

Investigating soft matter

Experimental techniques

Experimental techniques

- General
- Fluctuations - correlation functions
- Scattering techniques - general aspects/theory
 - ⇒ Neutron scattering
 - ⇒ Light scattering
 - Raman/IR spectroscopy
 - Photon correlation spectroscopy

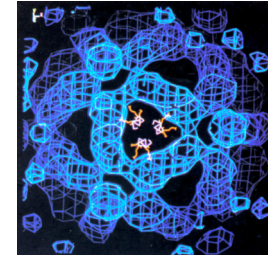
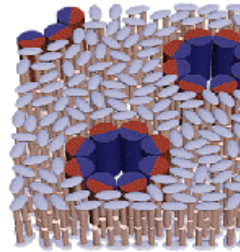
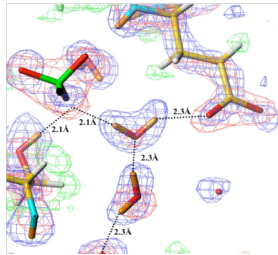
Literature

- Slides from this lecture
- Slides Johan Bergenholtz seminar on rheology

Time and length scales

Length scale in nm

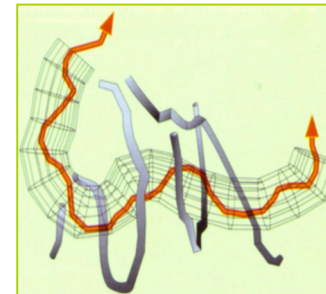
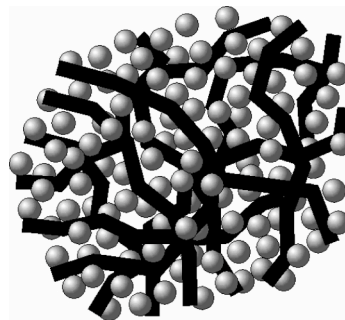
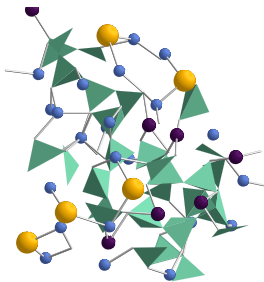
0.01 0.1 0.3 1.0 3.0 10 30 100



Need to investigate *structure* and *dynamics* over wide time and length scales!

10^{-13} Time scale (seconds)

10^{-7} - 10^3

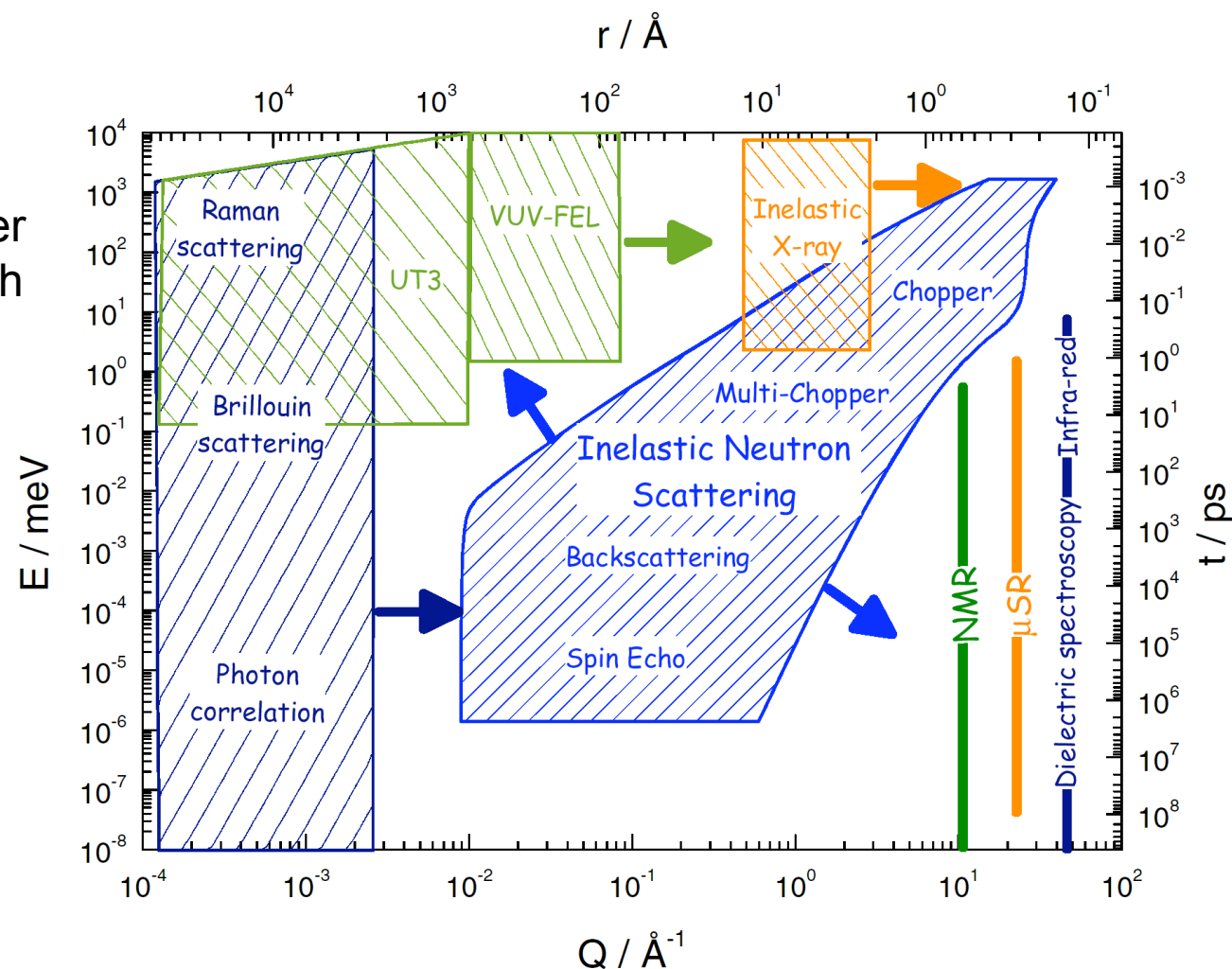


Combining techniques

With complementary techniques we can cover relevant time and length scales in soft matter

Length scale:
 Q ($\text{\AA}^{-1}$) or r ($\text{\AA}$)

Time scale or energy:
 τ (s) or E (meV)



Selection of techniques

Technique

Rheology

Nuclear Magnetic Resonance

Optical microscopy

Confocal microscopy

Vibrational spectroscopy

Dynamic light scattering

Dielectric spectroscopy

Calorimetry

x-ray & neutron scattering

AFM

Electron microscopy

Selection of techniques

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Electron microscopy

Mechanical properties, shear deformation

$$\sigma = \eta(\omega)\dot{\gamma} \quad , \quad G = G(\omega)$$

Selection of techniques

Technique

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Nuclear Magnetic Resonance

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Dielectric spectroscopy

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AFM

Electron microscopy

Utilizes nuclear magnetic spins
Probes local structure, diffusion (μs)
Species selective (H, D, C, F ...)

Selection of techniques

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Electron microscopy

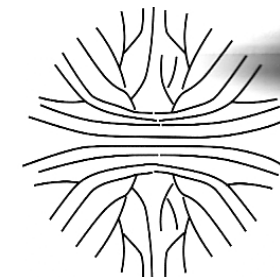
Morphology, optical anisotropy

Resolution down to 1 μm



10 μm x 10 μm

Microscopy image of a crystal of high density poly(ethylene) - viewed while “looking down” at the lamella



Selection of techniques

Technique

Rheology

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Vibrational spectroscopy

Dynamic light scattering

Dielectric spectroscopy

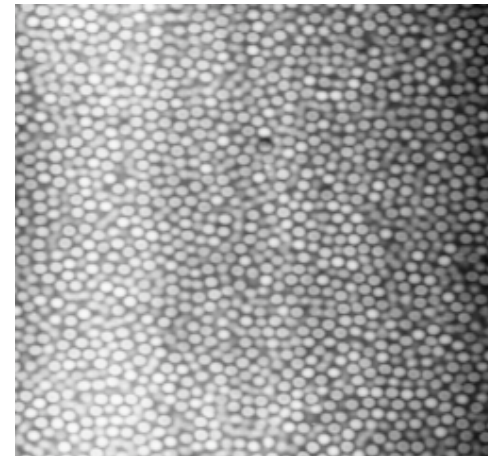
Calorimetry

x-ray & neutron scattering

AFM

Electron microscopy

Tracking of individual particles:
colloids, cells, ...
3-D images, resolution down to 1 μm (x&z)



PMMA particles, 2.3 μm

<http://www.physics.emory.edu/~weeks/lab>

Selection of techniques

Technique

Rheology

Nuclear Magnetic Resonance

Optical microscopy

Confocal microscopy

Vibrational spectroscopy

Dynamic light scattering

Dielectric spectroscopy

Calorimetry

x-ray & neutron scattering

AFM

Electron microscopy

Differential scanning calorimetry (DSC)

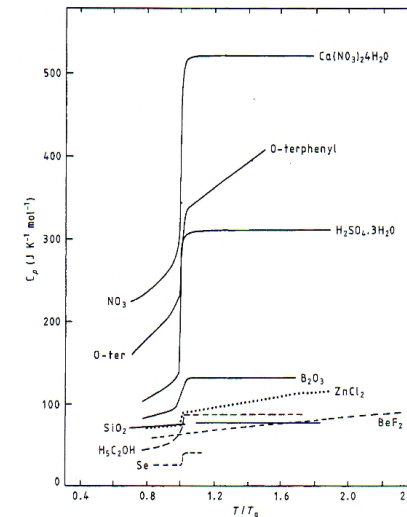


Figure 10. Specific heat C_p against reduced temperature T/T_g in the vicinity of the glass transition temperature T_g for different glass forming liquids. Note that for SiO_2 and BeF_2 a jump in C_p at T_g is not discernible (from Brawer 1983).

follow phase transitions, e.g. glass trans.

Experimental techniques

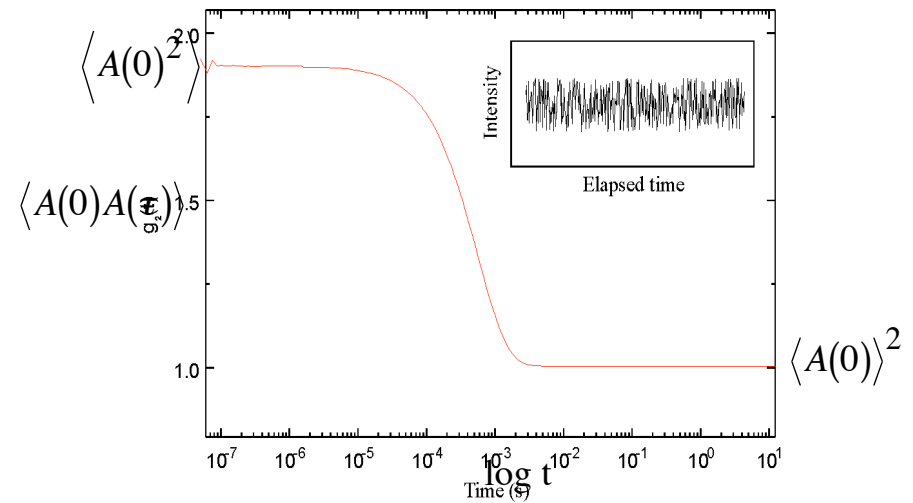
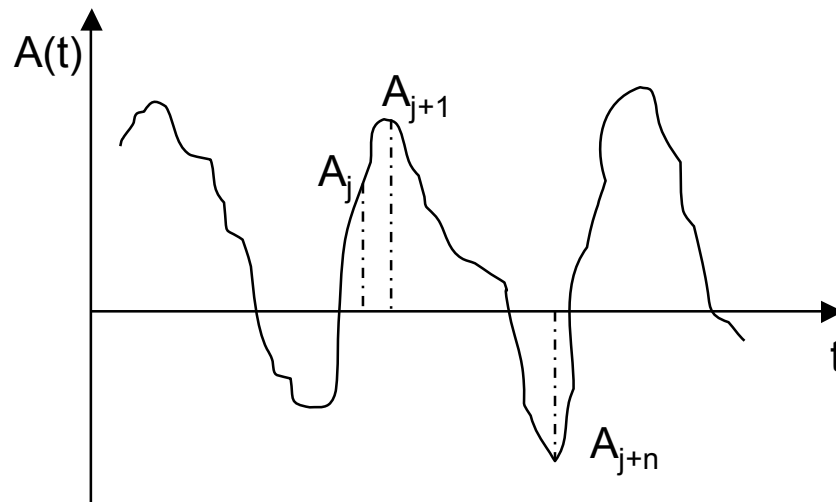
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Fluctuations - Correlation functions

Fluctuations in the property $A(\varepsilon, \rho, c, \dots)$
(vibrations, rotations, translations, ...)

Autocorrelation function

$$\langle A(0)A(\tau) \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt A(t)A(t + \tau)$$



$\Rightarrow$ Determine $\langle A(0)A(\tau) \rangle$ to learn about the dynamics of the system

$g(r,t)$ - van Hove correlation function

$$g(r,t) = \frac{1}{N} \sum_{i,j} \int \langle \delta\{r' - R_j(0)\} \delta\{r' + r - R_i(t)\} \rangle dr' = \frac{1}{N} \int dr' \langle \rho(r',0) \rho(r' + r,t) \rangle$$

$$\rho(r,t) = \sum_i \delta\{r - R_i(t)\} \quad \begin{array}{l} \text{- particle density operator} \\ \text{- } R_i(t) \text{ - position of particle } i \text{ at time } t \end{array}$$

Self correlation function

$$g_s(r,t) = \frac{1}{N} \sum_i \int \langle \delta\{r' - R_i(0)\} \delta\{r' + r - R_i(t)\} \rangle dr'$$

Distinct correlation function

$$g_d(r,t) = \frac{1}{N} \sum_{i \neq j} \int \langle \delta\{r' - R_j(0)\} \delta\{r' + r - R_i(t)\} \rangle dr'$$

$$g(r,t) = g_s(r,t) + g_d(r,t)$$

$g(r,t)$ - van Hove correlation function

$$g_s(r,t) = \frac{1}{N} \sum_i \int \langle \delta\{r' - R_i(0)\} \delta\{r' + r - R_i(t)\} \rangle dr'$$

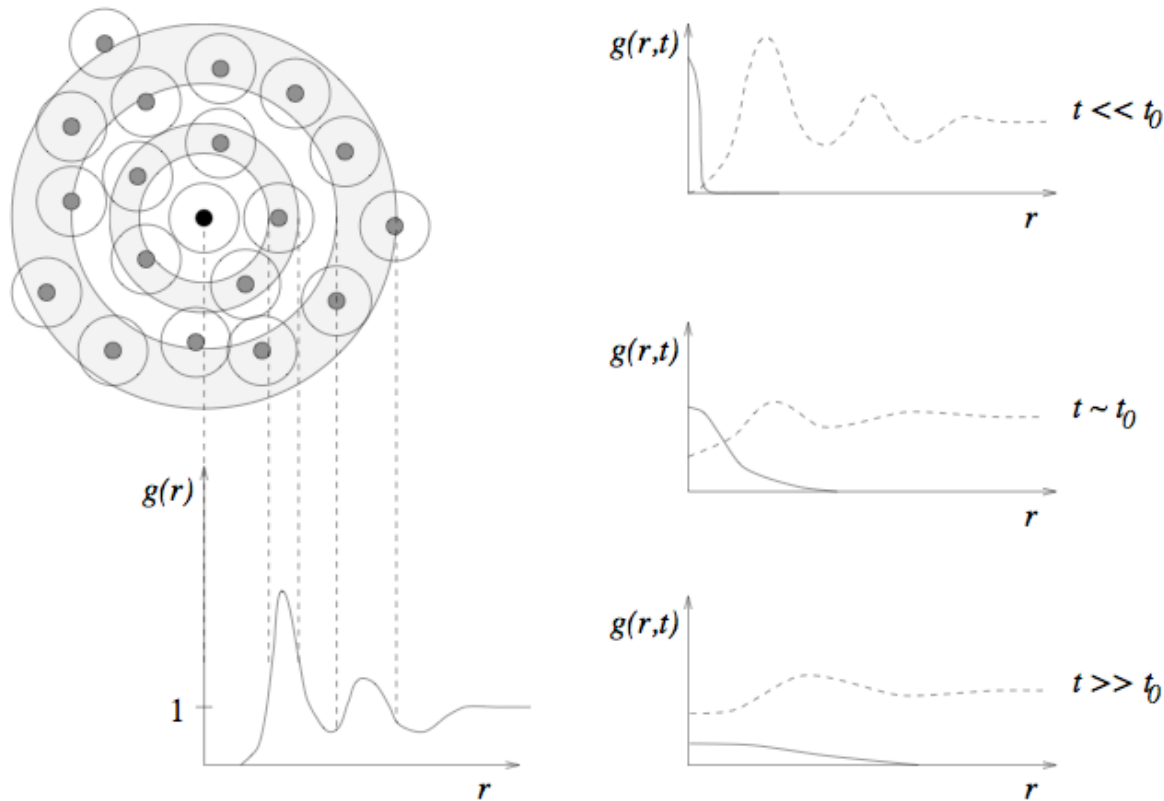
$$g_d(r,t) = \frac{1}{N} \sum_{i \neq j} \int \langle \delta\{r' - R_j(0)\} \delta\{r' + r - R_i(t)\} \rangle dr'$$

In the limit $t \rightarrow 0$

$$g(r,0) = \delta(r) + \sum_i \langle \delta(r - R_i(0) + R_0(0)) \rangle = \delta(r) + \sum_i \langle \delta(r - R_i + R_0) \rangle = \delta(r) + g(r)$$

$g(r)$ - static pair distribution $\Rightarrow$ *the structure of the material*

$g(r,t)$ - van Hove correlation function



$$g(r,0) = \delta(r) + \sum_i \langle \delta(r - R_i + R_0) \rangle = \delta(r) + g(r)$$

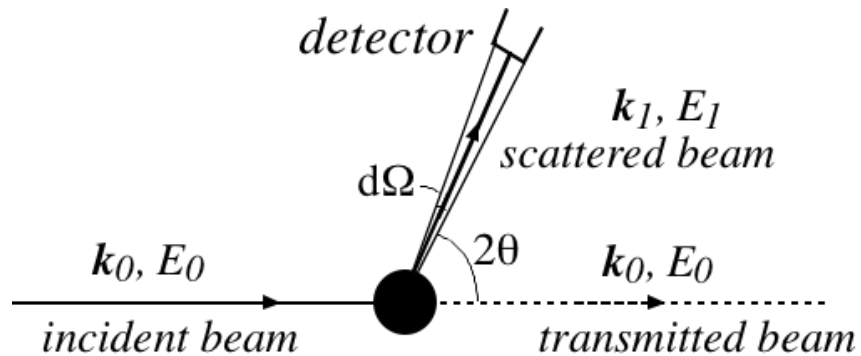
$$g_s(r,t) = \frac{1}{N} \sum_i \int \langle \delta\{r' - R_i(0)\} \delta\{r' + r - R_i(t)\} \rangle dr'$$

$$g_d(r,t) = \frac{1}{N} \sum_{i \neq j} \int \langle \delta\{r' - R_j(0)\} \delta\{r' + r - R_i(t)\} \rangle dr'$$

Experimental techniques

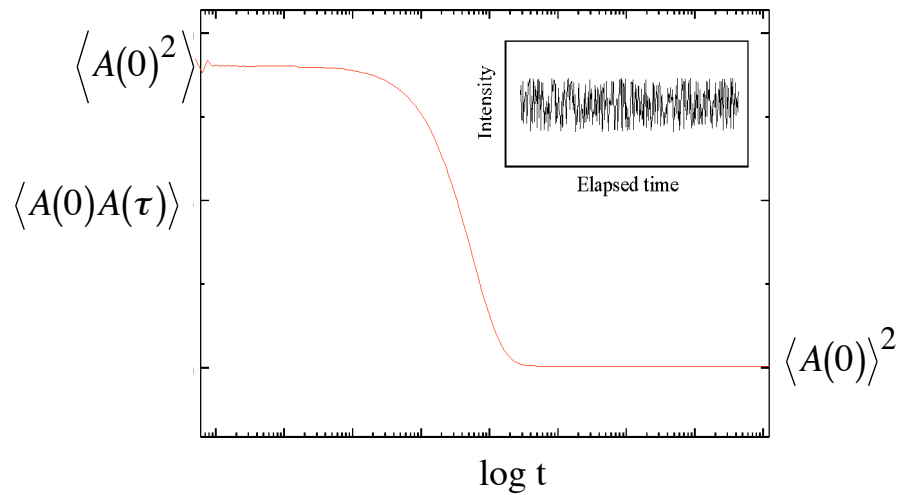
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Scattering experiment



Scattering of particles:

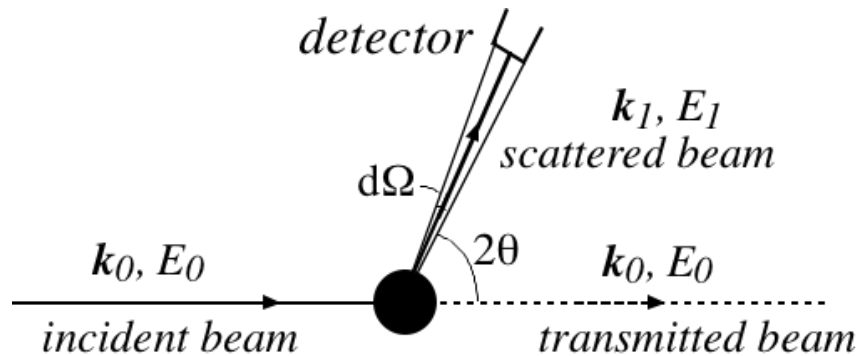
- Neutrons
- electrons
- photons
- ...



