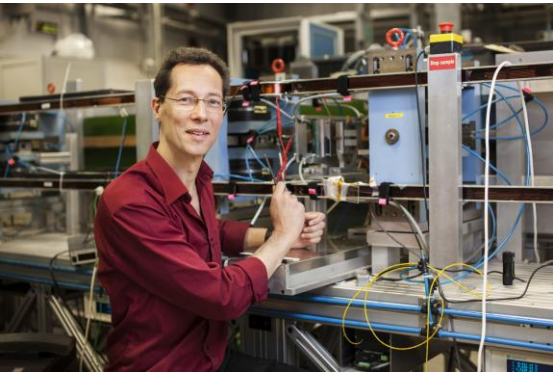
Diffraction from non-crystalline materials 1

Wim Bouwman, Delft University of Technology

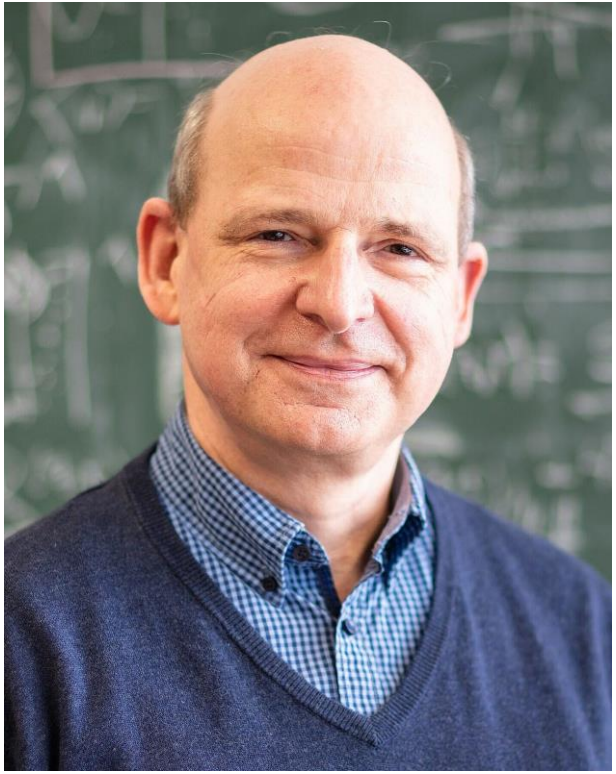
Oxford School of Neutron Scattering

Wim Bouwman



- Spin-echo small-angle neutron scattering (SESANS)
- Reactor Institute Delft
- Food

Stefan Egelhaaf



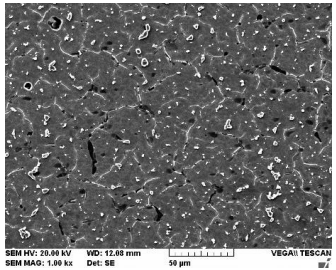
Diffraction from non-crystalline materials 1

- Non-crystalline materials?
- Small-angle approximation
- Phase map
- Single particle scattering, form factor
- Concentrated scattering, structure factor

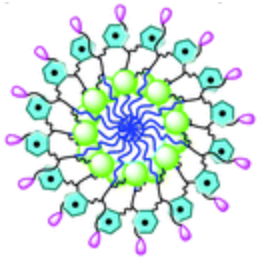
Diffraction from non-crystalline materials 2

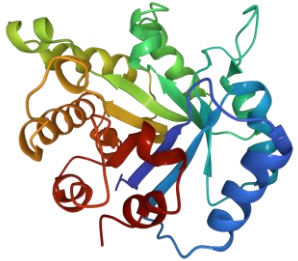
- Structure factor again
- Intensity
- Contrast variation

Non-crystalline materials



- Metals
  - Defects
  - Precipitates
  - Magnetic domains
- Polymers
  - Conformation of polymer molecules in solution and in the bulk
  - Structure of micro-phase separated block copolymers
  - Factors affecting miscibility of polymer blends
- Chemistry
  - Structure and interactions in colloid suspensions, micro-emulsions, surfactant phases etc.
  - Mechanisms of molecular self-assembly in solutions
- Biology
  - Organization of biomolecular complexes in solution
  - Conformation changes affecting function of proteins, enzymes, protein/DNA, complexes, membranes etc
  - Mechanisms and pathways for protein folding and DNA supercoiling

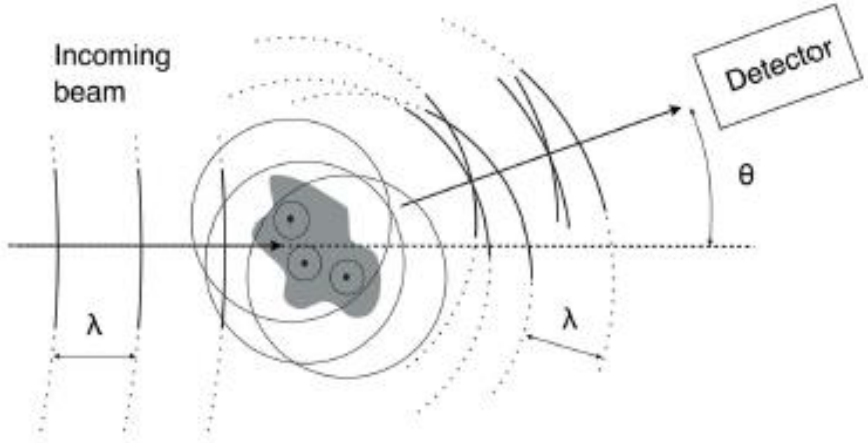




Non-crystalline materials

- Length scales >> interatomic distances
- Small angles (reciprocal space)

Huygens wave scattering

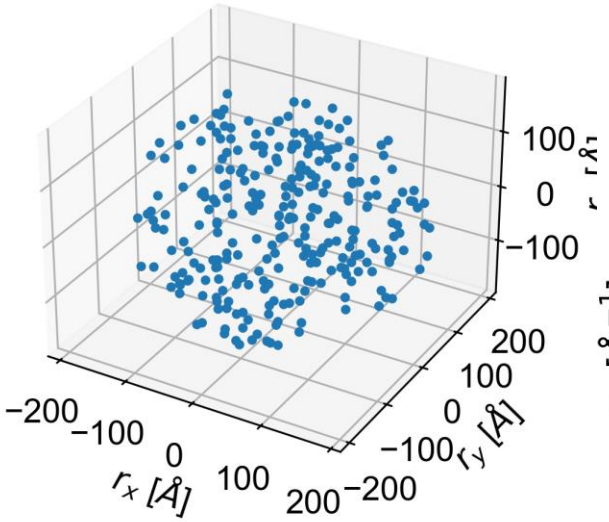


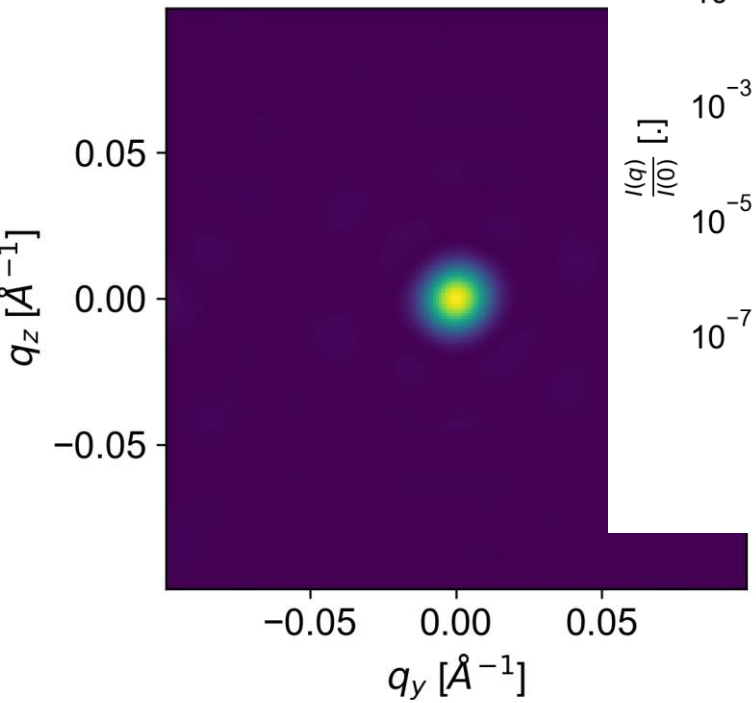
$$A = b_1 \exp(i\phi_1) + b_2 \exp(i\phi_2) + \cdots$$

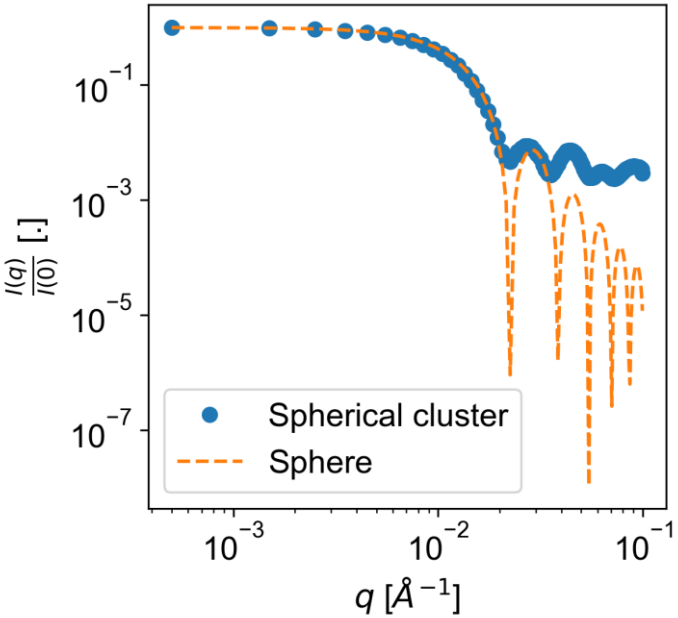
$$\phi_n = \mathbf{q} \cdot \mathbf{r_n}$$

$$\frac{d\sigma}{d\Omega} = |\sum_n b_n \exp(i\mathbf{q} \cdot \mathbf{r_n})|^2$$

Numerical approach: Lassi Tiihonen

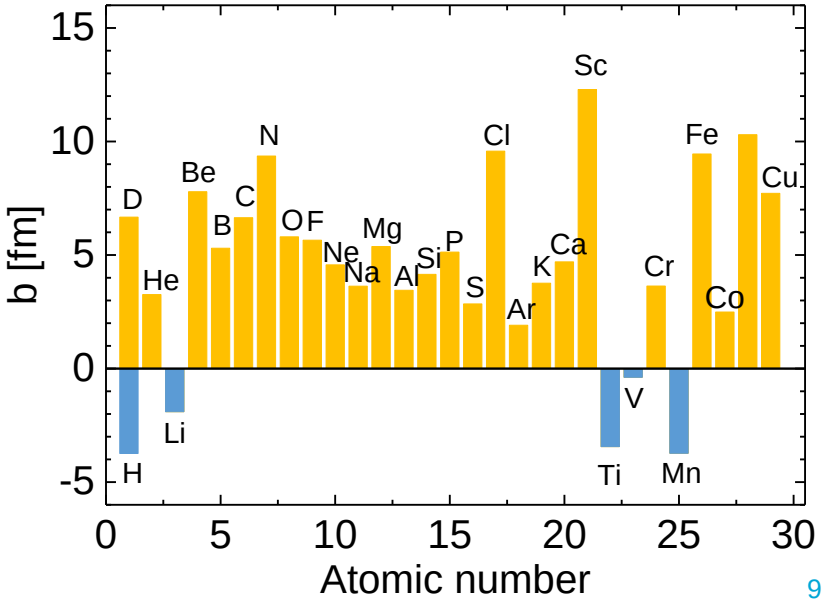






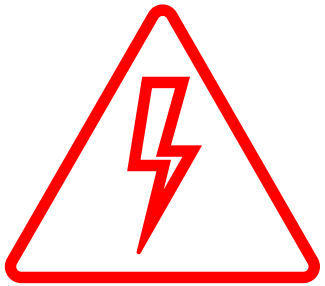
Reminder: Scattering length density ρ

$$\rho = SLD = \sum_i N_i b_i$$



Many symbols and definitions used

- *SLD*, *Nb*, N_b, ρ
- $\theta, 2\theta, \alpha$
- *Q*, -*Q*, *q*, -*q*
- *P*(*q*), *F*(*q*)
- *I*(*q*), $\frac{d\sigma}{d\Omega}(q)$



Small-angle approximation

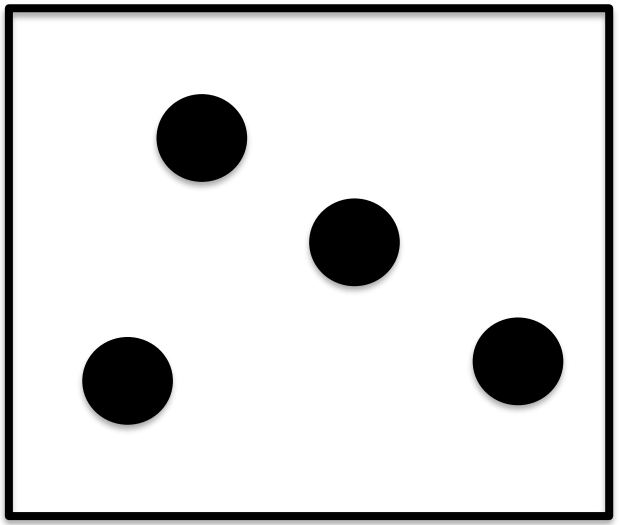
$$\frac{d\sigma}{d\Omega} = \left|\sum_n b_n \exp(i\mathbf{q}\cdot\mathbf{r_n})\right|^2$$

$$qa << 2\pi$$

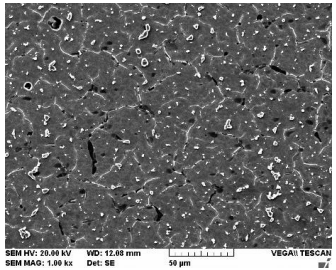
$$\frac{d\sigma}{d\Omega} = \left|\int \rho(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r}) d\mathbf{r}\right|^2$$

