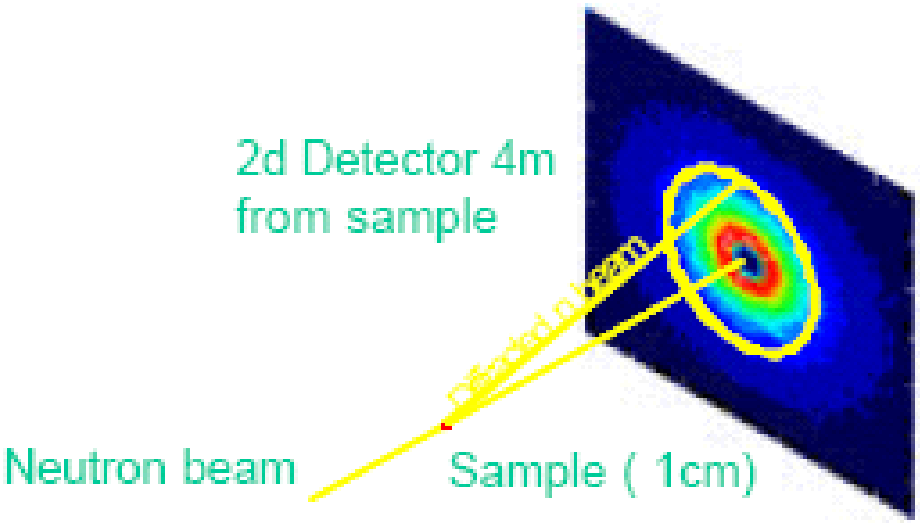
SANS

Scattering (or diffraction) of X-rays, light, or neutrons at small angles is used to examine objects that are large compared to the wavelength (λ) of the radiation used.

LOQ at ISIS



Sizes of interest = “large scale structures” = 1 – 300 nm or more

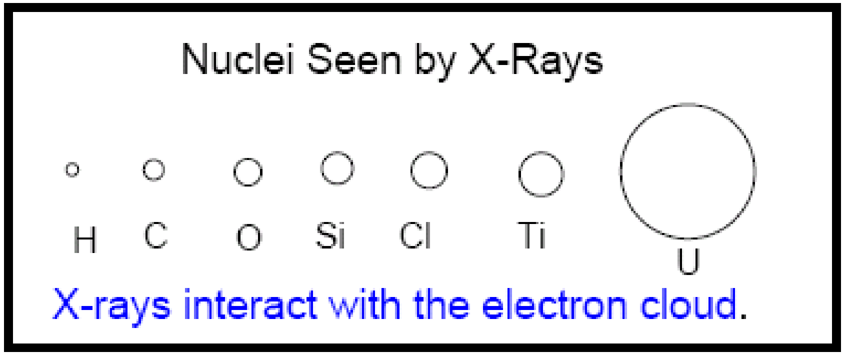
- Mesoporous structures
- Biological structures (membranes, vesicles, proteins in solution)
- Polymers
- Colloids and surfactants (micelles and more)
- Magnetic films and nanoparticles
- Voids and Precipitates

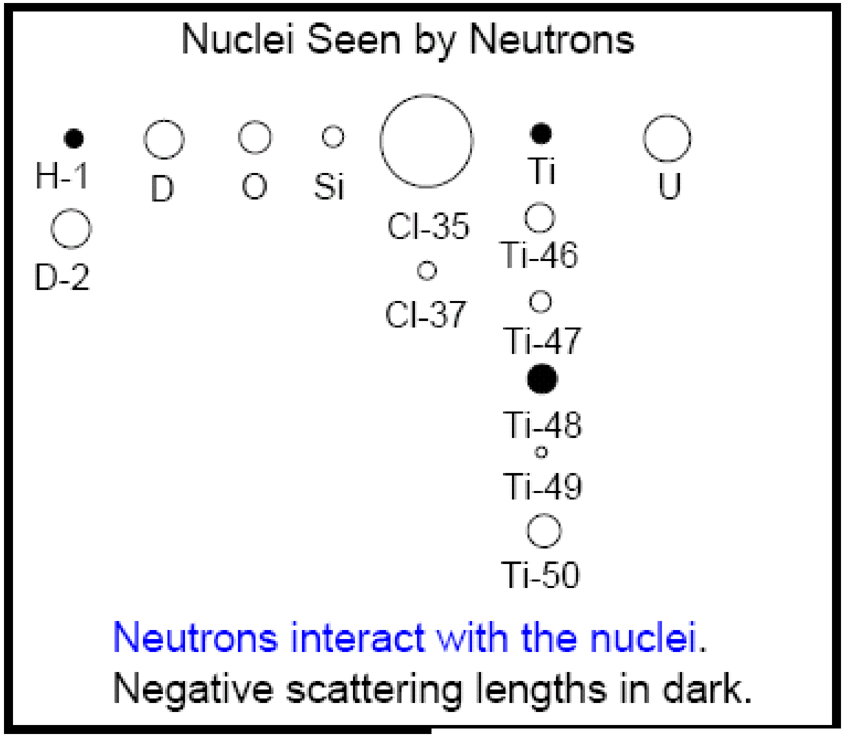
WHY USE NEUTRONS?

-- Neutrons interact through short-range nuclear interactions. They have no charge and are very penetrating and do not destroy samples.

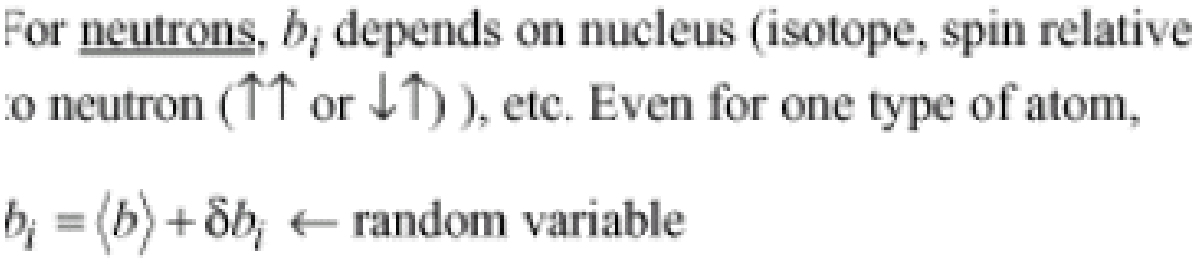
-- Neutron wavelengths are comparable to atomic sizes and interdistance spacings.

-- Neutrons interactions with hydrogen and deuterium are widely different making the deuterium labeling method an advantage.





In the case of light or X-rays, the scattering cross-section of an atom (a concept which may be likened to the collision cross-section encountered in the classical derivation of chemical kinetic theory) increases in direct proportion to the number of electrons present; that is, it increases with increasing atomic number, Z. However, the strength of the neutron-nucleus interaction varies completely irregularly with Z; not even isotopes of the same element have the same *neutron scattering cross-section*, σ . The most significant isotopic variation occurs when Z = 1. Hydrogen has a (coherent) σ_{coh} of 1.75´ 10^{-24} cm^{2} (or, in physicists units, 1.75 barns) which is roughly the same as that of manganese. On the other hand, for deuterium σ_{coh} = 5.6 barns, similar to the value for carbon-12. Thus, and unlike X-rays, not only can neutrons "see" hydrogen isotopes, but they can differentiate between them.


For <u>neutrons</u>, b_i depends on nucleus (isotope, spin relative o neutron (↑↑ or ↓↑)), etc. Even for one type of atom,

$$b_i = \langle b \rangle + \delta b_i \leftarrow \text{random variable}$$

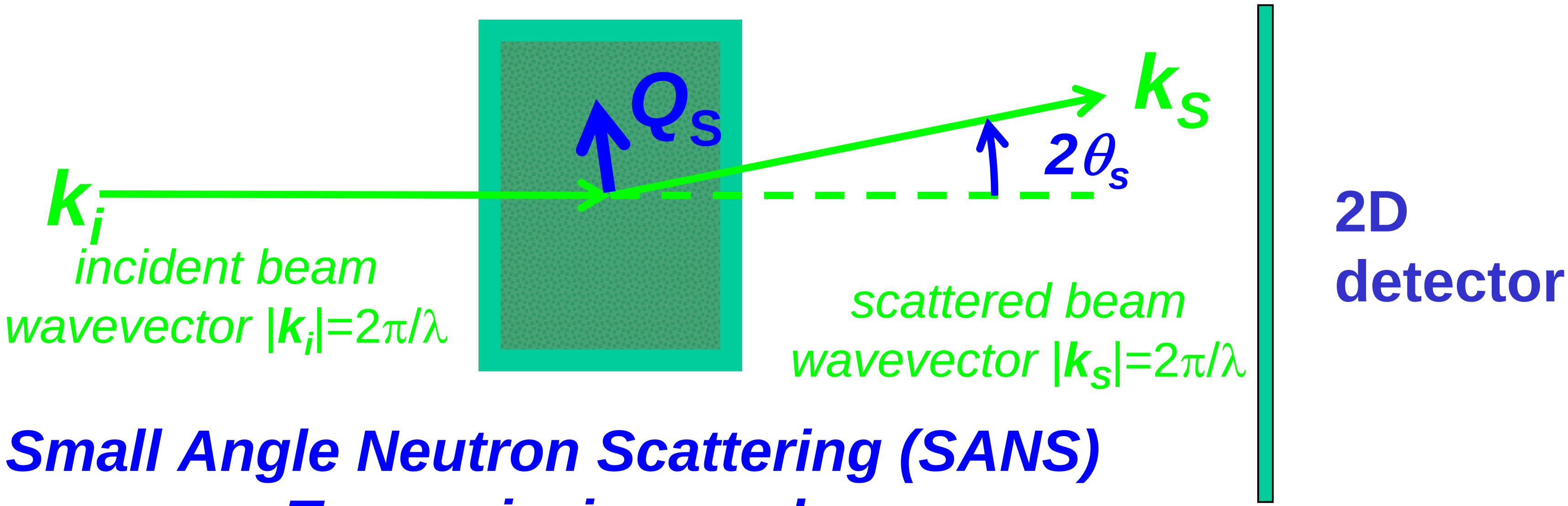
- Neutron “contrast variation” provides powerful and often unique insights.
- Carefully designed experiments provide information on much more than “structure” alone.

The Neutron has Both Particle-Like and Wave-Like Properties

- Mass: $m_n = 1.675 \times 10^{-27}$ kg
- Charge = 0; Spin = ½
- Magnetic dipole moment: $\mu_n = -1.913\, \mu_N$
- Nuclear magneton: $\mu_N = eh/4\pi m_p = 5.051 \times 10^{-27}$ J T^{-1}
- Velocity (v), kinetic energy (E), wavevector (k), wavelength (λ), temperature (T).
- $E = m_n v^2/2 = k_B T = (hk/2\pi)^2/2m_n$; $k = 2\pi/\lambda = m_n v/(h/2\pi)$

	Energy (meV)	**Temp (K)**	**Wavelength (nm)**
Cold	**0.1 – 10**	**1 – 120**	**0.4 – 3**
Thermal	**5 – 100**	**60 – 1000**	**0.1 – 0.4**
Hot	**100 – 500**	**1000 – 6000**	**0.04 – 0.1**

λ (nm) = 395.6 / v (m/s)
E (meV) = $0.02072\, k^2$ (k in nm^{-1})



$\mathbf{k}_i$

incident beam wavevector $|\mathbf{k}_i|=2\pi/\lambda$

$\mathbf{Q}_S$

$\mathbf{k}_S$

$2\theta_s$

scattered beam wavevector $|\mathbf{k}_S|=2\pi/\lambda$

2D detector

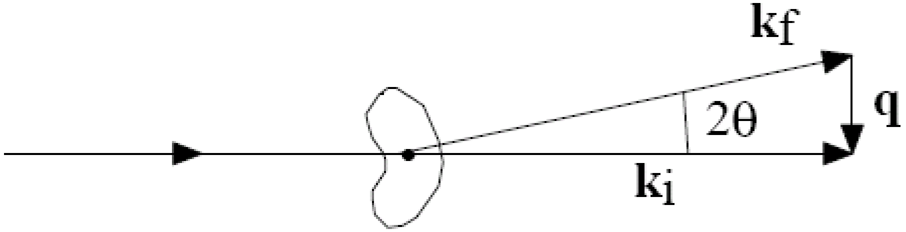
Small Angle Neutron Scattering (SANS) Transmission mode

(elastic scattering) $\mathbf{k}_S = \mathbf{k}_i+\mathbf{Q}_s$

$Q_s=|\mathbf{Q}_s|=4\pi \sin\theta_s / \lambda$

A diffraction pattern is obtained (not a direct image)

- **Rather than use scattering angle $2\theta_s$ to show the diffraction pattern we use the scattering vector Q (in “reciprocal space”**



Constructive interference from structures in the direction of **q**

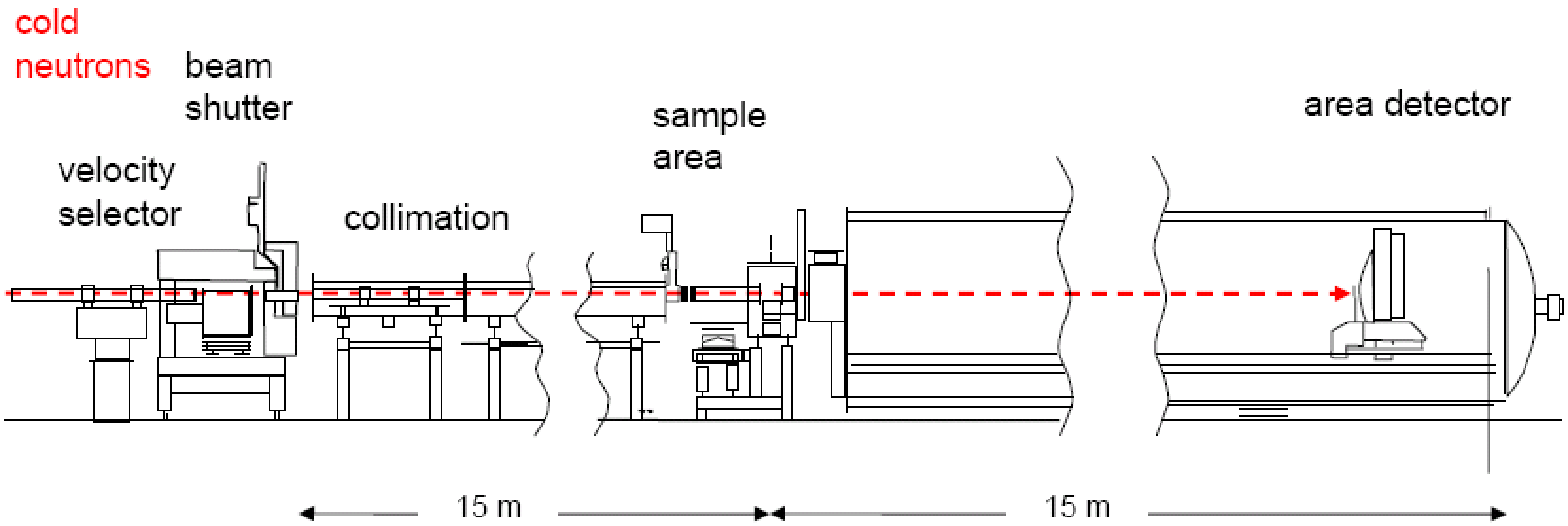
Diffraction length scale $d \approx 2\pi / q$

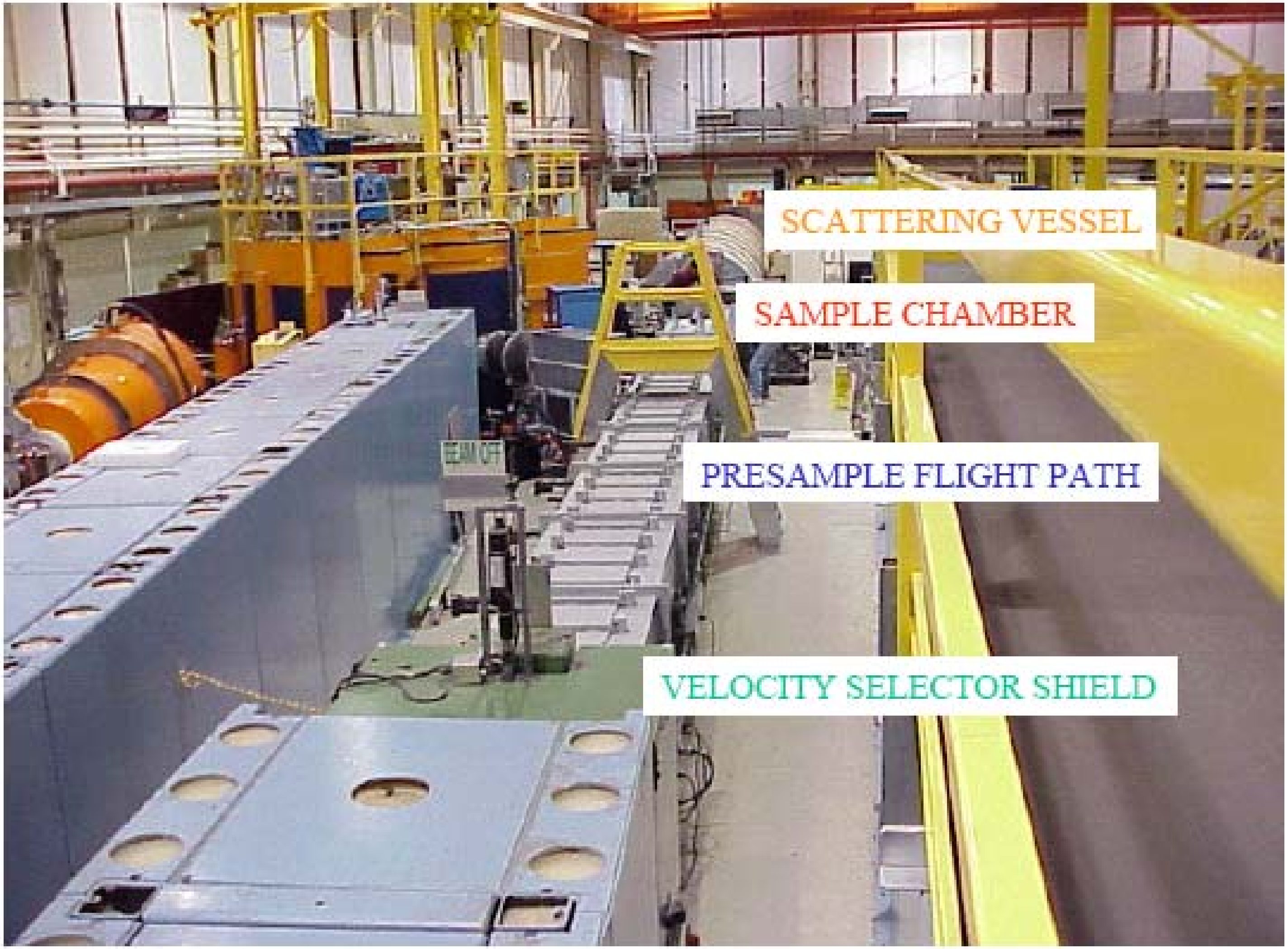
$$2\theta \approx \frac{\lambda}{d} \approx \frac{6\dot{A}}{60 \text{ to } 1000\dot{A}}$$

$$2\theta \approx 0.3^\circ \text{ to } 5^\circ$$

Scattering is at small angles - non-zero but smaller than classical diffraction angles

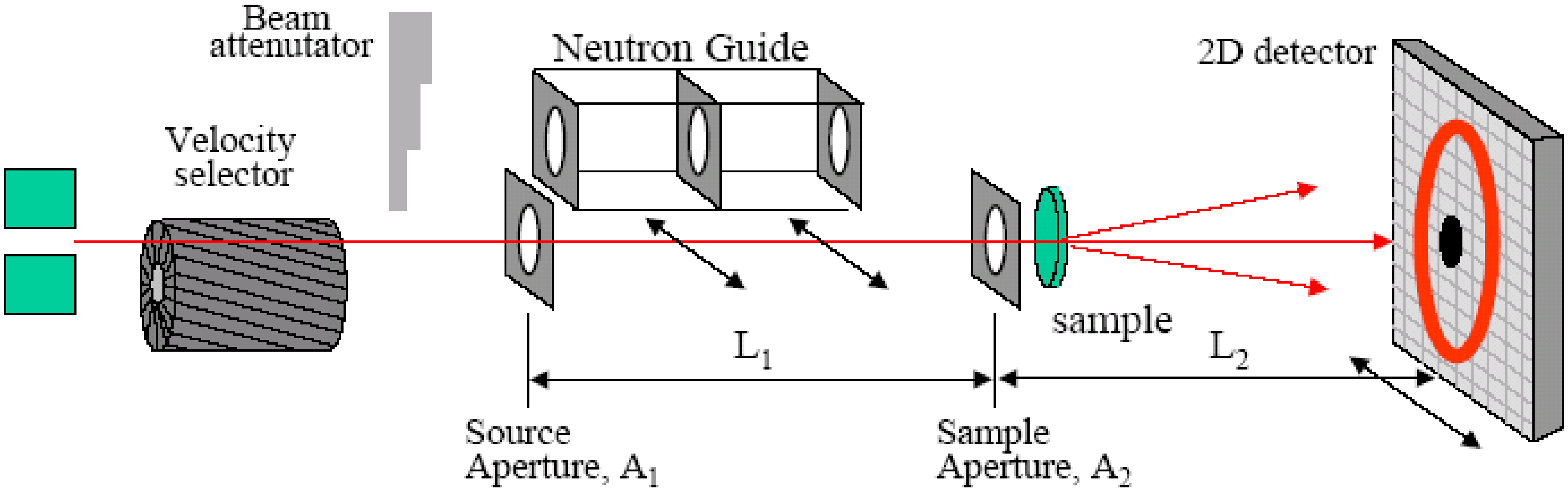
The NG3 30 m NIST-SANS Instrument




SCATTERING VESSEL
SAMPLE CHAMBER
BEAM OFF
PRESAMPLE FLIGHT PATH
VELOCITY SELECTOR SHIELD

30 m NIST-SANS Instrument Characteristics

Source:	neutron guide (NG3), 6 x 6 cm^2
Monochromator:	mechanical velocity selector with variable speed and pitch
Wavelength Range:	variable from 5 Å to 20 Å
Wavelength Resol.:	10% to 30% for $\Delta\lambda/\lambda$ (FWHM)
Source-to-Sample Dist.:	3.5 to 15m in 1.5m steps via insertion of neutron guides
Sample-to-Detector Dist.:	1.3 to 13.2 m continuously variable for NG3
Collimation:	circular pinhole collimation
Sample Size:	0.5 to 2.5 cm diameter
Q-range:	0.001 to 0.6 Å^{-1}
Size Regime:	10 Å to 6000 Å
Detector:	64 x 64 cm^2 He-3 position-sensitive area detector proportional counter (0.5 cm^2 resolution).

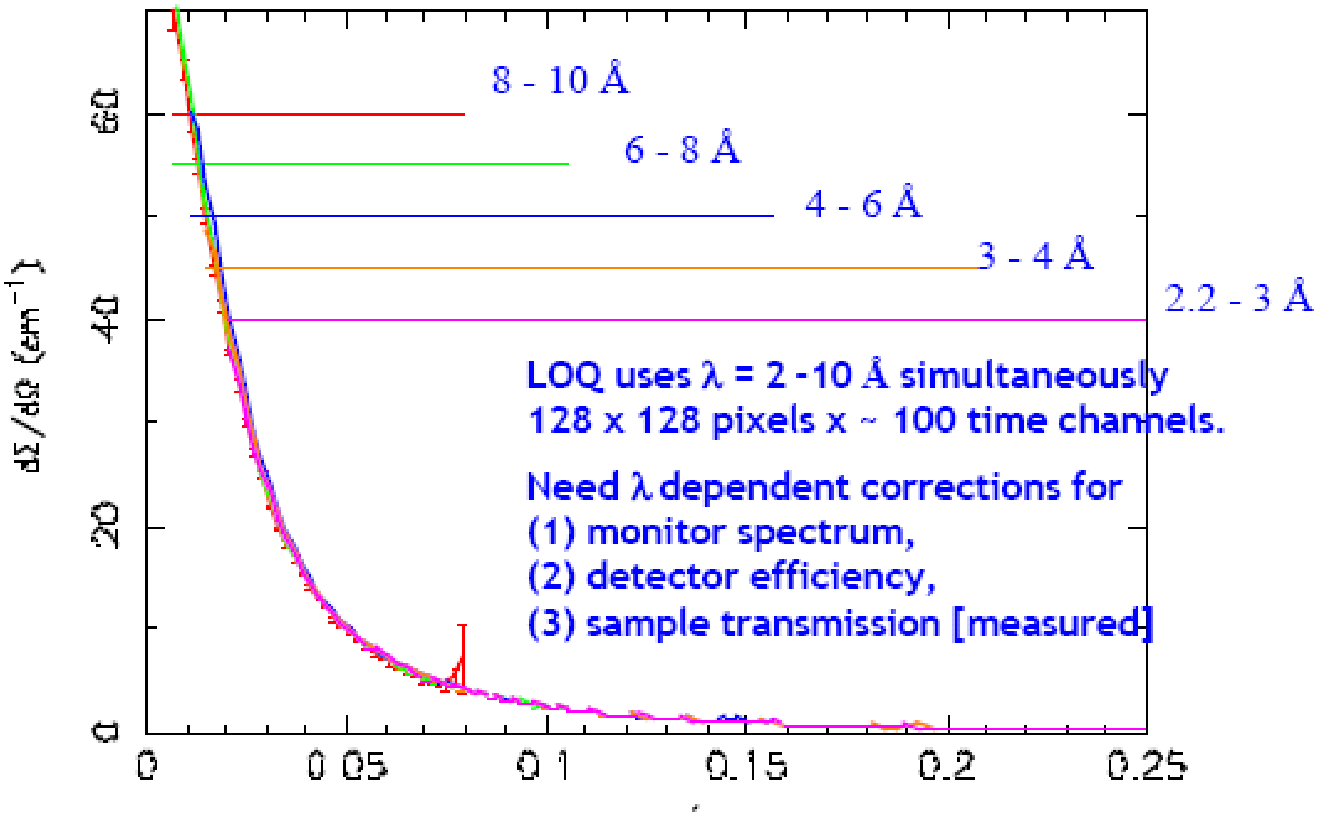


Why such a long instrument ?

When you perform an experiment you'll always try to have as much intensity as possible with a good resolution (δQ). Essentially $L_1 \approx L_2$

TOF instruments

LOQ data reduction, (e.g. for 49% d-PS/ h-PS)



LOQ uses λ = 2 -10 Å simultaneously
128 x 128 pixels x ~ 100 time channels.

Need λ dependent corrections for
(1) monitor spectrum,
(2) detector efficiency,
(3) sample transmission [measured]

$$Q = \frac{4\pi}{\lambda}\sin(\theta/2)$$

R.K.Heenan, J.Penfold & S.M.King, J.Appl.Cryst. 30(1997)1140-1147

Small Angle Samples

Neutrons –

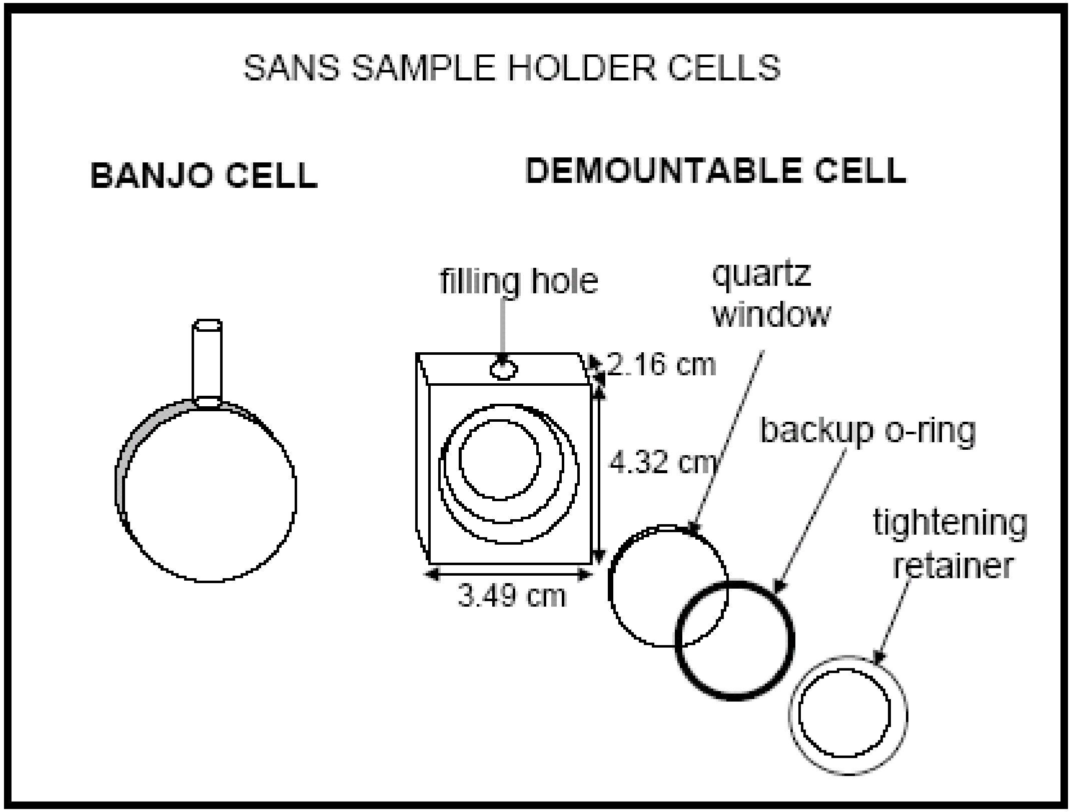
- 8-12 mm diameter beam
- 1mm thick (2mm in D_2O)
- Quartz glass cells
  (as for UV spectroscopy, no Boron which adsorbs neutrons, as does Cadmium)
- Pressure, shear cells, cryostat, furnace etc, fairly easy

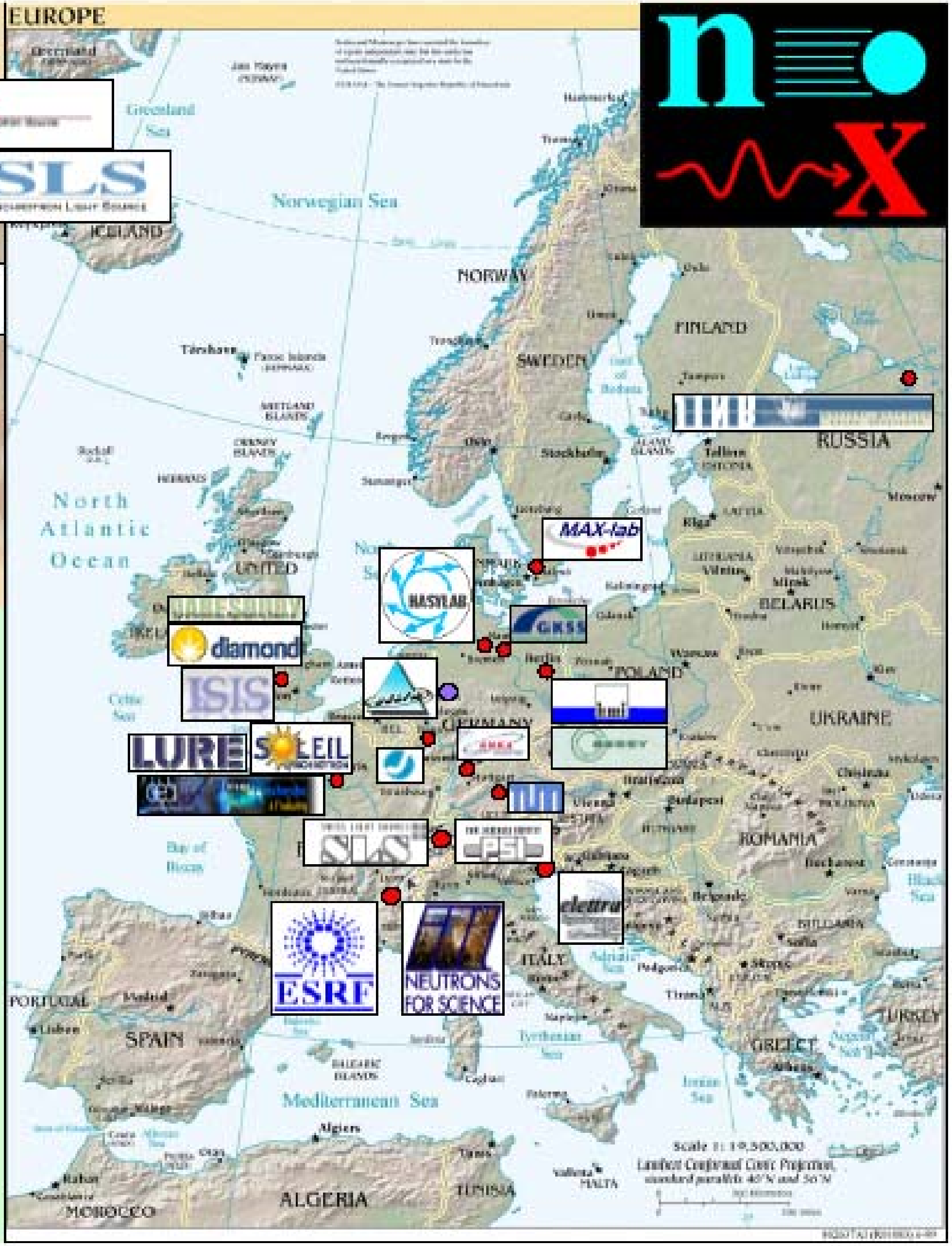
X-Rays –

- << 1mm beam
- Thin samples
- Mica window cells
- Radiation damage and/or heating ?
- Powerful synchrotron X-ray beams do now allow more complex sample environment – but samples still fry!

SANS SAMPLES AND CELL HOLDERS

SANS samples can be solid, gels, solutions or powders.
Sample thicknesses are 1 mm to 2 mm.
Sample diameter can vary between 0.5 cm and 2 cm.





