Inorganic colloids and their assembling

From colloids to materials

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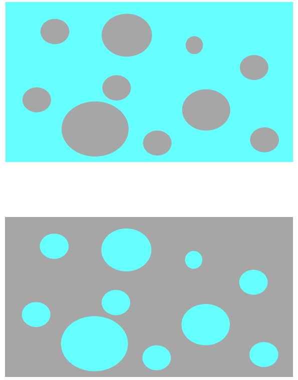
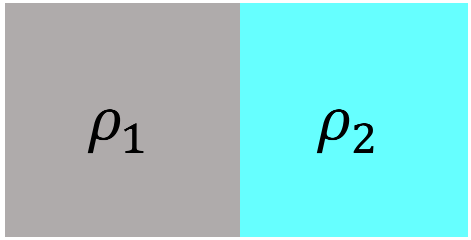
Scattering Intensity I^{abs}

$$\boldsymbol{I^{abs}}(q) = \frac{N}{V_{probed}} . \Delta\rho^2 . V^2 . P(q) . S(q)$$

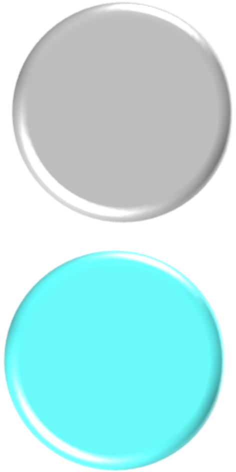
Density of object in the probed volume



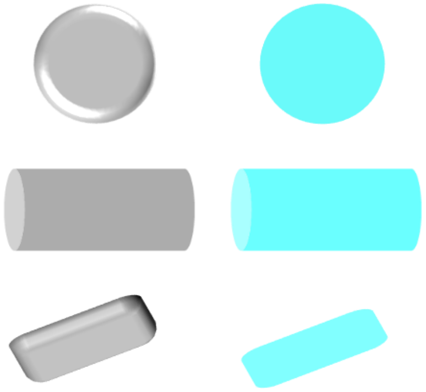
Scattering lenght density contrast



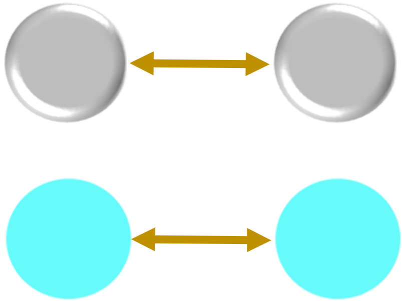
Object volume



Form factor

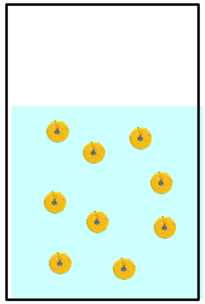


Structure factor



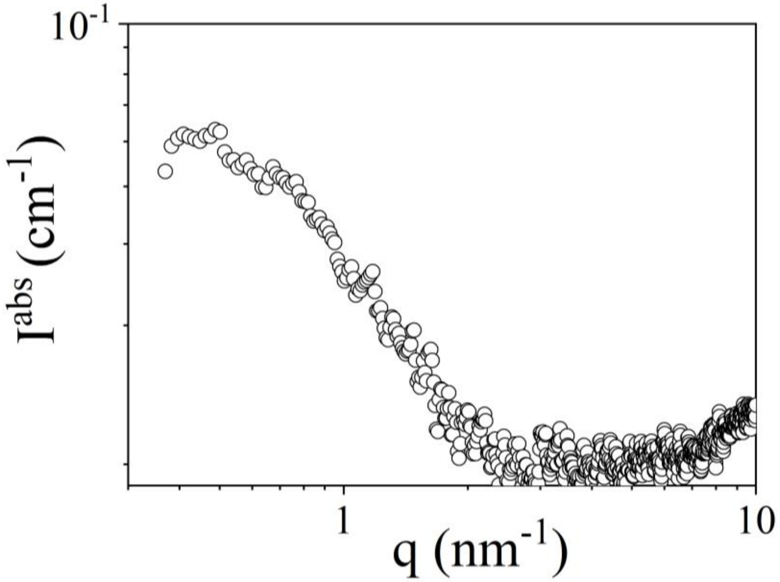
Isotropic diluted system

Scattering objects are randomly oriented and scatter independently



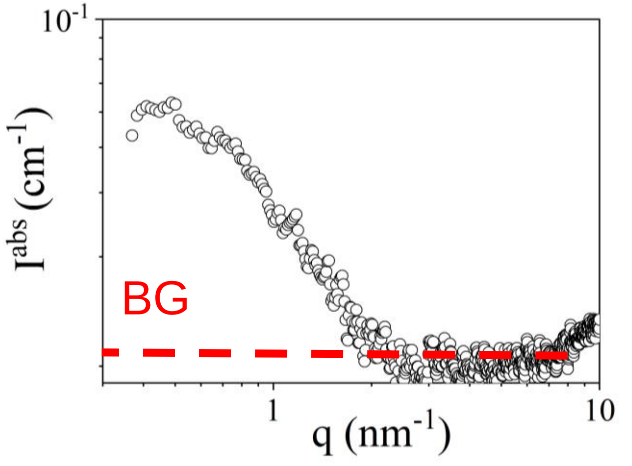
Diluted media

$$S(q) = 1$$

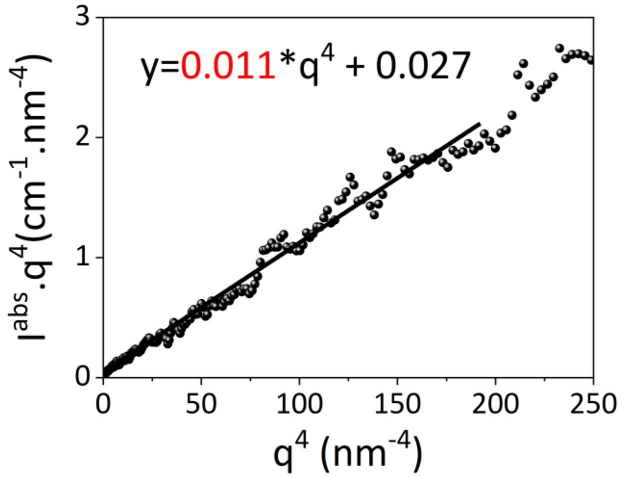


$$I^{abs}(q) = \frac{N}{V_{probed}}.\Delta\rho^2.V^2.P(q)$$

Method 1: BG at q→∞



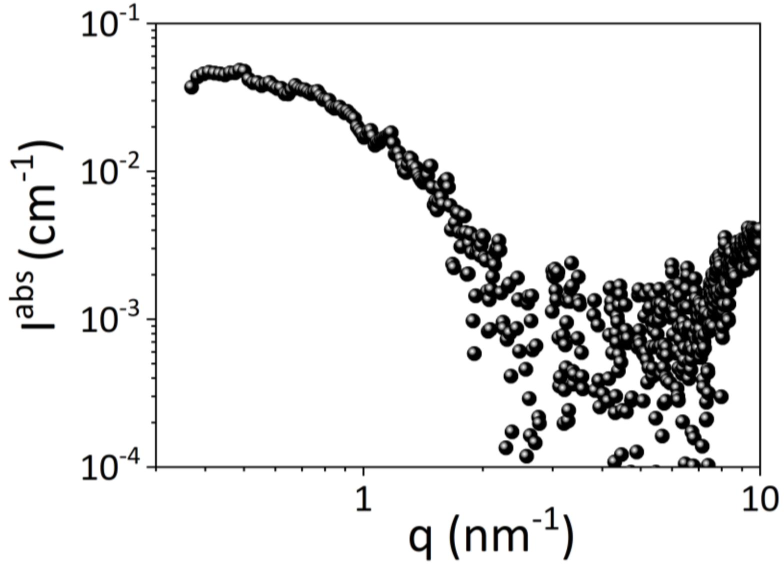
Method 2: plot $\boldsymbol{I}^{\boldsymbol{abs}}.q^4(q^4)$



Porod law

$$\lim_{\boldsymbol{q}\to\infty} \boldsymbol{I}^{\boldsymbol{abs}}(q) = 2\pi(\Delta\rho)^2\Sigma\frac{1}{q^4}$$

