

Chemical Engineering 160/260
Polymer Science and Engineering

**Lecture 4 - Direct Measures of
Molecular Weight: Osmometry and
Light Scattering**

January 24, 2001

Outline

- Chemical potential of dilute solutions
- Raoult's Law
- Osmotic pressure
- Van't Hoff Equation
- Virial expansion
- Light scattering

Experimental Approaches

- **Direct** measures of molecular weight may be obtained from osmometry, light scattering, and ultracentrifugation.
- **Indirect** measures of molecular weight, such as viscometry and gel permeation chromatography, yield relative estimates that must be calibrated.

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

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



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.

Semipermeable Membrane Construction

- Membranes for different solvents
 - ◆ Organic - cellulose, gel cellophane
 - ◆ Aqueous - cellulose acetate, nitrocellulose
 - ◆ Corrosive - glass
- Membrane porosity
 - ◆ Must consider pore size and its distribution
- Membrane conditioning
 - ◆ Membranes shipped in isopropanol/water
 - ◆ Programmed sequence of solvent mixtures
 - ◆ Dried-out membranes should be discarded

Derivation of Van't Hoff Equation

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

$$\mu_s = f(P, x_p)$$

$$x_p = 1 - x_s$$

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, $d\mu_s = 0$

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

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

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

\bar{V}_s = partial molar volume of solvent

Since the order of differentiation is immaterial, we have

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

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

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



$$\bar{V}_s$$



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

Substitution leads to

$$\int_{P_o}^{P_o+\pi} \bar{V}_s dP = RT \int_0^{x_p} \frac{dx_p}{1-x_p}$$

Derivation of Van't Hoff Equation

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

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

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

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

For the case where $N_s \gg N_p$,

$$x_p = \frac{N_p}{N_s + N_p} \cong \frac{N_p}{N_s}$$

$$N_s \bar{V}_s = V_s \cong V(\text{solution})$$

Derivation of Van't Hoff Equation

Substitution yields

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

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

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

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

\bar{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.

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

A_2 = second virial coefficient

A_3 = third virial coefficient

Alternative expressions:

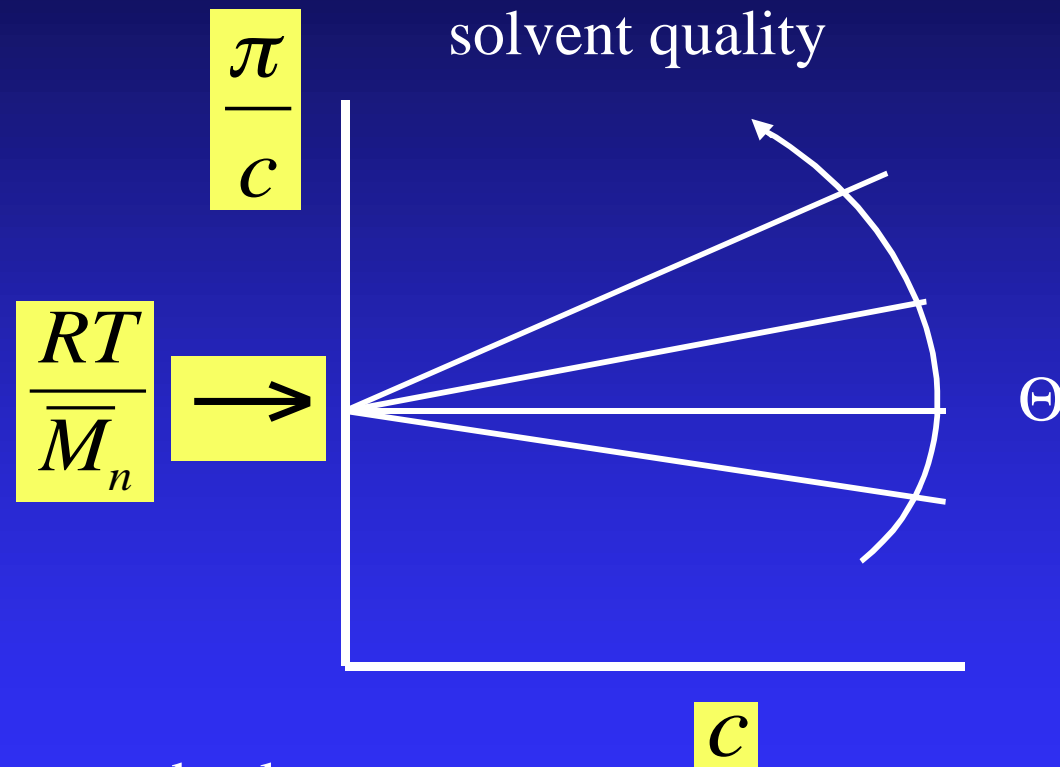
$$\frac{\pi}{c} = \left(\frac{\pi}{c}\right)_{c=0} \left[1 + \Gamma_2 c + \Gamma_3 c^2 + L \right]$$

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

The forms are equivalent if:

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

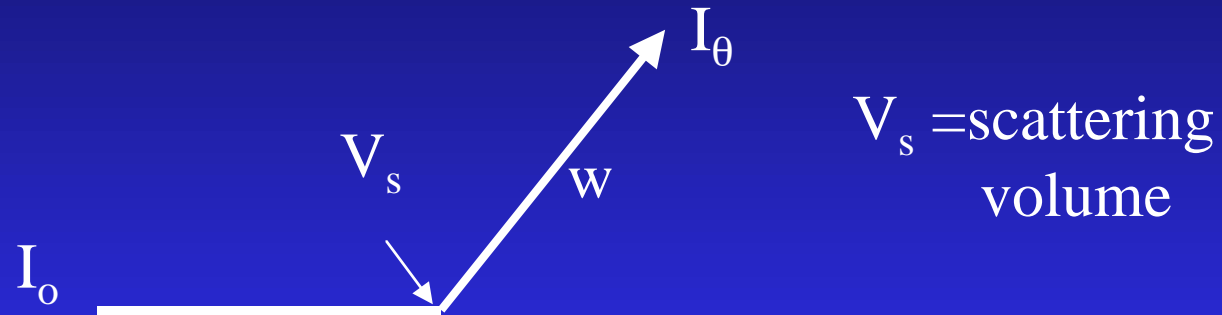
Effect of Solvent Quality on Osmotic Pressure



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

Light Scattering

We will only summarize the results -- for background, see, e.g., Allcock and Lampe, 2nd ed., pp 348-363.



