Particle Sizing Techniques

Dispersions in liquids: suspensions, emulsions, and foams

ACS National Meeting

March 21 – 22, 2009

Salt Lake City

Microscopy – the first laboratory instrument

Always look at particles in the microscope before doing any other type of size analysis!!

Microscope results are almost always the referee for a new technique.

Image analysis:

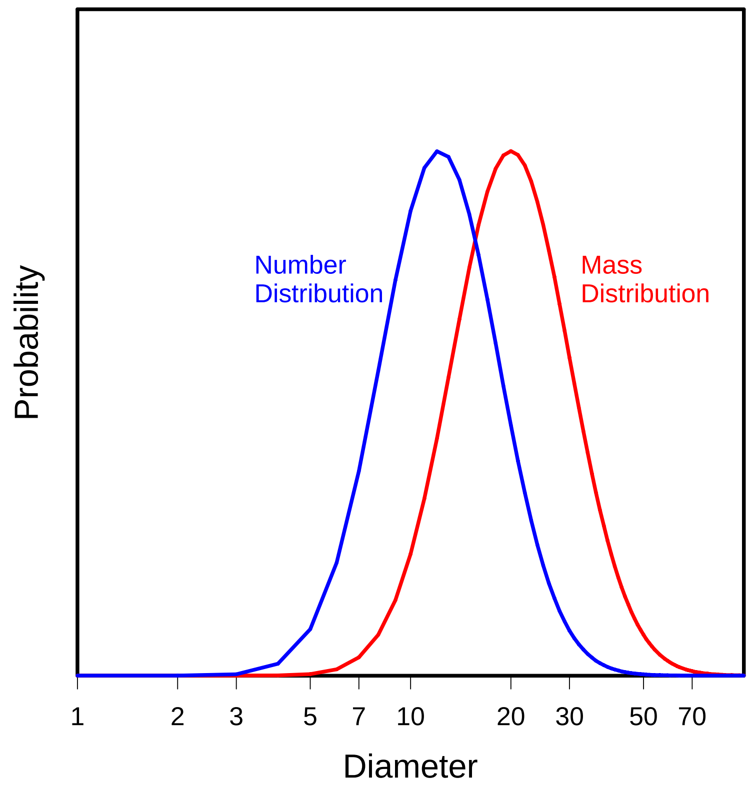
- Reticle
- Photograph
- Digitized photograph
- Digitized video

For particle sizing by measuring Brownian motion with dark field illumination: www.nanosight.co.uk

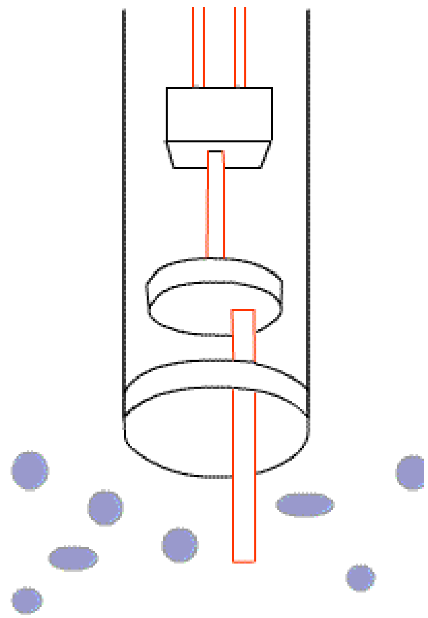
Electron microscopy

- Orders of magnitude higher resolution
- But samples are in vacuum at high temperature
- Cryogenic TEM's are nice-ish.

