Light scattering occurs when polarizable particles in a sample are placed in the oscillating electric field of a beam of light. The varying field induces oscillating dipoles in the particles and these radiate light in all directions. Light scattering has been utilized in many areas of science to determine particle size, molecular weight, shape, thermodynamic properties, diffusion coefficients etc.

Static Light Scattering
In static light scattering the time average value of the scattered intensity is measured as function of the scattering angle. This allows to determine the weight average of the molar mass $M_w$, the z-average of the squared radius of gyration $<R_z^2>$ and the
second virial coefficient of the osmotic pressure $A_2$. As mentioned above the oscillating electric field of light induces oscillating dipoles within molecules and these therefore radiate light in all directions. The wavelength of the scattered light is identical with the wavelength of the incident beam.

Rayleigh applied the Maxwell theory of electrodynamics and derived the so called Rayleigh ratio of scattered intensity and primary beam intensity for gases:

$$
R(\theta) = \frac{I^2}{I_0} - \frac{8\pi^2}{\lambda_0^4} \sum_{k=1}^{N_k} \alpha_k^2 (1 + \cos^2 \theta)
$$

1

$R(\theta)$: Rayleigh ratio as a function of scattering angle
$I$: Intensity of the scattered light
$I_0$: Intensity of the primary beam
$r$: Distance of detector and scattering volume
$\lambda_0$: Wavelength of the primary beam in vacuum
$N_k$: Number of scattering centers
$\alpha_k$: Polarizability of the scattering center $k$ (polarization $p = \alpha E$)
$\theta$: Angle between primary and scattered beam

Using vertically polarized light of a laser the scattering intensity (of small particles) is independent from the scattering angle and the so called polarization term $(1 + \cos^2 \theta)$ equals 2.

The absolute scattering intensity of several pure liquids (e.g. toluene or benzene) are utilized as calibration standards and with their help the absolute scattering intensity of other liquids and solutions are determined. All specific parameters of the scattering apparatus (e.g. distance $r$ of the detector, size of the scattering volume, primary beam intensity of the laser) are therefore eliminated. For the measurement of the Rayleigh ratio of any solution the following formula has to be applied:

$$
R(\theta) = \frac{I_{\text{solution}}}{I_{\text{standard}}} \cdot RR_{\text{standard}}
$$

2

$RR_{\text{standard}}$: Absolute scattering intensity of the standard. (for toluene at 90° scattering angle, 23°C, the value is $14.02 \times 10^{-6}$ cm$^{-1} @ 633$ nm)

Einstein developed the fluctuation theory for the scattering in a solution. Scattering can only occur if there are differences of the refractive index of a small volume compared to its neighborhood. Since $\theta$ in a liquid or a solution is described as a function of fluctuations of the density and the fluctuation of the concentration due to
thermal movements of the molecules,

\[
R(\theta) = \frac{4\pi^2}{L_0^2 N_L} \rho \cdot n_0^2 \left( \frac{dn}{d\theta} \right)^2 R \beta + \left( n_0 \frac{dn}{dc} \right)^2 R \beta \frac{M_0}{\rho_0} \left( -\frac{d\Delta \mu}{dc} \right)
\]

(3)

\( L_0 \): Avogadro constant
\( \rho, \rho_0 \): Density of the solution and solvent
\( n, n_0 \): Refractive index of solution and solvent
\( \beta \): Isothermal compressibility
\( M_0 \): Molar mass of the solvent
\( \Delta \mu \): Difference of the chemical potential of solution and solvent

There are two contributions for the Rayleigh ratio (density fluctuations and concentration fluctuations). For diluted solutions it can be assumed that the contribution of the density fluctuations of solution and solvent are the same. Therefore the scattering of the dissolved substance is given by:

\[
R(\theta) = R(\theta)_{\text{solution}} - R(\theta)_{\text{solvent}} = \frac{4\pi^2 n_0^2}{L_0^2 N_L} \left( \frac{dn}{dc} \right)^2 \frac{RT M_0 c}{\rho_0} \left( -\frac{d\Delta \mu}{dc} \right)
\]

(4)

