Structural Analyses of Polymers by Small Angle Neutron Scattering

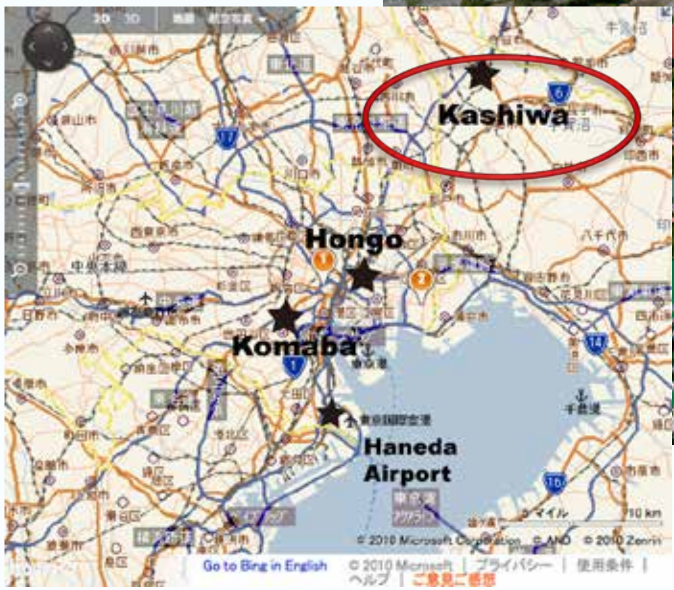
M. Shibayama, ISSP, U. Tokyo
https://www.shibayamalab.issp.u-tokyo.ac.jp/

from Kashiwa/Tsukuba
4/5 Mori
4/19 Shibayama
4/26 Yoshinobu
5/10 Sasaki
5/24 Amemiya
5/31 Yamamuro

1. Introduction
2. Neutron
3. Neutron Scattering
4. SANS Applications to Polymeric Systems
5. Neutron Scattering of Gels
6. Structure of Critical Clusters and Biomedical Application
7. Report

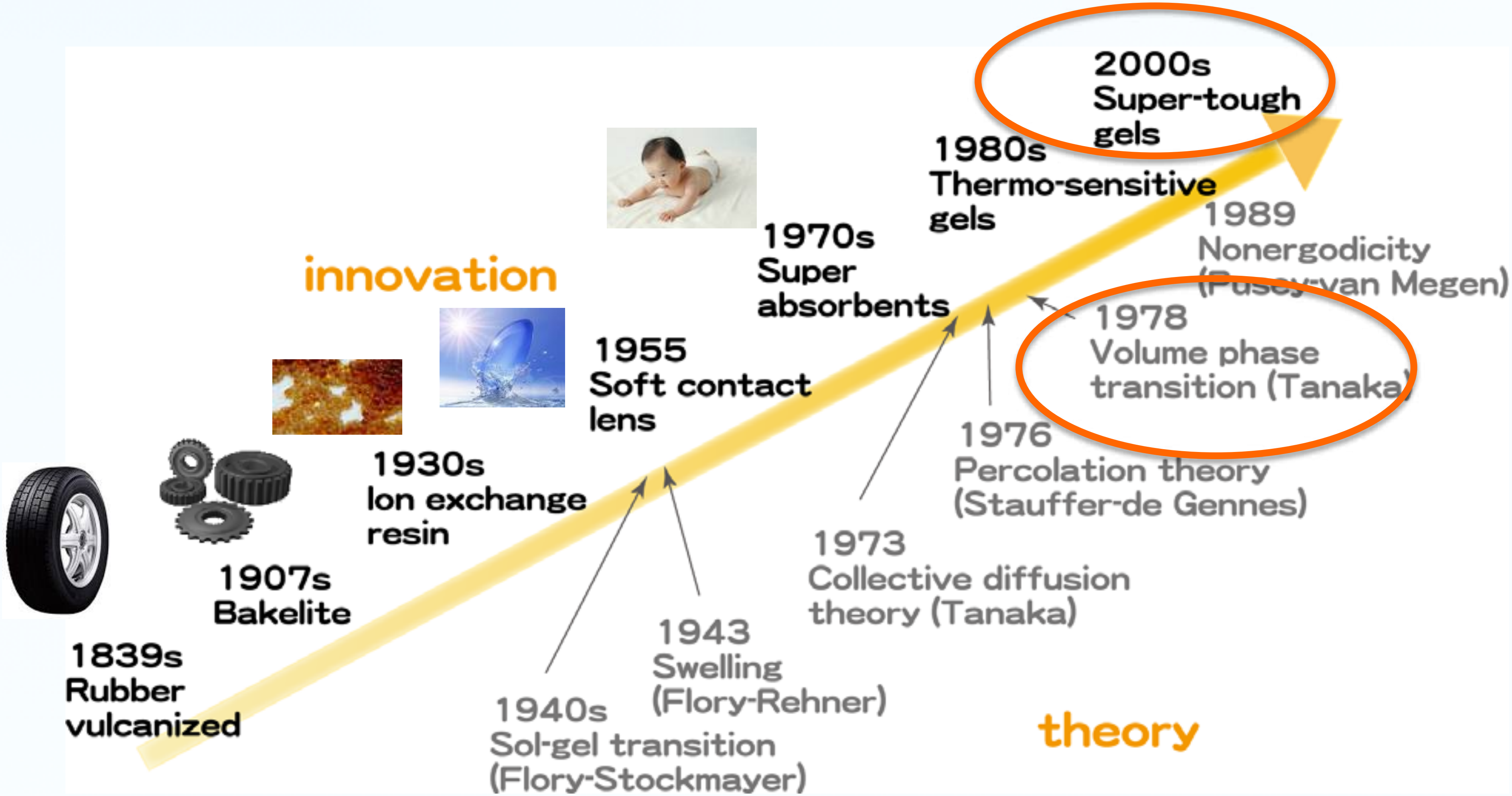
Guidance schedule:
Apr. 28 (Sat)、June 2 (Sat) *Chem. Div.*
June 2 (Sat) *Institute for Solid State Physics*
June 2 (Sat) Material Science Course, School of Frontier Science

Kashiwa Campus, U. Tokyo

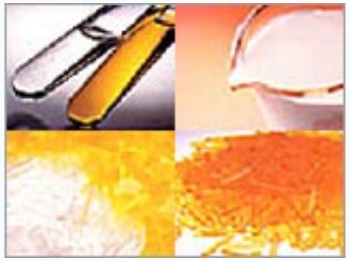


One of three major campuses of U. Tokyo

History of network polymer and gels



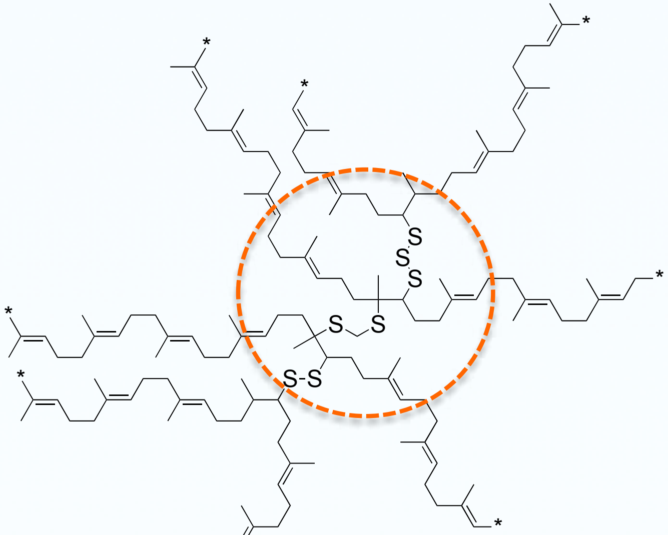
Historical innovations in network polymers

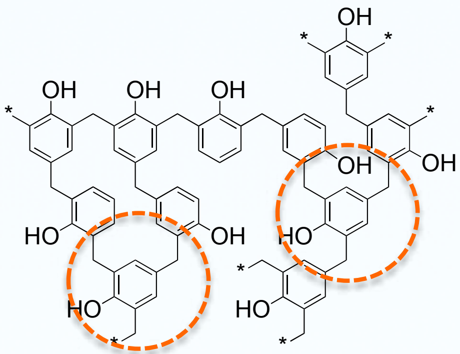


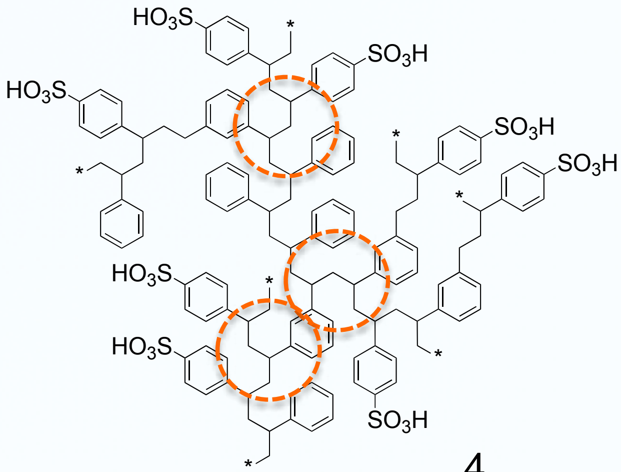
Rubber, Ebonite,
Goodyear (1839)

Bakelite
Dr. Leo Bakeland (1907)

Ion exchange resin
(1935)







Still keep their significance as industrial materials since their discovery.

Biomedical application

失われた人体の機能を人工的に取り戻すー
その試みは、古代エジプトの義歯にはじまるという。・・・

1 Intraocular lens (眼内レンズ)

2 Cochlear implant (人工内耳)

3 Artificial tooth root (人工歯根)

4 Deep brain stimulation device (脳深部刺激装置)

5 pacemaker (ペースメーカー)

6 Artificial blood vessel (人工血管)

7 Auxiliary artificial heart (補助人工心臓)

8 dialysis (人工透析)


The Asahi Shimbun GLOBE globe.asahi.com
人工臓器、日本のギャップ
Overcoming Medical Device Lag

Asahi News Paper Globe, 2010.3.22

Biomedical application

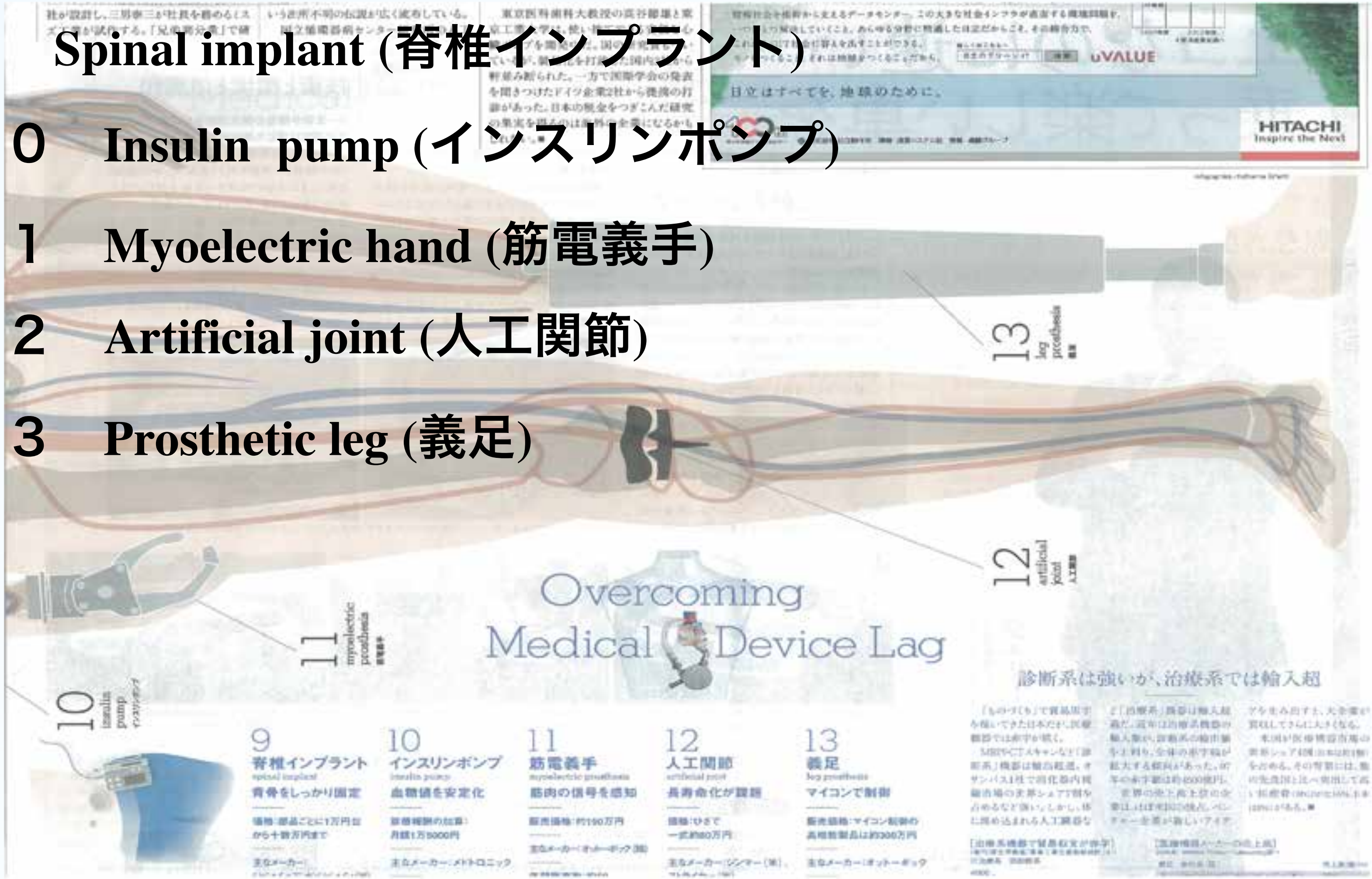
９　Spinal implant (脊椎インプラント)

１０　Insulin pump (インスリンポンプ)

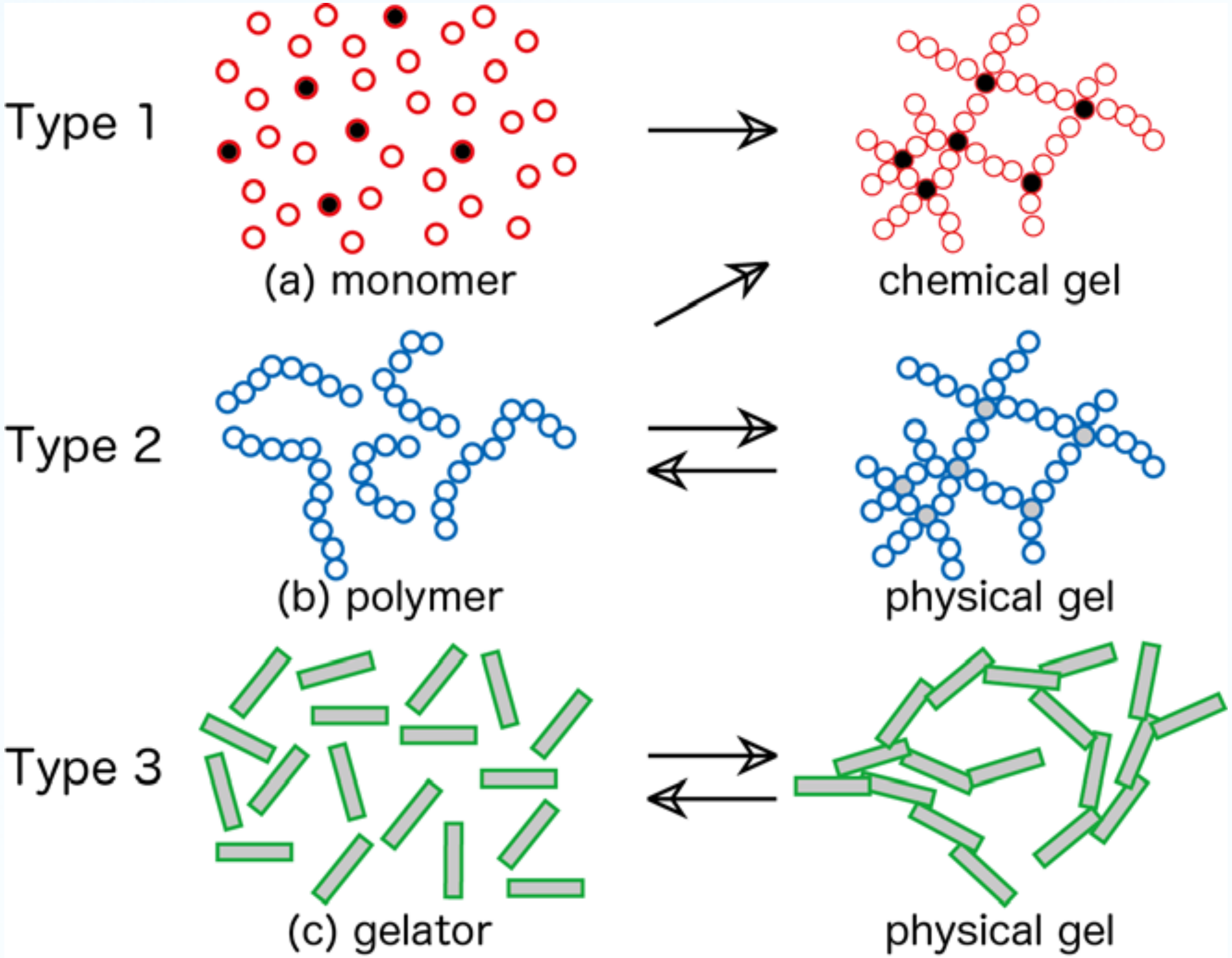
１１　Myoelectric hand (筋電義手)

１２　Artificial joint (人工関節)

１３　Prosthetic leg (義足)

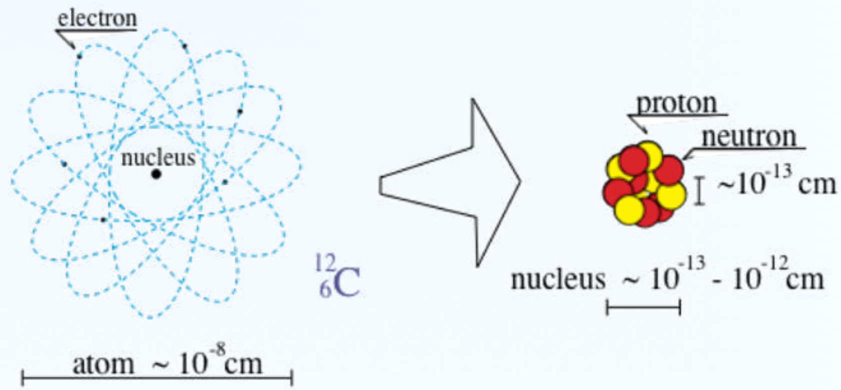


various types of gels



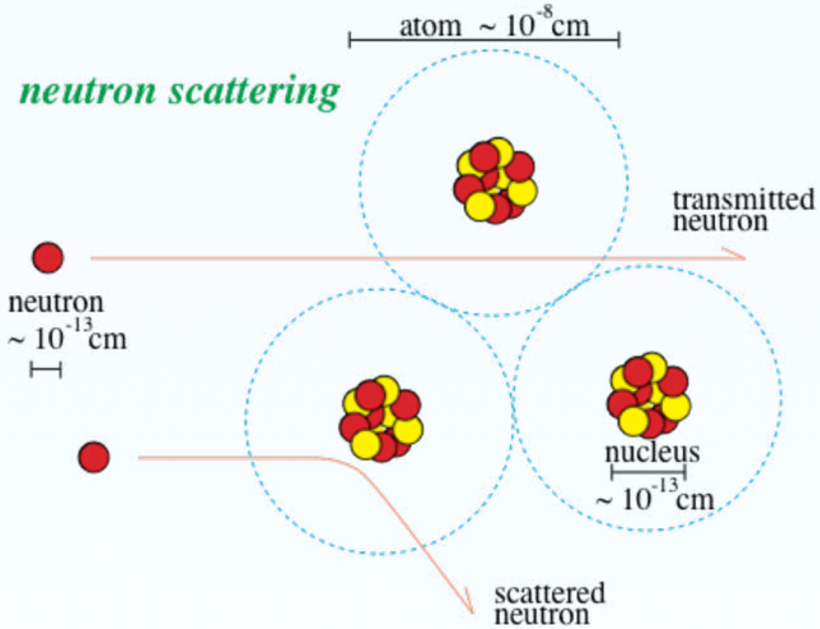
2. Neutron

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.

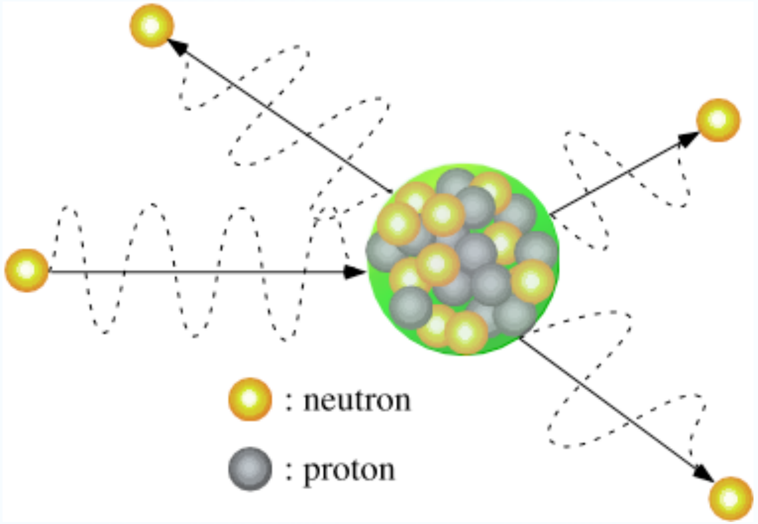
For ex.:
If an atom is a Colosseo size (188m (long axis)), the nucleus is ca. 2mm!

