Scattering theory by pictures

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Reading:

M. Rubinstein and R.H. Colby, *Polymer Physics*, Oxford (2003)

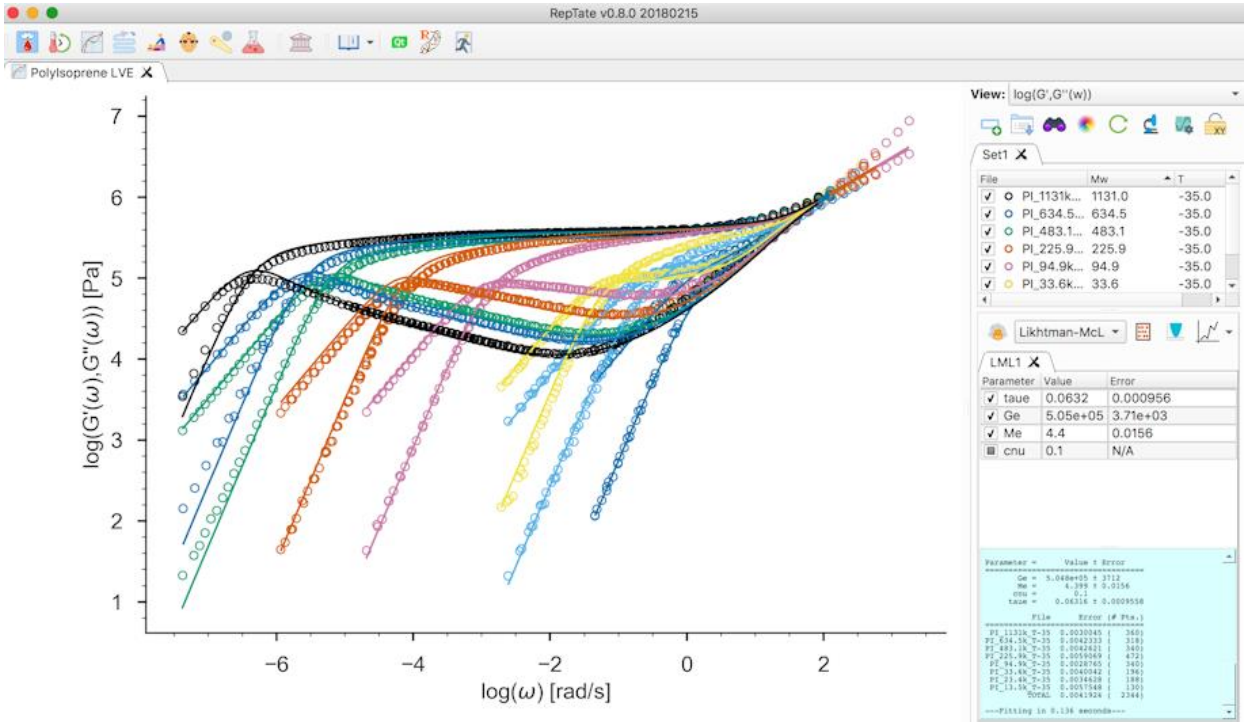
Chapters 2, 4

Adverts!

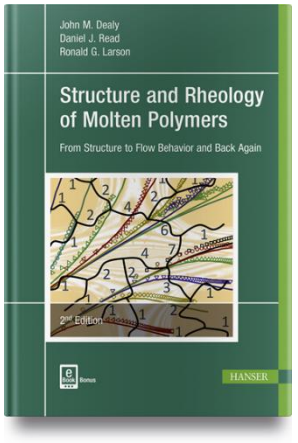
Useful software for rheology: **Reptate**

https://reptate.readthedocs.io/

RepTate (Rheology of Entangled Polymers: Toolkit for Analysis of Theory & Experiment) is a free and open source software package for viewing, exchanging and analysing experimental data.



And…..



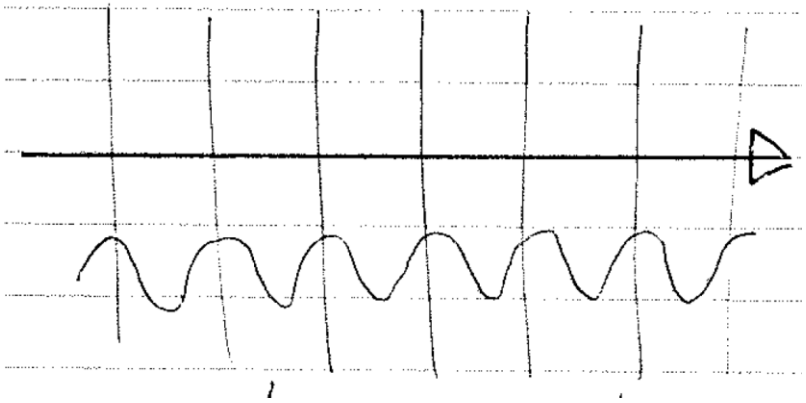
Waves

Wave described by amplitude and phase

$$A = A_0 \cos(kx - \omega t)$$

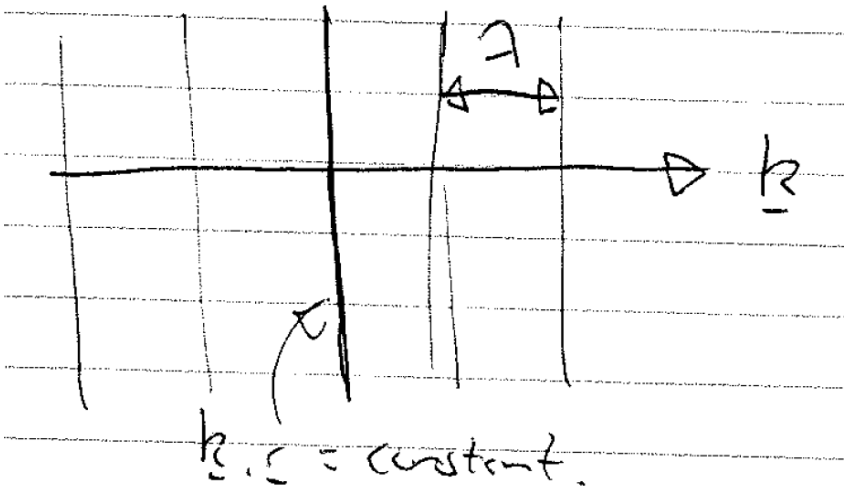
amplitude, phase

$$A = A_0 e^{i(kx - \omega t)}$$



In 3D, the phase varies with position as:

$\phi = \underline{k} \cdot \underline{r}$ $\underline{k}$ = wavevector, $\underline{r}$ = position.



$\Delta\phi = 2\pi = |\underline{k}|\lambda$

So... $|\underline{k}| = \frac{2\pi}{\lambda}$

Waves – the "phase clock"

