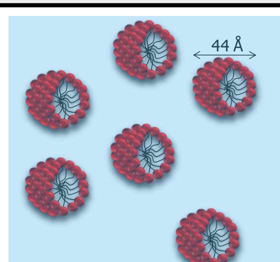
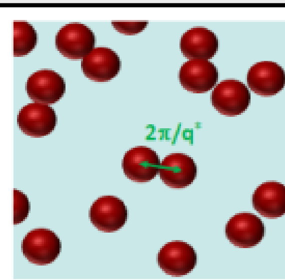
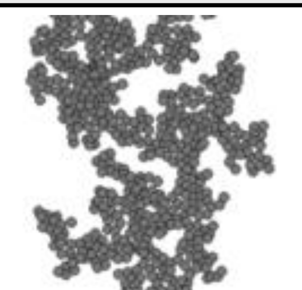
From the diluted regime to the concentrated regime :

the case of spherical systems (colloids, spherical micelles, globular proteins..)

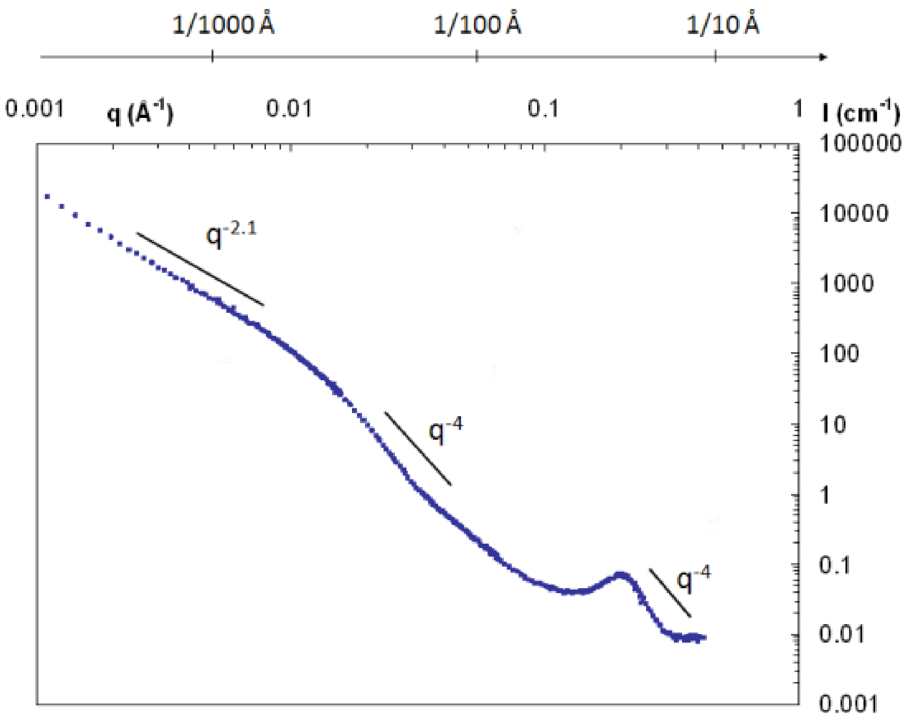
Fabrice.cousin@cea.fr







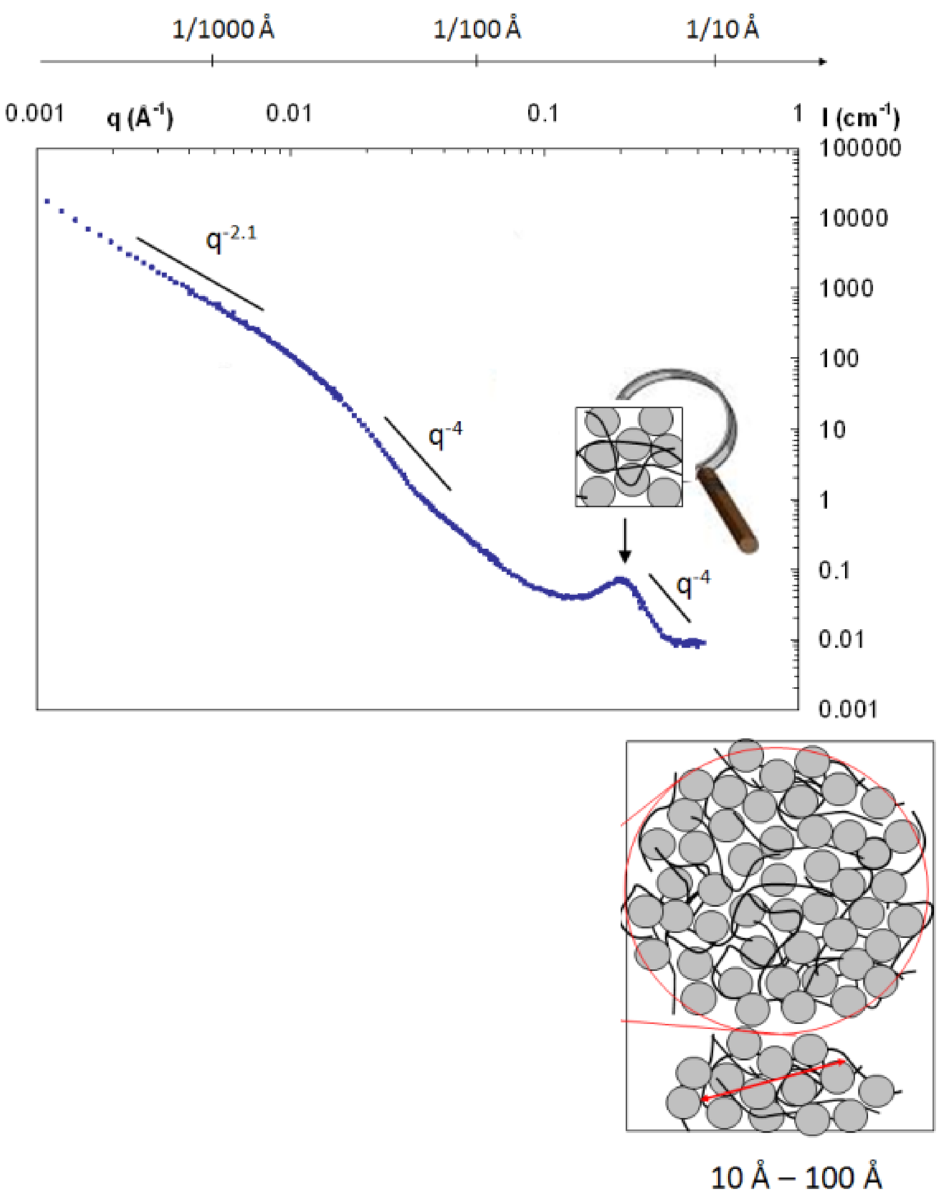
On the importance to look at correlations between objects…



What is the structure at different scales ?

F. Cousin *et al*, Langmuir, **2010**, *26(10)*, 7078–7085.

On the importance to look at correlations between objects…



What is the structure at different scales ?

- Aggregation of spheres

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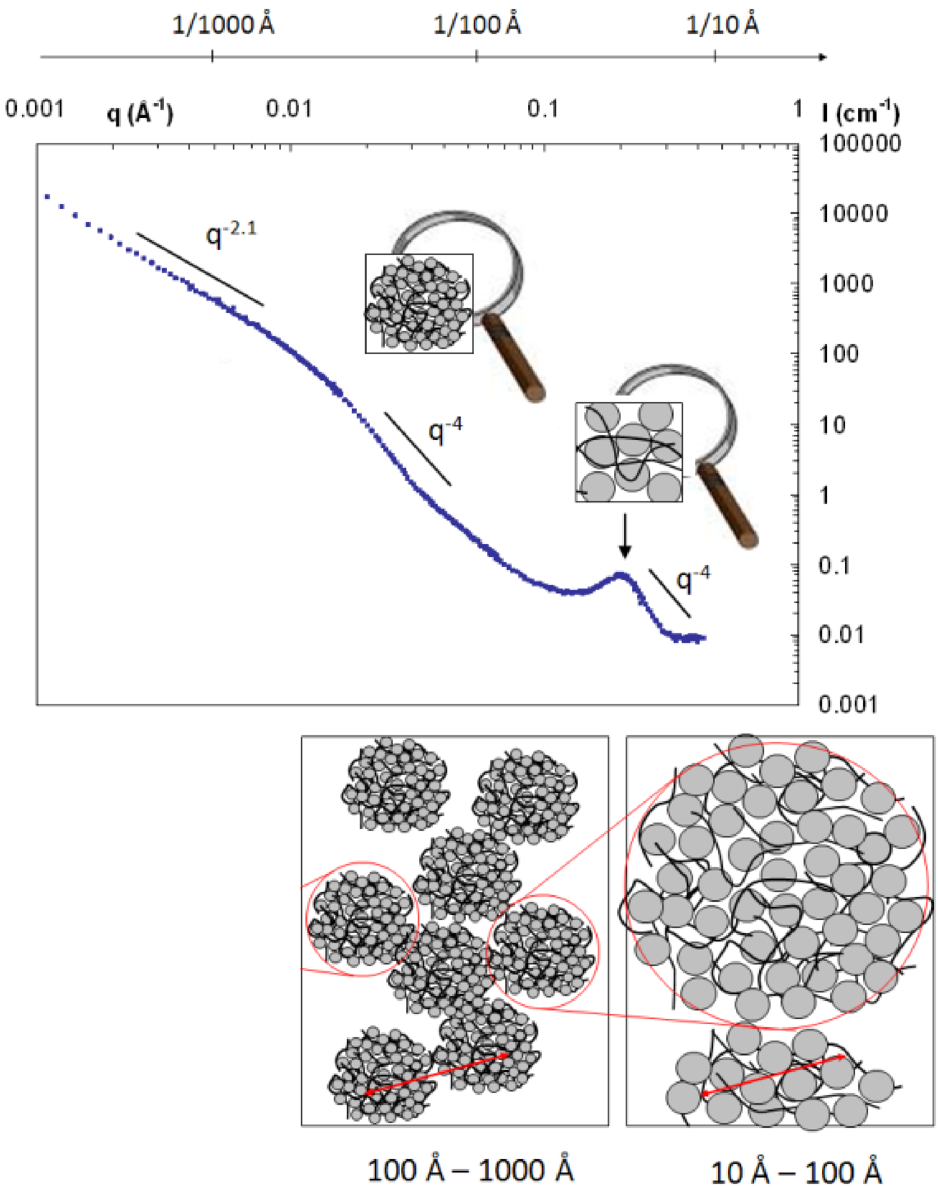

What is the structure at different scales ?

- Aggregation of spheres
- Dense aggregates

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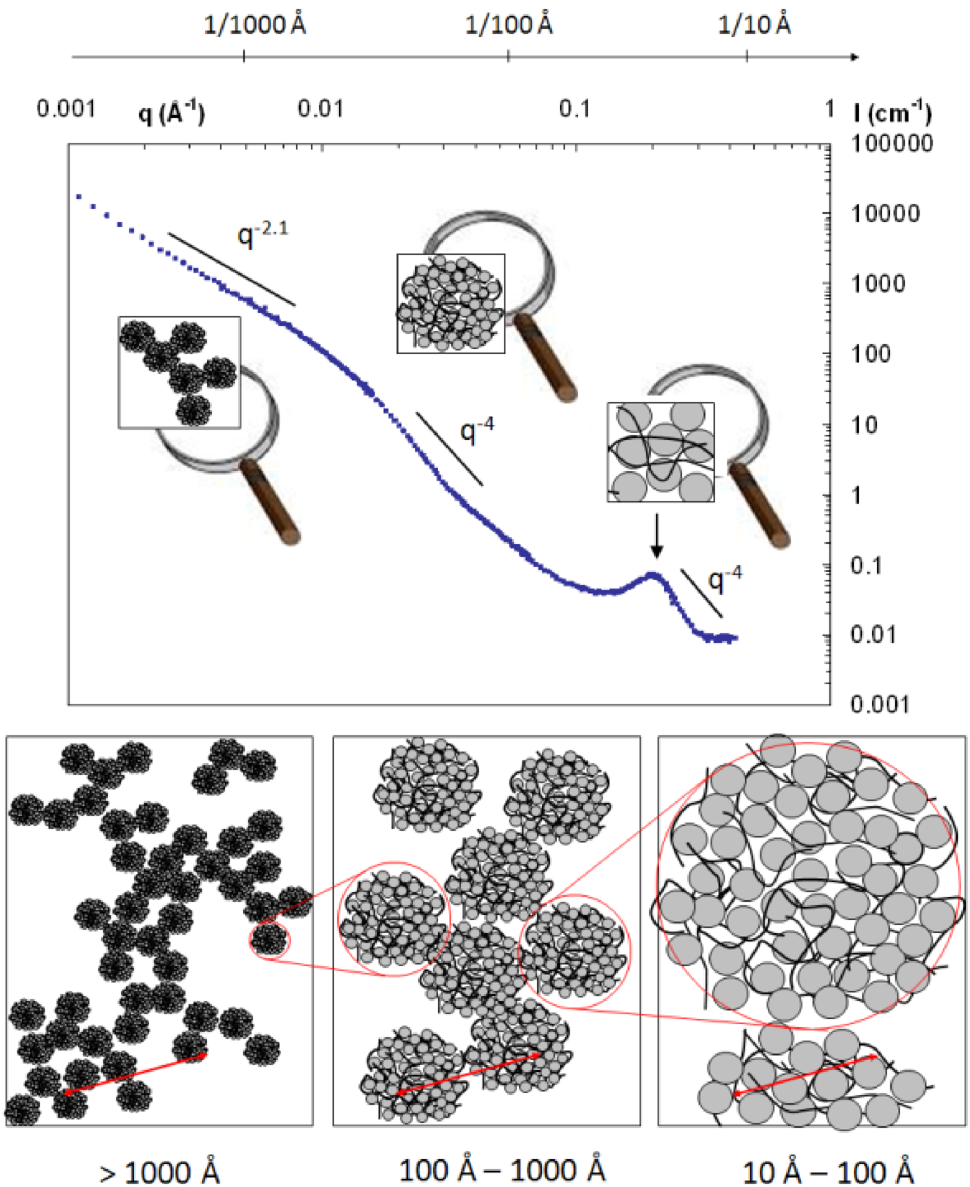
On the importance to look at correlations between objects…

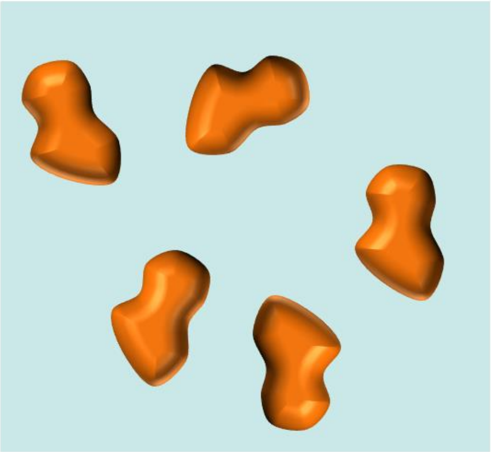


What is the structure at different scales ?

- Aggregation of spheres
- Dense aggregates
- Open Aggregates of dense aggregates !

F. Cousin *et al*, Langmuir, **2010**, *26(10)*, 7078–7085.

Form Factor/Structure factor



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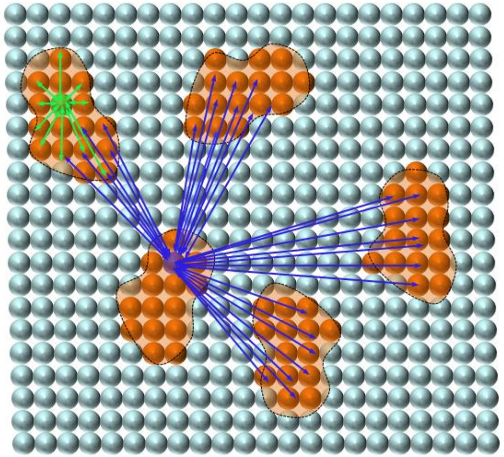


$$\frac{1}{V}\cdot\frac{d\sigma}{d\Omega}(q)$$

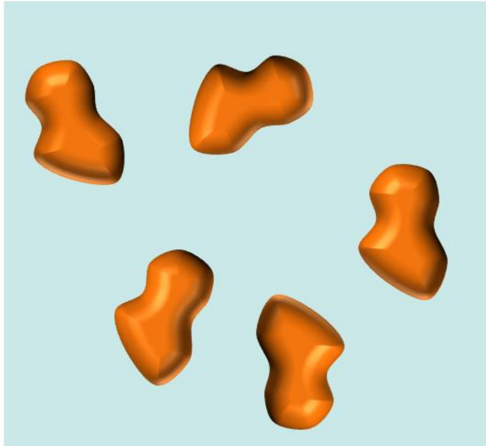
$$\frac{\Sigma(q)}{\boxed{\left(\rho_{obj}-\rho_{media}\right)^2} v_{obj}{}^2} = \sum_{\alpha}^{n}\sum_{\beta}^{n}\sum_{i}^{N}\sum_{j}^{N} e^{i\vec{q}\cdot\left(\vec{r}_i^{\,\alpha}-\vec{r}_j^{\,\beta}\right)}$$

contrast

n objects

N elementary scatterer per object

Form Factor/Structure factor



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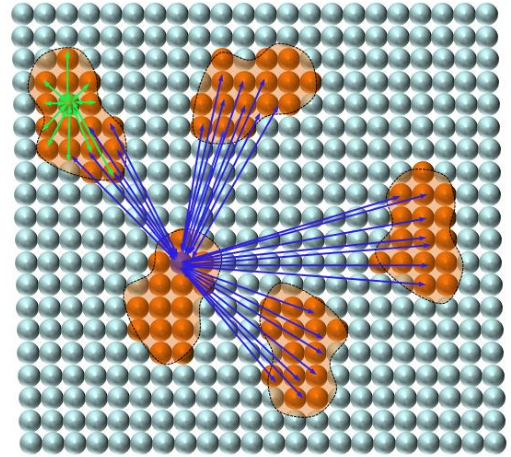


contrast

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

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

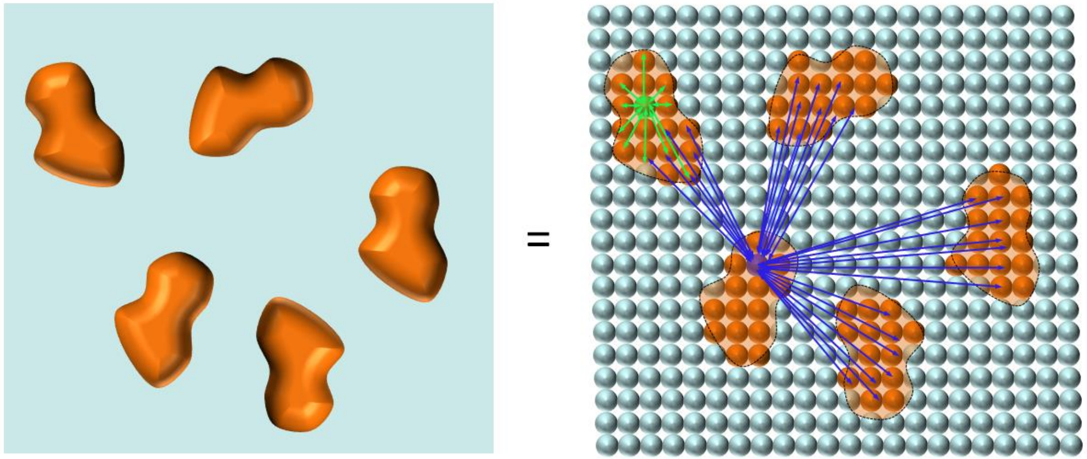
$$\boxed{Q(q)} = \frac{1}{N^2}\sum_{i^\alpha}^{N}\sum_{j^\beta}^{N} e^{i\vec{q}.\left(\vec{r}_i^{\alpha}-\vec{r}_j^{\beta}\right)}$$

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

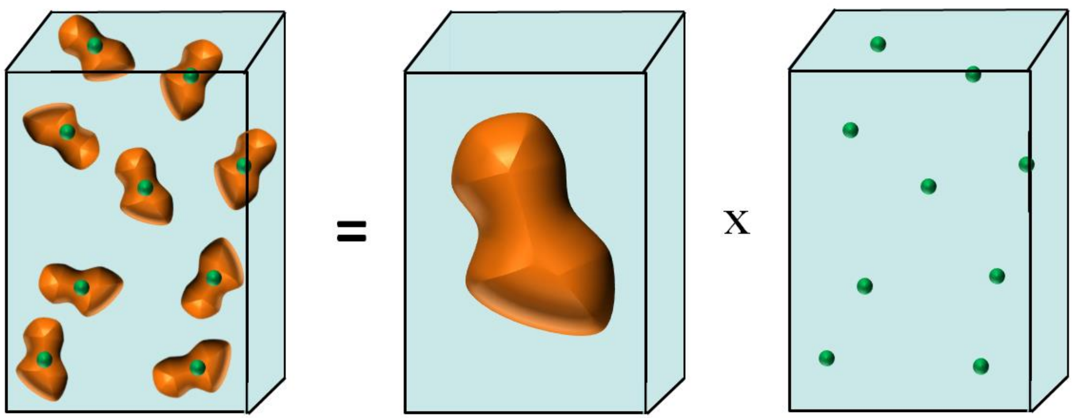
Cf lecture Pierre Roblin

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

Form Factor/Structure factor



For rigid centrosymmetrical objects :