Synchrotron- and Neutron Scattering Places

- Easier to think in terms of material properties rather than atomic properties
- Define a "Scattering Length Density"

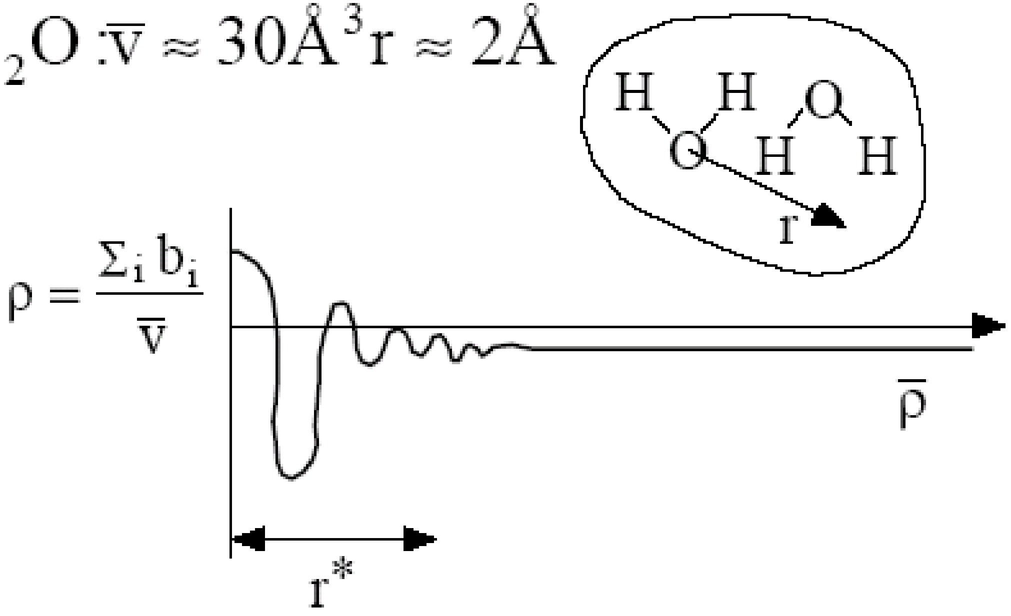
$$\rho(\vec{r}) = b_i\delta(\vec{r} - \vec{r}_i)$$

or

$$\rho = \frac{\sum_{i}^{n} b_i}{\overline{V}}$$

$\overline{V}$ is the volume containing the n atoms

- Can we really use scattering length densities?
- consider $H_2O : \bar{v} \approx 30\text{Å}^3 \, r \approx 2\text{Å}$



$$1/q > r^* \quad r^* \approx 10\text{Å} \quad q \leq 0.1\text{Å}^{-1}$$

≈ 100 molecules

- We can use material properties rather than atomic properties when doing small-angle scattering

Neutron scattering length densities

$$\rho = \frac{\sum n_i b_i}{V}$$

V can be any suitable volume, e.g. one molecule

$$V_{MOLAR} = \frac{\rho_{BULK} N_A}{M}$$

e.g. water $$V = \frac{1.0 g.cm^{-3}\, 6.023\times10^{23}}{18.0152 g.mol^{-1}} = 29.915\times10^{-24} cm^3 = 29.915 \quad Å^3$$

H_2O $$\rho = \frac{(2\times(-0.3739)+0.580)\times10^{-12} cm}{29.915\times10^{-24} cm^3} = -0.56\times10^{10} cm^{-2}$$

D_2O $$\rho = \frac{(2\times0.667+0.580)\times10^{-12} cm}{29.915\times10^{-24} cm^3} = 6.40\times10^{10} cm^{-2}$$

NOTE units of length per unit volume!

$\times 10^{10}$ cm^{-2} is the same as **$\times 10^{-6}$ Å^{-2}**, **1Å = 10^{-8} cm = 0.1nm**

^{1}H (^{7}Li, ^{62}Ni, ^{48}Ti etc) have a negative *b* due to phase shift via neutron spin interaction.

Digression - useful units!

Distances in Angstrom, 1 Å = 10^{-10} m = 10^{-8} cm = 0.1 nm

Scattering lengths are in femtometres, 1 fm = 10^{-15} m

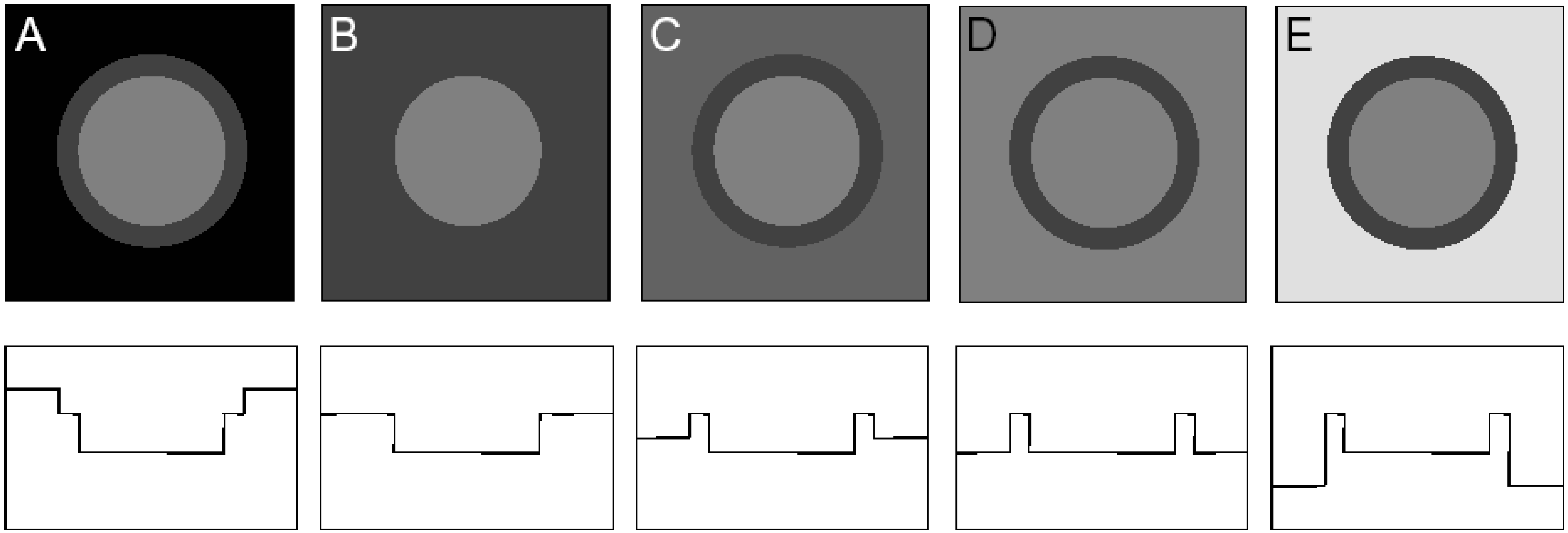
Total and absorption cross sections in "barns", 1 barn = 10^{-24} cm^2

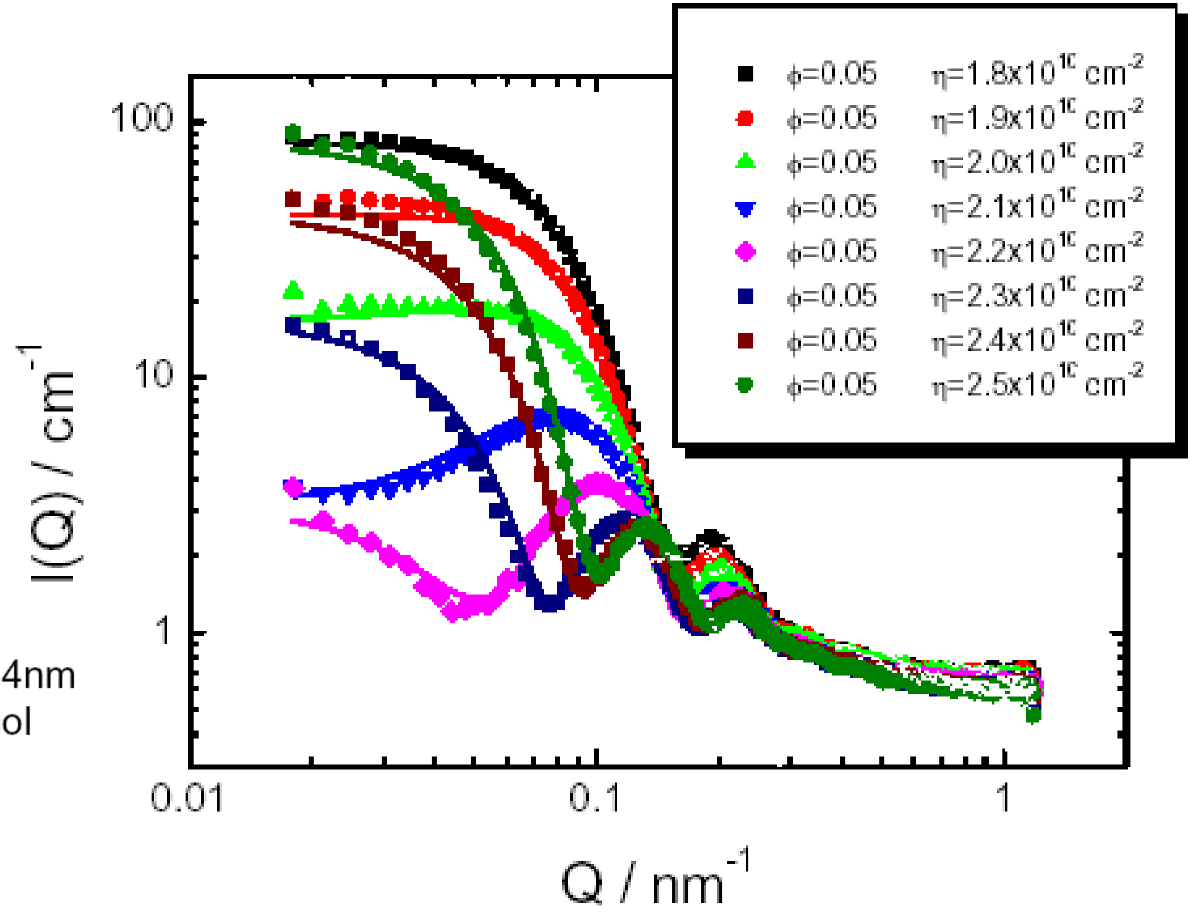
Neutron wide angle diffraction scattering cross sections are often "barns per molecule" or "barns per atom"

To go from SANS type cm^{-1} to barns per molecule (both have implied "per steradian" for scattering probability per unit solid angle) multiply by V_{MOLAR} in Å^3.

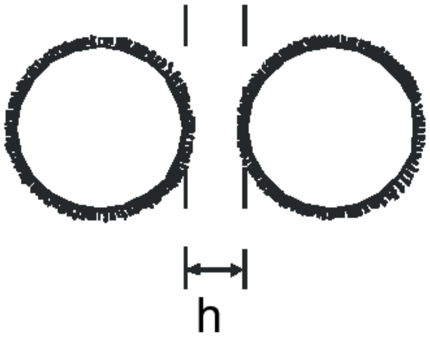
$$
\begin{aligned}
(\partial\Sigma/\partial\Omega)\,[\mathrm{cm}^{-1}] \times V\,[\text{Å}^3] &= (\partial\Sigma/\partial\Omega)\,[\mathrm{cm}^{-1}]\,V\,[10^{-24}\,\mathrm{cm}^3] \\
&= (\partial\Sigma/\partial\Omega)'\,[\,10^{-24}\,\mathrm{cm}^2] \\
&= (\partial\Sigma/\partial\Omega)'\,[\mathrm{barns}]
\end{aligned}
$$

matching the contrast of different parts of a spherical shell by varying solvent deuteration



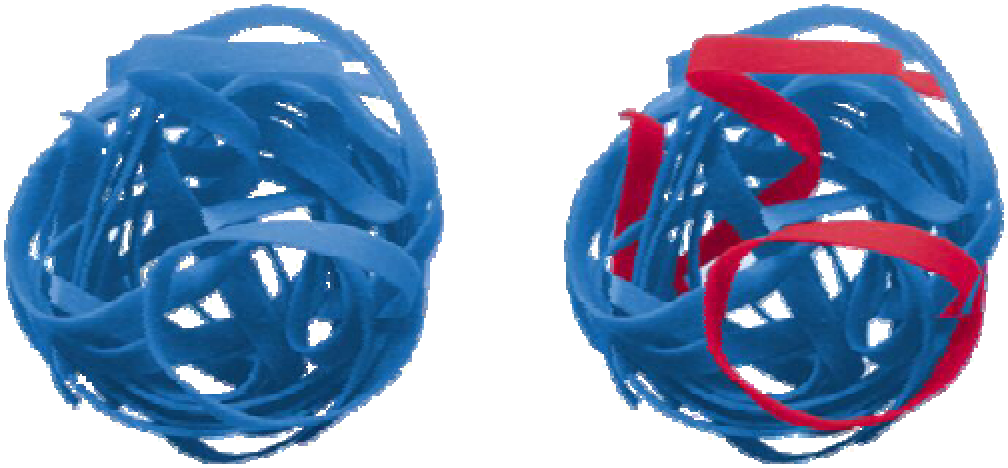


colloidal silica spheres R=34nm
coated with stearyl alcohol
in toluene



Specific deuteration enhances the contrast and/or “strains” parts of a macromolecular complex or single polymer chains in a matrix

contrast variation in polymer melts



Small Angle Neutron Scattering (SANS)

Macromolecular structures: polymers, micelles,complex fluids, precipitates,porous media, fractal structures

Measure: Scattered Intensity => Macroscopic cross section
= (Scattered intensity(Q) / Incident intensity) T d

$$\frac{d\Sigma}{d\Omega}\left[\vec{Q}_S\right]=\frac{\left|\iiint_{V_S}\Delta\rho[\vec{r}]\exp\left[i\vec{Q}_S.\vec{r}\right]d^3\vec{r}\right|^2}{V_S}$$

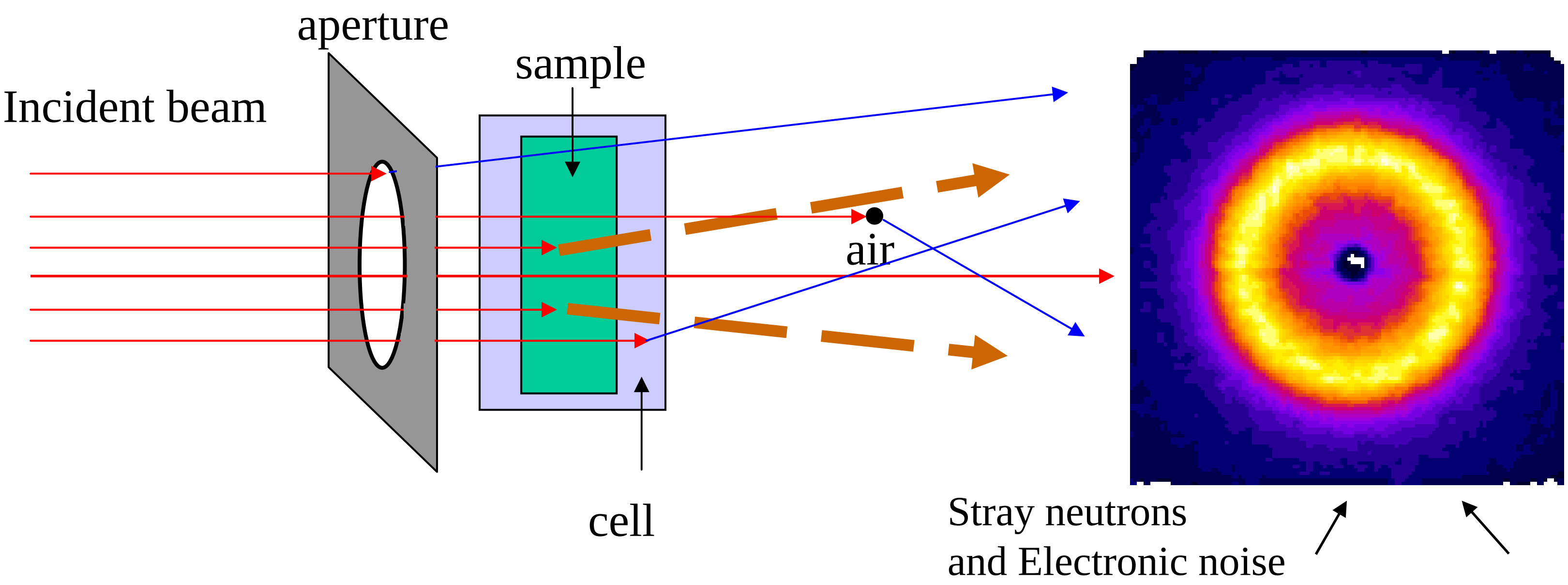
|3-D Fourier Transform of scattering contrast|^2
normalized to sample scattering volume

Reciprocity in diffraction:
Fourier features at Q_S => size d ~ $2\pi/Q_S$
Intensity at smaller Q_S (angle) => larger structures

Sample Scattering

- Contribution to detector counts

1) Scattering from sample
2) Scattering from other than sample (neutrons still go through sample)
3) Stray neutrons and electronic noise (neutrons don’t go through sample)



$$\mathbf{I_{meas}(i) = \Phi\ t\ A\ \varepsilon(i)\ \Delta\Omega\ T_{c+s}[(d\Sigma/d\Omega)_s(i)\ d_s + (d\Sigma/d\Omega)_c(i)\ d_c] + I_{bgd}\ t}$$

SANS DATA ACQUISITION

-- Choose neutron wavelength (λ= 6 Å) and wavelength spread ($\Delta\lambda/\lambda$=15%).

-- Choose source-to-sample distance L_1 and sample-to-detector distance L_2.

-- Choose counting time.

-- Measure scattering:
  - Empty cell scattering
  - Sample scattering
  - Blocked beam scattering

-- Measure transmission:
  - Cell transmission
  - Empty cell transmission

-- Neutron transmission is the ratio of the transmitted beam to the incident beam.

SANS DATA REDUCTION

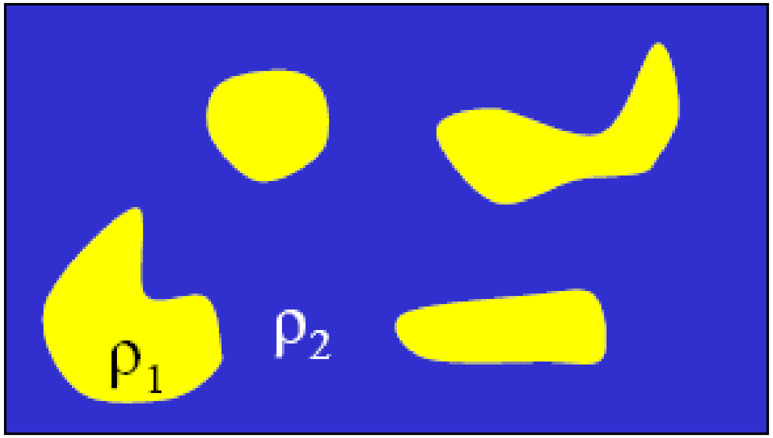
Correct for empty cell and blocked beam scattering.

$$I(Q) = [I_{\text{sample+cell}} - I_{\text{blocked beam}}]/T_{\text{sample+cell}} - [I_{\text{cell}} - I_{\text{blocked beam}}]T_{\text{cell}}$$

Rescale the SANS intensity to an absolute scale (units of cm^{-1}).

Perform the radial averaging for isotropic scattering to obtain the Q-dependent macroscopic cross section $I(Q) = d\Sigma(Q)/d\Omega$.

General Two-Phase System



- Incompressible phases of scattering length density ρ_1 and ρ_2

$$V = V_1 + V_2$$

$$\rho(r) = \begin{cases} \rho_1 \text{ in } V_1 \\ \rho_2 \text{ in } V_2 \end{cases}$$

- break the total volume into two sub-volumes

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{1}{V}\left|\int_{V_1}\rho_1 e^{i\vec{q}\cdot\vec{r}}\,d\vec{r}_1 + \int_{V_2}\rho_2 e^{i\vec{q}\cdot\vec{r}}\,d\vec{r}_2\right|^2$$

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{1}{V}\left|\rho_1\int_{V_1} e^{i\vec{q}\cdot\vec{r}}\,d\vec{r}_1 + \rho_2\left\{\int_{V} e^{i\vec{q}\cdot\vec{r}}\,d\vec{r} - \int_{V_1} e^{i\vec{q}\cdot\vec{r}}\,d\vec{r}_1\right\}\right|^2$$

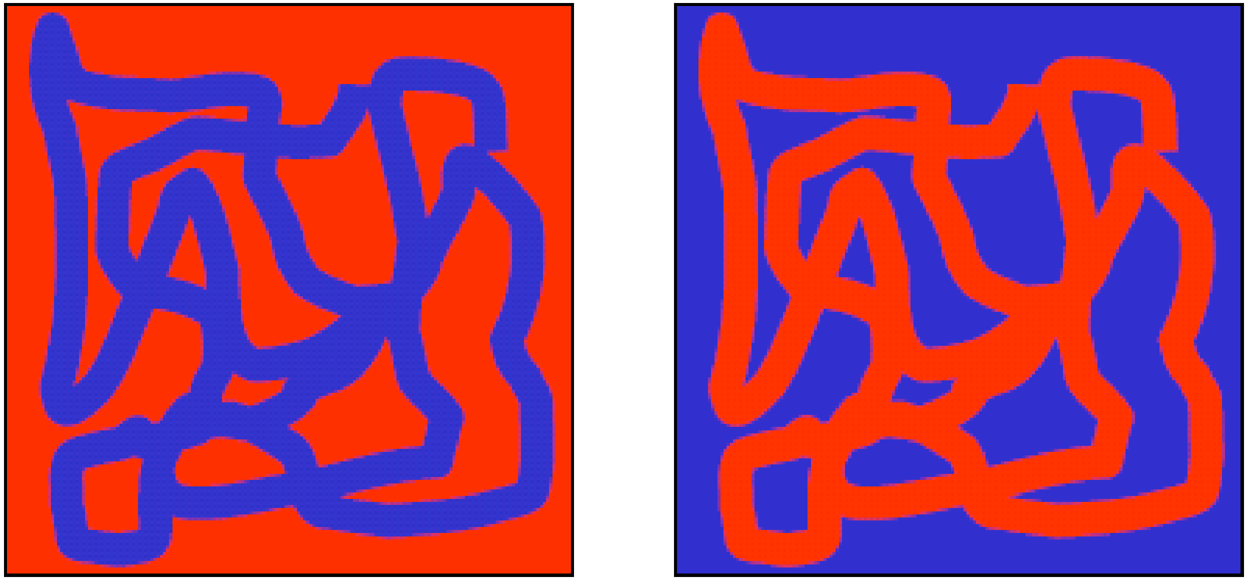
- So at non-zero q-values:

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{1}{V}(\rho_1 - \rho_2)^2\left|\int_{V_1} e^{i\vec{q}\cdot\vec{r}}\,d\vec{r}_1\right|^2$$

Material Properties
+
Radiation Properties

Spatial Arrangement
of Material

Babinet's Principle

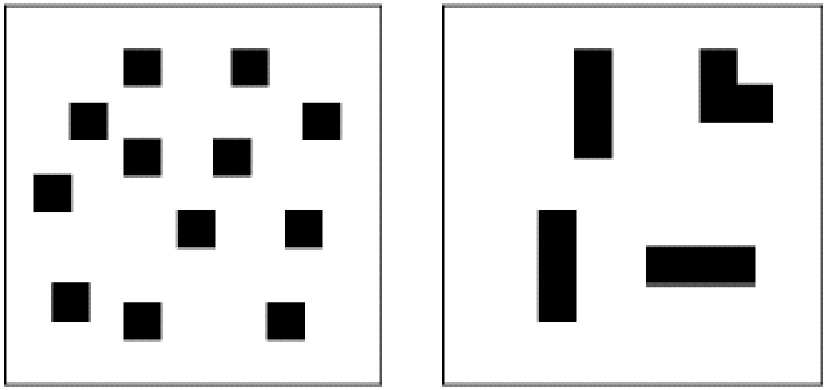


Two structures give the same scattering

$$\frac{d\Sigma}{d\Omega}(\vec{\mathbf{q}}) \propto (\rho_1 - \rho_2)^2$$

*incoherent scattering may be different

Scattering Invariant



10 % black
90 % white
in each square

- Scattered intensity for each would certainly be different

$$Q_I \equiv \int_0^\infty q^2 \frac{d\Sigma}{d\Omega}(q)\, dq$$

- For an incompressible, two-phase system:

$$Q_I = 2\pi^2 \Delta\rho^2 \phi (1 - \phi)$$

- <u>Domains can be in any arrangement</u>

Dilute particles – subtract uniform solvent & sum over one particle:

$$P(Q) = N\int_V \int_V (\rho(\underline{r}_1) - \rho_S)(\rho(\underline{r}_2) - \rho_S)\exp\{-iQ(\underline{r}_1 - \underline{r}_2)\} dV_1 dV_2$$

$$= NV^2(\Delta\rho)^2 F^2(Q)$$

Note NV = ϕ volume fraction

Randomly oriented or centro-symmetric particle, ONLY gives information on average radial density distribution ρ(r) or g(r) :

$$F(Q) = \int 4\pi r^2 \rho(r) \frac{\sin(Qr)}{Qr} dr$$

[This is a Fourier transform: small Q is for large *r*, high Q for small *r*]

SANS from Dilute (i.e. Independent) Particles

"Dilute" means:

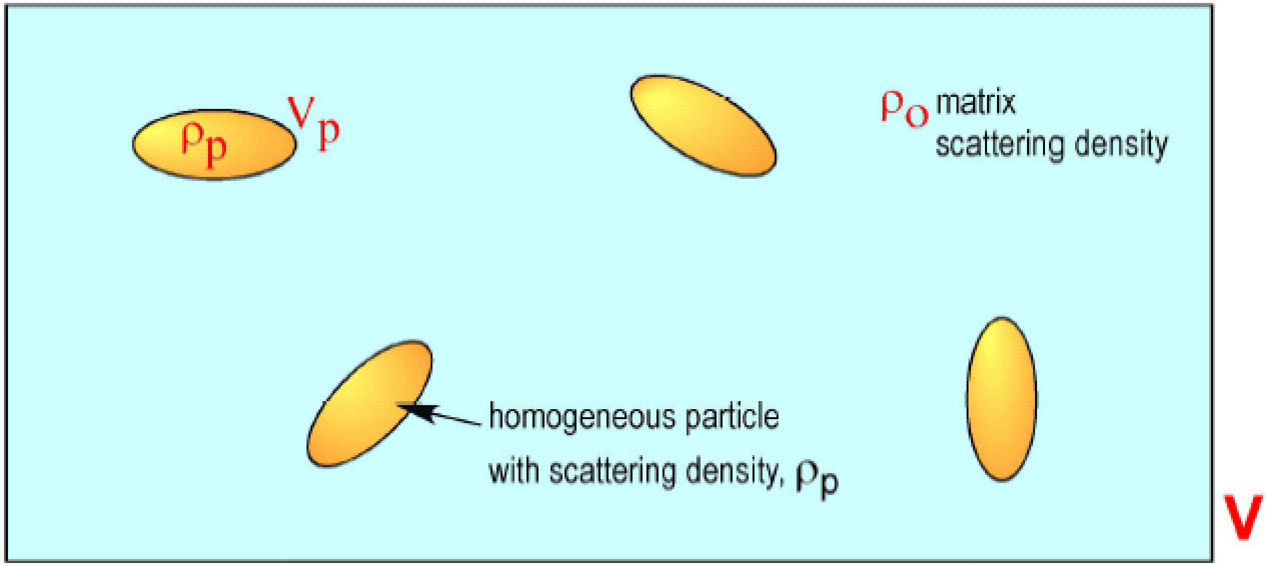
- no correlation between positions or orientations of particles

"Particle" means:

- any discrete submicron scale material inhomogeniety

Simple (uniform) Particles
- macromolecules, e.g., proteins, polymer chains
- single phase precipitates in metal alloys
- voids, pores, microcracks, etc.
- simple colloids, e.g., latex

Scattering from Dilute, Homogeneous Particles



$$I(\vec{Q}) \propto \frac{d\Sigma(\vec{Q})}{d\Omega} = \frac{1}{V}\left|\int_V \rho(\vec{r})\, e^{i\vec{Q}\cdot\vec{r}}\, d\vec{r}\right|^2$$

for identical particles

$$\frac{d\Sigma(\vec{Q})}{d\Omega} = \frac{N}{V}\left(\rho_p - \rho_o\right)^2 V_p^2 \left|\frac{1}{V_p}\int e^{i\vec{Q}.\vec{r}}\, d\vec{r}\right|^2$$

Contrast Factor

Particle Shape

$$\left|F_p(\vec{Q})\right|^2$$ Form Factor

SANS From Randomly Oriented Particles

- Guinier Approximation for Low-Q Scattering

average over orientations

$$I_p(Q) \propto \frac{d\Sigma(Q)}{d\Omega} = \frac{1}{V}\left\langle \left| \int_V \rho(\vec{r})\, e^{i\vec{Q}\cdot\vec{r}}\, d\vec{r} \right|^2 \right\rangle$$

$$\frac{d\Sigma(Q)}{d\Omega} = \frac{1}{V}\iint_V \rho(\vec{r})\rho(\vec{r}\,')\left\langle e^{i\vec{Q}\cdot(\vec{r}-\vec{r}\,')} \right\rangle d\vec{r}\, d\vec{r}\,'$$

$$\frac{\sin(Q|\vec{r}-\vec{r}\,'|)}{Q|\vec{r}-\vec{r}\,'|} \sim 1 - \frac{1}{6}(Q|\vec{r}-\vec{r}\,'|)^2 + \ldots$$

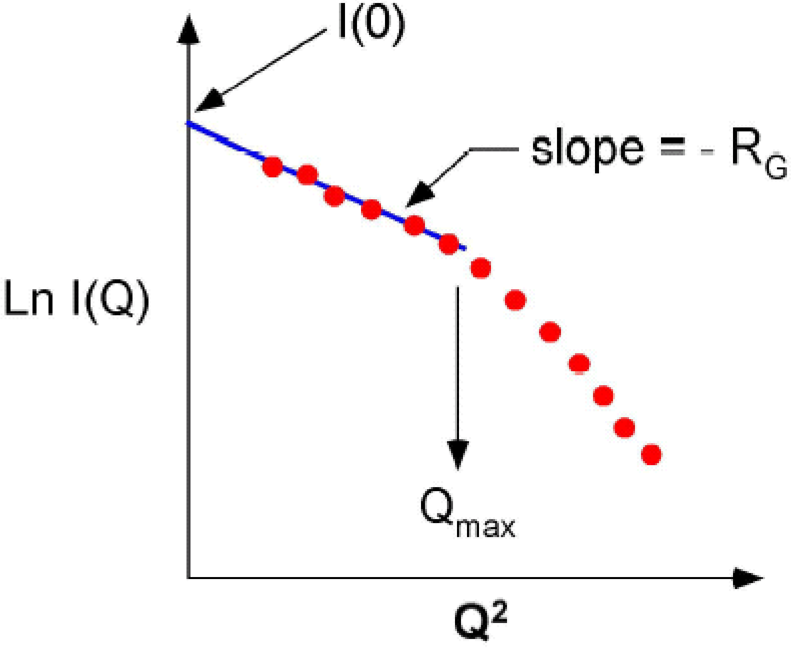
$$\vdots$$

$$\frac{d\Sigma(Q)}{d\Omega} = \frac{1}{V}\left(\int_V \rho(\vec{r})\, d\vec{r} \right)^2 \left[1 - \frac{1}{3}Q^2 R_G^2 + \ldots \right]$$

$$I_p(Q) \cong I_p(0)\, e^{-\frac{1}{3}Q^2 R_G^2} \quad \text{when } Q R_G \le 1, \quad \text{Guinier law}$$

Guinier Appoximation: $I(Q) \cong I(0)e^{-\frac{1}{3}R_G^2Q^2}$

Guinier Plot $\ln[I(Q)] = \ln[I(0)] - Q^2R_G^2/3$

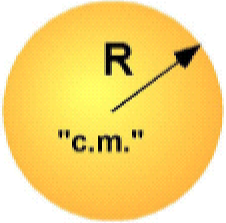


$$Q_{max}R_G \leq 1$$

Guinier Radius, R_G

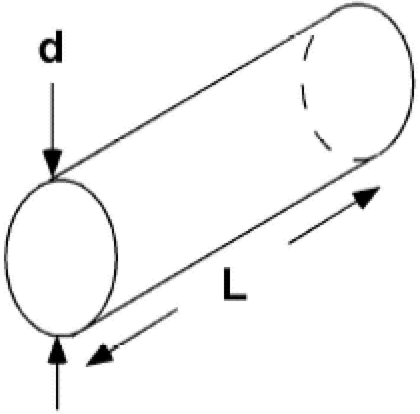
- rms distance from "center of scattering density"

1) Spherical Particles



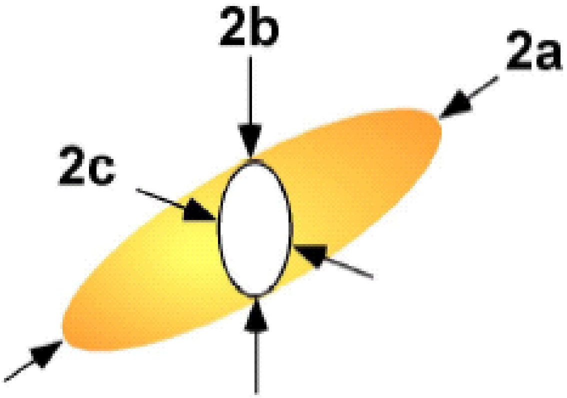
$$R_G^2 = \langle r^2 \rangle = \frac{\int \eta(\vec{r})\, r^2 \, d\vec{r}}{\int \eta(\vec{r})\, d\vec{r}} = \frac{3}{5} R^2$$

2) Cylinders (Rods or Disks)



$$R_G^2 = \frac{L^2}{12} + \frac{d^2}{8}$$

3) Ellipsoids (major axes 2a, 2b, 2c)



$$R_G^2 = \frac{1}{5}(a^2 + b^2 + c^2)$$

4) Gaussian chain

$$R_G^2 = \frac{1}{6}\overline{L^2} \quad \overline{L^2} =$$ **average square of the end-to-end distance**

