SANS From Dilute Particle Systems

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NIST

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CHRNS Center for High Resolution Neutron Scattering NIST

Outline

1. General Features of Scattering from Dilute, Uniform Particles
   - Oriented Particles
   - Randomly Oriented Particles
2. Monosized, Uniform Particles
   - Guinier approximation
   - Molecular weight determination
   - Form factors for various particle shapes
   - Effect of polydispersity on Rg
   - Determination of particle shape: P(r)
3. Compound Particles
   - contrast matching
4. Non-Uniform, Monosized, Particles
   - contrast variation methods

SANS from Dilute (i.e. Independent) Particles

"Dilute" means:

- no correlation between positions or orientations of particles

"Particle" means:

- any discrete submicron scale material inhomogeneiety

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

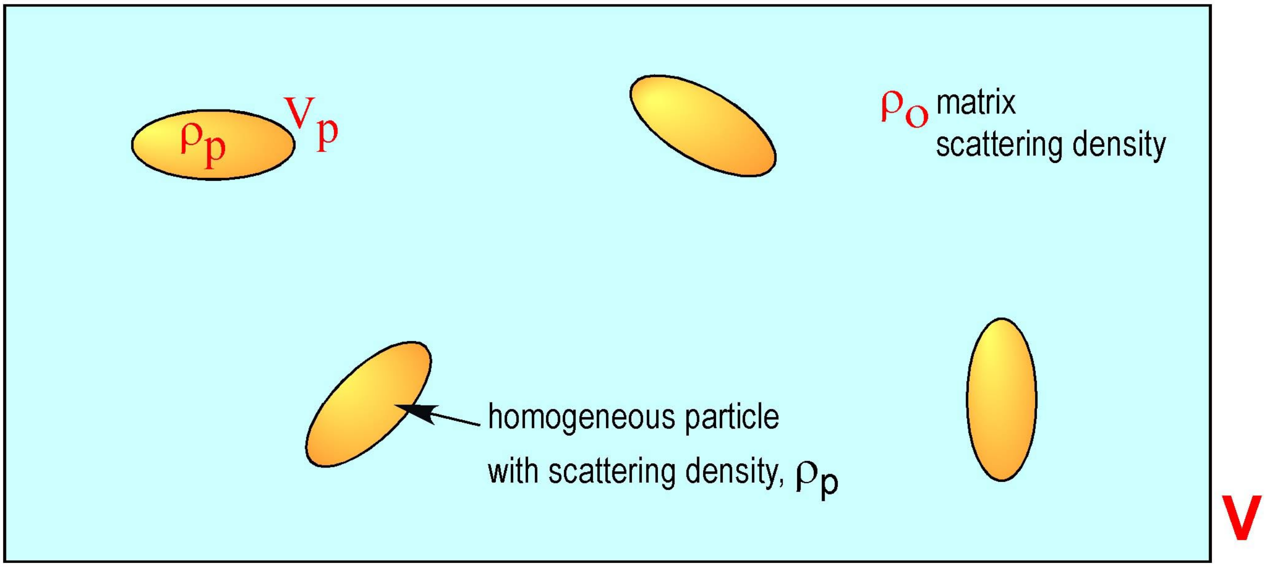
Compound (non-uniform) Particles
- DNA/protein complexes, viruses, etc.
- block copolymers
- particles with labelled subunits

Consequences:

- No interparticle interference effects

- Total scattered intensity is the sum of scattering from individual particles

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

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

Contraste Factor Particle Shape

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

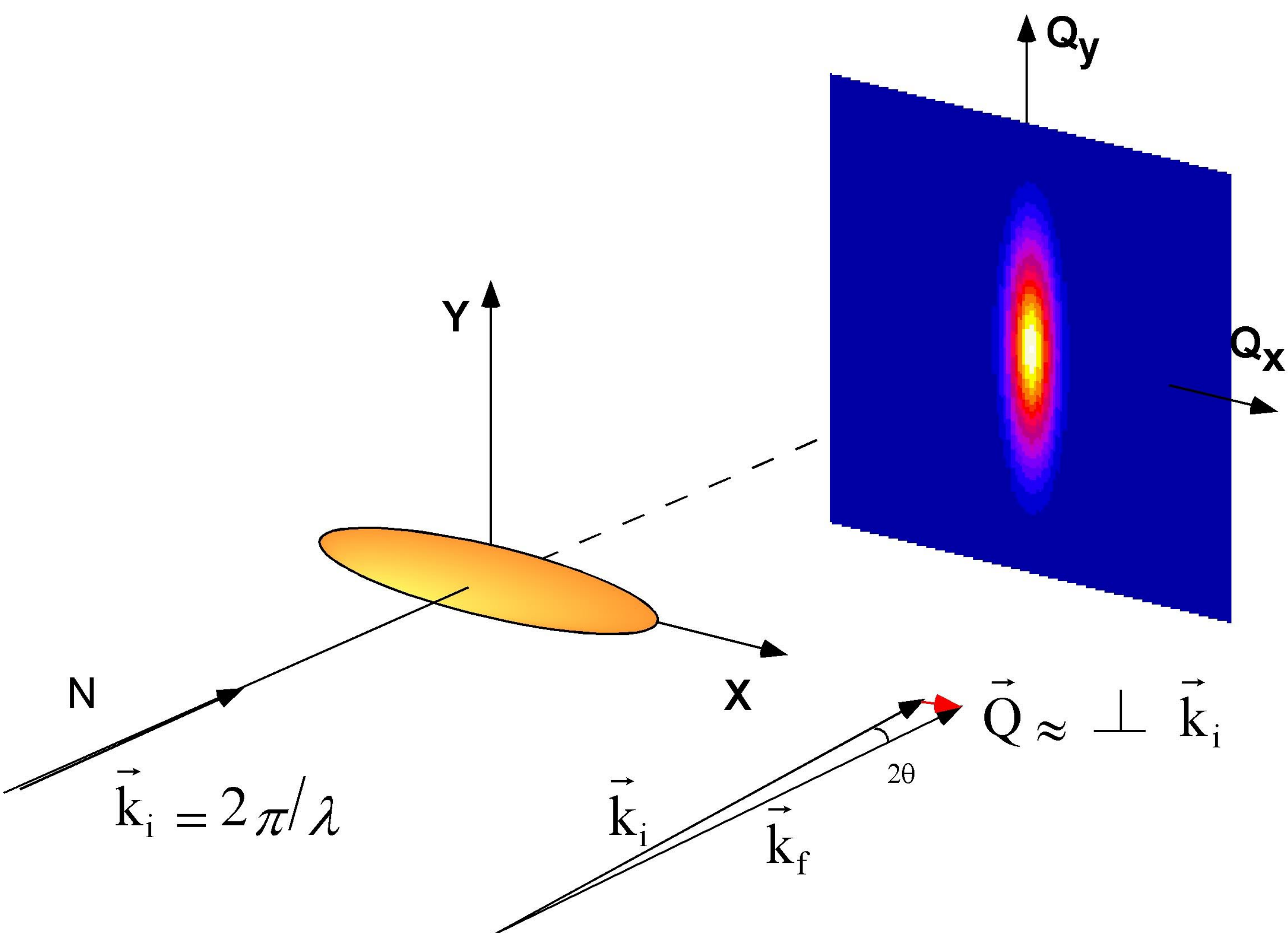
SANS from Oriented Particles

$$I(\vec{Q}) \propto \left|F(\vec{Q})\right|^2 = \left|\frac{1}{v_p}\int_{v_p} e^{i\vec{Q}\cdot r}\, d\vec{r}\right|^2 = \left|\frac{1}{v_p}\int_{v_p} e^{iQ\, r_Q}\, d\vec{r}\right|^2$$

