Chapter 2

Dynamic Light Scattering

2.1 Introduction

Light scattering is a powerful technique to study the physical (structural and dynamical) properties of a system (particularly of solutions). Among many advantages of this technique, the most important that can be emphasized is a non-perturbative technique, provided the intensity of light should not be high enough to ionize the system. Depending on the change in the energy between the incident and the scattered light, the scattering phenomena can be called either as an elastic scattering (Rayleigh Scattering) or quasi-elastic scattering (Rayleigh-Brillouin Scattering) or inelastic scattering (Raman Scattering). The elastic light scattering comprises of static light scattering (SLS) and Dynamic Light Scattering (DLS). The combination of these two provides a powerful tool to study the complete physical properties of the system. In the static light scattering the information about static physical properties (like molecular weight, radius of gyration, second virial coefficient of inter and intra-particle interaction, etc.) of the macromolecules are contained in the angular dependence of the scattered intensity. In contrast, the dynamic light scattering probes the transport properties (like diffusion coefficient, hydrodynamic radius, etc.) of the macromolecules under different thermodynamical and hydrodynamic environments. Let us compare the sensitivity of this technique vis-à-vis other methods. If a particle of radius ‘r’ is to be observed, in a viscosity experiment the particle size is proportional to mass and hence the viscosity (which is the measured parameter) will vary as $r^3$. In an optical microscopy experiment, the sensitivity will vary, as $r$ whereas in light scattering it will
be $r^6$. So a very small change in size produces a large change in the measured intensity of the scattered light.

It has long been realized that any excitation, which modulates the refractive index of a condensed matter medium, can give rise to scattering of light. For example, a perfect homogeneous crystal scatters no light in all directions except in the forward direction. The reason being that in a perfectly ordered crystal the scattered light coming out of the lattice point interferes destructively and hence the effective intensity is negligibly small. So the implication is that, to get finite intensity, the destructive interference has to be incomplete. But in reality at any point of time any substance has got a finite heat content due to which it gives rise to finite scattered intensity. From the above discussion it is clear that light will be scattered only if the local change in concentration is accompanied by a change in refractive index, i.e., $(\partial n / \partial c) \neq 0$.

Before discussing about DLS in details it is worthwhile to discuss the salient feature of scattering in general. In a typical experiment, light is scattered from a macromolecular solution and detector is placed at an angle $\theta$ with respect to the direction of propagation of light. The physical state of the incident light is characterized by frequency $\omega$, wave vector $\vec{K}_i$ and state of polarization $P_i$. The corresponding parameters describing the scattered light will be $\omega_s$, $\vec{K}_s$ and $P_s$. During the scattering experiment, the energy, momentum and the state of polarization of the incident light can undergo considerable change. However since we are only interested in quasi-elastic scattering, it is safe to consider the scattered energy $E_s$ ($= \hbar \omega_s$) is almost same as the incident energy $E_i$ ($= \hbar \omega_i$) and consequently the magnitude of the corresponding wave vectors are almost equal, i.e., $K_s \approx K_i$. Let us consider one element of the macromolecular solution is at a position 'r' with respect to an arbitrary origin in a medium with refractive index 'n' Fig. 2.1. Since, we have argued that in a quasi-elastic light scattering experiment $K_s \approx K_i$, one can write this as [1].
\[ K_s = K_i = \frac{2\pi n}{\lambda_0} = \frac{2\pi}{\lambda} \]

where \( \lambda_0 \) is the wavelength in the free-space and \( \lambda \) is the corresponding wavelength in the medium.

The phase difference \( \Delta \phi \) in the wave-zone between the contributions to the scattering from the points 'R' and 'O' is \( 2\pi n / \lambda_0 \) times the path difference (OQ-PR), i.e.,

\[ \Delta \phi = K_s \cdot r - K_i \cdot r = (K_s - K_i) \cdot r = K \cdot r \]

Where, we have defined the scattering wave vector \( \vec{K} \) as,

\[
\vec{K} = \left( \vec{K}_s - \vec{K}_i \right) \\
\Rightarrow K^2 = K_s^2 + K_i^2 - 2K_sK_i \cos(\theta) \\
= K_i^2 + K_i^2 - 2K_sK_i \cos(\theta) \\
= 2K_i^2 (1 - \cos \theta) \\
= 4K_i^2 \sin^2(\theta / 2) \\
K = 2K_i \sin(\theta / 2) \\
\Rightarrow K = \frac{4\pi n}{\lambda_0} \sin(\theta / 2) \quad (2.1) \]

Where, '\( \theta \)' is the scattering angle between \( \vec{K}_i \) and \( \vec{K}_s \) as shown in Fig.2.1 (b)

![Fig. 2.1. (a) Scattering Geometry; (b) geometrical construction for the scattering wave vector \( \vec{K} \).](image)

The reciprocal of the scattering wave vector \( \vec{K} \) physically signifies the length scale over which the sample is probed. It is clear from the above (Eq. 2.1) that the probing length depends on wavelength of the light as well as on the scattering angle. As long as
the characteristic length of the macromolecule is less than this length scale, one would see the signature of the Rayleigh scattering.

In light scattering the typical accessible length scale is \( \sim 50\text{Å} \) to \( 2000\text{Å} \), where as in the case of neutron scattering it is \( \sim 5 \text{ Å} \) to \( 50 \text{ Å} \) and in the case of x-ray scattering it is \( 1\text{Å} \) to \( 5\text{Å} \). If one wishes to study samples smaller than this size, one has to go over to electron scattering.

2.2 Theory of Light Scattering

Let us consider only the scattering geometry most commonly used in the laboratory, shown schematically in Fig. 2.2. The incident light, a vertically plane-polarized monochromatic wave, traverses the scattering volume \( V_s \) containing \( N_s \) particles. The component \( E_s \) of the scattered electric field, polarized perpendicular to the scattering plane, is observed at the distant point \( r_s \) from the scattering volume and at an angle \( \theta \).

