Small Angle Neutron Scattering

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- Outline
  - Scattering events, flux
  - Scattering vector
  - Interference terms
  - Autocorrelation function
  - Single particle scattering
  - Concentrated systems
  - Nonparticulate scattering

Small Angle Neutron Scattering

- Measures (in the ideal world…)
  - Particle Size
  - Particle Shape
  - Polydispersity
  - Interparticle Interactions
  - Internal Structure
- Model-free Parameters
  - Radius of gyration – R_g
  - Specific surface – S/V
  - Compressibility: $\left(\frac{\partial \Pi}{\partial \rho}\right)^{-1} \Rightarrow$ molecular weight
- Much information as *part* of an integrated approach involving many techniques

References

- Vol. 21, part 6, Journal of Applied Crystallography, 1988.
- Chen, S.-H. Ann. Rev. Phys. Chem. 37, 351-399 (1986).
- Hayter, J.B. (1985)in Physics of Amphiphiles: Micelles, Vesicles, and Microemulsions, edited by V. Degiorgio, pp. 59-93.
- Roe, R.-J. (2000) Methods of X-ray and Neutron Scattering in Polymer Science.

Different Radiations

- Light (refractive index or density differences)
  - laboratory scale, convenient
  - limited length scales, control of scattering events (contrast)
  - dynamic measurements (diffusion)
- X-rays (small angle) (electron density differences)
  - laboratory or national facilities
  - opaque materials
  - limited contrast control
- Neutrons (small angle) (atomic properties)
  - national facilities
  - great contrast control

Neutrons

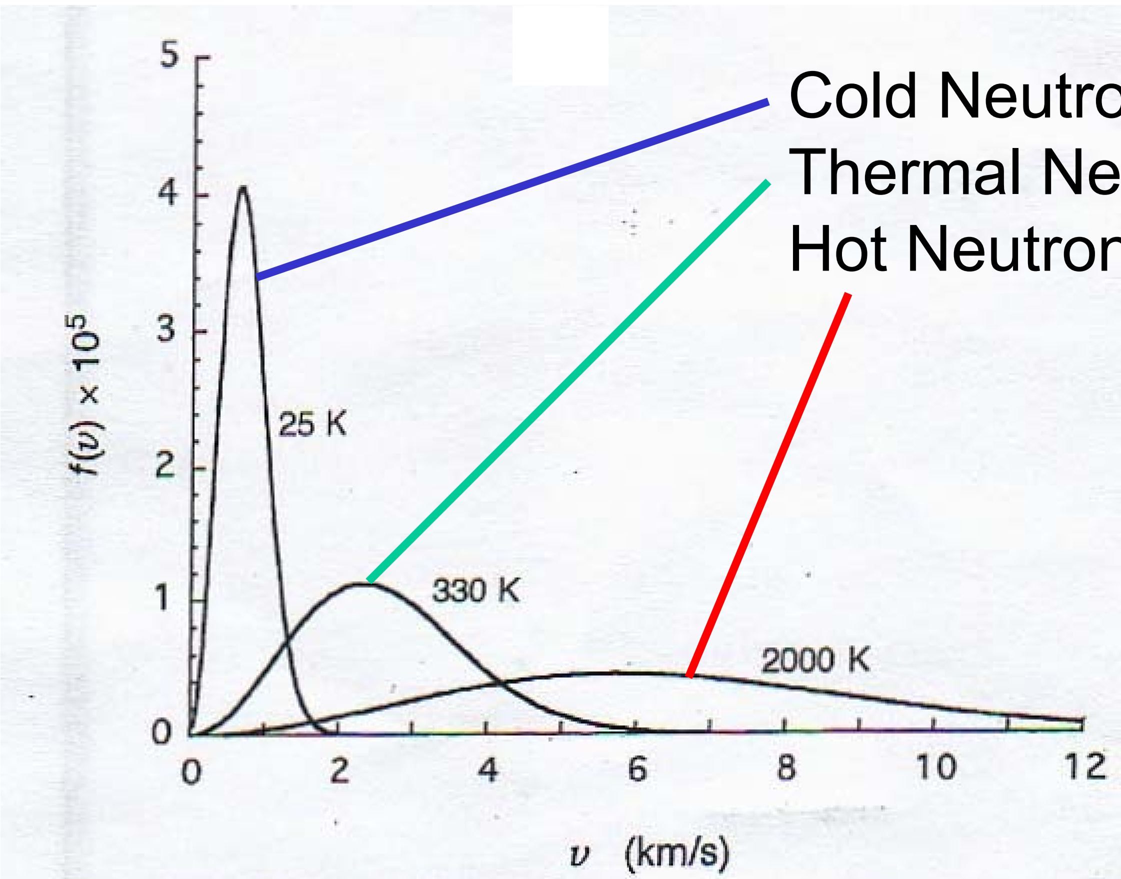
- Sources
  - nuclear reactor
    - US: NIST
  - spallation sources (high energy protons impact a heavy metal target)
    - US: Spallation Neutron Source (SNS)
      - 1.4 billion dollars, complete 2006
- Both cases produce high energy neutrons that must be 'thermalized' for materials science studies

SNS Overview

www.sns.gov

Maxwell Distribution

velocity distribution: $f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{1}{2}mv^2/kT\right)$



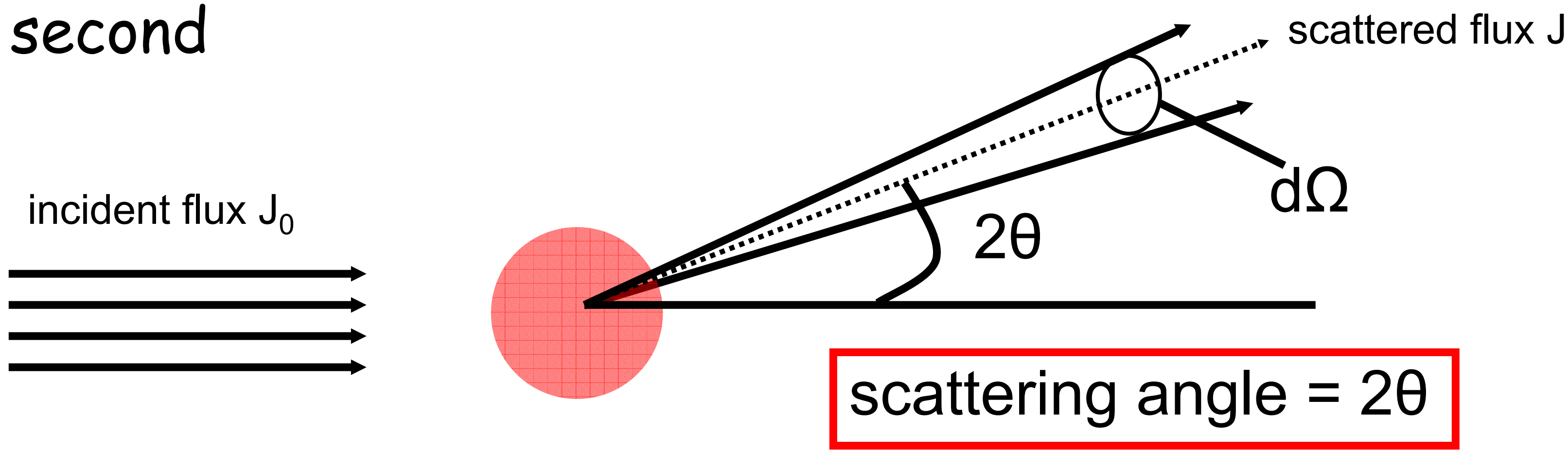
Cold Neutrons: D_2O at 25K
Thermal Neutrons: D_2O at 300K
Hot Neutrons: Graphite at 2000K

$$\lambda = \frac{h}{mv}$$

T = 25K
v = 642 m/s
E = 2.16 meV
λ = 6.2 A

Flux, cross-section, intensity

- Flux (plane wave): number per unit area per second
  - for a wave of amplitude A, the flux $J = |A|^2 = AA^*$
- Flux (spherical wave): number per unit solid angle per second

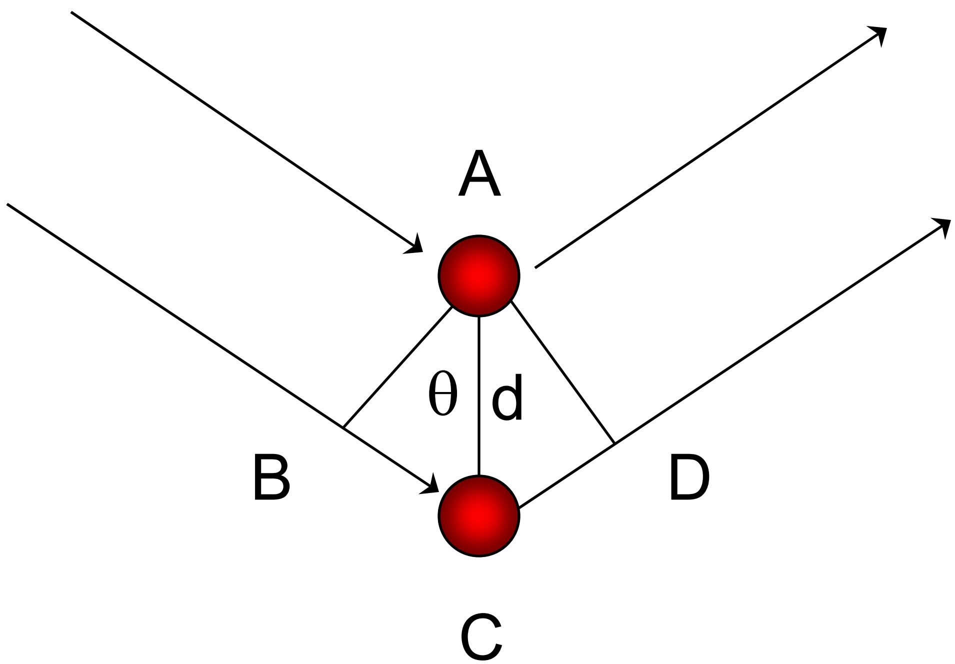


$$\frac{\text{number of particles scattered into unit solid angle in a given direction per second}}{\text{flux of the incident beam}} = \frac{J}{J_o} = \boxed{\frac{d\sigma}{d\Omega}}$$

differential scattering cross-section

= intensity (I)

Bragg Condition for Interference



$$\sin\theta = \frac{BC}{AC}$$

$$\sin\theta = \frac{DC}{AC}$$

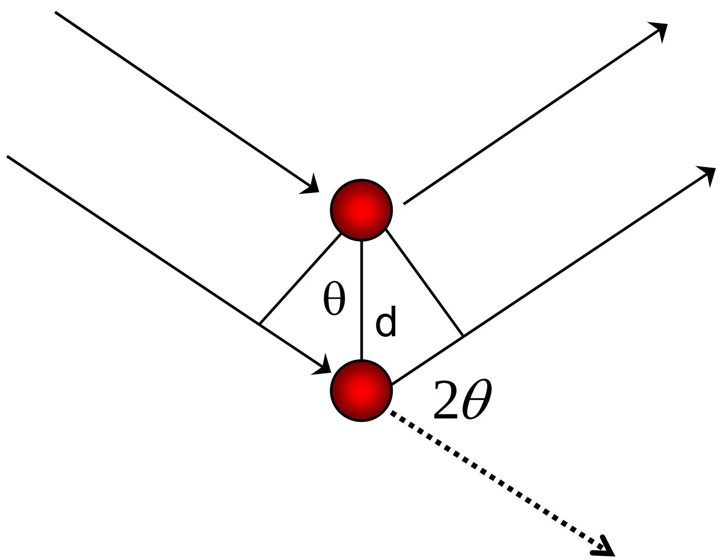
$$BC + CD = 2d\sin\theta$$

When extra distance is equal to one wavelength

$$m\lambda = 2d\sin\theta$$

Dealing with Colloidal Dimensions

Recall that interference between two particles is a function of the scattering angle and the separation between scattering centers



$$m\lambda = 2d\sin\theta$$

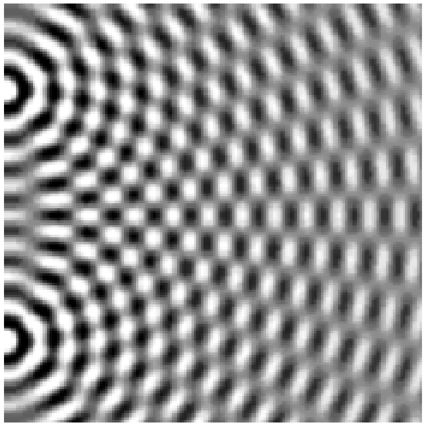
or

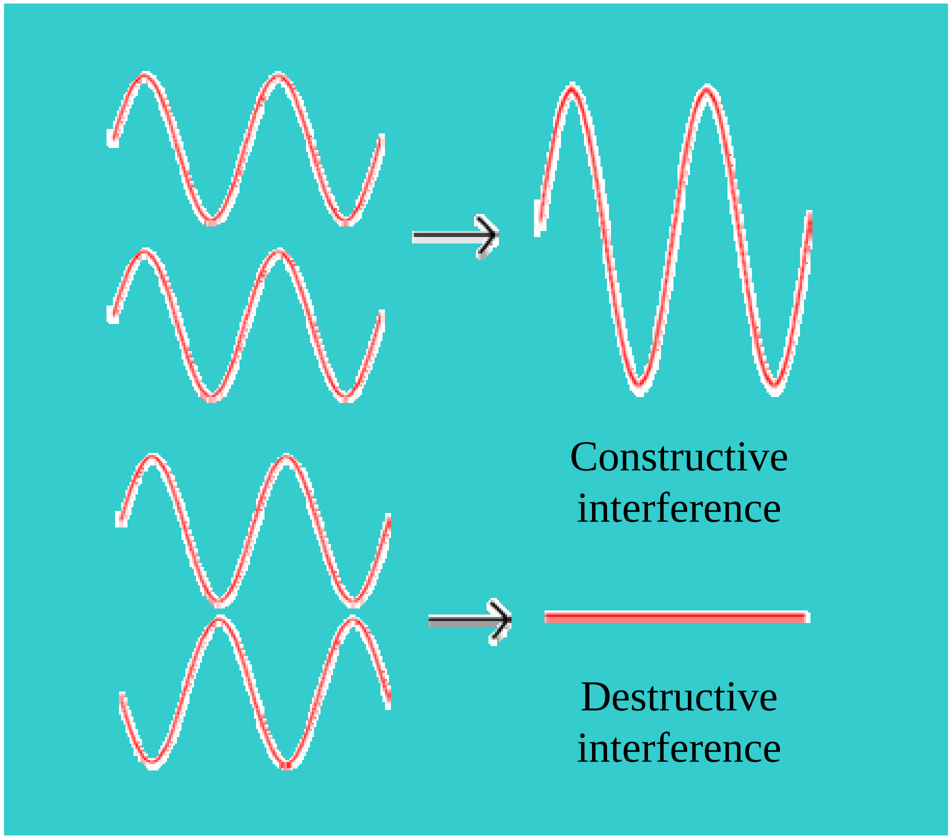
$$\frac{1}{d} = \frac{2\sin\theta}{\lambda}$$

so the size explored varies *inversely* with the scattering angle

For d = 100 nm, λ = 1nm, $\sin\theta = 0.005$, so $\theta \approx 0.005$

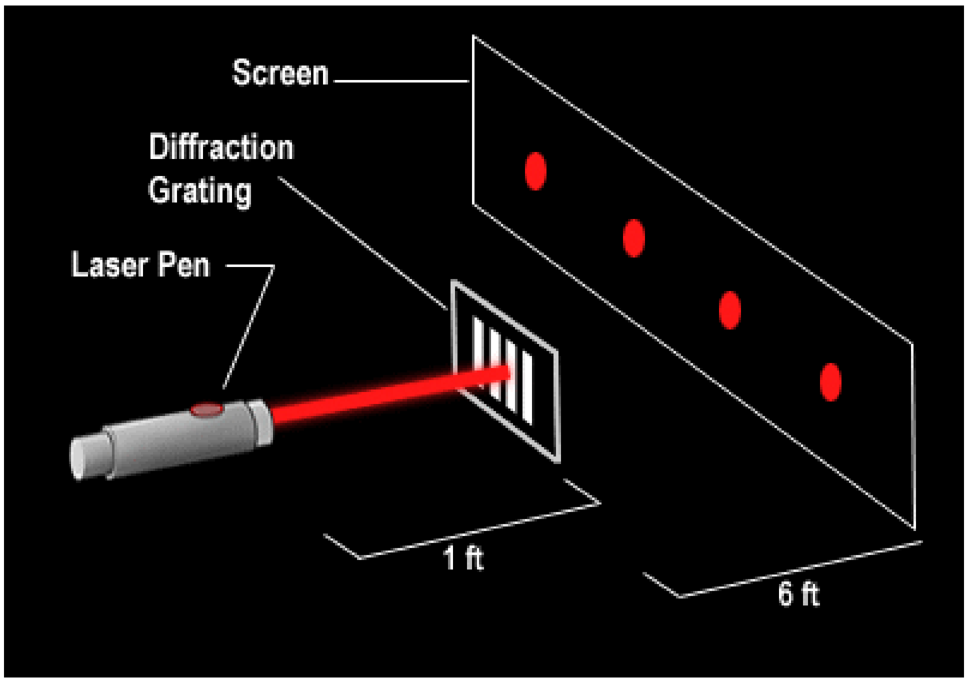
Example of Interference





Constructive and destructive interference can lead to more (or less) intensity

Another Example of Interference



Constructive and destructive interference from path length differences

Light waves only interfere if they are polarized in the same direction.

