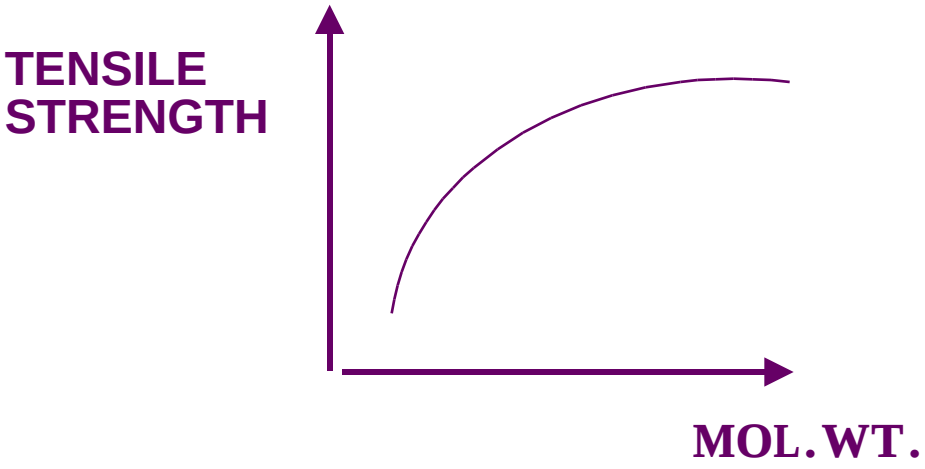
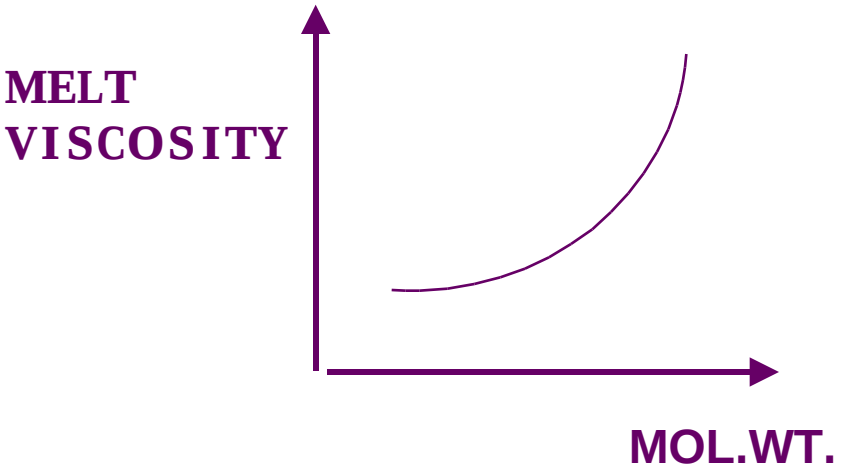
MOLECULAR WEIGHT

"Drop the idea of large molecules. Organic molecules with a molecular weight higher than 5000 do not exist."
—Advice given to Hermann Staudinger*

