Small-angle scattering from nanostructures

Australian Soft Matter Scattering Workshop

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http://deb.li/IntroSANS

General small-angle scattering equation

Measured scattering intensity, $I(Q)$:

$$I(Q) = (\rho_\mathrm{p} - \rho_\mathrm{s})^2 \; \phi_\mathrm{p} \; V_\mathrm{p} \; P(Q) \; S(Q)$$

- contrast *scattering length density*
- concentration
- size of each scattering centre
- "shape" of each scattering centre *form factor*
- arrangement of particles in dispersion *structure factor*

For dilute dispersions of non-interacting particles, $S(Q) = 1$.

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Introduction
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Small-angle scattering experiments for nanostructures

Form factor, $P(Q)$
- shape of particle
- well known for some shapes (spheres, cylinders, core-shell particles)
- can be calculated for others (slowly)

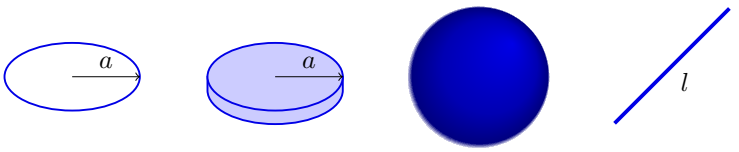
Structure factor, $S(Q)$
- typical distance between particles
- self avoiding? aggregating?
- can write down for very few systems

Contrast, SLD, $\Delta\rho$
- like refractive index
- can vary with isotopes
- H $\rightarrow$ D most useful in colloids (H_2O, D_2O)

Overview

1. $P(Q)$
   - approximations to form factors
   - Guinier & Porod
2. $\Delta\rho$
   - varying contrast
   - using contrast variation
3. $S(Q)$
   - understanding structure factors
   - calculating structure factors

Approximations to shapes: radius of gyration



circular ring | thin disc | sphere | thin rod

$R_g = a$ | $R_g = \frac{a}{\sqrt{2}}$ | $R_g = \sqrt{\frac{3a}{5}}$ | $R_g = \frac{l}{\sqrt{12}}$

radius of gyration, $R_g = \frac{1}{V}\int_V r^2 \, d\vec{r}$

root-mean-square radius averaged over the volume of the particle

Approximations to form factors

Low-Q region

Take a Taylor expansion of $P(Q)$. (remember: $\cos x = 1 - \frac{x^2}{2} + \ldots$)

$$\begin{aligned} P(Q) &= \frac{1}{V_\mathrm{p}^2}\left|\int_{V_\mathrm{p}} \exp(-i\vec{Q}\cdot\vec{r})\,\mathrm{d}\vec{r}\right|^2 \\ &= \frac{1}{V_\mathrm{p}^2}\left|\int_{V_\mathrm{p}} 1 - \frac{(\vec{Q}\cdot\vec{r})^2}{2} + \ldots\,\mathrm{d}\vec{r}\right|^2 \\ &= \left[1 - \frac{R_\mathrm{g}^2}{3}Q^2 + \ldots\right] \end{aligned}$$

Approximations to form factors

Low-Q region

Take a Taylor expansion of $P(Q)$. (remember: $\cos x = 1 - \frac{x^2}{2} + \ldots$)

$$P(Q) = \left[1 - \frac{R_\mathrm{g}^2}{3}Q^2 + \ldots\right]$$

So for low-Q region, dilute solution (*i.e.* $S(Q) = 1$):

$$\begin{aligned} I(Q) &= \Delta\rho^2 N_\mathrm{p} V_\mathrm{p}^2 P(Q) \\ &= \Delta\rho^2 N_\mathrm{p} V_\mathrm{p}^2 \left(1 - \frac{R_\mathrm{g}^2}{3}Q^2 + \ldots\right) \end{aligned}$$

Approximations to form factors

Starting with: $I(Q) = \Delta\rho^2 N_\mathrm{p} V_\mathrm{p}^2 \left(1 - \frac{R_\mathrm{g}^2}{3}Q^2 + \ldots\right)$

Zimm

$$1 - x \approx \frac{1}{1+x}$$

$$1 - \frac{R_\mathrm{g}^2}{3}Q^2 \approx \frac{1}{1 + \frac{R_\mathrm{g}^2}{3}Q^2}$$

$$\frac{1}{I(Q)} = \frac{1}{\Delta\rho^2 N_\mathrm{p} V_\mathrm{p}^2}\left(1 + \frac{R_\mathrm{g}^2}{3}Q^2\right)$$

Used with Gaussian polymer coils.