Exercise class

Models for $\rho(\mathbf{r})$



Non-crystalline materials



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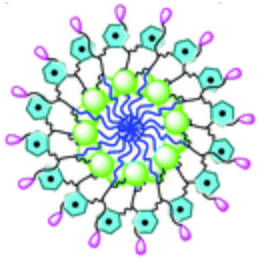
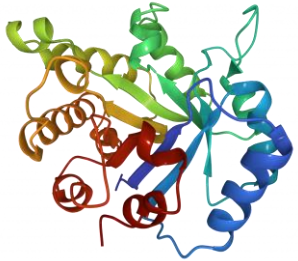
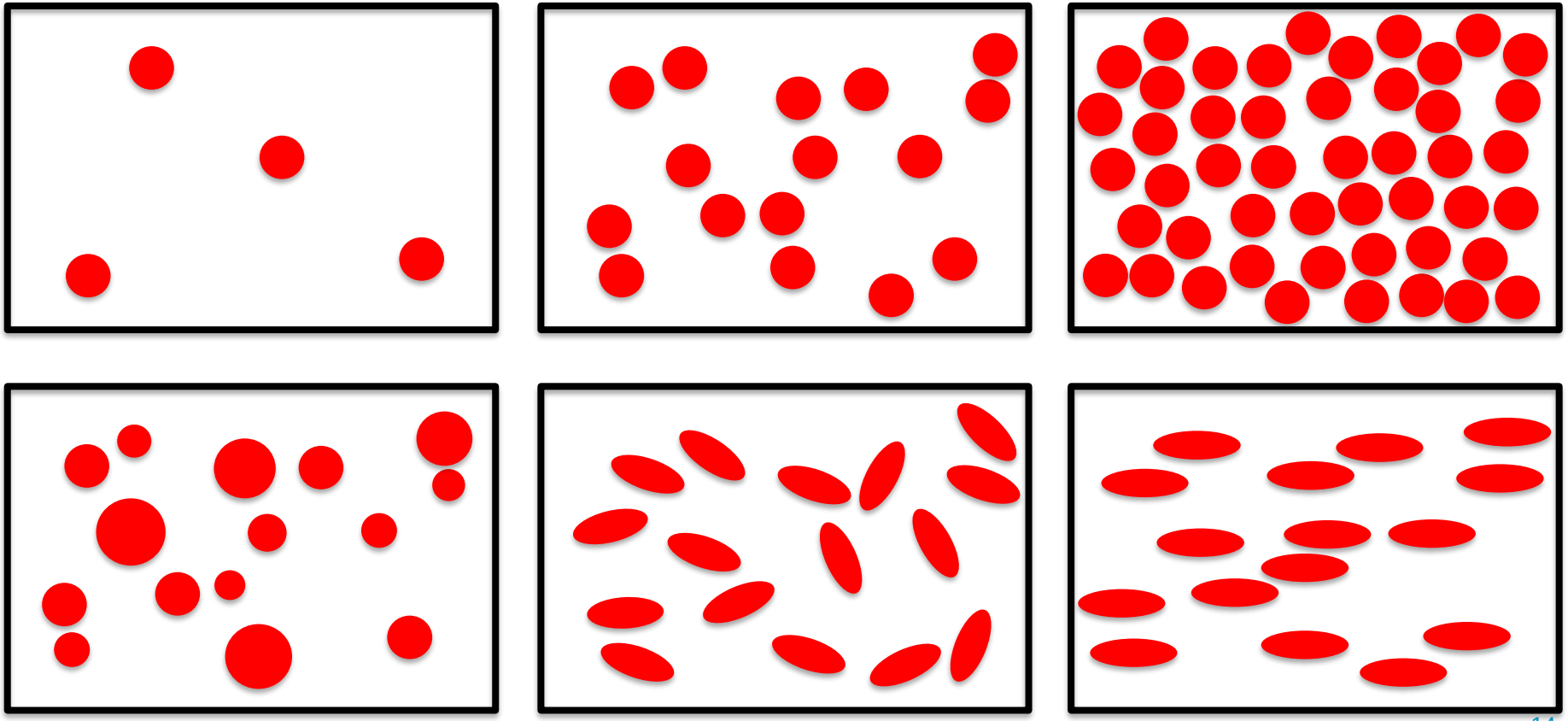
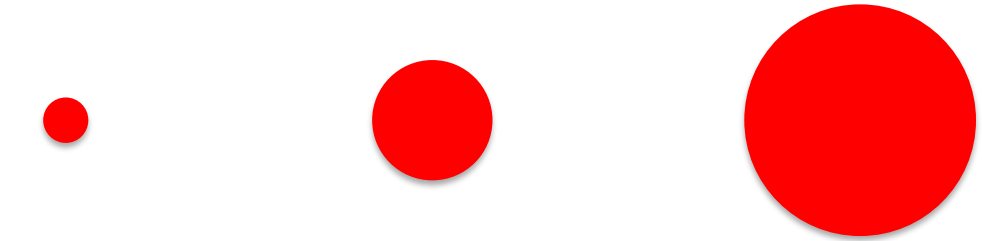




2-phase models for $\rho(\mathbf{r})$

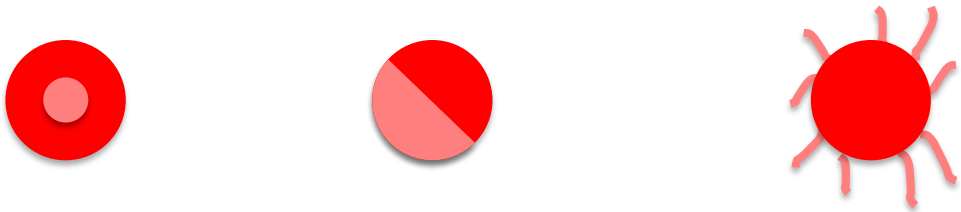


Characterisation particles
Form factor $P(q)$



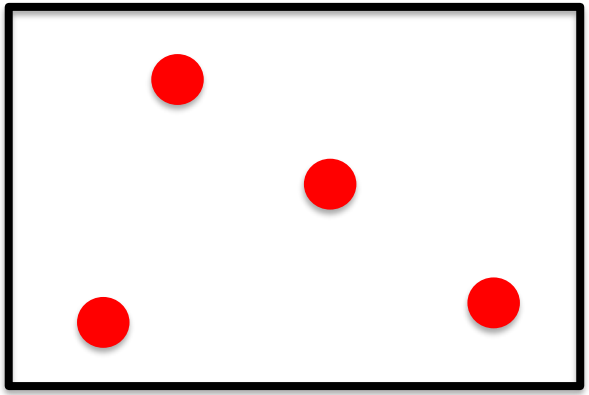
Size

Shape

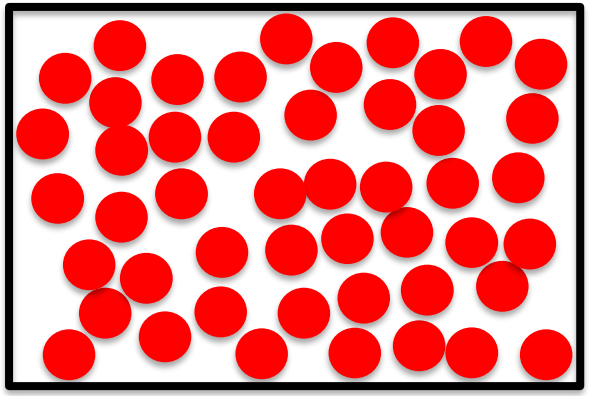


Structure

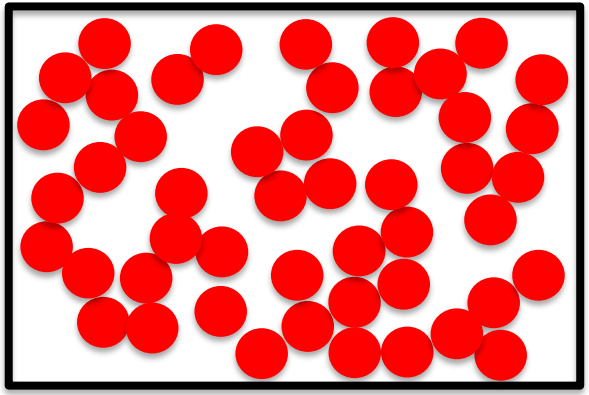
Characterisation organisation particles
Structure factor $S(q)$



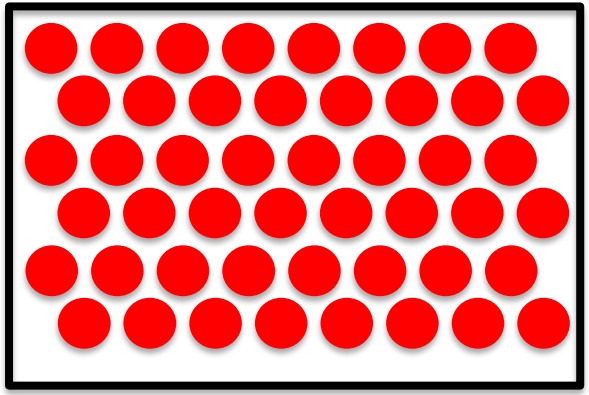
Dilute



Hard sphere



Attractive



Repulsive

2 phase: particles in solvent

Concentration [particles/volume]

Scattering length density contrast [length/volume]

Structure factor [-] (between particles)

$$\frac{d\sigma}{d\Omega}(q) = cV^2(\Delta\rho)^2 P(q) S(q)$$

Volume particle [volume]

Form factor [-] (of particle)

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Small-angle scattering for beginners

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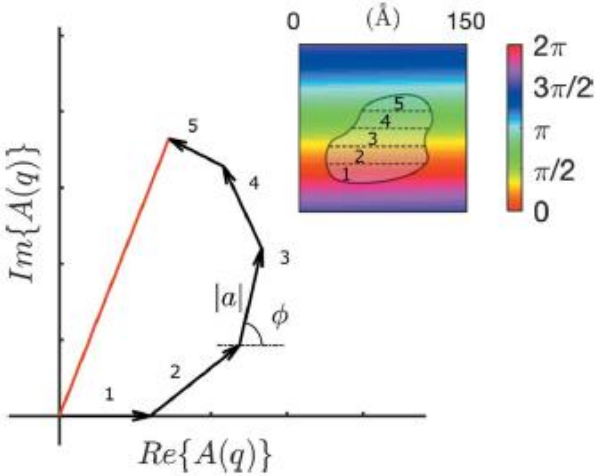
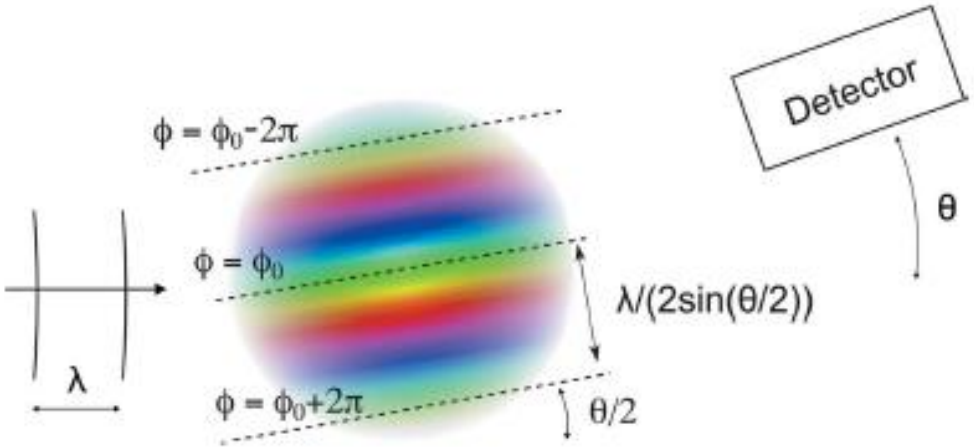


J. Appl. Cryst. (2021). 54

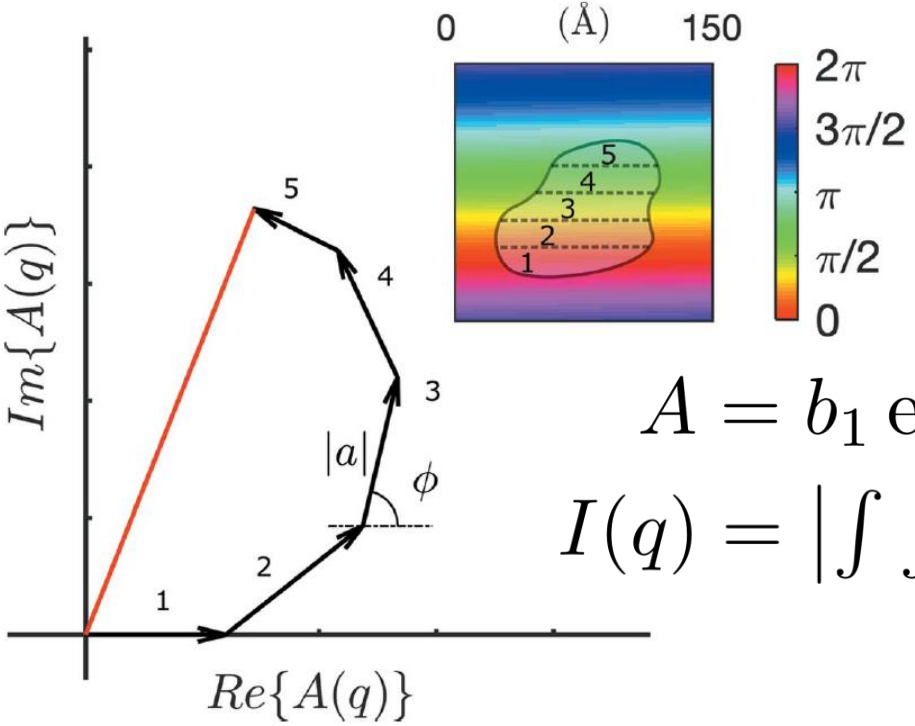
Phase map

$$\frac{d\sigma}{d\Omega} = |\int \rho(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r}) d\mathbf{r}|^2$$



