Small-Angle Scattering:
Principles and Practice

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CHRNS CENTER FOR HIGH RESOLUTION NEUTRON SCATTERING NIST

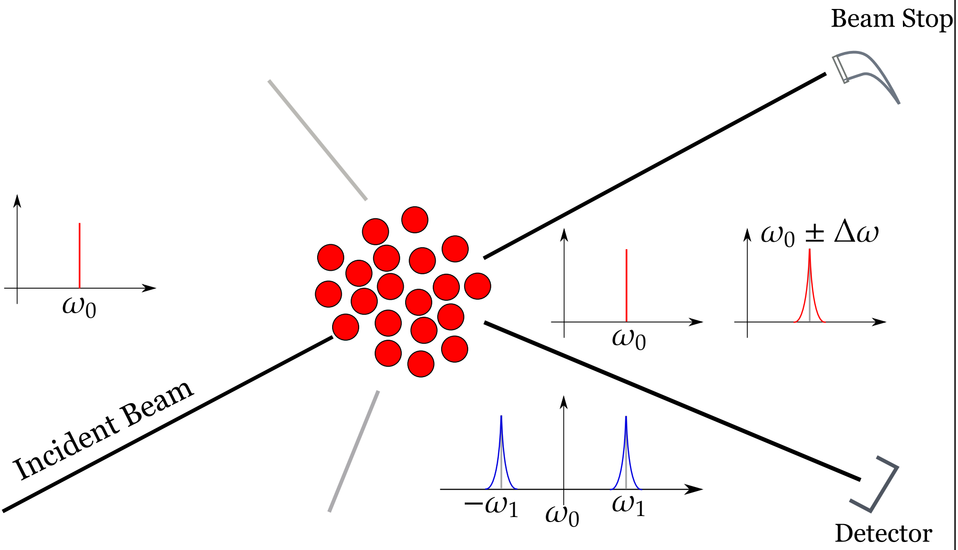
NIST Center for Neutron Research

The 28th CHRNS School on Methods and Applications of Small Angle Neutron Scattering and Neutron Reflectivity

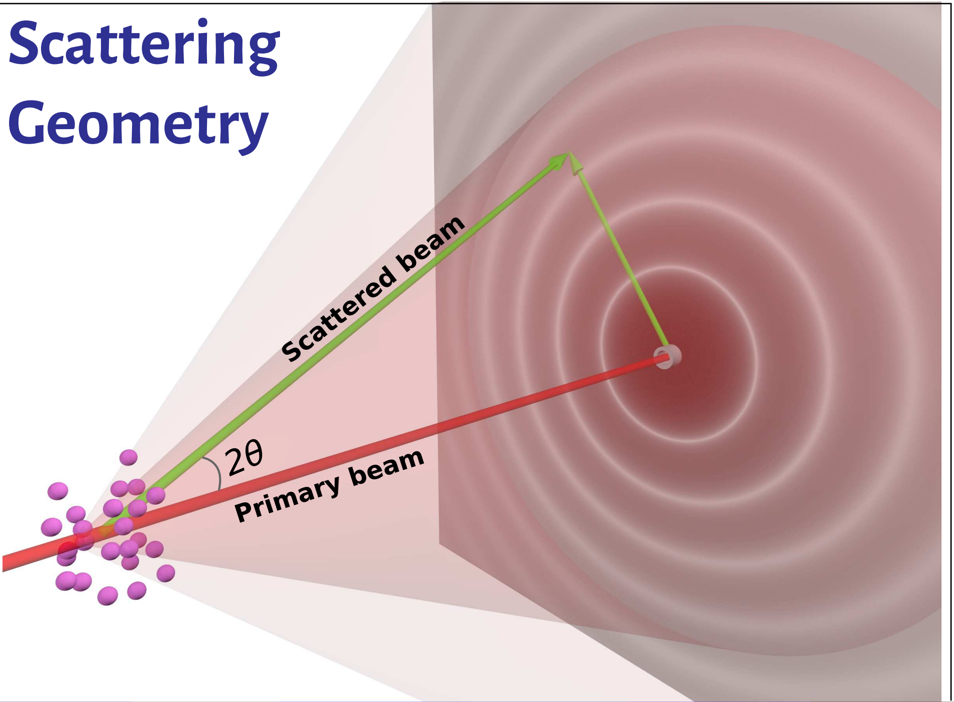
Oct. 17-21, 2022, NCNR

An Overview of Different Scattering Phenomena

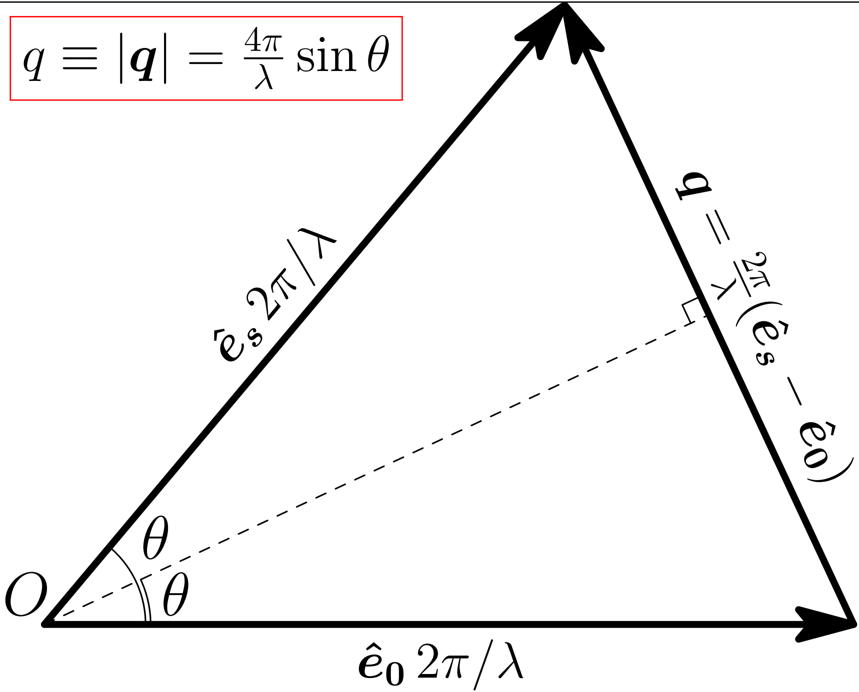
Elastic scattering experiment measures the intensity change as a function of angle



Scattering Geometry



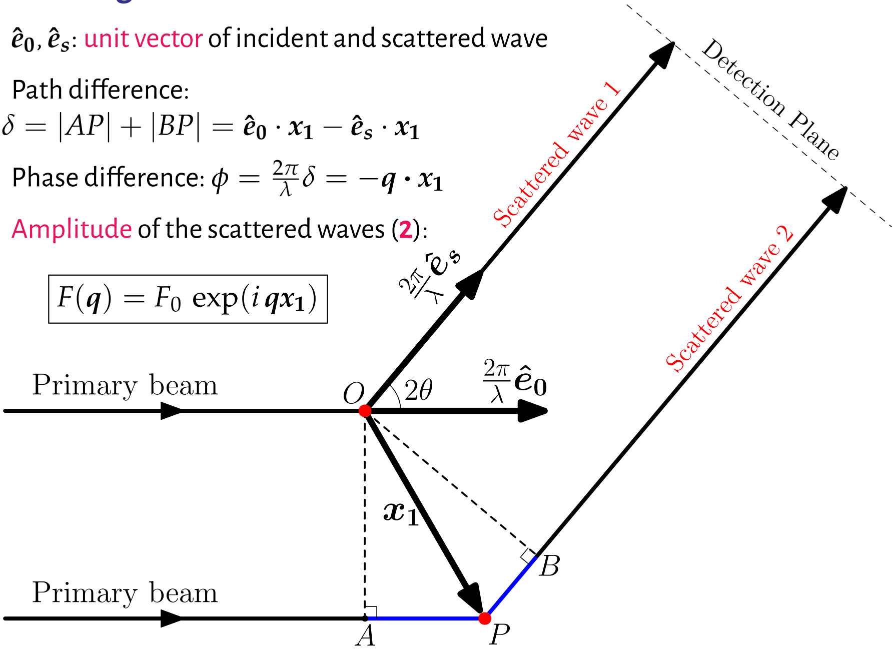
$$q \equiv |\boldsymbol{q}| = \frac{4\pi}{\lambda} \sin\theta$$