Differ in:

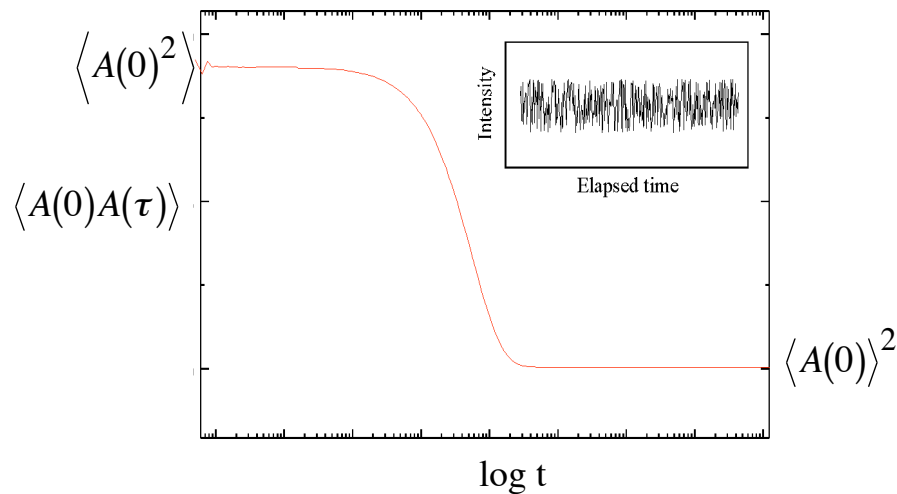
- wavelength
- interaction mechanism
- cross section
- detection
- resolutions
- ...

Scattering experiment



Scattering of particles:

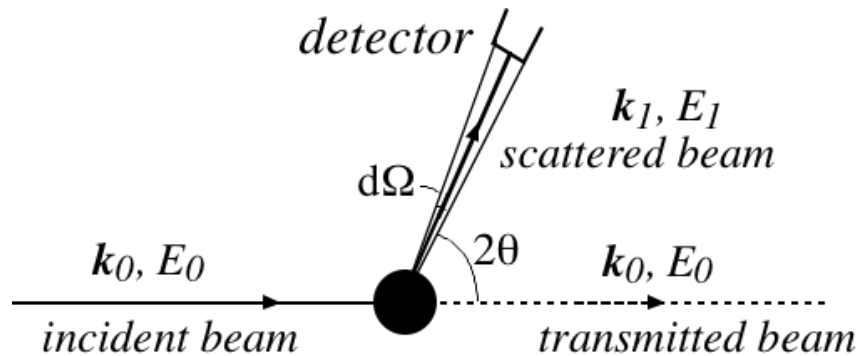
- Neutrons - 1 - 30 Å
- electrons - 0.1 - 1 Å
- photons - 1 - 5000 Å
- ...



Differ in:

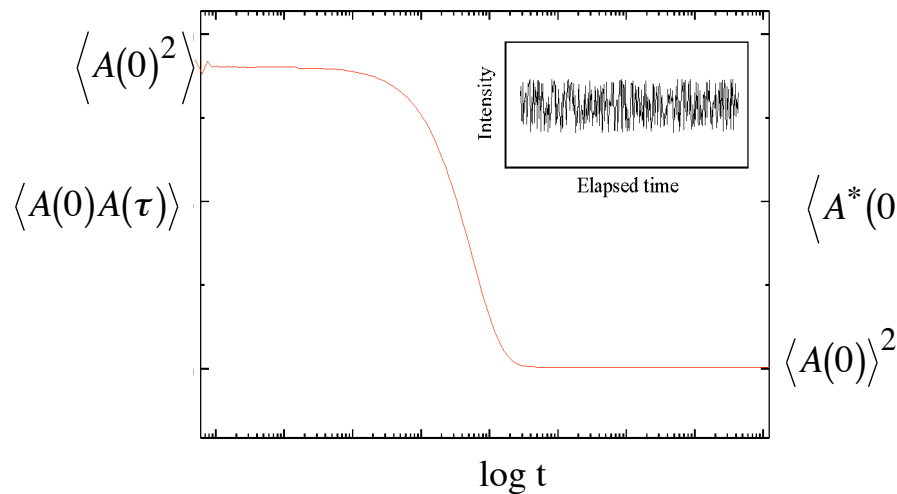
- wavelength
- interaction mechanism
- cross section
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Scattering experiment



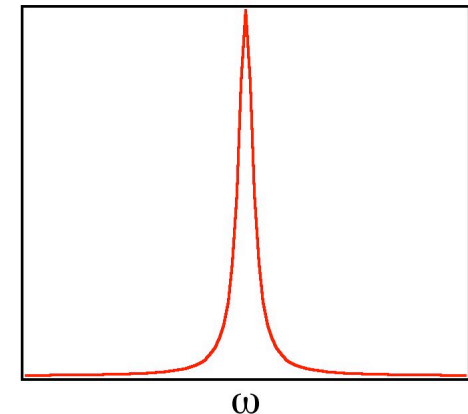
Obtaining the correlations function:

- Directly in time domain
(PCS, transient grating ...)
- In frequency domain
(Brillouin, Raman, neutron,...)
 $\Rightarrow$ spectral density $I(\omega)$

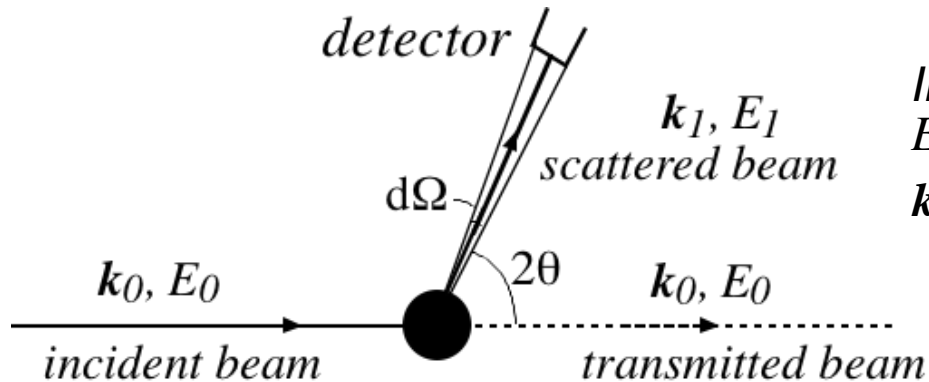


$$\langle A^*(0)A(\tau) \rangle = \int_{-\infty}^{\infty} d\omega e^{i\omega\tau} I(\omega)$$

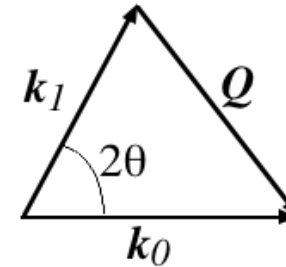
$I(\omega)$



Scattering experiment



In the scattering process we can exchange
 $E_0 - E_1 = \pm \hbar \omega$ - energy transfer
 $k_0 - k_1 = G \pm Q$ - momentum transfer



$$\Delta E = \hbar \omega = E_0 - E_1 = \frac{\hbar}{2m} (\bar{k}_0^2 - \bar{k}_1^2)$$

$$Q^2 = |\bar{k}_1 - \bar{k}_0|^2$$

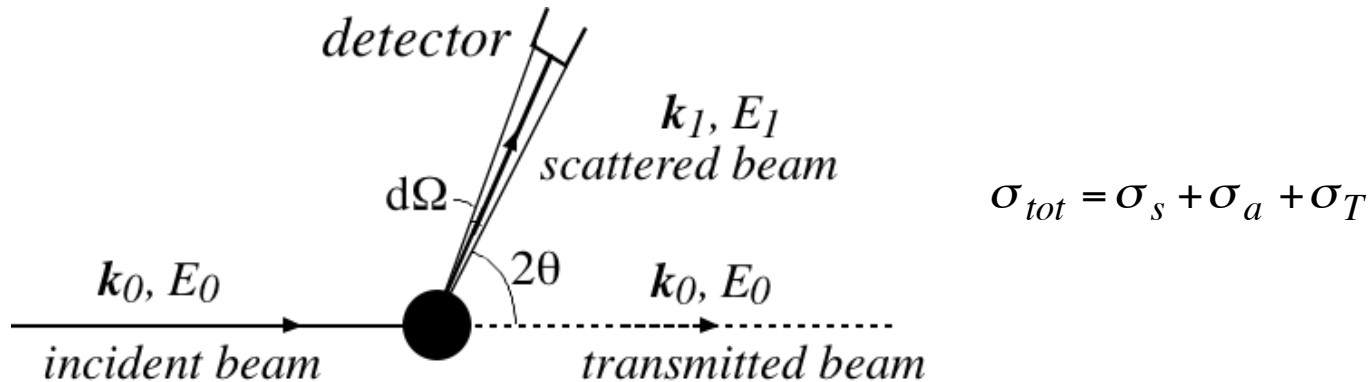
$$\text{if } |\bar{k}_1| \approx |\bar{k}_0| \Rightarrow Q^2 = 4k_0^2 \sin^2 \frac{\theta}{2}$$

$$Q = 2k_0 \sin \frac{\theta}{2} = \frac{4\pi n}{\lambda_0} \sin \frac{\theta}{2}$$

$$\lambda = 2\pi n/k$$

light scattering
 n - refractive index

Scattering experiment



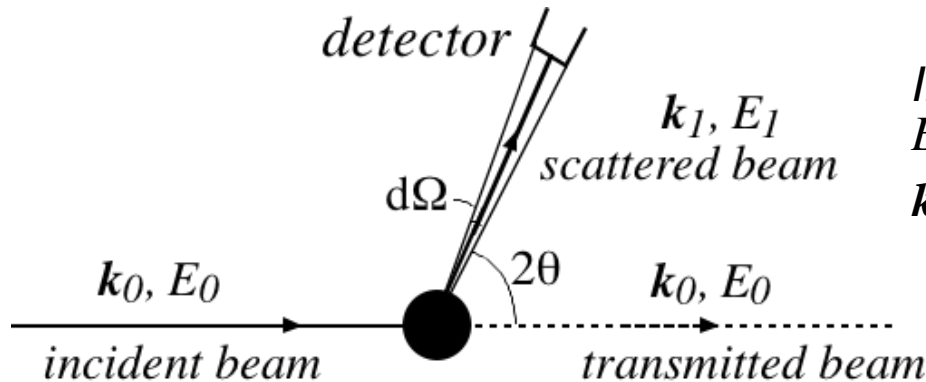
In the experiment we measure the double differential scattering cross section

$$\Rightarrow \frac{\partial^2 \sigma_s}{\partial \Omega \partial \omega} ; \quad \sigma_s = \iint \frac{d^2 \sigma}{d\Omega d\omega} d\omega d\Omega \quad - \text{ total scattering cross section}$$

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \propto \int dt \int dr e^{-i(\omega t - Qr)} \underbrace{\langle \rho(r, 0) \rho(r' + r, t) \rangle}_{\text{Dynamic structure factor}} = S(Q, \omega)$$

$$g(r, t) \Leftrightarrow S(Q, \omega) \text{ (Fourier transforms)}$$

Scattering experiment



In the scattering process we can exchange
 $E_0 - E_1 = \pm \hbar \omega$ - energy transfer
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$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \propto \int dt \int dr e^{-i(\omega t - Qr)} \langle \rho(r, 0) \rho(r' + r, t) \rangle = S(Q, \omega)$$

express in fourier components

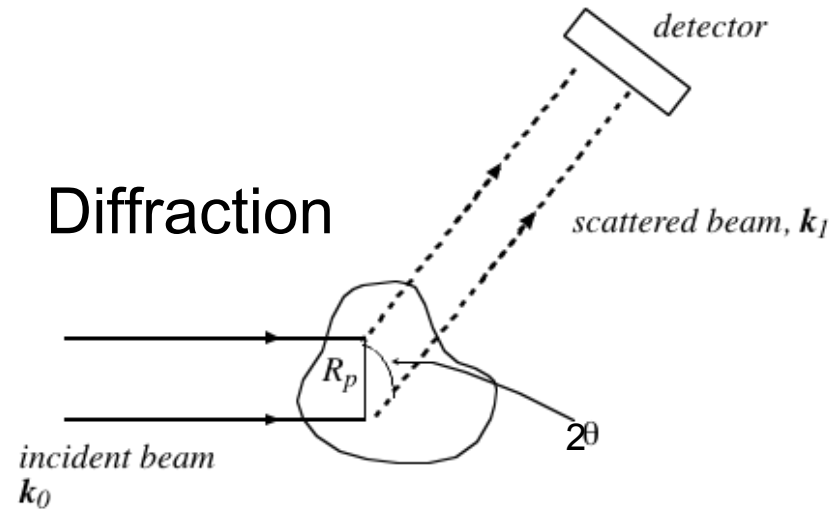
$$\rho(r, t) = \sum_i \delta\{r - R_i(t)\} = \frac{1}{(2\pi)^3} \int \rho_Q(t) \exp(iQr) dQ$$

$$\rho_Q(t) = \sum_i \exp\{-iQR_i(t)\}$$



$$S(Q, \omega) = \int \exp\{-i\omega t\} \sum_{i,j} \langle \exp\{-iQr_j(0)\} \exp\{iQr_j(t)\} \rangle dt$$

Scattering experiments - structure

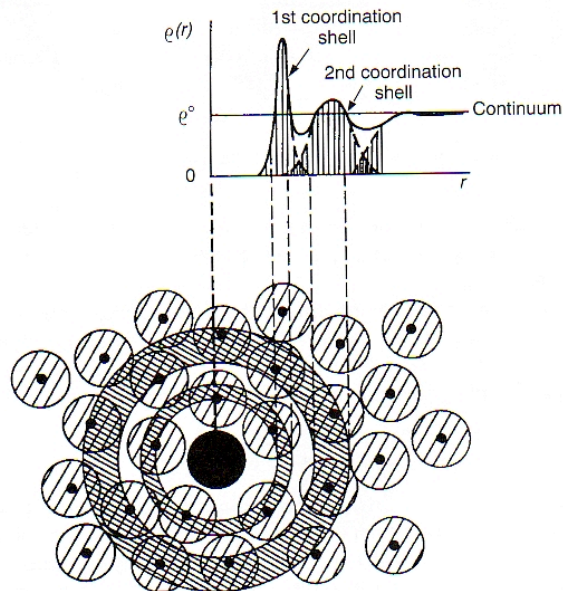


$$g(r,0) = \delta(r) + \sum_i \langle \delta(r - R_i + R_0) \rangle = \delta(r) + g(r)$$



$$g(r,0) \Rightarrow \int S(Q,\omega) d\omega = S(Q)$$

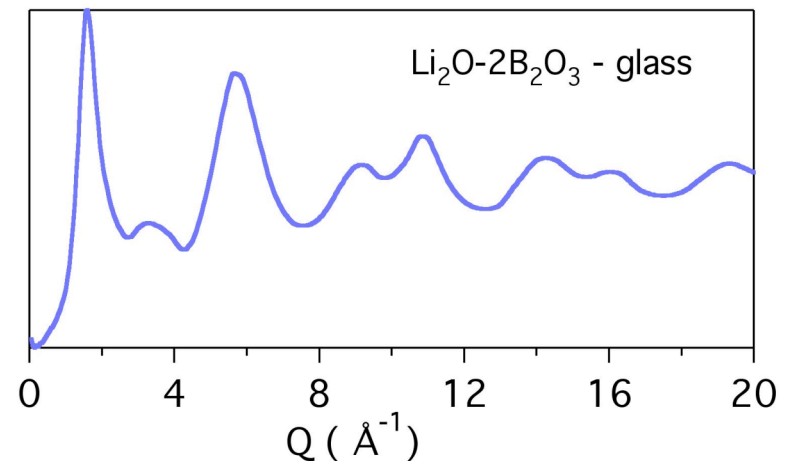
$$g(r) = \frac{1}{(2\pi)^3 \rho_0} \int (S(Q) - 1) \frac{\sin Qr}{Qr} 4\pi Q^2 dr + 1$$



F.T



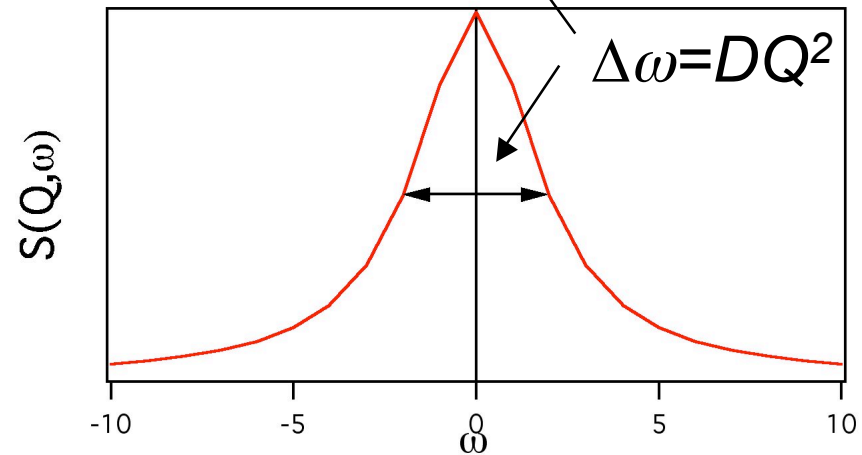
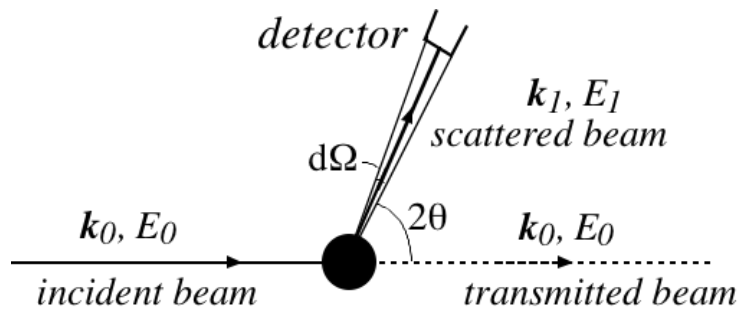
$S(Q)$ (arb. units)



Scattering experiments - dynamics

Liquid like diffusion / Brownian motion

$$g_s(r, t) = (4\pi Dt)^{-3/2} \exp\left\{-\frac{r^2}{4Dt}\right\} \Rightarrow S_{inc}(Q, \omega) = \frac{1}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2}$$

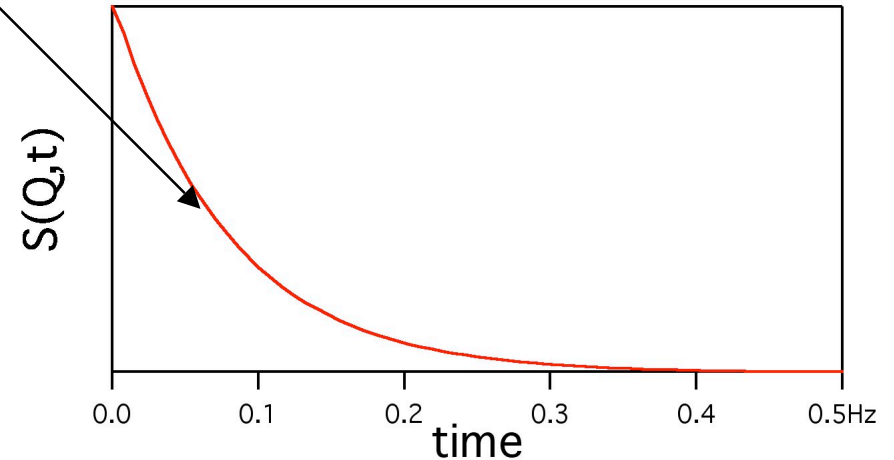
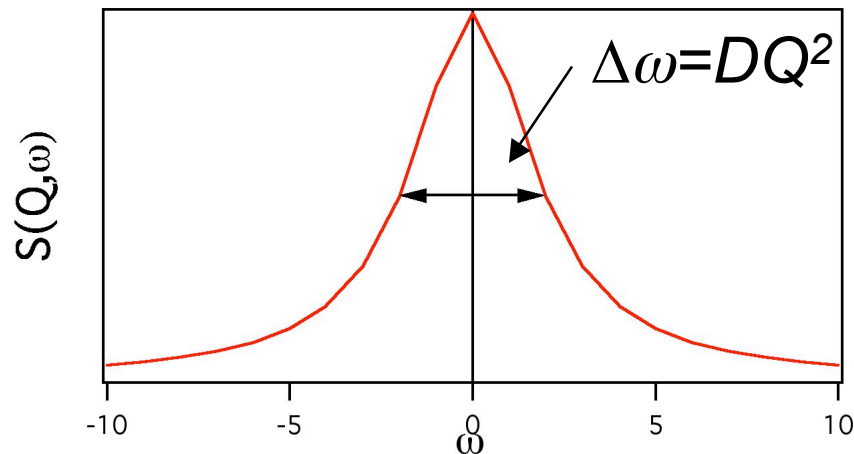


Scattering experiments - dynamics

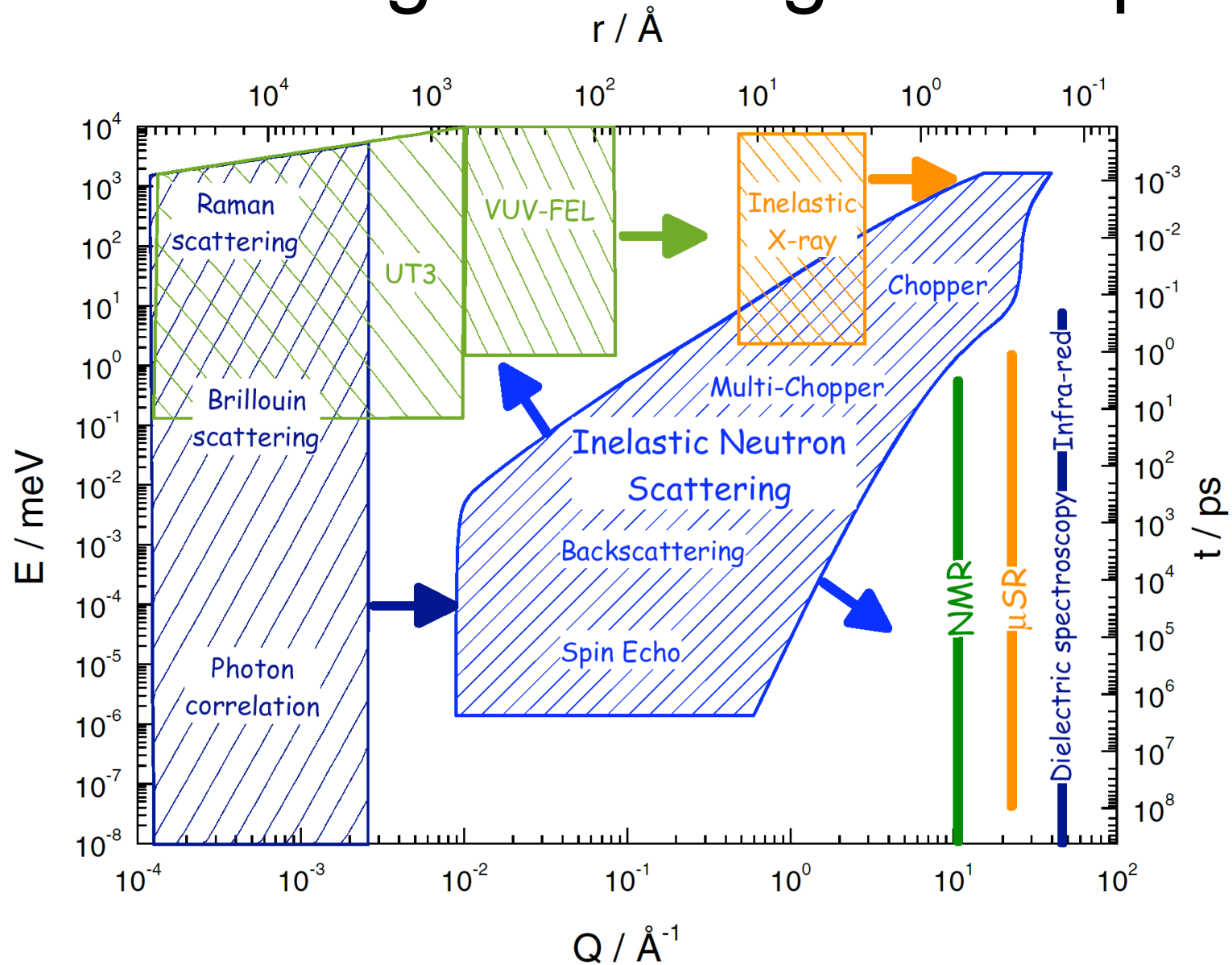
Liquid like diffusion / Brownian motion

$$g_s(r,t) = (4\pi Dt)^{-3/2} \exp\left\{-\frac{r^2}{4Dt}\right\} \Rightarrow S_{inc}(Q,\omega) = \frac{1}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2}$$

$$S(Q,\omega) \Rightarrow S(Q,t) \propto \exp\{-t/\tau\} \quad \tau = \frac{1}{DQ^2}$$



Combining scattering techniques



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Neutron scattering

The Nobel Prize in Physics 1994

Clifford G. Shull, MIT, Cambridge, Massachusetts, USA, winner one half of the 1994 Nobel Prize in Physics for development of the neutron diffraction technique.