MOLECULAR WEIGHT

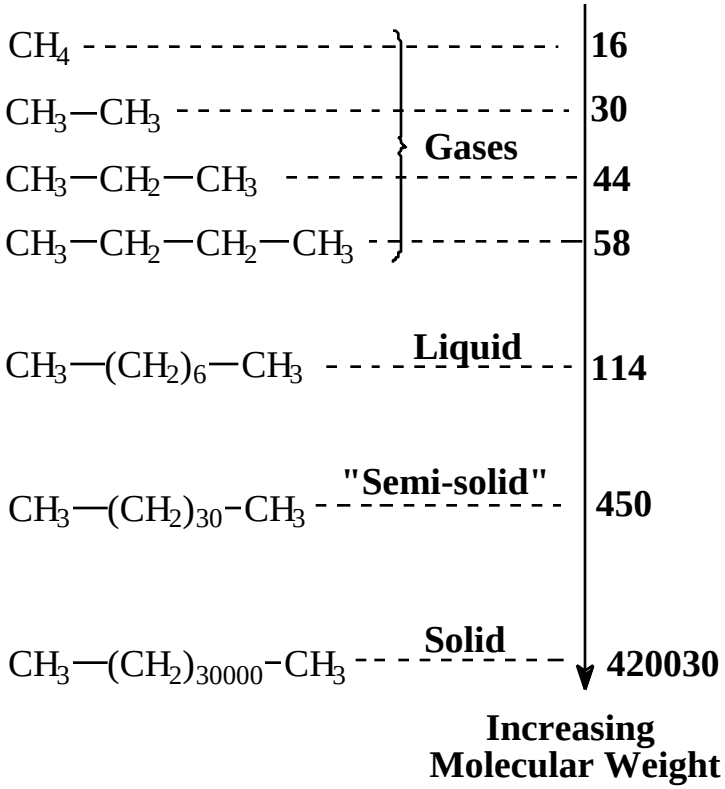
WHY IS IT IMPORTANT ?





Molecular Weight - Some Initial Observations

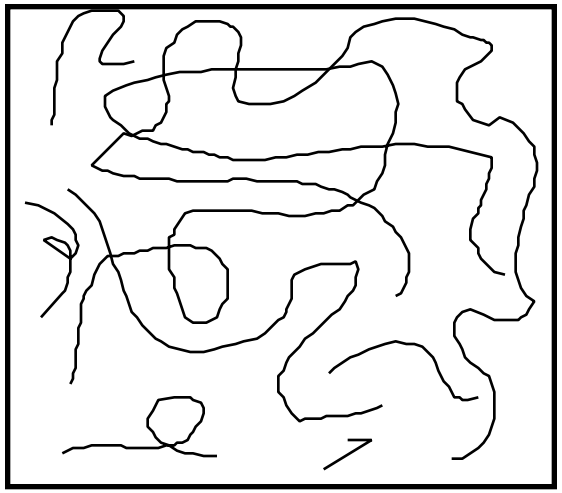
How does the molecular weight of a high polymer differ from that of a low-molecular-weight substance ?



Molecular weight M simply:

(# C atoms x 12) + (# H atoms x 1)

But for most polymers there is a *Distribution of Chain Lengths*



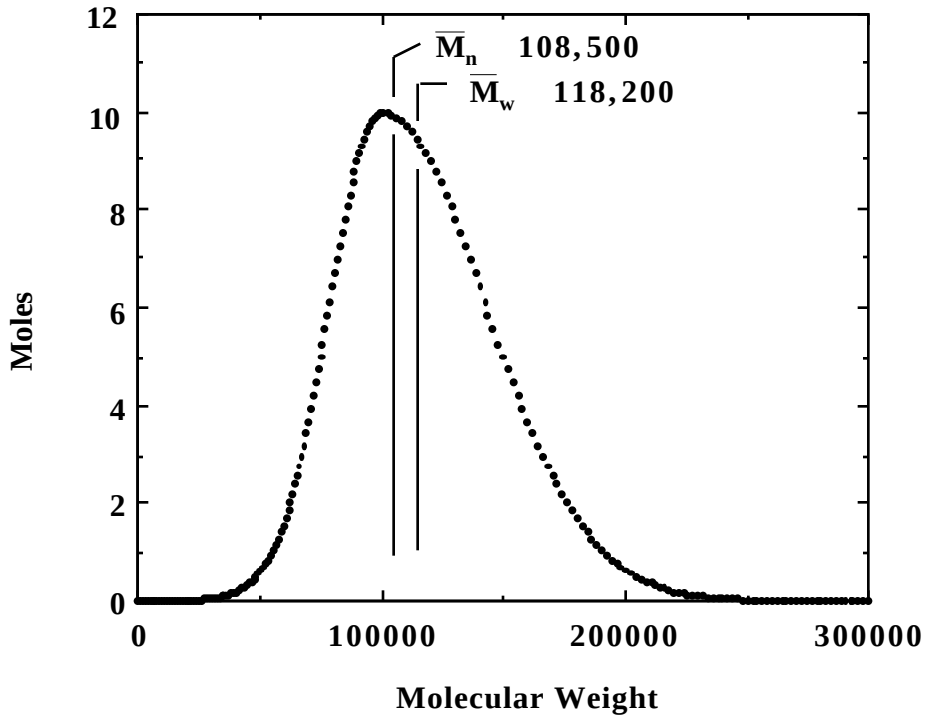
We must therefore define an *Average Degree of Polymerization* ($\overline{DP}$)

