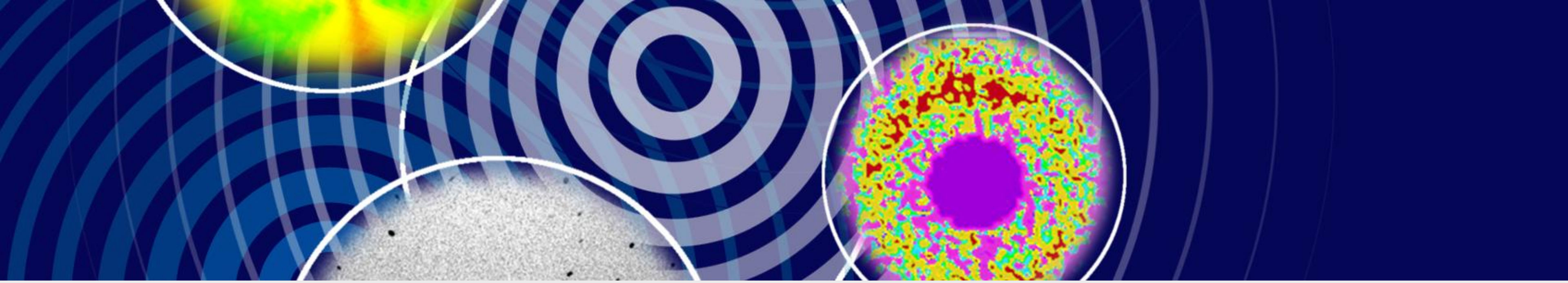
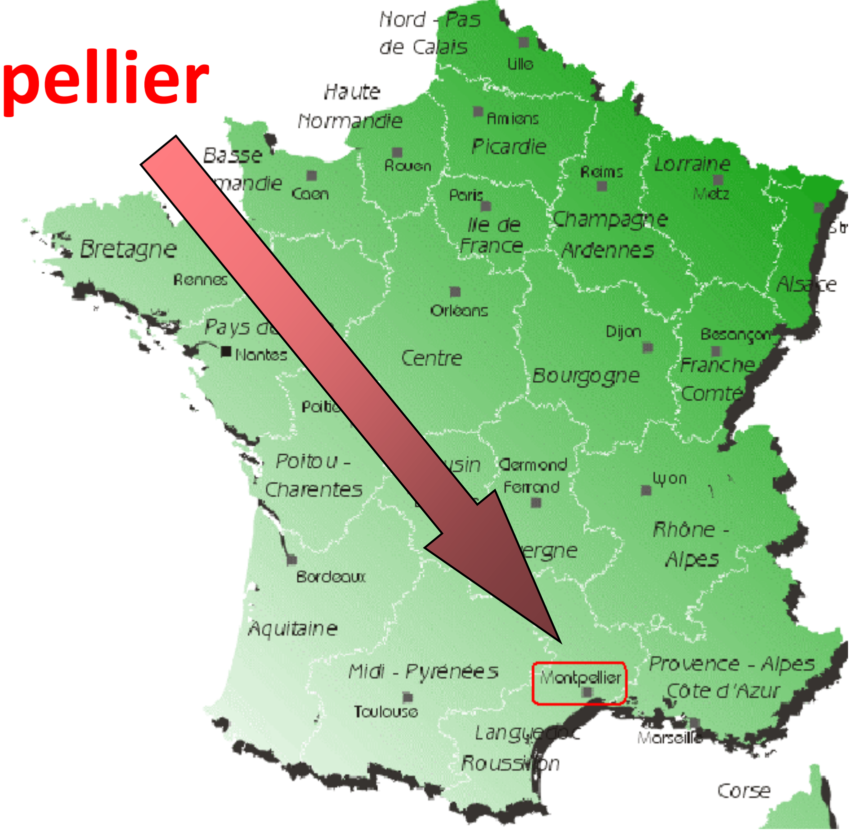


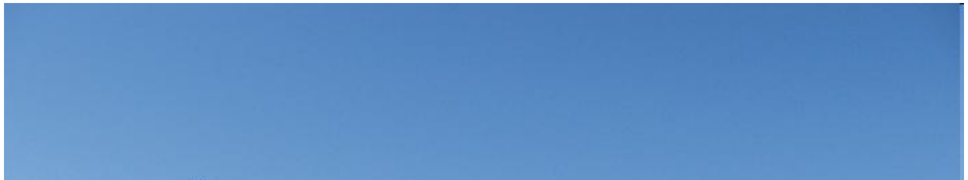
Small Angle Neutron Scattering

Fabrice Cousin and Julian Oberdisse

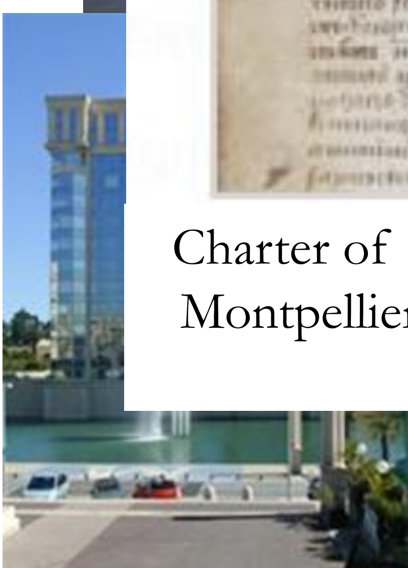
Fabrice.cousin@cea.fr

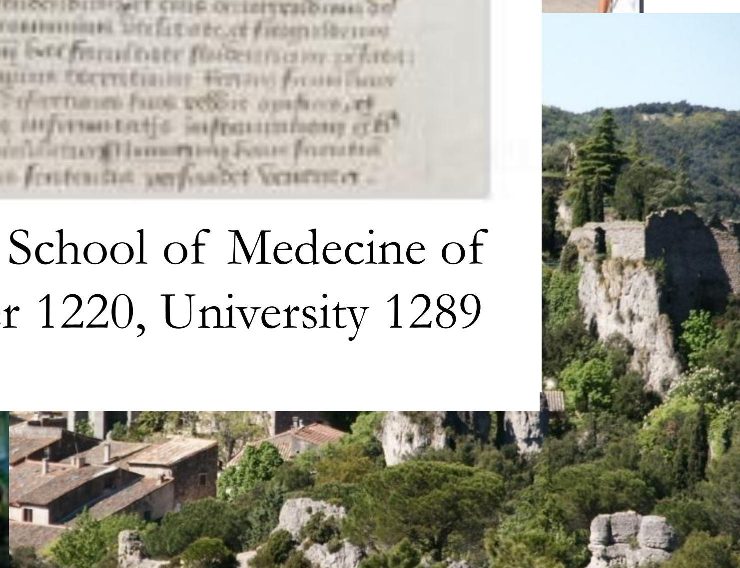
Montpellier



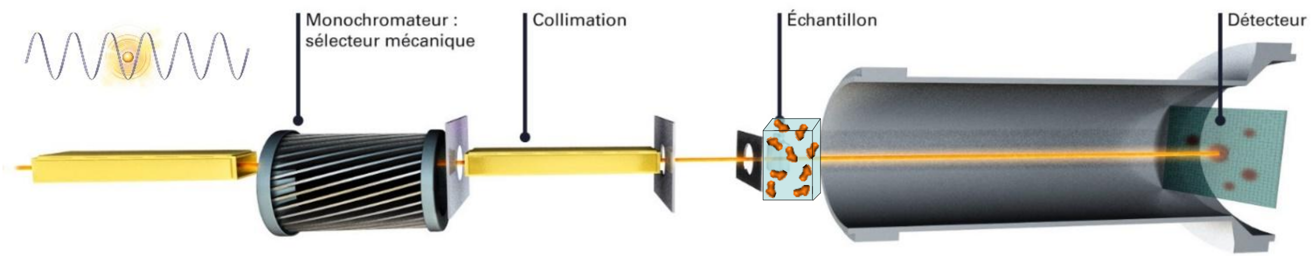


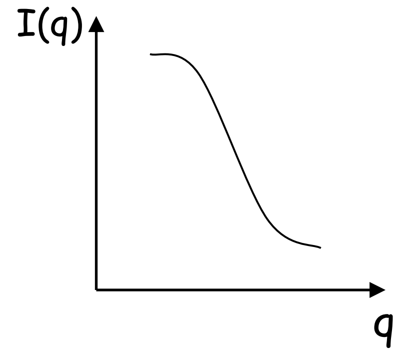
Charter of School of Medecine of Montpellier 1220, University 1289





What can be measured with SANS?





q = 4π/λ sin (θ/2)

Characteristic sizes: From ~ **5 Å** to ~ **2000 Å**

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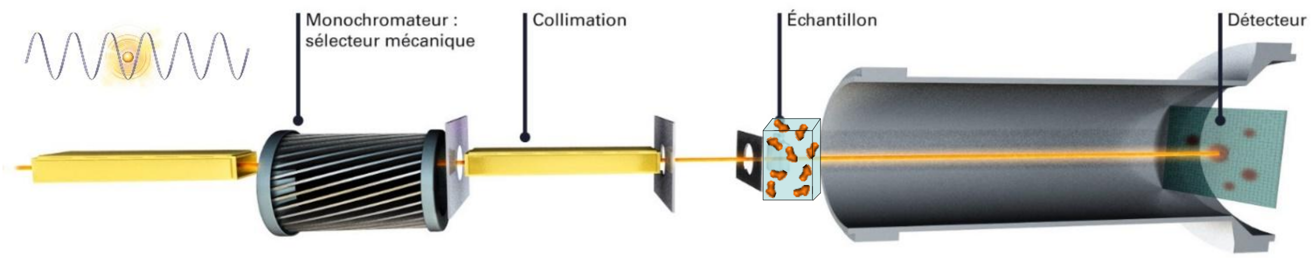

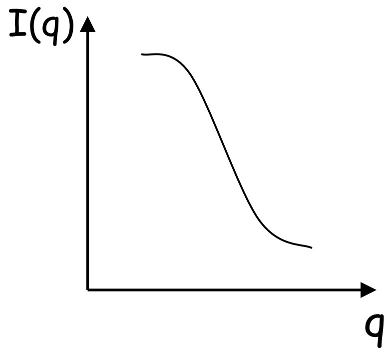

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- **Form and size of objects**
- **Structure between objets**
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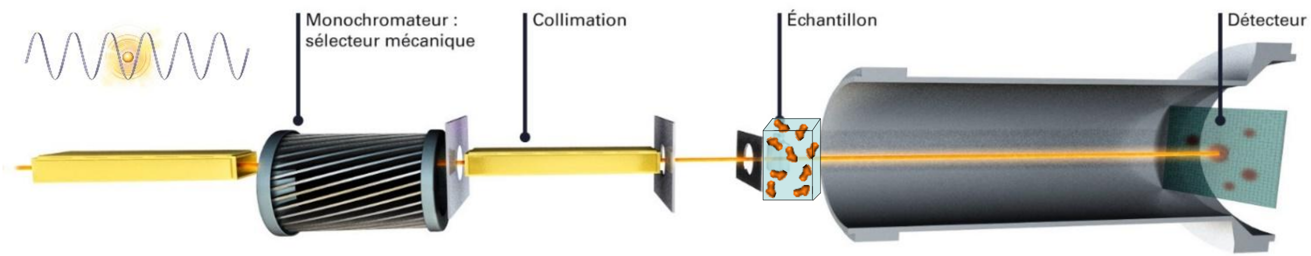

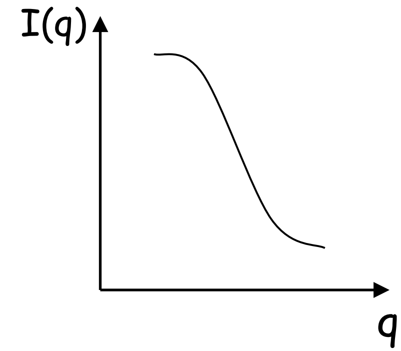

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Characteristic sizes: From ~ **5 Å** to ~ **2000 Å**

- **Form and size of objects**
- **Structure between objets**
- **Specific surface (porosity)**

Samples : a few cm^{-3} → Very large number of objects (~ Na)

Stastistical measurement

Small Angle (Neutron) Scattering: experimental

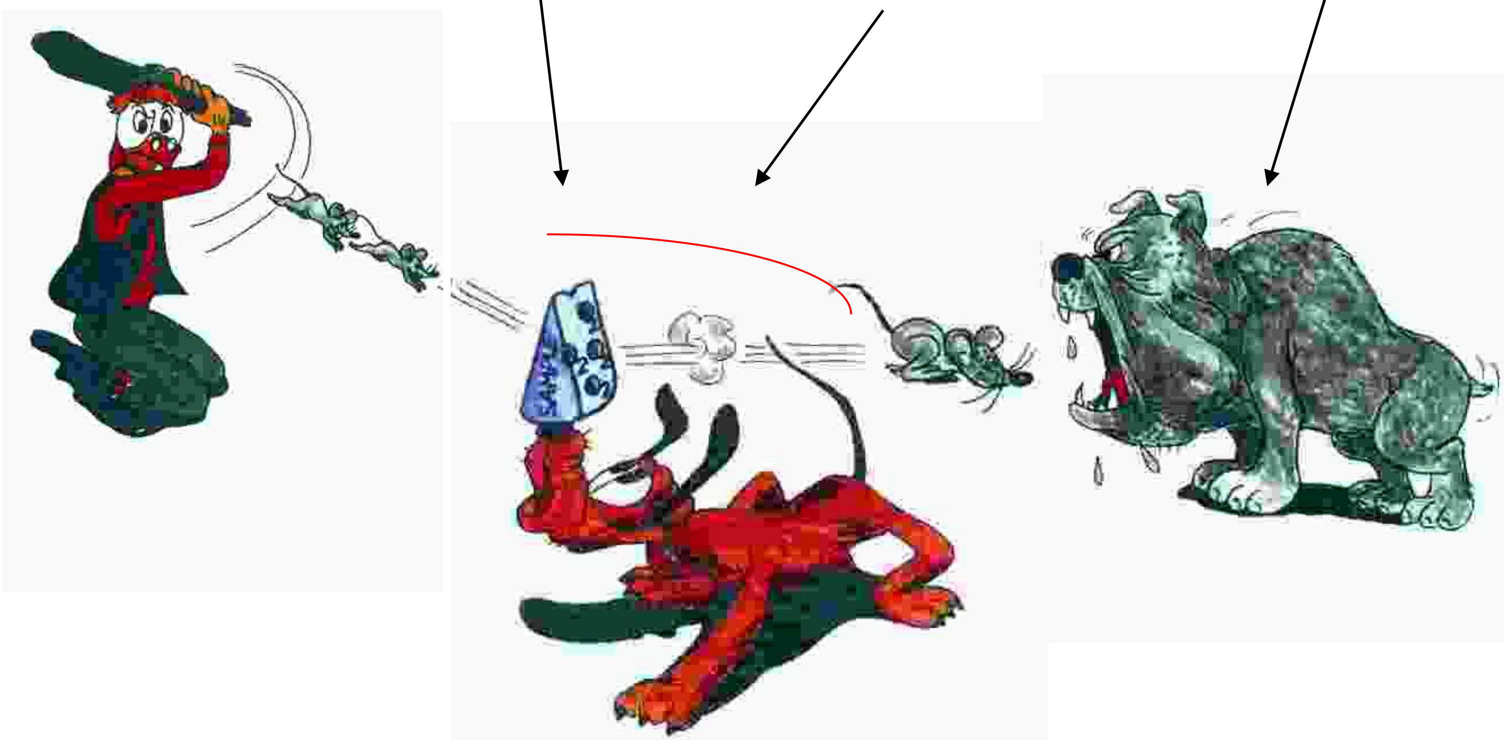
neutron production

and monochromator

sample

detector

scattering angle



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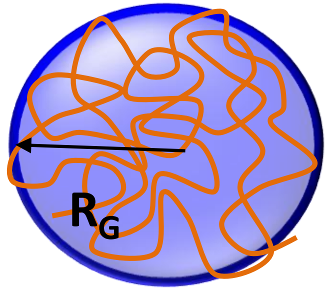
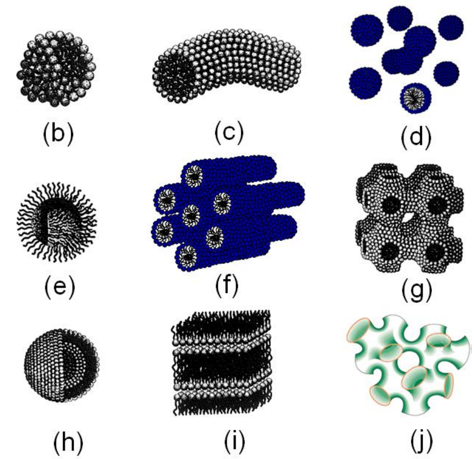
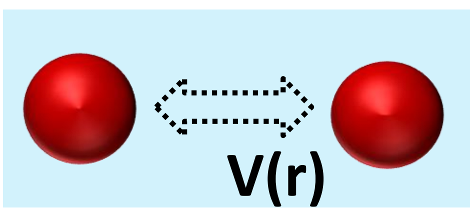
Mass…

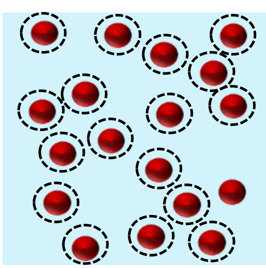


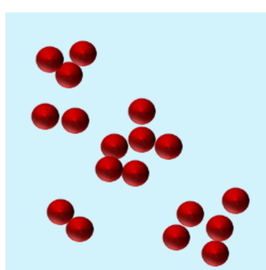
Gyration radius…

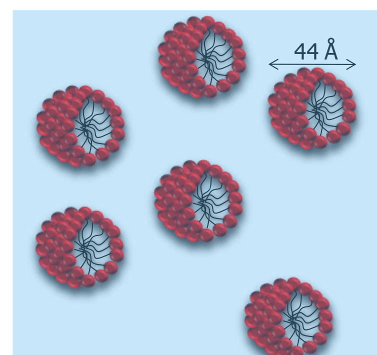


Morphology…









Interactions ? …

Advantages and neutron specificities

- Weak **absorption**
- **Interaction with nuclei** and not electronic cloud

  vary from one isotope to another

  Contrast variation
- Sensitive to **magnetism**
- **Weak energy** of neutrons (few meV)

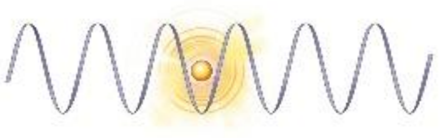
  Not destructive
- Weak fluxes (max $10^6 n/cm^2/s$)

  Long counting times

Outline

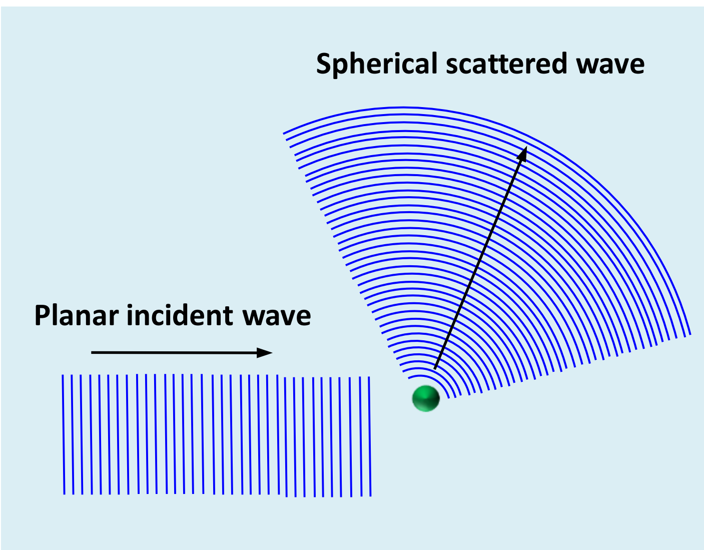
- <u>**Neutron scattering : Principles**</u>
- **Scattering Length Density /Contrast variation**
- **Form Factor/Structure factor**
- **Systems of non-interacting objects : Form factor**
- **Interactions between objects : Structure factor**
- **SANS diffractometer**

Incident beam ≅ plane incident wave



Individual nuclei (10^{-13} cm) will interact with neutrons following a spherical interaction potential.

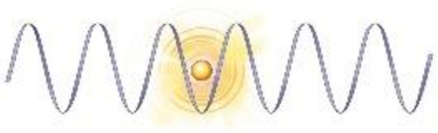
The neutron wave scattered by a nucleus is spherical



$$\Psi_s = \frac{-b}{r} e^{i(k_i . r - \omega' t)}$$

The amplitude of the spherical scattered wave is ***proportional to b*, the scattering length**

Incident beam ≅ plane incident wave



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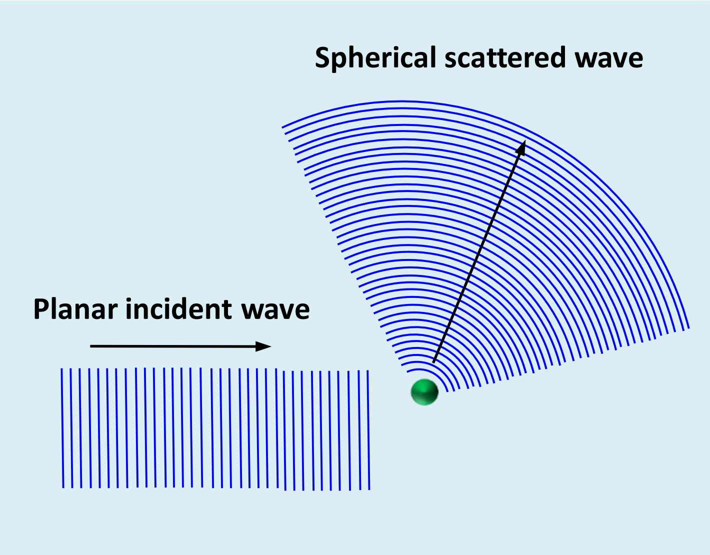

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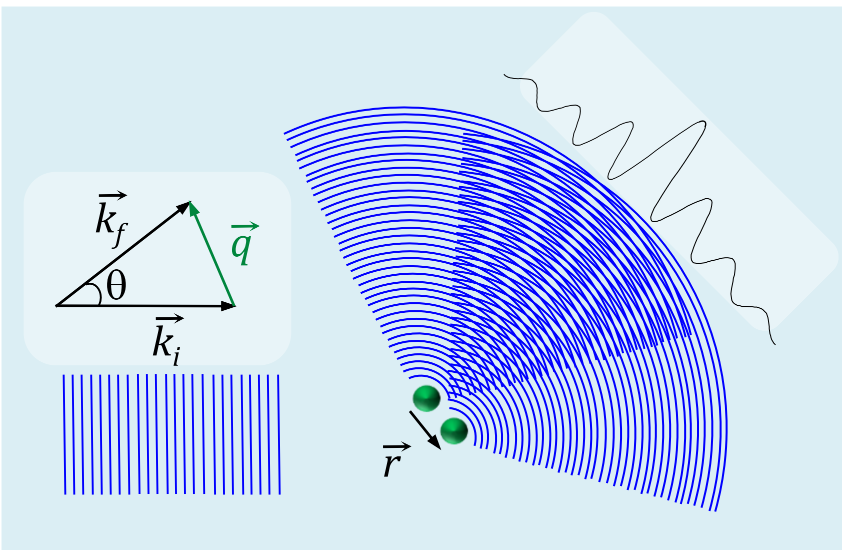
Neutron scattering : Principles

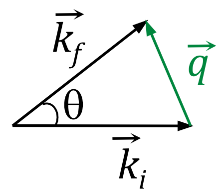
For **n** nuclei ➡ **n** spherical waves ➡ **interferences**

The scattered wave : ➡ **superposition of spherical waves scattered by each nuclei,** corrected by a phase factor due the **phase difference** of the incident wave to reach the position of another nucleus at $\vec{r}$



Phase shift $\Delta\phi = \vec{r}\,.\,(\vec{k_f} - \vec{k_i})$

Scattering vector



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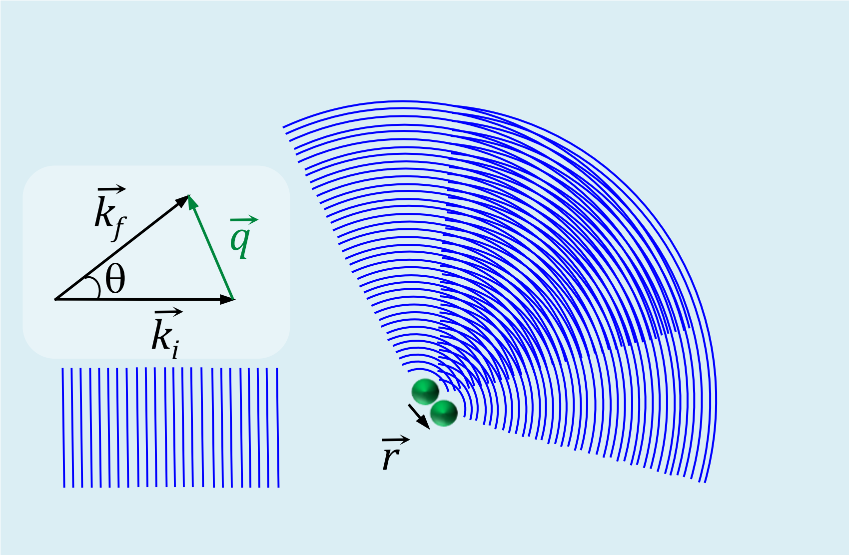

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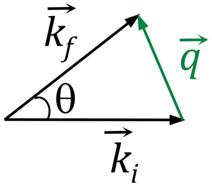

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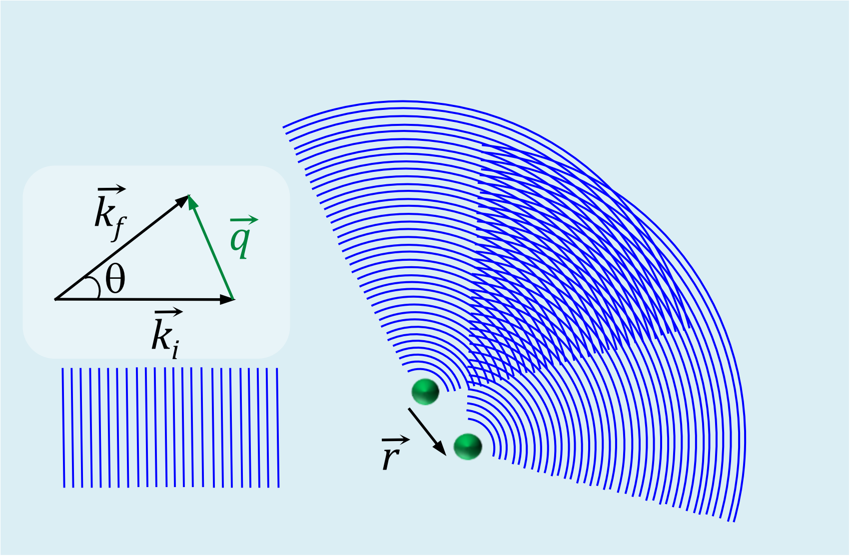

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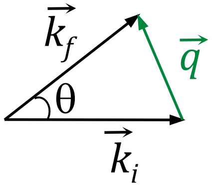

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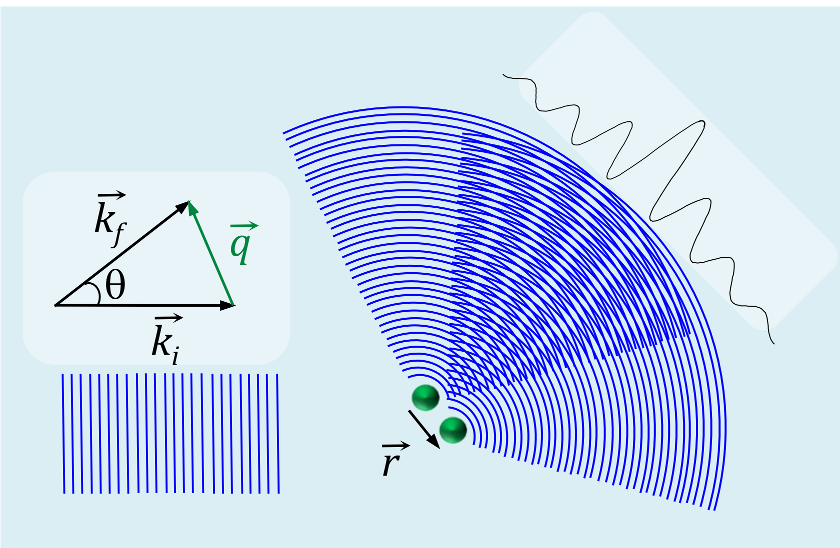

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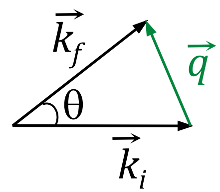

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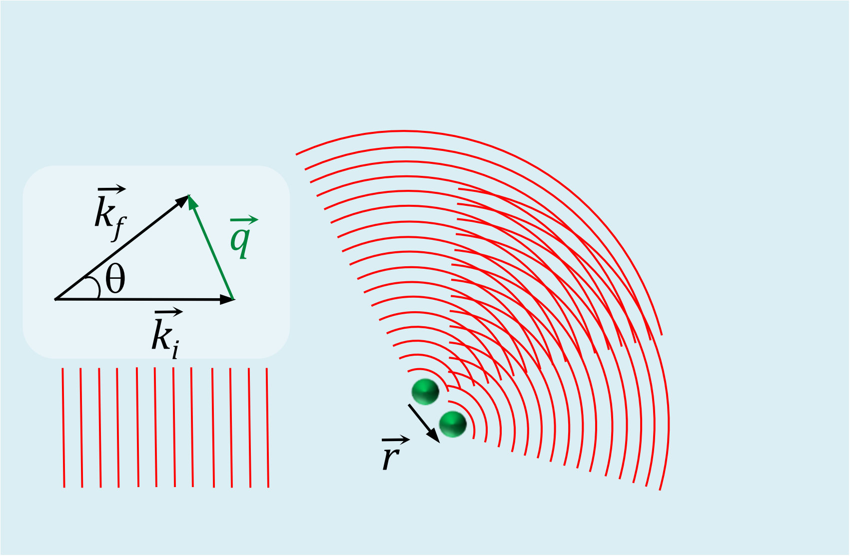

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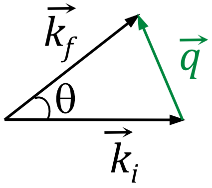

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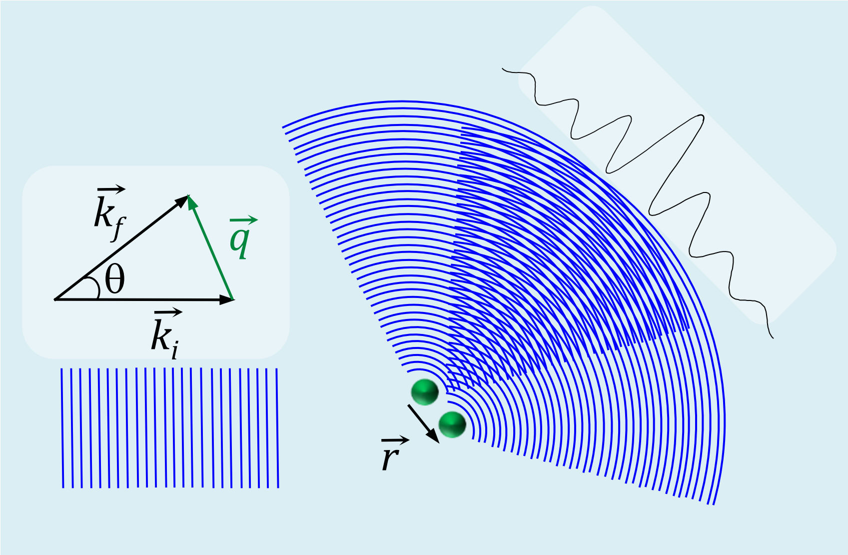
The neutron detector is not sensitive to the phase of the wave, but :

Square of the amplitude $|\Psi|^2 = \Psi.\Psi^*$

We define the differential scattering cross-section **dσ/dΩ (q) by** :

$$\frac{d\sigma}{d\Omega}(q) = \sum_{i,j} b_i b_j \exp(-i\vec{q}.(\vec{r}_i - \vec{r}_j))$$



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dσ/dΩ (q) is analogous to a **surface** (cm²).

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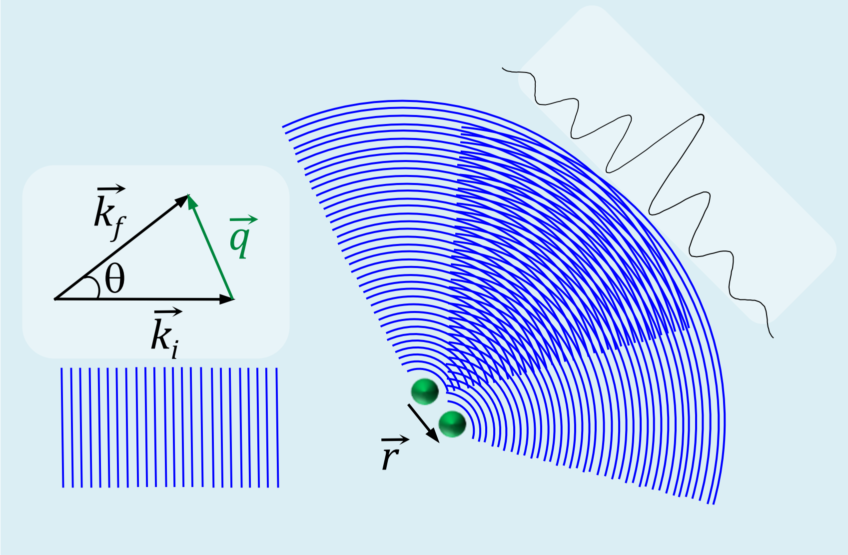

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Probability to find a nucleus of scattering length b_i and another nucleus of scattering length b_j distant of a vector $\vec{r}_i - \vec{r}_j$

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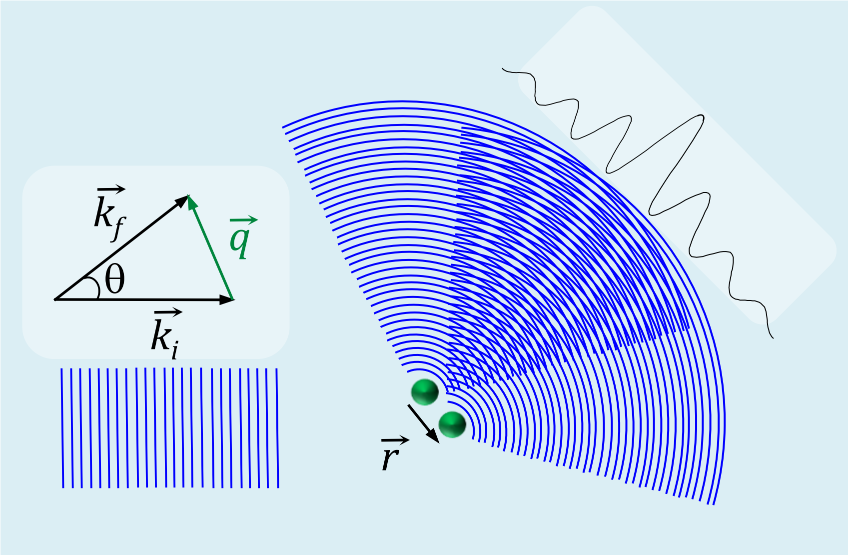

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Elastic scattering

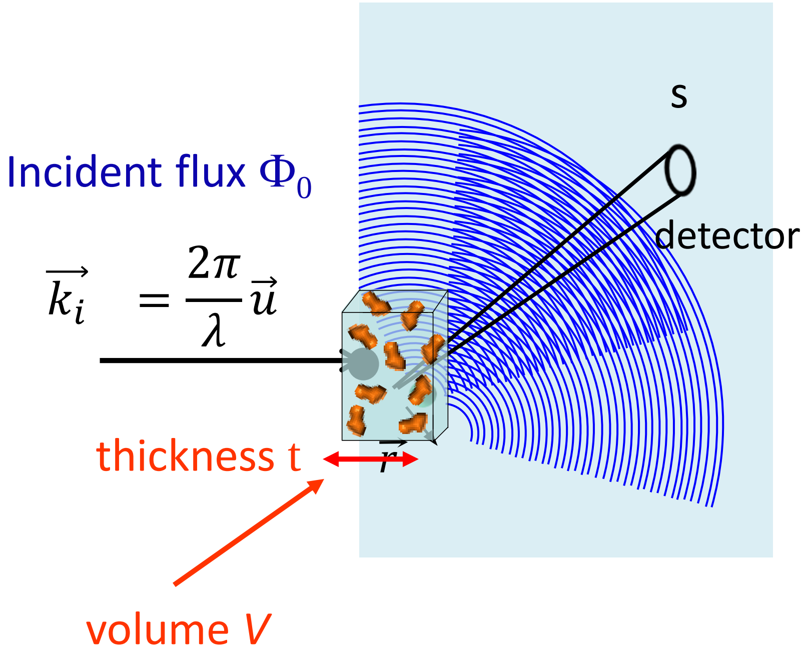
$\|\vec{k_f}\| = \|\vec{k_i}\|$ No exchange of energy

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

q: reverse of a length

q^{-1} is the observation scale

In practice, the **differential scattering cross-section dσ/dΩ (q)** is the number of neutrons measured by on the solid angle **ΔΩ** of a detector (area s at a distance D from the sample) normalized by incident flux unit.



