Introduction to Small Angle Neutron Scattering II

Form, structure factors and polydispersity

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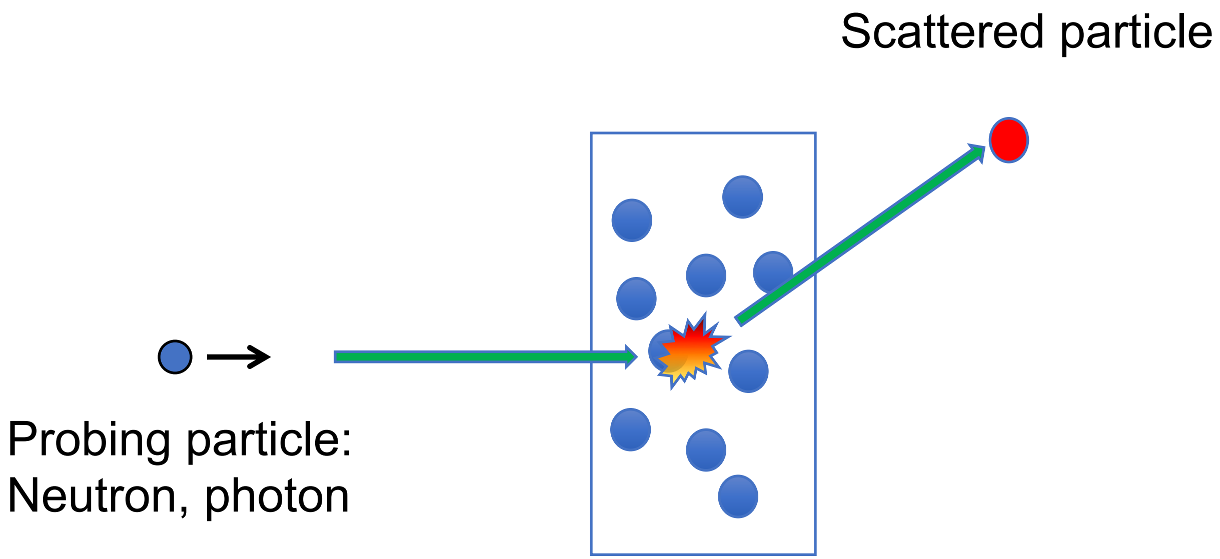
Goals

- Develop practical rather than theoretical understanding of subject
- Active participation is appreciated!
- Feel free to stop me at any time

Basic concepts of SANS

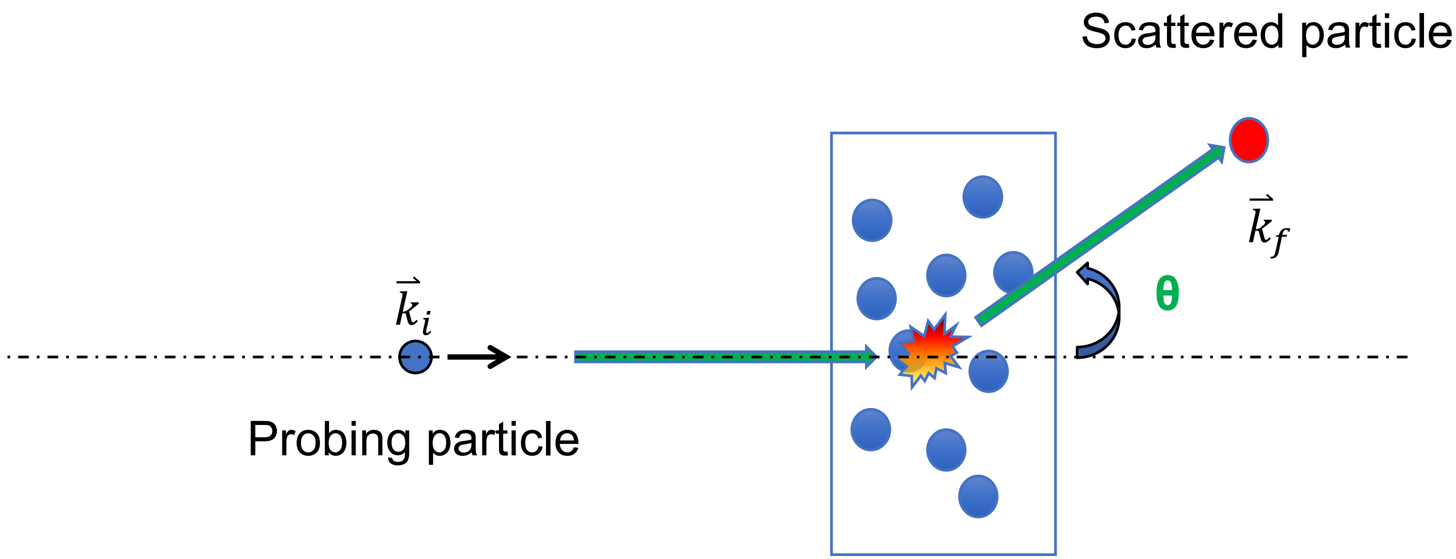
A typical scattering experiment setup

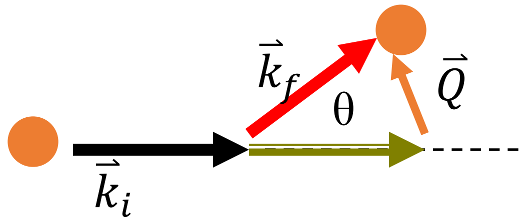


Adapted from Yun Liu

Basic concepts of SANS

A typical scattering experiment setup





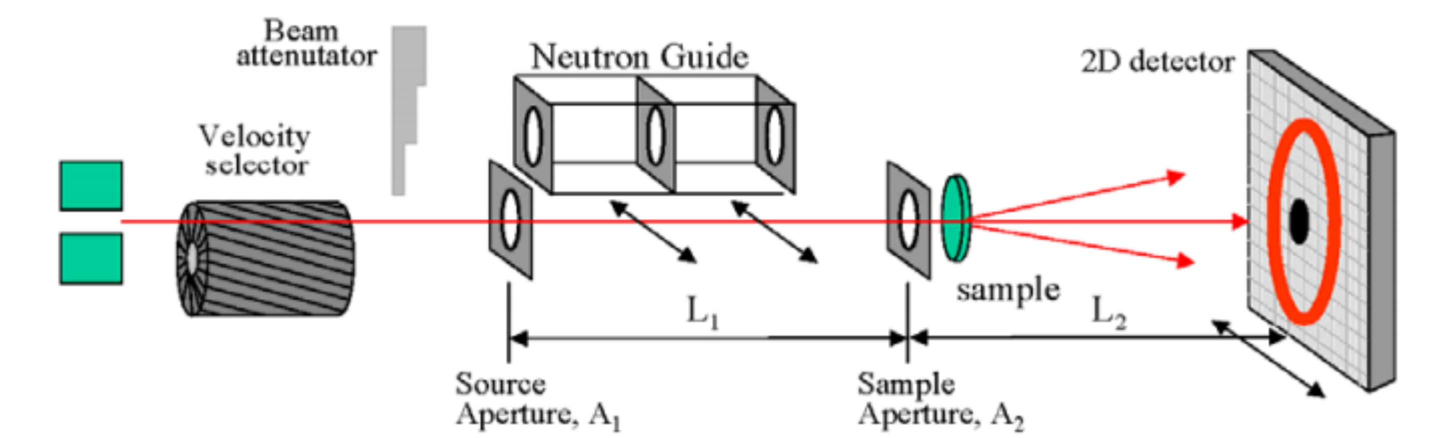
SANS measures the **scattering intensity function**, $\boldsymbol{I(\vec{Q})}$

When $k_i = k_f = k$,

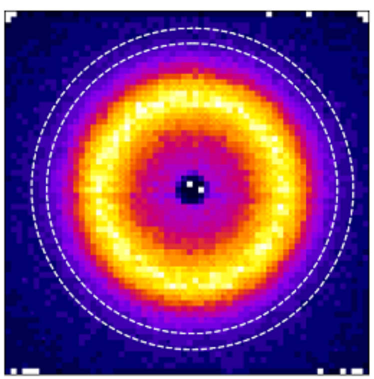
$Q = 2ksin\left(\frac{\theta}{2}\right) = \frac{4\pi}{\lambda}sin\left(\frac{\theta}{2}\right)$.