Multiple scattering effects are ignored, so that the complex amplitude of the scattered electric field \( E_s(K,t) \) can be taken as a sum of contributions from the individual scatterer and is given by

\[
E_s(K,t) = \sum_{j=1}^{N_s} a_j(t) \exp[i \vec{K} \cdot \vec{r}_j(t)]
\]  

(2.2)
Where $\vec{K}$ is the scattering wave vector, $a_j(t)$ the amplitude of the scattered electric field from the jth scattering particle, and $\vec{r}_j(t)$ the position of the center of particle j at time t. The magnitude of the scattering wave vector is given by Eq. (2.1)

$$K = \frac{4\pi n}{\lambda_0} \sin \frac{\theta}{2}$$

Where n is the refractive index of the medium and $\lambda_0$ the wavelength of the light in vacuum. The average intensity scattered from particles is

$$I_s = <|E_s(K,t)|^2> = <\sum_j \sum_j a_j a_j' \exp[i \vec{K}.(\vec{r}_j - \vec{r}_j')] >$$ (2.3)

where brackets stand for an ensemble average. The intensity $I_s$ can be obtained experimentally by measuring the excess of scattering of the solution with respect to the solvent, generally expressed in terms of the difference $\Delta R_\theta$ of the Rayleigh ratio of the solution and of the solvent:

$$\Delta R_{\theta, \text{solution}} - \Delta R_{\theta, \text{solute}} = \frac{I_s}{2I_0} I_s$$ (2.4)

where $I_0$ is the intensity of incident light. If we assume that the particles are optically isotropic, which is generally the case for micellar systems and microemulsions, $\Delta R_\theta$ is given by [2]

$$\Delta R_\theta = K_0 c MP(K) S(K)$$ (2.5)

with

$$K_0 = \frac{2\pi^2 n^2}{N_A \lambda_0^2} \left( \frac{dn}{dc} \right)^2$$ (2.6)

Where $N_A$ is Avogadro’s number, M the molecular weight of the particle scattering light and c its concentration (mass/volume), $P(K)$ the intraparticle interference factor, defined as the ratio of scattered intensity with interference over the scattered intensity without interference and $S(K)$ the time-averaged structure factor representing the interparticle interferences, defined by

$$S(K) = 1 + 4\pi N_p \int_0^\infty r^2 [g(r) - 1] \frac{\sin Kr}{Kr} dr$$ (2.7)
\( N_p \) is the number of particles per unit volume and \( g(r) \) is the particle-pair radial distribution function, with \( r \) the distance of interparticle center separation.

Since in this work we have not studied the static light scattering behavior of our systems, I do not discuss SLS and before continuing in DLS, let us have a brief brake and discuss the time correlation function in general.

2.3 Time Fluctuation and Correlation

Time dependent correlation functions have been familiar for a long time in the theory of noise and stochastic processes [3]. Correlation functions provide a concise method for expressing the degree to which two dynamical properties are correlated over a period of time. Let us discuss some of the basic properties of these functions that are relevant to our understanding of light scattering spectroscopy.

Let us consider a parameter 'A' that depends on position and momentum of all the particles in the system. Let us assume that due to thermal and collisional motions, these particles are constantly moving around, so their positions and momentum are changing with time and hence the property of \( A \). Although the constituent particles are moving according to Newton’s equations, their huge number in the system makes their motion appear to be somewhat random. The time dependence of the property \( A(t) \) will generally resemble a noise pattern. Hence the time average of \( A(t) \) can be expressed as

\[
< A(t) > = \lim_{T \to \infty} \frac{1}{T} \int_0^T A(t) \, dt
\]  

(2.8)

Any noise signal, like \( A(t) \), have following properties : the value of \( A \) at two different times \( t \), and \( t + \tau \) can in general have different values so that \( A(t) \neq A(t + \tau) \). Nevertheless when \( \tau \) is very small compared to time of fluctuations in \( A \), then \( A(t) \) will be very close to \( A(t + \tau) \). As \( \tau \) increases the deviation of \( A(t + \tau) \) from \( A(t) \) is more likely to be nonzero. Thus in some sense we can say that the value \( A(t + \tau) \) is correlated with \( A(t) \) when \( \tau \) is small but this correlation is lost as \( \tau \) becomes large compared with
the period of fluctuations. A measure of this correlation is the autocorrelation function of the property $A$, which is defined by

$$< A(t)A(t + \tau) >= \lim_{T \to \infty} \frac{1}{T} \int_0^T A(t)A(t + \tau) dt \quad (2.9)$$

Suppose that time is divided into discrete intervals $\Delta t$, such that $\tau = n \Delta t$ and $T = N\Delta t$ and $t + \tau = (j + n)\Delta t$ and suppose further that $A$ varies very little over the time interval $\Delta t$. Then from definition of ergodicity it follows that Eqs. (2.8) and (2.9) can be approximated by

$$< A(t) >= \lim_{N \to \infty} \frac{1}{N} \sum_{j=1}^{N} A_j$$

$$< A(t)A(t + \tau) >= \lim_{N \to \infty} \frac{1}{N} \sum_{j=1}^{N} A_j A_{j+n} \quad (2.10)$$

Where $A_j$ is the value of the property at the beginning of the $j$th interval. In dynamic light scattering experiments a correlator computes time correlation functions of the scattered intensity (which is a measurable and a positive quantity) in this discrete manner.

For times $\tau$ large compared to the characteristic time for the fluctuation of $A$, $A(t)$ and $A(t + \tau)$ are expected to become totally uncorrelated, thus

$$\lim_{\tau \to \infty} < A(t)A(t + \tau) > = < A(t) > < A(t + \tau) > = < A >^2 \quad (2.11)$$

And for times $\tau$ very small compared to the fluctuation time of $A$, $A(t)$ and $A(t + \tau)$ are expected to be correlated as

$$\lim_{\tau \to 0} < A(t)A(t + \tau) > = < A^2(t) > \quad (2.12)$$

So from the above two equations it can be noticed that the correlation function decays from its initial value $< A^2 >$ at $\tau = 0$ to $< A >^2$ as $\tau$ goes towards infinity. This has been depicted in Fig. 2.3. The time taken by the function to decay to (1/e) th of its initial value, $\tau_A$, is called the correlation time or coherence time.
The time correlation function, $< A(t)A(t + \tau) >$. Initially this function is $< A^2 >$. For times very long compared to the correlation time, $\tau_a$, the correlation function decays to $< A >^2$.

