

Polymer Blends

Good References on Polymer Blends:

- O. Olasbisi, L.M. Robeson and M. Shaw, *Polymer-Polymer Miscibility*, Academic Press (1979).
- D.R. Paul, S. Newman, *Polymer Blends*, Vol I, II, Academic Press (1978).
- Upper Critical Solution Temperature (UCST) Behavior
Well accounted for by F-H theory with $\chi = a/T + b$
- Lower Critical Solution Temperature (LCST) Behavior
FH theory cannot predict LCST behavior. Experimentally find that blend systems displaying hydrogen bonding and/or large thermal expansion factor difference between the respective homopolymers often results in LCST formation.

Why?

Phase Diagram for UCST Polymer Blend

Predicted from FH Theory

$$\chi = \frac{A}{T}; \text{ add a constant } B$$

$$x_1 = x_2 = N$$

$$\frac{\partial \Delta G_m}{\partial \phi} = 0 \quad \text{binodal}$$

$$\frac{\partial^2 \Delta G_m}{\partial \phi^2} = 0 \quad \text{spinodal}$$

$$\frac{\partial^3 \Delta G_m}{\partial \phi^3} = 0 \quad \text{critical point}$$

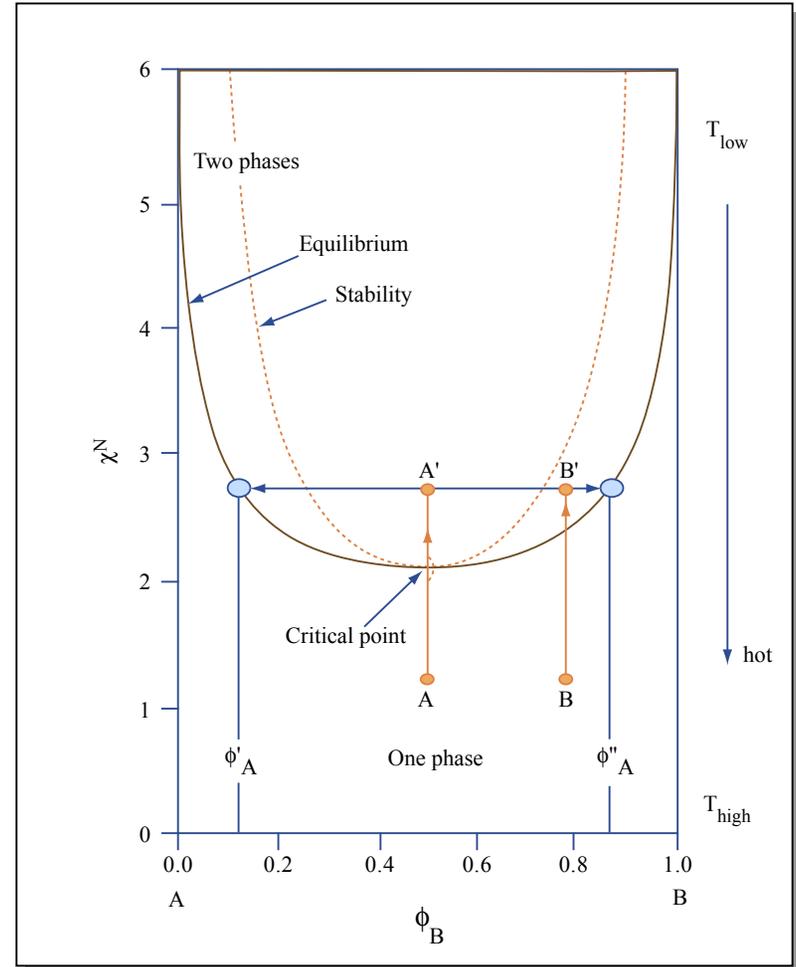


Figure by MIT OCW.

