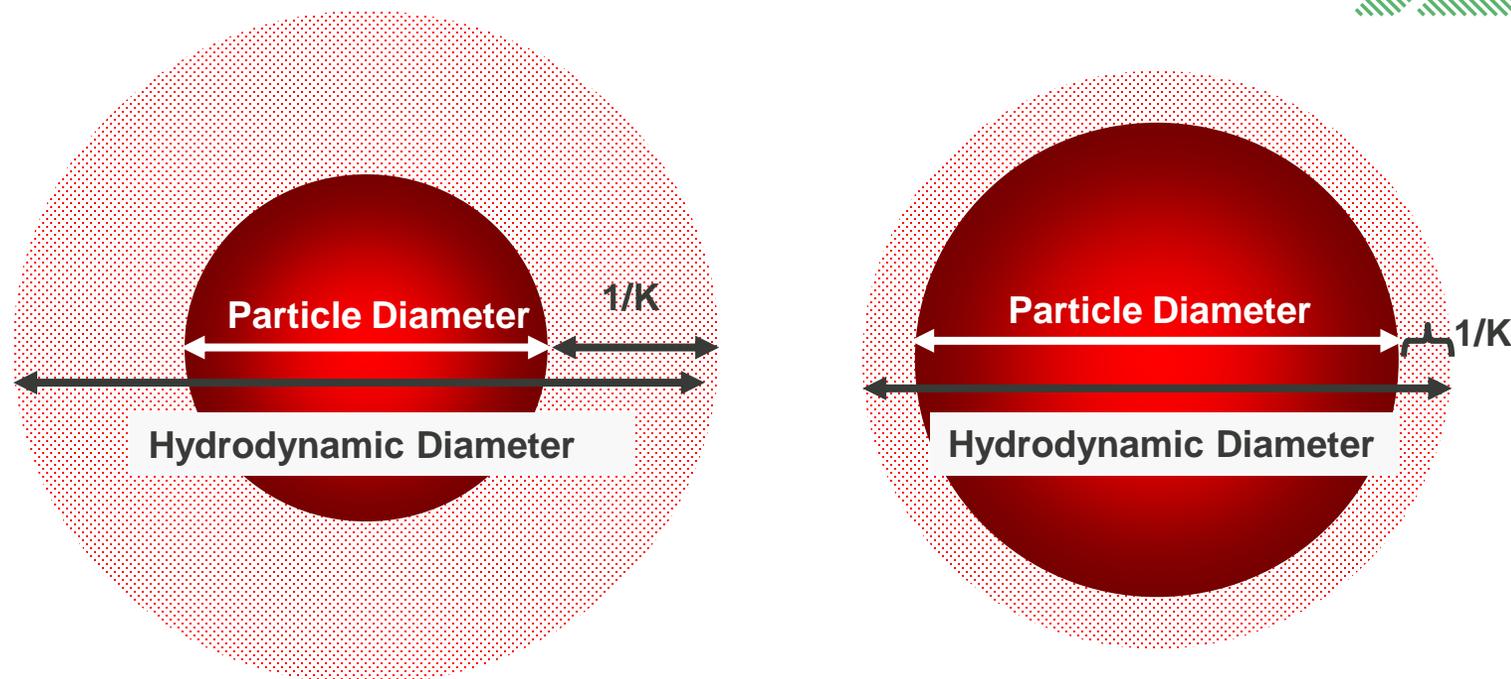
D = diffusion coefficient

Hydrodynamic diameter

- The diameter which is measured in DLS is a value that refers to how a particle moves within a liquid
- The hydrodynamic diameter reported will be based upon the sphere which has the same average diffusion coefficient as that of the particles



Hydrodynamic diameter : Ionic strength

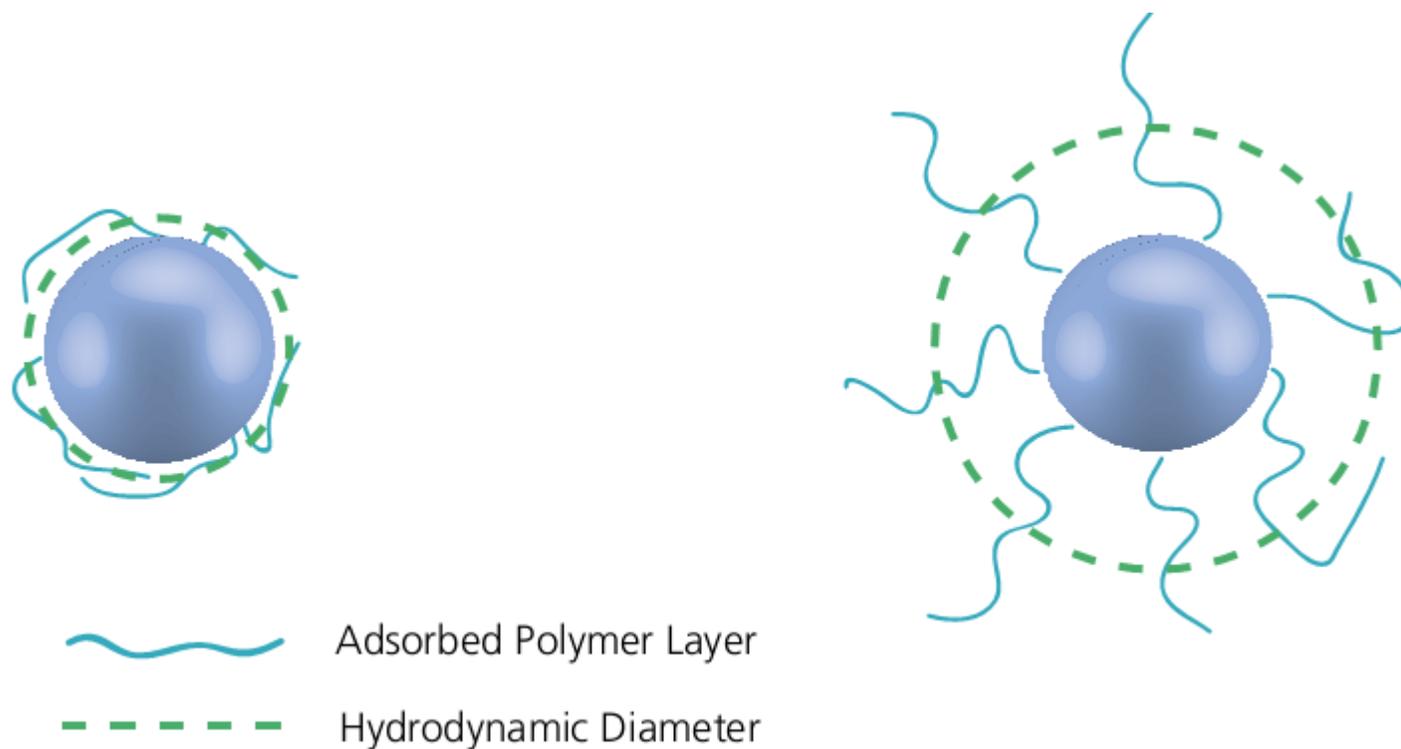


- $1/K$ (Debye Length) : the thickness of the electrical double layer
- It is dependent upon the ionic strength of the medium
- In low ionic strength media (DI water) the double layer is extended
- Latex standards should be diluted in 10mM NaCl to suppress the double layer and hence give the correct result (ISO13321)

