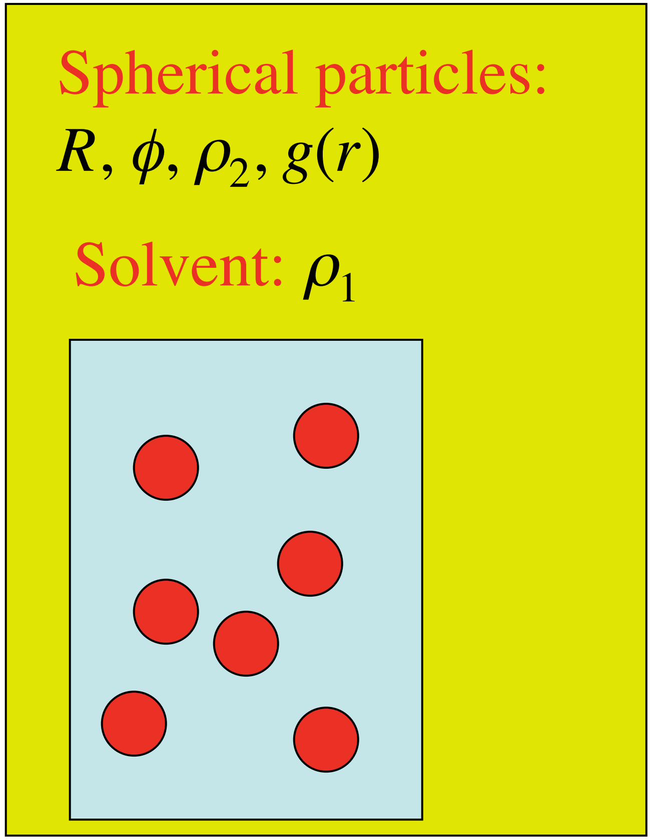
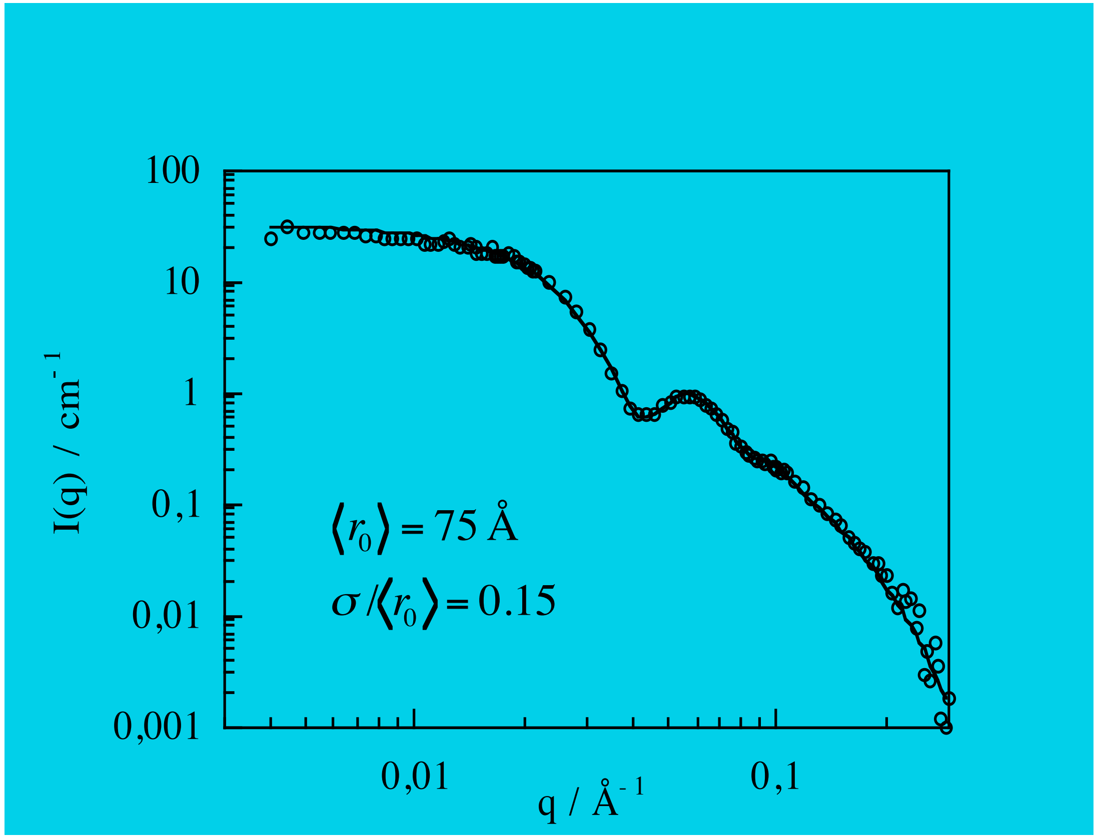
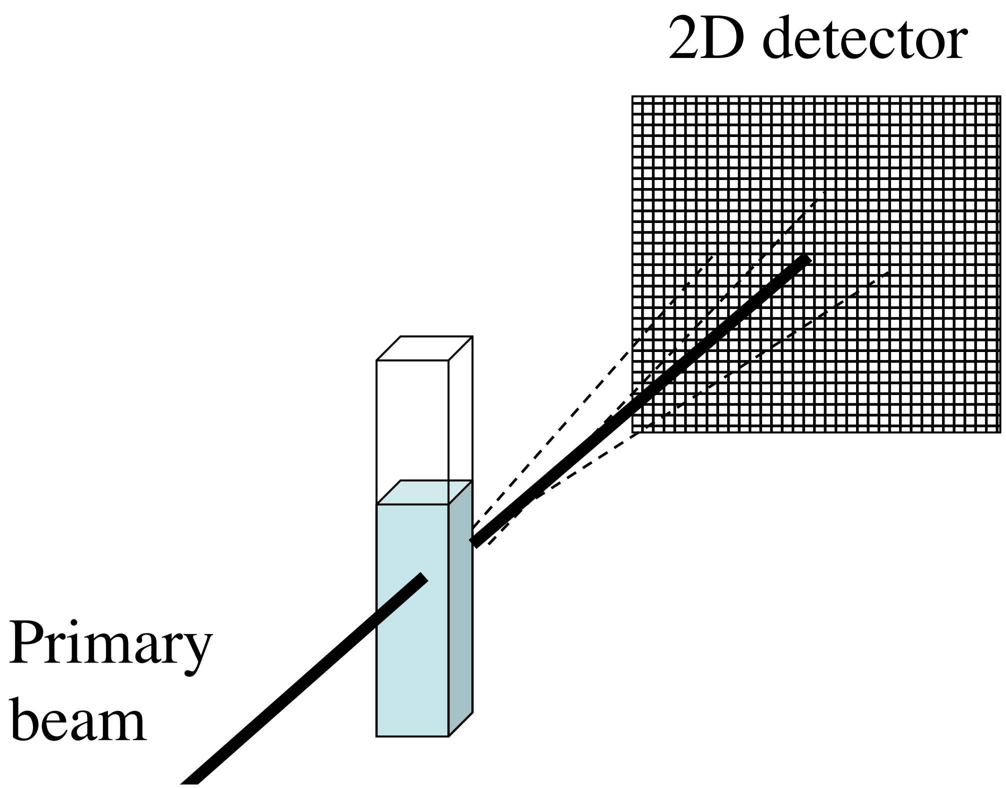
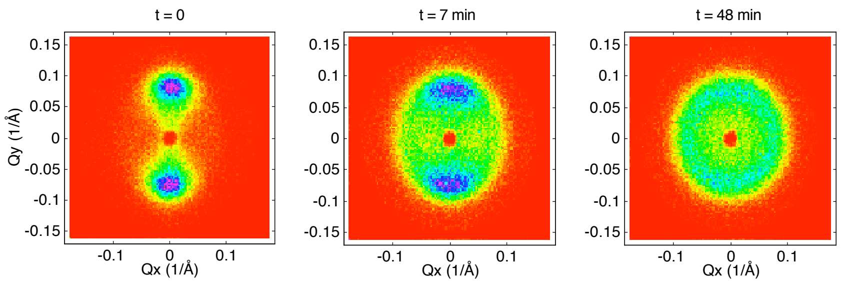
INTRODUCTION TO SMALL ANGLE SCATTERING FROM COLLOIDAL DISPERSIONS