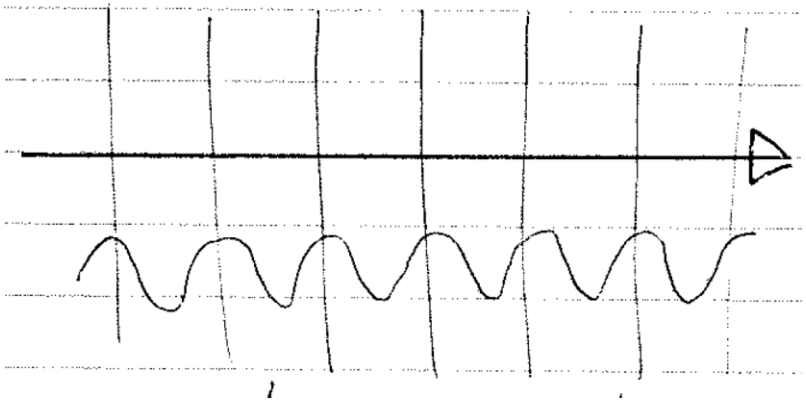
Wave described by amplitude and phase

$$A = A_0 \cos(kx - \omega t)$$

amplitude

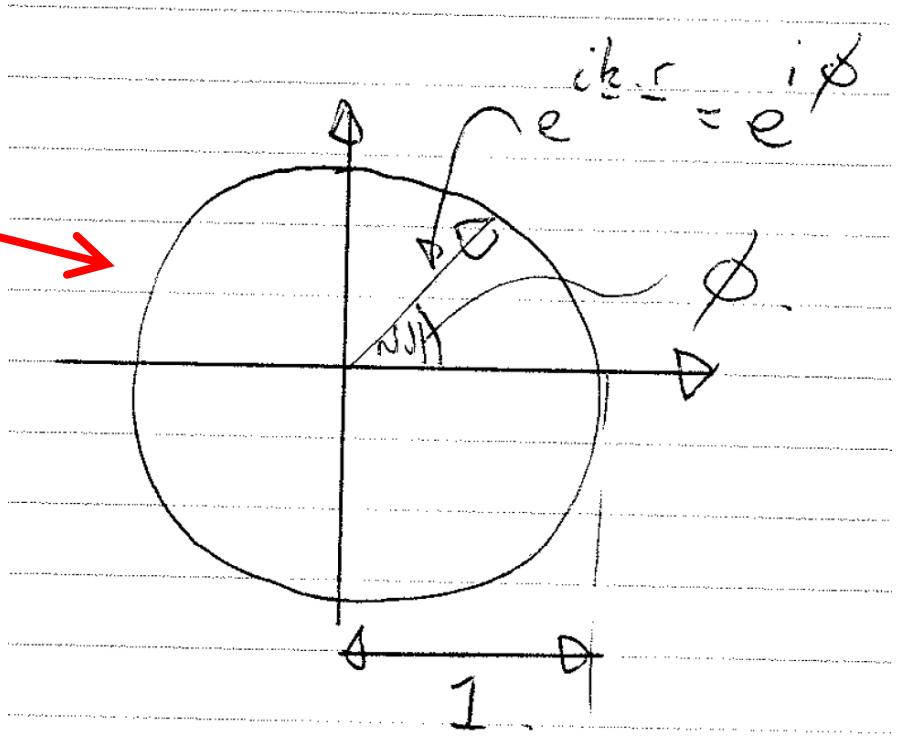
phase

$$A = A_0 e^{i(kx - \omega t)}$$

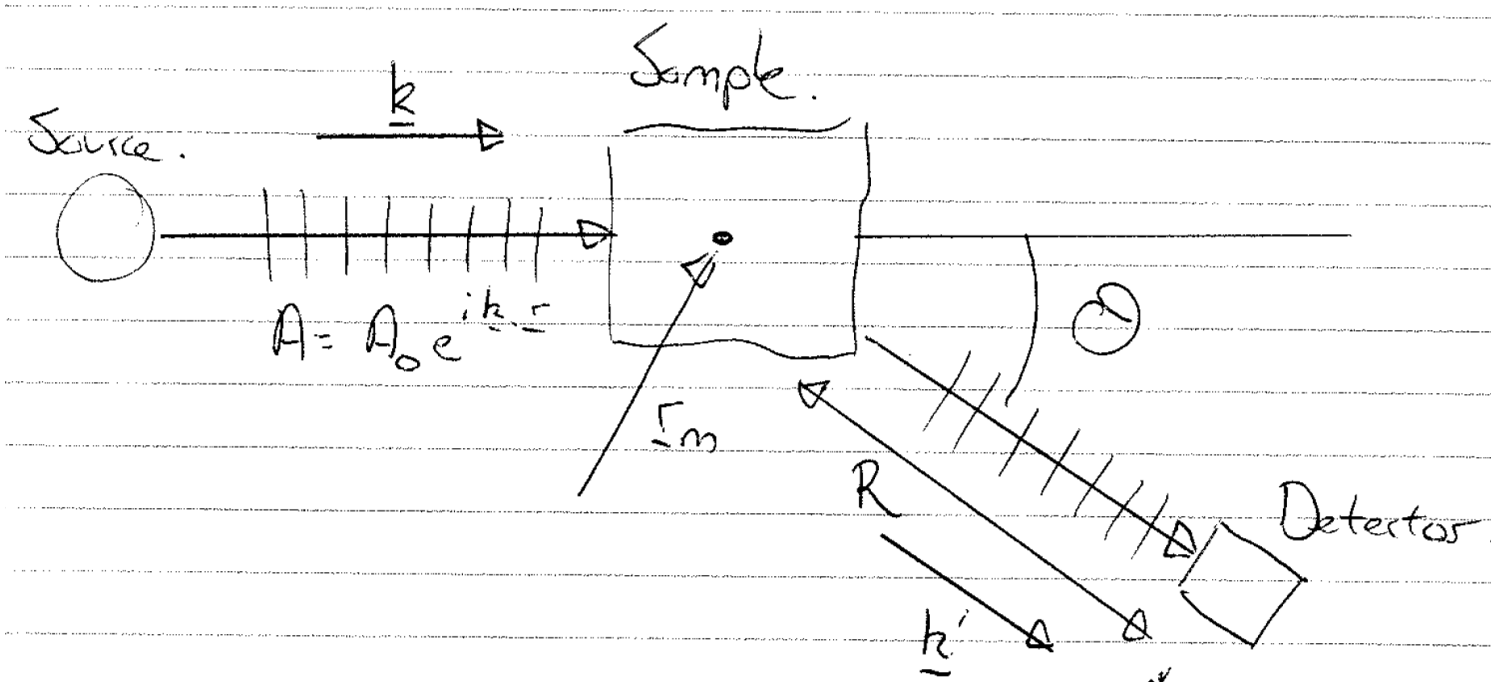


$$A = A_0 e^{i\underline{k}\cdot\underline{r}}$$

Think of this as an "anti-clockwise clock"

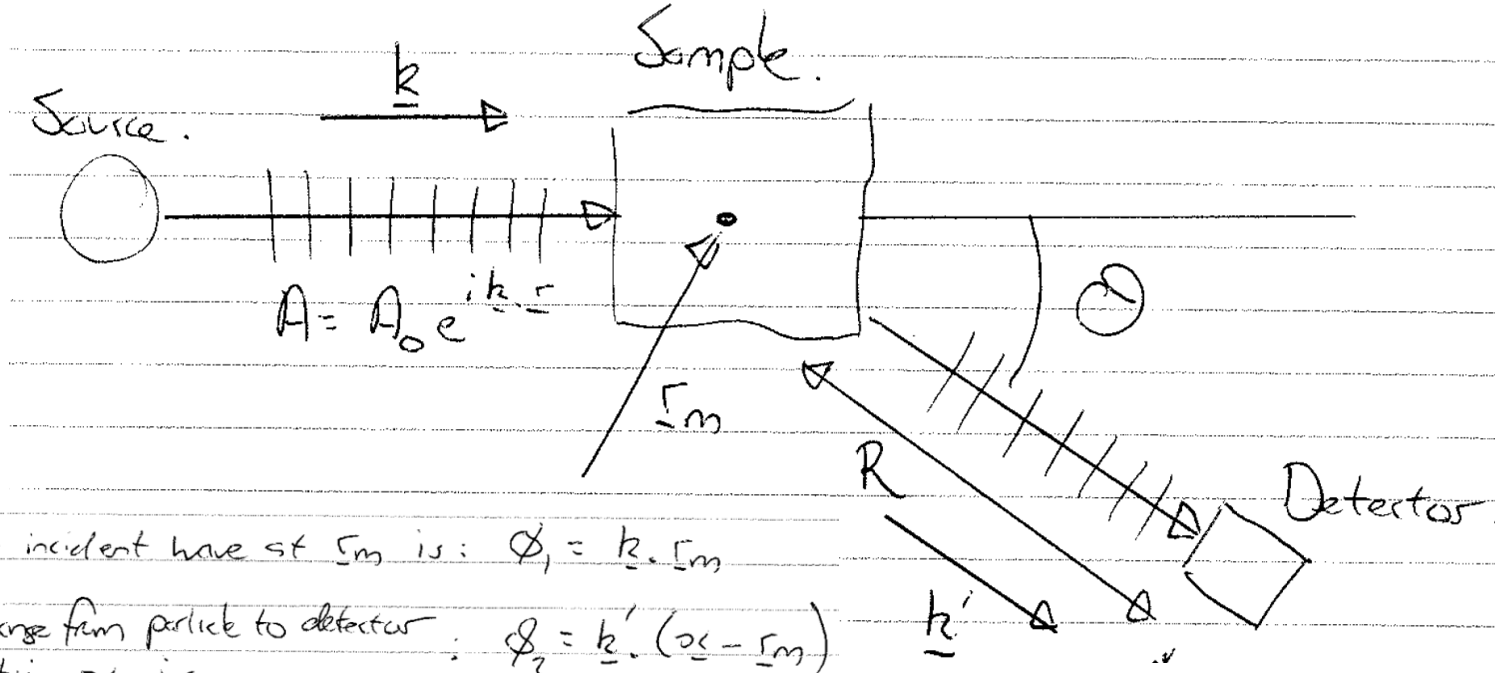


Geometry of a scattering experiment



- A_0 = amplitude of radiation from source (intensity = $I_0 = A_0^2$)
- θ = scattering angle to detector
- R = distance to detector
- $\underline{k}$ = wavevector of incident radiation
  $\underline{k}'$ = wavevector of scattered radiation.

Geometry of a scattering experiment



- Phase of incident wave at r_m is: $\phi_1 = k \cdot r_m$
- Phase change from particle to detector at position x is: $\phi_2 = k' \cdot (x - r_m)$

$$\phi = \phi_1 + \phi_2$$

$$= k \cdot r_m + k' \cdot (x - r_m)$$

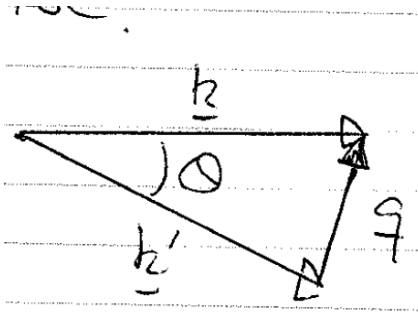
$$= k' \cdot x + (k - k') \cdot r_m = k' \cdot x + q \cdot r_m$$

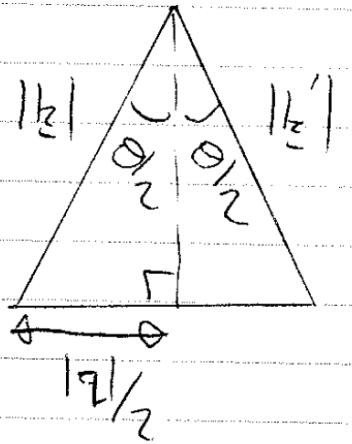
contribution from detector position: same for all particles

the bit which depends on particle position.

Scattering wavevector

$\underline{q} = \underline{k} - \underline{k}'$ is called the scattering wavevector.



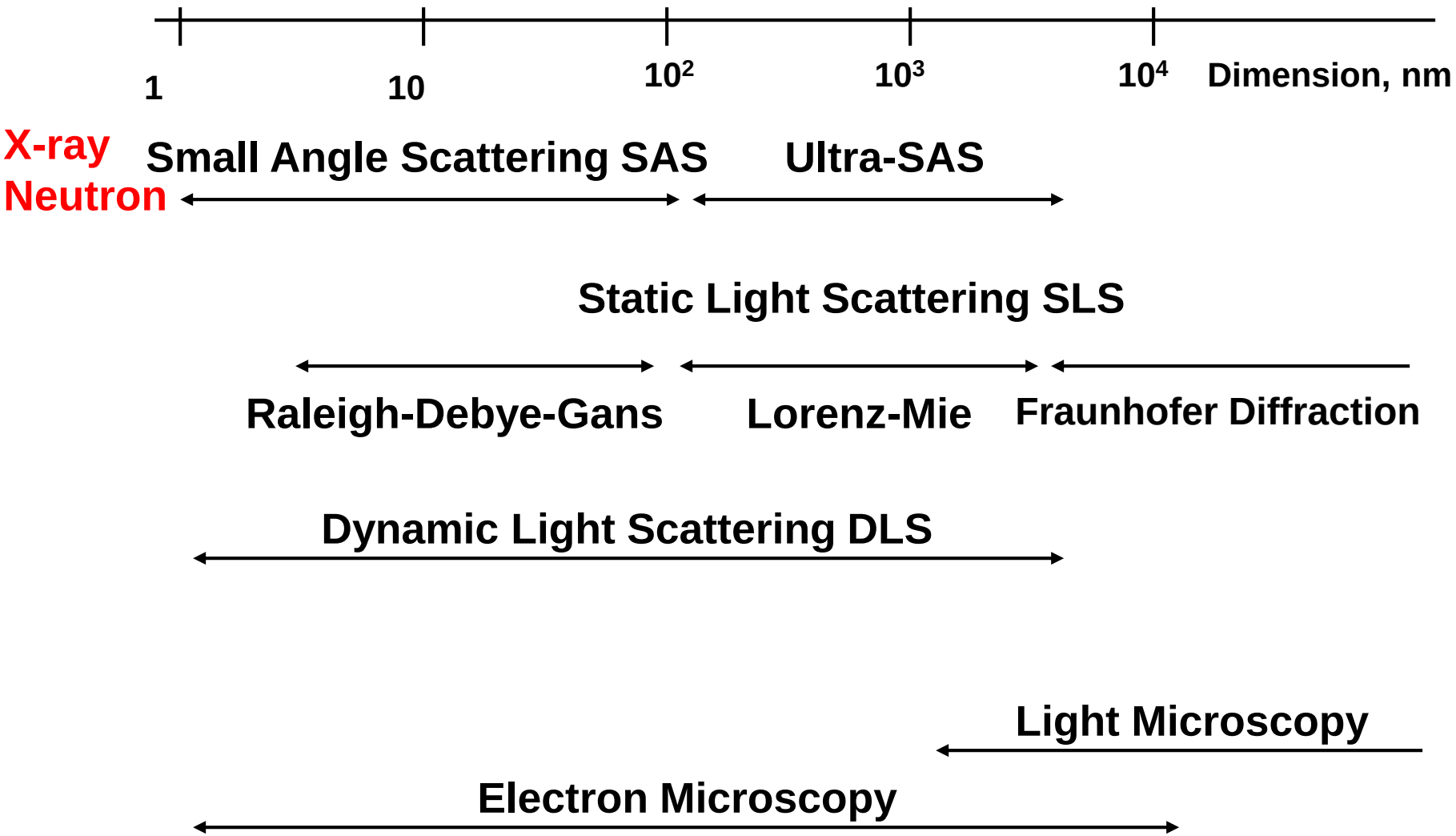


$\therefore$, $\frac{|\underline{q}|}{2} = |\underline{k}| \sin\frac{\theta}{2}$ (Isosceles Δ)