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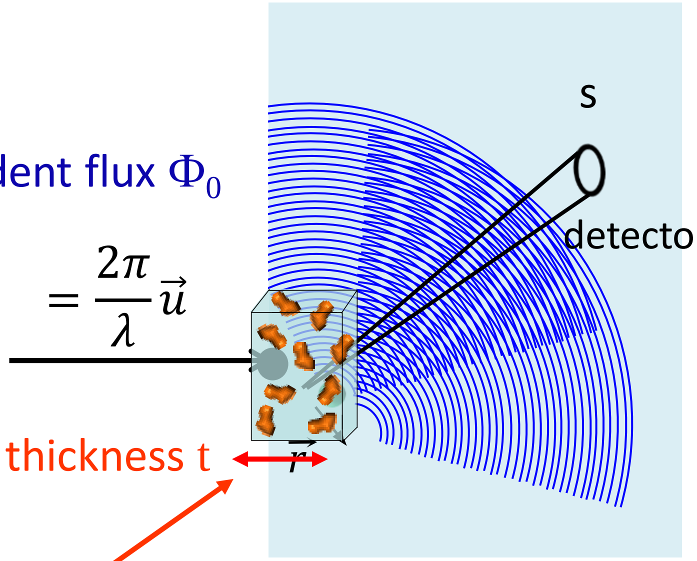
Incident flux Φ_0

$$\overrightarrow{k_i} = \frac{2\pi}{\lambda}\vec{u}$$



thickness t

volume V

A fraction of the incident flux ΔN is scattering in an elastic way in the direction of the vector q where is located the detector

$$\Delta N = \Phi_0 t T_r \frac{d\sigma}{d\Omega}(q)\,\Delta\Omega$$

T_r is the sample transmission

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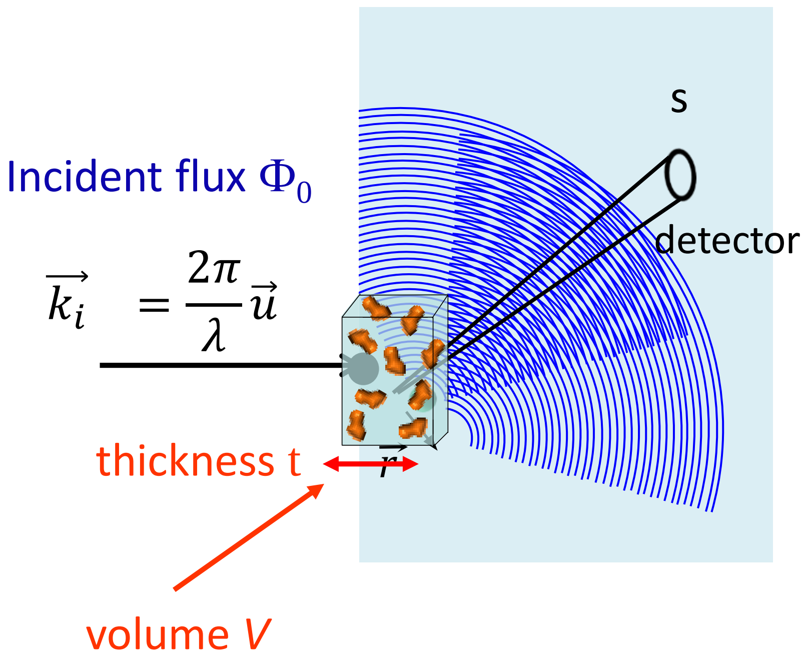

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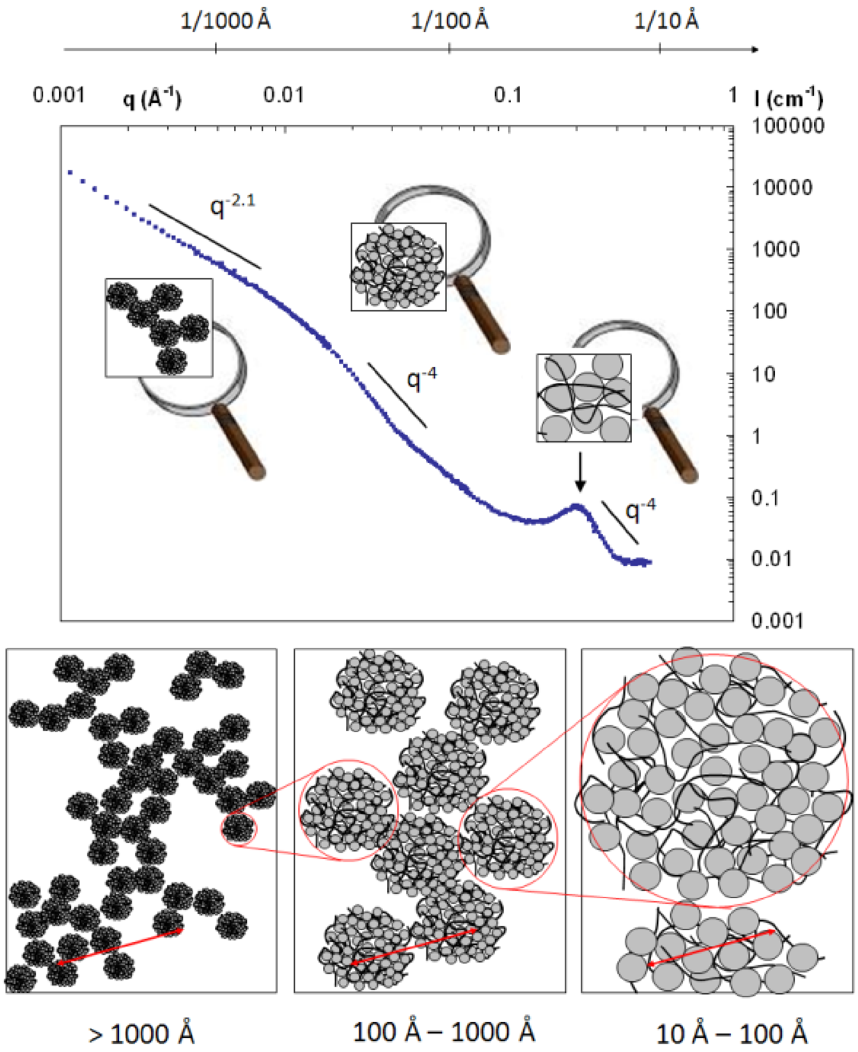
$$\Delta N = \Phi_0 t T_r \frac{d\sigma}{d\Omega}(q)\,\Delta\Omega$$

T_r is the sample transmission

The scattering intensity is the « scattering probability » (cm^2) per unit volume of the sample (cm^3) -> unit cm^{-1}

$$\boxed{I(q)_{cm^{-1}} = \frac{1}{V}\cdot\frac{d\sigma}{d\Omega}(q) = \frac{\Delta N(q)}{\Phi_0 T_r(\Delta\Omega).t}}$$

Neutron scattering : Principles



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

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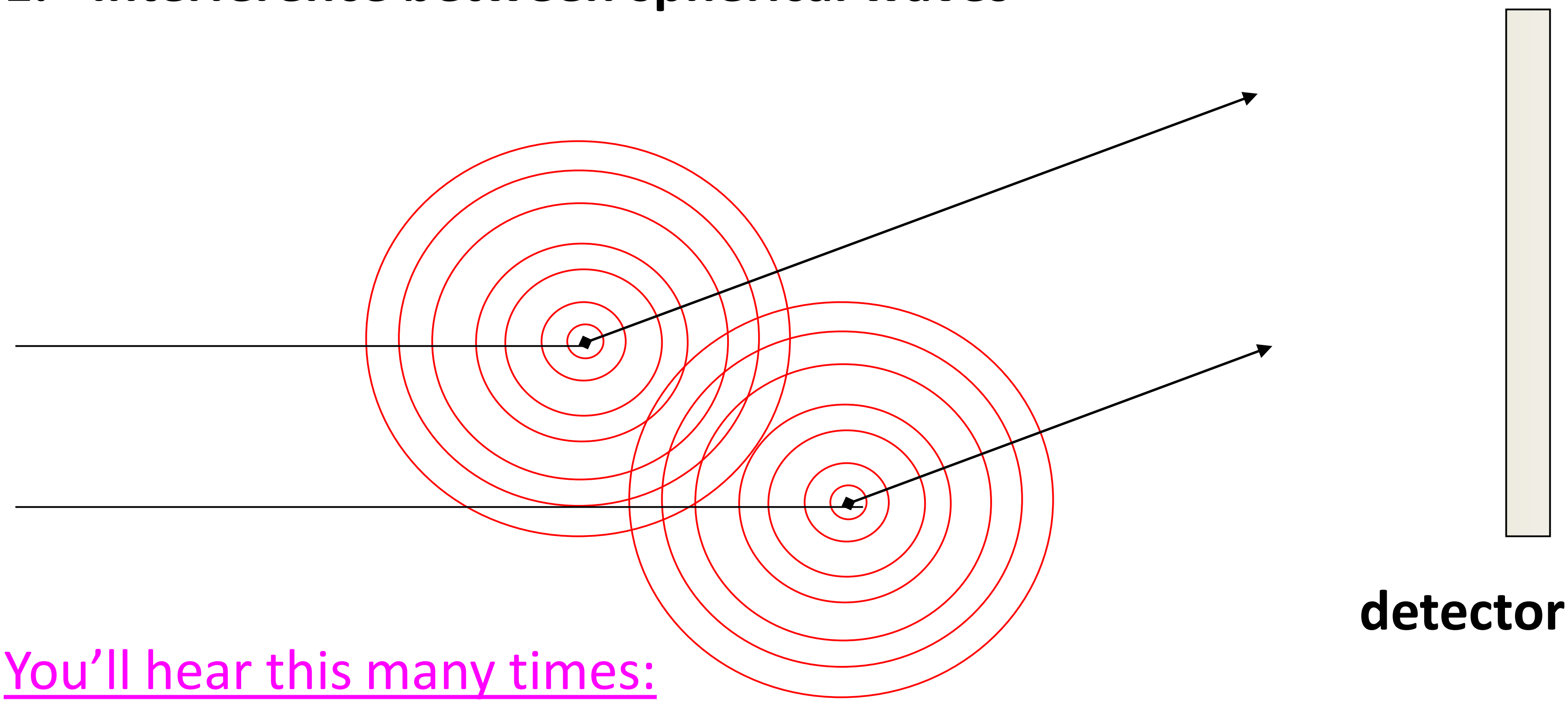
q^{-1} is the observation scale

Basic mechanism

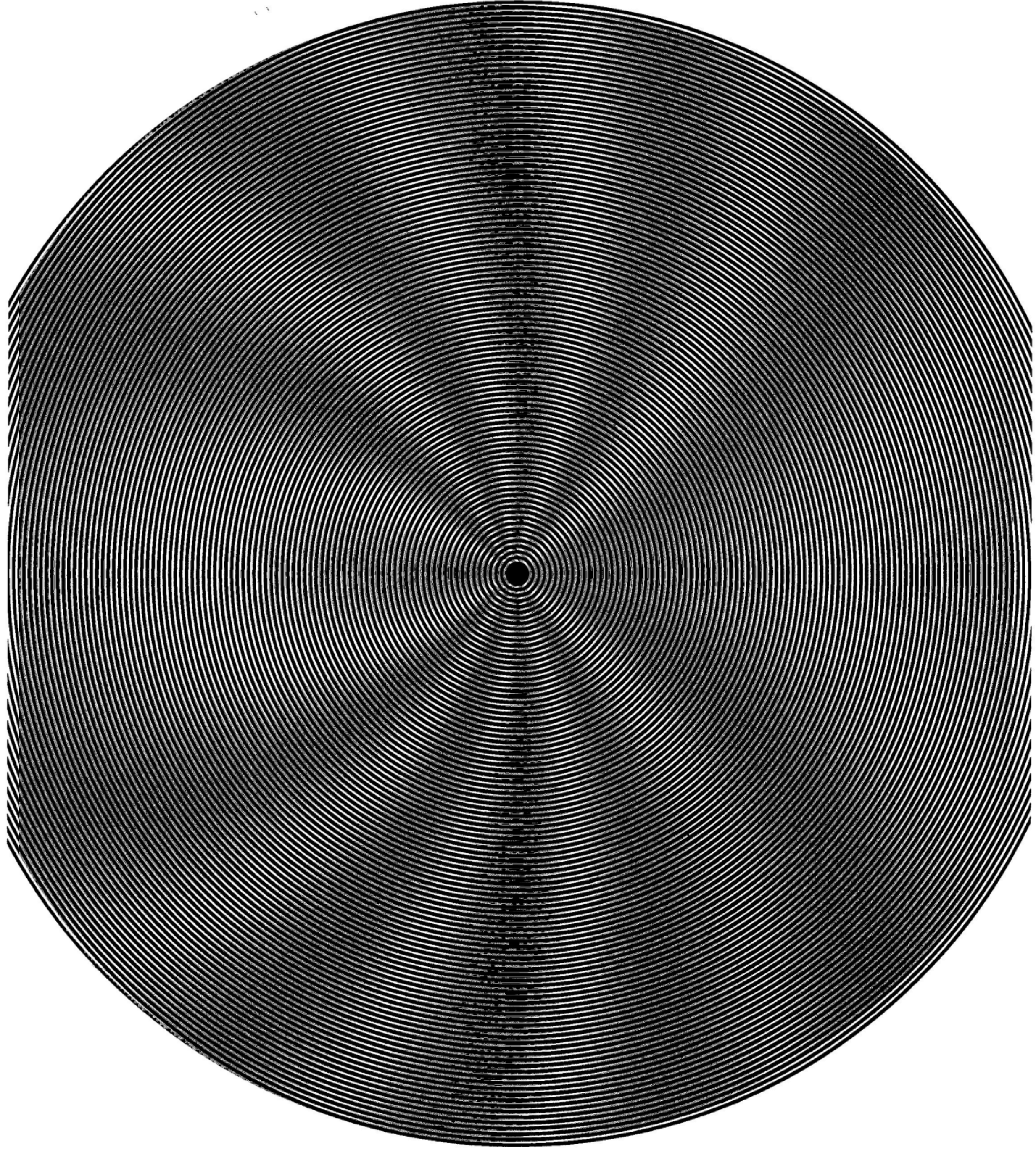
1. **Interference between spherical waves**



<u>You'll hear this many times:</u>

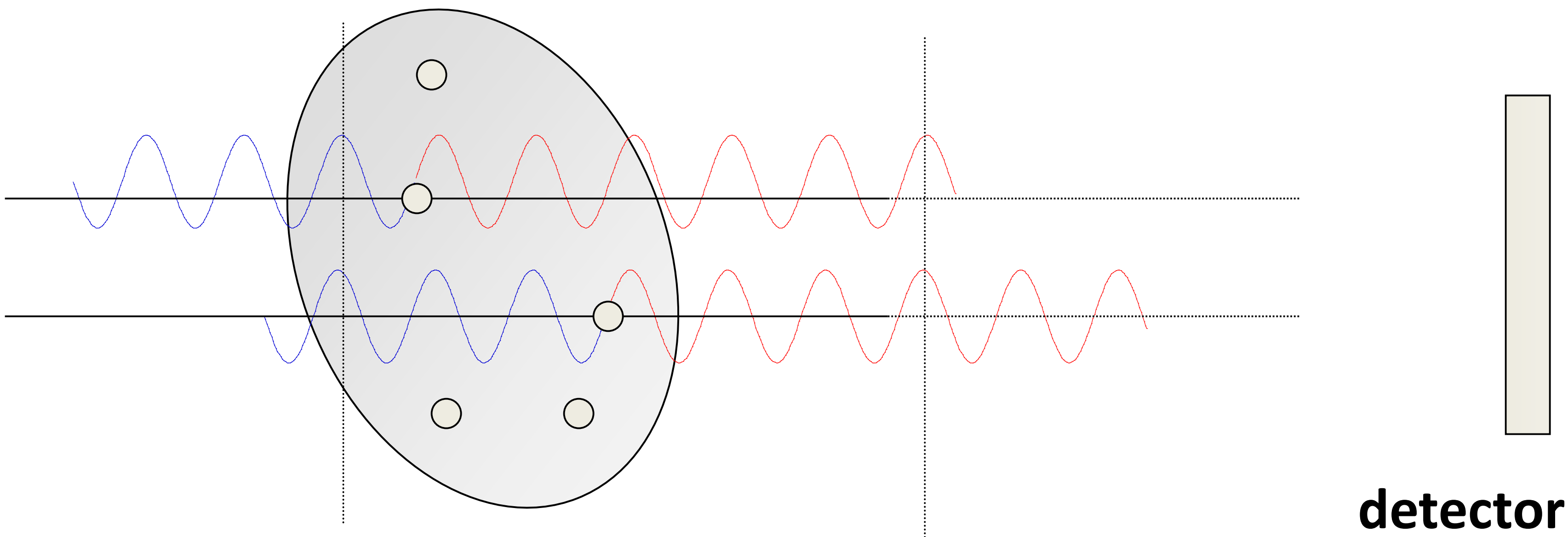
Small distances → large angles

Large distances → small angles



Basic mechanism

2. **Forward (q=0) scattering is additive**



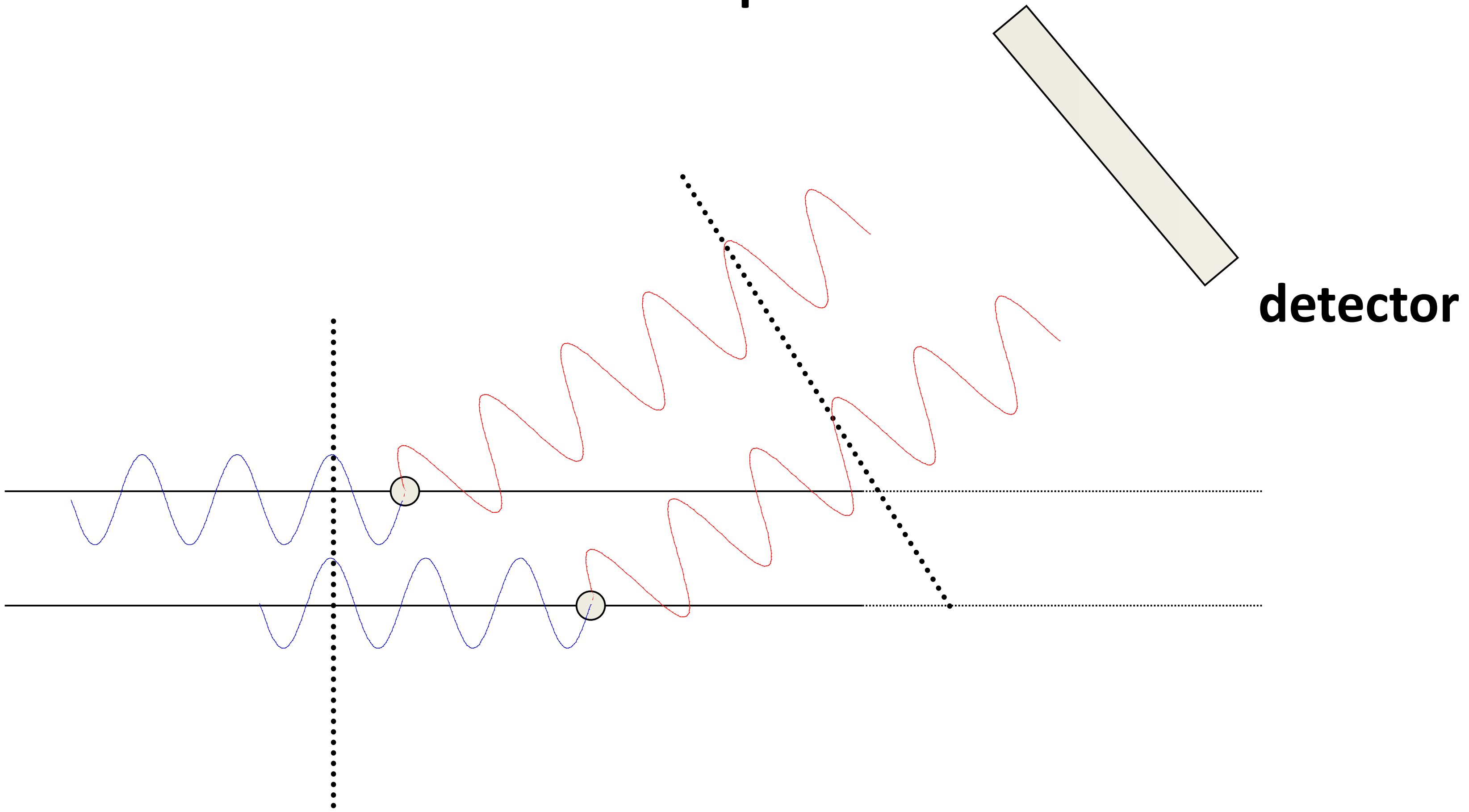
No phase shift → constructive interference on detector

Amplitude ∝ number of nuclei

I(q → 0) ∝ concentration * mass (meaning volume, same as Luca)

Basic mechanism

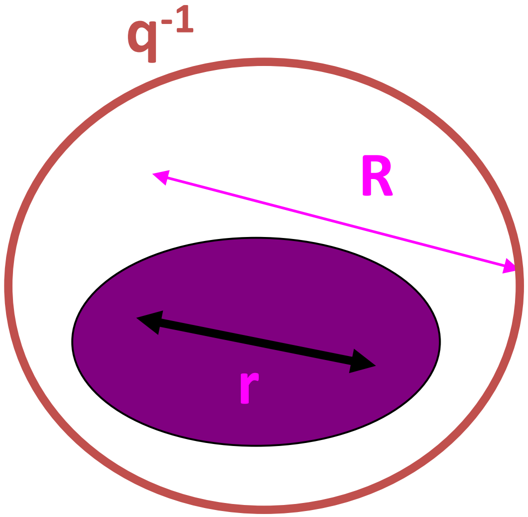
3. What mass is measured at q > 0 ?



Basic mechanism

3. What mass is measured at q > 0 ?

phase shift = **q** * r   with $q = 4\pi/\lambda \sin \Theta/2$



$R < q^{-1}$

$\rightarrow \; r < q^{-1}$

$\rightarrow$ qr = phase shift ≈ 0

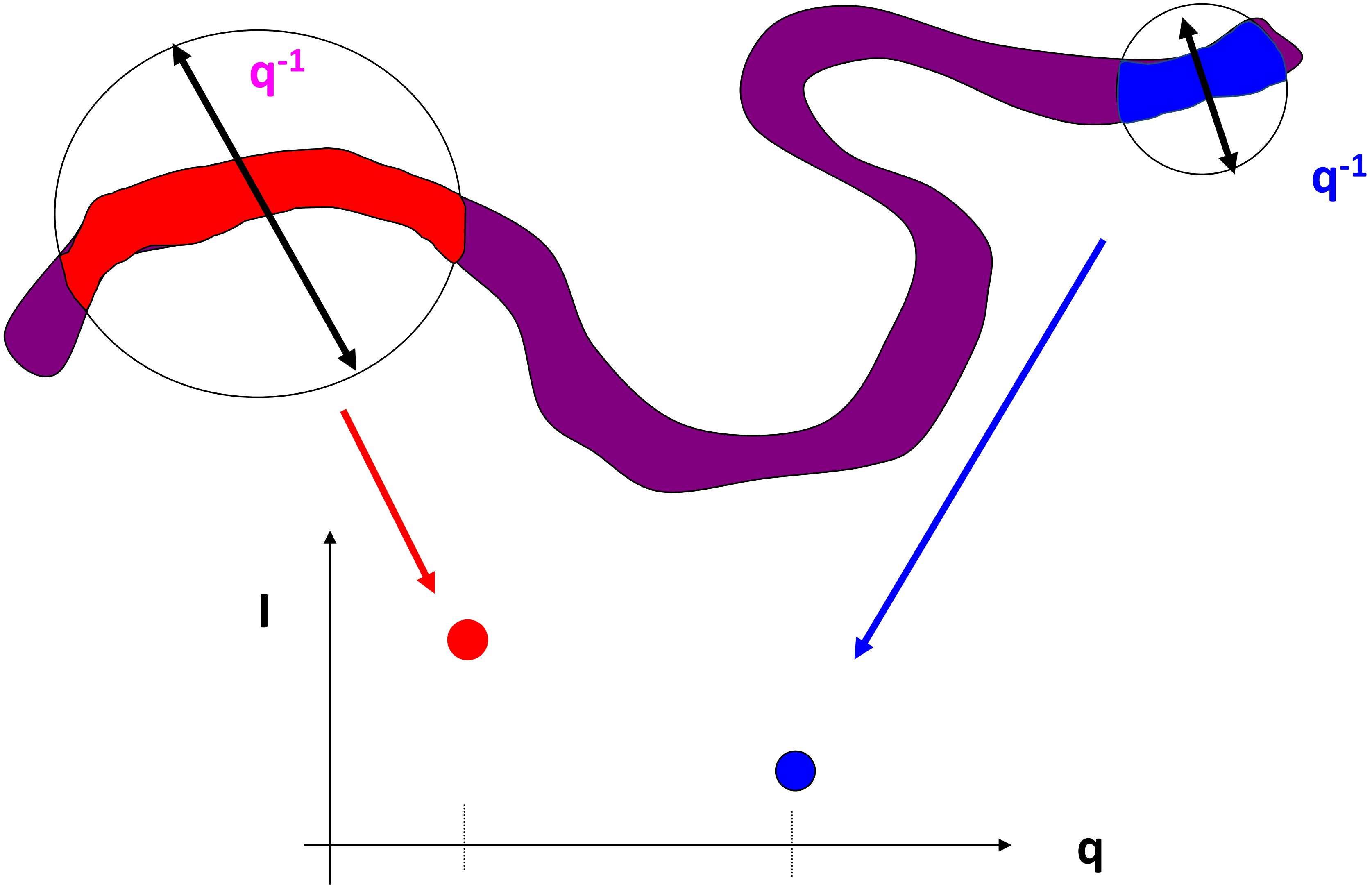
$\rightarrow$ I(q) = mass inside sphere q^{-1}

If you prefer mathematics: $e^{iqr} \approx 1$

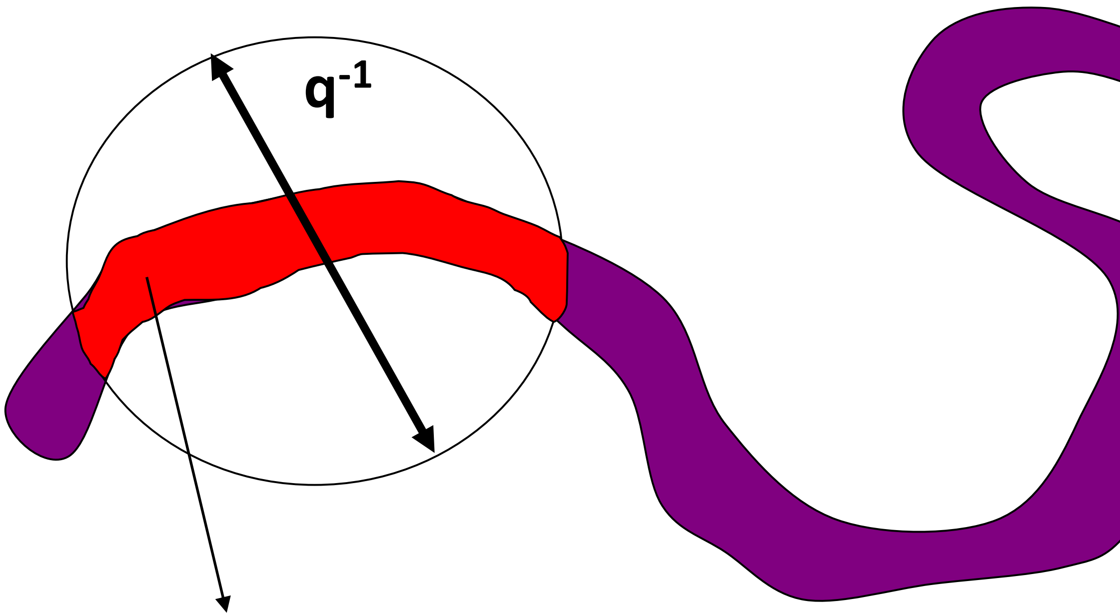
$$I(q<R^{-1}) = \frac{1}{V} \left| \int \rho(r)\, \cancel{e^{iqr}}\, d^3r \right|^2 \propto \frac{m}{V} * m$$

General scattering law

$I(q) \propto$ mass inside sphere of radius q^{-1}



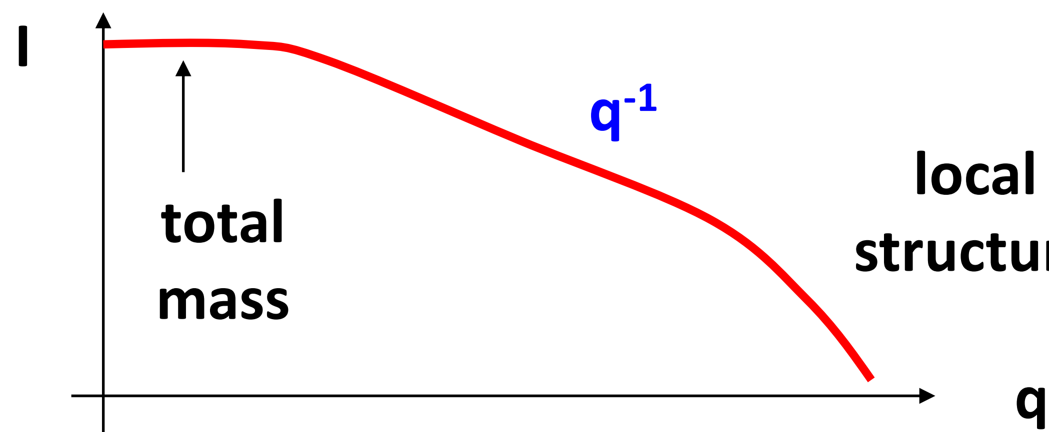
General scattering law: cylinders



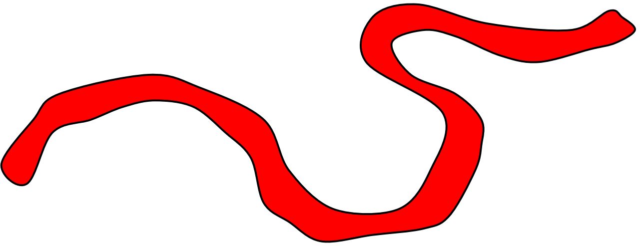
Loic Auvray, 1956-2016

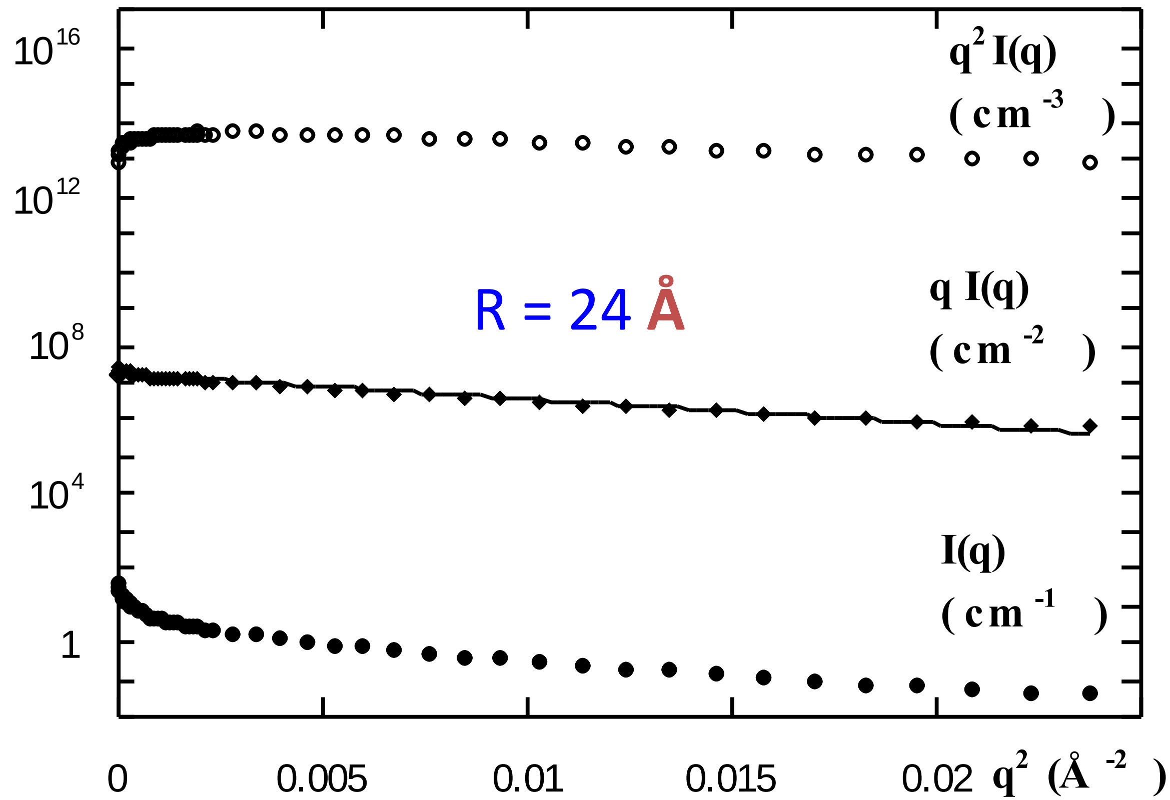
mass inside ≈ cylinder = Section x Length = $S\ q^{-1}$

$$I\,(q) \propto \Phi\ S\ q^{-1}$$



Example of cylinders

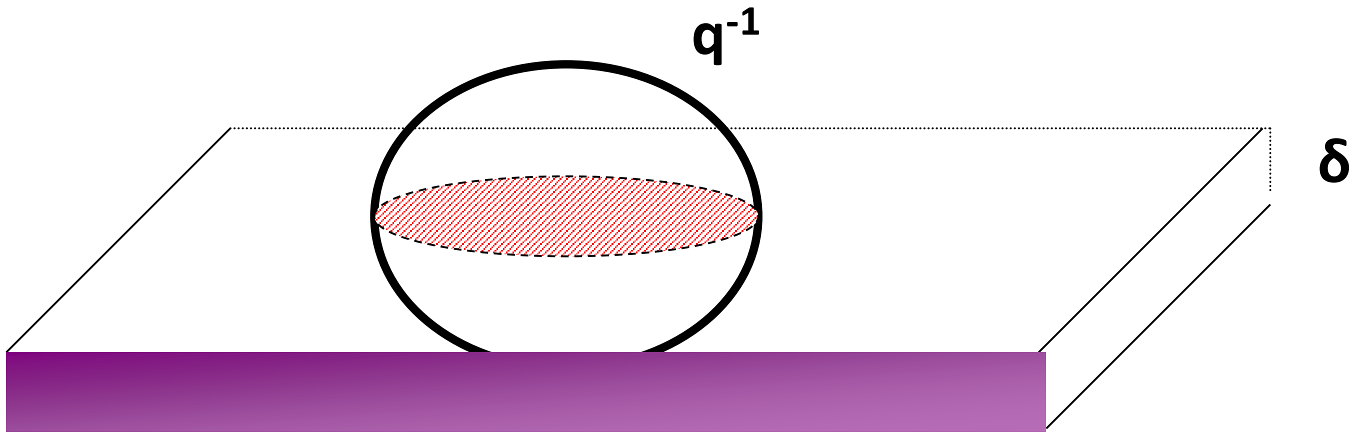




$$I\,(q) \propto \Phi\, S\, q^{-1}$$

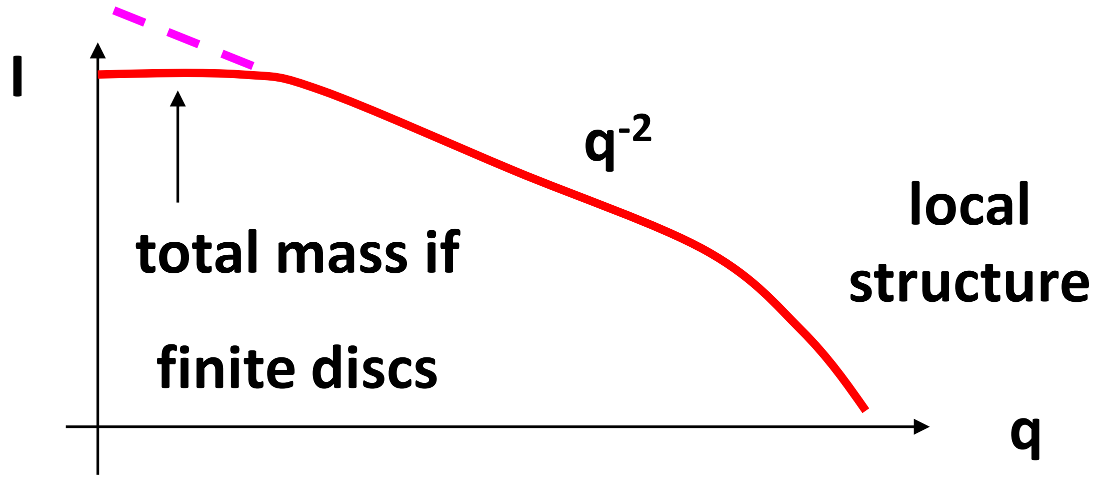
Cylinders, small q : $qI\,(q) = \pi\, \Phi\, \Delta\rho^2\, S\, \exp(-q^2R^2/4)$