Baron H. Brockhouse, McMaster University, Hamilton, Ontario, Canada, winner one half of the 1994 Nobel Prize in Physics for the development of neutron spectroscopy.

Neutrons behave as particles and as waves

The Royal Swedish Academy of Sciences has awarded the 1994 Nobel Prize in Physics for pioneering contributions to the development of neutron scattering techniques for studies of condensed matter.

Neutrons reveal structure and dynamics

S Shull made use of elastic scattering i.e. of neutrons which change direction without losing energy when they collide with atoms.

Because of the wave nature of neutrons, a diffraction pattern can be recorded which indicates where in the sample the atoms are situated. Even the placing of light elements such as hydrogen in metallic hydrides, or hydrogen, carbon and oxygen in organic substances can be determined.

The pattern also shows how atomic dipoles are oriented in magnetic materials, since neutrons are affected by magnetic forces. Shull also made use of this phenomenon in his neutron diffraction technique.

Neutrons show where atoms are

When the neutrons collide with atoms in the sample material, they change direction (see scattering) - elastic scattering.

Atoms in a crystalline sample

Research reactor

Neutrons bounce against atomic nuclei. They also react to the magnetism of the atoms.

Neutrons show what atoms do

3-axis spectrometer with magnetic crystals and variable sample

Atoms in a crystalline sample

When the neutrons penetrate the sample they start to vibrate (oscillate) in the atoms. If the neutrons change position or frequency, this shows atoms are vibrating (magnetic scattering).

Changes in the energy of the neutrons are first analysed in an analyser crystal...

...and the neutrons then counted in a detector.

Neutrons see more than X-rays

X-rays are scattered by electron clouds in atoms and molecules. Neutrons, on the other hand, are scattered by the nuclei of the atoms. This means that neutrons can see through light elements such as hydrogen and carbon, which are invisible to X-rays.

Neutrons reveal inner stresses

It tells the brain whether an object is under stress or not. The neutrons can see the internal stresses in a material, which are not visible to the eye.

Neutrons show what atoms are doing

Neutrons can see what atoms are doing. They can see the vibrations of atoms in a material, which are not visible to the eye.

Where it started

Brockhouse and Shull made their pioneering contributions at the first nuclear reactor in the USA and Canada back in the 1940s and 1950s. It was then that the neutron became available for scientific research.

... how it continues

Thousands of research teams are now working at the many neutron scattering centres throughout the world. New and more advanced neutron scattering facilities have been built and more are planned in Europe, the USA and Asia. At these neutron laboratories the researchers are studying the structure of new composite superconductors, material development on surfaces of interest for catalytic activity, drug design, stress measurement and the connections between the structure and the elastic properties of polymers.

Further reading:

Clifford G. Shull, *The Nobel Prize in Physics 1994*, Royal Swedish Academy of Sciences, Stockholm, 1994.

Baron H. Brockhouse, *The Nobel Prize in Physics 1994*, Royal Swedish Academy of Sciences, Stockholm, 1994.

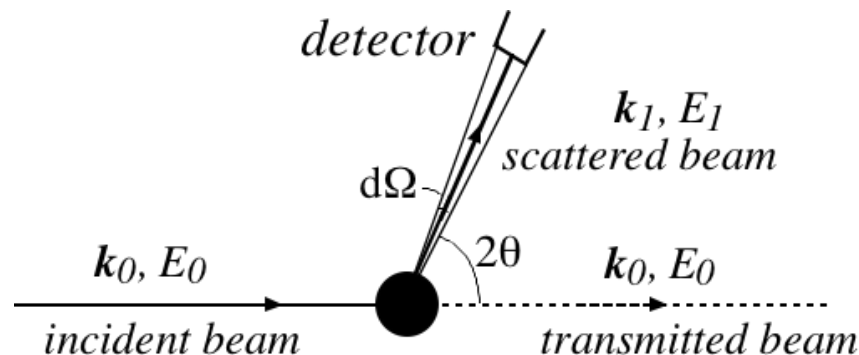
KUNGLIGA VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

Neutrons tell you where the atoms are and what the atoms do'
(Nobel Prize citation from Brockhouse and Shull 1994)

Neutron scattering

The neutron has a wavelength ($\text{\AA}$) and an energy (meV) comparable to typical atomic spacings and vibrational energies -

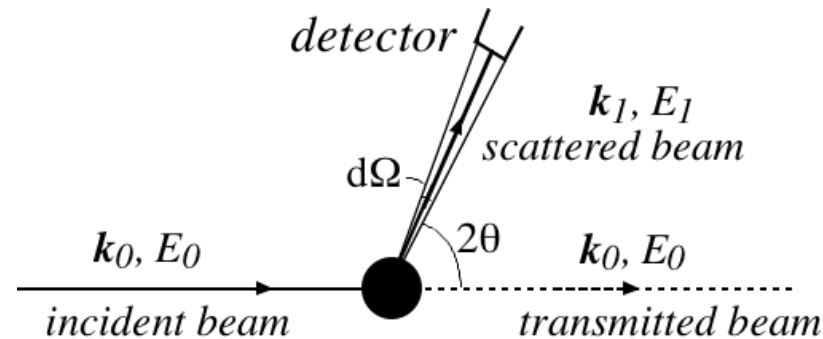
$\Rightarrow$ study both atomic structure and dynamics
(simultaneously if required)



Typical neutron energy: 0.1-100 meV

Typical wavelength: 30-1 $\text{\AA}$

Neutron scattering - dynamics



Incident neutron (E_0, k_0) can exchange energy and momentum in the scattering process to (E_1, k_1), $\omega = E_1 - E_0$, $q = k_1 - k_0$ due to interaction with the material

Typical neutron energy: 0.1-100 meV

$$\frac{d^2\sigma}{d\Omega d\omega} = N \frac{k_1}{k_0} \left(\langle b \rangle^2 S_{coh}(q, \omega) + \left(\langle b^2 \rangle - \langle b \rangle^2 \right) S_{inc}(q, \omega) \right)$$

$$S_{coh}(q, \omega) = \int_{-\infty}^{\infty} \exp^{-i\omega t} \sum_{i,j=1}^N \left\langle \exp^{-iq \cdot r_i(0)} \exp^{iq \cdot r_j(t)} \right\rangle dt$$

coherent scattering
(cross correlations)

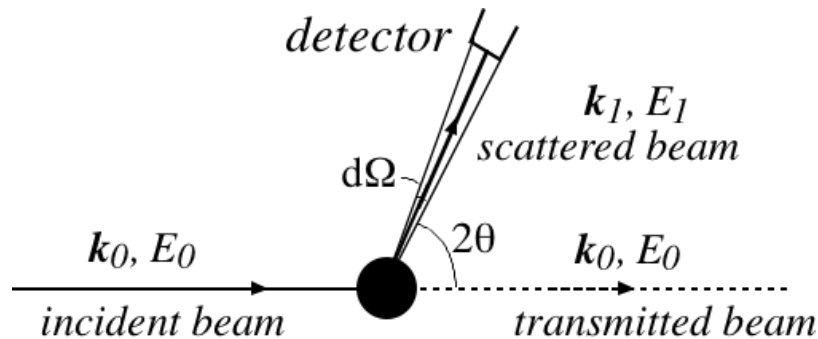
$$S_{inc}(q, \omega) = \int_{-\infty}^{\infty} \exp^{-i\omega t} \sum_{i=1}^N \left\langle \exp^{-iq \cdot r_i(0)} \exp^{iq \cdot r_i(t)} \right\rangle dt$$

Incoherent scattering
(self correlations)

$$\langle b \rangle^2 = \left(\frac{1}{N} \sum_{i=1}^N b_i \right)^2 \quad \text{and} \quad \langle b^2 \rangle = \left(\frac{1}{N} \sum_{i=1}^N b_i^2 \right)$$

$r_i(t)$ - atomic coordinate in the material

Neutron scattering - dynamics

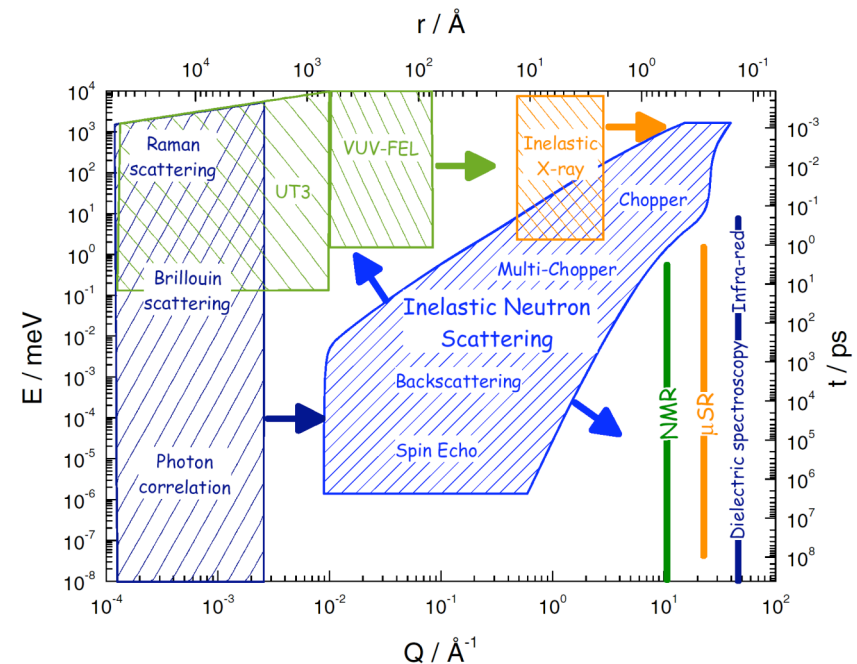


Incident neutron (E_0, k_0) can exchange energy and momentum in the scattering process to (E_1, k_1), $\omega = E_1 - E_0$, $q = k_1 - k_0$ due to interaction with the material

Typical neutron energy: 0.1-100 meV

Typical length scales: 1-1000 Å

- Vibrational dynamics
- Polymer dynamics - e.g. reptation
- Diffusion
- ...



Why neutrons?

Five good reasons:

- i) time and length scales*
- ii) cross sections*
- iii) weak probe*
- iv) high penetration*
- v) magnetic moment*

Why neutrons?

Five good reasons:

i) time and length scales

Probe both structure and dynamics – $\lambda \approx \text{\AA}$, $E \approx \text{meV}$

ii) cross sections

iii) weak probe

iv) high penetration

v) magnetic moment

Why neutrons?

Five good reasons:

i) *time and length scales*

ii) ***cross sections***

The scattering cross-section for neutrons (b) varies randomly through the periodic table and is isotope dependent

iii) *weak probe*

iv) *high penetration*

v) *magnetic moment*

Scattering cross section

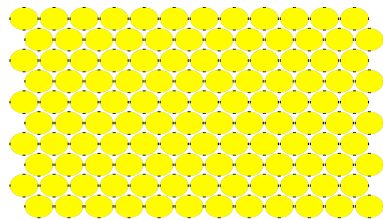
The scattering cross-section for neutrons varies randomly through the periodic table and is isotope dependent (x-rays $\Rightarrow$ Z-dependence)

$\Rightarrow$ distinguish light atoms in a matrix of heavy or atoms of similar Z
 $\Rightarrow$ contrast variation through isotopic substitution (keeping the chemistry)

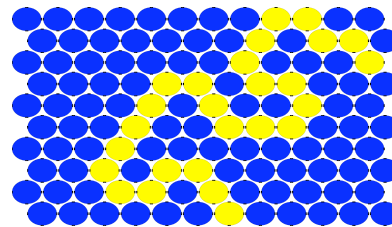
Especially valuable:

H and D have very different scattering cross sections

H:	$\sigma_{\text{coh}}=1.8$	$\sigma_{\text{inc}}=80.2$	(10^{-28} m^2)
D:	$\sigma_{\text{coh}}=5.6$	$\sigma_{\text{inc}}=2.0$	



H-polymer in H₂O



D-polymer in H₂O

Why neutrons?

Five good reasons:

i) *time and length scales*

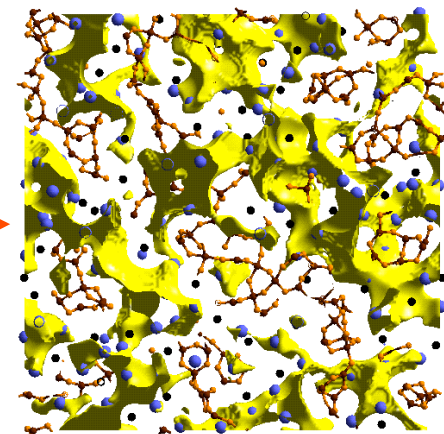
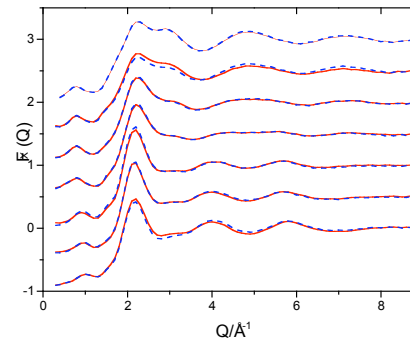
ii) *cross sections*

iii) **weak probe**

iv) *high penetration*

v) *magnetic moment*

The neutron is a weak probe - easy to model the scattering from computer simulation or theoretical calculations



reverse Monte Carlo model of glass structure from diffraction data

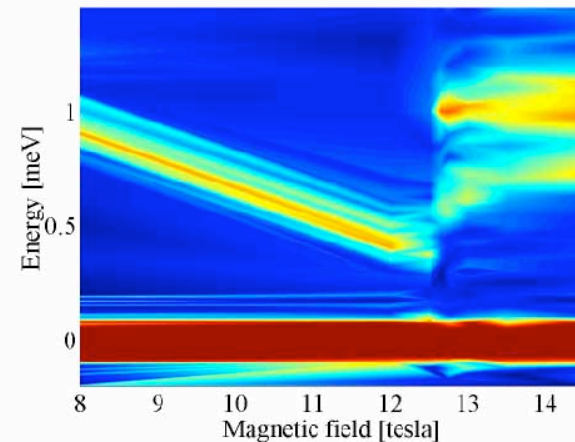
Why neutrons?

Five good reasons:

- i) time and length scales*
- ii) cross sections*
- iii) weak probe*
- iv) high penetration***
- v) magnetic moment*



Complex sample environment/
Extreme conditions
M: 0-15 T, T: mK-kK, P:



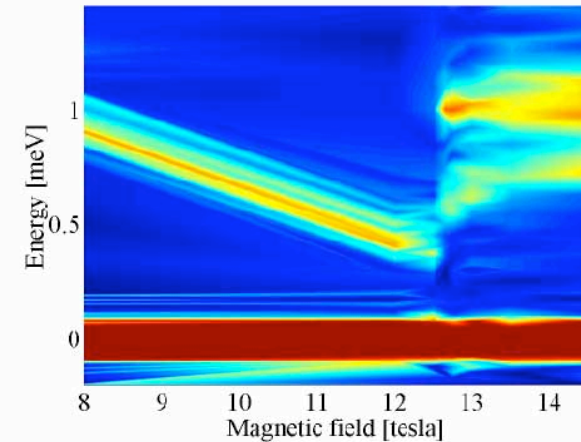
Why neutrons?

Five good reasons:

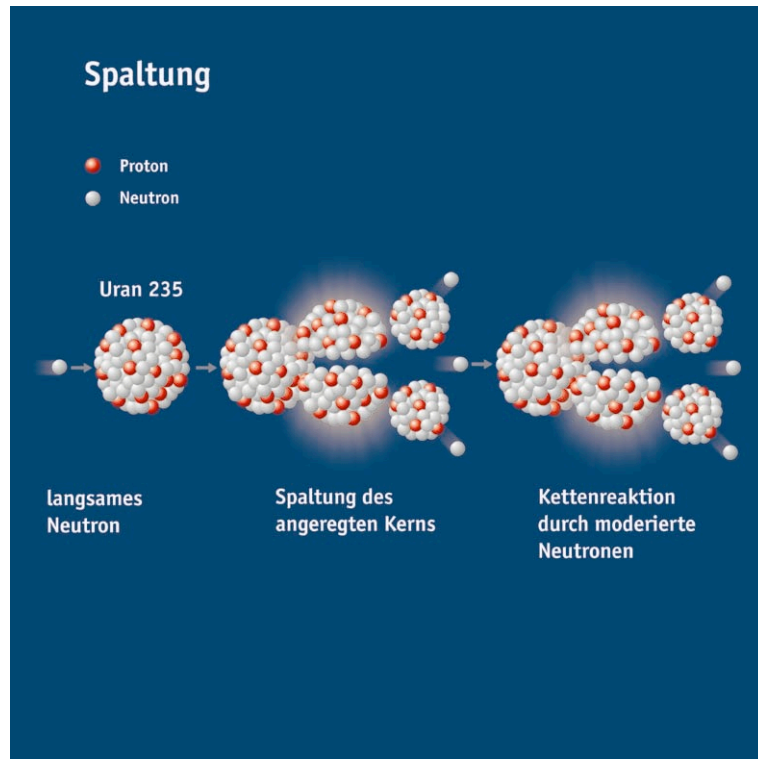
- i) time and length scales*
- ii) cross sections*
- iii) weak probe*
- iv) high penetration*

v) *magnetic moment*

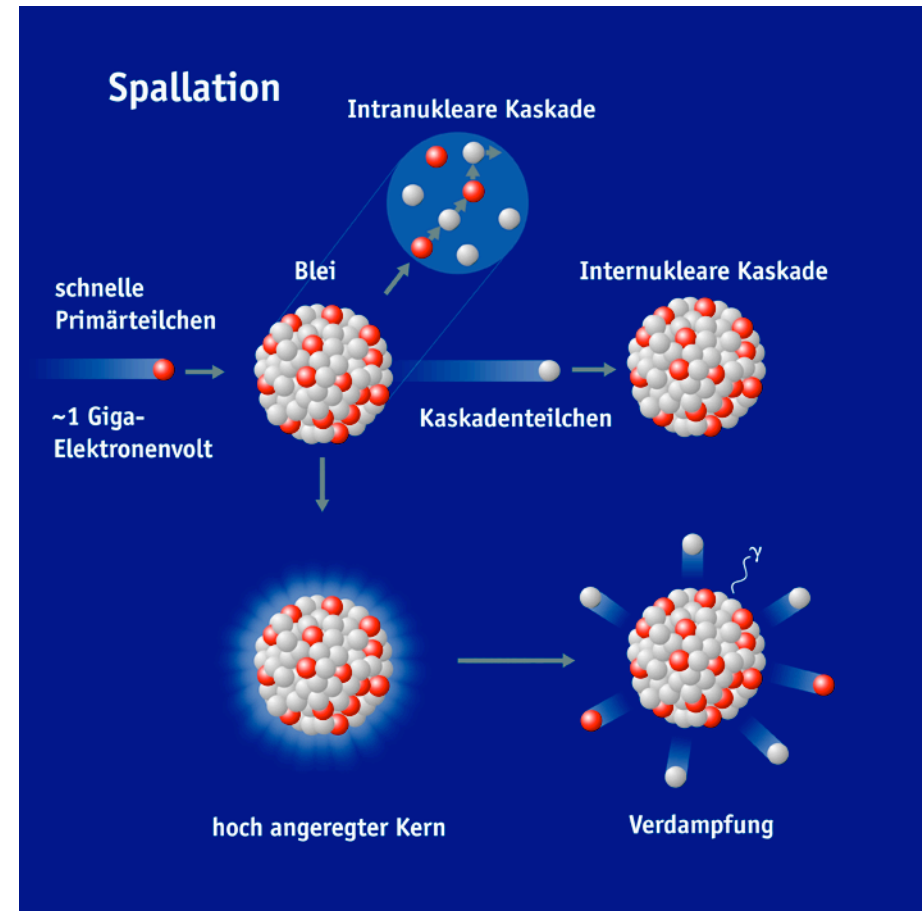
The neutrons have a magnetic moment
⇒ Studies of magnetic structure
and dynamics



Where do we get neutrons?