The average number of structural units in the polymer chain

And an *Average Molecular Weight* ($\overline{M}$)

The average degree of polymerization times the molecular weight of the structural unit, M_0

MOLECULAR WEIGHT



Number Average

$$\overline{M}_n = \frac{\sum N_x M_x}{\sum N_x}$$

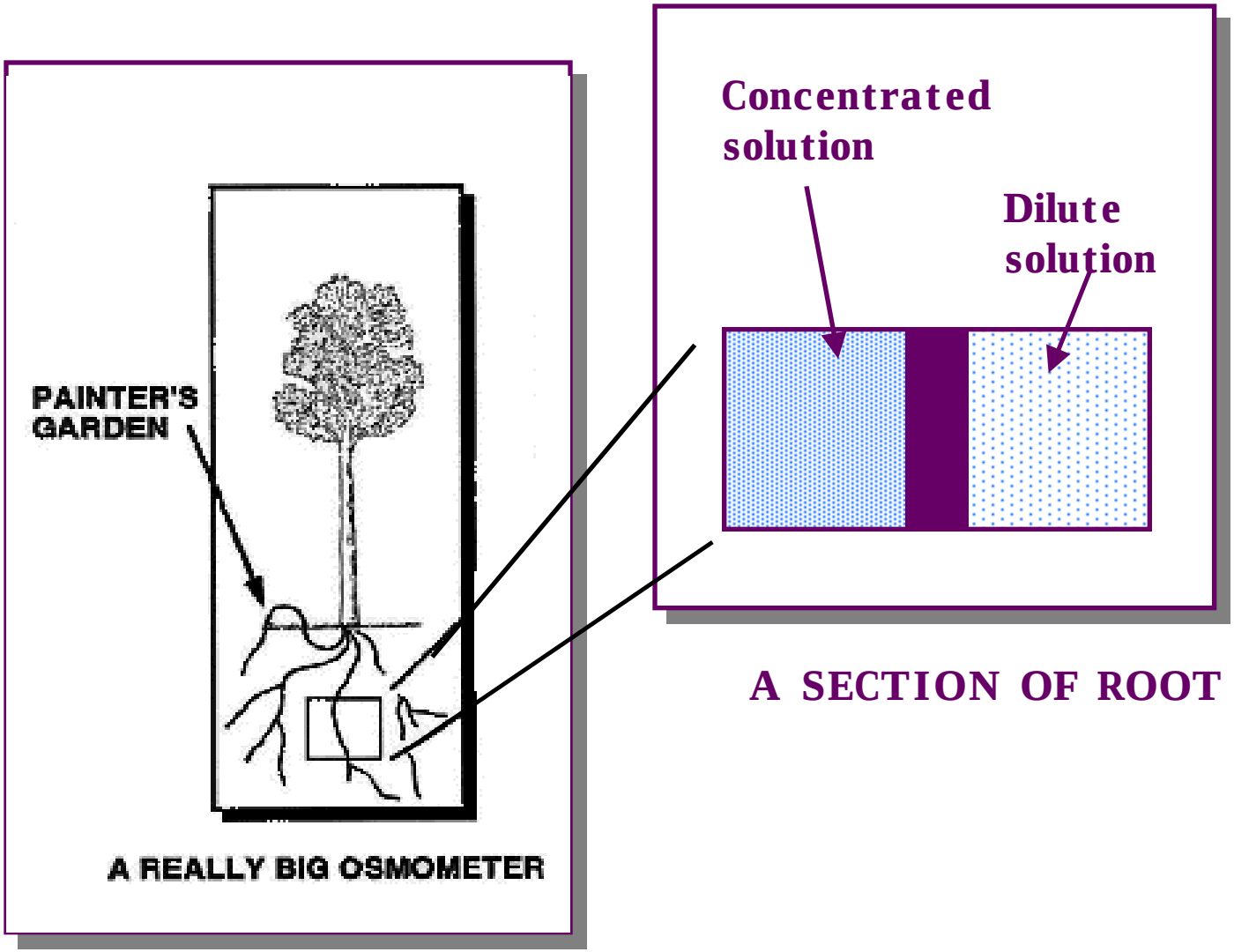
Weight Average

$$\overline{M}_w = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

