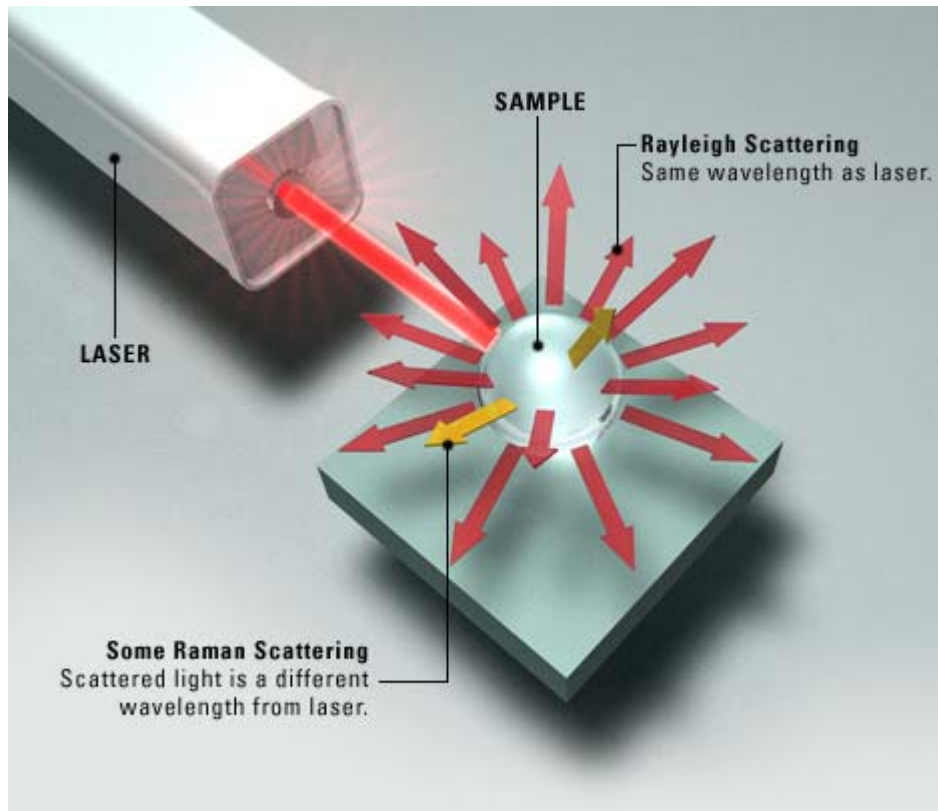


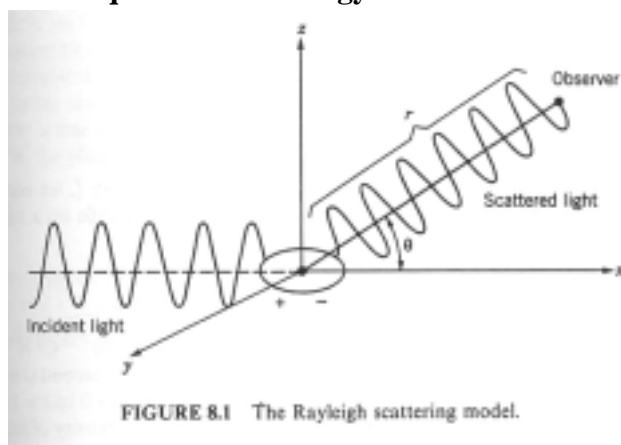
Part 8. Special Topic: Light Scattering

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** $\langle R^2 \rangle_z$ 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:

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

$R(\theta)$: 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

λ_0 : Wavelength of the primary beam in vacuum

N_k : Number of scattering centers

α_k : Polarizability of the scattering center k (polarization $p = \alpha E$)

θ : 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:

$$R(\theta) = \frac{I_{\text{solution}} - I_{\text{solvent}}}{I_{\text{standard}}} \cdot RR_{\text{standard}} \quad (2)$$

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

$$R(\theta) = \frac{4\pi^2}{\lambda_0^4 N_L} \left\{ \rho \cdot n_0^2 \left(\frac{dn}{d\rho} \right)^2 RT\beta + \left(n_0 \frac{dn}{dc} \right)^2 RT \frac{M_0}{\rho_0} \left(\frac{-d\Delta\mu}{dc} \right) \right\} \quad (3)$$