General scattering law for flat bilayers



mass inside $\approx$ cylinder = thickness x surface = $\delta \ \pi q^{-2}$

$$I(q) \propto \Phi\delta\, q^{-2}$$



Outline

- Neutron scattering : Principles
- <u>Scattering Length Density /Contrast variation</u>
- Form Factor/Structure factor
- Systems of non-interacting objects : Form factor
- Interactions between objects : Structure factor
- SANS diffractometer

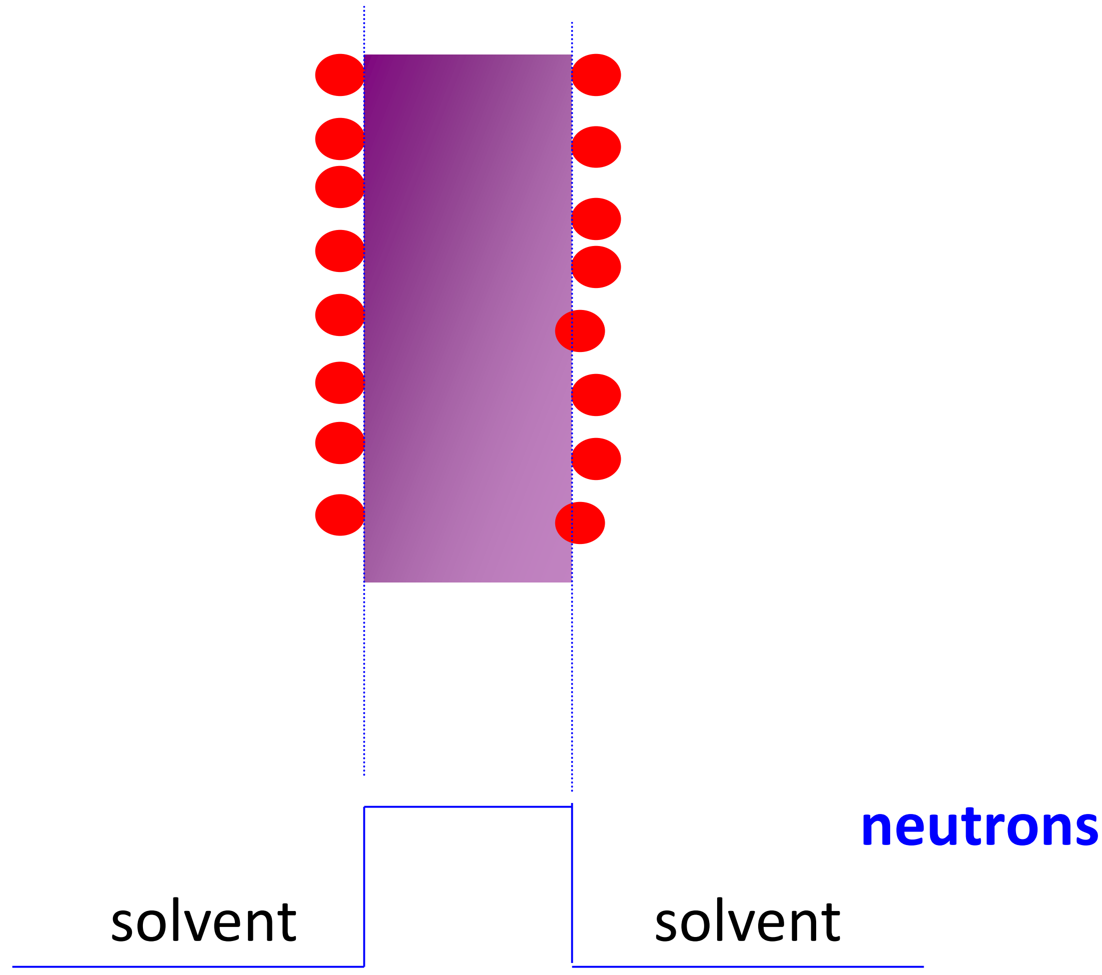
Contrast:

Contrast =

Difference in

Scattering length

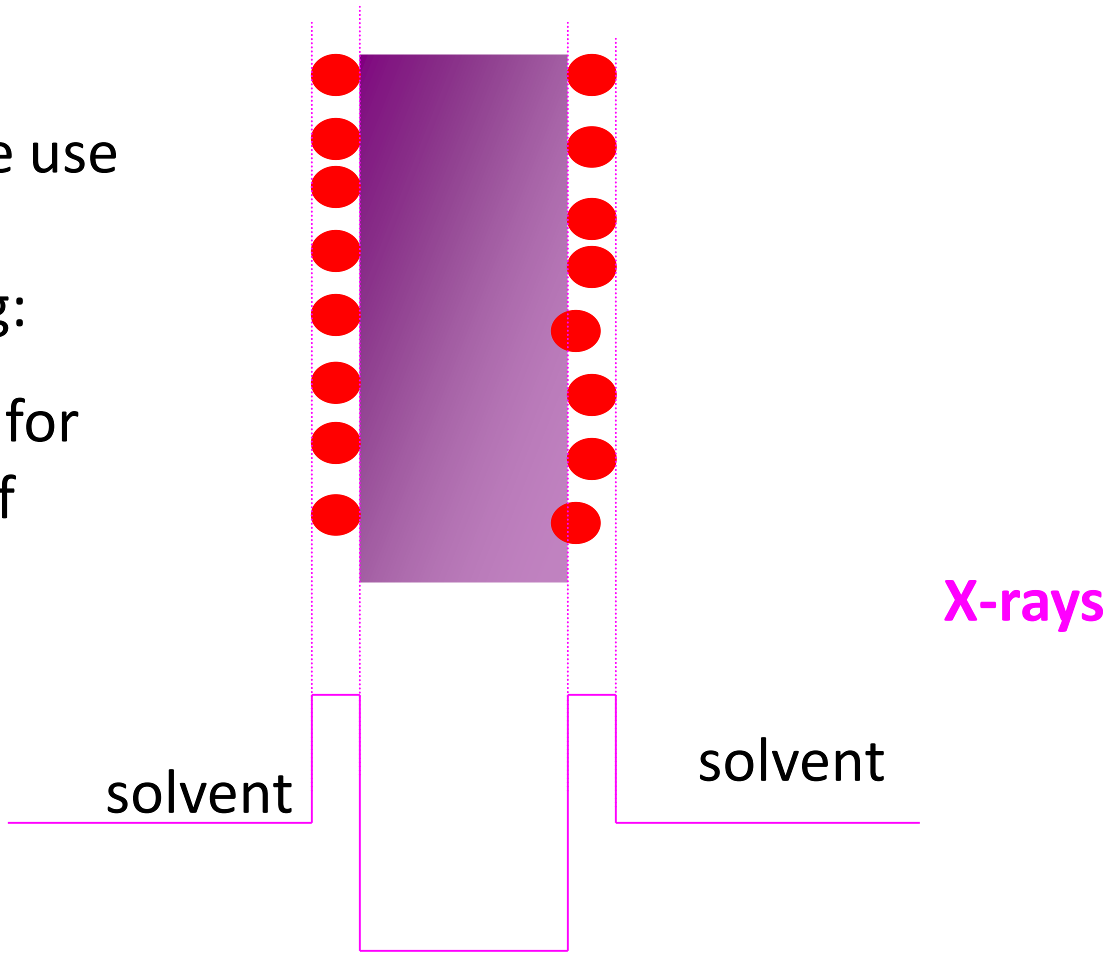
Density $\rho = \Sigma\, b_i/V$



Contrast

Sometimes people use such profiles for neutron scattering:

Core shell models for characterization of hydrophilic shell.

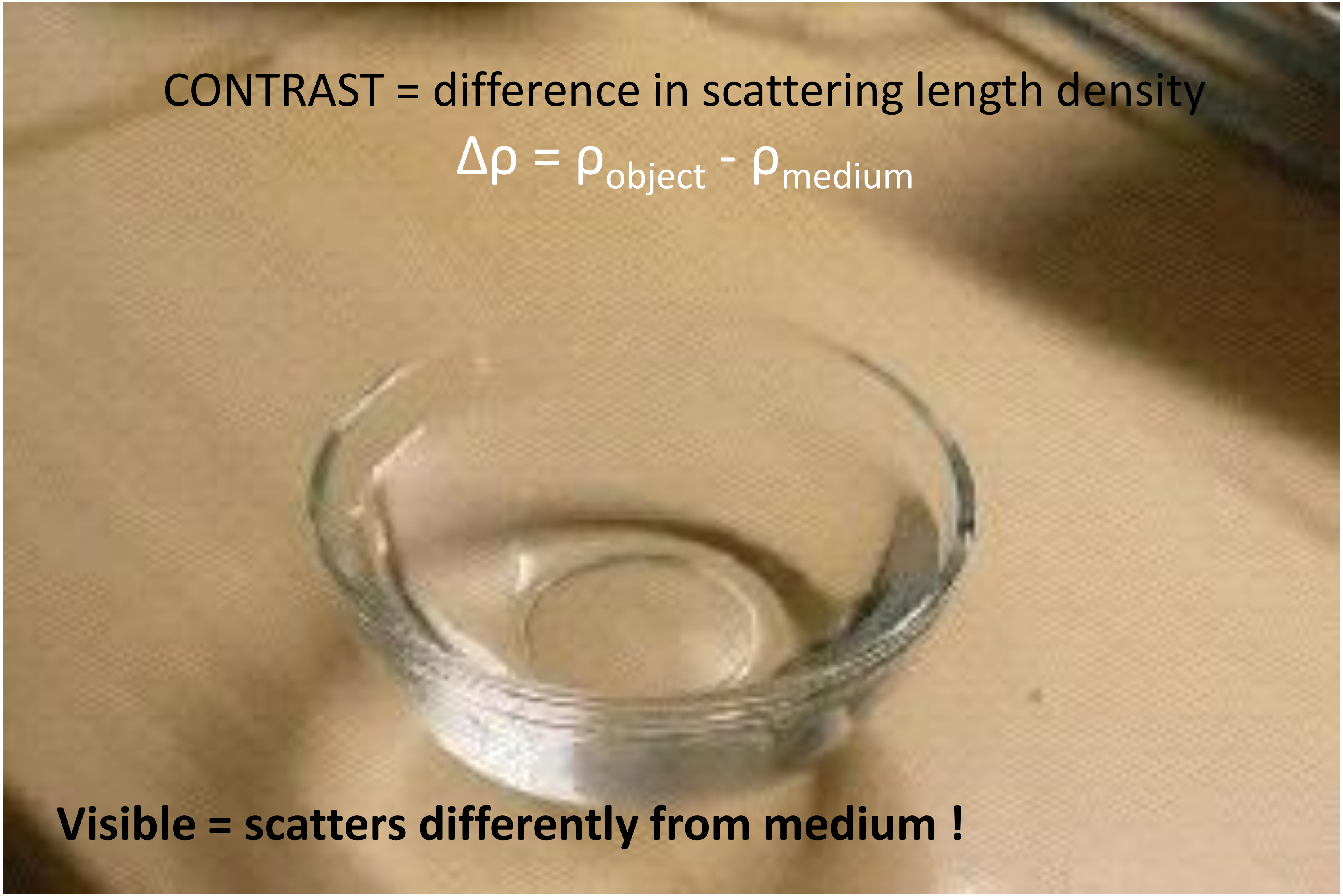


X-ray profile is more complicated. In the following discussion this is neglected

Contrast

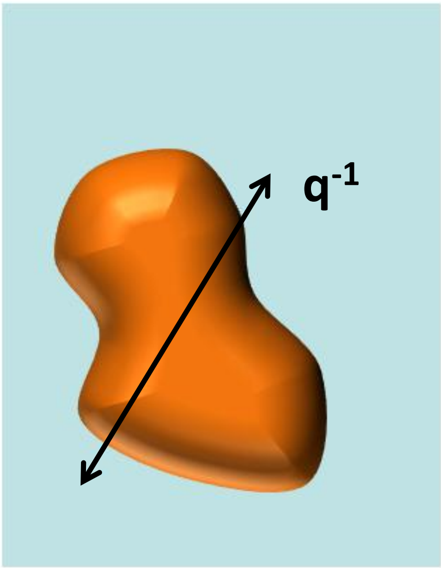
CONTRAST = difference in scattering length density

$$\Delta\rho = \rho_{object} - \rho_{medium}$$

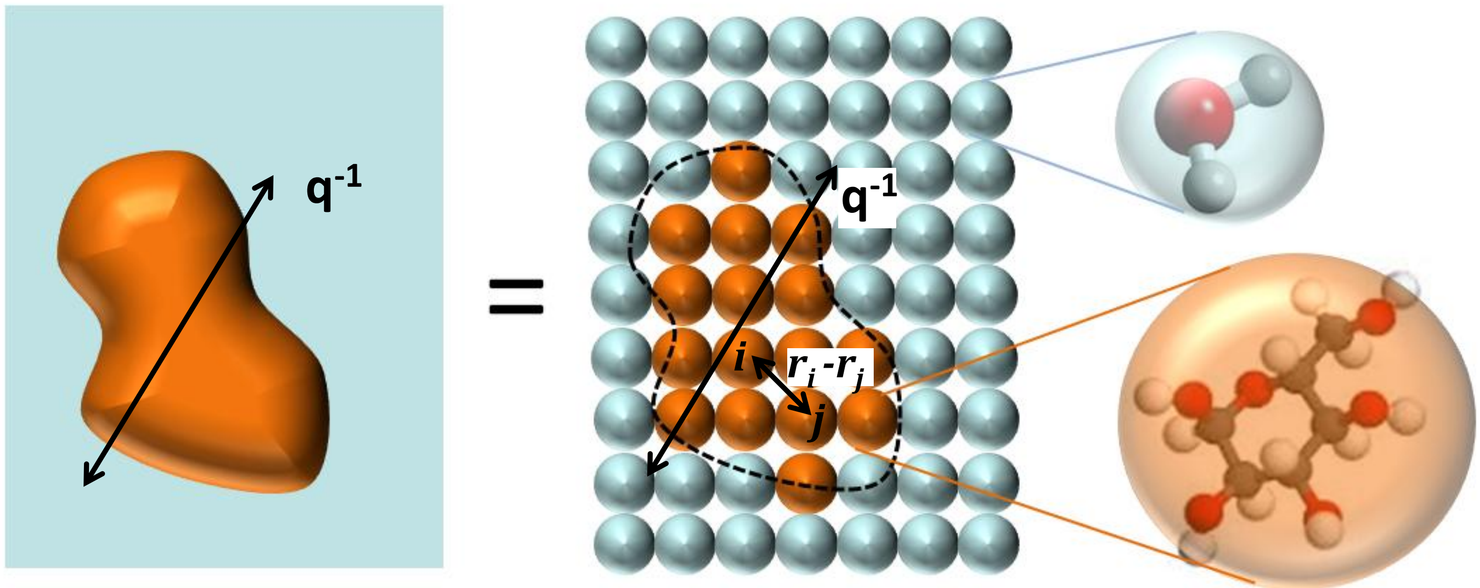


Visible = scatters differently from medium !

Scattering Length Density /Contrast variation



Scattering Length Density /Contrast variation

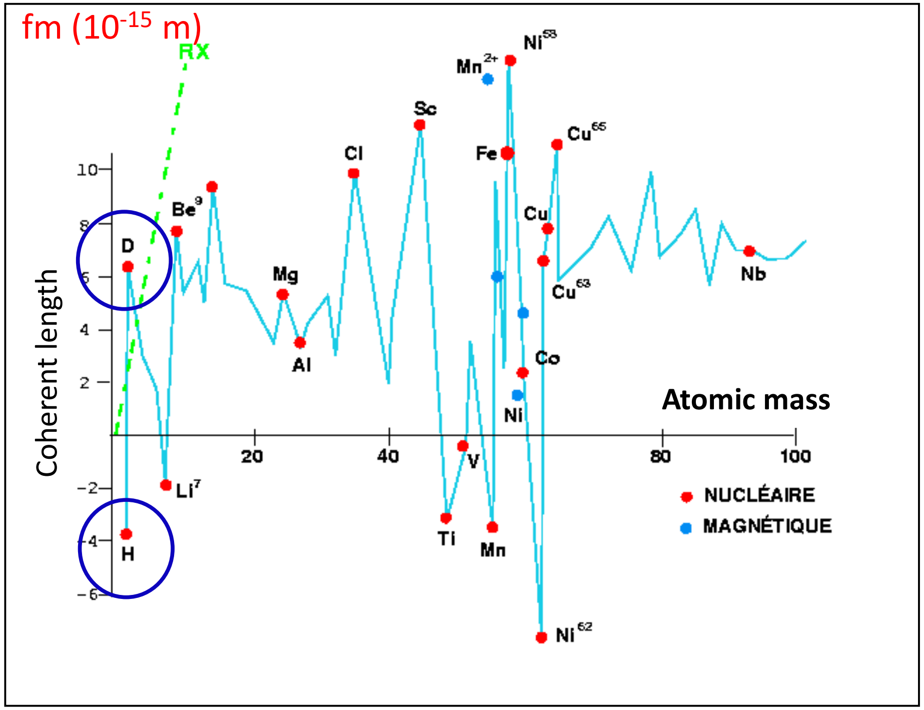


1/q >> size of Elementary Scatterer : ➡ $\boxed{e^{iq.r_{ij}} = 1}$

Relevant parameter for the contrast :

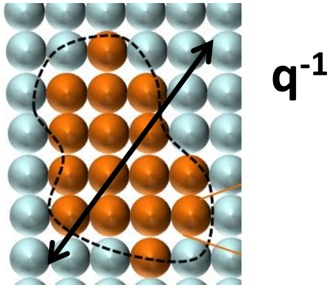
Scattering Length Density : ➡ $\rho = \dfrac{\sum_i b_i}{V_{mol.}} \qquad \dfrac{1}{V_{mol.}} = \dfrac{d\mathcal{N}_A}{M}$

Scattering Length Density /Contrast variation

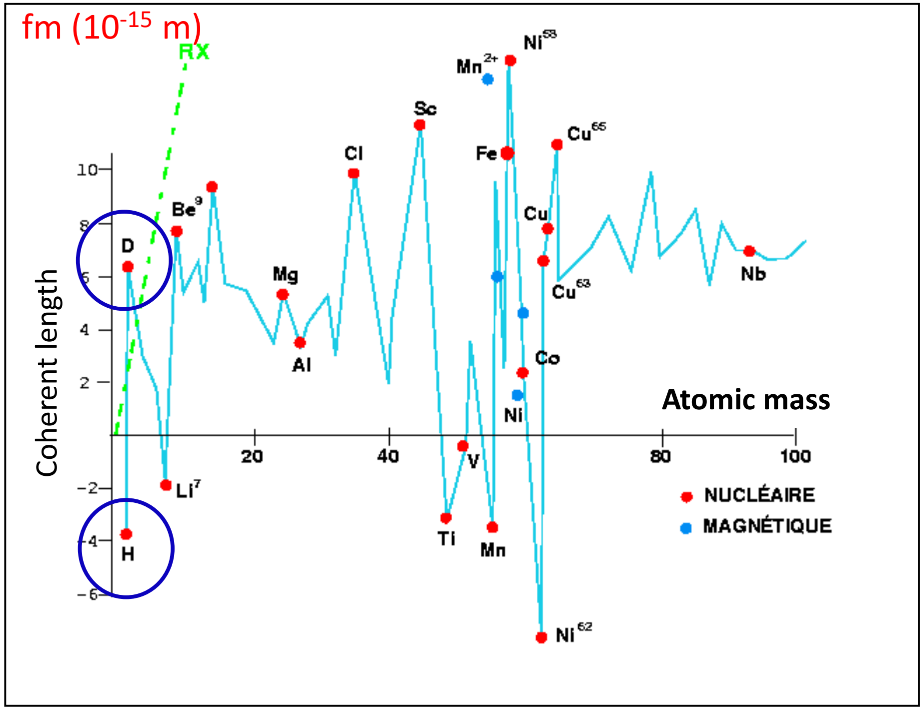


Atoms/ Molecules	b (10^{-12}cm)	ρ (10^{10}cm^{-2})
H	-0.373	
D	0.667	
O	0.58	
H_2O	-0.168	-0.563
D_2O	1.91	6.38
PS-h	2.32	1.42
PS-d	10.65	6.5

Neutron-Matter interaction varies from one isotope to the other



Scattering Length Density /Contrast variation



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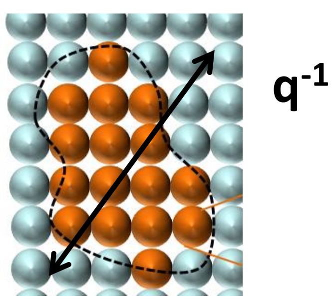
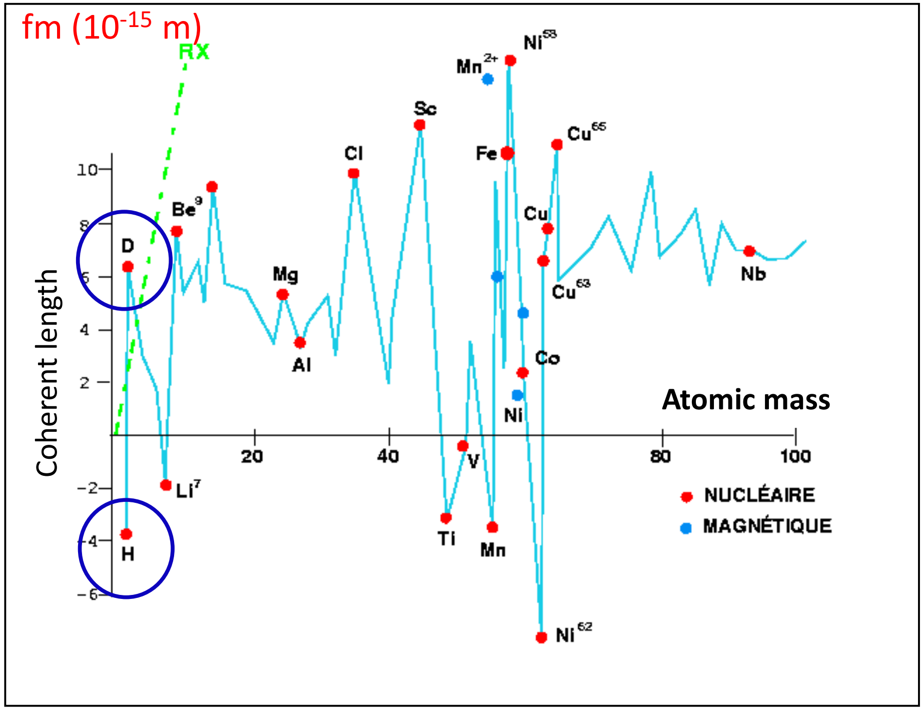


Scattering Length Density /Contrast variation



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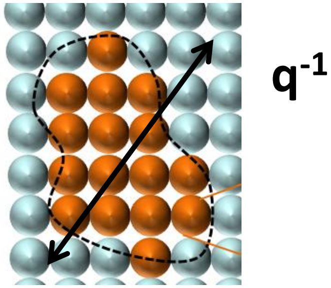
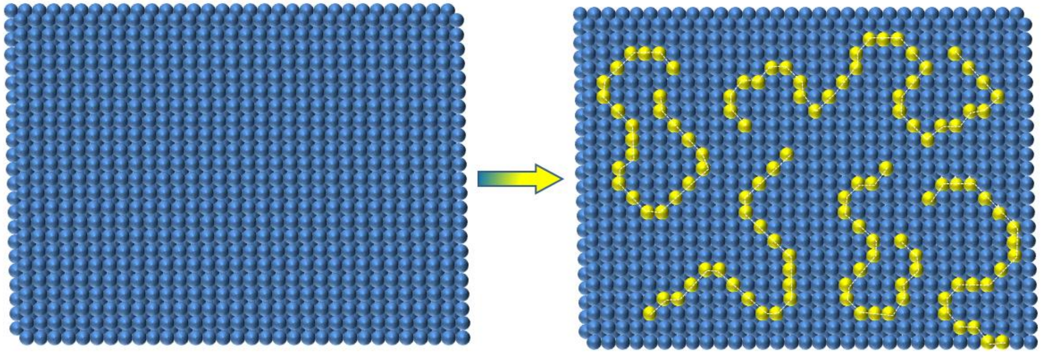


$$\rho = \frac{\sum_i b_i}{V_{mol.}} \qquad \frac{1}{V_{mol.}} = \frac{d\mathcal{N}_A}{M}$$

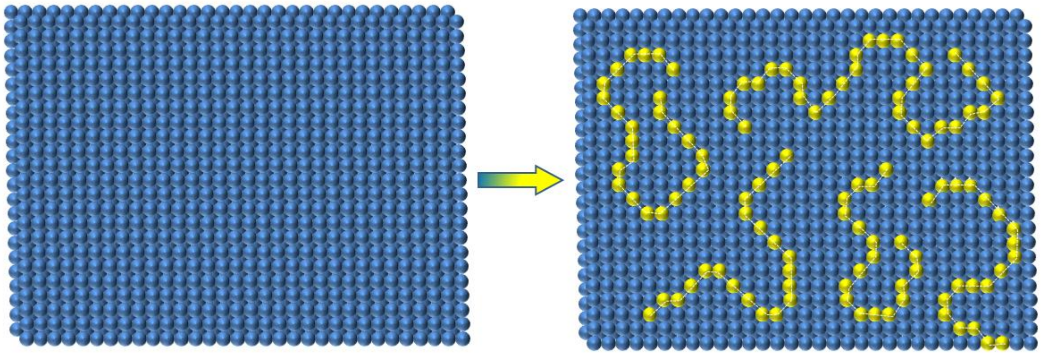
Scattering Length Density /Contrast variation

Binary systems

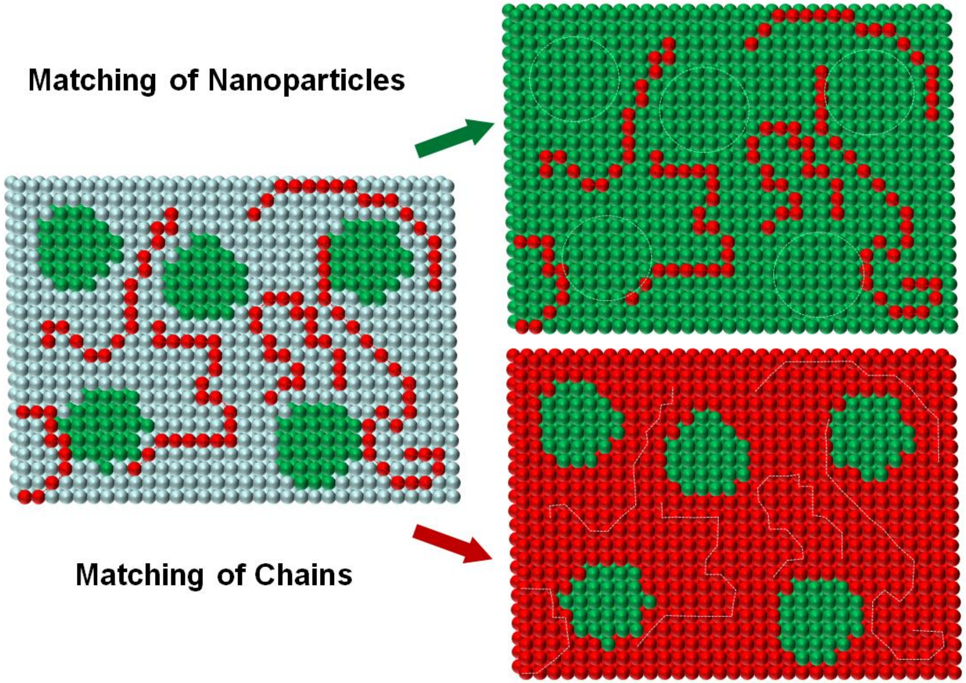


Scattering Length Density /Contrast variation

Binary systems



Ternary systems



Outline

- Neutron scattering : Principles
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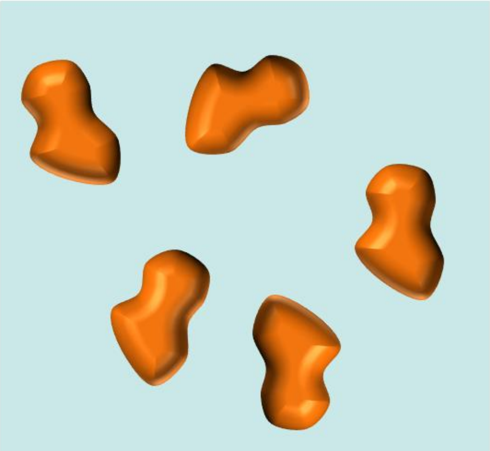
Form Factor/Structure factor



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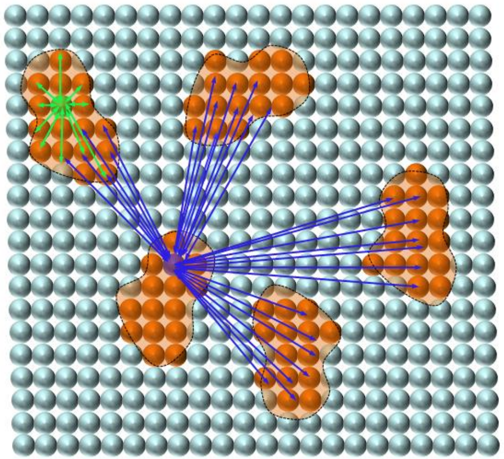


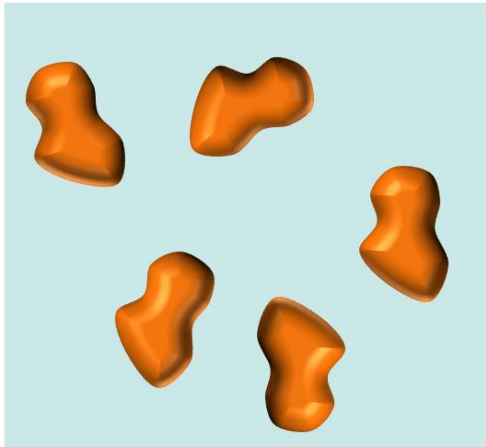
$\frac{1}{V}\cdot\frac{d\sigma}{d\Omega}(q)$

$$\frac{\Sigma(q)}{\boxed{\left(\rho_{obj}-\rho_{media}\right)^2} v_{obj}{}^2} = \sum_{\alpha}^{n}\sum_{\beta}^{n}\sum_{i}^{N}\sum_{j}^{N} e^{i\vec{q}\cdot\left(\vec{r}_i^{\,\alpha}-\vec{r}_j^{\,\beta}\right)}$$

contrast

n objects
N elementary scatterer per object

Form Factor/Structure factor



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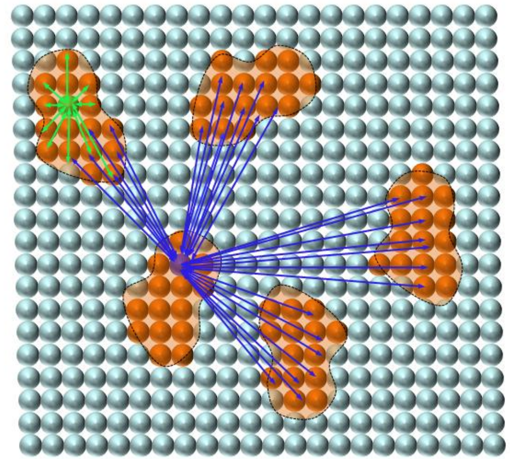


contrast

$$\frac{\Sigma(q)}{\boxed{\left(\rho_{obj}-\rho_{media}\right)^2} v_{obj}{}^2} = n\sum_{i,j}^{N} e^{i\vec{q}.\left(\vec{r}_i^{\alpha}-\vec{r}_j^{\alpha}\right)} + n^2 \sum_{i,j,\alpha\neq\beta}^{N} e^{i\vec{q}.\left(\vec{r}_i^{\alpha}-\vec{r}_j^{\beta}\right)}$$

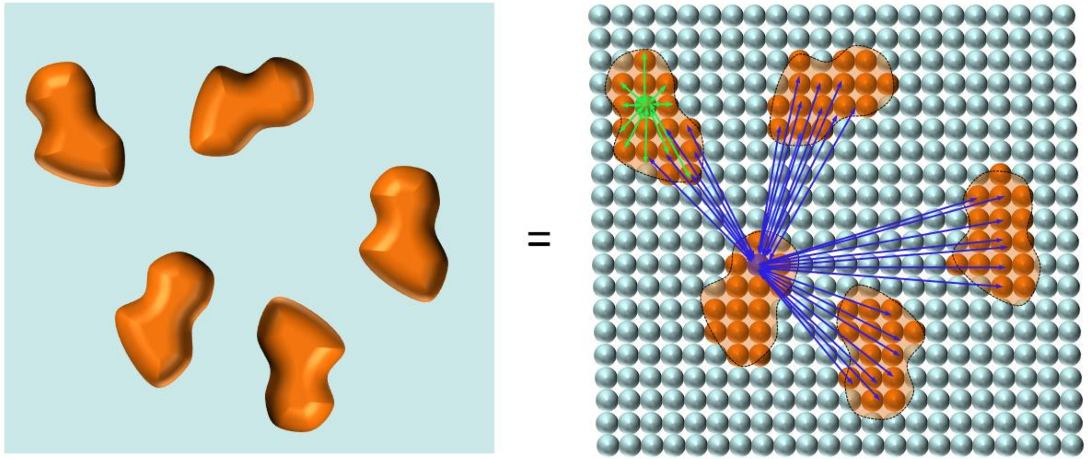
$$\boxed{P(q)} = \frac{1}{N^2}\sum_{i^{\alpha}}^{N}\sum_{j^{\alpha}}^{N} e^{i\vec{q}.\left(\vec{r}_i^{\alpha}-\vec{r}_j^{\alpha}\right)}$$

$$\boxed{Q(q)} = \frac{1}{N^2}\sum_{i^{\alpha}}^{N}\sum_{j^{\beta}}^{N} e^{i\vec{q}.\left(\vec{r}_i^{\alpha}-\vec{r}_j^{\beta}\right)}$$

Intra correlations : **Form factor P(q)** of objects (Mass, Size, shape, gyration radius…)

Inter correlations : **Structure factor Q(q)** (ou **S(q)**) of objects (Interactions, 2nd Virial coefficient..)