$I(\vec{Q})$ probes structure in direction of $\vec{Q}$

$$I(Q) \approx e^{-Q^2 \langle r_Q^2 \rangle} \quad \text{for} \quad Q\sqrt{\langle r_Q^2 \rangle} \le 1$$

$$\langle r_Q^2 \rangle = \frac{1}{v_p}\int r_Q^2\, d\vec{r}$$ mean square distance parallel to Q



SANS From Randomly Oriented Particles

- Guinier Approximation for Low-Q Scattering

average over orientations

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

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

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

$$\vdots$$

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

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

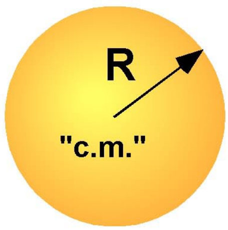
$$\text{where } R_G^2 = \frac{\int \rho(\vec{r})\, r^2\, d\vec{r}}{\int \rho(\vec{r})\, d\vec{r}} \quad \text{and} \quad \int \rho(\vec{r})\, \vec{r}\, d\vec{r} = 0$$

defines
"center of mass"

Guinier Radius, R_G

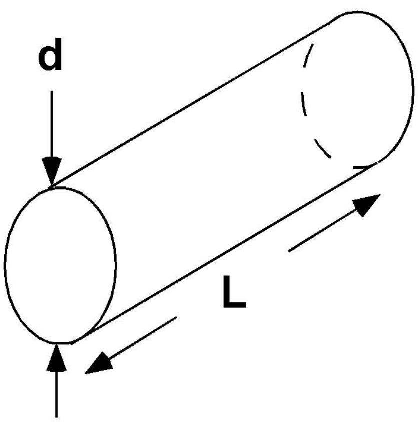
- rms distance from "center of scattering density"

1) Spherical Particles



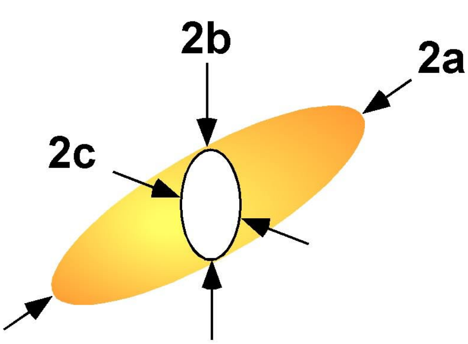
$$R_G^2 = \langle r^2 \rangle = \frac{\int \eta(\vec{r}) r^2 \, d\vec{r}}{\int \eta(\vec{r}) \, d\vec{r}} = \frac{3}{5} R^2$$

2) Cylinders (Rods or Disks)



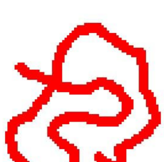
$$R_G^2 = \frac{L^2}{12} + \frac{d^2}{8}$$