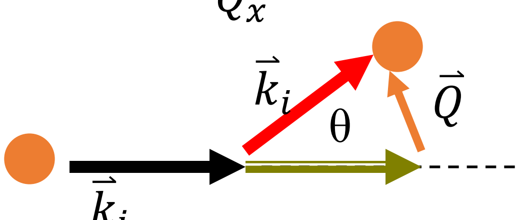
Adapted from Yun Liu

Basic concepts of SANS

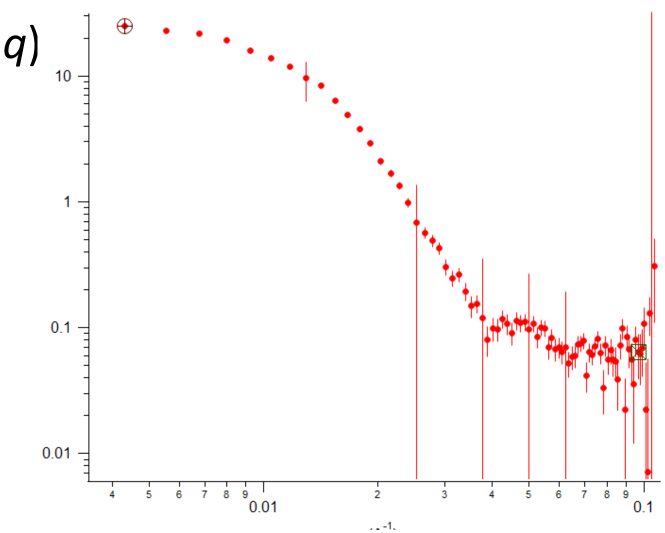


2D pattern $I(\vec{Q}) = I(Q_x, Q_y, Q_z \approx 0)$





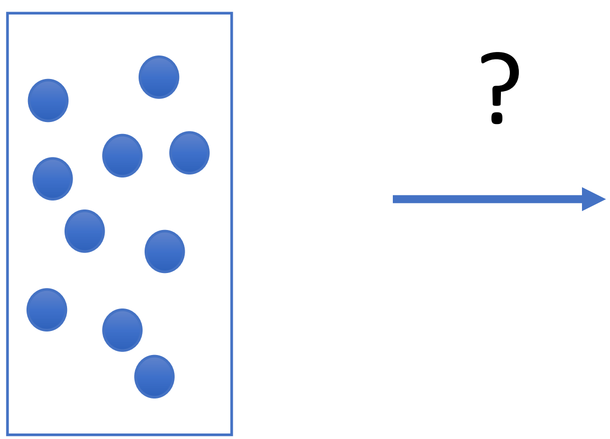
1D data: $I(Q)$

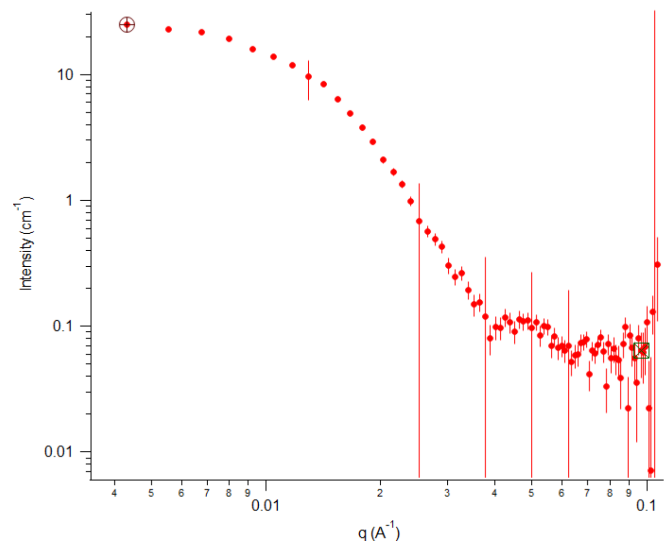


Adapted from Yun Liu

Question 1

What components should be included in the model to explain SANS data?





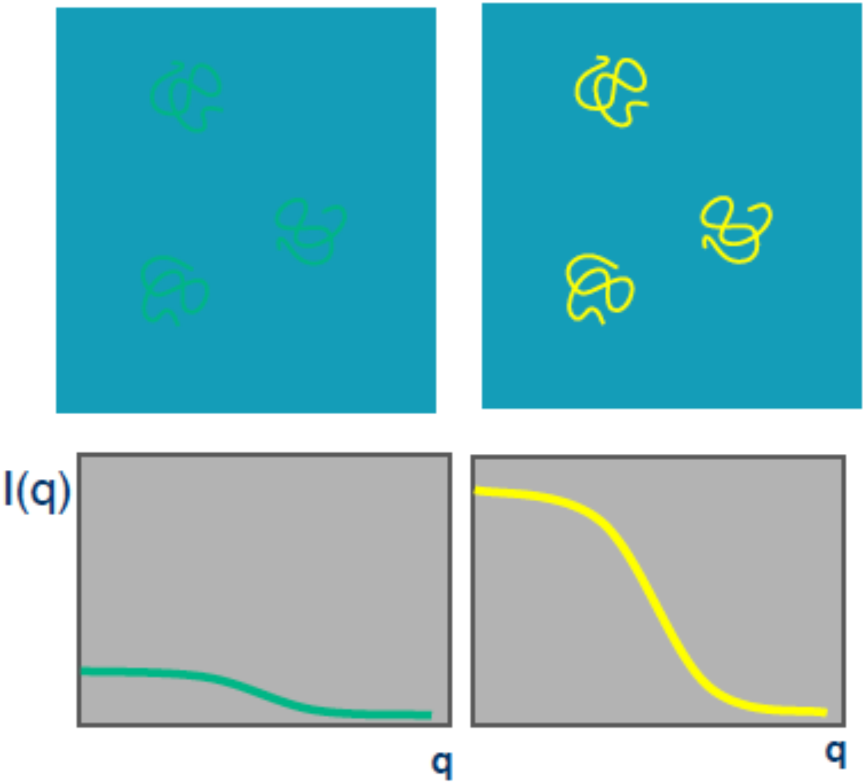
Scattering intensity

$$I(\mathrm{q}) = (\Delta\rho)^2\, nM^2\, P(\mathrm{q})\, S(\mathrm{q})$$

Intensity = Pre-factor * Form Factor * Structure Factor

Pre factor

$$I(q) = (\Delta\rho)^2\, nM^2\, P(q)\, S(q)$$

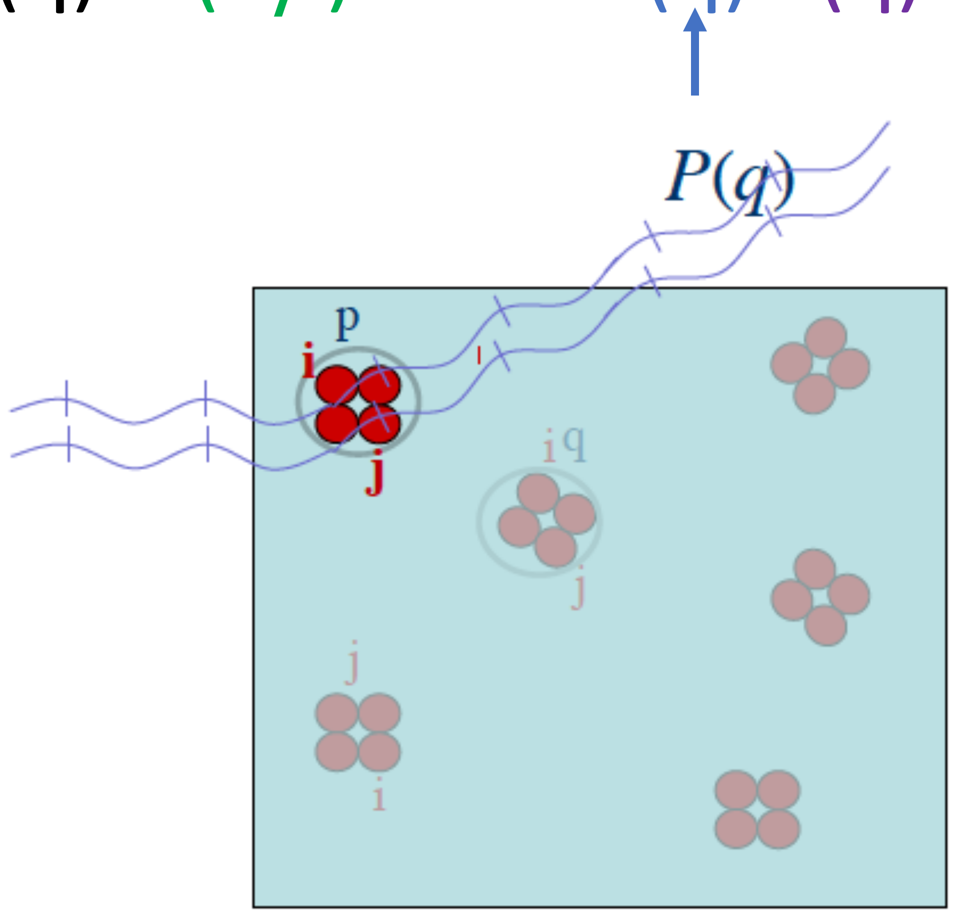


Pre-Factor given by
- Contrast Factor
- Number of Particles
- Mass of Particles

Adapted from Kell Mortensen, e-neutrons.org

Intra and inter particle interactions

$$I(q) = (\Delta\rho)^2 \, nM^2 \, P(q) \, S(q)$$

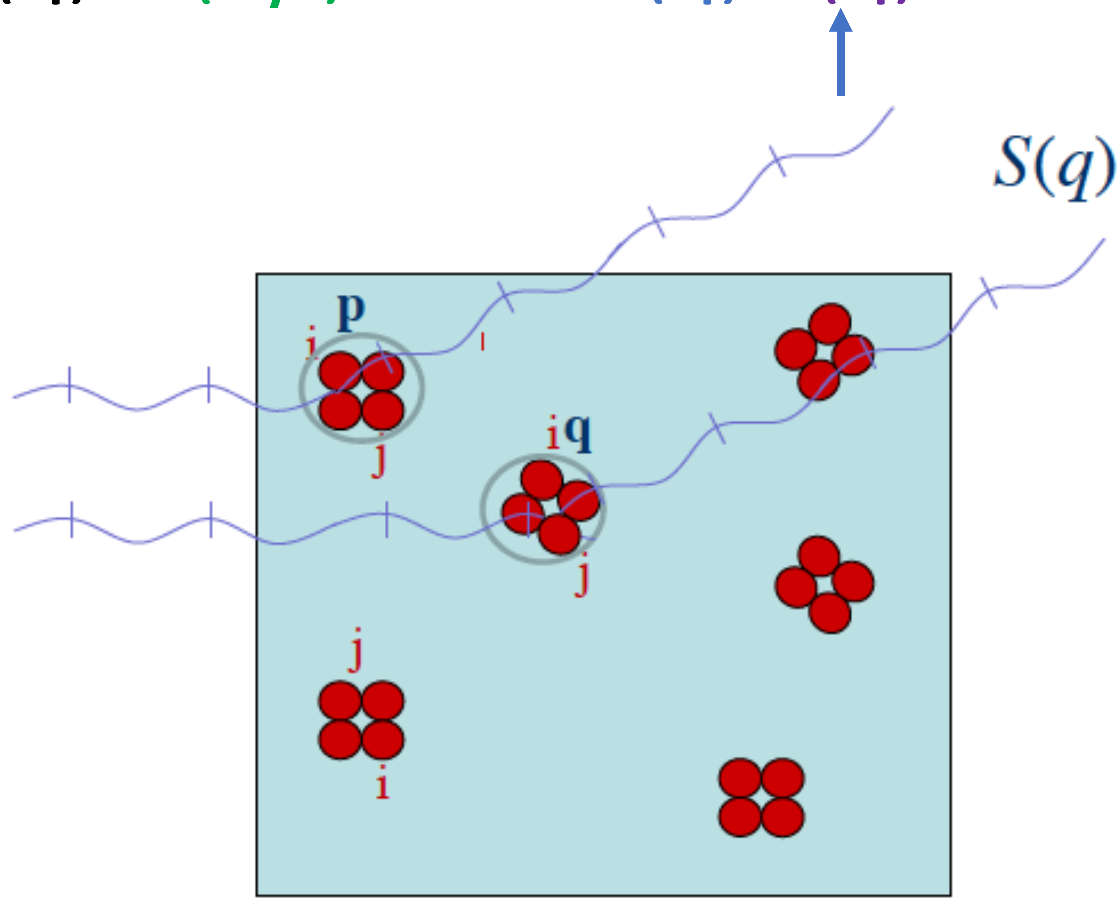


Form factor P(q) represents the interference of neutrons scattered from different parts of the same object

Adapted from Kell Mortensen, e-neutrons.org

Intra and inter particle interactions

$$I(q) = (\Delta\rho)^2\, nM^2\, P(q)\, S(q)$$



Structure factor S(q) represents interference between different objects.