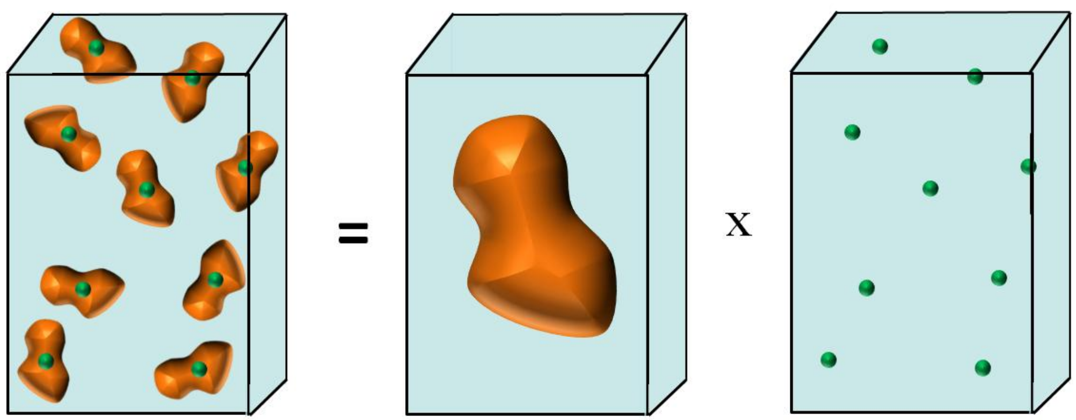
Form Factor/Structure factor



Intra correlations : **Form factor P(q)** of objects (Mass, Size, shape, gyration radius…)

Inter correlations : **Structure factor S(q)** of objects (Interactions, 2nd Virial coefficient..)

<u>For rigid centrosymmetrical objects :</u>



$$\boxed{I(q) = \Phi \Delta\rho^2 V_{obj} P(q) S(q)}$$

Outline

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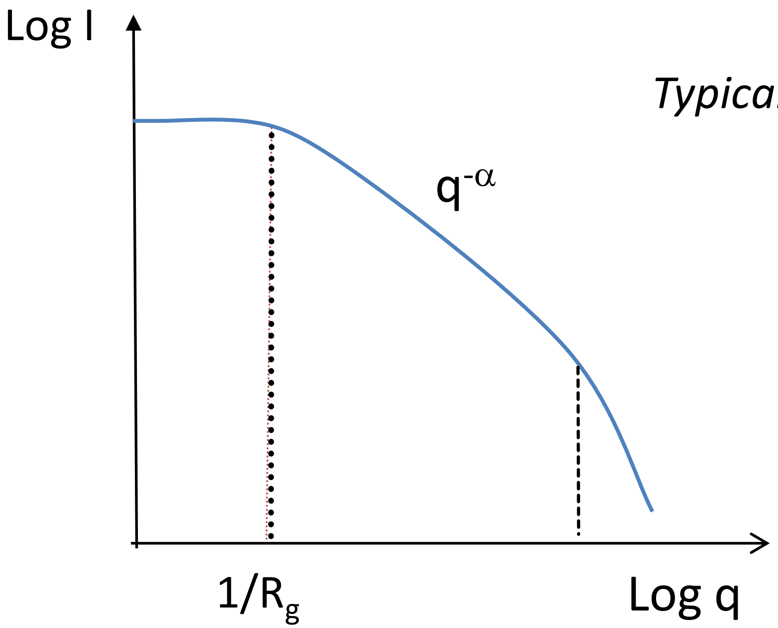
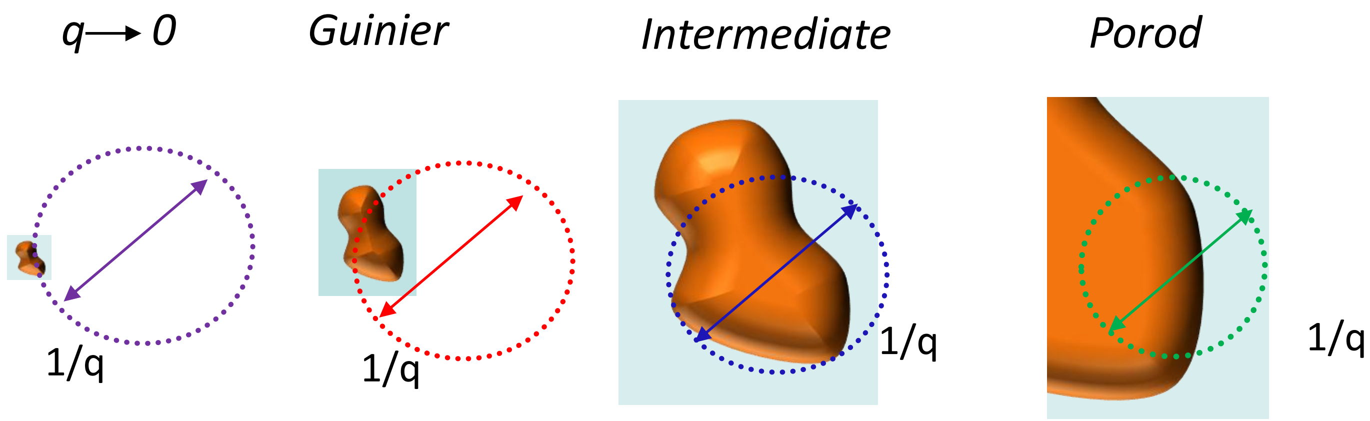
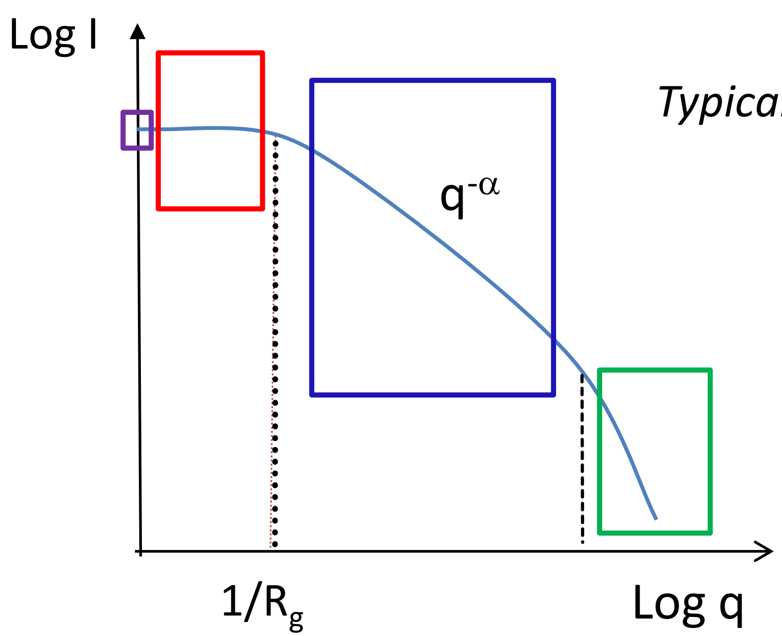
Systems of non-interacting objects : Form factor



Typical SANS spectra of non-interacting spectra…..

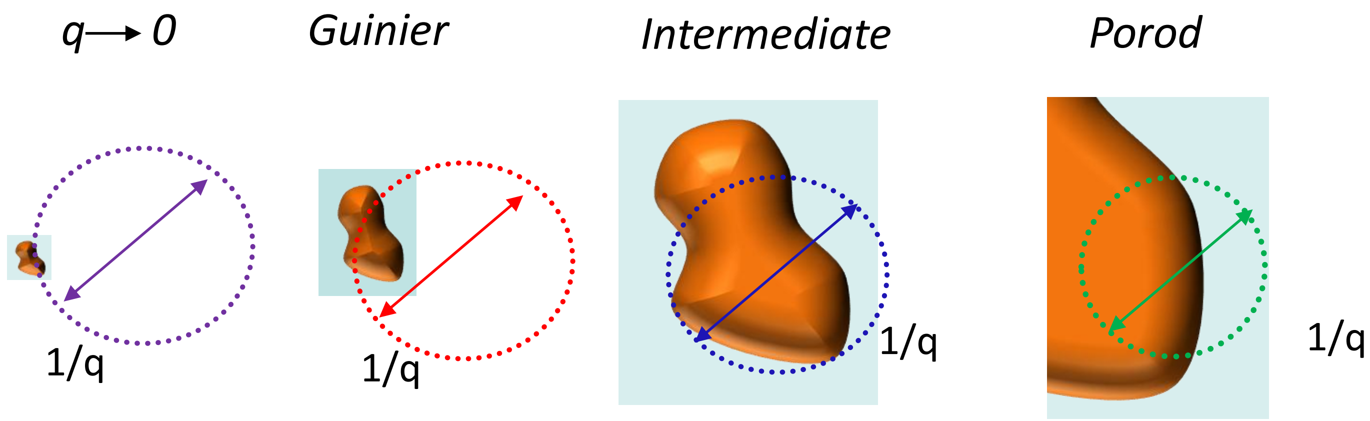
Systems of non-interacting objects : Form factor

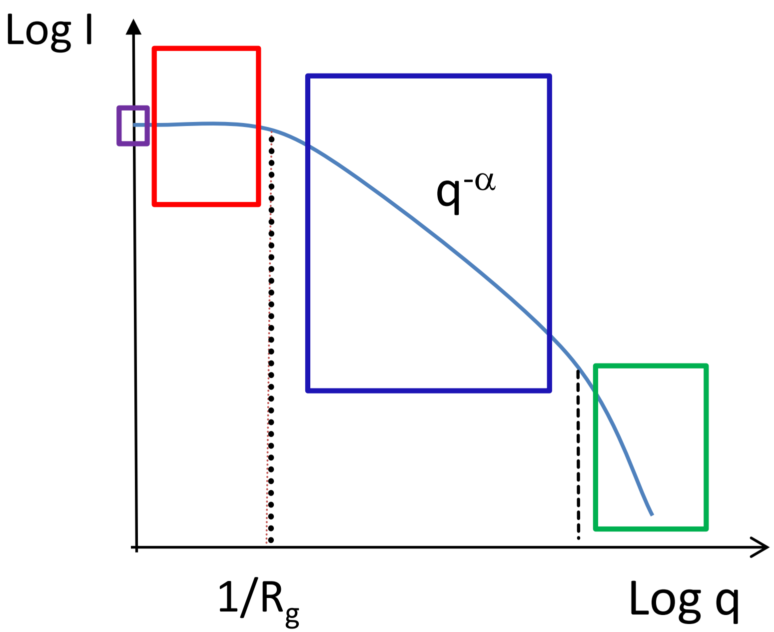




Typical SANS spectra of non-interacting spectra…..

Systems of non-interacting objects : Form factor



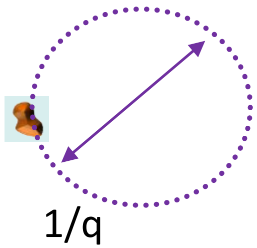


$$\Sigma(q) = \left(\rho_{obj} - \rho_{media}\right)^2 n V_{obj}{}^2 P(q)$$

with

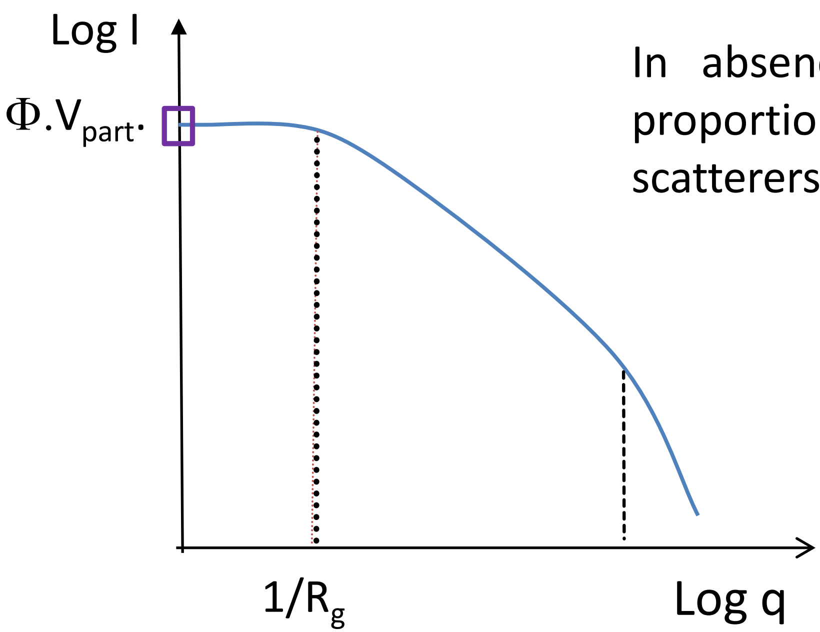
$$P(q) = \frac{1}{N^2}\sum_i^N \sum_j^N \langle e^{i\vec{q}.\vec{r}_{ij}} \rangle = \frac{1}{N^2}\sum_i^N \sum_j^N \frac{\sin(q r_{ij})}{q r_{ij}}$$

Form factor limit : $P(q)_{q->0}$



$q \rightarrow 0$, $P(q) \rightarrow 1$:

$I(q \rightarrow 0) = \mathbf{\Phi\, \Delta\rho^2\, V_{part.}} = \Phi\Delta\rho^2.M_W/d.N_A$

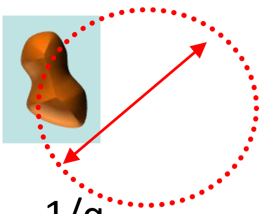


In absence of interactions, intensity at q=0 is proportional to the total number of elementary scatterers **(mass or volume)** of particles.

Systems of non-interacting objects : Form factor

Guinier Regime

$$P(q) = \frac{1}{N^2}\sum_i^N\sum_j^N \langle e^{i\vec{q}.\vec{r}_{ij}}\rangle = \frac{1}{N^2}\sum_i^N\sum_j^N \frac{\sin(qr_{ij})}{qr_{ij}}$$

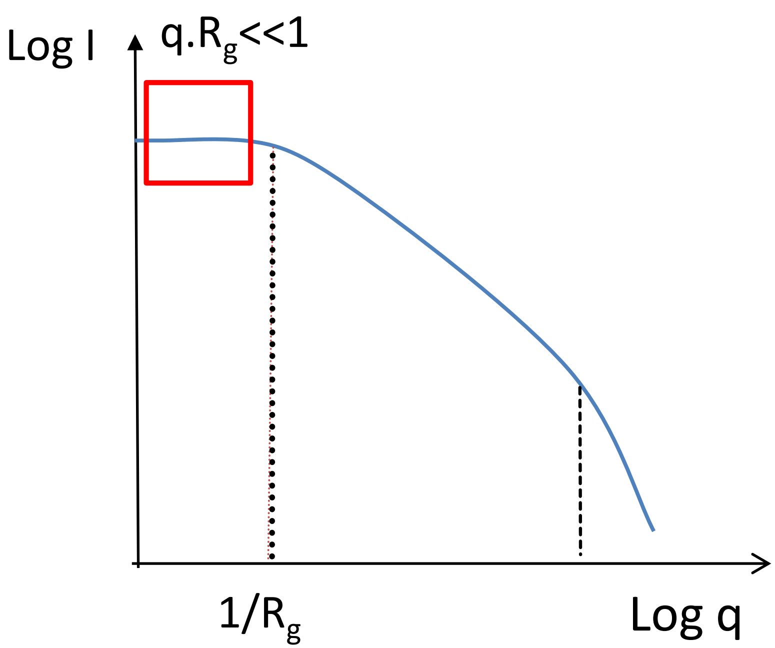


can be developped in the limit q->0 *(sin x = x – x³/3! + ox⁵)*
(i.e. when q<< 1/ largest dimension of the particle)

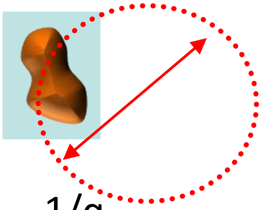
We obtain ∀ **form** the **Guinier approximation:**

$$\boxed{P_{Guinier}(q) = 1 - \frac{q^2}{3}\left[\frac{1}{2N^2}\sum_i^N\sum_j^N r_{ij}^2\right] = 1 - \frac{q^2R_g^2}{3}}$$

where R_g is the **radius of gyration of the object**



Guinier Regime



$$P(q) = \frac{1}{N^2}\sum_i^N\sum_j^N \langle e^{i\vec{q}.\vec{r}_{ij}}\rangle = \frac{1}{N^2}\sum_i^N\sum_j^N \frac{\sin(qr_{ij})}{qr_{ij}}$$

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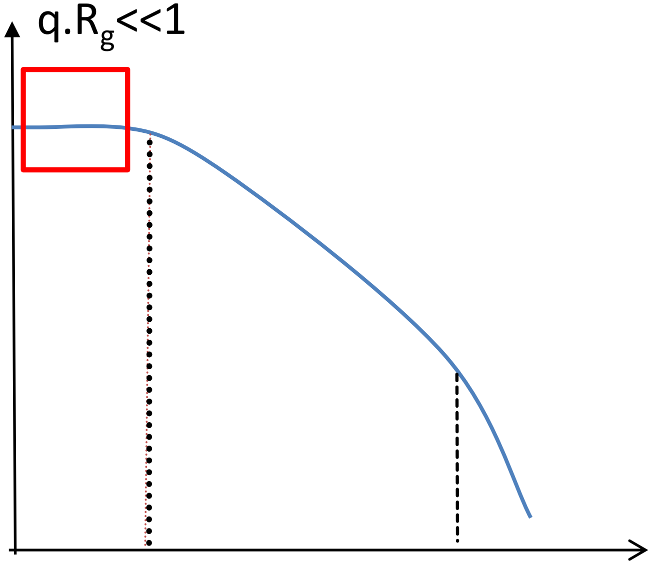
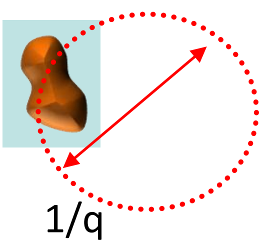
where R_g is the **radius of gyration of the object**

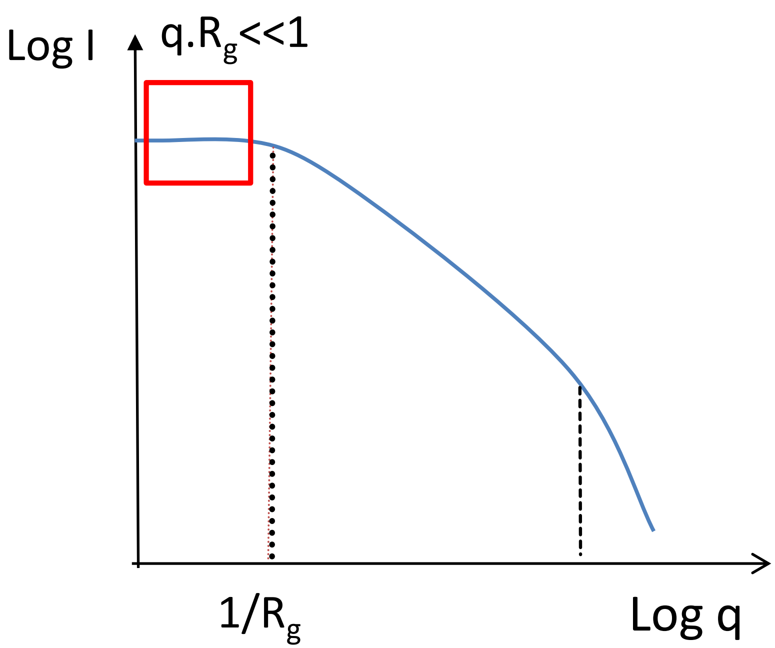


$$R_g^2 = \frac{1}{N}\sum_i^N r_i^2 = \langle r_i^2\rangle$$

R_g : size associated to the **moment of inertia of the object**($J=mR_g^2$)

Systems of non-interacting objects : Form factor





∀ **form** the **Guinier approximation:**

$$P(q) \propto \exp\left(\frac{-q^2 Rg^2}{3}\right)$$

Guinier representation :

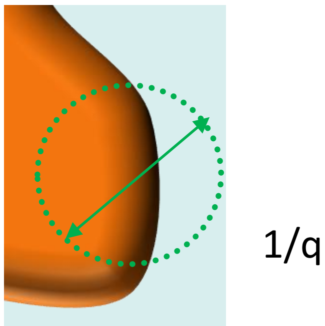
$\boxed{\textit{Ln(I(q)) versus } q^2 \text{ : slope } -R_g^2/3}$

$$R_g^2 = \frac{1}{N}\sum_i^N r_i^2 = \langle r_i^2 \rangle$$

R_g : size associated to the **moment of inertia of the object** ($J=mR_g^2$)

Systems of non-interacting objects : Form factor

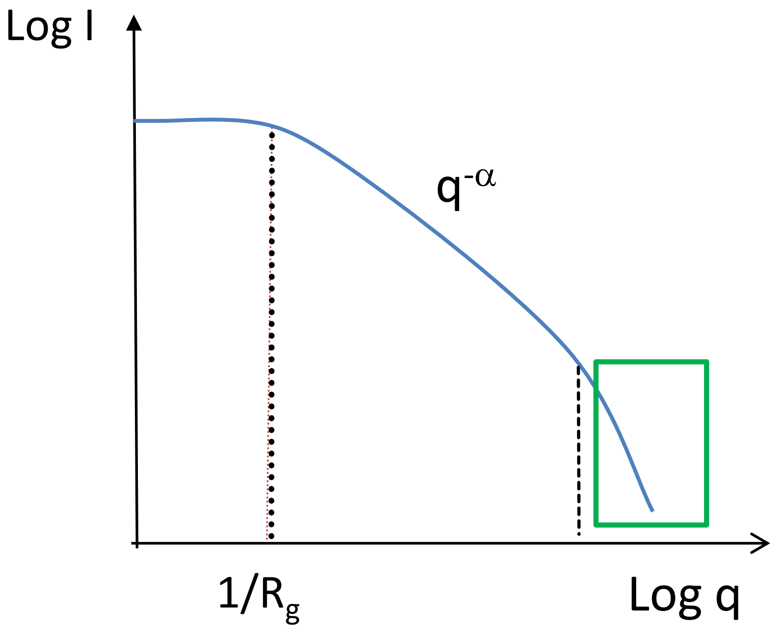
Porod regime



At high q values

the scale probed << characteristic size of scattering objects: we are looking at the **interfaces**.

When the interface between two homogeneous media is flat (abrupt), we obtain the scattering by surfaces



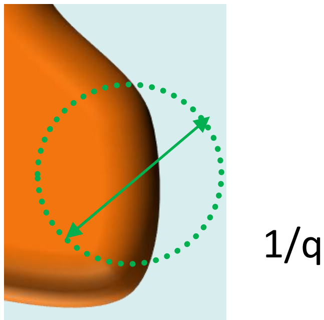
It gives the Porod's law (1951):

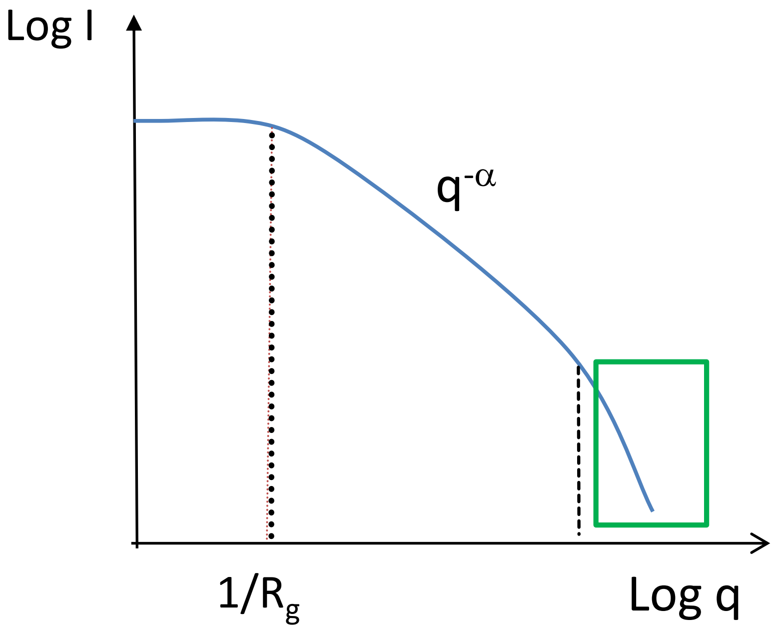
$$\boxed{\lim_{q\to\infty} I(q) = \frac{2.\pi.(\Delta\rho)^2}{q^4}\frac{S}{V}}$$

Q^{-4} is characteristic of abrupt interfaces.

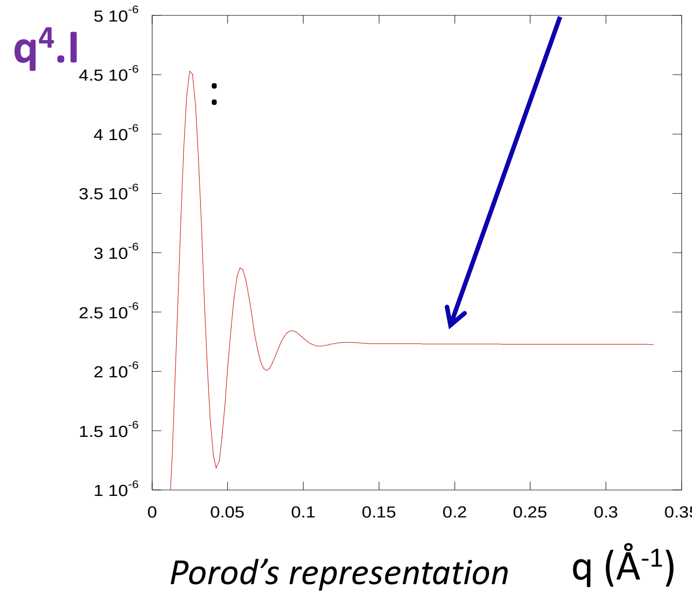
Systems of non-interacting objects : Form factor

Porod regime





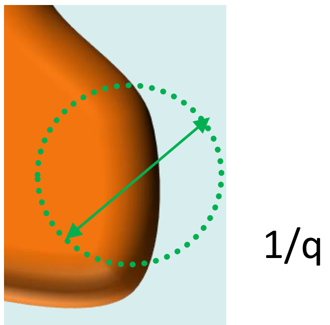
The plateau level (the Porod's constant A) is directly **proportionnal to the specific area S/V of the sample**.

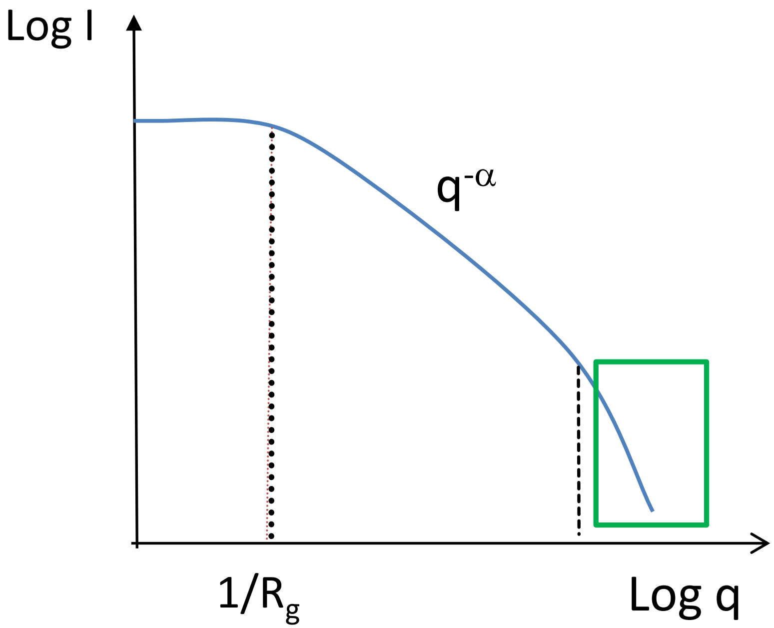


Porod's representation

Systems of non-interacting objects : Form factor

Porod regime





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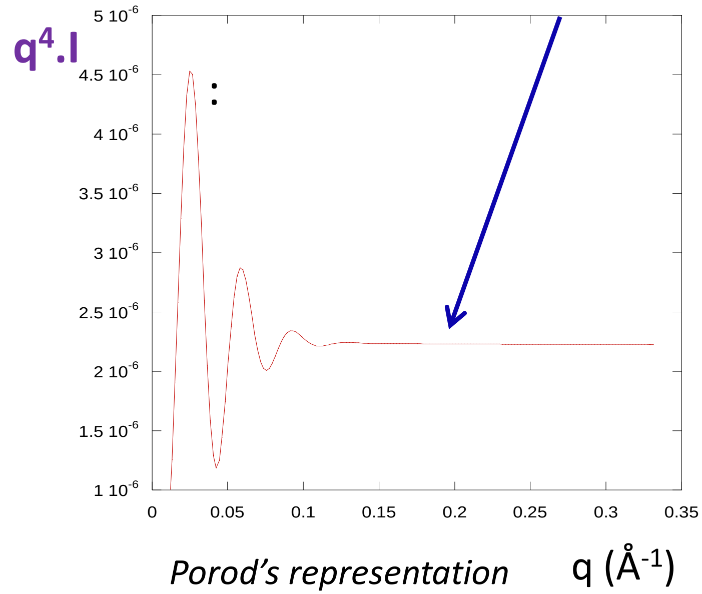


Porod's representation

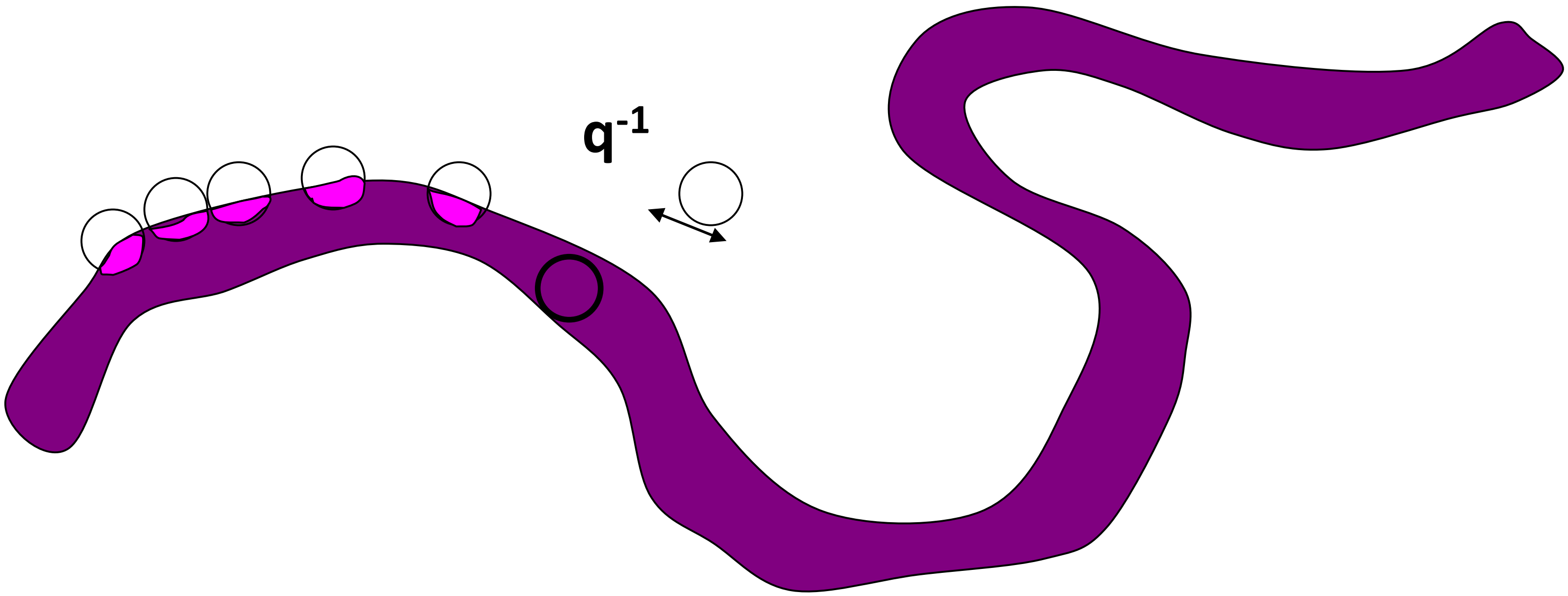
- Determination of specific area

(without any consideration of the geometry of the system).