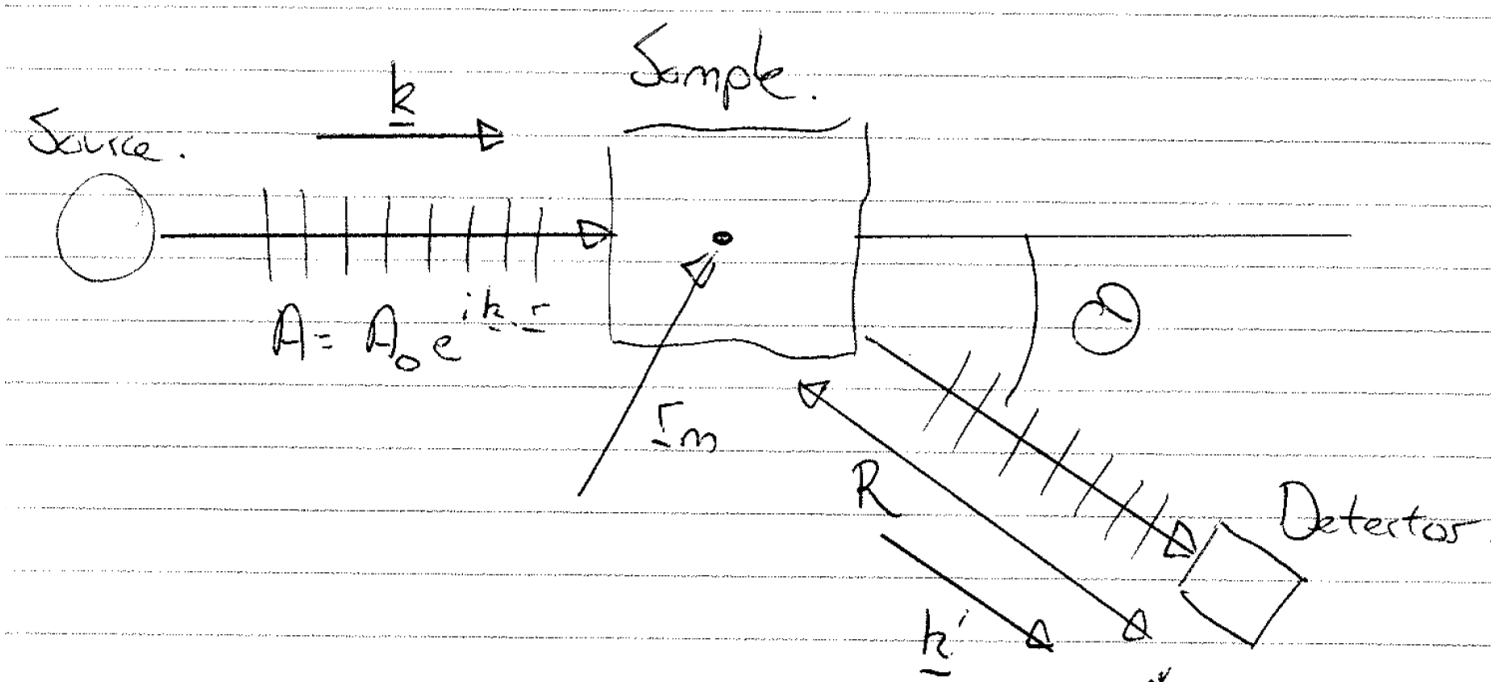
$$|\underline{q}| = 2|\underline{k}| \sin\frac{\theta}{2} = \frac{4\pi}{\lambda} \sin\frac{\theta}{2}.$$

- Large $|\underline{q}|$ probes small structures, small $|\underline{q}|$ probes larger structures.

Size range of different scattering methods



Scattering from one particle



Scattered wave at detector from particle at r_m is:

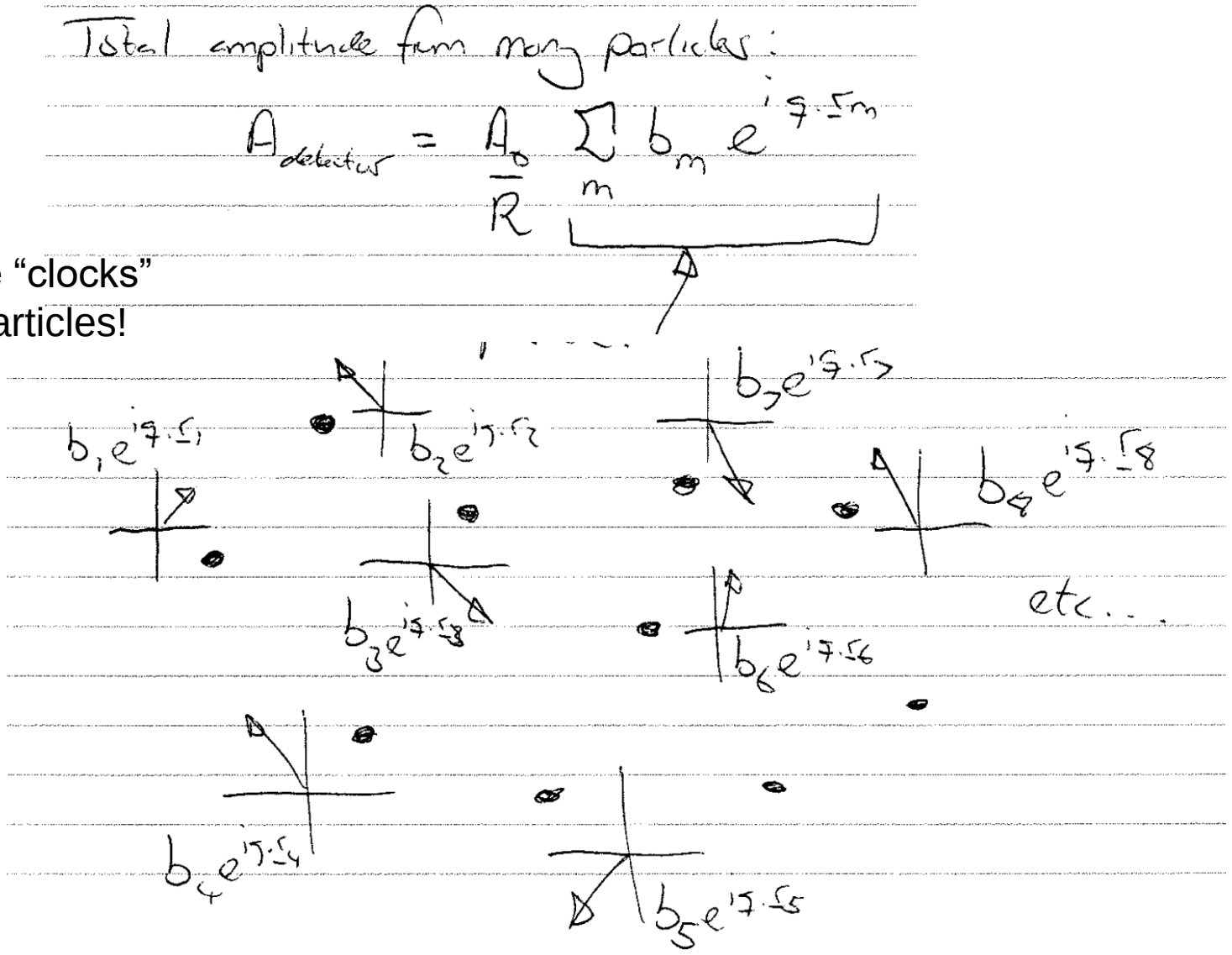
$$A_m = \frac{A_0}{R} b_m e^{i q \cdot r_m}$$

$\frac{1}{R}$ gives inverse square law for intensity.

b_m: scattering length

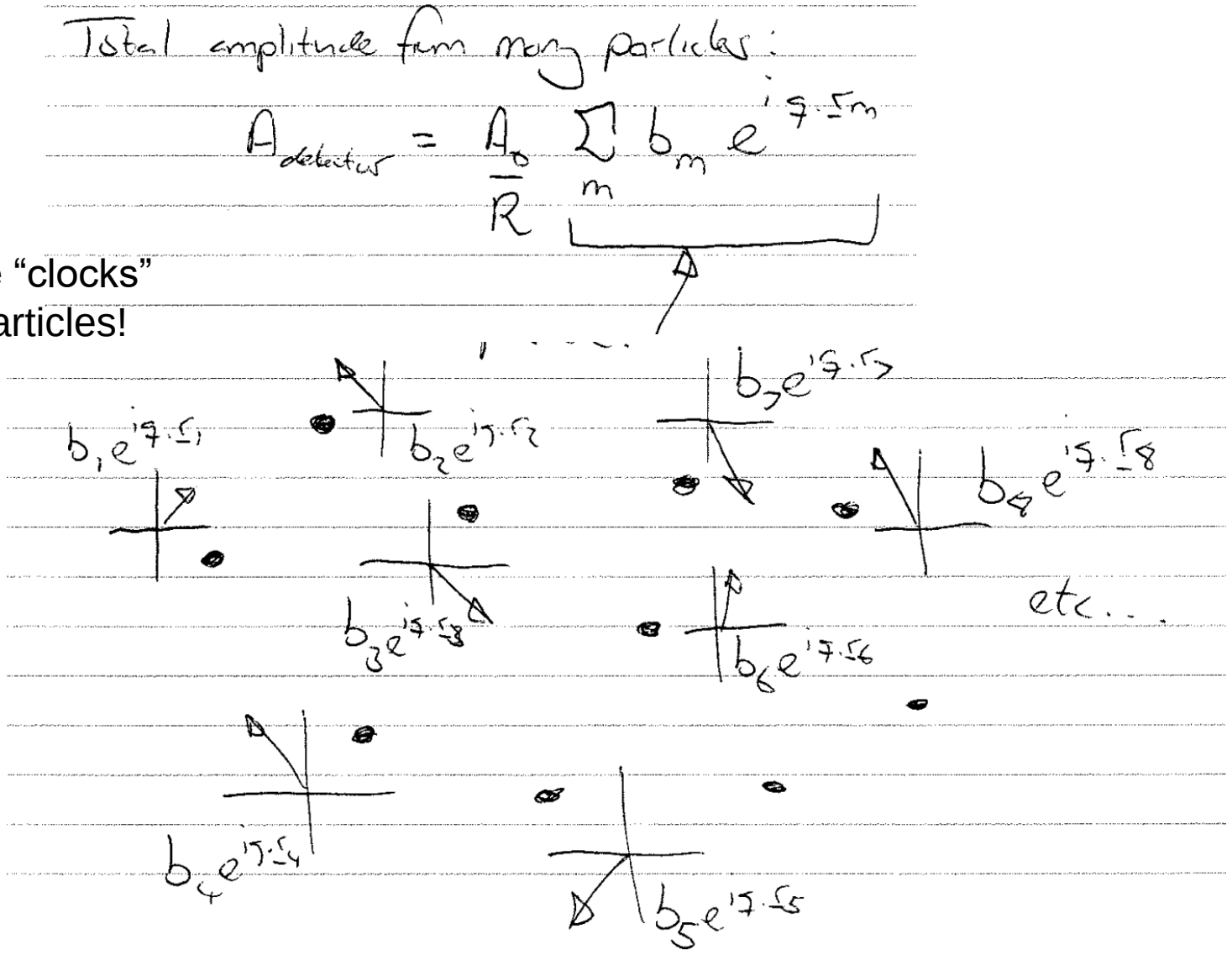
$e^{i q \cdot r_m}$: phase function (anticlockwise clock).