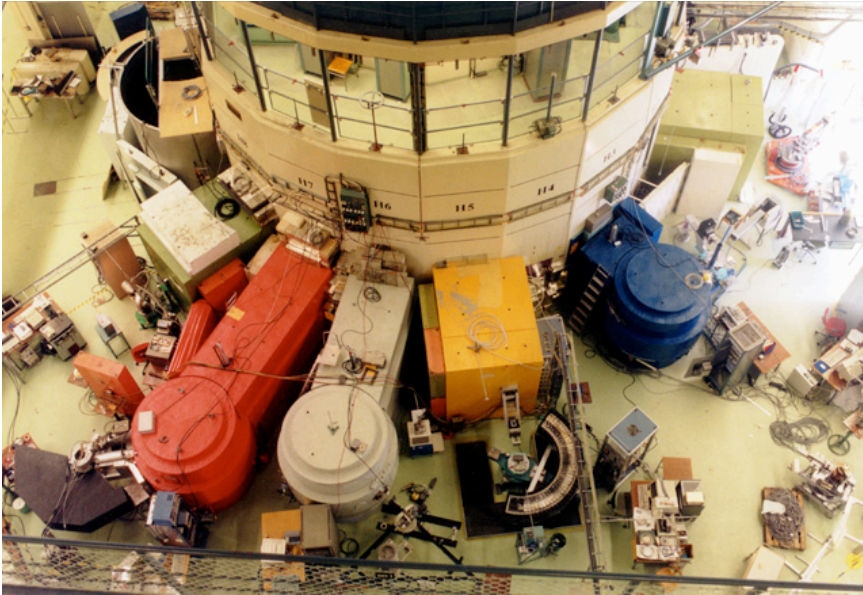


Fission in a nuclear reactor



Bombard heavy nucleus with high energy protons from an accelerator

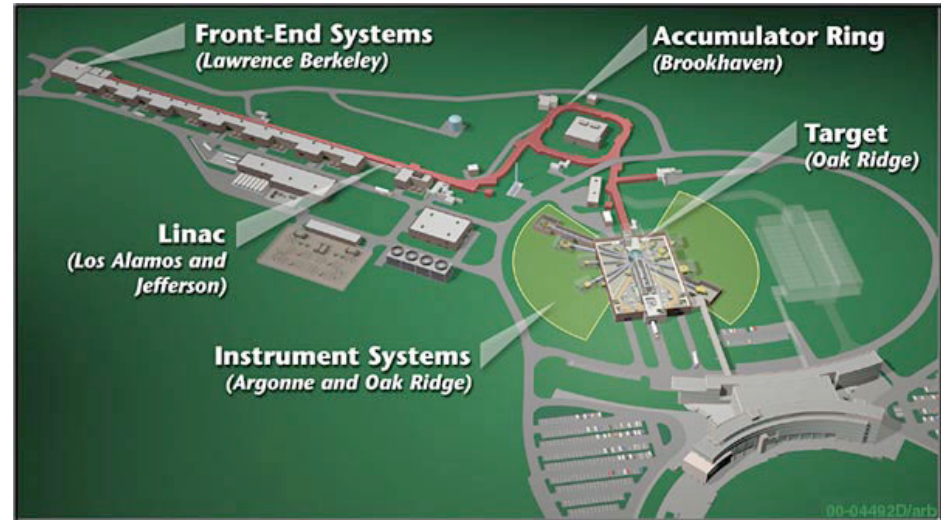
Where do we get neutrons?



Instruments at the Studsvik reactor
(now shut down)



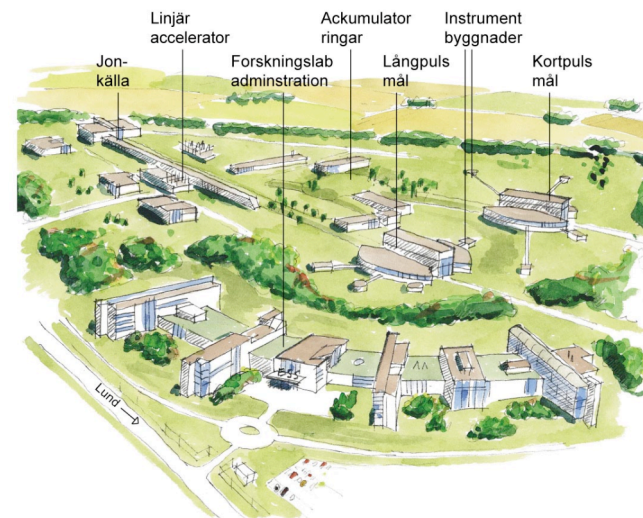
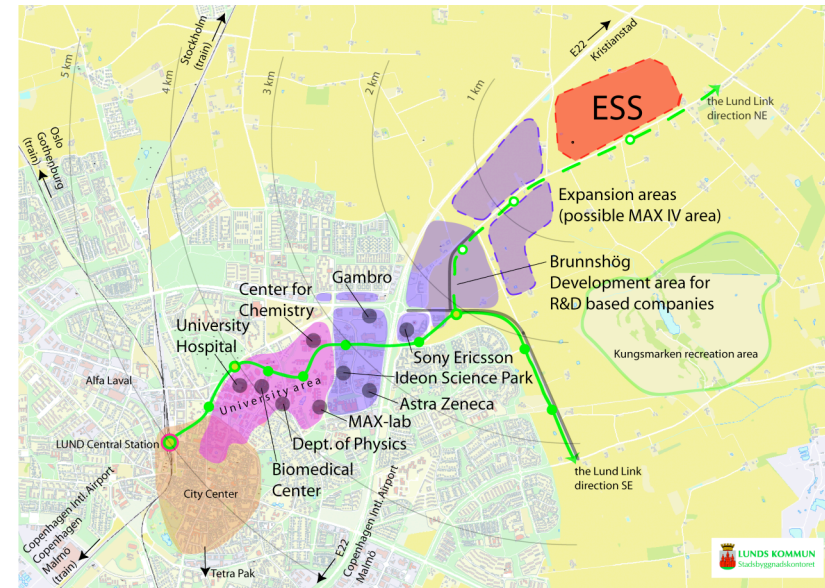
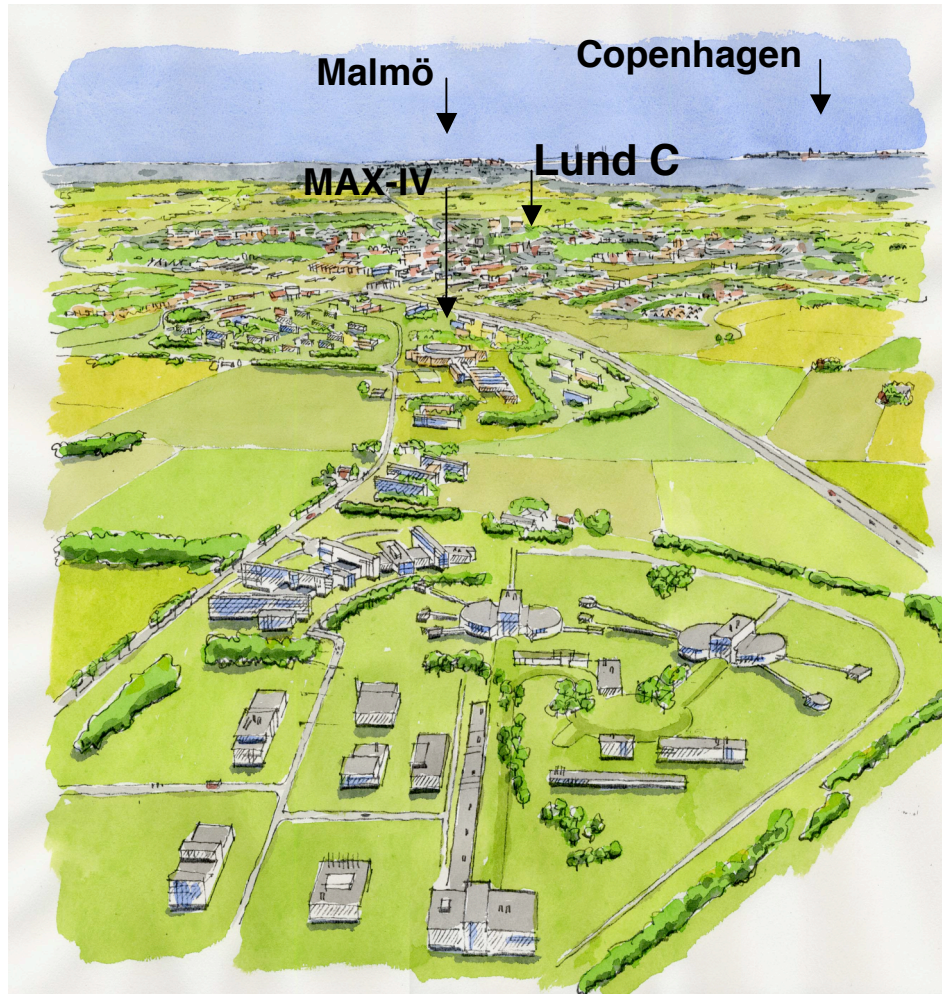
ILL, Grenoble
France



Sketch of spallation neutron source (SNS)

Also sources in UK and Japan

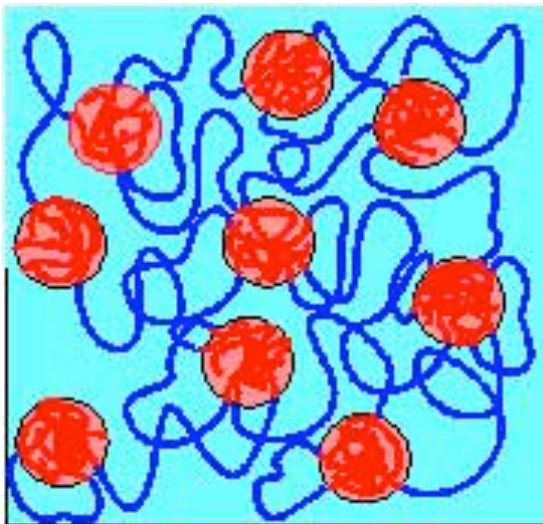
European Spallation Source in Lund?



Example: Structure under shear

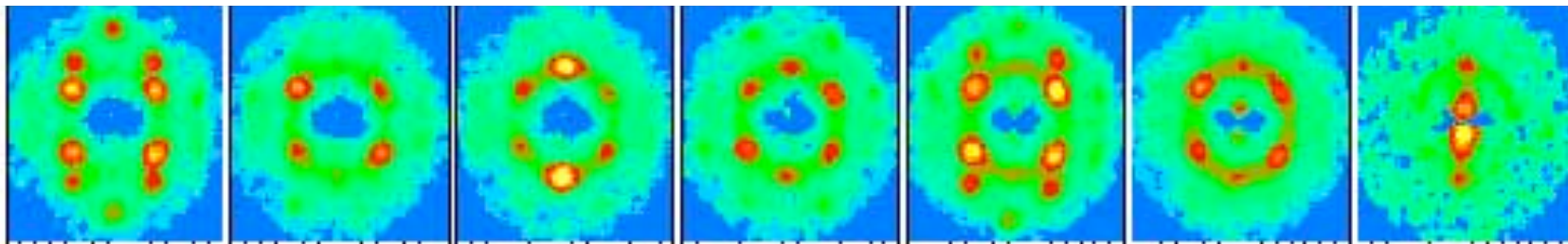
SANS - probes structure on length scales ($Q \approx 0.001 - 0.5 \text{ \AA}^{-1}$)

- radius of gyration
- size of phase separated regions
- size and shapes of pores in porous structures



Example (from Risø):

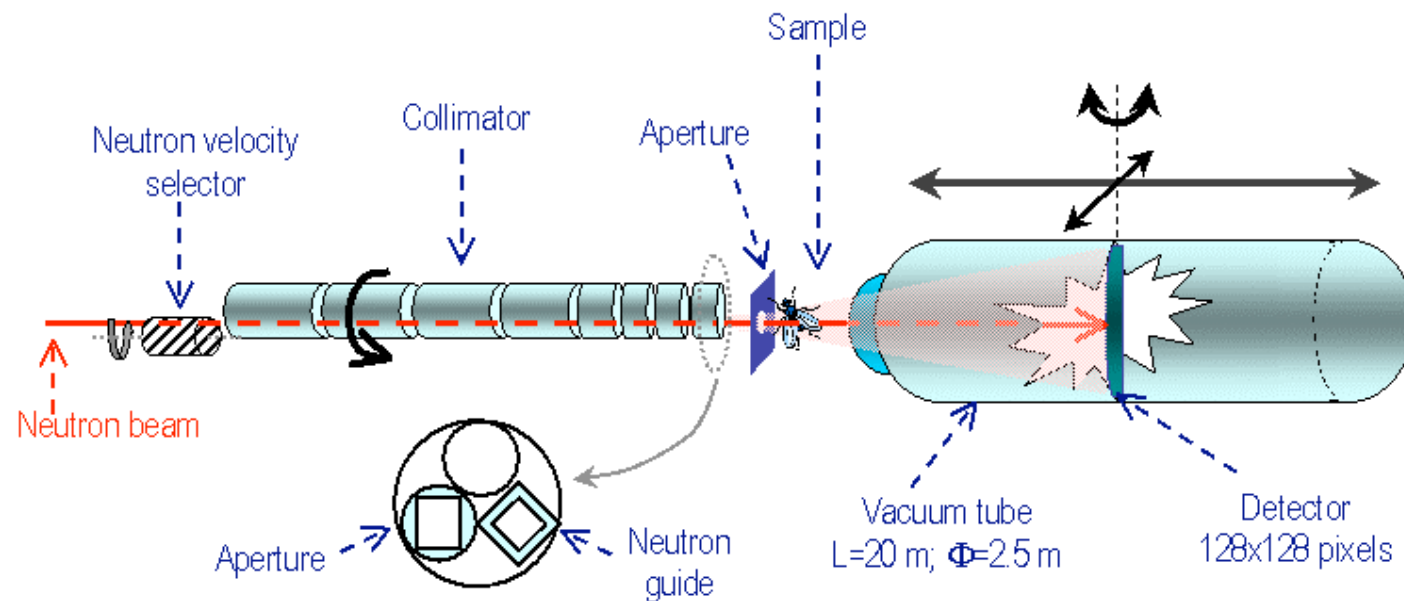
Neutron experiments in a shear cell to simulate processing conditions



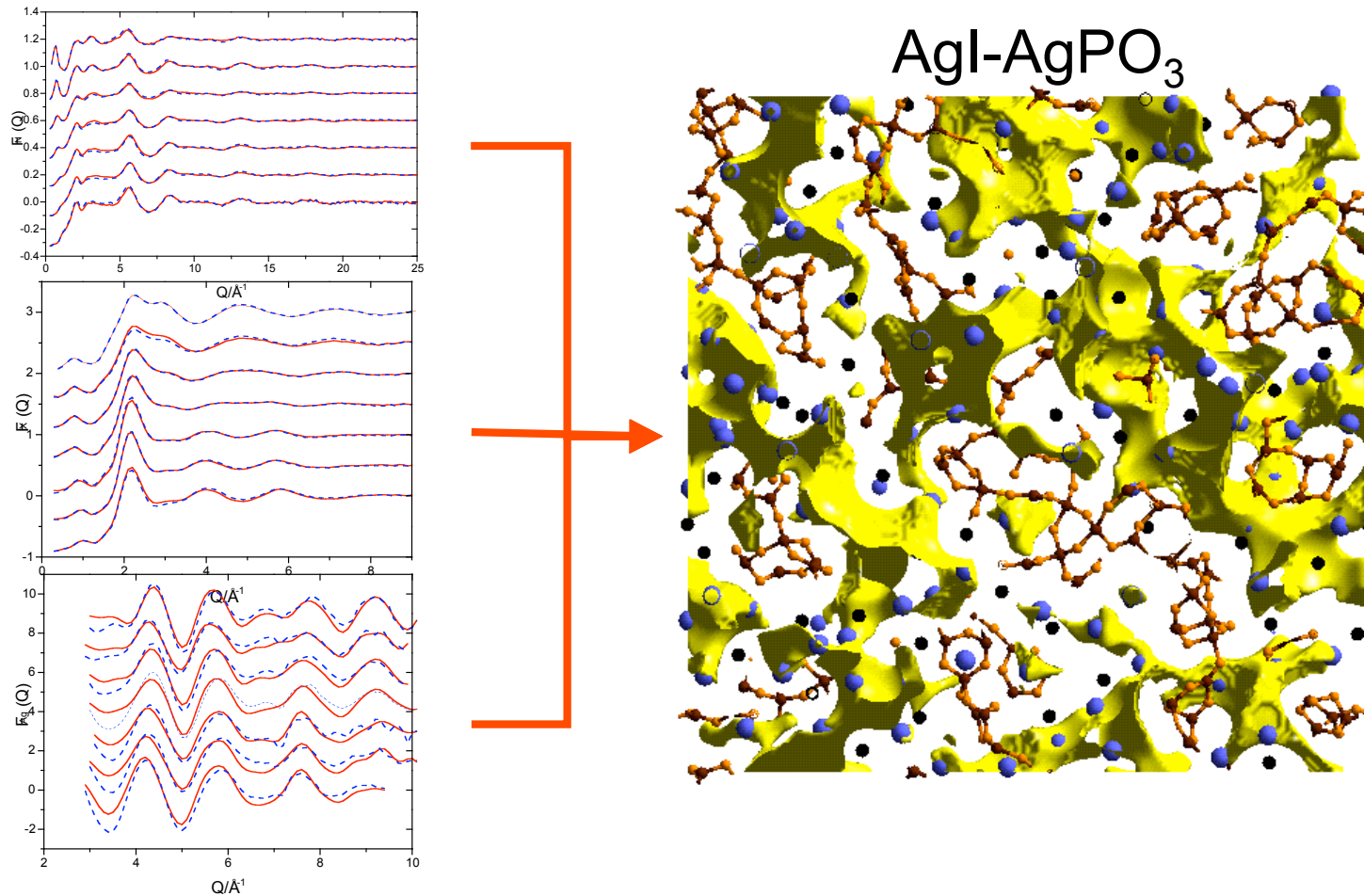
Small angle scattering

SANS - probes structure on length scales ($Q \approx 0.001 - 0.5 \text{ \AA}^{-1}$)

- radius of gyration
- size of phase separated regions
- size and shapes of pores in porous structures



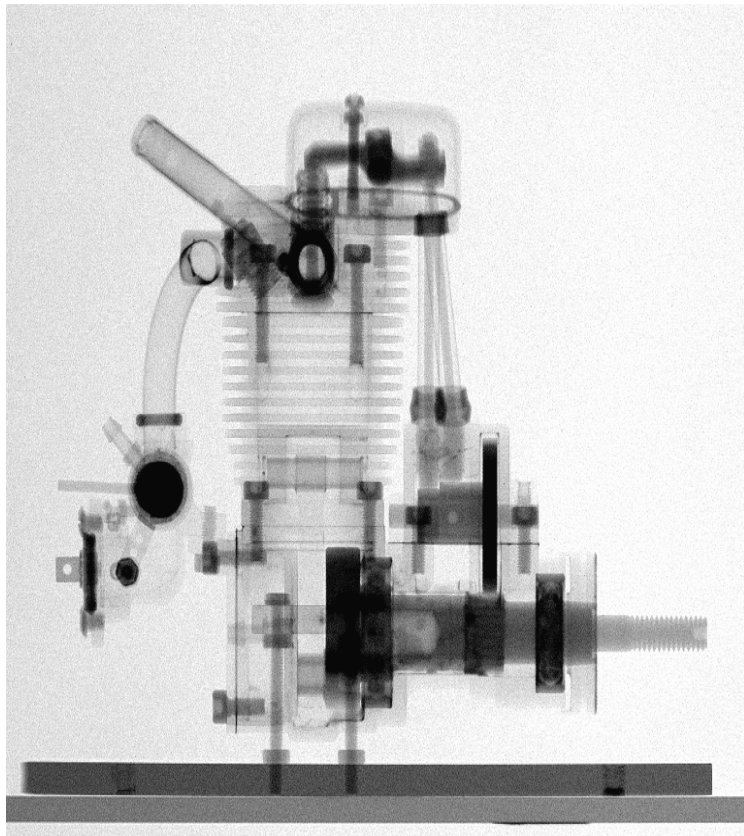
Example: Glass structure



Combination of ND, xrd, EXAFS and RMC to obtain a structural model

Example: Tomography

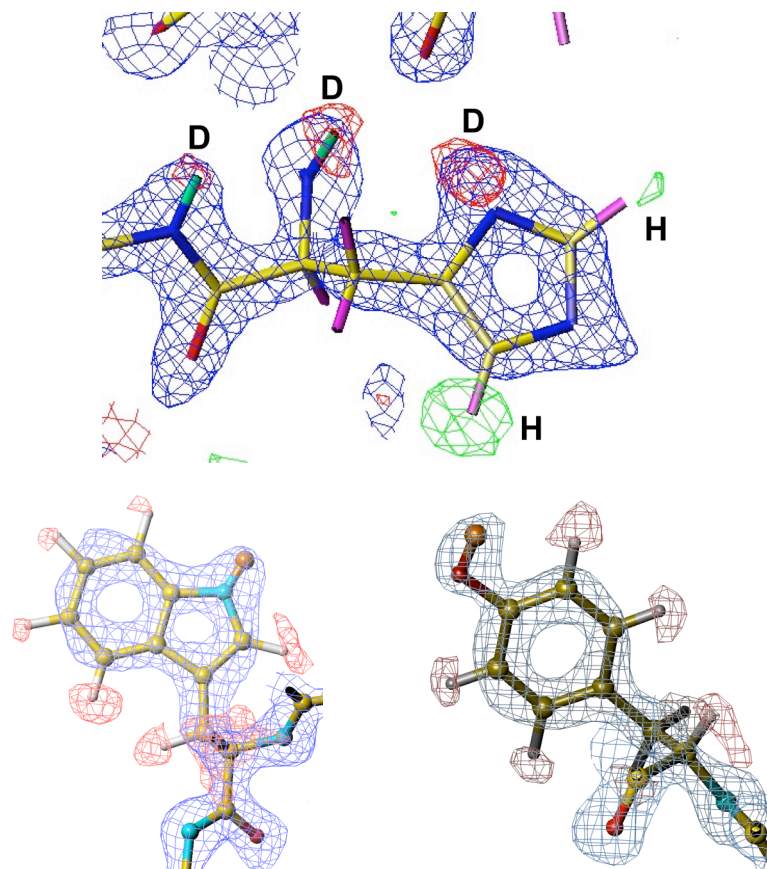
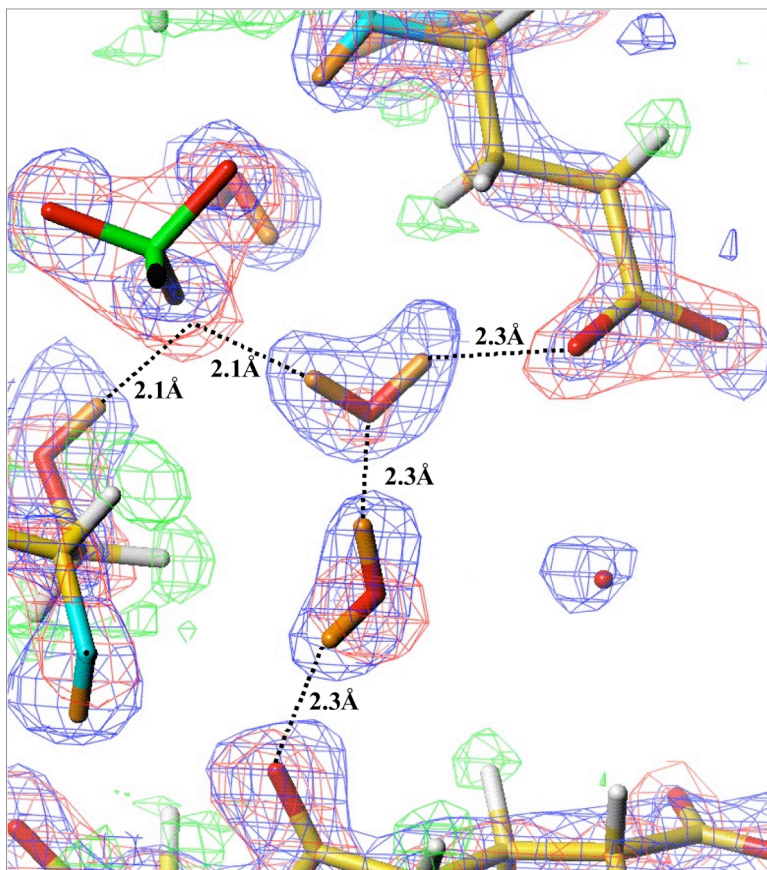
Real materials-Real Conditions-Real Time



