SANS and USANS

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1) Modified from Lecture from the NCNR Summer School on
Neutron Small Angle Scattering and Reflectometry from Submicron Structures
2) AONSA Summer School on Neutron small angle scattering and reflectometry
August 18 – 22, 2008

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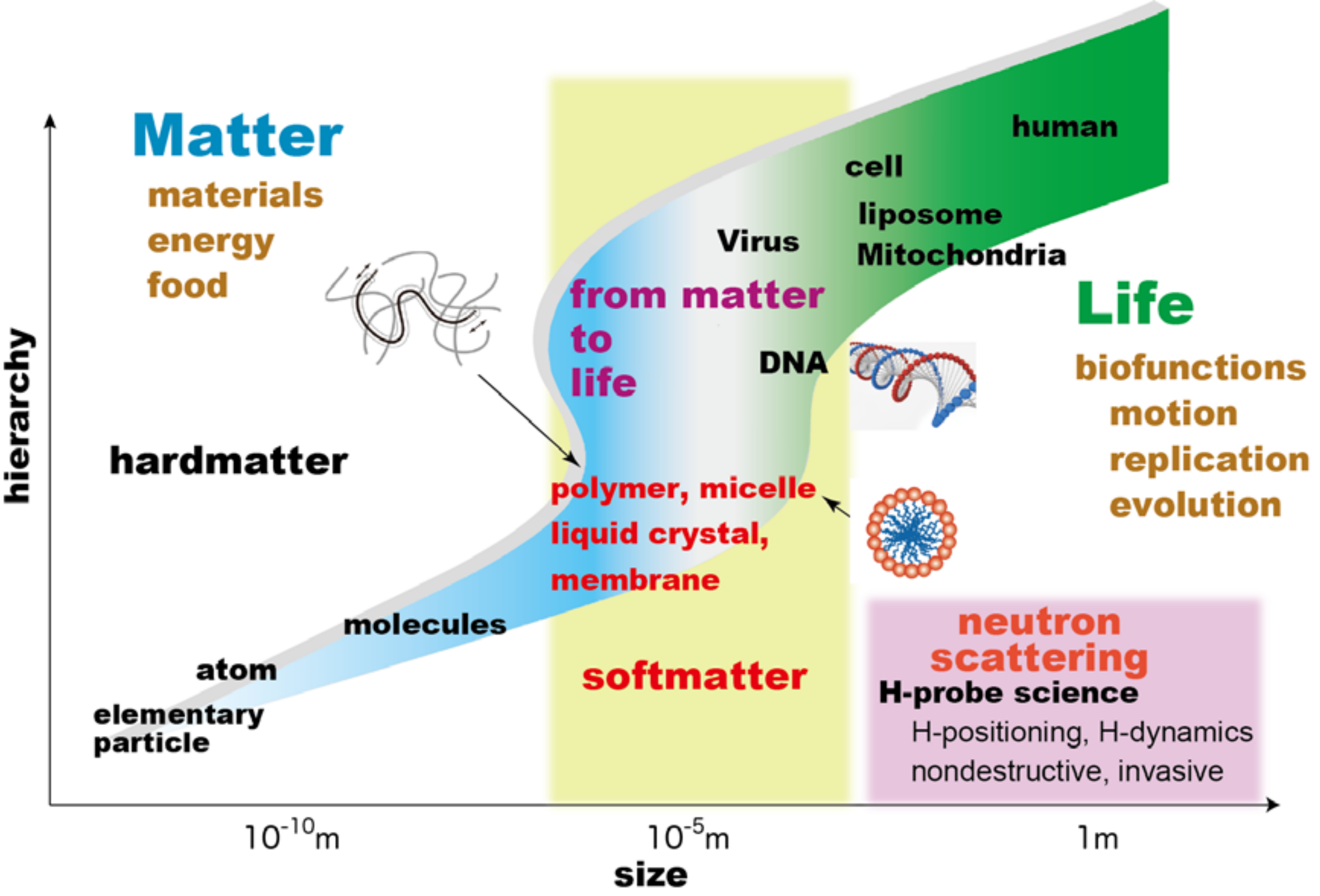
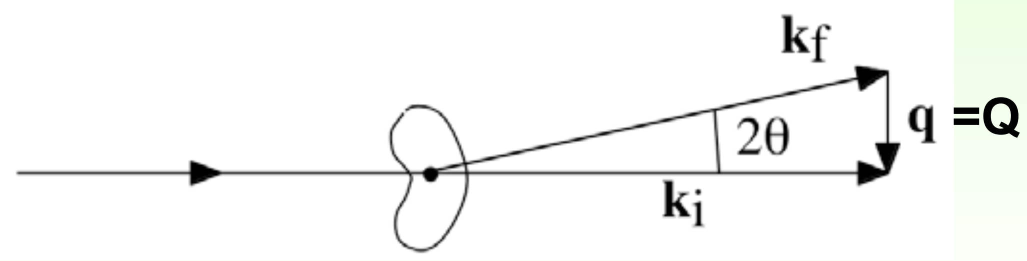
Size-hierarchy relationship of matter



M. Shibayama, in Neutron Scattering Applications in Chemistry, Materials Science and Biology, Fernandez-Alonso, F. and Price, D. L. Eds., Academic Press, 2017

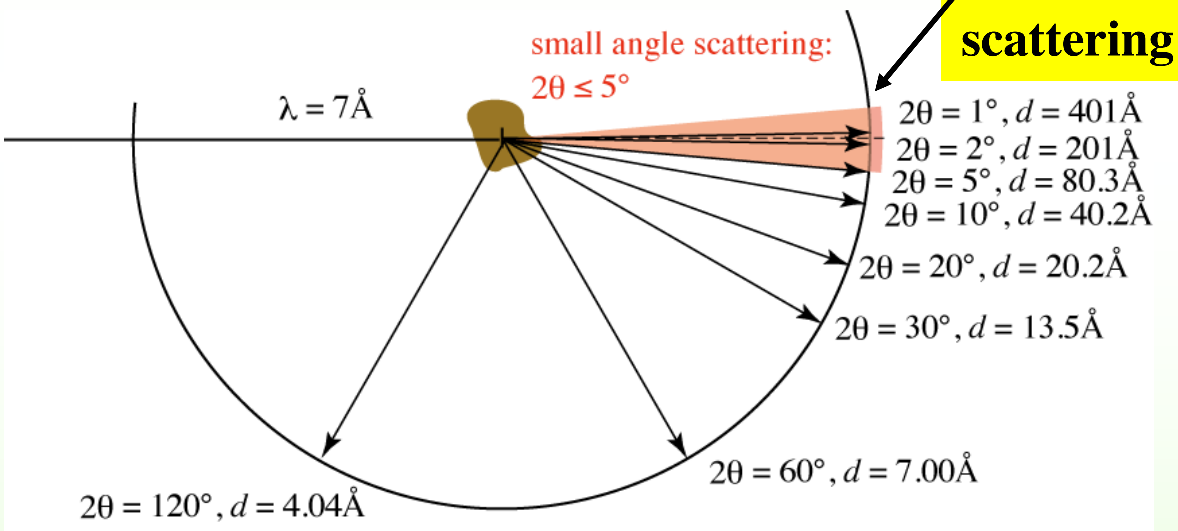
What is small-angle scattering?



- Constructive interference from structures in the direction of q

Nanometer Scale science

- Diffraction length scale



scattering

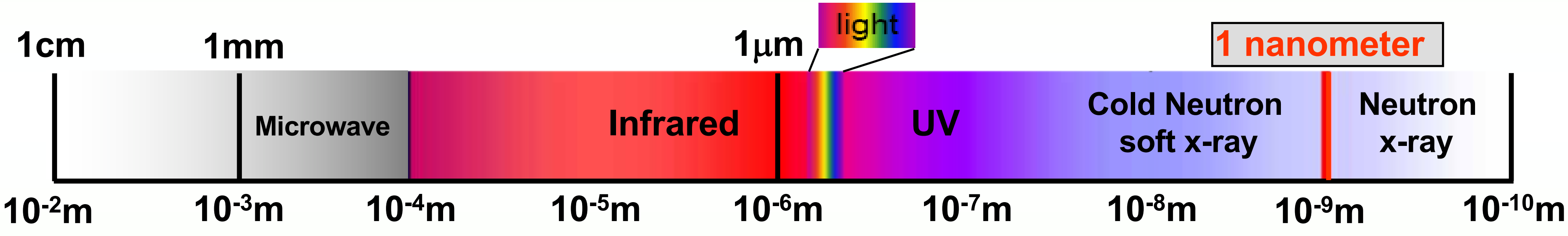
diffraction

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

Towards Nanometer Technology

Courtesy of S. Choi, KAIST

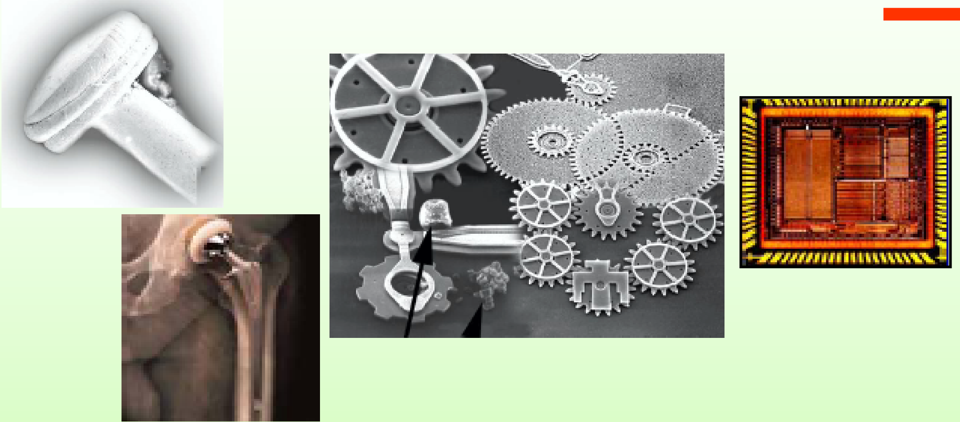
Natural

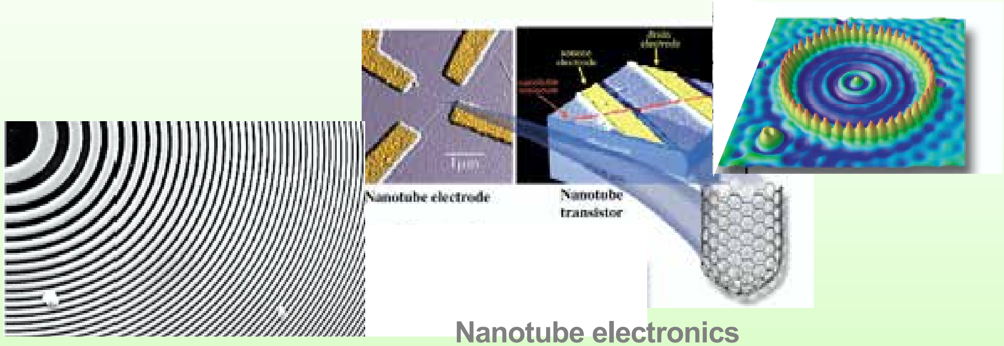

1cm
1mm
1μm
light
1 nanometer
Microwave
Infrared
UV
Cold Neutron
soft x-ray
Neutron
x-ray
10^{-2}m
10^{-3}m
10^{-4}m
10^{-5}m
10^{-6}m
10^{-7}m
10^{-8}m
10^{-9}m
10^{-10}m

Manmade

We need →

Electron Microscopy (destructive)
STM (surface)
In-situ analysis : Neutron & X-ray

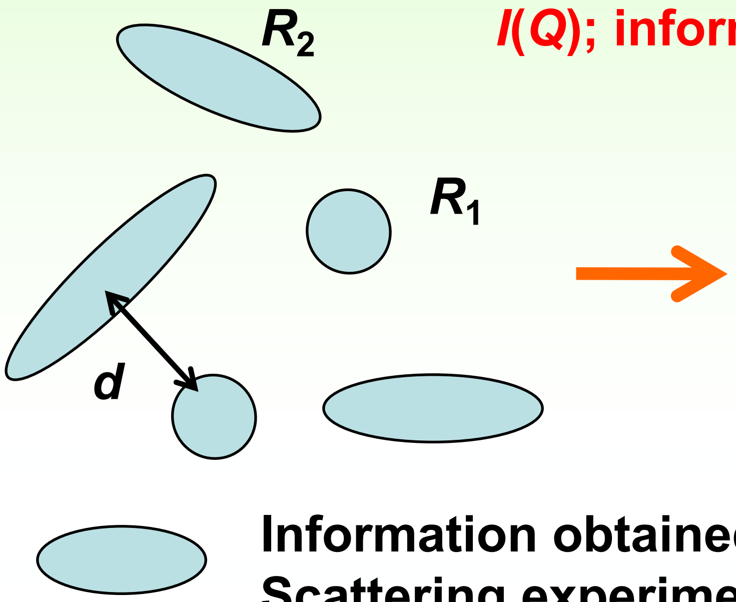




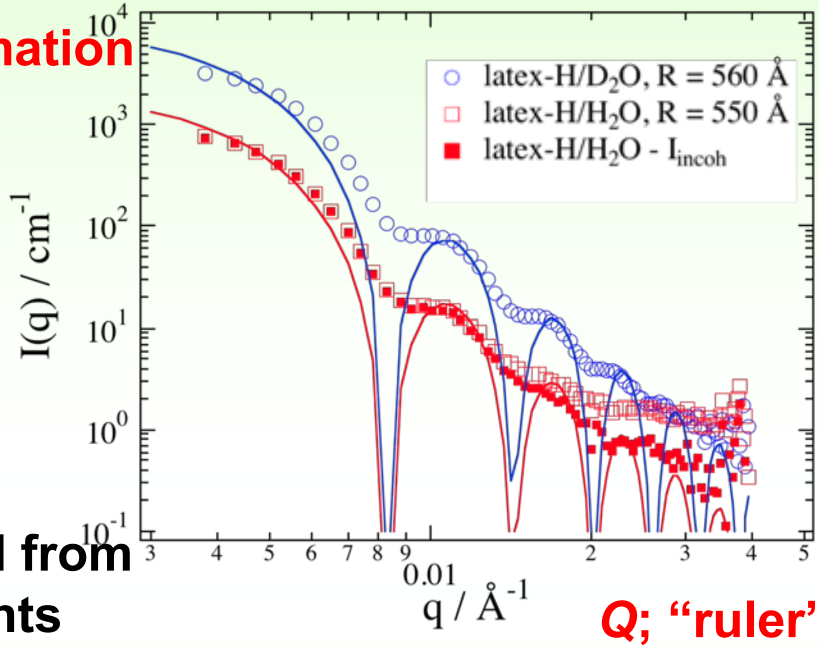
Nanotube electronics

Lecture note; M. Shibayama, AONSA Neutron School, Nov. 2018

Information obtained by small-angle scattering experiments



I(*Q*); information



Q; "ruler"

Information obtained from Scattering experiments

Structural Information
- size, R_1, R_2,
- shape,
- volume fraction, ϕ
- orientation,
- domain distance, d
- fractal dimension, D
- miscibility,
- specific surface, S/V
- ….

Ex. SANS function from a polystyrene latex (PS)

Lecture note; M. Shibayama, AONSA Neutron School, Nov. 2018

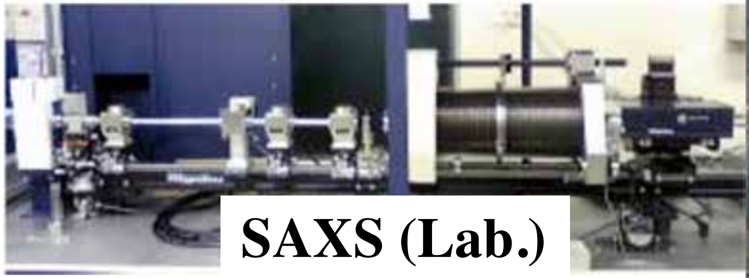
Methods of nano-structure characterization

SEM

AFM

Electron microscope
Atomic/scanning microscope
easy,
local structure, surface, …

Light scattering
mesoscopic structure,
size distribution



SAXS (Lab.)

SAXS (SPring-8)

X-ray scattering
(lab.): easy, weak intensity
(SOR): limited-machine time,
radiation damage

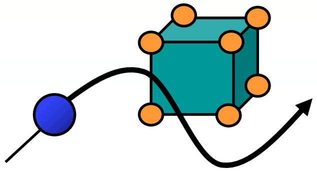
SANS (J-PARC/JRR-3)

Neutron scattering
limited-machine time,
low resolution (SANS),
large contrast (H/D, magnetic)

Why Neutrons ?

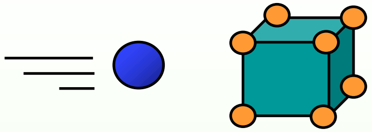
Mass **No Charge** **Spin 1/2**

No charge → Deep penetration



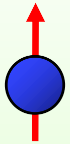
Wavelength ~ Å, nm → Atomic length scale & Nano length scale

(thermal & cold neutron)



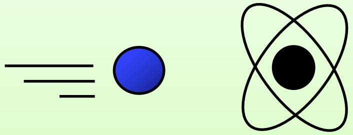
Energy ~ meV → Same magnitude as basic excitations in solids

(solid state physics)



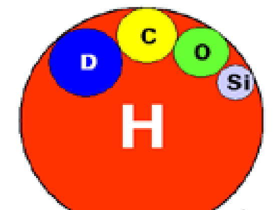
Spin =1/2 → Magnetic structure & dynamics

(solid state physics)



Interacts with nuclei → Contrast variation

(soft matter)



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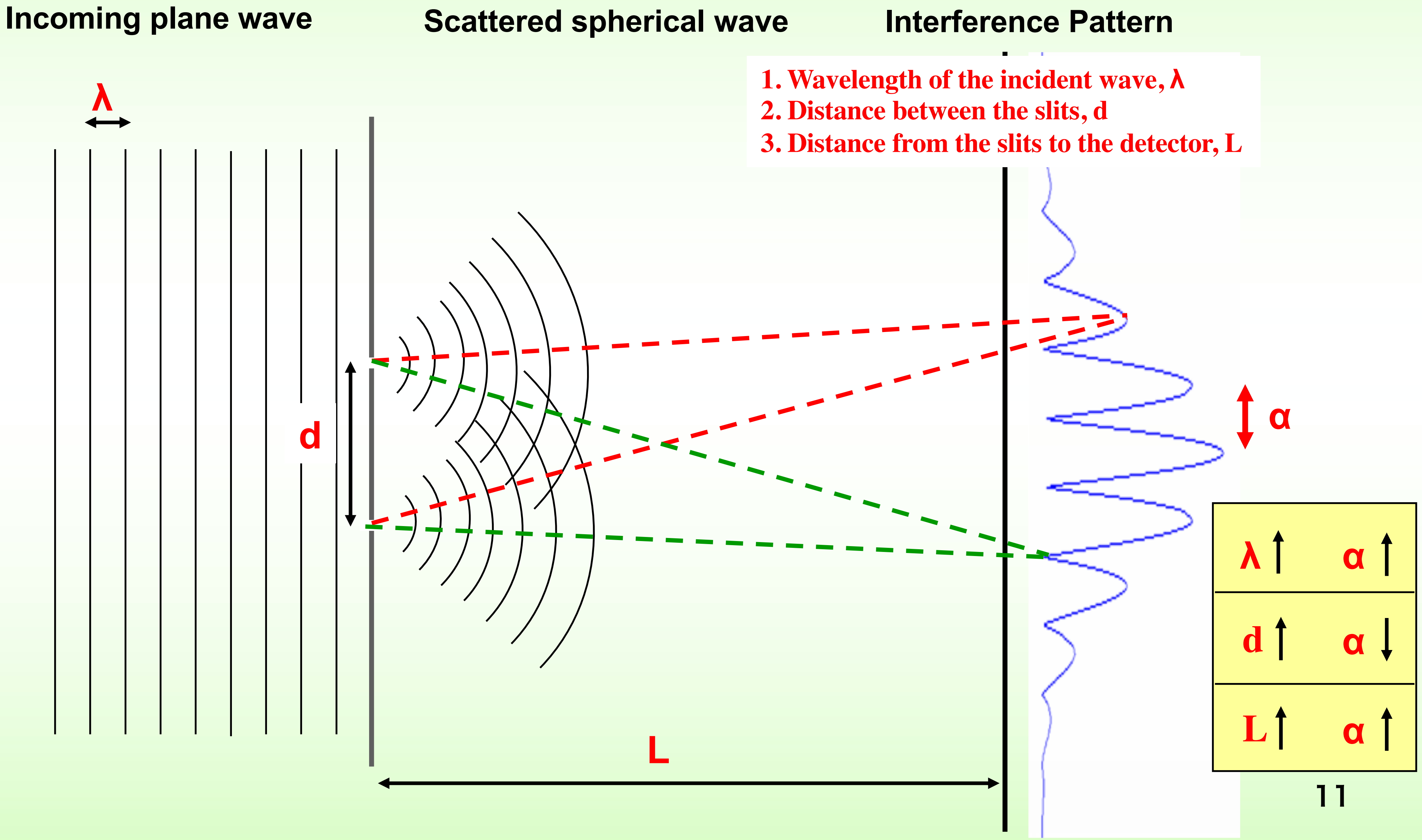
Young’s Double Slit Experiment