2. Neutron and Neutron Scattering

What is Neutron?

m_n~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 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

Part 1

3. Properties of neutron

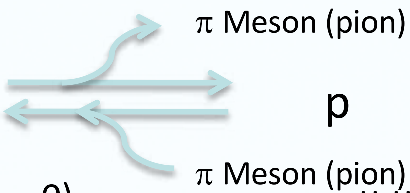
mass	m_n = 1.675 x 10^{-27} kg
Spin quantum number	s =1/2 (-1/2)；Fermion
Mag. moment	μ_n = -1.913 μ_N μ_N : nuclear mag. Moment, 3.152 x 10^{-14} MeV/T
Lamour freq.	29.16 (MHz/Tesla)
Life time	885.9 ±0.9 s (ca15min)
Quark comp.	u-d-d

Wikipedia

Annihilation of neutron（β^-annihilation）

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

n



p

Resonance state between n and p

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

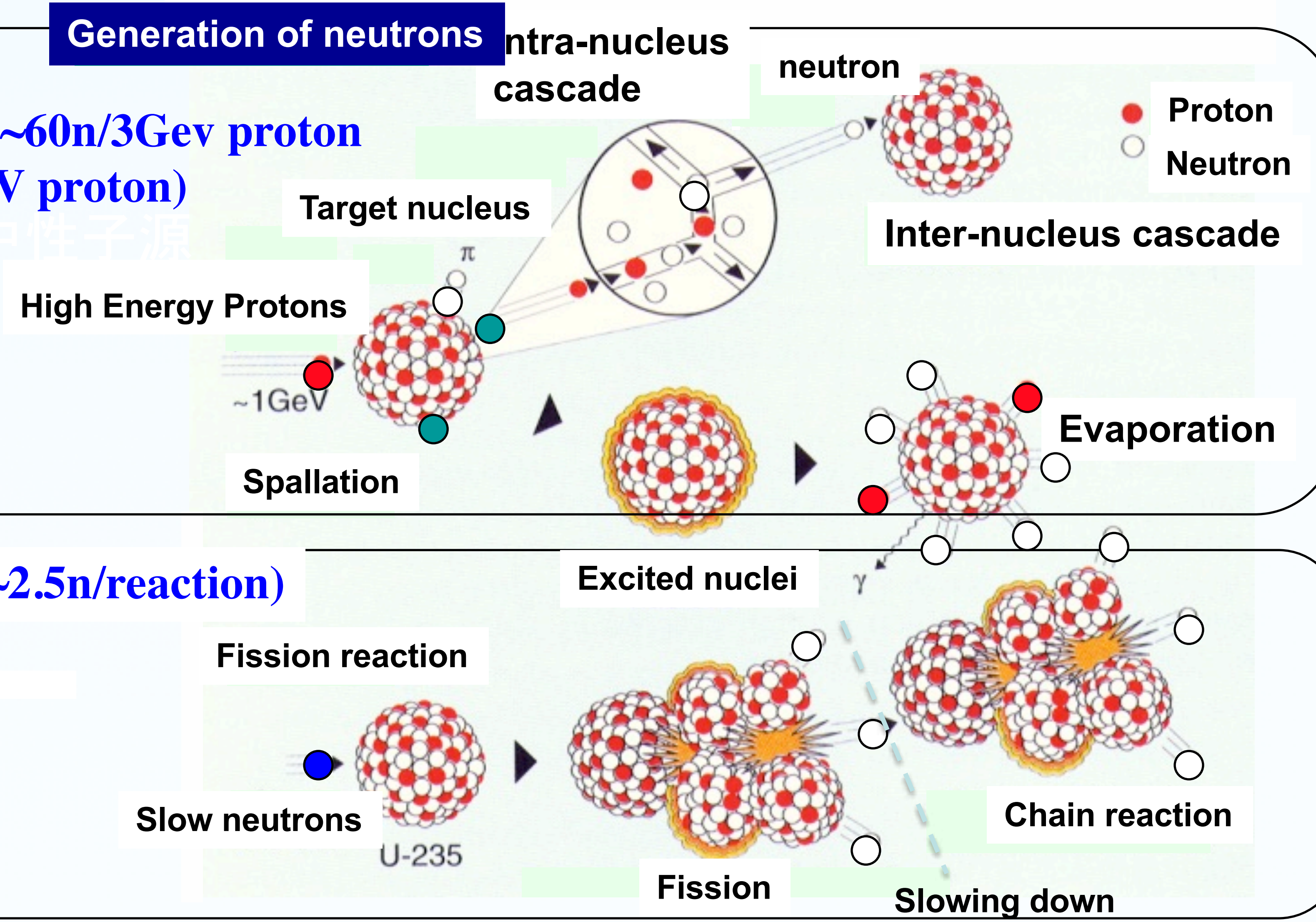
u-u-d (2/3, 2/3, -1/3 = 1)

4. Generation of neutrons

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

Generation of neutrons

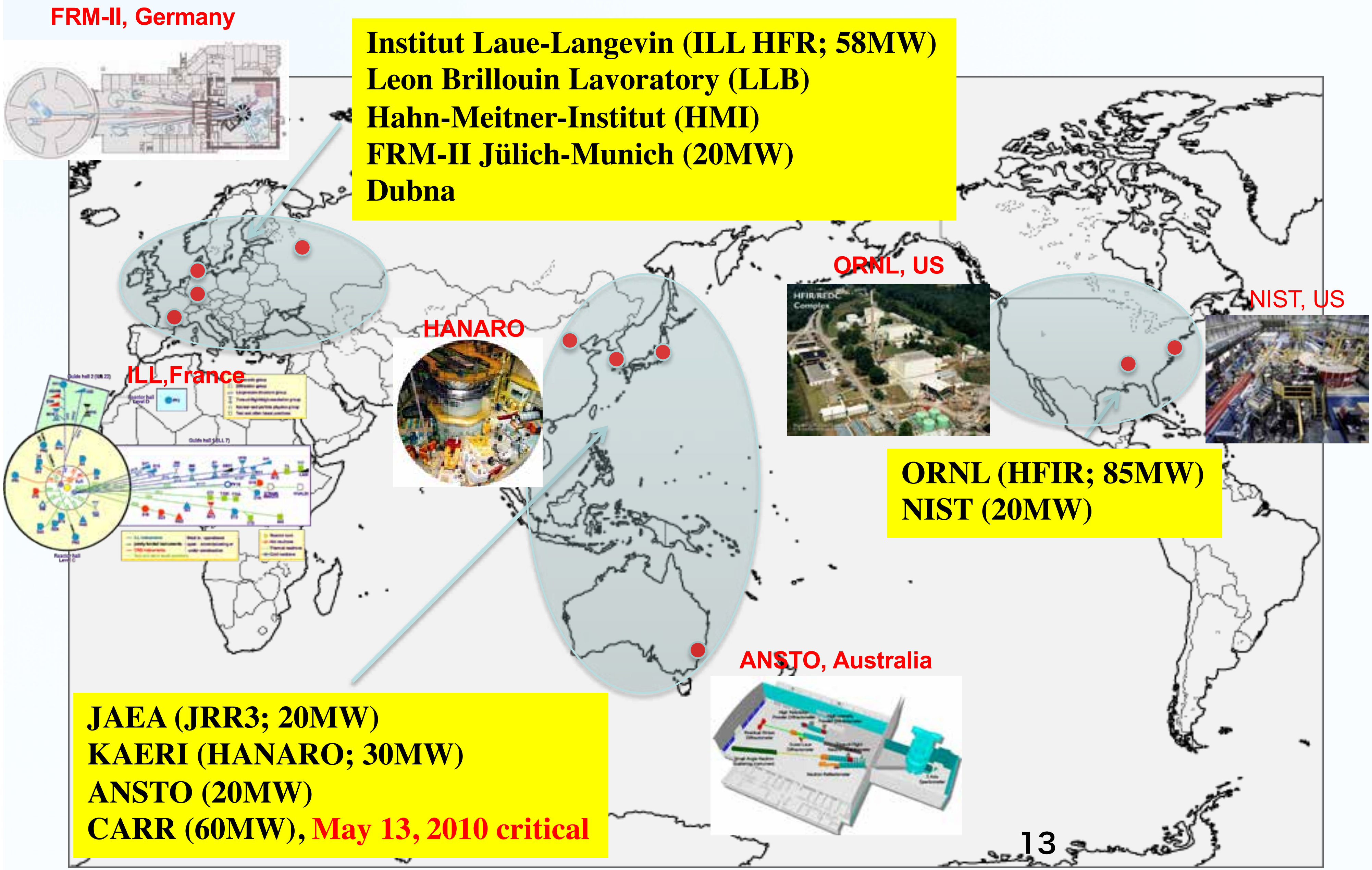
spallation(~60n/3Gev proton
~24n/1GeV proton)



fission(~2.5n/reaction)

reactor

5. Research reactors in the world



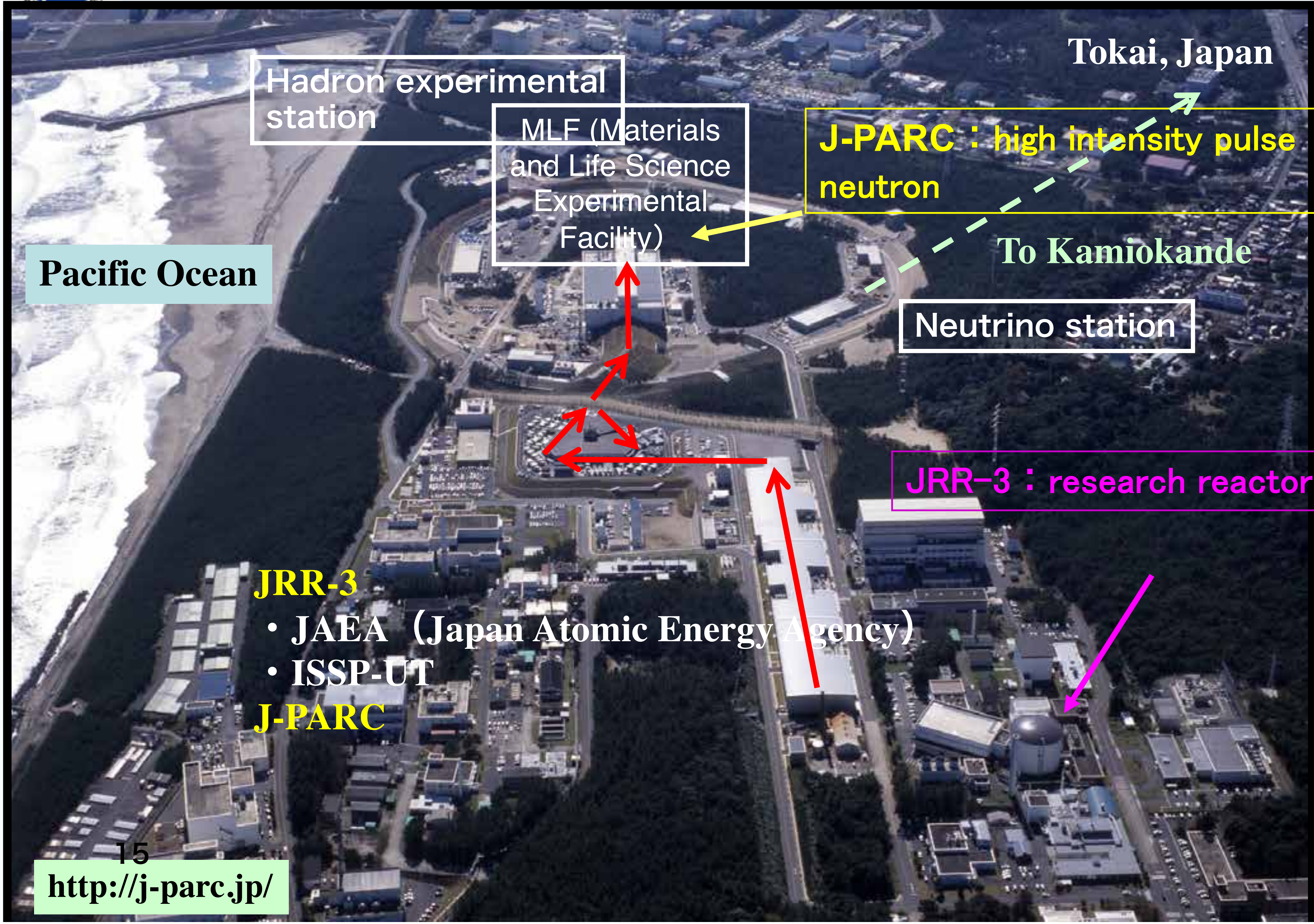
Institut Laue-Langevin (ILL HFR; 58MW)
Leon Brillouin Lavoratory (LLB)
Hahn-Meitner-Institut (HMI)
FRM-II Jülich-Munich (20MW)
Dubna

ORNL (HFIR; 85MW)
NIST (20MW)

JAEA (JRR3; 20MW)
KAERI (HANARO; 30MW)
ANSTO (20MW)
CARR (60MW), May 13, 2010 critical

6. Pulse Neutron Source in the world

7. Neutron Science at JRR-3 and J-PARC



Part 1

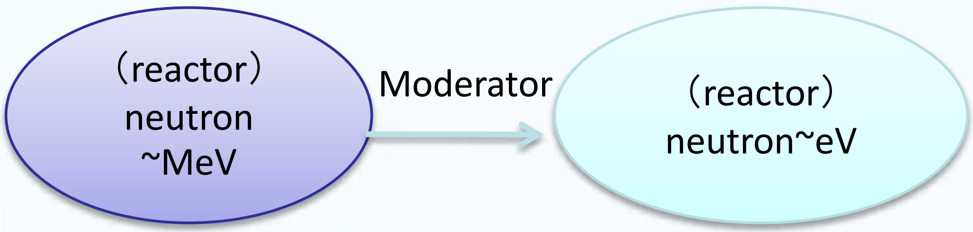
8. Reactor neutrons

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)

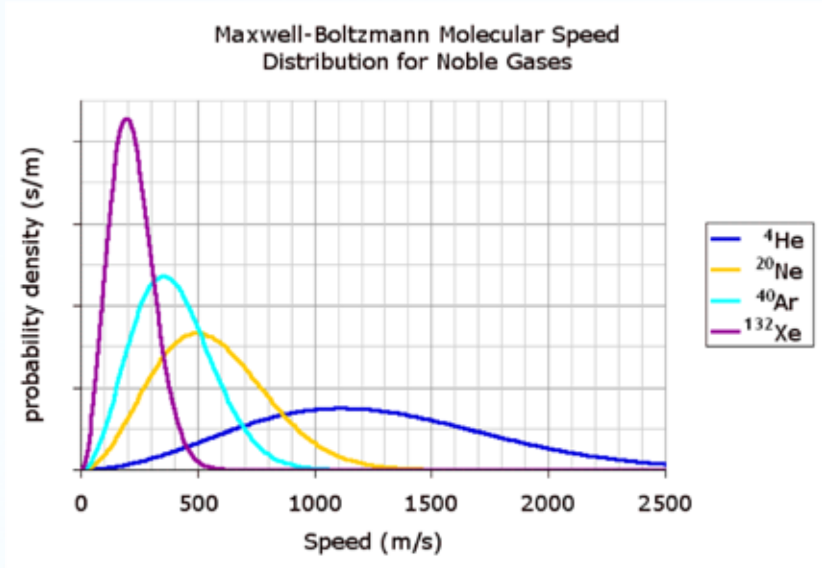


Maxwell distribution characterized by the temperature of the moderator

<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.

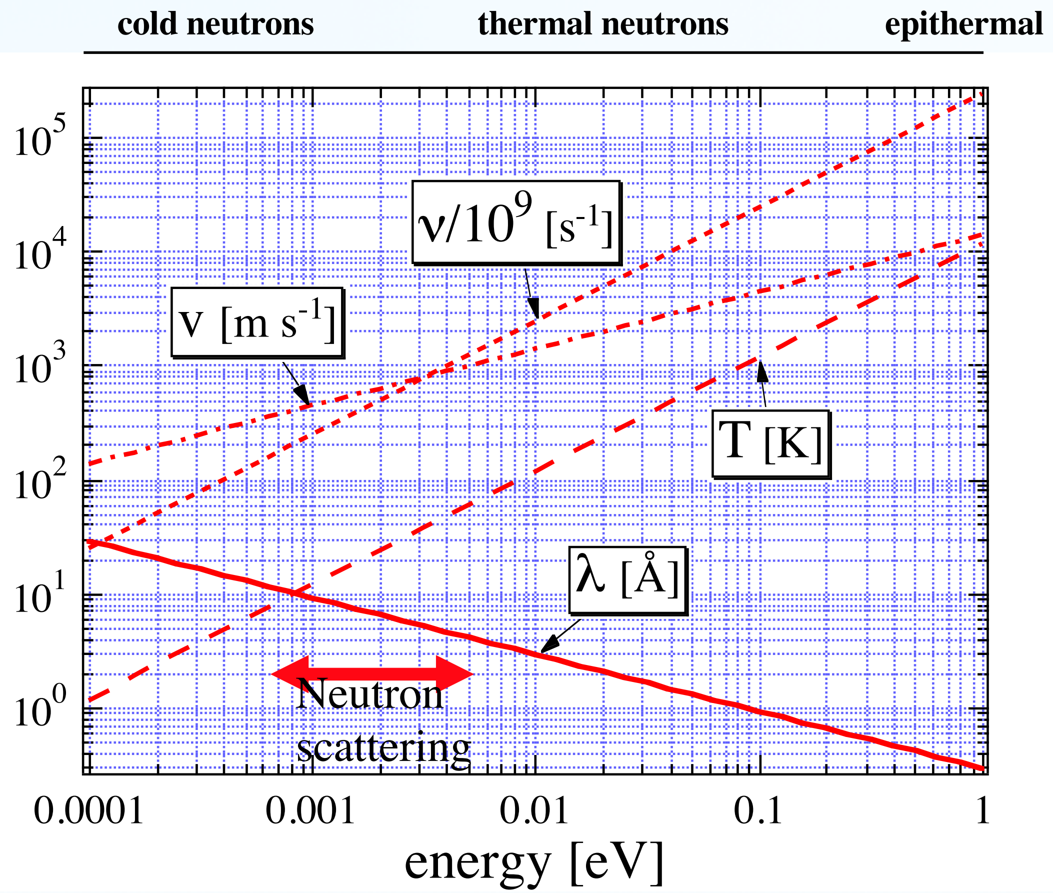
Q: Calculate the most probable velocity of argon gas at *T*=300K.

9. 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 ($T_{mod} \approx$ room temp.)
100 – 500 meV	hot neutron
> 500 meV	epithermal neutron

10. Velocity, wavelength, and wave number of neutrons



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

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

wave

$$E = kT \quad (3)$$

energy

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

Maxwell distribution

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

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

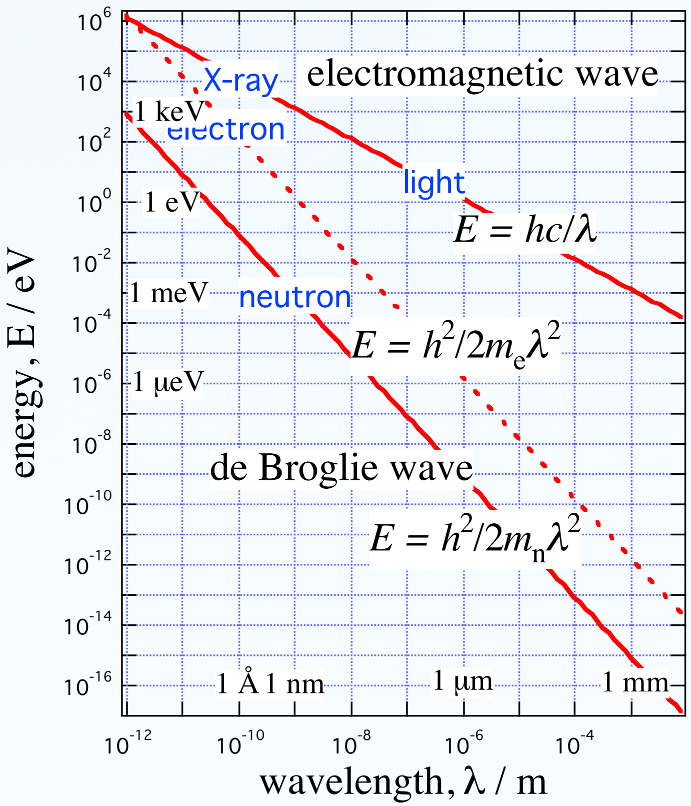
$$\lambda[\text{Å}] = \frac{0.2860}{\sqrt{E[eV]}} \quad (7)$$

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

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

11. Energy dispersion



Scattering by photon:

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

$$\varepsilon = \hbar\omega = \frac{hc}{\lambda} \qquad h = 6.626\times 10^{-34}\ \text{[J.s]}$$

For visible light $\varepsilon \approx 1\text{eV},\quad \lambda = 0.4 \sim 0.7\times 10^4\ \text{Å}$

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

For Å-ordered structures, photons with

$\varepsilon \approx 10^4\,\text{eV} = 10\text{keV}$ with are necessary and X-ray is the best means.

