Light Scattering

$$\frac{Kc_2}{\Delta R(\theta)} = \frac{1}{P(\theta)}\left[\frac{1}{\overline{\overline{M}}_w} + 2A_2c_2 + ...\right]$$

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

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

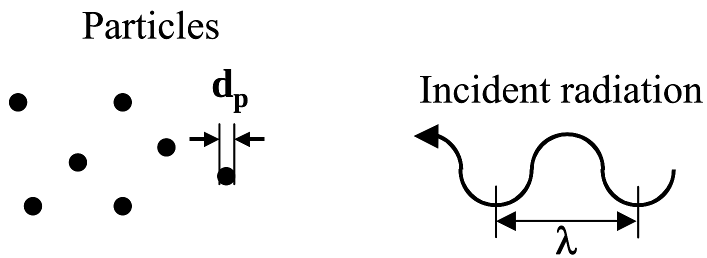
$\Delta R(\theta)$ = excess Raleigh ratio = $R_{solution} - R_{solvent}$ ~ excess scattering intensity

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 arises from Density Fluctuations

A dilute gas in vacuum

- Consider small particles: $d_p << \lambda_{radiation}$
  - (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)

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

ε = dielectric constant

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

Fundamental relationship: index of refraction ⟷ polarizability

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

Can approximate

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

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

c = conc. of particles per unit volume

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

Solving gives the polarizability

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

So by analogy for a polymer-solvent solution:

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

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

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

$$R = K\bullet M\bullet c$$

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:

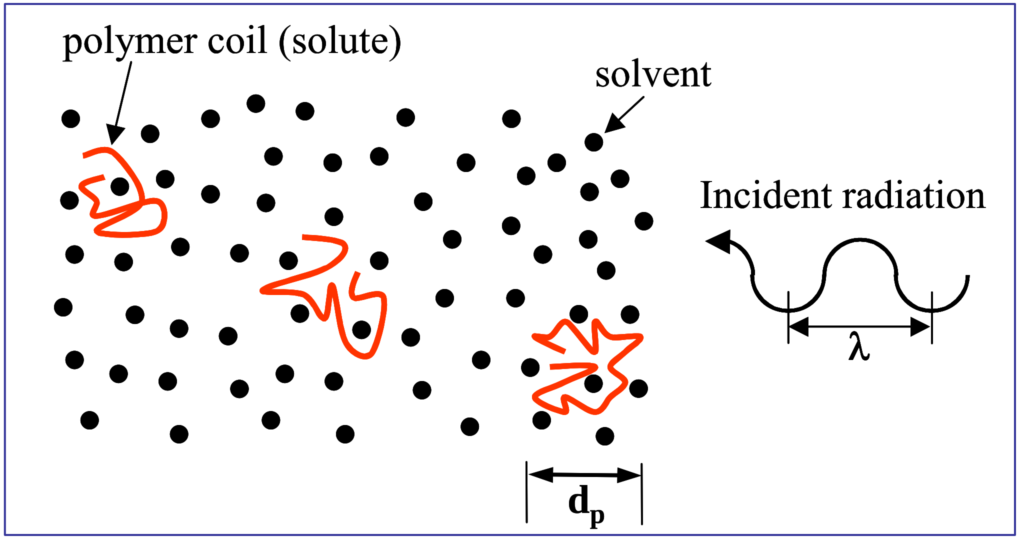
$$K \equiv \frac{2\pi^2 n_0^2\left(\frac{dn}{dc_2}\right)^2}{\lambda^4 N_{AV}}$$

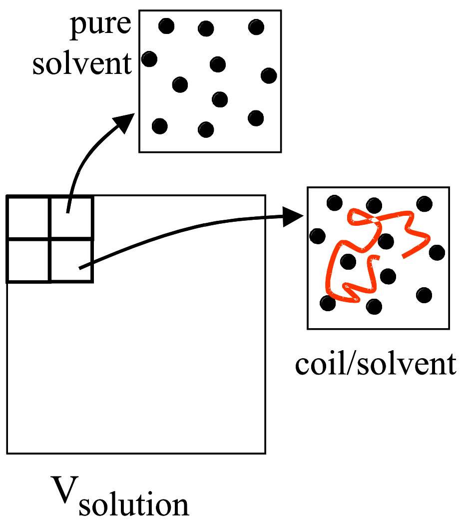
Rayleigh measured the molecular weight of gas molecules using light scattering!