$$\boldsymbol{I}^{\boldsymbol{abs}}.q^4(q^4) = 2\pi(\Delta\rho)^2\Sigma + \text{BG}q^4$$



Colloid morphology is unknown

Guinier approximation → Giration radius

Guinier approximation (Rice, 1956)

low *q* region

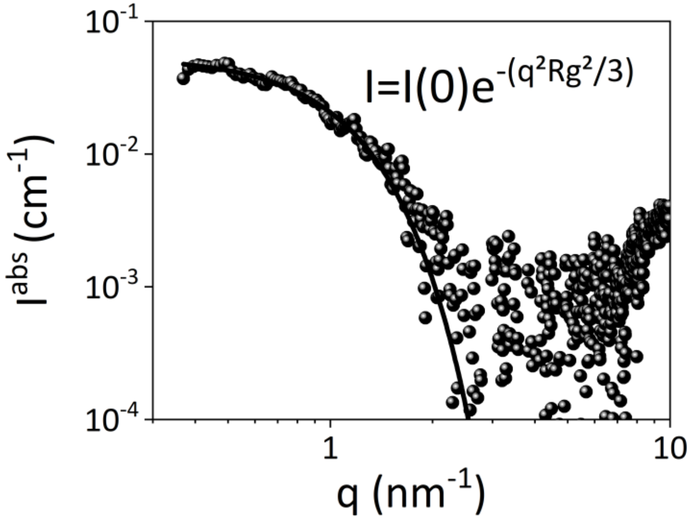
$$I^{abs} = I^{abs}(0)e^{-(\frac{q^2 R_g^2}{3})}$$

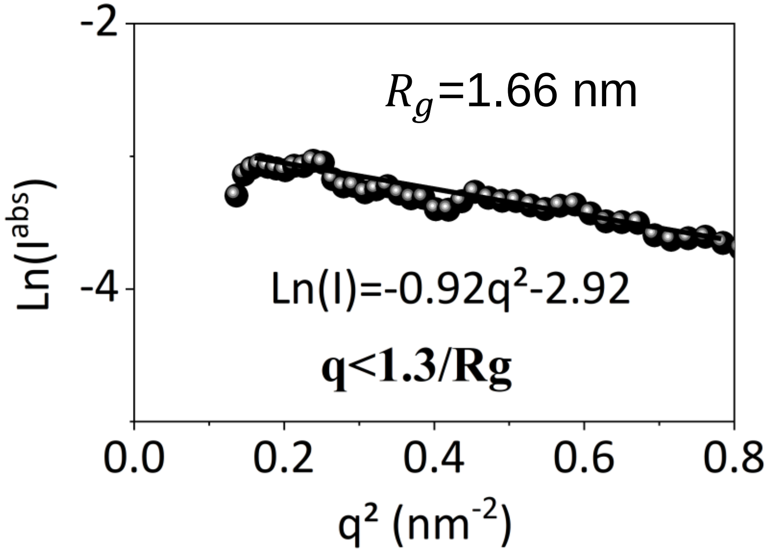
→ gyration radius of the average colloid

Guinier plot

$$\ln(I^{abs}) = \ln(I^{abs}(0) - \frac{R_g^2}{3} q^2$$

I.(qrg)²/I(0)=f(qRg)





Sphere $R_g = \sqrt{\frac{3}{5}}R$

Cylinder $R_g = \sqrt{\frac{R^2}{2} + \frac{L^2}{12}}$

Rice, S.A., 1956. Small angle scattering of X-rays. A. Guinier and G. Fournet. Wiley, New York, 1955. 268 pp. Journal of Polymer Science 19, 594–594.

Form factor of colloids P(Q)

Sphere (Guinier, 1955) $\boldsymbol{P(q)} = [3\frac{(\sin(qR) - qRcos(qR))}{(qR)^3}]^2$

Oscillation at high q

If wide distribution size → **Debye function of a sphere** $\boldsymbol{P(q)} = \frac{1}{(1 + 2^{\frac{1}{2}}(qR)^2/3)^2}$

Porod & Kratky, 1982
Peterlik & Fratzl, 2006

Cylinder (Guinier, 1955) $\boldsymbol{P(q)} = \int_0^{\frac{\pi}{2}} [\frac{2J_1(qRsin\alpha)}{qRsin\alpha} \frac{\sin\left(\frac{1}{2}qLcos\alpha\right)}{\frac{1}{2}qLcos\alpha}]^2$

....

Sasview!