Tomography

- ➡ *large field*
- ➡ *submillimeter resolution*
- ➡ *TOF structural mapping*

Example: Locating hydrogens



$$\begin{array}{ll} \text{H:} & \sigma_{\text{coh}}=1.8 \quad \sigma_{\text{inc}}=80.2(10^{-28} \text{ m}^2) \\ \text{D:} & \sigma_{\text{coh}}=5.6 \quad \sigma_{\text{inc}}=2.0 \end{array}$$

Example: Old stuff

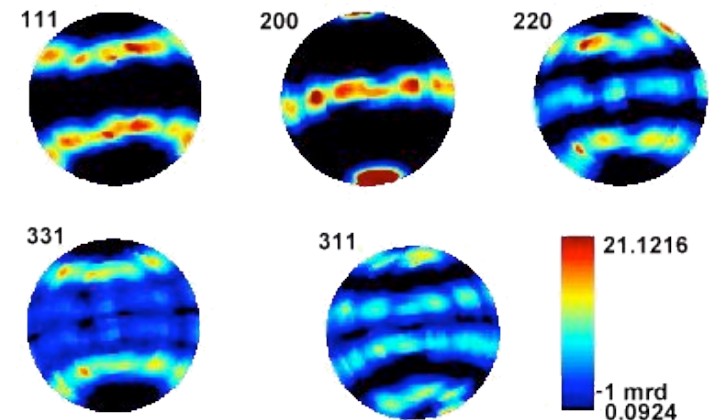


Copper axe (3.200 bc), iceman (Ötztal)

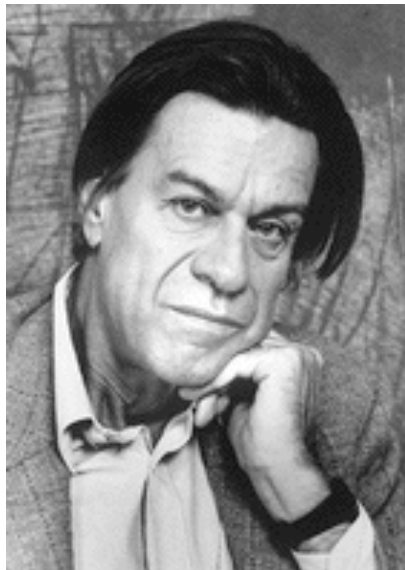
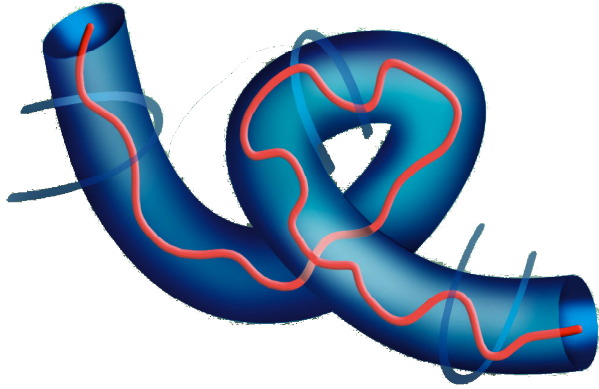


Ancient manufacturing history

- Heat treatment
- Mechanical treatment

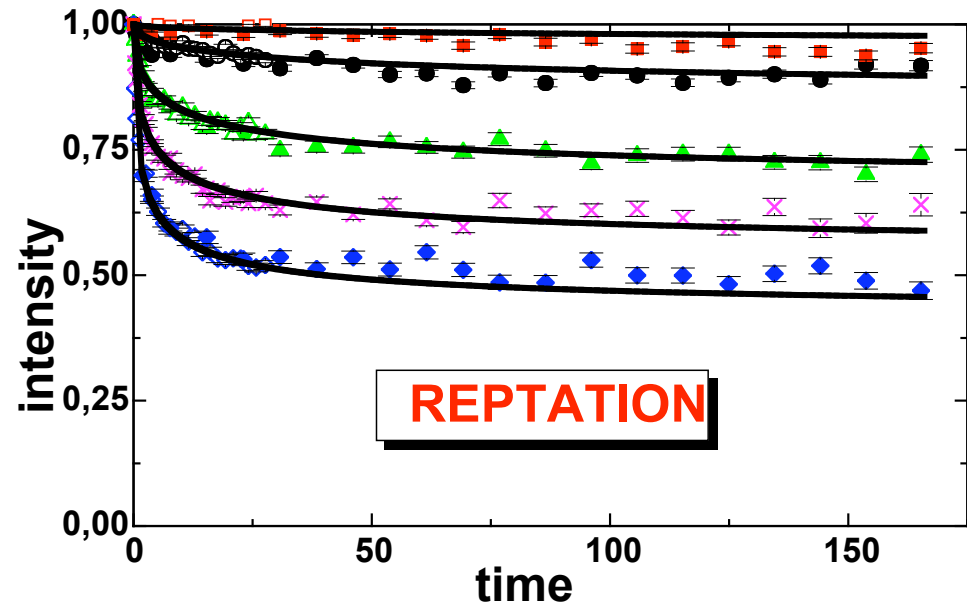


Dynamics - reptation model



P.G. De Gennes
ESPCI Paris
France

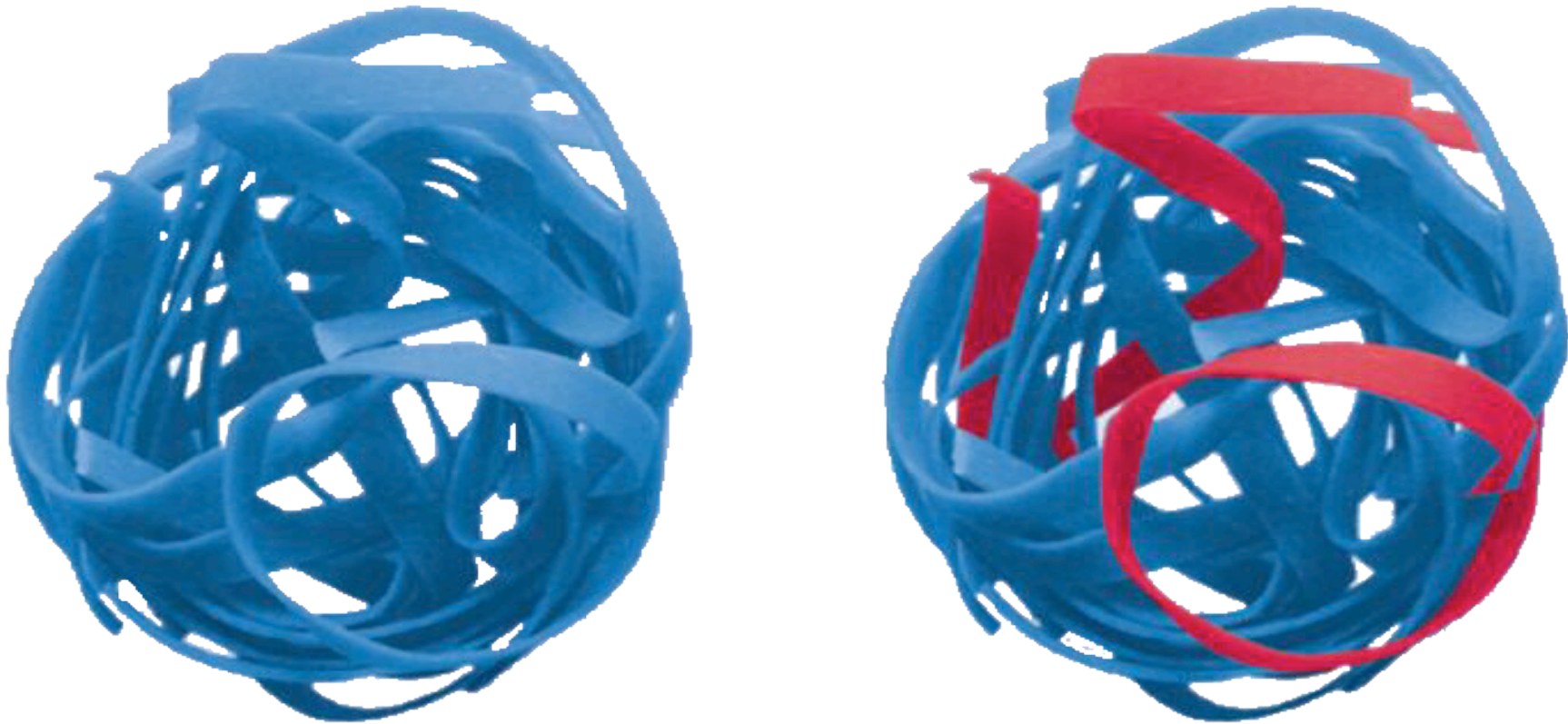
Nobel prize
1991



Confirmation by
Neutron Scattering
(NSE)

Contrast variation

Partial H-D substitution

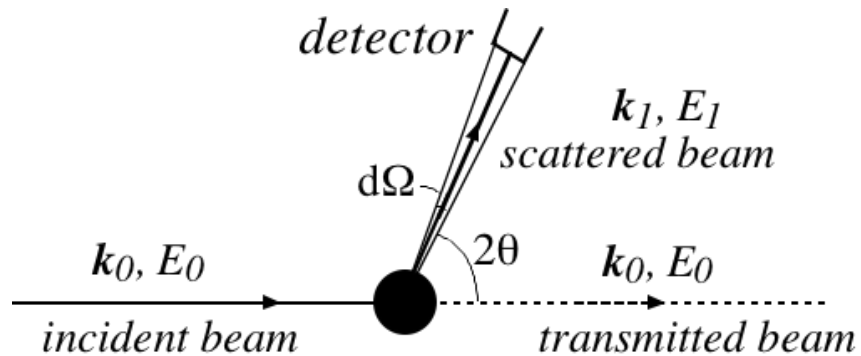


Isotopic contrasting in a polymer

Experimental techniques

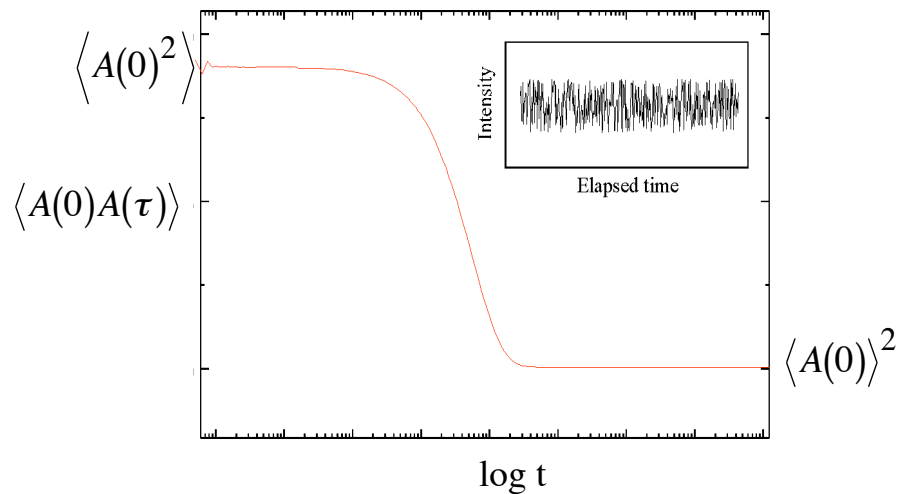
- General
- Fluctuations - correlation functions
- Scattering techniques - general aspects/theory
 - ⇒ Neutron scattering
 - ⇒ **Light scattering**
 - Raman/IR spectroscopy
 - **Photon correlation spectroscopy**

Scattering experiment



Scattering of particles:

- Neutrons
- electrons
- **photons: 1-1000 Å**
- ...



Differ in:

- wavelength
- interaction mechanism
- cross section
- detection
- resolutions
- ...

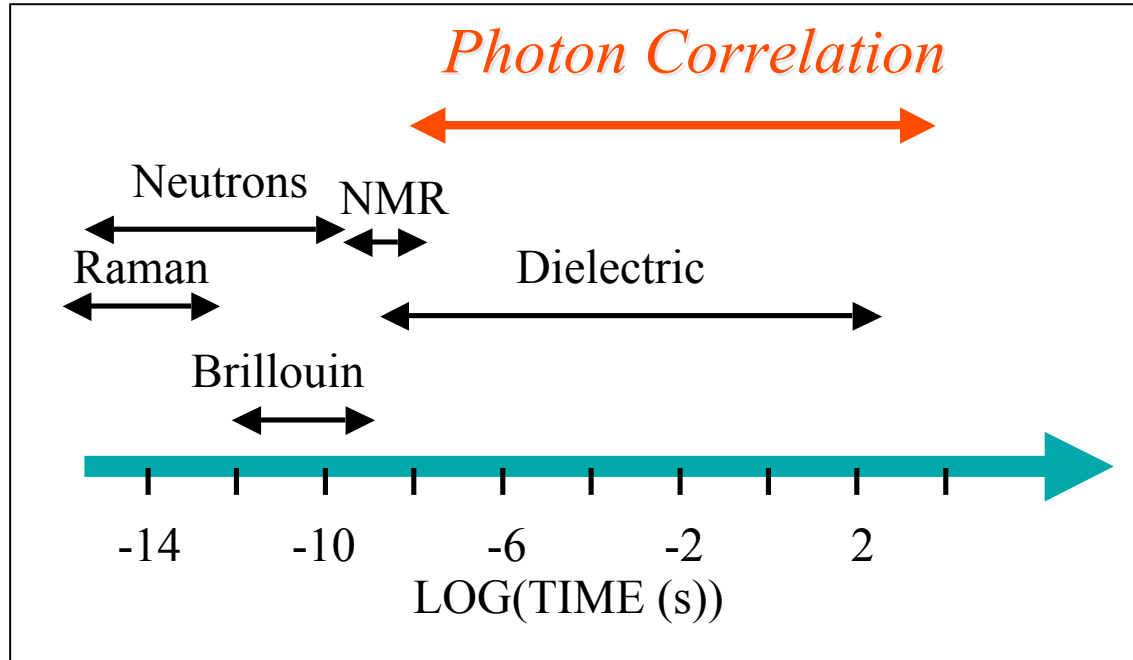
Photon Correlation Spectroscopy or dynamic light scattering

Laser spectroscopy to study dynamics in soft matter

Three examples:

- Determining particle size 5-1000 nm
- Radius of gyration and critical concentration in polymer solutions
- Glass transition dynamics - T_g and fragility

Time and Q range of PCS



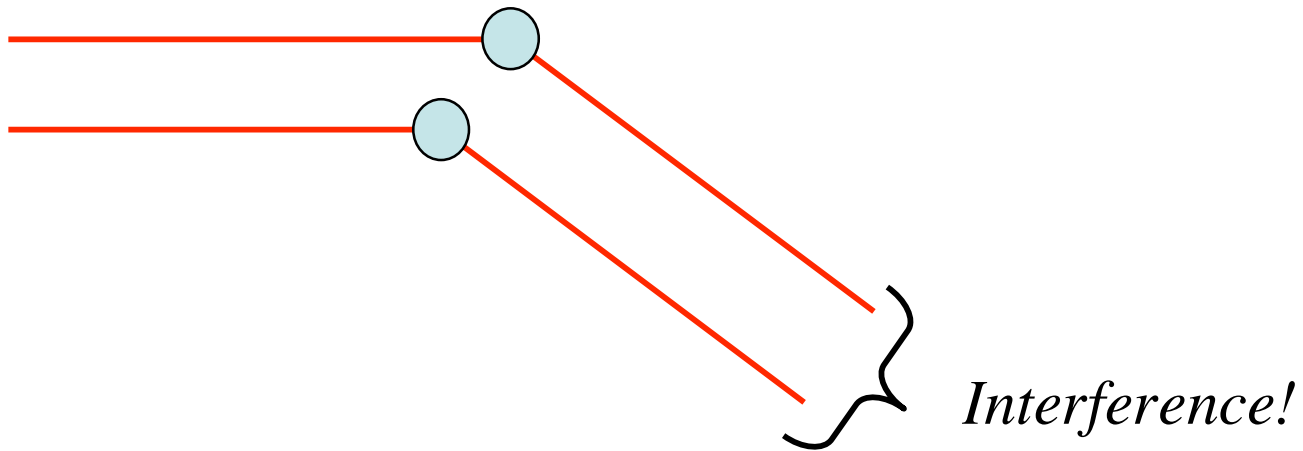
*PCS covers a
large time range!
 $t \approx 10^{-8} - 10^3$ s*

Visible light $\Rightarrow$ Q-range:

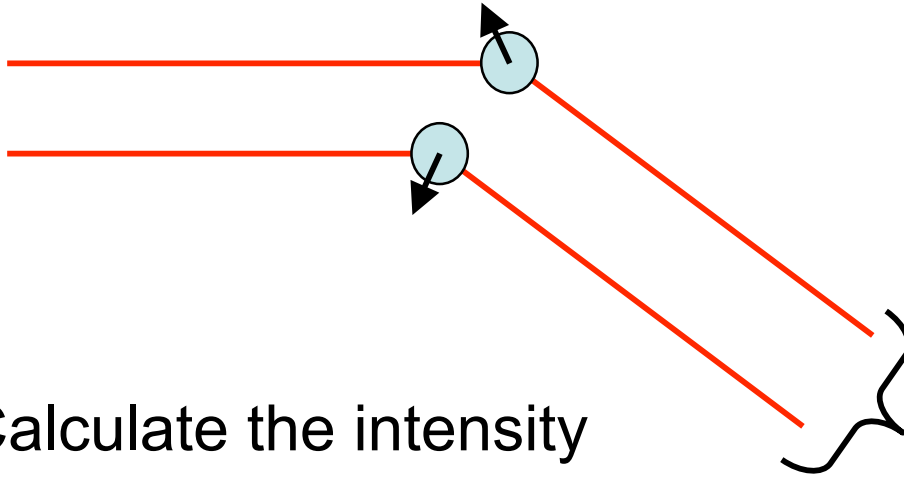
$$Q = 4\pi \sin(\theta/2) / \lambda \sim 10^{-3} \text{ \AA}^{-1}$$

$\Rightarrow$ length scales: $r \sim \mu\text{m}$

Dynamic light scattering



Dynamic light scattering



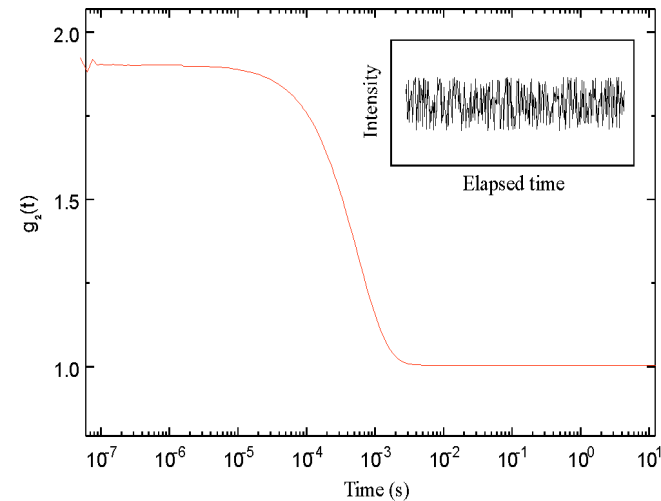
Calculate the intensity correlation function:

$$\langle I(t)I(t+\tau) \rangle = \frac{1}{N} \sum_{i=1}^N I(t_i)I(t_i+\tau)$$

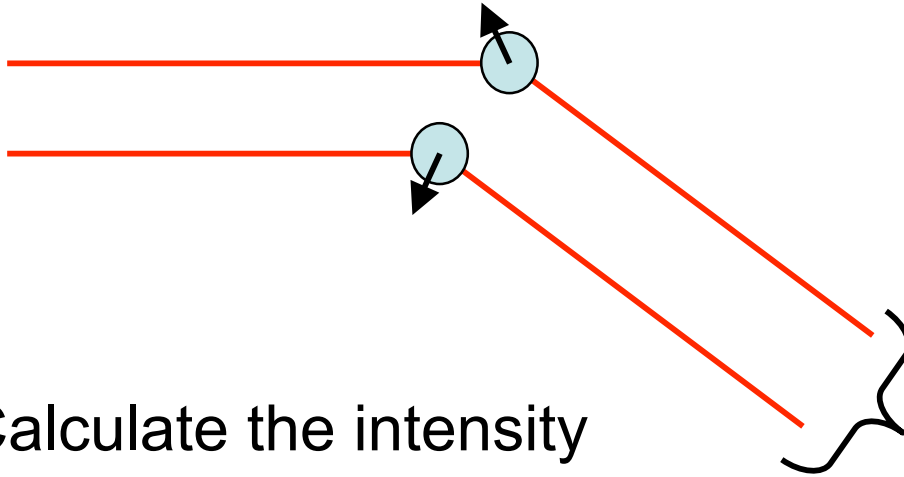
$$\lim_{\tau \rightarrow 0} \langle I(t)I(t+\tau) \rangle = \langle I^2(t) \rangle$$

$$\lim_{\tau \rightarrow \infty} \langle I(t)I(t+\tau) \rangle = \langle I(t) \rangle^2$$

Time-dependent interference!