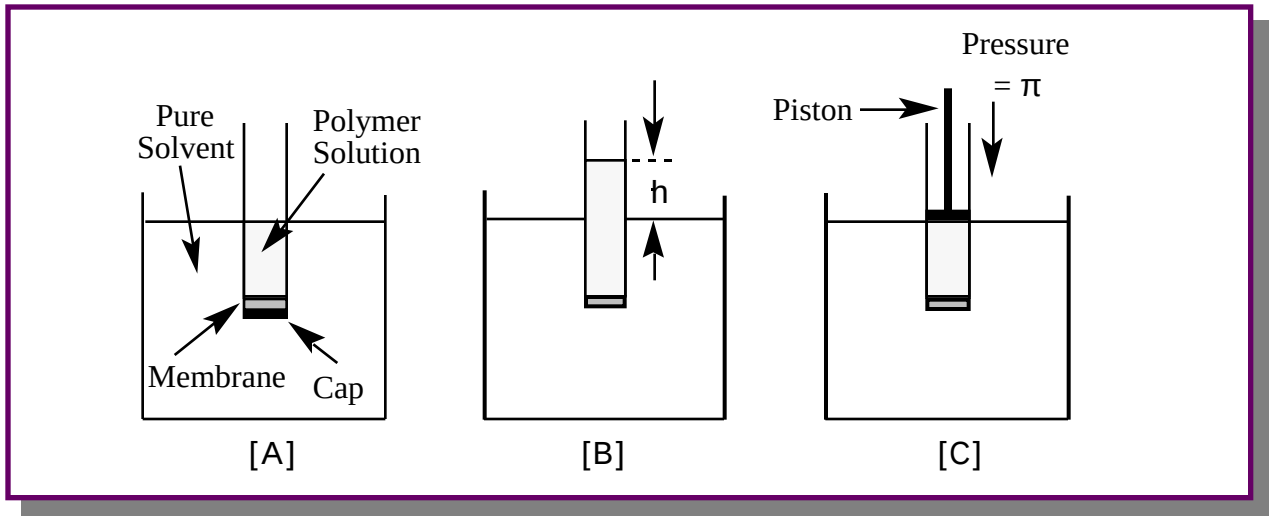
METHODS FOR THE DETERMINATION OF MOLECULAR WEIGHT

ABSOLUTE	END GROUP ANALYSIS	$\bar{M}_n$
	OSMOTIC PRESSURE	$\bar{M}_n$
	OTHER COLLIGATIVE PROPERTY MEASUREMENTS	$\bar{M}_n$
	LIGHT SCATTERING	$\bar{M}_w$
	ULTRA - CENTRIFUGATION	$\bar{M}_w$, $\bar{M}_z$
RELATIVE	SOLUTION VISCOSITY	$\bar{M}_v \sim \bar{M}_w$
	GPC	Complete distribution

