EUROPEAN
SPALLATION
SOURCE

Using neutrons to look at molecules in confinement

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FASEM - Lund - May 13, 2019

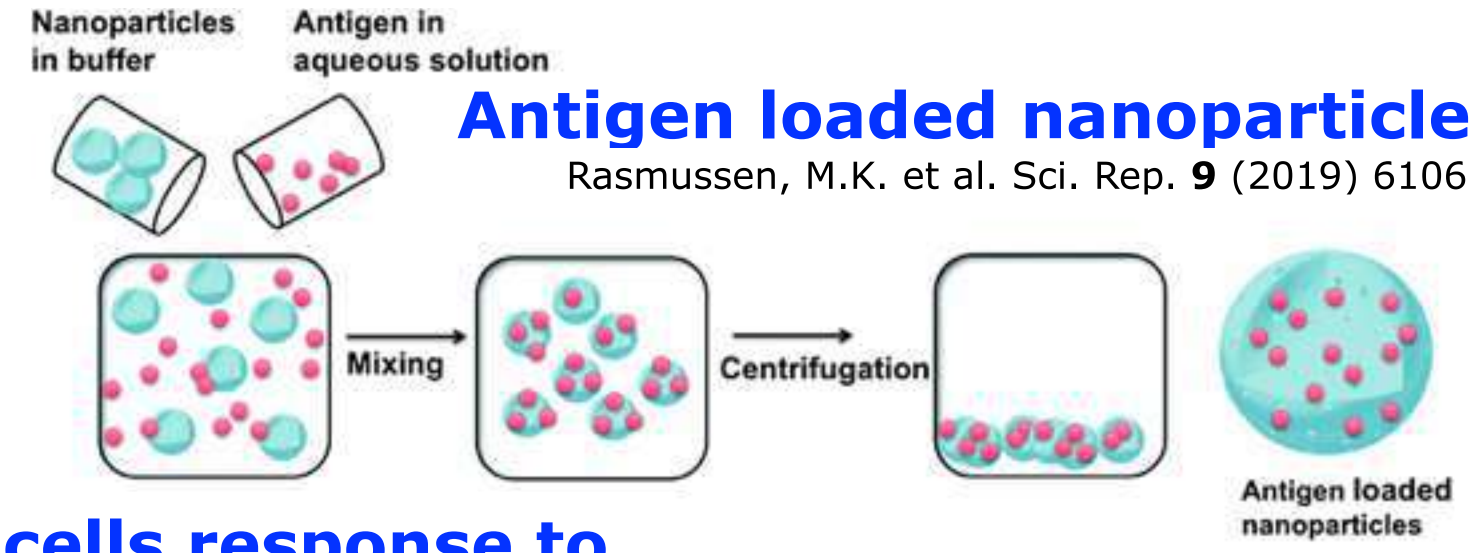
Imaging, Inelastic and Quasi-Elastic Neutron Scattering: Where are the hydrogen atoms and what are they doing?

Why dental cement cracks?

Benetti, A.R. et al. Sci. Rep. **5** (2015) 8972.
Berg, M.C. et al. ACS Applied Mat. & Interf. **10** (2018) 9904.

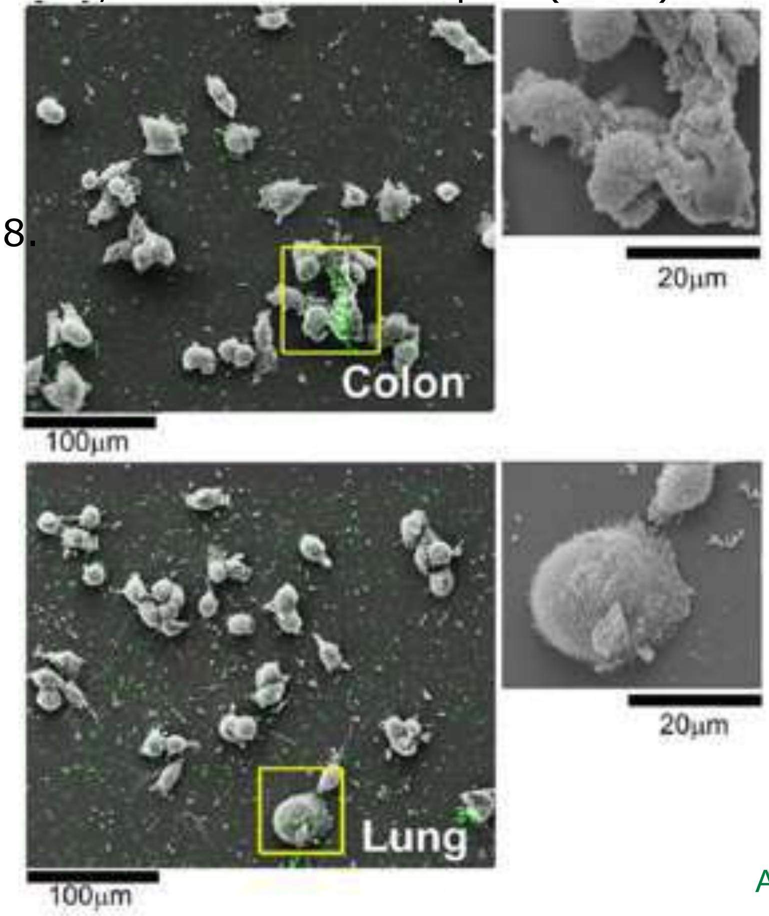
Antigen loaded nanoparticles

Rasmussen, M.K. et al. Sci. Rep. **9** (2019) 6106.



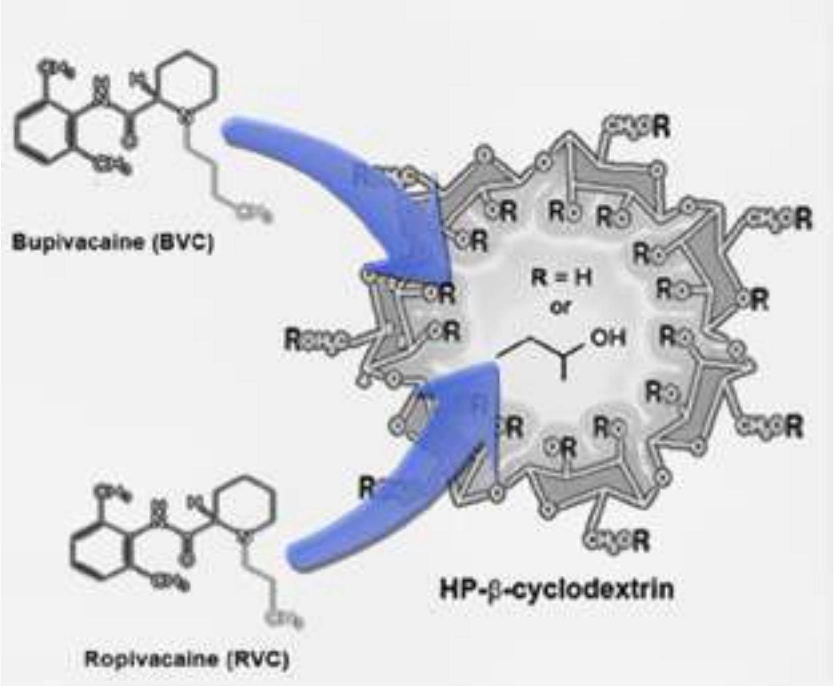
Cancer cells response to an new bio-nanocomposite

Martins, M.L. et al. Sci. Rep. **6** (2016) 22478.



Improving drugs: antibiotic resistance, local anaesthetics & antipsychotics

Martins, M.L. et al. Int. J. Pharm. **524** (2017) 397.
dos Santos, E.C. et al. Applied Clay **166** (2018) 288.
Pereira, J.E. - PhD Thesis (2018).

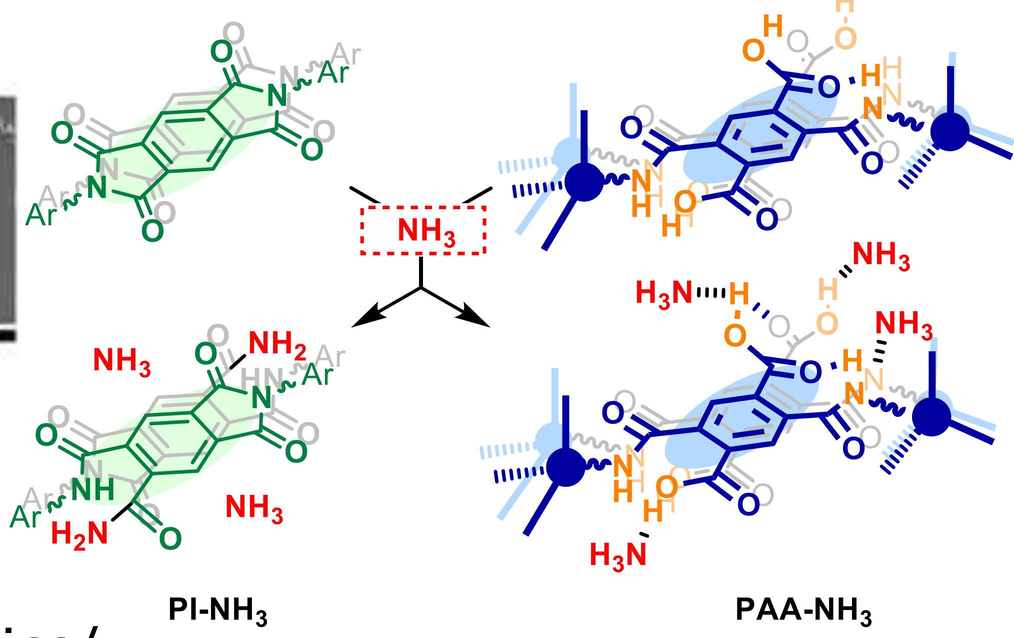


Porous Organic Polymers

R. Lima (UFCG) and J. Lee (KU)

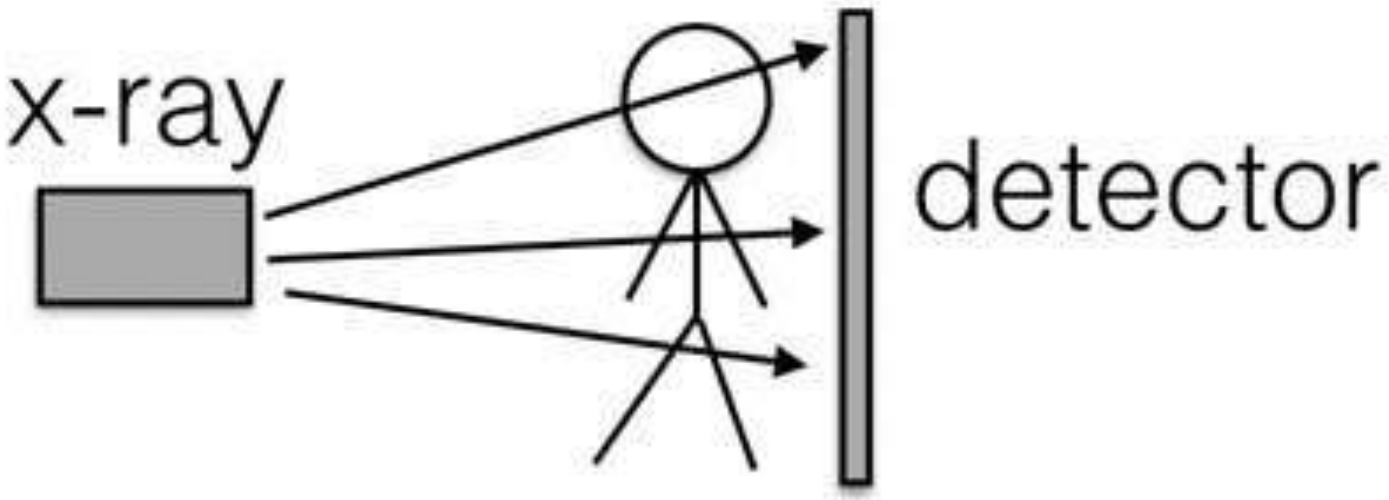
Polycyclic imide (**PI**)
- no H-bond donors
- lower NH_3 adsorption
- higher surface area
- chemical instability

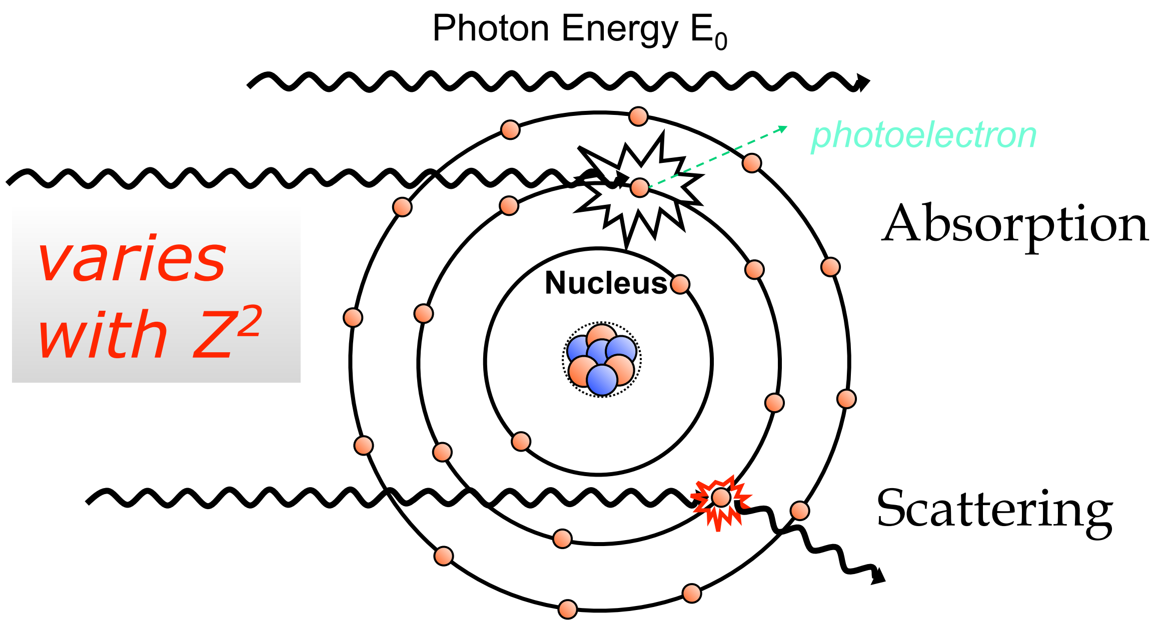
Poly(amic acid) (**PAA**)
- rich in H-bond
- higher NH_3 adsorption
- lower surface area
- structural integrity



http://xns.nbi.ku.dk/research/dynamics/

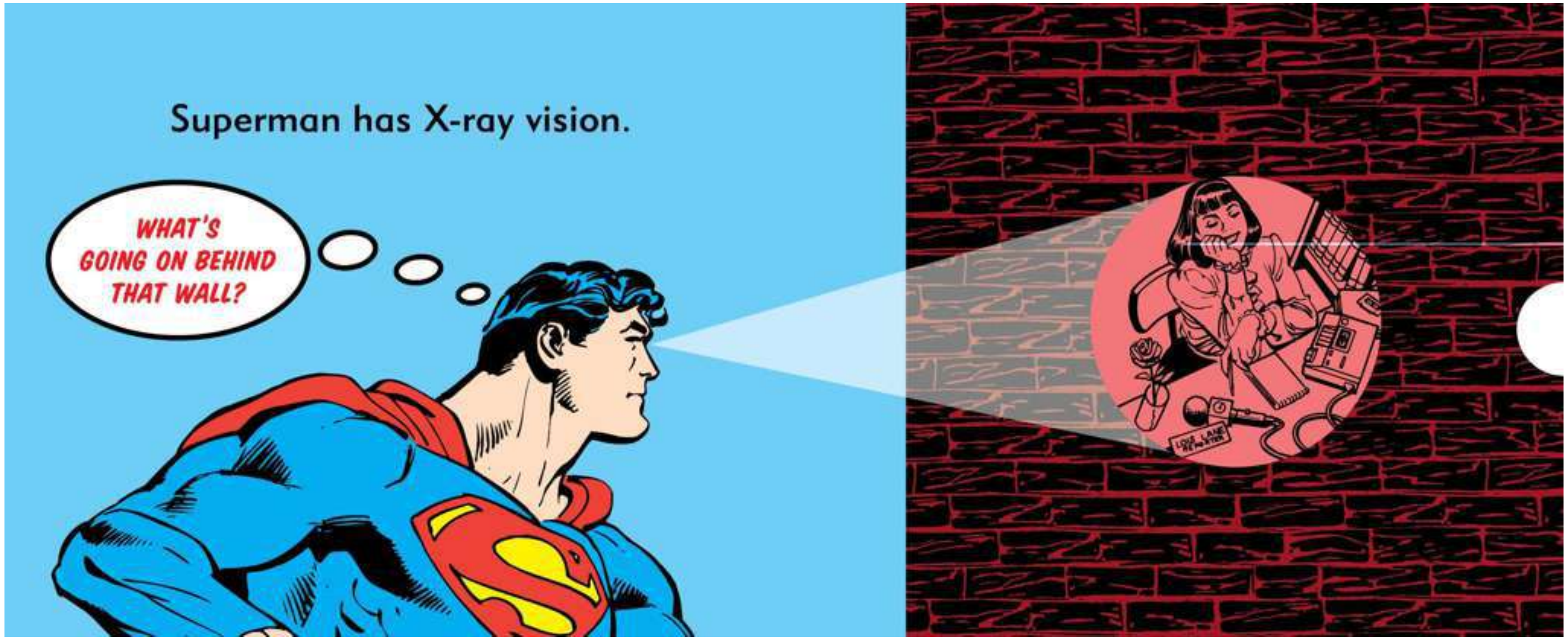
Superman X-rays (?) vision





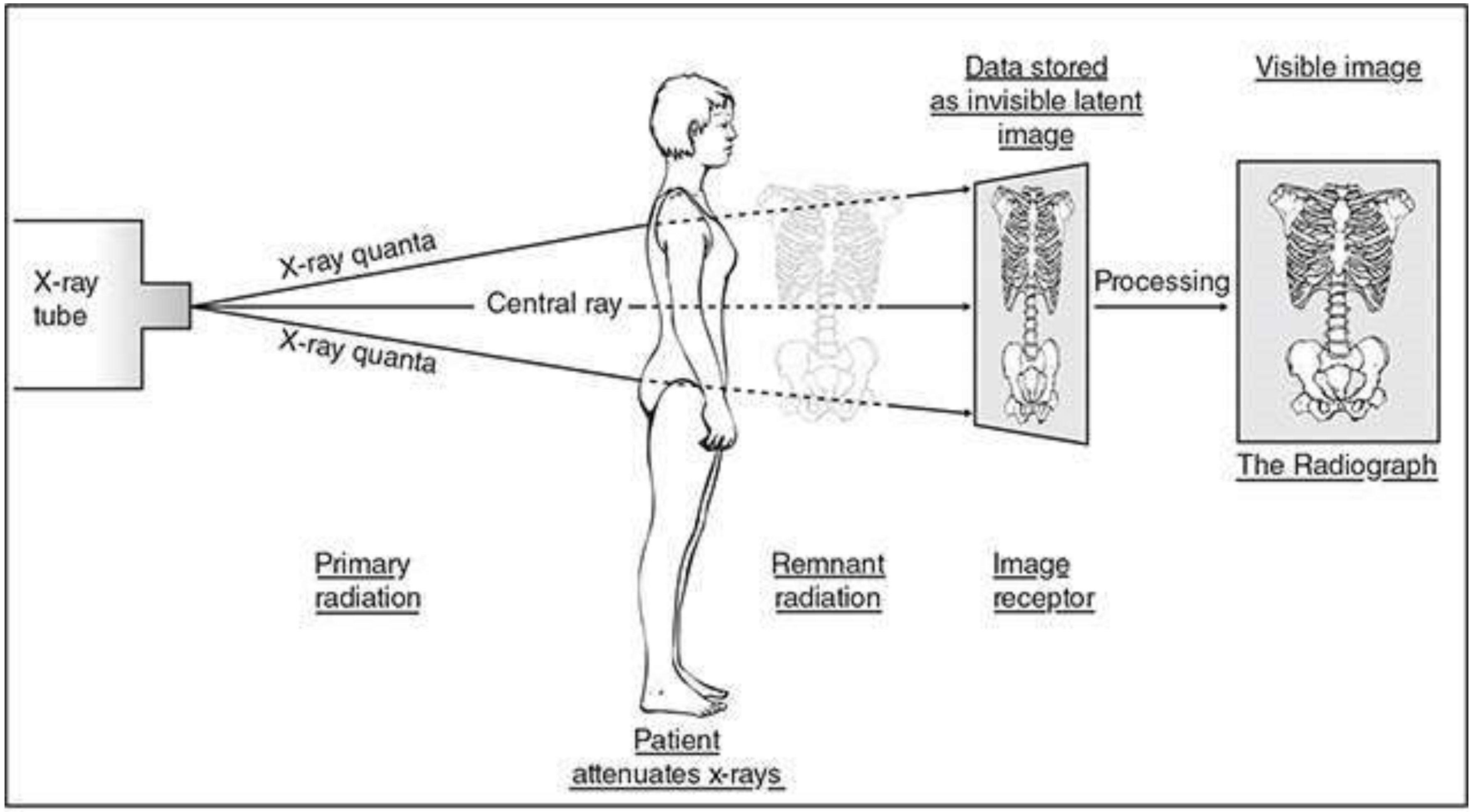
varies with Z^2

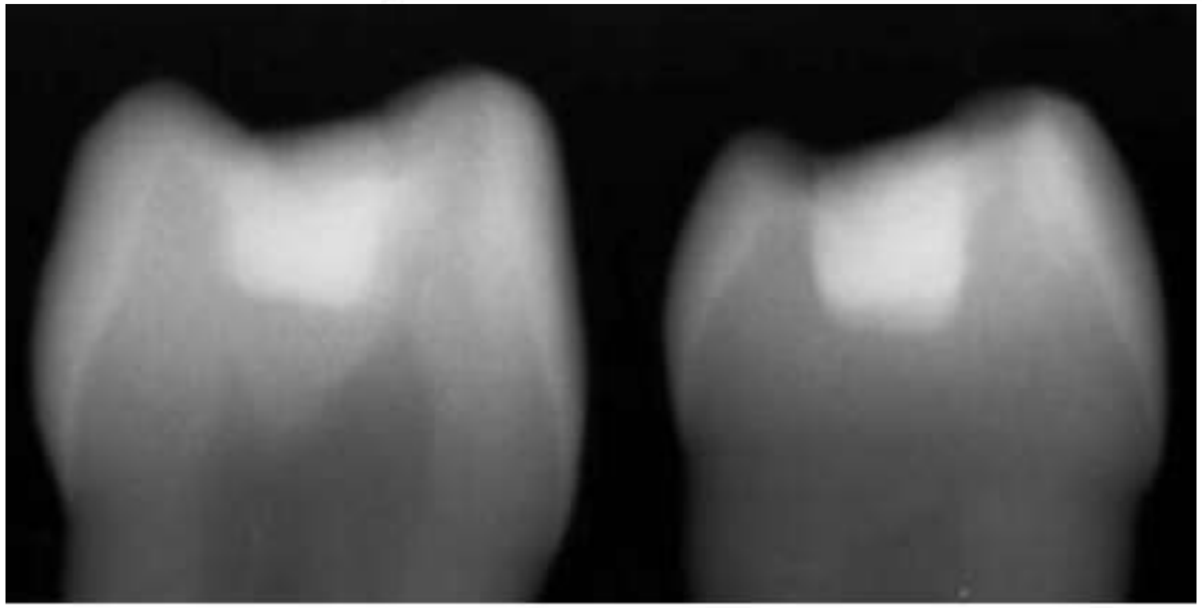
X-rays have a different wavelength (and frequency) they interact with matter differently than visible light.



Cartoon of making an x-ray image, by Rhett Allain.

