Chapter Two
Theoretical Background of Light Scattering and Rheology

2.1 Introduction

Light scattering is a very powerful technique to study the physical (structure and Dynamics) properties of a system (particularly of solutions). Among many advantages of this technique the most important one being it is a non-perturbative technique, provided the intensity should not be high enough to ionize the system. Depending on the change in energy between the incident light 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. Information about static physical properties like molecular weight, radius of gyration, second virial coefficient of inter and intra-particle interaction, etc. can be obtained from SLD data that is 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 thermodynamically and hydro dynamical environments. It has long been realized that any excitation 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 the directions except in the forward direction. The reason being that in a perfectly ordered crystal the scattered light coming out of the lattice-points 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., \((\partial \rho/\partial c) \neq 0\).

2.2 Theoretical Background

Before discussing about both SLS and DLS in details it is worthwhile to discuss the silent features of scattering in general. In a typical experiment, light is scattered from a macromolecular solution and the 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 \(\mathbf{K}_i\) and state of polarization \([p_1]\), the corresponding parameters describing the scattered light will be \(\omega_s\), \(\mathbf{K}_s\), and \([p_s]\). During the scattering experiment, the energy, momentum and the state of polarization of the incident light can undergo considerable change. But since, we are only interested in quasi-elastic light scattering, it is safe to consider the scattered energy \(E_s = (h\omega_s)\) is almost same as the incident energy \(E_i = (h\omega_i)\) and consequently, the magnitude of the corresponding wave vectors are almost equal, i.e., \(|\mathbf{K}_s| \approx |\mathbf{K}_i|\). Let us consider one element of the macromolecular solution is at a position \(r\) with respect to an arbitrary origin (Figure 2.1-a) in a medium with refractive index \(n\). Since, we have already argued that in a quasi-elastic light scattering experiment \(|\mathbf{K}_s| \approx |\mathbf{K}_i|\), one can write this as [1],

\[
|\mathbf{K}_s| \approx |\mathbf{K}_i| = |\mathbf{K}| = \frac{2m}{\lambda o} = \frac{2\pi}{\lambda} \tag{2.1}
\]
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 'Q' is $2\pi n/\lambda_0$ times the path difference (OQ-PR), i.e.

$$\Delta \phi = \vec{K}_s \vec{r} - \vec{K}_i \vec{r} = [\vec{K}_s - \vec{K}_i] \vec{r} = \vec{q} \vec{r}$$  \hspace{1cm} (2.2)$$

Where, we have defined the scattering wave-vector $\vec{q}$ as,

$$\vec{q} = [\vec{K}_s - \vec{K}_i]$$  \hspace{1cm} (2.3)$$

$$\Rightarrow q^2 = K_s^2 + K_i^2 - 2K_s \cdot K_i \cos \theta$$

$$= K_s^2 + K_i^2 - 2K_s \cdot K_i \cos \theta$$

$$= 2K_s^2 - 2K_s \cdot K_i \cos \theta$$

$$= 2K_s^2 \cdot 2 \sin^2 \theta / 2$$

$$|\vec{q}| = 2|\vec{K}_i| \sin \theta / 2$$

$$\Rightarrow |\vec{q}| = 2 \frac{2\pi}{\lambda} \sin \theta / 2 = \frac{4\pi}{\lambda_0} \sin \theta / 2$$ \hspace{1cm} (2.4)$$

Where, '0' is the scattering angle between $\vec{K}_i$ and $\vec{K}_s$ as shown in Figure. (2.1-b)

---

**Figure: 2.1.** (a) Scattering Geometry; (b) geometrical construction for the scattering wave vector $\vec{q}$.  

26
The reciprocal of the scattering wave-vector \( q \), physically signifies the length scale over which the sample is probed. It is clear from the above Eq. (2.4) 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. Beyond this one observes the Mie-Scattering.

In light scattering the typical accessible length scale is \( \sim 50 \, \text{Å} \) to \( 1000 \, \text{Å} \), whereas 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 \( \sim 1 \, \text{Å} \) to \( 5 \, \text{Å} \). If one wished to study samples smaller than this size, then one has to go over to electron scattering, after this let us shift over to the discussion on SLS and DLS.

2.3 Static Light Scattering (SLS)

Many excellent books and review articles [2-4] and conference proceedings of [5-8] are available which give a good description both of the theory and experimental techniques of scattering of electromagnetic radiation. Exhaustive treatments of static light scattering can be found in the book by Van de Hulst and Kerker [9, 10].

