Chap. 2. Molecular Weight and Polymer Solutions

2.1 Number Average and Weight Average Molecular Weight

A) Importance of MW and MW Distribution

M.W. ⟷ physical properties

As M.W.⇧ , toughness⇧ , viscosity⇧

1) Optimum MW, MW Distribution

depends upon application
via processing and performance tradeoffs

2) Typical MW values for commercial polymers

a) Vinyl polymers in the 10^5 and 10^6 range

b) Strongly H-bonding polymers in the 10^4 range

e.g., 15,000 - 20,000 for Nylon

Intermolecular Interactions

Increasing Interaction Strength

Type of Interaction	Characteristics	Approximate Strength	Examples
Dispersion Forces	Short Range Varies as $-1/r^6$	0.2 - 0.5 kcal/mole	Poly(ethylene) Polystyrene
Dipole/dipole Interactions	Short Range Varies as $-1/r^4$	0.5 - 2 kcal/mole	Poly(acrylonitrile) PVC
Strong Polar Interactions and Hydrogen Bonds	Complex Form but also Short Range	1 - 10 kcal/mole	Nylons Poly(urethanes)
Coulombic Interactions	Long Range Varies as $1/r$	10 - 20 kcal/mole	Surlyn (Ionomers)

Surlyn: copolymers such as ethylene/methacrylic acid, DuPont adds zinc, sodium, lithium or other metal salts.

B) Number Average Molecular Weight, $\overline{M}_n$

1) Very sensitive to the total number of molecules in solution and
   ∴ **sensitive to the low molecular weight monomers and oligomers**

   - Determined by End Group Analysis and Colligative Properties

(freezing point depression, boiling point elevation , osmotic pressure)

2)
$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

where N_i = # of molecules (or # of moles) having MW M_i

3) Example

9 moles of MW = 30,000 and 5 moles of MW = 50,000
$\Rightarrow \overline{M}_n \approx 37,000$

C) Weight Average Molecular Weight, $\overline{M}_w$

1) Sensitive to the mass of the molecules in solution

∴ **sensitive to the very highest MW species**

- Determined by Light Scattering and Ultracentrifugation

2)
$$\overline{M}_w = \frac{\sum W_i M_i}{\sum W_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

3) Example

9 moles of MW = 30,000 and 5 moles of MW = 50,000

$\Rightarrow M_w \approx 40,000$

4) Note:

a) $\overline{M}_w \geq \overline{M}_n$ b) $\dfrac{\overline{M}_w}{\overline{M}_n} = $ **polydispersity index (PDI)**

c) **For a sample having a single MW (Monodisperse)**

$\overline{M}_w = \overline{M}_n$ $\dfrac{\overline{M}_w}{\overline{M}_n} = 1$

d) **Polydisperse**

$\overline{M}_w > \overline{M}_n$ $\dfrac{\overline{M}_w}{\overline{M}_n} > 1$

D) General Molecular Weight Expression & $\overline{M}_z$ and $\overline{M}_v$

1) $$\overline{M} = \frac{\sum N_i M_i^{a+1}}{\sum N_i M_i^a}$$ $a = 0$ for $\overline{M}_n$ $0 < a < 1$ for $\overline{M}_v$
$a = 1$ for $\overline{M}_w$ $a = 2$ for $\overline{M}_z$

For polydisperse sample $\overline{M}_z > \overline{M}_w > \overline{M}_v > \overline{M}_n$

2) Z average, is closely related to processing characteristics $\Rightarrow$ a = 2

$$\overline{M}_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$

3) Viscosity average MW, $\overline{M}_v$, has $0 \le a \le 1$ and closer to 1 (i.e., to $\overline{M}_w$)

$$\overline{M}_v = \left(\frac{\sum N_i M_i^{a+1}}{\sum N_i M_i} \right)^{\frac{1}{a}}$$ $$\overline{M}_v = \left(\frac{\sum N_i M_i^{1.8}}{\sum N_i M_i} \right)^{\frac{1}{0.8}}$$

in a typical case

2.2 Polymer Solutions

A) Steps Dissolving a Discrete Molecule and a Polymer

    1) Discrete Molecule Dissolution Steps for a Crystalline Sample

    2) Polymer Dissolution Steps

        a) Solvent diffusion

            i) Solvation & swelling

            ii) Gel formation

            iii) Network polymers stop at this stage
                  Degree of swelling correlated with crosslink density

        b) True dissolution

            i) Untangling of chains

            ii) Very slow process and
                  may not occur on timescale of real world

B) Thermodynamics of Polymer Dissolution

1) Choosing a Solvent for Polymers

    a) Polymer Handbook!
      lists solvents and nonsolvents for common polymers

    b) Rule of Thumb: Like dissolves Like

2) $\Delta G = \Delta H - T\Delta S$

    a) ΔG must be negative for spontaneous dissolution

    b) ΔS will be positive because of greater mobility in solution

    c) $\therefore$ need ΔH to be negative or at least not too positive

3) $\Delta H_{mix} \propto (\delta_1 - \delta_2)^2$

   a) ΔH_{mix} = Enthalpy of mixing (dissolution)

   b) δ_1 = **Solubility Parameter** of one component

   c) δ_2 = Solubility Parameter of the other component

4) In practice, ΔH is seldom negative and we simply try to keep it from getting too positive

5) ∴ We see that we want the polymer and the solvent to have as similar of Solubility Parameters as possible

C) Solubility Parameters (δ)

1) δ is related to the heat of vaporization of the sample

$$\Delta H_{mix} = V_{mix}\left[\left(\frac{\Delta E_1}{V_1}\right)^{\frac{1}{2}} - \left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}}\right]^2 \phi_1\phi_2$$
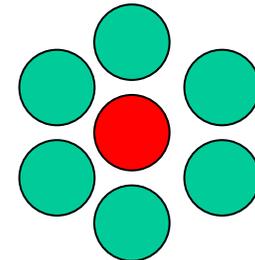
Where V_{mix} = total volume of mixture

V_1, V_2 = molar volumes

ϕ_1, ϕ_2 = volume fractions

ΔE_1, ΔE_2 = energies of vaporization

$$\frac{\Delta E_1}{V_1}, \frac{\Delta E_2}{V_2} = \text{cohesive energy desities (CED)}$$

$$\left(\frac{\Delta E}{V}\right)^{\frac{1}{2}} = \delta = \text{solubility parameter}$$

CED = energy needed to remove a molecule from its nearest neighbors $\cong$ heat of vapoization per volume for a volatile compound

2) For small molecules these can be measured experimentally

$$\Delta E = \Delta H_{vap} - RT$$

where ΔH_{vap} = latent heat of vaporization

R = gas constant

$$\delta_1 = \left(\frac{\Delta H_{vap} - RT}{V} \right)^{\frac{1}{2}}$$

3) $\therefore$ δ's of solvents are tabulated

4) For conventional polymers these can be estimated using tables

a) **Group Molar Attraction Constants**

b) Table 2.1 Group molar attraction constants

Group	$G[(cal\ cm^3)^{1/2}\ mol^{-1}]$	
	small	Hoy
CH_3—	214	147.3
—CH_2—	133	131.5
$>CH$—	28	85.99
$>C<$	-93	32.03
$=CH_2$	190	126.5
$=CH$—	19	84.51
$=C_6H_5$ (phenyl)	735	-
—$CH=$ (aromatic)	-	117.1
$>C=O$ (ketone)	275	262.7
—CO_2— (ester)	310	32.6

c)
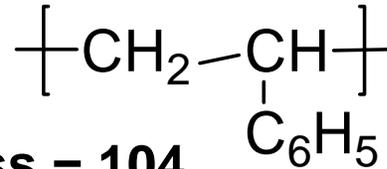
$$\delta = \frac{d \sum G}{M}$$

   i) G = the individual Group Molar Attraction Constants
      of each structural fragment

  ii) d = density

  iii) M = molecular weight

d) For polystyrene

$$\left[\text{CH}_2 - \underset{\underset{\text{C}_6\text{H}_5}{|}}{\text{CH}}\right]$$

  d = 1.05, repeating unit mass = 104

  Small's G values

$$\delta = \frac{1.05(133 + 28 + 735)}{104} = 9.0$$
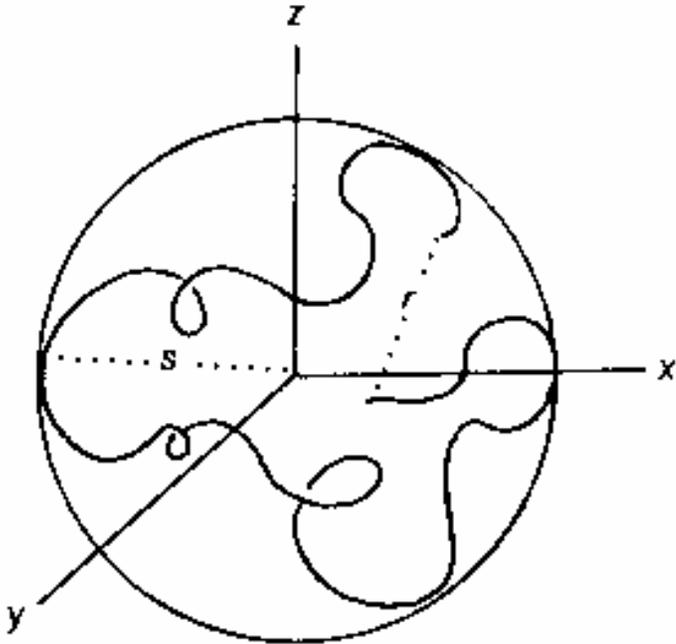
  Hoy's G values

$$\delta = \frac{1.05(131.5 + 85.99 + 6(117.1))}{104} = 9.3$$

e) Major problem with solubility parameters:
    They do not take into account strong dipolar forces
    such as hydrogen bonding.

D) Hydrodynamic Volume (V_h) in Solution

1) The apparent size of the polymer in solution

2) Reflects both the polymer chain itself and the solvating molecules in inner and outer spheres

r = end-to-end distance

s = radius of gyration

FIGURE 2.1. Schematic representation of a molecular coil, r = end-to-end distance; s = radius of gyration.
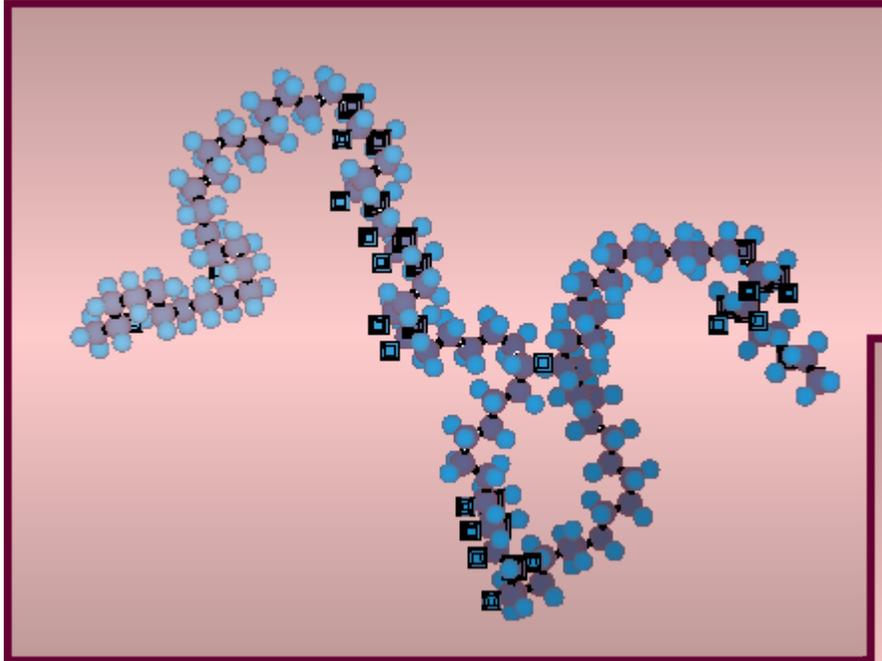
$\overline{r^2}$ = mean-square end-to-end distance
$\overline{s^2}$ = mean-square radius of gyration