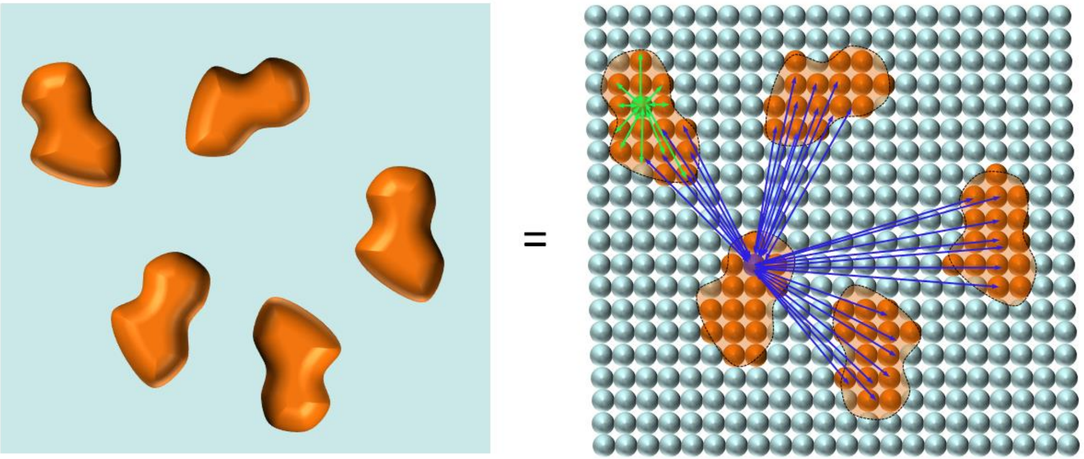


$$I(q) = \frac{n}{V}\,\Delta\rho^2 {V_{part}}^2 \; P(q).S(q)$$

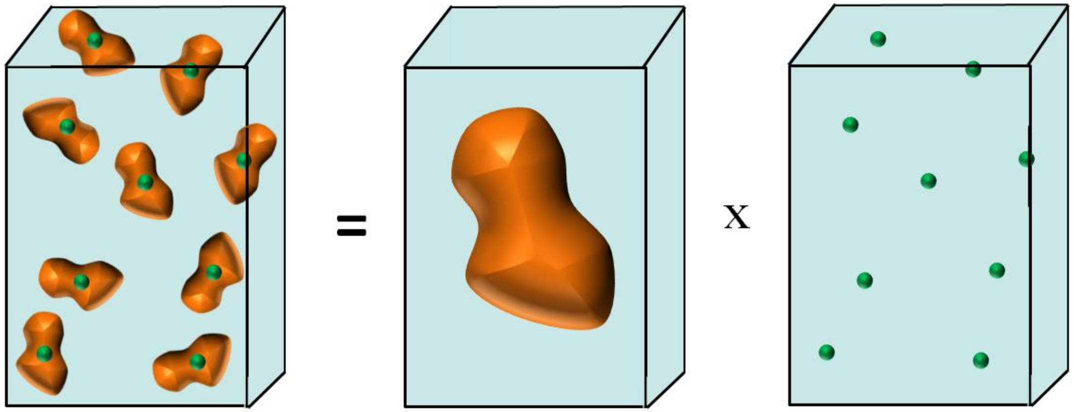
$$\Phi = \frac{n.V_{part.}}{V}$$

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

Form Factor/Structure factor



For rigid centrosymmetrical objects :



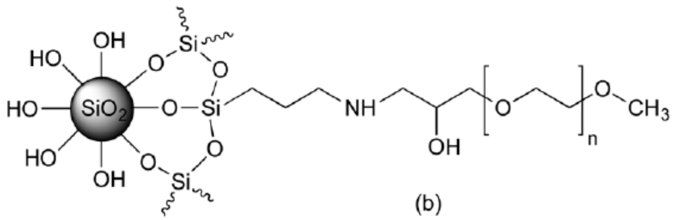
For no rigid centrosymmetrical objects : polymers, hydrogel, etc..

Cf lecture François Boué

How to obtain the structure factor ?

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

Silica nanospheres grafted by PEG

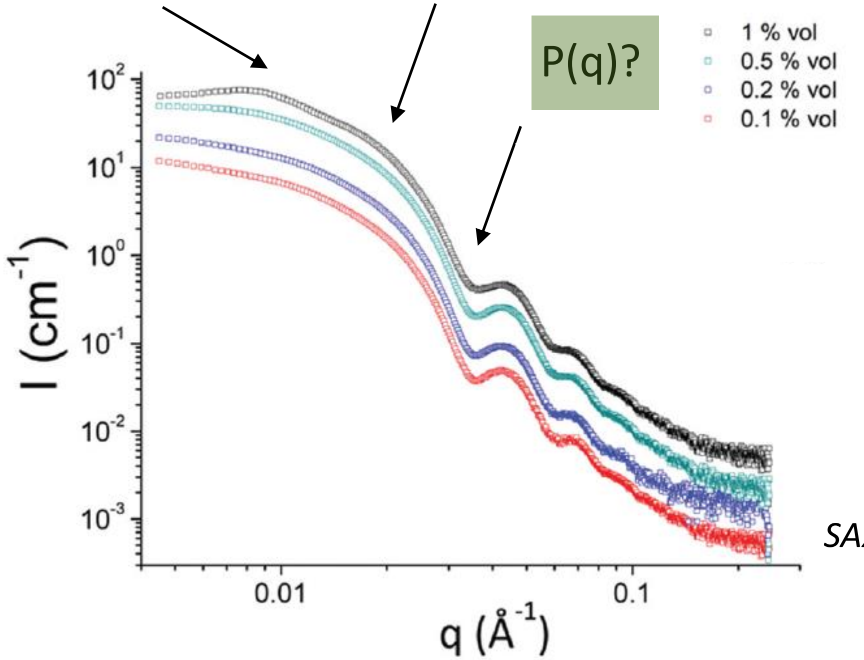


(b)

S(q)?

??

P(q)?



SAXS

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

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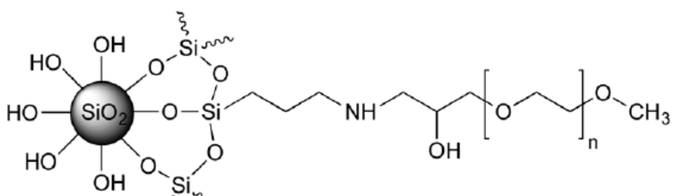
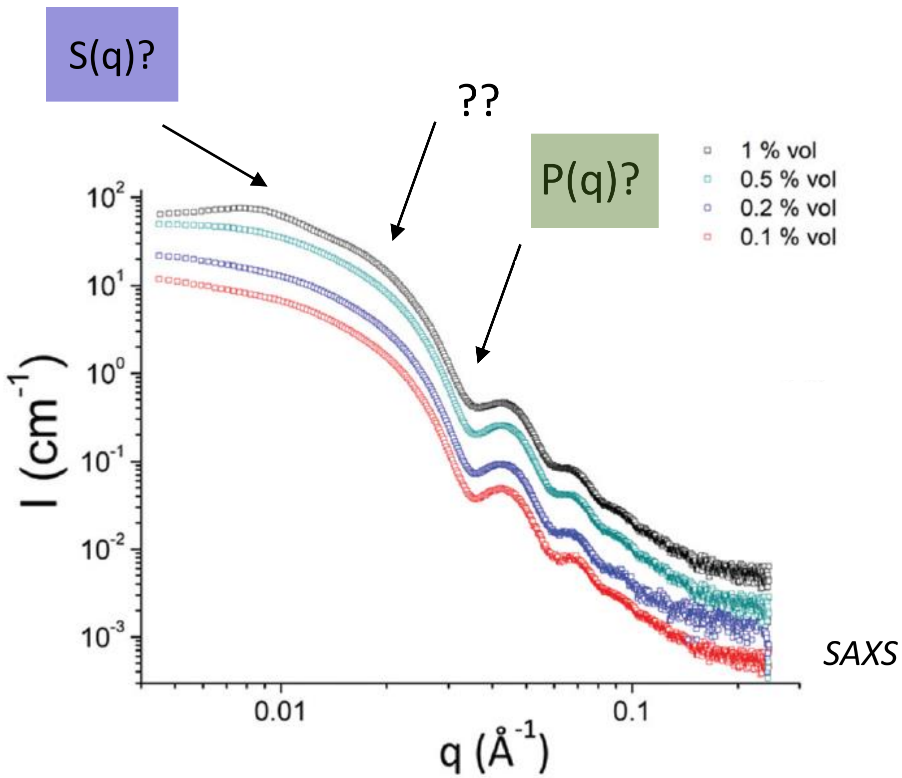


(b)



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

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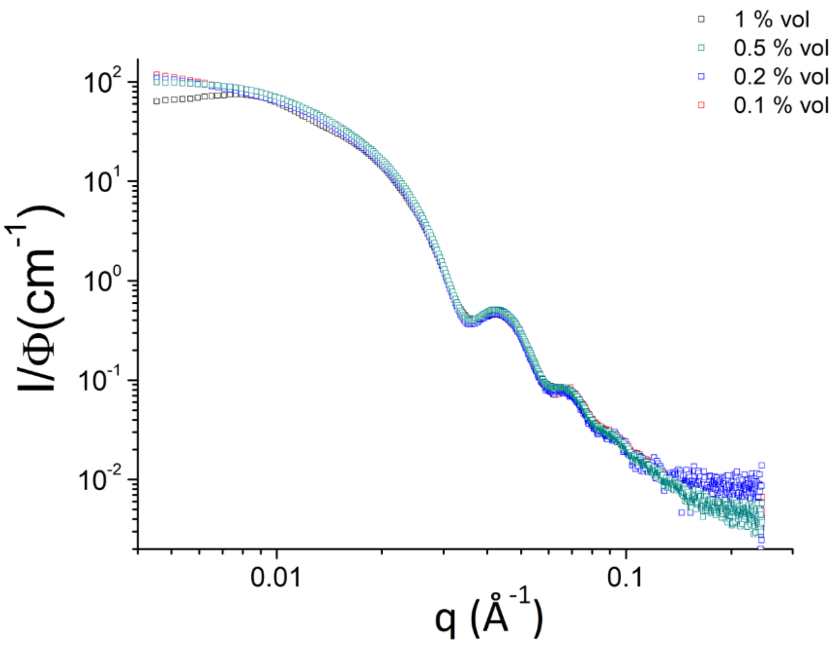

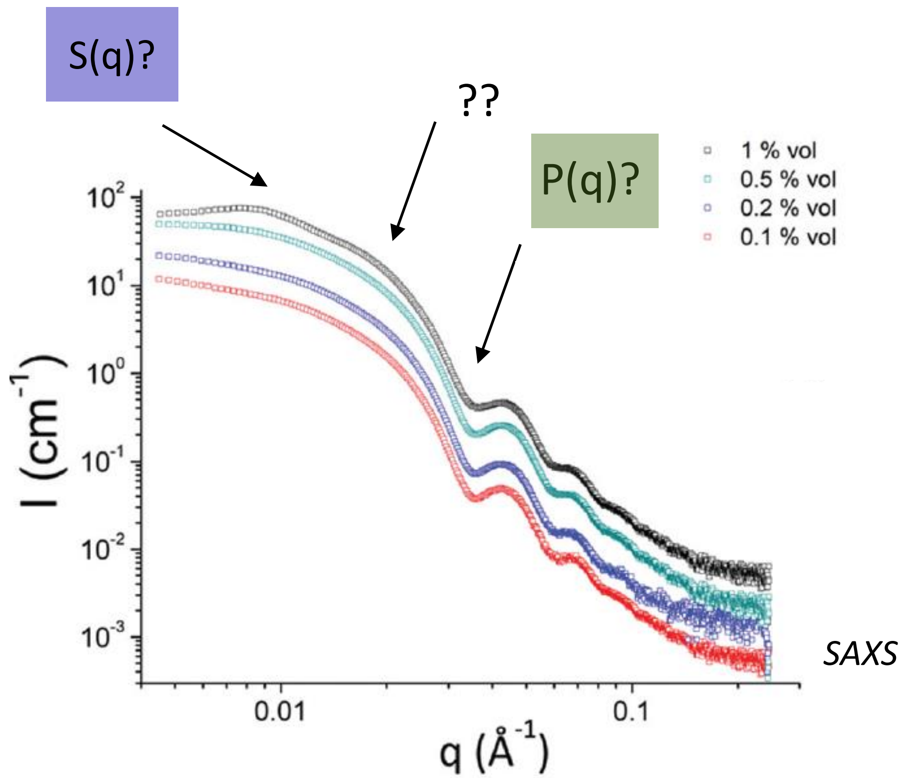

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S. Issa *et al*, Soft Matter, **2021**, *17*, 6552-6565

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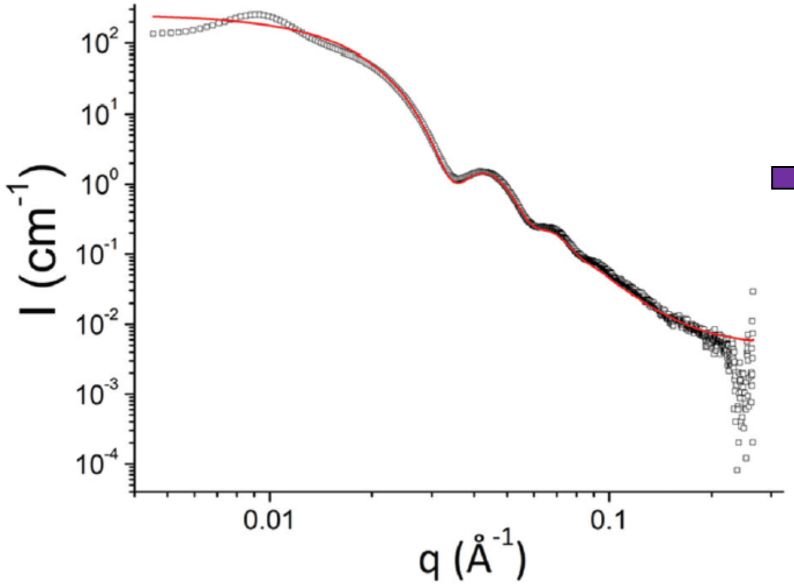

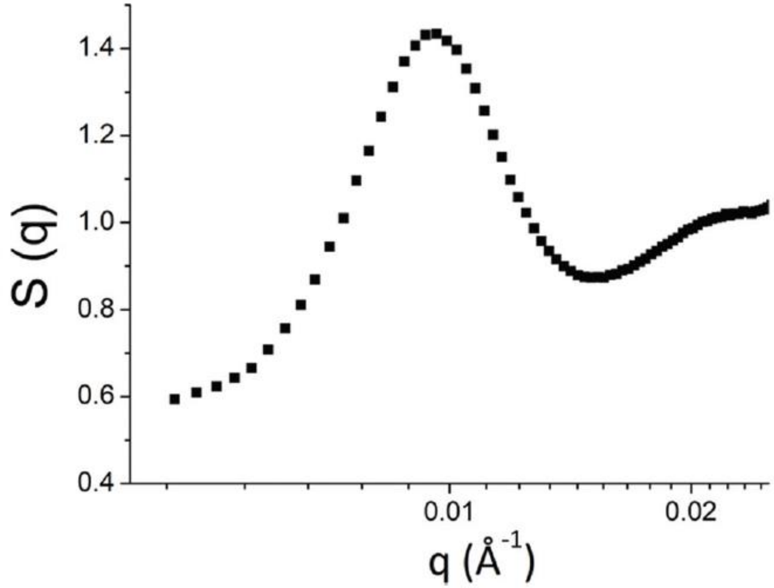

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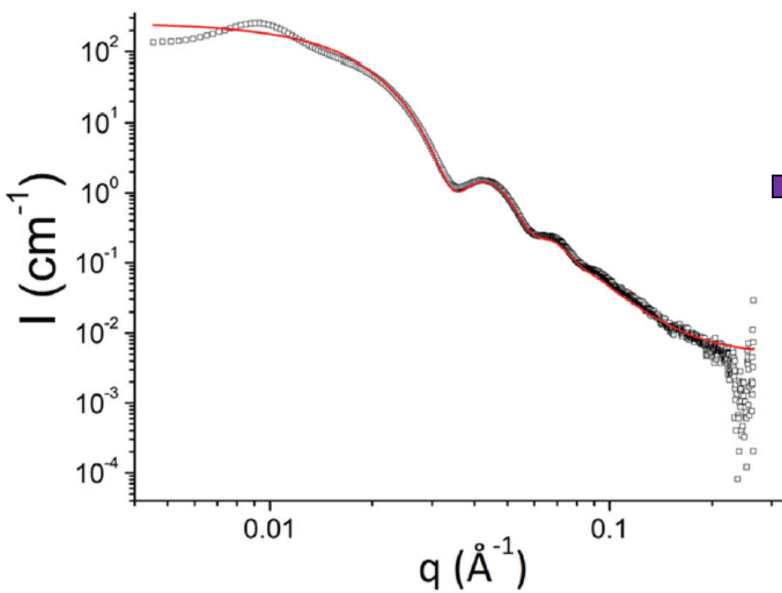
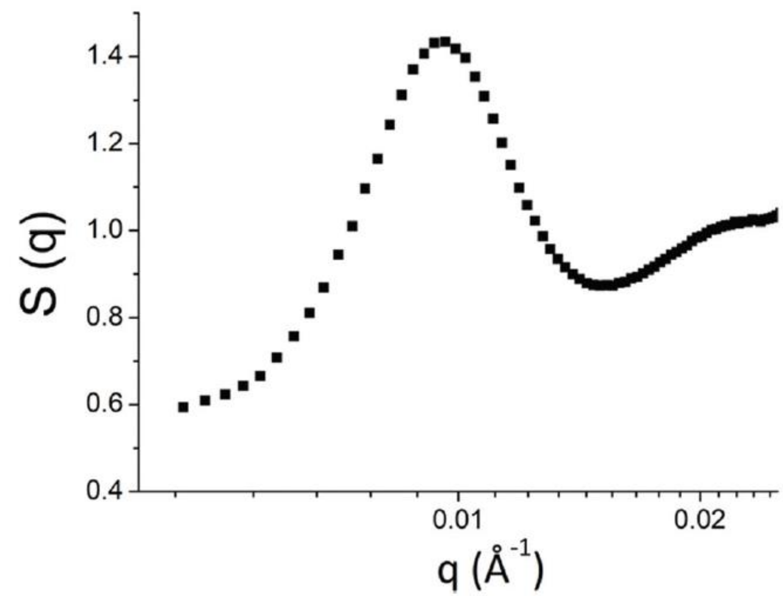


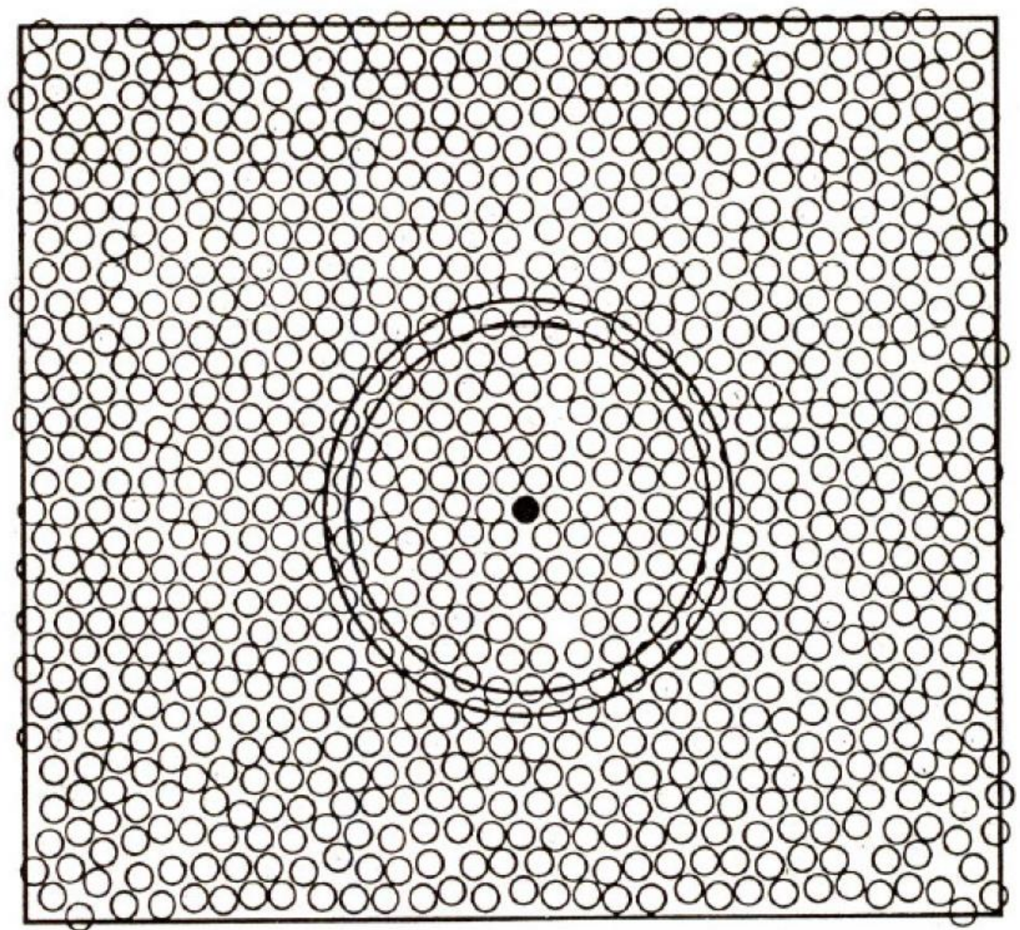


P(q) : usually plotted in log-log

S(q) : usually plotted in lin-lin

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

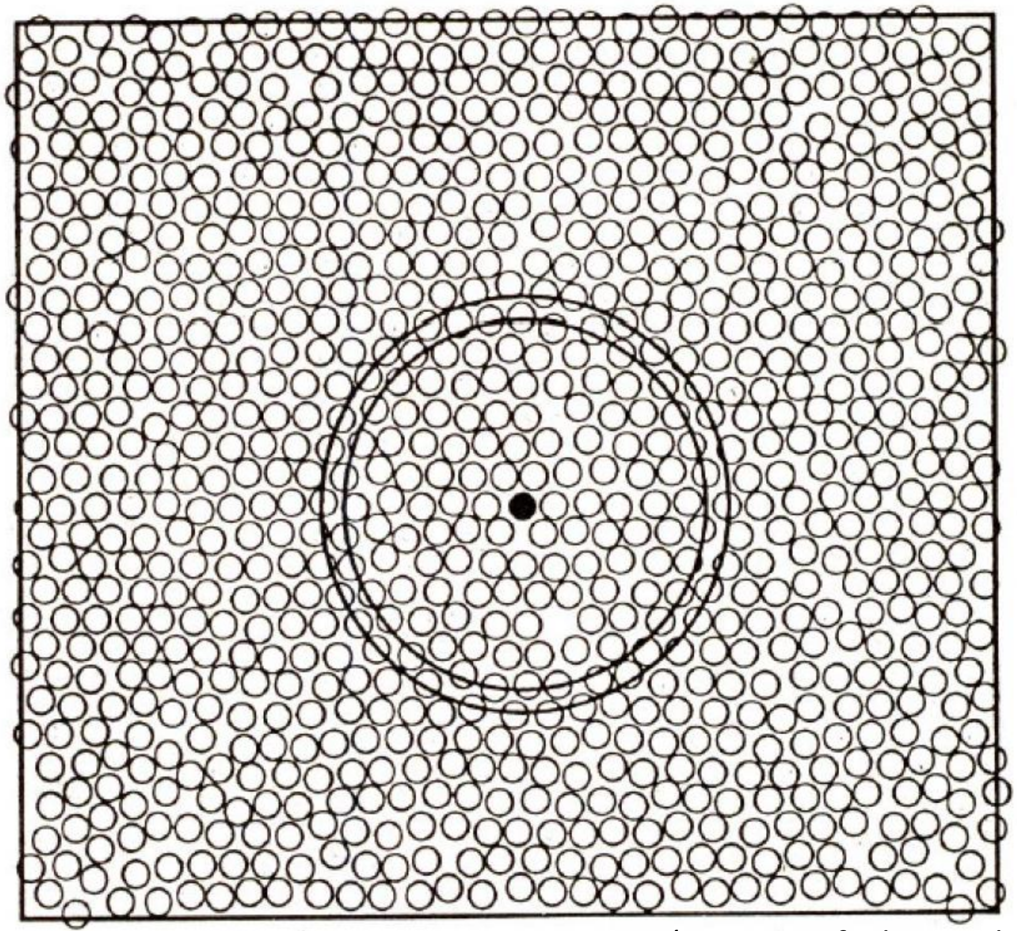
Link between S(q) and correlation function *g(r)*