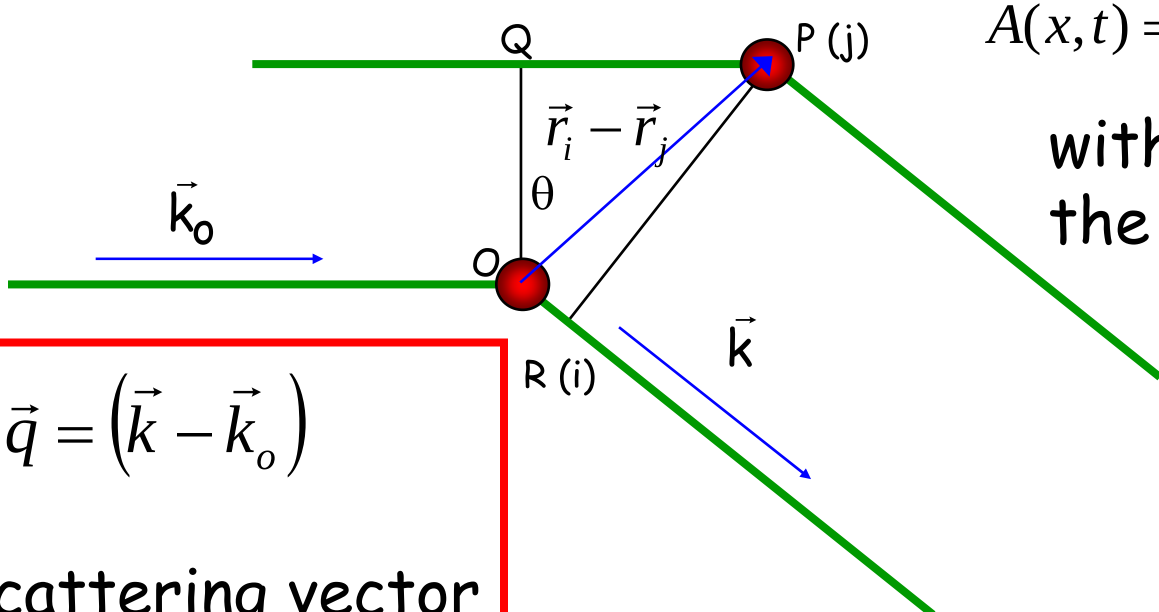
Interference Calculation

Consider a plane wave

$$A(x,t) = A\exp(-i2\pi(vt - x/\lambda))$$

with direction given by the wave vector k_o

$$k_o = \frac{2\pi}{\lambda} s_o$$ where s_o is a unit vector



$$\vec{q} = \left(\vec{k} - \vec{k}_o\right)$$

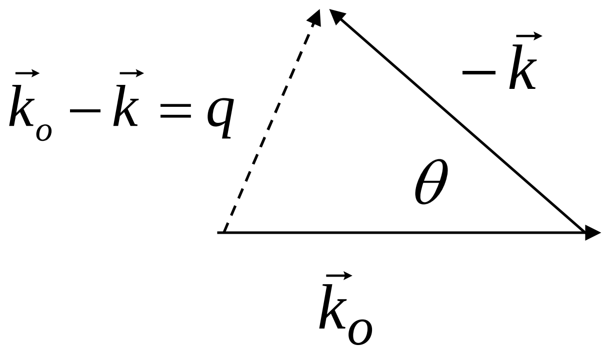
scattering vector

Then the phase difference between the two waves scattered from O and P is $\Delta\varphi = \frac{2\pi\delta}{\lambda} = \frac{2\pi(QP - OR)}{\lambda} = \frac{2\pi(k_o \cdot r - k \cdot r)}{\lambda} = -q \cdot r$

The scattering vector

$$\vec{q} = \left(\vec{k} - \vec{k}_o\right)$$

$$\left|\vec{q}\right| = q = \frac{4\pi \sin\theta}{\lambda}$$



q lies in the plane of the detector

Notation: q, k, h, s =q/2π

The Value of the Scattering Vector Corresponds to a Distance in Real Space

refractive index (~ 1.33 for water)

scattering angle (often 90°)

Light Scattering

$$\left|\vec{q}\right| = \frac{4\pi n}{\lambda}\sin\left(\frac{\theta}{2}\right) = \frac{2\pi}{d} \sim 0.054nm^{-1}$$

Wavelength (Argon = 514 nm)

$$d \sim 116nm$$

refractive index = 1

scattering angle (1 mrad)

Small Angle Scattering

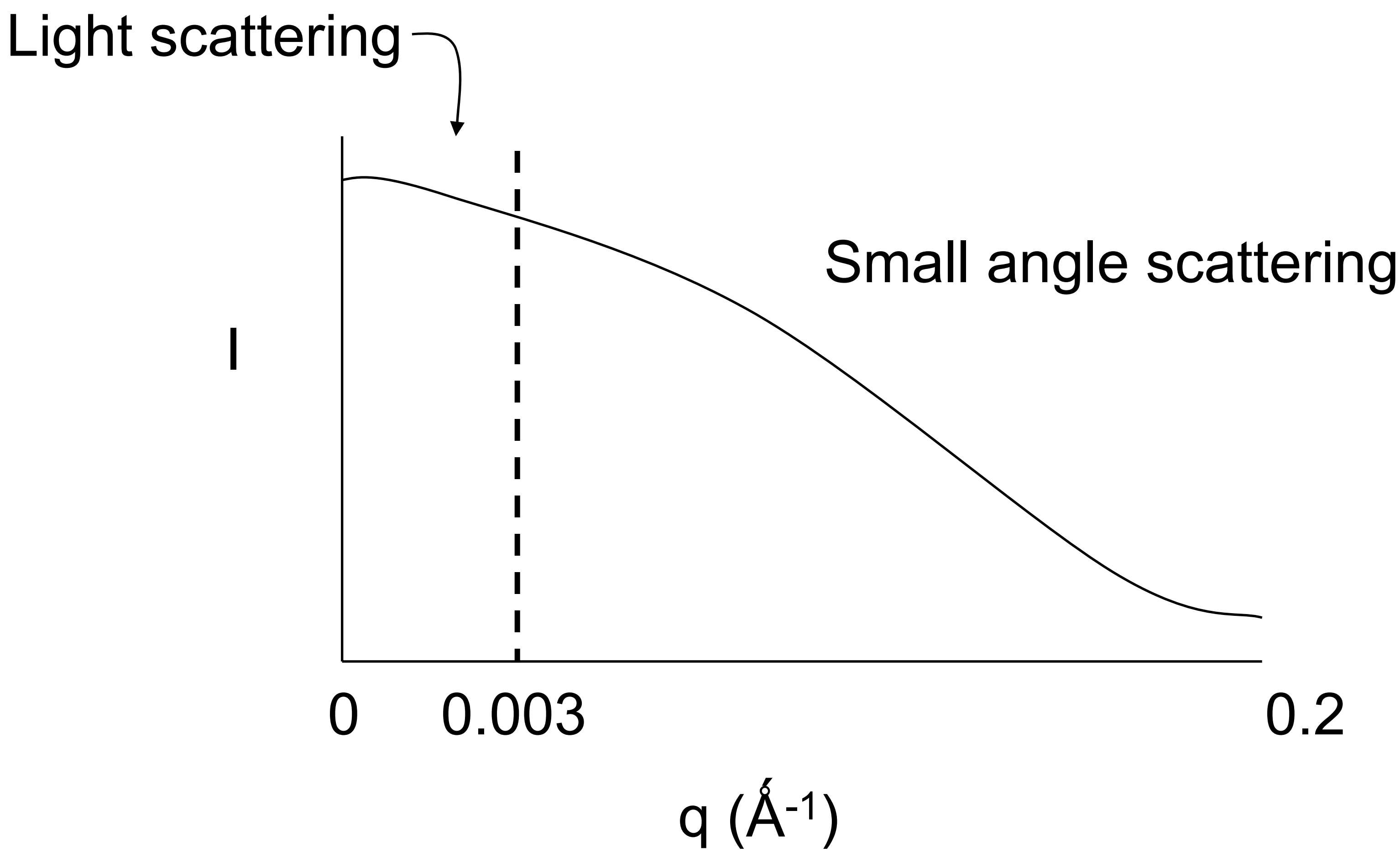
$$\left|\vec{q}\right| = \frac{4\pi n}{\lambda}\sin\left(\frac{\theta}{2}\right) = \frac{2\pi}{d} \sim 0.054nm^{-1}$$