From Scattering Extrapolated to Q=0

$$I(0) \propto \frac{d\Sigma(0)}{d\Omega} = \frac{1}{V}\left(\int_V \rho(\vec{r})\, d\vec{r}\right)^2$$

$$\frac{d\Sigma(0)}{d\Omega} = \frac{N}{V}\left(\rho_p - \rho_o\right)^2 V_p^2 \longleftarrow$$

for N uniform particles in volume, V, each with sld ρ_p and volume, V_p

in terms of:

c(particle concentration) [mg/ml] = $\dfrac{N \rho V_p}{V}$

M_W (particle molecular weight) = $\rho V_p N_A$

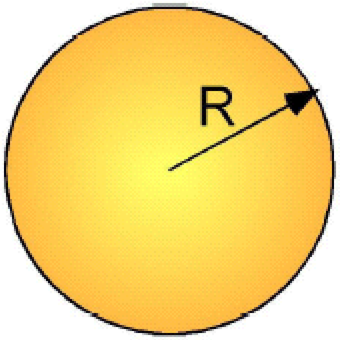
$$\frac{d\Sigma(0)}{d\Omega} = \frac{c\,\mathbf{M_W}}{\rho N_A}\left(\rho_p - \rho_o\right)^2$$

N_A = Avogadro's number

ρ = mass density

Form Factors for Some Simple Particle Shapes:

1) Spheres



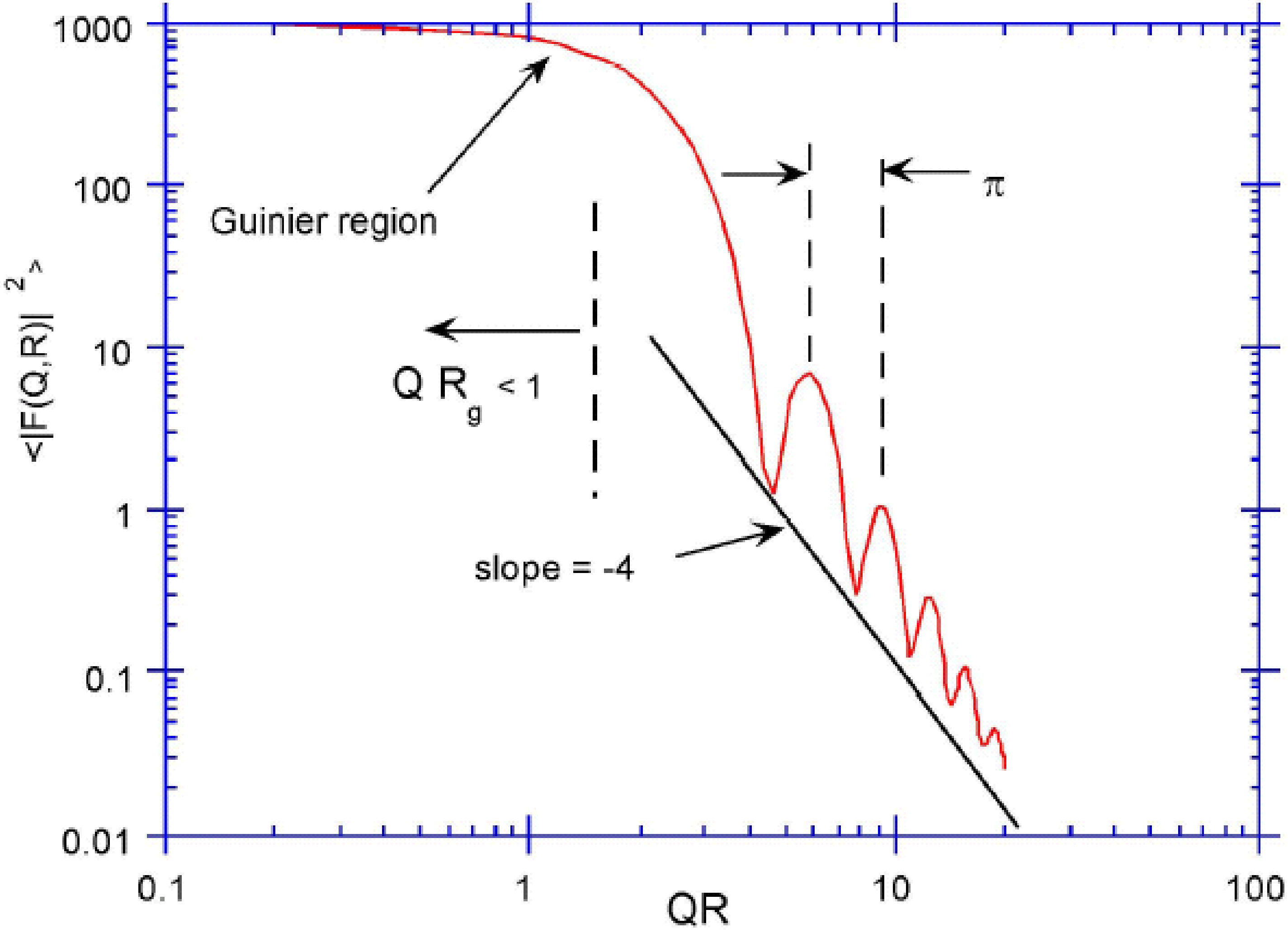
$$\left\langle |F(Q,R)|^2 \right\rangle = \left\langle \left| \frac{1}{V_p} \int_{V_p} e^{i\vec{Q}.\vec{r}}\, d\vec{r} \right|^2 \right\rangle$$

$$\left\langle |F(Q,R)|^2 \right\rangle = 9\left[\frac{\sin(QR) - QR\cos(QR)}{(QR)^3} \right]^2$$

$$I(Q) = NV^2(\Delta\rho)^2 P(Q) + BKG$$

$$P(Q) = F^2(Q,r) \rightarrow 1 \;\; as \;\; Q \rightarrow 0$$

(Form Factor) ^{2} for Monodispersed Spheres



Cylinder (rod or disc)

$$I(Q) = N(\Delta\rho)^2 V^2 \int_0^{\pi/2} F^2(Q)\sin(\gamma)d\gamma$$

$$F(Q) = \frac{\sin(\frac{1}{2}QL\cos\gamma)}{\frac{1}{2}QL\cos\gamma}\frac{2J_1(QR\sin\gamma)}{QR\sin\gamma}$$

Randomly oriented rods full length L, radius R, $V = \pi R^2 L$

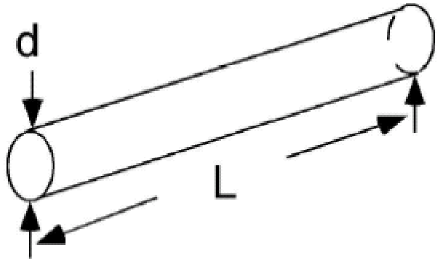
$J_1(x)$ = "first order Bessel function of the first kind"
is NOTsame as $j_1(x)$ on next slide!

As $x \rightarrow 0$, $J_1(x)/x \rightarrow ½$ & $\sin(x)/x \rightarrow 1$ so $P(Q \rightarrow 0)=1$

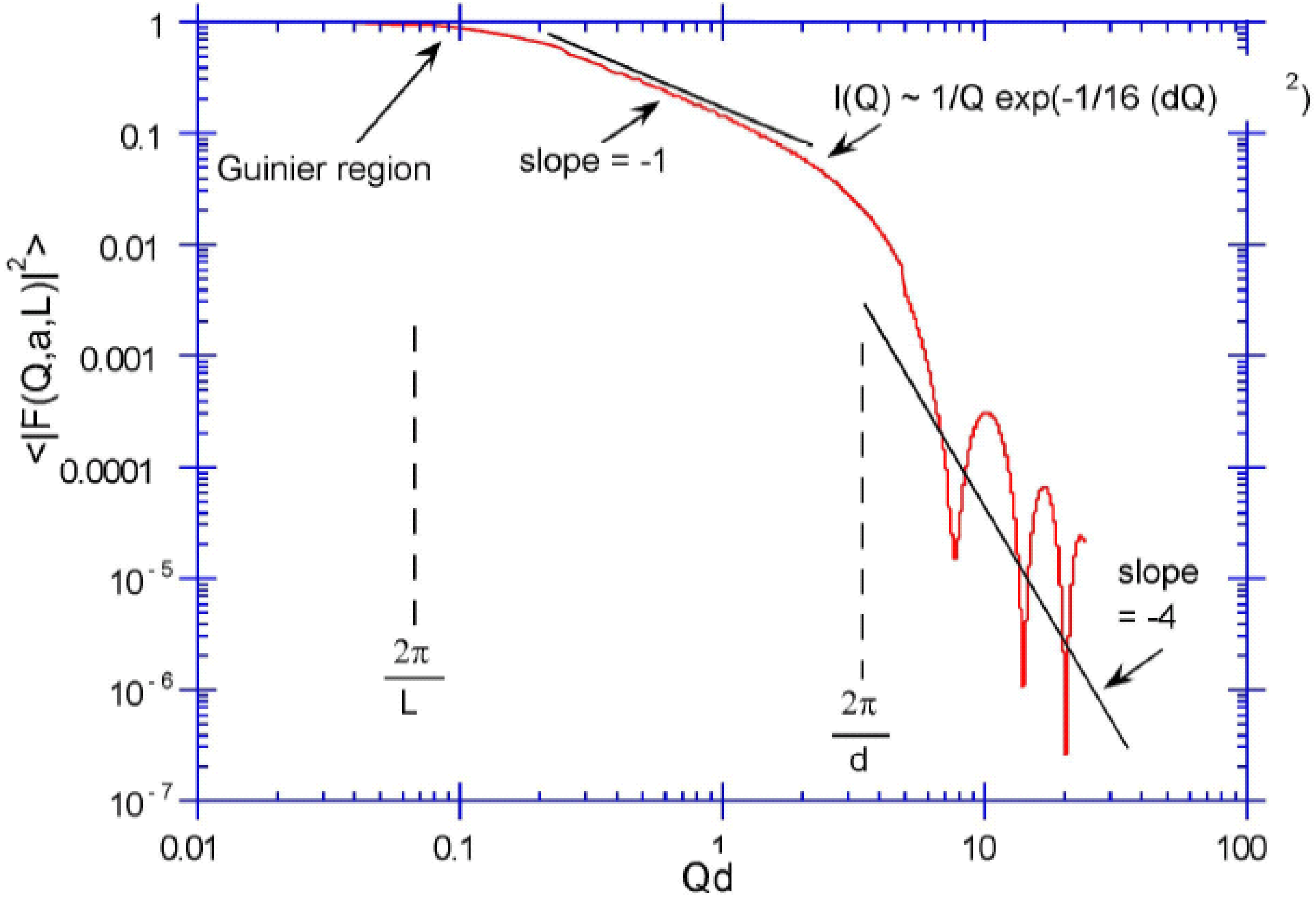
Integrate numerically over γ = angle between **Q** and rod axis.

Form Factors for Some Simple Particle Shapes:

2) Long Rods:

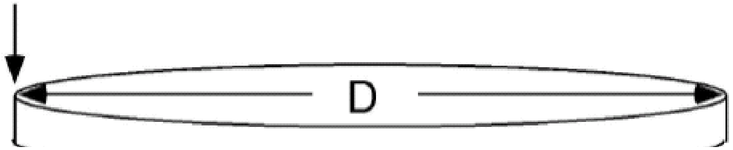


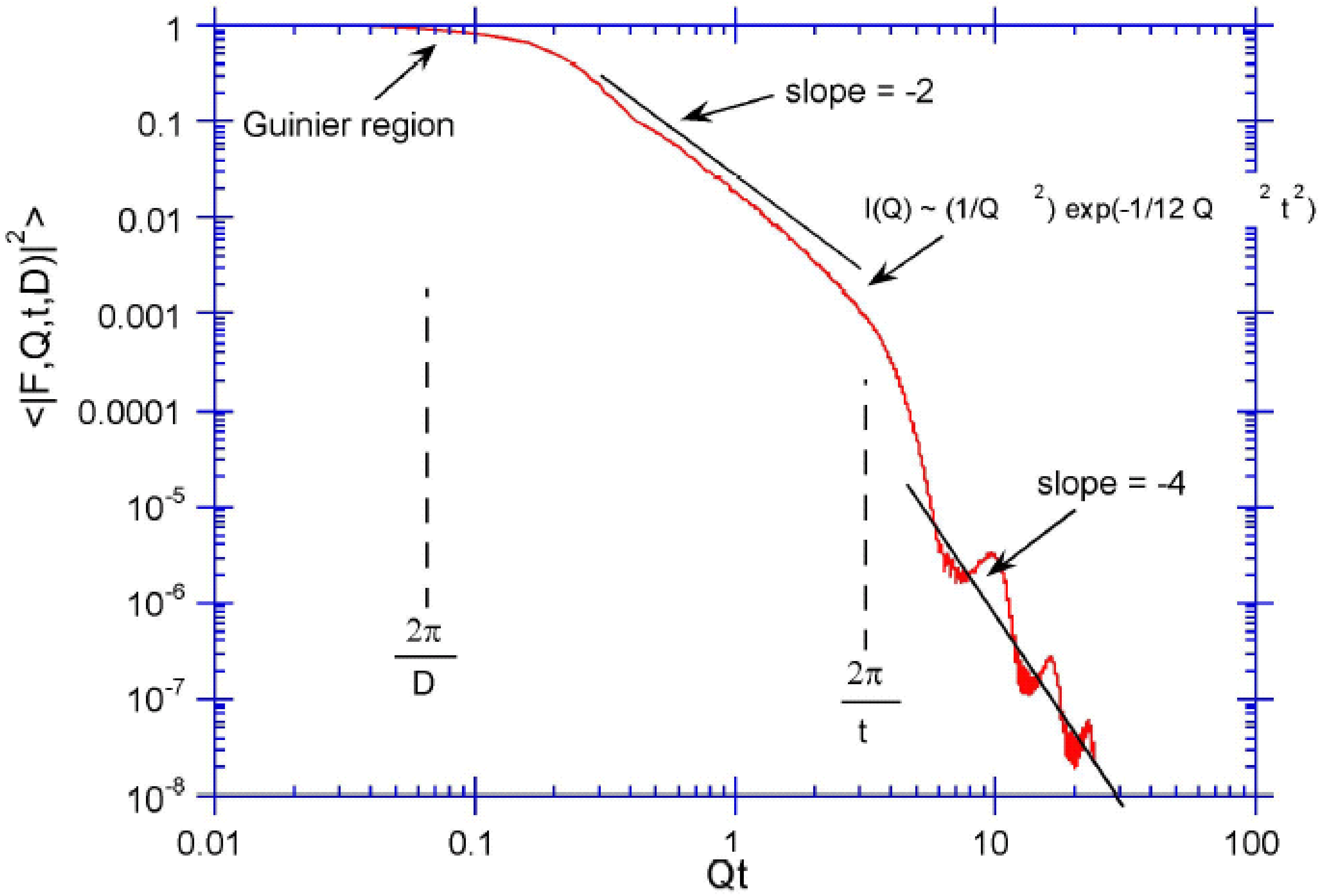
(Form Factor) ^{2} for Rods of and diameter, d = 4 nm



Form Factors for Some Simple Shapes:

3) Thin Disks




$(\text{Form Factor})^2$ for Thin Disks of Diameter, D = 80 nm, and Thickness, t = 4 nm

Ellipsoid

ellipsoid radii R, R, and XR

X>1 prolate (~ rugby ball),

X<1 oblate (~ pumpkin), X=1 sphere.

$$V = \tfrac{4\pi}{3} X R^3$$

$$I(Q) = N(\Delta\rho)^2 V^2 \int_0^{\pi/2} F^2(u)\sin(\gamma)d\gamma$$

$$F(u) = \frac{j_1(u)}{u} = \frac{3(\sin(u) - u\cos(u))}{u^3} \qquad u = QR\left(\sin^2\gamma + X^2\cos^2\gamma\right)^{1/2}$$

Note *F(u)* is same as *F(QR)* for sphere!

Change of variable to $\mu = \cos(\gamma)$ makes computation simpler:

$$I(Q) = N(\Delta\rho)^2 V^2 \int_0^1 F^2(u)d\mu \qquad u = QR\left((1-\mu^2) + X^2\mu^2\right)^{1/2}$$

Can be hard to distinguish X<1 and X>1, and also polydisperse spheres - absolute intensities, shape at high Q, and S(Q) may help.

Gaussian coil (ideal polymer)

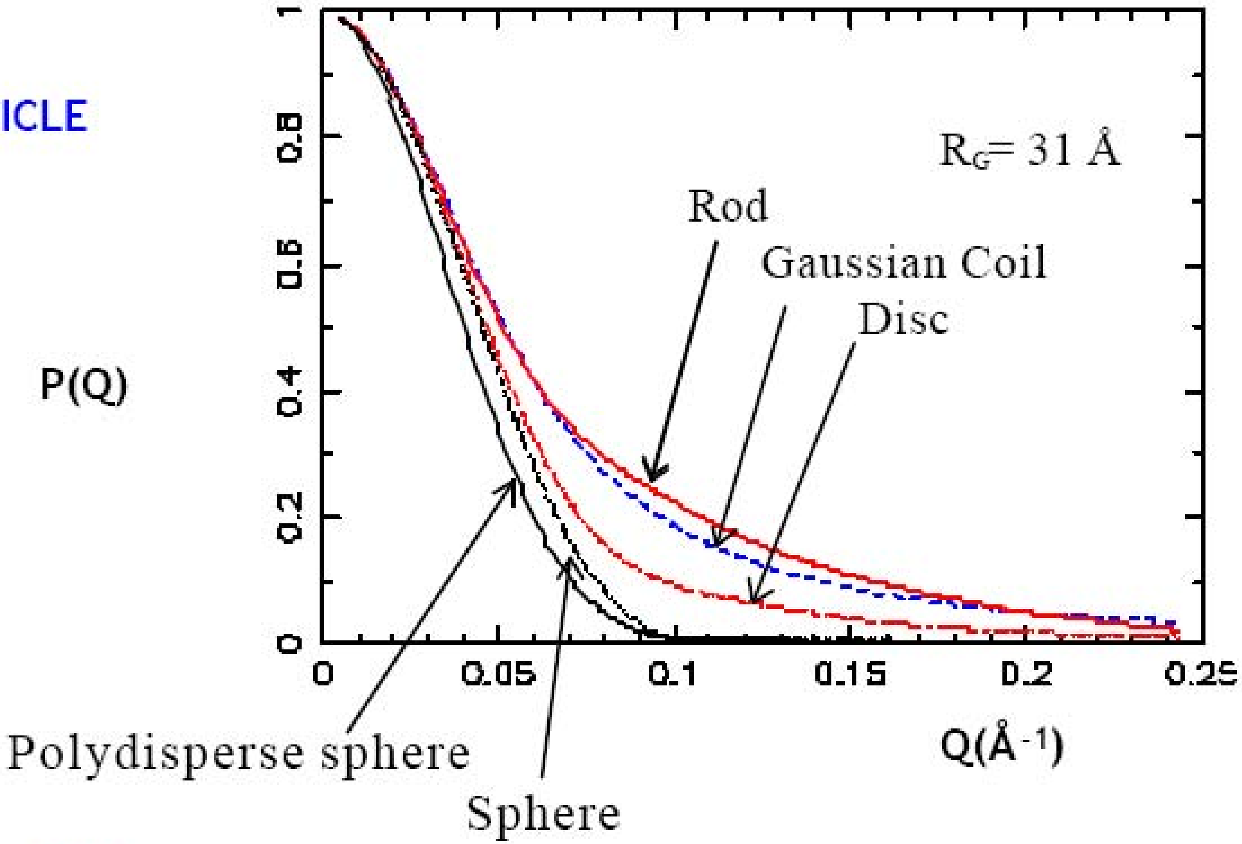
$$I(Q) = I_0.\left\{2\left(y - 1 + \exp(-y)\right)/\, y^2\right\}$$

$$y = (QR_G)^2$$

R_G = radius of gyration, the rms (root mean square) radius – same as in Guinier plot.

For dilute polymer, as usual $I_0 = NV^2(\Delta\rho)^2$

DILUTE PARTICLE SHAPE



R_G= 31Å (i.e. are same at small Q)

Rod R=10Å, L=104.5Å

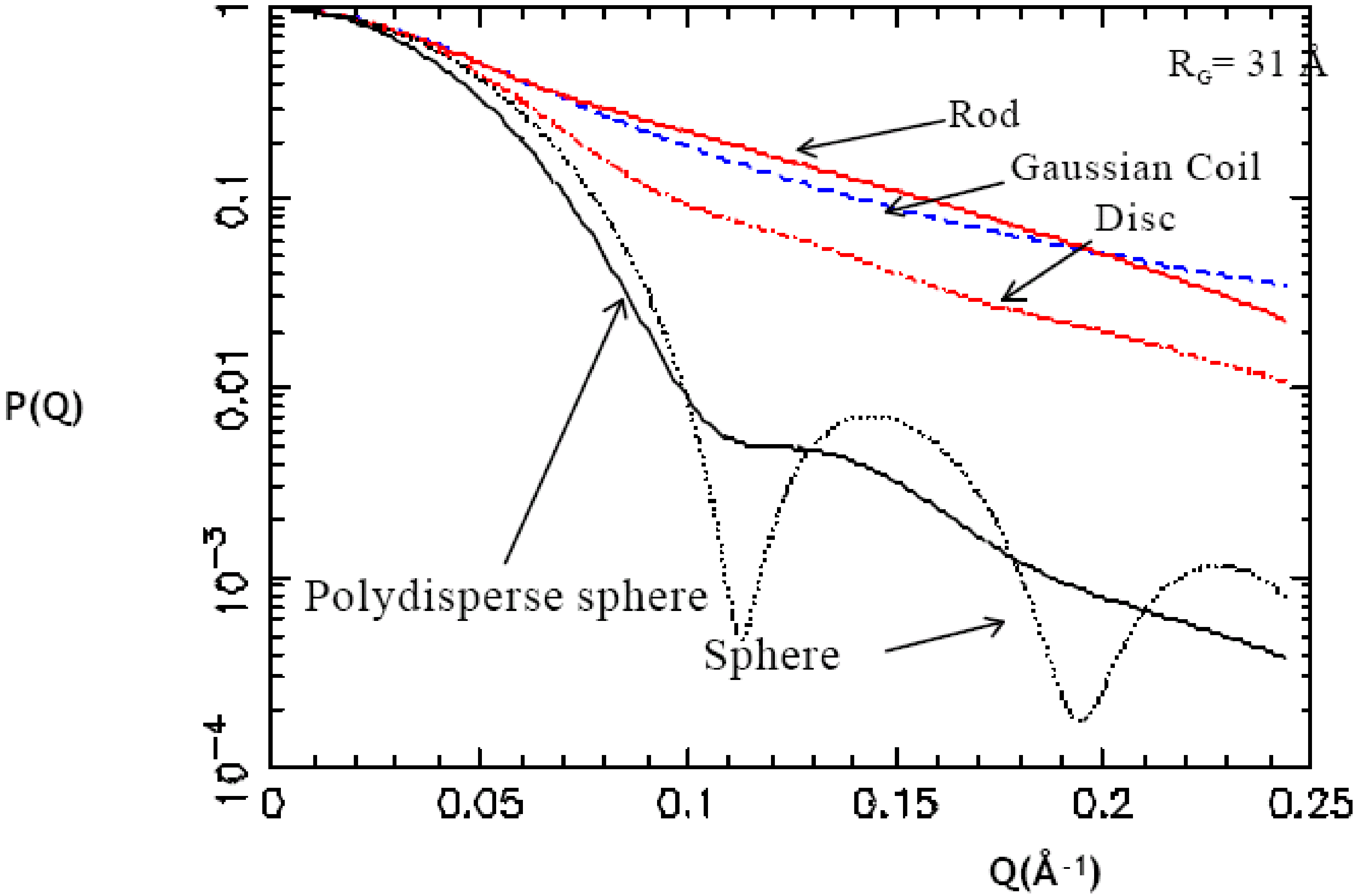
Disc R=43.6, L=10

Gaussian coil R_G= 31

Monodisperse sphere R = 40 has $R_G = 40 \times \sqrt{(3/5)} = 31$ Å, has resolution smearing.

Polydisperse (Schultz) R_{bar}= 40Å, σ/R_{bar} = 0.15, is steeper at small Q

DILUTE PARTICLE SHAPE log-linear plot



Absolute intensity of non-dilute samples & polymers

For dilute and concentrated (solid or melt) polymers and other particles:

$$I_0 = \phi(1-\phi)V(\Delta\rho)^2 = \frac{c}{d}(1-\frac{c}{d})\frac{M}{dN_A}(\Delta\rho)^2$$

ϕ = volume fraction

V = particle volume

$(\Delta\rho)^2$ = scattering length density difference

c = concentration (g.cm^{-3}),

M = molecular weight (g.mol^{-1}),

N_A =Avogadro's number,

d = bulk density (g.cm^{-3}).

NOTE at 50%vol, f (1-f) halves the usual intensity.

Polymer equations - often "disguised" with

(polymerisation index) × (monomer molecular weight,

segment length etc.)

For micelles M gives the aggregation number.

POROD’S LAW - surface to volume ratio from high Q limit

Well defined, sharp interface

$$I(Q) \rightarrow \frac{2\pi(\Delta\rho)^2 S}{Q^4}$$

If a plot of $Q^4 I(Q)$ will has a plateau value y [units $Å^4\ cm^{-1}$] then

$$S(cm^2 / cm^3) = \frac{10^{32} y}{2\pi(\Delta\rho)^2}$$

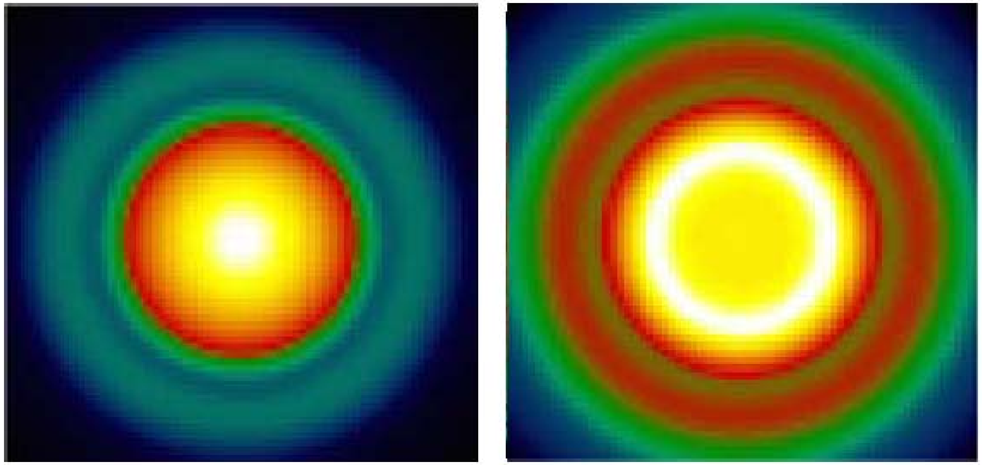
$\Delta\rho$ in cm^{-2}

A good “incoherent” background subtraction is vital !

Can try FIT to Q^{-4} and additional flat background.

[Other “power laws” may (or may not) relate to “fractal” materi als or rough surfaces, thins sheets, thin rods etc.]

silica spheres, R = 34 nm in toluene
(hard sphere interactions)

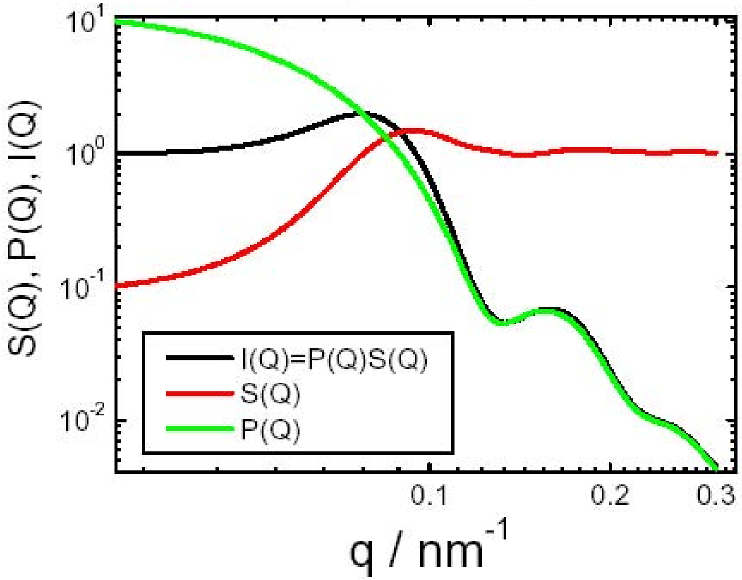


dilute hard spheres

concentrated hard spheres

$$I(q) \approx P(q)S(q)$$

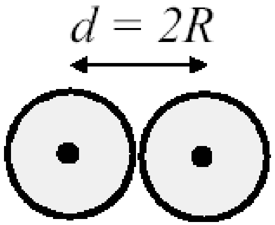
Approx. for monodisperse spherical symmetric particle

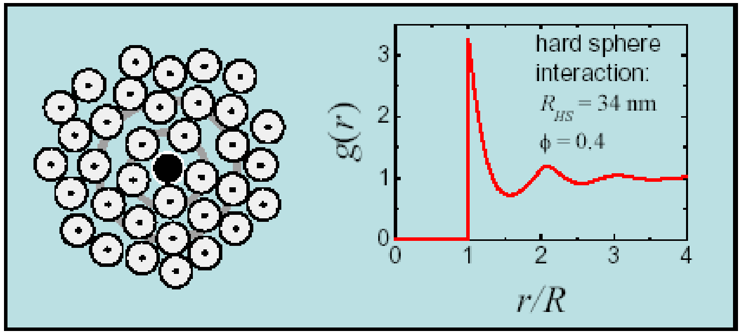


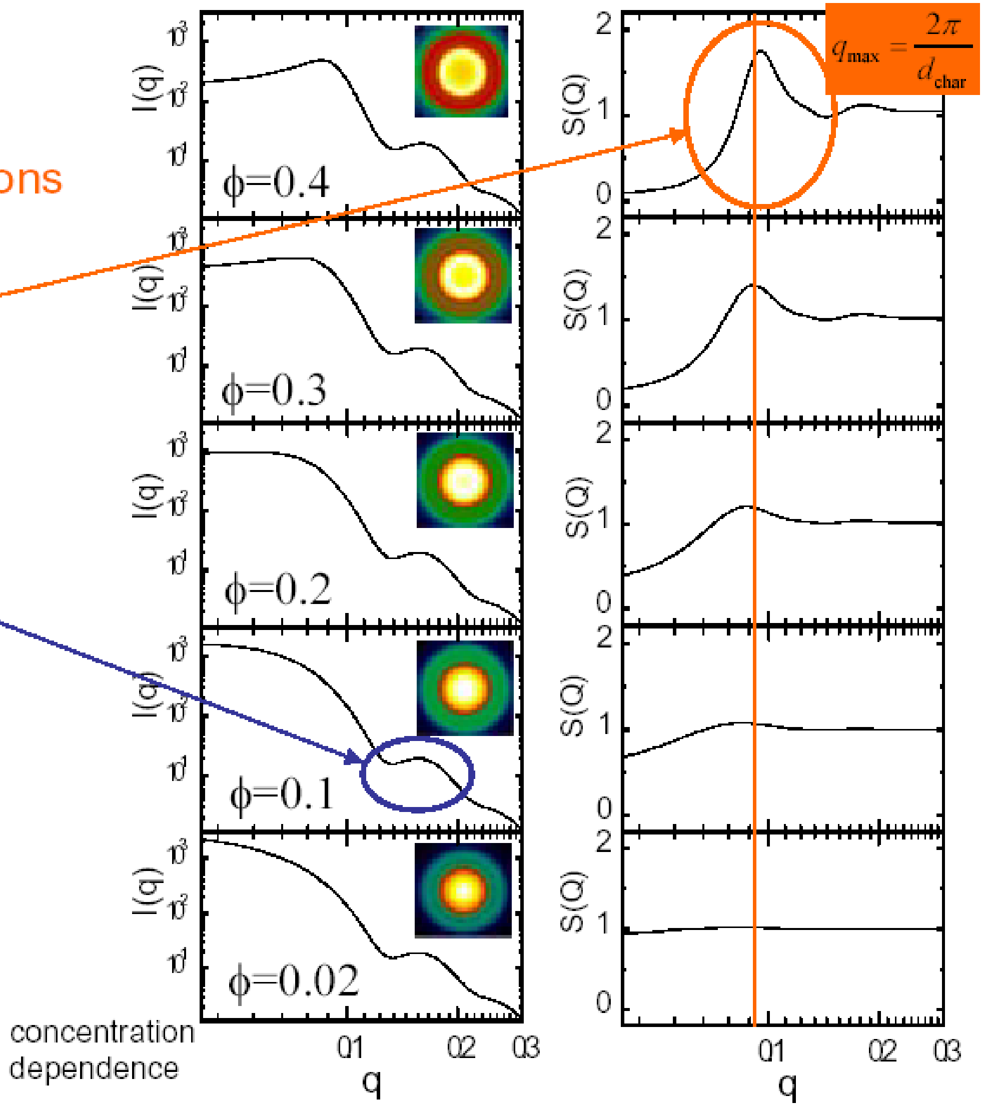
scattering intensity: contributions from

particle size and interparticle correlations

$$I(q) \approx P(q)S(q)$$

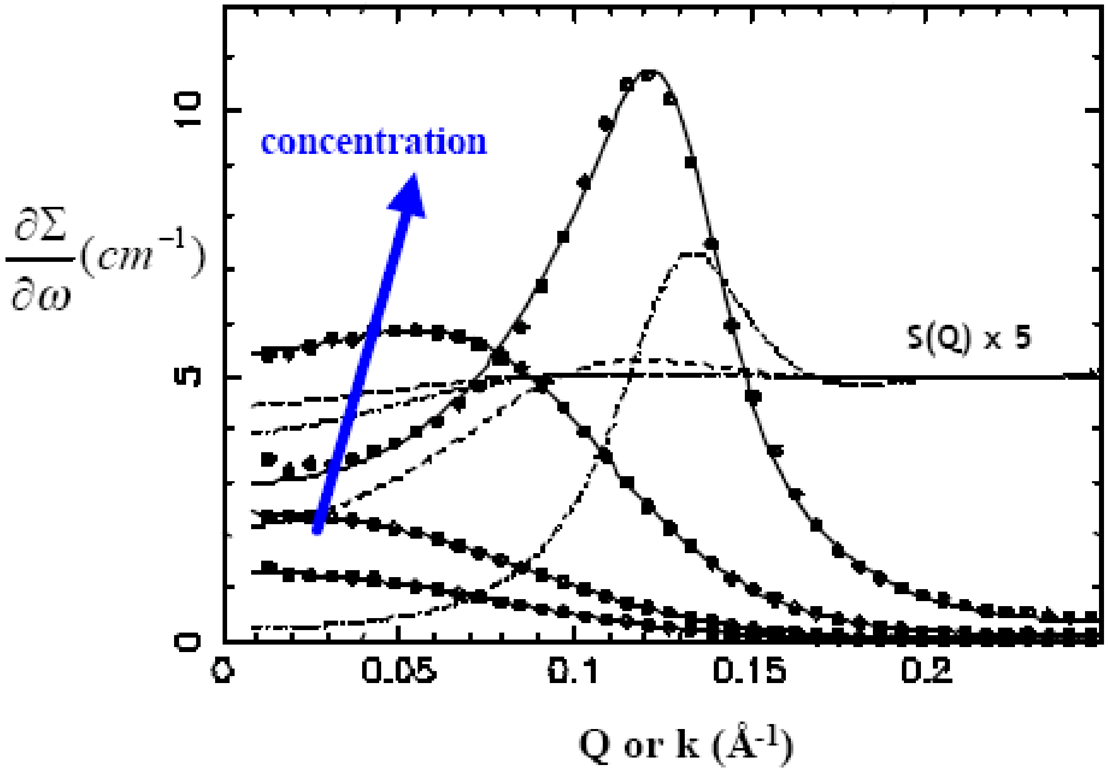


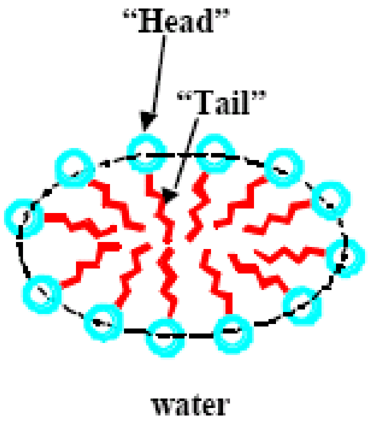




$$q_{\max} = \frac{2\pi}{d_{\mathrm{char}}}$$

SANS data (circles) for particles (surfactant micelles) in solution in D_2O, with increasing concentration (ignore the dashed lines, will see this again later when we explain the fits)   Data for 0.9, 1.8, 7 and 29 % vol.