OSMOTIC PRESSURE



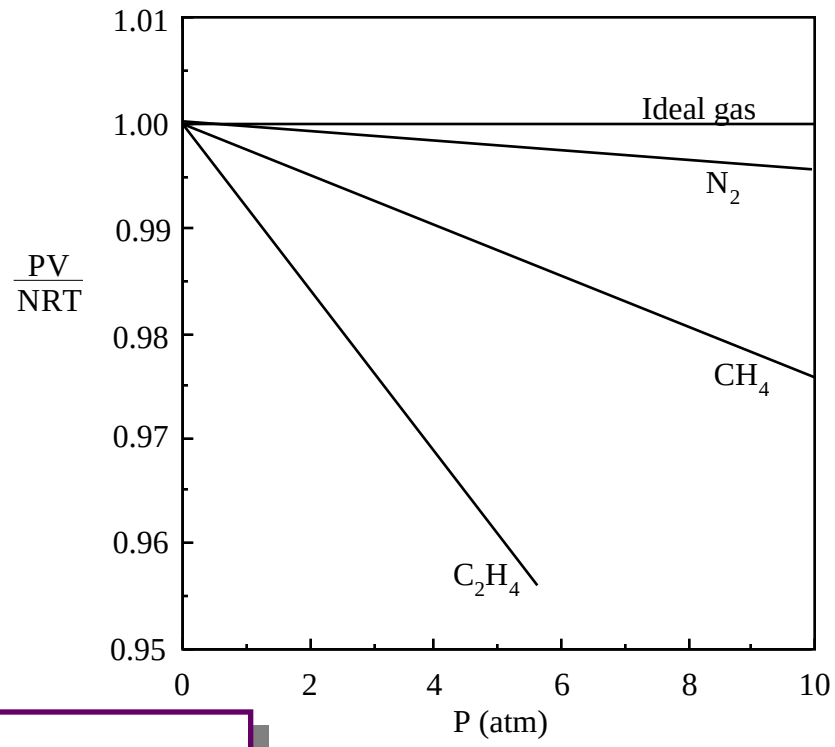
A SCHEMATIC OF A LABORATORY SCALE OSMOMETER



THE IDEA OF VIRIAL EQUATIONS

THE IDEAL GAS LAW

$$PV = nRT$$



VIRIAL EQUATION

$$\frac{PV}{nRT} = 1 + B'P + C'P^2 + D'P^3 + - - -$$

RELATIONSHIP TO MOLECULAR WEIGHT

$$PV = nRT$$

$$P\frac{V}{n} = RT$$

$$\frac{n}{V} = \frac{\#\ \text{moles}}{\text{volume}} = \frac{w}{M}\frac{1}{V} = \frac{c}{M}$$

