

Figure 3.5 illustrates the determination of Flory Θ temperature.

Table 3.6 lists polymers and their Θ temperature.

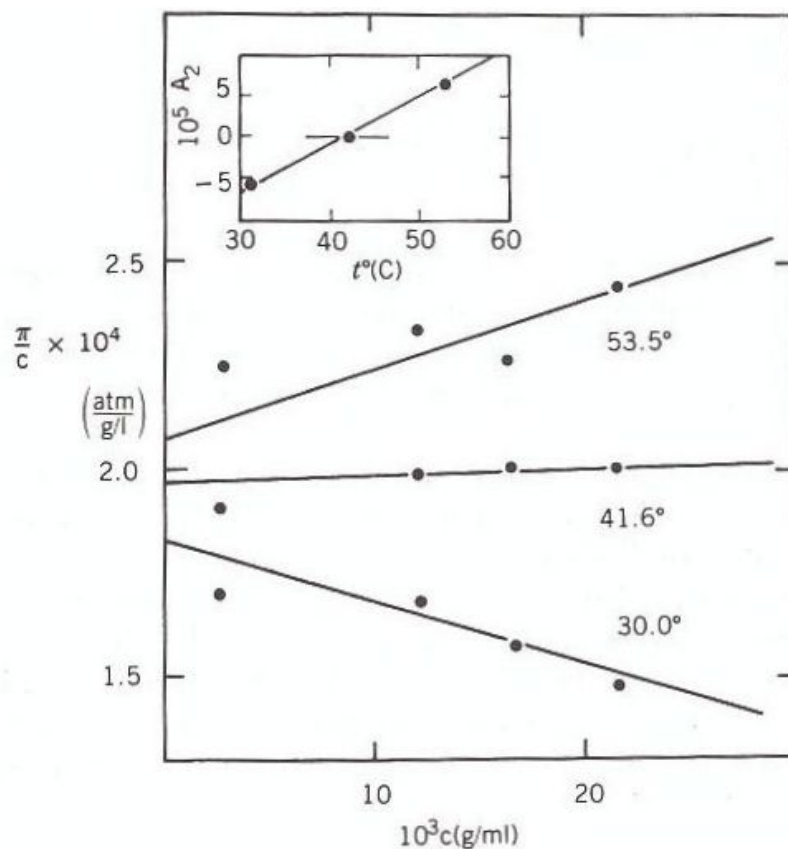


Figure 3.5 The osmotic pressure data for cellulose tricaproate in dimethylformamide at three temperatures. The Flory θ -temperature was determined to be $41 \pm 1^\circ\text{C}$ (25).

Table 3.6 Polymers and their θ -solvents (26)

Polymer	Solvent	Temperature ($^\circ\text{C}$)
<i>cis</i> -Polybutadiene	<i>n</i> -Heptane	-1
Polyethylene	Biphenyl	125
Poly(<i>n</i> -butyl acrylate)	Benzene/methanol 52/48	25
Polystyrene	Cyclohexane	34
Poly(oxytetramethylene)	Chlorobenzene	25
Cellulose tricaproate	Dimethylformamide	41

Source: J. Brandrup and E. H. Immergut, eds., *Polymer Handbook*, 2nd ed., Wiley-Interscience, New York, 1975.

3.6 Weight average mol weight and radii of gyration

Principal method to determine M_w = Light scattering

<Aside from SANS and X-ray scattering>

Reflection = Object size \gg Wavelength

Scattering = Object size approaches wavelength to atomic size: Blue sky and rainbow.

