Particle size, charge, and flow

Lecture 4

Brownian Motion is diffusion

The Einstein relation between particle size and its diffusion coefficient is:

$$D = \frac{kT}{6\pi\eta a}$$

However gravitational sedimentation tends to pull the particle to the bottom. When these two tendencies are in equilibrium, the concentration of particles is given by:

$$n = n_o \exp(-h/h_0)$$

$$h_0 = \frac{3kT}{4\pi a^3 \Delta\rho g}$$

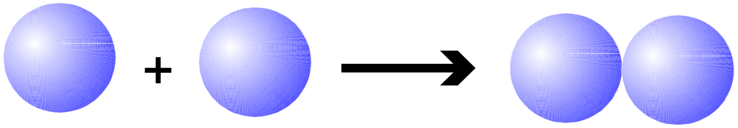
For a 500 *nm* radius particle, 2 gm/cm^3 in water at 25^{o}C, h_0 is about 1000 *nm*.

But Brownian motion is not the source of dispersion stability.

D is the diffusion constant
k is the Boltzmann constant
T is temperature
η is viscosity
a is particle radius
n is particle concentration
n_0 is the particle concentration at the bottom
h is the height
h_0 is the characteristic height
$\Delta\rho$ is the particle-liquid density difference
g is the gravitation constant

Brownian Collisions – Perikinetic Flow

Suspended particles collide because of Brownian motion:



Assuming that interparticle forces are not significant:

$$t_{1/2} = \frac{\eta \pi a^3}{\Phi k T}$$

where Φ is the volume fraction.

In water at 298°K: $$t_{1/2} = \frac{0.8 a^3}{\Phi} \sec$$

where *a* is in microns.

Microscopy

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.

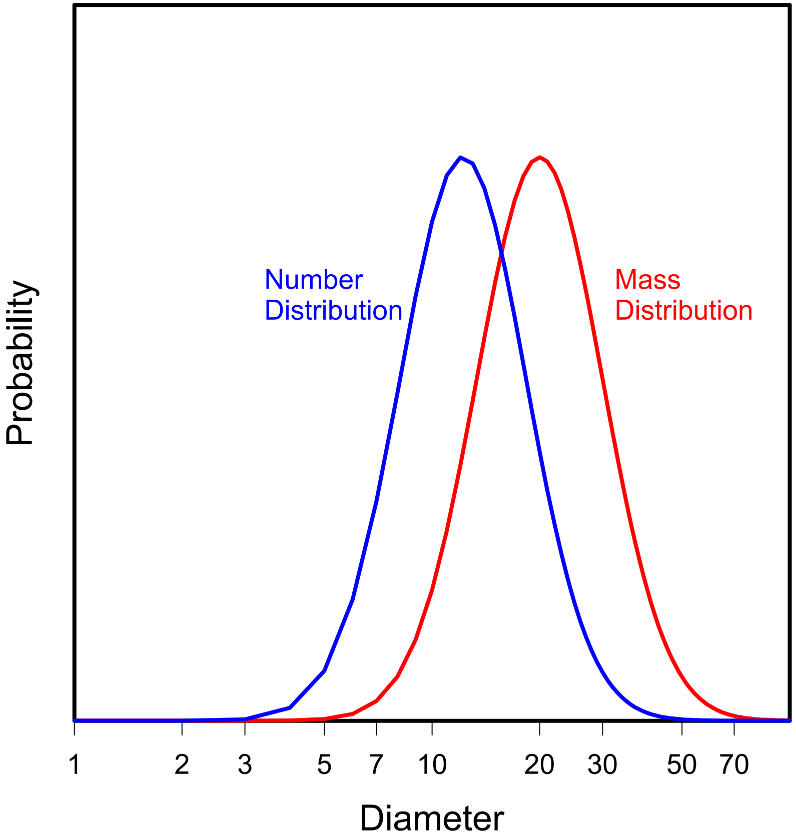
Image analysis:

- Reticle
- Photograph
- Digitized photograph
- Digitized video

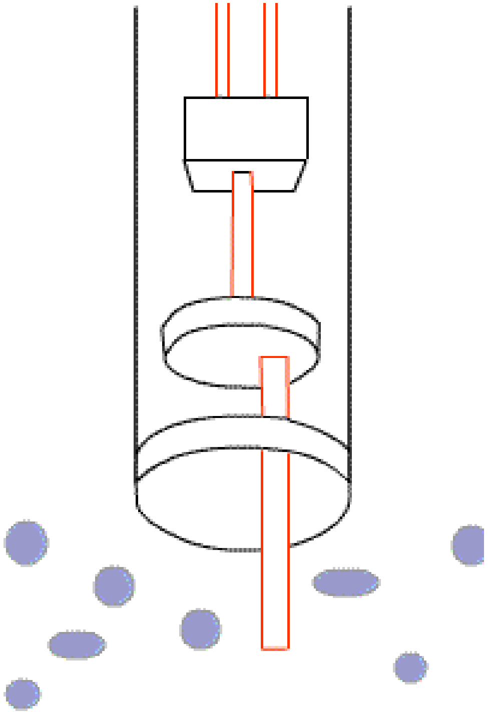
Electron microscopy

- Orders of magnitude higher resolution
- But samples are in vacuum at high temperature

