

Nanoparticle Technology

Brownian motion
Light scattering
Particle sizing
Rheology

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:

$$n = n_0 \exp(-h / h_0)$$

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

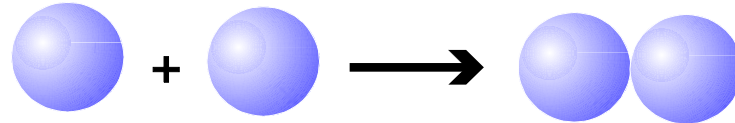
For a 500 *nm* radius particle, 2 gm/cm³ in water at 25°C, *h*₀ is about 1000 *nm*.

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

But Brownian motion is not the source of dispersion stability.

Brownian Collisions – Perikinetic Flow

Suspended particles collide because of Brownian motion:



Assuming that interparticle forces are not significant:

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

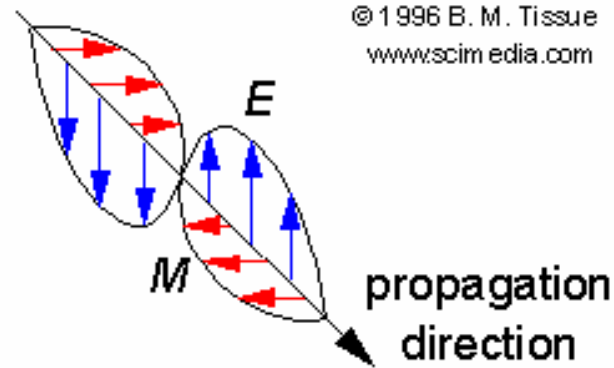
where Φ is the volume fraction.

In water at 298°K:

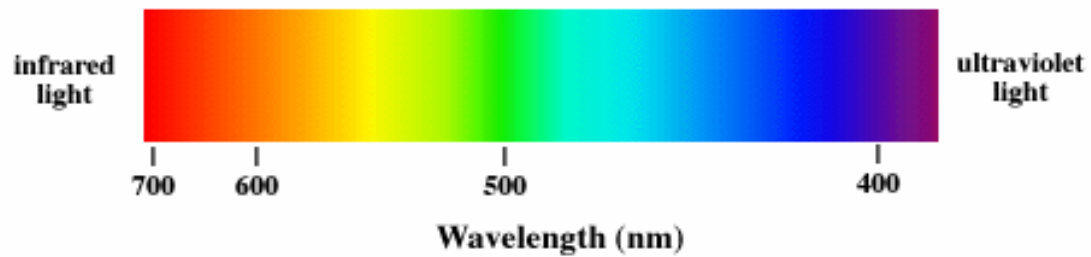
$$t_{1/2} = \frac{0.8a^3}{\Phi} \text{ sec}$$

where a is in microns.

Light

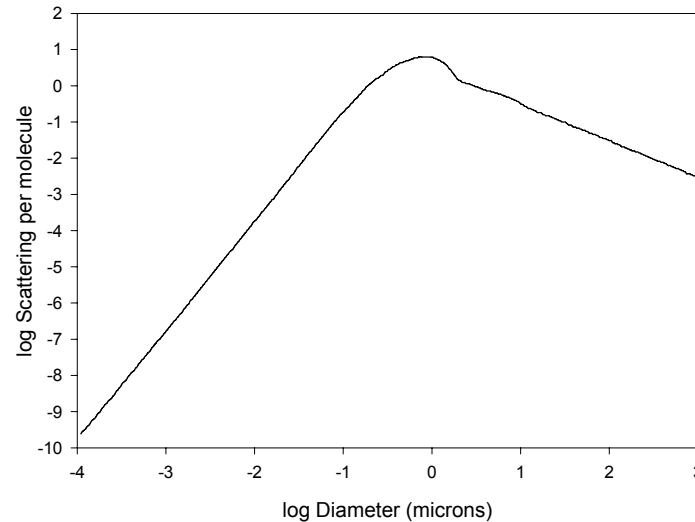


The Visible Spectrum



Total Scattering versus Particle Size

Scattering of visible light per water molecule



“Scattering by a molecule that belongs to a cloud droplet is about 10^9 times greater than scattering by an isolated molecule.”

Bohren, C.F. “Optics, Atmospheric”
Encyclopedia of Applied Physics, 1995, 12, 405-434. Figure 7.

Rayleigh Scattering

(Wavelength of light \gg 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

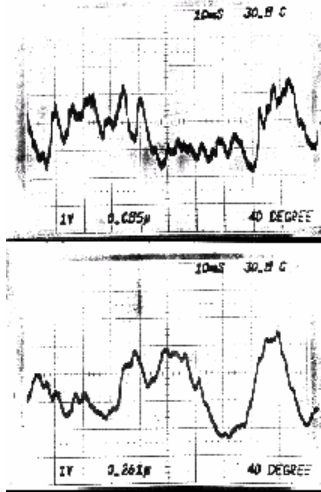
n = refractive index of medium

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

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

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.

