

# Introduction à la diffusion de rayonnement

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Objectif :

- suivre de façon critique une communication scientifique qui présente et interprète des expériences de diffusion de rayonnement (qualitatif).
- vous donner envie de pratiquer
- utiliser de manière éclairée les outils d'ajustement de courbes expérimentales (quantitatif).

## Radiation scattering: the principle

Scattering techniques: one of the most ubiquitous tools in physics. First image of the atom structure from Rutherford experiment

Light:  $\lambda=400\text{-}700\text{ nm}$

Angular dependence of the scattered intensity

X-Rays or neutrons:  $\lambda=0,1\text{-}2 \text{ nm}$

Small angle scattering

Scattering intensity is concentrated at  $qR < 1$

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

Scattering vector

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## The aim of a scattering experiment

**The determination of the structure and of the organisation of « particles » dispersed in a homogeneous medium**

J. P.Cotton Bombannes 1990

**Watch the units !**

colloids,  
macromolecules,  
their aggregates or  
pores in a solid

**Watch the scale !**  
**main graph: lin – lin**  
**inset : log – log**

Intensity  $\text{cm}^{-1}$

$10^0$     $10^{-2}$     $10^{-4}$     $10^0$     $10^{-2}$     $10^{-4}$     $10^0$     $10^{-2}$     $10^{-4}$

$10^0$     $10^{-2}$     $10^{-4}$     $10^0$     $10^{-2}$     $10^{-4}$     $10^0$     $10^{-2}$     $10^{-4}$

$10^0$     $10^{-2}$     $10^{-4}$     $10^0$     $10^{-2}$     $10^{-4}$     $10^0$     $10^{-2}$     $10^{-4}$

$10^0$     $10^{-2}$     $10^{-4}$     $10^0$     $10^{-2}$     $10^{-4}$     $10^0$     $10^{-2}$     $10^{-4}$

$q (\text{\AA}^{-1})$     $q (\text{\AA}^{-1})$     $q (\text{\AA}^{-1})$     $q (\text{\AA}^{-1})$

$0$     $0.1$     $0.2$     $0$     $0.01$     $0.02$     $0$     $0.01$     $0.02$

$0$     $0.01$     $0.02$     $0$     $0.01$     $0.02$     $0$     $0.01$     $0.02$

$0$     $0.01$     $0.02$     $0$     $0.01$     $0.02$     $0$     $0.01$     $0.02$

$0$     $0.01$     $0.02$     $0$     $0.01$     $0.02$     $0$     $0.01$     $0.02$

$10^0$     $10^{-2}$     $10^{-4}$     $10^0$     $10^{-2}$     $10^{-4}$     $10^0$     $10^{-2}$     $10^{-4}$

$10^0$     $10^{-2}$     $10^{-4}$     $10^0$     $10^{-2}$     $10^{-4}$     $10^0$     $10^{-2}$     $10^{-4}$

$10^0$     $10^{-2}$     $10^{-4}$     $10^0$     $10^{-2}$     $10^{-4}$     $10^0$     $10^{-2}$     $10^{-4}$

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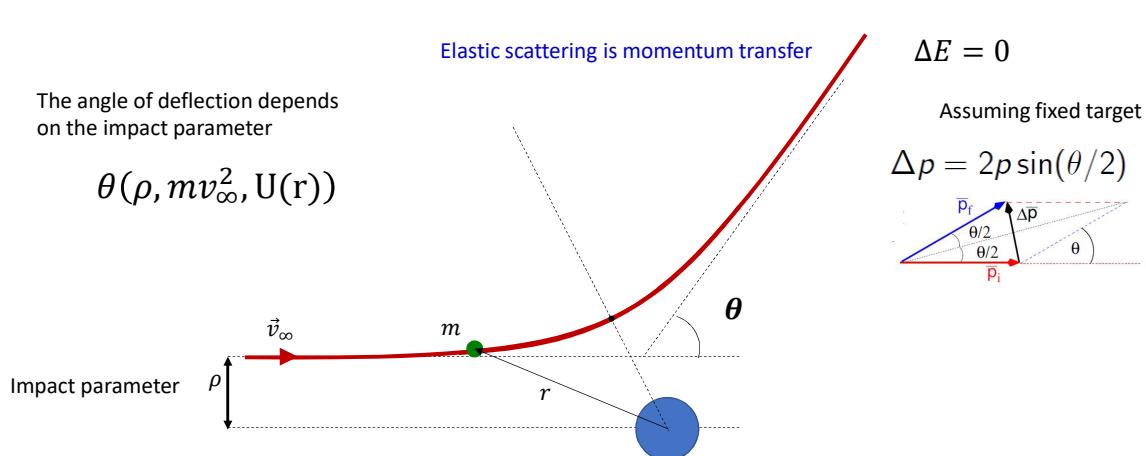
$q (\text{\AA}^{-1})$     $q (\text{\AA}^{-1})$     $q (\text{\AA}^{-1})$     $q (\text{\AA}^{-1})$

**Small-angle scattering for beginners**  
Cedric J. Gommès,<sup>a,\*</sup>‡ Sebastian Jakusch<sup>b</sup> and Henrich Frielinghaus<sup>b</sup>  
*J. Appl. Cryst.* (2021), 54, 1832–1843