Scattering by electrons:

Electrons with mass m_e has the following dispersion relationship.

$$\varepsilon = \frac{\hbar^2 k^2}{2m_e} = \frac{h^2}{2m_e\lambda^2} \qquad m_e = 9.109\times 10^{-31}\ \text{kg}$$

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

Scattering by neutrons:

The same dispersion eq. as for electrons

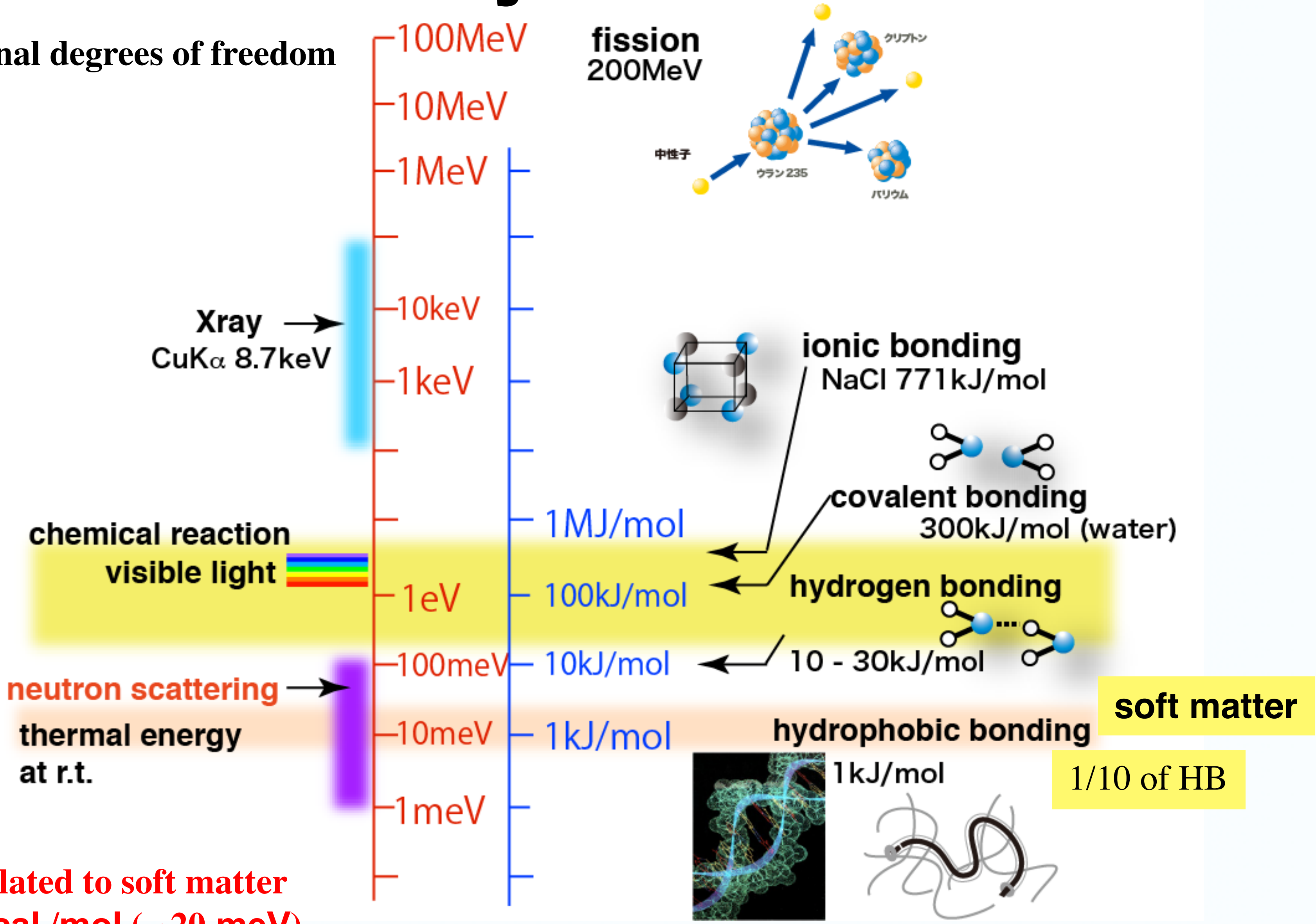
$$\varepsilon = \frac{\hbar^2 k^2}{2m_n} = \frac{h^2}{2m_n\lambda^2}$$

Note that the mass of neutron is very different from that of electron.
$m_n = 1.675\times 10^{-27}$ kg (ca 1800 times larger than e)

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

12. Energies governing soft matter dynamics

Large internal degrees of freedom (entropy)



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

Soft and flexible

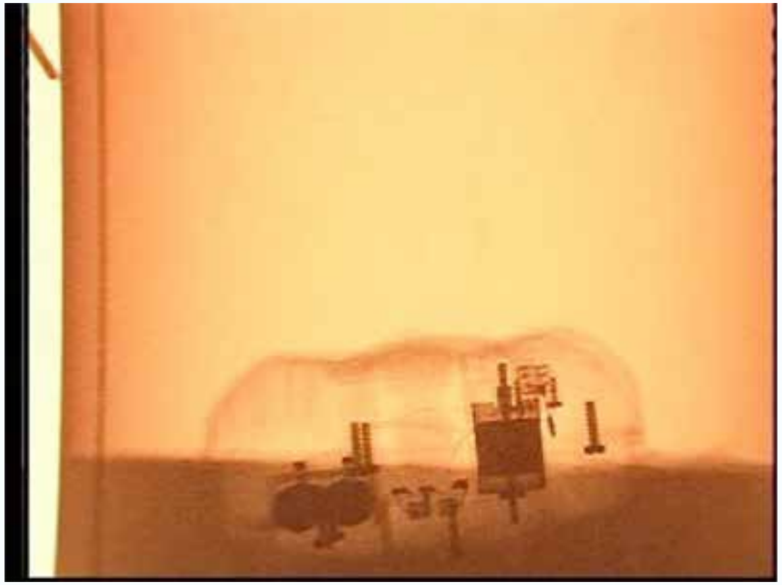
13. Comparison of X-ray and neutron

Water, H detection → Nondestructive visualization ← permeability

Fountain toy

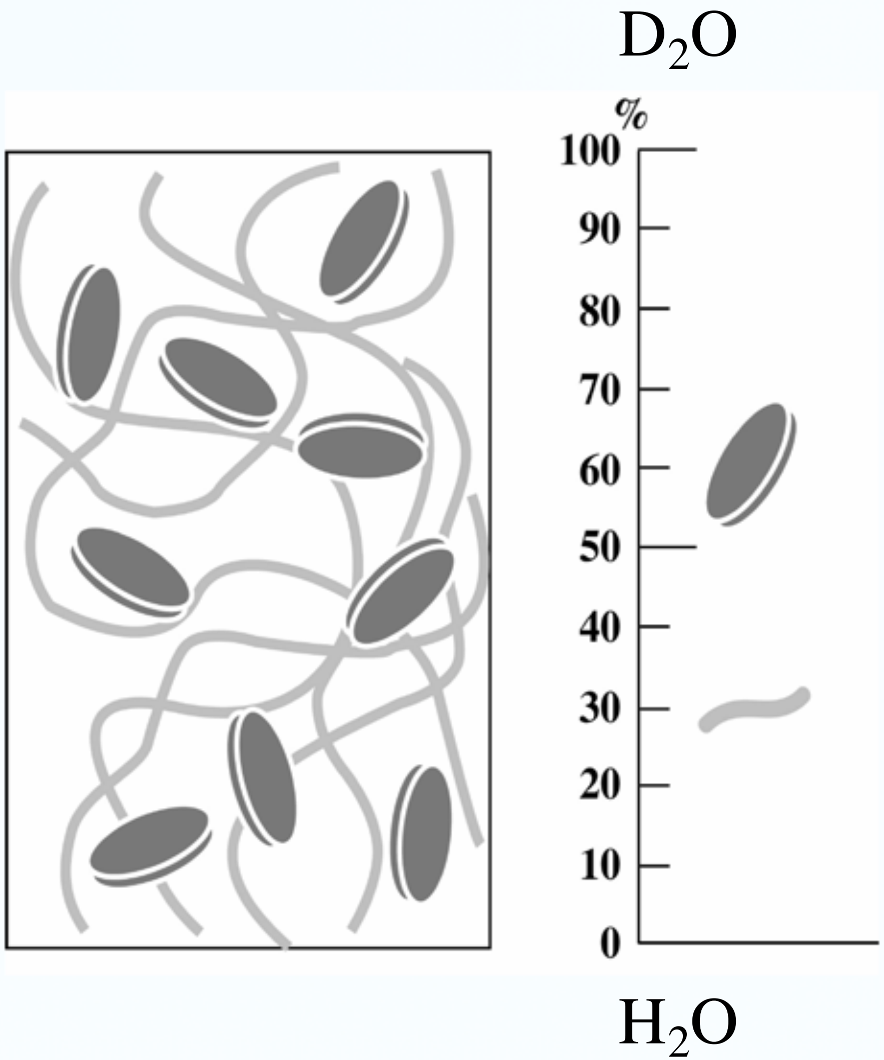
X -ray

neutron



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

14. Neutron contrast



labeling

Contrast matching

Part 1

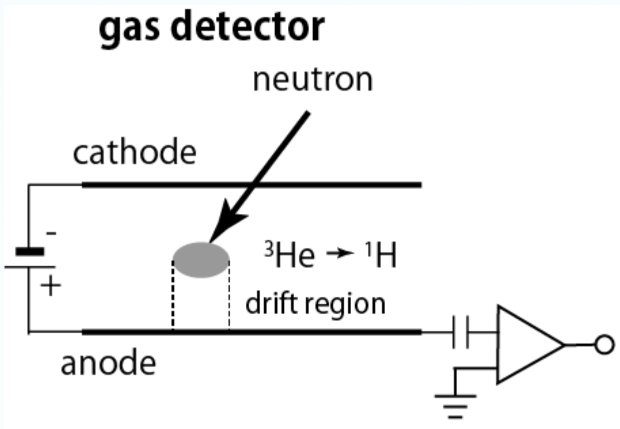
15. Detection of neutrons

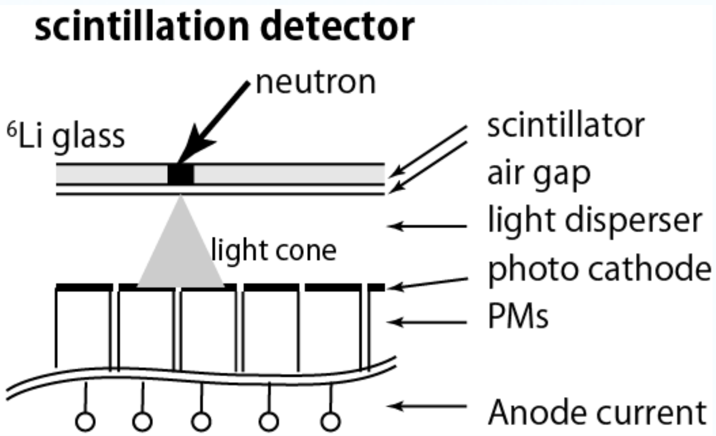
Neutron: electroneutral

By generating electric charges via nuclear reaction, and counting them

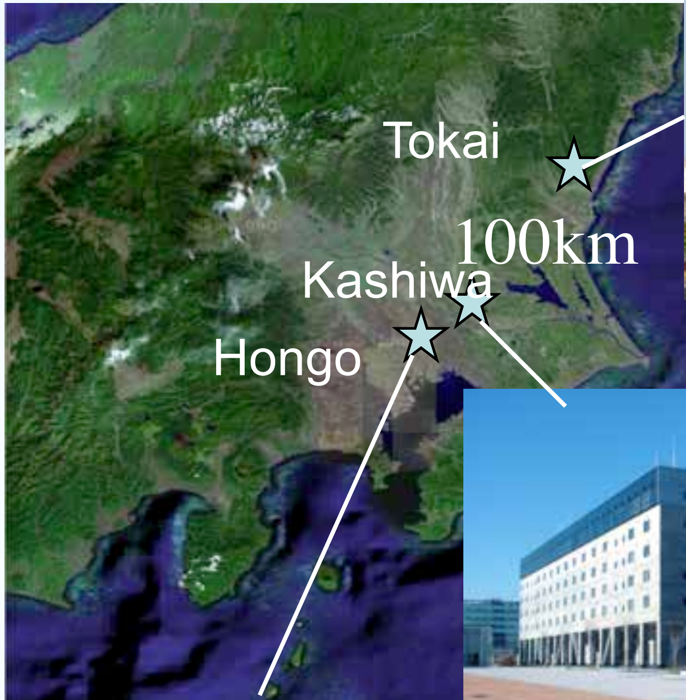
	Cross section、(25meV)	Generated particles	energy— [MeV]	Total energy[MeV]
n + ^{3}He	5333b	p, ^{3}T	0.57, 0.2	0.77
n + ^{6}Li	941b	^{3}T, ^{4}He	2.74, 2.05	4.79
n + ^{10}B	3838b	^{4}He, ^{7}Li, γ	1.47, 0.83, 0.48	2.30
n + ^{235}U	681b	fission		1 - 2

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





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

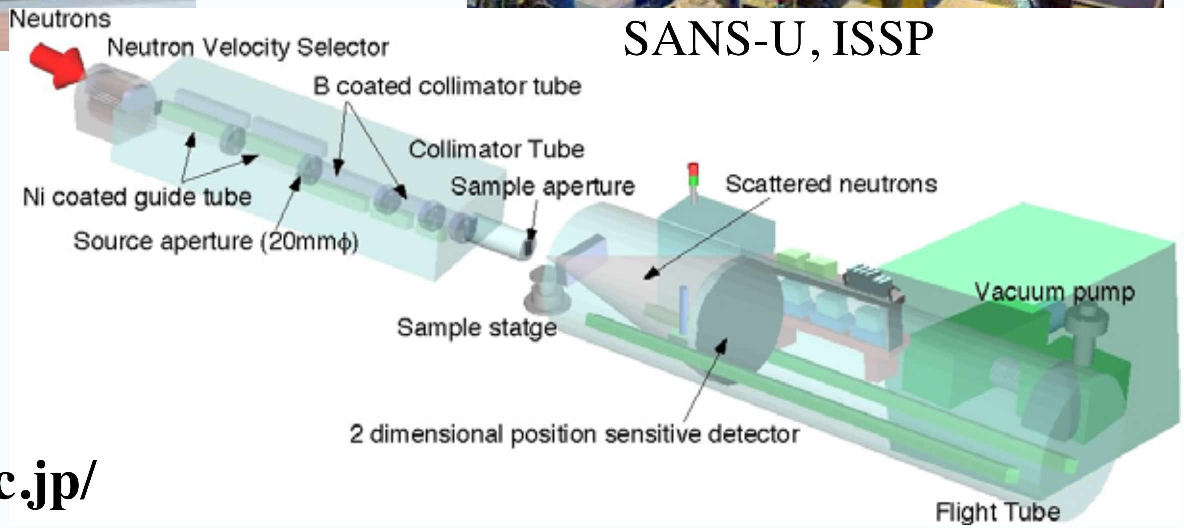


JRR-3@Japan Atomic Energy Agency
(20MW Research Reactor)

ISSP,
Kashiwa

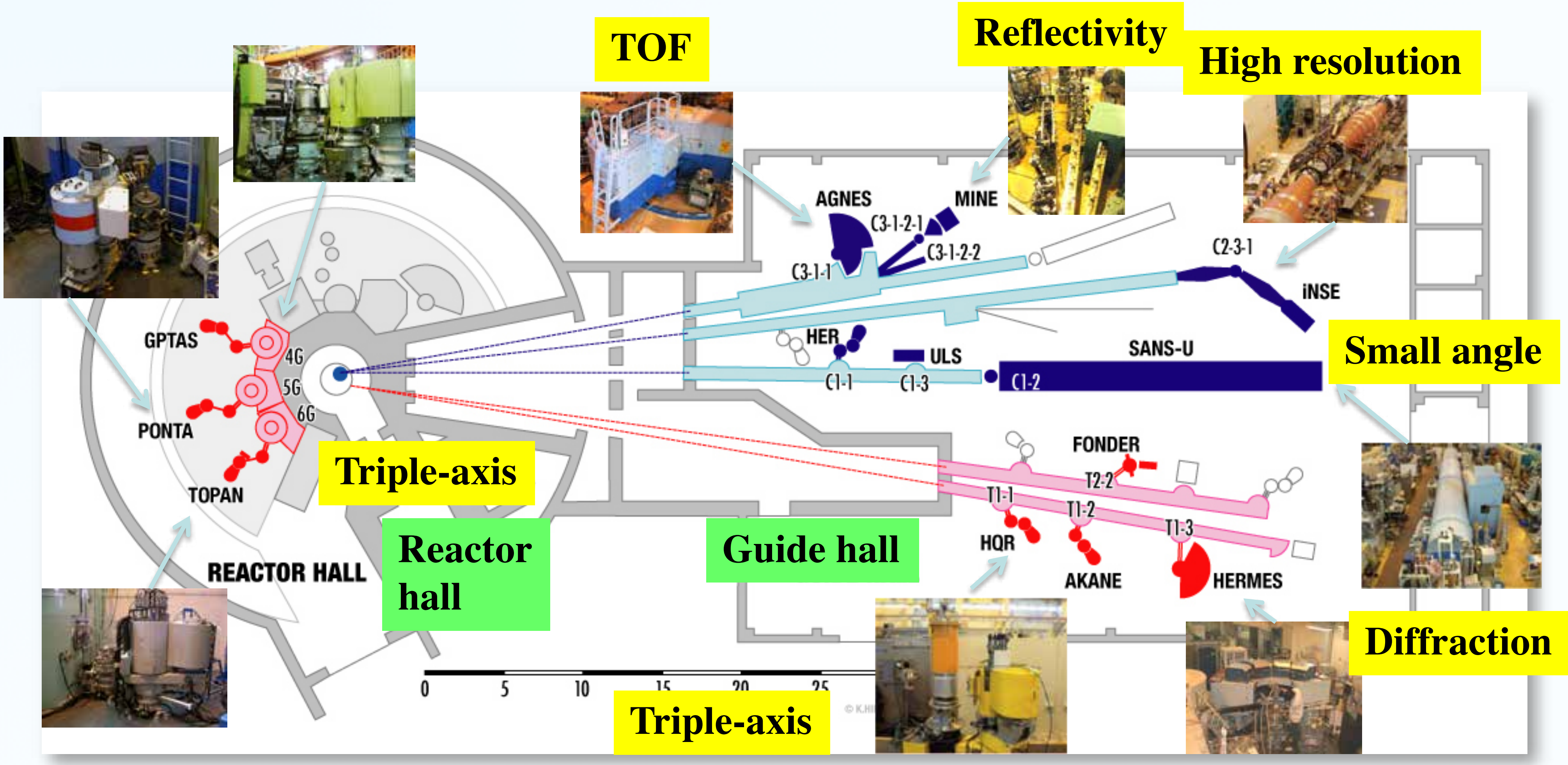
U. Tokyo

SANS-U, ISSP



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

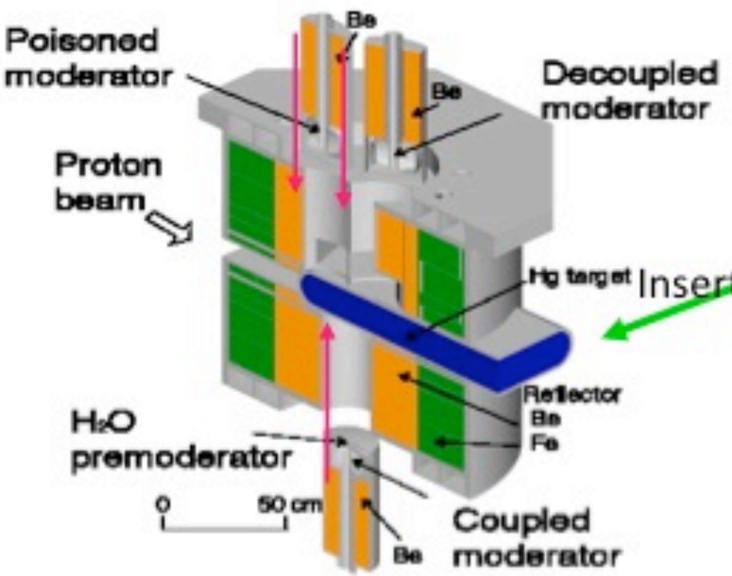
No. users (man.day)：in-house 2000, outside 5000, total 7000

