An introduction to small angle scattering

Saclay, November 2024

Marianne Impéror-Clerc

marianne.imperor@universite-paris-saclay.fr

website:

https://softqc.wordpress.com/scattering/

Ressources … you are not alone ! ☺

Books :

- Wim de Jeu, Basic X-ray Scattering for Soft Matter

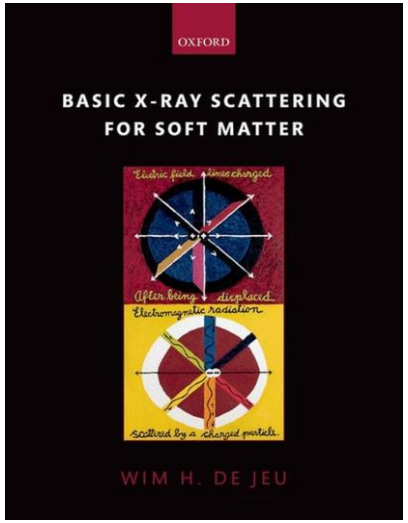
2016, Oxford University Press, ISBN: 9780198728665

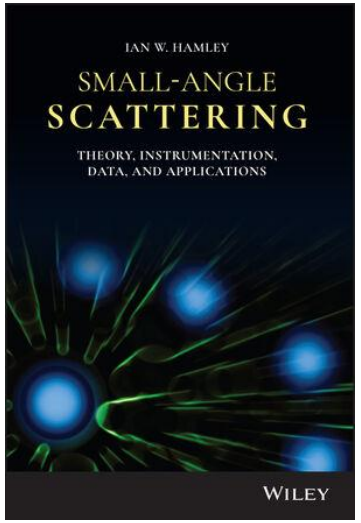
- Ian Hamley, Small-Angle Scattering: Theory, Instrumentation, Data and Applications

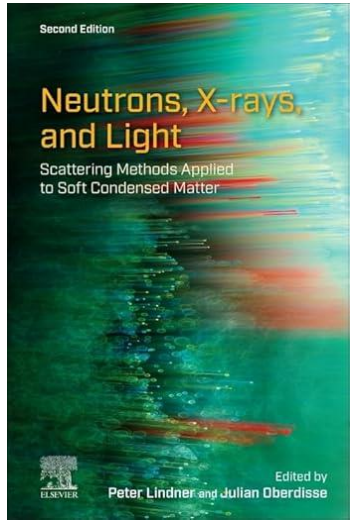
2021, John Wiley & Sons, 2021 ISBN: 9781119768302

- Neutrons, X-rays and light, Scattering methods applied to Soft Condensed Matter

2002 and 2024 revised version, Elsevier Science, Editors P. Lindner, Th. Zemb and Julian Oberdisse







Ressources … you are not alone ! ☺

An international community :

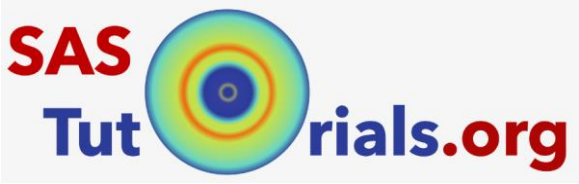
SAS Portal : http://www.smallangle.org

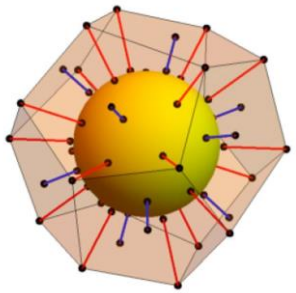
SasView software : https://www.sasview.org/

Online tutorials about SAS:

https://www.sasview.org/docs/user/tutorial.html

https://sastutorials.org/ (recent initiative in Copenhagen)





Crystallography for soft matter and nanomaterials

complex lattices and quasicrystals

HOME CRYSTALLOGRAPHY FRANK AND KASPER PHASES CLOSE PACKING

QUASICRYSTALS SCATTERING RESSOURCES BLOG CONTACT

https://softqc.wordpress.com/

anr

LPS ORSAY

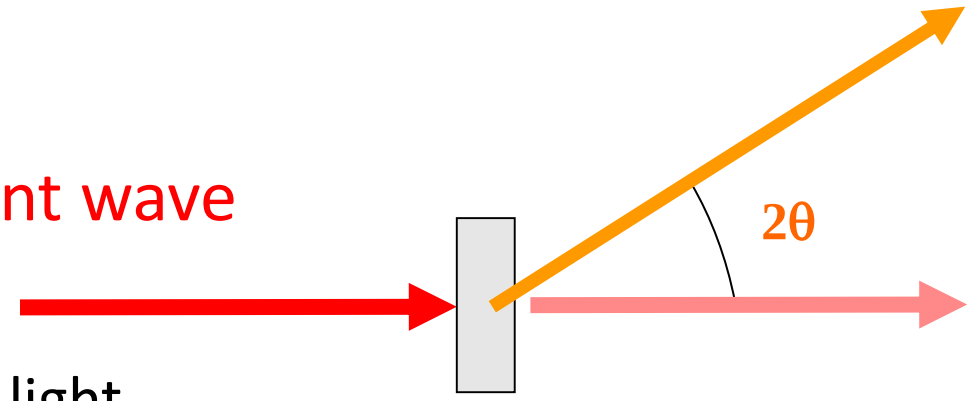
SESSION

1. Introduction
2. Scattering experiment
3. Some theory
4. Form factor: Spherical objects and other shapes
5. Data modelling
6. Structure factor: Hexagonal and lamellar mesophases

SESSION

1. Introduction
2. Scattering experiment
3. Some theory
4. Form factor: Spherical objects and other shapes
5. Data modelling
6. Structure factor: Hexagonal and lamellar mesophases

Scattering : a general physical process



X-rays, light

neutrons

…

electrons

nuclei

scattering

absorption

X-rays : diffraction, crystallography, SAXS

Light : DLS, Raman

Spectroscopy:

X-rays : EXAFS, XANES

Light: UV-vis

- Structure -> positions
- Dynamic -> motions

Elastic or inelastic scattering (energy transfer)

Scattering for soft matter

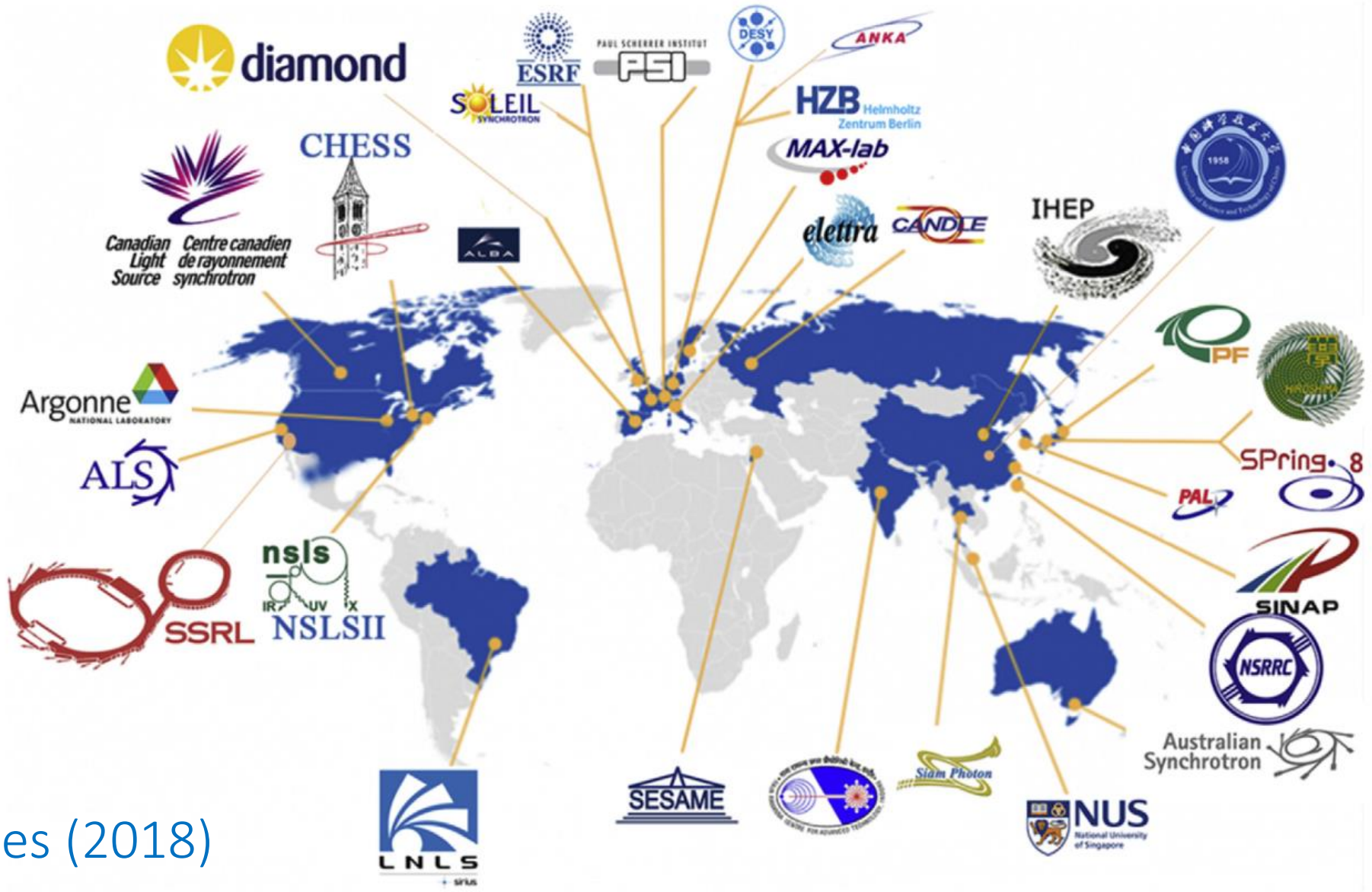
X-rays (SAXS for Small Angle X-ray Scattering) or
neutrons (SANS for Small Angle Neutron Scattering)

Multi-disciplinary field : Soft Matter / Biology / Material Science

Some examples :

- following in real-time the assembly of surfactant micelles
- nucleation/growth of nanoparticles during their synthesis
- folding/unfolding of globular proteins in solution
- polymer material deformation under mechanical strain

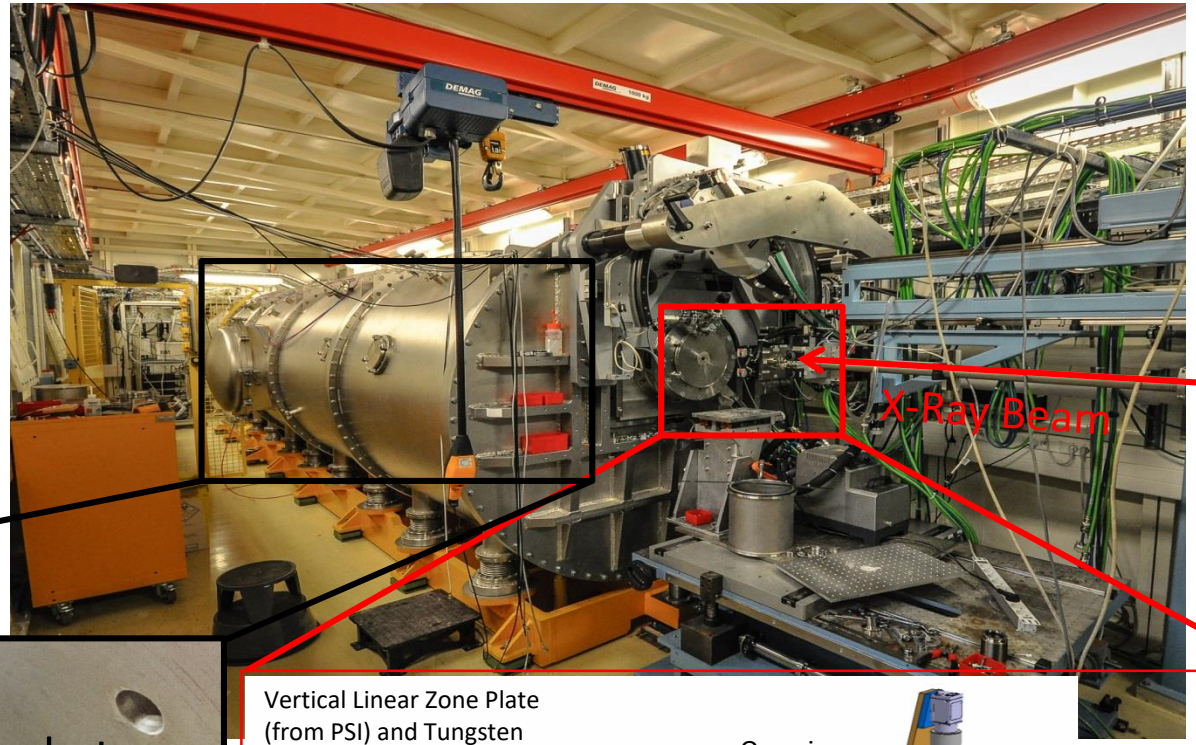
Synchrotron sources worldwide

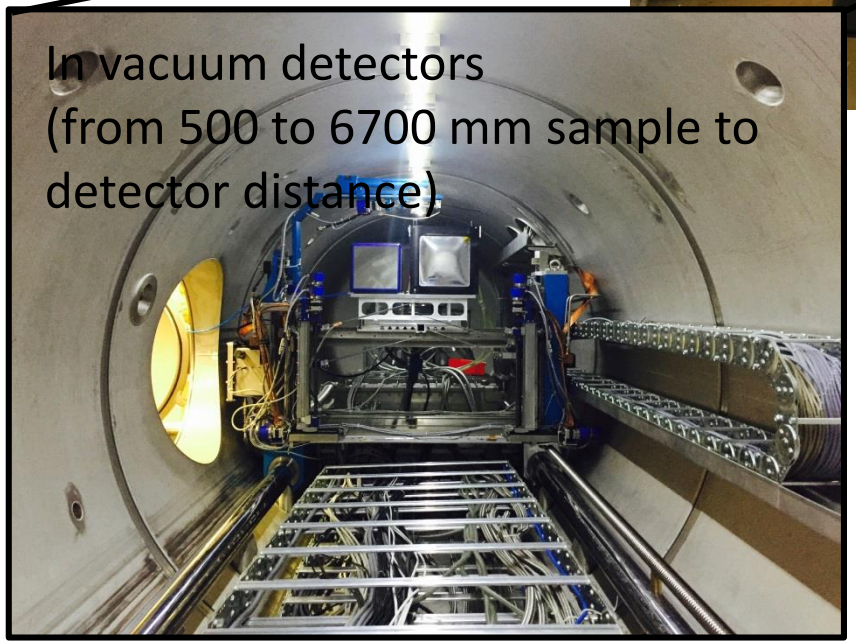


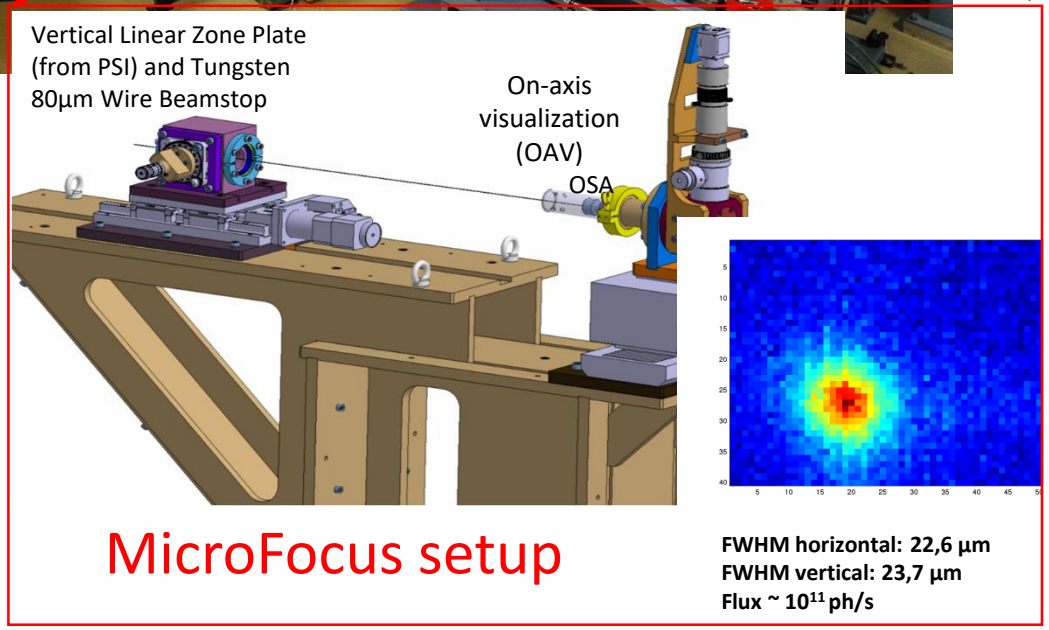
> 50 sources (2018)

SWING SAXS beamline

- **Source**: Onduleur U20 sous vide.
- **Gamme d'énergie**: 5-17 keV (Monochromateur 2 cristaux Si111).
- Deux **miroirs de focalisation**: horizontal (HFM) and vertical (VFM).
  Taille faisceau niveau échantillon:
  375 (H) x 25 (V) µm^2 (FWHM).



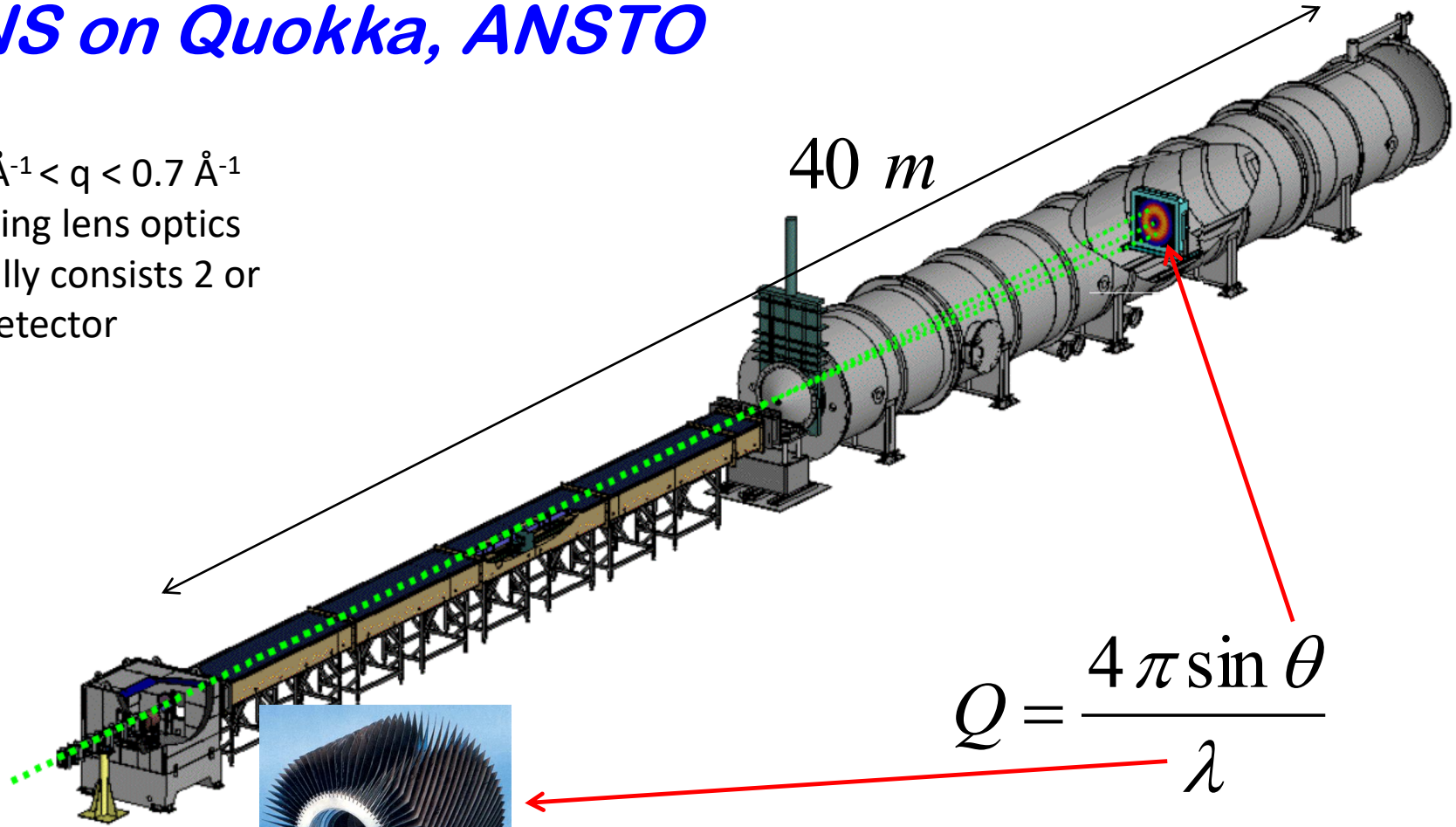




Australian neutron facility

Measuring SANS on Quokka, ANSTO

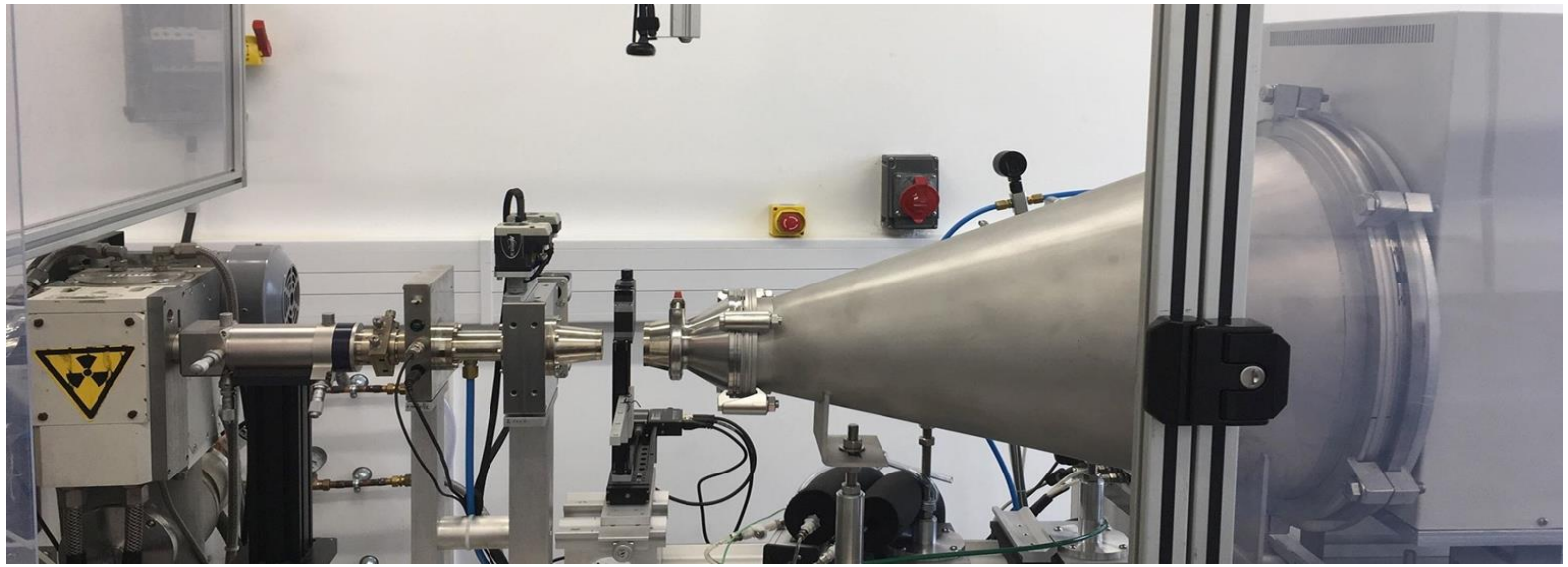
- q-range (standard): 4×10^{-3} Å^{-1} < q < 0.7 Å^{-1}
  q_{min} = 6×10^{-4} Å^{-1} with focusing lens optics
- a given measurement usually consists 2 or 3 camera settings (sample detector distances).



SAXS experiments at LPS

MORPHEUS LPS ORSAY

https://equipes2.lps.u-psud.fr/matrix/morpheus/



X-ray energy; wave-length
Mo: 17 keV; λ = 0.71 Å

X-ray energy; wave-length
Cu: 8 keV ; λ = 1,54 Å

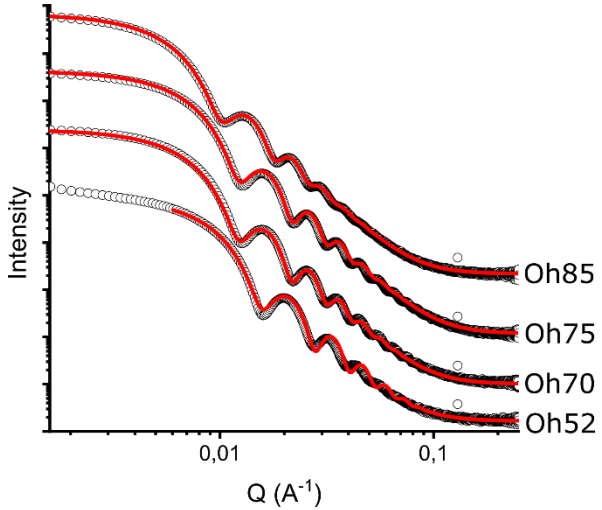
Scattering versus imaging

High statistics : ☺
average over about 10^{12} objects

In situ experiments ☺ during synthesis, temperature change, magnetic field …
Coupling with spectroscopy, rheology, stop-flow …

Use of synchrotron sources ☺

Indirect method ☹
Data modeling, reciprocal space, Fourier transform

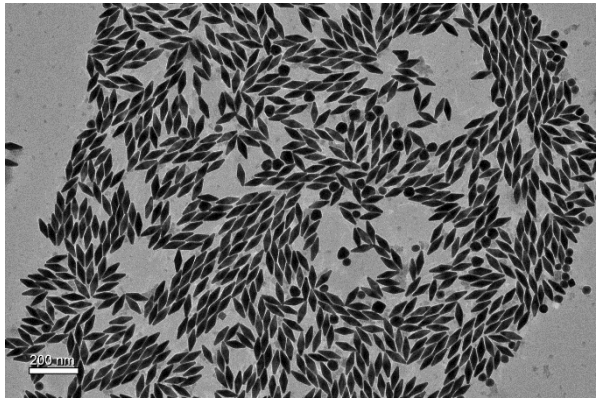


Pros and cons

Low statistics : ☹
Only a few 100's of objects on one image

TEM (Transmission Electron Microscopy) : ☹
demanding sample preparation conditions
under vacuum, drying, freezing … -> artefacts

Environmental TEM ☺



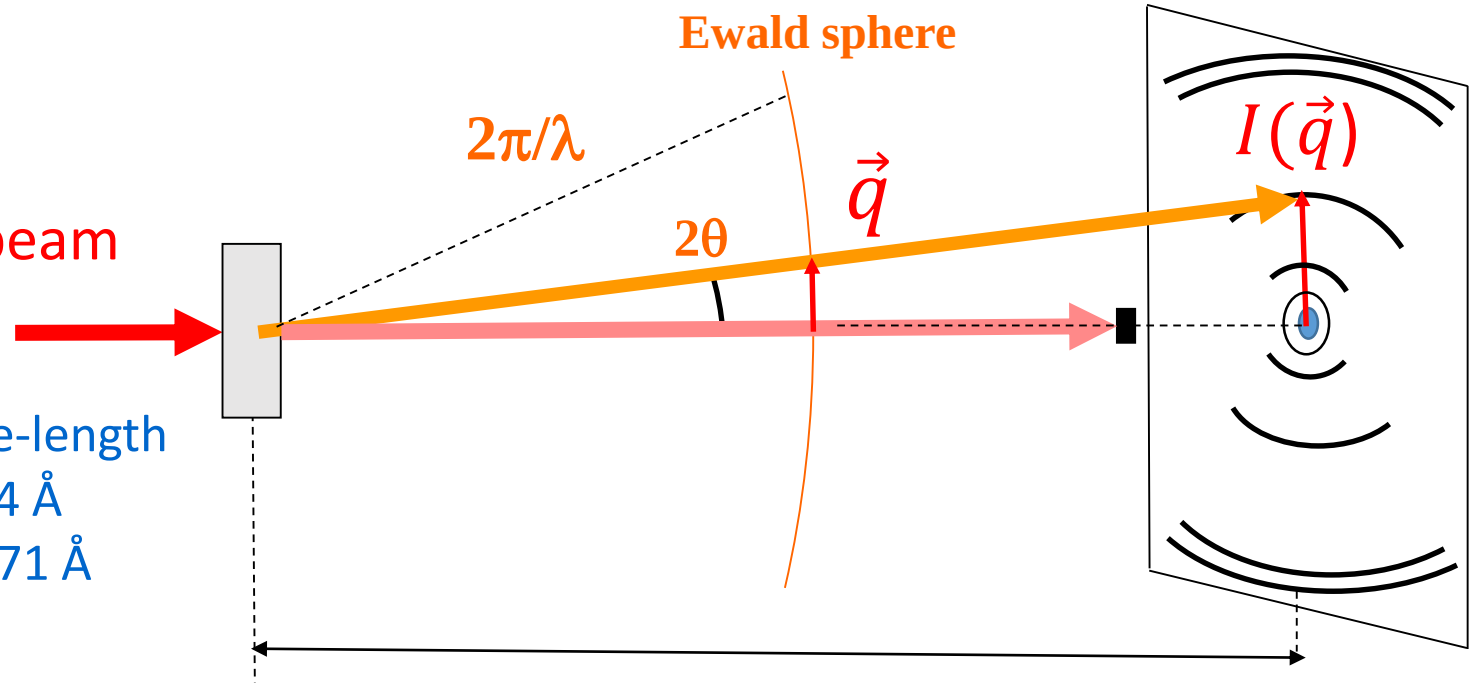
Direct method ☺
Image in real space !