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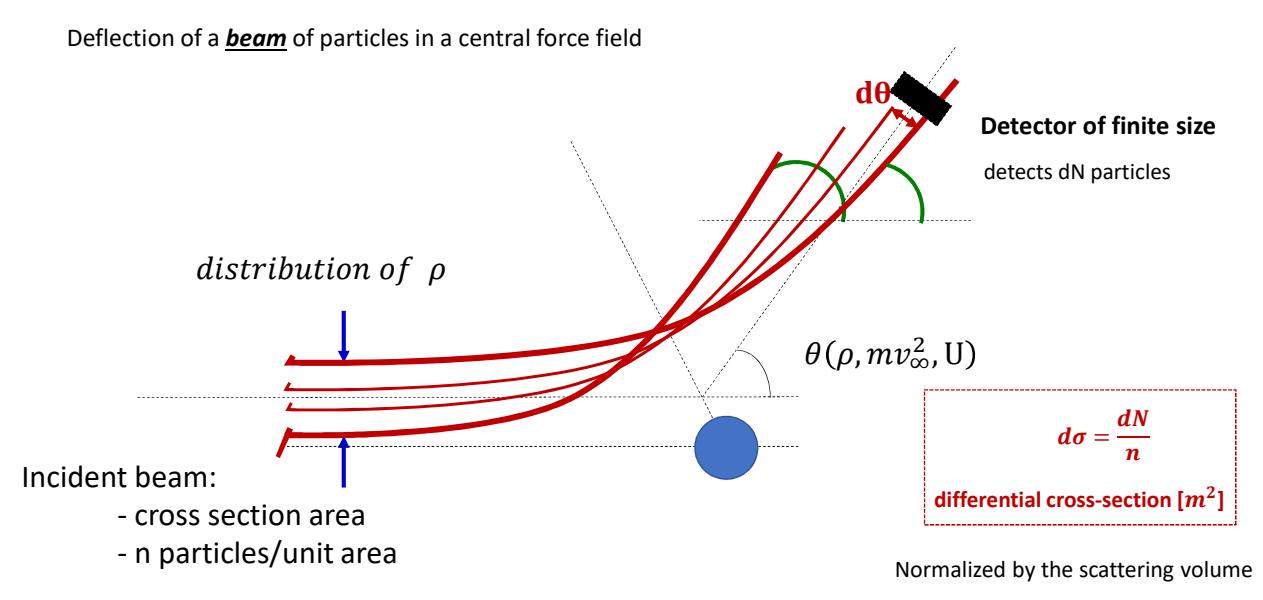
## Deflection of the trajectory of one single particle in a central repulsive force field



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## The scattering phenomenon



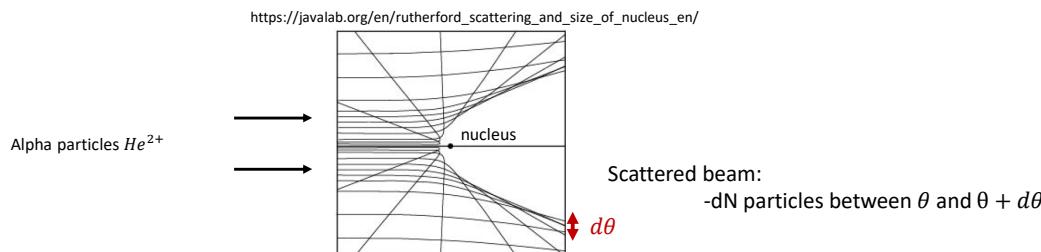
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## The scattering phenomenon

### Rutherford experiment

Coulomb interaction between alpha particles and the nucleus of the atom



Incident beam of constant cross-section  
n particles/unit area → Scattered beam of growing cross-section

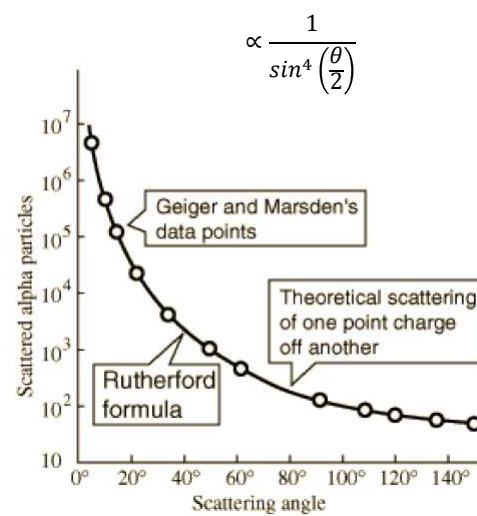
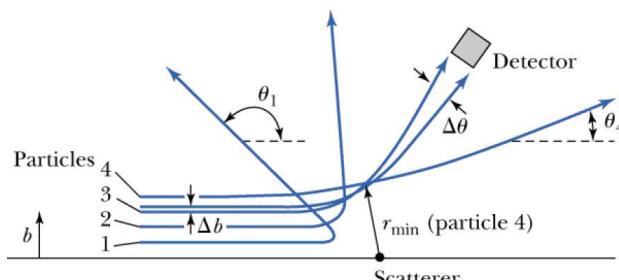
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## The scattering phenomenon

### Rutherford experiment

- Trajectories depend on the impact parameter.



[https://javab.org/en/rutherford\\_scattering\\_and\\_size\\_of\\_nucleus\\_en/](https://javab.org/en/rutherford_scattering_and_size_of_nucleus_en/)

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## Electromagnetic radiation scattering

The electric field of incoming wave induces dipole oscillation in the atoms

Accelerated charges emit radiation

Light : 2 eV ( $\lambda = 600\text{nm}$ )

Polarizability (Refractive index)

X-Rays:  $10^4$  eV ( $1 < \lambda < 5 \text{\AA}$ )

Electron density (Atomic number)

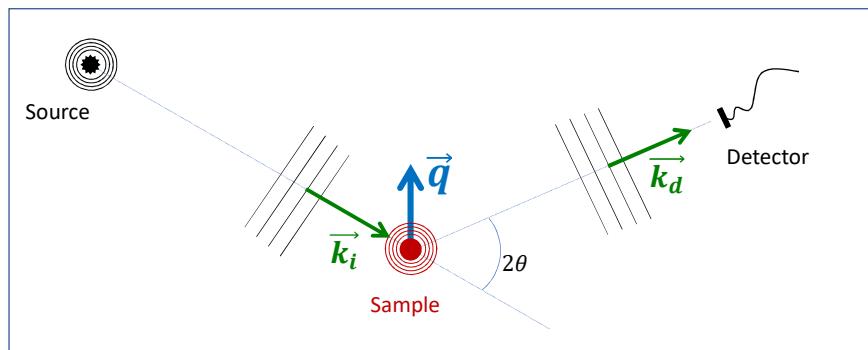
Neutrons:  $10^{-3}$ eV ( $(1 < \lambda < 20 \text{\AA})$ )

Scattering length density (nucleus spin)