In many applications the autocorrelation function decays like a single exponential so that [6]

$$< A(t)A(t + \tau) >= < A > + \left[ < A^2 > - < A >^2 \right] \exp\left( -\frac{\tau}{\tau_r} \right) \quad (2.13)$$

Where $\tau_r$ is called the relaxation time or the correlation time of the property. It represents the characteristic decay time of the property. If we define

$$\delta A(t) \equiv A(t) - < A > \quad (2.14)$$

which is the deviation of the instantaneous value of $A(t)$ from its average value, it is easy to show that

$$< \delta A(t)\delta A(t + \tau) >= < A(t)A(t + \tau) > - < A >^2 \quad (2.15)$$

and

$$< \delta A^2 >= < \delta A(0)\delta A(0) >= \left[ < A^2 > - < A >^2 \right] \quad (2.16)$$

combining Eqs. (2.13) (2.15) and (2.16) yields

$$< \delta A(t)\delta A(t + \tau) >= < \delta A^2 > \exp\left( -\frac{\tau}{\tau_r} \right) \quad (2.17)$$

$\delta A(t)$ is often referred to as fluctuation in that it represents the deviation of the property from its average value. Not all fluctuation decay exponentially. We often want to have some parameter that typifies the time scale for the decay of the correlations. We define the correlation time $\tau_c$ from Eq. (2.17) as
We note that for exponential decay $\tau_c = \tau_r$. In general, the correlation time will be a some complicated function of all the relaxation processes contributing to the decay of $\delta A$.

Thus as a summery, autocorrelation function is a measure of the similarity between two noise signals $A(t)$ and $A(t + \tau)$ (which is intensity in the case of dynamic light scattering). Then, at $\tau = 0$, these two signals are completely in phase with each other and $< A(t)A(t + \tau) >$ is large; as $\tau$ increases $A(t)$ and $A(t + \tau)$ get out of phase with each other and the autocorrelation function $< A(t)A(t + \tau) >$ is small.

Having discussed the time fluctuation and autocorrelation in general, let us go back to the DLS. Dynamic light scattering provides experimental estimates of $g^{(1)}(\tau)$, the normalized temporal autocorrelation function of the electric field amplitude and $g^{(2)}(\tau)$, the normalized temporal autocorrelation function of the intensity [4-6]:

$$g^{(1)}(K, \tau) = \frac{< E_s(K,t)E_s^*(K,t+\tau) >}{< |E_s(K,t)|^2 >}$$

$$g^{(2)}(K, \tau) = \frac{< E_s^*(K,t)E_s(K,t)E_s^*(K,t+\tau)E_s(K,t+\tau) >}{[< |E_s(K,t)|^2 >]^2}$$

Where $\tau$ is the delay time. Since scattered electric field in our case is originating from a isotropic solution, the scattered field is assumed to be a stationary Gaussian random process so that $g^{(1)}(\tau)$ and $g^{(2)}(\tau)$ are related by the Siegert relation given by [7]

$$g^{(2)}(K, \tau) = [g^{(1)}(K, \tau)]^2 + 1$$

Three lengths are relevant for the discussion of the scattering from particles. These lengths are: $2\pi/K$, which is a measure of the spatial scale being probed by a light scattering experiment; $\xi$, the correlation length, which defines the range of interaction
(in the high dilution limit \(\xi\) is simply a parameter characteristics of the particle size such as the radius); and \(N_p^{-1/3}\), the average interparticle spacing.

For simplicity we are considering separately the case \(K\xi/2\pi<<1\) and \(K\xi/2\pi>>1\).

### 2.4 Light Scattering in the Limit \(K\xi/2\pi<<1\)

If \(K\xi/2\pi<<1\), the electric field amplitude \(a_j\) of the light scattered by particle \(j\) is generally independent of both scattering wave vector \(\vec{K}\) and the time \(t\). The scattered electric field is therefore given by [see Eq. (2.2) ]

\[
E_s(k,t) = \sum_{j=1}^{N} a_j \exp[i\vec{k}.\vec{r}_j(t)]
\]  

(2.22)

The autocorrelation function \(g^{(1)}(K,\tau)\) can be written as

\[
g^{(1)}(K,\tau) = \frac{F(K,\tau)}{S(0)}
\]  

(2.23)

where the static structure factor, \(S(0)\) is

\[
S(0) = \frac{N_A}{M} K_b T \left( \frac{\partial \Pi}{\partial c} \right)^{-1}
\]  

(2.24)

Where \(c\) is concentration, \(\Pi\) is osmotic pressure, and \((\partial c/\partial \Pi)\) is osmotic compressibility and the dynamic structure factor is given by

\[
F(K,\tau) = \left( N_s a^2 \right)^{-1} \sum_j \sum_{j'} a_j a_{j'} \exp\{i\vec{K}.[\vec{r}_j(\tau) - \vec{r}_{j'}(\tau)]\}
\]  

(2.25)

With \(N_s a^2 = \sum_{j=1}^{N} a_j^2\) and the bar indicates an average over the distribution of scattering amplitudes.

For a polydisperse system, \(F(K,\tau)\) is a complicated function of \(K\) and \(\tau\). Simple expressions have been derived for \(F(K,\tau)\) by Pusey et al. [8,9] for various limiting conditions. Their model is based on the assumption proposed by Weismann [10] that particle size distribution dose not affect the particle correlation and the dynamics.
Then the temporal average and the particle size distribution can be separated in Eq. (2.25) to give

\[ F(K, \tau) = (1 - y)F'(K, \tau) + y F^S(K, \tau) \]  

(2.26)

Where

\[ y = 1 - \frac{a^2}{A^2} \]  

(2.27)

\[ F'(K, \tau) = \frac{1}{N_s} \sum_{j=1}^{N} \sum_{j'=1}^{N} < \exp[i \vec{K}.(\vec{r}_j(0) - \vec{r}_{j'}(\tau))] > \]  

(2.28)

\[ F^S(K, \tau) = < \exp[i \vec{K}.(\vec{r}(0) - \vec{r}(\tau))] > \]  

