NRC·CNRC
Canadian Neutron Beam Centre

University of Connecticut

Small Angle Neutron Scattering (SANS)

Mu-Ping Nieh (聂睦平)

Institute of Materials Science &
Dept. Chem. & Biomol. Eng.
Univ. of Connecticut, Storrs, CT, USA

Presented to CNBC, 2013 Neutron Scattering Summer School, June 5

National Research Council Canada
Conseil national de recherches Canada

Canada

University of Connecticut

Outline

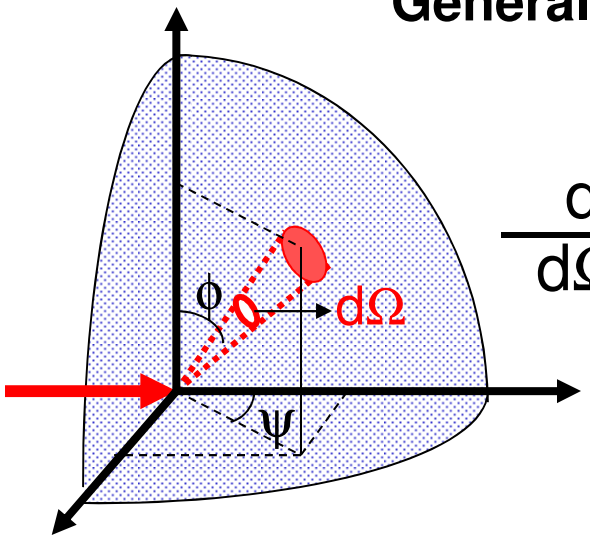
- Common Features of SANS
- Scattering Principle
- SANS Instrument & Data Reduction
- Contrast
- Dilute Particulate Systems – Form Factor
  - Data analysis
  - Examples
- Concentrated Particulate Systems – Structure Factor
  - Data analysis
  - Examples
- Dilute Polymer Solutions
  - Analysis for Gaussian Chain – Debye Function
  - More Generalized Analysis – Zimm Plot
- Small Angle Diffraction Analysis
- Model Independent Scaling Method Analysis
- Summary

Common Features & Advantages of SANS

1. The *Q* range of SANS : between 0.002 and 0.6 $Å^{-1}$
   – achievable with **long** wavelengths of neutrons and **low** detecting angles
2. A powerful technique for ***in-situ*** study on the ***global*** structures of ***isotropic*** samples
3. Easy to play contrast with isotope substitution
4. Data analysis:
   (A) Model dependent: well-defined particulate systems
   (possible non-unique solutions)
   (B) Model independent: general feature of the structure

Neutron Scattering Principle - I

General Equation



$$\frac{d^2\sigma}{d\Omega dE} = \frac{\text{The number of neutrons scattered per second into a solid angle } d\Omega \text{ with the final energy between E and E+dE}}{\text{neutron flux of the incident beam} \bullet d\Omega dE}$$

For Elastic Scattering

We do not analyze the energy but only count the number of the scattered neutrons

$$\frac{d\sigma}{d\Omega} = \int_0^\infty \frac{d^2\sigma}{d\Omega dE} dE = \frac{\text{The number of neutrons scattered per second into a solid angle } d\Omega}{\text{neutron flux of the incident beam} \bullet d\Omega}$$

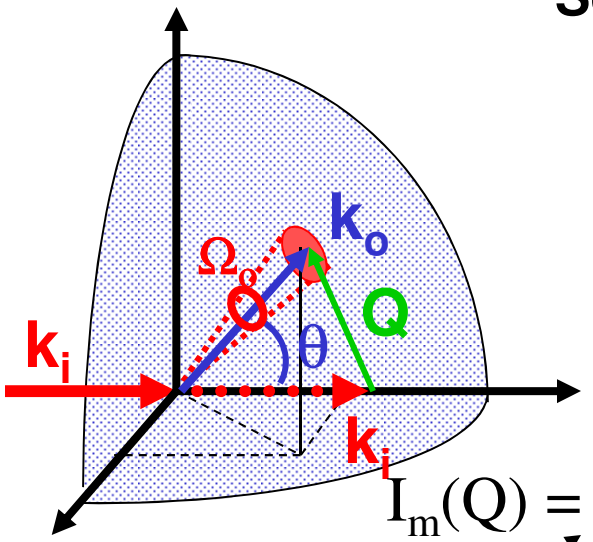
[time^{-1}]

[time^{-1}area^{-1}] **[area]**

Differential cross section

Neutron Scattering Principle - II

Scattering vector, Q



$$|\mathbf{Q}| = |\mathbf{k_o} - \mathbf{k_i}| = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

The measured intensity at Q (or θ), $I_m(Q)$ can be expressed as

$$I_m(Q) = I_F \cdot \Omega_o \cdot \varepsilon \cdot T \frac{d\sigma}{d\Omega} \rightarrow \left(\frac{d\sigma}{d\Omega}\right)_v \cdot A \cdot t$$

Beam area on the sample

Path length

Flux

Solid angle

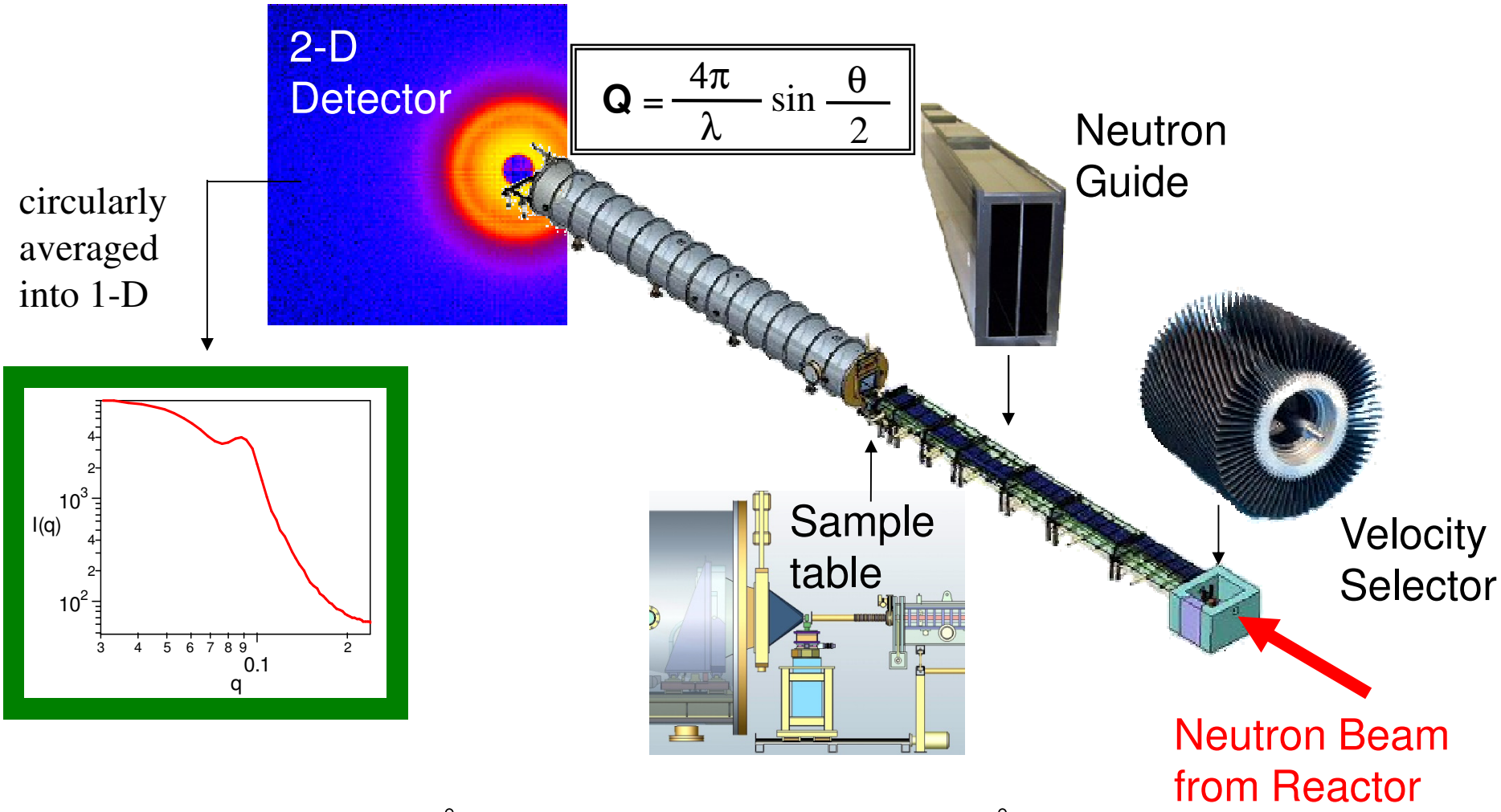
Detector efficiency

Sample transmission

Differential cross-section

$$\left(\frac{d\sigma}{d\Omega}\right)_{v,sam} = \left(\frac{d\sigma}{d\Omega}\right)_{v,std} \frac{I_{m,sam}(Q) \cdot A_{std} \cdot t_{std} \cdot T_{std}}{I_{m,std}(Q) \cdot A_{sam} \cdot t_{sam} \cdot T_{sam}}$$

Typical SANS Instrument



For $\lambda = 8$ Å and $\theta_{min} \sim 0.25^{o}$, $Q_{min} \sim 0.003$ Å^{-1}.
Max. attainable length scale = $2\pi/Q_{min} \sim 2000$ Å.

