POLYMERS and BIOMATERIALS LABORATORY

Dynamic Light Scattering application in size detection of molecules and molecular aggregates

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Theoretical background

When the light hits small particles, the light scatters in all directions (Rayleigh scattering) as long as the particles are small enough compared to the light wavelength (below 250nm).

The idea of light scattering experiment is presented in Figure 1.
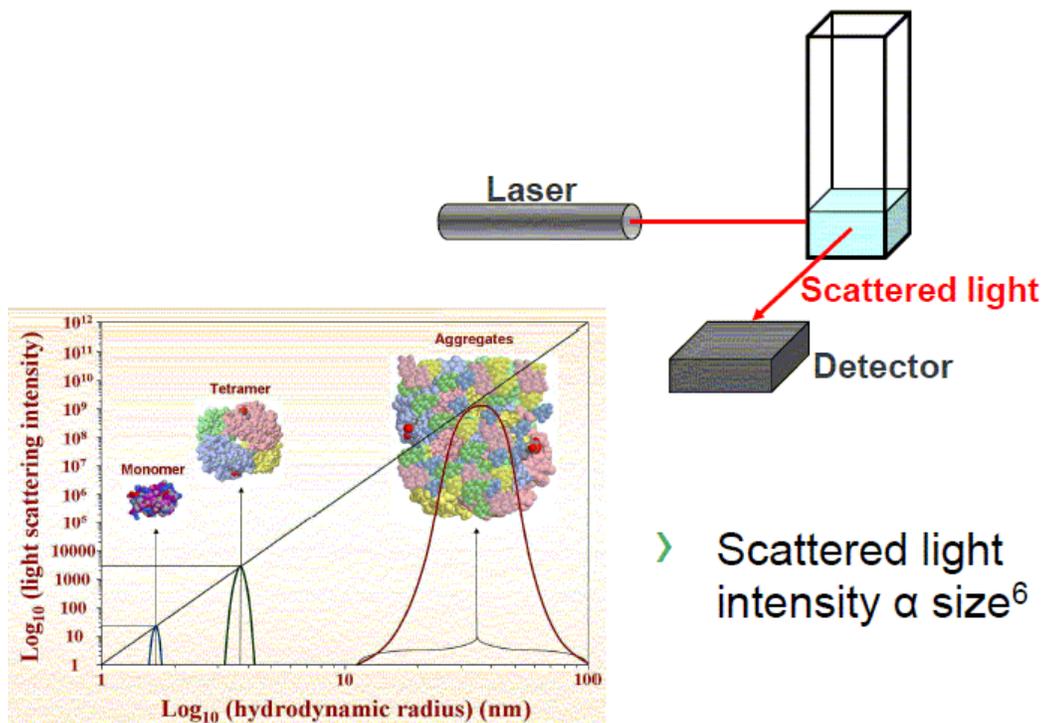
Figure 1. The idea of light scattering (Michael Caves, Malvern)

The scattering of electromagnetic radiation by liquids and solutions can be a useful source of structural information. Light scattering is consequent to refractive index differences (i.e. fluctuations) of adjacent volume elements caused by random thermal motion, and density as well concentration fluctuations. For a scattering particle characterized by a velocity $v0$, the

frequency of the scattered (or Doppler displaced) wave, $\Delta\nu$, is $\Delta\nu = \nu 0 - \nu sc = \nu /c$, where c is the speed of light and $\nu 0$ and νsc are source and scattered frequencies. The spectral distribution of the scattered light, $Isc(\nu)$, is broadened as compared to that of the incident wave, $I0(\nu)$. This effect (frequency broadening) caused by molecular motion is called Dynamic Light Scattering (DLS). DLS is also known as Photon Correlation Spectroscopy, Quasi-Elastic Light Scattering or Inelastic Rayleigh Scattering).

DLS technique measures Brownian motion in the liquids and solutions. The Brownian motion of molecules became more rapid when the size of particles scattering light are smaller. DLS was discovered shortly after gas lasers were applied as light sources in optical scattering investigations. Lasers are high intensity sharply monochromatic light sources; as a consequence the spectral broadening of the low intensity Rayleigh scattered radiation is relatively easy to detect.

The dynamic information of the particles scattered light is derived from the autocorrelation function of the intensity $g^2(q;\tau)$ registered during time and on the base of this function the second order autocorrelation curve is generated. The autocorrelation function at given wave vector, q (sometimes called „scattering vector"), decay time, τ and intensity, I, is the following: $g^2(q;\tau) = \dfrac{\langle\langle I(t)I(t+\tau)\rangle\rangle}{\langle I(t)\rangle^2}$. For the short decay time the correlation between scattered intensity of the initial and final states is high. The signals are almost unchanged. The situation is substantially different for

longer decay times. In this case signal decays exponentially. The reason is the motion of the particles causes that there is no correlation between scattered intensity of this the initial and final states. The exponential decay is straight related to the dynamic situation in the system it means to the motion of the particles and especially to their diffusion (to their diffusion coefficient). Assuming distribution the autocorrelation function can be fitted using numerical methods. If the sample is monodisperse then the decay is a single exponential. The Siegert equation relates the second-order autocorrelation function with the first-order autocorrelation function $g^1(q;\tau)$ as follows:

$$g^2(q;\tau) = 1 + \beta \left[g^1(q;\tau) \right]^2 \qquad (1)$$

where: the parameter β is a correction factor that depends on the geometry and alignment of the laser beam in the light scattering setup. The autocorrelation function involves on size determination of particles scattered light.