Hydrodynamic diameter : Surface structure



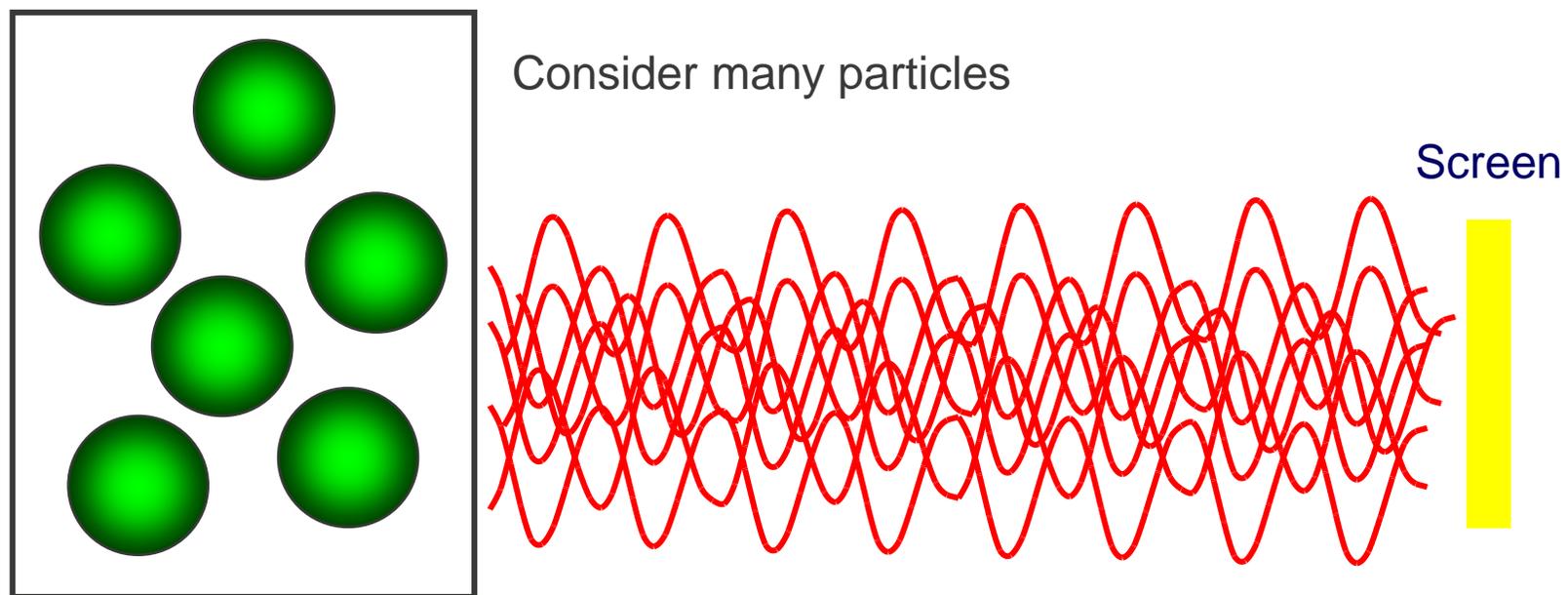
- A layer of molecules on the particle surface will slow the diffusion speed down
- The hydrodynamic diameter will therefore be influenced



How does a DLS experiment work ?

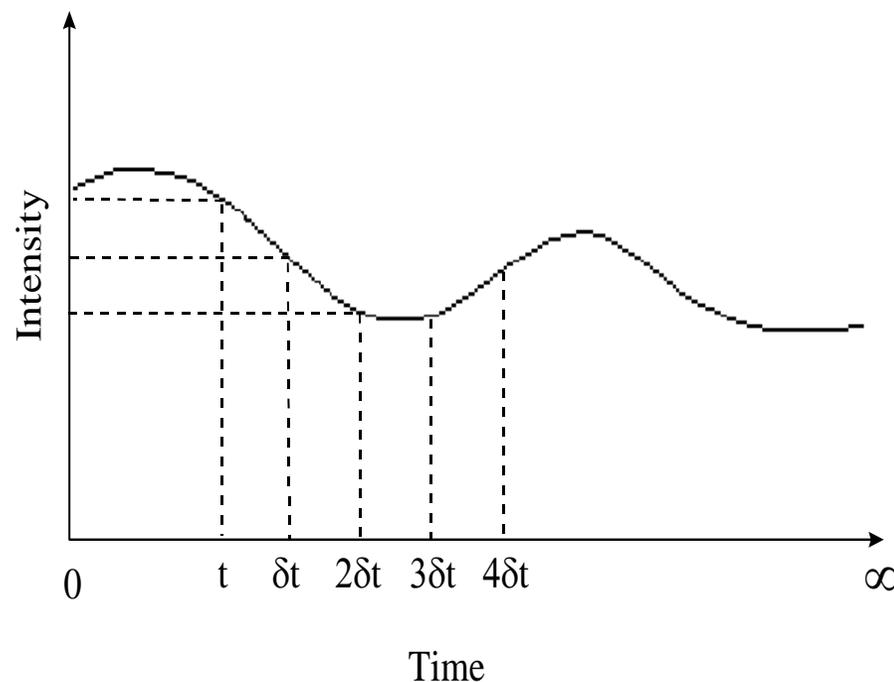
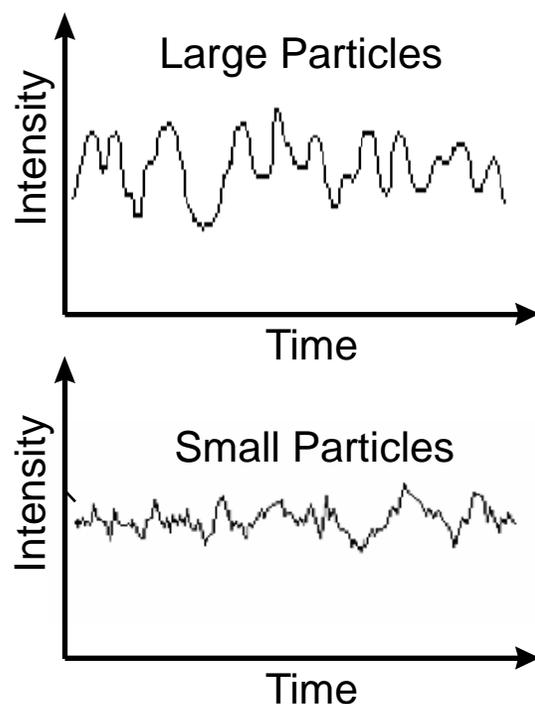