X-rays imaging: looking inside matter



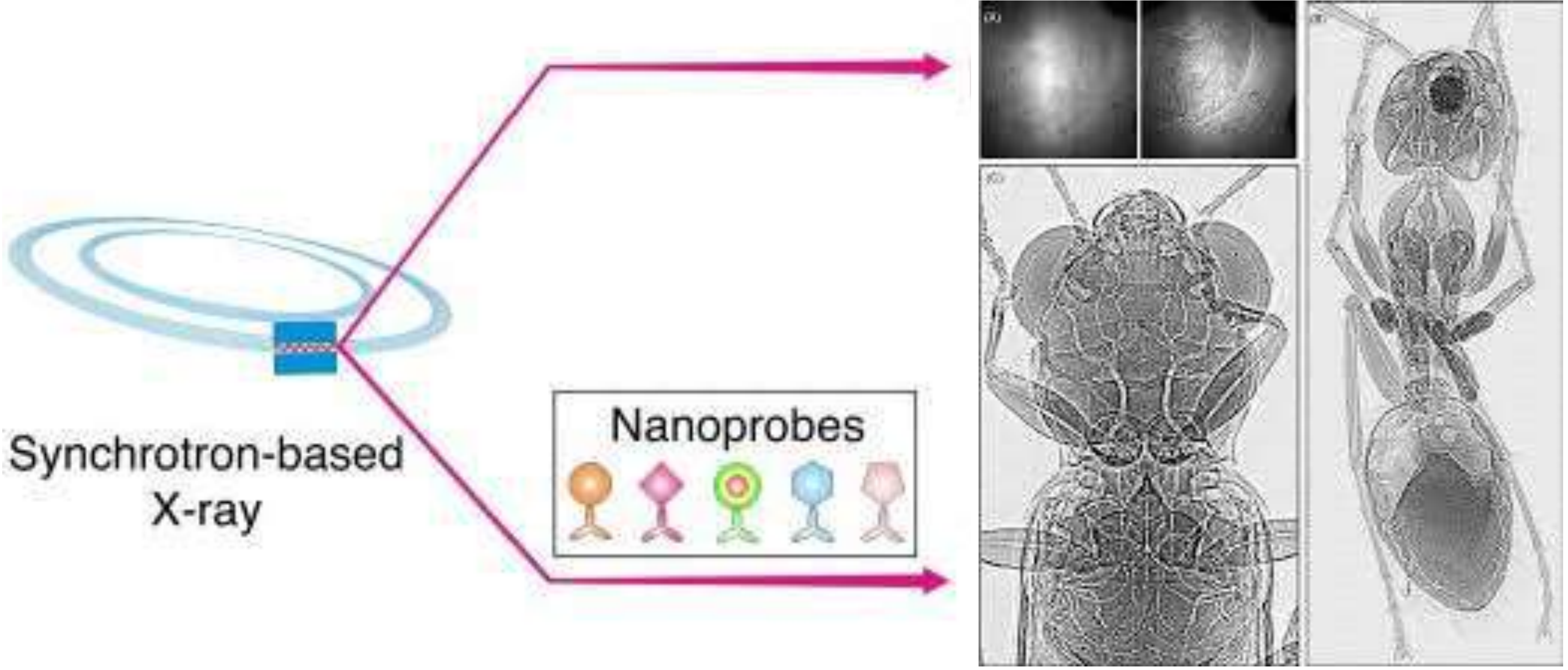


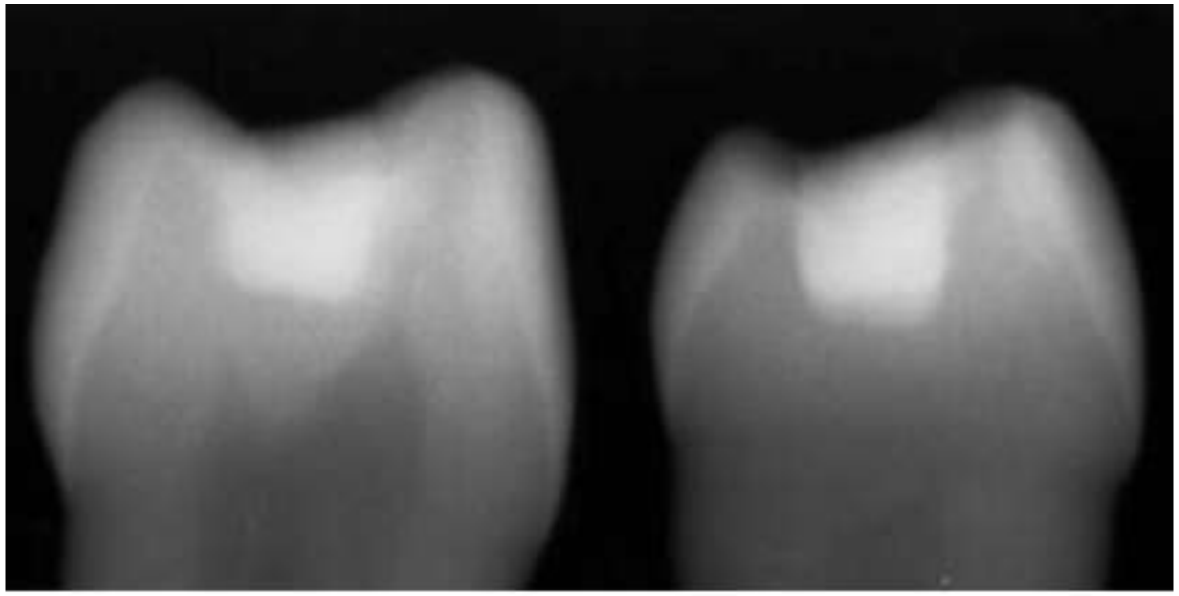
Ana R. Benetti
Odontology Faculty - KU

Conventional dental X-rays

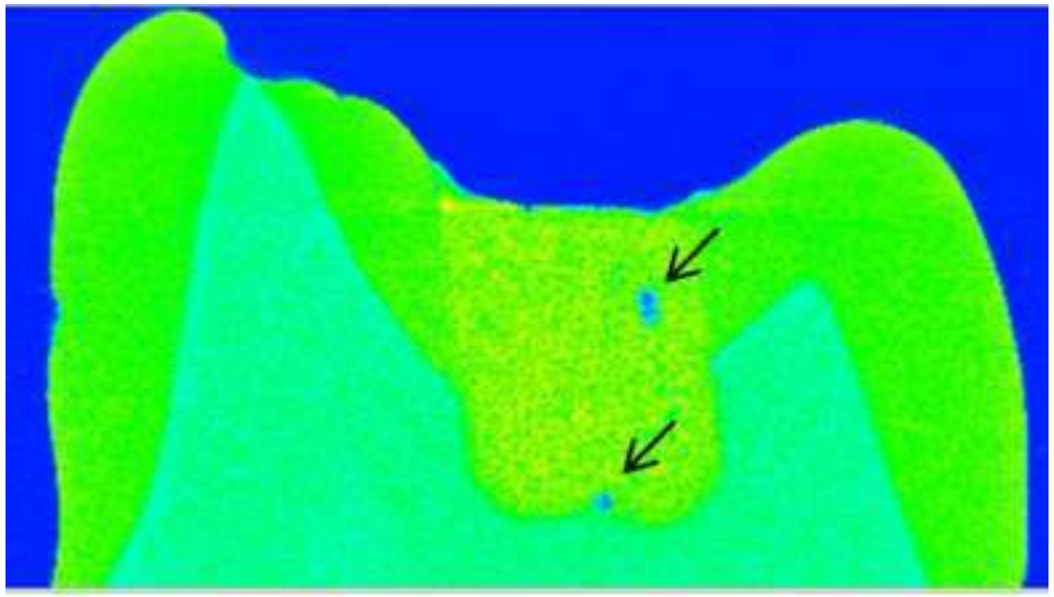
Cartoon of making a Musculoskeletal Imaging, by Lynn N. McKinnis.

Synchrotron X-rays imaging: looking inside smaller sizes





Conventional dental X-rays

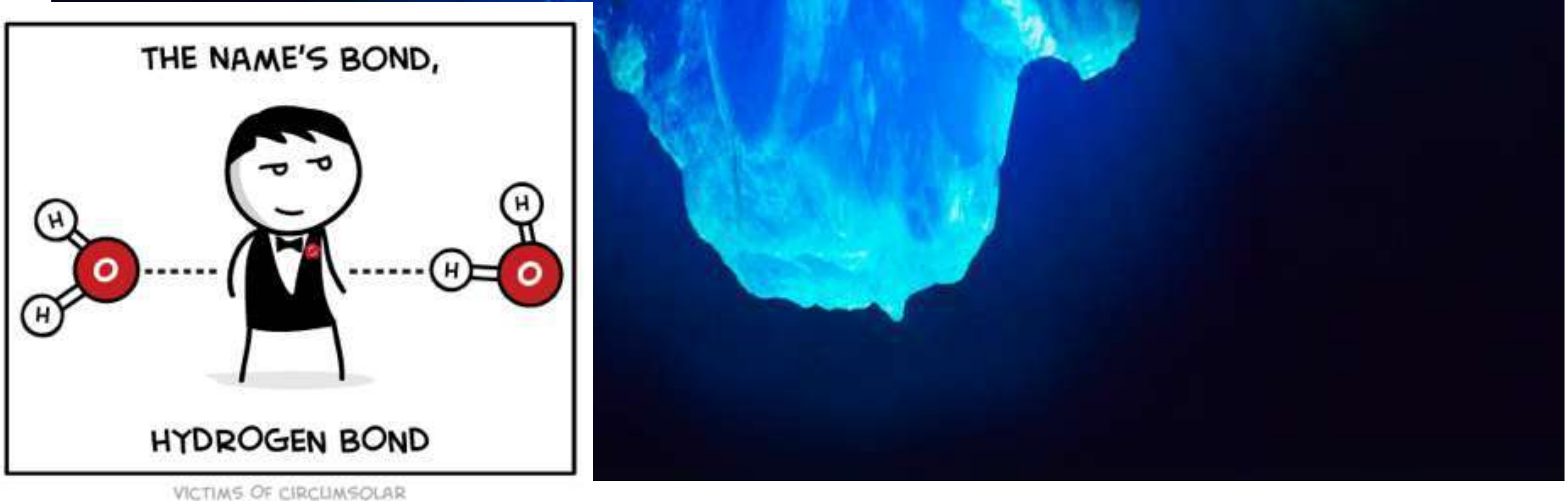


X-rays tomography

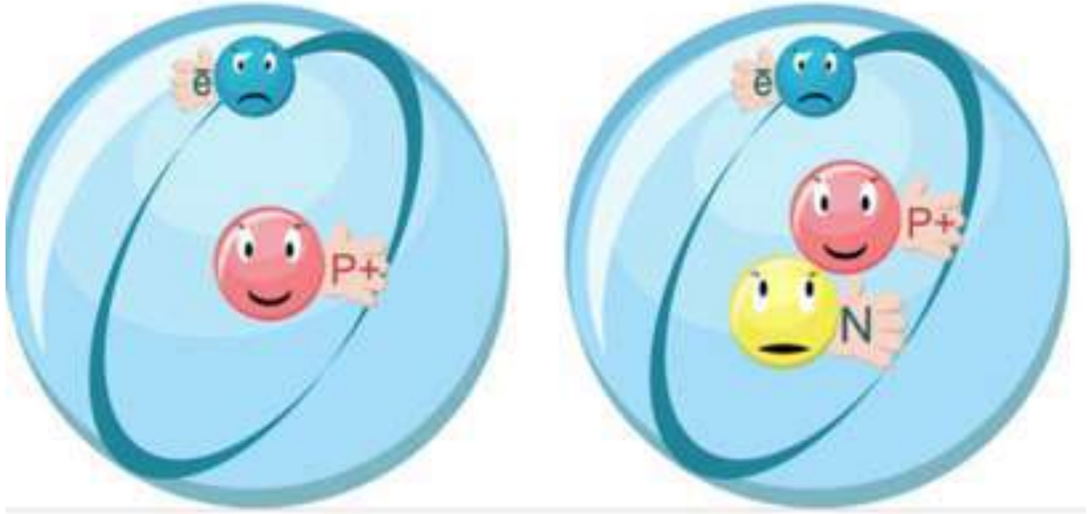
Respiratory Physiology & Neurobiology 173 Suppl:S65-73 · March 2010

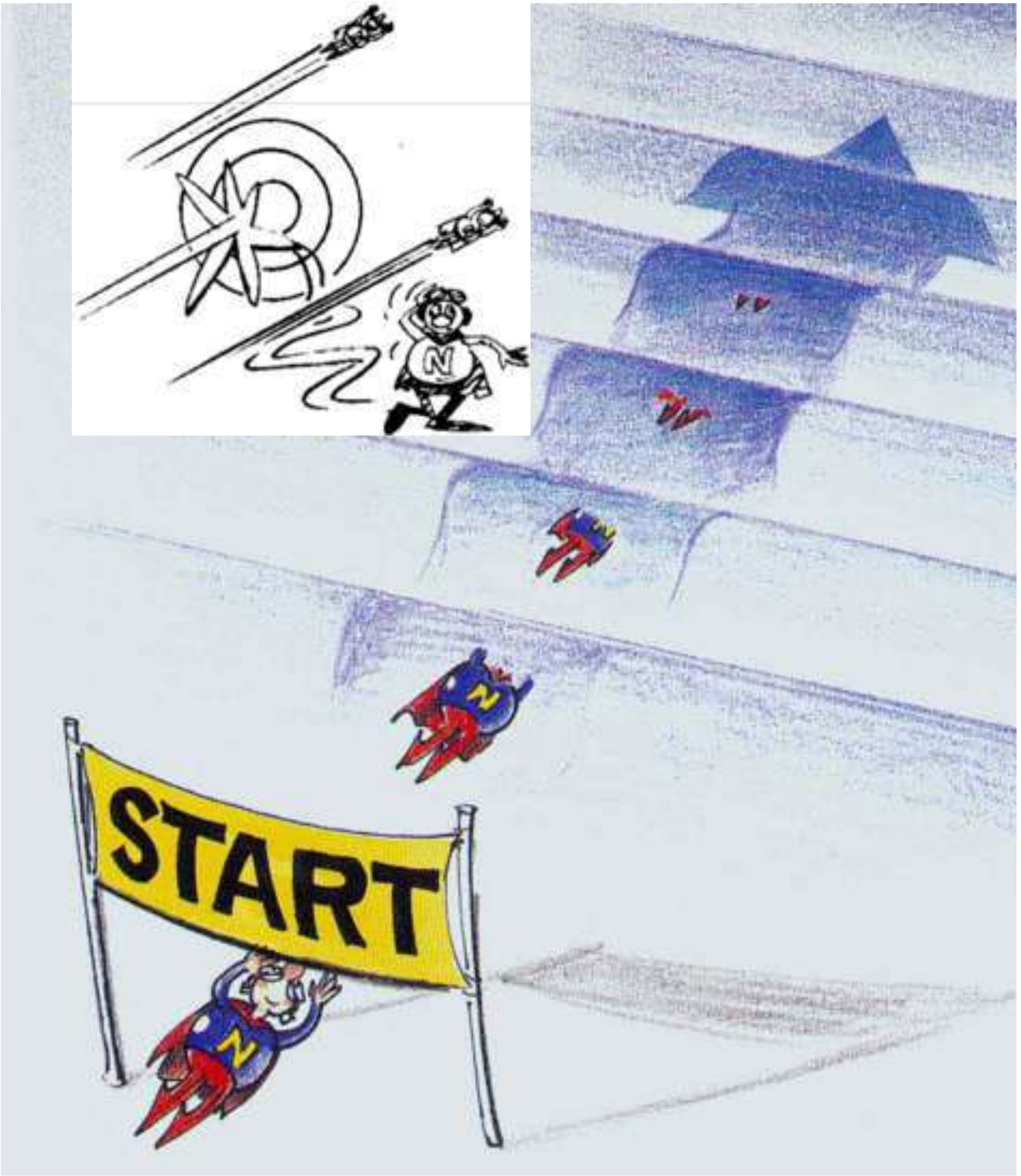
Benetti, A.R. et al. Sci. Rep. **5** (2015) 8972.

Then how can we 'see' the amazing H-bonds?



We need to call the neutron man!



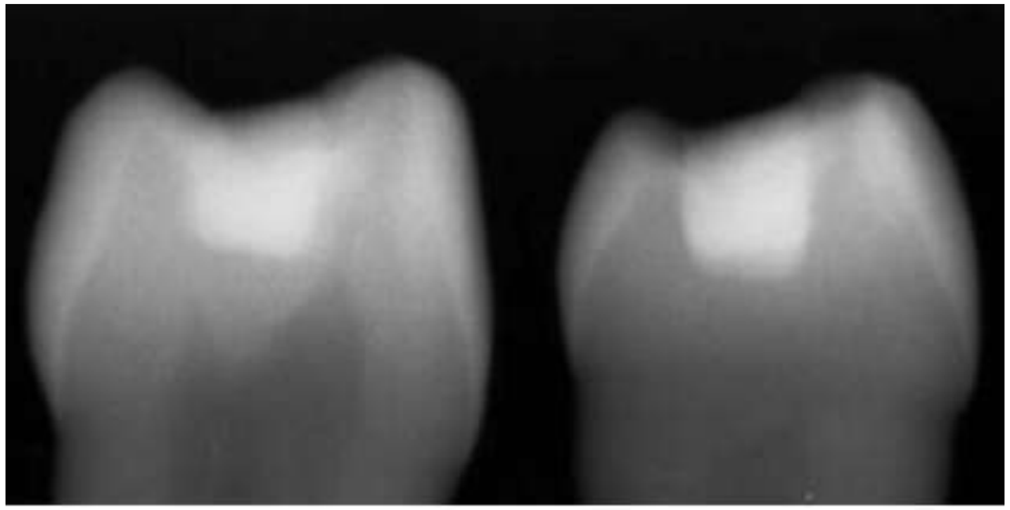


Neutron scattering a PRIMER by Roger Pynn.

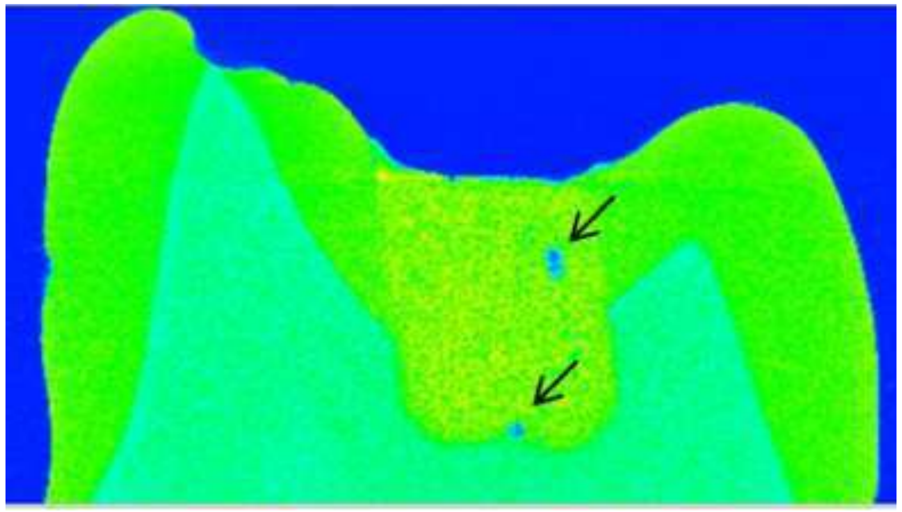
When the monster came, Lola, like the peppered moth and the arctic hare, remained motionless and undetected. Harold, of course, was immediately devoured.

Solvent matching (i.e. matching the scattering density of a molecule with the solvent) facilitates study of on component by rendering another “invisible.”

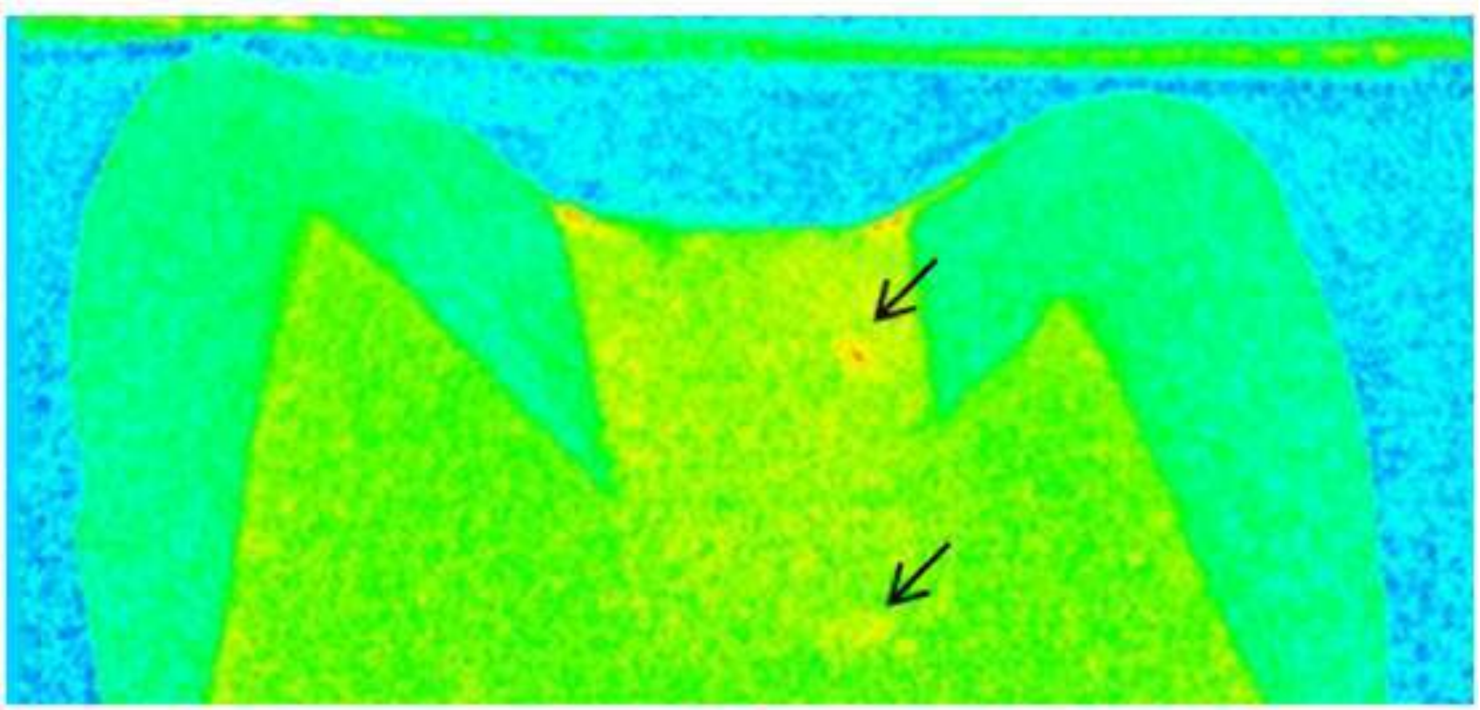
Neutrons help filling in the gaps: a better view



