Optical Crystals Demo

- use slides in General Microscopy
- try to guess shapes using the real optical crystals
- It's hard: from this we conclude that μscopy is superior to LS when you can get away with it.

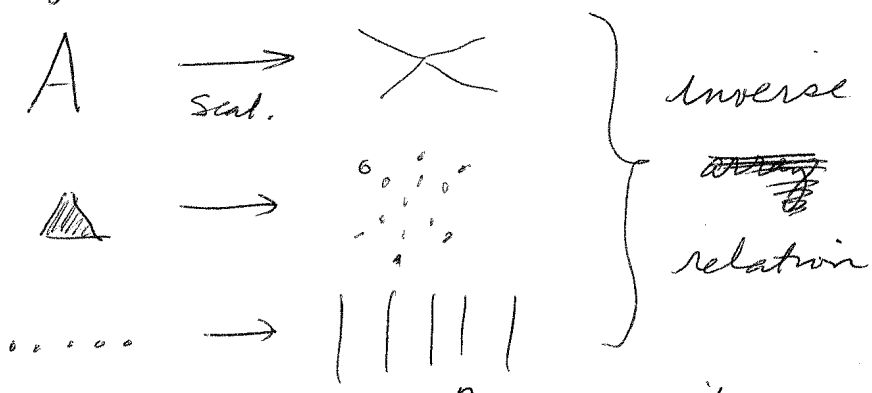
But....

- floppy objects better in LS
- averaging better in LS
- dynamics / kinetics
- quantization
- Theory

So let's look closer at the optical crystals observations

- Square array resulted in square diffractions
- hex " " " hex "
- intensity of points modulated by shape of particle

e.g.



But when we didn't know the answer, it was often hard. This is due to Phase Problem

Phase Problem: Cantor & Schimmel, Ch. 13

Image $\Longleftrightarrow$ Scattered Electric Field (perfect)

$|\text{Scattered E field}|^2 \Longleftrightarrow$ What you see (intensity) (imperfect)

$$I = S \cdot P$$

P ← form factor (e.g. ✕ for A)

S ← structure factor (e.g. square pattern for square array of A's)

High Polymer Physics Prize: all these prizes show us that there is powerful motivation to "see" molecules through scattering, despite the hardships. We may expect that some mathematical apparatus will be required to figure out why  =

Light Scattering: Outline

Increasingly Realistic

Observations, including diffraction which is a special case of scattering by regularly ordered objects

Small Molecules

<u>Gas</u>

A) Particle picture for a single particle.

B) Dilute picture: "matrix" type summation of electric fields

C) Molecular weights

<u>Two-Component Solution</u> (adapt from gas)

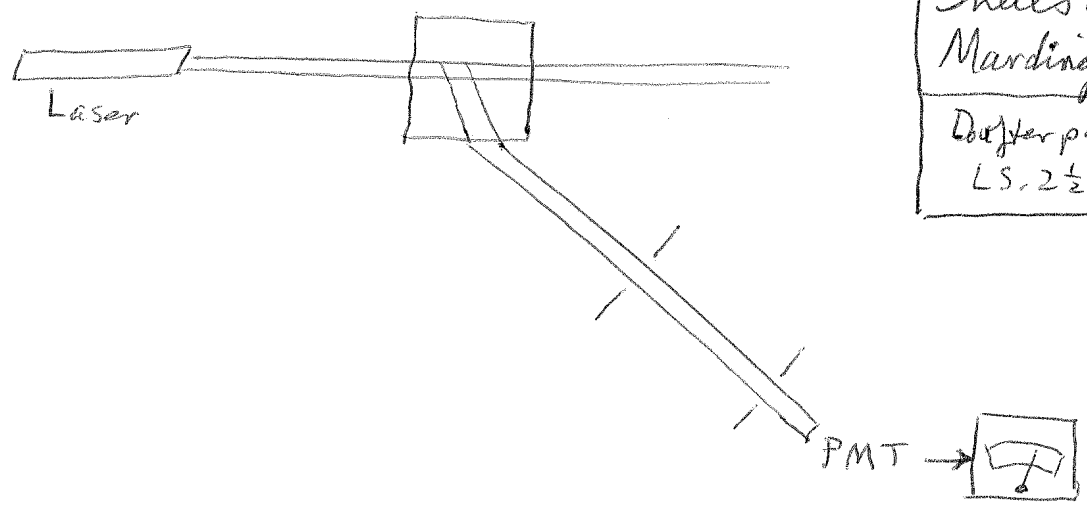
A) Simple adaptation from gas

B) Thermodynamic Viewpoint

Large Molecules

Preface: LS is relatively ignored by chemists who are mostly interested in <u>another</u> way that light interacts with matter: absorption. Nevertheless, scattering is as basic – and as important – as absorption.

The Nature of the LS experiment

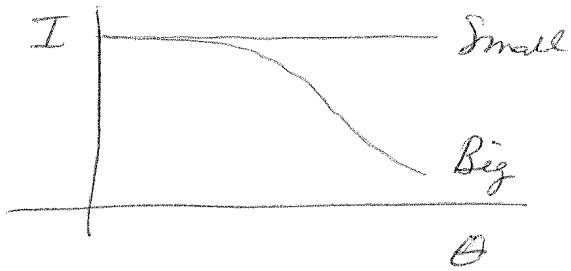


Snell's Law
Marding Demo
Doujter page
LS.2½

~~Experimental~~ Experiencial Observations

① Other things being equal, big particles scatter more than little ones

② Angular Dependence

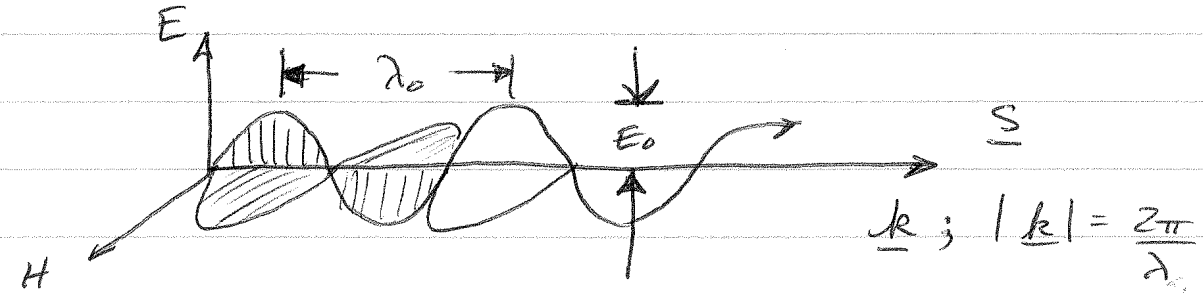


③ Blue sky .... but red sunsets
Polarized Sunlight
Sky seems far away .... but this is tricky!

④ All that optical crystal stuff

A word first about light.

We already discussed that light produces rapidly (10^{14}-10^{15} Hz) oscillating electrical fields. But there is more to it than that.



Poynting vector

$$\underline{S} = \frac{c}{4\pi} \underline{E} \times \underline{H}$$

$\underline{S}$ describes the <u>instantaneous</u> rate of energy flow at a point

Average over time to give I as energy per sec. per squared centimeter in direction of propagation

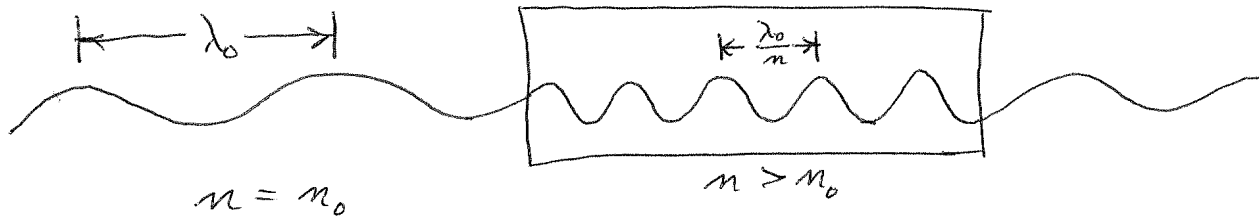
$$I = \frac{c}{8\pi} E_0^2$$

We will generally let $I \sim \underline{E}^* \underline{E}$

$\underline{k}$ describes the spatial frequency of the light and its direction. It has units of cm^{-1} and essentially gives how many "periods" per cm.

for visible light, $|\underline{k}| \simeq 10^5 cm^{-1}$

Refractive Index



typical values

Water $n = 1.33$

glass $n = 1.5$

$$\lambda = \frac{\lambda_0}{n} \qquad k = \frac{2\pi}{\left(\frac{\lambda_0}{n}\right)} = \frac{2\pi n}{\lambda_0} \qquad c = \frac{c_0}{n}$$

wavelength shortened — spatial frequency increased — speed reduced

Complex Refractive Index: Absorption

let $m = n + i\epsilon'$

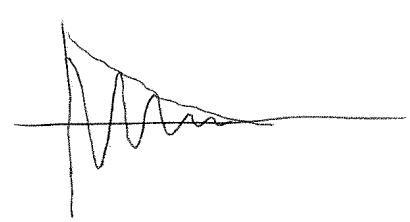
$$k = \frac{2\pi}{\lambda_0}\left(n + i\epsilon'\right) = \frac{2\pi n}{\lambda_0} + i\epsilon \qquad \left(\epsilon = \frac{2\pi}{\lambda_0}\epsilon'\right)$$

then consider a wave

$$E = E_0 e^{i(\omega t + kx)} \Rightarrow E_0 e^{i\omega t} e^{i\frac{2\pi n}{\lambda_0}x} e^{-\epsilon x}$$

$$= E_0 e^{i\left(\omega t + \frac{2\pi n}{\lambda_0}x\right)} \underbrace{e^{-\epsilon x}}_{\text{absorption!}}$$

time oscillator — spatial oscillator

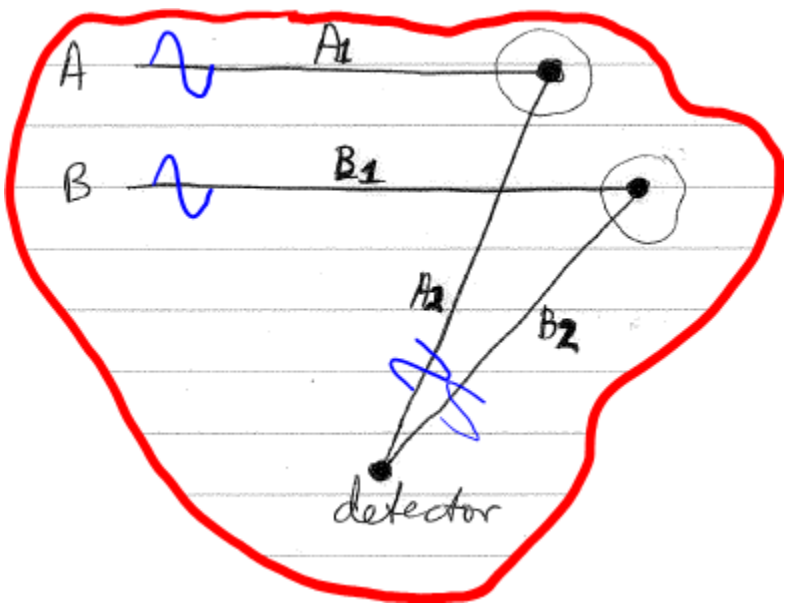


Why stuff scatters.