A polymer	x_1 segments	$v_1 \approx v_2$ & $x_1 \approx x_2$
B polymer	x_2 segments	

$$\chi = \frac{A}{T} + B$$

2 Principal Types of Phase Diagrams

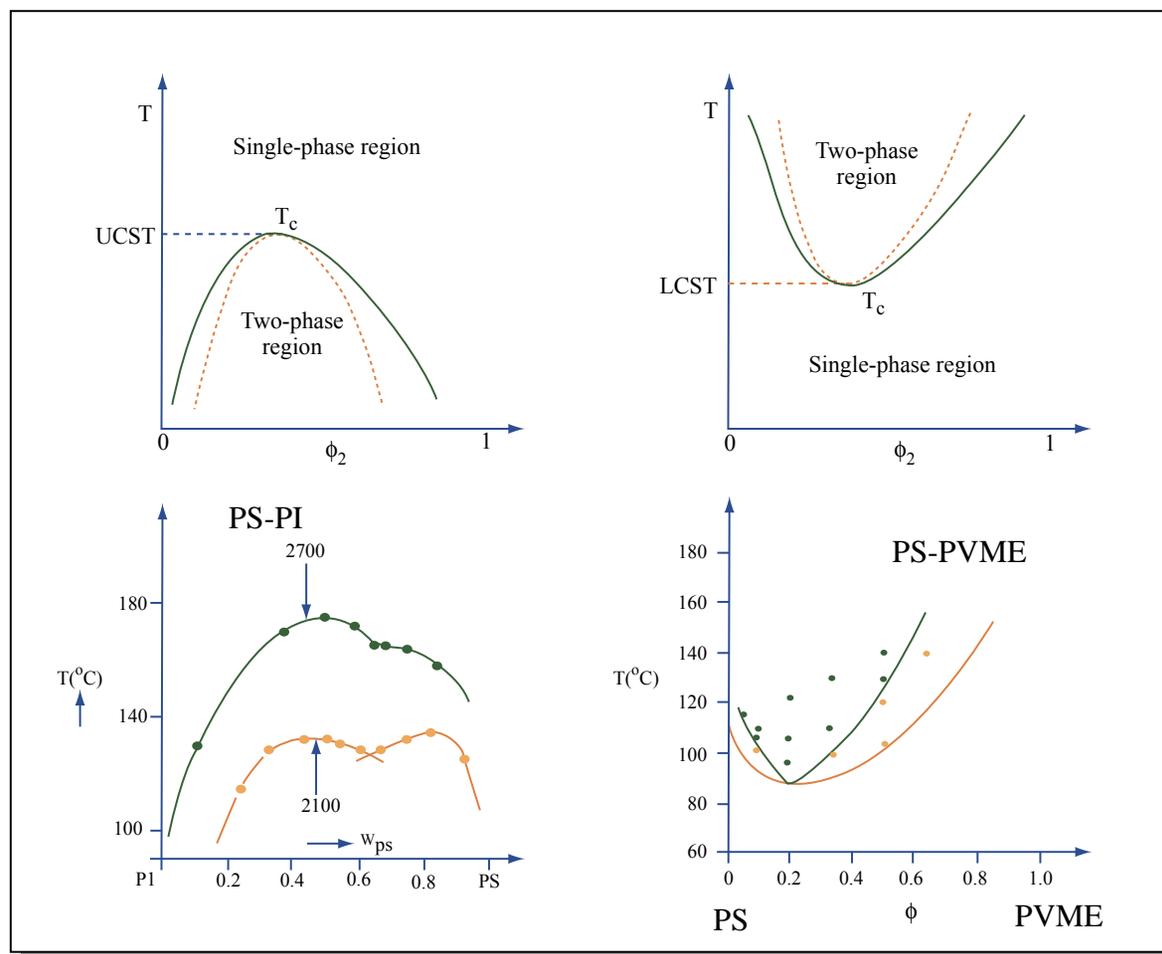


Figure by MIT OCW.