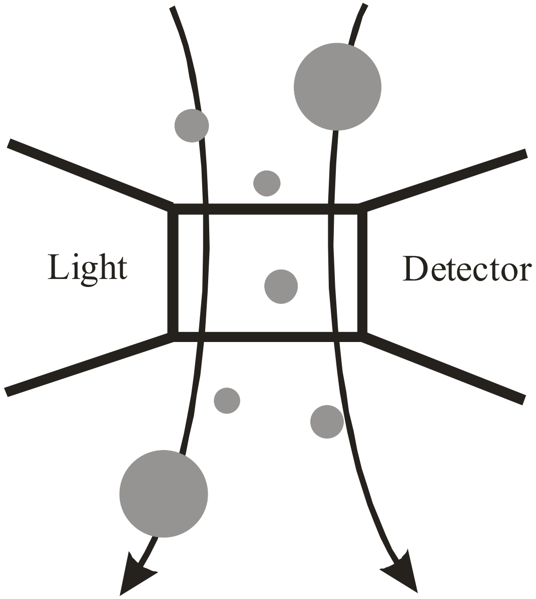
Number and Mass Distributions



Particle Size by Optical Scanning



Photozone Detection

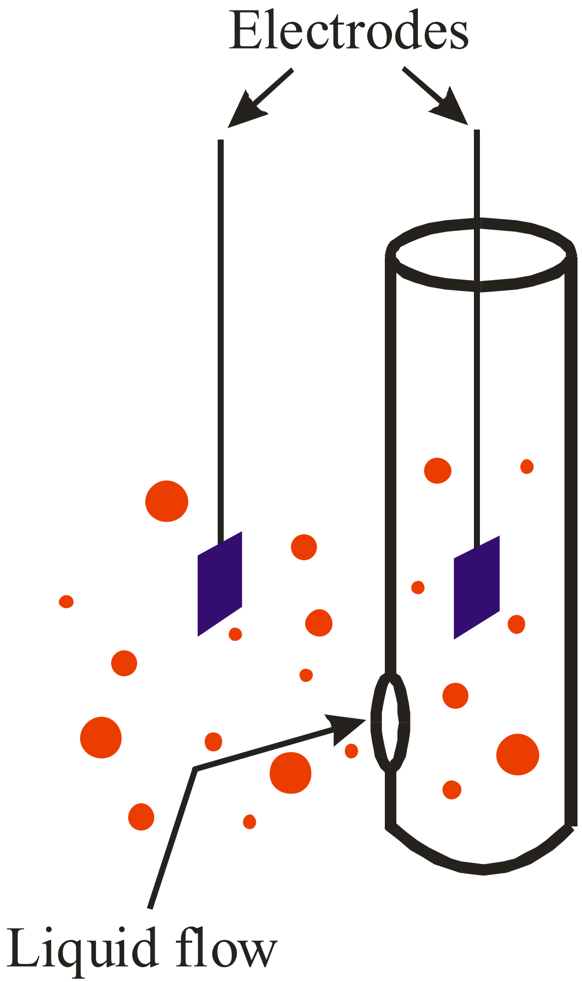


Data: Number versus cross-sectional area.

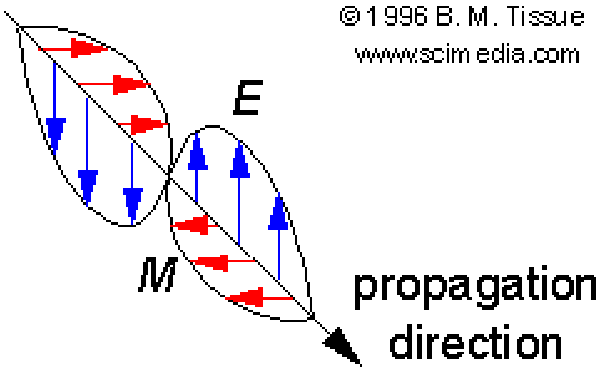
Lower limit with optical detection about 1 micron.

Optical detection good for all solvents.

Electrozone Detection (Coulter Principle)



Light



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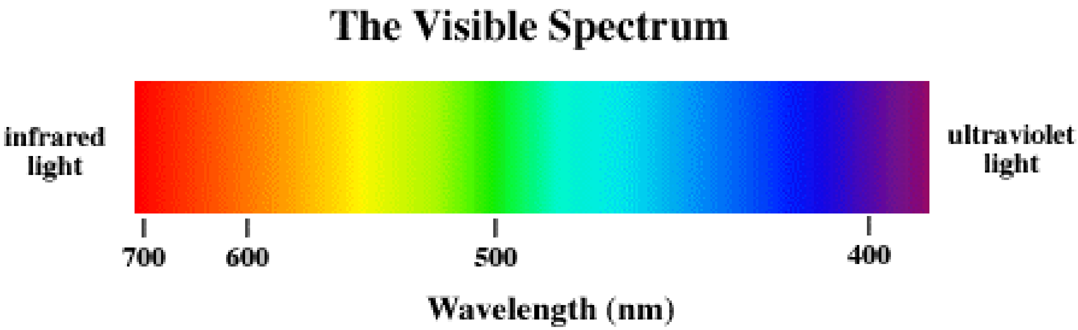


Rayleigh Scattering

(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.

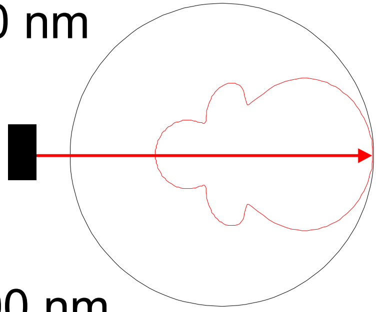
Angular Dependence of Scattered Light

Five monodisperse polystyrene dispersions in water.

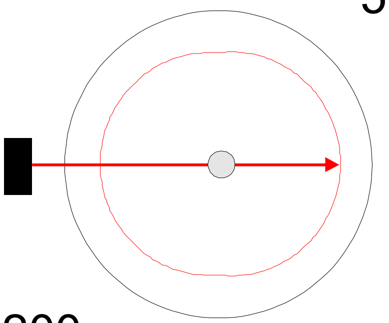
The laser beam enters each sample from the left. The red lines are the magnitude of the scattering as a function of angle.

The smallest particles scatter light equally in all directions. The largest particles scatter light mostly in the forward direction.

