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-SAS probes the structure of materials at the mesoscopic scale (1nm-1μm)

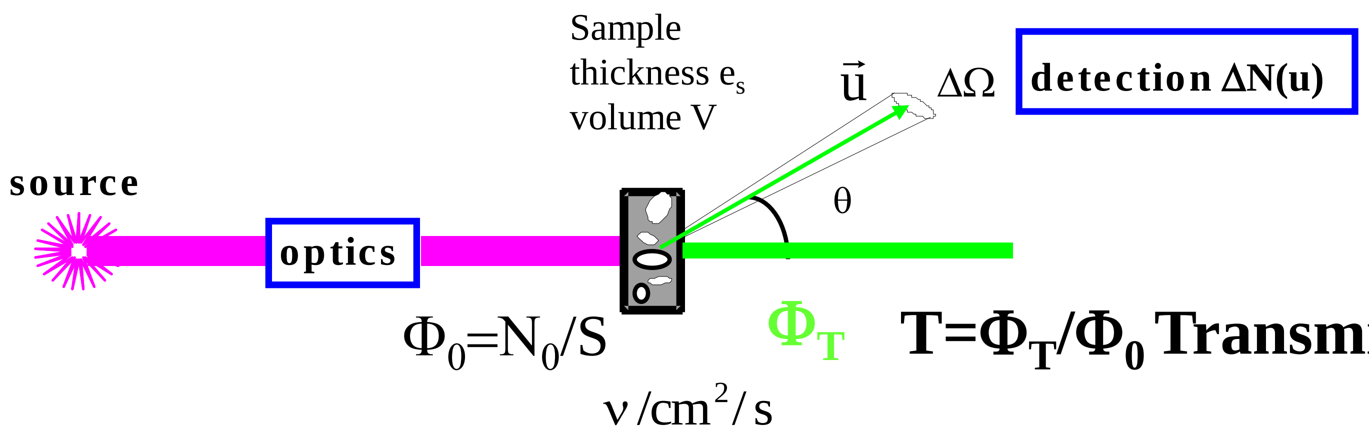
-Average physical quantities over the whole sample
-Sensitive to the form of particles
-Volume fraction and specific surface can be extracted independently of specific models

Theoretical aspects

-Definition of the scattered intensity

-Systems made of particles

-General theorems



$T = \Phi_T/\Phi_0$ Transmission

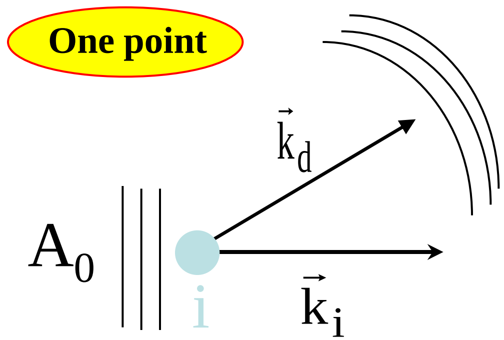
Differential scattering cross- section per unit volume

$$I = \frac{d\Sigma}{d\Omega} = \frac{1}{V}\frac{d\sigma}{d\Omega}(\vec{u}) = \frac{\Delta N}{N_0}\frac{1}{T e_s \Delta\Omega}$$

cm^{-1}

General expression of the scattered field

Theoretical side: **the interaction occurs with the field**



$$\frac{A_{sc,i}}{A_0} \propto b_i \frac{e^{-i\vec{k}_d.\vec{u}}}{L}$$

$$A_i \propto A_0 e^{i(wt-\vec{k}.\vec{r})}$$

X-ray convention of sign

$$k_i \approx k_d = \frac{2\pi}{\lambda} n$$ *Elastic scattering*

$$n = 1-\delta-i\beta \approx 1-i\beta$$

Refractive index of the sample
$\delta < 10^{-5}$ (X-ray)

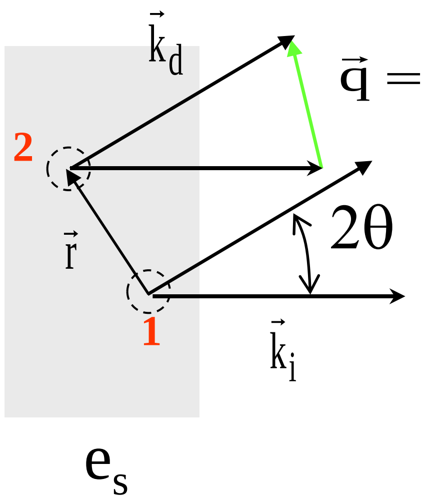
b_i : scattering length
of the element i
defines the degree of interaction
between the element i and the beam

X-rays :one electron in the small angle approximation

$$\mathbf{b_i = r_e = 2.82\ 10^{-15}\ m}$$

General expression of the scattered field

Two points

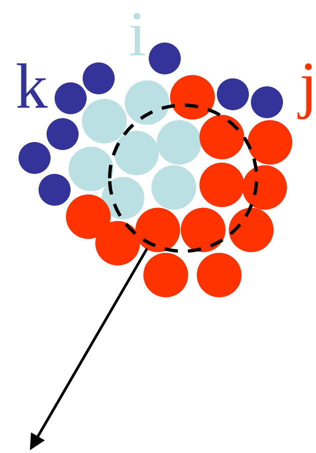


$$\vec{q} = \vec{k}_d - \vec{k}_i$$

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

Phase difference between volumes 1 and 2 $\quad \vec{q}.\vec{r}$

Summation over the volume



$$\rho(\vec{r}) = \sum \rho_i(\vec{r}) b_i \quad (cm^{-2})$$

Density of scattering length

$$A_{sc}(\vec{q}) = \frac{A_0}{L} e^{-\frac{2\pi\beta}{\lambda} e_s} \int_V \rho(\vec{r}) e^{i\vec{q}.\vec{r}} d\vec{r}$$

$$A(\vec{q})$$

General expression of the scattered intensity

By definition $\Delta N = A_{sc}(\vec{q}) A^*_{sc}(\vec{q})\ A_{\det}$

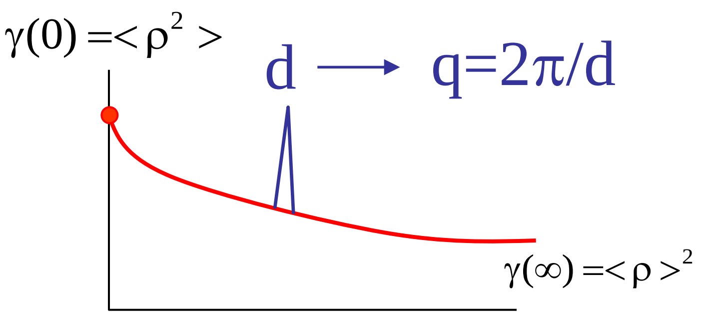
$$\Delta\Omega = \frac{A_{\det}}{L^2}$$

$$\frac{\Delta N}{\Delta\Omega} = A_0^2\ e^{-\frac{4\pi\beta}{\lambda}e_s} \int_V\int_V \rho(\vec{r})\rho(\vec{r}\,')e^{i\vec{q}.(\vec{r}-\vec{r}\,')}d\vec{r}d\vec{r}\,'$$

$$= \Phi_0 \quad T \quad \int_V\int_V \rho(\vec{r})\rho(\vec{r}\,')e^{i\vec{q}.(\vec{r}-\vec{r}\,')}d\vec{r}d\vec{r}\,'$$

$$\frac{d\Sigma}{d\Omega} = \frac{1}{V} < A(\vec{q})A^*(\vec{q}) > = \frac{1}{V}\int_V\int_V \rho(\vec{r})\rho(\vec{r}\,')e^{i\vec{q}.(\vec{r}-\vec{r}\,')}d\vec{r}d\vec{r}\,'$$

Introducing the **correlation** function $\gamma(\vec{r})$



$$\boxed{\gamma(\vec{r}) = \frac{1}{V}\int_V \rho(\vec{r}\,')\rho(\vec{r}+\vec{r}\,')d\vec{r}\,'}$$

leads to

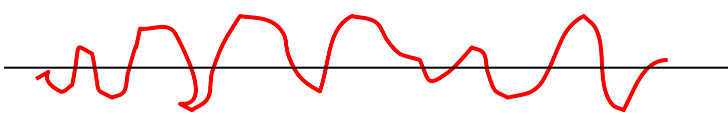
$$\boxed{I(\vec{q}) = \int_V \gamma(\vec{r})e^{i\vec{q}.\vec{r}}\,d\vec{r}}$$

The scattered intensity is the Fourier transform of the spatial correlation function

Fluctuations of ρ

Fluctuation of scattering length density

$$\boxed{\eta(\vec{r}) = \rho(\vec{r}) - <\rho>}$$



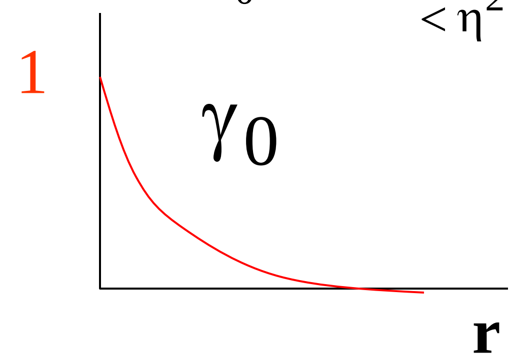
$<\rho>$

$$<\eta^2> = <\rho^2> - <\rho>^2$$

Normalized correlation function γ_0

$$\boxed{<\eta^2>\gamma_0(\vec{r}) = \frac{1}{V}\int_V \eta(\vec{r}\,')\eta(\vec{r}+\vec{r}\,')d\vec{r}\,'}$$

$$\gamma_0(\vec{r}) = \frac{\gamma(\vec{r}) - <\rho>^2}{<\eta^2>}$$



$$\boxed{I(\vec{q}) = <\eta^2> \int_V \gamma_0(\vec{r})e^{i\vec{q}.\vec{r}}d\vec{r} + <\rho>^2\,\delta(\vec{q})}$$

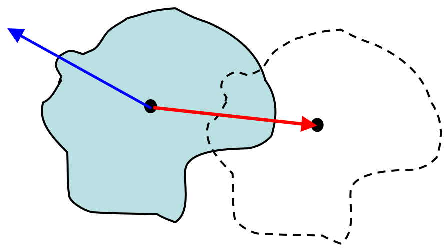
I_m

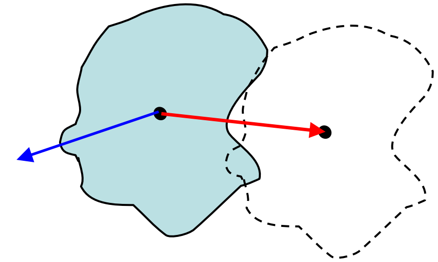
The fluctuations of density are the source of the scattering

