Instrumental Technique

Diffusing-wave spectroscopy:

Dynamic light scattering in the multiple scattering limit

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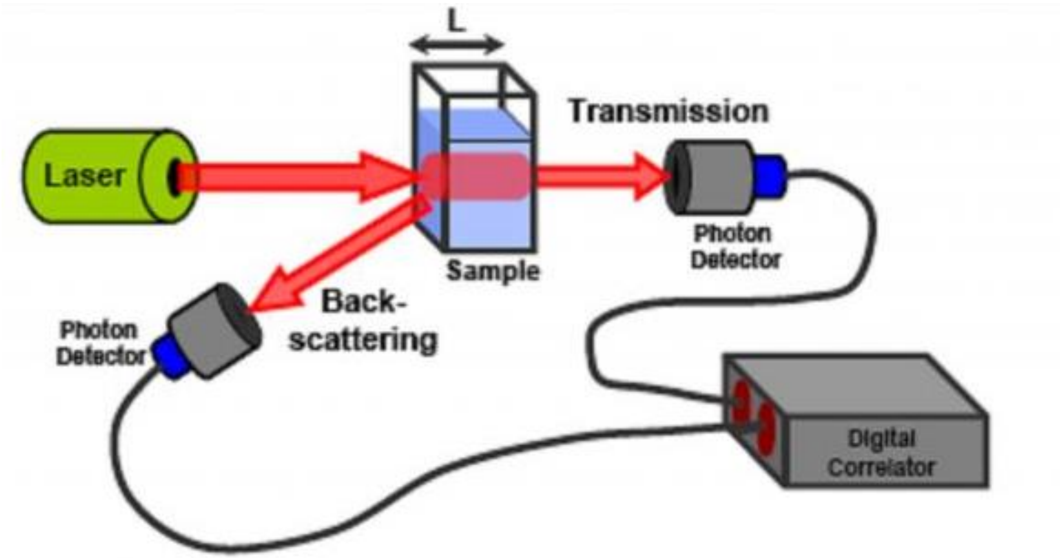
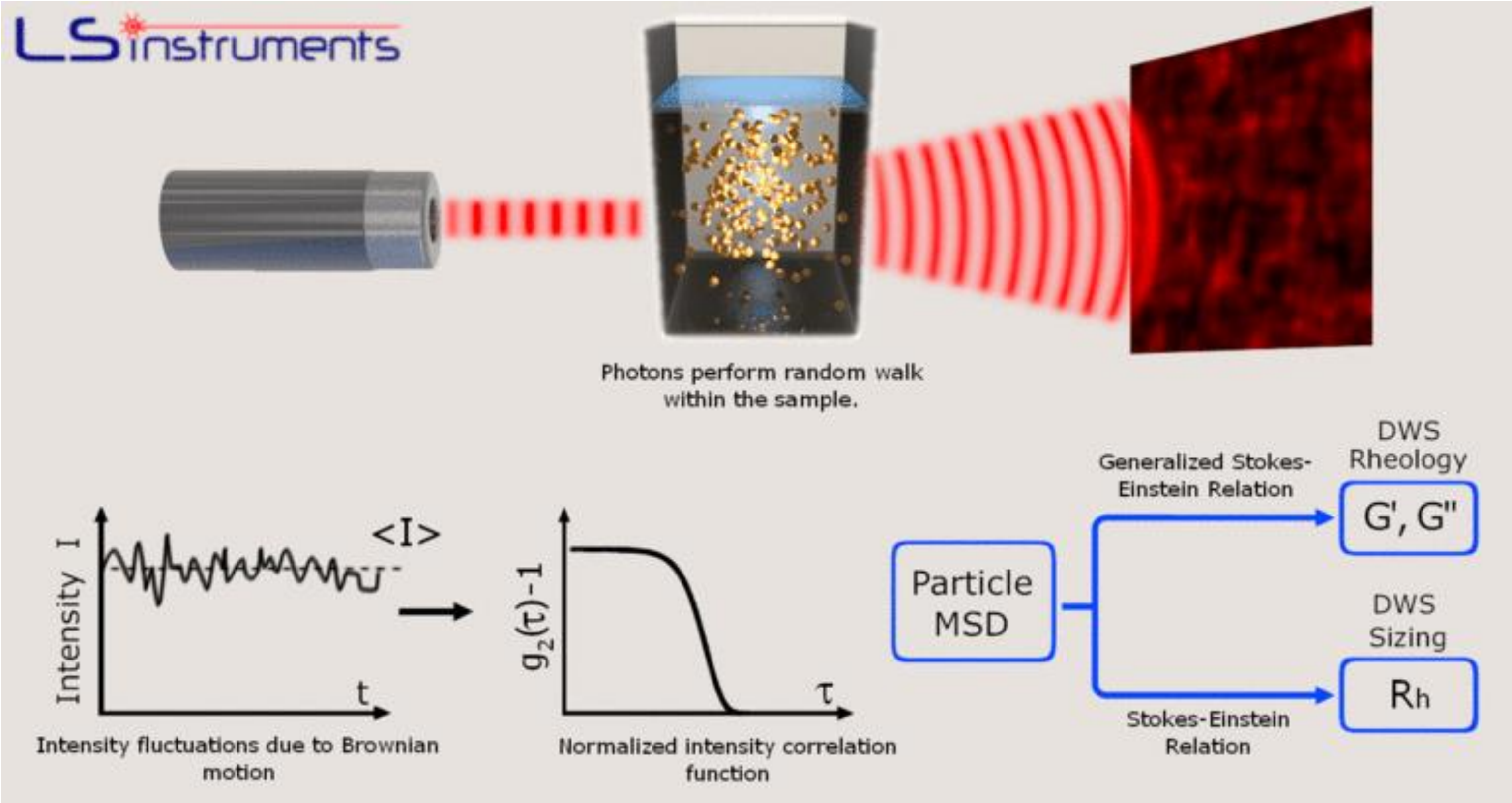
21.10.2017