Scattering Fundamentals: Interference

- $\hat{\boldsymbol{e}}_0, \hat{\boldsymbol{e}}_s$: unit vector of incident and scattered wave
- Path difference:
  $\delta = |AP| + |BP| = \hat{\boldsymbol{e}}_0 \cdot \boldsymbol{x}_1 - \hat{\boldsymbol{e}}_s \cdot \boldsymbol{x}_1$
- Phase difference: $\phi = \frac{2\pi}{\lambda}\delta = -\boldsymbol{q} \cdot \boldsymbol{x}_1$
- Amplitude of the scattered waves (2):

$$F(\boldsymbol{q}) = F_0 \exp(i\,\boldsymbol{q}\boldsymbol{x}_1)$$

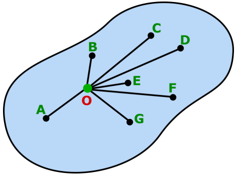


Scattered Intensity: N Particles

- **Superposed amplitude of waves scattered by N particles**

$$F(\boldsymbol{q}) = \sum_{i=1}^{N} b_i \exp(-i\boldsymbol{q}\cdot\boldsymbol{x}) = \int \rho(\boldsymbol{x}) \exp(-i\boldsymbol{q}\cdot\boldsymbol{x})\, \mathrm{d}\boldsymbol{x}$$

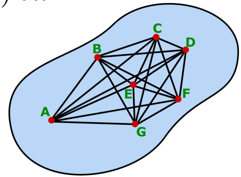
  * b_i: Scattering length (atomic scattering factor, f_i, in X-ray scattering).
  * $\rho(\boldsymbol{x})$: Scattering length density (SLD, electron density in X-ray scattering).



- **Scattered intensity due to N atoms**

$$\begin{aligned} I_N(\boldsymbol{q}) &= |F(\boldsymbol{q})|^2 \equiv F(\boldsymbol{q})F^*(\boldsymbol{q}) \\ &= \int \rho(\boldsymbol{x}) \exp(-i\boldsymbol{q}\cdot\boldsymbol{x})\, \mathrm{d}\boldsymbol{x} \int \rho(\boldsymbol{x}') \exp(i\boldsymbol{q}\cdot\boldsymbol{x}')\, \mathrm{d}\boldsymbol{x}' \\ &= \int \mathcal{P}(\boldsymbol{r}) \exp(-i\boldsymbol{q}\cdot\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}, \quad \text{where} \end{aligned}$$

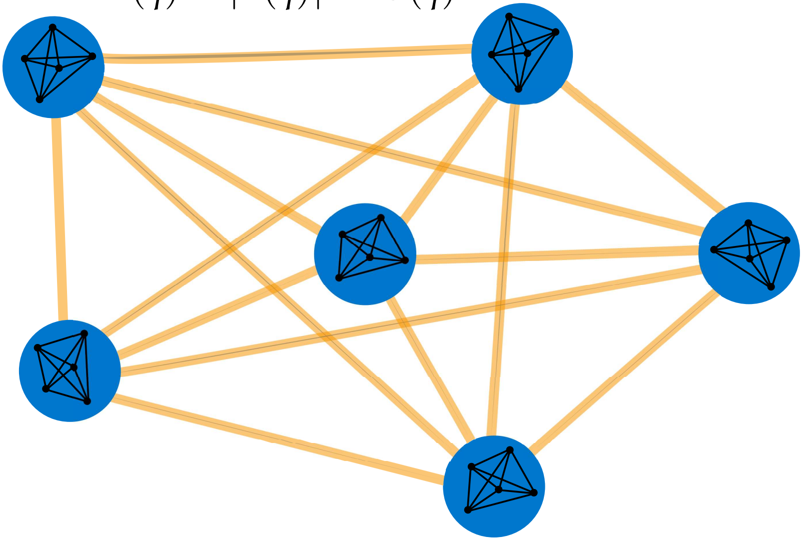
$$\mathcal{P}(\boldsymbol{r}) = \int \rho(\boldsymbol{x}'+\boldsymbol{r})\rho(\boldsymbol{x}')\, \mathrm{d}\boldsymbol{x}'$$



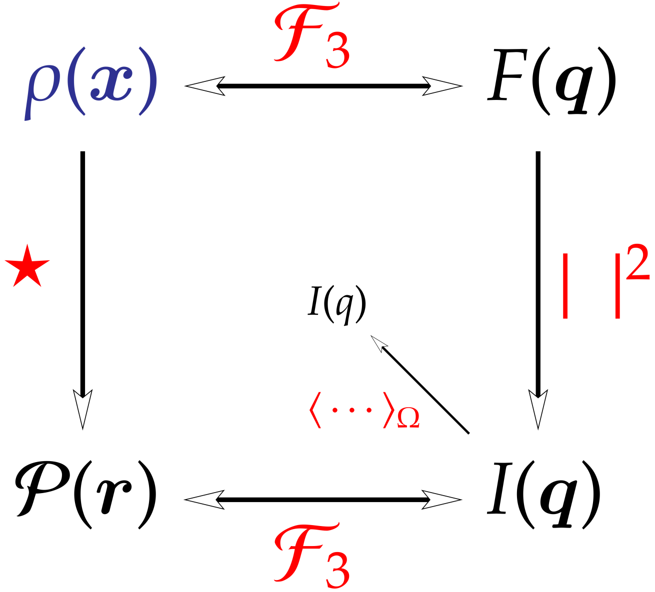
Form Factor & Structure Factor

Intra- & Inter-Particle Interference

$$I(q) \propto |F(q)|^2 \times S(q)$$



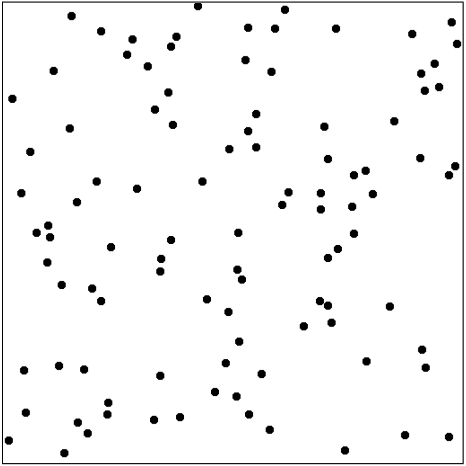
A Roadmap Toward Scattering Function: A Refresher



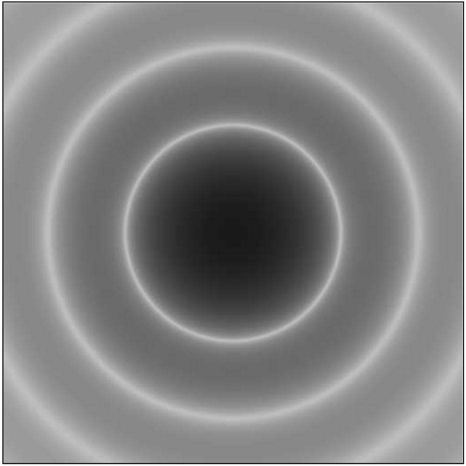
Form Factor & Structure Factor: Dilute Solution

$$S(q) = 1; \quad I(q) \propto |F(q)|^2$$

- Total scattering is a summation of scattering from each individual particle.