HENCE

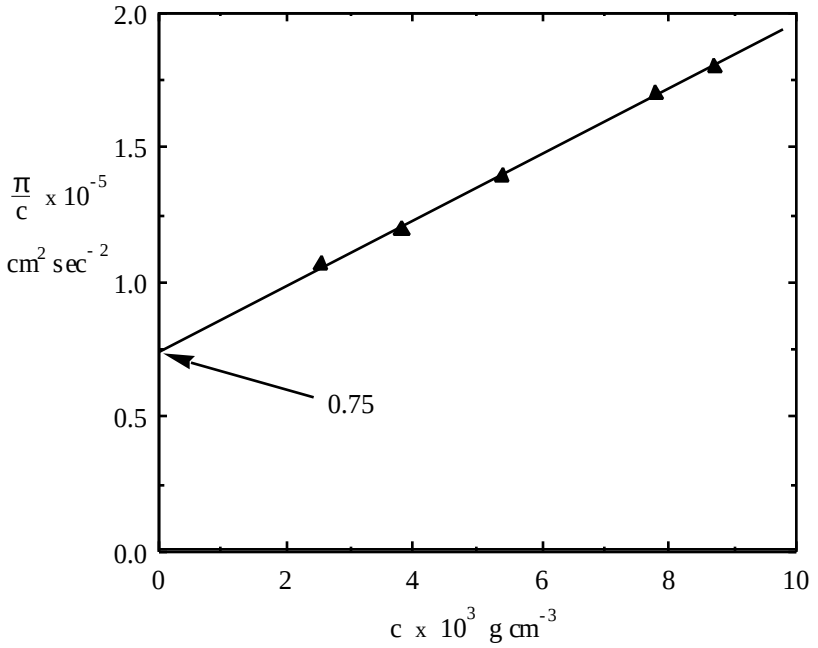
$$\frac{\Pi}{c} = \frac{RT}{M}$$

NOW CONSIDER AN IDEAL SOLUTION

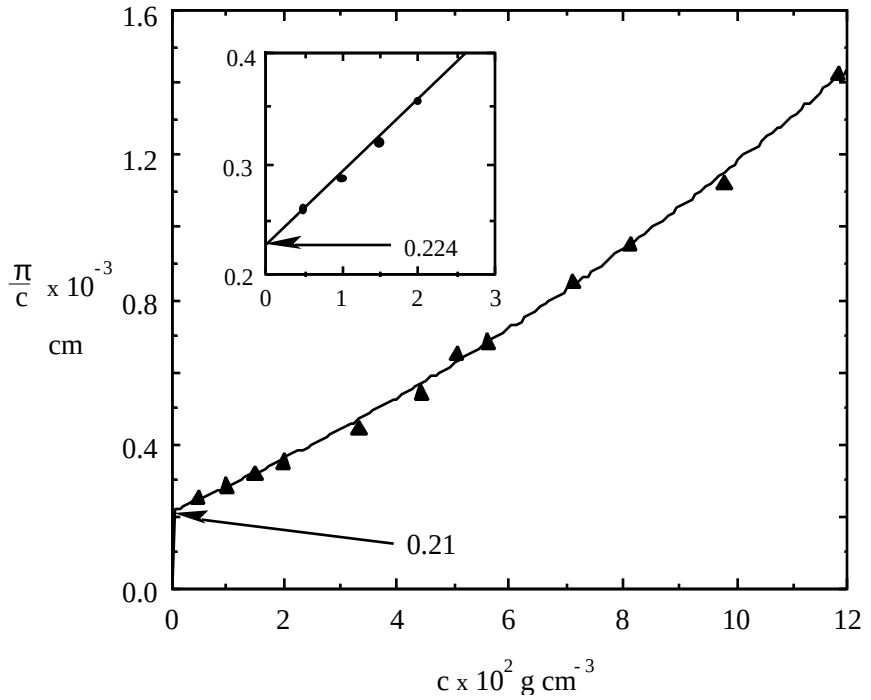
Osmotic Pressure

Ideal Solution $\frac{\pi}{c} = \frac{RT}{M}$

Not So Ideal Solution $\frac{\pi}{c} = \frac{RT}{\overline{M}_n} + Bc + Cc^2 + Dc^3 + \text{------}$



Graph of π/c versus c for polystyrene in toluene.



Graph of π/c versus c for polyisobutylene in chlorobenzene.

DERIVATION OF A VIRIAL EQUATION FROM THE FLORY - HUGGINS EQUATION

Osmotic pressure can Be related to the Chemical potential

$$\frac{\mu_s - \mu_s^0}{RT} = \ln \Phi_s + \left(1 - \frac{1}{\overline{M}_n}\right)\Phi_p + \Phi_p^2 \chi$$

$$\pi = - \frac{RT}{V_s}\left[\ln \Phi_s + \Phi_p \left(1 - \frac{1}{\overline{M}_n}\right) + \Phi_p^2 \chi\right]$$

Expanding the ln term

$$\ln \Phi_s = \ln \left(1 - \Phi_p\right) = - \Phi_p - \frac{\Phi_p^2}{2} - \frac{\Phi_p^3}{3} - \text{-------}$$