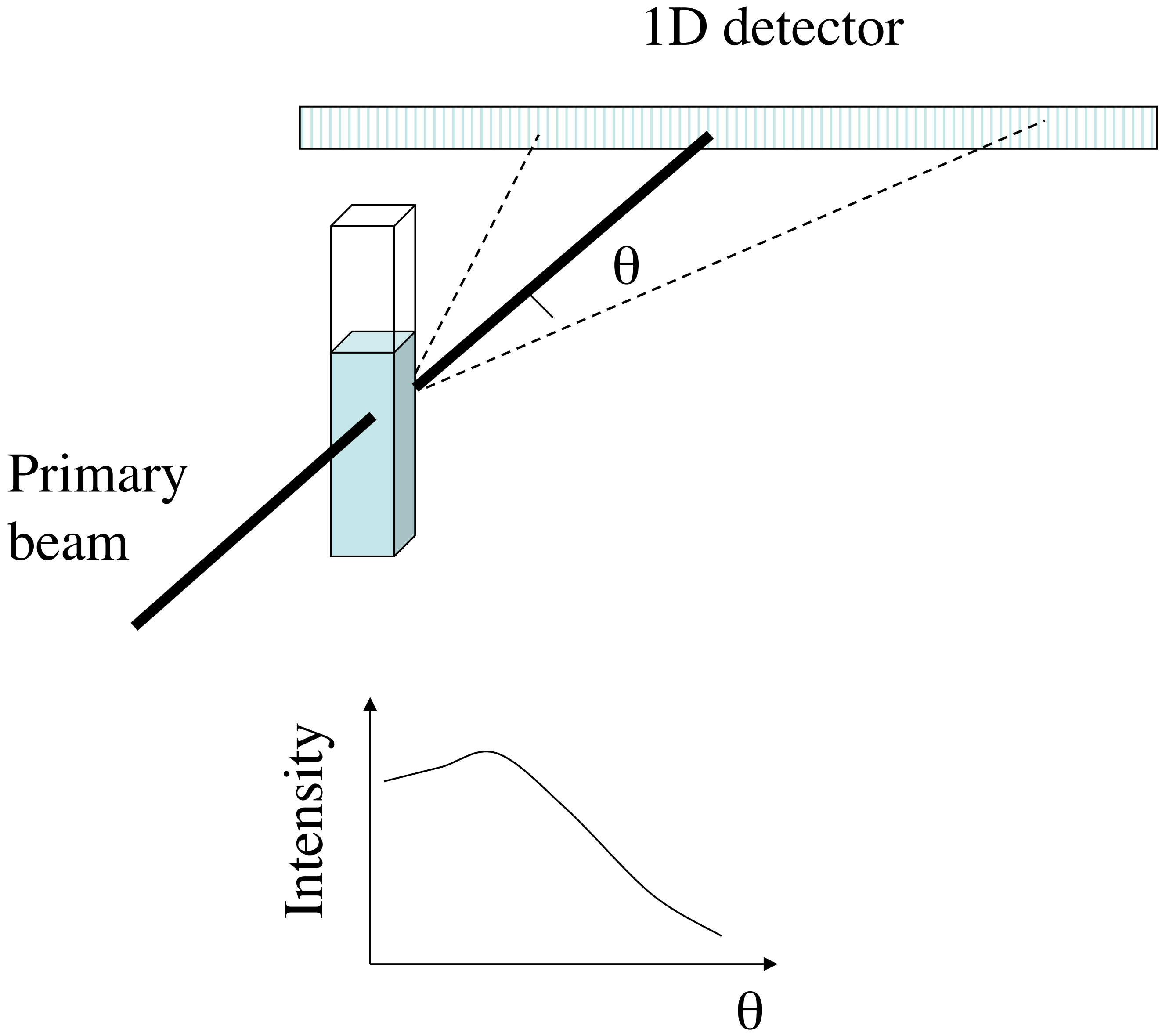
Analysis of small angle scattering data from an isotropic solution (dispersion) of spherical colloidal particles.



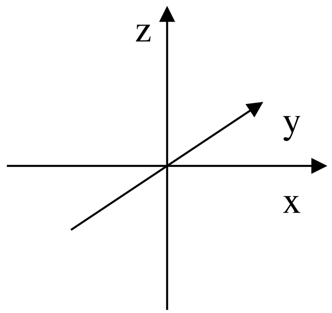


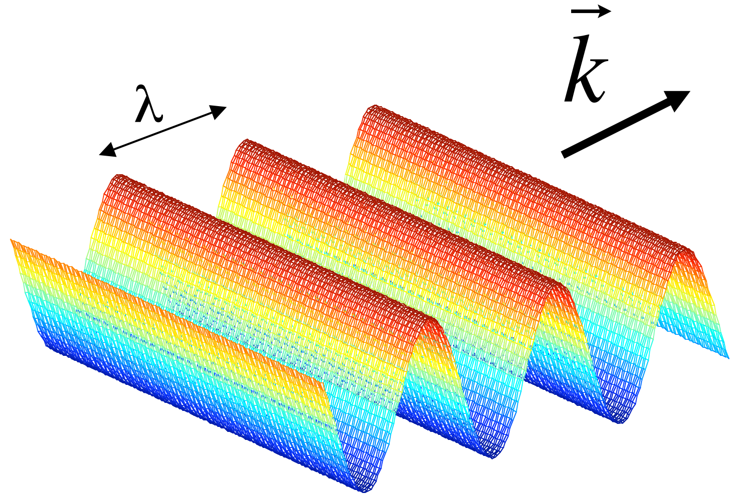

2D detector
Primary
beam


t = 0
t = 7 min
t = 48 min
Qy (1/Å)
Qx (1/Å)
0.15
0.1
0.05
0
-0.05
-0.1
-0.15
-0.1
0
0.1


