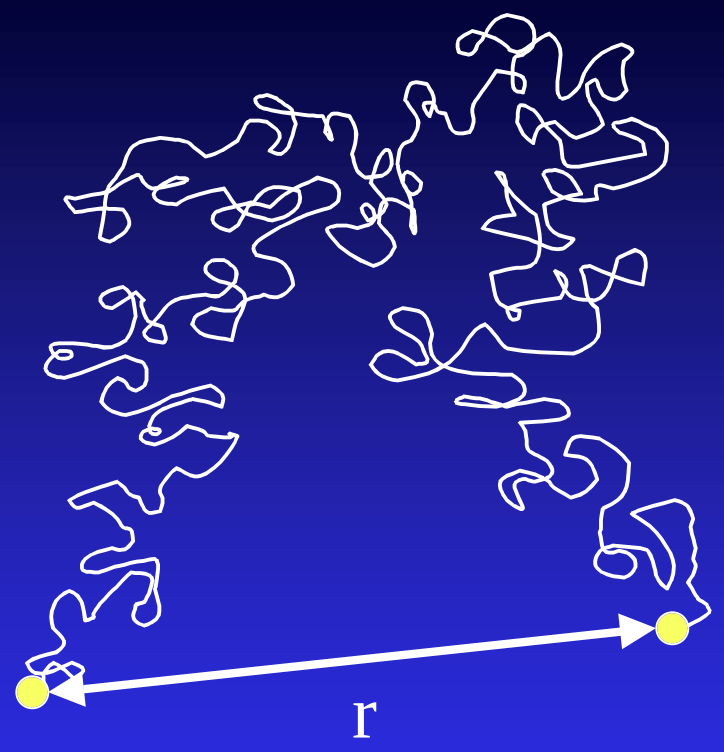
Chemical Engineering 160/260
Polymer Science and Engineering

Lecture 5 - Indirect Measures of Molecular Weight: Intrinsic Viscosity and Gel Permeation Chromatography

January 26, 2001

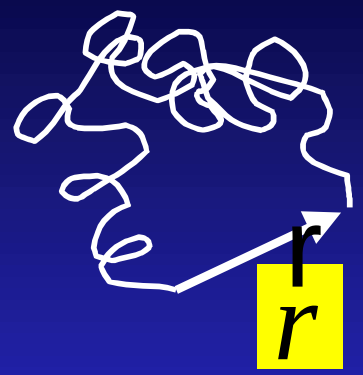
End-to-end Distance of a Random Coil



In general, we will express the end-to-end distance in terms of the root-mean-square statistical average.

$$\langle r^2 \rangle^{1/2}$$

Freely Jointed Model Polymer Chain: Mean-squared End-to-end Distance



$$\vec{r} = \sum_{i=1}^{n} \vec{l}_i$$

Vector sum

$$r^2 = \vec{r} \bullet \vec{r} = \sum_{i,j} \vec{l}_i \bullet \vec{l}_j = \sum_i l_i^2 + 2 \sum_{0<i<j\le n} \vec{l}_i \bullet \vec{l}_j$$

Average over all configurations.

$$\langle r^2 \rangle = \sum_i \langle l_i^2 \rangle + 2 \sum_{0<i<j\le n} \langle \vec{l}_i \bullet \vec{l}_j \rangle$$

$$\langle r^2 \rangle = nl^2 + 2 \sum_{i<j} \langle \vec{l}_i \bullet \vec{l}_j \rangle = nl^2$$

There is no bond correlation.

