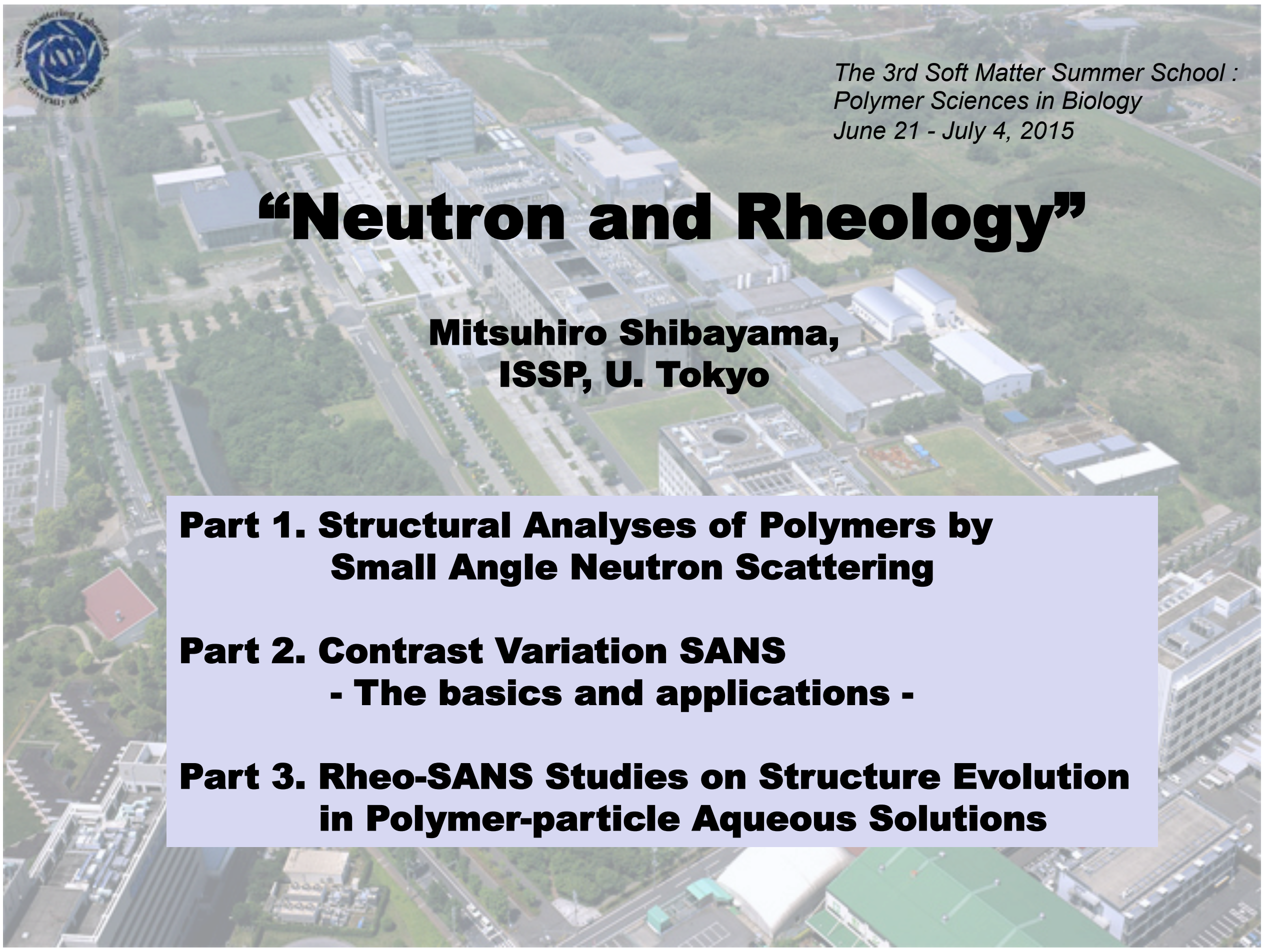

*The 3rd Soft Matter Summer School :*
*Polymer Sciences in Biology*
*June 21 - July 4, 2015*

# "Neutron and Rheology"

**Mitsuhiro Shibayama,**
**ISSP, U. Tokyo**

**Part 1. Structural Analyses of Polymers by Small Angle Neutron Scattering**

**Part 2. Contrast Variation SANS - The basics and applications -**

**Part 3. Rheo-SANS Studies on Structure Evolution in Polymer-particle Aqueous Solutions**

## Kashiwa Campus, U. Tokyo


One of three major campuses of U. Tokyo

The 3rd Soft Matter Summer School :
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1. **Introduction**
2. **Neutron and neutron scattering**
3. **Neutron scattering theory**
4. **Small angle Scattering**
5. **Applications**

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# Scattering vs spectroscopy

Spectroscopy
Scattering

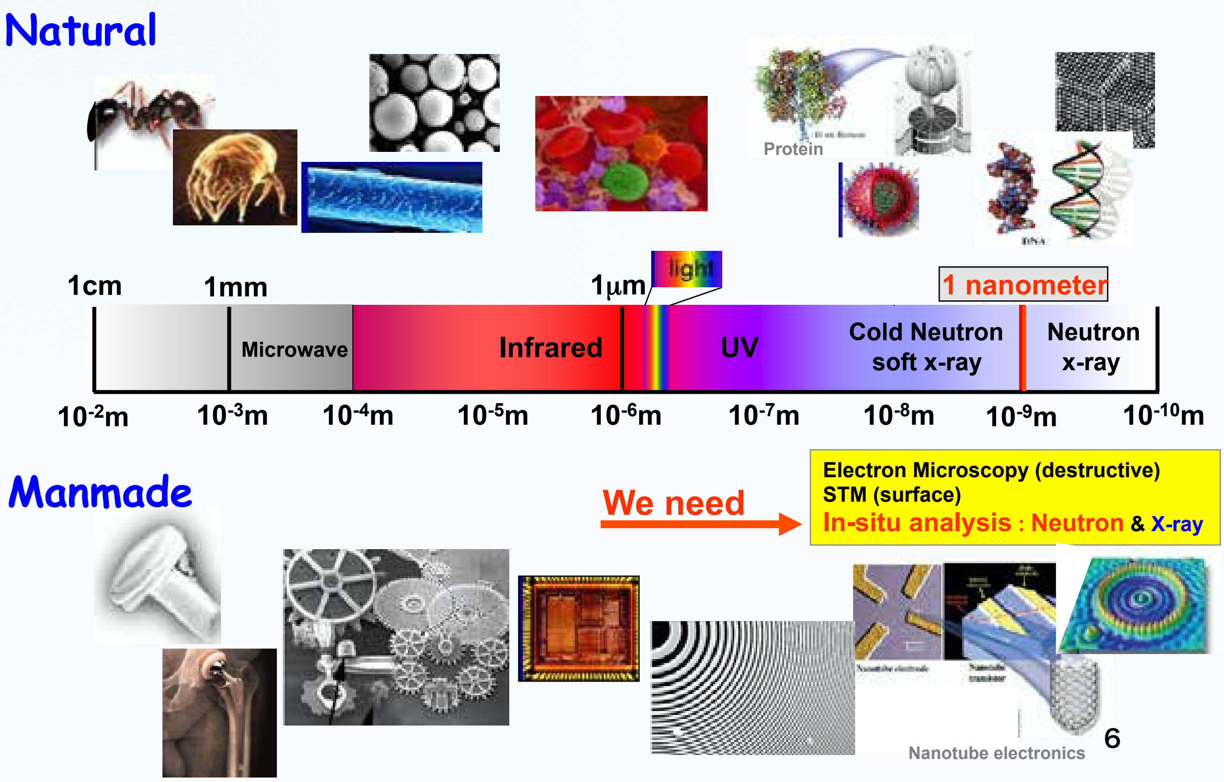
**The first observation of total ellipse in the South Pole**

~ 8 am, November, 24, 2003 by NHK
http://www.neptune.carina.gr.jp/same/solaec03/



# Towards Nanometer Technology

*Courtesy of S. Choi, KAIST*



# Nano-structure characterization

SEM

AFM

**Electron microscopy,**
**Atomic microscopy:**
*easy, but local structure,*
*thin film or surface only*


**Light scattering**
*mesoscopic structure*
*necessary to be transparent*

SAXS (Lab.)

SAXS (SPring-8)

**X-ray scattering**
*(lab): easy, but weak intensity*
*(large facility): strong beam,*
*but irradiation damage*


SANS (J-PARC/JRR-3)

**Neutron scattering**
*(large facility): difficult to get beam time,*
*low-resolution, difficult for deuteration,*
*but large contrast*

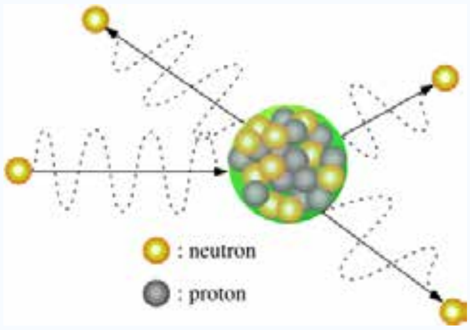


# Neutron

## What is Neutron?

$m_n \sim 1g/N_{Avogadro}$

Radius; 1.5 x $10^{-13}$ cm ($10^{-5}$ of the radius of hydrogen atom)
Mass; 1.6749 x $10^{-27}$ kg (nearly equal to that of proton)
Charge; $10^{-18}$ e (substantially zero)
Half-life time; 10.3 min (n -> p + meson)
Quantum spin number; 1/2




## Generation of neutrons:

Atomic reactor or accelerator

## Kinds of neutrons

Cold neutrons; $E \leq 0.002$ eV
Thermal neutrons; $0.002 \leq E \leq 0.5$ eV
Epithermal; $0.5 \leq E \leq 500$ eV
Fast neutrons; $500 \text{ eV} \leq E$

***Similar to***
***the electromagnetic wave,***
***i.e., g-ray, X-ray, UV, VL, IR, …***

## History of neutron scattering:

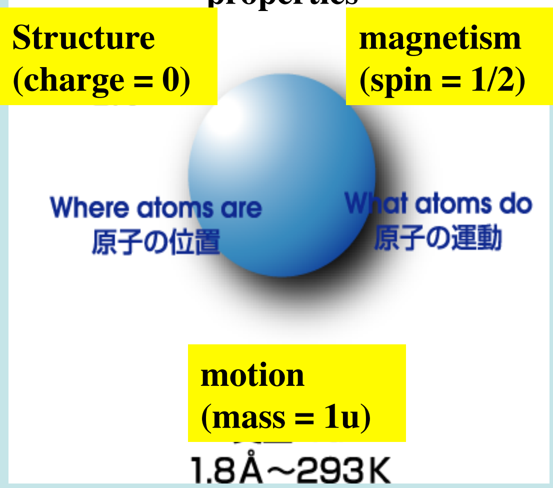
Discovery: Chadwick (1932)
Observation of diffraction (1936)
Polymer research by neutron scattering (1972)

Chadwick, Nobel winner, 1935

Brockhouse & Shull, Nobel winner, 1994

## Sizes of neutron and atom

Outstanding contribution to due to the three characteristic properties

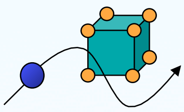



question:
If the diameter of Tokyo Dome (~ 100m), how large are the atom and neutron?
(1) apple (~ 10cm),
(2) orange (~ 5cm),
(3) Japanese pinball (11mm),
(4) Jintan ball (1mm)

## Why Neutrons ?

| Mass | No Charge | Spin 1/2 |
|---|---|---|

No charge → Deep penetration



Wavelength ~ Å, nm (thermal & cold neutron) → Atomic length scale & Nano length scale

Energy ~ meV → Same magnitude as basic excitations in solids

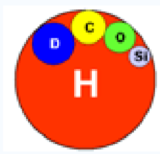
*(solid state physics)*

Spin =1/2 → Magnetic structure & dynamics

*(solid state physics)*

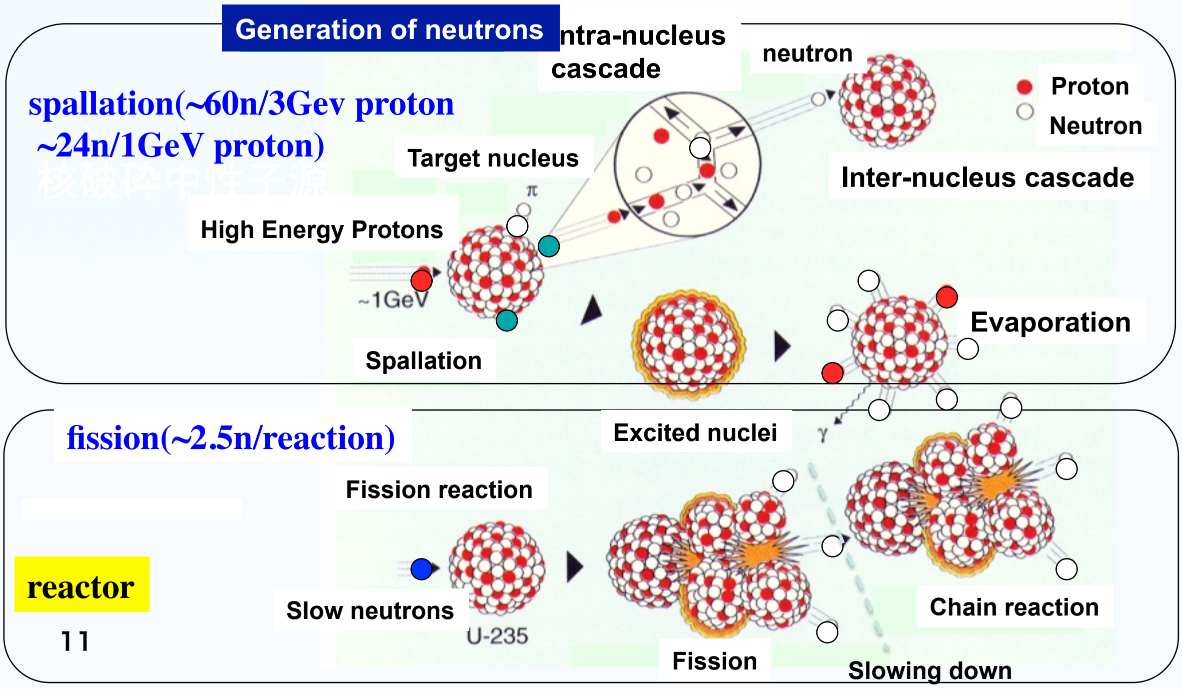
Interacts with nuclei → Contrast variation

*(soft matter)*



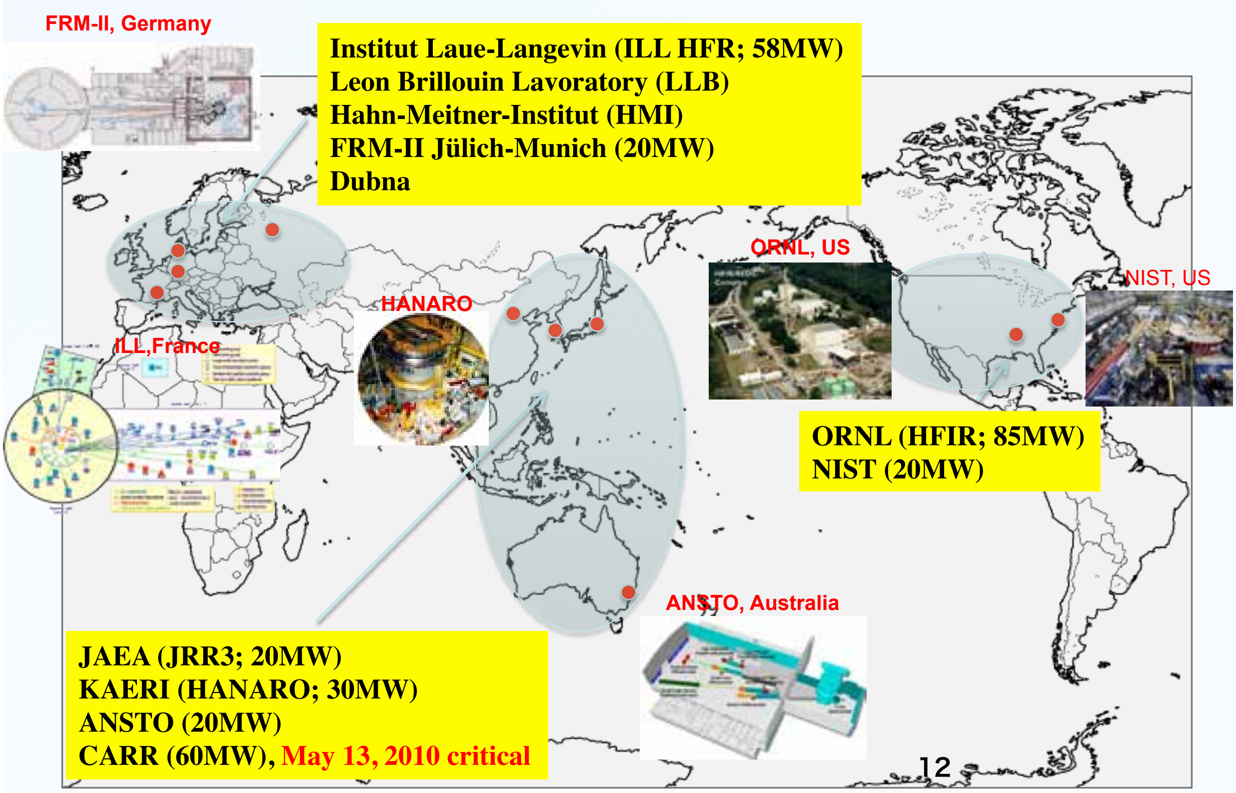
# Generation of neutrons

very effective (no. neutrons ∝ proton power)
(spallation 1MW ~ reactor 15MW)
low heat genaration (~ proton power)