1D detector
θ
Primary
beam
Intensity
θ

The planar wave





Amplitude:

$$A = A_0\, e^{i\vec{k}\bullet\vec{r}}$$

wave vector:

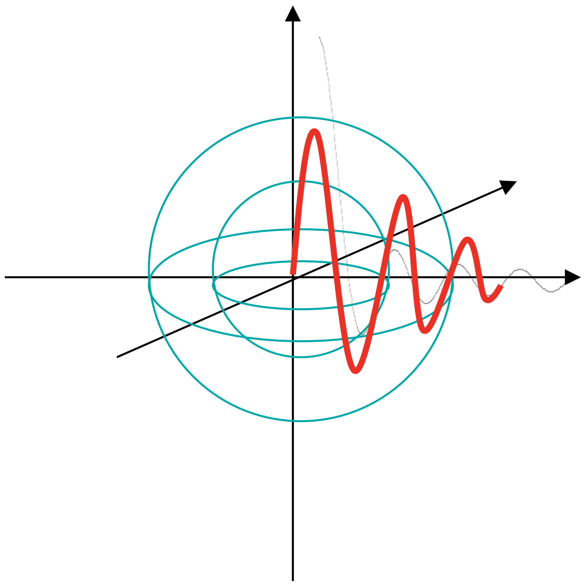
$$\left|\vec{k}\right| = \frac{2\pi}{\lambda}$$

Momentum:

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

$$\left|\vec{p}\right| = \frac{h}{\lambda} \qquad \text{(de Broigle)}$$

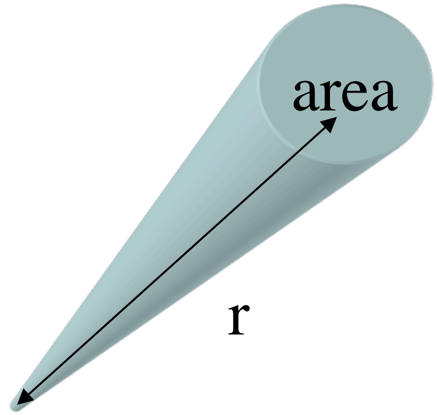
The spherical wave



Amplitude:

$$A = A_0 \frac{b}{r} e^{ikr}$$

INTENSITY

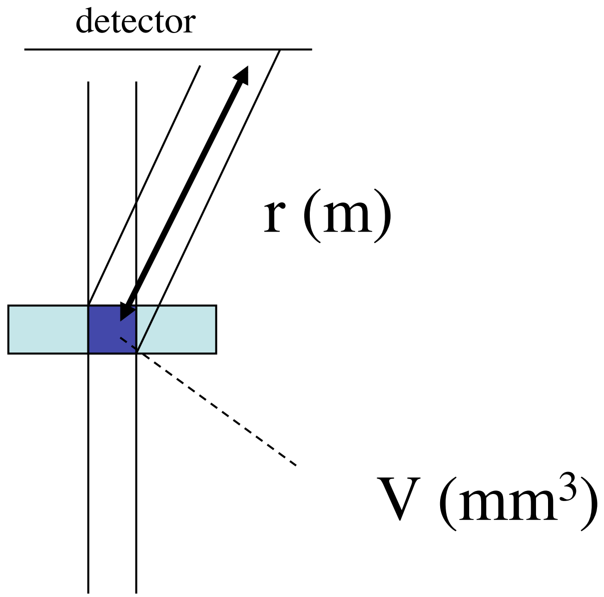


Intensity: $I = \left| A^2 \right|$

Energy flux / time & area $(\perp \vec{k})$

"Number of particles (e.g. photons) / time & area"

$$Area \sim r^2 \Rightarrow I \sim r^{-2} \Leftrightarrow A \sim r^{-1}$$

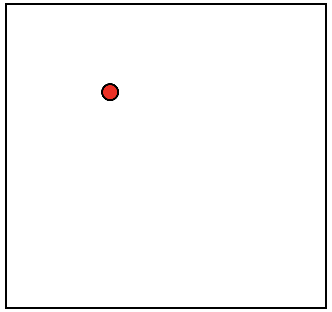


$$I = \frac{I_s}{I_0}\frac{r^2}{V}$$

[length^{-1}] [cm^{-1}]

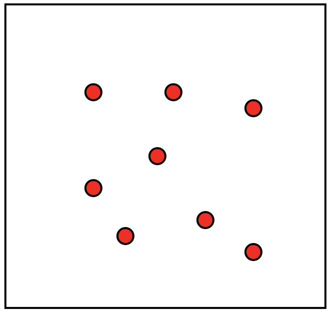
Outline

1)



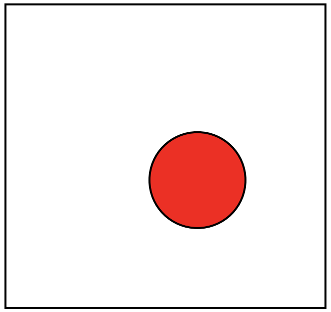
Single scattering centre

2)



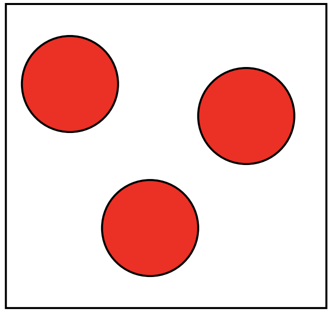
N scattering centra
=> interference

3)



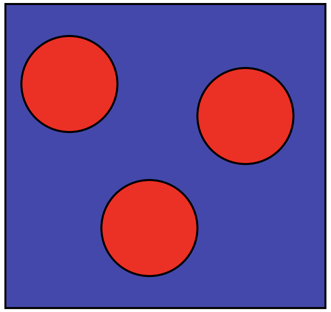
Continuum
Single colloidal particle

4)



N particles
=> interference

5)