A Guinier and G. Fournet, *Small-Angle Scattering of X-Rays*, John Wiley and Sons, New York, (1955)

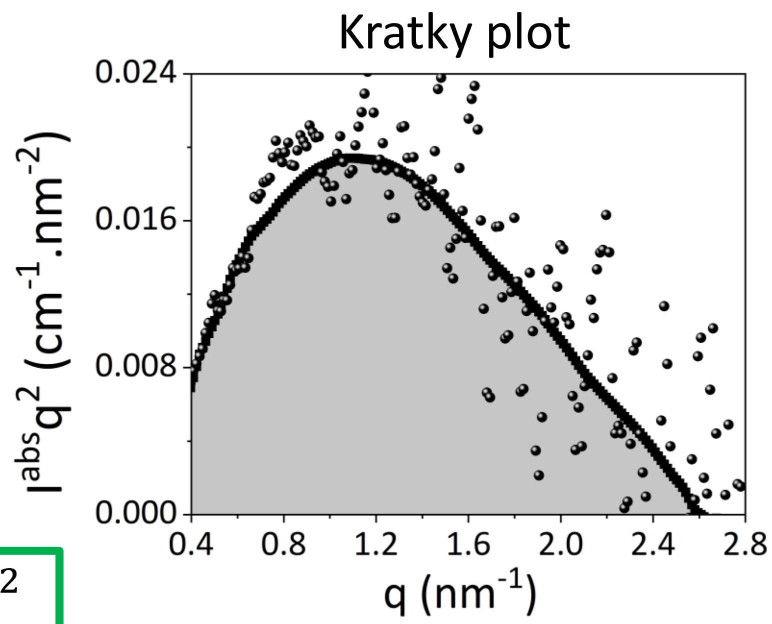
Volume and concentration of colloids

Invariant theorem

$$Q = \int_0^\infty I^{abs}(q).q^2.dq = 2\pi^2\varphi(1-\varphi)\Delta\rho^2$$

volume fraction of particles

Kratky plot: Integration of $Iq^2(q)$ in the probed q range



Diluted solution $\varphi \ll 1 \rightarrow (1-\varphi) \approx 1$ $\varphi = V_p N_p$ $Q \approx 2\pi^2 V_p N_p \Delta\rho^2$

$I^{abs}(q) = N_p.\rho^2.V_p^2.P(q)$ $P(0) = 1$ $I^{abs}(0) = V_p{}^2 N_p \Delta\rho^2$

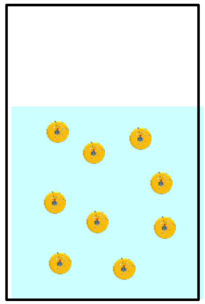
$$V_p(\text{nm}) = \frac{2\pi^2.I(0)}{Q}$$

if $\Delta\rho$ is known $\rightarrow N_p$

Colloidal fraction, distribution ratio….

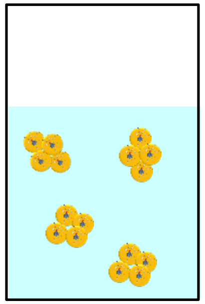
Brumberger, H. (Ed.), 1995. Modern Aspects of Small-Angle Scattering. Springer Netherlands, Dordrecht. https://doi.org/10.1007/978-94-015-8457-9

Assembling of primary scatters into larger aggregates



Diluted media

$S(q) = 1$ →



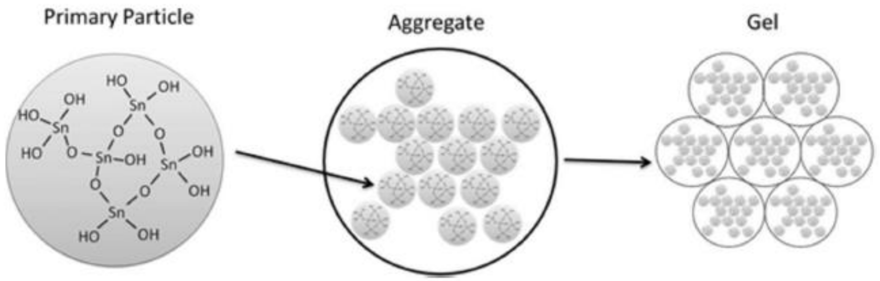
$S(q) \neq 1$

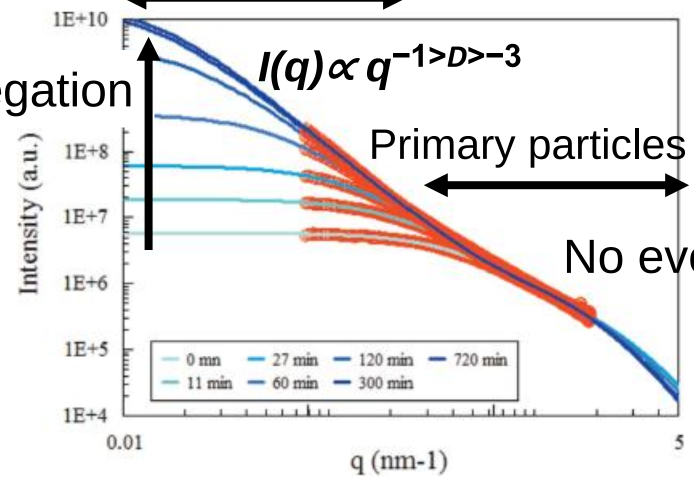
$$I^{abs}(q) = \frac{N}{V_{probed}} . \Delta\rho^2 . V^2 . P(q) . S(q)$$

Structure factor for fractal aggregates

For centrosymmetric particles in anisotropic system

Dumoulin et al, J. Appl. Cryst. (2016). 49, 366–374





$1 < D < 3$ => Mass fractal

Freltoft model

(Freltoft et al, 1986)

$$S(q) = 1 + \frac{B\sin[(D_f-1)\arctan(q\xi)]}{(1+(q\xi)^2)^{(D_f-1)/2} q\xi}$$

$1 + B$: average number of particles per aggregate (q→0)

ξ: limited size of aggregates

D_f: fractal dimension

$B = K(D_f-1)\Gamma((D_f-1)\xi^{D_f}$

Texeira model

(Texeira et al, 1988)

$$S(q) = 1 + \frac{\Gamma D_f(D_f-1)\sin[(D_f-1)\arctan(q\xi)]}{qR[1+\frac{1}{(q\xi)^2}]^{(D_f-1)/2}}$$

$R_g = \xi\left\{\frac{[D_f(D_f+1)]}{2}\right\}^{1/2}$ of aggregate

D_f

Reaction Limited Cluster Aggregation (**RLCA**) D_f =2.1

Diffusion limited cluster aggregation (**DLCA**) D_f = 1.80

Structure factor for fractal aggregates

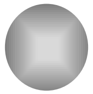
When several types of objects scattered

Beaucage unified scattering function

Combination of Guinier and power-law regimes

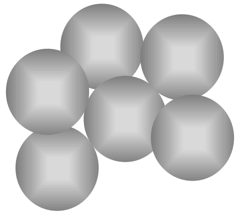
(Beaucage, 1995, 1996, 2004)

$$I^{abs}(q) = G_1 e^{\left(-\frac{q^2 R_{g1}^2}{3}\right)} + B_1 \left\{ \frac{\left[\mathrm{erf}\left(\frac{qkR_{g1}}{6^{\frac{1}{2}}}\right)\right]^3}{q} \right\}^{D_f}$$

