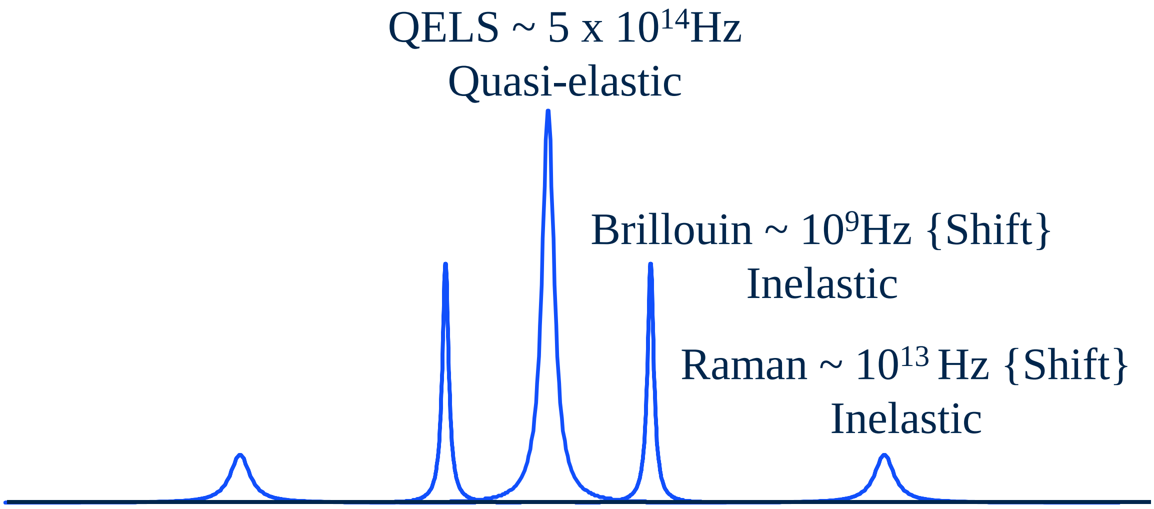
Scattering . 6 Inelastic scattering

Inelastic Scattering.

Light can also be scattered inelastically and if we use a very monochromatic light source we can see very clear evidence of energy (frequency changes) in the scattered light spectrum. The figure below which is not to scale show Brouillon scattering (from phonons) and Raman scattering from vibrations.



Photon Correlation Spectroscopy

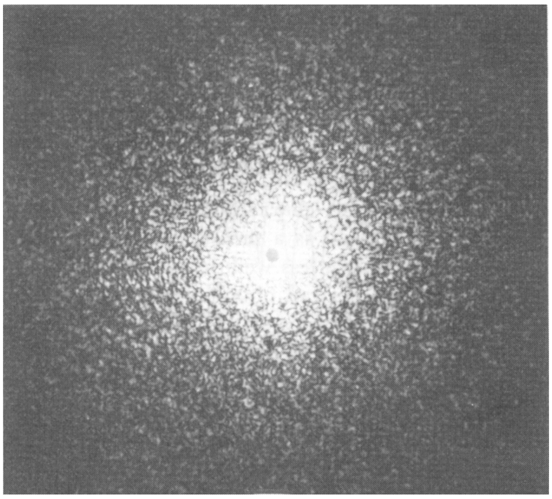
[1] K. J. Randle *Chemistry and Industry* **19** 74-81 [1980]
[2] S.J. Candau in Scientific Methods for the Study of Polymer Colloids and their Applications, Ed. F. Candau and R. H. Ottewill, Kluwer, [1990]

In PCS the scattered light intensity is modulated by the Brownian motion of the diffusing particles and the laser linewidth is broadened. By examining the spectral width Γ / Hz of the scattered light the diffusion of the particles can be measured. One simple approach is to use an analogy to the Doppler effect: the shift in frequency suffered by light scattered from a moving particle. Suppose a particle moving with a velocity u – 3 cm s^{-1} is illuminated by red light from a helium-neon laser of wavelength 633 nm (a frequency of 5 x 10^{14} Hz). This fractional shift in frequency is approximately u/c or 1 x 10^{-10}. The equivalent shift in frequency is very small and leads to a line broadening of the order of 10 to 10000 Hz. The detection of this change can be done using a photomultiplier which detects the difference frequency between the incident light and the scattered light.