It's actually more instructive to explain why stuff *doesn't* scatter.[1] Consider the construct below, showing two scattering volumes, A and B, in a sample. These regions aren't chosen at random; rather, they are selected such that the total distance from light source to detector through these two zones differs by a half wavelength (or multiple):

$A1 + A2 = B1 + B2 + \lambda/2$,

where λ is the wavelength. As a result, the waves arrive out of phase, leading to destructive interference…*but only if the scattering strength coming out of the A subvolume matches that coming out of the B subvolume.* If the contents of the two subvolumes are not identical, the destructive interference will be incomplete and scattering will occur.

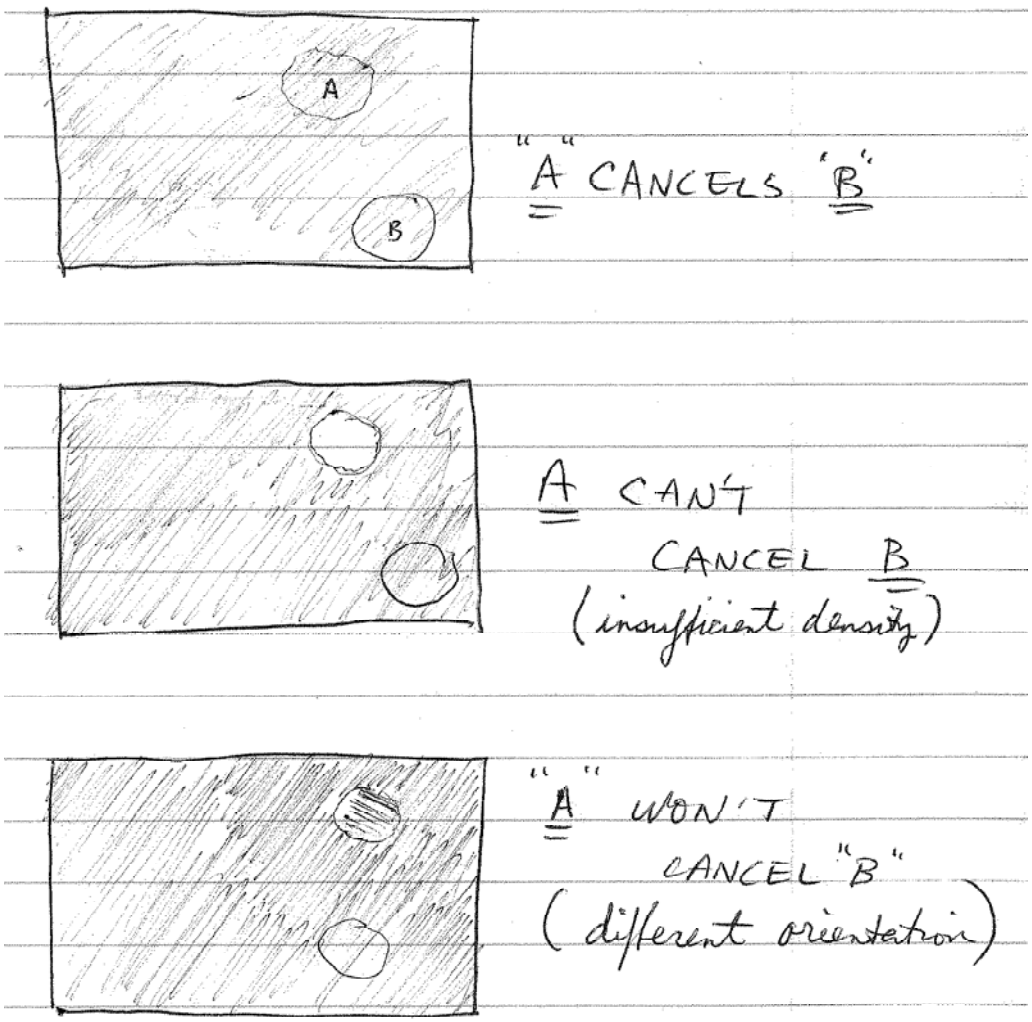


If the subvolumes A and B are identical, scattering cannot occur.

In a sufficiently large sample, any region A has a corresponding region B positioned so that the total scattering will null out if the contents of all pairs are identical. Now we have to consider how the contents can be the same.

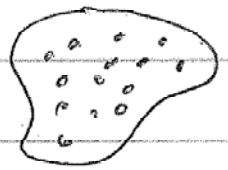
[1] Harkens back to "Slaughterhouse Five" by Ray Bradbury, in which a German Nazi randomly slaps an American prisoner of war. The American asks, "Why me?". His tormentor replies, "Why not you?".

Suppose the contents of A and B contain exactly the same number of identical molecules, randomly positioned and oriented; this would lead to cancellation and no scattering. If the two volumes contain differing numbers, the amplitude coming out of one is insufficient to cancel the scattering derived from the other; while the regions are positioned correctly for destructive interference, the effect is incomplete. Finally, suppose the number of molecules in each subvolume is the same, but their orientation differs. If the orientation is not only geometric but also optical, that could lead to *depolarized* scattering, in which the polarization sense of the outgoing beam differs from that of the incident.



Inhomogeneities lead to scattering.

Let us defer the orientation effects (or is that defects?) for now and consider scattering from systems containing just one component, such as pure nitrogen, pure water or pure carbon (as diamond). Even if each region A and B has identical size, differences in the number of scatterers within can exist due to normal fluctuations. For a sample of population N, the fluctuation δN is estimated as $\sqrt{N}$. It's easy to see that a 1% fluctuation should be expected if N = 10,000.



N particles

$\delta_N \sim \sqrt{N}$

Relative noise $\dfrac{\sqrt{N}}{N} = \dfrac{1}{\sqrt{N}}$

1% Relative noise $\Leftrightarrow$ $N \simeq 10{,}000$

We haven't said anything about the size of the subvolumes, but we should. It's important that the incident light remain in-phase as it crosses the subvolume. A good size, then, might be $\lambda/2$, but let's choose λ for convenience. All our arguments in this section are qualitative anyway. Let's get the pressure of a gaseous system that has a number density, $\nu = N/V$, corresponding to $10{,}000/\lambda^3$.

What pressure corresponds to $\nu = \frac{10{,}000 \text{ gas atoms}}{\lambda^3}$

$\lambda = 5000$ Å (green-blue)

$PV = NkT$

$P = \frac{N}{V} kT = \nu kT \qquad k = 1.38 \times 10^{-16} \frac{\text{erg}}{\text{mol} \cdot \text{K}}$

$T = 300\text{K}$

$$\Rightarrow \quad P = \frac{10{,}000}{(5000 \times 10^{-8} \text{cm})^3} \left(1.38 \times 10^{-16} \frac{\text{g cm}^2}{\text{s}^2 \text{K}}\right)(300\text{K})$$

$$= \text{Yuck!}$$

Try this instead

$$P = \frac{(10{,}000 / 6.02 \times 10^{23} \text{ mol})}{(5000 \times 10^{-8} \text{cm})^3} \left(82 \frac{\text{mL-atm}}{\text{mol K}}\right)(300\text{K})$$

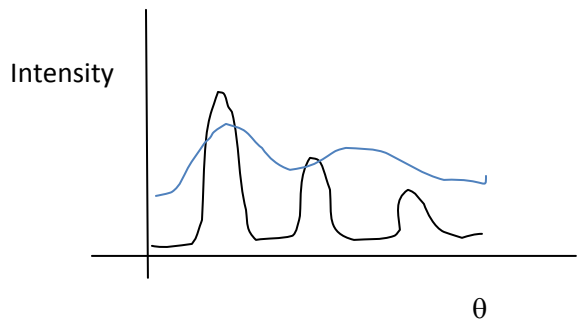
$$\Rightarrow 0.0033 \text{ Atm}$$

$$\equiv 2.5 \text{ mm Hg}$$

This pressure, which corresponds to Earth atmosphere at an altitude exceeding 100,000 ft (according to a quick Google search), is already sufficient to cause only 1% fluctuations in the particles within a box of volume λ^3. On the surface of earth, the fluctuations should be smaller still, yet it turns out even this density not enough to extinguish all the scattering from the particles. One needs even higher number densities. For example, the scattering by water is indeed very low; it is easy to show water has a number density of $\nu \approx 4$ billion/λ^3 so $\delta N/N \approx 0.002\%$. Such a low level of fluctuations is considered low enough, and it is often said that:

The scattering of light by a perfect fluid is zero (but no perfect fluid exists).

A perfect crystal, such as diamond also qualifies, but this leads to an interesting point: one cannot get to a density of many scatterers per λ^3 if λ is very small. Water and diamond both scatter x-rays well, but one sees the effect of crystallinity (diamond) or molecular correlation (water) in the scattering pattern, which fluctuates wildly with scattering angle, θ.



Returning to the scattering of visible wavelengths, one usually explains it not as fluctuations $\delta N/N$ but as fluctuations in density. This makes it clear that water will scatter more strongly near its boiling point, for example.

? What about a polymer solution, say $M = 100{,}000$ at $c = 1\ mg/mL$. How many scatterers in a volume of λ^3 then?

(1) First, let us agree that the number of solvent molecules is really huge. There will be some scattering due to density fluctuations, but it should be small (greater than air, due to the huge number of particles, but still very small on a <u>per particle</u> basis).

(2) Convert the concentration

$$\left(10^{-3}\ \frac{g}{mL}\right)\left(5000\times10^{-8}\ cm\right)^3\left(\frac{6\times10^{23}\ \text{particles}}{100{,}000\ g}\right) = 750$$

Two Things: 1) The <u>per particle</u> scattering of a polymer can be very large

2) $\frac{\sqrt{750}}{750}\times100 \simeq 3.5\%$ – significant fluctuations

We should expect an easy time measuring scattering from polymer solutions, but despite their high mass, one has to reach very high dilutions to measure single particles at once. If you see in the literature a study that claims to have been performed in the "single particle limit", it means something else—e.g., the particles are not interacting, though many are normally detected in the instrument.

Summary so far:

- It's not surprising that objects with a high density don't scatter much at visible wavelengths.
- We should expect polymers to scatter a bit better.

Before moving on, let's look at our four questions and/or observations:

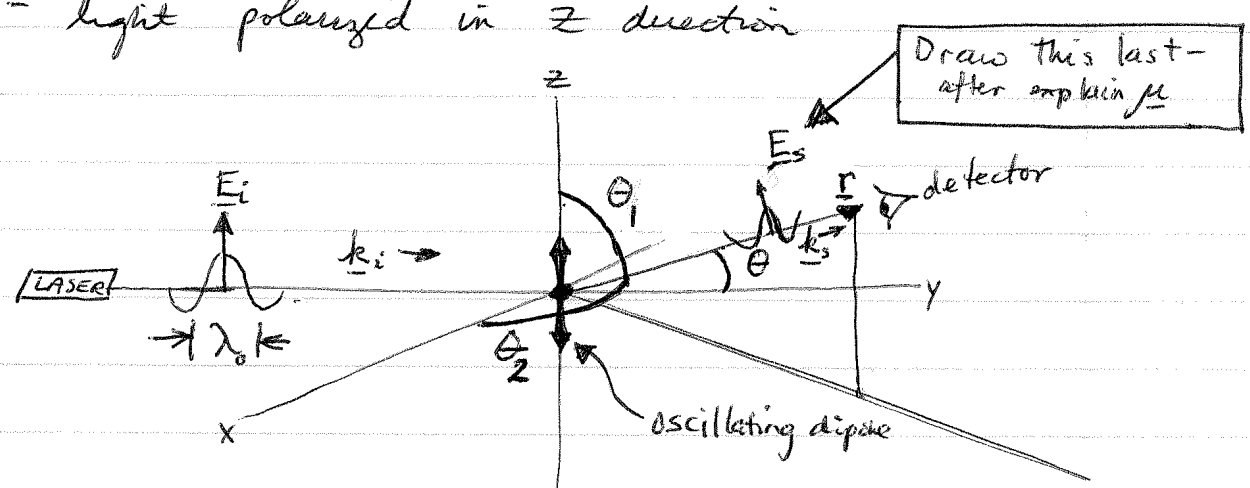
1. We haven't explained why big particles scatter more than small ones yet.
2. We haven't explained angular dependence yet.
3. We haven't explained why the sky is blue or sunsets are red, nor have we explained polarization or the reason why the sky seems distant. Nevertheless, from the above consideration it should should seem plausible that many miles of atmosphere could scatter light. Also, at the top of the atmosphere, the cancellation effect will be weak (but there are few scatterers to begin with, too).
4. We haven't explained diffraction…but we have pointed out that wild oscillations will occur when the interparticle distance approaches the wavelength. This is true of solids *and liquids* but the oscillations are less profound in the latter case.