We obtain

$$\pi = \frac{RT}{V_s}\left[\frac{\Phi_p}{\overline{M}_n} + \Phi_p^2\left(\frac{1}{2} - \chi\right) + \frac{\Phi_p^3}{3} + \text{------}\right]$$

LIGHT SCATTERING

Looks fiendishly difficult because Of all the equations

Crucial point:

We will end up with a virial equation, Just as in our treatment of osmotic Pressure

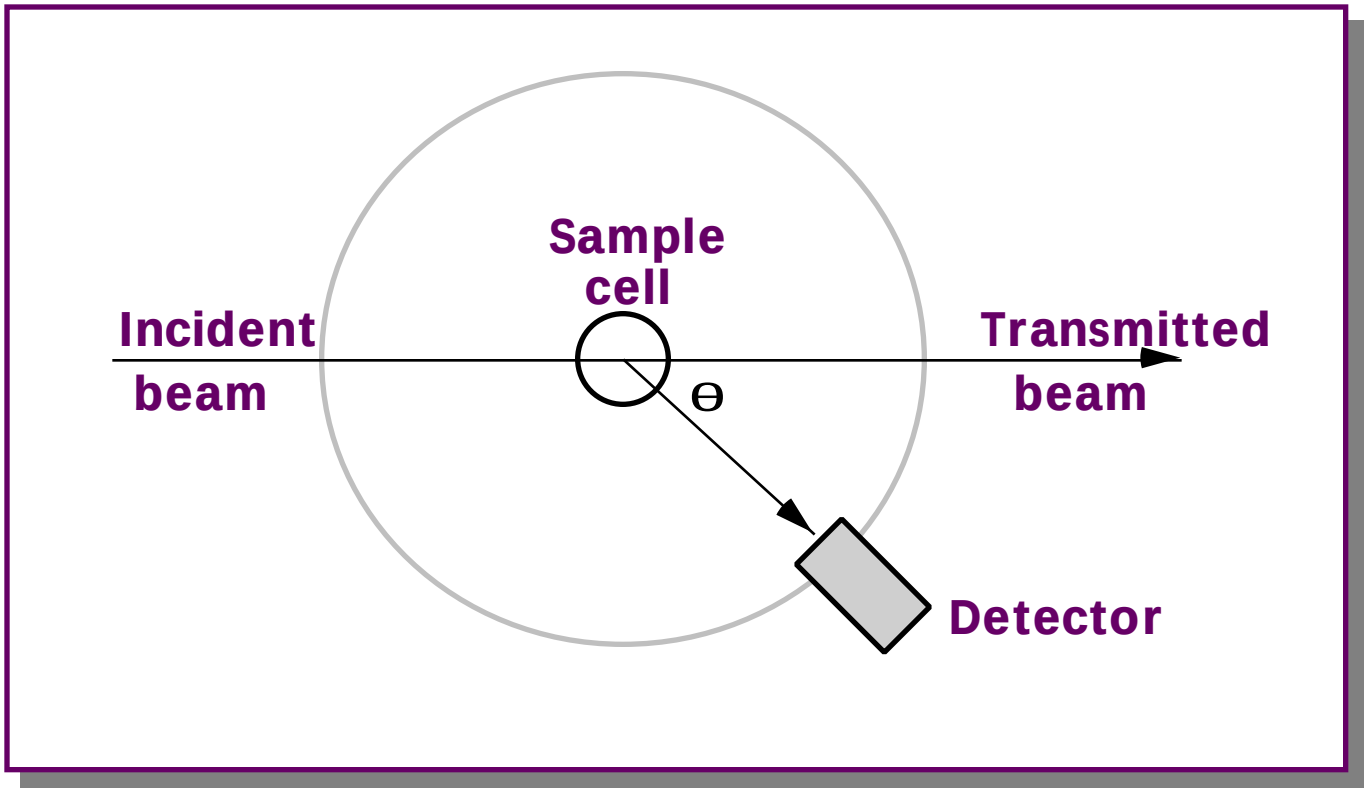
$$\frac{K(1+\cos^2\theta)\,c}{R_\theta} = \frac{1}{\overline{M}_w}\left(1 + 2\Gamma_2 c + \text{---}\right)\left(1 + S\sin^2\left(\frac{\theta}{2}\right)\right)$$