Number and mass distributions

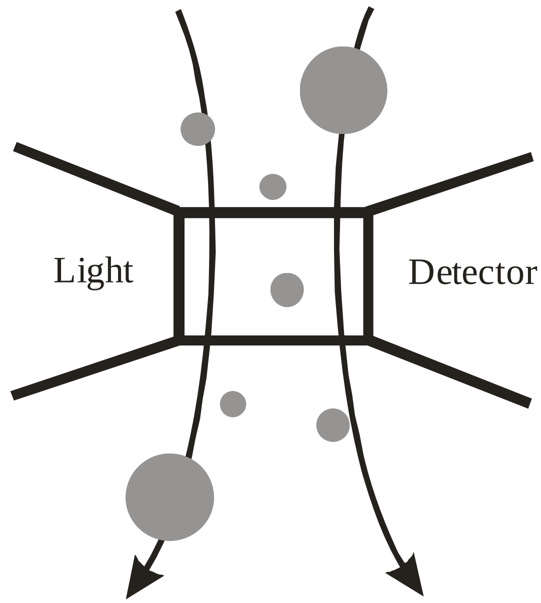


Particle size by optical scanning



Lasentec, Richmond, WA

Photozone detection

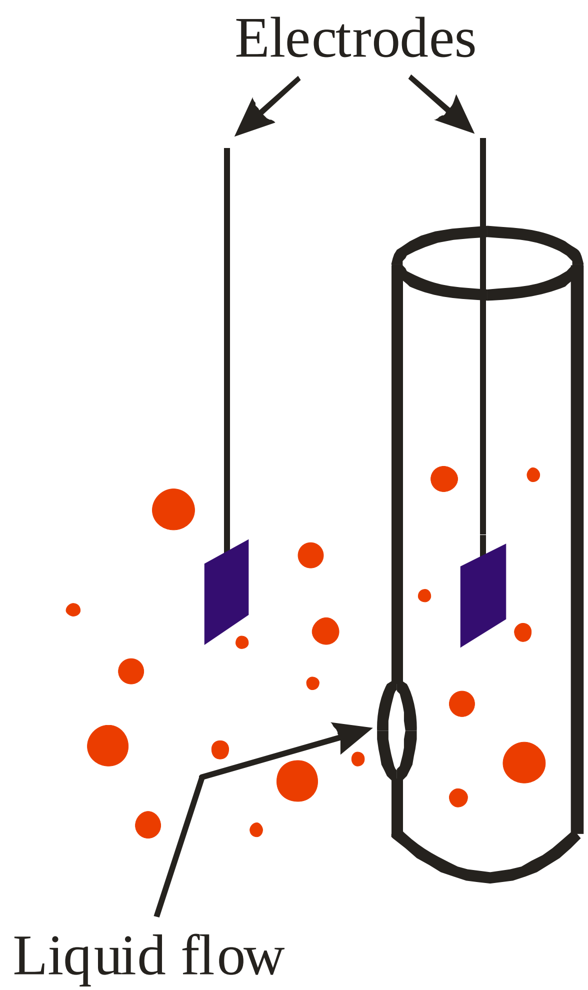


Data: Number versus cross-sectional area.

Lower limit with optical detection about 1 micron.

Optical detection good for all solvents.

Electrozone Detection (Coulter Principle)



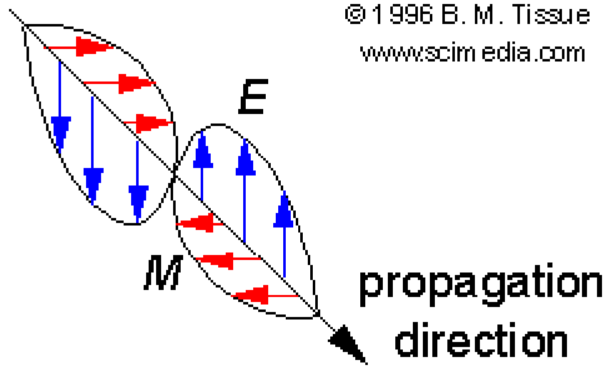
First issued
patent in 1953

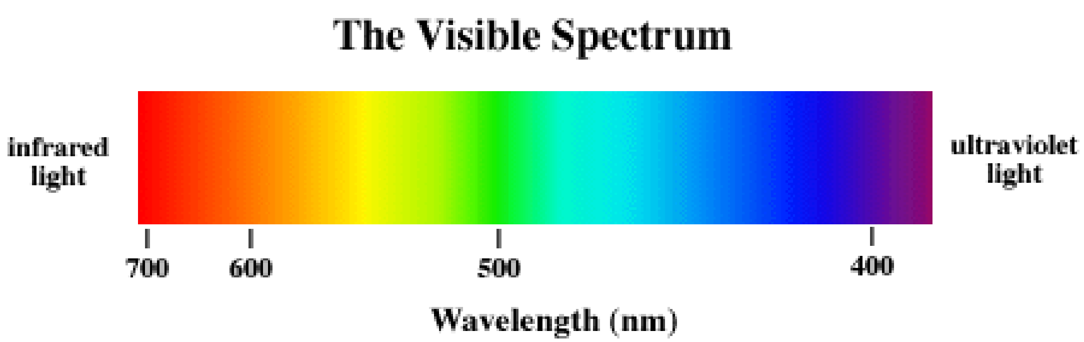
Wallace d.1998
Joe d.1995

Red blood cells:
6 – 8 μm

White blood cells:
10 - 12 μm

Light


©1996 B. M. Tissue
www.scimedia.com
E
M
propagation
direction


The Visible Spectrum
infrared
light
ultraviolet
light
700
600
500
400
Wavelength (nm)