Scattering from many particles



Sum of all the “clocks” from all the particles!

Scattering from many particles



Sum of all the “clocks” from all the particles!

But…. Detector measures intensity!

$$I = |A_{detector}|^2$$

$$= \frac{A_0^2}{R^2} \left| \sum_m b_m e^{i q \cdot r_m} \right|^2$$

If the volume of the sample is V, we often report:

$$\frac{I R^2}{I_0 V}$$ = normalised scattering.

(removes all details of experimental set-up, so result just depends on sample).

$$I_{norm} = \frac{1}{V} \left| \sum_m b_m e^{i q \cdot r_m} \right|^2.$$

This is what we try to calculate…
essentially the “square of the sum over clocks”

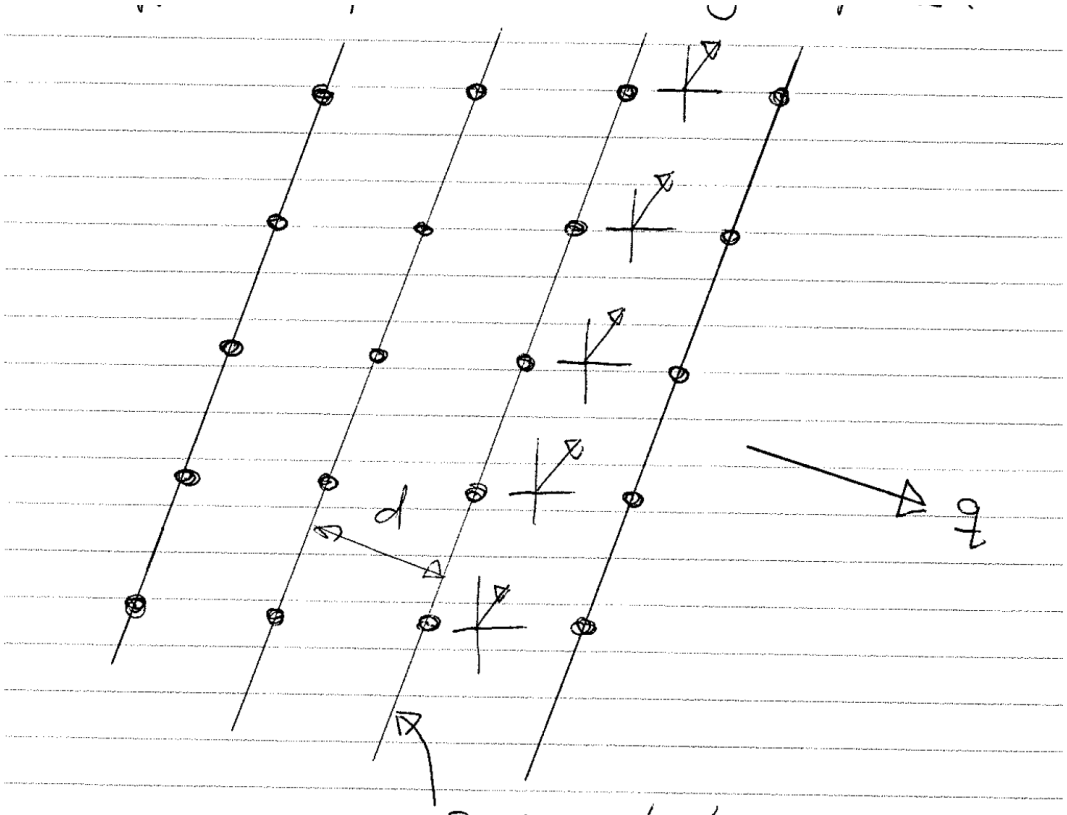
Scattering – introduction

A nice video!

https://www.youtube.com/watch?v=aiKrrGR57aI

Crystal scattering

If all particles lie in crystal planes perpendicular to **q**



$q \cdot r = \text{constant}$

$\Rightarrow$ ALL clocks have same phase!

$$\Delta\phi = |q| d$$

AND if $\Delta\phi = 2n\pi$ (a multiple of 2π)

Bragg law

$$|q| \cdot d = 2n\pi$$

$$\frac{4\pi}{\lambda} \sin\frac{\theta}{2} \cdot d = 2n\pi$$

$$2d \sin\frac{\theta}{2} = n\lambda$$

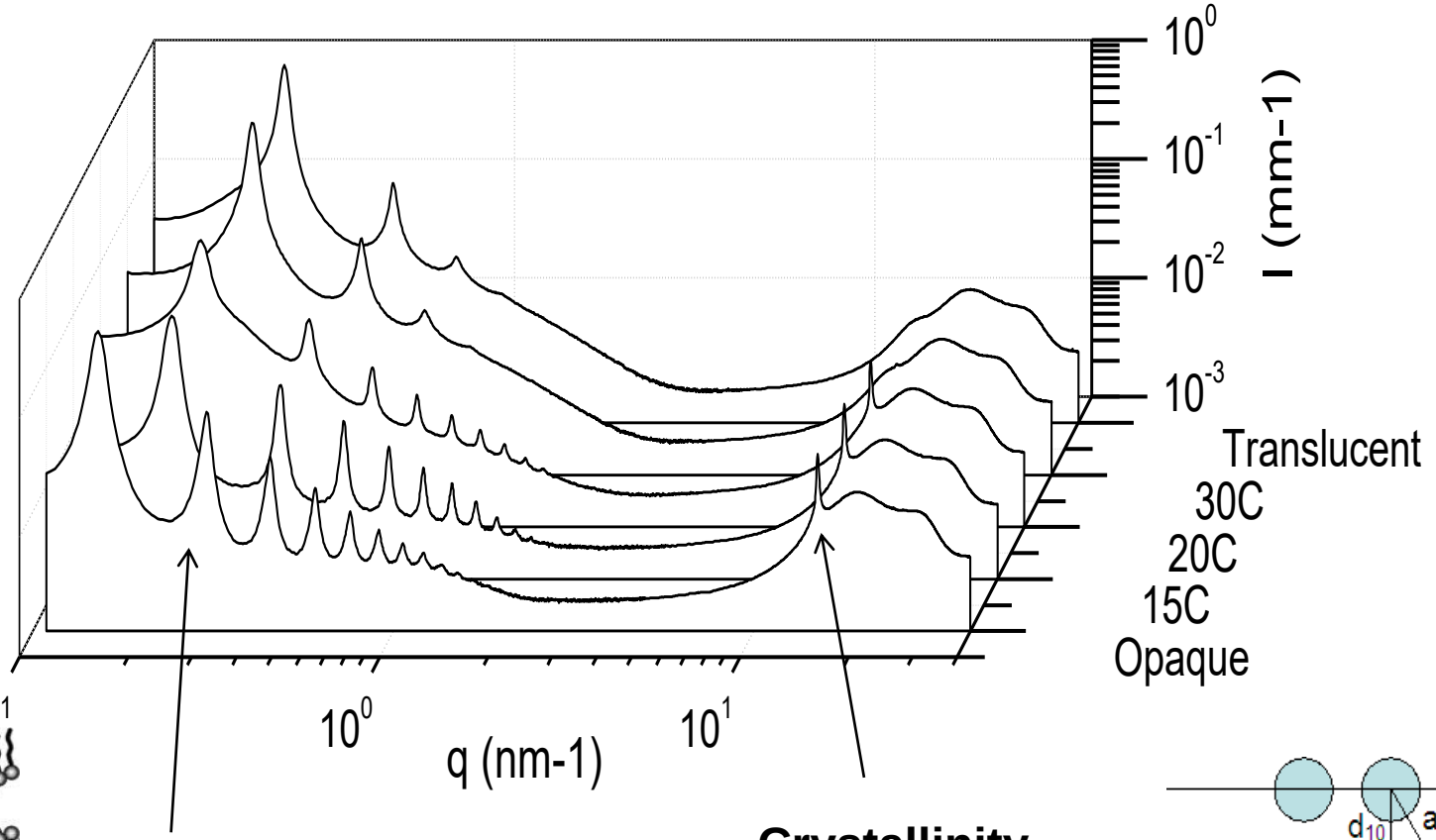
Indexing of crystal structures

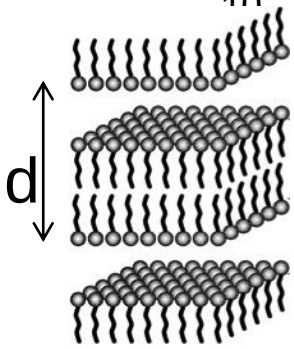
d is a function of chainlength, angle of inclination (if bilayer) and water layer thickness

Type of liquid crystal	d-values ratio	Diffraction Planes or Miller's indices {*hkl*}
Lamellar	1 : ½ : 1/3 : ¼	{1 0}, {2 0}, {3 0}, {4 0}
Hexagonal	1 : 1/√3 : 1/√4 : 1/√7 : 1/√9	{1 0}, {1 1}, {2 0}, {2 1}, {3 0}
Cubic (Pm3n, bicontinuous)	1 : 1/√2 : 1/√3 :1/√4 : 1/√6 : 1/√8 : 1/√9 :1/√10	{1 0 0}, {1 1 0}, {1 1 1}, {2 0 0}, {2 1 1}, {2 2 0}, {2 2 1}, and {3 1 0}
Cubic (Ia3d, bicontinuous)	1 : √3/√4 : √3/√7 : √3/√8 : √3/√10 : √3/√11 : √3/√12 : √3/√13	
Cubic (Fm3m or F23 or Im3m, discontinuous or primitive)	1 : 1/√2 : 1/√4 : 1/√6 : 1/√8 : 1/√10	{1 0 0}, {1 1 0}, {2 0 0}, {2 1 1}, {2 2 0} and {3 1 0}
Multilayer Vesicle	1 : ½ : 1/3 : ¼	{1 0}, {2 0}, {3 0}, {4 0}
Unilamellar vesicle	1 very broad peak	broad peak at *q** characteristic of the bilayer thickness

A. Svensson, et al, J. Phys. Chem B, **106**, 1013 (2002); K. Fontell, Colloid Polymer Sci. **268**, 264 (1990); **Colloids Surfaces A: Physicochemical and Engg Aspects;** 358, (2010), 50-56.