The mean density produces a signal in the forward direction only

Auto-correlation function

For one position x of the particle ***Average over the positions of the particle***





$$\gamma_{0,1}(\vec{r})$$

$$<\gamma_0(\vec{r})>=\gamma_0(r)$$

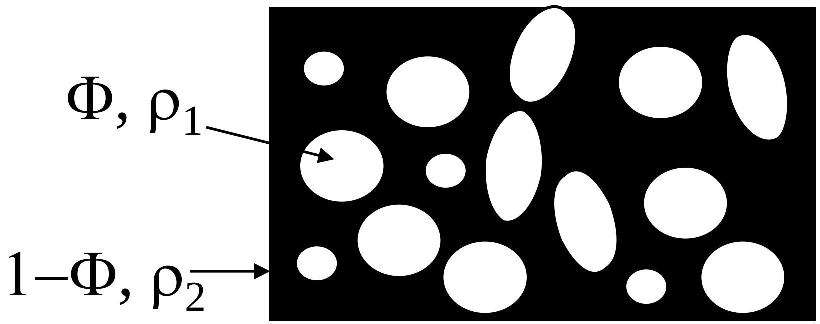
using $$\int_V f(r)e^{i\vec{q}.\vec{r}}\,d\vec{r} = 4\pi\int_0^{+\infty} f(r)r^2\frac{\sin(qr)}{qr}dr$$

One gets $$I_m(\vec{q}) =< \eta^2 > 4\pi\int_0^{+\infty} \gamma_0(r)r^2\frac{\sin(qr)}{qr}dr$$

Introducing the pair distance distribution function $$\gamma_0(r)r^2 = p(r)$$

$$\boxed{I_m(\vec{q}) =< \eta^2 > 4\pi\int_0^{+\infty} p(r)\frac{\sin(qr)}{qr}dr}$$

Importance of the contrast



$\Delta\rho=\rho_1-\rho_2$=contrast

$$<\eta^2>=<\rho^2>-<\rho>^2 \longrightarrow \boxed{<\eta^2>=\Phi(1-\Phi)(\Delta\rho)^2}$$

$$\boxed{I_m(q)=\Phi(1-\Phi)(\Delta\rho)^2\int_0^{+\infty}p(r)\frac{\sin(qr)}{qr}dr}$$

Density of scattering length

b_T Thomson scattering length for an electron $$b_T = \frac{e^2}{4\pi\varepsilon_0 m_e c^2} = \mathbf{2.82\ 10^{-15}\ m}$$

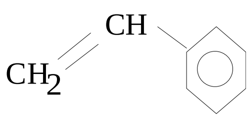
$$\rho_x\ (cm^{-2}) = \frac{N(e^-)}{V_{molecular}} * b_T$$

Example : polystyrene in water

Water

$$\left.\begin{array}{l} M_{eau} = 18.0152\ g/mol \\ d = 1\ g/cm^3 \\ N\ e^- = 8+2 = 10 \end{array}\right\}\ 0.334\ e^-/Å^3 \Rightarrow \rho_{water} = 9.38\ 10^{10}\ cm^{-2}$$

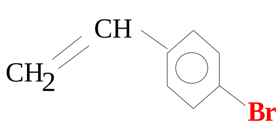
Styrene



$$\left.\begin{array}{l} M_{styrène} = 104.15\ g/mol \\ d_{styrène} = 1.06\ g/cm^3 \\ N\ e^- = 8*6+8 = 56 \end{array}\right\}\ 0.343\ e^-/Å^3 \Rightarrow \rho_{polystyrène} = 9.633\ 10^{10}\ cm^{-2}$$

$$\Delta\rho = 0.253\ 10^{10}\ cm^{-2}$$

Bromostyrene



$$\left.\begin{array}{l} M_{bromo} = 183\ g/mol \\ d_{bromo} = 1.5\ g/cm^3 \\ N\ e^- = 8*6+7+35 = 90 \end{array}\right\}\ 0.444\ e^-/Å^3 \Rightarrow \rho_{bromostyrène} = 12.47\ 10^{10}\ cm^{-2} \quad \Delta\rho = 3.09\ 10^{10} cm^{-2}$$

$\Delta\rho$ multiplied by 12

$(\Delta\rho)^2$ multiplied by 150

Systems made of uncorrelated particles

1- Scattering by a unique particle

$$A(\vec{q}) = \int_{V_{Part}} \Delta\rho(\vec{r})e^{i\vec{q}.\vec{r}}d\vec{r} = V_{Part}\, f(\vec{q})$$

$$\frac{d\sigma}{d\Omega} = A(\vec{q})A^{*}(\vec{q}) = V_{Part}^{2}F(\vec{q})$$

$$F(\vec{q}) = \frac{1}{V_{Part}^{2}} \iint_{V_{Part}} \Delta\rho(\vec{u})\Delta\rho(\vec{v})e^{i\vec{q}.(\vec{u}-\vec{v})}d\vec{u}d\vec{v}$$

$$F(0) = <\Delta\rho>^{2} \qquad F(\vec{q}) = <\Delta\rho>^{2} P(\vec{q})$$

By construction P(0)=1

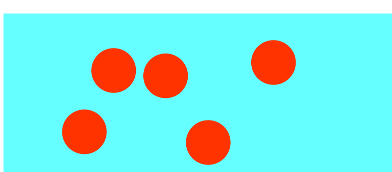
Form factor of the particle

$$P(\vec{q}) = \frac{1}{<\Delta\rho>^{2} V_{Part}} \int \gamma_{Par}(\vec{r})e^{i\vec{q}.\vec{r}}d\vec{r}$$

2- For N uncorrelated particles : addition of the intensities

N

V



$$\boxed{I_m(\vec{q}) = <\Delta\rho>^{2} \frac{N}{V} V_{Part}^{2} P(\vec{q}) = <\Delta\rho>^{2} \Phi V_{Part} P(\vec{q})}$$

Examples of form factor

1- Homogeneous sphere of radius R

$$\rho(\vec{r}) = \rho(r)$$

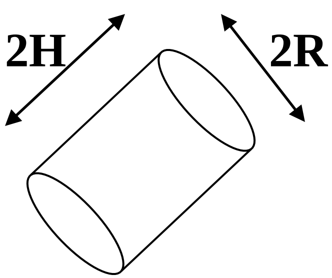
$$A(\vec{q}) = \int_{Vpart} \rho(\vec{r}) e^{i\vec{q}.\vec{r}} d\vec{r} \qquad A(q) = \Delta\rho \int_0^R 4\pi r^2 \frac{\sin(qr)}{qr} dr$$

$$= \Delta\rho \, 4\pi \frac{\sin(qR) - qR\cos(qR)}{q^3}$$

$$P(q) = \frac{A(q)A^*(q)}{V_{Part}^2 (\Delta\rho)^2}$$

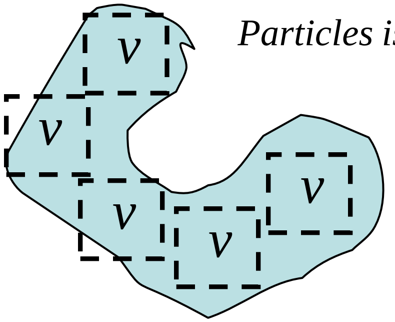
$$\boxed{P(q) = 9\frac{(\sin(qR) - qR\cos(qR))^2}{(qR)^6}}$$

2- disorientated cylinder



$$\boxed{P(q) = 4\int_0^{\pi/2} \frac{\sin^2(qH\cos(\alpha))}{[qH\cos(\alpha)]^2} \frac{J_1^{\,2}(qR\sin(\alpha))}{[qR\sin(\alpha)]^2} \sin(\alpha) d\alpha}$$

Numerical calculations for any shape



Particles is covered with small volumes v

$$\rho(\vec{r})\, d\vec{r} = \delta(\vec{r}_i)\rho_i(\vec{u})d\vec{u}$$

$$A(\vec{q}) = r_e f_v(q) \sum_i n(\vec{r}_i) e^{i\vec{q}.\vec{r}_i}$$

with $n(r_i)$ being the number of electrons in v at r_i and f(q) the amplitude factor of the elementary volume v

$$I(\vec{q}) = r_e^2 P_v(q) \sum_j \sum_i n(\vec{r}_j) n(\vec{r}_i) e^{i\vec{q}.\vec{r}_{ij}}$$

$$< I(\vec{q}) >_\Omega = r_e^2 P_v(q) \sum_{j=1}^{N} \sum_{i=1}^{N} n(\vec{r}_i) n(\vec{r}_j) \frac{\sin(qr_{ij})}{qr_{ij}}$$

$$P(q) = \frac{1}{\left(\sum_{i=1}^{N} n(\vec{r}_i) \right)^2} \sum_{j=1}^{N} \sum_{i=1}^{N} n(\vec{r}_i) n(\vec{r}_j) \frac{\sin(qr_{ij})}{qr_{ij}}$$