Konigsveld, Klentjens, Schoffeleers
Pure Appl. Chem. 39, 1 (1974)

Nishi, Wang, Kwei
Macromolecules, 8

Today - Measuring Polymer MW & Size

- c_2^*
- Intrinsic Viscosity -
 - alpha, M_v and more scaling exponents!
- Osmometry -
 - chi and M_n

Spinodal Decomposition of LCST Blend

Bicontinuous Structures

LCST

By *up-quenching* into the unstable spinodal regime and then after a short hold, rapidly cooling, one can trap the bicontinuous spinodal structure. Over-annealing results in coarsening and droplet formation (figure d) just like in metal alloys.

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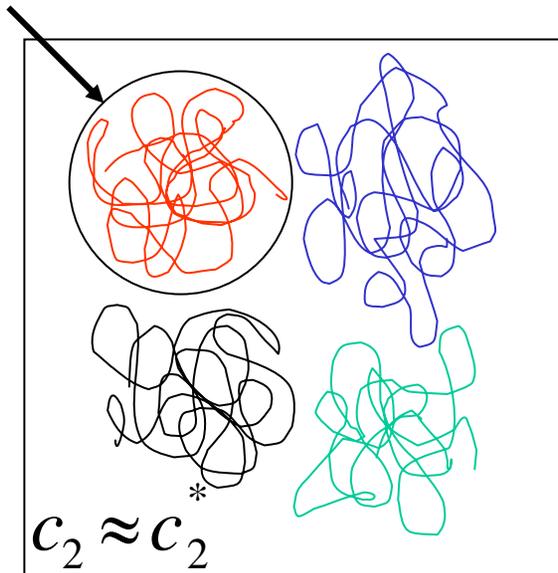
Please see Fig. 28 in Platzer, Norbert A. J. Copolymers, polyblends, and composites: a symposium. *Advances in Chemistry*, no. 142. Washington, DC: American Chemical Society, 1975.

Overlap Concentration c_2^*

c_2^* is the so called overlap concentration; the polymer concentration at which the coils of molecular weight M just begin to touch.

Note: at and above c_2^* the solution is reasonably uniform in composition (i.e. mean field situation, no large regions of pure solvent)

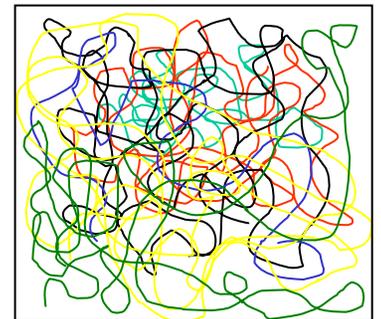
Sphere of pervaded volume



$$c_2^* \sim \frac{M / N_A}{\frac{4}{3} \pi \langle r^2 \rangle^{3/2}}$$

Volume of sphere

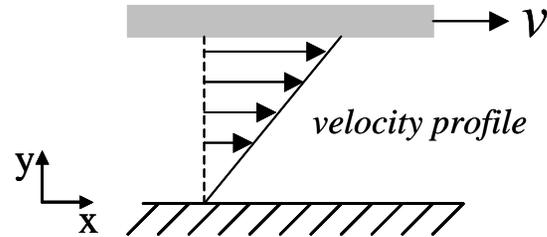
$c_2 > c_2^*$



Viscosity, η

- Basic information on chain dimensions in a particular solvent.

Shearing of a fluid



Boundary Conditions - no slip

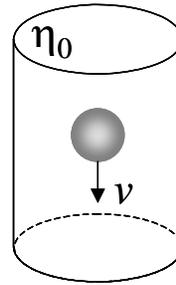
$$\tau = \frac{\text{viscous force}}{\text{area}} = \text{Pa} = \frac{\text{N}}{\text{m}^2}$$
$$\tau = \eta \frac{d\gamma}{dt}$$
$$\frac{d\gamma}{dt} = \frac{dv}{dy} = \frac{\text{cm/sec}}{\text{cm}} = \dot{\gamma} \text{ sec}^{-1}$$
$$\eta = \frac{\text{shear stress}}{\text{rate of shear}} = \text{Pa} \cdot \text{sec}$$

If $\eta \neq \eta(\gamma_{\text{tot}}, \dot{\gamma})$ the fluid is a *Newtonian* fluid Polymers are very nonNewtonian!