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## Electromagnetic radiation scattering



$$|\vec{k}_i| = \frac{2\pi}{\lambda}$$

$$\vec{p} = \hbar \vec{k}$$

$$\vec{q} = \vec{k}_d - \vec{k}_i$$

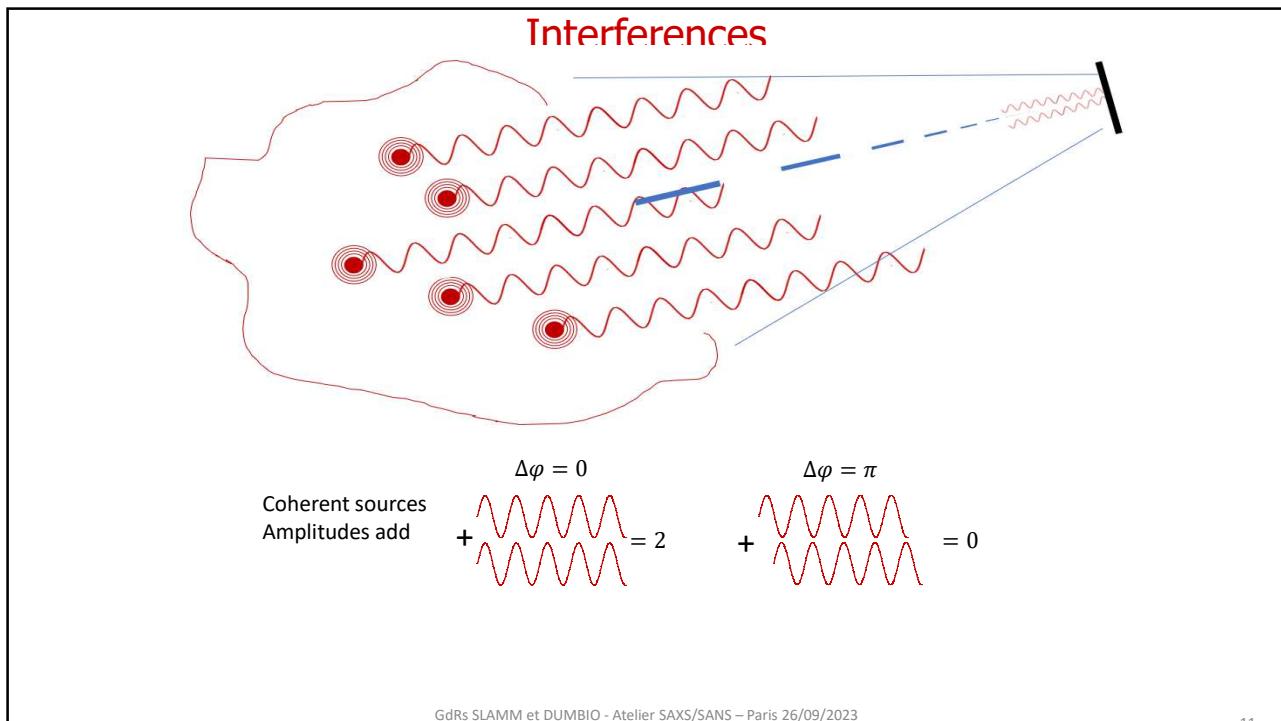
$$|\vec{k}_d| = \frac{2\pi}{\lambda}$$

Elastic scattering

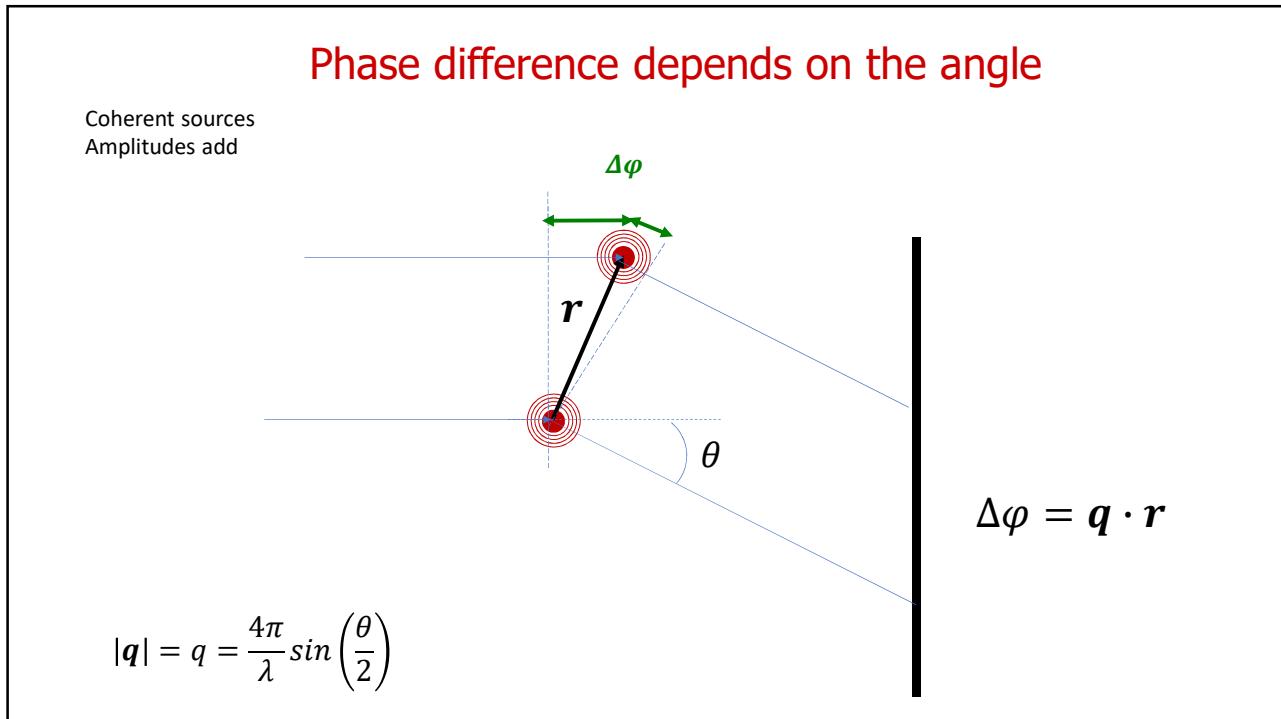
Scattering vector  
characterizes the momentum transfert