What is Diffusing-wave spectroscopy?

- ❖ Diffusing-wave spectroscopy (DWS) is an optical technique derived from dynamic light scattering (DLS) that studies the dynamics of scattered light in the limit of strong multiple scattering.
- ❖ DWS exploits the diffusive nature of the transport of light in strongly scattering media to relate the temporal fluctuations of the multiply scattered light to the motion of the scatterers.



- ✓ In DWS each detected photon is scattered by many particles; it is therefore more sensitive to small particle displacements compared with DLS, where photons are scattered only once.
- ✓ Whilst DLS typically can detect displacement of several nanometers, DWS can measure sub nanometer displacements.
- ✓ As a result, DWS is an excellent tool to study slow dynamics and non-ergodic samples such as gels, foams, and highly concentrated suspensions.



Particles in suspension undergo Brownian motion due to solvent molecule bombardment in random thermal motion.

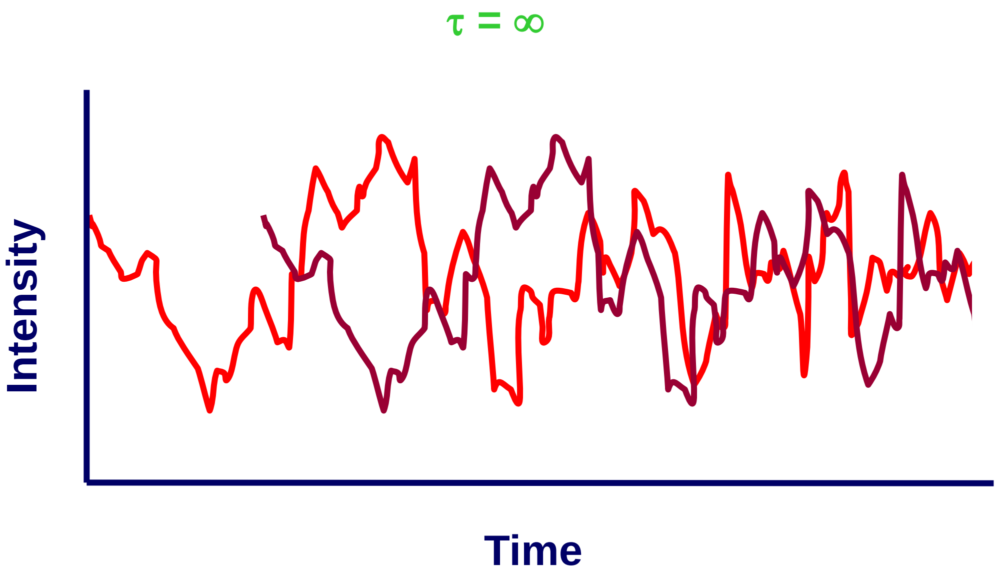
DLS measures fluctuations in the scattered intensity caused by Brownian Motion.