$$\lambda^* = \frac{2\pi}{q}$$

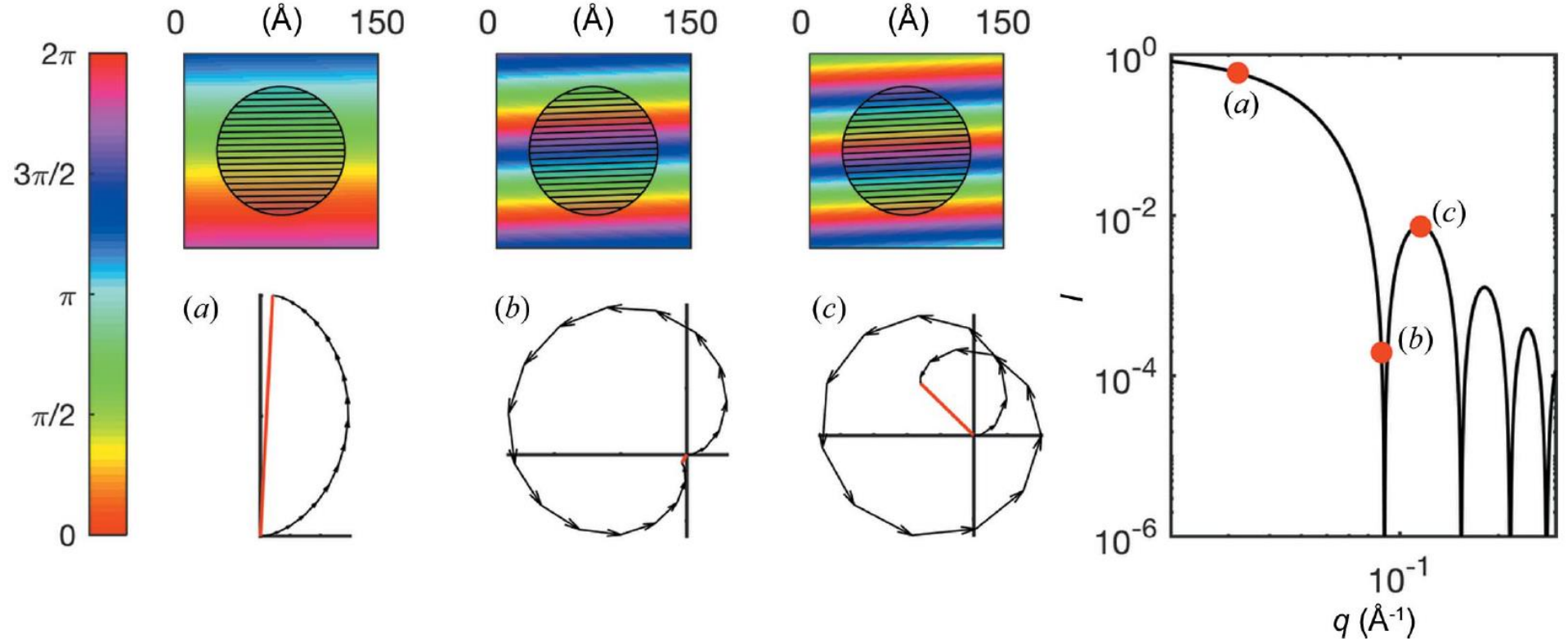
Addition atoms - integration density

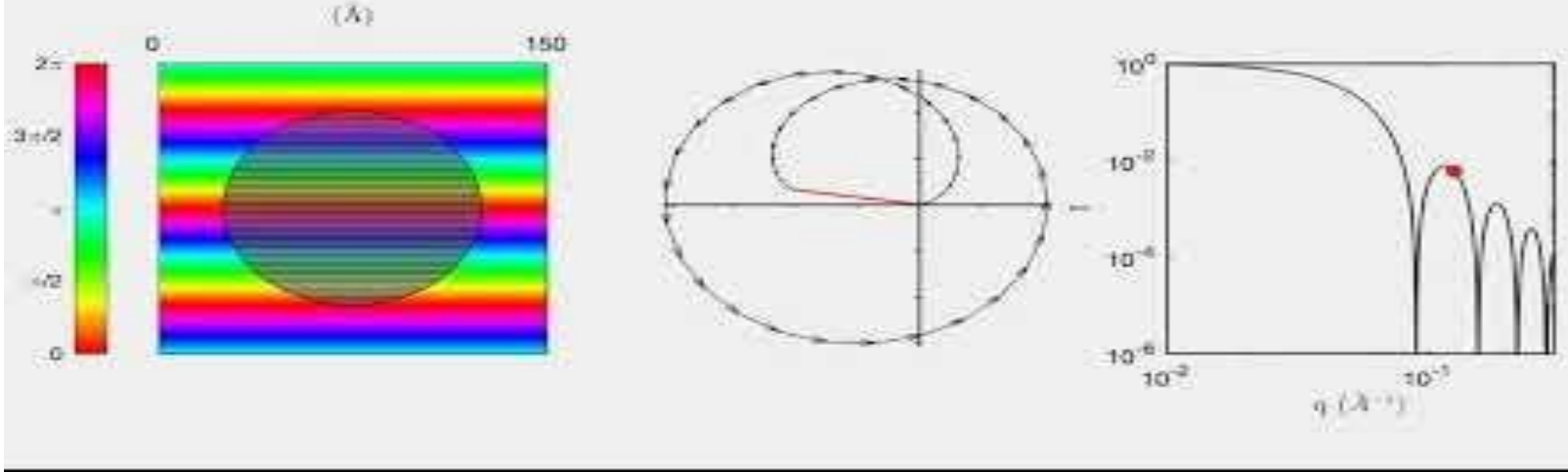


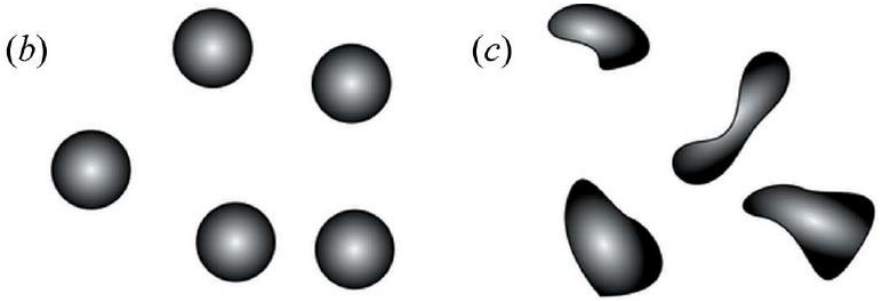
$$A = b_1 \exp(i\phi_1) + b_2 \exp(i\phi_2) + \cdots$$

$$I(q) = \left| \int \int \int \exp(iqy)\rho \, dx \, dy \, dz \right|^2$$

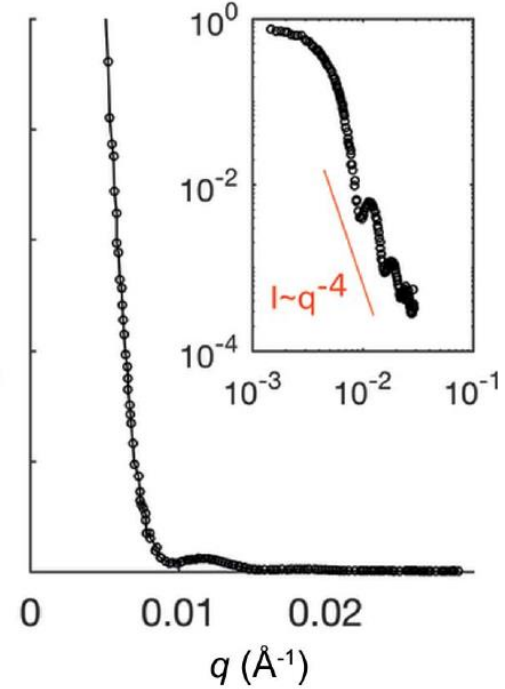
Single sphere, r = 50 Å




(Å)
0
150
2π
3π/2
π
π/2
0
10^{0}
10^{-2}
10^{-4}
10^{-6}
10^{-2}
10^{-1}
q (Å^{-1})



Amoebas?



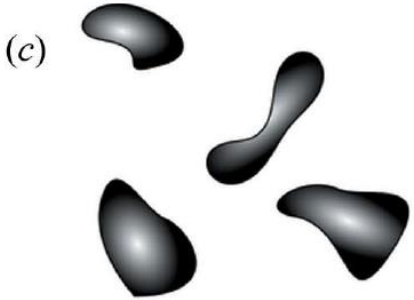
Guinier law:

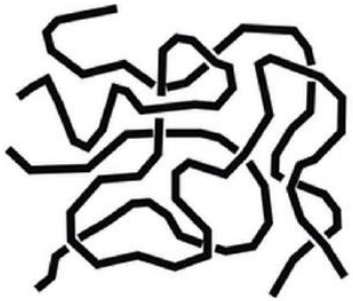
$$P(q) \approx \exp\left[-(qR_G)^2/3\right]$$

Discuss with your neighbour what you expect for:

Needles

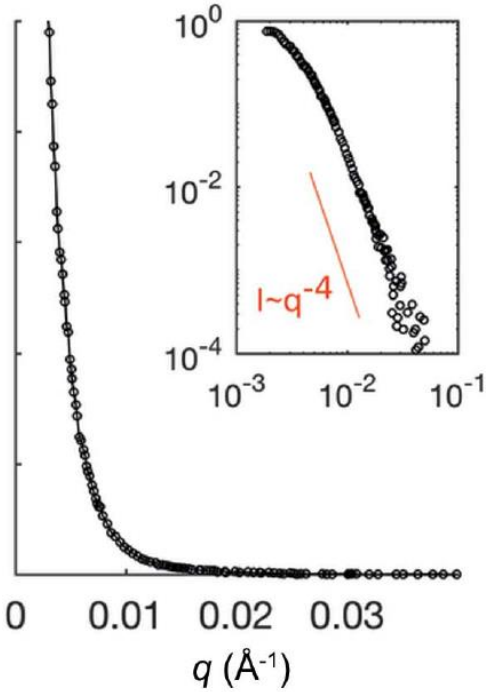
Plates





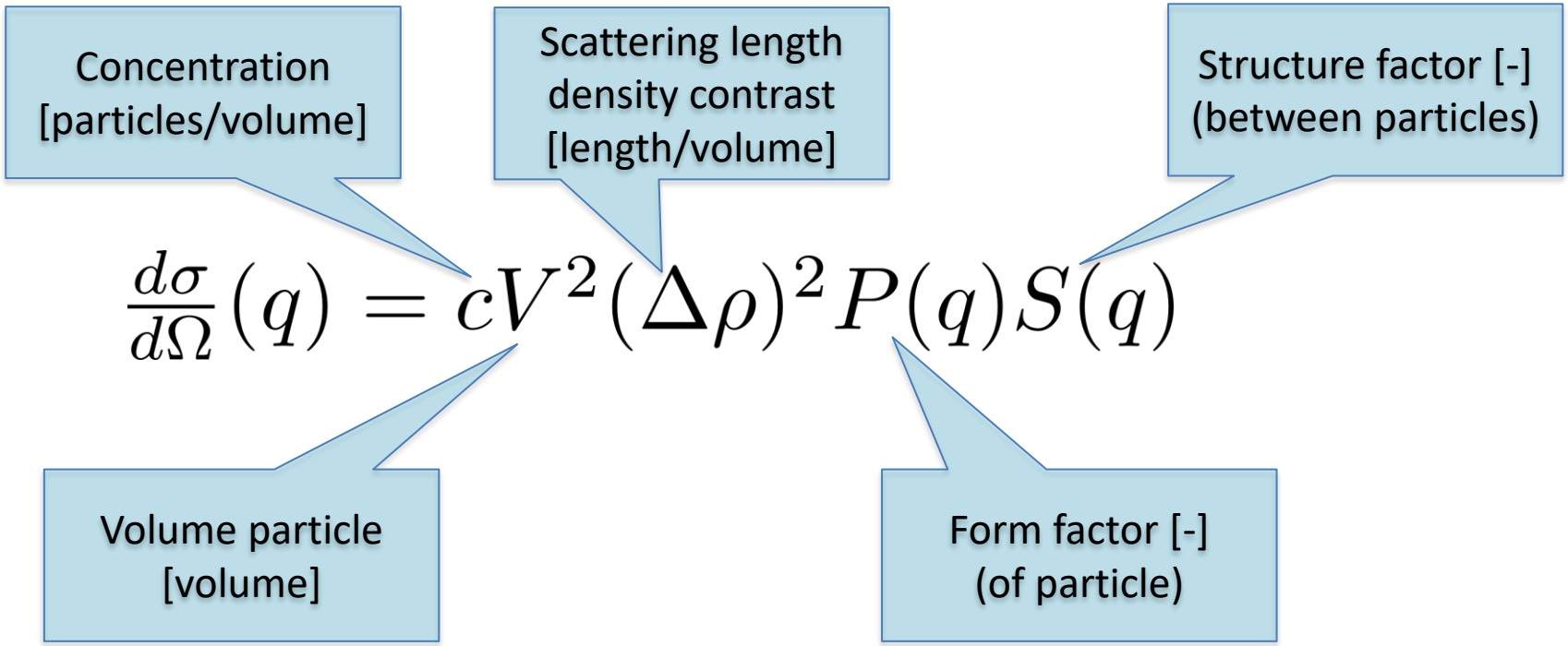
Other dimensions

Scattering exponent α	Underlying structure
1	Randomly oriented elongated objects (needles, rods *etc.*)
2	Randomly oriented flat objects (platelets, discs *etc.*)
2	Ideal polymer coil, *i.e.* modelled as a random walk
~1.7	Self-avoiding polymer coil
$1 \leq \alpha \leq 3$	Volume fractals (aggregates, house of cards *etc.*) with fractal dimension $D = \alpha$
$3 < \alpha < 4$	Surface fractals, with fractal dimension $D_s = 6 - \alpha$
4	Porod's law: any structure with sharp interfaces between contrasted domains
$4 < \alpha$	Smooth/progressive transitions between contrasted domains



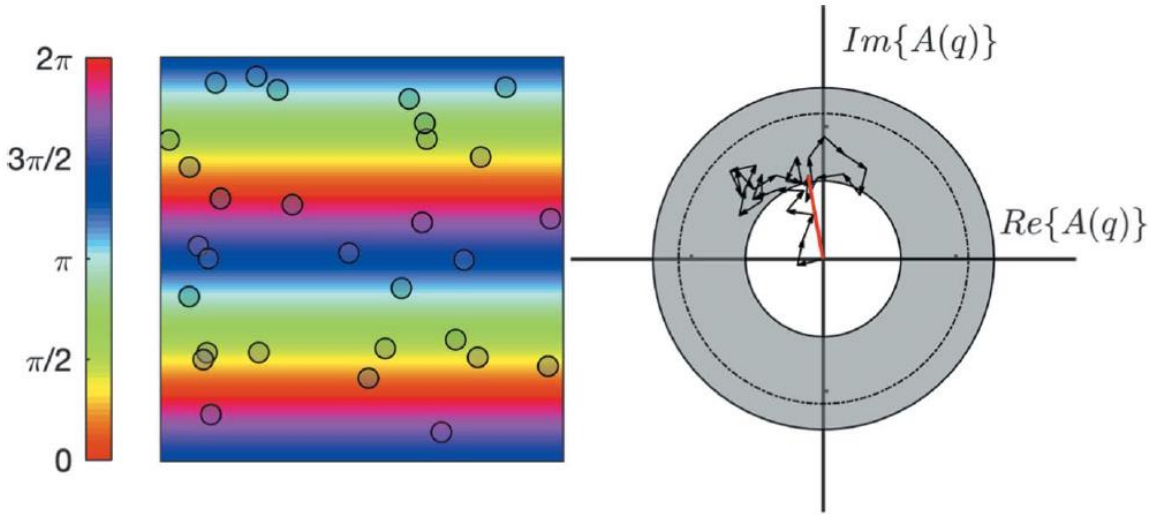
$$I(q) \propto q^{-\alpha}$$

2 phase: particles in solvent



Multiple particles, dilute

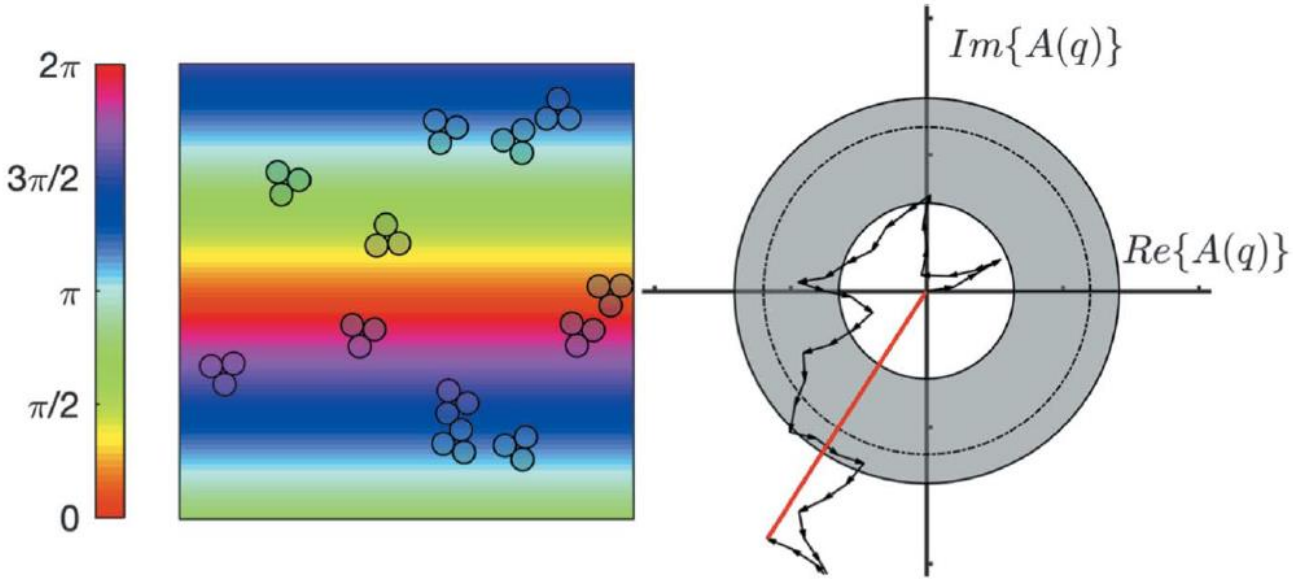
$$I(q) = \rho^2 V^2 P(q) \left| \exp(i\phi_1) + \exp(i\phi_2) + \cdots \right|^2.$$