We are interested in the effect of additives on the viscosity of simple (low molar mass) fluids.

- (1). suspension of **hard spheres** -- (*Stokes 1850, Einstein 1905*)
- (2). suspension of **polymer coils**

Stokes and Viscosity

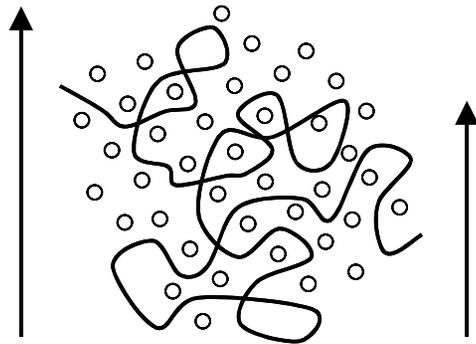


- sphere of size R_s falling through a fluid of viscosity η_0 with velocity v .

$F_{\text{viscous}} = f v$ f is the friction factor of the solution

$$f = 6 \rho \eta_0 R_s \quad \text{Stokes' Law}$$

- How to treat a **polymer molecule**?



x_2 segments/chain

2 Limiting Cases:

- I. Impenetrable Sphere
- II. Penetrable Coil

$$\langle R_g^2 \rangle \equiv \langle s^2 \rangle = \frac{\langle r^2 \rangle}{6}$$