Motion of Particles in Liquids

When a force is applied to a particle in a liquid, the particle will accelerate until the viscous drag just balances the applied force.

Stokes' equation for viscous drag is:

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

η is viscosity

a is radius

v is velocity

For any constant applied force, the velocity as a function of time is:

$$v = \frac{F_{applied}}{6\pi\eta a} \left[1 - \exp\left(-\frac{6\pi\eta a}{m} t\right) \right]$$

m is mass

t is time

Terminal Velocities

The terminal velocity is linear in the applied force:

$$v_t = \frac{F_{\text{applied}}}{6\pi\eta a}$$

The characteristic time is independent of the applied force:

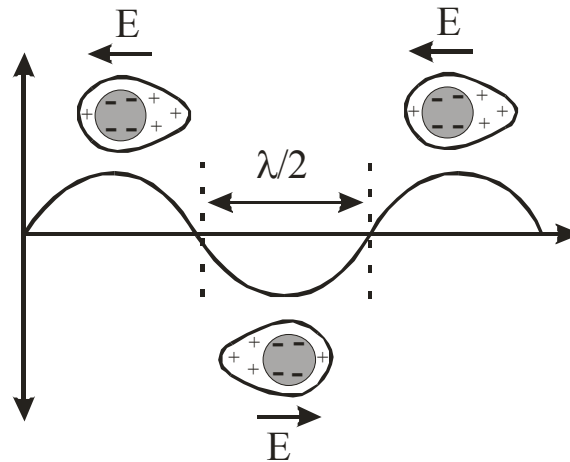
$$t_0 = \frac{m}{6\pi\eta a}$$

$3t_0$ is a typical measure of the time required to approach terminal velocity.

A particle 1 μm radius, 2 gm/cm^3 in water at 25°C, reaches terminal velocity in approximately:

$$3t_0 \approx 10^{-6} \text{ sec}$$

Electroacoustic Measurements

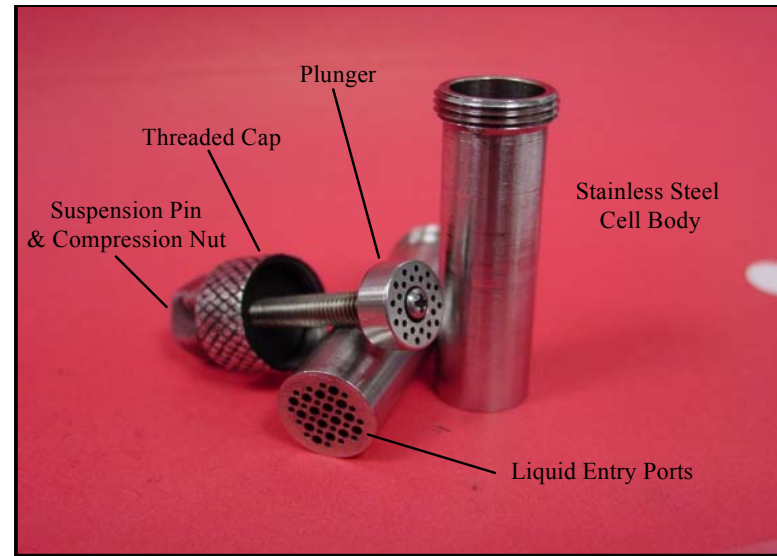
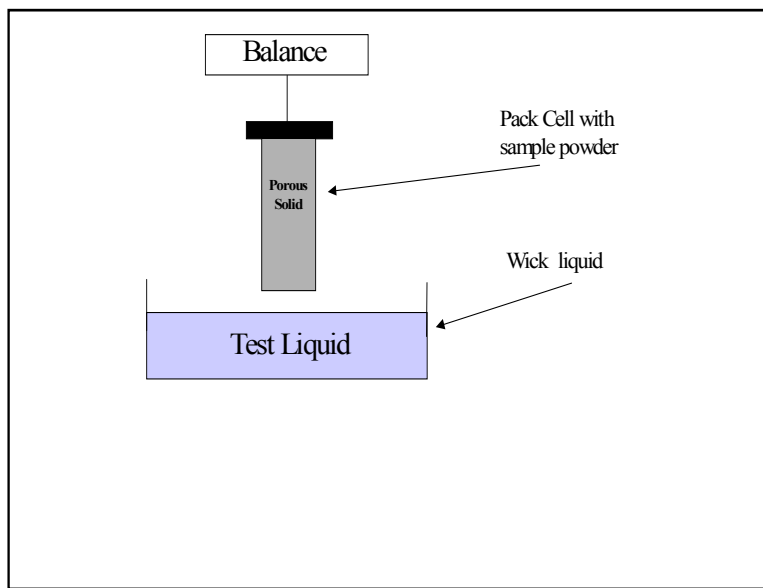