(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)*

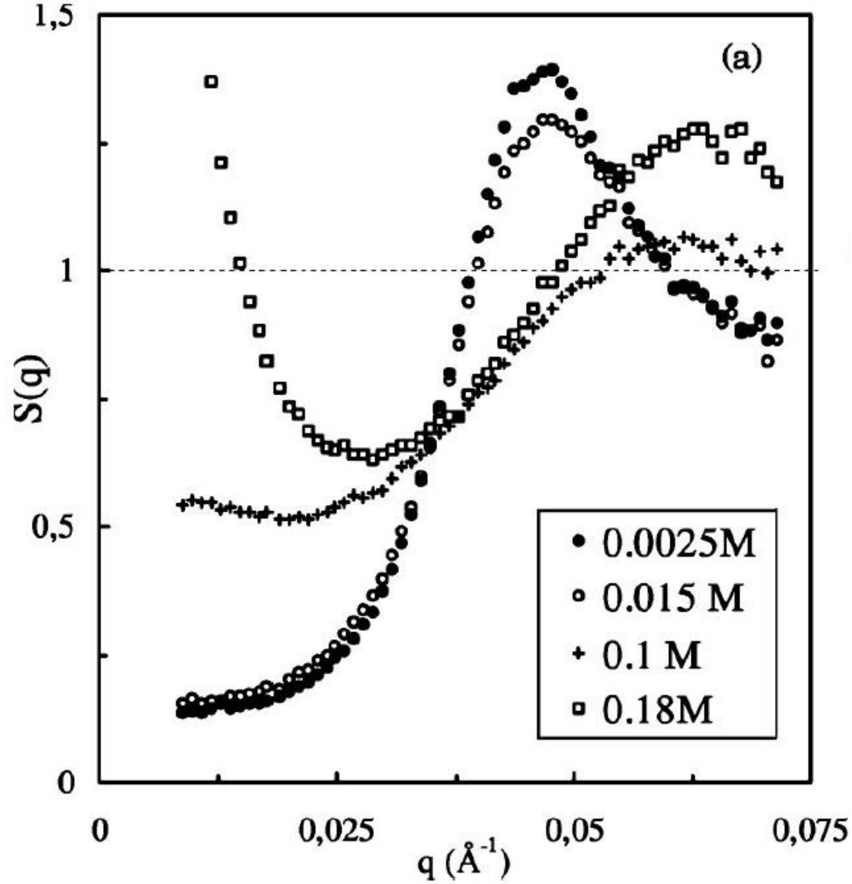


(courtesy of a lecture by J.S. Pedersen)

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

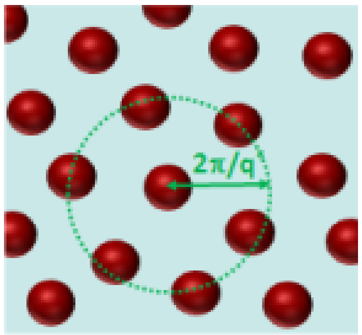
S(q) with hands : from repulsions to attractions…

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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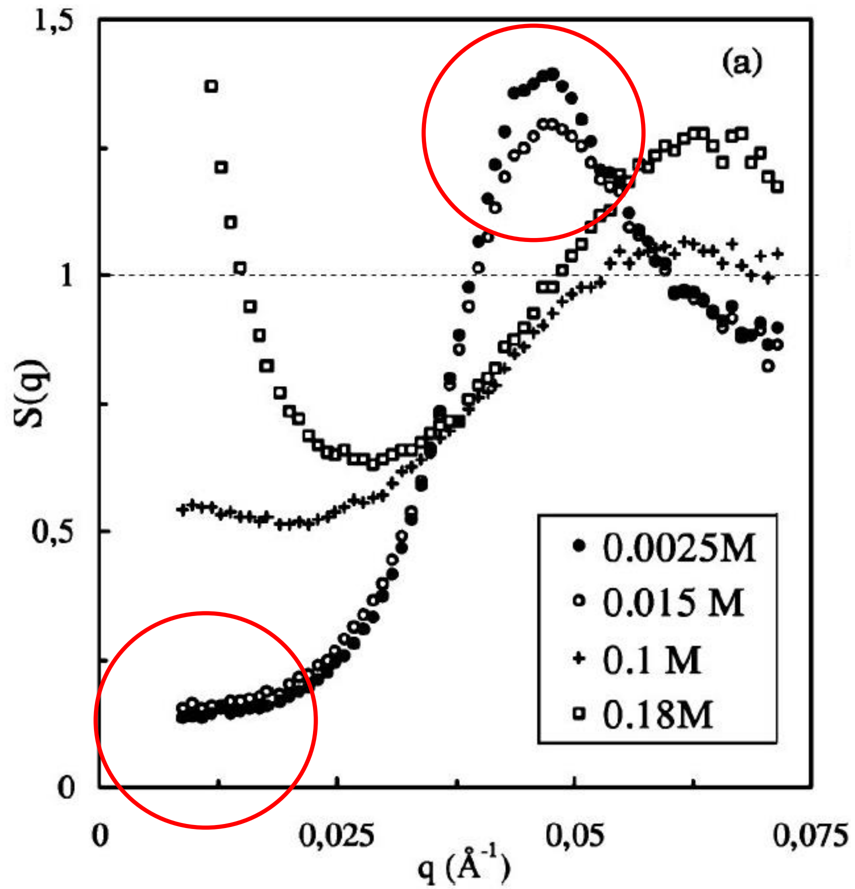

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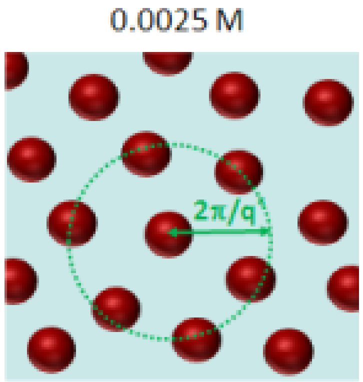

→ Strong correlation peak

→ Low intensity at low q

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

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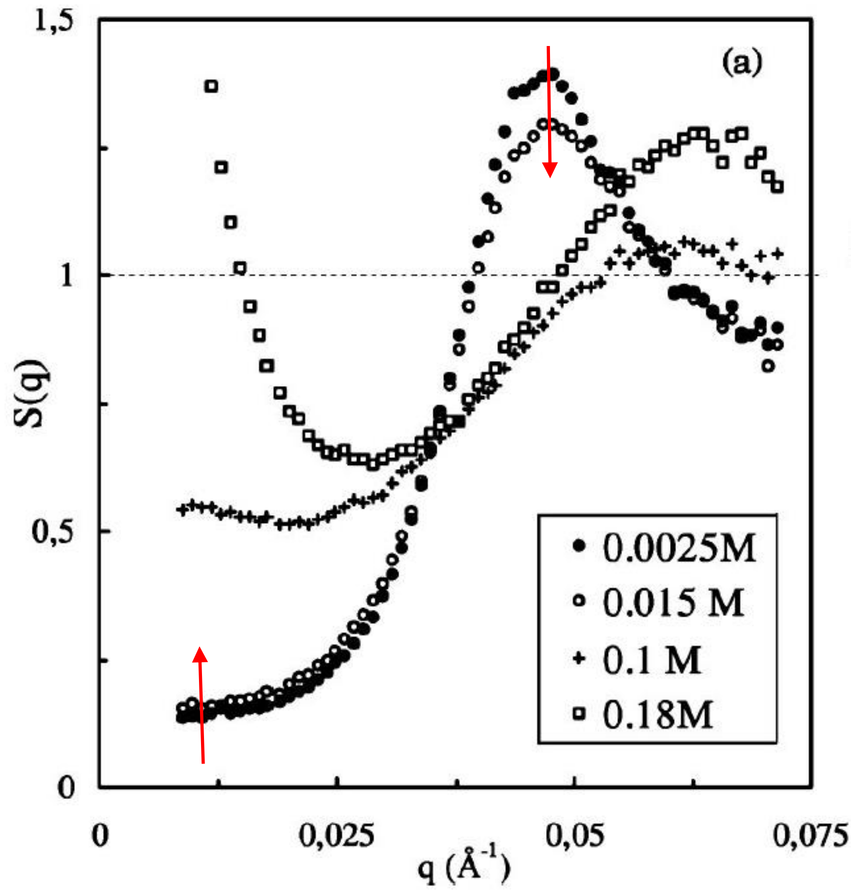

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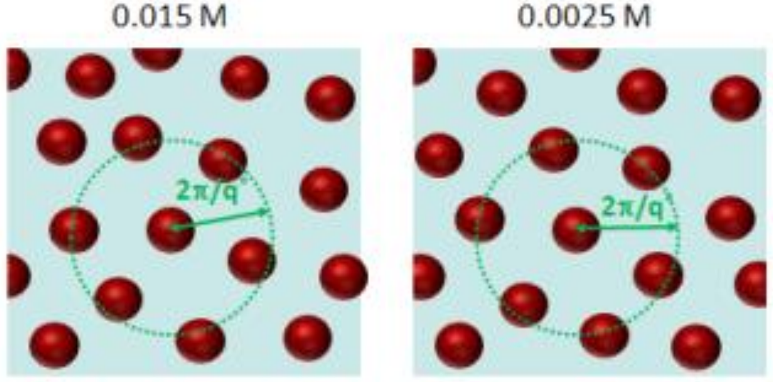

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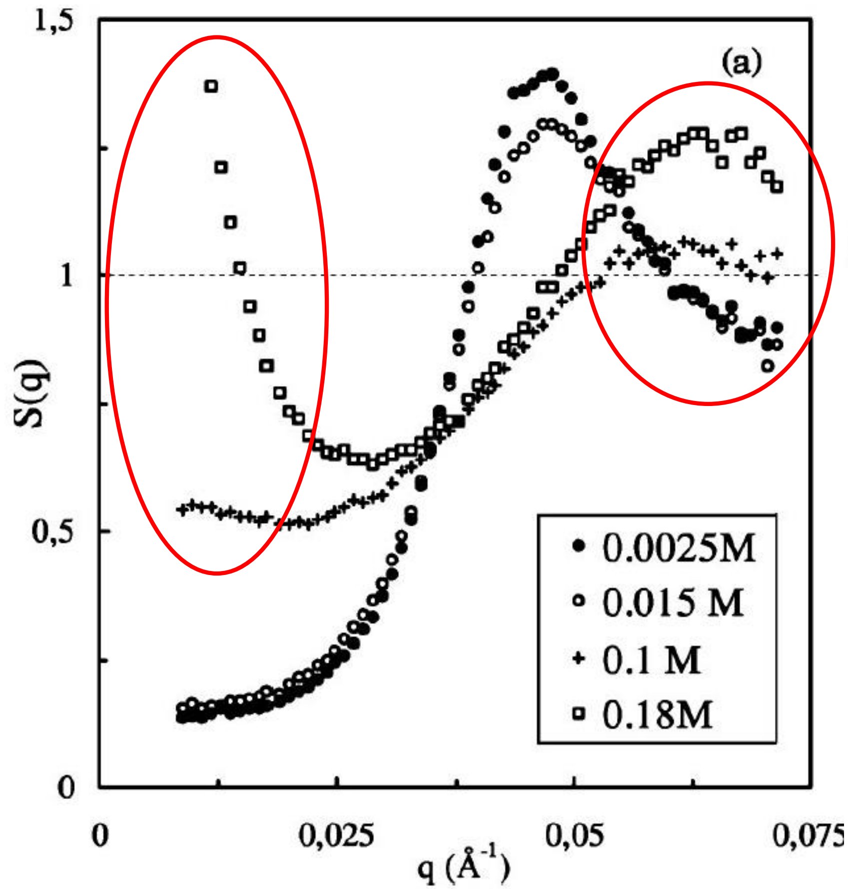
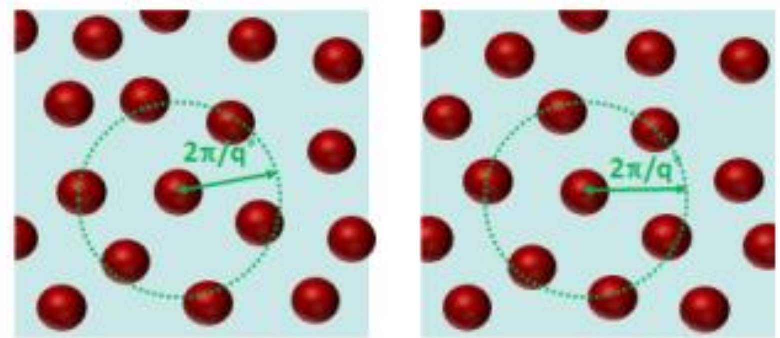


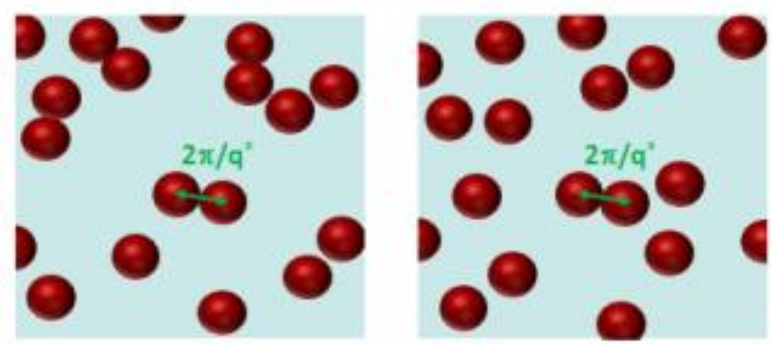
Low salinity : electrosatic repulsions

0.015 M 0.0025 M



Addition of salt :screening repulsions

0.18 M 0.1 M



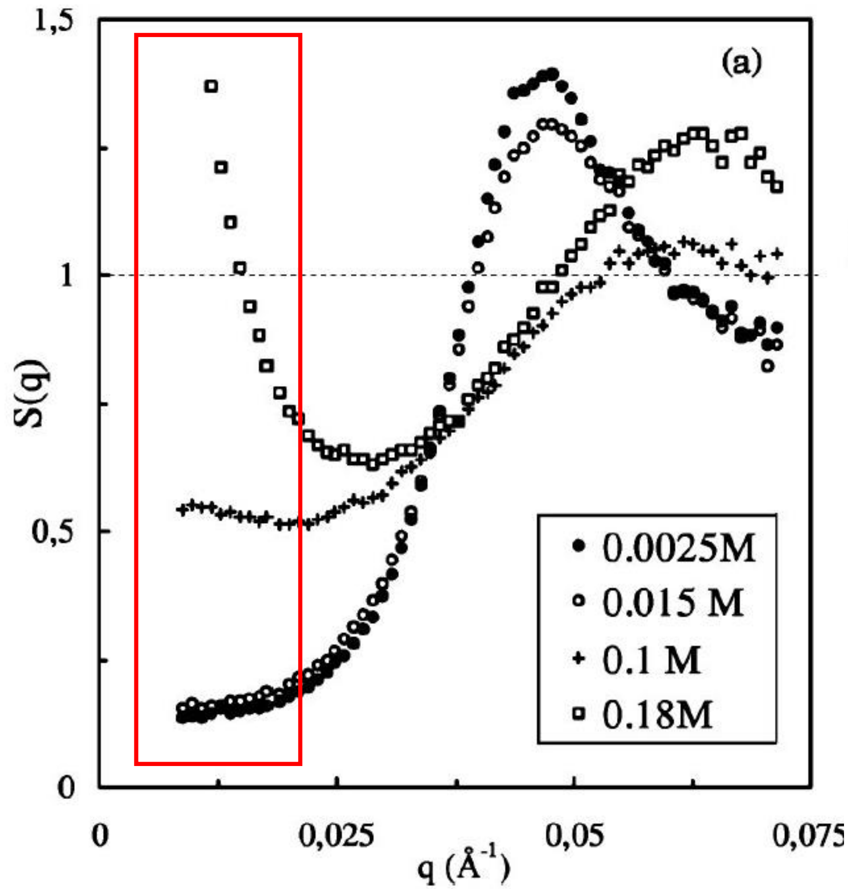
→ Progressive increase of intensity at low q

→ « contact peak »

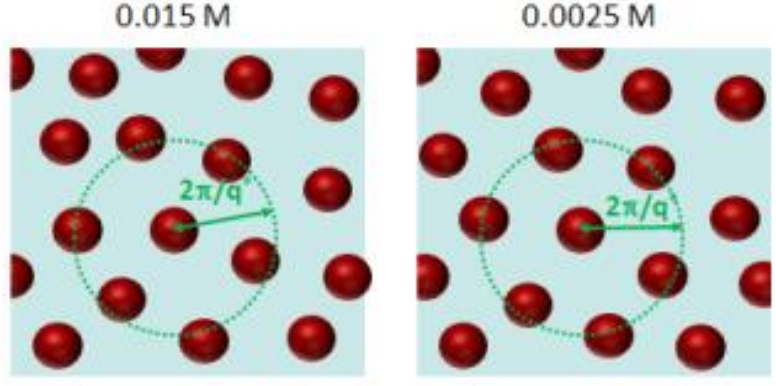
F. Cousin *et al*, *Phys. Rev. E*, **2003**, *68(2)*, 021405

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

Progressive addition of salt on an electrostatically stabilized colloidal suspension



Low salinity : electrosatic repulsions



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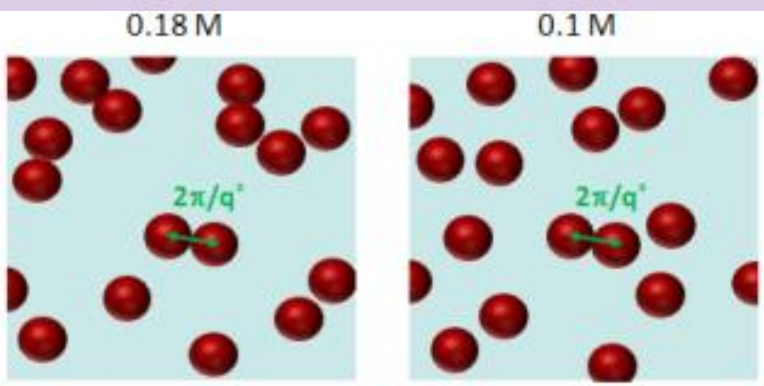


➢ **Informations at low q ?**

Isothermal compressibility χ and second virial coefficient A_2

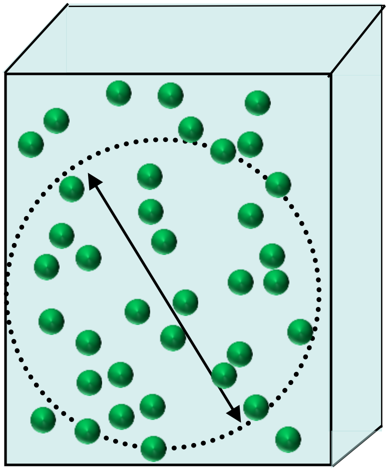
From statistical physics :

isothermal compressibility

Pair correlation function

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

Osmotic pressure



Density fluctuations at large scale (q→ 0)

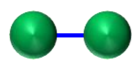
$$\left[\frac{\partial\Pi}{k_B T\partial\rho}\right]_T = \frac{1}{S(0)}$$