+ solvent

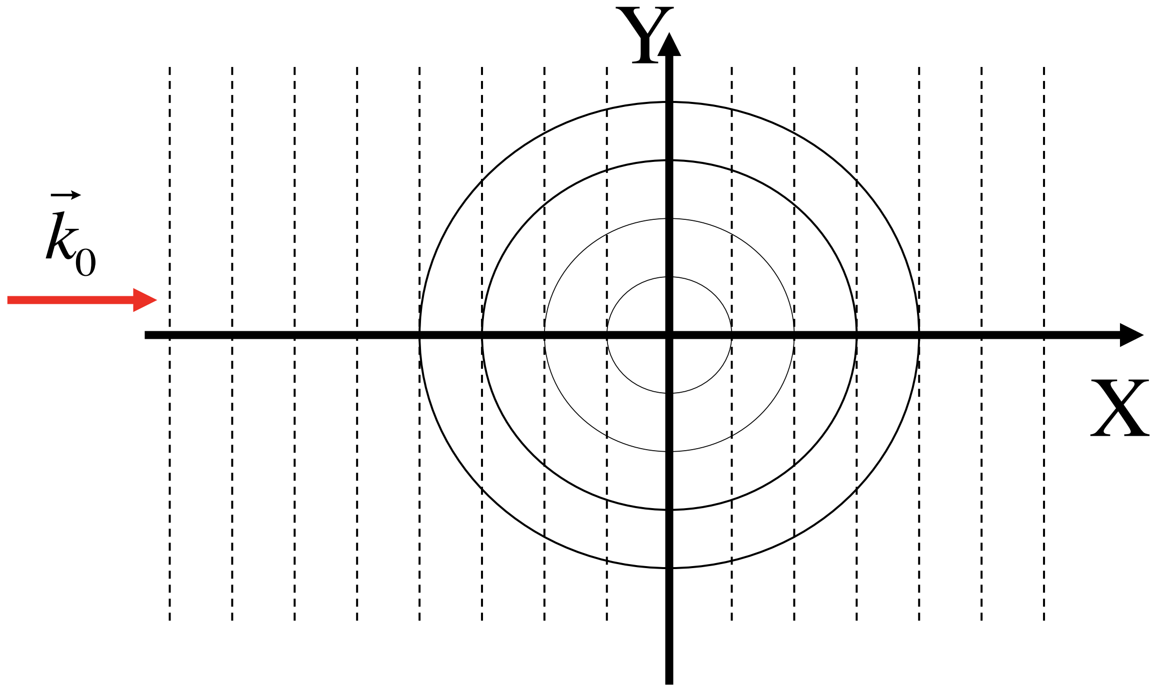
Single scattering centre (single event)

(X-rays: electron, neutrons: atomic nucleus)

$$A_{in} = A_0\, e^{i\vec{k}_0 \bullet \vec{r}}$$

$$A_s = A_0 \frac{b}{r} e^{i k_S r}$$

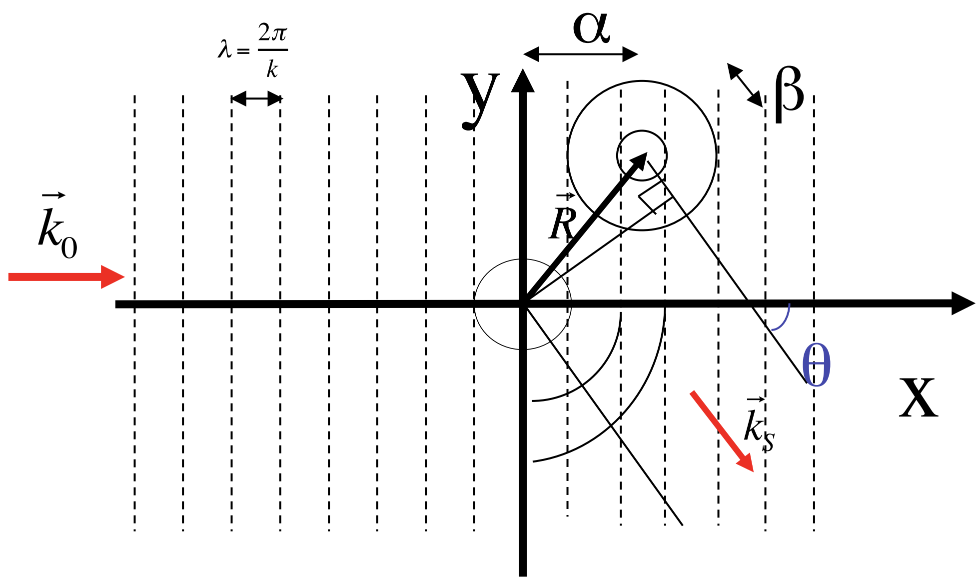
b = "scattering length"



- Coherent scattering: A_{in} and A_s in phase
- Elastic scattering: λ remains unchanged $\Leftrightarrow |\vec{k}_0| = |\vec{k}_S|$

Displaced from the origin - The phase shift

Assume detector distance $r >> R$



Phase shift=

$$= \frac{2\pi}{\lambda}\alpha + \frac{2\pi}{\lambda}\beta =$$

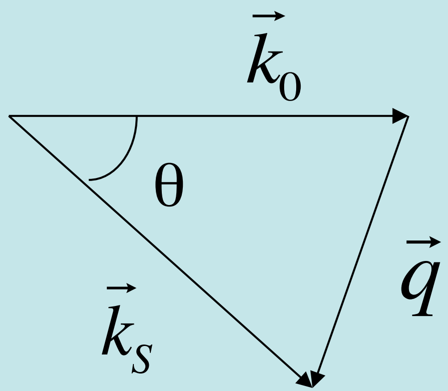
$$= \vec{k}_0 \cdot \vec{R} + \left(-\vec{k}_S \cdot \vec{R}\right) =$$

$$= -\left(\vec{k}_S - \vec{k}_0\right) \cdot \vec{R} = -\vec{q} \cdot \vec{R}$$

Scattering amplitude:

$$A_S = A_0 \frac{b}{r} e^{i k_S r} e^{-i \vec{q} \cdot \vec{R}}$$

The scattering vector $\vec{q}$

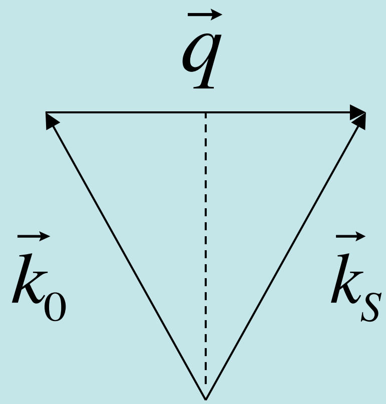


$$\vec{q} \equiv \vec{k}_S - \vec{k}_0$$

”momentum transfer”

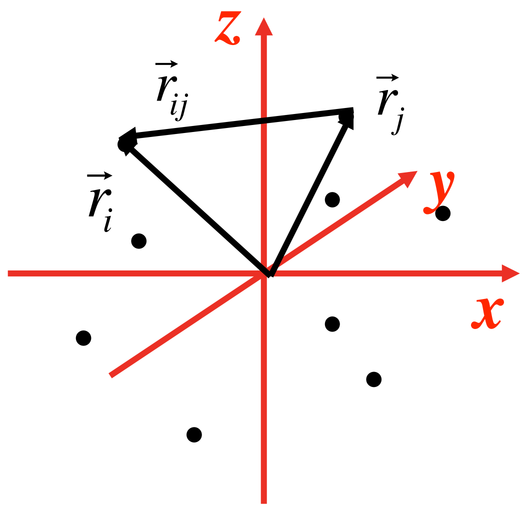
$$\left|\vec{k}_S\right| \equiv k_S = k_0 \quad \text{(elastic)}$$