When a beam of electromagnetic radiation strikes some element of a scattering particle, its constituent electrons get subjected to a force in one direction and its constituent nuclei to a force in opposite direction, creating a dipole moment ‘p’ in the particle. Let the electromagnetic beam be a plane-polarized beam of light, the electric field strength (E) of such a monochromatic beam of light is given as...
\[ \vec{E} = \vec{E}_0 \cos 2\pi (vt - x/\lambda) \]  

(2.5)

Where, \( E_0 \) is the maximum amplitude, 'v' is the frequency and '\( \lambda \)' is the wavelength of light in the medium. The dipole moment induced in this method is proportional to the electric field strength and the proportionality constant is called as the polarizability of particle, i.e.

\[ \vec{P} = \alpha \vec{E} \]  

(2.6)

We are considering particles much smaller in size than '\( \lambda \)' (for particle having size equal to or great than '\( \lambda \)' is called the Mie-Scattering). Thus each individual particle can be represented by a single value of 'x' the electric-field at each point of the particle, at any instant will be same. Combining Eq. (2.5) and (2.6) we have

\[ \vec{P} = \alpha \vec{E}_0 \cos 2\pi (vt - x/\lambda) \]  

(2.7)

An oscillating dipole, however itself acts as a source of electromagnetic radiation and this new radiation is known as scattered radiation. The scattered radiation field strength (\( E_s \)) is proportional to \( \frac{d^2 p}{dt^2} \). The oscillating dipole produces an oscillating electric field, which in turn, is accompanied by an oscillating magnetic field. The combination constitutes an electromagnetic wave. The scattered radiation is a spherical wave, extending in all directions, but the field strength depends on the direction. The residual field is perpendicular to the line from the observer and its strength at any given value 'r' is proportional to \( \sin (\theta_1) \), where \( \theta_1 \) is the angle between the dipole axis and the line joining to the point of observation to the dipole.
Another property is that the scattered field strength is proportional to $1/r$ to satisfy the law of conservation of energy.

So differentiating (2.7) two times with respect to ‘t’ and multiplying by $\sin(\theta_1)/r$ and dividing by $c^2$, where ‘c’ is the velocity of light to make it dimensionally consistent, we have,

$$E_s = \frac{4\pi^2 v^2 \alpha E_0 \sin \theta_1}{c^2 r} \cos 2\pi(\nu - x/\lambda)$$  \hspace{1cm} (2.8)

Where $E_s$ is the scattered electric field and having the same frequency as the incident beam frequency indicating it is an elastic scattering.

But the experimentally measured quantity is intensity instead of electric field strength, which is proportional to $E^2$ by poynting theorem, i.e.

$$I_s = |E_s|^2 = \frac{16\pi^4 \alpha^2 \sin^2 \theta_1}{\lambda^4 r^2} I_0$$

$$\Rightarrow \frac{I_s}{I_0} = \frac{16\pi^4 \alpha^2 \sin^2 \theta_1}{\lambda^4 r^2}$$  \hspace{1cm} (2.9)

Where $\lambda = c/\nu$. This Eq. (2.90) was first derived by Rayleigh. One of the most striking features of this equation is that the scattered intensity ($I_s$) is inversely proportional to $4^{th}$ power of wavelength of light.

From the above Eq. (2.9) it is clear that the angular dependence of the scattering is due to $\sin^2 \theta_1$. But in most of the experiments the incident light used are unpolarized.
rather than polarized. An unpolarized light can be thought of as superposition of two plane-polarized beams, independent in phase, equal in intensity and with perpendicular planes of polarization to one another. So, for an unpolarized light, instead of \( \sin^2 \theta_1 \) we will have \( \sin^2 \theta_1 + \sin^2 \theta_2 = (1 + \cos^2 \theta)/2 \), where \( \theta_1 \) and \( \theta_2 \) represent the angles made by the line of observation with the ‘y’ and ‘z’ axis respectively, when the incident beam is in x-direction. \( \theta \) is the angle between the line of observation and the x-axis, i.e., between the line of observation and the direction of incident light. The factor of \( \frac{1}{2} \) comes because each term represents the scattering from half the incident intensity, i.e., \( (1/2). (I_s/I_0) \). So Eq. (2.9) becomes,

\[
\frac{I_s}{I_0} = \frac{8\pi^2 \alpha^2}{\lambda^4 r^2} (1 + \cos^2 \theta)
\]

(2.10)

This is the basic Rayleigh equation of light scattering for a single scattering element.