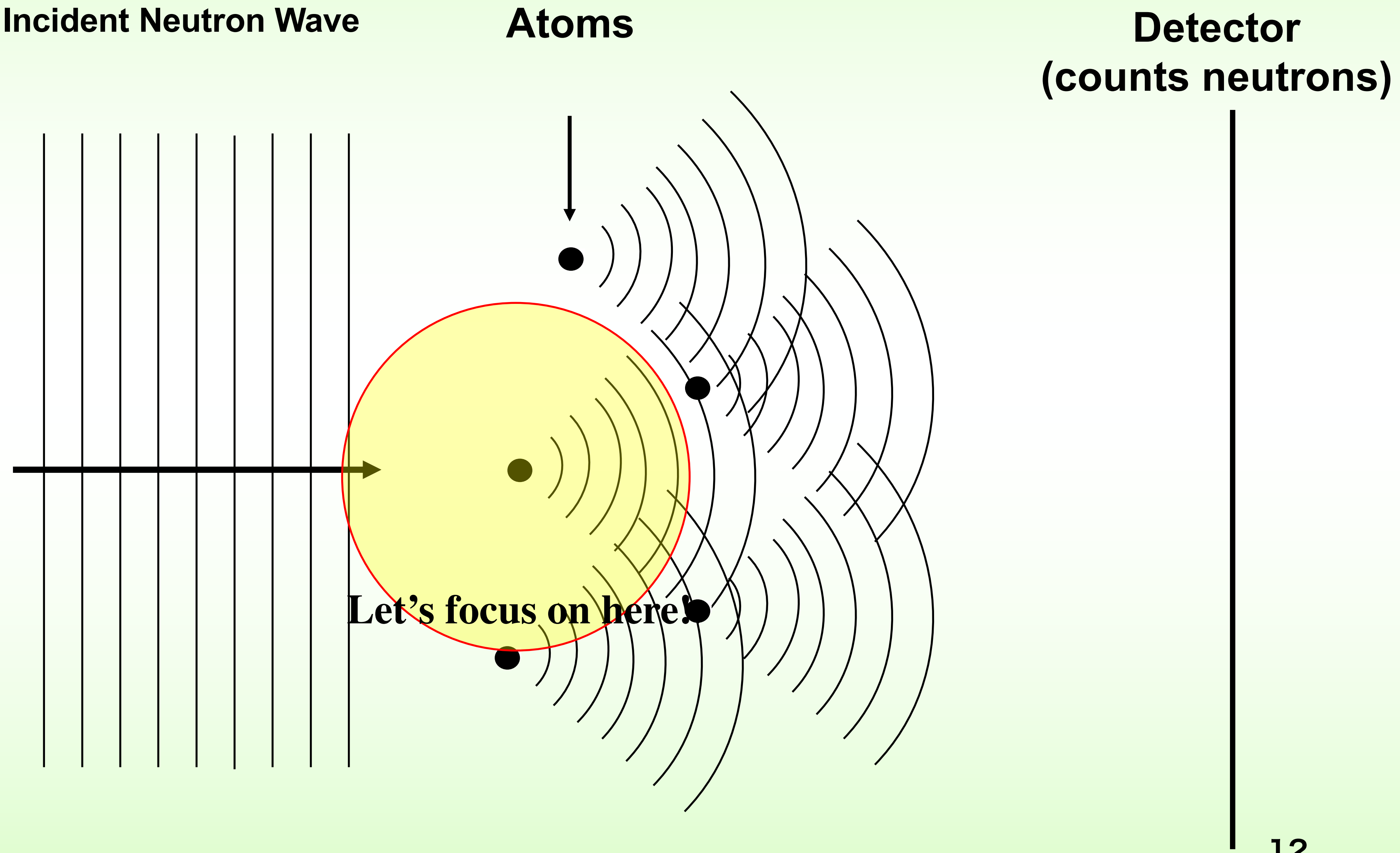
1. Wavelength of the incident wave, λ
2. Distance between the slits, d
3. Distance from the slits to the detector, L

λ ↑	α ↑
d ↑	α ↓
L ↑	α ↑

Lecture note; M. Shibayama, AONSA Neutron School, Nov. 2018

Neutron Scattering

Young's Experiments with Neutron Wave and Atoms



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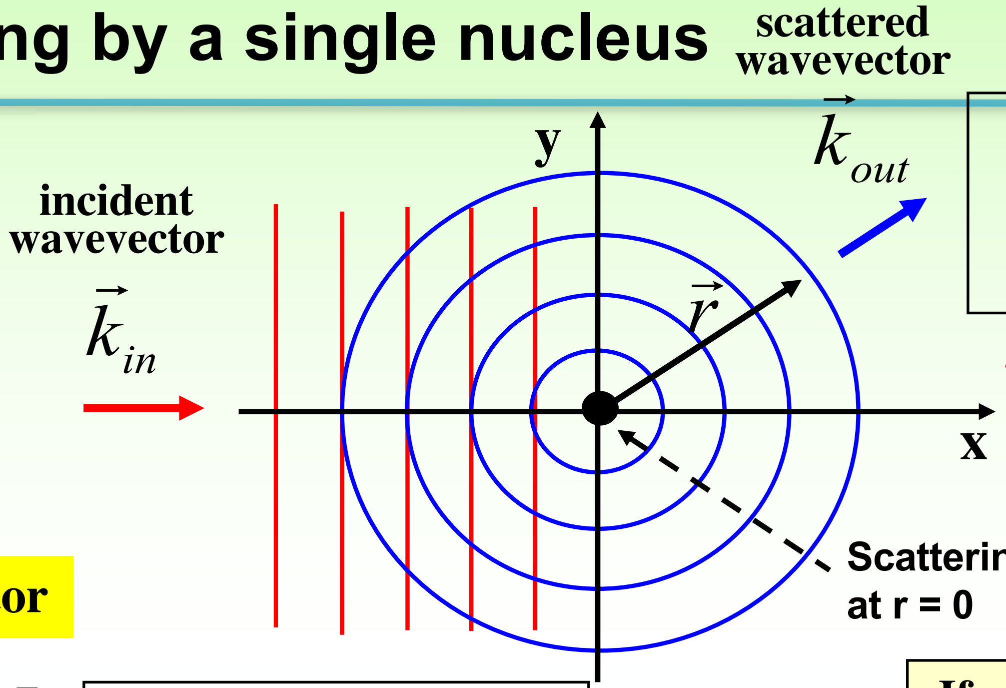
Scattering by a single nucleus



Scattering center
at r = 0

$$\psi_{inc}(\vec{r}=0) = e^{i\vec{k}_{in}\cdot 0} = 1$$

Scattered Spherical Wave

$$\psi_{scat} = \frac{-b}{r} e^{i\vec{k}_{out}\cdot\vec{r}}$$

b **= scattering length of a nucleus**

(3) Scattering length

(2) Scattering vector

$$\left|\vec{k}_{in}\right| = \left|\vec{k}_{out}\right| = k = \frac{2\pi}{\lambda}$$

(elastic scattering)

Incident Plane wave

$$\psi_{inc} = e^{i\vec{k}_{in}\cdot\vec{r}}$$

If scattering center is at $\vec{r} = \vec{R}$

$$\psi_{scat} = e^{i\vec{k}_{in}\cdot\vec{R}} \frac{-b}{\left|\vec{r}-\vec{R}\right|} e^{i\vec{k}_{out}\cdot(\vec{r}-\vec{R})}$$

(1) Scattering cross section

No. of incident neutrons passing through unit area per second

$$\Phi = \mathrm{v}\left|\psi_{inc}\right|^2 = \mathrm{v}$$

V: Neutron velocity

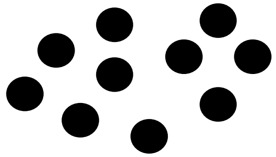
No. of scattered neutrons passing throu

$$\mathrm{v}\left|\psi_{scat}\right|^2 dS = \mathrm{v}\left(\frac{b^2}{r^2}\right) dS = \mathrm{v}\, b^2\, \mathrm{d}\Omega$$

$$\sigma_{total} = \int \frac{d\sigma}{d\Omega} d\Omega = 4\pi b^2$$

$$\frac{d\sigma}{d\Omega} = \frac{\text{No. of Neutrons Scattered per sec. into d}\Omega}{\Phi \mathrm{d}\Omega} = \frac{\mathrm{v}\left|\psi_{\mathrm{scat}}\right|^2 dS}{\mathrm{v}\mathrm{d}\Omega} = \frac{\mathrm{v}\, b^2\, \mathrm{d}\Omega}{\mathrm{v}\mathrm{d}\Omega} = b^2$$

Scattering by Many Nuclei



The scattered wave from many nuclei located at $\vec{R}_j$

$$\psi_{scat} = \sum_j e^{i\vec{k}_{in}\cdot\vec{R}_j} \frac{-b_j}{\left|\vec{r}-\vec{R}_j\right|} e^{i\vec{k}_{out}\cdot(\vec{r}-\vec{R}_j)} = e^{i\vec{k}_{out}\cdot\vec{r}} \sum_j \frac{-b_j}{\left|\vec{r}-\vec{R}_j\right|} e^{-i(\vec{k}_{out}-\vec{k}_{in})\cdot\vec{R}_j}$$

(1) Scattering cross-section

Therefore

$$\frac{d\sigma}{d\Omega} = \frac{\mathrm{v}\left|\psi_{scat}\right|^2 dS}{\mathrm{v}d\Omega} = \frac{dS}{d\Omega}\left| e^{i\vec{k}_{out}\cdot\vec{r}} \sum_j \frac{b_j}{\left|\vec{r}-\vec{R}_j\right|} e^{-i\underline{(\vec{k}_{out}-\vec{k}_{in})}\cdot\vec{R}_j} \right|^2$$

If we measure far enough away so that $r >> R_i$, then $\left|\vec{r}-\vec{R}_i\right| \approx r$

$$d\Omega = \frac{dS}{r^2}$$

$$\boxed{\frac{d\sigma}{d\Omega} = \left|\sum_j b_j e^{-i\vec{Q}\cdot\vec{R}_j}\right|^2 = \sum_{i,j} b_i b_j e^{-i\vec{Q}\cdot(\vec{R}_i-\vec{R}_j)}}$$

$$\left|e^{i\vec{k}_{out}\cdot\vec{r}}\right|^2 = 1$$

where the wavevector transfer $\vec{Q}$ is defined as

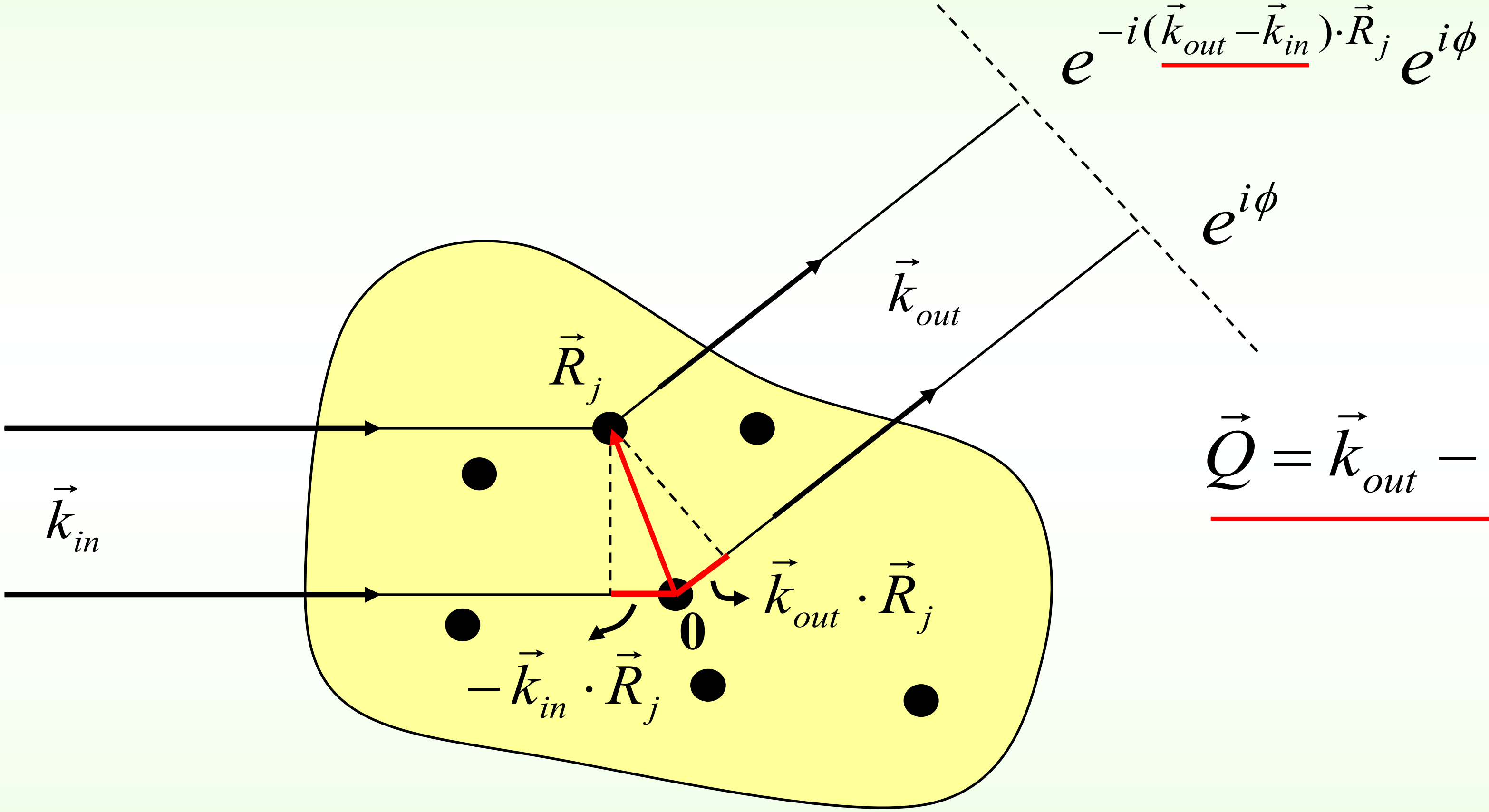
$$\boxed{\vec{Q} = \vec{k}_{out} - \vec{k}_{in}}$$

(2) Scattering vector

Lecture note; M. Shibayama, AONSA Neutron School, Nov. 2018

Scattering vector *Q*

(2) Scattering vector

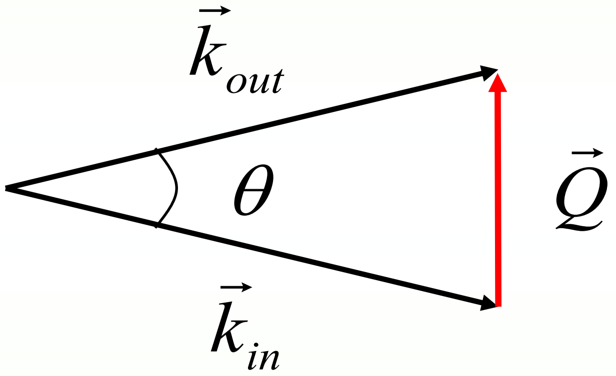


$$\vec{Q}=\vec{k}_{out}-\vec{k}_{in}$$

Scattering vector *Q*

(2) Scattering vector

$$\vec{Q} = \vec{k}_{out} - \vec{k}_{in}$$



For elastic scattering

$$\left|\vec{k}_{in}\right| = \left|\vec{k}_{out}\right| = k = \frac{2\pi}{\lambda}$$

$$\left|\vec{Q}\right| = 2k \sin\frac{\theta}{2}$$

$$\boxed{Q = \left(\frac{4\pi}{\lambda}\right)\sin\left(\frac{\theta}{2}\right)}$$

Note: **The dimension of *Q* = 1/Length**

$$\boxed{Q = \frac{2\pi}{d} \quad \text{or} \quad d = \frac{2\pi}{Q}}$$

Lecture note; M. Shibayama, AONSA Neutron School, Nov. 2018

What we measure in Neutron Scattering Exp. ?

(1) Scattering cross-section

Differential Neutron Scattering Cross-Section

$$\frac{d\sigma}{d\Omega}(\vec{\mathbf{Q}}) = \left\langle \left| \sum_j b_j e^{-i\vec{\mathbf{Q}}\cdot\vec{R}_j} \right|^2 \right\rangle$$

σ = total scattering cross section

Ω = solid angle

$\vec{Q}$ = scattering vector

b_j = coherent scattering length of atom j

$\vec{R}_j$ = position of atom j

Lecture note; M. Shibayama, AONSA Neutron School, Nov. 2018

Neutron Scattering : Fourier Transform

(1) Scattering cross-section

- ☐ **Differential scattering cross-section**

$$\frac{d\sigma}{d\Omega}(\vec{Q}) = \left\langle \left| \sum_j b_j e^{-i\vec{Q}\cdot\vec{R}_j} \right|^2 \right\rangle$$

Dirac delta function

$$\int \delta(\vec{\mathrm{r}})d\vec{r} = 1$$

$$\int f(\vec{r})\delta(\vec{\mathrm{r}} - \vec{\mathrm{R}})d\vec{r} = f(\vec{\mathrm{R}})$$

$n(\vec{r}) = \sum_j \delta(\vec{r} - \vec{R}_j)$: **Atomic number density**

$\rho_{\mathrm{sld}}(\vec{r}) = \sum_j b_j \delta(\vec{r} - \vec{R}_j)$: **Scattering length density**

$$\mathrm{F.T.}\{\rho_{\mathrm{sld}}(\vec{r})\} = \int \rho_{\mathrm{sld}}(\vec{r}) e^{-i\vec{Q}\cdot\vec{r}} d\vec{r} = \int \sum_j b_j \delta(\vec{r} - \vec{R}_j) e^{-i\vec{Q}\cdot\vec{r}} d\vec{r} = \sum_j b_j e^{-i\vec{Q}\cdot\vec{R}_j}$$

$$\boxed{\frac{d\sigma}{d\Omega}(\vec{Q}) = \left\langle \left| \int \rho_{sld}(\vec{r}) e^{-i\vec{Q}\cdot\vec{r}} d\vec{r} \right|^2 \right\rangle}$$

Scattering Length

(3) Scattering length

☐ Neutron Interaction Potentials

Nuclear Interaction (Neutron-Nucleus)

$$V_N(\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} b_N \delta(\mathbf{r})$$

Magnetic Interaction (Neutron-Unpaired Electron)

$$V_M(\mathbf{r}) = -\underset{\uparrow}{\boldsymbol{\mu}} \cdot \mathbf{B}(\mathbf{r})$$

B-field induced unpaired spin

Magnetic moment of neutron

☐ Scattering length, *b*

Fourier Transform of V(r)

$$b = \frac{m_n}{2\pi\hbar^2} V(\mathbf{Q})$$

Pauli operator for neutron

Magnetic form factor

$$\boxed{b = \underbrace{b_N}_{\text{Nuclear}} + \underbrace{b_M}_{\text{Magnetic}} = b_N + \gamma r_e \boldsymbol{\sigma} \cdot \mathbf{S}_\perp f(Q)}$$

Spin component perpendicular to Q

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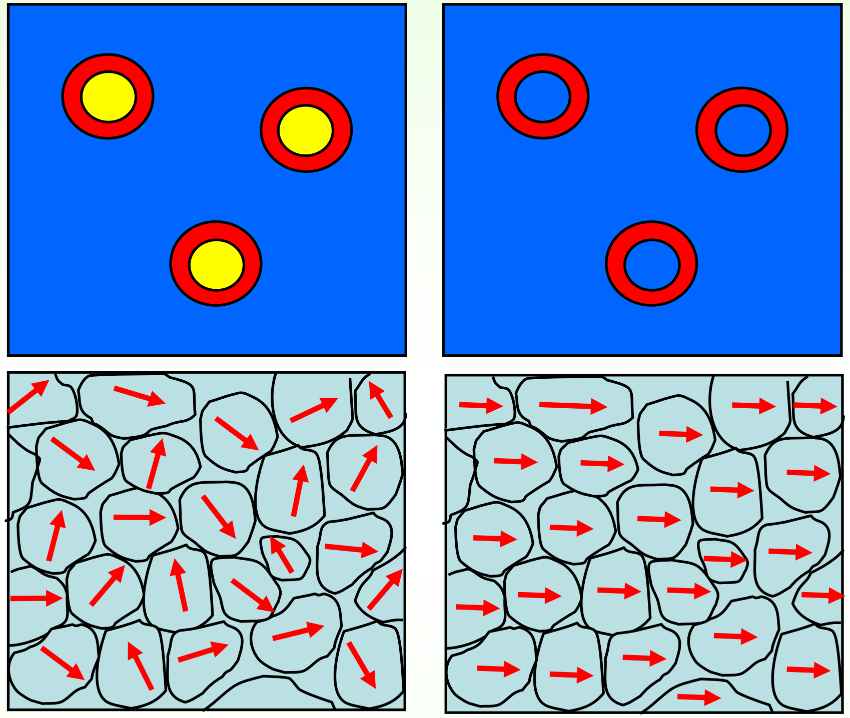
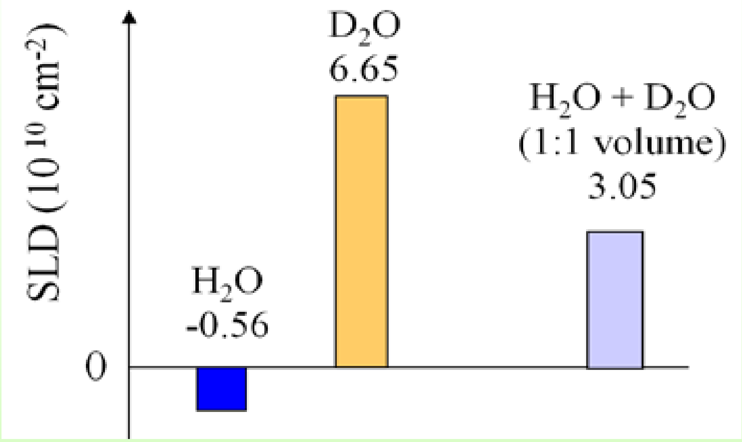
Scattering Length Density

