

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 to make the chemical potential $\mu(\pi) = \mu_1^0$

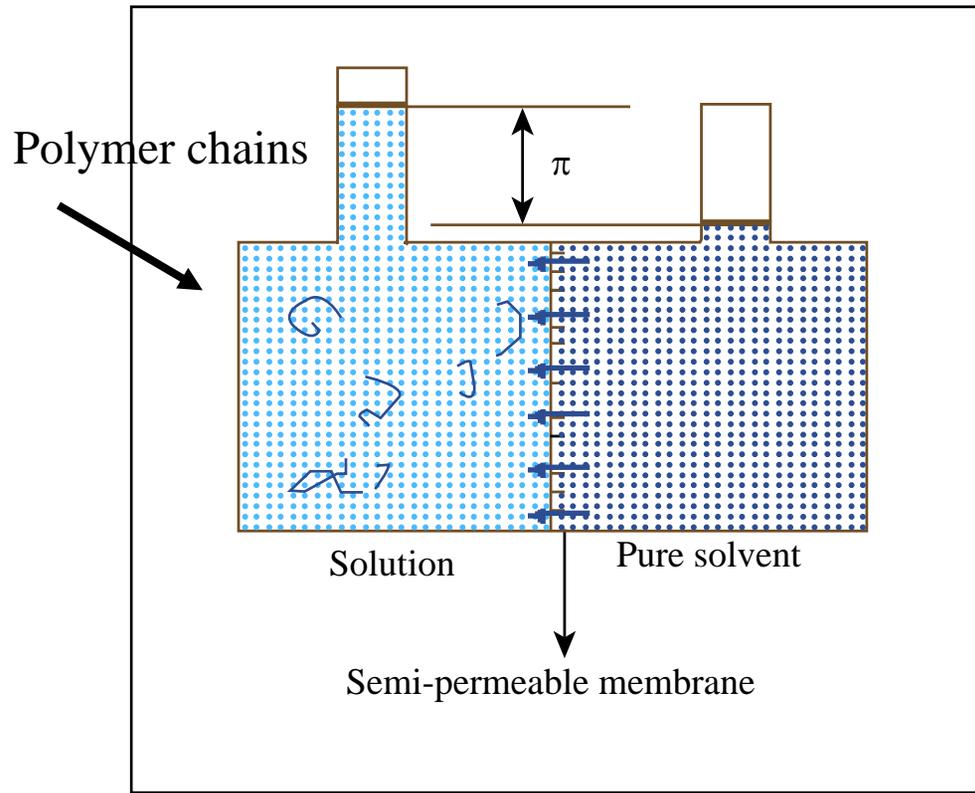


Figure by MIT OCW.

$$\mu_1^0 = \mu_1 + \int_{P_0}^{P_0 + \pi} \frac{\partial \mu_1}{\partial P} dP$$

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

$$dG = Vdp - sdT + \mu dn$$

$$\text{so } \frac{\partial G}{\partial P} = V \quad \text{since } T, n \text{ fixed}$$

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

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: $V \cong n_1 \bar{V}_1$

recall

$$\phi_2 \cong \frac{n_2 x_2}{n_1}$$

$$\pi = RT \left[\left(\frac{n_2}{V} \right) + \left(\frac{1}{2} - \chi \right) \left(\frac{n_2}{V} \right)^2 \bar{V}_1 x_2^2 \right]$$

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

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

Hence the osmotic pressure can be written

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

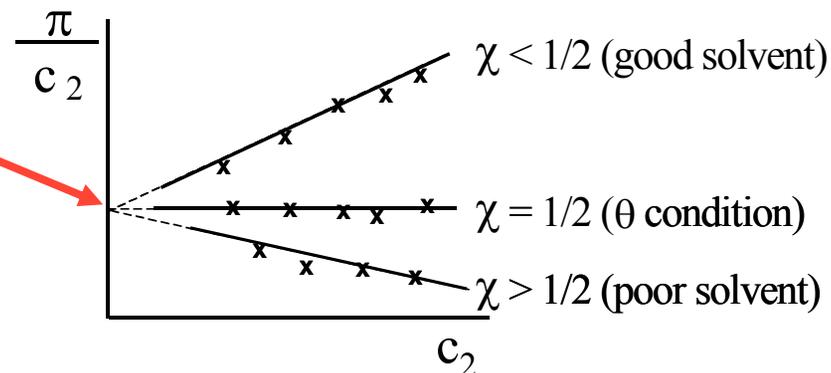
- The “reduced osmotic pressure” when plotted as a function of the solute (i.e. polymer) concentration will give a straight line with:

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

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

- 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, ie we have a way to *experimentally determine χ* .