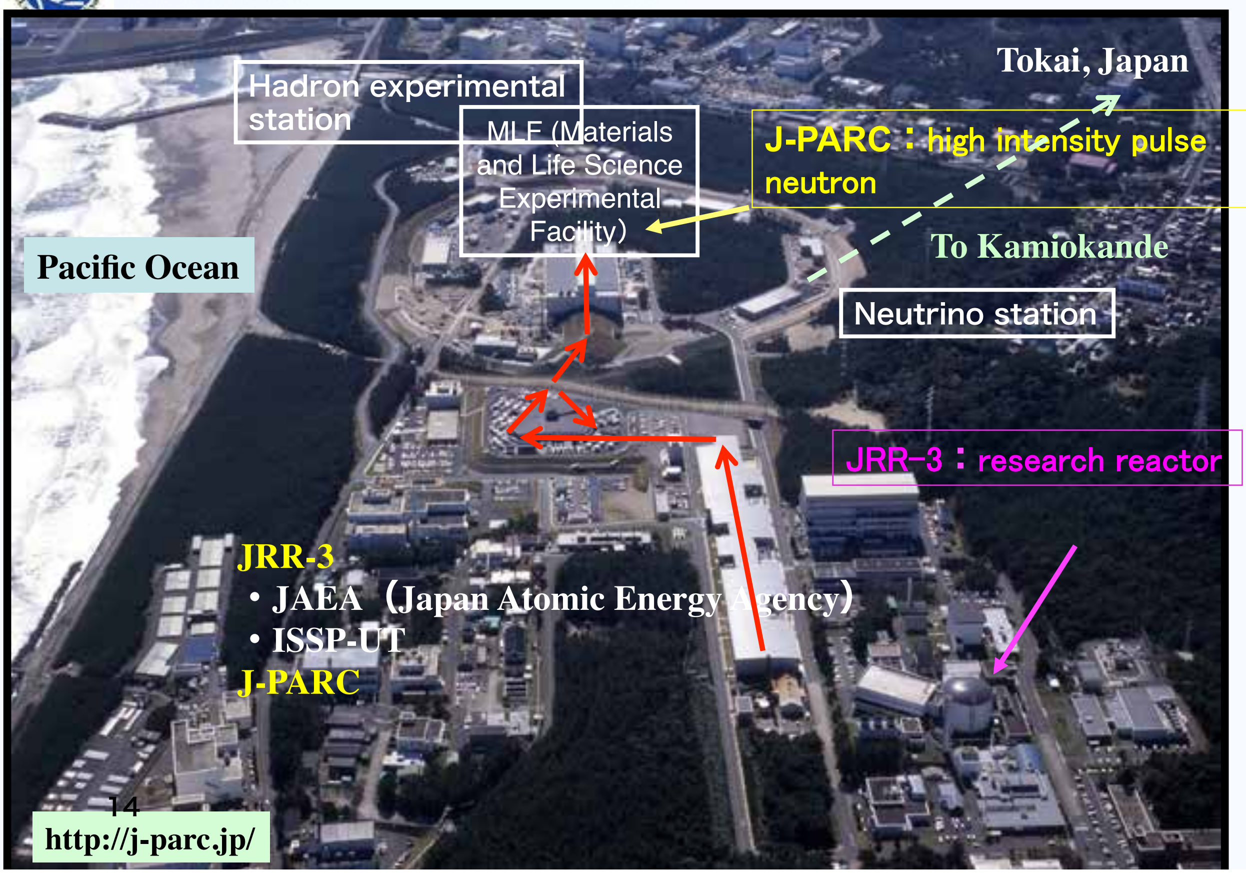



# Research reactors in the world



## Pulse Neutron Source in the world


## Neutron Science at JRR-3 and J-PARC

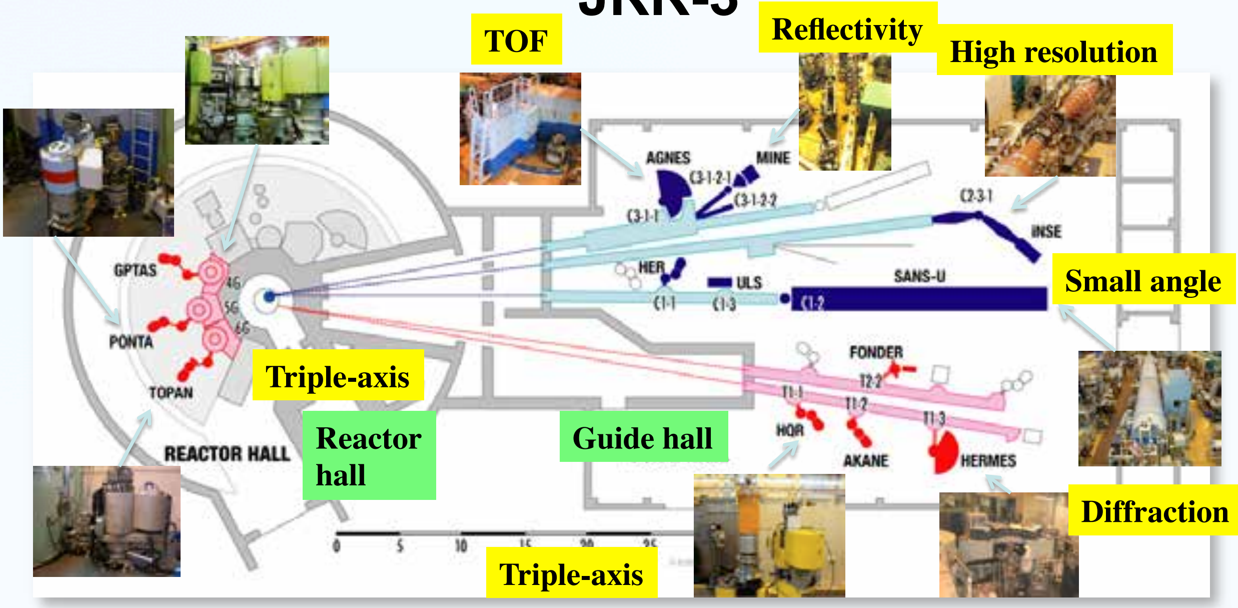


## Neutron Science Lab., ISSP, U. Tokyo
## NSL-ISSP ：SANS-U


**http://neutrons.issp.u-tokyo.ac.jp/**



## University-owned Instruments at JRR-3




University-owned instruments: 14, ISSP 9, Tohoku U. 3, Kyoto U. 2
No. proposals: ~300
No. users (man.day)：in-house 2000, outside 5000, total 7000
No. papers：~100 /y



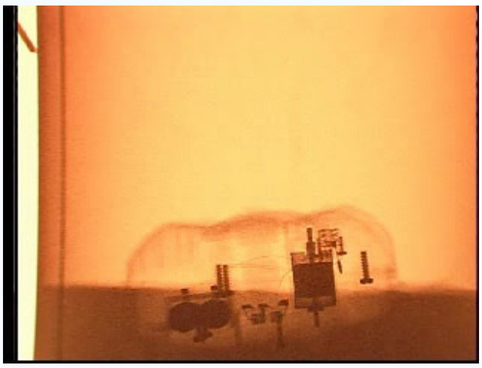

# Comparison of X-ray and neutron

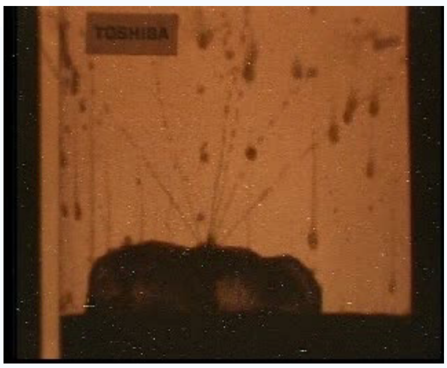
Water, H detection → Nondestructive visualization ← permeability

X-ray

Fountain toy

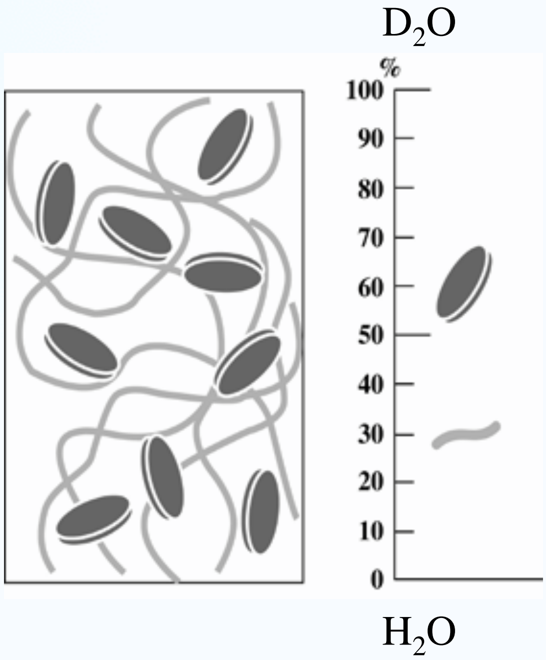
neutron






Matsubayashi (JAEA), Mochiki (Musashino Inst. Tech. ), Toshiba

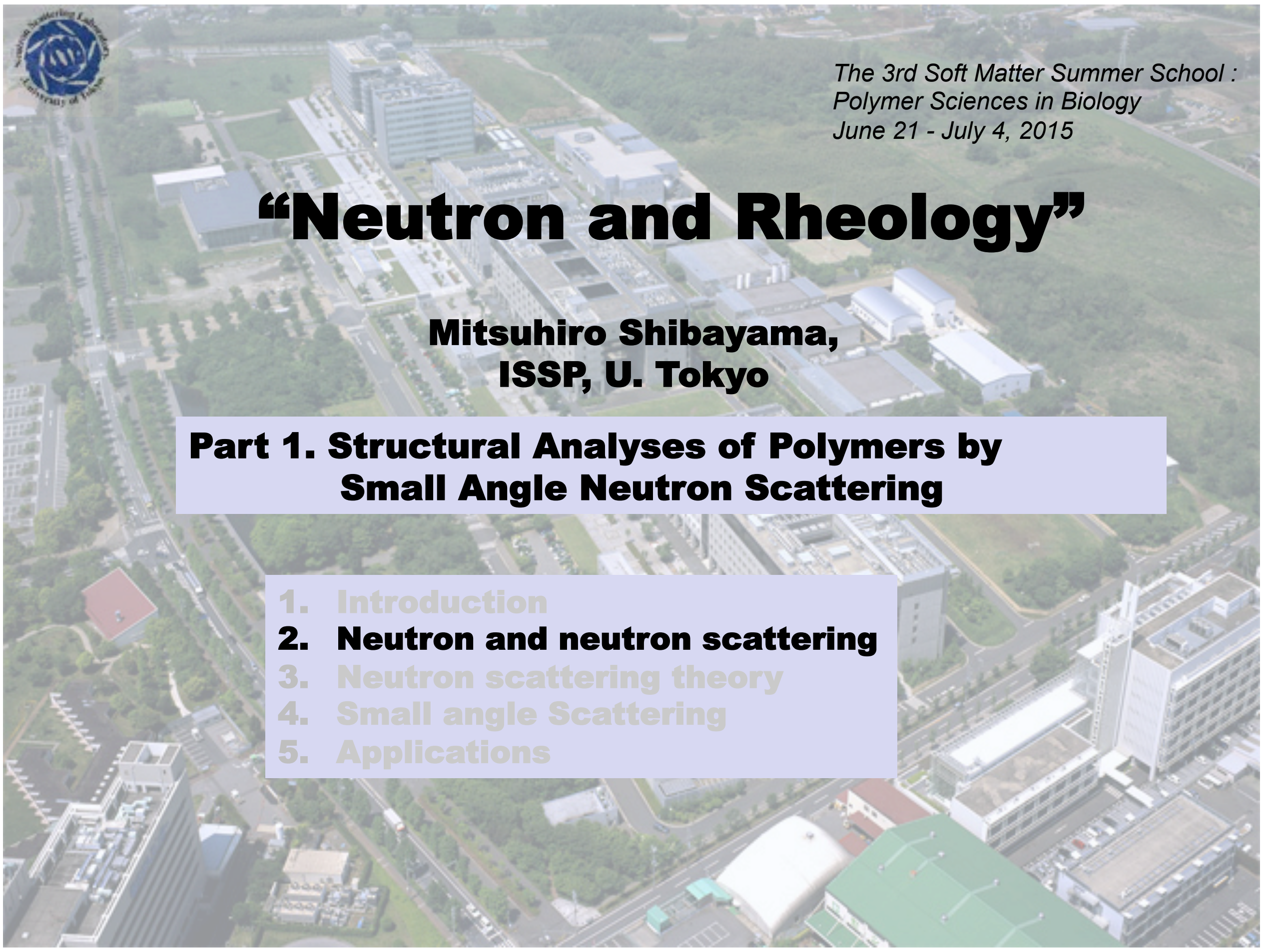
# Neutron contrast




labeling

Contrast matching





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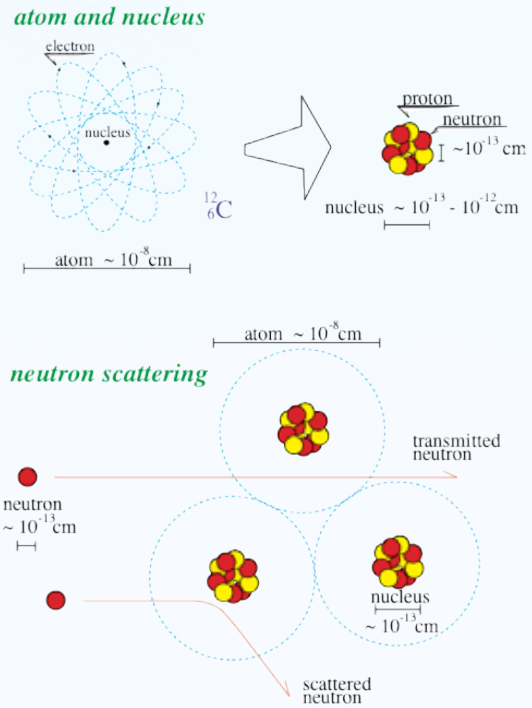
# 1. Atom and Neutron




**Size of an atom**
**(≈ 0.1 nm = $10^{-8}$cm)**

**A neutron is about $1/10^5$(≈ $10^{-13}$ cm) as large as an atom.**
**(A neutron is 1 cm large if an atom is 1 km large.)**

**With an eye of neutron, the nuclei in materials are so dilute that most of neutrons pass through the materials without scattering.**

**When a neutron passes near an nucleus, nuclear scattering takes place.**



Part 1

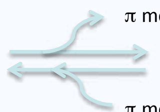
# 2. Properties of neutron

| | |
|---|---|
| mass | $m_n$ = 1.675 x $10^{-27}$ kg |
| Spin quantum number | $s$ =1/2 (-1/2) ; Fermion |
| Mag. moment | $\mu_n$ = -1.913 $\mu_N$<br>$\mu_N$ : nuclear mag. Moment, 3.152 x $10^{-14}$ MeV/T |
| Lamor freq. | 29.16 (MHz/Tesla) |
| Life time | 885.9 ±0.9 s (ca15min) |
| Quark comp. | u-d-d |


Wikipedia

Annihilation of neutron (β⁻annihilation)

$$n \to p^{+} + e^{-} + \bar{\nu}(+0.77\text{MeV})$$

n  p Resonance state between n and p



u-d-d (2/3, -1/3, -1/3 = 0) u-u-d (2/3, 2/3, -1/3 = 1)

Part 1

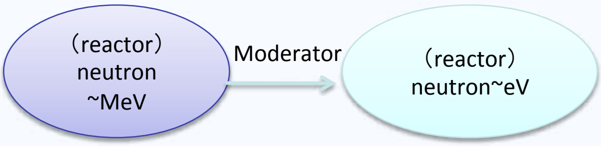
# 3. Generation of neutron (1)

## 1. reactor : fission of $^{235}$U

$$^{235}\mathrm{U} + \mathrm{n} \rightarrow {}^{95}\mathrm{Y} + {}^{139}\mathrm{I} + 2\mathrm{n}$$

235 + 1 > 95 + 139 + 2 mass defect $\Delta E = mc^2$
(236) (244)

* Generation of 2~3 neutron by 1 fission
* Energy of ca. 200MeV ≈ 3.2 x $10^{-11}$ J
  (8.2 x $10^{10}$ J/1g U)

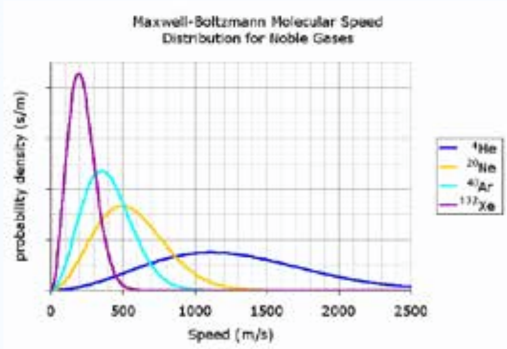



Maxwell distribution characterized by the temperature of the moderator

<ref.> velocity distribution of noble gas

$$f(\mathbf{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m\mathbf{v}^2}{2kT}\right), \quad v = (v_x, v_y, v_z)$$

$$f(v)\mathrm{d}v = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) v^2 \mathrm{d}v$$



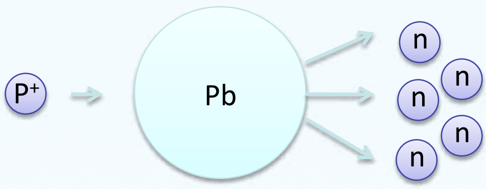

The velocity distribution of neutrons is the Same as that of noble gas.