No. papers：~100 /y

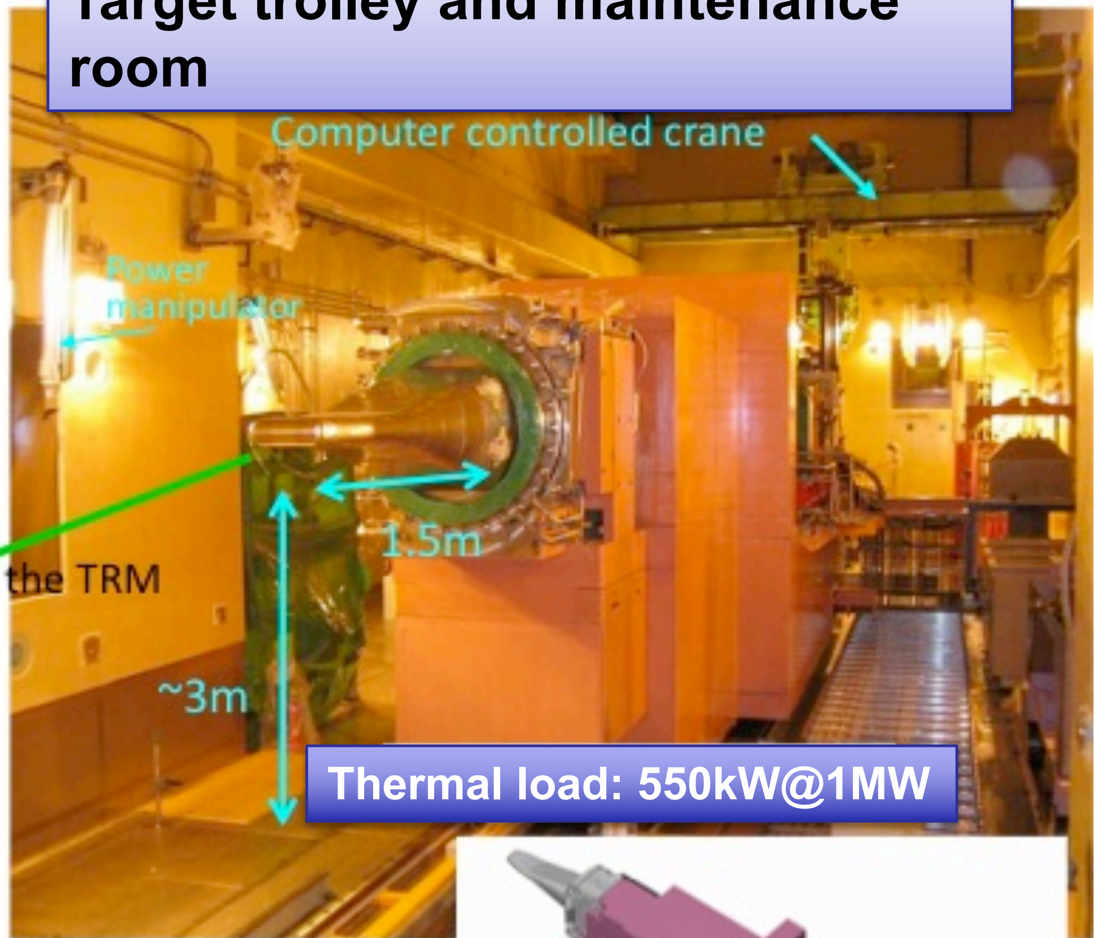
ISSP : SANS-U

Mercury target, moderator, reflector system

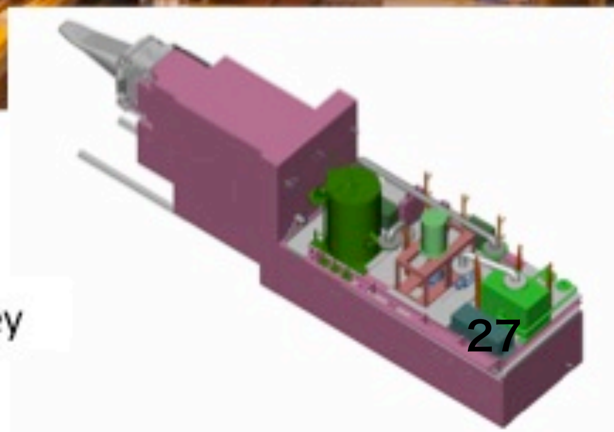
Three H_2 moderators



Target trolley and maintenance room



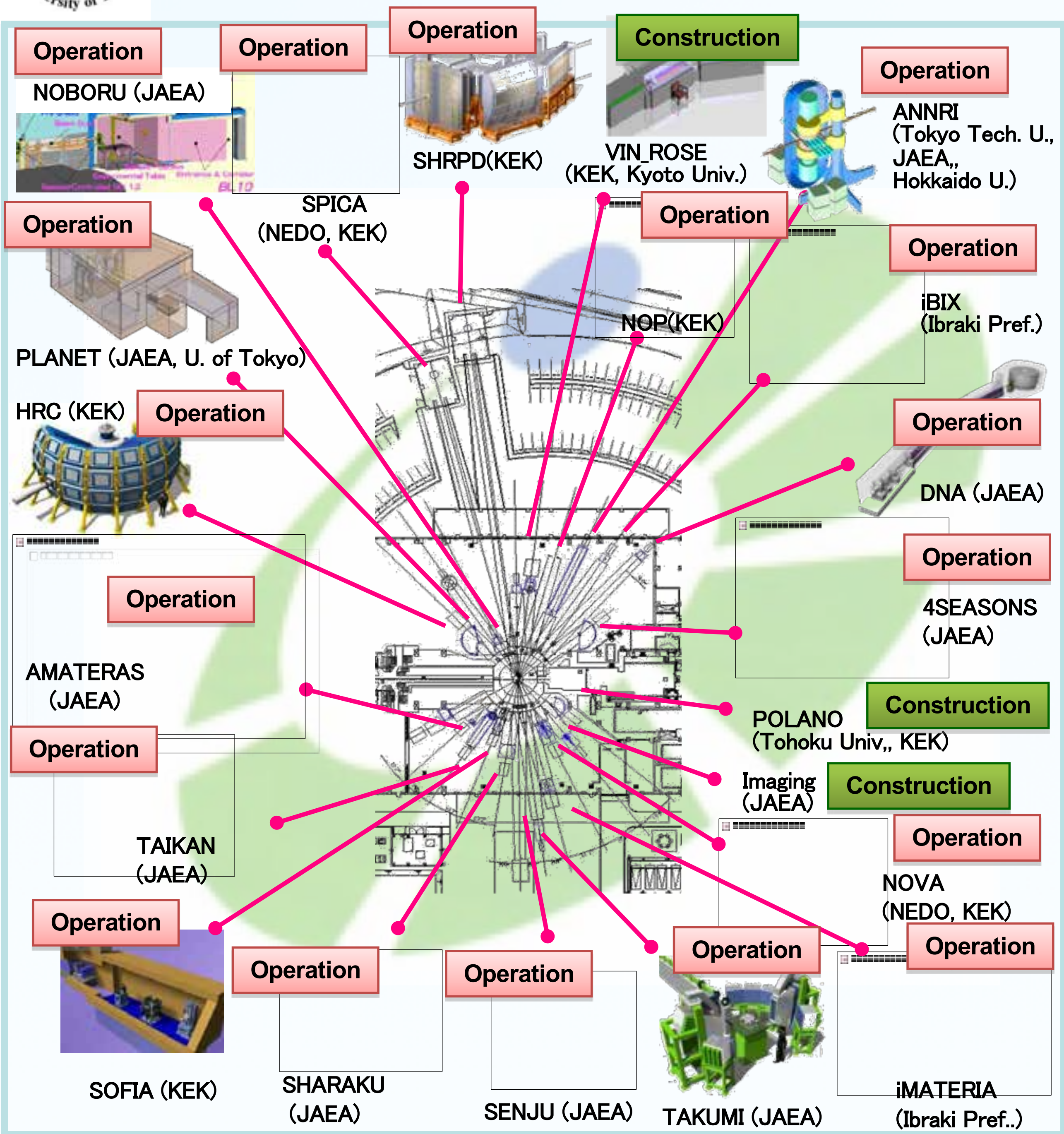
Thermal load: 550kW@1MW



Mercury loop on the trolley

Enhance cold neutron flux
and
intrinsic narrow peak width

Neutron Instruments at MLF

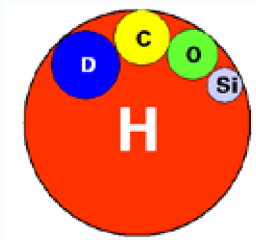


- The first neutron in May, 2008
- 23 Neutron Beam Ports
- From Fundamental Physics to Industrial Uses
- In operation: 18
  Under construction: 3
- Constructed by
  - KEK
  - JAEA } J-PARC MLF
  - Ibaraki Prefecture
  - Government (Direct funding)
- Operation days/Year
  200days/year
  (176days in 2012)
- Staffs and out-sourcing
  150+70
  relevant organ. altogether

Why Neutrons ?

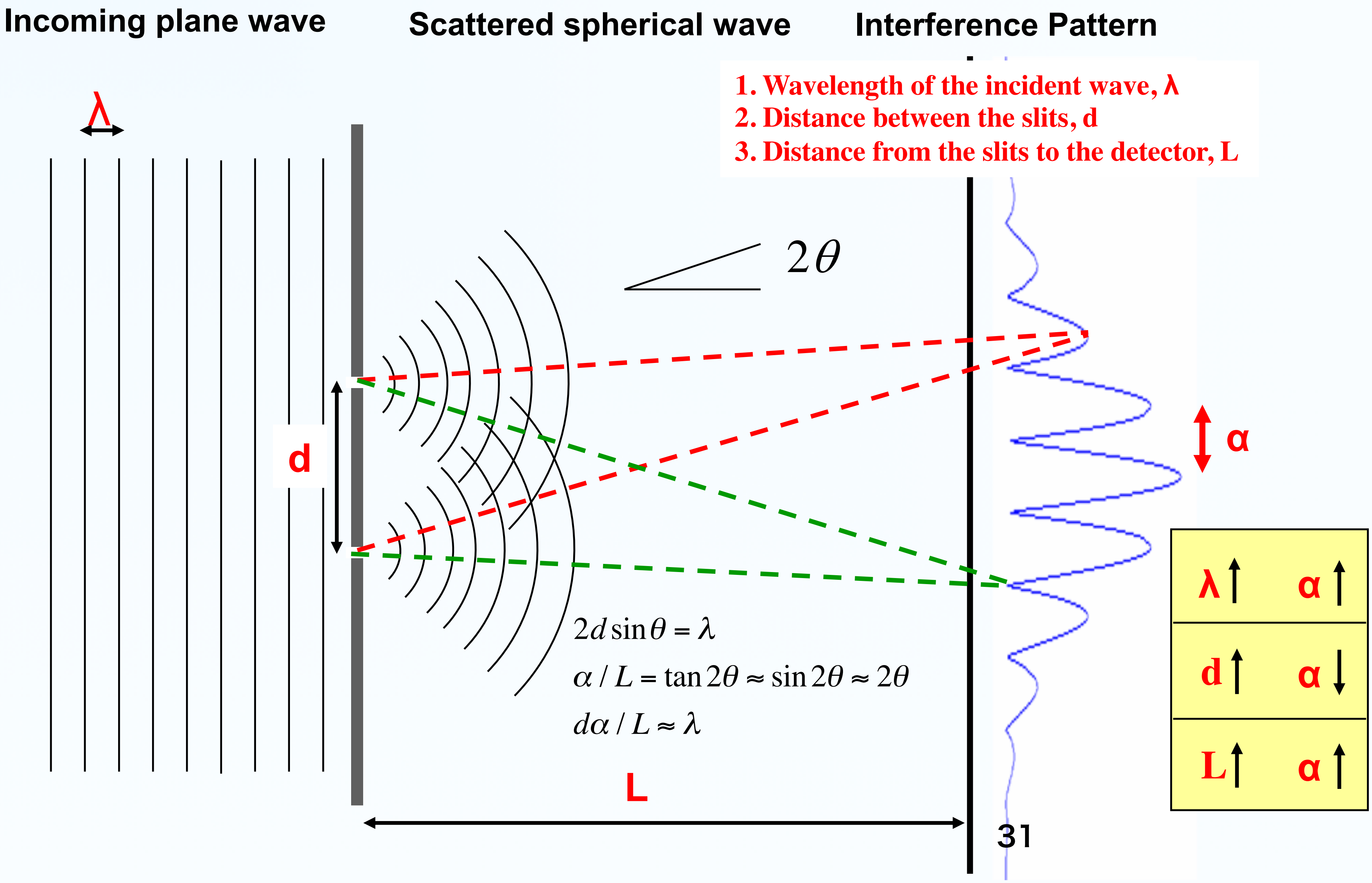
Mass　　No Charge　　Spin 1/2

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)*



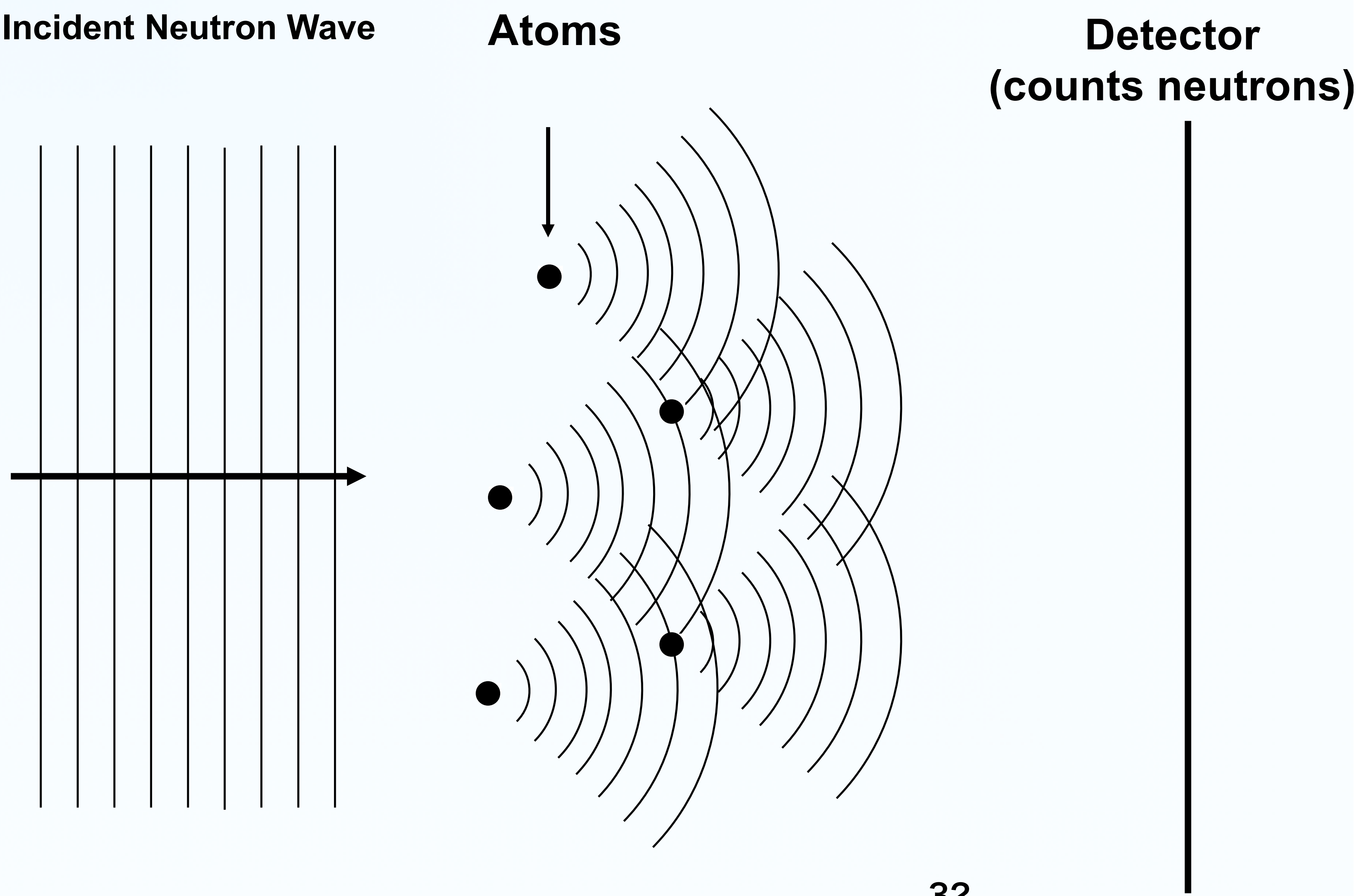
3. Neutron Scattering

Young's Double Slit Experiment

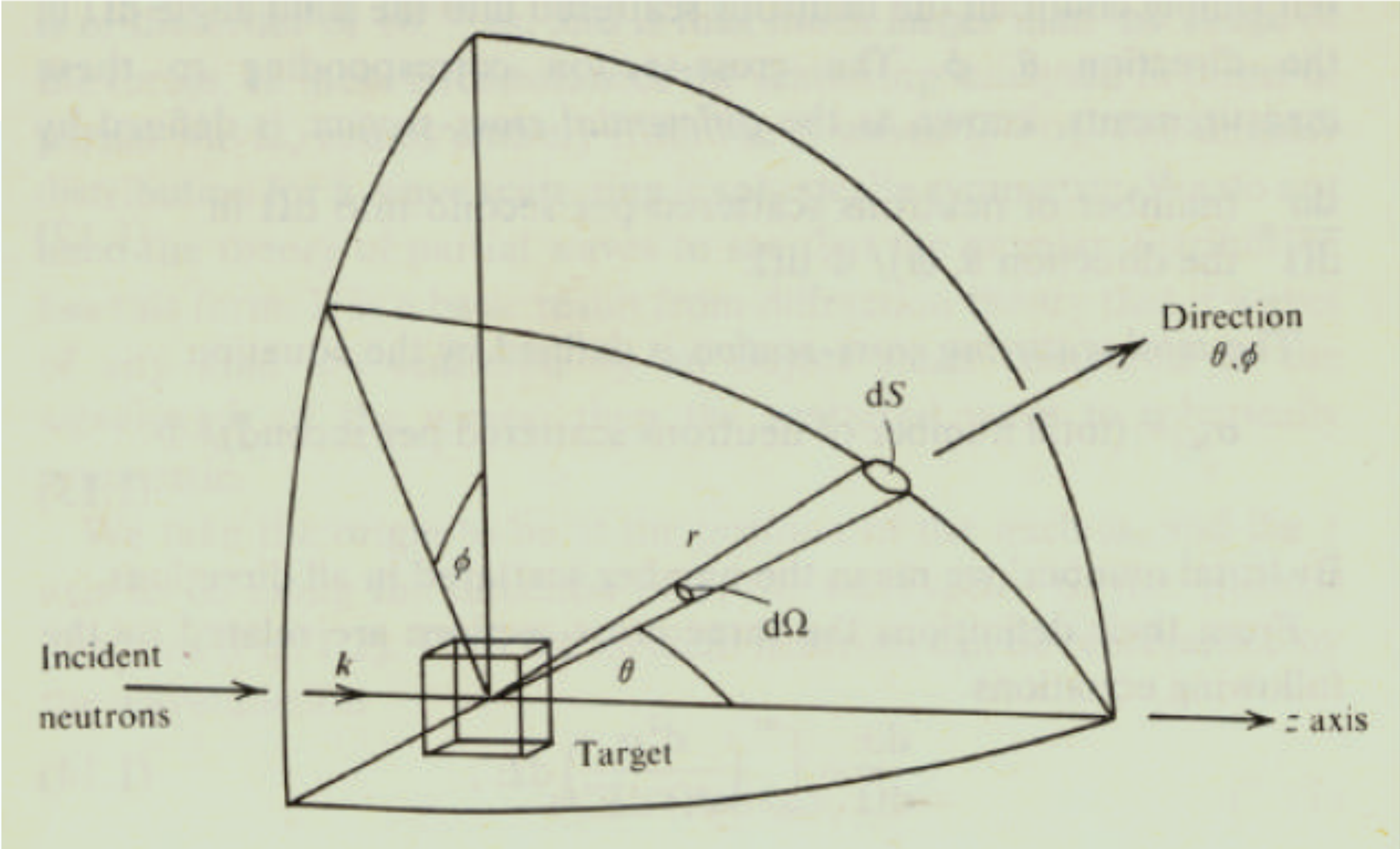


Neutron Scattering

Young's Experiments with Neutron Wave and Atoms



Neutron Scattering Cross Section



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

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

σ measured in barns

$1 \text{ barns} = 10^{-24} \text{ cm}^2$

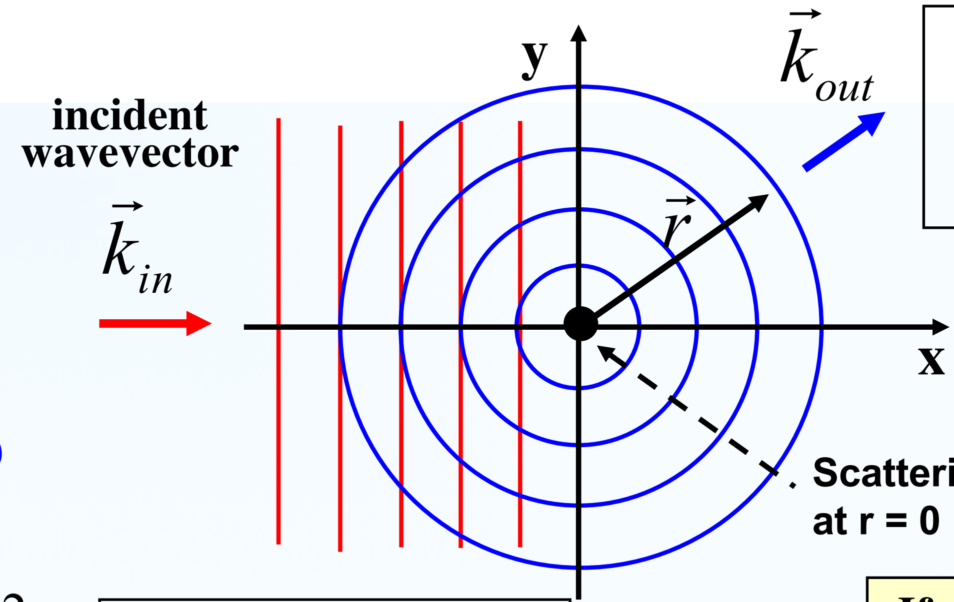
Elastic →

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

Inelastic →

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

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**

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

See, Part 2, 3 (p.14)

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

(elastic scattering)

Incident Plane wave

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

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

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

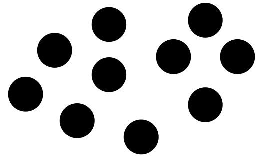
No. of incident neutrons passing through unit area per second $\Phi = \mathrm{v}\left|\psi_{inc}\right|^2 = \mathrm{v}$ **V: Neutron velocity**

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

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

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

Scattering by Many Nuclei



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

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

Therefore

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

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

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

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

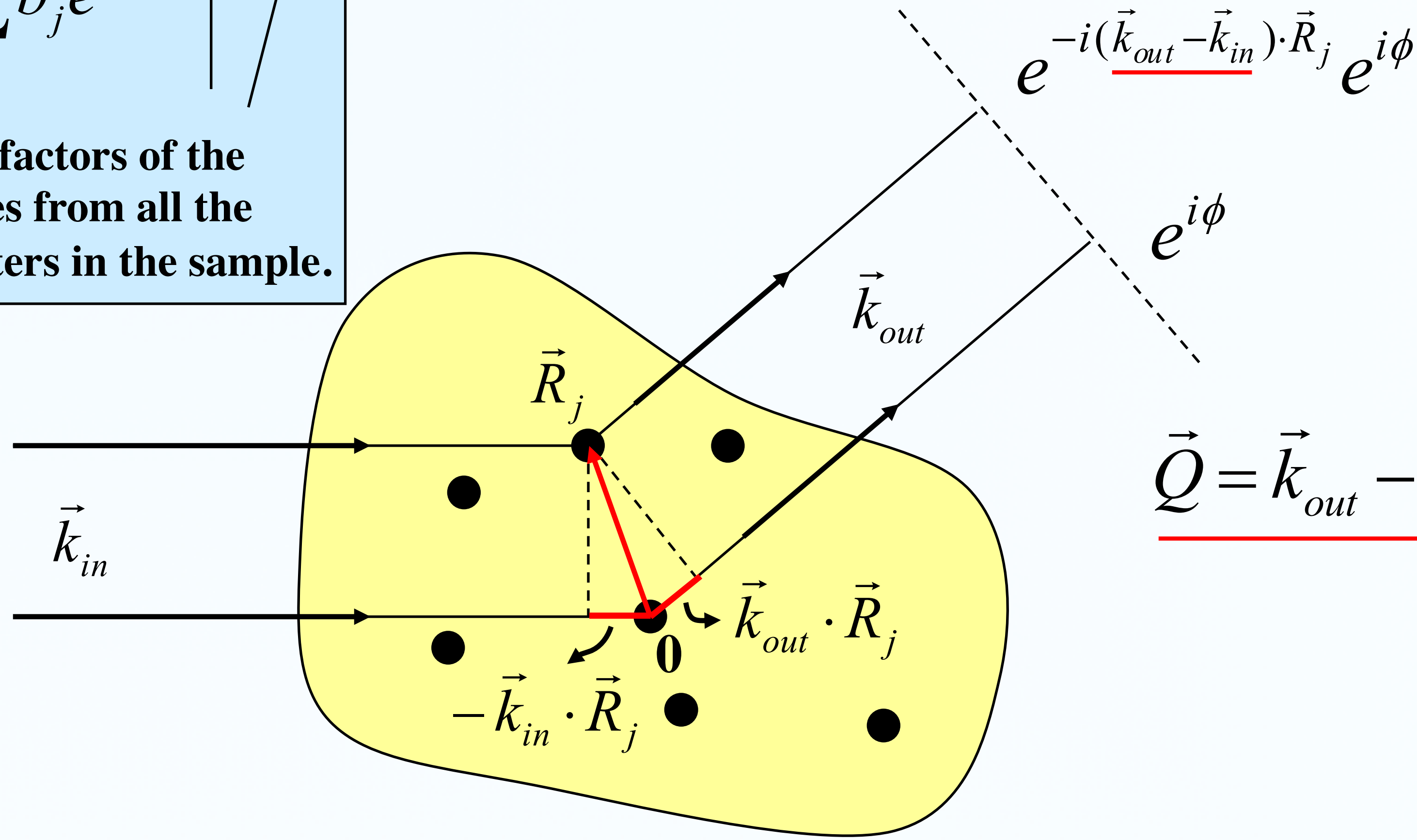
where the wavevector transfer $\vec{Q}$ is defined as

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

Scattering vector Q and Scattering Cross Section

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

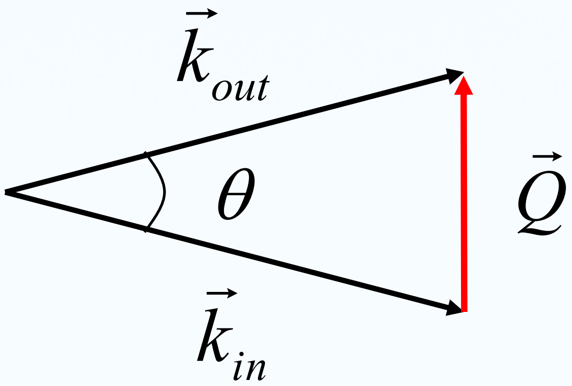
Add up phase factors of the scattered waves from all the scattering centers in the sample.