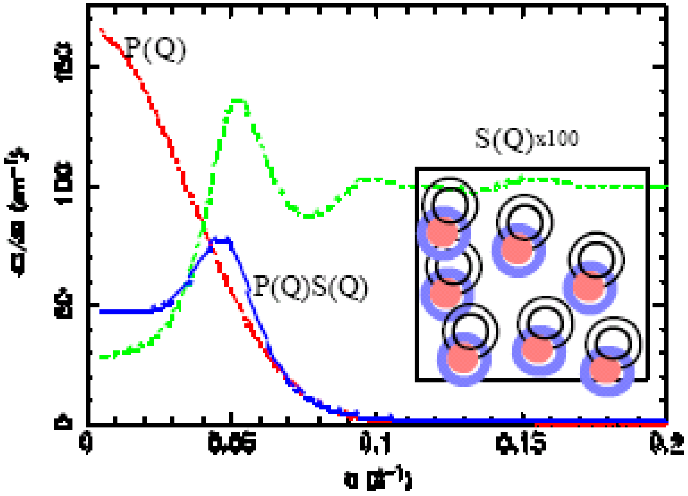




Does not look like Bragg scatter from a crystal, except for peak at the highest concentration – "Bragg peak" from a very disordered array of micelles !
SANS fits give size, shape (aggregation number) and charge on the micelle. Particle radius ~ 19 Å, axial ratio X ~ 1.7

D.J.Barlow, M.J.Lawrence, T.Zuberi, S.Zuberi & R.K.Heenan, Langmuir <u>16</u>(2000)10398-10403.

Example: interacting spheres:



10% R=40 Å radius spheres, in "core" contrast,
(polydispersity $\sigma/R_{bar}= 0.15$, $\Delta\rho=6\text{x}10^{10}\text{cm}^{-2}$).
plus another 16% in invisible 15 Å coating gives hard sphere $S(Q)$ of 26 % vol & R = 55 Å
$S(Q) \rightarrow 1$ at high Q

At higher volume fractions we start to see interference from waves scattered by adjacent particles (it was there all along, but at smaller Q, inside the beam stop!). $I(Q=0)$ is now decreased!

To first approximation we multiply P(Q) by an "inter-particle structure factor" S(Q) which depends on "long range" interparticle interactions. S(Q) comes from a Fourier transform of interparticle g(r) & hence interaction potential for colloids or Bragg $d = 2\pi/Q_{peak}$ in "liquid crystal".

$$\frac{\partial\Sigma}{\partial\omega} = I(Q) = NV^2(\Delta\rho)^2 P(Q)S(Q) + BKG$$

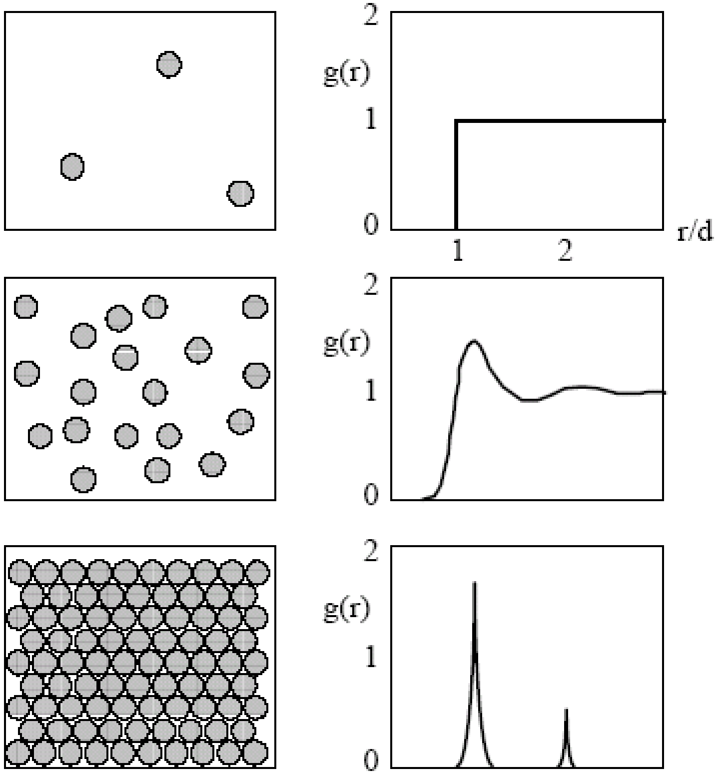
$$\langle S(\vec{q}) \rangle = S(q) = 1 + 4\pi n_p \int_0^\infty [g(r) - 1] \frac{\sin qr}{qr} r^2 dr$$

Note:

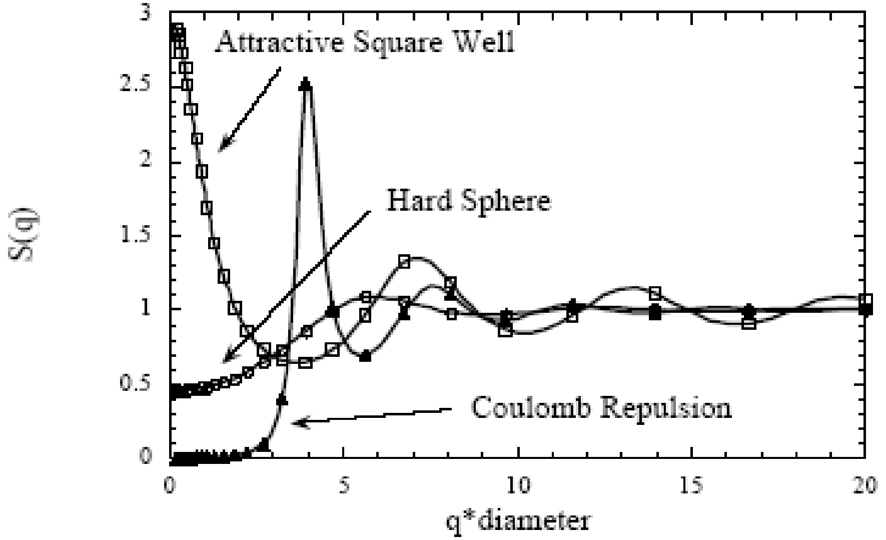
- S(q) is proportional to the number density of particles
- S(q) depends on g(r), the pair correlation function

- $n_p g(r)$ is a “local” density of particles

- Spatial arrangement set by interparticle interactions and indirect interactions



- The form of the interparticle potential has a great effect on the low q value of S(q)

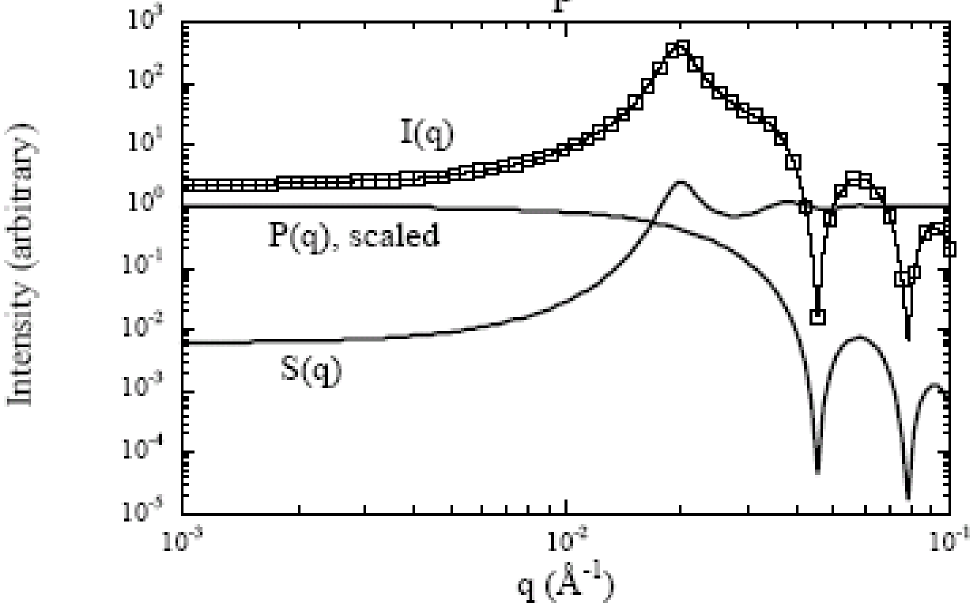


- The low q limit is proportional to the osmotic compressibility

$$S(q = 0) = kT\left(\frac{\partial n}{\partial \pi}\right)$$

  - Attractive interactions ⇒ more compressible
  - Repulsive interactions ⇒ less compressible

$I(q) = n_p P(q) S(q)$



- The form of the interparticle potential has a great effect on the low q value of S(q)
- Example of charged spheres:
    - development of "interaction peak"
    - change in low-q slope and I(0)
- Must fit model to data
    - know P(q)
    - ?calculate S(q)?

- Ornstein Zernicke Equation:

$$h(r) = g(r) - 1 = c(r) + n\int c\left(\left|\vec{r} - \vec{x}\right|\right)h(x)d\vec{x}$$

  - c(r) = direct correlation function
  - Integral = all indirect interactions
- A second relation is necessary to relate c(r) and g(r)
- Percus-Yevick Closure - an approximation

$$c(r) = g(r)\left[1 - e^{\beta u(r)}\right]$$

  - correct closure gives correct results
  - in general a difficult problem

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

POLYDISPERSITY

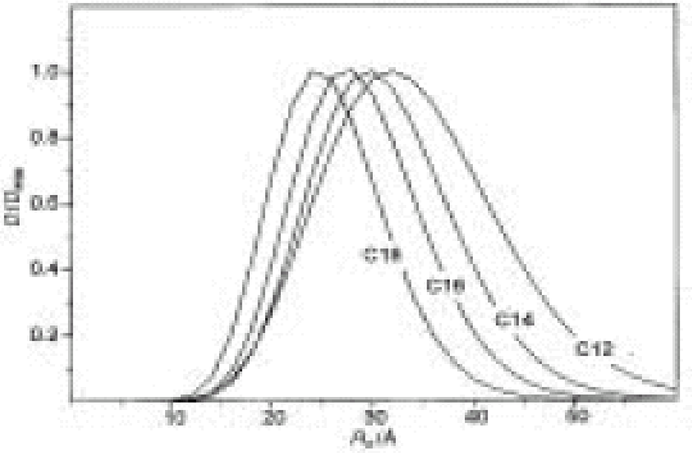
Sum SANS over size distribution - Gaussian, log-normal, uniform, etc. "Schultz distribution" is similar to log-normal but I(Q) is analytic. Generally SANS is only sensitive to mean R_{bar} and "polysdispersity" $\sigma(R)/R_{bar}$ where $\sigma(R)$ is the standard deviation.

Schultz distribution:

$$N(r) = \left[\frac{(Z+1)}{R_{bar}}\right]^{Z+1} \frac{r^Z}{\Gamma(Z+1)} \exp\left\{\frac{-(Z+1)r}{R_{bar}}\right\}$$

$$\frac{\sigma}{R_{bar}} = \frac{1}{(Z+1)^{1/2}}$$

$$Z = \left(\frac{R_{bar}}{\sigma}\right)^2 - 1$$

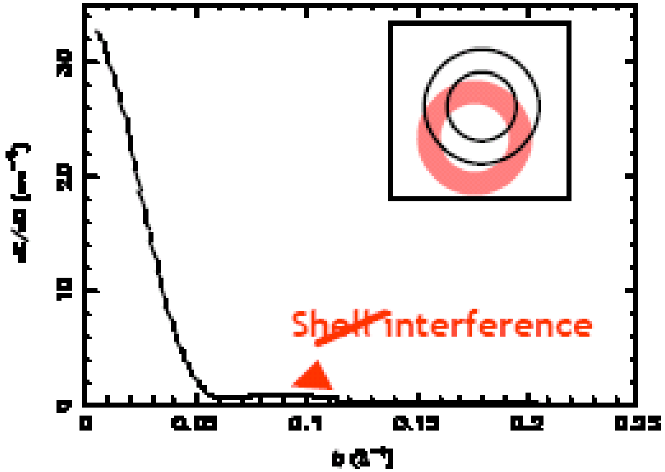


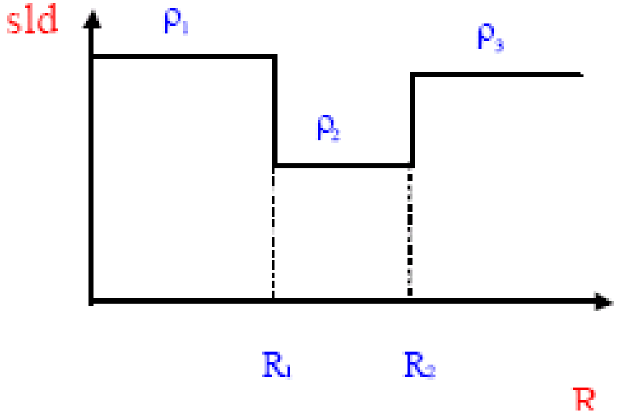
NOTE: at large σ the Schultz is very skewed and has significant numbers of small particles. Gamma function $\Gamma(n) = (n-1)!$ Care is needed in numerical calcs as Z may be large.

Contrast variation - introduction

For core plus shell spherical particle

e.g. Spherical Shell R_1 = 40 Å (R_2-R_1) = 15 Å (with 15% polydispersity)





$$I(Q)=N\{(\rho_1-\rho_2)V_1F(Q,R_1)+(\rho_2-\rho_3)V_2F(Q,R_2)\}^2$$

$$F(Q,r)=\frac{3(\sin(Qr)-Qr\cos(Qr))}{(Qr)^3}$$

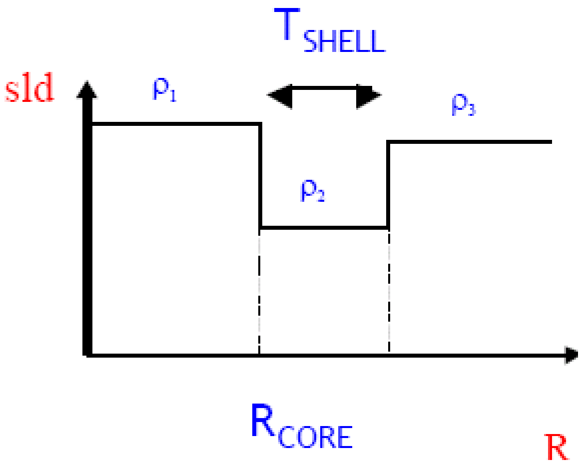
I(Q=0) not so simple now !

At "contrast match" $\rho_1 = \rho_3$, then we see "hollow shell" with oscillation in I(Q) which is very sensitive to the details of the structure.

Practical computations

Please note – the way that equations are presented in scientific papers may not be the best way to use them in a computer program.

There are many ways to re -arrange the equations, e.g. the core/shell sphere on the previous slide can become:



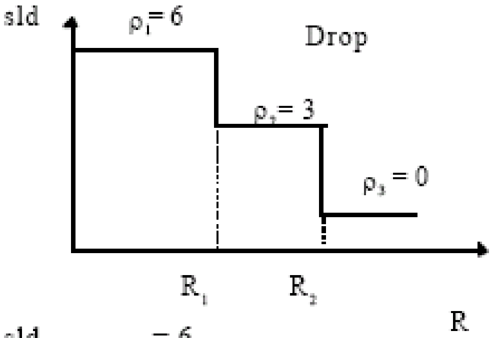
$$I(Q)=\frac{16\pi^2 N}{Q^6}\left\{(\rho_1-\rho_2)f(Q,R_{CORE})+(\rho_2-\rho_3)f(Q,R_{CORE}+T_{SHELL})\right\}^2$$

$$f(Q,r)=\left(\sin(Qr)-Qr\cos(Qr)\right)$$

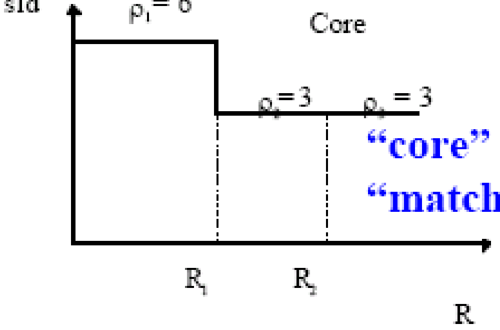
Where there are N particles per unit volume (usually per cm^3).
Note that we may need to include a factor 10^{48} to convert Q(Å^{-1})^6 to cm^{-6}.

CONTRAST VARIATION -CORE/SHELL PARTICLES

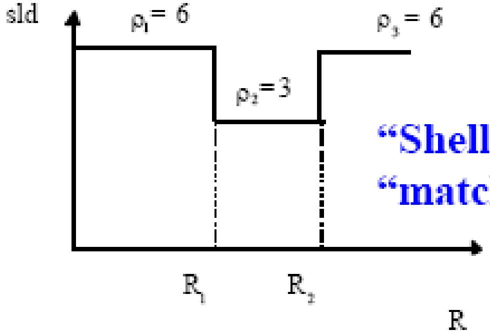
e.g. Core $\rho 1 = 6\mathrm{x}10^{10}$ cm^{-2}, mean $R_1 = 40$Å, $\phi = 1\%$, $\sigma/R_{bar} = 15\%$
$R_2 - R_1 = 15$ Å shell $\rho_2 = 3\mathrm{x}10^{10}$ cm^{-2}.



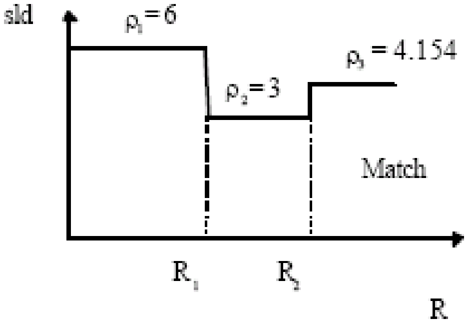
"drop" contrast sees whole particle
(here some effect of the shell)



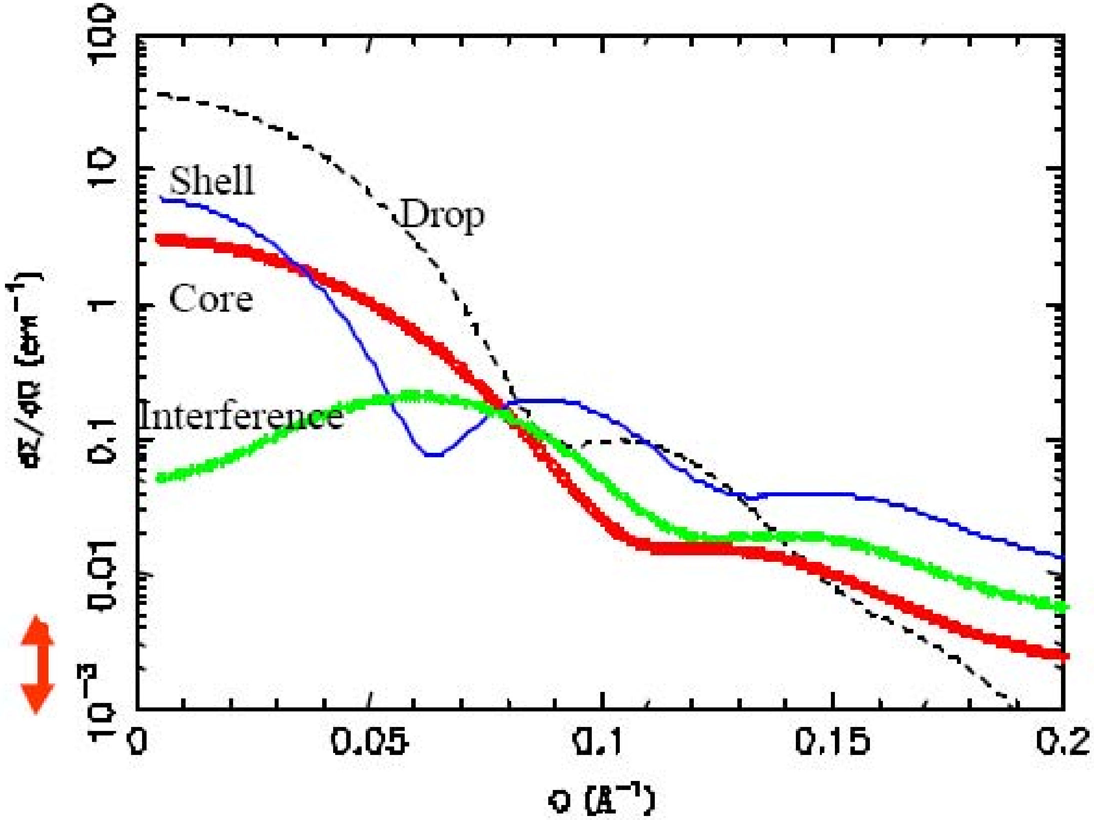
"core" - solvent
"matches" shell



"Shell" - solvent
"matches" core



"interference" – rarely seen, but be aware! Solvent between "core" & "shell" matches the average sld of the whole particle.
Small Q, long dist. SANS ~ zero,
High Q, short distances some scatter!

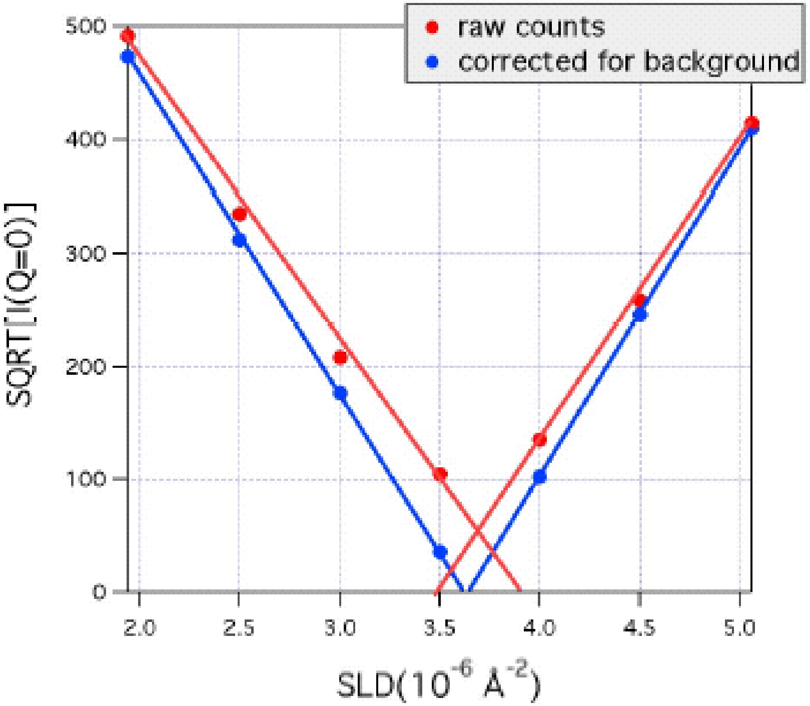


typical background levels ?

NOTE **I(Q) from “shell contrast” scales non-linearly with particle size and layer thickness - trial calculations are useful to plan experiments.**

Determining the Contrast Match Point

$$I(Q=0)=\frac{N}{V}(\rho_p-\rho_o)^2V_p^2$$



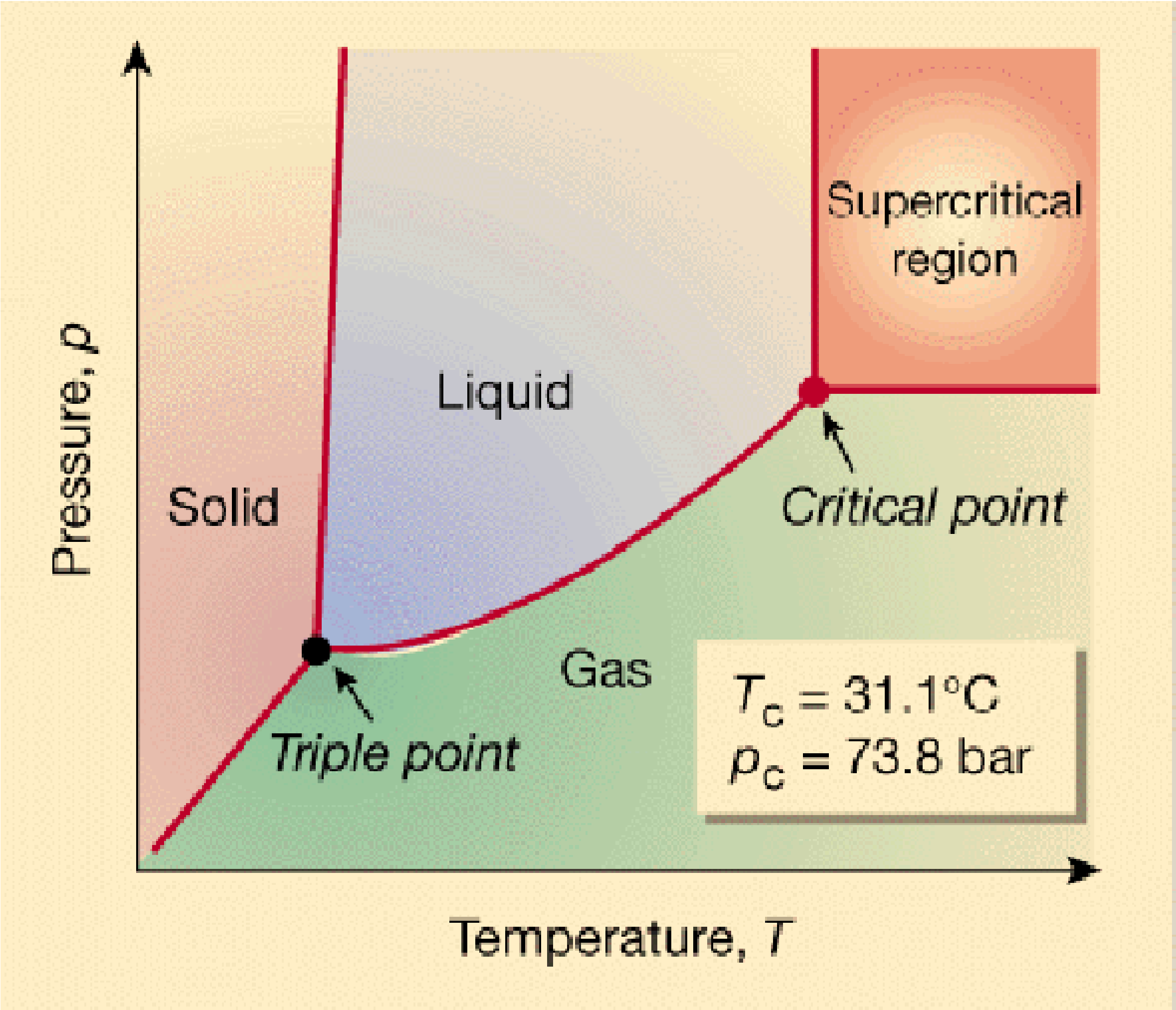
**Need "dilute" particles and "low" Q

- Make several measurements at different solvent SLDs
- Keep the same concentration
- Extrapolate data to I(Q=0)
- Plot sqrt(IQ=0) vs. SLD

- Don't forget to correct for the incoherent background contribution

- For composite particles, I(Q=0) will never reach zero - but it will be a minimum at the average particle contrast

The CO_2 Phase Diagram



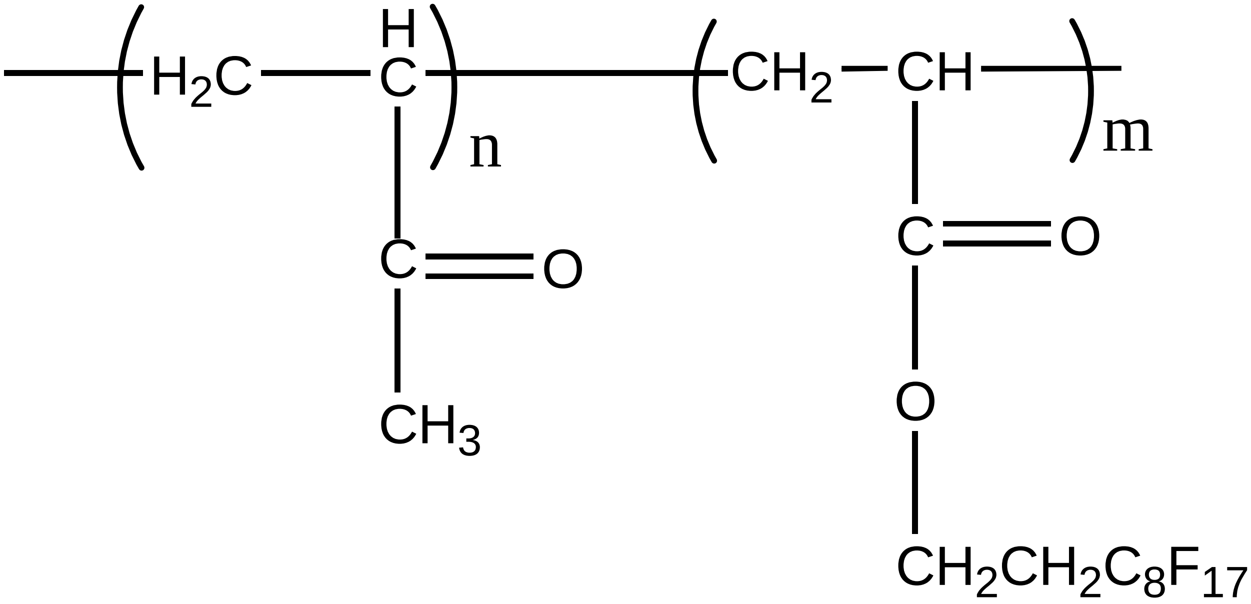
W. Leitner, Nature, vol. 405, 11 May 2000

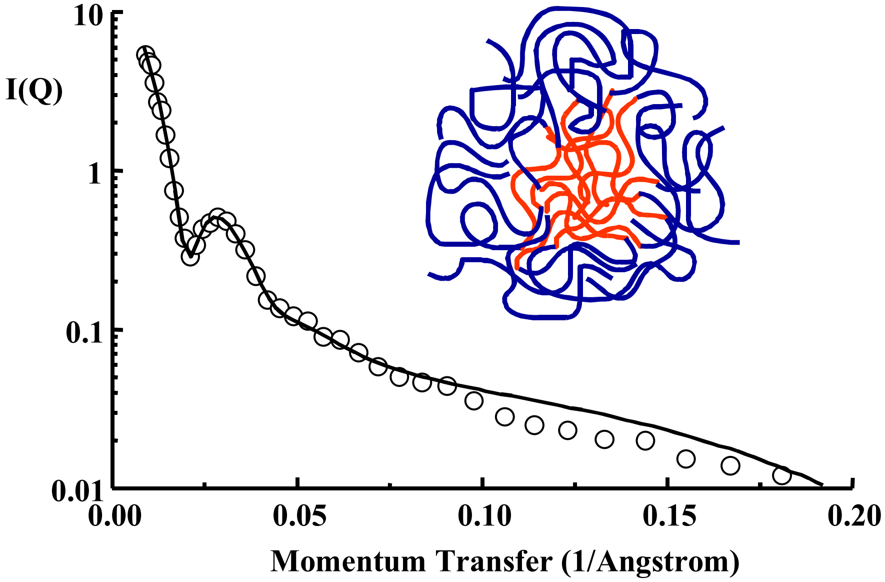
$scCO_2$ is a very poor solvent for most high MW polymers, with the possible exception of fluoropolymers, silicones, and poly(ether-carbonate)

(T. Sarbu, T.Styranec and E.J. Beckman, Nature, vol. 405, 11 May 2000)

It is then possible to design copolymers with a CO_2-phobic and a CO_2-philic portion that behave as surfactants, giving micellar-like aggregates in certain conditions