N_L : Avogadro constant

ρ, ρ_0 : Density of the solution and solvent

n, n_0 : Refractive index of solution and solvent

β : 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:

$$R(\theta) = R(\theta)_{\text{solution}} - R(\theta)_{\text{solvent}} = \frac{4\pi^2 n_0^2}{\lambda_0^4 N_L} \left(\frac{dn}{dc} \right)^2 \frac{RTM_0c}{\rho_0 \left(\frac{-d\Delta\mu}{dc} \right)} \quad (4)$$

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

$$-\left(\frac{d\Delta\mu}{dc} \right) = \frac{M_0}{\rho_0} \left(\frac{d\Pi}{dc} \right) \quad (5)$$

Π : Osmotic pressure

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

$$\left(\frac{d\Pi}{dc} \right) = RT \left(\frac{1}{M} + 2A_2c + 3A_3c^2 + \dots \right) \quad (6)$$

A_2, A_3 : Virial coefficients of the osmotic pressure

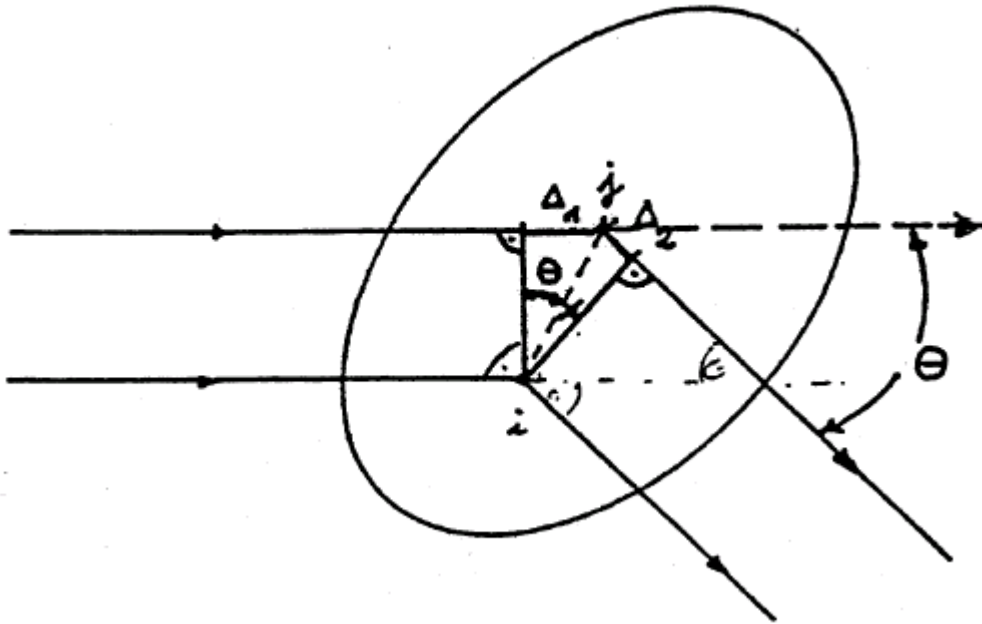
Inserting eqs. 5 and 6 in eq 4 yields:

$$\frac{Kc}{R(\theta)} = \left(\frac{1}{M} + 2A_2c + 3A_3c^2 + \dots \right) \quad (7)$$

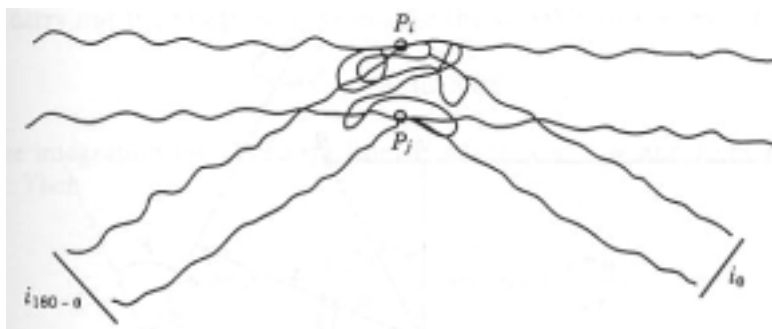
$$K = \frac{4\pi^2 n_0^2}{\lambda_0^4 N_L} \left(\frac{dn}{dc} \right)^2 : \text{Optical constant}$$