Guinier

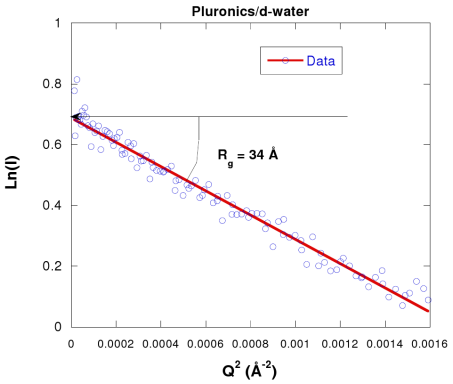
$$1 - x \approx \mathrm{e}^{-x}$$

$$1 - \frac{R_\mathrm{g}^2}{3}Q^2 \approx \exp\left(-\frac{R_\mathrm{g}^2}{3}Q^2\right)$$

$$I(Q) = \Delta\rho^2 N_\mathrm{p} V_\mathrm{p}^2 \exp\left(-\frac{R_\mathrm{g}^2}{3}Q^2\right)$$

Gives R_g for any shape.

Guinier approximation



Low angle means $QR_\mathrm{g} < 1$.

Plot: $\ln I(Q)$ vs Q^2

Slope: $-R_\mathrm{g}^2/3$

Data: SANS on pluronic surfactant P85 in $\mathrm{D_2O}$
Slope: $-400\,\text{Å}^2$

$$I(Q) = \Delta\rho^2 N_\mathrm{p} V_\mathrm{p}^2 \exp\left(-Q^2 \frac{R_\mathrm{g}^2}{3}\right)$$

Pluronic = poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)

Data from Boualem Hammouda, NIST

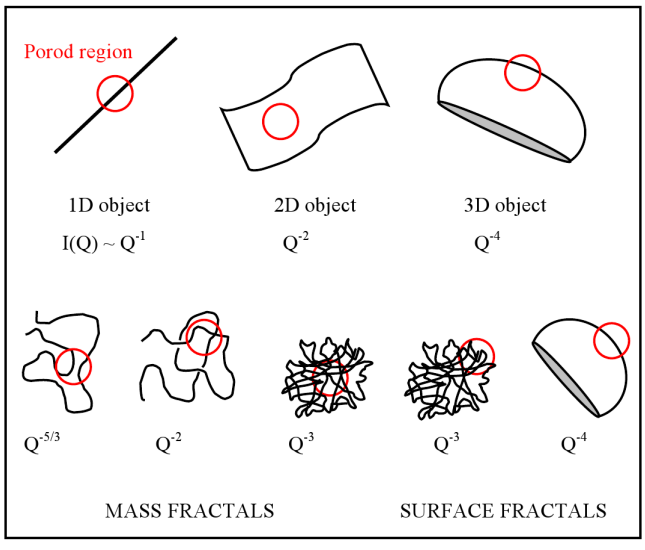
High-Q approximation: Porod region

Another very useful approximation is at high-Q.

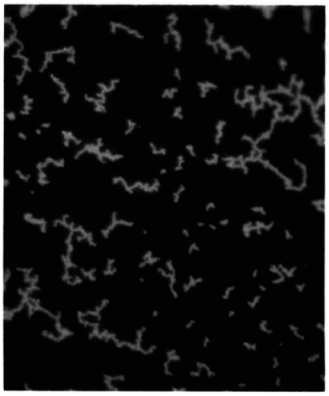
$$I(Q) = \frac{A}{Q^n} + B \qquad \Rightarrow \qquad \log(I(Q) - B) = \log(A) - n\log(Q)$$

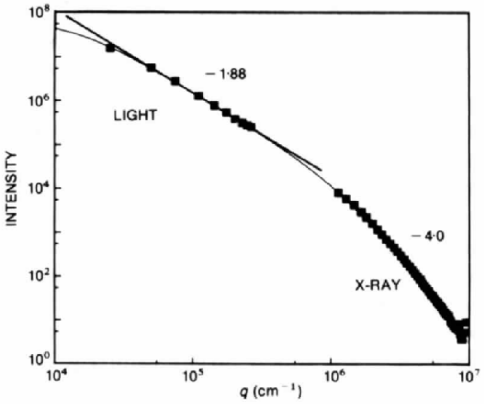
i.e. a plot of $\log I(Q)$ vs $\log Q$ gives a straight line with slope $-n$.
High-Q $\Rightarrow$ small length scales