Current CNBC SANS Setup

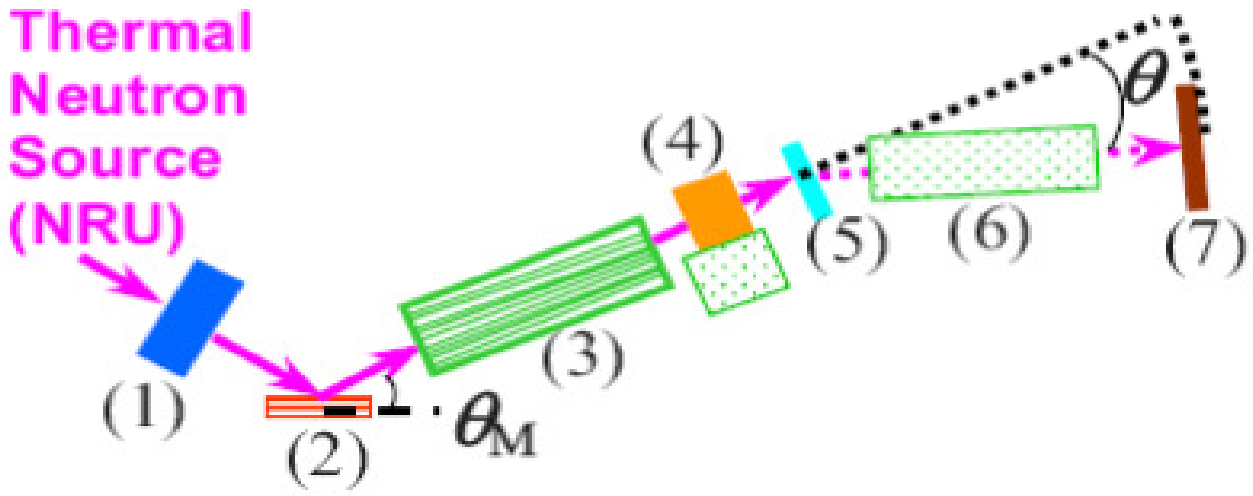


FIG. 1. (Color online) Schematic of the N5-SANS adapted from a triple-axis spectrometer to an instrument capable of SANS measurements. The components are as follows: (1) sapphire or Be filter. (2) Monochromator. (3) 23-channel CSC. (4) PG filter/21.6 cm long HSC/open. (5) Sample. (6) 48 cm long HSC. (7) 32-wire position sensitive detector.

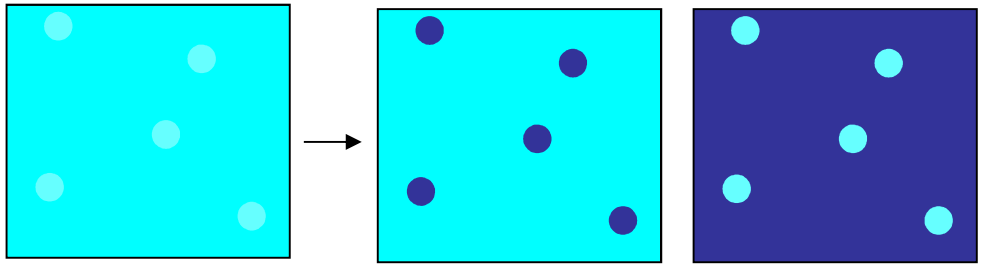
M.-P. Nieh Y. Yamani, N. Kučerka and J. Katsaras
Rev. Sci. Instrum. (**2008**) *79*, 095102

Q_{min} ~ 0.006 Å^{-1}: Max. attainable length = $2\pi/Q_{min}$ ~ 1000 Å.

University of Connecticut

Contrast – A Key Parameter

$$\left(\frac{d\sigma}{d\Omega}\right)_V = \frac{N}{V}\left(\rho_p - \rho_o\right)^2 V_p^2 P\left(\vec{Q}\right) S\left(\vec{Q}\right)$$



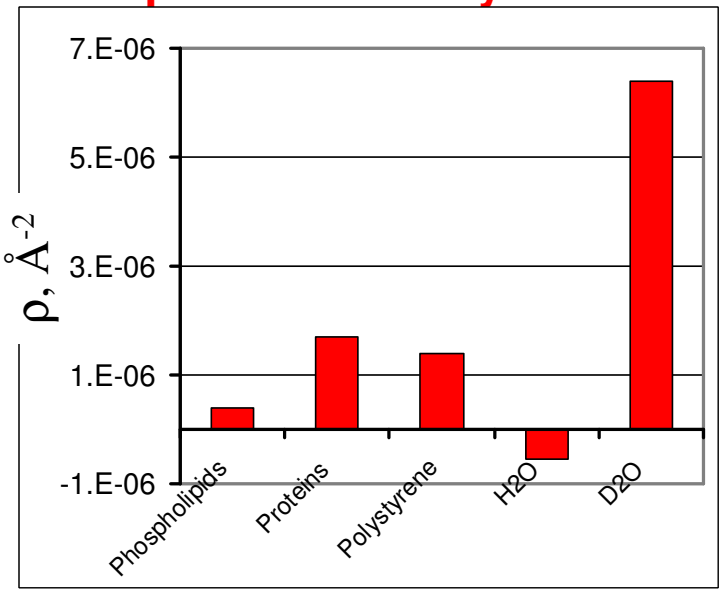
low contrast — 2 ways of increasing contrast

Scattering intensity is proportional to "the square of the scattering length density difference between studied materials and medium" (known as "contrast factor").

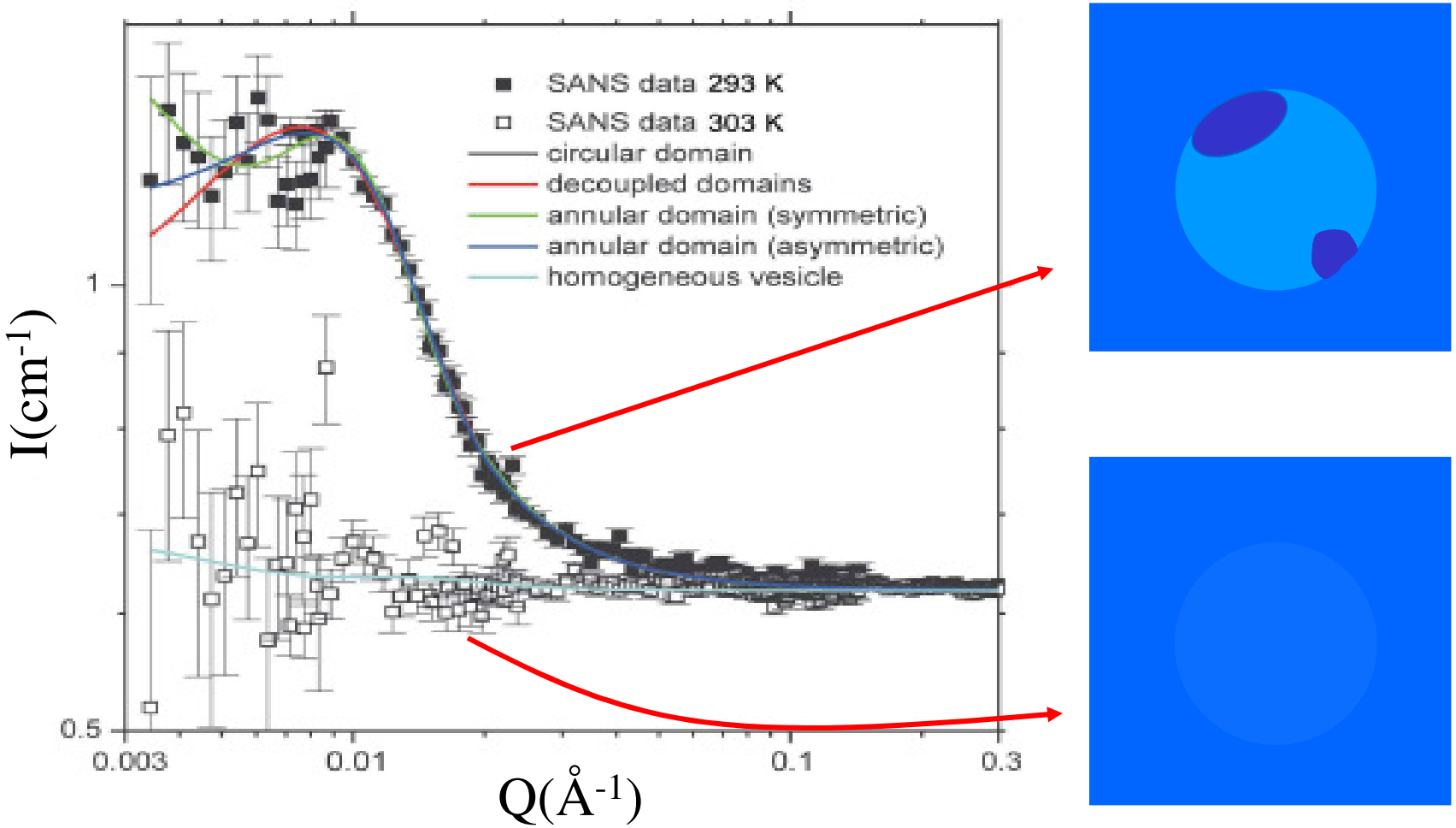
Ideally, we would like to increase the contrast yet without changing the chemical properties of the system. This is one of the greatest advantages using neutron scattering, since the neutron scattering lengths of isotopes can be very different.