It might seem like little progress has been made, but you are beginning to think like a scatterbrain.

Scattering from a single, small particle in a gas.

References: Tanford p. 278
Van Holde Ch. 9
Zimm, Stein & Doty Polym. Bull. 1 (415) 90-119 (1945)
Johnson & Gabriel, Laser LS, Dover, Mineola NY (1981)

- Consider a gas atom (size $\ll \lambda$) located at origin
- light incident along y axis
- light polarized in z direction



let $\underline{k}_s$ = vector ∥ scattered light, magnitude $2\pi/\lambda_0$
let $\underline{k}_i$ = vector ∥ incident light, magnitude $\frac{2\pi}{\lambda_0}$.
let θ_1 = The polar angle (what we often call ϕ or θ)
θ_2 = angle between x axis & scattering direction
θ = "the" scattering angle = angle btwn. $\underline{k}_i$ & $\underline{k}_s$
$\underline{r}$ = vector btwn. scatterer & detector
$\underline{\mu}$ = induced dipole at origin, as electrons respond to the incident field $\underline{E}_i$

DK – That's the set-up. Now what happens?

- $\underline{E}_i$ is a rapidly oscillating E & H (magnetic) field
- The $\underline{E}$ field is ∥ to $\underline{z}$ direction. The magnitude of $\underline{E}_i$ varies at $\sim 10^{14}-10^{15}$ Hz.
- Inside the atom, the electrons & protons dance to the tune of the incident light.
- To first approximation, the electrons do most of the moving (proton is 1836 times heavier).
  [Born Approximation]

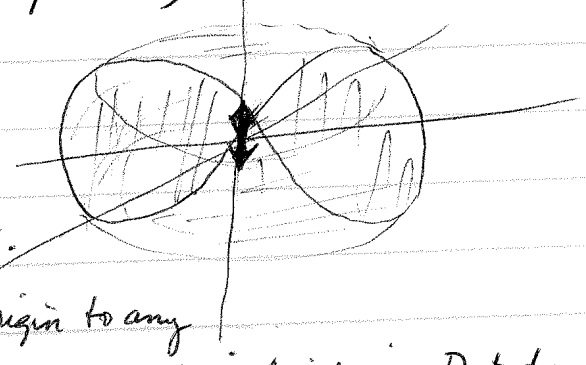
$$\underline{\mu} = \alpha \underline{E}_i$$

{ assume $\underline{\mu} \parallel \underline{E}_i$
This actually <u>isn't</u> true

Units: $(\text{esu-cm}) = \alpha_{\text{units}} (\text{esu-cm}^{-2})$
α_{units} are cm^3 (α related to volume)

- An oscillating dipole re-radiates light. This is how antennae work. Now the intensity radiated by an oscillating dipole has a well known pattern, like a donut with no hole in it.

take a figure 8 on its side & rotate it around z axis.

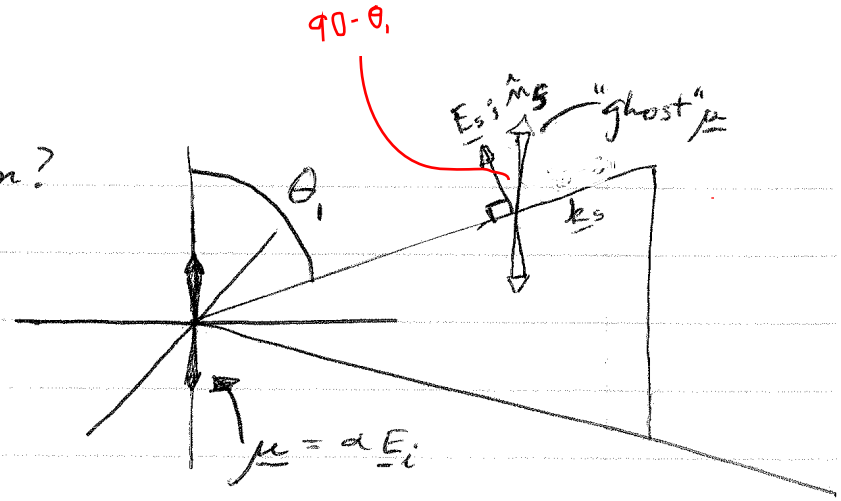


The distance from origin to any point on donut represents the intensity in that direction.

$\cos(90-\theta_1) = \sin(\theta_1)$

Why the donut pattern?

translate the $\underline{\mu}$ dipole to some remote point (call this "ghost" $\underline{\mu}$)



- It is a property of light that the propagation direction is exactly $\perp$ to the electric field. So $\underline{E}_s$ is $\perp$ to $\underline{k}_s$
- The amplitude of $\underline{E}_s$ depends on θ_1
- From the drawing, it can be seen that $|\underline{E}_s| \sim \sin\theta_1$
- So to get the most scattering, operate in the x, y plane.

<u>Now</u> we can do the math.

<u>At the origin</u> $\quad \underline{E}_i = \hat{z}\, E_0\, e^{i(\omega t)} \qquad \omega = 2\pi c/\lambda_0$

: will be directed as shown. Call this vector $\hat{n}_s$

$\underline{E}_s$: will be proportional to $\sin\theta_1$

: will be proportional to $\left(\frac{d^2\mu}{dt^2}\right)\left(\frac{1}{rc^2}\right)$

{ <u>Why?</u> because $\frac{d\mu}{dt}$ is a current, and accelerating current gives rise to radiation. The rc^2 term: energy intensity dies as r^{-2}. The c^2 part is dimensionally correct at least }

: will be modified by a phase factor $\underline{k}_s \cdot \underline{r}$ by the time we measure it at the detector.

$$\underline{E}_s = \frac{\hat{n}_s \frac{d^2\mu}{dt^2}}{rc^2} = \left(\frac{d^2}{dt^2}\left[\alpha E_0 e^{i(\omega t - \underline{k}_s \cdot \underline{r})}\right]\sin\theta_1\right)\hat{n}_s\left(\frac{1}{rc^2}\right)$$

- The two derivatives bring down $(i\omega)^2 = -\omega^2$
- Everything else comes back as it was, since $\frac{d}{dx} e^x = e^x$

Thus $$\underline{E}_s = \frac{\hat{n}_s}{rc^2}\left(\alpha E_0 (-\omega^2)\, e^{i\omega t} e^{-i\underline{k}_s\cdot\underline{r}} \sin\theta_1\right)$$

oscillations

spatial phase term

geometry

<u>Useful to dissect this</u>

incident light strength

Scattered light field goes up as square of frequency — comes from E&M: radiation is acceleration of current.

The direction $\perp$ to $\underline{k}_s$ in which E field lies

Polarizability = Scattering Strength

field fades as $\frac{1}{r}$

c^2 from E&M (some squared velocity is needed by dimensions)

− sign says that there is a 180° phase change on scattering.

Instantaneous Intensity is actually $\sim |\underline{E} \times \underline{H}|$ but we do OK to compute $\underline{E}^*\underline{E}$ which gives $I_{average}$.

$$I_s = \underline{E}_s^* \underline{E}_s = \frac{1}{r^2 c^4}\, \alpha^2 E_0^2\, \omega^4 \sin^2\theta_1$$

$$\left\{\begin{array}{l} \nu = c/\lambda_0 \\ \omega = 2\pi\nu = 2\pi c/\lambda_0 \\ \left(\omega/c\right)^4 = \left(\frac{2\pi}{\lambda_0}\right)^4 = \frac{16\pi^4}{\lambda_0^4} \end{array}\right.$$

$$\frac{I_s}{I_i} = \frac{\alpha^2}{r^2}\left(\frac{16\pi^4}{\lambda_0^4}\right)\sin^2\theta_1$$

geometry

blue scatters more than red

$I_s \sim (\text{volume})^2$

fades like r^2

$$\left\{\text{let } E_0^2 = I_i\right.$$

Note: the λ_0^4 in this expression came via <u>frequency</u> terms. It would still be λ_0^4 even in a general medium of $RI^* = n$. However, for large particles, we will see that λ_0/n also enters — not here in the fundamental scattering power, but rather in the angular dependence.

*(RI = refractive index).

Still Single Particle Dilute Gas, but now convert from α to n.

The Debye relation: $\boxed{n^2 - 1 = 4\pi\nu\alpha}$ $\left\{ \begin{array}{l} \text{esu units} \\ \text{gas phase} \\ \nu = \#\text{density} \end{array} \right.$

But for dilute gas, $n^2 \simeq 1$, so expand:

$$n^2(c) = \underbrace{n^2_{(c=0)}}_{1} + 2n\left(\frac{\partial n}{\partial c}\right)_{(c=0)} c + \dots \quad \left\{ \begin{array}{l} c = \text{conc. of gas as} \\ g/mL \end{array} \right.$$

$$\Rightarrow n^2(c) - 1 = 2 \cdot \underbrace{n}_{1} \cdot \left(\frac{\partial n}{\partial c}\right)_{c=0} c$$

or... $\boxed{n^2 - 1 = 2c\left(\frac{\partial n}{\partial c}\right)}$ $\left\{ \begin{array}{l} \text{drop explicit } c=0 \\ \text{reminders} \end{array} \right.$

Comparing the 2 boxed equations: $\alpha = \dfrac{2c(\partial n/\partial c)}{4\pi\nu}$

But $\nu = \dfrac{c}{M}\mathcal{N}$, so: $\alpha = \dfrac{2M(\partial n/\partial c)}{4\pi\mathcal{N}}$

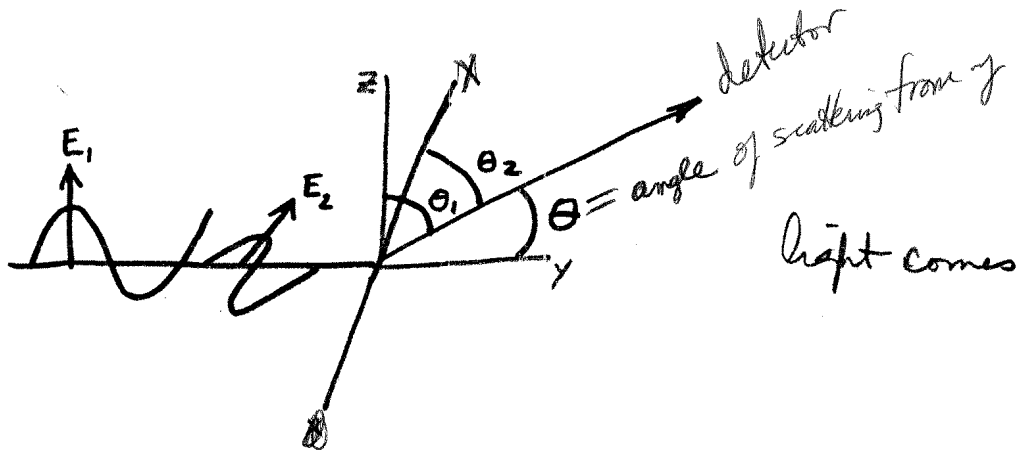
$$\boxed{\alpha = \frac{M(\partial n/\partial c)}{2\pi\mathcal{N}}}$$