1	rigid rods (1D particles)
2	sheets, plates (2D particles)
4	smooth particle surface, *e.g.* spheres (3D particles)
5/3	fully swollen coil (good solvent)
$2 < 3$	"mass fractal", gels, networks
2	dilute Gaussian polymer chain
3	collapsed polymer coil (poor solvent)
$3 < 4$	"surface fractals" fractal dimension D gives $n = 6 - D$



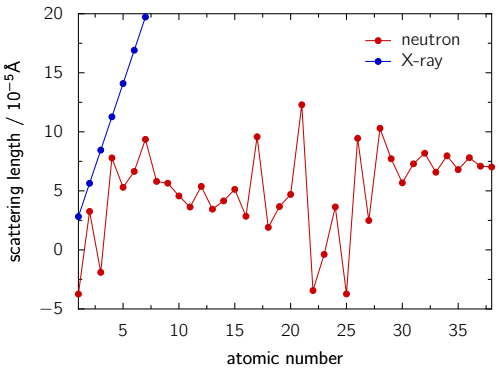
Example analysis





Martin & Hurd *Scattering from fractals* J. Appl. Cryst., **1987**, 20, 61-78.

Comparison of scattering lengths for atoms



neutrons:
scatter off nucleus, isotope also matters

X-rays:
scatter off electrons, only atomic number matters

`http://www.ncnr.nist.gov/resources/n-lengths/`

Neutron scattering length density

$$\rho_{\mathrm{N}} = \frac{1}{V_{\mathrm{m}}} \sum_i n_i b_i = \frac{\rho_{\mathrm{m}} N_{\mathrm{A}}}{M} \sum_i n_i b_i$$

- V_{m} is the molecular volume
- ρ_{m} is the mass density
- M is the molecular weight
- n_i is the number of atoms in the molecule of type i
- b_i is the scattering length of atom i

nucleus	$b_{\mathrm{coh}}/10^{-5}$ Å	$b_{\mathrm{inc}}/10^{-5}$ Å	$b_{\mathrm{abs}}/10^{-5}$ Å
^{1}H	-3.741	25.3	1.5
^{2}D	6.671	4.04	0
^{12}C	6.646	5.56	0
^{14}N	9.37	11.0	0
^{16}O	5.803	4.23	0
Cd	4.87	3.04	142

Calculating SLDs

$$\rho_{\mathrm{N}} = \frac{\rho_{\mathrm{m}} N_{\mathrm{A}}}{M} \sum_i n_i b_i$$

nucleus	$b_{\mathrm{coh}}/10^{-5}$ Å
^{1}H	-3.741
^{2}D	6.671
^{16}O	5.803

H_2O

$$\begin{aligned}\rho_{\mathrm{N}} &= \frac{1.0\,\mathrm{g\,cm^{-3}} \times 6.022 \times 10^{23}\,\mathrm{mol^{-1}}}{18\,\mathrm{g\,mol^{-1}}}(2 \times b_{\mathrm{H}} + b_{\mathrm{O}}) \\ &= -0.56 \times 10^{-6}\,\mathrm{Å^{-2}}\end{aligned}$$

D_2O

$$\begin{aligned}\rho_{\mathrm{N}} &= \frac{1.1\,\mathrm{g\,cm^{-3}} \times 6.022 \times 10^{23}\,\mathrm{mol^{-1}}}{20\,\mathrm{g\,mol^{-1}}}(2 \times b_{\mathrm{D}} + b_{\mathrm{O}}) \\ &= 6.38 \times 10^{-6}\,\mathrm{Å^{-2}}\end{aligned}$$

X-ray scattering length density

$$\rho_{\mathrm{X}} = \frac{\rho_{\mathrm{m}} N_{\mathrm{A}}}{M} \sum_i n_i b_{\mathrm{e}} z_i$$

- ρ_{m} is the mass density
- M is the molecular weight
- n_i is the number of atoms in the molecule of type i
- z_i is the atomic number of atom i
- $b_{\mathrm{e}} = \dfrac{\mu_0 e^2}{4\pi m} = 2.85 \times 10^{-5}$Å
- μ_0 is the permeability of free space, $\mu_0 = 4\pi \times 10^{-7}\,\mathrm{N\,A^{-2}}$
- e is the elementary charge, $e = 1.6021 \times 10^{-19}\,\mathrm{C}$
- m is the mass of an electron, $m = 9.109 \times 10^{-31}\,\mathrm{kg}$