Scattering from Fluctuations II

Debye: Re-identify fluctuations as chains in a solvent and extend Rayleigh's idea to polymers in solution

A dilute "gas" of polymer chains in solution





Now for polymer coils: $\lambda \sim d_p$

Recognize 4 features in a binary component system:

1. Each cell has on average, the same number of solvent molecules but there are variations. Fluctuations in solvent density will give rise to some (weak) scattering (subtract off pure solvent scattering).
2. Fluctuations in the number of solute molecules (chains) will give rise to significant scattering
3. Fluctuations in the concentration of solute create osmotic forces
4. Polymer chains are large and cannot treat them as point scatterers

   $P(\theta) \neq 1$

The Features of Excess Scattering

- Feature 1.

  Define $\Delta R = R_{solution} - R_{pure\ solvent}$ = "Excess Rayleigh Ratio"
- Feature 2.

  Remaining scattering arises from fluctuations in solute concentration

$$I'_\theta = \frac{I_0 2\pi^2 (1+\cos^2\theta)}{\lambda^4 r^2 (N/V)} \left(\frac{dn}{dc}\right)^2 c^2 \qquad \Delta R \text{ depends on } \left(\frac{dn}{dc_2}\right)^2 \text{ and } \left\langle (\delta c_2)^2 \right\rangle$$

Einstein-Smoluchowski mean squared concentration fluctuation per unit vol.

$$\left\langle (\delta c_2)^2 \right\rangle = \frac{RTc_2}{\delta V N_{AV} (\partial\pi / \partial c_2)}$$

- Feature 3.

  A local osmotic pressure will arise due to local concentration differences, this effect acts to suppress solute concentration fluctuations. Note in the gas-vacuum system, such an effect is not present.

$$\frac{\pi}{c_2} = RT\left[\frac{1}{M} + \frac{(\frac{1}{2} - \chi)}{V_1 \rho_2^2} c_2 + \cdots\right]$$

$$\frac{\partial\pi}{\partial c_2} = RT\left[\frac{1}{M} + 2A_2 c_2 + \cdots\right]$$

Feature 3 cont'd

$$R_{solution} - R_{solvent} = \frac{2\pi^2 n_0^2 \left(\frac{dn}{dc_2}\right)^2 c_2}{\lambda^4 N_{AV}\left[\frac{1}{M} + 2A_2c_2 + \cdots\right]}$$

Polymer in solution

$$\Delta R = Kc_2\left[\frac{1}{\left(\frac{1}{M} + 2A_2c_2 + \cdots\right)}\right]$$

Gas in vacuum

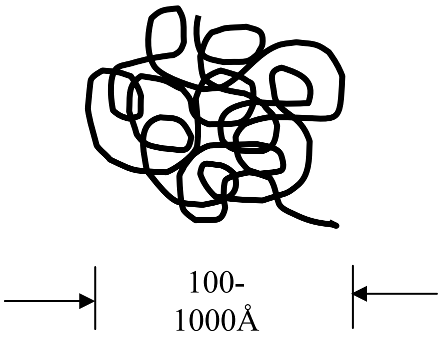
$$R = \frac{2\pi^2 \left(\frac{dn}{dc}\right)^2 M\ c}{\lambda^4\ N_{AV}}$$

ΔR similar to the Rayleigh scattering for gases but with a new term depending A_2

Scattering from Polymer Solutions

- <u>Feature 4.</u>

  Polymer chains are large and can not be assumed as point scatterers for visible light



- λ ~ 6,328Å He-Ne laser
- Coil size ~ typically 100-1000 Å

  depending on molecular weight of polymer
  Therefore need to consider self-interference
  of monomers in polymer coil on scattered intensity