Dilute hard sphere suspension

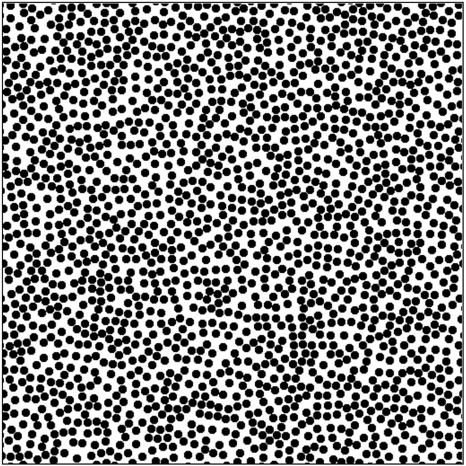


The scattering pattern

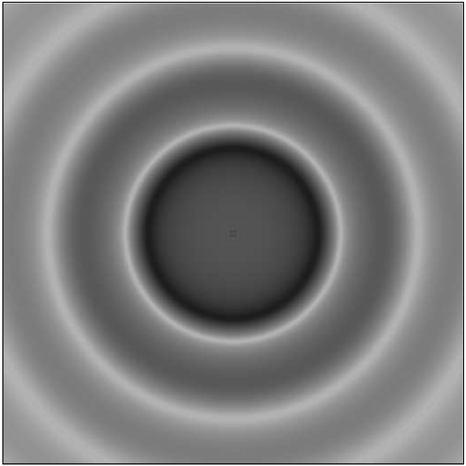
Form Factor & Structure Factor: Concentrated Solution

$$S(q) \neq 1; \quad I(q) \propto S(q) \, |F(q)|^2$$

- Need to consider interference of the scattered waves from different particles.



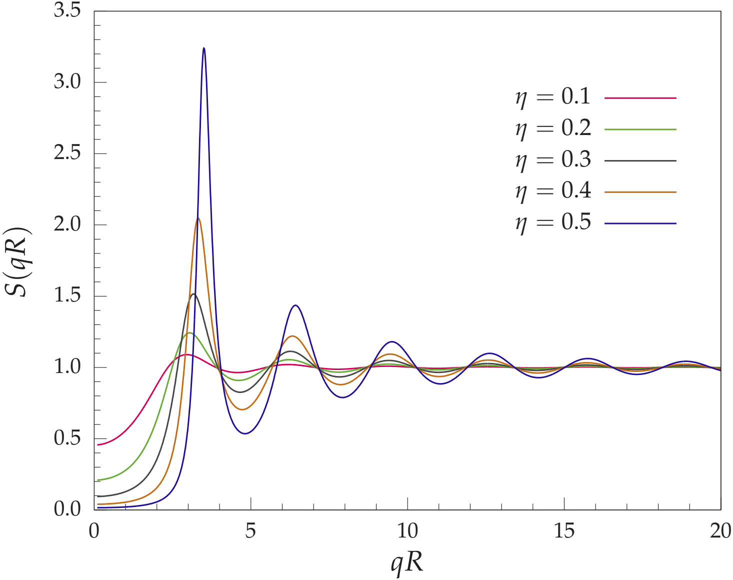
Concentrated hard sphere suspension



The scattering pattern

Structure Factor: An Example of Hard-Shpere Model[1–3]

1. J. K. Percus, G. J. Yevick; *Phys. Rev.*, **110**(1958) : 1-13. 2. M. S. Wertheim; *Phys. Rev. Lett.*, **10**(1963) : 321-323. 3. E. Thiele; *J. Chem. Phys.*, **39**(1963) : 474-479.



X-Ray, Light, and Neutron

- **X-ray & visible light are electromagnetic waves**

$$E = E_0 \exp(i\omega t)$$

E: EM field; ω: angular frequency

- **X-ray interacts with electrons, light with electron cloud**

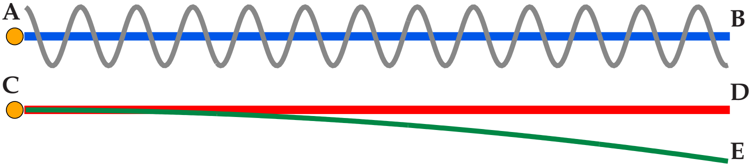
$$p = \frac{e^2/m}{\omega_0^2 - \omega^2} \cdot E$$

p: induced-dipole moment
e: elementary charge; e=1.6×10^{-19} C
m: electron mass; m=9.1×10^{-31} kg

- **Neutrons are particles (mass=1.68×10^{-27} kg)**

$$\lambda = h/p$$

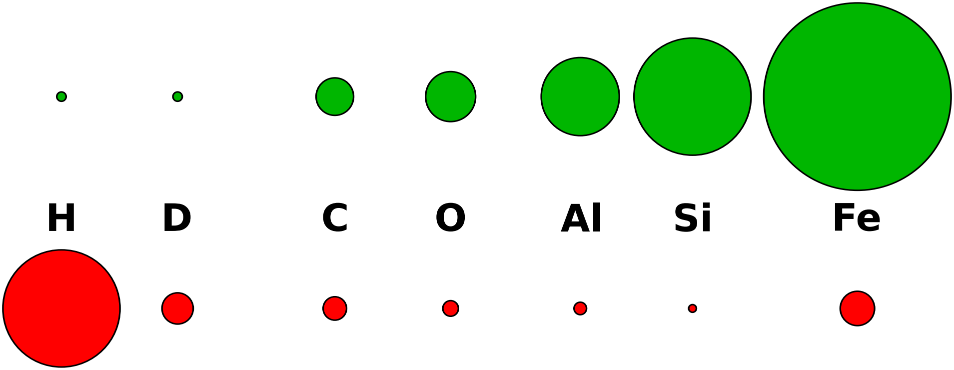
λ: (particle) wavelength; h: Planck's constant
p: (particle) momentum



Schematics: propagation of a EM wave (A-B) and neutron beam (C-E).

X-ray & Neutron as Complementary Probes

X-ray scattering cross section



Neutron scattering cross section

* Illustration, not in absolute scale.

Scattering Length Density

https://www.ncnr.nist.gov/resources/activation/

$$\rho = \frac{\sum_{i=1}^{N} b_i}{V_m}$$

- ρ: scattering length density
- b_i: coherent scattering length of the i-th atom
- V_m: volume of the molecule

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Home Instruments

Material

H2O

Neutron Activation

For rabbit system Calculate

Thermal flux	Cd ratio	Thermal/fast ratio
1e8	0	0
Mass	Time on beam	Time off beam
	10	1 y

Absorption and Scattering

Calculate

Density	Thickness
1.0	1
Source neutrons	Source X-rays
1 Ang	Cu Ka

Scattering from H2O

Source neutrons: 1.000 Å = 81.80 meV = 3956 m/s
Source X-rays: 1.542 Å = 8.042 keV
Sample in beam: H2O at 1.00 g/cm^3

1/e penetration depth (cm)		Scattering length density (10^{-6}/Å^2)		Scattering cross section (1/cm)		X-ray SLD (10^{-6}/Å^2)	
abs	80.836	real	-0.561	coh	0.004	real	9.469
abs+incoh	0.178	imag	-0.000	abs	0.012	imag	-0.032
abs+incoh+coh	0.177	incoh	21.180	incoh	5.621		

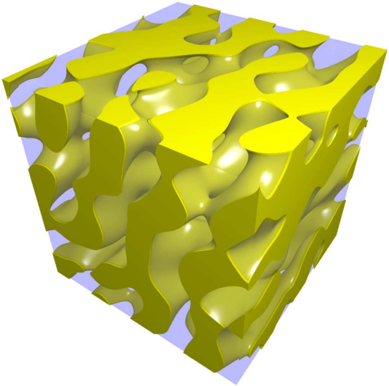
Neutron transmission is 0.358% for 1 cm of sample (after absorption and incoherent scattering).
Transmitted flux is 3.576e+5 n/cm^2/s for a 1e8 n/cm^2/s beam.