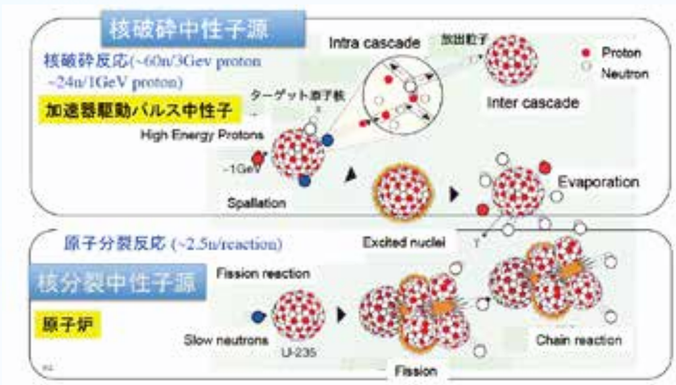
Q: Calculate the most probable velocity of argon gas at $T$=300K.

Part 1

# 3. Generation of neutron (2)

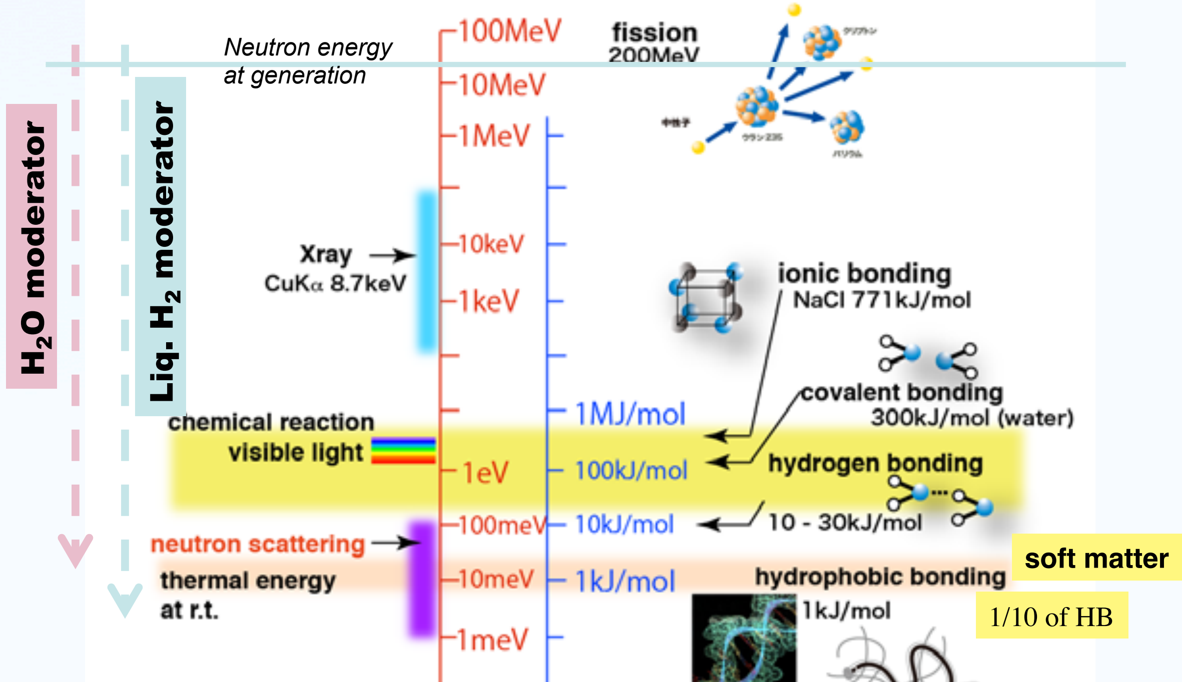
## 2. spallation




**By a collision of a proton with 1GeV with a target nucleus, 20 ~ 25 of high energy neutrons come out.**

## 4. Energies of neutrons, chemical reactions, and soft matter dynamics




**Energy related to soft matter**
***kT* ≈ 0.6kcal /mol (~ 20 meV)**



**Soft and flexible**

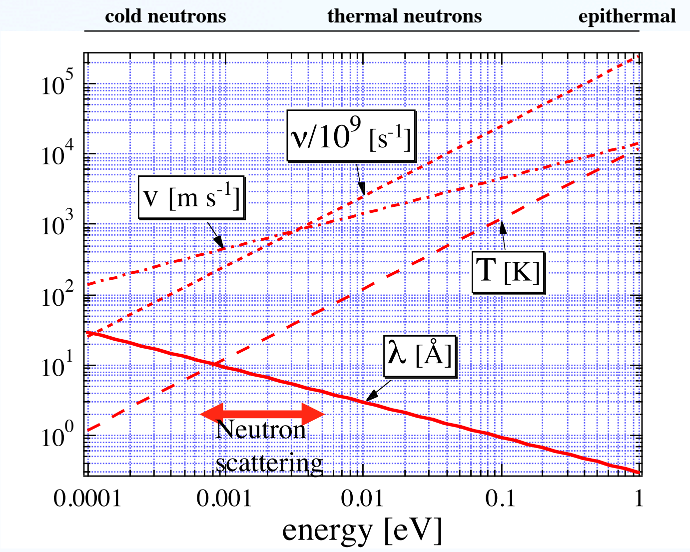
Part 1

## 5. Properties of neutrons

| | suchness |
|---|---|
| energy | $E = mv^2/2 = p^2/2m$; (Einstein, particle wave) |
| wavelength | $\lambda = h/mv = h/p$; (de Brogile wave) |
| temperature | $E = kT$ |
| velocity | $v = (2E/m)^{1/2}$ |
| flux | $\Phi(v) \sim v^3 \exp(- mv^2/2kT_{mod})$ ($T_{mod}$; moderator temperature) |

| | category |
|---|---|
| $10^{-7}$ eV | ultra cold neutron |
| **0.1 - 10 meV** | **cold neutron (moderator: liquid $H_2$)** |
| **10 – 100 meV** | **thermal neutron ($T_{mod}$ ≈ room temp.)** |
| 100 – 500 meV | hot neutron |
| > 500 meV | epithermal neutron |

# 6. Velocity, wavelength, and wave number of neutrons




$E = \frac{1}{2}mv^2$ (Einstein), **particle** (1)

$E = h\nu$; $p = mv = \frac{h}{\lambda}$ (de Broglie) **wave** (2)

$E = kT$ **energy** (3)

$\lambda_{mean} = \frac{h}{\sqrt{3m_n kT}} \sim T^{-1/2}$ **Maxwell distribution** (4)

$\lambda_{max} = \sqrt{\frac{3}{2}}\lambda_{mean} = \frac{30.81}{\sqrt{T}}[Å]$ (5)

$T[K] = 11.605 \times 10^3 E[eV]$ (6)

$\lambda[Å] = \frac{0.2860}{\sqrt{E[eV]}}$ (7)

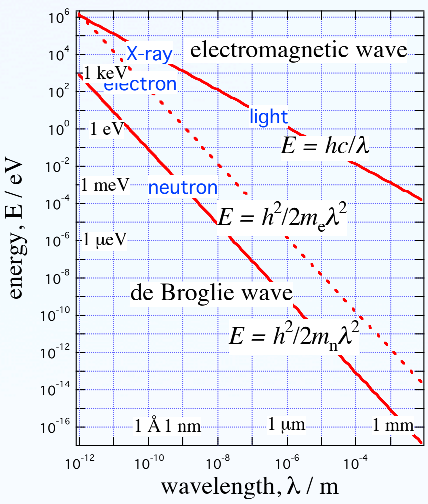
$v[m/s] = 1.383 \times 10^4 \sqrt{E[eV]}$ (8)

**Neutron has wave-particle duality.**
**The velocity, wavelength, and wave number of neutrons depend on temperature.**
**Only cold neutrons and thermal neutrons are used for small angle neutron scattering.**



Part 1

# 7. Energy dispersion




Scattering by photon:
For photons, the relationship between energy $\varepsilon$ and wavenumber $k = 2\pi/\lambda$ is given by

$$\varepsilon = \hbar\omega = \frac{hc}{\lambda} \qquad h = 6.626\times10^{-34}\ [\mathrm{J.s}]$$

For visible light $\varepsilon \approx 1\mathrm{eV}, \quad \lambda = 0.4 \sim 0.7\times10^4\,Å$

Hence, light is a suitable probe for μm-ordered structures.

For Å-ordered structures, photons with $\varepsilon \approx 10^4\mathrm{eV} = 10\mathrm{keV}$ with are necessary and X-ray is the Best means.

Scattering by electrons:
Electrons with mass $m_e$ has the following dispersion relationship.

$$\varepsilon = \frac{\hbar^2 k^2}{2m_e} = \frac{h^2}{2m_e\lambda^2} \qquad m_e = 9.109\times10^{-31}\ \mathrm{kg}$$

$\lambda = 1Å, \quad \varepsilon \approx 100\mathrm{eV}$

Scattering by neutrons:
The same dispersion eq. as for electrons

$$\varepsilon = \frac{\hbar^2 k^2}{2m_n} = \frac{h^2}{2m_n\lambda^2}$$

Note that the mass of neutron mass is very different from that of electron.
$m_n = 1.675\times10^{-27}$ kg (ca 1800 times larger than e)

$\lambda = 1Å, \quad \varepsilon \approx 0.05\mathrm{eV}$ ~ thermal energy

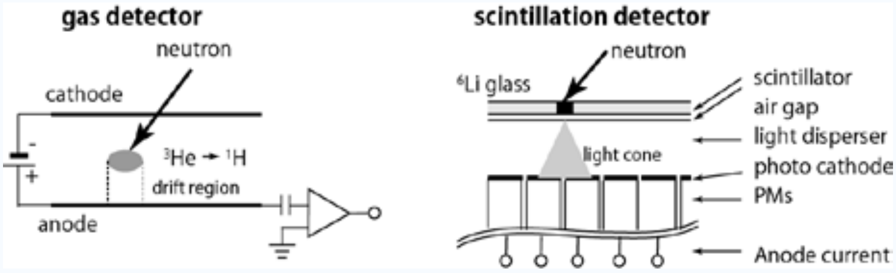
Part 1

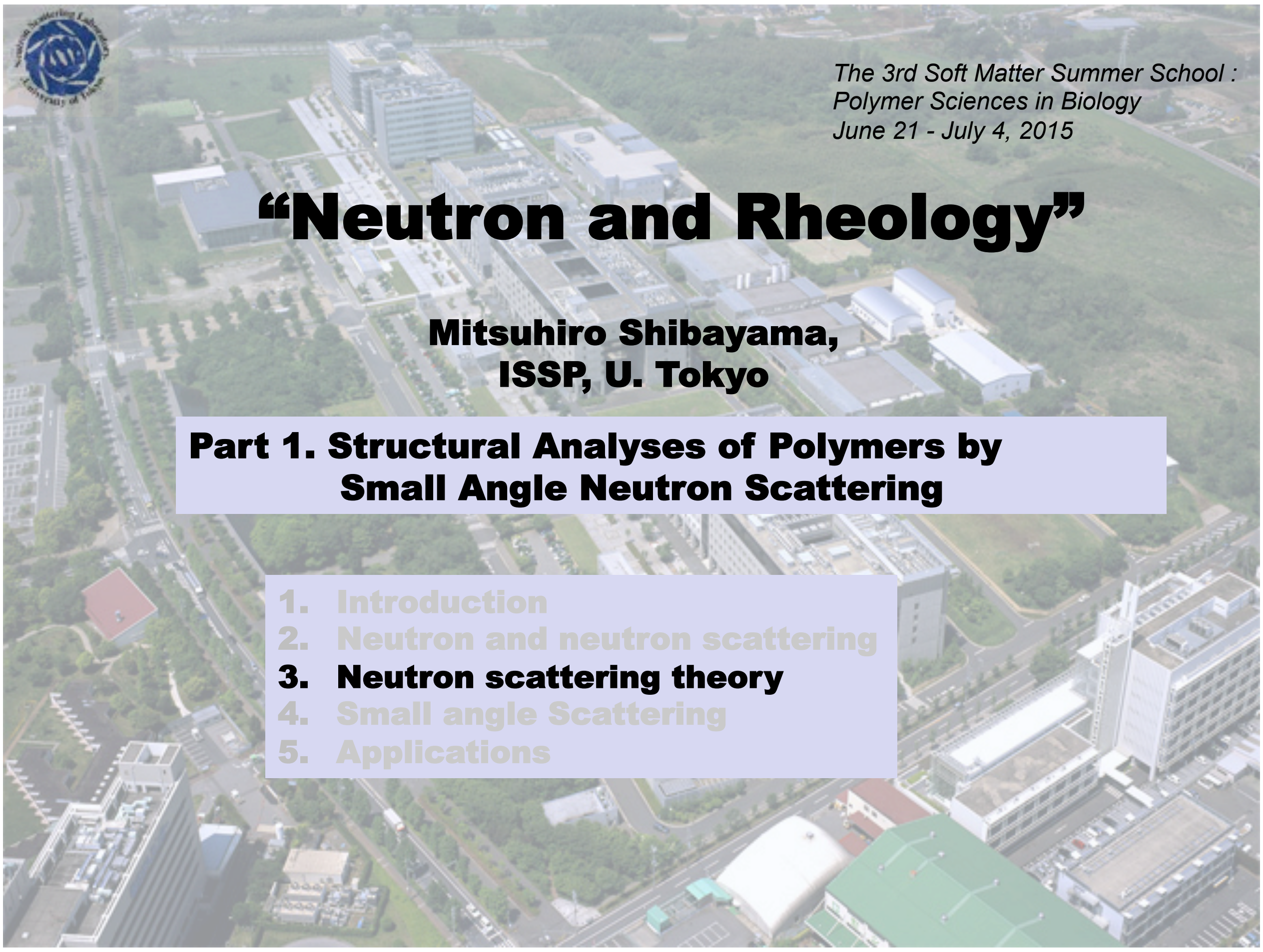
# 8. Detection of neutrons

Neutron: electroneutral
By generating electric charges via nuclear reaction, and counting them

| | Cross section、(25meV) | Generated particles | energy— [MeV] | Total energy[MeV] |
|---|---|---|---|---|
| n + $^3He$ | 5333b | p, $^3T$ | 0.57, 0.2 | 0.77 |
| n + $^6Li$ | 941b | $^3T$, $^4He$ | 2.74, 2.05 | 4.79 |
| n + $^{10}B$ | 3838b | $^4He$, $^7Li$, γ | 1.47, 0.83, 0.48 | 2.30 |
| n + $^{235}U$ | 681b | fission | | 1 - 2 |

b ; a unit of scattering cross section b = barn($10^{-24}$ $cm^2$)



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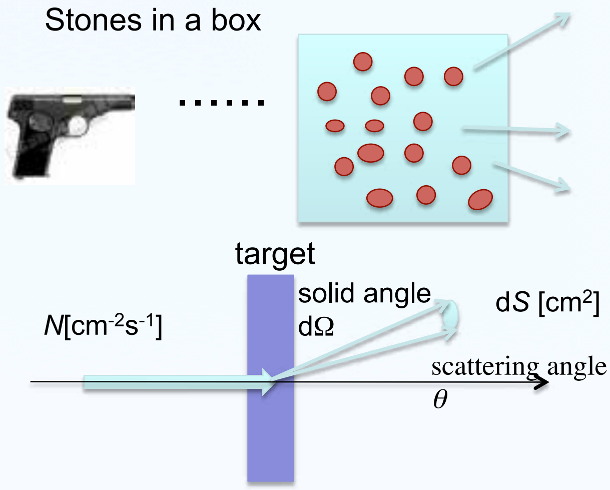
Part 2

# 1. What is scattering?




By randomly shooting a gun, you may guess what in the box are.