Conventional dental X-rays



X-rays tomography



Neutrons tomography

Benedict Lenhoff
BSc thesis

Johan Jacobsen
MSc thesis

Solveig Hedal
MSc thesis

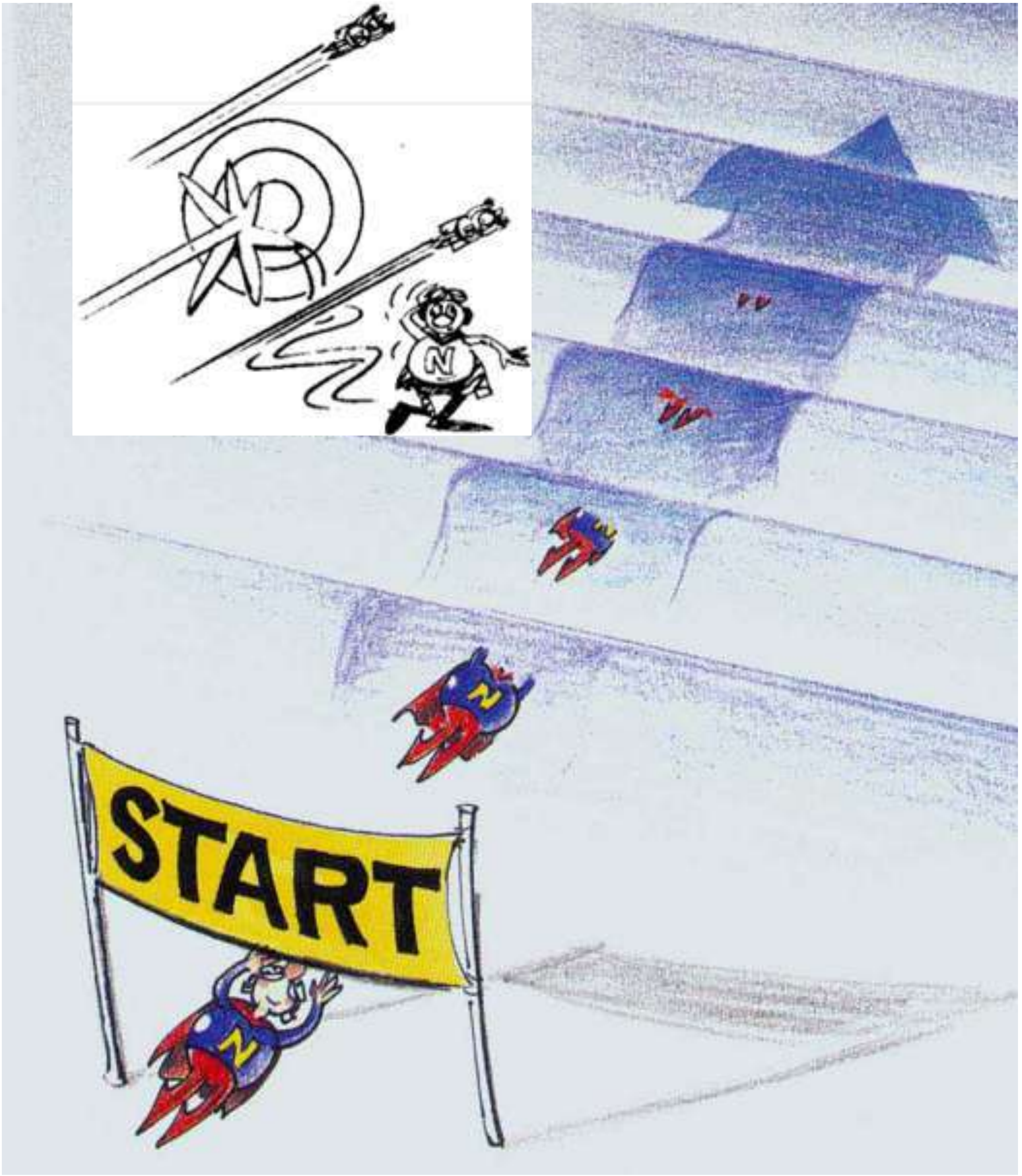
Casper Madsen
MSc thesis

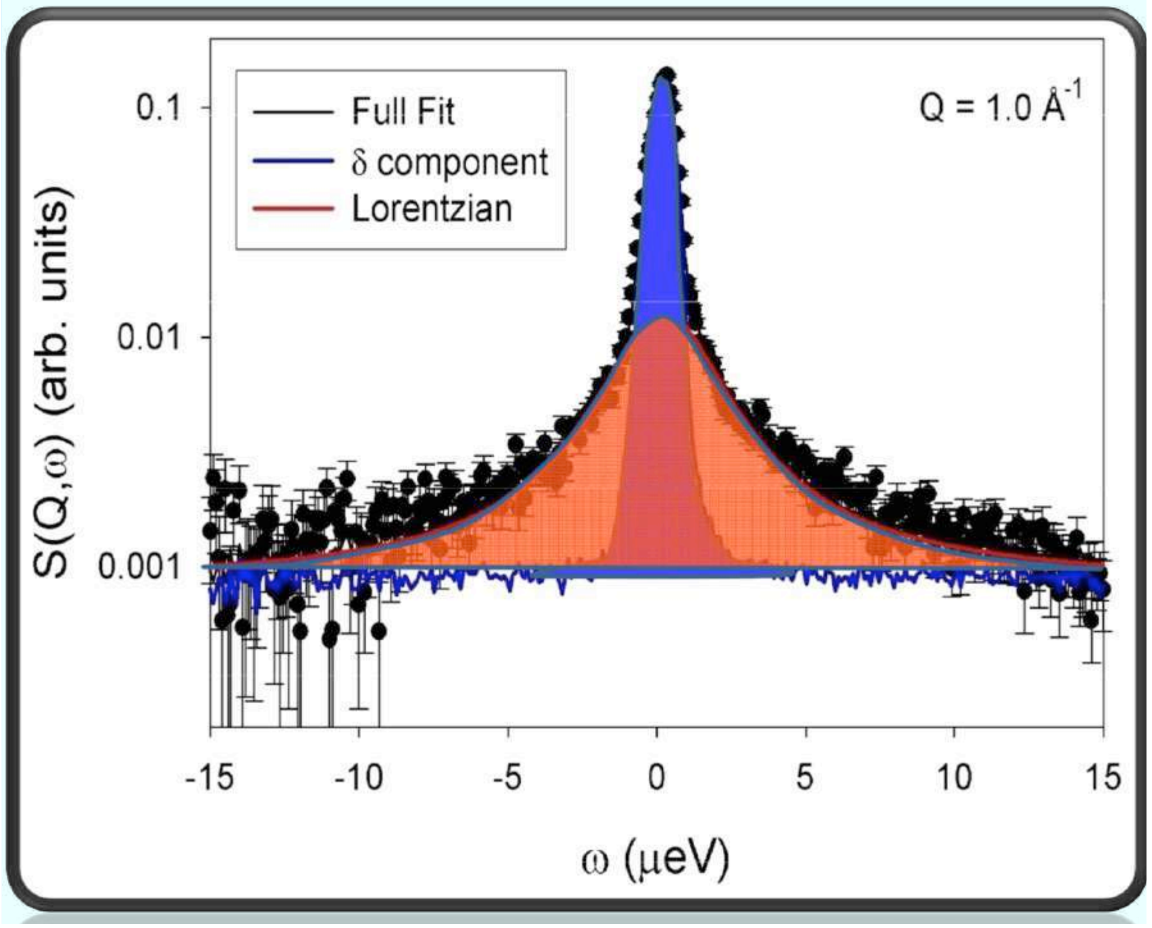
Marcella C. Berg
PhD thesis

Murillo L. Martins
Postdoctoral Fellow

Benetti, A.R. et al. Sci. Rep. **5** (2015) 8972.

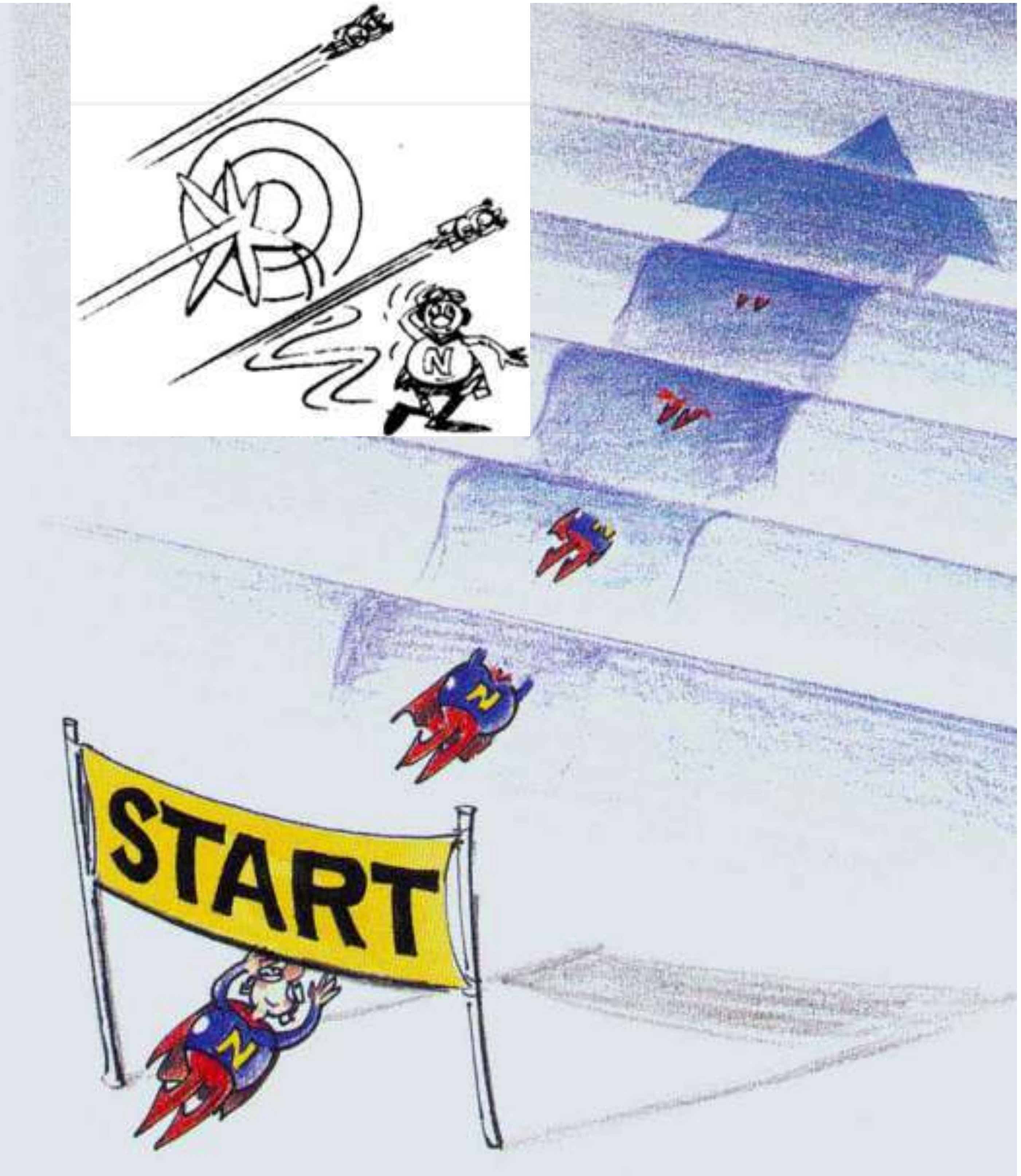
Neutron man can also tell us about dynamics





Berg, M.C. et al. ACS Applied Materials & Interfaces, **10** (2018) 9904–9915.

Neutron man can also tell us about dynamics



Berg, M.C. et al. ACS Applied Materials & Interfaces, **10** (2018) 9904–9915.

NS: Basically two types of instruments

The the £4million diffraction detector from Polaris at ISIS.

The BASIS instrument at SNS.

Diffractometers: 1- 10Å
Measure structures
neutron : Wave
Bragg's law : $2d\sin\theta=n\lambda$
$E_i=E_f$ & $k_i=k_f$

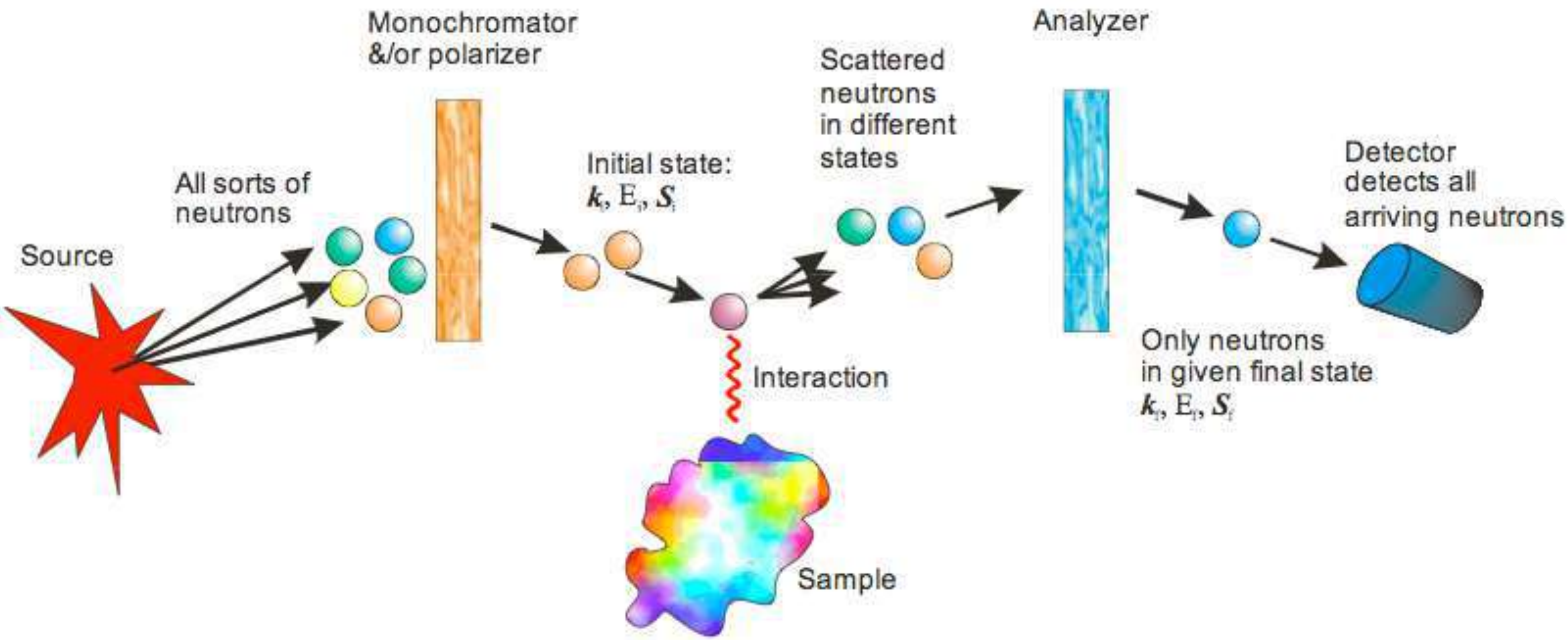
Spectrometers:
-30 to 1000meV
Measure dynamics
neutron : particle
Newton's law
$E_i\neq E_f$ & $k_i\neq k_f$

Crash course in Neutron Instrumentation

☑ one can not manipulate its initial state

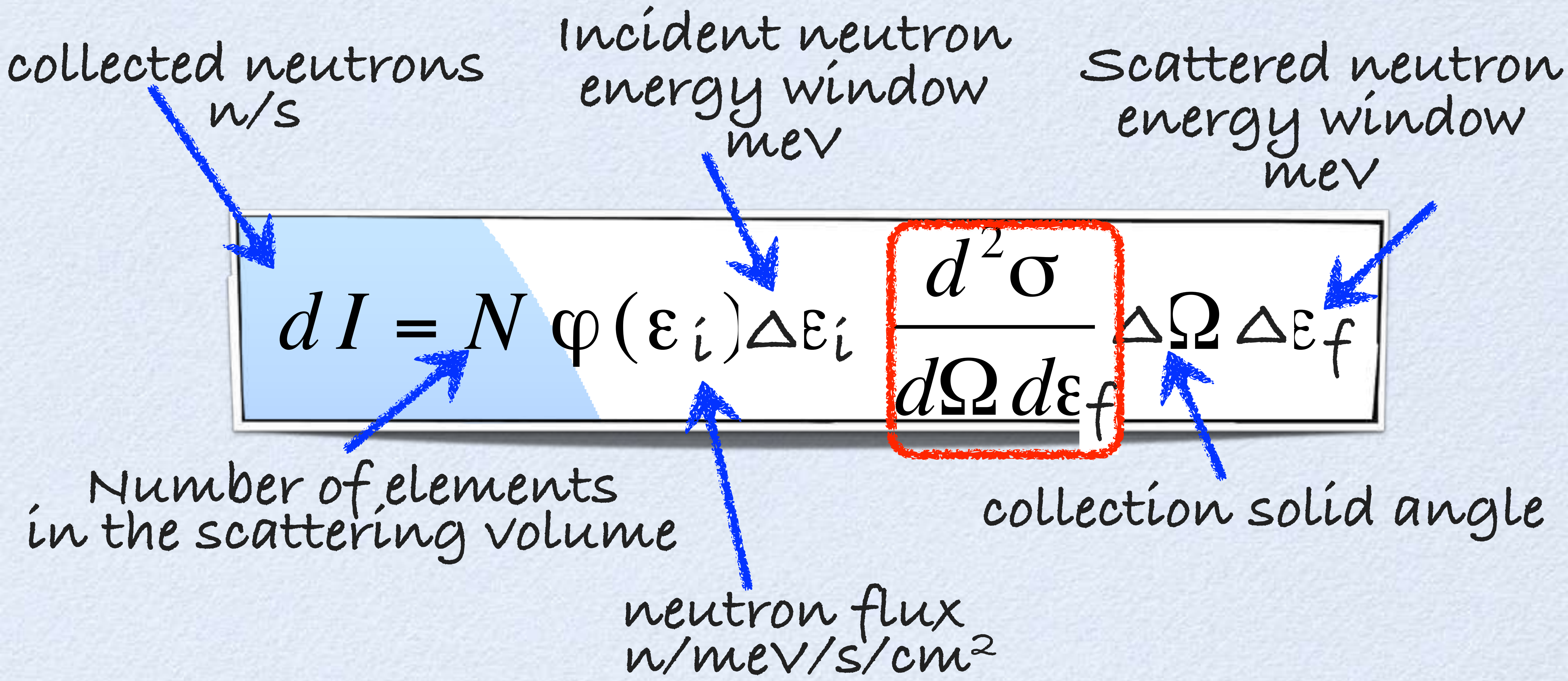
☑ often one cannot measure its final state

Solution:‘filters’ - monochromator and analysers



High price: most neutrons are lost twice!

SCATTERING CROSS SECTION



$$dI = N\,\varphi(\varepsilon_i)\,\Delta\varepsilon_i\,\boxed{\frac{d^2\sigma}{d\Omega\,d\varepsilon_f}}\,\Delta\Omega\,\Delta\varepsilon_f$$

collected neutrons
n/s

Incident neutron
energy window
meV

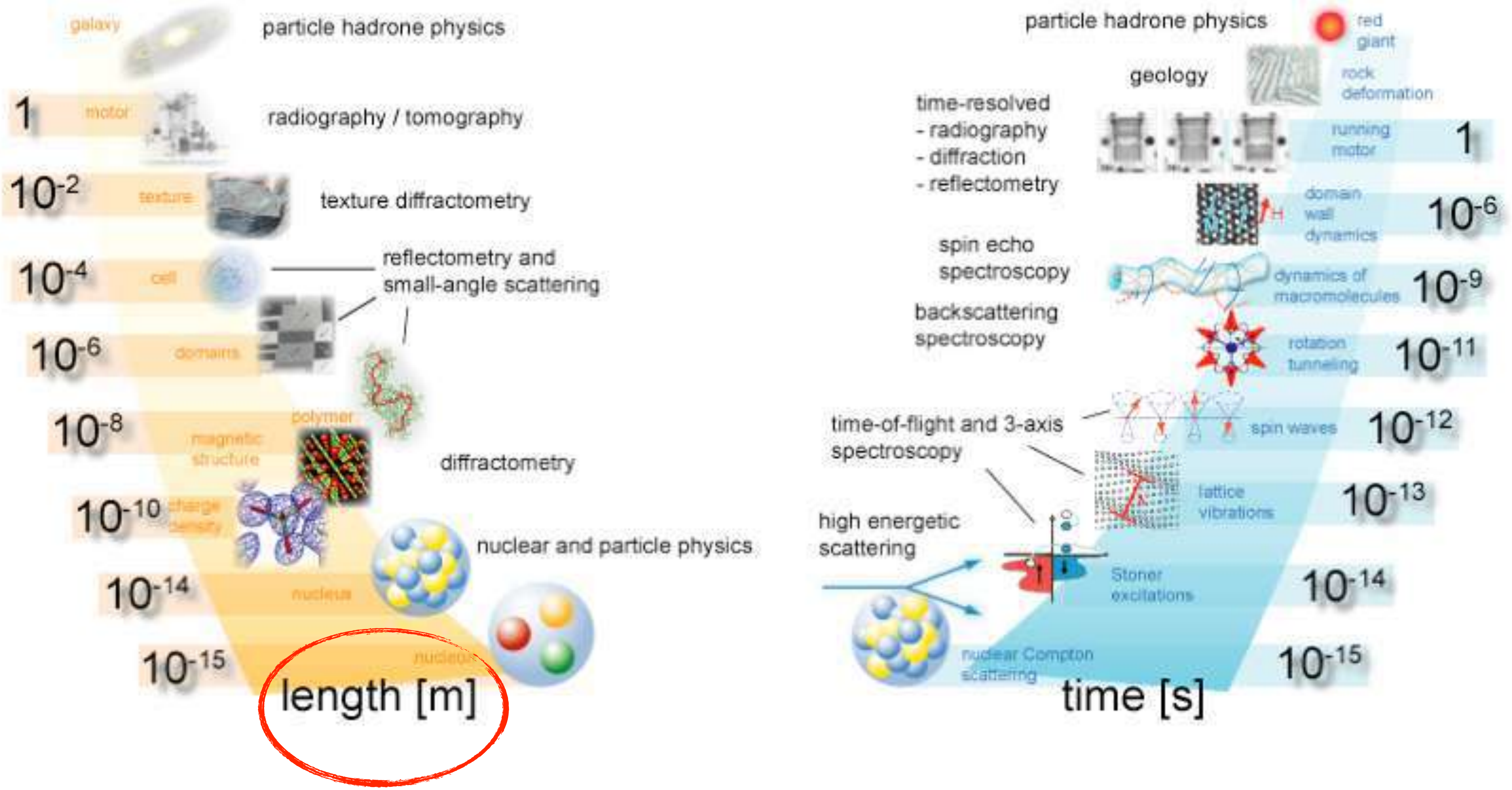
Scattered neutron
energy window
meV

Number of elements
in the scattering volume

neutron flux
n/meV/s/cm^2

collection solid angle

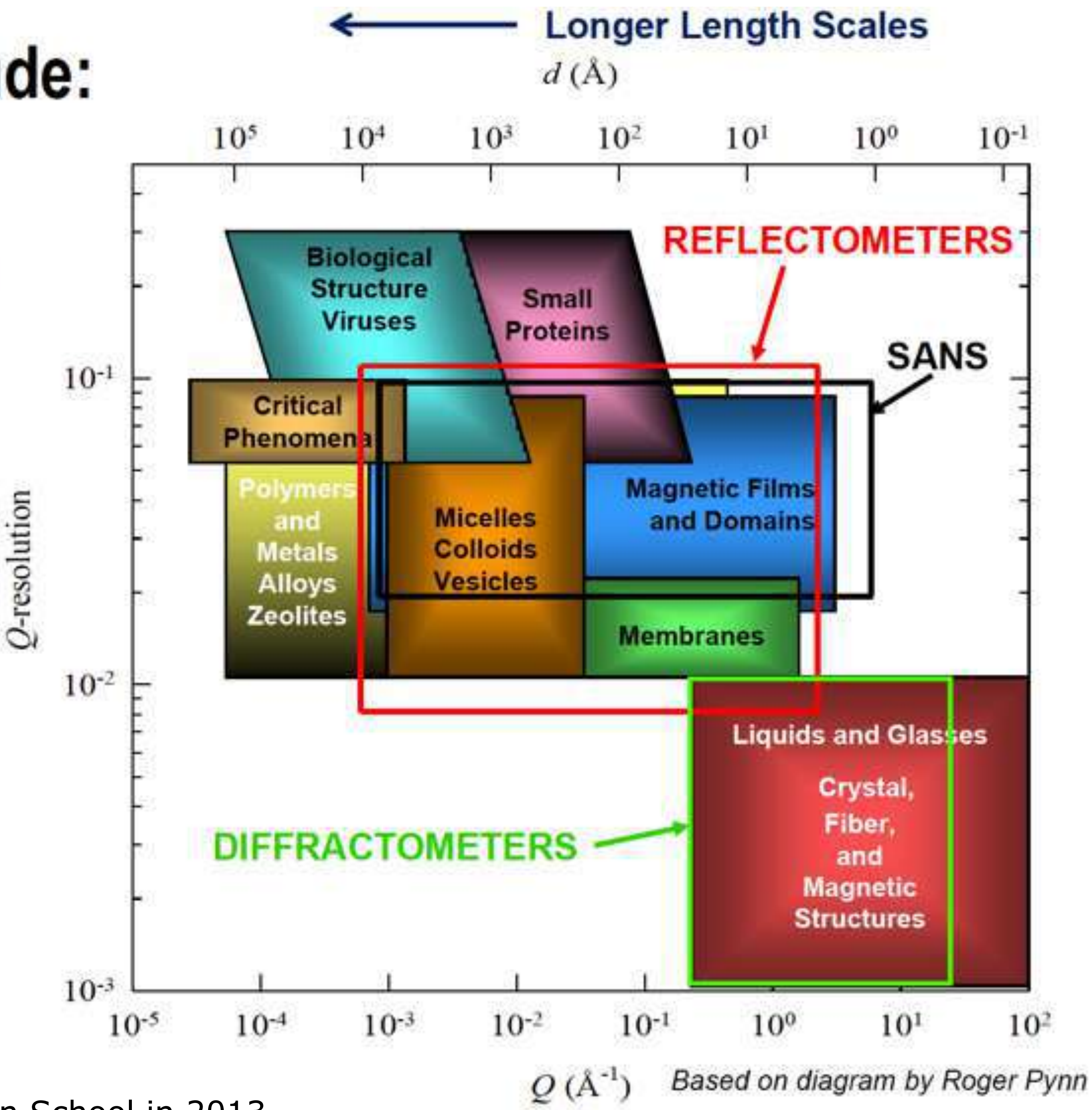
Elastic Neutron Scattering: Applications



Elastic Neutron Scattering instruments

- **Elastic instruments include:**
  - Powder diffraction
  - Single Crystal diffraction
  - SANS (typical)
  - Reflectometry

- **Used to determine the average structure of materials (i.e. how the atoms are arranged)**



Based on diagram by Roger Pynn

Based on L. Robertson presentation at the SNS Neutron School in 2013

Using Neutrons: Single differential cross section

For a "thin" sample, the total integrated scattering is:

$$I_S = \phi N \sigma_S .$$

The measured intensity in a diffraction experiment (on a "thin" sample) is related to the single differential cross section:

$$I_S(E_i, 2\theta) = \phi N \left(\frac{d\sigma}{d\Omega} \right) \Delta\Omega$$

solid angle

The single differential cross section is related to the "structure factor" S(Q) .