- For gases, the pressure is often developed 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 as:

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

Comments about Osmometry

1. We assumed *mean field conditions* - local environment is similar everywhere.
2. We employed a dilute solution approximation with $\phi_2 \ll 1$.

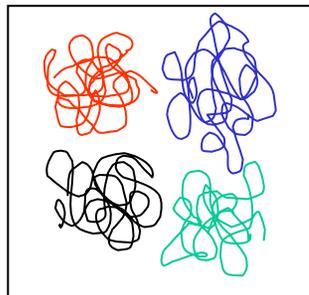
The requirements force the experimental conditions to be chosen such that:

- (1) System is “thermodynamically concentrated” $c_2 > c_2^*$
- (2) System is “mathematically dilute” $\phi_2 \ll 1$

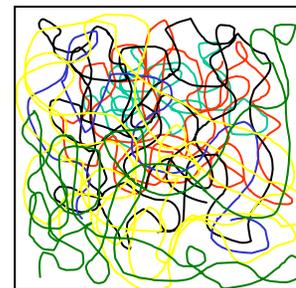
c_2^* is the so called overlap concentration; the polymer concentration at which the coils just begin to touch and hence the solution is reasonably uniform in composition (i.e. mean field situation, no large regions of pure solvent)

$$c_2^* \equiv \text{concentration at overlap} \cong \frac{\text{mass of polymer molecule}}{\text{volume of coil}} = \frac{M / N_A}{\left(\langle r^2 \rangle^{1/2}\right)^3}$$