The quantity actually measured in experiment is the Rayleigh ratio \( (R_{\theta}) \) which is defined as

\[
R_{\theta} = \frac{r^2 I_s(\theta)}{I_0(1 + \cos^2 \theta)}
\]

(2.11)

Now, let us calculate \( \alpha^2 \). The polarizibility is related to dielectric constant ‘\( D \)’ (at frequency ‘\( \nu \)’) and hence to the refractive index ‘\( n \)’ by,

\[
D - 1 = n^2 - 1 = 4\pi N\alpha
\]

(2.12)

Where ‘\( N \)’ is the number of molecules / c.c. For dilute gas ‘\( n \)’ is close to unity and can be expanded by Taylor series as,
\[ n = 1 + \left[ \frac{dn}{dc} \right] c + \ldots \]

\[ \Rightarrow n^2 - 1 = 2 \left[ \frac{dn}{dc} \right] c = 4\pi N\alpha \quad (2.13) \]

\[ \Rightarrow \alpha = c \frac{\left[ \frac{dn}{dc} \right]}{2\pi N} = \frac{M}{2\pi N \Lambda} \left[ \frac{dn}{dc} \right] \quad (2.14) \]

Where ‘M’ is the molecular weight of the particles, ‘N’ is their number per cubic centimeter (cc). \( N_A \) is the Avogadro’s number and ‘c’ is the concentration of the particles in the gas, so that \( M/N_A = c/N \) is equal to the mass per particle. Putting this in Eq. (2.10), we well have

\[ \frac{I_S}{I_0} = \frac{2\pi^2 M^2 \left[ \frac{dn}{dc} \right]^2 (1 + \cos^2 \theta)}{N_A \Lambda^2 \lambda^2} \quad (2.15) \]

A more useful result is the intensity of scattering from unit volume, assuming that the particles are randomly located so that the total intensity is the sum of that of individual particles with \( N = N_A c/M \) particles per cc

\[ \frac{I_S}{I_0} = \frac{2\pi^2 (1 + \cos^2 \theta) \left[ \frac{dn}{dc} \right]^2 M c}{N_A \Lambda^2 \lambda^2} \quad (2.16) \]

If the scattering molecules are immersed in a solvent having refractive index, \( n_0 \) instead of in free-space in which the refractive index is ‘1’, we well have \( n^2 - n_0^2 = 4\pi N\alpha \) as the total polarizibility per unit volume instead of \( n^2 - 1 = 4\pi N\alpha \).

Actually ‘\( \alpha \)’ is the difference between the polarizibility of the solute molecules and the
solvent, which it replaces. So instead of Eq. (2.13) we will have

\[ n^2 - n_0^2 = 2n_0 \left( \frac{dn}{dc} \right) c = 4\pi\alpha \]. And the final expression (Eq. 2.16) will become

\[
\frac{I_s}{I_0} = \frac{2\pi^2 (1 + \cos^2 \theta)n_0^2 \left( \frac{dn}{dc} \right)^2 M.c.}{N_A \lambda^4 r^2} \quad (2.17)
\]

2.4 Fluctuation Theory

But in the case of a solution one no longer deal with non-interacting particles. Since, at finite concentration, some sort of interaction will always exist between the particles. In this case it is more appropriate to express the scattered intensity in terms of concentration fluctuation, which in turn, depends on the chemical potential.

Let us consider a solution made up of small elements of volume δv. The dimension of δv << λ, so that the entire element can be considered as a single scattering source. But it should be big enough to contain many solvent molecules and few solute molecules N = 1/δv.

Let us say the concentration of the solution at any point of time can be given by,

\[ c(t) = \bar{c} + \Delta c(t) \quad (2.18) \]

Where \( \bar{c} \) is the average concentration and \( \Delta c(t) \) is the fluctuation in concentration (can be +ve or -ve). Due to fluctuation in concentration, there will also be fluctuation in polarizibility designated by
\[ a(t) = \bar{a} + \Delta a(t) \tag{2.19} \]

Where \( \bar{a} \) is the average polarizibility and \( \Delta a \) is the fluctuation in polarizibility.

Putting Eq.(2.19) in Eq. (2.10) we will have, expression for scattered light from any one volume element at a particular instant of time, i.e.,

\[ \frac{I_s}{I_0} = \frac{8\pi^4 (\bar{a} + \Delta a)^2 (1 + \cos^2\theta)}{\lambda^4 r^2} \tag{2.20} \]

The term \((\bar{a} + \Delta a)^2\) in Eq. (2.20) when expanded will become, \((\bar{a}^2 + 2\bar{a}\Delta a + \Delta a^2)\).

The contribution due to \(\bar{a}^2\) is same for each element and thus cancels for the same reason which makes the scattering from a perfect crystal equal to zero. The average value of \(\Delta a\) must also vanish since positive and negative value of \(\Delta a\) must also are equally likely. So Eq. (2.20) will reduce to

\[ \frac{I_s}{I_0} = \frac{8\pi^4 (\Delta a^2) (1 + \cos^2\theta)}{\lambda^4 r^2} \tag{2.21} \]

The expression for scattered light of 'N' volume elements/ cc is given by

\[ \frac{I_s}{I_0} = \frac{8\pi^4 N(\Delta a^2)(1 + \cos^2\theta)}{\lambda^4 r^2} = \frac{8\pi^4 (\Delta a^2)(1 + \cos^2\theta)}{(\delta \nu)\lambda^4 r^2} \tag{2.22} \]