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



$$\frac{q}{2} = k_0 \sin\left(\frac{\theta}{2}\right)$$

N scattering centra



Sum up all the scattered waves:

$$A_S = A_0 \frac{b}{r} e^{ikr} \sum_{i=1}^{N} e^{-i\vec{q}\cdot\vec{r}_i}$$

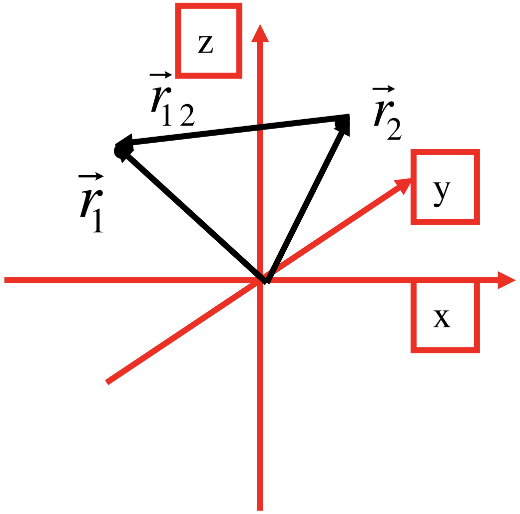
Intensity is the square of the amplitude

$$I = \left\langle |A|^2 \right\rangle = \frac{\left\langle |A_S|^2 \right\rangle}{A_0^2} \frac{r^2}{V}$$

$$I = \frac{1}{V} \left\langle b^2 \sum_{i=1}^{N} \sum_{j=1}^{N} e^{-i\vec{q}\cdot\vec{r}_{ij}} \right\rangle$$

$$\vec{r}_{ij} \equiv \vec{r}_i - \vec{r}_j$$

The basic idea



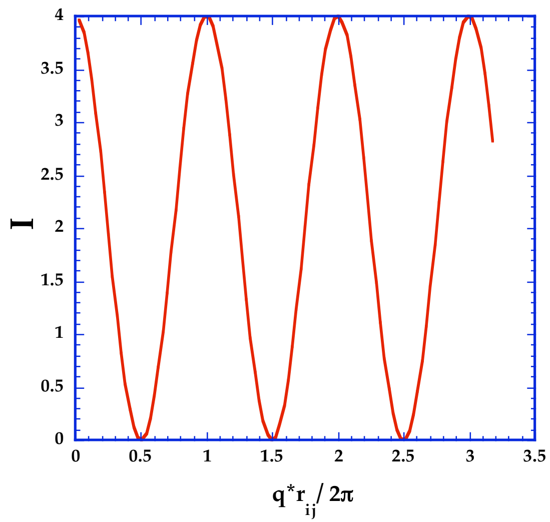
$$I(q) \sim \left(e^{i\vec{q}\cdot\vec{r}_1} + e^{i\vec{q}\cdot\vec{r}_2}\right)\left(e^{-i\vec{q}\cdot\vec{r}_1} + e^{-i\vec{q}\cdot\vec{r}_2}\right) =$$

$$= 2 + \left(e^{i\vec{q}\cdot\vec{r}_{12}} + e^{-i\vec{q}\cdot\vec{r}_{12}}\right) =$$

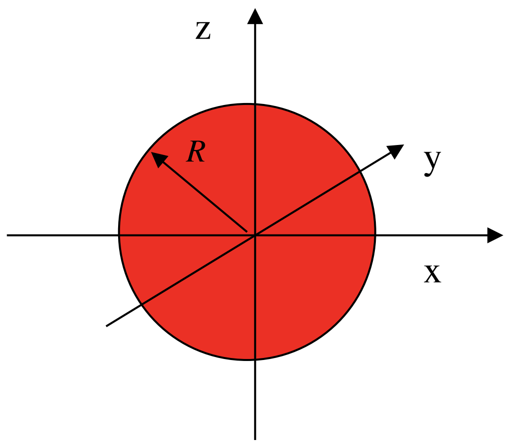
$$= 2\left(1 + \cos\left(\vec{q}\cdot\vec{r}_{12}\right)\right)$$

N (=2) $\quad P(q)$ (=1) $\quad S(q)$

- Maximum for qr_{12}=n2π.
- $I(q)$ probe correlations at separations 2π/q.



Collect the "atoms" in a sphere
The particle "form factor"



$$I(\vec{q}) = |A|^2 = \frac{1}{V}\left|\sum_i b\, e^{i q \bullet \vec{r}_i}\right|^2$$

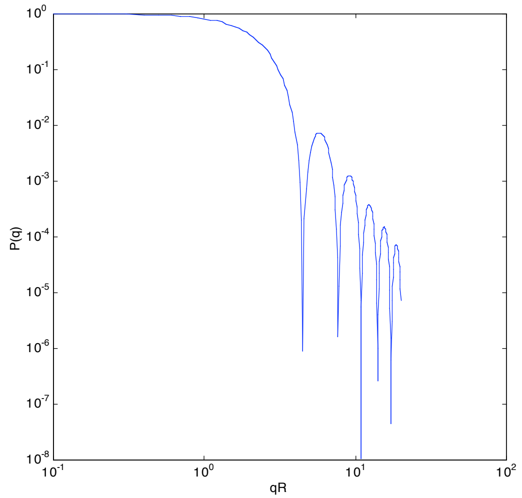
$$\approx \frac{1}{V}\left|\int_{V_{sphere}} d\vec{r}\, \rho(\vec{r})\, e^{i\vec{q}\bullet\vec{r}}\right|^2$$

$$= \frac{1}{V} P(\vec{q})$$

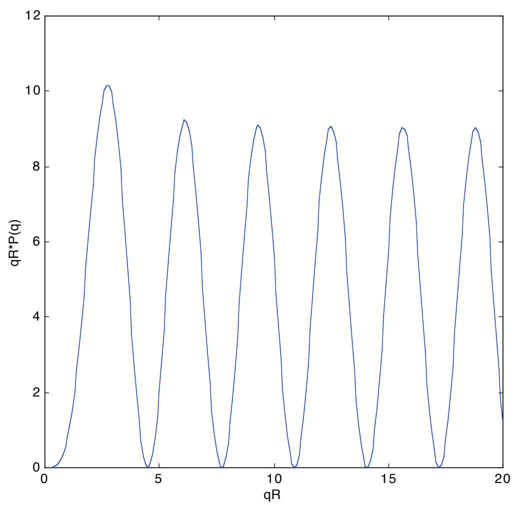
$P(\vec{q})$: "form factor" or single particle scattering function.

$\rho(\vec{r}) = \frac{\partial b}{\partial V}$: "Scattering length density"

The form factor of a sphere.