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

Scattering vector Q

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



For elastic scattering

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

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

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

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

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

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)

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

$\boldsymbol{\mu}$: Magnetic moment of neutron
$\mathbf{B}$: B-field induced unpaired spin

Scattering length, *b*

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

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

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

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

Part 2

10. 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 σ_{coh} σ_{inc} σ_s σ_a

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

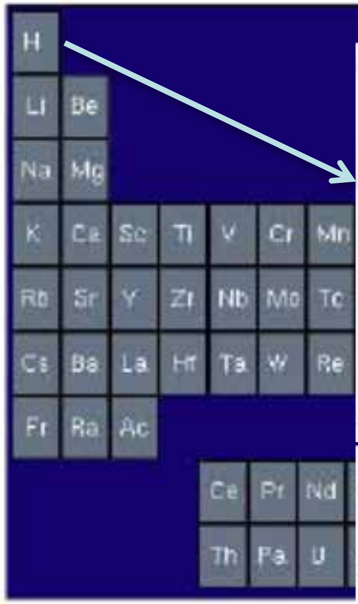
http://www.ncnr.nist.gov/resources/n-lengths/

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 elements and isotopes is also available.

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

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

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

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

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

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

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

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

$$b_i = \langle b \rangle + \delta b_i \qquad \text{where } \delta b_i \text{ averages to zero}$$

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

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

If $i \neq j$, $\langle b_i b_j \rangle = \langle b \rangle^2$

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

Therefore,

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

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

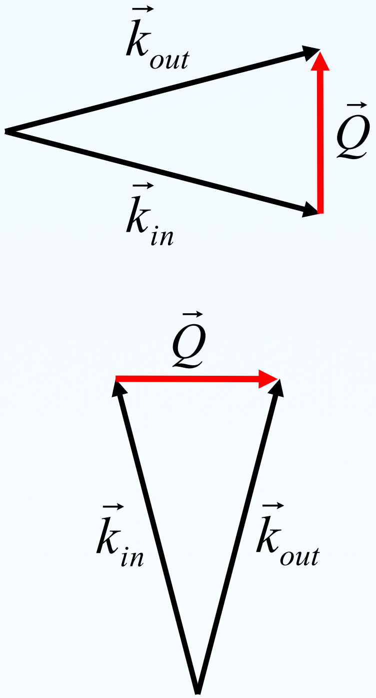
$$\frac{d\sigma}{d\Omega} = \left\langle \sum_{i,j} b_i b_j e^{-i\vec{Q}\cdot(\vec{R}_i - \vec{R}_j)} \right\rangle = \sum_{i,j} \langle b_i b_j \rangle e^{-i\vec{Q}\cdot(\vec{R}_i - \vec{R}_j)} = \langle b \rangle^2 \sum_{i,j} e^{-i\vec{Q}\cdot(\vec{R}_i - \vec{R}_j)} + N\left(\langle b^2 \rangle -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

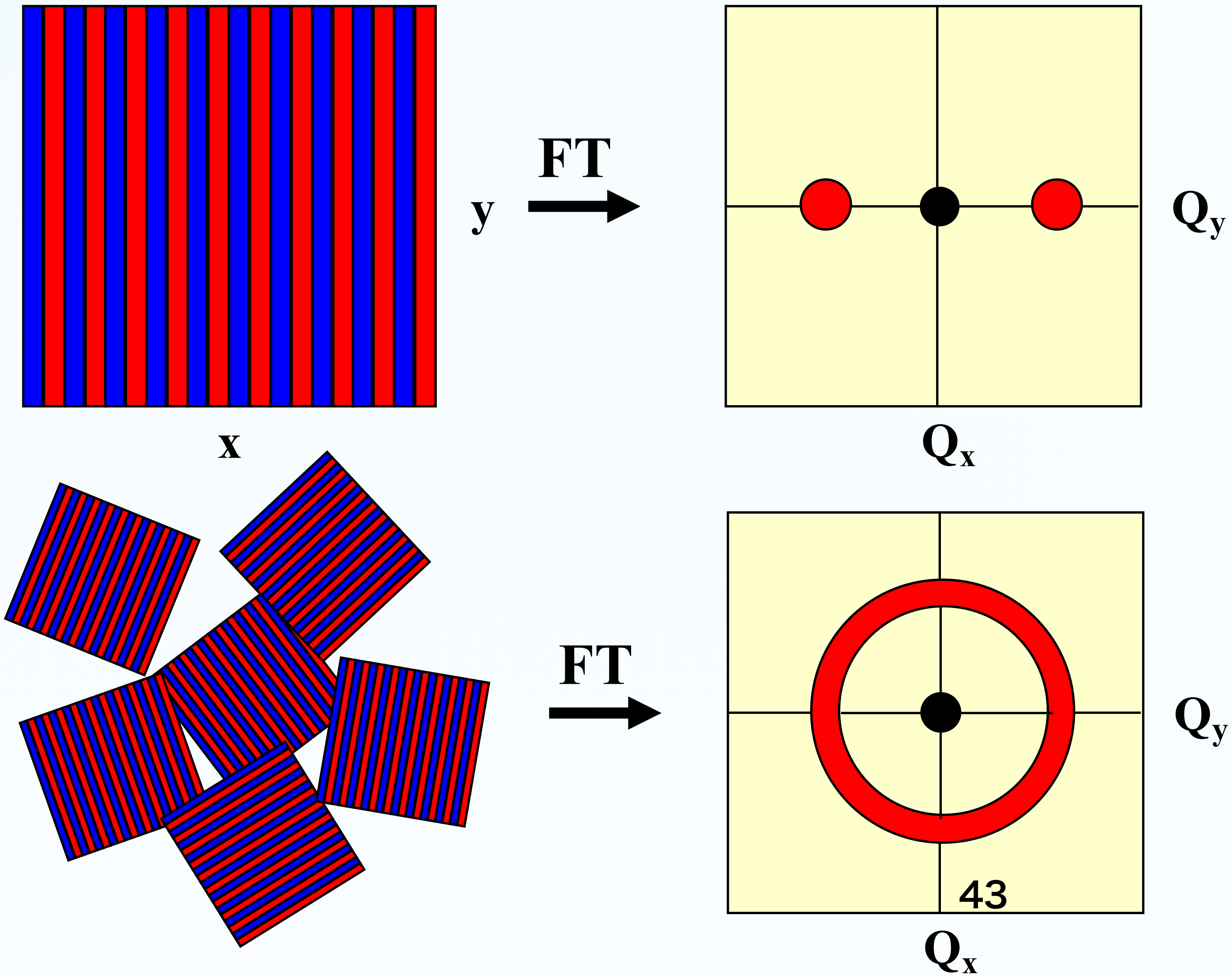
Coherent scattering Incoherent scattering

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

Fourier Transform

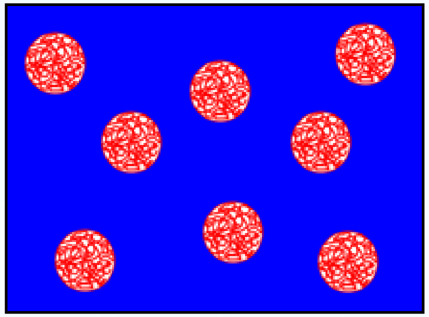
$\vec{Q}$ probes the space along $\vec{r}$ parallel to $\vec{Q}$

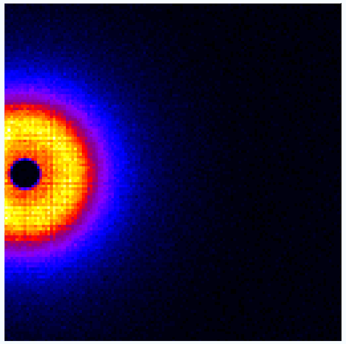


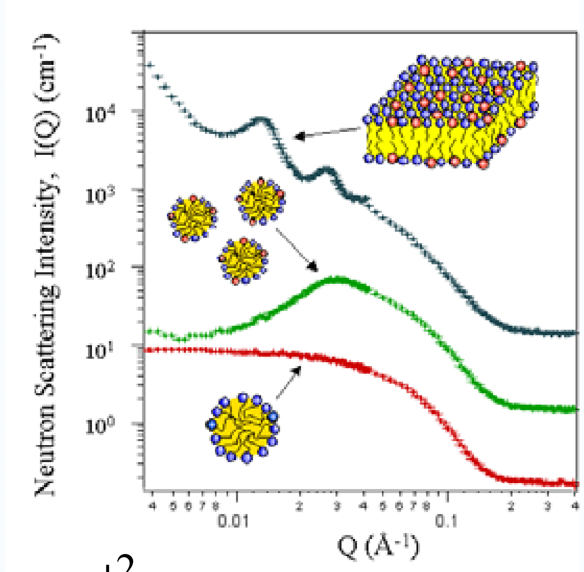


4. SANS Application to Polymeric Systems

What Information from SANS ?
: Particulate Systems







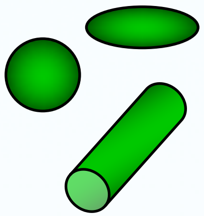
$$\frac{d\Sigma}{d\Omega}(\mathbf{Q}) = \left|\text{Fourier Transfom of } \rho(\mathbf{r})\right|^2$$

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

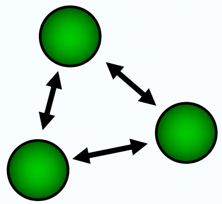
Number density

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

Shape and dimensions of particles



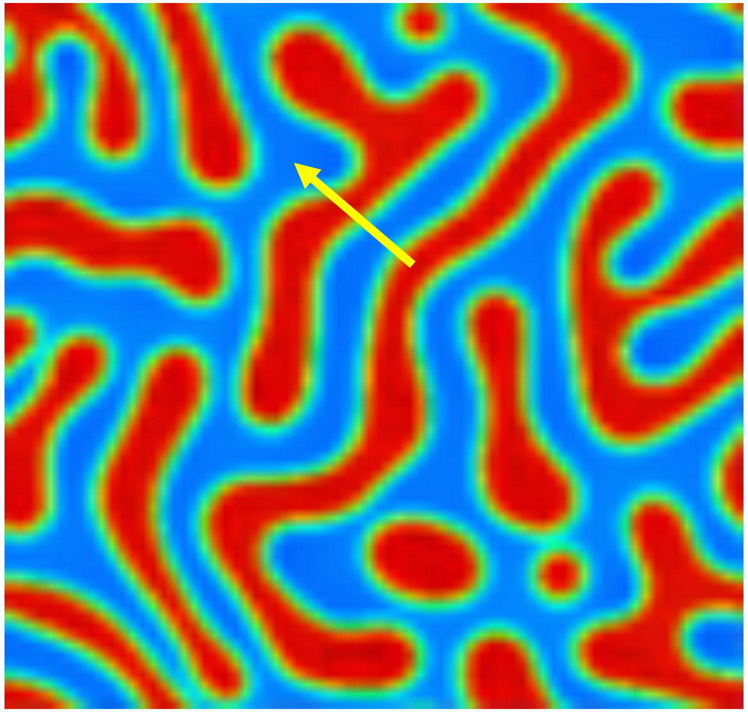
Interaction between particles



Intra-Particle interference
: Form factor

Inter-Particle interference
: Structure factor

What Information from SANS ? : Non-Particulate Systems



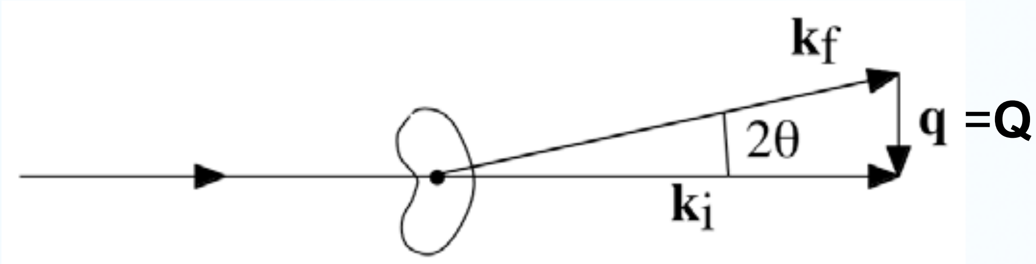
$$\frac{d\Sigma}{d\Omega}(Q) = 4\pi\left\langle(\Delta\rho)^2\right\rangle\int_V \gamma(r)\frac{\sin(Qr)}{Qr}r^2dr$$

Contrast — Correlation function — Orientation average

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

Part 4

Small-angle scattering
1. what is small-angle scattering?

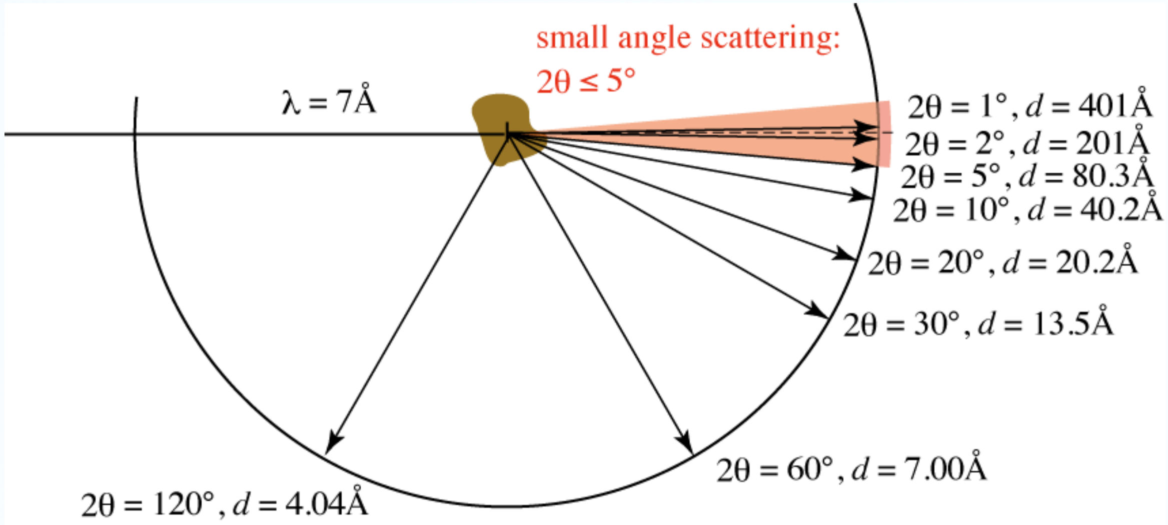


- **Constructive interference from structures in the direction of q**

- **Diffraction length scale**

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

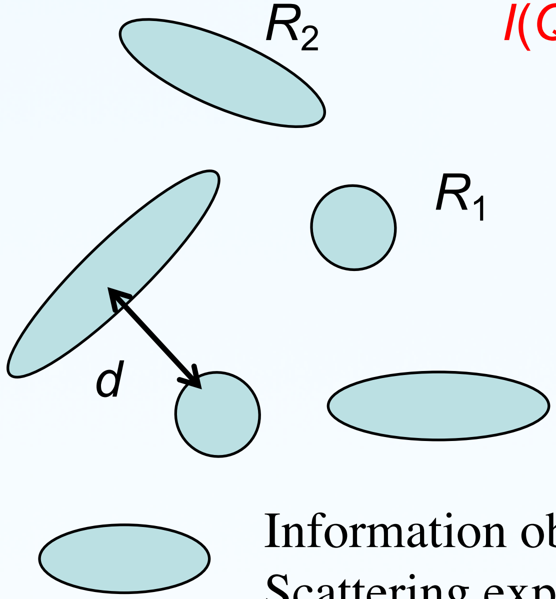
$$2\theta \approx 0.5° \sim 10°$$

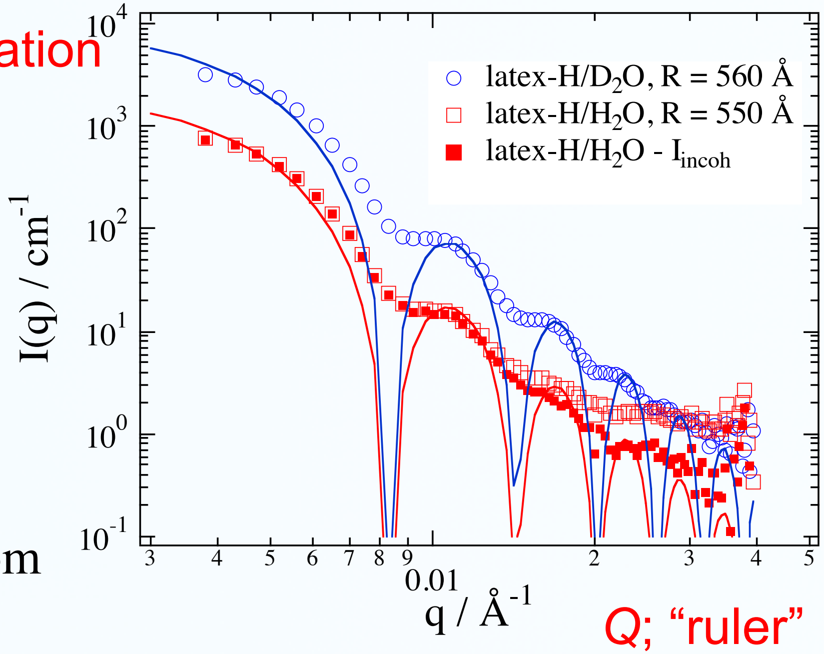


- **Scattering is at small angles - non-zero but smaller than classical diffraction angles**

Part 4

Information obtained by small-angle scattering experiments



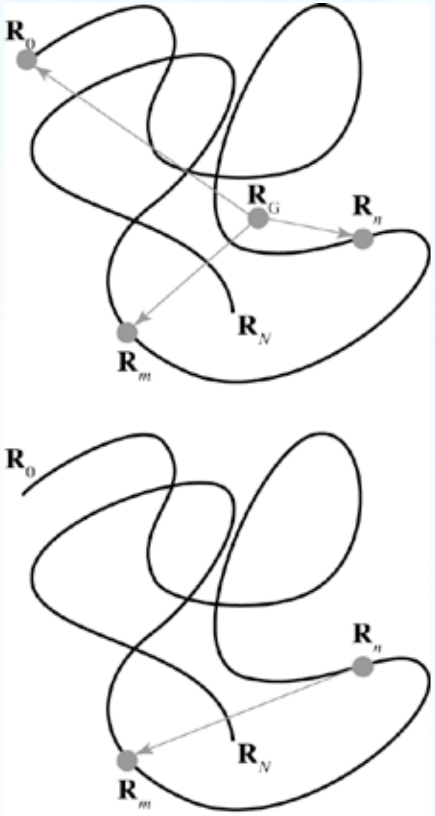


Information obtained from Scattering experiments

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)

Scattering function from a polymer chain



the radius of gyration

$$\mathbf{R}_{\mathrm{G}} = \frac{1}{N}\sum_{n=1}^{N}\mathbf{R}_n$$

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

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

N; the degree of polymerization

the Debye fn.

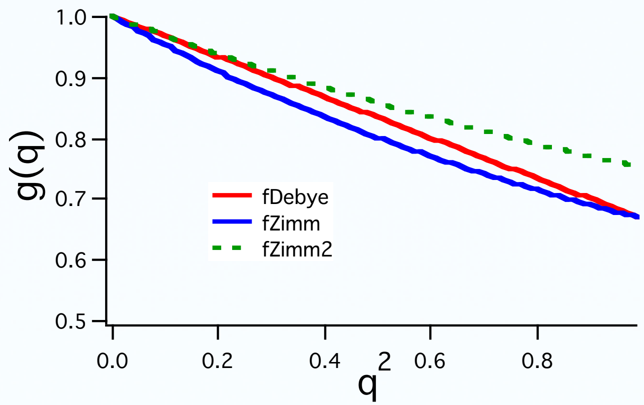
$$g(\mathbf{r}) = \frac{1}{N}\sum_n\sum_m\left\langle\exp\left[i\mathbf{Q}\cdot\left(\mathbf{R}_m - \mathbf{R}_n\right)\right]\right\rangle$$

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

$$= Nf_{\mathrm{D}}\left(\left(QR_{\mathrm{g}}\right)^2\right)$$

b; the segment length

$$f_{\mathrm{D}}\left(\left(QR_{\mathrm{g}}\right)^2\right) \equiv f_{\mathrm{D}}(x) = \frac{2}{x^2}\left(e^{-x} - 1 + x\right)$$



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

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

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

Summary (3)

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)

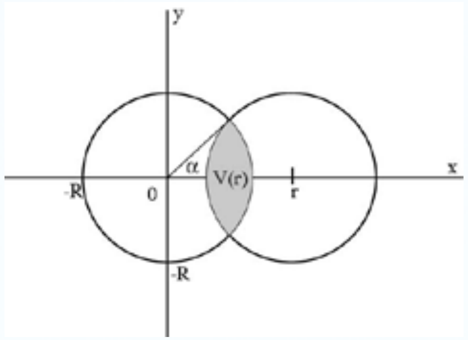
$$g(r) = \exp\left[-\frac{r^2}{2\left(R_g{}^2/3\right)}\right] \longleftrightarrow I(Q) \sim \exp\left(-\frac{R_g{}^2}{3}Q^2\right)$$

Scattering from isolated particles

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

Lorentz fn. (semi-dilute polymer solutions)