Biomaterials

Atom	Nucleus	b_c (10^{-12} cm)	σ_c (10^{-24} cm^2)	σ_i (10^{-24} cm^2)	σ_{abs}* (10^{-24} cm^2)
Hydrogen	^{1}H	-0.374	1.76	79.7	0.33
Deuterium	^{2}H	0.667	5.59	2.01	0
Carbon	^{12}C	0.665	5.56	0	0
Nitrogen	^{14}N	0.930	11.1	0	1.88
Oxygen	^{16}O	0.580	4.23	0	0
Fluorine	^{19}F	0.556	4.03	0	0
Phosphorous	P†	0.513	3.31	0	0.17
Chlorine	Cl†	0.958	11.53	5.9	33.6



Contrast Variation



J. Pencer, V. N. P. Anghel, N. Kučerka and J. Katsaras,
***J. Appl Cryst* 40** (2007) 513-525

SANS Analysis – Dilute Particulate Systems

$$\left(\frac{d\sigma}{d\Omega}\right)_V = \frac{N}{V}(\rho_p - \rho_o)^2 V_p^2 P(\vec{Q}) S(\vec{Q})$$

orientational average

$$\left(\frac{d\sigma}{d\Omega}\right)_v = \frac{N}{V}\iint \rho(\vec{r}_1)\rho(\vec{r}_2) \langle e^{-i\vec{Q}\cdot(\vec{r}_1 - \vec{r}_2)} \rangle \, d\vec{r}_1 d\vec{r}_2$$

$$= \frac{N}{V}\left|\int_{V_p} \Delta\rho(\vec{r}) \cdot \langle e^{-i\vec{Q}\cdot\vec{r}} \rangle \, d\vec{r}\right|^2$$

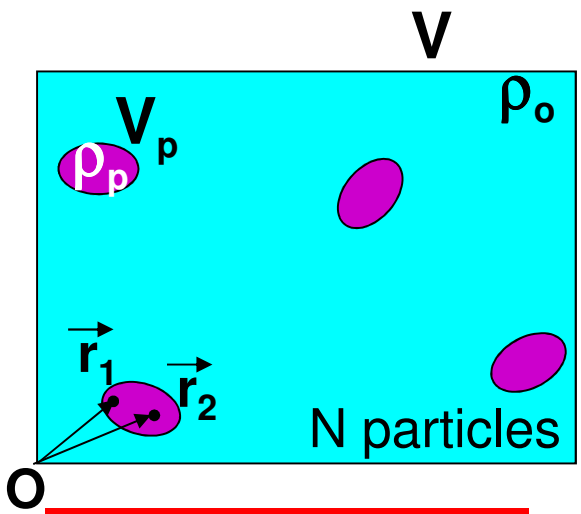
$$= \frac{N}{V}(\rho_p - \rho_o)^2 \cdot V_p^2 \cdot P(\vec{Q})$$

Particle Form Factor

$$= \frac{(\rho_p - \rho_o)^2 N}{V} \sum_{k=1}^{} |A_k(\vec{Q})|^2$$

Amplitude of the Form Factor

$$A_k(\vec{Q}) = \int_{\text{particle k}} \langle e^{-i\vec{Q}\cdot\vec{r}} \rangle \, d\vec{r}$$



$\vec{r}_1$ and $\vec{r}_2$ are vectors of scattering center from **one particle**

The form factor is determined by the structure of the particle.

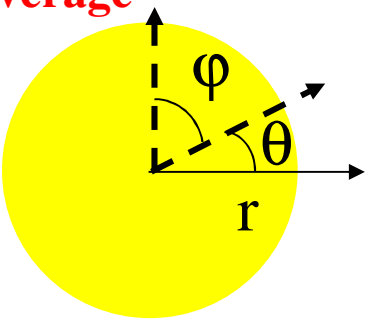
SANS Analysis – Dilute Particulate Systems

Simulation of a particular system - Spheres

$$P(q) = \frac{1}{V_{sphere}^2}\left|\iiint_{V_{sphere}} e^{-i\vec{Q}\cdot\vec{r}}\,d\vec{r}\right|^2$$

Since spheres are isotropic, there is no need to do orientational average

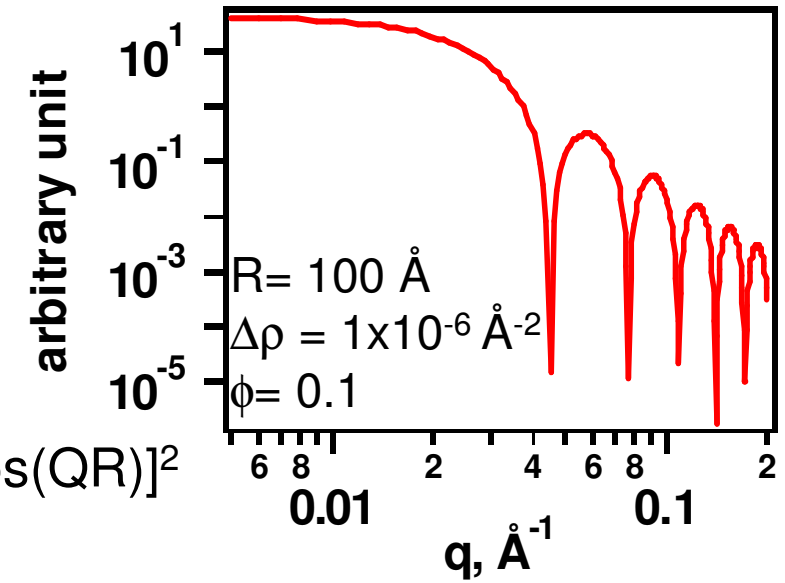
$$= \frac{1}{V_{sphere}^2}\left|\int_{r=0}^{r=R}\int_{\theta=0}^{\theta=\pi}\int_{\varphi=0}^{\varphi=2\pi} e^{-iQr\cdot\cos\theta}\, r^2 \sin\theta\, d\varphi\, d\theta\, dr\right|^2$$



$$= \frac{9}{(QR)^6}[\sin(QR) - qR\cdot\cos(QR)]^2$$

$$\left(\frac{d\sigma}{d\Omega}\right)_v = \frac{N}{V}(\rho_{sphere} - \rho_o)^2 \cdot V_{sphere}^2 \cdot P(\vec{Q})$$

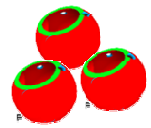
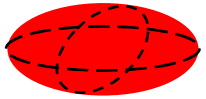
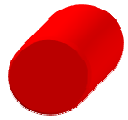
$$= \phi_{sphere} V_{sphere} \Delta\rho^2 \frac{9}{(QR)^6}[\sin(QR) - QR\cdot\cos(QR)]^2$$



University of Connecticut

SANS Analysis – Dilute Particulate Systems

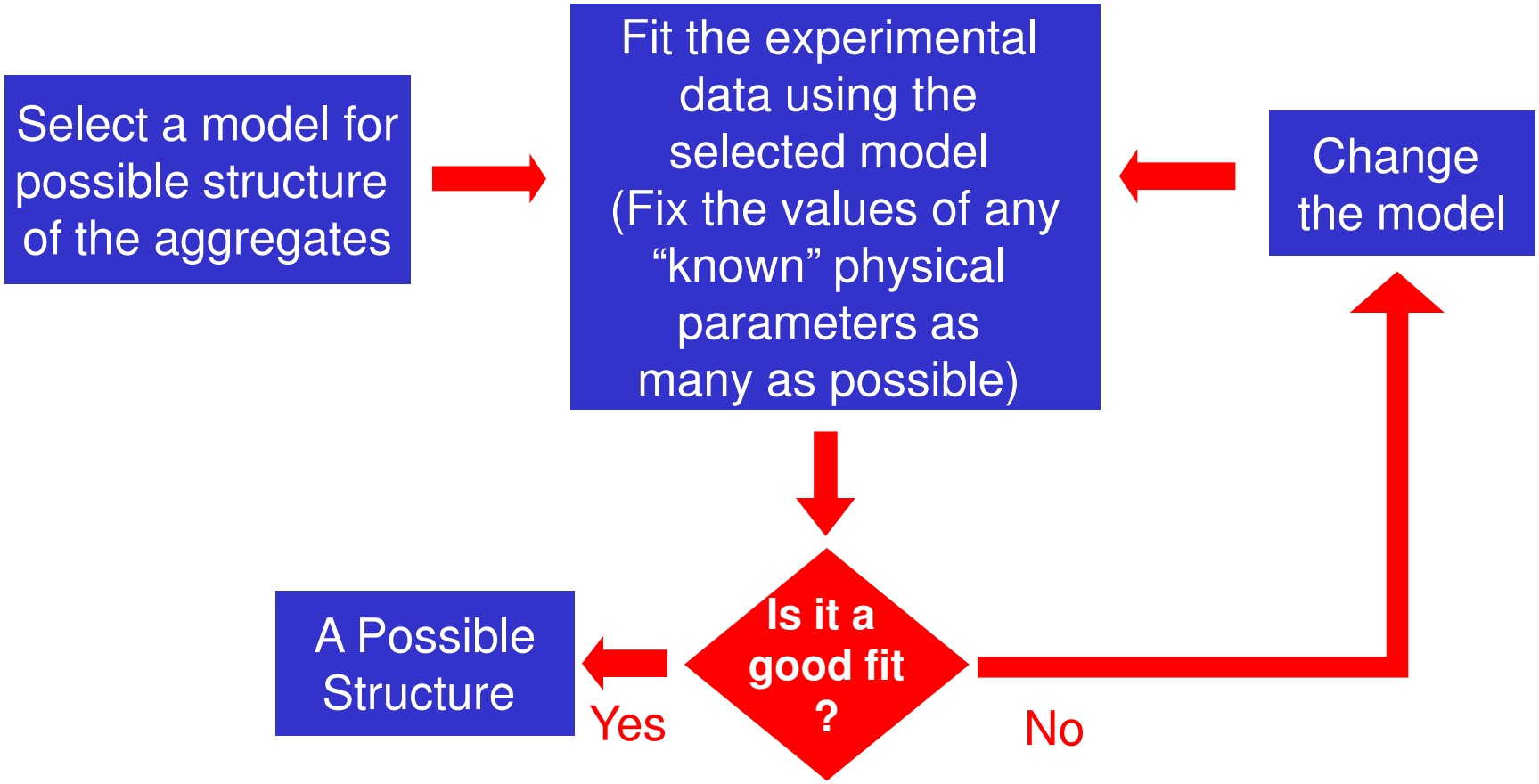
Common form factors of particulate systems