For a linear polymer: $\overline{r^2} = 6\,\overline{s^2}$

$$V_h \propto \left(\overline{r^2}\right)^{\frac{3}{2}}$$
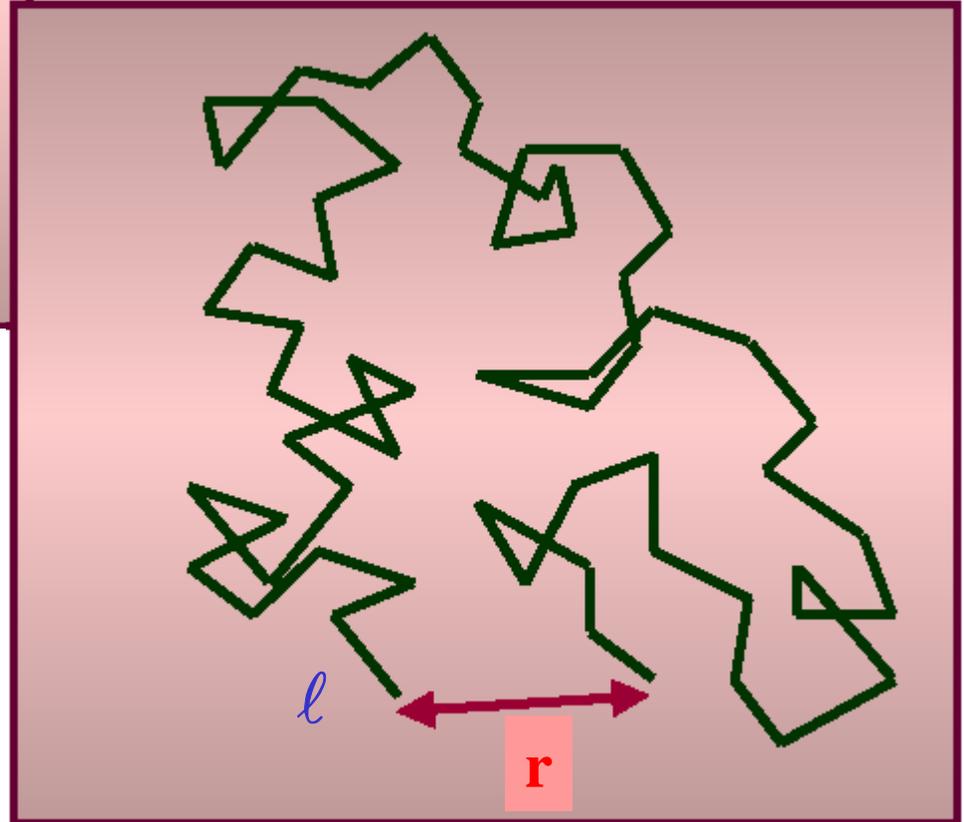
Root-Mean-Square End-to-End Distance

$$\overline{r_o}^2 = N \ell^2$$

$$(\overline{r_o^2})^{0.5} = N^{0.5} \ell$$

If N = 10,000, ℓ = 1;

$$(\overline{r_o^2})^{0.5} = 100 \ ! \ ! \ !$$

ℓ

r

3) Hydrodynamic Volume is related to an Expansion Factor, α

**a) The greater the affinity of solvent for polymer,
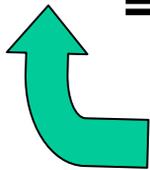the larger will be the sphere.**

$$\overline{r^2} = \overline{r_0}^2\alpha^2$$

$$\overline{s^2} = \overline{s_0}^2\alpha^2$$

$$\alpha = \left(\frac{\overline{r^2}}{\overline{r_0}^2}\right)^{\frac{1}{2}} = \left(\frac{\overline{s^2}}{\overline{s_0}^2}\right)^{\frac{1}{2}}$$

r_0, s_0 = **unperturbed dimension**

= **size of macromolecule exclusive of solvent effects**

**combination of
free rotation and
intramolecular steric and
polar interactions**

α = **expansion factor**

interactions between solvent & polymer

**b) α = 1 for the "non-expanded" polymer in the
"ideal" statistical coil having the smallest possible size**

**c) as α increases, so does the Hydrodynamic Volume of
the sample**

E) *Theta* **(Ѳ) State**

1) Solubility varies with temperature and the nature of the solvent

2) ∴ **There will be a minimal dissolution temperature call the *Theta Temperature* and at that point the solvent is said to be the *Theta Solvent***

3) The *Theta State* at this point is the one in which the last of the polymer is about to precipitate

4) Compilations of Theta Temperatures & Solvents are available in the literature

F) Intrinsic Viscosity & Molecular Weight

1) [ɳ] = Intrinsic Viscosity

$$\eta_{rel} = \frac{\eta}{\eta_0} \qquad \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \qquad \eta_{red} = \frac{\eta_{sp}}{c}$$

$$\eta_{inh} = \frac{\ln \eta_{rel}}{c} \qquad [\eta] = \left(\frac{\eta_{sp}}{c}\right)_{c=0} = (\eta_{red})_{c=0} = (\eta_{inh})_{c=0}$$

2) Flory-Fox equation

$$[\eta] = \frac{\phi\left(\overline{r^2}\right)^{\frac{3}{2}}}{\overline{M}} = \frac{\phi\left(\overline{r_0^2}\alpha^2\right)^{\frac{3}{2}}}{\overline{M}}$$

where ϕ = proportionality constant = Flory constant $\cong$ 3 x 10^{24} mol^{-1}

$$V_h \propto \left(\overline{r^2}\right)^{\frac{3}{2}} \propto [\eta]\overline{M}$$

Rearranged to

$$[\eta] = \phi\left(\overline{r_0^2}\alpha^2\right)^{\frac{3}{2}}\overline{M}^{-1} = \phi\left(\overline{r_0^2}\,\overline{M}^{-1}\right)^{\frac{3}{2}}\overline{M}^{\frac{1}{2}}\alpha^3 = K\overline{M}^{\frac{1}{2}}\alpha^3$$

where
$$K = \phi\left(\overline{r_0^2}\,\overline{M}^{-1}\right)^{\frac{3}{2}} \qquad \because \overline{r_0^2} \propto M$$

At T = θ, α = 1

$$[\eta]_\theta = K\overline{M}^{\frac{1}{2}} \qquad \theta \text{ solvent}$$

At T $\neq$ θ, α = $\alpha(M) \propto M^{0\sim0.1}$

$$[\eta] = K\overline{M}^{0.8} \qquad \text{good solvent} \qquad \because \alpha \propto M^{0.1}$$

3) Mark- Houwink-Sakurada Equation

a)
$$[\eta] = K\overline{M}_v{}^a$$

b) K and a are characteristic of the particular solvent/polymer combination

c) a = 0.5 (θ solvent) ~ 0.8 (good solvent)

2.3 Measurement of Number Average Molecular Weight M_n

● **General Considerations**

1) Most methods give **only averages**

 Exceptions are: **GPC, Light Scattering, MS**

2) Most methods' results vary depending on the **structure of the sample**

 ∴ need to calibrate each sample and/or know some **structural information** such as branching

3) Most methods have **limited sensitivities** and/or **linear ranges**

4) Most methods require **expensive instrumentation**

5) There can be substantial **disagreements** between the results of **different techniques**

2.3.1 End- group Analysis

1) Basic principles

a) The structures of the end groups must be different from that of the bulk repeating units (e.g., CH_3 vs. CH_2 in an ideal polyethylene)

b) ∴ If you detect the concentration of the end group and know the total amount of sample present you can calculate the average MW, $\overline{M}_n$.

i) need to have either a perfectly linear polymer (i.e., two end groups per chain) or need to know information about the amount of branching

ii) ∴ the $\overline{M}_n$ values that come out for "linear" polymers must typically be considered an upper bound since there may be some branching

c) Detection of concentrations of end groups

i) Titration, using either indicators or potentiometric techniques

ii) Spectroscopy - IR, NMR, UV-Vis

iii) Elemental Analysis

iv) Radioactive or Isotopic labels

Linear polyerster
HOOC~~~~~OH

$$\overline{M}_n = \frac{\text{sample weight}}{\dfrac{[COOH]+[OH]}{2}} = \frac{2\times\text{sample weight}}{[COOH]+[OH]}$$

2) Strengths

    a) The requisite instruments are in any department

    b) can be quite quick

    c) Sometimes this information comes out "free" during polymer structural studies

3) Weaknesses

    a) does not give MW distribution information

    b) need to know information about the structure

      - identity and number of end groups in each polymer molecule

    c) limited to relatively low MW for sensitivity reasons

          i) Practical upper limit ; 50,000

        ii) 5,000 - 20,000 is typical MW range

        iii) Can be high with some detections types

            • **radioactive labeling of end groups**

            • **fluorescent labeling of end groups**

2.3.2 **Membrane Osmometry**

Static equilibrium method:
    No counterpressure,
    Long time

Measuring tubes

Δh

Solution

Solvent

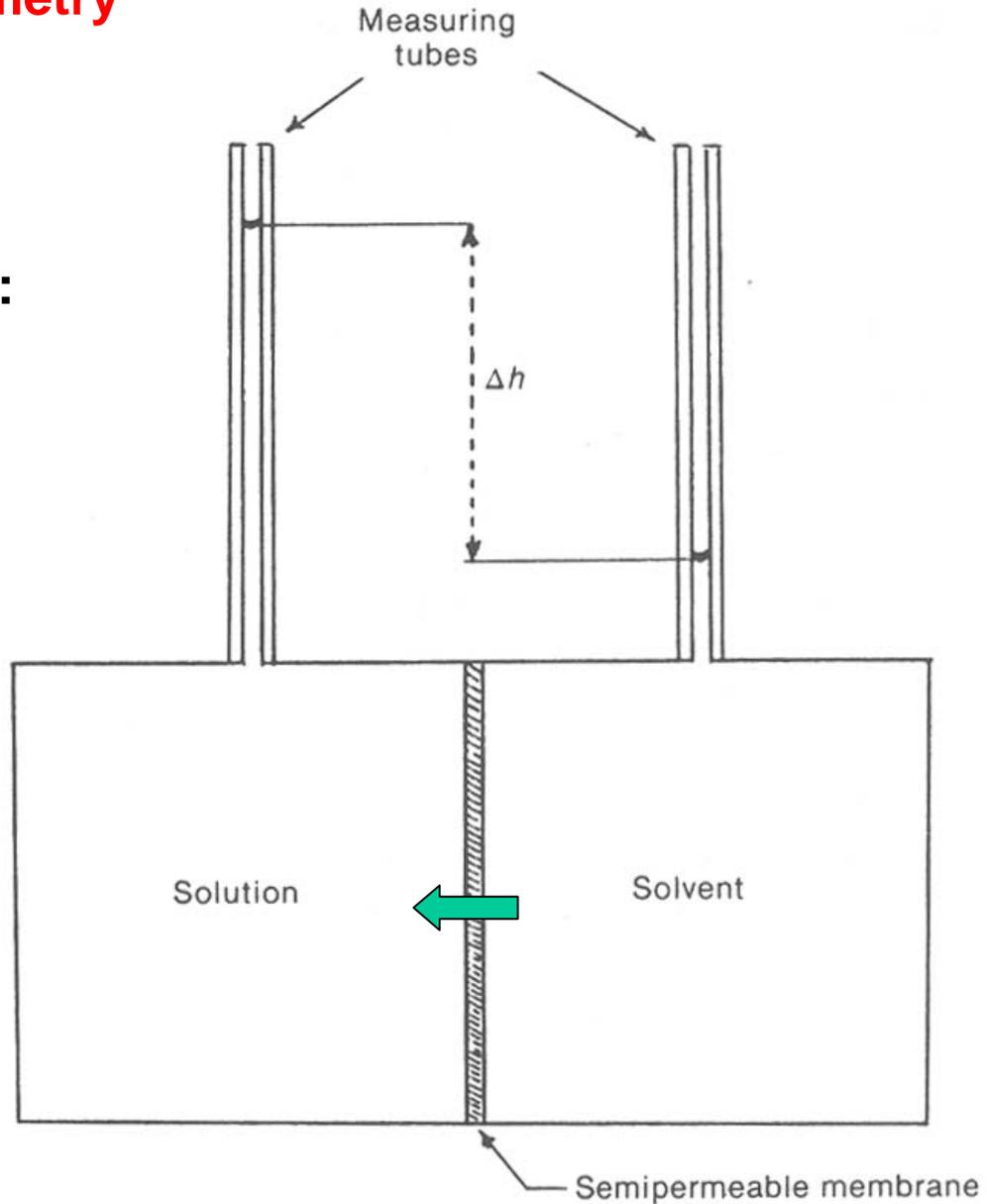Semipermeable membrane

Fig. 2.2 Membrane Osmometry

Dynamic equilibrium method: Counterpressure, short time
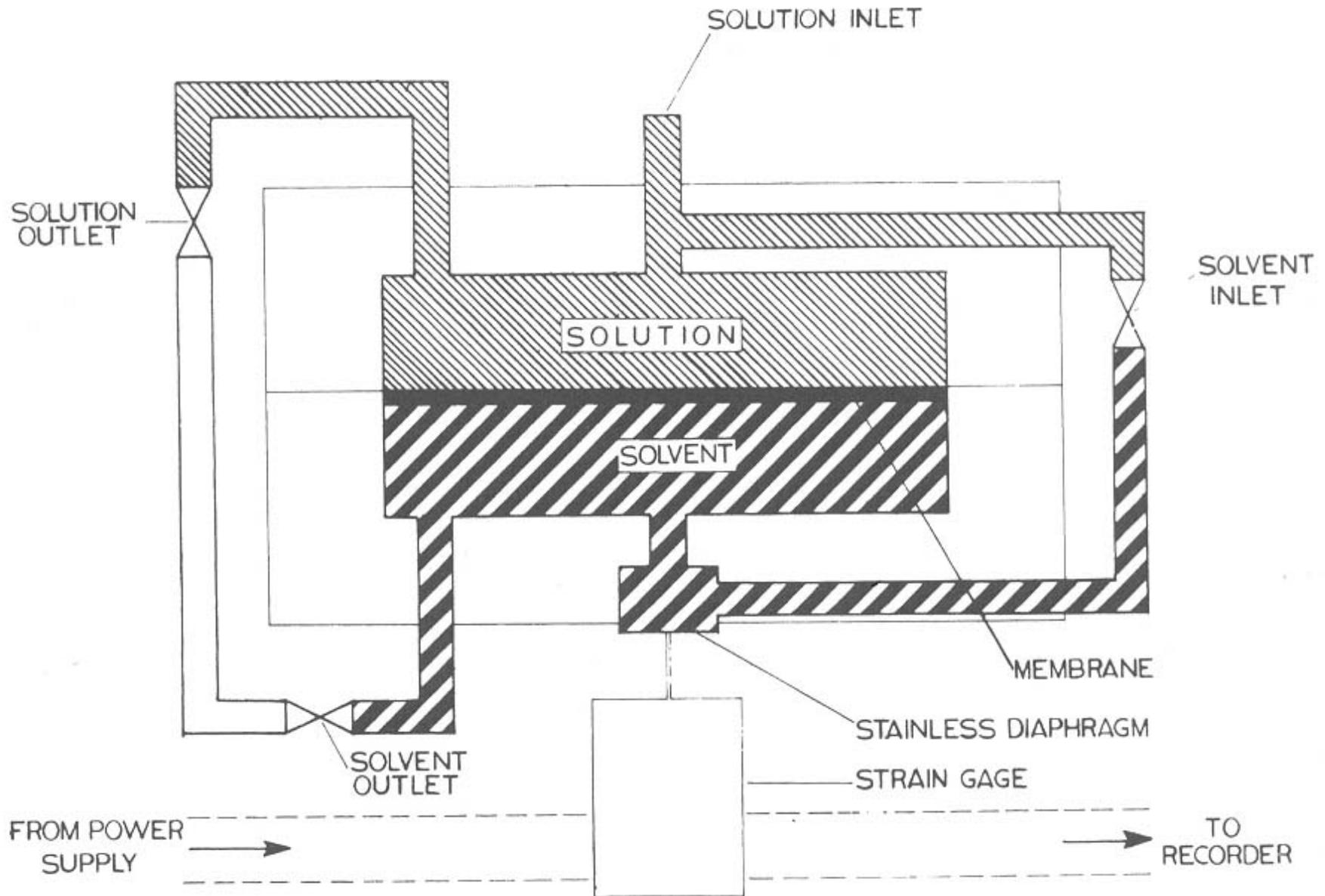
Fig. 2.3 Automatic Membrane Osmometry