Isothermal compressibility χ and second virial coefficient A_2

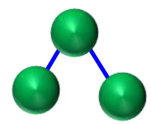
Virial development of osmotic pressure

(Kamerlingh Onnes 1902)

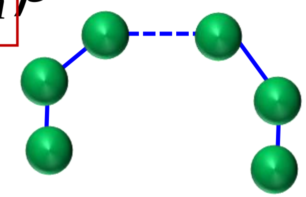
$$\frac{\Pi}{kT} = \rho + \boxed{A_2}\rho^2 + \boxed{A_3}\rho^3 + \ldots \boxed{A_n}\rho^n$$



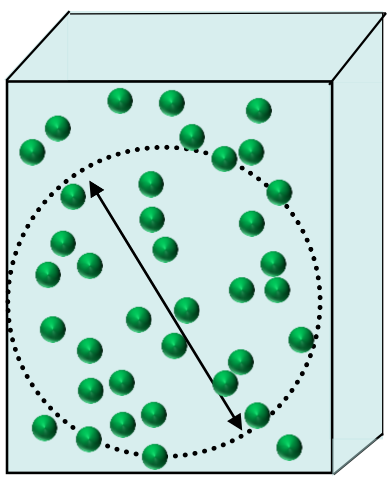
2-body correlations



3-body correlations



n-body correlations



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

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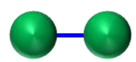

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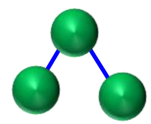

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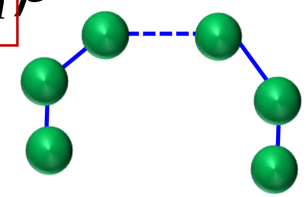

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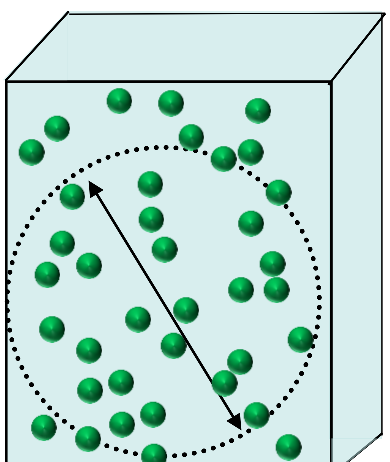

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In weakly and/or dilute systems

One can show that :

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

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

Isothermal compressibility χ and second virial coefficient A_2

Virial development of osmotic pressure

(Kamerlingh Onnes 1902)

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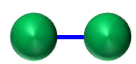

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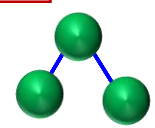

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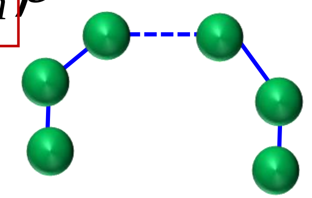

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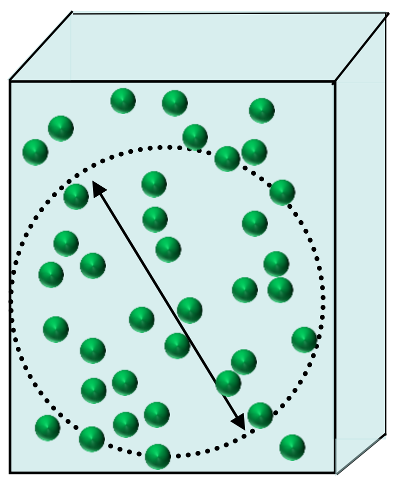

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One can show that :

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

One can show that :

Isothermal compressibility χ and second virial coefficient A_2

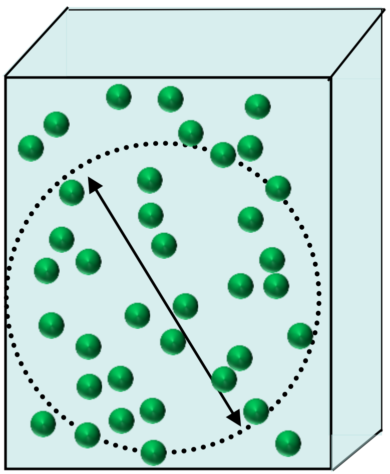
$$I(q) = \Phi\, \Delta\rho^2\, V_{part}\quad P(q).S(q)$$

Determination of A_2 : several measurements at concentrations at low q

At low q :

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

Zimm Plot



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

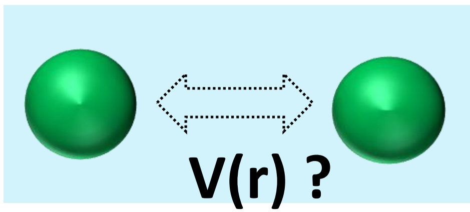
In weakly and/or dilute systems

One can show that :

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

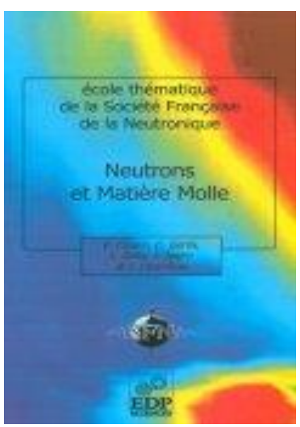
Link between V(r), g(r) and S(q)

How to go further in descriptions of interactions ?



g(r) – S(q)

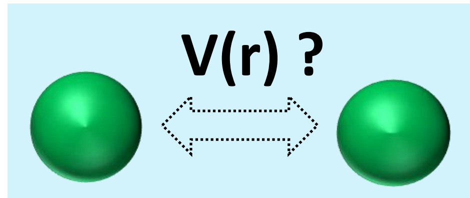
Simulations, integral equations

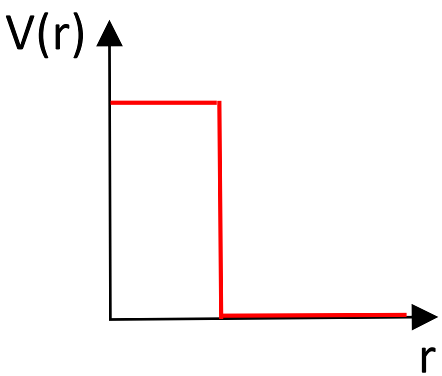


See, for example

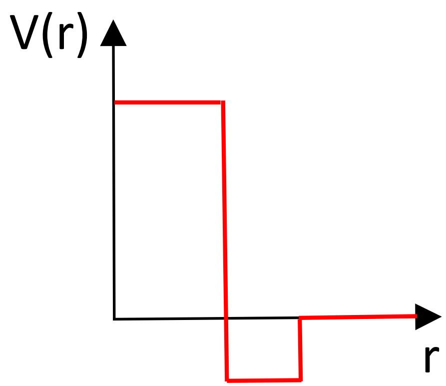
Chapter from Luc Belloni *(in french)*

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

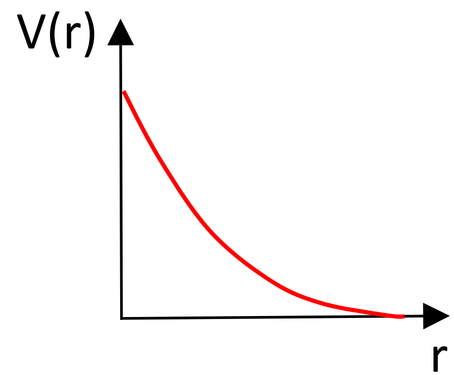




Hard spheres



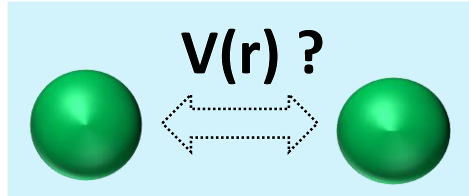
Sticky Hard sheres

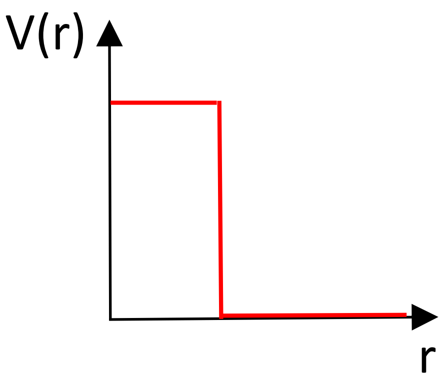


Screened Coulombian Potential
(Debye Hückel)

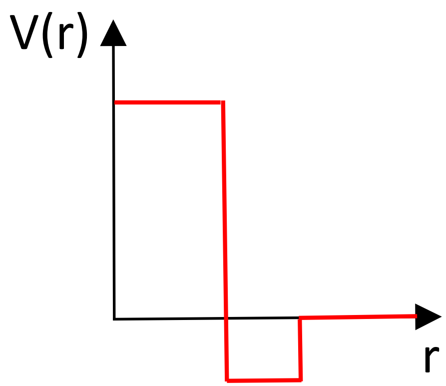
Implemented in SasView

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

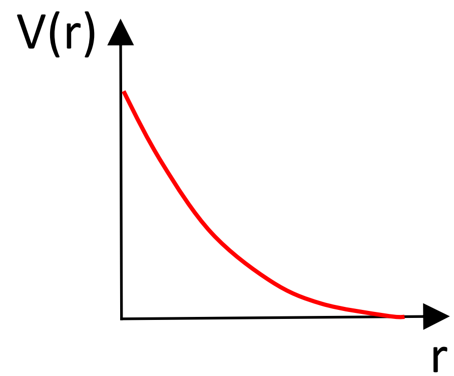




Hard spheres



Sticky Hard sheres



Screened Coulombian Potential
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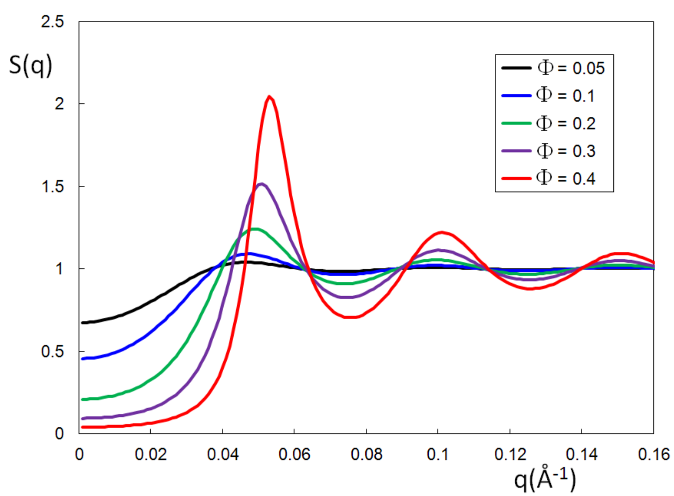
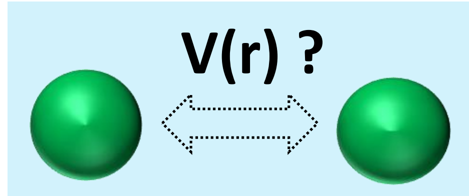
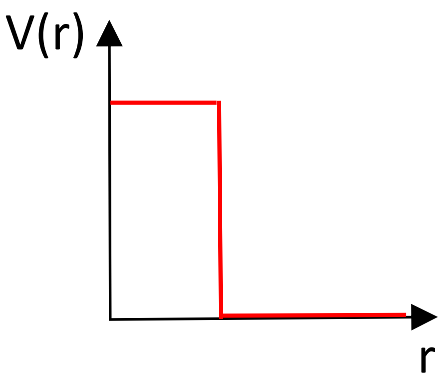


Percus-Yevick : analytical form

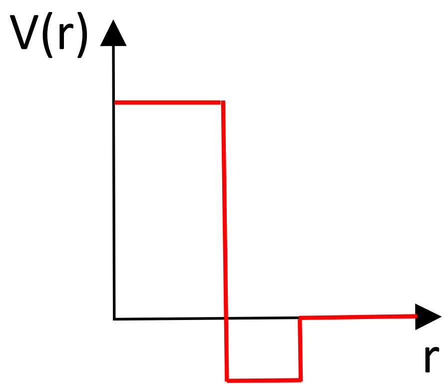
Implemented in SasView

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

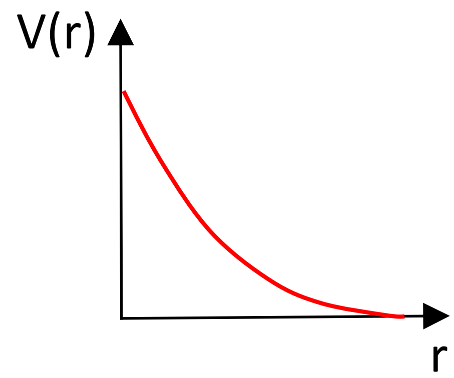




Hard spheres



Sticky Hard sheres



Screened Coulombian Potential
(Debye Hückel)

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

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

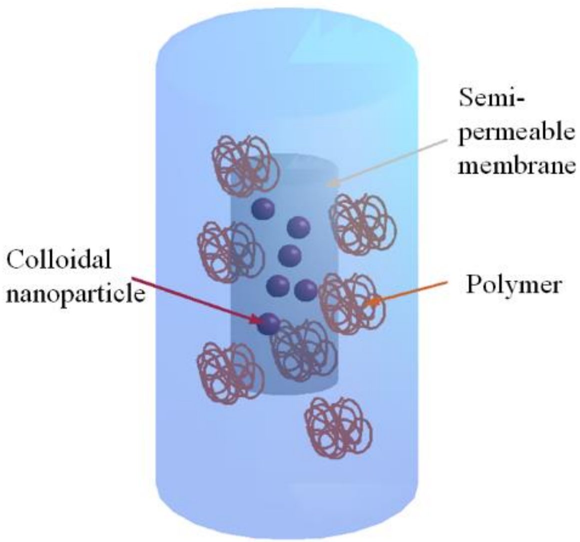
$$\kappa^2 = \frac{2e^2 I}{\varepsilon\varepsilon_0 kT}$$ with $$I = \frac{1}{2}\sum_i c_i z_i^2$$

Hayter-Penfold : many parameters!

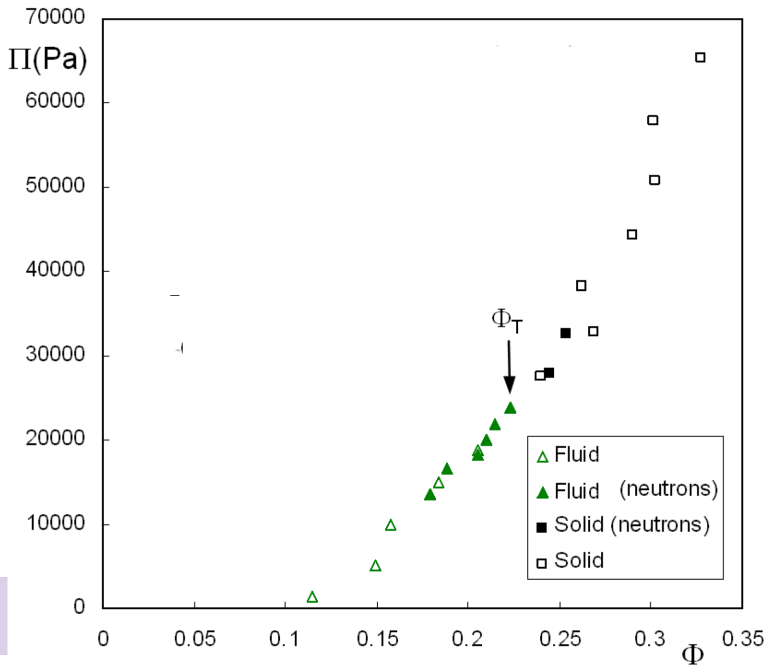
Implemented in SasView

Evolution of structure factor with concentration in highly repulsive systems

Silica spheres in aqueous suspensions



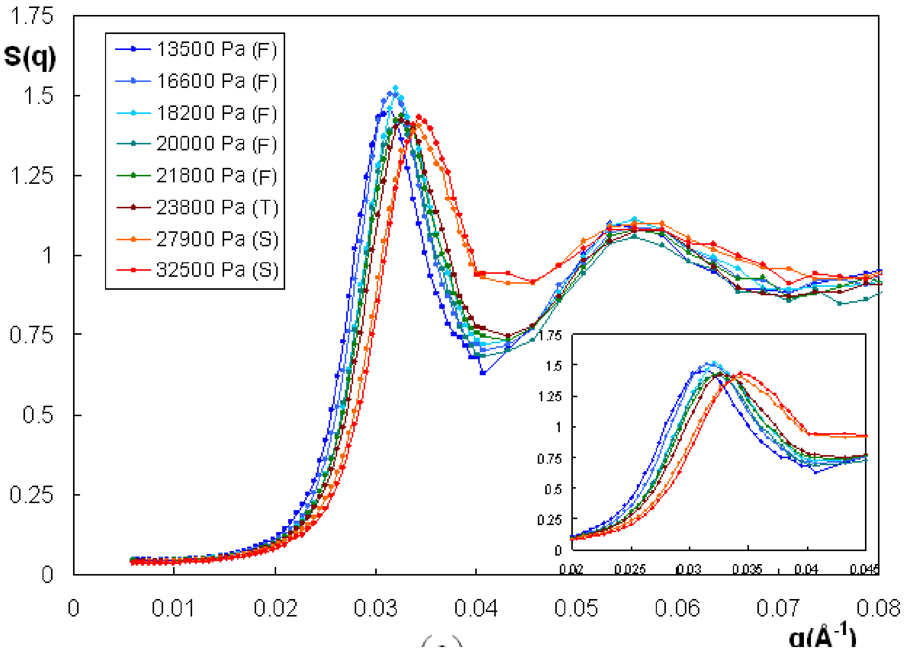
Osmotic stress : variation of Π at fixed salinity

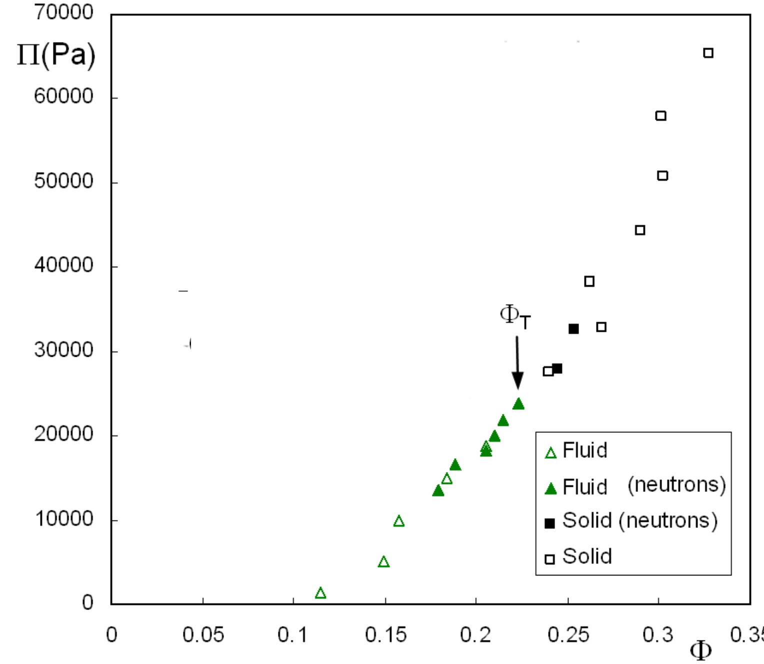


A.S. Robbes *et al*, *Braz. J. of Physics*, **2009**, *37(1A)*, 156-162

Evolution of structure factor with concentration in highly repulsive systems

Silica spheres in aqueous suspensions





- Different structure for liquid and solid glassy samples

A.S. Robbes *et al*, *Braz. J. of Physics*, **2009**, *37(1A)*, 156-162

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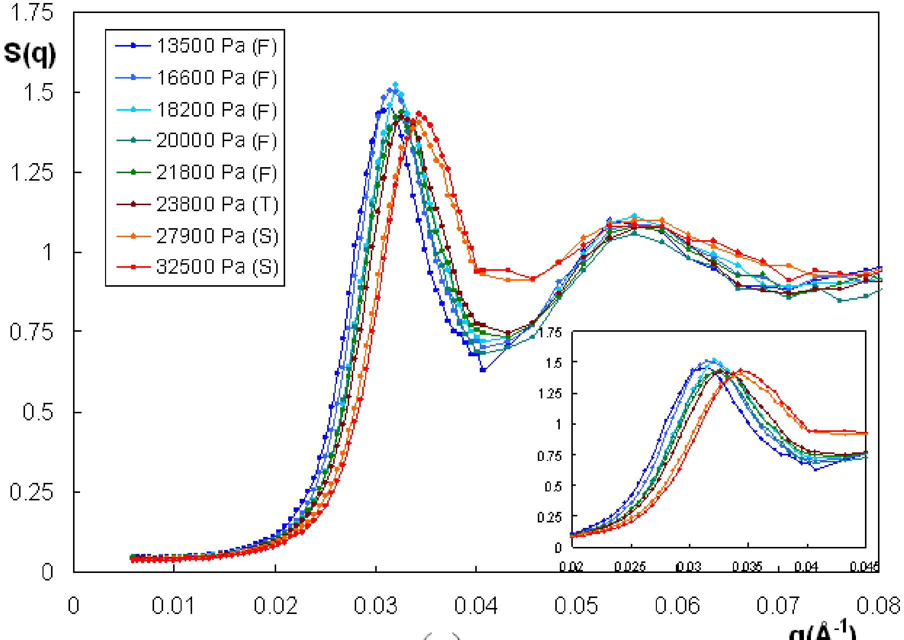
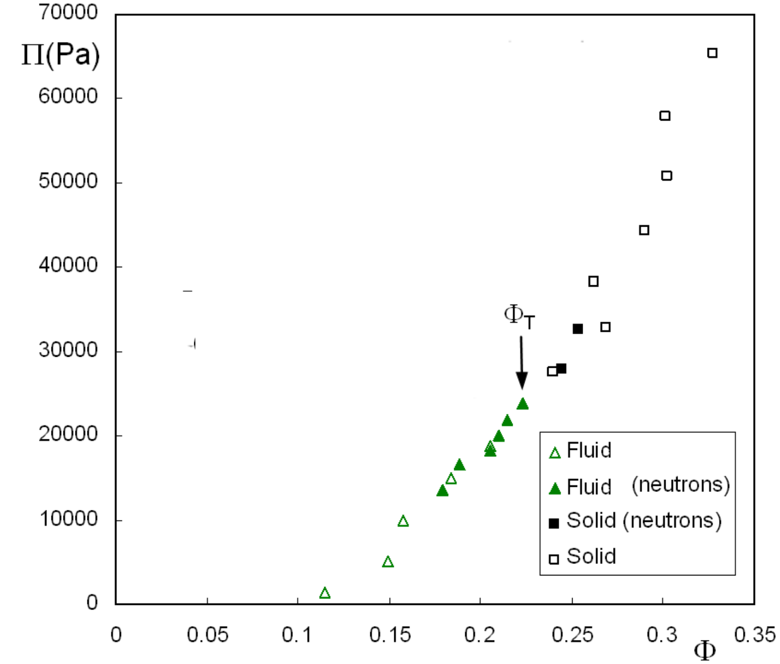
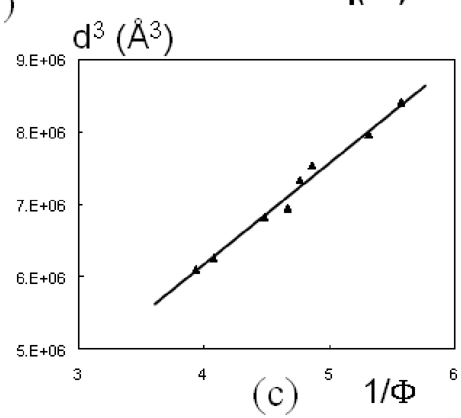