Morphologies	P(Q)	Morphologies
Spheres (radius :R)	$\frac{9}{(QR)^6}[\sin(QR) - QR\cdot\cos(QR)]^2 = A_{sph}^2(QR)$	
Spherical shells (outer radius: R_1 inner radius: R_2)	$\frac{[R_1^3\cdot A_{sph}(QR_1) - R_2^3\cdot A_{sph}(QR_2)]^2}{(R_1^3 - R_2^3)^2}$	
Triaxial ellipsoids (semiaxes: a,b,c)	$\int_0^1\int_0^1 A_{sph}^2[Q\sqrt{a^2\cos^2(\pi x/2) + b^2\sin^2(\pi x/2)(1-y^2)_1 + c^2y^2}\,]\,dx\,dy$	
Cylinders (radius: R length: L)	$4\int_0^1 \frac{J_1^2[QR\sqrt{1-x^2}\,]}{[QR\sqrt{1-x^2}\,]^2}\,\frac{\sin^2(QLx/2)}{(QLx/2)^2}\,dx$	
	$J_1(x)$ is the first kind Bessel function of order 1	
Thin disk (radius: R)	By setting L = 0 $\quad \frac{2 - J_1(2QR)/QR}{Q^2R^2}$	
Long rod (length: L)	By setting R = 0 $\quad \frac{2}{QL}\int_0^{QL}\frac{\sin(t)}{t}\,dt - \frac{\sin^2(QL/2)}{(QL/2)^2}$	

"Structure Analysis by Small Angle X-Ray and Neutron Scattering" L. A. Feigen and D. I. Svergun

SANS Analysis – Dilute Particulate Systems

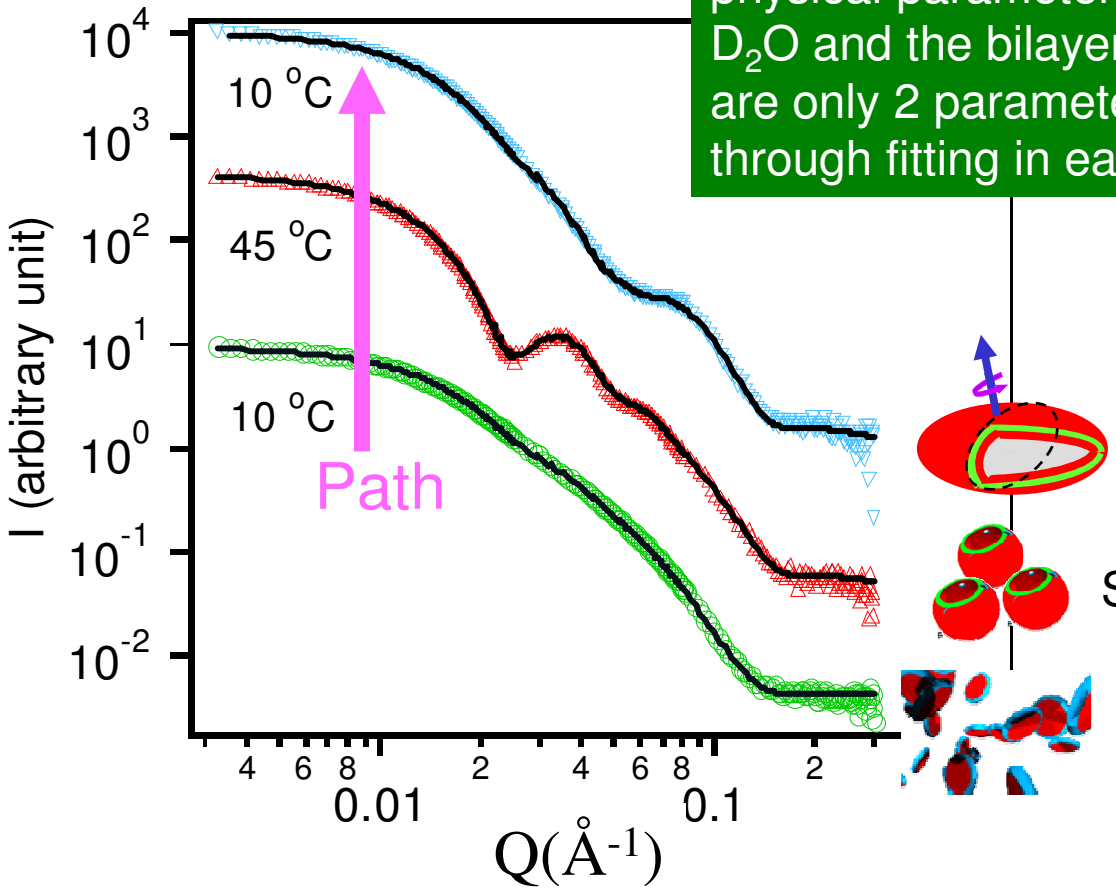
Procedure of Data Analysis



Examples of A Dilute Particulate System

Sample: A mixture of dimyristoyl and dihexanoyl phosphatidylcholine (DMPC, DHPC), and dimyristoyl phosphatidylglycerol (DMPG) in D_2O;
total lipid conc. = 0.1 wt.%

In these cases, the known (or constrained) physical parameters are SLDs of lipid and D_2O and the bilayer thickness. Thus, there are only 2 parameters to be determined through fitting in each case.



Oblate shells: a=180 Å, b=62 Å

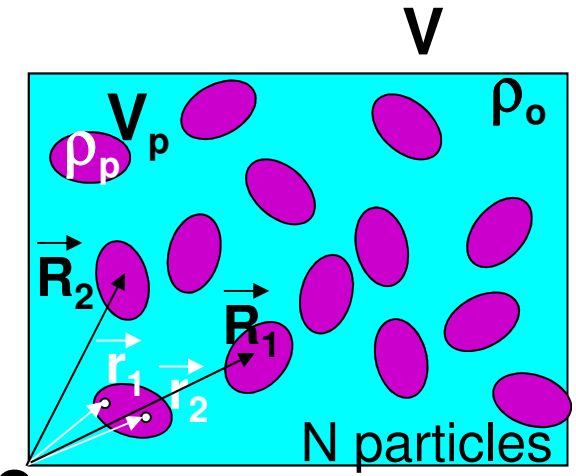
Spherical shells: R=133 Å, p= 0.15

Bilayer disks: R=156 Å, L= 45 Å

SANS Analysis –Concentrated Particulate Systems

$$\left(\frac{d\sigma}{d\Omega}\right)_V = \frac{N}{V}(\rho_p - \rho_o)^2 V_p^2 P(\vec{Q}) S(\vec{Q})$$

$$\left(\frac{d\sigma}{d\Omega}\right)_v = \frac{N}{V}\iint \rho(\vec{r}_1)\rho(\vec{r}_2) \langle e^{-i\vec{Q}\cdot(\vec{r}_1 - \vec{r}_2)} \rangle d\vec{r}_1 d\vec{r}_2$$



$$= \frac{1}{V}\sum_{k=1}^{N} \langle |A_k(\vec{Q})|^2 \rangle + \frac{1}{V}\left\langle \sum_{k=1}^{N}\sum_{j\neq k}^{N} A_k(\vec{Q}) A_j^*(\vec{Q}) e^{-i\vec{Q}\cdot(\vec{R}_k - \vec{R}_j)} \right\rangle_O$$

$$\sim \frac{1}{V}\sum_{k=1}^{N} \langle |A_k(\vec{Q})|^2 \rangle \{1 + \sum_{j\neq k}^{N} \langle e^{-i\vec{Q}\cdot(\vec{R}_k - \vec{R}_j)} \rangle\}$$