$$c_2 \approx c_2^*$$



$$c_2 > c_2^*$$



Schematic Polymer-Solvent Structure at Various c_2

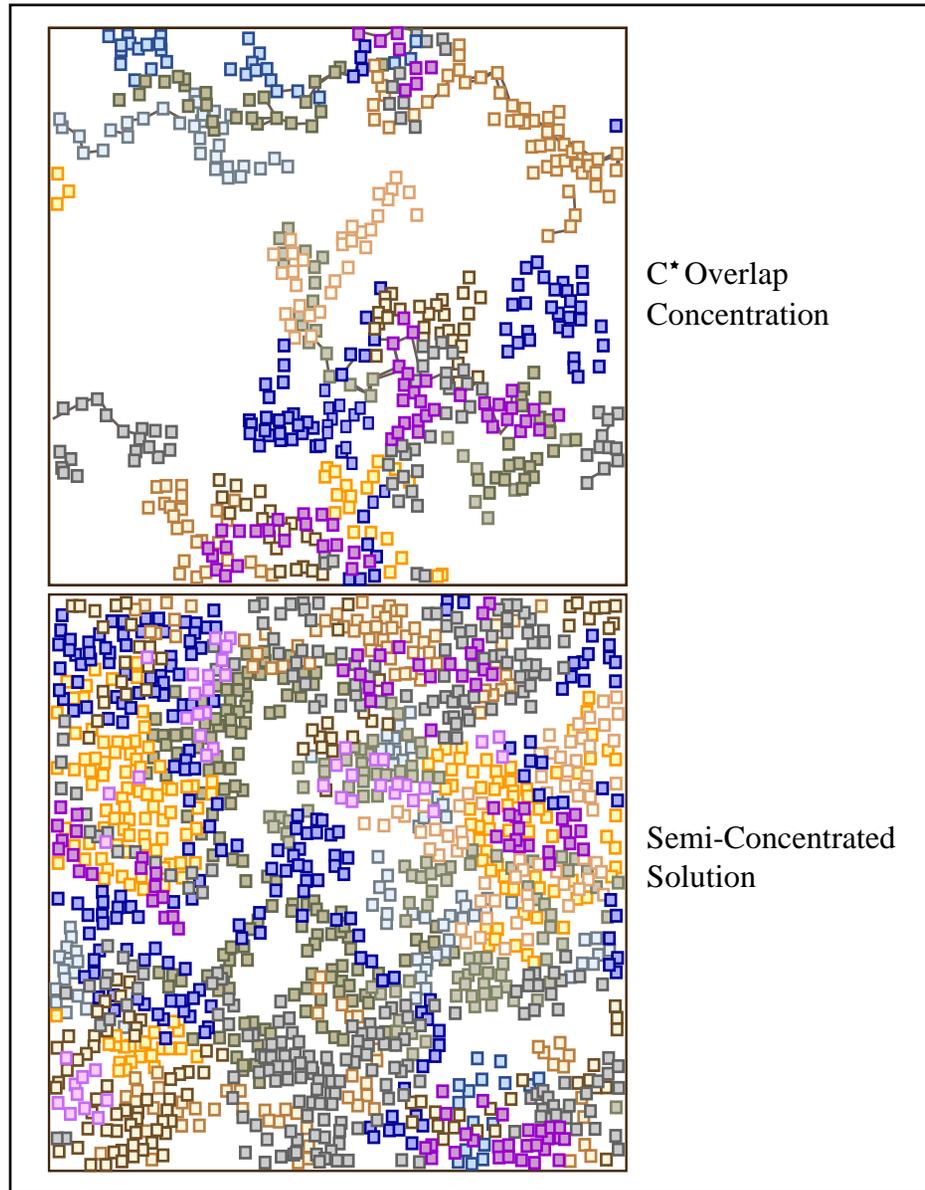
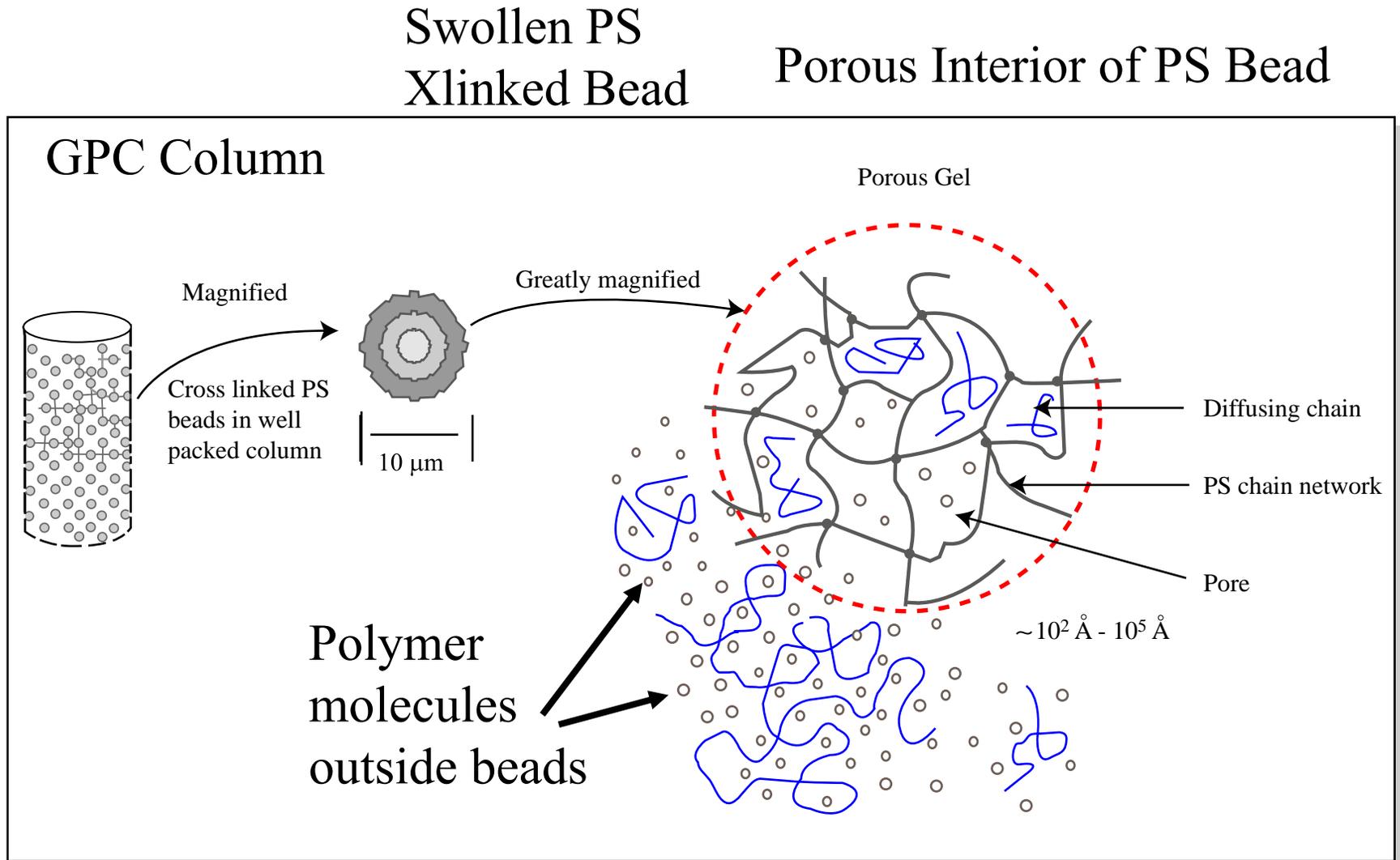


Figure by MIT OCW.