Polymer Molecule in Shear Flow

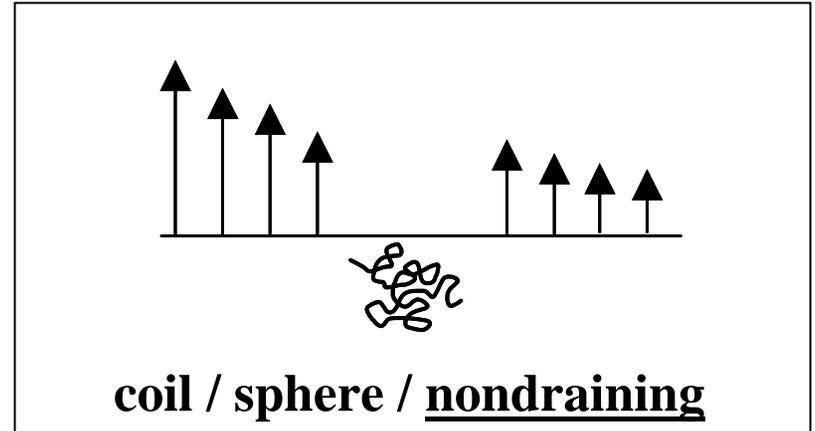
- Case I: Impenetrable Sphere

$$f = 6 \pi \eta_0 R_H$$

$$R_H \sim \langle R_g^2 \rangle^{1/2}$$

$$\text{so } f \sim x_2^{1/2}$$

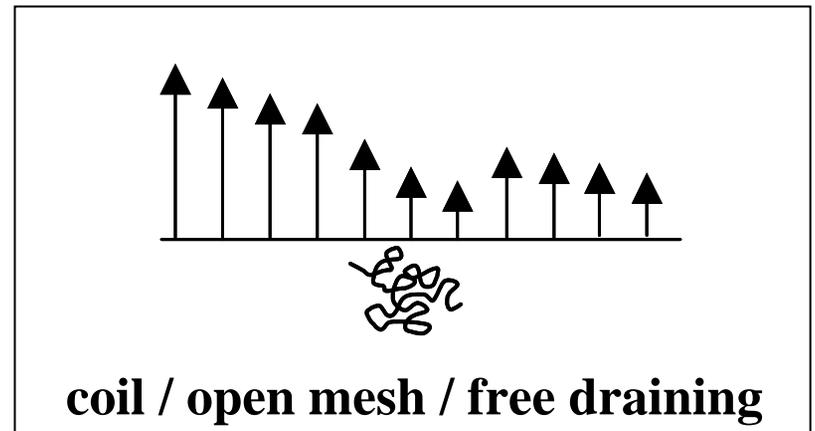
R_H is the hydrodynamic radius



- Case II: Penetrable Coil
Solvent passes through coil

$$\text{so } f \sim \xi x_2$$

where ξ is the monomeric friction factor



The model that is most appropriate depends on the size of the polymer

Scaling Behavior of Friction Factor

$$f \sim X_2^a$$

a	Condition
1	low MW coil or any rod
1/2	θ condition (Gaussian coil: RW)
3/5	good solvent (coil: SARW)

- For high MW flexible chain molecules correct model is nondraining, impenetrable units

$$f = 6\pi\eta_0 R_H$$

$$R_H = \gamma \langle R_g^2 \rangle^{1/2} \quad \gamma \approx 0.85$$

- To develop expression for viscosity use Einstein equation for viscosity of a solution containing impenetrable spheres of volume fraction ϕ_{hs} :

$$\eta(\phi_{hs}) = \eta_0 (1 + 2.5\phi_{hs} + \dots)$$

- choose θ condition and dilute solution ($\phi_2 \ll 1$), $c_2 \ll c_2^*$
- c_2^* = overlap concentration, note: $\phi_2 \neq \phi_{hs}$, indeed $\phi_2 \ll \phi_{hs}$

2 Important Viscosities

- **Specific viscosity** $\eta_{sp} = \frac{\eta}{\eta_o} - 1 = 2.5\phi_{hs}$

$$\phi_{hs} = \frac{(\# \text{ sphere}) (\text{vol. of sphere})}{\text{Total Volume}} = \left(\frac{c_2}{M/N_{AV}} \right) \frac{4}{3} \pi \gamma^3 \langle R_g^2 \rangle^{3/2}$$

- **Intrinsic viscosity**

$$[\eta] \equiv \lim_{c_2 \rightarrow 0} \frac{\eta_{sp}}{c_2} = \frac{2.5\phi_{hs}}{c_2}$$

$$[\eta] = 2.5 \left(\frac{\frac{4\pi}{3} \gamma^3 N_{AV} \langle R_g^2 \rangle^{3/2}}{M} \right)$$

At θ condition and collect constants into prefactor K_θ $[\eta]_\theta = K_\theta M^{1/2}$

For other solvent conditions use α solvent quality factor

$$R_g \rightarrow \alpha R_{g\theta}$$

in general:

$$[\eta] = KM^a$$

Expt'l method for
obtaining alpha

$$[\eta] = \alpha^3 [\eta]_\theta \quad \text{with} \quad K = \alpha^3 K_\theta$$

Intrinsic Viscosity - Key Idea

- A simple method to quickly assess a sample's molecular weight is to utilize the dependence of the viscosity of a polymer solution (in a good solvent) on the molecular weight of the polymer. The viscosity depends not only on molecular weight and on solvent quality, but also on polymer concentration, so one has to extrapolate to zero concentration to determine the “*intrinsic*” effect of the addition of the polymer to the increase in viscosity of the solution.

$$[\eta] \equiv \lim_{c_2 \rightarrow 0} \frac{\eta_{sp}}{c_2}$$

\bar{M}_v Viscosity-average molecular weight

$$[\eta] = k\bar{M}_v^a$$

$$\bar{M}_v = \left(\frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right)^{1/a} \quad (\text{See following page for derivation})$$