Comparison of scattering lengths for molecules

material	$\rho_{\mathrm{N}}/10^{-6}$Å^{-2}	$\rho_{\mathrm{X}}/10^{-6}$Å^{-2}
H_2O	-0.56	9.4
D_2O	6.38	9.4
$-(CH_2)-$	-0.3	6.5
$-(CD_2)-$	7.9	6.5
h-polystyrene	1.41	9.5
D_2O:H_2O (28:72)	1.41	9.4
h-SDS	0.34	7.7
d-SDS	5.83	7.7
D_2O:H_2O (15:85)	0.34	9.4
D_2O:H_2O (92:8)	5.83	9.4

Calculating SLDs of mixtures

$$\rho_{\text{mix}} = \frac{V_1\rho_1 + V_2\rho_2}{V_1 + V_2}$$

H_2O:D_2O mixture 50:50 v/v

$\rho_{D_2O} = 6.38 \times 10^{-6}$ Å^{-2} $\rho_{H_2O} = -0.56 \times 10^{-6}$ Å^{-2}

$$\begin{aligned}\rho_{\text{mix}} &= \frac{V_{H_2O}\rho_{H_2O} + V_{D_2O}\rho_{D_2O}}{V_{H_2O} + V_{D_2O}} \\ &= (0.5 \times -0.56 + 0.5 \times 6.38) \times 10^{-6}\,\text{Å}^{-2} \\ &= 2.88 \times 10^{-6}\,\text{Å}^{-2}\end{aligned}$$

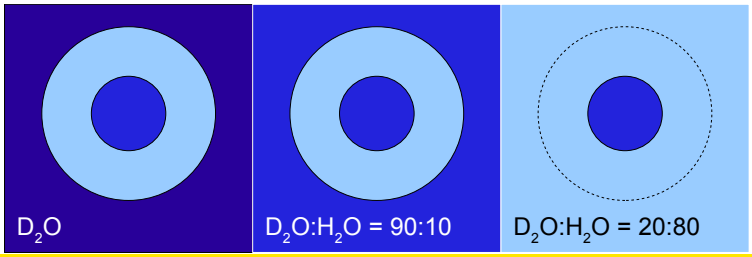
On-line calculator:
`https://www.ncnr.nist.gov/resources/activation/`

Contrast to give more information

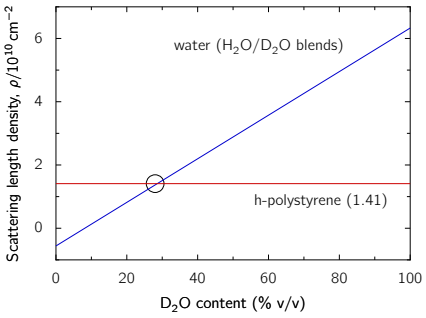
H and D scatter differently

- deuteration of one part of a structure changes scattering
- several different experiments are then possible
- deuteration of polymers and surfactants is expensive and difficult

D-polymer core, H-polymer corona:



Scattering length densities for mixtures



Contrast matching:

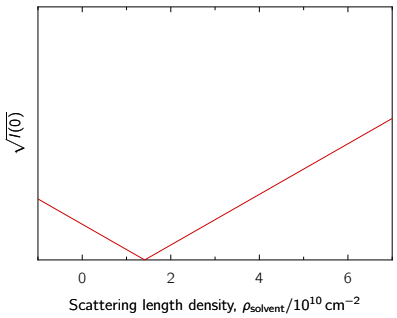
$$\rho_{\text{solvent}} = \frac{V_1\rho_1 + V_2\rho_2}{V_1 + V_2}$$

h-polystyrene spheres with d-SDS on the surface.

h-polystyrene "invisible" at ∼28% v/v D_2O.

Theoretical approach to finding SLD match

Scattering length densities for mixtures



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h-polystyrene spheres with d-SDS on the surface.