(3) Scattering length





- ❑ **Scattering length density, ρ**

$$\rho = \frac{\sum_{j}^{n} b_j}{\bar{V}}$$

b_j = **bound coherent scattering length of atom *j***

$\bar{V}$ = **volume containing the *n* atoms**

- ❑ **Contrast variation**

- bound coherent scattering length (10^{-13} cm)

b_H = -3.749 fm **b_D = 6.671 fm**

Lecture note; M. Shibayama, AONSA Neutron School, Nov. 2018

Calculation of scattering lengths

(3) Scattering length

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

$$b \equiv b_{molecule} = \sum_i r_i b_{atom,i}$$

Ex. benzene C_6H_6

$$b_{\mathrm{benzene}} = 6b_H + 6b_C$$

$$= 6 \times (-3.739 \times 10^{-13}) + 6 \times (6.646 \times 10^{-13})$$

$$= 17.442 \times 10^{-13} [\mathrm{cm}]$$

Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
	%	fm (=10^{-13}cm)	fm	barn(=10^{-24}cm^2)	barn	barn	barn
isotope	Conc.	Coh. Scatt. length	Inc. scatt. length	Coh. Cross section	Inc. cross section	Scattering cross secdtion	Absorption cross section
H	---	-3.739	---	1.7568	80.26	82.02	0.3326
^{1}H	99.985	-3.7406	25.274	1.7583	80.27	82.03	0.3326
^{2}H	0.015	6.671	4.04	5.592	2.05	7.64	0.000519
C	---	6.646	---	5.551	0.001	5.551	0.0035
N	---	9.36	---	11.01	0.5	11.51	1.9
O	---	5.803	---	4.232	0.0008	4.232	0.00019

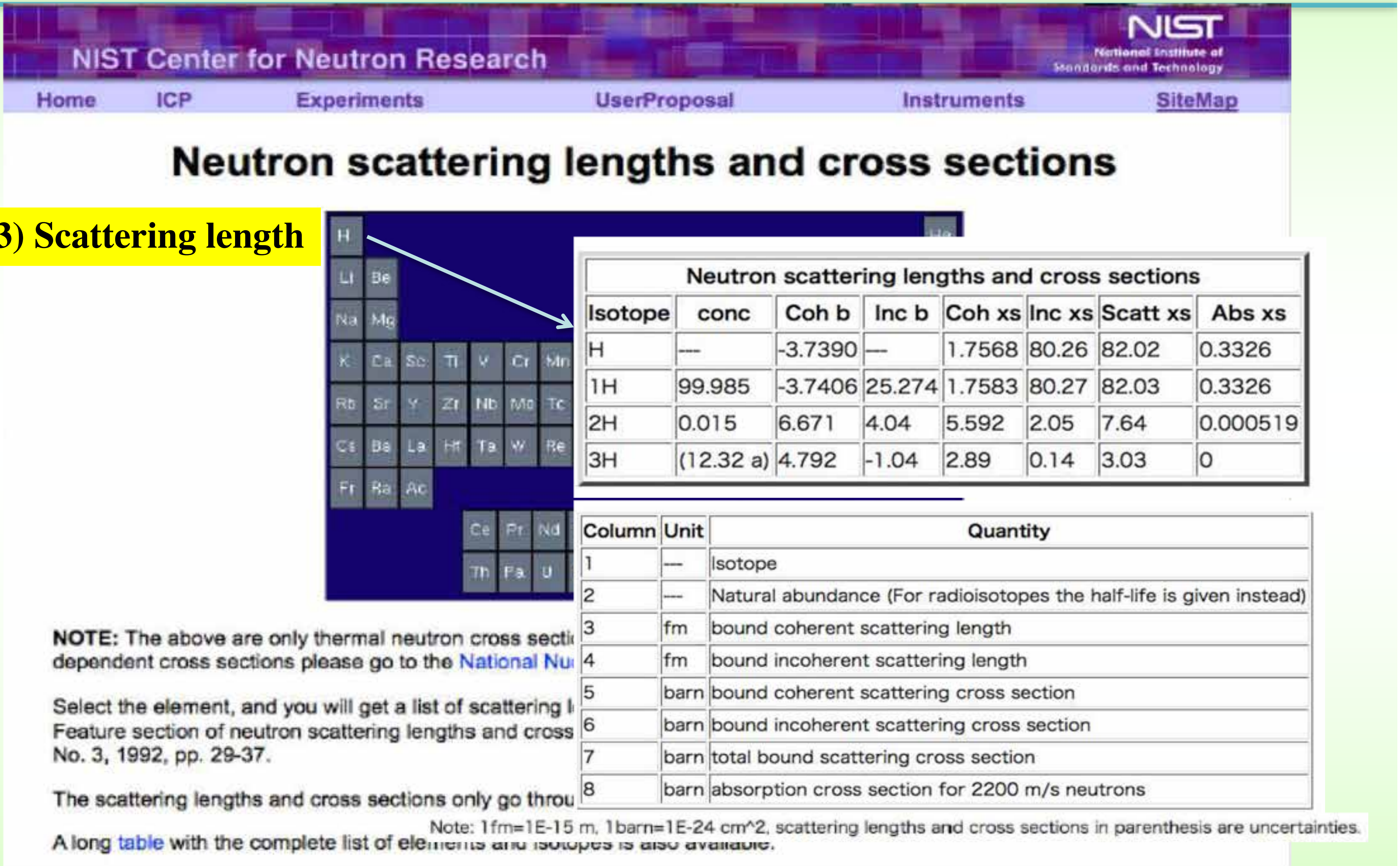
b σ_{coh} σ_{inc} σ_s σ_a

Q: Calculate the scattering lengths of light (H_2O) and heavy (D_2O) waters?

Lecture note; M. Shibayama, AONSA Neutron School, Nov. 2018

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

(3) Scattering length



Neutron scattering lengths and cross sections

Neutron scattering lengths and cross sections

Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
H	---	-3.7390	---	1.7568	80.26	82.02	0.3326
1H	99.985	-3.7406	25.274	1.7583	80.27	82.03	0.3326
2H	0.015	6.671	4.04	5.592	2.05	7.64	0.000519
3H	(12.32 a)	4.792	-1.04	2.89	0.14	3.03	0

Column	Unit	Quantity
1	---	Isotope
2	---	Natural abundance (For radioisotopes the half-life is given instead)
3	fm	bound coherent scattering length
4	fm	bound incoherent scattering length
5	barn	bound coherent scattering cross section
6	barn	bound incoherent scattering cross section
7	barn	total bound scattering cross section
8	barn	absorption cross section for 2200 m/s neutrons

Note: 1fm=1E-15 m, 1barn=1E-24 cm^2, scattering lengths and cross sections in parenthesis are uncertainties.

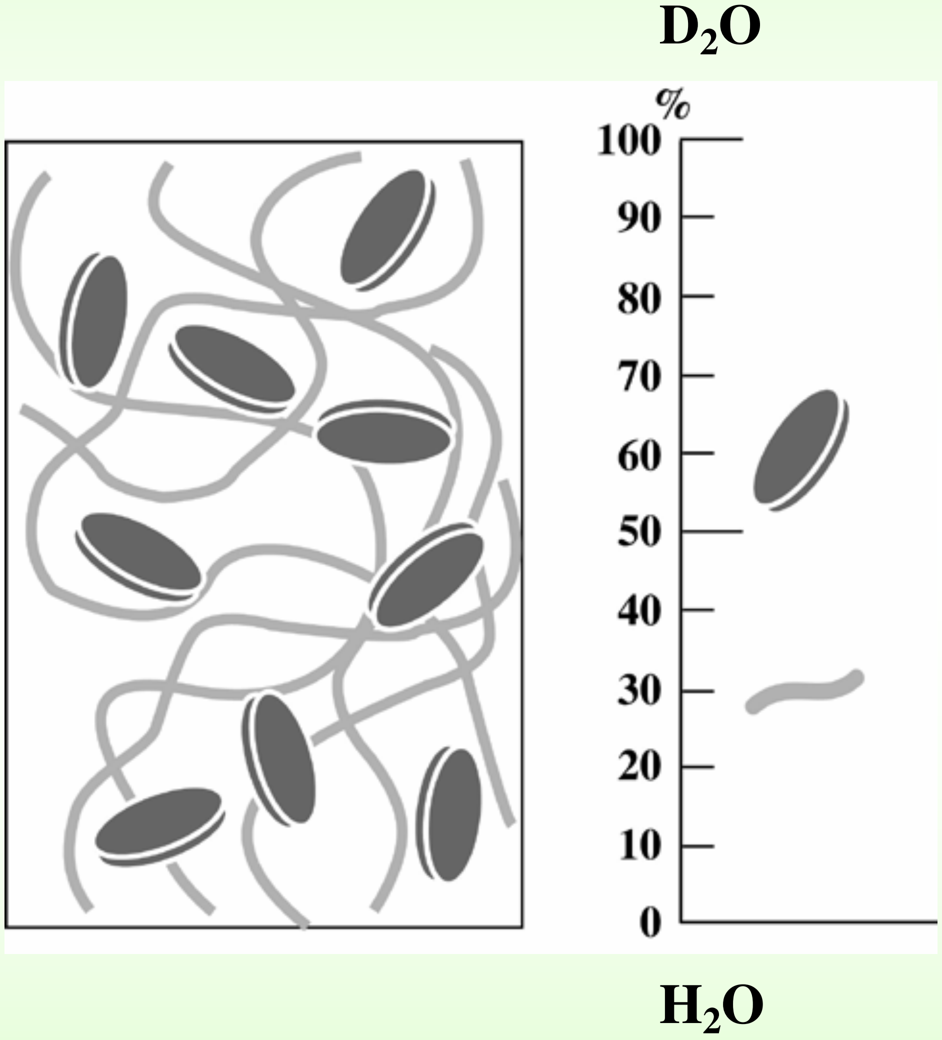
NOTE: The above are only thermal neutron cross secti
dependent cross sections please go to the National Nu

Select the element, and you will get a list of scattering l
Feature section of neutron scattering lengths and cross
No. 3, 1992, pp. 29-37.

The scattering lengths and cross sections only go throu

A long table with the complete list of ele

Neutron contrast



labeling

Contrast matching

Coherent and Incoherent Scattering

The scattering length, *b_i*, depends on the nuclear isotope, nuclear spin relative to neutron spin. For a single nucleus,

Random fluctuation due to isotope and spin

$$b_i = \langle b\rangle + \delta b_i$$

where δb_i averages to zero

$$b_i b_j = \langle b\rangle^2 + \langle b\rangle(\delta b_i + \delta b_j) + \delta b_i \delta b_j$$

$$\text{Note: } \langle \delta b_i\rangle = 0 \text{ and } \langle \delta b_i \delta b_j\rangle = 0 \text{ unless i = j}$$

$$\text{If i} \neq \text{j}, \quad \langle b_i b_j\rangle = \langle b\rangle^2$$

$$\text{If i = j}, \quad \langle b_i b_j\rangle = \langle b_i{}^2\rangle = \langle b^2\rangle = \langle b\rangle^2 + \langle \delta b_i{}^2\rangle \quad \text{-->} \langle \delta b_i{}^2\rangle = \langle b^2\rangle - \langle b\rangle^2$$

Therefore,

$$\langle b_i b_j\rangle = \langle b\rangle^2 + \delta_{ij}\left(\langle b^2\rangle - \langle b\rangle^2\right)$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{scatt} = \left(\frac{d\sigma}{d\Omega}\right)_{Coh} + \left(\frac{d\sigma}{d\Omega}\right)_{Inc}$$

$$\frac{d\sigma}{d\Omega} = \left\langle \sum_{i,j} b_i b_j e^{-i\vec{Q}\cdot(\vec{R}_i - \vec{R}_j)} \right\rangle = \sum_{i,j} \langle b_i b_j\rangle e^{-i\vec{Q}\cdot(\vec{R}_i - \vec{R}_j)} = \underline{\langle b\rangle^2 \sum_{i,j} e^{-i\vec{Q}\cdot(\vec{R}_i - \vec{R}_j)}} + \underline{N\left(\langle b^2\rangle - \langle b\rangle^2\right)}$$

Coherent scattering **Incoherent scattering**

- **scattering depends on Q**
- **contains structural information**

Lecture note: M. Shibayama, AONSA Neutron School, Nov. 2018

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5. Applications
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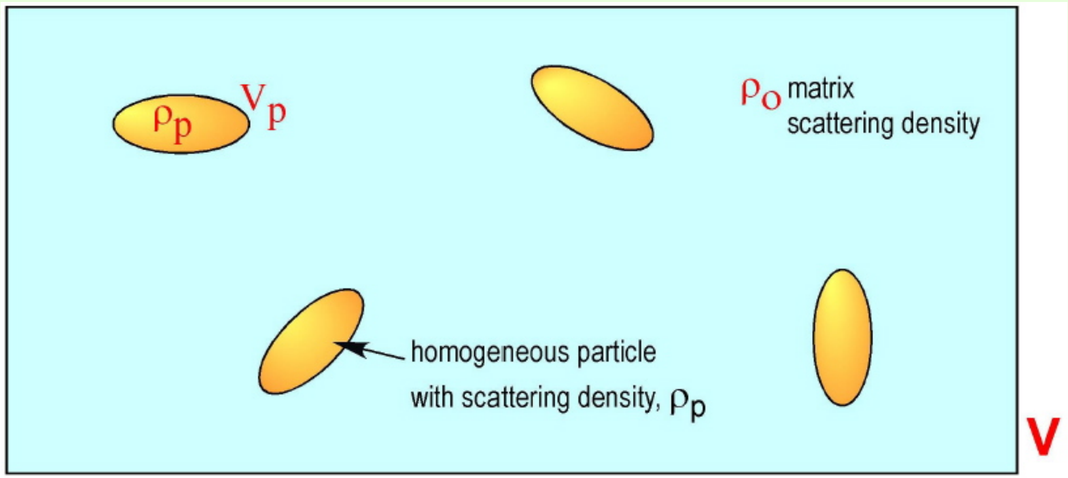
Scattering from Dilute, Homogeneous Particles



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

Number of particles

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

Contrast Factor

Particle Shape

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

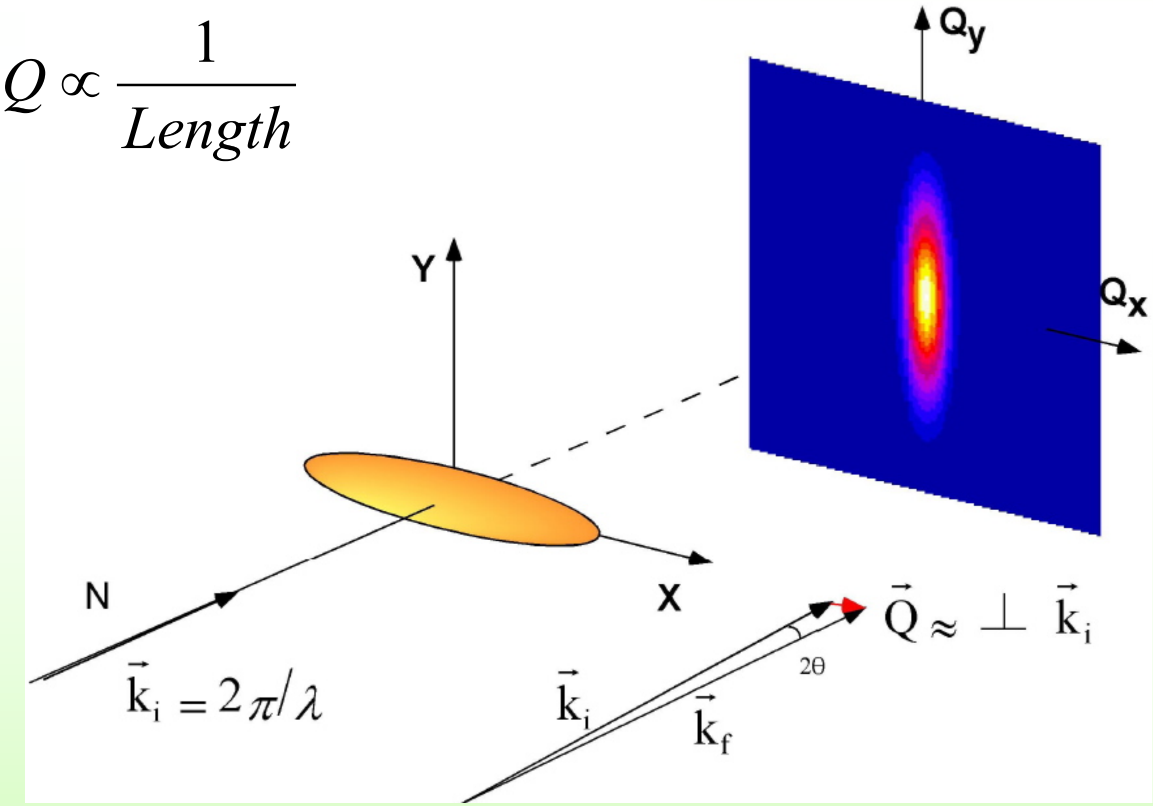
SANS from oriented dilute particles

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

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

$$Q \propto \frac{1}{Length}$$

$$\mathbf{Q}\cdot\mathbf{r} = Qr\cos\theta$$



SANS from randomly oriented particles

Guinier Approximation for Low-Q Scattering

average over orientations

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

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

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

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

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

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

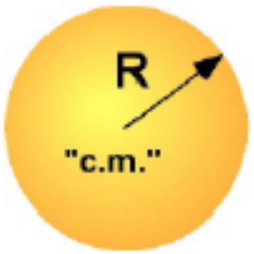
defines
"center of mass"

Guinier Radius, R_g

Guinier Radius, R_G

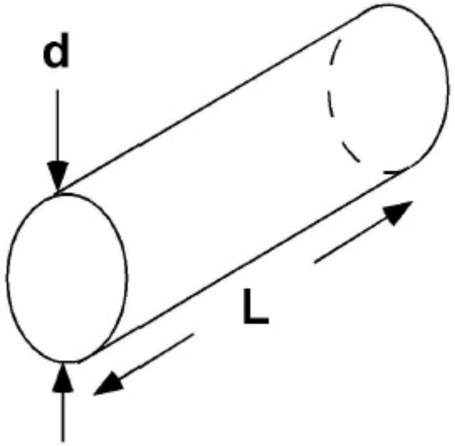
- rms distance from "center of scattering density"

1) Spherical Particles



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

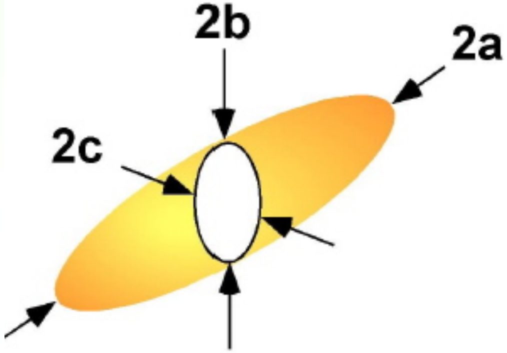
2) Cylinders (Rods or Disks)



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

Guinier Radius, R_g

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



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

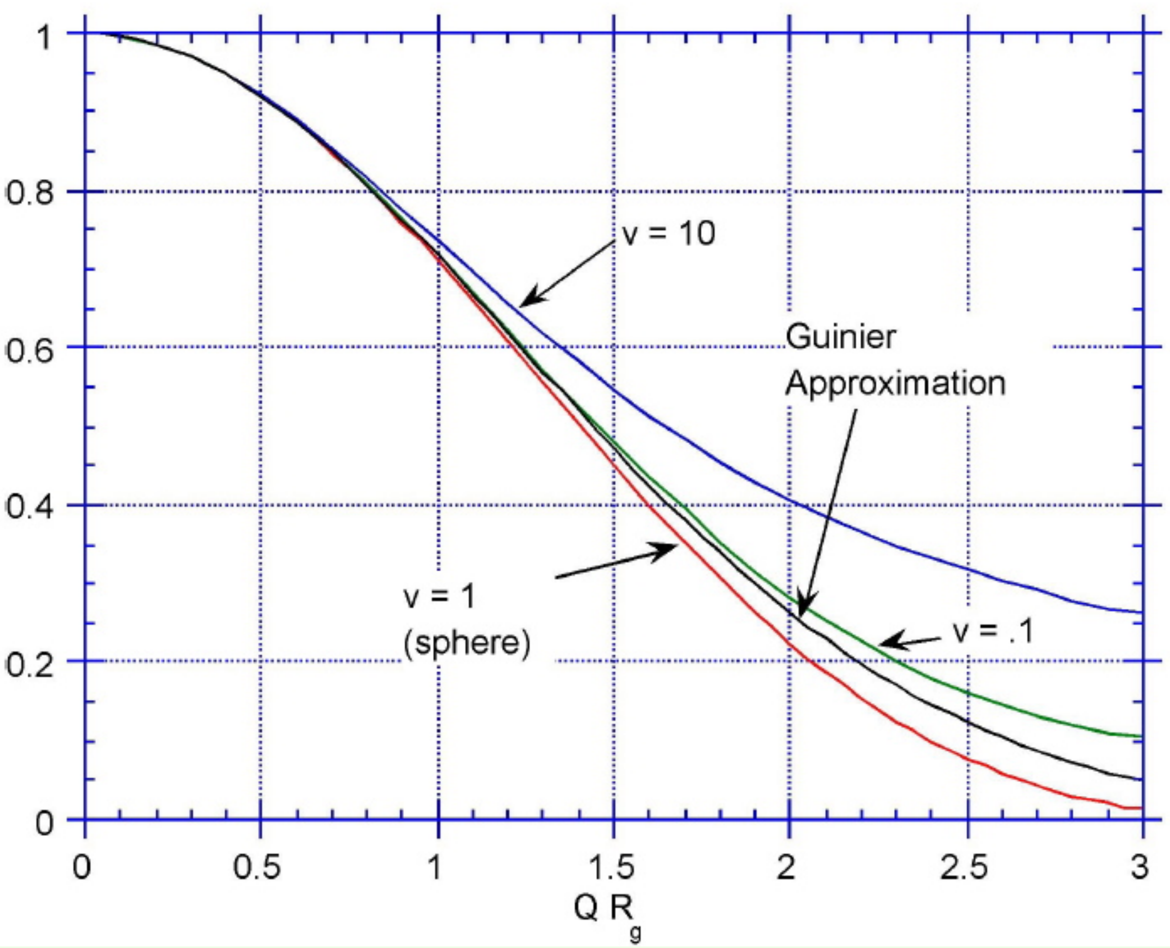
4) Gaussian chain

$$R_G^2 = \frac{1}{6}\overline{L^2} \qquad \overline{L^2} =$$

average square of the end-to-end distance

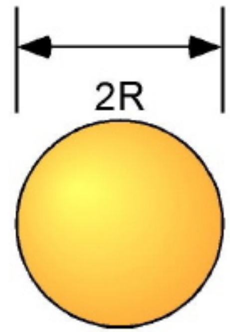
Scattering intensity from ellipsoid of revolution