But \(\Delta a\) \((P, T, c)\) can be written as

\[ \Delta a = \left[ \frac{\partial a}{\partial P} \right]_{T, c} \Delta P + \left[ \frac{\partial a}{\partial T} \right]_{P, c} \Delta T + \left[ \frac{\partial a}{\partial c} \right]_{T, P} \Delta c \] \tag{2.23} \]
The first two terms on the right hand side of Eq. (2.23) are assumed for dilute solutions to be same as the corresponding terms leading to scattering from the pure solvent and ignored. So Eq. (2.23) can be written as

\[ \Delta \alpha = \frac{\partial \alpha}{\partial c} \Delta c \]  

(2.24)

Putting Eq. (2.24) in Eq.(2.22) we will have

\[ \frac{I_r}{I_0} = \frac{8\pi^4 (\Delta c)^2 (1 + \cos^2 \theta)}{(\delta\nu) \lambda^2 r^2} \left[ \frac{\partial \alpha}{\partial c} \right]_{r,r'}^2 \]  

(2.25)

From Eq. (2.13) we have

\[ n^2 - 1 = 4\pi Na. \]

\[ \Rightarrow 2n \left| \frac{dn}{dc} \right| = 4\pi N \left| \frac{\partial \alpha}{\partial c} \right| \]

\[ \Rightarrow \left[ \frac{\partial \alpha}{\partial c} \right] = \frac{n \left| \frac{dn}{dc} \right|}{2\pi} \]  

(2.26)

And from the thermodynamic theory of fluctuation, the mean square concentration fluctuation is given by,

\[ \Delta c^2 = \frac{k_b T}{\partial^2 F/\partial c^2} = \frac{k_b TV_1 c}{\partial \mu_1 / \partial c} \]  

(2.27)

Where, 'F' is the total free- energy, '\mu_1' is the chemical potential of the solvent is solution and V_1 is the molar volume of the solvent.

Putting Eq. (2.26) and (2.27) in Eq. (2.25), we have
\[
\frac{I_s}{I_0} = \frac{2\pi^2 n^2 \left( \frac{dn}{dc} \right)^2 c. (1 + \cos^2 \theta)}{\lambda^4 r^2 \left[ \left( \frac{1}{V} \right) \frac{\partial \mu_i}{\partial c} \right]}
\] (2.28)

But

\[
-\frac{1}{V_k T} \left[ \frac{\partial \mu_i}{\partial c} \right] = N_A \left[ \frac{1}{M} + 2A_2 c + 3A_3 c^2 + \ldots \right]
\]

Where \( A_2 \) is the second virial coefficient. Therefore,

\[
\frac{I_s}{I_0} = \frac{2\pi^2 n^2 \left( \frac{dn}{dc} \right)^2 c. (1 + \cos^2 \theta)}{\lambda^4 r^2 N_A \left[ \frac{1}{M} + 2A_2 c + \ldots \right]}
\] (2.29)

Let us consider

\[
\frac{2\pi^2 n^2 \left( \frac{dn}{dc} \right)^2 c}{\lambda^4 N_A} = K \text{ (constant)}
\]

And form Eq. (2.11) \( R_0 = r^2 I_s / I_0 (1 + \cos^2 \theta) \) so Eq.(2.29) can be written as [11]

\[
\frac{K c}{R_0} = \left[ \frac{1}{M} + 2A_2 c + \ldots \right]
\] (2.30)

2.5 Size and Shape-effects

For scatterers with dimension much less than the wavelength of light \((\leq \lambda / 20)\) the electric field of the incident light is almost constant over the volume of the scatterer.
and the Eq. (2.30) holds good. But in the case of longer particles having dimension of the order of wavelength of light (in the case of macromolecules, biopolymers, etc), the scattered intensity will generally be reduced because of the interference between the scattered radiation originated between the different parts of the same molecule. The interference effect can be incorporated into Eq. (2.30) by including the multiplicative angle dependent form factor, \( P(q) \). Modified Eq. (2.30) can be written as [11].

\[
\frac{Kc}{R_g} = \frac{1}{M + 2Ac + \ldots} P(q)
\]  

(2.31)

Evaluation of \( P(q) \) for various geometrical shape particles can be found in literature. The most precise method of finding \( P(q) \) is Mie-method. If the scatterer are sufficiently small to satisfy the Rayleigh-Gans criterion (i.e., \((n-n_0)L \ll 4\pi\lambda\)) then \( P(q) \) in given by,

\[
P(q) = \frac{1}{V} \int e^{iq\cdot v} dv
\]

(2.32)

Where ‘\( v \)’ is the volume of the scatterer.