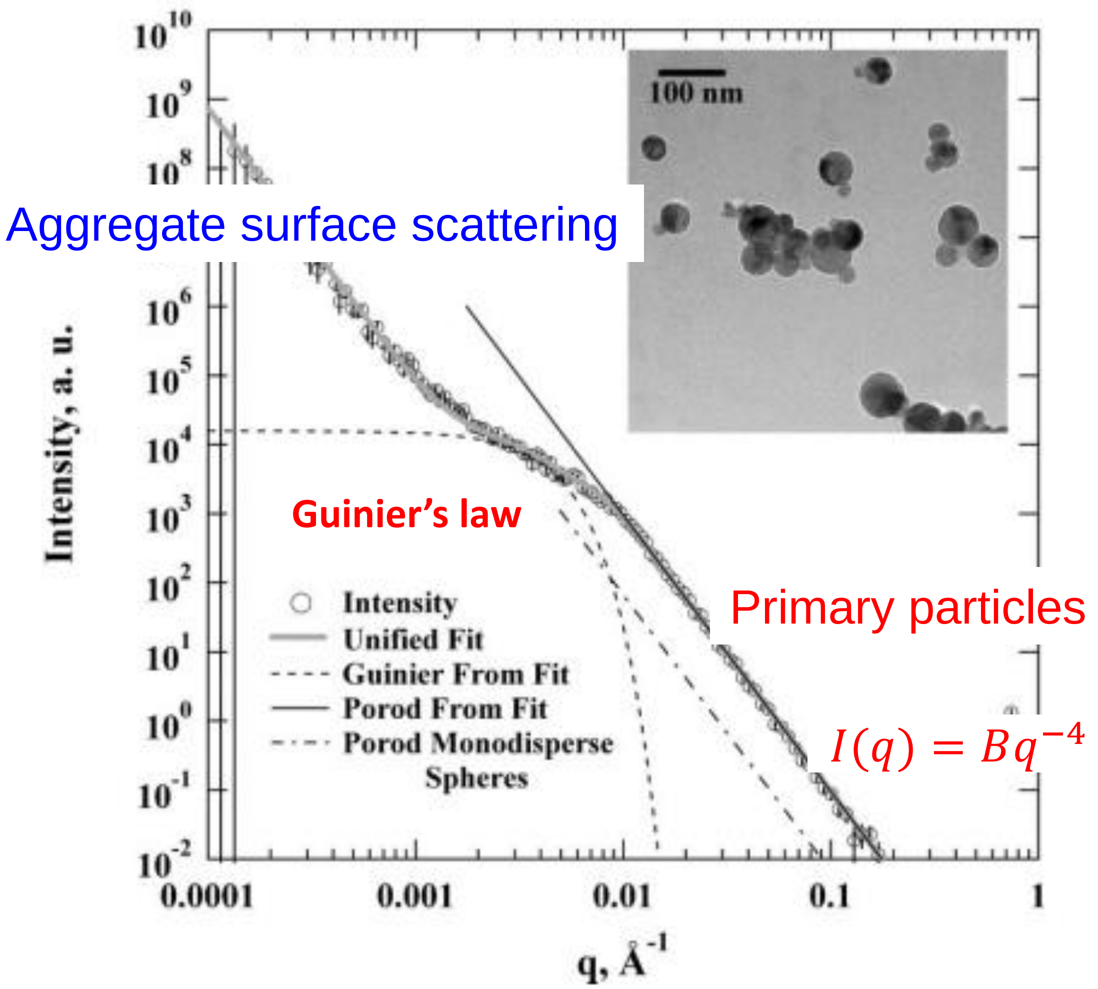


Primary particles

$$+ G_2 e^{\left(-\frac{q^2 R_{g2}^2}{3}\right)} + B_2 e^{\left(-\frac{q^2 R_{g1}^2}{3}\right)} \left\{ \frac{\left[\mathrm{erf}\left(\frac{q1.06R_{g2}}{6^{\frac{1}{2}}}\right)\right]^3}{q} \right\}^{D_f}$$



Aggregate



k=1.06 for mass or surface fractal object

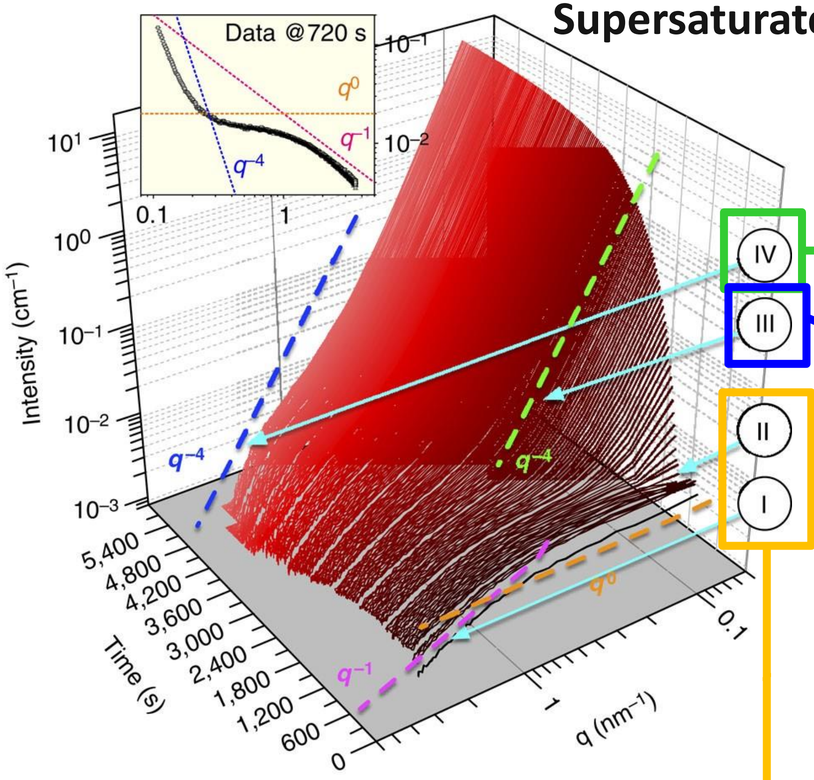
k=1 for other object

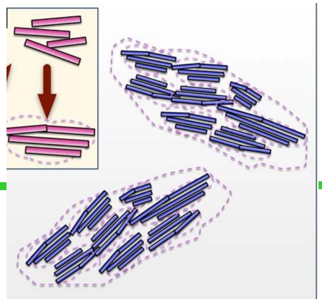
- Average surface area for a primary particle
- Density of primary particles….