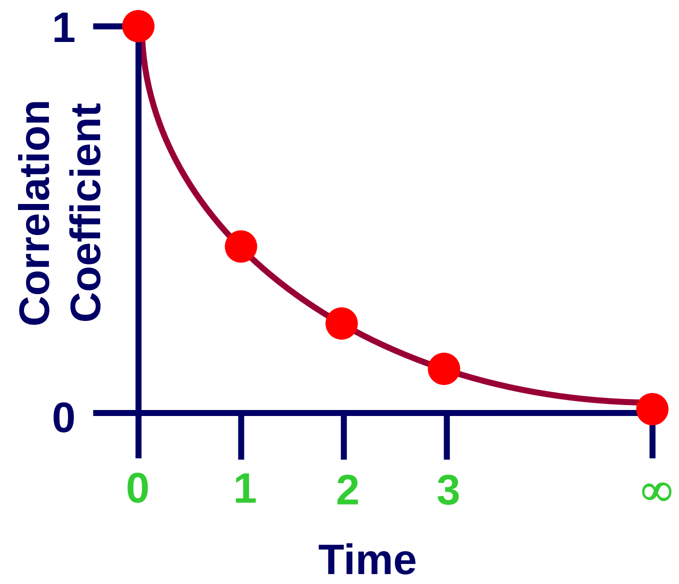
Small Particle = Fast Brownian motion = Fast Intensity Fluctuations
Large Particle = Slow Brownian motion = Slow Intensity Fluctuations

$$P(r,t|0,0)=(4\pi Dt)^{-3/2}\ \exp\left(-r^2/4Dt\right)$$

$$D=k_B T/6\pi\eta a$$

Random fluctuations are interpreted in terms of the Auto Correlation Function





The dynamic information of the particles is derived from an autocorrelation of the intensity trace recorded during the experiment.

$$g^2(q;\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2}$$

Principles of DWS

The correlation function of a path consisting of n scattering events,

$$g_1^n(t) = \left\langle \exp\left\{ -i \sum_{j=1}^{n} \mathbf{q}_j \cdot \Delta \mathbf{r}_j(t) \right\} \right\rangle$$

q scattering vector
Δr displacement of the scattering particle

Scattering events are independent,

$$g_1^n(t) = \left\langle \exp\left\{ -i\mathbf{q} \cdot \Delta \mathbf{r}(t) \right\} \right\rangle_q^n$$

Neglecting the conservation of momentum at each step

$$g_1^n(t) = \exp\left\{ -2(\tau/\tau_0)(s/l^*) \right\}$$

l* transport mean free path

$$\frac{l}{l^*} = \frac{\langle q^2 \rangle}{2k_0^2} \quad s = nl$$

$$\tau_0 = 1/k_0^2 D_0$$

k_0 incident wave vector
D_0 diffusion coefficient

Full auto correlation function,

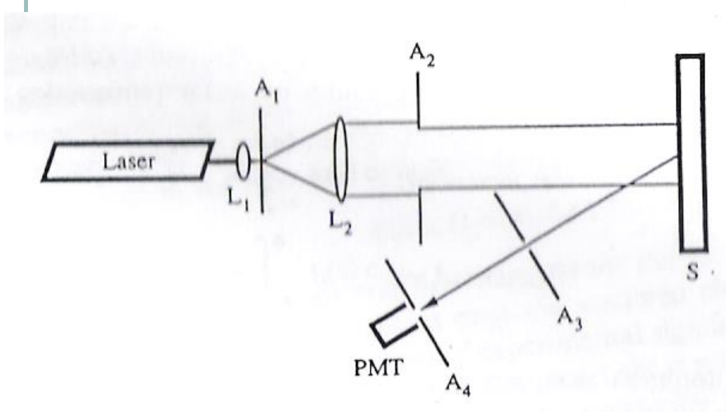
$$g_1(t) = \int_0^\infty P(s)\, e^{-2(\tau/\tau_0)(s/l^*)}\, ds$$