► Scattering from small spherical particles ($a < \lambda/20$) → **Rayleigh scattering** (Extended to include large particle using form factor),

► Scattering from large spherical particles ($a \rightarrow 50 \mu\text{m}$) → **Mie scattering** (mathematically complicated)

Scattering from a single electron provides a beginning:

As EM wave approaches electron → Electron absorbs energy and oscillates (**Figure 3.6**) → **Reradiates energy in all directions** (Radiator)

→ **Scatterings**

[Scan Figure 3.6 here](#)

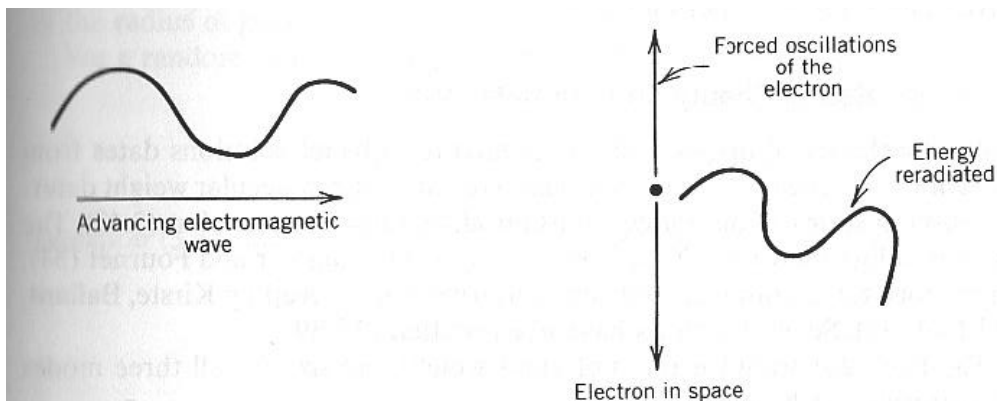


Figure 3.6 The effect of an electromagnetic wave on a free electron. The forced oscillations of the electron involve accelerations and decelerations, which cause the electromagnetic energy to be re-radiated.

Diffraction:

If atom, molecule, particles are organized in a regular array → Radiation is **diffracted**: Scattering is observed only at a special angle (X-rays by a crystal) (All other angles give total **destructive interference** among the scattered radiations).

If structures are not organized in a regular array → Scattering is observed in all angles: **Angular variation of the scattering intensity provides a measure of the size of structures** <form factor>.

► Scattering is caused by **fluctuations in the refractive index** of the medium on the molecular or supermolecular scale.

▷ Scatterings at gas molecules-Vacuum interfaces → **Blue sky**

▷ Slight fluctuations in the spacing of water molecules → Blue sea water

▷ Scattering at crystal-amorphous interfaces → Haze

Application of light scattering to polymer MW is based on the fluctuation of refractive index in liquid (Smoluchowski and Einstein) →

Fluctuation of refractive index of solvent is replaced by the change caused by the polymer molecules (Debye and Zimm).

The final result relates scattering intensity - osmotic pressure (π):

$$\frac{Hc}{R(\theta)} = \frac{1}{RT} \left(\frac{\partial \pi}{\partial c} \right)_T \quad (3.42)$$

$R(\theta)$ = Rayleigh's ratio = $I_\theta w^2 / I_0 V_s$

I_θ = Scattered light intensity observed at angle θ .

V_s = Scattering volume

I_0 = Incident light intensity

w = Distance from the source

H (or K) = Optical constant defined as

$$H = \frac{2\pi^2 n_0^2 (dn/dc)^2}{N_A \lambda^4} \quad (3.43)$$

n_o =Refractive index at a wavelength λ (Both for solvent)

$$\pi_1=3.14$$

N_A =Avogadro's number

dn/dc must be determined for each polymer-solvent pair

H =Constant for polymer-solvent pair, determined experimentally.