Oscillations damped with q^{-4}



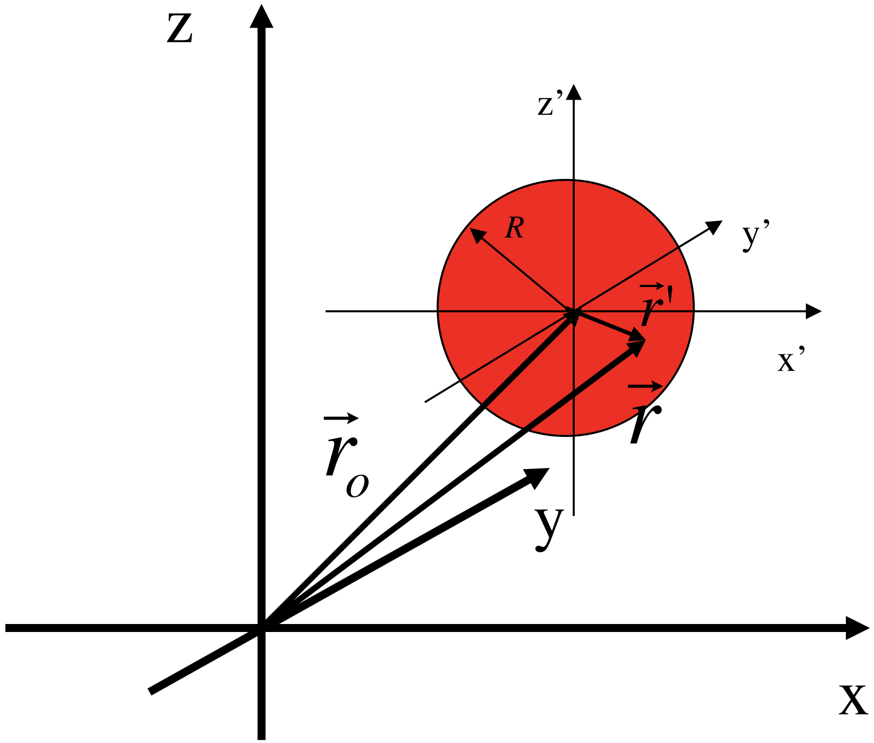
$$P(q) = \rho^2 \left| \int_{V_{sphere}} d\vec{r}\, e^{i\vec{q}\bullet\vec{r}} \right|^2 =$$

$$= \rho^2 \left(3 \frac{4\pi R^3}{3} \frac{\sin\{qR\} - qR\cos\{qR\}}{(qR)^3} \right)^2 =$$

$$= \rho^2 \left(3 \frac{4\pi R^3}{3} \frac{j_1(qR)}{qR} \right)^2$$

- $j_1(x)$: spherical Bessel function
- Zeros at $qR = \tan\{qR\}$

Displacement $\vec{r}_o$



[x,y,z]: "lab-frame" coordinate system

[x',y',z']: local coordinate system

$$\vec{r} = \vec{r}_o + \vec{r}\,'$$

$$I(q) = \left| \rho \int_{V_{sphere}} d\vec{r}\,' e^{i\vec{q} \bullet (\vec{r}\,' + \vec{r}_o)} \right|^2 = \left| \left(\rho \int d\vec{r}\,' e^{i\vec{q} \bullet \vec{r}\,'} \right) e^{i\vec{q} \bullet \vec{r}_o} \right|^2$$

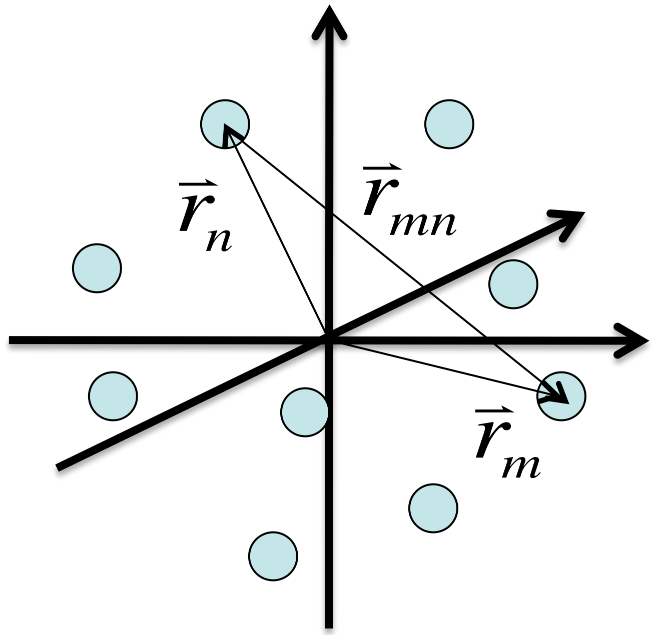
$$I(q) = \frac{1}{V}\left\langle \left| \sum_{m=1}^{N} \rho \left(\int_{V_s} d\vec{r}\,' e^{i\vec{q}\bullet\vec{r}\,'} \right) e^{i\vec{q}\bullet\vec{r}_m} \right|^2 \right\rangle =$$

$$= \frac{1}{V} P(q) \left\langle \sum_{m=1}^{N} \sum_{n=1}^{N} e^{i\vec{q}\bullet\vec{r}_{mn}} \right\rangle =$$

$$= \frac{1}{V} P(q) \left\langle N + \sum_{m} \sum_{n\neq m} e^{i\vec{q}\bullet\vec{r}_{mn}} \right\rangle =$$

$$= \frac{N}{V} P(q) \left\langle 1 + \frac{1}{N} \sum_{m} \sum_{n\neq m} e^{i\vec{q}\bullet\vec{r}_{mn}} \right\rangle =$$