-Deviation from the Porod's law:

roughness effects (modification of the surface) effect of interfaces curvature, measurement of adsorbed layers …

Surfaces: Porod's law



1. Full or empty spheres do not contribute at $q > 0$.

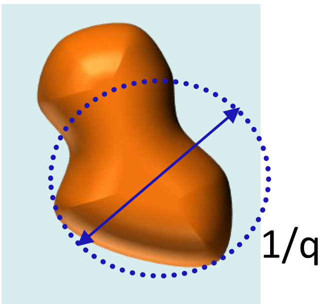
2. Number of half empty spheres = surface / $\pi R^2 \propto A\, q^2$

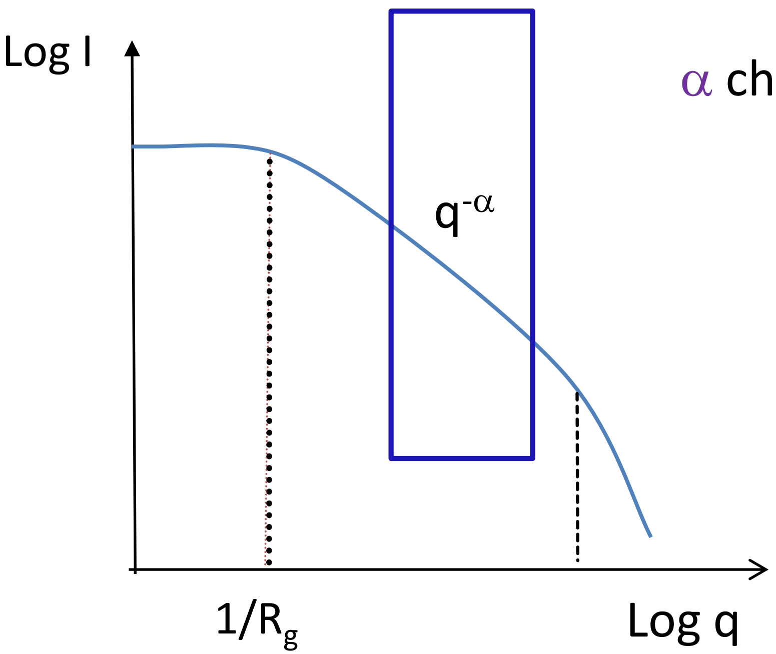
3. Each sphere on surface contributes: mass $\propto R^3 \propto q^{-3}$

=> Porod law for smooth surfaces: $I \propto$ number x mass^2

$I \propto A/q^4$ => **Specific surface S/V**

Intermediate regime



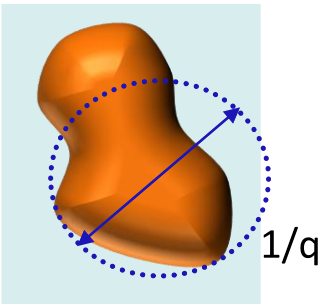


$I(q) \sim q^{-\alpha}$

α characteristic of the shape of the object

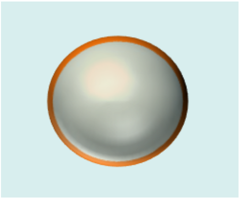
Systems of non-interacting objects : Form factor

Intermediate regime

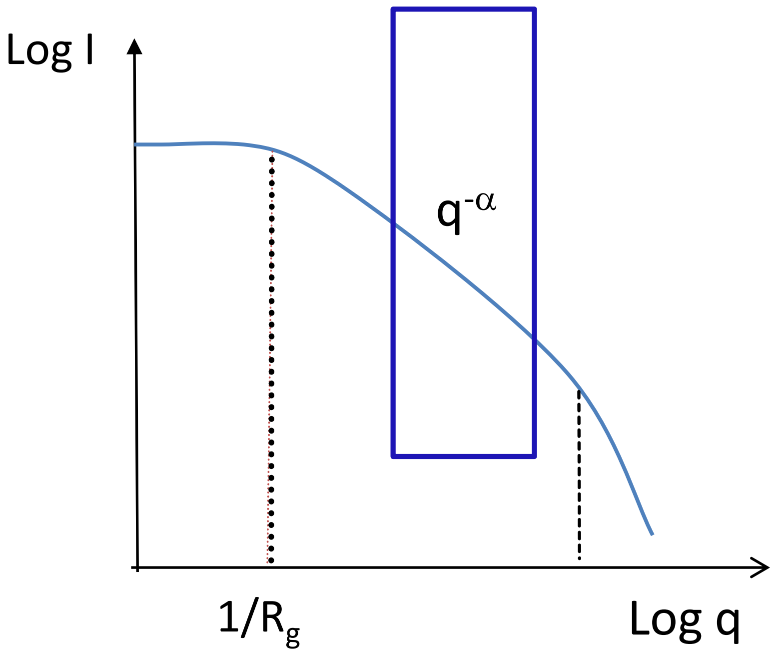


$$P(q) = \frac{1}{N^2}\sum_i^N\sum_j^N \langle e^{i\vec{q}.\vec{r}_{ij}}\rangle = \frac{1}{N^2}\sum_i^N\sum_j^N \frac{\sin(qr_{ij})}{qr_{ij}}$$

<u>Form factor of well-defined geometrical objetcs</u>

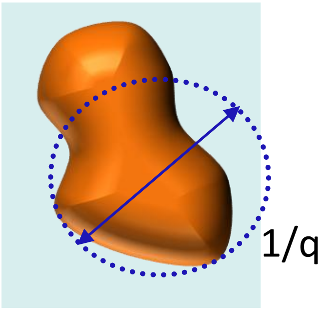


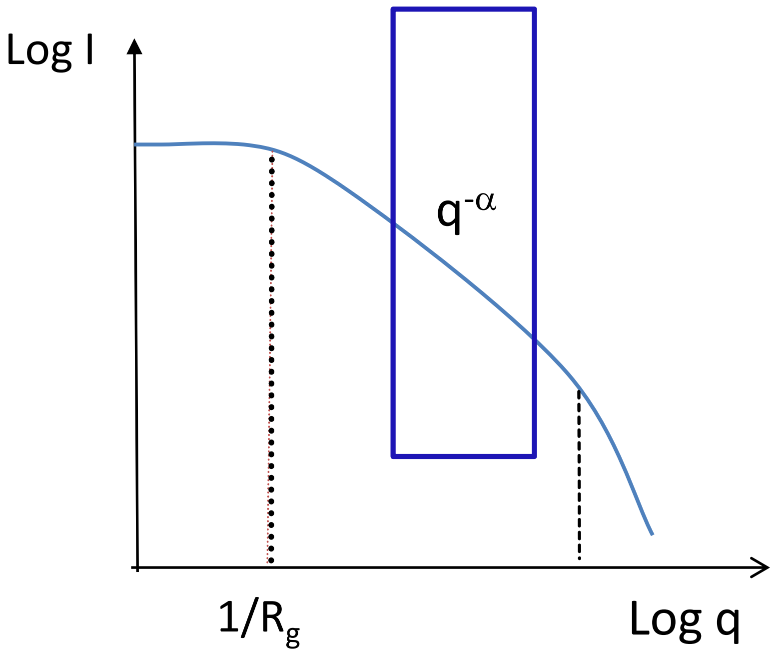
$$P_{empty\ sphere}(q) = \left[\frac{\sin(qR)}{qR}\right]^2$$



Systems of non-interacting objects : Form factor

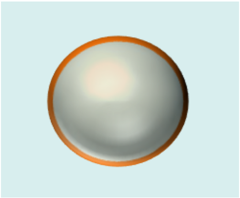
Intermediate regime



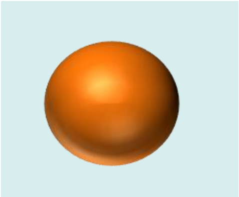


$$P(q) = \frac{1}{N^2}\sum_i^N \sum_j^N \langle e^{i\vec{q}.\vec{r}_{ij}} \rangle = \frac{1}{N^2}\sum_i^N \sum_j^N \frac{\sin(q r_{ij})}{q r_{ij}}$$

<u>*Form factor of well-defined geometrical objetcs*</u>



$$P_{empty\ sphere}(q) = \left[\frac{\sin(qR)}{qR}\right]^2$$



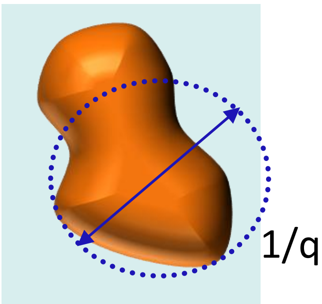
$$P_{sphere}(q) = \left[\int_0^R 4\pi r^2 \frac{\sin(qr)}{qr}\, dr\right]^2$$

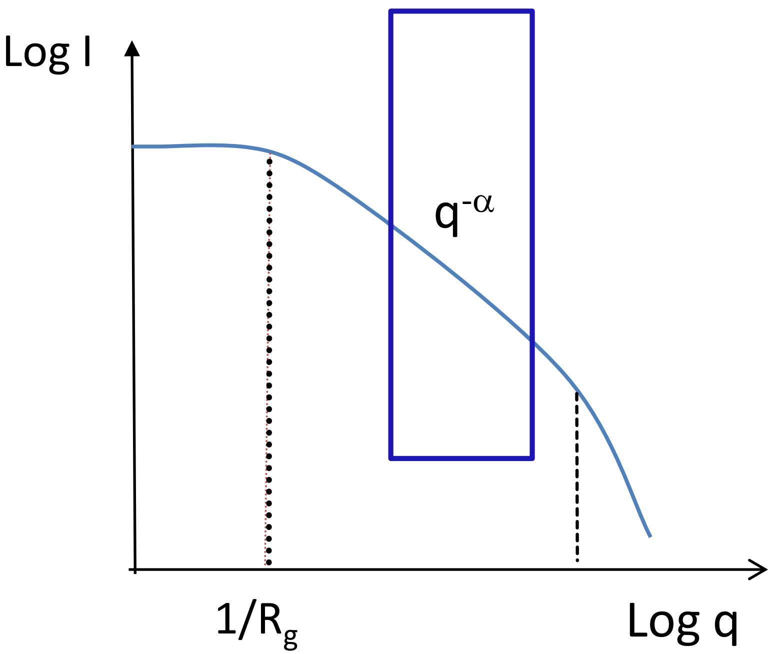
By integration :

$$\boxed{P_{sphere}(q) = \left[\frac{\sin(qR) - qR\cos(qR)}{qR^3}\right]^2}$$

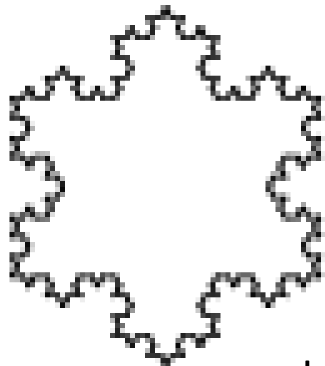
Systems of non-interacting objects : Form factor

Intermediate regime





Case of fractal objects



Self similar structure : $\forall$ scale (< R_{object}), the structure looks the same.

$$N(r) \sim M \sim r^{D_f}$$

where D_f is the fractal dimension of the object (N the number of elementary scatterer)

The pair distribution function is a probability :

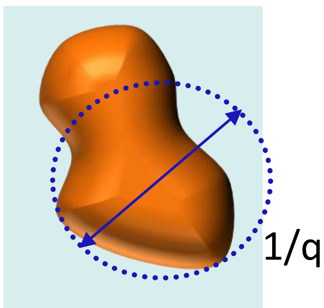
$$g(r) = \frac{N(r)}{r^d}$$

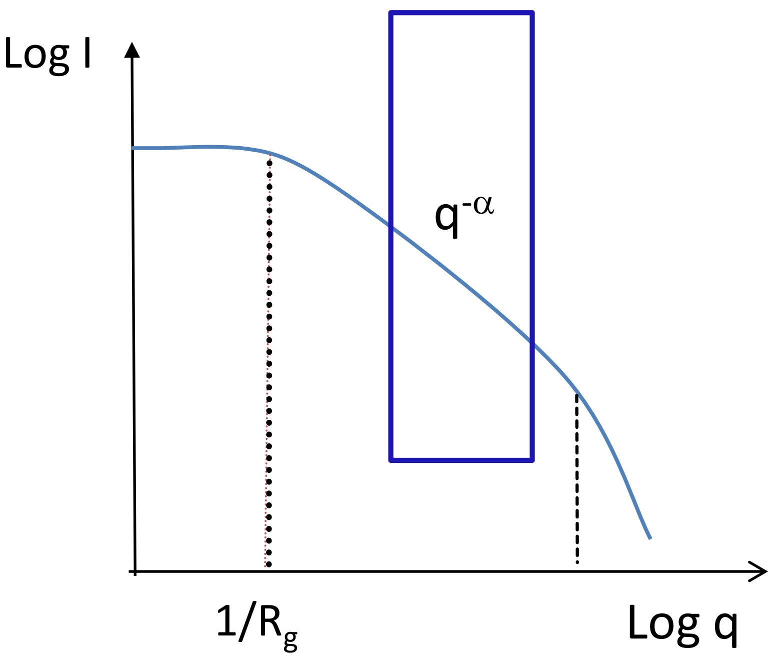
where d is the dimension space (3 in bulk)

I(q) = *F.T.* of g(r) in the space of dimension d :

$$\boxed{P(q) \sim q^{-D_f}}$$

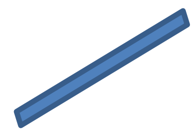
Intermediate regime



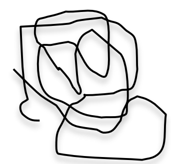


Case of fractal objects

Discs (Df = 2), $I(q) \sim q^{-2}$



Rods (Df = 1), $I(q) \sim q^{-1}$



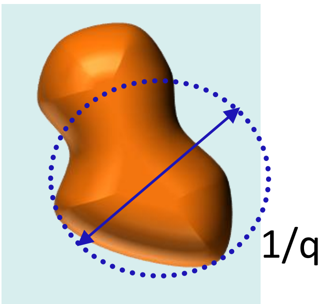
Polymers

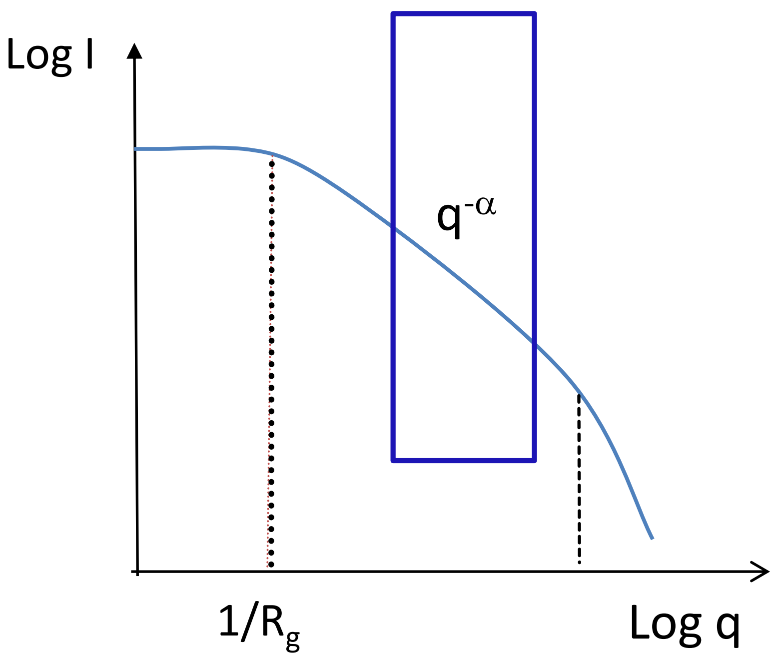
Good solvent (Df = 5/3), $I(q) \sim q^{-5/3}$

Theta solvent (Df = 2), $I(q) \sim q^{-2}$

Systems of non-interacting objects : Form factor

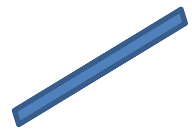
Intermediate regime



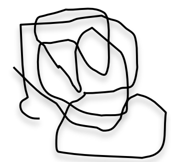


Case of fractal objects

Discs (Df = 2), $I(q) \sim q^{-2}$



Rods (Df = 1), $I(q) \sim q^{-1}$



Polymers

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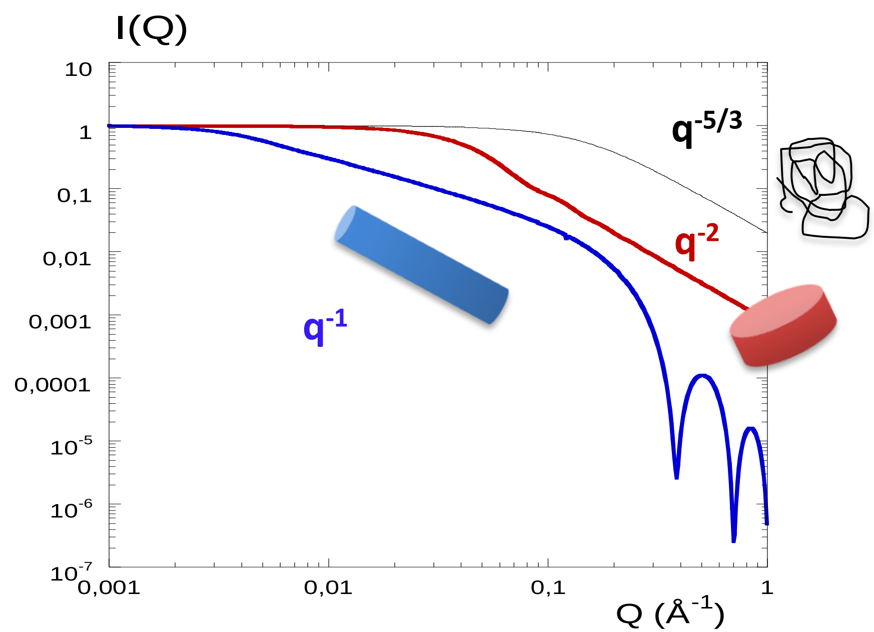
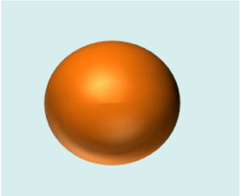
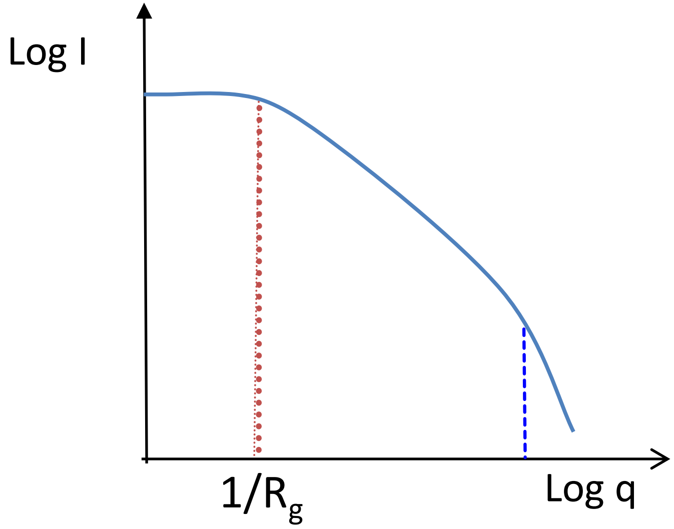


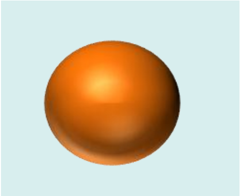
Example of measurement : Sphere



$$P_{sphere}(q, \boldsymbol{R}) = \left[3\,\frac{(\sin(qR) - qR.\cos\,(qR))}{(qR)^3}\right]^2$$



Example of measurement : Sphere



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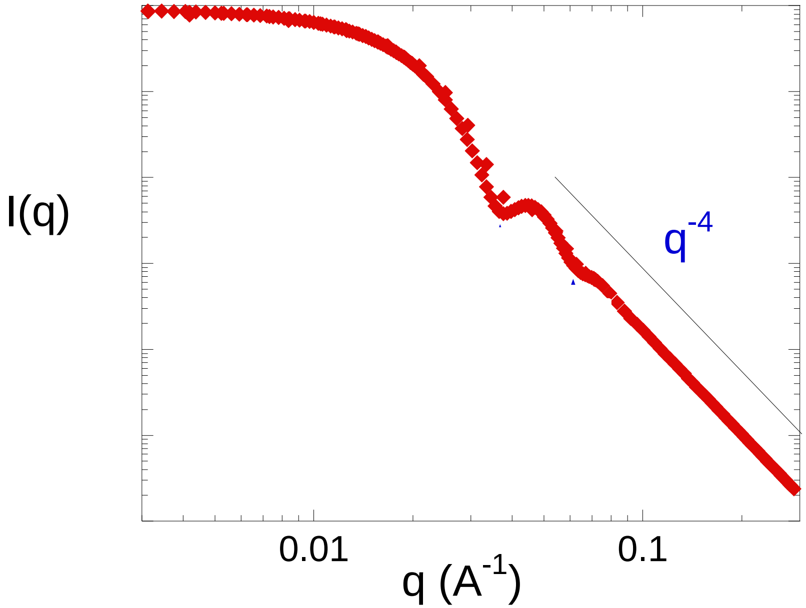
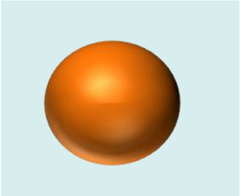


Systems of non-interacting objects : Form factor

Example of measurement : Sphere



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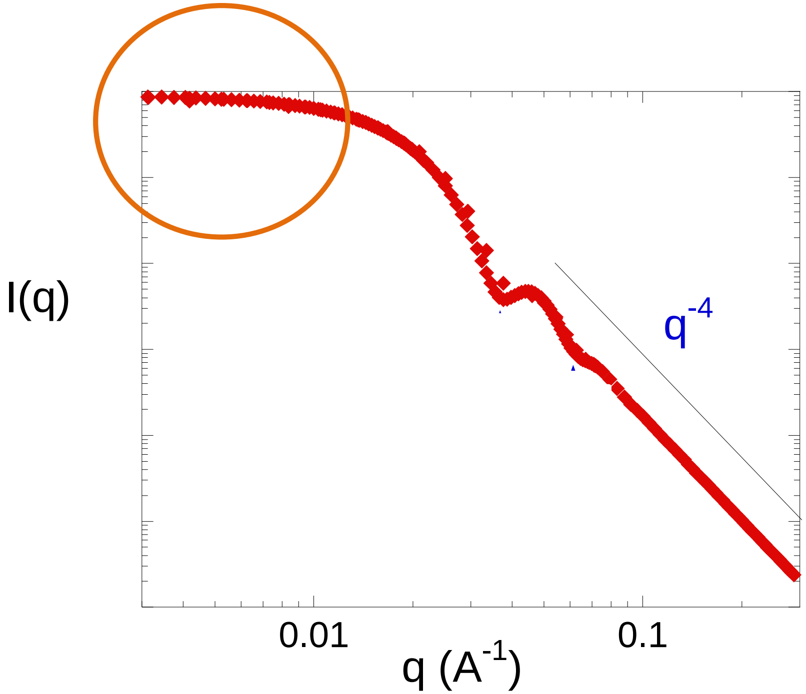
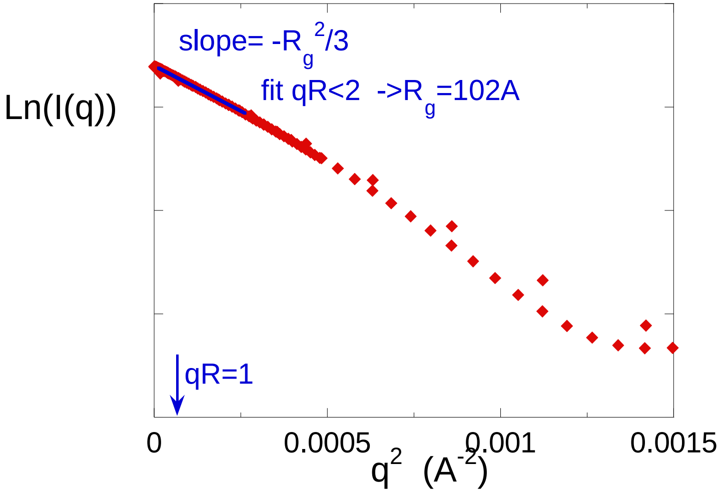


Guinier Regime

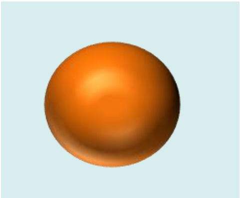
$$\underset{q.R_g \ll 1}{\mathrm{I(q)}} \sim \exp\left(-\frac{q^2 R_g^2}{3}\right)$$



$$R_g^2 = \frac{3}{5} R^2 \quad \text{for sphere}$$

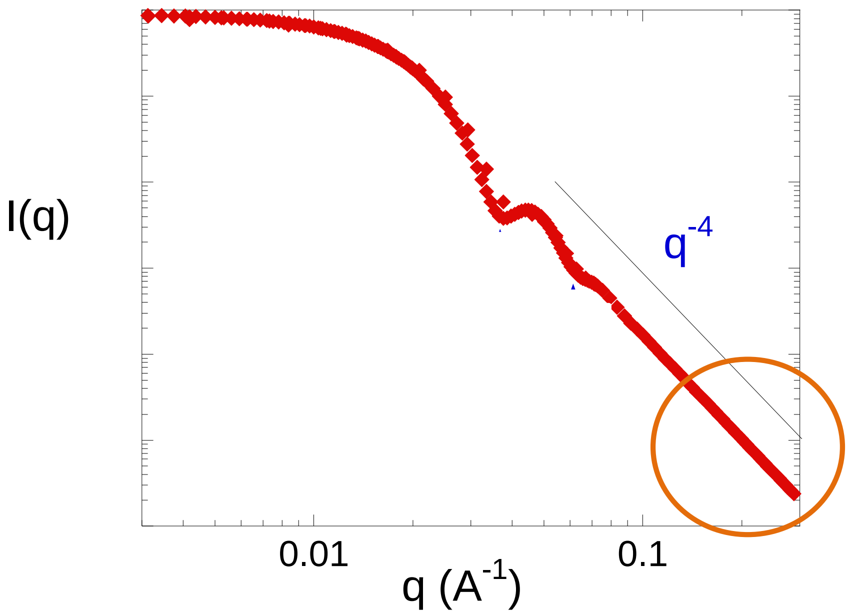
Systems of non-interacting objects : Form factor

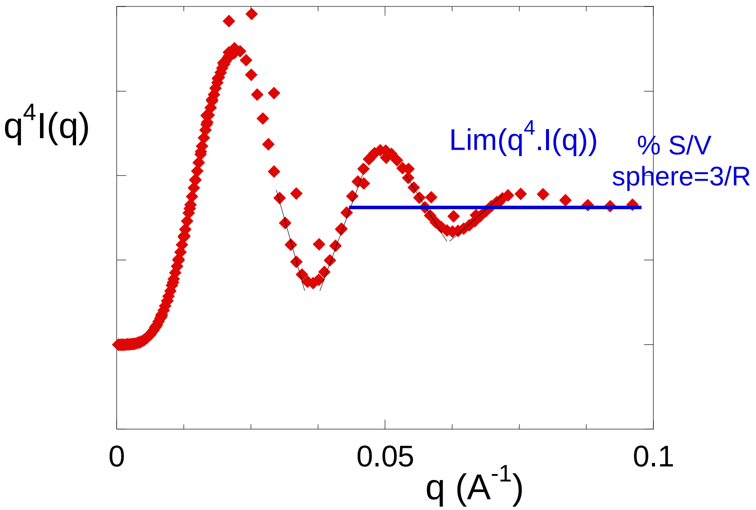
Example of measurement : Sphere



$$P_{sphere}(q, \boldsymbol{R}) = \left[3\,\frac{(\sin(qR) - qR.\cos(qR))}{(qR)^3}\right]^2$$

Porod Regime



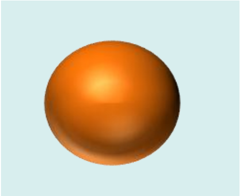


$$\lim_{q\to\infty} q^4 I(q) = 2.\pi.(\Delta\rho)^2\,\frac{S}{V}$$

3/R for sphere

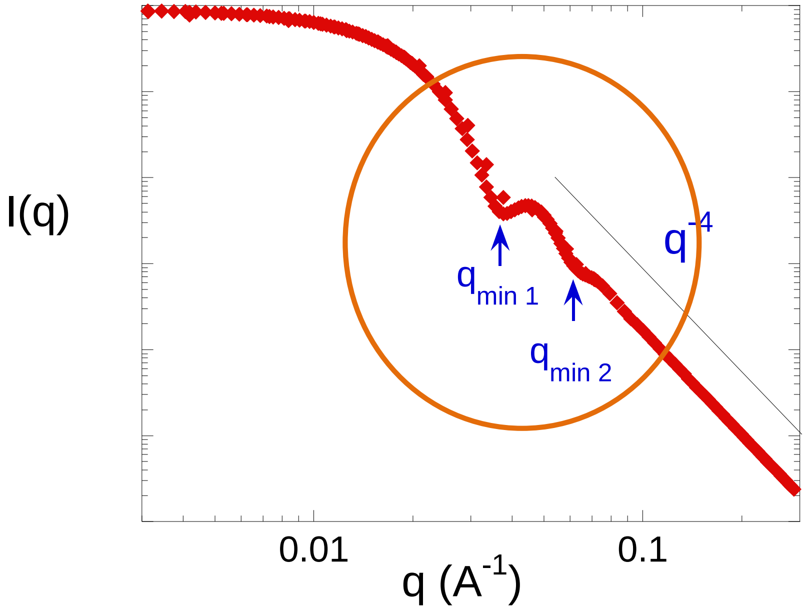
Systems of non-interacting objects : Form factor

Example of measurement : Sphere



$$P_{sphere}(q, \boldsymbol{R}) = \left[3\frac{(\sin(qR) - qR.\cos(qR))}{(qR)^3}\right]^2$$

Intermediate regime



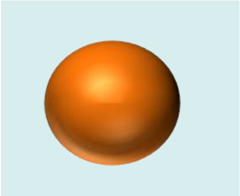
Oscillations whose q-positions is directly linked to the radius

qR = 4.47; qR = 7.70, qR..

Damped by…
- Instrumental resolution
- polydispersity

Systems of non-interacting objects : Form factor

Example of measurement : Sphere



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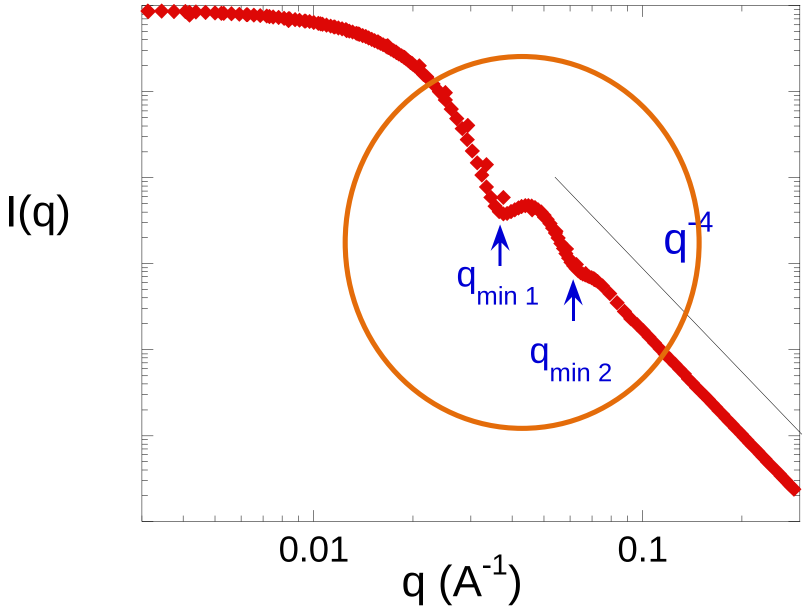
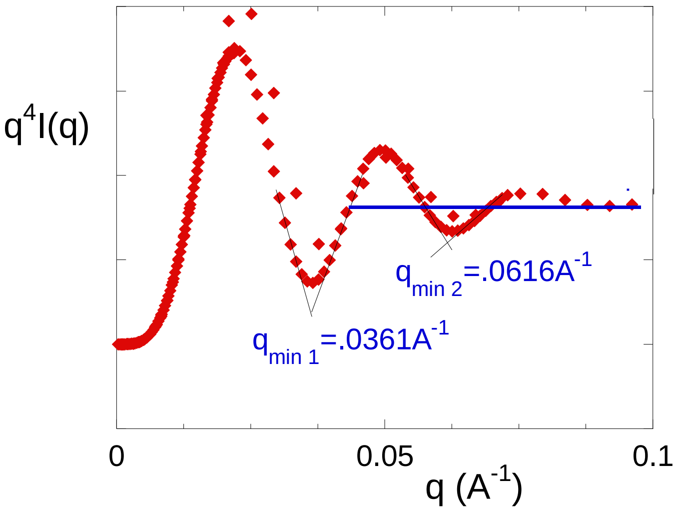
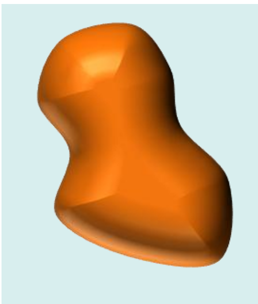
Intermediate regime





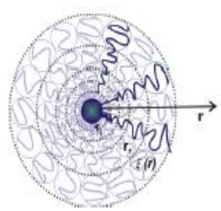
qR = 4.47; qR = 7.70, qR..

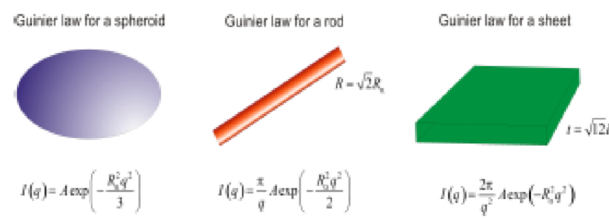
Systems of non-interacting objects : Form factor

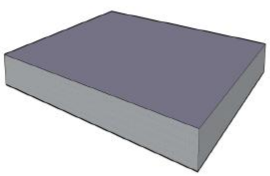


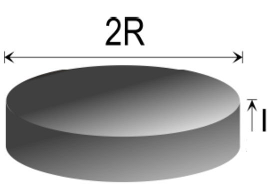
Calculation of various form factors....