Rayleigh Scattering

(Wavelength of light >> Particle size)

$$I_u = \frac{\pi^4 d^6}{4r^2\lambda^4}\left(\frac{n_p^2 - n^2}{n_p^2 + 2n^2}\right)^2$$

I_u = scattered intensity with unit illumination
d = particle diameter
r = distance to detector
λ = wavelength of light
n_p = refractive index of particle
n = refractive index of medium

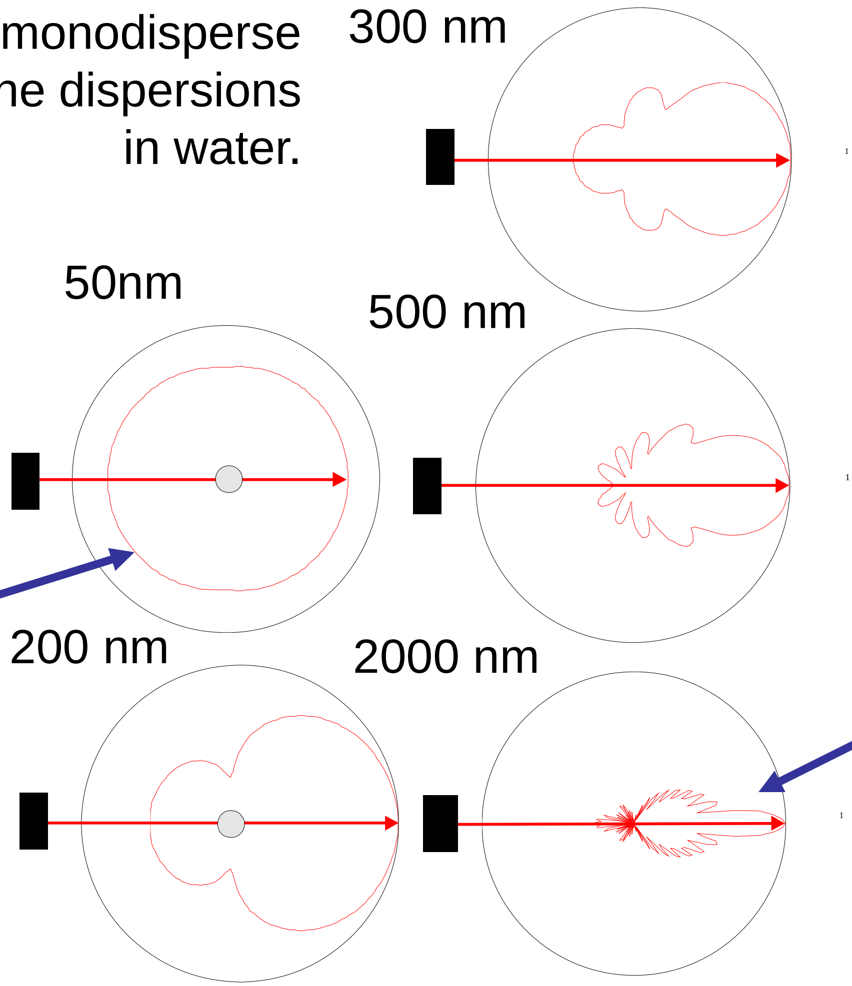
The Tyndall effect – the larger the particles, the more the scattering.

Why the sky is blue – the shorter the wavelength, the more the scattering.

Angular dependence of scattered light

Five monodisperse polystyrene dispersions in water.

The laser beam enters each sample from the left.