Van't Hoff equation

$$\frac{\pi}{c} = \frac{RT}{\overline{M_n}} + A_2 c$$

where

π = **osmotic pressure**

   = $\rho g \Delta h$

R = gas constant = 0.082 L atm mol^{-1}K^{-1}

                    = 8.314 J mol^{-1}K^{-1}

c = concentration [g L^{-1}]

ρ = solvent density [g cm^{-3}]

g = acceleration due to gravity

   = 9.81 m s^{-2}

Δh = difference in heights of solvent and solution [cm]
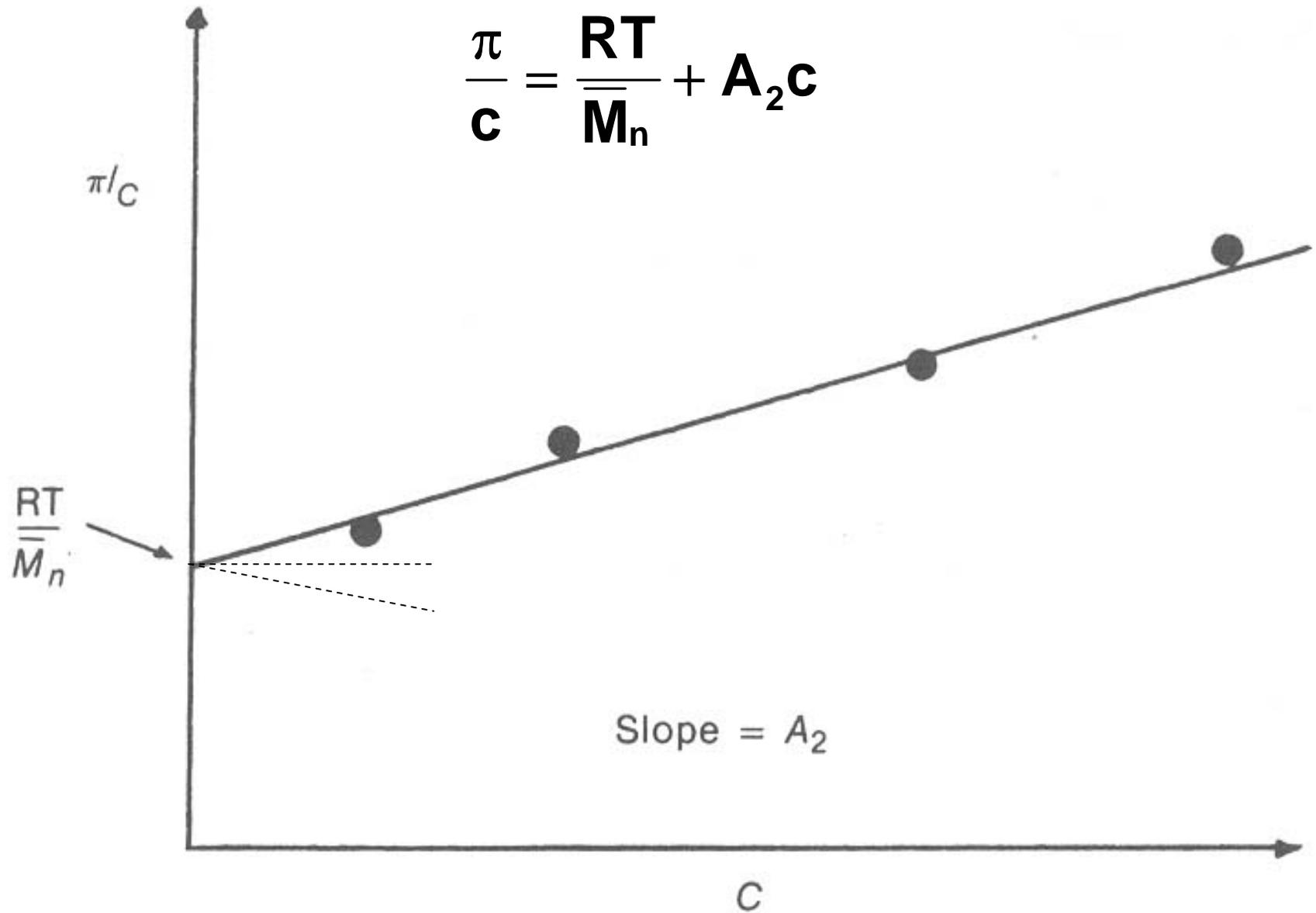
A_2 = **second virial coefficient** = **measure of interaction** between
     solvent and polymer

$A_2 = 0$ at $T = \theta$, $A_2 > 0$ at $T > \theta$

Major source of error: **low-M.W.-species diffuse** through membrane

$\therefore$ M_n (**obtained**) **>** M_n (actual)

 50,000 < M_n < 2,000,000

$$\frac{\pi}{c} = \frac{RT}{\overline{\overline{M}}_n} + A_2 c$$

π/c

$\dfrac{RT}{\overline{\overline{M}}_n}$

Slope $= A_2$

C

Chemical Potential of Dilute Solutions

The **chemical potential** of a solvent in a solution is

$$\mu_s = \mu_s^o + RT \ln a_s$$

μ_s^o = chemical potential for pure solvent at T

a_s = activity of solvent

$$\mu_s = \left(\frac{\partial G}{\partial n_s} \right)_{T,P,n_p}$$

If the solvent vapor obeys the **ideal gas law**, we have

$$\mu_s = \mu_s^o + RT \ln \frac{P_s}{P_s^o}$$

$$P_s < P_s^o$$

$$\mu_s < \mu_s^o$$

P_s = vapor pressure above the solution at T

P_s^o = vapor pressure above the pure solvent at T

Raoult's Law

In general, the **activity** is related to vapor pressure by
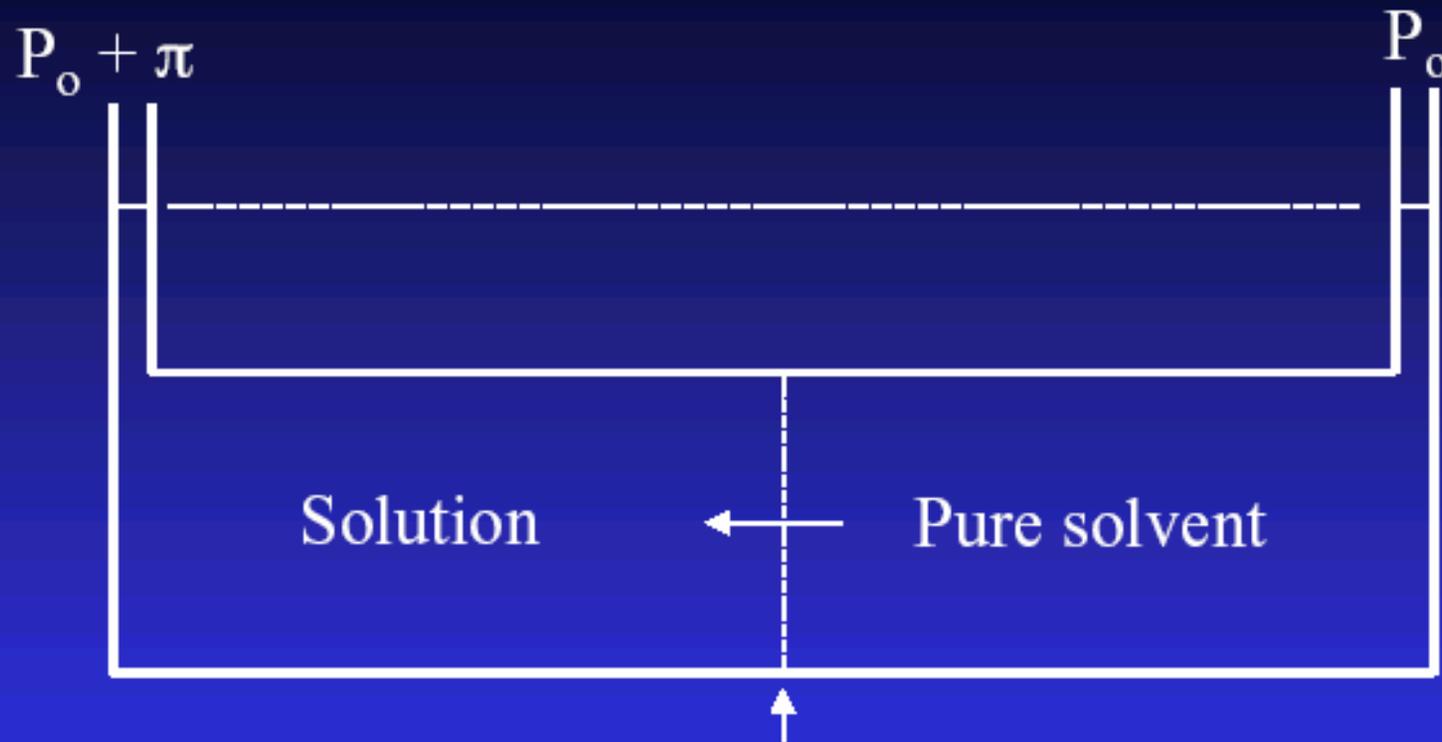
$$a_s = \frac{P_s}{P_s^o}$$

If the solution is sufficiently dilute, **Raoult's Law** will be obeyed

$$a_s = x_s = \frac{P_s}{P_s^o}$$

x_s = mole fraction of solvent in solution

$$\mu_s = \mu_s^o + RT \ln x_s$$

Osmotic Pressure

$$P_o + \pi \qquad\qquad\qquad\qquad\qquad\qquad P_o$$

Solution $\longleftarrow$ Pure solvent

Semipermeable membrane

The **osmotic pressure** π is the additional pressure that must be imposed to keep solvent and solution sections at the same level. This static method requires a long time to reach equilibrium.

Derivation of Van't Hoff Equation

At constant temperature, the chemical potential depends upon both pressure and composition.

$$\mu_s = f(P, x_p) \qquad\qquad x_p = 1 - x_s$$

The total derivative of the chemical potential is then

$$d\mu_s = \left(\frac{\partial \mu_s}{\partial P}\right)_{T,x_p} dP + \left(\frac{\partial \mu_s}{\partial x_p}\right)_{T,P} dx_p$$

If no solvent flow occurs, $d\mu_s = 0$

$$\left(\frac{\partial \mu_s}{\partial P}\right)_{T,x_p} dP = -\left(\frac{\partial \mu_s}{\partial x_p}\right)_{T,P} dx_p$$

dE = TdS - PdV

dH = d(E + PV)
   = TdS – PdV + PdV – VdP
   = TdS + VdP

dG = d(H - TS)
   = TdS + VdP - TdS – SdT
   = - SdT + VdP

dG = - SdT + VdP (+ $\mu_s$dn$_s$ + $\mu_p$dn$_p$)

$$\left(\frac{\partial \mathbf{G}}{\partial \mathbf{P}}\right)_{T,n_s,n_p} = \mathbf{V}$$

Derivation of Van't Hoff Equation

The chemical potential is defined by

$$\mu_s = \left(\frac{\partial G}{\partial n_s}\right)_{T,P,x_p}$$

n_s = moles of solvent

n_p = moles of polymer

G = Gibbs free energy

Partial differentiation with respect to P yields

$$\left(\frac{\partial \mu_s}{\partial P}\right)_{T,x_p} = \frac{\partial^2 G}{\partial P\,\partial n_s}$$

Derivation of Van't Hoff Equation

The volume of the system is given by

$$\left(\frac{\partial G}{\partial P}\right)_{T,x_p} = V$$

Partial differentiation with respect to n_s yields

$$\frac{\partial^2 G}{\partial n_s \, \partial P} = \left(\frac{\partial V}{\partial n_s}\right)_{T,x_p,P} = \overline{V}_s$$

$\overline{V}_s$ = partial molar volume of solvent

Since the order of differentiation is immaterial, we have

$$\left(\frac{\partial \mu_s}{\partial P}\right)_{T,x_p} = \overline{V}_s$$

Derivation of Van't Hoff Equation

Recall the chemical potential

$$\mu_s = \mu_s^o + RT \ln x_s$$

$$\left(\frac{\partial \mu_s}{\partial x_s}\right)_{T,P} = \frac{RT}{x_s}$$

Note that $x_s = 1 - x_p$ and $\frac{dx_s}{dx_p} = -1$

Partial differentiation with respect to x_p yields

$$\left(\frac{\partial \mu_s}{\partial x_p}\right)_{T,P} = \left(\frac{\partial \mu_s}{\partial x_s}\right)_{T,P}\left(\frac{dx_s}{dx_p}\right) = -\frac{RT}{1 - x_p}$$

Derivation of Van't Hoff Equation

Recall that for conditions of no solvent flow, $d\mu = 0$ and

$$\left(\frac{\partial \mu_s}{\partial P}\right)_{T,x_p} dP = -\left(\frac{\partial \mu_s}{\partial x_p}\right)_{T,P} dx_p$$

$\overline{V}_s$

$-\dfrac{RT}{1-x_p}$

Substitution leads to

$$\int_{P_o}^{P_o+\pi} \overline{V}_s \, dP = RT \int_{0}^{x_p} \frac{dx_p}{1-x_p}$$

Derivation of Van't Hoff Equation

If the partial molar volume is independent of pressure, we have

$$\pi = -\frac{RT}{\overline{V}_s}\ln\left(1 - x_p\right)$$

For the very dilute solutions that obey Raoult's Law,

$$\ln\left(1 - x_p\right) = -x_p - \frac{x_p^2}{2} - \frac{x_p^3}{3} - \cdots \cong -x_p$$

For the case where $n_s >> n_p$

$$x_p = \frac{n_p}{n_s + n_p} \cong \frac{n_p}{n_s}$$

$$n_s \overline{V}_s = V_s \cong V(solution)$$

Derivation of Van't Hoff Equation

Substitution yields

$$\pi = RT \frac{n_p}{V(solution)}$$

Compare this expression to the **ideal gas law**.