- Therefore P(θ) term is important

Scattering of Polymer Solutions

Introduce finite size chain scattering factor P(θ)

$$\Delta R = Kc_2 \frac{1}{\left(\frac{1}{\overline{M}_w} + 2A_2 c_2 + \cdots\right)} P(\theta)$$

For a Gaussian coil $P(\theta) \equiv \frac{2}{u^2}\left(u - 1 + e^{-u}\right)$ (Debye, 1939)

where $u = \left[\frac{4\pi n_0}{\lambda} \sin\left(\frac{\theta}{2}\right)\right]^2 \langle R_g{}^2 \rangle$

q = scattering vector, $u = q^2 \langle R_g{}^2 \rangle$

In the limit of very small θ, P(θ => 0) = 1

Useful approximation for small, nonzero θ

$$P(\theta) \approx 1 - \frac{u}{3} \quad \text{and} \quad \frac{1}{P(\theta)} \approx 1 + \frac{u}{3} \quad \textit{for} \;\; u^{1/2} << 1$$

Scattering in a Polymer-Solvent System

- In general, $P(\theta) \neq 1,\ c_2 \neq 0,\ A_2 \neq 0$

therefore rewrite excess Rayleigh ratio as

$$\frac{\mathrm{Kc_2}}{\Delta \mathrm{R}} = \left[\frac{1}{\mathrm{M}} + 2\mathrm{A_2 c_2} + \cdots\right]\left[1 + \frac{\mathrm{u}}{3}\right] \qquad u = q^2 \langle R_g{}^2 \rangle$$

$$\frac{Kc_2}{\Delta R} = \left[\frac{1}{M} + 2A_2 c_2 + \cdots\right]\left[1 + \frac{16\pi^2 n_0^2}{3\lambda^2} \sin^2\left(\frac{\theta}{2}\right)\langle R_g{}^2 \rangle\right]$$

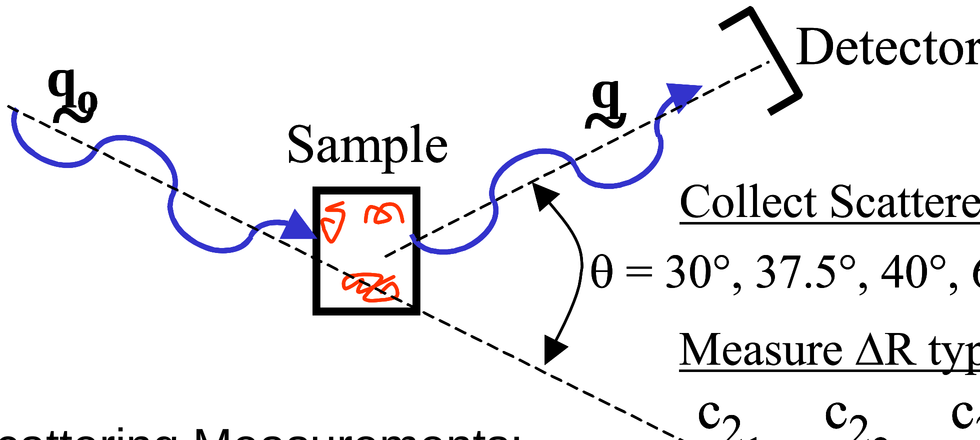
Equation is valid for dilute solutions and scattering angles θ such that

$$\mathrm{u}^{1/2} << 1$$

Next: how to plot scattered intensity vs. c_2 and versus q^2 to extract M and A_2

Zimm Plot – Analysis of Light Scattering Data

Light Scattering Experiment



Collect Scattered Intensity at typically 8 angles:

θ = 30°, 37.5°, 40°, 60°, 75°, 90°, 105°, 120°

Measure ΔR typically for 5 solute concentrations:

c_{2_1} , c_{2_2} , c_{2_3} , c_{2_4} , c_{2_5}

Scattering Measurements:

1. Pure (no dust!) solvent $R_{solvent}$
2. Polymer solutions [$c_{2,i}$, $I(\theta_i)$] $R_{polymer}$
3. Construct Zimm Plot

$$\Delta R = R_{polymer} - R_{solvent}$$

Note: $\dfrac{Kc_2}{\Delta R_\theta}$ is a function of 2 variables, c_2 and θ.