SEC/GPC (Size Exclusion Chromatography)/(Gel Permeation Chromatography)

- SEC allows measurement of the entire molar mass distribution enabling all molecular weight averages to be computed for comparison with other techniques. Preparative GPC uses 25-50 mg of a polymer per run and allows one to fractionate polydisperse samples.
- Apparatus: Set of columns (2-6) containing solvent swollen crosslinked PS beads. The beads are selected to have pore sizes in the range of $10^2 - 10^5 \text{ \AA}$. A run consists of injecting 0.05 ml of a dilute solution (requires only ~ 0.1 mg of polymer !), then allowing the solution to transverse the columns and monitoring the eluting polymer molecules using various detectors. In order to “see” the molecules, one needs sufficient “contrast” between the solvent and solute (polymer). Three types of detectors are commonly used:
 - Ultra violet absorption : UV Detector
 - Infrared absorption : IR Detector
 - Refractive index changes : RI Detector
- The solvent is chosen to be a good solvent for the polymer, to have a different refractive index from the polymer and to not have light absorption in the range for which the polymer is absorptive.

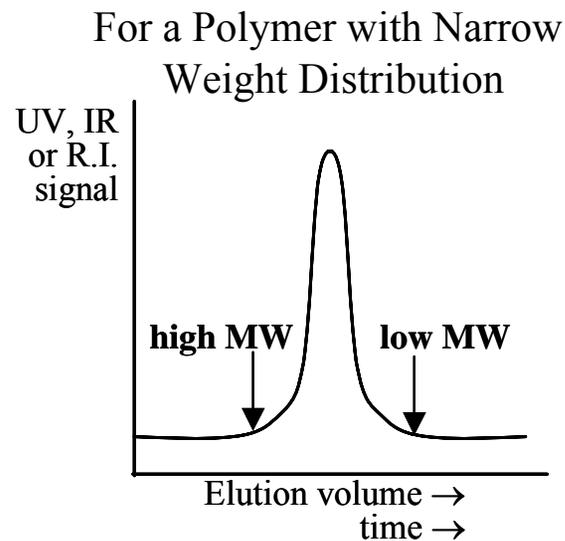
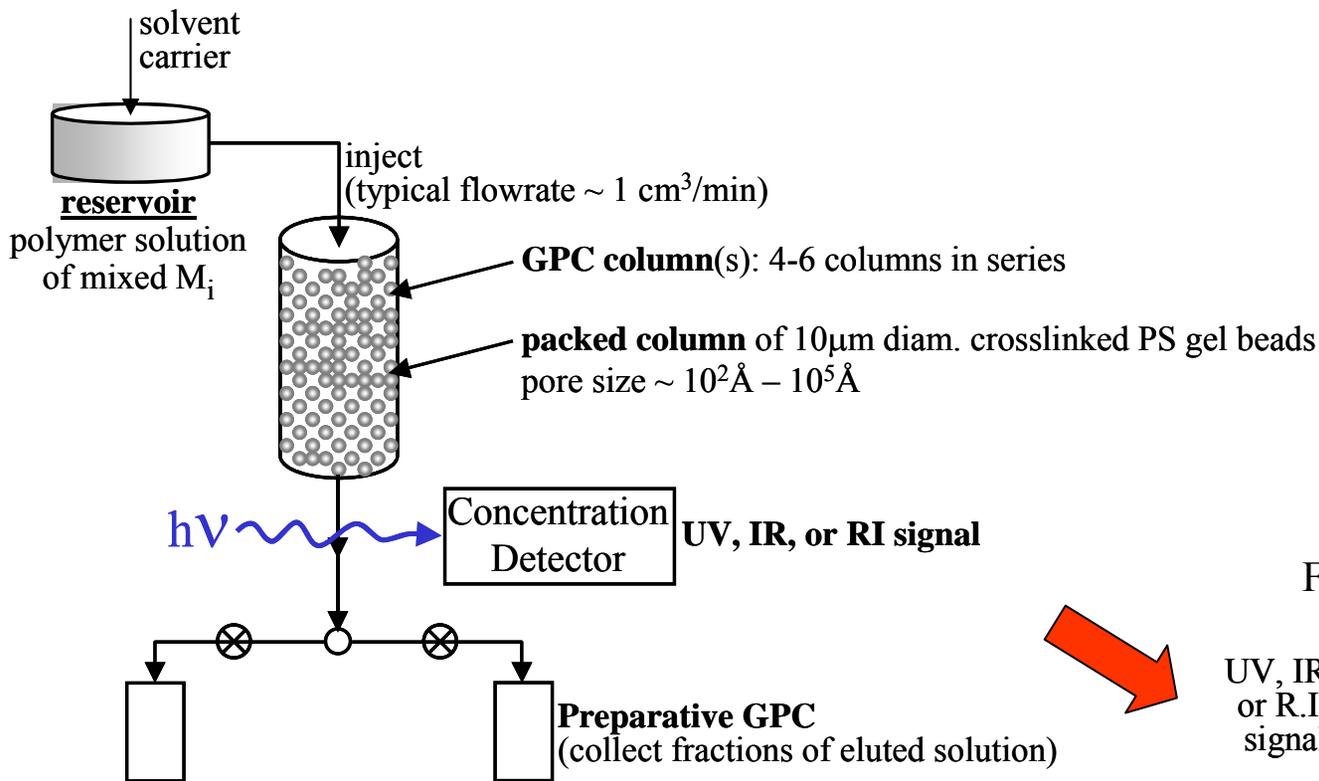
Schematic of SEC Separation Process



Principles behind SEC involves...