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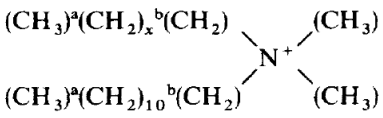
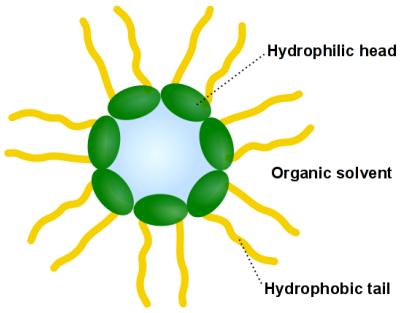
Experimental approach to finding SLD match

Understanding microemulsions

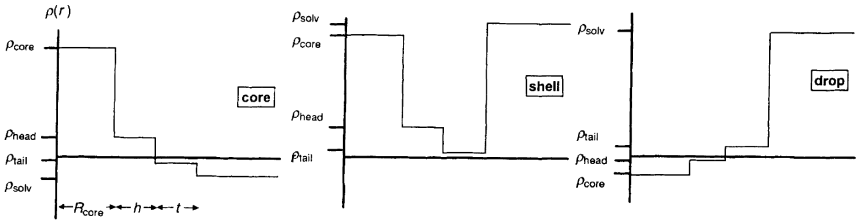
Two-tailed surfactant, DDAB:



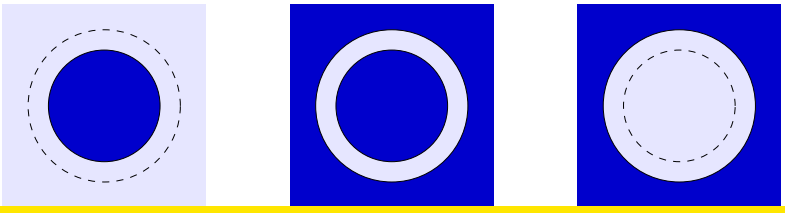
water-in-oil microemulsions

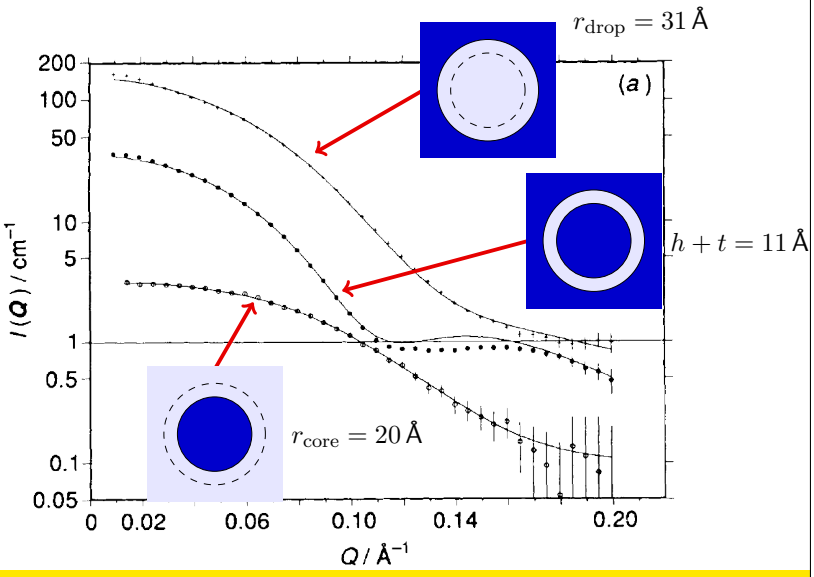


Eastoe, *Structure in microemulsions of di-chained surfactants* J. Chem. Soc., Faraday Trans, **1996**, 92, 65–72

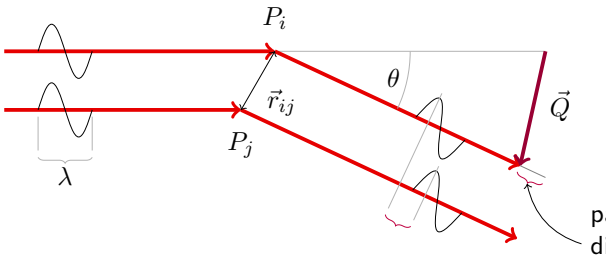


d-water	d-water	h-water
h-surfactant	h-surfactant	h-surfactant
h-oil	d-oil	d-oil





Structure factors



Radial distribution functions

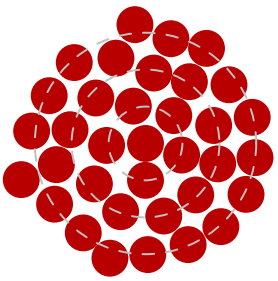
Radial distribution function

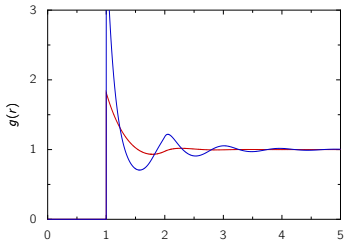
Hard-sphere particles of radius R.
$g(r)$ probability of finding another particle at distance r

$$g(r) = \frac{N_{\mathrm{p}}(r)}{N_{\mathrm{p}}}$$

N_{p} average number density
$N_{\mathrm{p}}(r)$ number density in shell at radius r (thickness δr)