3.6.1 Scattering theory and formulation

Debye determined absolute molecular weight in terms of H (Eq. 42)

<X-ray by Guinier, SANS by Kirste et al>

Sub (41) into (42), after differentiation gives

$$\frac{\pi}{c} = RT \left(\frac{1}{M_n} + A_2c + A_3c^2 + \dots \right) \quad (3.41) \rightarrow \frac{Hc}{R(\theta)} = \frac{1}{RT} \left(\frac{\partial \pi}{\partial c} \right)_T \quad (3.42)$$

$$\rightarrow \frac{Hc}{R(\theta)} = \frac{1}{M_w} + 2A_2c$$

Correcting for solvent scatterings, and chain conformation ($P(\theta)$):

$$\frac{Hc}{R(\theta) - R(\text{solvent})} = \frac{1}{M_w P(\theta)} + 2A_2c \quad (3.44)$$

For particle diameter, $a < 0.05 \lambda$

$P(\theta)=1$ (Intensity distribution is symmetrical)

For $a > 0.05 \lambda$

$P(\theta)$ = Form factor which describes the angular scattering.

► $P(\theta)$ independent of particle shape as $\Theta \rightarrow 0$.

► For $K^2 R_g^2 < 1$ (Guinier region, Very small angle (Eq 49)

→ $P(\theta)$ is a measure of R_g ,

▷ For random coil, $P(\Theta)$ is expressed by

$$P(\theta) = \frac{2}{R_g^4 K^4} \{R_g^2 K^2 - [1 - \exp(-R_g^2 K^2)]\} \quad (3.47)$$

Expand this for small x using $e^x = 1 + x + x^2/2! + \dots$ gives

$$P(\theta) = 1 - \frac{K^2 R_g^2}{3} + \dots \quad (3.48)$$

Wave vector (K) is defined as $K = \frac{4\pi_1}{\lambda} \sin\left(\frac{\theta}{2}\right)$ (3.49)

► As $\theta \rightarrow 0$, $K=0$, $P(0)=1$, then Eq 44 relates light scattering intensity to

M_w (Zimm)(Also neglect $R(\text{solvent})$):

$$\frac{Hc}{R(\theta) - R(\text{solvent})} = \frac{1}{M_w P(\theta)} + 2A_2 c \quad (3.44)$$

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

► As $c \rightarrow 0$, Eq 44 becomes upon subbing 49 → 48 → 44 (Zimm):

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

$\lambda' = \lambda_o / n_o$ (Wavelength of the light in solution)

To construct a Zimm plot (50) and (51) are added and the concentration term is usually multiplied by an arbitrary factor to make the concentration term similar to angle term.

→ M_w , R_g^2 , A_2 are determined.

A useful practical eq to determine R_g from $H \frac{c}{R(\theta)}$ vs $\sin^2 \frac{\theta}{2}$ is

$$R_g^2 = \frac{3(\lambda')^2(\text{initial slope})}{16\pi_1^2(\text{intercept})} \quad (3.52)$$

See [Table 3.7](#) for light scattering units.

Convenient light-scattering units are shown in Table 3.7.

Table 3.7 Convenient light-scattering units

$H = \frac{\text{mol} \cdot \text{cm}^2}{\text{g}^2}$	$A_2 = \frac{\text{mol} \cdot \text{cm}^3}{\text{g}^2}$
$c = \frac{\text{g}}{\text{cm}^3}$	$R(\theta) = \text{cm}^{-1}$ $\theta = \text{degrees}$ $\left(\sin^2 \frac{\theta}{2} \text{ for } 90^\circ \text{ is } 0.500, \text{ unitless} \right)$
$M_w = \frac{\text{g}}{\text{mol}}$	

The optical constant (H) depends on the radiation type.

$$H = \frac{2\pi_1^2 n_0^2 (dn/dc)^2}{N_A \lambda^4} \quad \text{<Light scattering>} \quad (3.43)$$

$$H = N_a i_e \left(\frac{\partial \rho_e}{\partial c} \right)^2 = \frac{N_a i_e}{e^2} (\rho_{e_s} - \rho_{e_p})^2 \quad \text{<X-ray>} \quad (3.53)$$

$$H = \frac{N_a}{M_p^2} \left[a_s \left(\frac{V_p}{V_s} \right) - a_p \right]^2 \quad \text{<Neutron scattering>} \quad (3.54)$$

See the nomenclature in Sperling for 53 and 54.