$P_v(q) \approx 1$ *for small v*

Debye Formulae

For an homogeneous particle $\mathbf{n(r_i) = n(r_j)}$

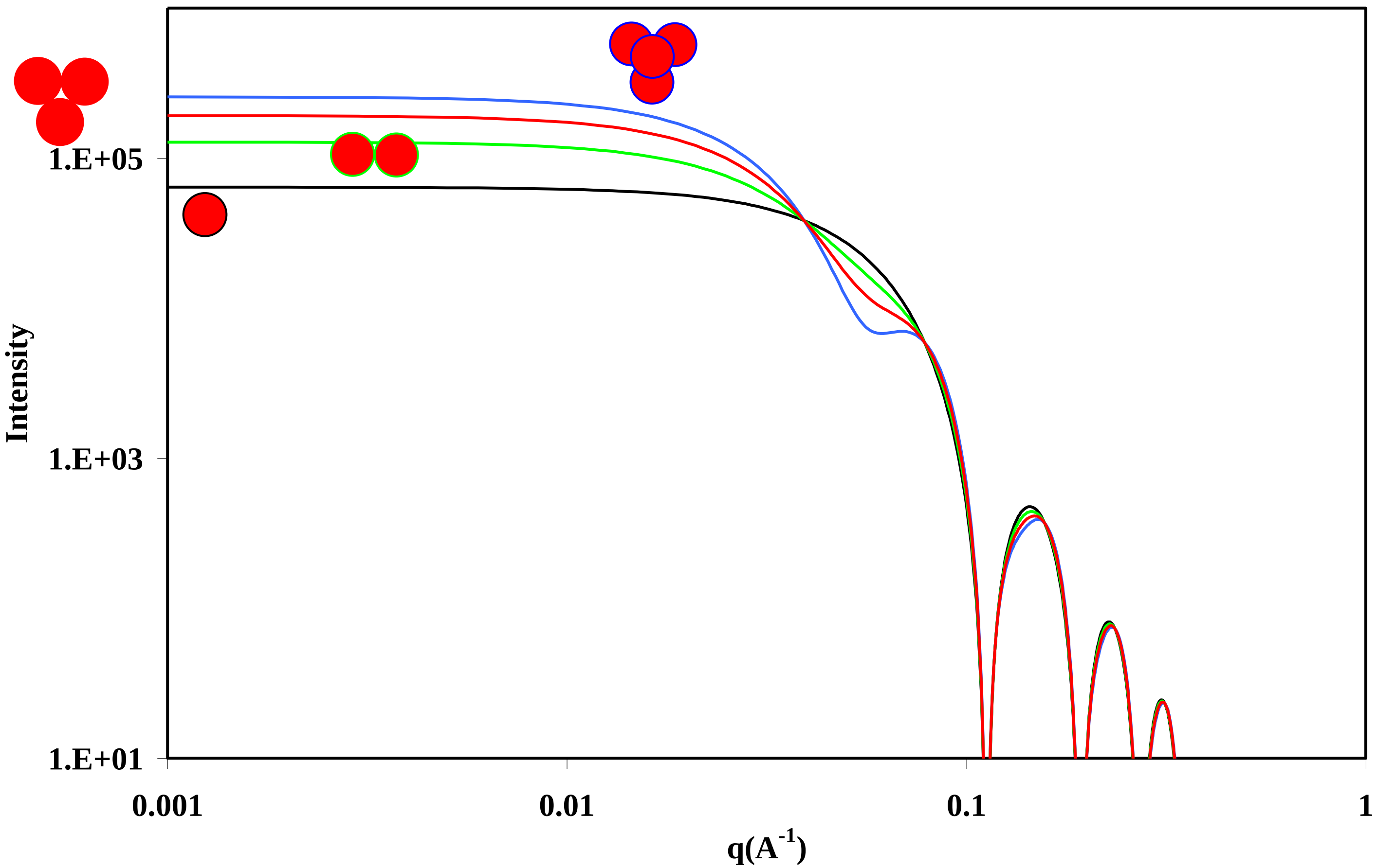
$$\boxed{P(q) = \frac{1}{N^2} \sum_{j=1}^{N} \sum_{i=1}^{N} \frac{\sin(qr_{ij})}{qr_{ij}}}$$

Multiplets of spheres

$$I_m = (v\Delta\rho)^2 P_v(q) \sum_{j=1}^{N}\sum_{i=1}^{N} \frac{\sin(qr_{ij})}{qr_{ij}}$$

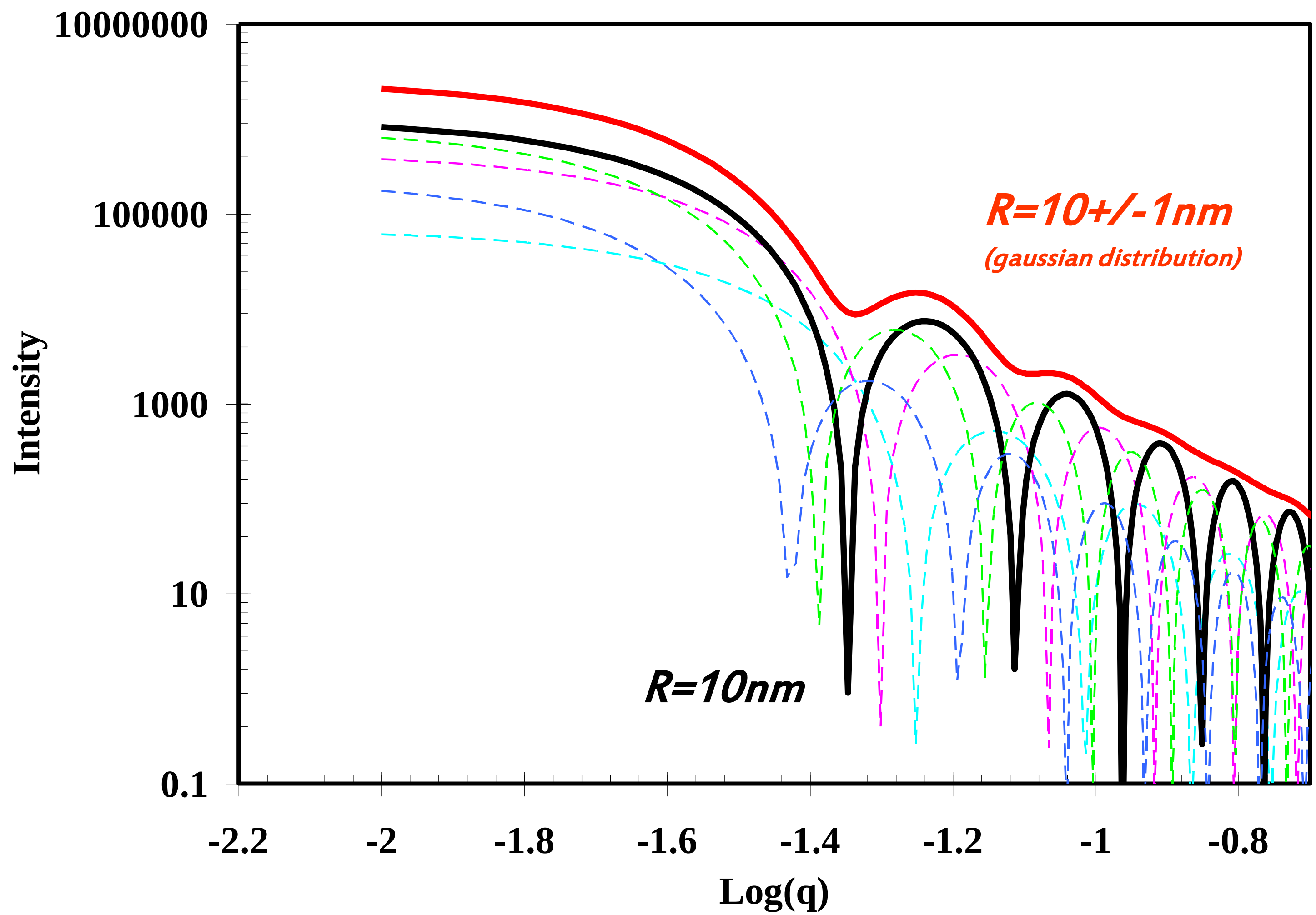
$$\frac{I_m}{NI_0} = \frac{1}{N}\sum_{j=1}^{N}\sum_{i=1}^{N} \frac{\sin(qr_{ij})}{qr_{ij}}$$

$$I_0 = (v\Delta\rho)^2 P_v(q)$$ *being the scattering of one sphere*



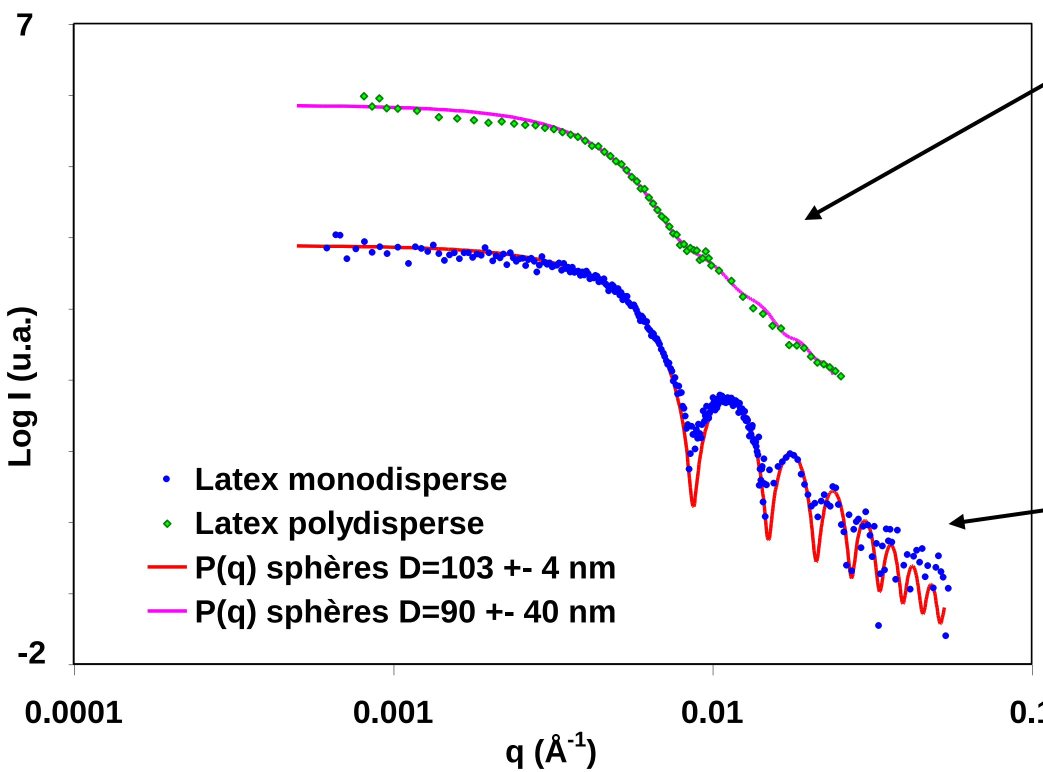
Effect of polydispersity

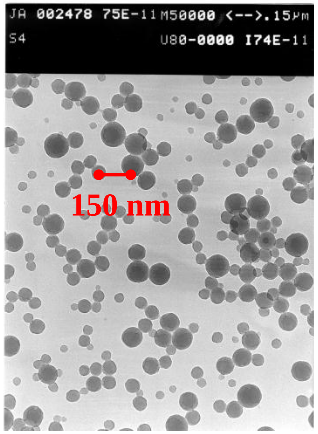
$$I = (\Delta\rho)^2 N \int f(R) V^2 \, P(q) dR$$

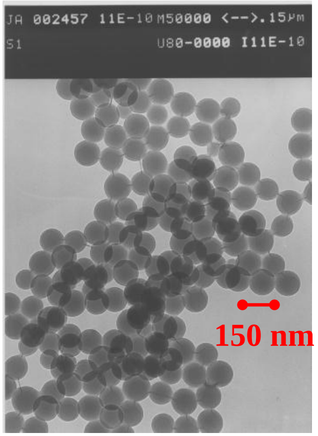


Effect of polydispersity-example

Bromostyrene
Sample 1 : D= 103 nm Polydispersity : 4 %
Sample 2 : D= 90 nm Polydispersity : 40 %