Measurements and Fluctuations

As we saw before that scattering is due to fluctuations in refractive index/dielectric constant which are proportional to fluctuations in concentration. In PCS we are interested in both the Q and time dependence of these fluctuations $\delta c(Q,t)$.
In practise we measure these fluctuations in concentration in the time domain:

$I(t).I(t+\tau) \propto \delta c(Q,t)$ [6.1] .This can be envisaged as the light falling on the detector varies randomly due to the Brownian motion of the observed particles. The instantaneous velocity of the particle v will be damped by the viscous force of the surroundings so using Newton's law for force $F = ma$ [6.2] where m is the mass of the particle and a its acceleration. The viscous force is the Stokes force $F = 6\pi\eta R_H$ [6.3] where η *is the viscosity of the medium and* R_H is the hydrodynamic radius of the particle .Hence



$$m\frac{dv}{dt} = -6\pi\eta a v$$ [6.4] whose solution is

$$v = v_o \exp(-t/\tau_B)$$ where $\tau_B = m/6\pi\eta a$ [6.5]

τ_B is the Brownian relaxation time which for a 100nm polystyrene particle in water is ~ 5.8 x 10^{-10} s. This is the typical time for which this particular velocity persists. Collusions and frictional dissipation see to it! We measure these fluctuations as a speckle pattern.
The signal falling on the detector is an a direct measure of these fluctuations

Correlation functions:-

The correlation function is defined as follows: $$\langle I(0)I(\tau)\rangle = \lim_{T\to\infty}\frac{1}{T}\int_0^T dt\ \ I(t)I(t+\tau)$$ [6.6]

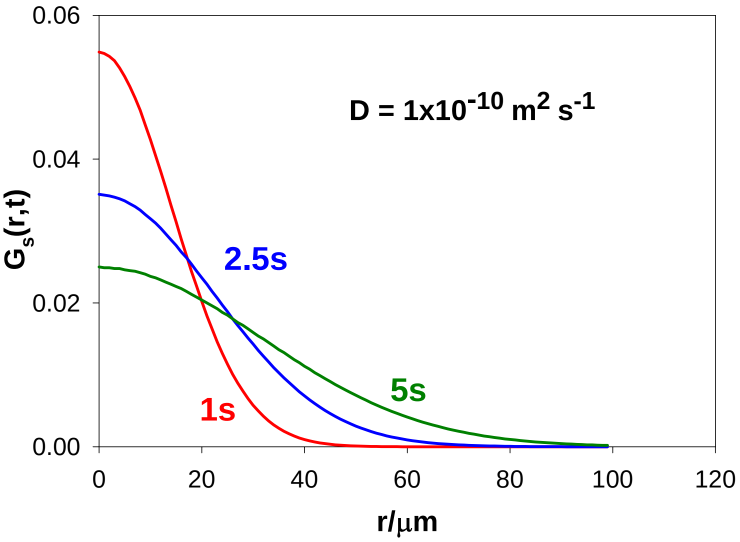
where τ is the correlation time and the average is taken over the time interval T in the limit as T tends to infinity. We van define another correlation function $G_s(\overline{r},t)$ as the total self-correlation function. It is essentially the probability that a particle at $\overline{r}$ *at* $t=0$ *is at* $(\overline{r}+\delta\overline{r})$ *at* $(t+\delta t)$ [6.7]
For isotropic motion $G_s(\overline{r},t)$ is the solution of the 3-dimensional diffusion equation

$$\frac{\partial G_s(\overline{r},t)}{\partial t} = D\frac{\partial^2 G_s(\overline{r},t)}{\partial \overline{r}^2}$$ [6.8]

which is one of Fick's Law, where *D* is the diffusion coefficient . For motion in 3D

$$D = \langle r^2\rangle/6t$$ [6.9]

The form of $G_s(\overline{r},t)$ is a gaussian which is characteristic of random motion.



$$G_s(\bar{r},t) = \frac{1}{(4\pi Dt)^{3/2}}\exp(-r^2/4Dt) \quad [6.10]$$

In 1 dimension the solution is a gaussian function as before in distance [x] and we can write an analogous equation for the propagation of the fluctuations due to diffusion: $\delta c(x,t) = \frac{A}{(4Dt)^{0.5}}\exp(-x^2/4Dt)$ [6.11]

where D is the diffusion coefficient and A is a constant. On scattering we require a solution in Q space which is reciprocal to x. By Fourier transform we can convert the representation:

$$\delta c(Q,t) = \frac{A'}{(4Dt)^{0.5}}\int_{-\infty}^{\infty}\exp(-x^2/4Dt)\exp(iQx)dx \quad [6.12]$$

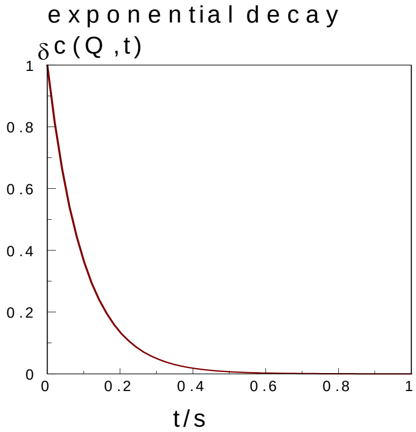
This is a standard Integral: $\int_{-\infty}^{\infty}\exp(-p^2x^2+qx)dx = \frac{\pi^{0.5}}{p}\exp\left(\frac{q^2}{4p^2}\right)$