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



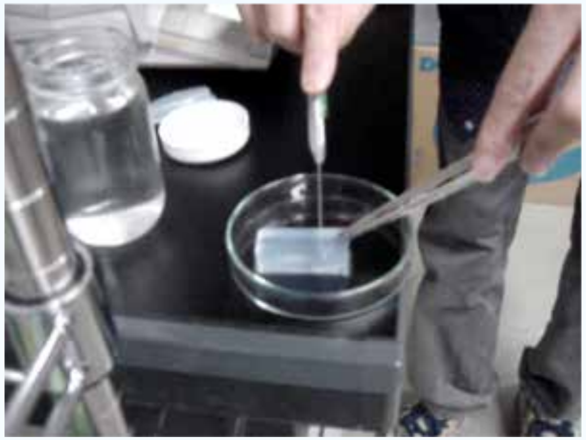
Polymer chains

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

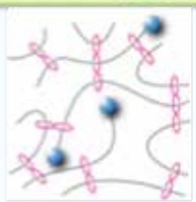
The volume $V(r)$ of the shaded part

5. Neutron Scattering on Gels

Tough hydrogels



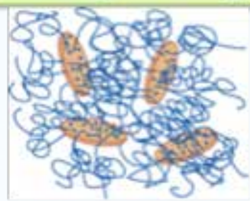
Slide-ring gel



Okumura, Adv. Mater., 2001

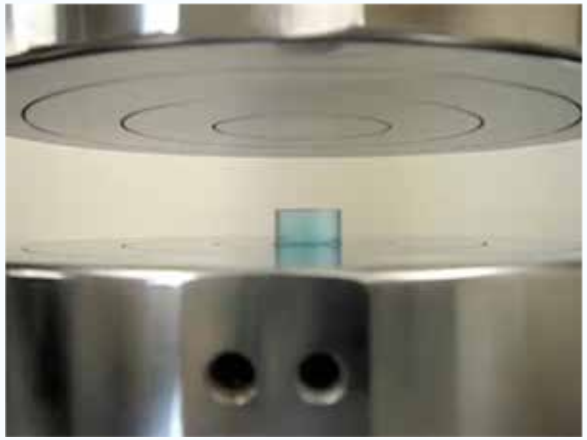
K. Ito

Nanocomposite gel

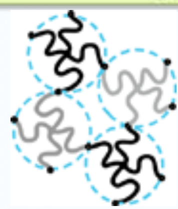


Haraguchi, Adv. Mater., 2002

K. Haraguchi



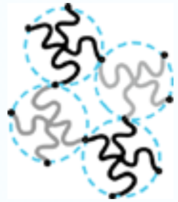
Tetra-PEG gel



Sakai et al., Macromol., 2008

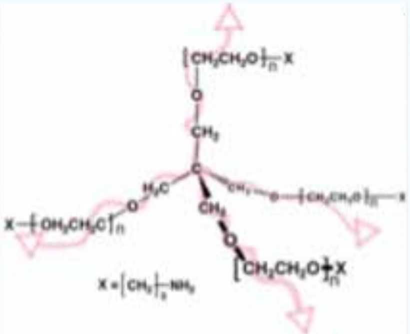
T. Sakai

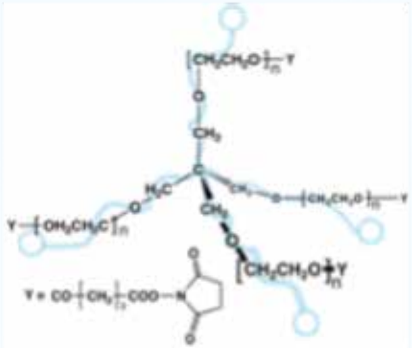
Tetra-PEG gels



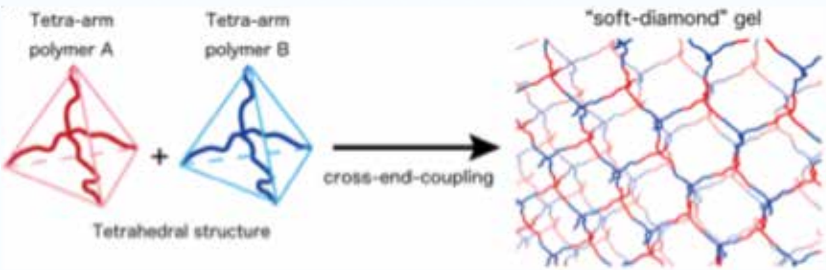
TC 304 (Mar 17, 2017)

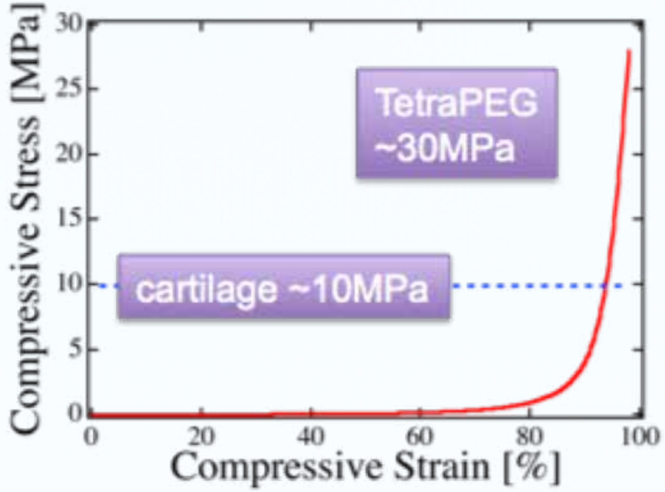
Sakai, et al., Macromolecules, 41, 5739 (2008)



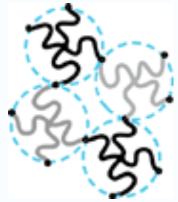


amine *N-hydroxysuccinimide-glutarate*





Preparation of Tetra-PEG



3x speed
~ 1 min

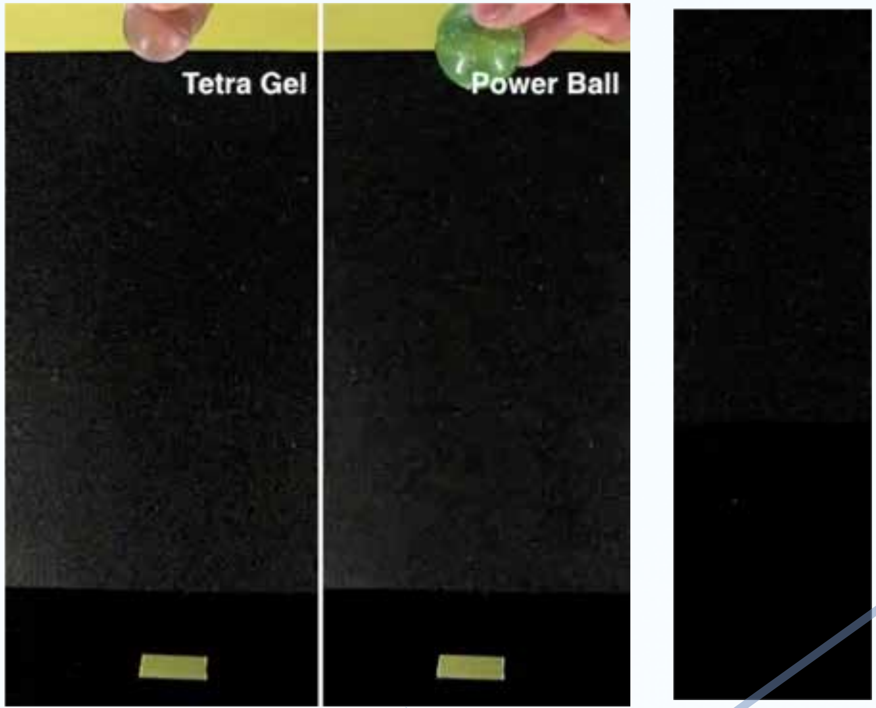
Advanced physical, chemical, and biological properties
1. high compressive toughness (compatible to cartilage)
2. high transparency
3. biocompatible and nontoxic
4. easy and quick preparation

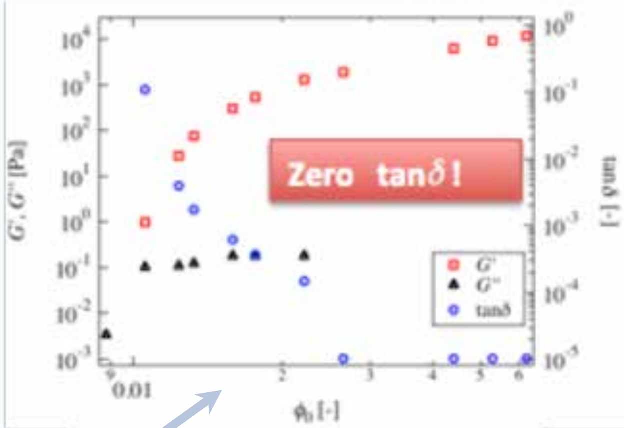
Etc.

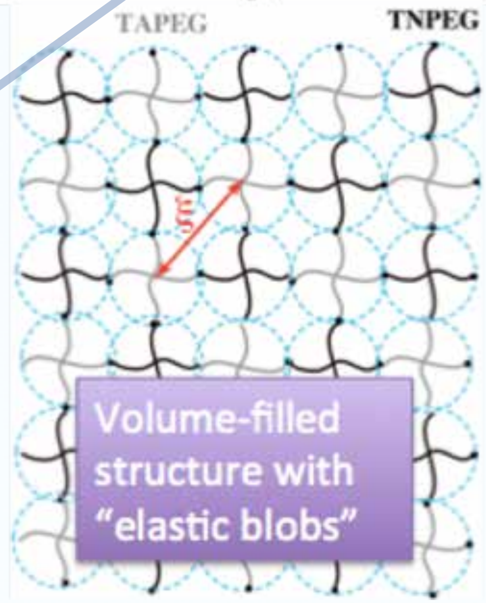
remarkable mechanical properties owing to “elastic blobs”

Macromolecules, 43, 488 (2010)

Tetra PEG gel ball vs power ball

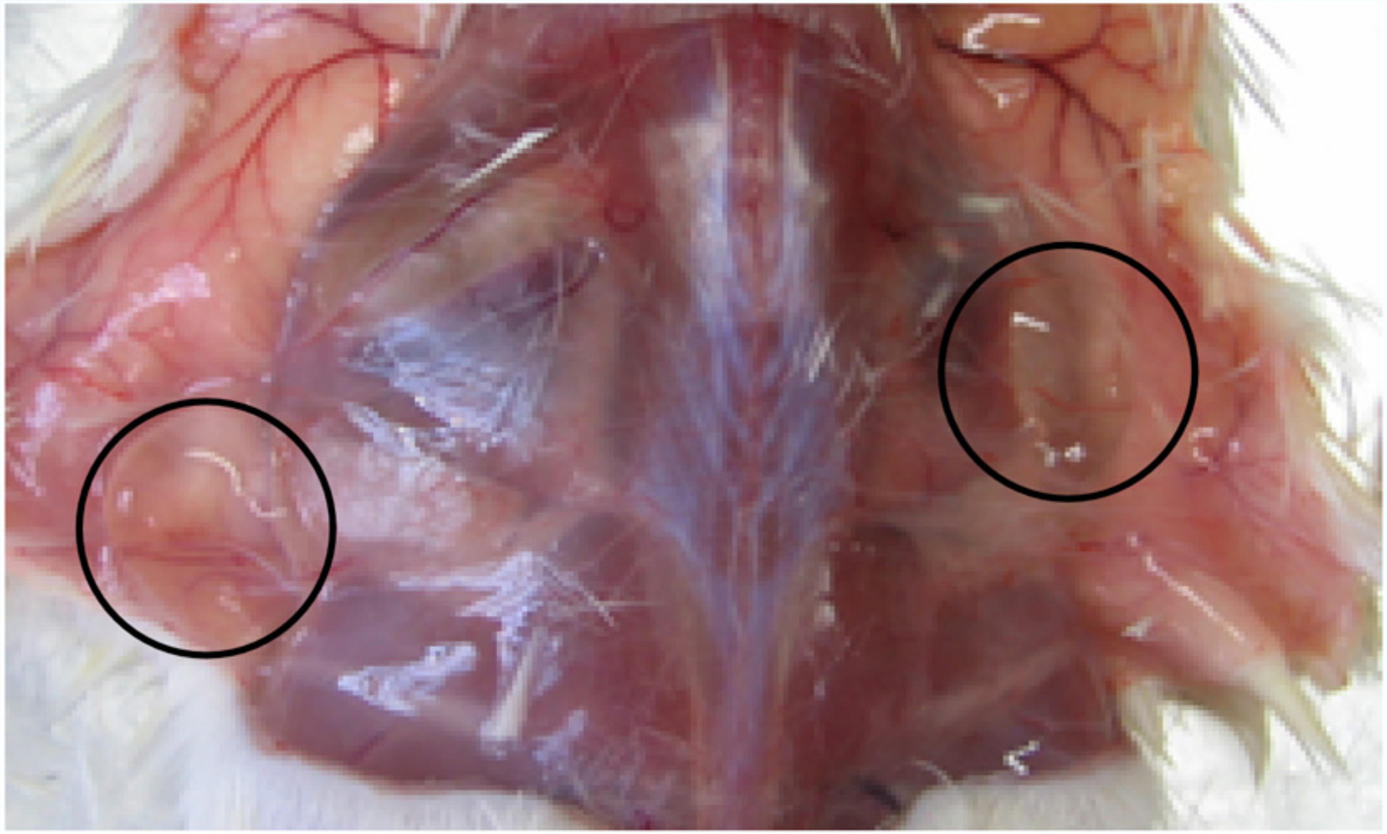






- Remarkable repulsion coefficient and infinitesimally small loss tangent
- Ideal networks with no entanglements and no defects

subcutaneous implantation of Tetra-PEG gel



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

scattering functions of polymer gels

$$I(q) = I_{soln}(q) + I_{ex}(q)$$

Liquidlike component (Lorentz)

$$I_{soln}(q) = \frac{I_{soln}(0)}{1+\xi^2 q^2}$$

Excess scattering

(i) another Lorentz function

$$I_{ex}(q) = \frac{I_{ex}(0)}{1+\xi_G{}^2 q^2}$$

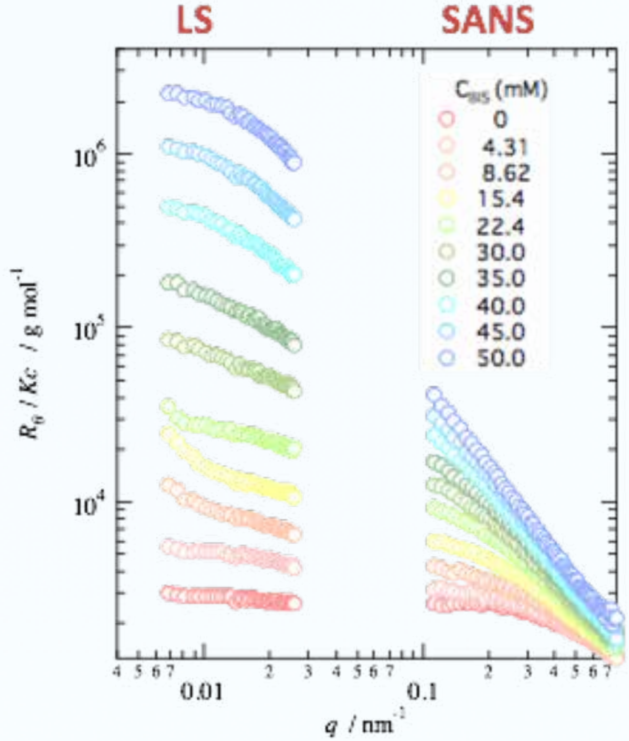
(ii) a stretched exponential function

$$I_{ex}(q) = I_{ex}(0)\exp\left[-(q\Xi)^{\alpha}\right]$$

(iii) a Debye-Bueche function

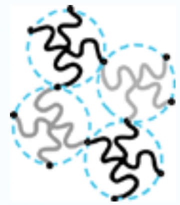
$$I_{ex}(q) = \frac{I_{ex}(0)}{\left(1+b^2q^2\right)^2}$$

Cross-link density dependence of I(q) for NIPA gels

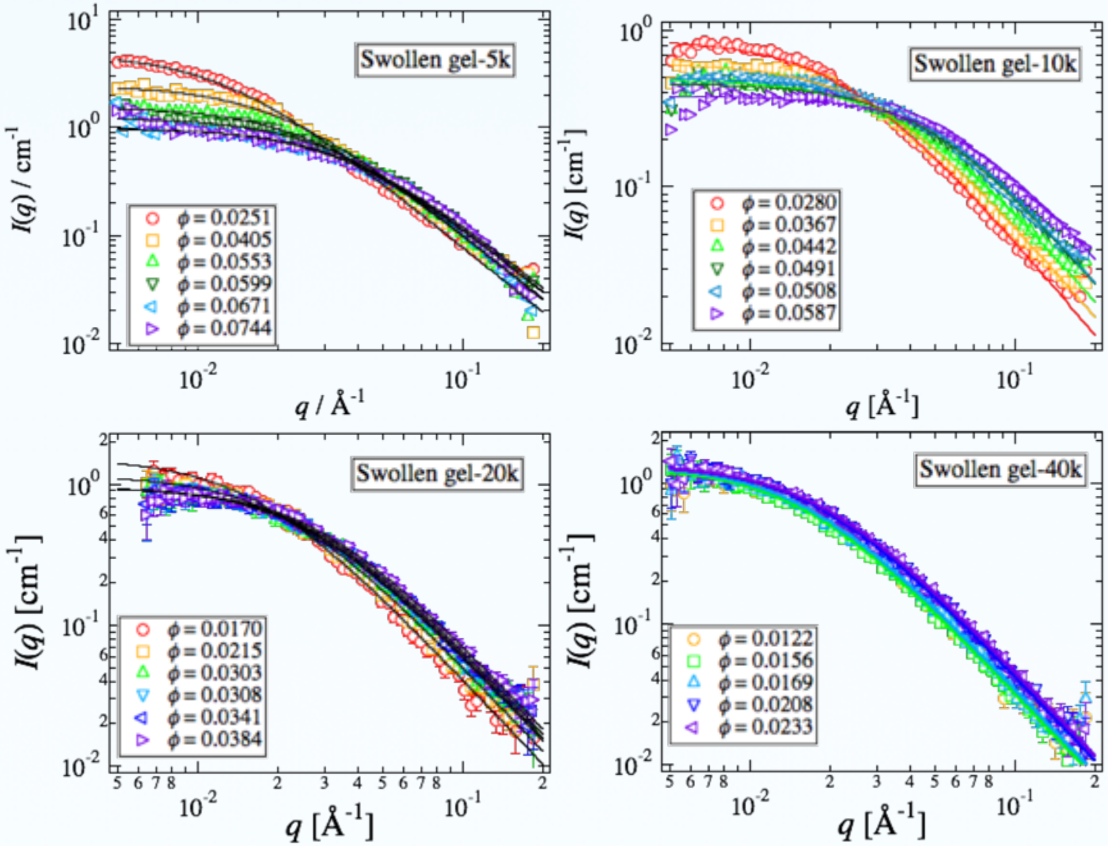


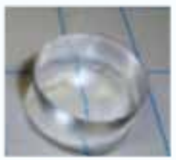
Macromolecules, 2002, 35, 4779.

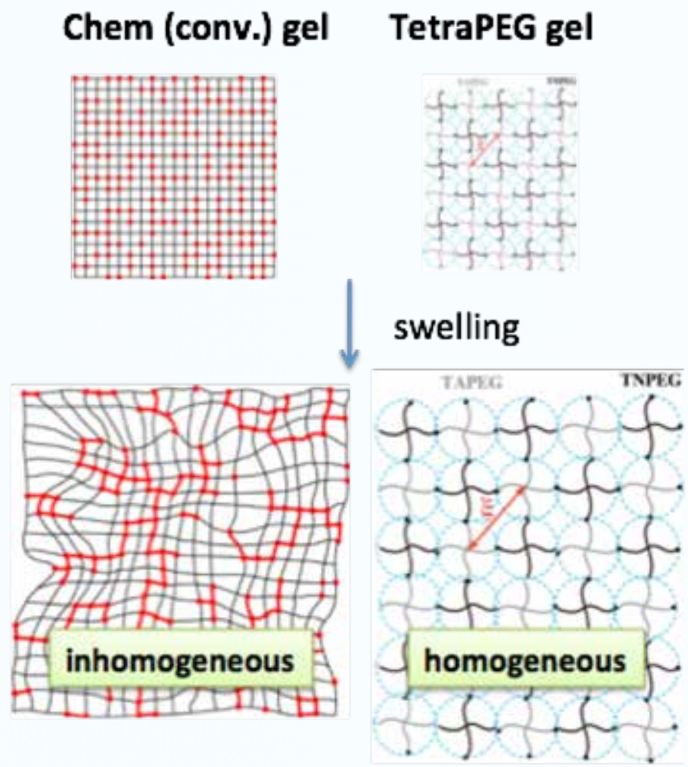
SANS of Tetra-PEG gels



Macromolecules, 42, 1344 (2009); 42, 6245 (2009)



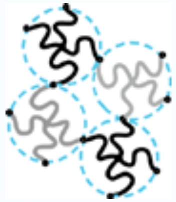




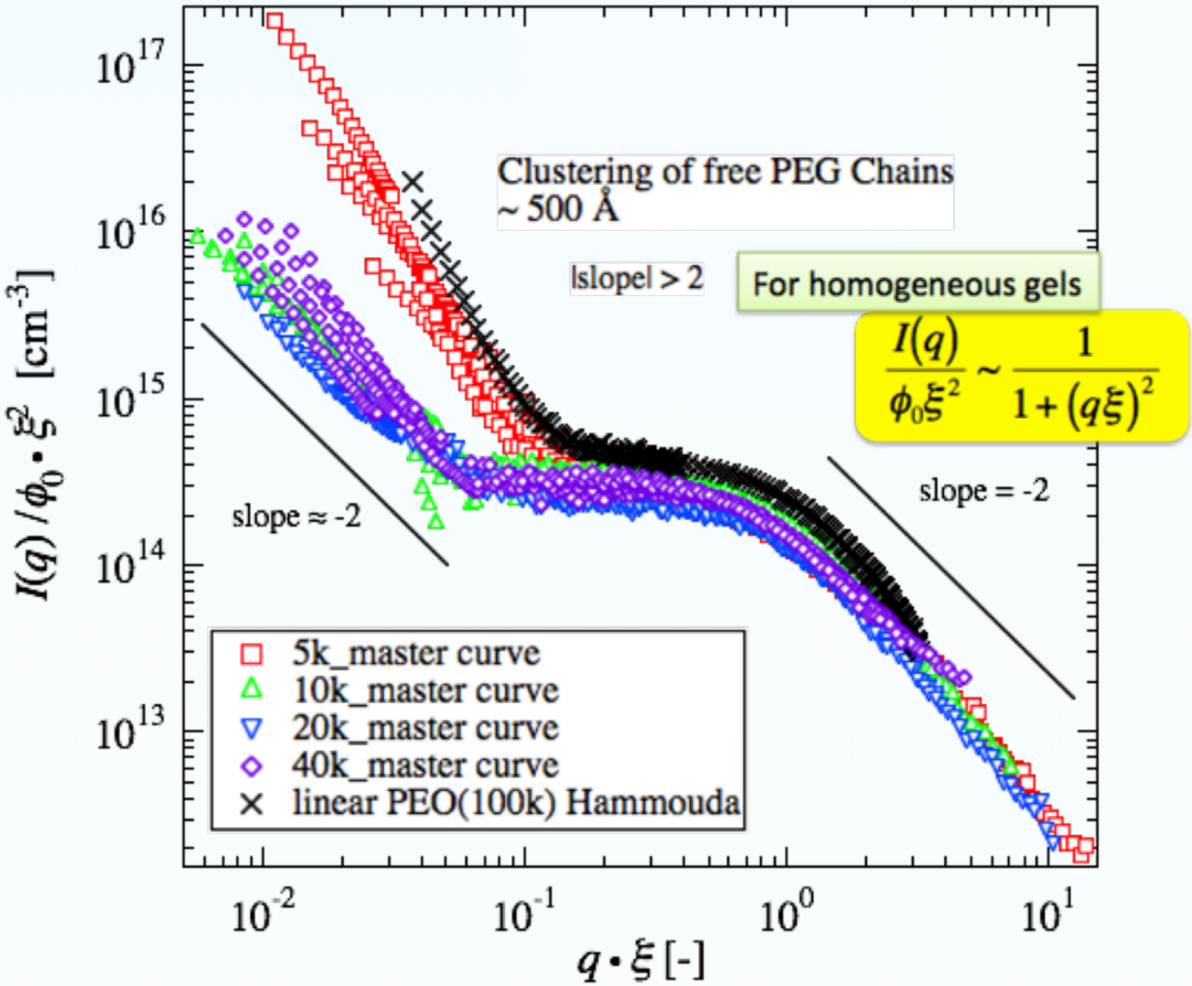
Macromolecules, 42, 1344-1351 (2009),
Macromolecules, 42, 6245-6252 (2009)

1. No inhomogeneity appears even after swelling.
2. For high MW gel, the network structure in swollen state is independent of t

SANS master plot



Macromolecules, 42, 6245 (2009)



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

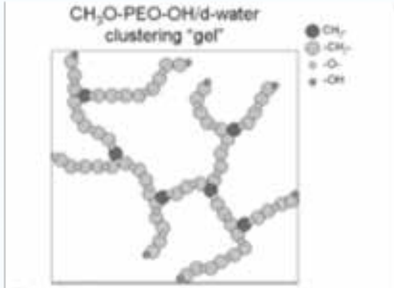
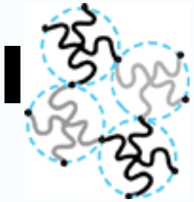


Figure 6. Schematic rendering (not to scale and not realistic) of the PEO/d-water clusters in the case with different chain ends ($-OCH_3$ and $-OH$). The $-OH$ end groups stay dissolved in water, whereas the $-OCH_3$ end groups are expelled from water regions and end up sticking to other hydrophobic (CH_2CH_2) groups on the PEO chain. PEO chains are tethered at one end.