(2.29)

and \( F'(K, \tau) \) and \( F^S(K, \tau) \) are, respectively, the "ideal" full and self dynamic structure factors that would apply to monodisperse systems. In hydrodynamic regime, that is, when \( 2\pi / K \) is much larger than the most probable interparticle spacing, the full dynamic structure factor \( F'(K, \tau) \) describes the dynamics of sinusoidal spatial variations. These variations are expected to decay by a linear diffusive mechanism [11,12] so that

\[ F'(K, \tau) = S(0) \exp(-D_c K^2 \tau) \]  

(2.30)

Where \( D_c \) is the collective diffusion coefficient, which can be written as the ratio of an osmotic driving force \( \partial \Pi / \partial N_p \) and a friction coefficient \( f_c \):

\[ D_c = (f_c)^{-1} \frac{\partial \Pi}{\partial N_p} \]  

(2.31)

Since \( N_p = (N_M/c) \), from Eqs. (2.24) and (2.31),

\[ D_c = S(0)^{-1} (f_c)^{-1} K_b T \]  

(2.32)

The coefficient \( D_c \) is the same as that measured in the macroscopic gradient diffusion.
The self-dynamic structure factor $F^S(K, \tau)$ describes the motion of a single particle through the suspension and decays exponentially in time

$$F^S(K, \tau) = \exp(-D_s K^2 \tau)$$  \hspace{1cm} (2.33)$$

Where $D_s$ is the self-diffusion coefficient, which is given by

$$D_s = k_B T (f_s)^{-1}$$  \hspace{1cm} (2.34)$$

Where $f_s$ is the frictional coefficient for the self diffusion of the particles. Equations (2.26), (2.30), and (2.33) lead to

$$F(K, \tau) = (1 - y) S(0) \exp(-D_c K^2 \tau) + y \exp(-D_s K^2 \tau)$$  \hspace{1cm} (2.35)$$

For mono-disperse systems, $y = 0$ in Eq. (2.35) and therefore $F(K, \tau)$ measures only the collective diffusion process:

$$F(K, \tau) = S(0) \exp(-D_c K^2 \tau)$$  \hspace{1cm} (2.36)$$

For very dilute systems, $S(0) = 1$, and the frictional coefficients $f_c$ and $f_s$ are both equal to $f_0$, which is given by the Stokes expression:

$$f_0 = 6 \pi \eta_0 R_H$$  \hspace{1cm} (2.37)$$

with $\eta_0$ the viscosity of the continuous phase and $R_H$ the hydrodynamic radius of the particle. Therefore the dynamic structure factor is

$$F(K, \tau) = \exp(-D_0 K^2 \tau)$$  \hspace{1cm} (2.38)$$

Where $D_0$ is the free-particle diffusion coefficient as given by

$$D_0 = \frac{k_B T}{6 \pi \eta_0 R_H}$$  \hspace{1cm} (2.39)$$
For polydisperse noninteracting systems, $F(K, \tau)$ is, as is well known, a sum of exponentials, one for each species of particles:

$$
\lim_{c \to 0} F(K, \tau) = F_0(K, \tau) = \frac{\sum N_i a_i^2 \exp(-D_{0i} K^2 \tau)}{\sum_i N_i a_i^2} \tag{2.40}
$$

Where $N_i$ is the number of particles with diffusion coefficient $D_{0i}$ and electric field amplitude $a_i$. For narrow size distribution, the exponentials in Eq. (2.40) can be expanded about a mean value [13,14]

$$
F_0(K, \tau) = \exp\left(-<D_0>K^2\tau\right)\left[1 + \frac{V}{2} <D_0>^2 K^4 \tau^2 + O(\tau^3)\right] \tag{2.41}
$$

Where

$$
<D_0> = \frac{\sum_i N_i a_i^2 D_{0i}}{\sum_i N_i a_i^2} \tag{2.42}
$$

and the variance is given by

$$
V = \frac{<D_0^2>}{<D_0>^2} - 1 \tag{2.43}
$$

and

$$
<D_0^2> = \frac{\sum_i N_i a_i^2 D_{0i}^2}{\sum_i N_i a_i^2} \tag{2.44}
$$

In micellar systems, as described in Chapter one, the micelles exists only above the critical micellar concentration. Equation (2.30) shows that the measurements of the first cumulant of the autocorrelation function in the vicinity of the CMC will provide a $z$ average diffusion coefficient $<D_0>$. The average hydrodynamic radius being related to $<D_0>$ through Eq. (2.39). The second cumulant in Eq. (2.41) gives the variance $V$, which is a measure of the width of the distribution of decay rates.
2.5 Light Scattering in the $K \xi / 2\pi >> 1$

If the particle size or the correlation length is not very small compared to the wavelength of the incident light, interference effects produce both reduction of the scattered intensity and a broadening of the dynamic structure factor. For large spherical particles, the autocorrelation function $g^{(1)}(\tau)$ of a scattered electric field still decays exponentially in time according to Eqs. (2.23) and (2.36).

For non-spherical particle, Pecora has derived the expanded expression [6]

$$g^{(1)}(\tau) = S_0(KL)\exp(-K^2D_0\tau) + S_1(KL)\exp(-(K^2D_0 + 6\Theta_r)\tau) + \cdots \quad (2.45)$$

Where the $S$'s are called dynamic form factors, $L$ is the longest dimension of the particle and $\Theta_r$ is the rotational diffusion coefficient. The dynamic form factors have been calculated by Pecora for the case of rigid-road particles and can be found in [6]. When $KL$ increases, $S_0$ decreases and $S_1$ increases. In the case of very flexible cylindrical micelles, an expression similar to Eq. (2.45) can be written [6]

$$g^{(1)}(\tau) = S_0(K^2R_G^2)\exp(-K^2D_0\tau) + S_2(K^2R_G^2)\exp(-(K^2D_0 + \frac{2}{\tau_1})\tau) \quad (2.46)$$

$S_2$ is a dynamic form factor and $\tau_1$ is the relaxation time of the first normal mode of the Gaussian coil. Expansions (2.45) and (2.46) are valid only in a limited range of $KR_G$, typically $3 < K^2R_G^2 < 5$.