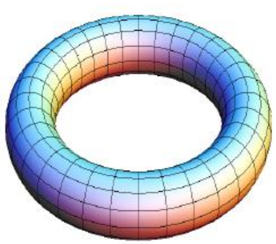
From SASFIT (https://kur.web.psi.ch/sans1/SANSSoft/sasfit.html)
Sasview (practice)

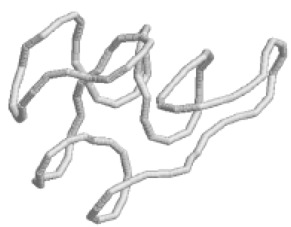


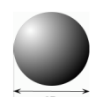


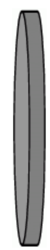


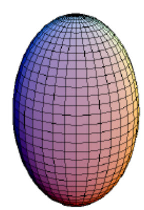


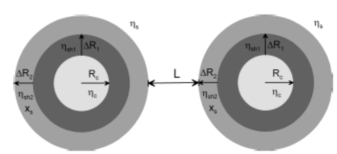








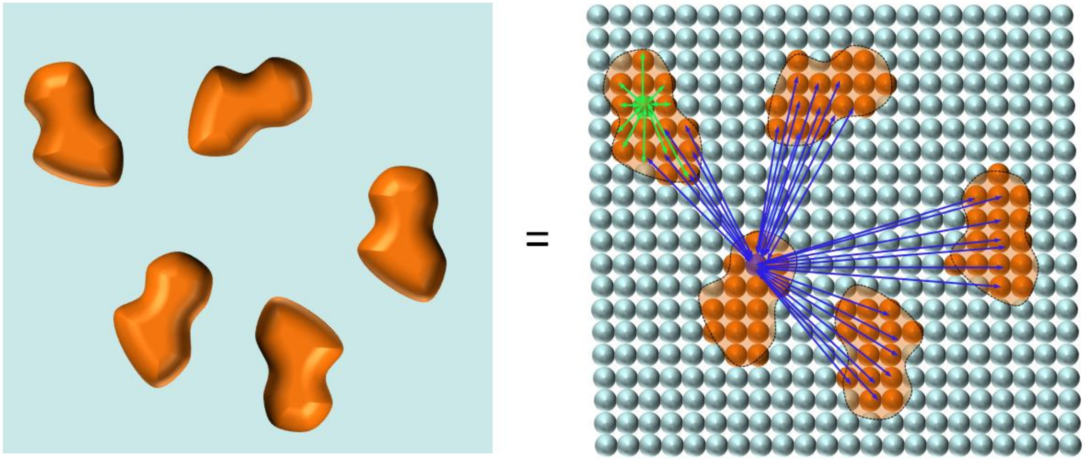




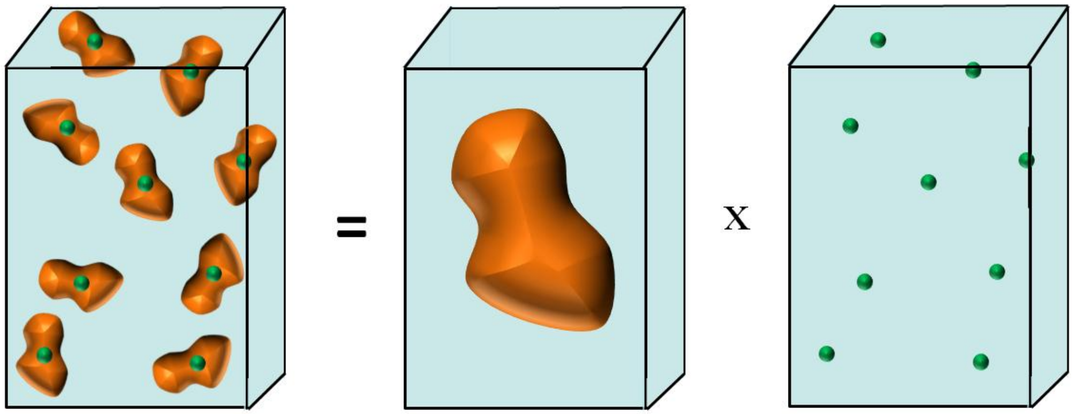
Outline

- Neutron scattering : Principles
- Scattering Length Density /Contrast variation
- Form Factor/Structure factor
- Systems of non-interacting objects : Form factor
- Interactions between objects : Structure factor
- SANS diffractometer

Form Factor/Structure factor



For rigid centrosymmetrical objects :



$$I(q) = \frac{n}{V}\,\Delta\rho^2 {V_{part}}^2 \; P(q).S(q)$$

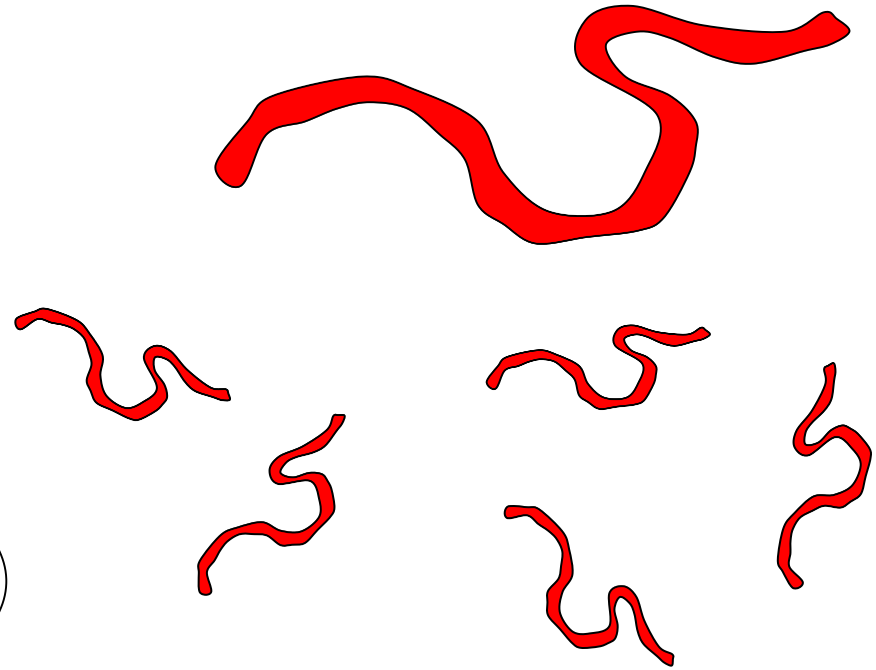
$$\Phi = \frac{n.V_{part.}}{V}$$

$$I(q) = \Phi\,\Delta\rho^2\,{V_{part}}^2 \; P(q).S(q)$$

Form and structure

Shape $\rightarrow$ Form factor P(q)

Scattering from individual objects



Structure factor S(q)

Scattering from interacting objects

What can one do ?

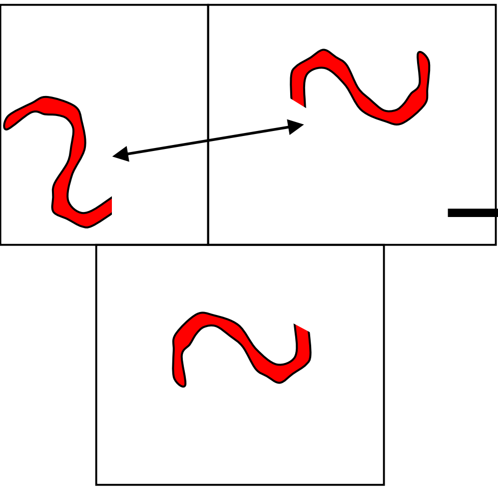
$\rightarrow$ Observe **scaling** (dilution…)

$\rightarrow$ Use simple models: I = S*P

$\rightarrow$ Use more complicated models

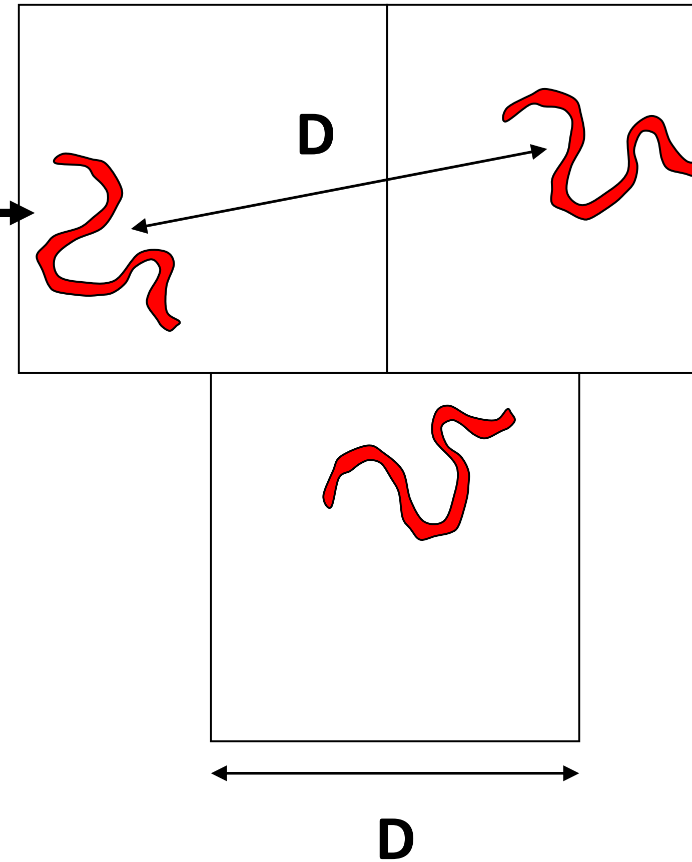
or simulations (cf. Luc Belloni)

Growth of charged objects: scaling laws



Growth of micelles

at constant concentration

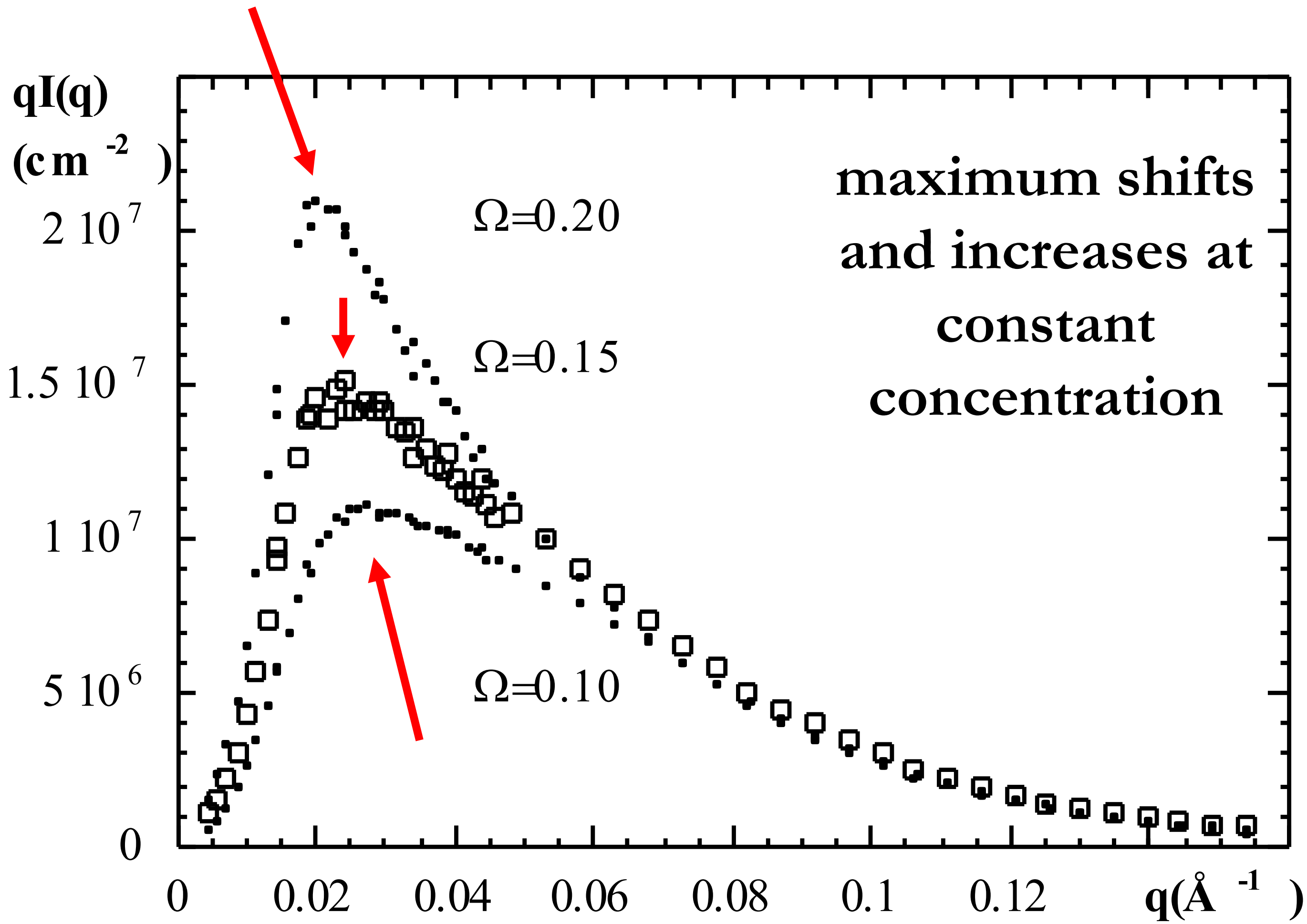


Simple cubic cell model $D^3 * \Phi = V_{object}$

Mass and average distance D increase:

- => maximum intensity ↑
- => $2\pi/D$ ↓: approximate position of correlation peak

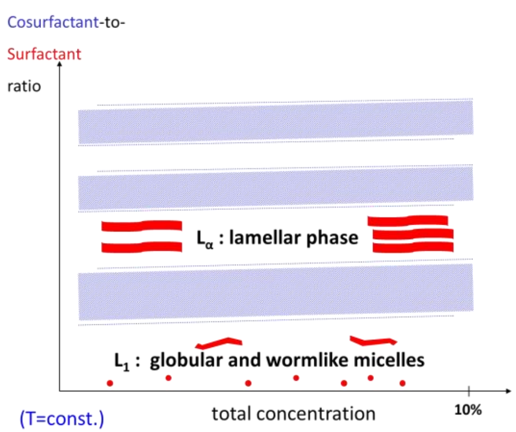
Growth of charged objects: scaling laws



Check growth:

Cubic model

$$D^3 * \Phi = V_{object}$$



Ω is the mixing ratio between cosurfactant and surfactant

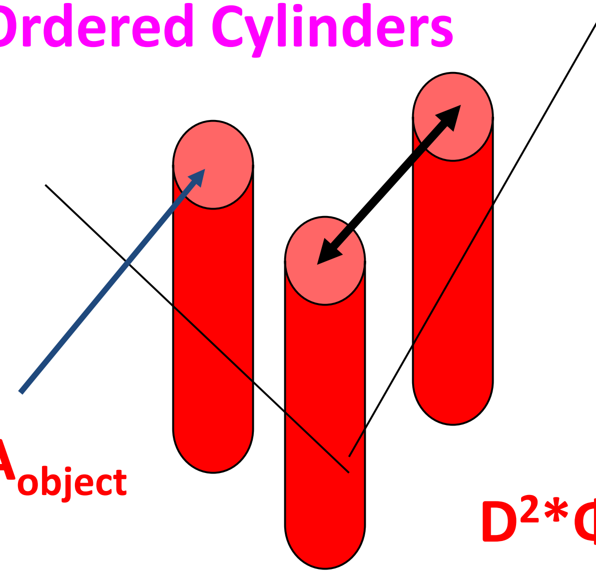
Interactions in practice: dilution laws

Globular objects

Conc.

Cubic model: $D^3 * \Phi = V_{object}$

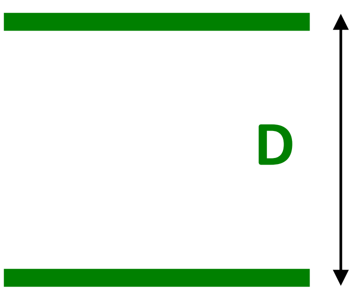
Ordered Cylinders



A_{object}

$D^2 * \Phi = A_{object}$

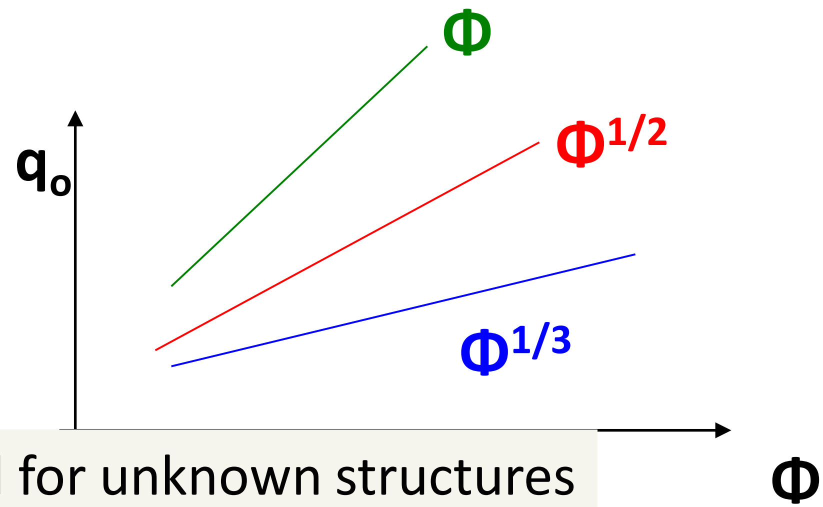
Flat bilayers



D

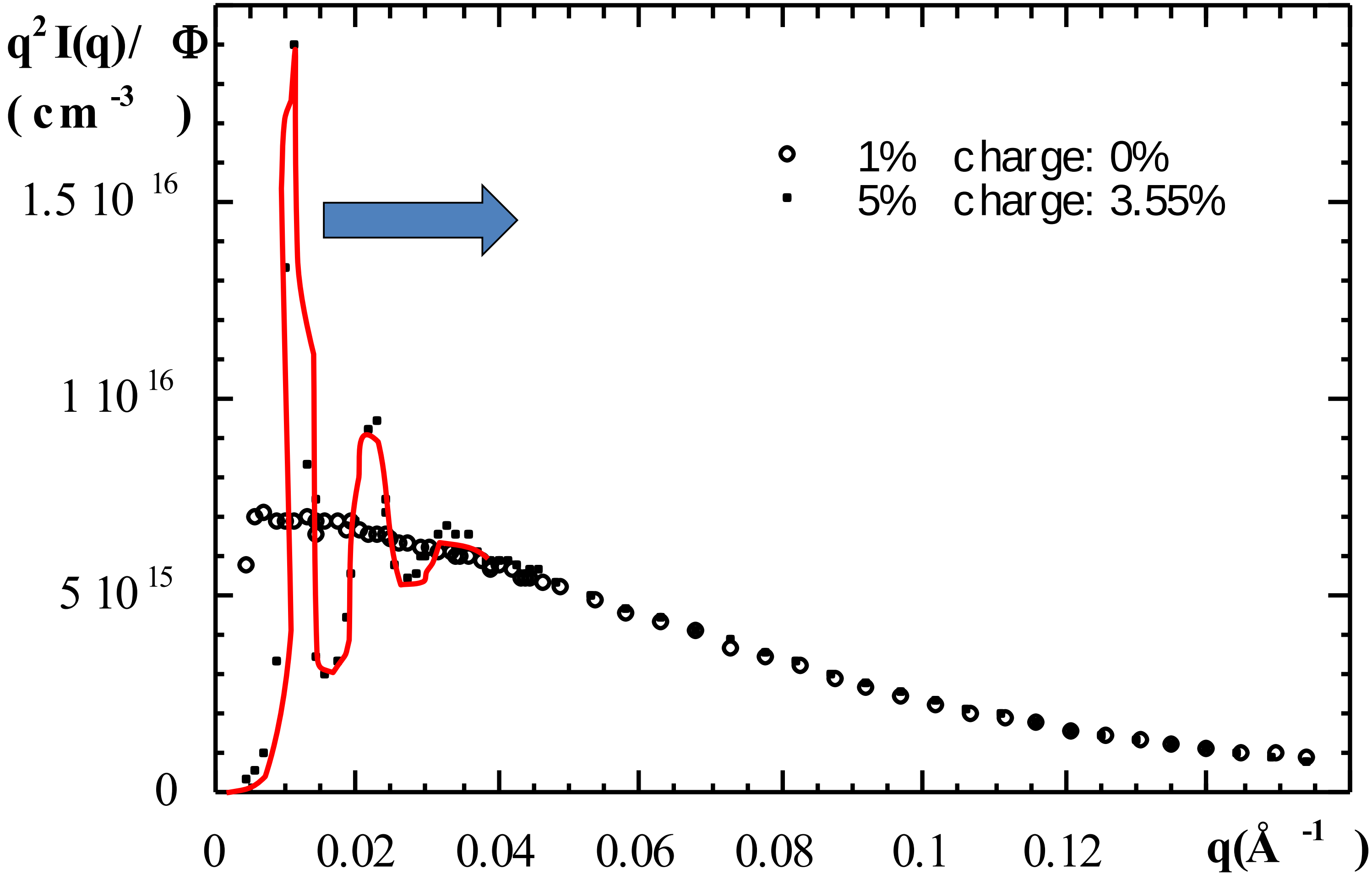
δ

$D * \Phi = \delta$



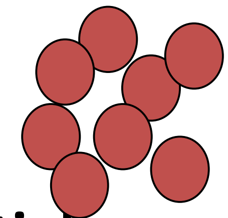
Dilution laws: very useful for unknown structures
(cf. microemulsions)

Lamellar phase: correlation + dilution law



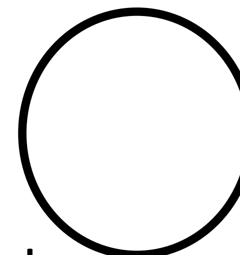
Lamellar phase: correlation + dilution law

TAKE HOME MESSAGE:

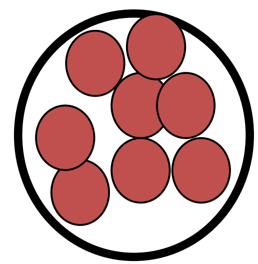


- Structure may give an estimate of **dry mass/volume:**

- **Form factor** (e.g. Guinier) may give an idea of the **spatial extent** ('wet size'):



The **ratio** can give you the hydration, or the internal volume fraction, or compacity:



0 0.05 0.1 0.15 0.2 0.25 0.3 Φ

Summary Part 2 : Scattering

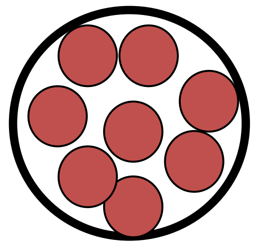
Shape = Form Factor = mass distribution

I

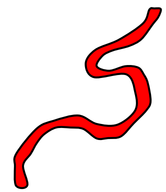
q^{-1}

You will find different aspects of this approach in other lectures:

- **Aggregates**



- **Polymers**

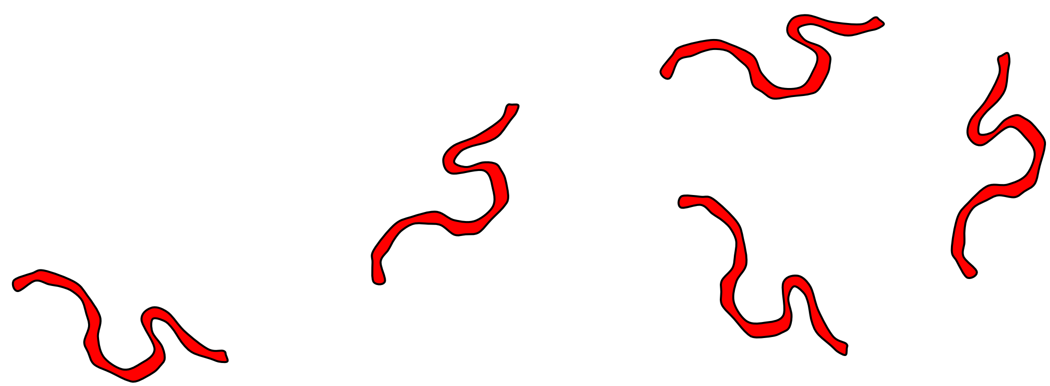


- etc…

q

Interactions = Structure Factor

1. Check scaling (dilution)
2. First *understand* data
3. Then do modelling:

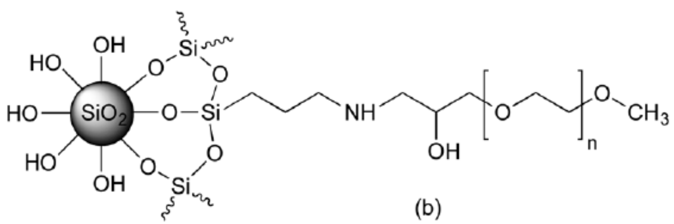


I = P(q) S(q) etc… warning: for monodisperse spherical objects only!

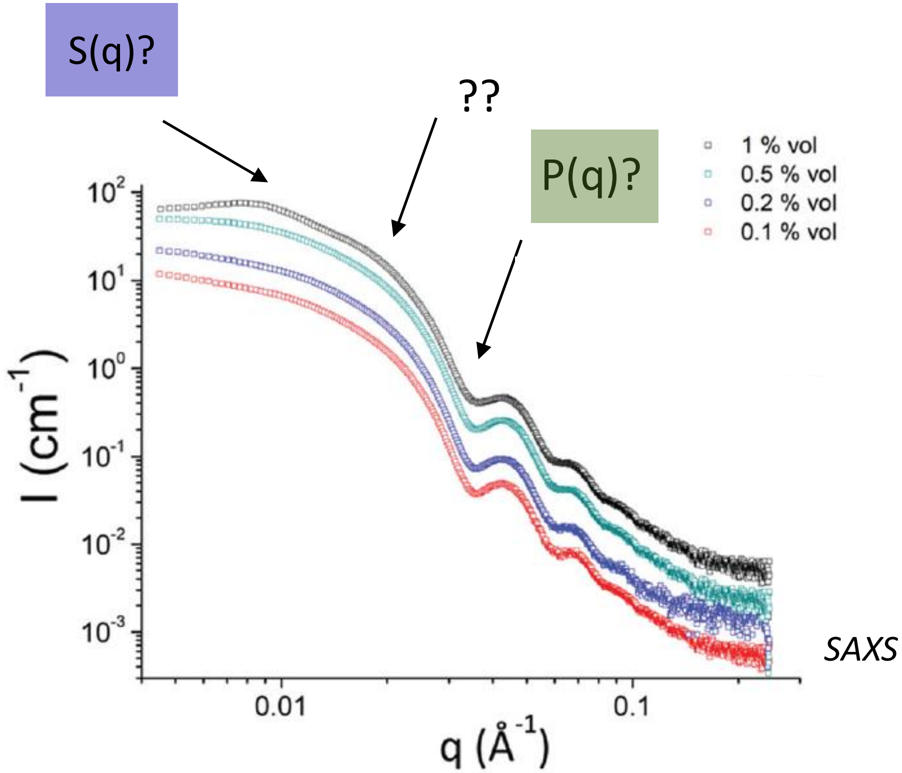
How to obtain the structure factor ?

$$I(q) = \Phi\, \Delta\rho^2\, V_{part}^{\ 2}\ P(q).S(q)$$

Silica nanospheres grafted by PEG



(b)



S. Issa *et al*, Soft Matter, **2021**, *17*, 6552-6565

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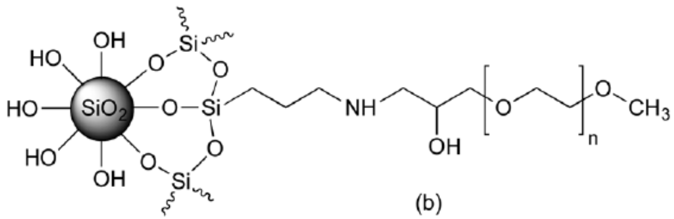

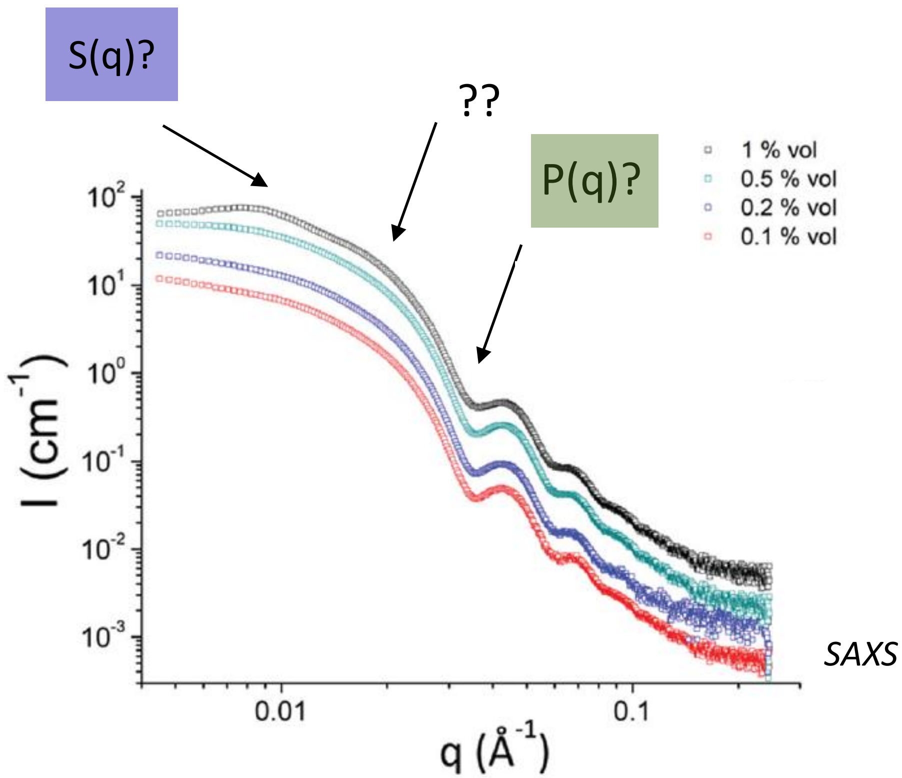

- Measurement in a system *without interactions*
- Dilution of the system (extrapolation to zero concentration)
- *Kill* the interactions, by adding salt for instance (more risky!)

S. Issa *et al*, Soft Matter, **2021**, *17*, 6552-6565

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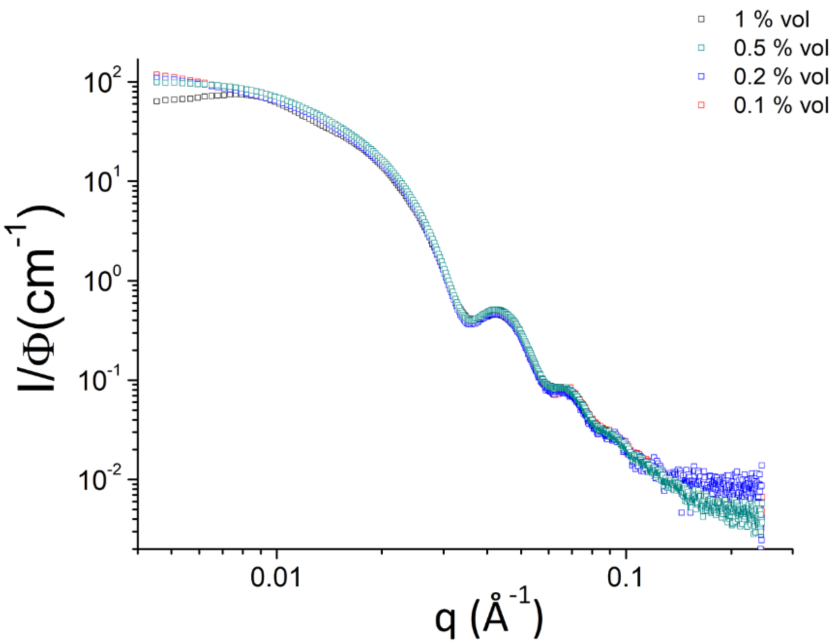

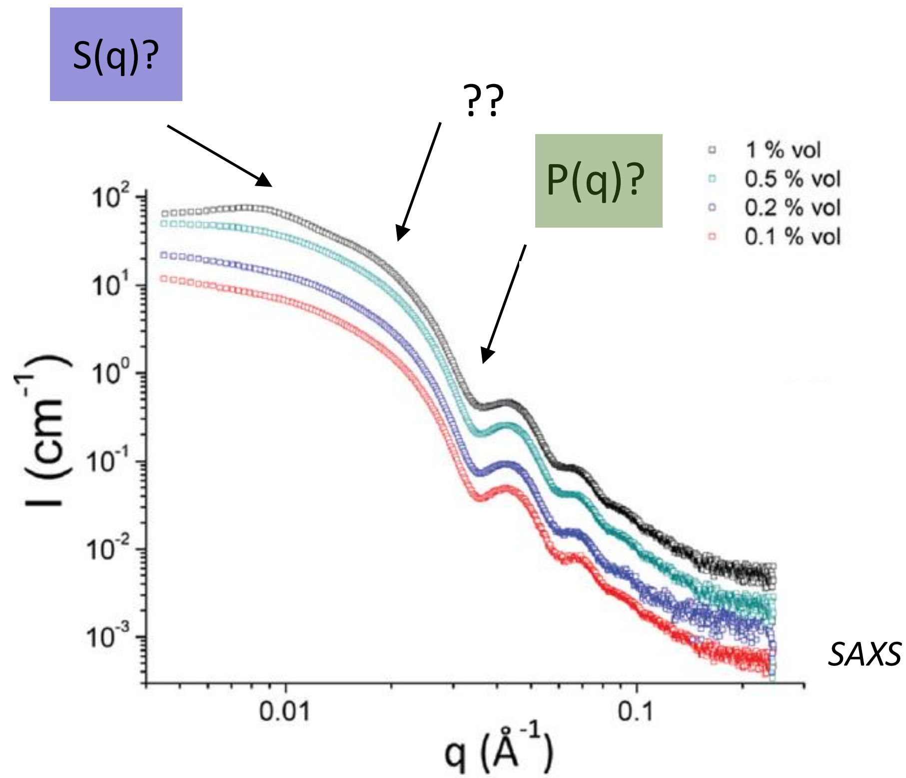

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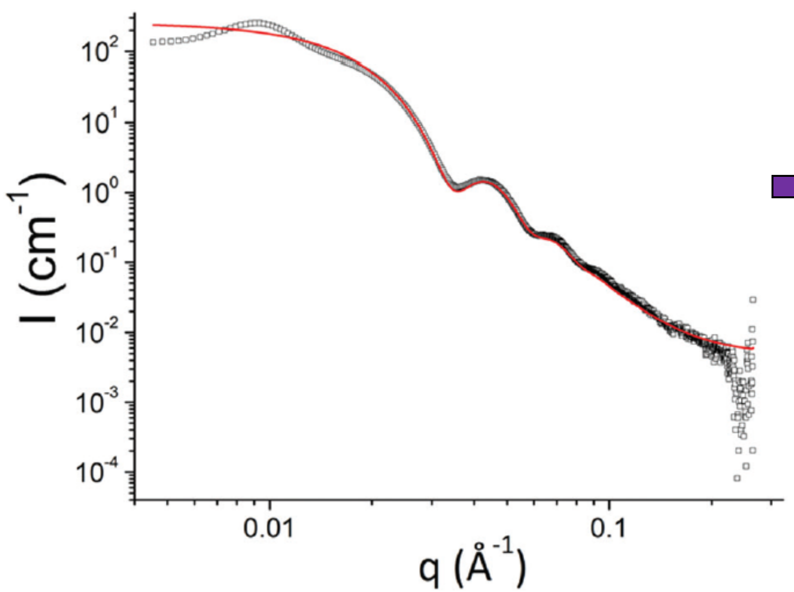

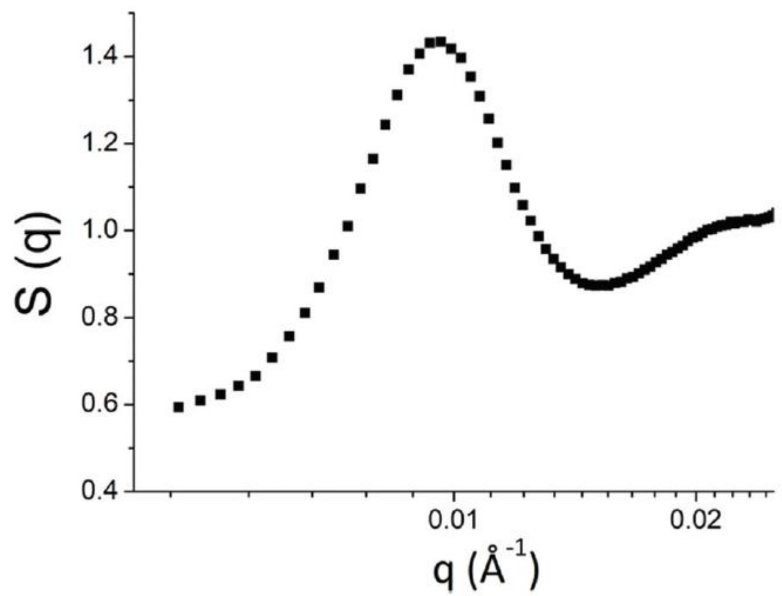

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S. Issa *et al*, Soft Matter, **2021**, *17*, 6552-6565