- Competition between 2 types of entropy
 1. ΔS_{mix} favorable entropy of mixing of polymer and solvent inside pores.
 2. ΔS_{conf} unfavorable loss of conformation entropy of large size polymers (high MW) when entering smaller pores in the gel (column packed with swollen Xlinked PS beads).
- The interplay of both types of entropies results in substantially different *residence times* in the column for the different polymer molar masses.
 1. Mixing entropy gain drives smaller chains to enter and diffuse throughout entire gel
 2. Intermediate size chains access a portion (the larger pores) of the pore volume in the gel
 3. Conformational entropy loss prevents larger chains from entering the gel
- GPC is *not* an absolute method so it is necessary to calibrate the MW vs. elution volume curve using known narrow fraction samples of the same polymer in the same solvent at the same temperature. Normally researchers employ PS in THF at 23°C for PS-based calibration. Thus samples are referred to as eg “60,000 g/mol on a PS-basis,” meaning that the particular sample exited the column at an elution volume corresponding to a 60,000 g/mol PS sample going through the same column using THF at 23°C (a good solvent) as the carrier medium.

A Simple GPC Chromatograph



SEC cont'd

- The volume eluted V_e consists of 2 parts:

External to the Beads: “Void” Volume V_o (outside volume)

Internal to the Beads: Pore Volume V_i (inside volume)

- Depending on the size of the molecule passing through the column all or only a portion of the total volume is visited/explored (called pore permeation) by the diffusing molecules.

pure solvent eluted volume

$$V_{es} = V_o + V_i$$

polymer solution eluted volume

$$V_{ep} = V_o + V_i K_{se}$$

- where K_{se} is the *size exclusion equilibrium constant*.

$$K_{se}(x_2) \equiv \frac{\text{polymer concentration inside bead}}{\text{polymer concentration outside bead}} = \frac{c_{2i}(x_2)}{c_{2o}(x_2)}$$

$K_{se} = 1$ for $x_1 = 1$ solvent, i.e. no exclusion

$K_{se} = f(x_2) < 1$ for $x_2 > x_1$ $K_{se} \rightarrow 0$, ie total exclusion from pores for $x_2 \rightarrow \infty$

$\Delta G_{pp} = G_o - G_i$ change in Gibbs free energy for pore permeation by polymer

- Solvent and column material are chosen such ΔH_{pp} of the polymer is = 0

$$\Delta G_{pp} = -T\Delta S_{pp} = -RT \ln K_{se}$$

ΔS_{pp} is the change in entropy for pore permeation. This depends mainly on the relative sizes of the polymer chain and the pore. solving $K_{se} = e^{\Delta S/R}$

SEC cont'd

Furthermore, we can approximate:

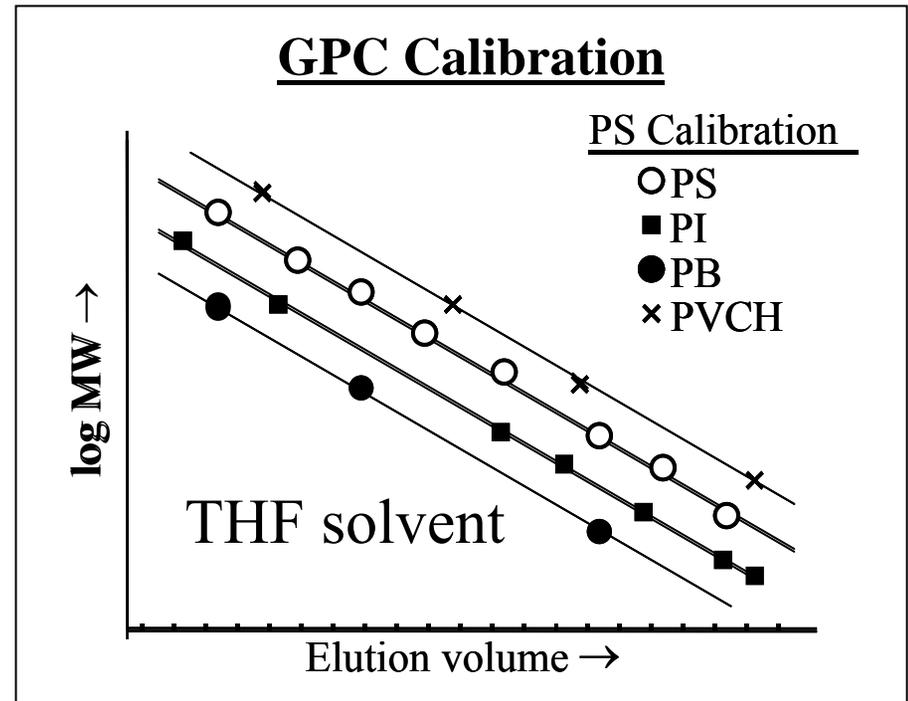
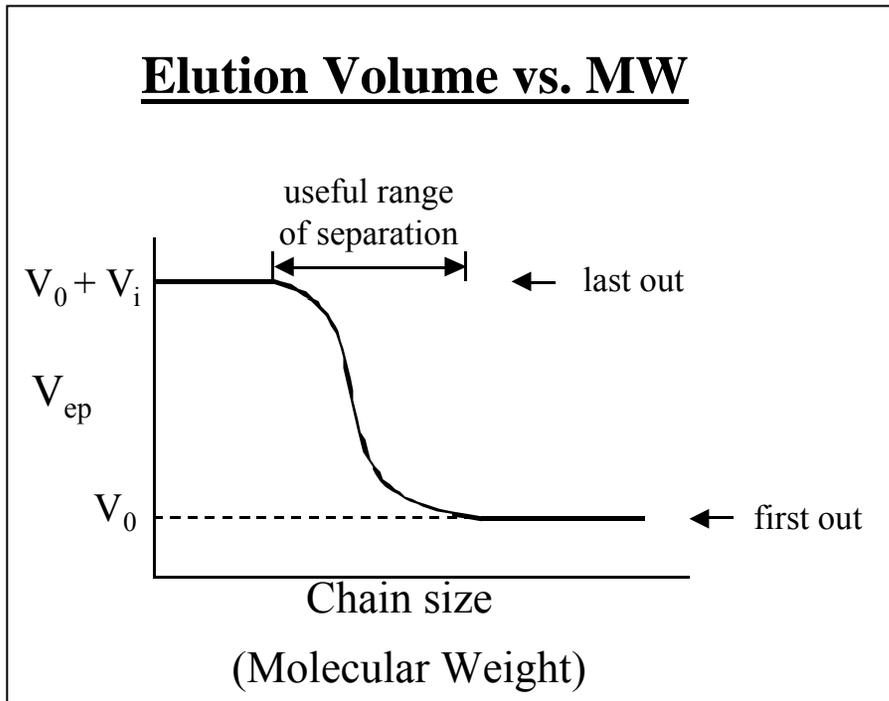
$$\Delta S_{pp} = -R \left[\left(\frac{\text{pore surface area}}{\text{volume of pore}} \right) (\text{diameter of chain}) \right]$$

