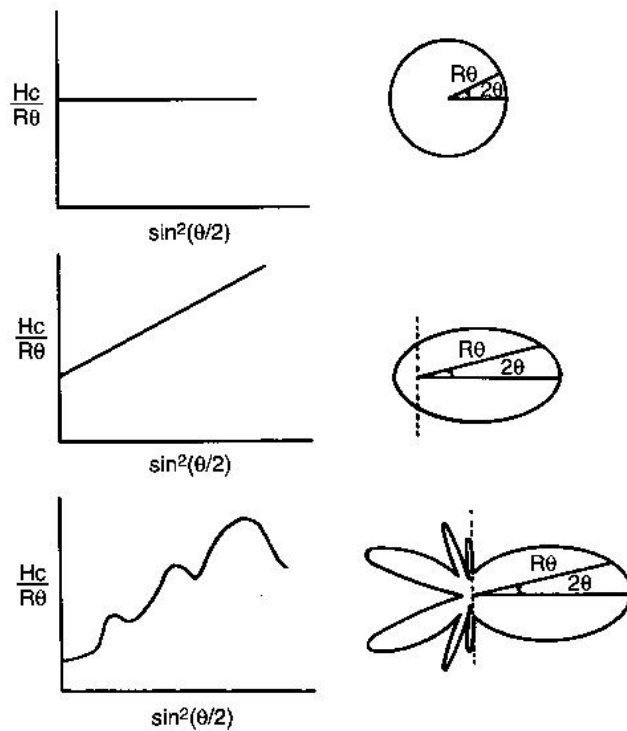Figure 3.8 middle: Until 180° phase difference is attained scattering intensity decreases with increasing angle. Scattering must be observed for angle smaller than $KR_g=1$ (Eq 55) to determine R_g.

Figure 3.8 Scattering intensity envelopes for small, medium, and large particles. The G region contains both the small and medium ranges, but the medium range is far more used for scattering experiments.

For ordinary sized polymer, R_g= O (100-200A)

→For light scattering, Θ is measured in 45°< Θ <135° because λ is 5000A.

$$< \; K = \frac{4\pi_1}{\lambda}\sin\left(\frac{\theta}{2}\right) \; > \qquad (3.49)$$

→For X ray (λ =1-2A), thermal neutrons (λ =5A)→ Θ<1°.

Note R_g is the mean square distance away from the center of gravity:

$R_g{}^2 = (1/N)\sum r_i{}^2)$ (N=Total number of scattering points)

For random coil,

$$R_g^2 = \frac{r^2}{6} \qquad (3.56) \quad (r=\text{End-to-end distance}).$$

Depending on the geometry P(Θ) is given by

Sphere

$$P(\theta) = \left[\frac{3}{x^3}(\sin x - x\cos x)\right]^2 \qquad x = \frac{ksD}{2} \qquad (3.57)$$

D=Diameter of sphere, ks=K

Rod

$$P(\theta) = \frac{1}{x}\int_0^{2x}\frac{\sin w}{w}dw - \left(\frac{\sin x}{x}\right)^2 \qquad x = \frac{ksL}{2} \qquad (3.58)$$

L=Length of rod

Coil

$$P(\theta) = \frac{2}{x^2}[e^{-x} - (1 - x)] \qquad x = \frac{k^2 s^2 r^2}{6} \qquad (3.59)$$

R=rms of end-to-end distance

Note (59) is rearranged to (49).

3.6.3 The Zimm plot

Plotting of the data is shown in Figure 3.10.

$$\left(H\frac{c}{R(\theta)}\right)_{\theta=0} = \frac{1}{M_w} + 2A_2 c + \cdots \quad (3.50)$$