Questions? Last modified

Neutron activation: Dave Brown <david.brown@nist.gov>
Scattering calculations: Paul Kienzle <paul.kienzle@nist.gov>

Contrast: Why Structures Can be Probed at All

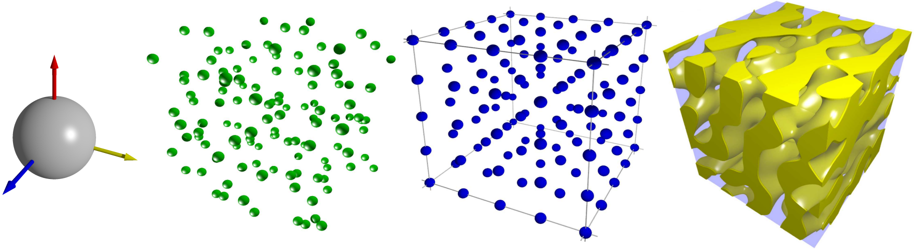
- **Structure**: **spatial variation** of **some 'property'**
- **To examine a structure, there must be a sufficient contrast between the objectives and the surroundings.**
- **Interpret** $\Delta\rho = \rho_p - \rho_s$; **what does** ρ **refers to?**
  - **NS**: scattering length density
  - **XS**: electron density
  - **LS**: polarizability

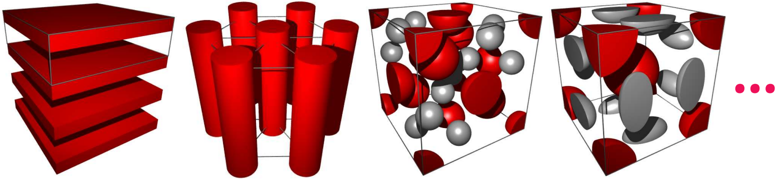


'Density' difference between the two phasess makes the bi-continous structure 'visible'.

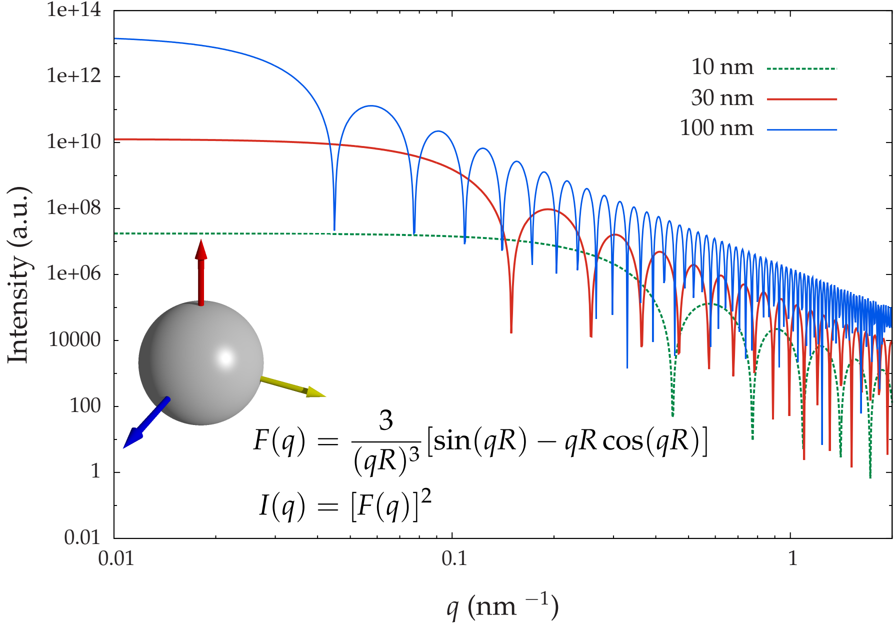
A General Definition of Structure: The Essence of $\rho(x)$

- Variation of some material property over space.

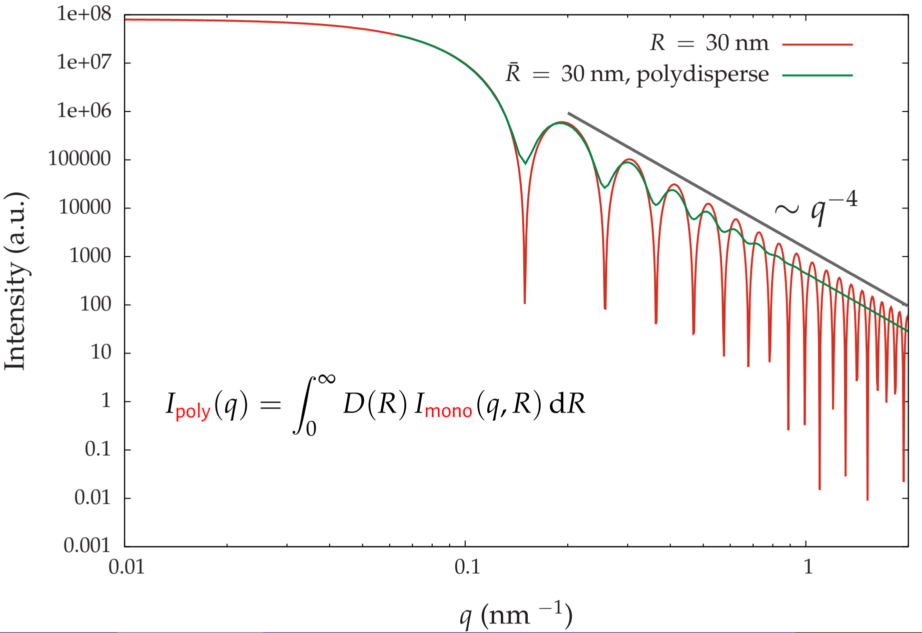




Scattering Function of Particulate System: General Features



Influence of Polydispersity



Guinier Approximation

$$I(q) = \sum_i \sum_i f_i f_j \frac{\sin(qr_{ij})}{qr_{ij}}$$

$$\frac{\sin(qr)}{qr} \approx 1 - \frac{q^2r^2}{6} + \frac{q^4r^4}{120} + \mathcal{O}(qr)$$

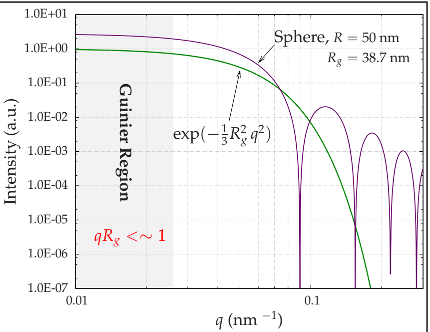
$$I(q) \approx \sum_i \sum_j f^2 - \sum_i \sum_j f^2 \frac{q^2 r_{ij}^2}{6}$$