-> combine both methods ☺

SESSION

1. Introduction
2. Scattering experiment
3. Some theory
4. Form factor: Spherical objects and other shapes
5. Data modelling
6. Structure factor: Hexagonal and lamellar mesophases

X-ray Scattering



Incident X-ray beam

X-ray energy; wave-length
Cu: 8 keV ; λ = 1,54 Å
Mo: 17 keV; λ = 0.71 Å

SWING : 5-17 keV

WAXS
Wide Angle X-ray Scattering

SAXS
Small Angle X-ray Scattering

Intensity : $I(\vec{q})$

$$E = h\upsilon = \frac{hc}{\lambda}$$

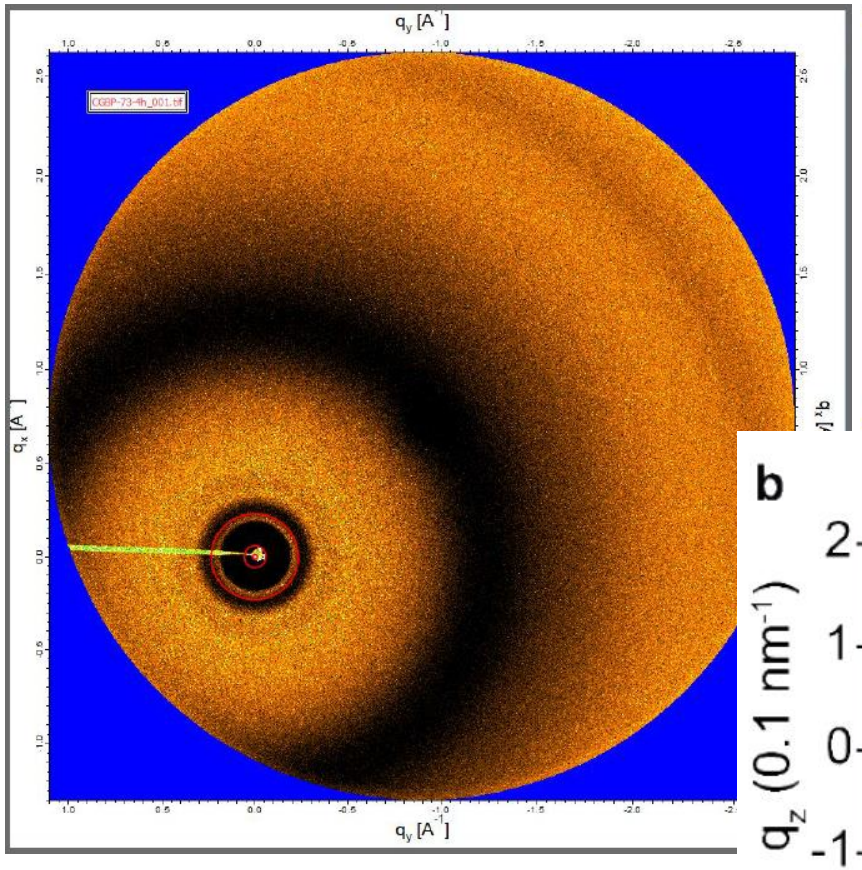
elastic scattering

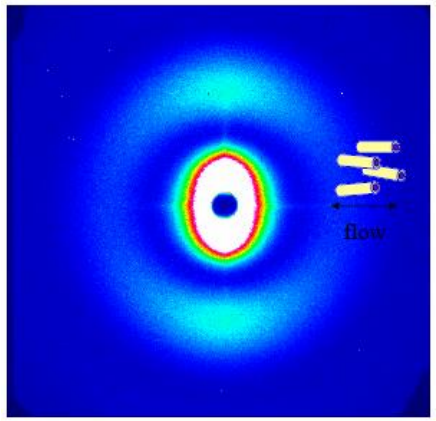
scattering angle 2θ

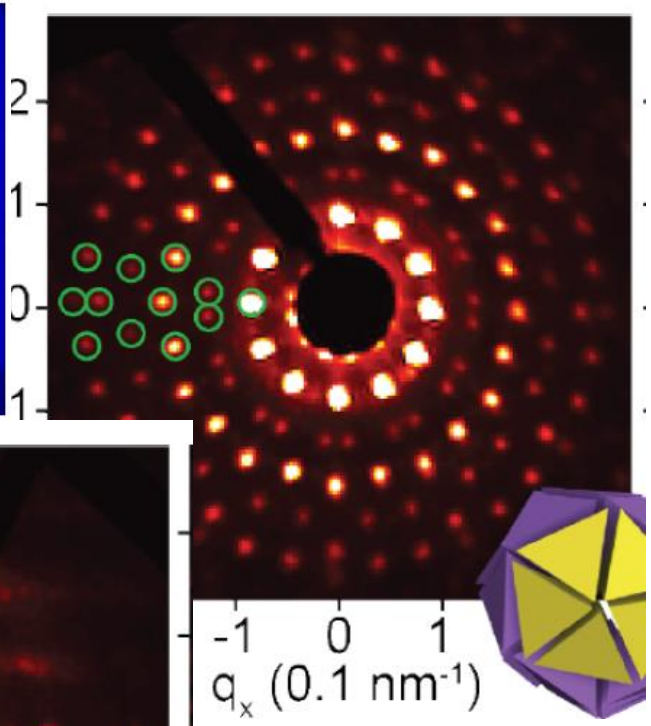
scattering vector $\vec{q}$

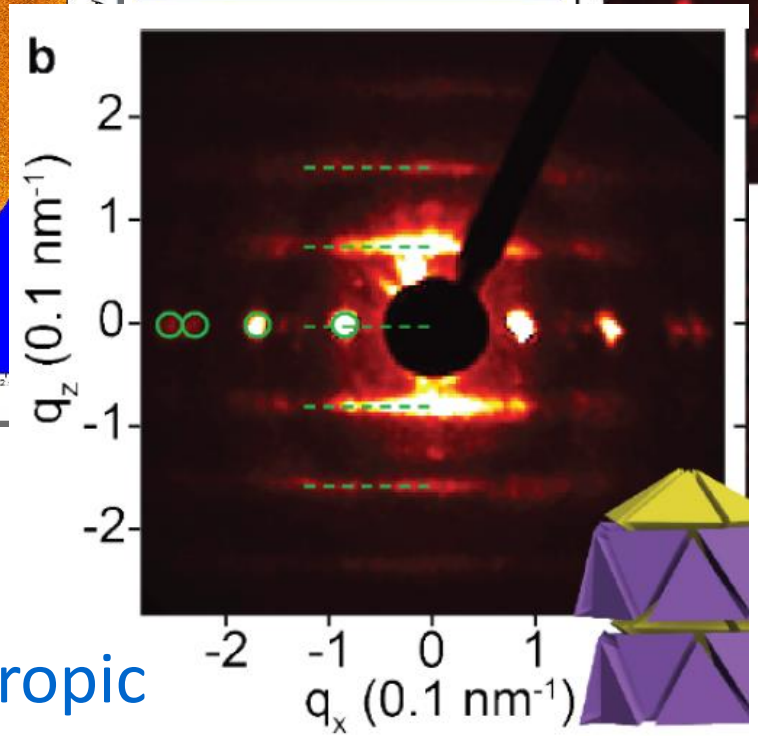
$$|\vec{q}| = \frac{4\pi}{\lambda} sin\theta$$

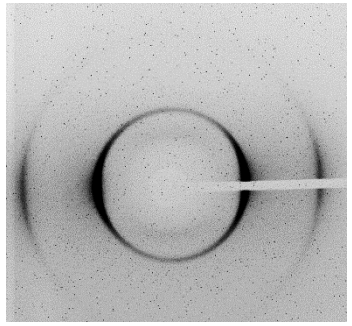
Scattering images

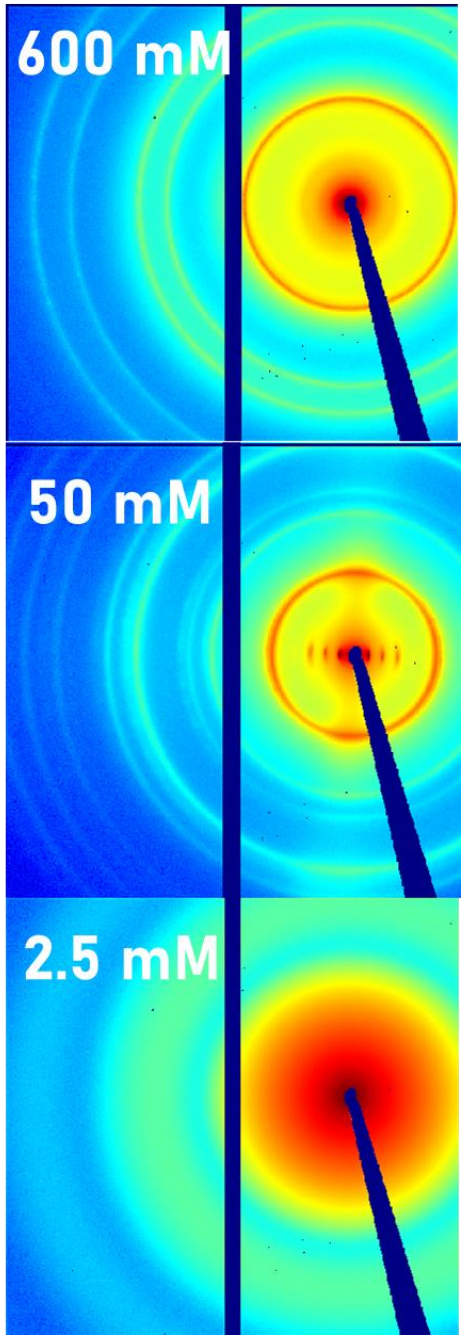






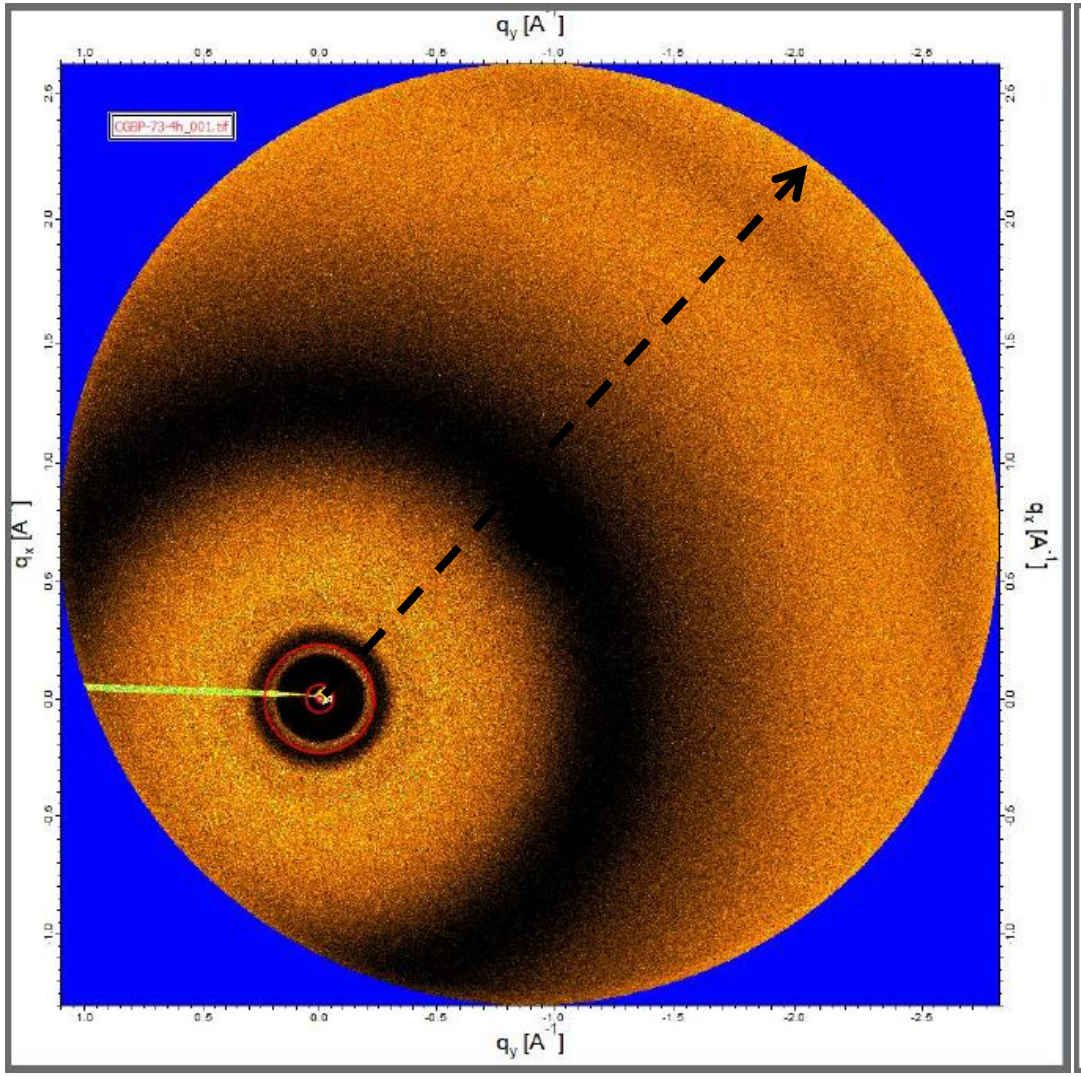


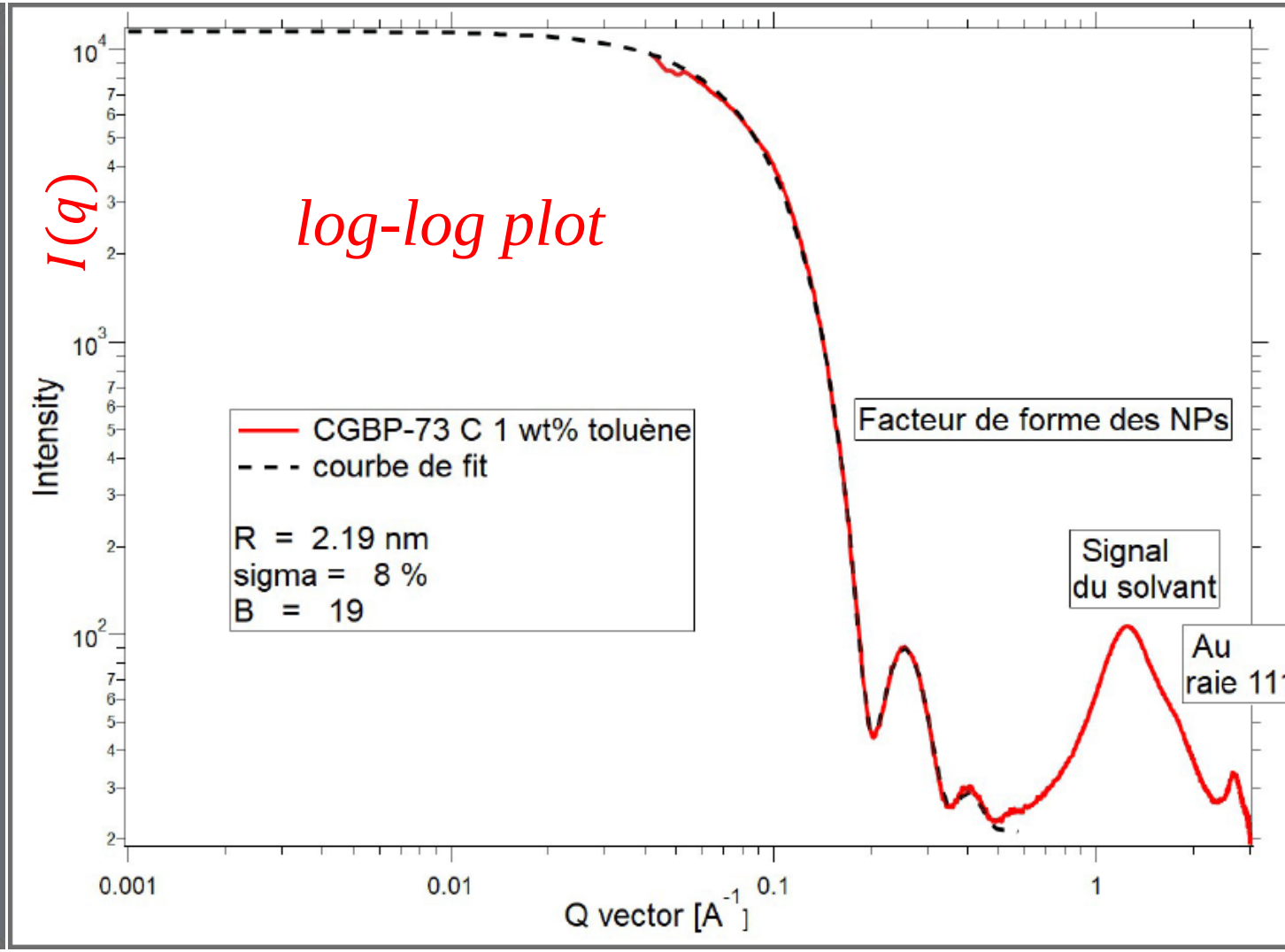




Isotropic *versus* anisotropic

Data reduction





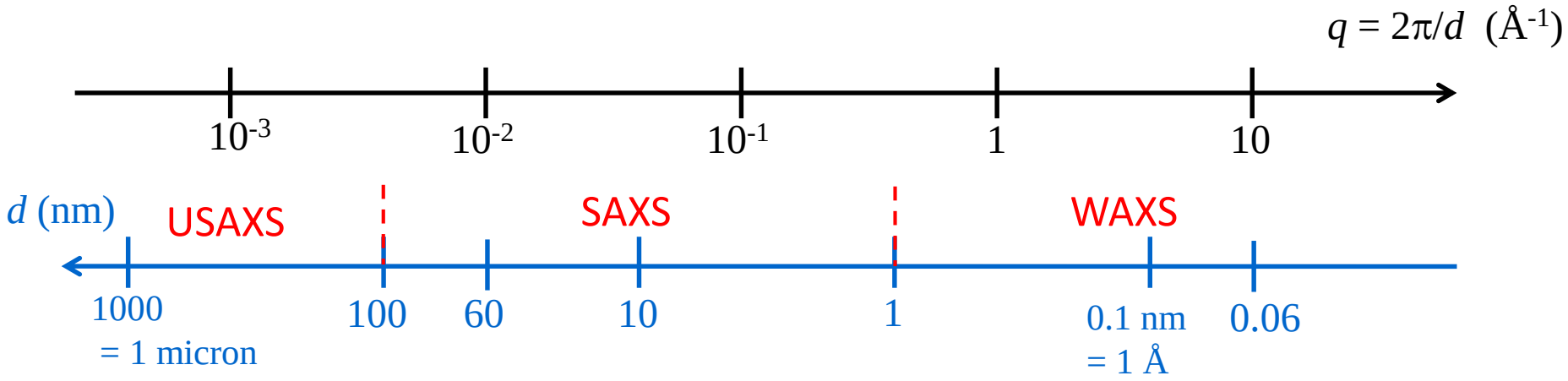
2D image

1D profile

$q = |\vec{q}| = 2\pi/d$

Scattering vector units

$$q = |\vec{q}| = (4\pi/\lambda)\sin\theta = 2\pi/d \quad (\text{Å}^{-1})$$



Crystallography

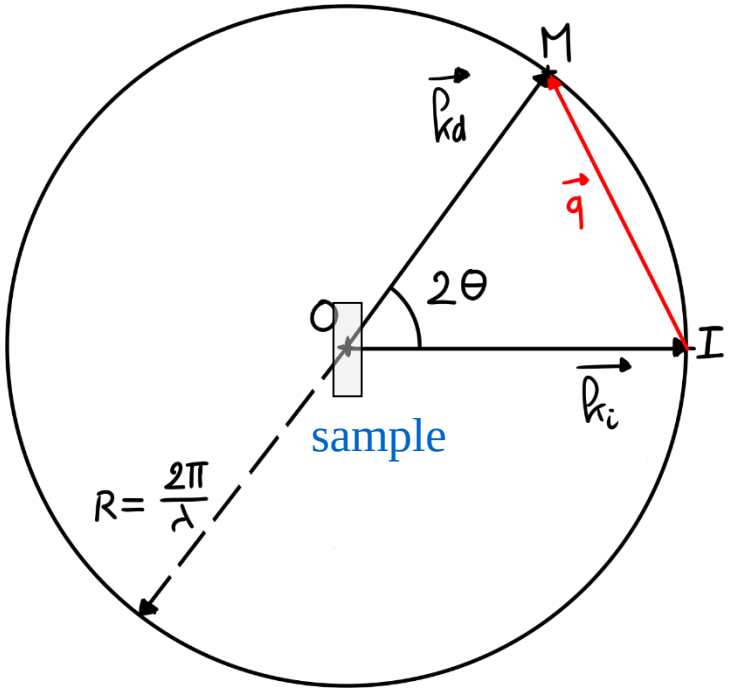
WAXS: atomic structure	d ≅ 0.1-1 nm
SAXS: supramolecular scale	d ≅ 1-100 nm
USAXS: micron size objects	d ≅ 0.1-10 μm

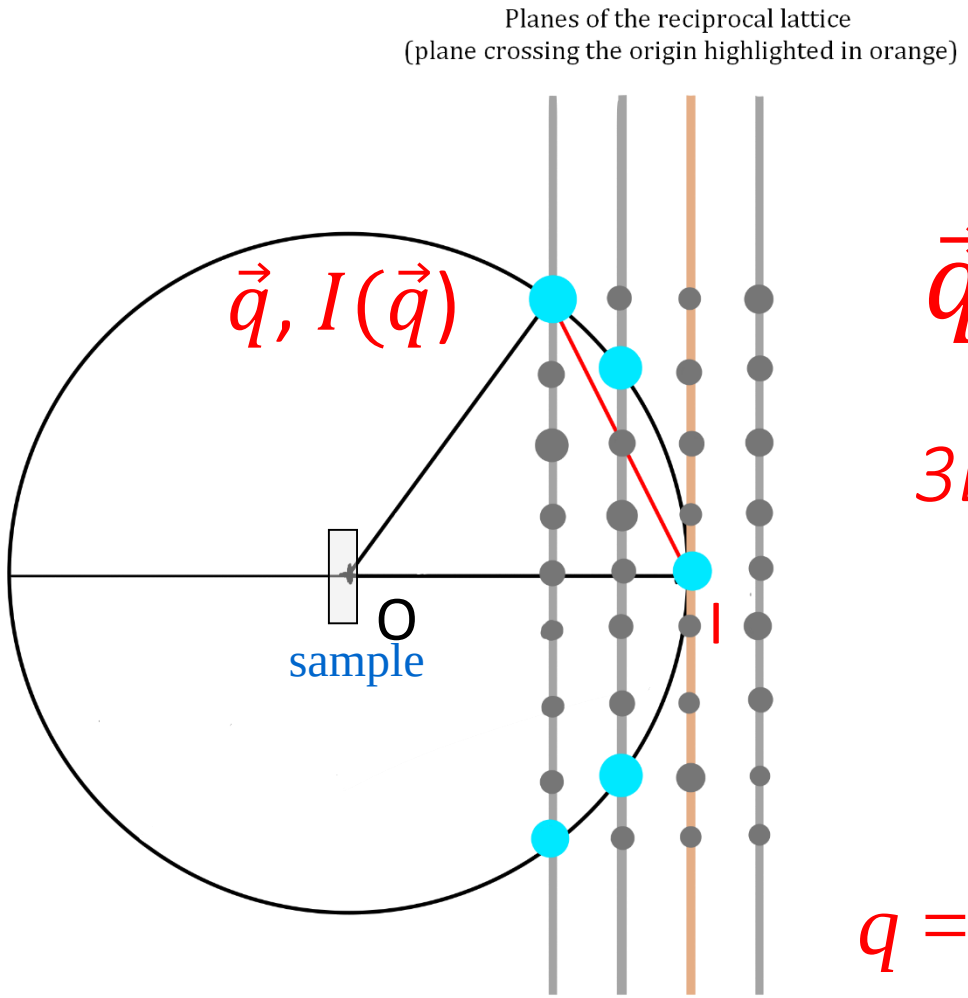
Bragg's law

$$2\,d\sin\theta = \lambda$$

Reciprocal space

Ewald sphere





$\vec{q}$ space

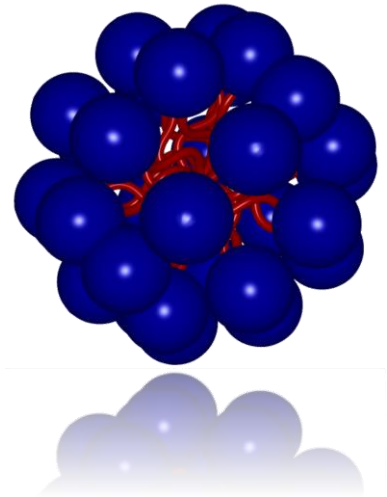
3D-vector

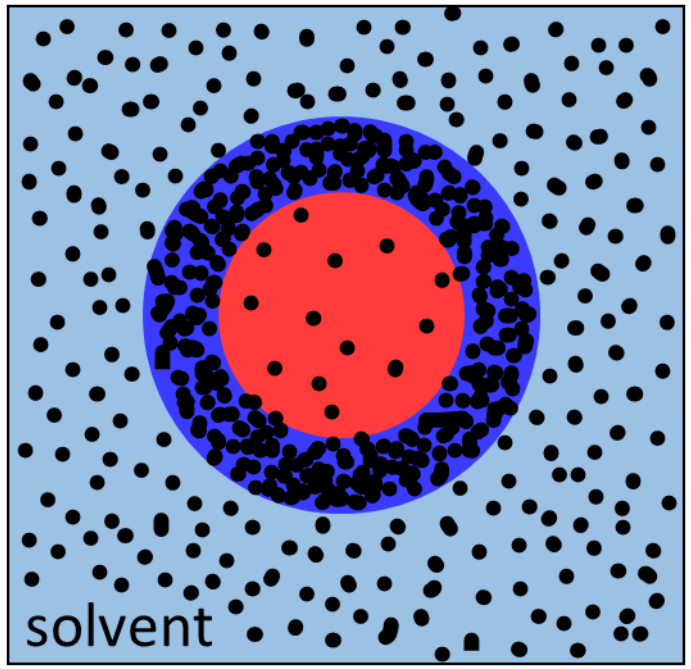
$q = |\vec{q}| = 2\pi/d$

Intersection between Ewald sphere and 3D reciprocal space

X-rays are scattered by electrons in matter

Micellar aggregate





atomic coordinates WAXS

number of electrons per unit volume SAXS

-> continuous function :

the electron density $\rho_e(\vec{r})$

OR

the scattering length density $\rho_{SLD}(\vec{r})$

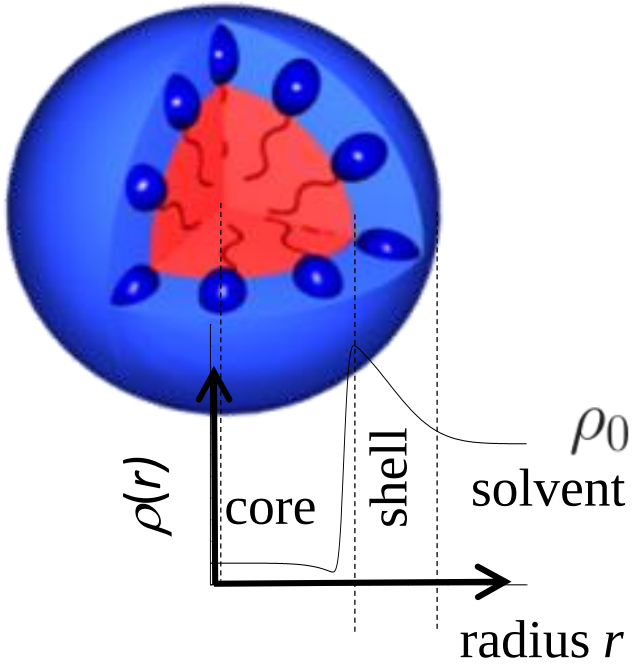
contrast between high and low density regions