$$V_{ep} = V_o + V_i K_{se}$$

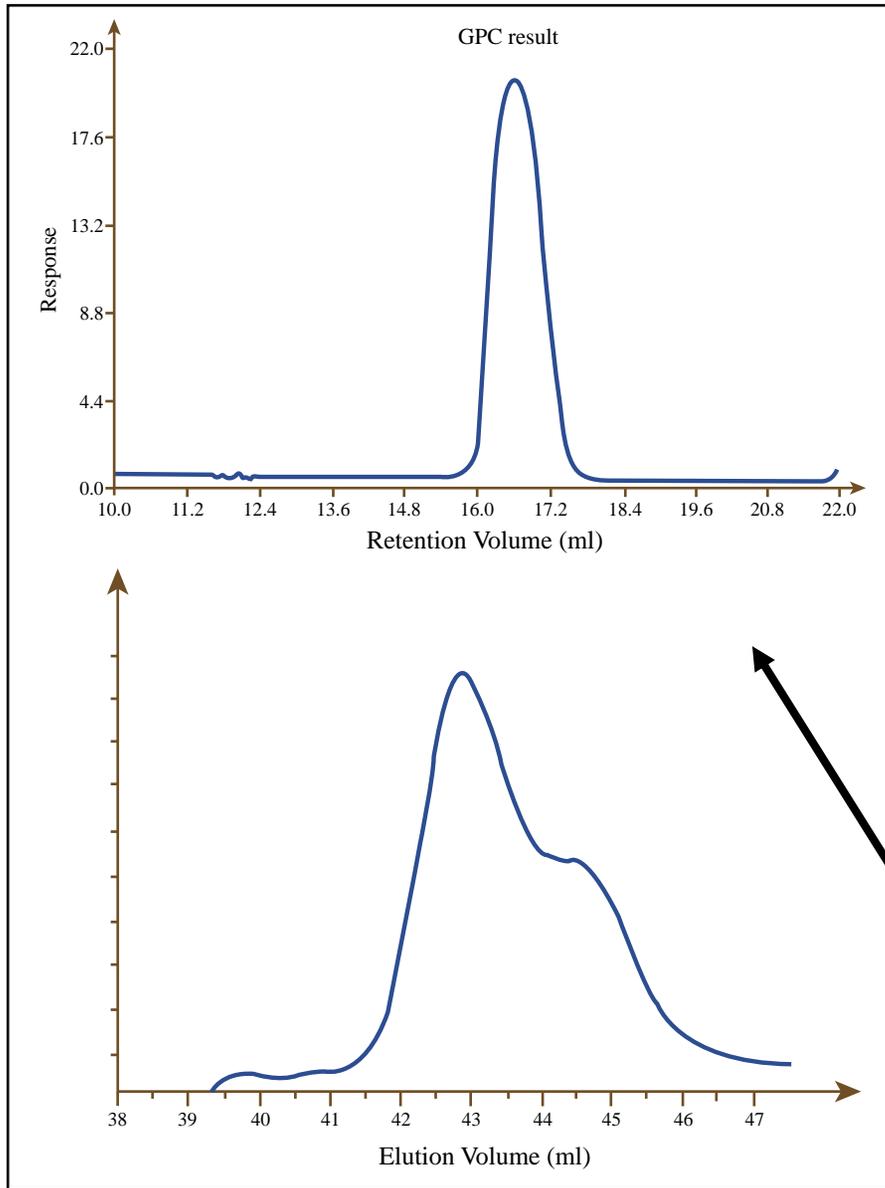
$$V_{ep} = V_o + V_i e^{-\left(A_s \langle r^2 \rangle^{1/2} \right)}$$

here V_{ep} is the elution volume of the polymer and A_s is the pore S/V ratio

A_s depends on the pore/column and $\langle r^2 \rangle^{1/2}$ depends on solvent, T and the MW of that polymer chain entering the pore



Detector Sensitivity/Selectivity: An Example



Polydispersity Index (PDI)

$$PDI = \frac{M_w}{M_n}$$

2 Column GPC
PDI = 1.12, apparently
a nice sample...

6 Column GPC (high resolution)

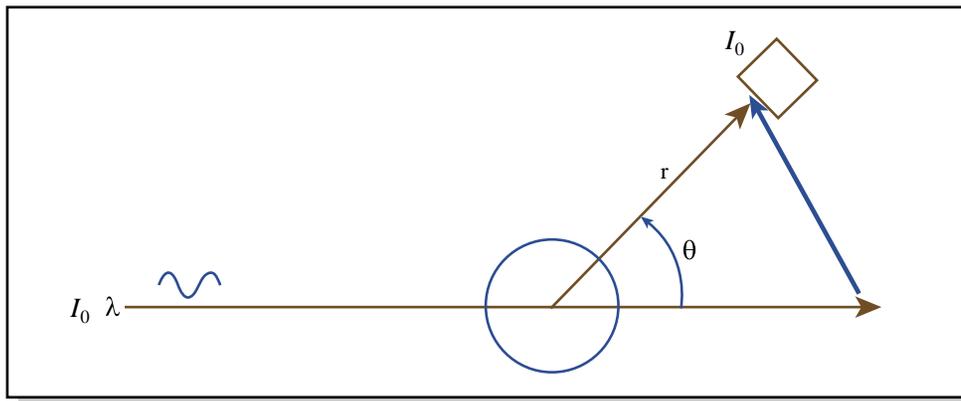
PDI >> 1.12!!

[The Truth hurts!!]

Note very different elution volume values

Scattering of Radiation: Dilute Polymer Solution

- \overline{M}_w , $A_2(\chi)$ and $\langle R_g^2 \rangle$ (Zimm plot)
- SALS (small angle light scattering)
SAXS (small angle X-ray scattering)
SANS (small angle neutron scattering)



$$q = \frac{4\pi}{\lambda/n_o} \sin \theta/2$$

Figure by MIT OCW.