Limits:
$N_{\mathrm{p}}(r) = 0$ for $r < 2R$
$N_{\mathrm{p}}(r) = 1$ for $r \to \infty$





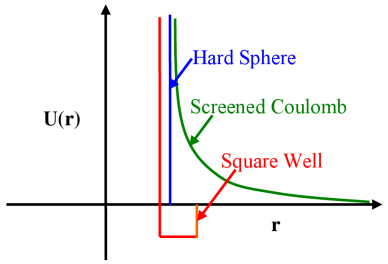
Start with the radial distribution function...

Ornstein–Zernike equation

$$g(r) = \exp\left[\frac{-U(r)}{k_B T}\right]$$

$$U(r) = \sum_{i,j} w_{i,j}(r) + \sum_{i,j,k} w_{i,j,k}(r) + \ldots$$

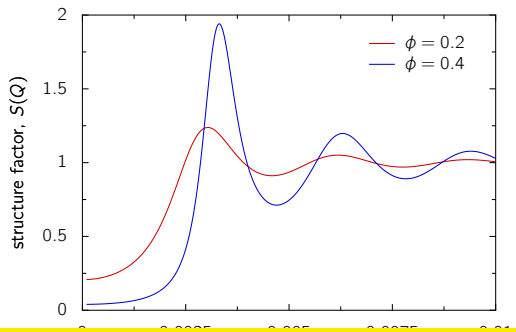
where $w_{i,j,\ldots}(r)$ are the binary, ternary etc interaction energies.



...to calculate structure factor

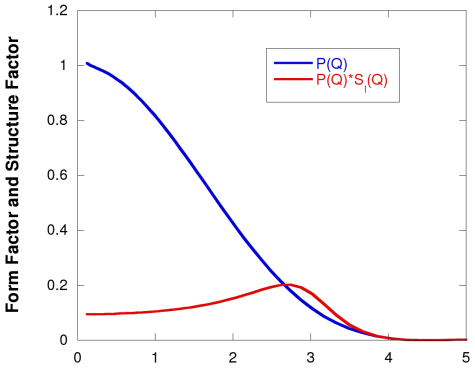
Structure factor

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



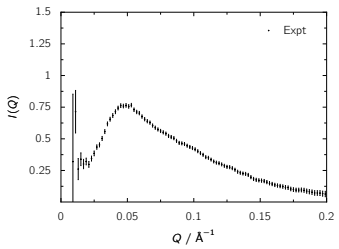
$S(Q)$ calculated for 100 nm hard spheres

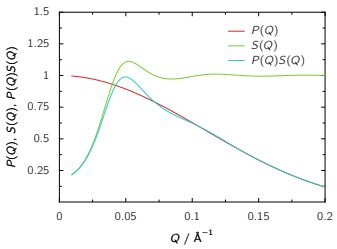
Comparison with form factor



- $P(Q)$ for a sphere has series of maxima, but falls at $\sim Q^{-4}$
- $S(Q) \ll 1$ for small Q.
- $S(Q)$ also oscillatory around 1 for larger Q
- interaction peak

Example: Hayter–Penfold structure

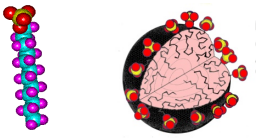




SDS micelles at 4×cmc

Final fitting gives:

micelle radius, r	38 Å
micelle charge	17.5
Debye length $1/\kappa$	3.4 nm



Hayter & Penfold, Molecular Physics, **1981**, 42, 109–118

Approximations to form factors

- Guinier analysis: $\ln I(Q)$ vs Q^2 has slope $R_g^2/3$
- Porod region: $\log I(Q)$ vs $\log Q$ has slope n characteristic of particle / network / fractal / coil nature

Contrast

- scattering length density, calculated from atomic composition and either molecular volume or bulk density
- isotopes matter, particularly H & D
- SLD of a mixture from volumes used
- can tune the contrast to vary (extra data) or match (hide)

Structure factors

- longer range structure of dispersion
- based on potential between scattering centres
- easy to do hard spheres, charged particles (micelles, nanoparticles), sticky square wells