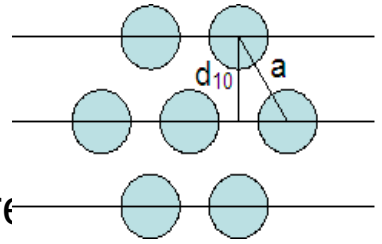
SAXS of Lamellar Gel Network in Beauty Products





Bragg peaks: **d-spacing**
Harmonics: 1, 2, 3...
lamellar phase

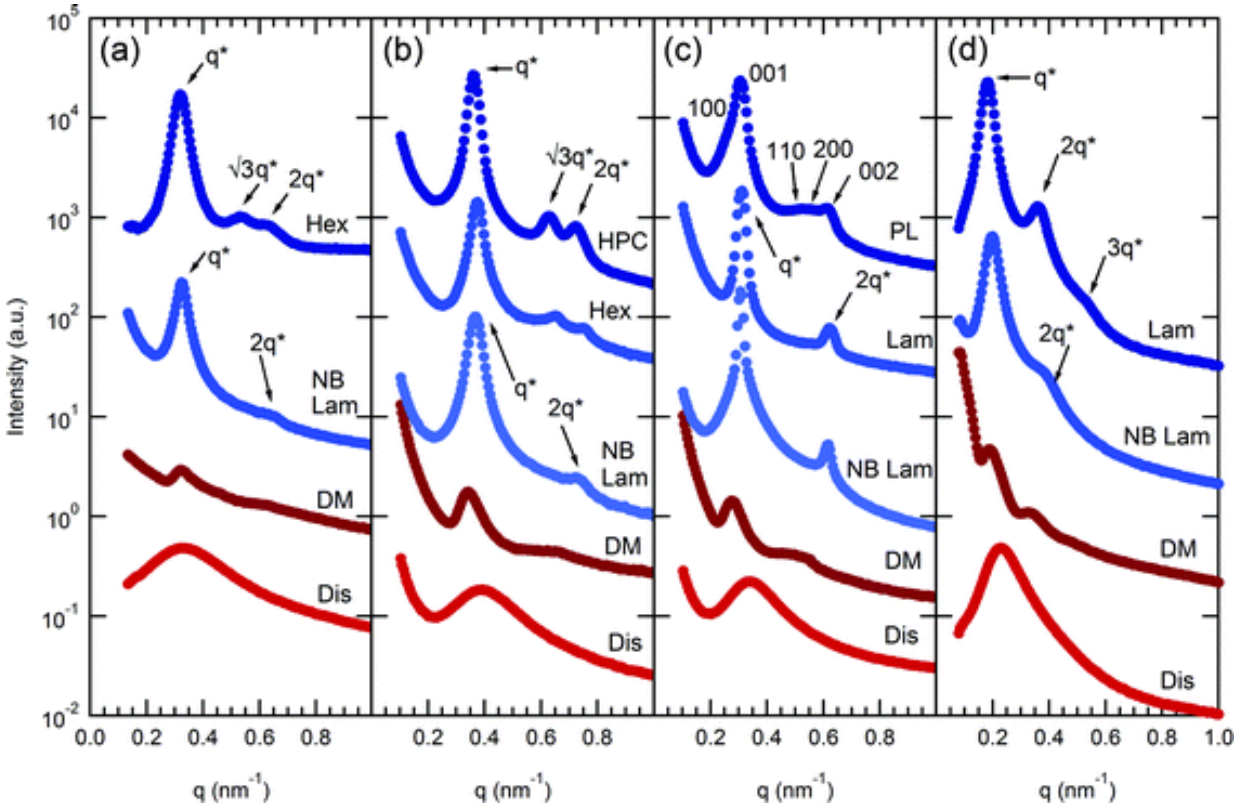
Crystallinity
Harmonics: 1, √3...
Hexagonal structure



a ~ 4.5Å

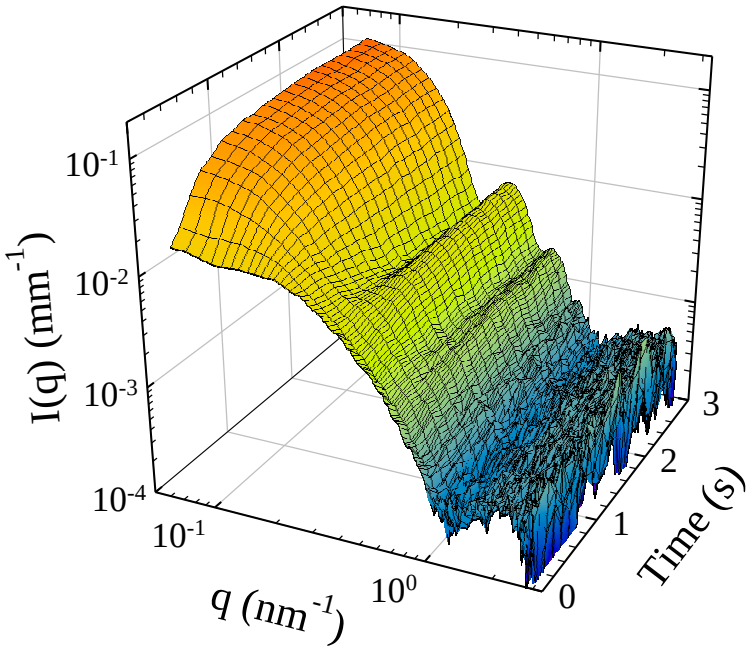
Identification of soft matter phases using scattering

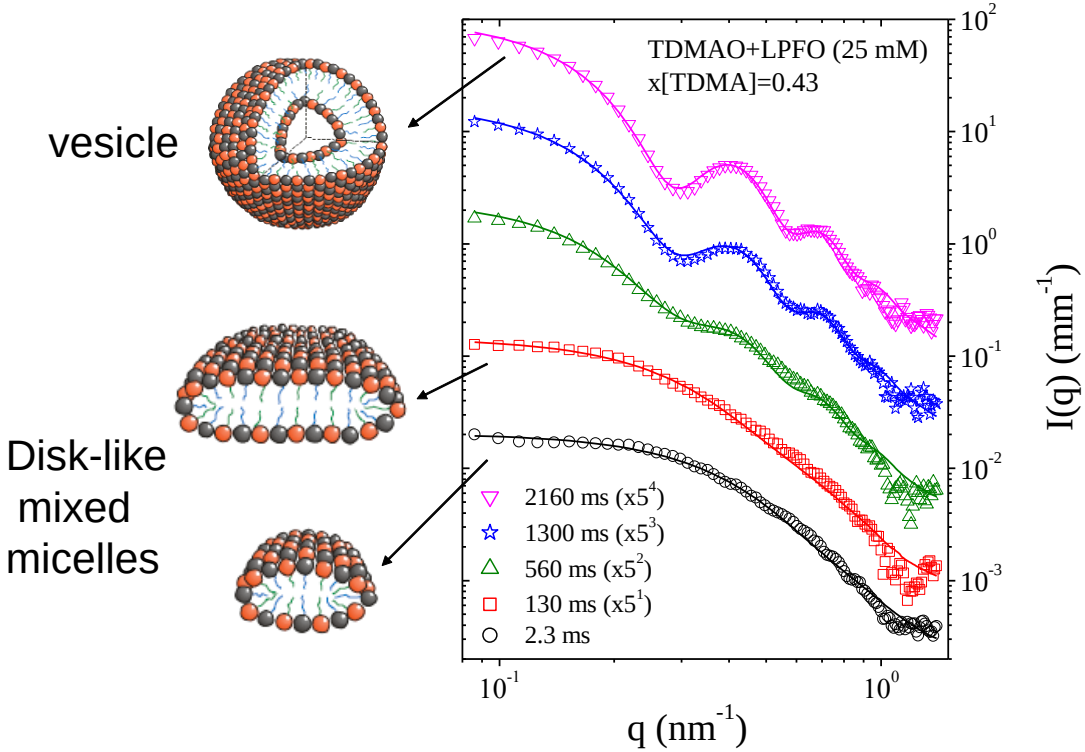
e.g. Christopher N. Lam and Bradley D. Olsen Soft Matter, 2013, 9, 2393-2402



Rapid Formulation: Investigate Surfactant Aggregation Like Vesicle Formation in Real Time

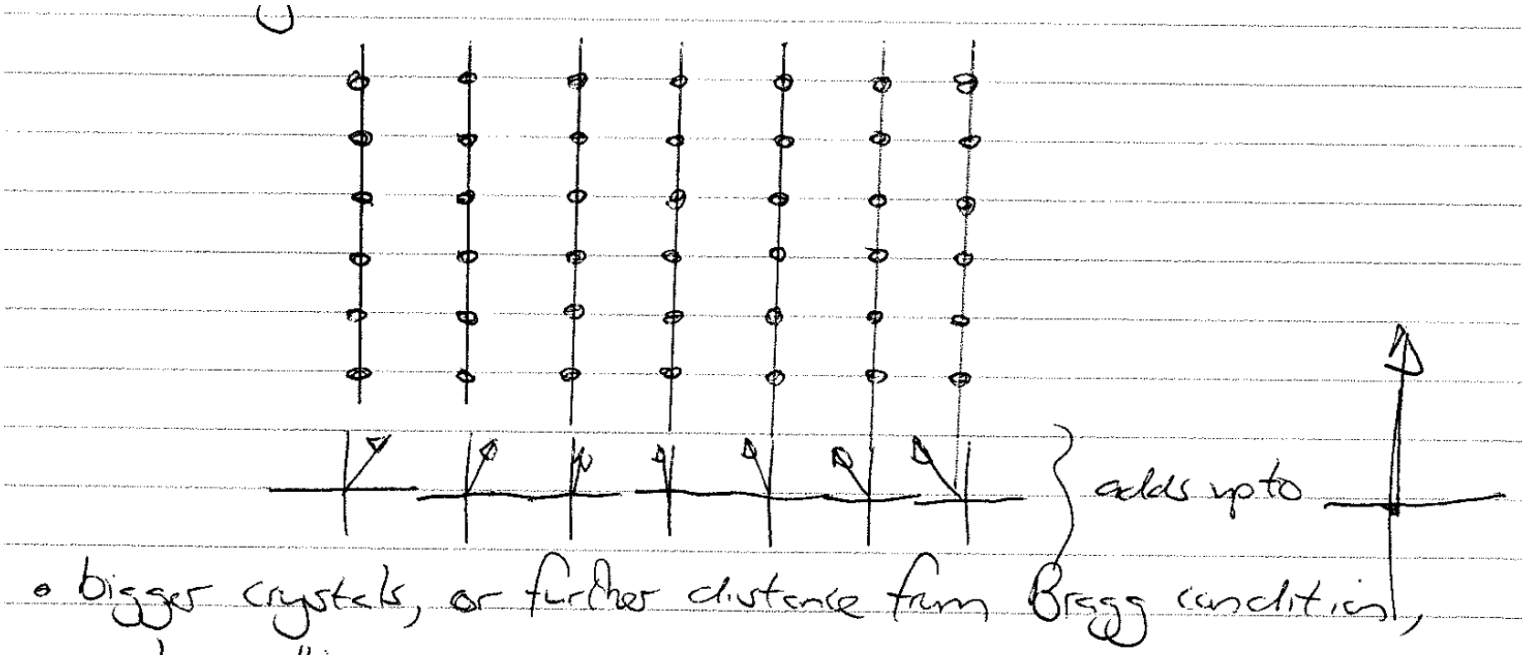
Mixing anionic and zwitterionic surfactants