Convert to concentration units of mass/volume and take the limit as concentration goes to zero

$$\lim\left(\frac{\pi}{c}\right) = \frac{RT}{\overline{M}_n}$$

$\overline{M}_n$ = number average molecular weight

At last, we have the **Van't Hoff Equation**. Note that it is applicable only at **infinite dilution**.

Virial Expression for Osmotic Pressure

In order to account for **concentration effects** in polymer solutions, a virial expression is often used.

$$\left(\frac{\pi}{c}\right) = RT\left(\frac{1}{\overline{M}_n} + A_2 c + A_3 c^2 + \cdots\right)$$

A_2 = second virial coefficient
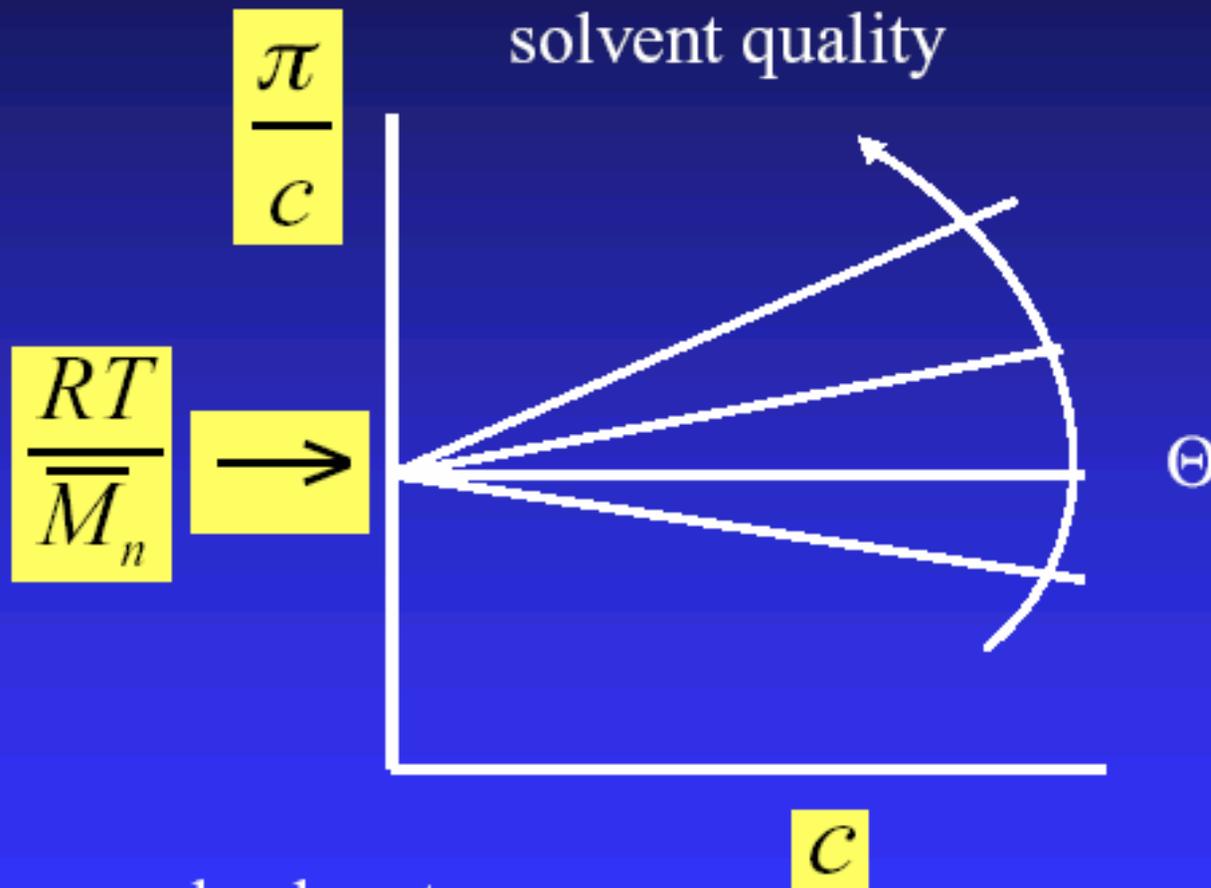A_3 = third virial coefficient

Alternative expressions:

$$\frac{\pi}{c} = \left(\frac{\pi}{c}\right)_{c=0}\left[1 + \Gamma_2 c + \Gamma_3 c^2 + \cdots\right]$$

$$\frac{\pi}{c} = \left(\frac{RT}{\overline{M}_n}\right) + Bc + Cc^2$$

The forms are equivalent if:

$$B = RTA_2 = \left(\frac{RT}{\overline{M}_n}\right)\Gamma_2$$

Effect of Solvent Quality on Osmotic Pressure

$$\frac{\pi}{c}$$

solvent quality

$$\frac{RT}{\overline{M}_n} \quad \rightarrow$$

Θ

c

$A_2 > 0$ for a good solvent
$A_2 = 0$ for a theta solvent
$A_2 < 0$ for a poor solvent

2.3.3 Cryscopy and Ebulliometry

Freezing-point depression (ΔT_f)   **Boiling-point elevation (ΔT_b)**

$$\left(\frac{\Delta T_f}{c}\right)_{c=0} = \frac{RT^2}{\rho \Delta H_f \overline{M_n}} + A_2 c \qquad\qquad \left(\frac{\Delta T_b}{c}\right)_{c=0} = \frac{RT^2}{\rho \Delta H_v \overline{M_n}} + A_2 c$$
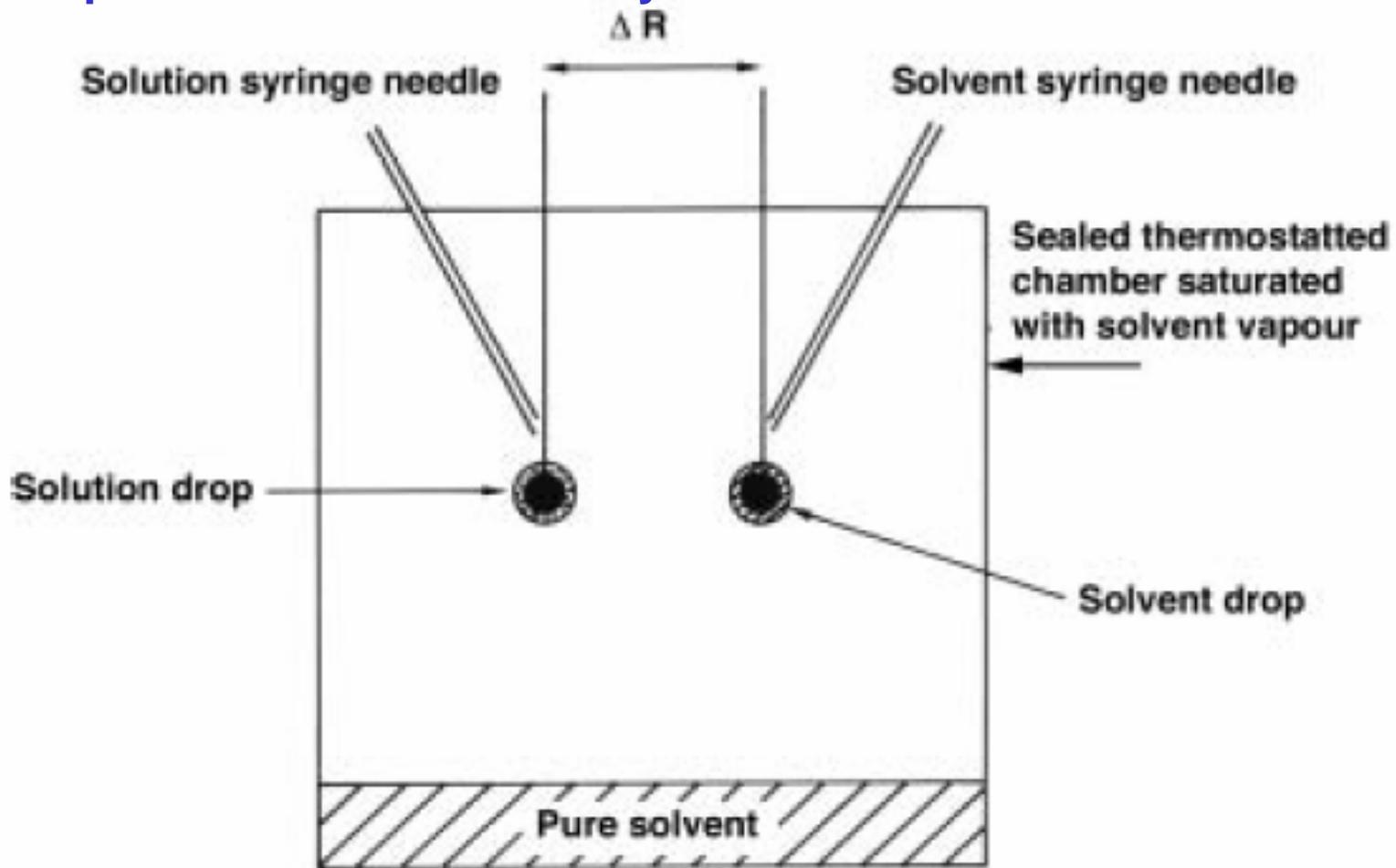
where
- T = freezing point or boiling point of the solvent
- ρ = solvent density
- ΔH_f = **latent heat of fusion**
- ΔH_v = **latent heat of vaporization**
- A_2 = second virial coefficient

The **most sensitive thermister** ; 1×10^{-4} °C
Upper limit $\approx$ **40,000**

2.3.4 Vapor Pressure Osmometry

- **Polymer solution** and **pure solvent** are placed on **thermistor beads.**
- **Solvent vapor condenses onto polymer solution.**
- **Temp rise of solution** due to heat of evaporization.
- **Vapor pressure of solution is increased** to that of pure solvent.
- **Temperature difference** between the solution and the solvent droplet is measured as the resistance difference ΔR between the thermistor beads.

In a dilute solution, the vapor pressure of a solvent is given by **Raoult's Law**

$$P_1 = P_1^0 \, x_1$$

where
P_1 = partial pressure of solvent in solution
P_1^0 = vapor pressure of pure solvent
x_1 = mole fraction of solvent

$$x_1 = 1-x_2$$

x_2 = mole fraction of solute

$$P_1 = P_1^0 \, (1-x_2)$$

vapor pressure lowering $= \Delta P \equiv P_1^0 - P_1 = P_1^0 x_2$

It is assumed that T, ΔH_v, and P = constant.

Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{P\Delta H_v}{RT^2}$$

where
P = vapor pressure
T = absolute temperature
ΔH_v = enthalpy of vaporization
R = gas constant

integrated to yield

$$\Delta T = \frac{RT^2 \Delta P}{P\Delta H_v}$$

Substitution of the equations

$$\Delta T = \frac{RT^2 P_1^o x_2}{P \Delta H_v}$$

For small pressure changes, $P_1^0 = P$

$$\Delta T = \frac{RT^2 x_2}{\Delta H_v}$$

$$x_2 = \frac{n_2}{n_1 + n_2}$$

where
n_1 = number of moles of solvent
n_2 = number of moles of solute

For very small n_2

$$x_2 = \frac{n_2}{n_1}$$

$$\Delta T = \frac{RT^2}{\Delta H_v} \frac{n_2}{n_1} = \frac{RT^2}{\Delta H_v} \frac{\frac{w_2}{M_2}}{\frac{w_1}{M_1}} = \frac{RT^2}{\Delta H_v} \frac{w_2}{w_1 M_2} M_1 = \frac{RT^2}{\Delta H_v} \frac{m_2}{M_2} \frac{M_1}{1000}$$

where
w_1 = weight of solvent
w_2 = weight of solute

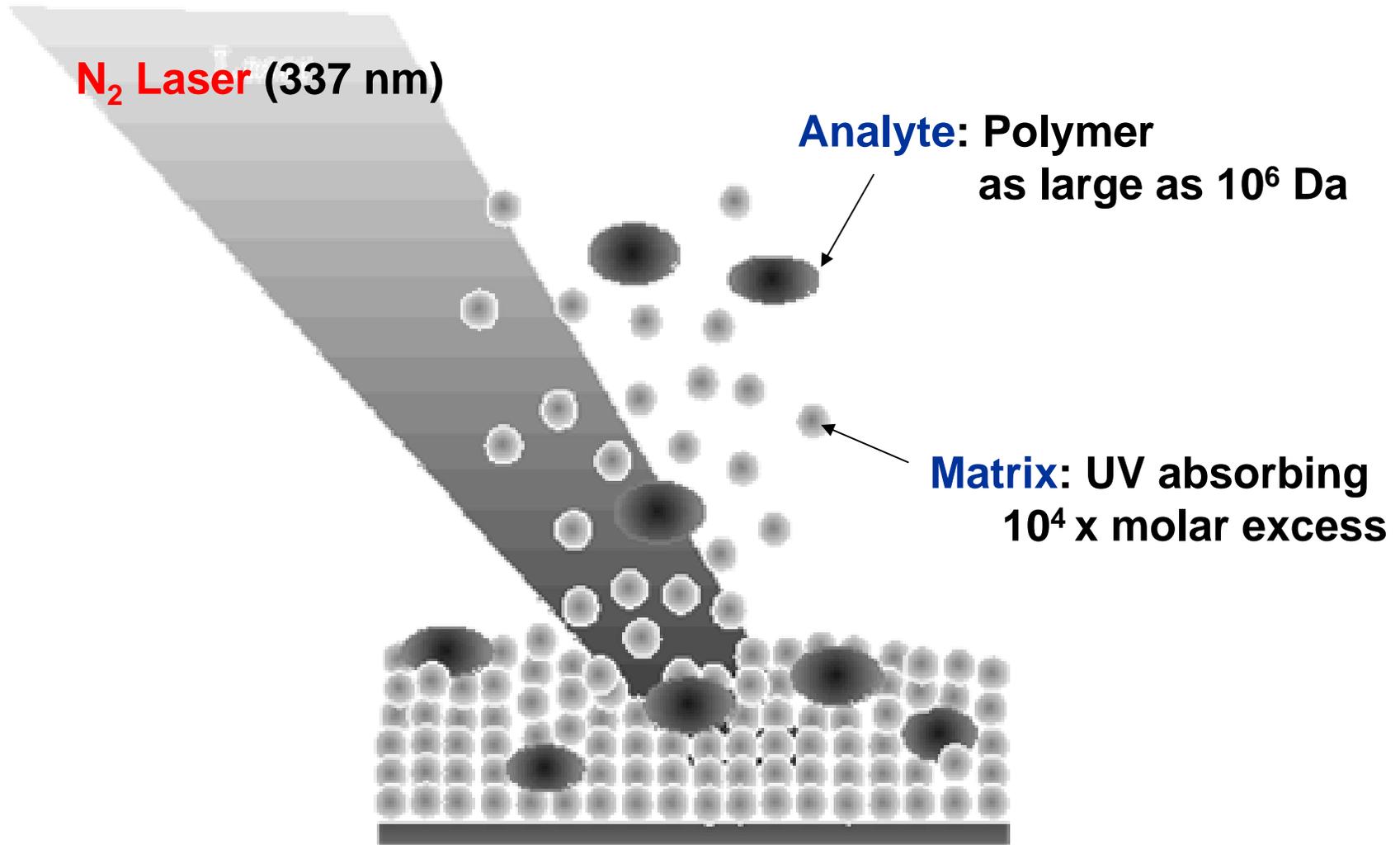$$m_2 = \frac{w_2}{\frac{w_1}{1000}} = \text{molality} \left(\frac{g}{kg}\right)$$

$$\Delta T = \frac{RT^2}{\Delta H_v} \frac{m_2}{M_2} \frac{M_1}{1000} = \frac{RT^2}{\dfrac{\Delta H_v}{M_1}} \frac{m_2}{M_2} \frac{1}{1000} = \frac{RT^2}{1000\lambda} \frac{m_2}{\overline{\overline{M}}_n}$$

Where λ = heat of vaporization per gram of solvent

$$\boxed{\Delta T = \frac{RT^2}{1000\lambda} \frac{m}{\overline{\overline{M}}_n}}$$

2.3.5 Matrix-Assisted Laser Desorption Ionization Mass Spectrometry (MALDI-MS or MALDI-TOF)

N$_2$ Laser (337 nm)

Analyte: Polymer
as large as 10^6 Da

Matrix: UV absorbing
10^4 x molar excess

The energy of laser beam is transferred to the matrix which is partially vaporized, carrying intact polymer into the vapor phase and charging the polymer chains.

Field free drift region

Sample

Detector

$$t = D\sqrt{m/2zV}$$

HV
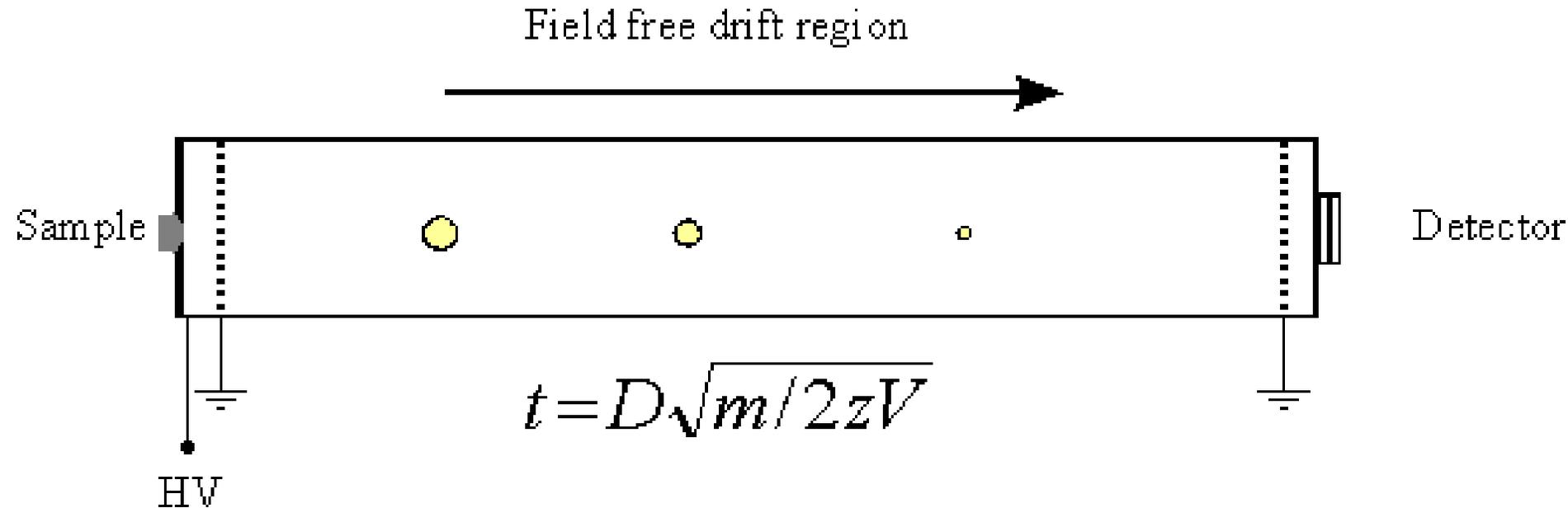
All **ions** are rapidly **accelerated** to ideally the **same high-kinetic energy** by an **electrostatic field** and expelled into a **field-free region** (flight-tube) where they physically separate from each other based on their **mass-to-charge (m/z) ratios**.

Linear time-of-flight matrix-assisted laser desorption ionization mass spectrometer
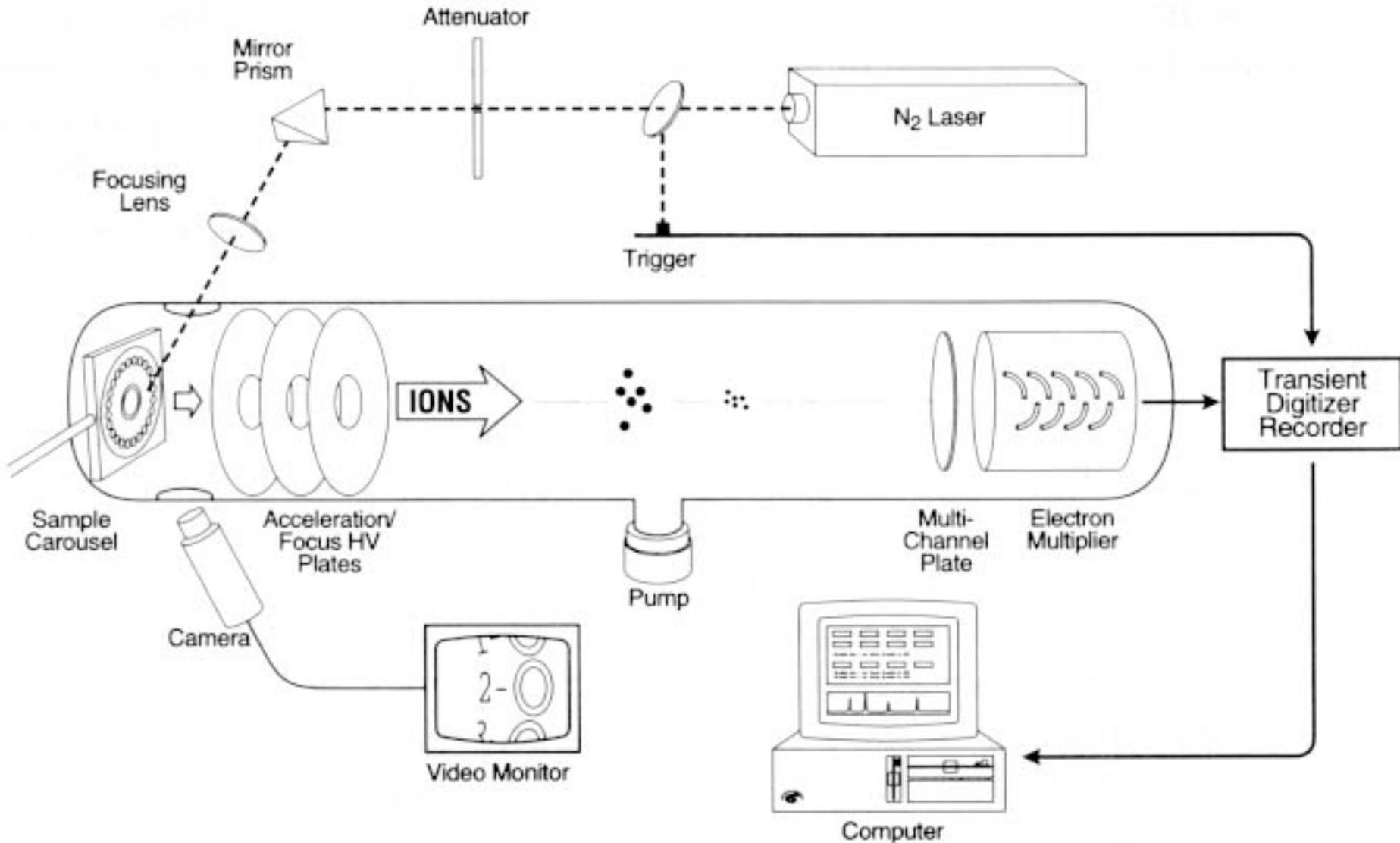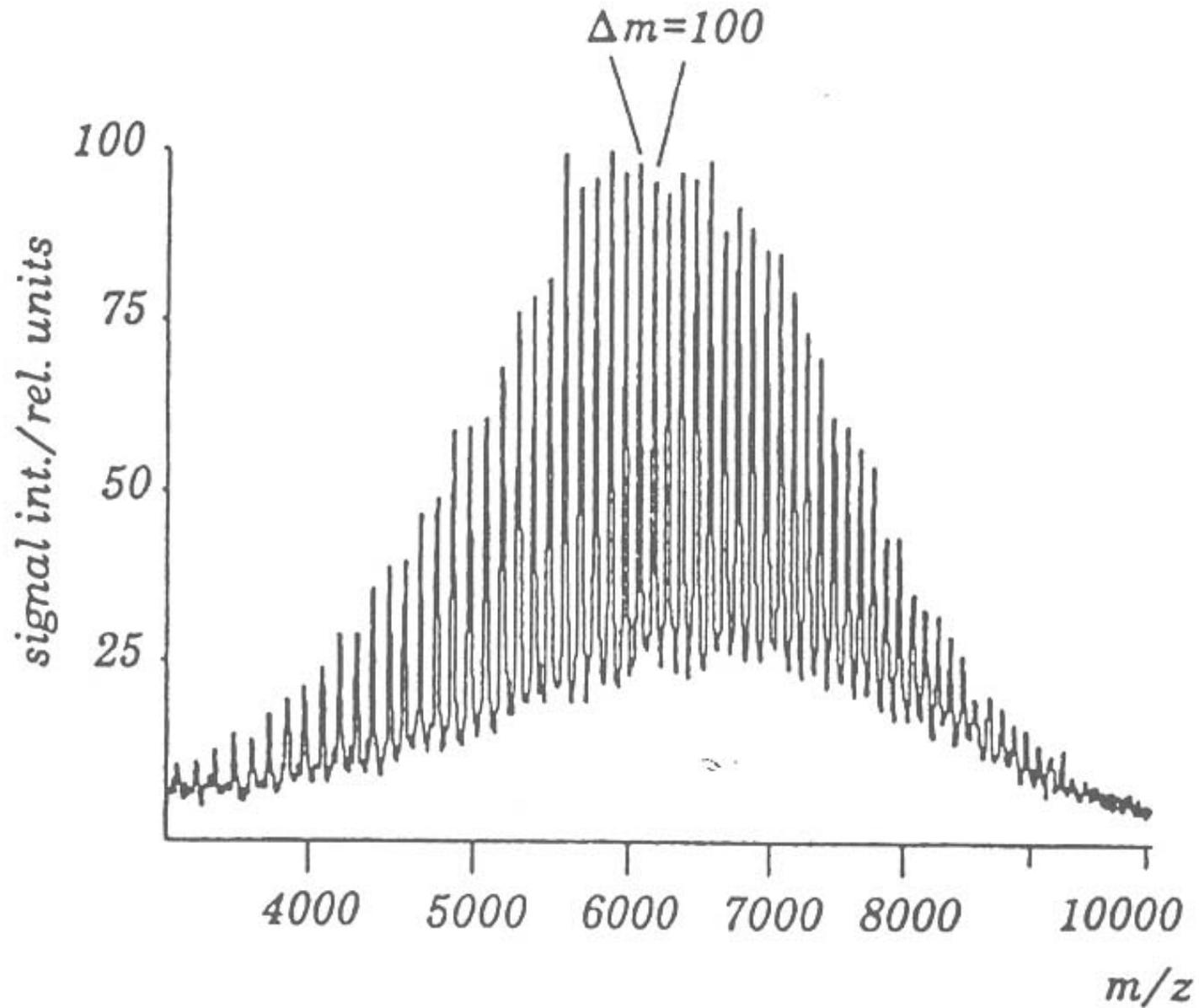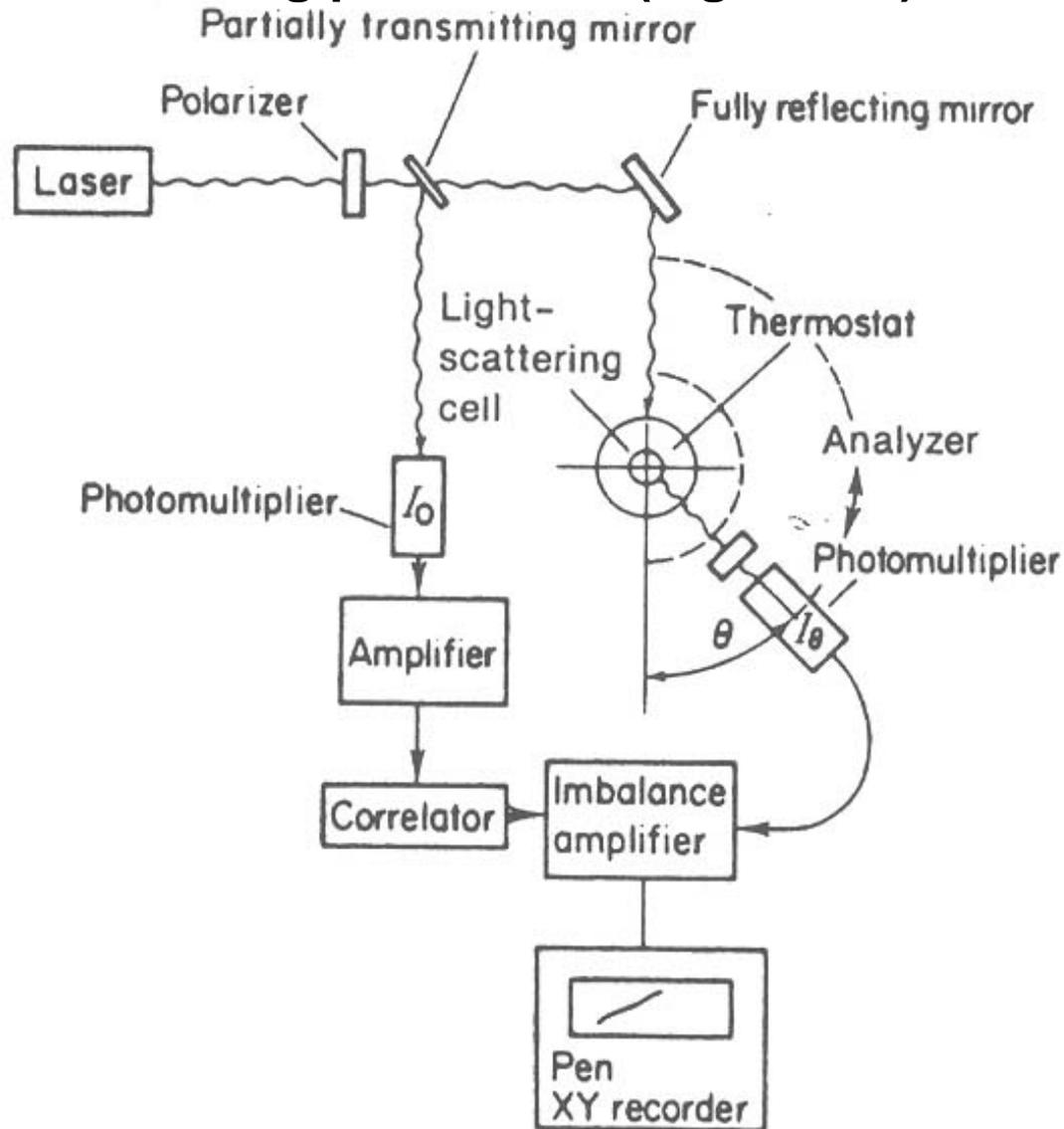
Figure 2.5 MALDI mass spectrum of low-molecular-weight PMMA