Zimm's cool idea was to plot y(p,q) *vs* (p+q) to separate out dependence on each variable: called ***Zimm plot***

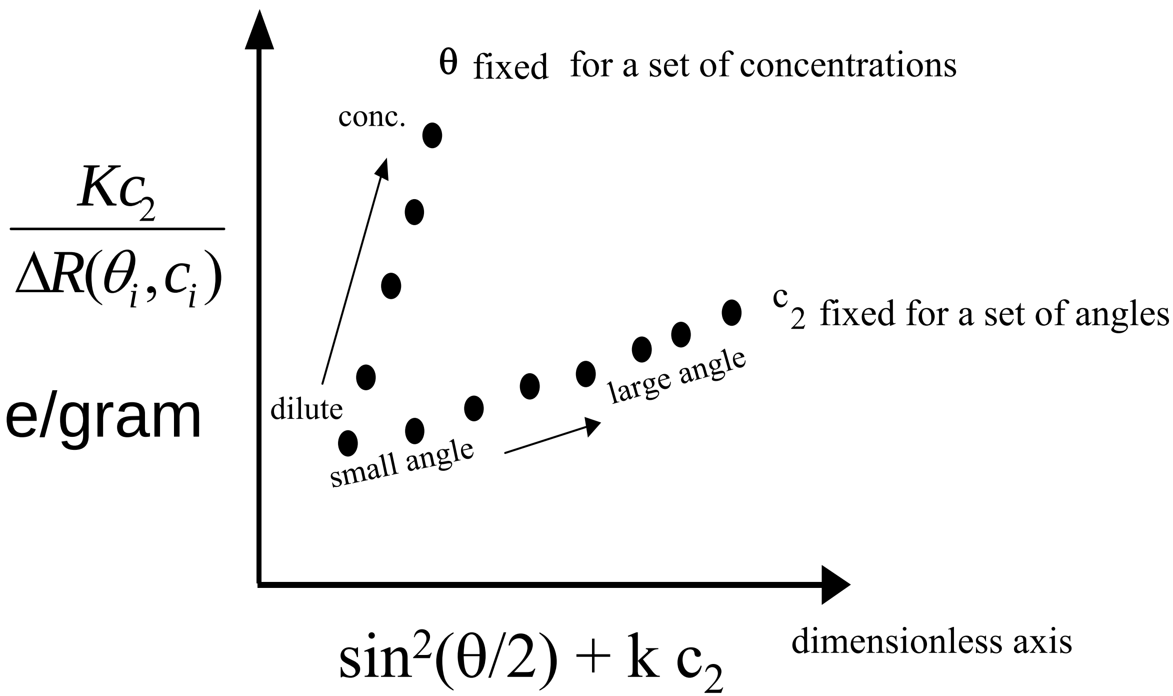
Construction of a Zimm Plot

<u>The Master Equation:</u>

$$\frac{Kc_2}{\Delta R} = \left(\frac{1}{\overline{M}_w} + 2A_2 c_2 + \ldots\right)\left(1 + \frac{16\pi^2 n_0^2 \sin^2\frac{\theta}{2}}{3\lambda^2}\langle R_g^{\,2}\rangle\right)$$

do *double* extrapolation: $\theta \rightarrow 0^o$ A_2 & $\overline{M}_w$

$c_2 \rightarrow 0$ $<R_g^{\,2}>$ & $\overline{M}_w$



Mole/gram

Units

Zimm Plot Sample Data Set

	$\frac{Kc_2}{\Delta R(\theta_i, c_i)}$	θ										
		30°	***37.5°***	***45°***	***60°***	***75°***	***90°***	***105°***	***120°***	***135°***	***142.5°***	***150°***
c_2 g/cm^3	***2×10^{-3}***	3.18	3.26	3.25	3.45	3.56	3.72	3.78	4.01	4.16	4.21	4.22
	1.5×10^{-3}	2.73	2.76	2.81	2.94	3.08	3.27	3.4	3.57	3.72	3.75	3.78
	1×10^{-3}	2.29	2.33	2.37	2.53	2.66	2.85	2.96	3.12	3.29	3.38	3.37
	0.75×10^{-3}	2.10	2.14	2.17	2.32	2.47	2.64	2.79	2.93	3.10	3.21	3.2
	0.5×10^{-3}	1.92	1.95	1.98	2.16	2.33	2.51	2.66	2.79	2.96	3.11	3.12