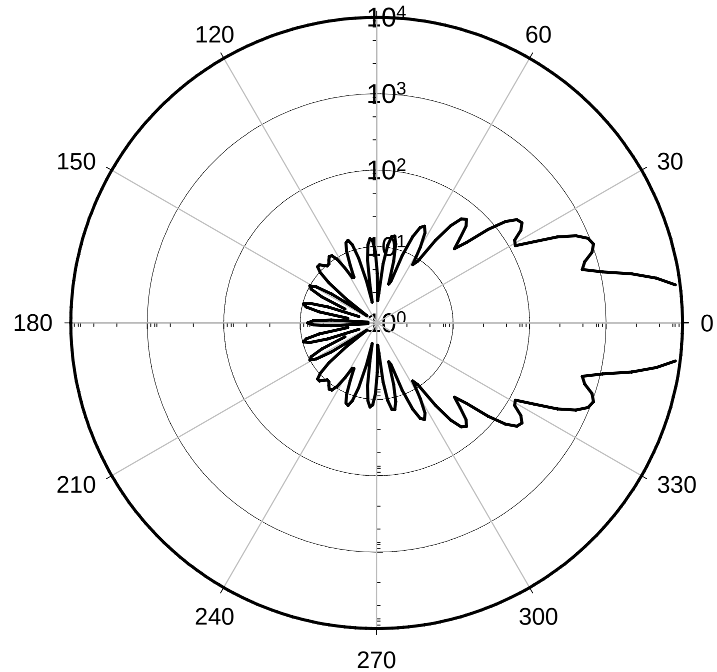


The red lines are the magnitude of the scattering as a function of angle.

The smallest particles scatter light equally in all directions.

The largest particles scatter light mostly in the forward direction.

Mie Theory – Classical light scattering



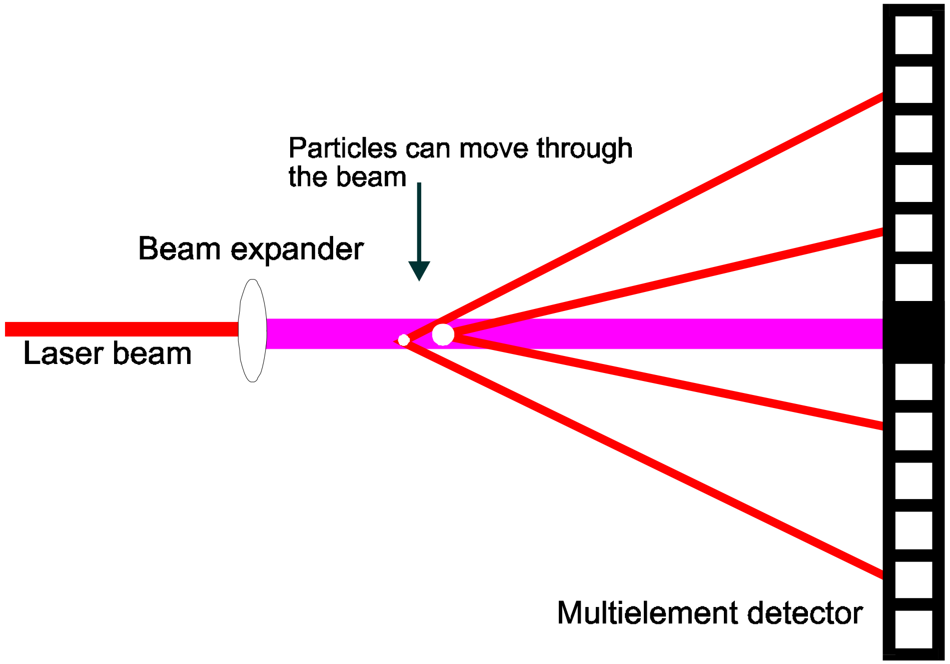
Light intensity as a function of angle for a 500 nm polystyrene particle suspended in water.

Fraunhofer diffraction

For particles greater than a micron.

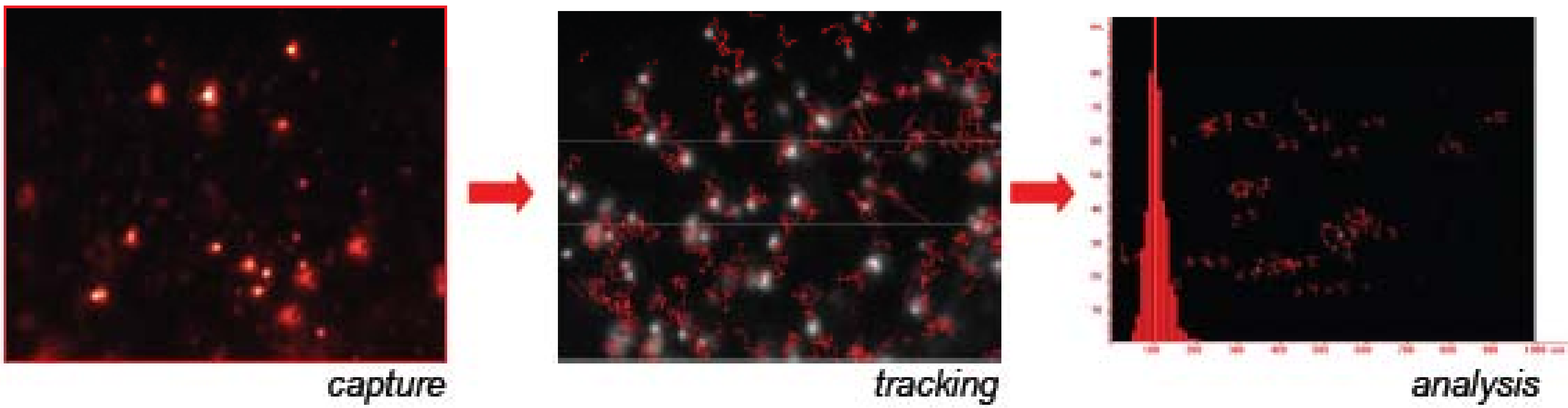
Works really well for sprays.