The change of the chemical potential with the concentration can be described as a change of the osmotic pressure with concentration:

\[
-\left( \frac{d\Delta \mu}{dc} \right) = \frac{M_0}{\rho_0} \left( \frac{d\Pi}{dc} \right)
\]

(5)

\( \Pi \): Osmotic pressure

Use of a series development of the osmotic pressure with respect to concentration yields:

\[
\left( \frac{d\Pi}{dc} \right) = RT \left( \frac{1}{M} + 2A_2c + 3A_3c^2 + \ldots \right)
\]

(6)

\( A_2, A_3 \): Virial coefficients of the osmotic pressure

Inserting eqs. 5 and 6 in eq 4 yields:

\[
\frac{Kc}{R(\theta)} = \left( \frac{1}{M} + 2A_2c + 3A_3c^2 + \ldots \right)
\]

(7)
Furthermore, for polymers with dimensions in the range of the wavelength of the light applied (particles larger than $\lambda/20$), interference of the scattered light occurs:

At the angle $\theta = 0^\circ$ the path difference of the scattered elemental waves is zero, therefore the scattered intensity of large particles is not influenced by interference effects. Extrapolating the scattered intensity to zero angle allows us to interpret the result in terms of the Rayleigh theory. (however, measurements at $\theta = 0$ are not possible because the primary beam intensity is much larger than the scattered beam intensity (factor of $10^6$)).

For large particles the dependence of the scattered intensity is expressed by the form factor $P(q)$. For the calculation of $P(q)$ it has to be considered that due to thermal (Brownian) motion a particle adopts all possible orientations in space. Therefore an
average value of all possible orientations and distances are measured:

\[ P(\vec{q}) = \frac{1}{N^2} \sum_i \sum_j \left\{ \exp(i\vec{q} \cdot \vec{r}_{ij}) \right\} \]  

(8)

\[ q = \|\vec{q}\| = \frac{4\pi n}{\lambda_0} \sin\left(\frac{\theta}{2}\right) \] : Norm of the scattering vector \( \vec{q} \)

**N:** Number of scattering centers within a particle  
**\( r_{ij} = r_i - r_j \):** Distance of scattering centers \( i \) and \( j \)  
**\( n \):** Refractive index of the solvent

Integration over all possible orientations yields:

\[ P(\vec{q}) = \frac{1}{N^2} \sum_i \sum_j \left\{ \sin(qr_{ij}) \right\} \] with \( i \neq j \)

(9)

For small values of the scattering vector \( q \), the form factor \( P(q) \), which only depends on shape and size of the particle, can be rewritten as a polynomial series:

\[ P(q) = 1 - \frac{q^2}{3lN^2} \sum_i \sum_j \left\{ q^2 r_i^2 \right\}^{\frac{1}{2}} + \ldots \quad \text{(break off after the 2nd term)} \]  

(10)

The mean squared radius of gyration is defined by:

\[ \langle r_i^2 \rangle = \frac{1}{N} \sum_i \left\{ r_i^2 \right\} = \frac{1}{2N^2} \sum_i \sum_j \left\{ r_i^2 \right\} \]

(11)

\( \vec{r}_i \): Distance vector of scattering center \( i \) from the center of mass of the particle

Application of eqs 10 and 11 yields for monodisperse particles:

\[ P(q) = 1 - \frac{1}{3} q^2 \langle r_i^2 \rangle + \ldots \]  

(12)

Polydispersity does not only influence the form factor but also the mean squared radius of gyration:

\[ \langle \langle r_i^2 \rangle \rangle = \frac{\sum_{i} m_i M_i \langle R_{i}^2 \rangle_i}{\sum_{i} m_i M_i} \]

(13)
\[ \left\langle r_{z}^2 \right\rangle_i : \text{z-average of the square of the radius of gyration} \]
\[ \left\langle r_{z}^2 \right\rangle_i : \text{Square of the radius of gyration of particle } i \]

\( m_i : \text{Mass of the particle } i \)
\( M_i : \text{Molar mass of the particle } i \)

Therefore we can rewrite eq 7:

\[
\frac{Kc}{R(0)} = \frac{1}{M_w P_2(q)} + 2 A_2 c + 3 A_3 c^2 + \ldots \tag{14}
\]