Our equation was $\dfrac{I_s}{I_i} = \dfrac{\alpha^2}{r^2}\left(\dfrac{16\pi^4}{\lambda_0^4}\right)\sin^2\theta_1$

With expression for α we get: $\boxed{\dfrac{I_s}{I_i} = \dfrac{4\pi^2}{\lambda_0^4 r^2}\left(\dfrac{M}{\mathcal{N}}\right)^2\left(\dfrac{\partial n}{\partial c}\right)^2 \sin^2\theta_1}$

Scattering from one gas particle

Extension to Unpolarized Light



light comes in along y axis

Unpolarized light = $E_1 \parallel$ to z direction plus $E_2 \parallel$ x direction where there is arbitrary phase relationship ~~to random~~ between E_1 and E_2. Both E_1 and E_2 have same intensity.

$$\frac{I_{1,s}}{\frac{1}{2}I_i} = \frac{4\pi^2 \sin^2\theta_1 \left(dn/dc\right)^2 M^2}{N^2 \lambda^4 r^2}$$

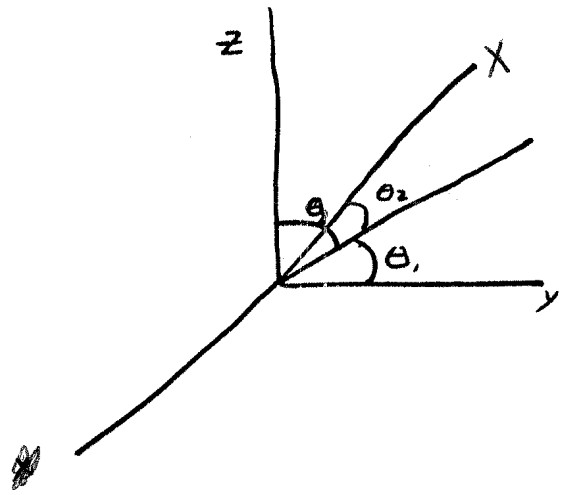
$$\frac{I_{2,s}}{\frac{1}{2}I_i} = \frac{4\pi^2 \sin^2\theta_2 \left(dn/dc\right)^2 M^2}{N^2 \lambda^4 r^2}$$

$$\Rightarrow \quad I_s(\theta) = \frac{2\pi^2 \left(dn/dc\right)^2 M^2}{N^2 \lambda^4 r^2} \left(\sin^2\theta_1 + \sin^2\theta_2\right)$$

unpolarized light will be indicated by $I_s(\theta)$ rather than I_s

But $\sin^2\theta_1 + \sin^2\theta_2 = 1 + \cos^2\theta$

Why:



Because $\theta_1, \theta_2, \theta$ are direction angles we know that:

$$\cos^2\theta_1 + \cos^2\theta_2 + \cos^2\theta = 1$$

$$\left(\text{from } x^2+y^2+z^2 = r^2 \Rightarrow (x/r)^2 + (y/r)^2 + (z/r)^2 = 1\right)$$

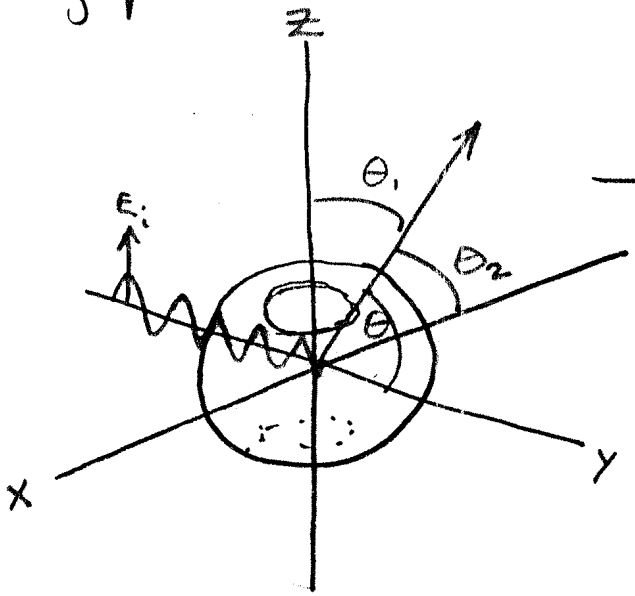
$$\Rightarrow \quad 1 - \sin^2\theta_1 + 1 - \sin^2\theta_2 + \cos^2\theta = 1$$

$$\Rightarrow \quad \sin^2\theta_1 + \sin^2\theta_2 = 1 + \cos^2\theta \qquad \text{QED}$$

$$\therefore \quad \frac{I_s(\theta)}{I_i} = \frac{2\pi^2 \left(\frac{dn}{dc}\right)^2 M^2}{N \lambda^4 \Omega^2}\left(1 + \cos^2\theta\right)$$

This produces a different dependence on angle than for polarized.

Summary of Rayleigh

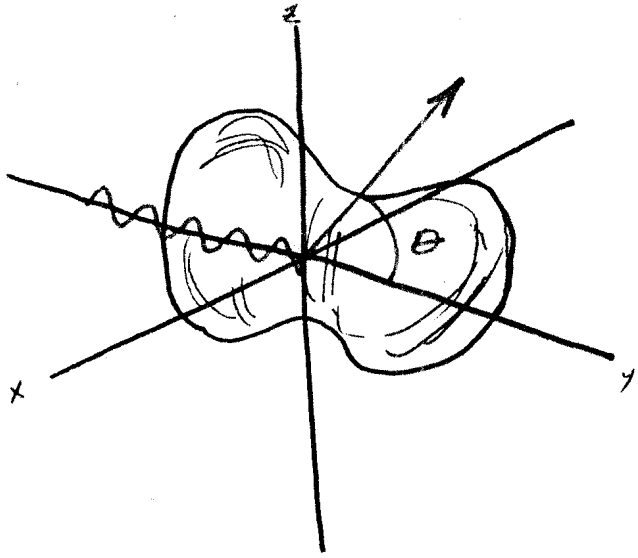


Polarized Rayleigh

Donut shaped figure represents the intensity of the scattered light in various directions

At const θ_1, θ_2 & θ can be varied anywhere

$$\frac{I_s}{I_i} = \frac{4\pi^2 \sin^2\theta_1 M^2 (\partial n/\partial c)^2}{\lambda^4 r^2 N^2}$$



PEANUT SHAPED

Rayleigh Unpolarized

Dumbell shaped shape gives intensity of scattered light in various directions

$$\frac{I_s(\theta)}{I_i} = \frac{2\pi^2 M^2 (\partial n/\partial c)^2}{\lambda^2 r^2 N^2} (1+\cos^2\theta)$$

More Than One Particle: Dilute Gas

Now, electric field at detector will be sum of many terms:

$$\underline{E}_{detector} = \underline{E}_1 + \underline{E}_2 + \underline{E}_3 + \dots \underline{E}_n$$

$$I_{detector} \propto \begin{pmatrix} \underline{E}_1^* \cdot \underline{E}_1 & + \underline{E}_1^* \cdot \underline{E}_2 + \dots & \dots \underline{E}_1^* \cdot \underline{E}_n \\ \vdots & \ddots & \vdots \\ \underline{E}_n^* \cdot \underline{E}_1 & \dots & \underline{E}_n^* \cdot \underline{E}_n \end{pmatrix}$$

Remember: Instantaneously, this isn't really true! $I \propto \underline{E} \times \underline{H}$, but letting it be $\underline{E}^* \cdot \underline{E}$ will suit our purposes for time averaged intensity

$$E_i = E_0 \sin(\omega t + \phi_i) \equiv E_0 e^{i(\omega t + \phi_i)}$$

phase factor giving position of particle w/res. source and detector.

For unstructured gas, off-diagonal terms go off to zero, because phase is random. ⇒ Only diagonal terms survive. Averaging over time gives:

$$I_{detector} \propto n E_0^2$$

{ Note similarity to $\langle r^2 \rangle = n l^2$ }

Thus $I(N \text{ molecules in a gas}) = N\, I(\text{one molecule in a gas})$

$$\frac{I_s}{I_i} = \frac{2\pi^2 N M^2 (\partial n/\partial c)^2}{\lambda_0^4 r^2 \mathcal{N}^2} G$$

G ← geometry factor

$G = 2\sin^2\theta_1$ Vert. Pol.

or $(1+\cos^2\theta)$ Random Pol.

Use one M and one $\mathcal{N}$ and The N

1) ÷ both sides by V = scattering volume

2) $\dfrac{NM}{\mathcal{N} V} = \dfrac{gz}{V} = c$

$$\boxed{\frac{1}{V}\frac{I_s}{I_i} = \frac{2\pi^2 c M (\partial n/\partial c)^2}{\lambda_0^4 r^2 \mathcal{N}} G}$$

dilute, multiparticle gas

$G = 2$ for usual arrangement $\theta_1 = 90°$

$$\boxed{I_s \sim c M \equiv n M^2 \equiv n R^6}$$

Two-component solution: small particles at low concentration.

For gas, we had:

$$n^2 - 1 = 2c\left(dn/dc\right)$$

If we examine the <u>excess</u> scattering, this becomes:

$$n^2 - n_0^2 = 2n_0 c\left(\frac{dn}{dc}\right)$$

$$\therefore \frac{1}{V}\frac{I_s}{I_i} = \frac{2\pi^2 n_0^2 \left(dn/dc\right)^2 Mc}{N \lambda_0^4 R^2} G(\theta)$$

geometry factor
$2\sin^2\theta$, (polarized)
$(1+\cos^2\theta)$ (unpolarized)

Molecular Weight

We will soon see that the equation must be modified for: 1) thermodynamic interaction
2) finite size.

But it's a good time to see what the equation can do in the ideal gas limit.

The equation says $\boxed{I_s \sim cM}$

What average do we get for a polydisperse gas?

$$I_s \sim \sum c_i M_i \underset{\text{define}}{=} c_{total} M_{LS}$$

Thus, $$M_{LS} = \frac{\sum c_i M_i}{c_{total}} = \frac{\sum \left(\frac{g_i}{V}\right) M_i}{\left(\frac{\sum g_i}{V}\right)}$$

$$M_{LS} = \sum w_i M_i \equiv M_w$$

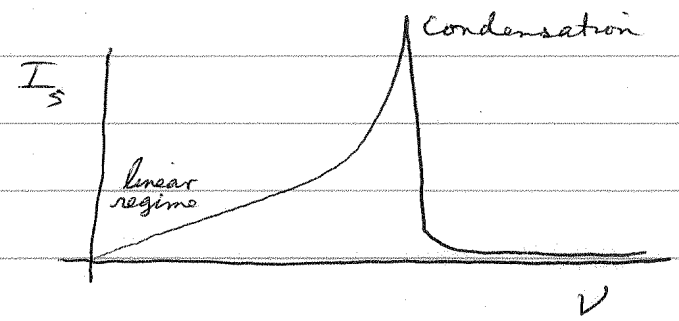
LS gives weight average mass!

This result is for dilute solution limit, but later we shall see how we can always <u>extrapolate to this limit</u>.