Wavelength 1 nm

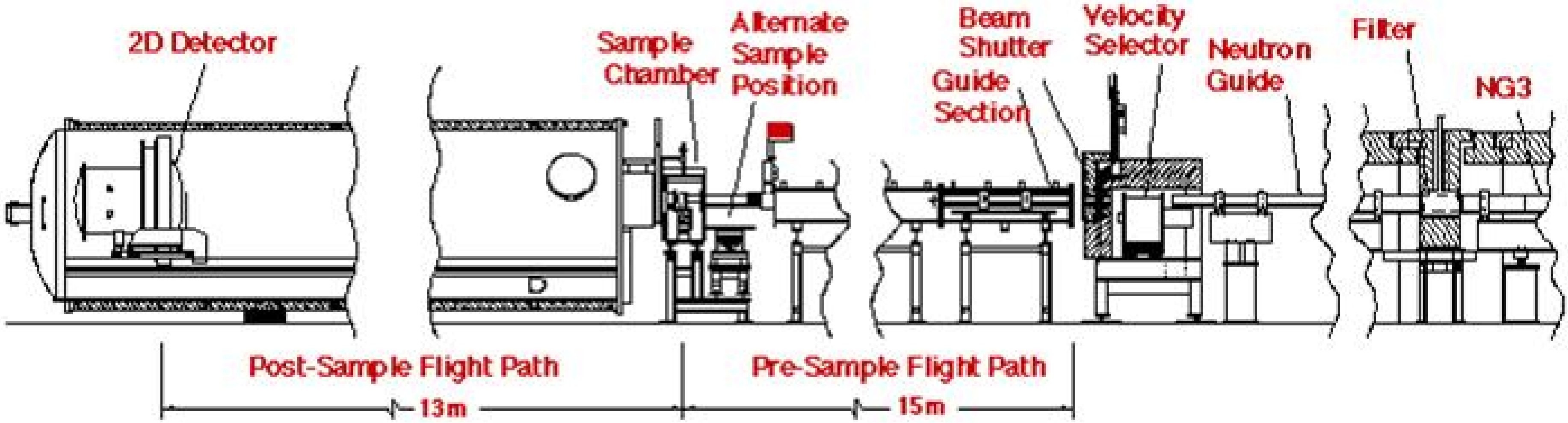
$$d \sim 116nm$$

Characteristic distance, d, that is measured in the experiment

Comparison of light and small-angle x-ray or neutron scattering



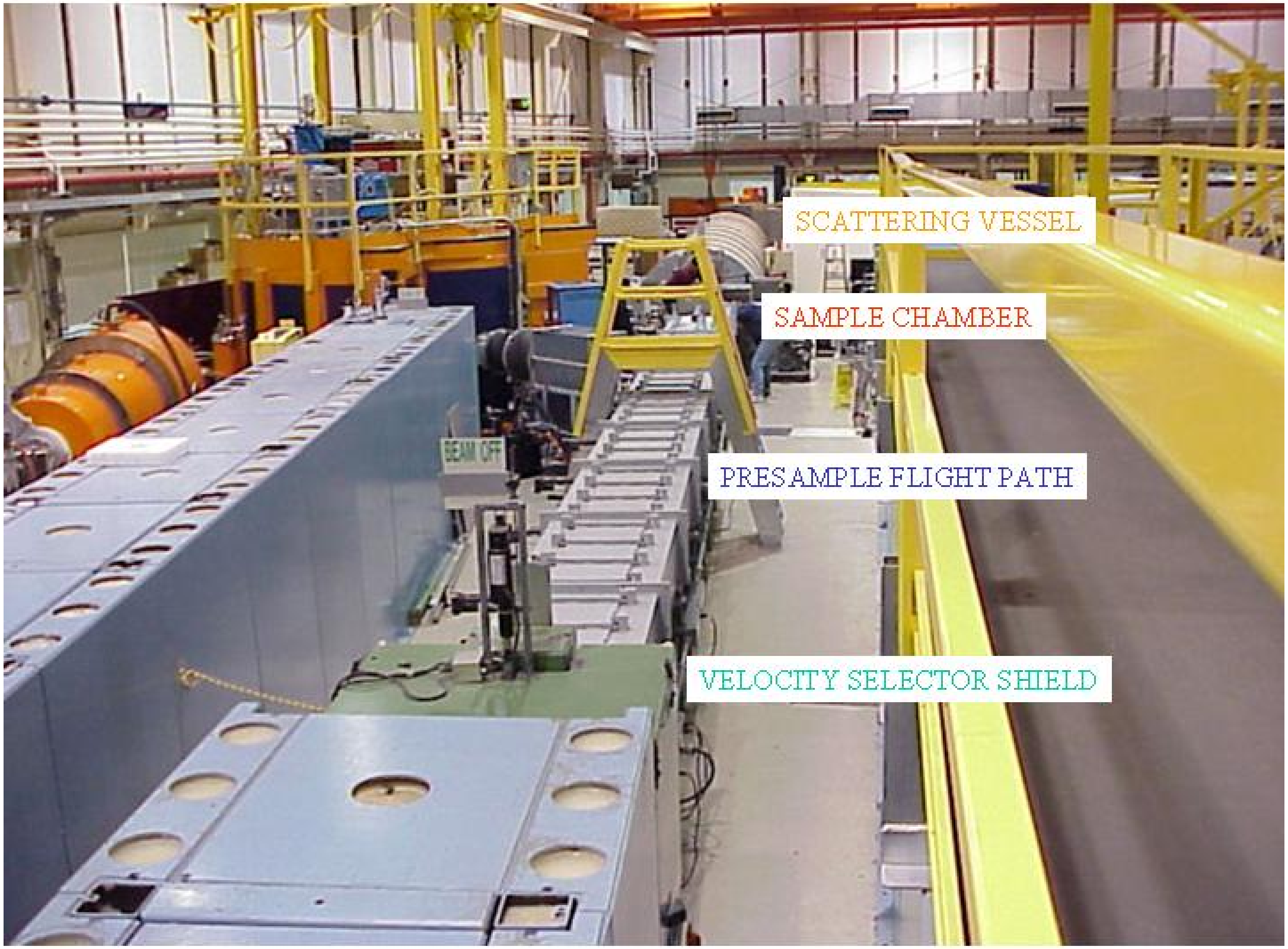
CHRNS 30 METER SANS INSTRUMENT



NIST
National Institute of Standards and Technology

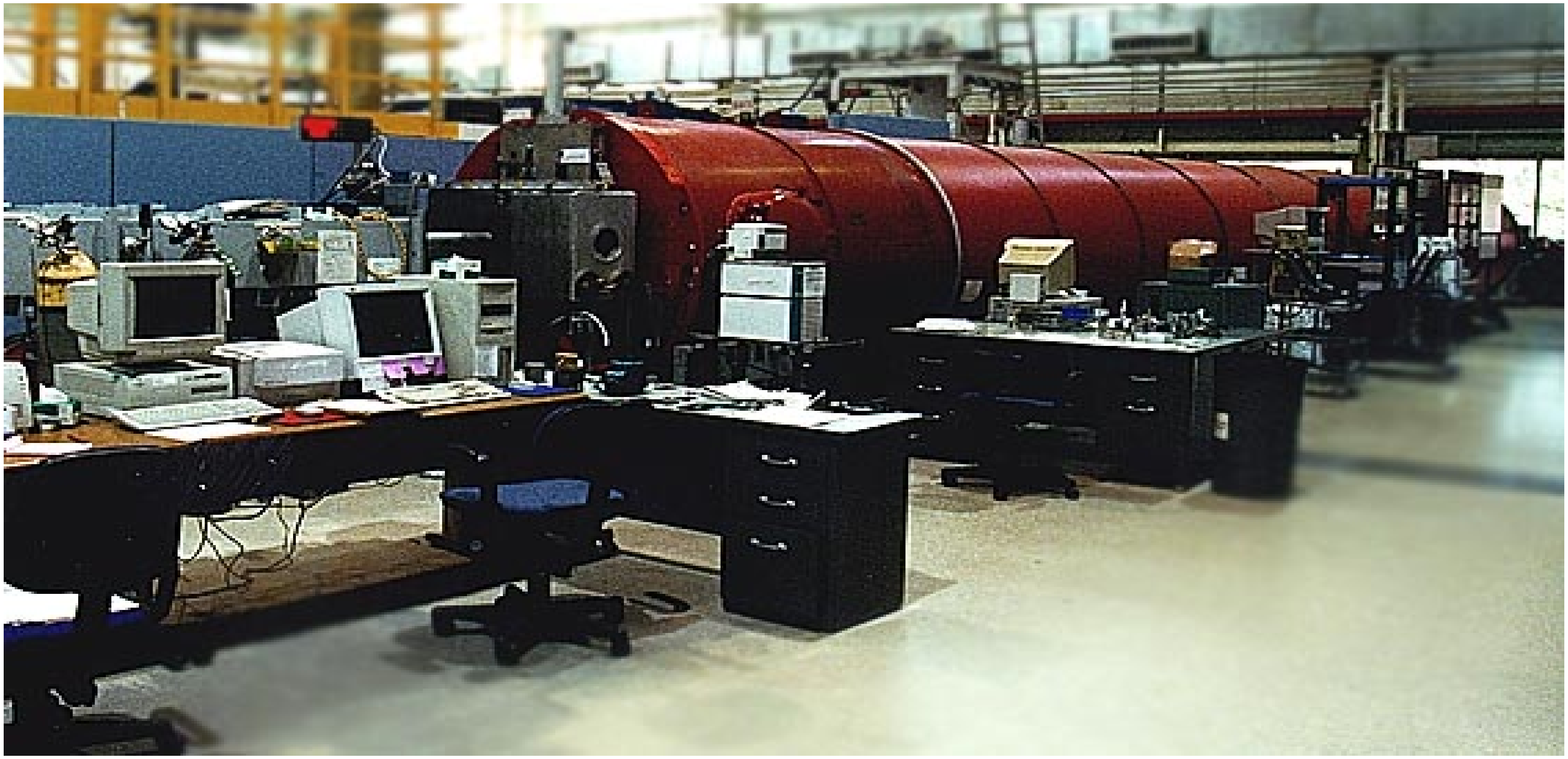
CHRNS NIST

Small Angles… Big Machines

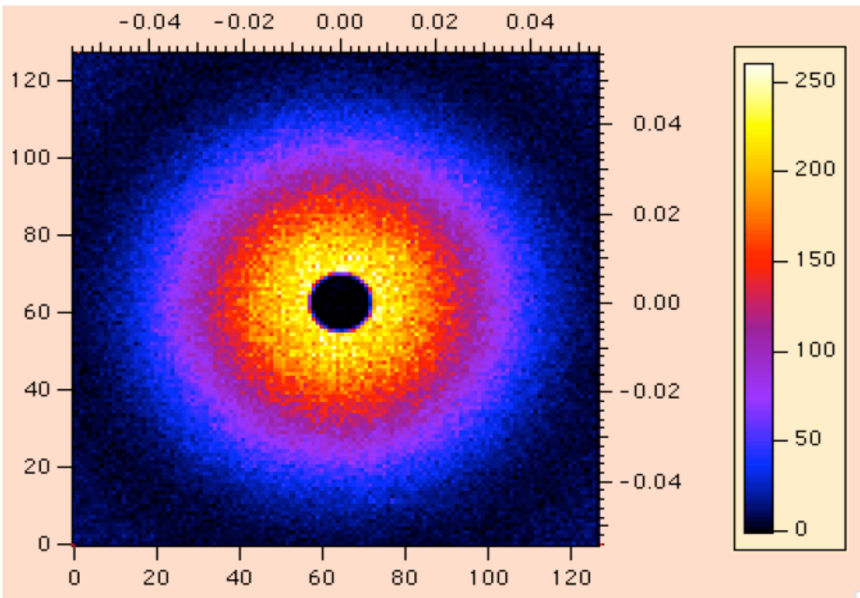


http://www.ncnr.nist.gov/instruments/ng3sans/ng3_sans_photos.html

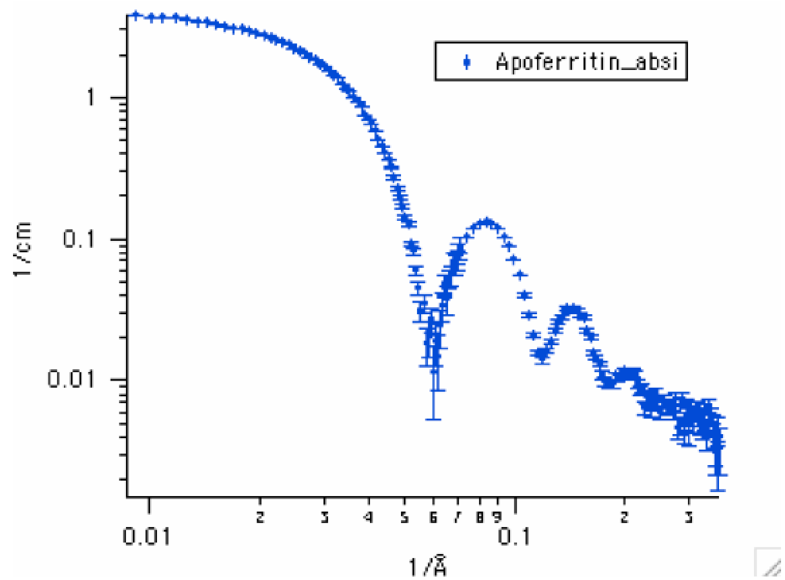
Small Angle Scattering Instrument (NG-7) at NIST, Gaithersburg, MD



SANS Data Reduction
NIST examples



Two Dimensional Data



Reduced to I(q)

Interference continued

- Now write the (spherical) scattered wave from particle 1 (at O)

$$A_1(x,t) = A_o b \exp(-i2\pi(vt - x/\lambda))$$

scattering length

incident amplitude

- And the spherical scattered wave from particle 2 (at P)

$$A_2(x,t) = A_1(x,t)\exp(i\Delta\phi) = A_o b \exp(-i2\pi(vt - x/\lambda))\exp(-iq\cdot r)$$

- The combined wave on the detector is $A = A_1 + A_2$

$$A(x,t) = A_o b \exp(-i2\pi(vt - x/\lambda))(1 + \exp(-iq\cdot r))$$

- And the flux is

$$J = A(x,t)A^*(x,t) = A_o^2 b^2 (1 + \exp(-iq\cdot r))(1 + \exp(iq\cdot r))$$

which only depends on q·r

Interference continued

- For N scatterers,

$$A(q) = A_o b \sum_{j=1}^{N} \exp(-iq \cdot r_j)$$

- and for a distribution of scatterers

$$A(q) = A_o b \int_V n(r) \exp(-iq \cdot r) d^3 r$$

- where n(r)dr is the number of scatterers in a volume element and V is the sample volume.

So What is Special About Neutrons?

- Neutrons have spin $\frac{1}{2}$
- Neutrons are scattered from atomic nuclei, and the scattering event depends on the nuclear spin.
- There are coherent and incoherent scattering lengths tabulated for elements and isotopes
  - coherent – information about structure
  - incoherent – arises from fluctuations in scattering lengths due to nonzero spins of isotopes and has no structural information

Neutron cross-sections

- Hydrogen is special. Spin =1/2, with different spin up and spin down scattering, gives rise to a very large incoherent scattering (this is bad for structure measurements, but good for dynamics)
- Deuterium is spin 1, with much lower incoherent scattering

Element	$b_{coh}(10^{-12}cm)$
^{1}H	-0.374
^{2}D	0.667
C	0.665
O	0.580

For a molecule, the scattering length density

$SLD = \Sigma b_i$/molecular volume

H/D substitution changes the scattering power and gives control of n(r): this is called contrast variation.

Autocorrelation Function

- Setting $A_o = 1$, defining the scattering length density $\rho(r) = \Sigma n(r)\, b$ then

$$A(q) = \int_V \rho(r)\exp(-iq\cdot r)d^3r$$

weak scattering (kinematic theory)

and

$$I(q) = |A(q)|^2 = \left|\int_V \rho(r)\exp(-iq\cdot r)d^3r\right|^2$$

$$I(q) = |A(q)|^2 = \left\langle\left|\int_V \rho(r)\exp(-iq\cdot r)d^3r\right|^2\right\rangle$$

really an ensemble average...

- With some calculus…

$$I(q) = A(q)A(q)^*$$

$$= \left[\int \rho(u')e^{-iqu'}du'\right]\left[\int \rho(u)e^{-iqu}du\right] \text{and set r} = \text{u'-u}$$

$$= \int \left[\int \rho(u)\rho(u+r)du\right]e^{-iqr}dr$$

$$= \int p(r)e^{-iqr}dr$$

$$where\ p(r) \equiv \int \rho(u)\rho(u+r)du$$

is the autocorrelation function of ρ(r) and is the Fourier transform pair of I(q)

Data Analysis

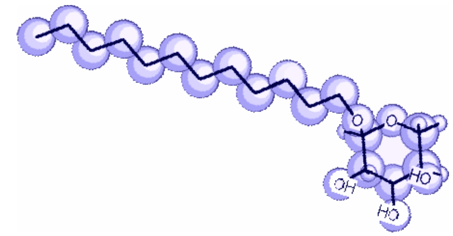
$$I(q) = \int p(r) e^{-iqr} dr$$

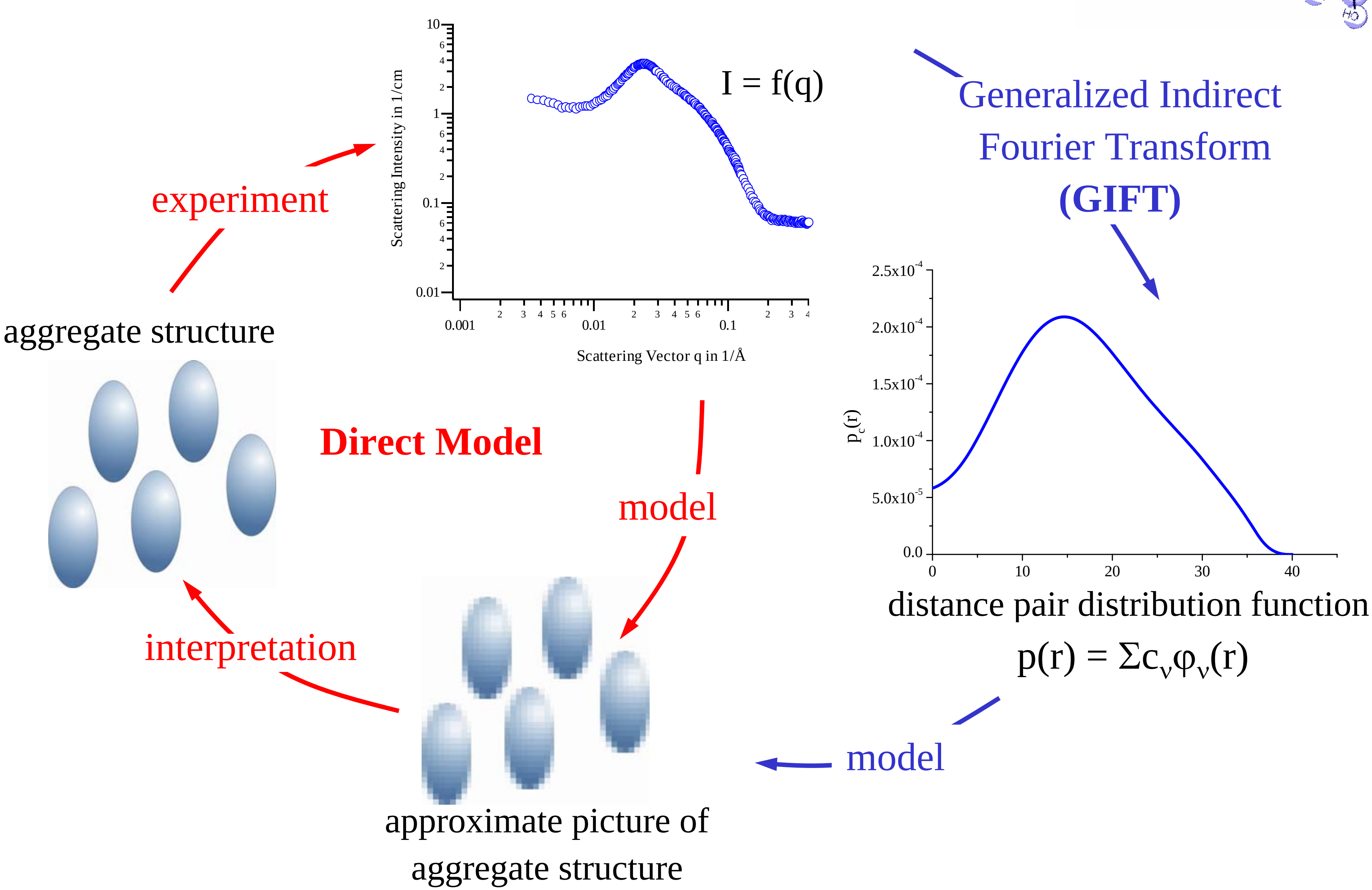
$$p(r) \equiv \int \rho(u)\rho(u+r) du$$

To find ρ(r), either

1. Inverse Fourier Transform
2. Propose a model and fit the measured I(q)

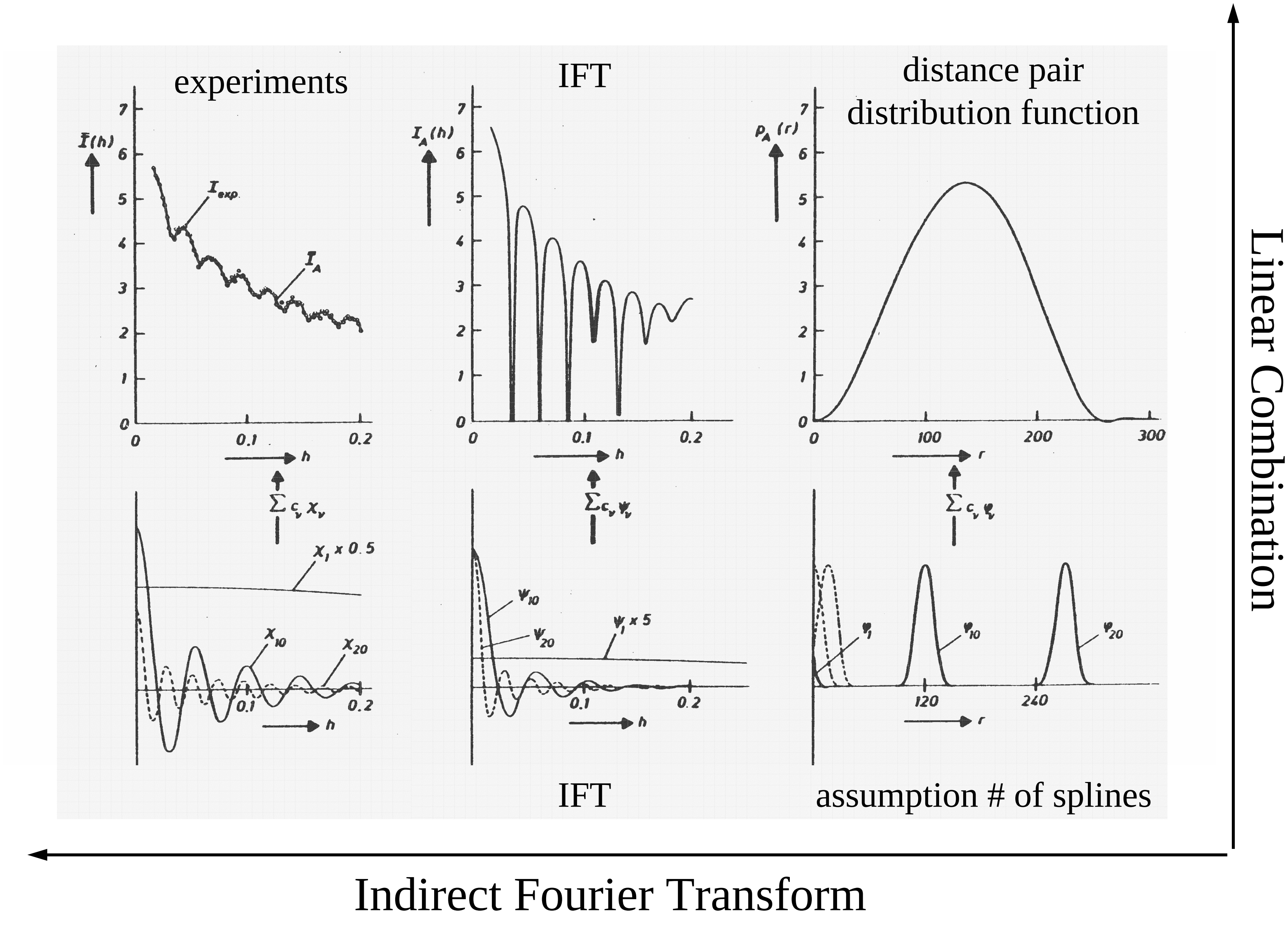
Data Interpretation





Glatter, O. *J. Appl. Cryst.* 1977, 10, 415-421; 1980, 30, 431-442

Method of Global Indirect Fourier Transform



DILUTE LIMIT: Scattering from Particles
Intraparticle Interference

Scattering from larger particles can constructively/destructively interfere, depending on size (relative to the size of the object) and shape of the particles.