- numbers of bullets per unit area and time $N$[cm$^{-2}$s$^{-1}$]
- number of bullets scattered in the solid angle d$n$[s$^{-1}$]

$$dn \propto N dS / r^2 = N d\Omega$$

$$dn = N\sigma(\theta) d\Omega$$

σ(θ): proportional const.

dimension $[\sigma] = \frac{[dn d\Omega]}{[N]} = \frac{[s^{-1}]}{[cm^{-2}s^{-1}]} = [cm^2]$

σ(θ):scattering cross section

| Bullet (probe) | Stones (target) |
|---|---|
| photon | atom |
| neutron | nucleus |
| electron | molecule |
| proton | elemental particle |
| …. | …. |

Total cross section $\sigma_{tot} = \int \sigma(\theta) d\Omega$

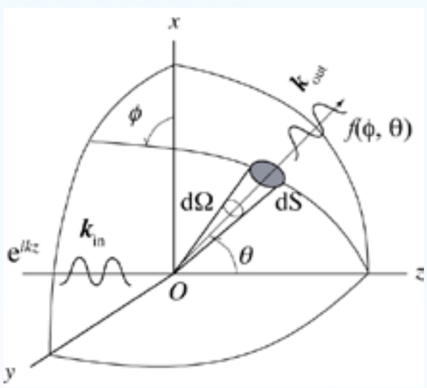
| Scattering by an atom | Scattering by a nucleus |
|---|---|
| Bohr radius $a_0$ = 5.29 x $10^{-9}$ cm<br>-> $\sigma_{tot} \approx a_0^2$ = 2.80 x $10^{-17}$ cm$^2$ | $\sigma_{tot}$ ~ $10^{-24}$ cm$^2$ |



Part 2

# 2. Scattering amplitude

Scattered wave




$$\psi(\mathbf{r}) = \frac{1}{r} f(\Omega) e^{i\mathbf{k}\cdot\mathbf{r}}$$

$f(\mathbf{r})$ :scattering amplitude

Stationary wave

$$H = H_0 + V(\mathbf{r})$$

V(**r**) :potential

$$H_0 = \frac{p^2}{2\mu}$$

$\mu$: reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$

$p$: momentum

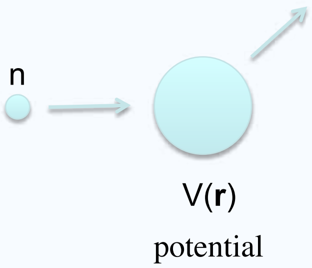
Schrödinger eq.

$$H\psi = E\psi$$

$$\psi(r,t) = \varphi(r) e^{-iEt/h}$$

$\phi(\mathbf{r})$ : a solution of the eigen function

$$\left[-\frac{\hbar^2 \Delta}{2\mu} + V(\mathbf{r})\right]\varphi(\mathbf{r}) = E\varphi(\mathbf{r}), \quad E = \frac{p^2}{2\mu} = \frac{\hbar^2 k^2}{2\mu}$$



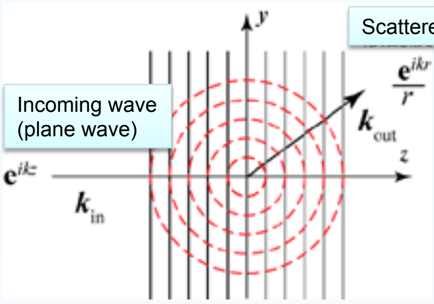

Let $V(\mathbf{r}) \equiv (\hbar^2/2\mu) U(\mathbf{r})$ , and

$$\left[\Delta + k^2 - U(\mathbf{r})\right]\varphi(\mathbf{r}) = 0$$

Part 2

# 3. Scattering cross section and amplitude

The wave equation for scattering is a sum of plane wave $e^{ikz}$ and $\sim e^{ikr}/r$.




$$\varphi_k(\mathbf{r}) \underset{r\to\infty}{\sim} e^{ikz} + f_k(\theta,\varphi)\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{r}$$

Plane wave Scattering amp.

Calculation of scattering cross section

Flux density: $J(r) = \frac{1}{\mu}\mathrm{Re}\left[\varphi^*(r)\frac{\hbar}{i}\nabla\varphi(r)\right]$

In-coming wave $J_{in} = \frac{\hbar k}{\mu}$

Scattered wave: $J_{out}(r) = \frac{\hbar k}{\mu}\frac{1}{r^2}\left|f_k(\theta,\varphi)\right|^2$

Hence, $\mathrm{d}n = J_{out}\mathrm{d}S = J_{out}r^2\mathrm{d}\Omega = \frac{\hbar k}{\mu}\left|f_k(\theta,\varphi)\right|^2\mathrm{d}\Omega$

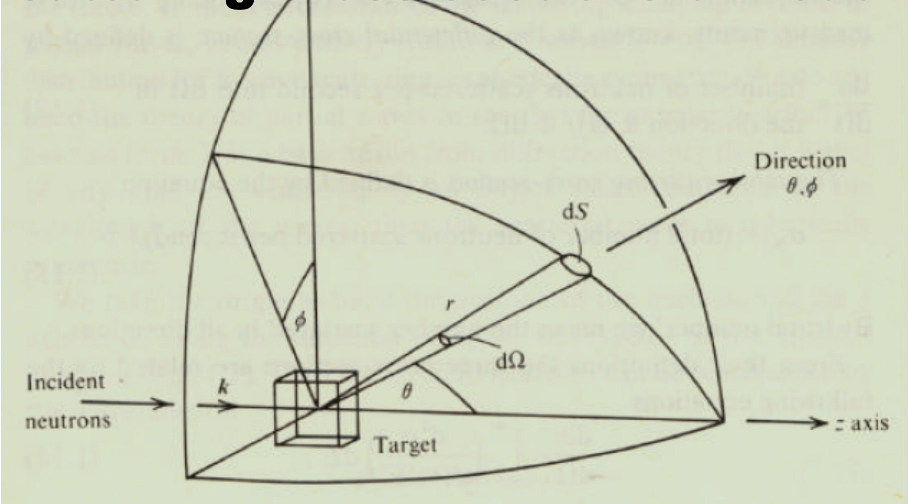
From the definition of cross section, $\mathrm{d}n = J_{in}\sigma\mathrm{d}\Omega = \frac{\hbar k}{\mu}\sigma\mathrm{d}\Omega$

$$\sigma = \left|f_k(\theta,\varphi)\right|^2$$

Note: the cross section is a square of the scattering amplitude



# 4. Scattering cross sections of neutrons




$\Phi$ = No. of incident neutrons per $cm^2$ per second

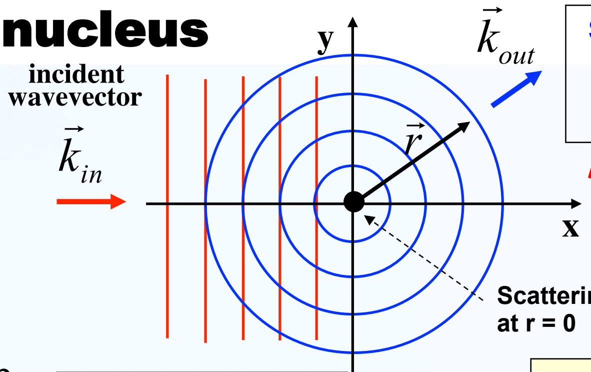
$\sigma$ = Total No. of neutrons scattered per second/$\Phi$

| |
|---|
| $\sigma$ measured in barns |
| 1 barns = $10^{-24}$ $cm^2$ |

Elastic → $$\frac{d\sigma}{d\Omega} = \frac{\text{No. of neutrons scattered per second into d}\Omega}{\Phi\mathrm{d}\Omega}$$

Inelastic → $$\frac{d^2\sigma}{d\Omega dE} = \frac{\text{No. of neutrons scattered per second into d}\Omega\text{ and dE}}{\Phi\mathrm{d}\Omega\mathrm{dE}}$$

# 5. Scattering by a single nucleus




**Scattered Spherical Wave**

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

***b*** **= scattering length of a nucleus**

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

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

**(elastic scattering)**

**Incident Plane wave**

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

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

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

**No. of incident neutrons passing through unit area per second** $\Phi = \mathrm{v}|\psi_{inc}|^2 = \mathrm{v}$ **V: Neutron velocity**

**No. of scattered neutrons passing thr**... $\mathrm{v}|\psi_{scat}|^2 dS = \mathrm{v}\left(\frac{b^2}{r^2}\right) dS = \mathrm{v}\, b^2\, d\Omega$

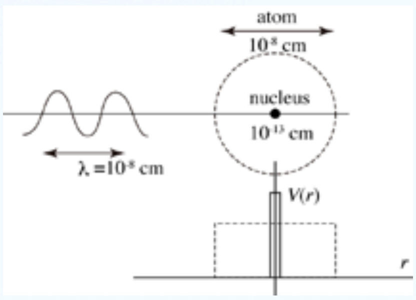
$$\sigma_{total} = \int \frac{d\sigma}{d\Omega} d\Omega = 4\pi b^2$$

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



Part 2

# 6. Fermi's pseudo potential




$$V(r) = \frac{2\pi\hbar^2}{m} b\delta(\mathbf{r}-\mathbf{R})$$

The interaction potential for nuclear scattering is given by A delta function.
b : the scattering length

$b = b_1 + ib_2$ ; complex number
(imaginary part: absorption)

Differential cross section (Born approx.)

$$\sigma^{(B)}(\theta,\varphi) = \frac{\mu^2}{4\pi^2\hbar^4}\left|\int d^3r e^{-i\mathbf{Q}\cdot\mathbf{r}} V(r)\right|^2$$

$$= \frac{\mu^2}{4\pi^2\hbar^4}\left|\int d^3r e^{-i\mathbf{Q}\cdot\mathbf{r}} \frac{2\pi\hbar^2}{m} b\delta(\mathbf{r}-\mathbf{R})\right|^2$$

$$= |b|^2$$

Note: the scattering cross section does not depend on Q.
(A Fourier tr. of a delta fn. is a constant.)

$$U(r) = \frac{2\mu}{\hbar^2} V(r) = 4\pi b\delta(\mathbf{r}-\mathbf{R})$$

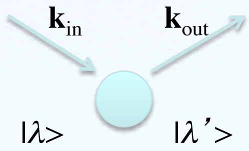
The scattering amplitude

$$f(\theta,\varphi) = -\frac{1}{4\pi}\int d^3r' e^{-i\mathbf{Q}\cdot\mathbf{r}'} U(r') = -b$$

*b*: the scattering length

Part 2

# 7. Inelastic scattering




In the case of inelastic scattering, the wavelength is also changed as follows,

$$\left(\frac{d\sigma}{d\Omega}\right)_{k,\lambda\to k',\lambda'} = \frac{k'}{k}\left(\frac{m}{2\pi\hbar^2}\right)^2 \langle k'\lambda' | V | k\lambda\rangle^2$$

On the other hand, the energy and momentum transfer are preserved.

$$\left(\frac{\partial^2\sigma}{\partial\Omega\partial\omega}\right)_{k,\lambda\to k',\lambda'} = \frac{k'}{k}\left(\frac{m}{2\pi\hbar^2}\right)^2 \sum_\lambda P_\lambda \langle k',\lambda' | V | k,\lambda\rangle^2 \delta(\hbar\omega + E_\lambda - E_{\lambda'})$$

$P_\lambda$: distribution of λ



# 8. Scattering by many nuclei

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

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

**Therefore**

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

**If we measure far enough away so that** $r >> R_i$, **then** $|\vec{r}-\vec{R}_i| \approx r \quad d\Omega = \frac{dS}{r^2}$

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

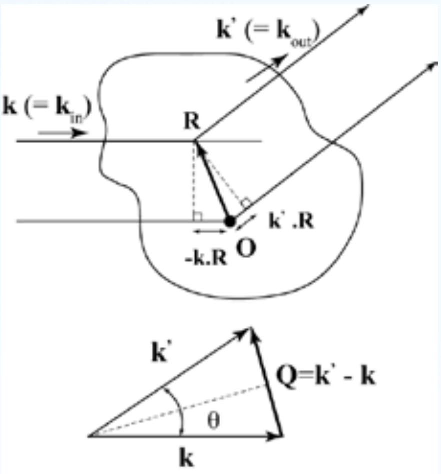
$$\left|e^{i\vec{k}_{out}\cdot\vec{r}}\right|^2 = 1$$

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

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

Part 3

# 9. Scattering vector



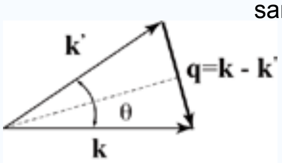

$$\mathbf{Q} \equiv \mathbf{k}_{out} - \mathbf{k}_{in} = \mathbf{k}' - \mathbf{k}$$

Path difference $= \mathbf{k}'\cdot\mathbf{R} - \mathbf{k}\cdot\mathbf{R} = (\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}$
$= \mathbf{Q}\cdot\mathbf{R}$

$$|\mathbf{k}| = |\mathbf{k}'| = k = \frac{2\pi}{\lambda}$$

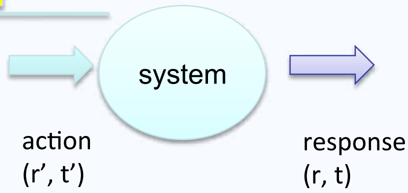
$$\mathbf{Q} = 2k\sin\left(\frac{\theta}{2}\right)$$

Cf. From the viewpoint of momentum transfer from incoming particle to sample, the following definition is better.




$$\hbar\mathbf{q}: \quad \hbar\mathbf{k} \rightarrow \hbar\mathbf{k}'$$

$$\mathbf{q} \equiv \mathbf{k} - \mathbf{k}'$$




response＝＜after｜action｜before＞

Part 2

# 10. Coherent and incoherent scattering

Neutron scattering is also dependent on isotopes and the relative orientation of spins. Here, we consider scattering from an assembly of isotopes with $\{R_l, b_l\}$.

Fermi potential

$$V(r) = \frac{2\pi\hbar^2}{m}\sum_l b_l \delta(\mathbf{r} - \mathbf{R}_l)$$

The scattering amplitude

$$\langle k'|V|k\rangle = \frac{2\pi\hbar^2}{m}\sum_l b_l \int d^3 r e^{-i\mathbf{k}'\cdot\mathbf{r}}\delta(\mathbf{r}-\mathbf{R}_l)e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$= \frac{2\pi\hbar^2}{m}\sum_l b_l e^{i\mathbf{Q}\cdot\mathbf{R}_l}$$

The scattering Cross section $\quad \dfrac{d\sigma}{d\Omega} = \left(\dfrac{m}{2\pi\hbar^2}\right)^2 \left|\langle k'|V|k\rangle\right|^2$

Now, we need to take care of the change of spin states,

$$s \rightarrow s'$$

$$\frac{d\sigma}{d\Omega} = \sum_{s,s'} P_s \sum_{l,l'} e^{i\mathbf{Q}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})}\left|\langle s'|b_{l'}^* b_l|s\rangle\right|^2$$

If the scattering is not dependent on The spin states and is dependent only on random distribution of isotopes,

$$\frac{d\sigma}{d\Omega} = \sum_{l,l'} e^{i\mathbf{Q}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})}\left|\langle b_{l'}^* b_l\rangle\right|^2$$

$$\langle b_{l'}^* b_l\rangle = (1-\delta_{ll'})\bar{b}^2 + \delta_{ll'}\overline{b^2}$$

Hence,

$$\frac{d\sigma}{d\Omega} = N\left(\overline{b^2} - \bar{b}^2\right) + \bar{b}^2 \sum_{l,l'} e^{i\mathbf{Q}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})}$$

incoherent　　coherent

# 11. 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)**

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

Magnetic moment of neutron ($\boldsymbol{\mu}$); B-field induced unpaired spin ($\mathbf{B}(\mathbf{r})$)

## Scattering length, *b*

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

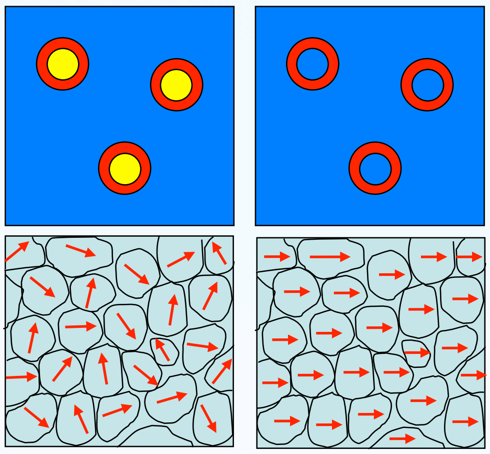
Fourier Transform of V(r) ($V(\mathbf{Q})$)

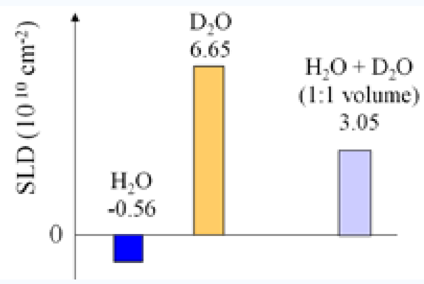
$$b = b_N + b_M = b_N + \gamma r_e \boldsymbol{\sigma} \cdot \mathbf{S}_\perp f(Q)$$

- $b_N$: Nuclear
- $b_M$: Magnetic
- $\boldsymbol{\sigma}$: Pauli operator for neutron
- $f(Q)$: Magnetic form factor
- $\mathbf{S}_\perp$: Spin component perpendicular to Q



# 12. Scattering Length Density






## Scattering length density, ρ

$$\rho = \frac{\sum_j^n b_j}{\overline{V}}$$

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

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

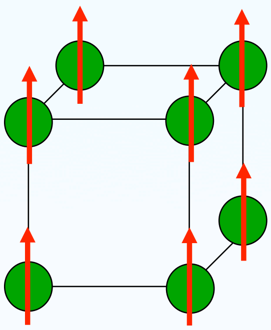
## Contrast variation

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

$b_H$ = -3.749 fm  $b_D$ = 6.671 fm

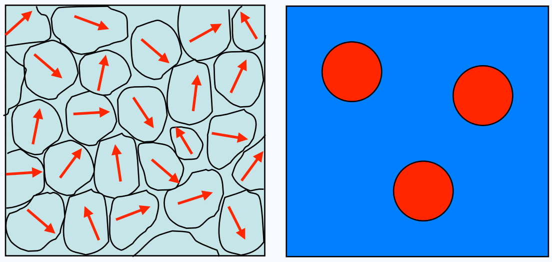
## What Contrast Do We Use in Neutron Scattering ?