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

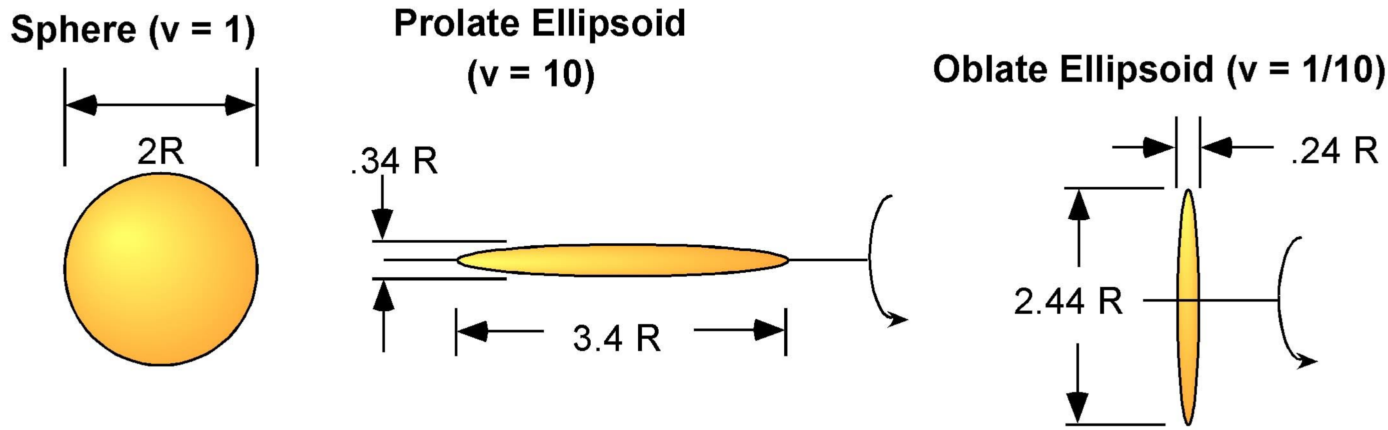


$$R_G^2 = \frac{1}{5}(a^2 + b^2 + c^2)$$

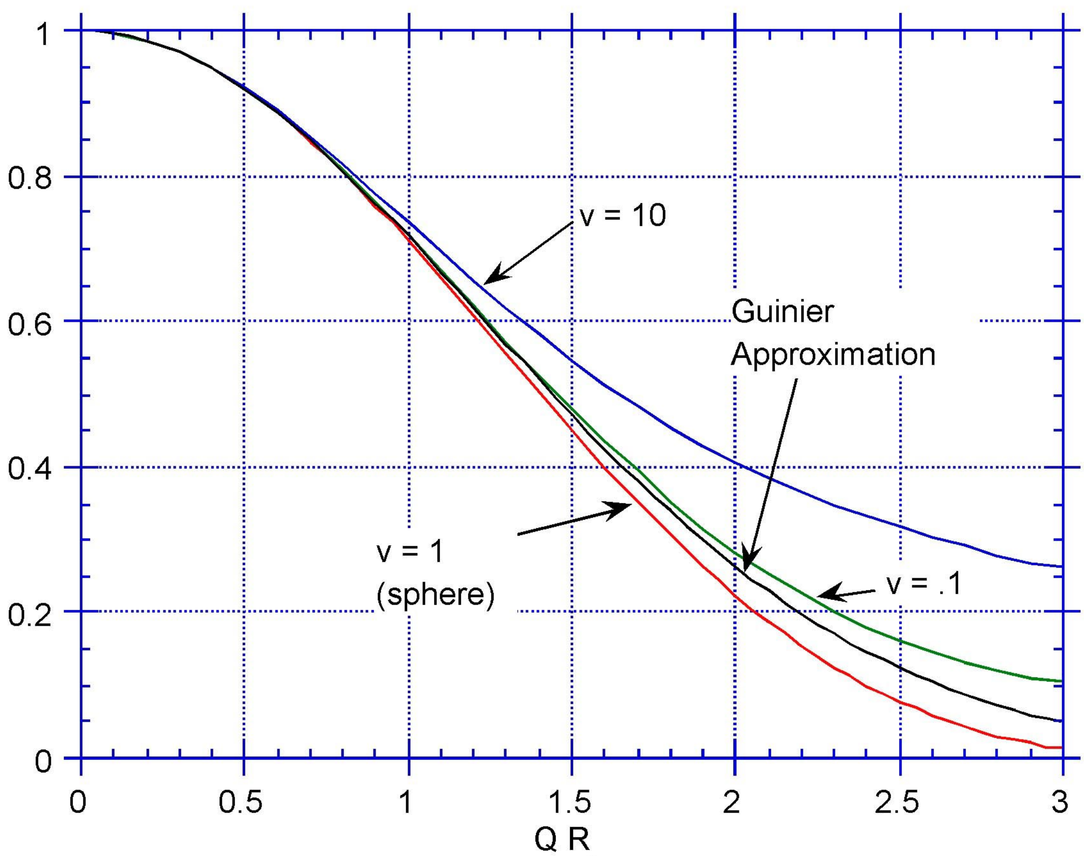
4) Gaussian chain



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



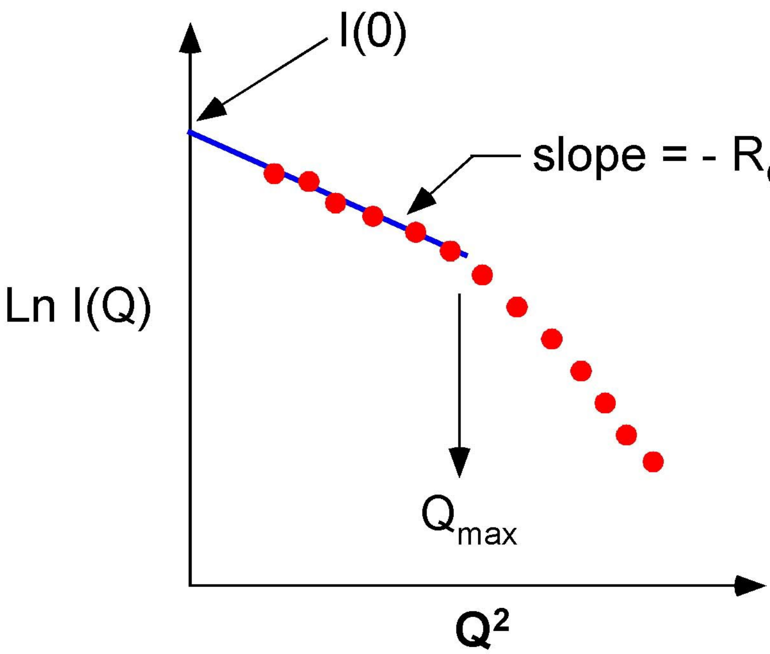
Scattered Intensity from Ellipsoids of Revolution of Axes 2R, 2R, 2vR



$$R_g = R\sqrt{\frac{2+v^2}{5}}$$

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

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



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

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

If Particles Have a Distribution of Sizes:

$$I(Q) \propto \int N(R)\, V_p^2(R)\, |F(Q,R)|^2\, dR$$

N(R) - Number of Particles (Spheres) with Radius R

$V_p(R)$ - Particle Volume

Guinier law still applies, but with

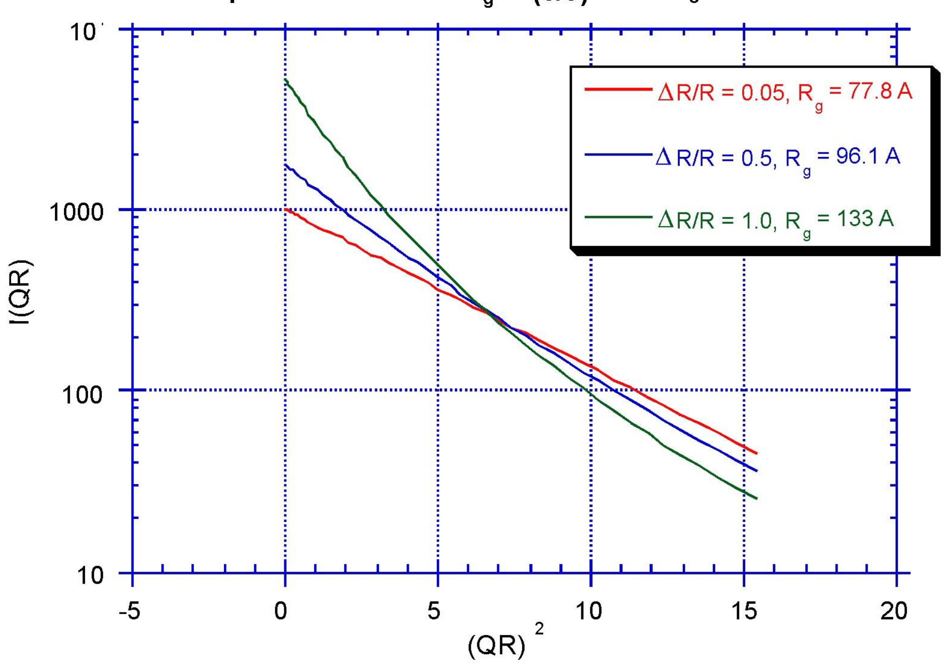
average over N(R)

$$R_g^2 = \frac{3}{5}\frac{\langle R^8 \rangle}{\langle R^6 \rangle}$$

weighted toward larger particles

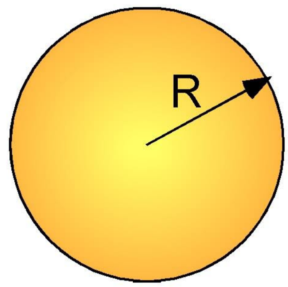
Guinier Plots of Scattering from Spherical Particles with mean radius, R_o = 100 Å, and a Gaussian Size Distribution.