For a random coil in the very low scattering angle, limit, \( P(q) \) is given by,

\[
P(q) \equiv 1 - \frac{q^2 R_g^2}{3}
\]

Where \( R_g = \text{Radius of gyration} \). Putting this in Eq. (2.31), we have
\[ \frac{K_c}{R_\theta} = \left[ \frac{1}{M} + 2A_2c + ... \right] \left[ 1 + \frac{q^2R_g^2}{3} \right] \]  

(2.33)

2.6 Zimm-Plot

If experimental of $K_c/R_\theta$ is plotted against $\sin^2(\theta/2)$ where ‘A’ is a constant, we will obtain ‘Linear-Plot’ as drawn in Fig. (2.2). Extrapolation of all the points to $\theta = 0$ and $c = 0$ will give rise to molecular weight of the particle which is nothing but the intercept in y-axis.

\[ \lim_{q \to 0} \frac{K_c}{R_\theta} = \frac{1}{M} \]  

(2.34)

Extrapolation of all points at constant $\theta$ to $c = 0$ gives a line which is

\[ \left. \frac{K_c}{R_\theta} \right|_{c \to 0} = \left[ 1 + \frac{q^2R_g^2}{3} \right] \frac{1}{M} \]  

(2.35)

Knowing the value of ‘M’ from Eq. (2.34) one can find out $R_\theta$, the Radius of gyration.

Extrapolation of all points at constant $c$ to $\theta = 0$ gives

\[ \left. \frac{K_c}{R_\theta} \right|_{\theta \to 0} = \left[ \frac{1}{M} + 2A_2c + ... \right] \]  

(2.36)

Similarly, knowing the value of ‘M’ from Eq. (2.34) one can find out $A_2$, the second virial coefficient. This constitutes the zimm plot method [12].
2.7 Dynamic Light Scattering (DLS)

In a light scattering experiment a monochromatic laser beam impinges on a sample and scattered into a detector placed at an angle 'θ' with respect to the incident beam. When the molecules in this scattering volume are exposed to the incident beam, their constituent charges experience a force and a dipole moment gets induced in the scattering volume which in return radiates secondary light into the detector. This secondary radiation of light is known as the scattered light. But in the case of a scattering from a solution the molecules in the scattering volume are perpetually translating, rotating and vibrating due to thermal interactions and collision by solvent molecules. Due to these constant motions the position of the charges are randomly changing and the scattered light at the detector will fluctuate in the time about the average value and the rate at which these spontaneous fluctuations decay to equilibrium value is directly dependent on the dynamics of the molecules. This can give information like: diffusion coefficient, hydrodynamic radius, etc., of the molecules.

Both the thermal and collisional motions of the molecules are random, so the total scattered intensity varies randomly at the detector. A recording of this looks like a noise pattern. Hence, the fluctuation dissipation theory of noise and random fluctuation provide an ideal framework to study these processes involved in light scattering spectroscopy.

2.8 Fluctuations and Time Correlation Functions

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 motion these particles are constantly moving around, so their positions and momentum are
changing in the time, and hence the property 'A'. The time-dependence of A(t) will
generally resemble a noise pattern. It can be argued through the central limit theorem
that property A(t) is very much close to a Gaussian random variable. This led us to the
following properties.

(i) A(t) ≠ A(t+τ) when 'τ' is of the order of the fluctuation relaxation time.
(ii) A(t) ≈ A(t+τ) when 'τ' is much smaller than the fluctuation relaxation time
     and they are statistically dependent hence correlated.
(iii) When 'τ' is much longer than the relaxation correlation time A(t) and
     A(t+τ) are statically independent, and, hence uncorrelated.
Hence the time-average of A(t) can be expressed as

\[ \langle A(t) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T A(t) dt \]  \hspace{1cm} (2.33)

and the time correlation function is defined as

\[ A(t)A^*(t+τ) = \lim_{T \to \infty} \frac{1}{T} \int_0^T \langle A(t)A^*(t+τ) \rangle dt \]  \hspace{1cm} (2.33)

Where A* is complex conjugate of 'A'. There are two extreme limits, one, when τ =
0, we have

\[ \langle A(t) A^*(t+τ) \rangle = \langle A^2(t) \rangle \]  \hspace{1cm} (2.39)

And the second one when τ → ∞ we, have

\[ \langle A(t) A^*(t+τ) \rangle = \langle A^2(t) \rangle = \langle A \rangle < \langle A(t+τ) \rangle > = \langle A^2 \rangle \]  \hspace{1cm} (2.40)
So from the above two equations it can be noticed that the correlation functions
decays from its initial value \( \langle A^2 \rangle \) at \( τ = 0 \) to \( \langle A^2 \rangle \) as 'τ' goes towards infinite. This
has been depicted in Figure 2.2. The time taken by the function to decay to \((1/e)^{th}\) of its initial value is called the correlation time or coherence time.