Thermodynamic Approach

It isn't quite as deep as wave-particle duality in quantum mechanics, but LS has a dual nature, too: sometimes, a particle approach is best, while at other times it may be better to adopt a thermodynamic viewpoint. The thermodynamic picture is more general and should reduce to the particle picture in the dilute limit.

To begin with, consider I_s vs. ν where ν is the number density of small particles, say H_2O particles in air.



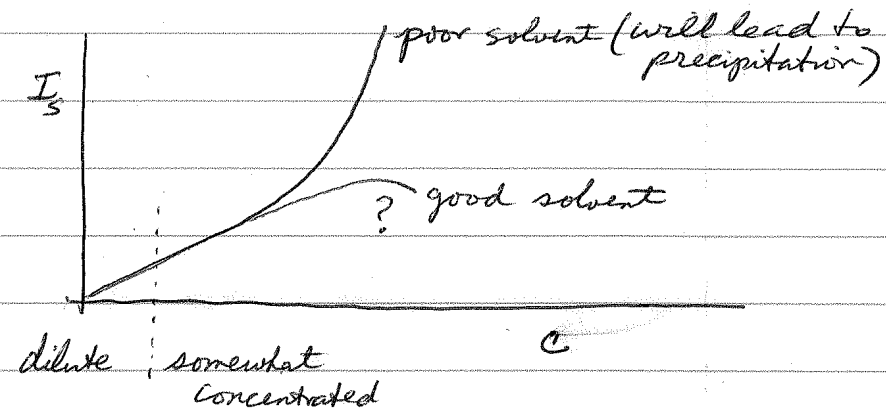
The maximum scattering is when the particles have a size $\approx \lambda$. Particles larger than that do scatter a lot, but only to the forward direction. This is why one can see through rain but not fog. (R. Stein, F2000).

At low number density, there is a linear increase, as we have discussed by "matrix-like" summation on p. LS-12.

Let us now recast this as a polymer/solute problem rather than water/air.

Two-component, non-dilute solutions (Tanford)

overall trend



The turnaround in good solvents is implicit in that a pure, crud-free, glassy polymer (like PMMA) scatters little.

<u>dilute</u>: we can adapt from gas limit

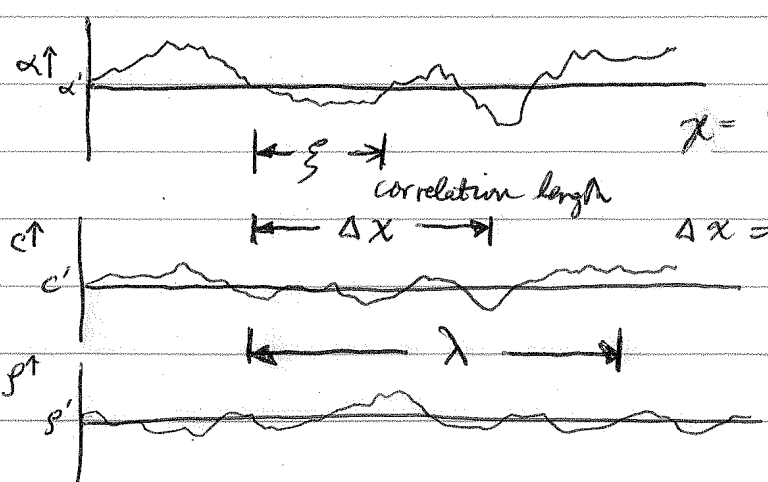
<u>somewhat concentrated</u>: we need thermo, and it should behave well in the dilute limit, too.

To do thermo approach, we go all the way back to:

$$\frac{I_s}{I_0} = \frac{16\pi^4}{\lambda_0^4 r^2}\,\alpha^2 \sin^2\theta_1$$

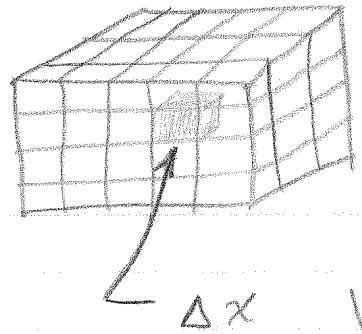
let's stipulate that $\theta_1 = 90°$, so $\sin^2\theta_1 = 1$

<u>3 PLOTS</u>



x = "a direction in space"

Δx = a side of one subvolume



m volume elements

Δx Volume $= \Psi = (\Delta x)^3$

⇒ We want scattering from a single volume element – like single particle case but scat. arises out of α fluctuations.

⇒ We must consider how to add these together.

☆ $\Psi = (\Delta x)^3$ must be large enough to constitute a thermodynamic system.

☆ We want the interaction length ξ to be $< \Delta x$. Then $\delta\alpha_1$ in one volume element and $\delta\alpha_2$ in another are unconnected. The product $\delta\alpha_1 \delta\alpha_2$ could be + or −

☆ <u>But</u> Δx must be less than λ, so that each volume can be treated as a point source.

i.e. $\boxed{\xi < \Delta x < \lambda}$ ☆ Actually $\frac{2\pi}{q}$ probably better gauge than λ.

These are tough demands.

– Cannot treat phase separating systems since $\xi \Rightarrow \infty$

– May be problems with v. large molecules, larger than λ, possibly worst in really dilute solutions?

Maybe the real Zimm treatment deals with this OK.

You might write

$$\frac{I_s}{I_0} = \frac{16\pi^4}{\lambda_0^4 r^2}\left(\alpha' + \delta\alpha_i\right)^2$$

= intrinsic scattering power of
<u>one</u> <u>isolated</u> volume element, i.

What will the scattering be from all of the elements?

$$E_s = (\alpha' + \delta\alpha_1)\, e^{\phi_1} + (\alpha' + \delta\alpha_2)\, e^{\phi_2} + \ldots\ldots$$

$$\Rightarrow I_s = \begin{pmatrix} (\alpha'+\delta\alpha_1)^2 + (\alpha'+\delta\alpha_1)(\alpha'+\delta\alpha_2)\, e^{\overbrace{\phi_2-\phi_1}^{\phi_{12}}} + \ldots & + \\ (\alpha'+\delta\alpha_1)(\alpha'+\delta\alpha_2)\, e^{\phi_{21}} + (\alpha'+\delta\alpha_2)^2 + \ldots & + \\ \vdots & \vdots \\ \cdots & \ddots \end{pmatrix}$$

Although the formalism is by now familiar, this is different. The phase factors are not random, as when the indexes on them represented mobile gas atoms. They are fixed, representing the location of a pair of subvolumes.

In general, this won't be easy to simplify. However, if the correlation length is not too long, we stand a good chance of the fluctuation $\delta\alpha_i$ being uncorrelated from $\delta\alpha_j$. In this case, maybe the <u>excess</u> scattering can be estimated from the diagonals

Somewhat simpler case 1

If long-range interactions are weak, off diagonals go to zero, at least insofar as the $\delta\alpha$ effects are concerned.

$$I_s \sim \sum_{i=1}^{m} (\alpha' + \delta\alpha_i)^2 = \sum_{i=1}^{m} \left(\alpha'^2 + 2\alpha'\delta\alpha + (\delta\alpha)^2\right)$$

$\sum \alpha'^2$ term We could take this one & subdivide very finely i.e. right down to the angstrom level because α is the same in any volume element, no matter what its size. This term is liquid-like and goes to zero. Keeping it would only represent an artifact of the coarse-grained subdivision of volume elements that we have used in our matrix and in computing the phase factors ϕ.

$\sum_i 2\alpha'\delta\alpha_i$ term $\Rightarrow 0$ because $\alpha \sum_i \delta\alpha_i = 0$

The only term that contributes is $\sum (\delta\alpha)^2 = m\,\overline{\delta\alpha^2}$

$$I_s \sim m \sum \overline{\delta\alpha^2}$$

Now.... how to get $\overline{\delta\alpha^2}$?

let $\delta\alpha = \underbrace{\delta\alpha_\rho}_{\text{density fluctuations; occur for both solution and pure solvent}} + \underbrace{\delta\alpha_c}_{\text{concentration fluctuations don't occur for pure solvent.}}$

$$\overline{\delta\alpha^2} = \cancel{\overline{\delta\alpha_\rho^2}} + \cancel{2\,\overline{\delta\alpha_\rho\,\delta\alpha_c}} + \overline{\delta\alpha_c^2}$$

Assume to be the same for solvent and solution. So if we talk about <u>excess</u> intensity scattered above solvent then we are OK to ignore this term.

assume $\delta\alpha_\rho\,\delta\alpha_c$ is uncoupled $\Rightarrow$ average $= 0$

Then $\overline{\delta\alpha^2} = \overline{\delta\alpha_c^2}$

2 assumptions

We will now develop $\overline{\delta\alpha_c^2}$

Let us regroup some: We have shown

$$I_s \sim m\,\overline{\delta\alpha_c^2}$$

excess above solvent

m = # volume elements

$\xi < \Delta x < \lambda$

Plug into the multiple particle, random phase expression:

$$\frac{1}{V}\frac{I_s}{I_i} = \frac{m}{V}\left(\frac{16\pi^4}{\lambda_0^4 R^2}\sin^2\theta_1\right)\overline{\delta\alpha_c^2}$$

assumes V polarization

note: $\dfrac{m}{V} = \dfrac{1}{\psi} = \dfrac{1}{(\Delta x)^3}$

$$\frac{1}{V}\frac{I_s}{I_i} = \frac{1}{\psi}\left(\frac{16\pi^4}{\lambda_0^4 R^2}\sin^2\theta_1\right)\overline{\delta\alpha_c^2}$$

Recall, we had

As for gases, we must get from α to c.

Recall for gases: $n^2 - 1 = 2c(dn/dc)$ [expansion of $n^2 = n_0^2 + 2n_0\left(\frac{dn}{dc}\right)_0$]

$n^2 - 1 = 4\pi\nu\alpha$ [Clausius-Mosotti Eqn.]

$$\Rightarrow \alpha = \frac{c\,(dn/dc)}{2\pi\nu}$$

For polymer solutions: (eqA) $n^2 - n_0^2 = 2n\,\delta c\,(dn/dc)$ [expand about pure solvent]

(eqB) $n^2 - n_{c'}^2 = 4\pi\nu\,\frac{d\alpha_c}{}$

assuming ρ terms vanish for the reasons discussed

Assuming $n_{c'}^2 \simeq n_0^2$ then equate A & B

$$\frac{\delta\alpha_c}{\delta c} = \frac{n_0\,(dn/dc)}{2\pi\nu}$$

or... $$\overline{(d\alpha)^2} = \frac{n_0^2\,(dn/dc)^2}{4\pi^2\nu^2}\,\overline{(dc)^2}$$

But $\nu = \frac{m}{V} = \frac{1}{\psi}$

So $$\overline{(d\alpha)^2} = \frac{n_0^2\,\psi^2\,(dn/dc)^2}{4\pi^2}\,\overline{(dc)^2}$$

Now put this into eqn. from previous page. One power of ψ cancels. A $4\pi^2$ cancels, too.

So... $\frac{1}{V}\frac{I_s}{I_o} = \frac{4\pi^2 \psi n_o^2 (\partial n/\partial c)^2 \overline{(\delta c)^2}}{\lambda_o^4 r^2}$ Same as Tanford eq. 17-18 except we limited to $\theta_1 = 90°$

Now we require an expression for $\overline{(\delta c)^2}$, the mean square concentration fluctuation. This is going to come from Boltzmann statistics.

$$P(\delta c) = e^{-\Delta G(\delta c)/kT}$$

= probability density of an element being at a concentration $c' + \delta c$.

where ΔG is the free energy difference between concentrations $c' + \delta c$ and c' on a per molecule basis.