Scattering Intensity from a Solution of Polymer Chains in Solvent

- Geometry of apparatus: sample detector distance r , scattering angle θ
- Optical constants and material properties:
 λ , $n(\text{or } \alpha)$, dn/dc_2
- Thermodynamics of polymer-solvent system: c_2 , \overline{M}_w and $A_2(\text{chi})$

Basic Scattering Equation

$$\frac{Kc_2}{\Delta R(\theta)} = \frac{1}{P(\theta)} \left[\frac{1}{M_w} + 2A_2c_2 + \dots \right]$$

We will derive this. Note the nice set of variables...that we would like to be able to determine

K = optical constants

c_2 = polymer concentration

$P(\theta)$ = particle scattering factor, known for various particle geometries

$$A_2 = \frac{\left(\frac{1}{2} - \chi \right)}{\rho_2^2 V_1} = 2^{\text{nd}} \text{ virial coefficient}$$

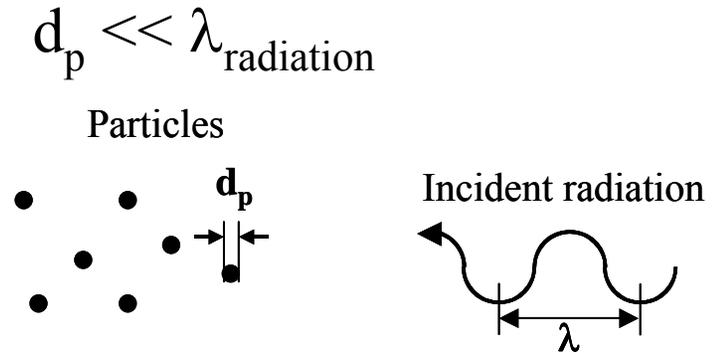
$\Delta R(\theta)$ = excess Raleigh ratio = $R_{\text{solution}} - R_{\text{solvent}} \sim$ excess scattering intensity

Scattering arises from...		
Light	$(\Delta\alpha)^2$	polarizability fluctuations
X-ray	$(\Delta\rho)^2$	electron density variations
Neutron	$(\Delta b)^2$	neutron scattering length variation

Scattering I: from Density Fluctuations

A dilute gas in vacuum

- Consider small particles:
 - (situation: ~ point scatterers)



- Scattered Intensity at scattering angle θ to a detector r away from sample:

$$I_{\theta} = \frac{I_0 8\pi^4 (1 + \cos^2 \theta)}{\lambda^4 r^2} \alpha^2$$

α = polarizability of molecule

I_0 = incident beam intensity

- For N particles in total volume V (assume dilute, so no coherent scattering)

$$I'_{\theta} = \frac{N}{V} I_{\theta} \quad \epsilon = 1 + 4\pi \left(\frac{N}{V} \right) \alpha$$

ϵ = dielectric constant

$\epsilon = n^2$, $\epsilon(\omega)$ = frequency dependent

Fundamental relationship: index of refraction \longleftrightarrow polarizability

$$n = \sqrt{1 + 4\pi \frac{N}{V} \alpha}$$

Can approximate

$$n_{\text{gas}} \cong 1 + \frac{dn}{dc} c$$

$\frac{dn}{dc}$ = refractive index increment

c = conc. of particles per unit volume

$$n_{\text{gas}}^2 = \left(1 + \frac{dn}{dc} c\right)^2 \cong 1 + 2\left(\frac{dn}{dc}\right) c + \dots$$

Solving gives
the polarizability

$$\alpha = \frac{1}{2\pi} \frac{(dn/dc) c}{(N/V)}$$

So by analogy for a polymer-solvent solution:

$$n \cong n_0 + \frac{dn}{dc_2} c_2 \qquad n^2 \cong n_0^2 + 2n_0 \frac{dn}{dc_2} c_2$$

Rayleigh and Molecular Weight of Gases

$$I'_\theta = \left(\frac{N}{V}\right) \frac{8\pi^2 (1 + \cos^2 \theta)}{\lambda^4 r^2} \left(\frac{(dn/dc)c}{2\pi(N/V)}\right)^2$$

simplifying $I'_\theta = \frac{I_0 2\pi^2 (1 + \cos^2 \theta)}{\lambda^4 r^2 (N/V)} \left(\frac{dn}{dc}\right)^2 c^2$ and since $\frac{N}{V} = \frac{c}{M/N_{AV}}$

This expression contains several parameters dependent on scattering geometry, so we define

Rayleigh Ratio, R as

$$R = \frac{I'_\theta}{I_0 (1 + \cos^2 \theta) / r^2}$$

which equals

$$R = \frac{2\pi^2 \left(\frac{dn}{dc}\right)^2 M c}{\lambda^4 N_{AV}}$$

Or just

$$R = K \cdot M \cdot c$$

Where K is a lumped optical constant

$$K \equiv \frac{2\pi^2 \left(\frac{dn}{dc}\right)^2}{\lambda^4 N_{AV}}$$

Note, for polymer-solvent solution:

$$K \equiv \frac{2\pi^2 n_0^2 \left(\frac{dn}{dc_2}\right)^2}{\lambda^4 N_{AV}}$$

**Rayleigh measured the molecular weight of gas molecules
using light scattering!**