- › In DLS, the intensity fluctuations of scattered light arising from Brownian motion are measured



Many scattered beams interfere with one another resulting in a very complex intensity pattern of 'speckles'

Intensity fluctuations and correlation



- If the particles are large, the signal will be changing slowly and the correlation will persist for a long time
- If the particles are small and moving rapidly then the correlation will disappear more rapidly

Analysing the correlation function



- The correlation function contains the diffusion coefficient information required to be entered into the Stokes-Einstein equation
- These diffusion coefficients are obtained by fitting the correlation function with a suitable algorithm
- Two methods of analysis are used
 - *Cumulants analysis*
 - Determines a mean size and polydispersity index
 - *Distribution analysis*
 - Determines actual size distribution from suitable data

Cumulants analysis

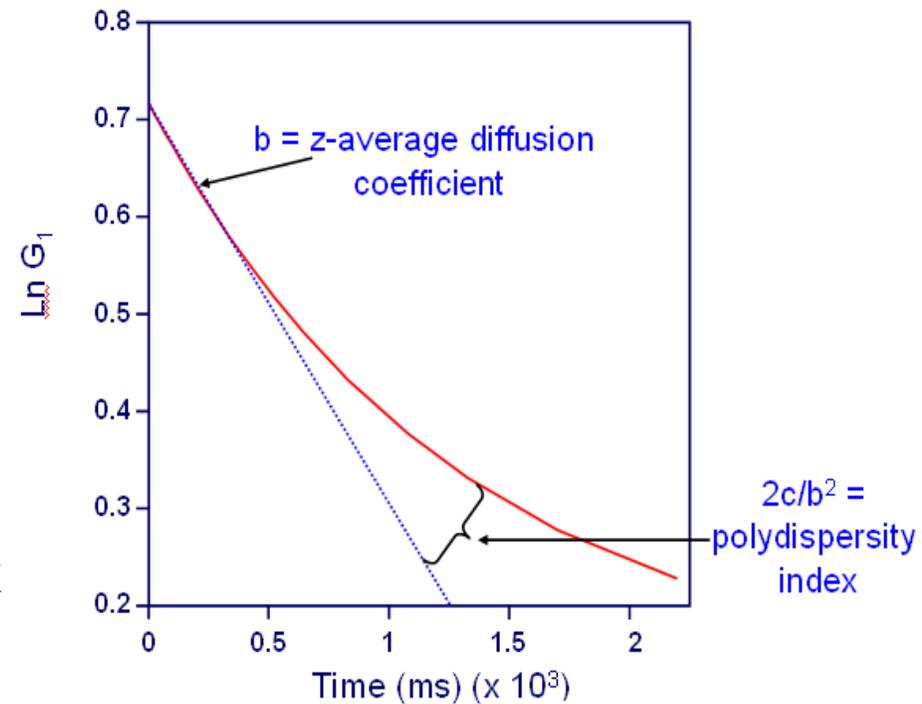
- ISO13321 states that a 3rd order fit of a polynomial should be used
- This analysis only gives a mean particle size (z-average) and an estimate of the width of the distribution (polydispersity index)

$$\text{Ln}[G_1] = a + b\tau + c\tau^2$$

where,

τ is the delay time of the correlator

- › $b = z\text{-average diffusion coefficient (Initial slope)}$
- › $2c/b^2 = \text{polydispersity index (Curvature away from the initial slope)}$



Distribution analysis



- Default algorithms present in the Zetasizer software for calculating the size distribution are:

General Purpose (non-negative least squares, NNLS)

: suitable for the majority of samples where no knowledge of the distribution is available

Multiple Narrow Modes (NNLS)

: suitable for samples suspected to contain discrete populations

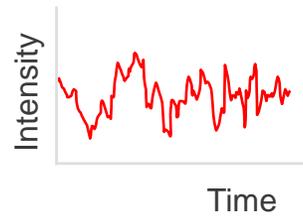
Protein Analysis (L-curve)

: suitable for protein samples (give narrow peaks)

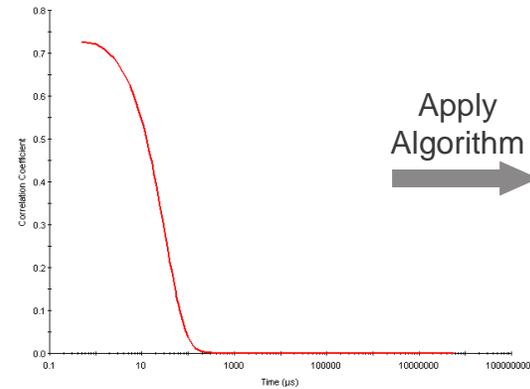
Intensity fluctuations (Correlation & particle size)