(a)





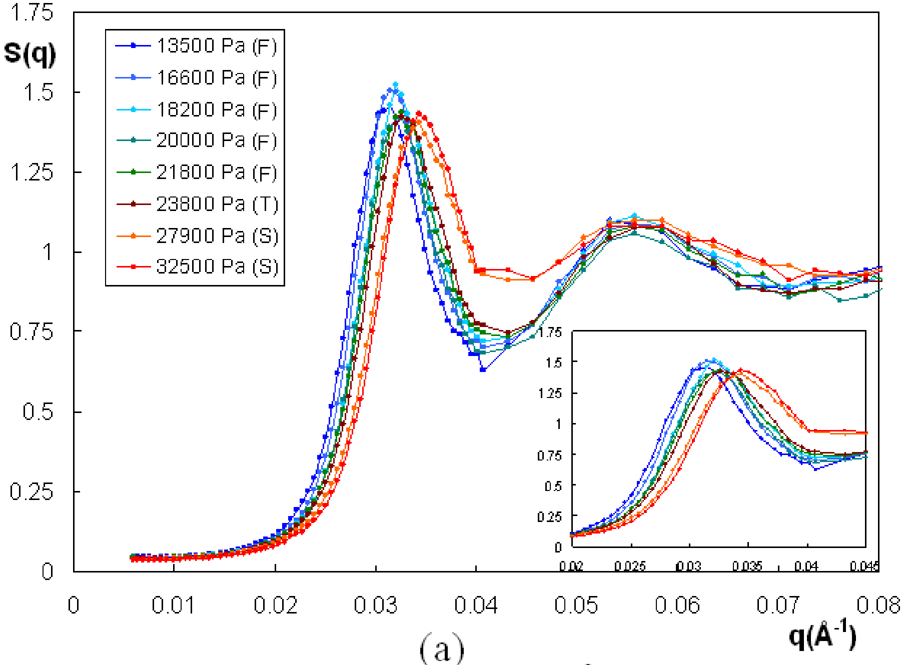
(c)

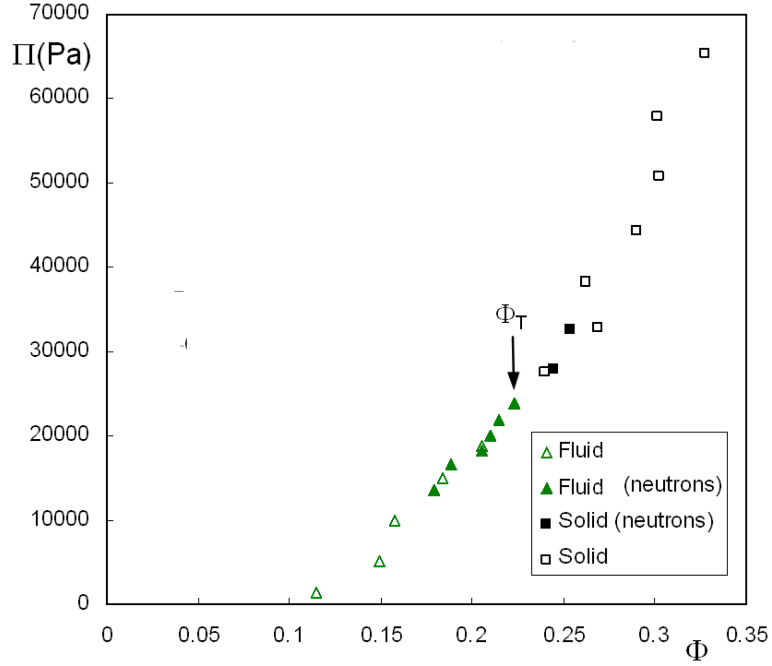
- ➢ Different structure for liquid and solid glassy samples
- ➢ Dilution law

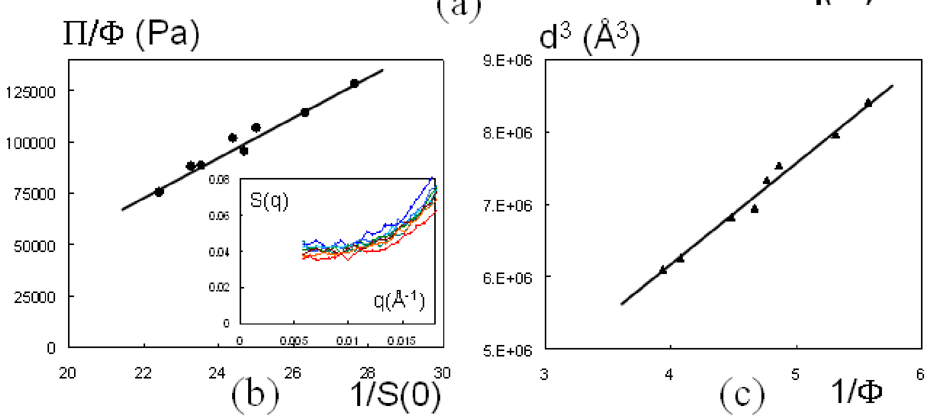
A.S. Robbes *et al*, *Braz. J. of Physics*, **2009**, *37(1A)*, 156-162

Evolution of structure factor with concentration in highly repulsive systems

Silica spheres in aqueous suspensions





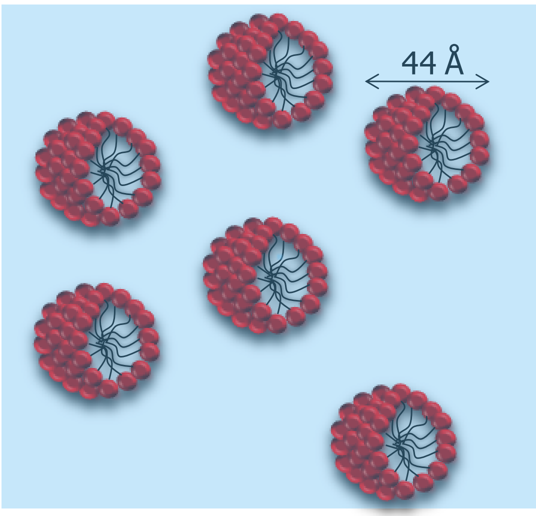


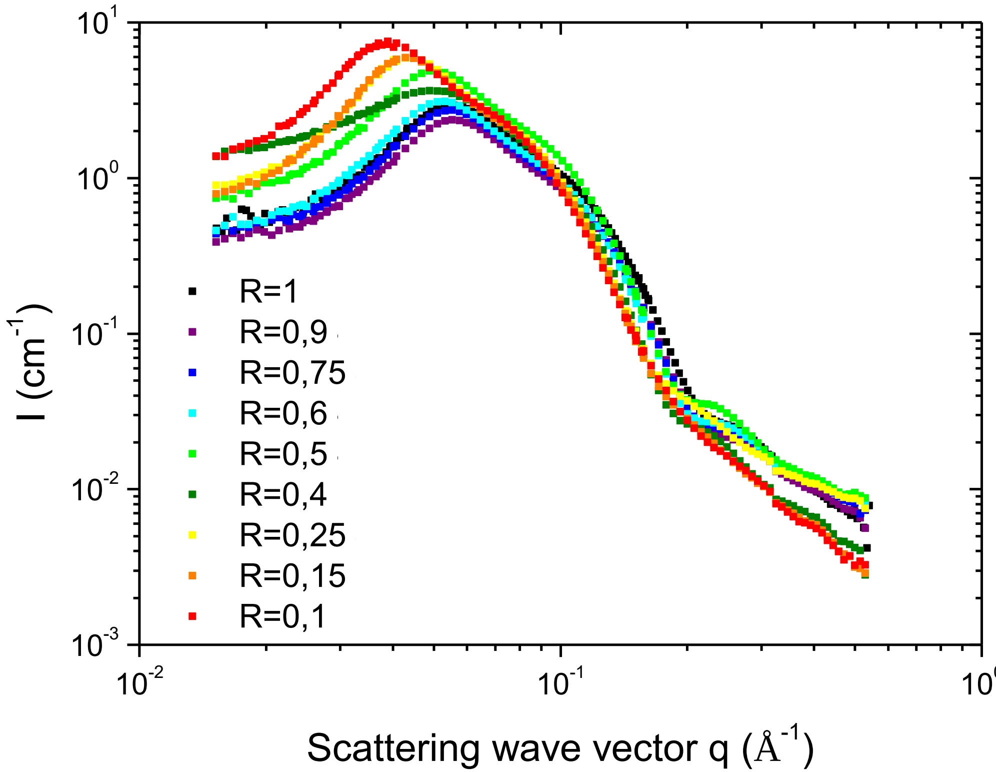
- Different structure for liquid and solid glassy samples
- Dilution law
- Link between S(0) and Π

A.S. Robbes *et al*, *Braz. J. of Physics*, **2009**, *37(1A)*, 156-162

Interacting micelles of surfactants

Aqueous mixture of stearic acid and 12-hydroxystearic acid at **fixed total concentration of surfactants**





- Be careful : aggregation number (and **form factor**) may change with physico-chemical conditions

De Almeida *et al*, *Molecules*, **2023,** 28(17), *6317*

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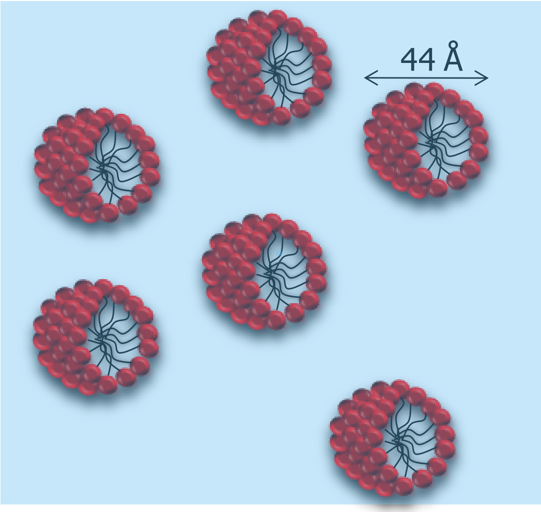
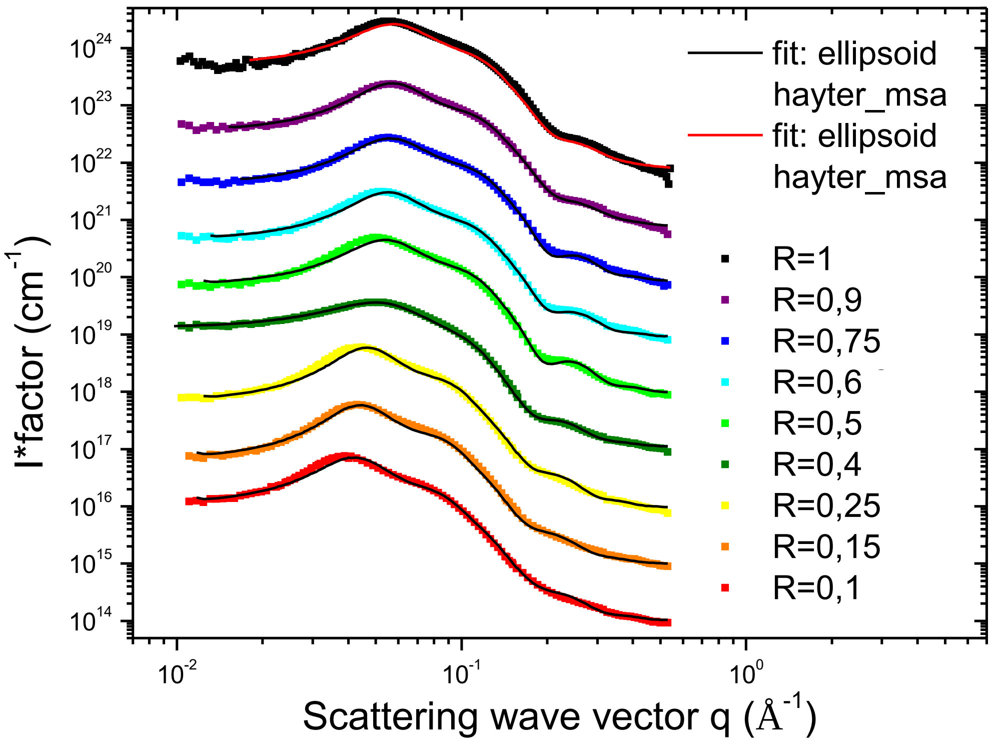


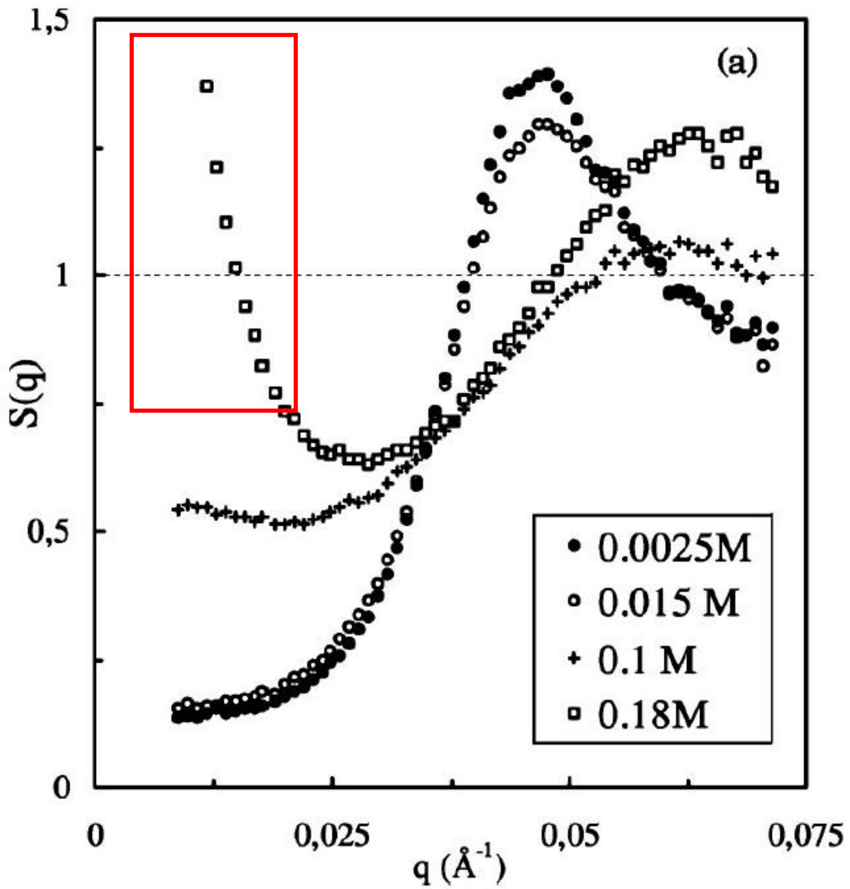


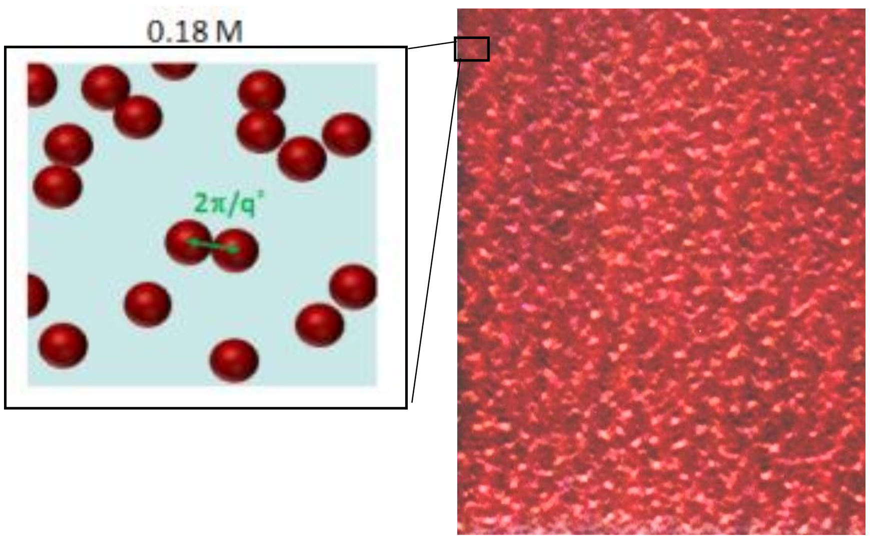
- Be careful : aggregation number (and **form factor**) may change with physico-chemical conditions
- Fitting of structure factor by **Hayter Penfold** is usually sucessful

De Almeida *et al*, *Molecules*, **2023,** 28(17), *6317*

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

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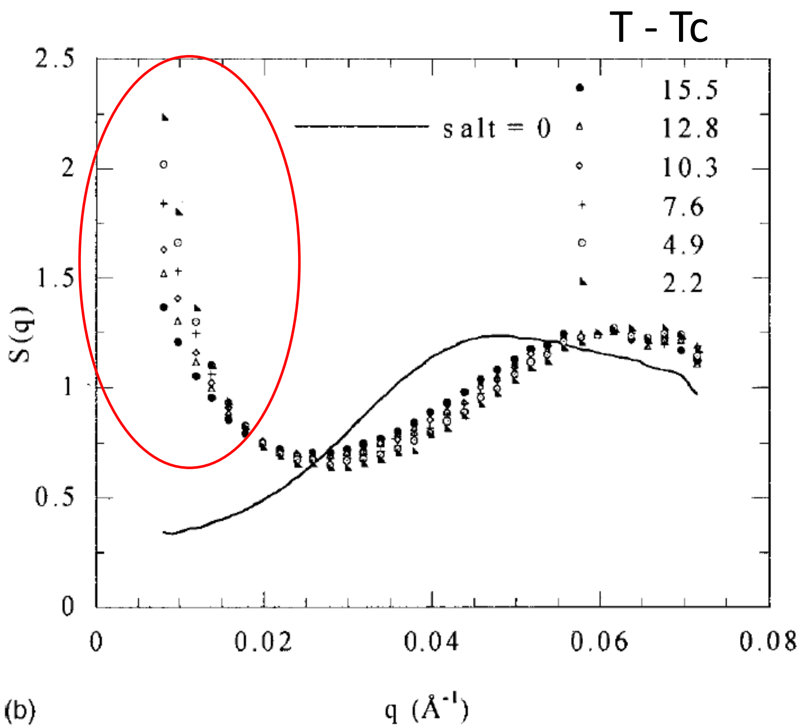
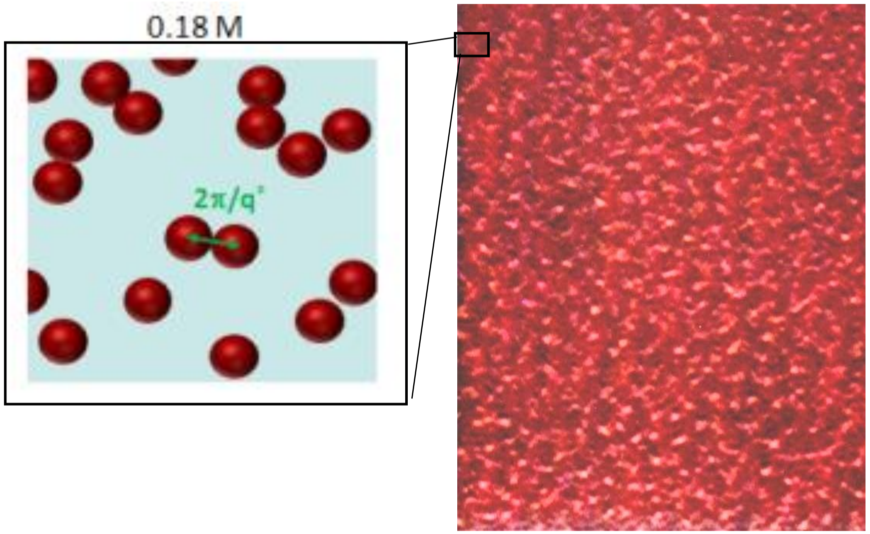