Dynamic light scattering



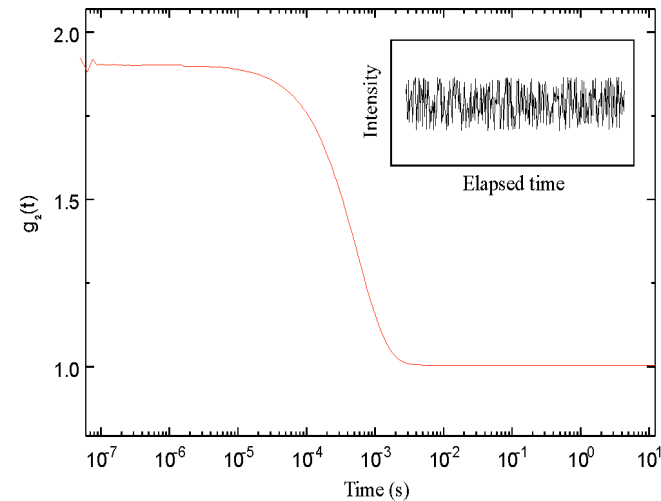
Calculate the intensity correlation function:

$\langle I(t)I(t + \tau) \rangle \Rightarrow \langle I(0)I(t) \rangle$ start time not important

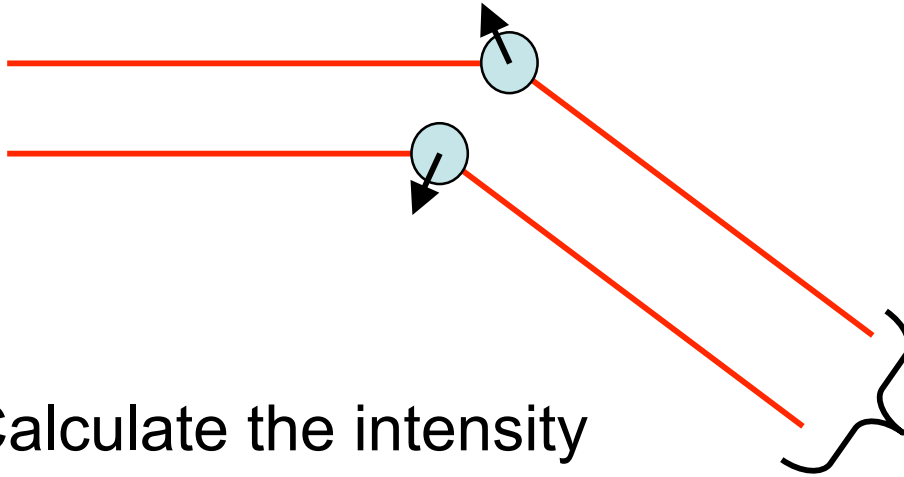
Normalized intensity auto - correlation function

$$g_2(t) = \frac{\langle I(0)I(t) \rangle}{\langle I(t) \rangle^2}$$

Time-dependent interference!



Dynamic light scattering



Calculate the intensity correlation function:

$$\langle I(t)I(t+\tau) \rangle \Rightarrow \langle I(0)I(t) \rangle \text{ start time not important}$$

Normalized intensity auto-correlation function

$$g_2(t) = \frac{\langle I(0)I(t) \rangle}{\langle I(t) \rangle^2}$$

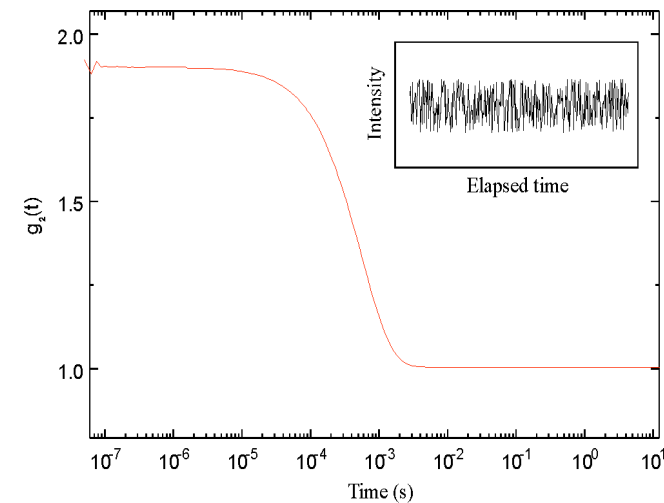
$$g_2(t) = \frac{\langle I(0)I(t) \rangle}{\langle I(t) \rangle^2}$$

short times - no decorrelation, $g_2(t) = 2$

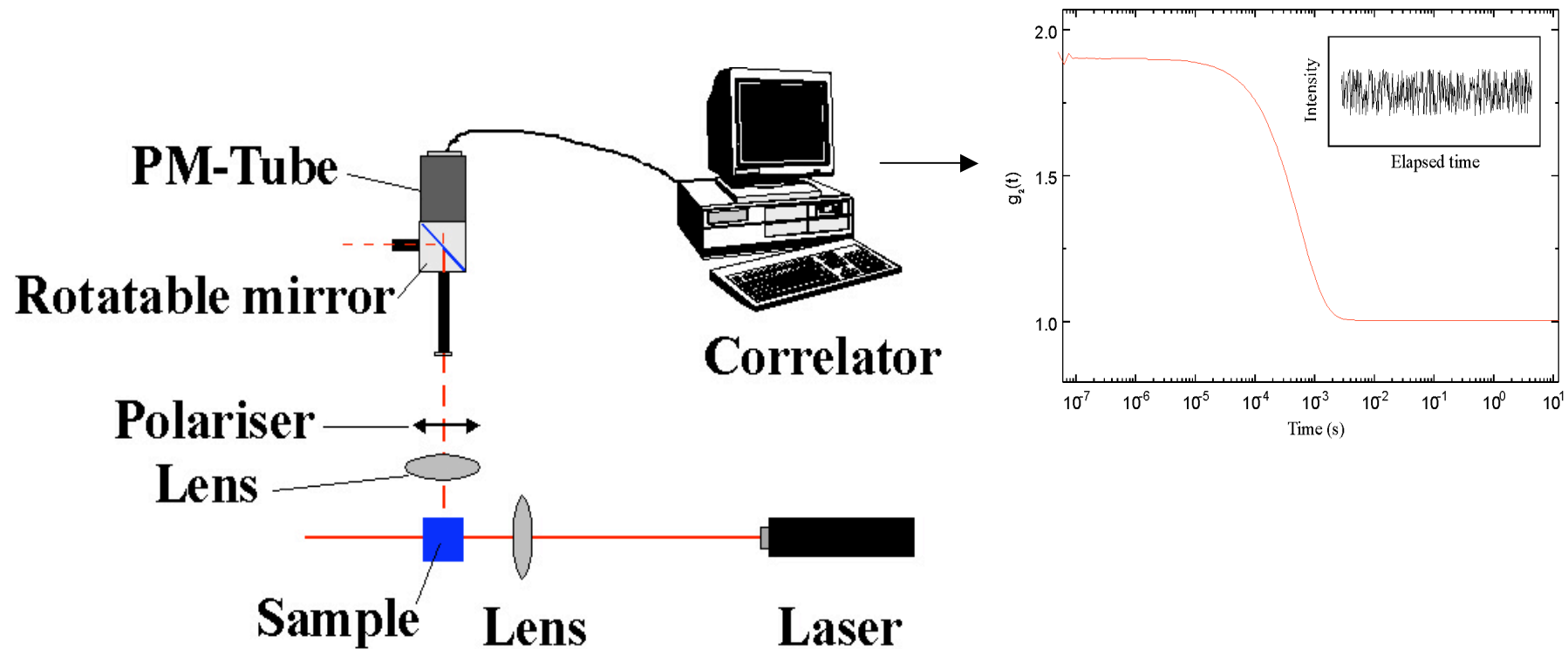
long times - total decorrelation, $g_2(t) = 1$

$$g_1(t) = \frac{\langle E^*(0)E(t) \rangle}{\langle E(t) \rangle^2}, \quad g_2(t) = 1 + \sigma |g_1(t)|^2$$

Time-dependent interference!



Schematic set-up for PCS



Determining particle size

Brownian motion of particles in a solution -> Stokes-Einstein equation

$$D = \frac{k_B T}{6\pi\eta r}$$

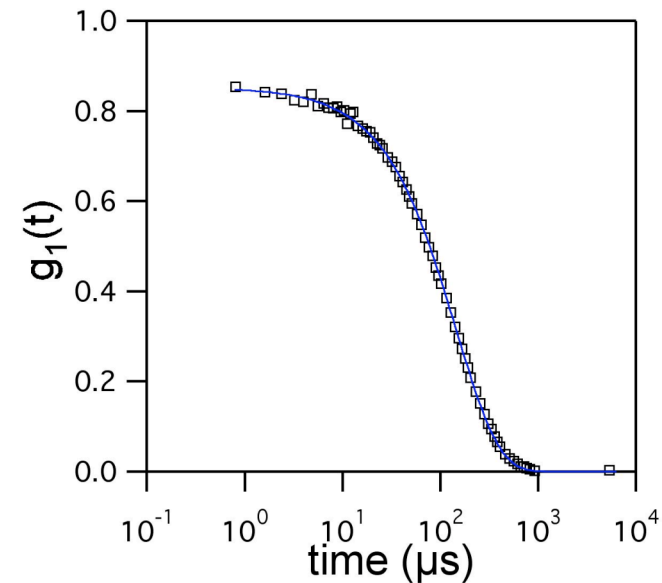
- D diffusion constant
- T temperature
- η viscosity of solvent
- r radius of particles

For mono-disperse particles:

$$g_1(t) = \exp\left(\frac{-t}{\tau}\right), \quad \tau_q = \frac{1}{Dq^2} \quad \text{for free diffusion}$$

$$q = \frac{4\pi n}{\lambda} \sin(\theta/2)$$

$$\Rightarrow \tau_q = \frac{6\pi\eta r}{k_B T q^2} \quad \text{or} \quad r = \frac{\tau_q k_B T q^2}{6\pi\eta}$$



Determining particle size

Brownian motion of particles in a solution -> Stokes-Einstein equation

$$D = \frac{k_B T}{6\pi\eta r}$$

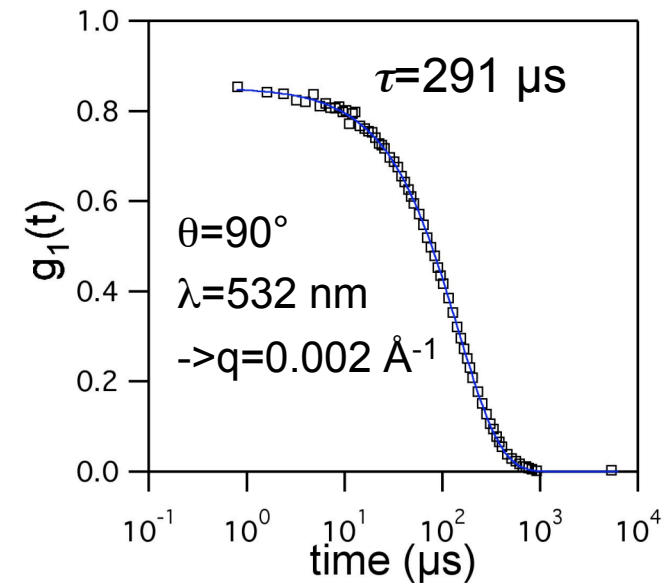
- D diffusion constant
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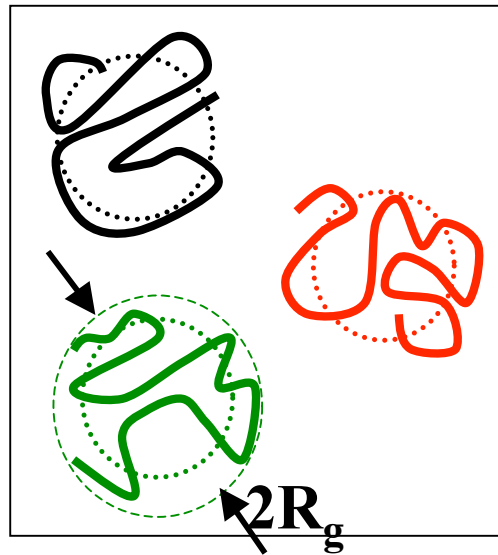
Polystyrene sphere in water:

$n=1.33$, $\eta=0.89 \cdot 10^{-3}$ Pas, $T=293$ K

-> $r=28$ nm

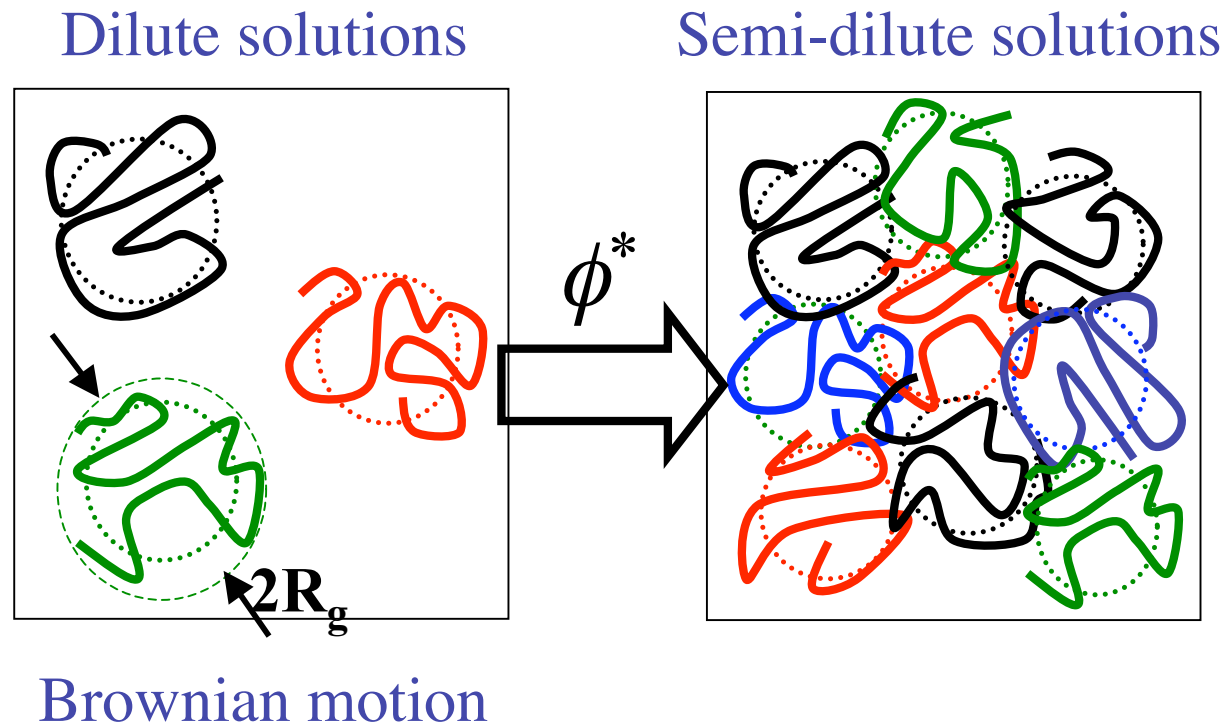
Polymer Dynamics

Dilute solutions

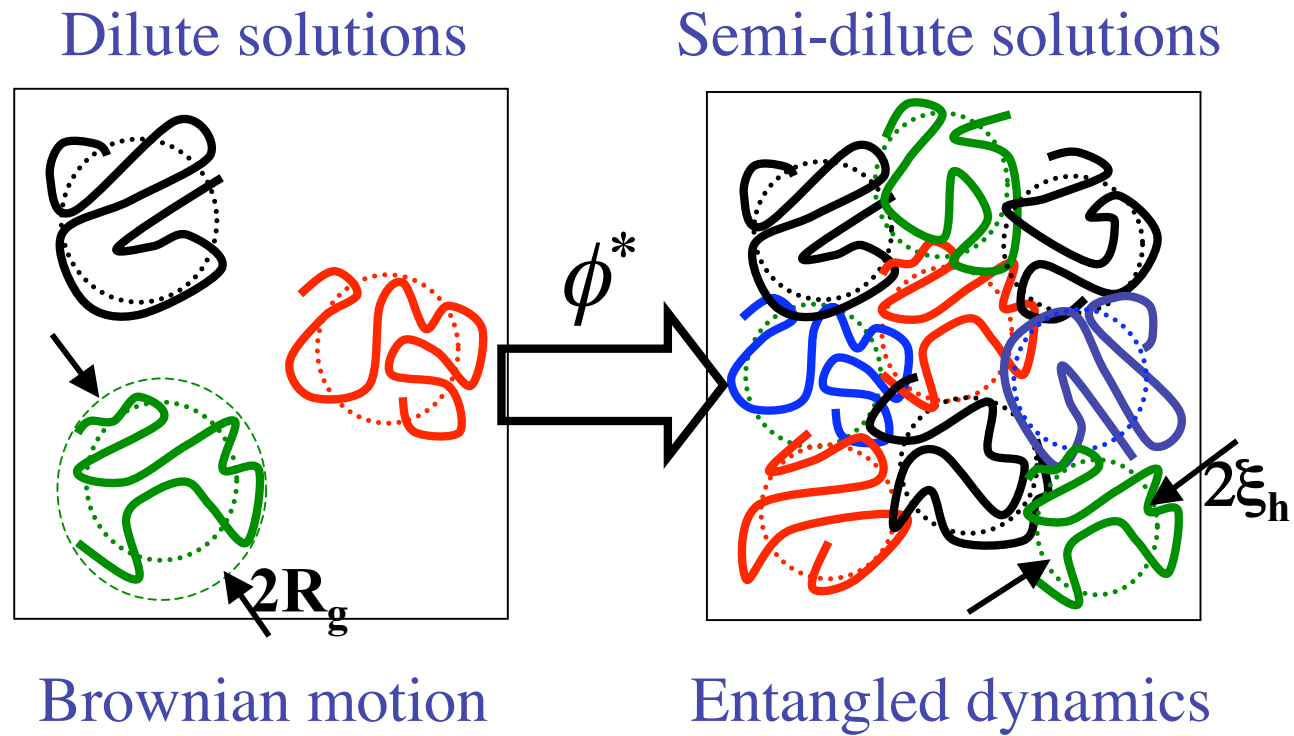


Brownian motion

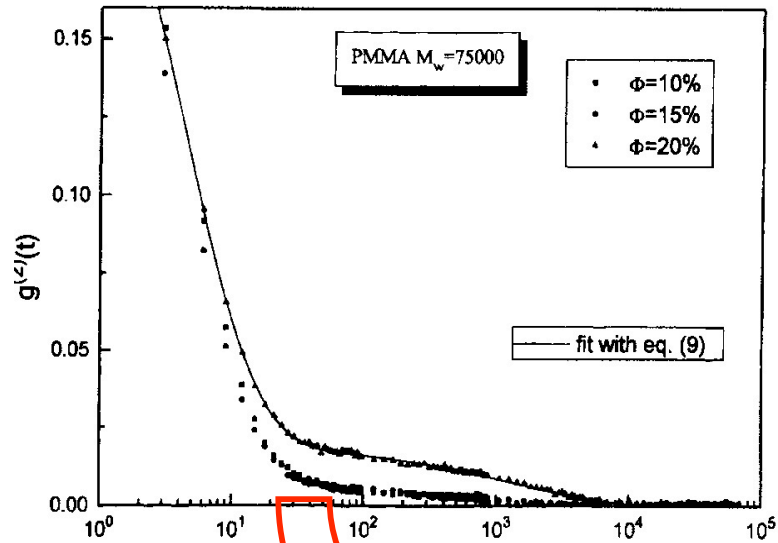
Polymer Dynamics



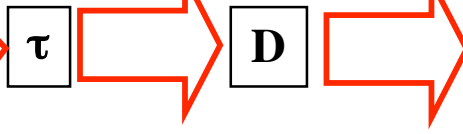
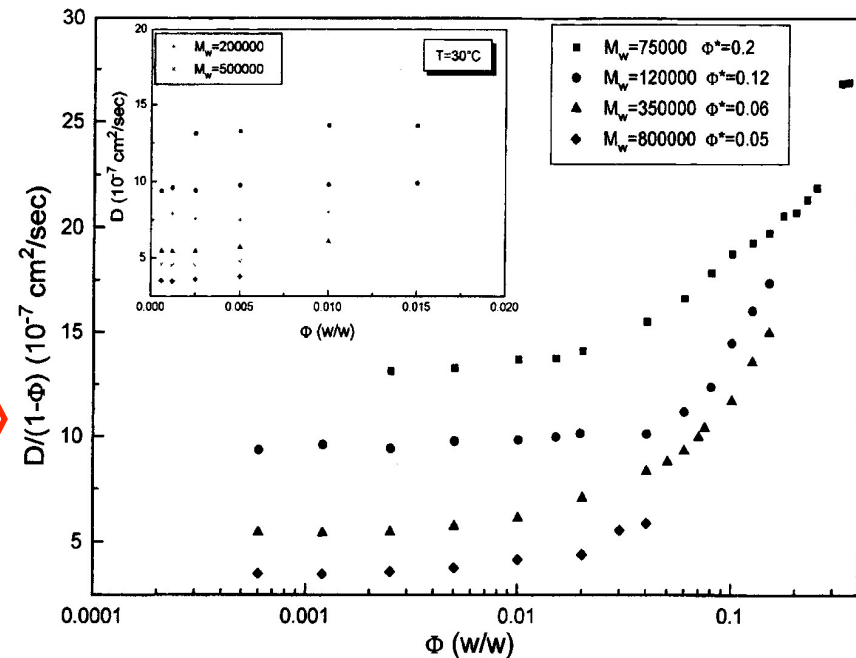
Polymer Dynamics