2.6 Principle of Operation of Correlator

Correlators are instruments capable of obtaining the correlation function of an electric signal. Mathematically a correlation function is defined as
\[ g^{(2)}(\tau) = \lim_{T \to \infty} T^{-1} \int_{0}^{T} I(t)J(t+\tau)dt \]  

(2.47)

Where \( I(t) \) and \( J(t) \) are signals which depend upon time. \( g^{(2)}(\tau) \) is called autocorrelation function or cross-autocorrelation function depending on whether \( I(t) \) and \( J(t) \) are the same or different signals respectively. A block diagram of a typical digital correlator is shown in [15] Fig. 2.4. The timing and operation of the correlator is controlled by the Sample Time Generator, which divides time into intervals of equal duration, \( \Delta \tau \). The number of pulses at input \( A \) occurring during each sample time is counted by the Shift Register Counter. This situation is illustrated in Fig. 2.5, where \( n_0, n_1, ... \), are the number of pulses appearing at point \( A \) and counted by the Shift Register Counter.

Fig. 2.4. Block diagram of a correlator. Operational principles are discussed in the text.

At the end of each sample time the number in the Shift Register Counter is entered into the first stage of the Shift Register, the number that was in the first stage is shifted to the second, the number that was in the second stage is shifted to the third, etc. As a consequence, after the correlator has been in operation for a brief period of time, the first stage contains \( I(t - \Delta \tau) \), the second \( I(t - 2\Delta \tau) \), the third \( I(t - 3\Delta \tau) \) and the \( k \)th stage contains \( I(t - k\Delta \tau) \).
During the present sample time each pulse appearing at input A is processed by the Adders in the correlator to add each of the numbers stored in the Shift Register to the number stored in the associated channel of the Correlation Function Memory. As an example, consider the pulse sequence in Fig. 2.5. During sample time interval 2, the product \( n_2 n_3 = 0 \) is added to channel 1 of Correlation Function Memory, the product \( n_2 n_4 = 6 \) is added to channel 2, \( n_2 n_5 = 0 \) is added to channel 3, etc.

Thus the correlator will accumulate in the first channel

\[
g^{(2)}(\Delta \tau) = n_1 \tilde{\eta}_1 + n_2 \tilde{\eta}_2 + n_3 \tilde{\eta}_3 + \cdots = \sum_{i=0}^{N-1} n_i \tilde{\eta}_{i+1}
\]

And in the second channel

\[
g^{(2)}(2\Delta \tau) = n_2 \tilde{\eta}_2 + n_3 \tilde{\eta}_3 + n_4 \tilde{\eta}_4 + \cdots = \sum_{i=0}^{N-1} n_i \tilde{\eta}_{i+2}
\]

Fig. 2.5. The train of pulses processed by a correlator.

In general, the \( k \)th channel will contain

\[
g^{(2)}(k\Delta \tau) = n_1 \tilde{\eta}_k + n_2 \tilde{\eta}_{k+1} + n_3 \tilde{\eta}_{k+2} + \cdots = \sum_{i=0}^{N-1} n_i \tilde{\eta}_{i+k}
\]

which is a good approximation to the true correlation function whenever the change in the value of correlation function during the time \( \Delta \tau \) is small. In each of these expressions the numbers \( n_i \) represents the number of times the content of each stage of
the shift register is added to its representative correlation function memory channel and the number $n_{i+k}$ are the numbers stored in the shift register.

The characteristic of a correlator that are important in light scattering experiments are the efficiency of operation, the capacity of the shift register counter and, therefore of the shift register, the range of the sample time available, and the number of channels. We will briefly discuss each of these characteristics bearing in mind that they match the requirements imposed by the majority of experimental condition.

The efficiency with which a correlator performs the sums of equations (2.48)-(2.50) depends critically on the architecture of the correlator. The instrument illustrated in Fig. (2.5) employs a separate adder and multibit counter for each channel. Each adder must handle only a 4-bit by 4-bit sum (assuming the shift register has a 4-bit capacity) and this may be done by a single integrated circuit. Multi-bit counters are not expensive. If the adder is capable of doing a sum every $10^{-7}$ sec, the rate of obtaining sums in a 64-channel correlator is $64 \times 10^7$ sums/sec. An instrument with these abilities will operate at nearly 100% efficiency at sample time of 100 nsec or longer.

The capacity of shift register is measured by the number of bits of information used to represent the intensity during each sample time. Correlators intended for use with fluctuation spectrometers generally use either one or four bits. The one bit or clipped correlator introduces a zero into the shift register if the number of photons detected during a sample time is less than or equal to a preset number (called the clipping level) and a one if the photon count exceeds the clipping level. While it may appear that the correlation function obtained in this way would bear little relationship to the true correlation function, but clipped correlation function is proportional to the true correlation function if the signal is random in the proper way. In particular, the clipped correlation function is proportional to the true function if the signal obeys Gaussian random statistics. This is the case whenever the signals originates from a large number of independent scatterers, and is independent of the form of the correlation function.
However, if the sample contains a few scatterers or the scatterers are coupled together, the clipped correlation function may be distorted.

Correlators having 4-bit shift registers obtain an accurate correlation function for a wide range of input signals, although it is still possible that certain classes of input signals will exceed the operating range of the correlator. For example, a signal having two (or more) greatly different intensities each with small but important fluctuations, would yield erroneous results. In addition to permitting a wide range of input signals, the 4-bit correlator is easier to use because the adjustment of the clipping level is either easier or unnecessary.

The sample-times available to the user are for all practical purposes unlimited at long end. The shortest sample time is consequently the factor of importance. For most fluctuation spectroscopy applications a minimum sample time of 100 nsec is satisfactory, and a number of instruments are available at this speed at moderate prices. Several correlators in the 20nsec or faster category are available at much higher prices. They are largely single-bit instruments intended for use in high speed velocity measurements and do not offer any significant advantage in our present study.