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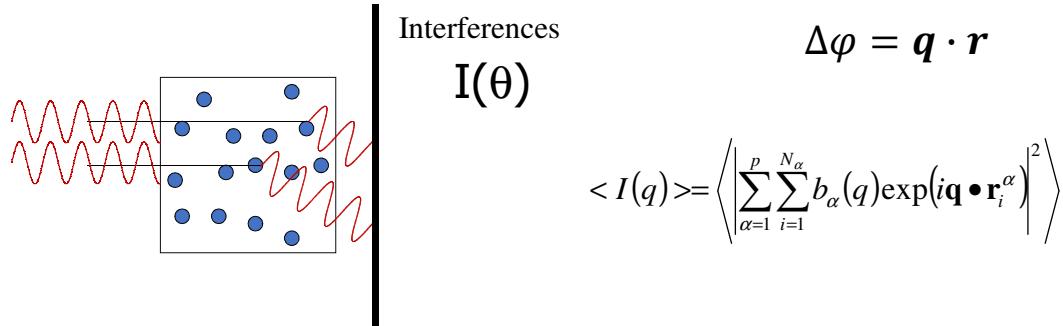
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## The scattered intensity results from interferences



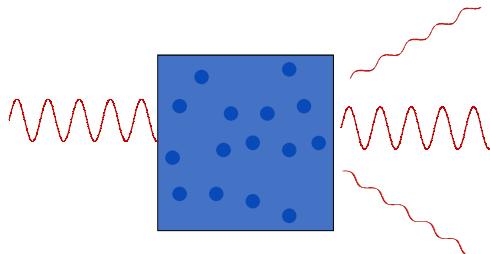
**Intensity patterns of scattered radiation are histograms of distances (Glatter)**

## Radiation scattering contrast



From a completely homogeneous medium,  
there is no net scattered intensity except at zero angle (propagation)

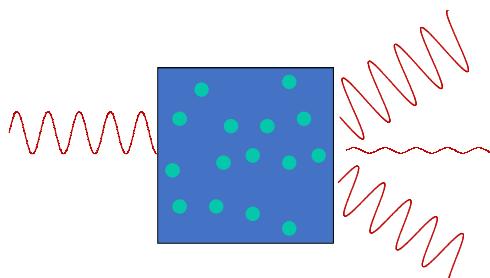
## Radiation scattering contrast



For the sum not to cancel at  $\theta \neq 0$ ,  
the scattering power must vary from place to place.

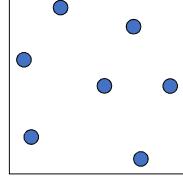
Scattered intensity reveals  
composition fluctuations

## Radiation scattering contrast



When transmittance decreases due to  
scattering = turbidity

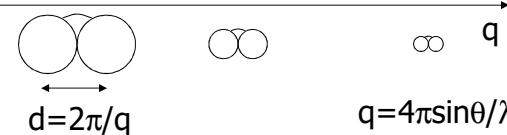
### Hand waving Fourier transform of the pair correlation function

Dilute suspension 

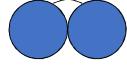
Measuring the angular variation of the scattered intensity  $\Leftrightarrow$

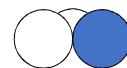
Scanning the sample with a pair of glasses with the following rules :

- Rule 1: The size of the glasses is  $1/q$  (interferences)



$I = \sum i$

$i=0$  

$i=1$  

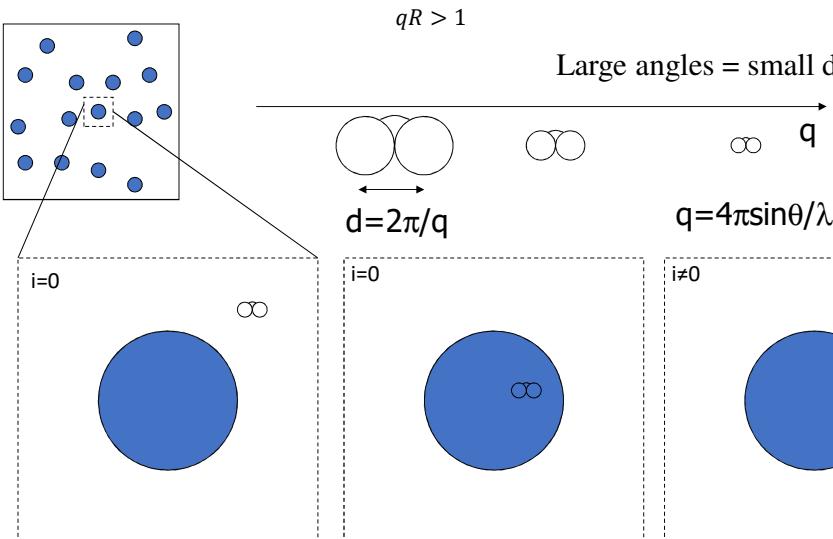
-Rule 2: Each scanning step contributes to the scattered intensity if each glass of the pair do not see the same thing (contrast)

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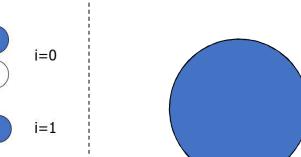
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### At large angles=scanning with small glasses