This $\Delta G(\delta c)$ will come from an expansion:

$$\Delta G(\delta c) = G(c' + \delta c) - G(c') = \left(\frac{\partial G}{\partial c}\right)_{c'} \delta c + \frac{1}{2!}\left(\frac{\partial^2 G}{\partial c^2}\right)(\delta c)^2 + \ldots$$

But c' is the <u>equilibrium concentration</u>. By definition $\left(\frac{\partial G}{\partial c}\right)_{c'} = 0$.

$$\therefore \quad \Delta G(\delta c) \simeq \frac{1}{2}\left(\frac{\partial^2 G}{\partial c^2}\right)_{c'} (\delta c)^2$$

and $$P(\delta c) = e^{\underbrace{-\frac{1}{2}\left(\frac{\partial^2 G}{\partial c^2}\right)_{c'}}_{\text{Just a constant Call it } A} (\delta c)^2 / kT}$$

NOT A BAD PLACE TO CONTEMPLATE WHAT HAPPENS WHEN $\frac{\partial^2 G}{\partial c^2} > 0$

actually from $-\infty$ to ∞ but does not really require it because (δc) is squared

$$\therefore \quad \overline{(\delta c)^2} = \frac{\int_{\delta c = 0}^{\delta c = \infty} (\delta c)^2 e^{-A(\delta c)^2} d(\delta c)}{\int_0^\infty e^{-A(\delta c)^2} d(\delta c)}$$

{ Integrals of type $\int_0^\infty x^2 e^{-Ax^2} dx$ and $\int_0^\infty e^{-Ax^2} dx$ }

The result of evaluating these standard integrals is:

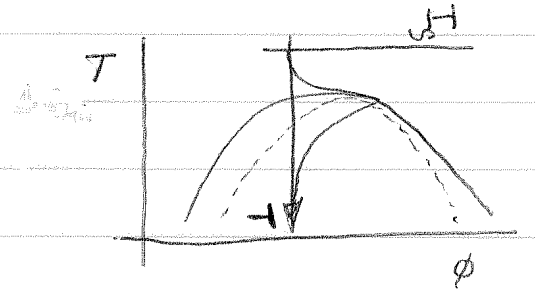
$$\overline{(\delta c)^2} = \frac{kT}{\left(\frac{\partial^2 G}{\partial c^2}\right)_{T,p}\Bigg|_{c=c'}}$$

↑ Henceforth, it is understood that derivatives are evaluated at c'

Does it make sense? Well, G is within a constant of ΔG_{mix} and we saw that at $\frac{\partial^2 \Delta G_{mix}}{\partial c^2} = 0$ we have the SPINODAL CURVE, which means that BIG concentration fluctuations occur without hesitation.

$\overline{(\delta c)^2}$ does not really go off to ∞ because the terms we truncated prevent that.

So, in fact, the scattering just gets real large.



I_s vs. T is actually used to locate spinodals, in a method called PICS: pulse induced critical scattering.

Now we must calculate $(\partial^2 G/\partial c^2)$.

Let n_1 and n_2 be mole #'s such that *

$$n_1 \bar{V}_1 + n_2 \bar{V}_2 = \Psi$$

Tanford claims $\bar{V}_1 = \bar{V}_1(c')$.
Not true, I think, but a close approximation.

$$\Rightarrow dn_1 = -dn_2 \frac{\bar{V}_2}{\bar{V}_1} \quad \text{since } \Psi = \text{constant}$$

Now $dG = \mu_1 dn_1 + \mu_2 dn_2$ @ const T, P

$$dG = \left(\mu_1\left(\frac{-\bar{V}_2}{\bar{V}_1}\right) + \mu_2\right) dn_2 \qquad \boxed{\text{EQ. A}}$$

But $\frac{n_2}{\Psi} = \frac{c}{M}$ That is.... $\frac{\text{mol}}{\text{mL}} = \frac{\left(\frac{g}{\text{mL}}\right)}{\left(\frac{g}{\text{mol}}\right)}$

So... $dn_2 = \frac{\Psi}{M} dc \qquad \boxed{\text{EQ. B}}$

PLUG B into A $\Rightarrow$ $dG = \left(\mu_1\left(\frac{-\bar{V}_2}{\bar{V}_1}\right) + \mu_2\right)\left(\frac{\Psi}{M}\right) dc$

So... $\frac{\partial G}{\partial c} = \left(\mu_2 - \frac{\bar{V}_2}{\bar{V}_1}\mu_1\right)\left(\frac{\Psi}{M}\right)$

* It can be argued (Dr. Carpenter) that if Ψ is fixed and T, P are also, is not the system then fixed? Answer: No! Because composition can still fluctuate.

So... take 2nd deriv to get:

$$\left(\frac{\partial^2 G}{\partial c^2}\right)_{T,P} = \left(\frac{\partial \mu_2}{\partial c} - \frac{\bar{V}_2}{\bar{V}_1}\frac{\partial \mu_1}{\partial c}\right)\frac{\Psi}{M}$$

we have assumed $\frac{\partial}{\partial c}\left(\frac{\bar{V}_2}{\bar{V}_1}\right) = 0$

Now apply Gibbs-Duhem: $d\mu_2 = -\frac{n_1 d\mu_1}{n_2}$

$$\left(\frac{\partial^2 G}{\partial c^2}\right)_{T,P} = \underbrace{\left(\frac{-n_1}{n_2} - \frac{\bar{V}_2}{\bar{V}_1}\right)}\left(\frac{\partial \mu_1}{\partial c}\right)\frac{\Psi}{M}$$

appears to be no real physical significance to this term, but it does simplify.

$$\left(\frac{\partial^2 G}{\partial c^2}\right)_{T,P} = -\left(\frac{n_1\bar{V}_1 + n_2\bar{V}_2}{n_2 M}\right)\left(\frac{\partial \mu_1}{\partial c}\right)\frac{\Psi}{\bar{V}_1}$$

$$= -\left(\frac{1}{c}\right)\left(\frac{\partial \mu_1}{\partial c}\right)\frac{\Psi}{\bar{V}_1}$$

Thus, $\overline{(\delta c)^2} = \dfrac{kT}{\left(\frac{\partial^2 G}{\partial c^2}\right)_{T,P}} \Rightarrow \dfrac{-kT\, c\bar{V}_1}{\Psi\left(\partial\mu_1/\partial c\right)}$

But we had $\dfrac{1}{V}\dfrac{I_s}{I_i} = \dfrac{4\pi^2 \Psi n_0^2 \left(\partial n/\partial c\right)^2}{\lambda_0^4 r^2}\overline{(\delta c)^2}$

So this evolves to:

$$\frac{1}{V}\frac{I_s}{I_i} = \left(\frac{4\pi^2 \Psi n_0^2 (\partial n/\partial c)^2}{\lambda_0^4 r^2}\right) \times \left(\frac{-kTc\bar{V}_1}{\Psi(\partial\mu_1/\partial c)}\right)$$

Note: Ψ cancels out, as it must because we defined it sort of vaguely <u>BUT</u> to meet specific criteria. So we needed it .... and we needed to get rid of it!

$$\frac{1}{V}\frac{I_s}{I_i} = \frac{4\pi^2 n_0^2 (\partial n/\partial c)^2}{\lambda_0^4 r^2} \quad \frac{c}{\left(\frac{-1}{kT\bar{V}_1}\right)(\partial\mu_1/\partial c)}$$

But what is $\partial\mu_1/\partial c$? It clearly represents the energy to generate a concentration fluctuation. If it takes lots of energy to make a fluctuation, then they will not occur .... and scattering declines.

Well, we have a formalism for all this already.

$$-\pi V_1^\circ \simeq \mu_1 - \mu_1^\circ = -RT\bar{V}_1 c\left(\frac{1}{M} + A_2 c + A_3 c^2 + \cdots\right)$$

$$\Rightarrow \partial\mu_1/\partial c = -RT\bar{V}_1\left(\frac{1}{M} + 2A_2 c + 3A_3 c^2 + \cdots\right) = -V_1^\circ\left(\frac{\partial\pi}{\partial c}\right)$$

Then $$\frac{-1}{kT\bar{V}_1}\left(\frac{\partial\mu_1}{\partial c}\right) = N\left(\frac{1}{M} + 2A_2 c + 3A_3 c^2 + \cdots\right) = \frac{-N}{RT}\left(\frac{\partial\pi}{\partial c}\right)$$

$$\frac{1}{V}\frac{I_s}{I_i} = \overbrace{\frac{4\pi^2 n_0^2 \left(\partial n/\partial c\right)^2}{\lambda_0^4 r^2}}^{\text{OPTICAL STUFF}} \overbrace{\frac{c}{N\left(\frac{1}{M} + 2A_2 c + 3A_3 c^2 + \dots\right)}}^{\text{THERMODYNAMIC STUFF}}$$

$$\text{or....} \quad \frac{1}{V}\frac{I_s}{I_i} = \frac{4\pi^2 n_0^2 \left(\partial n/\partial c\right)^2}{N \lambda_0^4 r^2} \frac{c}{\frac{1}{RT}\left(\partial \pi/\partial c\right)}$$

So... The LS experiment gives you everything the osmometer does (for monodisperse samples anyway).

This is often rearranged into new terms.

Define: $\mathcal{R} = \frac{r^2}{V}\frac{I_s}{I_i}$ = Rayleigh factor $\left\{\begin{matrix}\text{not "ratio" as is} \\ \text{often said}\end{matrix}\right\}$

UNITS: cm^{-1}

$$K = \frac{4\pi^2 n_0^2 \left(\partial n/\partial c\right)^2}{\lambda_0^4 N} = \text{"optical constant"}$$

Then we have $\mathcal{R} = \frac{Kc}{\frac{1}{RT}\left(\partial \pi/\partial c\right)}$

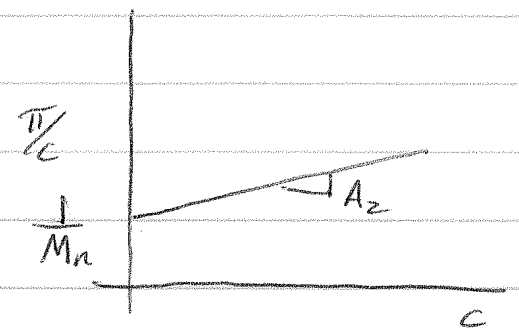
$$\text{or...} \quad \boxed{\frac{Kc}{\mathcal{R}} = \frac{1}{RT}\left(\partial \pi/\partial c\right)} = \frac{1}{RT}\left(RT\left(\frac{1}{M} + 2A_2 c + \dots\right)\right)$$

easily memorized forms

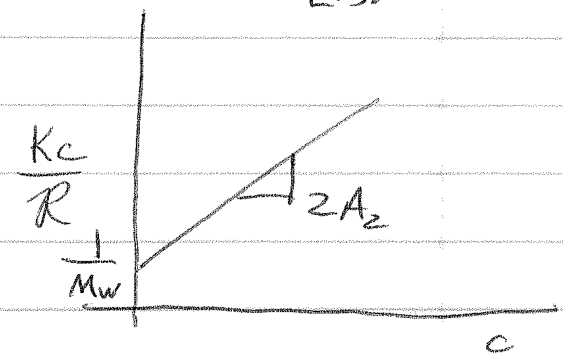
$$\text{or} \quad \boxed{\frac{Kc}{\mathcal{R}} = \frac{1}{M} + 2A_2 c + \dots}$$

Graphically, with comparison to osmometer & limitations & characteristics

OSMOMETER



L.S.