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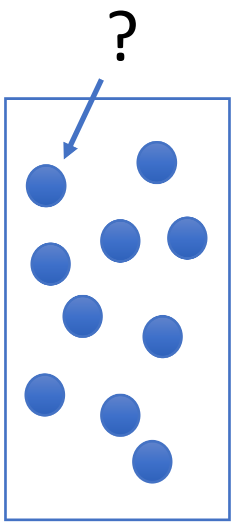
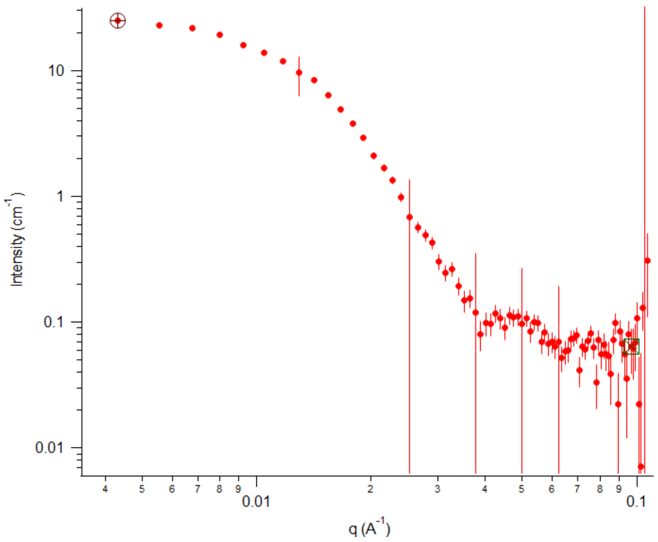
Adapted from Kell Mortensen, e-neutrons.org

Question 2

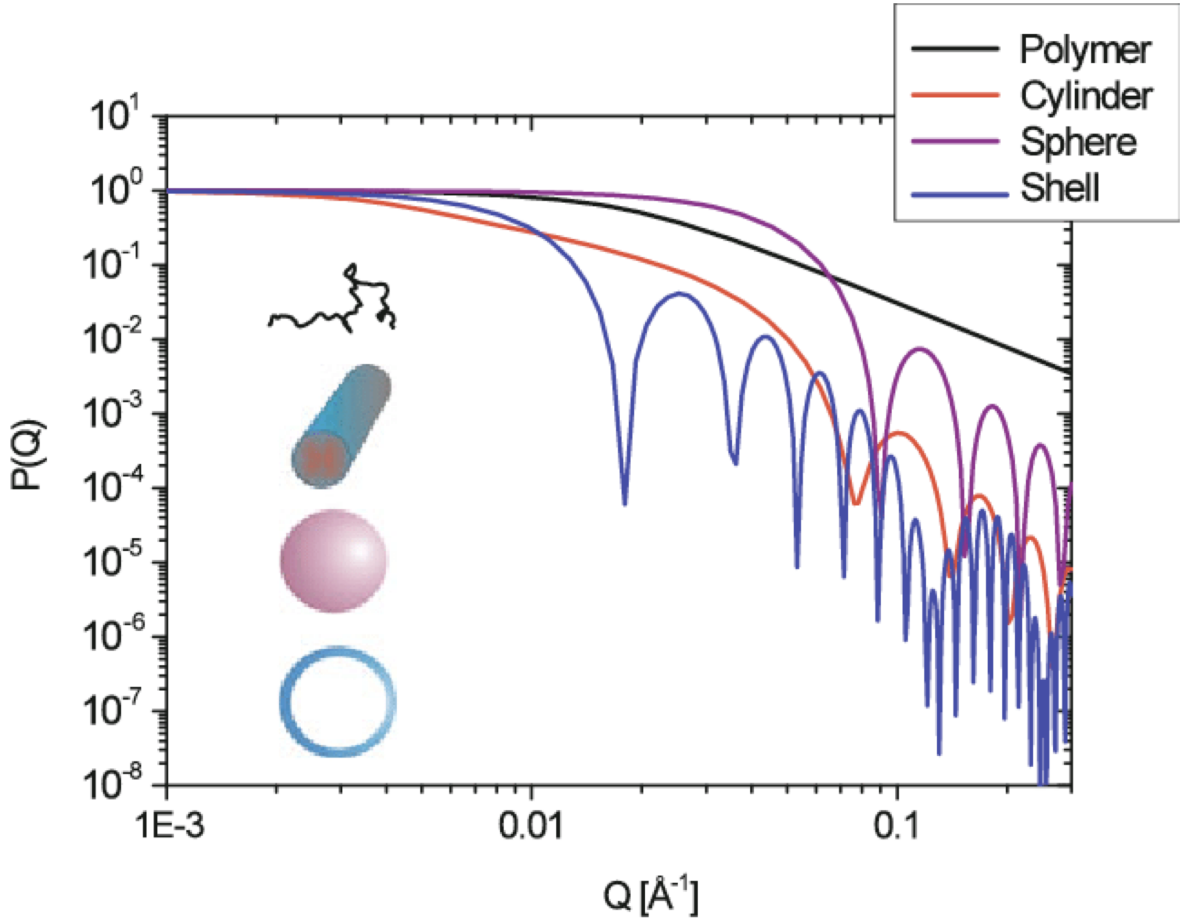
How to define form factor?



Pre, **Form** and Structure Factors

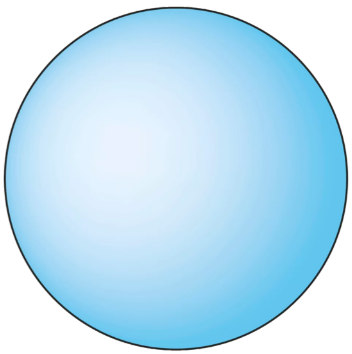


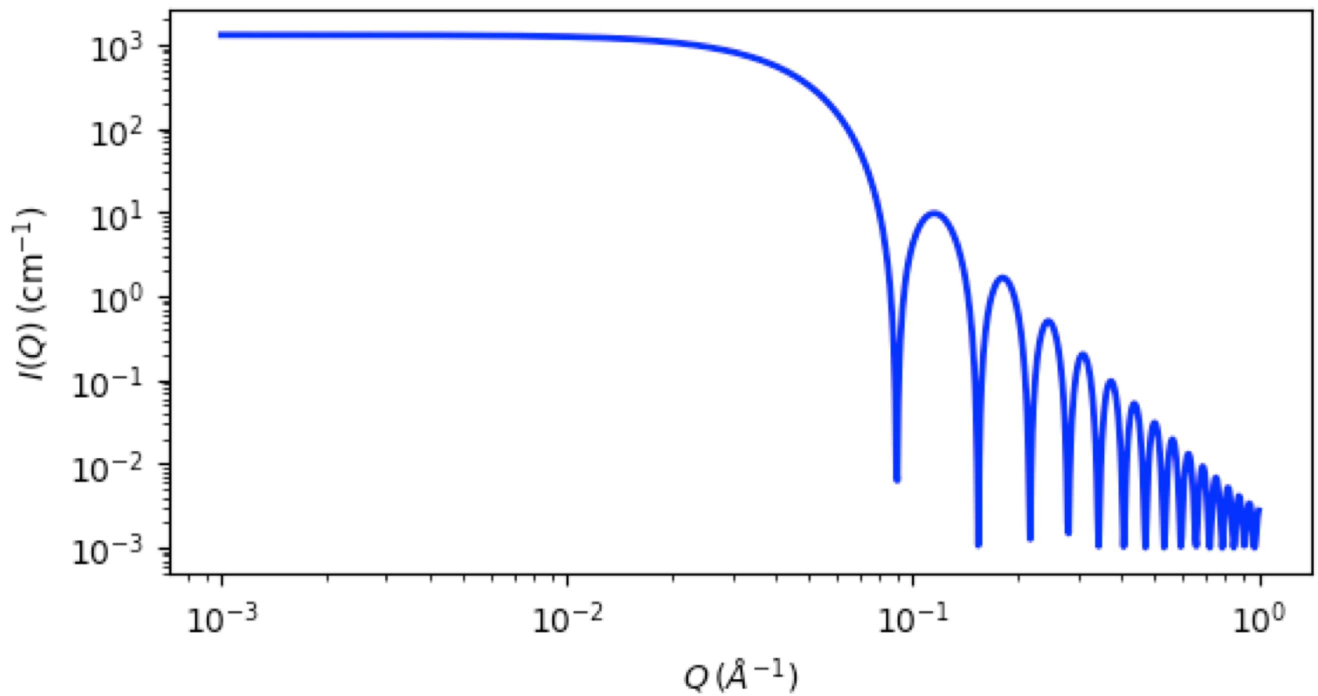
Form factors determined for different shapes



Credit: Reidar Lund (DOI:10.1007/12_2012_204)