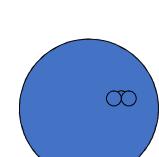
$qR > 1$

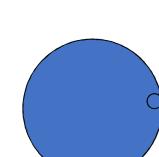
Large angles = small distances 

$I = \sum i$

$i=0$  

$i=1$  

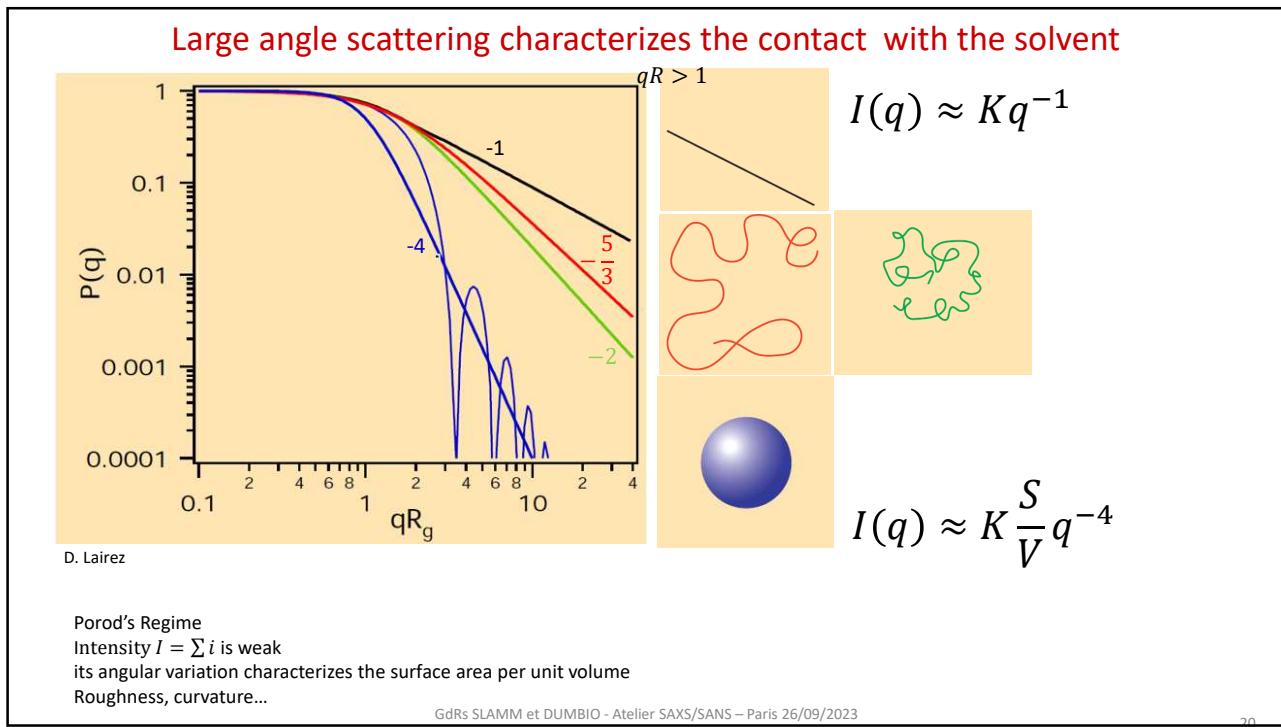
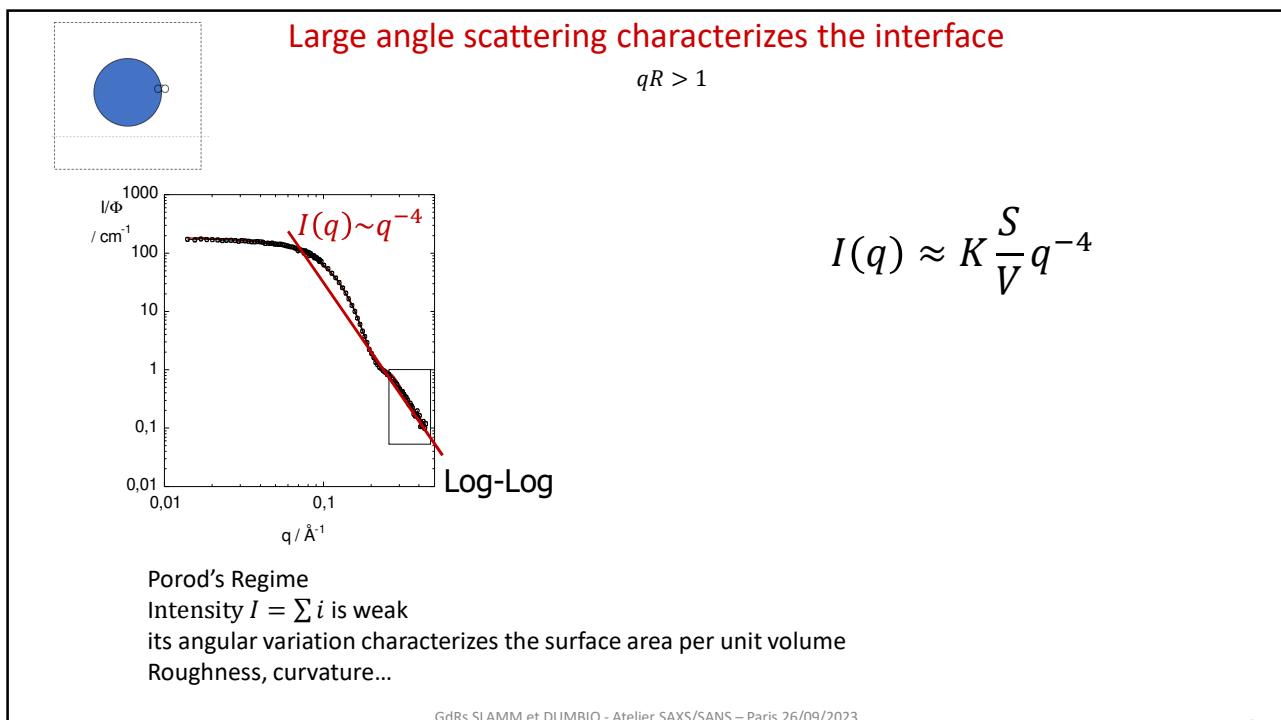
$i=0$  

$i=0$  

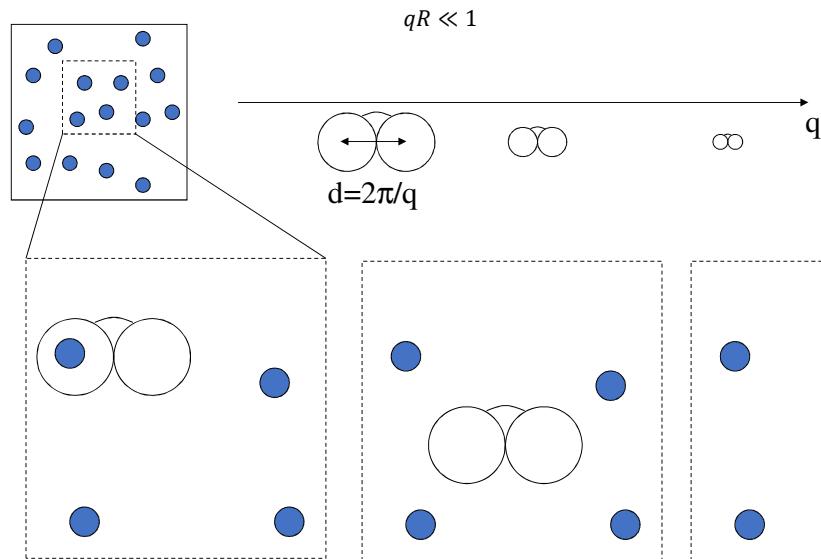
Most often  $i=0$   
 $i \neq 0$  only at interface