J. Gummel, M. Sztucki, T. Narayanan and M. Gradzielski, **Soft Matter** 2011

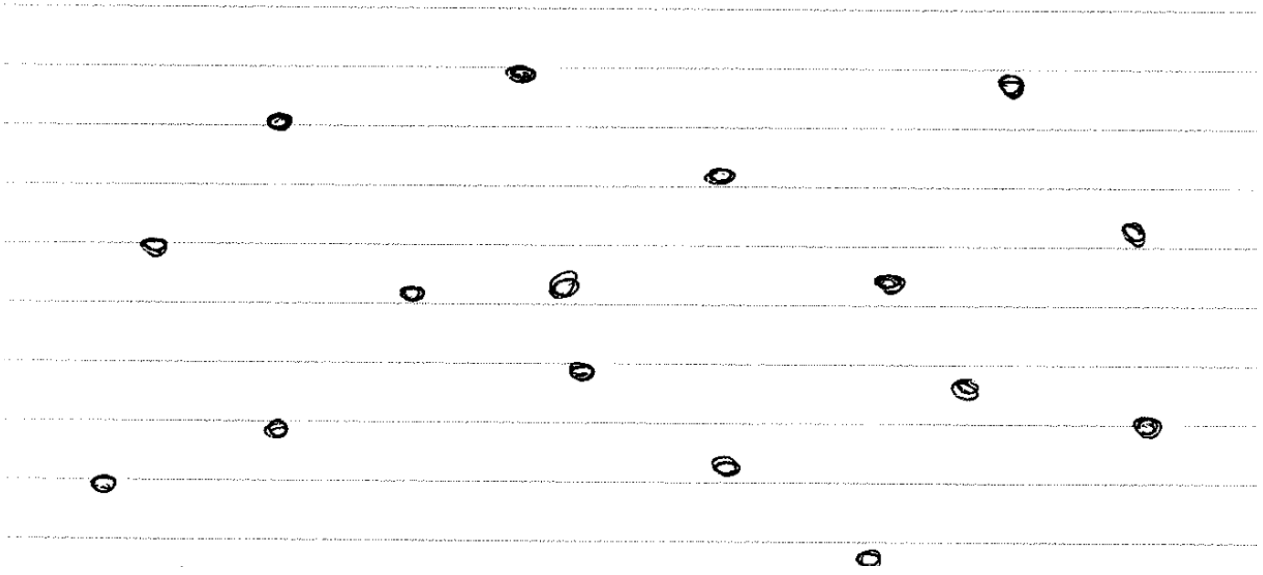
Finite crystals….



- bigger crystals, or further distance from Bragg condition, makes allignment worse.

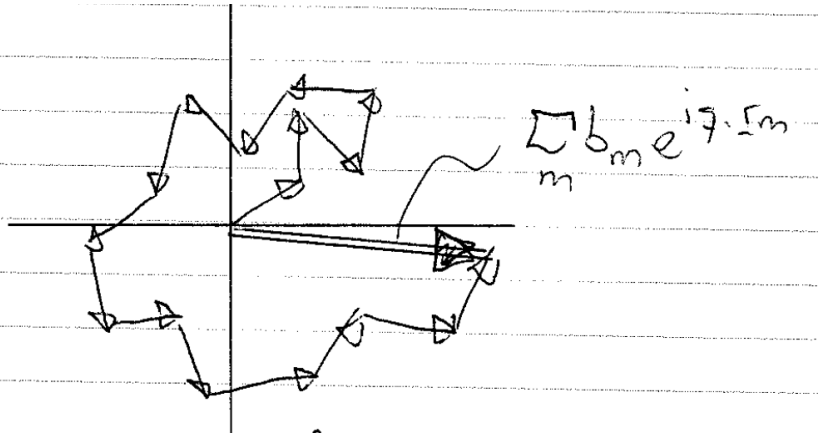
So... width of scattering peak is a measure of size of crystals!

Scattering from random particles



$\sum_m b_m e^{i q \cdot r_m}$ ≡ a sum over randomly directed arrows, each of size b

≡ RANDOM WALK!!



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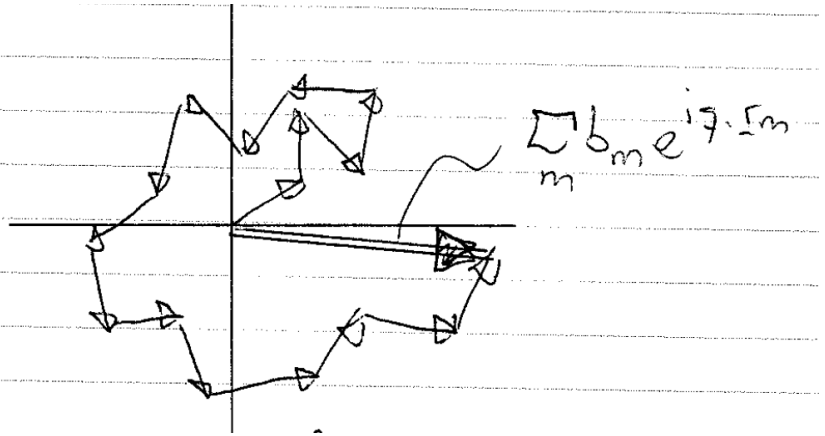


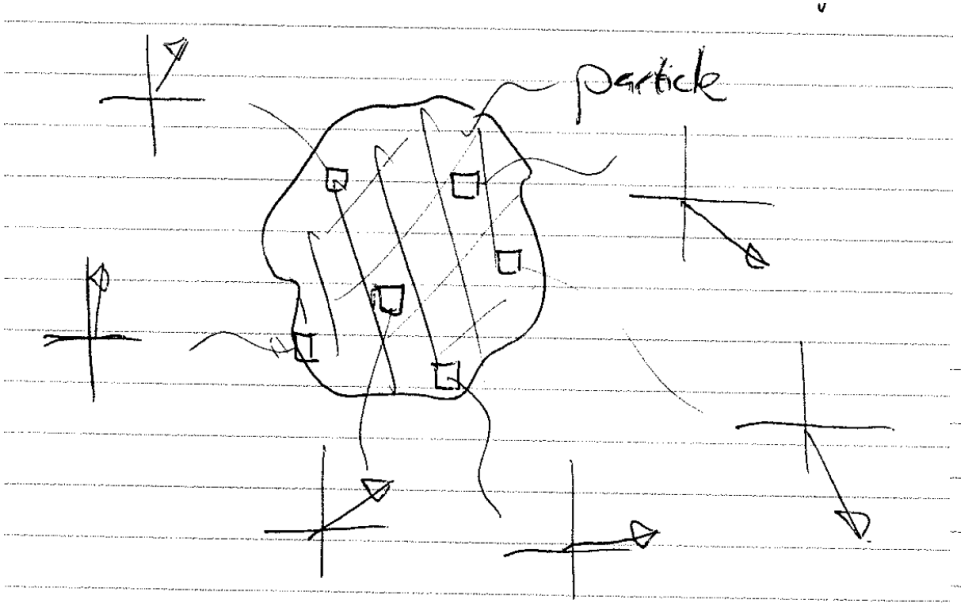
$$\langle R^2 \rangle = Nb^2$$

$$\left\langle \left| \sum_m b_m e^{i\mathbf{q}\cdot\mathbf{r}_m} \right|^2 \right\rangle = Nb^2$$

N: number of particles; b: sphere of scattering length

"Form" factor

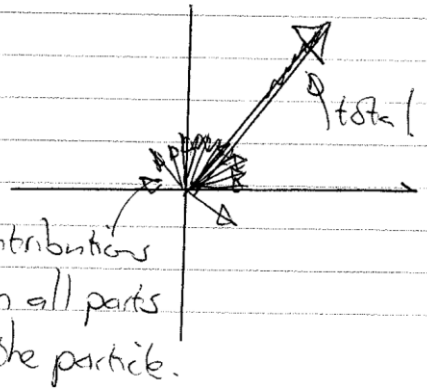
Finite sized particle…..



$$P(q) = \left| \sum_{m \text{ in particle}} b_m e^{i q \cdot r_m} \right|^2$$

= FORM FACTOR for particle.