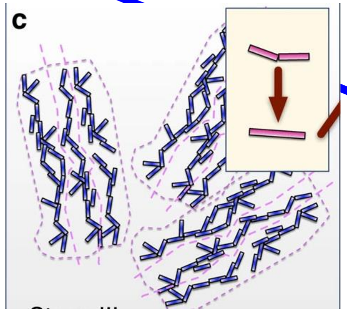
Example: Colloids assembling - Precipitation

Stawski et al, 2016

Supersaturated solution of $CaSO_4$ 50 mmol.L^{-1}

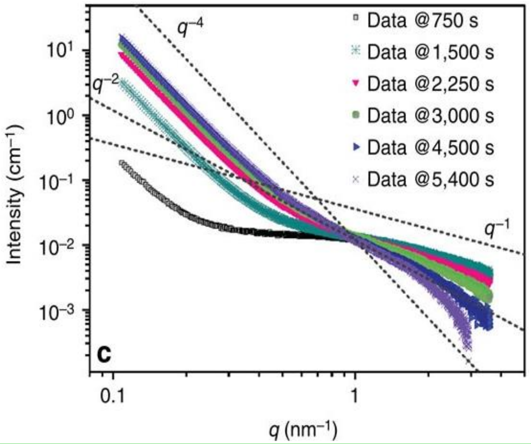






Individual scatterers coalescence

Growth and coalescence of the primary species within the aggregates



Self assembling of primary scatters into larger aggregates

$I(q) \propto q^{-3>\alpha>-4}$

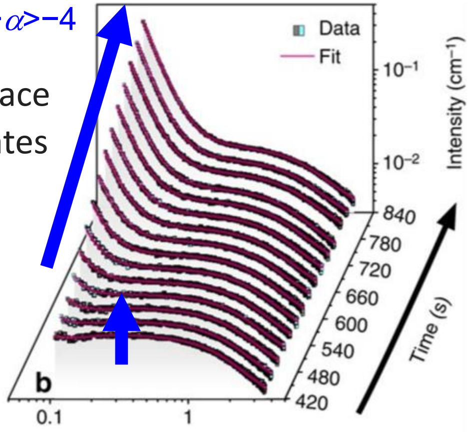
Rough fractal surface
Growth of aggregates

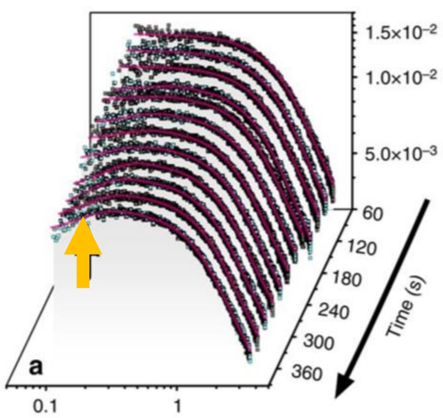
$I(q) \propto q^{D_s-6}$ $\quad 3 < 6 - D_s < 4$

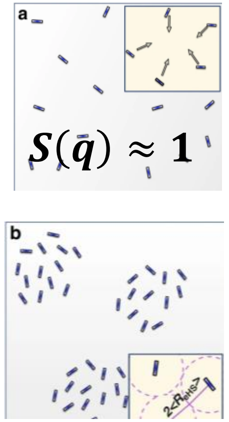
Surface fractal

Wong et al, 1988

$$I(q) = A\frac{\Gamma(5-D_s)\sin[\pi(3-D_s)/2]}{(3-D_s)}q^{D_s-6}$$







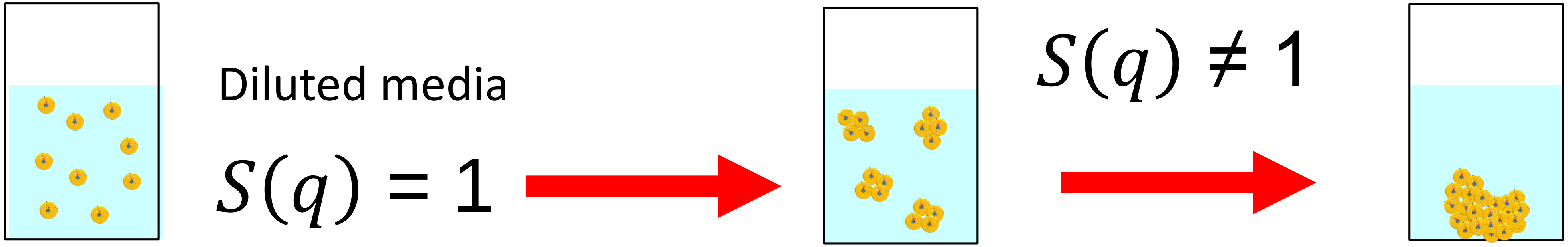
Small primary scatterers < 3nm

Non-aggregated and non-interacting individual species of elongated, anisotropic shapes

Interactions between primary species

$S(q) \neq 1$ Polydisperse structure factor

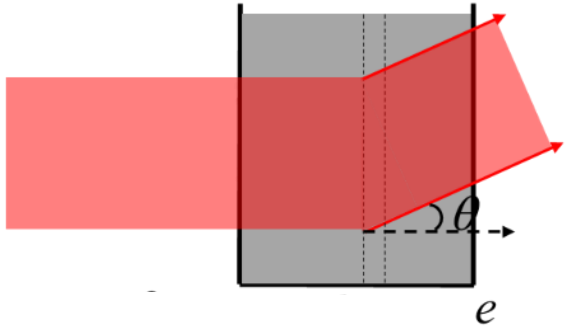
Assembling of aggregates into porous material



$$\boldsymbol{I}^{\boldsymbol{abs}}(q) = \frac{N_{pores}}{V_{probed}}.\Delta\rho^2.V_{pores}^2.P(q).\,S(q)$$