For Monodispersed Particles: $R_g = (3/5)^{1/2}$ R_o = 77.5 Å



Form Factors for Some Simple Particle Shapes:

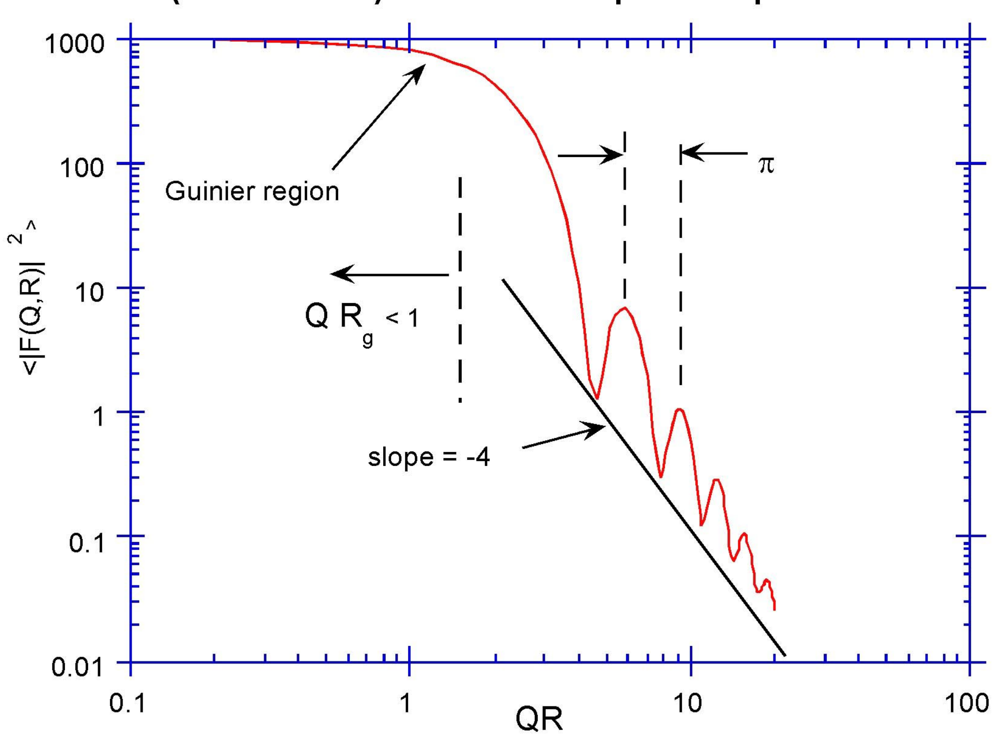
1) Spheres



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

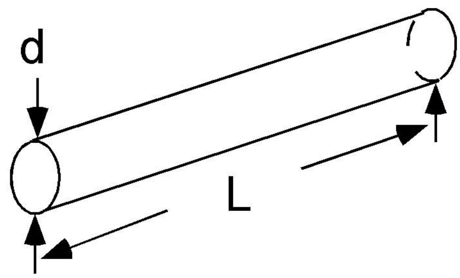
$$\left\langle |F(Q,R)|^2 \right\rangle = 9 \left[\frac{\sin(QR) - QR\cos(QR)}{(QR)^3} \right]^2$$

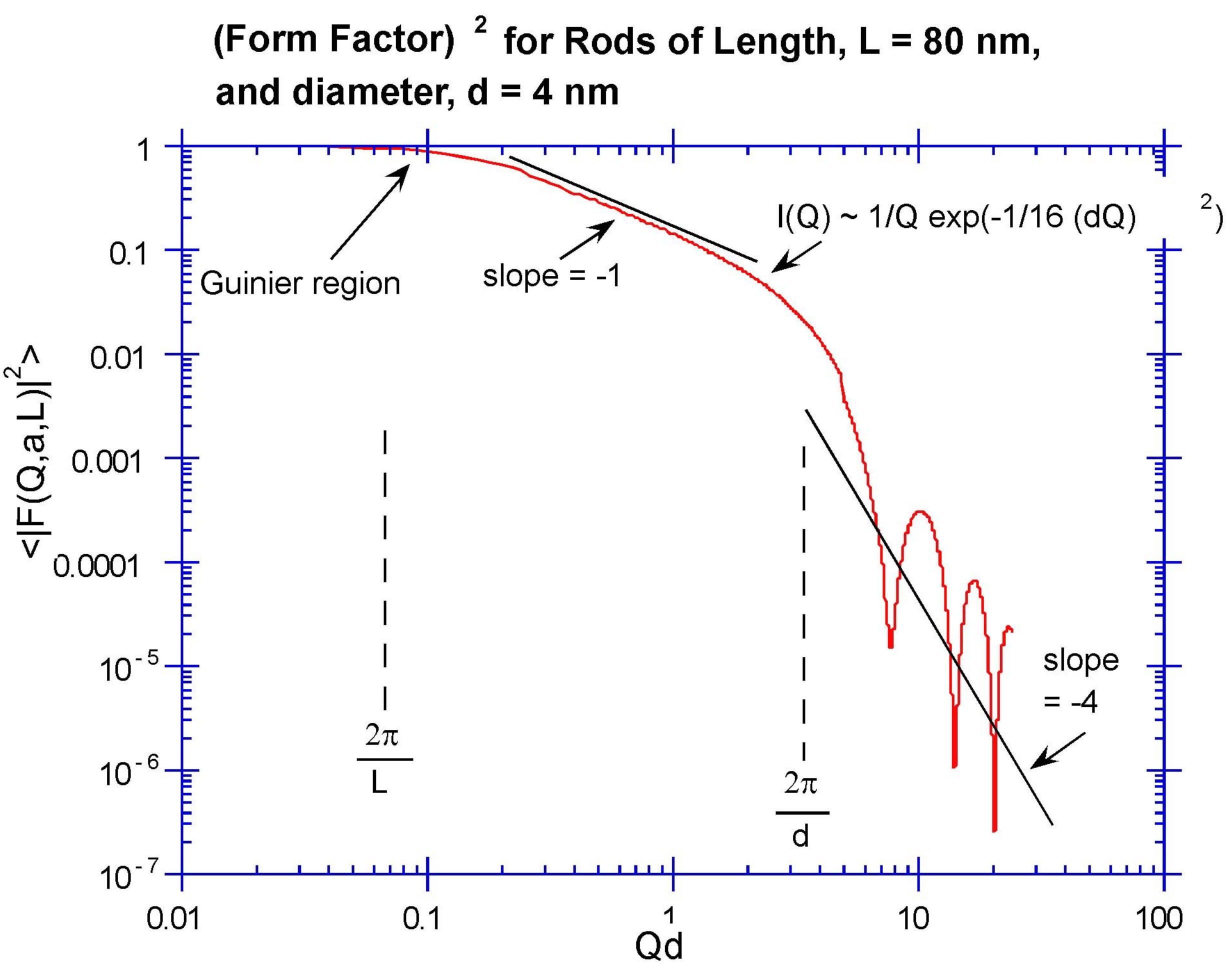
(Form Factor) ^{2} for Monodispersed Spheres



Form Factors for Some Simple Particle Shapes:

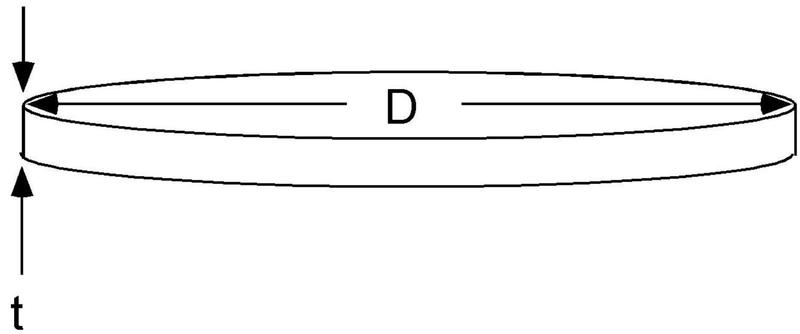
2) Long Rods:



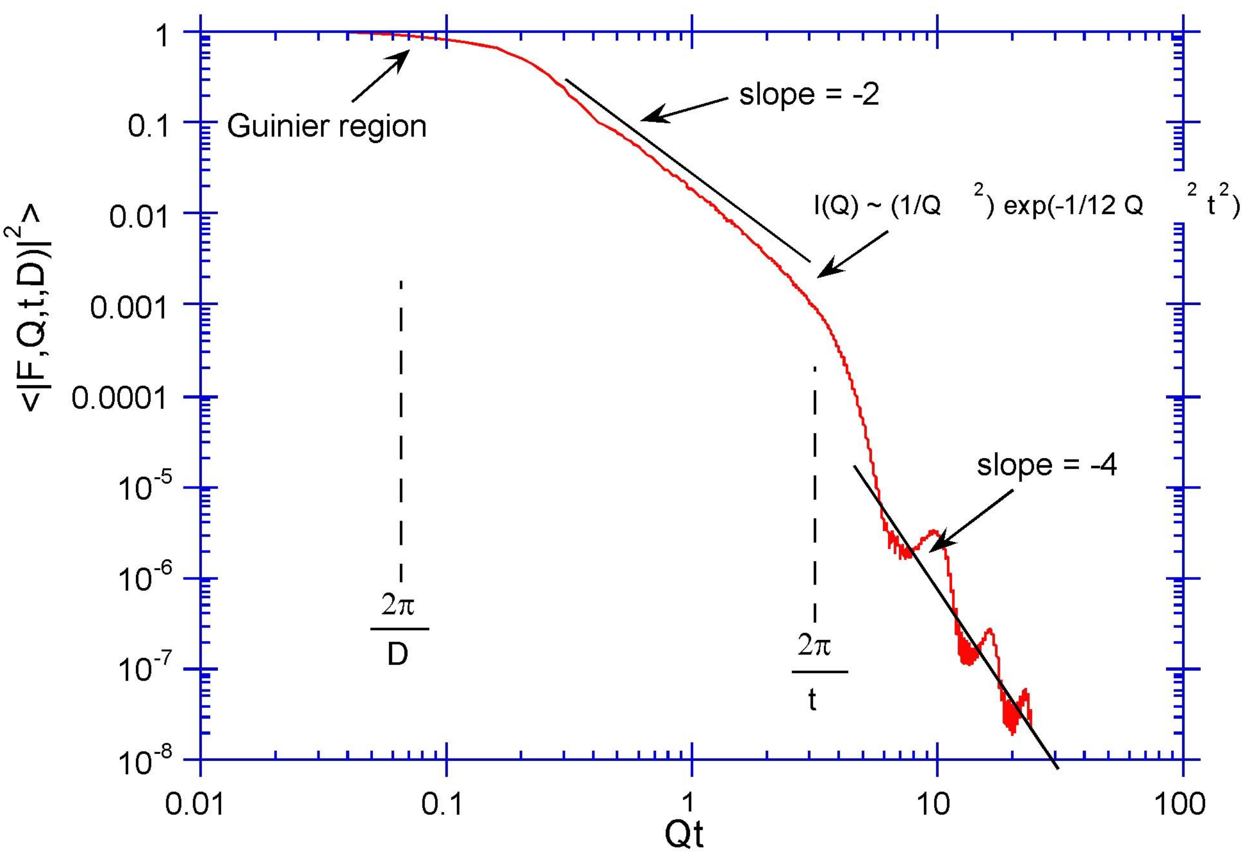


Form Factors for Some Simple Shapes:

3) Thin Disks



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



Shape Determination for Dilute, Randomly Oriented, Uniform Particles

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

particle shape ??

Recall, in terms of Porod-Debye correlation function

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

If I(Q) is measured over a wide enough Q-range to extrapolate to Q = 0 and Q = ∞, then can compute inverse transform:

$$\gamma(r) = \frac{1}{2\pi^2 r} \int Q I_p(Q) \sin(Qr)\, dQ$$

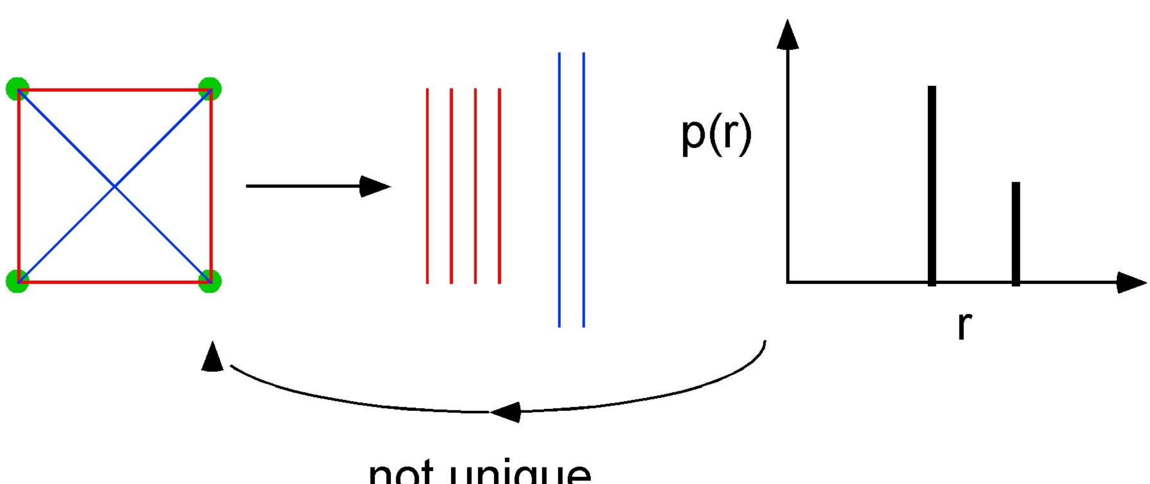
Distance Distribution Function: p(r)

$$p(r) \equiv 4\pi r^2 \ \gamma(r)$$ ← correlation function

$$p(0) = 0 \qquad\qquad p(D_{max}) = 0$$

recall,
$$R_G^2 = \frac{\int p(r)\, r^2\, dr}{2\int p(r)\, dr}$$

p(r) is $\propto$ probability that 2 randomly chosen points in particle are distance r apart