Limits

$10^4 \lesssim M_n \lesssim 10^6$

↑ due to membrane

↑ due to sensitivity

Limits

$500 \lesssim M_w \lesssim 10^8$

↑ due to sensitivity

↑ due to need to go to low angles (see below) depends on how good you are!

CHARACTERISTICS

responds slowly to energy required to make large, macroscopic pressure changes, distance scale $\simeq$ cm.

CHARACTERISTICS

responds instantly to small energies required to thermally stimulate small pressure changes over microscopic distances ($\simeq \lambda_0/n$, see below).

Problem: - leaks

- not easily automated / coupled to other techniques

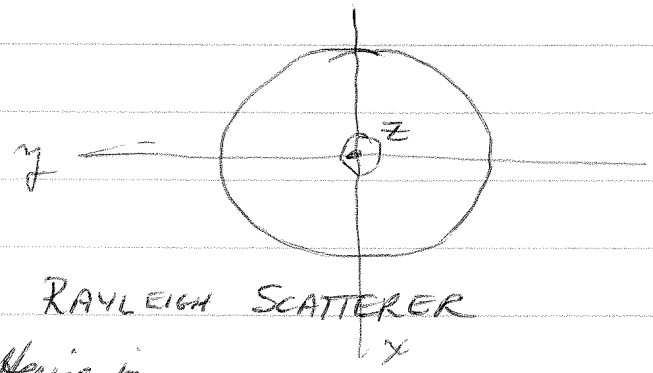
Problem: dust, finite size.

EXTENSION TO LARGE PARTICLES

The development so far is due to some of the greatest minds in science – Einstein, Smoluchowski, Debye, Rayleigh – and much of the development preceeds belief in large molecules.

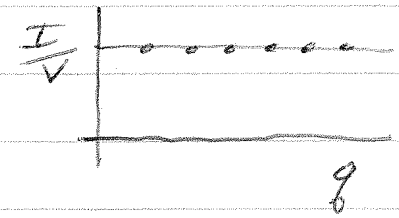
But surely the observation concerning the unusual behavior – distorted donut – of large particles must have been made.

Looking down on a donut, z polarized incident light

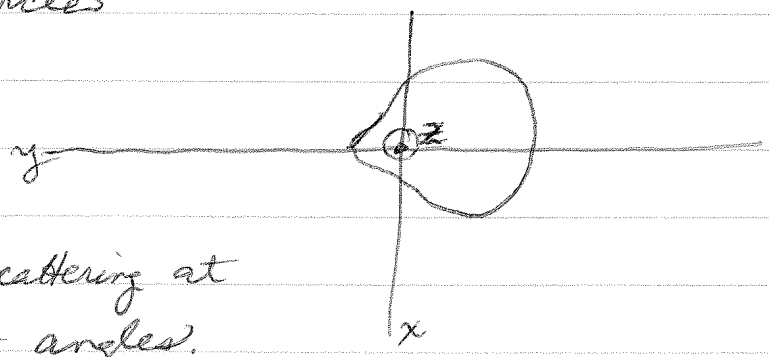


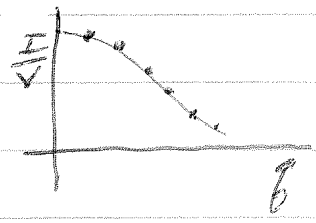
Small particle: RAYLEIGH SCATTERER

uniform scattering in all directions in the horizonal plane



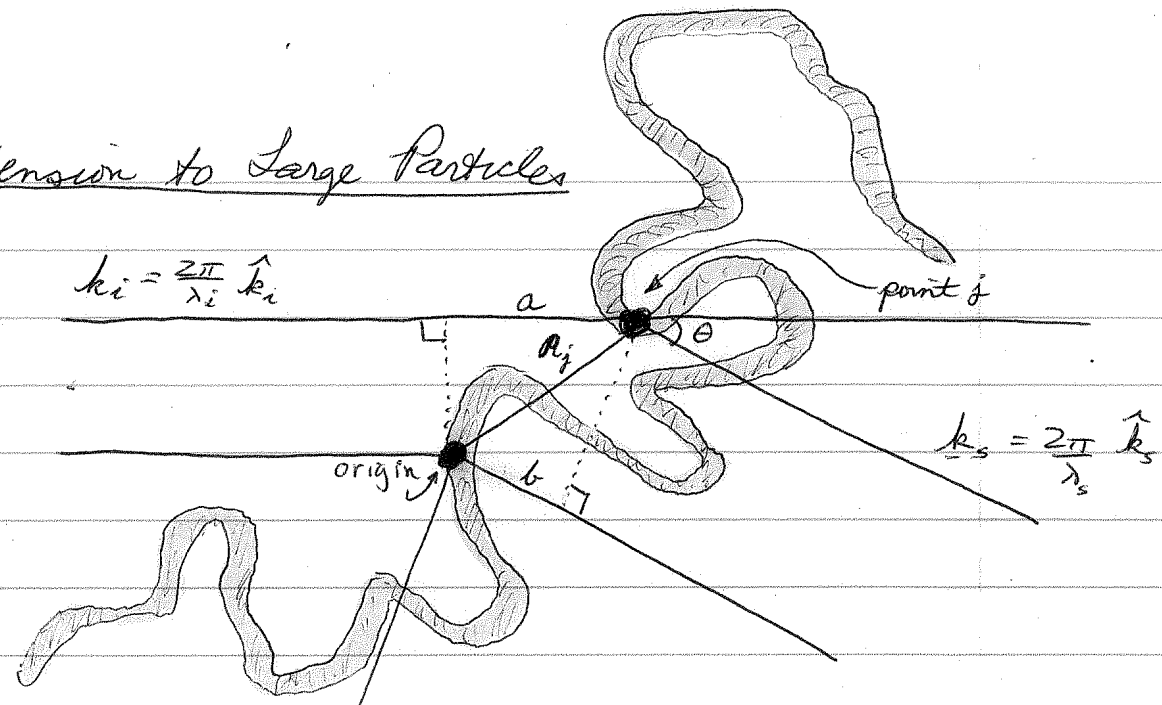
Large particles





reduced scattering at larger angles.

Extension to Large Particles



$\underline{q} = \underline{k}_s - \underline{k}_i$ (bisects them)

Note: all λ's are λ_0/n here, where n = solution refractive index
it is assumed that $\lambda_i = \lambda_s$

extra distance of ray through point j compared to origin:

$$= a - b$$

$$\frac{\text{phase shift}}{2\pi} = \frac{\phi}{2\pi} = (\underline{R}_j \cdot \underline{k}_i) - (\underline{R}_j \cdot \underline{k}_s)$$

$$= -\underline{q} \cdot \underline{R}_j$$

Before we start adding fields & squaring, let's look at $|\underline{q}|$

It turns out that the <u>magnitude</u> of $\underline{q}$ is useful because we can often assume that molecules re-orient randomly & rapidly w/res. to $\underline{q}$.

$$q = |\underline{q}| = \sqrt{(\underline{k}_i - \underline{k}_s)\cdot(\underline{k}_i - \underline{k}_s)}$$

$$= \sqrt{k_i^2 - 2k_i k_s \cos\theta + k_s^2}$$

$$= \sqrt{\left(\frac{2\pi}{\lambda}\right)^2 (2 - 2\cos\theta)}$$

$$= \frac{2\pi}{\lambda}\sqrt{2(1-\cos\theta)}$$

But trig. tells us that $1-\cos\theta = 2\sin^2\frac{\theta}{2}$

so... $q = \frac{2\pi}{\lambda}\sqrt{2\left(2\sin^2\frac{\theta}{2}\right)} = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$

Recall $\lambda = \lambda_0/n$

So... $q = \frac{4\pi n}{\lambda_0}\sin\frac{\theta}{2}$

Other symbols for q : K, s, h, u

Now we must add & square the fields E_j from all the N scatterers in the molecule

$$E_j = E_0 e^{i(\omega t + \phi)} = E_0 e^{i(\omega t - \underline{q}\cdot\underline{R}_j)}$$

$$E_s = \sum_{j=1}^{N} E_j = E_0 e^{i\omega t} \sum_{j=0}^{N} e^{-i\underline{q}\cdot\underline{R}_j}$$

$$I_s(\theta) = |E_0|^2 \sum_{i,j}^{N} e^{i\underline{q}\cdot\underbrace{(\underline{r}_i - \underline{r}_j)}_{\text{call this } \underline{r}_{ij}}}$$

<u>q=0 CASE</u> Clearly, from this equation, at $q=0$ we get:

$$I_s(0) = |E_0|^2 \sum_{i=1}^{N}\sum_{j=1}^{N} 1 = N^2 |E_0|^2$$

Note how different this is from our finite angle gas expression where we added and then squared the ~~phases~~ fields of many particles, scattered to finite ~~[illegible]~~ angles. Because those particles can change their ϕ at finite q, we can "wipe out" the off-diagonal terms. Here, no matter how the scattering segments move, at $q=0$ they stay in phase.

I think this bears a formal resemblance to the "shot noise" term in DLS

<u>q = finite case</u> Interpretation: we won't get exactly zero off diagonals as in the independent particles case because particles <u>are</u> correlated now due to connectedness.

Define $P(\theta) = \dfrac{I_s(\theta)}{I(0)}\Big|_{c=0}$ So $P(\theta)$ is <u>always</u> <1 since $I(\theta)$ is the in phase intensity.

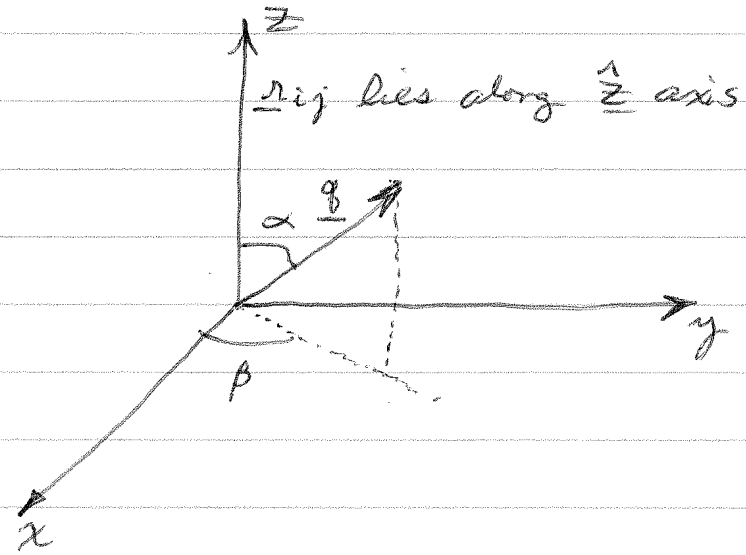
A note: even at this point the inverse nature of LS is evident: for $q=0$ see nothing high $q \Rightarrow$ high magnification

$$\Rightarrow P(\theta) = \frac{1}{N^2} \sum_{i,j=1}^{N} e^{i\underline{q}\cdot\underline{r}_{ij}}$$

Orientational Averaging

The foregoing expression gives $P(\theta)$ for one orientation of $\underline{r}_{ij}$ with respect to $\underline{q}$. But in normal solutions, $\underline{r}_{ij}$ can reorient freely. Typically, many reorientations will occur in the time required to complete an intensity measurement, so we should perform an average of $\underline{r}_{ij}$ w/respect to some fixed $\underline{q}$.

Equivalently, we could let $\underline{r}_{ij}$ "stand still" and let $\underline{q}$ assume all orientations:



This kind of problem occurs often in physics.