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

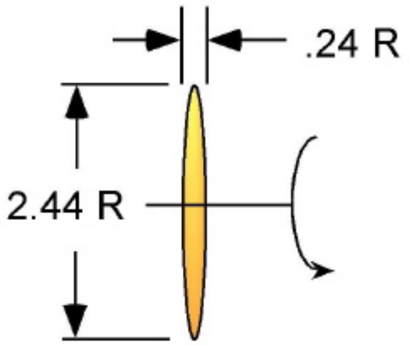


$$R_g = R\sqrt{\frac{2+v^2}{5}}$$

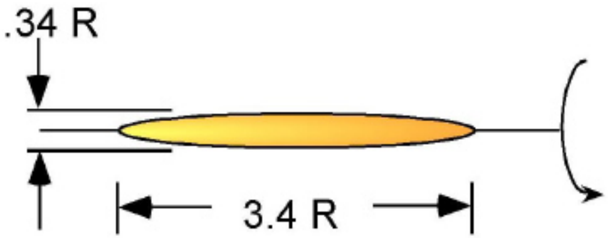
Sphere (v = 1)



Oblate Ellipsoid (v = 1/10)



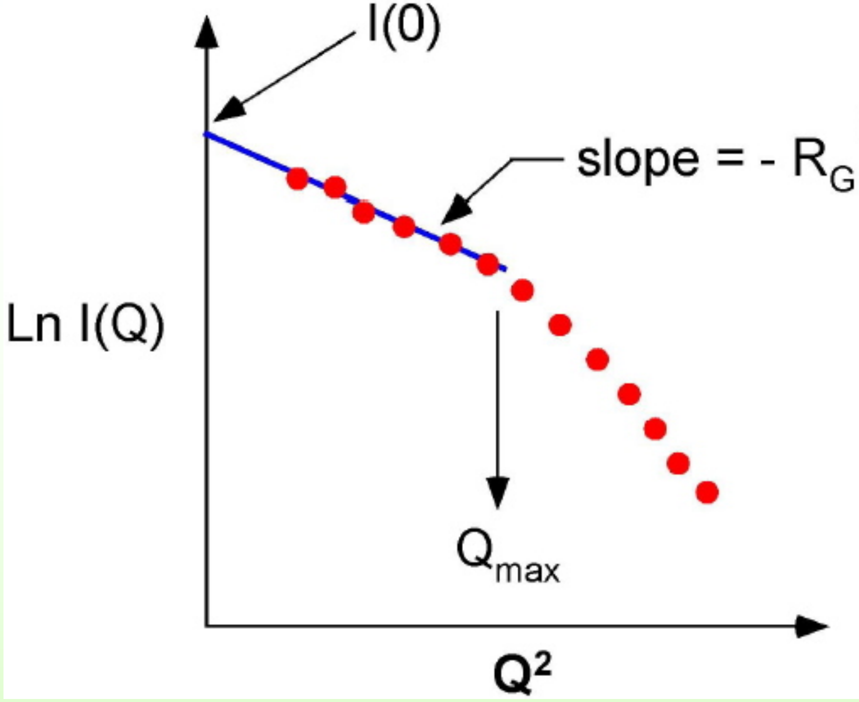
Prolate Ellipsoid (v = 10)



Guinier Approximation

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

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



$Q_{max} R_G \le 1$

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Extrapolation to *Q* = 0

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

$$= \frac{N}{V}\left(\rho_p - \rho_o\right)^2 V_p^2$$

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

Expressing in terms of
c (molecular concentration) [mg/ml] = $\frac{N \rho V_p}{V}$
M_W (molceular weight)= $\rho V_p N_A$

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

N_A = Avogadro's number

ρ = mass density

Particles having a size distribution

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

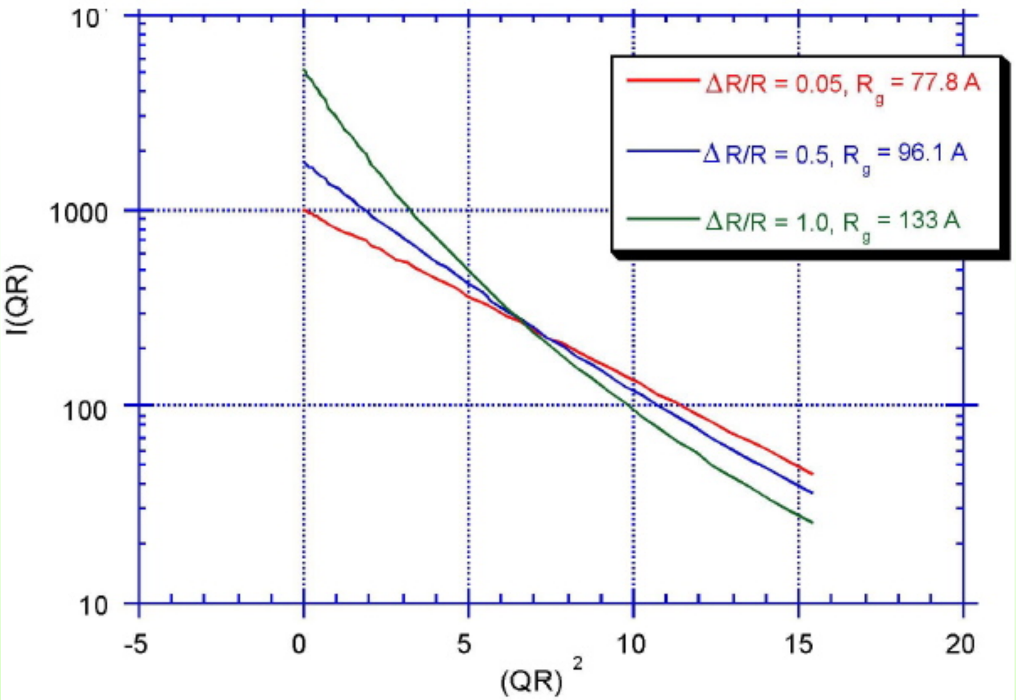
↖ Weighed by the square of the particle volume!

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

$V_p(R)$ - Particle Volume

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



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

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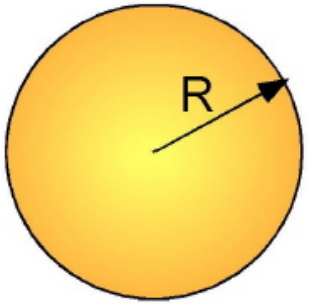
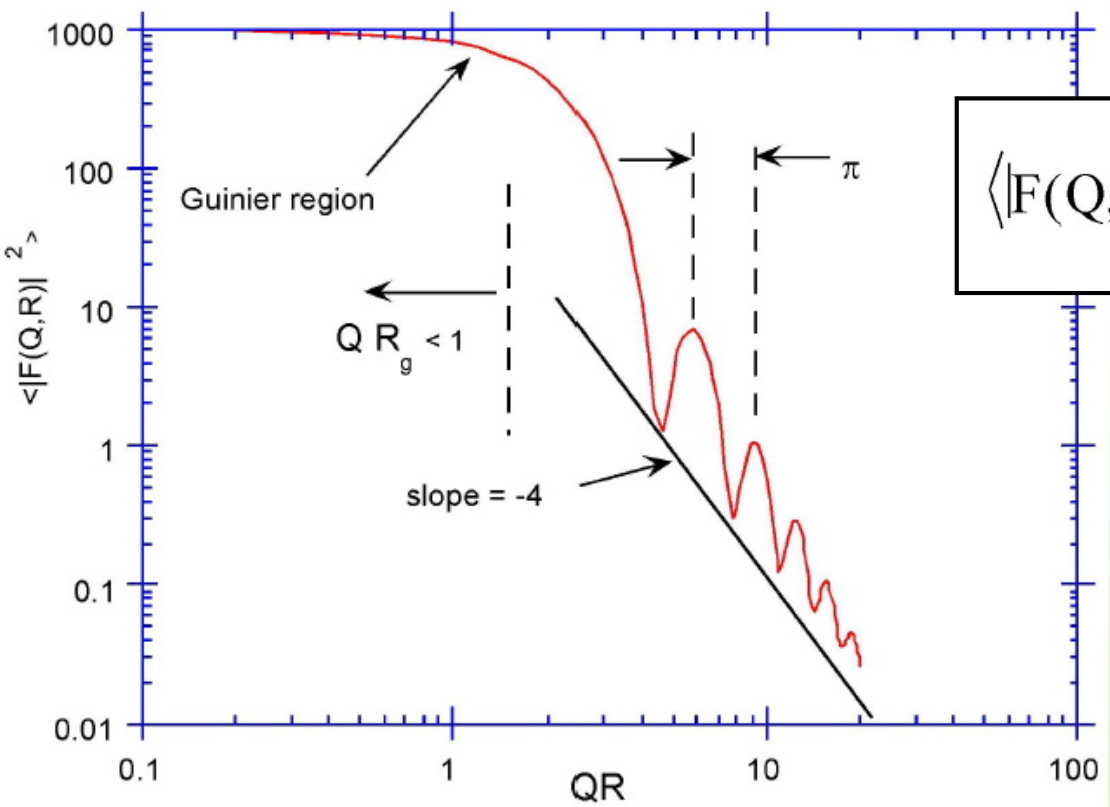
Form Factors for Simple Particle Shapes

1) Spheres



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

(Form Factor) ^{2} for Monodispersed Spheres



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

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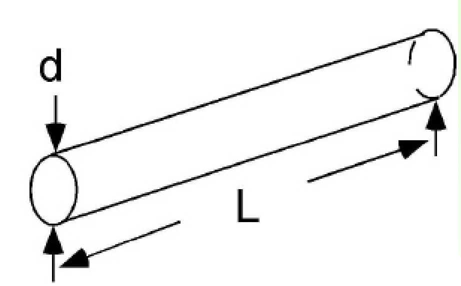
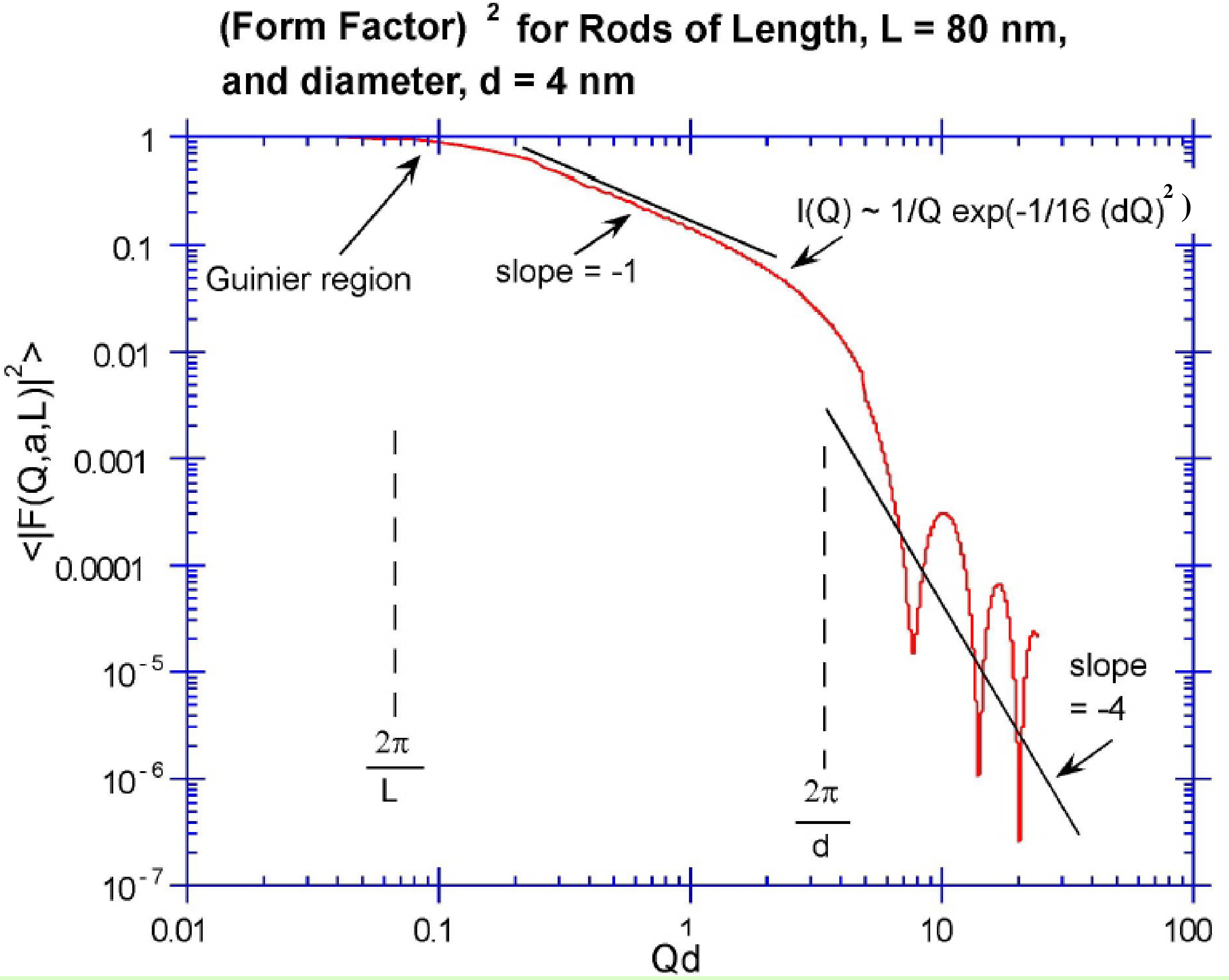
Form Factors for rods



$$\left|F_p(Q)\right|^2 = \int_0^{2\pi} \left[\frac{2J_1(QR\sin\alpha)}{QR\sin\alpha} \frac{\sin((QL\cos\alpha)/2)}{QL\cos\alpha)/2} \right]^2 \sin\alpha d\alpha$$

R=d/2



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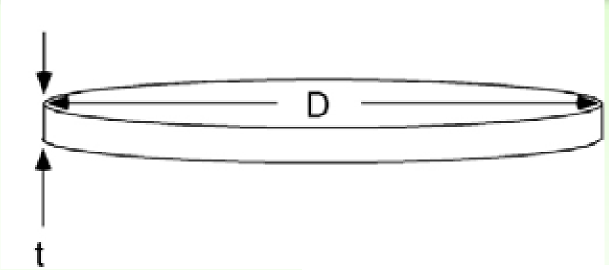
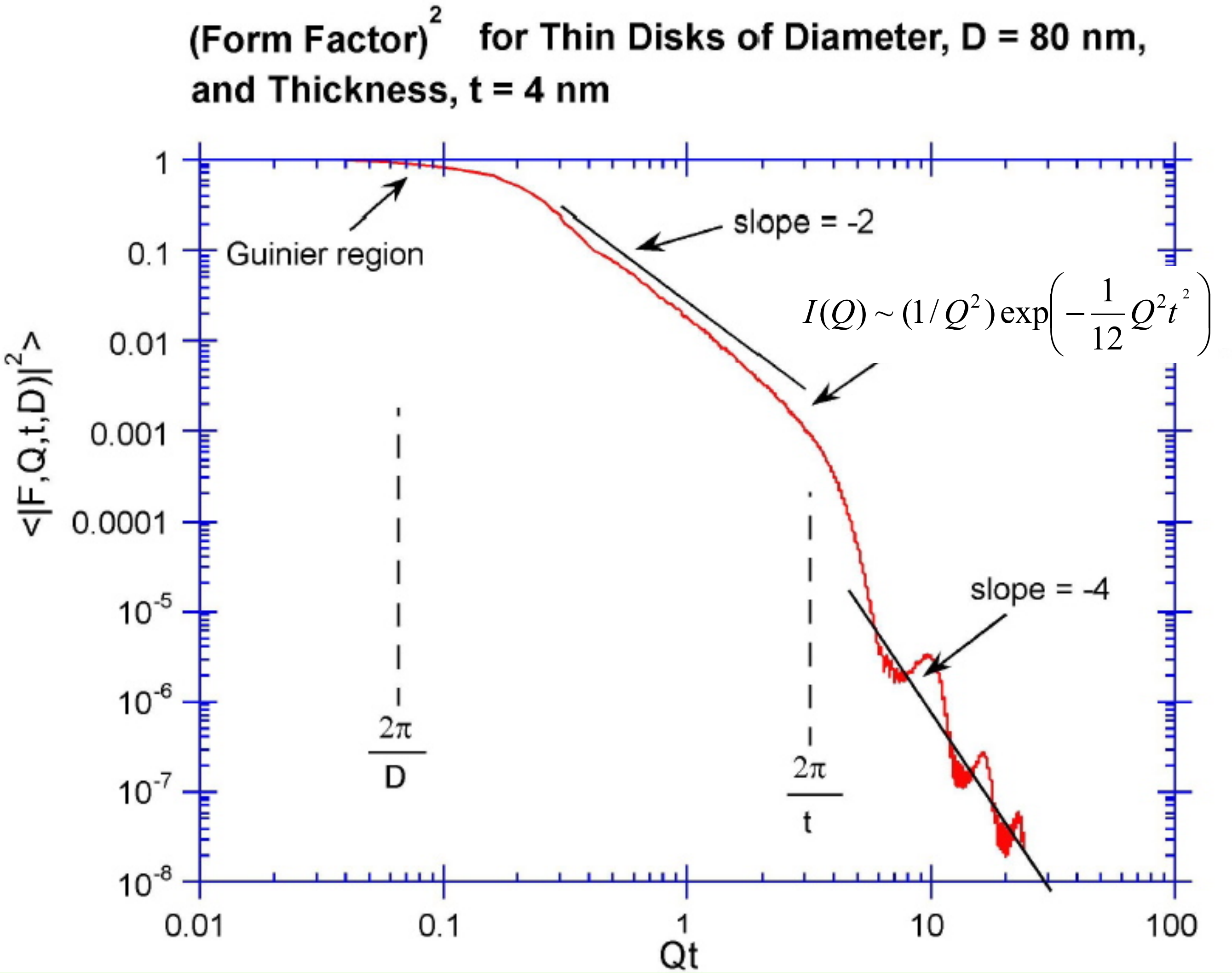
Form Factors for thin discs



$$\left|F_p(Q)\right|^2 = \int_0^{2\pi} \left[\frac{2J_1(QR\sin\alpha)}{QR\sin\alpha} \frac{\sin((QL\cos\alpha)/2)}{QL\cos\alpha)/2} \right]^2 \sin\alpha d\alpha$$


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

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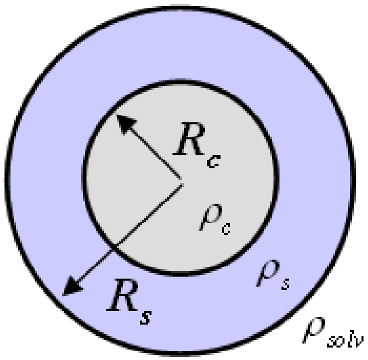
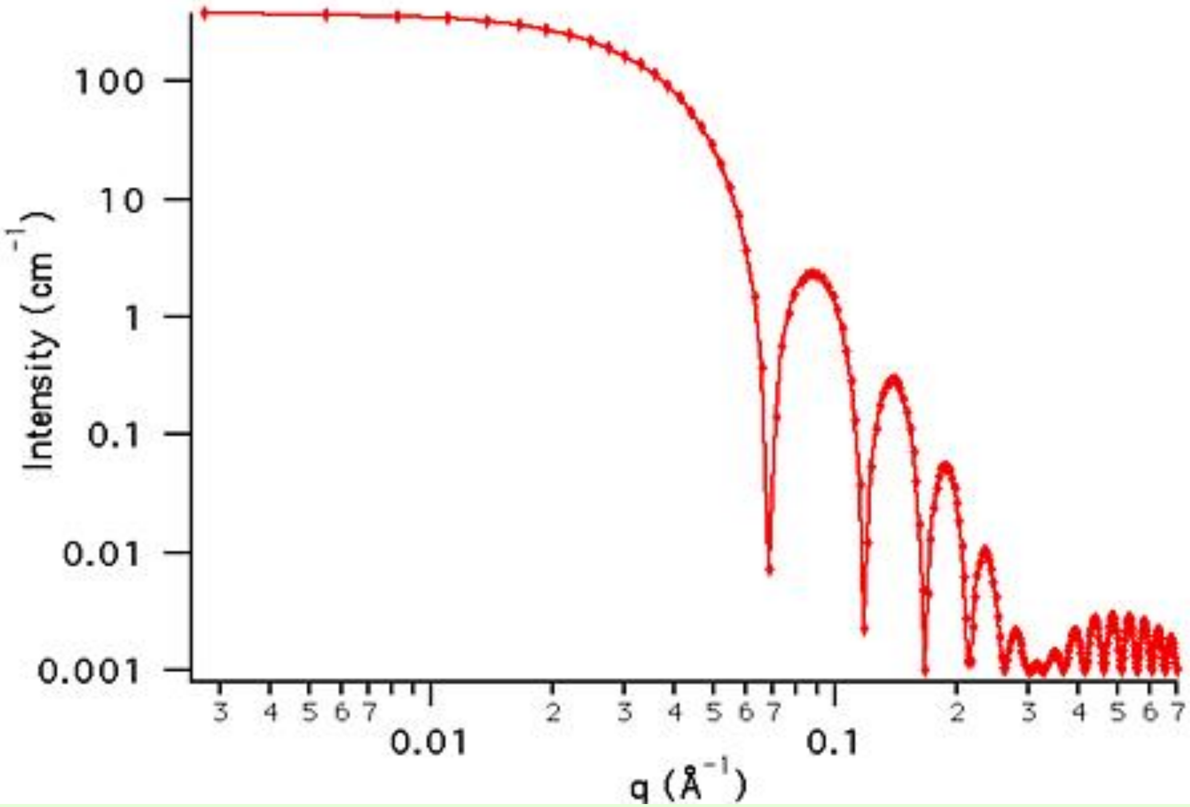
Spherical Core-Shell



$$|F_p(Q)|^2 = \left[\frac{3V_c(\rho_c - \rho_s)J_1(QR_c)}{QR_c} + \frac{3V_s(\rho_s - \rho_{solv})J_1(QR_s)}{QR_s} \right]^2$$