2.4 Measurement of M_w

2.4.1 Light Scattering

1) Laser light-scattering photometer (Figure 2.7)

2) Polymer molecule in solution (and its associated solvent molecules) has a different refractive index than neat solvent

∴ **they behave as tiny lenses and scatter light**

a) **scan detector over a range of angles or use multiple detectors**

b) **measure scattered intensity as a function of angle and concentration**

c) **Use "Zimm" plot to extrapolate to infinite dilution and to zero degrees**

$$\frac{Kc(1+\cos^2\theta)}{R_\theta} = \frac{1}{\overline{M}_w}\left(1 + \frac{16\pi^2}{3\lambda}\overline{s^2}\sin^2\left(\frac{\theta}{2}\right)\right) + 2A_2c$$

where

$$K = \frac{2\pi^2 n_o^2\left(\dfrac{dn}{dc}\right)^2}{\lambda^4 N_o}$$

n_o = refractive index of the solvent
λ = wavelength of the incident light
N_o = Avogadro's number

$\dfrac{dn}{dc}$ = specific refractive increment

$R_\theta = \dfrac{I_\theta r^2}{I_o}$ = Rayleigh Ratio

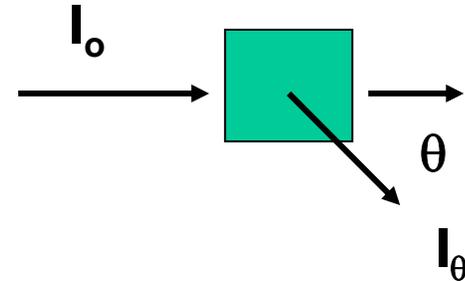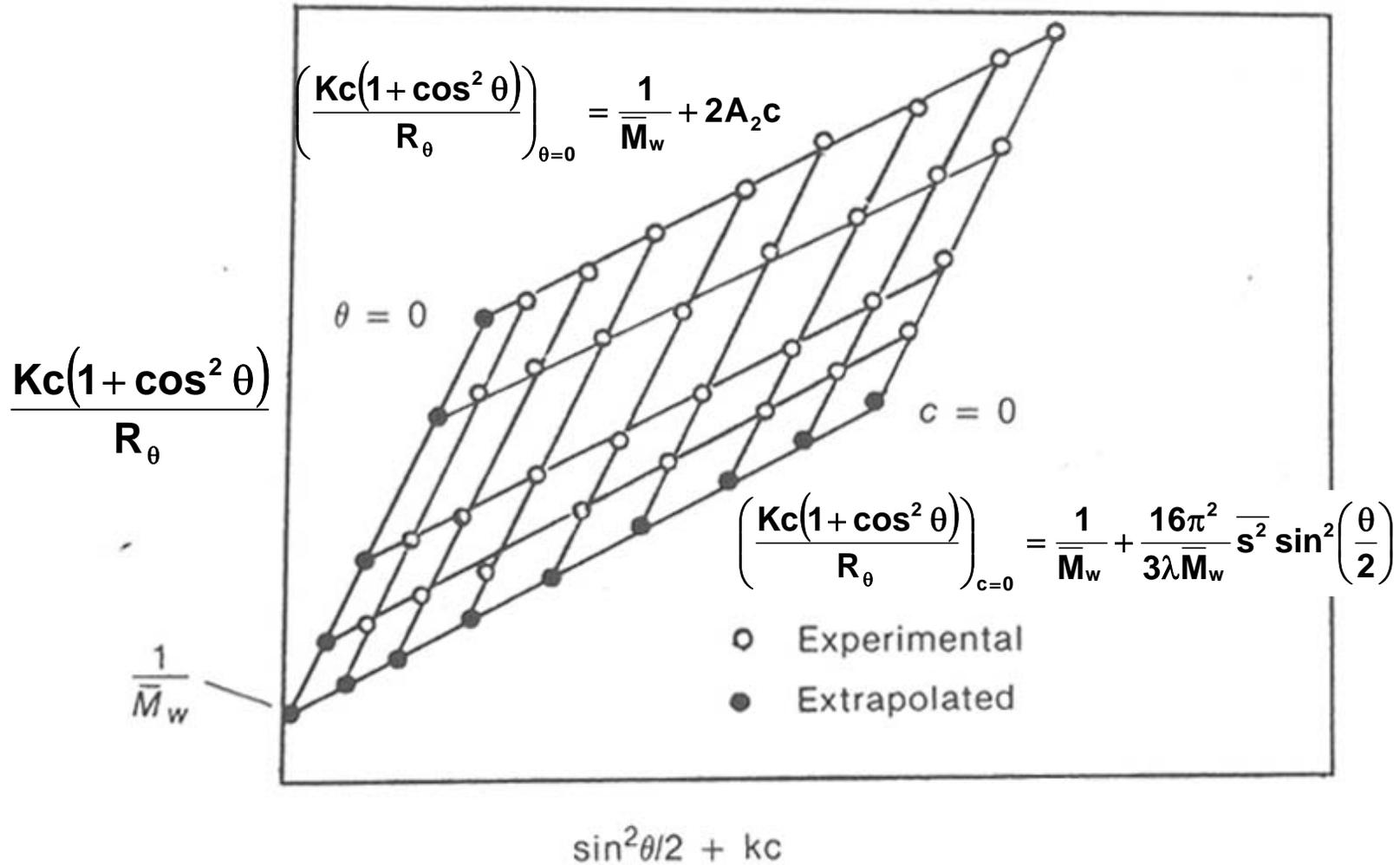r = distance from scatterer to detector

I_o

θ

I_θ

Figure 2.6 Zimm plot of light-scattering data

$$\frac{Kc(1+\cos^2\theta)}{R_\theta} = \frac{1}{\overline{M}_w}\left(1+\frac{16\pi^2}{3\lambda}\overline{s^2}\sin^2\left(\frac{\theta}{2}\right)\right)+2A_2c$$

$$\left(\frac{Kc(1+\cos^2\theta)}{R_\theta}\right)_{\theta=0} = \frac{1}{\overline{M}_w}+2A_2c$$

$$\frac{Kc(1+\cos^2\theta)}{R_\theta}$$

$$\theta = 0$$

$$c = 0$$

$$\left(\frac{Kc(1+\cos^2\theta)}{R_\theta}\right)_{c=0} = \frac{1}{\overline{M}_w}+\frac{16\pi^2}{3\lambda\overline{M}_w}\overline{s^2}\sin^2\left(\frac{\theta}{2}\right)$$

- ○ Experimental
- ● Extrapolated

$$\frac{1}{\overline{M}_w}$$

$$\sin^2\theta/2 + kc$$

k = scaling factor

2.5 Viscometry

Not an absolute method
Measured at concentrations of about 0.5g/100mL of solvent

A) Viscosity Measurement

1) Table 2.2 Dilute Solution Viscosity Designations

Common Name	IUPAC Name	Definition
Relative viscosity	Viscosity ratio	$\eta_{rel} = \dfrac{\eta}{\eta_o} = \dfrac{t}{t_o}$
Specific viscosity	-	$\eta_{sp} = \dfrac{\eta - \eta_o}{\eta_o} = \dfrac{t - t_o}{t_o} = \eta_{rel} - 1$
Reduced viscosity	Viscosity number	$\eta_{red} = \dfrac{\eta_{sp}}{C} = \dfrac{\eta_{rel} - 1}{C}$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = \dfrac{\ln \eta_{rel}}{C}$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = \left(\dfrac{\eta_{sp}}{C} \right)_{C=0} = (\eta_{inh}) C = 0$