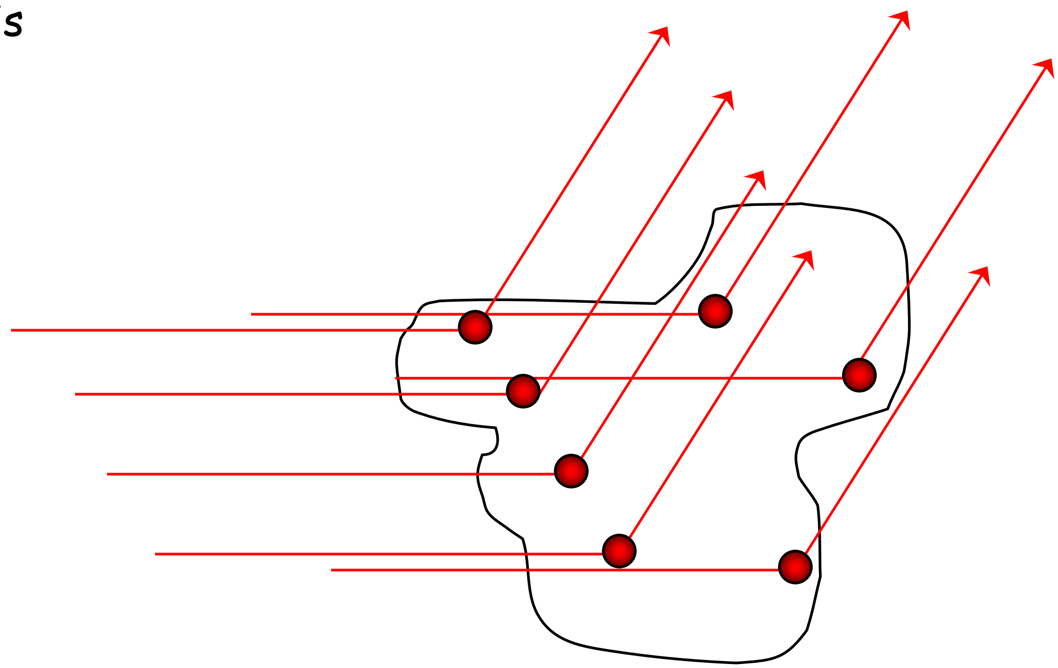
- Size (how big is big?)
  - Scattering vector, q, which gives the length probed
  - Introduce dimensionless quantity, 'qR', that indicates how big the particles are relative to the wavelength.

- Shape
  - Introduce the Form Factor, P(q), the define the role of particle shape in the scattering profiles
  - P(q) for Spheres, leading to Guinier Plots
  - P(q) for vesicles, which are different than spheres
  - P(q) for Gaussian Coils/Polymers, leading to Zimm Plots

Intraparticle Interference Arises from Scattering from the Particle

Generate constructive and destructive interference which is related to FORM

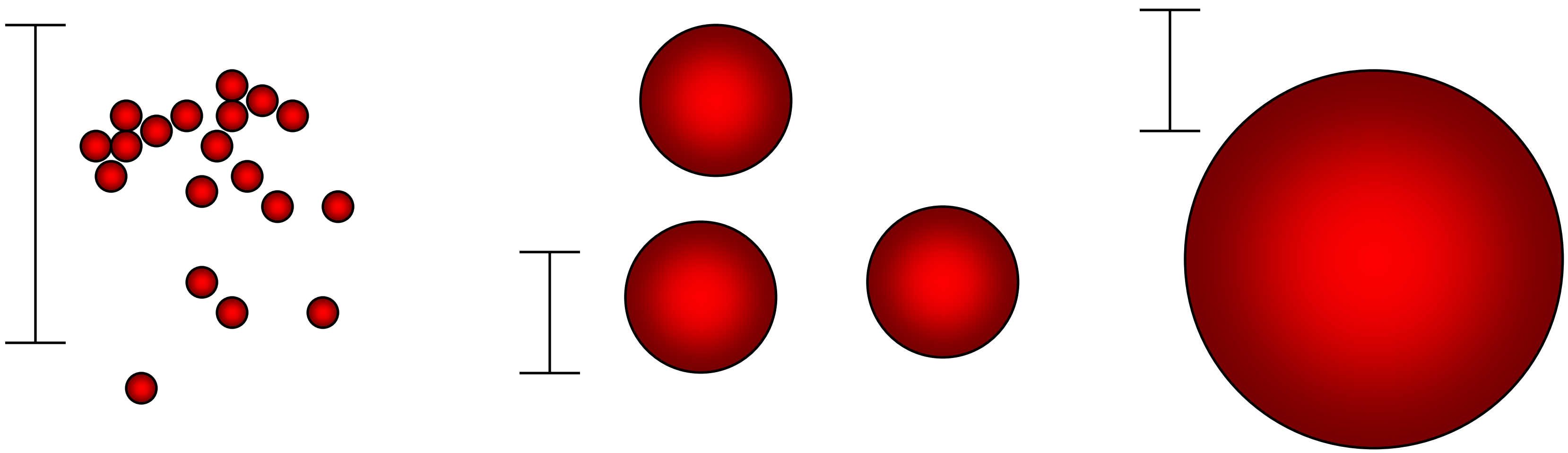
each point scatters



A some angle, the effect depends on the wavelength of the light, size of the aggregate and the shape of the aggregate.

Introduce a Dimensionless Quantity to Answer the Question 'How Long is Long?'

small-q limit		large-q limit
$qR << \pi$	$qR \approx \pi$	$qR >> \pi$



collective properties

individual properties

Intraparticle Form Factor, P(q) is an Integral Over the Structure

Integral over the volume of the sample

phase difference for two scatterers in the volume (as with definition of q)

$$A(q) = \int_{v} \rho(r) e^{-iq \bullet r} d^3 r$$

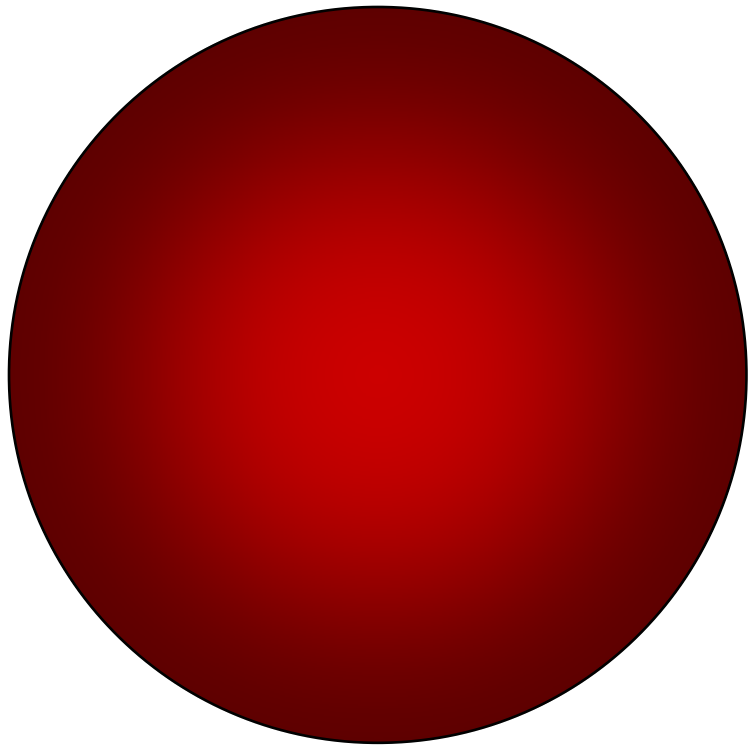
radial density of the particle

Each shape is different, so each integral and each form factor will be different

$$I(q) = \frac{1}{V} N_p \left| A(q) \right|^2 = n_p P(q)$$

P(q) is the particle form factor

Form Factors for Spheres

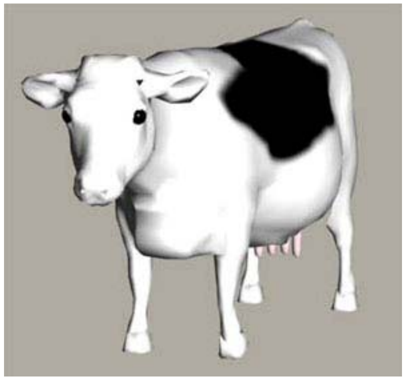


Form Factor for a Cow

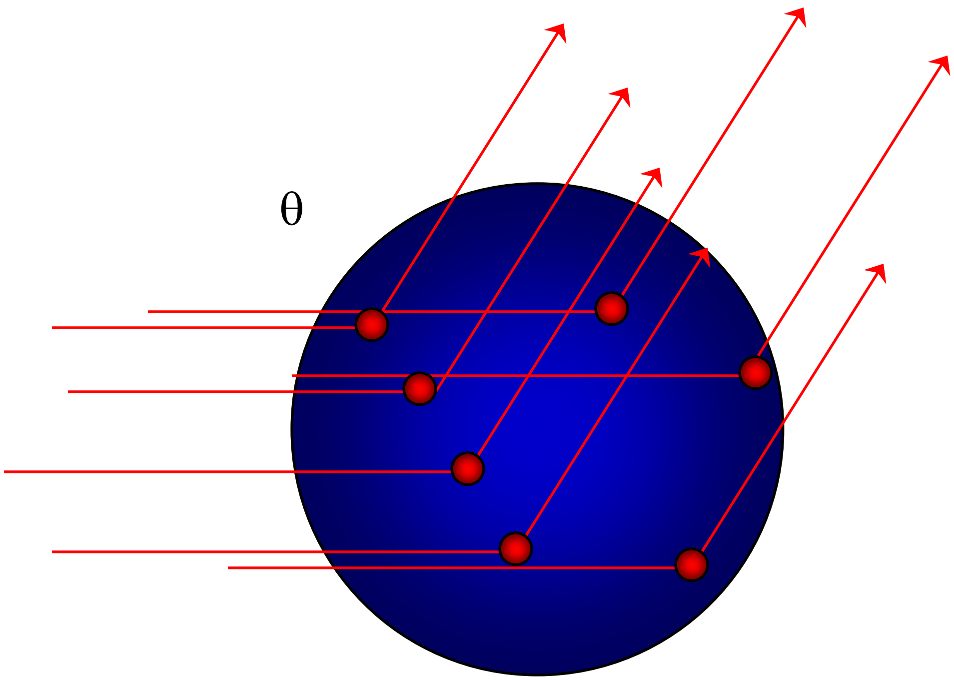
Perry, R.L., and Speck, E.P. "Geometric Factors for Thermal Radiation Exchange Between Cows and Their Surroundings", American Society of Agricultural Engineers Paper #59-323.

For evaluating thermal radiant exchange between a cow and her surroundings, the cow can be represented by an equivalent sphere. The height of the equivalent sphere above the floor is 2/3 of the height at the withers. The origin of the sphere is about 1/4 of the withers-to-pin-bone length back of the withers. The sphere size differs for floor and ceiling, side walls, and front and back walls. For the model surveyed, the radius of the equivalent sphere is 2.13 feet for exchange with floor and ceiling, 2.38 feet for side walls, and 2.02 feet for the front and back walls. These values are 1.8, 2.08, and 1.78 times the heart girth. An equation in spherical coordinates is given for the variation of the size of the equivalent sphere with the angle of view measured from the vertical and transverse axes.

The shape factor for exchange with an adjacent cow in a stanchion spacing of 3'8" was found to be 0.1.



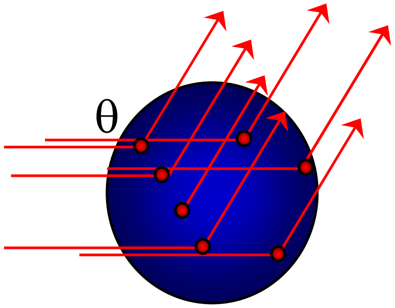
Form Factor for Sphere



Integrate the scattering over the entire sphere, which gives an analytical solution to the intra-particle form factor.