M : Molar mass of the dissolved material

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:

$$P(\bar{q}) = \frac{1}{N^2} \sum_1^N \sum_1^N \langle \exp(i\bar{q}\bar{r}_{ij}) \rangle \quad (8)$$

$$q = |\bar{q}| = \frac{4\pi n}{\lambda_0} \sin\left(\frac{\theta}{2}\right) : \quad \text{Norm of the scattering vector } \bar{q}$$

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:

$$P(q) = \frac{1}{N^2} \sum_i^N \sum_j^N \left\langle \frac{\sin(qr_{ij})}{qr_{ij}} \right\rangle \text{ with } i < j \quad (9)$$

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:

$$P(q) = 1 - \frac{q^2}{3!N^2} \sum_i^N \sum_j^N \langle r_{ij}^2 \rangle + \dots \quad (\text{break off after the 2nd term}) \quad (10)$$

The mean squared radius of gyration is defined by:

$$\langle R_g^2 \rangle = \frac{1}{N} \sum_i^N \langle \bar{r}_i^2 \rangle = \frac{1}{2N^2} \sum_i^N \sum_j^N \langle r_{ij}^2 \rangle \quad (11)$$

\bar{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:

$$P(q) = 1 - \frac{1}{3} q^2 \langle R_g^2 \rangle + \dots \quad (12)$$

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

$$\langle R_g^2 \rangle_z = \frac{\sum_i m_i M_i \langle R_g^2 \rangle_i}{\sum_i m_i M_i} \quad (13)$$

$\langle R_g^2 \rangle_z$: z-average of the square of the radius of gyration

$\langle R_g^2 \rangle_i$: Square of the radius of gyration of particle i

m_i : Mass of the particle i

M_i : Molar mass of the particle i

Therefore we can rewrite eq 7:

$$\frac{Kc}{R(\theta)} = \left(\frac{1}{M_w P_z(q)} + 2A_2c + 3A_3c^2 + \dots \right) \quad (14)$$

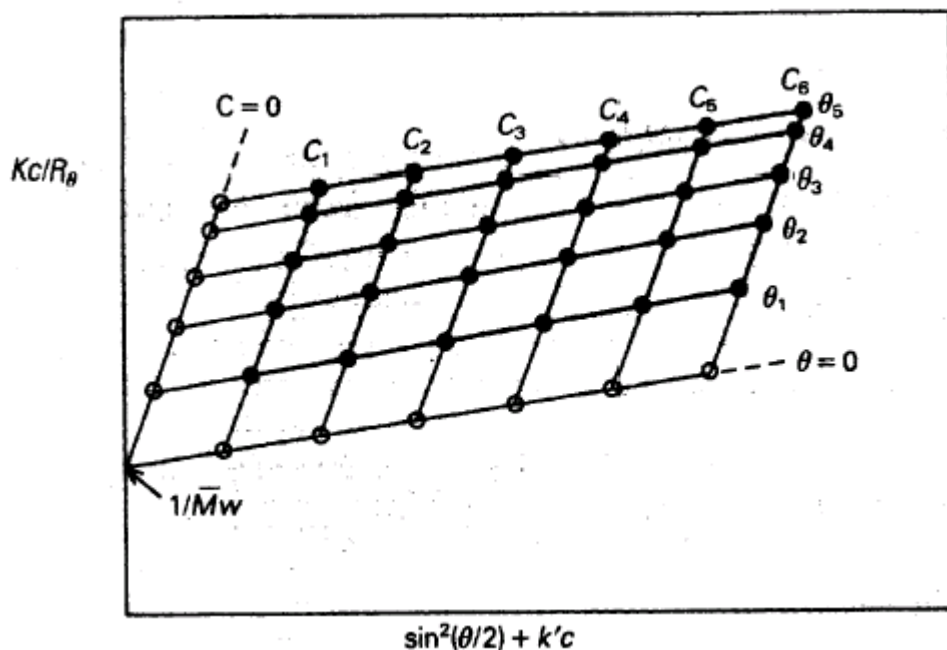
Using the relationships in eq 14

$$\frac{1}{1+x} \cong 1-x, \text{ or } \frac{1}{1-x} \cong 1+x$$

we get the famous Zimm Equation:

$$\frac{Kc}{R(\theta)} = \frac{1}{M_w} \left(1 + \frac{1}{3} q^2 \langle R_g^2 \rangle_z \right) + 2A_2c + \dots \quad (15)$$

By plotting the data $\frac{Kc}{R(\theta)}$ as a function of $q^2 + kc$, we can extrapolate for $c = 0$ and $q^2 = 0$. 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 $\langle R_g^2 \rangle_z$ (from q^2 dependence) and A_2 (from c dependence).