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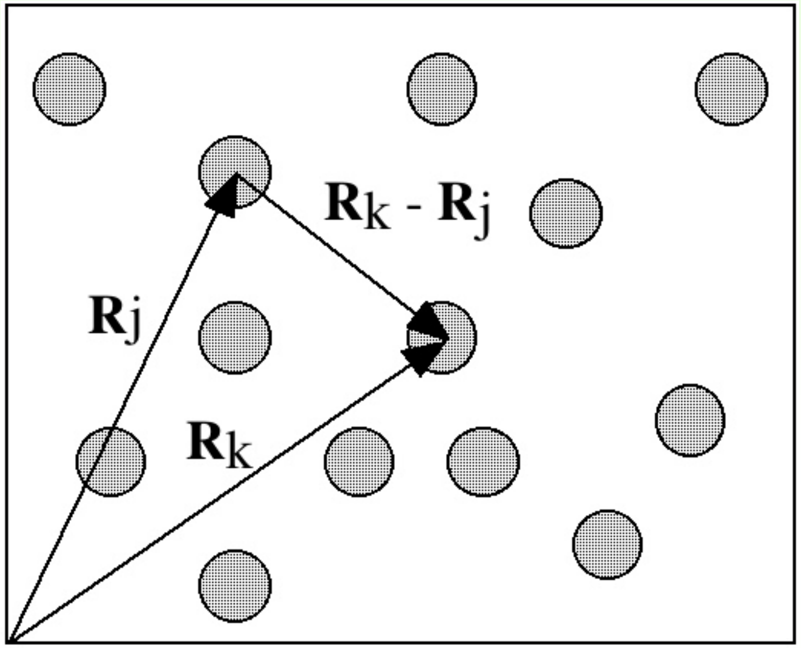
Interparticle Interference Effects

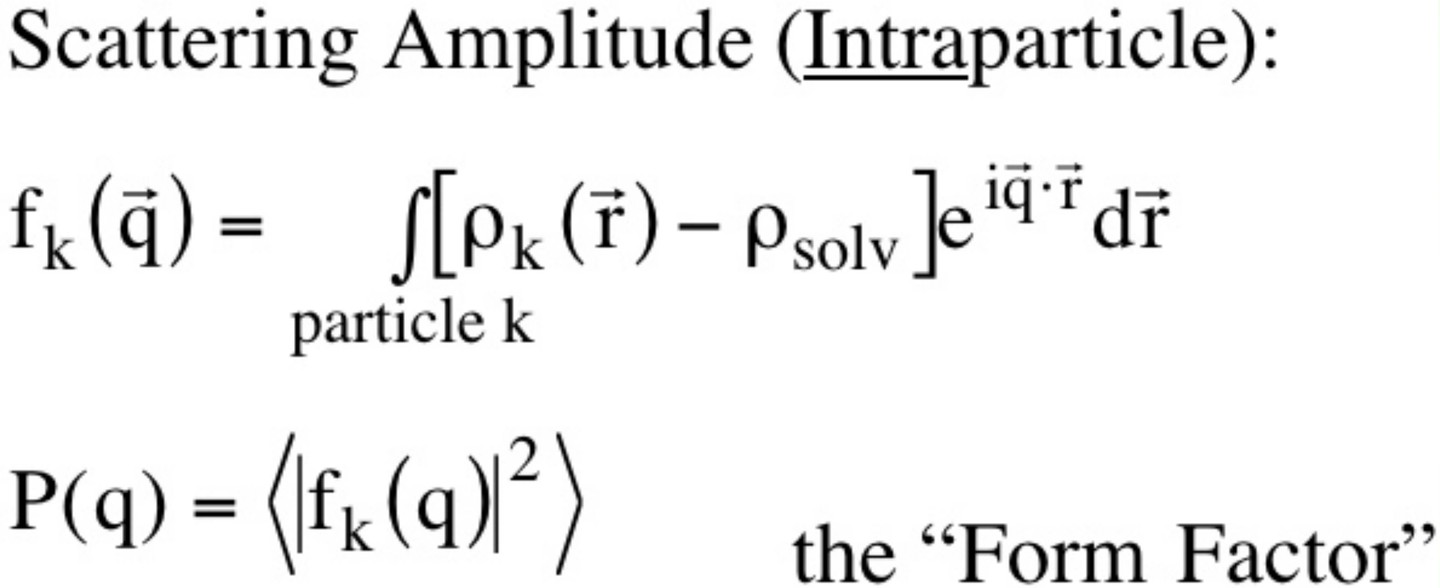


Scattered Intensity:

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{1}{V}\sum_{k=1}^{N_p}\left\langle |f_k(\vec{q})|^2 \right\rangle + \frac{1}{V}\left\langle \sum_{k=1}^{N_p}\sum_{\substack{j=1\\ j\neq k}}^{N_p} f_k(\vec{q}) f_j^*(\vec{q}) e^{i\vec{q}\cdot(\vec{r}_k - \vec{r}_j)} \right\rangle$$

Intra- Inter-

Interparticle Interference Effects



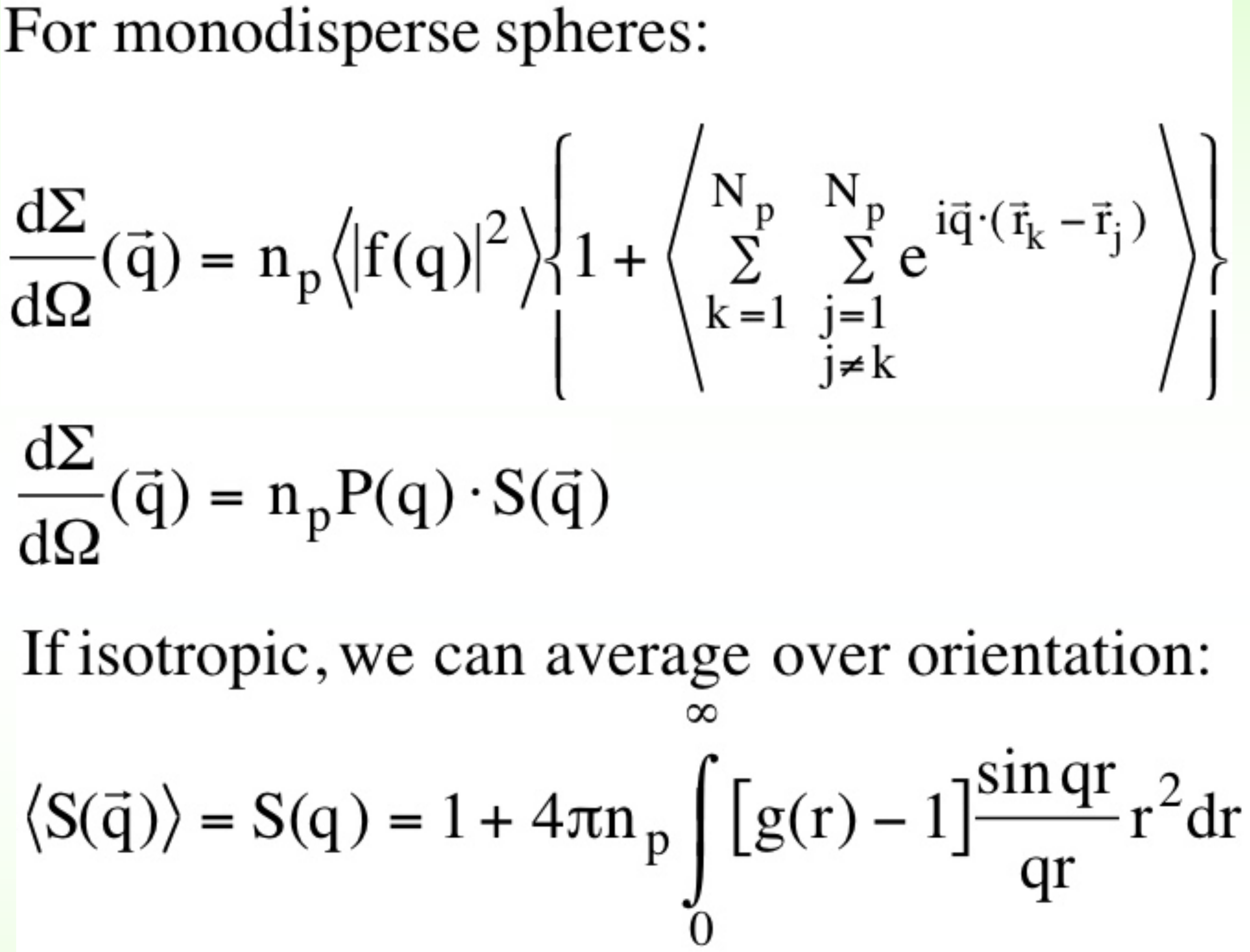
Scattering Amplitude (Intraparticle):

$$f_k(\vec{q}) = \int_{\text{particle k}} [\rho_k(\vec{r}) - \rho_{solv}] e^{i\vec{q}\cdot\vec{r}} d\vec{r}$$

$$P(q) = \left\langle |f_k(q)|^2 \right\rangle$$

the “Form Factor”

The Structure Factor



For monodisperse spheres:

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = n_p \left\langle |f(q)|^2 \right\rangle \left\{ 1 + \left\langle \sum_{k=1}^{N_p} \sum_{\substack{j=1 \\ j\neq k}}^{N_p} e^{i\vec{q}\cdot(\vec{r}_k - \vec{r}_j)} \right\rangle \right\}$$

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = n_p P(q) \cdot S(\vec{q})$$

If isotropic, we can average over orientation:

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

Note:

- S(q) is proportional to the number density of particles

- S(q) depends on g(r), the pair correlation function

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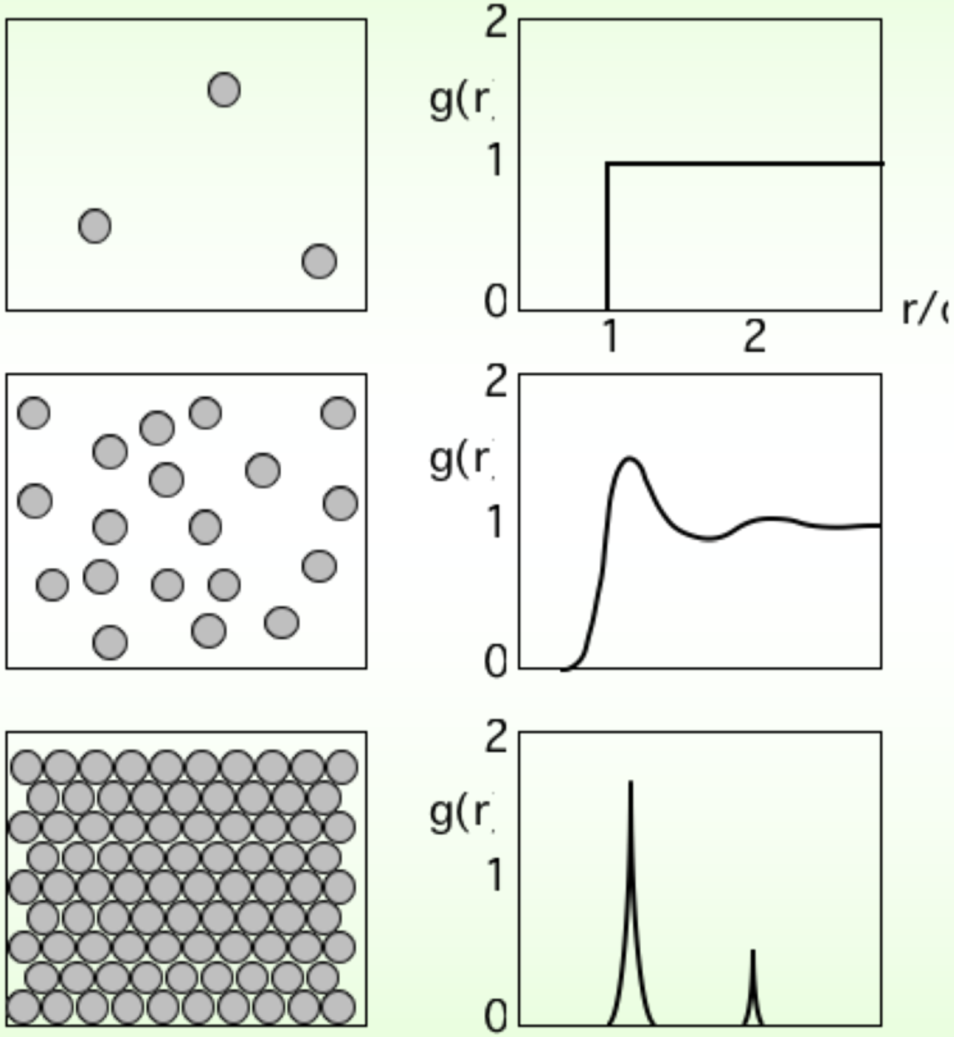
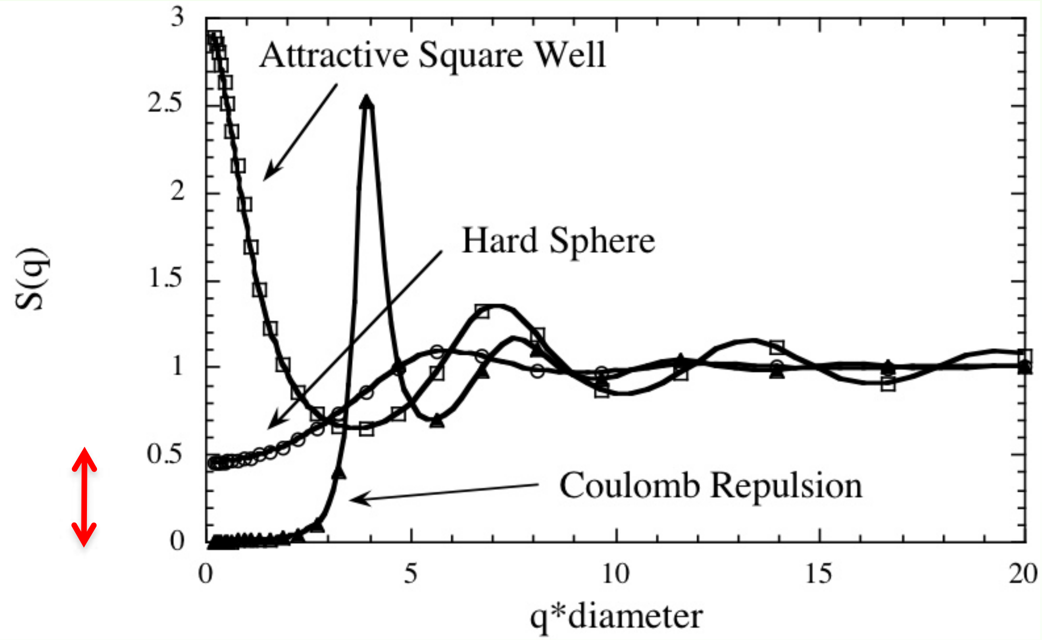
The Pair Correlation Function

- **$n_p g(r)$ is a "local" density of particles**
- **Spatial arrangement set by interparticle interactions and indirect interactions**



S(*q*) and Statistical Thermodynamics

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



Cf. compressibility of gases

$$\beta_T = -\frac{1}{V}\left(\frac{dV}{dP}\right)_T$$

$$I(q) \sim 1/\beta_T$$

The low q limit is proportional to the osmotic compressibility

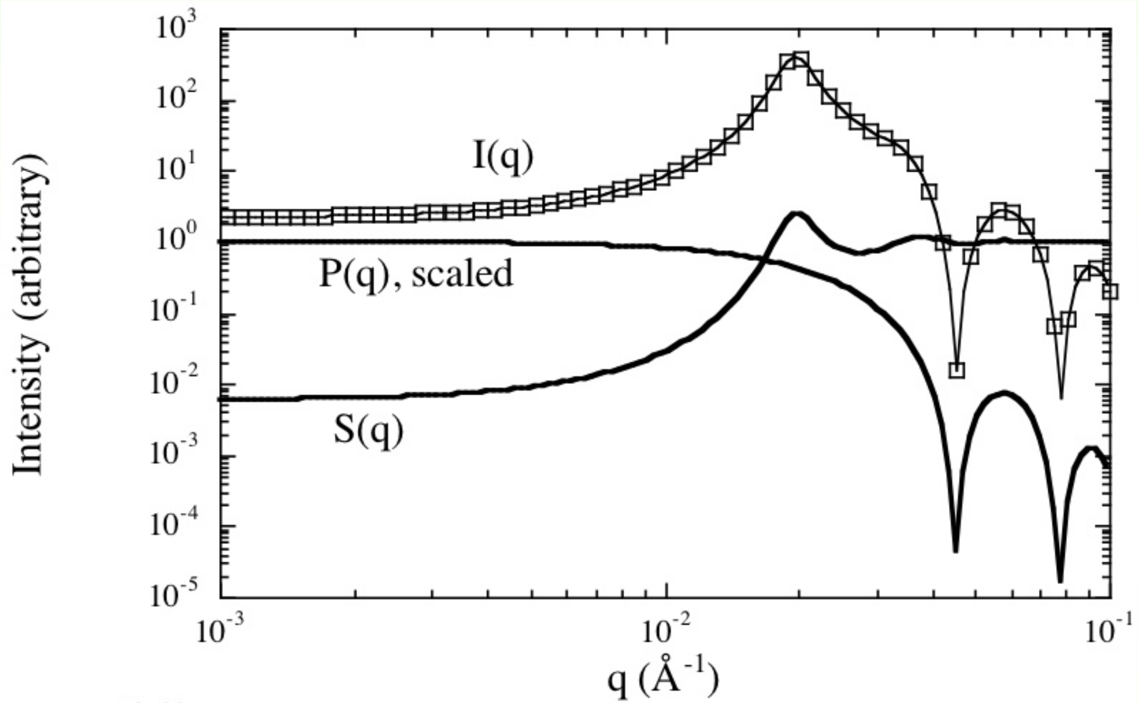
$$S(q=0) = kT\left(\frac{\partial n}{\partial \pi}\right)$$

Attractive interactions ⇒ more compressible
Repulsive interactions ⇒ less compressible

n; the number density of the particle (1/volume)

S(*q*) Reflected in the Low-*q* Intensity

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



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)?