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

$$\rho_{SLD}(\vec{r}) = r_e\rho_e(\vec{r})$$

SLD : Scattering Length Density

Micellar aggregate



$$\Delta\rho(\vec{r}) = \rho - \rho_0$$

$$\rho_{SLD}(\vec{r}) = \frac{1}{V_{\vec{r}}} \sum_{i(atoms)\in V_{\vec{r}}} b_i$$

$$b_i = Z_i r_e$$

$$r_e = 2.81794{*}10^{-15} m$$

$$\rho_e(\vec{r}) = \frac{1}{V_{\vec{r}}} \sum_{i(atoms)\in V_{\vec{r}}} Z_i$$

$$\rho_{SLD}(\vec{r}) = r_e \rho_e(\vec{r}) \qquad [L^{-2}]$$

Values of electron densities and SLDs

$$\rho_e(e/nm^3) = \frac{N_e}{v(nm^3)} = \frac{N_e N_{Avogadro} d(g/cm^3)}{10^{21} M(g/mol))} = \frac{602 N_e d(g/cm^3)}{M(g/mol))}$$

$$r_e = 2.81794^{*}10^{-15} m$$

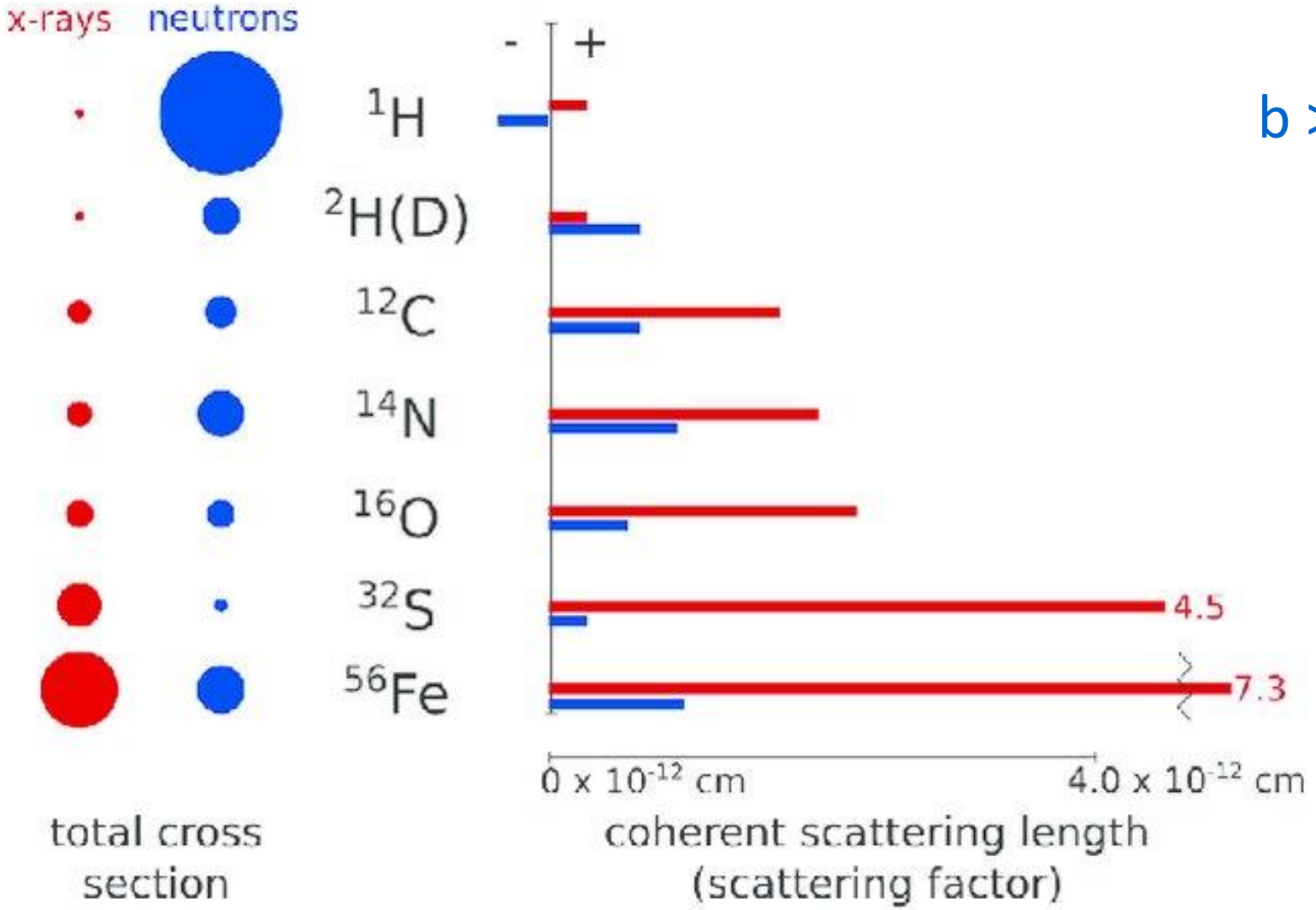
$$\rho_{SLD} = r_e \rho_e$$

$$[L^{-2}]$$

Compound	ρ_e	ρ_{SLD}	N_e	M	d
	e/nm3	*10^{-6} A^{-2}*		*g/mol*	*g/cm³*
water	334	9.41	10	18.016	0.998
toluene	283	7.97	50	92.14	0.867
hexane	229	6.45	50	86.18	0.655
SiO_2	661	18.63	30	60.09	2.2
Ag	2757	77.69	47	108	10.49
Au	4659	131.29	79	196	19.3
Pt	5163	145.49	78	195	21.45
PO (propylene oxide)	333	9.38	32	58.078	1.004
EO (ethylene oxide)	371	10.45	24	44.052	1.13
dodecane	259	7.30	98	170.328	0.7487
hexadecane	267	7.52	130	226.432	0.7733
-CH2	295	8.31	8	14.026	0.86
-CH3	168	4.73	9	15.034	0.466
-C12H25	276	7.78	97	169.32	0.8

Neutrons versus X-rays

$$b_i = Z_i r_e$$

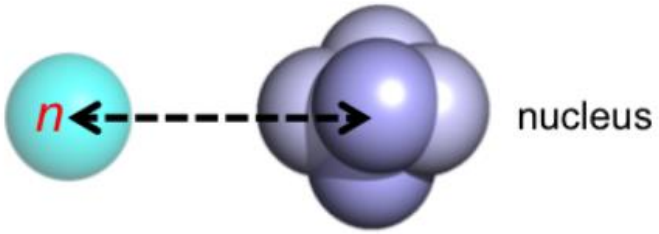


b > 0 or b <0

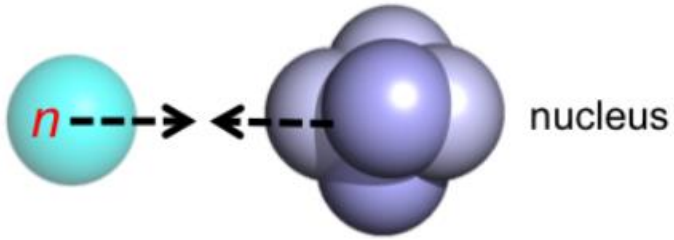
Neutrons

b > 0

Repulsive energy potential



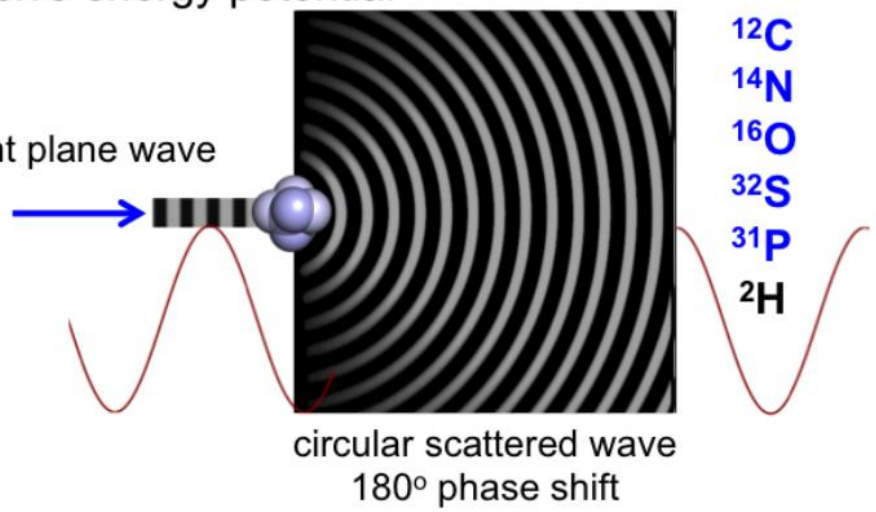
Attractive energy potential



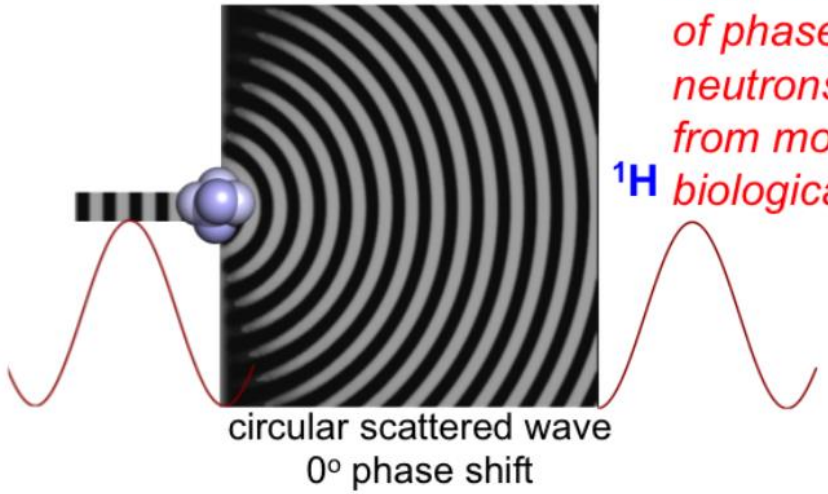
b < 0

In 2-dimensions: elastic coherent scattering

Repulsive energy potential



Attractive energy potential



Neutrons scattered from ^{1}H are 180° out of phase with neutrons scattered from most other biological isotopes!

$$-\frac{b}{r}e^{-i\vec{q}\cdot\vec{r}}$$

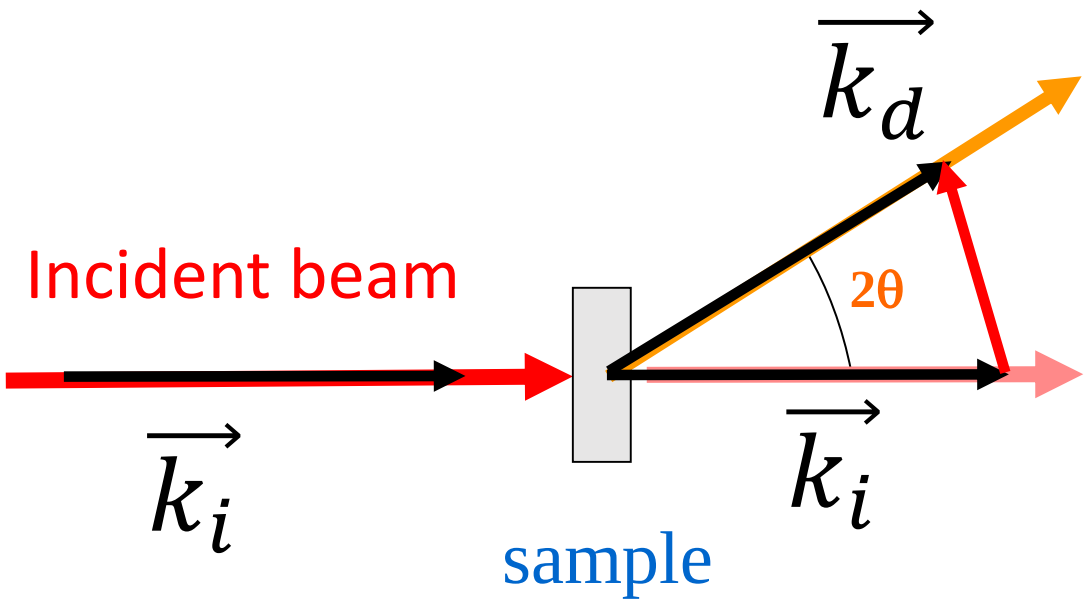
Cy M. Jeffries, Zuzanna Pietras and Dmitri I. Svergun,
EPJ Web of Conferences 236, 03001 (2020) , https://doi.org/10.1051/epjconf/202023603001

SESSION

1. Introduction
2. Scattering experiment
3. Some theory
4. Form factor: Spherical objects and other shapes
5. Data modelling
6. Structure factor: Hexagonal and lamellar mesophases

Elastic scattering

no change in energy/wavelength : $\left|\overrightarrow{k_i}\right| = \left|\overrightarrow{k_d}\right|$



$\vec{q} = \overrightarrow{k_d} - \overrightarrow{k_i}$

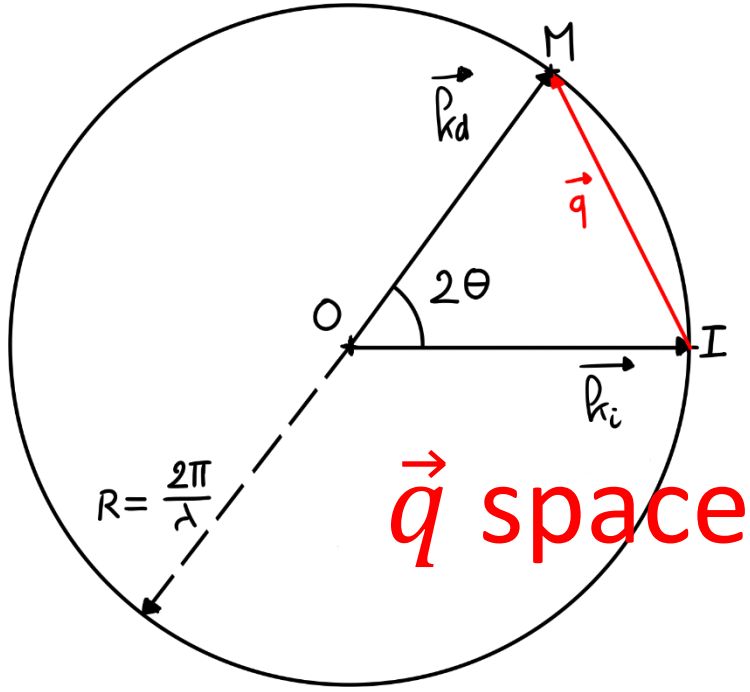
scattering vector

wave vector

$\left|\overrightarrow{k_i}\right| = \frac{2\pi}{\lambda}$

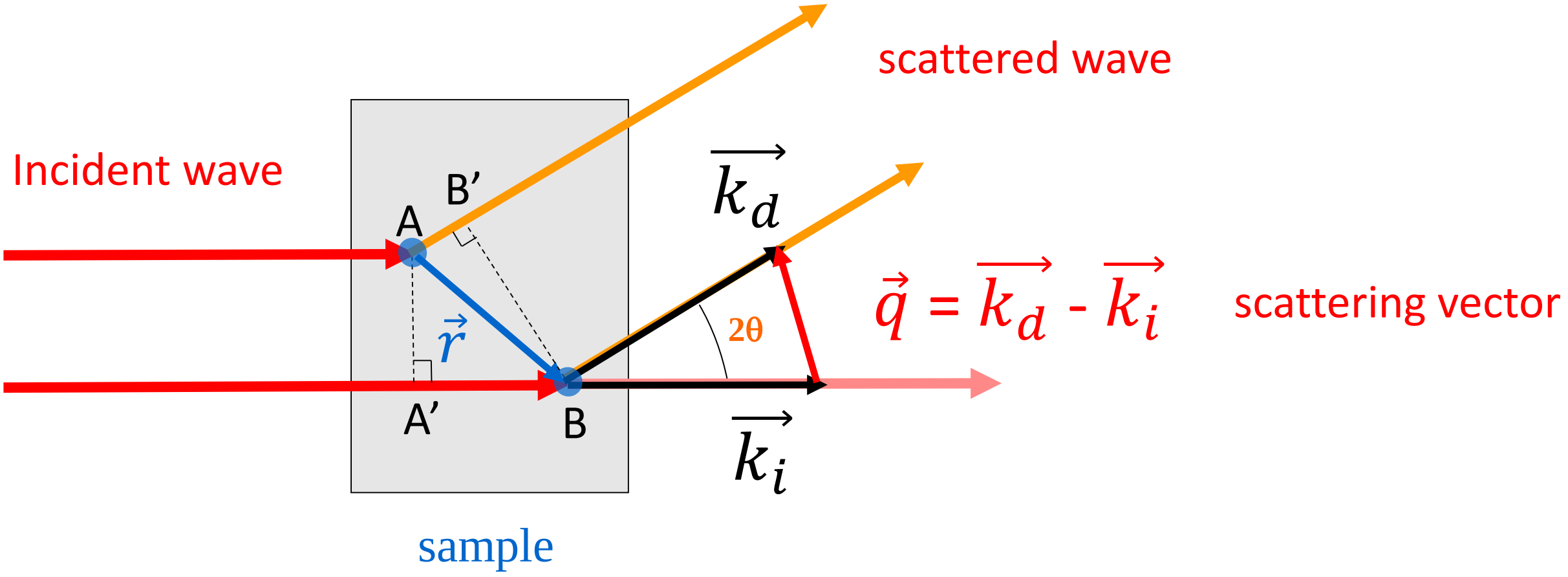
$|\vec{q}| = \frac{4\pi}{\lambda} sin\theta$

Ewald sphere



3D reciprocal space

Phase shift between two scattering points



$$e^{\frac{2i\pi}{\lambda}(A'B-AB')} = e^{+i\overrightarrow{k_i}\cdot\vec{r}-i\overrightarrow{k_d}\cdot\vec{r}} = e^{-i\vec{q}\cdot\vec{r}}$$

3D Fourier transform

Basic relations

Scattering amplitude

$$A(\vec{q}) = \int_{V_{tot}} \rho(\vec{r}) e^{-i\vec{q}\cdot\vec{r}} d\vec{r}$$

$[L]$

3D Fourier transform of the SLD function

Intensity == measured quantity

$$I(\vec{q}) = \frac{1}{V_{tot}} \langle |A(\vec{q})|^2 \rangle_t$$

$[L^{-1}]$

Normalisation per unit volume, average over acquisition time

V_{tot} == Sample volume inside the X-ray beam

Absolute Intensity

What we measure during one acquisition == Number of photons in a pixel

$$N_{pixel}(\vec{q}) = \eta\,(\phi_0\,A\,T)\;\; t_{acq}\;\Delta\Omega\;\; e\;\; I(\vec{q}) + \mathrm{BG}$$

$[L^{-1}]$ $\quad I(\vec{q}) = \dfrac{1}{V_{tot}}\langle|A(\vec{q})|^2\rangle_t$

$[L]$ $\quad A(\vec{q}) = \displaystyle\int_{V_{tot}} \rho(\vec{r})e^{-i\vec{q}\cdot\vec{r}}d\vec{r}$

$[L^{-2}]$ $\quad \rho(\vec{r}) = r_e\,\rho_e(\vec{r})$: SLD

$[L^{-3}]$ $\quad \rho_e(\vec{r})$: electron density

r_e = 2.81794×10^{-15} m
Classical radius of electron

- η: detector efficency
- ϕ_0: incident flux == photons number per unit time and surface area
- A : section of the X-ray beam on the sample
- T : sample transmission
- $(\phi_0\,A\,T)$: integrated transmitted flux
- t_{acq} : acquisition time
- e : sample thickness
- $A\,e = V_{tot}$: sample volume inside the X-ray beam
- Δ: pixel size; r : distance between sample and pixel
- $\Delta\Omega = \left(\dfrac{\Delta}{r}\right)^2$: solid angle for one pixel

case 0

Scattering by a single particle
(micelle, NP …) === Form Factor

Shape, size and orientation of the particle

case 1

Scattering by an assembly of identical/similar particles

AND

NO interference terms

(dilute conditions)

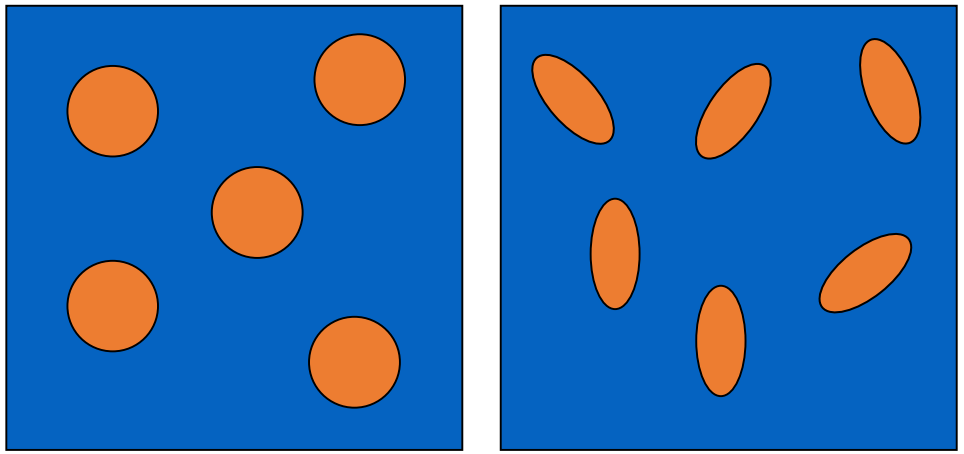
=== total intensity is the sum of the individual intensities scattered by each particle

Statistical average Form Factor

(shape, size, polydispersity, orientationnal average)

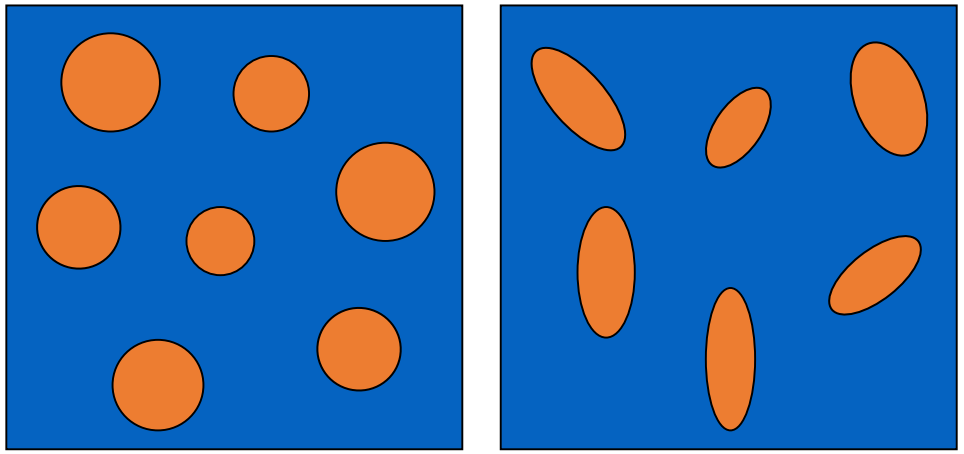
Average Form Factor

$$I(\vec{q}) = \frac{N}{V_{tot}} P(\vec{q})$$



$$P(\vec{q}) = \frac{1}{N} < \sum_{i=1}^{N} |F_i(\vec{q})|^2 >_t$$

Orientation average (no need for spheres)



Polydispersity == Average over size distribution

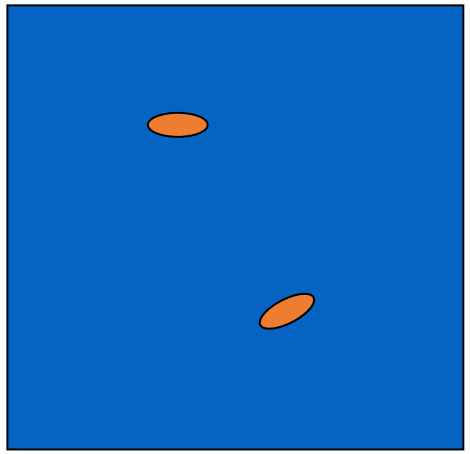
$$P(\vec{q}) = \int_0^\infty D(r, R_{ave}, \sigma) |F(\vec{q}, r)|^2 dr$$

case 2

Scattering by an assembly of identical/similar particles
AND
Interference terms
(spatial correlations between the positions of the particles need to be taken into account)

Combination of form factor and structure factor

Interference term with two particles



$$I(\vec{q}) = \frac{1}{V_{tot}} < |A_1(\vec{q}) + A_2(\vec{q})|^2 >_t$$

$$I_1(\vec{q}) = \frac{1}{V_{tot}} < |A_1(\vec{q})|^2 >_t = \frac{1}{V_{tot}} < A_1(\vec{q}) A_1^*(\vec{q}) >_t$$

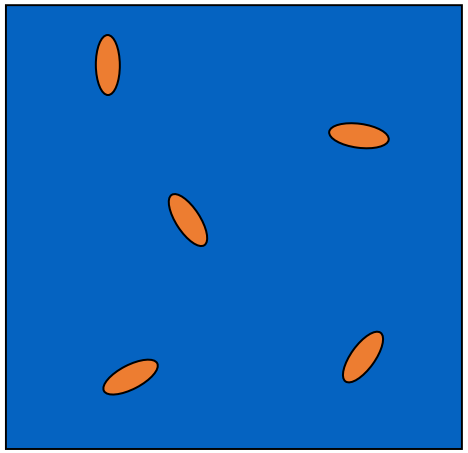
$$I(\vec{q}) = I_1(\vec{q}) + I_2(\vec{q}) + \frac{1}{V_{tot}} < A_1(\vec{q}) A_2^*(\vec{q}) + A_2(\vec{q}) A_1^*(\vec{q}) >_t$$

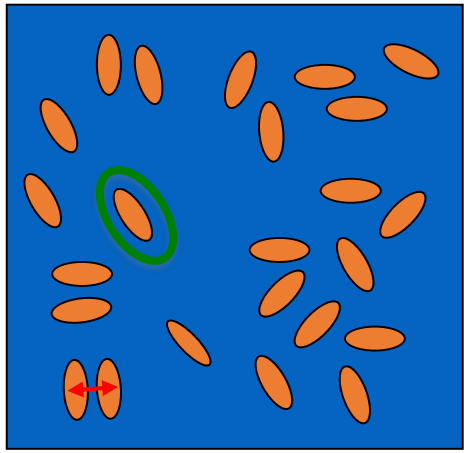
Interference term

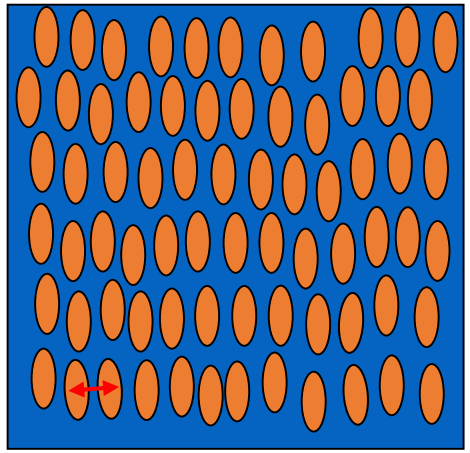
Form factor and structure factor

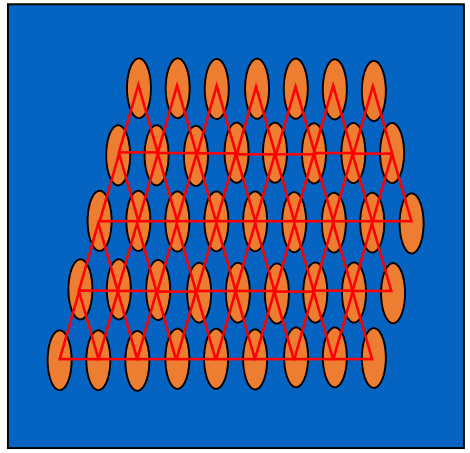
$$n = \frac{N}{V_{tot}}$$

N identical particles









Dilute conditions

form factor only

Local order

Long-range order

== lattice

$$I(\vec{q}) = n\,P(\vec{q})$$

$$I(\vec{q}) = n\,P(\vec{q})\,S(\vec{q})$$

same orientation for non spherical particles !!!