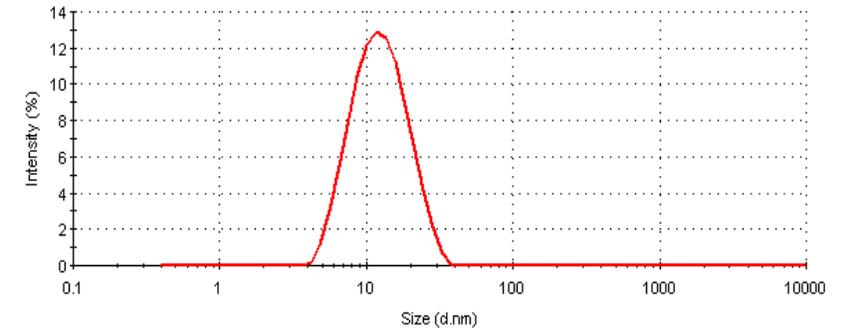
Small particles



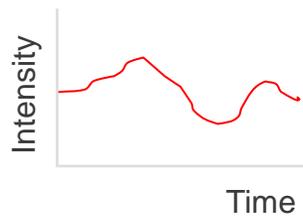
Correlate →



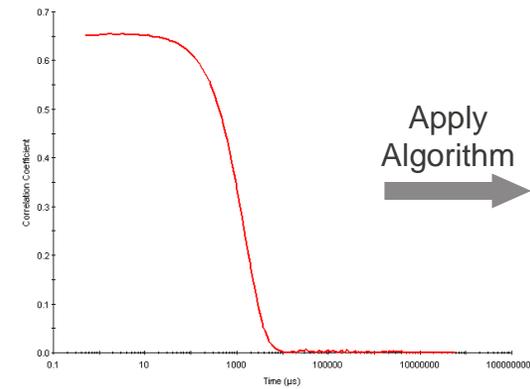
Apply Algorithm →



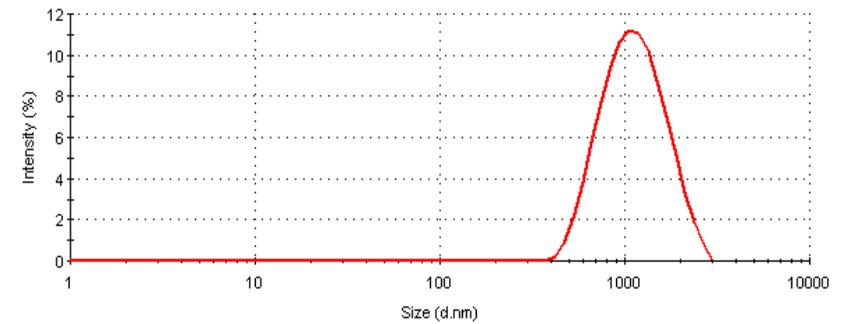
Large particles



Correlate →



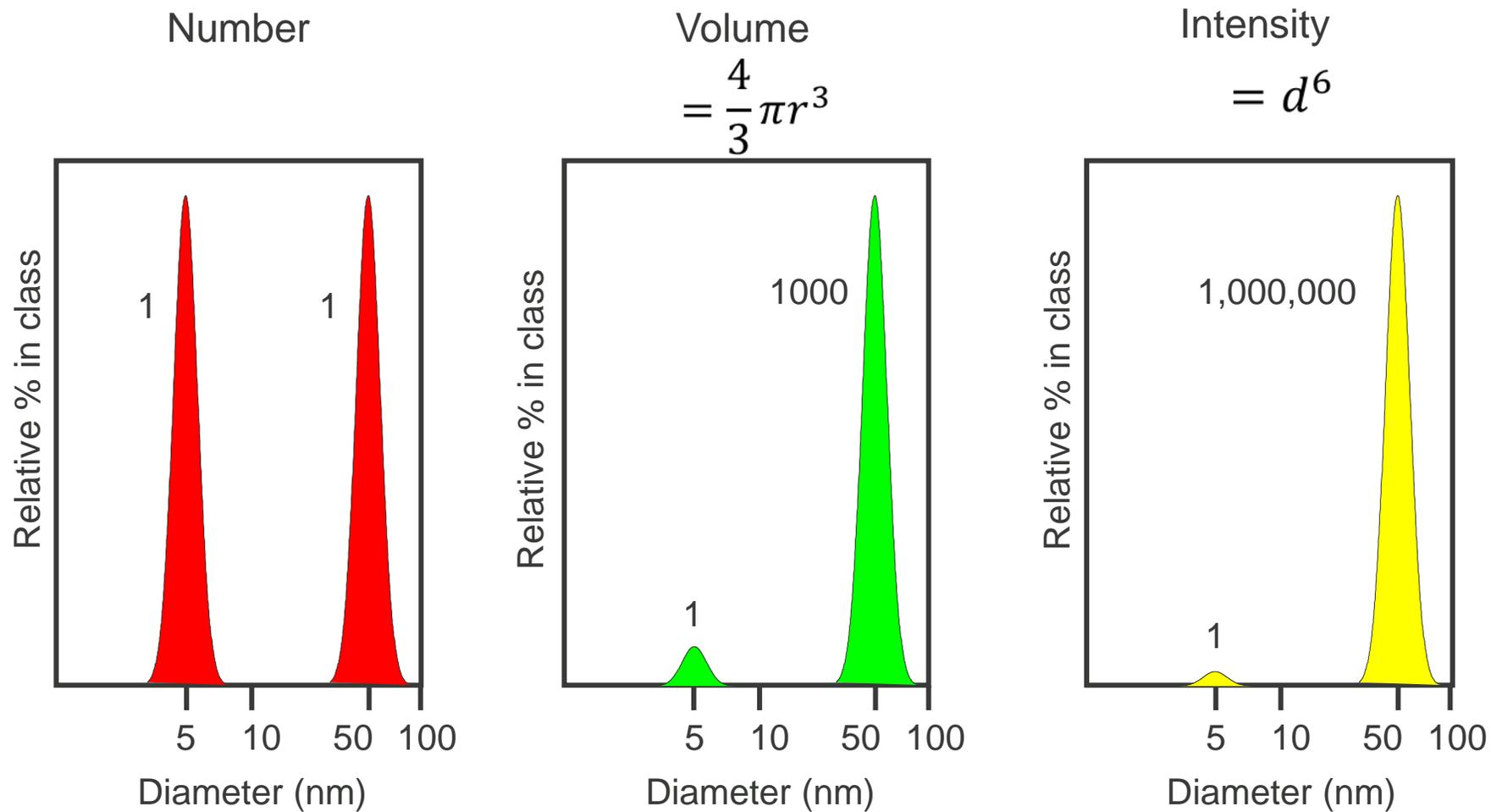
Apply Algorithm →



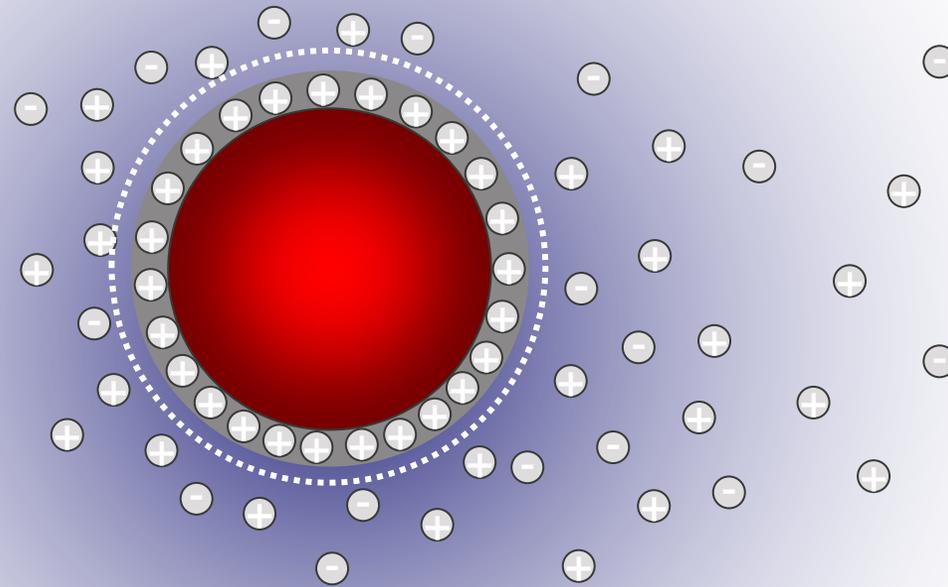
Intensity, volume and number distributions