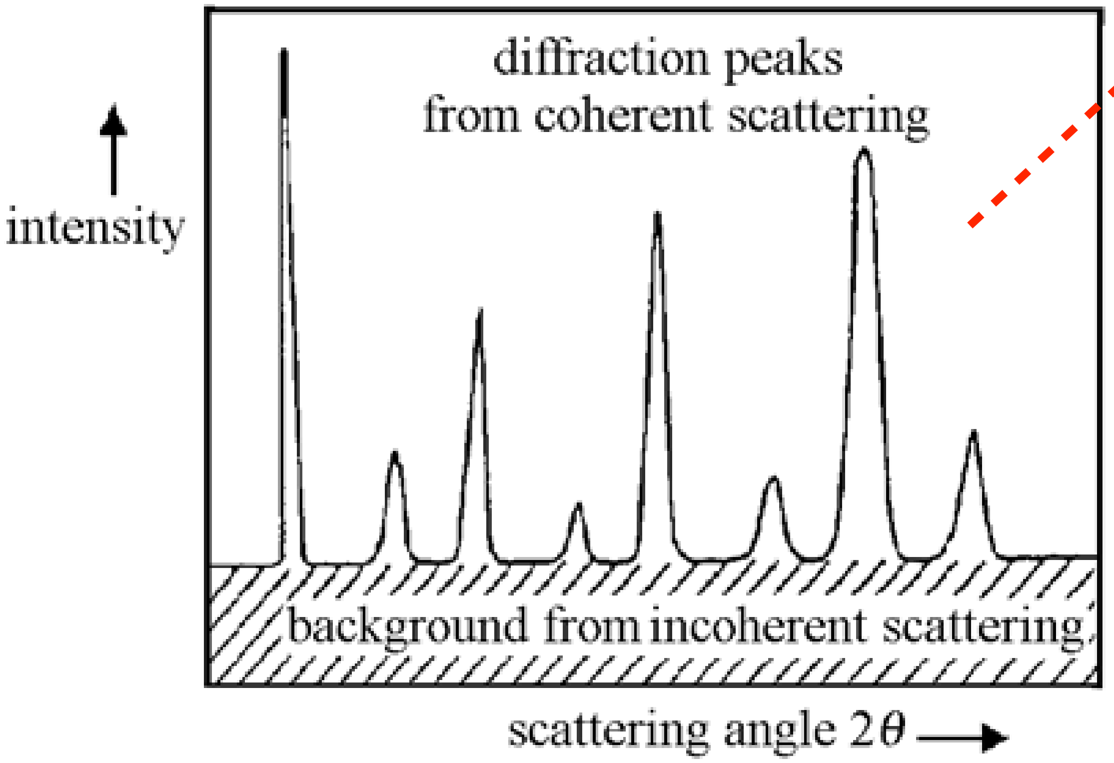
When there is one type of atom we obtain, in the static approximation,

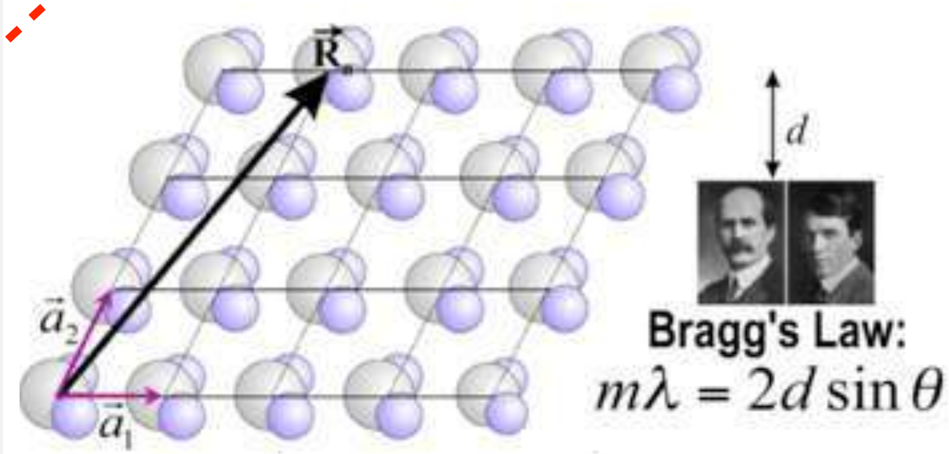
$$\frac{d\sigma}{d\Omega}(E_i, 2\theta) = \frac{\sigma_S}{4\pi} \boxed{S(Q)}$$

ONLY DEPENDS ON THE SAMPLE

No exchange in energy

$$\frac{\partial\sigma}{\partial\Omega} = \sum_{n} \frac{\sigma_{\text{inc},n}}{4\pi} + \left\langle \sum_{m,n} b_{\text{coh},m} b_{\text{coh},n}\, e^{i\mathbf{Q}\cdot(\mathbf{R}_m - \mathbf{R}_n)} \right\rangle$$





Bragg's Law:
$m\lambda = 2d\sin\theta$

Small Angle Neutron Scattering

Blobs !!! Not atoms!!!

“large scale structures” = 1 – 300 nm or more

Mesoporous structures

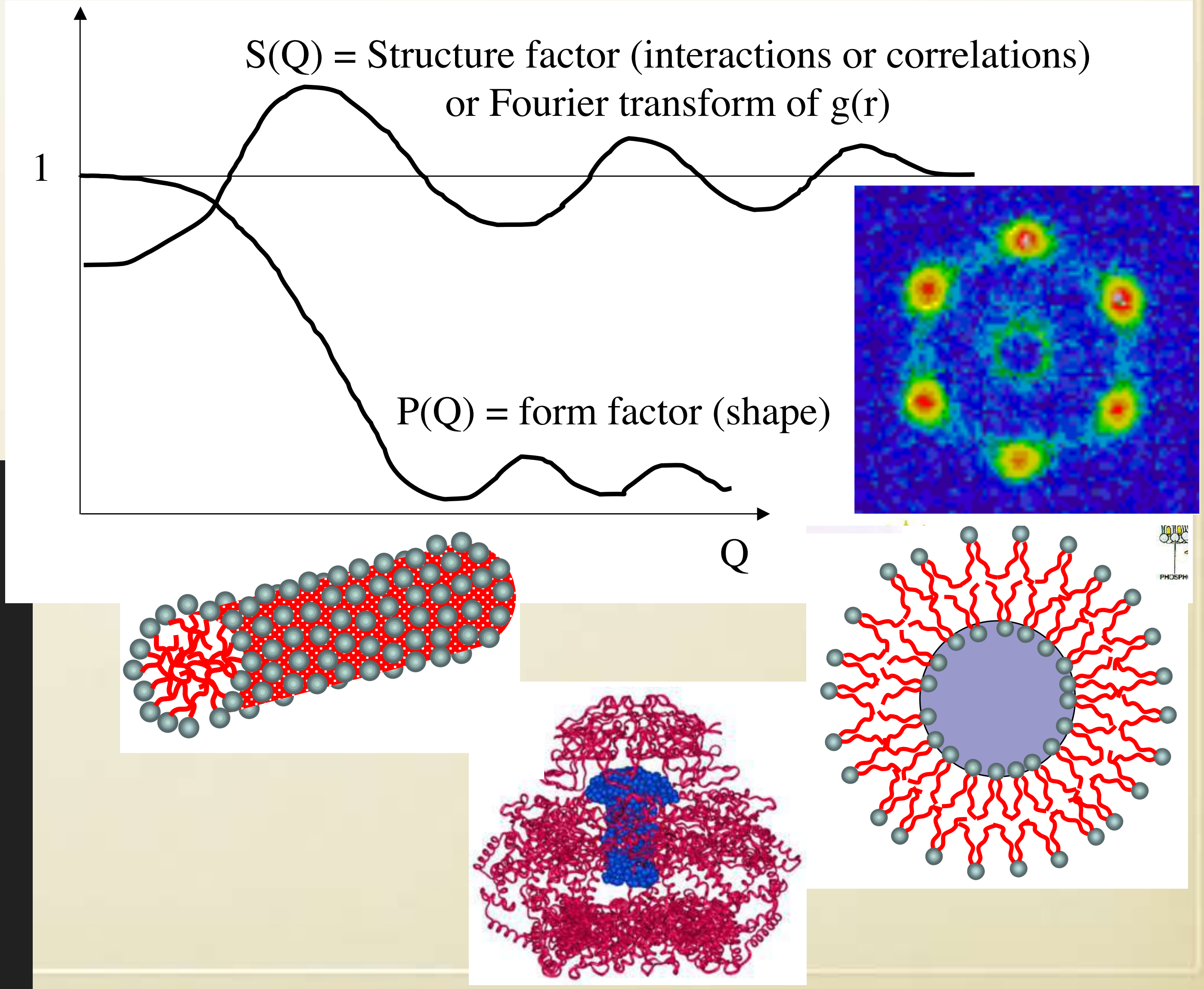
Biological structures (membranes, vesicles, proteins in solution)

Polymers

Colloids and surfactants

Nanoparticles

Voids and Precipitates

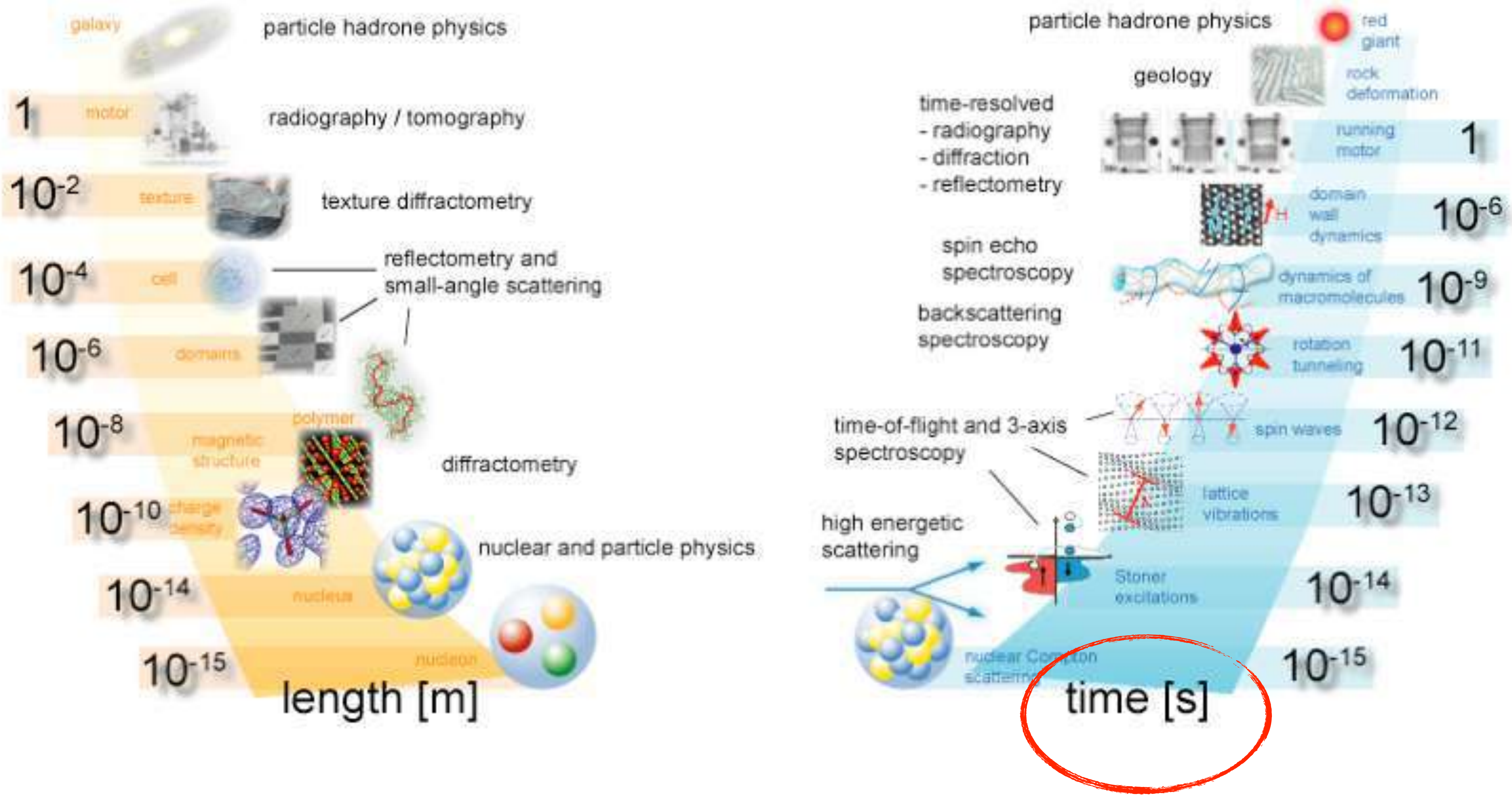


Bragg’s law : $2d\sin\theta=\lambda$

$Q = \frac{4\pi\sin\theta}{\lambda}$, for small θ

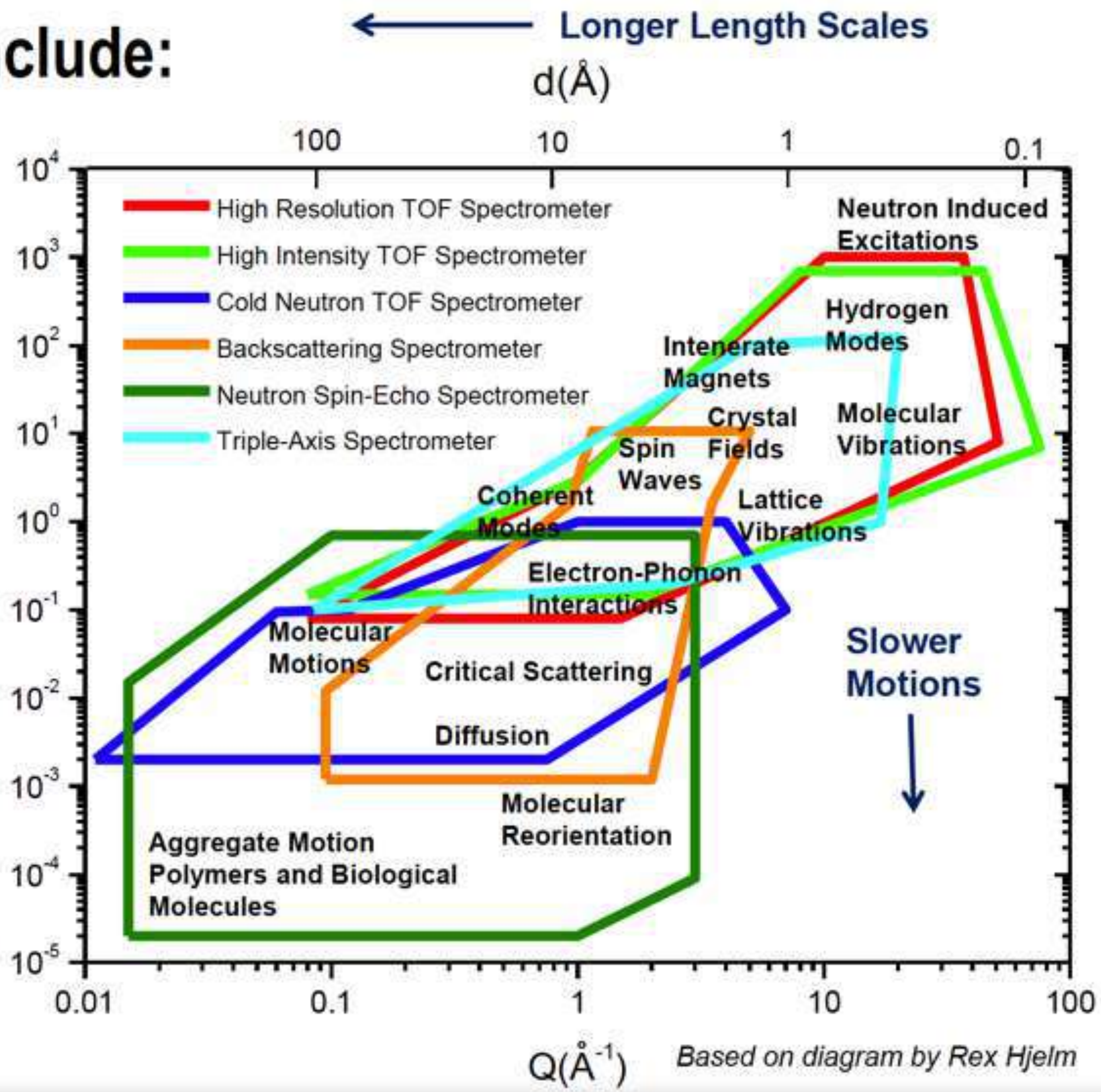
$$d = \frac{\lambda}{2\theta}$$

Inelastic Neutron Scattering: Applications



Inelastic Neutron Scattering

- **Inelastic instruments include:**
  - Direct Geometry TOF Spectrometers
  - Indirect Geometry TOF Spectrometers
  - Triple-Axis Spectrometers
  - Backscattering Spectrometers
  - Neutron Spin-Echo Spectrometers
- **Used to study dynamics such as phonons, magnons, and diffusion (i.e. what the atoms are doing)**



Based on diagram by Rex Hjelm

Based on L. Robertson presentation at the SNS Neutron School in 2013

Double differential cross section

The measured intensity in a spectroscopy experiment is related to the double differential cross section:

$$I_S\left(E_i, 2\theta, E_f\right) = \phi N \left(\frac{d^2\sigma}{d\Omega dE_f}\right)\Delta\Omega\Delta E_f .$$

energy window

The double differential cross section is related to the "scattering function"

$$S\left(Q,\omega\right)$$

When there is one type of atom,

$$\frac{d^2\sigma}{d\Omega dE_f}\left(E_i, 2\theta, E_f\right) = \frac{\sigma}{4\pi\hbar}\frac{k_f}{k_i}S\left(Q,\omega\right),$$

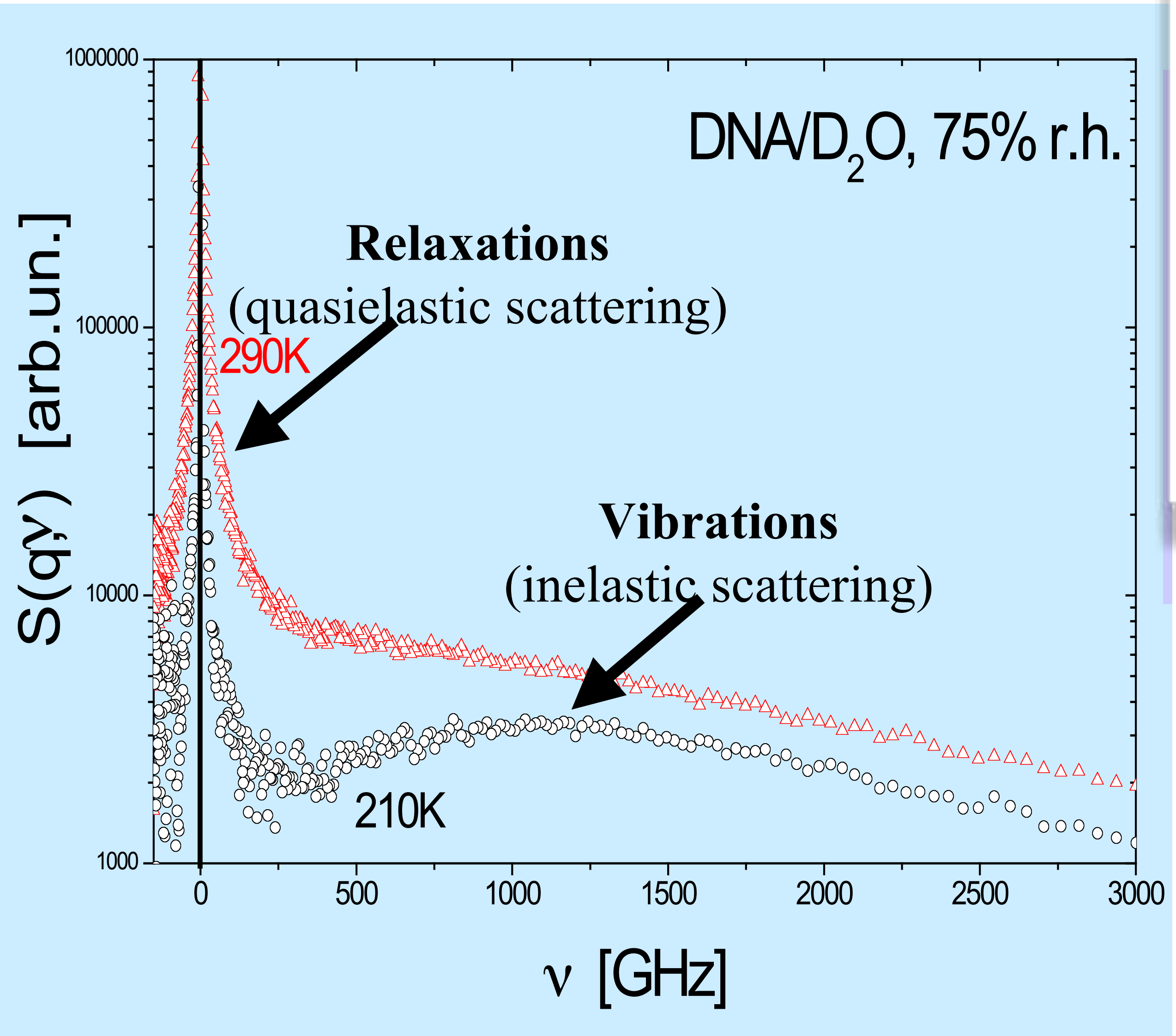
ONLY DEPENDS ON THE SAMPLE

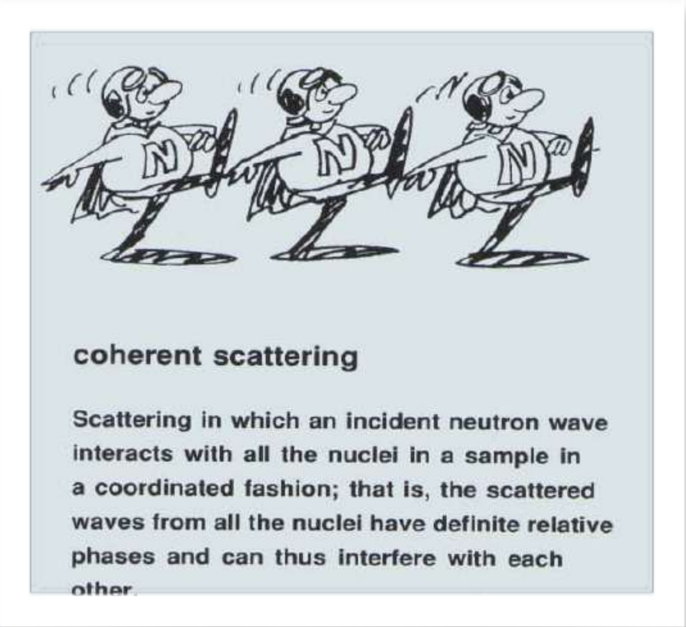
if there is an energy exchange

$$\frac{d^2\sigma}{d\Omega\, d\varepsilon_f} = \frac{\sigma_{coh}}{4\pi\hbar}\frac{k_f}{k_i} S(Q,\omega) + \frac{\sigma_{inc}}{4\pi\hbar}\frac{k_f}{k_i} S_S(Q,\omega)$$

collective motion
(phonon)

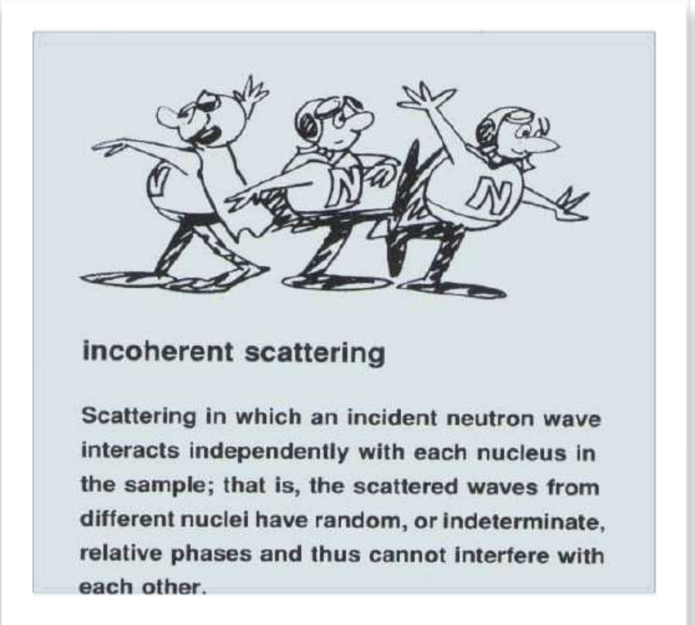
single particle
(diffusion)





coherent scattering

Scattering in which an incident neutron wave interacts with all the nuclei in a sample in a coordinated fashion; that is, the scattered waves from all the nuclei have definite relative phases and can thus interfere with each other.



incoherent scattering

Scattering in which an incident neutron wave interacts independently with each nucleus in the sample; that is, the scattered waves from different nuclei have random, or indeterminate, relative phases and thus cannot interfere with each other.