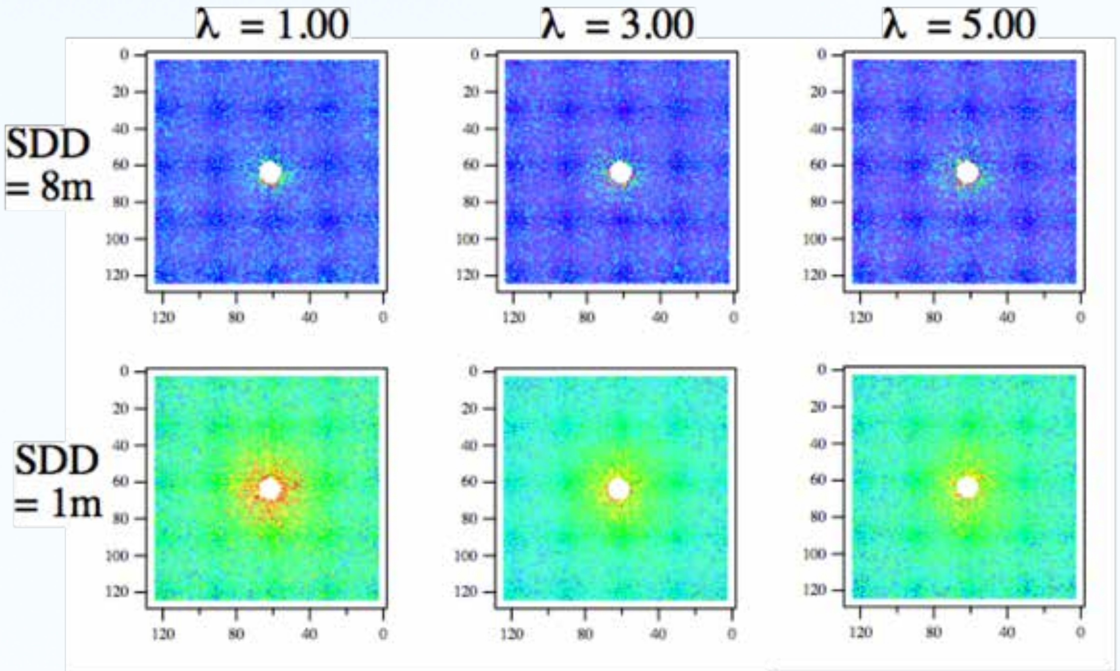
$$I(Q) = A/Q^n + C/\{1 + (QL)^m\} + B$$

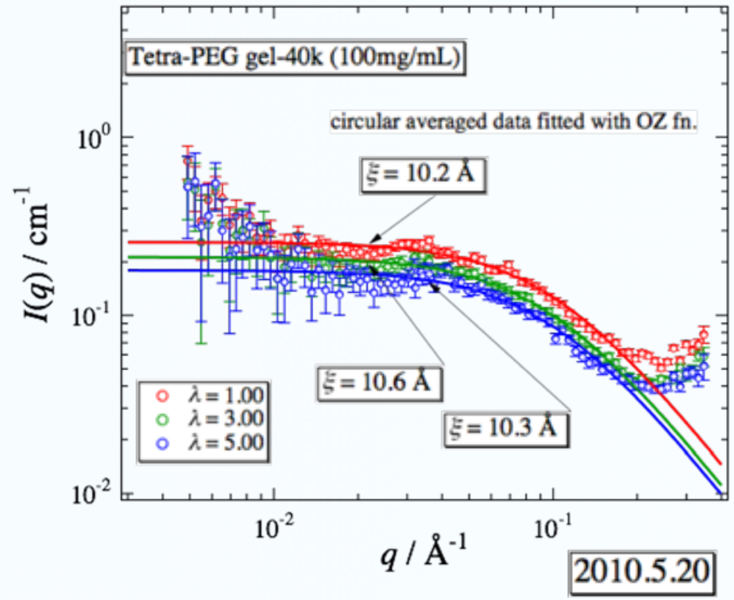
Hammouda et al.,
Macromolecules,
2002, 35, 8578,
2004, 37, 6932.

Deformation SANS for Tetra-PEG gel

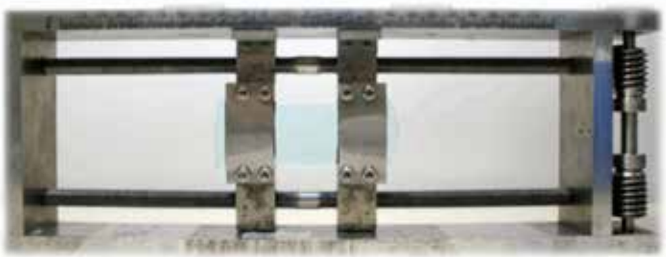


Macromolecules, 44, 1203 (2011)



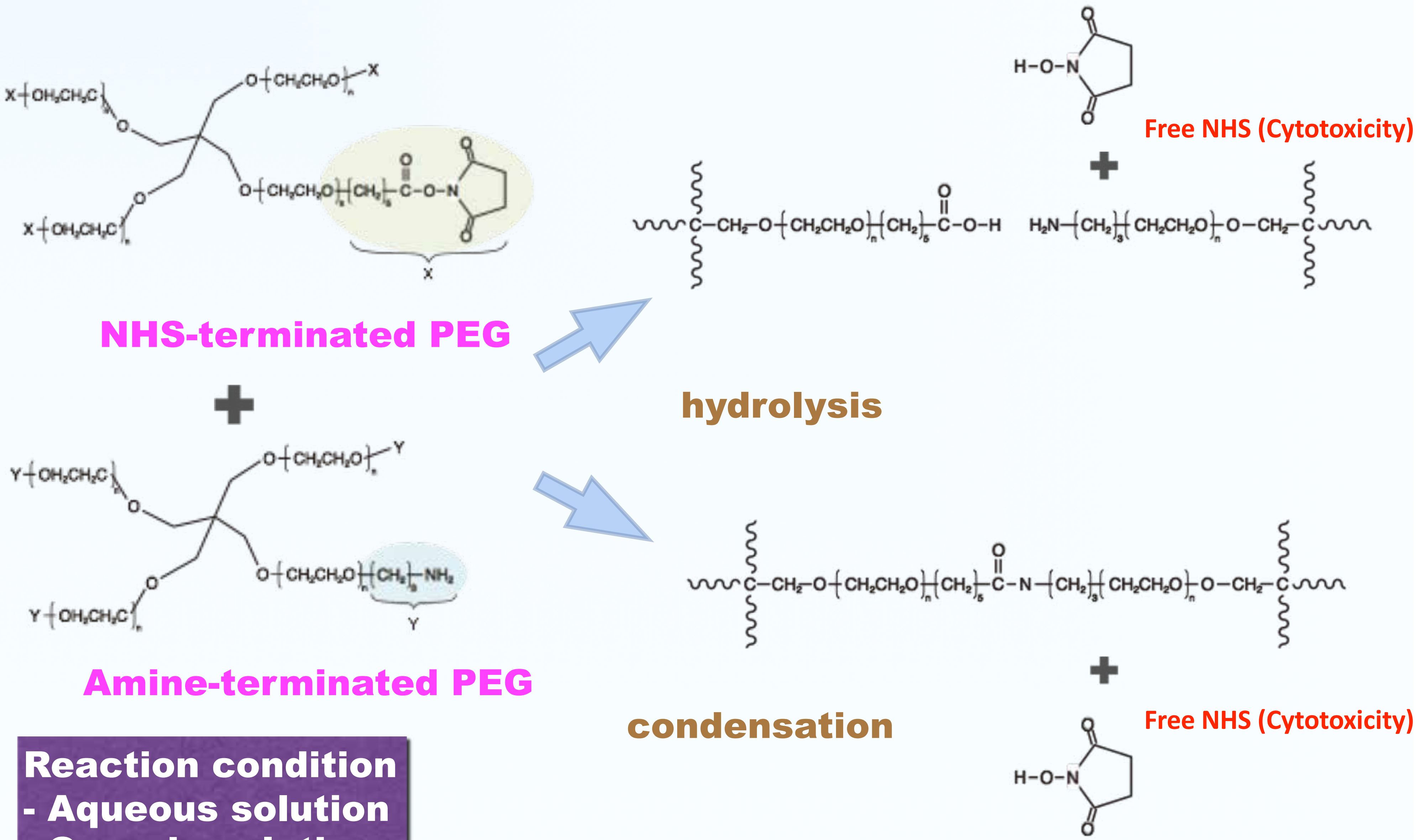


No anisotropy due to isotropic thermal motion



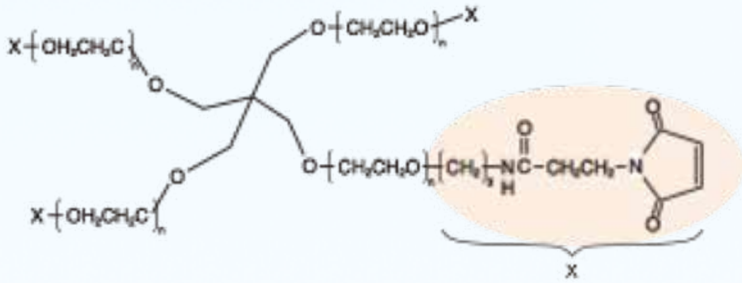
6. Structure of Critical Clusters And Biomedical Application

Cross-end-coupling 1



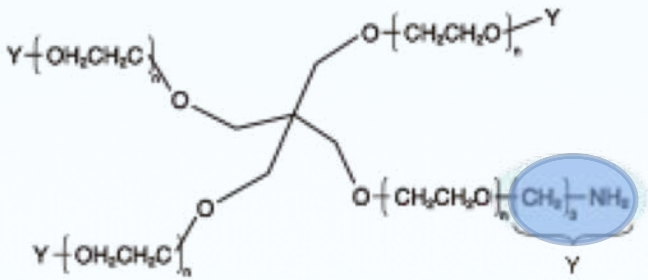
Reaction condition
- **Aqueous solution**
- **Organic solution**

Cross-end-coupling 2



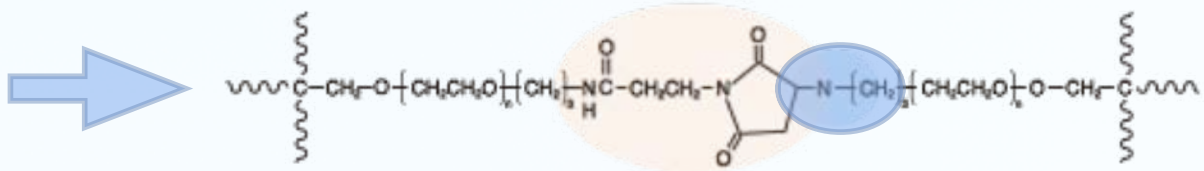
Maleimide-terminated PEG

+



Amine-terminated PEG

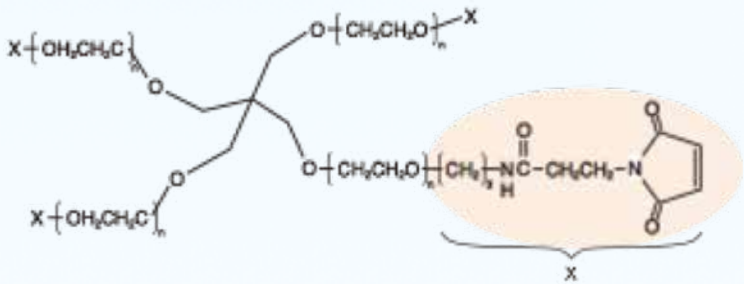
No byproduct !



addition

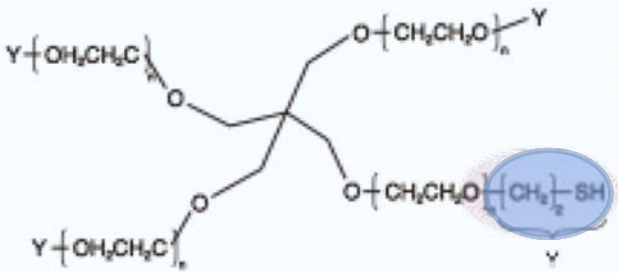
Reaction condition
- Organic solution

Cross-end-coupling 3



Maleimide-terminated PEG

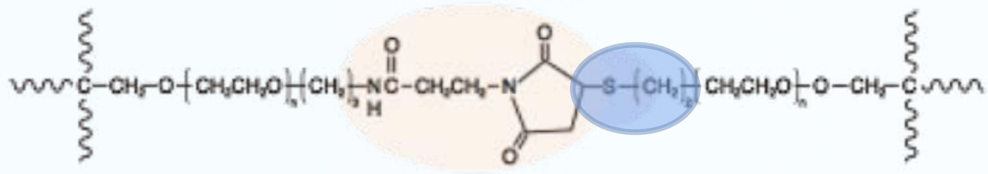
+



Thiol-terminated PEG

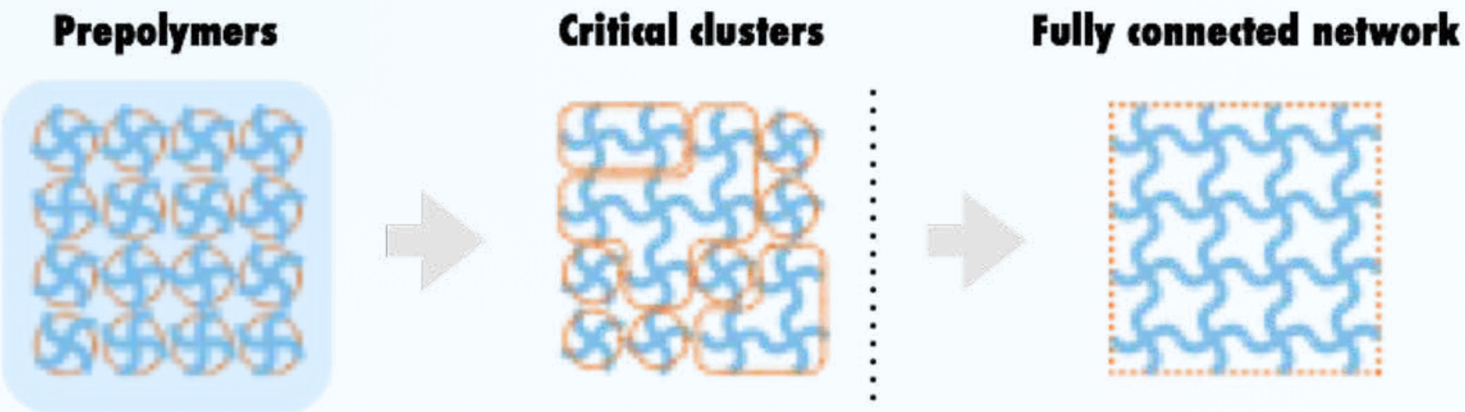
addition

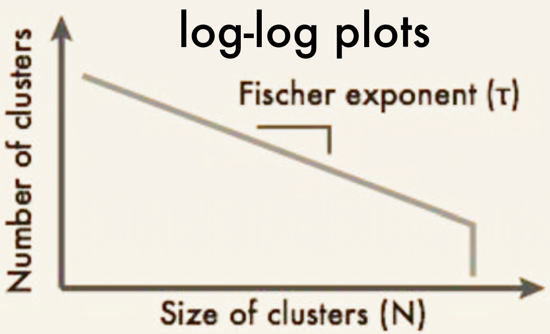
No byproduct !



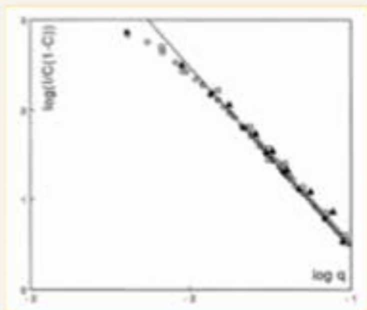
Reaction condition
- **Aqueous solution** (No hydrolysis pH<7)
- **Organic solution**

Critical clusters



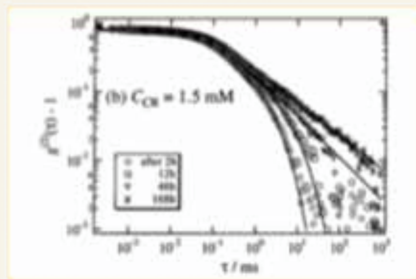


Patton, E. V. et al., Macromolecules, 1989



Small angle scattering

Adam, M. et al., *Physical Review Letters*, 1991.



Dynamic light scattering

Shibayama, M. et al., *Macromolecules*, 2002.

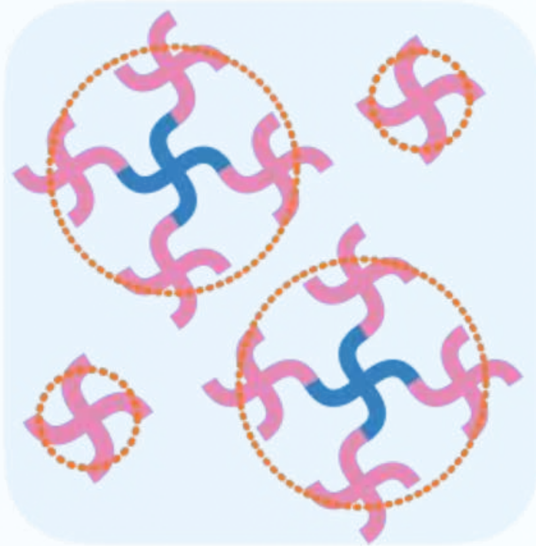
Attributed to the scaling relation between clusters sizes and their numbers, numerous scaling relations have been found by scattering and rheology.

A new type critical clusters

Mix two different prepolymers with an unbalanced ratio

Wait until reaction ends,

Prepolymers



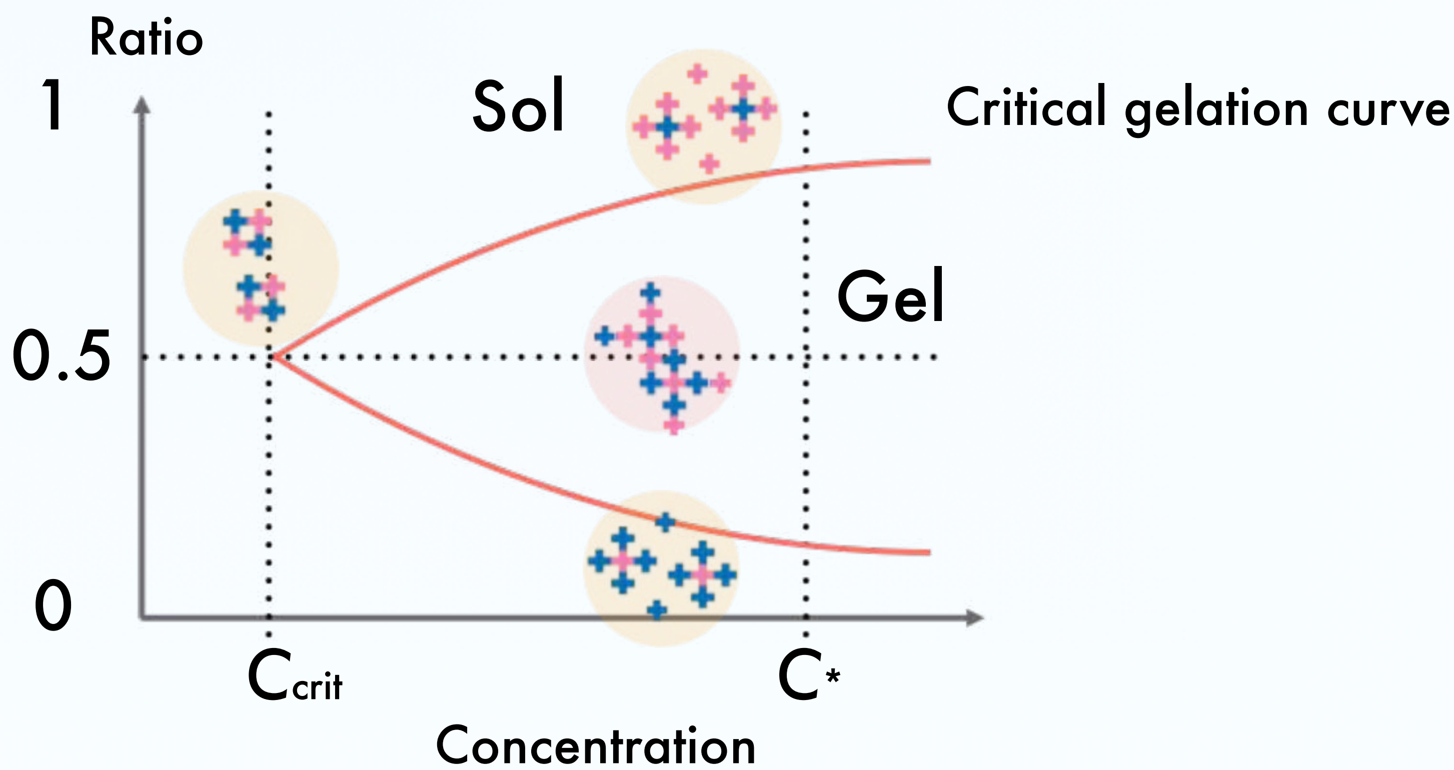
Critical clusters

If one adds one more blue unit,
the system will percolate.