SESSION

1. Introduction
2. Scattering experiment
3. Some theory
4. Form factor: Spherical objects and other shapes
5. Data modelling
6. Structure factor: Hexagonal and lamellar mesophases

case 0

Scattering by a single particle
(micelle, NP …) === Form Factor

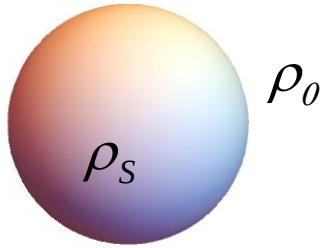
Shape, size and orientation of the particle

Form factor for a spherical particle

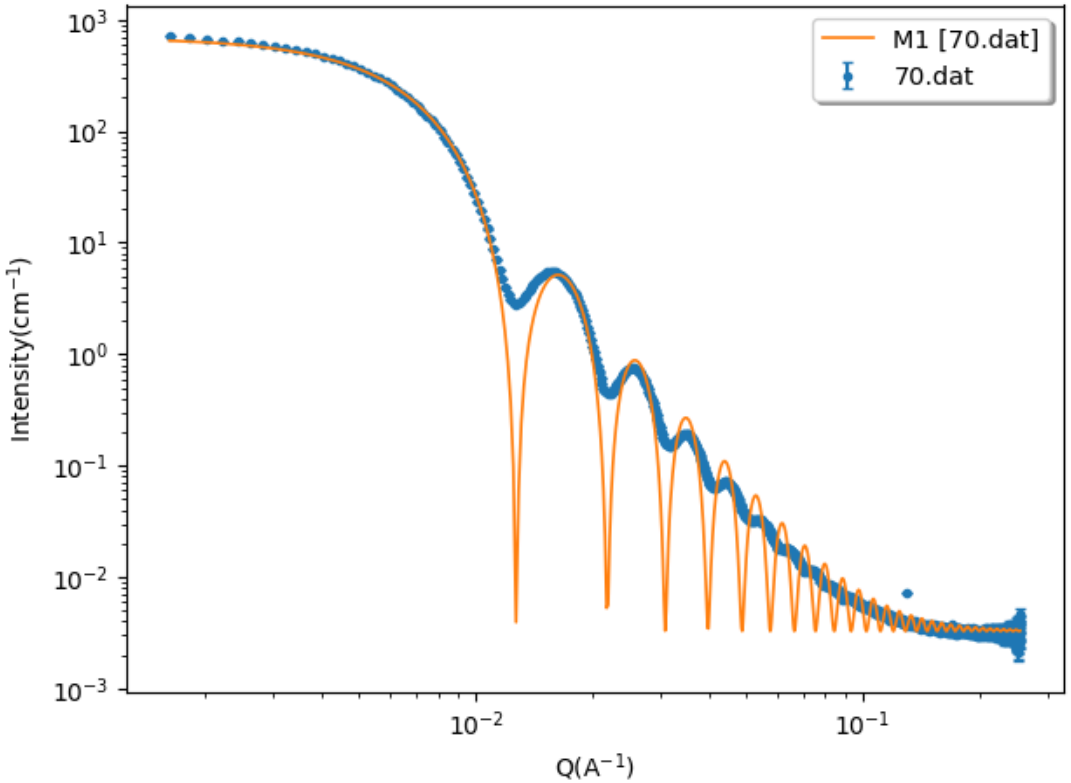
Scattering amplitude for a sphere of radius *R* and contrast $\Delta\rho$

$$F_s(q,R) = \Delta\rho \int_{V_s(R)} e^{-i\vec{q}.\vec{r}} d^3\vec{r}$$

$$P_s(q,R) = |F_s(q,R)|^2$$



$$\Delta\rho = \rho_S - \rho_0$$

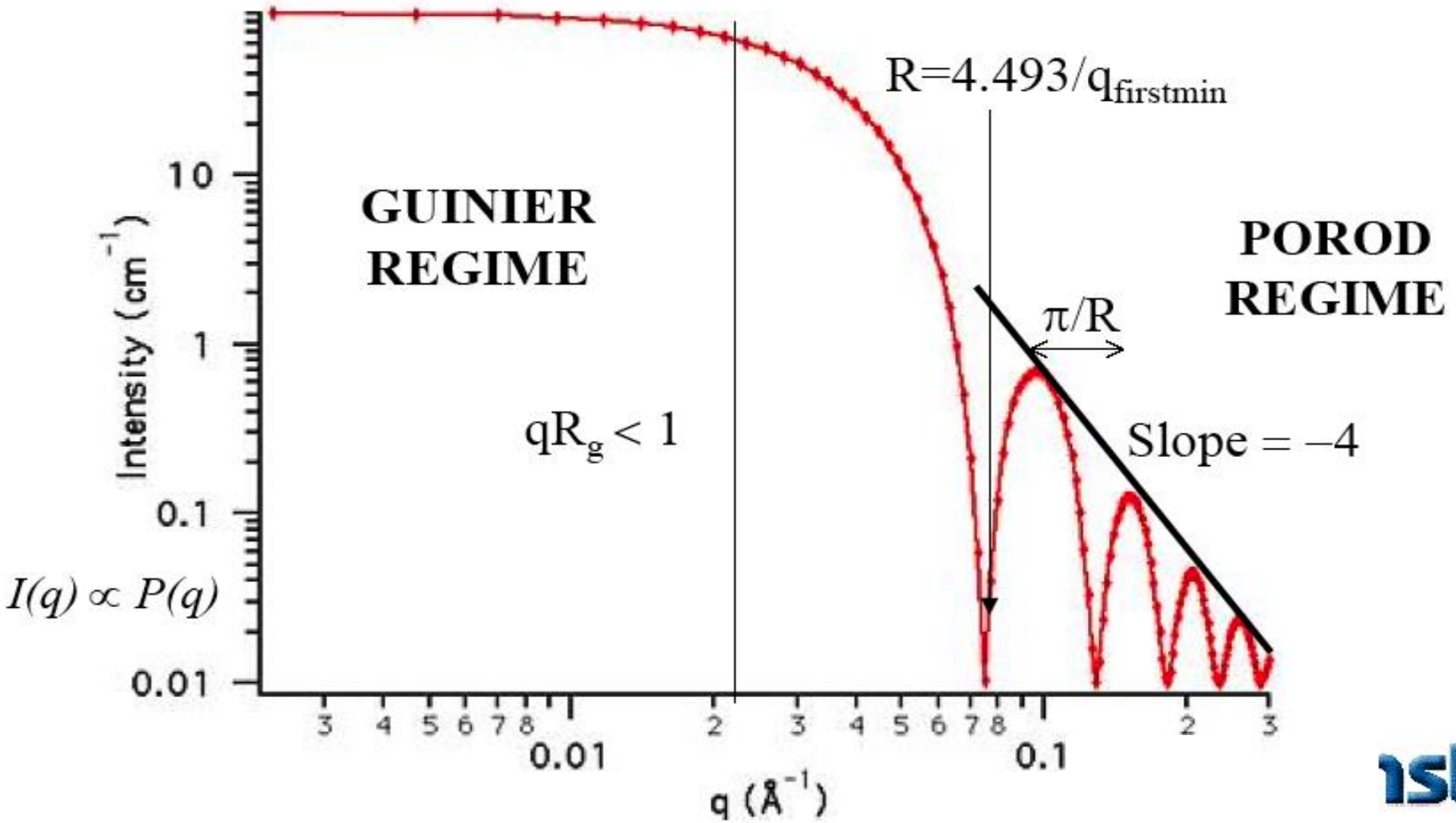


$$F_s(q,R) = \Delta\rho V_s(R) f_s(q,R)$$

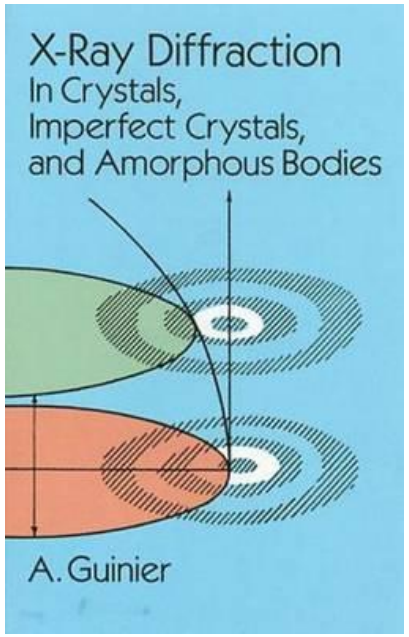
$$f_s(q,R) = 3\left(\frac{sin(qR) - qRcos(qR)}{(qR)^3}\right)$$

$$V_s(R) = \frac{4\pi}{3}R^3$$

Dilute monodisperse spheres



André Guinier
(1911-2000)



Guinier Law

$$I(q) = n(\Delta\rho)^2 V^2 \exp\left(\frac{-q^2 R_g^2}{3}\right)$$

V = volume of particles

R_g = radius of gyration (root mean square distance from center of gravity)

The main assumptions of the Guinier Law are that:

- q is much smaller than 1/Rg
- Particles scatter independently of each other.
- The scattering bodies are isotropically distributed in the sample.
- Useful for estimating size of particles

LPS ORSAY *History of Science*

Porod Law

-4 slope

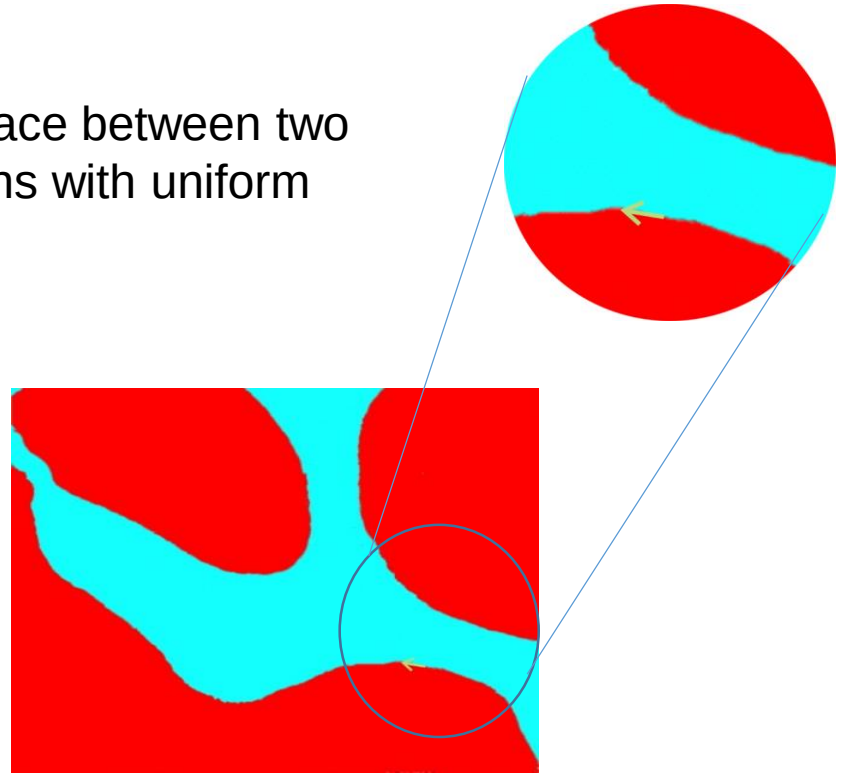
$$\lim_{q \to \infty} I(q) = \frac{K_p}{q^4}$$

$$K_p = \frac{2\pi S}{V_{tot}} (\Delta\rho)^2$$

S: total interface area

SLD contrast between the two regions

Interface between two regions with uniform SLDs

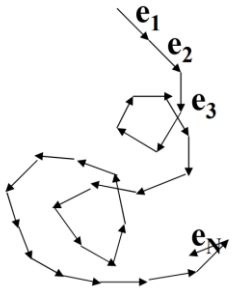


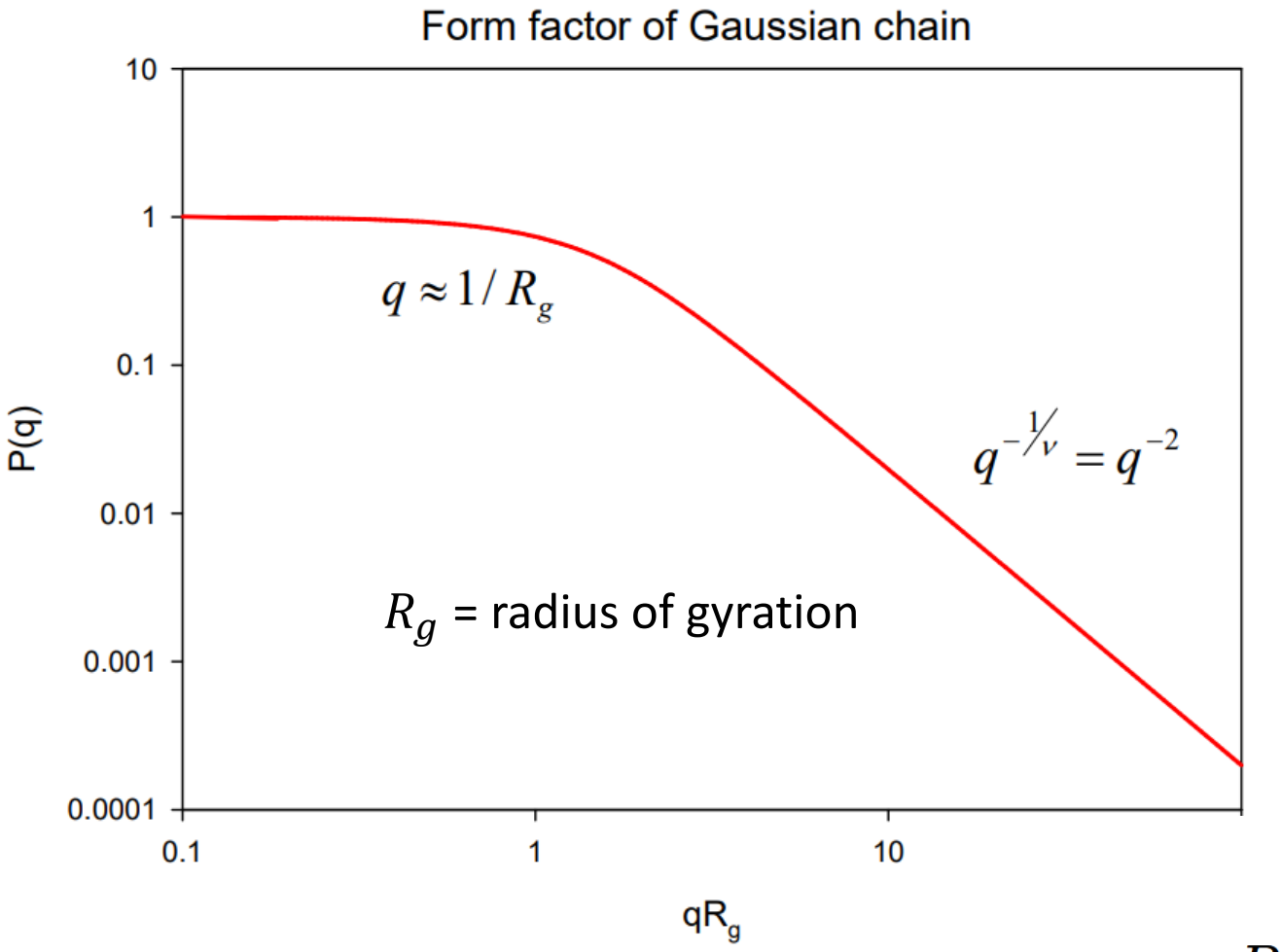
Günther Porod
(1919-1984)

Otto Kratky
(1902-1995)

History of Science

Polymer gaussian chain: Debye model





Peter Debye
(1884-1966)

History of Science

Random walk

N rigid segments of length b

$$R_g^2 = \frac{Nb^2}{6}$$

$$I_0 = \phi_{\text{poly}} \cdot V \cdot (\rho_{\text{poly}} - \rho_{\text{solv}})^2$$

$$P(q) = 2[\exp(-Z) + Z - 1]/Z^2$$

$$Z = (qR_g)^2$$

$$V = M/(N_A \delta)$$

case 1

Scattering by an assembly of identical/similar particles

AND

NO interference terms

(dilute conditions)

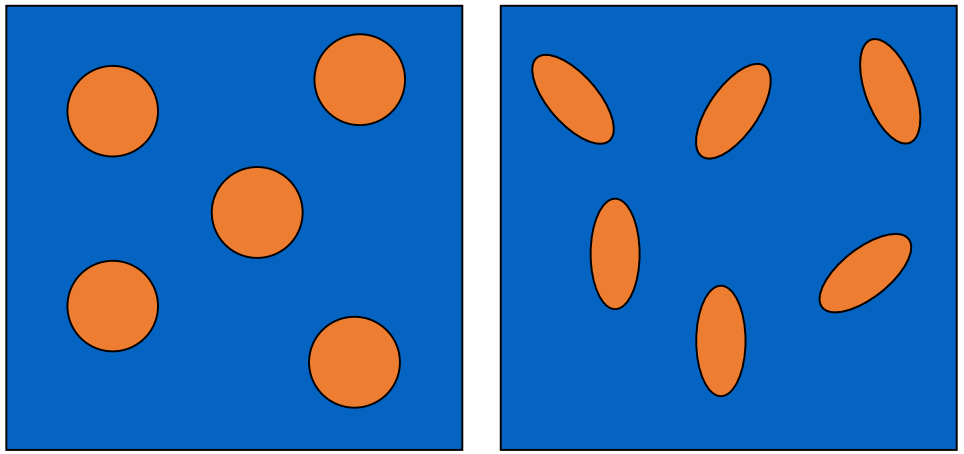
=== total intensity is the sum of the individual intensities scattered by each particle

Statistical average Form Factor

(shape, size, polydispersity, orientationnal average)

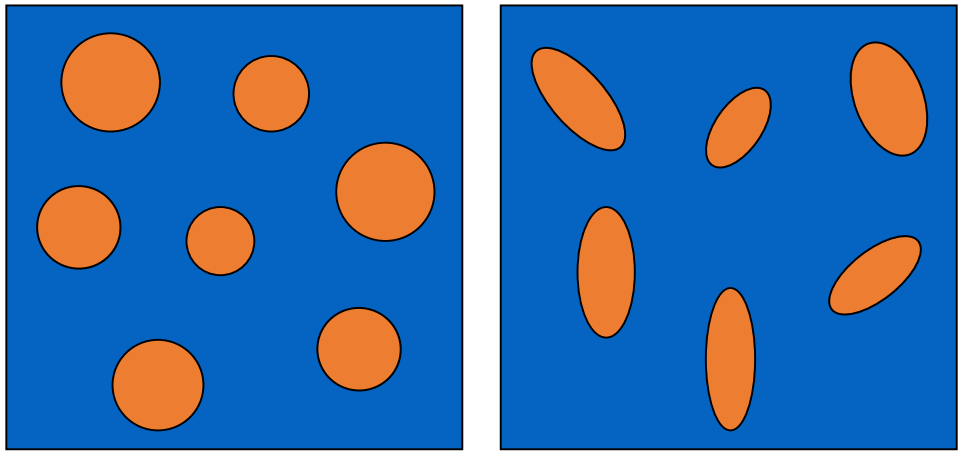
Average Form Factor

$$I(\vec{q}) = \frac{N}{V_{tot}} P(\vec{q})$$



$$P(\vec{q}) = \frac{1}{N} < \sum_{i=1}^{N} |F_i(\vec{q})|^2 >_t$$

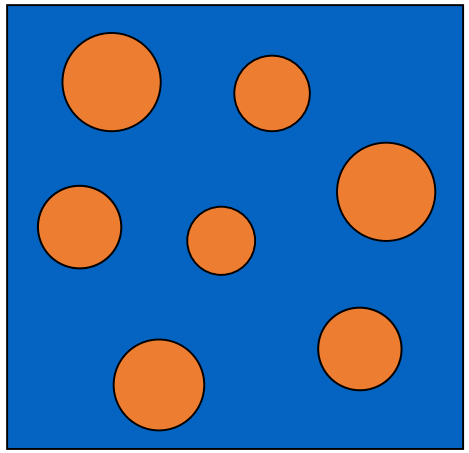
Orientation average (no need for spheres)