Mixture containing equal numbers of 5nm and 50nm spherical particles



Colloidal system and Zetapotential

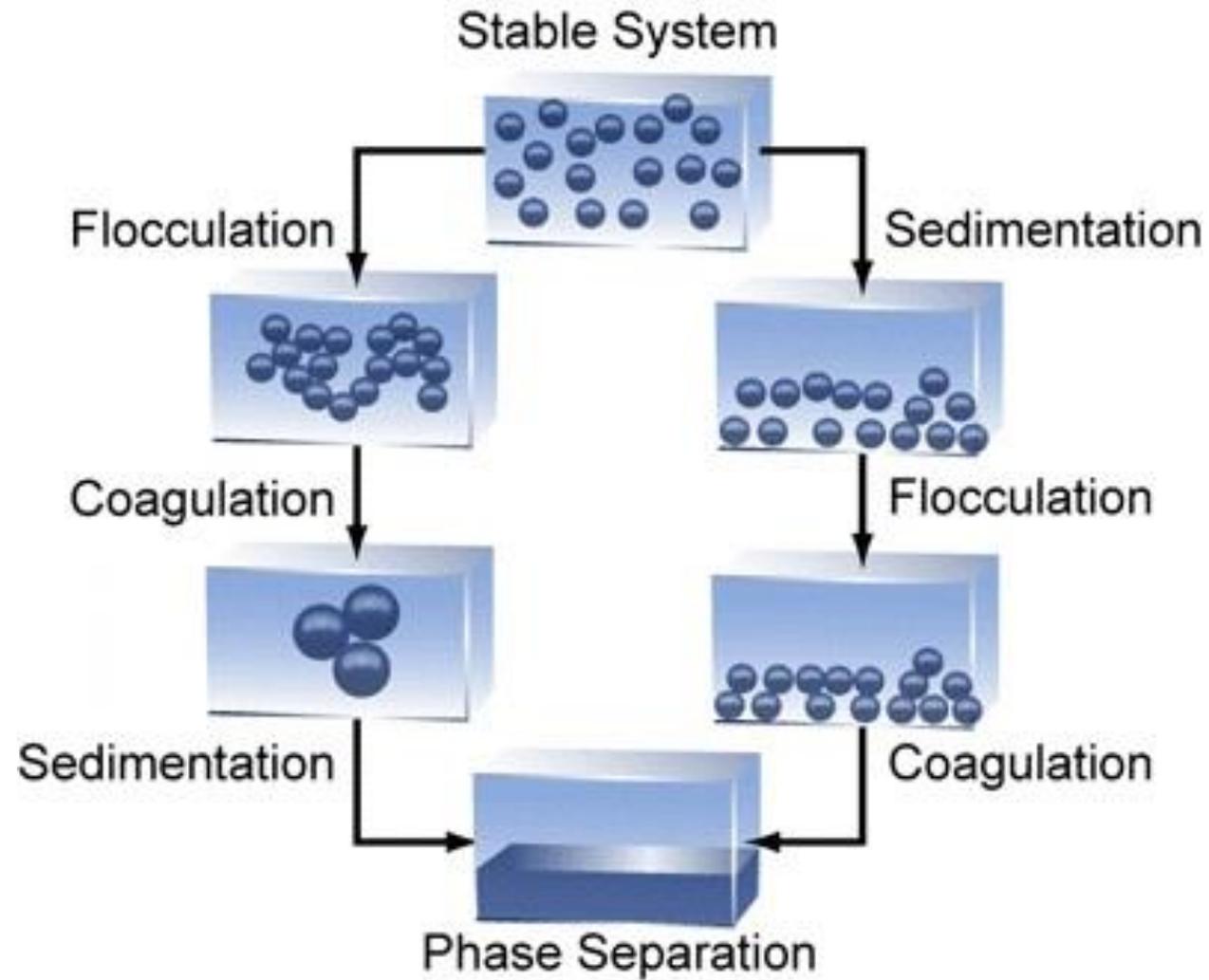


Colloidal system



- Three states of matter - gas, liquid and solid
- If one of these states is finely dispersed in another then we have a **Colloidal system**
- Examples of colloidal systems
 - Aerosols : fine liquid droplets or solid particles in a gas
(e.g. fogs, smokes)
 - Emulsions : fine droplets of fat in an aqueous phase (e.g. milk)
 - Inverse Emulsions : aqueous phase in a non aqueous phase
(e.g. crude oil)
 - Colloidal Suspensions : fine solid particles in a liquid medium
(e.g. paints, muds, slurries)

Colloidal instability



Colloidal stability : DVLO theory

- Derjaguin, Verwey, Landau and Overbeek developed a theory describing colloidal stability
- DVLO theory suggests that the stability of a particle in solution is dependent upon its total potential energy function V_T
- V_T is the balance of several competing contributions:

$$V_T = V_A + V_R + V_S$$

$$V_A = -A/(12\pi D^2)$$

A = Hamaker constant
D = particle separation

$$V_R = 2 \pi \varepsilon a \zeta^2 \exp(-\kappa D)$$

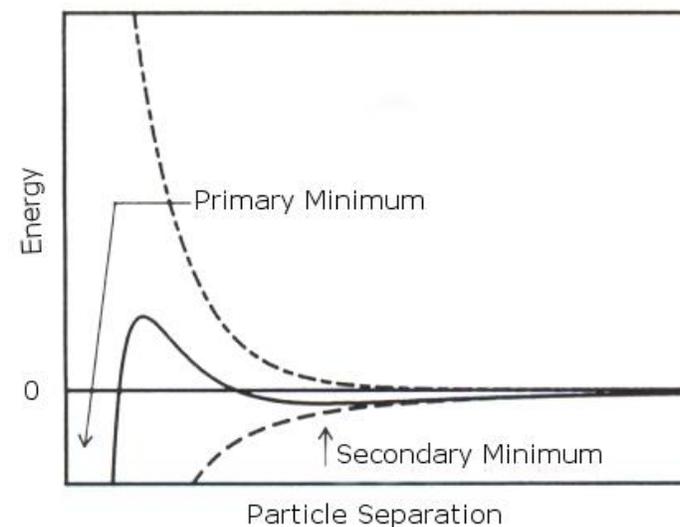
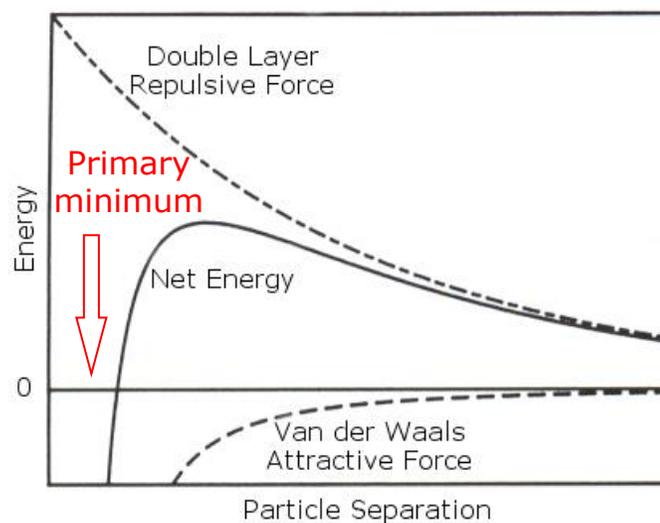
a = particle radius
 ε = solvent permeability
 κ = Debye length
 ζ = zeta potential

V_S = potential energy due to the solvent
(negligible contribution)

Colloidal stability : DVLO theory



- An energy barrier resulting from the repulsive force prevents two particles approaching one another and adhering together
- In certain situations (e.g. in high salt concentrations), there is a possibility of a “secondary minimum” where a much weaker and potentially reversible adhesion between particles exists together