Useful to track size changes with time.



Each particle acts as a small lens and forms a series of concentric rings of scattered light. The number and spacing of the diffraction rings depend on the particle diameters.

Submicron particle sizing

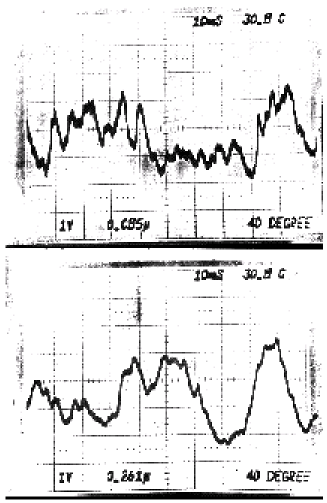


Submicron particles are visible with dark field illumination.
The motion of individual particles are tracked by analysis of captured video.
A number **size distribution** is generated assuming Brownian diffusion.

Nanosight Ltd., http://www.nanosightuk.co.uk/

Quasi-elastic light scattering

Because suspended particles are always moving, and the light they scatter can interfere with each other constructively and destructively, the intensity of scattered light varies with time.



The upper oscilloscope trace is for 85 *nm* styrene particles in water. The lower is for 261 *nm* polystyrene particles in water. (Each signal is 0.1 sec long.)

The motion of the smaller particles appears more random, less correlated.

The autocorrelation function is a mathematical transform similar to the Fourier transform.

The autocorrelation of the intensity data for monodisperse spheres undergoing Brownian motion (like this data) produces a simple exponential.

The exponential constant is inversely proportional to the particle diameter. The technique is absolute.

Stokes sedimentation

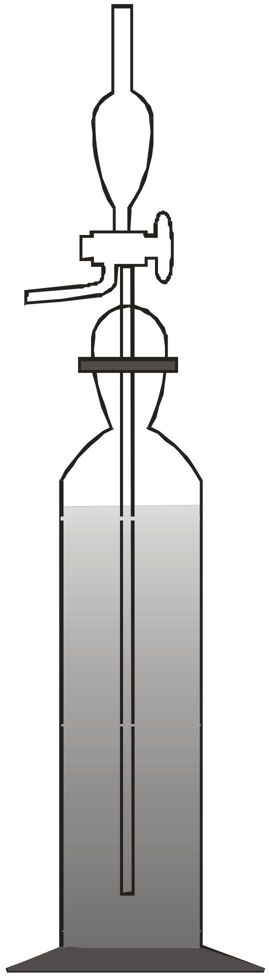
The “terminal” velocity is the ratio of the gravitational pull and viscous drag:

$$v_t = \frac{F_{applied}}{6\pi\eta a} = \frac{m_{apparent}\, g}{6\pi\eta a} = \frac{2g}{9} \bullet \frac{a^2 \Delta\rho}{\eta}$$

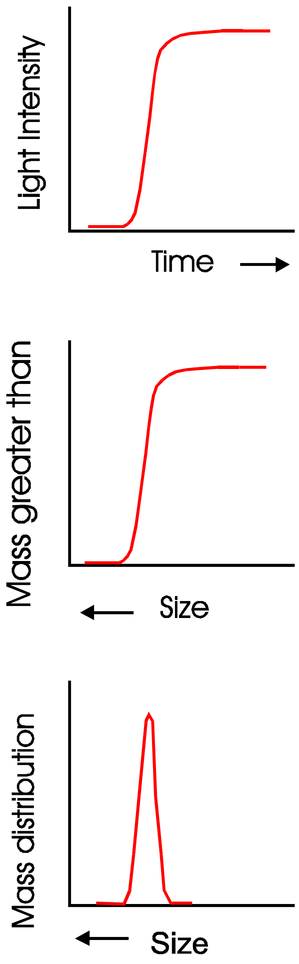
Where *g* is gravitational acceleration, *a* is the particle radius, $\Delta\rho$ is the density difference, and η is the liquid viscosity.

