Light Scattering

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

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

\[ A_2 = \left( \frac{1}{2} - \chi \right) \]

\( A_2 = \frac{1}{\rho_2^2 V_1} = 2^{\text{nd}} \) virial coefficient

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

<table>
<thead>
<tr>
<th>Scattering arises from…</th>
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</thead>
</table>
| **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: \( d_p << \lambda_{\text{radiation}} \)
  - (situation: ~ point scatterers)

Scattered Intensity at scattering angle \( \theta \) to a detector \( r \) away from sample:

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

- \( \alpha = \) polarizability of molecule
- \( I_0 = \) incident beam intensity

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

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

- \( \varepsilon = \) dielectric constant
- \( \varepsilon = n^2, \quad \varepsilon(\omega) = \) frequency dependent
Fundamental relationship: index of refraction $\leftrightarrow$ polarizability

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

Can approximate

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

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

$c = \text{conc. of particles per unit volume}$

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

Solving gives the polarizability

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

So by analogy for a polymer-solvent solution:

$$n \approx n_0 + \frac{dn}{dc_2} c_2$$

$$n^2 \approx n_0^2 + 2 n_0 \frac{dn}{dc_2} c_2$$
Rayleigh and the Molecular Weight of Gases

\[ I_\theta = \left( \frac{N}{V} \right) \frac{8\pi^2(1 + \cos^2 \theta)}{\lambda^4 r^2} \left( \frac{\text{dn} / \text{dc}}{2\pi(N/V)} \right)^2 \]

simplifying

\[ I'_\theta = \frac{I_0}{\lambda^4 r^2 (N/V)} \left( \frac{\text{dn}}{\text{dc}} \right)^2 c^2 \]

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

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

Or just

\[ R = K \cdot M \cdot c \]

Where \( K \) is a lumped optical constant

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

Note, for polymer-solvent solution:

\[ K \equiv \frac{2\pi^2 n_0^2 \left( \frac{\text{dn}}{\text{dc}_2} \right)^2}{\lambda^4 N_{AV}} \]

Rayleigh measured the molecular weight of gas molecules using light scattering!
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 $\Delta R = R_{\text{solution}} - R_{\text{pure solvent}} = \text{“Excess Rayleigh Ratio”}$

• Feature 2.
  Remaining scattering arises from fluctuations in solute concentration.
  
  $$I_o = \frac{I_0 2\pi^2 (1 + \cos^2 \theta) (\frac{dn}{dc})^2 c^2}{\lambda^4 r^2 (N/V)}$$

  $\Delta R$ depends on $\left(\frac{dn}{dc}\right)$ and $\langle (\delta c_2)^2 \rangle$

  Einstein-Smoluchowski mean squared concentration fluctuation per unit vol.

  $$\langle (\delta c_2)^2 \rangle = \frac{RT c_2}{\delta VN_{AV} \left( \frac{\partial \pi}{\partial c_2} \right)}$$

• 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.

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

  $$\frac{\partial \pi}{\partial c_2} = RT \left[ \frac{1}{M} + 2A_2 c_2 + \cdots \right]$$
Feature 3 cont’d

\[ R_{\text{solution}} - R_{\text{solvent}} = \frac{2\pi^2 n_0^2 \left( \frac{dn}{dc_2} \right)^2 c_2}{\lambda^4 N_{AV} \left[ \frac{1}{M} + 2A_2 c_2 + \cdots \right]} \]

Polymer in solution

\[ \Delta R = K c_2 \left[ \frac{1}{\frac{1}{M} + 2A_2 c_2 + \cdots} \right] \]

Gas in vacuum

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

\( \Delta R \) similar to the Rayleigh scattering for gases but with a new term depending \( A_2 \)
Scattering from Polymer Solutions

• **Feature 4.**
  
  Polymer chains are large and can not be assumed as point scatterers for visible light

• $\lambda \sim 6,328\text{Å}$ He-Ne laser

• Coil size $\sim$ 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 $P(\theta)$ term is important
Scattering of Polymer Solutions

Introduce finite size chain scattering factor \( P(\theta) \)

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

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

where

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

\( q = \) scattering vector,

\[u = q^2 \left\langle R_g^2 \right\rangle\]