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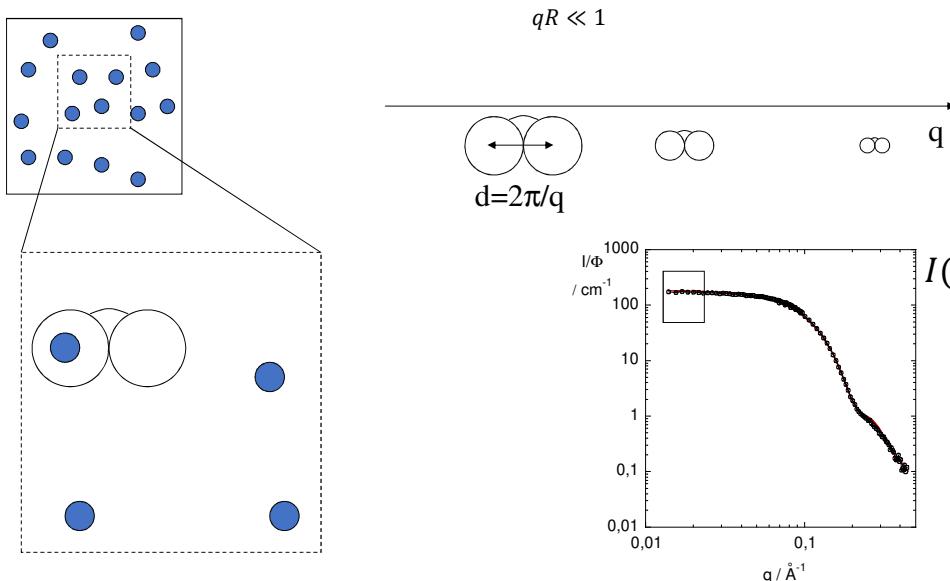
### At small angles=scanning with large glasses



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### At small angles=scanning with large glasses

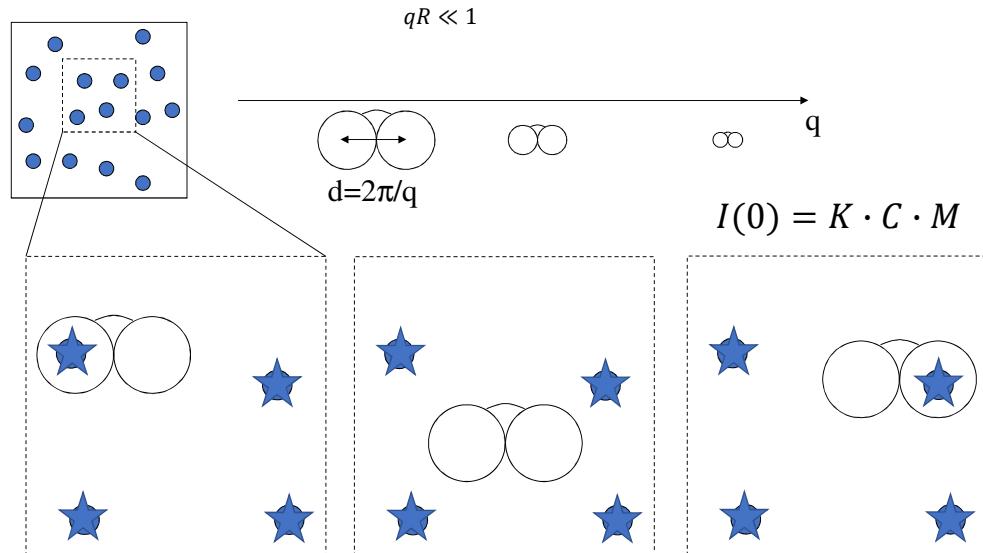


Dilute regime:  $I(0)$  proportional to the concentration and to the mass of particle

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### At small angles=scanning with large glasses



No information about the shape nor the size of the particles

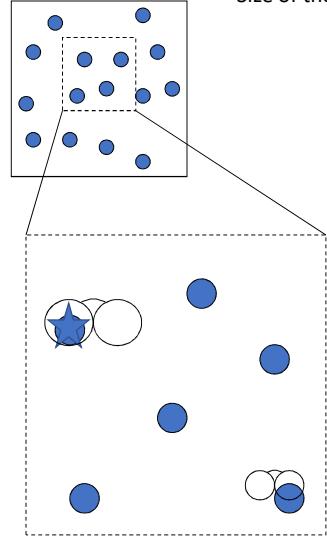
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### At intermediate angles

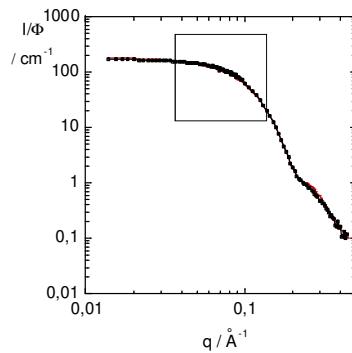
Size of the glasses = size of the particle

$qR \approx 1$



$$P(q) \approx \exp \left[ -\frac{(qR_g)^2}{3} \right]$$

Guinier approximation

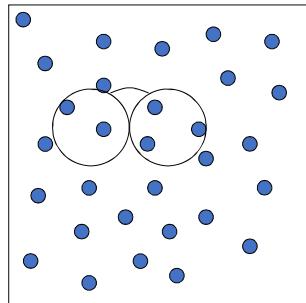


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### Concentrated solutions small angles

$$qR \ll 1$$



$$I(0) = Kc \left( \frac{d\pi}{dc} \right)^{-1}$$

$$S(0) = c \left( \frac{d\pi}{dc} \right)^{-1}$$

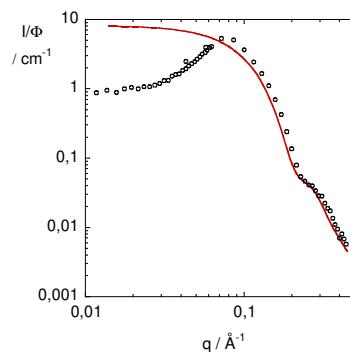
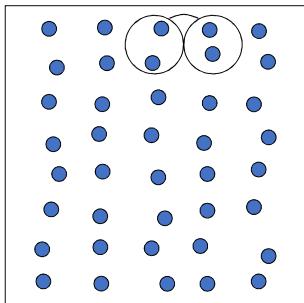
$$\Pi = RTc(1 + A_2c + A_3c + \dots)$$