Determining R_g and ϕ_c from PCS



PCS experiment on PMMA/acetone solutions

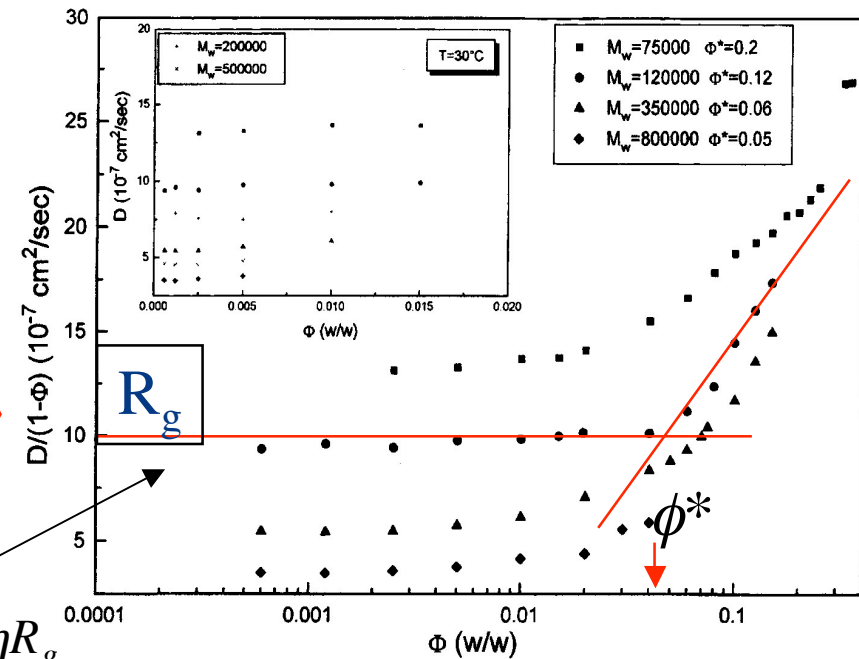
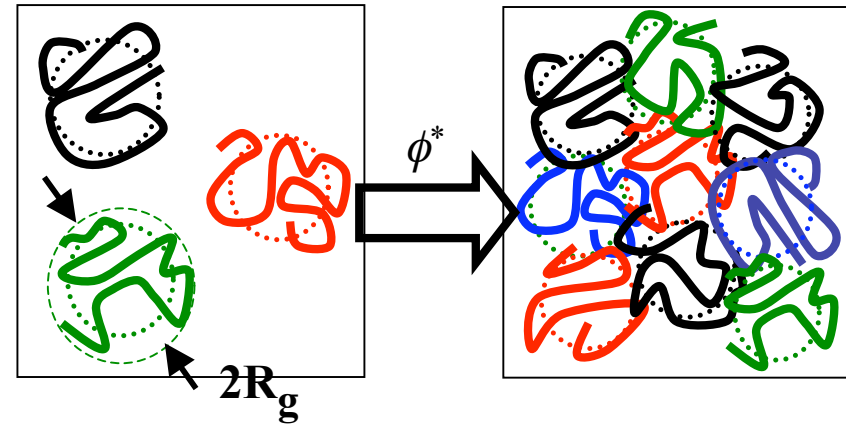
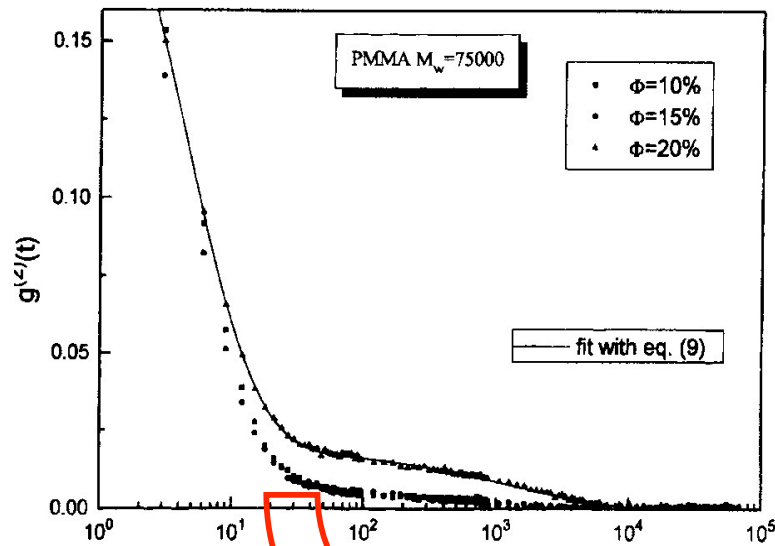


Obtain diffusion coefficient by measuring the relaxation time for several q

$$\tau_q = \frac{1}{Dq^2}$$

A. Faraone *et al.* *Macromolecules* **1999**, 32, 1128

Determining R_g and ϕ_c from PCS



Calculate radius of gyration from the diffusion coefficient

$$\tau_q = \frac{1}{Dq^2}$$

$$\tau_q = \frac{6\pi\eta R_g}{k_B T q^2}$$

Glass transition dynamics

a glass forming polymer - poly(propylene glycole)

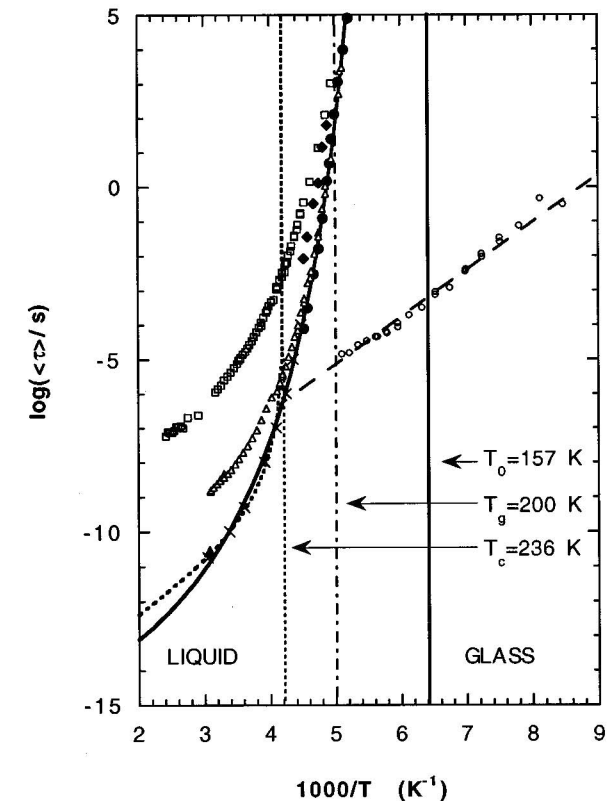
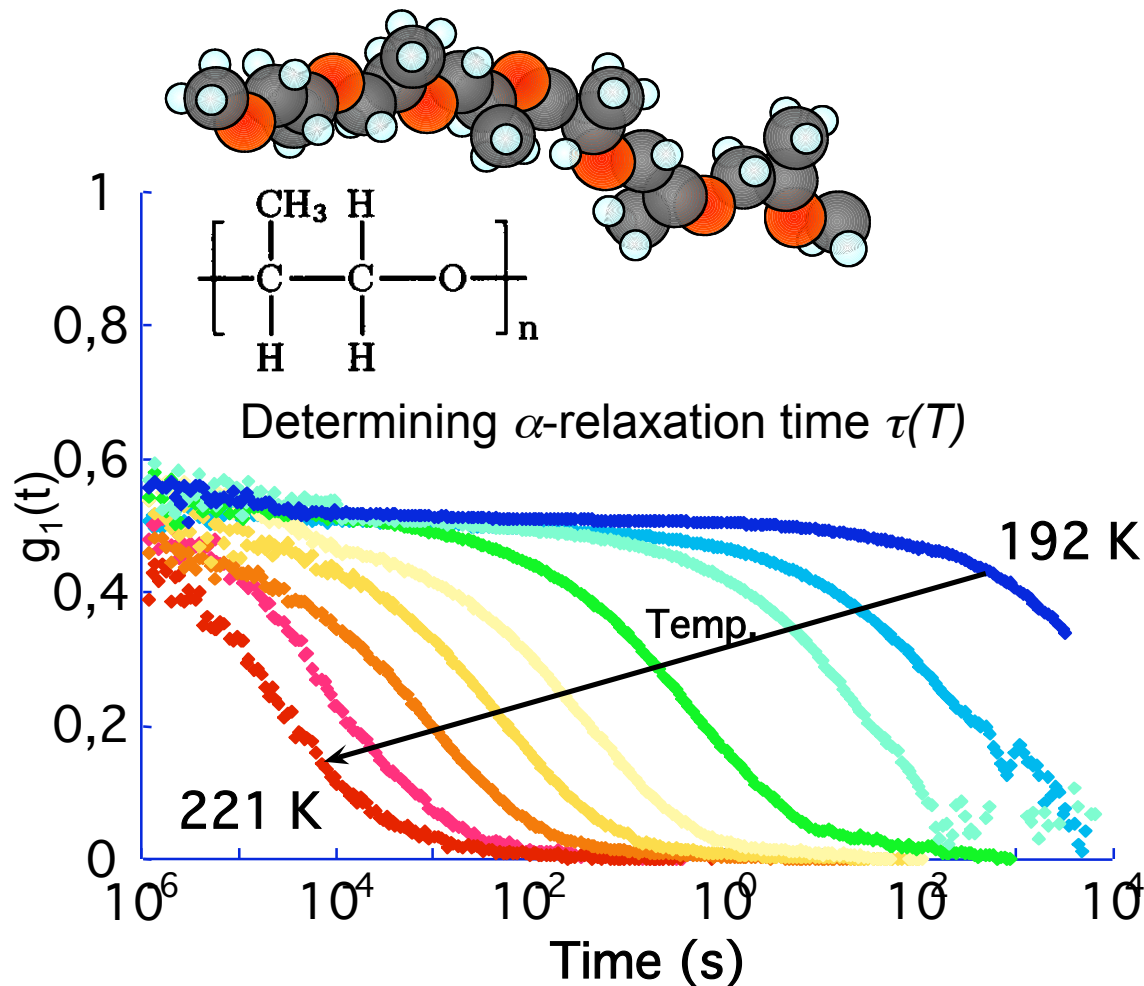
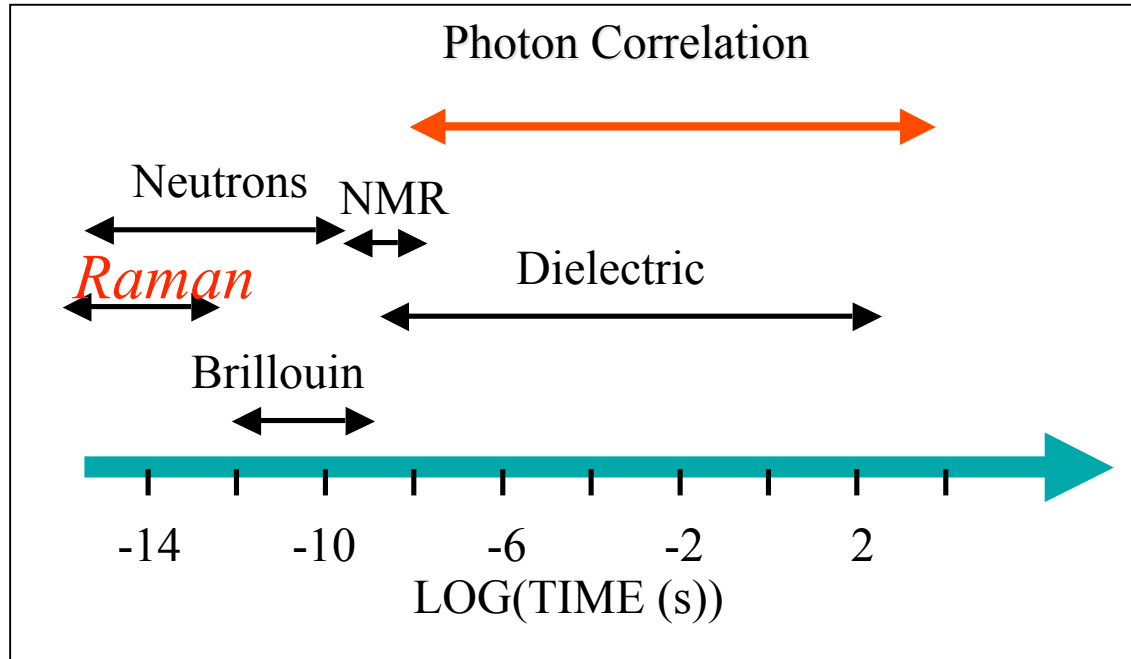


FIG. 4. Arrhenius plot of the mean relaxation times for PPG 300). Photon correlation data for the main α process are marked with filled circles, whereas data for the α' relaxation are marked with filled diamonds. ISS (Ref. 33) and Brillouin data (Ref. 32) are marked with crosses and a filled triangle, respectively. Dielectric data reported by Schönhals *et al.* (Refs. 30 and 31) for the α' , α , and β relaxations are marked with open squares, open triangles, and open circles, respectively. Solid curve represents a fit of the VFT equation [Eq. (3)] to the α process observed with the different light-scattering techniques, the dotted curve represents a fit of the MCT power law [Eq. (5)] to the high-temperature data and the dashed curve represents an Arrhenius equation through the dielectric β relaxation.

Experimental techniques

- General
- Fluctuations - correlation functions
- Scattering techniques - general aspects/theory
 - ⇒ Neutron scattering
 - ⇒ **Light scattering**
 - **Raman/IR spectroscopy**
 - Photon correlation spectroscopy

Vibrational spectroscopy



Probing molecular vibrations

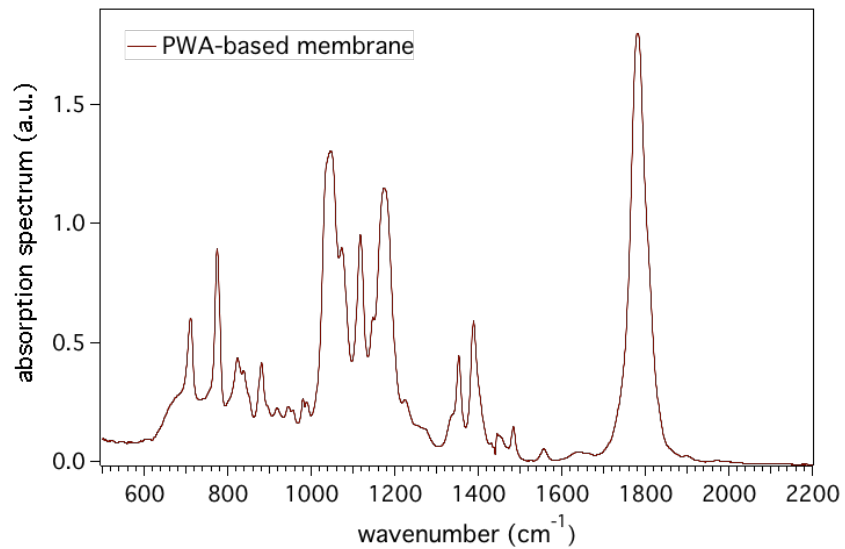
Time scale:
 $\Rightarrow$ fs-ps processes

Length scale:
 $q \approx 10^{-3} \text{ \AA}^{-1}$
but probing local vibrations

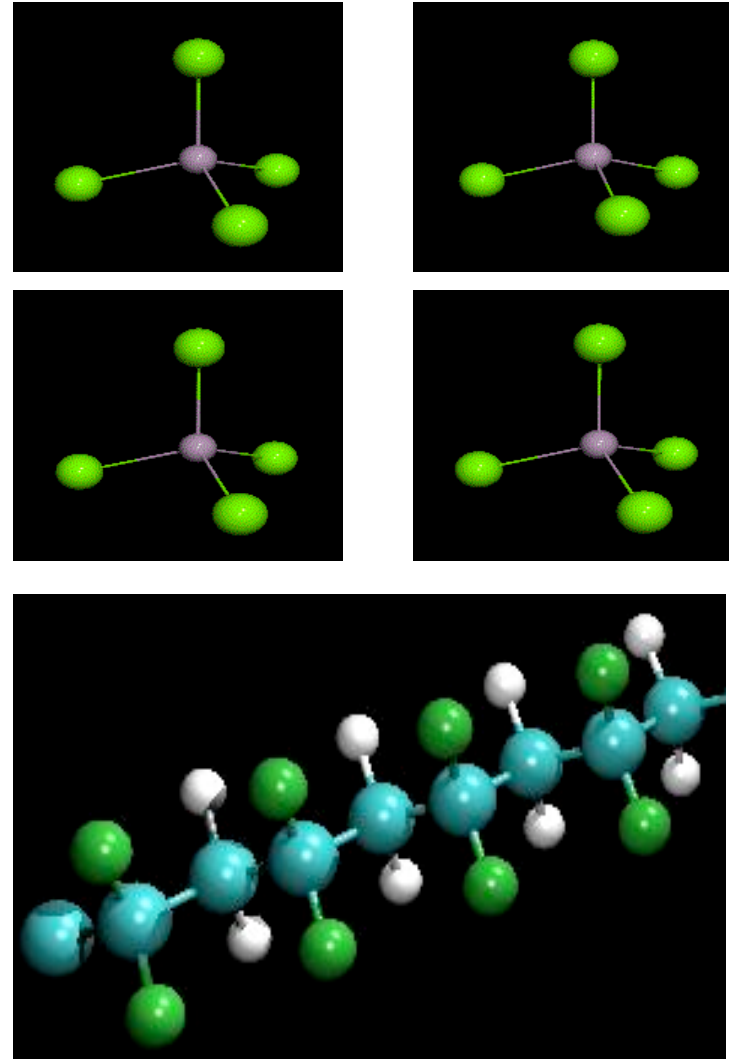
- Composition, coordination, conformation
- Interactions & reactions
- Mapping spatial distributions

Vibrational spectroscopy

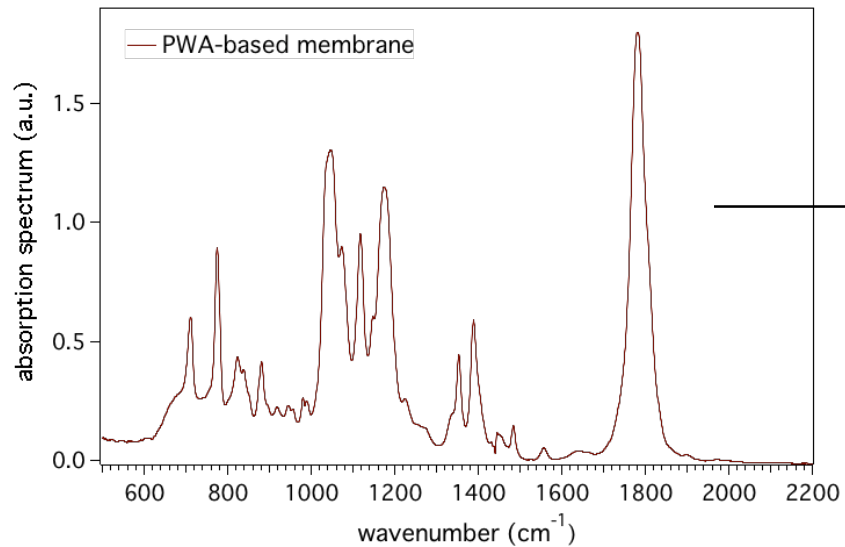
- potential energy, $V(r)$
- chemical bonds/forces, F_i
- $\Rightarrow$ frequency of vibration, ν_k



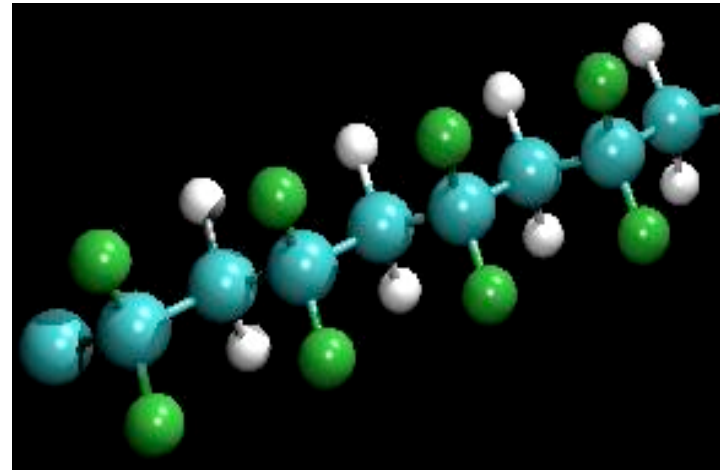
3N-6 vibrational modes



Vibrational spectroscopy



- composition
- coordination
- conformations
- interactions



Vibrational levels

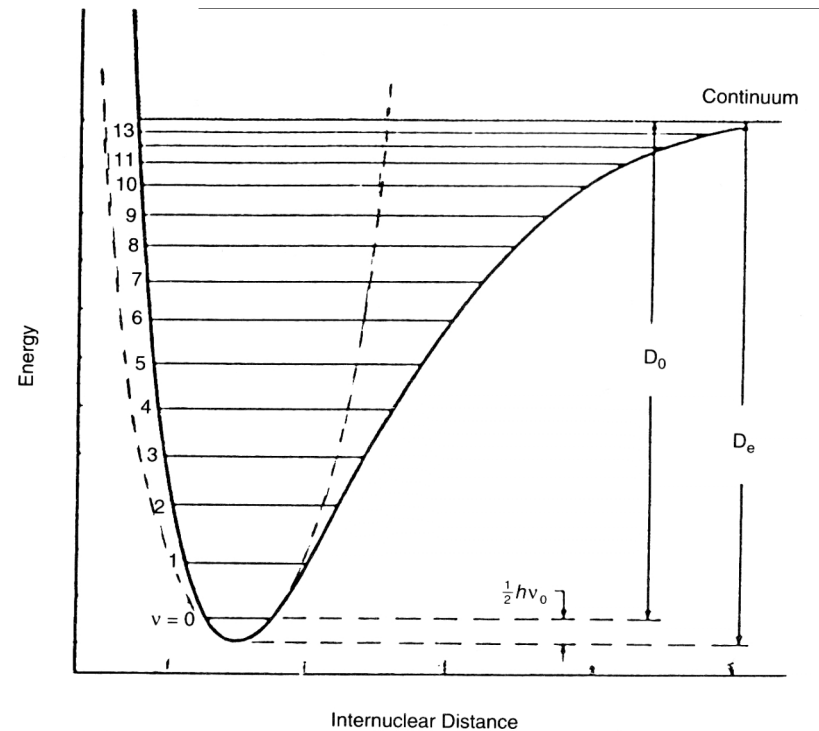
- molecular motion is quantized; vibrational quantum levels (quantum number “v”)

$$E_v = \left(v + \frac{1}{2}\right) \hbar \omega = \left(v + \frac{1}{2}\right) h \nu$$