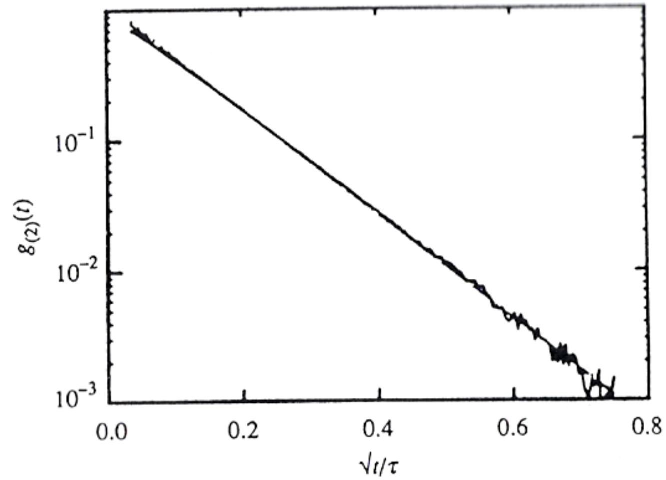
P(S) probability that light travels a pathlength of S

$$D_0 = k_B T / 6\pi \eta a$$

a particle radius,
η viscosity

Backscattering geometry





Backscattering measurements from an aqueous suspension of polystyrene spheres at a volume fraction $\phi = 0.05$. The data are plotted logarithmically as a function of the square root of the reduced time. The smooth line through the data represents fits

$$g_1(t) = \exp\left\{-\gamma\sqrt{6\tau/\tau_0}\right\}$$

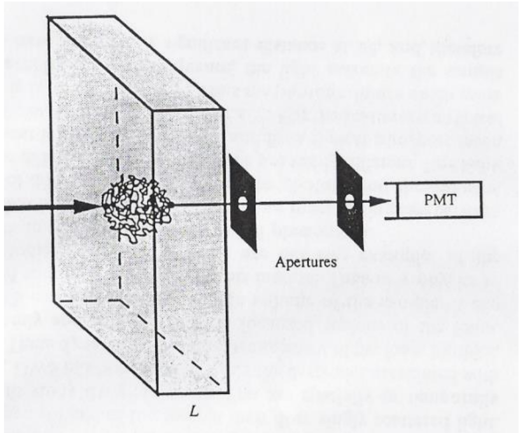
$$\tau_0 = 1/k_0^2 D_0$$

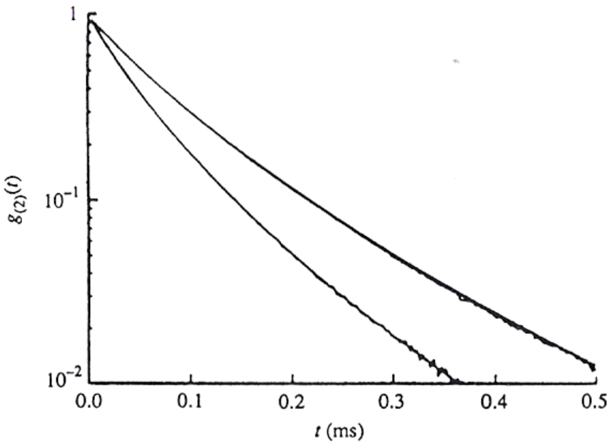
γ independent of *l**: no need to know/measure *l**!

Need to determine γ

γ is a coefficient that depends on the sample and the polarization of the scattered light

Transmission geometry





$$g_1(t) \approx \frac{\left(\frac{L}{l^*} + \frac{4}{3}\right)\sqrt{\frac{6t}{\tau_0}}}{\left(1 + \frac{8t}{3\tau_0}\right)\sinh\left[\frac{L}{l^*}\sqrt{\frac{6t}{\tau_0}}\right] + \frac{4}{3}\sqrt{\frac{6t}{\tau_0}}\cosh\left[\frac{L}{l^*}\sqrt{\frac{6t}{\tau_0}}\right]}$$

$$\tau_0 = 1/k_0^2 D_0$$

Need to determine *l**

Application

DWS

Sizing

Rheology

(when photons probe mechanical properties)

Thank You