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

Form Factor for Sphere



$$P(q) = |A(q)|^2 = \left| \int_v \rho(r) e^{-iq\bullet r} d^3 r \right|^2$$

solid sphere of radius R, $\Delta\rho = \rho - \rho_{solvent}$

$$A(q) = \Delta\rho \int_0^R \int_0^\pi \int_0^{2\pi} e^{-iq\bullet r} r^2 dr \sin\theta d\theta d\phi$$

$$q \cdot r = qr\cos\theta$$

$$A(q) = \Delta\rho(2\pi) \int_0^R \int_0^\pi e^{-iqr\cos\theta} r^2 dr \sin\theta d\theta$$

$$= \Delta\rho(2\pi) \int_0^R \int_{-1}^1 e^{-iqrx} r^2 dr dx$$

$$= \Delta\rho(2\pi) \int_0^R \frac{e^{iqr} - e^{-iqr}}{iqr} r^2 dr$$

$$= \Delta\rho(2\pi) \int_0^R \frac{2i\sin qr}{iqr} r^2 dr$$

$$A(q) = \Delta\rho \frac{4\pi}{q} \int_0^R r \sin qr dr$$

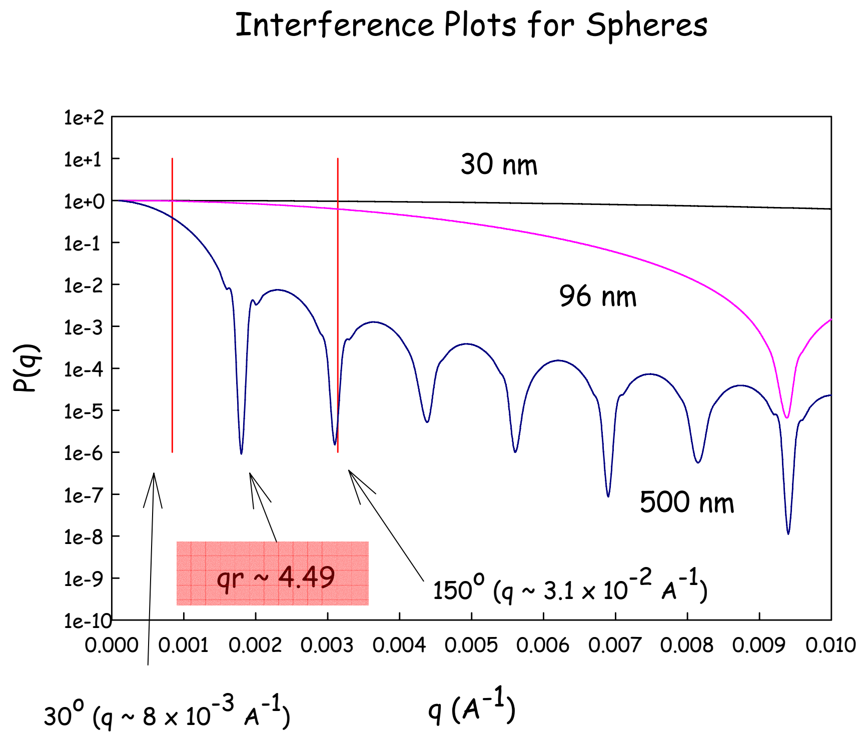
$$= \Delta\rho \frac{4\pi}{q} \left[\frac{\sin qR}{q^2} - \frac{qR\cos qR}{q^2} \right]$$

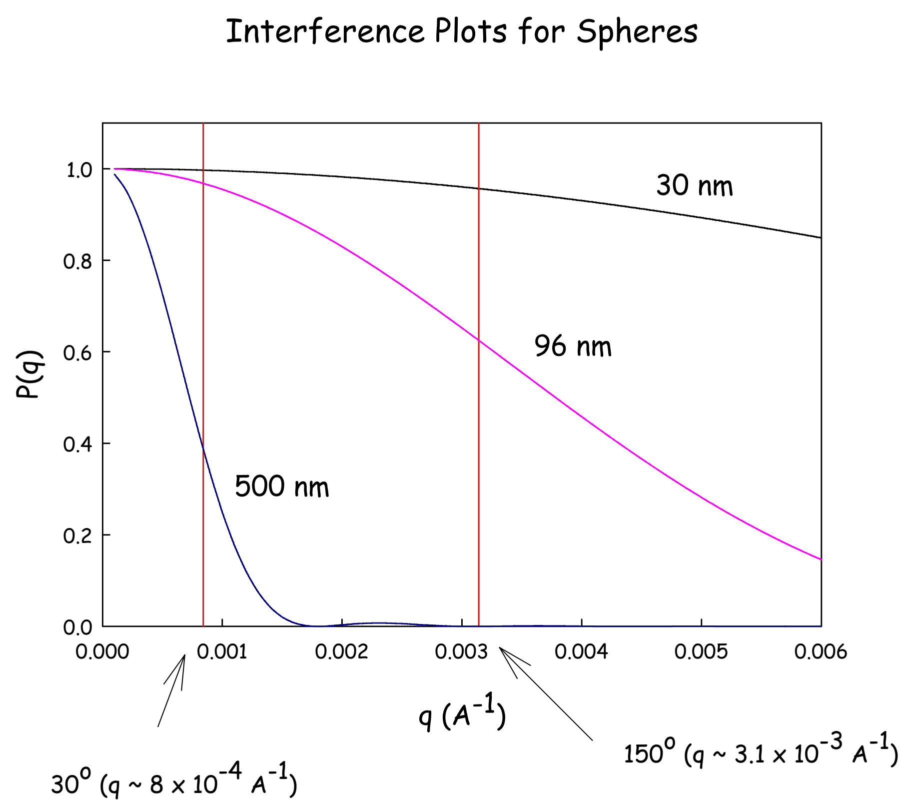
$$= \Delta\rho(4\pi R^3) \left[\frac{\sin qR}{(qR)^3} - \frac{qR\cos qR}{(qR)^3} \right]$$

$$= 3\Delta\rho V_p \left[\frac{\sin x - x\cos x}{x^3} \right]$$

$$P(q) = |A(q)|^2 = (\Delta\rho)^2 V_p^2 \left[3\frac{\sin x - x\cos x}{x^3} \right]^2$$

Shape of the Form Factor

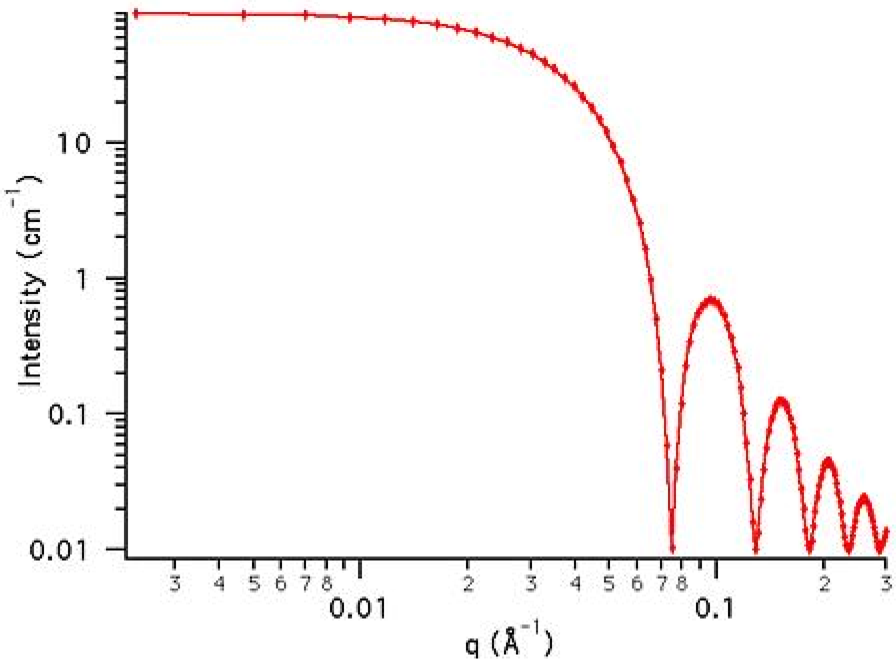




The sizes denote the diameter of the particles; the red lines denote the q values accessible with typical light scattering measurements

Sphere Form Factor

- 6 nm monodisperse sphere



Guinier Expression

Back in the day… intensities were weak, so special care was taken at the low-q region

$$\frac{I}{I_o} = P(q) \approx 1 + aq^2 + bq^4 \ldots \approx 1 - \frac{{R_g}^2 q^2}{3}$$

Note that an exponential can be expanded as a power series

$$e^{-x} \approx 1 - x + \frac{x^2}{2!} - \ldots$$

so this suggested that in general

$$I = I_o e^{-\frac{{R_g}^2 q^2}{3}}$$

where R_g is the radius of gyration

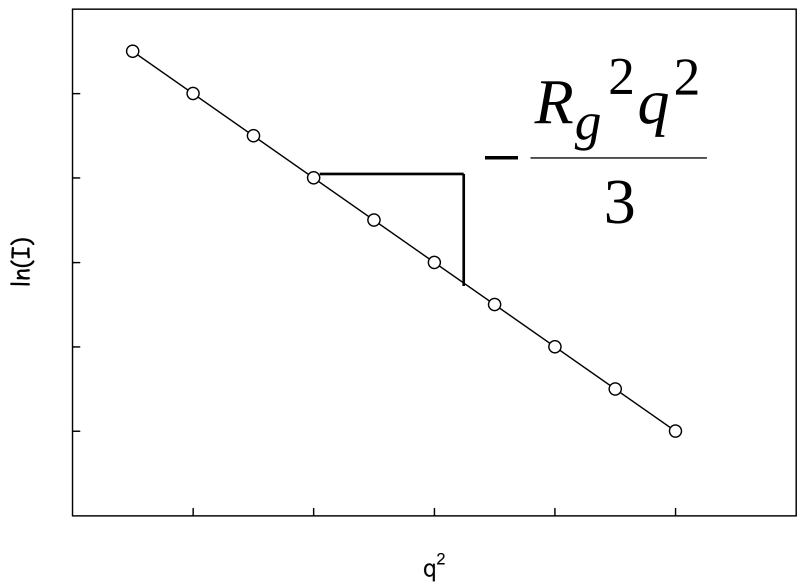
(Guinier radius)

General Feature - Guinier Region ($qa < \pi$)

Onset of the angle dependence of the scattering

$$I(q) = I_o P(q) \approx I_o e^{-\frac{R_g{}^2 q^2}{3}}$$

Guinier Plot



Then, taking the natural logarithm of the expression

$$\ln I = \ln I_o - \frac{R_g{}^2 q^2}{3}$$

The plotting the ln I versus q^2, leads to a plot with the slope proportional to the square of the scattering vector

Guinier continued

- In general, for monodisperse objects

$$R_g^2 = \frac{\int r^2(\rho(r)-\rho_s)d^3r}{\int (\rho(r)-\rho_s)d^3r}$$

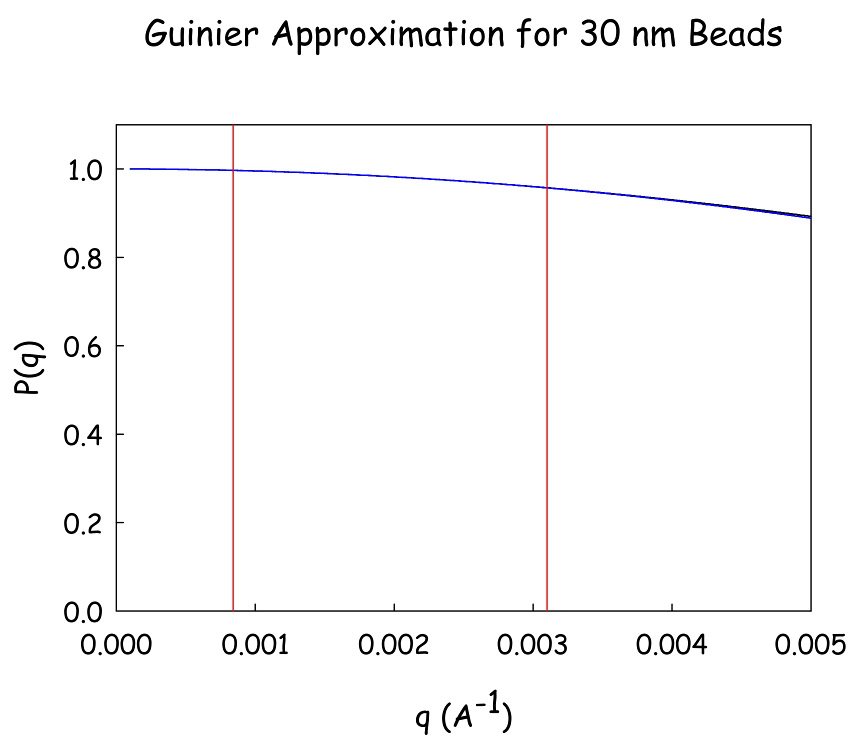
- Example- solid sphere

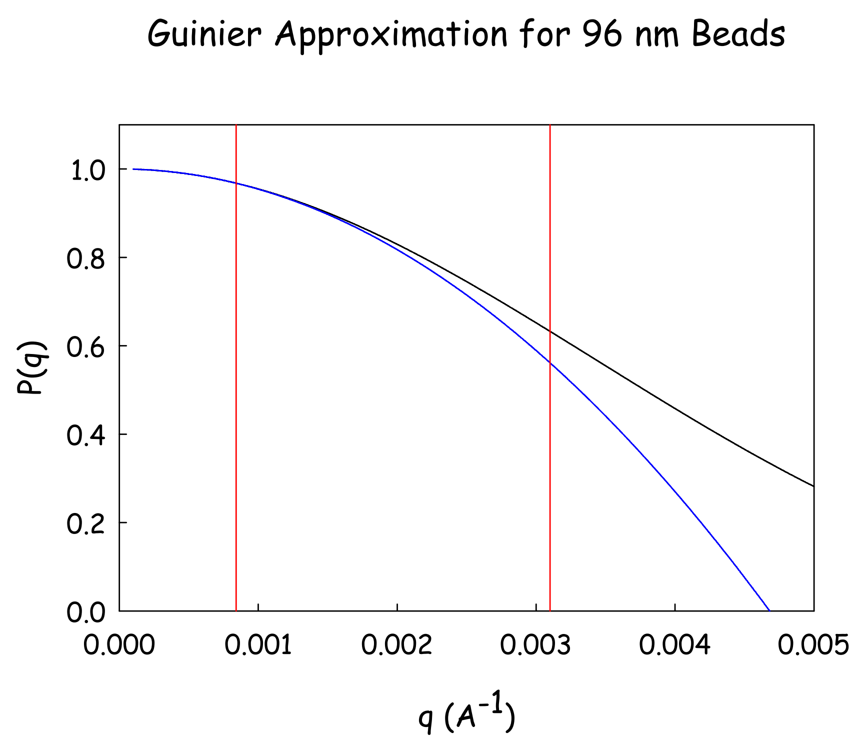
$$R_g^2 = \frac{\int r^2 r^2 dr}{\int r^2 dr} = \frac{3}{5}R^2$$

or $R_g = 0.77$ R

- Aside – for polydisperse spheres measure $\langle R_g^2 \rangle_z$

How Good Are Guinier Approximations?

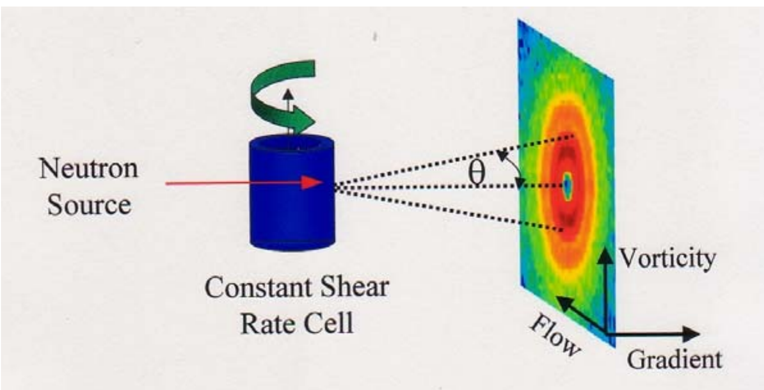


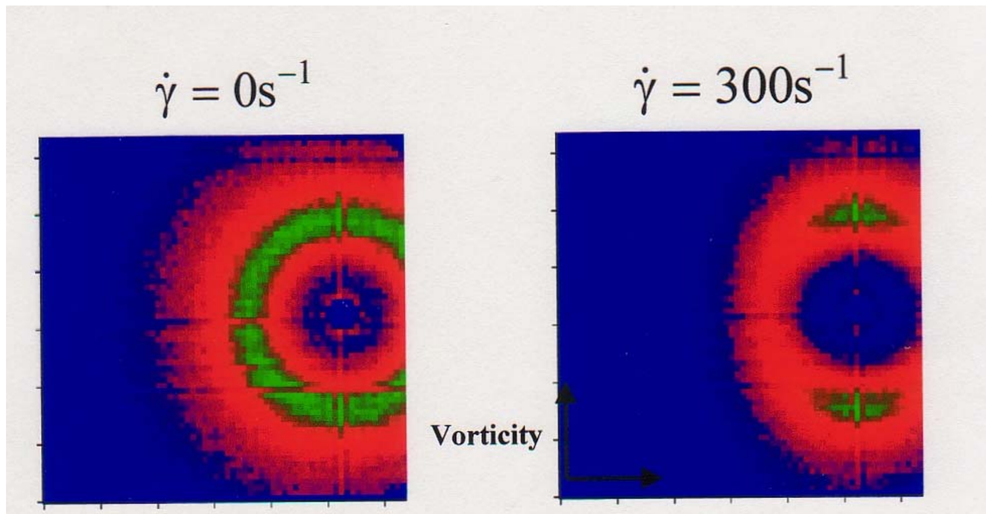


- Guinier Approximations work well provide 'qa' is small
  (black- full expression of P(q); blue- Guinier Approximation)
- As particles get larger, the angles must be far smaller
- Limit ~ 100 nm for LS measurements, using smaller angles

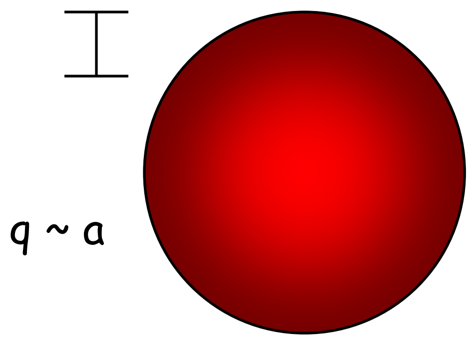
Anisotropic Scatterers

- Rods or disks may not always be isotropic
  - Above analysis is for **I(q)** = I(q)
- Alignment may give additional information