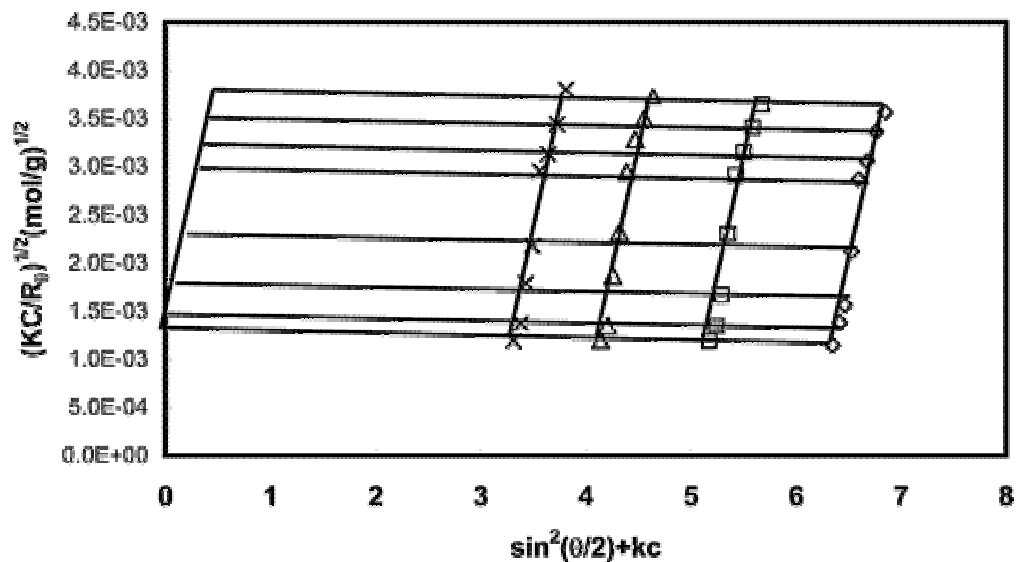


(1) Berry plot

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:

$$\left(\left(\frac{Kc}{R(q,c)} \right)^0 \right)^{1/2} = \left(\frac{1}{M} \right)^{1/2} \{ 1 + R_G^2 q^2 / 6 + \dots \} \quad (16)$$

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

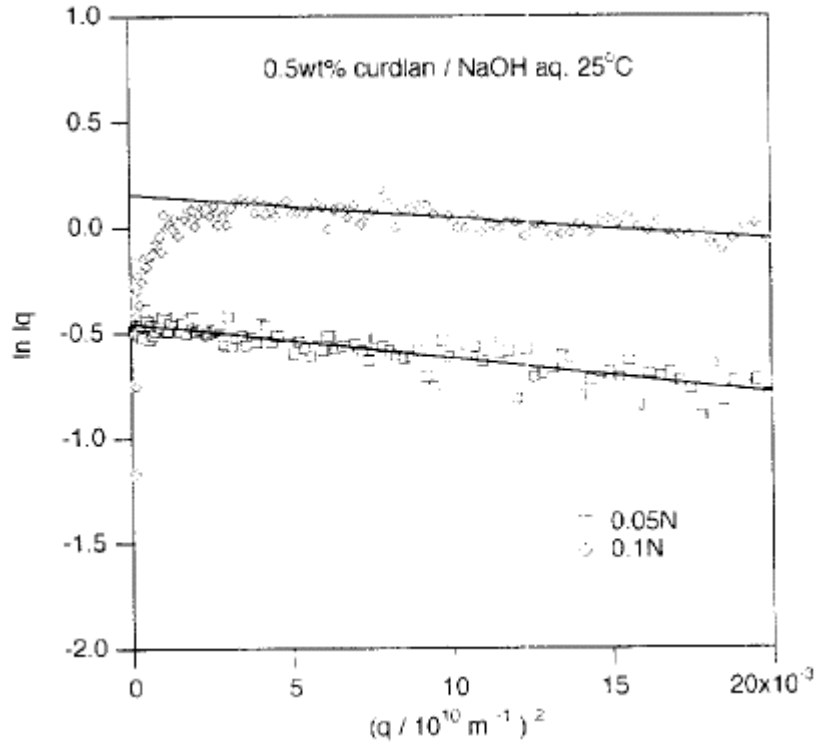


(2) Guinier plot (Another way to obtain $\langle R^2 \rangle_z$)