The contrast comes from the osmotic compressibility,  
It means on how easy it is for the concentration to fluctuate,  
to get away from average.

$$\chi = c \left( \frac{d\pi}{dc} \right)^{-1}$$

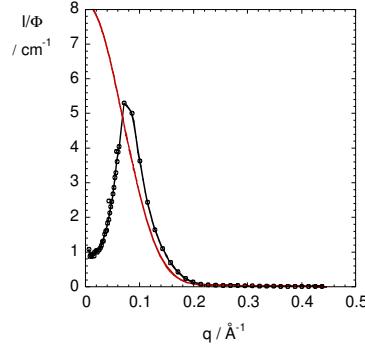
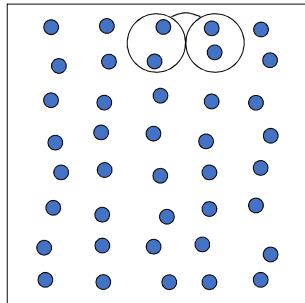
### Concentrated solutions small angles

#### Repulsive interactions



Concentrated solutions  
small angles

**Repulsive interactions**

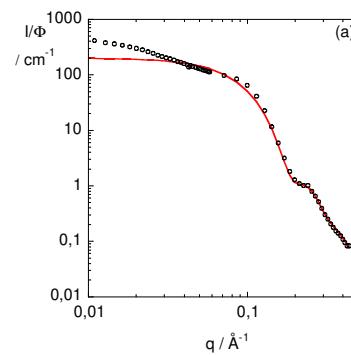
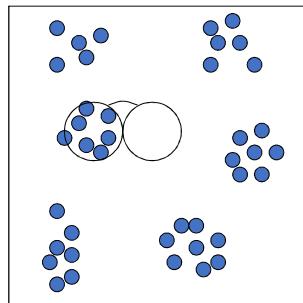


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Concentrated solutions  
small angles

**Attractive interactions**

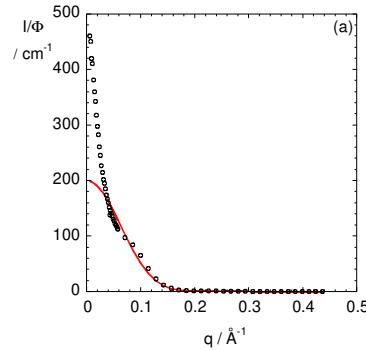
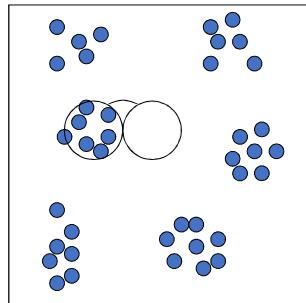


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## Concentrated solutions small angles

### Attractive interactions

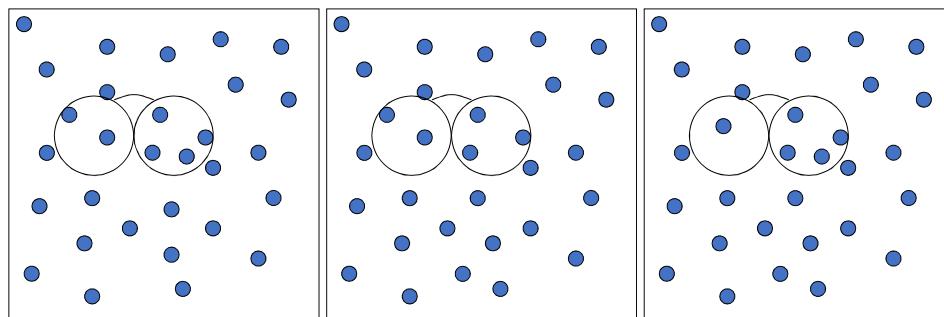
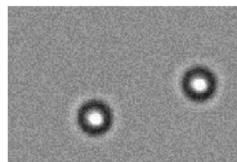


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## Dynamic light scattering

Diffusion coefficient measurement

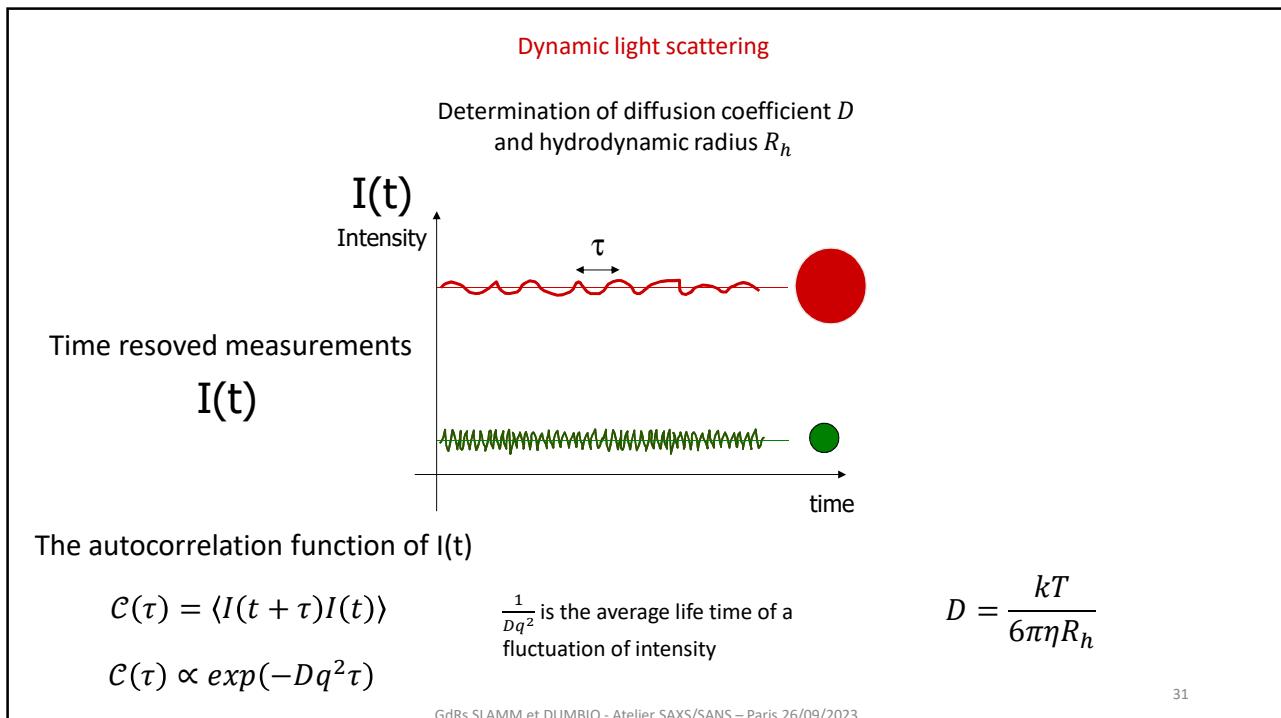


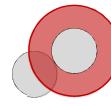
$$I(q, t)$$

Scattered intensity is not constant over time, because  
particle particles diffuse.