(optical microscopy)

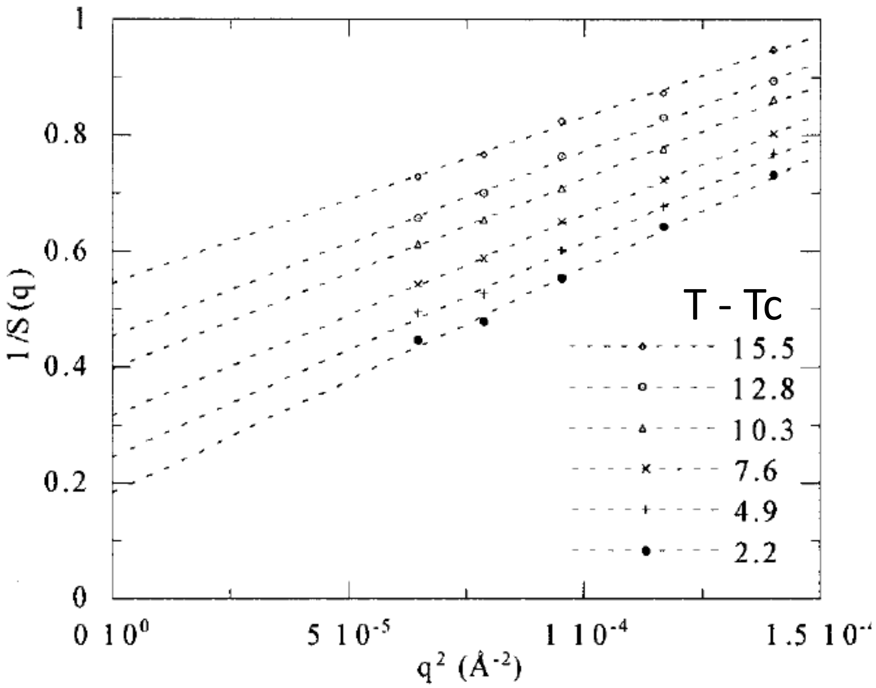
Approach of critial point by temperature at fixed salinity

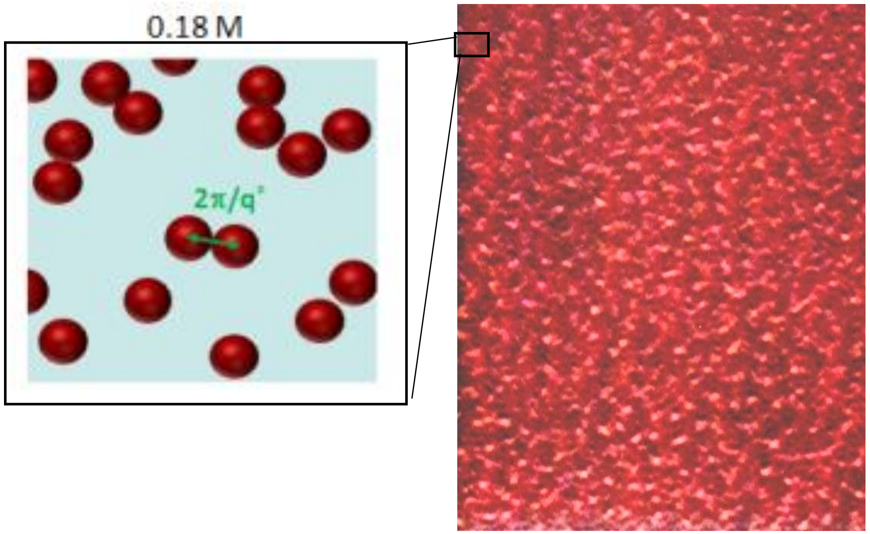
→ Divergence of fluctuations

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





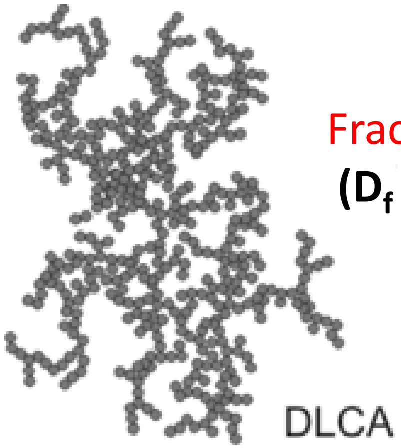
(optical microscopy)

Approach of critial point by temperature at fixed salinity

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

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

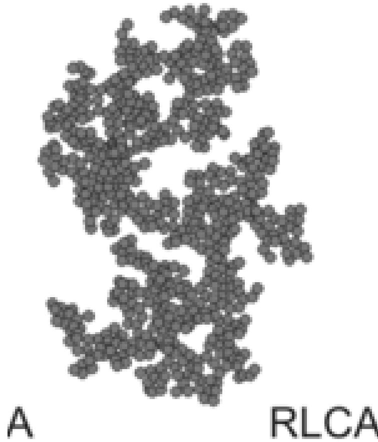
Attractions in colloid : Fractal aggregates



Fractal final structure

(D_f = 1.78)

Diffusion Limited Cluster Aggregation



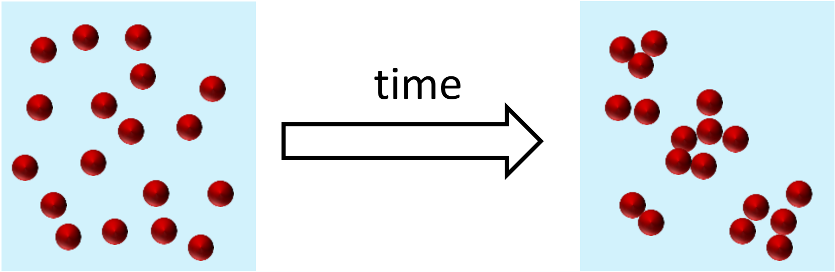
Fractal final structure

(D_f = 2.1)

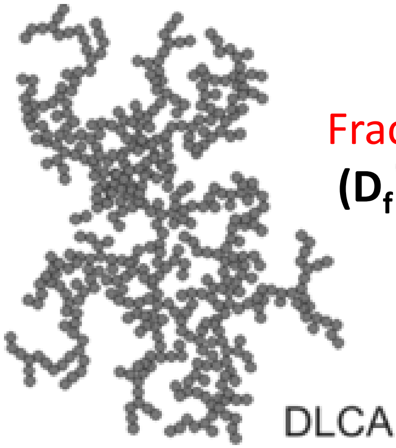
Reaction Limited Cluster Aggregation

<u>2 limit cases of aggregation processes :</u>

(without strong attractions)

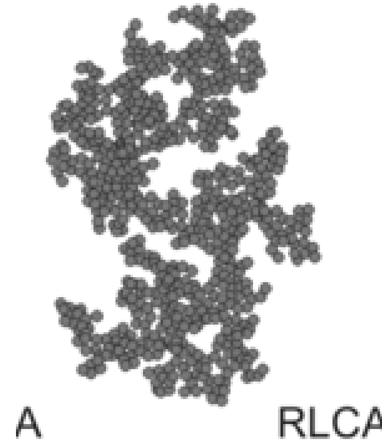


Attractions in colloid : Fractal aggregates



Fractal final structure
(D_f = 1.78)

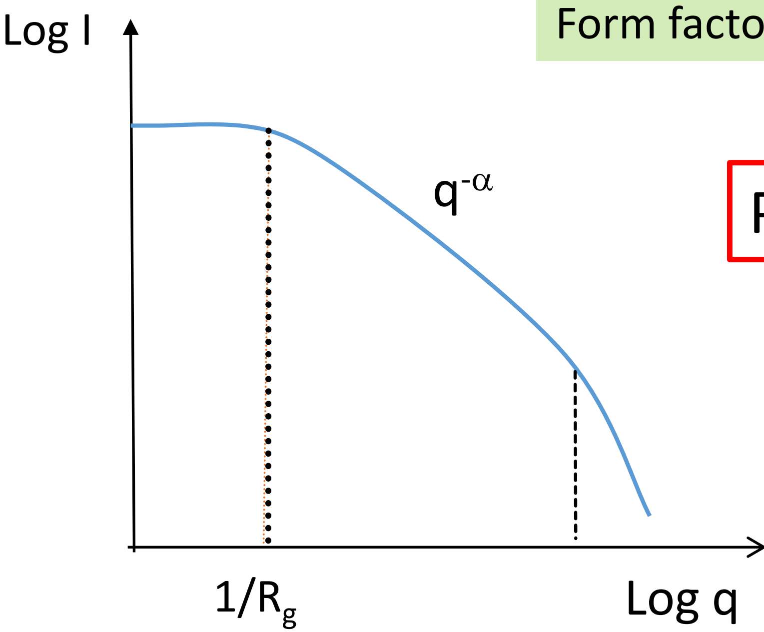
Diffusion Limited Cluster Aggregation



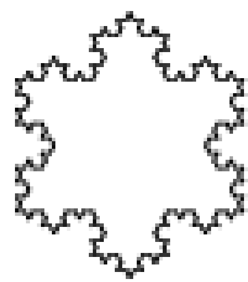
Fractal final structure
(D_f = 2.1)

Reaction Limited Cluster Aggregation

Form factor of a fractal object

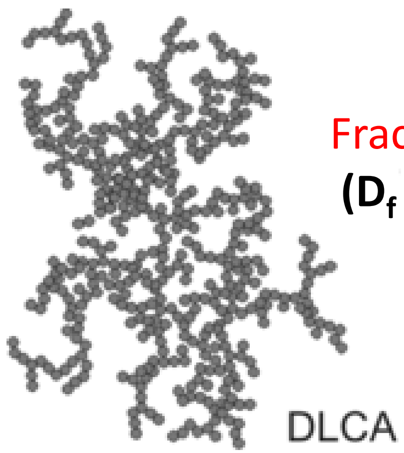


$$\boxed{P(q) \sim q^{-Df}}$$



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

Attractions in colloid : Fractal aggregates



Fractal final structure
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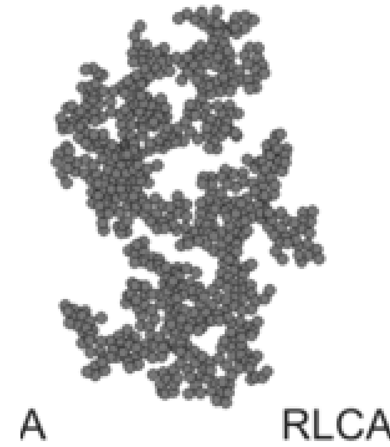
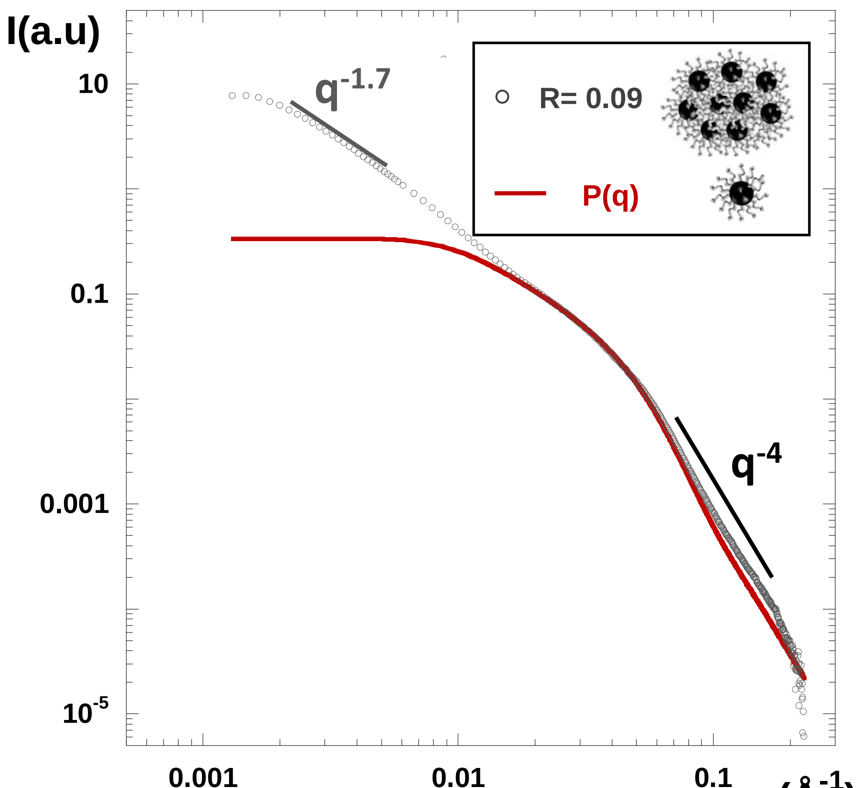
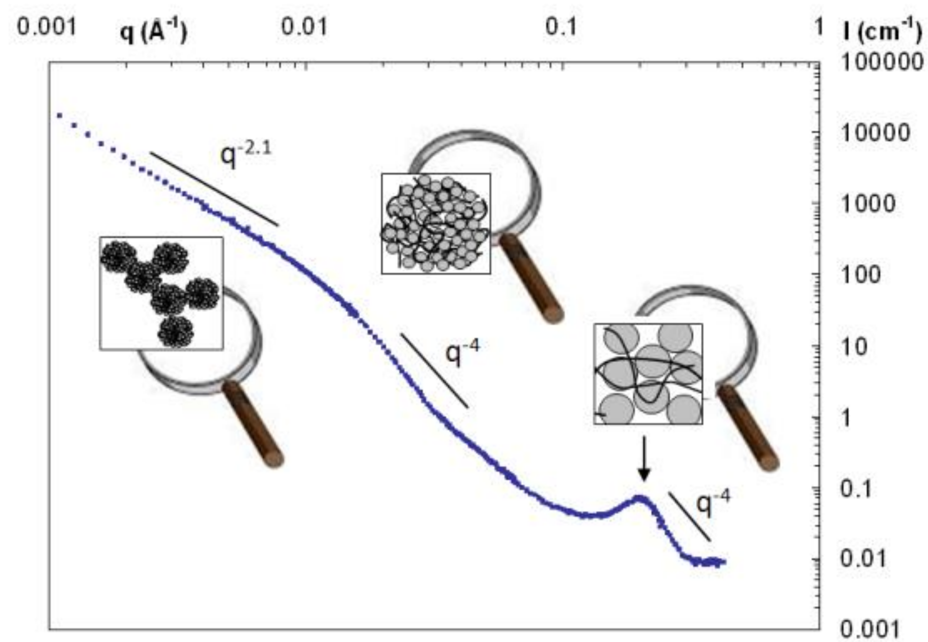
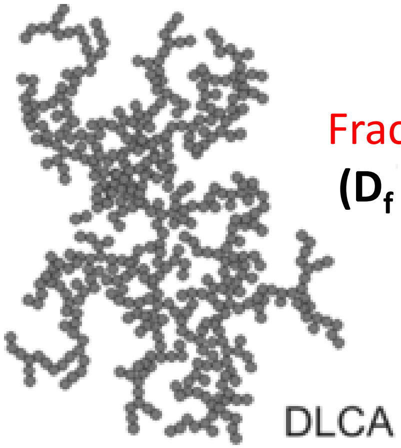


Fractal final structure
(D_f = 2.1)



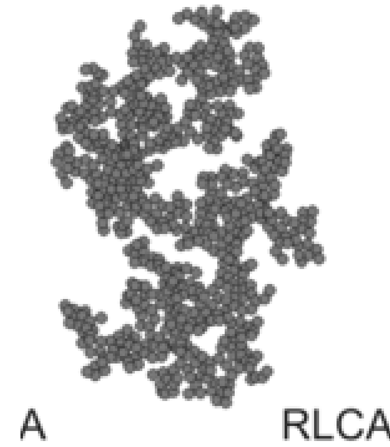


Attractions in colloid : Fractal aggregates



Fractal final structure

(D_f = 1.78)



Fractal final structure

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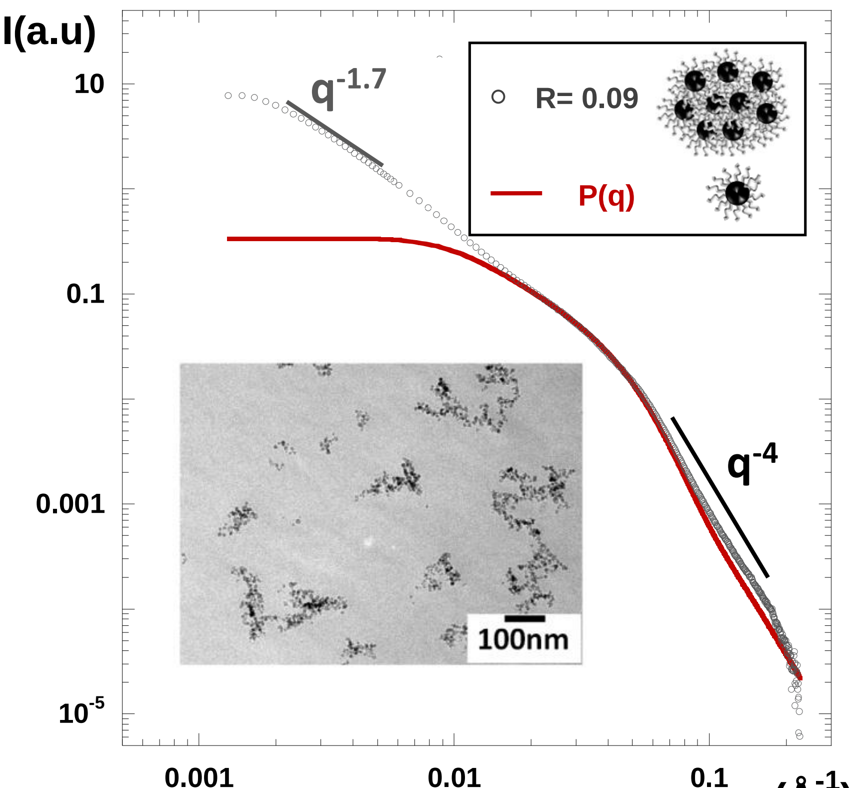
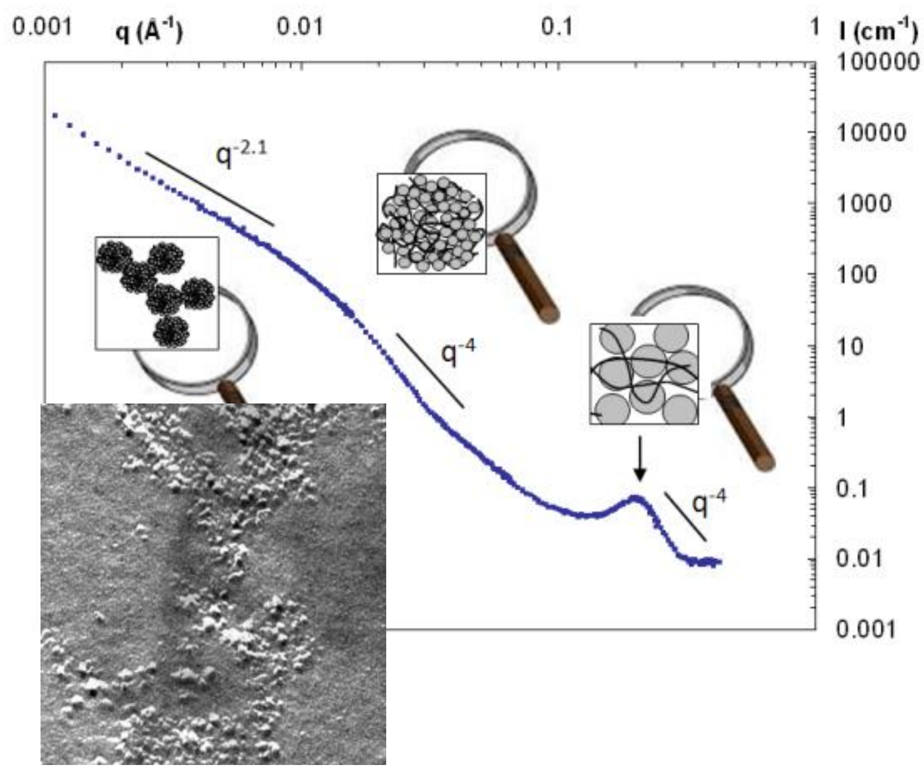
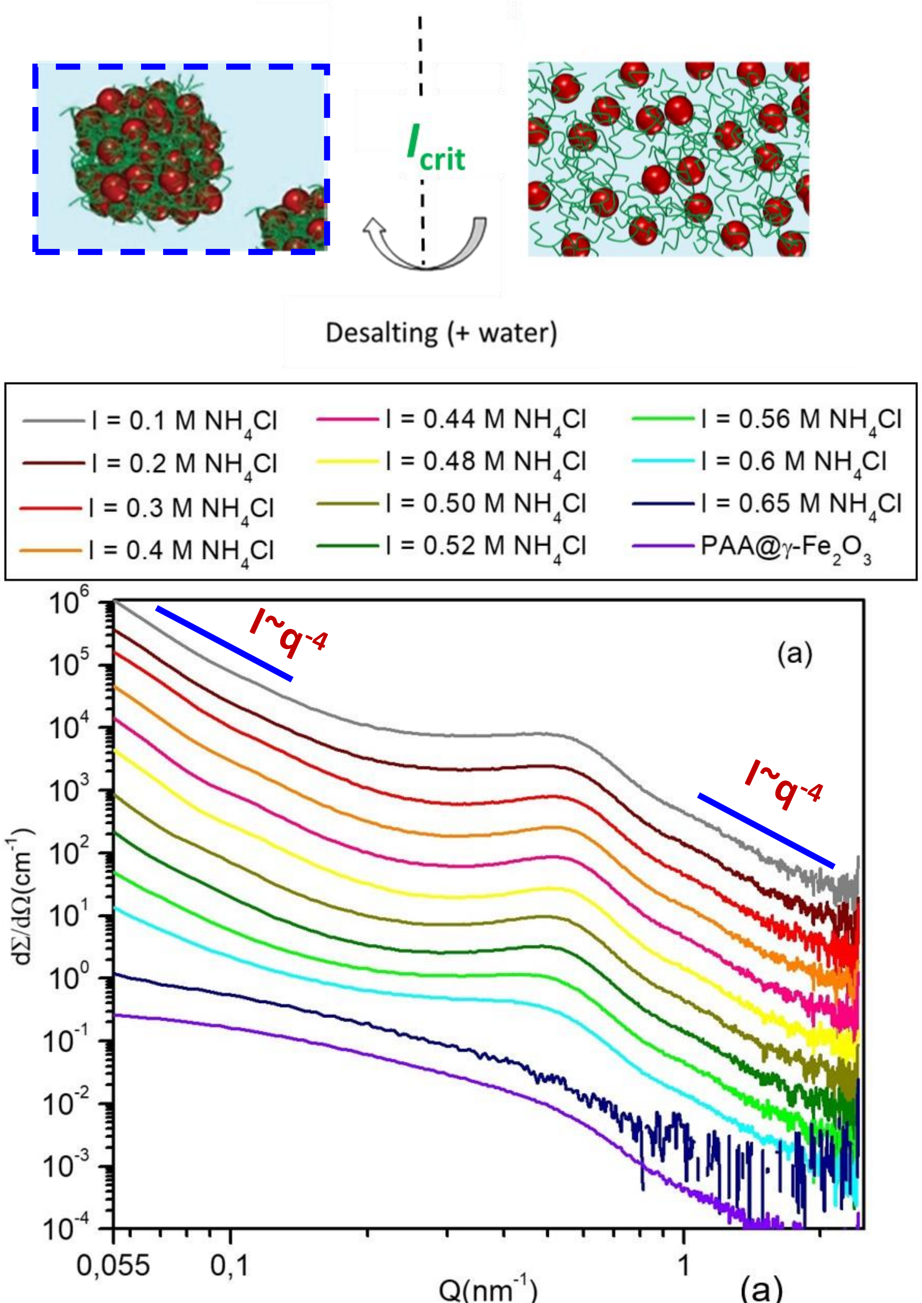