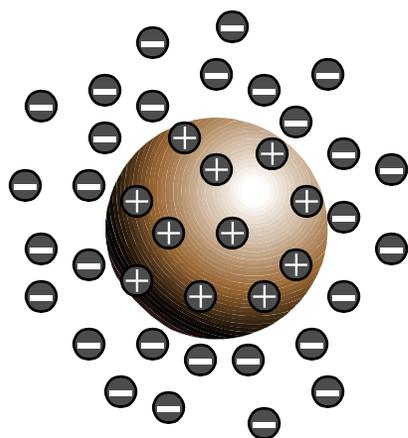
Maintaining dispersion stability



- To maintain dispersion stability, the repulsive forces must be dominant
- Two fundamental mechanisms that affect dispersion stability:

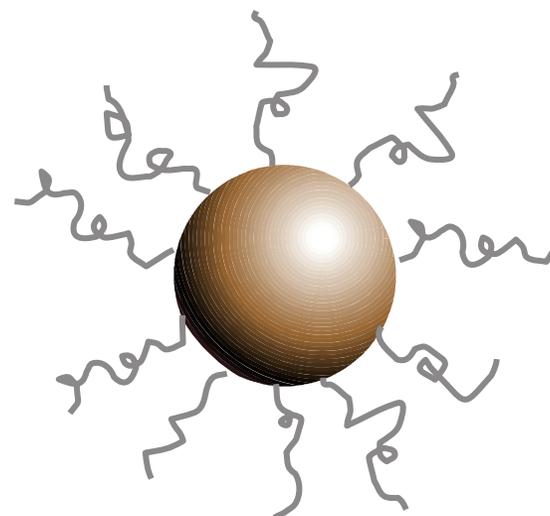
Electrostatic

- › Easy to measure the controlling parameter (zeta potential)
- › Reversible
- › May only require change in pH or ion concentration



Steric

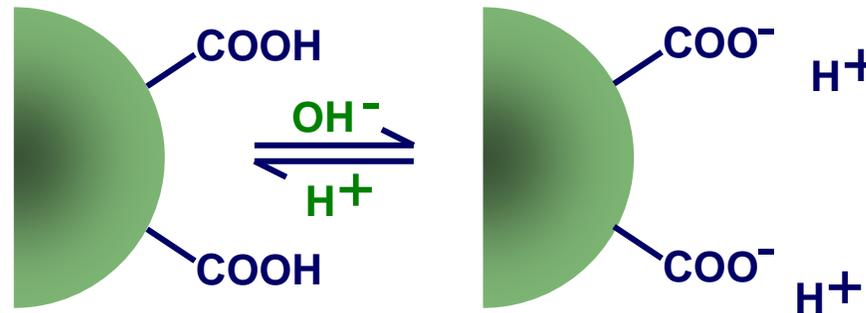
- › Simple, but limited options
- › Irreversible
- › An extra component



Origins of surface charge in aqueous media



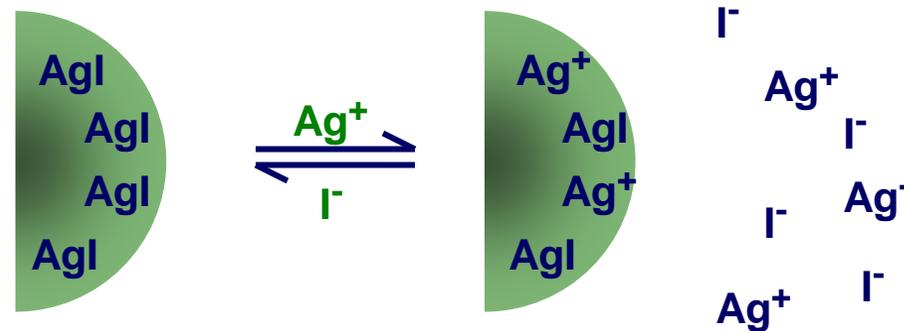
- Many origins depending upon the nature of the particle and surrounding medium
 - *Ionisation of surface groups*



Origins of surface charge in aqueous media



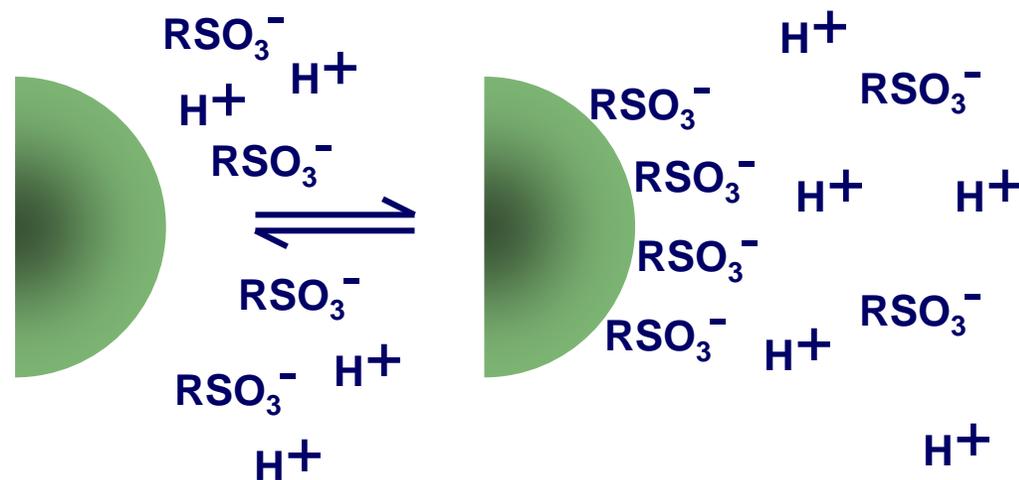
- Many origins depending upon the nature of the particle and surrounding medium
 - *Ionisation of surface groups*
 - *Preferential loss of ions from the particle surface*



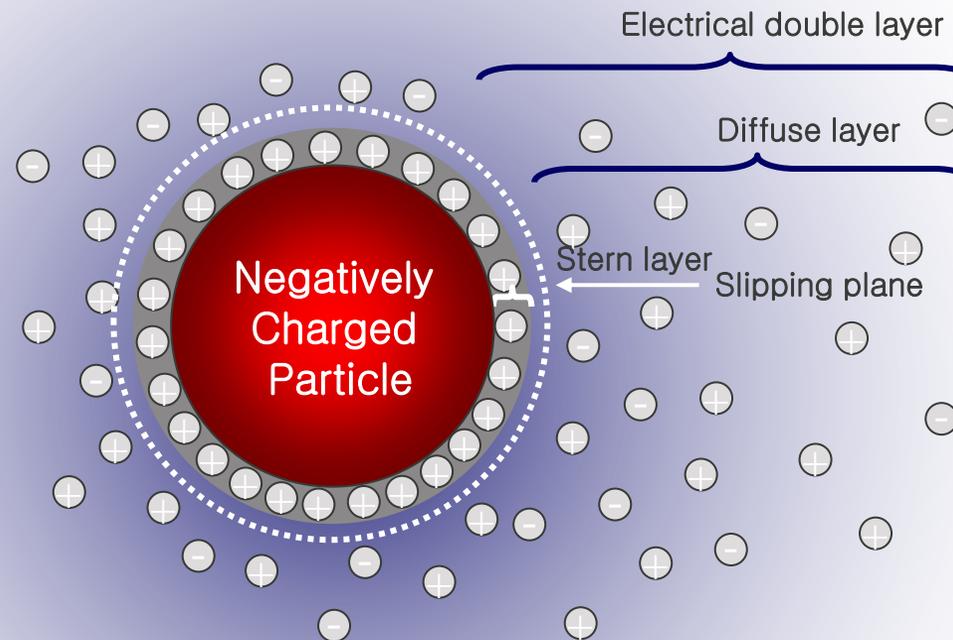
Origins of surface charge in aqueous media