❑ **Thermal Neutron Diffraction**



- **Use atomic properties**
  **: Scattering length**

❑ **SANS/REF**



- **Use material properties**
  **: Scattering length density**



Part 2

## 13. Calculation of scattering lengths

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

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

Ex. benzene $C_6H_6$

$$b_{\text{benzene}} = 6b_H + 6b_C$$
$$= 6 \times (-3.739 \times 10^{-13}) + 6 \times (6.646 \times 10^{-13})$$
$$= 17.442 \times 10^{-13} [\text{cm}]$$

| 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 |
| | | $b$ | | $\sigma_{coh}$ | $\sigma_{inc}$ | $\sigma_s$ | $\sigma_a$ |

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

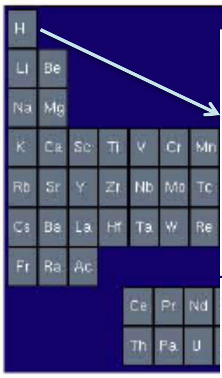
http://www.ncnr.nist.gov/resources/n-lengths/

NIST Center for Neutron Research

NIST National Institute of Standards and Technology

Home ICP Experiments UserProposal Instruments SiteMap

## 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... is also available.

# 14. Neutron Scattering : Fourier Transform

- **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**

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

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

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

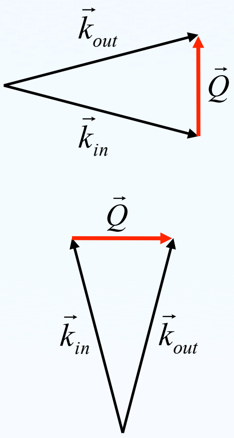
$\rho_{\mathrm{sld}}(\vec{r}) = \sum_j b_j \delta(\vec{r}-\vec{R}_j)$ : **Scattering length density**

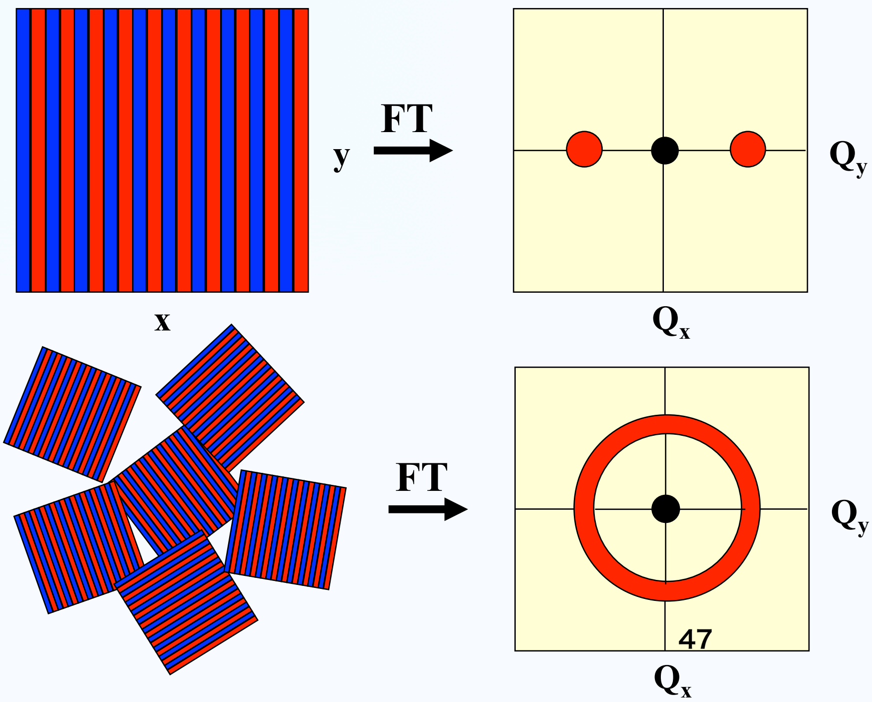
$$\mathrm{F.T.}\{\rho_{\mathrm{sld}}(\vec{r})\} = \int \rho_{\mathrm{sld}}(\vec{r}) e^{-i\vec{Q}\cdot\vec{r}} d\vec{r} = \int \sum_j b_j \delta(\vec{r}-\vec{R}_j) e^{-i\vec{Q}\cdot\vec{r}} d\vec{r} = \sum_j b_j e^{-i\vec{Q}\cdot\vec{R}_j}$$

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

# 15. Fourier Transform

$\vec{Q}$ probes the space along $\vec{r}$ parallel to $\vec{Q}$






Part 3

# 16. From scattering cross section to absolute intensity

Total cross section : the sum of scattering cross section $\sigma_s$ and absorption cross section $\sigma_a$.
The scattering cross section: coherent scattering cross secdtion $\sigma_{coh}$ and
incoherent scattering cross section $\sigma_{inc}$.

$$\sigma_{tot} = \sigma_s + \sigma_a$$

$$\sigma_s = \sigma_{coh} + \sigma_{inc}$$

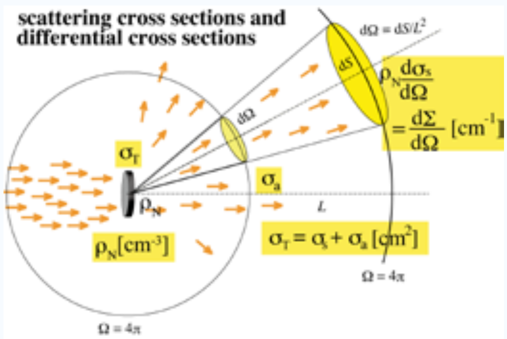
Scattering intensity (differential scattering cross section)

The differential scattering cross section is given by normalizing the scattering cross section by the number density of the scatterers in the sample.

$$\frac{d\sigma}{d\Omega}(Q)\left[\mathrm{cm}^2\right] \xrightarrow[\times N/V]{} \frac{N}{V}\frac{d\sigma}{d\Omega}(Q)\left[\mathrm{cm}^{-1}\right] = \rho_N \frac{d\sigma}{d\Omega}(Q)\left[\mathrm{cm}^{-1}\right] = \frac{d\Sigma}{d\Omega}(Q)\left[\mathrm{cm}^{-1}\right]$$

**(one particle)**

$$\rho_N \equiv \frac{N_A d\left[\mathrm{g/cm}^3\right]}{m\left[\mathrm{g/mol}\right]}\left[\mathrm{cm}^{-3}\right] \quad \text{Number density}$$




$\frac{d\Sigma}{d\Omega}(Q)\left[\mathrm{cm}^{-1}\right]$ : commonly-used unit for scattering intensity

$$\frac{d\Sigma}{d\Omega}(Q)\left[\mathrm{cm}^{-1}\right] \xrightarrow[\Omega]{} \Sigma\left[\mathrm{cm}^{-1}\right]$$ : total cross section of the sample

# Summary: Comparison of scattering amplitudes

**neutron**

$$f^{(1)}(\theta) = -b$$

constant

**X-ray**

$$f^{(1)}(\theta) = \frac{e^2}{m_e c^2} A(\theta), \quad A(\theta = 0) = Z$$

angular dependent

**electron**

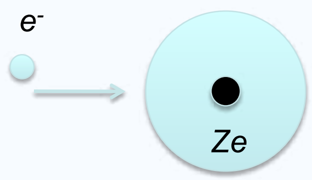
Two contributions; from the nucleus, and the electron clouds

$$f^{(1)}(\theta) = \frac{2m_e e^2}{\hbar^2} \frac{Z - A(\theta)}{Q^2}, \quad A(\theta = 0) = Z$$

$$V(r) = -\frac{Ze^2}{r} + \int d^3r' \frac{(-e)(-e)^2 \rho(r')}{|r - r'|}$$

↑ Atom and Incoming electron

↑ Electron cloud and incoming electron




$$\int d^3 r \rho(r) \equiv Z$$



Part 2

# Summary: scattering variables

Total cross section

$$\sigma_{tot} = \int \sigma(\theta,\varphi) d\Omega$$

Differential scattering cross section

$$\sigma = \left| f_k(\theta,\varphi) \right|^2$$

Fermi's pseudo potential

$$V(r) = \frac{2\pi\hbar^2}{m} b\delta(\mathbf{r} - \mathbf{R})$$

Scattering length

$$f(\theta,\varphi) = -\frac{1}{4\pi} \int d^3r' e^{-i\mathbf{Q}.\mathbf{r}'} U(r') = -b$$

Scattering vector

$$Q \equiv \mathbf{k}_{\text{out}} - \mathbf{k}_{\text{in}} = \mathbf{k}' - \mathbf{k}$$

Scattered wave

$$\psi(r) = -\frac{b}{r} e^{ikr}$$

Scattering cross section for a particle

$$\frac{d\sigma}{d\Omega} = b^2$$

Coherent scattering cross section

$$\sigma_{\text{coh}} \equiv 4\pi \bar{b}^2$$

Incoherent scattering cross section

$$\sigma_{\text{inc}} \equiv 4\pi \left( \overline{b^2} - \bar{b}^2 \right)$$

The 3rd Soft Matter Summer School :
Polymer Sciences in Biology
June 21 - July 4, 2015

# “Neutron and Rheology”

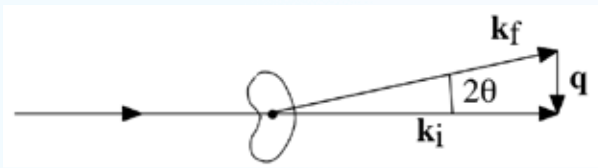
**Mitsuhiro Shibayama,**
**ISSP, U. Tokyo**

## Part 1. Structural Analyses of Polymers by Small Angle Neutron Scattering

1. Introduction
2. Neutron and neutron scattering
3. Neutron scattering theory
4. **Small angle Scattering**
5. Applications

Part 4

# 1. what is small-angle scattering?

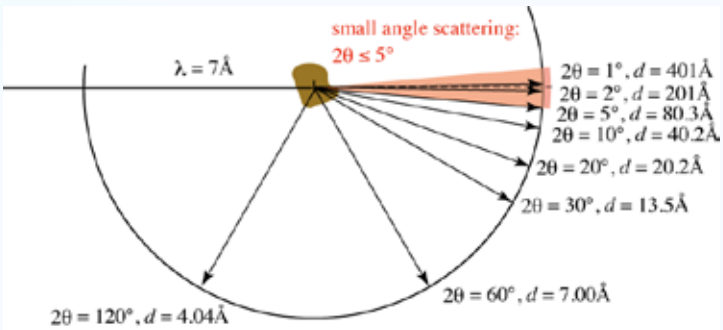



- **Constructive interference from structures in the direction of q**

- **Diffraction length scale**

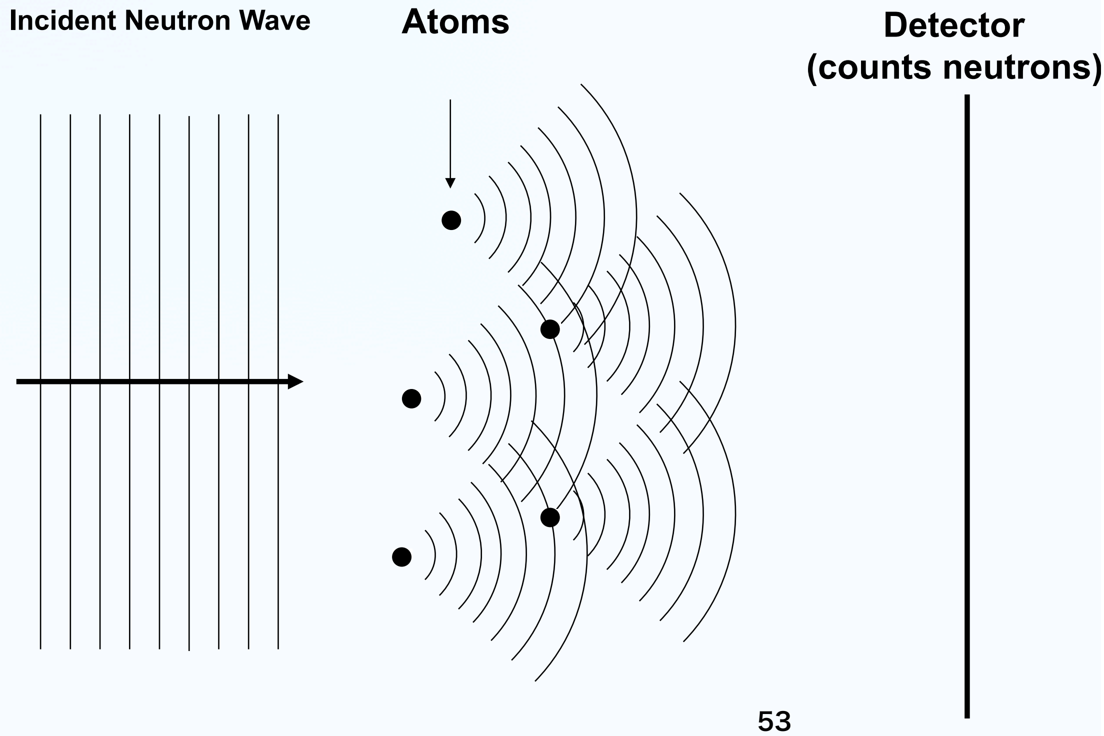
$$d \approx \frac{2\pi}{q}, \quad 2\theta \approx \frac{\lambda}{d} \approx \frac{7\text{Å}}{40 \sim 800\text{Å}}$$

$$2\theta \approx 0.5° \sim 10°$$



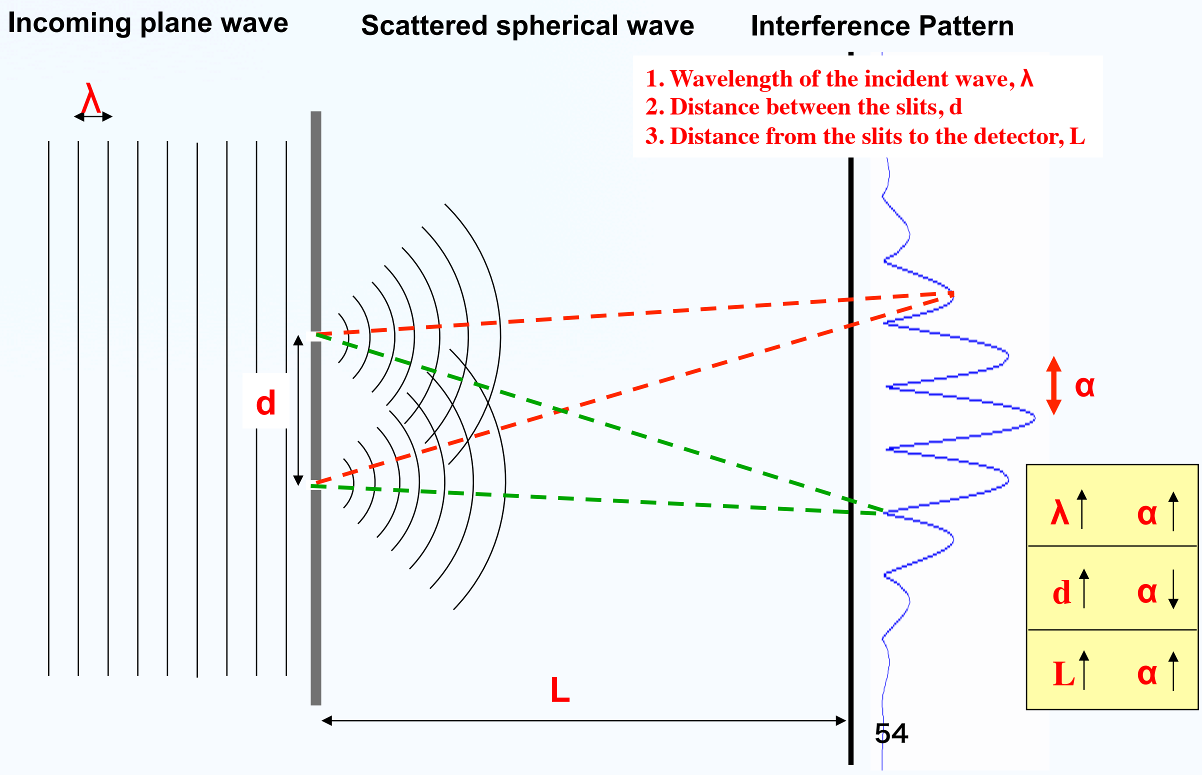

- **Scattering is at small angles - non-zero but smaller than classical diffraction angles**

# 2. Young's Double Slit Experiment (1)



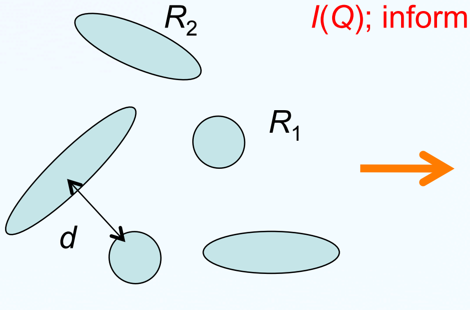



# 2. Young's Double Slit Experiment (2)

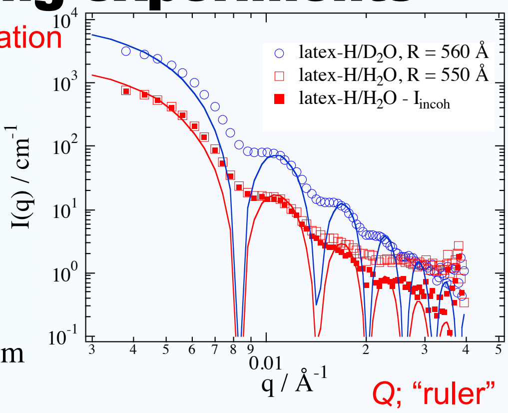


Part 4

# 3. Information obtained by small-angle scattering experiments




*I*(*Q*); information




Q; "ruler"

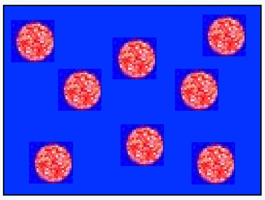
Information obtained from Scattering experiments