Viscosity-Average Molecular Weight

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1$$

For a polydisperse solution with n_i moles of species i of molecular weight M_i ,

$$\eta_{sp, \text{soln}} = \sum_i \eta_{sp, i} \quad [\eta]_i = KM_i^a$$

conc of i th species in g/vol. of solution $c_i = \frac{n_i M_i}{V}$

Number average MW

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

$$[\eta]_{\text{soln}} = \lim_{c_2 \rightarrow 0} \frac{\eta_{sp, \text{soln}}}{c_2}$$

$$[\eta]_{\text{soln}} = \lim_{c_2 \rightarrow 0} \frac{\sum_i \eta_{sp, i}}{\sum_i c_i} = \lim_{c_2 \rightarrow 0} \frac{\sum_i \eta_{sp, i}}{\sum_i n_i M_i / V}$$

$$[\eta]_{\text{soln}} = \lim_{c_2 \rightarrow 0} \frac{\sum_i c_i [\eta]_i}{\sum_i n_i M_i / V} = \lim_{c_2 \rightarrow 0} \frac{\sum_i n_i M_i / V \cdot KM_i^a}{\sum_i n_i M_i / V}$$

$$[\eta]_{\text{soln}} = K \frac{\sum_i n_i M_i^{1+a}}{\sum_i n_i M_i} \equiv K \bar{M}_v^a \quad \text{or} \quad \bar{M}_v = \left(\frac{\sum_i n_i M_i^{1+a}}{\sum_i n_i M_i} \right)^{1/a}$$

Note:

For $a = 1$ $\bar{M}_v = \bar{M}_w$

But in general $0.5 \leq a \leq 0.8$ so

$$\bar{M}_n \leq \bar{M}_v \leq \bar{M}_w$$

Mark-Houwink-Sakurada

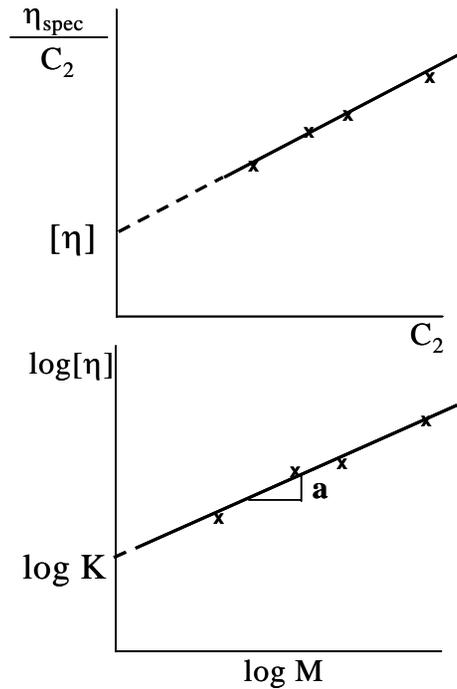
$$[\eta] = KM^a$$

- K and a depend on solvent quality; more scaling exponents!
 - $a < 1/2$ poor solvent
 - $a = 1/2$ θ conditions
 - $a > 1/2$ good solvent
- It turns out α is weakly dependent on coil size (the interior of the coil expands more than the periphery) so longer chains expand more in a good solvent than do shorter chains.

$$\alpha \sim M^{1/10}$$

which results in $a = 8/10$ for high MW chains in a good solvent

Determination of Intrinsic Viscosity



For a series of concentrations

$$C_2 < C_2^*$$

$$\frac{\eta_{sp}}{C_2} = [\eta] + \text{slope} \cdot C_2$$

For a series of MWs

$$[\eta] = K M^a$$

Slopes:

θ solvent

$$a = 1/2$$

good solvent $8/10 > a > 1/2$; MW dependent

	Solvent	K x 10 ²	a
Atactic Polystyrene in (at 25°C)	Benzene	1.23	0.72
	Butanone	3.9	0.58
	Chloroform	0.7	0.76
	Cyclohexane	10.8	0.48
	Dichloromethane	2.10	0.66
	THF	1.10	0.725
	Toluene	1.05	0.73
θ condition	Cyclohexane $\theta = 36^\circ\text{C}$		0.5