Light scattering arises from **fluctuations in refractive index**, which can be related to the osmotic pressure.

Rayleigh's Ratio, $R(\theta)$

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

$$R(\theta) = \frac{I_\theta w^2}{I_o V_s}$$

w = scattering distance
 V_s = scattering volume

$$H = \frac{2\pi^2 n_o^2 \left(\frac{dn}{dc} \right)^2}{N_A \lambda^4}$$

λ = incident wavelength
 n_o = refractive index at λ
 N_A = Avogadro's number

Relationship to Weight Average Molecular Weight and Second Virial Coefficient

$$\frac{Hc}{R(\theta) - R(\text{solvent})} = \frac{1}{\overline{M}_w P(\theta)} + 2A_2$$

$P(\theta)$ is the single chain **form factor**, which accounts for the **finite size** of the macromolecule relative to the wavelength of incident light.

Single Chain Form Factor for a Random Coil

For **particles larger than $\lambda/20$** , $P(\theta)$ is not unity.
For small angles (in the Guinier region) and a **random coil** structure,

$$P(\theta) = \frac{2}{R_g^4 k^4} \left\{ R_g^2 k^2 - \left[1 - \exp(-R_g^2 k^2) \right] \right\}$$

R_g is the radius of gyration, which is a measure of the three-dimensional structure of the random coil.

$$k = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

This is also referred to as q .

Zimm Plot

Extrapolations to zero angle and zero concentration allow for determination of \mathbf{M}_w , \mathbf{A}_2 , and \mathbf{R}_g .

Eliminate shape effects:

$$\left[\frac{Hc}{R(\theta)} \right]_{\theta=0} = \frac{1}{\overline{M}_w} + 2A_2c$$

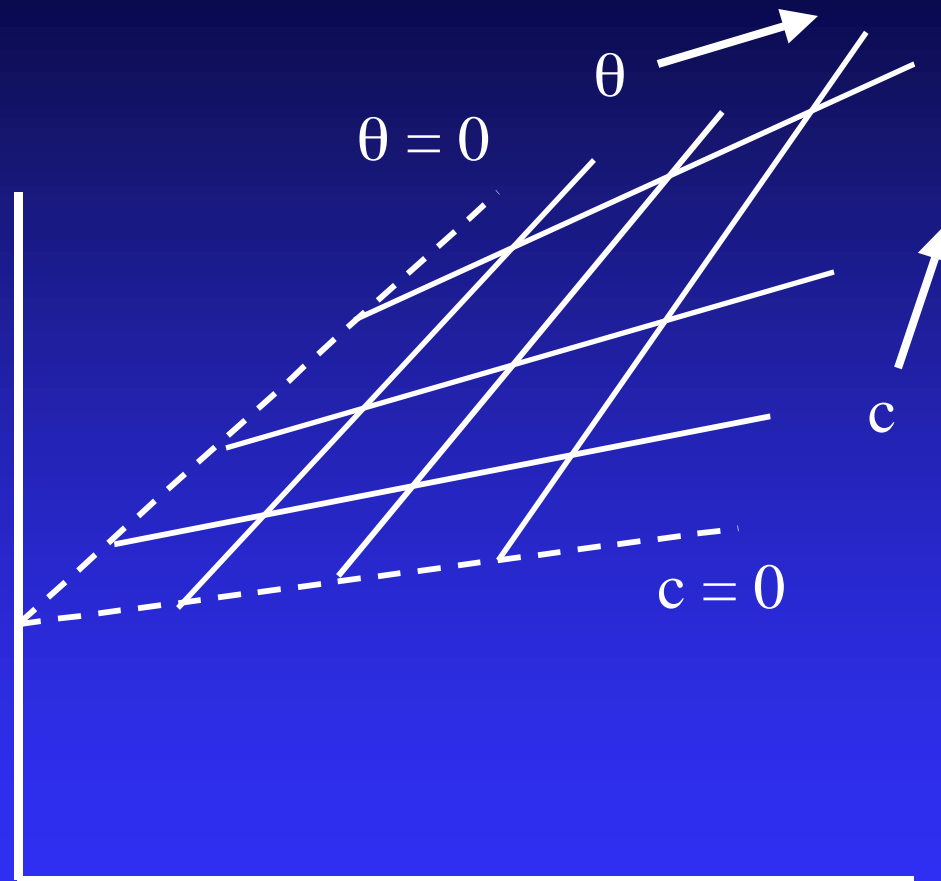
Eliminate intermolecular interactions:

$$\left[\frac{Hc}{R(\theta)} \right]_{c=0} = \frac{1}{\overline{M}_w} \left[1 + \frac{1}{3} \left(\frac{4\pi}{\lambda \odot} \right)^2 R_g^2 \sin^2 \left(\frac{\theta}{2} \right) + L \right]$$

$$\lambda \odot = \frac{\lambda_o}{n_o}$$

Zimm Plot

$$\frac{3Hc}{16\pi R(\theta)}$$



$$100c + \sin^2\left(\frac{\theta}{2}\right)$$