$$\langle |A|^2 \rangle = N|a|^2$$

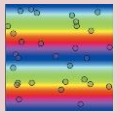
$$I(q) = c\rho^2 V^2 P(q)$$

Aggregation, structure factor $S(q)$

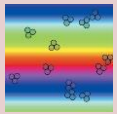


$$I(q) = c\rho^2 V^2 P(q)\, S(q)$$

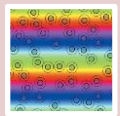
Discuss neighbour: $S(q << 2\pi/R)$



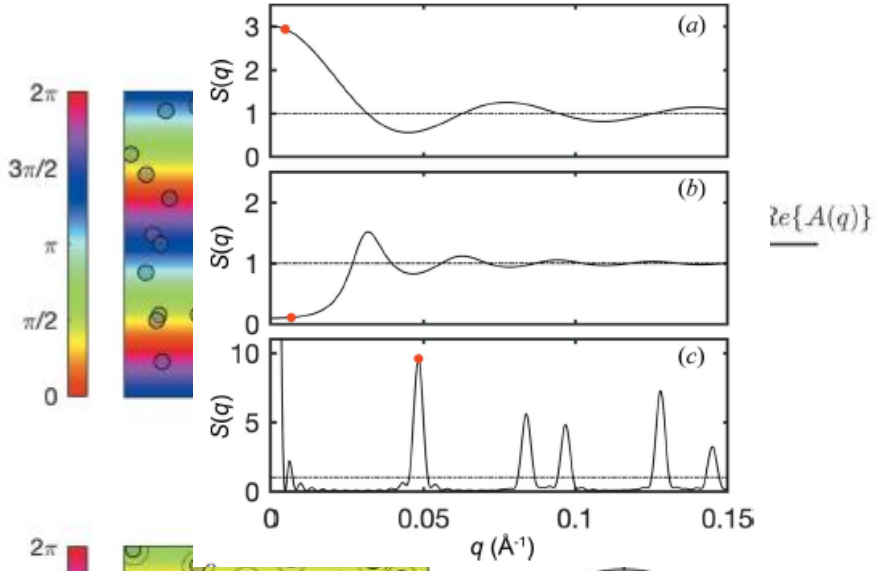
Dilute



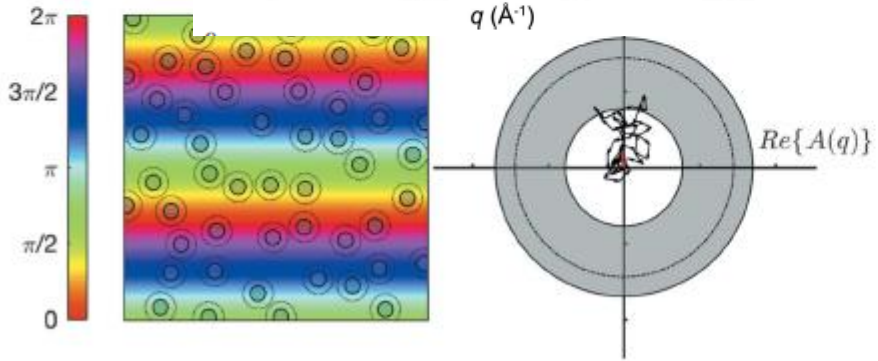
Trimers

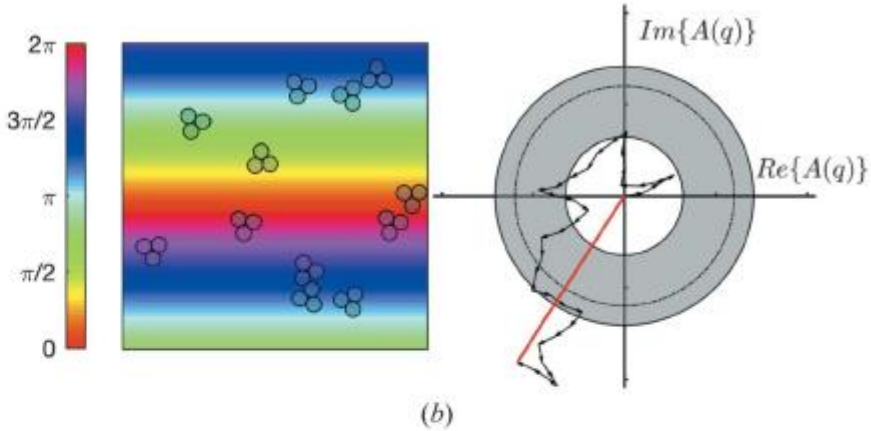


Repulsion

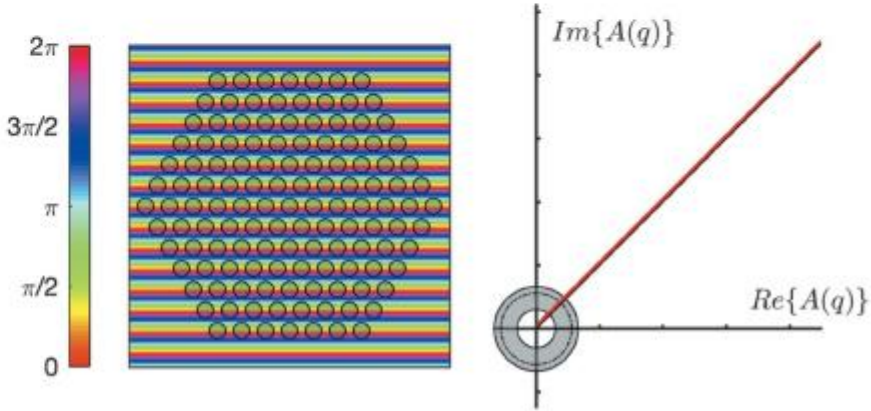

2π
3π/2
π
π/2
0
S(q)
(a)
(b)
(c)
0
0.05
0.1
0.15
q (Å⁻¹)
Re{A(q)}

(c)


2π
3π/2
π
π/2
0
Re{A(q)}


2π
3π/2
π
π/2
0
Im{A(q)}
Re{A(q)}

(b)


2π
3π/2
π
π/2
0
Im{A(q)}
Re{A(q)}

(d)

Figure 8

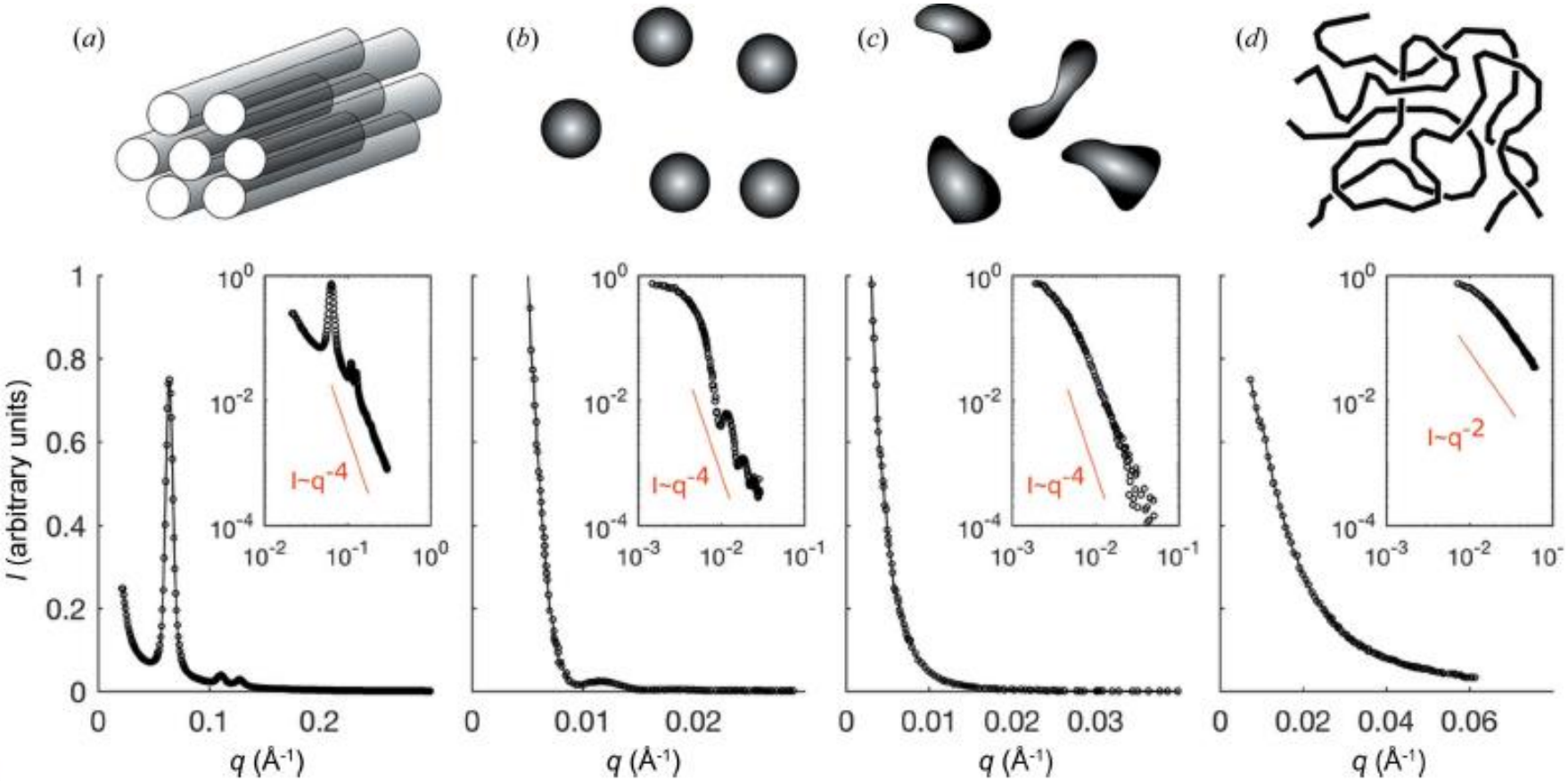
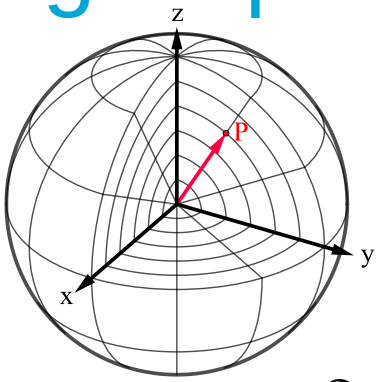


Figure 4

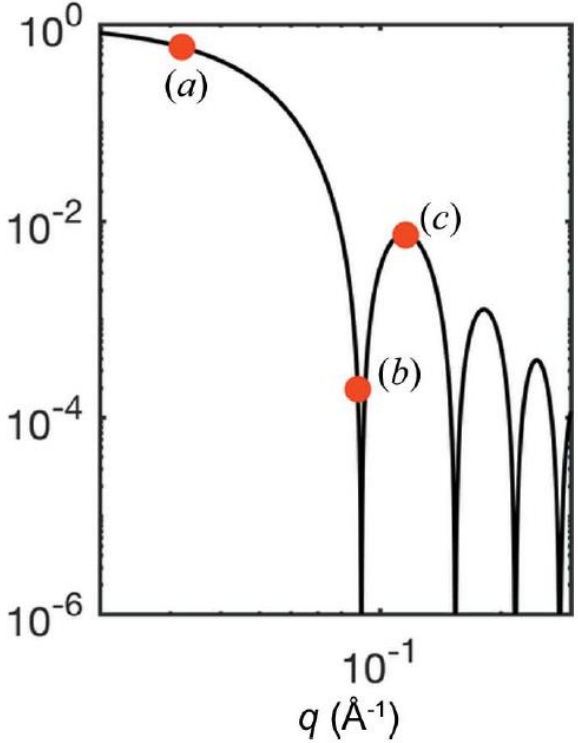
Analytical single sphere

$$I(q) = \rho^2 V^2 P(q)$$



$$P(q) = \left| \frac{1}{V} \int_V \exp(-\mathbf{q} \cdot \mathbf{r}) dV \right|^2$$

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



Exercise class

SasView expressions for shapes

- Cylinder Functions
  - barbell
  - capped_cylinder
  - core_shell_bicelle
  - core_shell_bicelle_elliptical
  - core_shell_bicelle_elliptical_belt_rough
  - 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_paracrystal
- Paracrystal Functions
  - bcc_paracrystal
  - fcc_paracrystal
  - sc_paracrystal
- Parallelepiped Functions
  - core_shell_parallelepiped
  - 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
  - multilayer_vesicle
  - onion
  - polymer_micelle
  - raspberry
  - sphere
  - spherical_sld
  - superball
  - vesicle

Looking at Nothing

A weblog about small-angle scattering

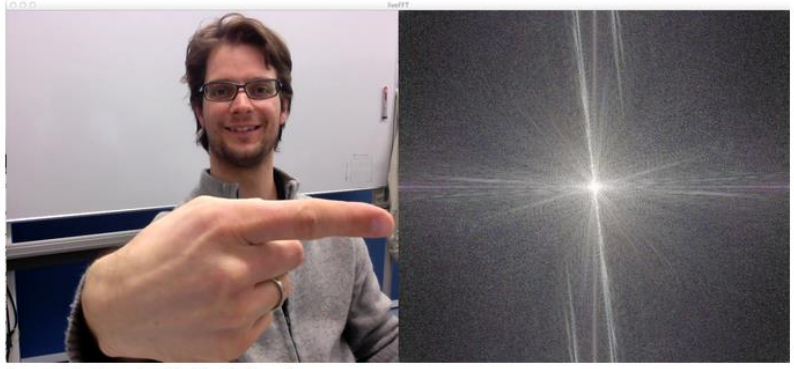
LOOKING AT NOTHING

A SA(X)S WEBLOG

ABOUT SA(X)S | MEASURE WITH US | PUBLICATIONS | SOFTWARE | VIDEOS | ABOUT ME

New Live Fourier Transform code

2014-01-27 Brian Blog posts, Presentations and teaching, Software 0



A screenshot from the Live Fourier Transform program

*More about this next week, but **Ingo** has kindly provided a Windows executable version of one of the latest development builds of the Monte Carlo code (with GUI). While I have not yet had the chance to test it (being on a mac myself), please go ahead and get it **from here**!*

BRIAN'S TWEETS

RT @JustMyTweet: #MakeTrumpNervousIn4Words Greta Thunberg made TIME!! https://t.co/QexuUrsPO7 about 3 hours ago

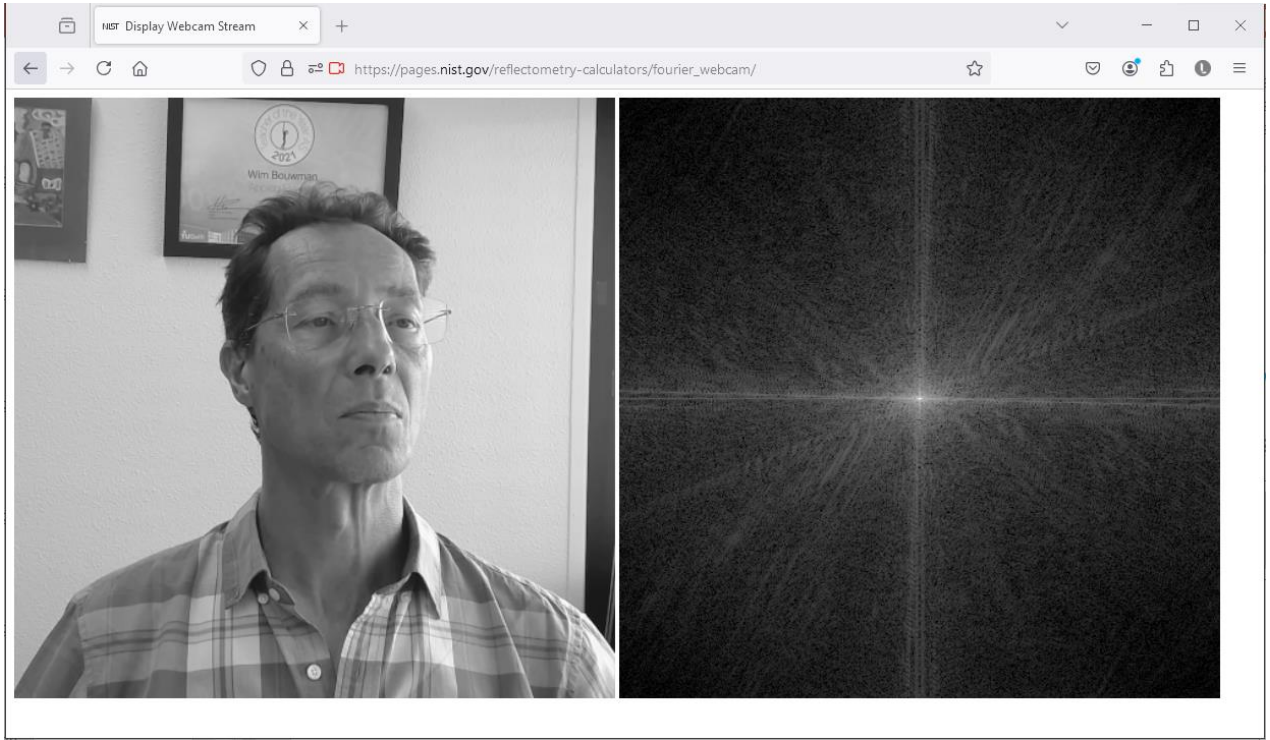
RT @GretaThunberg: "The difference is about the same as a decade of fossil fuel emissions from the UK, Germany, France and Canada put toget... about 4 hours ago