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

$$\ln(I(q)) = \ln(I(0)) - \frac{q^2 R_g^2}{3} \quad (17)$$

Thus plotting $\ln I$ against q^2 gives $\langle R^2 \rangle_z$ directly. Example $\ln I \times q$ against q : (slopes give $\langle R^2 \rangle_z$)



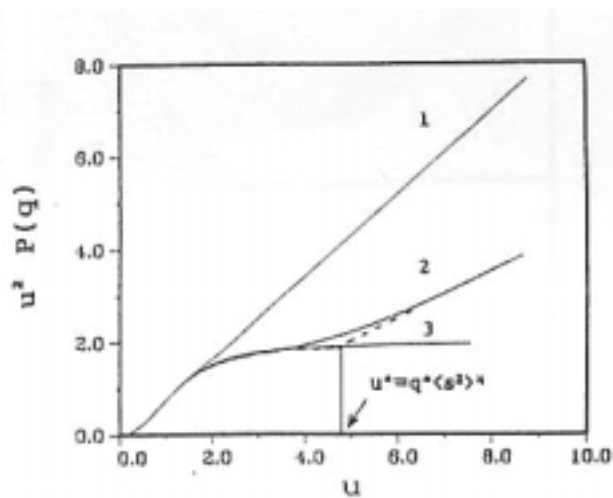
(3) Kratky plot (Kratky-Porad plot)

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

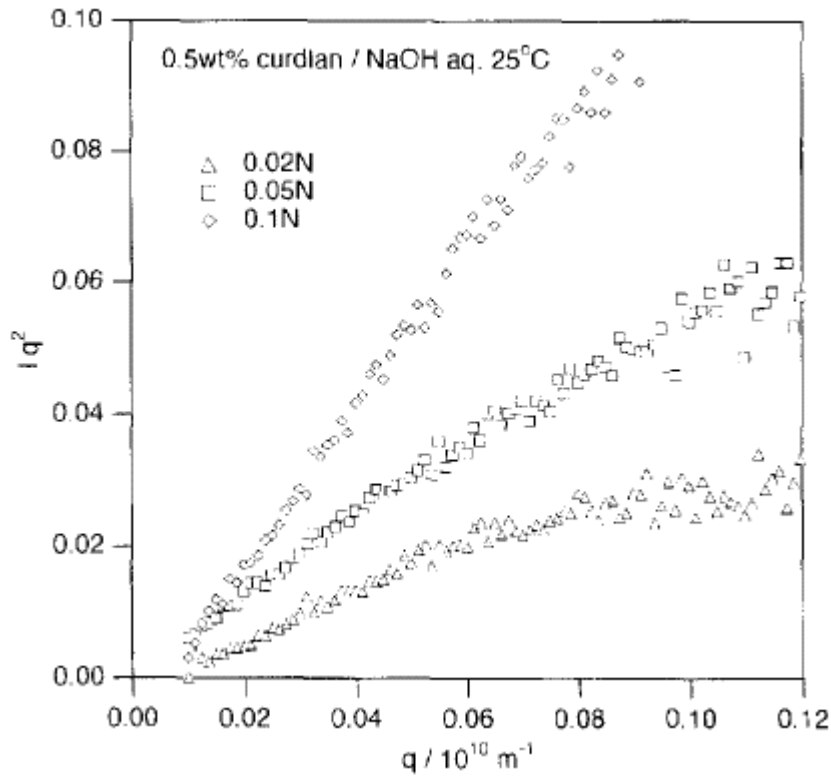
- Features:
- (1) straight line: rigid rod
 - (2) a well-developed plateau: Gaussian coil
 - (3) a combination of (2) & (3): kink-point defines q^*

“coil-like-to-rod-like transition” $l_k = 12 / \pi q^*$

Problem: is difficult to identify in a coil-like behavior plot (Kratky plot)