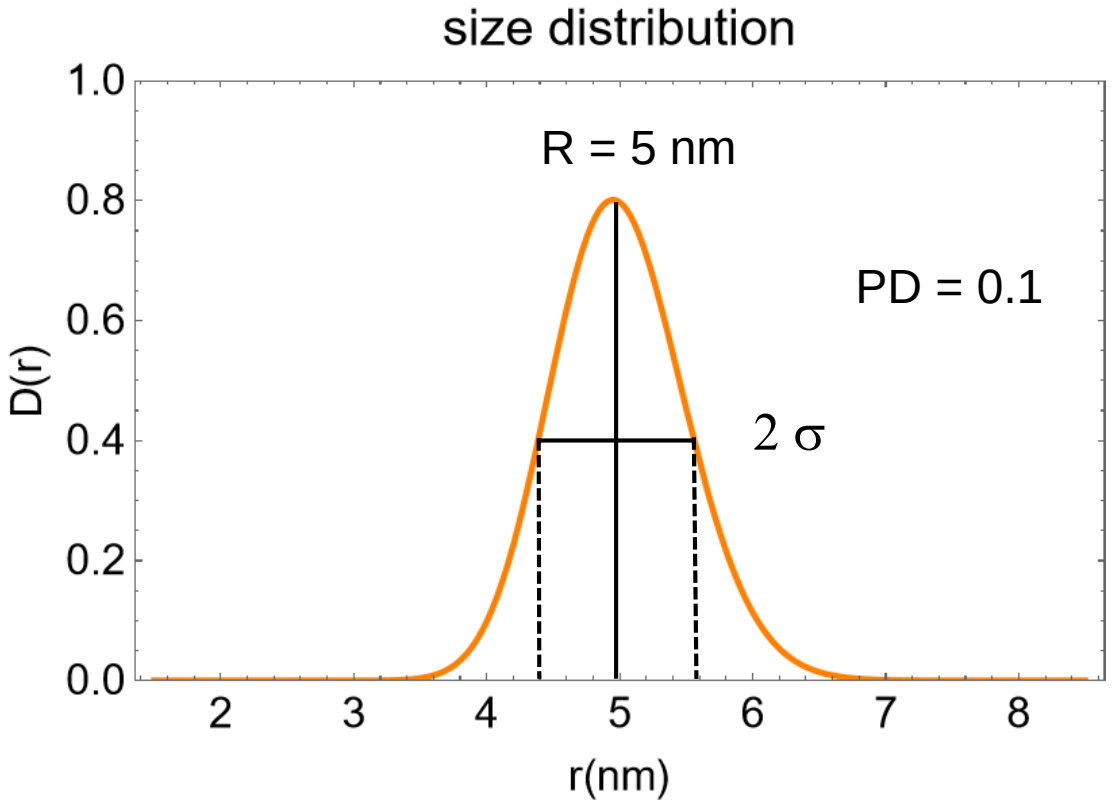


Polydispersity == Average over size distribution

$$P(\vec{q}) = \int_0^\infty D(r, R_{ave}, \sigma) |F(\vec{q}, r)|^2 dr$$

Polydispersity in size





D(r): size distribution function

R : average size

σ : standard deviation

PD : polydispersity index

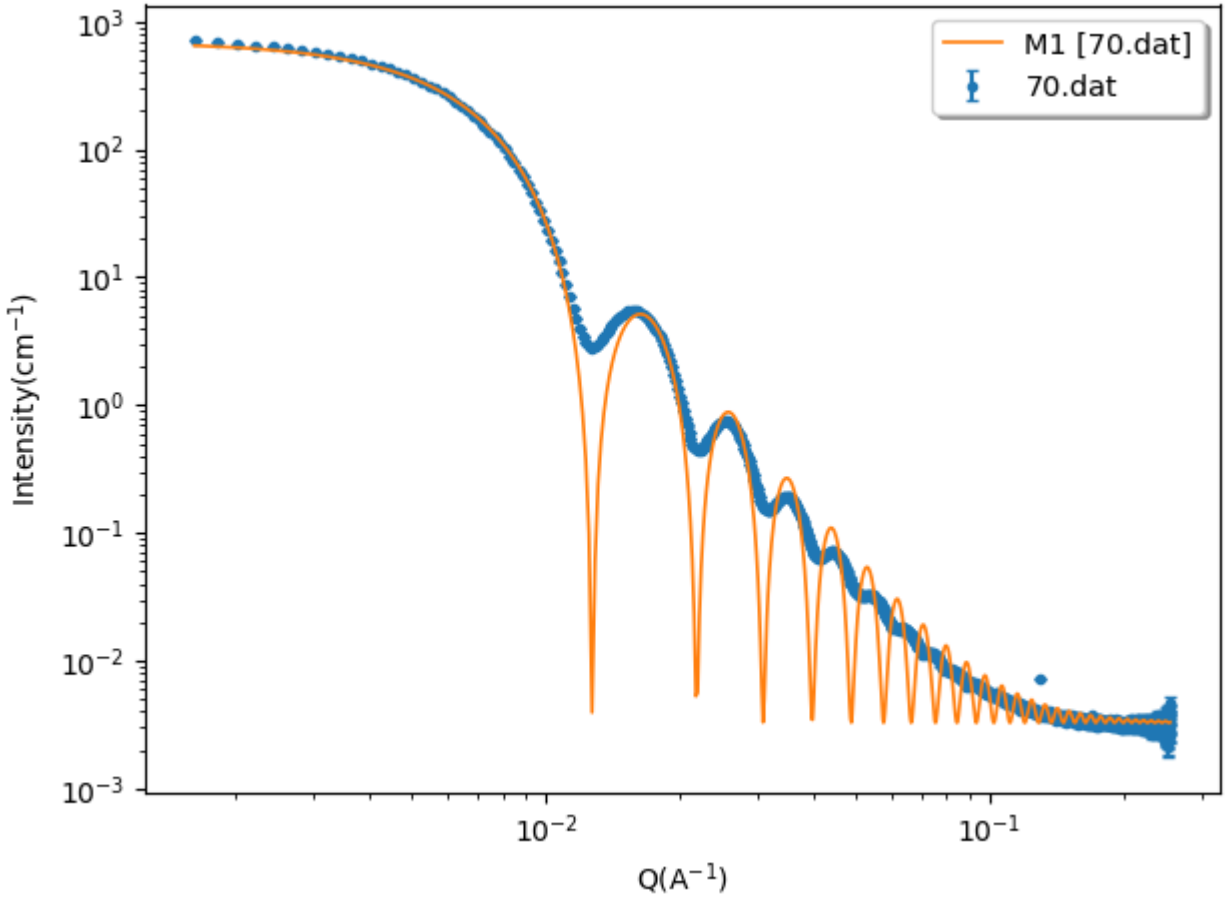
$$\sigma^2 = \frac{1}{R^2}\int D(r)(r-R)^2 dr$$

$$\sigma = PD\ \ R$$

Spherical form factor, no polydispersity

R=35.3 nm

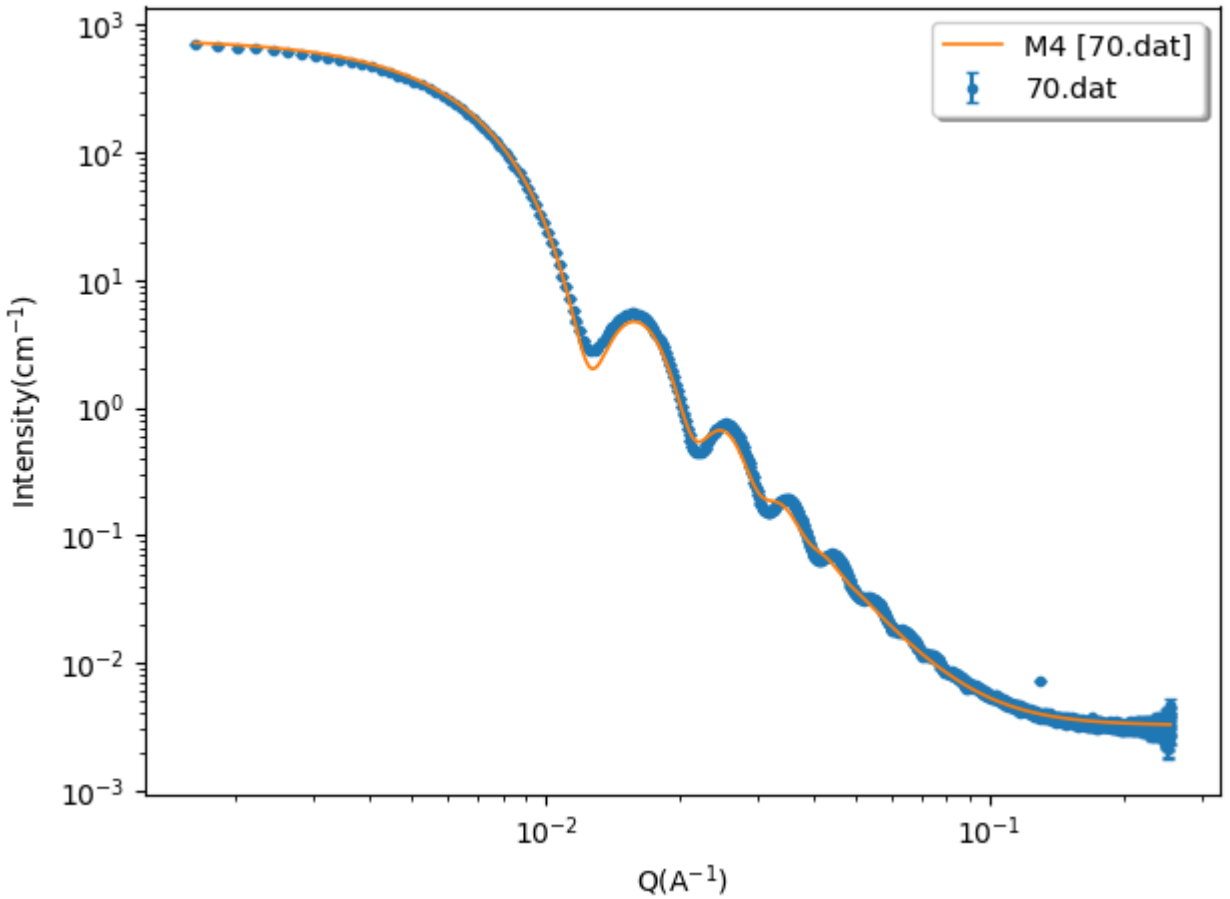
PD=0



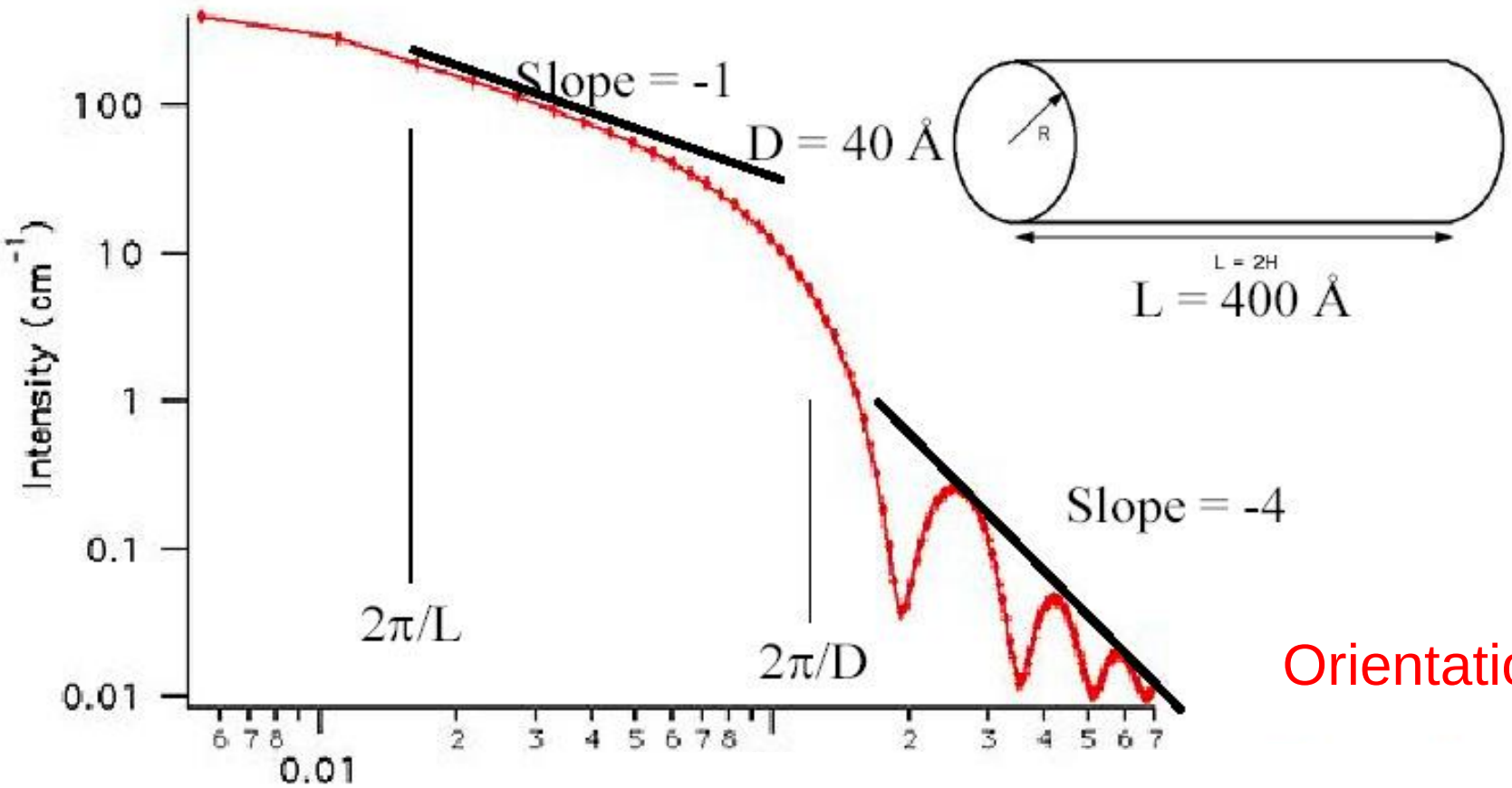
Spherical form factor with polydispersity

R=35 nm

PD=0.09



Dilute randomly oriented monodisperse rods



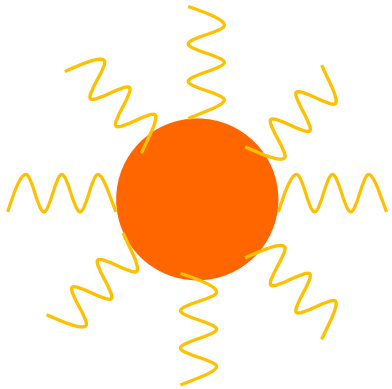
Orientation average

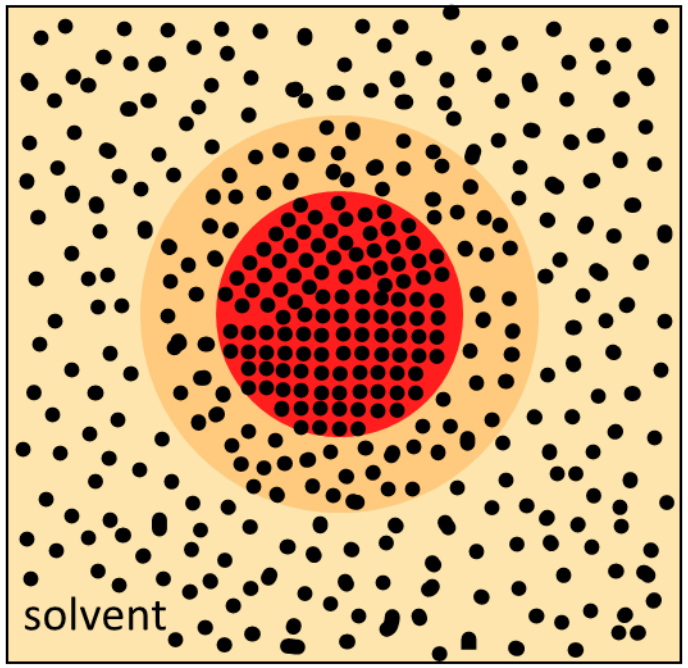
$$P(\vec{q}) = \frac{1}{N} < \sum_{i=1}^{N} |F_i(\vec{q})|^2 >_t$$

Spherical gold nanoparticle in SAXS

Gold nanocrystal

Surface stabilizers : Organic ligands





$$I(q) = n\, P_S(q, R)$$

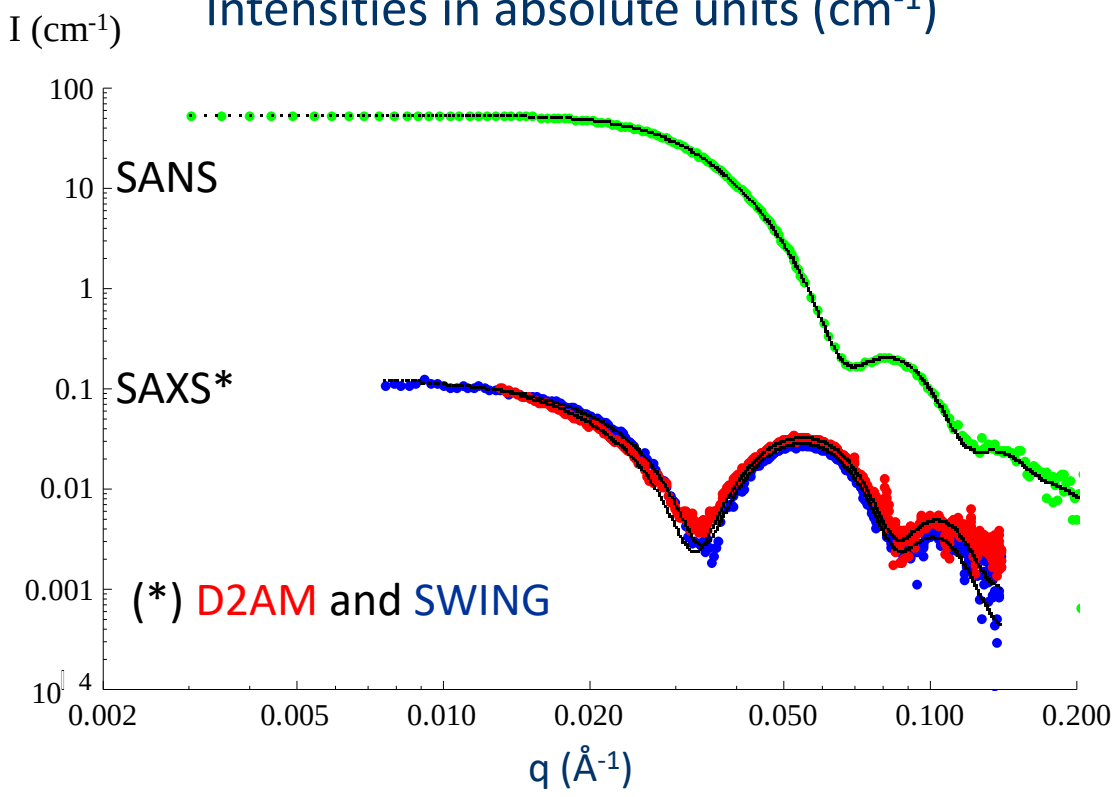
$$n = \frac{N}{V_{tot}}$$

contrast between gold and solvent : $\Delta\rho$

Gold volume fraction of nanoparticles : $\phi = n\ V_S(R)$

$$I(q) = \phi(\Delta\rho)^2 V_S(R) |f_S(q, R)|^2$$

P123 spherical micelles



Combination of SANS and SAXS analysis

$$I(q) = n\,(\rho_{core} - \rho_0)^2\,P(q)$$

core/shell form factor

Rcore = 6 nm

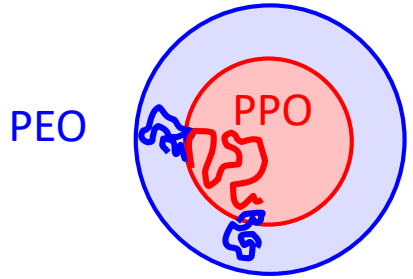
Rtot = 9 nm

polydispersity 10 %

Hydration:

Shell: 90 %

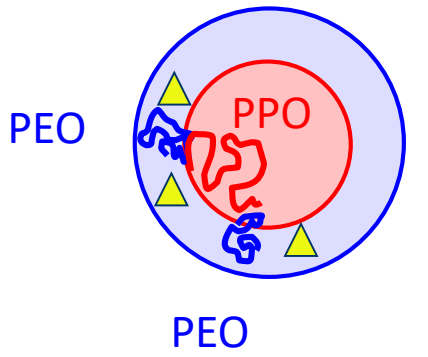
Core: 20 %

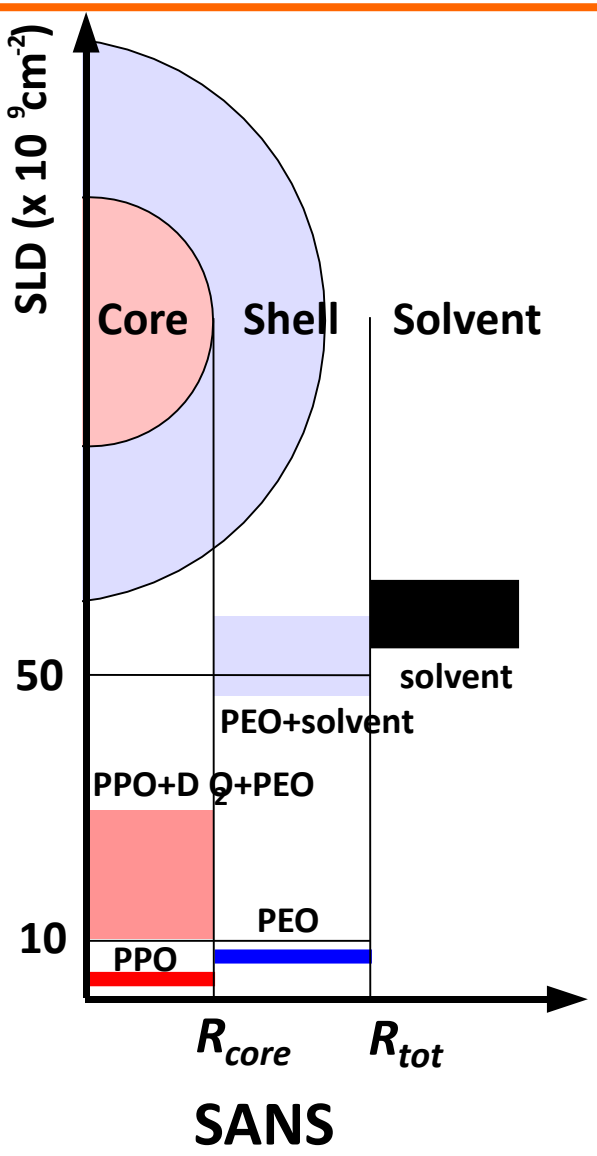


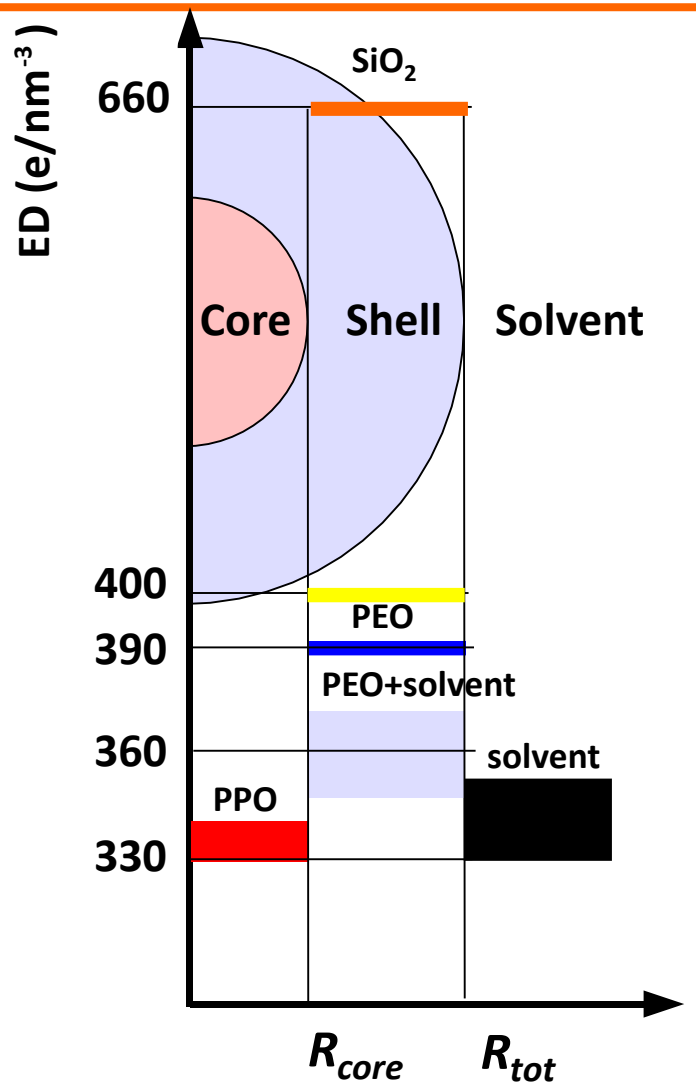
$EO_{20}\,PO_{70}\,EO_{20}$

Manet, S. et all., J. Phys. Chem. B (2011)
Structure of micelles of a non-ionic copolymer determined by SANS and SAXS

Core-shell model







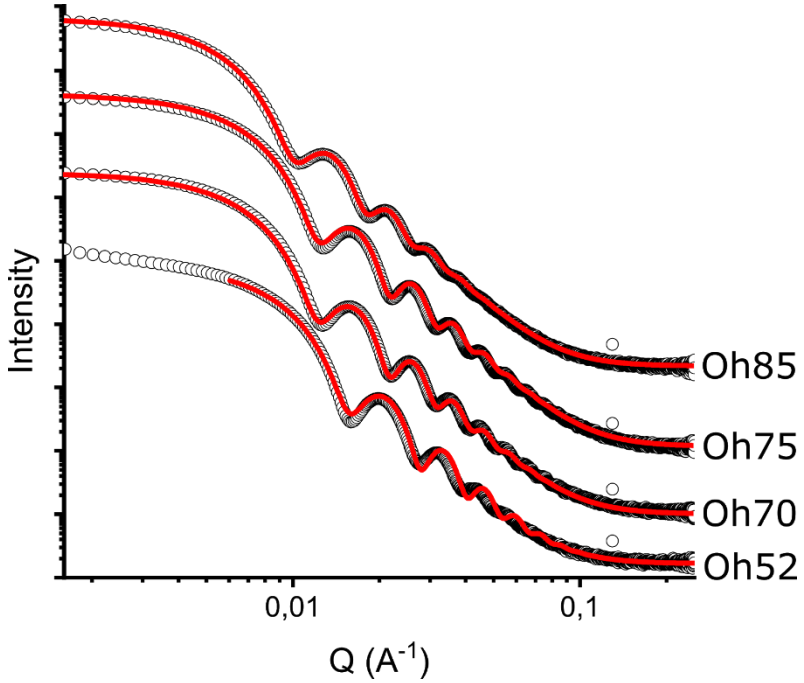
Manet, S. et all., J. Phys. Chem. B (2011)

SESSION

1. Introduction
2. Scattering experiment
3. Some theory
4. Form factor: Spherical objects and other shapes
5. Data modelling
6. Structure factor: Hexagonal and lamellar mesophases

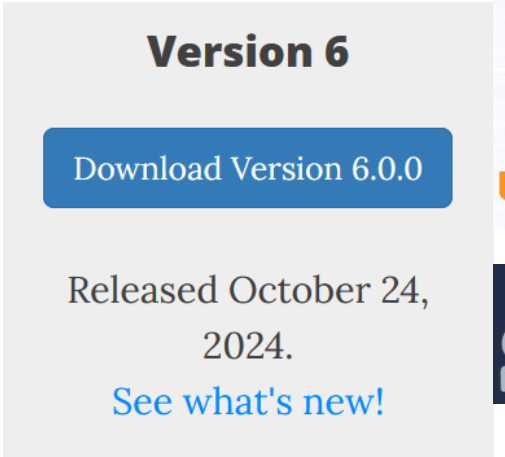
Data modelling

- Calculate scattering based on mathematical model. Estimate parameters based on that model.
- Catalog of many possible shapes ☺
- Not stand alone, i.e. that model fits does guarantee that you have a unique structural solution. Better add another technique like TEM.
- Minimize the number of free parameters