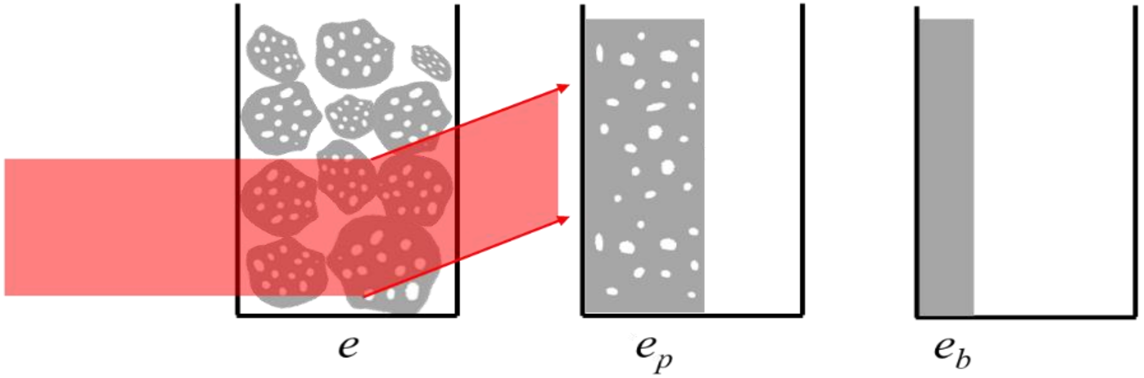
Importance of sample thickness for porous granular media

1st case: dense phase



$\boldsymbol{e}$ = capillary thickness

2d case: porous granular media $\boldsymbol{e} = e_b$ thickness of the solid part