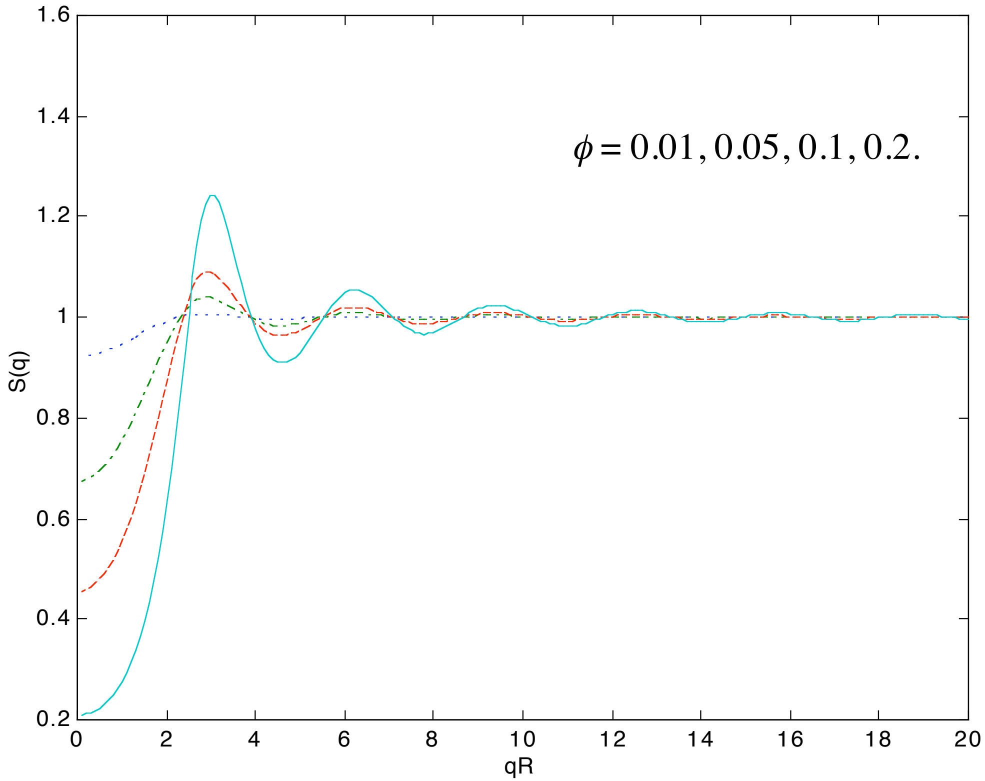
$$= \frac{N}{V} P(q) S(q)$$

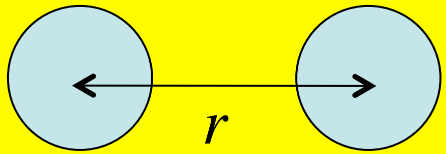


$S(q)$: "Structure factor"

Hard sphere structure factor

For the analytical expression see *e.g*.
Kinnig and Thomas *Macromolecules* 17, 1712 (1984)



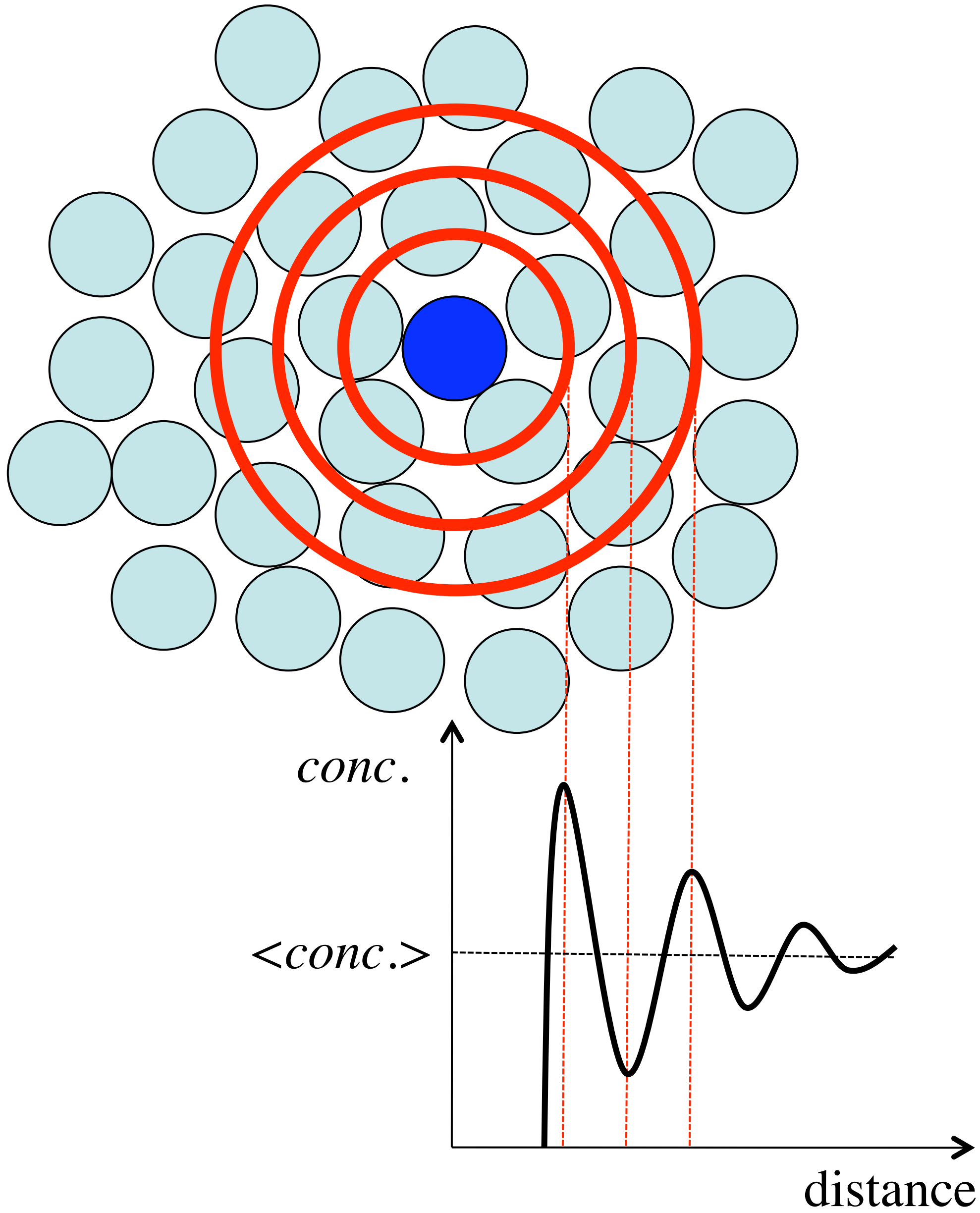


$$U(r) = \begin{cases} \infty & r < 2R \\ 0 & r \geq 2R \end{cases}$$

$S(q)$ -> 1 when ϕ ->1.
i.e. $I(q) \approx P(q)$ at low ϕ.

$S(q)$ -> 1 when q -> ∞.
i.e. $I(q) \approx P(q)$ at high q.

The radial distribution function, *g(r)*



The local variation of the concentration of particle centers outside a given test particle.