(note: $\frac{Kc}{R(q)} = \frac{1}{M_w P(q)}$)



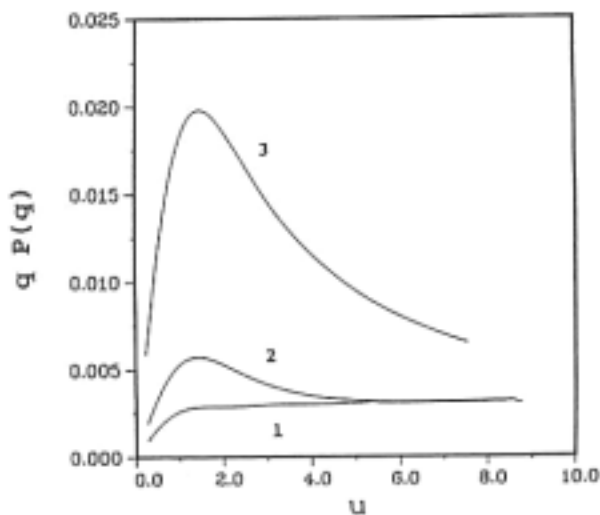
(4) Holtzer plot (Cassasa-Holtzer plot)

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

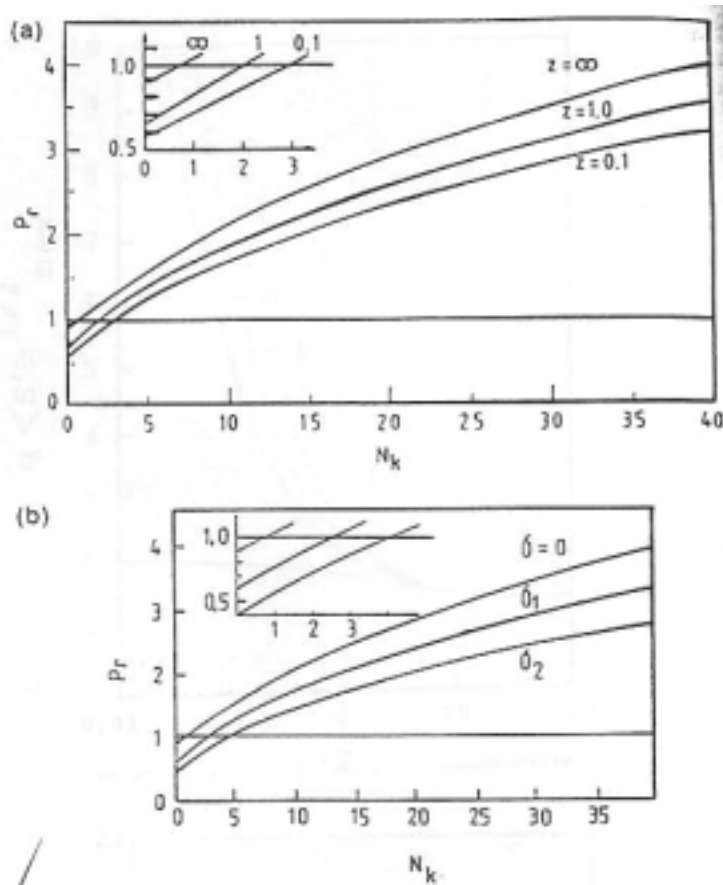
Features: (1) rod

(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 .

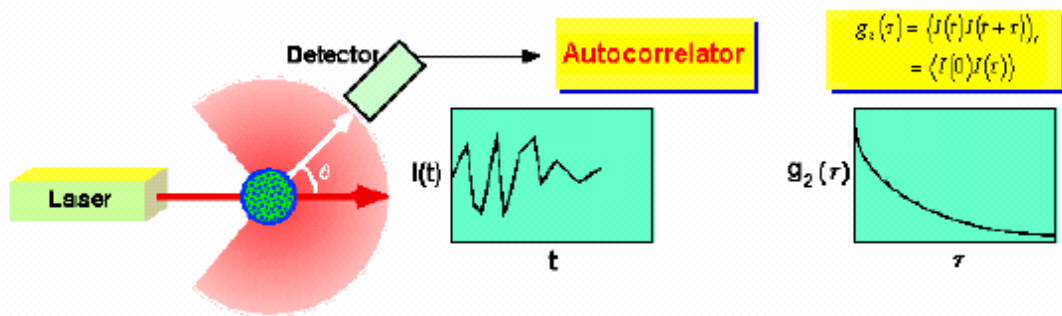
(3) coil



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 $t=n \cdot \Delta t$ with n the number of time intervals Δt . Typically