![Time Correlation Function](image)

Fig. 2.2 The time correlation function, \(\langle A(t)\rangle\langle A(t+\tau)\rangle\). Initially this function is \(\langle A^2 \rangle\). For times very long compared to the correlation time, \(\tau_A\), the correlation function decays to \(\langle A\rangle^2\).

2.6 Theoretical Background of DLS

According to Einstein’s formalism, in a condensed matter, medium, thermal density fluctuations contribute to the creation of local dielectric constant (or refractive index) fluctuations, which in turn scatters light. The intensity of the scattered light is directly proportional to the strength of these fluctuations. At any instant of time the instantaneous dielectric constant \(\varepsilon(r, t)\) is given by,

\[
\varepsilon(r, t) = \langle \varepsilon \rangle + \Delta \varepsilon(r, t)
\]

(2.41)

Where \(\langle \varepsilon \rangle\) is the average dielectric constant and \(\Delta \varepsilon\) is the fluctuation in it. All the thermodynamic variables like pressure \((P)\), volume \((V)\), entropy \((S)\), concentration \((c)\), etc., can be described in the form of Eq. (2.41). For the scattering of light from a macromolecular solution, one can express the Einstein relation as,
Let us say, $\varepsilon = \varepsilon(T, c)$. Then one can write,

$$\Delta \varepsilon(r, t) = \left( \frac{\partial \varepsilon}{\partial T} \right)_c \Delta T(r, t) + \left( \frac{\partial \varepsilon}{\partial c} \right)_T \Delta c(r, t)$$  \hspace{1cm} (2.43)

The temporal auto-correlation function of the scattered electric field $E_s(t)$ is given as

$$\langle E(t)E_s^*(t + \tau) \rangle \sim \left( \frac{\partial \varepsilon}{\partial T} \right)_c^2 \langle \Delta T(t)\Delta T^*(t + \tau) \rangle + \left( \frac{\partial \varepsilon}{\partial c} \right)_T^2 \langle \Delta c(t)\Delta c^*(t + \tau) \rangle$$ \hspace{1cm} (2.44)

The dielectric constant is expressed as a function two thermodynamic variables, which are adequate to describe the system. Equation (2.44) has two time-dependent terms. The explicit behavior of concentration fluctuation is accounted for by Fick's diffusion equation.

$$\frac{\partial (\Delta c)}{\partial t} = D_z \nabla^2 (\Delta c)$$  \hspace{1cm} (2.45)

Where $D_z$ is the transnational diffusion coefficient. The solution of Eq. (2.45) in q-space is

$$\Delta c(q, t) = \Delta c(q, 0) \exp (-D_z q^2 t)$$ \hspace{1cm} (2.46)

This indicates the concentration fluctuation relaxes to equilibrium through an exponential process. Likewise the temperature fluctuation can be completely characterized through Fourier heat equation analogues to Eq. (2.45) [13] and $\Delta T$ relaxes exponentially like Eq. (2.46)

$$\Delta T(q, t) = \Delta T(q, 0) \exp (-D_m q^2 t)$$ \hspace{1cm} (2.47)

Where $D_m$ in the thermal diffusivity. The temporal auto-correlation function of $\Delta c(q, t)$ and $\Delta T(q, t)$ is given by
\[
\langle \Delta c (q, t), \Delta c^* (q, t+\tau) \rangle = \langle |\Delta c (q, 0)|^2 \rangle \exp(-Dz q^2 \tau) \tag{2.48}
\]

and

\[
\langle \Delta T(q, t), \Delta T^* (q, t+\tau) \rangle = \langle |\Delta T(q, 0)|^2 \rangle \exp(-D_\text{int} q^2 \tau) \tag{2.49}
\]

Putting Eq. (2.48) and (2.49) in Eq. (2.44), we will get

\[
\langle E(t)E_s^*(t+\tau) \rangle = \left( \frac{\partial \epsilon}{\partial T} \right)_{\epsilon}^2 \exp(-D_\text{int} q^2 \tau) + \left( \frac{\partial \epsilon}{\partial c} \right)_{\epsilon}^2 \exp(-D_q q^2 \tau)
\]

(2.50)

The normalized temporal auto-correlation function of the scattered electric field is defined as \[14]\]

\[
g_\text{s}(\tau) = \frac{\langle E_s(t)E_s^*(t+\tau) \rangle}{\langle |E_s(t)|^2 \rangle} \approx A \exp(-D_\text{int} q^2 \tau) + B \exp(-D_q q^2 \tau) \tag{2.51}
\]

Since both these processes occur in different time scales in a particular experiment, one only measures one of these quantities. Since, one is mostly interested in the mass diffusion behavior, the correlation function for scattered electric field \( E_s(t) \) of our interest will be

\[
g_\text{s}(\tau) = \frac{\langle E_s(t)E_s^*(t+\tau) \rangle}{\langle |E_s(t)|^2 \rangle} \approx \exp(-D_q q^2 \tau) \tag{2.52}
\]

But, actually experimentally measured quantity is intensity, not electric field. So the temporal auto-correlation function of intensity is given as \[10,14]\]

\[
g_\text{i}(\tau) = \frac{\langle I_s(t)I_s^*(t+\tau) \rangle}{\langle |I_s(t)|^2 \rangle} \tag{2.53}
\]

For a Gaussian distribution \( g_2 (\tau) \) and \( g_1 (\tau) \) are connected through the Siegert equation \[12\] as.
Where \( a \) is the background as \( \tau \to \infty \) and \( b \) is the coherence area factor, which basically quantifies the signal to noise situation.