Calculation of *S*(*q*)

Ornstein Zernike Equation:

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

- **c(r) = direct correlation function**
- **Integral = all indirect interactions**

• A second relation is necessary to relate c(r) and g(r)

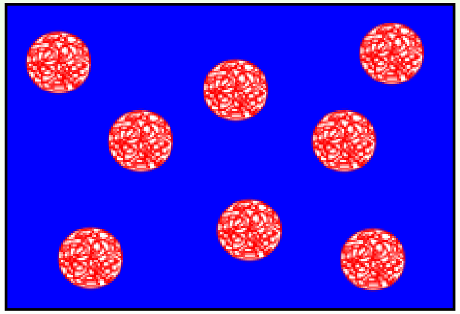
Percus-Yevick Closure - an approximation

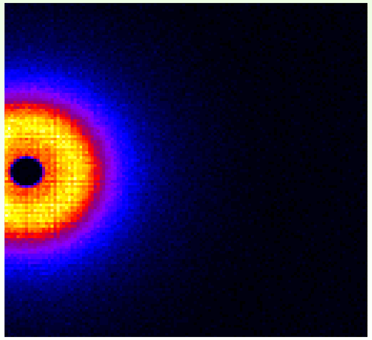
$$c(r) = g(r)\left[1 - e^{\beta u(r)}\right] \qquad \beta \equiv 1/kT$$

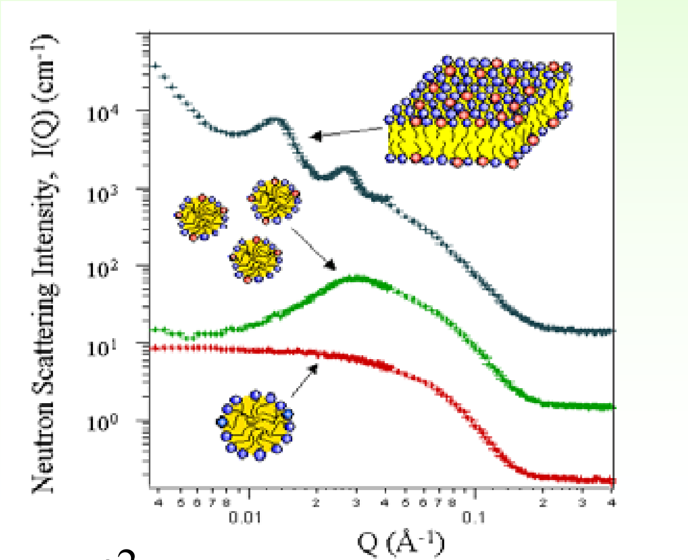
- **correct closure gives correct results**
- **in general a difficult problem**

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

What Information from SANS ?
: Particulate Systems







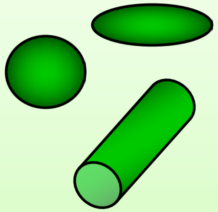
$$\frac{d\Sigma}{d\Omega}(\mathbf{Q}) = \left|\text{Fourier Transfom of } \rho(\mathbf{r})\right|^2$$

$$= \frac{N_p}{V}\left|F(Q)\right|^2 \frac{1}{N_p}\left\langle \sum_i^{N_p}\sum_j^{N_p} e^{i\mathbf{Q}\cdot(\mathbf{r}_i-\mathbf{r}_j)} \right\rangle$$

Number density

$$= n_p P(Q) S(Q)$$

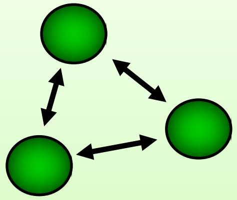
Shape and dimensions of particles



Intra-Particle interference
: Form factor

Inter-Particle interference
: Structure factor

Interaction between particles



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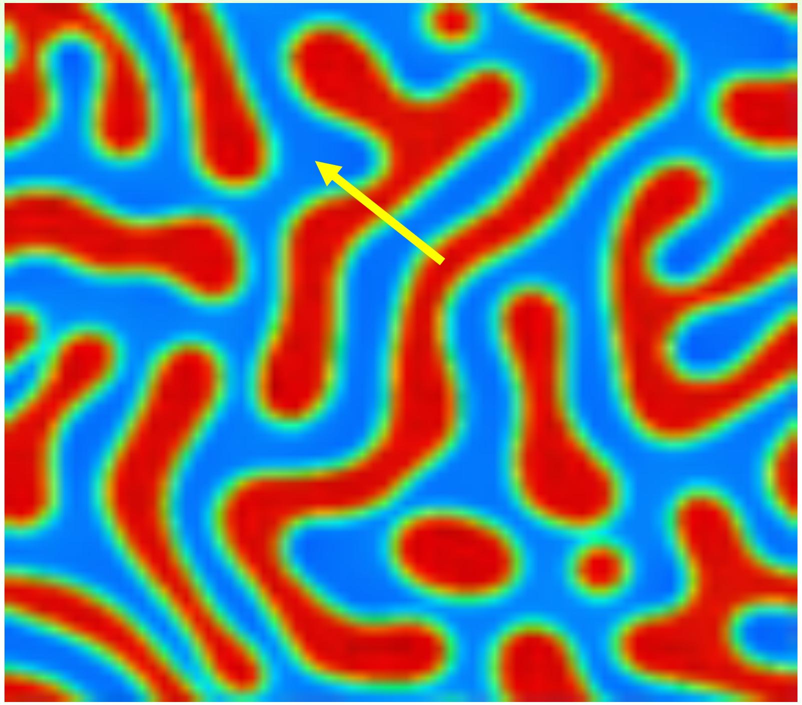
What Information from SANS ?
: Non-Particulate Systems



$$\frac{d\Sigma}{d\Omega}(Q) = 4\pi\left\langle(\Delta\rho)^2\right\rangle\int_V \gamma(r)\frac{\sin(Qr)}{Qr}r^2dr$$

Contrast

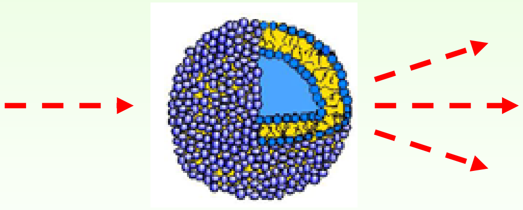
Correlation function

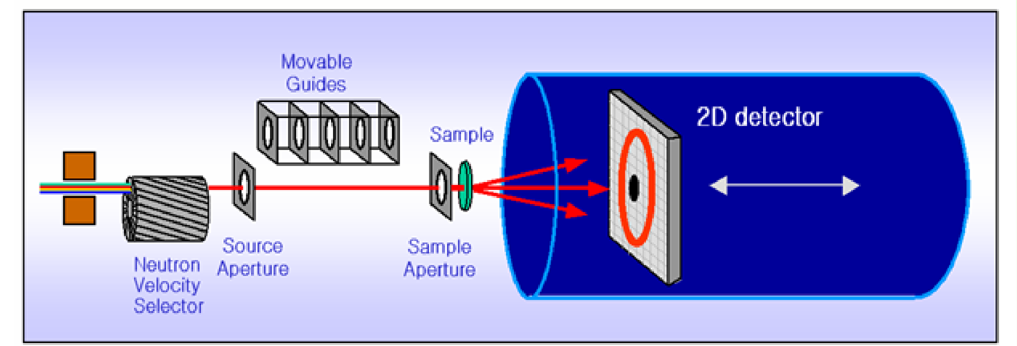
Orientation average

$$\gamma(r) = \frac{\int\langle\Delta\rho(\mathbf{r}')\Delta\rho(\mathbf{r}'+\mathbf{r})\rangle d\mathbf{r}'}{\int\langle\Delta\rho(\mathbf{r}')\Delta\rho(\mathbf{r}')\rangle d\mathbf{r}'}$$

Contents

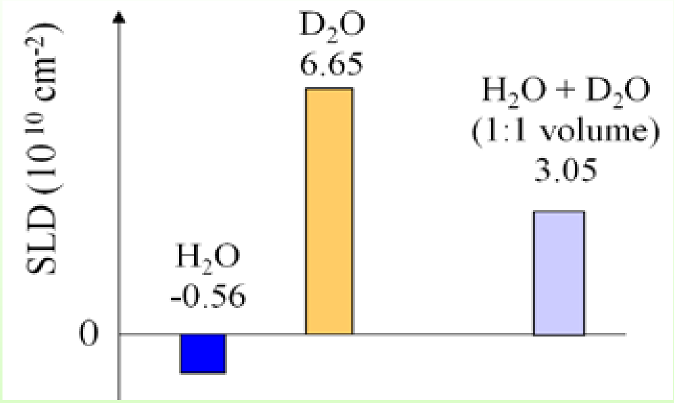
Systems that SANS Can Measure



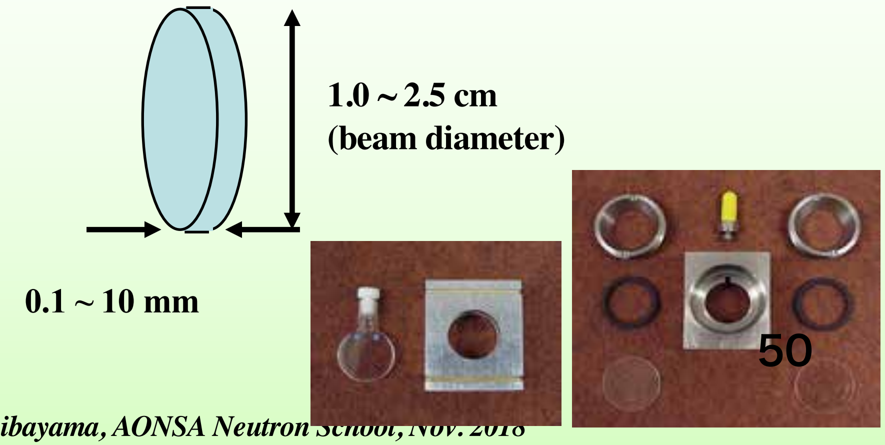


- SANS measures the bulk nanostructures of 1nm – 100's nm in solids, liquids, gel or mixtures.
- Practically, anything that has proper
  1) length scale, 2) neutron contrast and 3) sample volume

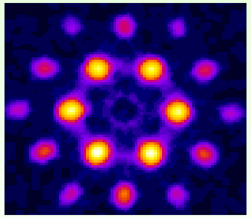
Neutron scattering length density

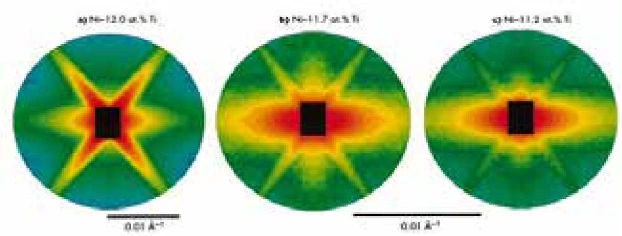


Typical sample volume

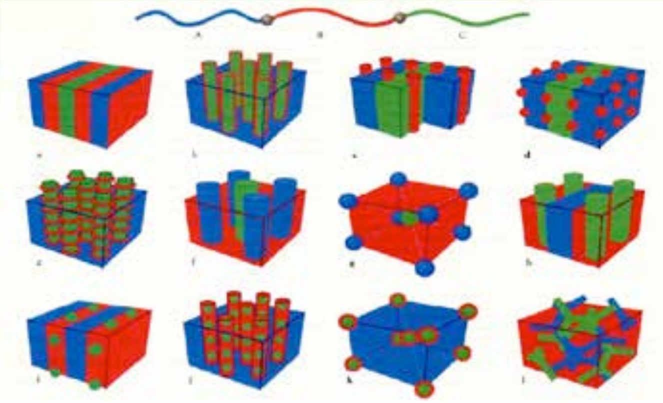


Applications of Small Angle Neutron Scattering

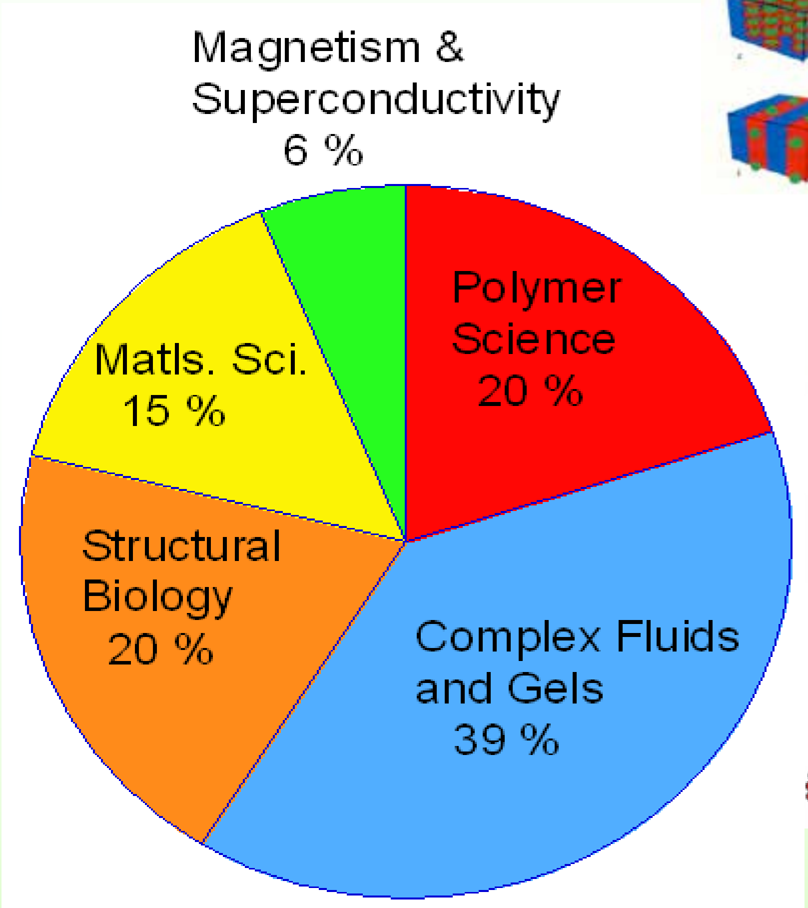




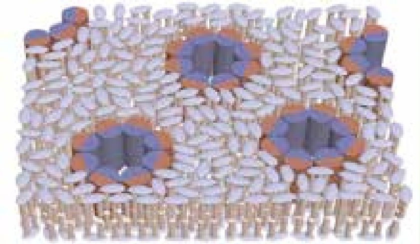
(Kostorz et al)



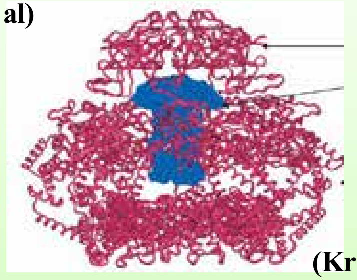
(Bates FS et al)



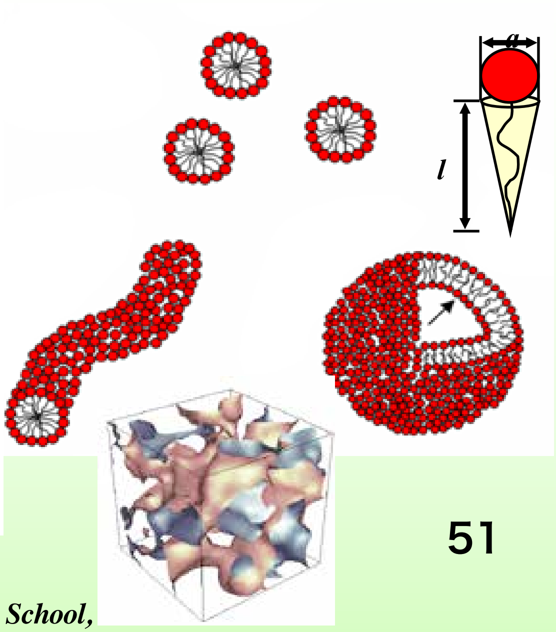
(NIST)



(Huang et al)



(Krueger et al)



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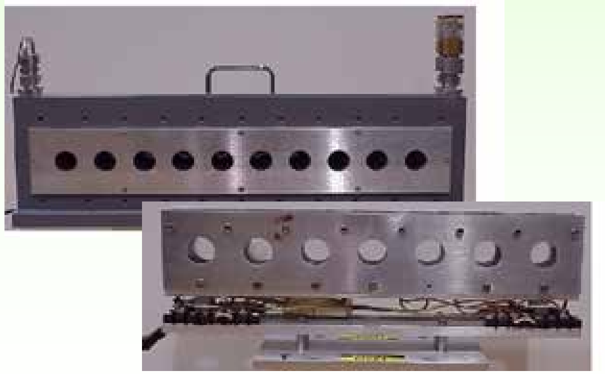
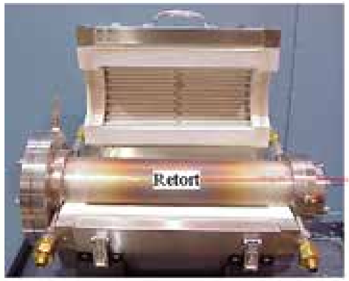
Sample Environments for SANS Exp.

Temperature control

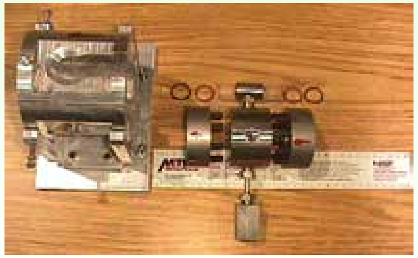


Furnace (~450C)

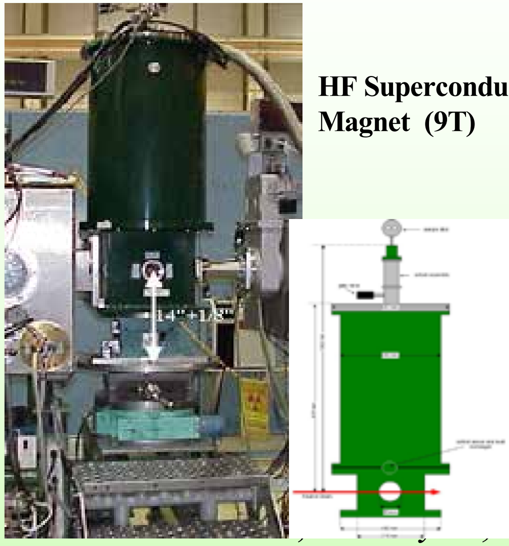


Low Temperature (CCR)

Pressure Cell (~60 kpsi)



Horizontal Field Electromagnet

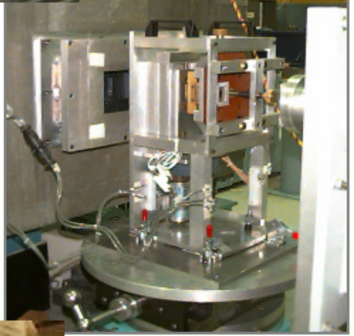


HF Superconducting Magnet (9T)

(NIST Center for Neutron Research)

Couette Shear Cell

Plate/Plate Shear Cell (Polymer melts)

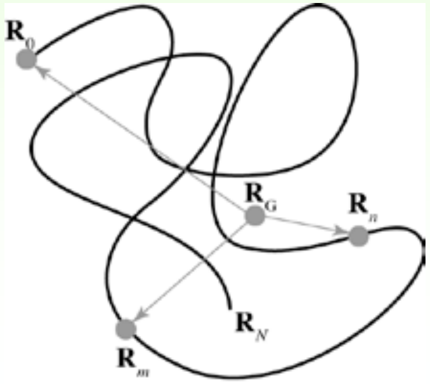


SANS Rheometer

Polymeric systems:

Radius of gyration: A measure of chain size

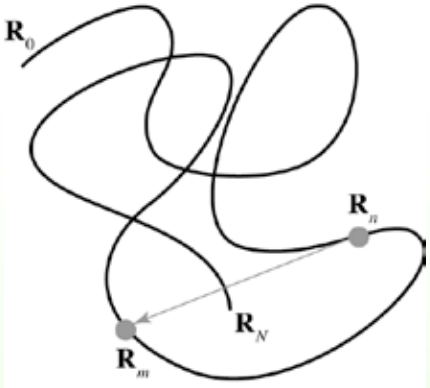
the radius of gyration



$$\mathbf{R}_G = \frac{1}{N}\sum_{n=1}^{N}\mathbf{R}_n$$

$$R_g^2 = \frac{1}{N}\sum_{n=1}^{N}\left\langle\left(\mathbf{R}_n - \mathbf{R}_G\right)^2\right\rangle$$

$$R_g^2 \equiv \frac{1}{2N^2}\sum_{n=1}^{N}\sum_{m=1}^{N}\left\langle\left(\mathbf{R}_m - \mathbf{R}_n\right)^2\right\rangle$$



for a large chain (N >> 1)

$$\left\langle\left(\mathbf{R}_n - \mathbf{R}_m\right)^2\right\rangle \approx |n-m|b^2$$

$$R_g^2 = \frac{b^2}{2N^2}\sum_{n=1}^{N}\sum_{m=1}^{N}|n-m| = \frac{Nb^2}{2}\int_0^1 x^2 \mathrm{d}x$$

$$= \frac{Nb^2}{6}$$

$$\boxed{R_g{}^2 = \frac{Nb^2}{6}}$$

ideal chain

$$R_g{}^2 = \frac{3}{5}R^2$$ **for a spherical object**

Lecture note; M. Shibayama, AONSA Neutron School, Nov. 2018

Debye fn.: the scattering function for a Gaussian chain

the segment pair corr. fn.

$$g_n(\mathbf{r}) = \sum_{m=1}^{N} \left\langle \delta\left\{\mathbf{r} - (\mathbf{R}_m - \mathbf{R}_n)\right\}\right\rangle$$

$$g(\mathbf{r}) = \frac{1}{N}\sum_{n=1}^{N} g_n(\mathbf{r}) = \frac{1}{N}\sum_{n=1}^{N}\sum_{m=1}^{N} \left\langle \delta\left\{\mathbf{r} - (\mathbf{R}_m - \mathbf{R}_n)\right\}\right\rangle$$

the form factor

$$g(\mathbf{q}) = \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} g(\mathbf{r}) = \frac{1}{N}\sum_{n=1}^{N}\sum_{m=1}^{N} \underline{\left\langle \exp\left[i\mathbf{q}\cdot(\mathbf{R}_m - \mathbf{R}_n)\right]\right\rangle}$$

Double summation

$$g(\mathbf{q}) = \frac{1}{N}\sum_{n=1}^{N}\sum_{m=1}^{N}\left[1 - \left\langle i\mathbf{q}\cdot(\mathbf{R}_m - \mathbf{R}_n)_\alpha\right\rangle - \frac{1}{2}q_\alpha q_\beta \left\langle (\mathbf{R}_m - \mathbf{R}_n)_\alpha (\mathbf{R}_m - \mathbf{R}_n)_\beta \right\rangle + \ldots\right]$$

$$= \frac{1}{N}\sum_{n=1}^{N}\sum_{m=1}^{N}\left[1 - \frac{1}{6}q^2\left\langle (\mathbf{R}_m - \mathbf{R}_n)^2\right\rangle + \ldots\right]$$

$$= g(0)\left(1 - \frac{R_g^2}{3}q^2 + \ldots\right)$$

$$\left\langle r_\alpha \right\rangle = 0, \quad \left\langle r_\alpha r_\beta \right\rangle = \frac{\left\langle r^2 \right\rangle}{3}\delta_{\alpha\beta}$$

$$\left\langle \exp\left[i\mathbf{q}\cdot(\mathbf{R}_m - \mathbf{R}_n)\right]\right\rangle = \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} \left(\frac{3}{2\pi|n-m|b^2}\right)^{3/2} \exp\left(-\frac{3r^2}{2|n-m|b^2}\right)$$

$$= \left\langle \exp\left[iq_\alpha(\mathbf{R}_{n\alpha} - \mathbf{R}_{m\alpha})\right]\right\rangle$$

$$= \exp\left[-\frac{1}{2}q_\alpha^{\,2}(\mathbf{R}_{n\alpha} - \mathbf{R}_{m\alpha})\right] = \exp\left[-\frac{|m-n|}{6}b^2q^2\right]$$

FT of Gaussian function

the Debye fn.

$$g(\mathbf{r}) = \frac{1}{N}\sum_n\sum_m \left\langle \exp\left[i\mathbf{q}\cdot(\mathbf{R}_m - \mathbf{R}_n)\right]\right\rangle = \frac{1}{N}\sum_n\sum_m \exp\left[-\frac{|m-n|}{6}b^2q^2\right]$$

$$= Ng_D\left((qR_g)^2\right)$$

$$g_D\left((qR_g)^2\right) \equiv g_D(x) = \frac{2}{x^2}\left(e^{-x} - 1 + x\right)$$

$$g_D(x) = \frac{2N}{x^2}\left(e^{-x} - 1 + x\right), \quad x \equiv R_g^{\,2}q^2$$

$$g_D(q) = \begin{cases} N(1 - q^2R_g^{\,2}/3), & qR_g << 1 \\ 2N/q^2R_g^{\,2}, & qR_g >> 1 \end{cases}$$