As it was mentioned the intensity of scattered light registered during DLS experiment is a source of the autocorrelation function generation. Next different mathematical approaches are employed to obtain from it information about particles scattered light. The simplest approach assumes that the first order autocorrelation function is for single exponential decay. This is appropriate for populations which are monodisperse. The autocorrelation function for such populations is the following:

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$$g^1(q, \tau) = \exp(-\Gamma\tau) \quad (2)$$

where: Γ is the decay rate. Depending on the wave vector q the translational diffusion coefficient D_t can be derived at a single angle or at range of angles. The relation between Γ and D_t is through wave vector q as follows:

$$\Gamma = q^2 D_t \quad (3)$$

with

$$q = \frac{4\pi n_0}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (4)$$

where: λ is the incident laser wavelength, η_o is the refractive index of the sample and Θ is angle at which scattered light is detected. Note, that q is a function of scattering angle and incident light frequency, and varies with experimental conditions (temperature, pressure, concentration etc.). Assuming a spherical shape of particles translational diffusion coefficient D_t can be used to calculate the hydrodynamic radius through the Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi \eta r} \quad (5)$$

which is true for diffusion of spherical particles through liquid.

In practice samples are polydisperse. In such cases the autocorrelation function is a sum of the exponential decays corresponding to each of the species present in the population. There are employed different methods which have been developed to extract information about analyzed

population from autocorrelation function. Among the most popular are: Cumulant and Contin.

Generally, in practice the time-averaged intensity of scattered light at given angle, frequency, and averaging times, $I_{SC}(v, \theta, <t>)$ thus depends on the dynamics of decay of the refractive index fluctuations, and hence on relaxation rate (decay rate) and diffusion constant.

The typical correlation functions for small and large particles in comparison to perfect correlation are shown in Figure 2.
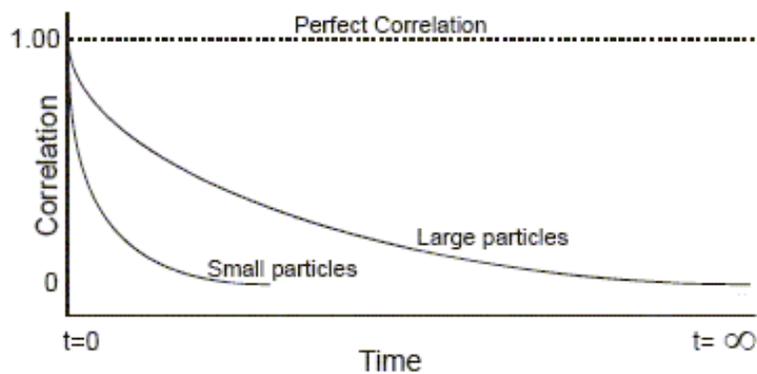
Figure 2. Correlation functions for large and small particles .

Example of the population size distribution in studied system extracted from autocorrelation function is given in Figure 3.
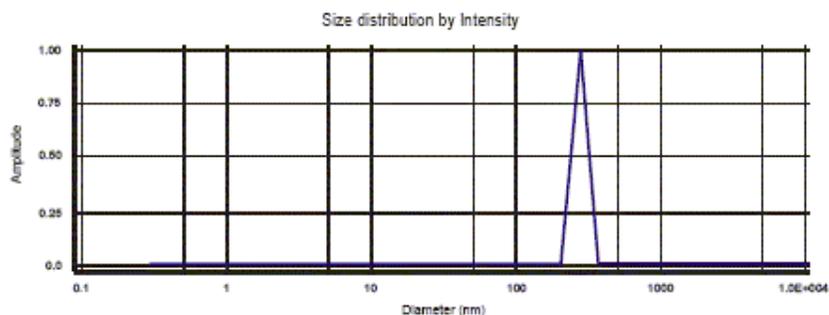
Figure 3. A typical size distribution.

The implementation of DLS requires high-speed digital processing of stochastic optical signals and usually involves photon counting (detection) over regularly timed intervals of variable length. The statistical and stochastic concepts used in photon correlation techniques discussed in detail by Schätzel (1993).

A method for calculation of the dynamic scattering function is clearly described by Akcasu (1993), but unfortunately numerically exact solutions are only possible for highly idealized cases. There is no tractable general theory that encompasses all regions of concentration and temperature. Even so, theoretical models do exist which describe the (n x n) dynamic scattering matrix, $S(q,t)$, for limiting dilute or semi-dilute conditions. $S(q,t)$, sometimes called the dynamic structure factor, can be represented by a superposition of exponential modes with different relaxation frequencies. The interpretation proceeds to resolve such modes into the so-called slow and fast (or short and long time) mobilities. The scattering lengths probed in DLS usually lie between $10^2 \div 10^4$ Å and are often expressed in terms of the inverse scattering vector q^{-1}. Recent advances in DLS techniques have made it possible to measure accurate autocorrelation functions covering 12 decades in delay time (i.e. from ~12.5ns to ~10^4 seconds) allowing practical application of DLS to the study of dilute and semidilute polymer solutions (Brown and Nicolai 1993) as well as proteins, micelles, emulsions, nanoparticles or colloids.

Presently, DLS is one of the widely used light scattering techniques because it allows particles and molecules sizing down to 0.5nm radius.

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