$$\left(H\frac{c}{R(\theta)}\right)_{c=0} = \frac{1}{M_w}\left[1 + \frac{1}{3}\left(\frac{4\pi_1}{\lambda'}\right)^2 R_g^2 \sin^2\frac{\theta}{2} + \cdots\right] \quad (3.51)$$
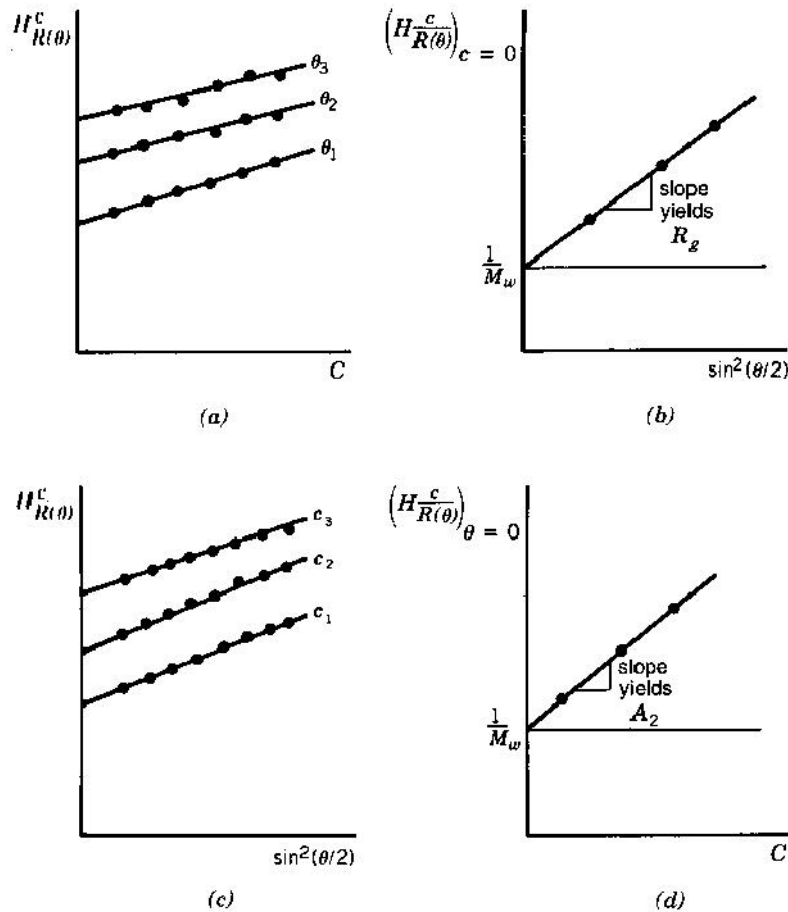

Figure 3.10 Illustration of a light-scattering calculation.

(a) $\left(H\frac{c}{R(\theta)}\right)$ vs concentration plot for three angles extrapolated to c=0.

(b) Replot of the intercept from (a) vs $\sin^2\frac{\theta}{2}$ to yield M_w and R_g.

(c) Same data as (a) are replotted against $\sin^2\frac{\theta}{2}$

(d) Intercepts of (c) are plotted against concentration to yield M_w and A_2.

Note the intercept of (b) and (d) must be equal.

Most powerful Zimm plot is obtained by plotting $\left(H\dfrac{c}{R(\theta)}\right)$ vs a function of both angle and concentration to calculate M_w, R_g, A_2 from a single master curve (Figure 3.11a). Concentration is multiplied by a constant (1×10^3) which is divided out for the final answer.

Scan Figure 3.11 here (Better plot is shown on the next page)
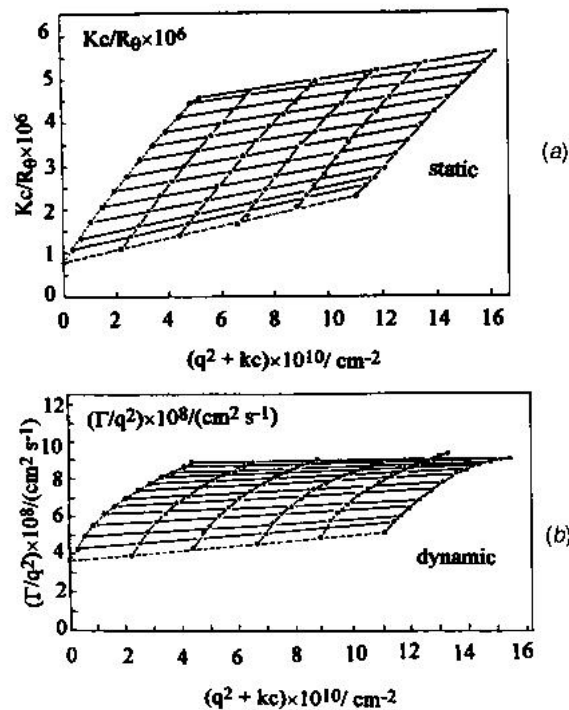
Figure 3.11 Zimm plots of a bacterial polysaccharide in 0.1 M NaCl. Top: Static, bottom: Dynamic light scattering. $\lambda_0 = 488$ nm, $dn/dc = 0.145$ cm^3/g. Static light-scattering yields R_g, M_w, and A_2. Dynamic light-scattering yields the diffusion coefficient, D. Results: $M_w = 1.25 \times 10^6$ g/mol, $D_z = 3.58 \times 10^{-9}$ cm^2/s. Terms: $q = (4\pi/\lambda)\sin(\theta/2)$, $\Gamma = Dq$.