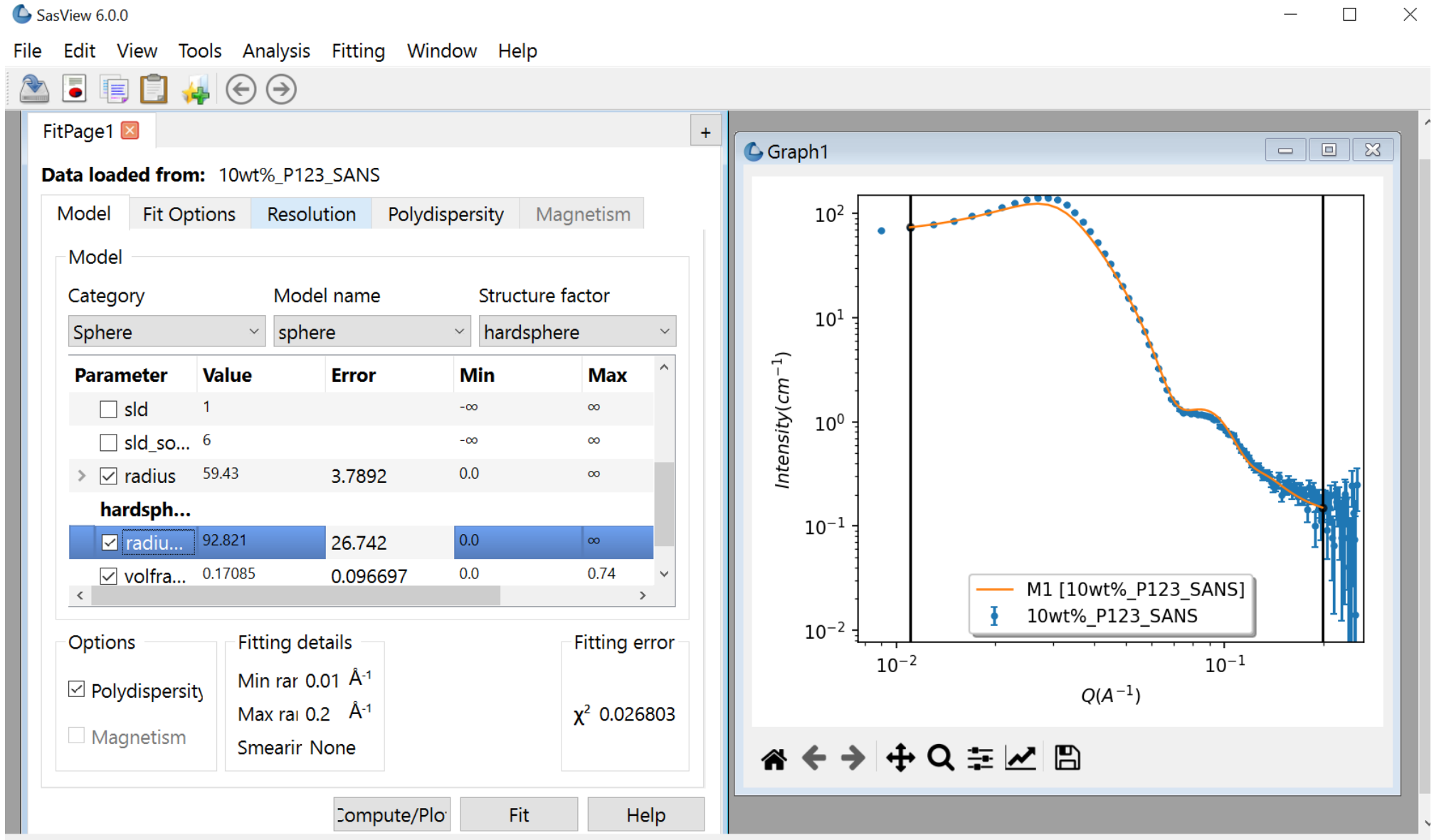


https://www.sasview.org/

Release of SasView 6.0 in October 2024

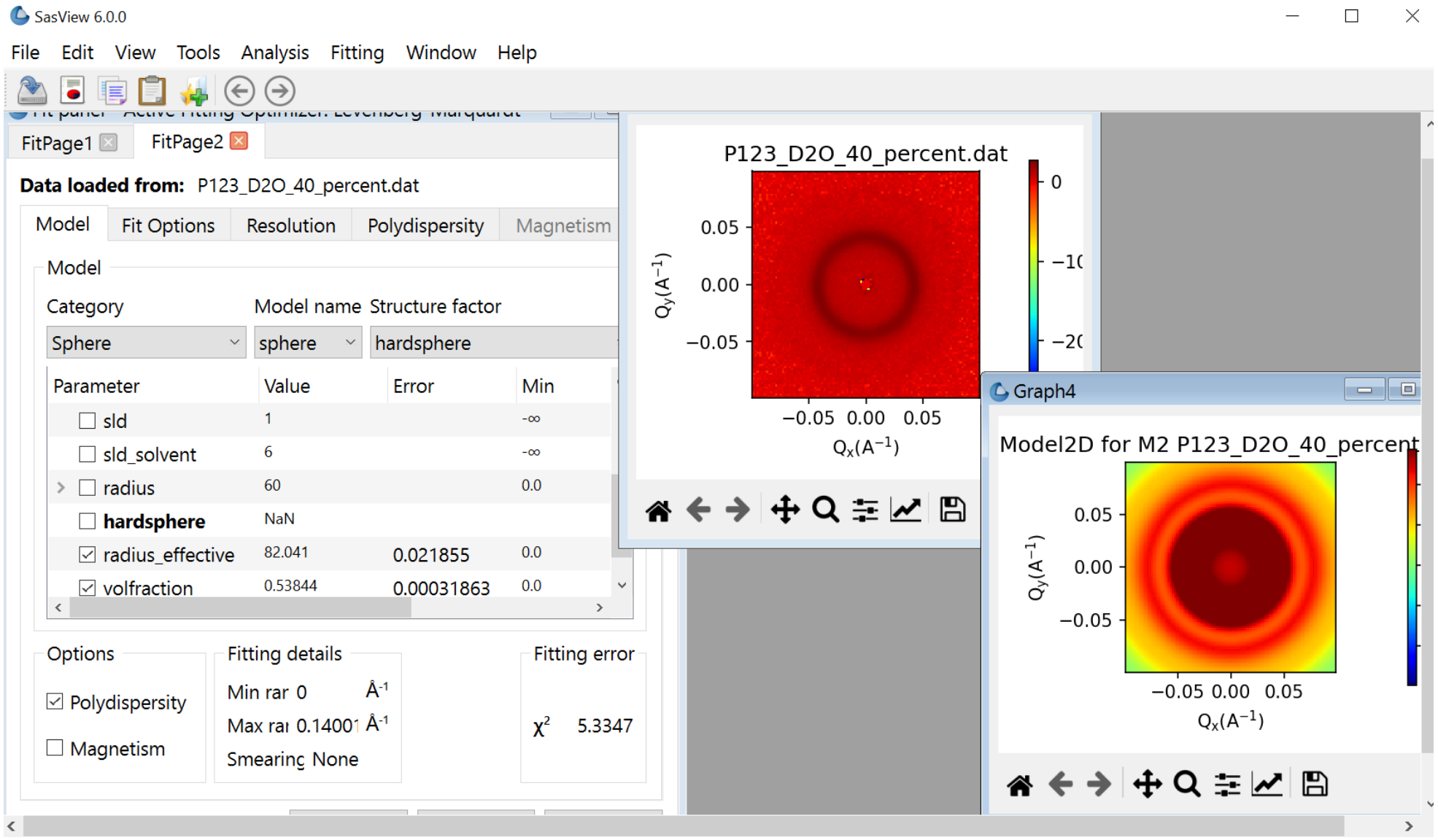


SASView GUI


SasView 6.0.0
File Edit View Tools Analysis Fitting Window Help
FitPage1
Data loaded from: 10wt%_P123_SANS
Model Fit Options Resolution Polydispersity Magnetism
Model
Category Model name Structure factor
Sphere sphere hardsphere
Parameter Value Error Min Max
sld 1 -∞ ∞
sld_so... 6 -∞ ∞
radius 59.43 3.7892 0.0 ∞
hardsph...
radiu... 92.821 26.742 0.0 ∞
volfra... 0.17085 0.096697 0.0 0.74
Options
Polydispersity
Magnetism
Fitting details
Min rar 0.01 Å-1
Max rai 0.2 Å-1
Smearir None
Fitting error
χ2 0.026803
Compute/Plo
Fit
Help
Graph1
Intensity(cm−1)
Q(A−1)
M1 [10wt%_P123_SANS]
10wt%_P123_SANS

SASView GUI

Works with 2D images as well !



Criterium for a good fit

Least-squared method

Reduced chi squared

$$\chi^2_R = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{(I^i_{data} - I^i_{model})}{\Delta I^i_{data}}\right|^2$$

Data set $I^1_{data}, I^2_{data}, \ldots, I^N_{data}$

Errors $\Delta I^1_{data}, \Delta I^2_{data}, \ldots, \Delta I^N_{data}$

$$\chi^2_R \simeq 1$$

Make sure that errors have realistic values

SASView models

SasView User Documentation » Model Functions

Model Functions

- Cylinder Functions
  - barbell
  - capped_cylinder
  - core_shell_bicelle
  - core_shell_bicelle_elliptical
  - core_shell_bicelle_elliptical_belt_r
  - core_shell_cylinder
  - cylinder
  - elliptical_cylinder
  - flexible_cylinder
  - flexible_cylinder_elliptical
  - hollow_cylinder
  - pearl_necklace
  - pringle
  - stacked_disks
- Ellipsoid Functions
  - core_shell_ellipsoid
  - ellipsoid
  - triaxial_ellipsoid
- Lamellae Functions
  - lamellar
  - lamellar_hg
  - lamellar_hg_stack_caille
  - lamellar_stack_caille
  - lamellar_stack_paracrys
- Paracrystal Functions
  - bcc_paracrystal
  - fcc_paracrystal
  - sc_paracrystal
- Parallelepiped Functions
  - core_shell_parallelepipe
  - hollow_rectangular_prism
  - hollow_rectangular_prism_thin_walls
  - parallelepiped
  - rectangular_prism
- Sphere Functions
  - adsorbed_layer
  - binary_hard_sphere
  - core_multi_shell
  - core_shell_sphere
  - fuzzy_sphere
  - linear_pearls
  - micromagnetic_FF_3D
  - multilayer_vesicle
  - onion
  - polymer_micelle
  - raspberry
  - sphere
  - spherical_sld
  - superball
  - vesicle
- Shape-Independent Functions
  - be_polyelectrolyte
  - broad_peak
  - correlation_length
  - dab
  - fractal
  - fractal_core_shell
  - gauss_lorentz_gel
  - gaussian_peak
  - gel_fit
  - guinier
  - guinier_porod
  - line
  - lorentz
  - mass_fractal
  - mass_surface_fractal
  - mono_gauss_coil
  - peak_lorentz
  - poly_gauss_coil
  - polymer_excl_volume
  - porod
  - power_law
  - rpa
  - spinodal
  - star_polymer
  - surface_fractal
  - teubner_strey
  - two_lorentzian
  - two_power_law
  - unified_power_Rg
- Structure Factors
  - hardsphere
  - hayter_msa
  - squarewell
  - stickyhardsphere

- Lots of contributors: community based approach
- Online documentation, possibility to combine models
- Implement you own models (python and c code)
- https://marketplace.sasview.org/models/
- Can run from python script or jupyter notebook instead of GUI

SESSION

1. Introduction
2. Scattering experiment
3. Some theory
4. Form factor: Spherical objects and other shapes
5. Data modelling
6. Structure factor: Hexagonal and lamellar mesophases

case 2

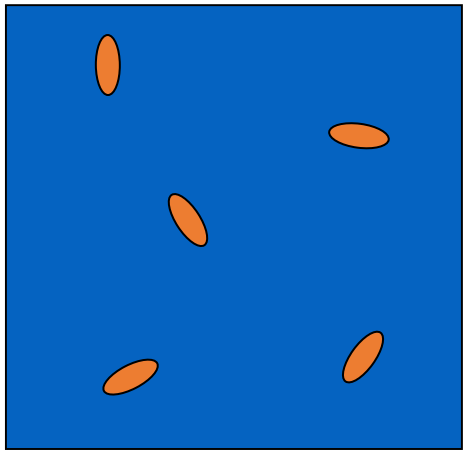
Scattering by an assembly of identical/similar particles
AND
Interference terms
(spatial correlations between the positions of the particles need to be taken into account)

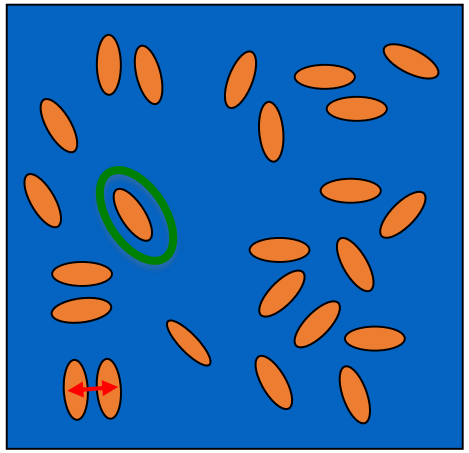
Combination of form factor and structure factor

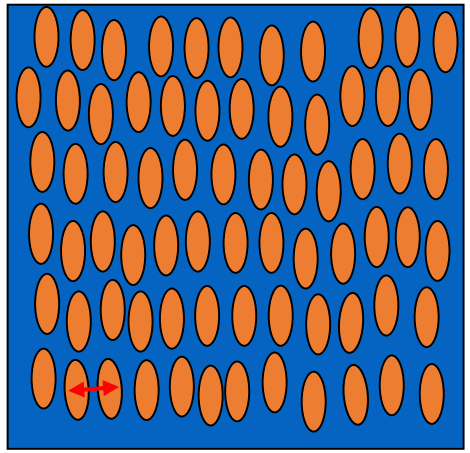
Form factor and structure factor

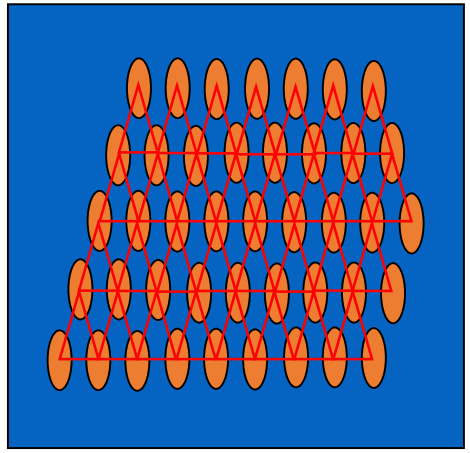
$$n = \frac{N}{V_{tot}}$$

N identical particles









Dilute conditions

form factor only

Local order

Long-range order

== lattice

$$I(\vec{q}) = n\,P(\vec{q})$$

$$I(\vec{q}) = n\,P(\vec{q})\,S(\vec{q})$$

same orientation for non spherical particles !!!

Structure factor

-> Distances between two particles

- Local order: broad correlation peaks
- Long range order: sharp diffraction peaks

Structure factor for *N* identical particles

$$I(\vec{q}) = n\,P(\vec{q})\,S(\vec{q})$$

$$S(\vec{q}) = \left\langle \frac{1}{N} \sum_{\{i\}} e^{-i\vec{q}\vec{R}_i} \sum_{\{j\}} e^{i\vec{q}\vec{R}j} \right\rangle$$

interference term

Sum over all the positions Ri of the particles

For a periodic lattice == Bragg peaks == diffraction

$$\mathbf{L}(x, N) = \left(\frac{\sin(Nx)}{\sin(x)} \right)^2$$

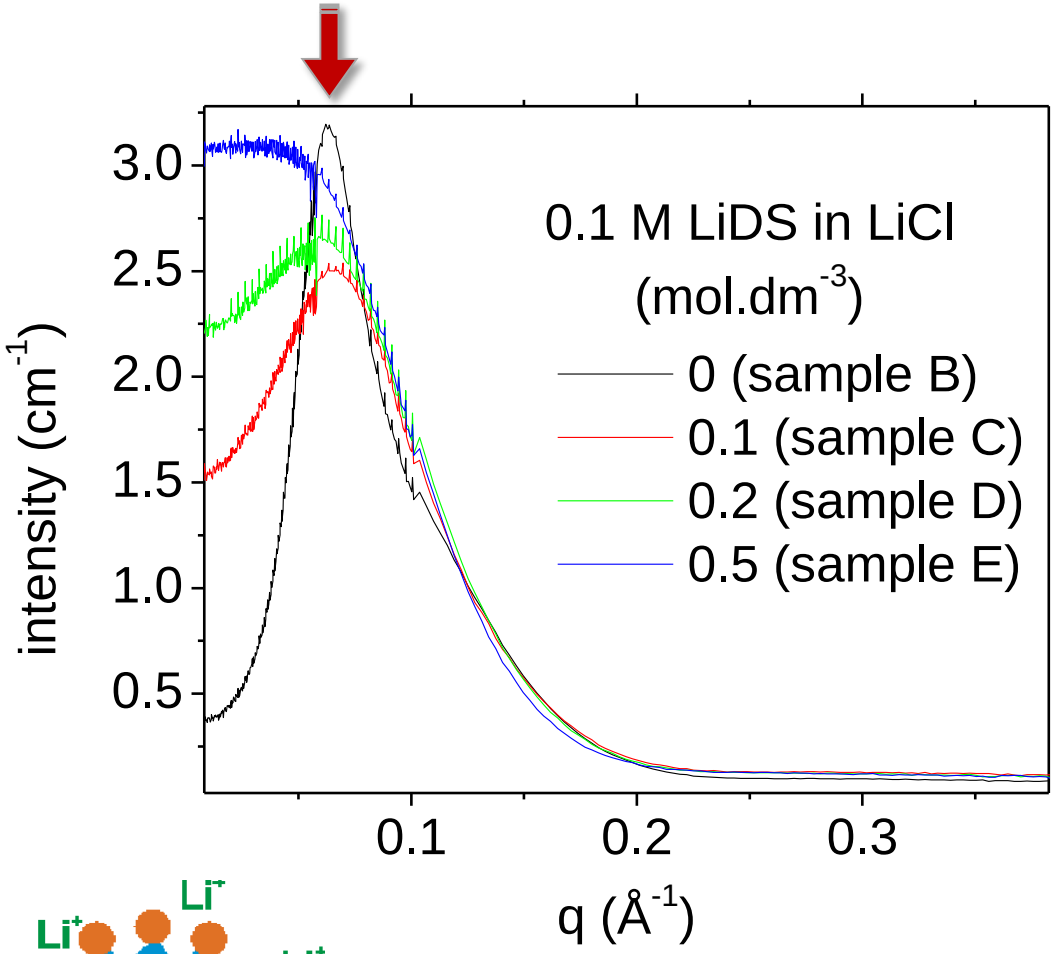
Laue function

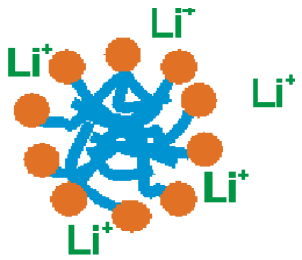
$$S(\vec{q}) = \frac{1}{N} \mathbf{L}\left(\frac{\vec{q}\cdot\vec{a}}{2}, N_a\right) \mathbf{L}\left(\frac{\vec{q}\cdot\vec{b}}{2}, N_b\right) \mathbf{L}\left(\frac{\vec{q}\cdot\vec{c}}{2}, N_c\right)$$

3D lattice

Structure Factor : local order

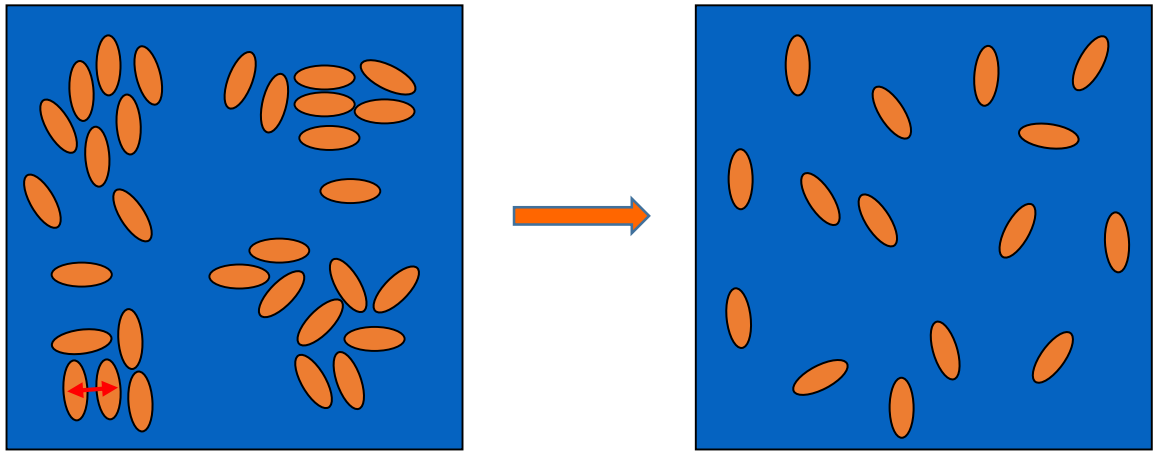
$S(\vec{q})$





$$\kappa = \left(\frac{4\pi e^2}{\epsilon_r \epsilon_o kT} \sum z_k^2 n_k \right)^{1/2}$$

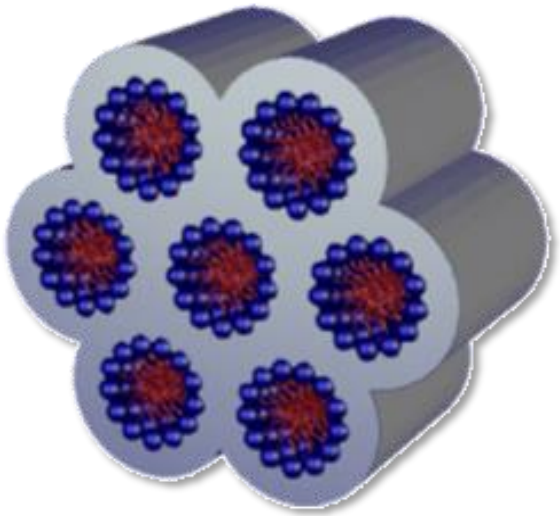
- Interactions between particles lead to constructive interference.
- Electrostatic interaction screened by salt addition. Debye Length (nm^{-1})
- The charge on a particle is determined by the number of bound counter-ions (Li^+)



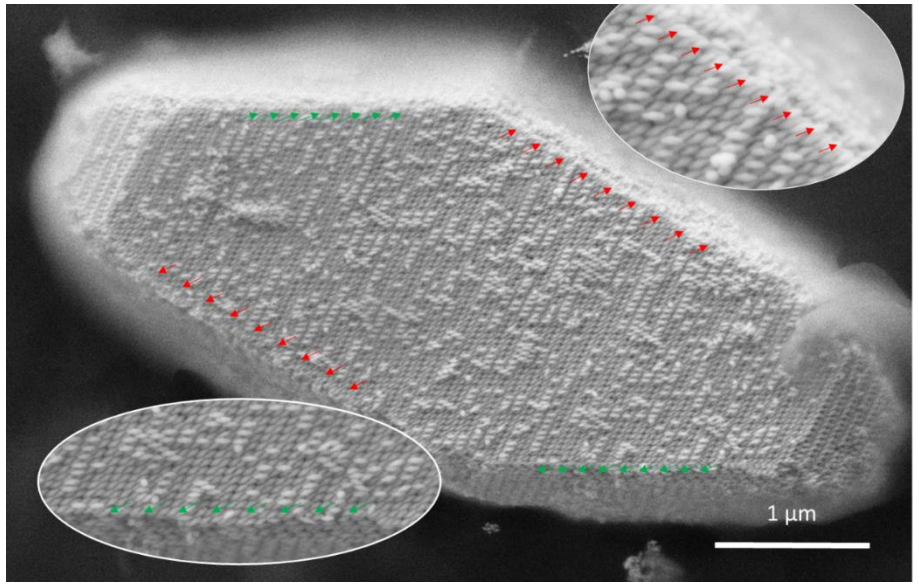
Diffraction or scattering ?

Diffraction -> long-range order == lattice in real space

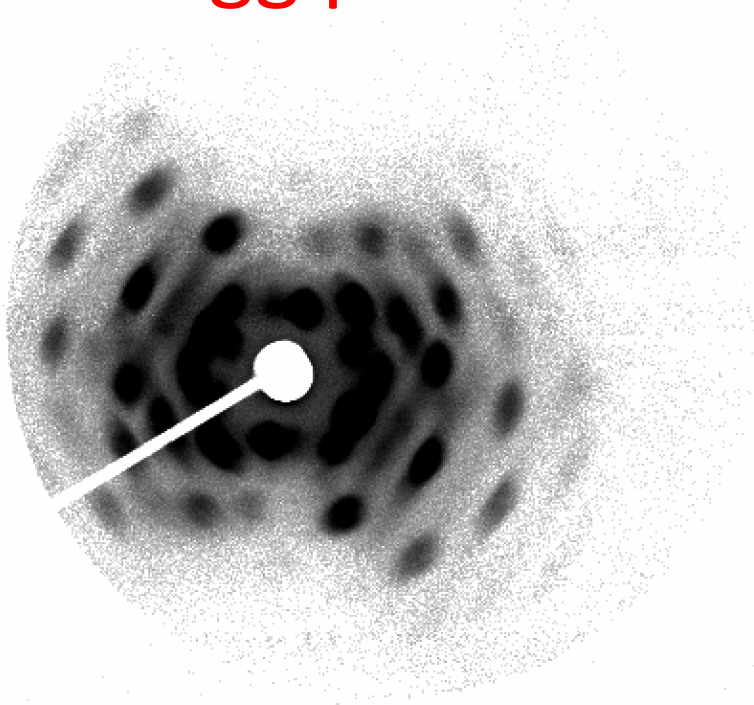
mesophase



Supercrystal of nanoparticles

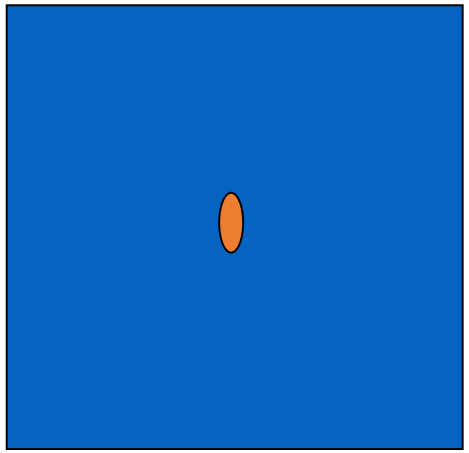


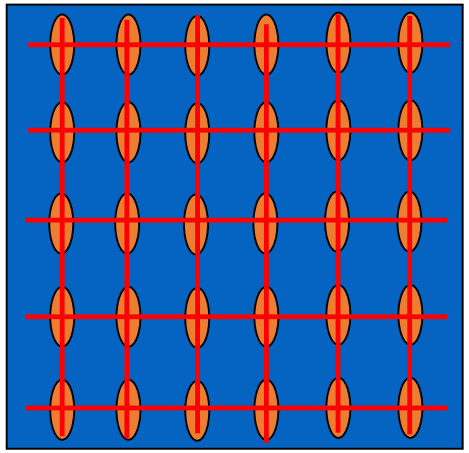
Bragg peaks

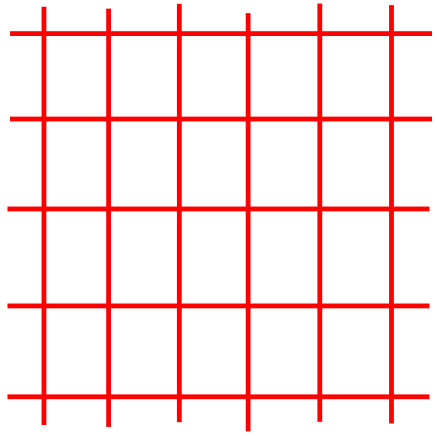


reciprocal space

In real space: convolution product of a particle and a lattice





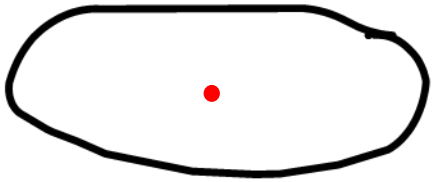


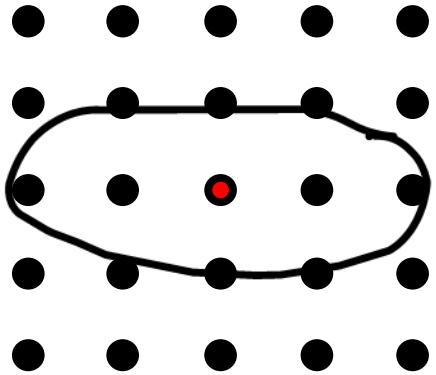
In reciprocal space: product of the Fourier transforms