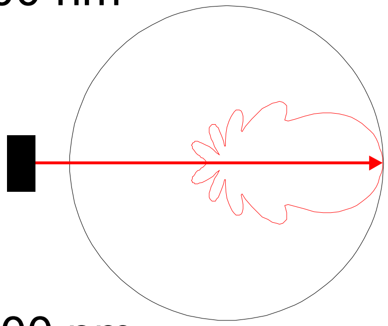
300 nm



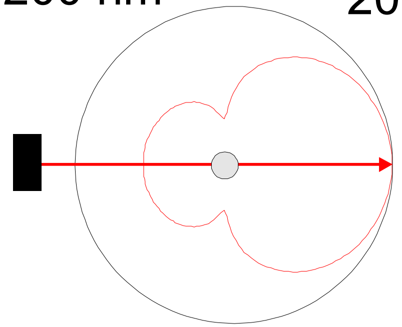
50nm



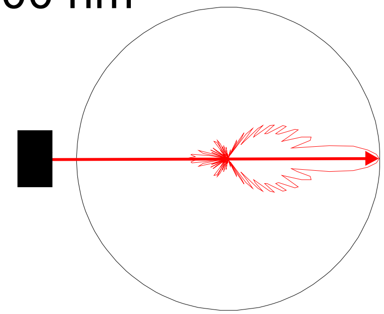
500 nm



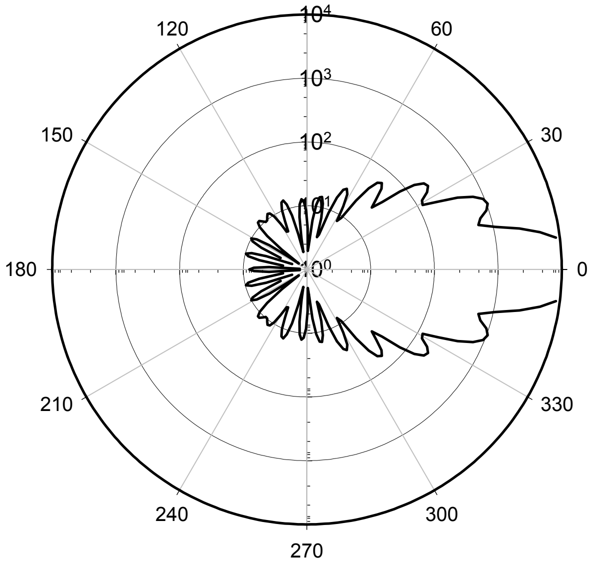
200 nm



2000 nm



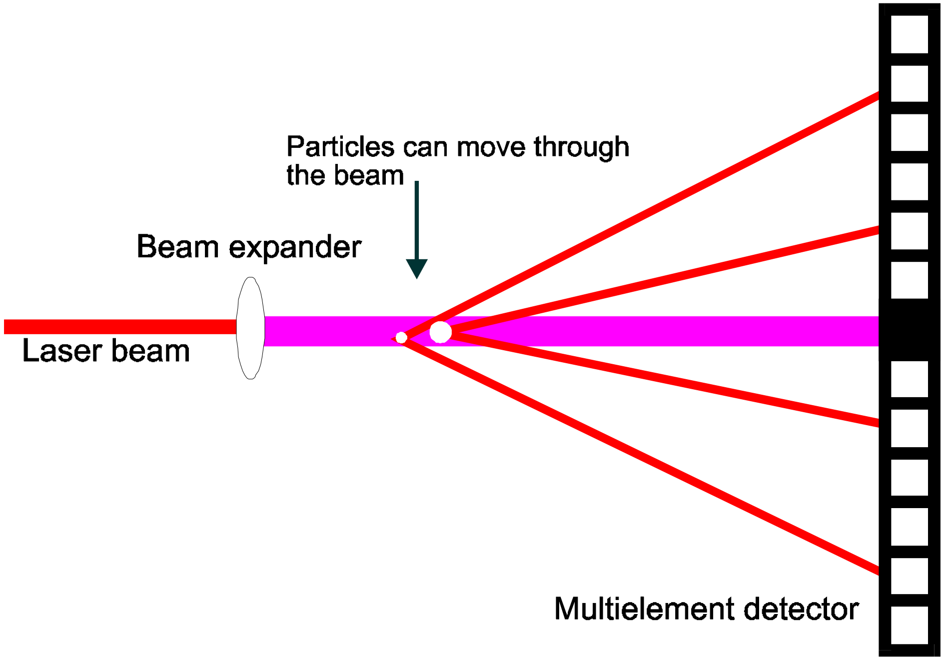
Mie Scattering –
Classical Light Scattering



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

Fraunhofer Diffraction

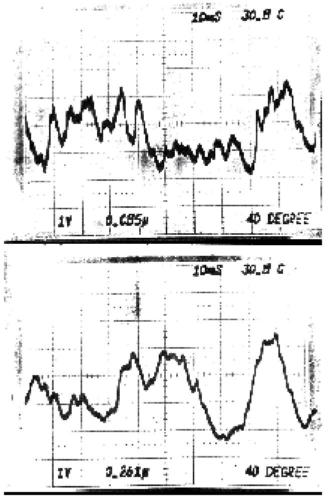
For particles greater than a micron.



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.

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.

Sedimentation Velocities

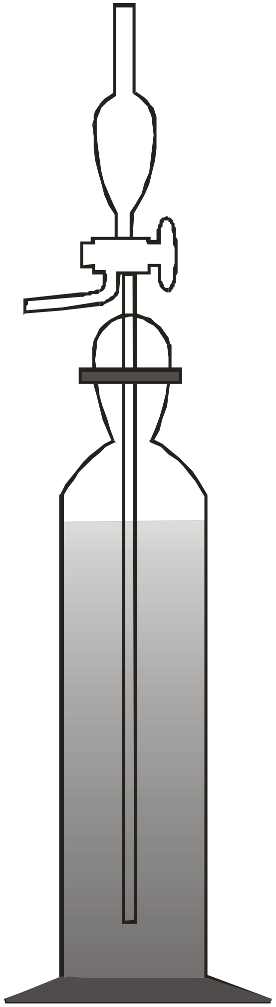
The “terminal” velocity is the ratio of the gravitational pull and viscous drag:

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

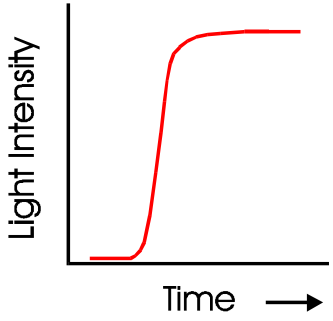
Where *g* is gravitational acceleration, *a* is the particle radius, $\Delta\rho$ is the density difference, and η is the liquid viscosity.