Low q regime : radius of gyration

Absence of interaction $I_m(q) = <\Delta\rho>^2 \Phi V_{Part} P(q)$

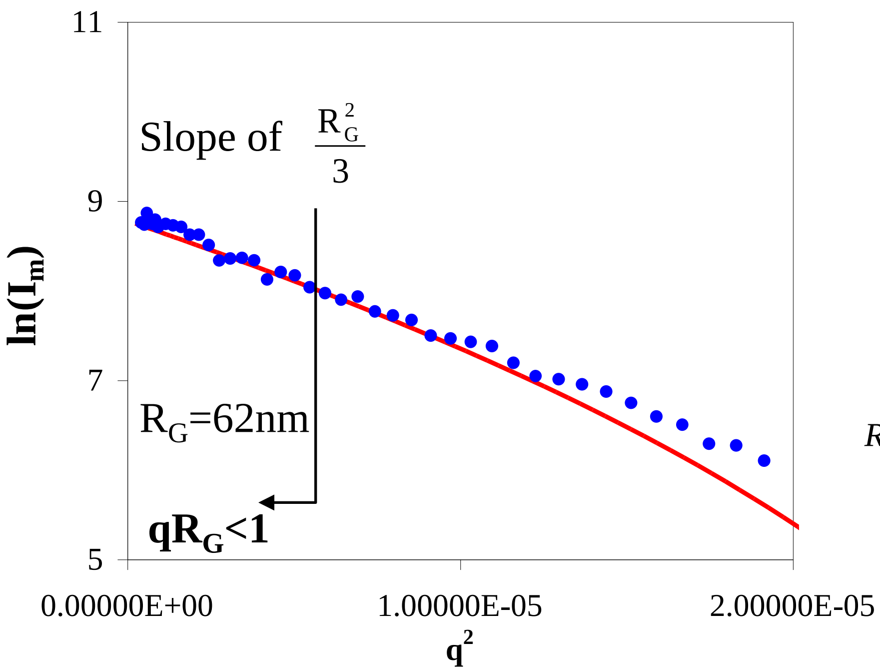
Averaged over orientation $$P(q) = \frac{1}{V_{Part} <\Delta\rho>^2} 4\pi \int_0^D \gamma_{Part}(r) r^2 \frac{\sin(qr)}{qr} dr$$

$$I_m(q) \approx <\Delta\rho>^2 \Phi V_{Part} \left[1 - \frac{(qR_G)^2}{3} + \ldots\right] \approx <\Delta\rho>^2 \Phi V_{Part} e^{-\frac{(qR_G)^2}{3}}$$

Guinier approximation

Valid for $qR_G<1$ ***(Guinier regime)***

The R_G radius of gyration of the particle can be extracted from the decrease of the intensity at low q



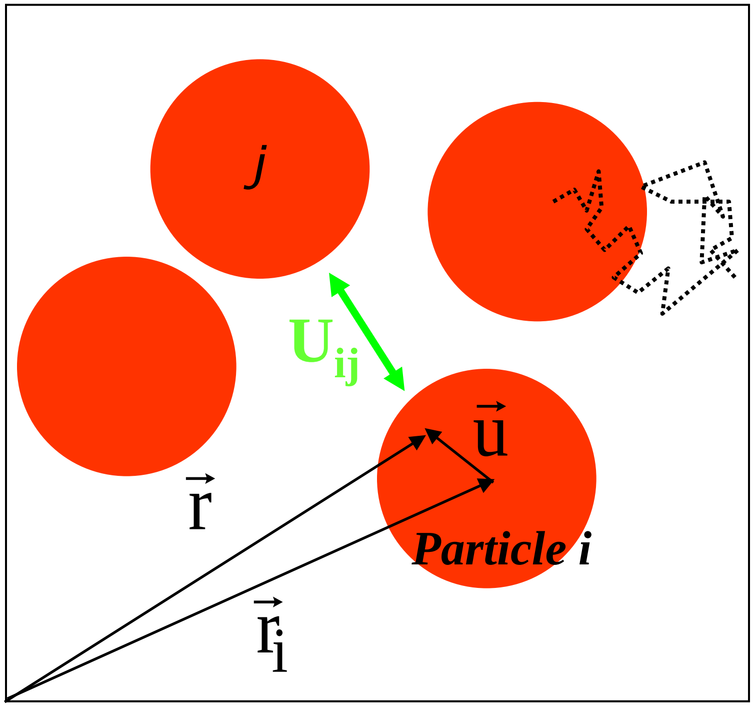
$$R_G^2 = \frac{1}{2} \frac{\int r^4 \gamma(r) dr}{\int r^2 \gamma(r) dr}$$

$$R_G^2 = \frac{\int_{V_{Part}} r^2 \rho(r) d\vec{r}}{\int_{V_{Part}} \rho(r) d\vec{r}}$$

Homogeneous sphere

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

Systems made of correlated particles



$$\frac{d\Sigma}{d\Omega} = \frac{1}{V} < A(\vec{q})A^*(\vec{q}) >$$

$$= \frac{1}{V} < \left\{ \sum_{i=1}^{N} e^{-i\vec{q}.\vec{r}_i} \int_{V_{Part}} \rho(\vec{u}) e^{i\vec{q}.\vec{u}} d\vec{u} \right\} \left\{ \sum_{j=1}^{N} e^{i\vec{q}.\vec{r}_j} \int_{V_{Part}} \rho(\vec{v}) e^{-i\vec{q}.\vec{v}} d\vec{v} \right\} >$$

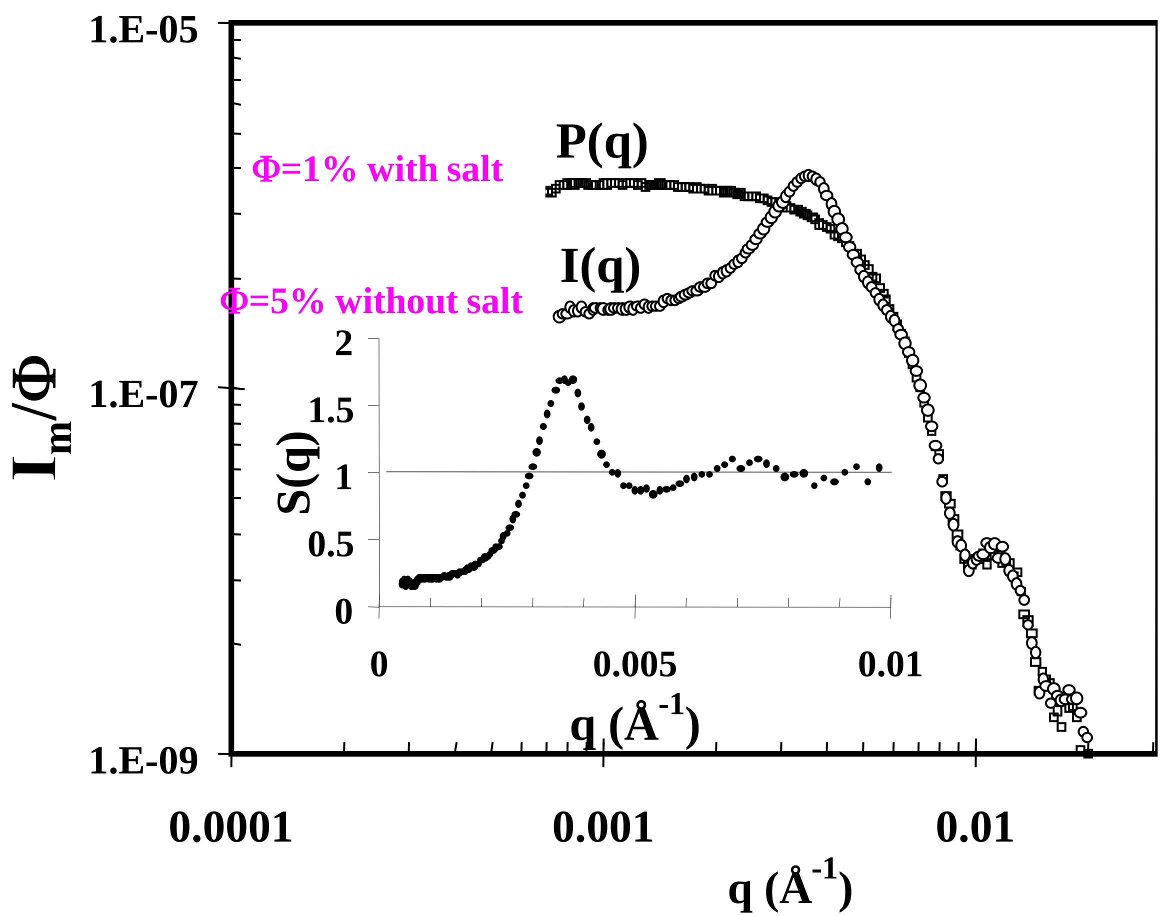
$$= \frac{N}{V} < \left\{ \iint_{V_{Part}} \rho(\vec{u})\rho(\vec{v}) e^{i\vec{q}.(\vec{u}-\vec{v})} d\vec{u} d\vec{v} \right\} \left\{ \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} e^{-i\vec{q}.(\vec{r}_j - \vec{r}_i)} \right\} >$$

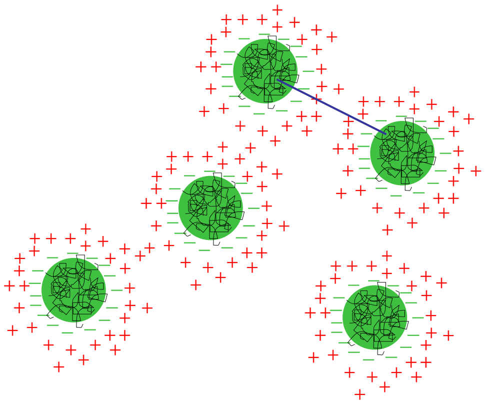
$$\boxed{I_m(q) = < \Delta\rho >^2 \; \Phi V_{Part} P(q) S_m(q)}$$

$$S_m(q) = 1 + \frac{N-1}{V} \int_V (g(r)-1) e^{-i\vec{q}.\vec{r}} d\vec{r}$$

Interaction can have very strong effects on scattering diagrams

Examples





Aqueous dispersion
of
charged latices

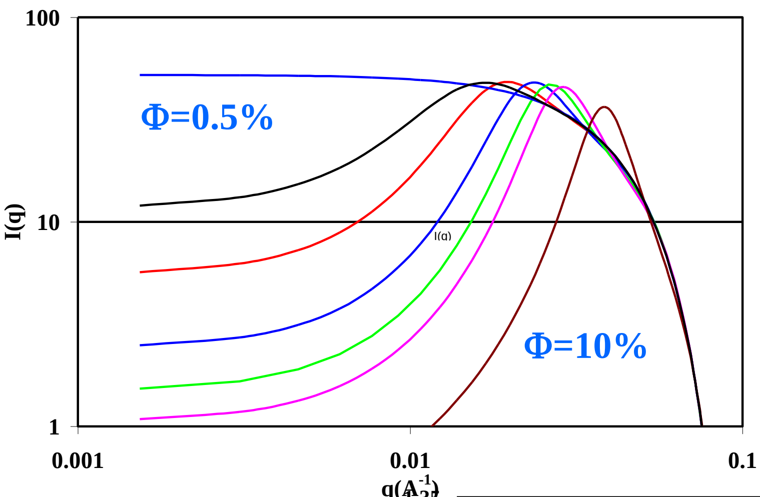
The volume of the particle cannot be extracted when interactions are present
There is no Guinier regime