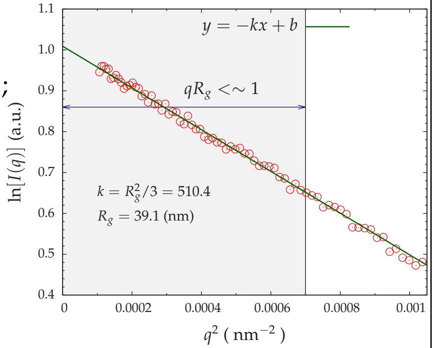
$$\sum_i \sum_j r_{ij}^2 = 2N^2R_g^2 \rightsquigarrow I(q) \approx Nf^2 \left(1 - \frac{q^2R_g^2}{3}\right);$$

$$e^{-q^2r^2/3} \approx 1 - \frac{q^2r^2}{3} + \frac{q^4r^4}{18} + \mathcal{O}(qr)$$

$$I(q) \propto \exp(-q^2R_g^2/3)$$

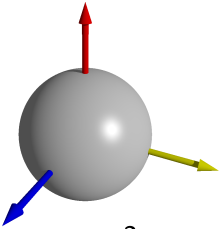
when $qR <\sim 1$

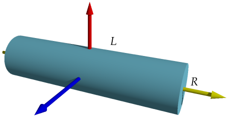


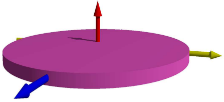


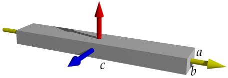
Radius of Gyration

$$R_g^2 = \frac{\int_V \rho(\mathbf{r}) r^2 \, \mathrm{d}v}{\int_V \rho(\mathbf{r}) \, \mathrm{d}v}; \quad R_g^2 = \frac{1}{2N^2} \sum_i \sum_j r_{ij}^2$$







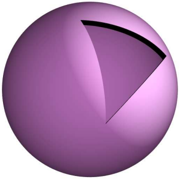


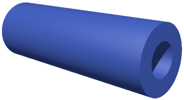
$$R_g^2 = \frac{3}{5} R^2$$

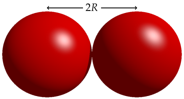
$$\frac{1}{2} R^2 + \frac{1}{12} L^2$$

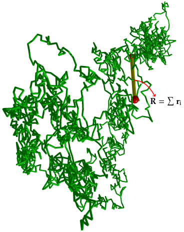
$$\frac{1}{2} R^2 + \frac{1}{12} d^2$$

$$\frac{1}{12} (a^2 + b^2 + L^2)$$









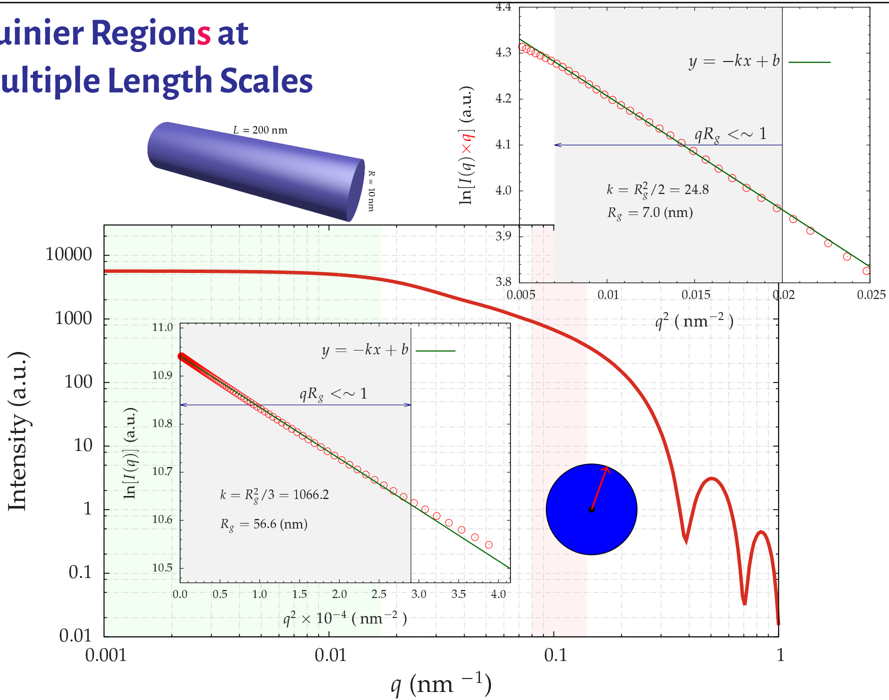
$$R_g^2 = \frac{3}{5} \frac{R_1^5 - R_0^5}{R_1^3 - R_0^3}$$

$$\frac{1}{2} \frac{R_1^4 - R_0^4}{R_1^2 - R_0^2} + \frac{1}{12} L^2$$

$$2R^2$$

$$\frac{1}{2} N b^2$$

Guinier Regions at Multiple Length Scales



Correlation function & Distance Distribution Function

$$I(\boldsymbol{q}) = \mathcal{F}[\mathcal{P}(\boldsymbol{r})]$$

$$\langle I(\boldsymbol{q})\rangle_\Omega \equiv I(q) = \rho^2 \int_0^\infty \overline{V(r)}\,\frac{\sin(qr)}{qr}\,4\pi r^2\,\mathrm{d}r$$

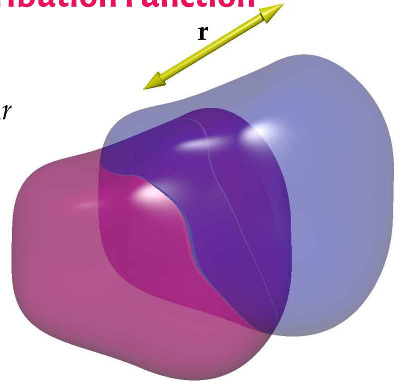
where

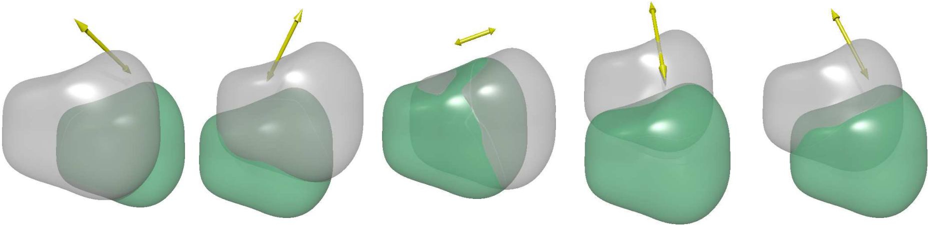
$$\rho^2\,\overline{V(r)} = \langle \mathcal{P}(\boldsymbol{r})\rangle_\omega$$

Define

$$\gamma_0(r) = \overline{V(r)}/V(0) \equiv \overline{V(r)}/V$$

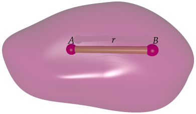
$$p(r) = 4\pi r^2 V \gamma_0(r)$$





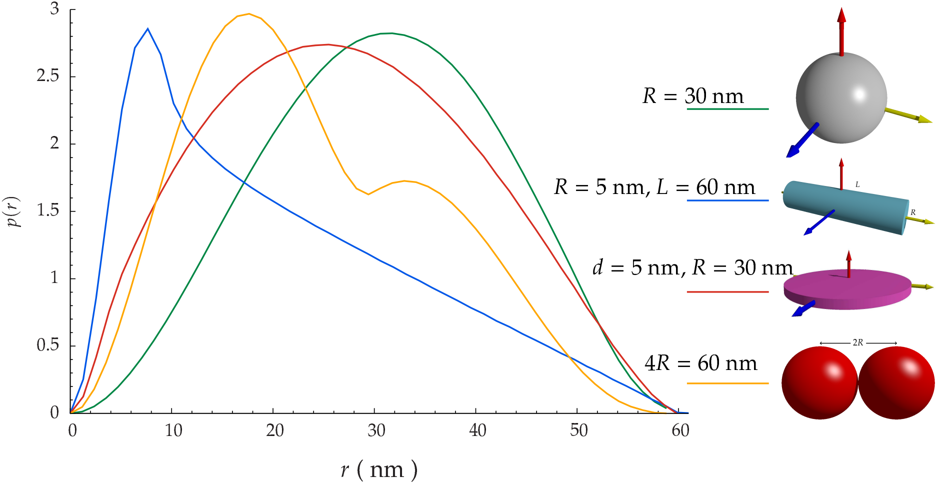
Particles and their phantom identicals shifted by $\boldsymbol{r}$, at the same $r = |\boldsymbol{r}|$