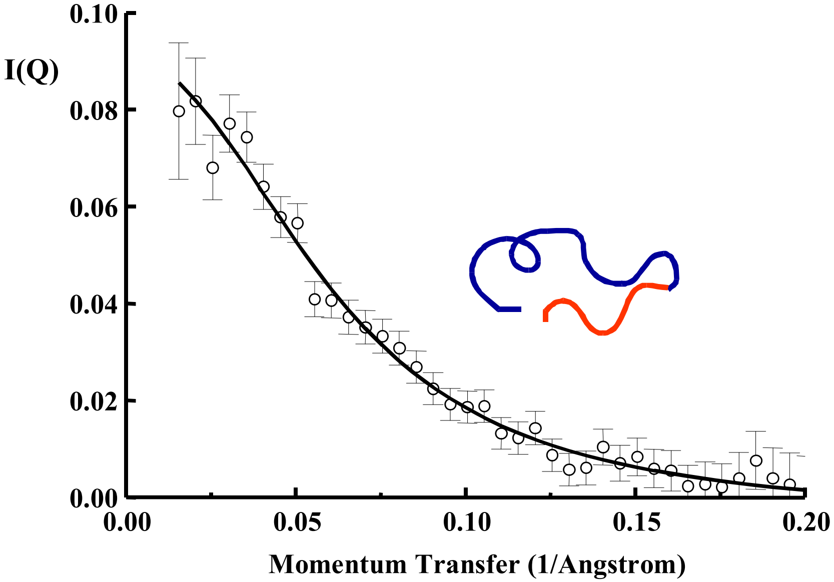
PVAC-b-PTAN

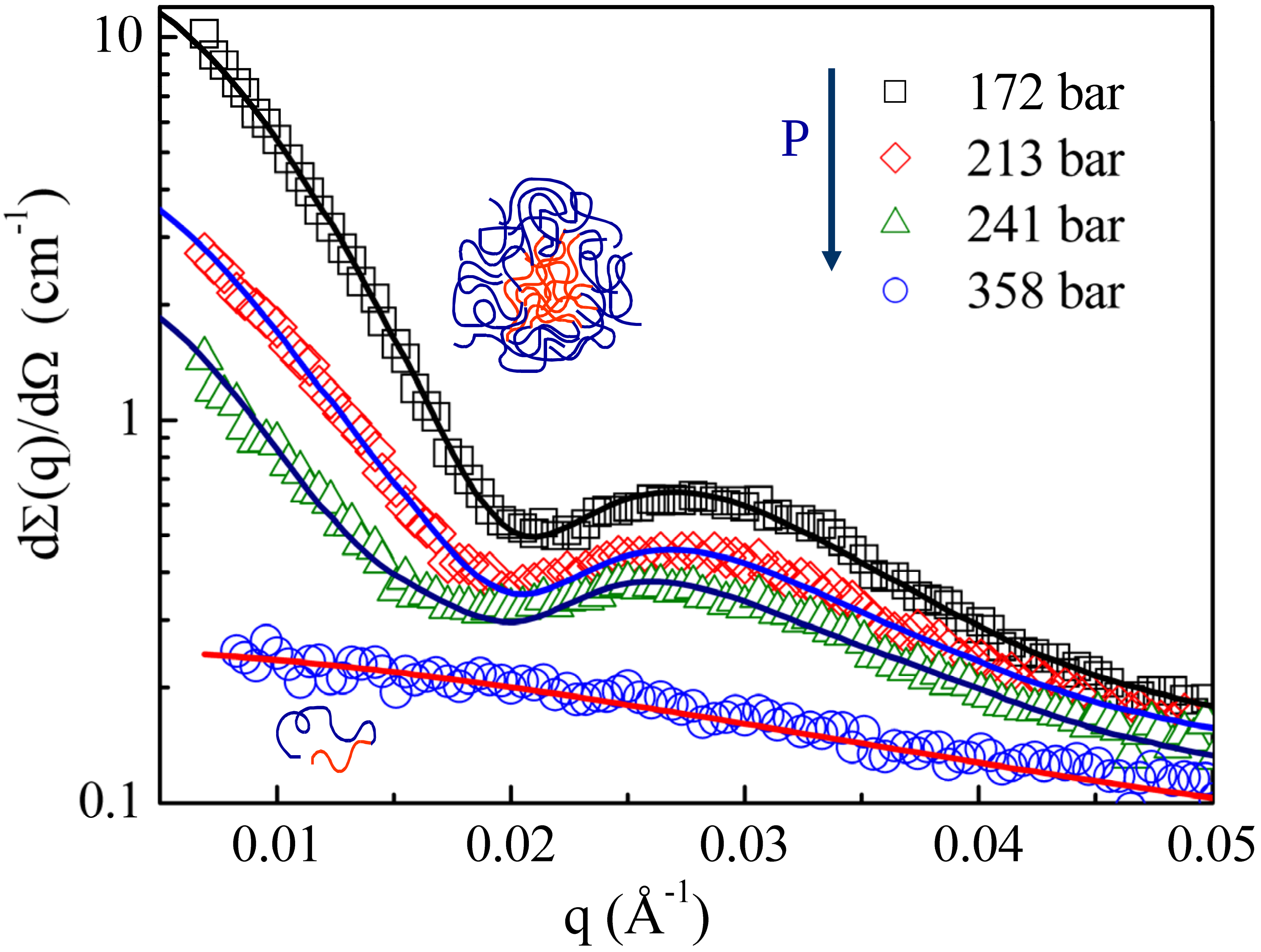


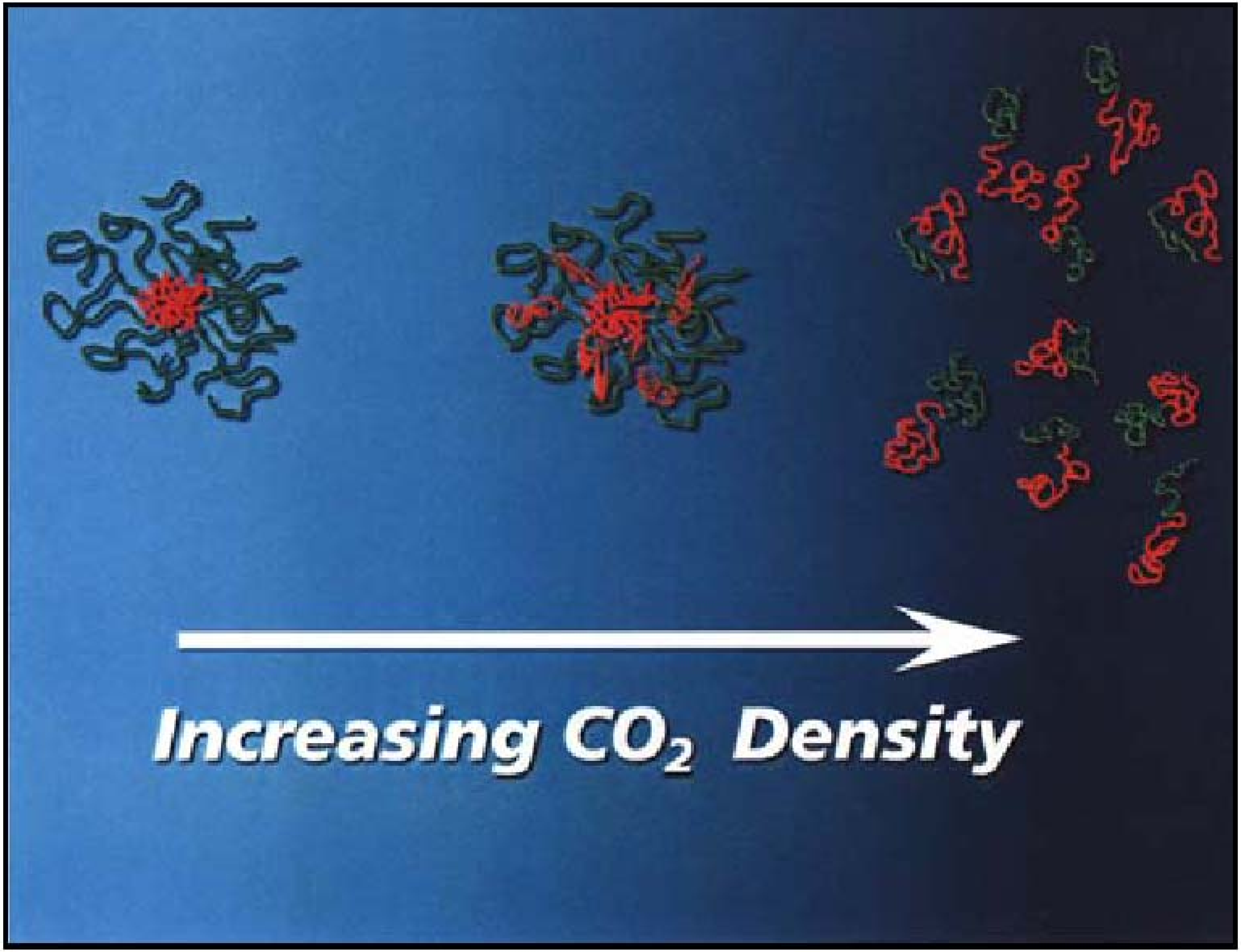


Low Pressure
(Low Density)

High Pressure
(High Density)




dΣ(q)/dΩ (cm^{-1})
10
1
0.1
0.01
0.02
0.03
0.04
0.05
q (Å^{-1})
P
□ 172 bar
◇ 213 bar
△ 241 bar
○ 358 bar


Increasing CO_2 Density

- Model

$$d\Sigma(Q)/d\Omega = N_p[d\Sigma(Q)/d\Omega]_{RC}+N_{Agg}[d\Sigma(Q)/d\Omega]_{Agg}$$

Random coils + Aggregates

$$2\,N_p[(QR_g)^2 + \exp[-(QR_g)^2]-1]/(QR_g)^4 \quad + \quad N_{agg}\,P(Q)\,S(Q)$$

P. Debye (1944)

Core+shell
(polydisperse)
spheres

\+

PY hard spheres
\+
ECF
$(=I(0)/[1+(Q\xi)^2])$

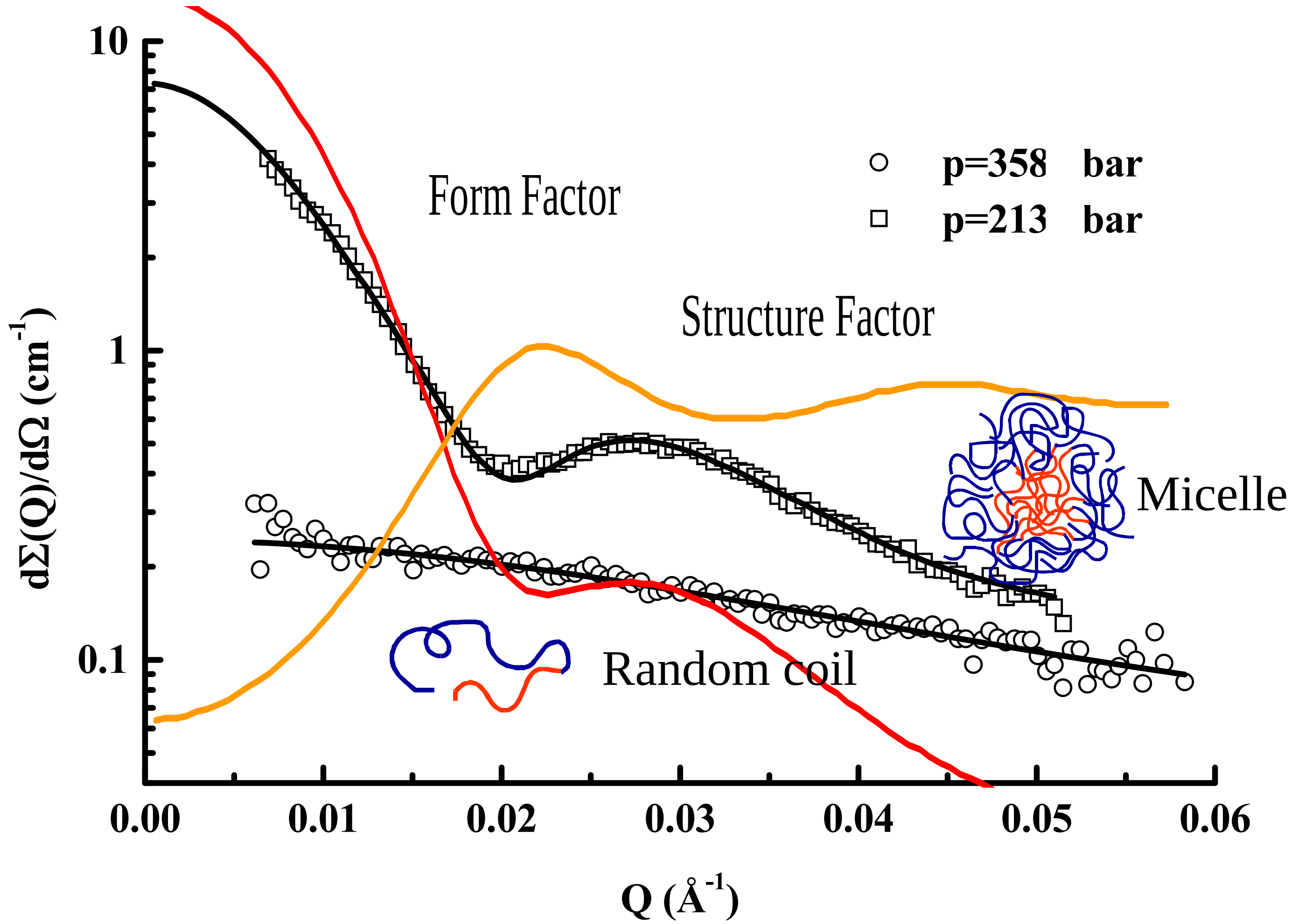
$$P(q) = \left[V_1 (\rho_1 - \rho_2) \frac{3 j_1 (q R_1)}{q R_1} + V_2 (\rho_2 - \rho_0) \frac{3 j_1 (q R_2)}{q R_2} \right]^2$$

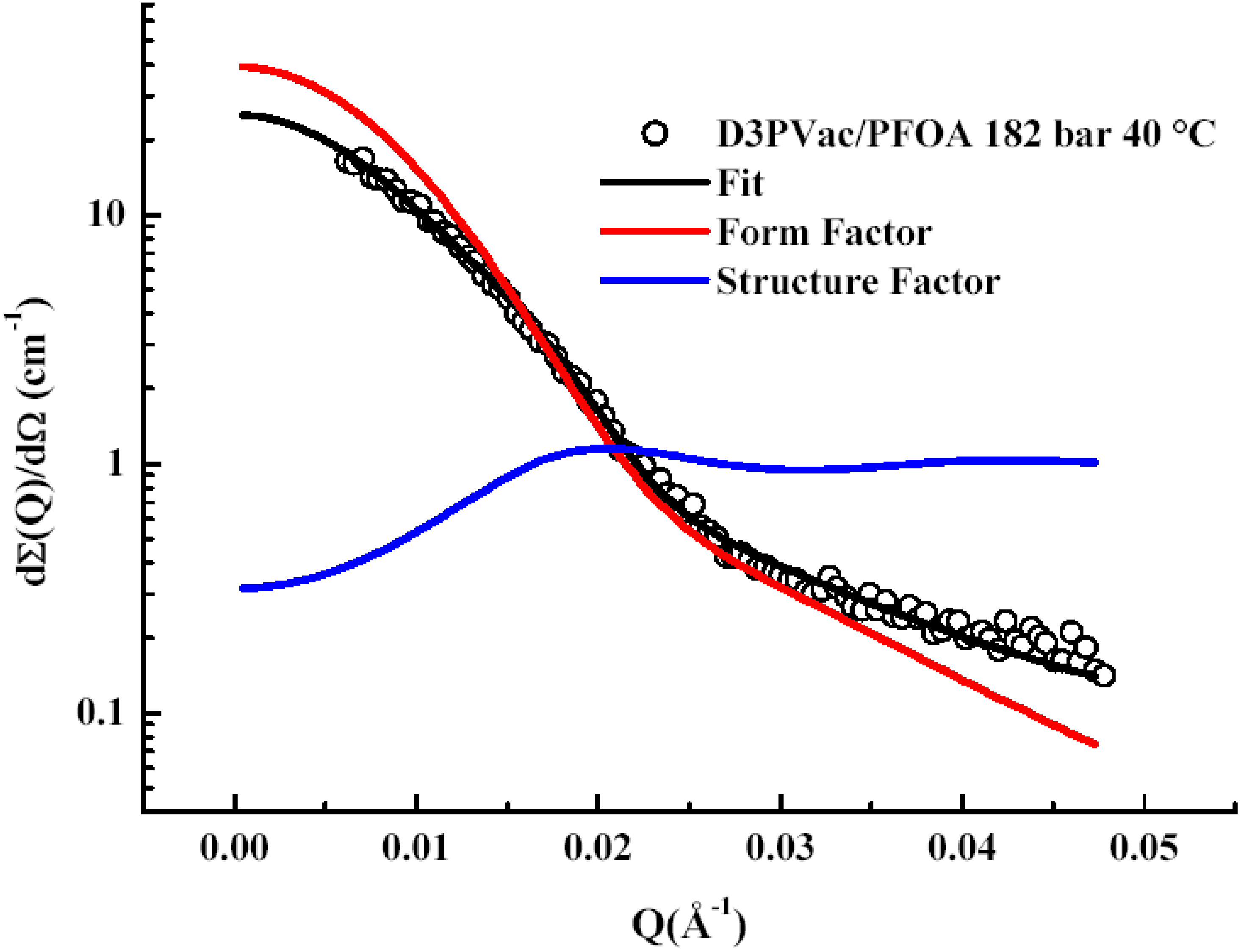
$$j_1(x) = \frac{\sin(x) - x \cos(x)}{x^2}$$

$$S(q) = \frac{1}{1 + 24 \phi \dfrac{G(2qR_{\mathrm{HS}}, \phi)}{2qR_{\mathrm{HS}}}}$$

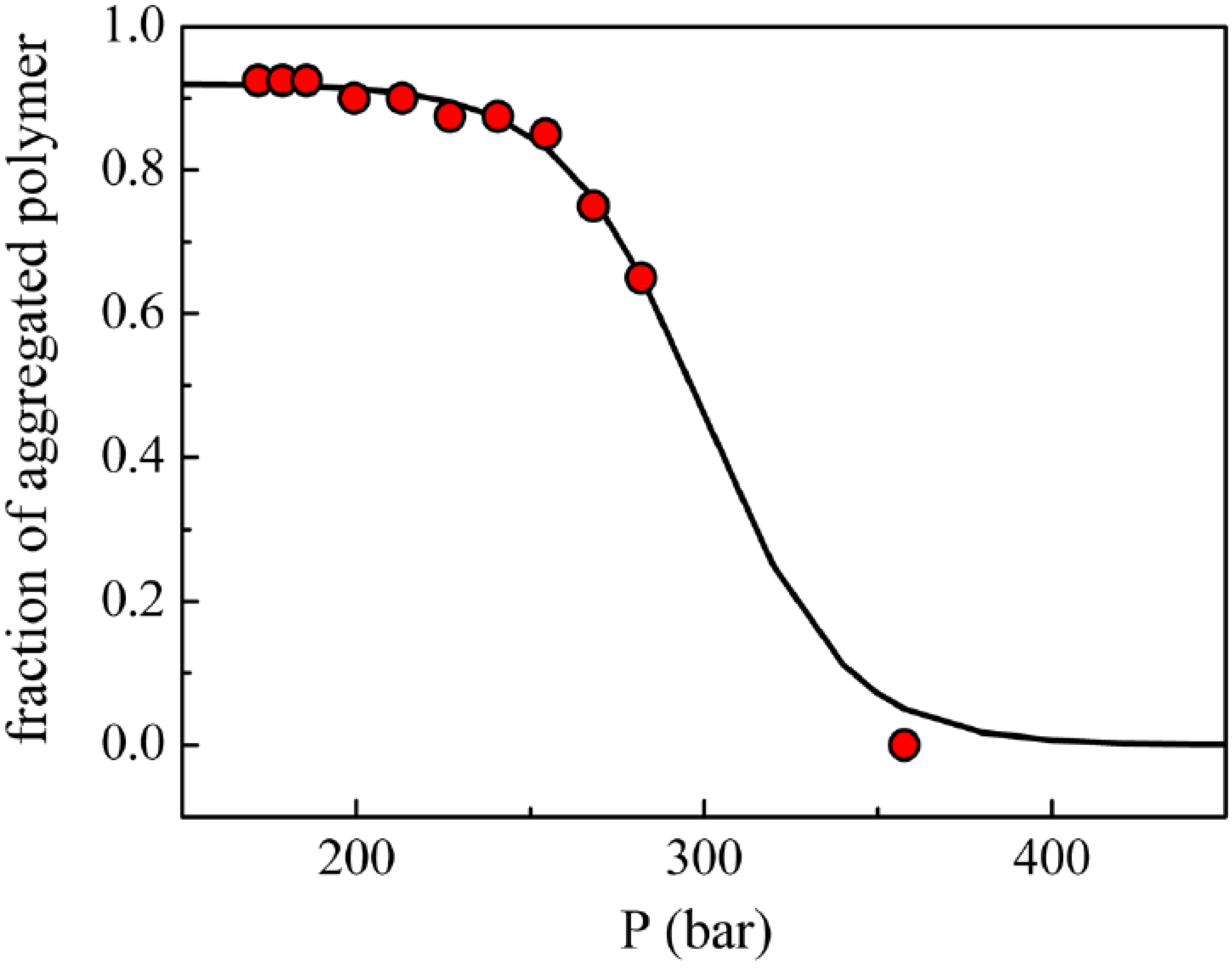
$$G(x,\phi) = \frac{(1+2\phi)^2}{(1-\phi)^4 x^2} (\sin x - x \cos x) - \frac{6\phi (1+\phi/2)^2}{(1-\phi)^4 x^3} \left[2x \sin x + (2 - x^2) \cos x - 2 \right] +$$

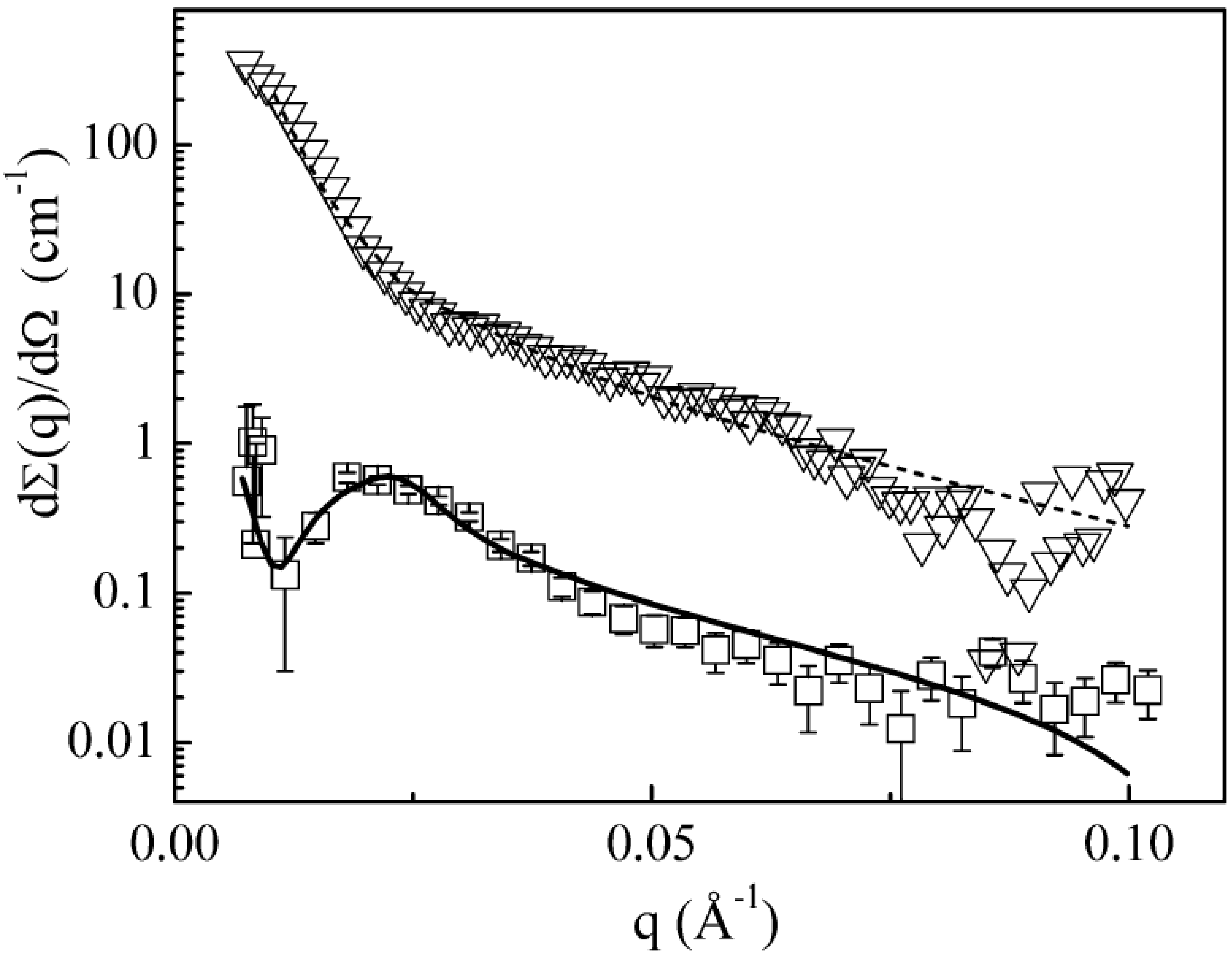
$$+ \frac{\phi (1+2\phi)^2}{2(1-\phi)^4 x^5} \left\{ -x^4 \cos x + 4 \left[(3x^2 - 6) \cos x + (x^3 - 6x) \sin x + 6 \right] \right\}$$

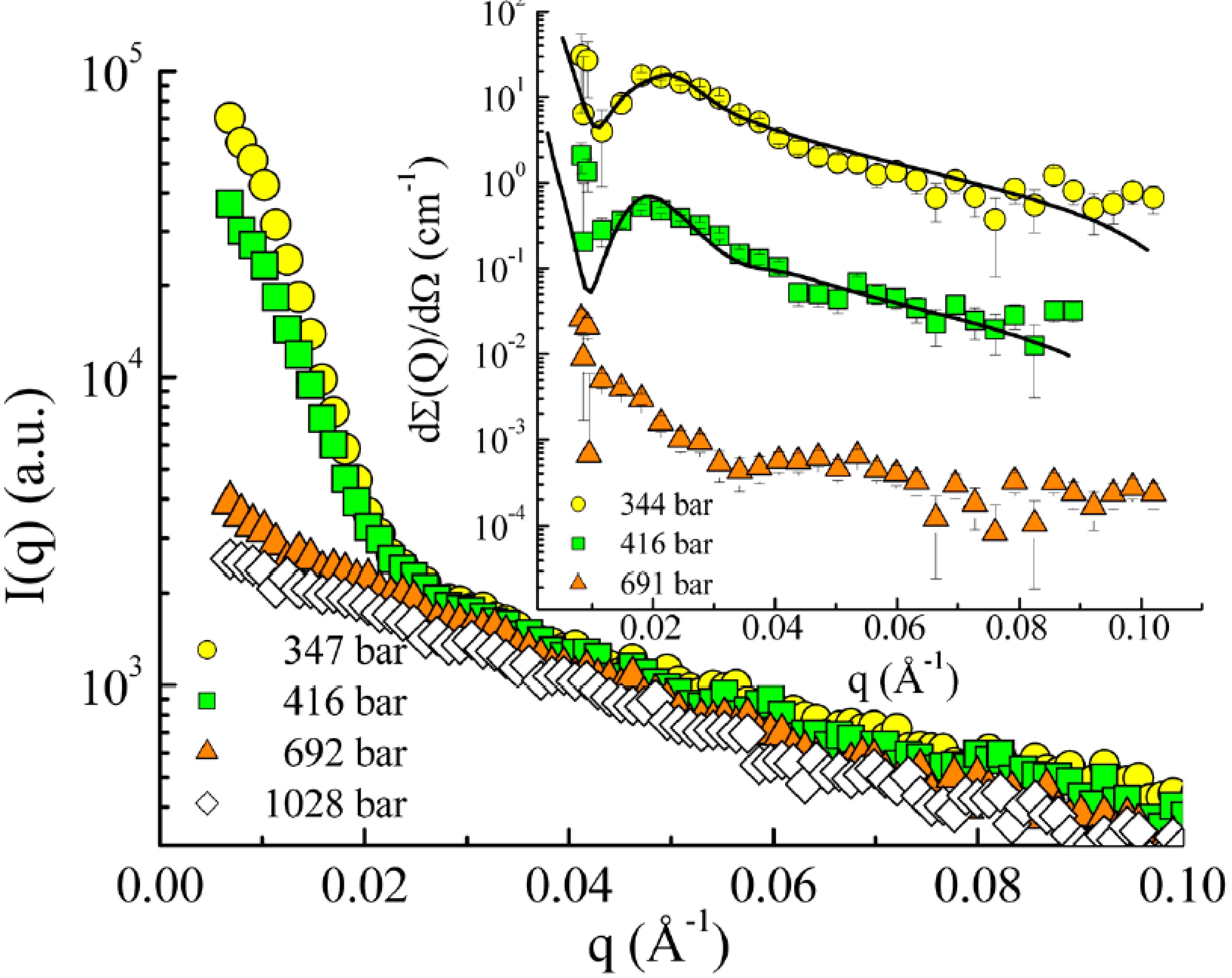

10
1
0.1
dΣ(Q)/dΩ (cm-1)
0.00
0.01
0.02
0.03
0.04
0.05
0.06
Q (Å-1)
○ p=358 bar
□ p=213 bar
Form Factor
Structure Factor
Micelle
Random coil


D3PVac/PFOA 182 bar 40 °C
Fit
Form Factor
Structure Factor
dΣ(Q)/dΩ (cm-1)
10
1
0.1
0.00
0.01
0.02
0.03
0.04
0.05
Q(Å-1)

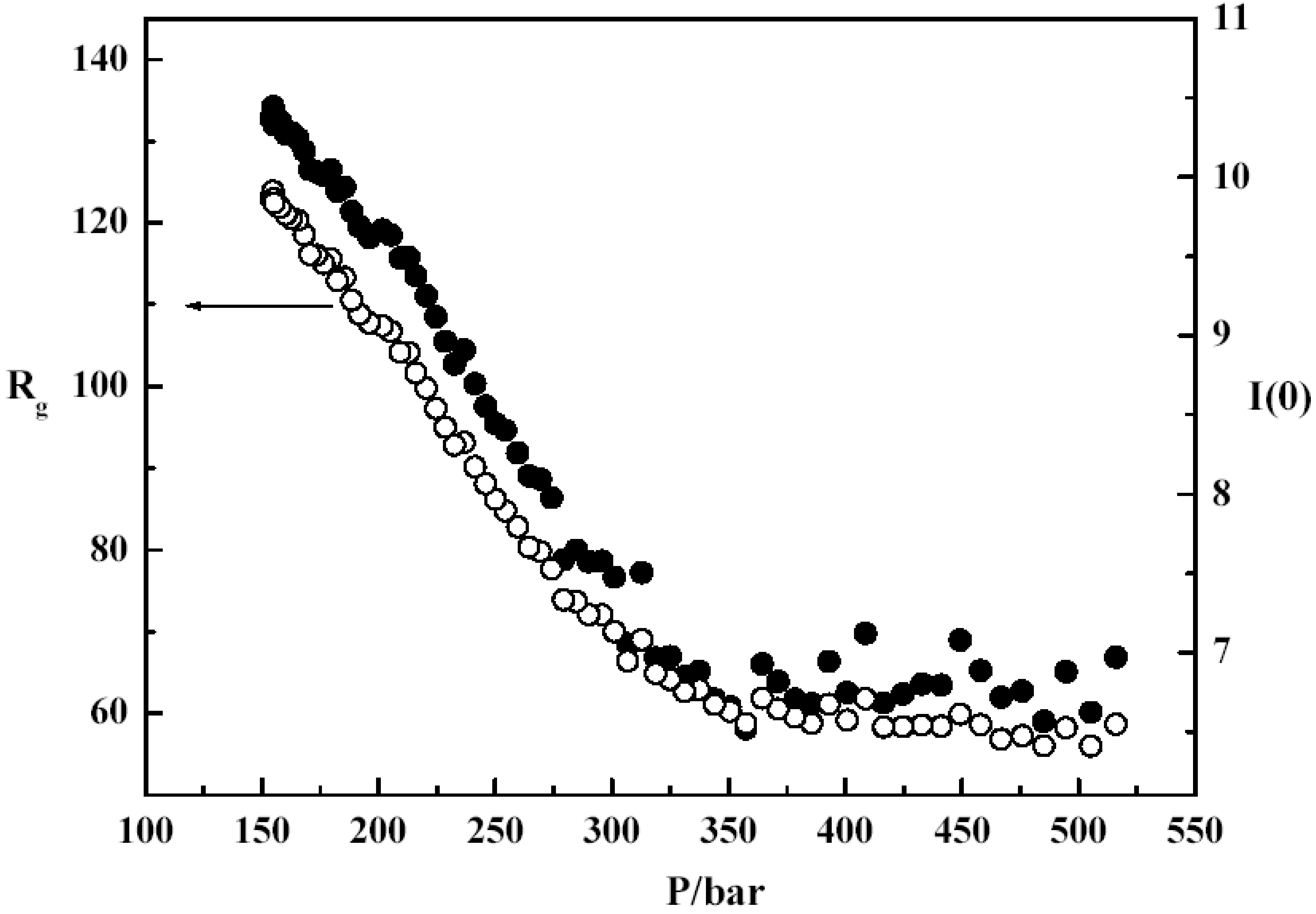
P	(1-uom)	ρ	CS	Agg.	Z
172	0.925	0.821	1.00	29.5(1)	17.0(1)
179	0.925	0.830	1.0(1)	29.3(3)	17.0(1)
186	0.925	0.838	1.1(1)	29.2(5)	17.4(1)
199	0.900	0.849	1.1(1)	28.0(3)	19.5(3)
213	0.900	0.858	1.1(1)	24.8(5)	18.4(5)
227	0.875	0.868	1.1(2)	21.7(2)	18.0(2)
241	0.875	0.879	1.1(3)	19.4(2)	17.0(2)
255	0.850	0.889	1.1(1)	18.6(2)	17.0(2)
268	0.750	0.900	1.6(2)	14.8(3)	17.0(2)
282	0.65	0.909	1.8(2)	12.0(2)	10.0(2)
295		transition zone, 0.91 g/cm^3			
310		transition zone, 0.92 g/cm^3			
357		0.917	Random coil, Rg 43.5 Å		