$n=100-500$ and $\tau=1-1000 \mu \text{ sec}$. The autocorrelation function $g_2(t)$ is then calculated as

$$g_2(t) = \langle I(t=0) \cdot I(t=n \cdot \tau) \rangle \quad (18)$$

where the brackets $\langle \dots \rangle$ 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**

$$g_2(t) = A(1 + \beta |g_1(t)|^2) \quad (19)$$

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

$$A = \lim_{t \rightarrow \infty} g_2(t) = \langle I \rangle^2 \quad (20)$$

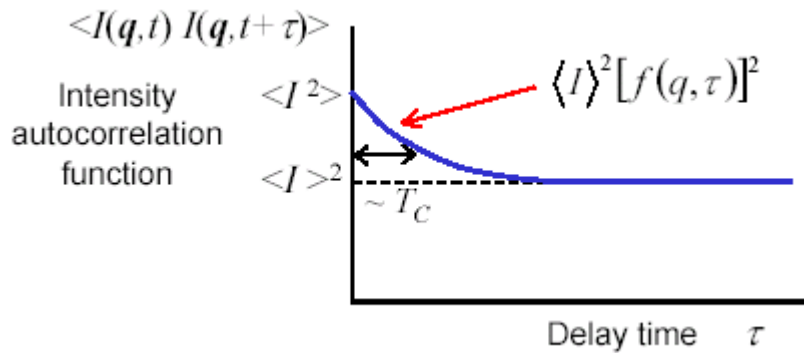
In this limit the intensities $I(t=0)$ and $I(t \rightarrow \infty)$ are not correlated, i.e.

$$\langle I(t=0)I(t \rightarrow \infty) \rangle = \langle I(t=0) \rangle \langle I(t \rightarrow \infty) \rangle = \langle I \rangle^2 \quad (21)$$

Since

$$\lim_{t \rightarrow 0} g_2(t) = \langle I^2 \rangle \quad (22)$$

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



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

$$g_1(\tau) = \exp(-\Gamma \tau) \quad (23)$$

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 $q \rightarrow 0$ and $c \rightarrow 0$.

$$D(q, c) = D_o(1 + Cq^2 R_g^2 + \dots) \times (1 + k_D c + \dots) \quad (24)$$

applying the Stokes-Einstein equation we can calculate the hydrodynamic radius of a corresponding sphere:

$$R_h = \left\langle \frac{1}{R_h} \right\rangle_z = \frac{kT}{6\pi\eta_0 D_z} \quad (25)$$

where k Boltzmann factor, T temperature in K, η_0 viscosity of the solvent. The $\langle R^2 \rangle_z^{1/2}/R_h$ 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 $g(t)$

$$\ln g^{(1)}(t) = -\Gamma_1 t + (\Gamma_2 / 2!)t^2 - (\Gamma_3 / 3!)t^3 + \dots \quad (26)$$

Comparison of LLS, SAXS, and SANS

Table I.B.1

	LLS ⁽¹⁾			SAXS ⁽¹⁾		SANS ⁽¹⁾
Momentum transfer						
Representative wavelength (nm)	300			0.15	λ^*	0.4
Scattering angle (rad)	Min. 5×10^{-2}	Typical $\pi/2$	Max. π	Min. 5×10^{-4}	Typical 10^{-2}	Typical 10^{-2}
K (nm^{-1})	1.05×10^{-3}	2.96×10^{-2}	4.19×10^{-2}	2.09×10^{-2}	0.419	0.157
K^{-1} (nm)	952	33.8	23.9	47.9	2.39	6.37
d ($= 2\pi/K$, nm)	5.98×10^3	212	150	301	15.0	40.0
Energy transfer						
$\Delta\gamma$ (wave number, cm^{-1})	Typical 8×10^{-9}					Typical 8×10^{-3}
$\hbar\Delta\omega$ (eV)	10^{-12}					10^{-4}
τ (μsec)	4×10^3					4×10^{-3}

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 α (proportional to the square of index of refraction).