Lecture note; M. Shibayama, AONSA Neutron School, Nov. 2018

Interacting systems (polymer solutions, polymer blends)

Polymer solutions

$$\frac{(b_1 v_0 / v_1 - b_0)^2 N_A c}{I(q) m^2} = \frac{1}{zmP(q)} + \frac{N_A v_{ex}}{m^2} c$$

$$= \frac{1}{MP(q)} + 2A_2 c$$

m; the monomer molecular weight, N_A; the Avogadro number, v_{ex}; the excluded volume, *M*; the molecular weight

the second virial coefficient

$$A_2 = \frac{N_A v_{ex}}{2m^2} = \frac{N_A b^3}{2m^2}(1 - 2\chi)$$

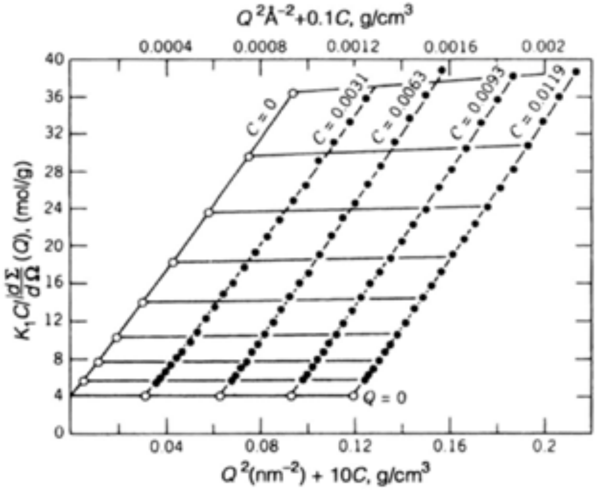
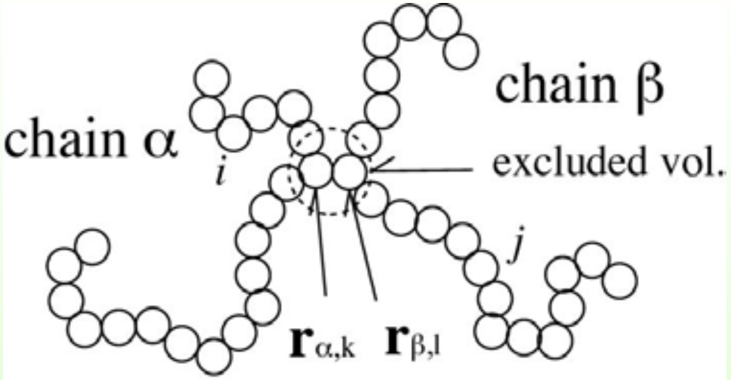


Fig. 8.2 Zimm plot of data in Fig. 8.1. The open circles are the result of extrapolation to zero *C* and zero *Q* (≡ *q*) (Kirste *et al.* 1975). Reprinted with permission from Wignall (1987).

the scattered intensity (*Zimm equation*)

$$\frac{(a_1 v_0 / v_1 - a_0)^2 N_A c}{I(q) m^2} = \frac{1}{M}\left[1 + \frac{1}{3} R_g{}^2 q^2 + \ldots\right] + 2A_2 c$$



the *de Gennes scattering function* for polymer blend

$$\frac{(b_1 - b_2)^2}{v_0} \cdot \frac{1}{I(q)} = \frac{1}{S(q)} = \frac{1}{\phi_1 z_1 g_D(q, z_1)} + \frac{1}{\phi_2 z_2 g_D(q, z_2)} - 2\chi$$

Self-standing nano-emulsion

Kawada, et al., Langmuir, *2010*, **26**, 2430.

self-standing
Nano-emulsion

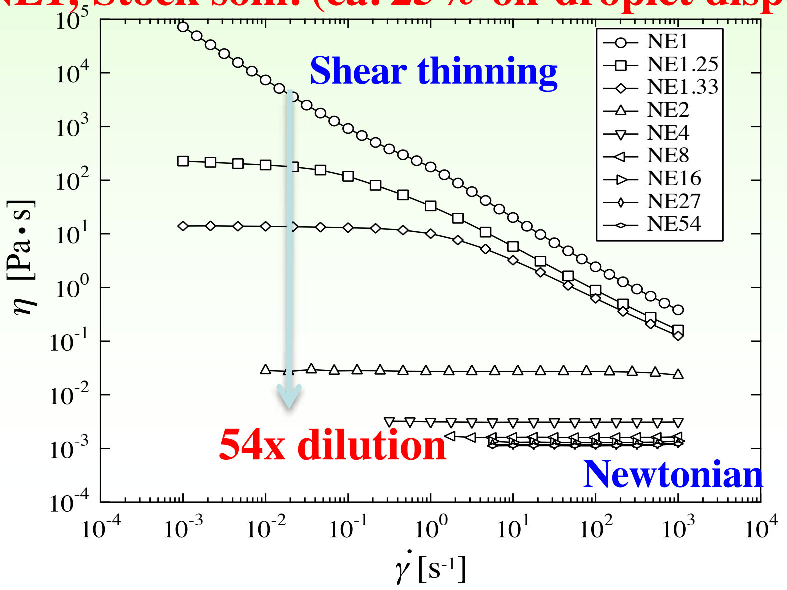
Transmission micrograph

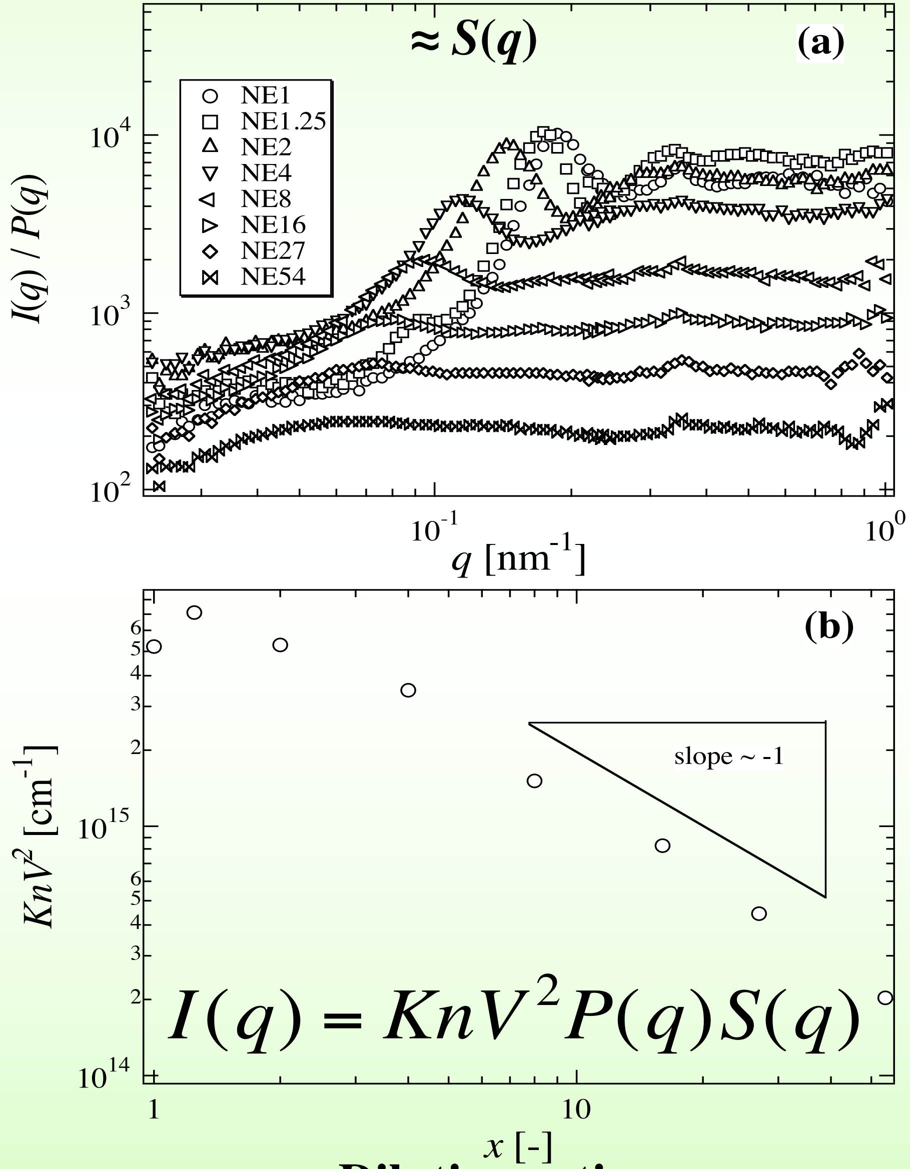
About 25% oil droplet
with small amount of anionic surfactant
obtained by high-pressure extrusion

Kao Co. Ltd.

Rheological behavior

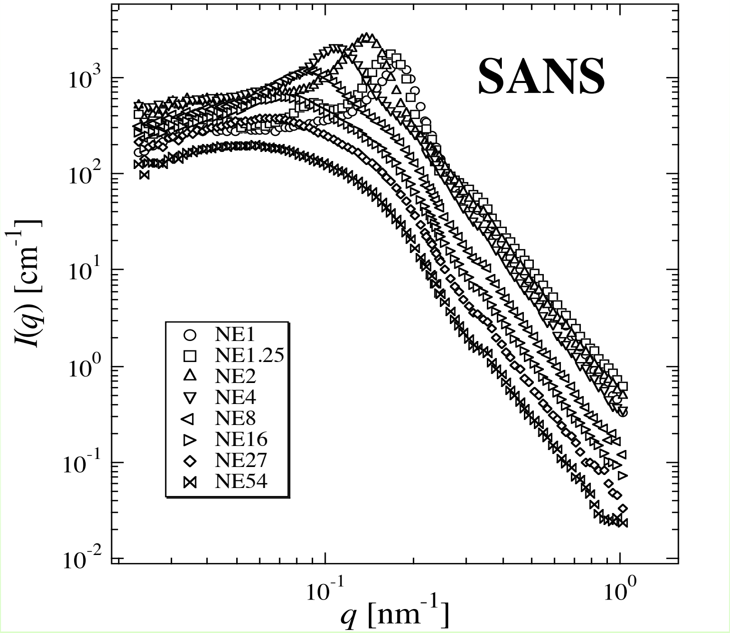
NE1; Stock soln. (ca. 25% oil-droplet dispersion)





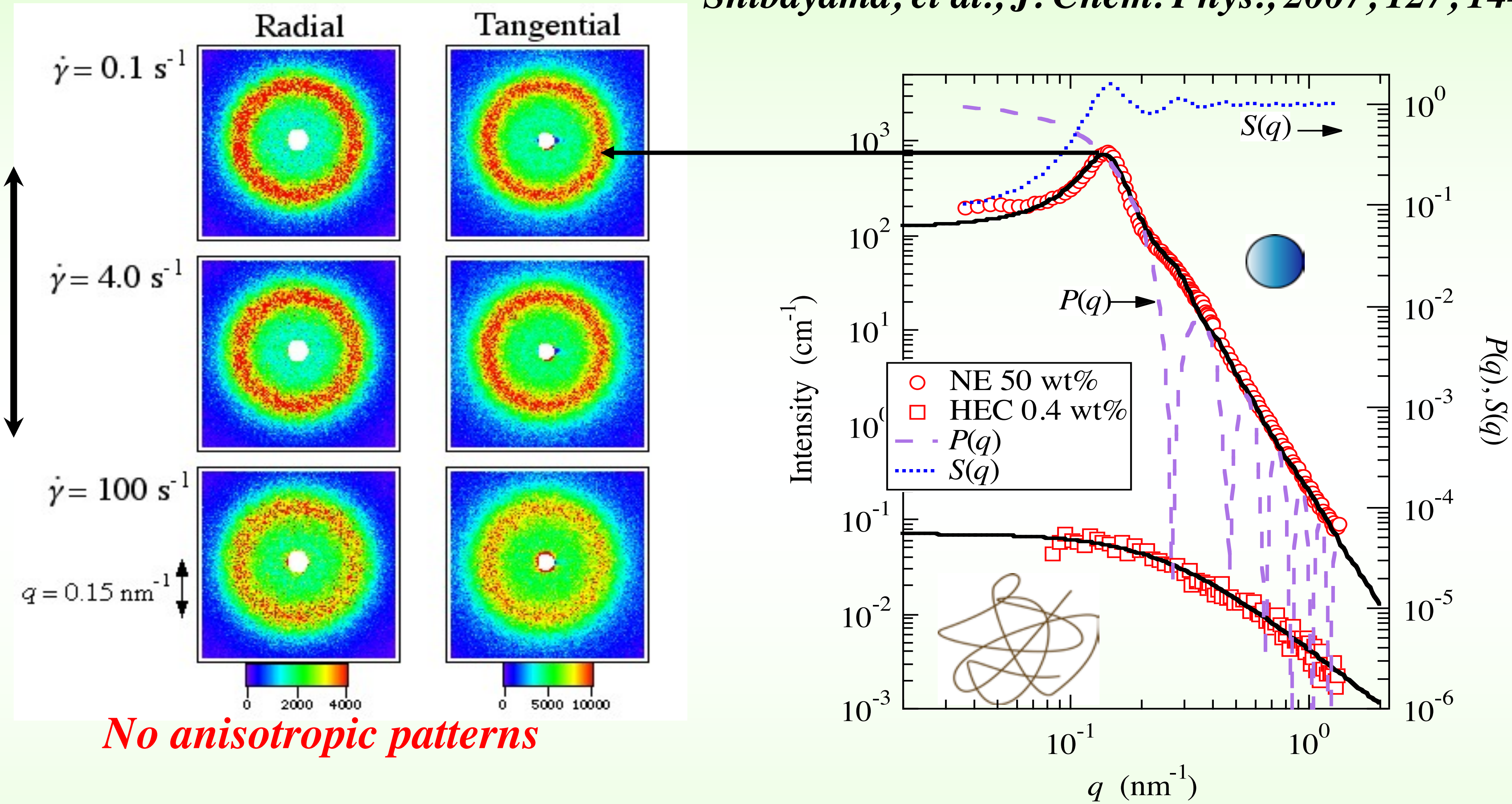
$$I(q) = KnV^2P(q)S(q)$$

Dilution ratio, *x*



2D SANS Patterns of Shake Gel

Shibayama, et al., J. Chem. Phys., 2007, 127, 144507.



No anisotropic patterns

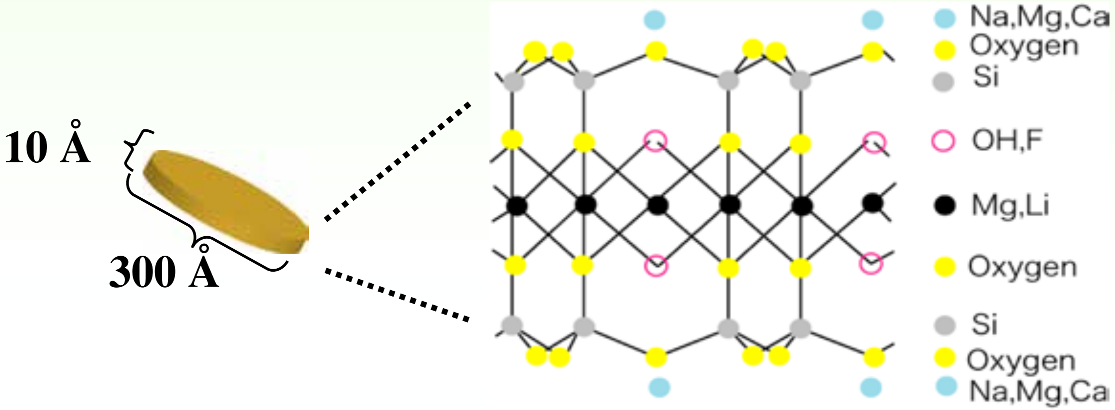
The shape of the NE and the inter-particle distance are preserved and only the long-range inhomogeneities increase by shearing.

shake gel composed of clay-PEO mixture

Takeda, et al., Macromolecules, 2010, 43, 7793.

samples

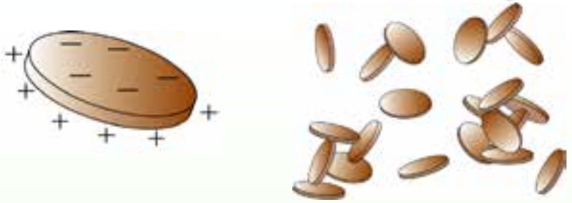
- **Laponite (XLG) (clay platelet)**



- **poly(ethylene oxide) (PEO)**

  $M_w = 400{,}000$

$\left[CH_2CH_2O\text{--} \right]_n$



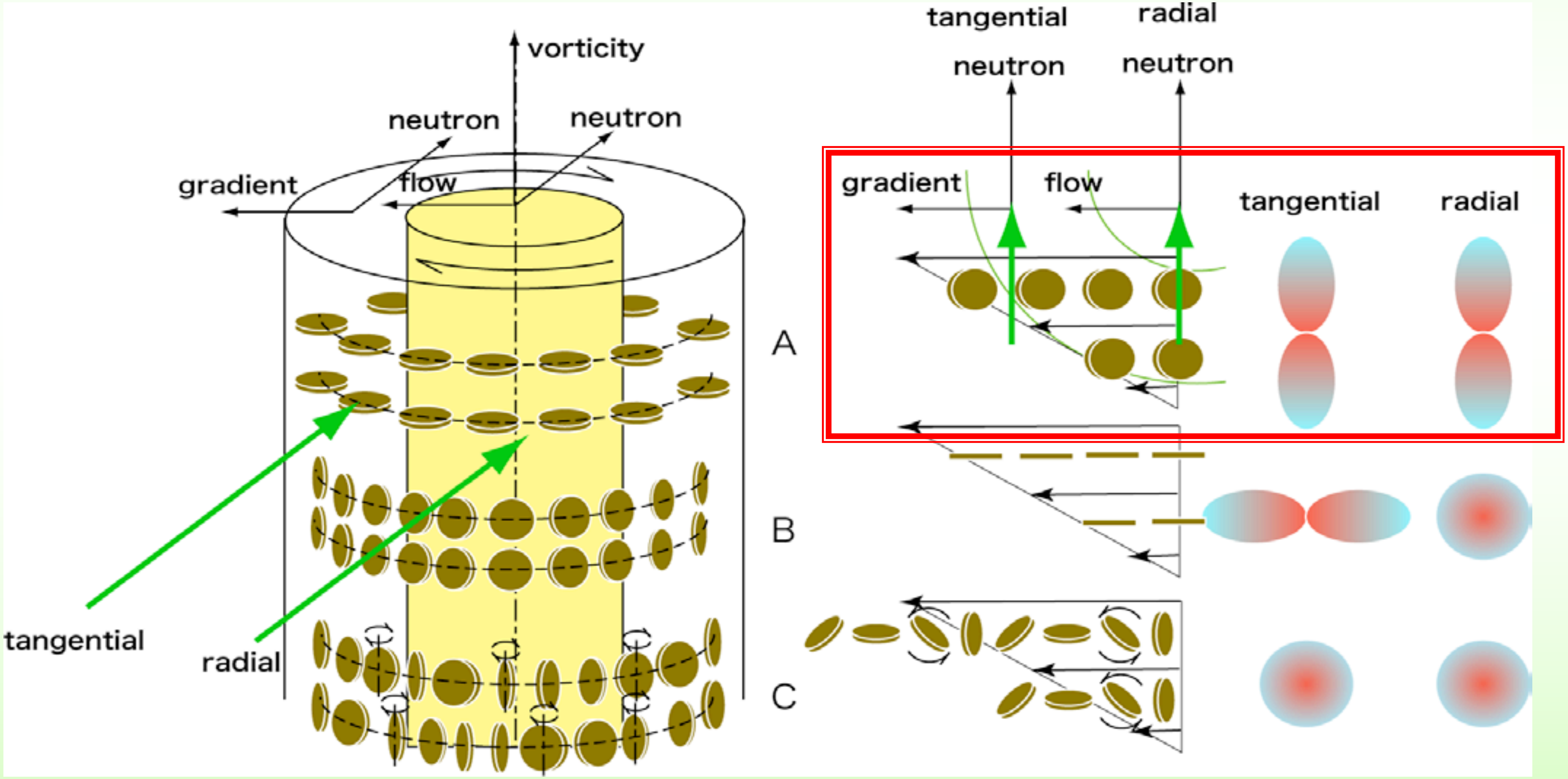
- **water**

H_2O and D_2O mixtures for SANS
(contrast variation SANS)

Clay Orientation in a flow field

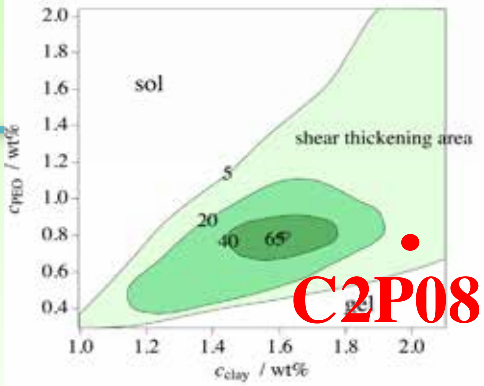
"Gedankenexperiment"

Schematic illustration showing the relationship between the anisotropy of scattering intensity and clay's orientation.