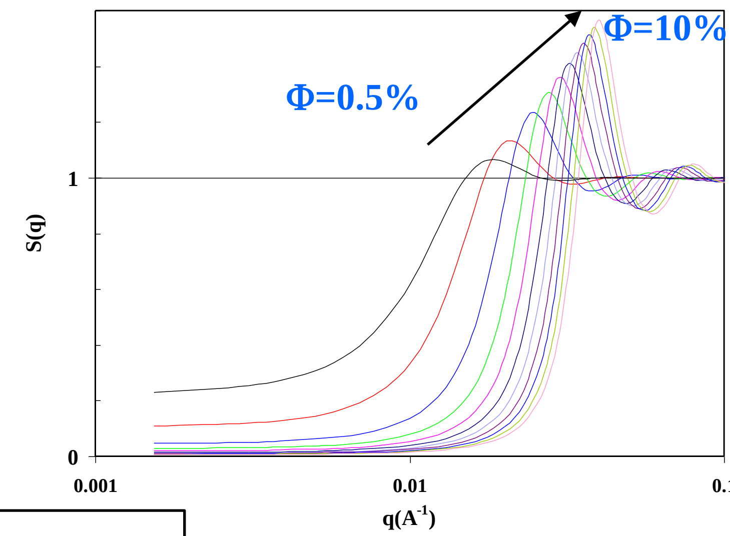
$$I_m(q) = <\Delta\rho>^2 \Phi V_{Part} P(q) S_m(q)$$

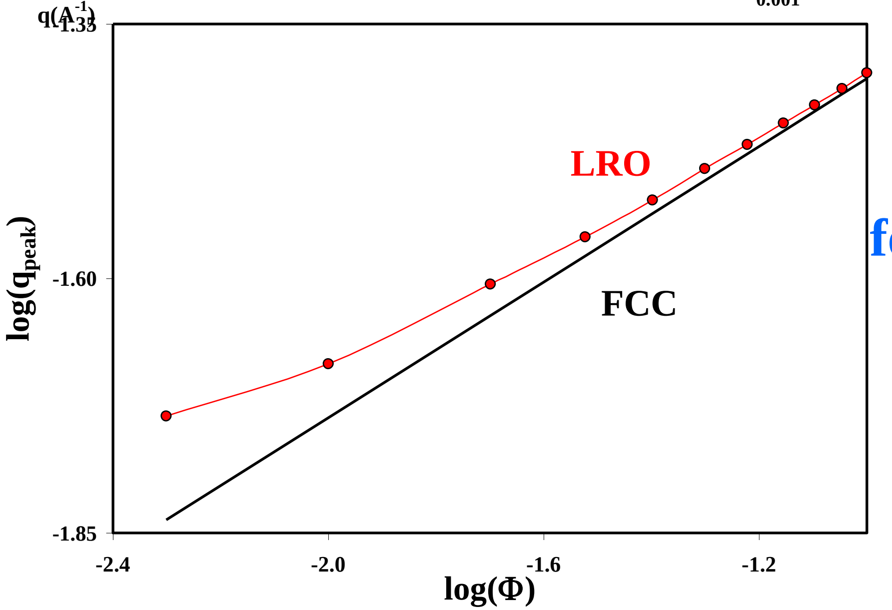
Concentration effects on the peak position

R=5nm, Z=30, K^{-1}=9.6nm

S(q) can be calculated using statistical mechaniscs



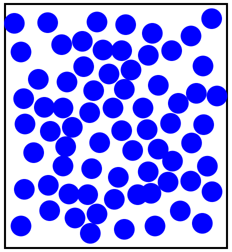




Swelling law for coulombic liquid system equivalent to FCC

$$(q\sigma)^3 = (2\pi)^2 9\sqrt{3}\,\Phi$$

Scattering by a solvent



$$I(q) = \frac{N}{V_{Tot}} (\Delta\rho)^2 \, V_{Part}^2 \; P(q)S(q)$$

For solvent molecules, Small angle scattering regime corresponds to qR<<1

$$P(q) = 1$$

For solvent molecules, small angle scattering regime corresponds to q=0

$$S(0) = \frac{N}{V_{Tot}} kT \chi_T$$

$$I(q) = \left(\frac{N}{V_{Tot}}\right)^2 (\Delta\rho V_{Part})^2 \; kT \chi_T$$

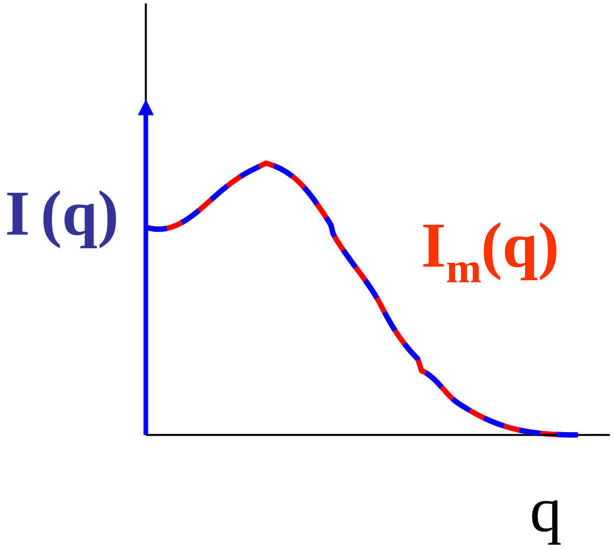
$$I(q) = \left(\frac{N}{V_{Tot}}\right)^2 b^2 \; kT \chi_T$$

Integral theorem

$$I_m(\vec{q}) = I(\vec{q}) - <\rho>^2 \delta(\vec{q}) = <\eta^2> \int_V \gamma_0(\vec{r}) e^{i\vec{q}.\vec{r}} d\vec{r}$$

Using the inverse Fourier transform

$$\frac{1}{(2\pi)^3} \int I_m(\vec{q}) e^{-i\vec{q}.\vec{r}} d\vec{q} = <\eta^2> \gamma_0(\vec{r})$$



For r=0

$$\int I_m(\vec{q}) d\vec{q} = (2\pi)^3 <\eta^2>$$

For isotropic system, one gets

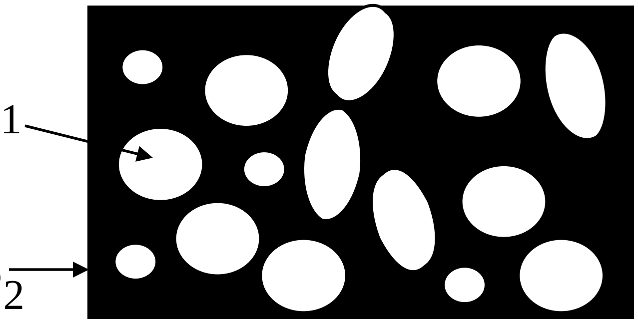
$$\boxed{\int I_m(q)\, q^2\, dq = 2\pi^2 <\eta^2>}$$

Application to two level systems

$$<\eta^2> = <\rho^2> - <\rho>^2$$

$\Phi,\ \rho_1$

$1-\Phi,\ \rho_2$



$\Delta\rho = \rho_1 - \rho_2 =$ contrast

$$\boxed{<\eta^2> = \Phi(1-\Phi)(\Delta\rho)^2}$$

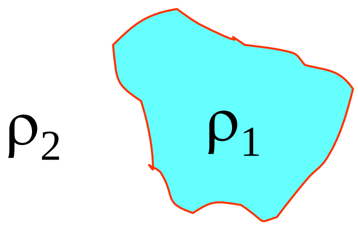
$$\int I_m(\vec{q})d\vec{q} = (2\pi)^3\Phi(1-\Phi)(\Delta\rho)^2$$

For isotropic system, one gets

$$\boxed{Q = \int_0^\infty I_m(q)q^2dq = 2\pi^2\Phi(1-\Phi)(\Delta\rho)^2}$$

Q is named the invariant
because it does not depend on the structure
but only on the volume fraction and contrast

Measure of the volume of a particle



P(0)=1

$$I_m(0) = (\Delta\rho)^2 \Phi V_{Part}$$

Valid for $\Phi \ll 1$

$$\Delta\rho = \rho_1 - \rho_2$$

Using the invariant $Q = 2\pi^2 \Phi(1-\Phi)(\Delta\rho)^2 \approx 2\pi^2 \Phi (\Delta\rho)^2$

One gets

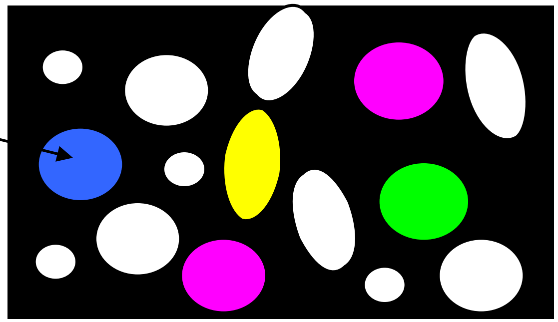
$$\boxed{V_{Part} = 2\pi^2 \frac{I_m(0)}{Q}}$$

When the particles are not correlated ($\Phi \ll 1$), their volume can be extracted Directly.
This measure does not require the absolute scaling of the intensity

Application to many level systems

$$<\eta^2>=<\rho^2>-<\rho>^2$$

Φ_i, ρ_i



$$\sum_i \Phi_i = 1$$

$$<\rho^2>=\sum_i \Phi_i \rho_i^2 \qquad <\rho>=\sum_i \Phi_i \rho_i$$

More complete Exercise!

$$<\eta^2>=\frac{1}{2}\sum_i\sum_j \Phi_i\Phi_j(\rho_i-\rho_j)^2$$

In practice, useless beyond 3-levels systems

Synthesis of gold nanoparticles by reduction in presence of ligands

"Single-Phase and Gram-Scale Synthesis of Au and Other Noble Metal Nanocrystals", N. R. Jana, X. Peng, ***J. Am. Chem. Soc.***, 2003, vol 125, p 14280

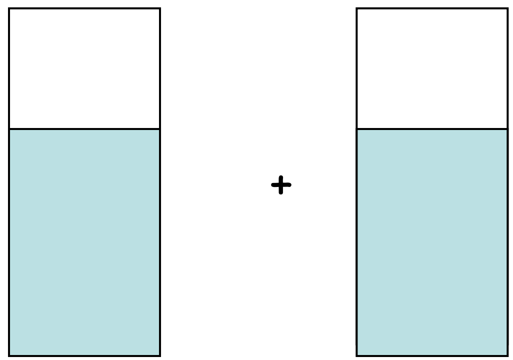
BH_4^- $(C_4H_9)_4N^+$

$AuCl_3$ dissolved in

Toluene +DDAB

(didodecyldimethyl ammonium bromide)