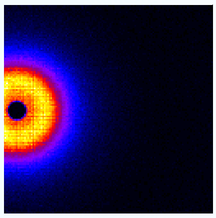
**Structural Information**
- **size, $R_1$, $R_2$,**
- **shape,**
- **volume fraction, $\phi$**
- **orientation,**
- **domain distance, *d***
- **fractal dimension, *D***
- **miscibility,**
- **specific surface, *S/V***
- **….**

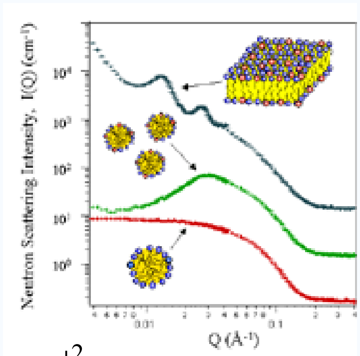
Ex. SANS function from a polystyrene latex (PS)



# 4. What Information from SANS ? : Particulate Systems







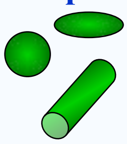

$$\frac{d\Sigma}{d\Omega}(\mathbf{Q}) = \left|\text{Fourier Transform of } \rho(\mathbf{r})\right|^2$$

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

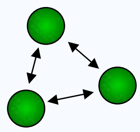
**Number density**

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

**Shape and dimensions of particles**



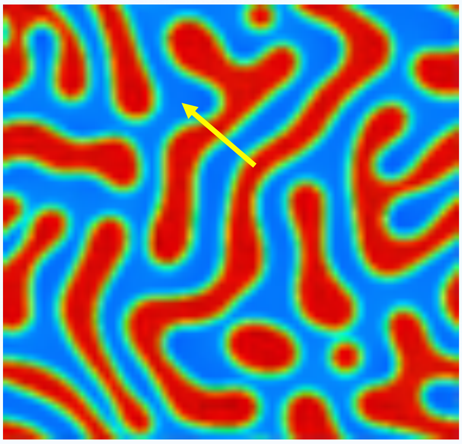
**Interaction between particles**



**Intra-Particle interference**
**: Form factor**

**Inter-Particle interference**
**: Structure factor**

# 4. What Information from SANS ? : Non-Particulate Systems



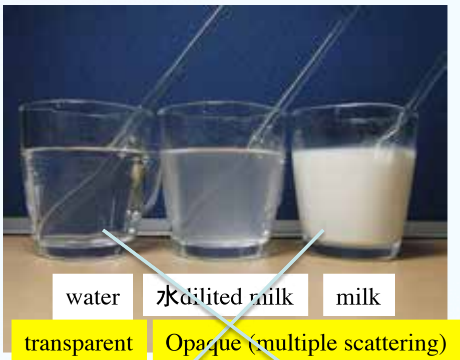
$$\frac{d\Sigma}{d\Omega}(Q) = 4\pi\left\langle(\Delta\rho)^2\right\rangle \int_V \gamma(r)\frac{\sin(Qr)}{Qr}r^2 dr$$

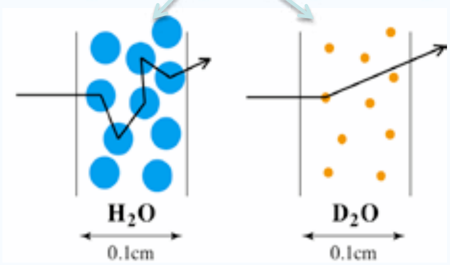
Contrast | Correlation function | Orientation average

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



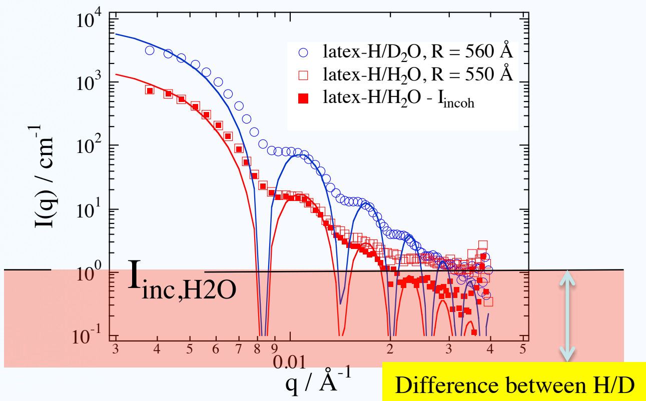
# 5. Multiple scattering by H




MFP ≈ 0.15cm   MFP ≈ 1.6cm

$$\text{mean free path (MFP)} = \frac{1}{\rho\sigma_T} = \frac{1}{\Sigma_T}\ [\text{cm}] = \frac{1}{\text{total cross section}}$$



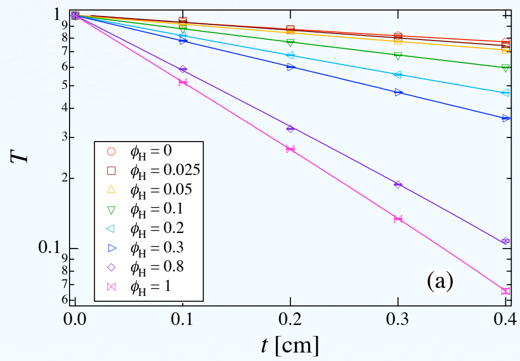

Ex. Polystyrene latex

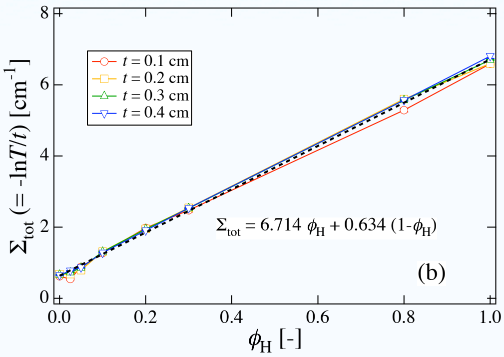
If incoherent scattering is large, Information at large q cannot be obtained.

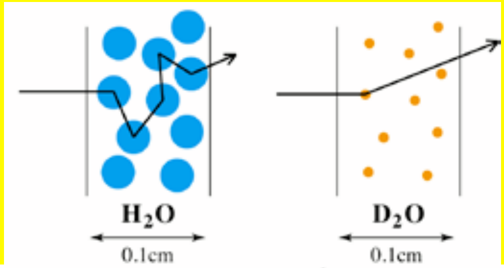
Need to design to lower incoherentscattering

Part 3

# 6. Transmission of $H_2O/D_2O$




$$\text{mean free path (MFP)} = \frac{1}{\rho\sigma_T} = \frac{1}{\Sigma_T}\ [\text{cm}] = \frac{1}{\text{total cross section}}$$

$$T \equiv \frac{I_{tr}}{I_0} = \exp(-\Sigma_{tot} t)$$

The Lambert-Beer law holds even $T \approx 0.05$.

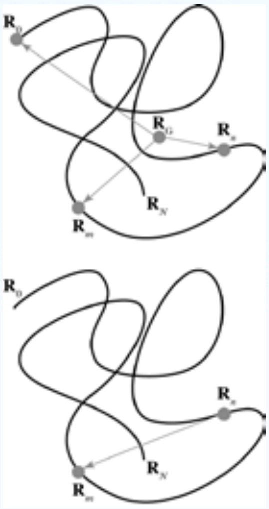
$$\Sigma_{tot} = 6.714\phi_H + 0.634(1-\phi_H)$$

A linear relationship holds all fractions irrespecective of sample thickness.

Shibayama, et al., J. Appl. Crystallogr. 2009, 42, 621.

Part 4

# 7. Scattering function from a polymer chain




**the radius of gyration**

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

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

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

*N*; the degree of polymerization

**the Debye fn.**

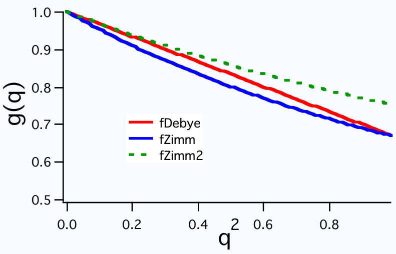
$$g(\mathbf{r}) = \frac{1}{N}\sum_n\sum_m\left\langle\exp[i\mathbf{Q}\cdot(\mathbf{R}_m - \mathbf{R}_n)]\right\rangle$$

$$= \frac{1}{N}\sum_n\sum_m\exp\left[-\frac{|m-n|}{6}b^2Q^2\right]$$

$$= Nf_D\left((QR_g)^2\right)$$

*b*; the segment length

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




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

$$R_g = \frac{N^{1/2}b}{\sqrt{6}}$$

Q: Discuss the asymptotic behavior of the Debye function near *x*=0 and *x*=large.

Part 4

# Summary:

correlation functions and scattering intensity for various systems

$$g(r) \Leftrightarrow I(Q) = \int g(r)\exp(i\mathbf{Q}\cdot\mathbf{r})d\mathbf{r} = \int g(r)\frac{\sin Qr}{Qr}4\pi r^2 dr$$

**corr. fns.** **scatt. fns.**

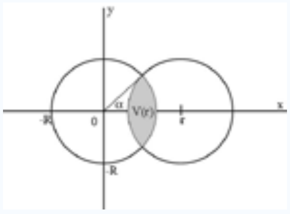
---

**Gaussian fn. (scattering from an assembly of non-interacting particles)**

$$g(r) = \exp\left[-\frac{r^2}{2(R_g{}^2/3)}\right] \longleftrightarrow I(Q) \sim \exp\left(-\frac{R_g{}^2}{3}Q^2\right)$$

**Scattering from isolated particles**

$$g(r) \equiv \frac{V(r)}{4\pi R^3/3} = 1 - \frac{3}{4}\frac{r}{R} + \frac{1}{16}\left(\frac{r}{R}\right)^3 \longleftrightarrow I(Q) \sim \Phi^2(QR) = \left\{\frac{3[\sin(QR) - qR\cos(QR)]}{(QR)^3}\right\}^2$$




**Lorentz fn. (semi-dilute polymer solutions)**

$$g(r) = \frac{1}{r}\exp\left(-\frac{r}{\xi}\right) \longleftrightarrow I(Q) \sim \frac{1}{1+Q^2\xi^2}$$

**Polymer chains**

**The volume *V(r)* of the shaded part**

$$g(\mathbf{r}) = \frac{1}{N}\sum_{n=1}^{N}\sum_{m=1}^{N}\left\langle \delta\{\mathbf{r} - (\mathbf{R}_m - \mathbf{R}_n)\}\right\rangle \longleftrightarrow f_D(x) = \frac{2}{x^2}\left(e^{-x} - 1 + x\right) \quad x \equiv (QR_g)^2$$



# Summary: Scattering functions

***Differential Cross section*** ***Scattering is a Fourier transform of the contrast variation square***

$$\frac{d\Sigma}{d\Omega}(q) = |\text{Fourier Transfom of } \rho(\mathbf{r})|^2 = (\Delta\rho)^2 \times$$

$$n_p P(q) S(q) = \begin{cases} n_p P(q) & \textbf{Particle dispersion (dilute)} \quad ( S(q) = 1 ) \\ n_p P(q) S(q) & \textbf{Particle dispersion (semi-dilute)} \end{cases}$$

$S(q)$ **Non-particulate system**

$$S(q) = \frac{S(0)}{1+\xi^2 q^2}$$ **Concentration fluctuations (one phase)**

| | | | |
|---|---|---|---|
| $\Delta\rho$ | **Scattering contrast** | $P(q)$ | **form factor** |
| | | $S(q)$ | **structure factor** |
| $n_p$ | **Number density of the particles** | $\xi$ | **correlation length** |

**Memo: "Fluctuations" mean space or time fluctuations of densities (electron or scattering length density), concentration, dipole moment, spin, etc.**

*The 3rd Soft Matter Summer School : Polymer Sciences in Biology*
*June 21 - July 4, 2015*

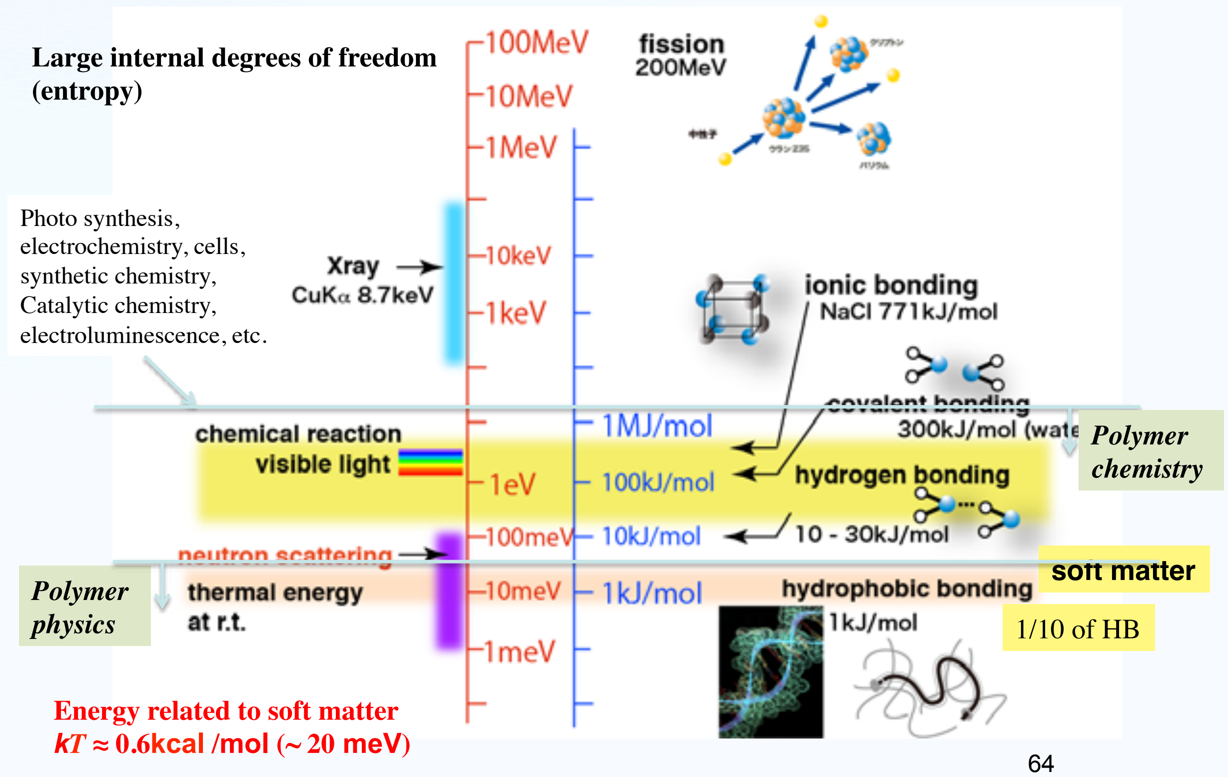
# "Neutron and Rheology"

**Mitsuhiro Shibayama,**
**ISSP, U. Tokyo**

## Part 1. Structural Analyses of Polymers by Small Angle Neutron Scattering

1. Introduction
2. Neutron and neutron scattering
3. Neutron scattering theory
4. Small angle Scattering
5. **Applications**

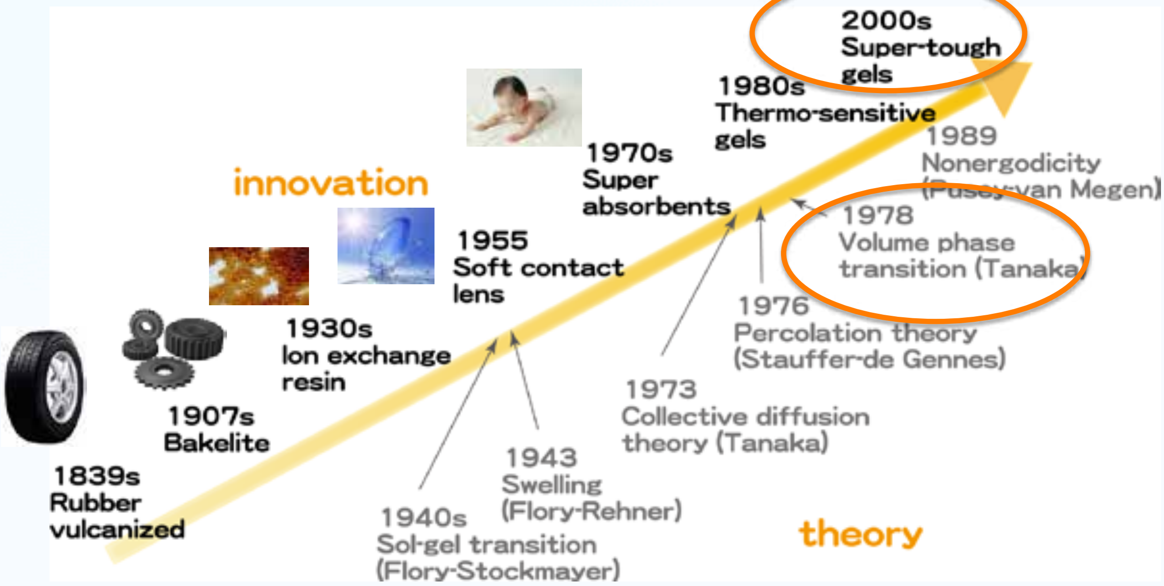
# Energies governing soft matter dynamics