Membrane Osmometry (M_n , A_2 , χ)

- Osmotic pressure, π , is a colligative property which depends only on the number of solute molecules in the solution.
- In a capillary membrane osmometer, solvent flow occurs until π increases until the chemical potential $\mu(\pi) = \mu_1^\circ$

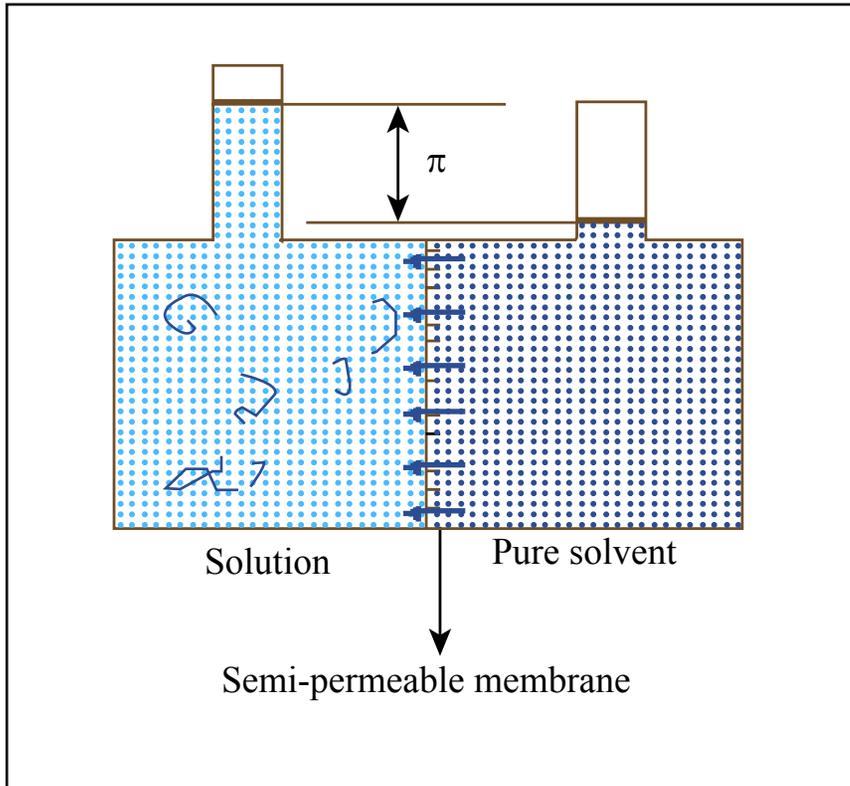


Figure by MIT OCW.

$$\mu_1^\circ = \mu_1 + \int_{P_0}^{P_0 + \pi} \frac{\partial \mu_1}{\partial P} dP$$

$$\frac{\partial \mu_1}{\partial P} = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial n_1} \right) = \frac{\partial}{\partial n_1} \left(\frac{\partial G}{\partial P} \right)$$

$$dG = Vdp - sdT + \mu dn \quad T, n \text{ fixed}$$

$$\text{so } \frac{\partial G}{\partial P} = V$$

$$\frac{\partial}{\partial n_1} (V) \equiv \bar{V}_1 \quad (\text{partial molar volume of pure solvent})$$

Membrane Osmometry cont'd

$$\mu_1^\circ = \mu_1 + \int_{P_0}^{P_0 + \pi} \bar{V}_1 dP = \mu_1 + \pi \bar{V}_1$$

$$\mu_1 - \mu_1^\circ = -\pi \bar{V}_1$$

Recall F-H expression for a dilute solution (ϕ_2 small):

$$\mu_1 - \mu_1^\circ = RT \left[\frac{-\phi_2}{x_2} + (\chi - 1/2) \phi_2^2 \right]$$