$p(r)$: Distance Distribution Function



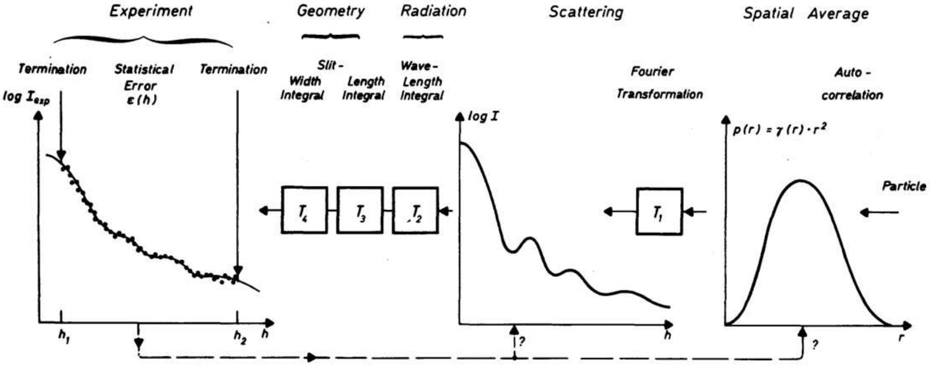
$$I(q) = \int_0^\infty \rho^2 V \gamma_0(r) \operatorname{sinc}(qr) 4\pi r^2 \, dr = \int_0^\infty p(r) \operatorname{sinc}(qr) \, dr$$

$$p(r) \propto \int_0^\infty I(q) qr \sin(qr) \, dq$$



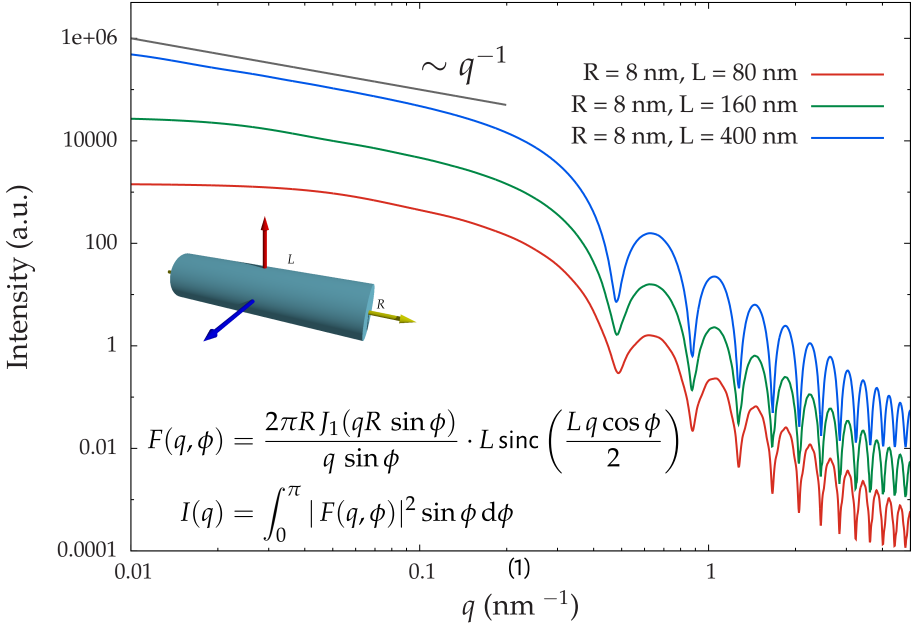
Obtaining $p(r)$: Indirect Fourier Transform

$$p(r) = \sum_{\nu=1}^{N} c_\nu \varphi_\nu(r); \quad I(q) = \sum_{\nu=1}^{N} c_\nu \Phi_\nu(q); \quad \text{where} \quad \Phi_\nu(q) = \mathcal{F}[\varphi_\nu(r)]$$



O. Glatter; *Small Angle X-Ray Scattering*, Academic Press, 1982, Chapter 4.

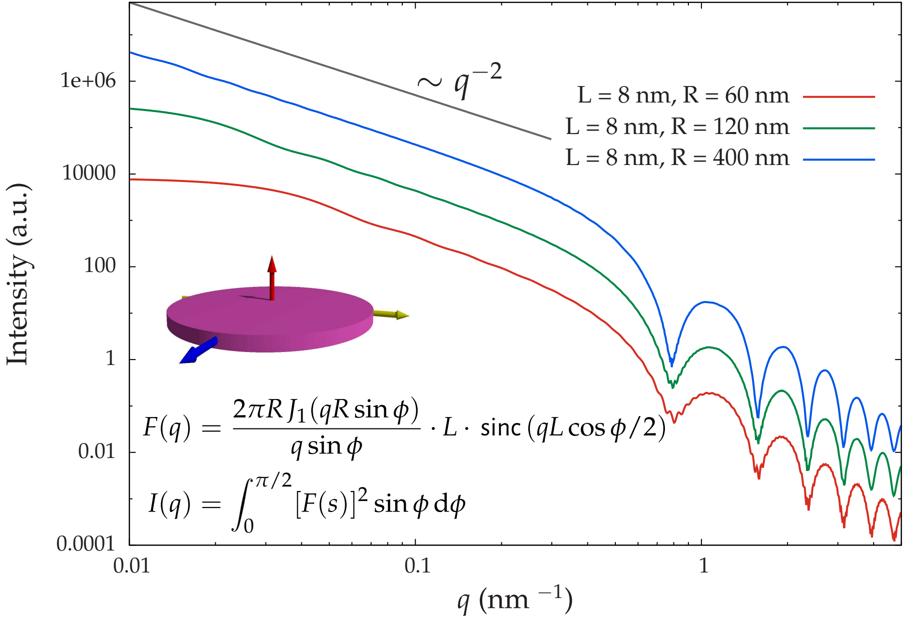
Computing 1D Scattering Curve: Rod



$$F(q,\phi) = \frac{2\pi R\, J_1(qR\,\sin\phi)}{q\,\sin\phi} \cdot L\,\mathrm{sinc}\left(\frac{L\,q\cos\phi}{2}\right) \qquad (1)$$

$$I(q) = \int_0^{\pi} |\,F(q,\phi)|^2 \sin\phi\, \mathrm{d}\phi$$

Computing 1D Scattering Curve: Disk



$$F(q) = \frac{2\pi R\, J_1(qR\sin\phi)}{q\sin\phi} \cdot L \cdot \mathrm{sinc}\,(qL\cos\phi/2)$$

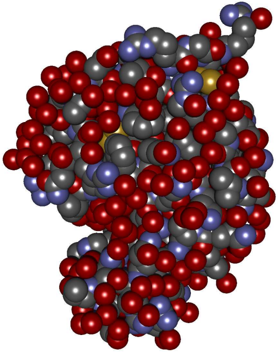
$$I(q) = \int_0^{\pi/2} [F(s)]^2 \sin\phi\, \mathrm{d}\phi$$