Outline

- Definitions
- Equivalent sphere and Einstein relationship
- Effect of concentration
- Mark-Houwink-Sakurada equation
- Gel permeation chromatography
- Molecular weight summary

Definitions

Relative viscosity

$$\eta_{rel} = \frac{\eta(solution)}{\eta_o(solvent)} = \frac{t(solution)}{t_o(solvent)}$$

Specific viscosity

$$\eta_{sp} = \frac{\eta(solution) - \eta_o(solvent)}{\eta_o(solvent)} = \eta_{rel} - 1$$

Reduced viscosity

$$\eta_{red} = \frac{\eta_{sp}}{c}$$

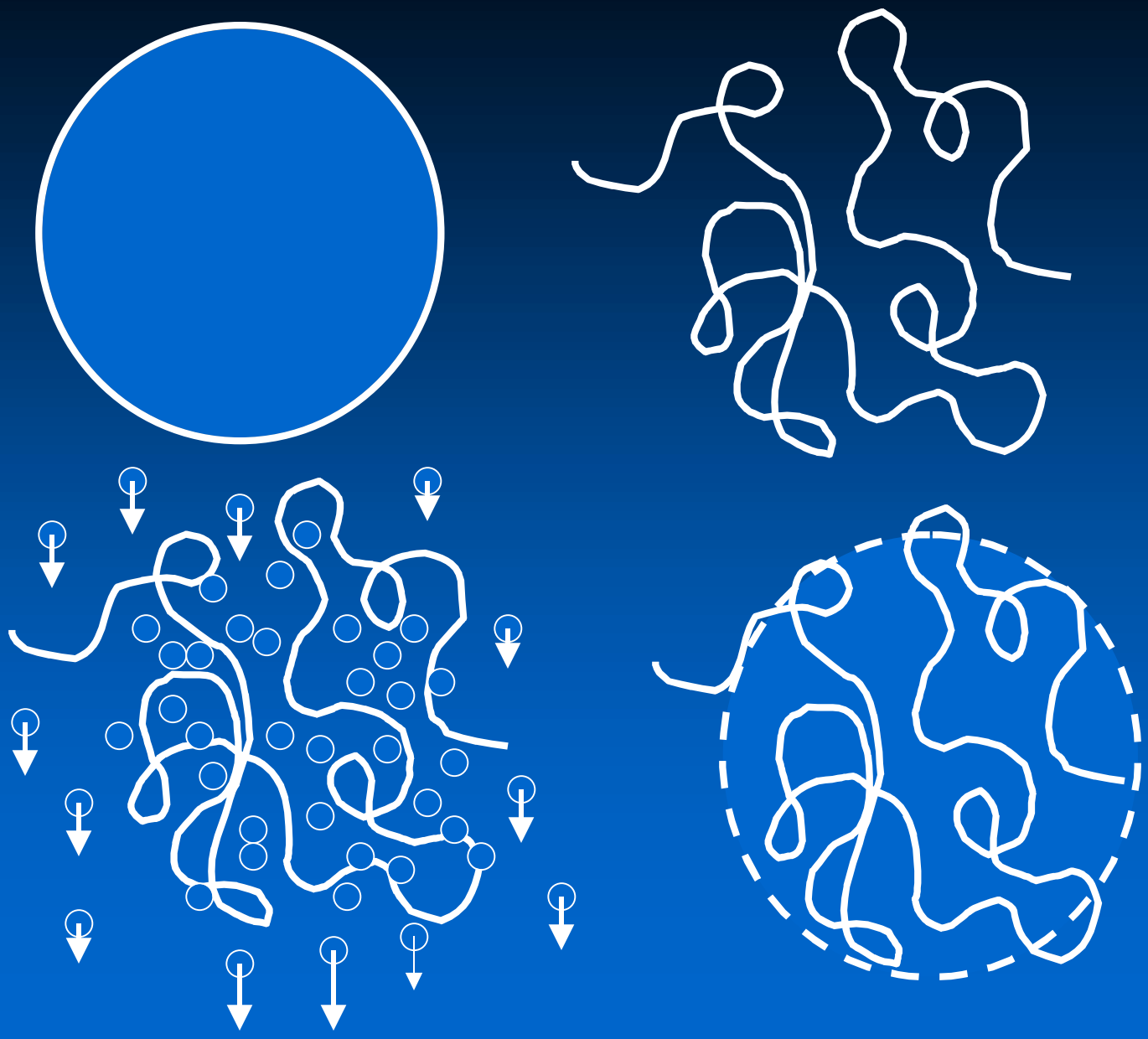
Inherent viscosity

$$\eta_{inh} = \frac{\ln \eta_{rel}}{c}$$

Intrinsic viscosity

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

Equivalent Sphere



Einstein Relationship

For a **suspension** containing volume fraction ϕ of suspended material with shape factor ω, Einstein found that