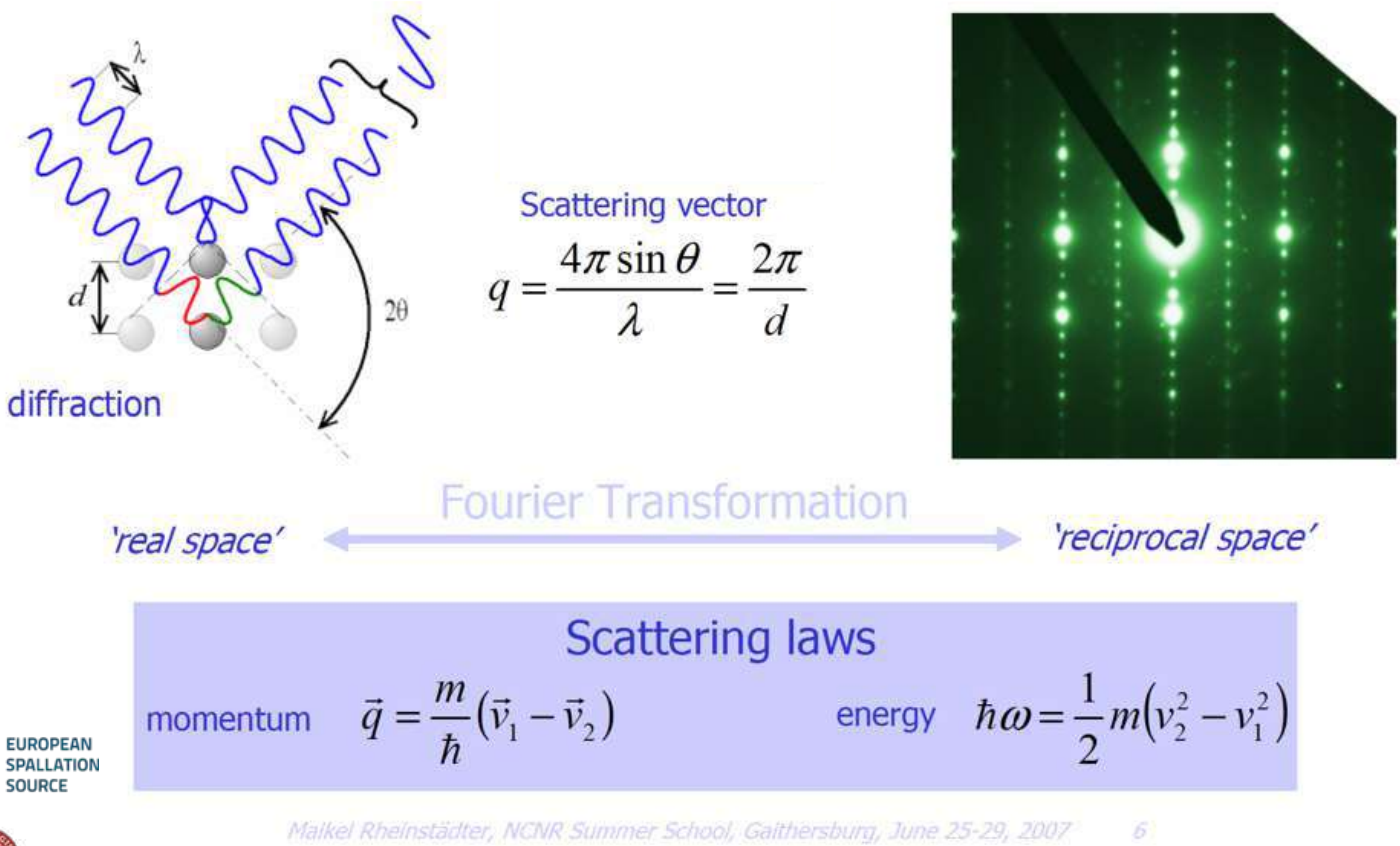
- Quasielastic scattering (a relaxation-like contribution) usually dominates the spectra at higher T.
- It is traditionally approximated by a sum of a few Lorentzians. This approximation assumes a few single exponential relaxation processes.


COFFEE
BREAK

All you need to understand

(or… the key questions you need to answer to be an ‘expert level 1’ in neutron scattering

Scattering Laws



diffraction

Scattering vector

$$q = \frac{4\pi \sin\theta}{\lambda} = \frac{2\pi}{d}$$

Fourier Transformation

'real space' ⟷ *'reciprocal space'*

Scattering laws

momentum $\vec{q} = \frac{m}{\hbar}(\vec{v}_1 - \vec{v}_2)$

energy $\hbar\omega = \frac{1}{2}m(v_2^2 - v_1^2)$

Maikel Rheinstädter, NCNR Summer School, Gaithersburg, June 25-29, 2007 6

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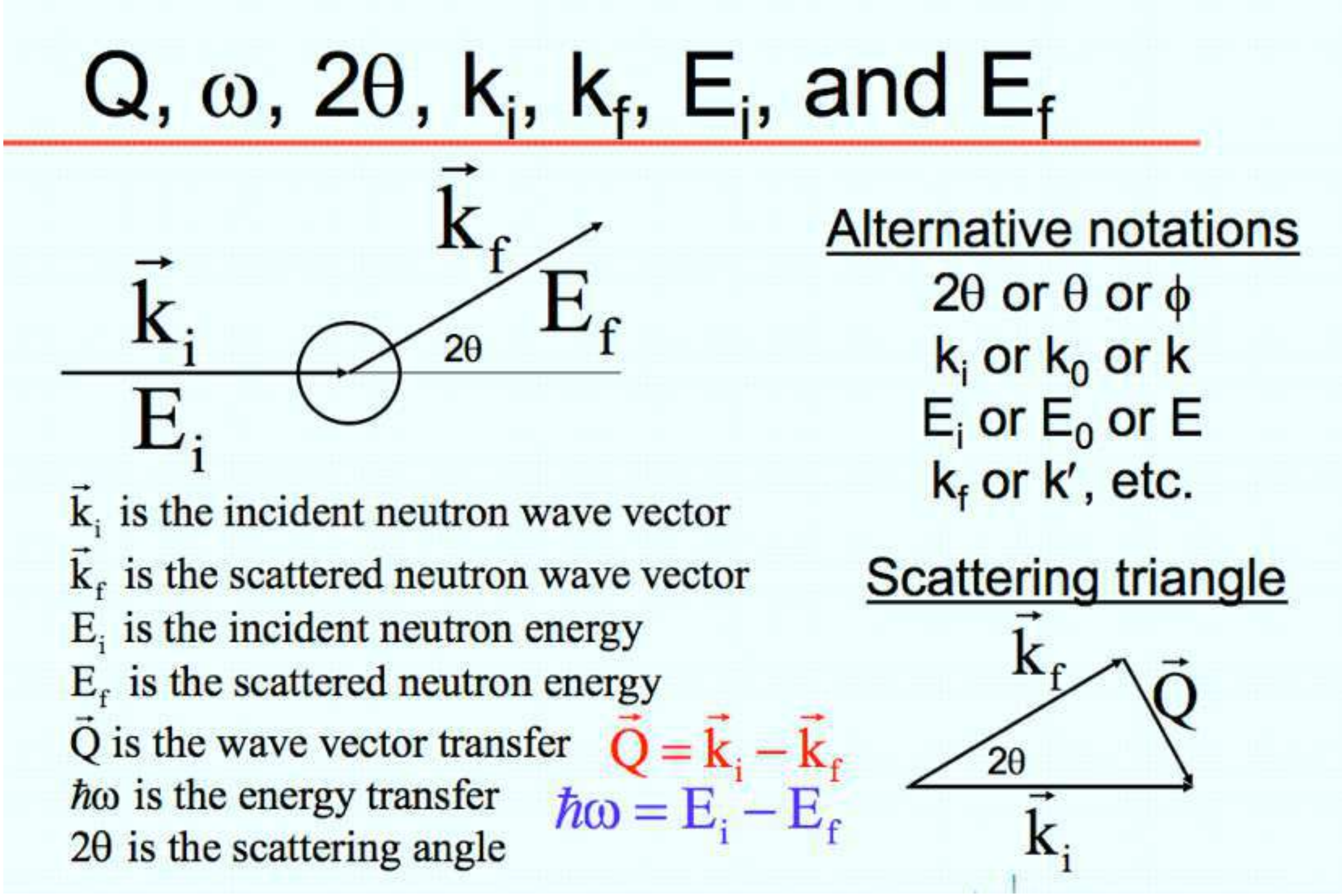
Neutron and X-rays variables



Q, ω, 2θ, k_i, k_f, E_i, and E_f

$\vec{k}_i$ is the incident neutron wave vector

$\vec{k}_f$ is the scattered neutron wave vector

E_i is the incident neutron energy

E_f is the scattered neutron energy

$\vec{Q}$ is the wave vector transfer $\vec{Q} = \vec{k}_i - \vec{k}_f$

$\hbar\omega$ is the energy transfer $\hbar\omega = E_i - E_f$

2θ is the scattering angle

Alternative notations

2θ or θ or ϕ

k_i or k_0 or k

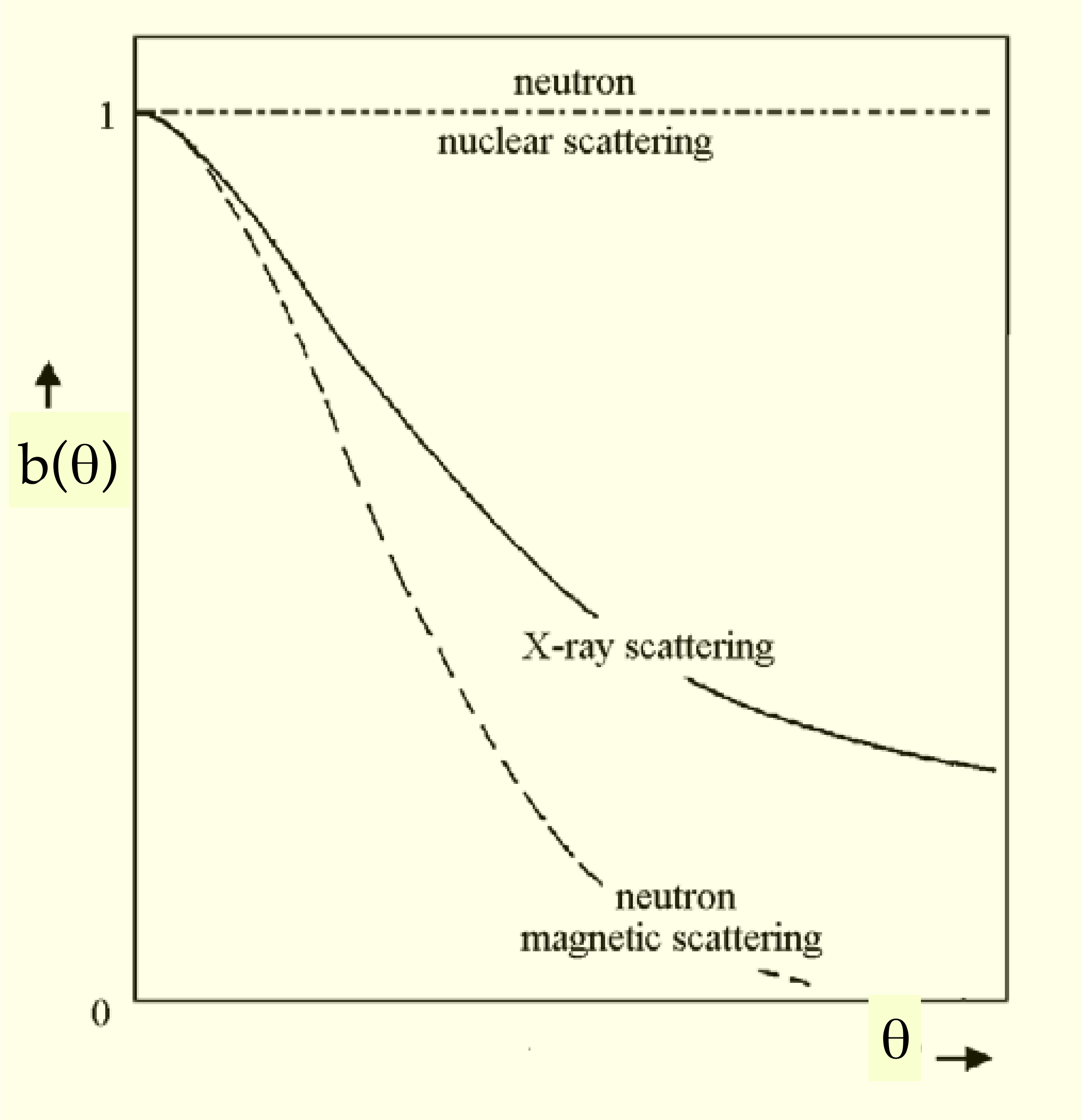
E_i or E_0 or E

k_f or k′, etc.

Scattering triangle

… (or in other words: scattering length)…

$$\sigma = 4\pi b^2$$



- ☑ X-rays scatter from the electrons around nuclei. Therefore they have a form factor & the scattering strength depends on the scattering angle.
- ☑ Neutrons scatter from the nucleus itself, a much smaller object and there is no form factor.
- ☑ For magnetic neutron scattering the neutron interacts with the outer unpaired electrons and this scattering also has a form factor.

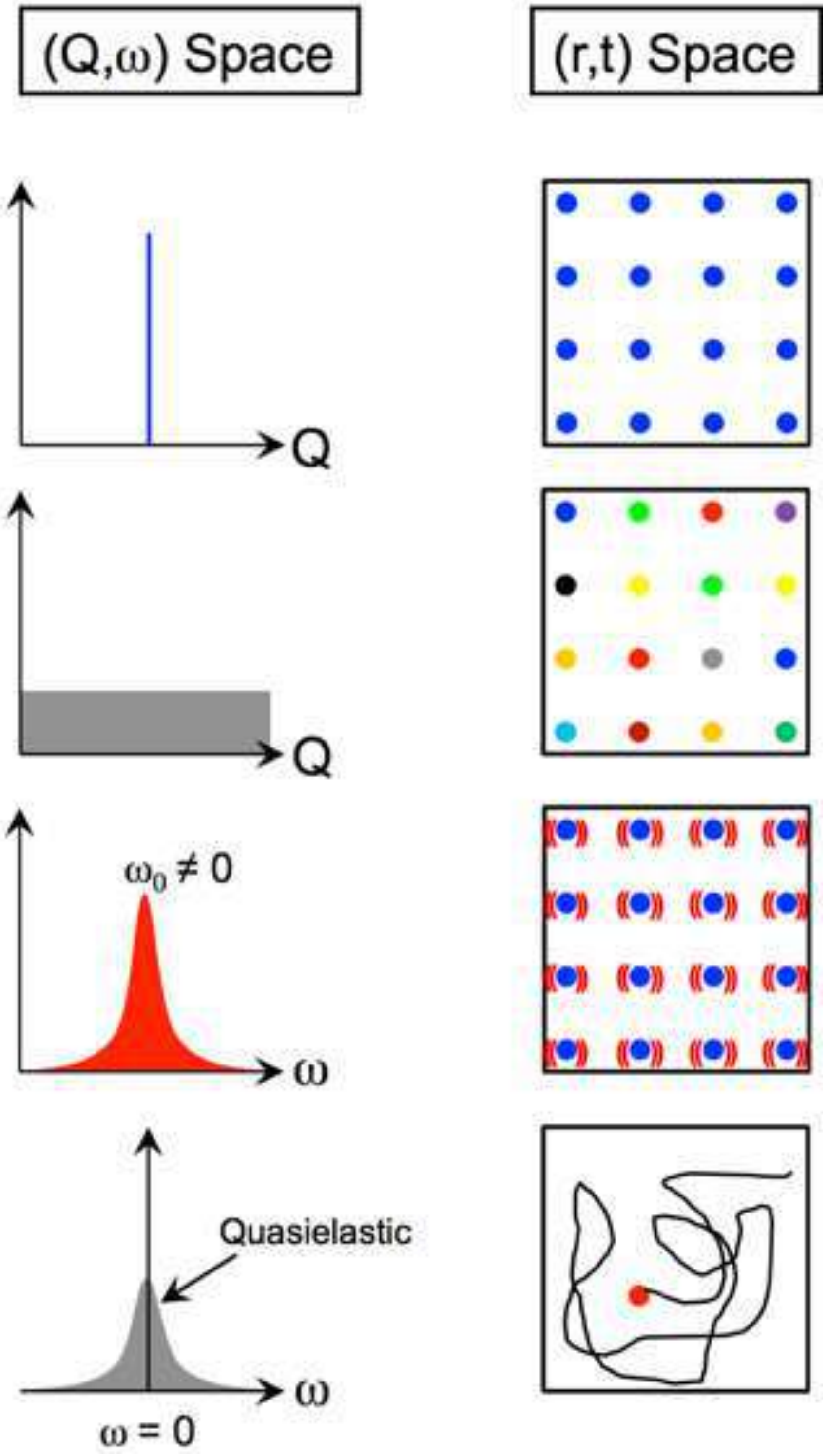
Summary of cross sections:

$$\left.\frac{d\sigma}{d\Omega}\right|_{coh} = \frac{\sigma_{coh}}{4\pi} S(Q)$$

$$\left.\frac{d\sigma}{d\Omega}\right|_{inc} = \frac{\sigma_{inc}}{4\pi}$$

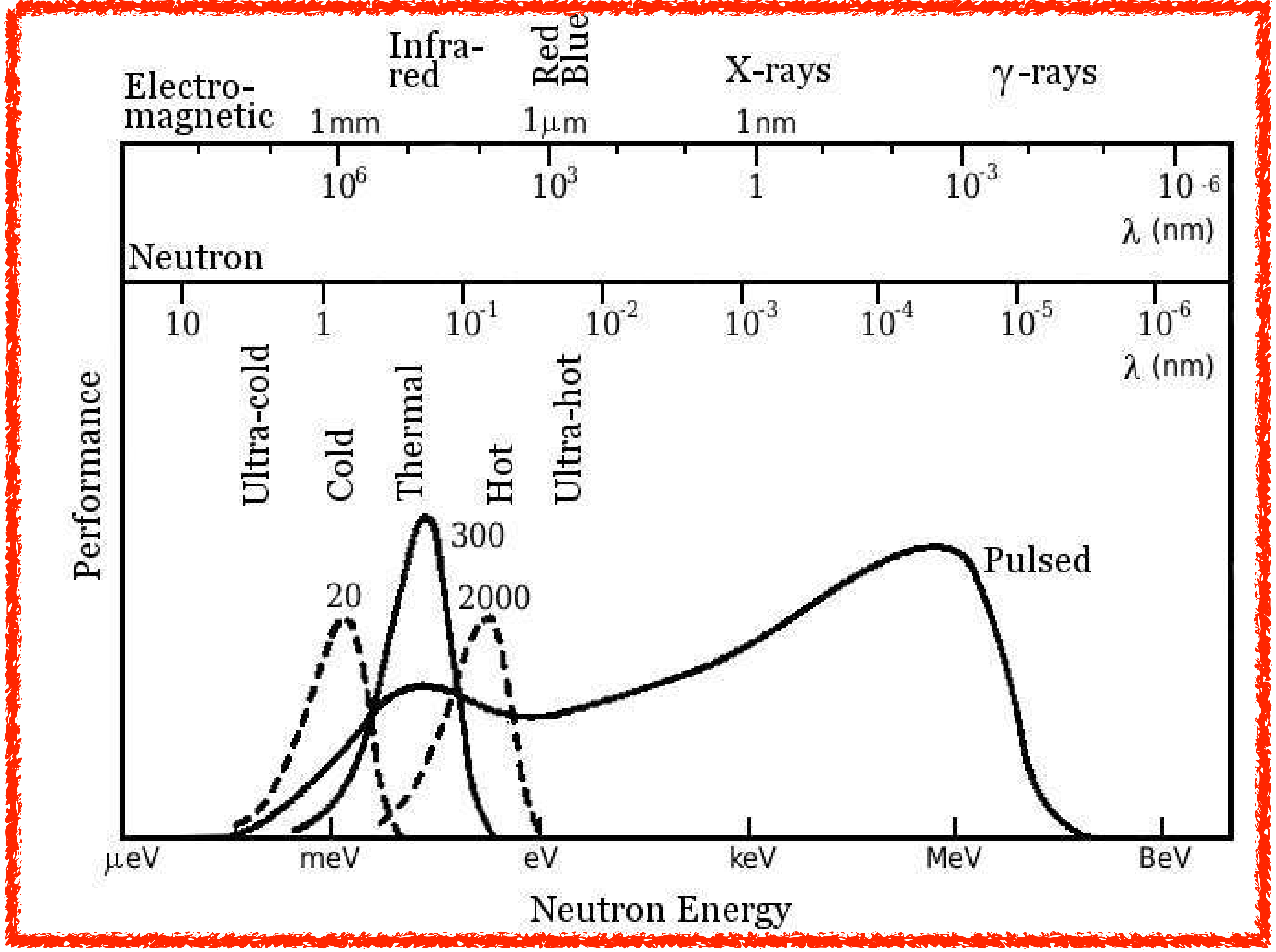
$$\left.\frac{d^2\sigma}{d\Omega dE_f}\right|_{coh} = \frac{k_f}{k_i} \frac{\sigma_{coh}}{4\pi} S_{coh}(Q,\omega)$$

$$\left.\frac{d^2\sigma}{d\Omega dE_f}\right|_{inc} = \frac{k_f}{k_i} \frac{\sigma_{inc}}{4\pi} S_{inc}(Q,\omega)$$



by Peter M. Gehring

… and the complementary to other techniques…



)