The experiment is to measure the time it takes for a particle to settle a known distance.

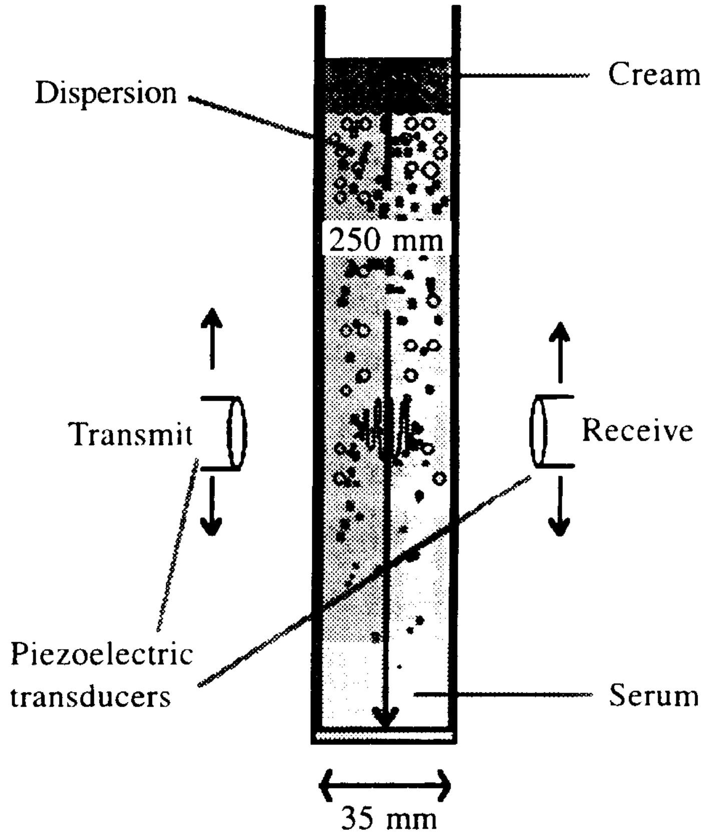
Andreasen sedimentation pipette



Measure the light transmission at a fixed height.



Ultrasound profiling



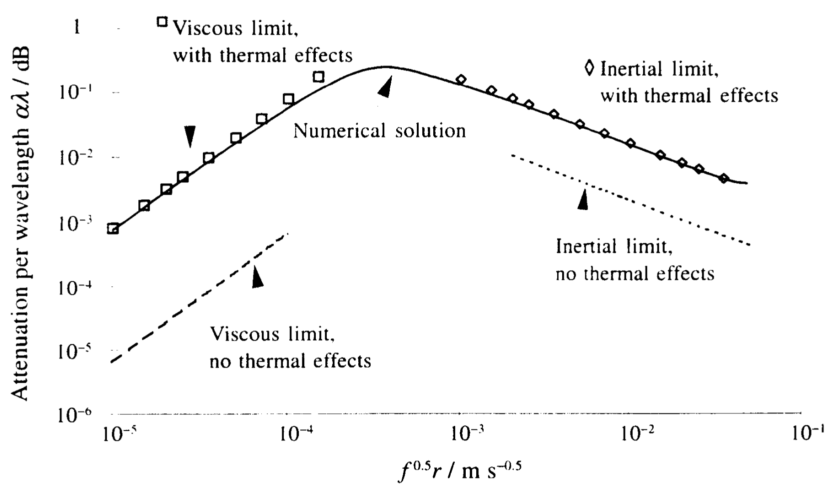
The speed of sound is a linear function of the volume fraction!!!

(Light transmission is exponential.)