Substituting the value of \( g_1(\tau) \) in Eq. (2.54), we will have the expression for temporal intensity auto-correlation function, which is equal to

\[
g_2(\tau) = g_1(\tau)^2
\]  

(2.54)

Where \( g_1(\tau) \) is the coherence area factor, which basically quantifies the signal to noise situation.

Substituting the value of \( g_1(\tau) \) in Eq. (2.54), we will have the expression for temporal intensity auto-correlation function, which is equal to

\[
g_2(\tau) = a + b \exp(-2D_2q^2\tau) = a + b \exp(-2\Gamma\tau)
\]  

(2.55)

Where \( \Gamma = D_2q^2 \), is half width at full maximum of the exponential. So measuring \( \Gamma \) and knowing \( q^2 \), one can find out the value of diffusion coefficient. The diffusion coefficient \( D_2 \) is related to frictional coefficient through Einstein relation

\[
D_2 = \frac{K_BT}{f_T}
\]  

(2.56)

Where \( f_T \) is the transnational frictional coefficient from Stokes-Einstein relation, one knows that for spherical particles \( f_T \) is given as,

\[
f_T = 6\pi\eta_0R_{II}
\]  

(2.57)

Where \( \eta \) is the solvent viscosity and \( R_{II} \) is the hydrodynamic radius, which is different from the actual radius because of the hydration layer around it.

2.7 Rheology

2.7 What is rheology? Newton (c.1700) was the first to formulate a mathematical description of the resistance of a fluid to deform or flow when a stress was applied to it. He described this resistance as the viscosity. From that time until Coquette developed the first rotational viscometer (c.1890), viscosity was measured using stress driven (gravity) flow. Many techniques that use this principle, such as flow cups, u-tubes, capillaries, etc. are still very popular. The term 'Rheology' was suggested by
Bingham of Lafayette College, Easton PA. This definition was officially accepted when the American Society of Rheology was founded in 1929. Rheology can be defined as "The science of the deformation and flow of matter." Rheology plays a part in everyday life in some form or another. For instance, why does the water run out of a bath when the plug is removed? How does the manufacturer ensure that toothpaste can be squeezed from a tube yet can retain its shape without slumping through the bristles of a toothbrush? Can you imagine how painful it would be if you blinked and there was no fluid in eye? These and many more examples show every one is affected by rheology. To this end, it can be assumed that any action or process that involves fluids or semi-solids can be regarded as being rheological.

Dynamic or oscillatory tests are performed to study the viscoelastic properties of a sample. The tests are called microscale experiments compared to macroscale tests like rotational or viscometry tests. Viscoelastic samples have both elastic (solid) and viscous (liquid) properties, the extreme described by Hooke’s law of elasticity and Newton’s law of viscosity.

2.7.1 Basic rheological ideas Viscosity

1687: Isaac Newton addresses liquids and steady simple shearing flow in his "Principia" "The resistance which arises from the lack of slipperiness of the parts of the liquid, other things being equal, is proportional to the velocity with which the parts of the liquid are separated from one another.”

Viscosity is a quantity that describes a sample's resistance to flow in contradiction to quantities as plasticity, elasticity and viscoelasticity. Sample is forced to flow by the
force F (see figure 2.4). When force is removed the sample stops to flow. This is described by the force emanating from dashpot. The dashpot driven flow is a symbol for Newtonian flow according to Newton’s viscosity law.

Newton's law describes ideal flow behavior using a constitutive equation in which stress (\(\sigma\)) and rate of strain (\(\gamma\)) are related through proportionality constant called the viscosity. Newton’s Law: \(\sigma = \eta \gamma\) (2.58)

Where \(\eta\) is the coefficient of viscosity. If you double the stress, you double the shear rate.

![Figure 2.4: Purely Viscous Response Newtonian Liquid](image)

2.7.2 Basic rheological concept of Elasticity

1678: Robert Hooke develops his “True Theory of Elasticity” “The power of any spring is in the same proportion with the tension thereof” (stress = G x strain) where G is the rigidity modulus for materials that do not flow but show solid properties and spring is used to describe such a system. Elastic samples are studied by pulling the spring with a force F (Figure 2.5). The larger F the larger is the spring deformation. When force F is removed the sample returns to original shape and position.
Hooke’s and Newton’s laws are *linear* laws. They assume direct proportionality between stress and strain, or shear rate no matter what the stress. Most materials we work with obey these laws over a limited range of stresses. Beyond this limited range a material behaves *non-linearly*.