Form factor of sphere





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

Adapted from Kell Mortensen, e-neutrons.org

Form factor of sphere - derivation

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

Use, that the scattering amplitude from a homogeneous volume V can be written

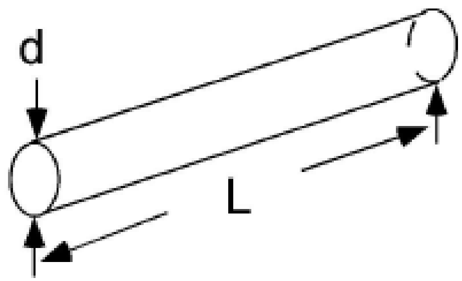
$$A(\mathbf{q}) = \frac{1}{V}\int_{sphere} \rho(\mathbf{r}) \exp[-i\mathbf{q}\cdot\mathbf{r}] d\mathbf{r}$$

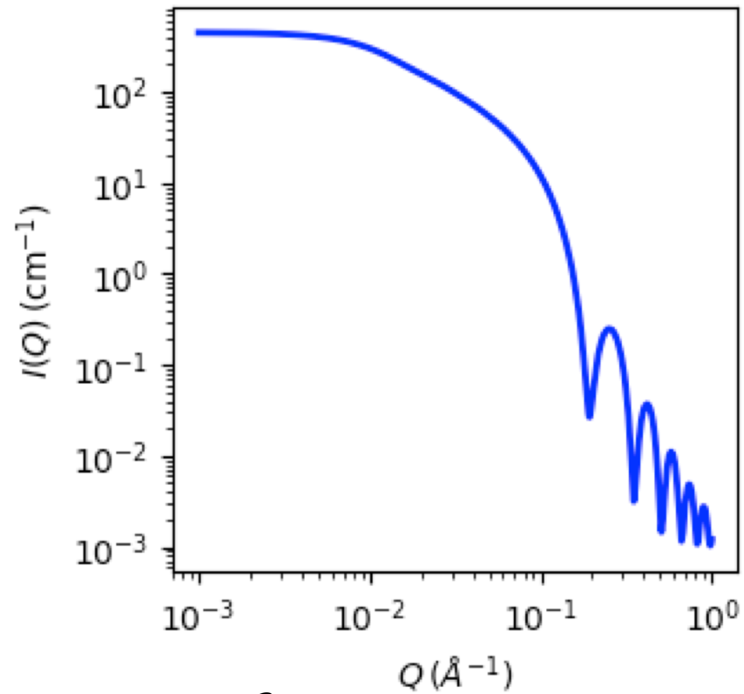
to calculate the form factor P(q)
of a homogeneous sphere of radius R.

You may need the integral formula

$$\int x \sin x \, dx = \sin x - x\cos x$$

Form factor for cylinder



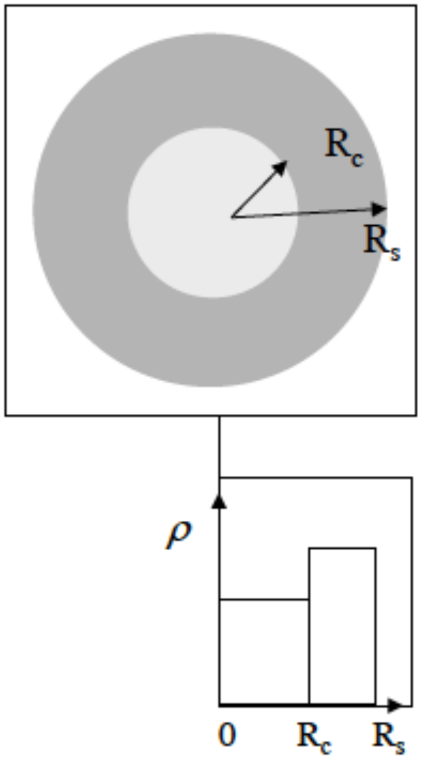


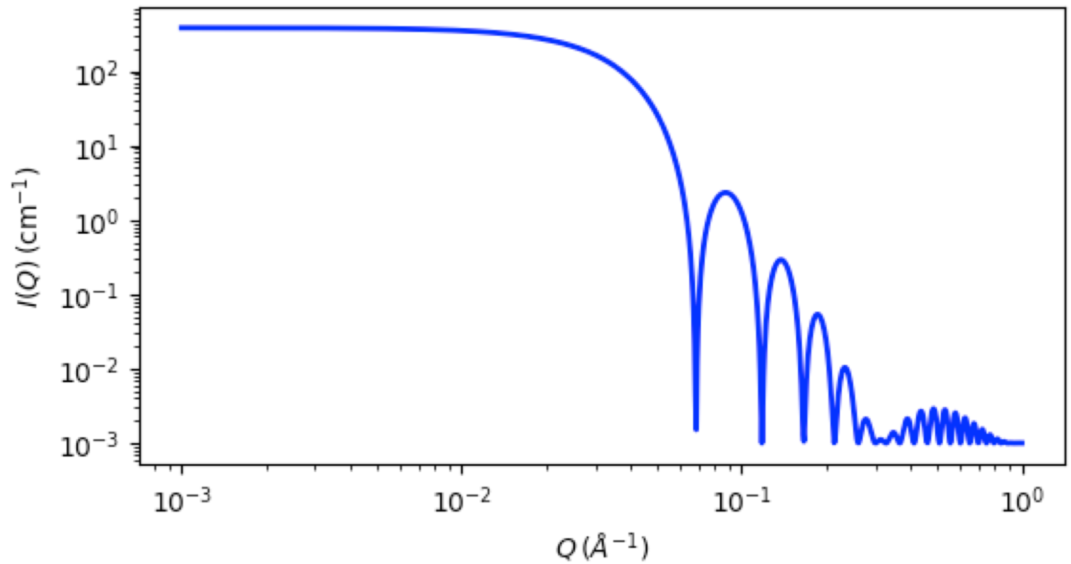
$$\mathrm{P}(Q) = \frac{1}{2}\int_0^{\pi} \frac{\sin^2\left(Q\,\frac{L}{2}\cos\alpha\right)}{\left(Q\,\frac{L}{2}\cos\alpha\right)^2} \frac{\left[2J_1\left(Q\sin\alpha\,\frac{d}{2}\right)\right]^2}{\left(Q\,\frac{d}{2}\sin\alpha\right)^2} \sin\alpha\, d\alpha$$

where J_1 is the first order Bessel function and α is defined as the angle between the cylinder axis and the scattering vector q.