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<b>What is size ?</b>		
Radius of gyration $R_g$	The radius of the spherical shell which would have the same momentum of « inertia » From $P(\theta)$	$R_g^2 = \frac{1}{p} \left\langle \sum_{i=1}^p (\vec{r}_i - \vec{r}_M)^2 \right\rangle$
Hard sphere radius $R_{HS}$	The radius of the sphere which would have the same excluded volume Impossible to find two centers of particle closer than $2R_{HS}$ From 2nd Virial coefficient $B$	 $\frac{Kc}{I(c)} \propto \frac{1}{M} + 2A_c c$ $q \rightarrow 0$
Hydrodynamic radius $R_h$	The radius of the sphere which would have the same diffusion coefficient From autocorrelation function of $I(t)$	$D = \frac{k_B T}{6\pi\eta R_h}$

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## Extracting informations from scattering data

For monodispersed isotropic objects

$$I(q) = KV^2v \cdot P(q) \cdot S(q)$$

K: contrast, **composition**

v: number density of particles, **concentration**

V: volume of particles, **size** (Large objects biased)

### Form factor

- $P(q)$ : **size, shape**
- Dominant at large  $q$
- $P(0)=1$
- $P(q)$  decreases when  $q$  increases

Analytical expressions exist  
for many shapes

### Structure factor

- $S(q)$ : **Inter-objects distances, Interactions**
- $S(q) \approx 1$  when  $v \rightarrow 0$
- Dominant at small  $q$
- $S(q \rightarrow \infty) = 1$

## Extracting informations from scattering data

As a macromolecular chemist

$$I(q) = KV^2v \cdot P(q) \cdot S(q)$$

$$\frac{KV^2v \cdot P(q)}{I(q)} = \frac{1}{S(q)}$$

$$P(q \rightarrow 0) = 1$$

$$\frac{Kc}{R_\theta^0} = \frac{1}{M_W} + 2A_2c + 3A_3c^2 + \dots = S(0)^{-1}$$

More relevant for light  
because  $\lambda$  is so large

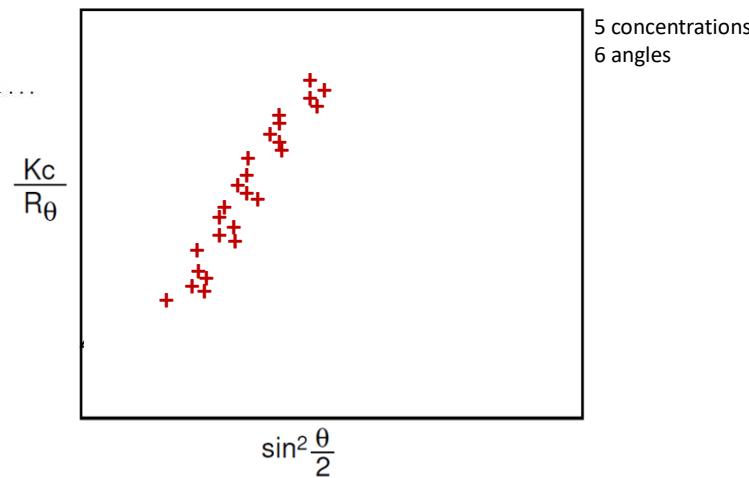
$R_\theta^0$  is the Rayleigh ratio at zero angle in  $cm^{-1}$

$$R_\theta = \frac{1}{V_{scat}} \frac{I_{scattered}}{I_{incident}} (d_{detector-sampel})^2 \cong \text{Absolute intensity } [L]^{-1}$$

## Extracting informations from scattering data

As a macromolecular chemist

$$\frac{Kc}{R_\theta^0} = \frac{P(\theta)}{M_W} + 2A_2c + 3A_3c^2 + \dots$$



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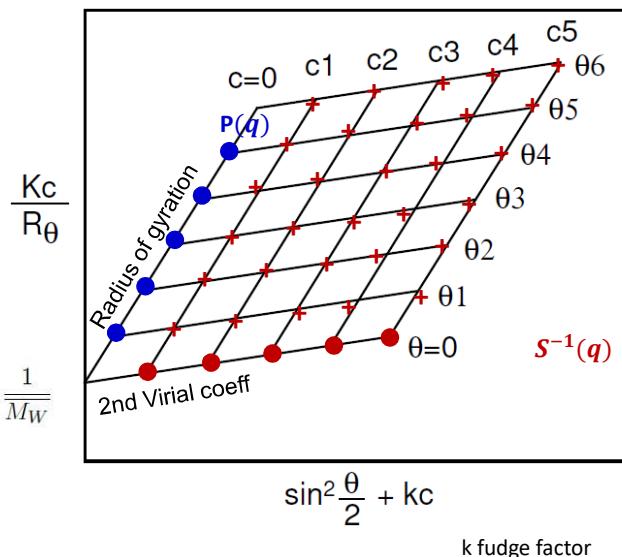
## Extracting informations from scattering data

As a macromolecular chemist

Zimm-plot

$M_w$  in g/mol  
If  $c$  in g/ml

$$\text{intercept} = \frac{1}{M_W}$$



$$\frac{Kc}{R_\theta^0} = \frac{P(\theta)^{-1}}{M_W} + 2A_2c + 3A_3c^2 + \dots$$

$$\frac{1}{P(\theta)} \approx 1 + \frac{q^2 R_g^2}{3}$$

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