The number of channels required depends on the nature of the correlation function to be studied. If the correlation function consists of a single exponential or a narrow distribution of exponentials, a 64-channel instrument will provide all the detail in the correlation function that can sensibly be used. However, if a broad range of exponential time constants (greater than a factor of 5 between maximum and minimum time constants) or if an oscillatory correlation function is involved, a larger instrument is warranted. In any case, a correlator should have several channels that may be delayed a substantial amount in order to establish a base line.
2.7 Signal to Noise Behavior

In every DLS experiment there are some sources of noise that limit our ability to measure the properties of the scattered light with arbitrary high precision. They are effects due to the small intensity of the scattered light; effects due to a finite duration of the experiment and the effects due to light scattered by unwanted effects (dust, for example). Let us review briefly each of these contributions.

A contribution to fluctuation in the scattered light intensity is caused by the fact that the number of photons detected during each sample time is finite. Suppose that laser beam of power $P_0$ is focused to a beam of radius $r$ on the studying sample by means of a lens. Pecora [15], showed that the total scattered energy incident on the detector (PMT) for each time constant is

$$P_s = P_0 \frac{c}{32\pi Dr \sin \theta \sin^2(\theta/2)} \quad (2.51)$$

Where $c$ is the concentration of the sample, $D$ is the diffusion coefficient and $\theta$ is the scattered angle. Thus, equation (2.51) shows directly that an increase in $P_0$ or $c$ or decrease in $r$ or $\sin \theta \sin^2(\theta/2)$ will all increase the light energy detected by each exponential decay constant. It might appear from this equation that arbitrarily values of solute concentration $c$ could be studied by increasing the detected light energy through the other three factors. There is, however, a practical limit achieved when the light scattered by the solvent is roughly equal in intensity to that scattered by the solute molecules.

The second limitation in accuracy is due to the fact that data are collected for a finite number of decay times of the correlation function. If the correlation function decays as $g^{(2)}(\tau) = 1 + \exp(-DK^2\tau)$ and the total duration of the experiment is $T$, then the number of
decay times during the experiment is $DK^2T$ (the parameters have the same meaning as before). The corresponding signal to noise ratio, even if the detected light level is high, is $S/N = (DK^2T)^{1/2}$. The only way to improve this contribution to the signal/noise ratio (other than increasing the duration of the experiment) is to increase $\Gamma = DK^2$, which requires that light be scattered at a larger angle.

The existence of unwanted signals in the scattered light provides the third limitation to the quality of the light scattering results. Included in this category are such effects as

- Fluctuations in laser intensity.
- Unwanted laser light due to reflections that has not been scattered but acts as a local oscillator.
- Dust, air bubbles, glass particles, bacteria and other foreign matter in the solution.
- Molecules or other artifacts resulting from improper or inadequate sample preparation.
- Light scattered by the solvent.

The first effect can be overcome by starting the experiment half an hour after switching on the laser to let the fluctuation of it to be stabilized.

In considering the second effect, if a small amount of light (small compared to the real scattered light) is unscattered and is able to act as a local oscillator, the correlation function will contain two exponentials, one with a decay of $2DK^2$ and another at $\Gamma = DK^2$ proportional to the intensity of the local oscillator. If the resulting correlation function is fitted to a single exponential, the calculated decay rate will differ from the correct result according to

$$\frac{\Delta \Gamma}{\Gamma} = -\frac{16}{9} \frac{I_{lo}}{I_s},$$

Where $\Delta \Gamma/\Gamma$ is fractional error in the measured decay time constant. Equation (2.52) shows that extreme caution must be taken to avoid small amount of local oscillator if the greatest possible accuracy is to be obtained. This can be done by alignment of the
setup and calibrating it with known dispersed samples, like polystyrene spherical particles.

The light scattered by the solvent cannot, of course, be eliminated. Fortunately it usually does not contribute to systematic effects because it has a broad spectrum. The one example in which this is not true is when relatively large molecules are included in the solvent as, for example, when glucose is added to a solution to alter the viscosity. In this case the correlation function deriving directly from the solvent will cause a significant systematic error. If in doubt it is best to study correlation functions of the solvent alone. They should be flat, when using sample times of relevance to the experiment. If they are not flat, it may be possible to subtract their effect from the final correlation function using careful curve-fitting procedures.

The elimination of dust from a solution is considered by many to be black art. This may be because each sample requires slightly different procedures. For this reason it is not possible to give a single prescription that is guaranteed to lead to clean solutions. There are, however, some methods that should lead to clean solution if combined with sufficient effort on the behalf of the experimenter. These are distillation (usually used only with the solvent), filtering and centrifugation. All the glassware used for preparation of the sample and the cuvette or sample cell should be cleaned so that when filled with clean solvent, no bright scatterers are seen when tested with the focused laser beam. A dirty cuvette (that is, one with the residue of earlier experiments on the inner walls) should be cleaned in acid according to the cuvette maker's instructions. It should next be soaked for a day or more in a solution of water and detergent. For faster cleaning, ultrasonic bath can be used to give better result within one hour. Finally, the cuvette should be rinsed in many volumes of clean water followed the final rinse by distilled water and dried in a warm oven before use.

Centrifugation is one of the important factors in increasing signal to noise ratio by eliminating the foreign matters (like dust particles) in preparing uniform size distribution in general, particularly in micellar solutions.
2.8 Data analysis

The form of the correlation functions we have discussed so far depends on the nature of the sample and can have several kinds of forms. These functions can take single exponential form, two exponential forms and some other forms that is shown in Table 2.1. below. Here $A$, $B$ are constants, $D_R$ is the rotational diffusion coefficient, $M$ is molecular weight, $q$ is the wave number and others have their meaning as before.

Table 2.1. Theoretical form of correlation functions corresponding to various physical processes.