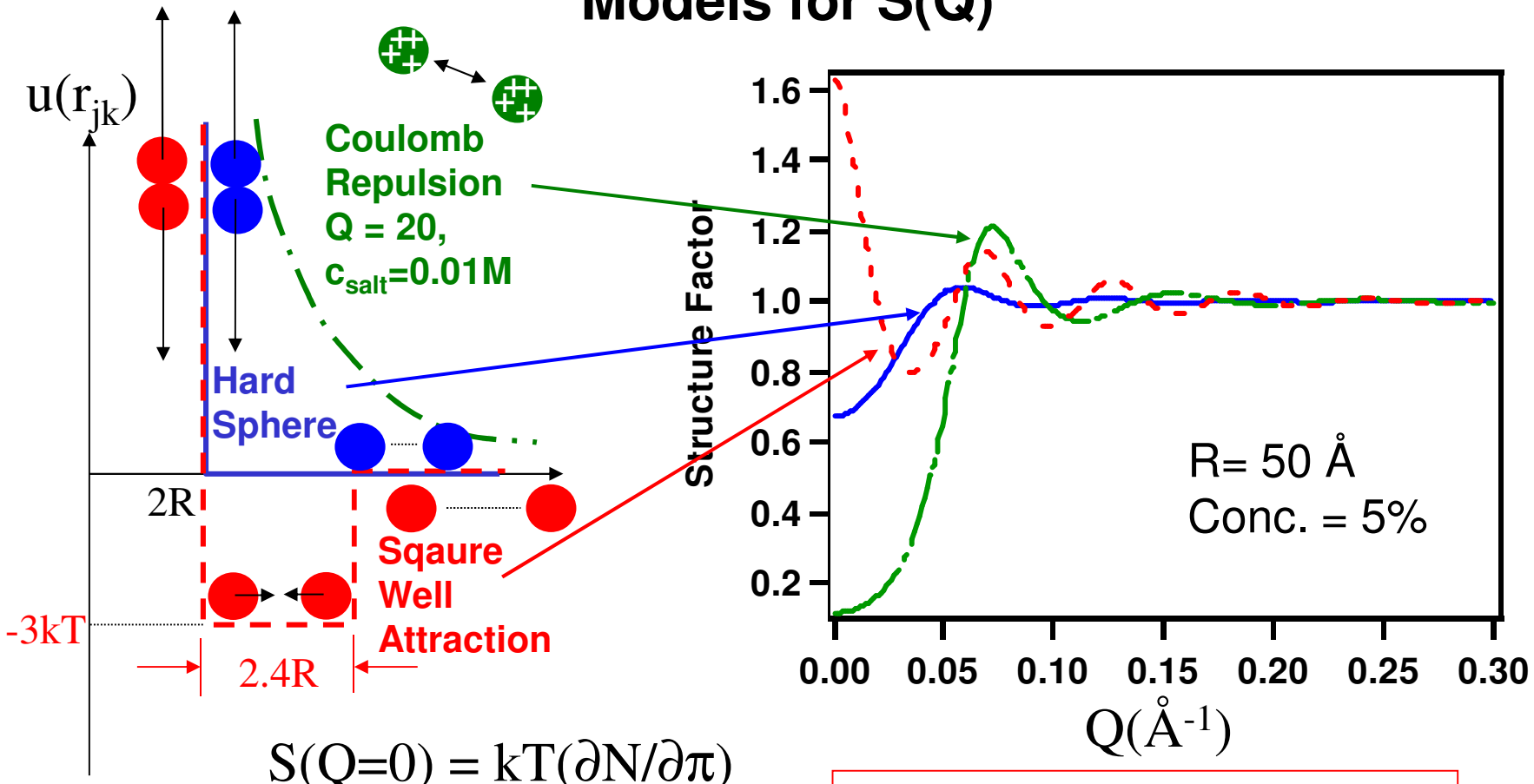
Structure Factor

$$= \frac{N}{V}(\rho_p - \rho_o)^2 \cdot V_p^2 \cdot P(\vec{Q})\, S(\vec{Q})$$

In dilute solution, $S(\vec{Q}) = 1$

SANS Analysis –Concentrated Particulate Systems

Models for S(Q)



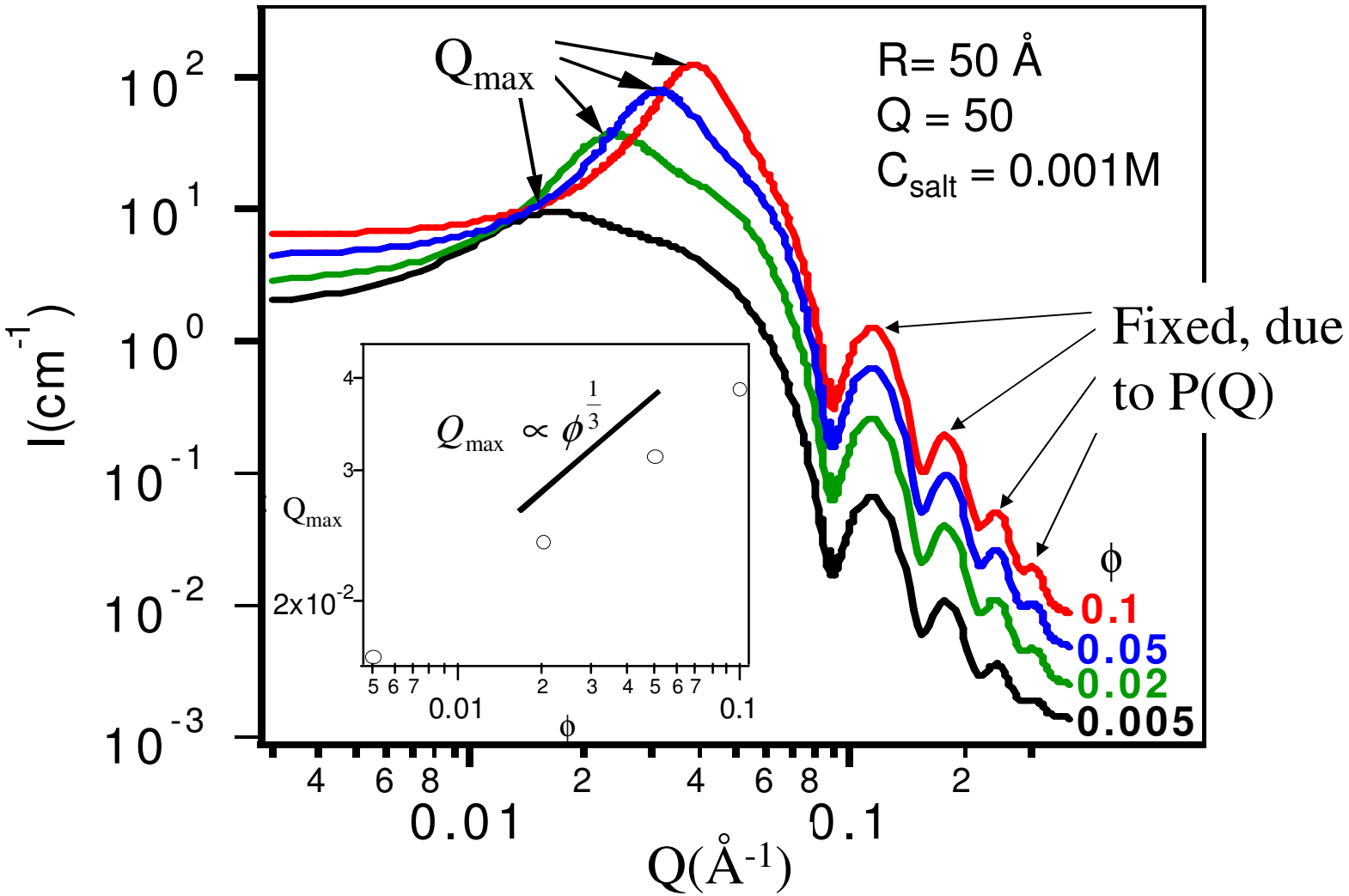
$$S(Q=0) = kT(\partial N/\partial \pi)$$

Osmotic compressibility →

S(0)>1 more compressible
S(0)<1 less compressible

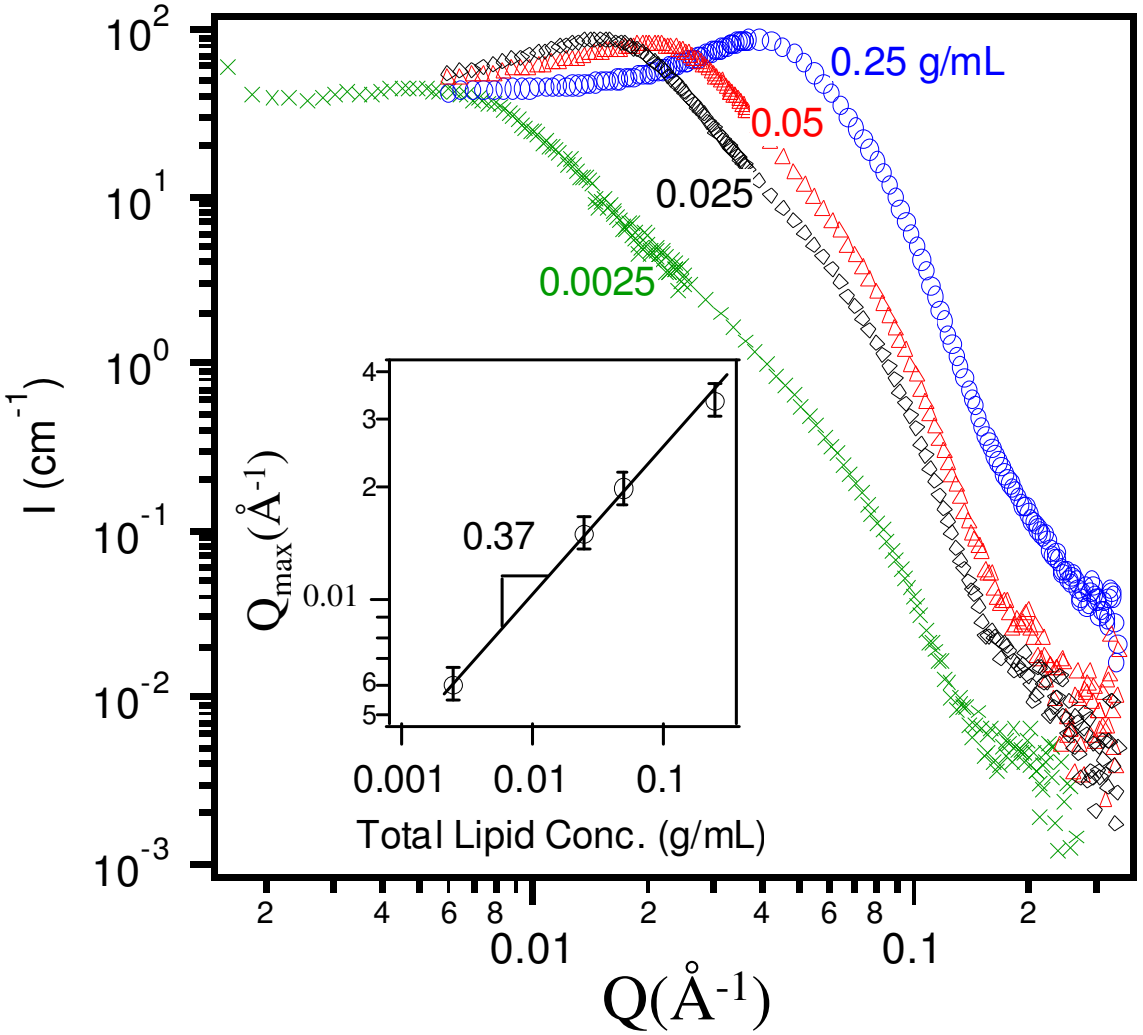
SANS Analysis –Concentrated Particulate Systems