Rearranging:

$$\pi = RT \left[\left(\frac{\phi_2}{\bar{V}_1 x_2} \right) + \left(\frac{1}{2} - \chi \right) \left(\frac{\phi_2^2}{\bar{V}_1} \right) \right]$$

Since solution is dilute:
recall $\phi_2 \cong \frac{n_2 x_2 V}{n_1} \cong \frac{n_2 x_2}{n_1} V \cong n_1 V_1$ so $\bar{V}_1 \cong V_1$

$$\pi = RT \left[\left(\frac{n_2}{V} \right) + \left(\frac{1}{2} - \chi \right) \left(\frac{n_2}{V} \right)^2 V_1 x_2^2 \right]$$

The osmotic pressure is a power series in $\left(\frac{n_2}{V} \right)$ i.e., π depends on the number of molecules of solute per unit volume of the solution.

Osmotic Pressure cont'd

- For a polydisperse polymer solution, $n_2 = \sum_i n_i$ where n_i is the number of moles of polymer of molecular weight M_i in the solution. The number average molecular weight of the polymer is simply $\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{m}{n_2}$

- The concentration in grams/cm³ of the polymer in the solution is just c_2 . Hence the osmotic pressure can be written

$$c_2 = \frac{m}{V} = \frac{n_2 \bar{M}_n}{V} \text{ or } \left(\frac{n_2}{V} \right) = \frac{c_2}{\bar{M}_n}$$

written

$$\frac{\pi}{c_2} = RT \left[\frac{1}{\bar{M}_n} + \left(\frac{1}{2} - \chi \right) \frac{V_1 x_2^2}{\bar{M}_n^2} c_2 \right]$$

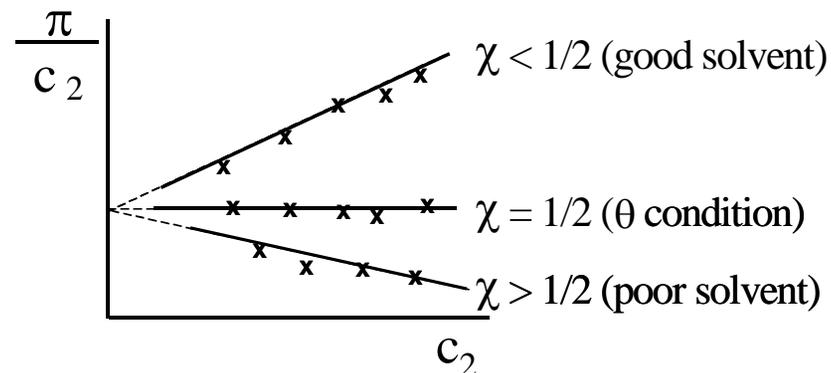
- The “reduced osmotic pressure” when plotted as a function of the solute (i.e. polymer) concentration will give a straight line with:

Key Information:

Intercept: $\frac{RT}{\bar{M}_n}$

Slope: $\left(\frac{1}{2} - \chi \right) \frac{V_1 x_2^2}{\bar{M}_n^2}$

Three types of behavior:



Osmometry cont'd

- At the θ condition, 2nd term disappears (recall $\chi = 1/2$) and solution is ideal

$$\pi V \cong n_2 RT$$

- The slope of the reduced osmotic pressure yields a measure of the polymer segment-solvent F-H interaction parameter, so we have a way to experimentally determine the important χ parameter

- For gases, the pressure is often developed in a virial expansion as a function of concentration

$$P = RT(A_1 c + A_2 c^2 + A_3 c^3 + \dots)$$

- We can therefore identify the virial coefficients A_1 and A_2 from $\frac{\pi}{c_2}$

$$A_1 = \frac{1}{M_n} \quad A_2 = \frac{\left(\frac{1}{2} - \chi\right)}{\rho_2^2 V_1}$$