Interrelationships Among Parameters

For **dilute** solutions,

$$\ln \eta_{rel} = \ln(\eta_{sp} + 1) \cong \eta_{sp} - \frac{\eta_{sp}^2}{2} + \cdots$$

$$\left[\frac{\ln \eta_{rel}}{c}\right]_{c=0} = [\eta]$$

Compare this to

$$\left[\frac{\eta_{sp}}{c}\right]_{c=0} \equiv [\eta]$$

Effect of Concentration in Dilute Solution

Huggins Equation

$$\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c$$

Kraemer Equation

$$\frac{\ln \eta_{rel}}{c} = [\eta] - k_K [\eta]^2 c$$

For many polymers in good solvents

$k_H = 0.4 +/- 0.1 \qquad k_K = 0.05 +/- 0.05$

1) Basic Principles

 a) Mark-Houwink-Sakurada Equation

$$[\eta] = K\overline{M}_v{}^a$$

$$\log[\eta] = \log K + a \log M_v$$

 i) K and a are characteristic of the particular solvent/polymer combination

 ii) $\overline{M}_v$ = Viscosity Average Molecular Weight

$$\overline{M}_v = \left(\frac{\sum N_i M_i{}^{a+1}}{\sum N_i M_i} \right)^{\frac{1}{a}}$$
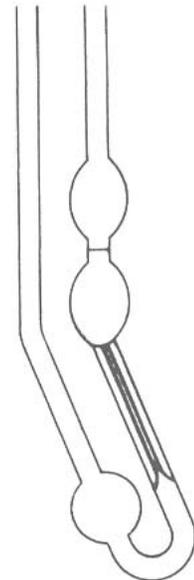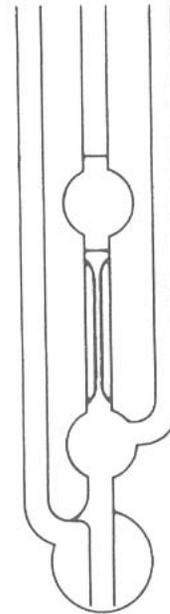
 iii) a = 0.5 (θ solvent) ~ 0.8 (good solvent)

b) Measurement of [η]

i) Make up 5-6 solutions at different concentrations of the same sample and of pure solvent

ii) measure the time it takes each of them to flow through the viscometer

iii) extrapolate to viscosity at zero concentration which gives the intrinsic viscosity

Capillary viscometers: **Ubbelohde**   **Cannon-Fenske**

c) Measurement of [η], K and a

Plot the [η] values against the MW values from another technique and get K and a from the intercept and slope

$$\log[\eta] = \log K + a \log M_v$$

d) Determination for a polymer of known structure
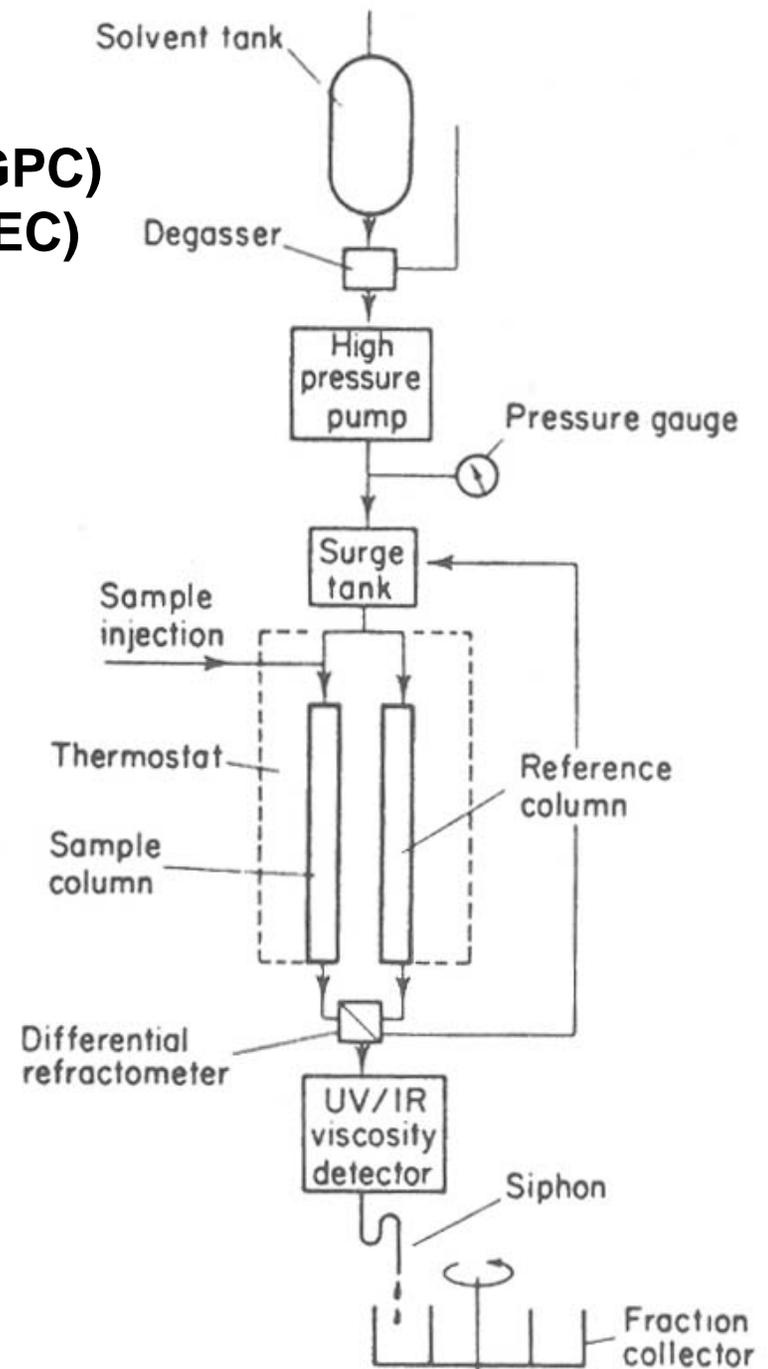
i) Look up K and a in the Polymer Handbook (Table 2.3)

ii) Use the [η] values to calculate $\overline{M_v}$ directly

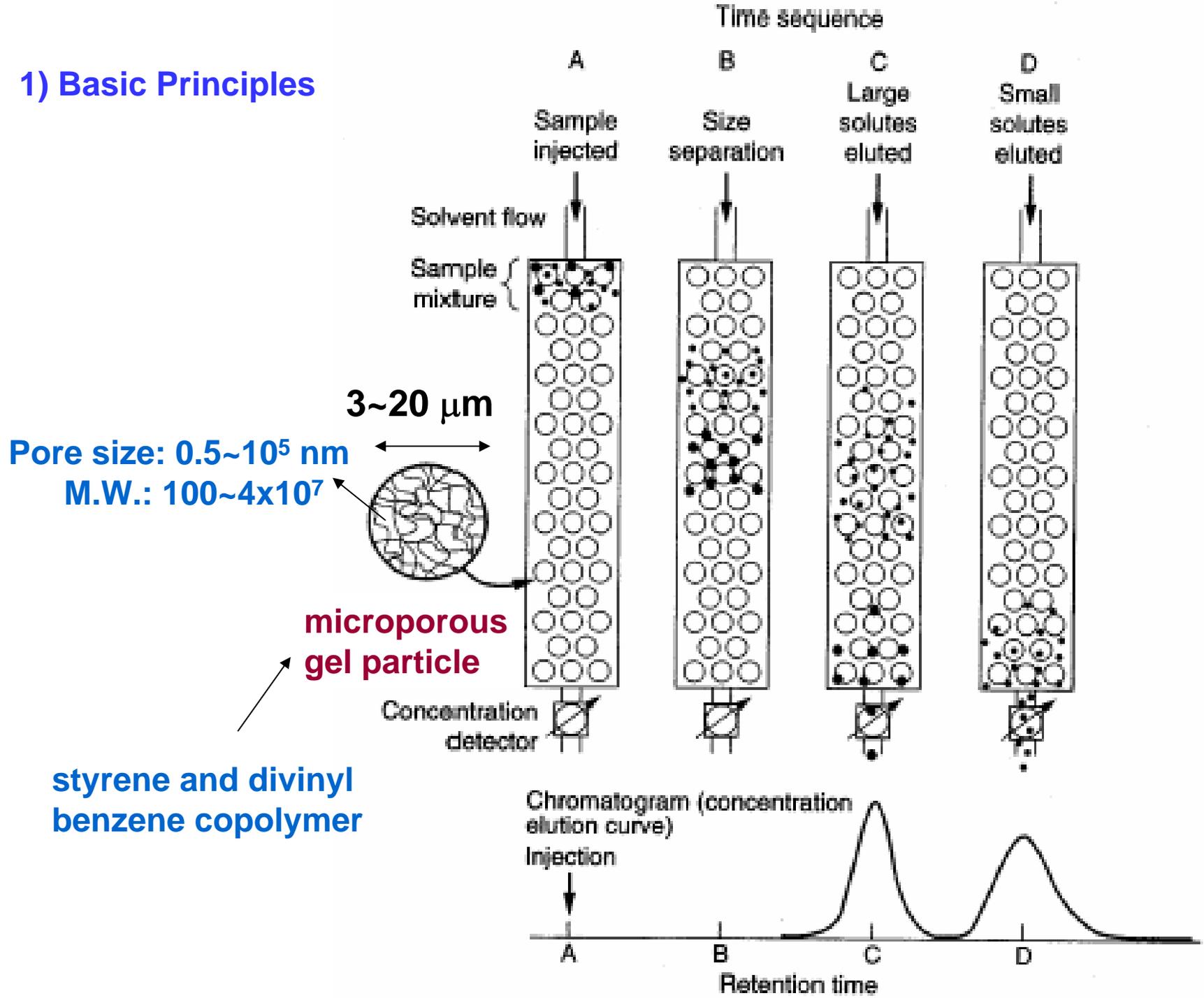# Table 2.3 Representative Viscosity-Molecular Weight Constants [a]

Polymer	Solvent	Temperature ℃	Molecular Weight Range $\times 10^{-4}$	$K^b \times 10^3$	a^b
Polystyrene (atactic)[c]	Cyclohexane	35[d]	8-42[e]	80	0.50
	Cyclohexane	50	4-137[e]	26.9	0.599
	Benzene	25	3-61[f]	9.52	0.74
Polyethylene (low pressure)	Decalin	135	3-100[e]	67.7	0.67
Poly(vinyl chloride)	Benzyl alcohol	155.4[d]	4-35[e]	156	0.50
	cyclohexanone	20	7-13[f]	13.7	1.0
Polybutadiene					
98% cis-1,4, 2%1,2	Toluene	30	5-50[f]	30.5	0.725
97% trans-1,4, 3% 1,2	Toluene	30	5-16[f]	29.4	0.753
Polyacrylonitrile	DMF[g]	25	5-27[e]	16.6	0.81
	DMF	25	3-100[f]	39.2	0.75
Poly(MMA-co-St)					
30-7- mol %	1-Chlorobutane	30	5-55[e]	17.6	0.67
71-29 mol %	1-Chlorobutane	30	4.8-81[e]	24.9	0.63
PET	m-Cresol	25	0.04-1.2[f]	0.77	0.95
Nylon 66	m-Cresol	25	1.4-5[f]	240	0.61

2.6 M.W. Distribution

2.6.1 Gel Permeation Chromatography (GPC)
**   = Size Exclusion Chromatography (SEC)**

1) Basic Principles

3~20 μm

Pore size: 0.5~10^5 nm
M.W.: 100~4×10^7

microporous
gel particle

styrene and divinyl
benzene copolymer

Time sequence

A — Sample injected
B — Size separation
C — Large solutes eluted
D — Small solutes eluted

Solvent flow

Sample mixture

Concentration detector

Chromatogram (concentration elution curve)