Using the relationships in eq 14

\[
\frac{1}{1+x} \equiv 1 - x, \text{ or } \frac{1}{1-x} \equiv 1 + x
\]

we get the famous Zimm Equation:

\[
\frac{Kc}{R(0)} = \frac{1}{M_w} \left( 1 + \frac{1}{3} q^2 \left\langle r_{z}^2 \right\rangle_i \right) + 2 A_2 c + \ldots \tag{15}
\]

By plotting the data \( \frac{Kc}{R(0)} \) as a function of \( q^2 + kc \), we can extrapolate for \( c \to 0 \) and \( q^2 \to 0 \). From the intercept of both the c-dependence as well as the \( q^2 \) dependence we can calculate \( M_w \) and from the slopes we get \( <R_z>z \) (from \( q^2 \) dependence) and \( A_2 \) (from c dependence).
(1) Berry plot

Sometimes Zimm plot does not give a linear plot (Zimm plot is excellent in fitting mid-size particles 20~50 nm), an alternative plot is thus tested. Similar to the Zimm plot, the data \((Kc/R(\theta))^{1/2}\) is plotted as a function of \(q^2 + kc\) (Berry plot) according to the following equation:

\[
\left( \frac{Kc}{R(\theta)} \right)^{1/2} = \left( \frac{1}{M} \right)^{1/2} \{ 1 + R_G^2q^2/6 + \ldots \}
\]  

(16)

Berry plot is useful for high molecular weight flexible polymers (>50 nm).

(2) Guinier plot (Another way to obtain \(<R_z^2>\))

Guinier used the expression: \(\ln(I-x) \approx -x\) to obtain the equation:

\[
\ln(I(q)) = \ln(I(0)) - \frac{q^2R_z^2}{3}
\]

(17)

Thus plotting \(\ln I\) against \(q^2\) gives \(<R_z^2>\) directly. Example \(\ln I \times q\) against \(q\): (slopes give \(<R_z^2>\))
(3) Kratky plot (Kratky-Porod plot)

A plot of $\frac{q^2 R(q)}{Kc}$ vs. $q$ (or $\frac{u^2 R(q)}{Kc}$ vs. $u$, where $u$ is is dimensionless $q = q < R >^{1/2}$).

Features:  
(1) straight line: rigid rod  
(2) a well-developed plateau: Gaussian coil  
(3) a combination of (2) & (3): kink-point defines $q^*$  
“coillike-to-rodlike transition” $I_k = 12 / \pi q^*$

Problem: is difficult to identify in a coillike behavior plot (Kratky plot)

\[ \frac{Kc}{R(q)} = \frac{1}{M_n P(q)} \]
(4) Holtzer plot (Cassasa-Holtzer plot)

A plot of \( \frac{qR(q)}{Kc} \) vs. \( q \) (or \( \frac{qR(q)}{Kc} \) vs. \( u \))

Features: (1) rod

(2) wormlike chain (semirigid): plateau value at large \( q = \pi M_L \) (where \( M_L \) is the mass per unit length); the ratio of maximum height/ asymptotic plateau height determines the number of Kuhn segments \( N_K \).

(3) coil
Monodisperse chains: $u_{max} = 1.4$; polydisperse chains: $u_{max}$ is a function of polydispersity.

Dynamic Light Scattering (Quasi-elastic Light Scattering or Photon Correlation Spectroscopy)

In dynamic light scattering the fluctuations of the scattering intensity due to Brownian motion of the particles are correlated by means of an intensity-time autocorrelator. The correlator monitors the scattering intensities in small time intervals over a total observation time $t = n \Delta t$ with $n$ the number of time intervals. Typically
\( n = 100 - 500 \) and \( \square = 1 - 1000 \) \( \square \) sec. The autocorrelation function \( g_2(t) \) is then calculated as

\[
g_2(t) = \left\langle I(t = 0) \cdot I(t = n \cdot \tau) \right\rangle
\]

where the brackets \( \langle \ldots \rangle \) denote an average over typically \( 10^6 - 10^8 \) single correlations. For ergodic medium, the ensemble average equals to the time average. From \( g_2(t) \) the electric field correlation function \( g_1(t) \) is derived by the Siegert relation

\[
g_2(t) = A(1 + \beta |g_1(t)|^2)
\]

where \( A \) is a measured baseline and \( \beta \) is a parameter \( (< 1) \) depending on the coherence of the detection. The baseline \( A \) can be determined as

\[
A = \lim_{t \to \infty} g_2(t) = \left\langle I \right\rangle^2
\]