$$\eta = \eta_o\left[1 + \omega\phi\right]$$

where η is the viscosity of the suspension and η_o is the viscosity of the suspending fluid. For a **sphere or random coil, ω = 2.5**.

If the polymer is treated as an **equivalent hydrodynamic sphere** with volume V_e and radius R_e we obtain

$$\eta_{sp} = 2.5\left(\frac{n_p}{V}\right)V_e \qquad \frac{n_p}{V} = \frac{cN_A}{M_v} \qquad V_e = \left(\frac{4\pi}{3}\right)R_e^3$$

$$\left[\frac{\eta_{sp}}{c}\right]_{c=0} \equiv [\eta] = \frac{2.5N_A V_e}{M_v}$$

Excluded Volume

That portion of the solution volume that is inaccessible to polymer chain segments due to prior occupancy by other chain segments is known as the **excluded volume**.

As a consequence of the volume exclusion, the overall spatial dimensions of a real polymer chain must **increase** relative to those predicted by the simple chain models.

One can **compensate** for chain expansion due to excluded volume through placing the polymer in a **poor solvent** such that interactions between polymer segments and solvent molecules are **thermodynamically unfavorable**. Such a solvent, at a given temperature, is a **theta solvent**.

Excluded Volume of a Flexible Chain

$$\langle r^2 \rangle = \alpha^2 \langle r^2 \rangle_o$$

α = expansion factor

For large α, $\alpha \propto M^{0.10}$

Effect of solvent on chain dimensions:

- Good solvent - chain expansion
- Poor solvent - chain contraction
- Theta solvent - chain contraction exactly compensates for excluded volume effect

$$\langle r^2 \rangle = \langle r^2 \rangle_o$$

$$\alpha = 1$$

$A_2 = 0$ for theta solvent

Expansion Factor

$$\frac{V_e}{\overline{M}_v} = \frac{4\pi}{3}\frac{R_e^3}{\overline{M}_v} = \frac{4\pi}{3}\left(\frac{R_e^2}{\overline{M}_v}\right)^{3/2} M_v^{1/2}$$

~ constant

Define an **expansion factor** for a coil in a **good solvent** compared to a theta solvent.

$$R_e = R_{eo}\alpha$$

$$[\eta] = 2.5\left(\frac{4\pi}{3}\right) N_A \left(\frac{R_{eo}^2}{\overline{M}_v}\right)^{3/2} \overline{M}_v^{1/2}\alpha^3$$

$$\alpha^3 = \frac{[\eta]}{[\eta]_\Theta}$$

Interrelationships Among Parameters

For **dilute** solutions,

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

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

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 k_K = 0.05 +/- 0.05

Intrinsic Viscosity and Molecular Weight

An empirical relationship that works well for correlating **intrinsic viscosities** and molecular weights of fractionated samples is the **Mark-Houwink-Sakurada equation**.

$$[\eta]_i = KM_i^a$$

For a sample at **infinite dilution**,

$$(\eta_{sp})_i = [\eta]_i c_i + k_H [\eta]_i^2 c_i^2 \cong [\eta]_i c_i = KM_i^a c_i$$

For the unfractionated solution,

$$\eta_{sp} = K \sum_i M_i^a c_i$$

Intrinsic Viscosity and Molecular Weight

The observed **intrinsic viscosity** may be obtained from

$$[\eta] = \lim(c \rightarrow 0)\left[\frac{\eta_{sp}}{c}\right] = K\sum_i M_i^a\left(\frac{c_i}{c}\right)$$