Porod Region (qa >> π)



Recall that…

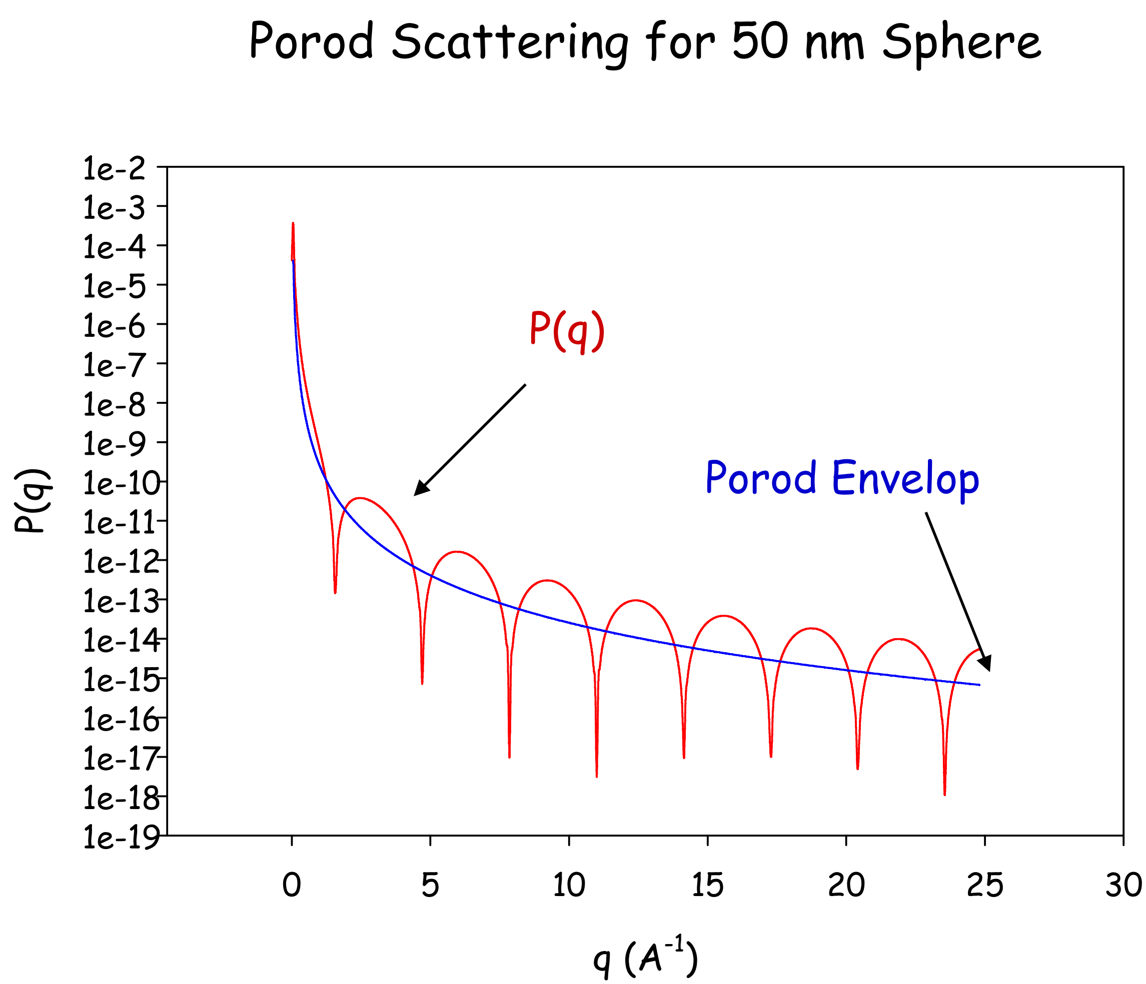
$$P(qR) = \left(\frac{3}{(qR)^3} (\sin(qR) - qR\cos(qR)) \right)^2$$

'qR' dominates summation

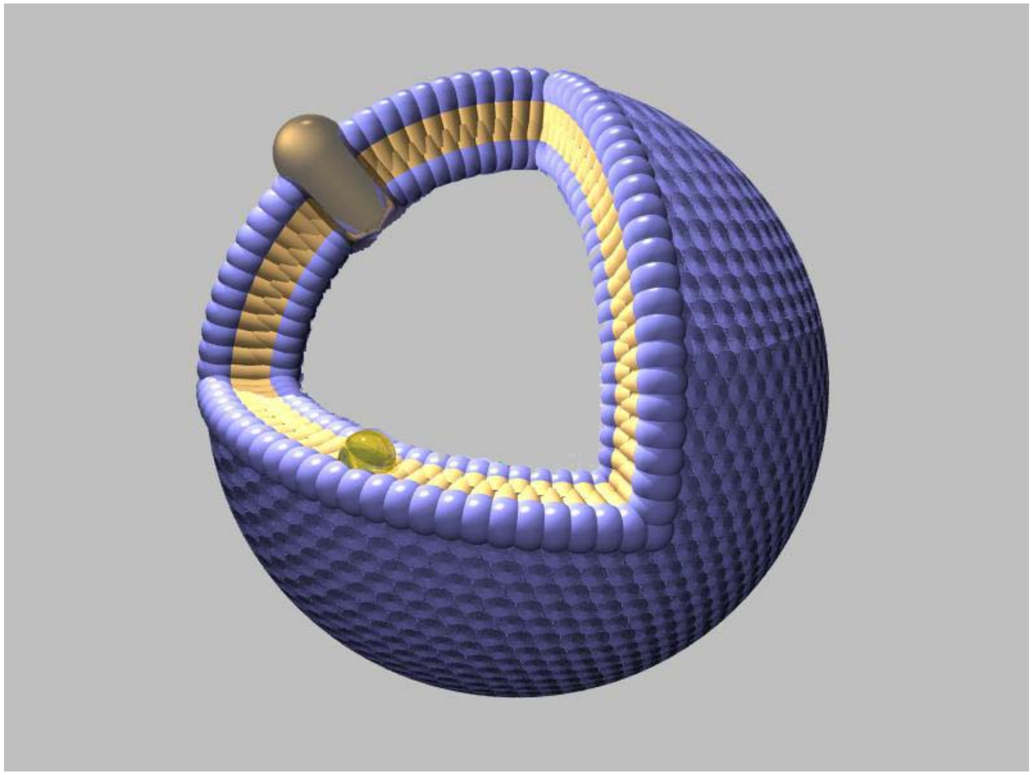
In the limit that 'qR' is large

$$P(qR) \approx \left(\frac{-3qR\cos(qR)}{(qR)^3} \right)^2 \approx \left(\frac{1}{(qR)^2} \right)^2 \cos^2(qR) \approx \frac{1}{(qR)^4} \approx (qR)^{-4}$$

P(q) is Dominated by q^{-4} Term



Form Factor for Vesicles

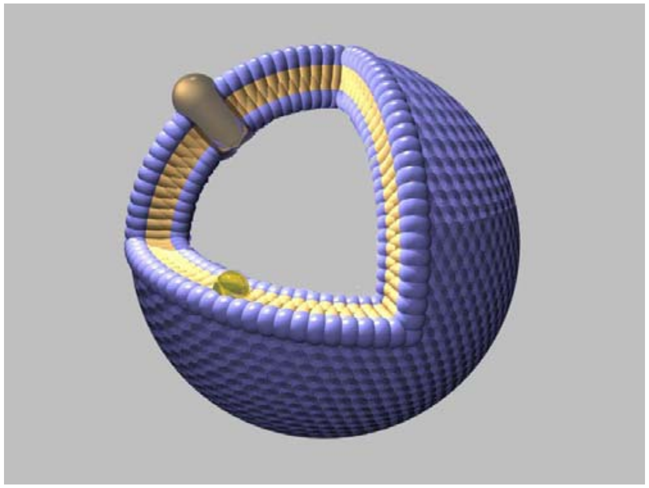


Form Factor of Vesicles Versus Spheres

Form factor for a sphere is given as:

$$P(q) = (A(q))^2$$

$$A(qR) = \frac{3}{qR}(\sin(qR) - qR\cos(qR))$$



Form factor for a vesicle is outside sphere minus the inside spheres

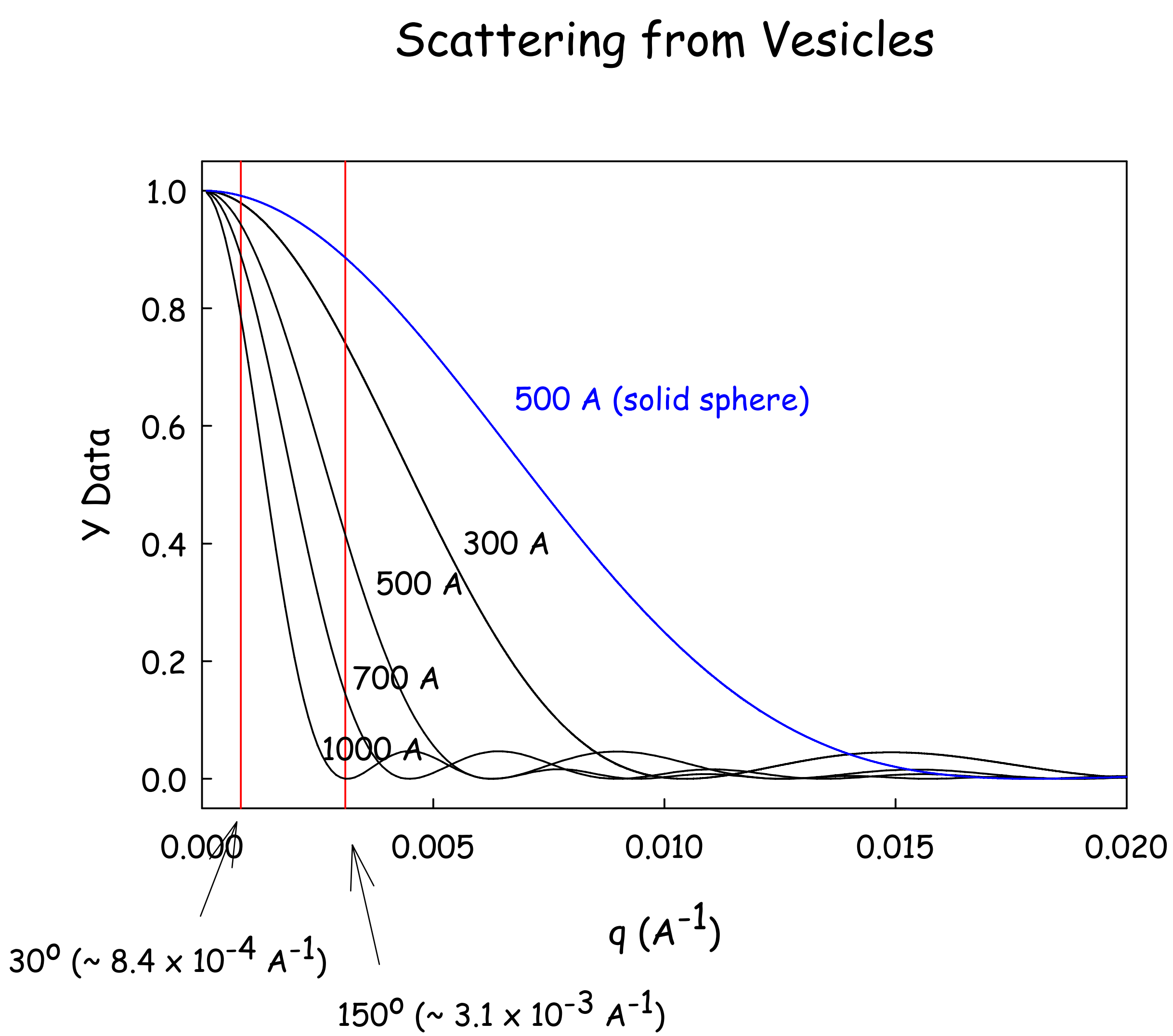
$$P(q) = (F_{outside}(q) - F_{inside}(q))^2$$

$$P(q) = \left(\frac{3}{{R_o}^3 - {R_i}^3}\right)^2 \left(\frac{{R_o}^3}{qR_o} J_1(qR_o) - \frac{{R_i}^3}{qR_i} J_1(qR_i)\right)^2$$

Where $J_1(q)$ is the first order Bessel Function

$$J_1(qR) = \frac{\sin(qR)}{(qR)^2} - \frac{\cos(qR)}{qR}$$

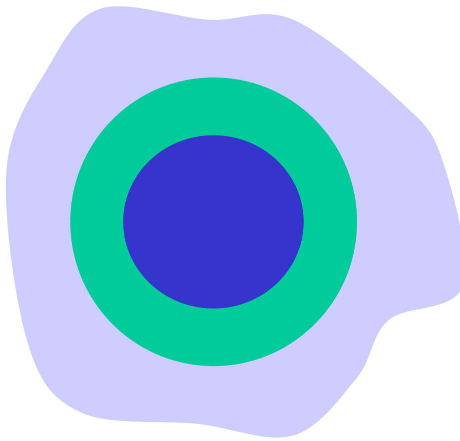
Form Factor of Vesicles Versus Spheres



Which looks very different than a sphere, for the same size

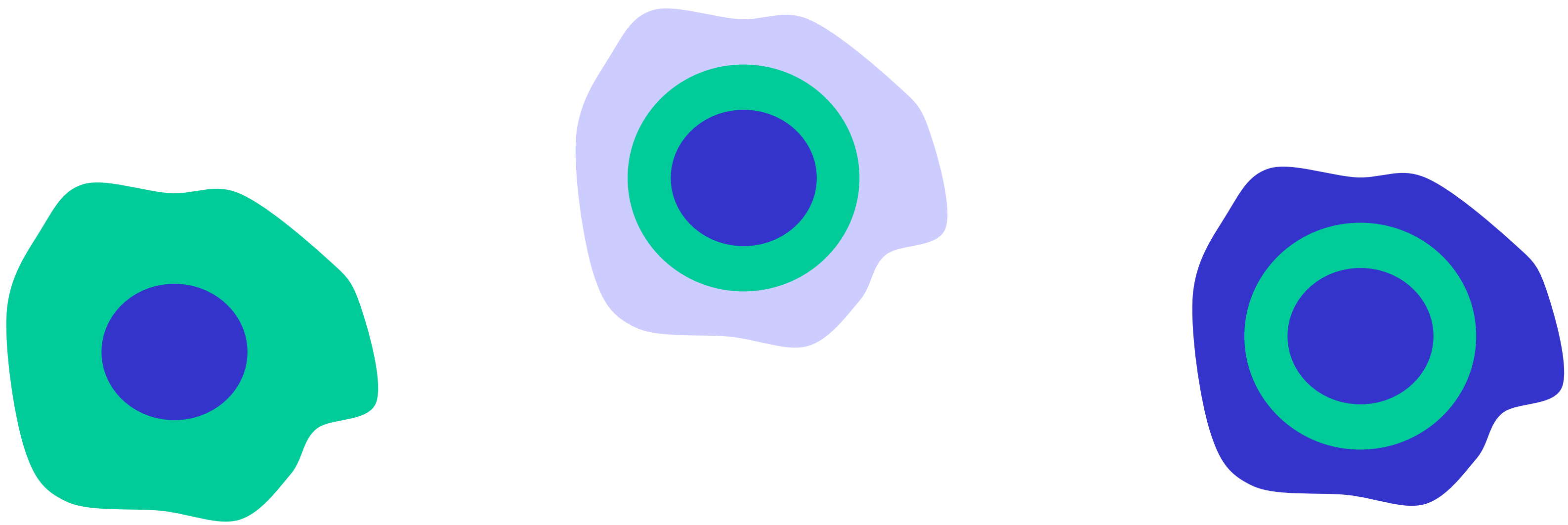
Contrast variation

- Consider a core and shell morphology:



- and change the solvent (H/D) to match the SLD of the core and shell, separately