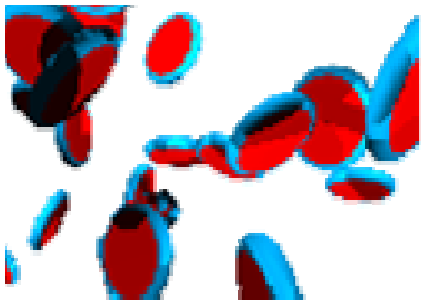
Simulation Result using Coulomb Repulsive Model



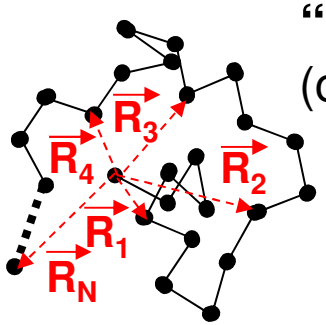
SANS Analysis –Concentrated Particulate Systems

"Bicelles" composed of DMPC/DHPC and small amount of Tm^{3+}





Gaussian Chain



"Gaussian Chain" Model : The effective bond length, a, of one step (composed of several segments of the chain) has a Gaussian distribution.

$$a^2 = \sum_{n=1}^{N} \frac{\left|\vec{R}_n - \vec{R}_{n-1}\right|^2}{N}$$

The distribution vector between any two "steps" m, n, i.e., ($\vec{\mathbf{R}}_n$ - $\vec{\mathbf{R}}_m$) is Gaussian

$$\Phi(\vec{\mathbf{R}}_n - \vec{\mathbf{R}}_m, n\text{-}m) = \left[\frac{3}{2\pi a^2 |n\text{-}m|}\right]^{3/2} \exp\left[-\frac{3(\vec{\mathbf{R}}_n - \vec{\mathbf{R}}_m)^2}{2a^2|n\text{-}m|}\right]$$

This model is adequate for describing long polymer chains in a theta solvent, where the segment-segment and segment-solvent interaction and the excluded volume effect are canceled out. Such polymer chains are also known as "phantom" chains.

"The Theory of Polymer Dynamics" M. Doi and S. F. Edwards (1992)

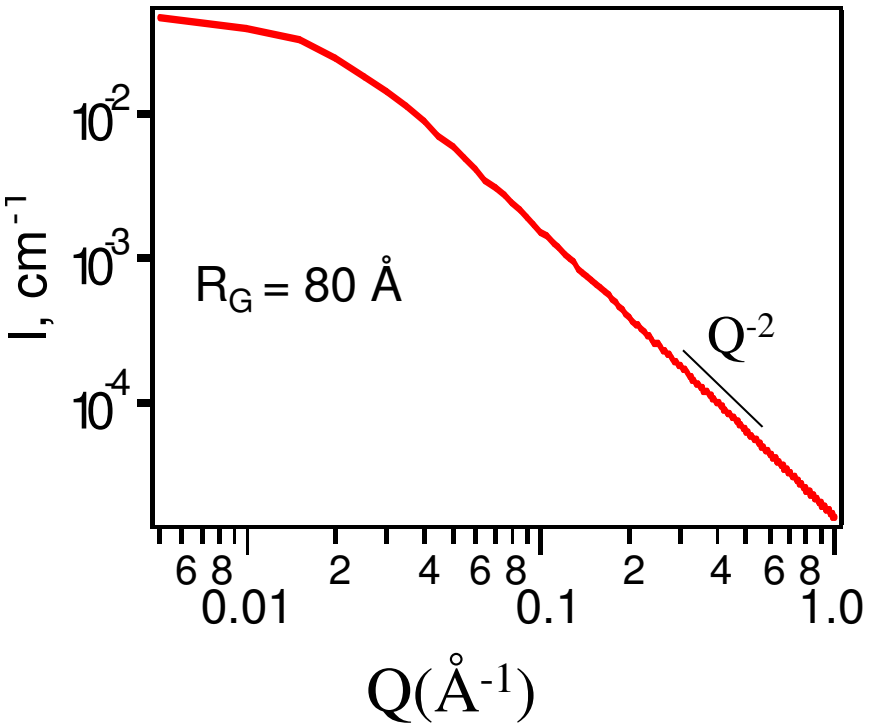
SANS Analysis – Dilute "Gaussian Chain" Solutions

The scattering from a Gaussian Chain can be described as a Debye function

$$\left(\frac{d\sigma}{d\Omega}\right)_v = N_p \phi_p (\rho_p - \rho_o)^2 V_M \boxed{\frac{2}{Q^4 R_G^4}\left(e^{-Q^2 R_G^2} - 1 + Q^2 R_G^2\right)}$$

Debye Function

V_M: molecular volume of monomer
N_p : degree of polymerization

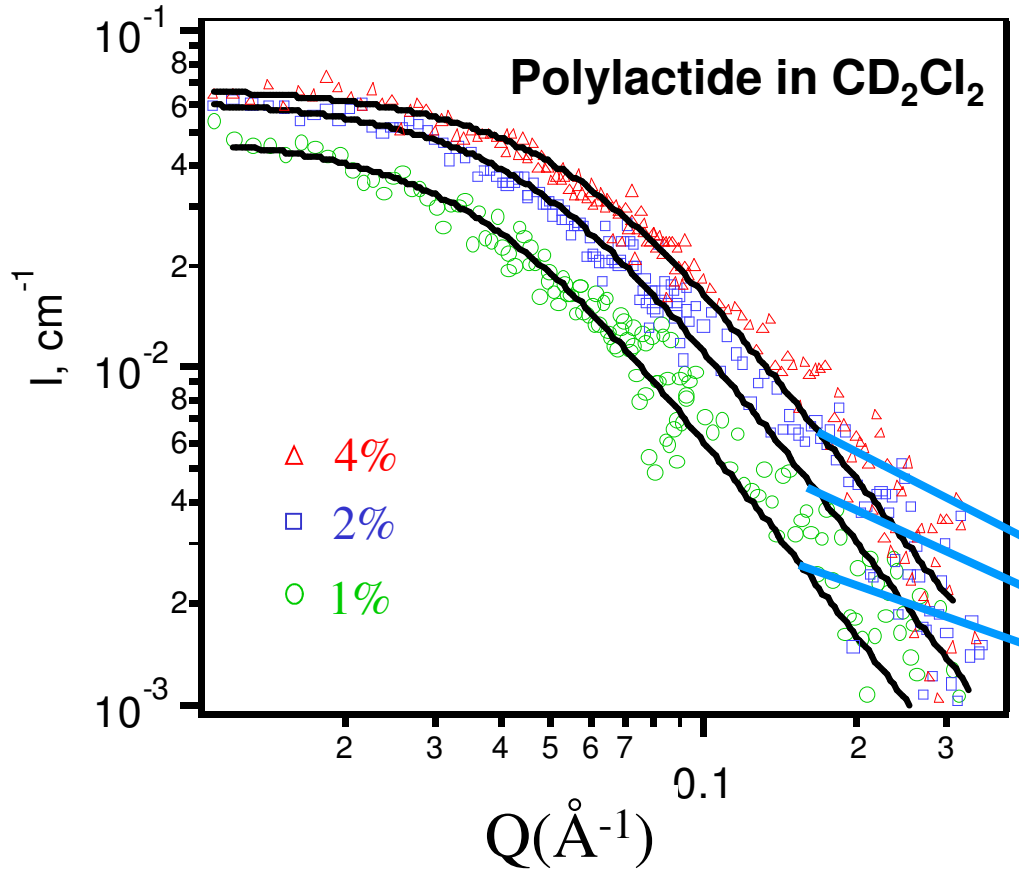


Radius of Gyration, $R_G^2 = \frac{1}{2N^2}\sum_{m,n} \langle (R_n - R_m)^2 \rangle$

Example – Polymer Solutions

Debye function is not always adequate to describe the polymer conformation!

An example is that as polymers are in a good solvent, the intensity at high Q regime will decay with $Q^{-5/3}$ instead of Q^{-2}.



ϕ_p	N_p	R_G (Å)
1%	111	39
2%	74	32
4%	42	27

deviation from the data!