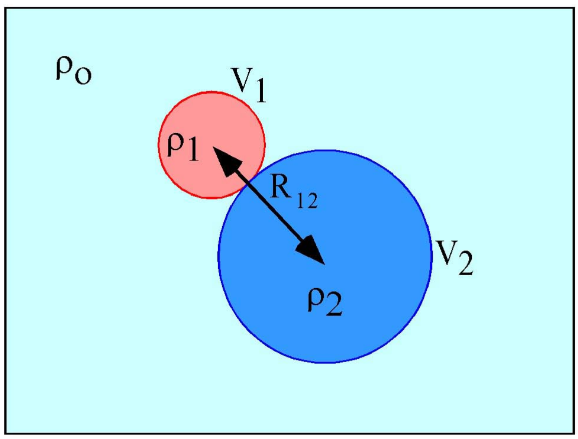


Compound Particles:

- model as assembly of uniform particle subunits

e.g. nucleosomes (protein/DNA complexes)

ribosomes (multiple protein/RNA complexes)



$$I(Q) = \left\langle \left| \int_V (\rho(r) - \rho_o) e^{i\vec{Q}.\vec{r}} d\vec{r} \right|^2 \right\rangle \qquad V = V_1 + V_2$$

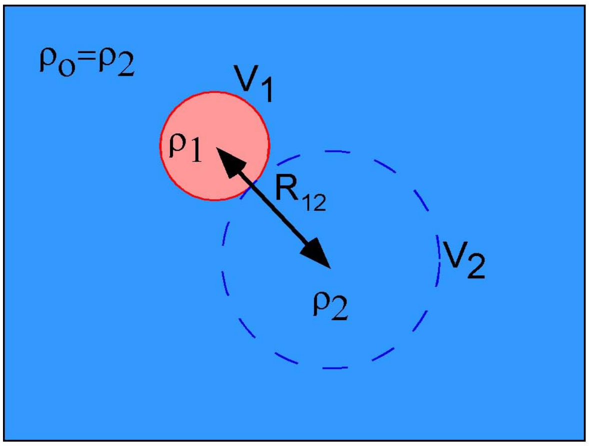
$$I(Q) = \left\langle \left| (\rho_1 - \rho_o) \int_{V_1} e^{i\vec{Q}.\vec{r}} d\vec{r}_1 + (\rho_2 - \rho_o) \int_{V_2} e^{i\vec{Q}.\vec{r}} d\vec{r}_2 \right|^2 \right\rangle$$

$$I(Q) = (\rho_1 - \rho_o)^2 \left\langle |F_1(Q)|^2 \right\rangle + (\rho_2 - \rho_o)^2 \left\langle |F_2(Q)|^2 \right\rangle$$

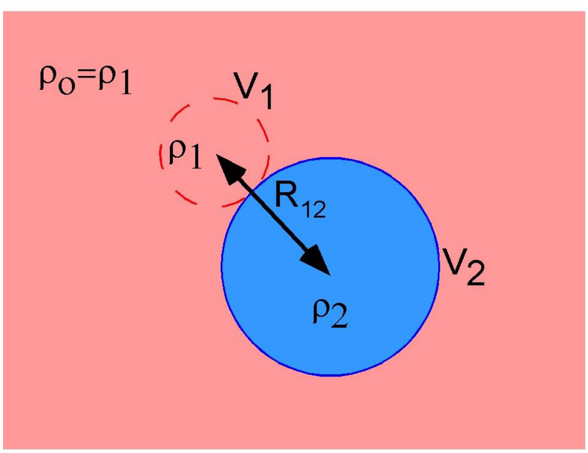
$$+ (\rho_1 - \rho_o)(\rho_2 - \rho_o)|F_1||F_2| \frac{\sin(QR_{12})}{QR_{12}}$$

Compound Particles:

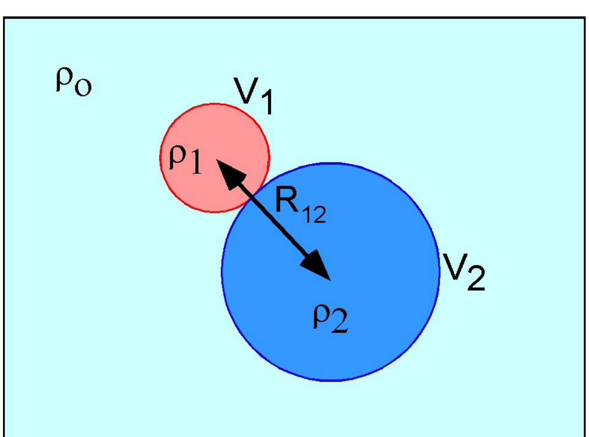
- Use Contrast Variation to Separate Terms