Experimentally measured parameters

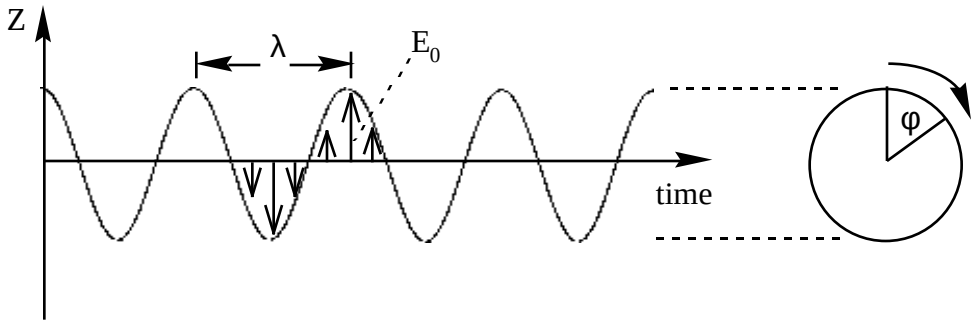
Virial expansion

Dependence on angle of observation

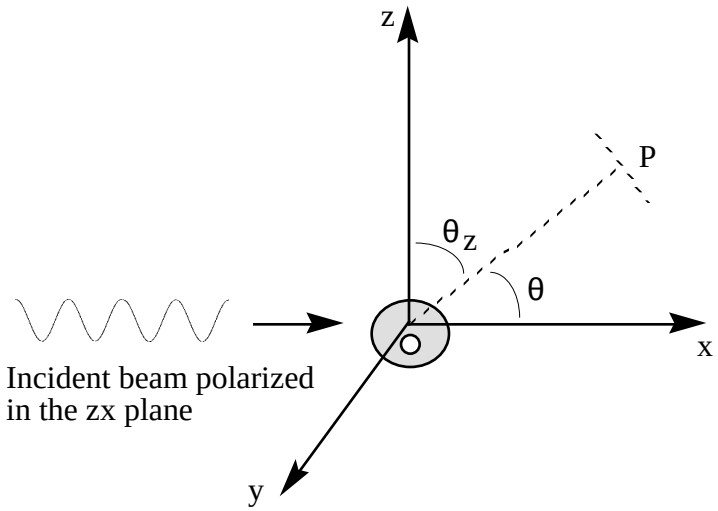
THE EXPERIMENT



THE ORIGIN OF LIGHT SCATTERING



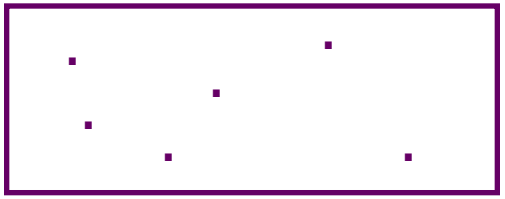
LIGHT AS AN OSCILLATING ELECTRIC FIELD



**Classical description -
The electric field of
The incident light induces
Oscillations of the
Electrons in the molecule,
So that the molecule now
Emits light in all directions**

SCATTERING FROM A GAS

FOR SCATTERING FROM A BUNCH OF RANDOMLY LOCATED OSCILLATORS



$$i'_\theta = \left(\frac{N}{V}\right)\left(\frac{I_0\, 8\pi^4}{\lambda^4}\right)(\alpha^2)\left(\frac{1+\cos^2\theta}{r^2}\right)$$

 # scatterers per unit volume

Characteristics of the incident beam

Polarizability

Geometry of observation