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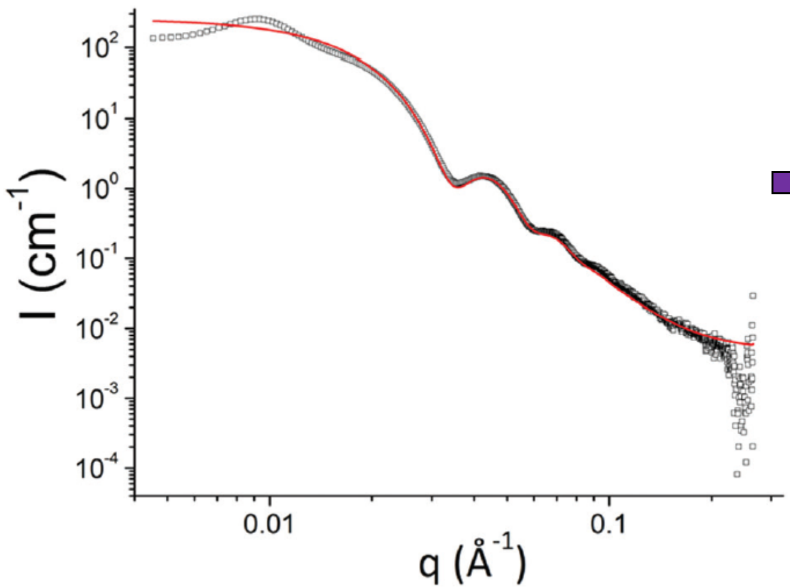
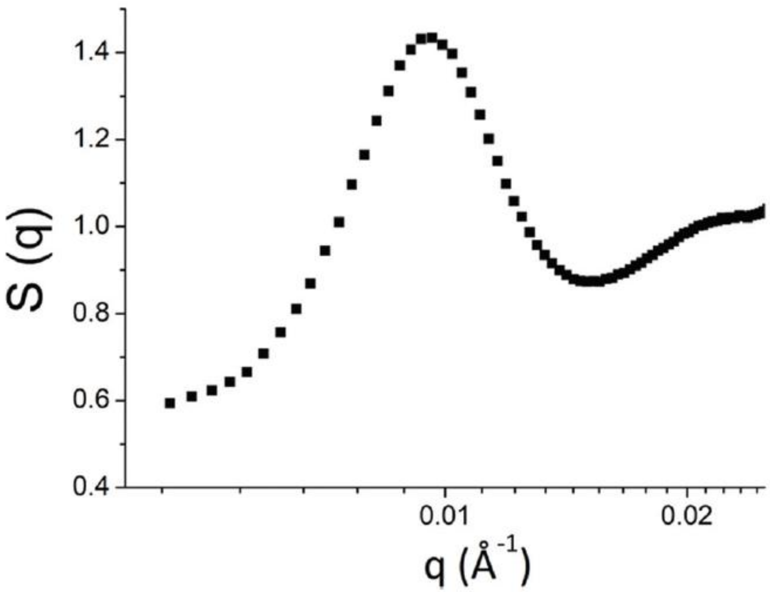


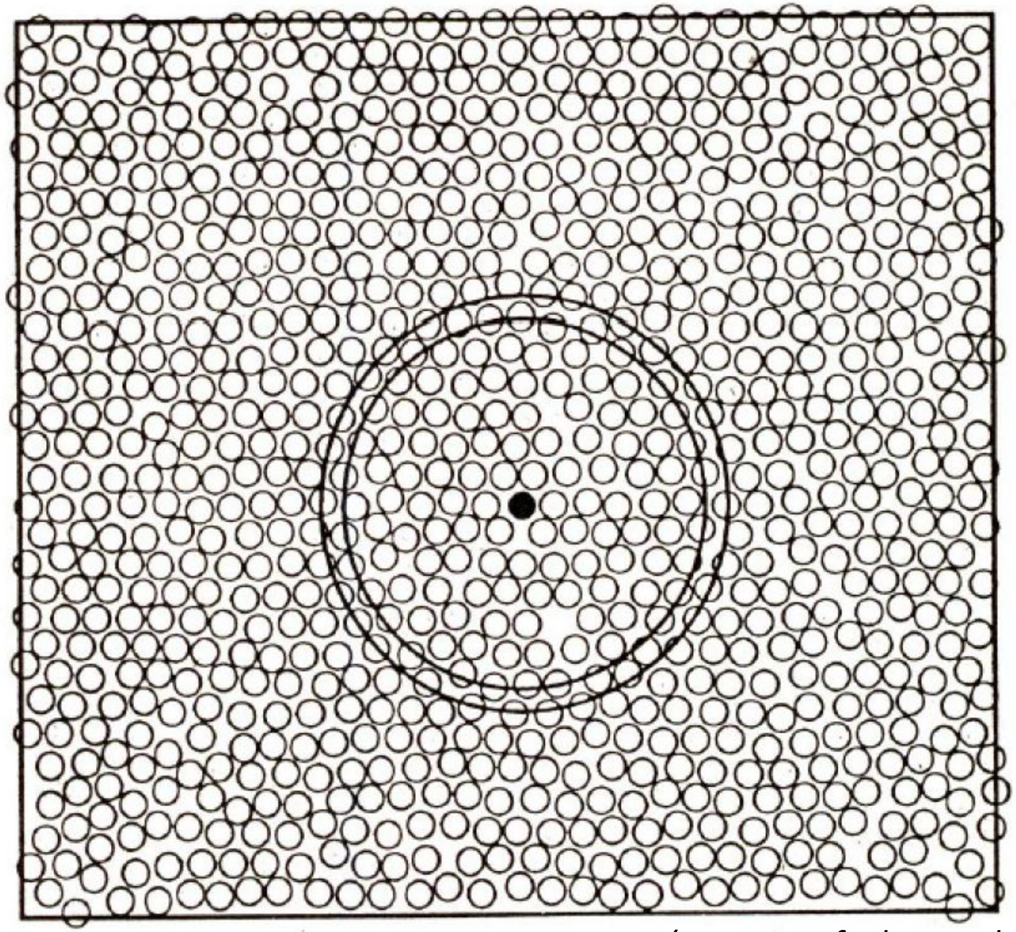


P(q) : usually plotted in log-log

S(q) : usually plotted in lin-lin

S. Issa *et al*, Soft Matter, **2021**, *17,* 6552-6565

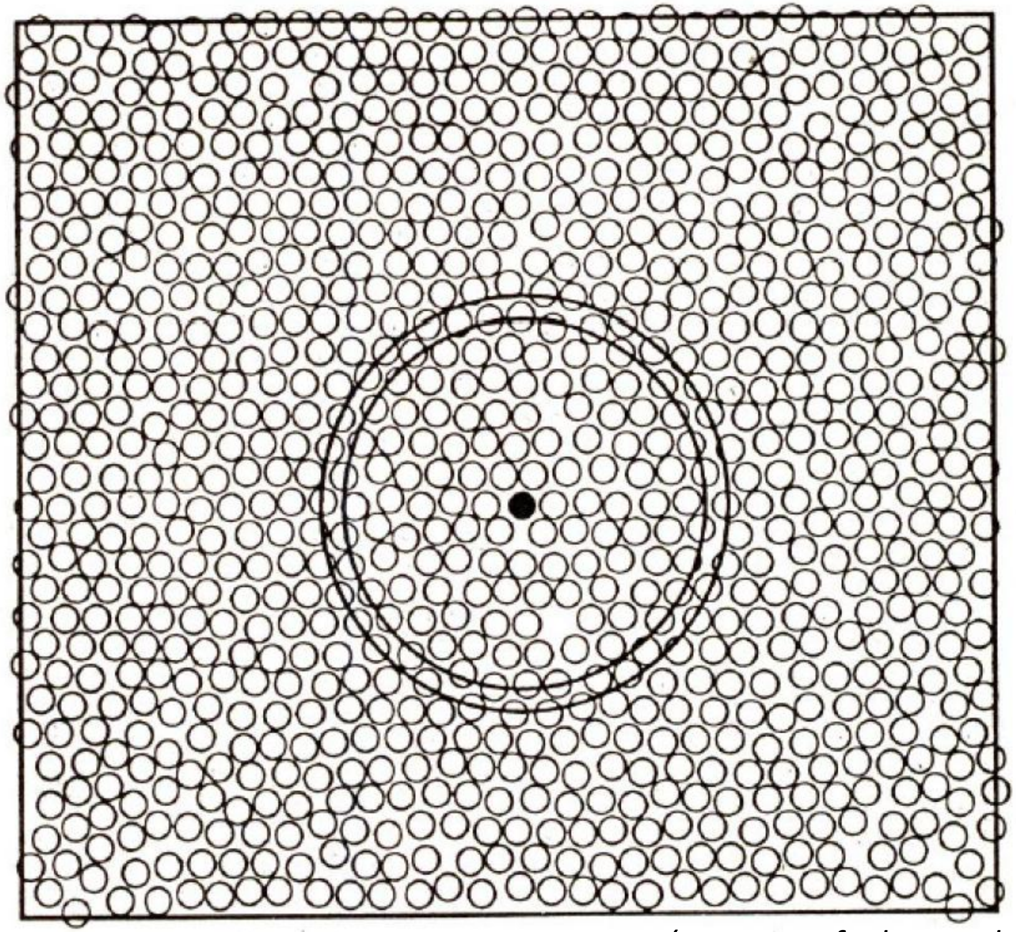
Link between S(q) and correlation function *g(r)*



(courtesy of a lecture by J.S. Pedersen)

g(r) : Average of the normalized density of objects in a shell [r, r+dr] from the center of a particle

Link between S(q) and correlation function *g(r)*

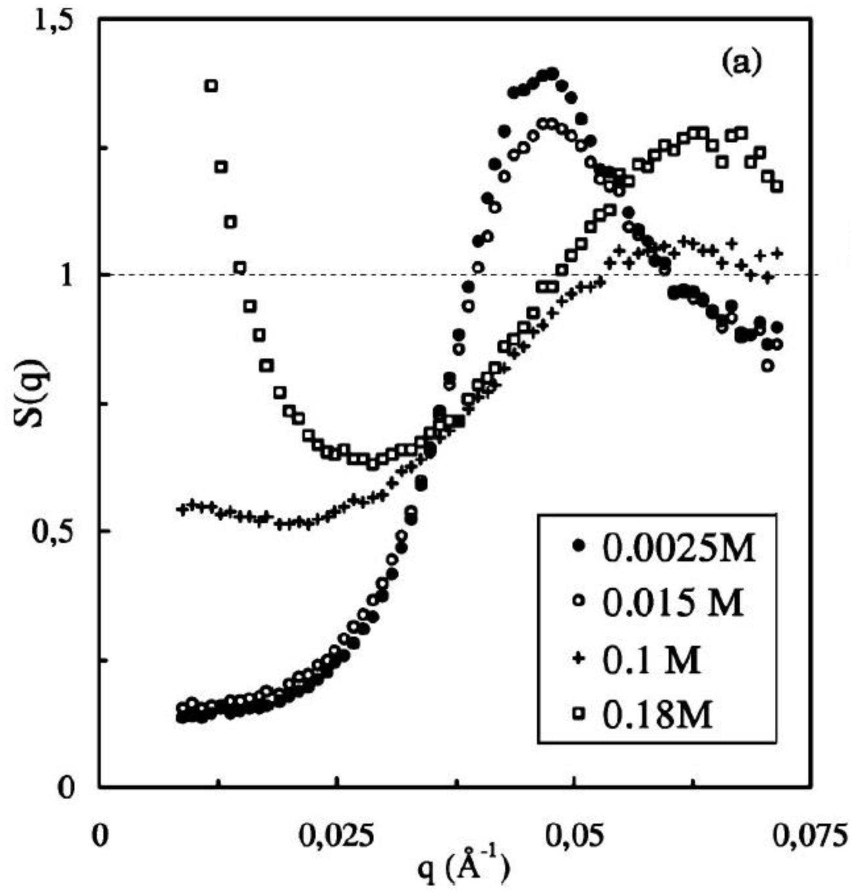


(courtesy of a lecture by J.S. Pedersen)

$$S(q) = 1 + n\,4\pi \int (g(r)-1)\frac{\sin(qr)}{qr} r^2\,dr$$

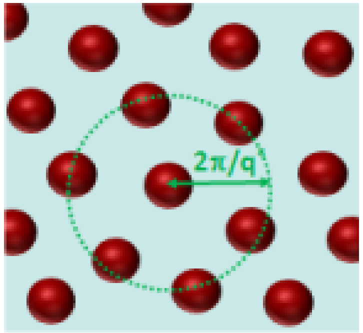
S(q) with hands : from repulsions to attractions…

Progressive addition of salt on an electrostatically stabilized colloidal suspension



Low salinity : electrosatic repulsions

0.0025 M



F. Cousin *et al*, *Phys. Rev. E*, **2003**, *68(2),* 021405

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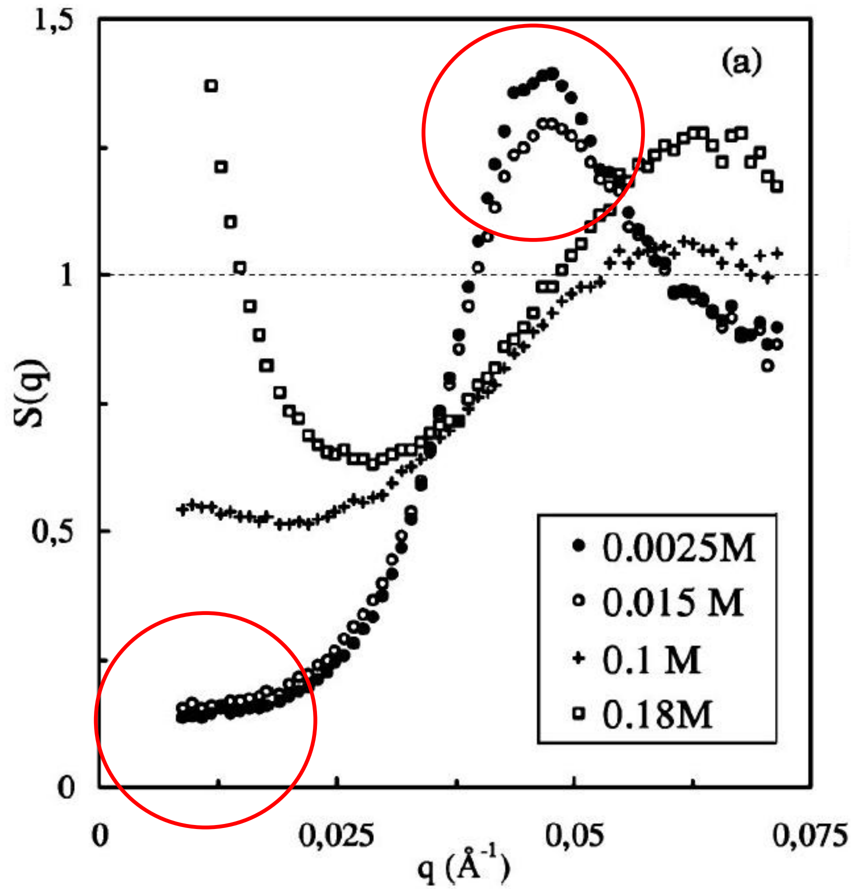

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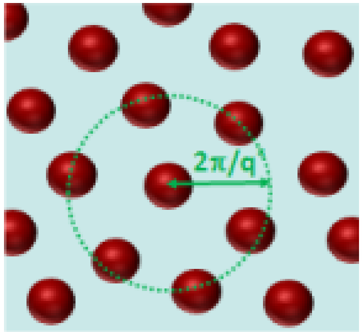

→ Strong correlation peak

→ Low intensity at low q

F. Cousin *et al*, *Phys. Rev. E*, **2003**, *68(2),* 021405

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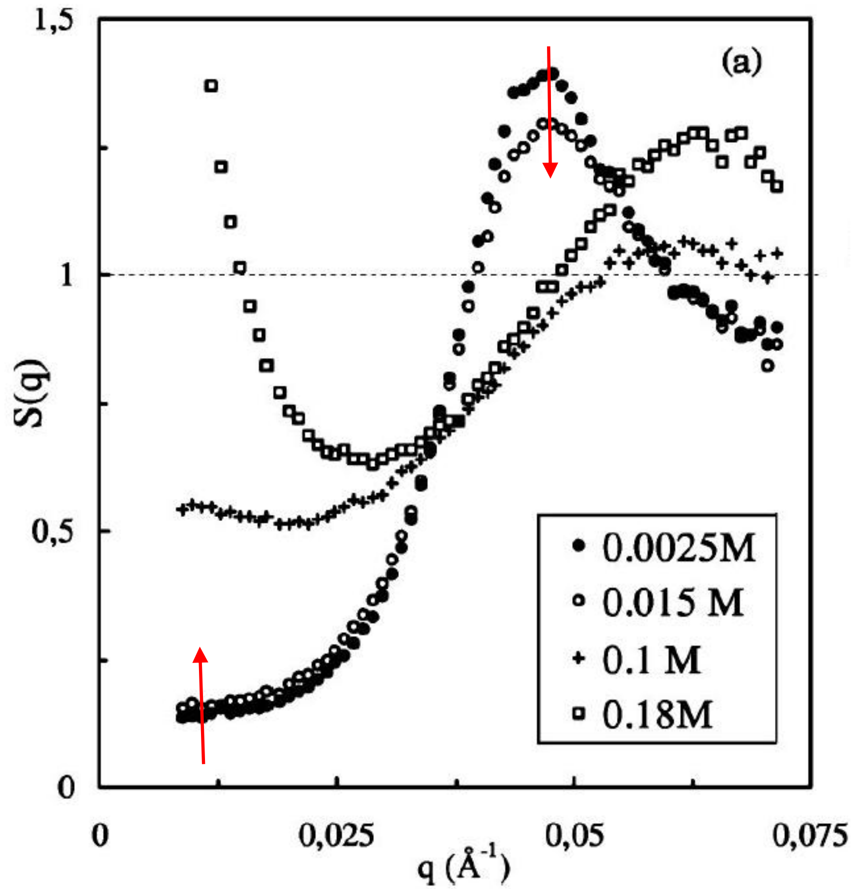

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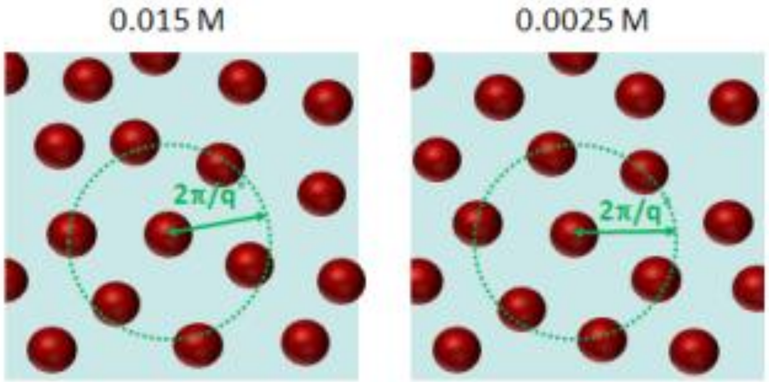

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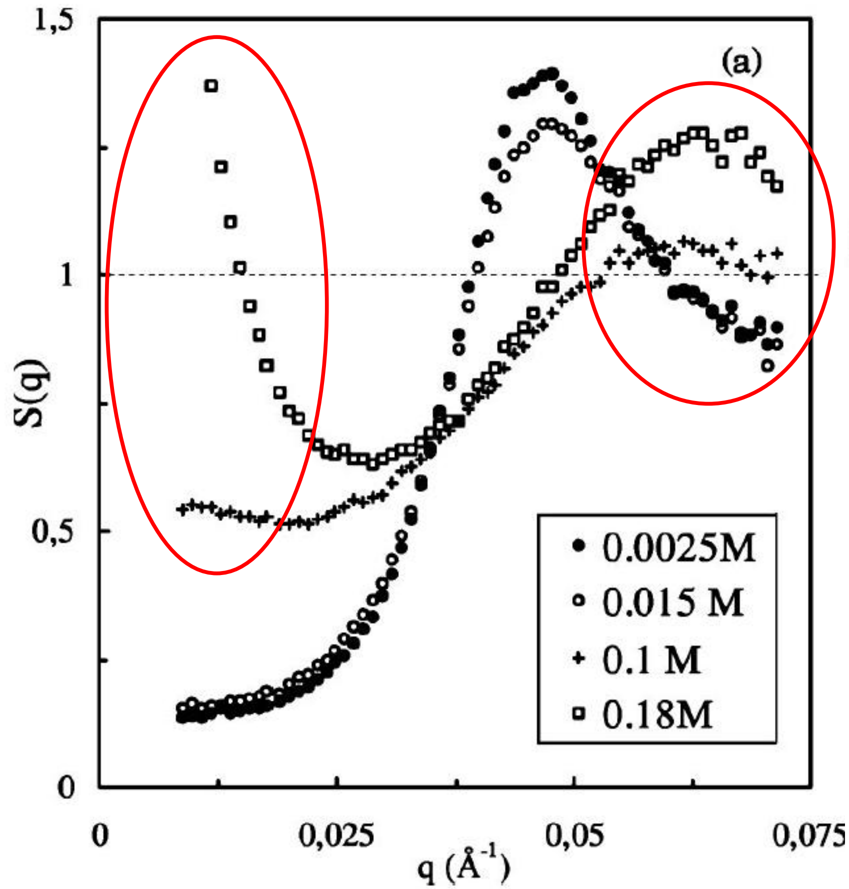
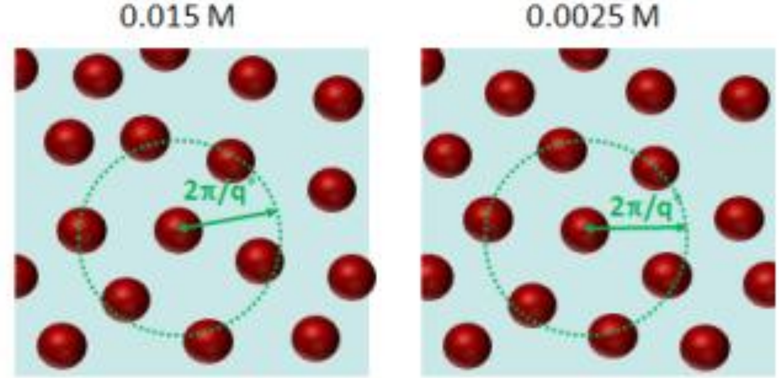
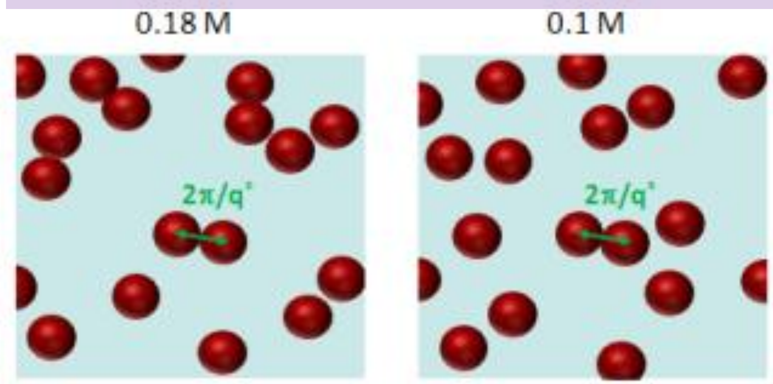


Low salinity : electrosatic repulsions



Addition of salt :screening repulsions



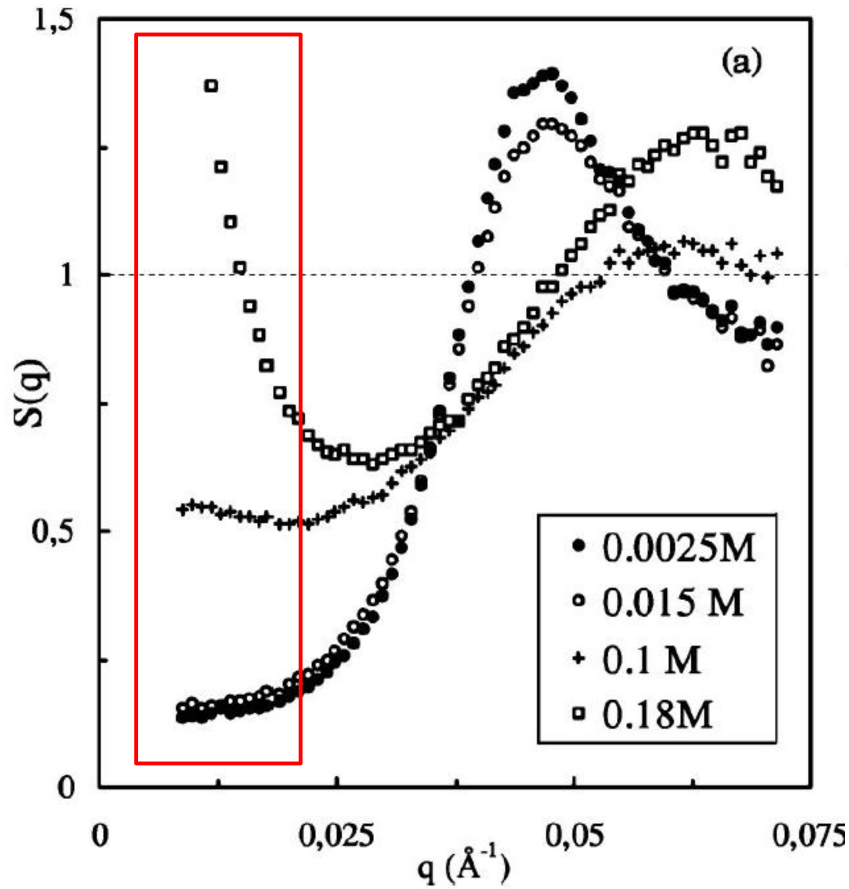
→ Progressive increase of intensity at low q

→ « contact peak »

F. Cousin *et al*, *Phys. Rev. E*, **2003**, *68(2),* 021405

S(q) with hands : from repulsions to attractions…

Progressive addition of salt on an electrostatically stabilized colloidal suspension



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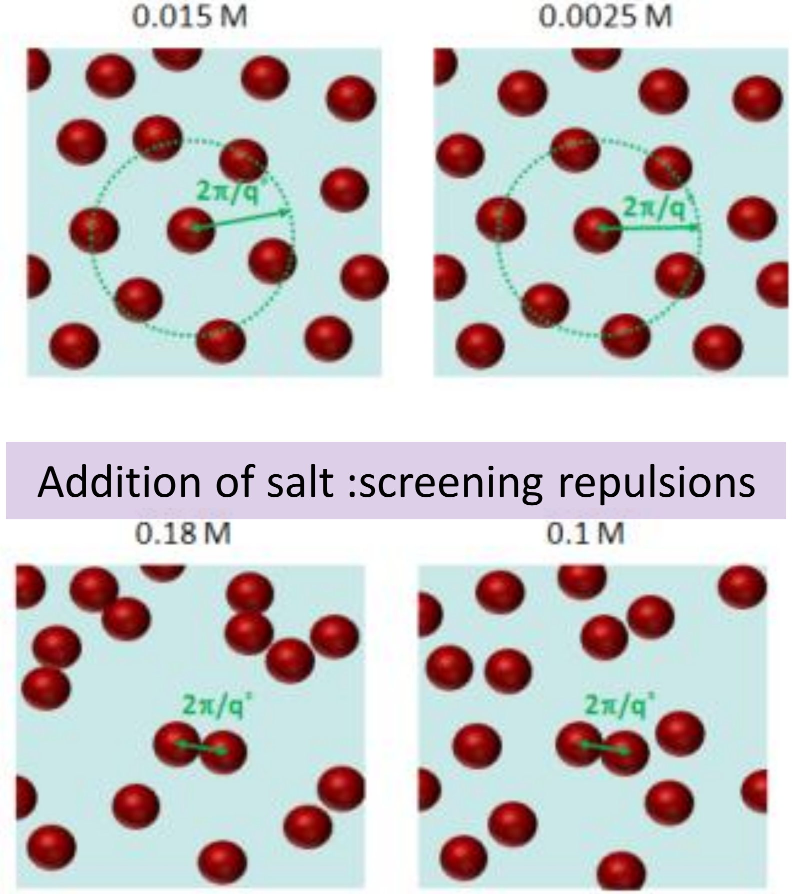


➤ **Informations at low q ?**

Isothermal compressibility χ and second virial coefficient A_2

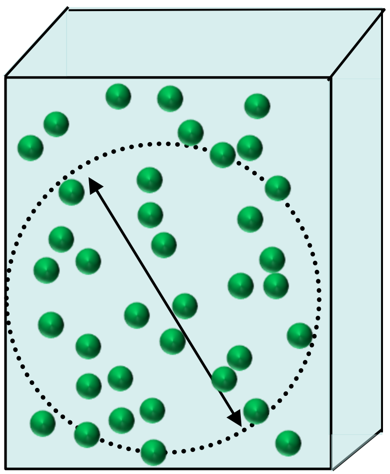
From statistical physics :

isothermal compressibility

Pair correlation function

$$\chi = kT \frac{\partial \rho}{\partial \Pi}\Big)_{\Phi,T} = \boxed{\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}} = 1 + \rho \int_0^\infty (g(r) - 1) 4\pi r^2 dr$$

Osmotic pressure



Density fluctuations at large scale ($q \rightarrow 0$)

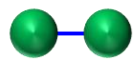
$$\left[\frac{\partial \Pi}{k_B T \partial \rho} \right]_T = \frac{1}{S(0)}$$

Isothermal compressibility χ and second virial coefficient A_2

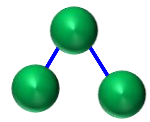
<u>Virial development of osmotic pressure</u>

(Kamerlingh Onnes 1902)

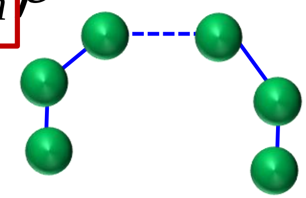
$$\frac{\Pi}{kT} = \rho + \boxed{A_2}\rho^2 + \boxed{A_3}\rho^3 + \dots\boxed{A_n}\rho^n$$



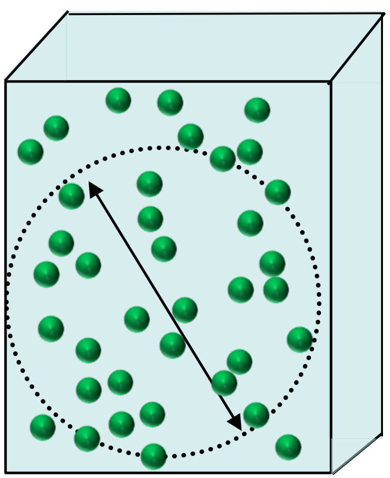
2-body correlations



3-body correlations



n-body correlations



$$\left[\frac{\partial \Pi}{k_B T \partial \rho}\right]_T = \frac{1}{S(0)} = 1 + \rho A_2 + \rho^2 A_3 + \rho^3 A_4 + \dots$$

Isothermal compressibility χ and second virial coefficient A_2

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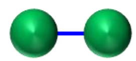

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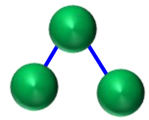

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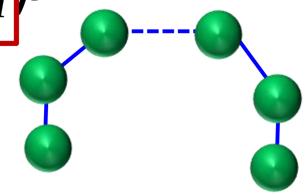

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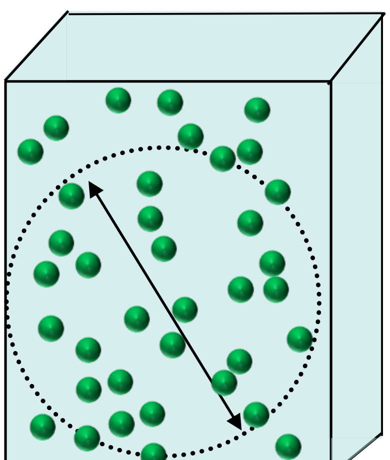

$$\left[\frac{\partial \Pi}{k_B T \partial \rho}\right]_T = \frac{1}{S(0)} = 1 + \rho A_2 + \cancel{\rho^2 A_3 + \rho^3 A_4 + \ldots}$$

In weakly and/or dilute systems

If $V(r) > 0$ (repulsive regime), A_2 has a positive value

If $V(r) < 0$ (attractive regime), A_2 has a negative value

One can show that :

Isothermal compressibility χ and second virial coefficient A_2

Virial development of osmotic pressure

(Kamerlingh Onnes 1902)

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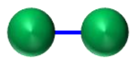

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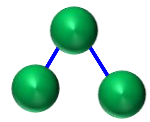

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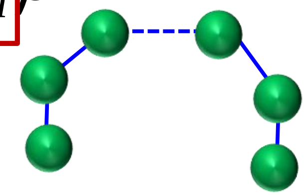

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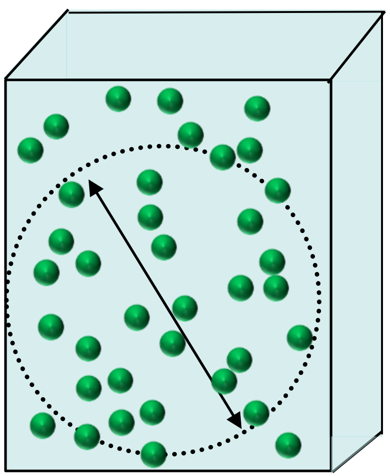


$$\left[\frac{\partial \Pi}{k_B T \partial \rho}\right]_T = \frac{1}{S(0)} = 1 + \rho A_2 + \cancel{\rho^2 A_3 + \rho^3 A_4 + \dots}$$

In weakly and/or dilute systems

One can show that :

$$A_2 = \frac{1}{2}\int_0^\infty \left(1 - e^{-\frac{V(r)}{kT}}\right) 4\pi r^2 dr$$

One can show that :

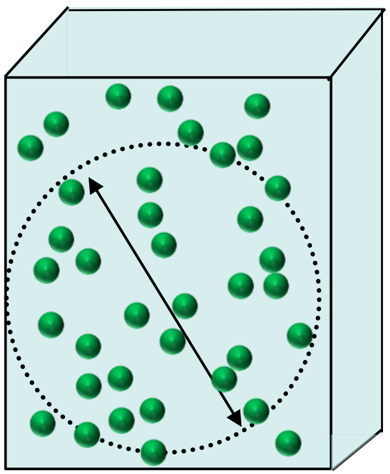
Isothermal compressibility χ and second virial coefficient A_2

$$\boxed{I(q) = \Phi\,\Delta\rho^2\,{V_{part}}^2\,P(q).S(q)}$$

Determination of A_2 : several measurements at concentrations at low q

At low q : $$P_{Guinier}(q) = 1 - \frac{q^2}{3}\left[\frac{1}{2N^2}\sum_i^N\sum_j^N r_{ij}^2\right] = 1 - \frac{q^2 R_g^2}{3}$$

$\Rightarrow$ $\boxed{\textbf{Zimm Plot}}$



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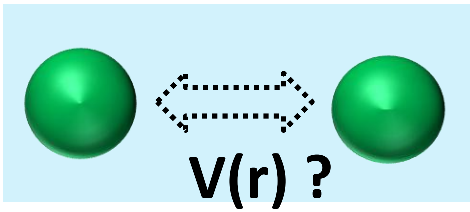
One can show that : $$A_2 = \frac{1}{2}\int_0^\infty\left(1 - e^{-\frac{V(r)}{kT}}\right)4\pi r^2 dr$$

Link between V(r), g(r) and S(q)

How to go further in descriptions of interactions ?