RT @BlackPhysicists: Regularized integral equation methods for elastic scattering problems in three dimensions https://t.co/aYLwwgAbMT via... about 5 hours ago

RT @NCStinn: Scientists: you should wash your hands because of Coronavirus. People: I'm gonna stop flying, hoard masks, work from home & t... about 5 hours ago

Discrete Fourier Transform

https://pages.nist.gov/reflectometry-calculators/fourier_webcam/



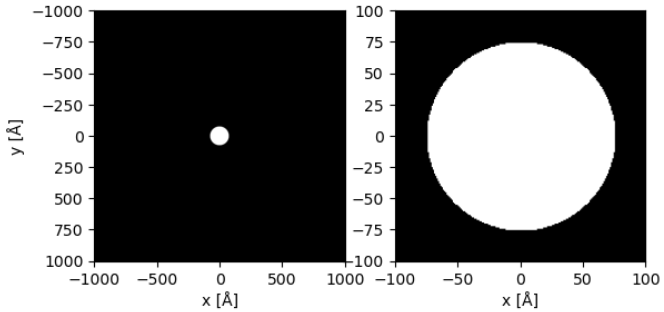
Do it yourself

•[6]:
```
# The next line(s) of code define(s) the structure "M" we want to study. You can edit this to create other structures
radius = 75
M =  np.sqrt(X**2 + Y**2) < radius
# Above this line was the last line defining the structure "M" we will study.

# plt.subplots(figsize=(10,3.5))
# The full plot
plt.subplot(121)
exts = [x[0], x[-1], y[-1], y[0]]
plt.imshow(M, extent=exts, cmap='gray')
plt.xlabel("x [Å]")
plt.ylabel("y [Å]")

# The zoom
plt.subplot(122)
zoom = 200
start = int(len(x)/2-zoom/2)
end = start + zoom
M_zoom = M[start:end,start:end]
exts_zoom = [x[start], x[end], y[start], y[end]]
plt.imshow(M_zoom, extent=exts_zoom, cmap='gray')
plt.xlabel("x [Å]")
plt.ylabel("y [Å]")
```

[6]:
```
Text(0, 0.5, 'y [Å]')
```



https://wimbouwman.nl/oxford.php

Oxford neutron school material with lectures Wim Bouwman

Phase map article

Small-angle scattering for beginners

Cedric J. Gommes, Sebastian Jaksch, and Henrich Frielinghaus

Applied Crystallography 54 (2021) 1832-1843

https://doi.org/10.1107/S1600576721010293

Discrete Fourier Transform

If you are familiar with Jupyter Notebooks, you can use this notebook I adapted to experiment with calculating the scattering from some 2D objects.

If you are not familiar with Python, you can make drawings and show them to the camera of your laptop while you look at https://ncnr.nist.gov/instruments/magik/calculators/fourier_webcam/.

A nice demonstration of this kind of software is given by Brian Pauw.

Diffraction from non-crystalline materials 1

- Non-crystalline materials?
- Small-angle approximation
- Phase map
- Single particle scattering, form factor
- Concentrated scattering, structure factor

Diffraction from non-crystalline materials 2

- Structure factor again
- Intensity
- Contrast variation

Diffraction from non-crystalline materials 2

Wim Bouwman, Delft University of Technology

Oxford School of Neutron Scattering

Diffraction from non-crystalline materials 1

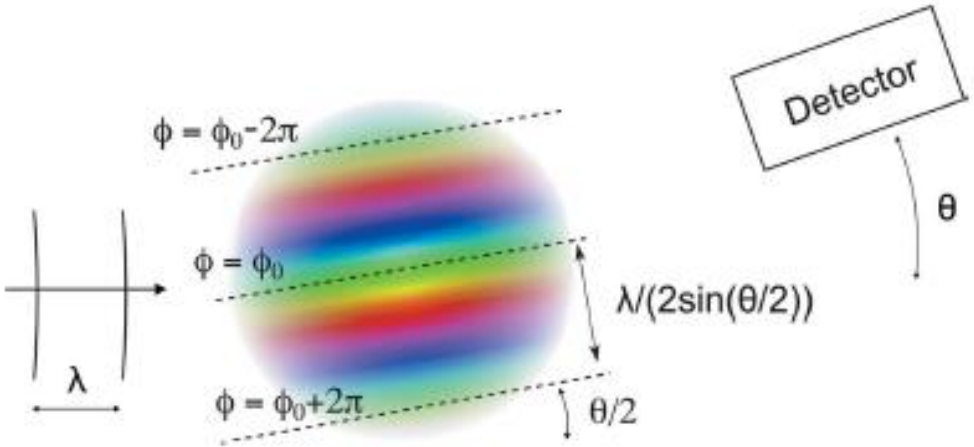
- Non-crystalline materials?
- Small-angle approximation
- Phase map
- Single particle scattering, form factor
- Concentrated scattering, structure factor

Diffraction from non-crystalline materials 2

- Structure factor again
- Intensity
- Contrast variation

Phase map

$$\frac{d\sigma}{d\Omega} = |\int \rho(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r}) d\mathbf{r}|^2$$



$$\lambda^* = \frac{2\pi}{q}$$

2 phase: particles in solvent

Concentration [particles/volume]

Scattering length density contrast [length/volume]

Structure factor [-] (between particles)

$$\frac{d\sigma}{d\Omega}(q) = cV^2(\Delta\rho)^2 P(q) S(q)$$

Volume particle [volume]

Form factor [-] (of particle)

Isotropic - density correlation function

$$r = |\mathbf{r}| \qquad \left\langle e^{-i\mathbf{Q}\cdot\mathbf{r}} \right\rangle = \frac{\sin Qr}{Qr}$$

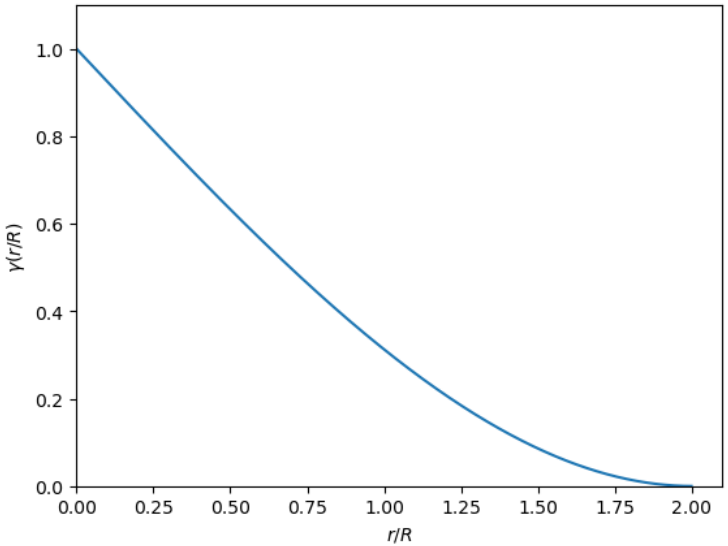
$$\frac{d\sigma}{d\Omega} = \left| \int \rho(\mathbf{r}) \exp(i\mathbf{Q}\cdot\mathbf{r}) d\mathbf{r} \right|^2$$

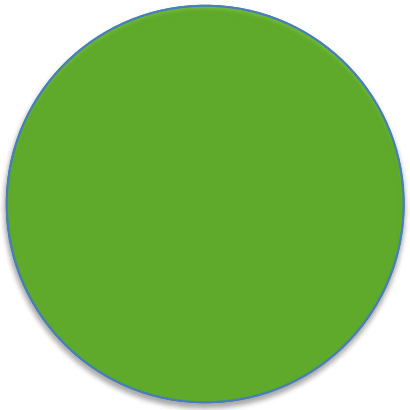
$$\frac{d\sigma}{d\Omega} = \left| \int \rho(r) \frac{\sin Qr}{Qr} dr \right|^2$$

$$\gamma(r) = \int \rho(\mathbf{r}')\rho(\mathbf{r}'+\mathbf{r}) d\mathbf{r}'$$

$$\frac{d\sigma}{d\Omega} = \int \gamma(r) \frac{\sin Qr}{Qr} 4\pi r^2 dr$$

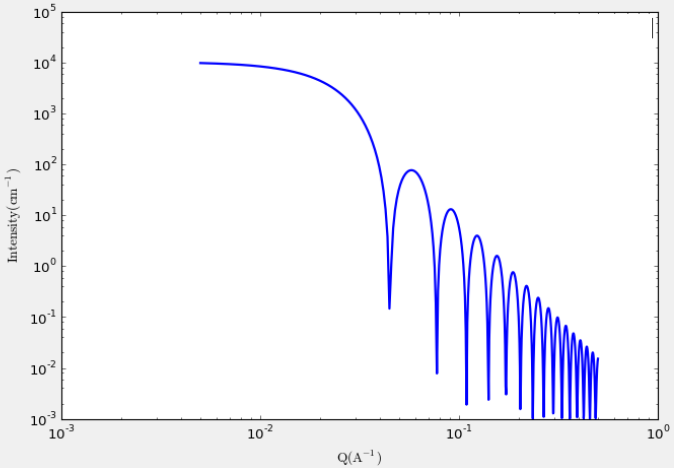
Correlation function sphere

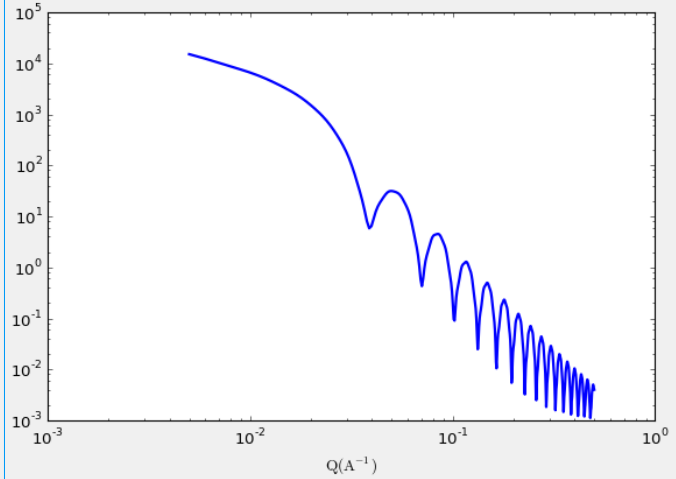




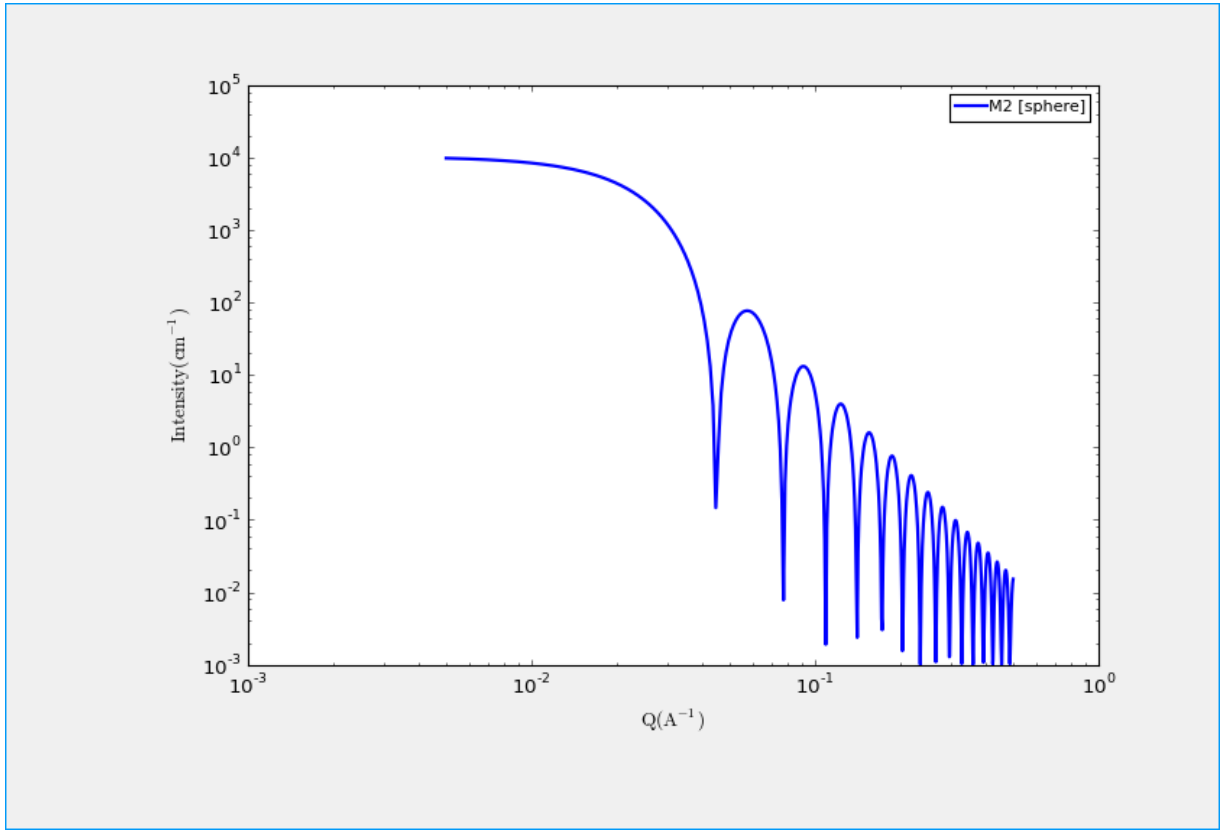
$$\gamma(r) = 1 - \frac{3}{4}\left(\frac{r}{R}\right) + \frac{1}{16}\left(\frac{r}{R}\right)^3$$

Cylinder Sphere?

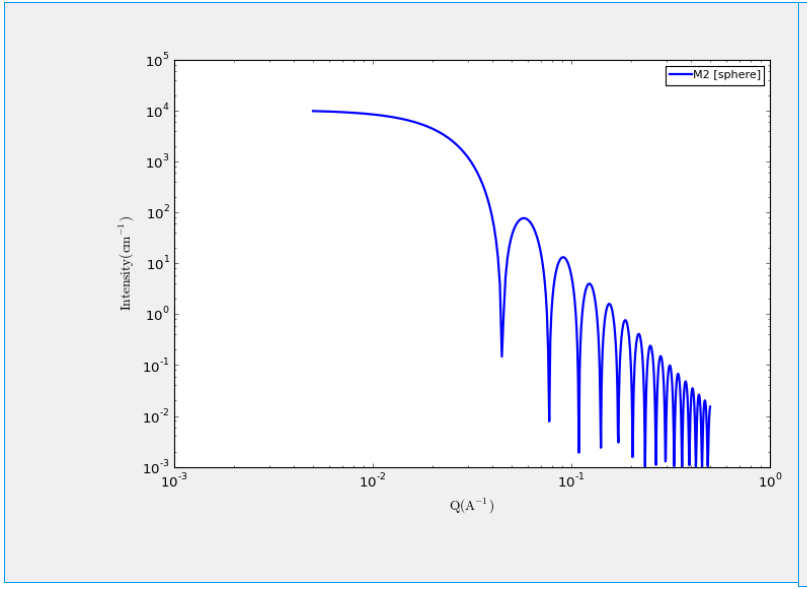


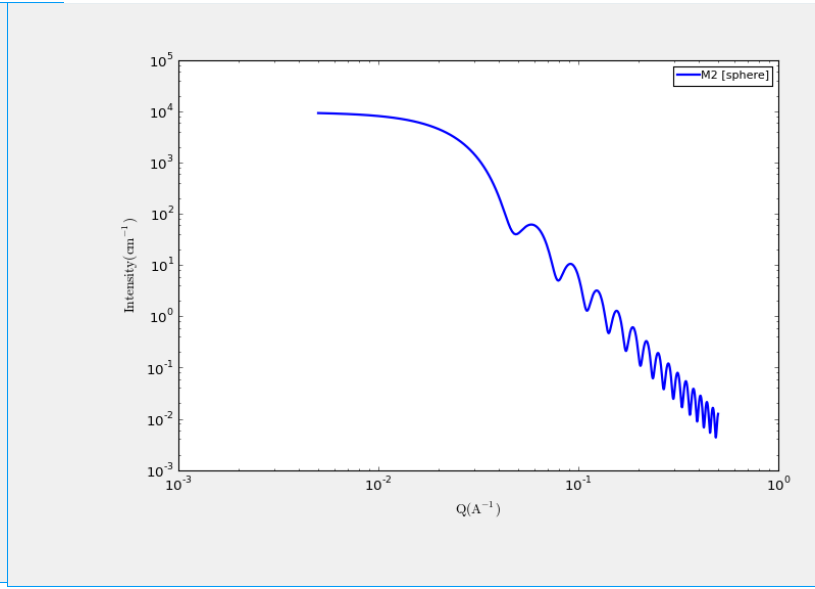


Radius? 1 Å, 10 Å or 100 Å



Most realistic outcome?