$$K = \frac{2\pi^2 n_0^{\,2}\left(\frac{dn}{dc}\right)^2}{\lambda^4 N_{AV}}$$

For $c_2 = 0.002$, $\theta = 30$ $\quad \frac{Kc_2}{\Delta R(\theta_i, c_i)} = 3.18$

$$n_0 = 1.5014 \qquad \lambda = 5.461\, x 10^{-5}\, cm$$

$$dn/dc = 0.106\, cm^3 g^{-1} \qquad N_{AV} = 6.02\, x 10^{-23}\, mole^{-1}$$

Plotting the Data

"vertical" data set
θ=30°
c_2 varies (decreases)

Extrapolating to zero concentration

(.267, 3.18)

"horizontal" data sets
θ variable
c_2=2x10^{-3}

$$\frac{Kc_2}{\Delta R_\theta}$$

Image removed due to copyright restrictions.

Please see, for example, http://web.umr.edu/~WLF/MW/orangeline.gif, from http://web.umr.edu/~WLF/MW/Zimm.html

Plot typical data point :

$$\theta = 30°, c_2 = 2\times 10^{-3}\, g/cm^3$$

y-axis: $\frac{Kc_2}{\Delta R_\theta} = 3.18$

x-axis: $\sin^2\left(\frac{30°}{2}\right) + k(2\times 10^{-3})$

$$= 0.067 + 100(2\times 10^{-3}) = 0.267$$

Pick constant to "spread" the plot

These points are determined by extrapolating the equations of each regression line

x = 0.067

Plotting the data cont'd

Extrapolating to zero scattering angle…

(.267, 3.18)

$100c_2$

Image removed due to copyright restrictions.

Please see, for example,
http://web.umr.edu/~WLF/MW/yellowline.gif, from
http://web.umr.edu/~WLF/MW/Zimm.html

Extrapolate the extrapolated data to obtain:

$$\overline{M}_w, \ A_2 \ \ \langle R_g{}^2 \rangle$$

$$\frac{Kc_2}{\Delta R_\theta}$$

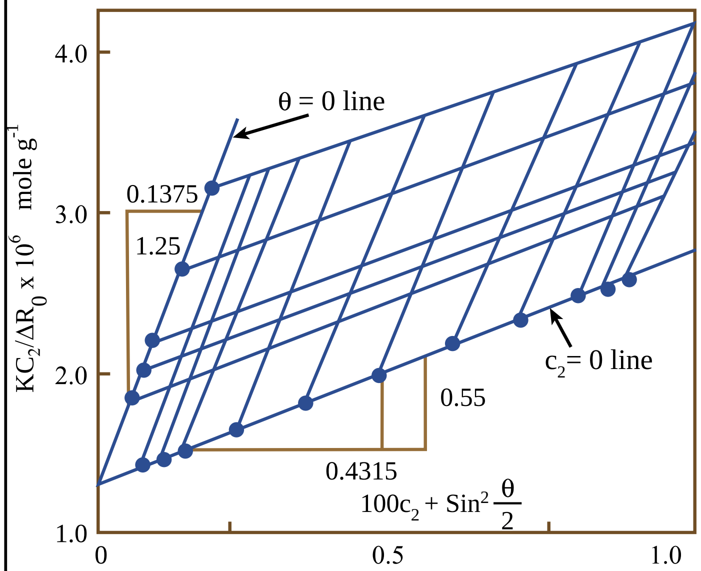
A_2

Image removed due to copyright restrictions.