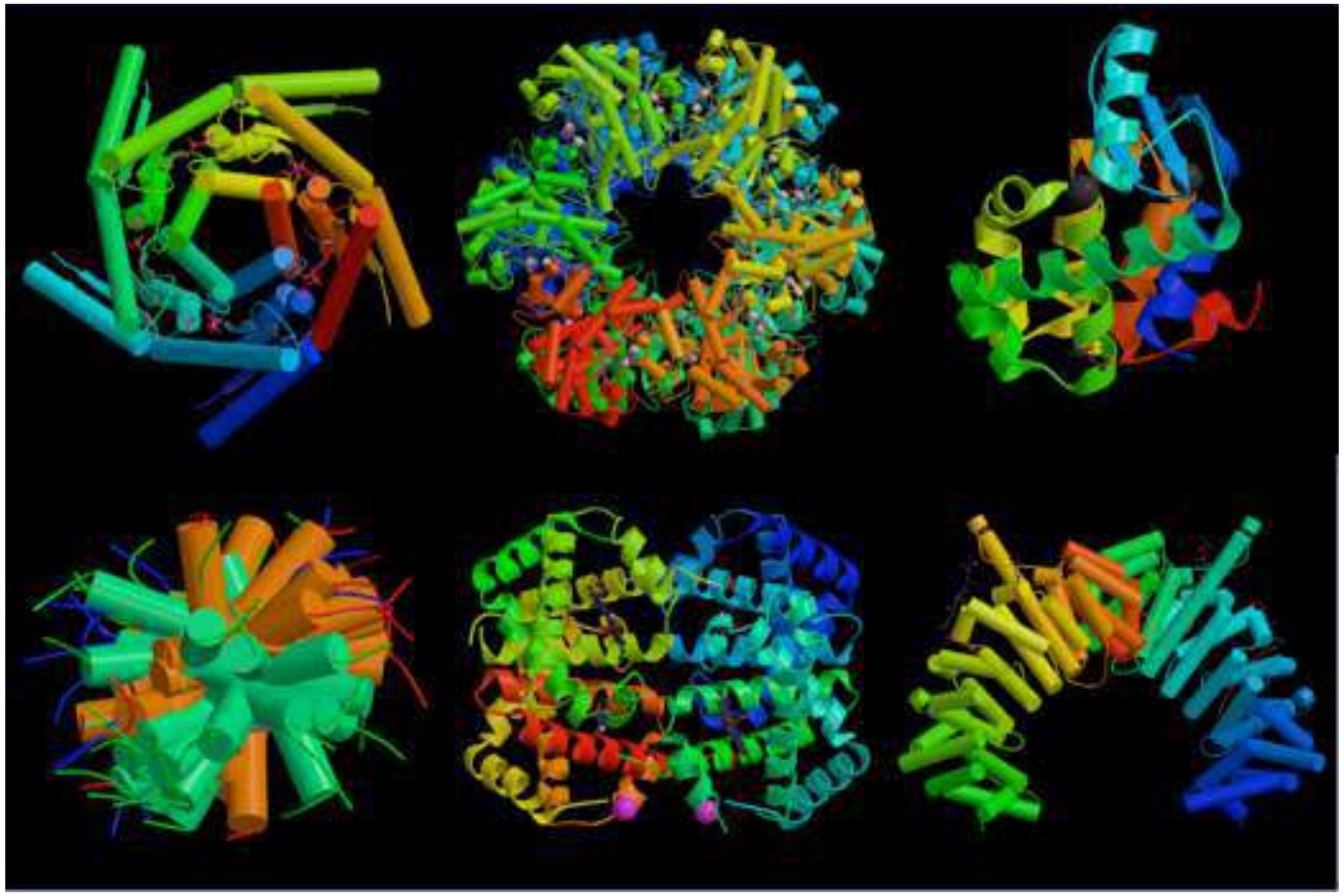
by D.N. Argyriou

Water mobility in concrete

- Largest volume of manufactured material produced on Earth: **1 ton for every person.**
- Over **1 trillion dollars** is invested in concrete production...
- That is about **1000 ESSs** per year! Compare this with…
- Worldwide **semiconductor industry: 213 billion U$ /year** and the **bank bailouts in the US: 2.7 - 3.6 trillion U$**
- The **cement industry produces 5-7% of global CO_2** emissions, which is linked to climate change!!!

Structure of cement… deciphering the puzzle...

After the war, Bernal resumed his professorial duties at Birkbeck, setting up the Biomolecular Research Laboratory in 1948. As well as groups working on organic crystals and proteins, he had others working on computers, the structure of cements (buildings and building materials were a life-long interest), and the structure of water. Rosalind Franklin later joined him to start work on virus structure, which she continued with Aaron Klug.



Use of Bagasse Ash in Concrete

- Compressive Strength[6]

Cement Replacement (%)	3 Day Strength (MPa)	7 Day Strength (MPa)	28 Day Strength (MPa)
0	20	27	36
5	22	30	42
10	27	35	43
15	28	35	42
20	27	35	40
25	25	32	35
30	20	25	32

[6] Amin, Noor-ul. "Use of Bagasse Ash in Concrete and its Impact on the Strength and Chloride Resistivity."*Journal of Materials in Civil Engineering*. (2010): n. page. Web. 1 Jun. 2012. <http://scitation.aip.org/getpdf/servlet/GetPDFServlet?filetype=pdf&id=JMCEXX000001000001000194000001&idtype=cvips&doi=10.1061/(ASCE)MT.1943-5533.0000227&prog=normal>.

Neutrons can help!

Local

Collapsed motorway bridge affecting traffic

Minor miracle that no-one was hurt

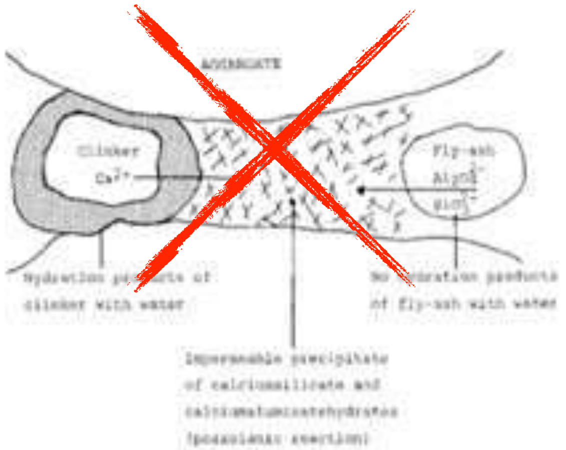
The police said they still werent sure why the bridge collapsed, but that a team of engineers were investigating (Photo: Scanpix)

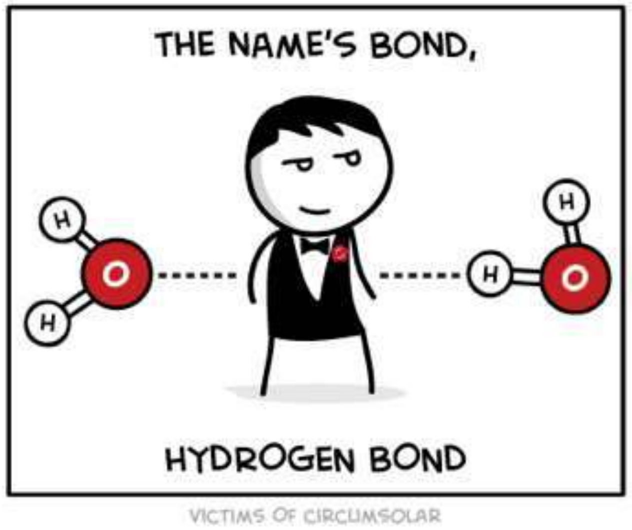
September 29, 2014
09:58

The collapse of a bridge onto the Copenhagen-Helsingør motorway has suspended the movement of traffic along the road in north Zealand.

18. SEP. 2013 KL. 06:30

Sukkerrør kan bane vejen for 'grøn' og stærk cement

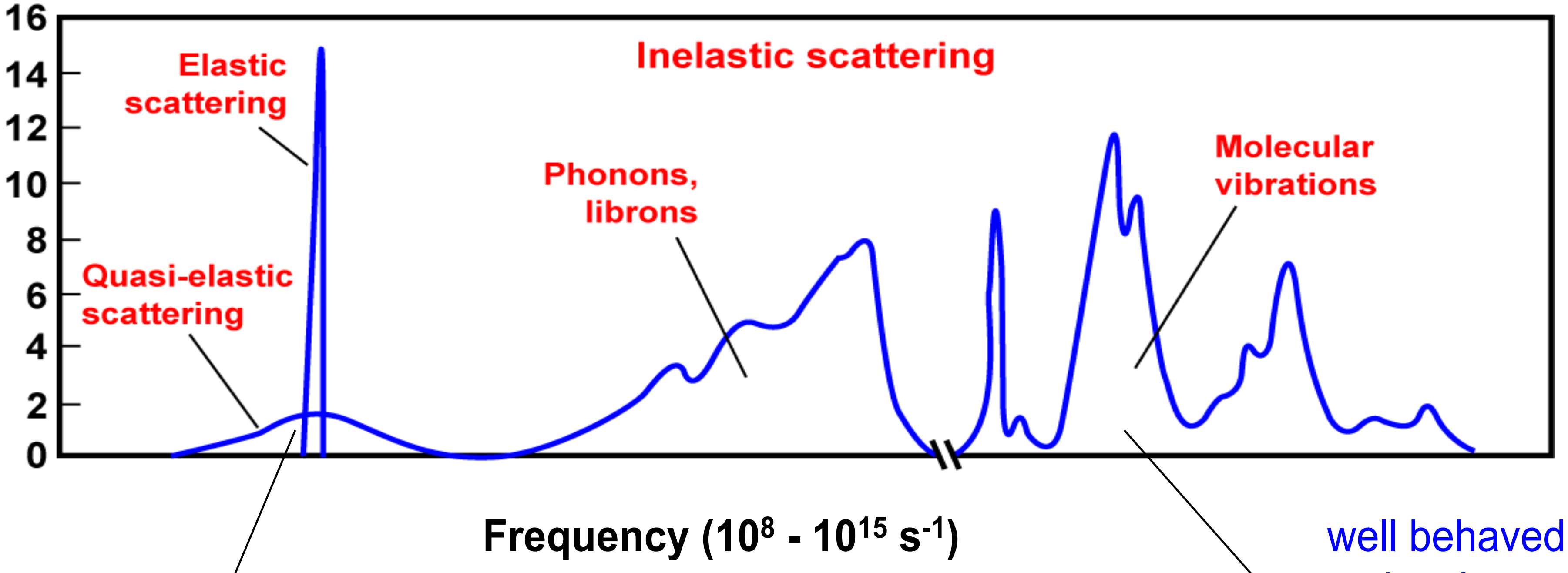




Jacobsen, J. et al.
Sci. Rep. **3** (2013) 2667.

"Generic" Incoherent Inelastic Neutron Scattering

(Incoherent spectrum dominated by motions involving H's)



elastic: structural information

quasielastic scattering:

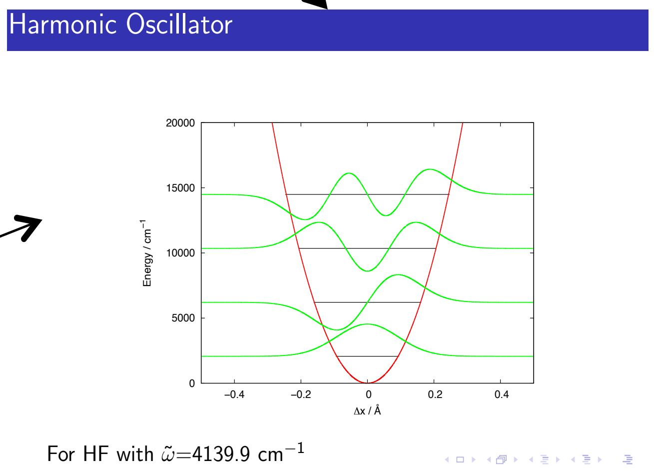
diffusive motions (rotational, translational, transport)

external modes:

whole-body librations, translations

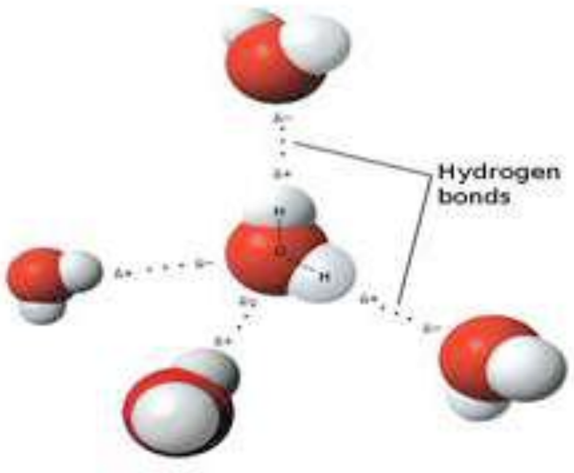
(internal) molecular vibrations:

well behaved molecules


Harmonic Oscillator

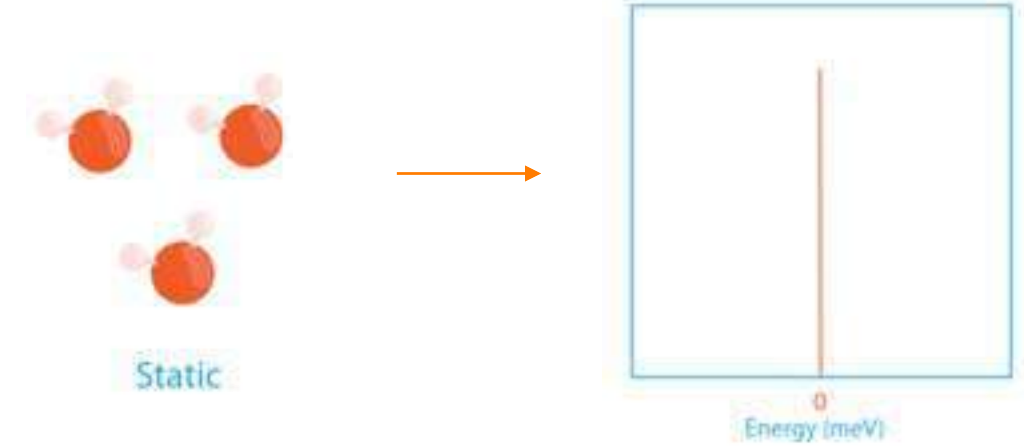
For HF with $\tilde{\omega}$=4139.9 cm^{-1}

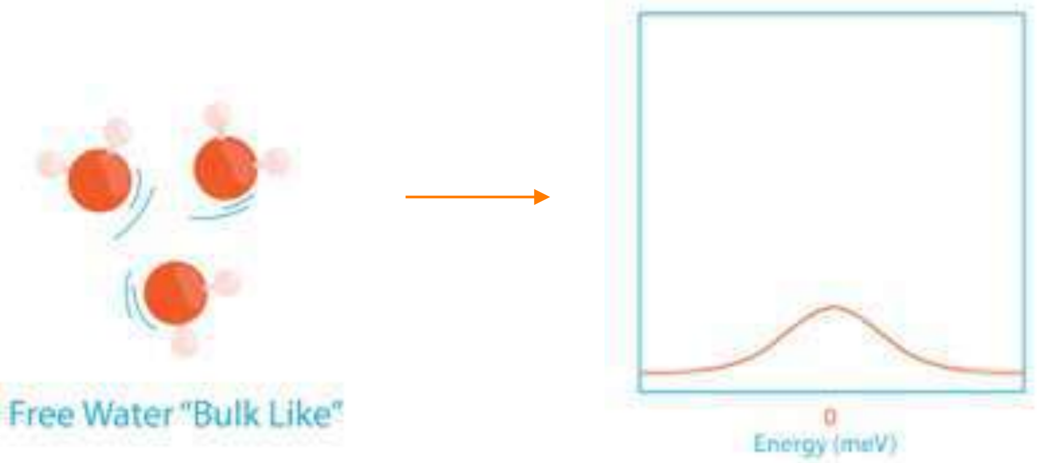
Badly behaved water molecules

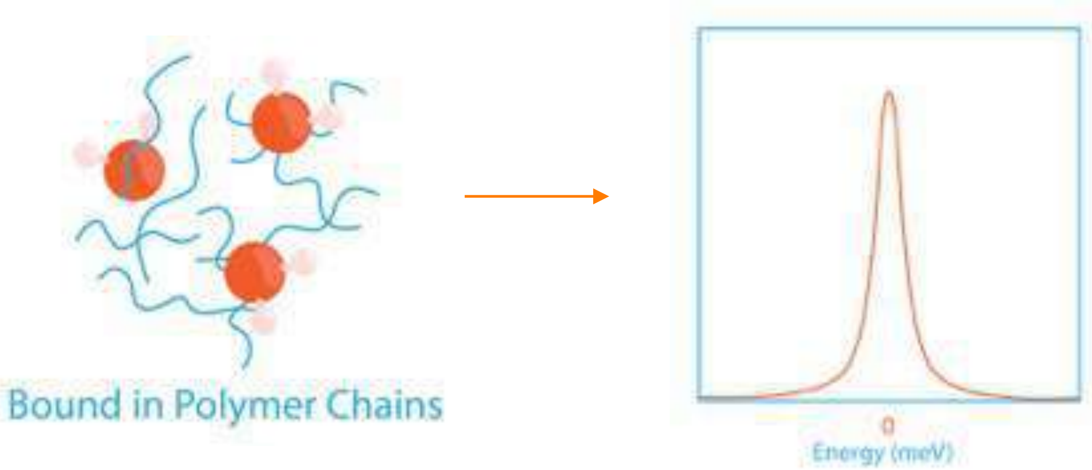


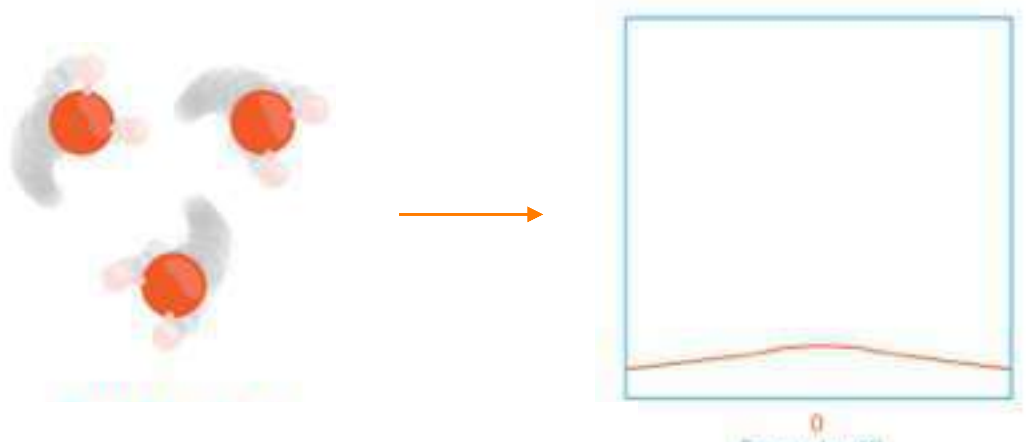
some of the time

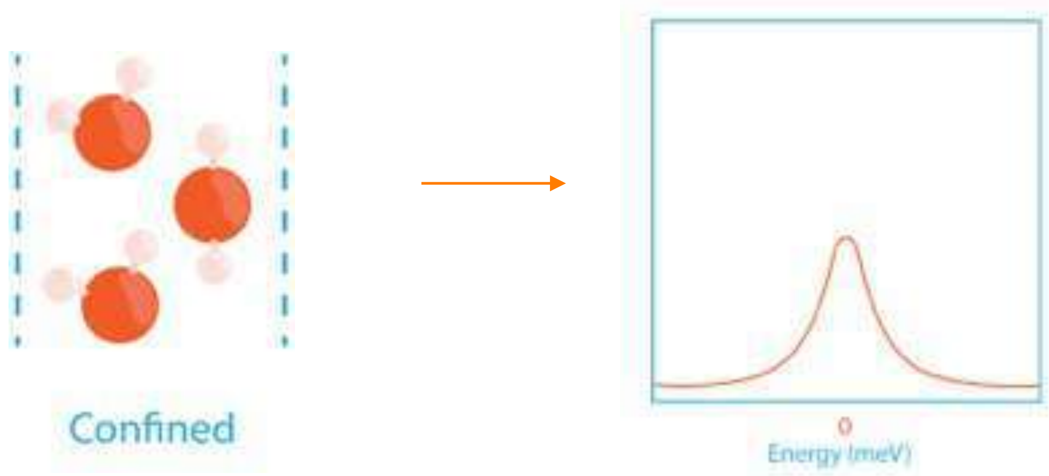
Understanding dynamics to improve structure