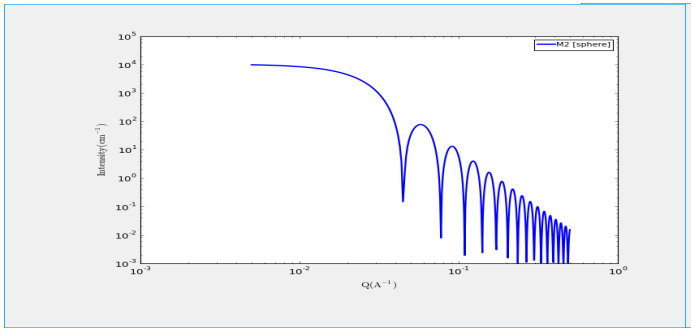


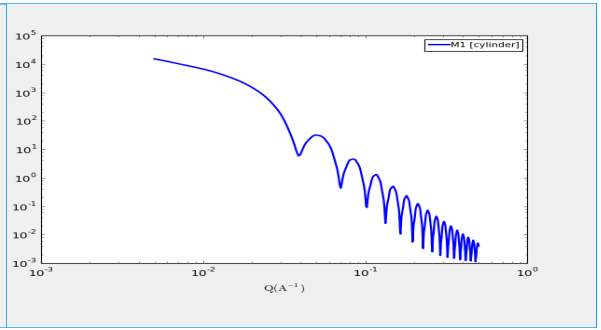


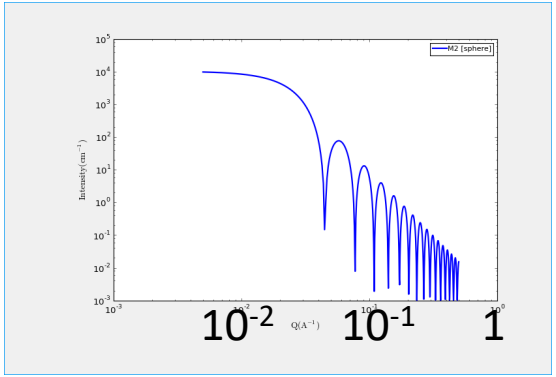
5 minutes, discuss in your group

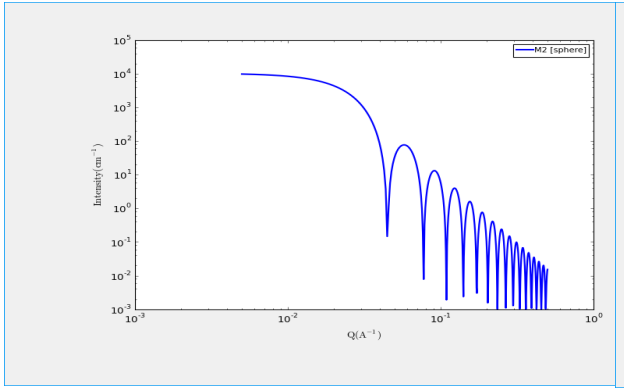
Cylinder Sphere?

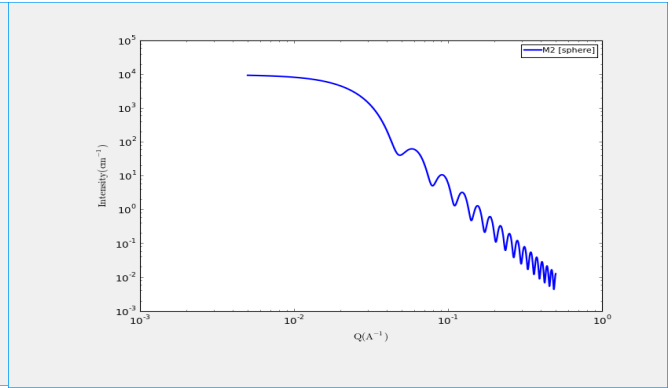
1, 10 or 100 Å?





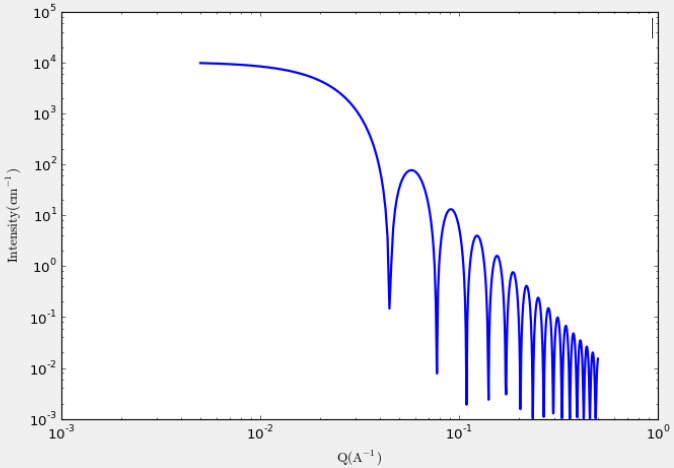


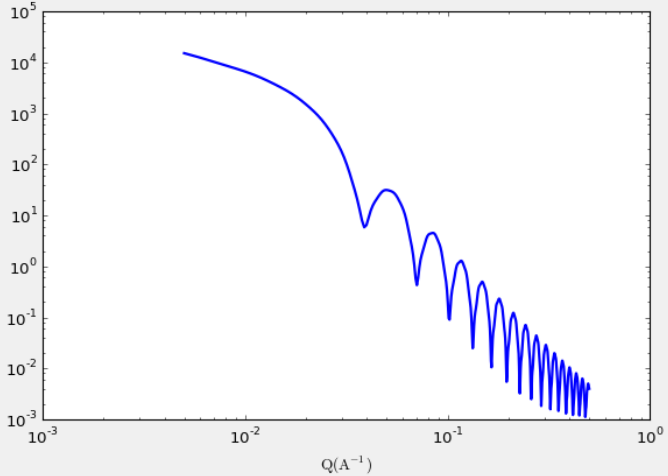




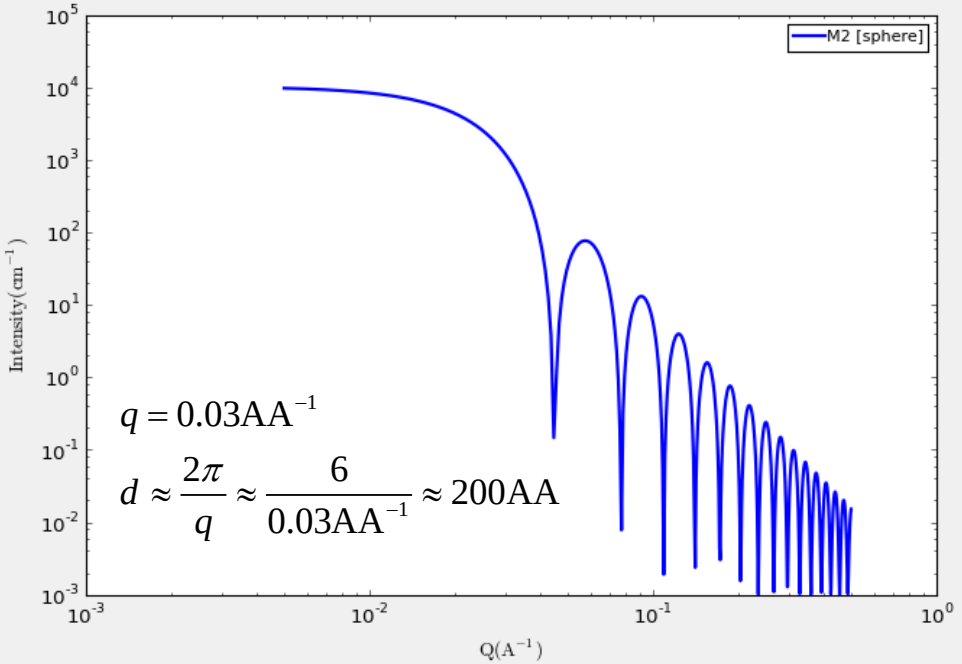
Most realistic?

Cylinder Sphere?



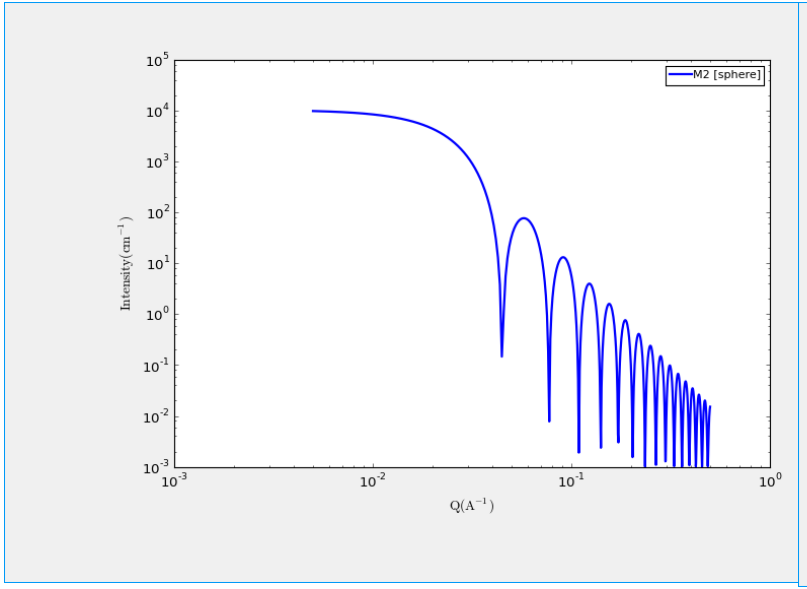


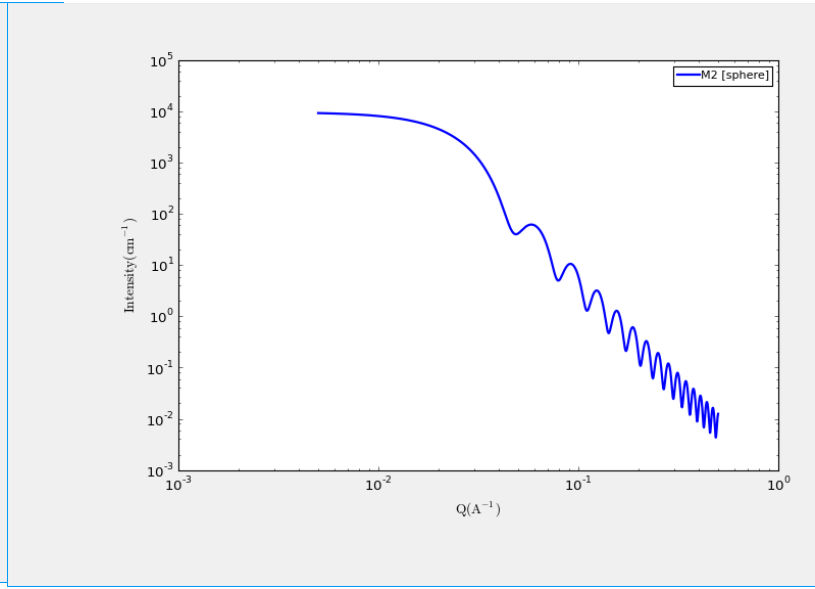
Radius? 1 Å, 10 Å or 100 Å



Most realistic outcome?

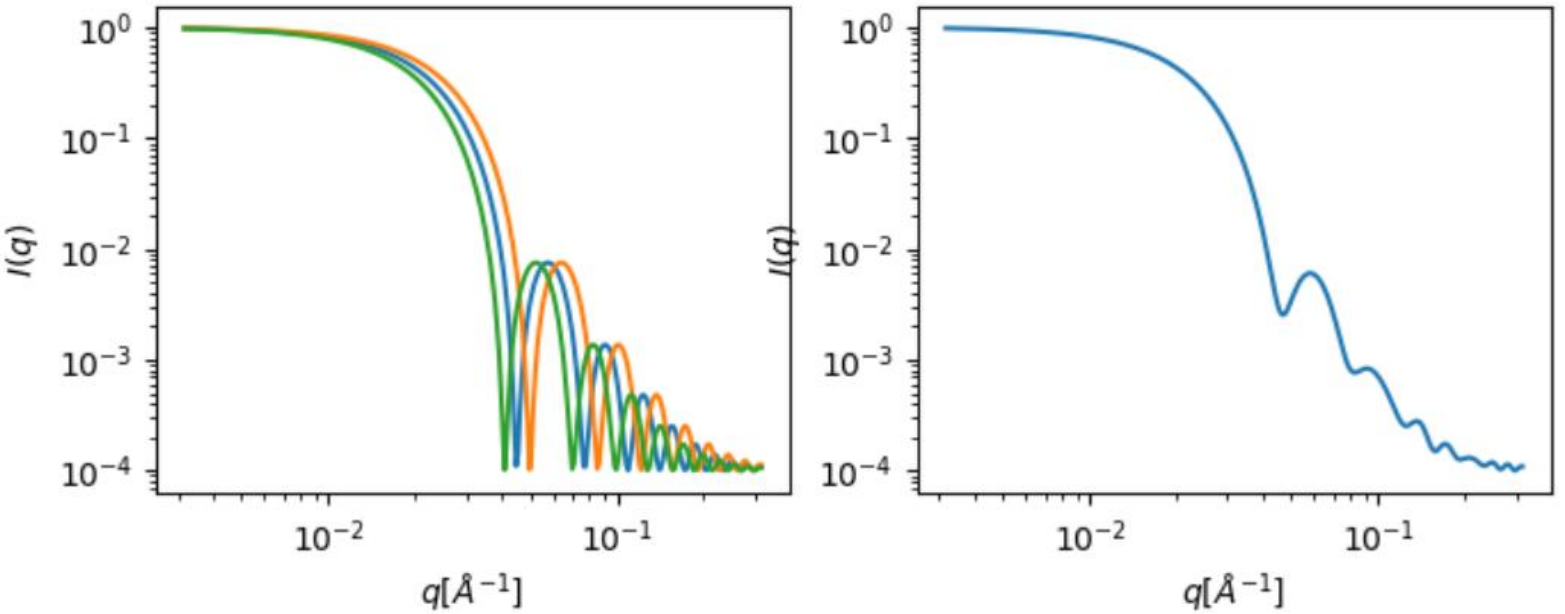
Resolution in SANS
or polydispersity in SAXS