The technique uses an ultrasonic pressure wave to perturb the equilibrium double layer. This polarization generates an alternating electric field called the Colloid Vibration Potential:

$$CVP = \frac{2p\phi}{\lambda_0} \left[\frac{\rho_2 - \rho_1}{\rho_1} \right] \frac{\epsilon_0 D \zeta}{\eta}$$

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

Wicking of liquids by powders



$$\frac{m^2}{t} = G_\theta \frac{\rho_L^2}{\eta} W_{SL}^{imm}$$

$$W_{SL}^{imm} = \sigma_L \cos \theta$$

m^2/t is the mass squared by time

G_θ is a packing factor

ρ_L is the liquid density

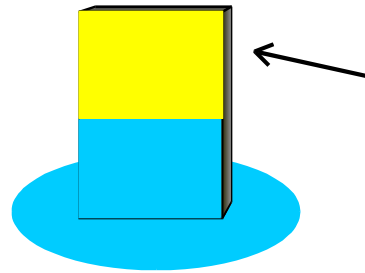
η is the liquid viscosity

W_{SL}^{imm} is the work of immersion

θ is the contact angle

σ_L is the surface tension of the liquid

A modification of the Washburn Method



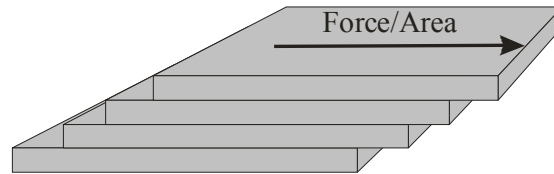
Coat a layer of pigment.

Measure the rate at which various liquids “wet” the packed bed.

Rheology – The Science of Flow

Shearing stress = Force/Area = F/A = Newton/m²

Rate of shear = Change of velocity with distance
= dv/dx = sec⁻¹



Newton's equation for viscous flow:

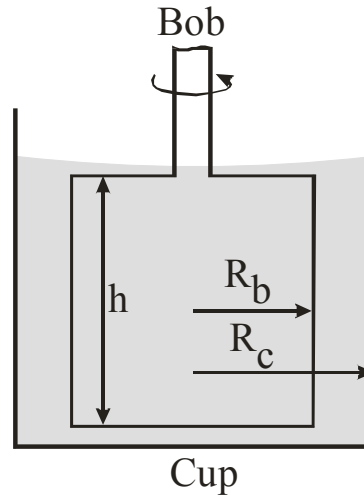
$$\frac{F}{A} = \eta \frac{dv}{dx}$$

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

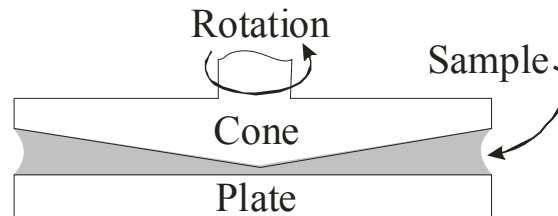
Couette Viscosimeter



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

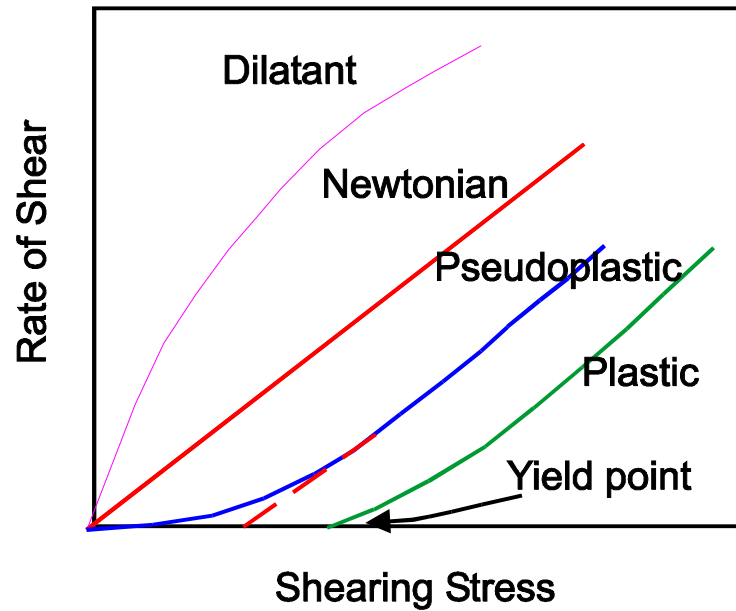


Consists of a flat plate and a cone with an apex angle of nearly 180°

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



Viscoelasticity

Solids are elastic – they deform when stress is applied but return to their original shape when the stress is removed.

Liquids are viscous – they flow steadily when stress is applied and do not return to their original shape when the stress is removed.

Viscoelastic flow – a combination of elastic and viscous flow.

Plastic – a material that deforms under stress, ceasing to flow when the stress is relieved; but that flows when the stress is sustained.