$$\sum_{m \text{ in particle}} b_m e^{i q \cdot r_m} \equiv$$



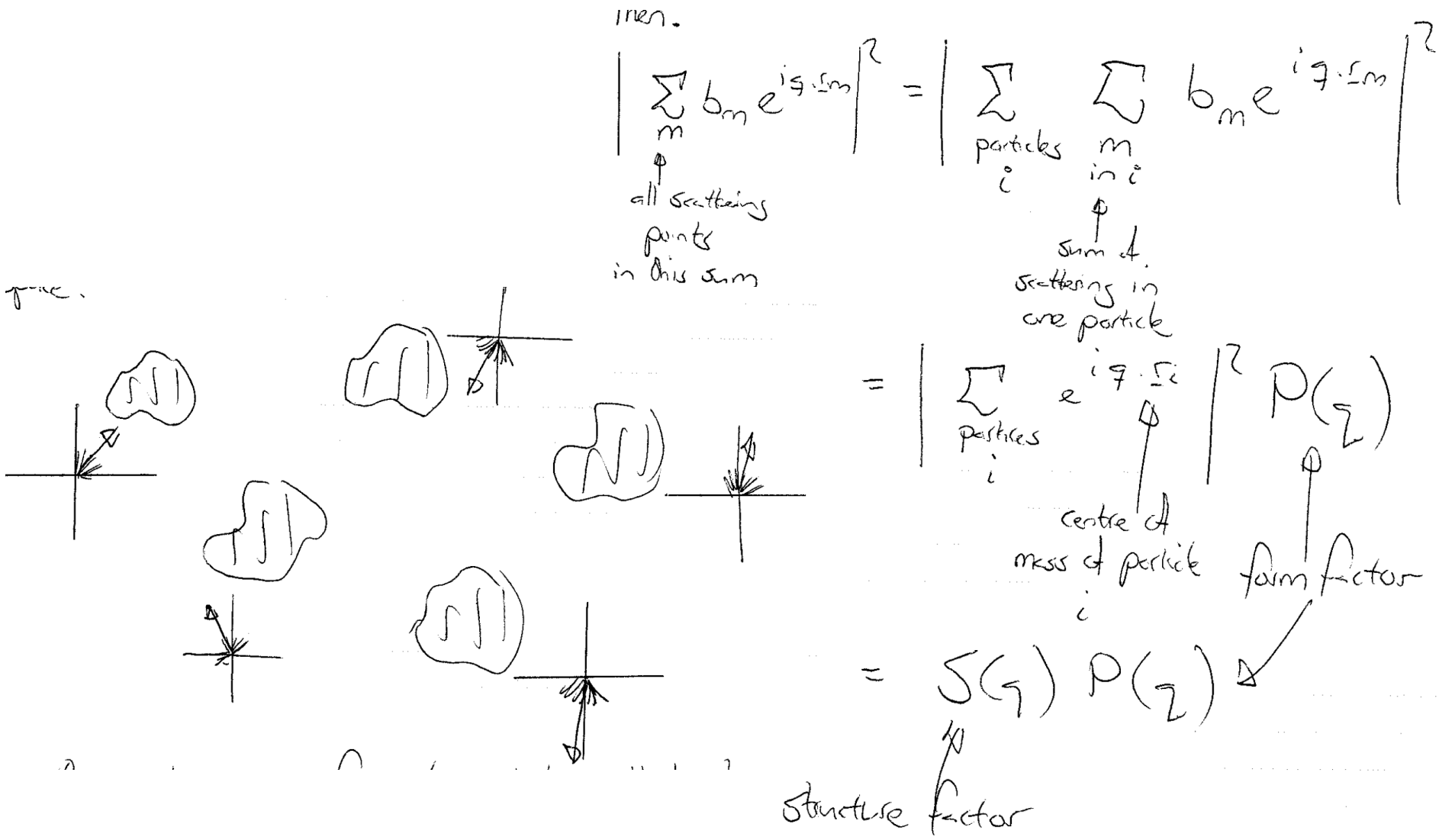
$$P(q) = P_0 \left(1 - \frac{q^2 R_g^2}{3} + \ldots \right)$$

R_g = "radius of gyration".

$P_0 = \left| \sum_m b_m \right|^2 \propto (\text{mass})^2$ of particle.

“Structure” factor

Finite sized particles….. With some arrangement in space



“Structure” factor and “Form” factor

STRUCTURE factor gives scattering contribution from arrangement of particles

FORM factor gives scattering from each individual particle

$$S(q)\,P(q)$$

e.g. 1. If particles are on a crystal lattice then

$S(q)$ gives Bragg peaks

$P(q)$ changes the peak intensity.

e.g. 2. If particles are randomly distributed, then:

$S(q) = N$ (no. of particles)

$P(q) = P_0\left(1 - \frac{q^2 R_g^2}{3} + \ldots\right)$

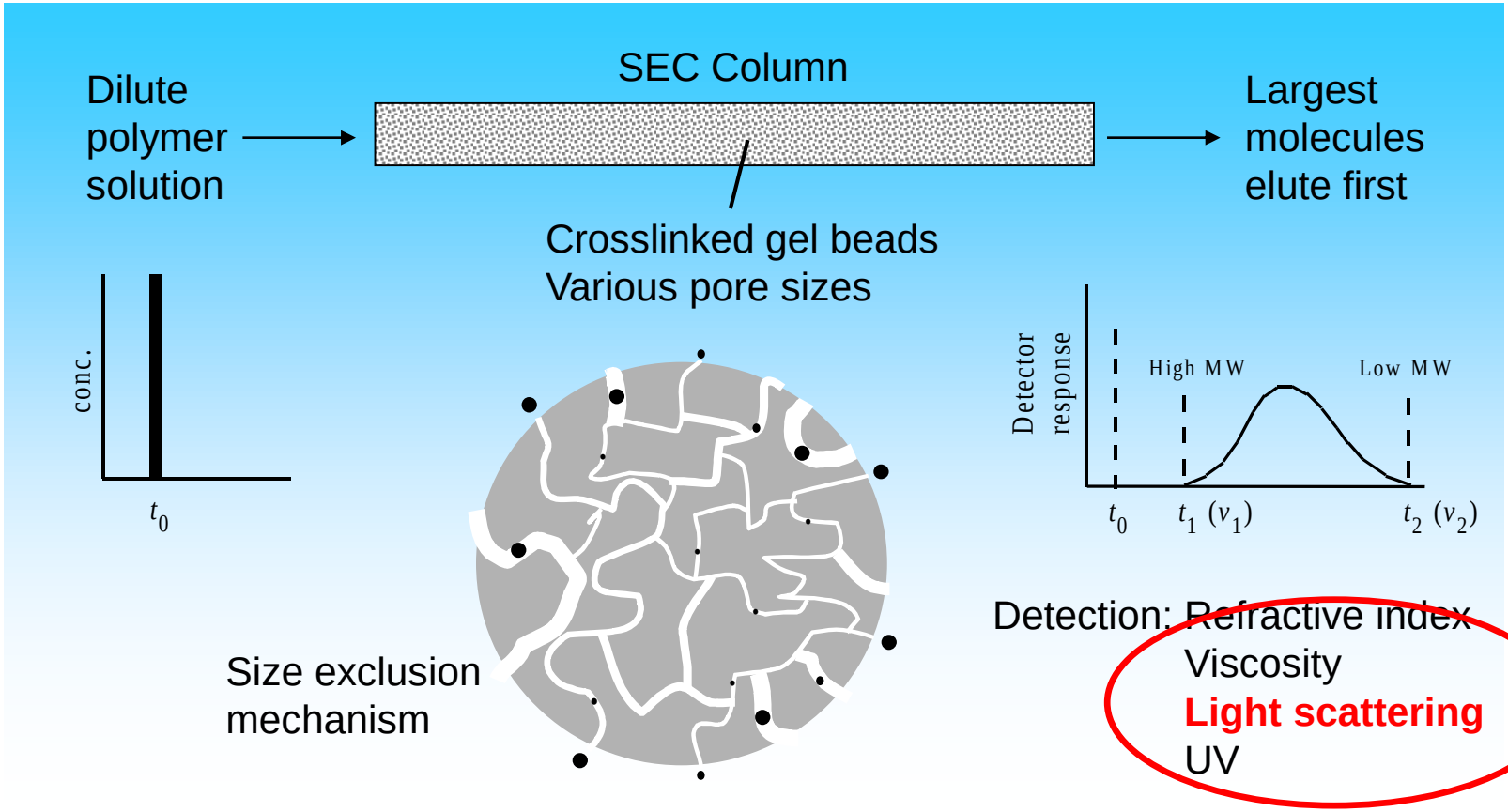
So, scattering measures R_g and P_0.

R_g: size

P_0: mass.

Size exclusion chromatography

- Apparatus and principle

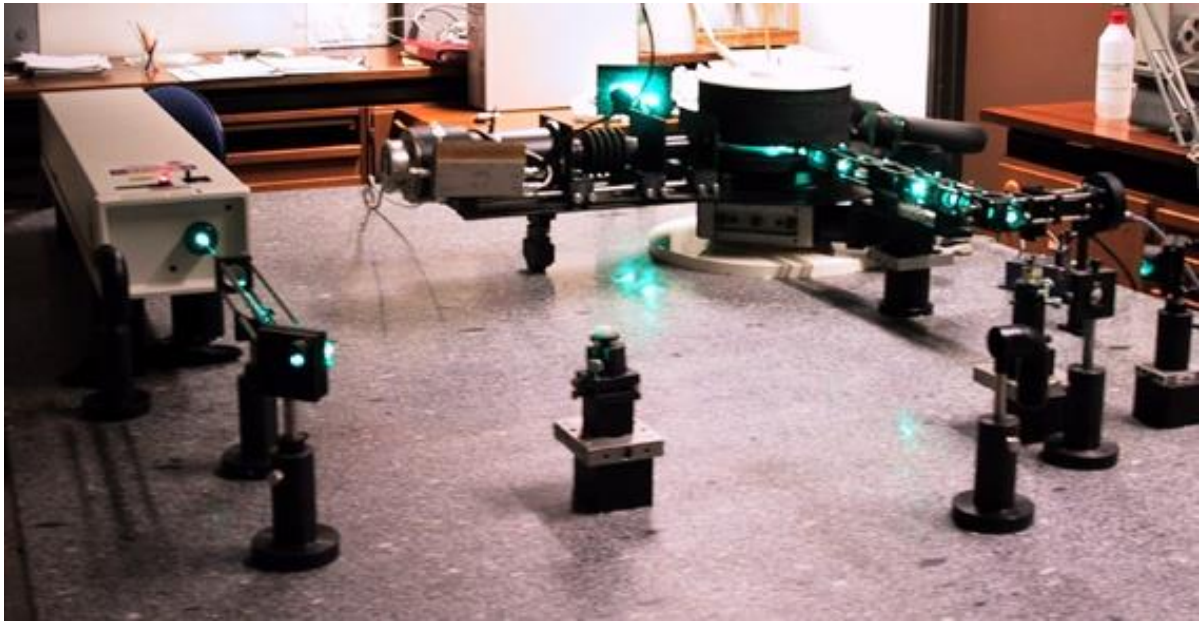


Light Scattering – a few comments

- Light-Scattering probes:

  (1) number density of chains (intensity)

  (2) radius of gyration (angle-dependence)