- Many origins depending upon the nature of the particle and surrounding medium
 - *Ionisation of surface groups*
 - *Preferential loss of ions from the particle surface*
 - *Adsorption of ions/ionic molecules*

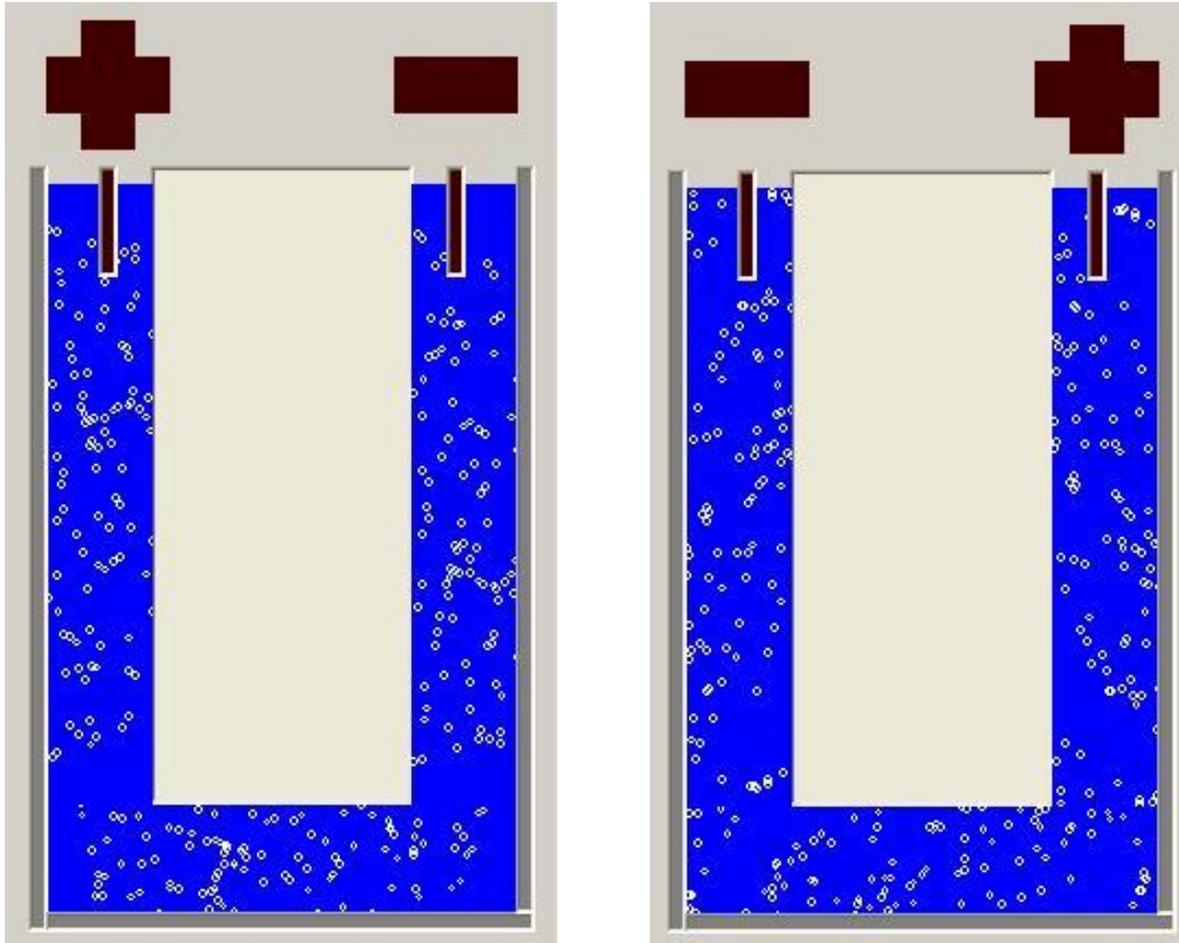


Zeta potential in aqueous media



Zeta Potential = Electrical potential at the slipping plane
(Charge a particle acquires in a particular medium)

Measuring zeta potential : electrophoresis



Folded Capillary Cell.exe



Measuring zeta potential : Henry equation



- If an electric field is applied across a sample in a capillary cell, charged particles suspended in the medium are attracted towards the electrode of opposite charge
- Zeta potential is related to the **electrophoretic mobility** by the **Henry equation**

$$U_E = \frac{2 \varepsilon z f(k a)}{3 \eta}$$

U_E = electrophoretic mobility

z = zeta potential

ε = dielectric constant

η = viscosity

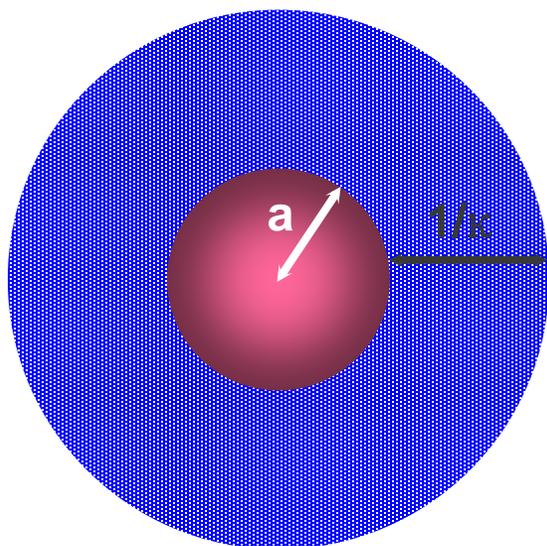
$f(k a)$ = Henrys function

Henry's Function $F(\kappa a)$



- κ = electrical double layer thickness (Debye length, κ^{-1} or $1/\kappa$)
- a = the particle radius
- $\kappa a = 1/\kappa \times a$: ratio of particle radius to double layer thickness (a/κ)