Contrast Variation for Composite Particle



Clean sphere scattering gives core dimension

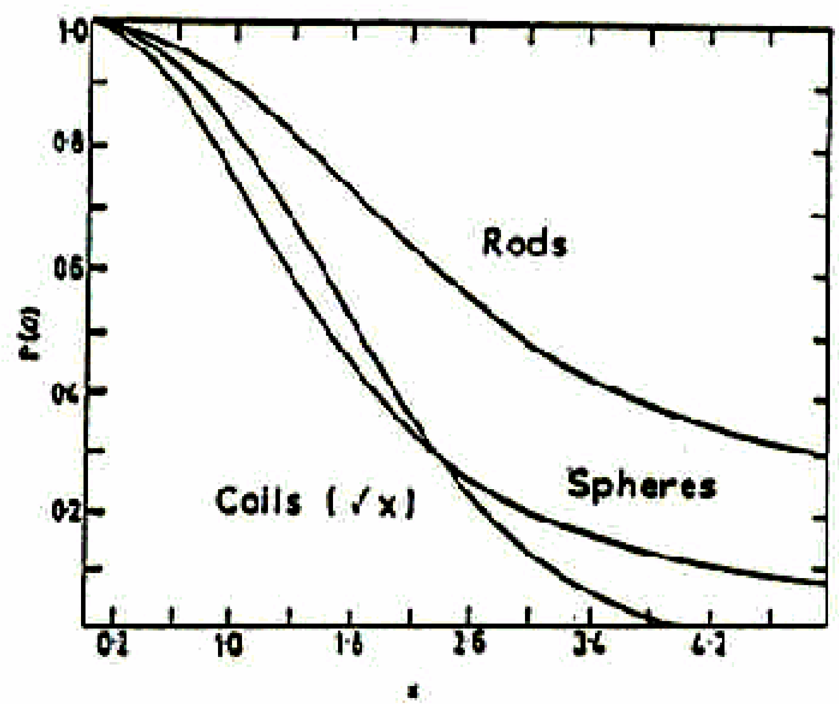
Clean shell scattering gives shell dimension

There are Other Forms of P(q)

Thin Rods: Length 2H; Diameter 2R; at low q

$$P(q) = \frac{e^{-q^2R^2/4}}{2qH}$$

$$R_g = \frac{R^2}{2} + \frac{H^2}{3}$$

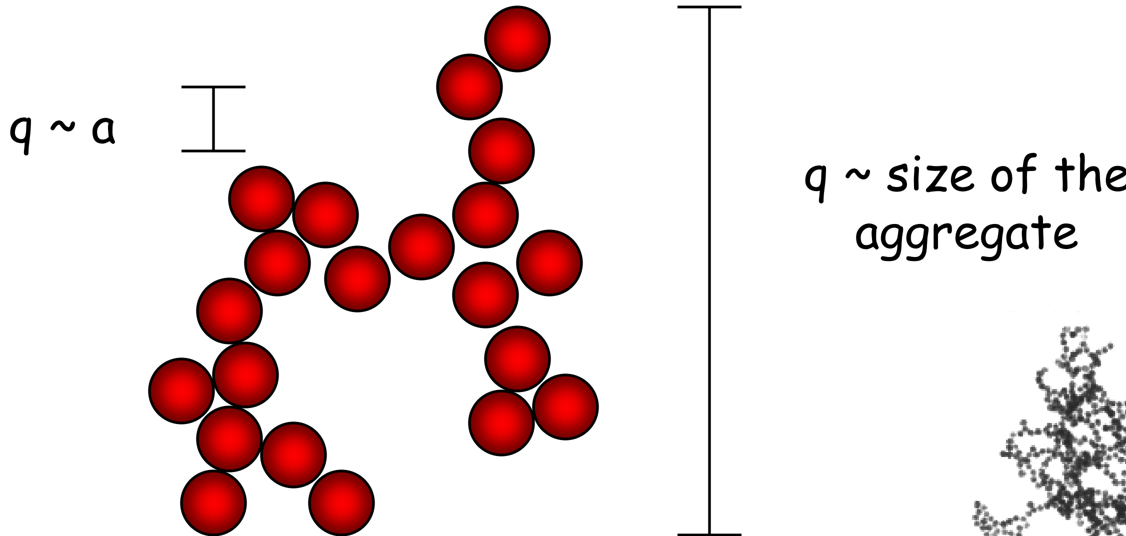


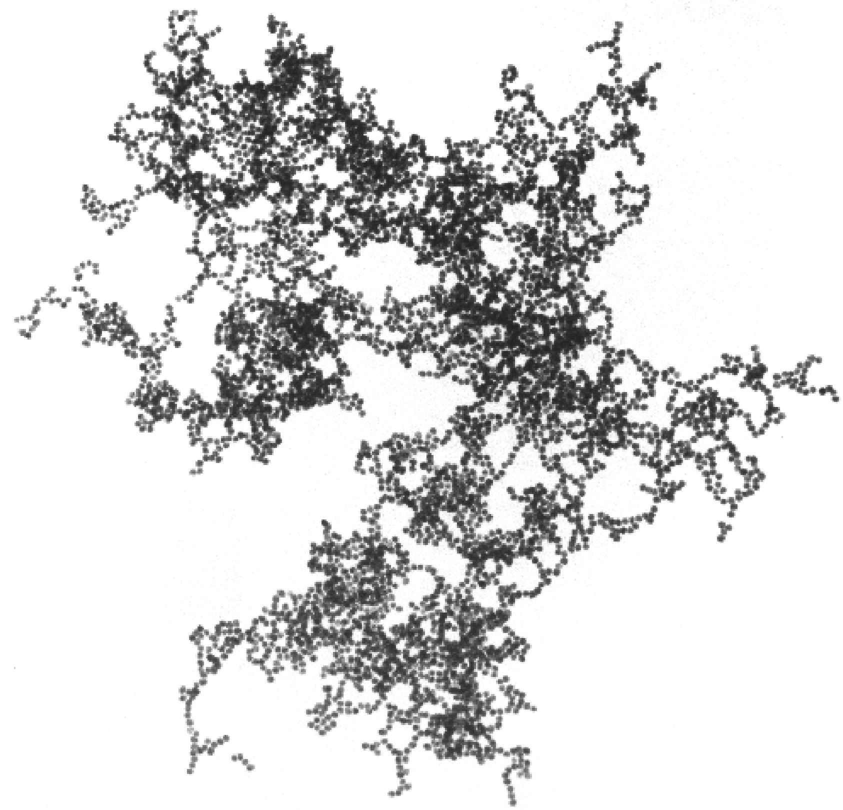
Disk: Thickness 2H; Diameter 2R

$$P(q) = \frac{e^{-q^2H^2/3}}{q^2R^2}$$

$$R_g = \frac{R^2}{2} + \frac{H^2}{3}$$

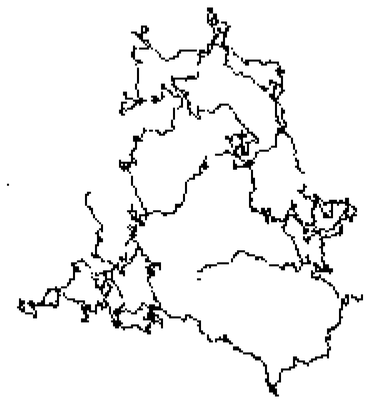
Fractal Region (qa ~ π)



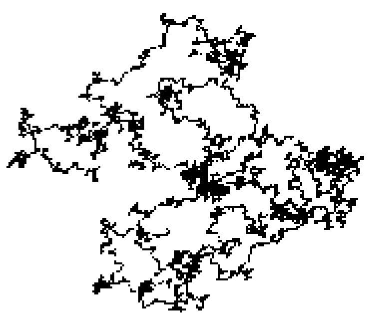


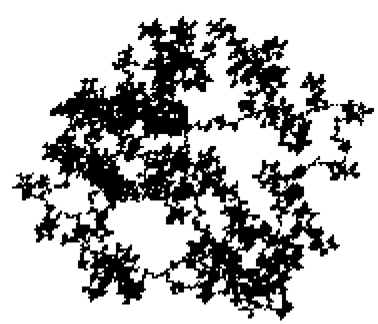
- Small q ~ size of the individual particles
- Large q ~ size of the individual aggregates

The Shape of Different Fractal Particles



Random fractal objects produced by using the band-limited Weierstrass functions and employed in experiments. Assigned fractal dimension was D = (a) 1.2, (b) 1.5, and (c) 1.8.

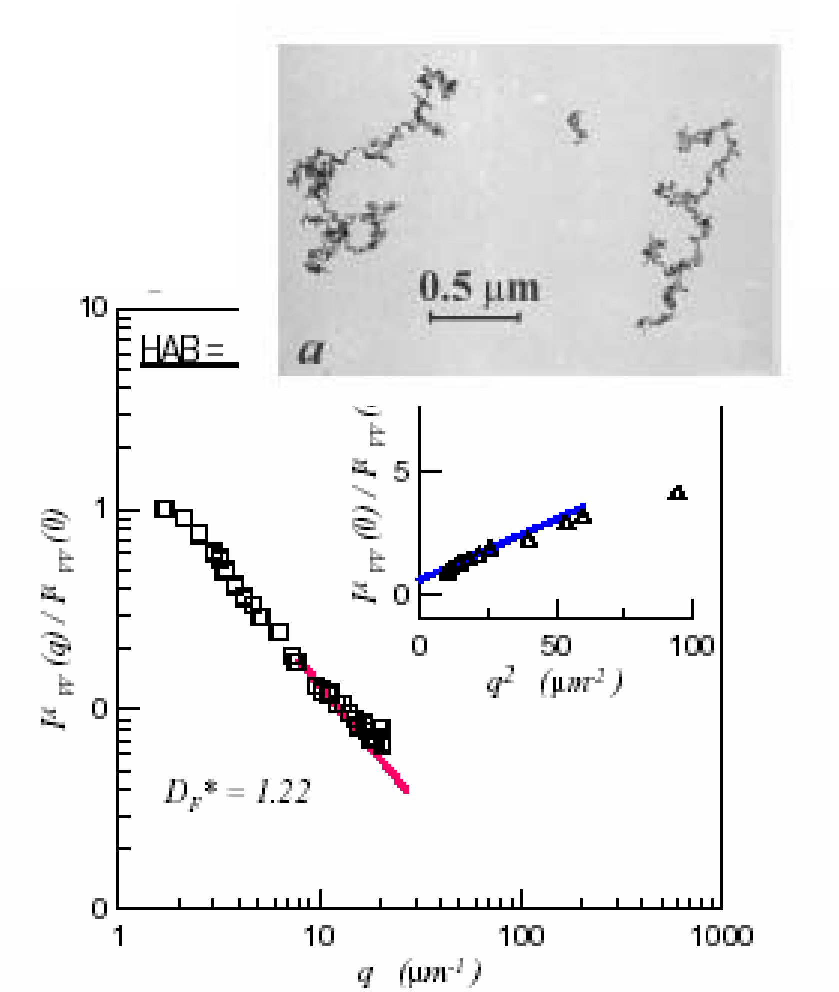




Fractal Region for Aerosol Aggregates

$$I(q) = I_o(q)P(q) \approx I_o e^{-d_f}$$

$$\ln I \approx -d_f \ln q$$



$$|\vec{q}| = \frac{4\pi(1.33)}{0.500\,\mu m} \sin\left(\frac{130}{2}\right) \approx 30\,\mu m^{-1}$$

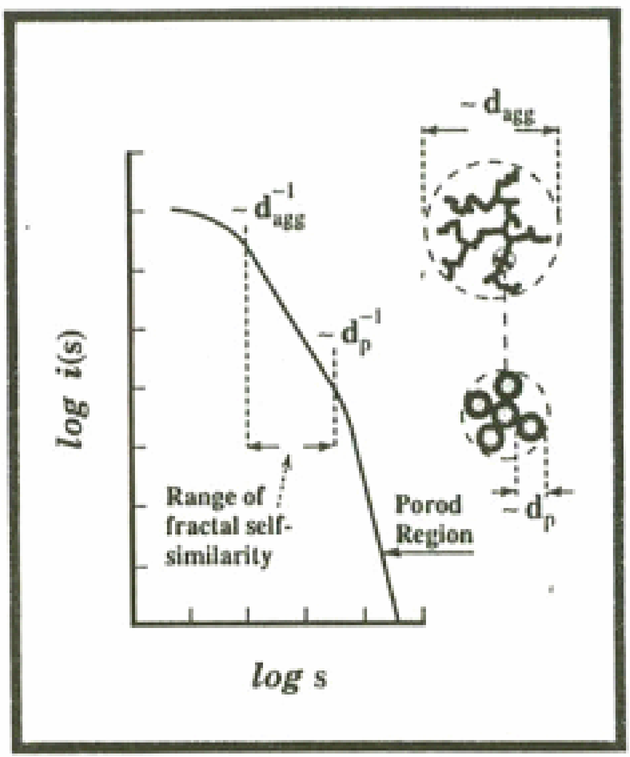
$$d \approx 1\,\mu m$$

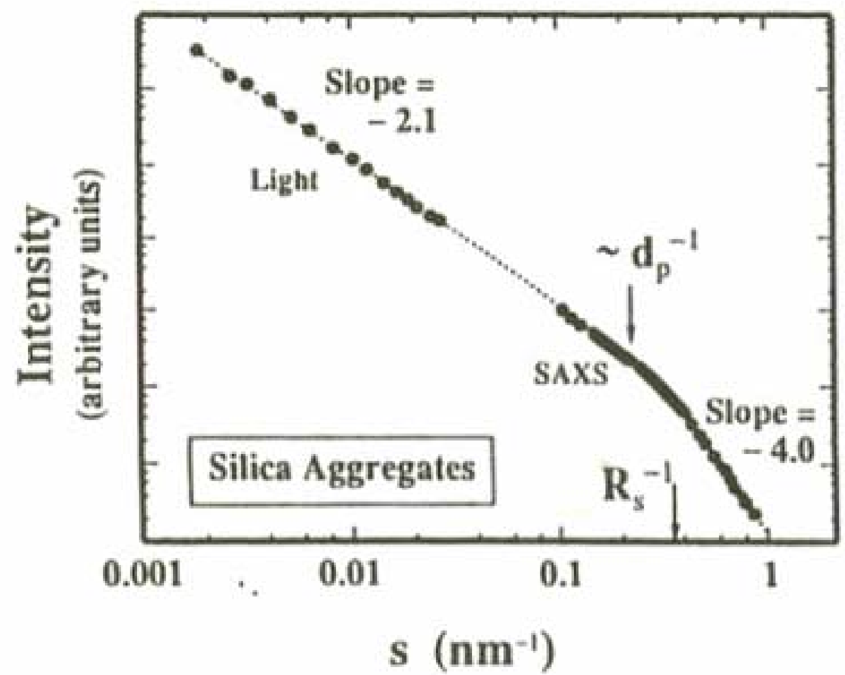
$$|\vec{q}| = \frac{4\pi(1.33)}{0.500\,\mu m} \sin\left(\frac{30}{2}\right) \approx 8\,\mu m^{-1}$$

$$d \approx 0.1\,\mu m$$

Allowing Characterization Over Many Distances

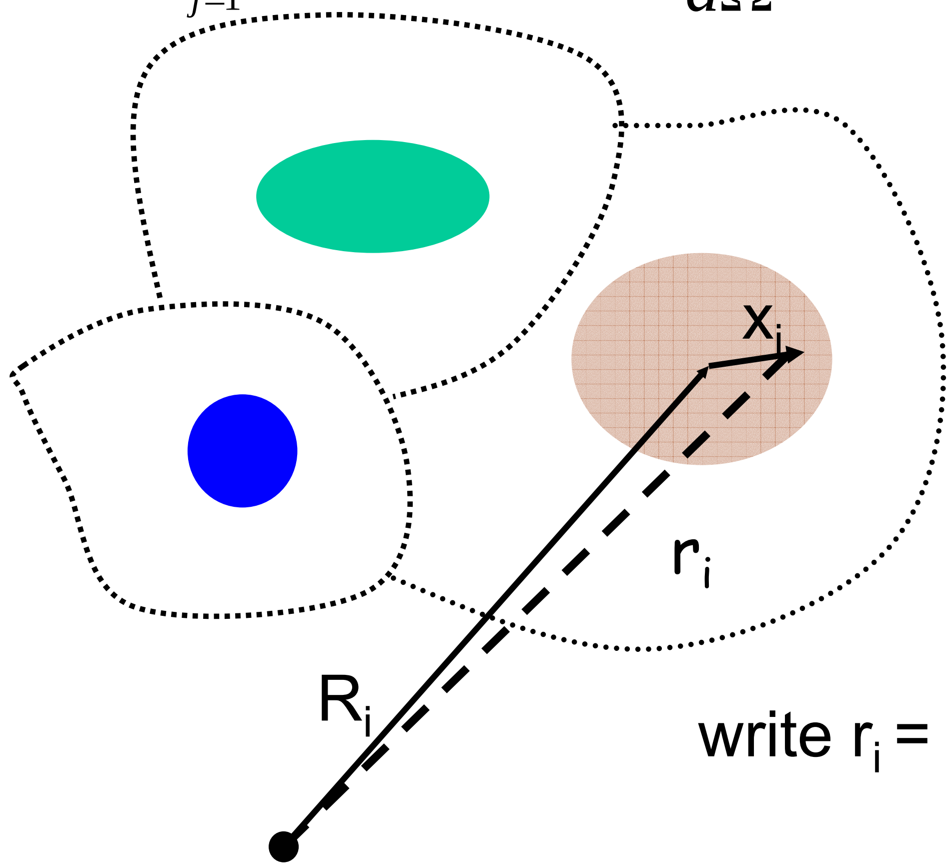
Logarithm-logarithm plots result in slopes that relate to the different levels of structures





Scattering from Particulate Systems

Recall: $A(q) = A_o b \sum_{j=1}^{N} \exp(-iq \cdot r_j)$ so $\frac{d\sigma}{d\Omega} \approx I(q) = \left\langle \left| \sum_i b_i e^{iq \cdot r_i} \right|^2 \right\rangle$



write $r_i = R_i + x_i$

Scattering from Particulate Systems

so $$\frac{d\sigma}{d\Omega} \approx I(q) = \left\langle \left| \sum_i b_i e^{iq \cdot r_i} \right|^2 \right\rangle$$

$$= \left\langle \left| \sum_{i=1}^{N_p} e^{iq \cdot R_i} \sum_{cell\,i} b_{ij} e^{iq \cdot x_j} \right|^2 \right\rangle$$

sum over the scatterers in each cell

sum over the number of cells

Scattering from Particulate Systems

now define a 'form factor' for each cell

$$A_i(q) = \sum_{celli} b_{ij} e^{iq \cdot x_j}$$

in the particle, define $\rho_i(r) = \sum_j b_{ij} \delta(r - x_j)$

in the solvent $\rho_i(r) = \rho_s$ (constant and uniform)

so $A_i(q) = \int_{celli} (\rho_i(r) - \rho_s) e^{iq \cdot r} dr + \rho_s \int_{celli} e^{iq \cdot r} dr$

$$= 0 + \int_{particle} (\rho_i(r) - \rho_s) e^{iq \cdot r} dr + \delta(q)$$

$= A(q)$ from above!