1.0
0.8
0.6
0.4
0.2
0.0
fraction of aggregated polymer
200
300
400
P (bar)

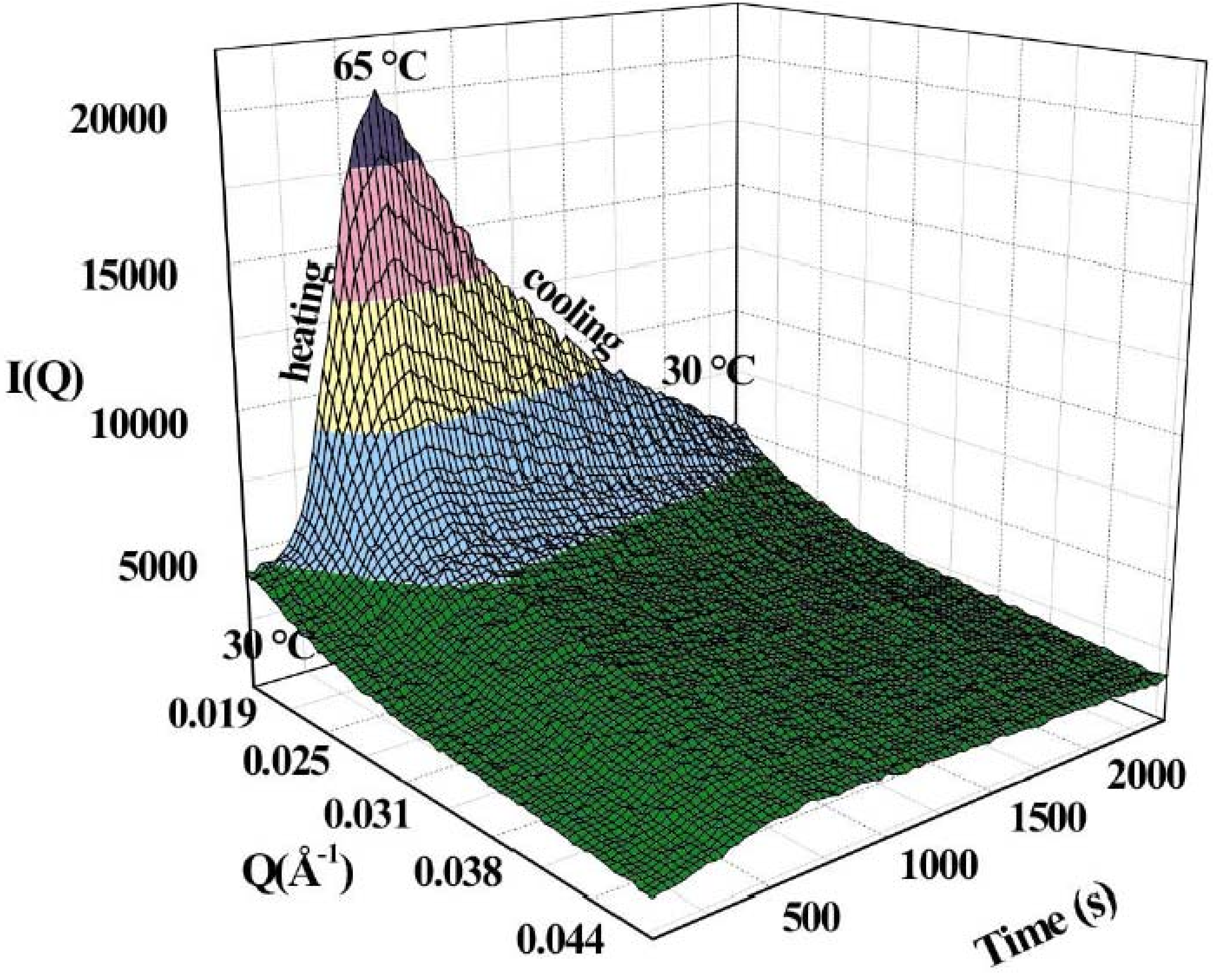

dΣ(q)/dΩ (cm-1)
100
10
1
0.1
0.01
0.00
0.05
0.10
q (Å-1)

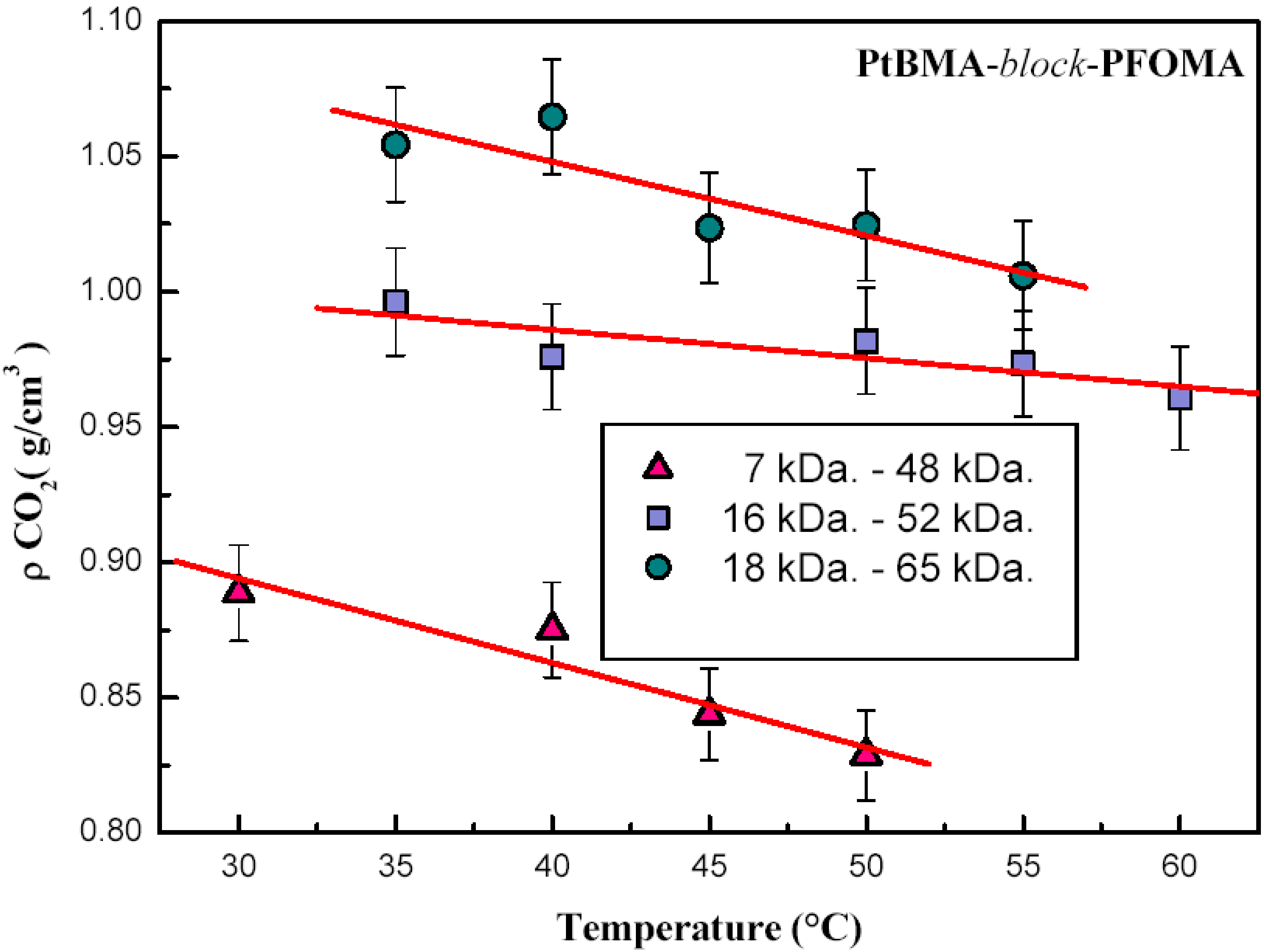


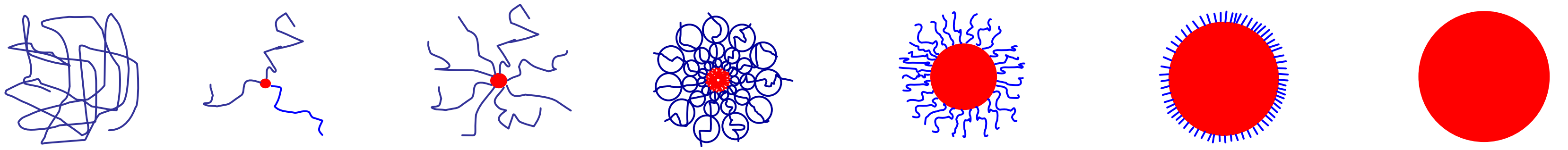
I(q) (a.u.)
10^5
10^4
10^3
0.00
0.02
0.04
0.06
0.08
0.10
q (Å^-1)
347 bar
416 bar
692 bar
1028 bar
dΣ(Q)/dΩ (cm^-1)
10^2
10^1
10^0
10^-1
10^-2
10^-3
10^-4
0.02
0.04
0.06
0.08
0.10
q (Å^-1)
344 bar
416 bar
691 bar



R_g
I(0)
P/bar
140
120
100
80
60
11
10
9
8
7
100
150
200
250
300
350
400
450
500
550


65 °C
heating
cooling
30 °C
30 °C
I(Q)
20000
15000
10000
5000
0.019
0.025
0.031
0.038
0.044
$Q(\AA^{-1})$
500
1000
1500
2000
Time (s)


PtBMA-*block*-PFOMA
▲ 7 kDa. - 48 kDa.
■ 16 kDa. - 52 kDa.
● 18 kDa. - 65 kDa.
ρ CO$_2$(g/cm^3)
1.10
1.05
1.00
0.95
0.90
0.85
0.80
30
35
40
45
50
55
60
Temperature (°C)



Gaussian Chains

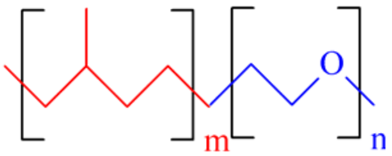
diffuse star-like

compact sphere-like

Hard Spheres

n»m

n≈m



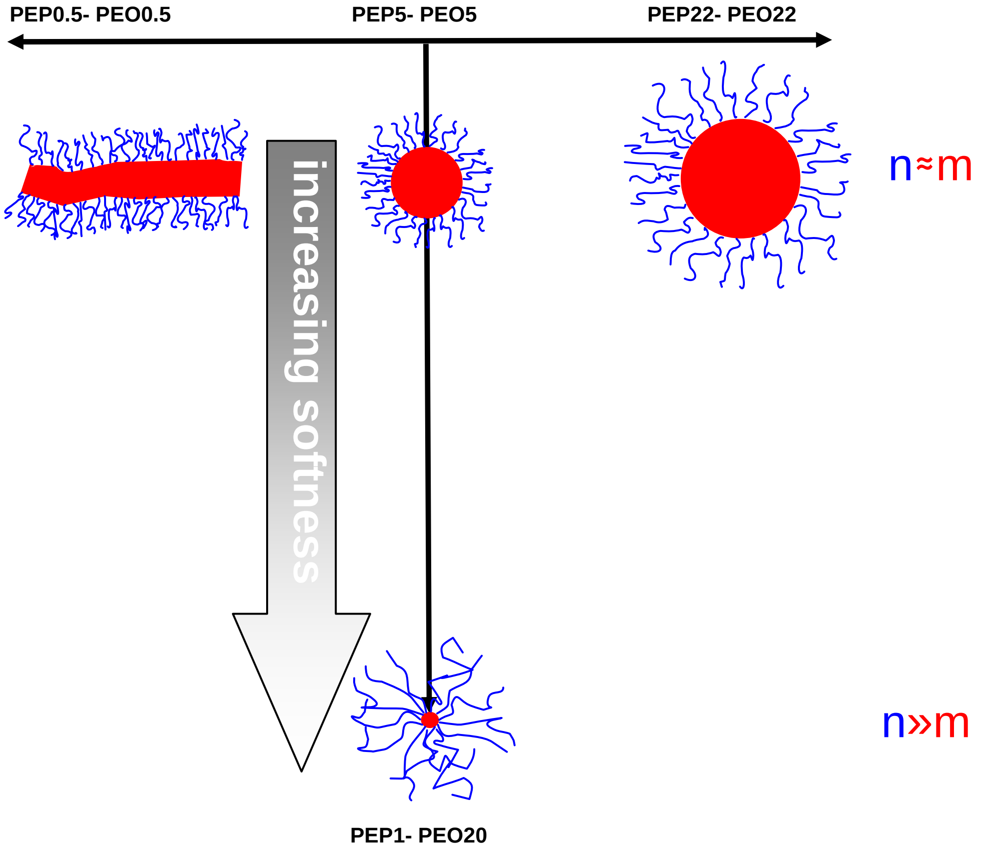
PEP

PEO

amphiphilic block copolymer:

- synthesized by anionic polymerisation
- predetermined M_W
- predetermined composition
- low polydispersity
- high interfacial tension (PEP/water)

micellar morphology in water



PEP0.5- PEO0.5

PEP5- PEO5

PEP22- PEO22

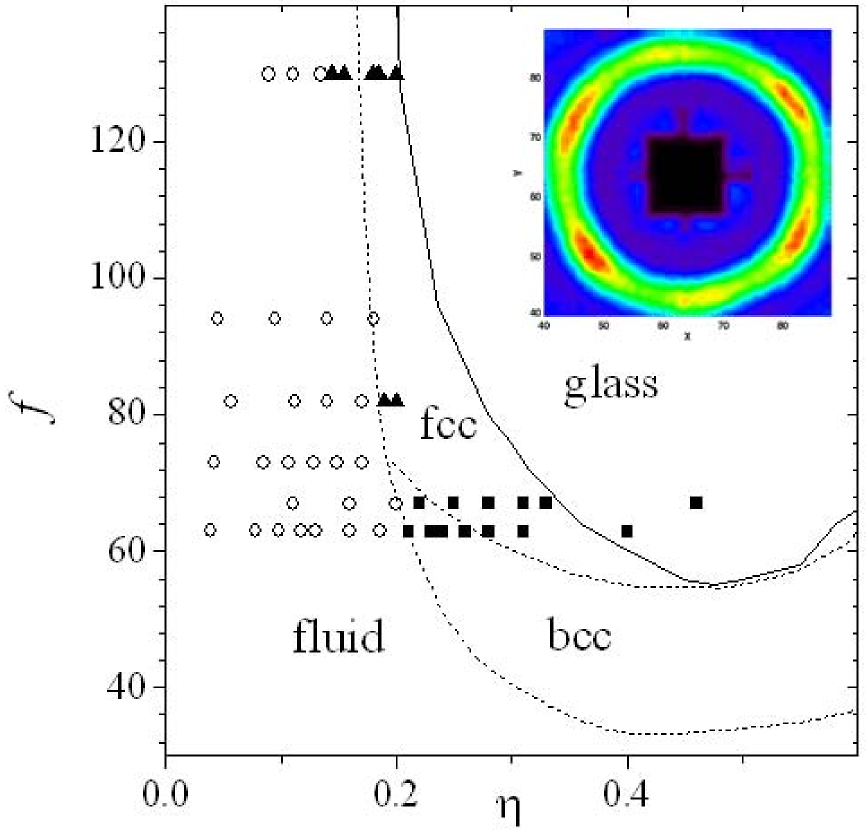
n≈m

increasing softness

n»m

PEP1- PEO20

J. Stellbrink, G. Rother, M. Laurati, R. Lund, L. Willner and D. Richter, *J. Phys.: Cond. Matter*, **16**, S3821-S3834, 2004.
R. Lund, L. Willner, J. Stellbrink, A. Radulescu and D. Richter, *Macromolecules*, **37**, 9984-9993, 2004.
R. Lund, L. Willner, J. Stellbrink, P. Lindner, and D. Richter, Phys. Rev. Letters, **96**, 068302, 2006.



-- eq. phases

— glass line MCT

○ fluid

■ bcc

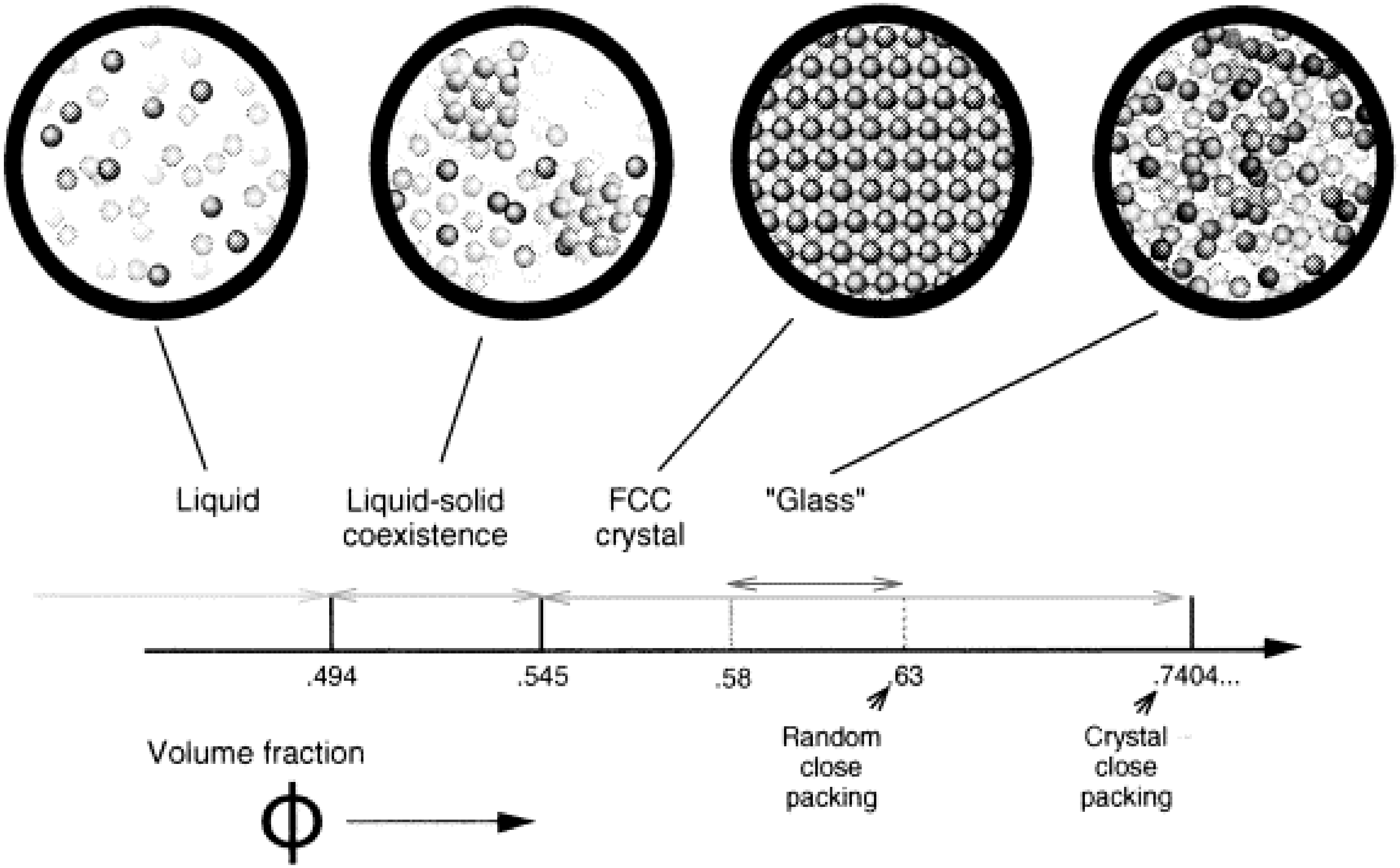
▲ amorphous solid

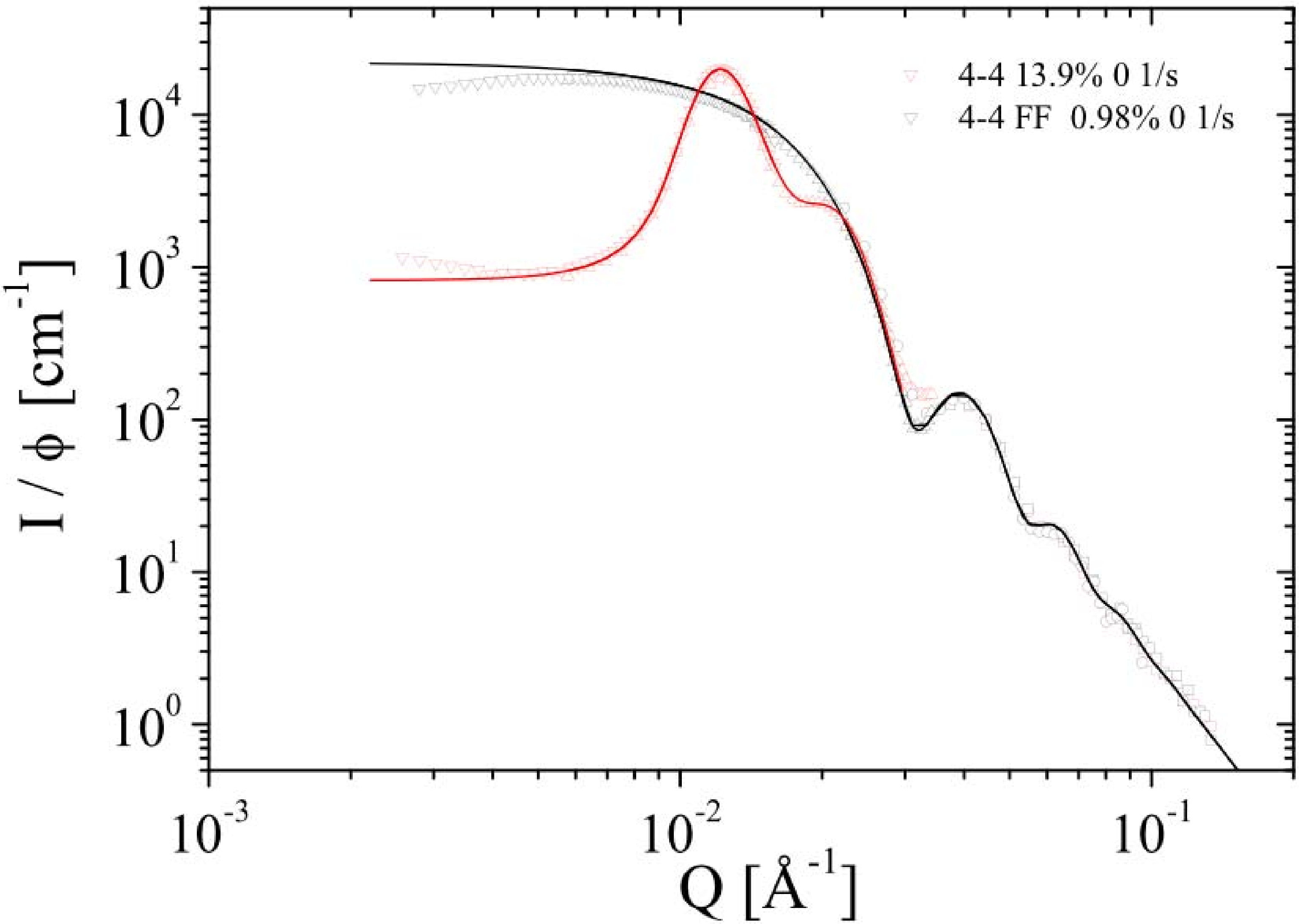
packing fraction: $\eta = N_z \frac{\pi}{6} \sigma^3$

Theory (Lines) M. Watzlawek et al. PRL 1999, G. Foffi et al. PRL 2003

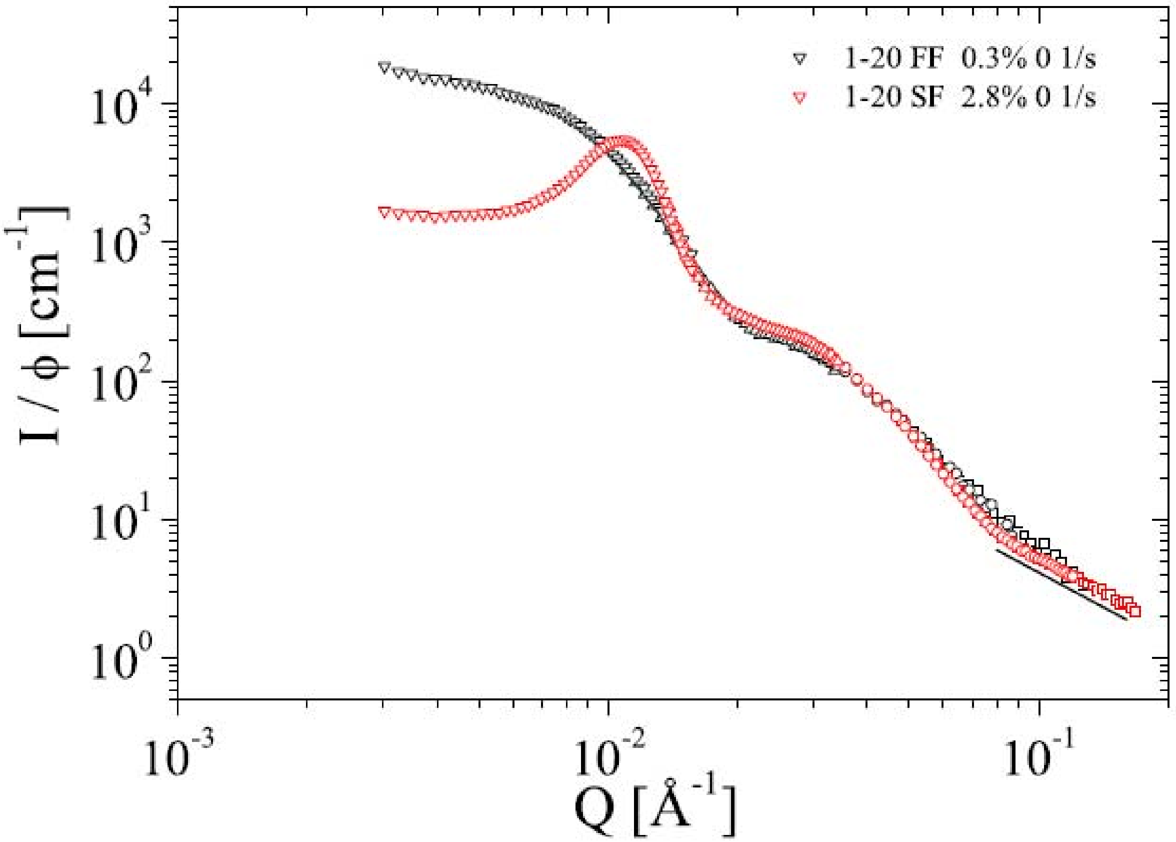
Experiment (Symbols) M. Laurati, J. Stellbrink, R. Lund, L. Willner, D. Richter, and E. Zaccarelli, *Phys. Rev. Letters*, **94**, 195504, 2005.

M. Laurati, J. Stellbrink, R. Lund, L. Willner, D. Richter, and E. Zaccarelli, PRE, 76, 041503, 2007

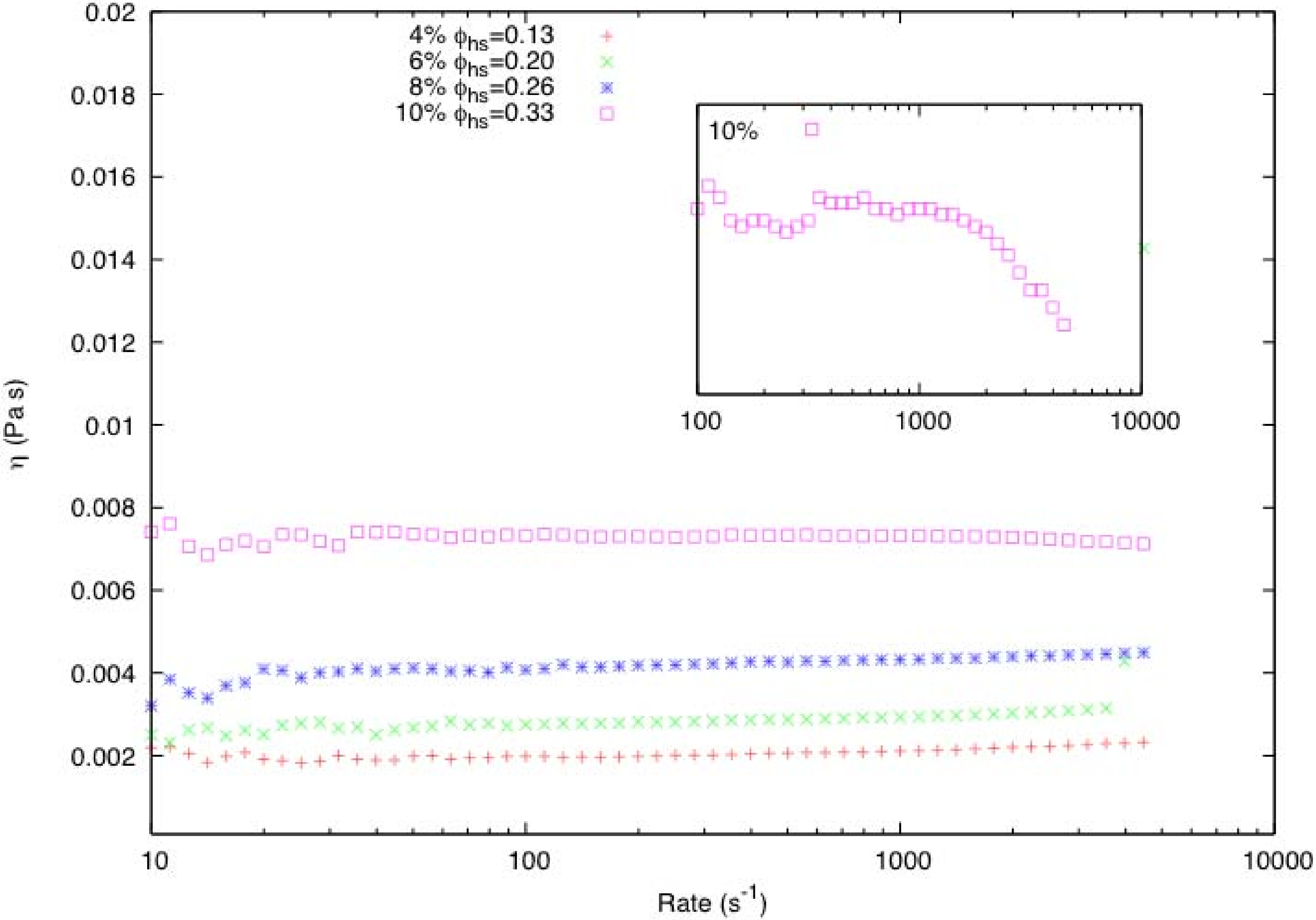

Liquid
Liquid-solid coexistence
FCC crystal
"Glass"
.494
.545
.58
.63
.7404...
Random close packing
Crystal close packing
Volume fraction
Φ



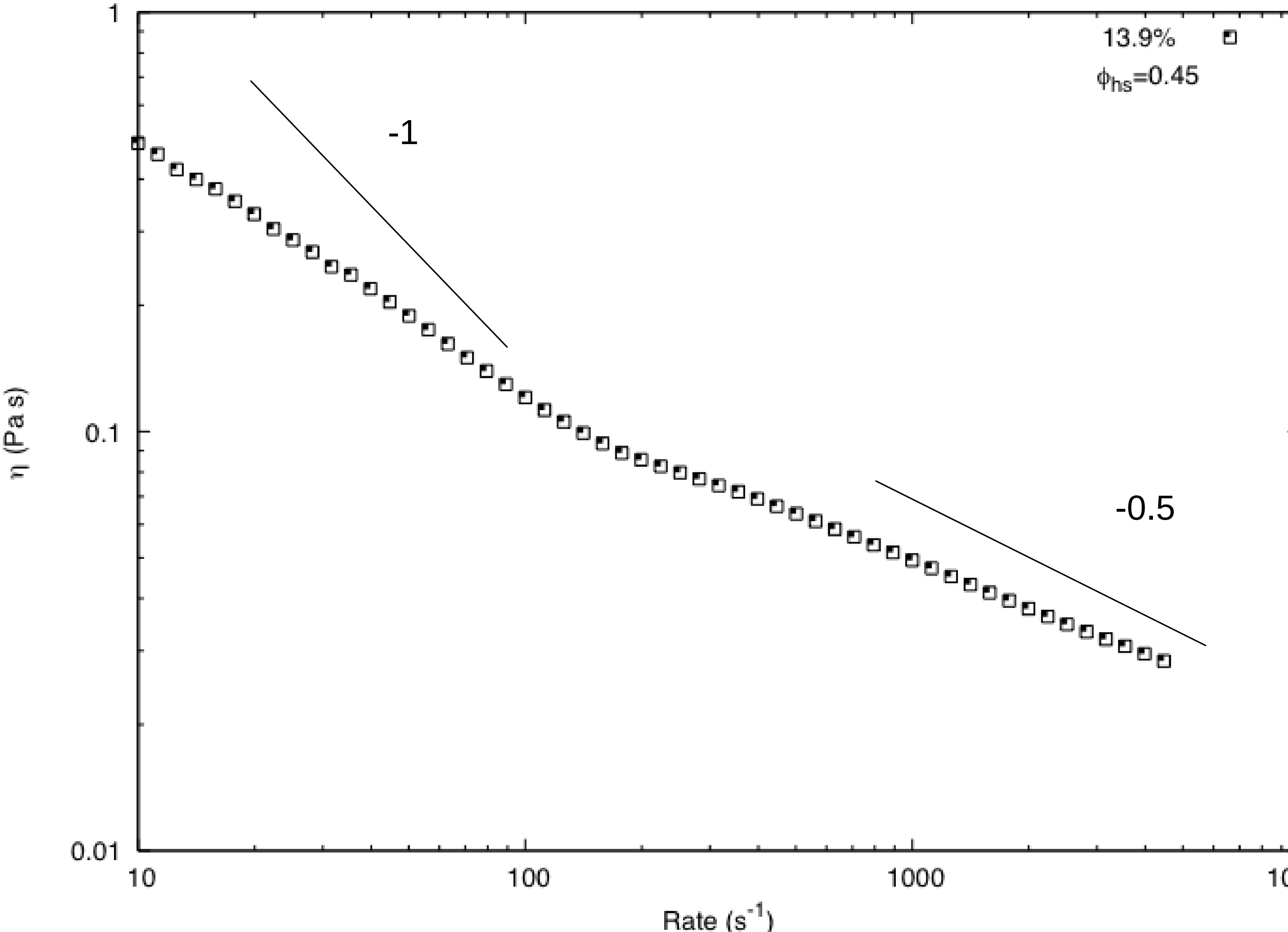
J. Stellbrink, B. Lonetti, G. Rother, L. Willner and D. Richter, J. Phys. Cond. Matter (in press)