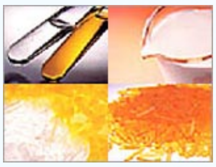

**Soft and flexible**

# History of network polymer and gels





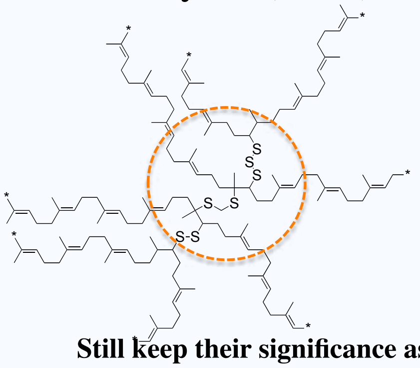
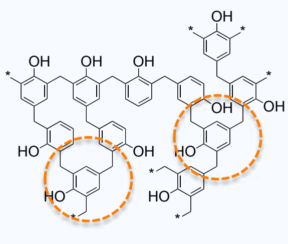
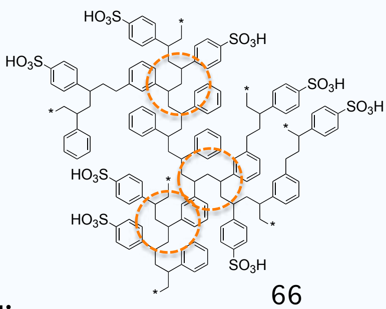

# Historical innovations in network polymers

**Rubber, Ebonite,** Goodyear (1839)

**Bakelite** Dr. Leo Bakeland (1907)

**Ion exchange resin** (1935)

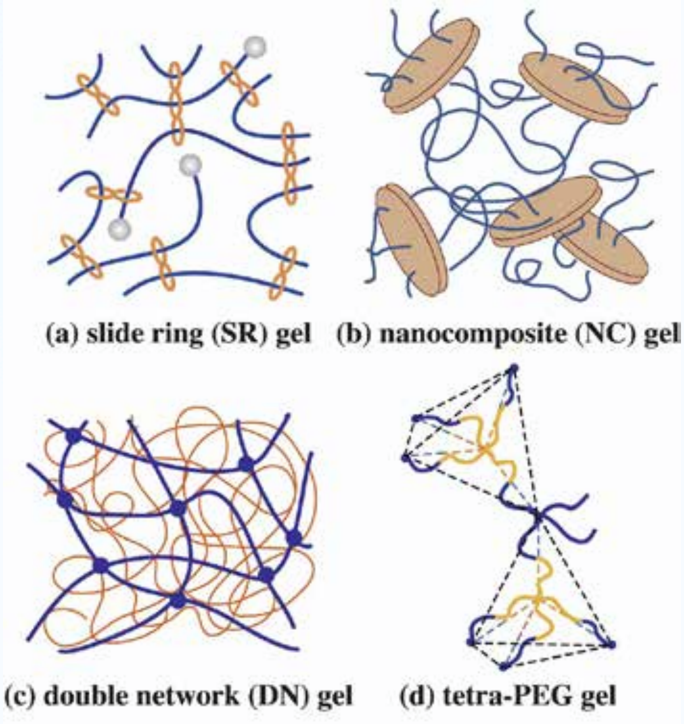


**Still keep their significance as industrial materials since their discovery.**

# Tough polymer gels

Itoh (2001)

Haraguchi (2002)



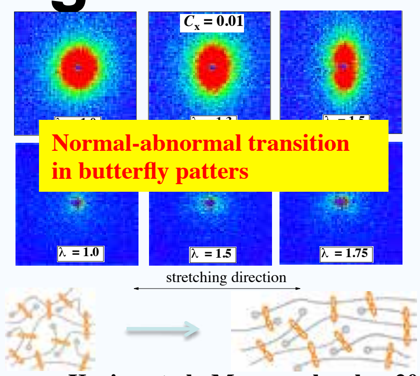

Gong (2003)

Sakai (2008)

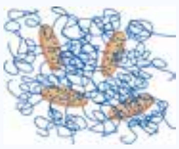


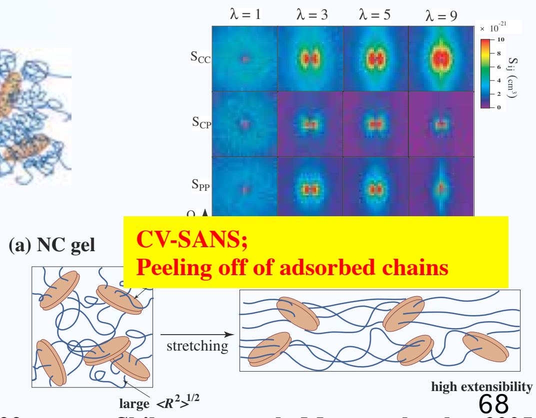
# Super tough gels

**Slide-ring gel** Okumura, Adv. Mater., 2001




Karino et al., Macromolecules, 2005.

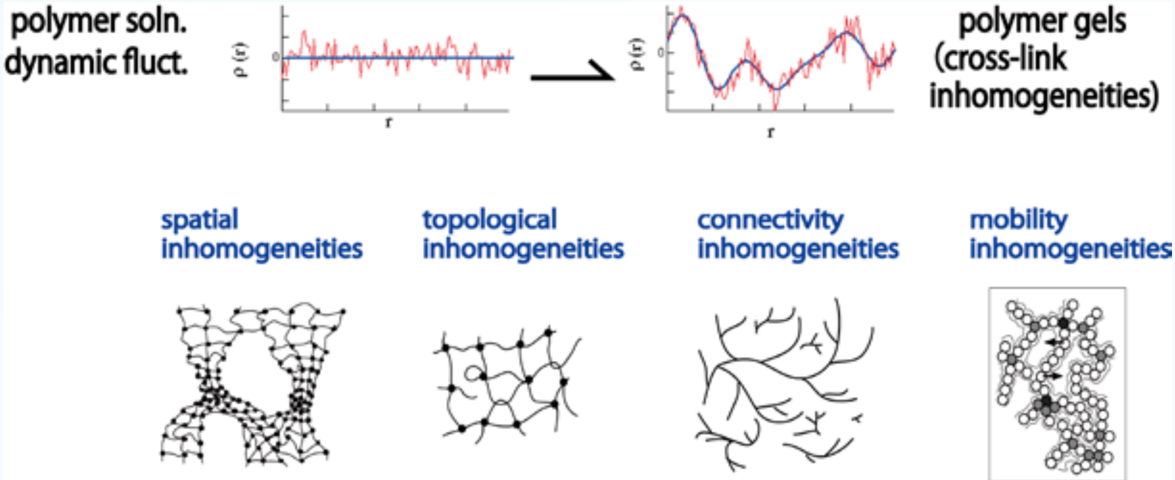





**Nanocomposite gel** Haraguchi, Adv. Mater., 2002

Shibayama et al., Macromolecules, 2005,
Nishida et al., PRE, 2009.

# Various types of inhomogeneities in polymer gels

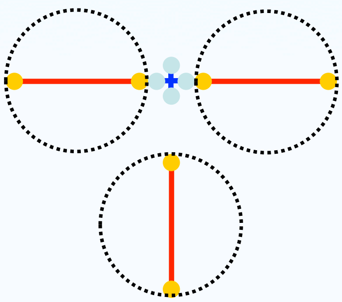


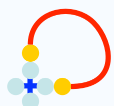

M. Shibayama, Bull. Chem. Soc. Jpn. 2002, 75, 641-659.



# Model Network

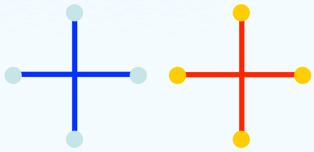
- **Buried reaction point**
- **Self-biting**





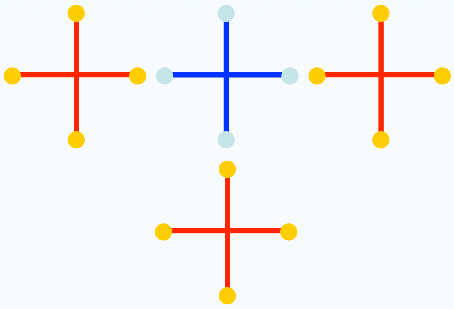
**Inhomogeneous structure**

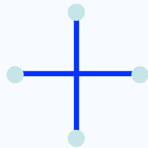
# Tetra Network



- Reaction front is always on the
- surface

- No self-biting

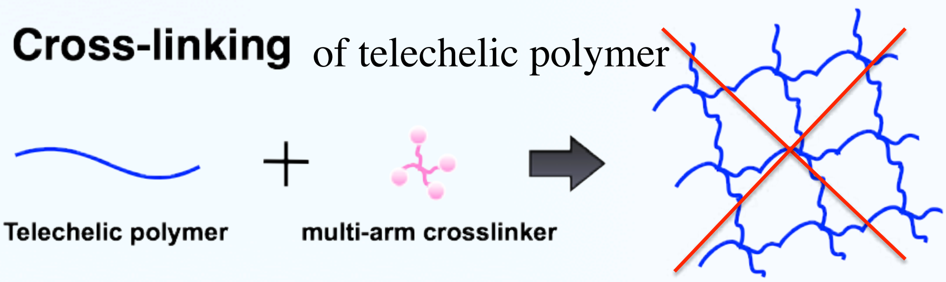




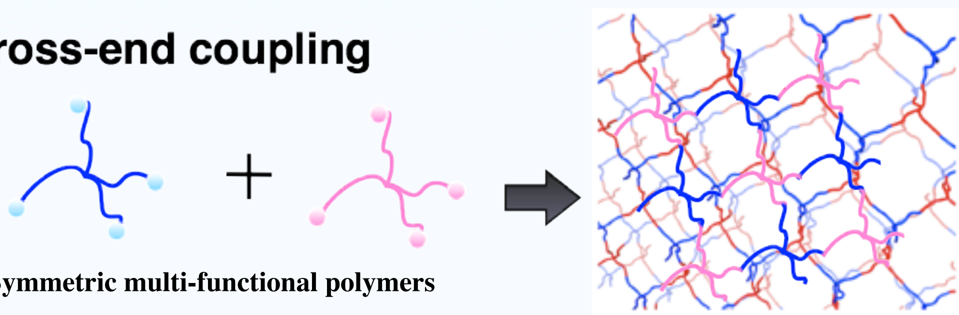
Homogeneous structure

# Exploration of realization of ideal-polymer network

**Cross-linking** of telechelic polymer




**Cross-end coupling**



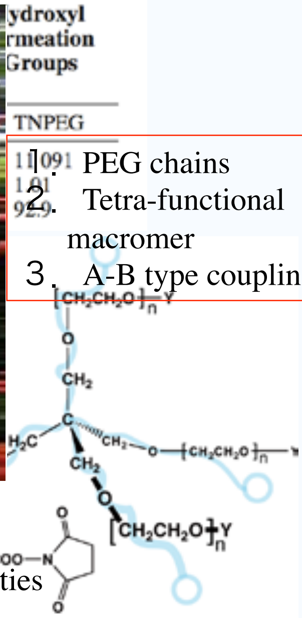
Symmetric multi-functional polymers

**New paradigm of Gel formation**
**Module assembling by "cross-end-coupling"**

# Tetra-PEG gel

*The Hakone Open Air Museum*

1. PEG chains
2. Tetra-functional macromer
3. A-B type coupling




A new type hydrogels with extremely low inhomogeneities like a “soft diamond”

amine

**TA**

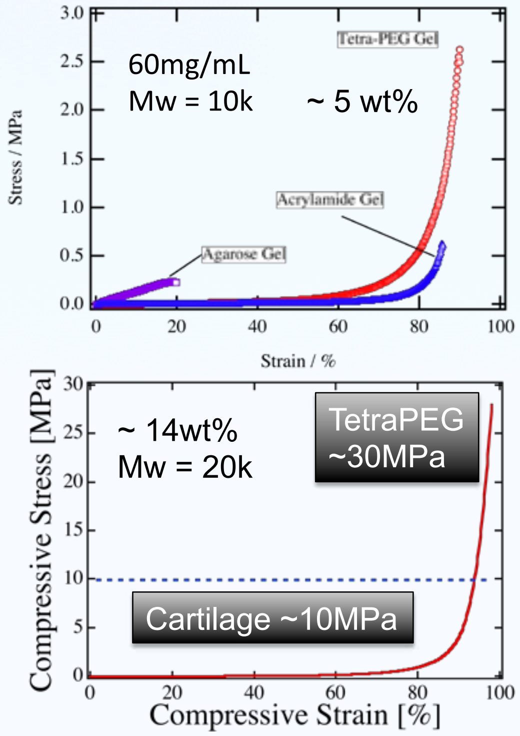
*N-hydroxysuccinimide-glutarate*

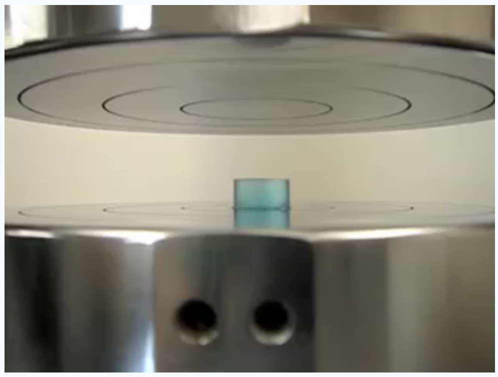
**TN**



T. Sakai et al. Macromolecules, 41, 5379-5384 (2008)

# Mechanical Properties





T. Sakai et al. Macromolecules, 41, 5379-5384 (2008)

# Tetra-PEG gel

**Advanced physical, chemical, and biological properties**
1. **high compressive toughness (superior to cartilage)**
2. **high transparency**
3. **biocompatible and nontoxic**
4. **easy and quick preparation**

**Etc.**

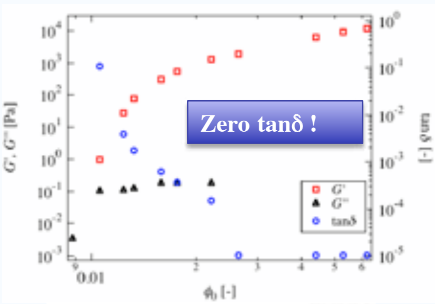
3x speed
~ 1 min

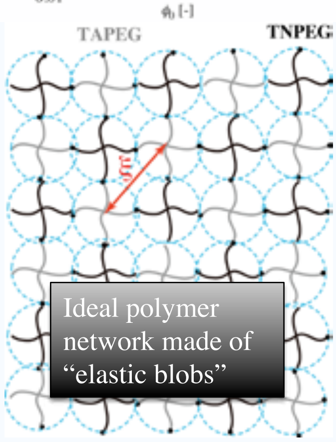


# Remarkable properties of Tetra-PEG gel

**Tetra-PEG ball vs power ball**


the reflection coefficient ≈ 0.84

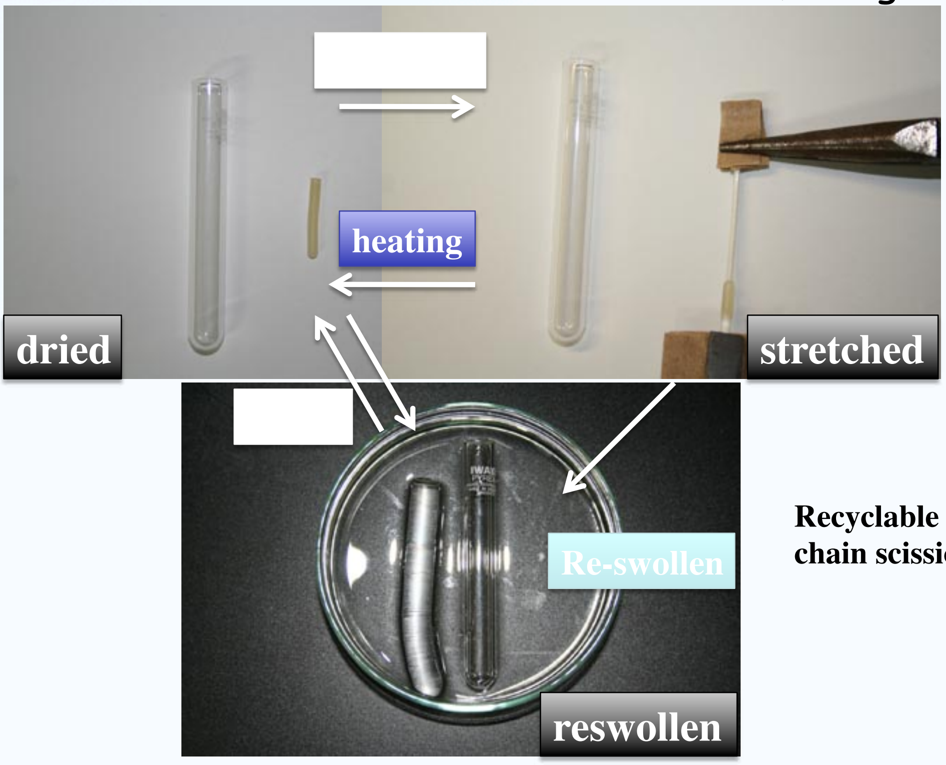



Macromolecules, 43, 488-493 (2010)