$$I_1(Q) = (\rho_1 - \rho_2)^2 F_1^2$$



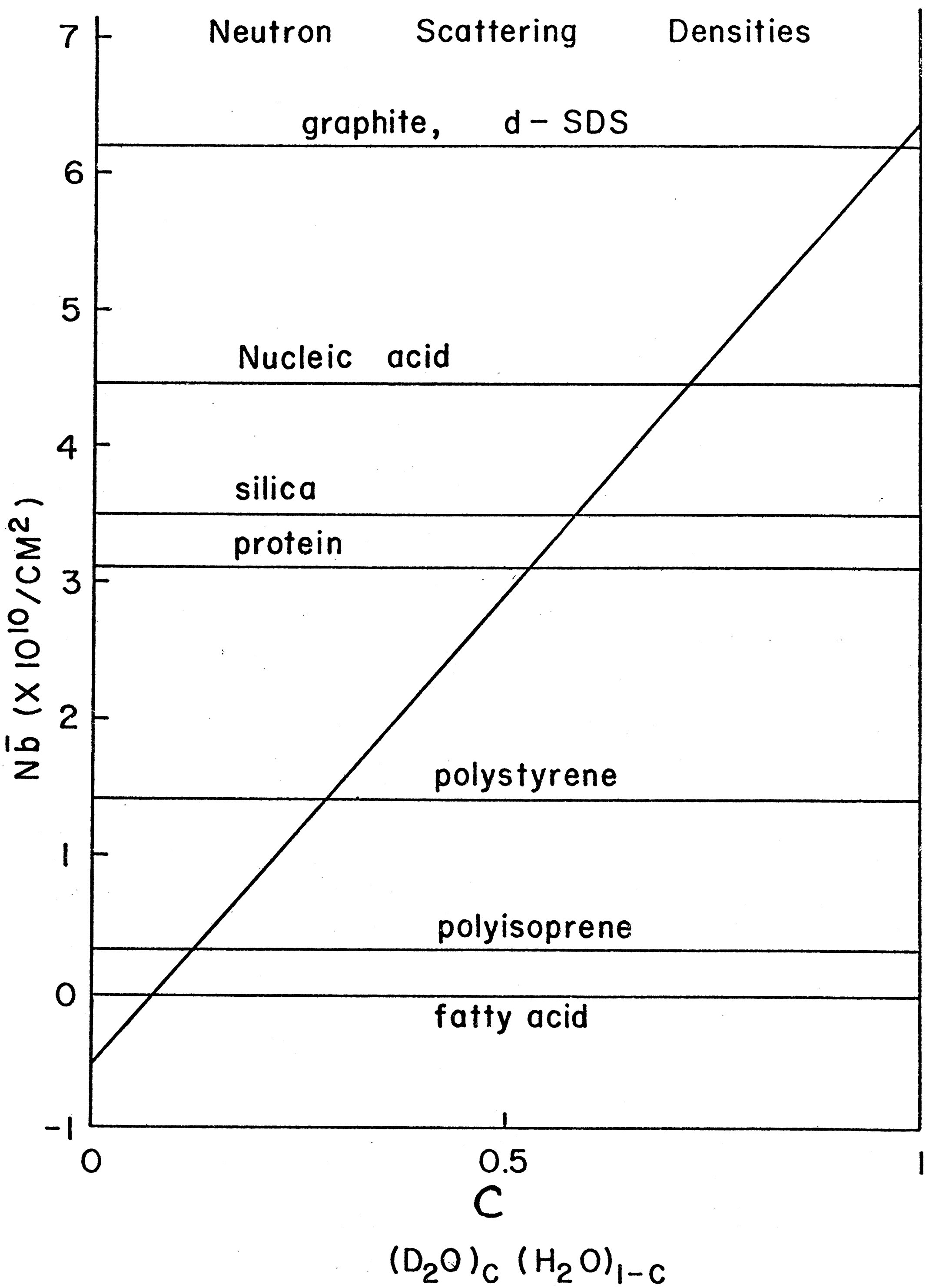
$$I_2(Q) = (\rho_2 - \rho_1)^2 F_2^2$$



$$I_3(Q) - \frac{(\rho_1 - \rho_o)^2}{(\rho_1 - \rho_2)^2} I_1(Q) - \frac{(\rho_2 - \rho_o)^2}{(\rho_1 - \rho_2)^2} I_2(Q)$$

$$= \underbrace{2(\rho_1 - \rho_o)(\rho_2 - \rho_o) F_1 F_2 \frac{\sin(QR_{12})}{QR_{12}}}$$

$=0$ at $Q = \pi / R_{12}$



Neutron Scattering Densities
graphite, d - SDS
Nucleic acid
silica
protein
polystyrene
polyisoprene
fatty acid
7
6
5
4
3
2
1
0
-1
$N\bar{b}$ (X 10^{10}/CM^2)
0
0.5
1
C
$(D_2O)_C (H_2O)_{1-C}$

STURHMANN ANALYSIS:

let $$\Delta\rho(\vec{r}) = \rho(\vec{r}) - \rho_o = \overline{\rho} + \rho_f(\vec{r}) - \rho_o = \overline{\Delta\rho} + \rho_f(\vec{r})$$

$$\overline{\Delta\rho} = (\overline{\rho} - \rho_o)$$

average contrast of particle with its surroundings

substitute in expression for R_G

$$\boxed{R_G^2 = R_\infty^2 + \frac{\alpha}{\overline{\Delta\rho}} - \frac{\beta}{\left(\overline{\Delta\rho}\right)^2}}$$

R_∞ : Guinier radius when average contrast is large (infinite); represents R_G of a uniform particle of the same shape.

$$\alpha = \frac{1}{V_p}\int \rho_f(\vec{r})\, r^2\, d\vec{r}$$

positive if exterior of particle has higher sld than interior; negative => reverse

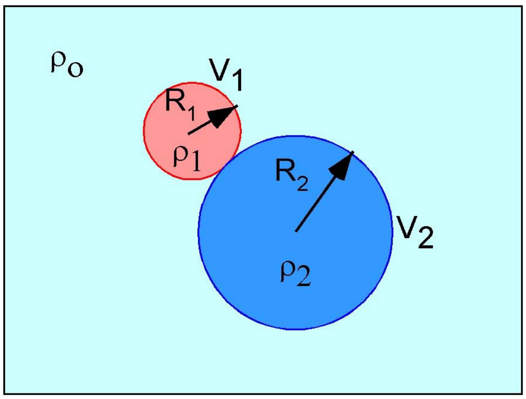
$$\beta = \frac{1}{V_p^2}\iint \rho_f(\vec{r})\,\rho_f(\vec{r}\,')\,\vec{r}\cdot\vec{r}\,'\,d\vec{r}\,d\vec{r}\,'$$

displacement of "center of mass" as a function of contrast; zero if particle constituents have concentric centers of mass

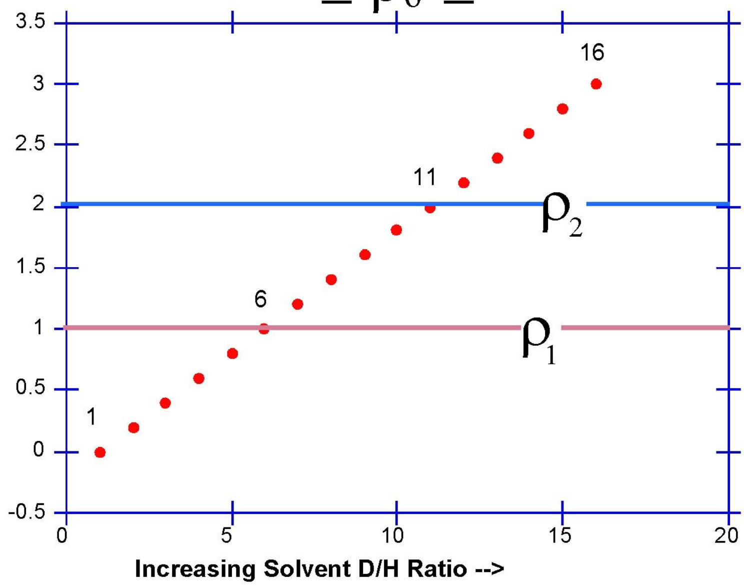
CONTRAST VARIATION EXAMPLE, Part I:

$\rho_1 = 1, \quad R_1 = 1$

$\rho_2 = 2, \quad R_2 = 2$

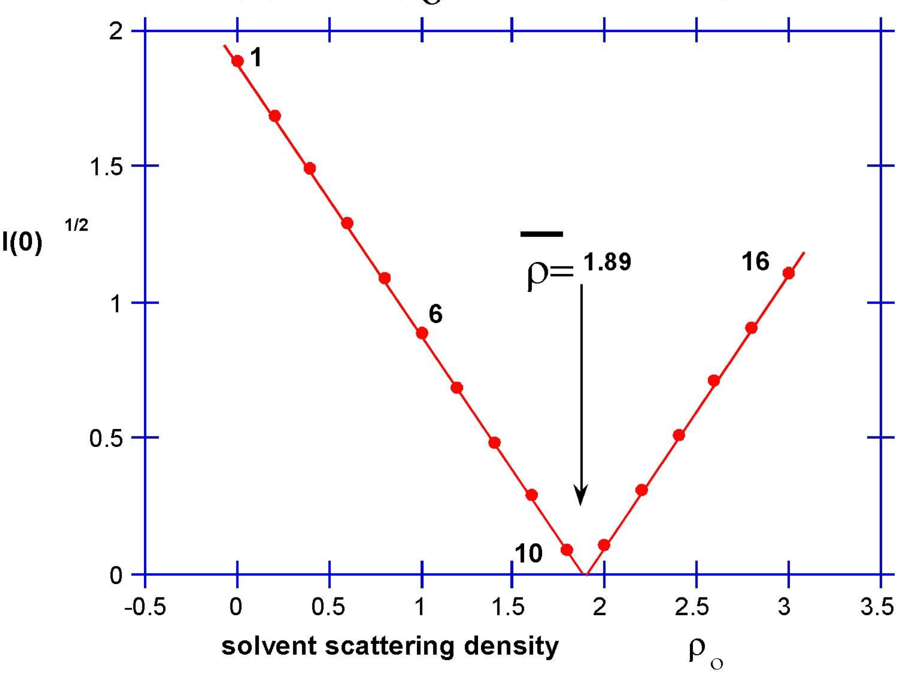


$0 \le \rho_o \le 3$



$$I(0) \propto (\bar{\rho} - \rho_o)^2, \ \bar{\rho} = \text{mean scattering density of compound particle}$$

Plot $I(0)^{1/2}$ vs ρ_O to determine $\bar{\rho}$

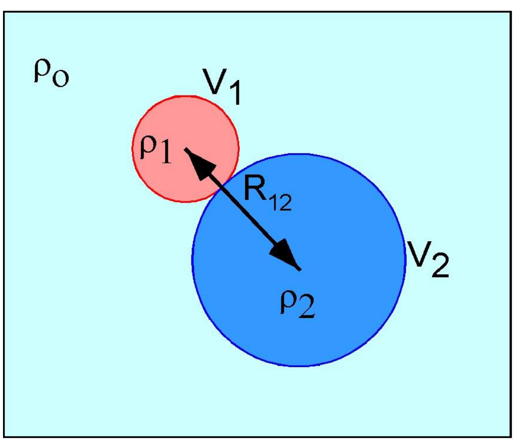


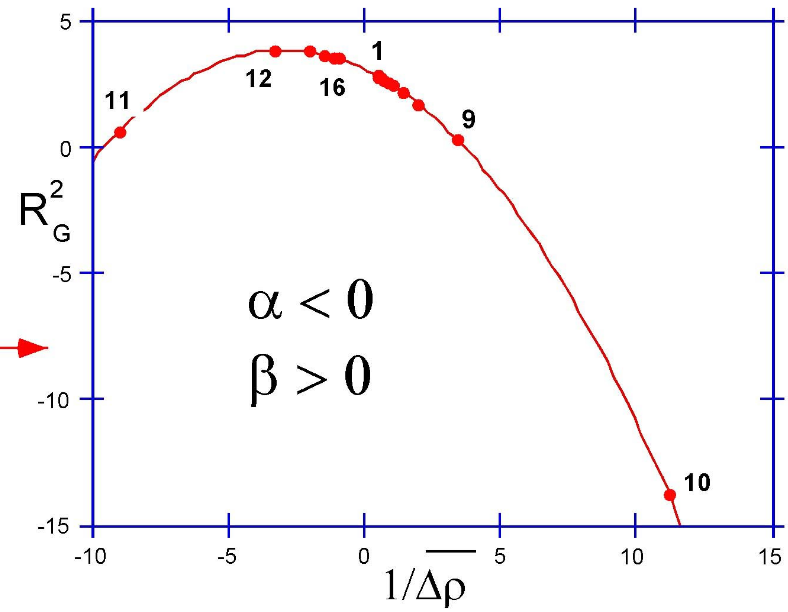
CONTRAST VARIATION EXAMPLE, Part II:

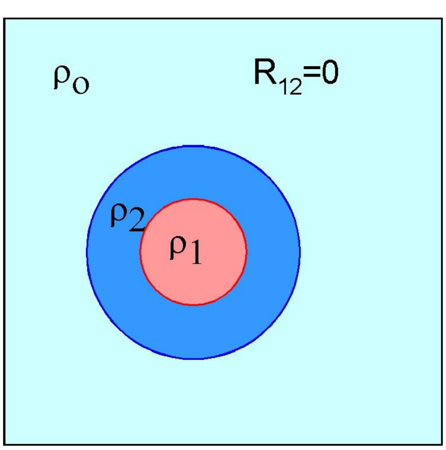
Recall $$R_G^2 = R_\infty^2 + \frac{\alpha}{\overline{\Delta\rho}} - \frac{\beta}{\left(\overline{\Delta\rho}\right)^2}$$

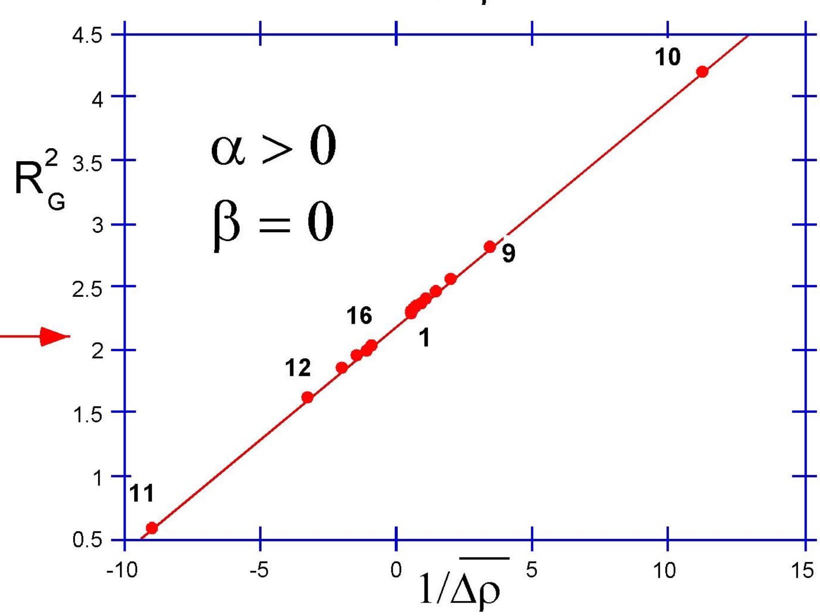
Make Stuhrmann plot of R_G^2 versus $1/\overline{\Delta\rho}$ where

$\overline{\Delta\rho} = (\overline{\rho} - \rho_O)$ and $\overline{\rho}$ is the mean sld of complex









Summary

Easy

- Average Particle Size (Rg)
- Molecular Weight [I(0)]
- Surface Area (I ~ S/Q4)
- Volume Fraction (Invariant)
- Particle Shape [P(r)]
- Internal Structure (contrast variation)
- Size Distributions

More Difficult