Please see, for example, http://web.umr.edu/~WLF/MW/first.gif, from http://web.umr.edu/~WLF/MW/Zimm.html

$\langle R_g{}^2 \rangle$

An example: A_2, $\langle R_g^2 \rangle$ and $\overline{M}_w$



Note: units on y-axis are mole/g. The x-axis is dimensionless.

$$\frac{Kc_2}{\Delta R_0} = \left(\frac{1}{M_w} + 2A_2c_2 + \qquad\right)\left(1 + \frac{16\pi^2 n_0^2 \sin^2(\theta/2)}{3\lambda^2} \langle \bar{s}^2 \rangle_z\right)$$

The intercept occurs at a y-value ($\frac{Kc_2}{\Delta R_0}$) of 1.36×10^{-6} mole/g. Hence, $\overline{M}_w$ = 7.35×10^5 g/mole.
Now, consider the $c_2 = 0$ line. Where $c_2 = 0$,

$$\frac{Kc_2}{\Delta R_0} = \frac{1}{M_w}\left(1 + \frac{16\pi^2 n_0^2 \sin^2(\theta/2)}{3\lambda^2} \langle \bar{s}^2 \rangle_z\right)$$

$$\text{slope} = \frac{1}{M_w}\left(\frac{16\pi^2 n_0^2 \langle \bar{s}^2 \rangle_z}{3\lambda^2}\right)$$

Measure the slope of the $c_2 = 0$ line.

From intercept,

$$\overline{M}_w = 735{,}000 \text{ g/mol}$$

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{5.5 \times 10^{-7} \text{mole/g}}{0.4375}$$

$$= 1.26 \times 10^{-6} \text{ mole/g}$$

$$\langle \bar{s}^2 \rangle_z = \frac{\text{slope } \overline{M}_w (3\lambda^2)}{16\pi^2 n_0^2}$$

$$= \frac{3(1.26 \times 10^{-6} \text{ mole/g})(7.35 \times 10^5 \text{g/mole})(5.461 \times 10^{-5})^2}{16\pi^2(1.5014)^2}$$

$$= 2.33 \times 10^{-11} \text{cm}^2$$

Figure by MIT OCW.

getting A_2, $\langle R_g^2 \rangle$ and $\overline{M}_w$

(i) $$< r^2 > \;=\; 6 < R_g^{\,2} >$$

$$= 6\,(2.33 \times 10^{-11}\ cm^2)$$

$$= 1.40 \times 10^{-10}\ cm^2$$

$$\langle r^2 \rangle^{1/2} = 1.182 \mathrm{x} 10^{-5}\ cm = 1{,}182\ \mathrm{A}$$

Pretty big molecules!

(ii) Now consider the $\theta = 0$ line. At $\theta = 0$ (neglecting higher order c_2 terms)

$$\frac{Kc_2}{\Delta R_\theta} = \frac{1}{\overline{M}_w} + 2A_2 c_2$$

slope = 2 A_2

The density of polystyrene (ρ_2) is 1.05g/cm³. The molar volume of benzene $V_1 = MW/\rho_1$. The molecular weight of benzene is 78.11 g/mole and its density is 0.8787g/cm³ (from CRC Handbook of Chemistry and Physics).

from the Zimm plot

$$slope = \frac{1.25\,x10^{-6}\ mole/g}{0.1375\,x10^{-2}\,g/cm^3} = 9.09x10^{-4}\ \frac{mole \cdot cm^3}{g^2} = 2\ A_2$$

$$A_2 = 4.55\mathrm{x}10^{-4}\ \frac{\mathrm{mole \cdot cm^3}}{\mathrm{g^2}}$$

A_2, $\langle R_g^{\,2} \rangle$ and $\overline{M}_w$

(ii) The relationship between A_2 and χ is given by:

$$\chi = \frac{1}{2} - A_2 V_1 \rho_2^2$$

Substituting the values,

$$\chi = \frac{1}{2} - \left(4.55x10^{-4} \frac{mole\ cm^3}{g^2} \right) \left(\frac{78.11\, g/mole}{0.8787\ g/cm^3} \right) \left(1.05\ g/cm^3\right)^2$$

$$\chi = 0.455$$

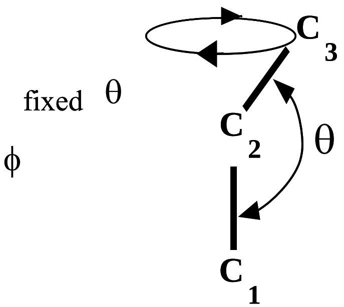
(So, of course, the polymer solution used for light scattering will be a single phase since $\chi < 1/2$ for miscibility of solvent and polymer).