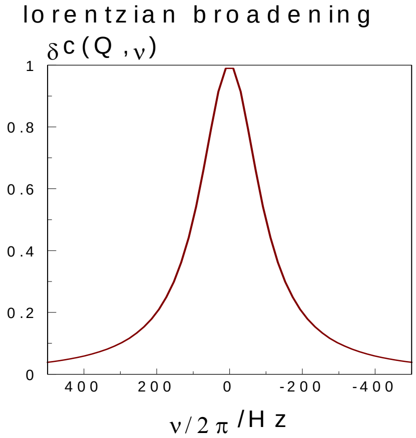
$\therefore p^2 = 1/4Dt$ *and* $q = iQ$ *then* $\delta c(Q,t) = A'\pi^{0.5}\exp(-Q^2Dt)$ [6.13]

Initial conditions $t = 0$ $\delta c(Q,t) = \delta c(Q,0)$ $\therefore$ $\delta c(Q,t) = \delta c(Q,0)\exp(-Q^2Dt)$ [6.14] i.e. in Q space we see an exponential decay of the concentration fluctuation with a time constant $\tau = 1/(Q^2D)$ [6.15]. A further insight into this is to Fourier transform [6.16] into the frequency domain [i.e. a reciprocal of time c.f. Q and x].

This gives a Lorentzian in the frequency domain:

. $\delta c(Q,\omega) = \delta c(Q,\omega_o)\frac{1}{1+Q^2(\omega^2-\omega_o^2)}$ [6.17] with a full width at half-height of $2Q^2D/2\pi$ Hz.





A closely related parameter is the normalised autocorrelation function $g^{(2)}(Q,\tau)$

$g^{(2)}(Q,\tau) = \frac{\langle I(Q,0).I(Q,\tau)\rangle}{\langle I(Q)\rangle^2}$ [6.18] which tends to 1 as τ tends to infinity

and so we often define $g^{(1)}(Q,\tau) = g^{(2)}(Q,\tau) - 1.$ ~ $\exp(-DQ^2\tau)$ [cf 6.14]

Particle size measurements

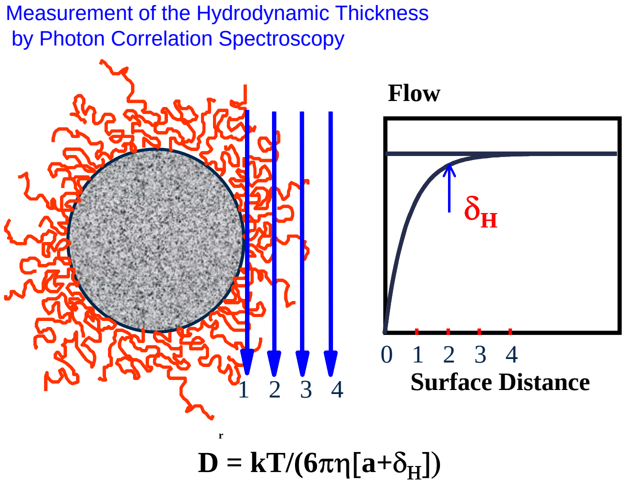
One of the major uses of PCs is to measure particle size and this can be done directly through measuring the correlation time τ and hence the diffusion coefficient and using the Stokes Einstein Equation:

$$D = \frac{kT_B}{6\pi\eta R_H} \quad [6.15]$$

If the sample is polydisperse then we see a distribution of exponentials [6.14] and this is not easy to separate though various averages of the particle size distribution can be found. If is the system is bimodal then two populations can be elicited.

Adsorbed layer Thickness

A simple extension of this idea is to measure the size of a colloidal particle before and after adsorbing a polymer. This then gives us a way of finding the hydrodynamic layer thickness.



Polymer solutions.

Polymer solutions can also be studied but this requires a modification of the simple Stokes Einstein equation [6.15] above as both D and the friction coefficient are functions of concentration. Equation [6.15] is basically the balance between the energy available and friction *f(c)*

$$D(c) = \frac{kT_B}{f(c)}$$ [6.16] . Osmotic pressure is the driving force for diffusion as before so we need to expand this equation in both *D* and *f.* This gives us the following result $D_m = D_o(1+\{2A_2M_w - k_{fm}\}c)$ [6.17] Where A_2 is (1/2 - χ) as before and k_{fm} is the mutual friction coefficient. Hence D can increase or decrease with concentration depending on the solvent quality.