1-20 FF 0.3% 0 1/s
1-20 SF 2.8% 0 1/s
I / φ [cm^{-1}]
10^0
10^1
10^2
10^3
10^4
10^{-3}
10^{-2}
10^{-1}
Q [Å^{-1}]

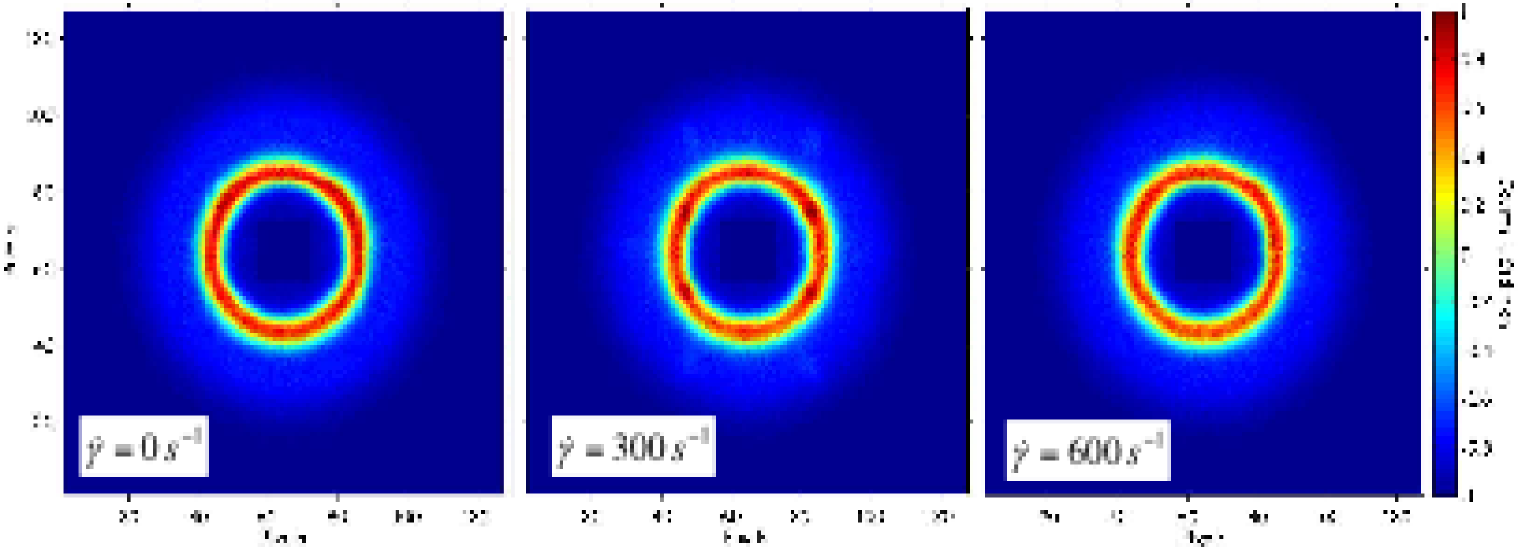
Rheology: Steady Shear

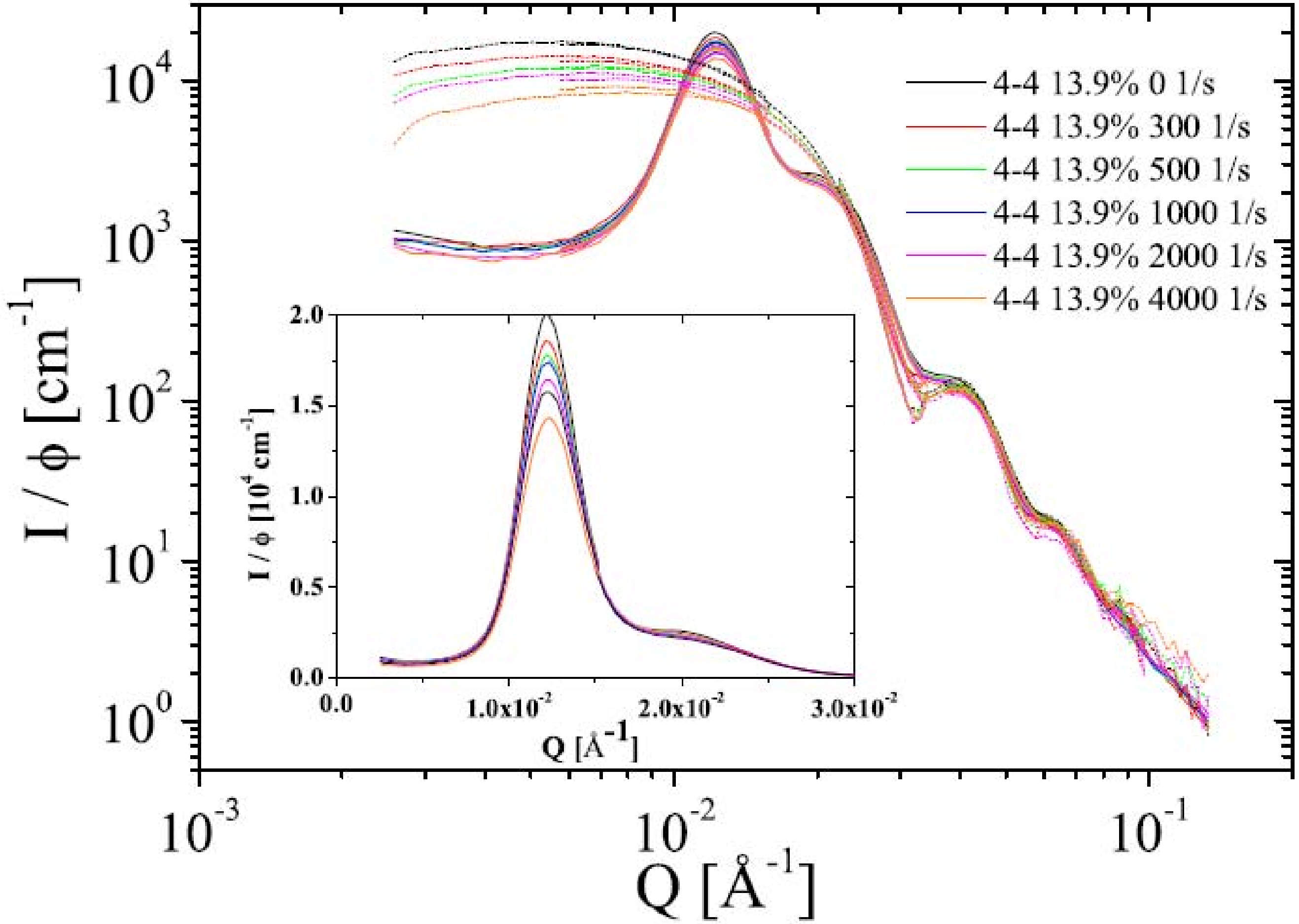


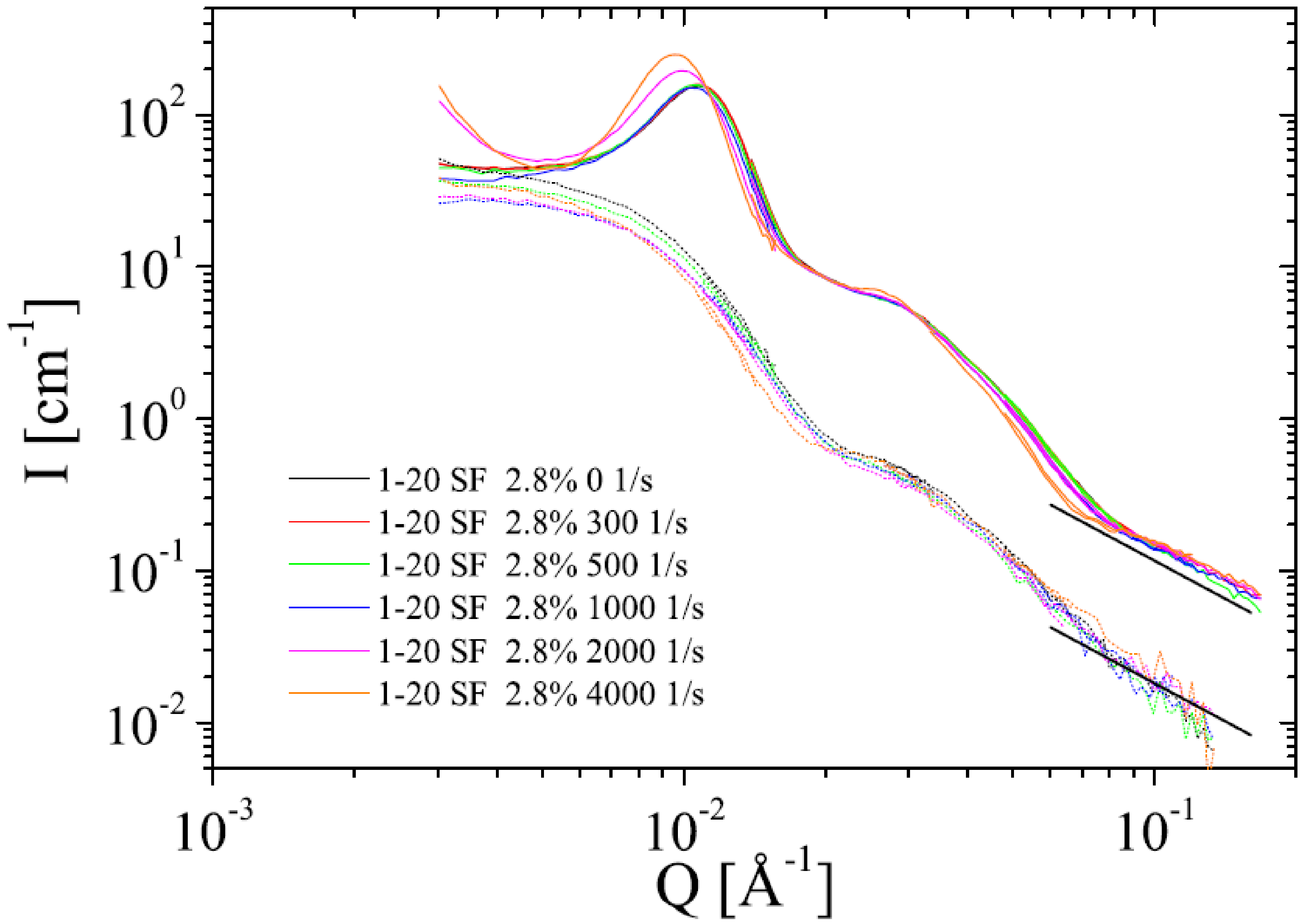
Rheology: Steady Shear



Rheo-SANS




I / φ [cm^{-1}]
Q [Å^{-1}]
10^{4}
10^{3}
10^{2}
10^{1}
10^{0}
10^{-3}
10^{-2}
10^{-1}
4-4 13.9% 0 1/s
4-4 13.9% 300 1/s
4-4 13.9% 500 1/s
4-4 13.9% 1000 1/s
4-4 13.9% 2000 1/s
4-4 13.9% 4000 1/s
I / φ [10^{4} cm^{-1}]
2.0
1.5
1.0
0.5
0.0
0.0
1.0x10^{-2}
2.0x10^{-2}
3.0x10^{-2}
Q [Å^{-1}]


I [cm^{-1}]
Q [Å^{-1}]
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-2}
10^{-1}
1-20 SF 2.8% 0 1/s
1-20 SF 2.8% 300 1/s
1-20 SF 2.8% 500 1/s
1-20 SF 2.8% 1000 1/s
1-20 SF 2.8% 2000 1/s
1-20 SF 2.8% 4000 1/s

Scattering From Fractal Systems

- Fractals are systems that are "self-similar" under a change of scale I.e. R -> CR
- For a mass fractal the number of particles within a sphere of radius R is proportional to R^D where D is the fractal dimension

Thus

$$4pR^2 dR.G(R) = \text{number of particles between distance R and R + dR} = cR^{D-1}dR$$

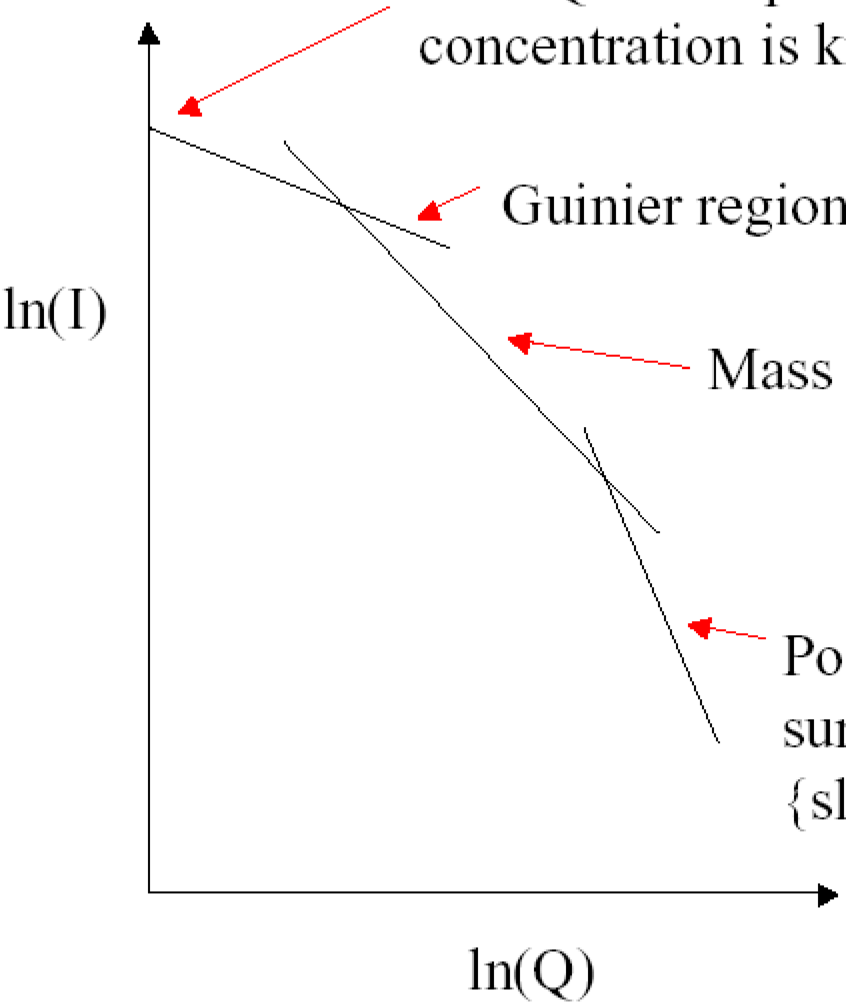
$$\therefore\ G(R) = (c/4\pi)R^{D-3}$$

$$\text{and}\ \ S(\vec{Q}) = \int d\vec{R}.e^{i\vec{Q}.\vec{R}}G(R) = \frac{2\pi}{Q}\int dR.R.\sin QR.(c/4\pi)R^{D-3}$$

$$= \frac{c}{2}\frac{1}{Q^D}\int dx.x^{D-2}.\sin x = \frac{const}{Q^D}$$

For a surface fractal, one can prove that $S(Q) \propto \dfrac{const}{Q^{6-D_s}}$ which reduces to the Porod form for smooth surfaces of dimension 2.

Typical Intensity Plot for SANS From Disordered Systems



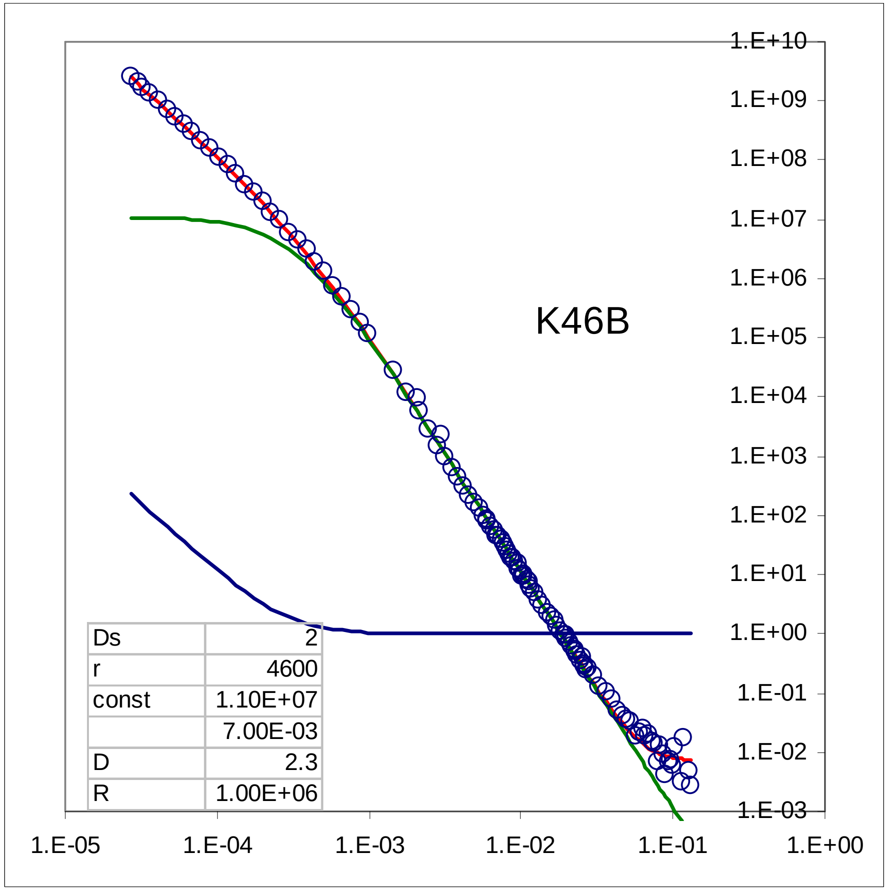
Zero Q intercept - gives particle volume if concentration is known

Guinier region (slope = $-r_g^2/3$ gives particle “size”)

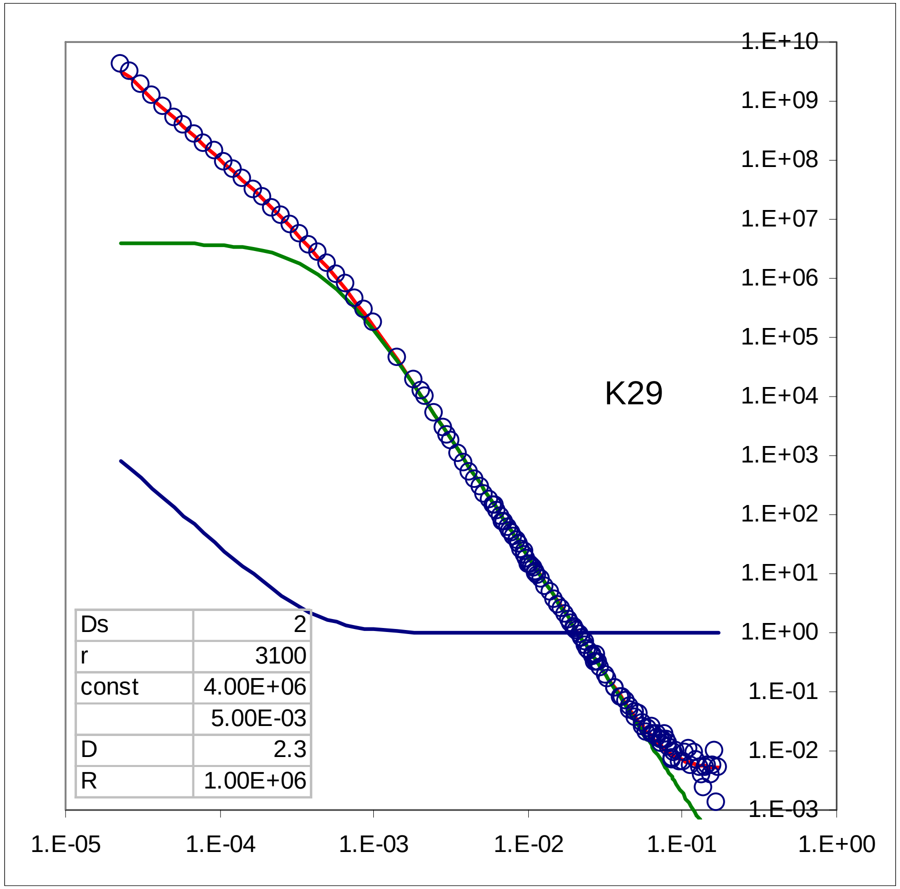
Mass fractal dimension (slope = -D)

Porod region - gives surface area and surface fractal dimension {slope = $-(6-D_s)$}

White marbles from Carrara (Italy)



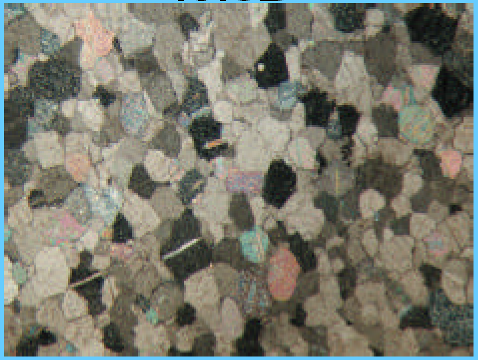
Ds	2
r	4600
const	1.10E+07
	7.00E-03
D	2.3
R	1.00E+06



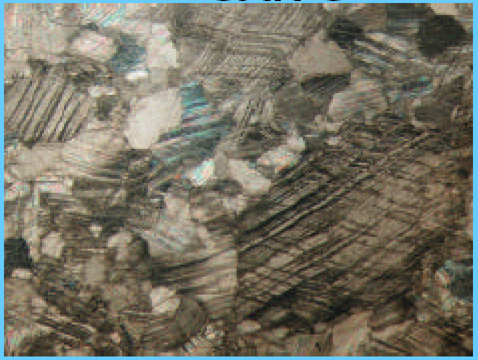
Ds	2
r	3100
const	4.00E+06
	5.00E-03
D	2.3
R	1.00E+06

MU2

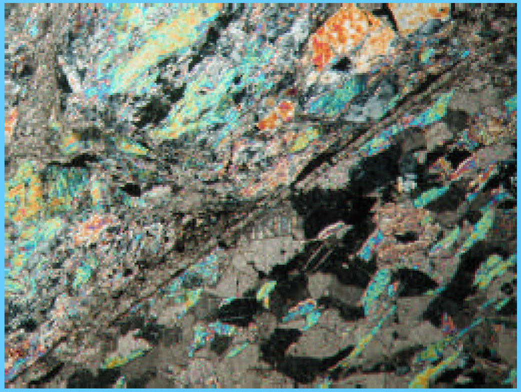
K46B



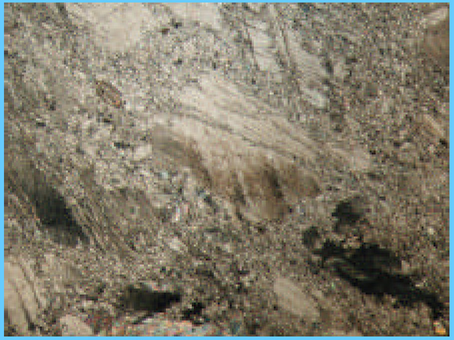
CAN C



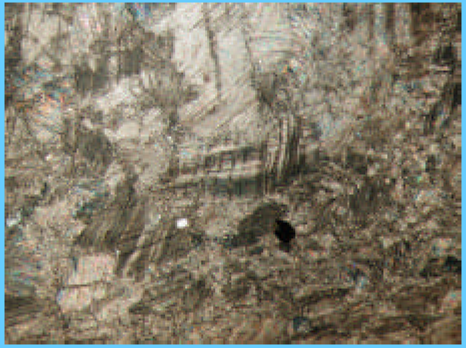
CD 11

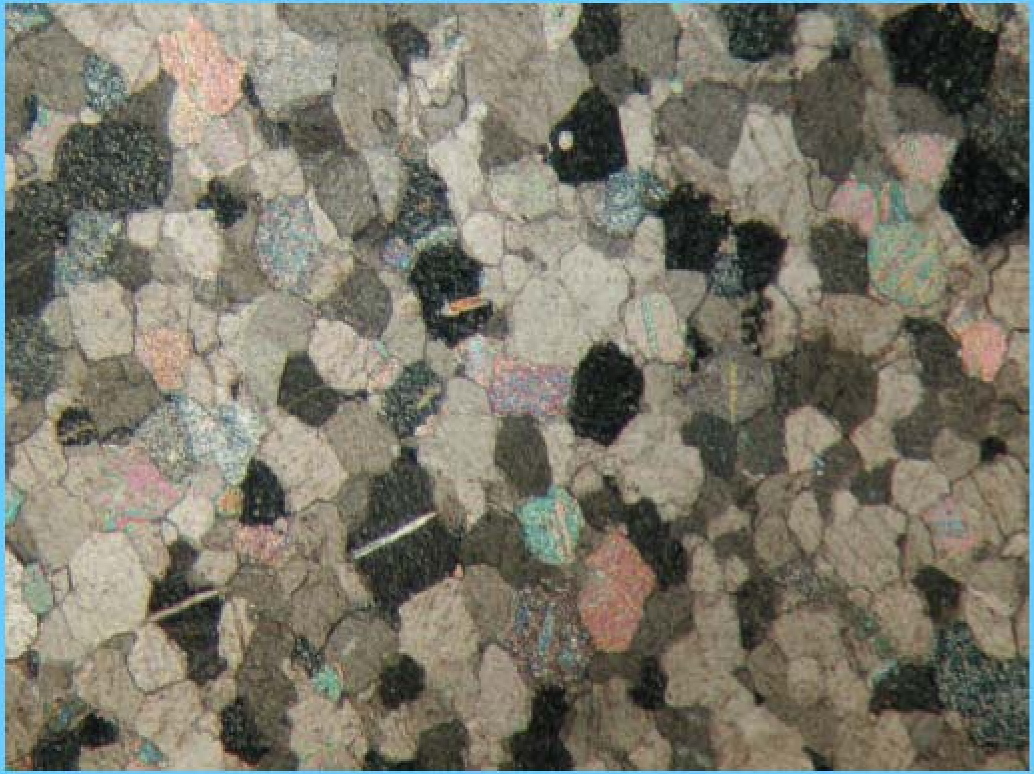


MU4



CV 9





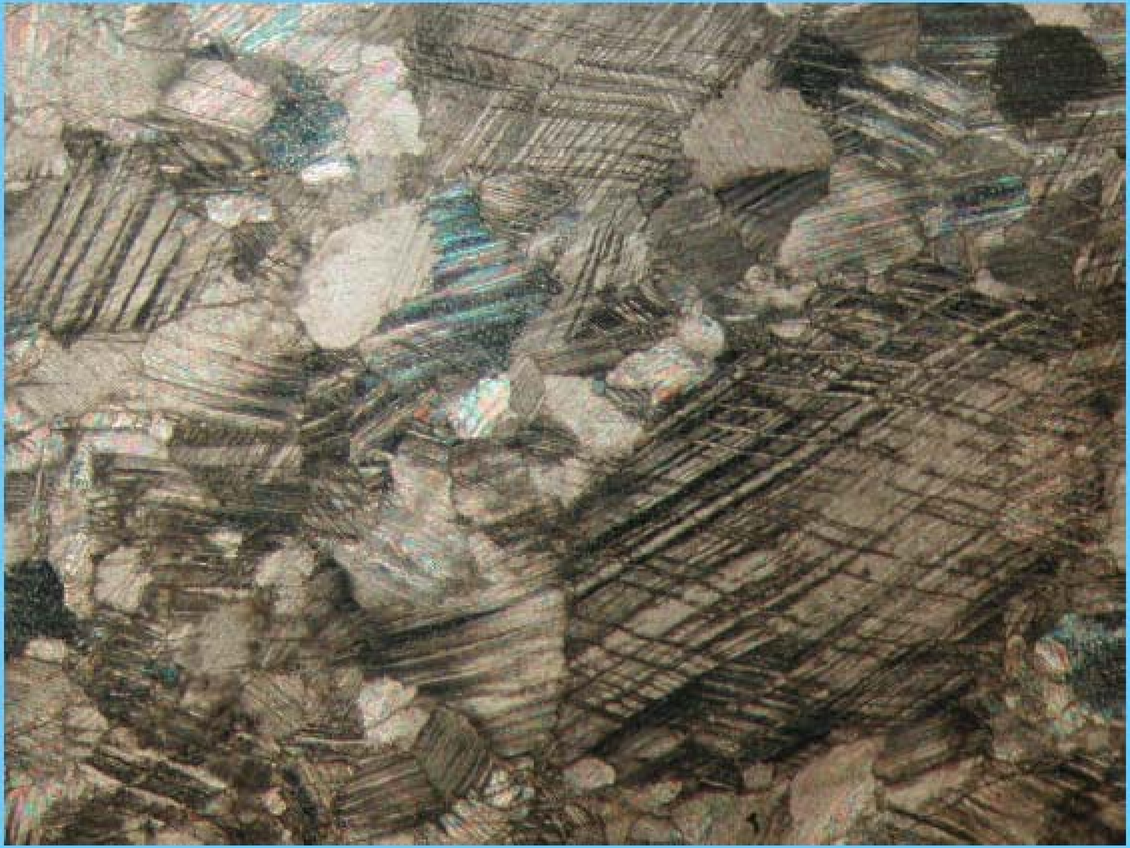
PA LA

MGS = ca. 4 mm with slightly irregular interfaces

Not very polydisperse

Medium Metamorphism (ca 400 °C)

Long time



CAN C

MGS = ca. 4-5 mm – Smeared Interfaces

time shorter than previous

Similar temperatures

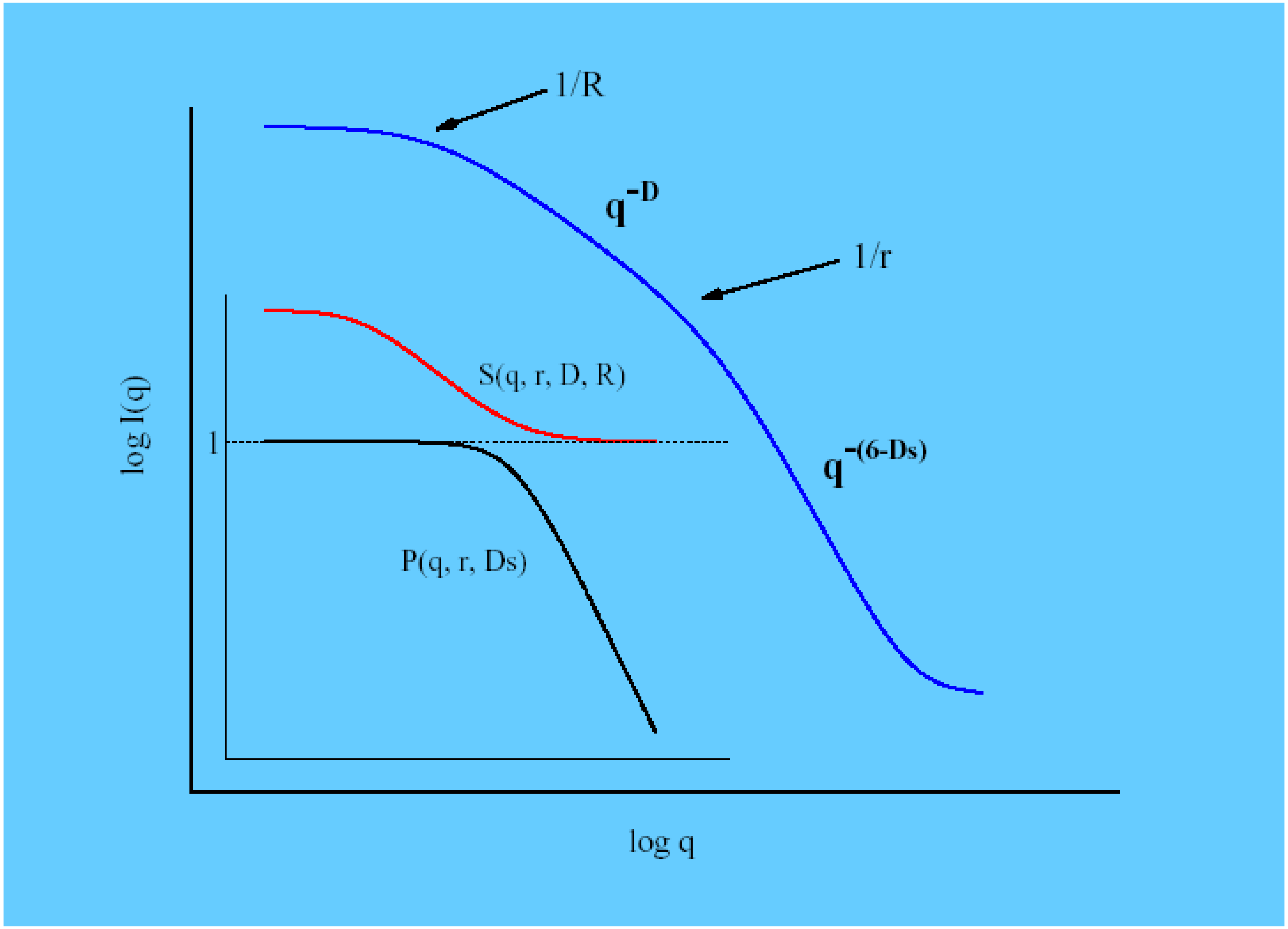
$$I(q) \propto P(q,r,Ds) \cdot S(q,r,D,R)$$