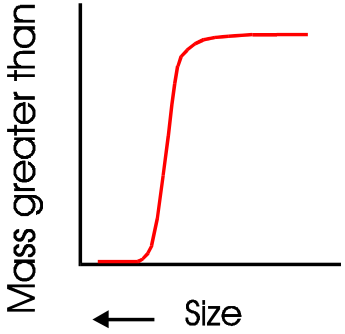
The experiment is to measure the time it takes for a particle to settle a known distance.

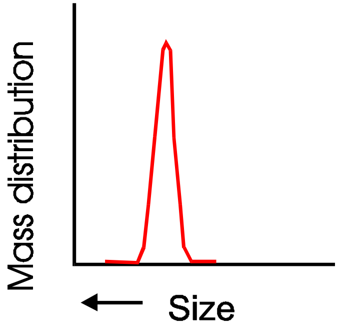
Andreasen Sedimentation Pipette



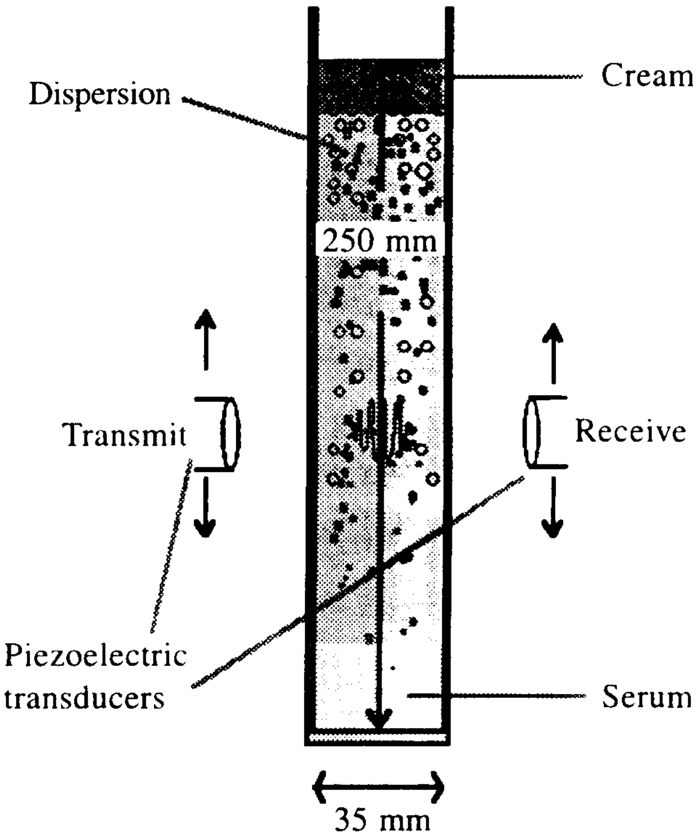
Sedimentation







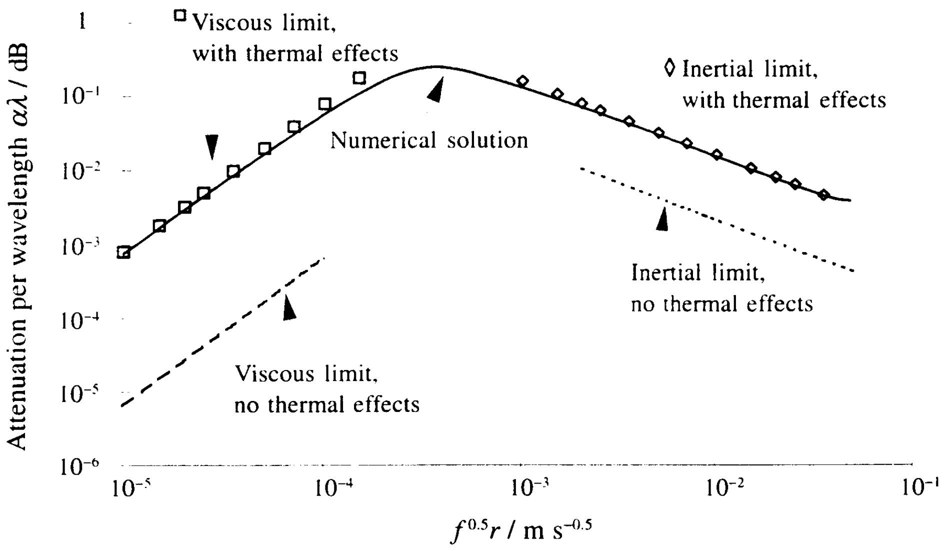
Ultrasound Profiling



The speed of sound is a linear function of the volume fractions.

Provey, p.79

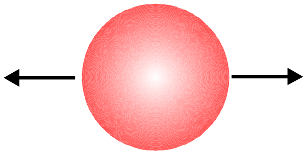
Ultrasound Absorption



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.

Povey, p. 7 and p. 119

Centrifugal Forces



Viscous drag

Centripetal force

The centripetal force on a particle in a centrifuge is:

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

The viscous drag is:

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

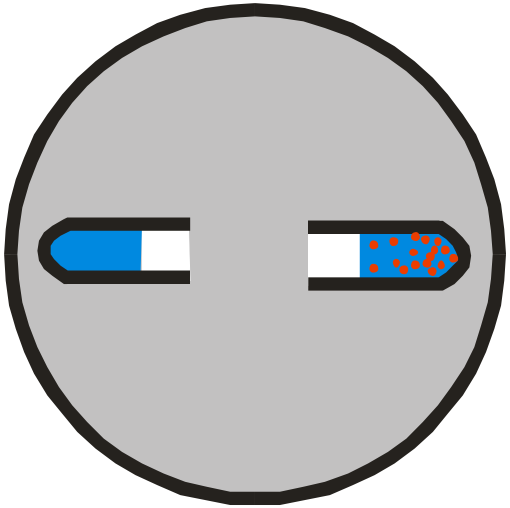
The terminal velocity is:

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

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

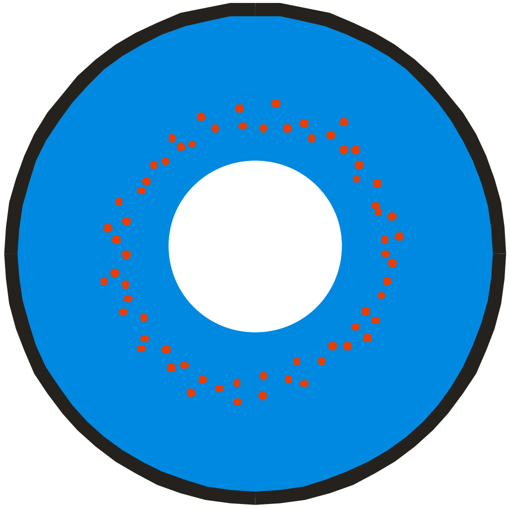
Centrifugation

Homogeneous
start



Gives cumulative
distribution.

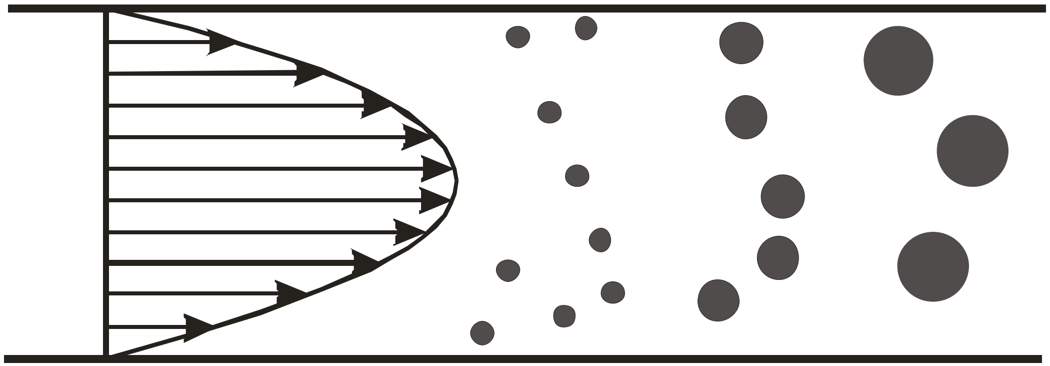
Line start



Gives size
distribution.

Hydrodynamic Chromatography

Separation of particles in a liquid flowing in a tube:

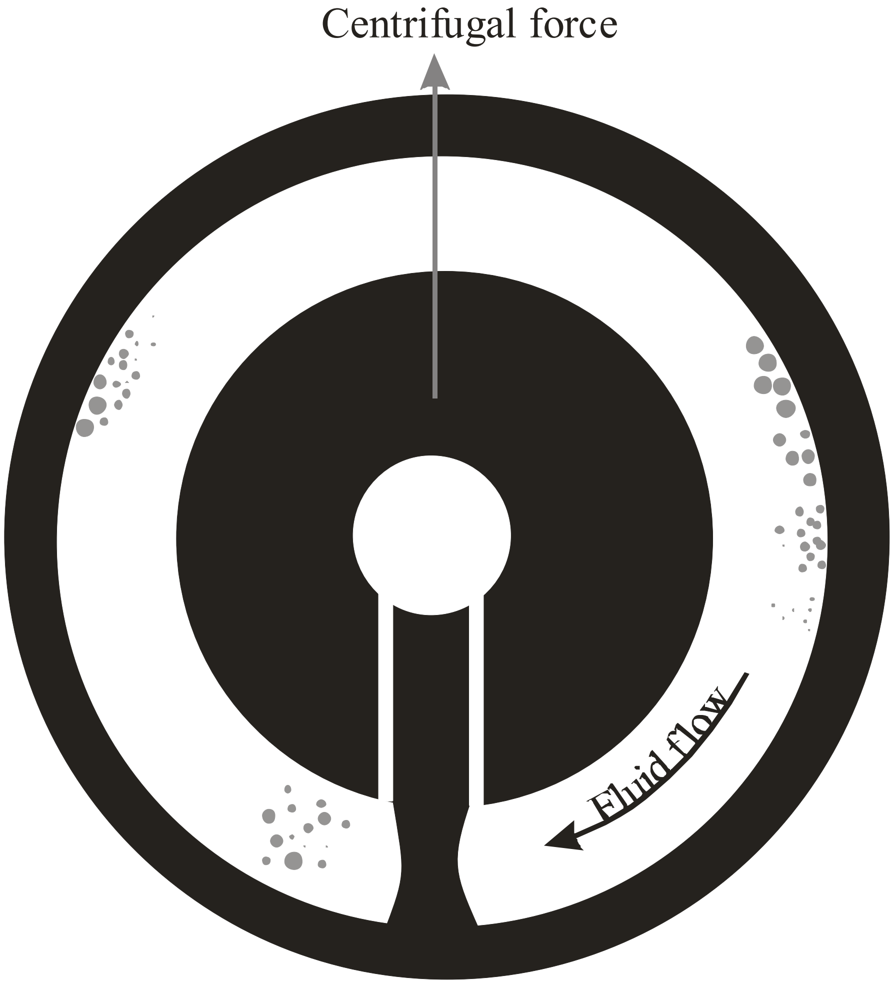


The liquid is moving slowest near the walls.

The smallest particles get closest to the walls.

Therefore, the smallest particles exit last.