## Tetra-PEG gel: dried, stretched, re-swollen

10,000 g/mol



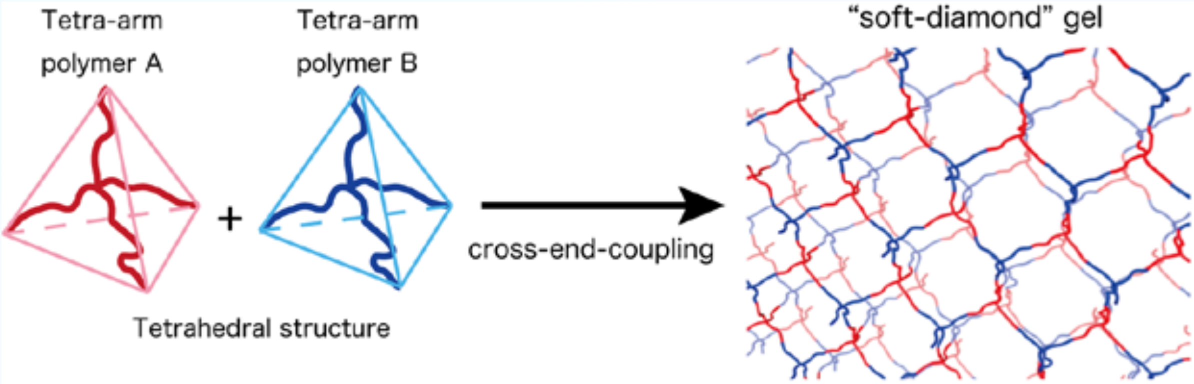

**Recyclable without chain scission**



## subcutaneous implantation of Tetra-PEG gel

**The back of immunocompetent mice**
**100mL of Tetra-PEG was implanted under anesthesia.**
**One week after implantation.**

# As-prepared gels

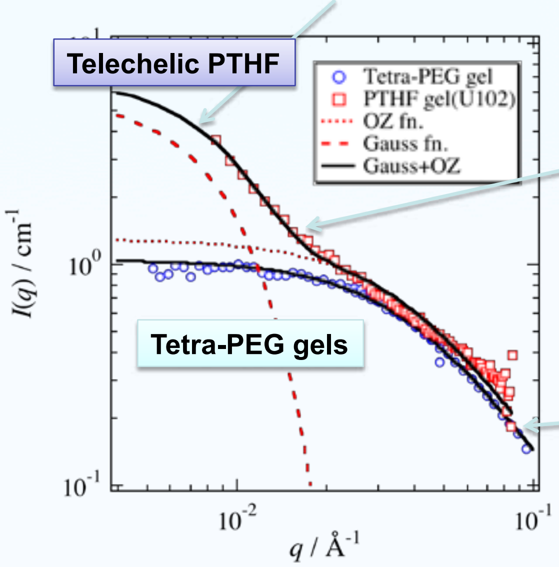



| TAPEG | TNPEG | |
|---|---|---|
| 5k | 5k | |
| 10k | 10k | |
| 20k | 20k | |
| 40k | 40k | *Symmetric condition* |



# Comparison of SANS functions of gels prepared by crosslinking of telechelic polymer vs Tetra-PEG gel

PTHF; made by end-coupling of telechelic PTHF (Takahashi, 1995)




For ordinary gels,

Inhom. Solution-like

$$I(q) = \frac{I(0)_{SL}}{\left(1+\Xi^2 q^2\right)^2} + \frac{I(0)_{OZ}}{1+\xi^2 q^2}$$

$$I(q) = I_G(0)\exp\left[-\frac{\Xi^2 q^2}{3}\right] + \frac{I(0)_{OZ}}{1+\xi^2 q^2}$$

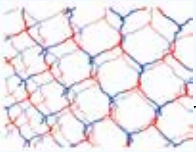
***Gauss*** ***OZ***

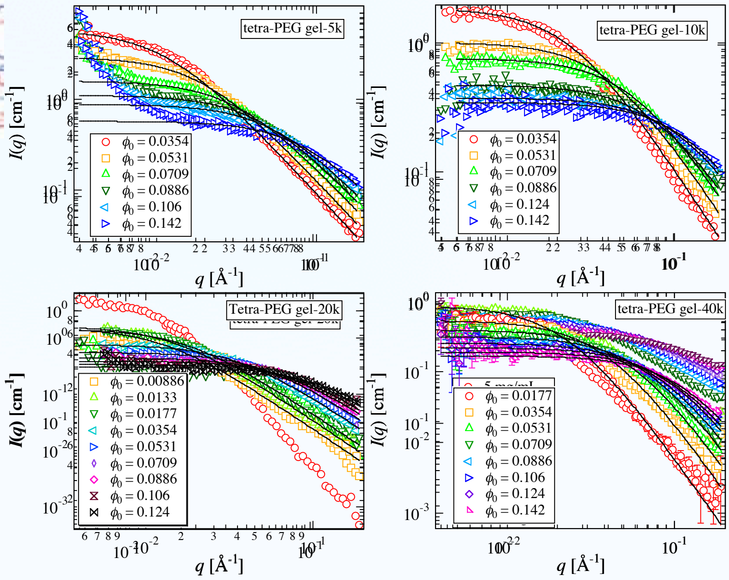
OZ function

$$I(q) \sim \frac{I(0)_{OZ}}{1+\xi^2 q^2}$$

**Note: Tetra-PEG gels can be described by only OZ fn.**

## Concentration and $M_w$ dependence





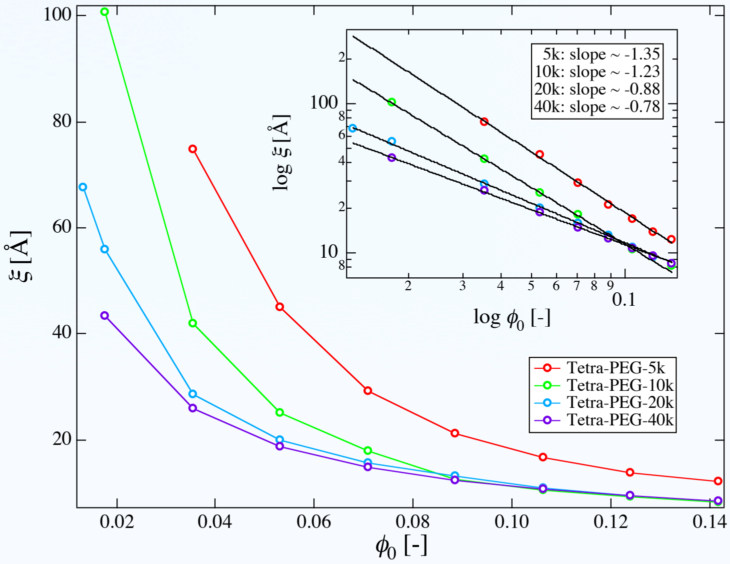

**As-prepared gels**

$$I(q) \sim \frac{I(0)_{OZ}}{1+\xi^2 q^2}$$

**Messages:**
**1. SANS functions are well fitted by the OZ equation.**
**2. There appears an upturn at low *q*'s, particularly for low Mw's.**



## $M_w$ dependence of $\xi$ for Tetra-PEG gel



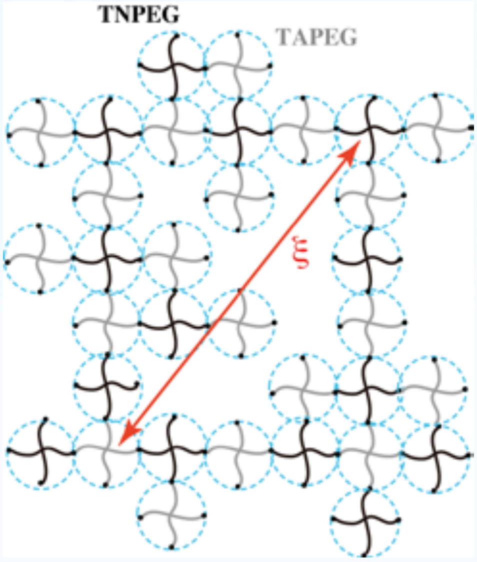

$$\xi \sim \phi_0^{-3/4}$$

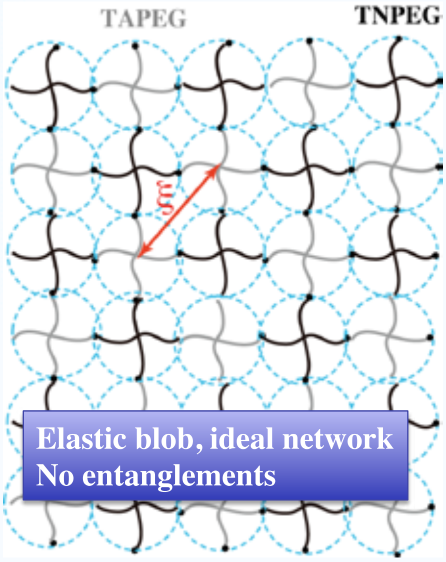
(Exclusively for -40k gel)

Note: $\xi(M_w\text{=40k}) < \xi(M_w\text{=5k})$!!

**Messages:**
**Tetra-PEG-40k recovers a proper behavior of polymer solutions In semidilute solutions, while Tetra-PEG-5k is far from it due to its short arm length.**

# Model of inhomogeneities in as-prepared gels



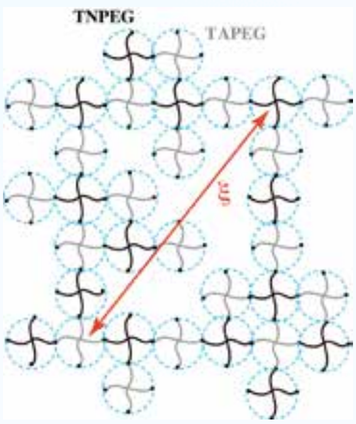




5k-Tetra-PEG gel

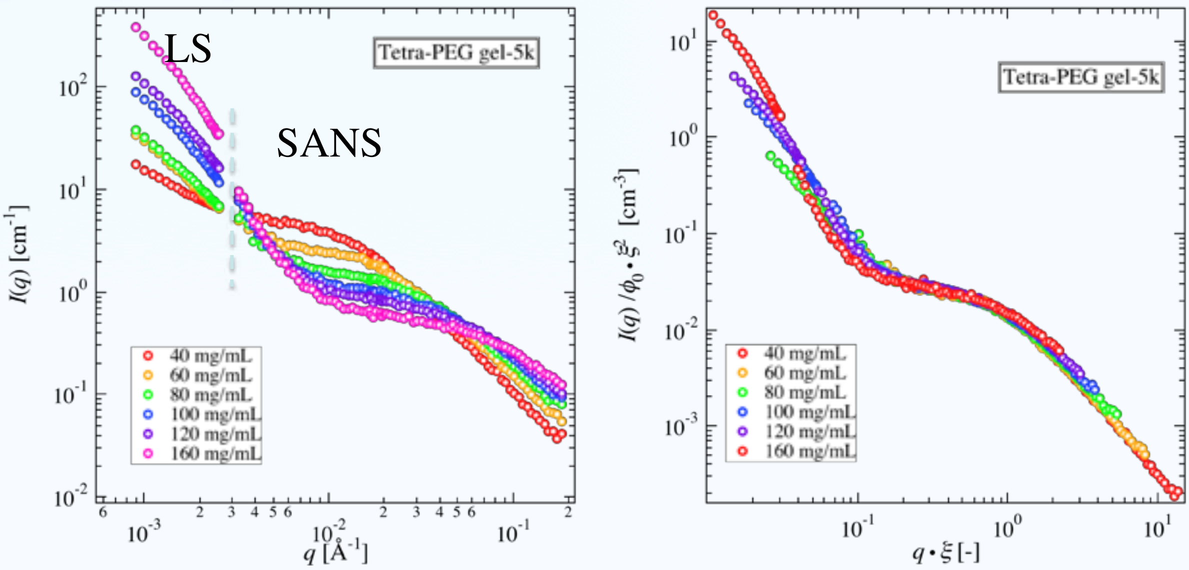
40k-Tetra-PEG gel



# Inhomogeneities in Tetra-PEG gels

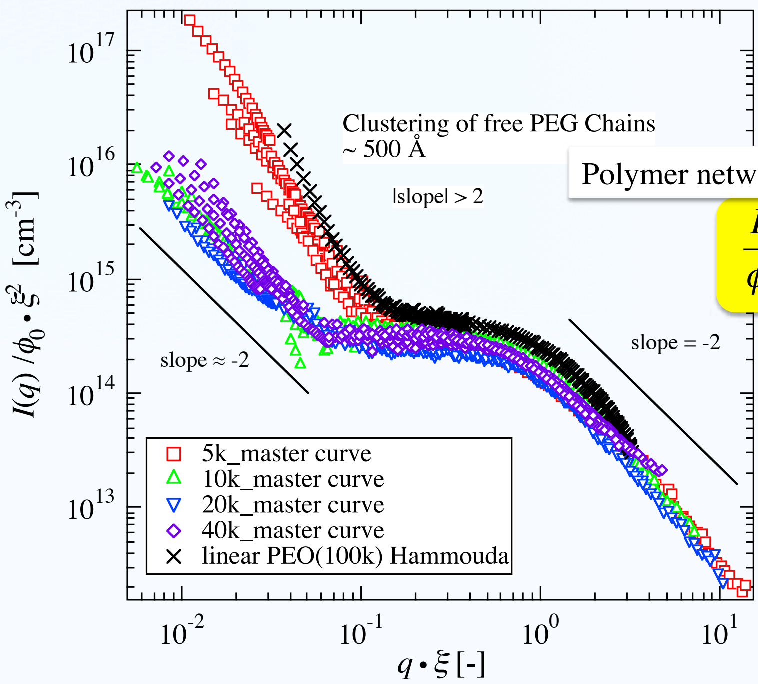


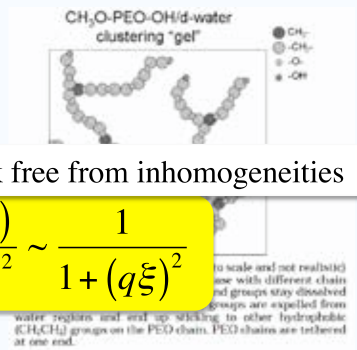
# Scattering curves and Master curves of Tetra-PEG gel-5k






# Master curves



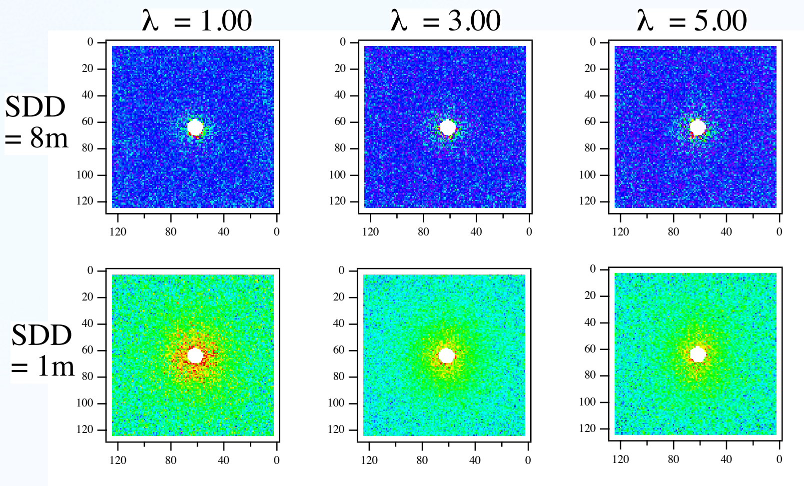

Polymer network free from inhomogeneities

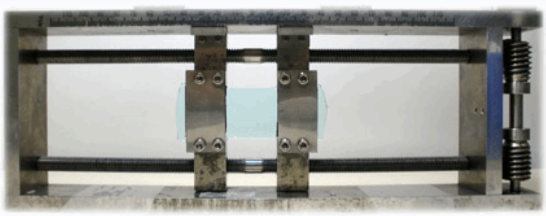
$$\frac{I(q)}{\phi_0 \xi^2} \sim \frac{1}{1+(q\xi)^2}$$

$$I(Q) = A/Q^n + C/\{1 + (QL)^m\} + B$$

Hammouda et al., Macromolecules, 2002, 35, 8578, 2004, 37, 6932.

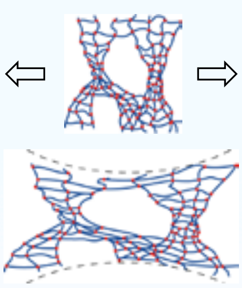
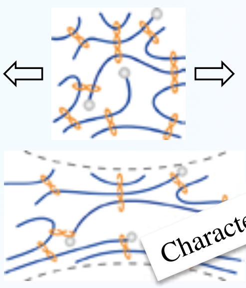
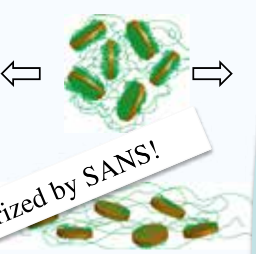
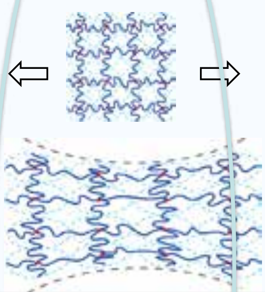
# Deformation SANS for Tetra-PEG



# Deformation mechanisms of super-tough gels

M. Shibayama, J. Phys. Soc. Jpn., 78, 041008 (2009)

| | Conv. Gel (chem. Gel) | Slide ring gel | Nanocomposite gel | Tetra-PEG gel |
|---|---|---|---|---|
| Deformation model |  |   |  |  |
| Mech. Prop. | brittle | High elasticity High deformability | High elasticity High deformability | High elasticity High deformability |
| inhomogeneities | Very large | Low $C_x$: decreasing High $C_x$: increasing | small | none |
| Scatt. pattern | Abnormal | Normal / abnormal liq. like/gel like | Normal liq. like/clay scatt. | isotropic $\times$ |
| Charac. feature | Inhomog. str. | Movable cross-links | Plane crosslink, large molec. wt. | Elastic blob |