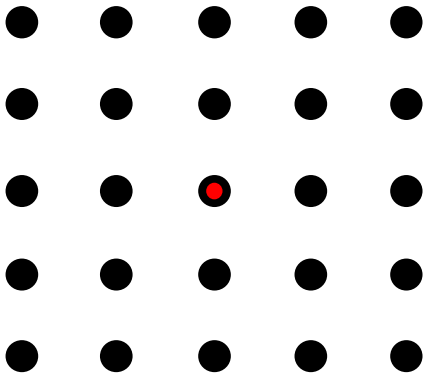
$P(\vec{q})$= form factor of a particle

$I(\vec{q}) = n\,P(\vec{q})\,S(\vec{q})$

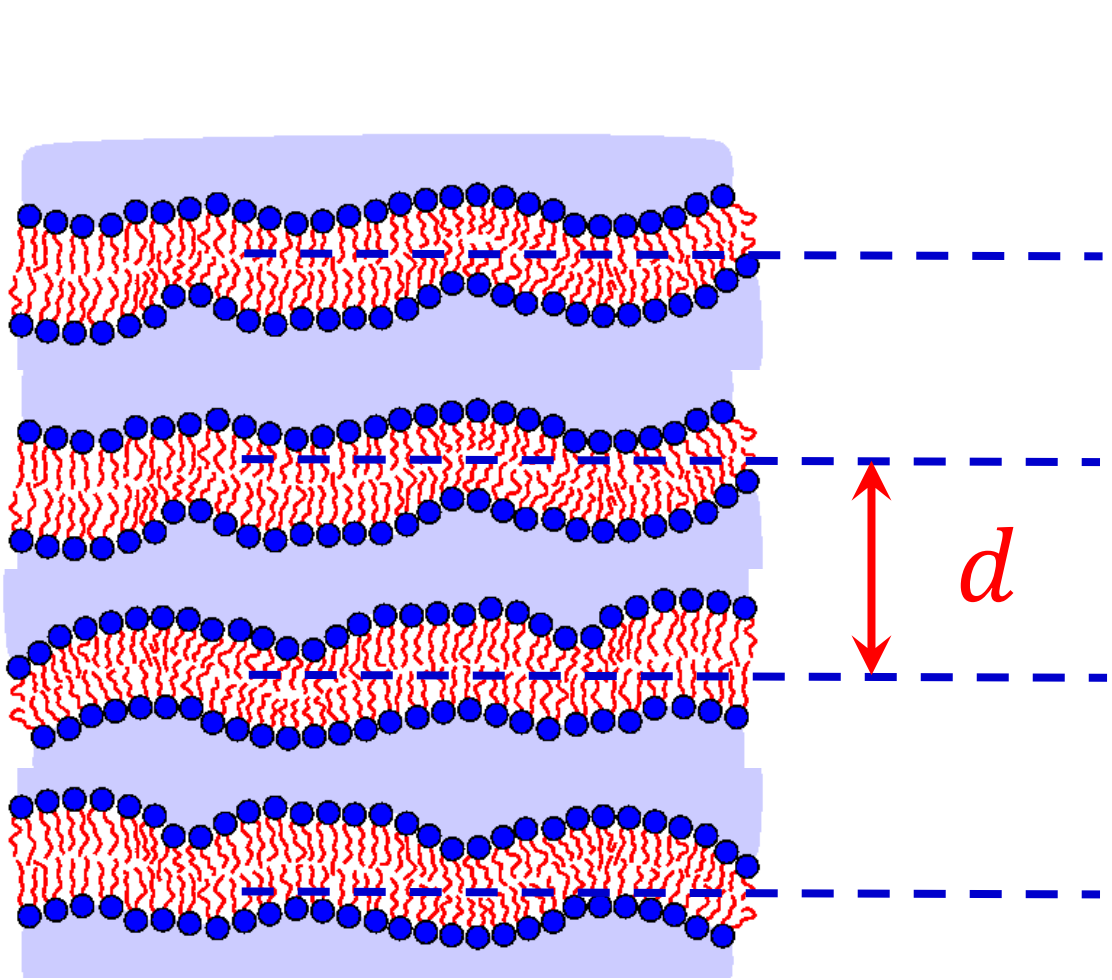
$S(\vec{q})$=TF the lattice

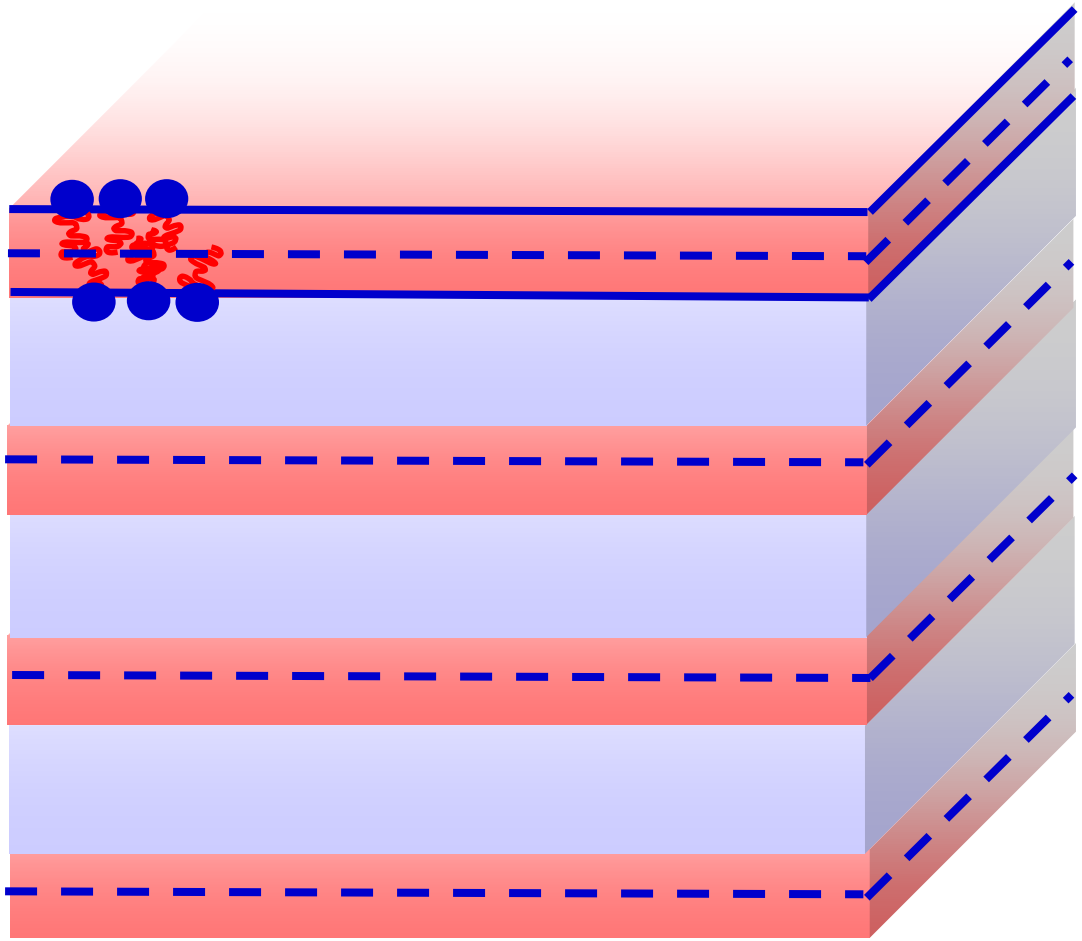




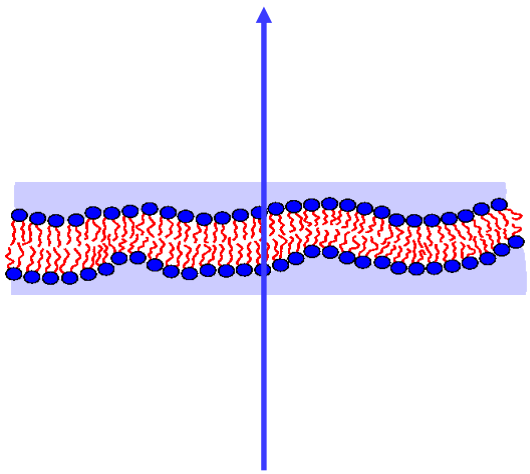


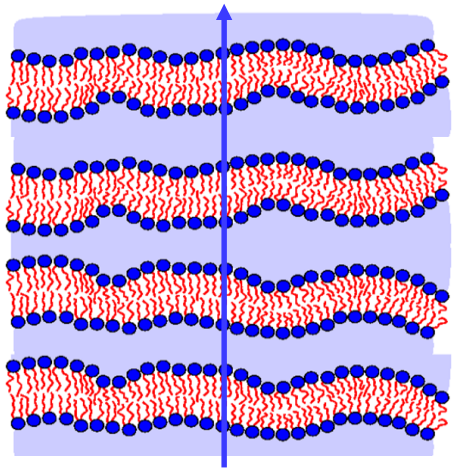
lamellar phase

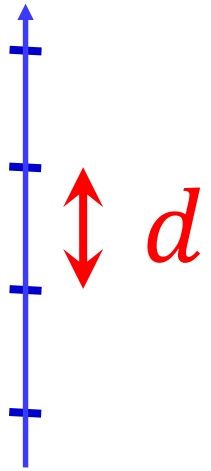




In real space: convolution product of a bilayer by a 1D lattice



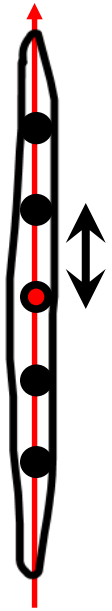




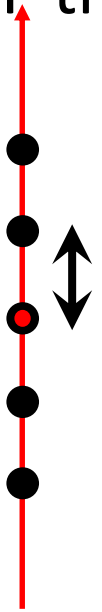
In reciprocal space: product of the Fourier transforms

$P(\vec{q})$=TF of one bilayer

$I(\vec{q}) = n\,P(\vec{q})\,S(\vec{q})$



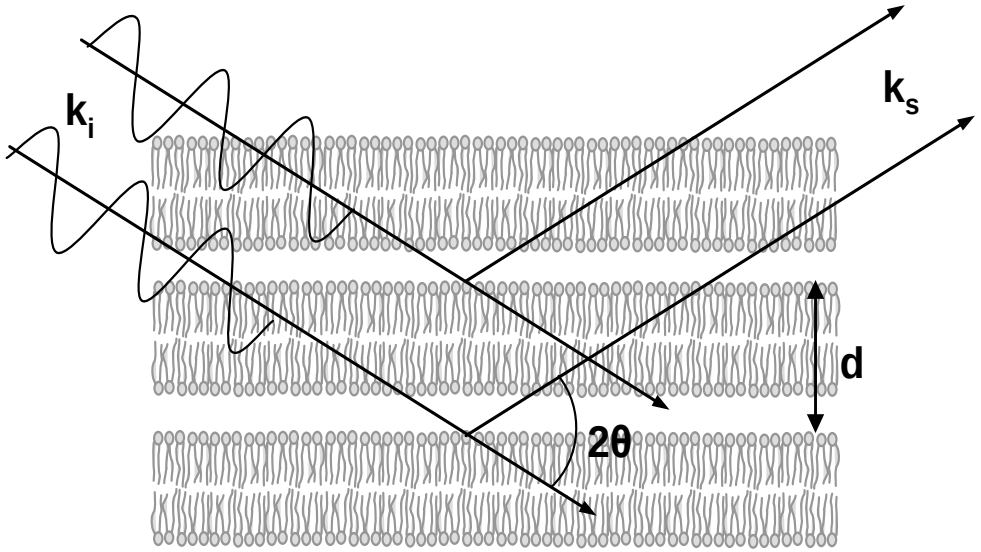
$S(\vec{q})$=TF the 1D lattice

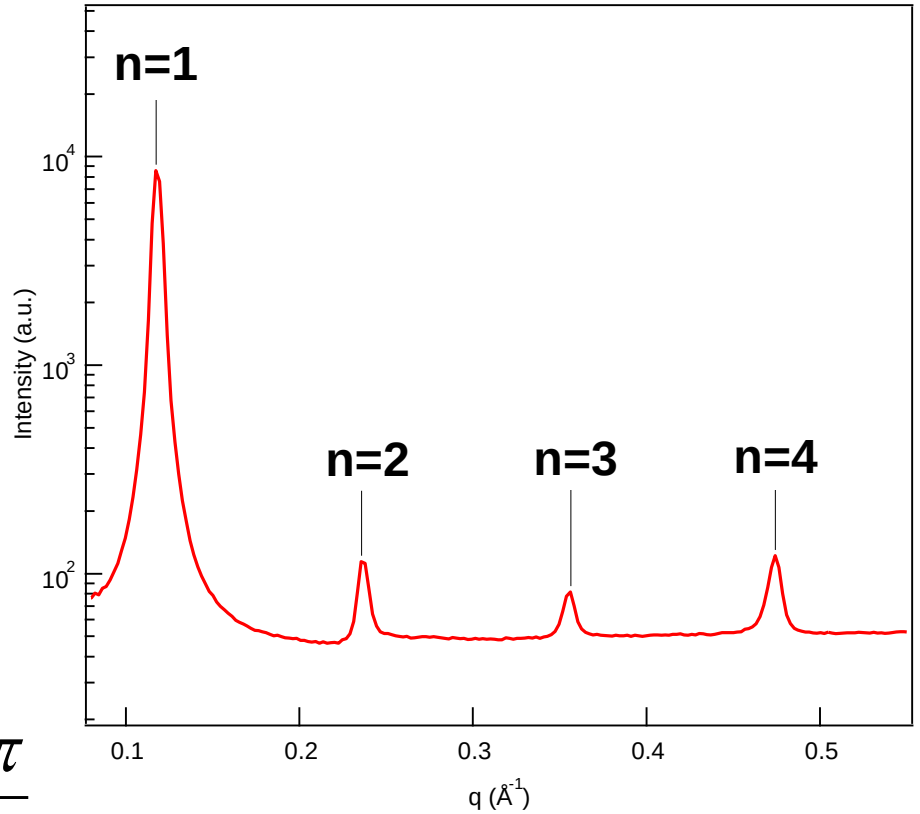


$$q_1 = \frac{2\pi}{d}$$

Lamellar phase

$$q_n = n\, q_1$$



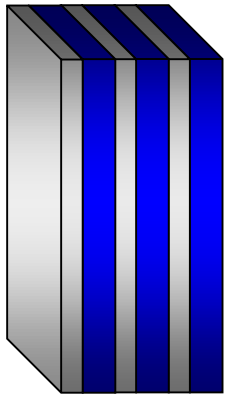


$$q = |\mathbf{q}| = |\mathbf{k}_s - \mathbf{k}_i| = \frac{4\pi \sin\theta}{\lambda}$$

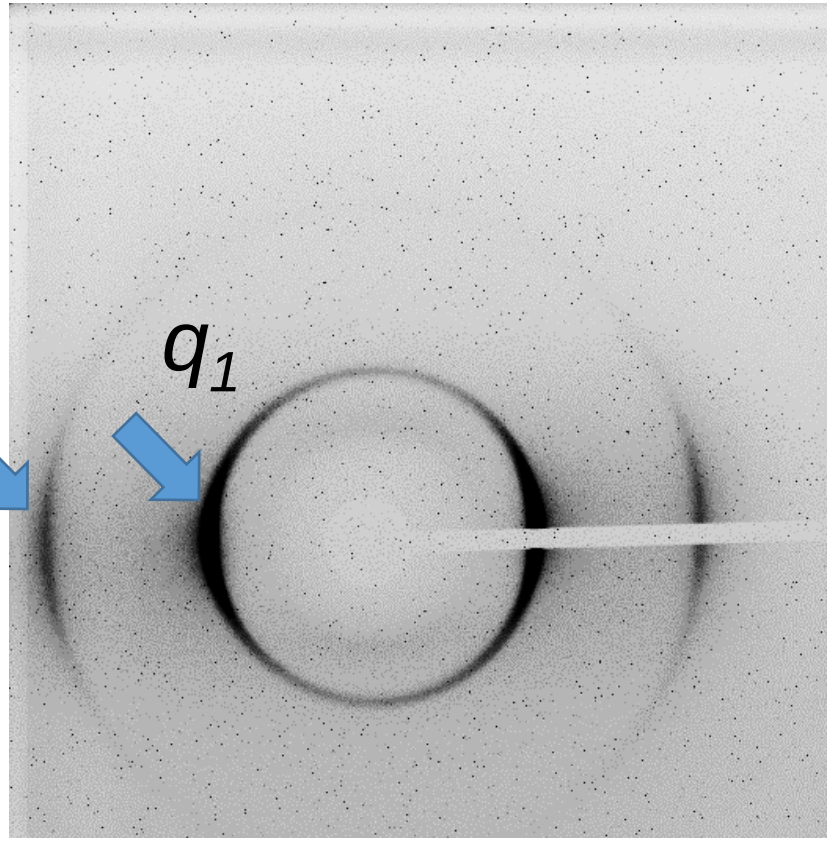
$$2d\sin\theta = n\lambda$$

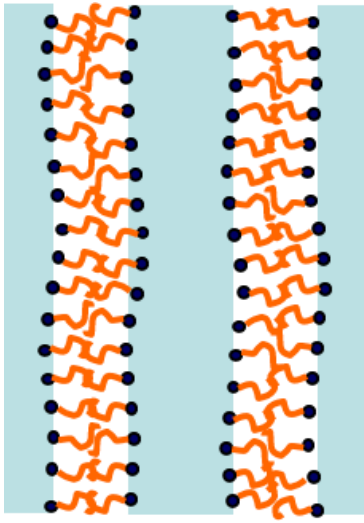
$$d = \frac{2\pi}{q_1}$$

2D image : preferred orientation



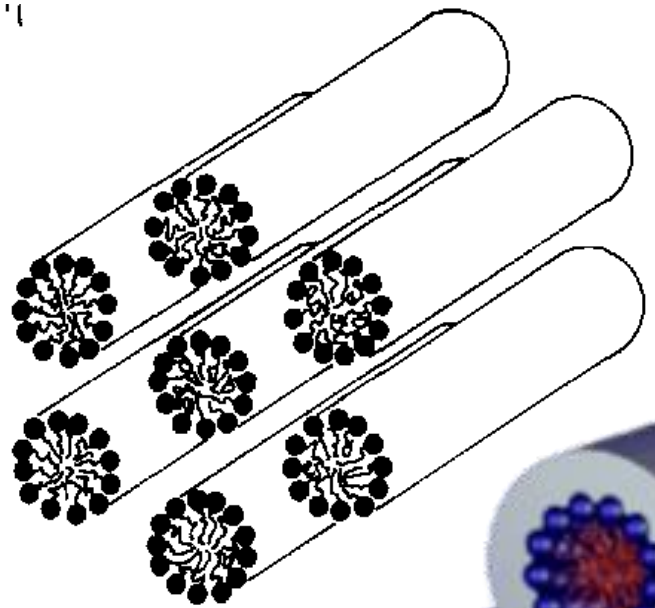
$preferred\ orientation$

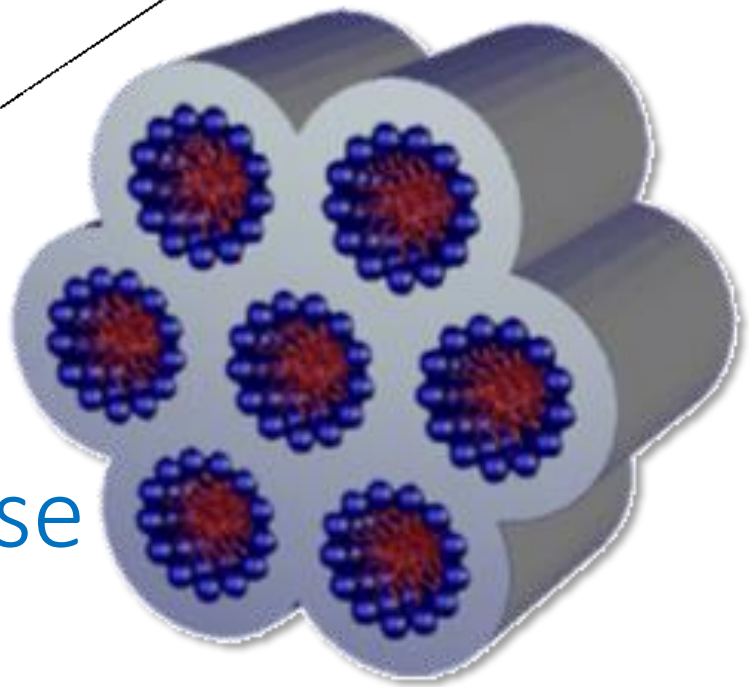




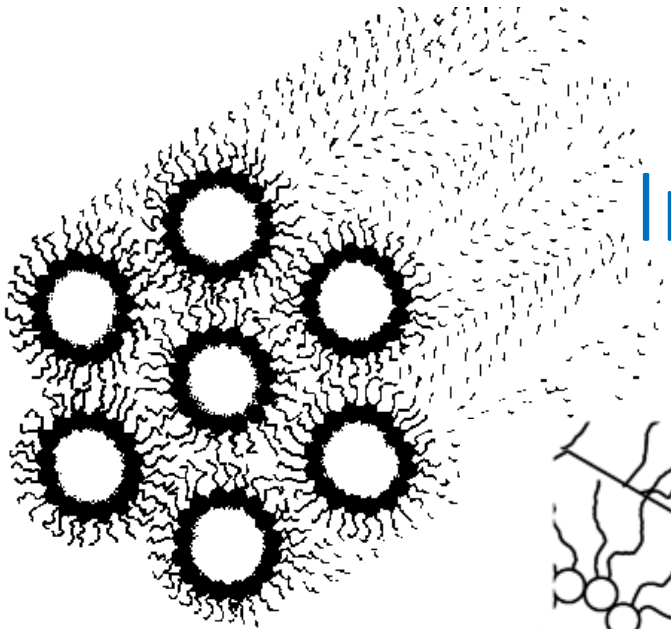
$d = 6.4\ nm$

2D hexagonal phase

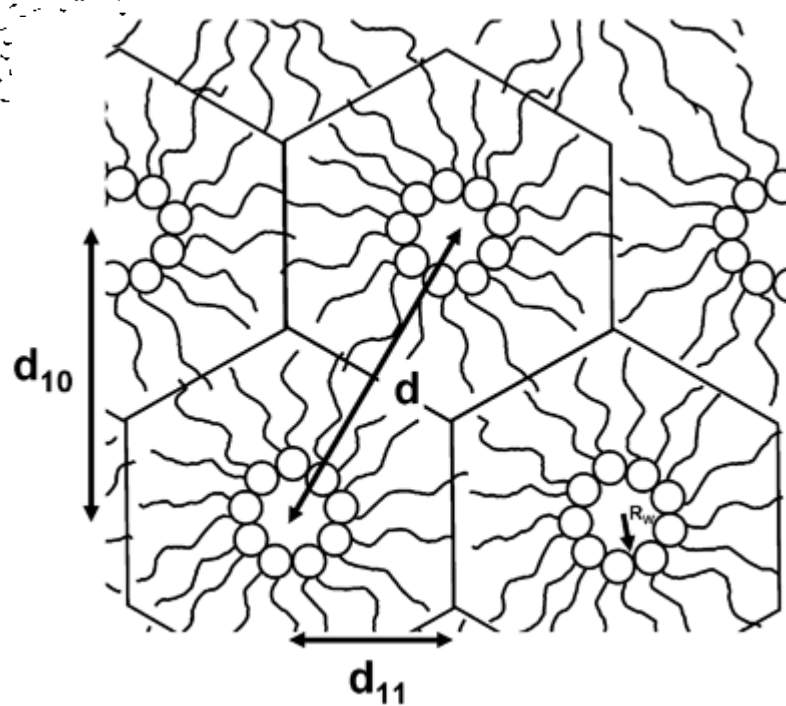




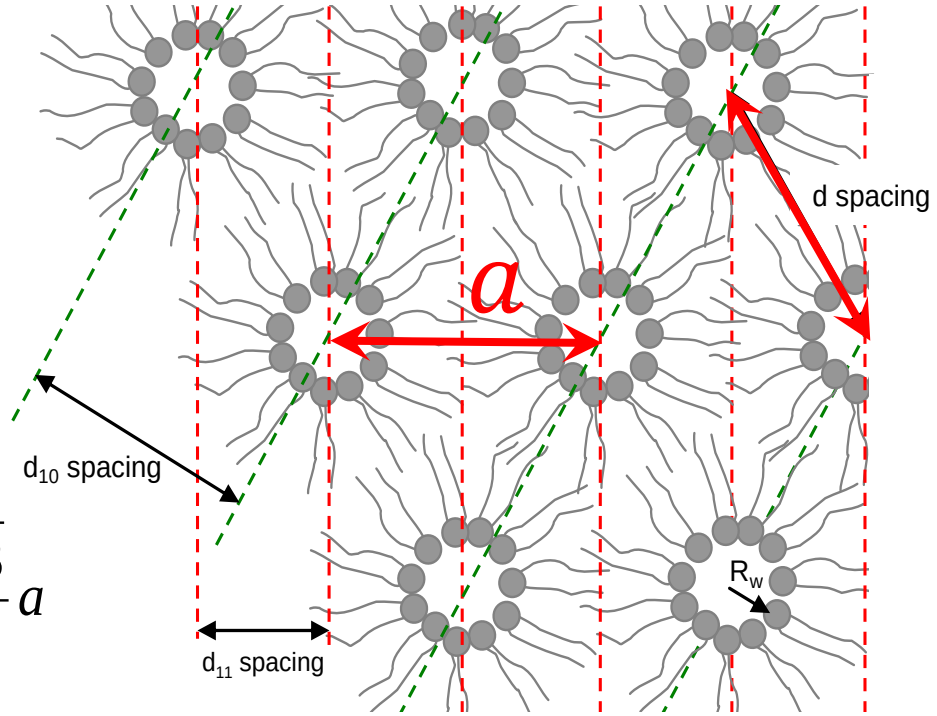
Direct phase



Inverse phase



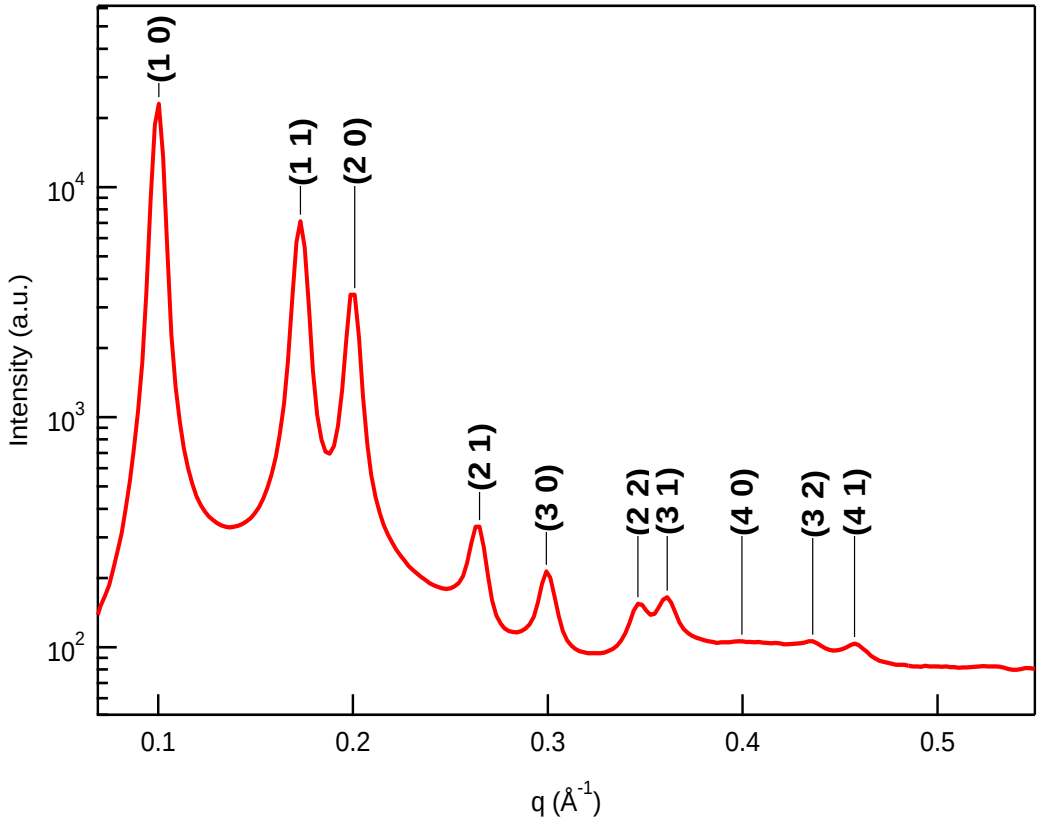
Hexagonal Phase



$$d_{10} = \frac{\sqrt{3}}{2} a$$

$$d_{11} = \frac{1}{\sqrt{3}} d_{10}$$

Bragg peaks == diffraction

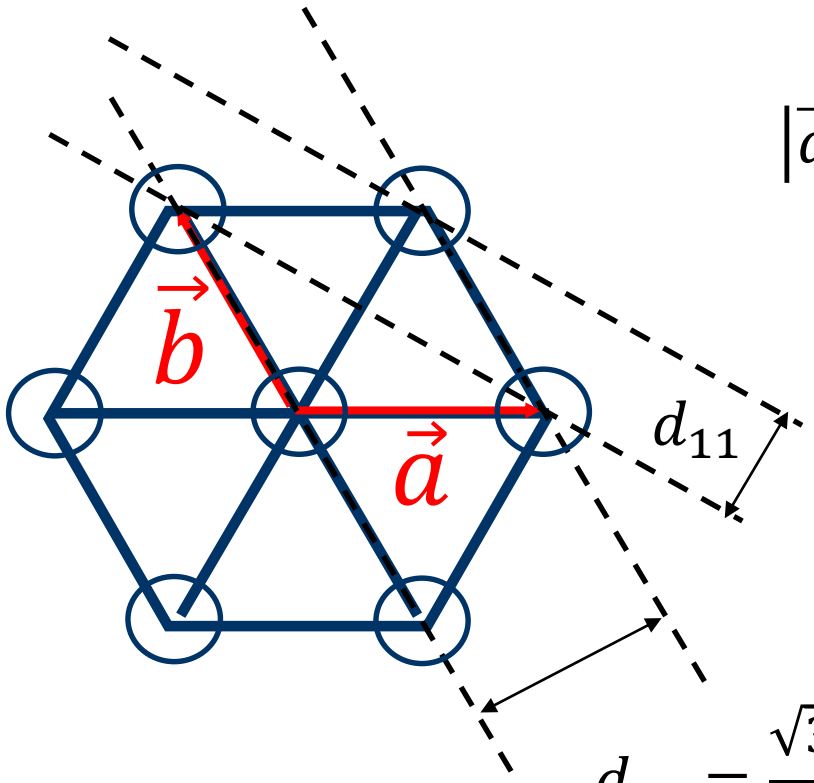


$$q_{hk} = q_{10}\sqrt{\left(h^2 + hk + k^2\right)}$$

$$1 : \sqrt{3} : \sqrt{4} : \sqrt{7} : \ldots$$

2D hexagonal phase

2D lattice



$$|\vec{a}| = \left|\vec{b}\right| = a$$

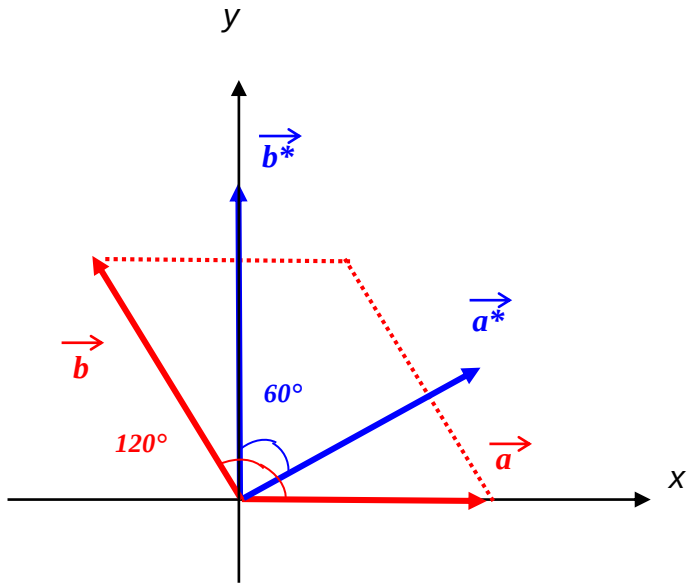
$$\left|\overrightarrow{a^*}\right| = \left|\overrightarrow{b^*}\right| = \frac{2}{\sqrt{3}}\,\frac{2\pi}{a} = \frac{2\pi}{d_{10}}$$