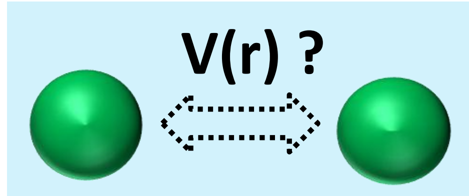
g(r) – S(q)

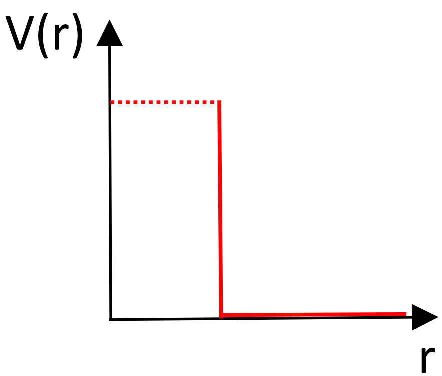
Simulations, integral equations

See, for example

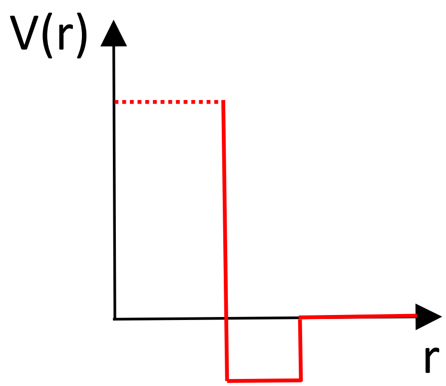
Chapter from Luc Belloni *(in french)*

Link between V(r), g(r) and S(q)

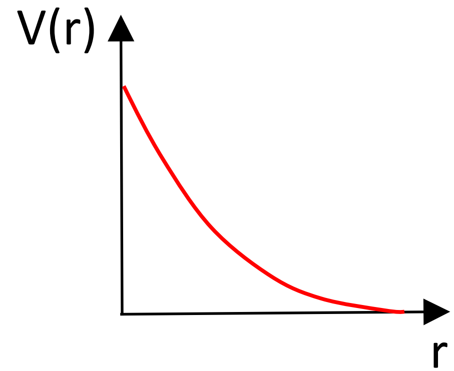




Hard spheres



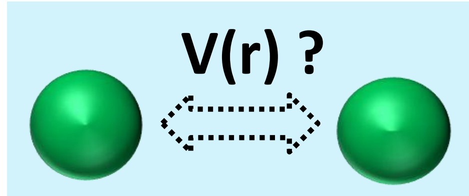
Sticky Hard sheres

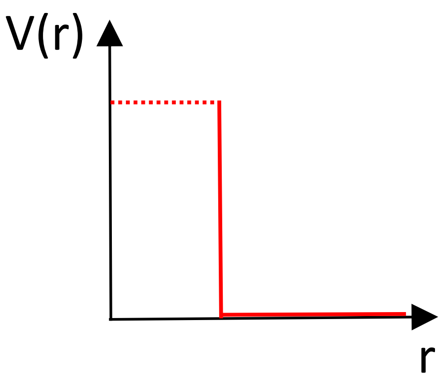


Screened Coulombian Potential
(Debye Hückel)

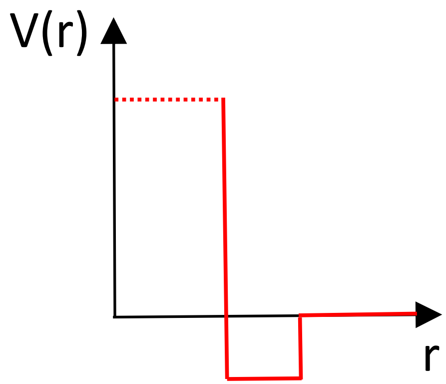
Implemented in SasView

Link between V(r), g(r) and S(q)





Hard spheres



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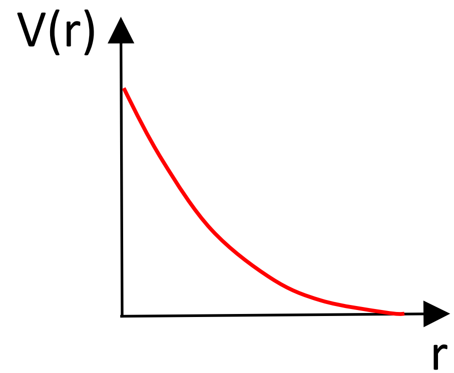

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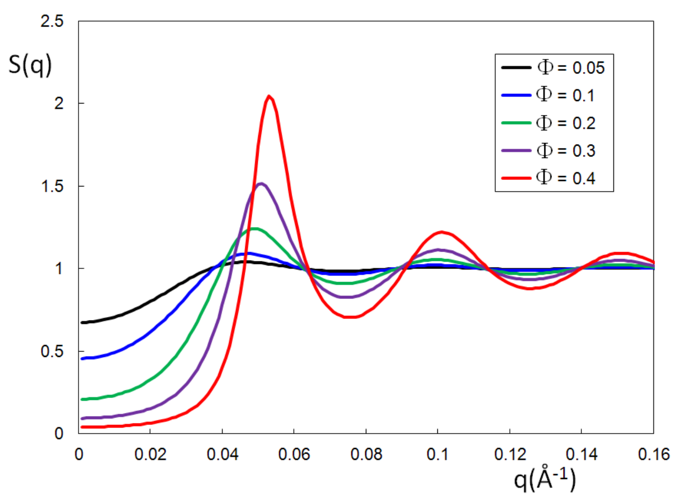
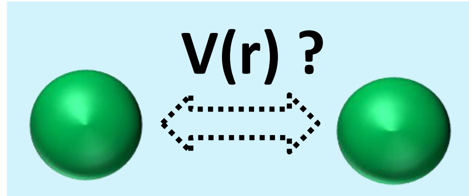
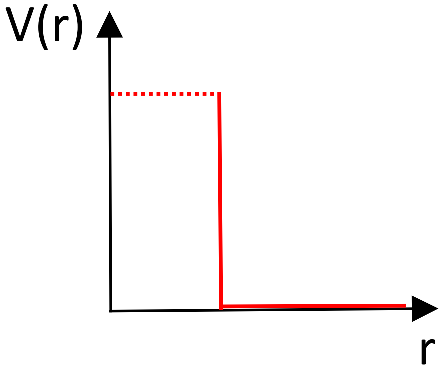


Percus-Yevick : analytical form

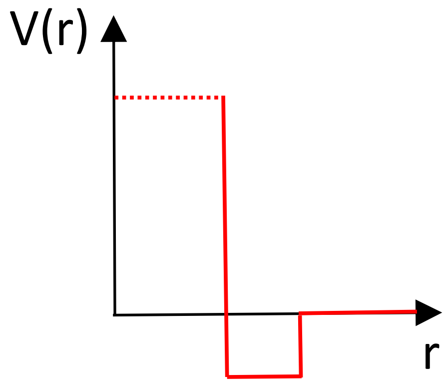
Implemented in SasView

Link between V(r), g(r) and S(q)





Hard spheres



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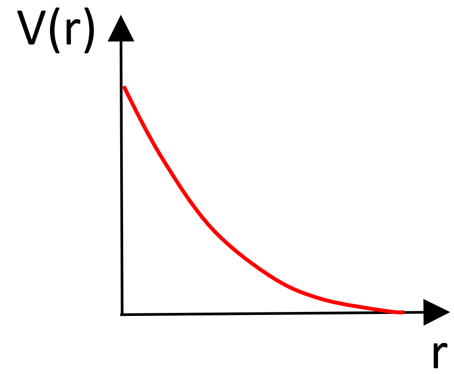


Screened Coulombian Potential
(Debye Hückel)

$$L_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon kT}$$

$$\boxed{\varphi_i(r) = \frac{z_i L_B}{r} e^{-\kappa r}}$$

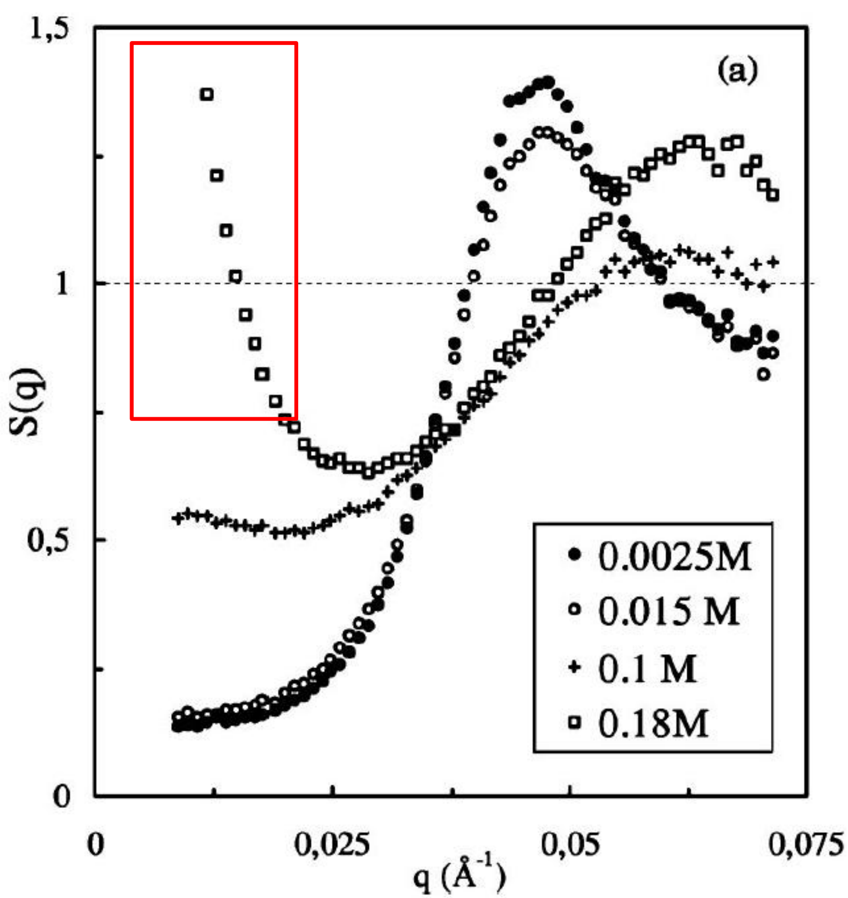
$$\kappa^2 = \frac{2e^2 I}{\varepsilon\varepsilon_0 kT} \quad \text{with} \quad I = \frac{1}{2}\sum_i c_i z_i^2$$

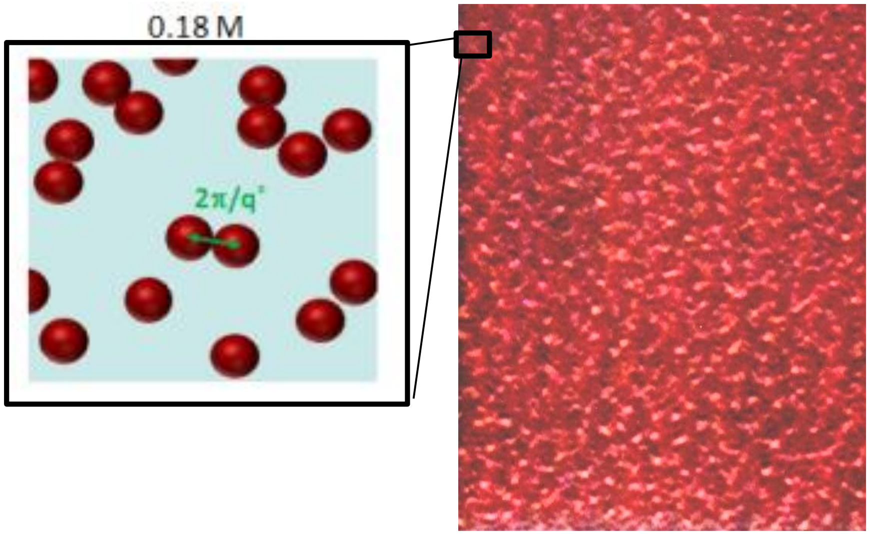
Hayter-Penfold : many parameters!

Implemented in SasView

Correlation length ξ in attractive systems

Progressive addition of salt on an electrostatically stabilized colloidal suspension





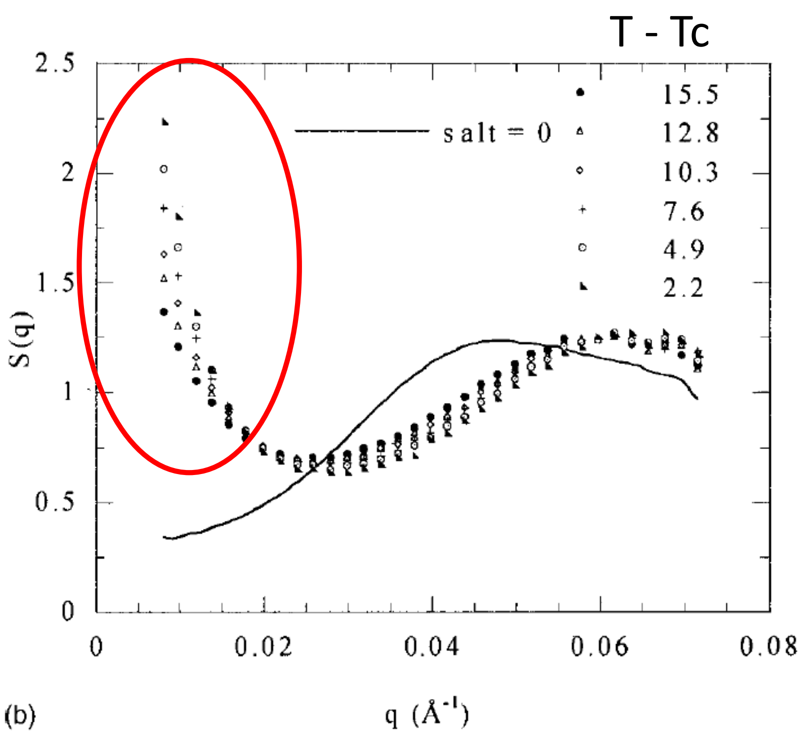
(optical microscopy)

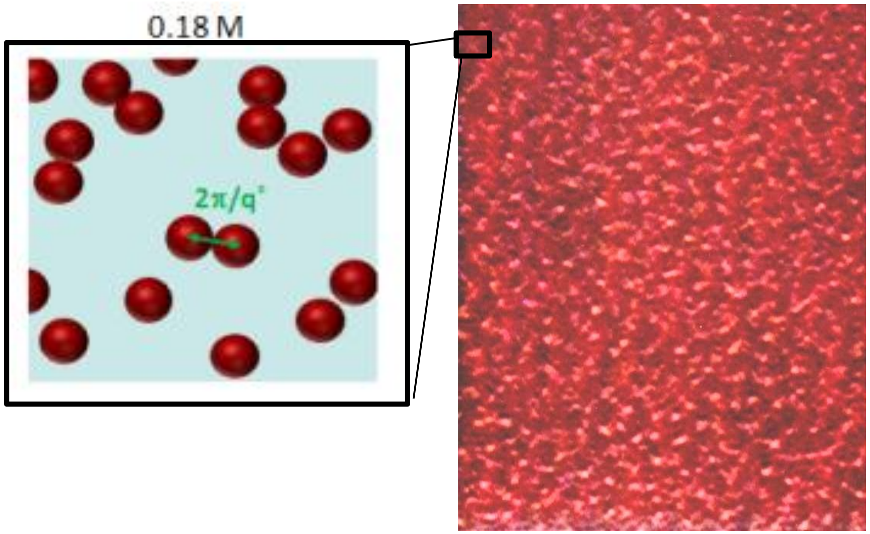
Approach of critial point by temperature at fixed salinity

F. Cousin *et al*, *J. Phys. Chem B*, **2001**, *115(13), 6051-6057*

Correlation length ξ in attractive systems

Progressive addition of salt on an electrostatically stabilized colloidal suspension





(optical microscopy)

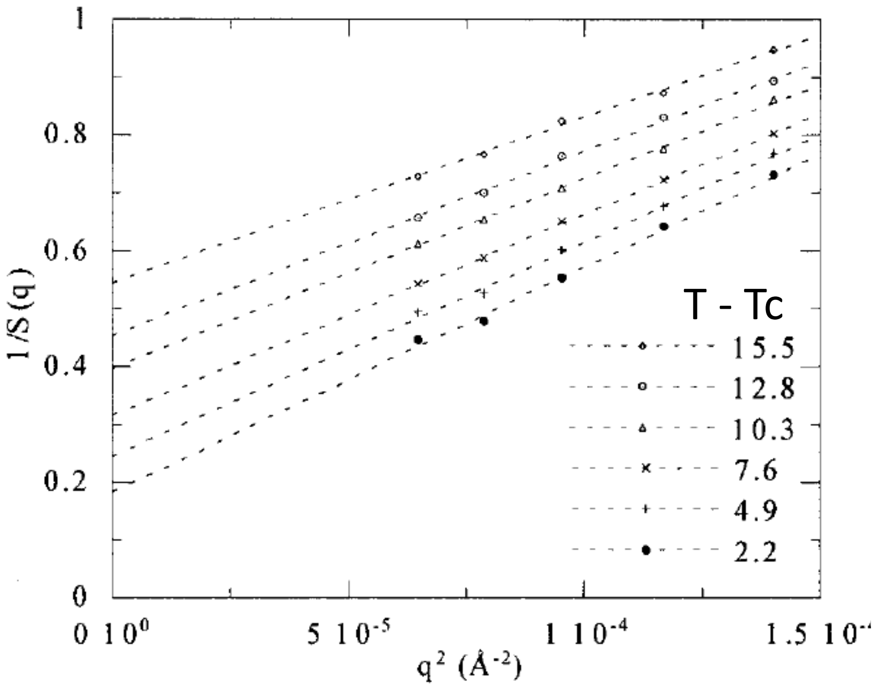
Approach of critial point by temperature at fixed salinity

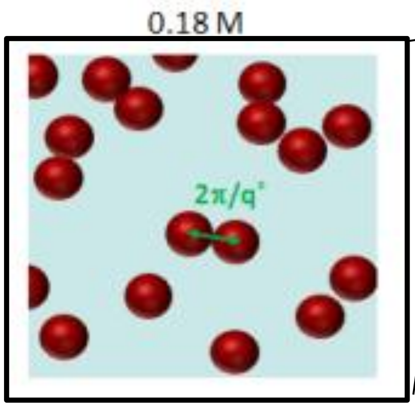
→ Divergence of fluctuations

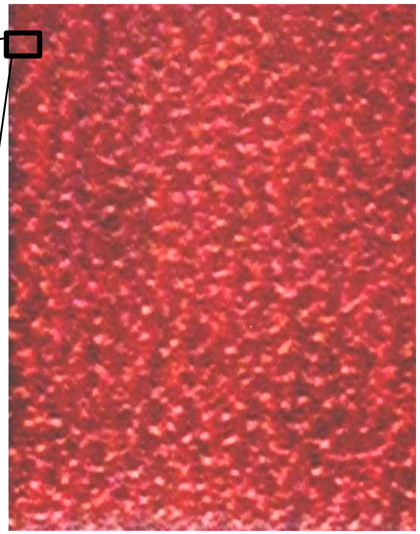
F. Cousin *et al*, *J. Phys. Chem B*, **2001**, *115(13), 6051-6057*

Correlation length ξ in attractive systems

Progressive addition of salt on an electrostatically stabilized colloidal suspension







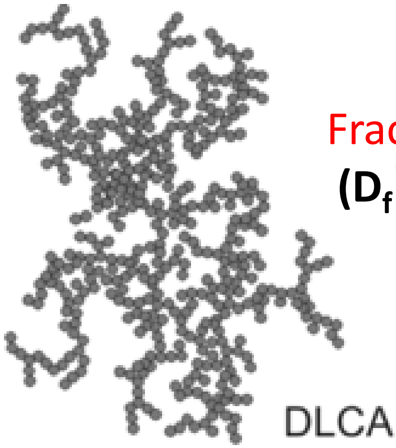
(optical microscopy)

Approach of critial point by temperature at fixed salinity

$$g(r) \propto \frac{e^{-r/\xi}}{r} \Rightarrow S(q) \propto \frac{1}{q^2+\xi^{-2}}$$

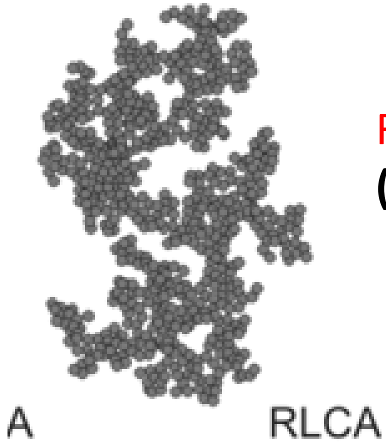
F. Cousin *et al*, *J. Phys. Chem B*, **2001**, *115(13), 6051-6057*

Attractions in colloid : Fractal aggregates



Fractal final structure
(D_f = 1.78)

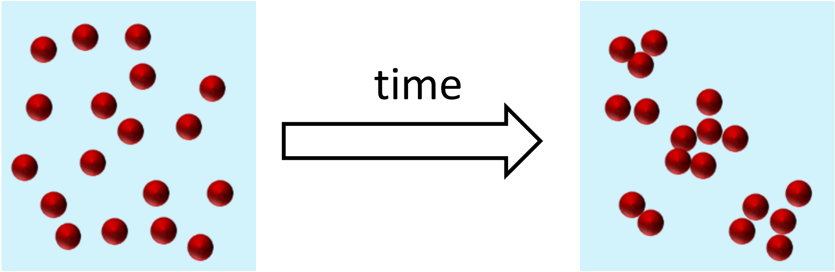
Diffusion Limited Cluster Aggregation



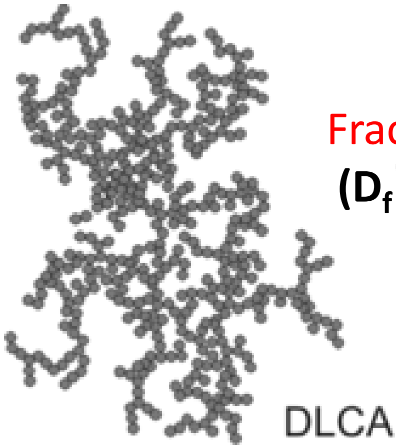
Fractal final structure
(D_f = 2.1)

Reaction Limited Cluster Aggregation

<u>2 limit cases of aggregation processes :</u>
(without strong attractions)

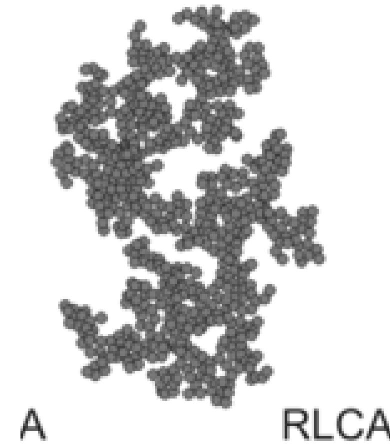


Attractions in colloid : Fractal aggregates



Fractal final structure
(D_f = 1.78)

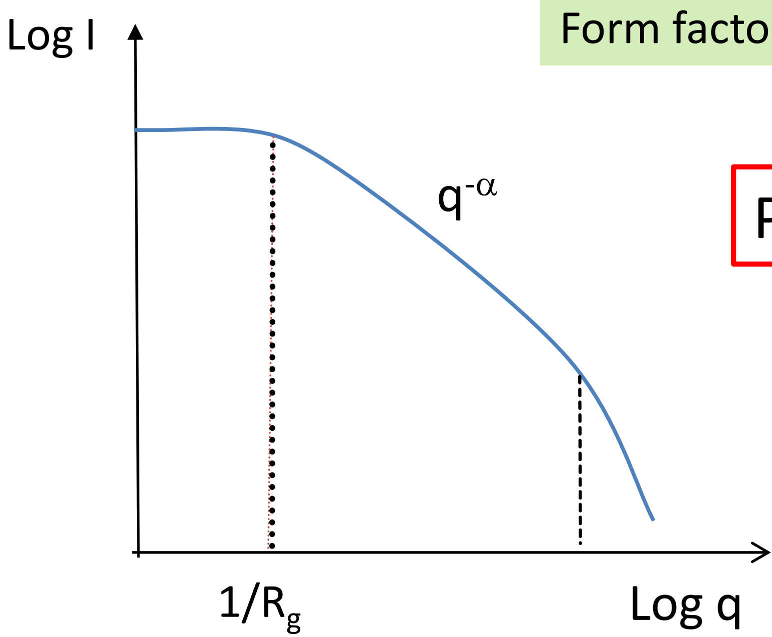
Diffusion Limited Cluster Aggregation



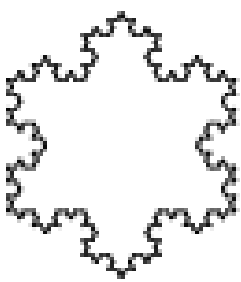
Fractal final structure
(D_f = 2.1)

Reaction Limited Cluster Aggregation

Form factor of a fractal object

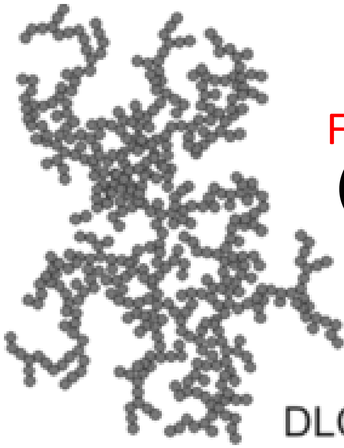


$$\boxed{P(q) \sim q^{-Df}}$$



J. Teixeira, *Journal of Applied Crystallography*, **1988**, *21 (6)*, 781-785

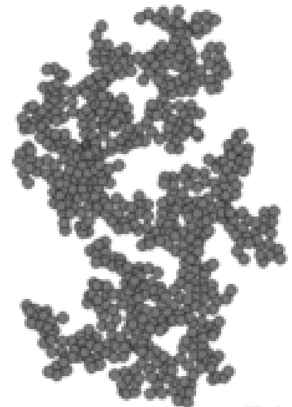
Attractions in colloid : Fractal aggregates



DLCA

Fractal final structure

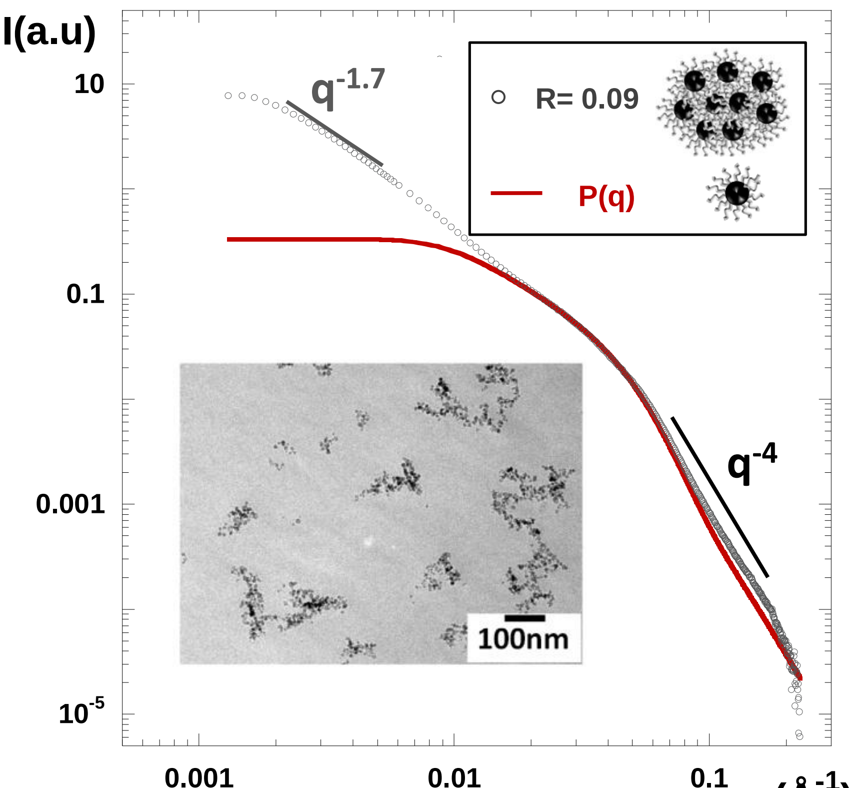
(D_f = 1.78)

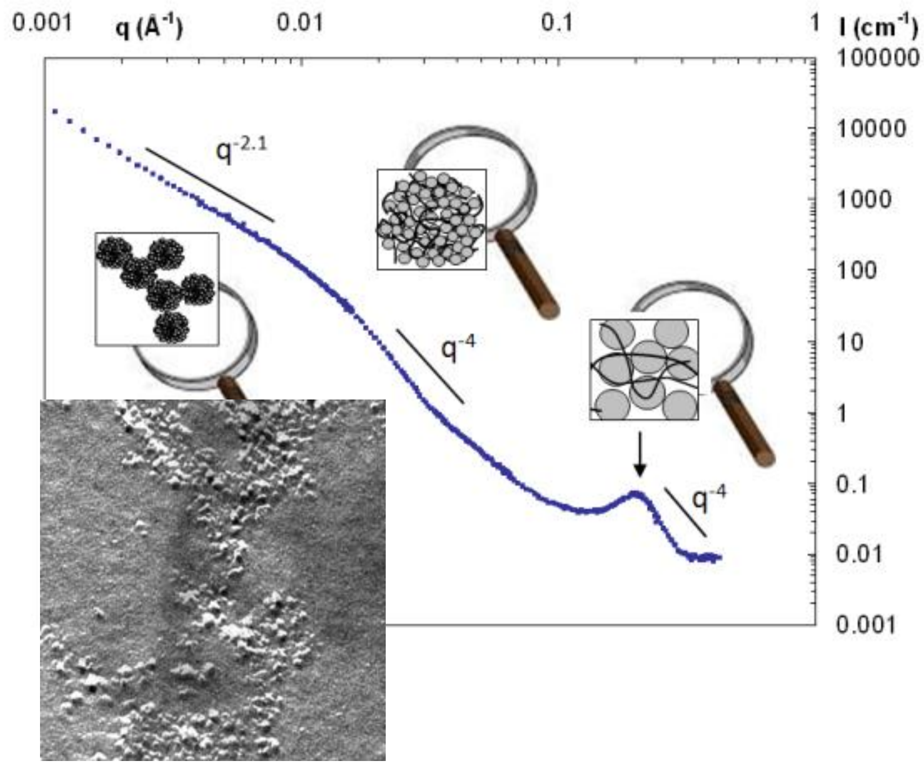


A RLCA

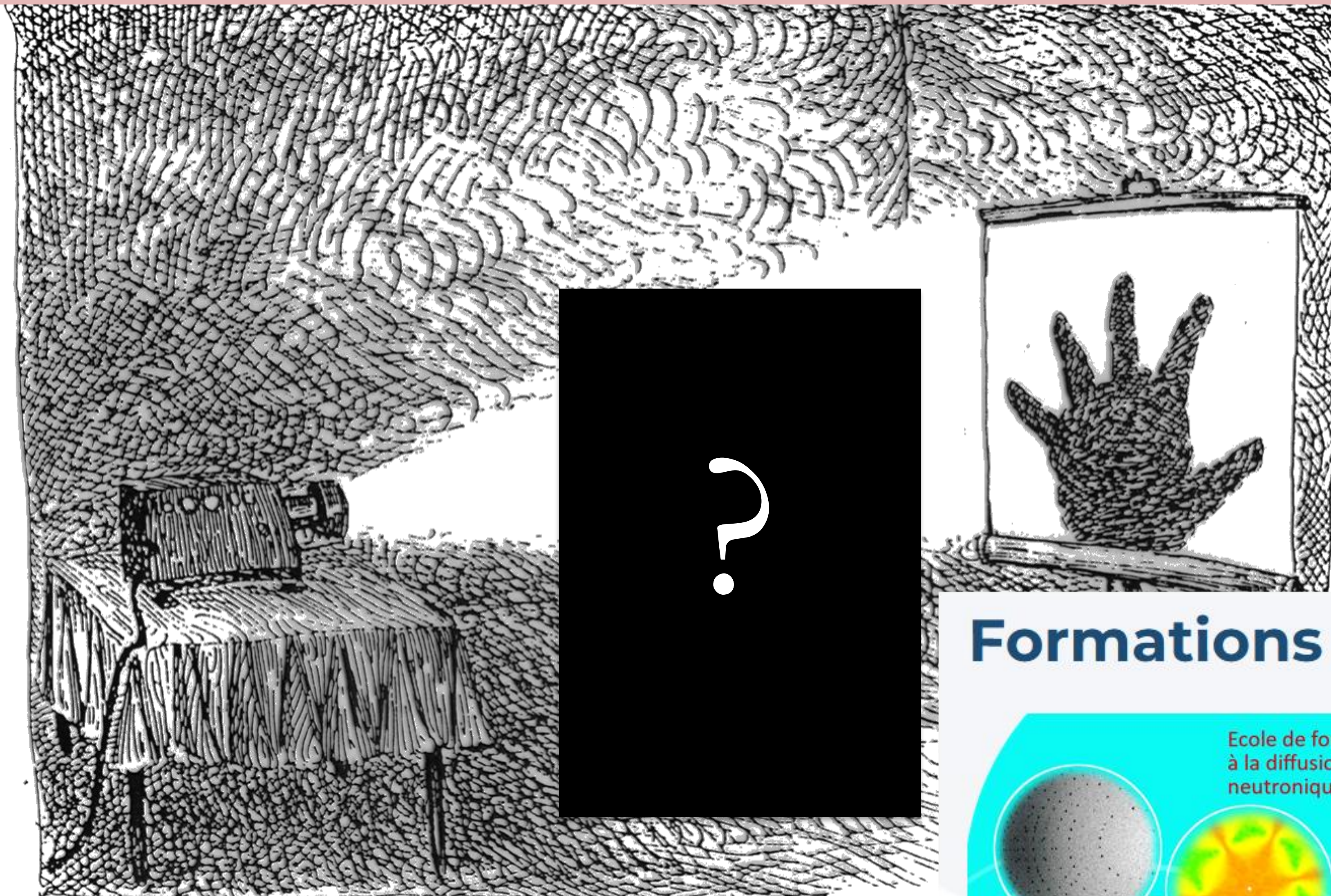
Fractal final structure

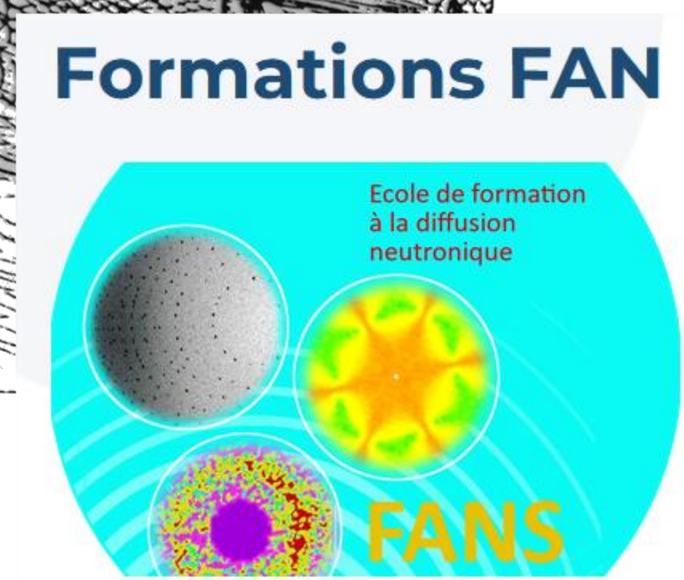
(D_f = 2.1)





Scattering: from the signal to structure (inversion)

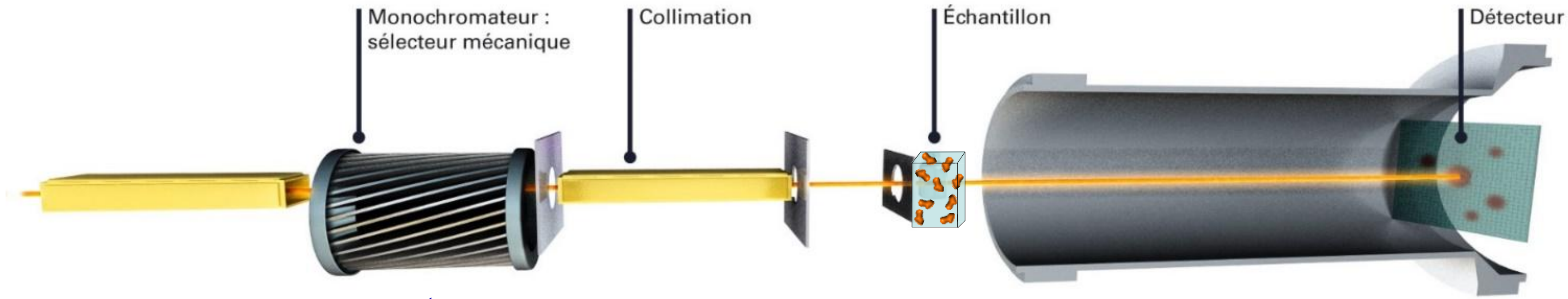




Outline

- Neutron scattering : Principles
- Scattering Length Density /Contrast variation
- Form Factor/Structure factor
- Systems of non-interacting objects : Form factor
- Interactions between objects : Structure factor
- <u>SANS diffractometer</u>

SANS diffractometer



Velocity selector

Detector PAXY
64cm*64cm*5mm

SANS diffractometer

SAM (CRG ILL)

SANS-LLB (PSI)

D22 (ILL)

Thanks for your attention