Scattering from Particulate Systems

so $$\frac{d\sigma}{d\Omega} \approx I(q) = \left\langle \left| \sum_i b_i e^{iq \cdot r_i} \right|^2 \right\rangle$$

$$= \left\langle \left| \sum_{i=1}^{N_p} e^{iq \cdot R_i} \sum_{celli} b_{ij} e^{iq \cdot x_j} \right|^2 \right\rangle$$

$$= \left\langle \left| \sum_{i=1}^{N_p} \underline{e^{iq \cdot R_i}} \, \underline{A_i(q)} \right|^2 \right\rangle$$

$A_i(q)$: particle shape, size, polydispersity

$e^{iq \cdot R_i}$: arrangement of particle centers

Scattering from Particulate Systems

so $$\frac{d\sigma}{d\Omega} \approx I(q) = \left\langle \left| \sum_{i=1}^{N_p} e^{iq\cdot R_i} A_i(q) \right|^2 \right\rangle$$

when the particles are 'dilute' the R_i are uncorrelated,

so $I(q) = N_p \left\langle \left| A_i(q) \right|^2 \right\rangle$ as before!

So, how do we find the R_i 's??

Scattering from Particulate Systems

so $\frac{d\sigma}{d\Omega} \approx I(q) = \left\langle \left| \sum_{i=1}^{N_p} e^{iq\cdot R_i} A_i(q) \right|^2 \right\rangle$

$$= \frac{1}{V} \sum_{i=1}^{N_p} \left\langle \left| A_i(q) \right|^2 \right\rangle + \frac{1}{V} \left\langle \sum_{i=1}^{N_p} \sum_{\substack{j=1 \\ j\neq i}}^{N_p} \exp(iq\cdot(R_i - R_j)) A_i(q) A_j^{*}(q) \right\rangle$$

again, in the simpliest case of monodisperse spheres,
all $\left\langle \left| A_i(q) \right|^2 \right\rangle = P(q)$

$$I(q) = \frac{N_p P(q)}{V} + \frac{P(q)}{V} \left\langle \sum_{i=1}^{N_p} \sum_{\substack{j=1 \\ j\neq i}}^{N_p} \exp(iq\cdot(R_i - R_j)) \right\rangle$$

$$= n_p P(q)(1 + \frac{1}{N_p} \left\langle \sum_{i=1}^{N_p} \sum_{\substack{j=1 \\ j\neq i}}^{N_p} \exp(iq\cdot(R_i - R_j)) \right\rangle)$$

Scattering from Particulate Systems

$$\frac{1}{N_p}\left\langle \sum_{i=1}^{N_p}\sum_{\substack{j=1\\ j\neq i}}^{N_p} \exp(iq\cdot(R_i - R_j)) \right\rangle$$

is related to the thermodynamic radial distribution function g(r), so we can finally write the master working equation as

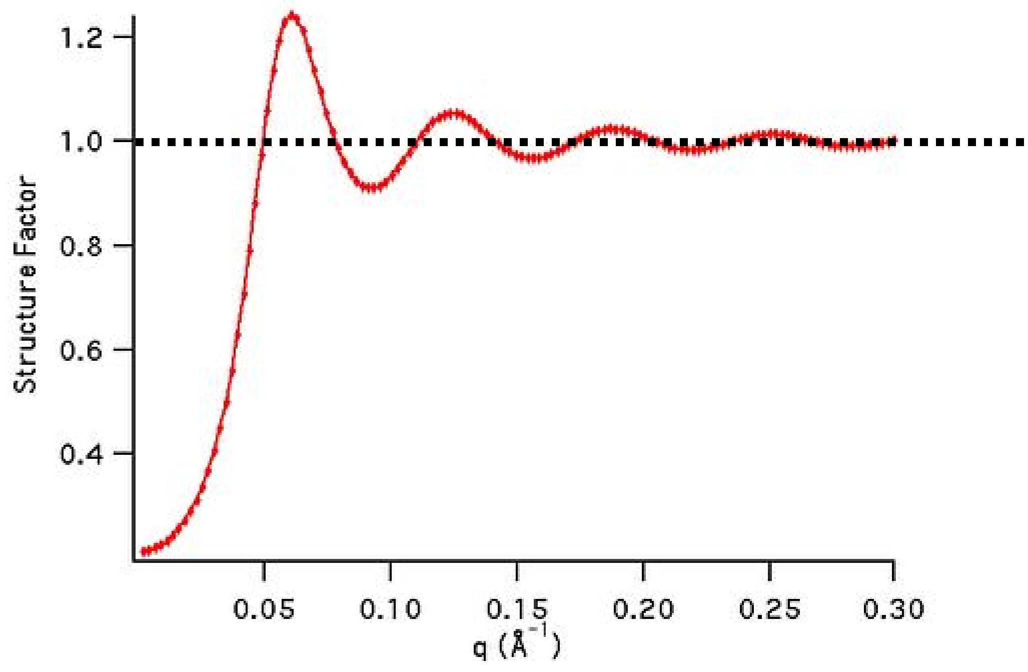
$$I(q) = n_p P(q)[1 + 4\pi n_p \int_0^\infty (g(r)-1)\frac{\sin qr}{qr} r^2 dr]$$

Fundamental working equation for monodisperse spherical particles, with the term in brackets called the structure factor, so

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

Structure Factor

- For 5 nm hard spheres, 20% volume fraction



Scattering from Particulate Systems

So how do we get $S(q)$?

Various thermodynamic models relate $g(r)$ (and thus $S(q)$) to the interparticle potential

There are two questions:

1. What is the nature of the potential?
    - Hard sphere?
    - Electrostatic?
    - Depletion?
    - Steric?
2. What thermodynamic formalism do you use to calculate $g(r)$?

Scattering from Particulate Systems

Potential	Solution (closure)	Comments
Hard Sphere	Percus-Yevick Rogers-Young	Excellent analytic, can be extended to polydisperse
Electrostatic	Mean-Spherical Approximation	Monodisperse
Square Well	Sharma&Sharma (PY)	Monodisperse

And many more… verified by computer simulations

Scattering from Particulate Systems

What about the real world…

polydisperse, nonspherical…

Various 'decoupling approximations' to deal with the issues of

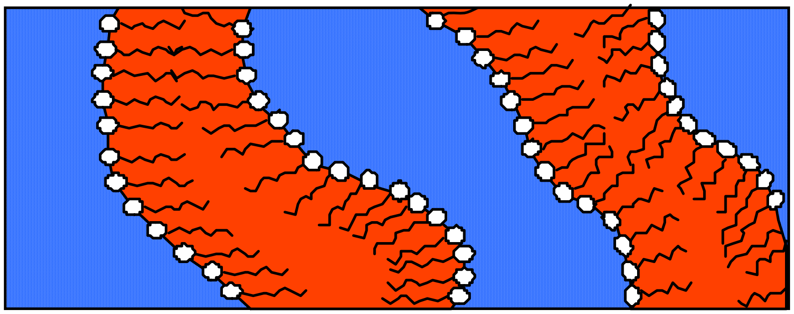
$$\frac{1}{V}\left\langle \sum_{i=1}^{N_p}\sum_{\substack{j=1\\ j\neq i}}^{N_p} \exp(iq\cdot(R_i - R_j))A_i(q)A_j^{*}(q)\right\rangle$$

These are best for repulsive potentials.

Data workup:
http://www.ncnr.nist.gov/programs/sans/manuals/available_SANS.html

Non-Particulate Scattering

Example: Teubner-Strey model for bicontinuous microemulsions



Using a free energy model derive correlation function for bicontinuous structures

Scattering Function

3-D Correlation Function

$$I(q) = \frac{8\pi\langle\eta^2\rangle c_2 V/\xi}{a_2 + c_1 q^2 + c_2 q^4} \xleftarrow{\text{Fourier Transform}} \gamma(r) = \frac{d}{2\pi r}\sin\left(\frac{2\pi r}{d}\right)\exp(-r/\xi)$$

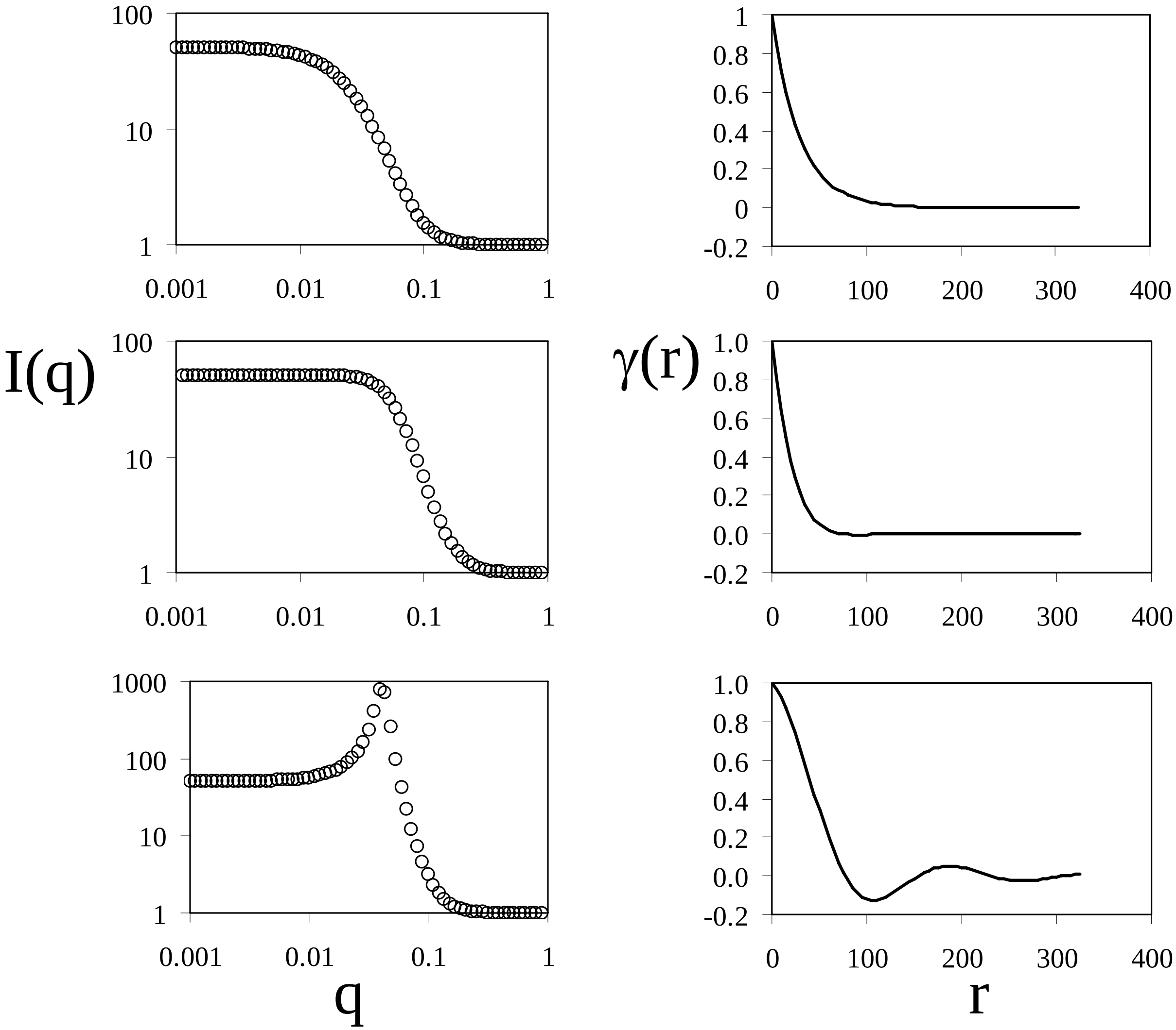
Structure characterized by 2 parameters:

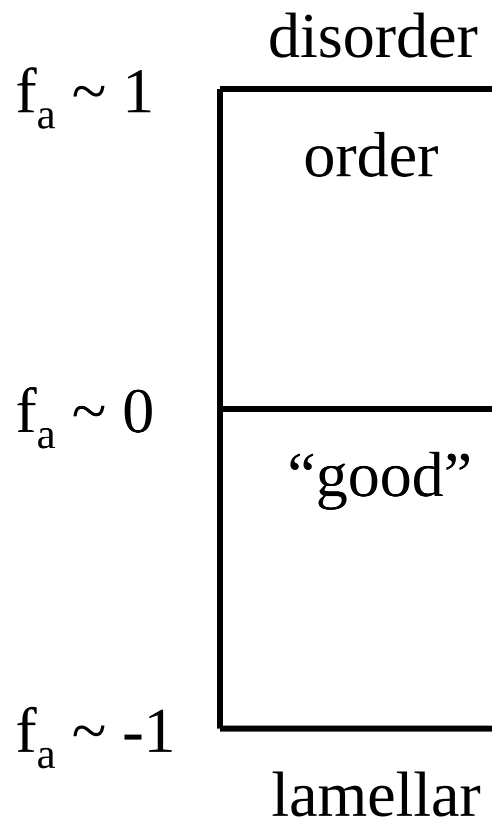
d : repeat length of microemulsion (oil + water domain)

ξ : correlation length

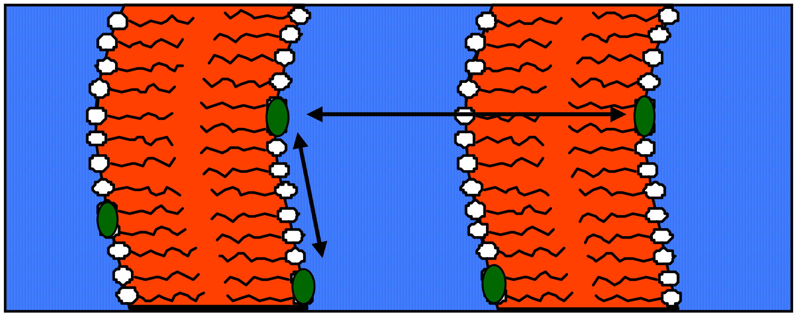
Amphiphilicity Factor

$$f_a = \frac{c_1}{\sqrt{4a_2c_2}}$$





Adding ionic surfactant to surfactant monolayer



Amphiphilicity Factor