Spalla et al, 2003

$$T = e^{-\mu_b e_b}$$

e_b → Equivalent thickness of the solid part

μ_b → Specific linear attenuation coefficient of solid part

https://henke.lbl.gov/optical_constants/atten2.html

$$\boldsymbol{e_b} = -\frac{\ln(T)}{\mu_b}$$

Porous materials made of aggregates

E 2 days

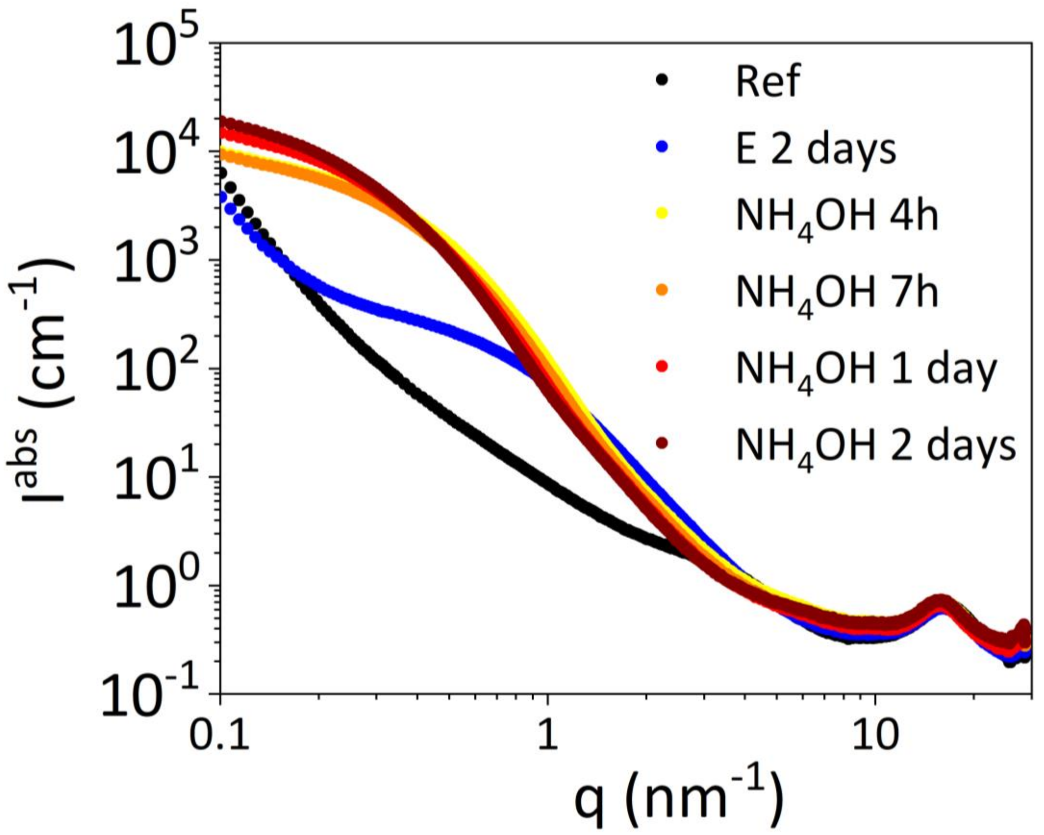
In water
2 days

Ageing 70°C

NH_4OH t

In NH_4OH
from 4h to 2 days

Aerogel prepared using acid catalysis **Ref**



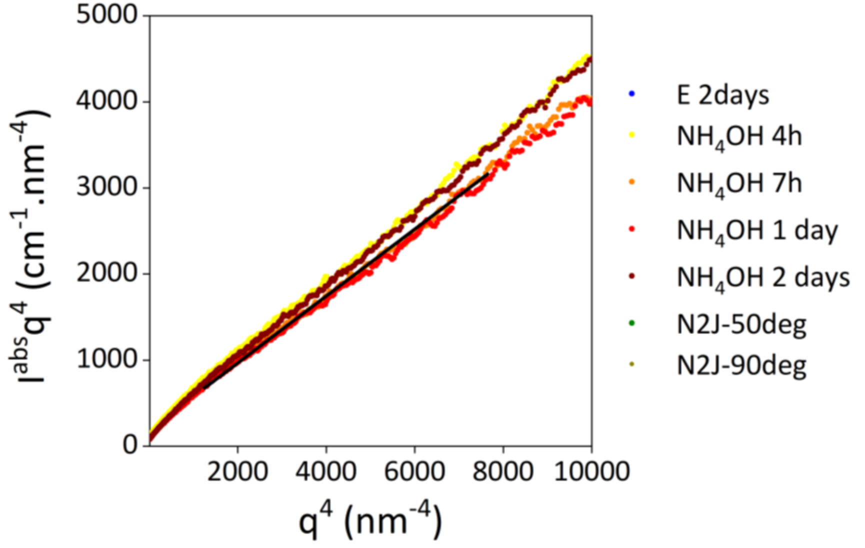
Surface area and porous volume

Fractal exponent close to 4→ Porod's law

$$\lim_{q\to\infty} I^{abs}(q) = 2\pi(\Delta\rho)^2\Sigma\frac{1}{q^4}$$

$$I^{abs}.q^4(q^4) = 2\pi(\Delta\rho)^2\Sigma + \text{BG}q^4$$

$$\boldsymbol{S_A = \frac{\Sigma}{\rho_m}}$$



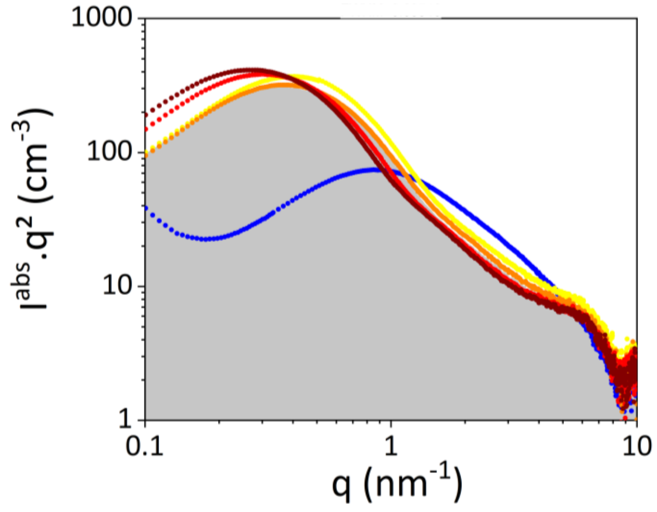
Invariant $Q = \int_0^\infty I^{abs}(q)q^2dq = 2\pi^2\,\varphi(1-\varphi)(\Delta\rho)^2$

$$\phi = \frac{Q}{2\pi^2\Delta\rho^2}$$

Spalla et al, 2003
Chavez Panduro, 2012

Sample	Φ	S_A $(m^{-2}.g^{-1})$	S_{BET} $(m^{-2}.g^{-1})$
E2J	0.25	312	
N4H	0.50	472	352
N7H	0.43	397	309
N1J	0.42	366	273
N2J	0.42	354	248

$$\boldsymbol{S_A > S_{BET}}$$



L. Auvray and P. Aurroy, Bombannes summer school lecture : Scatering by interfaces (1991)

Porous materials made of aggregates

2 contributions

Mass fractal (Texeira model)

$$\boldsymbol{S(q)} = 1 + \frac{\Gamma D_f (D_f - 1) sin[(D_f - 1)\arctan(q\xi)]}{q r_0 [1 + \frac{1}{(q\xi)^2}]^{(D_f - 1)/2}}$$

Teubner-Strey model (Teubner et al, 1987)

for networks of interconnected, coagulated particles

$$I(q) = \frac{8\pi < \Delta\rho^2 > / \xi_{TS}}{a^2 - 2bq^2 + q^4}$$

$$b = \left(\frac{2\pi}{d}\right)^2 - \frac{1}{\xi_{TS}^2}$$

d : quasi-periodic inter-domain distance

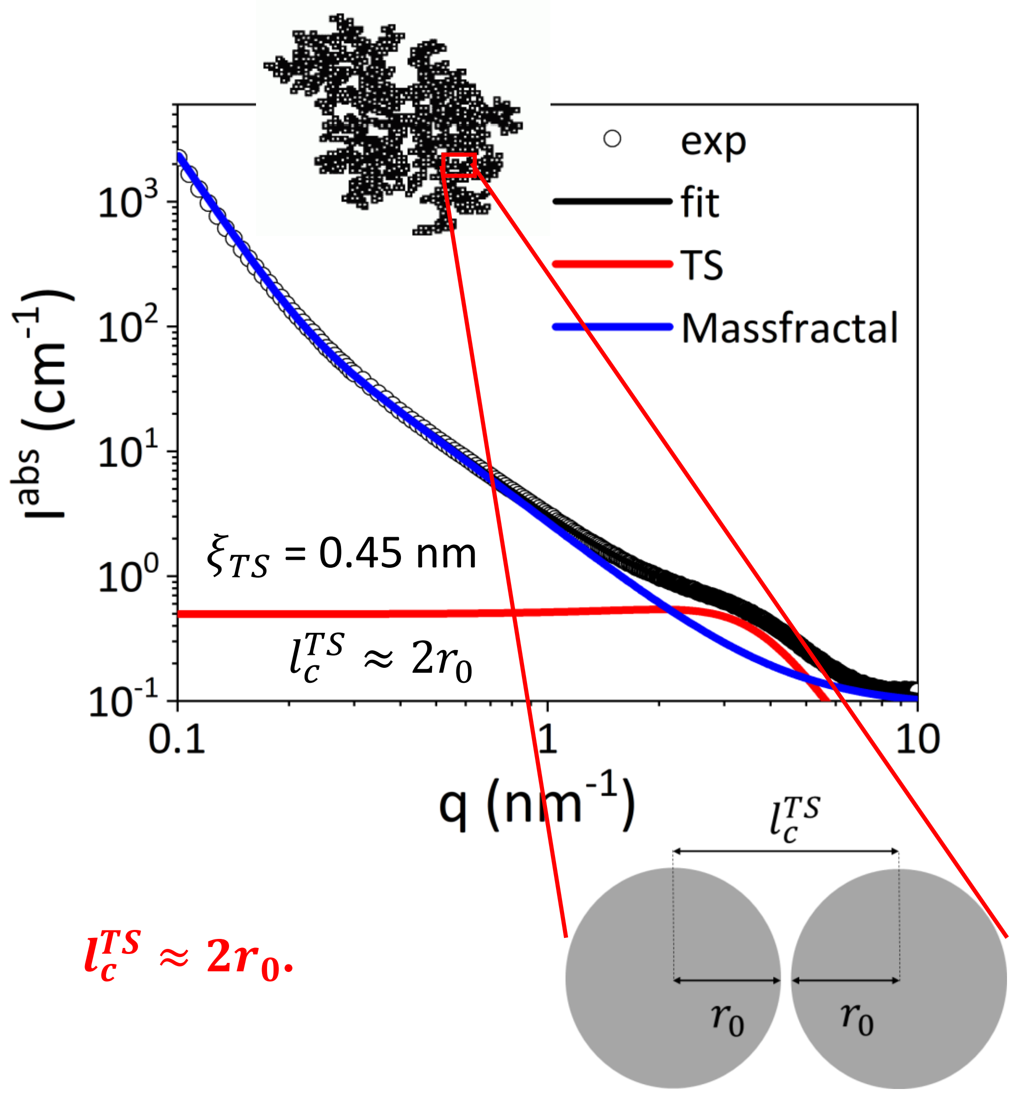
ξ_{TS} : characteristic domain size

correlation length

$$l_c^{TS} = \frac{d}{\pi} \arctan\left(\frac{2\pi\xi_{TS}}{d}\right)$$

$\boldsymbol{l_c^{TS} \approx 2r_0}$.