<table>
<thead>
<tr>
<th>Physical process</th>
<th>Theoretical form of $G(\tau)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Translational diffusion of</td>
<td>$A + Be^{-2Dq^2\tau}$</td>
</tr>
<tr>
<td>Single species</td>
<td></td>
</tr>
<tr>
<td>2. Translational diffusion of</td>
<td>$A + \left[ B(M)e^{-D(M)q^2\tau} \right]dM]^2$</td>
</tr>
<tr>
<td>Polydisperse sample</td>
<td></td>
</tr>
<tr>
<td>3. Rotational diffusion of</td>
<td>$A + \left{ \sum_{l\text{ even}} B_l \exp[-(Dq^2 + l(l+1)D_k)\tau] \right}^2$</td>
</tr>
<tr>
<td>Single species</td>
<td></td>
</tr>
<tr>
<td>4. Flexing molecule</td>
<td>$A + \left{ \sum_{m,n} P_{m,n} \exp \left[ - \left( Dq^2 + \frac{m}{\tau_n} \right) \tau \right] \right}^2$</td>
</tr>
<tr>
<td>5. Directed motion, propagating</td>
<td>$A + Be^{-\tau \omega} \cos \omega \tau$</td>
</tr>
<tr>
<td>waves</td>
<td></td>
</tr>
</tbody>
</table>

Given the diversity of the forms that are observed it is clearly impossible to give a single data analysis that will include all experiments. We can, however, discuss the steps that must be taken.

The first step in data analysis is thus the selection of the form (or combination of forms) expected in the correlation function. This selection depends on the experiment under consideration, and to a certain extent, prejudices the outcome of the experiment. Fortunately it is possible to use the well-known chi-squared test to determine if the
choice of the theoretical expression used to fit the correlation function is adequate for the job.

Having determined the form of the expected correlation function, the usual procedure is to write a general expression containing one or more parameters that may adjusted to make the theoretical expression have as nearly as possible the same values as the experimental correlation function. For example, if the correlation function is expected to have the form of single exponential, we would write the theoretical expression as

\[ g_{\text{th}}^{(2)}(\tau) = A + B \exp(-C\tau) \tag{2.53} \]

and vary \( A, B, \) and \( C \) to make \( g_{\text{th}}^{(2)}(\tau) \) resemble the measured correlation function, \( g_{\text{ex}}^{(2)}(\tau) \) as closely as possible at all values of \( \tau \). The theory of determining the best values of the parameters has been extensively developed \[17\]. Without discussing the details of the arguments, we simply state that the best values are those, which minimize \( \chi^2 \) (chi squared) defined as

\[ \chi^2 = \sum_{i=1}^{N} \left[ g_{\text{th}}^{(2)}(\tau_i) - g_{\text{ex}}^{(2)}(\tau_i) \right] / \sigma_i^2 \tag{2.54} \]

Where the sum is to be taken over all values of \( \tau \) for which \( g_{\text{ex}}^{(2)}(\tau) \) has been measured and \( \sigma_i \) is the expected error in \( g_{\text{ex}}^{(2)}(\tau) \). A computer using one of several standard techniques always performs the required minimization.

The quantity \( \sigma_i \) is the standard deviation for the quantity \( g_{\text{ex}}^{(2)}(\tau) \). If \( g_{\text{ex}}^{(2)}(\tau) \) were measured many times, and a plot made showing the number of times \( g_{\text{ex}}^{(2)}(\tau) \) takes on each value, a bell-shaped curve should be obtained with a peak at the true value of \( g_{\text{ex}}^{(2)}(\tau) \) and a half-width at half-height of \( \sigma \). Roughly 68% of all points would lie in the range between \( g_{i,\text{peak}}^{(2)} - \sigma_i \) and \( g_{i,\text{peak}}^{(2)} + \sigma_i \).
The quantity $\chi^2$ defined in equation (2.54) may be normalized by dividing $N-p$, where $N$ is the number of experimental points and $p$ is the number of parameters in the expression to be fitted to the data. The resulting quantity is expected to close to 1, particularly when $N-p$ is large (i.e., there are many more experimental points than parameters). The probability $P(\chi^2)$ that quantifies $\chi^2 / N-p$ will be in the range $\chi^2$ and $\chi^2 \Delta \chi^2$. The plot of $P(\chi^2)$ vs $\chi^2$ looks like a bell-shaped curve and if the resulting curve for the real experimental data is different from this shape it may be presumed that the chosen form for the correlation function is inadequate to represent the data.

2.8.1 Monodisperse System

Now let us discuss some of the specific mathematical techniques used in the analysis of dynamic light scattering data. The methods range from expansion techniques, such as the cumulant method, to the more powerful inverse Laplace transform methods. The general form of the correlation function is assumed to be

$$g^{(2)}(K,\tau) = \left[ \sum_{i=1}^{N} a_i(K) \exp[-\gamma_i(K)t] \right]^2 + B' + \epsilon(t)$$  \hspace{1cm} (2.55)

Where $a_i(K)$ is the relative amplitude of the $i$th decay process with decay rate $\gamma_i(K)$, $B'$ is a constant baseline, and $\epsilon(t)$ represents random fluctuating noise with the constraint that $<\epsilon(t)> = 0$. The simplest method of analysis of $g^{(2)}(K,\tau)$ is to represent the function by a single exponential function with a characteristic relaxation time $\tau_c$:

$$g^{(2)}(K,\tau) \sim A \exp \left[ -\frac{2\tau}{\tau_c} \right] + B$$  \hspace{1cm} (2.56)

where $B$ is a constant baseline. Since the value of $\tau$ characterizes the entire correlation function, its value may vary with the data collection interval $\Delta \tau$. Simple least squares methods are used to determine the adjustable variables $A$, $B$, and $\tau_c$. This is true for any monodisperse system.
2.8.2 Bimodal System

In order to characterize two widely separated relaxation regimes, one can characterize the correlation function as the sum of two exponential functions:

\[ g^{(2)}(K, \tau) \sim \left\{ A_1 \exp\left[ -\frac{\tau}{\tau_1} \right] + A_2 \exp\left[ -\frac{\tau}{\tau_2} \right] \right\}^2 + B \quad (2.57) \]

Nonlinear least squares methods to determine the five adjustable parameters \((A_1, A_2, \tau_1, \tau_2, \text{ and } B)\) may not converge if either the two amplitudes or the two relaxation times are of comparable value. This is because the iterative incremental adjustment to determine the new values of these parameters on successive calculations may be continually interchanged between the two relaxation modes.