Provey, p.79

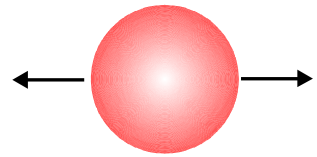
Ultrasound absorption

Povey, p. 7 and p. 119



Ultrasound	Light
Transducers are phase sensitive.	Transducers are phase insensitive.
Wavelength between cm and μm.	Wavelength between 0.5 and 1 μm.
Frequency between 0.1 and 10^{13} Hz.	Frequency between 3×10^{16} and 6×10^{16} Hz.
Coherence between pulses.	No coherence between pulses.
Responds to elastic, thermophysical, and density properties.	Responds to dielectric and permeability properties.
Particle motion parallel to the direction of propagation; no polarization.	Field displacement perpendicular to direction of propagation; polarization is therefore possible.
Propagates through optically opaque materials.	Sample dilution is normally required.

Centrifugation sedimentation

Viscous drag  Centrifugal force

The centrifugal force on a particle is:

$$F_{centrifugal} = \frac{4}{3}\pi a^3 \Delta\rho R\omega^2$$

The viscous drag is:

$$F_{drag} = 6\pi\eta a v$$

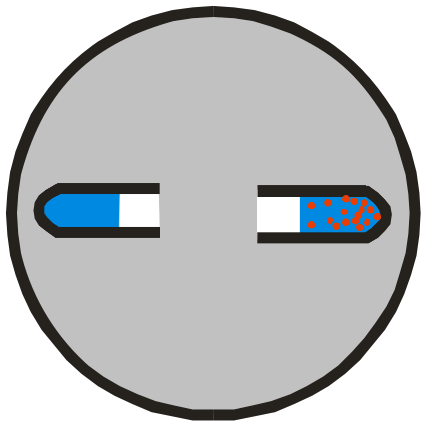
The steady velocity is:

$$v = \frac{2a^2\Delta\rho R\omega^2}{9\eta}$$

R is the radius of the centrifuge
ω is the angular velocity (radian/sec)

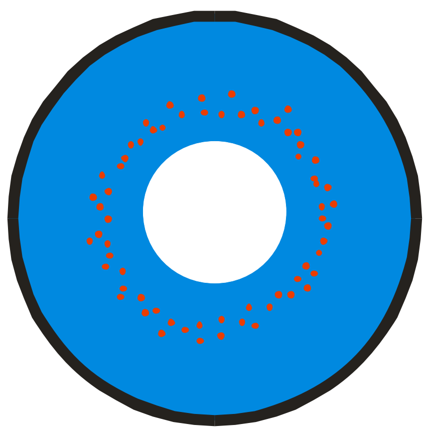
Centrifugation

Homogeneous start

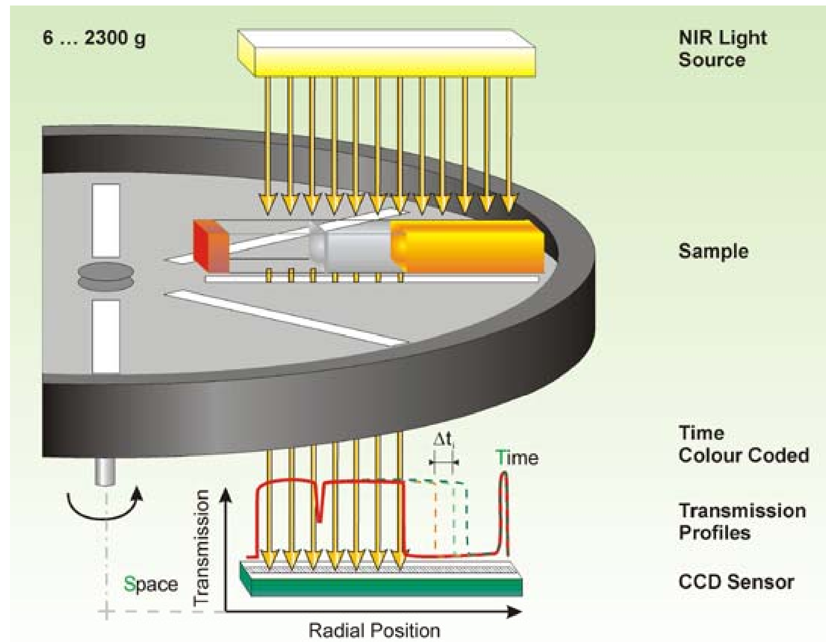


Gives cumulative distribution.