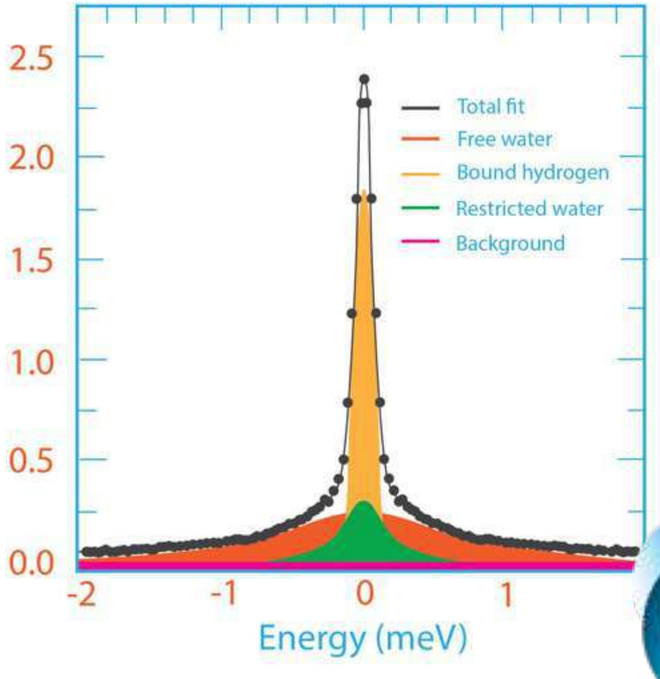








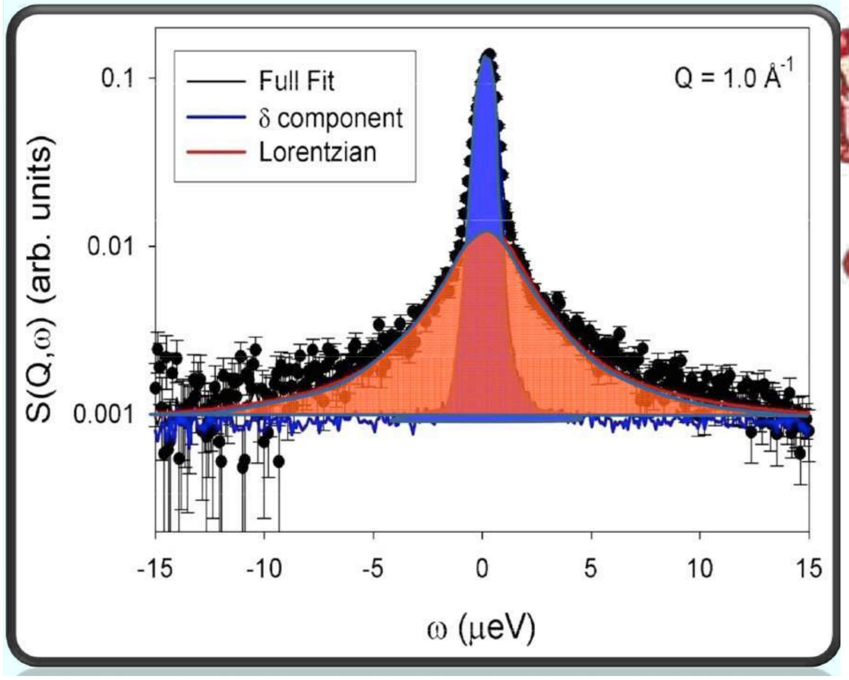


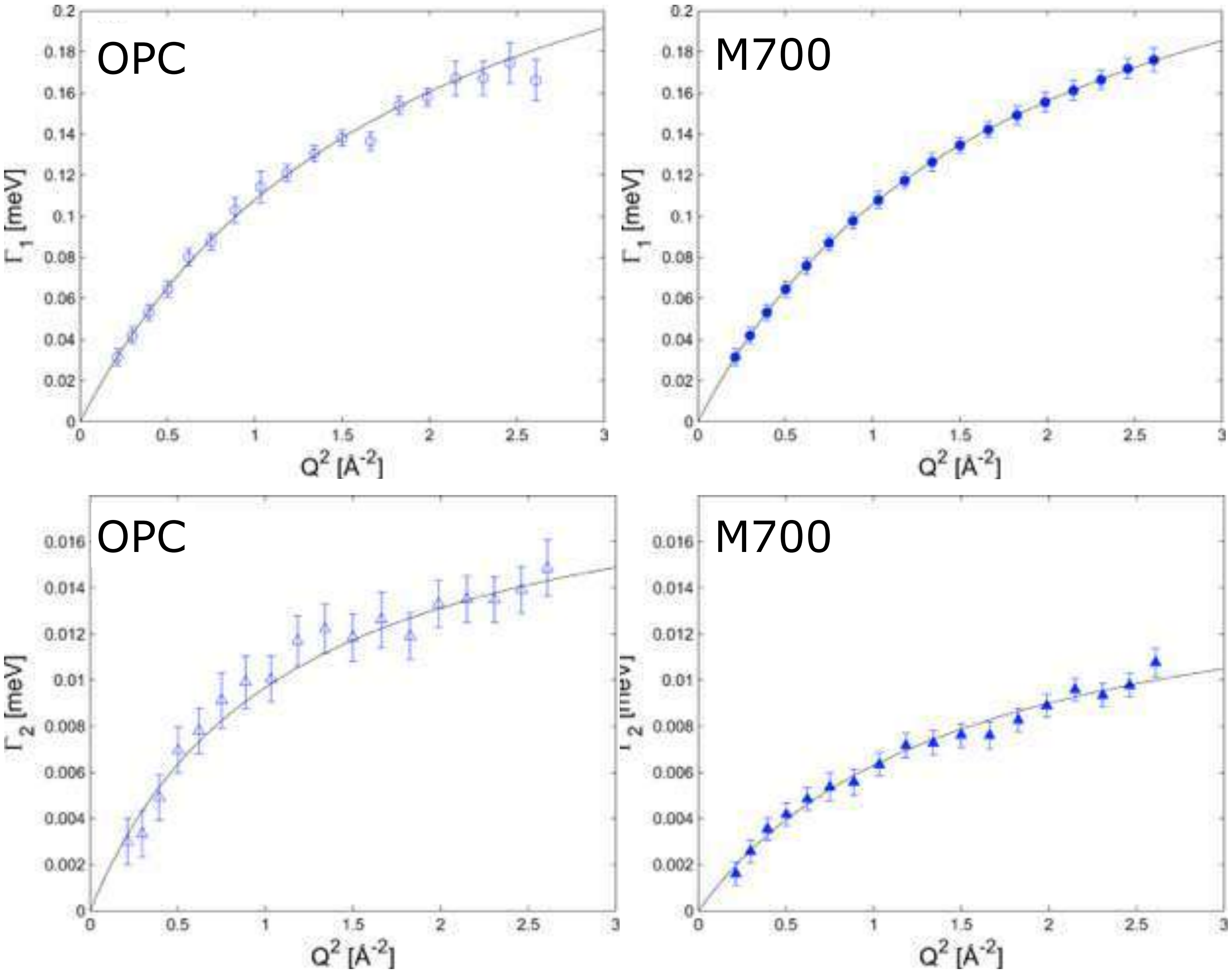


EUROPEAN
SPALLATION
SOURCE

by Marcella C. Berg

Why are greener cements better?





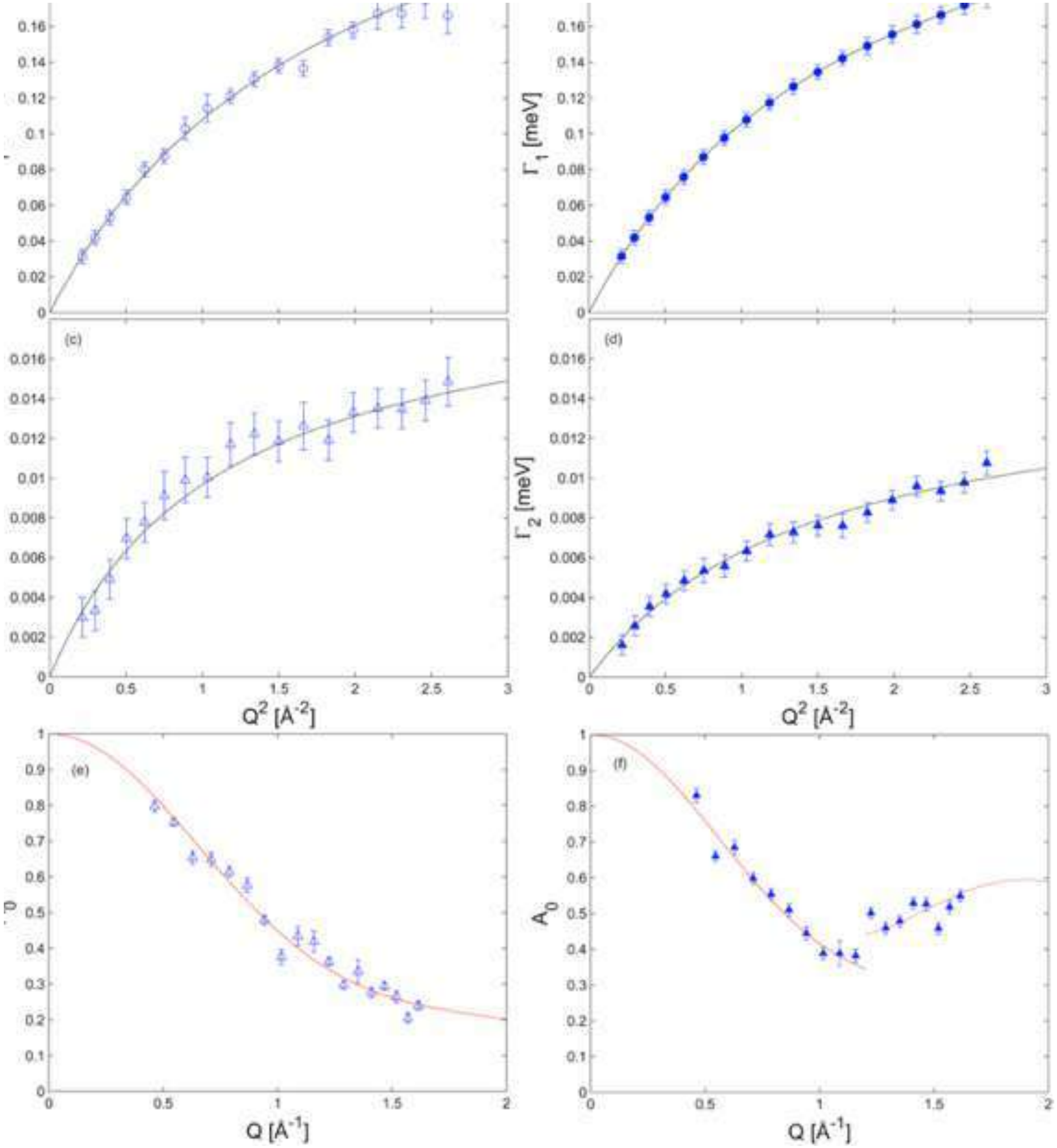
	τ_0 (ps)	D_t (10^{-9} m^2/s)
Bulk Water	1.57±0.12	2.49±0.07
OPC Γ_1	2.1±0.3	2.5±0.4
OPC Γ_2	32.3±0.5	0.28±0.04
M700 Γ_1	2.21±0.02	2.49±0.02
M700 Γ_2	41.9±0.3	0.16±0.01

Both samples contain bulk-like water

The glass-like water is more restricted in the M700 cement.

www.nature.com/scientificreports/

New hydrogen bonds network



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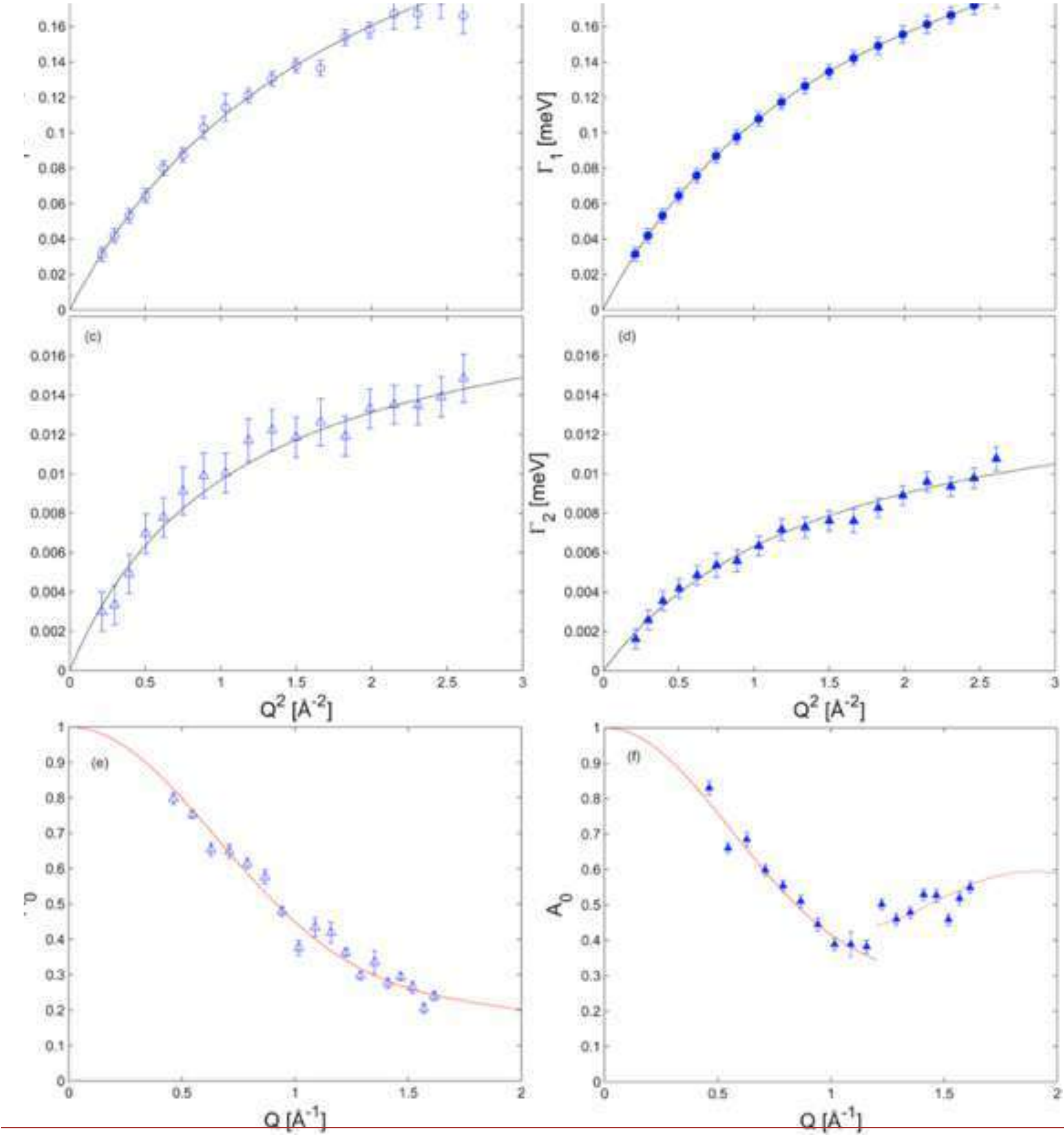

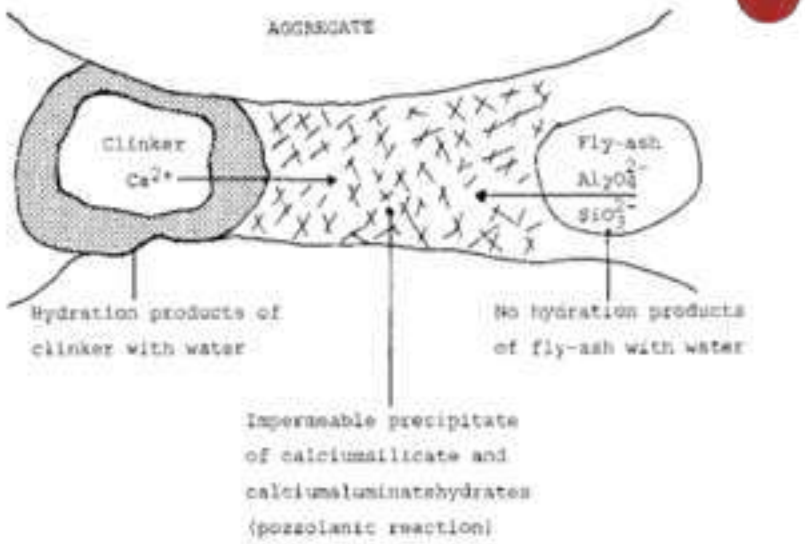

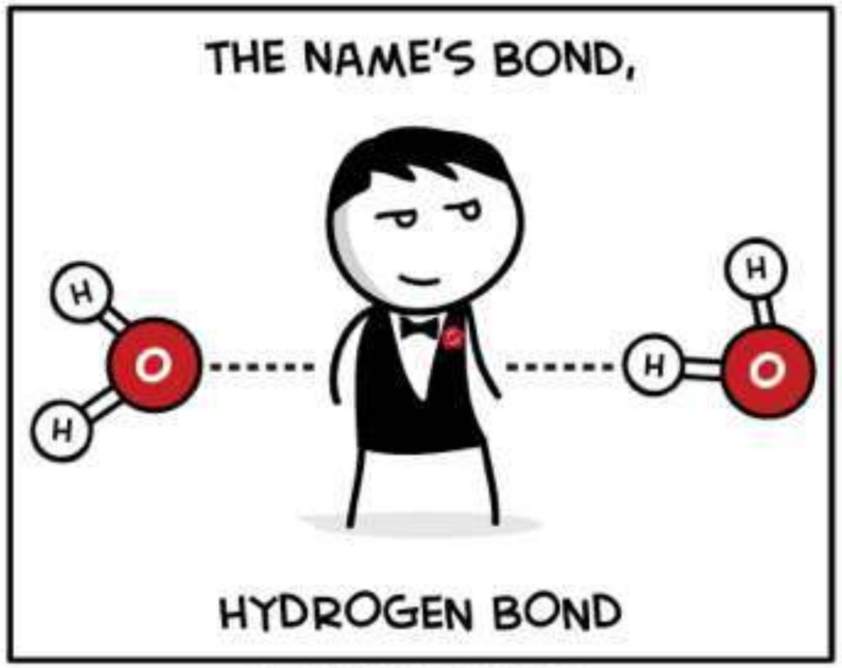

VICTIMS OF CIRCUMSOLAR

Jacobsen, J. et al.. Sci. Rep. **3** (2013) 2667.

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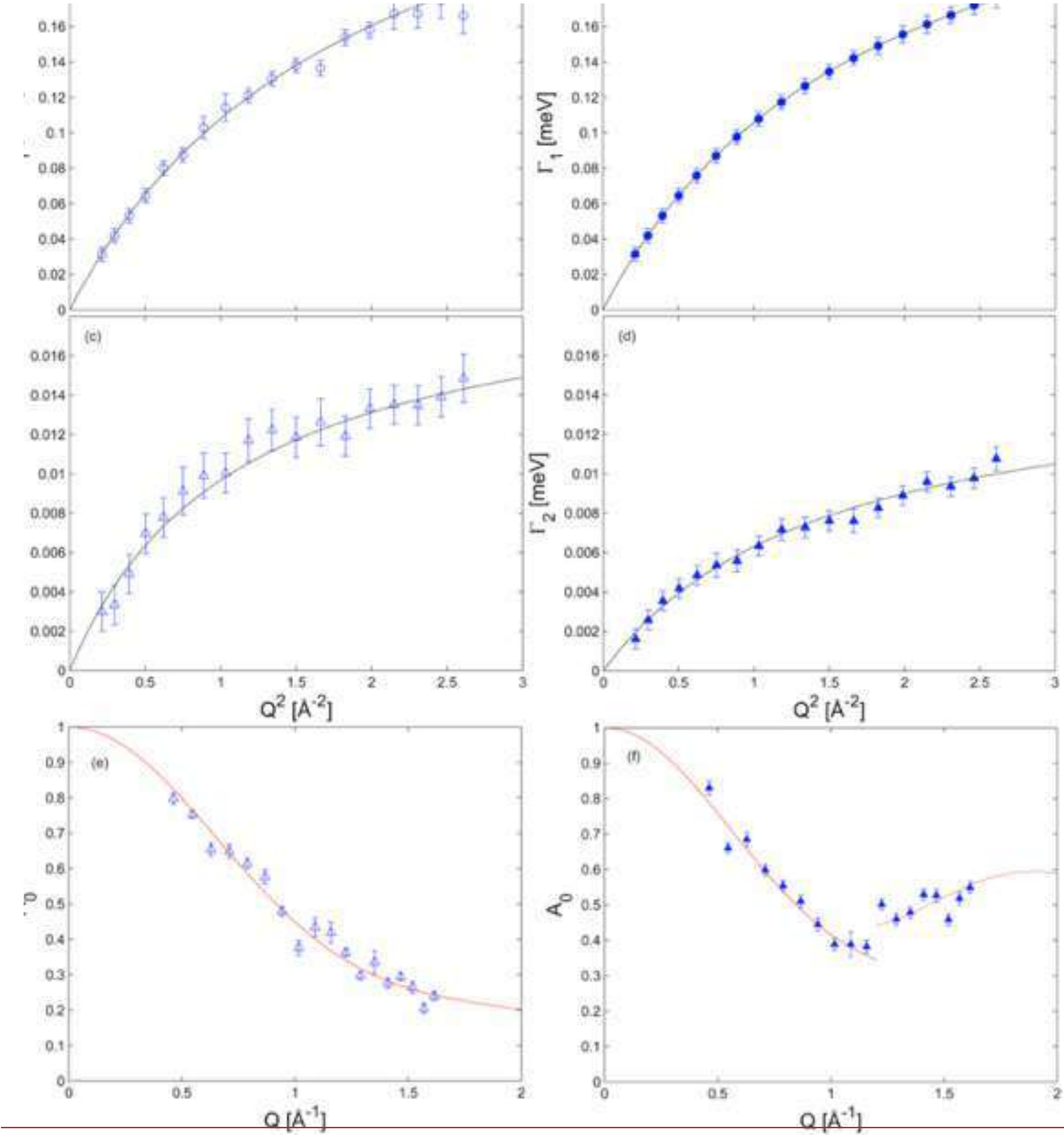

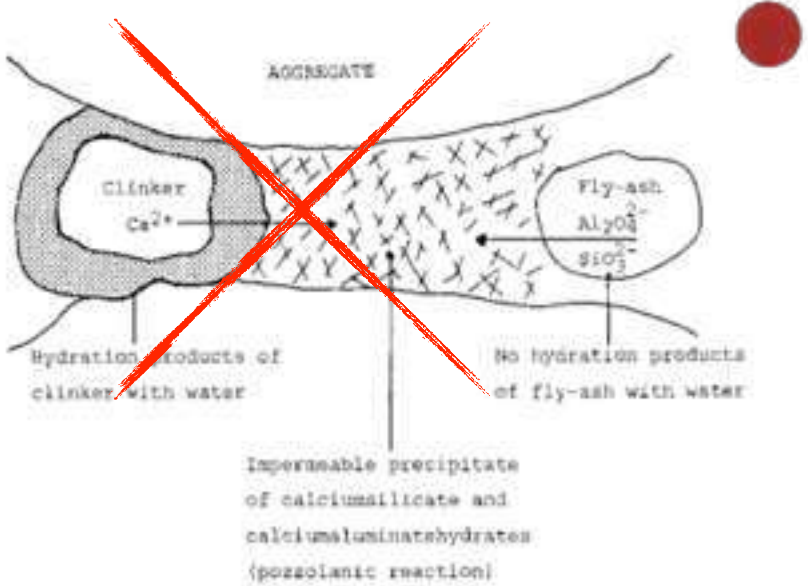

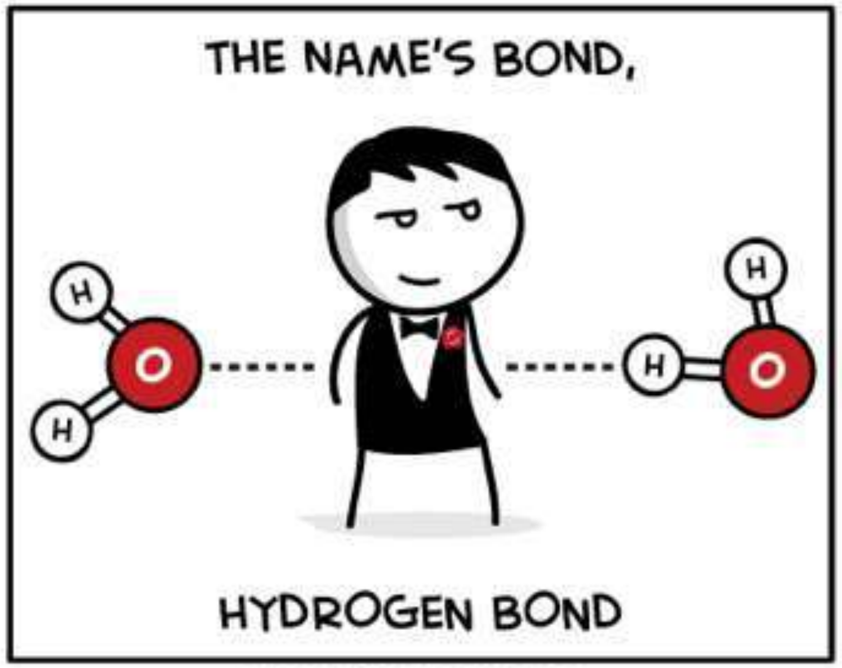

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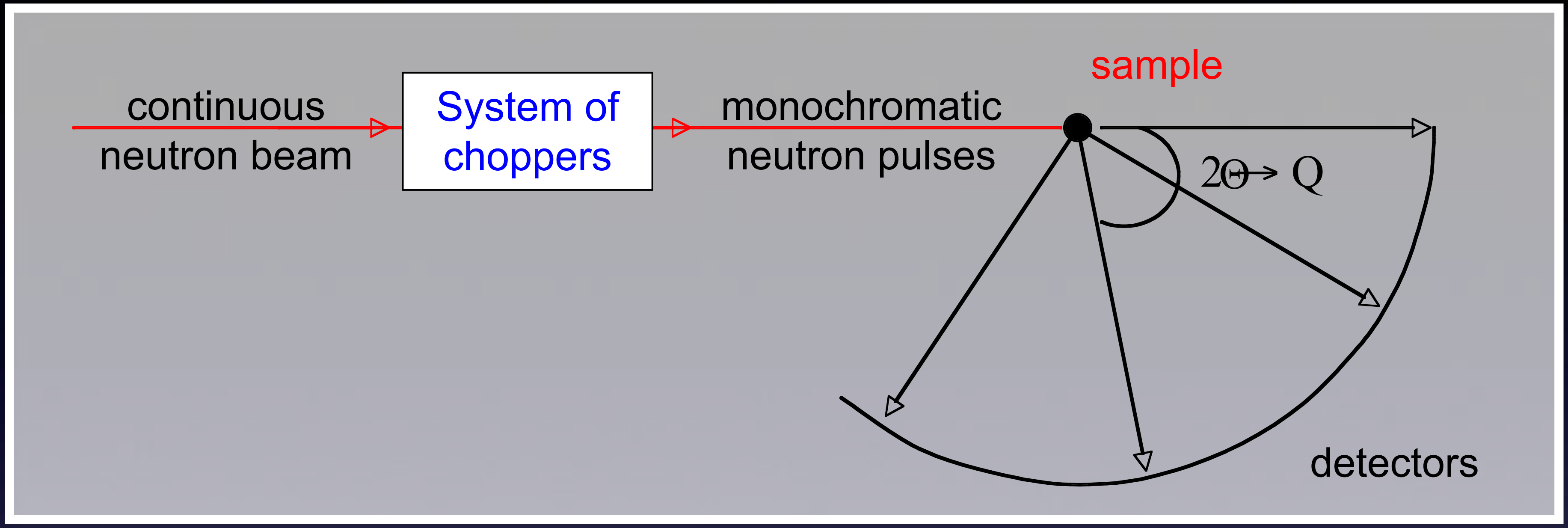
Time-averaged Mean-Squared Motions



continuous neutron beam

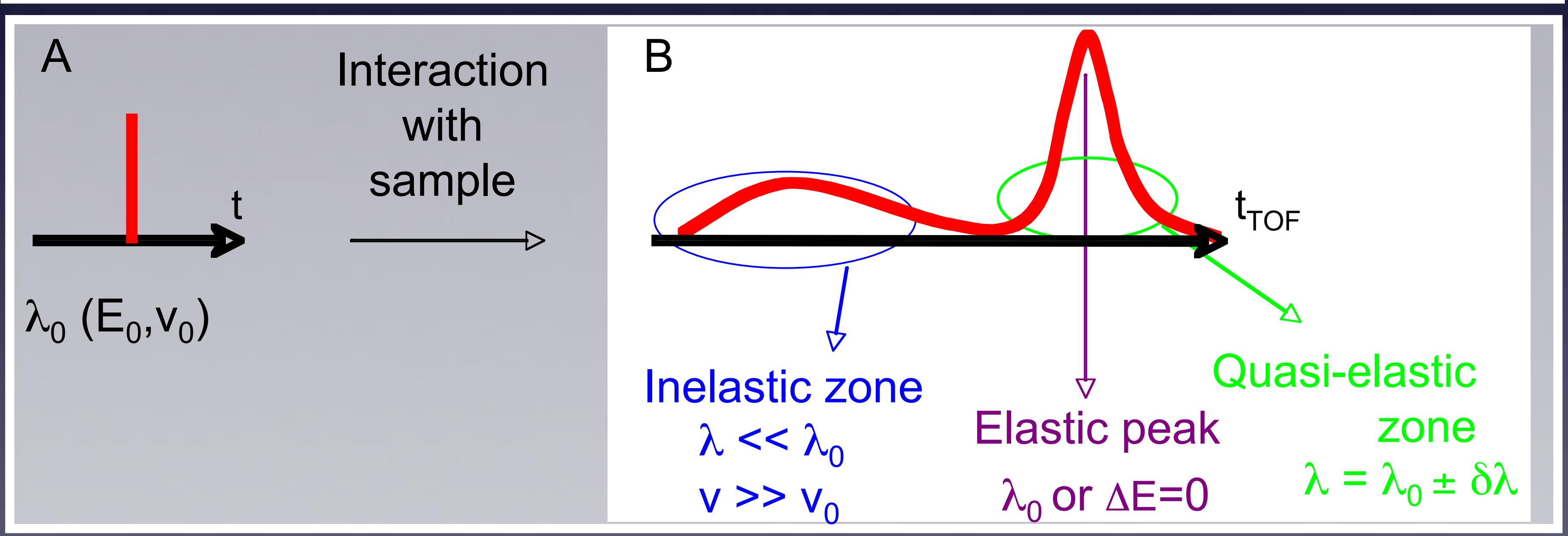
System of choppers

monochromatic neutron pulses

sample

2Θ → Q

detectors



A

t

λ_0 (E_0,v_0)