Debye Formula (Summation): Treating a Group of Particles

$$I(q) \equiv \langle |F(\boldsymbol{q})|^2 \rangle_\Omega = \left\langle \sum_i \sum_j F_i F_j \exp(i\boldsymbol{q}\cdot\boldsymbol{r}) \right\rangle$$

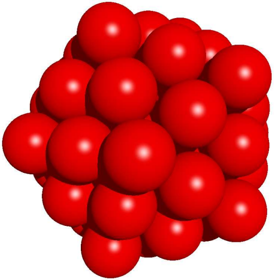
$$= \sum_i \sum_j F_i F_j \frac{\sin qr}{qr} = \sum_{i=1}^{N} I_i(q) + 2\cdot \sum\sum_{i\neq j} F_i F_j \frac{\sin qr}{qr}$$

Proteins



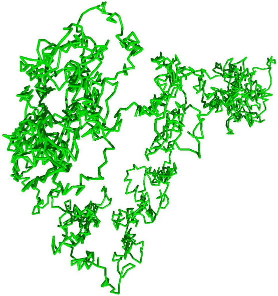
Lysozyme (1DPX)

Clusters



Icosahedron (55 particle)

Polymer Chains



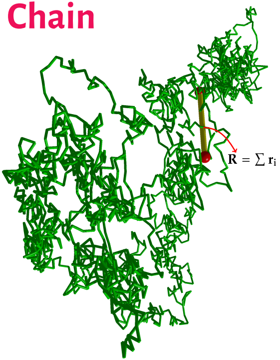
Gaussian Chain

Debye Function: Scattering from a Gaussian Chain

$$I(q) = \frac{1}{N} \sum_{i=0}^{N} \sum_{j=0}^{N} \left\langle \frac{\sin(qR_{ij})}{qR_{ij}} \right\rangle$$

$$\left\langle \frac{\sin(qr)}{qr} \right\rangle = \int_0^\infty \frac{\sin(qr)}{qr} W(r, \overline{R^2}) \cdot 4\pi r^2 \, \mathrm{d}r$$

$$= \exp[-q^2 \overline{R^2}/6]$$

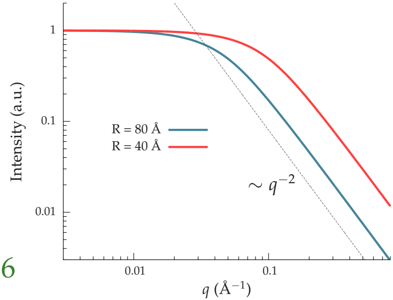


$$W(r, \overline{R^2}) = \left(\frac{3}{2\pi \overline{R^2}}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{r^2}{\overline{R^2}}\right)$$

$$I(q) = \frac{1}{N} \sum_{i=0}^{N} \sum_{j=0}^{N} \exp\left[-q^2(|i-j|)b^2/6\right]$$

$$= \frac{2}{N^2} \int_0^N (N-n) \exp(-q^2 n b^2/6) \, \mathrm{d}n$$

$$= 2x^{-2}(e^{-x} + x - 1) \quad \text{with} \quad x = q^2 \overline{R^2}/6$$



Spherical Harmonic Expansion

$$\sum_{i=0}^{N}\sum_{j=0}^{N}\frac{\sin(qR_{ij})}{qR_{ij}}$$

Acta Cryst. (1970). A**26**, 297

Interpretation of Small-Angle Scattering Functions of Dilute Solutions and Gases. A Representation of the Structures Related to a One-Particle-Scattering Function

BY HEINRICH B. STUHRMANN

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(*Received* 16 *July* 1969)

Small-angle scattering gives a much poorer resolution of the structure than does diffraction by perfect crystals, *i.e.* the loss of information due to the random orientations of the scattering molecules is far greater than that known from the phase problem. For a quantitative comparison the scalar field functions in physical and reciprocal space are expressed as a series of spherical harmonics Y_{lm}. From the rotational properties of spherical tensors it is deduced that the orientation of the partial structures described by the sum of the multipole components belonging to the same l has no influence on small angle scattering. There are no interference terms between these partial structures, *i.e.* the partial small angle scattering functions arising from the partial structures superimpose independently. Structures giving the same small angle scattering can be generated by displacing the coordinate system and rotating the partial structures in an arbitrary manner and sequence.

The calculations are greatly facilitated by the properties of the 3-*j* and 6-*j* coefficients widely used in nuclear physics. The Hankel transformations of the multipole components are reduced to an algebraic problem by the introduction of Laguerre polynomials.

Spherical Harmonic Expansion

- **Density (scalar field, real space) expansion**

$$\rho(r,\vartheta,\xi) \approx \sum_{l=0}^{L}\sum_{m=-l}^{l} \rho_{lm}(r) Y_{lm}(\vartheta,\xi)$$

$$\rho_{lm} = \int_0^{2\pi}\int_0^{\pi} \rho(r,\vartheta,\xi) Y^*_{lm}(\vartheta,\xi) \sin\vartheta \, \mathrm{d}\vartheta \, \mathrm{d}\xi$$

- **Amplitude expansion**

$$A(q,\phi,\psi) = \sum_{l=0}^{L}\sum_{m=-l}^{l} A_{lm}(q) Y_{lm}(\phi,\psi)$$

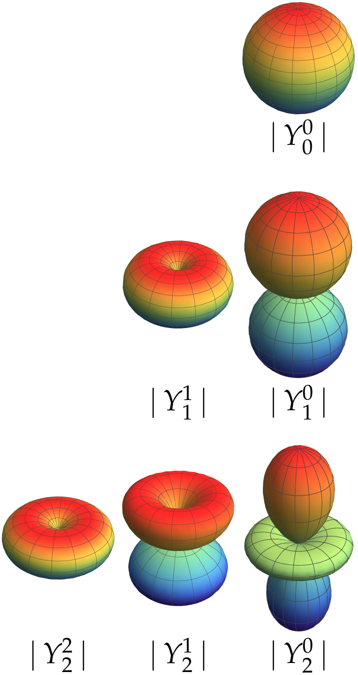
$$A_{lm}(q) = i^l \sqrt{\frac{2}{\pi}} \int_0^{\infty} j_l(qr)\rho_{lm}(r) r^2 \, \mathrm{d}r$$

$$\rho_{lm}(q) = (-i)^l \sqrt{\frac{2}{\pi}} \int_0^{\infty} j_l(qr) A_{lm}(r) q^2 \, \mathrm{d}q$$

- **Intensity expansion**

$$I(q) = \sum_{l=0}^{L} I_l(q) \propto \sum_{l=0}^{L}\sum_{m=-l}^{l} |A_{lm}(q)|^2; \quad \text{compare}$$

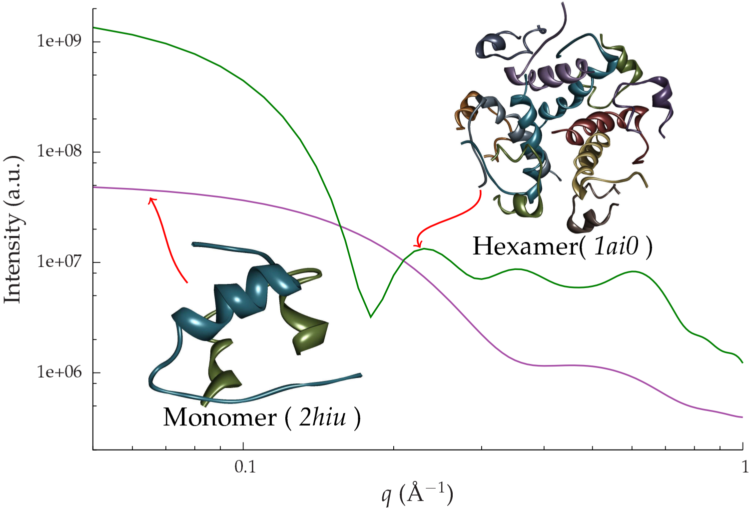
$$I(q) \propto \sum_i \sum_j \frac{\sin(qR_{ij})}{qR_{ij}}$$