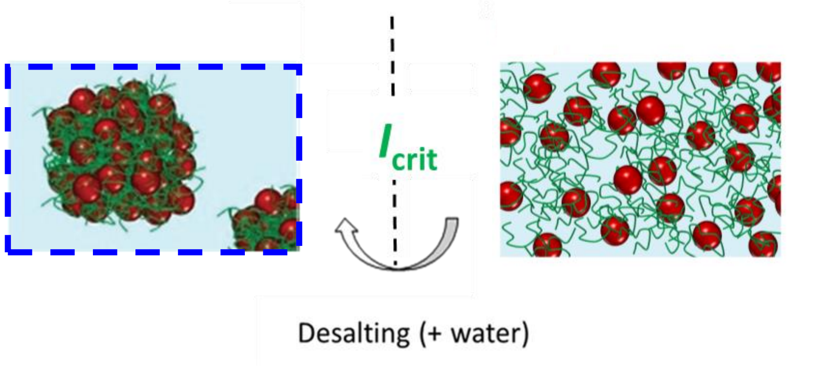


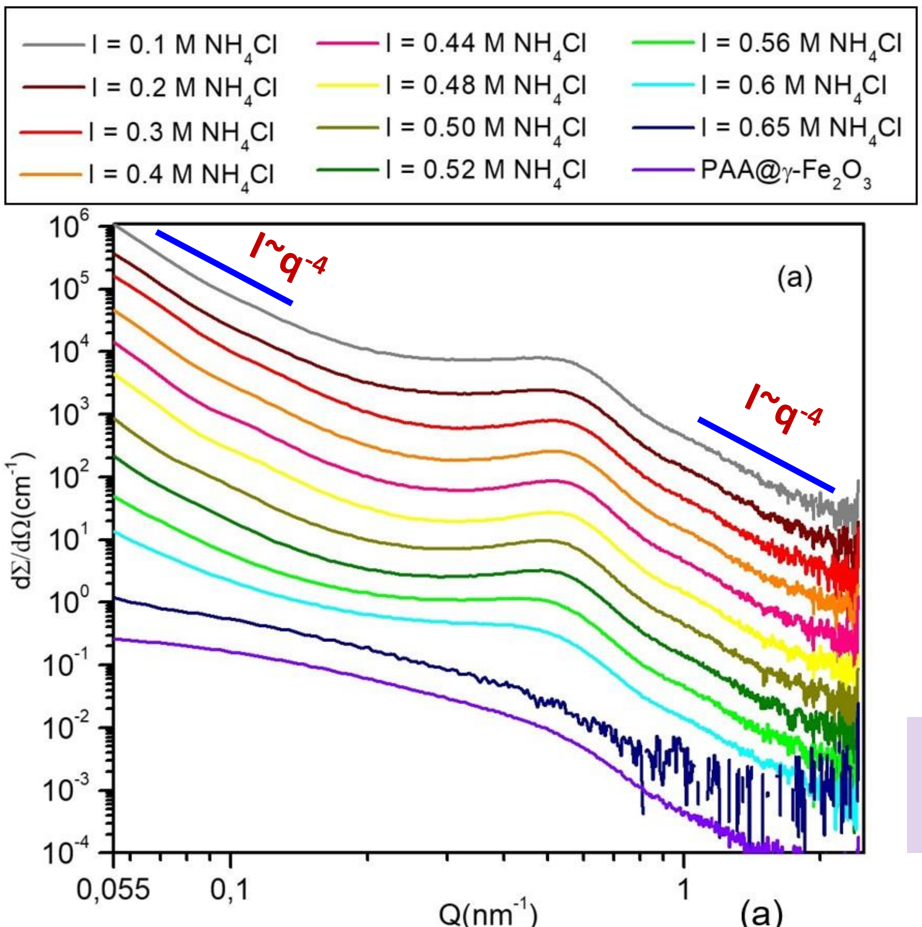
Dense aggregates

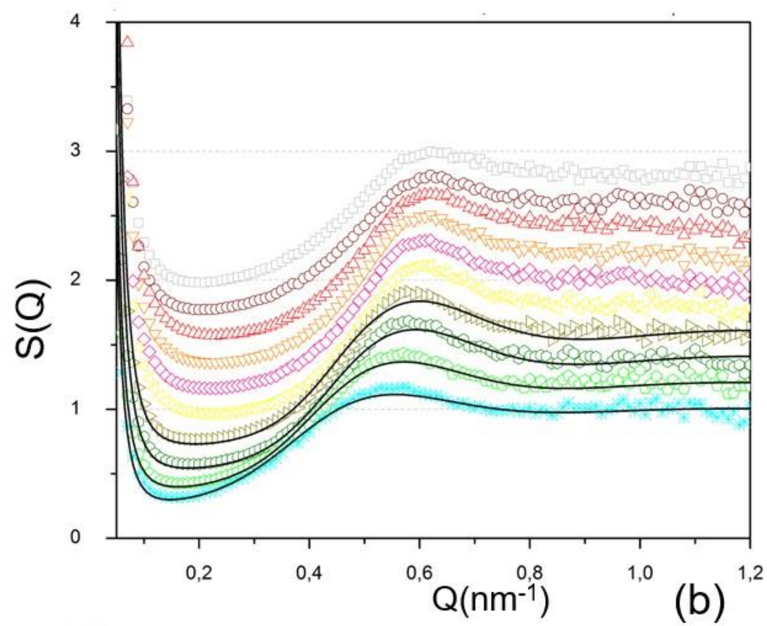


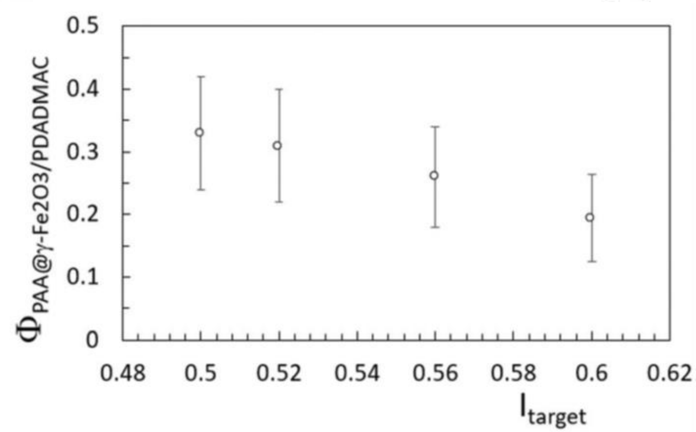
S. Mehan *et al*, *Soft Matter*, **2021**, *17, 8496-8505*

Dense aggregates





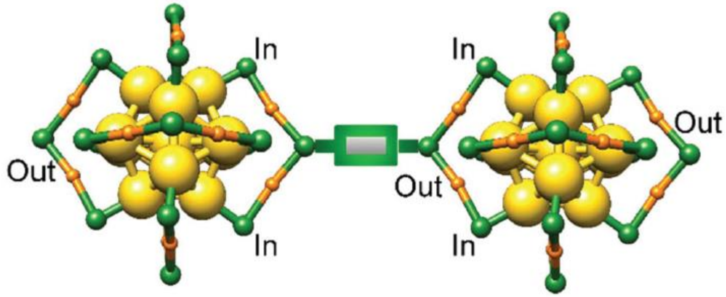




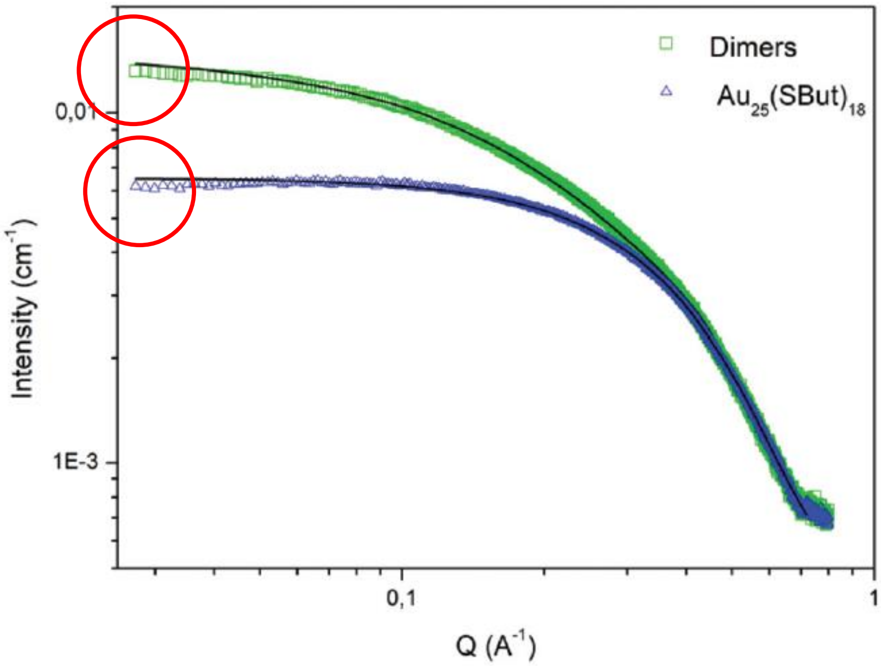
- Fit by Percus Yevick structure factor
- Determination of compactness of aggregates

S. Mehan *et al*, *Soft Matter*, **2021**, *17, 8496-8505*

Clusters of finite size



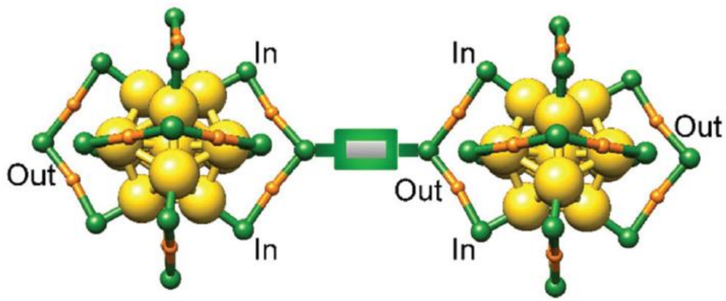
Clusters of gold assembled by ligands



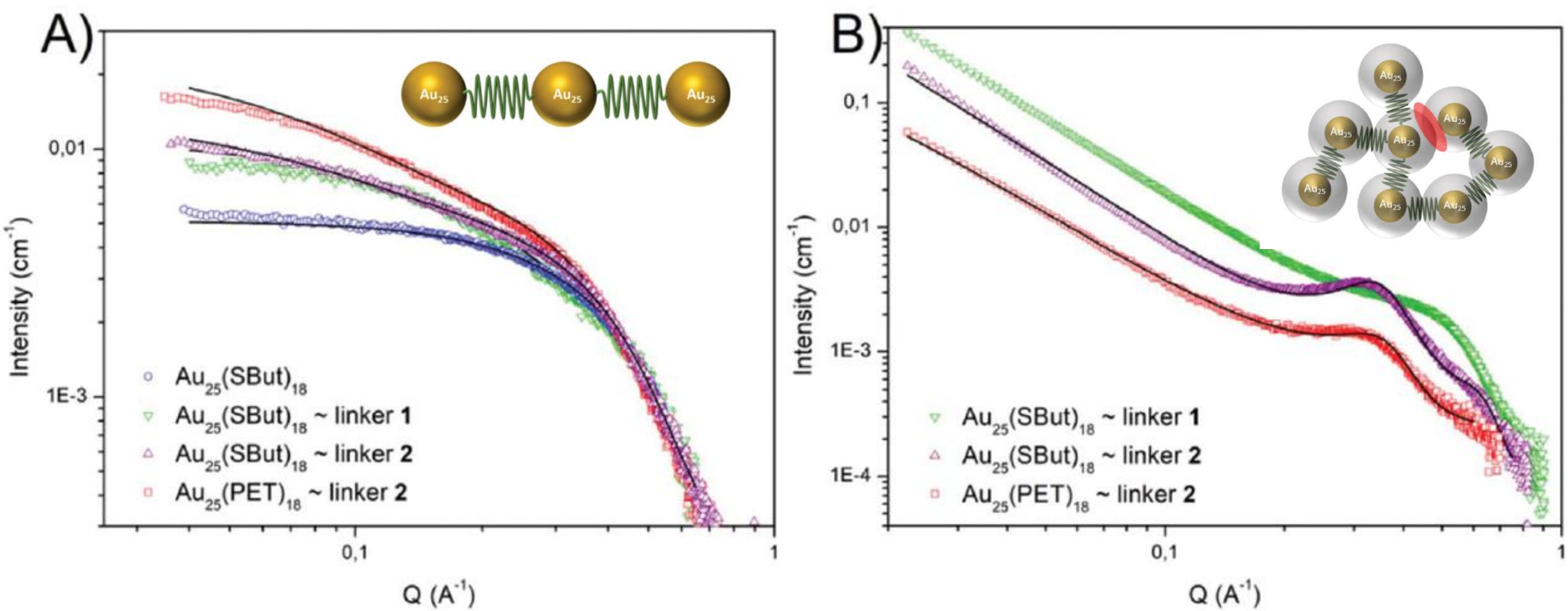
➢ **Aggregation number N_{agg}** from $I(q \to 0)$: $N_{agg} = I_{cluster}(0)/I_{individual\ object}(0)$

A. Sels *et al*, Nanoscale, **2018**, *10*, 12754-12762.

Clusters of finite size



Clusters of gold assembled by ligands

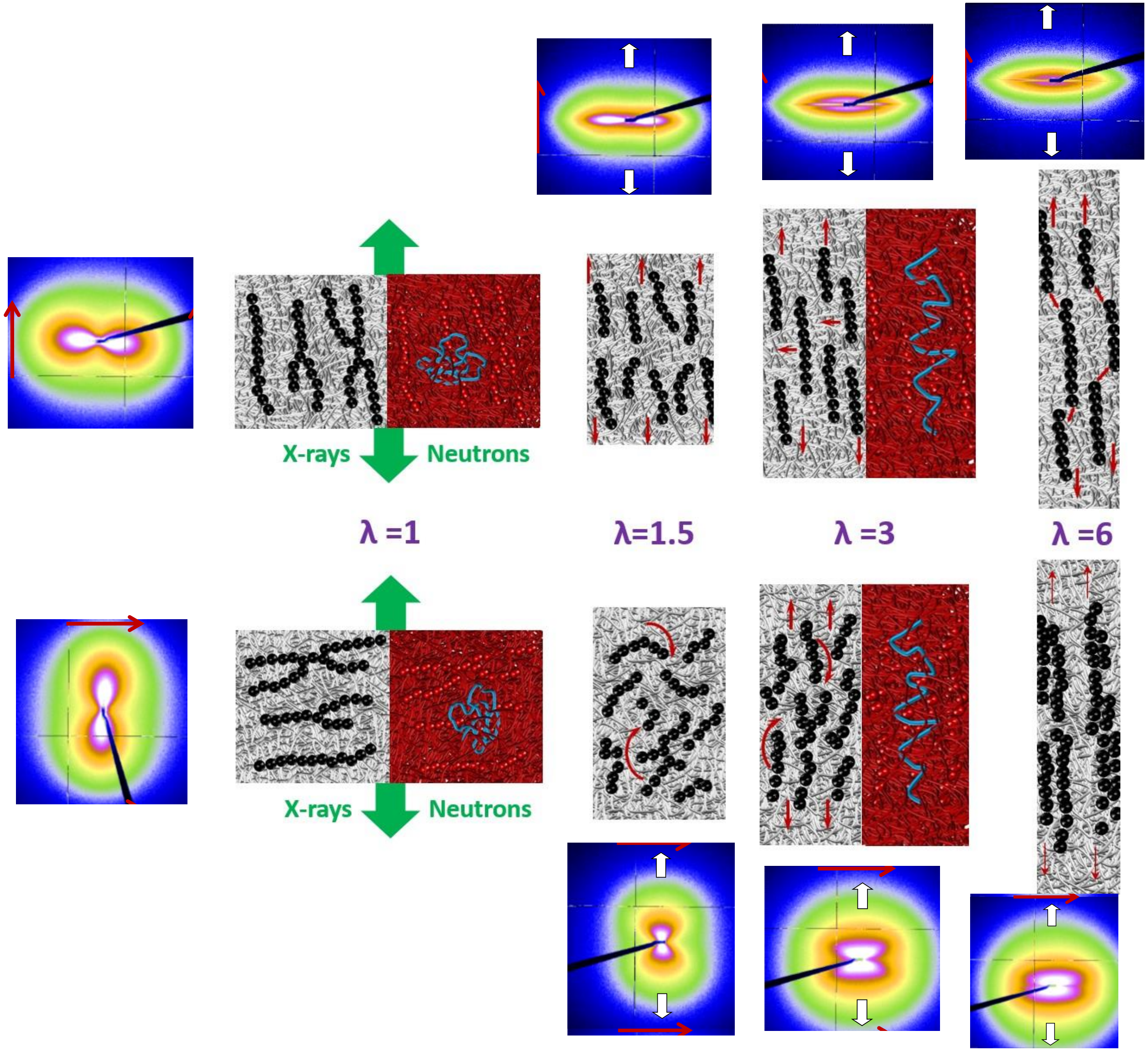


- **Fit by a form factor** (pearl necklace)

- **Fit by a structure factor** (sticky hard spheres)

A. Sels *et al*, Nanoscale, **2018**, *10*, 12754-12762.

Bonus : anisotropic systems based on spheres



S(q)$_{//}$ or S(q)$_{\perp}$ allows to describe qualitatively the structure

A.S. Robbes *et al*, *Macromolecules*, **2022**, *55(15)*, 6876–6889.


SANS FOR SOFT MATTER
24th-25th January 2024
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Villigen, Switzerland
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Prof. Harm-Anton Klok, EPFL, Lausanne
Prof. Peter Fischer, ETH, Zurich
Dr. Pierre Bauduin, ICSM, Marcoule
2F DN
Société Française de Neutronique
SSSN
SGN
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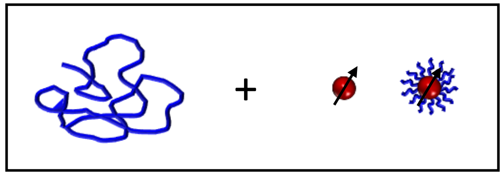
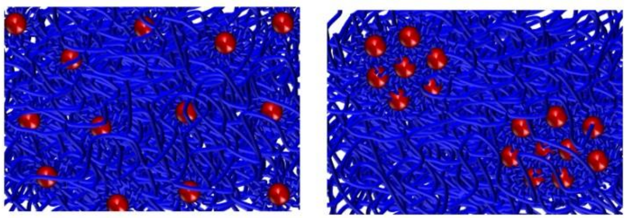
PSI

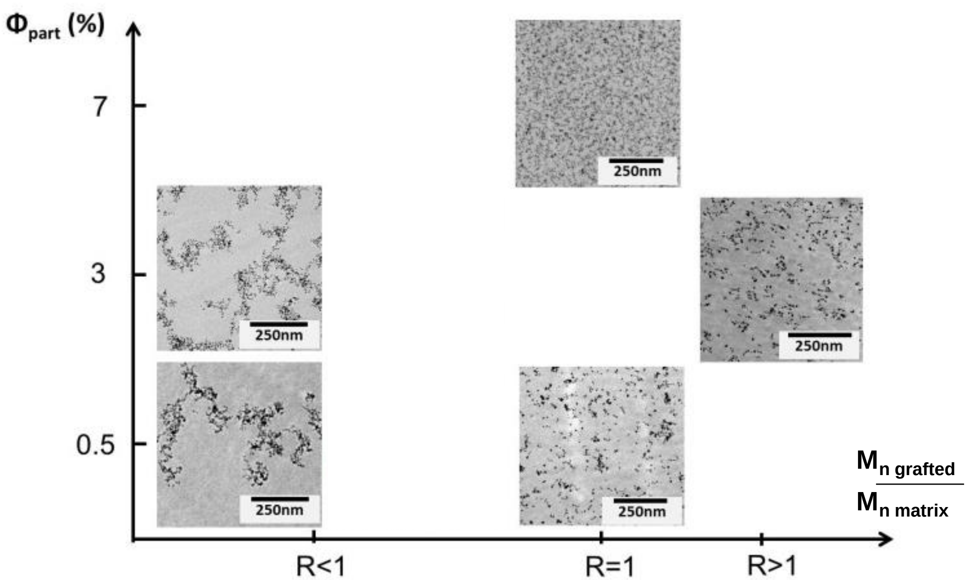
Sometimes the structure factor enables to obtain the… form factor!