Noncrystalline Materials

- The structure of noncrystalline materials (i.e. polymer glasses, amorphous polymer melts) is characterized by short range order (SRO)
- SRO – develops due to excluded volume and locally dense packing (glasses ~ are only 10% less dense than crystals)
- Pair distribution function g(r) is a dimensionless function used to quantify SRO. In polymers SRO is primarily due to covalent intra-molecular bonds and neighboring intermolecular packing.
- Properties of noncrystalline polymers are heavily influenced by τ^* , the characteristic relaxation time relative to an experimental observation time, t.

liquid (melt)	$t \gg \tau^*$	
rubbery	$t \leq \tau^*$	$\tau^*(T)$?
glassy	$t \ll \tau^*$	

SRO in Polymers

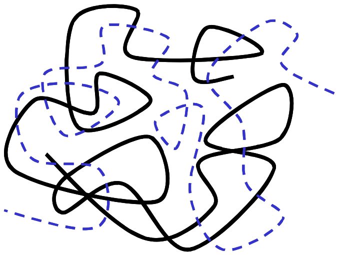


- Due to covalent intra-molecular bonds

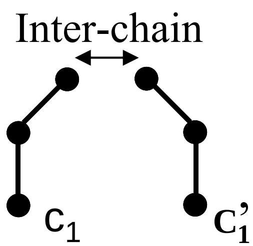
$$\left.\begin{array}{ll} C_1 - C_2 & = \text{constant} \\ C_1 - C_3 & = \text{constant} \end{array}\right\} \text{gives rise to peaks at large } q$$

$$C_1 - C_4 \quad = \text{varies}$$

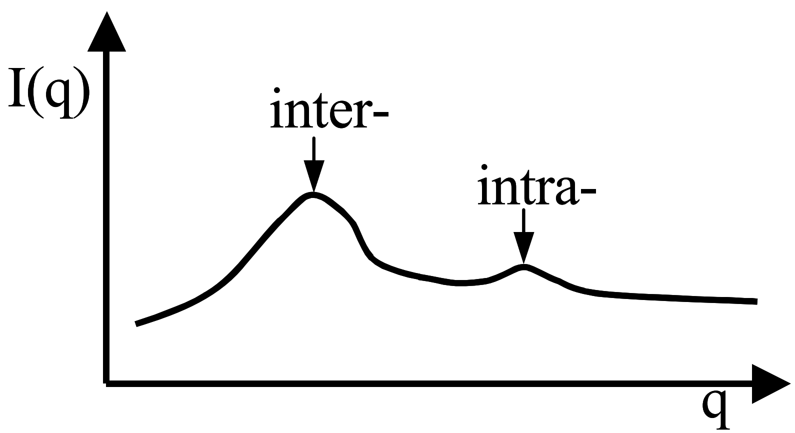
- Due to chain-chain inter-chain distances ~ 5Å



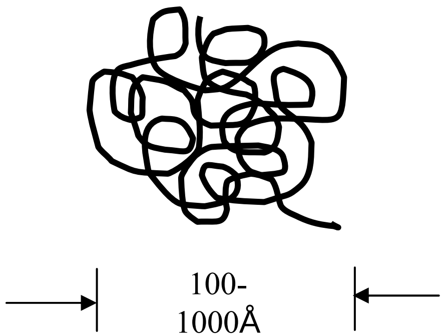
$C_1 – C'_1$ ~ 5Å



Typical X-ray signature of noncrystalline materials -
broad overlapping peaks from multiple distances:



Pair Distribution Function g(r)