$(C_{12}H_{25})_2NMe_2$ Br^-



TBAB (Tetrabutylammonium borohydride)

dissolved in

Toluene + DDAB

+ Ligands (R-COOH ou R'-NH_2)

Au(III) $\longrightarrow$ Au(0) NP

$m\ Au^{3+} + n\ red \rightarrow m\ Au^0 + n\ ox$

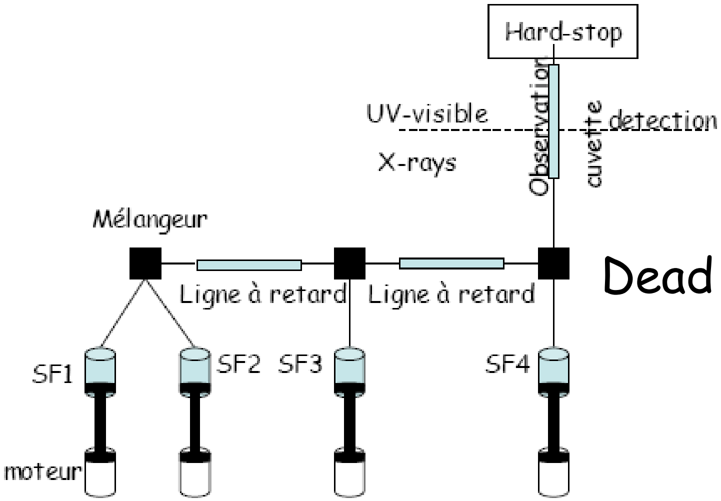
$M\ Au^0 \rightarrow (Au^0)_m$ nuclei

$(Au^0)_m + n\ Au^0 \rightarrow (Au^0)_{m+n}$

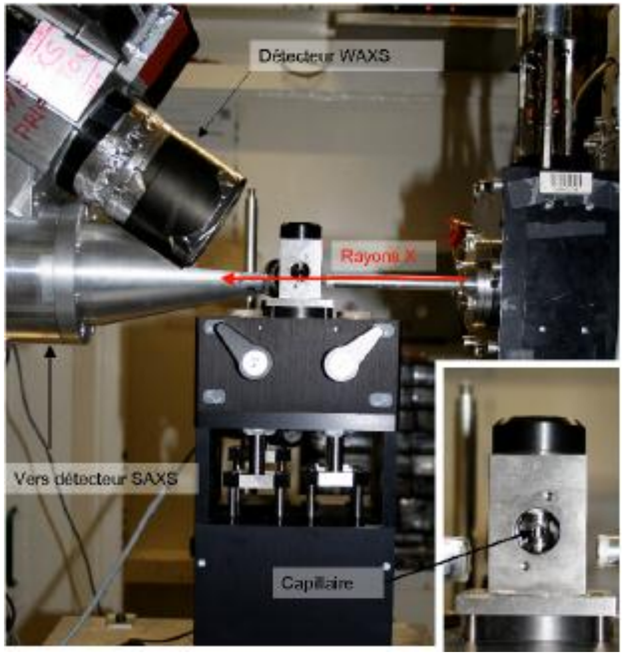
Homogeneous precipitation

In a few seconds

ID02 - ESRF (Grenoble)



Dead time: 4-16 ms



Stopped-flow adapted for non aqueous media

CCD Camera (Frelon)
Rapid Detection

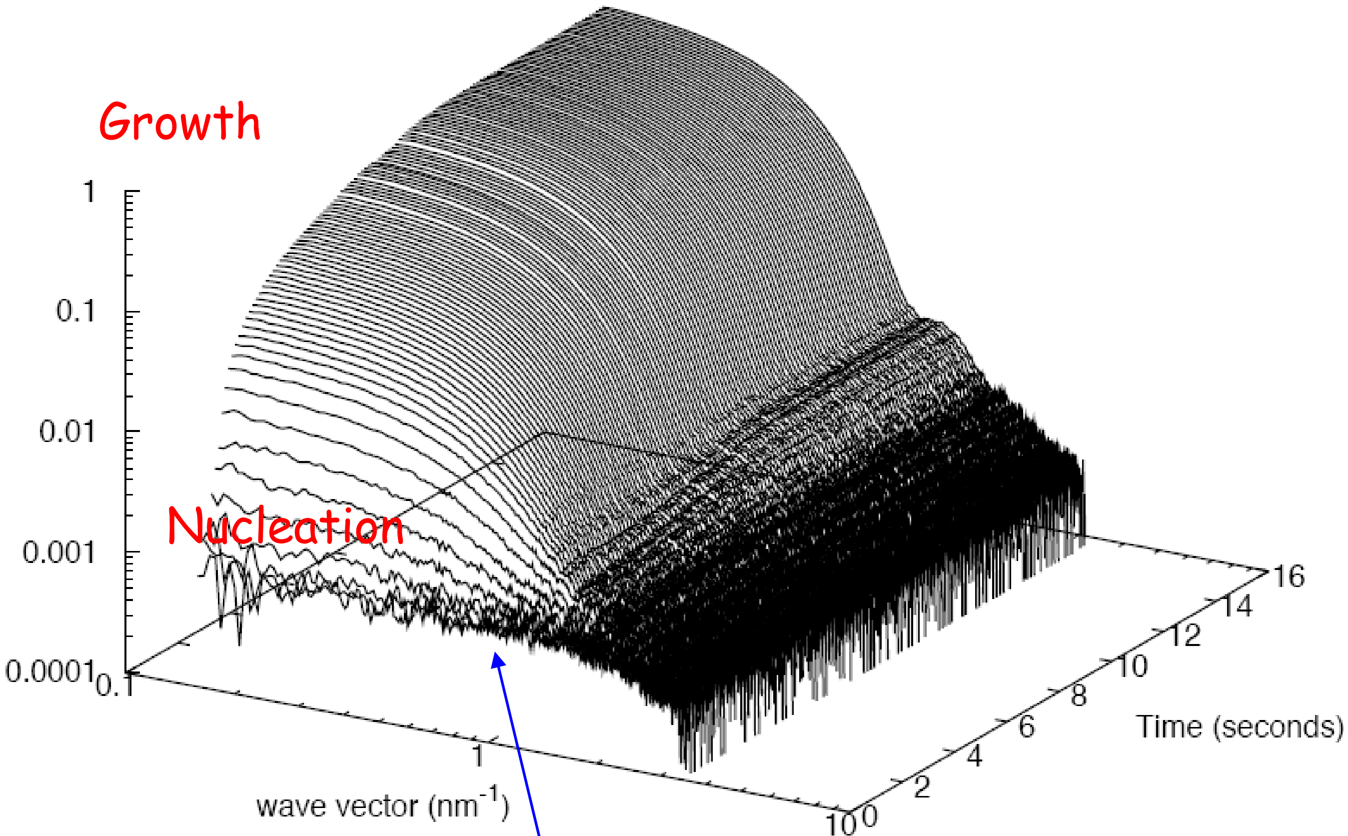
Acquisition time : 20-50 ms

Example of use of the invariant-3

SAXS : (E = 11.5 keV)

$[Au] = 3{,}5\ 10^{-3}$ mol/L
[Red] /[Au] = 4
[DDAB]/[Au] = 269
$[C_{10}OOH]$ /[Au] = 15

Growth



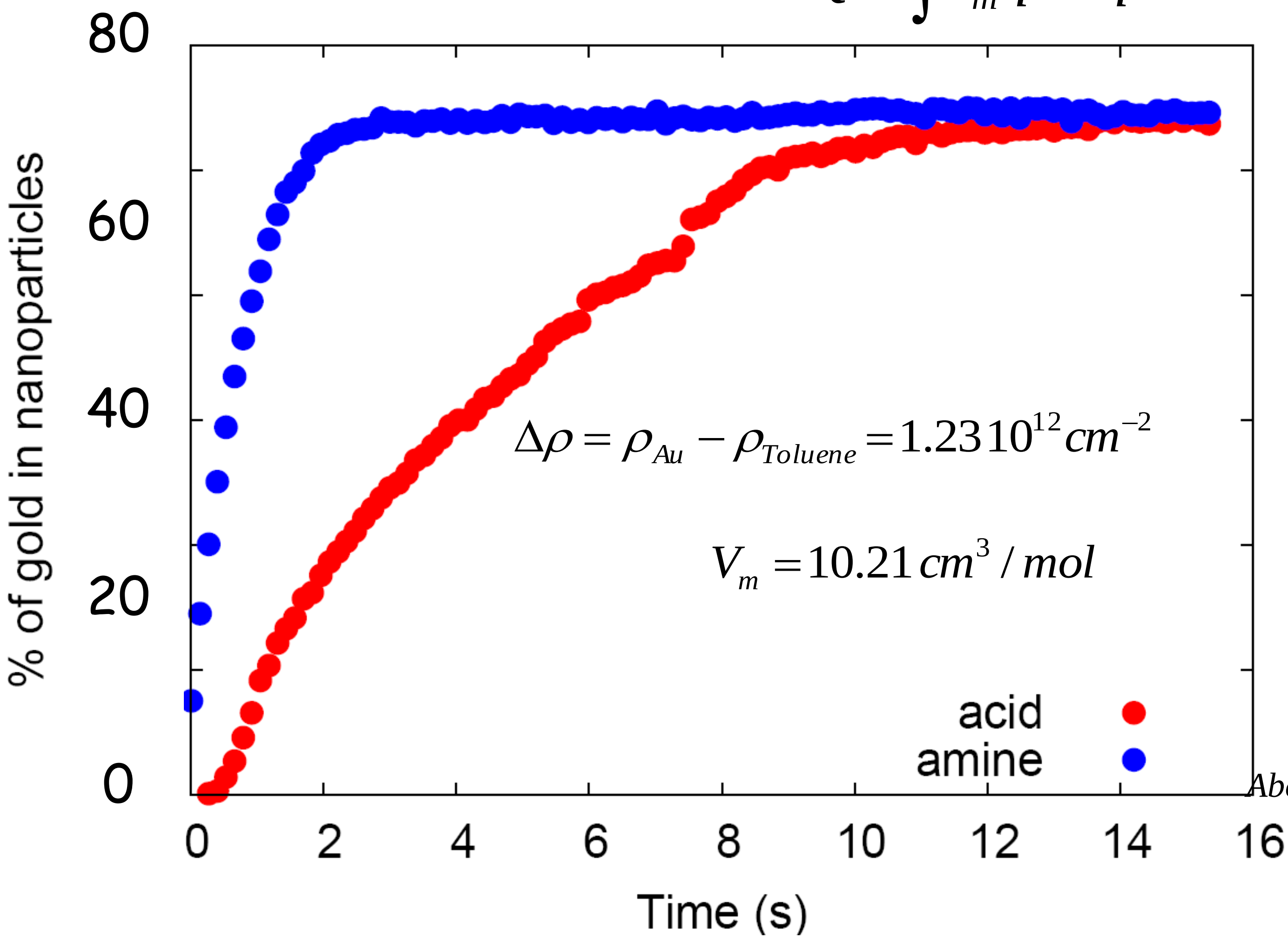
Nucleation

Weak scattering of the precursors solution

Example of use of the invariant-4

The yield of the reaction can be obtained

$$Q=\int I_m q^2\, dq = 2\pi^2 \Phi(1-\Phi)(\Delta\rho)^2$$



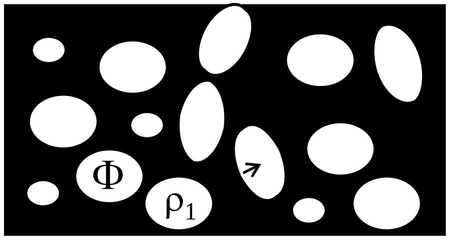
T=25°C

Abecassis et al Nanoletters 2007

- 67% of gold atoms are in the particles at the end (up to 100% at 45°C)
- reaction is faster with the amine ligands