2.8.3 Polydisperse Systems (Cumulant Analysis)

Cumulant analysis method was first introduced by Koppel [18] for obtaining the average decay rate and standard deviation for a polydisperse system. This method is based on a series expansion of the exponential functions comprising the normalized molecular correlation function,

\[ g^{(l)}(K, \tau) = \sum_{i=1}^{M} a_i(K) \exp(-\gamma_i \tau) \quad (2.58) \]

which in the limit of \(\tau \to 0\) (smaller delays) is given as a power series in \(\tau\):

\[ \ln[g^{(l)}(K, \tau)] \sim -K_1 \tau + \frac{1}{2} K_2 \tau^2 - \frac{1}{6} K_3 \tau^3 + \ldots \quad (2.59) \]

The \(n\)th cumulant \(K_n\) is defined as

\[ K_n = \left[ \frac{\partial^n \ln[g^{(l)}(K, \tau)]}{\partial \tau^n} \right]_{\tau=0} \quad (2.60) \]

The first two cumulants for center-of-mass diffusion are

\[ K_1(K) = \frac{\overline{D(K)}K^2}{1} \quad (2.61) \]
and

\[ K_2(K) = [\overline{D(K)}^2 - \overline{D(K)}^2]K^4 \]  

(2.62)

Where it is emphasized that diffusion coefficient may depend upon the scattering vector, \( K \). In the case of non-interacting identical particles, \( \overline{D(K)} \) is defined as

\[ D(K) = \frac{\sum_{i=1}^{M} P(K)N_iM_i^2D_i}{\sum_{i=1}^{M} P(K)N_iM_i^2} \]  

(2.63)

Where \( P(K) \) is the particle structure factor, \( N_i \) is the number of particles of type \( i \), \( M_i \) is the molecular weight of the particles of type \( i \), and \( D_i \) is their corresponding diffusion coefficient. For a long time cumulant analysis was extensively used to analyze correlation functions. However, this analysis is prone to serious error where the baseline cannot be deduced with sufficient accuracy.

### 2.8.4 Laplace Inversion Method

Intensity correlation function \( g^{(2)}(K, \tau) \) can be of the discrete form given in Eq. (2.55), or it can be represented by a continuous distribution of decay rates whose amplitude are determined by the distribution function \( G(\gamma) \):

\[ g^{(2)}(K, \tau) = \left[ \int_0^\tau \exp(-\gamma\tau)G(\gamma)d\gamma \right]^2 + 1 + \varepsilon(\tau) \]  

(2.64)

The Laplace inversion of these expressions represents an ill-posed problem because of the presence of the noise term, \( \varepsilon(\tau) \). The nature of the ill-conditioned behavior has been lucidly presented by Bott [19] and is summarized here. \( G(\gamma) \) is of the form

\[ G(\gamma) = \sum [A_j \cos(\omega_j\gamma) + B_j \sin(\omega_j\gamma)] \]  

(2.65)

hence the integral \( I \) in Eq. (2.64) has the analytic form

\[ I = \sum \frac{A_j \tau}{\omega_j^2 + \tau^2} + \frac{B_j \omega_j}{\omega_j^2 + \tau^2} \]  

(2.66)
It now becomes clear that the high-frequency components may make a large contribution to $G(\gamma)$ but a negligible contribution to $g^{(2)}(K,\tau)$. The situation is further complicated by the fact that the functions $g^{(2)}(K,\tau)$ are usually truncated, hence the baseline may not be reached in the time window examined. Premature truncation may lead to distortion of the low-frequency contribution.

From the above discussion it can be concluded that there exists a set of solutions $\{s\}$ to Eqs. (2.55) and (2.64) that lie within the experimental noise level $\varepsilon(\tau)$. Within $\{s\}$ there may be a subset of solutions $\{\{n\}\}$ that can be eliminated because they have no physical significance for example, those with negative amplitudes. This subset can be immediately eliminated. The problem, therefore, is to choose from the subset of feasible solutions $\{\{f\}\}$ the correct solution to the problem.

### 2.8.5 Exponential sampling

The degree of success in obtaining a reasonable representation of the distribution function $G(\gamma)$ is dependent upon the assumed functional form implicit in the treatment of the data. Mc Whirter and Pike [20] and Ostrowsky et al. [21] have truncated the frequency $\omega$ to the maximum value $\omega_{\text{max}}$, which more or less defines the noise level of the data. The choice of $\gamma$ value is given by

$$\gamma_n = \gamma_{n-1} \exp \left( \frac{\pi}{\omega_{\text{max}}} \right)$$

(2.67)

The exponential sampling recipe can provide an accurate reconstruction of amplitude distributions that have a high-frequency tail (smaller particles). Clearly, much smaller step sizes must be used on the low-frequency end of the distribution than on the high-frequency end of the distribution in order to resolve the detail. This type of sampling scheme is provided by exponentially spaced steps. On the other hand, the exponential sampling procedure does not provide information of comparable accuracy about a distribution with low-frequency tail. Sampling procedures using equally spaced linear step sizes may be more appropriate for these types of distributions.
2.8.6 CONTIN

Another approach to reduce the effect of noise is to employ a smoothing procedure that restricts curvature in the function $G(\gamma)$. Provincher [22,23] employed a smoothing procedure in the development of CONTIN. Such a procedure, however, assumes a relationship between adjacent and neighboring points in the distribution function. It may be difficult to resolve bimodal and multimodal distribution in $G(\gamma)$ since the smoothing reduces fluctuations in the curve. One must be cautioned that when the data are massaged, unwarranted correlation between points may result, thereby placing a bias on the optimal solution to the problem. CONTIN attempts to produce a Laplace inversion of $g^{(2)}(K,\tau)$ to establish $G(\gamma)$

$$G(\gamma) = \int g^{(2)}(K,\tau)\exp(-\gamma\tau)d\tau$$

It is particularly useful in dealing with noisy signals.

The CONTIN is a well-known program, which is composed of a core of 53 subprograms and 13 "USER" subprograms. The memory requirement is about 200 Kbytes. Aside from the initial entry of the experimental parameters (scattering angle, viscosity, temperature, etc., the integration limits for the Laplace variable, and the selection of particle structure factors), CONTIN is not a user-interactive program. However, it has found wide acceptability where polydispersity and poor background forbid largely the use of any other methods.
References