3.6.8 Polymer chain dimensions and random coils

Drop a string of beads (mers) to water→Conformation of the string changes continuously→Resemble random coiled or Gaussian chains

For random chains the two relationships are hold:

$$r^2 = CM \qquad (3.60) \qquad \text{C=C (Molecular structure)}$$

$$R_g^2 = \frac{1}{6}r^2 \qquad (3.61)$$

3.6.5 Scattering data

►1950s: Polymer chains in amorphous bulk state are similar to those under Flory Θ condition (But no bulk state data available)

►1970s: SANS determined bulk state and Θ condition gave substantially the same value of $(R_g^2/M_w)^{1/2}$.

►$(R_g^2/M_w)^{1/2}= R_g$ (in Λ) = Measure of chain stiffness.

 $(R_g^2/M_w)^{1/2}=0.475$ (PC), 0.275 (PS): PC is stiffer than PS

►Melt and solution viscosity depends on the R_g.

►Random coil theory is used in rubber elasticity, mechanical and relaxation calculations.

3.6.6 Dynamic light scattering

Make use of scattering from very small volume at very short time intervals, and correlates the scattering intensity fluctuations with time to measure diffusion coefficients and particle size in polymers and colloids.

Two approaches

1) Modified Doppler experiment

Frequency increases/decreases as molecules or particles moving toward/away from the beam→Frequency broadening is 10-100hz which is hard to be resolved.

2) Focus a laser light beam down to a waist of 0.1mm, yielding volume of 1×10^{-3} mm^3. Each measurement time is O (1μs).

▶Under these condition there exist scattering intensity-time (I-t) correlations (Autocorrelation).

▶Diffusion coefficient is determined by Stokes-Einstein relationship. For dilute solution

$$D_{app}(K, c) = D_{z0}(1 + CR_g^2K^2)(1 + k_{Dc}) \qquad (3.62)$$

$D_{app}(K, c)$=Diffusion coefficient at finite angle and concentration

D_{z0}=Corresponding z-average value at zero concentration and angle

C=Coefficient characteristic of the polymer

k_{Dc}=Dynamic interaction parameter

Figure 3.11 illustrate the DLS Zimm plot where Γ=DK^2, K=q→M$_w$=1.27x10^{6}g/mol, D$_z$=3.58x10^{-8}cm2/s.

Stokes-Einstein equation to determine D and d (More common)

▶For a solution of given viscosity (η), at a constant temperature (T), the rate of diffusion is given by the Stokes-Einstein equation (Accept),

$$D = \frac{kT}{6\pi\eta d}$$

- Measure intensity (I) at various time interval (τ),

- $I(0) = I(\tau)$ for short τ → "Correlated"

- Define anto-correlation function, **G(τ)= <I(t) I(t+τ)>**= Average of the intensity product. Correlation decreases as τ increases.

- High G(τ) means particles have not diffused away during τ.

- Thus G(τ) remaining high for a long time interval indicates large, slowly moving particles.

    The time scale of fluctuation is called decay time which is related to the particle size. Decay constant (Γ)≡1/Decay time

    Large, slowly moving particles →long decay time and small Γ