Spherical Harmonic Expansion: An Example Using CRYSOL

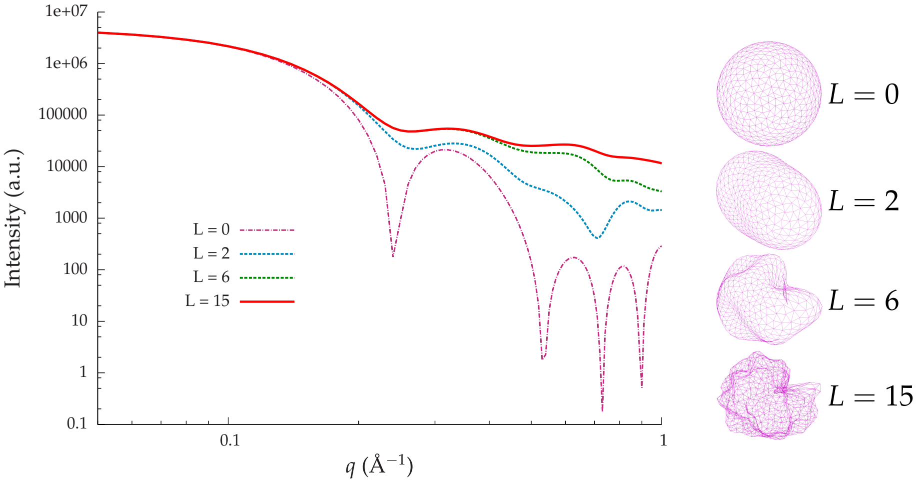
ATSAS by **EMBL** https://www.embl-hamburg.de/biosaxs/software.html

- Monodisperse system;
- Atomic coordinates (finite number) are known. (Then, why bother?)



Spherical Harmonic Expansion: Approaching Fine Details

- Low-order terms are for overall shape; high-order terms are for fine details.



SAXS curves of egg-white lysozyme. Atomic coordinates are from PDB file `6lyz`. Spherical harmonic expansion algorithm is implemented in `CRYSOL`; envelops are reconstructed using `MASSHA`. Both belongs to EMBL solution-SAXS toolkits `ATSAS`.

Planning for Your Experiment

- **What q-range do you need?**
  - Can we carry out some microscopic study beforehand?
  - Perhaps a visual inspection of your sample can provide some hints?
  - Can we do some simple calculation?
- **Where does the scattering contrast come from?**
  - electron density, scattering length density, polarizability...
- **What's the physical form of your sample?**
  - Liquid, film, powder, gel, *etc.*
  - Do I need to worry about radiation damage for biological samples?
- **Is kinetics of interest? How fast is the kinetic process?**
  - Shall we carry out the experiment using an in-house machine or at a synchrotron beamline?
- **What would be the scheme of scattering background manipulation?**

SANS Beamline, NG-7, 30 m, NIST Center for Neutron Research

SDD: A Practical Thinking of the Reciprocal Relation

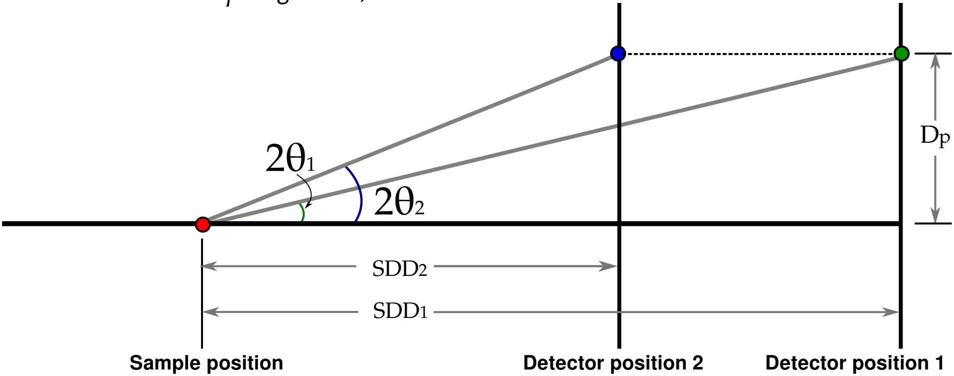
- $\tan 2\theta = D_p / SDD$

  $\uparrow$ SDD $\longmapsto$ Observed scattering angle $\downarrow$

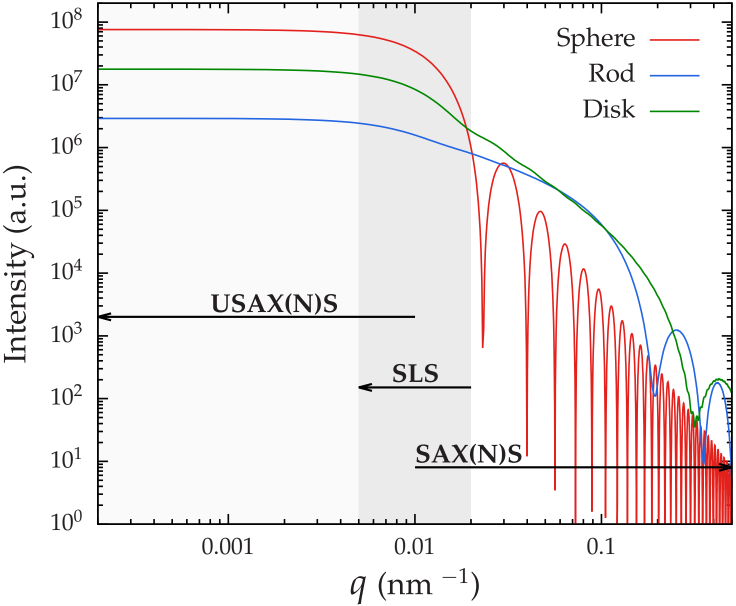
- $q = \frac{4\pi}{\lambda} \sin\theta = \frac{2\pi}{d}$

  $\downarrow \theta \longmapsto d \uparrow$

- To have a full-q range data, different SDDs are used.



Detection Range of Different SAS Techniques



$R_g = 150$ **nm**

Sphere:

$R = 194$ **nm**

Rod:

$R = 20$ **nm**

$l = 517$ **nm**

Disk:

$R = 212$ **nm**

$d = 20$ **nm**

Background Subtraction[1]

$$\frac{I_0}{I^0_{sam}} I_{cor} = \frac{I_0}{I^0_{sam}} (I_{sam} - I_{drk}) - (1-\phi)\frac{I_0}{I^0_{buf}} (I_{buf} - I_{drk}) - \phi \frac{I_0}{I^0_{cel}} (I_{cel} - I_{drk})$$

I_{cor} : Background subtracted/final corrected intensity

I_{sam} : Scattering intensity in **sample run** (`empty cell+solute+buffer`)

I_{buf} : Scattering intensity in **buffer run** (`empty cell+ buffer`)

I_{cel} : Scattering intensity in **empty cell run** (`empty cell`)

I_{drk} : Detector response NOT due to scattering event

I^0_{sam} : Transmitted intensity in **sample run** (`empty cell+solute+buffer`)

I^0_{buf} : Transmitted intensity in **buffer run** (`empty cell +buffer`)

I^0_{cel} : Transmitted intensity in **empty cell run** (`empty cell`)

ϕ : volume fraction of solute

[1] Koch, M. H., Vachette, P. & Svergun, D. I. Quart. Rev. Biophys., **36**, 147-227 (2003).