Structure factor

$$S(q) = 1 + \frac{1}{N}\left\langle \sum_{m} \sum_{n \neq m} e^{i\vec{q} \bullet \vec{r}_{mn}} \right\rangle$$

See *e.g.* J. P. Hansen, I. R. McDonald, "Theory of Simple Liquids", Ch. 5

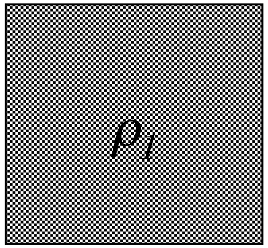
In terms of the radial distribution function:

$$S(q) = 1 + \langle c \rangle \int d\vec{r}\; g(\vec{r})\, e^{i\vec{q} \bullet \vec{r}}$$

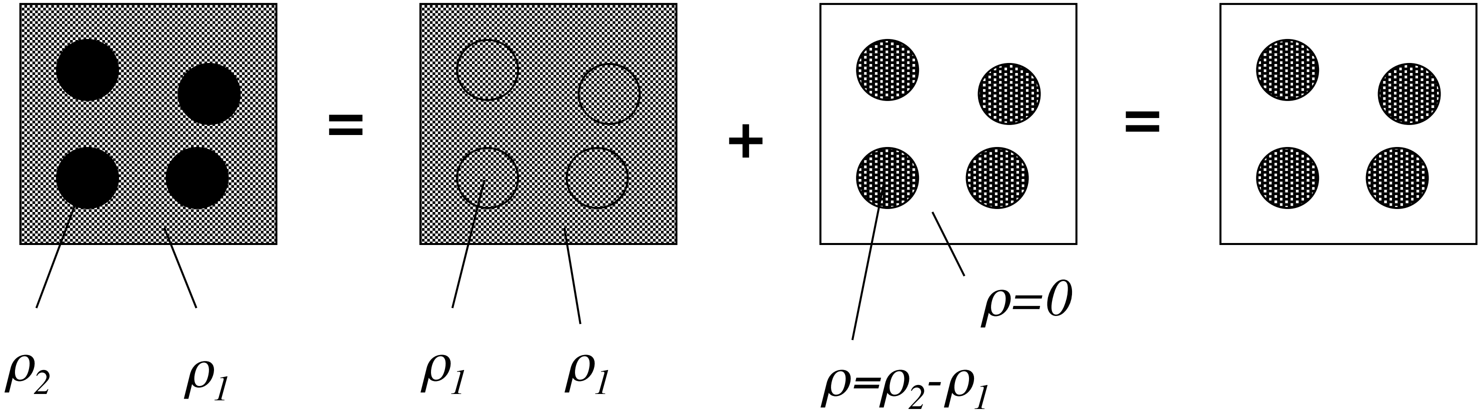
(or h(r)=g(r)-1)

g(r): the *radial distribution function*. The concentration profile of particles outside (around and away from) a given particle.

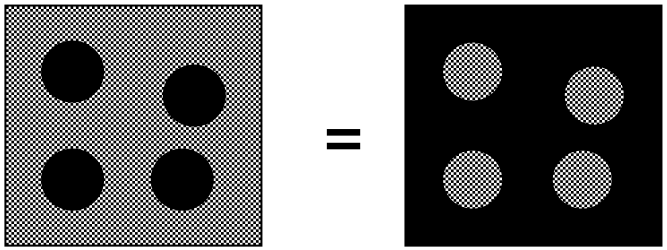
The principle of Babinet



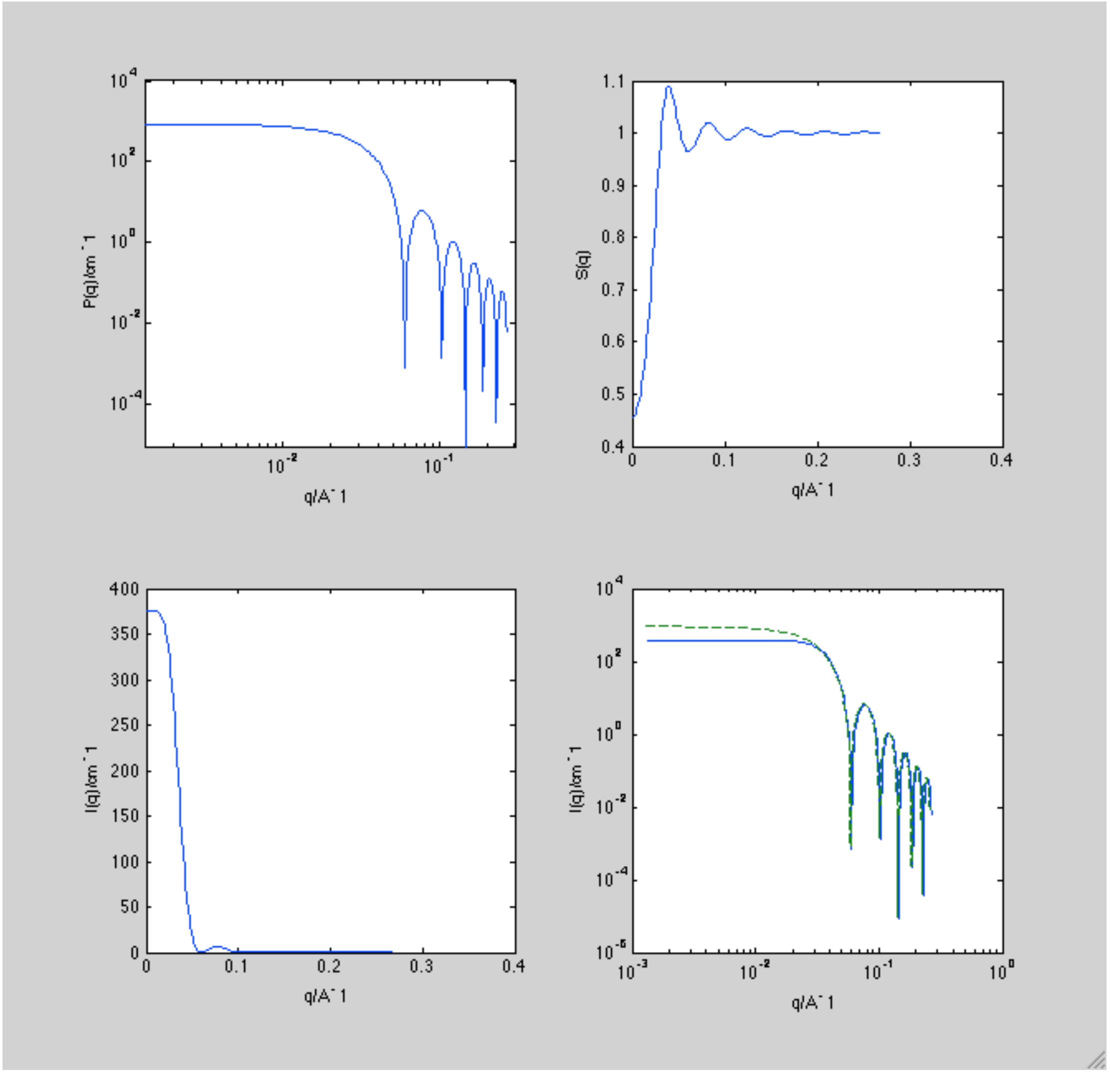
$$I(q) \sim \left(\int_{\Re^3} d\vec{r}\, e^{i\vec{q}\bullet\vec{r}} \right)^2 = \delta(\vec{q})$$



$$I(q) \sim (\Delta\rho)^2$$



$$I(q) = \frac{N}{V}\Delta\rho^2 S(q)\,P(q)$$



$$\phi = 0.1,\ R = 75\ \text{Å},\ \Delta\rho = 6.83\ 10^{10}\ \text{cm}^{-2}$$