Injection

Retention time
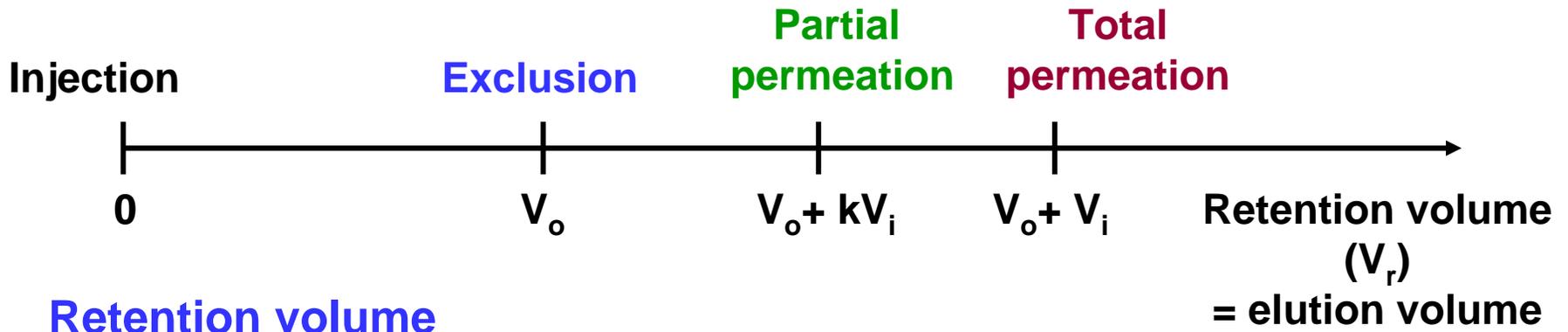
Gel Permeation Chromatography
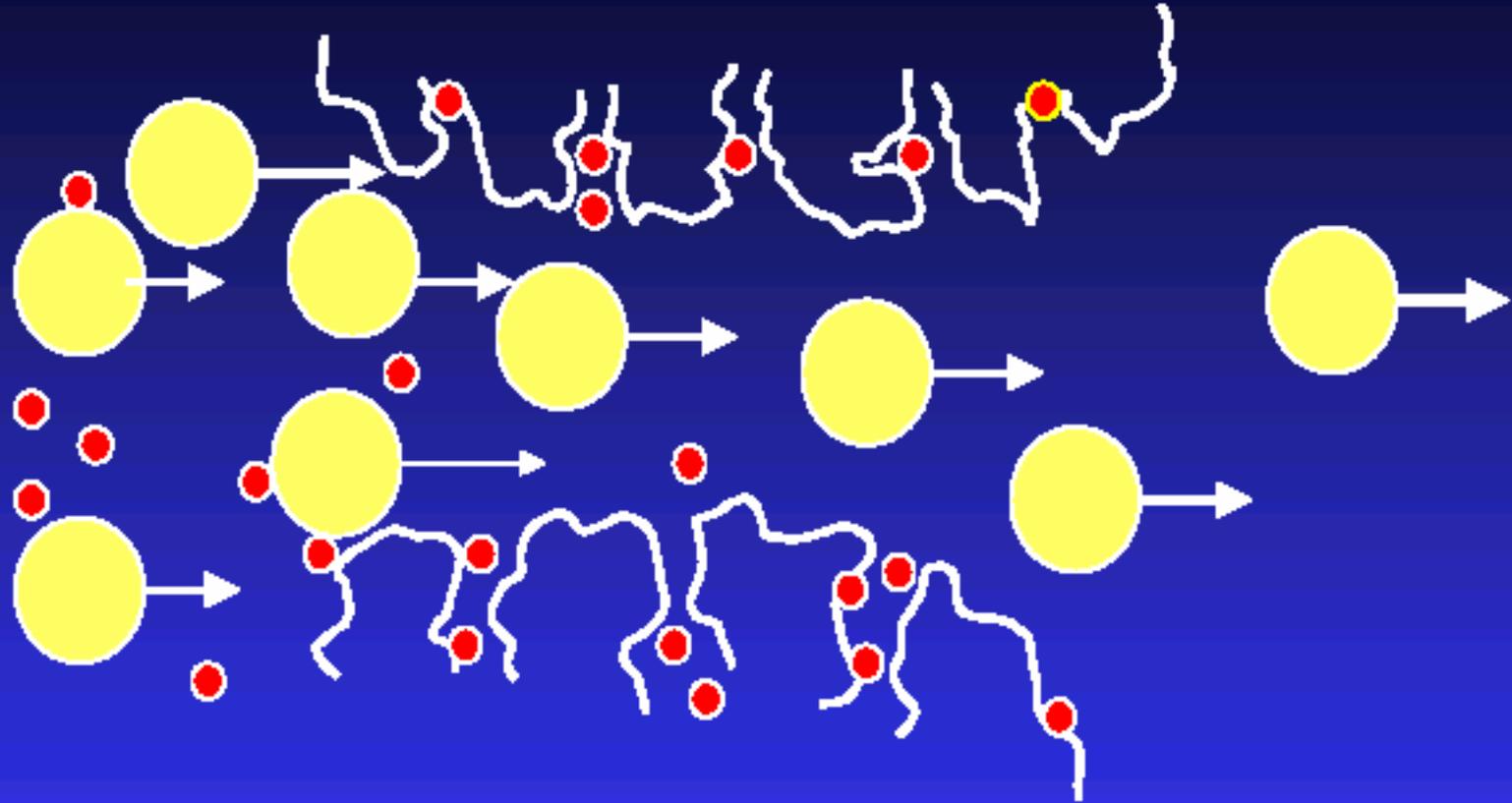
A mixture of different size solute molecules is eluted through a column of porous particles. Larger molecules are swept through unhindered, while small molecules are retarded in the pores.

Injection **Exclusion** **Partial permeation** **Total permeation**

$$0 \qquad V_o \qquad V_o + kV_i \qquad V_o + V_i \qquad \text{Retention volume} (V_r)$$

= elution volume

Retention volume

$$V_r = V_0 + kV_i$$

Where

V_0 = **Interstitial (or void) volume between** porous gel particles

V_i = **Pore volume within** the porous gel particles

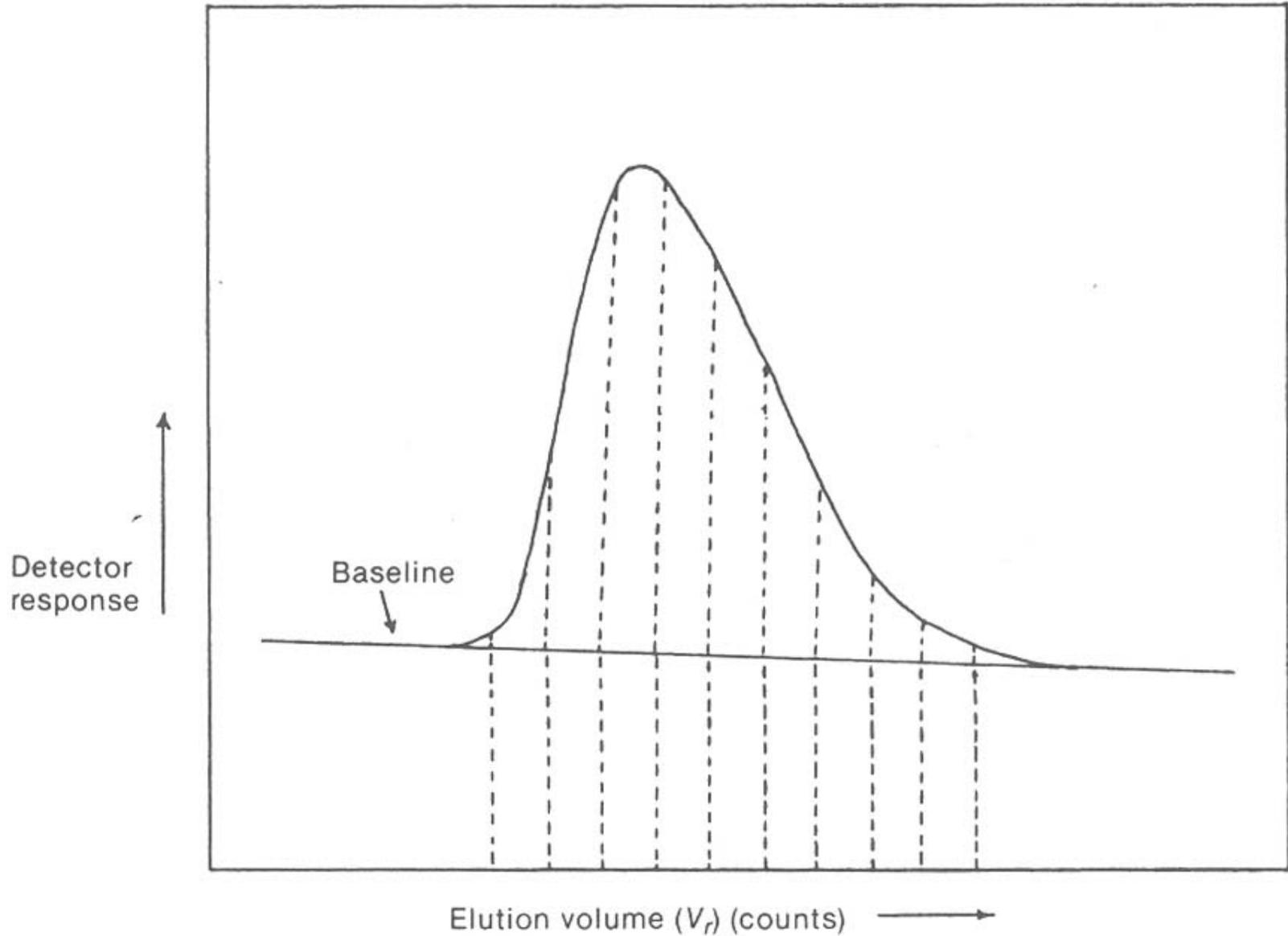k = **Partition coefficient** between V_i and the portion accessible to a given solute

= **0 ~ 1**

very large molecule

which cannot penetrate any available pore volume
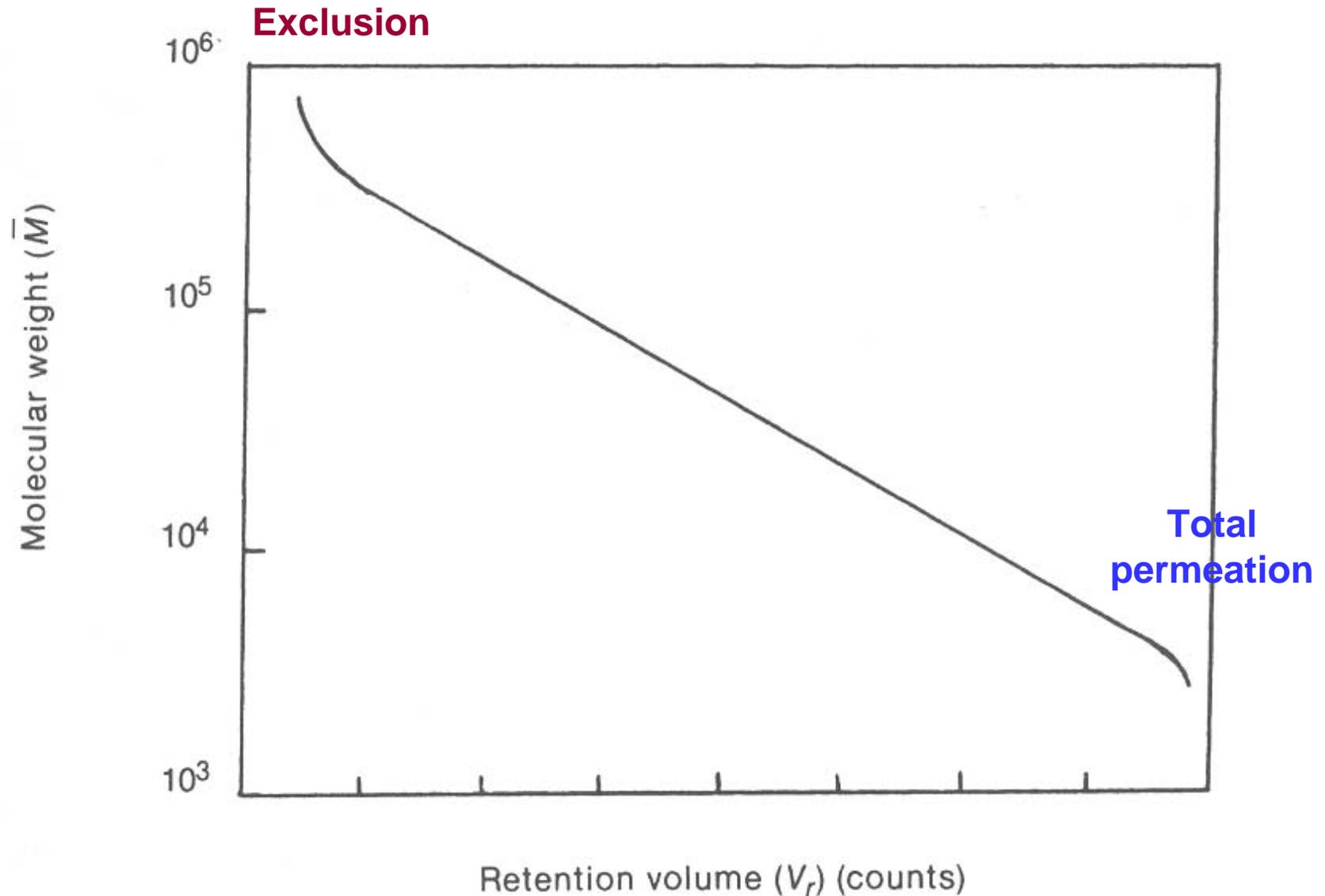
very small molecule

which can penetrate all the available pore volume

Figure 2.10 Typical gel permeation chromatogram

Gives Polystyrene (or Poly(vinyl alcohol)) Equivalent MWs

Figure 2.12 Typical semilogarithmic calibration plot

Reference polymer: monodisperse polystyrene or poly(vinyl alcohol)

2) **Universal calibration**

$$[\eta]\ M = 2.5\ N_A\ V_h$$ **Einstein viscosity relation**

= **universal calibration parameter**

= **constant for all polymers** for a given column, temp, and elution volume

Polymer 1 = reference polymer (e.g. polystyrene)
Polymer 2 = polymer to be fractionated

For equal elution volumes of two different polymers

$$[\eta]_1 M_1 = [\eta]_2 M_2$$

Mark-Houwink-Sakurada relationship

$$[\eta]_1 = K_1 M_1^{a_1} \qquad [\eta]_2 = K_2 M_2^{a_2}$$

$$K_1 M_1^{1+a_1} = K_2 M_2^{1+a_2}$$

$$\log K_1 + (1 + a_1) M_1 = \log K_2 + (1 + a_2) M_2$$

$$\log M_2 = \left(\frac{1}{1+a_2}\right) \log\left(\frac{K_1}{K_2}\right) + \left(\frac{1+a_1}{1+a_2}\right) \log M_1$$

Figure 2.11 **Universal calibration** for GPC

log([η]M) is plotted with V_r

All polymers fit on the same curve

Legend:
- ● Polystyrene (linear)
- ○ Polystyrene (comb)
- + Polystyrene (star)
- △ Heterograft copolymer
- × Poly (methyl methacrylate)
- ⊖ Poly (vinyl chloride)
- ▽ Styrene–methyl methacrylate graft copolymer
- ■ Poly (phenyl siloxane) (ladder)
- □ Polybutadiene

Axes: log([η]M), 10^9, 10^8, 10^7, 10^6, 10^5; Retention volume: 18 20 22 24 26 28 30