Adapted from Andrew Jacskon

Core-shell particle

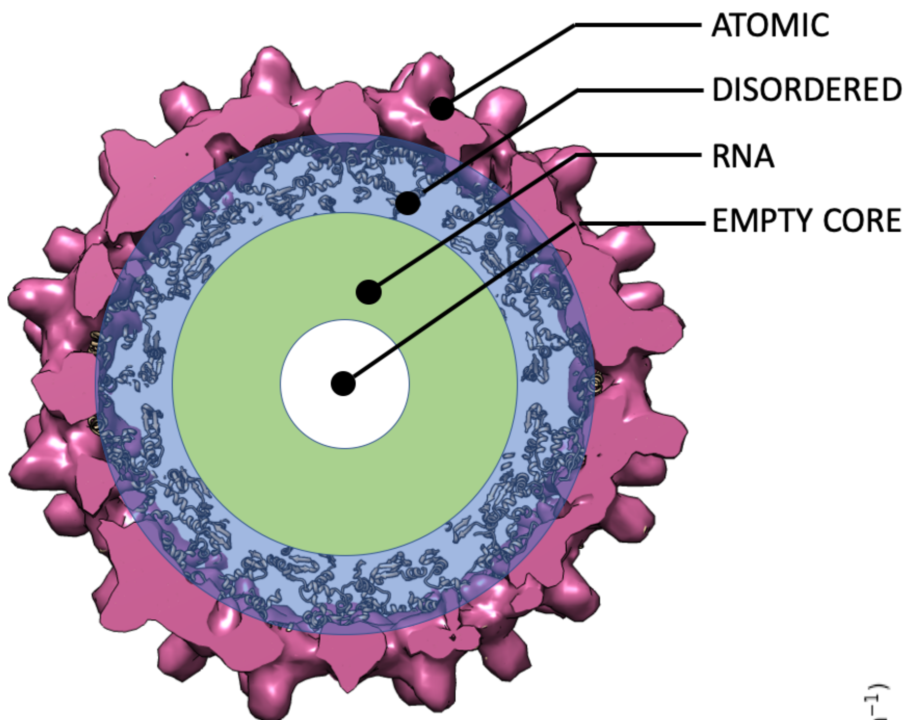


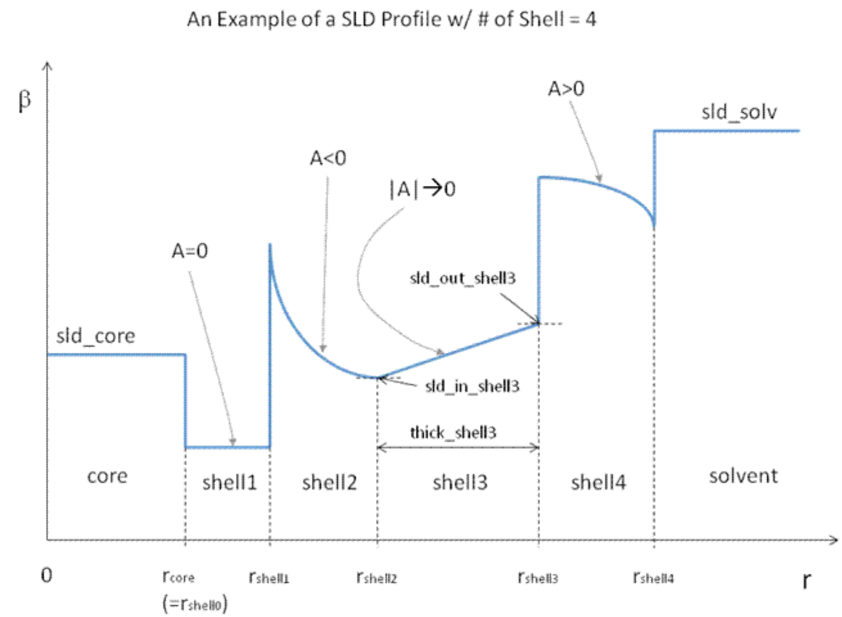


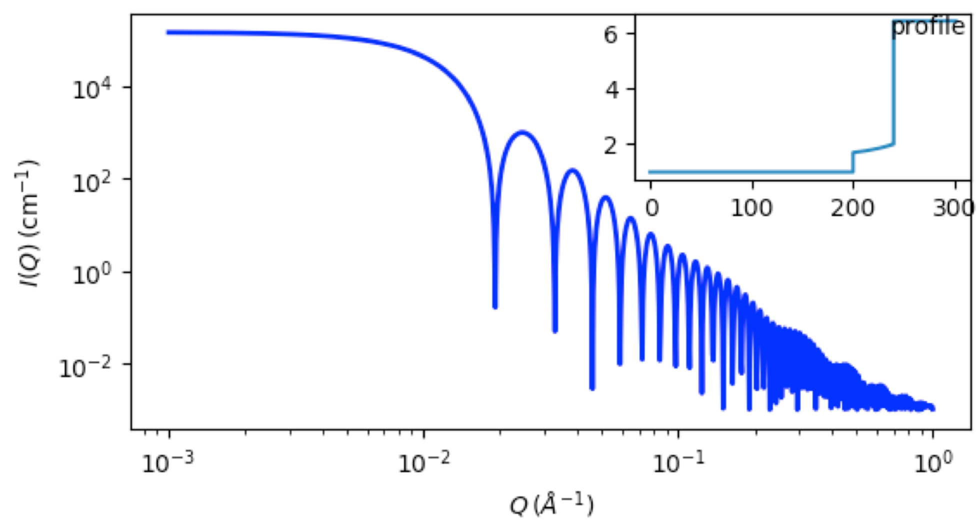
$$F(q) = \frac{3}{V_s}\left[V_c(\rho_c - \rho_s)\frac{\sin(qr_c) - qr_c\cos(qr_c)}{(qr_c)^3} + V_s(\rho_s - \rho_{\text{solv}})\frac{\sin(qr_s) - qr_s\cos(qr_s)}{(qr_s)^3}\right]$$

Adapted from Kell Mortensen, e-neutrons.org

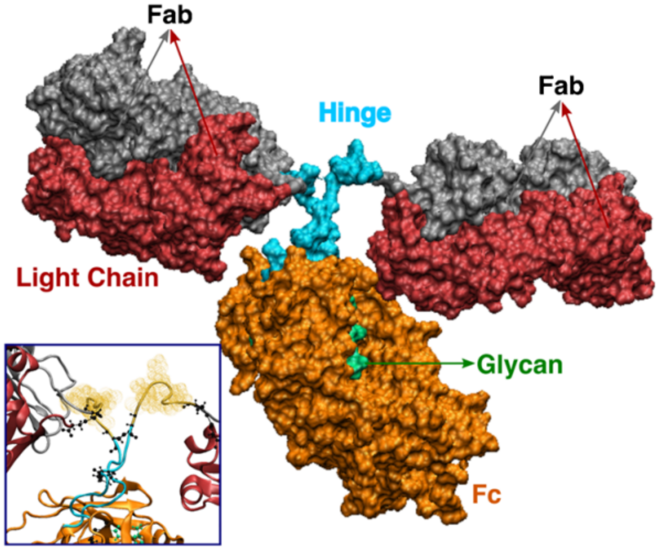
Onion model can be used to model virus capsids



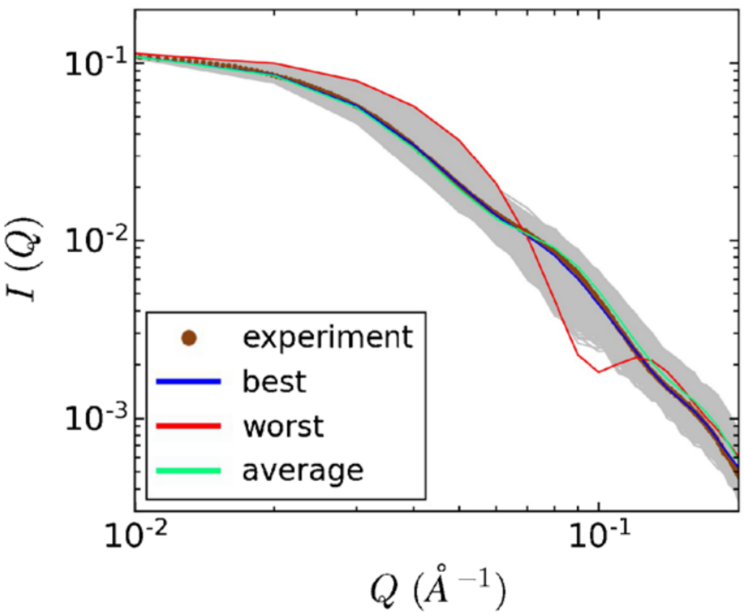




Proteins with the PDB structures



Monoclonal antibody protein



$$I(Q) = n \sum_i \sum_j b_i b_j \frac{sin(Q|\vec{r}_i - \vec{r}_j|)}{Q|\vec{r}_i - \vec{r}_j|}$$

b_i, b_j – atomic form factors

Maria Monica Castellanos et al. Analytical and Bioanalytical Chemistry (2018) 410:2141–2159

Form and Structure Factors

Lots of form and structure factors have
already been calculated ....

ELSEVIER

Advances in Colloid and Interface Science
70 (1997) 171–210

ADVANCES IN
COLLOID AND
INTERFACE
SCIENCE

Analysis of small-angle scattering data from colloids and polymer solutions: modeling and least-squares fitting[1]

Jan Skov Pedersen

Department of Solid State Physics, Risø National Laboratory, DK-4000 Roskilde, Denmark

Abstract

Analysis and modeling of small-angle scattering data from systems consisting of colloidal particles or polymers in solution are discussed. The analysis requires application of least-squares methods, and the basic principles of linear and non-linear least-squares methods are summarized with emphasis on applications in the analysis of small-angle scattering data. These include indirect Fourier transformation, square-root

Adapted from Andrew Jacskon

Form and Structure Factors

Lots of form and structure factors have already been calculated ....

SasView : http://www.sasview.org
SASFit : https://www.psi.ch/sinq/sansii/sasfit
NIST Igor : http://ncnr.nist.gov/programs/sans/data/red_anal.html

... and coded into software.

Adapted from Andrew Jacskon

Monte Carlo simulations

When everything fails…

↓

Do Monte Carlo simulations!

Monte Carlo simulations:

Form factors of polymer systems

Adapted from Jan Skov Pedersen

Monte Carlo simulations

- + Ideal for random structures with many degrees of freedom
- + Any parameter or function can be sampled: P(q), S(q)
- – P(q)/S(q) is not on analytical form

<u>Simple approach – trial-and-error:</u>

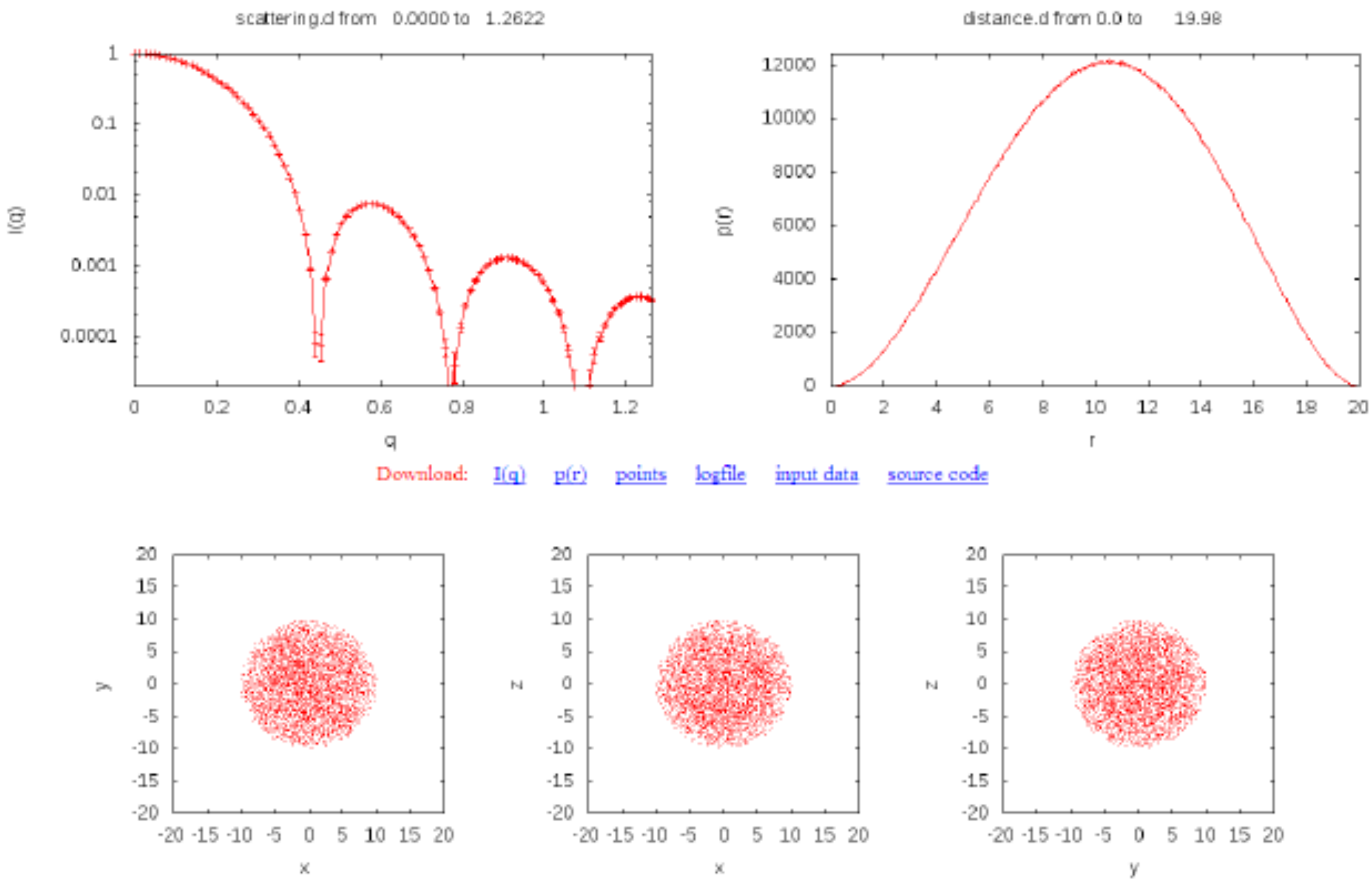
- Choose model and parameters*
- Generate random configurations – sample P(q)/S(q)
- Compare with experimental data