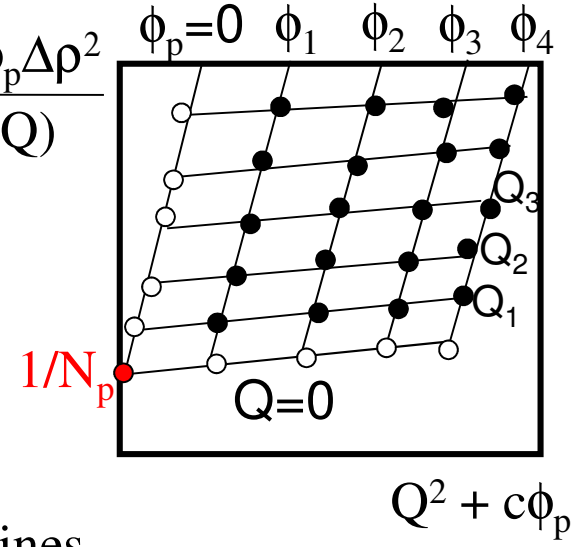
University of Connecticut

Zimm Plot

For dilute polymer solutions, the scattering intensity at low q regime (i.e., $q \cdot R_G < 1$) can be expressed as a function of R_G, M_W (molecular weight), A_2 (second virial coefficient) and ϕ_p (volume fraction of the polymer)

$$\frac{V_m \phi_p \Delta\rho^2}{I(Q)} = (1 + Q^2 R_G^2/3 + \ldots)\left(\frac{1}{N_p} + 2\phi_p A_2 + \ldots\right)$$

V_m is the molecular volume of the monomer
N_p is the degree of polymerization



R_G, N_p and A_2 can be obtained by Zimm plot, where $\frac{V_m \phi_p \Delta\rho^2}{I(Q)}$ is plotted against $(Q^2 + c\phi_p)$ and two extrapolation lines for Q=0 and ϕ_p=0 are also obtained (c is an arbitrary number.).

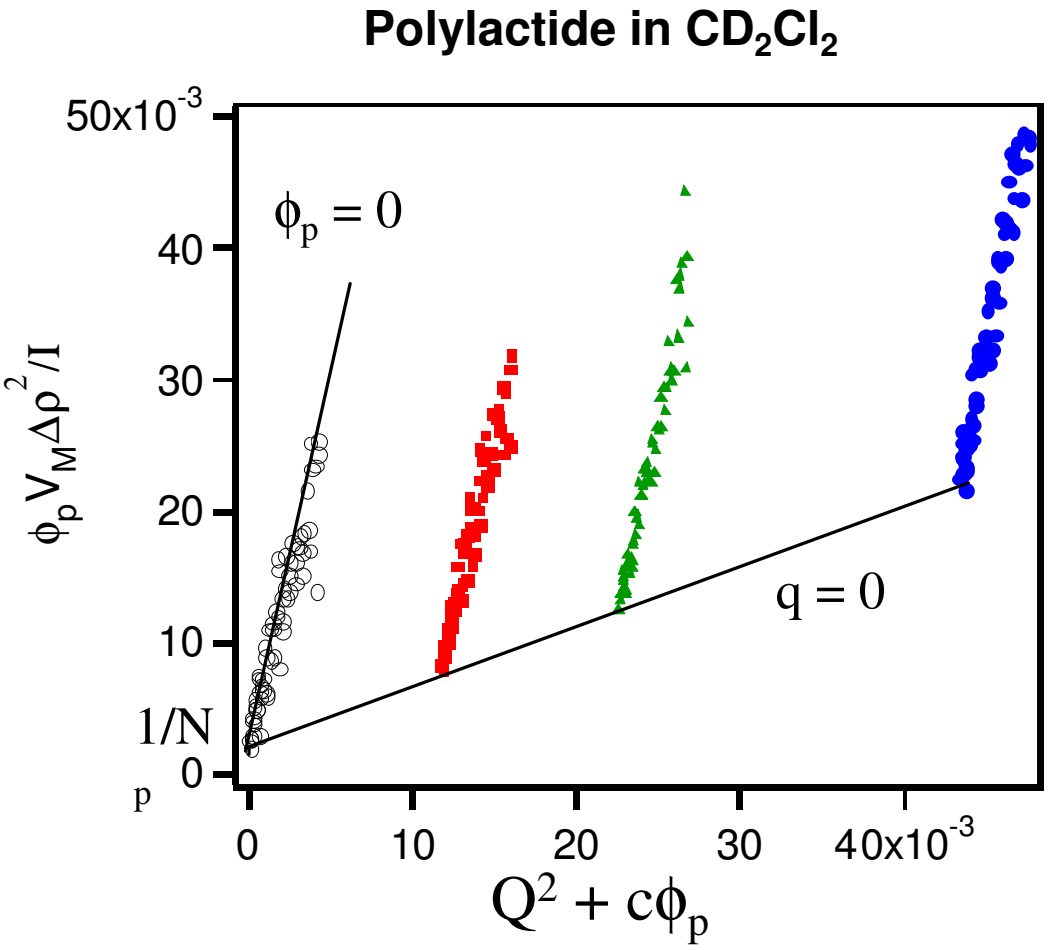
The slope of the extrapolation line for $\phi_p = 0$ is $R_G^2/3N_p$.

The slope of the extrapolation line for $Q = 0$ is $2A_2/c$.

The intercept of both extrapolation lines is $1/N_p$.

University of Connecticut

Application of Zimm Plot



$N_p = 387$
$R_G = 79$ Å
$A_2 = 88.6$

Compared to the result obtained from Debye fitting

ϕ_p	N_p	R_G (Å)
1%	111	39
2%	74	32
4%	42	27

It requires at least two concentrations to make up a Zimm plot.

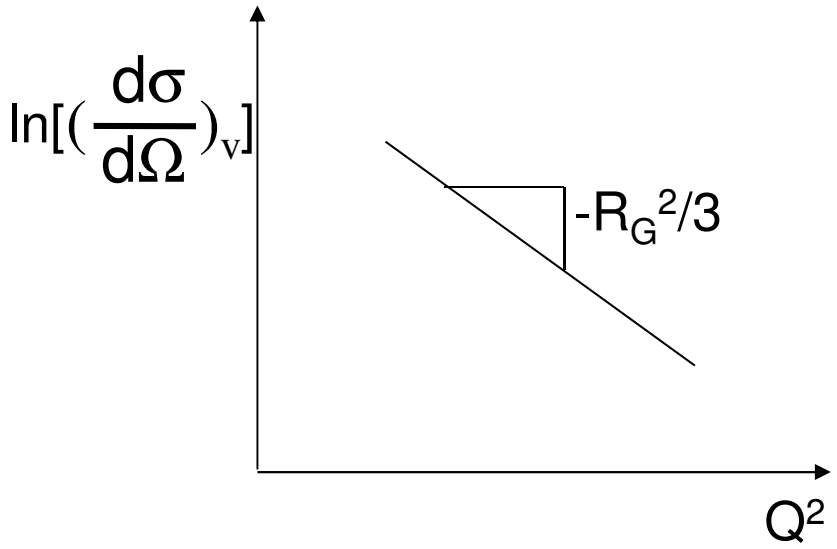
SANS Analysis – Model Independent Scaling Method

Guinier regime – low-Q scattering

$$\left(\frac{d\sigma}{d\Omega}\right)_v = \frac{N}{V}(\rho_p - \rho_o)^2 \cdot V_p^2 \cdot [1 - (QR_G)^2/3 + \ldots]$$

$$\sim \phi_p(\rho_p - \rho_o)^2 V_p e^{-Q^2R_G^2/3}$$

$$\ln\left[\left(\frac{d\sigma}{d\Omega}\right)_v\right] = \ln(I_o) - Q^2R_G^2/3$$



"Polymers and Neutron Scattering" J. S. Higgins and H. C. Benoit

SANS Analysis – Model Independent Scaling Method

Porod regime – high-Q (with respect to the length scale) scattering

The form factor of a sphere (radius of R)

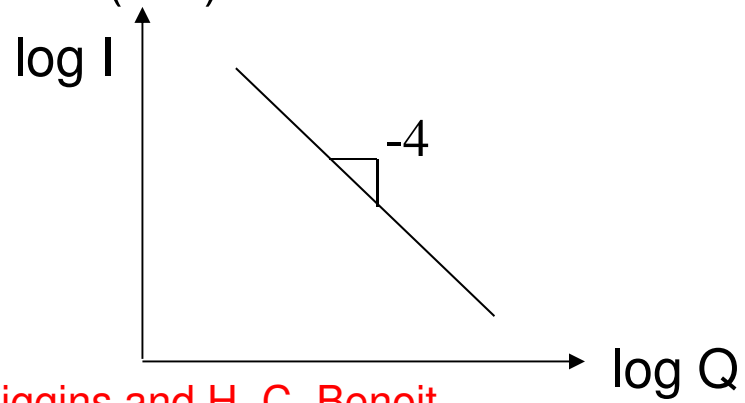
$$\left(\frac{d\sigma}{d\Omega}\right)_v = \phi_{sphere} V_{sphere} \Delta\rho^2 \frac{9}{(QR)^6} [\sin(QR) - QR\cdot\cos(QR)]^2$$

For QR>>1, i.e, focusing at smooth interface between two bulks 3-dimensionally

$$\left(\frac{d\sigma}{d\Omega}\right)_v \sim \frac{N_{sphere} V_{sphere}^2 \Delta\rho^2}{V} \frac{9}{2(QR)^4} = \frac{2\pi\Delta\rho^2 S_T}{VQ^4}$$