In the limit of very small \( \theta \), \( P(\theta \rightarrow 0) = 1 \)

Useful approximation for small, nonzero \( \theta \)

\[
P(\theta) \approx 1 - \frac{u}{3} \quad \text{and} \quad \frac{1}{P(\theta)} \approx 1 + \frac{u}{3} \quad \text{for} \quad u^{1/2} \ll 1
\]
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

\[
\frac{Kc_2}{\Delta R} = \left[ \frac{1}{M} + 2A_2c_2 + \cdots \right] \left[ 1 + \frac{u}{3} \right]
\]

\( u = q^2 \langle R_g^2 \rangle \)

\[
\frac{Kc_2}{\Delta R} = \left[ \frac{1}{M} + 2A_2c_2 + \cdots \right] \left[ 1 + \frac{16\pi^2 n_0^2}{3 \lambda^2} \sin^2 \left( \frac{\theta}{2} \right) \langle R_g^2 \rangle \right]
\]

Equation is valid for dilute solutions and scattering angles \( \theta \) such that

\( u^{1/2} \ll 1 \)

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:
\[ \theta = 30°, 37.5°, 40°, 60°, 75°, 90°, 105°, 120° \]

Measure \( \Delta R \) 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
2. Polymer solutions \([c_{2,i}, I(\theta_i)]\)
3. Construct Zimm Plot

\[ \Delta R = R_{\text{polymer}} - R_{\text{solvent}} \]

Note: \( \frac{Kc_2}{\Delta R_{\theta}} \) is a function of 2 variables, \( c_2 \) and \( \theta \).

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

The Master Equation:

\[
\frac{Kc_2}{\Delta R} = \left( \frac{1}{M_w} + 2A_2c_2 + \ldots \right) \left( 1 + \frac{16 \pi^2 n_0^2 \sin^2 \theta}{3 \lambda^2} \frac{2}{\langle R_g^2 \rangle} \right)
\]

do double extrapolation:

- \( \theta \to 0^\circ \)
- \( c_2 \to 0 \)
- \( \bar{\theta} \)
- \( \bar{M}_w \)

Units:

- Mole/gram
- Dimensionless axis

\( \sin^2(\theta/2) + k c_2 \) vs. \( \frac{Kc_2}{\Delta R(\theta_i, c_i)} \)
## Zimm Plot: Sample Data Set

<table>
<thead>
<tr>
<th>$c_2$ $\text{g/cm}^3$</th>
<th>$\frac{Kc_2}{\Delta R(\theta_i, c_i)}$</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$30^\circ$</td>
</tr>
<tr>
<td>$2 \times 10^{-3}$</td>
<td></td>
<td>3.18</td>
</tr>
<tr>
<td>$1.5 \times 10^{-3}$</td>
<td></td>
<td>2.73</td>
</tr>
<tr>
<td>$1 \times 10^{-3}$</td>
<td></td>
<td>2.29</td>
</tr>
<tr>
<td>$0.75 \times 10^{-3}$</td>
<td></td>
<td>2.10</td>
</tr>
<tr>
<td>$0.5 \times 10^{-3}$</td>
<td></td>
<td>1.92</td>
</tr>
</tbody>
</table>

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

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

\[
n_0 = 1.5014
\]

\[
dn/dc = 0.106 \text{ cm}^3 \text{g}^{-1}
\]

\[
\lambda = 5.461 \times 10^{-5} \text{ cm}
\]

\[
N_{AV} = 6.02 \times 10^{-23} \text{ mole}^{-1}
\]
Plotting the Data

Extrapolating to zero concentration

\( K_c^2 \)

\( \Delta R_\theta \)

“vertical” data set
\( \theta = 30^\circ \)
\( c_2 \) varies (decreases)

(0.267, 3.18)

“horizontal” data sets
\( \theta \) variable
\( c_2 = 2 \times 10^{-3} \)

Plot typical data point:
\( \theta = 30^\circ, c_2 = 2 \times 10^{-3} \text{ g/cm}^3 \)

\( y\text{-axis}: \quad \frac{K_c^2}{\Delta R_\theta} = 3.18 \)

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

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

Pick constant to “spread” the plot

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

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
Extrapolating to zero scattering angle...