Basic mathematical requirement to determine R_g :

$$K^2 R_g^2 < 1 \quad (3.55) \quad < K = \frac{4\pi_1}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (3.49) >$$

→ There must be only partial destructive interference between two waves striking the same particle so that the wave should not be out of phase by more than 180°

(Figure 3.7)

[Scan Figure 3.7 here](#)

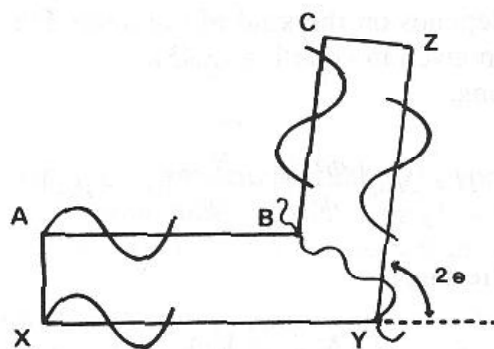


Figure 3.7 Schematic of the scattering phenomenon. When the waves are out of phase, intensity of scattered light is reduced.

Note A-X ⊥ Incidence radiation flux, C-Z ⊥ Scattered flux.

Before scattering, waves tend to be in phase (cohesive). On scattering from points B and Y at an angle 2θ , waves become out of phase. If the angle of scatter is large enough, waves are out of phase by 180° (One wave lags behind the other by $\lambda/2$) the radiation intensity observed at 2θ will be minimum. As θ further increases intensity increases until 360° phase difference is obtained. The practical destructive interference between the waves causes the intensity to vary according to the angle. (See [Figure 3.8 middle](#)). [Scan Figure 3.8 here](#)

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 .

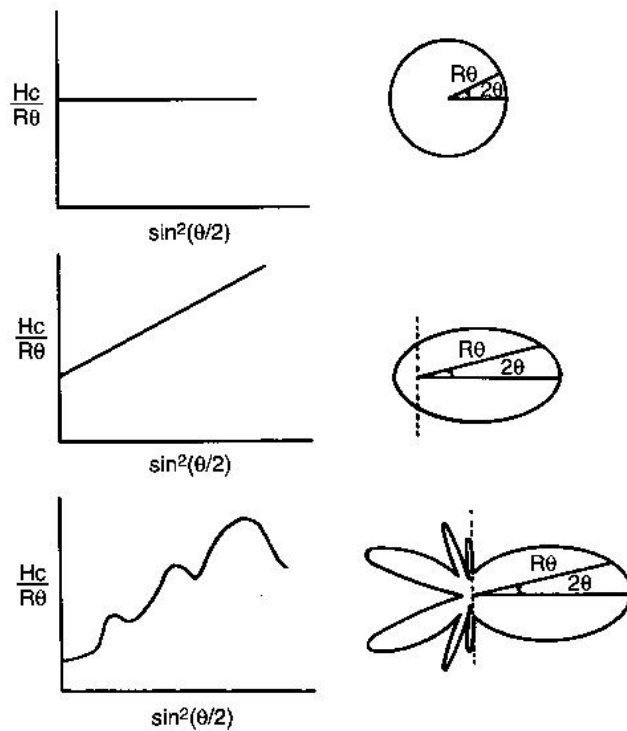


Figure 3.8 Scattering intensity envelopes for small, medium, and large particles. The Θ region contains both the small and medium ranges, but the medium range is far more useful for scattering experiments.

For ordinary sized polymer, $R_g = O(100-200\text{\AA})$

→ For light scattering, Θ is measured in $45^\circ < \Theta < 135^\circ$ because λ is 5000\AA .

$$\langle K = \frac{4\pi_1}{\lambda} \sin\left(\frac{\Theta}{2}\right) \rangle \quad (3.49)$$

→ For X ray ($\lambda = 1-2\text{\AA}$), thermal neutrons ($\lambda = 5\text{\AA}$) → $\Theta < 1^\circ$.

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