Hooke’s law describes ideal mechanical behavior using a constitutive equation in which stress and strain are related through a proportionality constant called the modulus $G$.

Hooke’s Law: $\sigma = G\gamma$ \hspace{1cm} (2.59)

If you double the stress, you double the strain.

### 2.7.3 Dynamic Mechanical Testing

An oscillatory (sinusoidal) deformation (stress or strain) is applied to a sample.

The material response (strain or stress) is measured.
The phase angle $\delta$, or phase shift, between the deformation and response is measured.

2.7.4 Dynamic Mechanical Testing Response for Classical Extremes

Purely Elastic Response (Hookean Solid)  Purely Viscous Response (Newtonian Liquid)

<table>
<thead>
<tr>
<th>Stress</th>
<th>Strain</th>
<th>Stress</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta = 0^\circ$</td>
<td>$\delta = 90^\circ$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.7.5 Dynamic Mechanical Testing Viscoelastic Material Response

Phase angle $0^\circ < \delta < 90^\circ$
2.7.6 The complex stress

The stress in a dynamic experiment is referred to as the complex stress \( \sigma^* \). The complex stress can be separated into two components: 1) An elastic stress in phase with the strain \( \sigma' = \sigma^* \cos \delta \sigma' \) is the degree to which material behaves like an elastic solid. 2) A viscous stress in phase with the strain rate. \( \sigma'' = \sigma^* \sin \delta \sigma'' \) is the degree to which material behaves like an ideal liquid.

\[ \sigma^* = \sigma' + i \sigma'' \]

2.7.7 Creep measurement

Stress is applied to sample instantaneously, \( t_1 \), and held constant for a specific period of time. The strain is monitored as a function of time \( \gamma(t) \). The stress is reduced to zero, \( t_2 \), and the strain is monitored as a function of time \( \gamma(t) \).
2.7.8 Creep Recovery Experiment

Response of Classical Extremes

**Elastic**
- Strain for \( t > t_1 \) is constant
- Strain for \( t > t_2 \) is 0

**Viscous**
- Strain rate for \( t > t_1 \) is constant
- Strain for \( t > t_1 \) increase with time
- Strain rate for \( t > t_2 \) is 0

Creep Recovery Experiment: Response of Viscoelastic Material

- Strain rate decreases with time in the creep zone, until finally reaching a steady state.
- In the recovery zone, the viscoelastic fluid recoils, eventually reaching an equilibrium at some small total strain relative to the strain at unloading.
2.7.9 The complex shear modulus $G^*$

The shear modulus (resulting from changing strain) is the ratio of the shear stress to the shear strain ($G^* = \text{Stress}^*/\text{Strain}$). It follows from the complex relationship [16].

$$G^* = G' + iG''$$

Where $G^*$ is the complex shear modulus, $G'$ is the in-phase storage modulus ($G' = (\text{stress}^*/\text{strain}) \cos \delta$) and $G''$ is the out-of-phase similarly-directed loss modulus ($G'' = (\text{stress}^*/\text{strain}) \sin \delta$); $|G^*| = (G'^2 + G''^2)^{1/2}$. The frequency where these parameters cross over corresponds to a relaxation time (t) specific for the material.

$$\tan(\delta) = G''/G'$$

Where tan(δ) quantifies the balance between energy loss and storage. As tan (45°) =1, a value for tan(δ) greater than unity indicates more "liquid" properties, whereas one lower than unity means more "solid" properties, regardless of the viscosity.

2.7.10 Complex viscosity

The viscosity measured in an oscillatory experiment is a complex viscosity much the same way the modulus can be expressed as the complex modulus. The complex viscosity contains an elastic component and a term similar to the steady state viscosity. The Complex viscosity is defined as:

$$\eta^* = \eta' - i\eta'' \quad \text{or} \quad \eta^* = G^*/\omega$$
Where the Dynamic Viscosity $\eta'$ is the part of the complex viscosity related to the steady state viscosity, the Dynamic viscosity is defined as: $\eta' = \frac{G''}{\omega}$ and the imaginary viscosity $\eta''$ measures the elasticity or stored energy and is related to the shear storage modulus. The imaginary viscosity is defined as: $\eta'' = \frac{G'}{\omega}$.

The Units of Viscosity are

SI unit is the Pascal.second (Pa.s)

cgs unit is the Poise

Poise is $\approx$ Pa.s by a factor of 10

10 Poise = 1 Pa.s

1 cP = 1 m Pa.

2.8 References