Ref (without ageing)



Porous materials made of aggregates

3 contributions

Mass fractal (Texeira model)

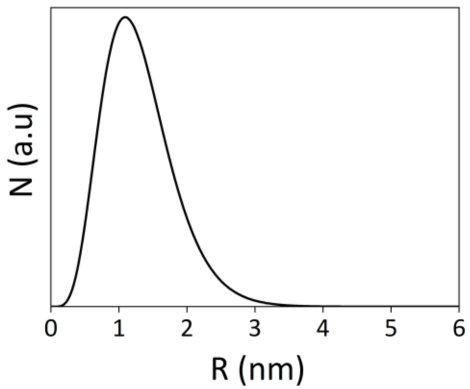
$$S(q) = 1 + \frac{\Gamma D_f (D_f - 1) sin[(D_f - 1)\arctan(q\xi)]}{q r_0 [1 + \frac{1}{(q\xi)^2}]^{(D_f - 1)/2}}$$

Teubner-Strey model

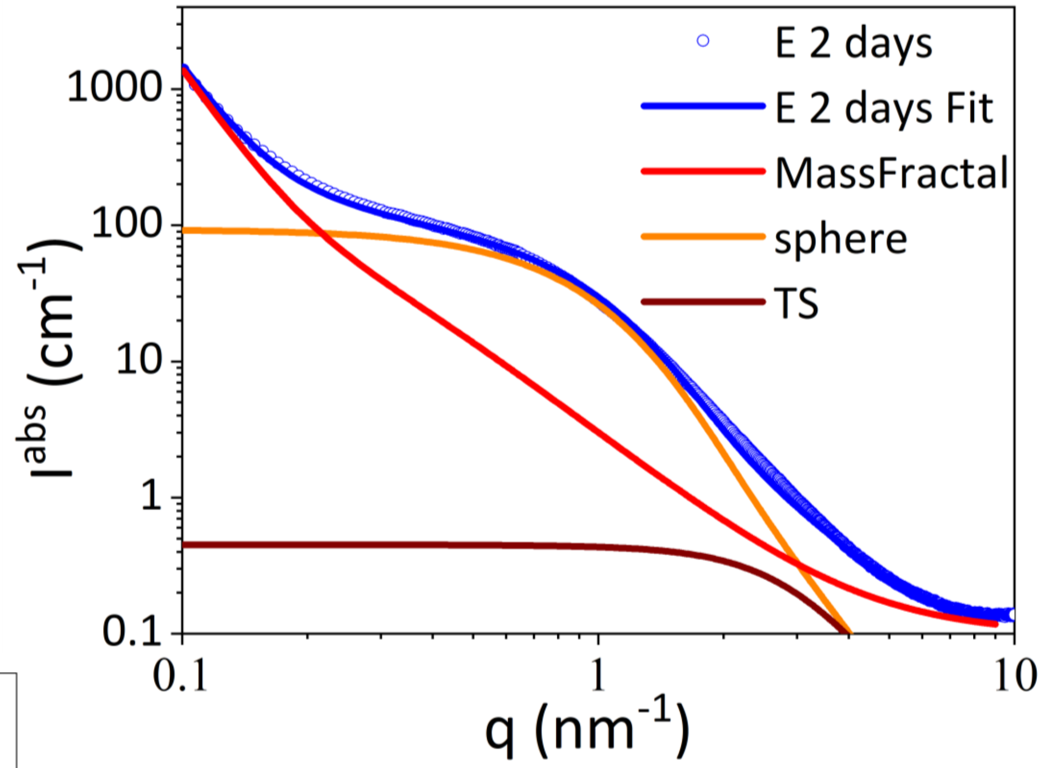
$$I(q) = \frac{8\pi < \Delta\rho^{2} > /\xi_{TS}}{a^2 - 2bq^2 + q^4}$$

Spherical pores with a Shulz-Zimm distribution

$$I_{sphere} = \frac{4}{3}\pi R^3 \Delta\rho 3 \frac{\sin qR - qR\cos qR}{(qR)^3}$$



Ageing in water during 2 days



Porous materials made of aggregates

Guinier-Porod model (Hammouda , 2010)

→Determination of the form factor of non-spherical object

2 contributions

$$I(q) = \frac{G}{q^s} e^{-\frac{q^2 R_g^2}{3-s}} \quad \text{for } q \leq q_1$$

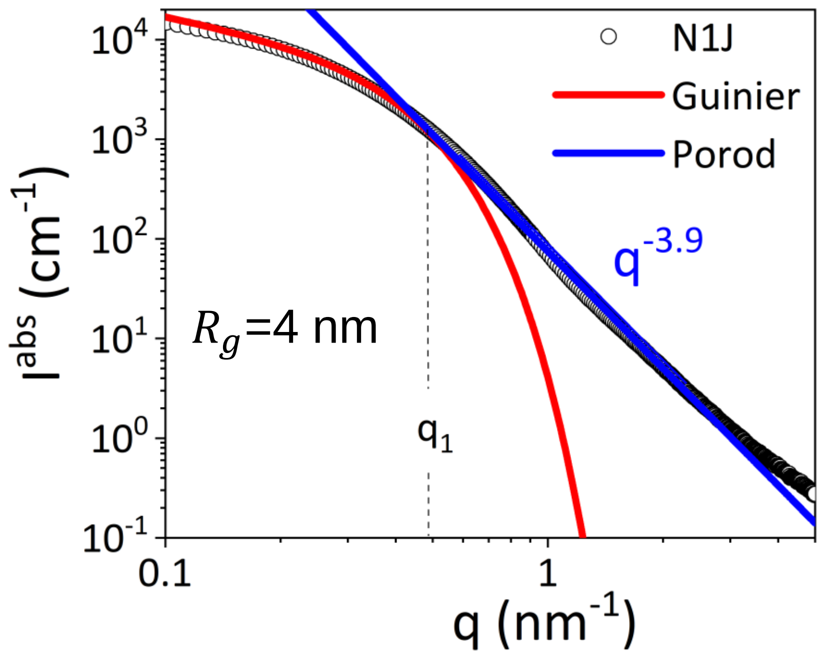
$$I(q) = \frac{D}{q^d} \quad \text{for } q \geq q_1$$

d : Porod exponent,
3-s : parameter given the object dimension

s = 0 sphere
S= 1 rod
S= 2 platelets

G : Guinier scale factor
D: Porod scale factor

After ageing in NH_4OH during 1 day



Sample	D	d	G (cm^{-1})	s	R_g (nm)
N4H	115	4.0	2300	0.65	2.95
N7H	90	4.0	2750	0.45	3.40
N1J	75	3.9	3600	0.70	3.95
N2J	65	3.9	4000	0.70	4.20

Thanks for your attention