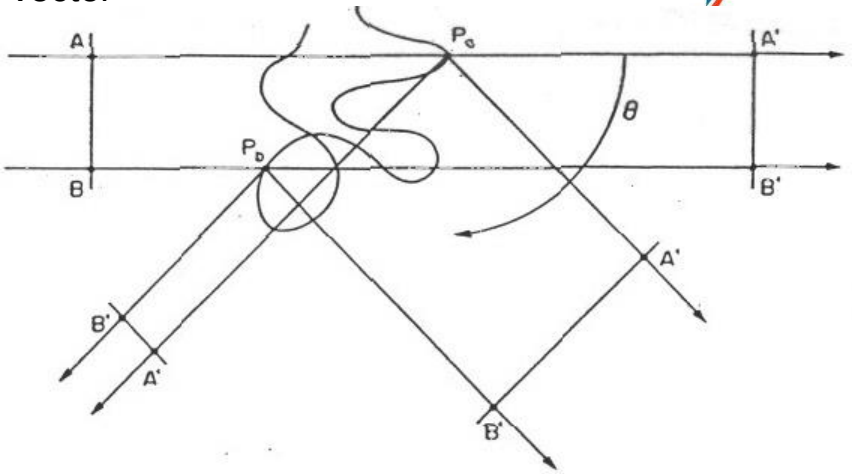


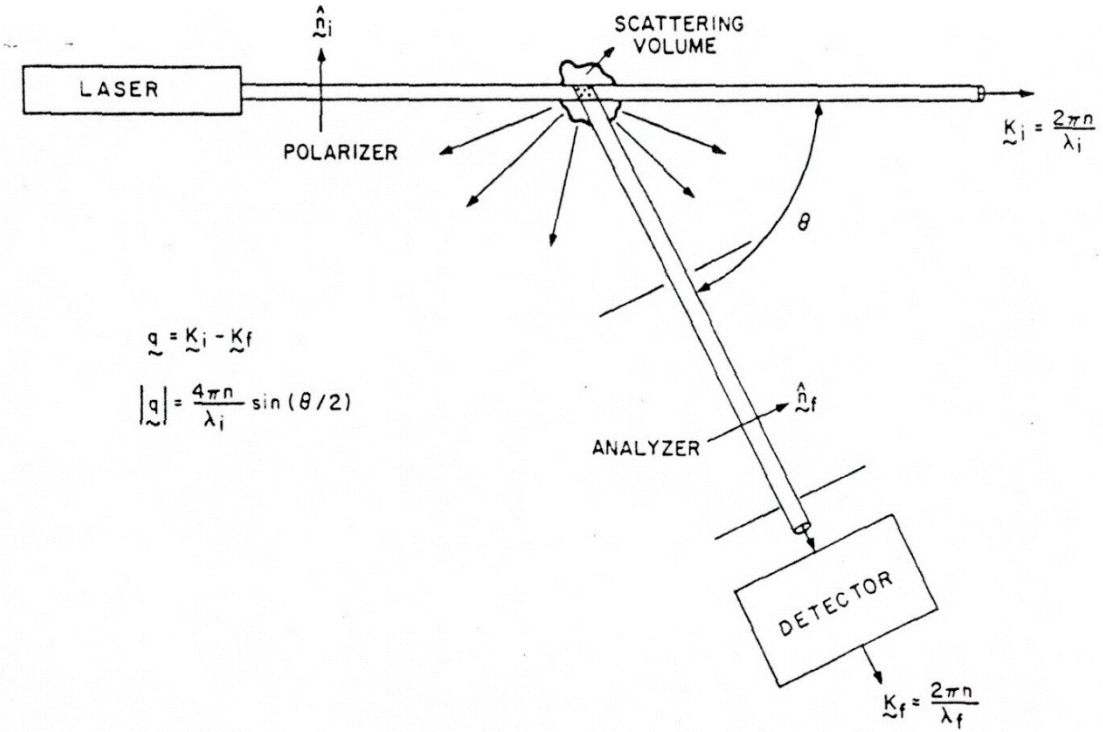
●θ information typically conveyed through the scattering vector

$$\vec{q} = \vec{K}_i - \vec{K}_f$$

where

$$|\vec{q}| = q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$





Light scattering

If it is a VERY dilute solution:

$$R_\theta = KcMP(\theta)$$

The Rayleigh Ratio

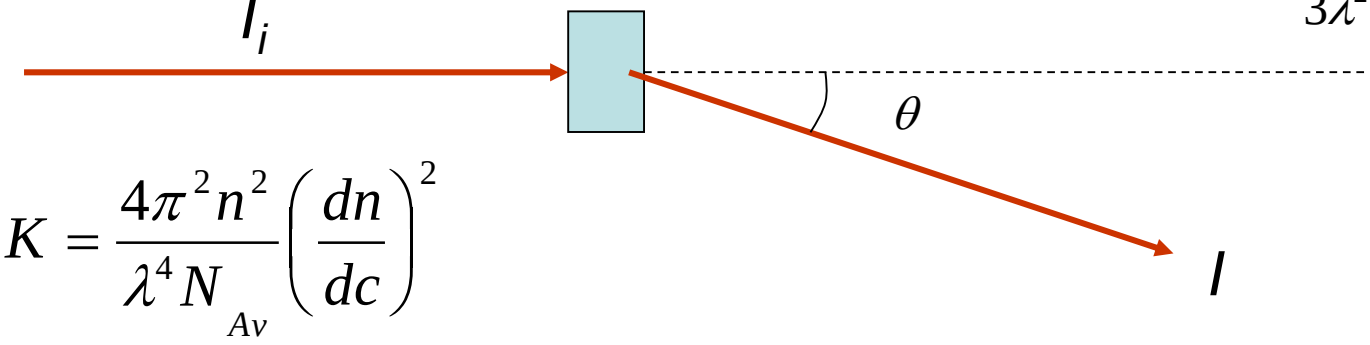
$$R_\theta = \frac{Ir^2}{I_i V}$$

Number of scatterers

Size of scatterers

$$P(\theta) = 1 - \frac{q^2}{3}\left\langle R_g{}^2 \right\rangle$$

$$= 1 - \frac{16\pi^2}{3\lambda^2}\left\langle R_g{}^2 \right\rangle \sin^2\left(\frac{\theta}{2}\right)$$



$$K = \frac{4\pi^2 n^2}{\lambda^4 N_{Av}}\left(\frac{dn}{dc}\right)^2$$

If it is a MORE CONCENTRATED dilute solution, then account for interactions between polymers:

$$\frac{Kc}{R_\theta} = \frac{1}{M\ P(\theta)} + 2A_2 c$$

STATIC LIGHT SCATTERING – More Detail

-assume incident light which is polarised perpendicular to the scattering plane

-scattering units of interest are monodisperse flexible polymer chains

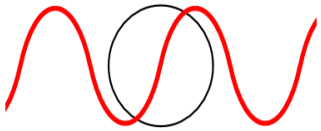
-no extreme interactions such as strongly interacting polyelectrolytes

-not too concentrated which would promote multiple scattering (n.b. transmittance should exceed 0.95)–Dilute solutions (mgs per ml)

$$\frac{Kc}{R_\theta} = \frac{1}{M\ P(\theta)} + 2A_2c \qquad \text{where} \qquad K = \frac{4\pi^2 n_0^2}{N_A \lambda_0^4}\left(\frac{dn}{dc}\right)^2 \qquad (1)$$

•WHAT YOU NEED

n_0	solvent refractive index
$c(g\ cm^{-3})$	concentration of solute in grams/ml
$N_A\ (mol^{-1})$	Avogadro's number
λ_0 (cm or nm)	vacuum wavelength of incident light
$*R_\theta\ (cm^{-1})$	excess Rayleigh Ratio
$*dn/dc\ (cm^3 g^{-1})$	refractive index increment



•WHAT YOU GET

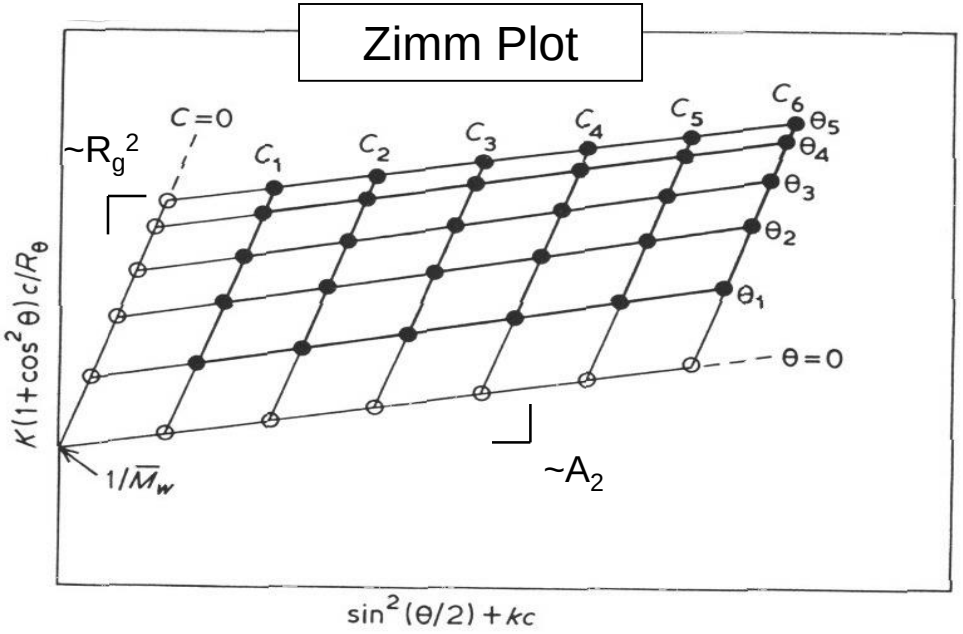
$M\ (g\ mol^{-1})$	molar mass
$*P(\theta)$	particle scattering factor that describes the angular variation in the intensity of the scattered light and leads to an indicator of size
$*A_2(cm^3\ mol\ g^{-2})$	second virial coefficient (solvent-solute interactions)

Pulling it all together…..

$$\left.\frac{Kc}{R_\theta}\right| = \frac{1}{M}\left[1+\frac{16\pi^2}{3\lambda^2}R_g{}^2\sin^2\left(\frac{\theta}{2}\right)\right]+2A_2c$$

C→0; θ→0

$\cos^2\theta$ deals with unpolarised radiation and becomes 1 for vertical polarisation



Filled symbols are data

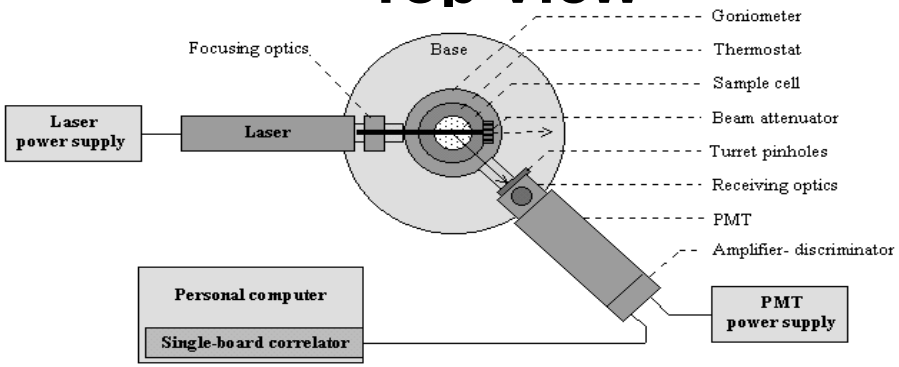
Open symbols are extrapolations

$$\left.\frac{Kc}{R_\theta}\right|_{C=0} = \frac{1}{M}+\frac{16\pi^2}{3M\lambda^2}R_g{}^2\sin^2\left(\frac{\theta}{2}\right)$$

$$\left.\frac{Kc}{R_\theta}\right|_{\theta=0} = \frac{1}{M}+2A_2c$$

When considering polydispersity, M is actually the weight average molecular weight, M_w and $\langle R_g^2\rangle$ is actually $\langle R_g^2\rangle_z$

Goniometer Style Laser Light Scattering- Top View



Multi-Angle Laser Light Scattering- Top View

(Wyatt Technology-www.wyatt.com)