Polystyrene



Nanoparticles of γ-Fe_2O_3
(magnetic, d ~ 10 nm)



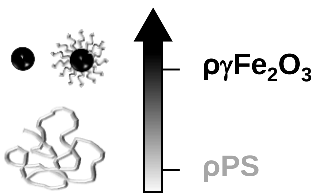


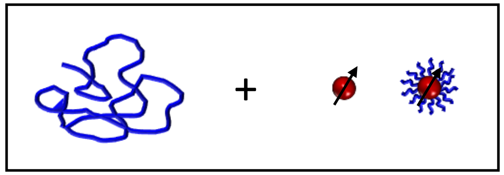
→ Control of dispersion of by grafting

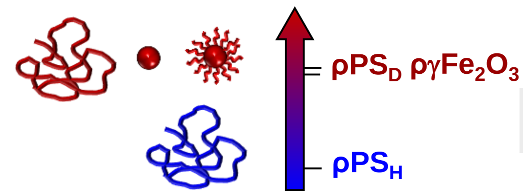
A.S. Robbes *et al*, *Macromolecules*, 2012, *45*, 9220−9231

Sometimes the structure factor enables to obtain the… form factor!

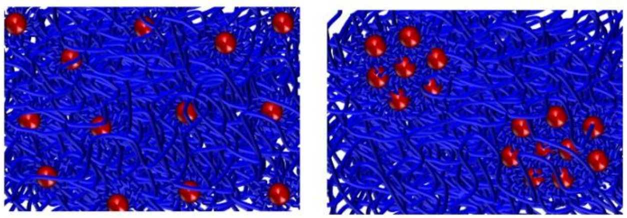
X Rays

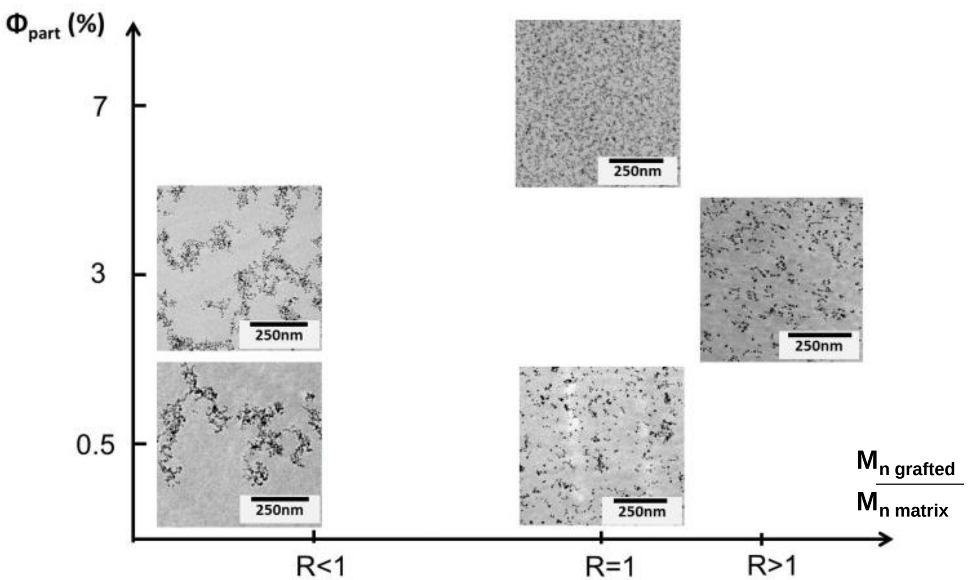




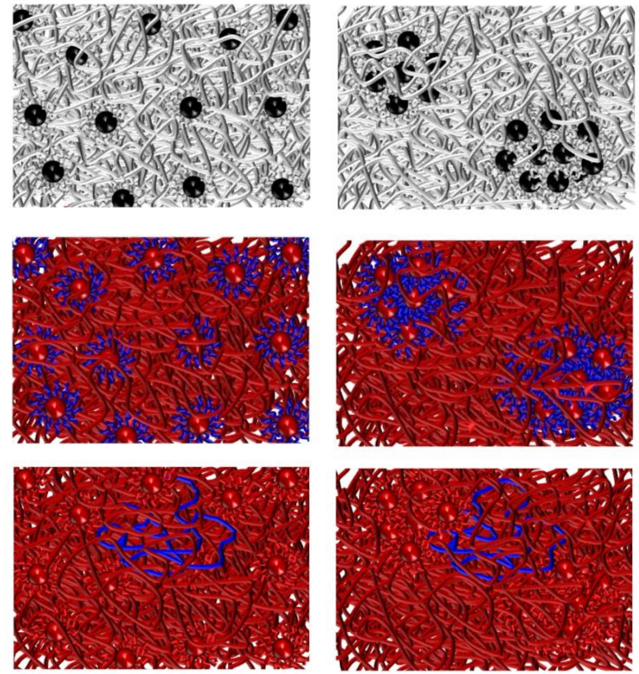


Neutrons





→ Control of dispersion of by grafting

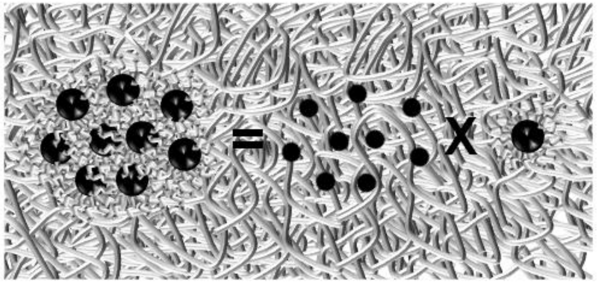


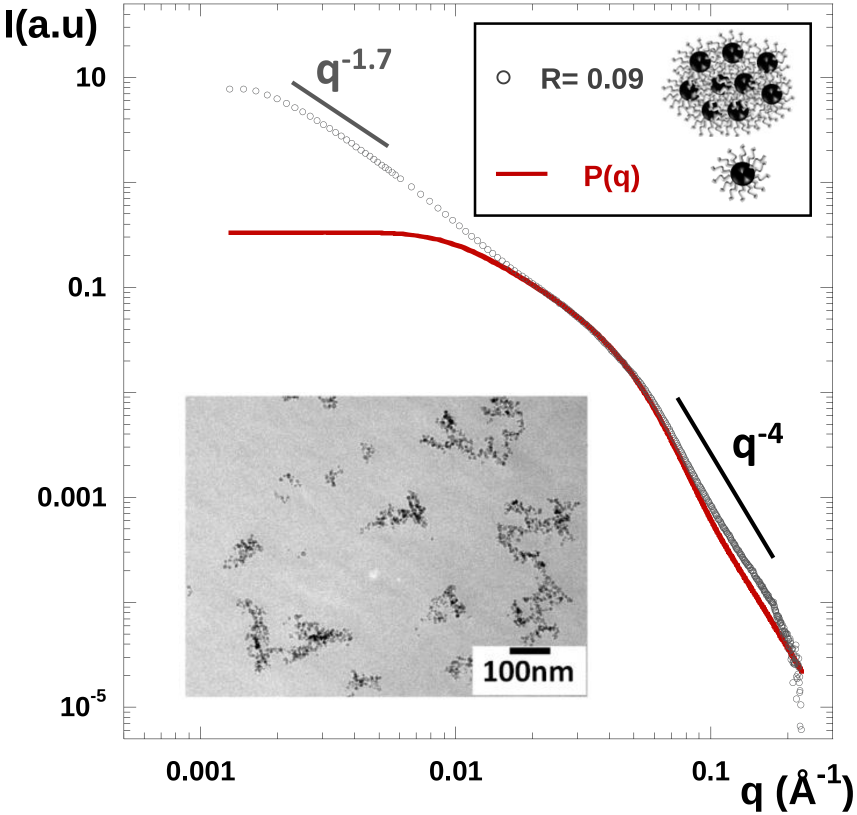
→ Conformation of chains of matrix

→ Conformation of corona

A.S. Robbes *et al*, *Macromolecules*, 2012, *45*, 9220−9231

Sometimes the structure factor enables to obtain the… form factor!

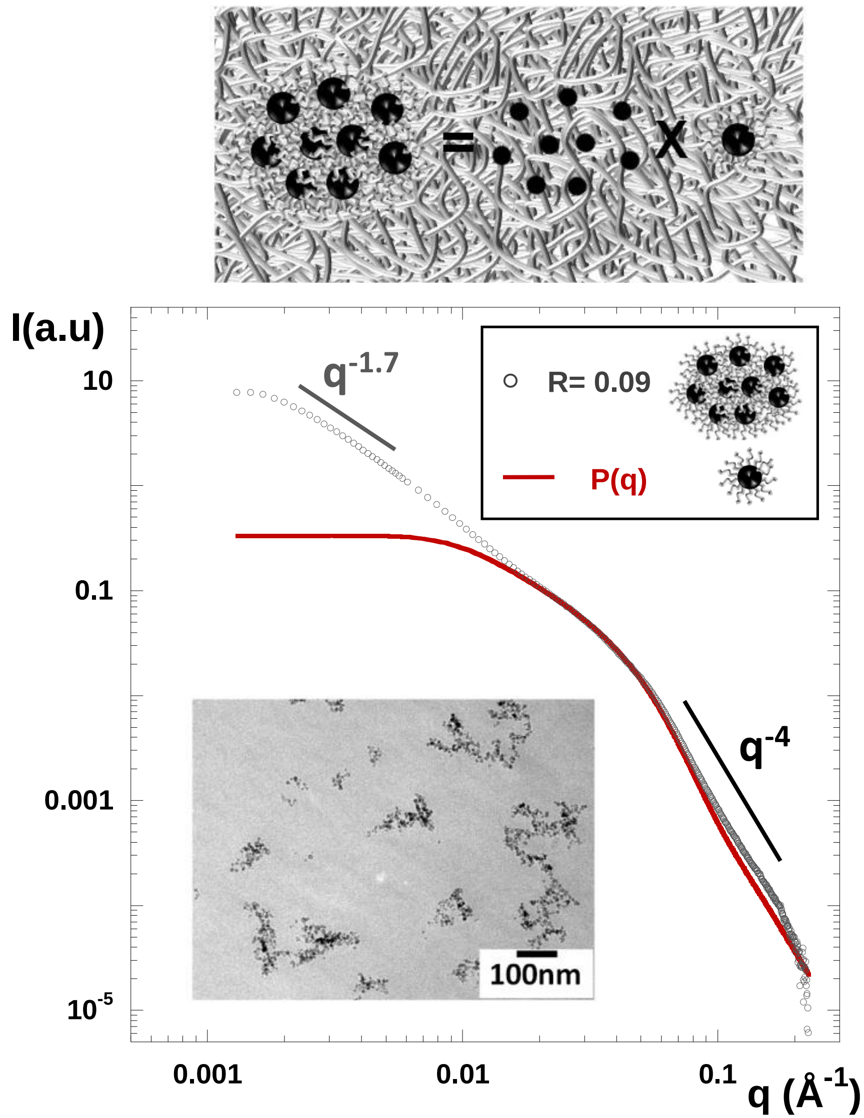




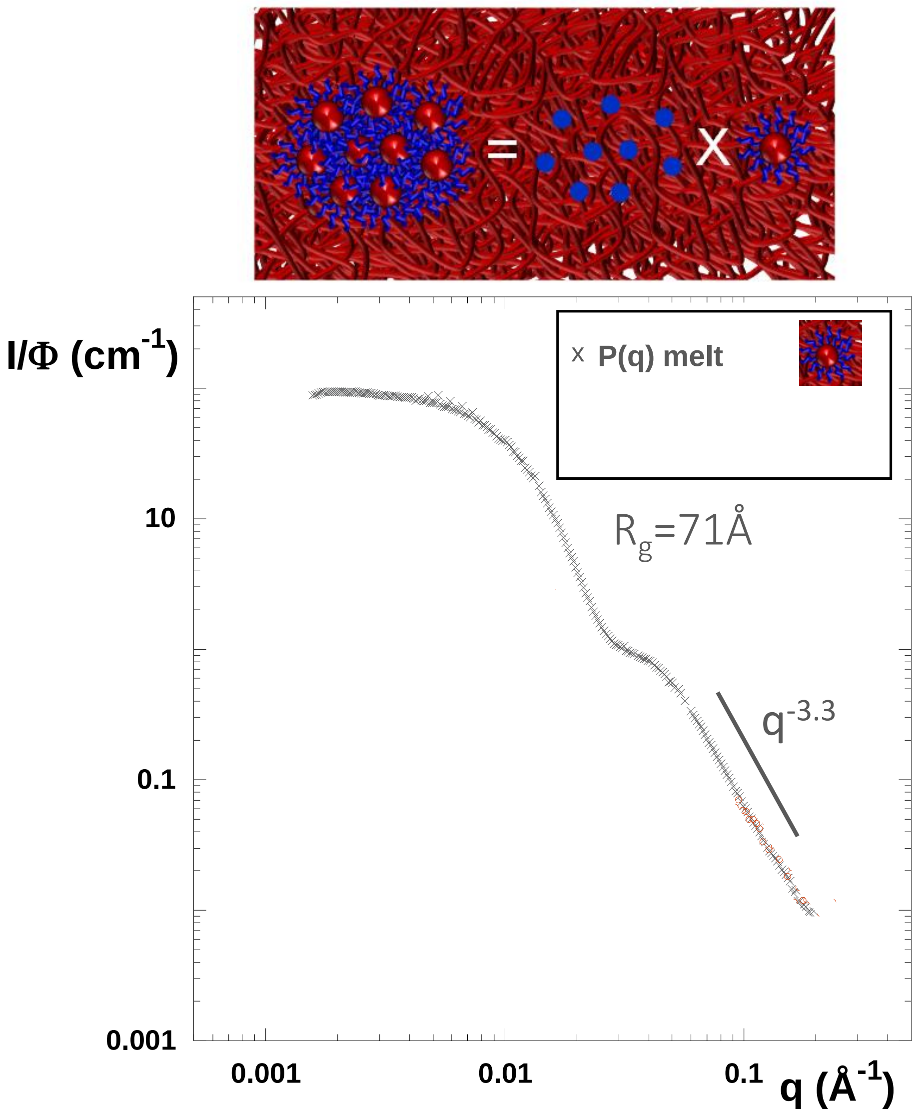
Ramified aggregates : obtention of S(q)

Photons and neutrons do not see the same things…

Sometimes the structure factor enables to obtain the… form factor!



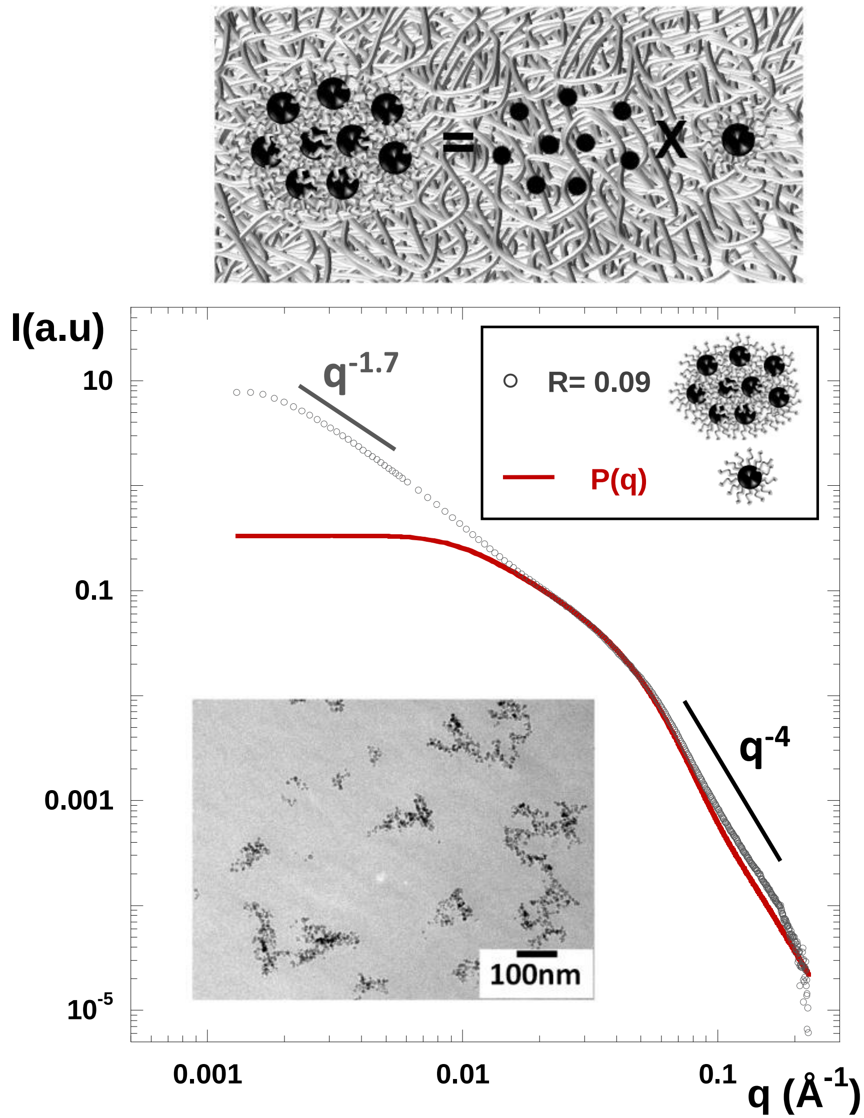
Ramified aggregates : obtention of S(q)

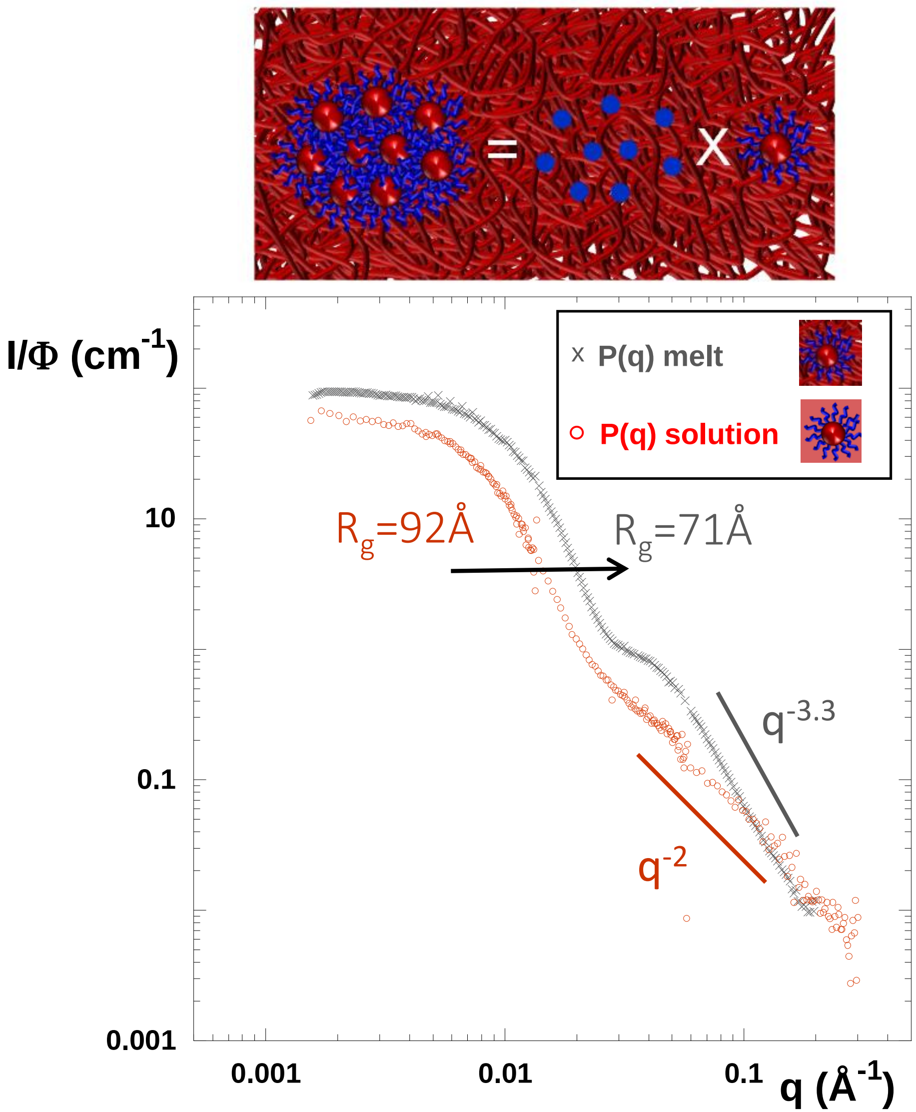


Conformation of corona

A.S. Robbes *et al*, *Macromolecules*, 2012, *45*, 9220–9231

Sometimes the structure factor enables to obtain the… form factor!





First experimental proof of collapse of chains of corona

Robbes *et al*, *Soft Matter*, 2012, *8*, 3407-3418   A.S. Robbes *et al*, *Macromolecules*, 2012, *45*, 9220−9231