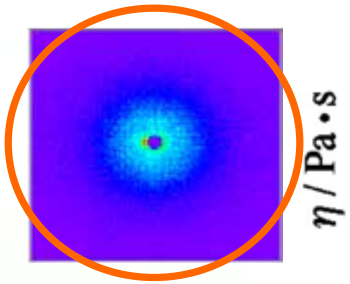
Lecture note; M. Shibayama, AONSA Neutron School, Nov. 2018

Rheology and SANS measurements

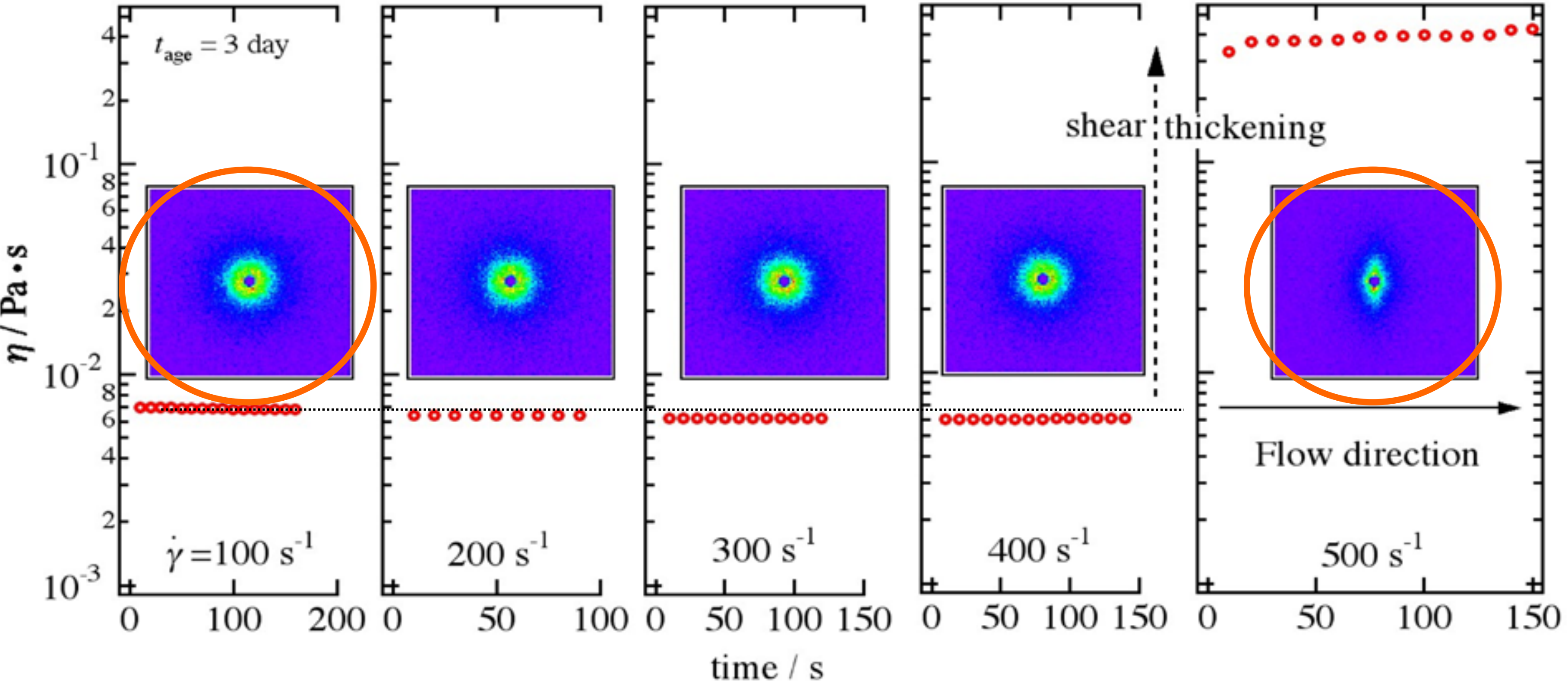


C2P08 ϕ_{D2O} =1 t_{age} = 3 day

SDD = 8 m, 4m



$\dot{\gamma}$= 0 s^{-1}

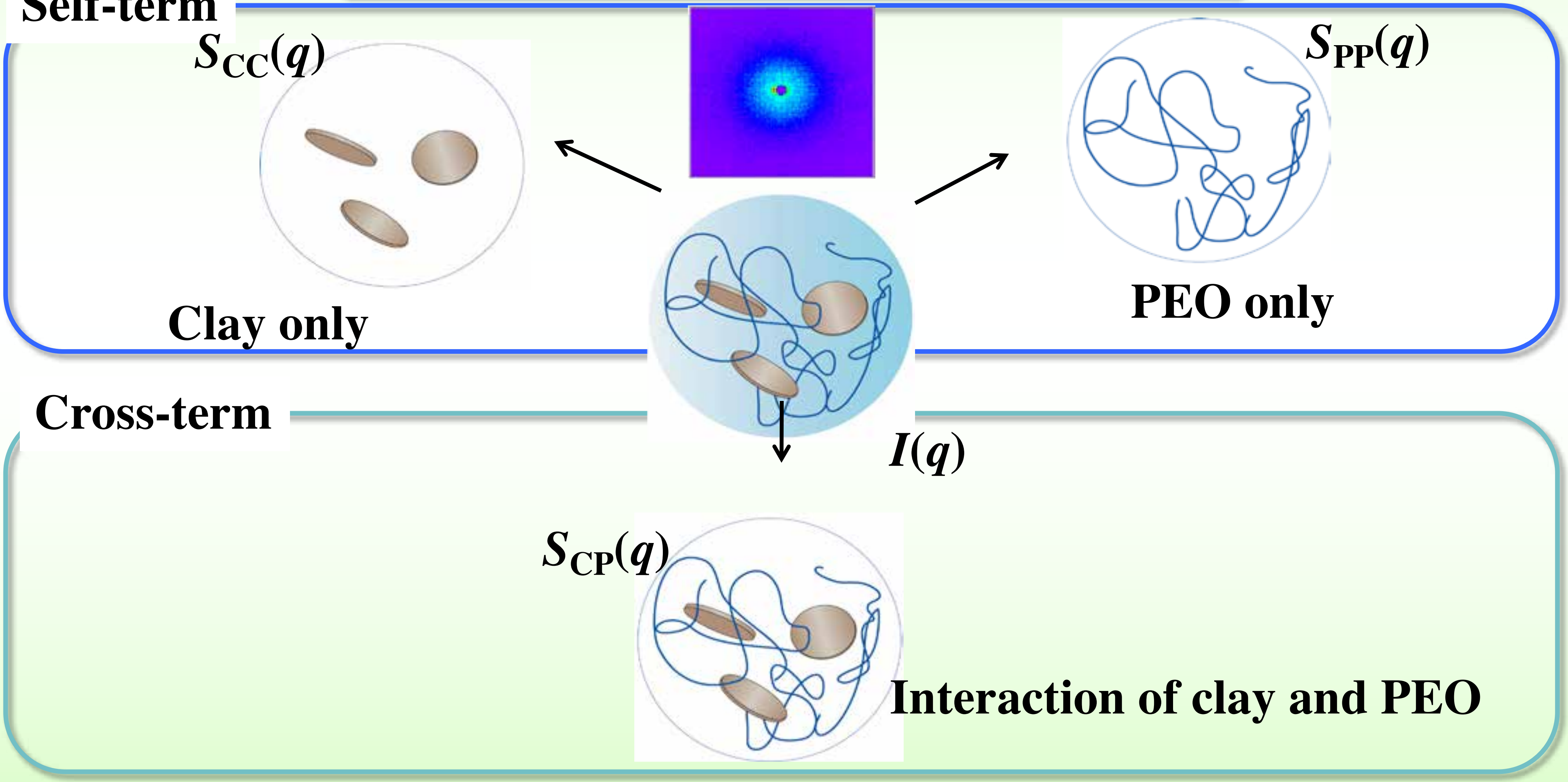


The scattering pattern changed to anisotropic at 500 s^{-1}.

To investigate $\dot{\gamma}$ = 0, 100, 500 s^{-1} more precisely, CV-SANS was applied.

Scattering from three-component systems

$$I(q) \approx \Delta\rho_{\mathrm{C}}{}^{2} S_{\mathrm{CC}}(q) + 2\Delta\rho_{\mathrm{C}}\Delta\rho_{\mathrm{P}} S_{\mathrm{CP}}(q) + \Delta\rho_{\mathrm{P}}{}^{2} S_{\mathrm{PP}}(q)$$



Self-term

$S_{\mathrm{CC}}(q)$

Clay only

$S_{\mathrm{PP}}(q)$

PEO only

$I(q)$

Cross-term

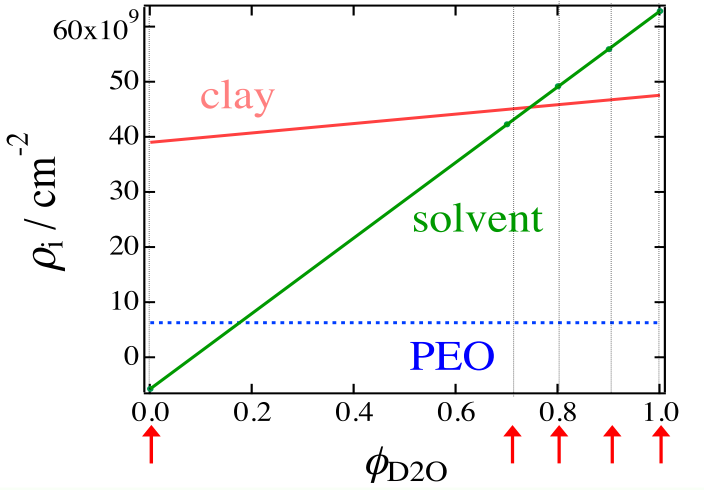
$S_{\mathrm{CP}}(q)$

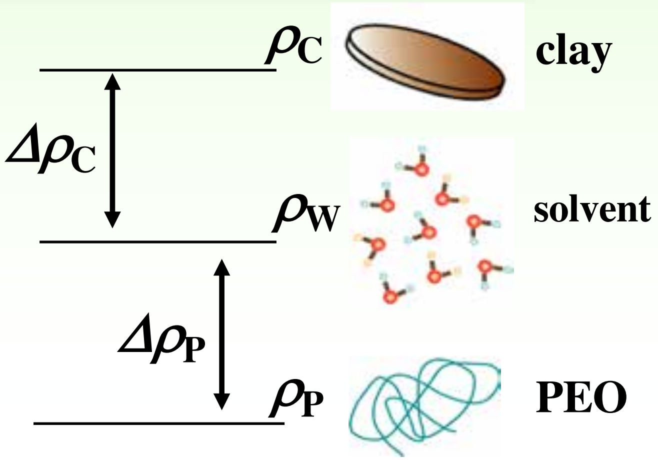
Interaction of clay and PEO

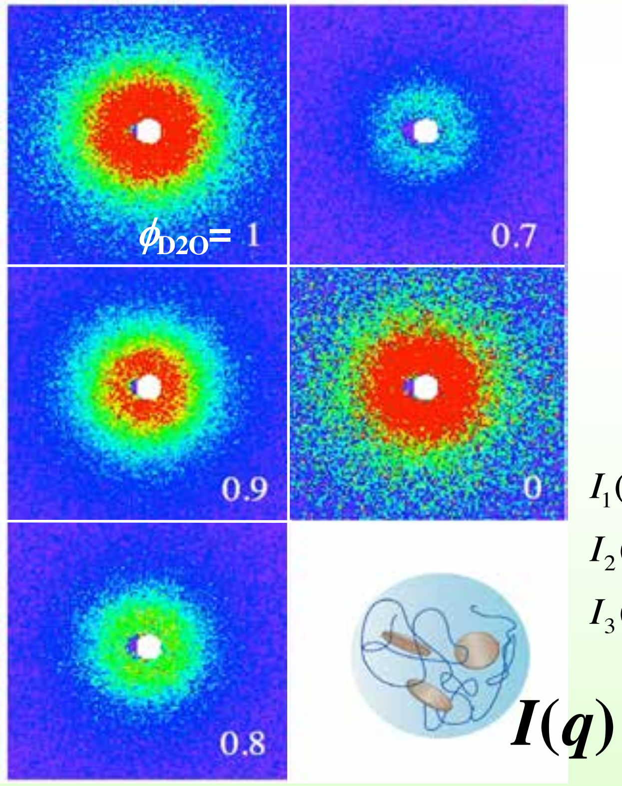
Lecture note; M. Shibayama, AONSA Neutron School, Nov. 2018

Contrast Variation SANS

$$I(q) \approx \Delta\rho_C{}^2 S_{CC}(q) + 2\Delta\rho_C \Delta\rho_P S_{CP}(q) + \Delta\rho_P{}^2 S_{PP}(q)$$







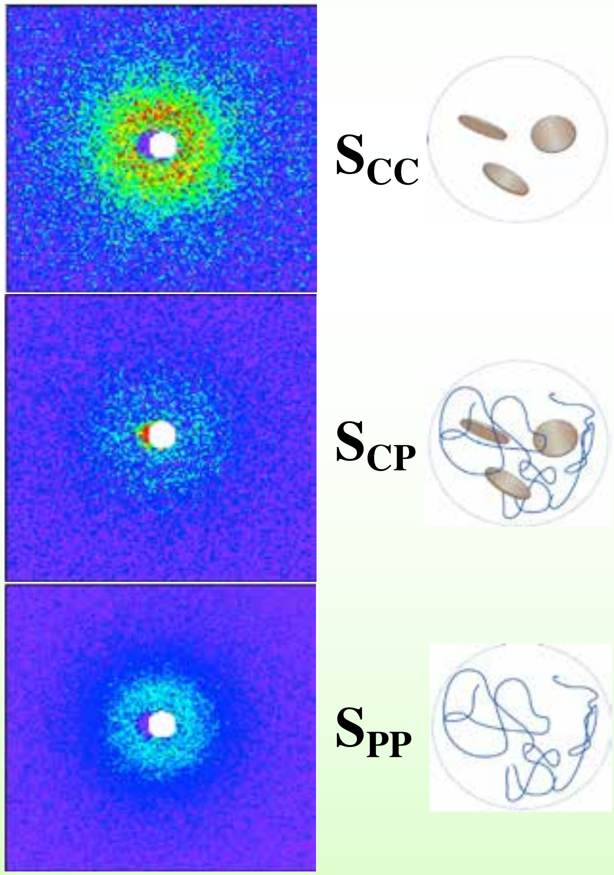
singular value decomposition

$$I_1(q) \approx {}^1\Delta\rho_C{}^2 S_{CC}(q) + 2{}^1\Delta\rho_C{}^1\Delta\rho_P S_{CP}(q) + {}^1\Delta\rho_P{}^2 S_{PP}(q)$$

$$I_2(q) \approx {}^2\Delta\rho_C{}^2 S_{CC}(q) + 2{}^2\Delta\rho_C{}^2\Delta\rho_P S_{CP}(q) + {}^2\Delta\rho_P{}^2 S_{PP}(q)$$

$$I_3(q) \approx {}^3\Delta\rho_C{}^2 S_{CC}(q) + 2{}^3\Delta\rho_C{}^3\Delta\rho_P S_{CP}(q) + {}^3\Delta\rho_P{}^2 S_{PP}(q)$$

$$\vdots$$

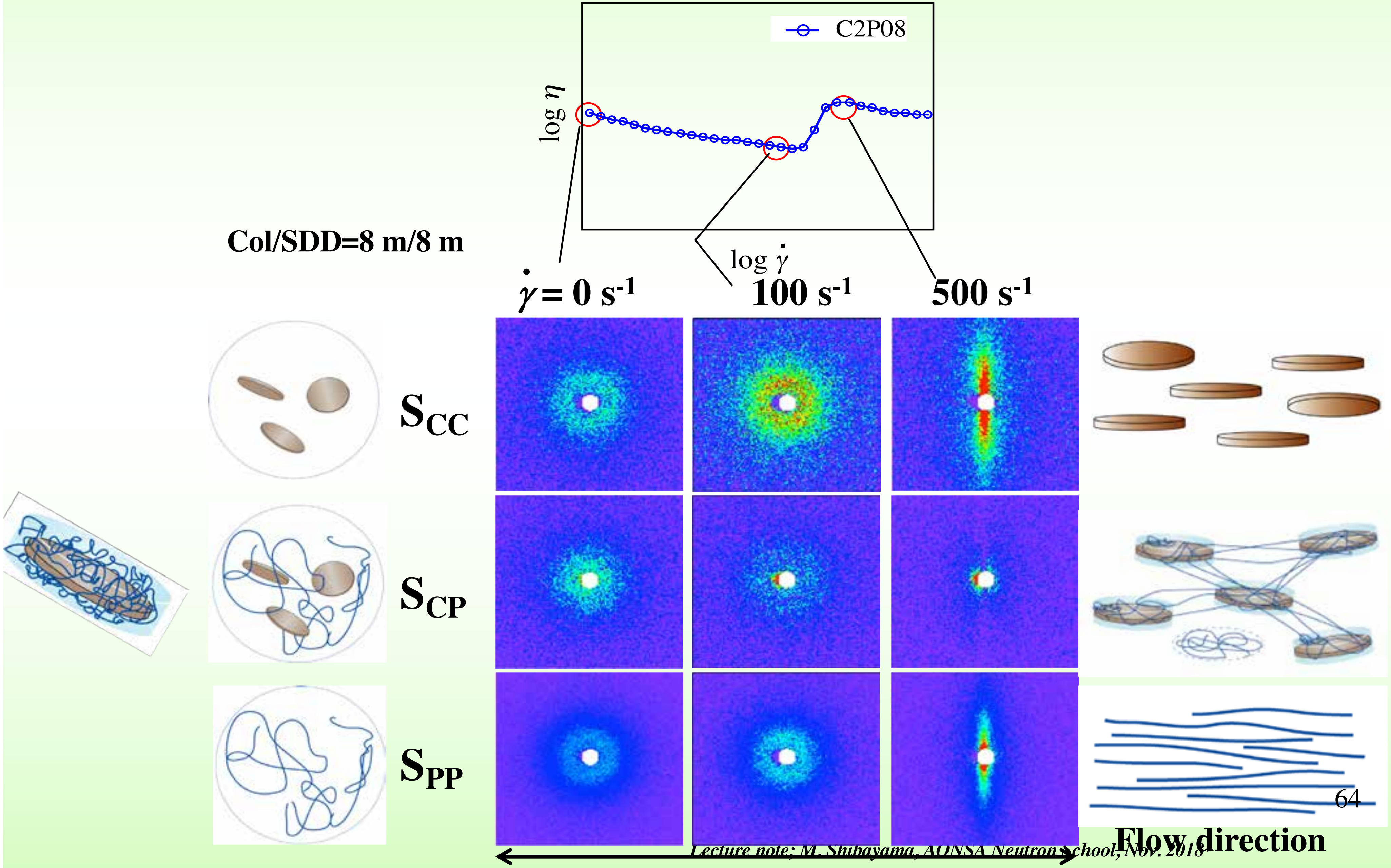


$I(q)$ measurements

Partial scatt. fun.

2D scattering Functions for C2P08

Col/SDD=8 m/8 m



Contents

1. Introduction
2. Basic theory
3. Dilute systems
4. Concentrated/bulk systems
5. Applications
6. **Summary and references**

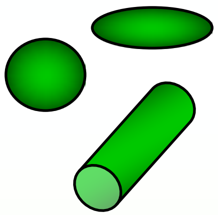
Summary: SANS

$$\frac{d\Sigma}{d\Omega}(\mathbf{Q}) = \left|\text{Fourier Transfom of } \rho(\mathbf{r})\right|^2$$

$$= \frac{N_p}{V}\left|F(Q)\right|^2 \frac{1}{N_p}\left\langle \sum_{i}^{N_p}\sum_{j}^{N_p} e^{i\mathbf{Q}\cdot(\mathbf{r}_i-\mathbf{r}_j)}\right\rangle$$

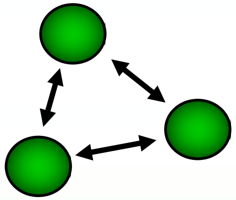
Number density

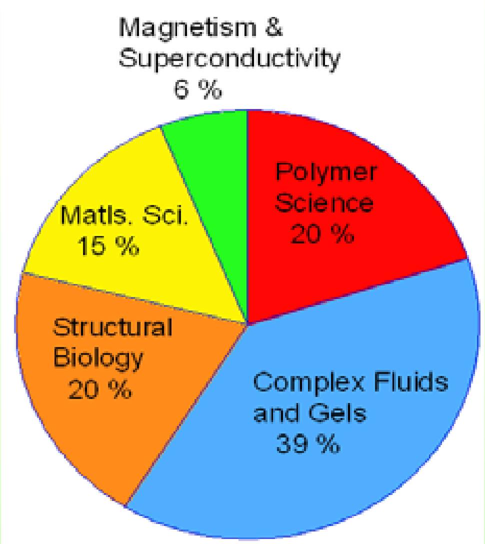
$$= n_p \underbrace{P(Q)}\underbrace{S(Q)}$$



Intra-Particle interference
: Form factor

Inter-Particle interference
: Structure factor





Small-angle neutron scattering is a very powerful technique to investigate nano-scale structures in a broad range of science and engineering.

Lecture note; M. Shibayama, AONSA Neutron School, Nov. 2018

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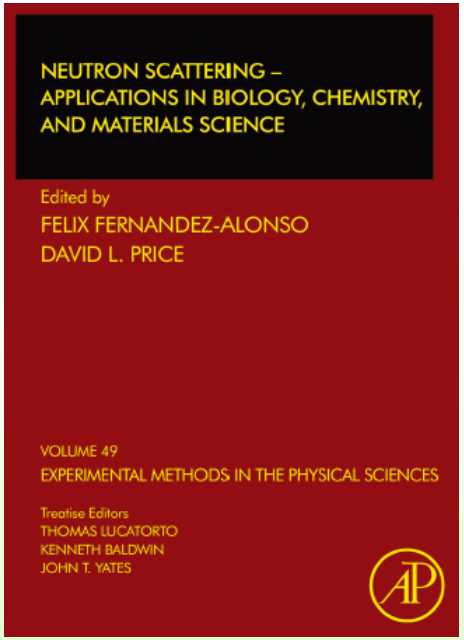

NEUTRON SCATTERING –
APPLICATIONS IN BIOLOGY, CHEMISTRY,
AND MATERIALS SCIENCE

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