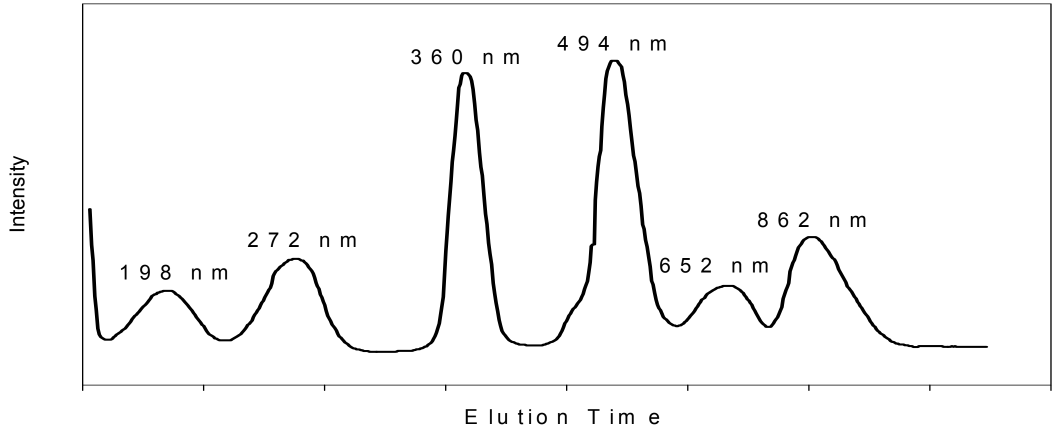
Sedimentation Field Flow Fractionation



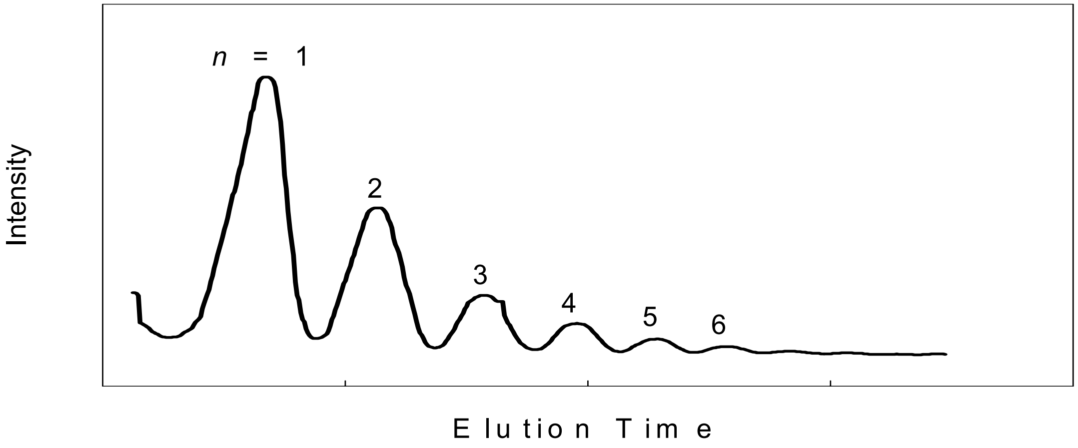
Larger particles are pushed to the outside where the fluid flow is the least.

Sedimentation Field Flow Fractionation

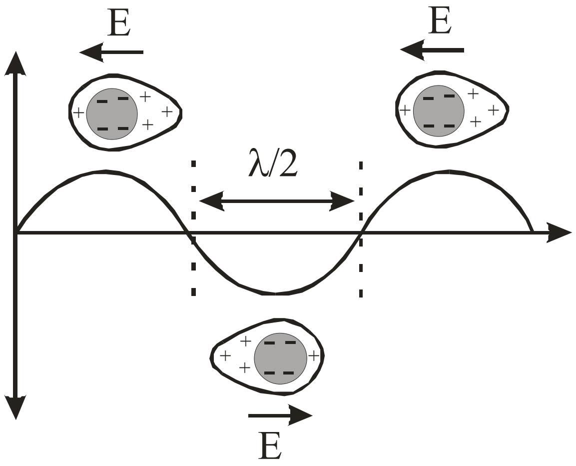
Polystyrene particles



PMMA particles



Particle charge – Electroacoustic Measurements



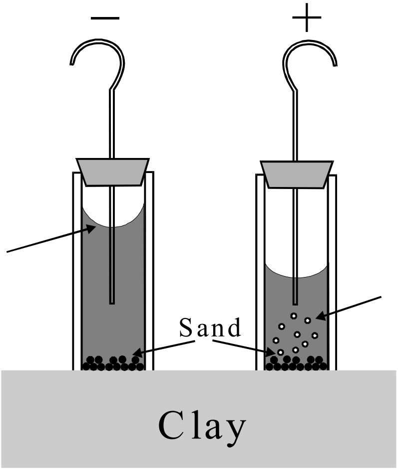
The technique uses an ultrasonic pressure wave to perturb the equilibrium double layer. This polarization generates an alternating electric field called the Colloid Vibration Potential:

$$CVP = \frac{2p\varphi}{\lambda_0}\left[\frac{\rho_2 - \rho_1}{\rho_1}\right]\frac{\varepsilon_0 D\zeta}{\eta}$$

If electrodes are spaced as shown in the diagram, this potential can be measured and the zeta potential calculated.

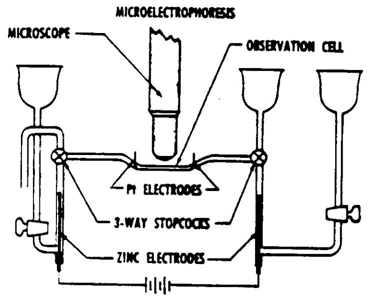
Electro-Osmosis and Electrophoresis

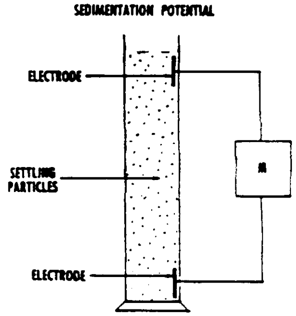
Electro-osmosis
of water.

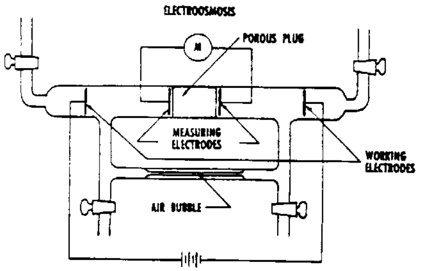


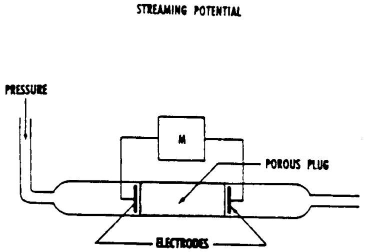
Electrophoreis
of clay particles.