Plotting the data cont’d

(.267, 3.18)

100c₂

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:

\[ \bar{M}_w, \quad A_2 \quad \left\langle R_g^2 \right\rangle \]

\[ \frac{Kc_2}{\Delta R_\theta} \quad A_2 \]

Image removed due to copyright restrictions.

An example: \( A_2, \langle R_g^2 \rangle \) and \( \bar{M}_W \)

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

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

The intercept occurs at a y-value \( \left( \frac{Kc_2}{\Delta R_0} \right) \) of 1.36 x 10^-6 mole/g. Hence, \( \bar{M}_w = 7.35 \times 10^5 \) g/mole.

Now, consider the \( c_2 = 0 \) line. Where \( c_2 = 0 \),

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

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

Measure the slope of the \( c_2 = 0 \) line.

\[
slope = \frac{\Delta y}{\Delta x} = \frac{5.5 \times 10^{-7} \text{mole/g}}{0.4375} = 1.26 \times 10^{-6} \text{ mole/g}
\]

\[
\langle s^2 \rangle_z = \frac{\text{slope} \bar{M}_w (3\lambda^2)}{16\pi^2n_0^2} = \frac{3(1.26 \times 10^{-6} \text{ mole/g})(7.35 \times 10^5 \text{ g/mole})(5.461 \times 10^{-5})^2}{16\pi^2(1.5014)^2} = 2.33 \times 10^{-11} \text{ cm}^2
\]

From intercept, \( \bar{M}_w = 735,000 \) g/mol

Figure by MIT OCW.
getting $A_2$, $\langle R_g^2 \rangle$ and $\overline{M_w}$

(i) \[
\langle r^2 \rangle = 6 \langle R_g^2 \rangle = 6 \left(2.33 \times 10^{-11} \text{ cm}^2\right) = 1.40 \times 10^{-10} \text{ cm}^2
\]

\[
\langle r^2 \rangle^{1/2} = 1.182 \times 10^{-5} \text{ cm} = 1,182 \text{ Å}
\]

Pretty big molecules!

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

\[
\frac{Kc_2}{\Delta R_0} = \frac{1}{M_w} + 2A_2 c_2
\]

slope = $2A_2$

The density of polystyrene ($\rho_2$) is 1.05g/cm$^3$. 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/cm$^3$ (from CRC Handbook of Chemistry and Physics).

*from the Zimm plot*

\[
slope = \frac{1.25 \times 10^{-6} \text{ mole/g}}{0.1375 \times 10^{-2} \text{ g/cm}^3} = 9.09 \times 10^{-4} \frac{\text{mole} \cdot \text{cm}^3}{g^2} = 2A_2
\]

\[
A_2 = 4.55 \times 10^{-4} \frac{\text{mole} \cdot \text{cm}^3}{g^2}
\]
\( A_2, \langle R_g^2 \rangle \) and \( \overline{M}_w \)

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

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

Substituting the values,

\[
\chi = \frac{1}{2} - \left( 4.55 \times 10^{-4} \frac{\text{mole cm}^3}{\text{g}^2} \right) \left( \frac{78.11 \text{ g/mole}}{0.8787 \text{ g/cm}^3} \right) (1.05 \text{ g/cm}^3)^2
\]

\[
\chi = 0.455
\]

(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 $\tau^*$, the characteristic relaxation time relative to an experimental observation time, $t$.

\begin{align*}
\text{liquid (melt)} & : t \gg \tau^* \\
\text{rubbery} & : t \leq \tau^* \\
\text{glassy} & : t \ll \tau^*
\end{align*}

$\tau^*(T)$ ?
Structural Features of Noncrystalline Polymers

SRO in Polymers

- Due to covalent intra-molecular bonds
  \[
  \begin{align*}
  C_1 - C_2 &= \text{constant} \\
  C_1 - C_3 &= \text{constant} \\
  C_1 - C_4 &= \text{varies}
  \end{align*}
  \]
gives rise to peaks at large q

- Due to chain-chain inter-chain distances \( \sim 5\text{Å} \)

Typical X-ray signature of noncrystalline materials - broad overlapping peaks from multiple distances:
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 \( j = 1 \ldots N \).
- \( g(r) \) 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 \( \langle \rho \rangle \)

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

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

• 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.