We have to average out each term involving $\underline{q} \cdot r_{ij}$ over all the possible orientations between $\underline{q}$ and r_{ij}.

$$\text{Average of one such term in } P(\theta) = \frac{\int_{\beta=0}^{2\pi} \int_{\alpha=0}^{\pi} e^{i\underline{q} \cdot \underline{r}_{ij}} \sin\alpha \, d\alpha \, d\beta}{4\pi}$$

{ This eqn. comes from $\iiint \sin\alpha \, d\alpha \, d\beta \, r^2 dr = \frac{4}{3}\pi R^3$
i.e. $d^3V = r^2 \sin\alpha \, dr \, d\alpha \, d\beta$ for spherical polar coordinates
We do not vary r in this problem, since r_{ij} is fixed in magnitude & only varies by orientation. }

$$\Rightarrow \frac{1}{4\pi} \int_0^{2\pi} d\beta \int_0^{\pi} e^{iqr_{ij}\cos\alpha} \sin\alpha \, d\alpha$$

$$\Rightarrow \frac{1}{2} \int_0^{\pi} e^{iqr_{ij}\cos\alpha} \sin\alpha \, d\alpha$$

let $iqr_{ij}\cos\alpha = u$

$$du = (-\sin\alpha)(iqr_{ij}) \, d\alpha$$

So... $\sin\alpha \, d\alpha = \dfrac{du}{-iqr_{ij}}$

$$\Rightarrow \frac{1}{2} \cdot \frac{1}{(-iqr_{ij})} \cdot \int e^u \, du$$

$$\Rightarrow \frac{-1}{2iqr_{ij}} \underbrace{e^{iqr_{ij}\cos\alpha}\Big|_0^{\pi}}_{e^{-iqr_{ij}} - e^{+iqr_{ij}}}$$

Now recall from complex variables that $\sin x = \dfrac{e^{ix} - e^{-ix}}{2i}$

Thus, $e^{-iqr_{ij}} - e^{+iqr_{ij}} = -2i \sin q r_{ij}$

So.... "average of one such term in $P(\theta)$" $= \dfrac{\sin q r_{ij}}{q r_{ij}}$

So... at last!

$$\boxed{P(\theta) = \frac{1}{N^2} \sum_{i,j=1}^{N} \frac{\sin q r_{ij}}{q r_{ij}}}$$

where $q = \dfrac{4\pi n}{\lambda_0} \sin \dfrac{\theta}{2}$

$r_{ij} = |\underline{r}_i - \underline{r}_j|$

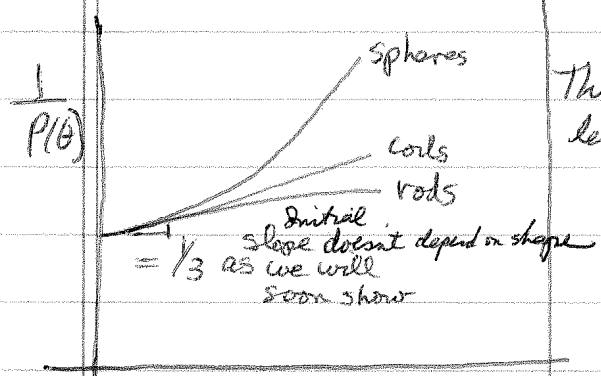
N = # scattering elements

It was assumed that all r_{ij} can orient w/res $\underline{q}$ <u>randomly</u>

Now there are 2 options, depending on a priori shape information and monodispersity info and overall size.

- Particle shape is known, or sample known monodisperse. Then it is possible to develop explicit equations for $P(\theta)$.

examples



Thin rod length L

$$P(\theta) = \frac{2}{x}\int_0^x \frac{\sin u}{u}\,du - \left(\frac{\sin(x/2)}{(x/2)}\right)^2$$

$$x = qL$$

$$R_g^2 = L^2/12$$

Uniform sphere radius R

$$P(\theta) = \left(\frac{3(\sin x - x\cos x)}{x^3}\right)^2$$

$$x = qR$$

$$R_g^2 = \frac{3}{5}R^2$$

So... if you know that the sample is monodisperse, you can generate $P(\theta)$ curves & see if they match experiment!

Gaussian Coil* $P(\theta) = \frac{2}{x^2}\left(e^{-x} - 1 + x\right)$

mean squared end to end length, $\langle r^2 \rangle$

$$x = q^2\frac{\langle r^2\rangle}{6} = q^2 R_g$$

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

*This "Debye equation" seems to work OK also for expanded coils that are not too large.

- Particle shape is not known, or sample polydisperse. Then it is still possible to obtain a radius of gyration, provided that measurements can be made at sufficiently low q R_g.

- Shape not known, continued.

To get R_g, regardless of shape, we obtain the limiting form of $P(\theta)$ at low q.

We had $$P(\theta) = \frac{1}{N^2} \sum_{i,j} \frac{\sin q r_{ij}}{q r_{ij}}$$

but $\sin x \simeq x - \frac{x^3}{3!} + \frac{x^4}{5!} \ldots$ at low x, i.e. low $q r_{ij}$

So $$\frac{\sin x}{x} \simeq 1 - \frac{x^2}{6}$$

$$P(\theta) = \frac{1}{N^2} \sum_{i,j} \left(1 - \frac{q^2}{6} r_{ij}^2\right)$$

But $\sum_{i,j} 1 = N^2$

and $\sum_{i,j} r_{ij}^2 = 2N^2 R_g^2$ { See Tanford Sec. 9j, eq. 9-34 p.167

<u>Inverse Plot</u>

So $$P(\theta) = 1 - \frac{q^2 R_g^2}{3} + \ldots$$

or... $$\frac{1}{P(\theta)} \simeq 1 + \frac{q^2 R_g^2}{3}$$ which explains the <u>initial slope</u> in figure on previous page.

If polydisperse, get Σ average of R_g^2 : $$R_{g_{LS}}^2 = \frac{\sum n_i M_i^2 R_g^2}{\sum n_i M_i^2}$$

Guinier Plot

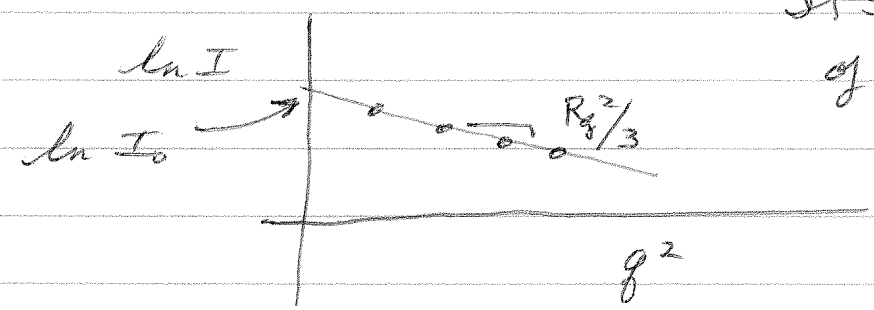
This limiting form has an important alternative form.

$$P(\theta) \cong 1 - \frac{q^2 R_g^2}{3} \approx e^{-q^2 R_g^2/3}$$

Thus $\ln P(\theta) = \ln\left(I/I_0\right) = \ln I - \ln I_0 = -\frac{q^2 R_g^2}{3}$

The important advantage of this form is that I_0 need not be estimated to get R_g! Just plot $\ln I$ vs. q^2

It's the miracle of logarithms at work.



Limitations

In order to use either the inverse or Guinier plots, $I(\theta)$ must actually be decreasing. This will be a sensitive function of radius because the decreasing term is the square of qR_g. As a practical guide, R_g should be bigger than $\simeq \lambda/20$. If not, you have to be very careful .... or consider another technique (dynamic LS or X-ray or neutron scattering).

laser	λ_0/Å	λ in toluene/Å	$\lambda/20$
Ar^+	4880	3250	163
Ar^+	5145	3430	172
HeNe	6328	4220	210

PUTTING IT ALL TOGETHER

THE WRONG WAY (However, you can find it in respected books – e.g. Kerker) also van Holde

"Pasting" the finite size results onto our previous thermodynamic results, which here would be valid only at $q = 0$.

Before we did finite size, we had: $\frac{Kc}{\mathcal{R}} = \frac{1}{M} + 2A_2 c + \dots$

recall that $\mathcal{R} = \frac{r^2 I_s}{V I_i}$ i.e. $\mathcal{R} \sim I_s$

So $\frac{Kc}{\mathcal{R}} \sim \frac{1}{I_s} \sim \frac{1}{I_s(0)\, P(\theta)}$

So we could "patch up" the small scatterer equation like this:
guess

$$\frac{Kc}{\mathcal{R}} \overset{?}{=} \frac{1}{P(\theta)} \left(\frac{1}{M} + 2A_2 c + \dots \right)$$

$$\overset{?}{=} \frac{1}{\left(1 - \frac{q^2 R_g^2}{3}\right)} \cdot \left(\frac{1}{M} + 2A_2 c + \dots \right)$$

$$\frac{Kc}{\mathcal{R}} \overset{?}{\approx} \left(\frac{1}{M} + 2A_2 c + \dots \right) \left(1 + \frac{q^2 R_g^2}{3} + \dots \right)$$

It's wrong ... but it's close, and it even behaves OK in the $c = 0$ or $q = 0$ limits:

$$\lim_{q \to 0} \frac{Kc}{\mathcal{R}} = \frac{1}{M} + 2A_2 c + \dots \qquad \lim_{c \to 0} \frac{Kc}{\mathcal{R}} = \frac{1}{M} \left(1 + \frac{q^2 R_g^2}{3} + \dots \right)$$

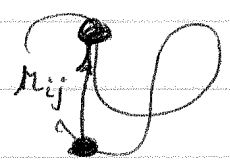
PUTTING IT ALL TOGETHER

THE RIGHT WAY (Zimm, J. Chem. Phys. 16(12), 1093-1116, 1948) (two papers)

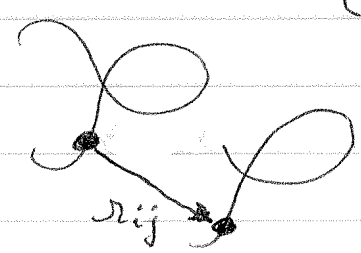
What he did: $I_s = \sum e^{i \underline{q} \cdot \underline{r}_{ij}}$

all possible segments, whether on same polymer or not

So, this way you can include these interferences (intramolecular)



as well as these ones (intermolecular)



So... that's pretty hard.

Assumptions:

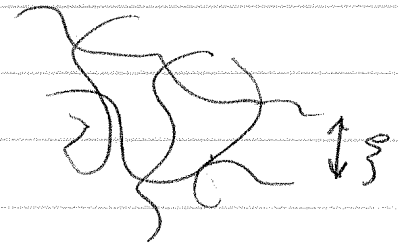
Result:

$$\frac{Kc}{\mathcal{R}} \simeq \frac{1}{M P(\theta)} + 2A_2 c$$

The $P(\theta)$ term applies only to the intercept, not to the virial term.

A MODERN CHOICE

forget molecular parameters. Leave it as a thermodynamic expression, modified by a "correlation length" representing the persistence of phase among all scatterers, whatever chain they may be on.



$$\frac{Kc}{\mathcal{R}} = \frac{1}{RT}\left(\frac{\partial \Pi}{\partial c}\right)_{T,P}\left(1 + q^2\xi^2\right)$$

$$\lim_{c \to 0} \xi^2 = \frac{R_g^2}{3}$$

$$\lim_{q \to 0} \frac{1}{RT}\left(\frac{\partial \Pi}{\partial c}\right)_{T,P} = \frac{1}{M}$$