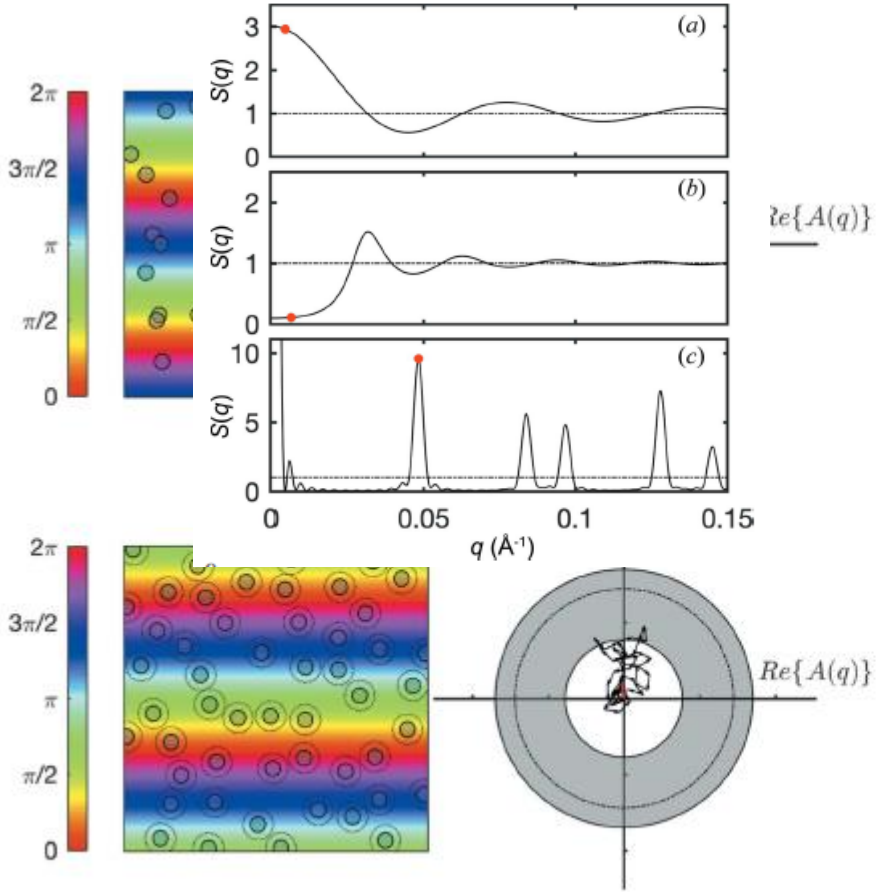




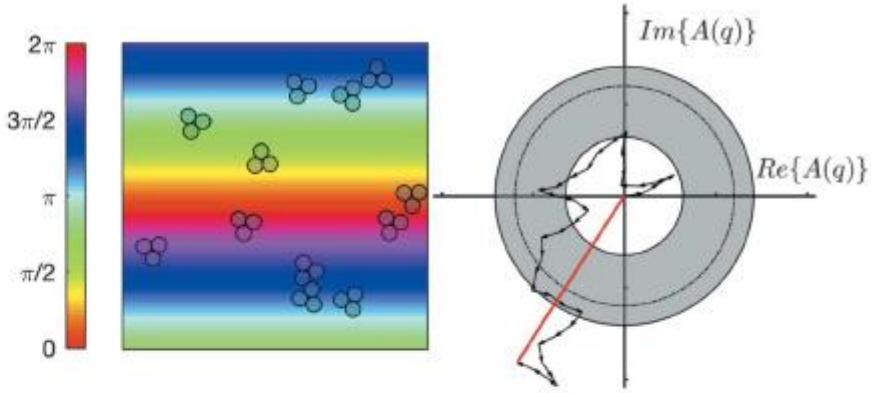
Polydispersity

$\Delta R/R=\pm 0.1$

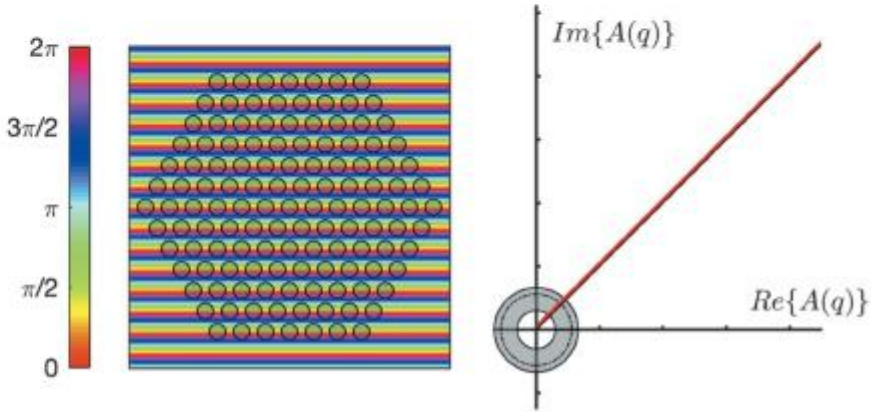



2π
3π/2
π
π/2
0
(a)
S(q)
(b)
(c)
0
0.05
0.1
0.15
q (Å⁻¹)
Re{A(q)}

(c)


2π
3π/2
π
π/2
0
Im{A(q)}
Re{A(q)}

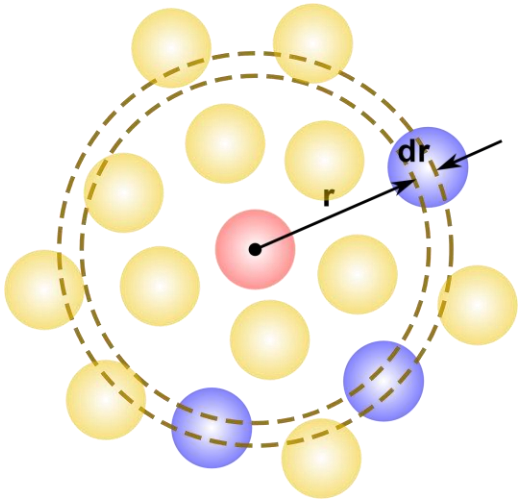
(b)

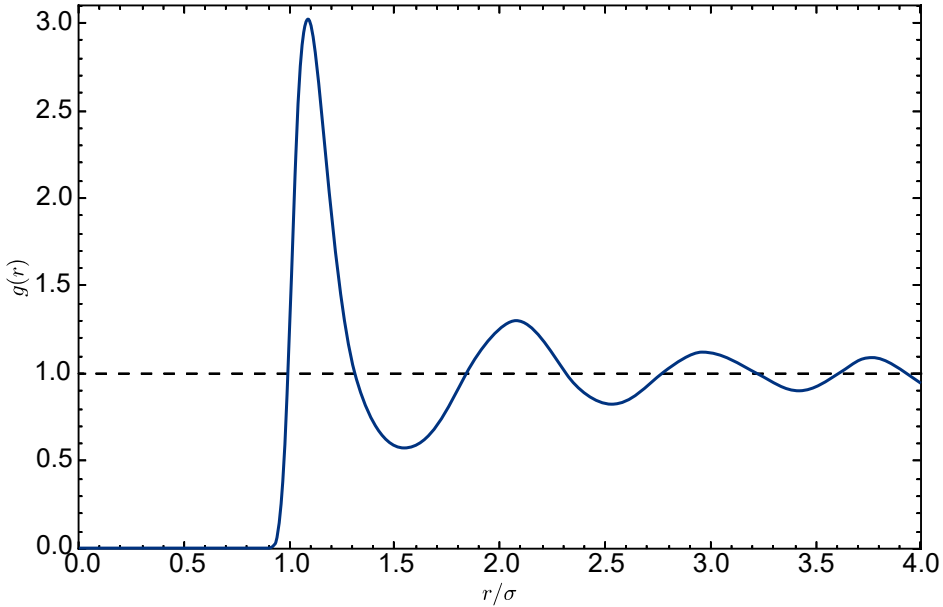

2π
3π/2
π
π/2
0
Im{A(q)}
Re{A(q)}

(d)

Figure 8

Radial distribution function $g(r)$





Average density at distance r from other particle $\rho g(r)$

By The original uploader was Wiki47222 at Wikimedia Commons.

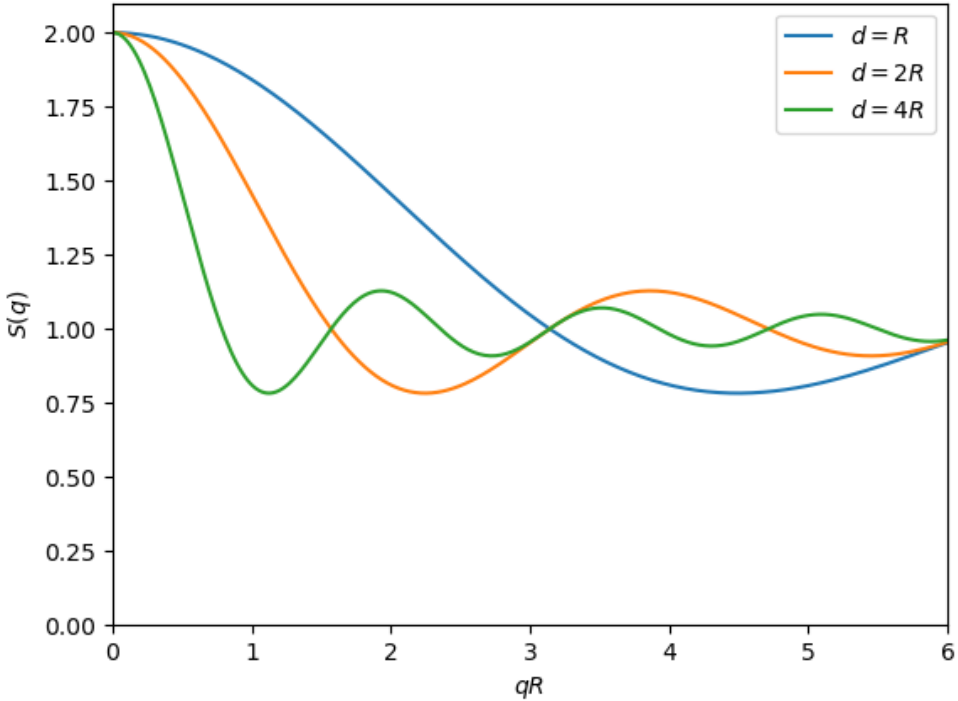
Structure factor

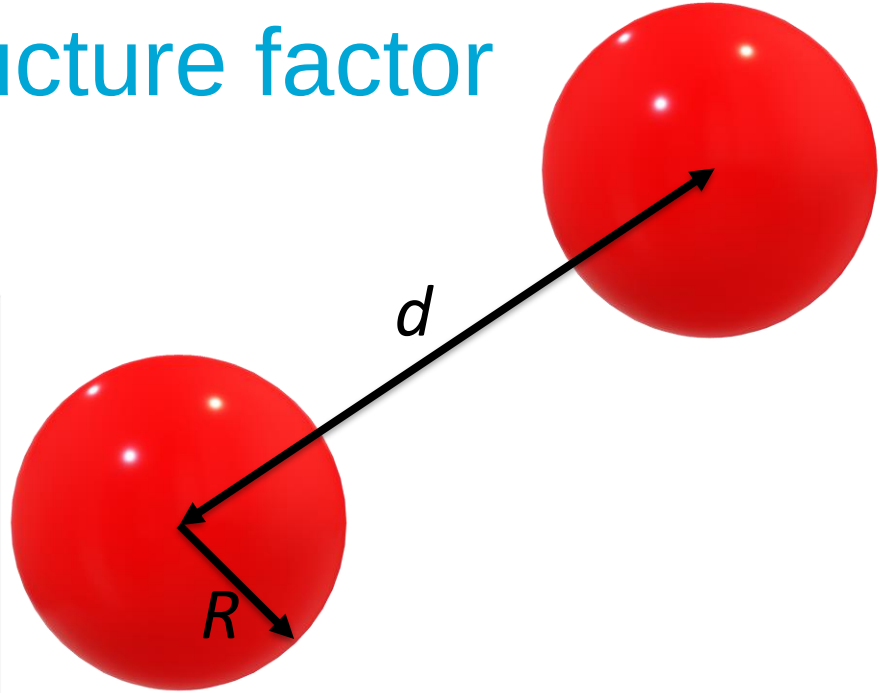
$$S(q) = \left|\sum_n \exp(i\mathbf{q}\cdot\mathbf{r_n})\right|^2$$