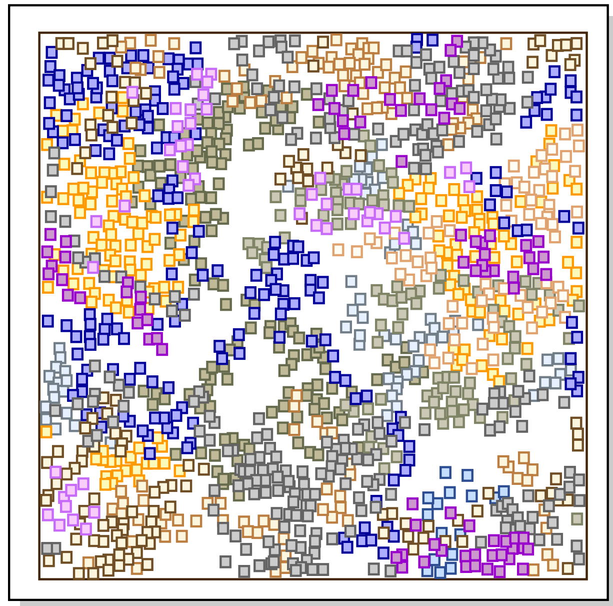


Figure by MIT OCW.

The Pair Distribution Function g(r) addresses the distances between the centers of mass of pairs of units. Since glasses and liquids are isotropic, the magnitude of the inter-unit distance is of interest.

The scalar distance r_{ij} between molecule i and molecule j is:

$$r_{ij} = |r_i - r_j|$$

g(r) cont'd

- $r_{ij} = |r_i - r_j|$
- Characterize the set of distances $\{r_{ij}\}$ from an average unit *i* to every other unit *j* =1 ….. N.
- g(r) counts the number of units *dn* in a small spherical shell sampling volume element of size *dv* at each distance r from a reference unit, $dv = 4\pi r^2 dr$
- The statistical average of these numbers for many units chosen as the reference is divided by the average unit density $\langle \rho \rangle$

Figure showing the pair-distribution functions for gas, liquid or glass, and monatomic crystal removed due to copyright restrictions.

See Figure 2.5 in Allen, S. M., and E.L. Thomas. *The Structure of Materials.* New York, NY: J. Wiley & Sons, 1999.

$$g(r) = \frac{1}{\langle \rho \rangle} \frac{dn(r, r+dr)}{dv(r, r+dr)}$$

Features of g(r) in Glasses & Liquids

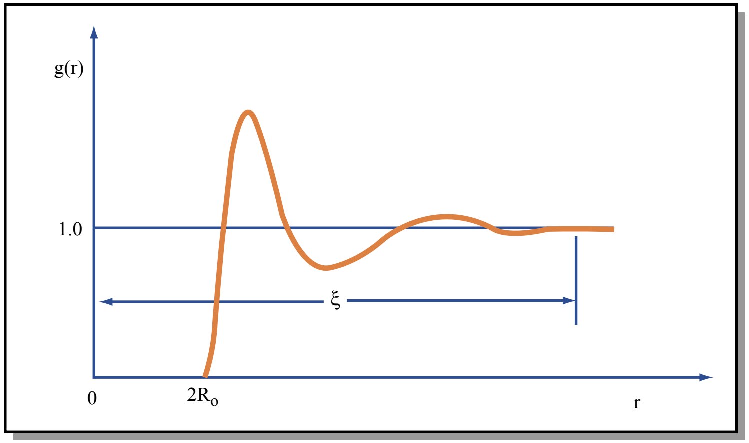


Figure by MIT OpenCourseWare.

At several unit diameters, the average number of units/vol. becomes constant

- Due to excluded volume, g(r) = 0 for distances less than $2R_o$
- Liquids and glasses are strongly correlated at the shortest distance between 2 units, the maximum occurs at slightly > $2R_o$, this largest peak is the average distance to the first shell to the nearest-neighbor unit.

$C_1 - C_2$	$g(r)_{intra}$	Superposed correlations
$C_1 - C_2 \searrow C_3$	$g(r)_{inter}$	