Since $\frac{c_i}{c} = \frac{c_i}{\sum_i c_i}$ the weight ratio is $\frac{w_i}{w} = \frac{w_i}{\sum_i w_i}$

and $$[\eta] = \frac{K\sum_i w_i M_i^a}{\sum_i w_i} = K\sum_i W_i M_i^a$$

Viscosity Average Molecular Weight

Define the **viscosity average molecular weight** by

$$\overline{M}_v \equiv \left(\sum_i W_i M_i^a \right)^{1/a}$$

The intrinsic viscosity then is related to molecular weight by

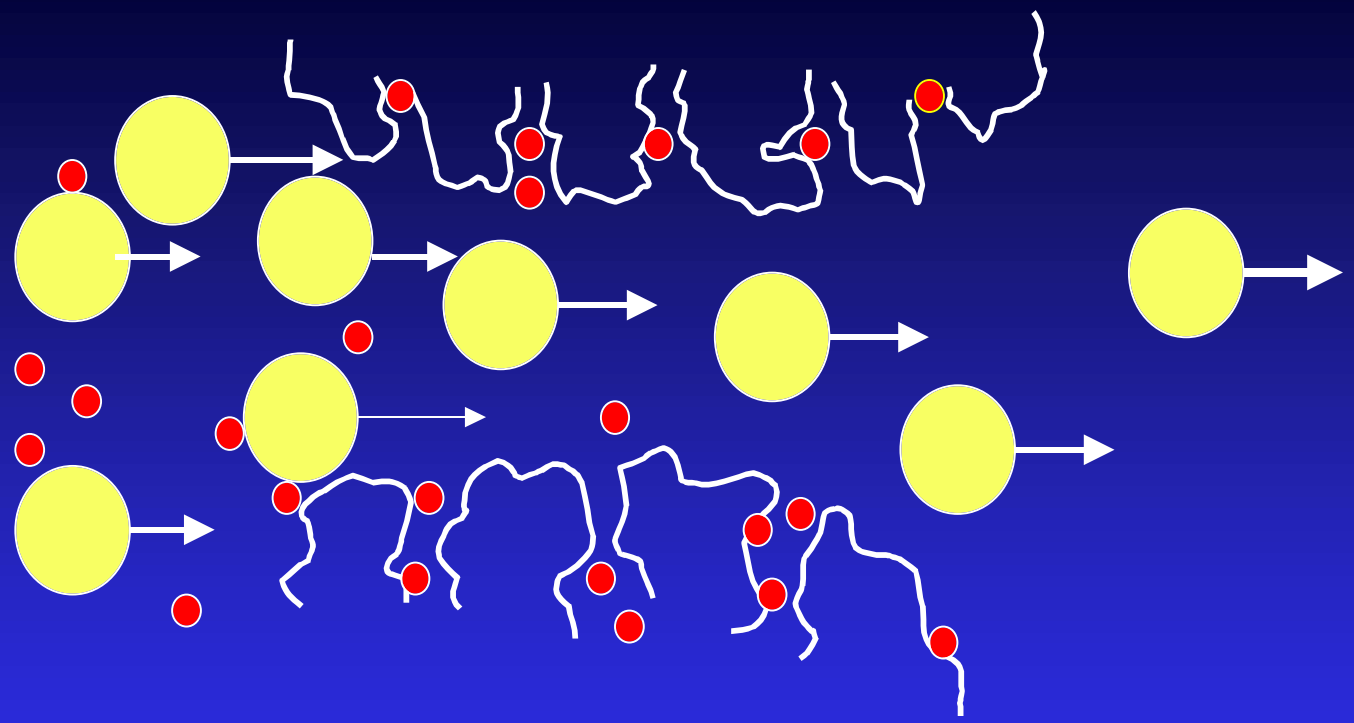
$$[\eta] = K \overline{M}_v^a$$

Typically, **0.5 < a < 0.8 for flexible polymers**, with **a = 0.5 for theta conditions** and increasing with increasing solvent quality. Also, a = 1 for semicoils and a = 2 for rigid rods.