Sakai, T. et al., Polymer Journal, 2016.

New type critical clusters

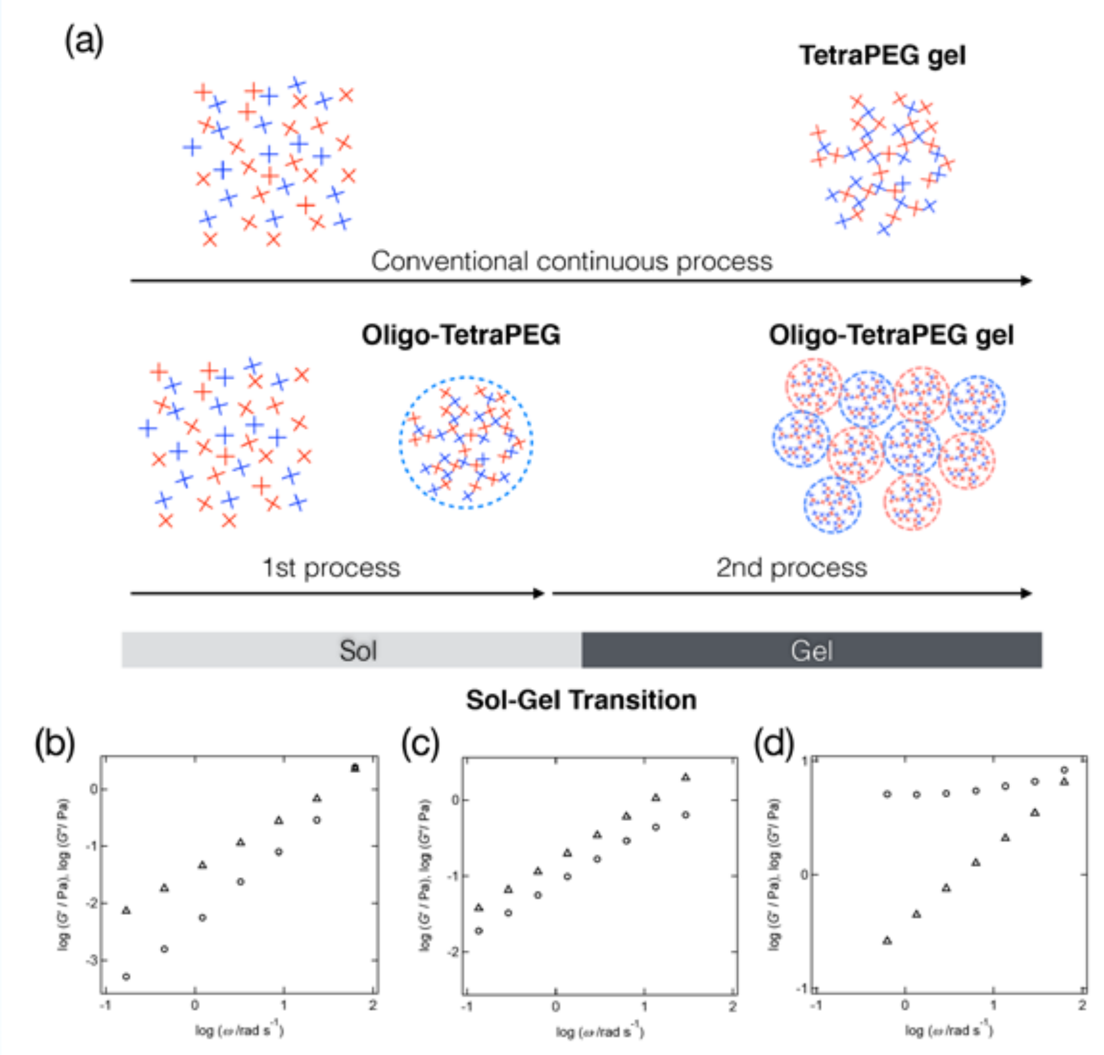
By tuning prepolymers' ratio and their concentrations,
one can obtain a series of different critical cluster solutions.



Sakai, T. et al., Polymer Journal, 2016.

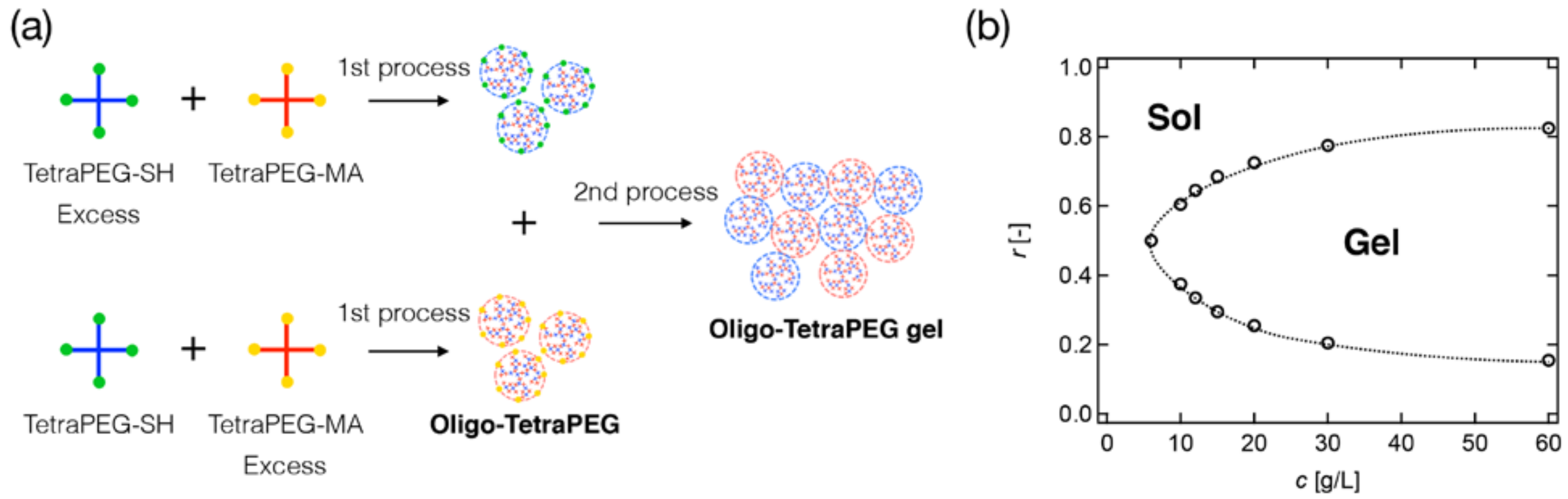
Do these critical clusters show the same scalings with conventional ones ?

Fast-forming hydrogel with ultralow polymeric content as an artificial vitreous body



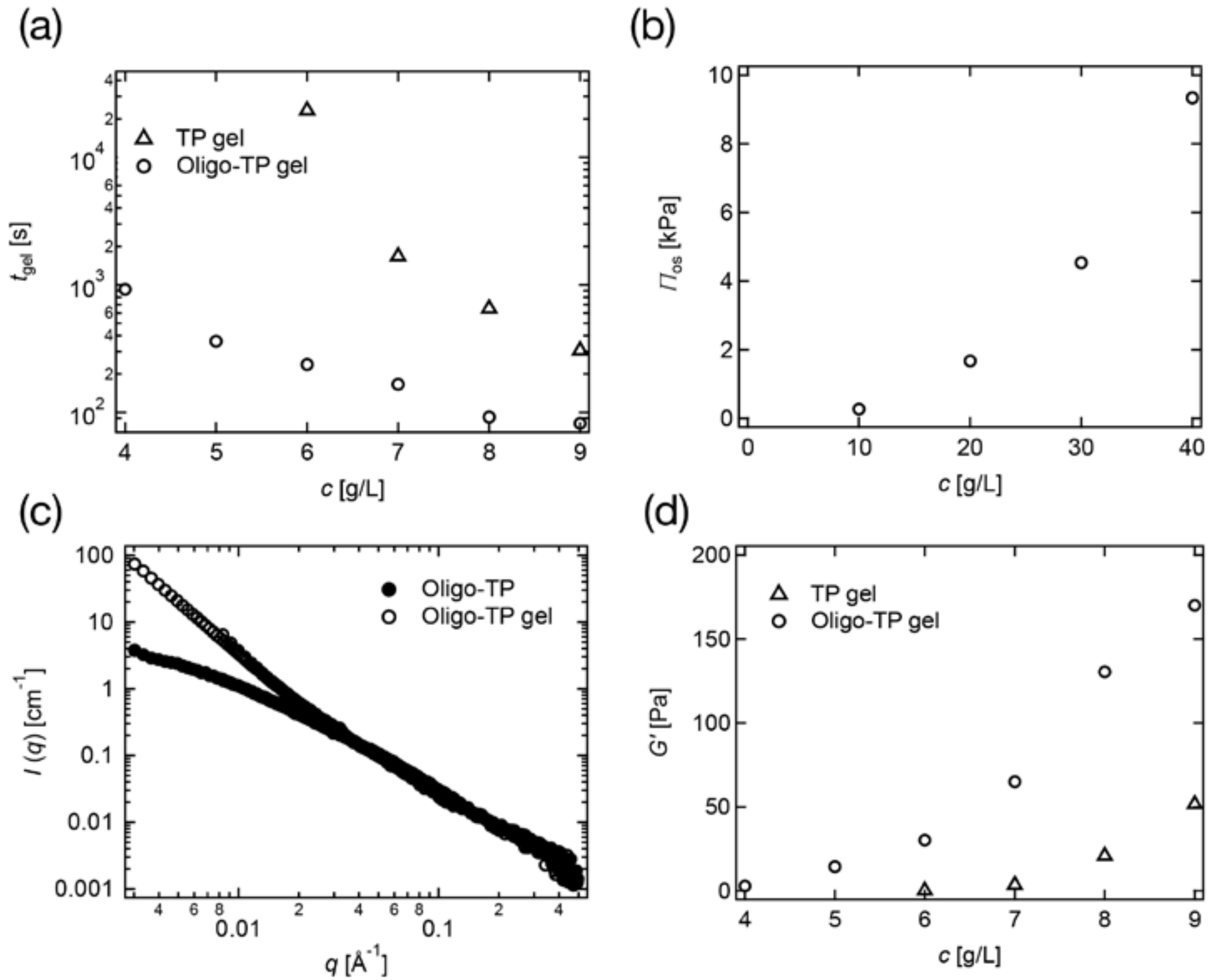
Hayashi et al., Nat. Biomedical Eng., 2017, 1, 0044

Fast-forming hydrogel with ultralow polymeric content as an artificial vitreous body



Hayashi et al., Nat. Biomedical Eng., 2017, 1, 0044

Fast-forming hydrogel with ultralow polymeric content as an artificial vitreous body



Hayashi et al., Nat. Biomedical Eng., 2017, 1, 0044

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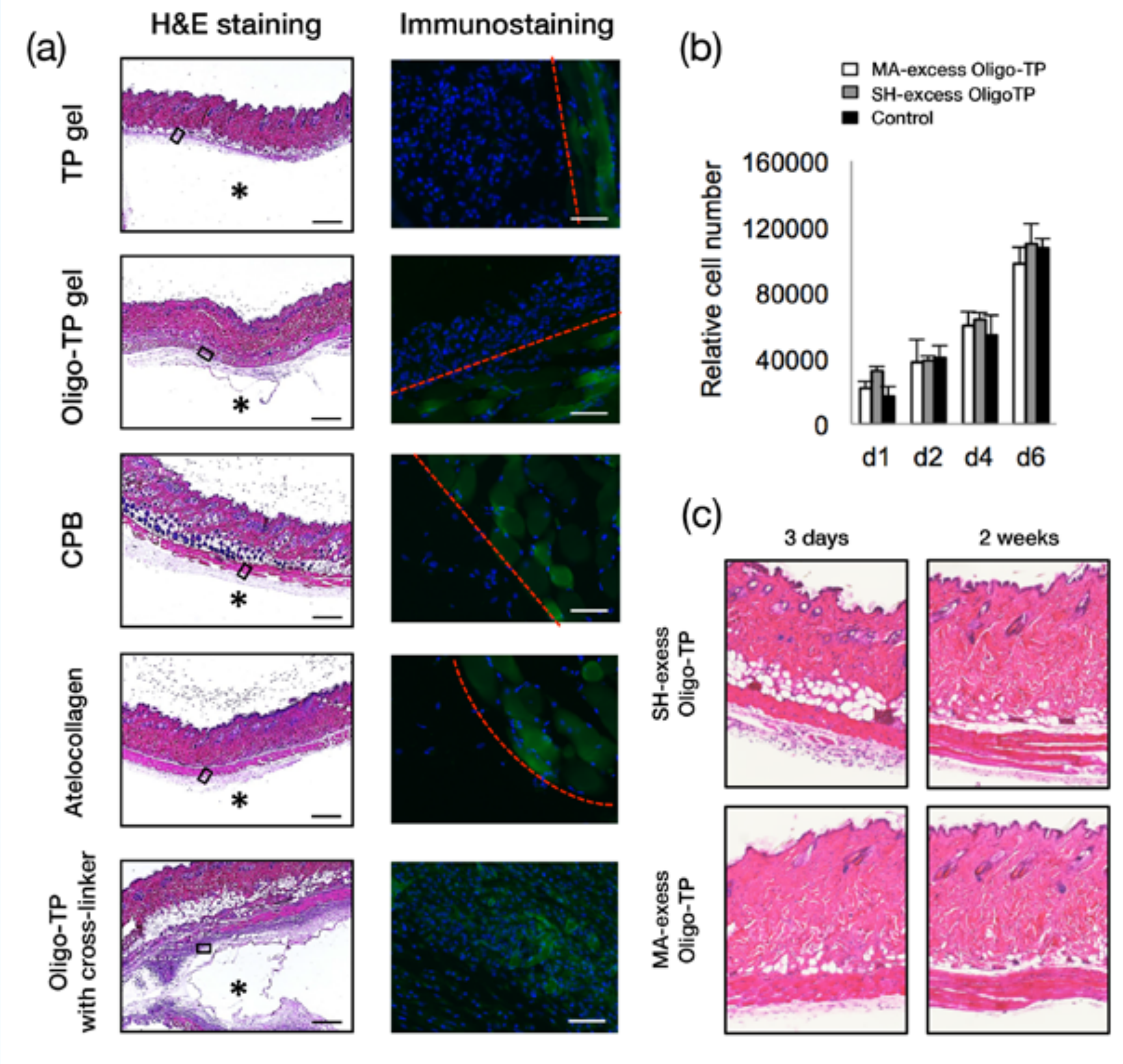

Hayashi et al., Nat. Biomedical Eng., 2017, 1, 0044

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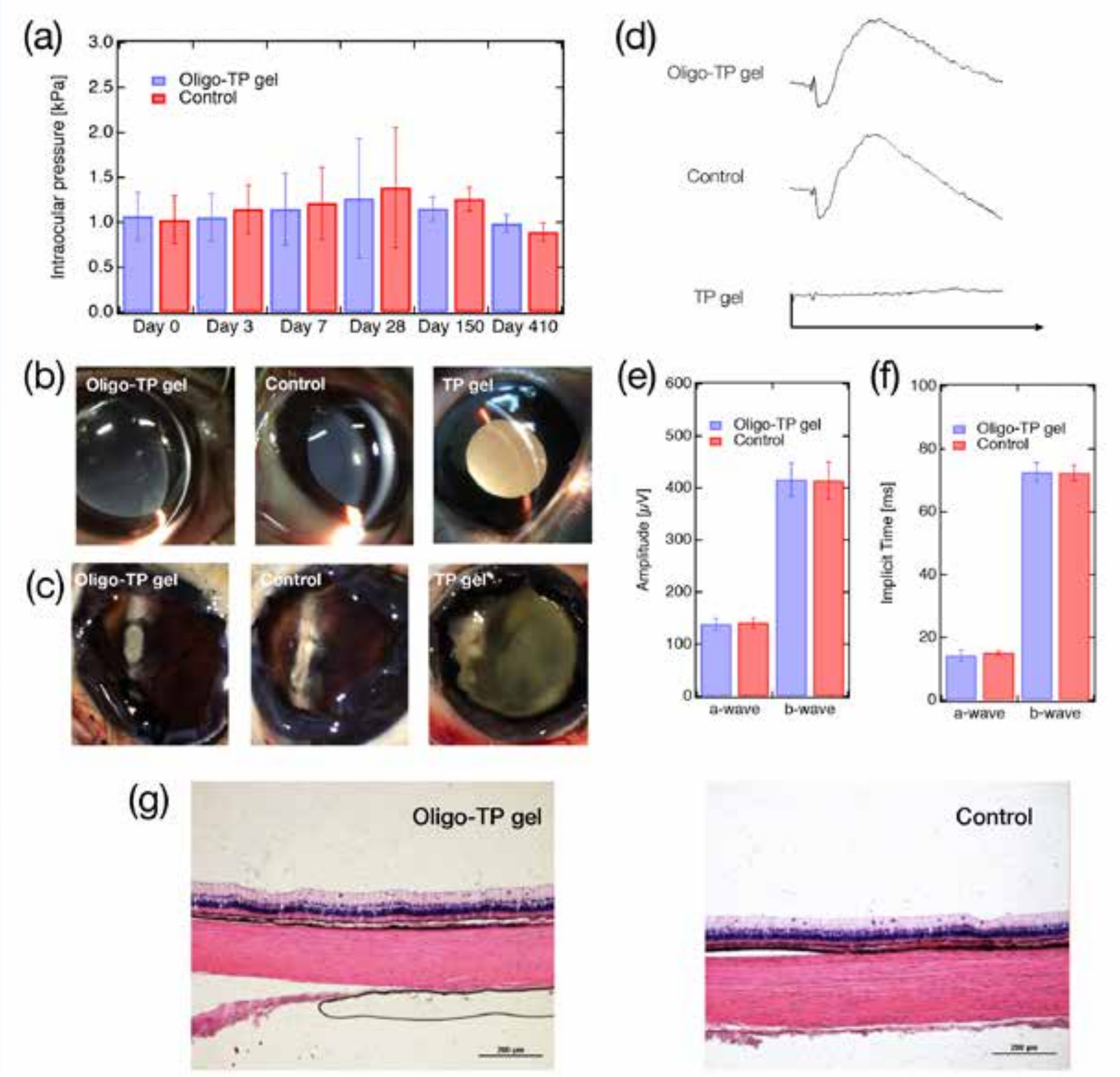
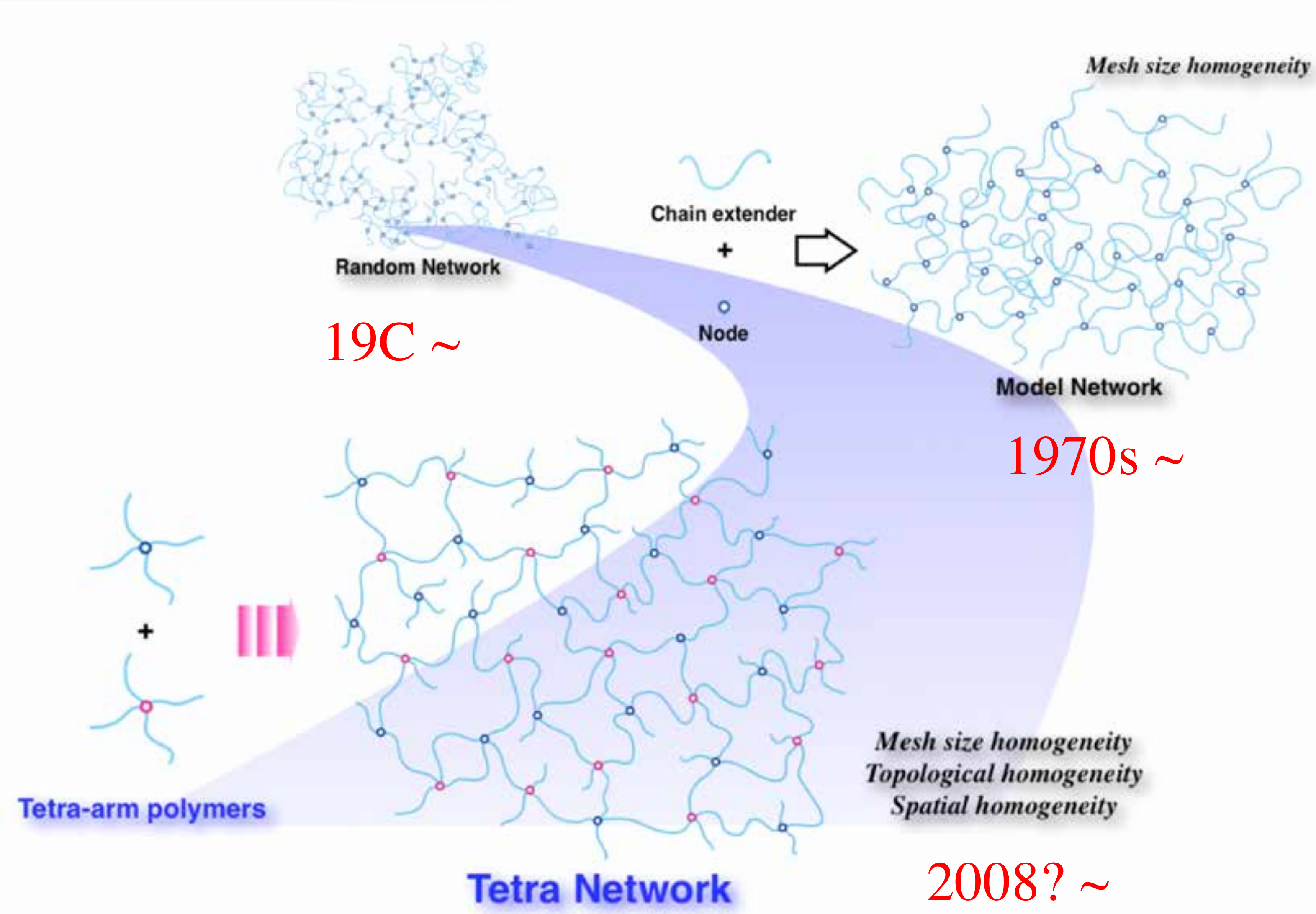


Hayashi et al., Nat. Biomedical Eng., 2017, 1, 0044

Toward Realization of ideal polymer network



T. Sakai et al. Macromol. Rapid Commun., 2010, 31, 1954.

7. Report

2019.4.19

1. Explain the difference between spectroscopy and scattering.
   Show some examples how these techniques are used in soft matter science.

2. Estimate the energies of X-ray, neutron, and electron with the wavelength of 1Å.
   Discuss how these probes are used structural analyses of soft matter.

3. Show some examples of neutron scattering studies on soft matter.