$$\vec{a}\cdot\overrightarrow{b^*} = \vec{b}\cdot\overrightarrow{a^*} = 0$$

$$\vec{a}\cdot\overrightarrow{a^*} = \vec{b}\cdot\overrightarrow{b^*} = 2\pi$$

$$d_{10} = \frac{\sqrt{3}}{2}\,a$$

reciprocal lattice



$$\vec{q}_{hk} = h\,\overrightarrow{a^*} + k\,\overrightarrow{b^*}$$

$$q_{hk} = \frac{2\pi}{d_{hk}} = \frac{4\pi}{\sqrt{3}a}\sqrt{h^2 + k^2 + hk}$$

2D hexagonal phase

hk	h^2+k^2+hk	M(hk)
10	1	6
11	3	6
20	4	6
21	7	12
30	9	6
22	12	6
31	13	12
40	16	6
32	19	12

$$q_{hk} = \frac{2\pi}{d_{hk}} = \frac{4\pi}{\sqrt{3}a}\sqrt{h^2 + k^2 + hk}$$

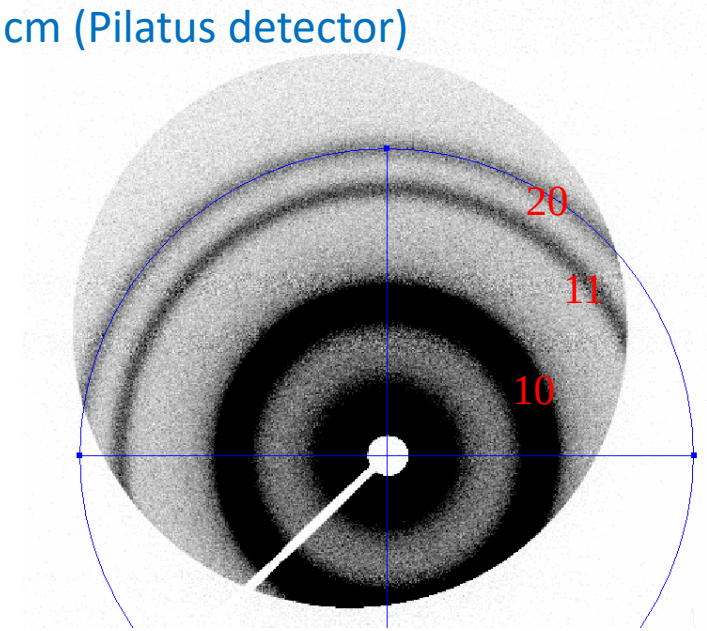
Powder sample

M(hk): Multiplicity term

2D hexagonal mesoporous materials

D : about 115 cm (Pilatus detector)

Cu-SAXS

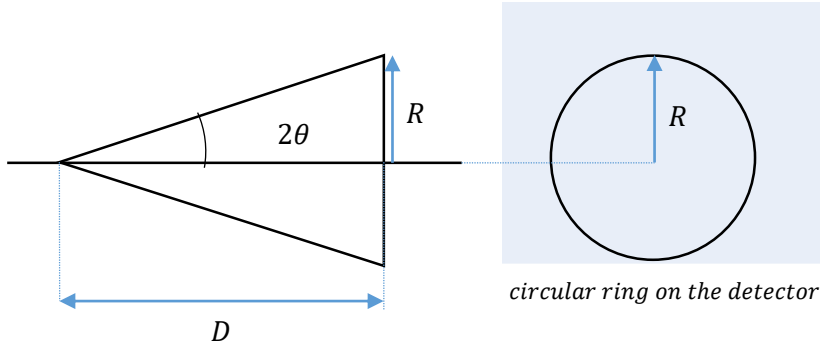


Ref LI34 mesoporous SBA15

hexagonal lattice parameter
(SWING SOLEIL march 2017)

a = 11.45 nm

hk	d_{ref} (nm)	q_{ref} (nm^{-1})
10	9.92	0.634
11	5.72	1.097
20	4.96	1.267

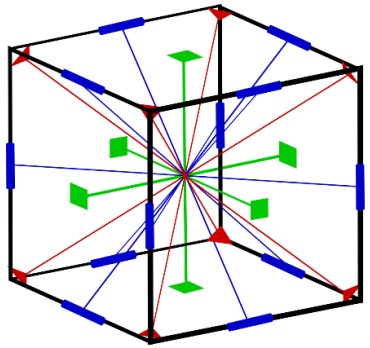


MCM powder

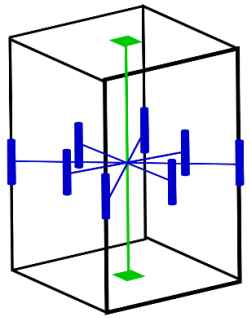
q_{10}=0.164 A^{-1}
q_{11}=0.284 A^{-1}
q_{20}=0.328 A^{-1}
q_{21}=0.434 A^{-1}

a = 4.4 nm

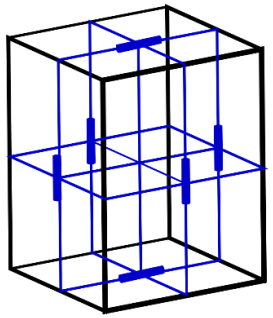
3D supercrystals



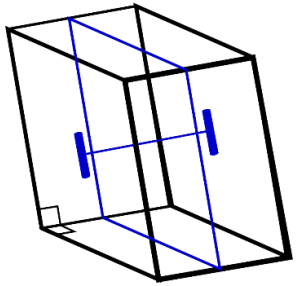
cubic



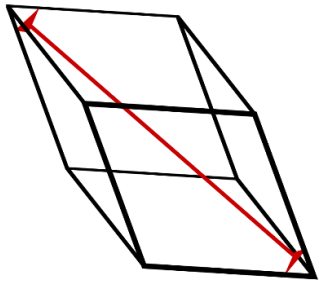
tetragonal



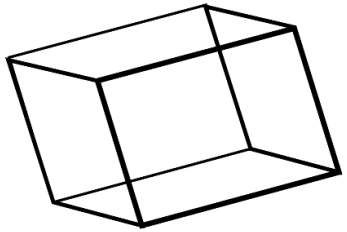
orthorhombic



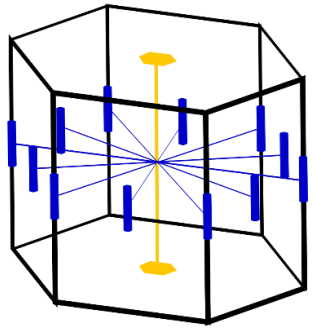
monoclinic



trigonal



triclinic

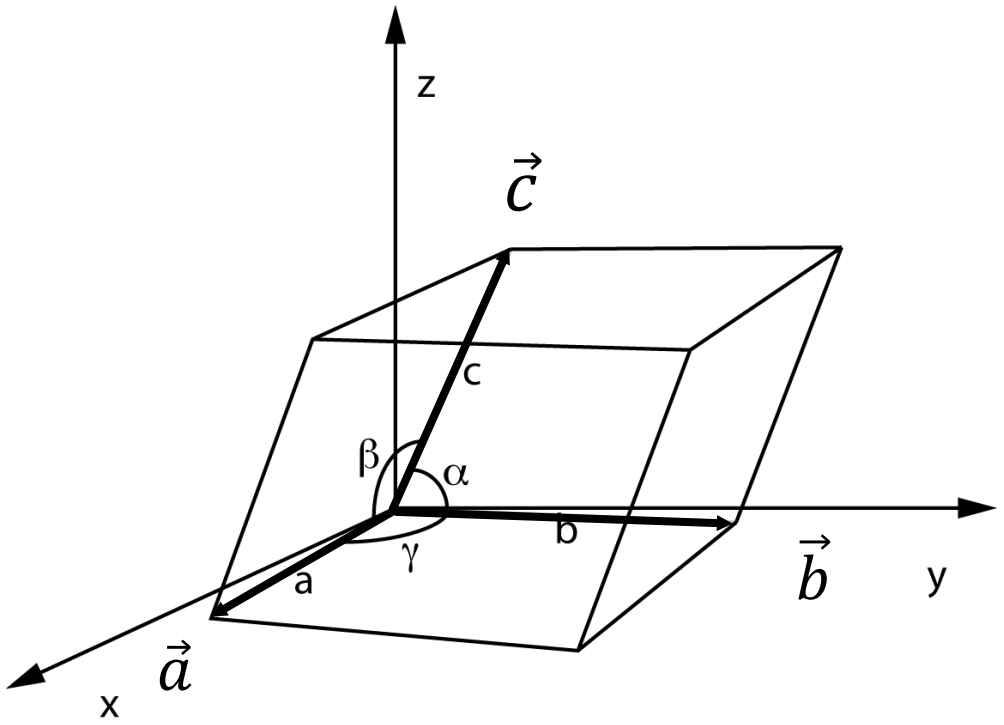


hexagonal

7 symmetry classes

3D unit cell and 3D reciprocal lattice

$\left(\vec{a}, \vec{b}, \vec{c}\right)$ $\left(\vec{a^*}, \vec{b^*}, \vec{c^*}\right)$ $\vec{q}_{hkl} = h\,\vec{a^*} + k\,\vec{b^*} + l\,\vec{c^*}$

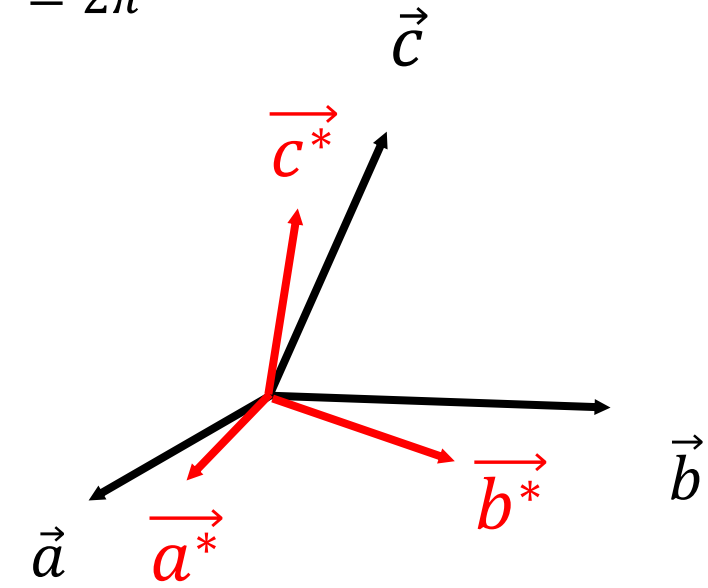


$$\vec{a} \cdot \vec{a^*} = \vec{b} \cdot \vec{b^*} = \vec{c} \cdot \vec{c^*} = 2\pi$$

$$\vec{a^*} = \frac{2\pi}{V_{cell}}\ \vec{b} \wedge \vec{c}$$

$$\vec{b^*} = \frac{2\pi}{V_{cell}}\ \vec{c} \wedge \vec{a}$$

$$\vec{c^*} = \frac{2\pi}{V_{cell}}\ \vec{a} \wedge \vec{b}$$



$$V_{cell} = \left|\vec{a} \cdot \left(\vec{b} \wedge \vec{c}\right)\right| =$$

$$abc\sqrt{1 + 2\cos\alpha\cos\beta\cos\gamma - \cos^2\alpha - \cos^2\beta - \cos^2\gamma}$$

$$\left|\vec{q}_{hkl}\right| = \frac{2\pi}{d_{hkl}}$$

- Triclinic: $a, b, c, \alpha, \beta, \gamma$ — $all\ d_{hkl}$

$$\frac{1}{d^2} = \frac{\frac{h^2}{a^2}\sin^2\alpha + \frac{k^2}{b^2}\sin^2\beta + \frac{\ell^2}{c^2}\sin^2\gamma + \frac{2k\ell}{bc}(\cos\beta\cos\gamma - \cos\alpha) + \frac{2h\ell}{ac}(\cos\gamma\cos\alpha - \cos\beta) + \frac{2hk}{ab}(\cos\alpha\cos\beta - \cos\gamma)}{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

- Monoclinic: $a, b, c, \beta\ (\alpha = \gamma = 90°)$

$$\frac{1}{d^2} = \left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{\ell^2}{c^2} - \frac{2h\ell\cos\beta}{ac}\right)\left(\frac{1}{sin^2\beta}\right)$$

- Orthorhombic: $a, b, c\ (\alpha = \beta = \gamma = 90°)$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{\ell^2}{c^2}$$

- Hexagonal: $a, c\ (b = a, \alpha = \beta = 90°, \gamma = 120°)$

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{\ell^2}{c^2}$$

- Tetragonal: $a, c\ (b = a, \alpha = \beta = \gamma = 90°)$

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{\ell^2}{c^2}$$

Trigonal : hexagonal or rhombohedral

- Rhombohedral unit cell: $a, \alpha\ (a = b = c, \alpha = \beta = \gamma)$

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + \ell^2)\sin^2\alpha + 2(hk + k\ell + h\ell)(\cos^2\alpha - \cos\alpha)}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$$

- Cubic: a

$$\frac{1}{d^2} = \frac{h^2 + k^2 + \ell^2}{a^2}$$

All 230 space groups

triclinic

1	P 1	1
2	P -1	$\bar{1}$

monoclinic

3	P 2	2
4	$P 2_1$	
5	C 2	
6	P m	m
7	P c	
8	C m	
9	C c	
10	P 2/m	2/m
11	$P 2_1/m$	
12	C 2/m	
13	P 2/c	
14	$P 2_1/c$	
15	C 2/c	

orthorhombic

16	P 2 2 2	2 2 2
17	$P 2 2 2_1$	
18	$P 2_1 2_1 2$	
19	$P 2_1 2_1 2_1$	
20	$C 2 2 2_1$	
21	C 2 2 2	
22	F 2 2 2	
23	I 2 2 2	
24	$I 2_1 2_1 2_1$	
25	P m m 2	m m 2
26	$P m c 2_1$	
27	P c c 2	
28	P m a 2	
29	$P c a 2_1$	
30	P n c 2	
31	$P m n 2_1$	
32	P b a 2	
33	$P n a 2_1$	
34	P n n 2	
35	C m m 2	
36	C m c 2_1	
37	C c c 2	
38	A m m 2	
39	A b m 2	
40	A m a 2	
41	A b a 2	
42	F m m 2	
43	F d d 2	
44	I m m 2	
45	I b a 2	
46	I m a 2	
47	P m m m	m m m
48	P n n n	
49	P c c m	
50	P b a n	
51	P m m a	
52	P n n a	
53	P m n a	
54	P c c a	
55	P b a m	
56	P c c n	
57	P b c m	
58	P n n m	
59	P m m n	
60	P b c n	
61	P b c a	
62	P n m a	
63	C m c m	
64	C m c a	
65	C m m m	
66	C c c m	
67	C m m a	
68	C c c a	
69	F m m m	
70	F d d d	
71	I m m m	
72	I b a m	
73	I b c a	
74	I m m a	

tetragonal

75	P 4	4
76	P 41	
77	$P 4_2$	
78	$P 4_3$	
79	I 4	
80	$I 4_1$	
81	P -4	$\bar{4}$
82	I -4	
83	P 4/m	4/m
84	$P 4_2/m$	
85	P 4/n	
86	$P 4_2/n$	
87	I 4/m	
88	$I 4_1/a$	
89	P 4 2 2	4 2 2
90	$P 4 2_1 2$	
91	$P 4_1 2 2$	
92	$P 4_1 2_1 2$	
93	$P 4_2 2 2$	
94	$P 4_2 2_1 2$	
95	$P 4_3 2 2$	
96	$P 4_3 2_1 2$	
97	I 4 2 2	
98	$I 4_1 2 2$	
99	P 4 m m	4 m m
100	P 4 b m	
101	$P 4_2 c m$	
102	$P 4_2 n m$	
103	P 4 c c	
104	P 4 n c	
105	$P 4_2 m c$	
106	$P 4_2 b c$	
107	I 4 m m	
108	I 4 c m	
109	$I 4_1 m d$	
110	$I 4_1 c d$	
111	P -4 2 m	$\bar{4}$ 2 m
112	P -4 2 c	
113	$P -4 2_1 m$	
114	$P -4 2_1 c$	
115	P -4 m 2	
116	P -4 c 2	
117	P -4 b 2	
118	P -4 n 2	
119	I -4 m 2	
120	I -4 c 2	
121	I -4 2 m	
122	I -4 2 d	
123	P 4/m m m	4/m m m
124	P 4/m c c	
125	P 4/n b m	
126	P 4/n n c	
127	P 4/m b m	
128	P 4/m n c	
129	P 4/n m m	
130	P 4/n c c	
131	$P 4_2/m m c$	
132	$P 4_2/m c m$	
133	$P 4_2/n b c$	
134	$P 4_2/n n m$	
135	$P 4_2/m n m$	
136	$P 4_2/m b c$	
137	$P 4_2/n m c$	
138	$P 4_2/n c m$	
139	I 4/m m m	
140	I 4/m c m	
141	$I 4_1/a m d$	
142	$I 4_1/a c d$	

trigonal

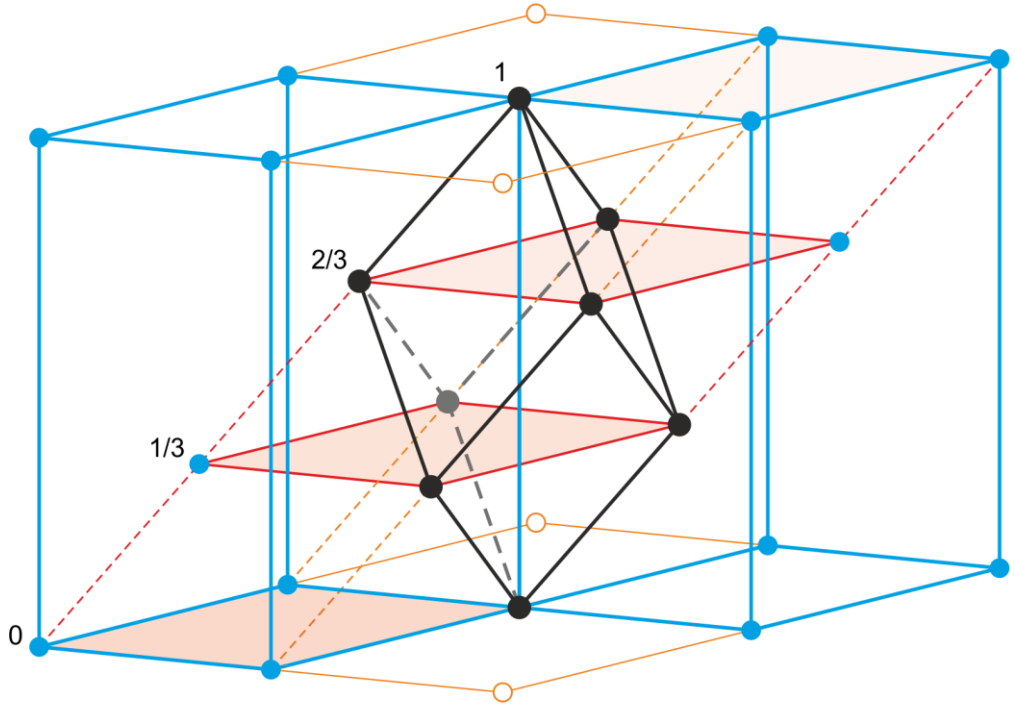
143	P 3	3
144	$P 3_1$	
145	$P 3_2$	
146	R 3	
147	P -3	$\bar{3}$
148	R -3	
149	P 3 1 2	3 2
150	P 3 2 1	
151	$P 3_1 1 2$	
152	$P 3_1 2 1$	
153	$P 3_2 1 2$	
154	$P 3_2 2 1$	
155	R 3 2	
156	P 3 m 1	3 m
157	P 3 1 m	
158	P 3 c 1	
159	P 3 1 c	
160	R 3 m	
161	R 3 c	
162	P -3 1 m	$\bar{3}$ m
163	P -3 1 c	
164	P -3 m 1	
165	P -3 c 1	
166	R -3 m	
167	R -3 c	

hexagonal

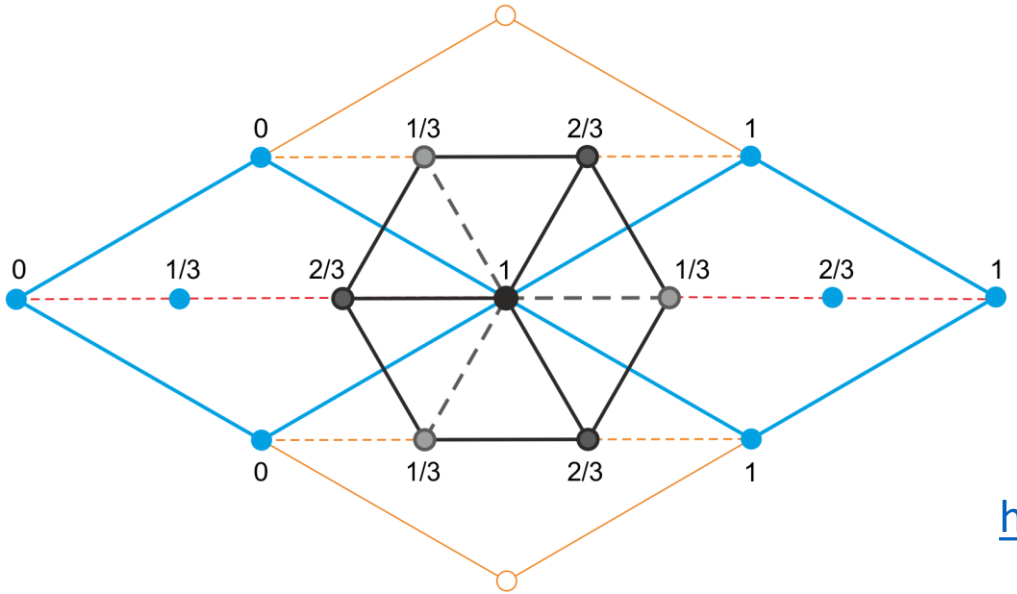
168	P 6	6
169	$P 6_1$	
170	$P 6_5$	
171	$P 6_2$	
172	$P 6_4$	
173	$P 6_3$	
174	P -6	$\bar{6}$
175	P 6/m	6/m
176	$P 6_3/m$	
177	P 6 2 2	6 2 2
178	$P 6_1 2 2$	
179	$P 6_5 2 2$	
180	$P 6_2 2 2$	
181	$P 6_4 2 2$	
182	$P 6_3 2 2$	
183	P 6 m m	6 m m
184	P 6 c c	
185	$P 6_3 c m$	
186	$P 6_3 m c$	
187	P -6 m 2	$\bar{6}$ 2 m
188	P -6 c 2	
189	P -6 2 m	
190	P -6 2 c	
191	P 6/m m m	6/m m m
192	P 6/m c c	
193	$P 6_3/m c m$	
194	$P 6_3/m m c$	

cubic

195	P 2 3	2 3
196	F 2 3	
197	I 2 3	
198	$P 2_1 3$	
199	$I 2_1 3$	
200	P m 3	m 3
201	P n 3	
202	F m 3	
203	F d 3	
204	I m 3	
205	P a 3	
206	I a 3	
207	P 4 3 2	4 3 2
208	$P 4_2 3 2$	
209	F 4 3 2	
210	$F 4_1 3 2$	
211	I 4 3 2	
212	$P 4_3 3 2$	
213	$P 4_1 3 2$	
214	$I 4_1 3 2$	
215	P -4 3 m	$\bar{4}$ 3 m
216	F -4 3 m	
217	I -4 3 m	
218	P -4 3 n	
219	F -4 3 c	
220	I -4 3 d	
221	P m 3 m	m 3 m
222	P n 3 n	
223	P m 3 n	
224	P n 3 m	
225	F m 3 m	
226	F m 3 c	
227	F d 3 m	
228	F d 3 c	
229	I m 3 m	
230	I a 3 d	



hexagonal and rhombohedral unit cells



https://www.periodni.com/crystal-systems-and-bravais-lattices.html