Measurements of Electrokinetic Phenomena







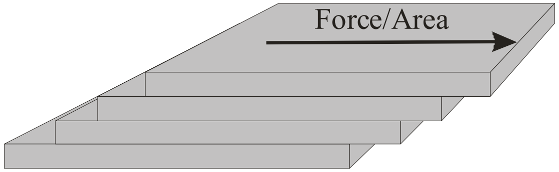


Rheology – The Science of Flow

Shearing stress = Force/Area = *F*/*A* = Newton/m^2

Rate of shear = Change of velocity with distance

= d*v*/d*x* = sec^{-1}



Newton's equation for viscous flow:

$$\frac{F}{A} = \eta \frac{dv}{dx}$$

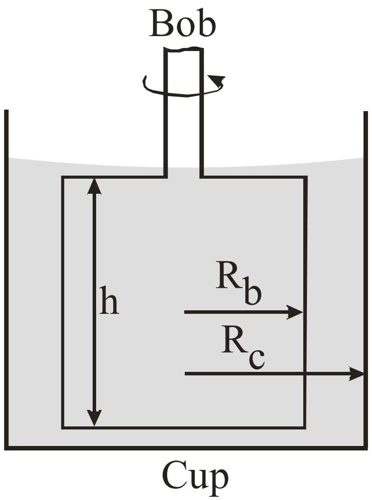
Where η is the viscosity coefficient. If η is constant, the fluid is called Newtonian.

$$\eta = \frac{\text{shear stress}}{\text{shear rate}} = \frac{\text{Newton} \times \text{sec}}{\text{m}^2} = \text{Pascal-sec}$$

Kinematic viscosity = Newtonian viscosity/density

= Stoke

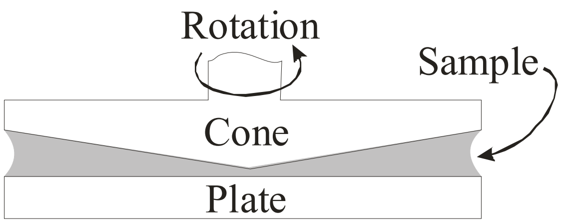
Couette Viscosimeter



In modern Couette viscosimeters the bob is either driven with a known stress and the resulting angular velocity measured or it is driven at a known angular velocity and the required stress measured. The first provides viscosity as a function of shear stress, the latter provides viscosity as a function of shear rate.

CW Macosko “Rheology: Principles, Measurements, and Applications” VCH:New York, **1994**.

Cone and Plate Rheometer

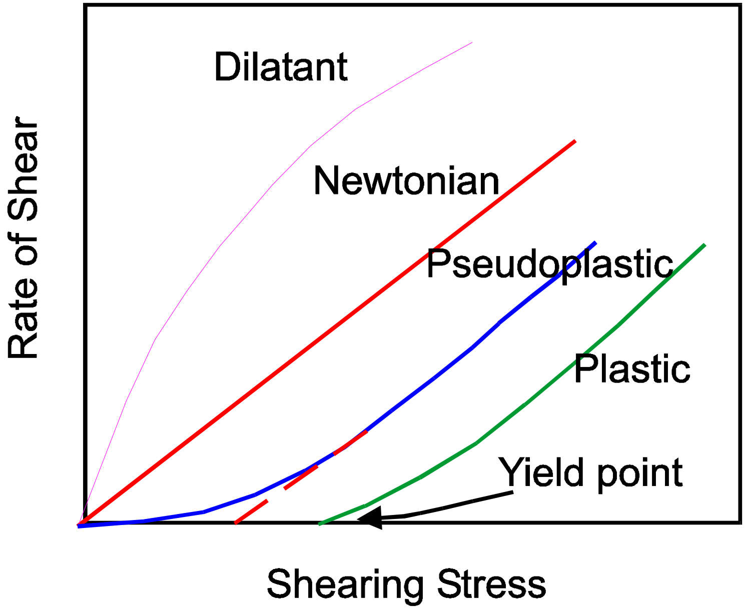


Consists of a flat plate and a cone with an apex angle of nearly 180°

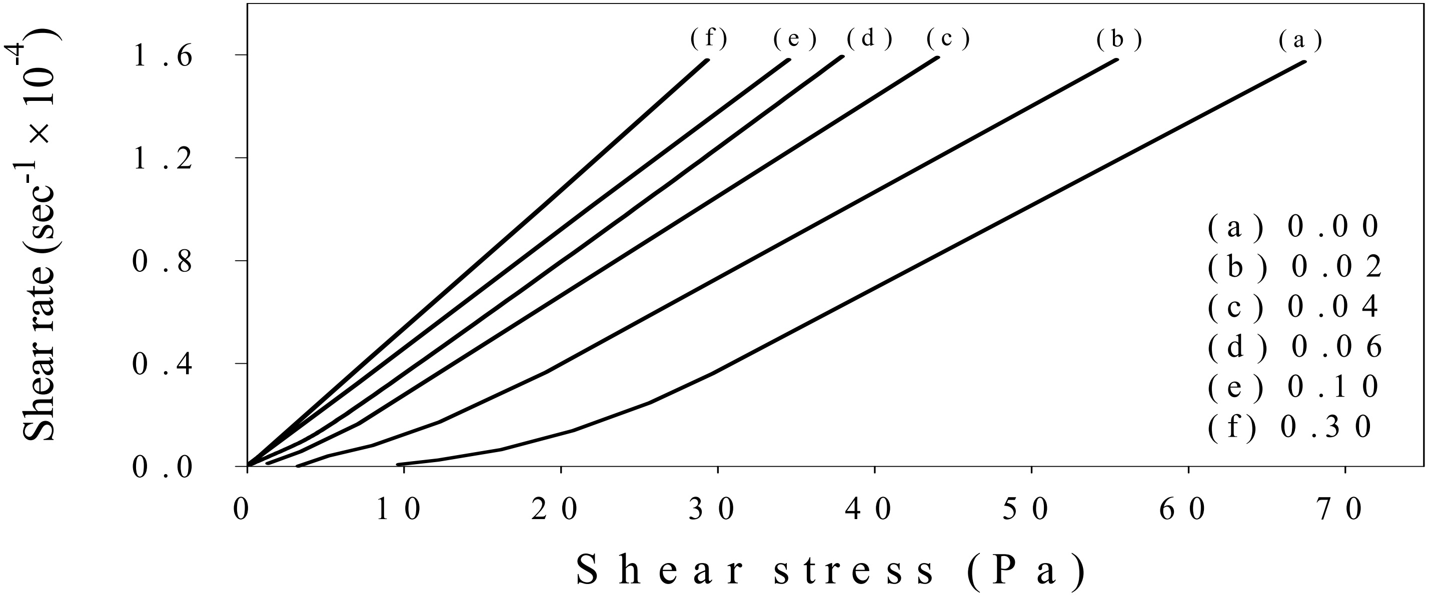
For such a geometry, the rate of shear is very nearly constant over the entire sample so that a well defined viscosity is measured.