Discuss with your neighbour *S*(*q*) dilute case

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

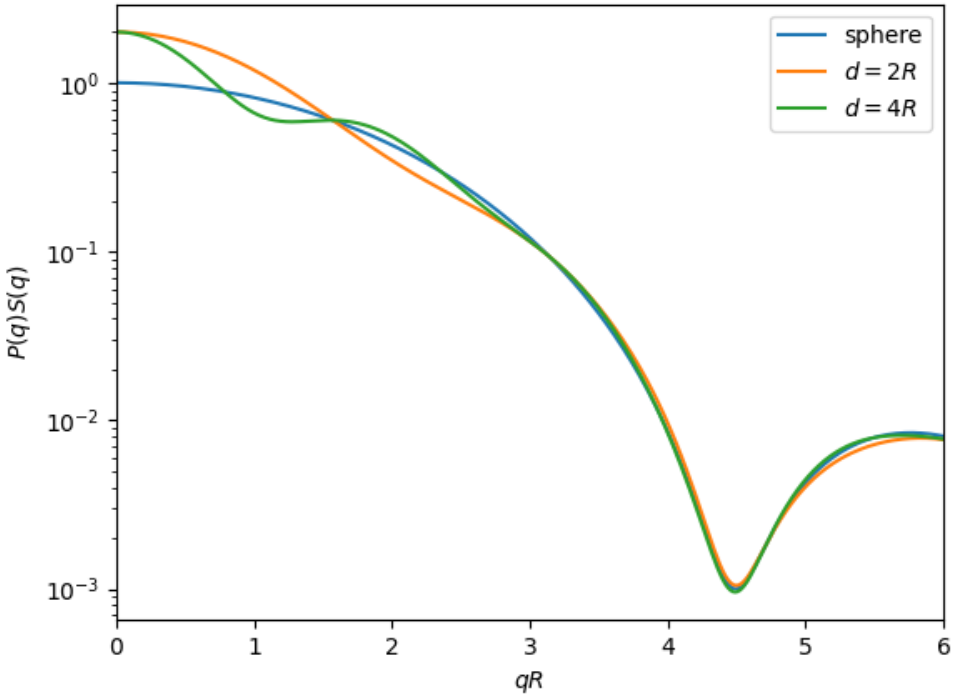
Dumbbell structure factor

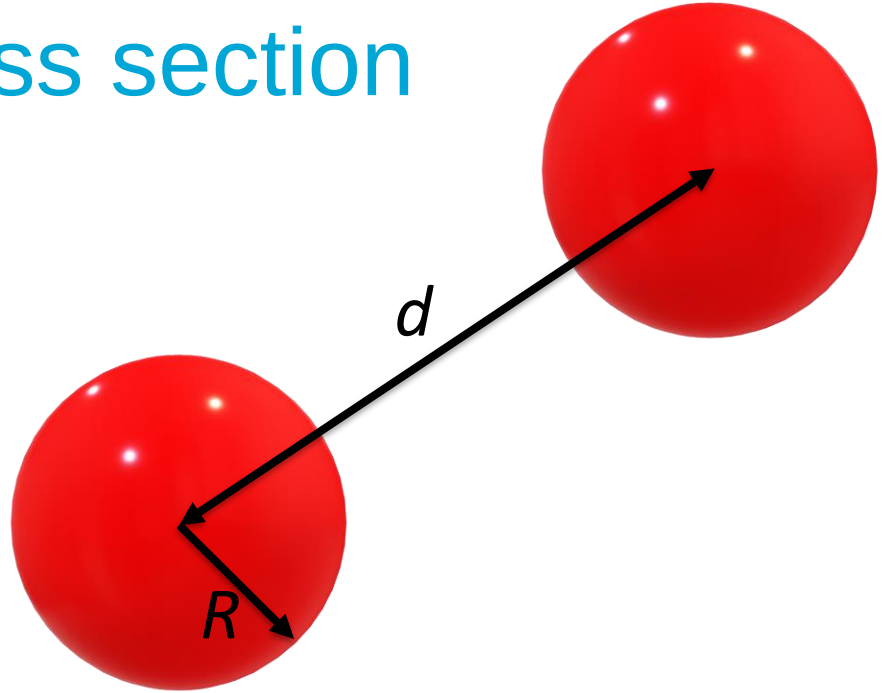




Exercise class

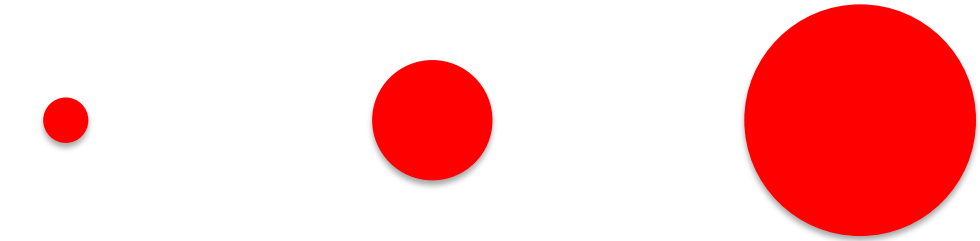
Dumbbell cross section





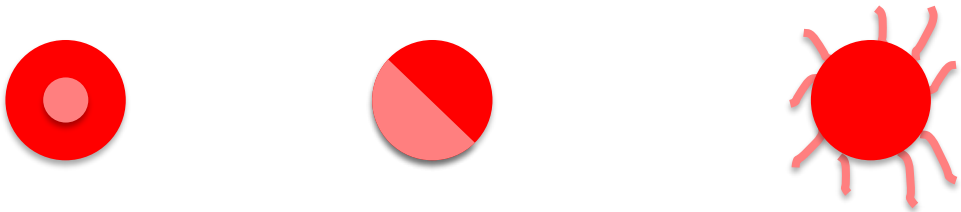
Exercise class

Characterisation particles
Form factor $P(q)$



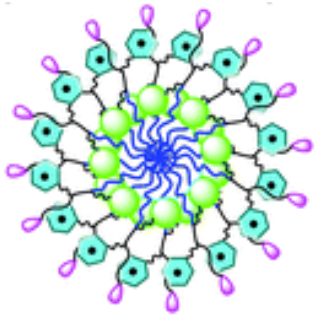
Size

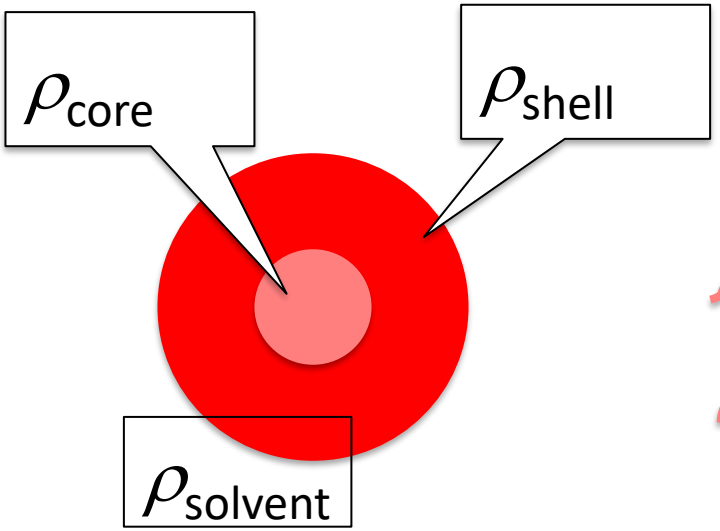
Shape

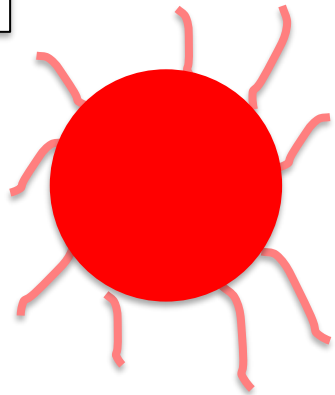


Structure

More than 2 densities







$$\frac{d\sigma}{d\Omega}(q) = cV^2(\Delta\rho)^2 P(q) S(q)$$

Contrast variation tunes visibility

Morna Fisken, Britlab
https://youtu.be/OZxtwIc3ieM

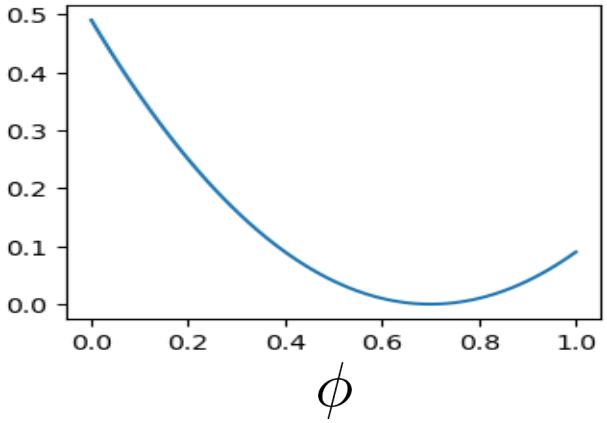
Why contrast variation solvent?

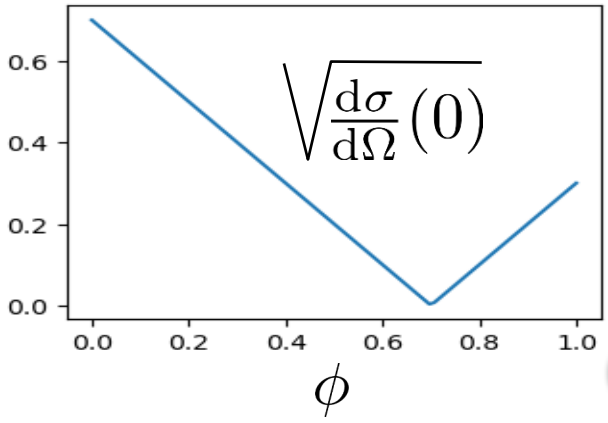
1. Increase signal
2. Decrease signal
3. Reduce background
4. Determine scattering length density
5. Light up different features

Contrast variation 1 density

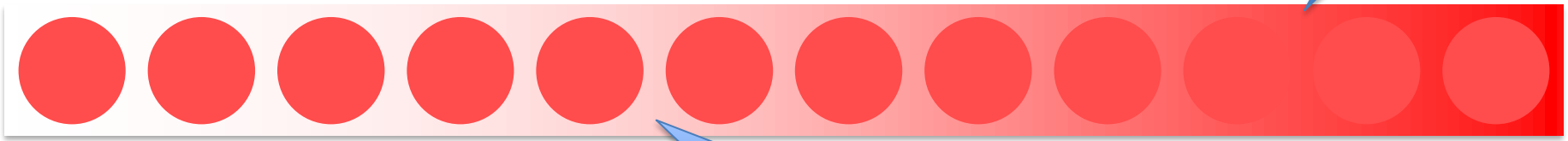
ρ_{H2O} = -0.56x10^{10} cm^{-2} ρ_{D2O} = 6.34x10^{10} cm^{-2}

$\frac{d\sigma}{d\Omega}(0)$



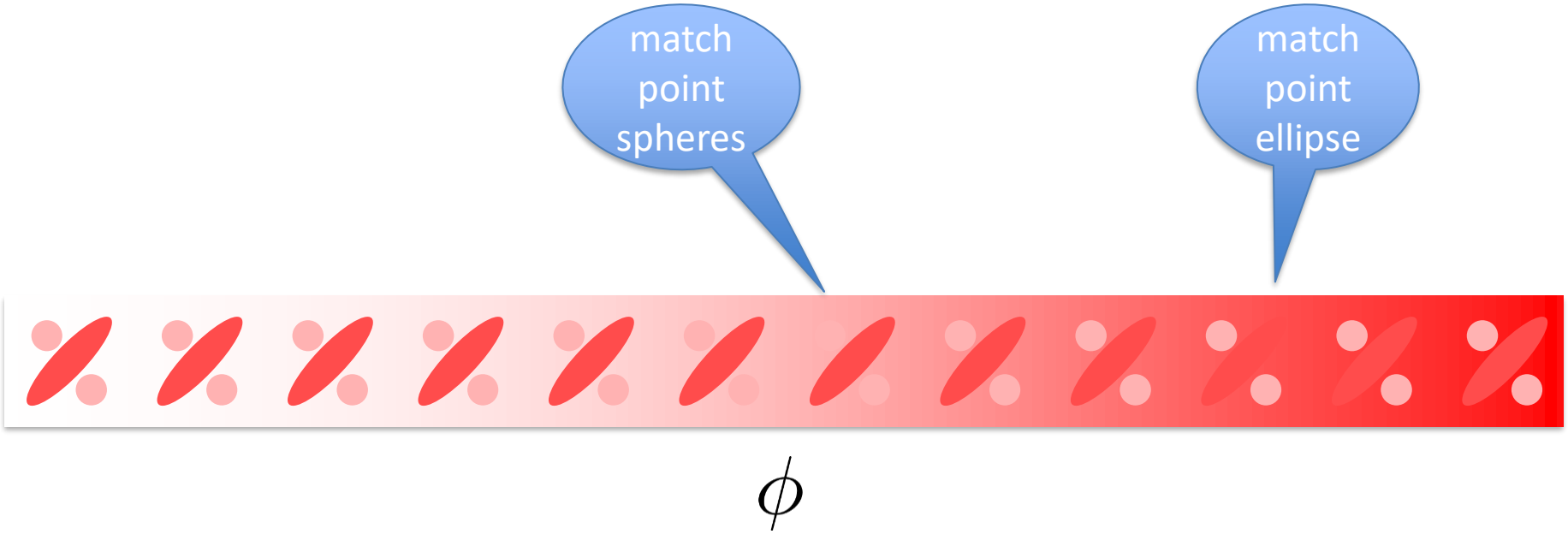


match point

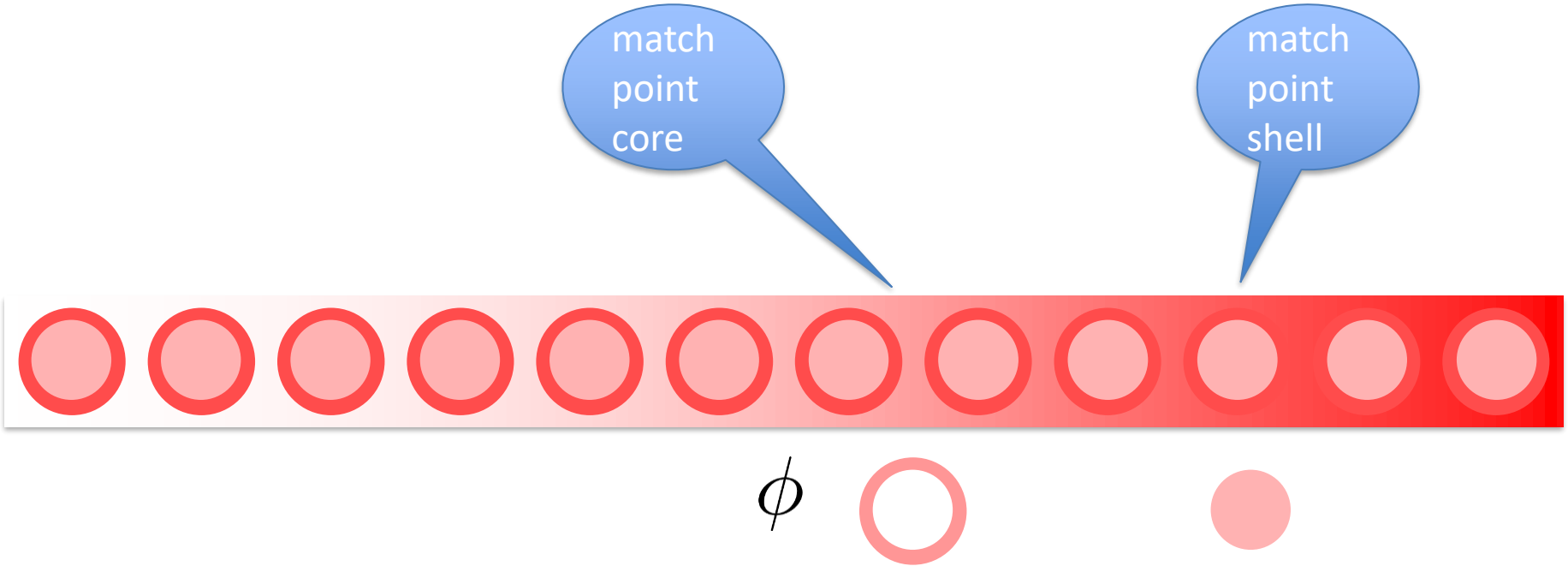


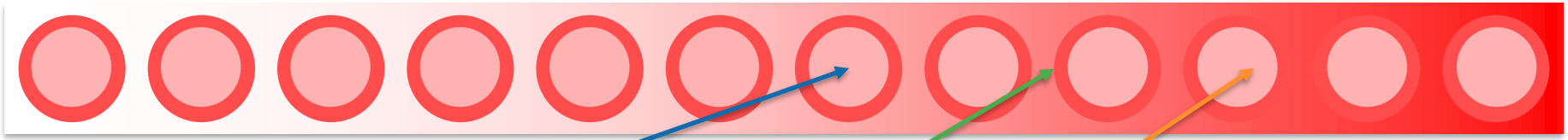
solvent

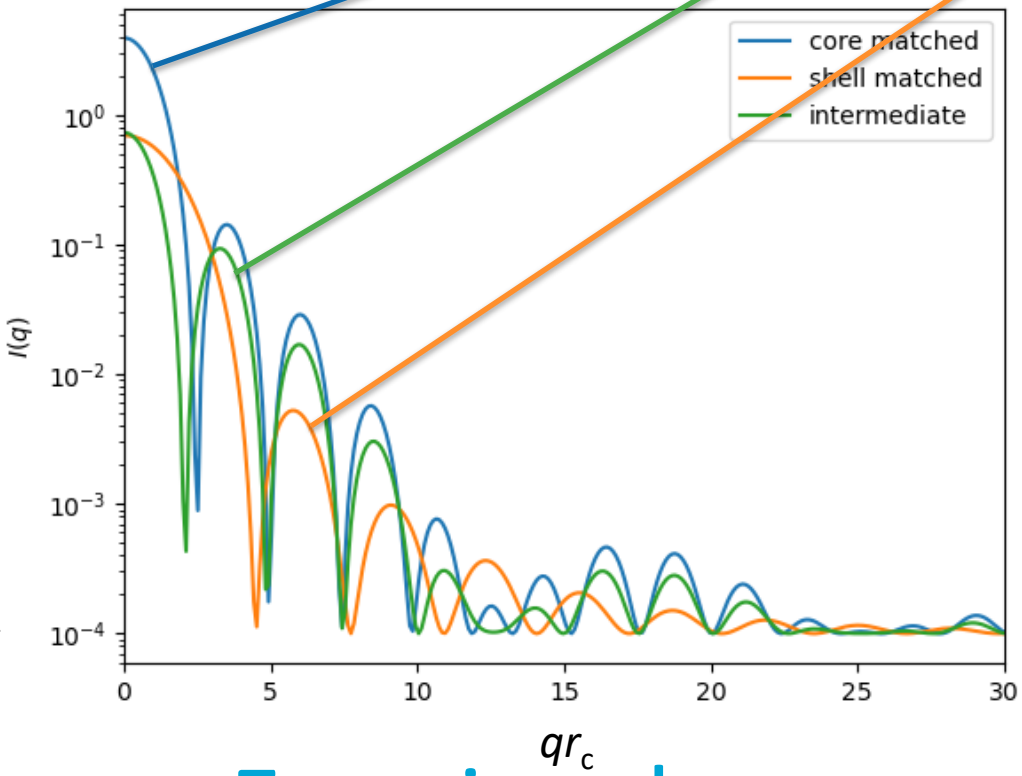
Contrast variation 2 component



Contrast variation core shell







$R_s = 1.5\ R_c$

$\rho_c = 2\text{x}10^{10}\ \text{cm}^{-2}$

$\rho_s = 4.5\text{x}10^{10}\ \text{cm}^{-2}$

$\rho_{int} = 3.0\text{x}10^{10}\ \text{cm}^{-2}$

Exercise class

Diffraction from non-crystalline materials 1

- Non-crystalline materials?
- Small-angle approximation
- Phase map
- Single particle scattering, form factor
- Concentrated scattering, structure factor

Diffraction from non-crystalline materials 2

- Structure factor again
- Intensity
- Contrast variation