Mark-Houwink-Sakurada Parameters

Polymer	Solvent	Temp.	Mol. Wt.	100K	a
PMMA	chloroform	25 C	80,000-1,400,000	0.48	0.80
	methyl ethyl ketone	25 C	80,000-1,400,000	0.68	0.72
	acetone	25 C	80,000-1,400,000	0.75	0.70
PS	benzene	20 C	1,200-140,000	1.23	0.72
	toluene	20-30 C	20,000-2,000,000	1.05	0.72
	methyl ethyl ketone	20-40 C	8,000-4,000,000	3.82	0.58

Gel Permeation Chromatography



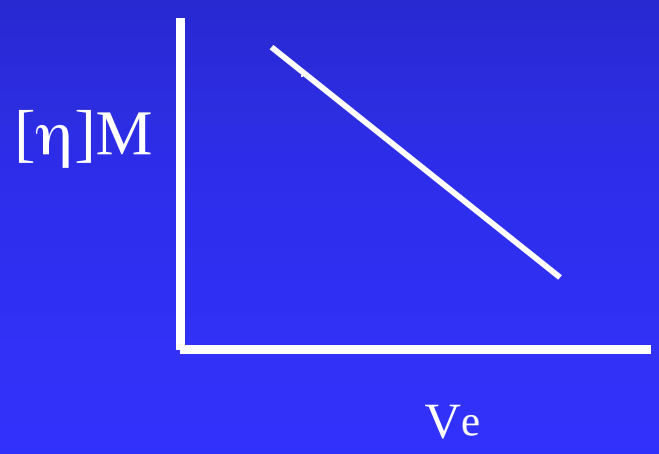
A mixture of different size solute molecules is eluted through a column of porous particles. Larger molecules are swept through unhindered, while small molecules are retarded in the pores.

GPC Calibration

The relationship between intrinsic viscosity and hydrodynamic volume is the basis for a “universal” calibration procedure.

$$\left[\frac{\eta_{sp}}{c}\right]_{c=0} \equiv [\eta] = \frac{2.5 N_A V_e}{M}$$

$$\ln([\eta]M) = \ln(2.5 N_A) + \ln[\lim(c \rightarrow 0) V_e]$$



GPC Calibration

Use the Mark-Houwink-Sakurada relation

$$[\eta]_i M_i = K_i M_i^{a_i+1}$$

For equal elution volumes of two different polymers,

$$[\eta]_1 M_1 = K_1 M_1^{a_1+1} = [\eta]_2 M_2 = K_2 M_2^{a_2+1}$$

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

Molecular Weight Summary: Averages

$$\overline{M}_n = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

$$\overline{M}_n = \frac{\sum_i c_i}{\sum_i \frac{c_i}{M_i}} = \frac{1}{\sum_i \frac{w_i}{M_i}}$$

$$\overline{M}_w = \frac{\sum_i c_i M_i}{\sum_i c_i} = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

$$\overline{M}_z = \frac{\sum_i n_i M_i^3}{\sum_i n_i M_i^2}$$

$$\overline{M}_v \equiv \left(\sum_i W_i M_i^a\right)^{1/a}$$

$$\overline{M}_z > \overline{M}_w > \overline{M}_v > \overline{M}_n$$

Molecular Weight Summary: "Most Probable" Distribution

$$N_x = p^{x-1}(1-p)$$

$$W_x = xp^{x-1}(1-p)^2$$

$$\bar{x}_n = \sum_x xp^{x-1}(1-p) = \frac{1}{1-p}$$

$$\bar{x}_w = \sum_x x^2 p^{x-1}(1-p)^2 = \frac{1+p}{1-p}$$

$$\frac{\bar{x}_w}{\bar{x}_n} = \frac{\overline{M}_w}{\overline{M}_n} = 1 + p \rightarrow 2$$