*) Simple enough to allow simulations – detailed enough to describe experimental data

Use efficient simulation algorithm

Adapted from Jan Skov Pedersen

Monte Carlo simulations



http://bayesapp.org/simtest/

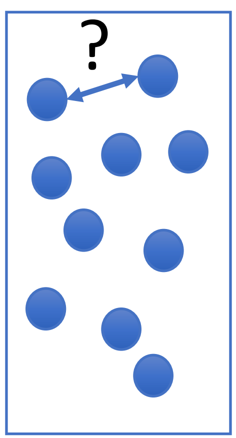
Scattering intensity

$$I(\mathrm{q}) = (\Delta\rho)^2\, nM^2\, P(\mathrm{q})\, S(\mathrm{q})$$

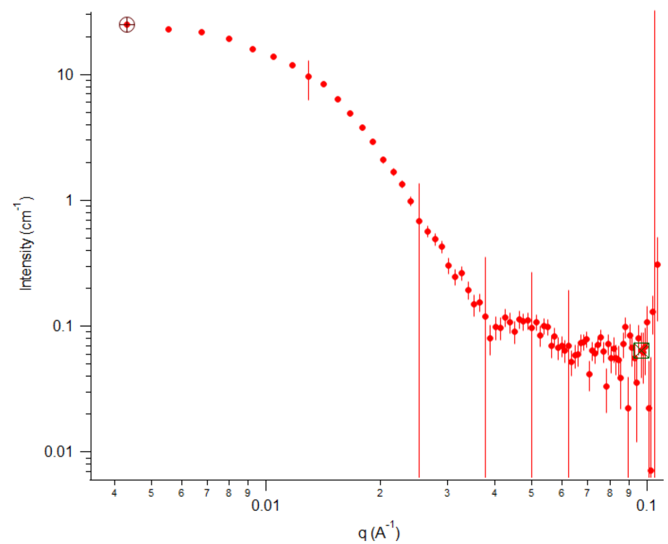
Intensity = Pre-factor * Form Factor * Structure Factor

Question 3

What should we considere when defining interparticle interactions?



Pre, Form and **Structure** Factors



Determination of Structure Factor

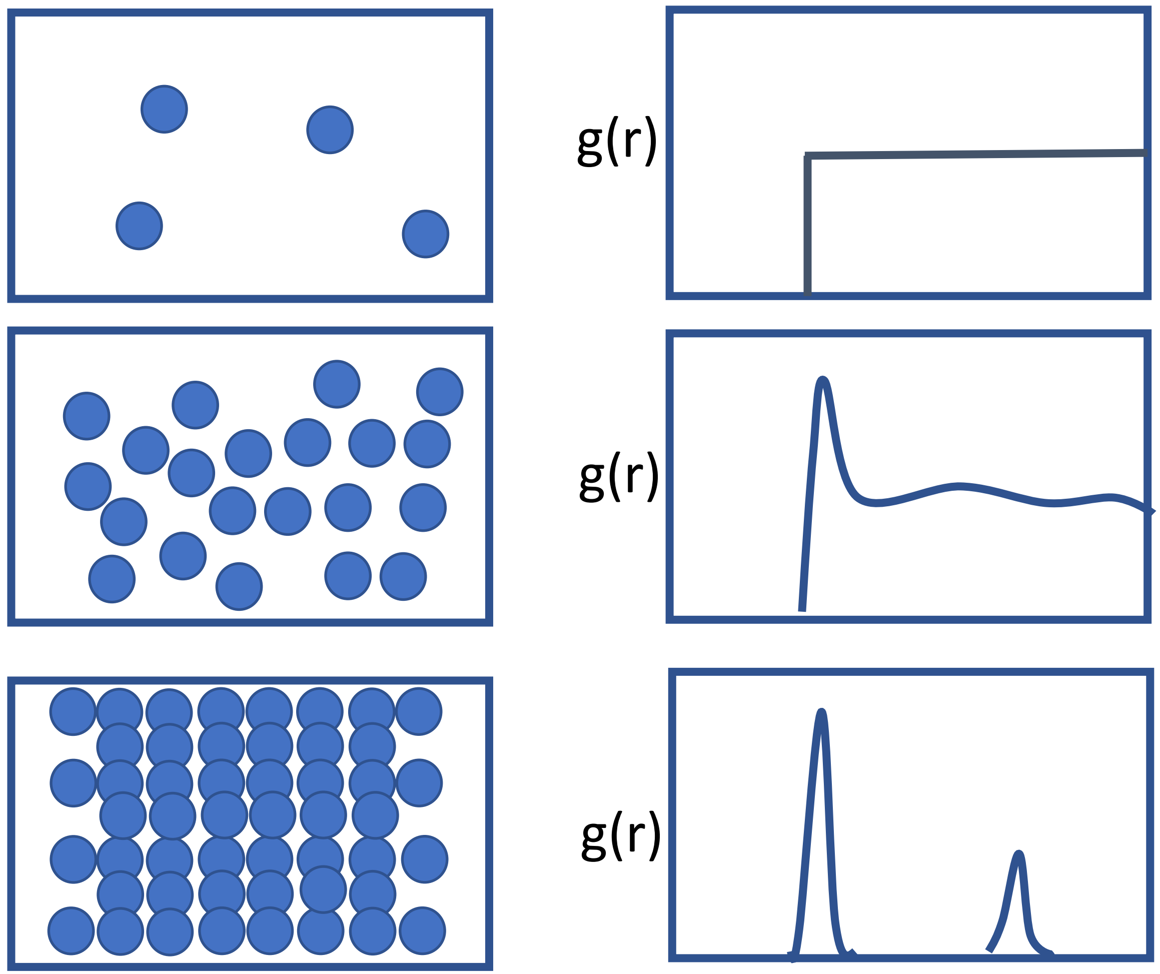
For an isotropic solution:

$$S(q) = 1 + 4\pi N_p \int_0^\infty [g(r) - 1] \frac{\sin(qr)}{qr} r^2 dr$$

Diluted

Concentrated

Ordered



Determination of Structure Factor

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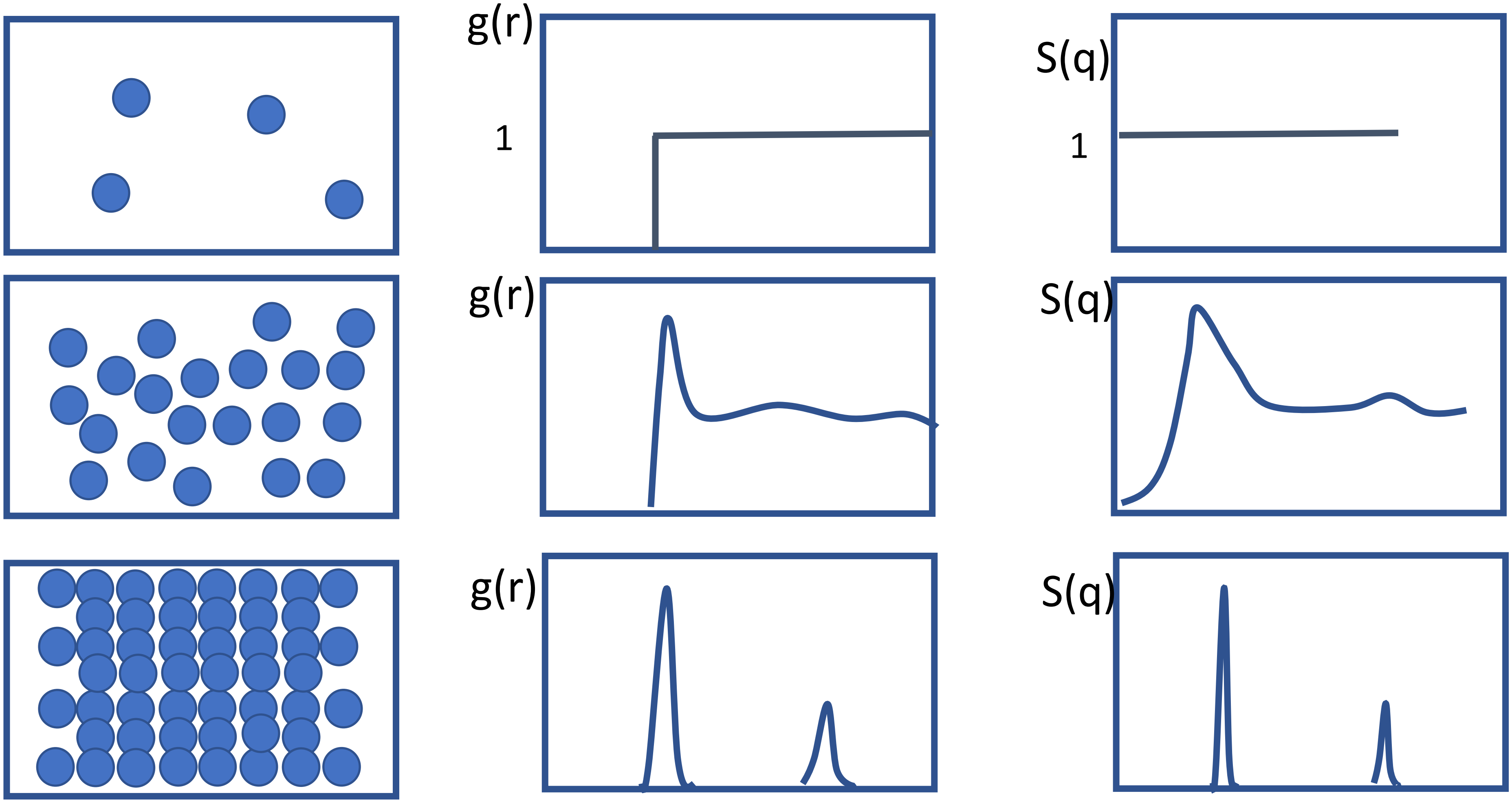
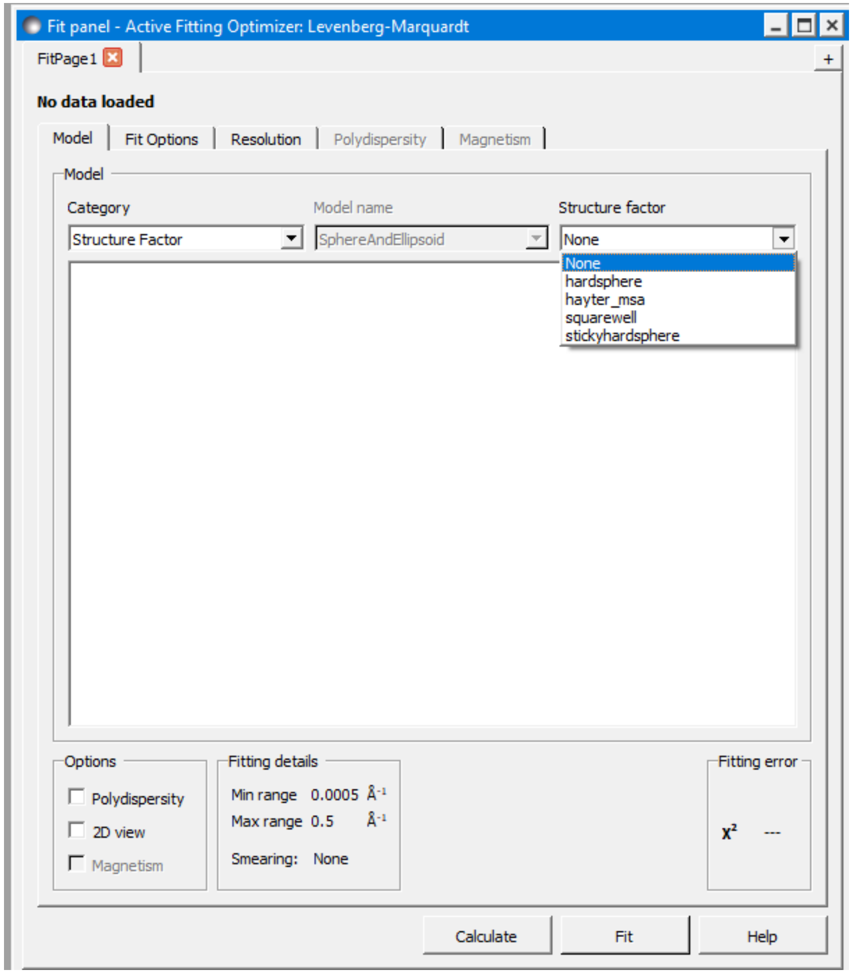


Models for S(Q) in SasView

$$I(q) = (\Delta\rho)^2\, nM^2\, P(q)\, S(q)$$



Four different type of interaction models:

1. Hardsphere
2. Hayter_MSA
3. Squarewell
4. Stickyhardsphere

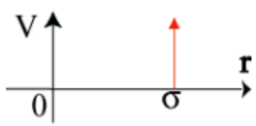
S(Q) : Hardsphere

$$I(q) = (\Delta\rho)^2\, nM^2\, P(q)\, S(q)$$

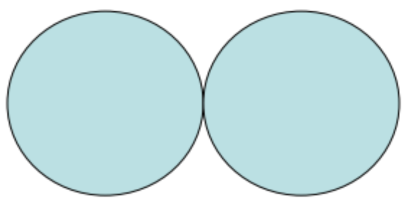
Four different type of interaction models:

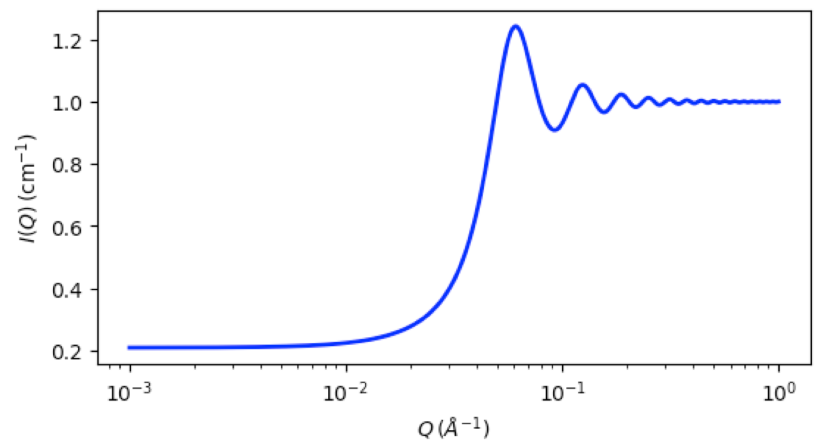
1. Hardsphere
2. Hayter_MSA
3. Squarewell
4. Stickyhardsphere

Spherical particles in solutions through hard-sphere Interactions (excluded volume).



$$V(r) = \begin{cases} +\infty & r < \sigma \\ 0 & r > \sigma \end{cases}$$





Most colloids are rigid objects: proteins, silicon nano-particle, …

S(Q): Hayter_MSA

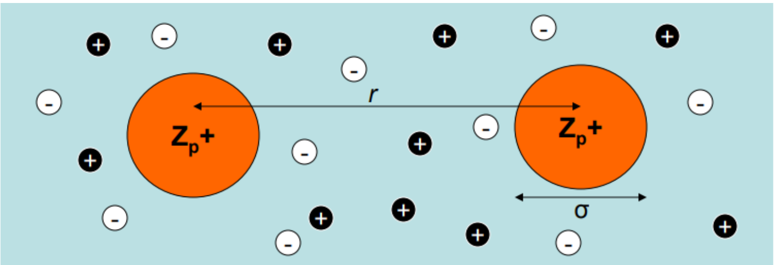
$$I(\text{q}) = (\Delta\rho)^2\, nM^2\, P(\text{q})\, S(\text{q})$$

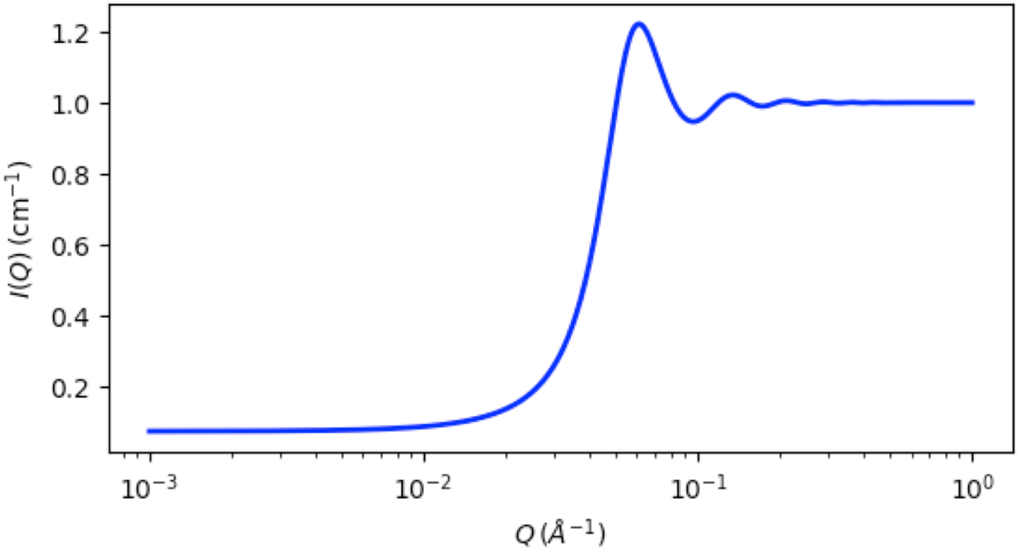
Colloidal particles with charge interactions.
(MSA closure)

Screened Coulombic repulsion between particles

Four different type of interaction models:

1. Hardsphere
2. Hayter_MSA
3. Squarewell
4. Stickyhardsphere





J. B. Hayter and J. Penfold, Mol. Phys. **46**, 651 (1981).

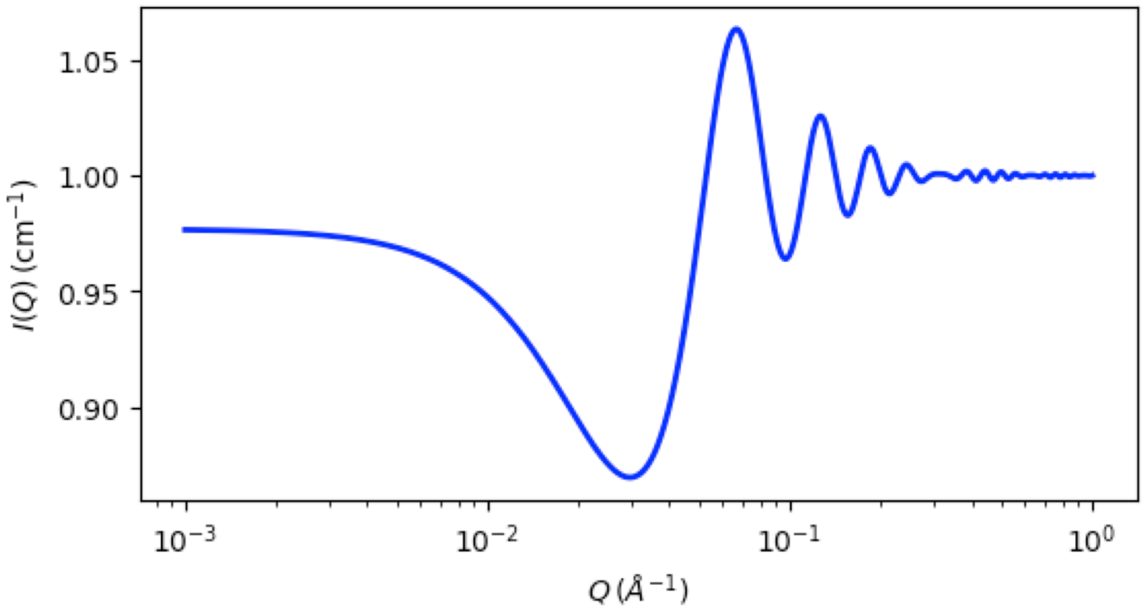
S(Q) : Squrewell

$$I(q) = (\Delta\rho)^2 \, nM^2 \, P(q) \, S(q)$$

Colloidal particles with narrow, attractive square well potential

Four different type of interaction models:

1. Hardsphere
2. Hayter_MSA
3. Squarewell
4. Stickyhardsphere



Colloidal Interactions in solution
https://cpb-us-w2.wpmucdn.com/sites.udel.edu/dist/4/1563/files/2014/03/ColloidsTutorial_final-283hizw.pdf

Methods to include structure factor

Monodisperse approximation (spherical symmetric interaction potential, independent of particle size)

$$\frac{d\sigma_i}{d\Omega}(Q) = \left[\int_0^\infty N_i(x;\mathbf{l}_i)F_i^2(Q;\mathbf{a}_i,x)dx\right] S_i(Q;\mathbf{s}_i)$$

Decoupling approximation (particles with small anisotropies and polydispersities, independent of particle size and orientation)

$$\frac{d\sigma_i}{d\Omega}(Q) = \int_0^\infty N_i(x;\mathbf{l}_i)F_i^2(Q;\mathbf{a}_i,x)dx + \frac{1}{n_i}\left[\int_0^\infty N_i(x;\mathbf{l}_i)F_i(Q;\mathbf{a}_i,x)dx\right]^2 \times [S_i(Q;\mathbf{s}_i) - 1]$$

with

$$n_i = \int_0^\infty N_i(x;\mathbf{l}_i)dx.$$

Local monodisperse approximation (particle of certain size is surrounded by the particles with the same size)

$$\frac{d\sigma_i}{d\Omega}(Q) = \int_0^\infty N_i(x;\mathbf{l}_i)F_i^2(Q;\mathbf{a}_i,x)S_i(Q;\mathbf{s}_i,R_i(\mathbf{a}_i,x))dx \qquad R_i(\mathbf{a}_i,x) = \sqrt[3]{\frac{3}{4\pi}V_i(\mathbf{a}_i,x)}.$$

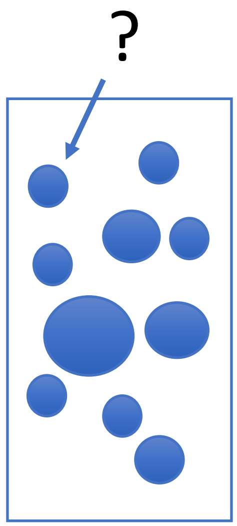
Polydispersity

Types of polydispersity:

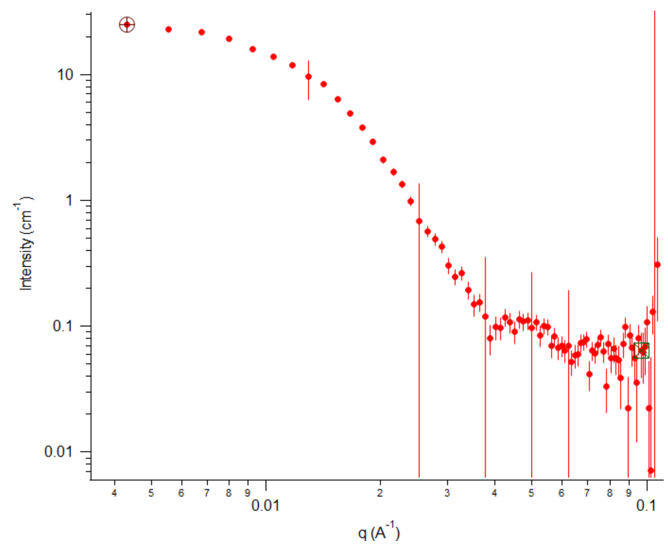
- Size - all particles have similar shape but differ in size, e.g. nanoparticles colloids
- Shape – different shape and size (e.g. oligomeric mixtures)
- Conformational – particles of identical molecular mass, which adopt different conformations, e.g. disordered or flexible proteins

Question 4

How to account for polydispersity?



Pre, Form and Structure Factors

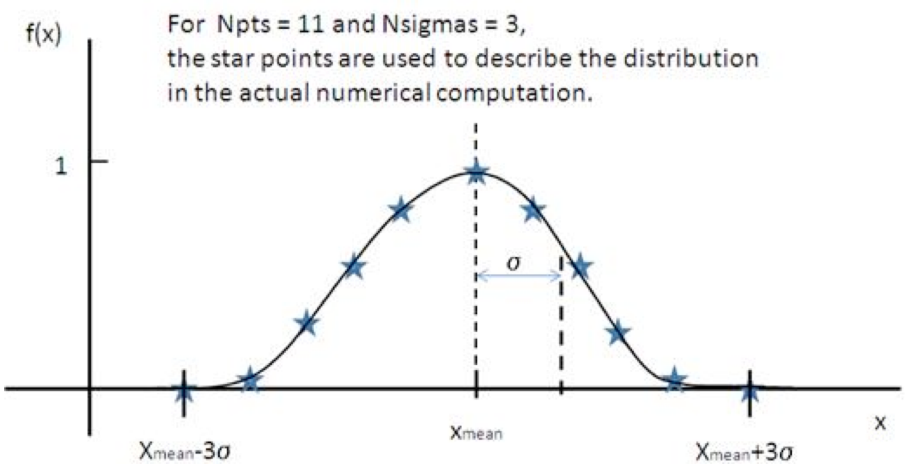


Size polydispersity

Average intensity for a population of particles that possess size distributions

The resultant intensity is then normalized by the average particle volume

$$P(q) = \frac{\text{scale}}{V} \int_{\mathbb{R}} f(x; \bar{x}, \sigma) F^2(q, x)\, dx + \text{background}$$



Shape polydispersity

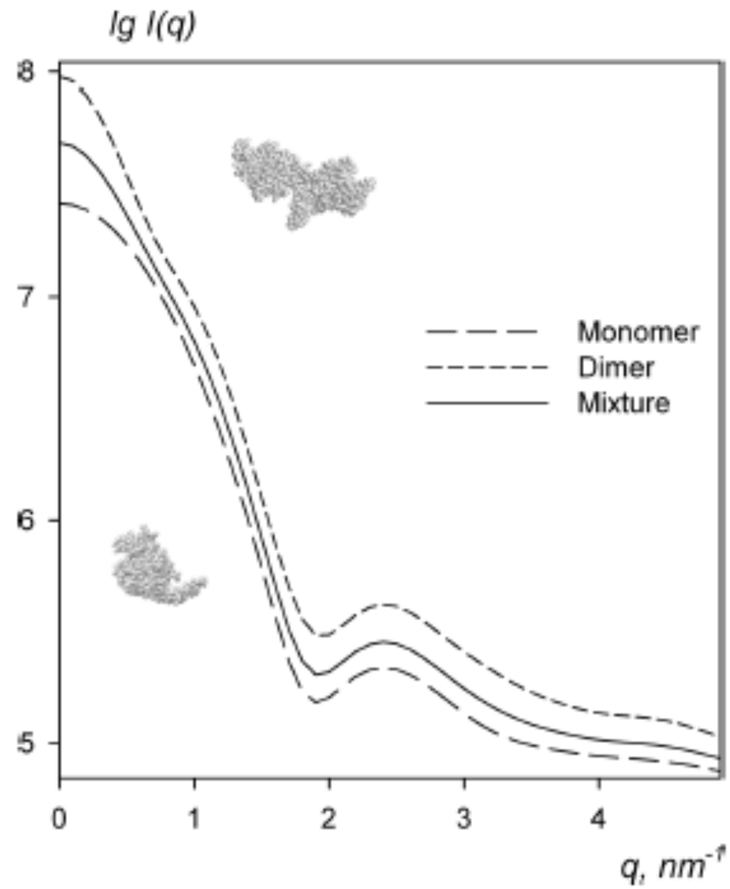
- Mixture of components gives combined scattering curve:

$$I(q_i) = \sum_{k=1}^{K} v_k i_k(q_i)$$

$v_k = n_k V_k$ volume fractions

$i_k(q) = I_k(q)/V_k$ normalized scattering intensities

- Combined curve can be fitted to experimental data $I_{exp}(q)$ to infer v_k



Conformational polydispersity

- Flexible and disordered proteins
- The same principle as for shape polydispersity:

$$I(q_i) = \sum_{k=1}^{K} v_k i_k(q_i)$$

$v_k = n_k V_k$ volume fractions

$i_k(q) = I_k(q)/V_k$ normalized scattering intensities

- Large number of parameters = high risk of overfitting

Summary

- Form factors represents the interference of neutrons scattered from different parts of the same object
- Structure factors represents interference between different objects.
- There are different ways to account for polydispersity

What hasn't been covered

- Rigorous derivations for form and structure factors (Orstein-Zernike equations)
- Backgrounds

$$I(q) = \frac{\text{scale}}{V} \cdot \left[3V(\Delta\rho) \cdot \frac{\sin(qr) - qr\cos(qr))}{(qr)^3}\right]^2 + \text{background}$$

- Resolution smearing
- Orientational and magnetic form factors
- And more…

Take home message

- We are working with low information content data
- Be careful when you add extra parameters
- Optimal experiment design is key to successful data analysis!

Questions?