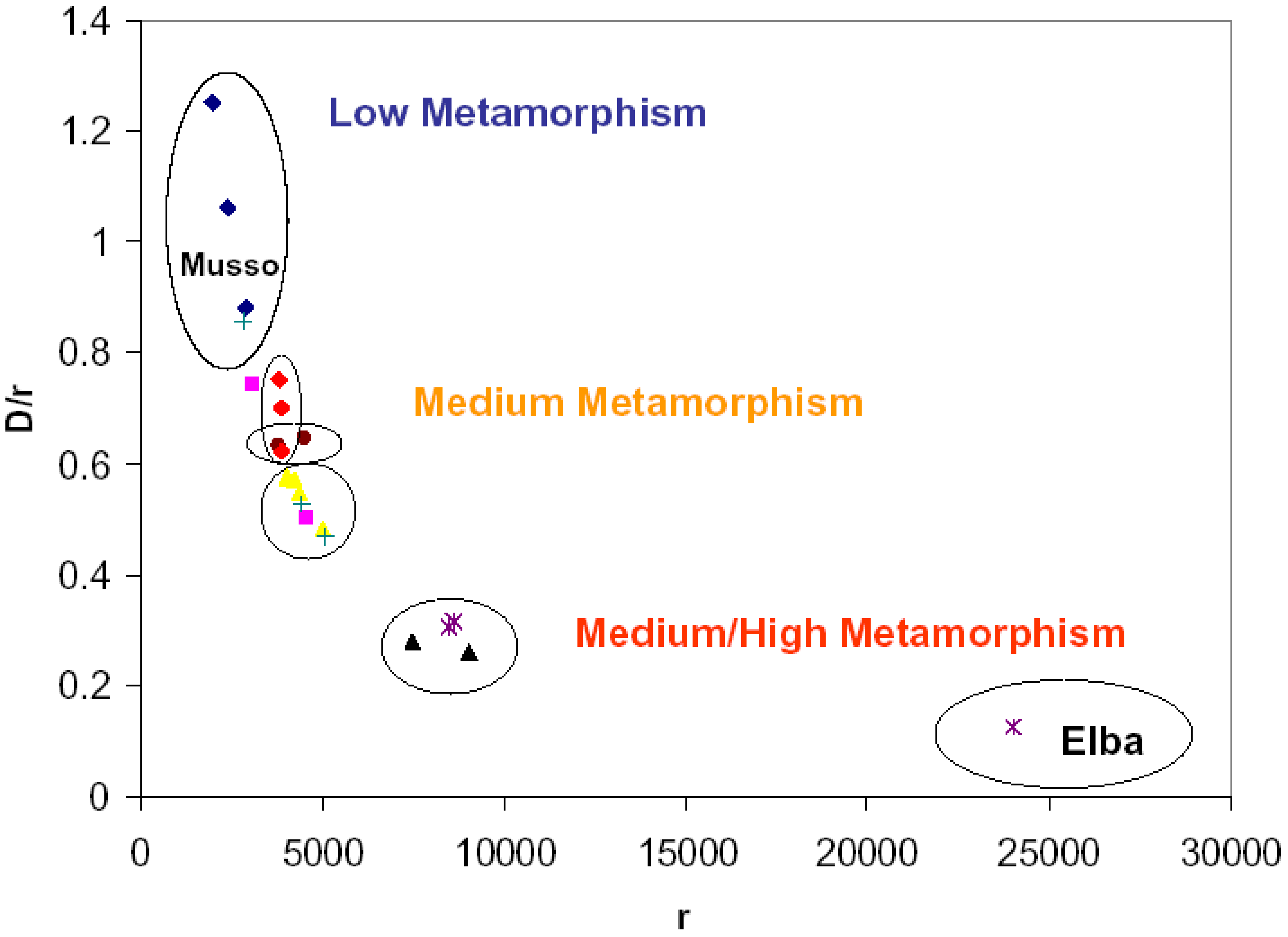
$$P(q,r,Ds) = \left(1 + \frac{\sqrt{2}}{3} q^2 r^2\right)^{\frac{Ds-6}{2}}$$

$$S(q,r,D,R) = 1 + \frac{D\Gamma(D-1)}{qr^D}\left(1 + \frac{1}{qR^2}\right)^{\frac{1-D}{2}} \sin[(D-1)\arctan(qR)]$$

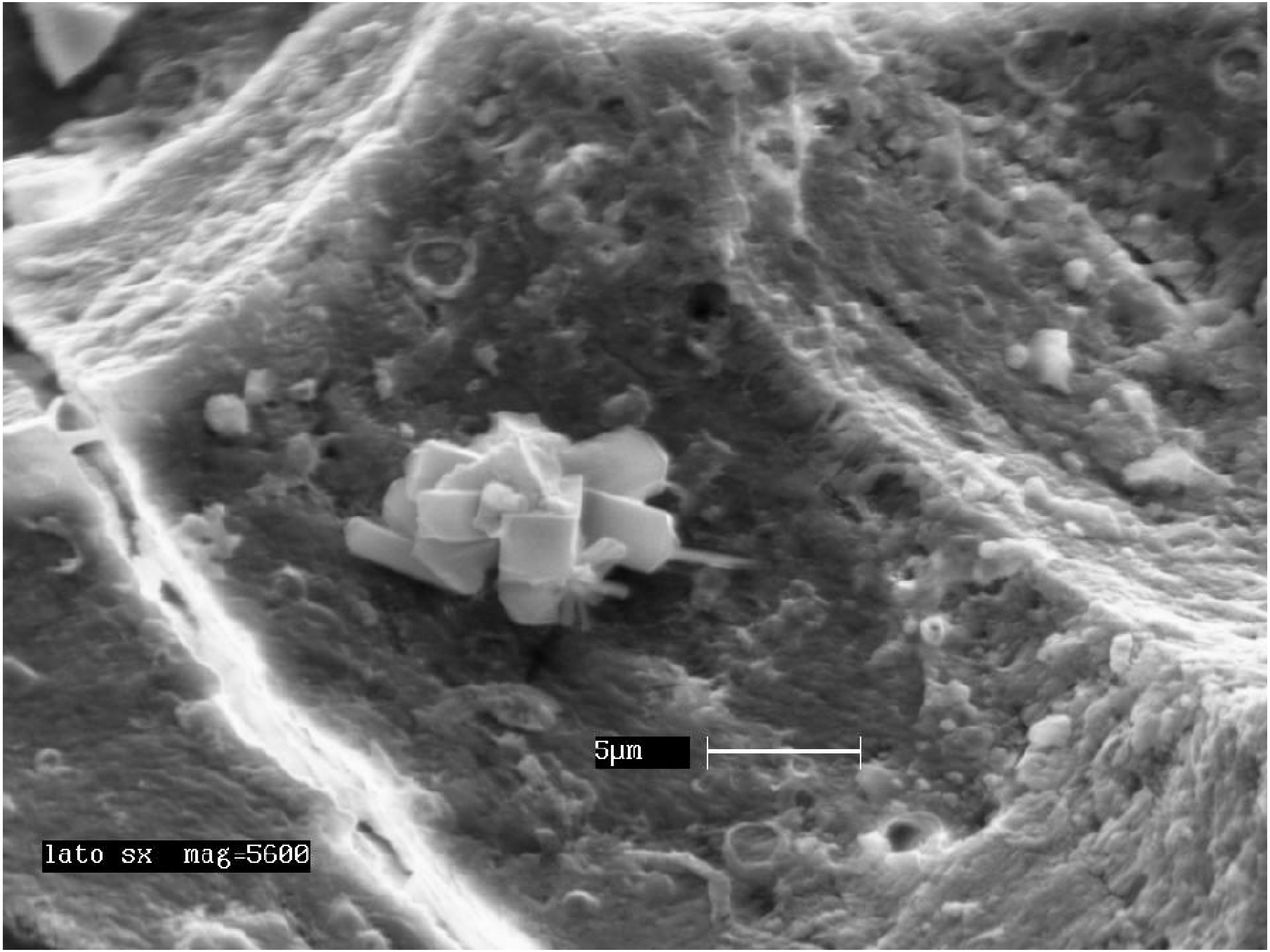
A. Emmerling et al., J. of Non Cryst. Sol. 185, 240 (1994)

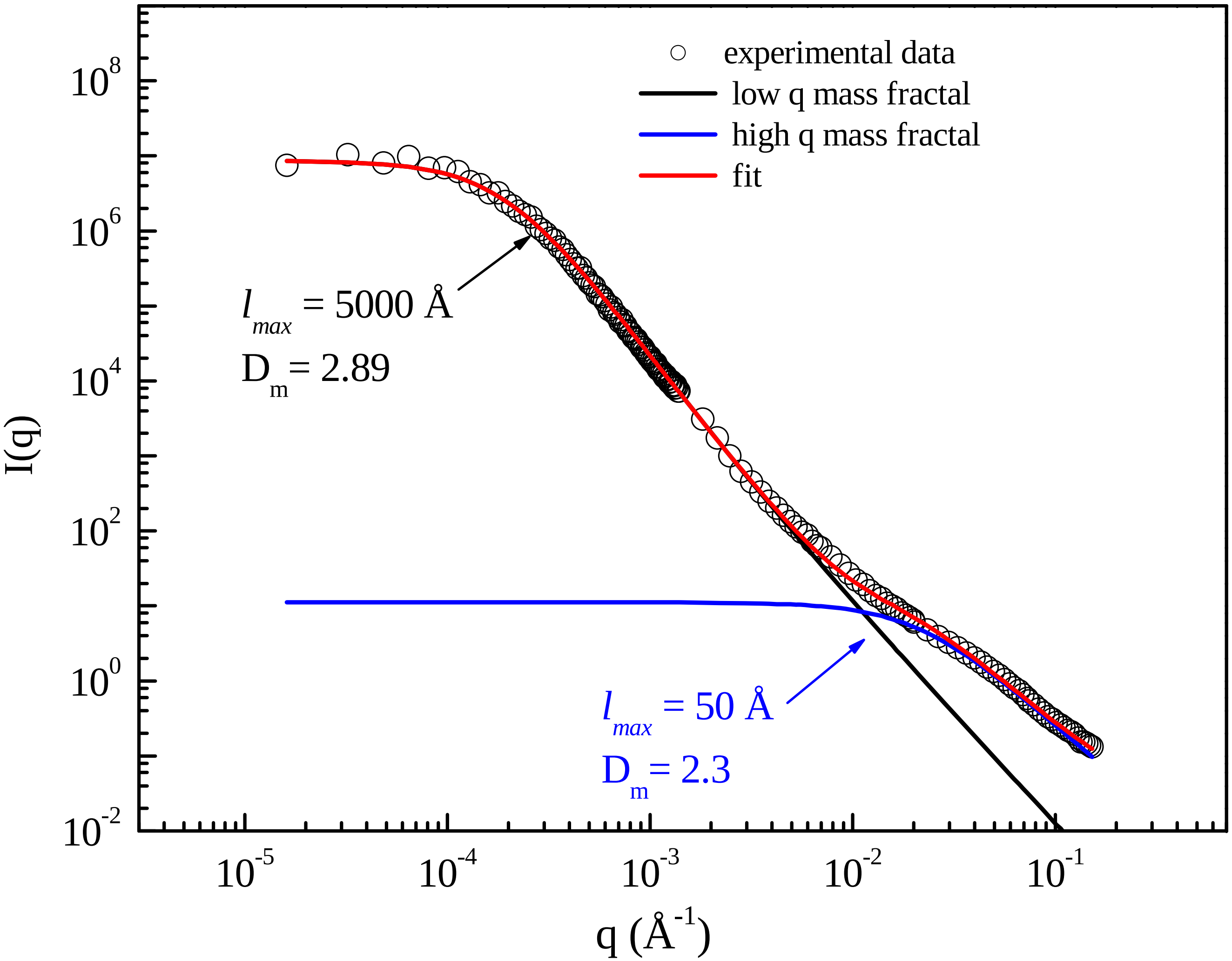
J. Teixeira, J. App. Cryst., 21, 781 (1988)


1/R
q^-D
1/r
S(q, r, D, R)
1
log I(q)
q^-(6-Ds)
P(q, r, Ds)
log q

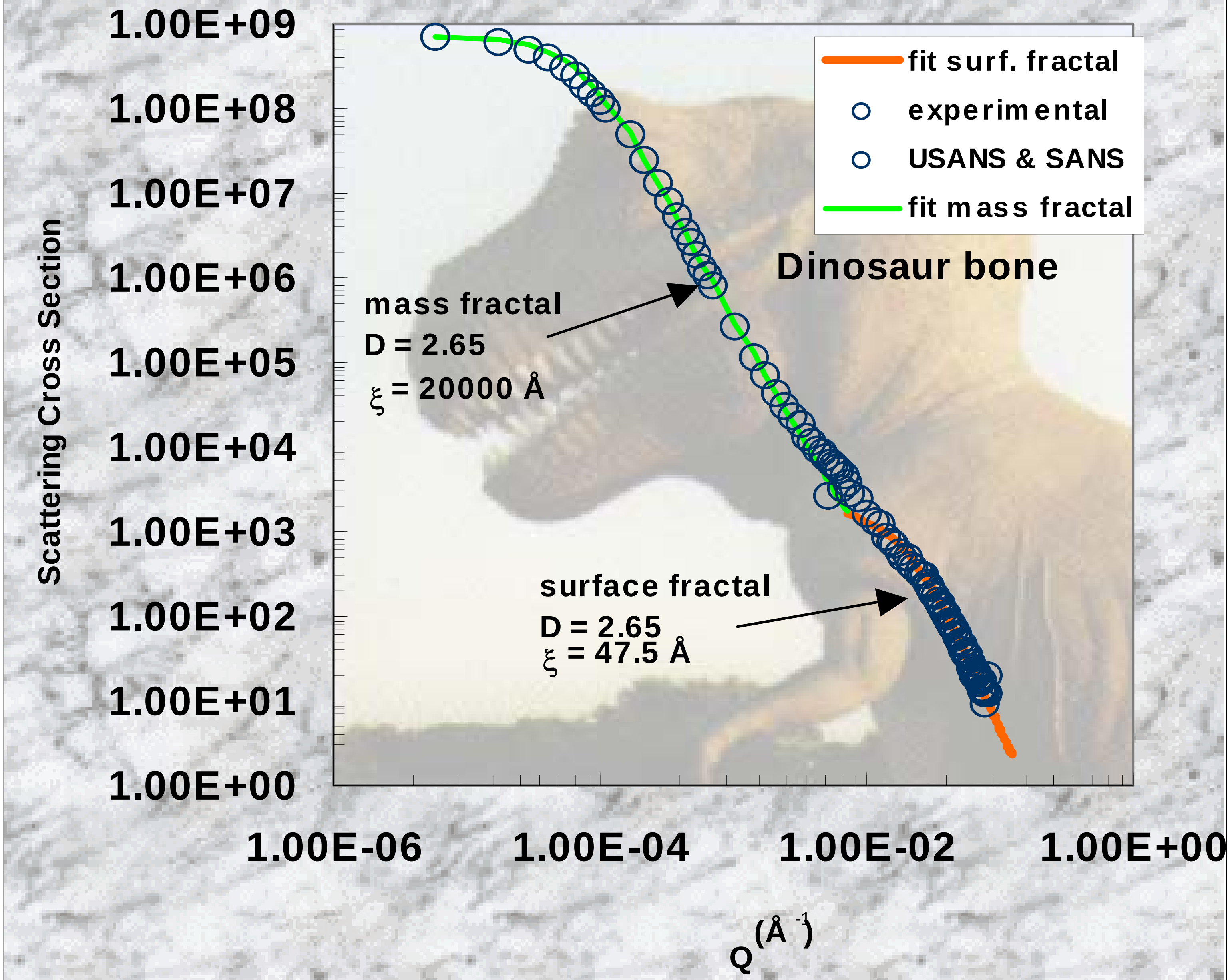

1.4
1.2
1
0.8
0.6
0.4
0.2
0
D/r
0
5000
10000
15000
20000
25000
30000
r
Low Metamorphism
Musso
Medium Metamorphism
Medium/High Metamorphism
Elba

biogenic platforms generated by *Dendropoma petraeum*


5µm
lato sx mag=5600



experimental data
low q mass fractal
high q mass fractal
fit
l max = 5000 Å
D m = 2.89
l max = 50 Å
D m = 2.3
I(q)
q (Å-1)
10-2
10^0
10^2
10^4
10^6
10^8
10-5
10-4
10-3
10-2
10-1



1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
Scattering Cross Section
1.00E-06
1.00E-04
1.00E-02
1.00E+00
Q (Å -1)
fit surf. fractal
experimental
USANS & SANS
fit mass fractal
Dinosaur bone
mass fractal
D = 2.65
ξ = 20000 Å
surface fractal
D = 2.65
ξ = 47.5 Å

- Basic Equations
- Model-independent methods
  - Guinier, Porod, Invariant
- Non-Linear Model Fitting
  - Particles, Polymers, Materials
- Global Fitting
- Anisotropic Scattering
- Transforms
- Ab initio modeling

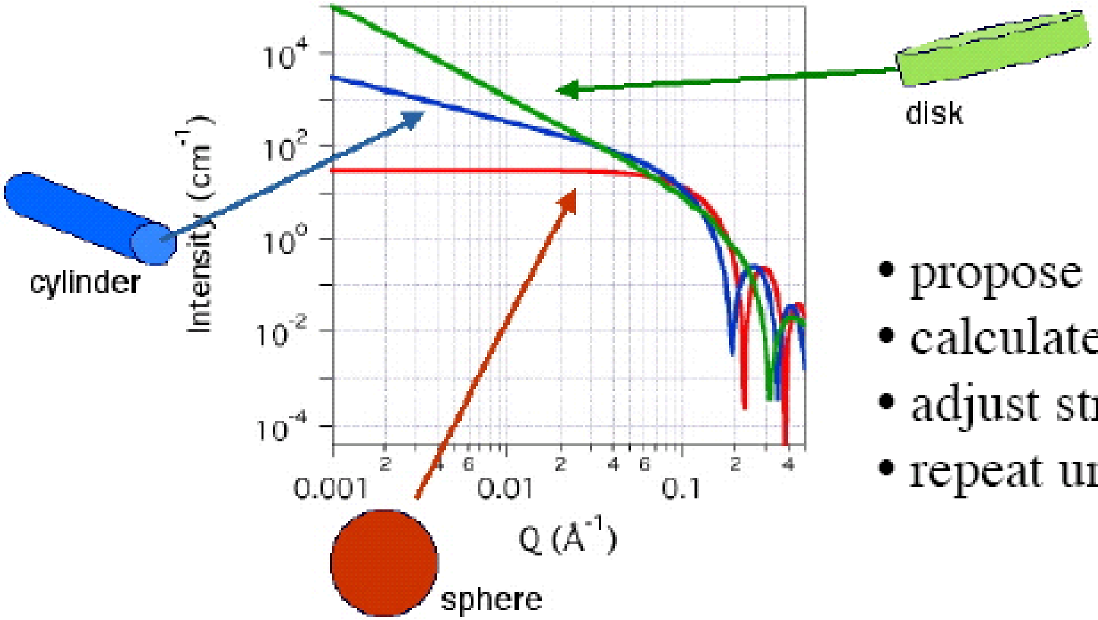
Easy

More involved

Non-Linear Model Fitting

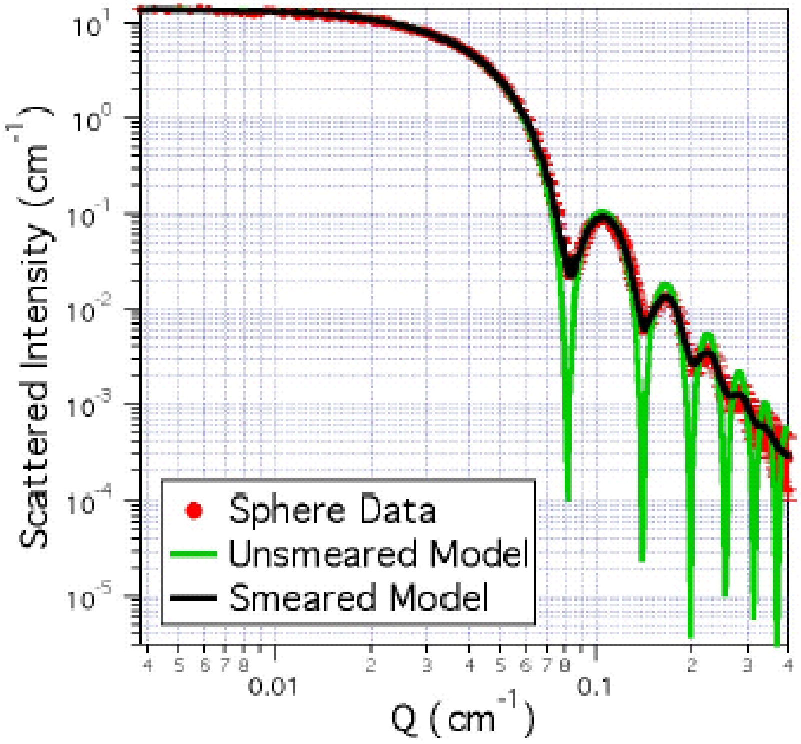
One of the most commonly used methods

- a “forward” calculation
- many structures and interactions to choose from



- propose a structural model
- calculate I(Q)
- adjust structural parameters
- repeat until done

Non-Linear Model Fitting



Point	parameters_sf	coef_sf	smear_coef_sf
0	scale	0.05	0.05
1	Radius (A)	55	55
2	contrast (Å-2)	2e-06	2e-06
3	bkgd (cm-1)	0	0

- Non-linear least squares fitting to experimental data

- Use all the information you can to reduce the number of free model parameters
  - -SLD's
  - -Concentrations
  - -Lengths

- A "good" fit does not necessarily guarantee a perfect representation of the structure in the sample

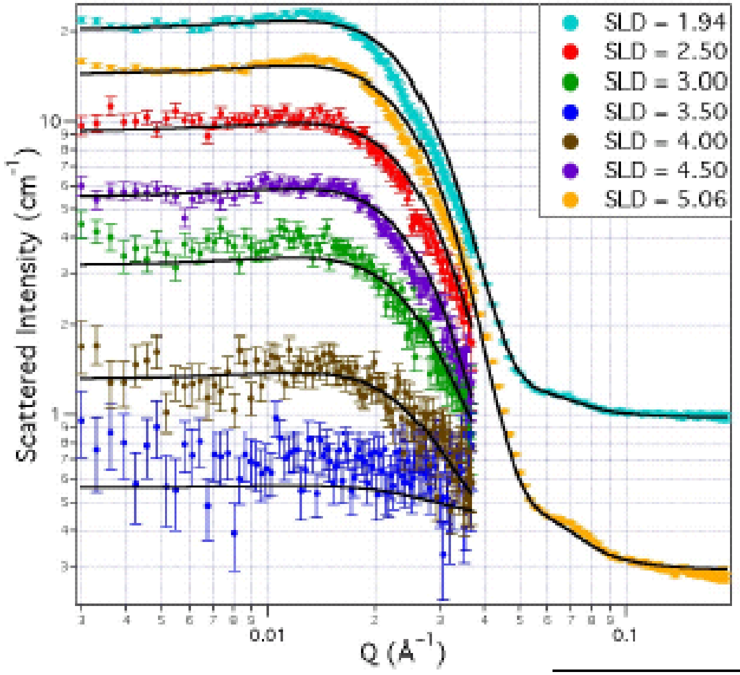
Global Fitting

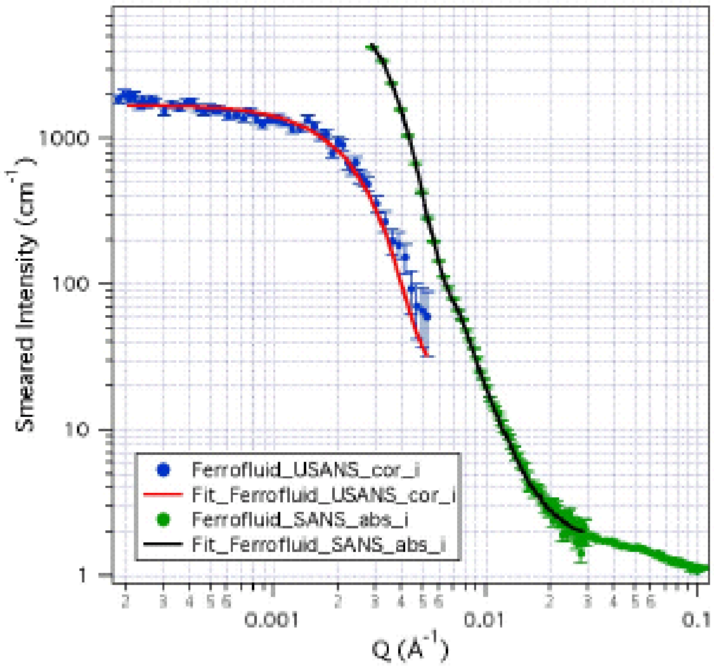
Contrast variation

- same particles, different solvent
- R, ρ_p, ϕ are the same
- ρ_{solv}, background are different

SANS + USANS data

- same sample (same cell)
- all parameters are the same
- smearing, scaling different

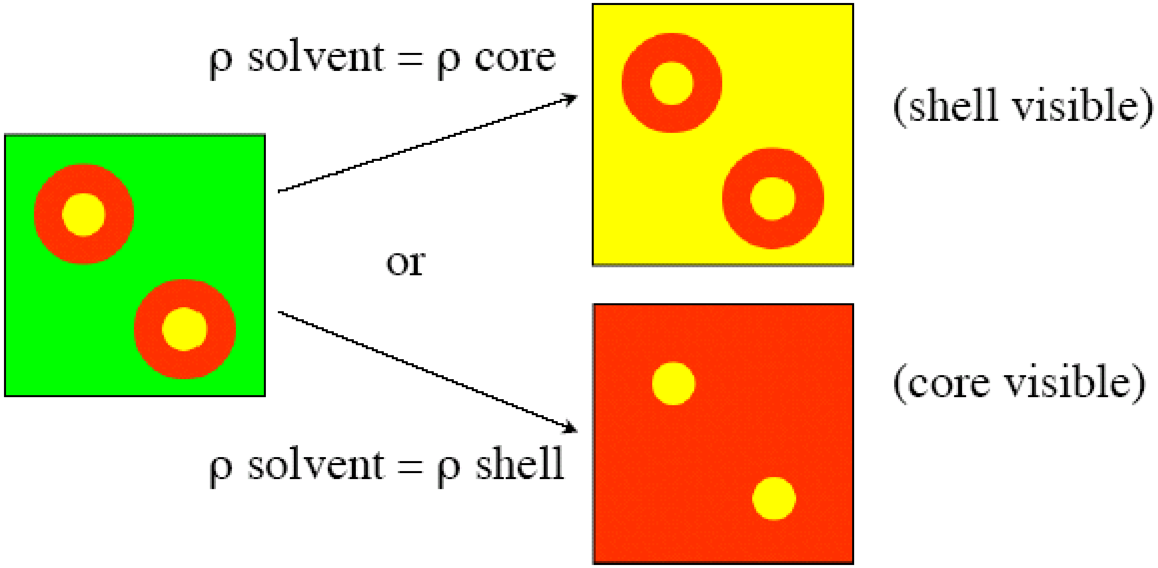




Contrast Variation

Contrast Matching

reduce the number of phases “visible”



ρ solvent = ρ core

(shell visible)

or

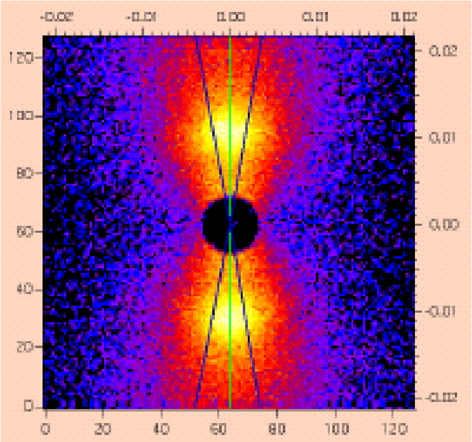
ρ solvent = ρ shell

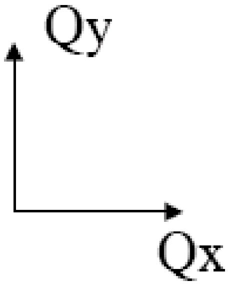
(core visible)

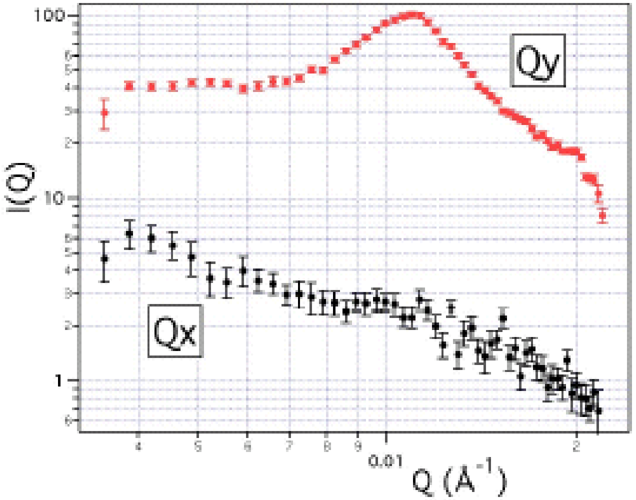
- The two distinct two - phase systems can be easily understood

Anisotropic Scattering

Elongated particles aligned by shear







Transforms - p(r)

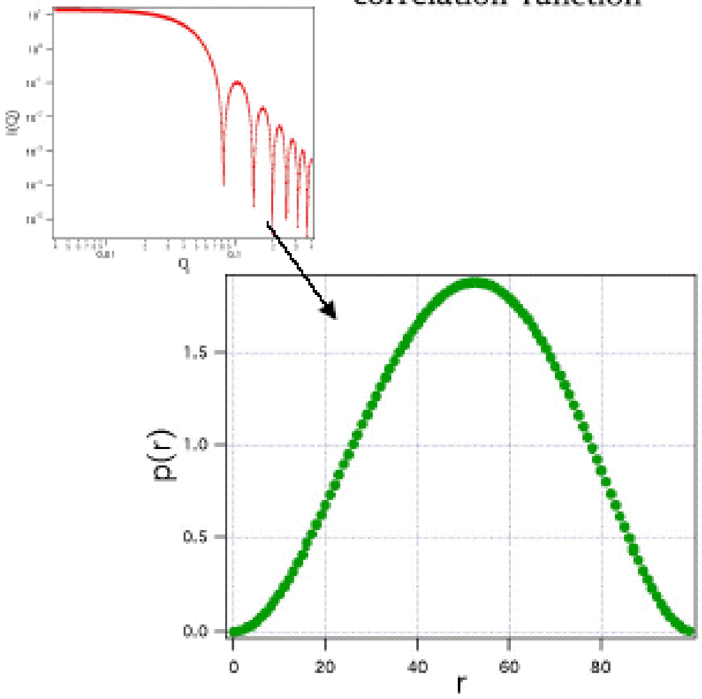
Distance Distribution Function: p(r)

average over orientations

$$I_p(Q) \propto \left\langle \int \gamma(\vec{r}) e^{i\vec{Q}\cdot\vec{r}}\, d\vec{r} \right\rangle = 4\pi \int r^2\, \gamma(r) \frac{\sin(Qr)}{Qr}\, dr$$

correlation function

p(r) is the probability that 2 randomly chosen points are at a distance r apart



If I(Q) is measured over a wide enough Q-range, then one can compute p(r) as the inverse transform:

$$p(r) = \frac{1}{2\pi^2} \int_0^\infty I(Q)(Qr)\sin(Qr)\, dQ$$

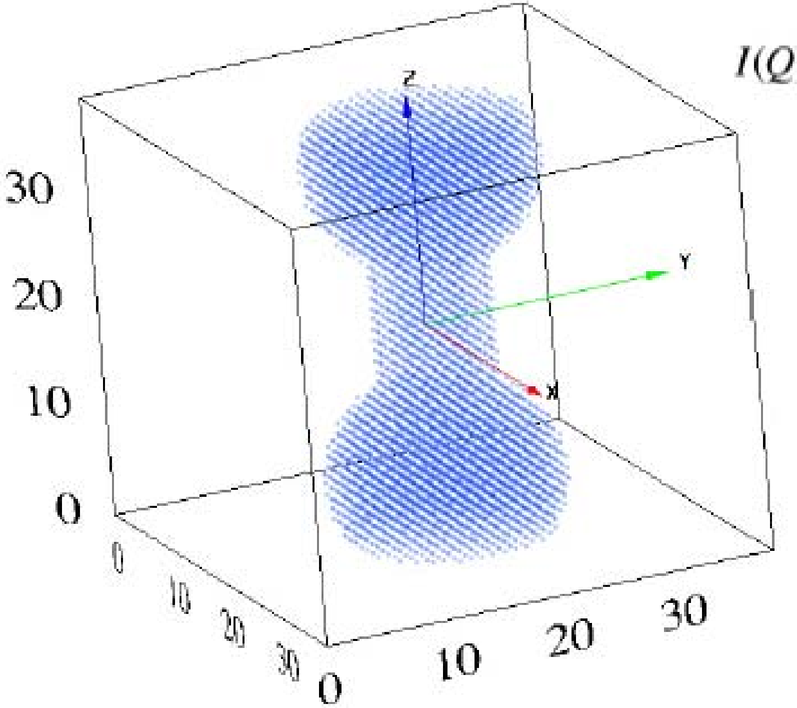
For a sphere:

$$p(r) = 12x^2(2 - 3x + x^3) \qquad x = r/D$$

*See: D. Svergun, O. Glatter

Ab initio methods

- Calculate I(Q) for complex structures
  - Biological molecules made up of subunits
  - non-standard geometric shapes



$$I(Q) = \sum_{i=1}^{n} I_i(Q) + 2\sum_{i \neq j}\sum F_i(Q)F_j(Q)\frac{\sin(Qr_{ij})}{Qr_{ij}}$$

- fill volume with spheres on a grid
- need distance between every pair
- can be computationally intensive
- can optimize shape

- packages available (D. Svergun)

**Need “dilute” particles and “burly” computer

Interesting Links:

http://scattering.tripod.com

http://www.isis.rl.ac.uk/LargeScale/LOQ/loq.htm

http://www.ncnr.nist.gov/resources/simulator.html