S_T → total surface area

$$Q^4\left(\frac{d\sigma}{d\Omega}\right)_v = \frac{2\pi\Delta\rho^2 S_T}{V}$$



"Polymers and Neutron Scattering" J. S. Higgins and H. C. Benoit

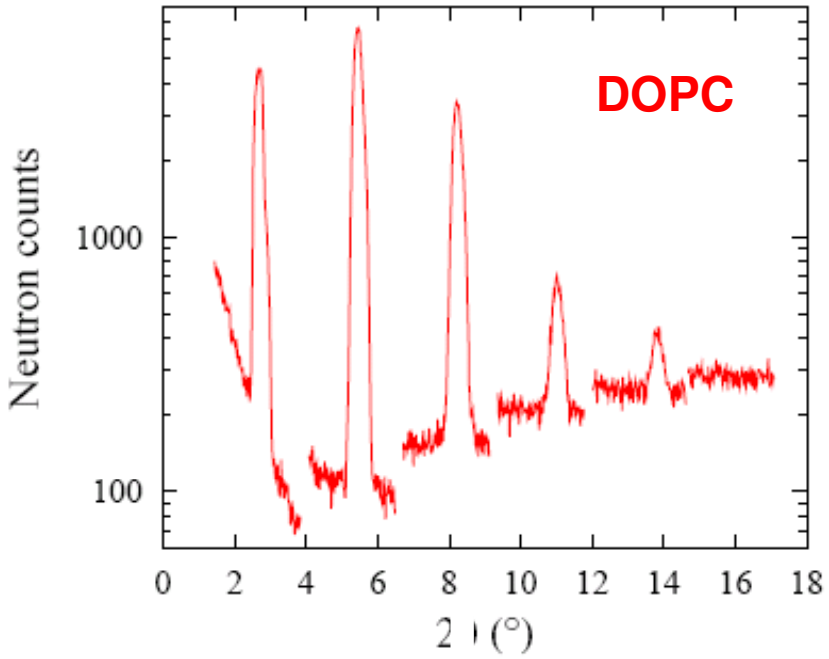
SANS Analysis – Model Independent Scaling Method

If $I_m(Q)$ scales with Q^{-n} over a wide range of Q. The "possible" structure can be obtained with some knowledge of the systems.

particles	n
•Long Rigid rod	1
•Smooth 2-D Objects	2
•Linear Gaussian Chain	2
•Chain with Excluded Volume	5/3
•Interfacial Scattering from 3-D Objects	
with Smooth Surface (Porod regime)	4
with fractal Surface	3 ~ 4

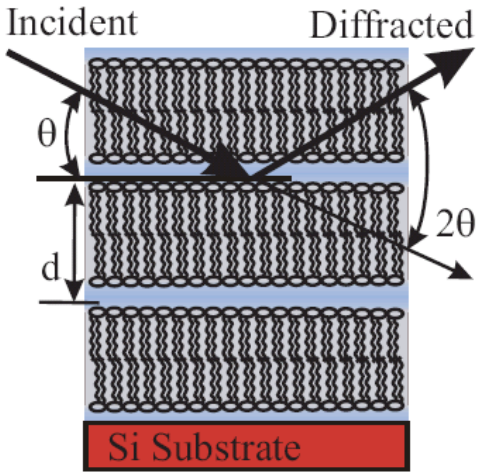
"Polymers and Neutron Scattering" J. S. Higgins and H. C. Benoit

Small Angle Diffraction

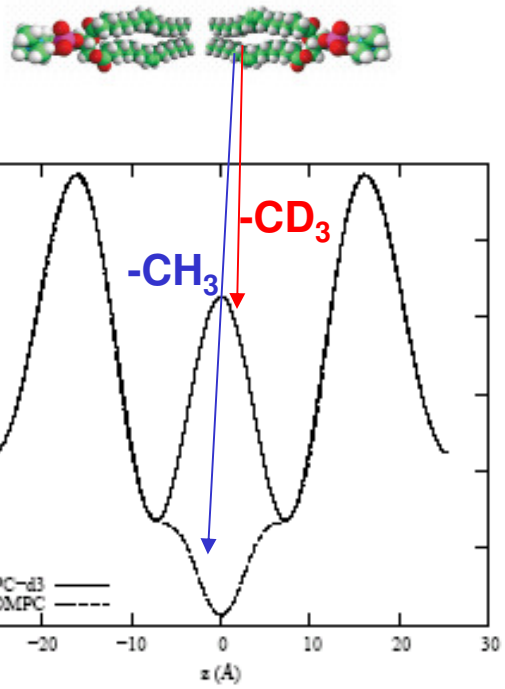


$$h\frac{Q}{2\pi} = \frac{h}{d} = \frac{2h\sin\left(\theta/2\right)}{\lambda}$$

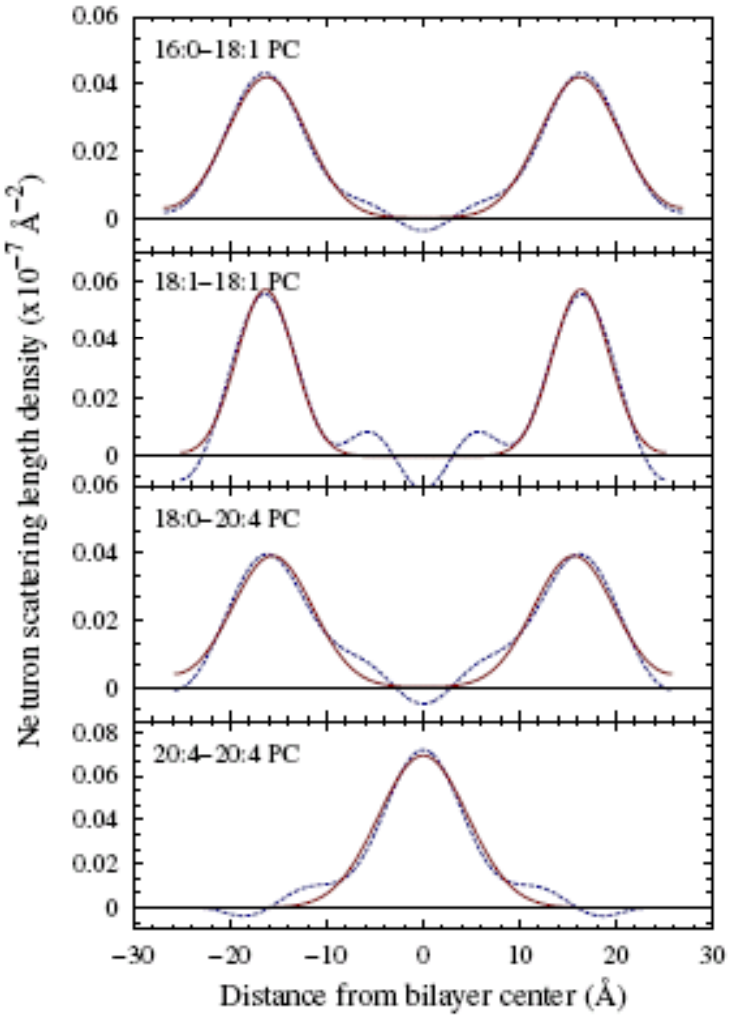
$$I \propto \left|F(Q)\right|^2 = \left|\sum b_i e^{-iQ\cdot z_i}\right|^2$$

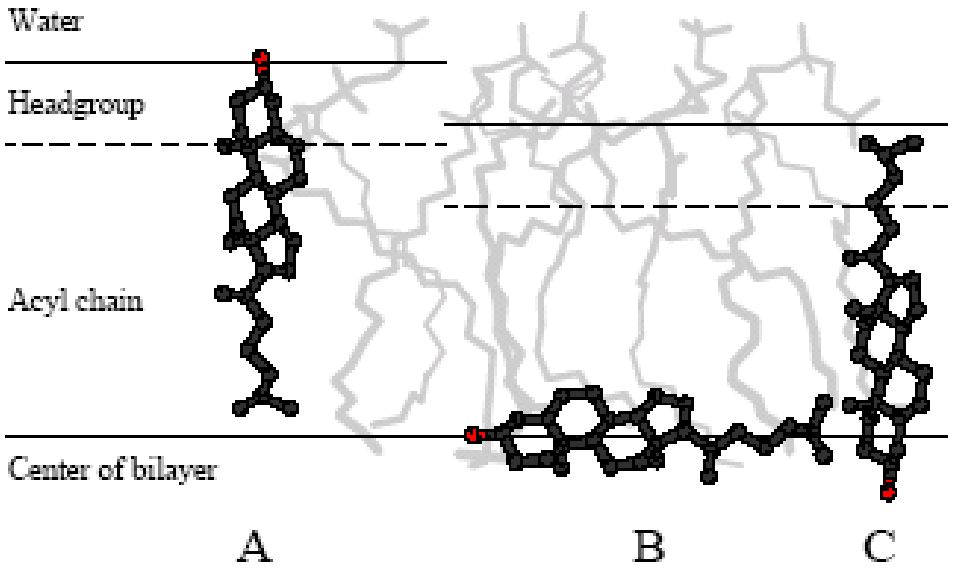


$$\rho(z) = \rho_0 + \sum_{h=1}^{h_{max}} F_h \cos(2\pi h z/d)$$



Example: Orientation of Cholesterol in Biomembrane





Harroun, T. A. et al. ***Biochemistry*** 45 (**2006**) 1227-1233.

Take Home Messages

• SANS is a powerful tool to study the **global structures** of isotropic systems in the length scales ranging from 10 to 1000 Å.

• It is easy to vary the contrast in a neutron scattering experiment without significantly changing the chemical properties of the systems.

• The scattering function is proportional to the product of **contrast factor**, **form factor** (intraparticle scattering function) and **structure factor** (interparticle interaction).

• Structural parameters can be obtained through model dependent approaches, while model independent scaling law can also reveal possible morphology of the studied system.