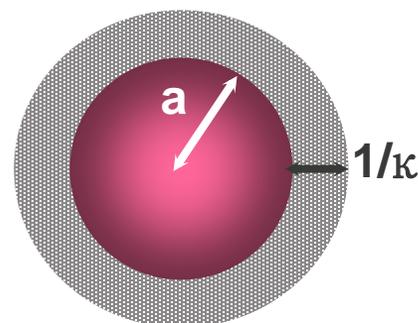
Non-polar media
(dielectric constant <20)



Huckel approx.

$$F(\kappa a) = 1.0$$

Polar media
(dielectric constant >20)



Smoluchowski approx.

$$F(\kappa a) = 1.5$$

κa	$F(\kappa a)$
0	1.000
1	1.027
2	1.066
3	1.101
4	1.133
5	1.160
10	1.239
25	1.370
100	1.460
∞	1.500

Affected factors of zeta potential



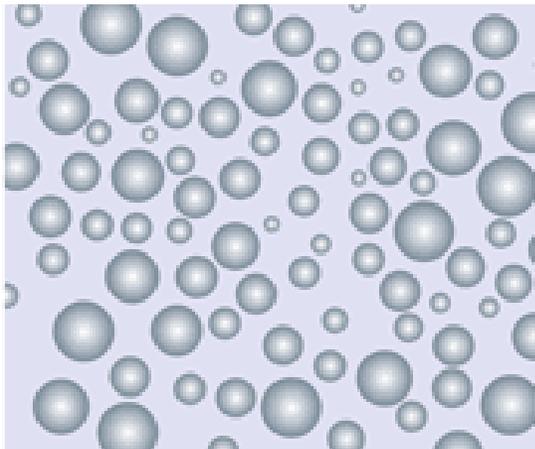
- Zeta potential can be affected by
 - *changes in pH,*
 - *conductivity (concentration and/or type of salt)*
 - *changes in the concentration of an additive (e.g. ionic surfactant, polymer)*
- Measurement of the zeta potential of a particle dispersion as a function of any of the above can lead to information in formulating the product to give maximum stability or in determining the optimum conditions for flocculation of the system

Zeta potential



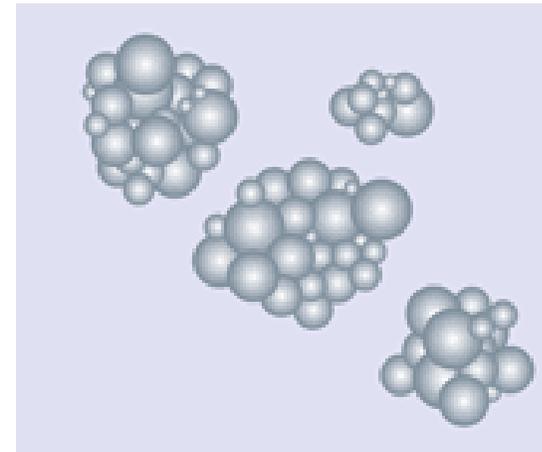
High Zeta Potential

- High interparticle repulsion
- **Stable suspension**



Low or Zero Zeta Potential

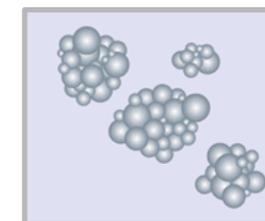
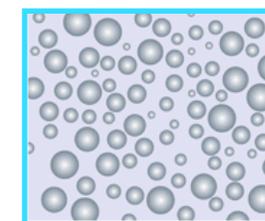
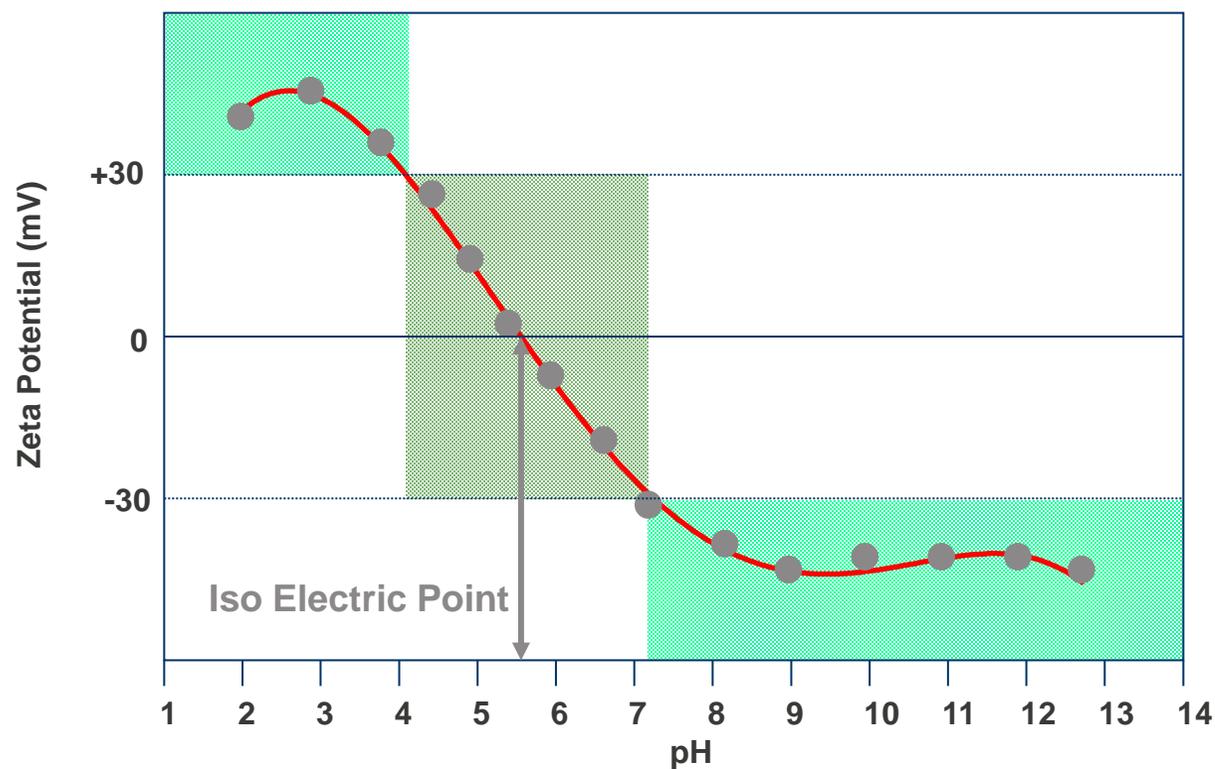
- Flocculation, aggregation, agglomeration, Ostwald ripening
- **Unstable suspension**



Zeta potential : pH



- The most important factor that affects zeta potential is pH
- IEP : very important from a practical consideration, least stable
- Aqueous dispersion stability dividing line $\approx \pm 30\text{mV}$



ISO standards

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2012-06-15

**Colloidal systems — Methods for zeta-
potential determination —**

Part 1:
**Electroacoustic and electrokinetic
phenomena**

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2012-06-15

**Colloidal systems — Methods for zeta-
potential determination —**

Part 2:
Optical methods



Q&A

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