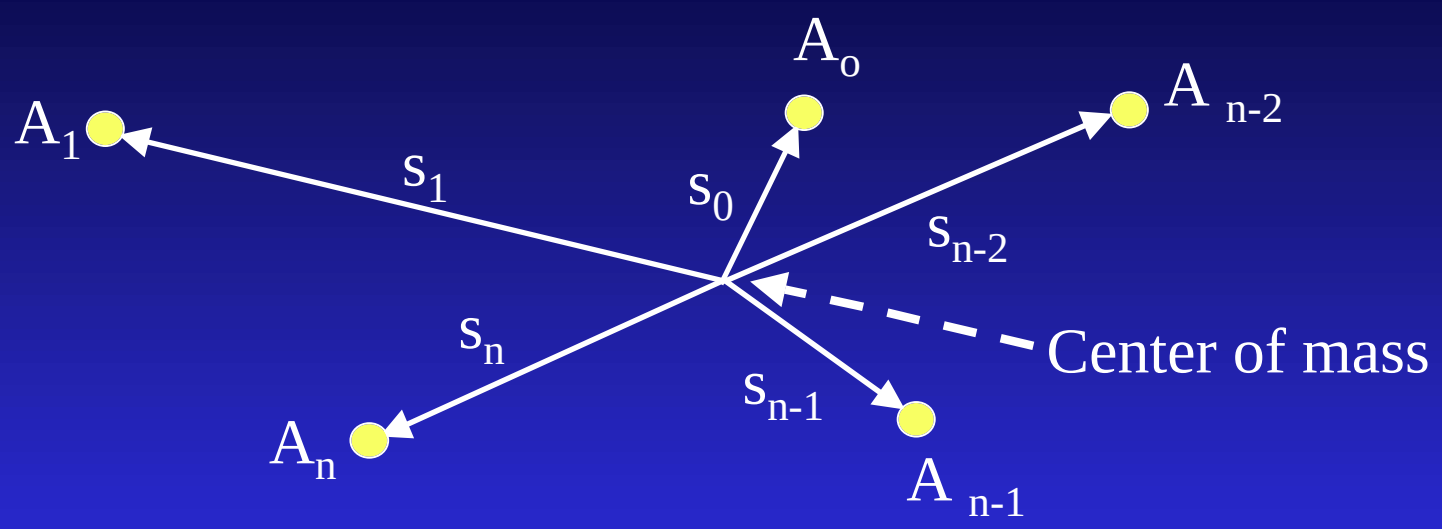
Molecular Weight Summary: Osmometry

$$\lim(c \rightarrow 0)\left[\frac{\pi}{c}\right] = \frac{RT}{\overline{M}_n}$$

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

Under **theta conditions, $A_2 = 0$**. For a particular polymer, the temperature at which this occurs depends on the solvent.

Mean-squared Radius of Gyration



$$s^2 = \frac{\sum_0^n m_i s_i^2}{\sum_0^n m_i} = \frac{m\sum_0^n s_i^2}{m(n+1)} = \frac{1}{n+1}\sum_0^n s_i^2$$

$$\langle s^2 \rangle^{1/2} \equiv R_g$$

Molecular Weight Summary: Light Scattering

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

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

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

$$\left[\frac{Hc}{R(\theta)}\right]_{\theta=0} = \frac{1}{\overline{M}_w} + 2A_2 c$$

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

Molecular Weight Summary: Intrinsic Viscosity

$$\eta_{sp} = \frac{\eta(solution) - \eta_o(solvent)}{\eta_o(solvent)} = \eta_{rel} - 1$$

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

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

Molecular Weight Summary: Gel Permeation Chromatography

$$\left[\frac{\eta_{sp}}{c}\right]_{c=0} \equiv [\eta] = \frac{2.5 N_A V_e}{M}$$