The rate of shear is changed by changing the rotational velocity of the cone.

Rheological Behavior



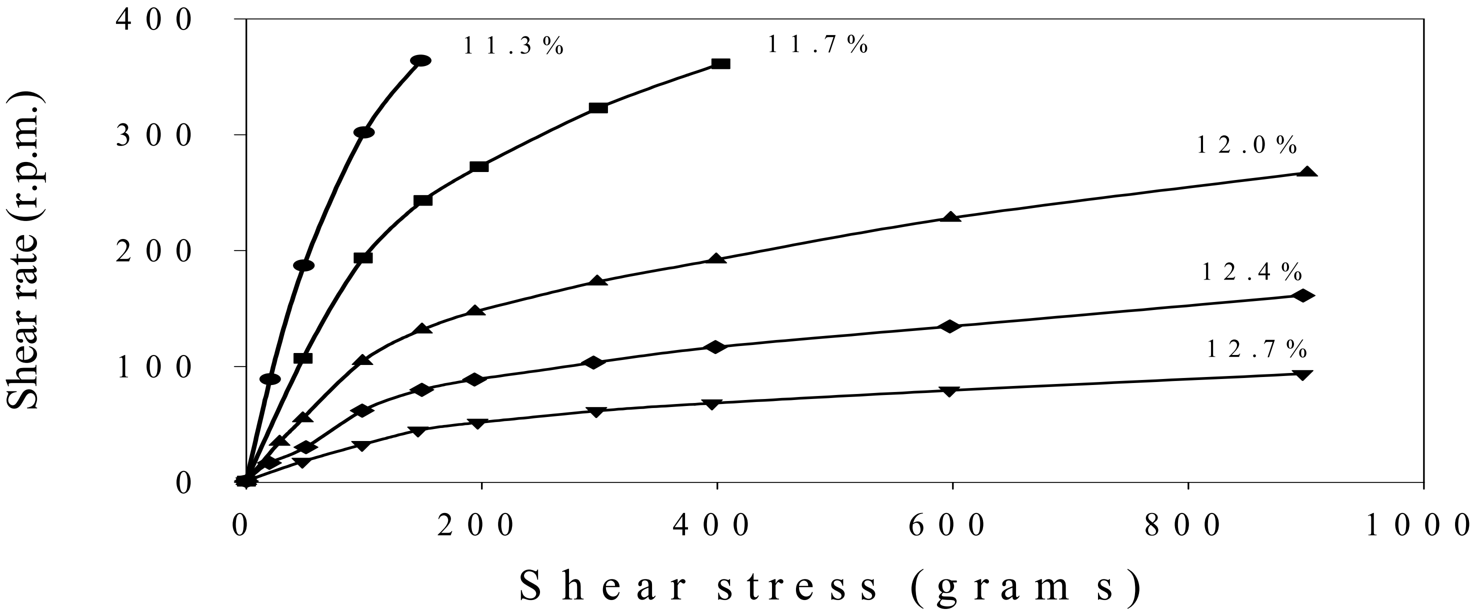
Pseudoplastic Flow



Rheograms of 20 w% deionized kaolin slurries at several levels of tetrasodium pyrophosphate addition. The figures on the curves indicate percent TSPP per weight of clay. An extrapolation of the linear region determines an apparent yield point.

$Na_4P_2O_7$

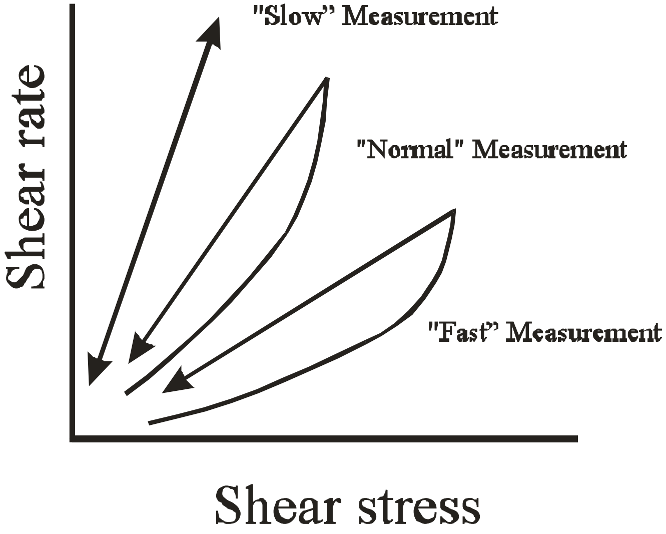
Dilatancy



Dilatant flow of a series of suspensions of red iron oxide in an aqueous solution of sodium lignin sulfonate at 10% concentration at 30° C. The volume concentrations of solids are noted on the curves.

Fischer p. 200

Thixotropy



Thixotropic behavior is a temporary destruction of structure by stirring or shaking, and may be measured as the time required to "heal." The diagram depicts rheological behavior of a thixotropic system as measured with a rotational viscosimeter. The area and nature of the thixotropic loop depends upon the type of instrument and the circumstances of measurement.