Babinet theorem

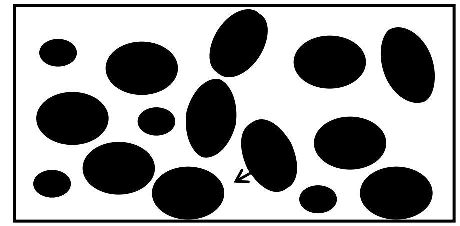
“white” holes in “black” matrix



Inverting phases

1 and 2

“black” grains in “white” solvent



$$A(\vec{q}) = \int_{\Phi V} \rho_1 e^{i\vec{q}.\vec{r}} d\vec{r} + \int_{(1-\Phi)V} \rho_2 e^{i\vec{q}.\vec{r}} d\vec{r}$$

$$A_i(\vec{q}) = \int_{\Phi V} \rho_2 e^{i\vec{q}.\vec{r}} d\vec{r} + \int_{(1-\Phi)V} \rho_1 e^{i\vec{q}.\vec{r}} d\vec{r}$$

$$A(\vec{q}) = \int_{\Phi V} (\rho_1 - \rho_2) e^{i\vec{q}.\vec{r}} d\vec{r} + \rho_2 \int_{V} e^{i\vec{q}.\vec{r}} d\vec{r}$$

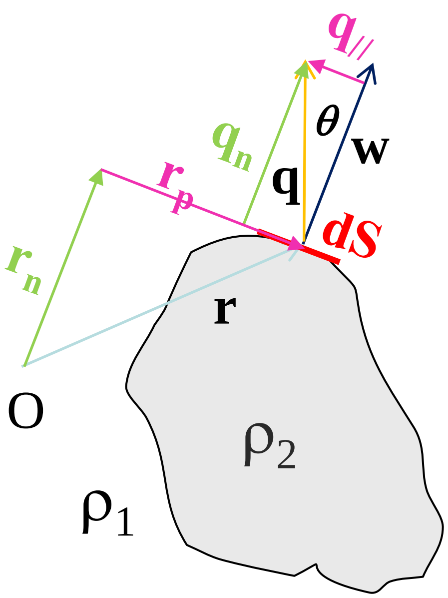
$$A_i(\vec{q}) = \int_{\Phi V} (\rho_2 - \rho_1) e^{i\vec{q}.\vec{r}} d\vec{r} + \rho_1 \int_{V} e^{i\vec{q}.\vec{r}} d\vec{r}$$

$$A(\vec{q}) = \int_{\Phi V} \Delta\rho e^{i\vec{q}.\vec{r}} d\vec{r} + \rho_2 \delta(\vec{q})$$

$$A_i(\vec{q}) = -\int_{\Phi V} \Delta\rho e^{i\vec{q}.\vec{r}} d\vec{r} + \rho_1 \delta(\vec{q})$$

Identical scattered intensities

Intensity as a surface integral



$$A(\vec{q}) = \int_V \Delta\rho \, e^{i\vec{q}.\vec{r}} \, d\vec{r}$$

Volume integral

Green–Ostograski theorem

$$A(\vec{q}) = -\Delta\rho \frac{i}{q^2} \int_S e^{i\vec{q}.\vec{r}} \, \vec{q}.d\vec{S}$$

Surface integral

$$A(\vec{q}) = \frac{\Delta\rho}{q} \int_S \cos(\theta) e^{i\vec{q}.\vec{r}_p} \, dS$$

Scattered intensity : $I(\vec{q}) = \frac{1}{V_e} \frac{(\Delta\rho)^2}{q^2} \iint dS_1 \cos(\theta_1) \iint dS_2 \cos(\theta_2) e^{i\vec{q}\vec{r}_{12}}$

Measure of the interface at large q – Porod theorem

When q is large, the contribution comes from (i) the small $r_{1,2}$

or

(ii) $\theta_2=\theta_1$ with $r_{1,2} \neq 0$

First term (i): when $r_{1,2} \to 0$ $\theta_2 \to \theta_1$

$$I(\vec{q}) \xrightarrow[q\to\infty]{} \frac{1}{V_e}\frac{(\Delta\rho)^2}{q^2}\iint dS \cos^2(\theta)\,(2\pi)^2\,\delta(\vec{q}_{//})$$

Average over the orientation of the object

$$I(q) = < I(\vec{q}) >_{\Omega}$$

Leads to

$$I(q) \xrightarrow[q\to\infty]{} (\Delta\rho)^2 \frac{2\pi}{q^4}\frac{S}{V_e}$$

Total surface of the objects

Volume of the sample

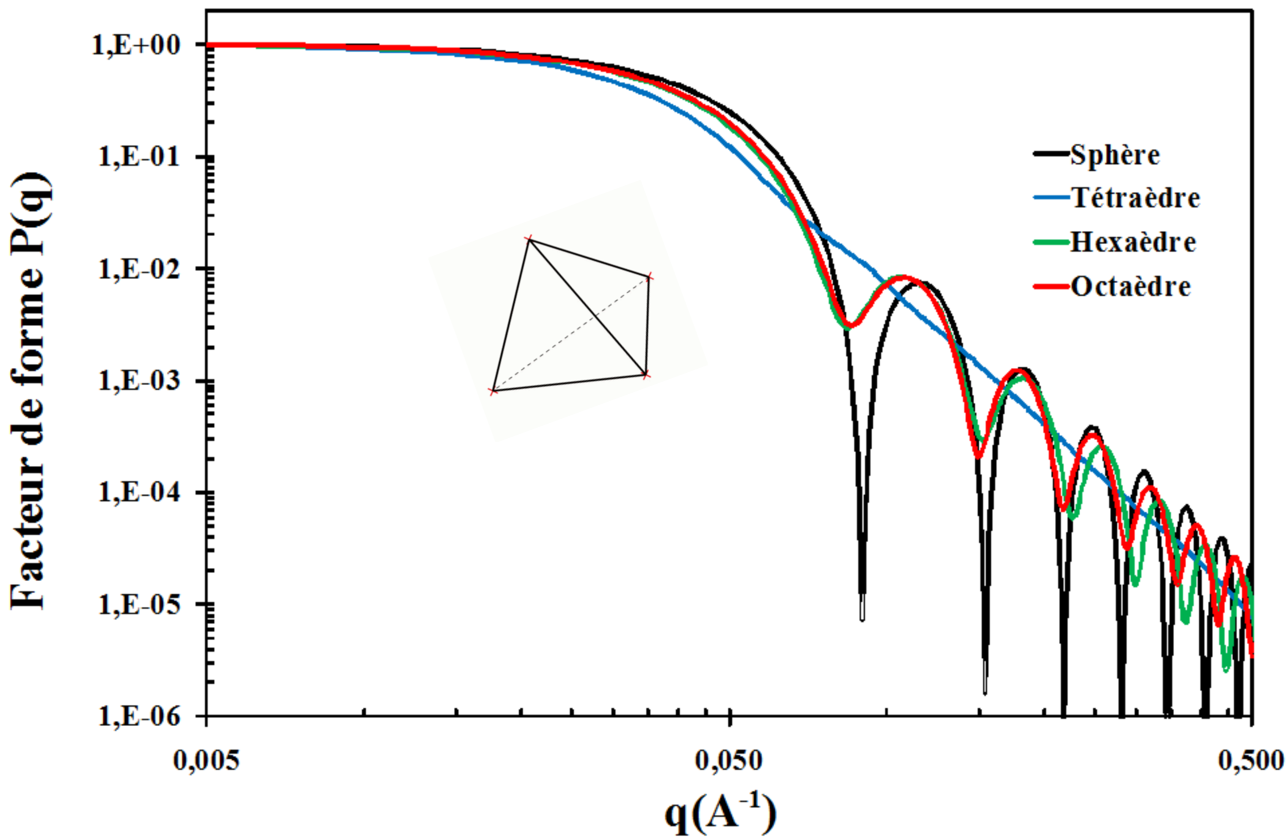
For an abrupt interface : **I decreases like q^{-4}**

is proportional to the specific surface of the sample

Oscillations in the Porod regime

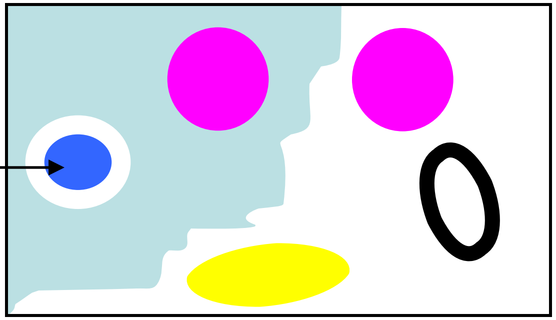
Second term (ii): contribution of $r_{1,2} \neq 0$ **with** $\theta_2 = \theta_1$