Interaction with sample

B

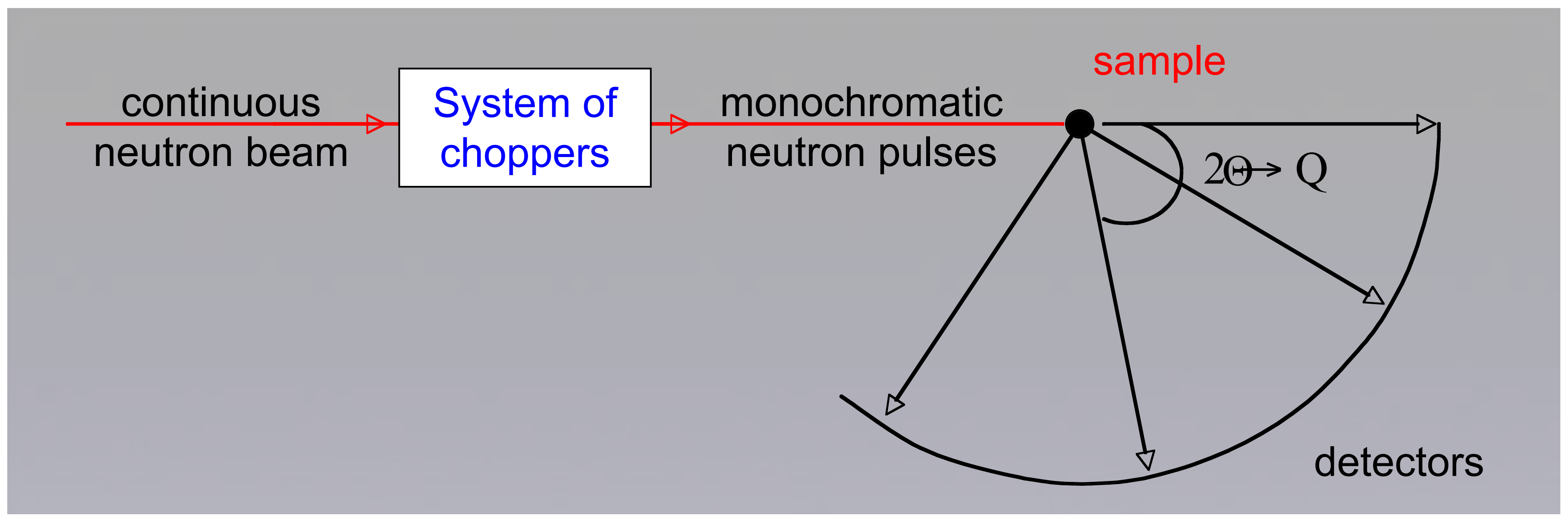
t_{TOF}

Inelastic zone
$\lambda << \lambda_0$
$v >> v_0$

Elastic peak
λ_0 or $\Delta E=0$

Quasi-elastic zone
$\lambda = \lambda_0 \pm \delta\lambda$

Time-averaged Mean-Squared Motions



continuous
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System of
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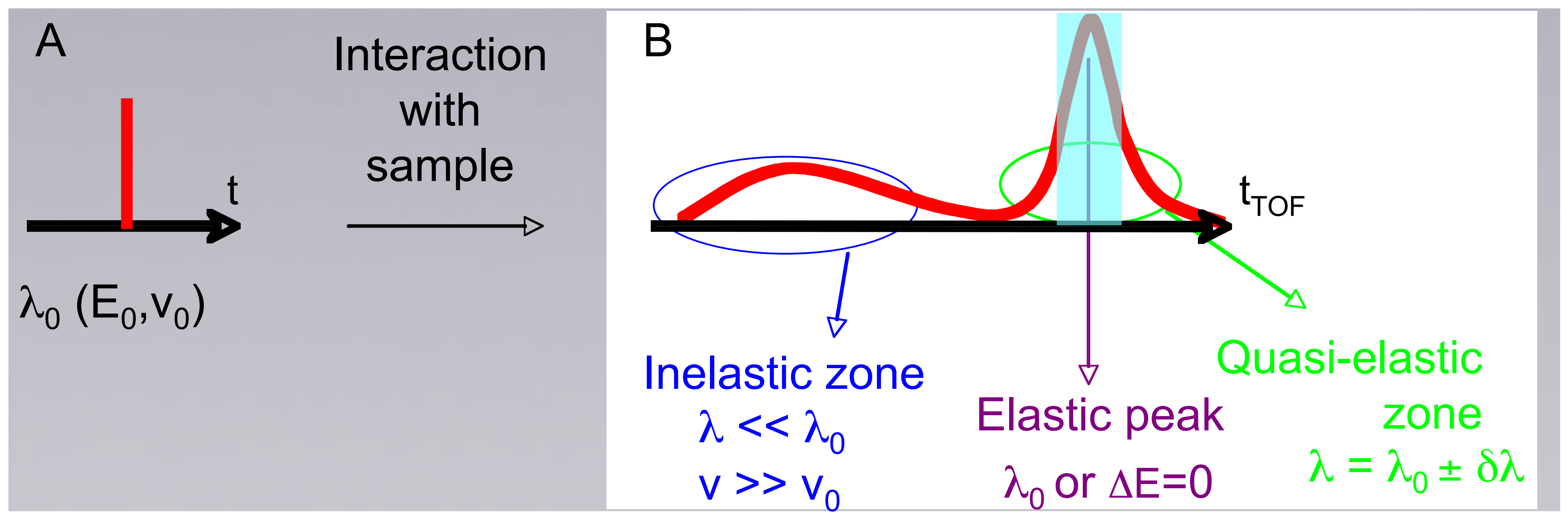

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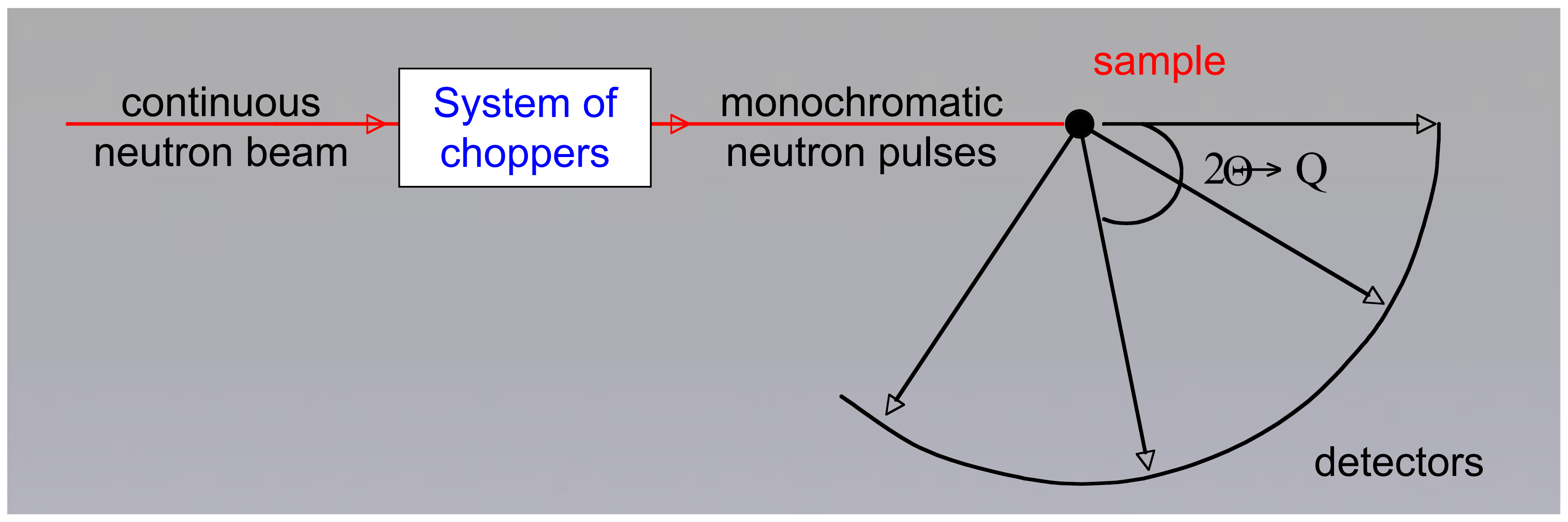
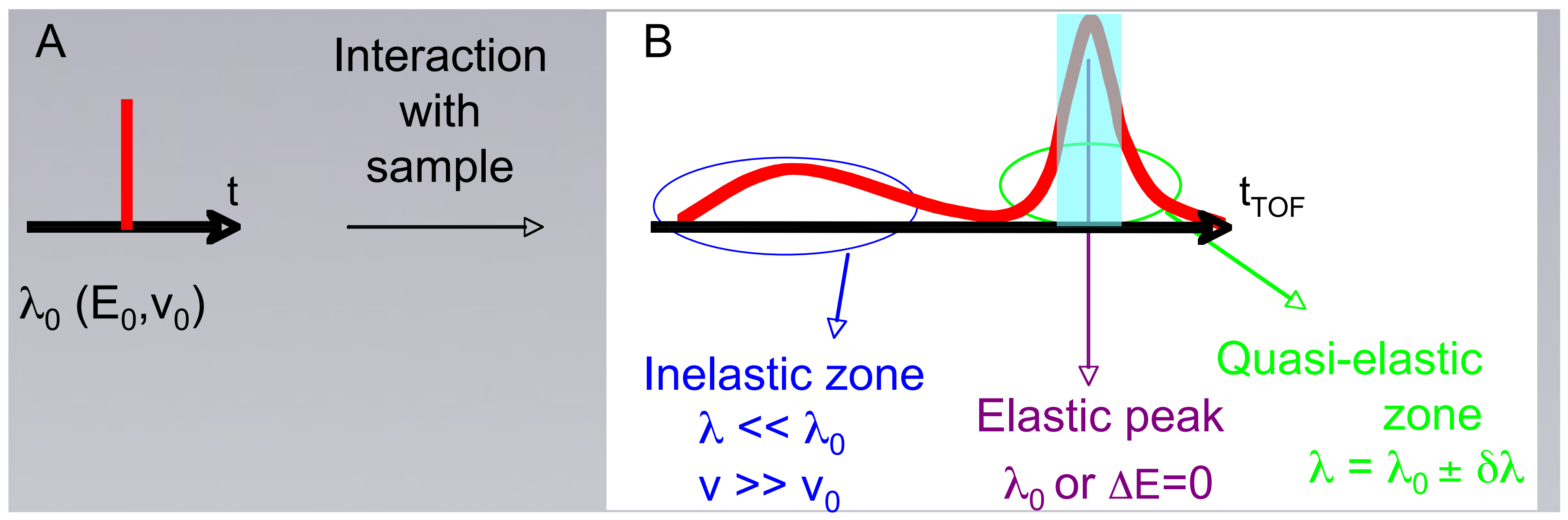
$$S(Q,\omega) = A_0(Q)\delta(\omega) + \sum_{i=1}^{N} A_i(Q)L_i(\omega)$$

$$A_0(Q) = a_0(Q)\exp^{\left(-\langle u^2\rangle Q^2\right)}$$

Time-averaged Mean-Squared Motions





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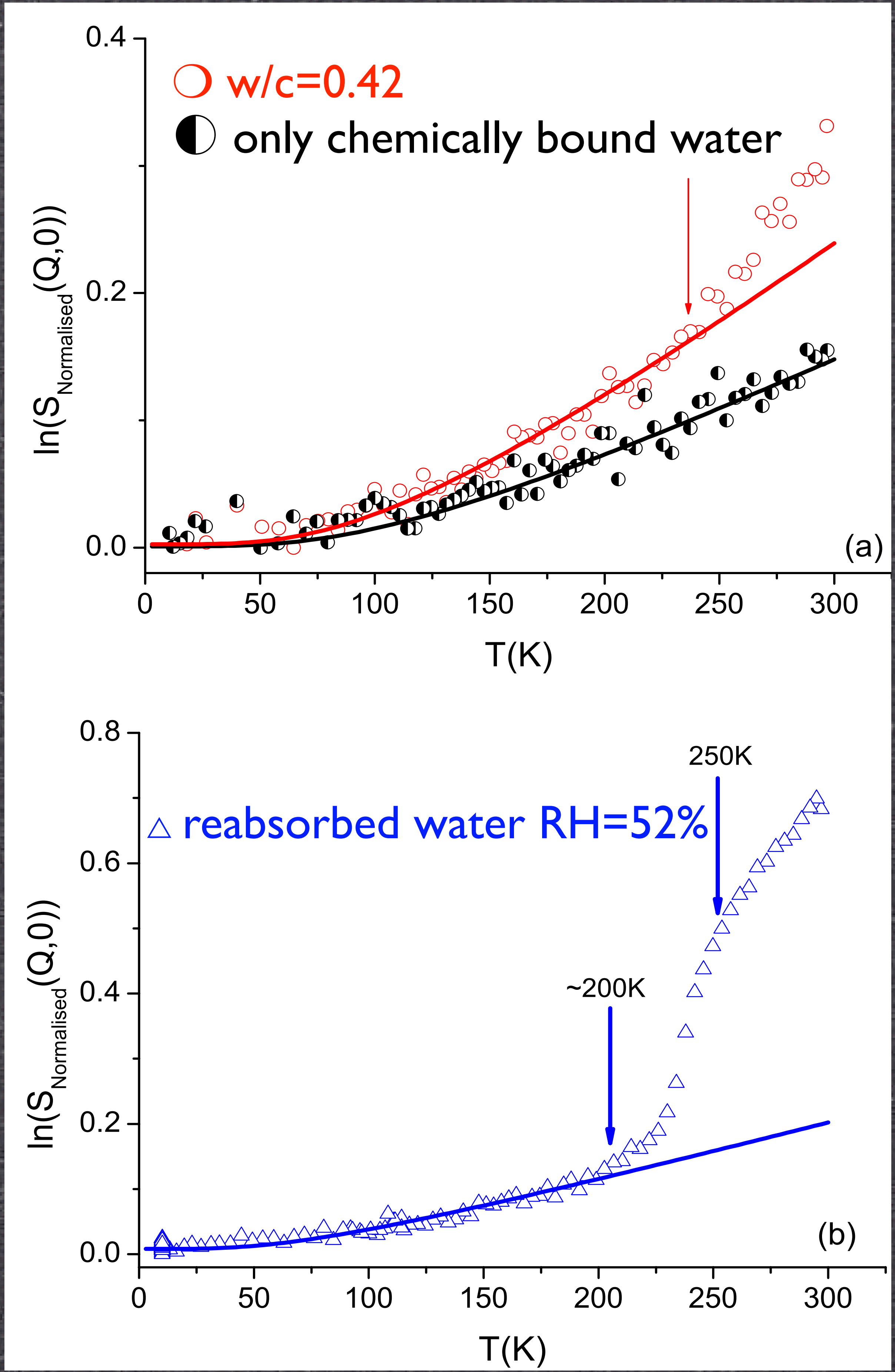
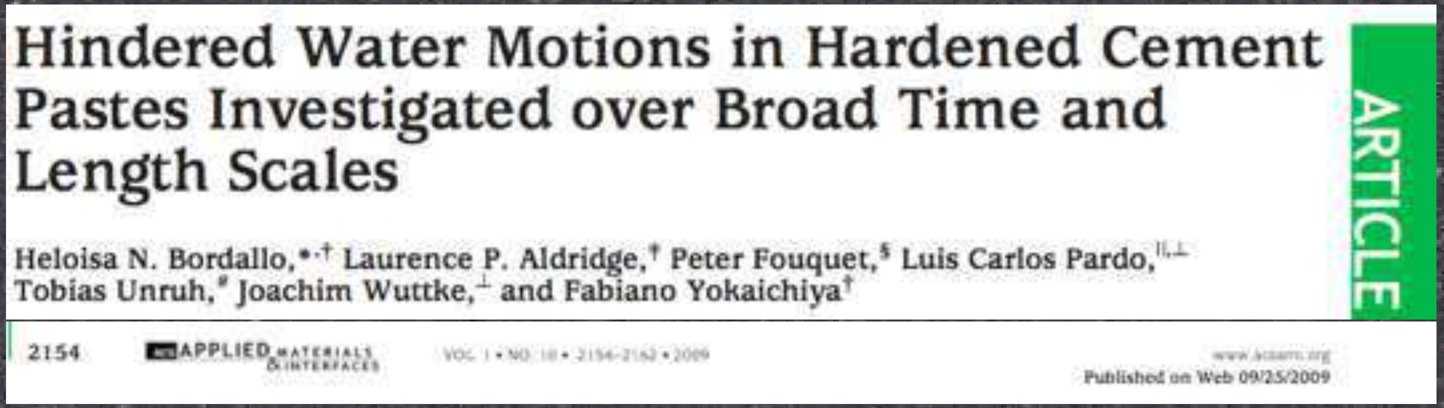
$$A_0(Q) = a_0(Q)\exp^{(-\langle u^2\rangle}$$

T

Harmonic Oscilator





Hindered Water Motions in Hardened Cement Pastes Investigated over Broad Time and Length Scales

Heloisa N. Bordallo,*,† Laurence P. Aldridge,† Peter Fouquet,§ Luis Carlos Pardo,∥,⊥ Tobias Unruh,# Joachim Wuttke,⊥ and Fabiano Yokaichiya†

ARTICLE

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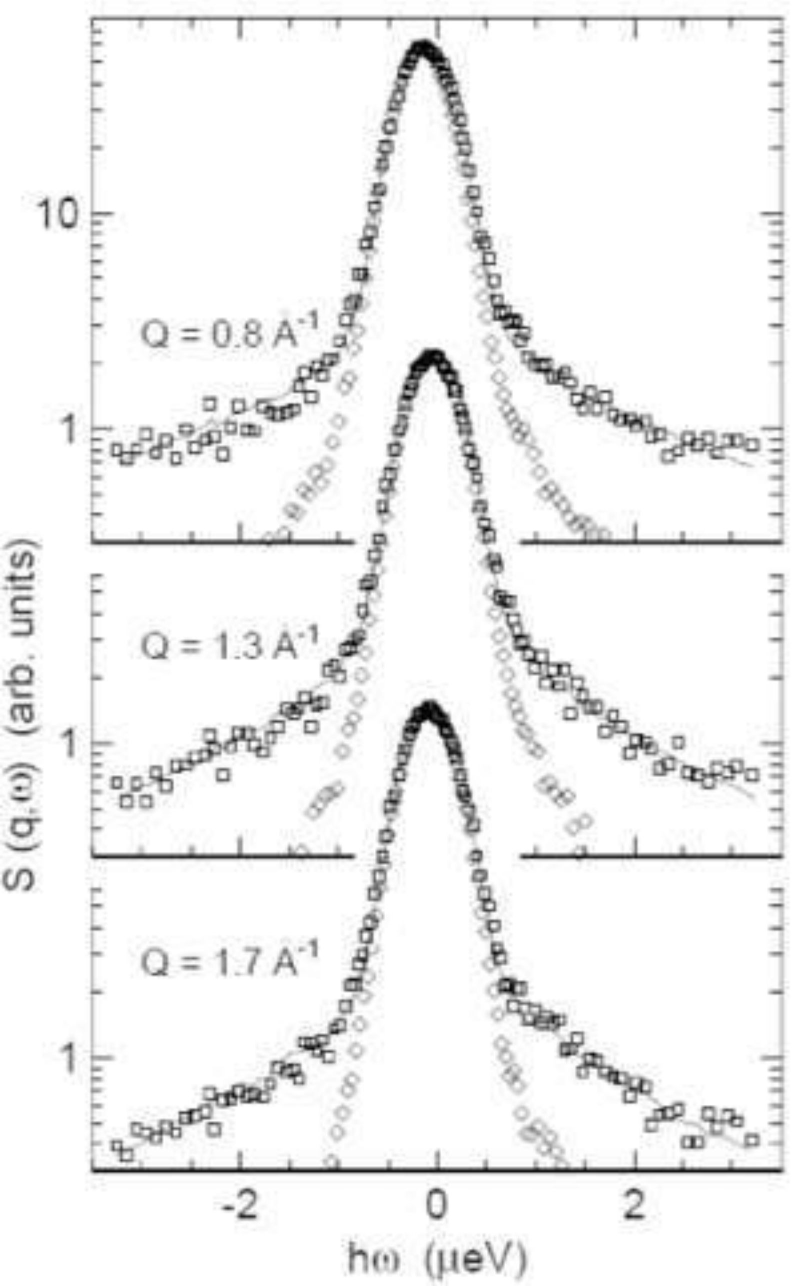

Take home message

☑ ToF to distinguish at least 3 types of water.

☑ Pastes made under different conditions show significantly different diffusivities!

☑ Water in gel pores diffuse ~ 10 times slower than bulk water.

☑ Our QENS results demonstrate that the development of a distinctive hydrogen bond network at the nano-scale is the key to the performance of these greener materials