In this limit the intensities \( I(t=0) \) and \( I(t \square \square) \) are not correlated, i.e.

\[
\left\langle I(t = 0) I(t = \infty) \right\rangle = \left\langle I(t = 0) \right\rangle \left\langle I(t = \infty) \right\rangle = \left\langle I \right\rangle^2
\]

Since

\[
\lim_{t \to 0} g_2(t) = \left\langle I^2 \right\rangle
\]

the intensity correlation function decays from \( \langle I^2 \rangle \) to \( \langle I \rangle^2 \).

\[
\langle I(q, t) I(q, t + \tau) \rangle = \langle I \rangle^2 \left[ f(q, \tau) \right]^\tau
\]

\[
\sim T_C
\]

In a dilute solution, for particles in Brownian motion, \( g_1(t) \) is reduced to:

\[
g_1(t) = \exp(-\Gamma t)
\]

where \( \Gamma = D^2 q \) is the relaxation rate and \( D \) is the diffusion coefficient. A dynamic Zimm plot can be used to obtain the z-average \( D \) as \( q \to 0 \) and \( c \to 0 \).

\[
D(q, c) = D_o \left( 1 + C q^2 R_g^2 + \ldots \right) \times \left( 1 + k_D c + \ldots \right)
\]

applying the Stokes-Einstein equation we can calculate the hydrodynamic radius of a corresponding sphere:
\[ R_t = \frac{1}{\left( n_R/2 \right)^{1/2}} = \frac{kT}{6\pi \eta_0 D_t} \]  

(25)

where \( k \) Boltzmann factor, \( T \) temperature in K, \( \eta_0 \) viscosity of the solvent. The \( <R_z^2>/R_t \) ratio is 1.0 for hard sphere, 1.23 for unperturbed coils, 1.5~1.7 for coils in good solvents.

Sometime, the cumulant expansion method is used to extract more information from \( g_1(t) \)

\[
\ln g^{(0)}(t) = -\Gamma_1 t + (\Gamma_2/2)t^2 - (\Gamma_3/3)t^3 + \ldots
\]

(26)

**Comparison of LLS, SAXS, and SANS**

<table>
<thead>
<tr>
<th>Table 1.B.1</th>
<th>LLS (nm)</th>
<th>SAXS (nm)</th>
<th>SANS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Representative wavelength (nm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scattering angle (rad)</td>
<td>Min. 5 x 10^{-2}</td>
<td>Typical π/2</td>
<td>Max. π</td>
</tr>
<tr>
<td></td>
<td>1.05 x 10^{-3}</td>
<td>2.96 x 10^{-3}</td>
<td>4.19 x 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>2.09 x 10^{-3}</td>
<td>0.419</td>
<td>0.157</td>
</tr>
<tr>
<td></td>
<td>1.5 x 10^{-4}</td>
<td>1.5 x 10^{-1}</td>
<td>1.5 x 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>4.0 x 10^{-1}</td>
<td>6.34</td>
<td>6.37</td>
</tr>
<tr>
<td></td>
<td>4.0 x 10^{-1}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy transfer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta f ) (wave number, cm^{-1})</td>
<td>Typical 8 x 10^{-4}</td>
<td>10^{-13}</td>
<td>10^{-13}</td>
</tr>
<tr>
<td>( E_{\text{iso}} ) (eV)</td>
<td>4 x 10^{-3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

X-rays are scattered by electrons (roughly proportional to the atomic number); neutrons are scattered by nuclei (characterized by “scattering length” \( b \), which is not a function of atomic number); and light is scattered according the polarizability \( \alpha \) (proportional to the square of index of refraction).