Gives an oscillating term proportional reflecting the symmetry of the sample



Porod theorem with multiple interfaces

$\sigma_{i,j}, \rho_i - \rho_j$



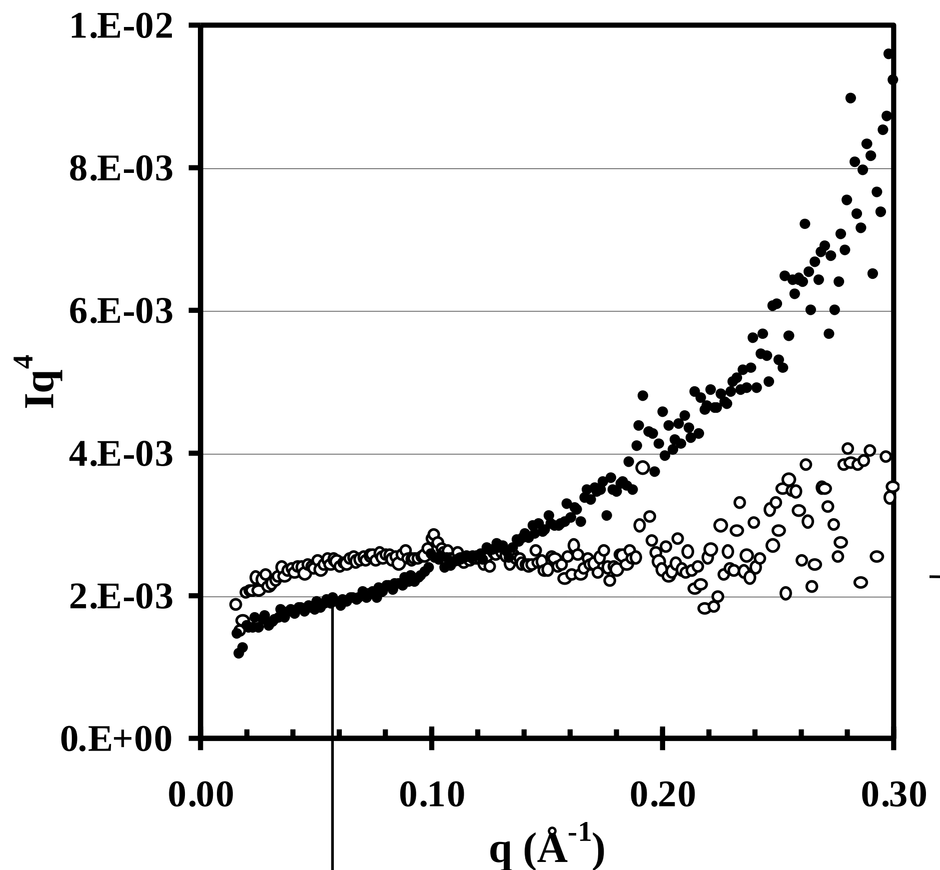
Volume V

-Core-shell particles
-Shell alone
-Sphere
-Anitropic objets

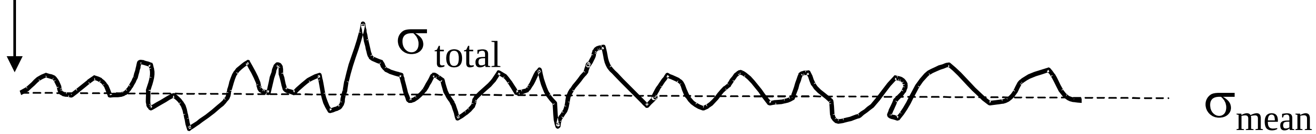
$$\lim I_{mq\to\infty} = \frac{2\pi}{q^4} \frac{\sum_V \sigma_{i,j}(\rho_i - \rho_j)^2}{V}$$

With the constraints that interface is abrupt (at 1/q scale)

Measure of the interface at large q - example



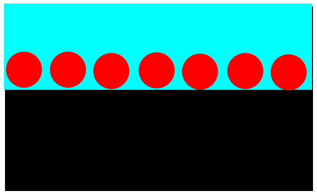
Porous silica: smooth interface
60m^2/g



Porous silica: rough interface
no Porod limit

Rough interface or equivalent layer

ρ_2 ρ_1



ρ_3

Non equivalent to

ρ_m

$$I_m q^4 = S(\rho_1-\rho_2)^2 + \sigma(\rho_3-\rho_2)^2$$

$$I_m q^4 = S(\rho_1-\rho_m)^2 + S(\rho_m-\rho_2)^2$$

avec $\rho_m = \Phi\rho_3 + (1-\Phi)\rho_2$

$$\frac{Iq^4}{S(\rho_1-\rho_2)^2} = 1 + \frac{\sigma}{S}\frac{(\rho_3-\rho_2)^2}{(\rho_1-\rho_2)^2}$$

$$\frac{Iq^4}{S(\rho_1-\rho_2)^2} = 1 + 2\Phi\left(\Phi\frac{(\rho_3-\rho_2)^2}{(\rho_1-\rho_2)^2} - \frac{\rho_3-\rho_2}{\rho_1-\rho_2}\right)$$

$\rho_3 = \rho_1$

Case of surface roughness

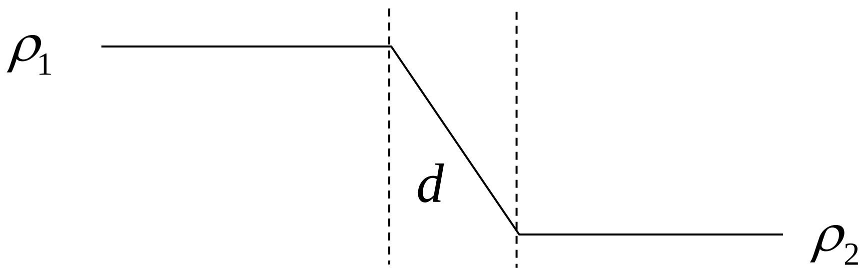
$$\frac{Iq^4}{S(\rho_1-\rho_2)^2} = 1 + \frac{\sigma}{S}$$

greater than 1

$$\frac{Iq^4}{S(\rho_1-\rho_2)^2} = 1 + 2\Phi(\Phi-1)$$

smaller than 1

Fuzzy interface-Continuous profile

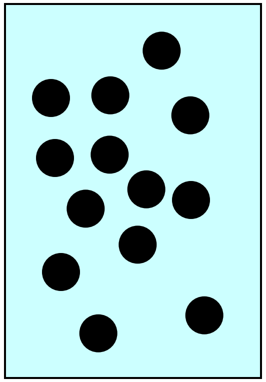


$$I = 2\pi \frac{S}{V}(2(\rho_1 - \rho_2)^2 \frac{1-\cos(qd)}{d^2 q^6})$$

For $qd << 1$ the Porod regime is still there

For $qd >> 1$ no more q-4 dependence

Summary of the GT

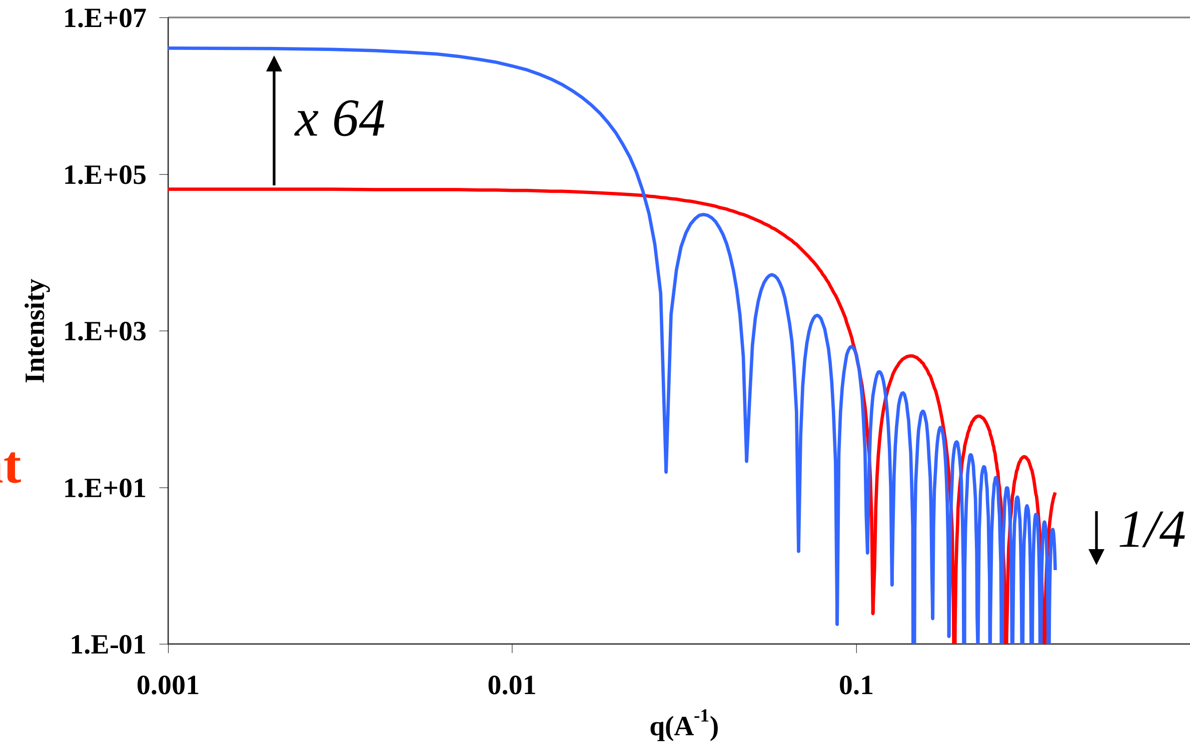


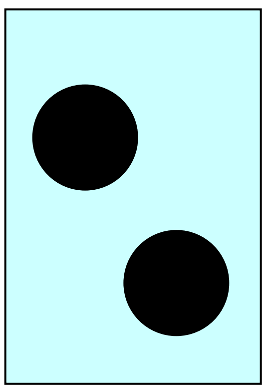
R_1

n_1

$S_1 \propto n_1 R_1^2$

Φ constant **Q is constant**





$R_2=4\ R_1$

$n_2=n_1/64$

$S_2 \propto n_2 R_2^2 = S_1 / 4$

$$I = (\Delta\rho)^2 \Phi\, V_{part}\ P(q) \qquad q=0 \quad P=1$$

Intensity is sensitive to :

- *the volume of the particle at q=0*
- *the surface of the particle at large q*
- *the concentration through the invariant*

Summary

Definitions

$$I(\vec{q}) = \frac{\Delta N}{N_0}\frac{1}{T\Delta\Omega}\frac{1}{e_s}$$

Correlation function

$$\gamma(\vec{r}) = \frac{1}{V}\int_V \rho(\vec{r}\,')\rho(\vec{r}+\vec{r}\,')d\vec{r}\,'$$

TF

$$I(\vec{q}) = \int_V \gamma(\vec{r})e^{i\vec{q}.\vec{r}}d\vec{r}$$

Theorems

Porod limit

$$\lim_{q\to\infty} I_m(q) = \frac{2\pi(\Delta\rho)^2}{q^4}\frac{S}{V}$$

Invariant

$$\int_0^\infty I_m(q)q^2dq = 2\pi^2\Phi(1-\Phi)(\Delta\rho)^2$$

Particles systems

$$I_m(q) = <\Delta\rho>^2 \Phi V_{Part} P(q)S(q)$$

$$I_m(q) \approx <\Delta\rho>^2 \Phi V_{Part} e^{-\frac{(qR_G)^2}{3}}$$

Guinier approximation q->0

Babinet