Line start



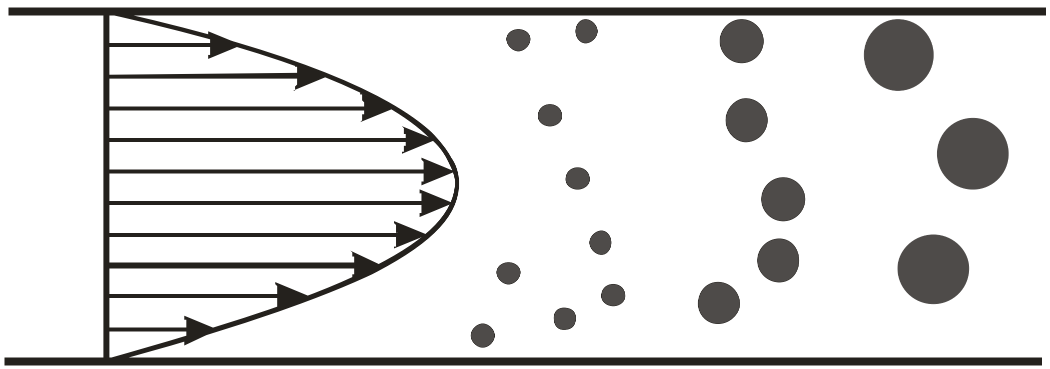
Gives size distribution.



www.lum-gmbh.com

Hydrodynamic chromatography

Separation of particles in a liquid flowing in a tube:



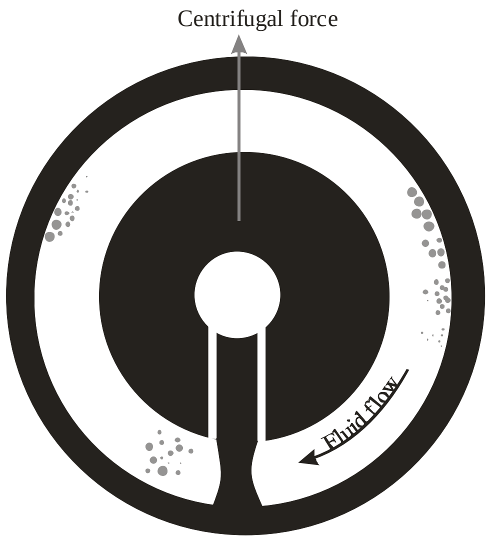
The liquid is moving slowest near the walls.

Next to the wall, the smaller the particle, the slower it moves.

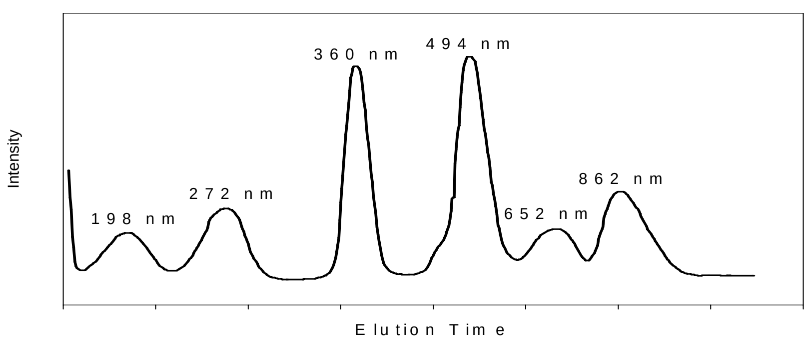
Therefore, the smallest particles exit last.

Real size distributions. (Size range claims from 10 *nm* to 3 μ*m*.)

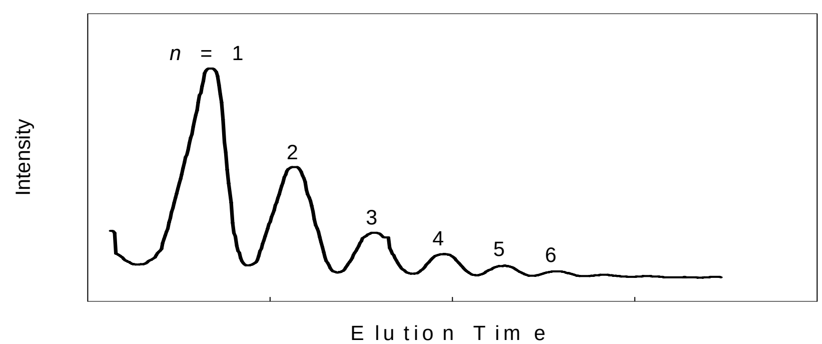
Sedimentation field flow fractionation



Larger particles are pushed to the outside where the fluid flow is the least.



Polystyrene particles



PMMA particles