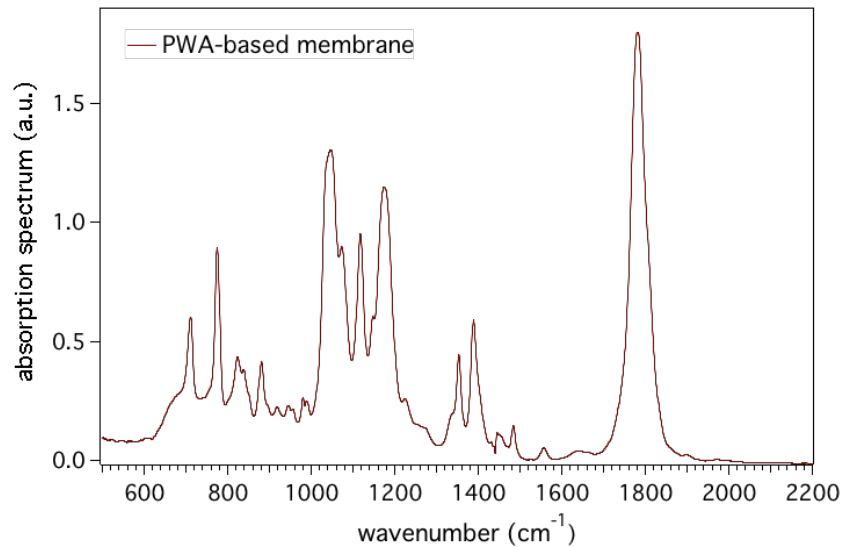
$$\hbar = \frac{h}{2\pi} \quad \omega = 2\pi \nu \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

- energy absorbed is energy difference between two levels; for SHO, spacing is same between ALL adjacent levels.

$$\Delta E_{v \rightarrow v+1} = \hbar \omega = h \nu = h \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$



Vibrational spectroscopy

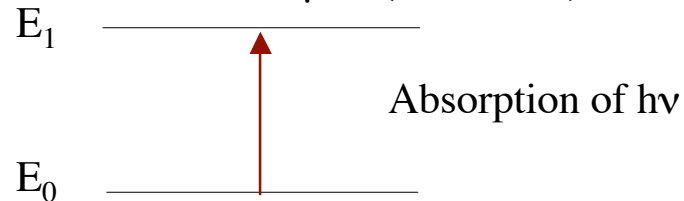


IR-spectroscopy

Polychromatic incident light

$$\lambda = h\nu$$

$\lambda \sim 0,7\text{-}1000\ \mu\text{m}$ (NIR-FIR)

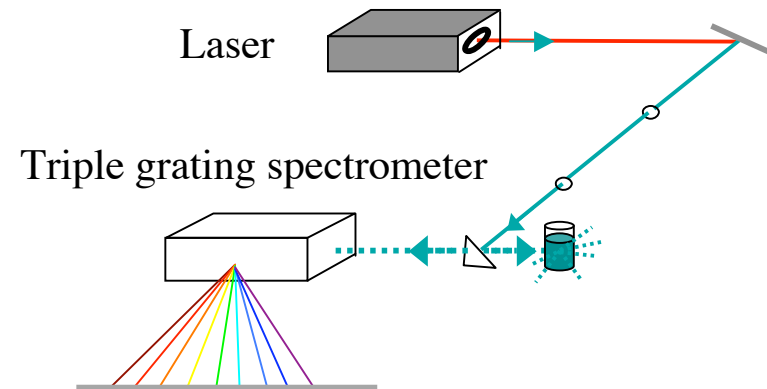
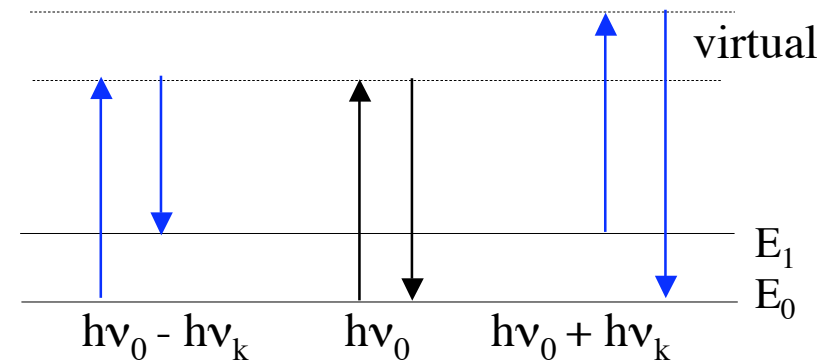


Raman spectroscopy

Monochromatic incident light

$$\lambda = h\nu_0$$

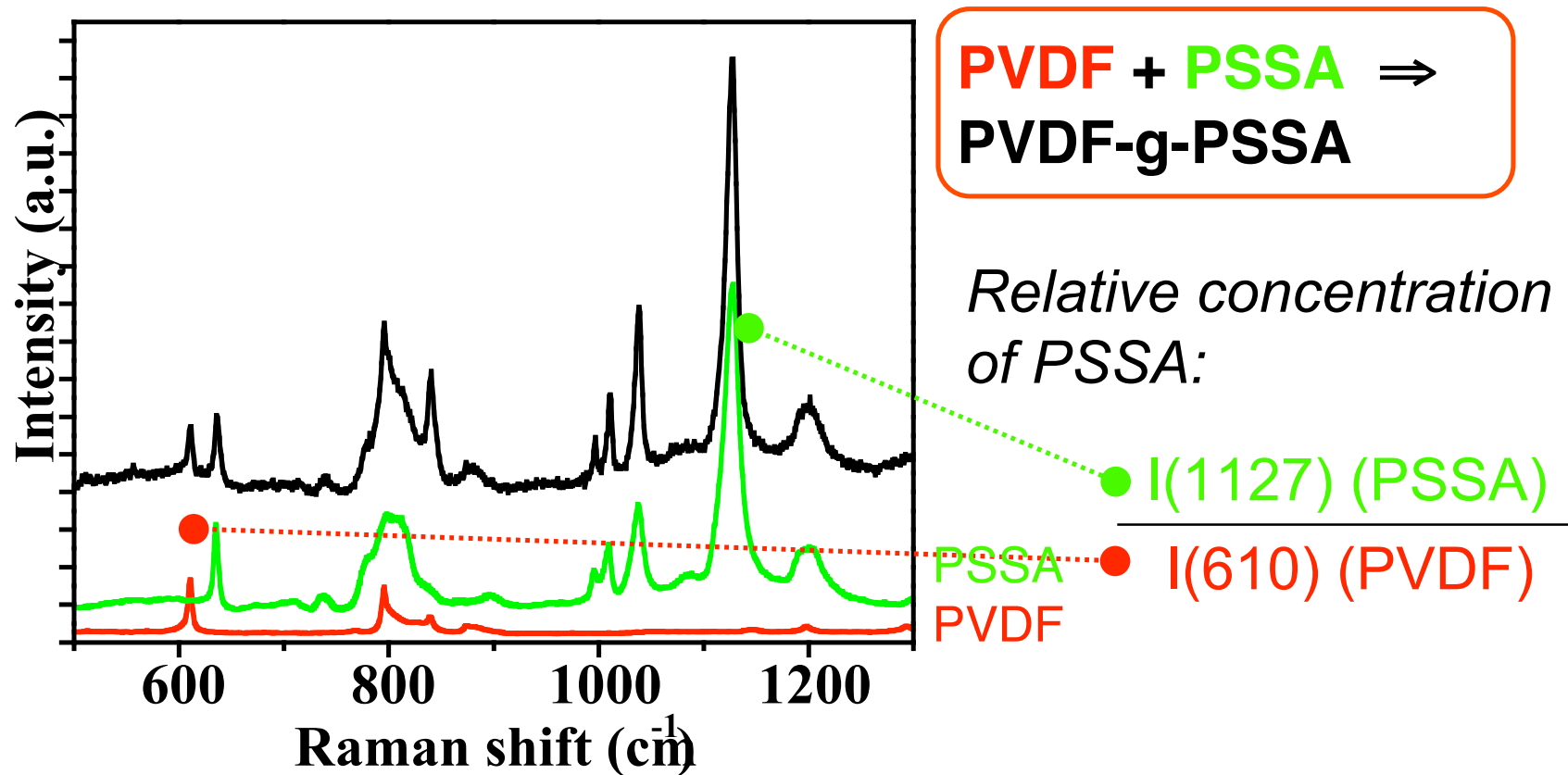
$\lambda \sim 400\text{-}700\ \text{nm}$



Raman vs. IR

	<u>Infrared Spectroscopy</u>	<u>Raman Spectroscopy</u>
Interaction	Absorption	Scattering
Excitation	Polychromatic	Monochromatic
Frequency measurement	Absolute	Relative
Activity	Dipole moment change $\partial\mu/\partial Q \neq 0$	Polarizability change $\partial\alpha/\partial Q \neq 0$
Band intensity	$I \propto (\partial\mu/\partial Q)^2$	$I \propto (\partial\alpha/\partial Q)^2$

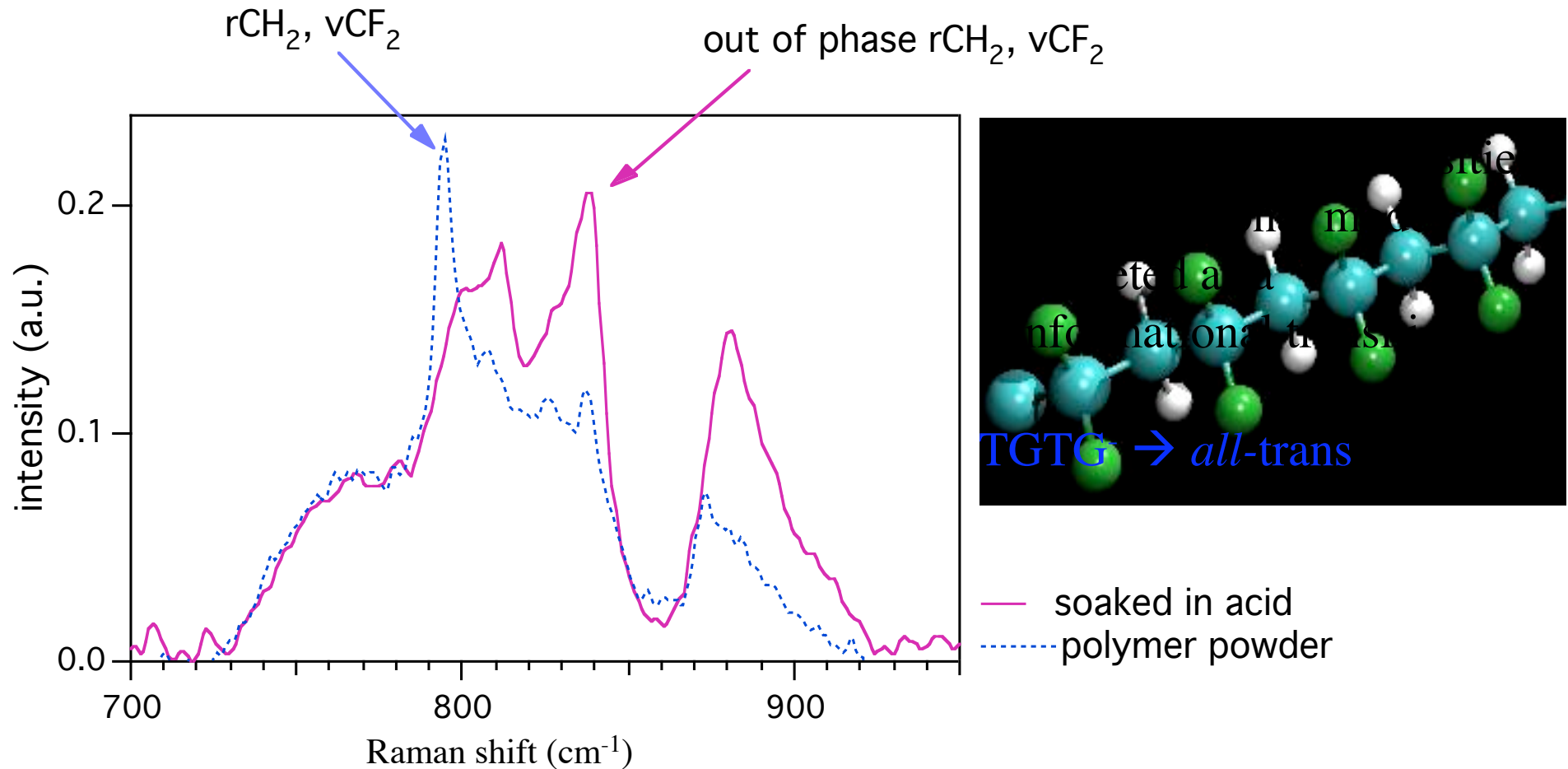
Composition



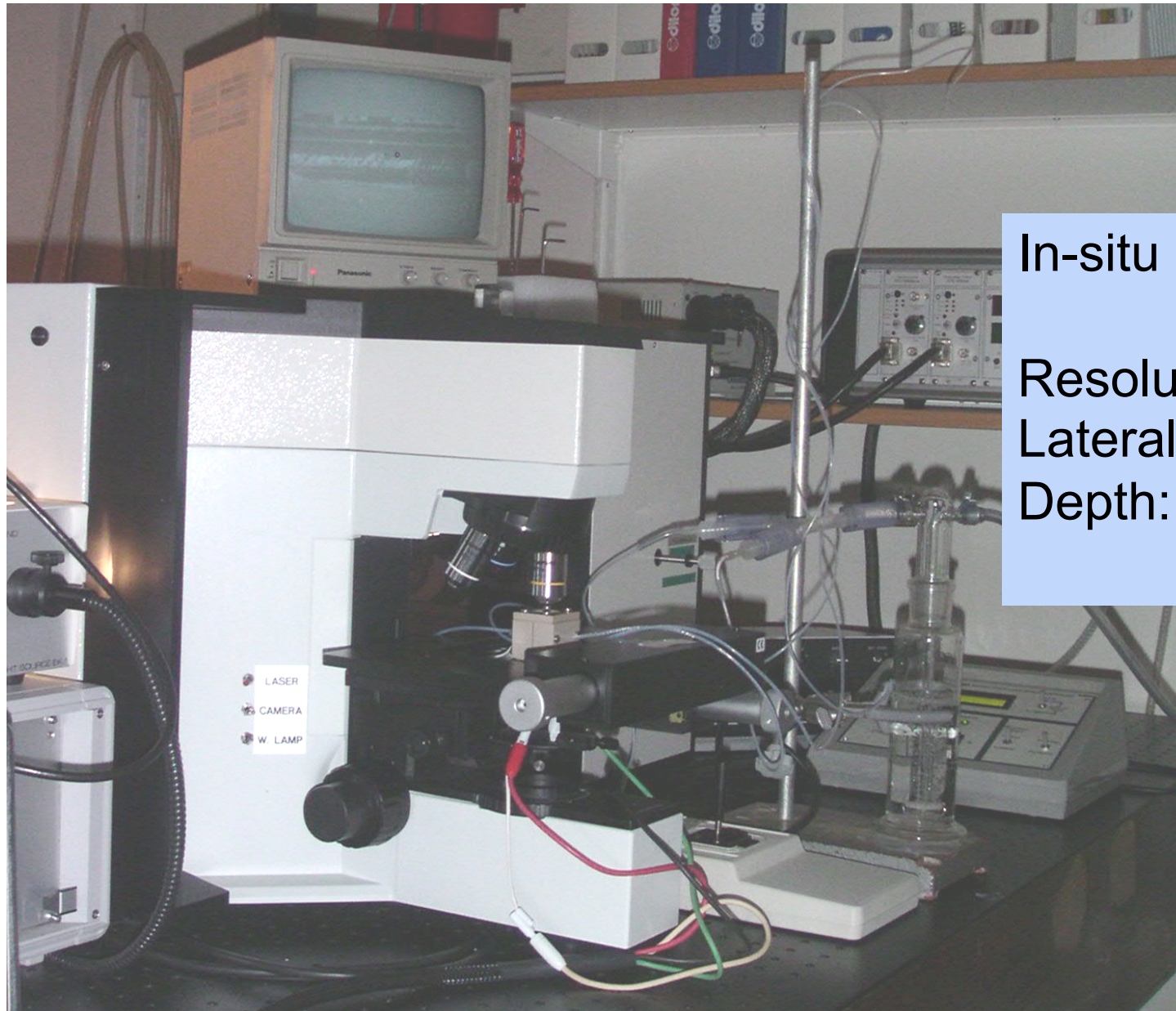
The vibrational spectrum is a "fingerprint" of a substance

Conformation

Raman spectra of PVDF in pure powder or in an membrane



Raman microscope



In-situ studies

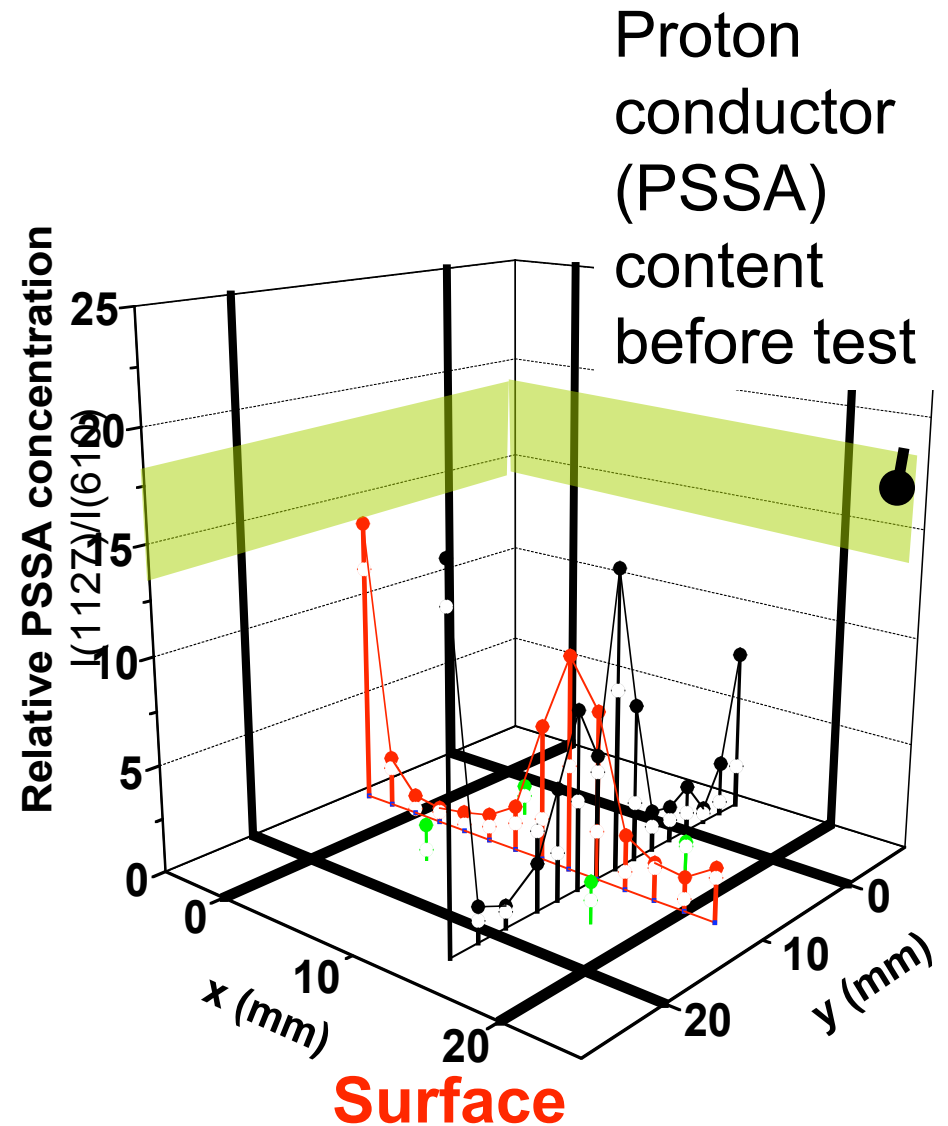
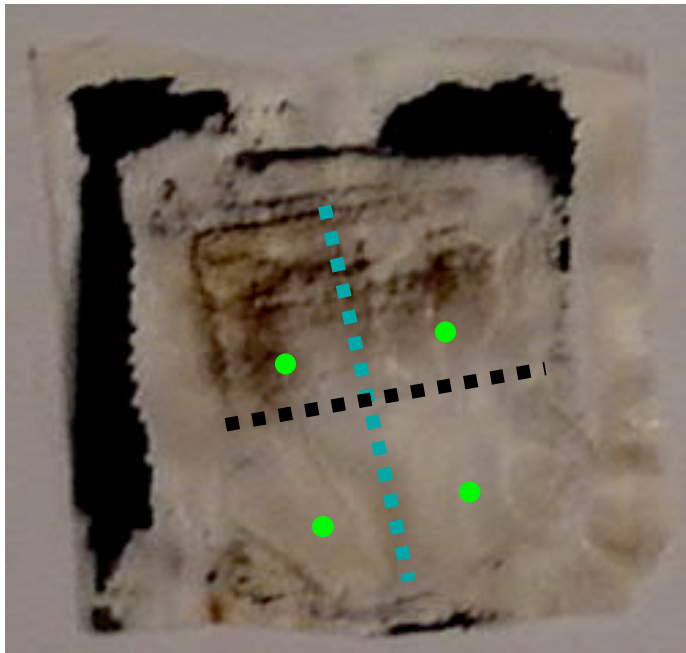
Resolution:

Lateral: $\approx 1 \mu\text{m}$

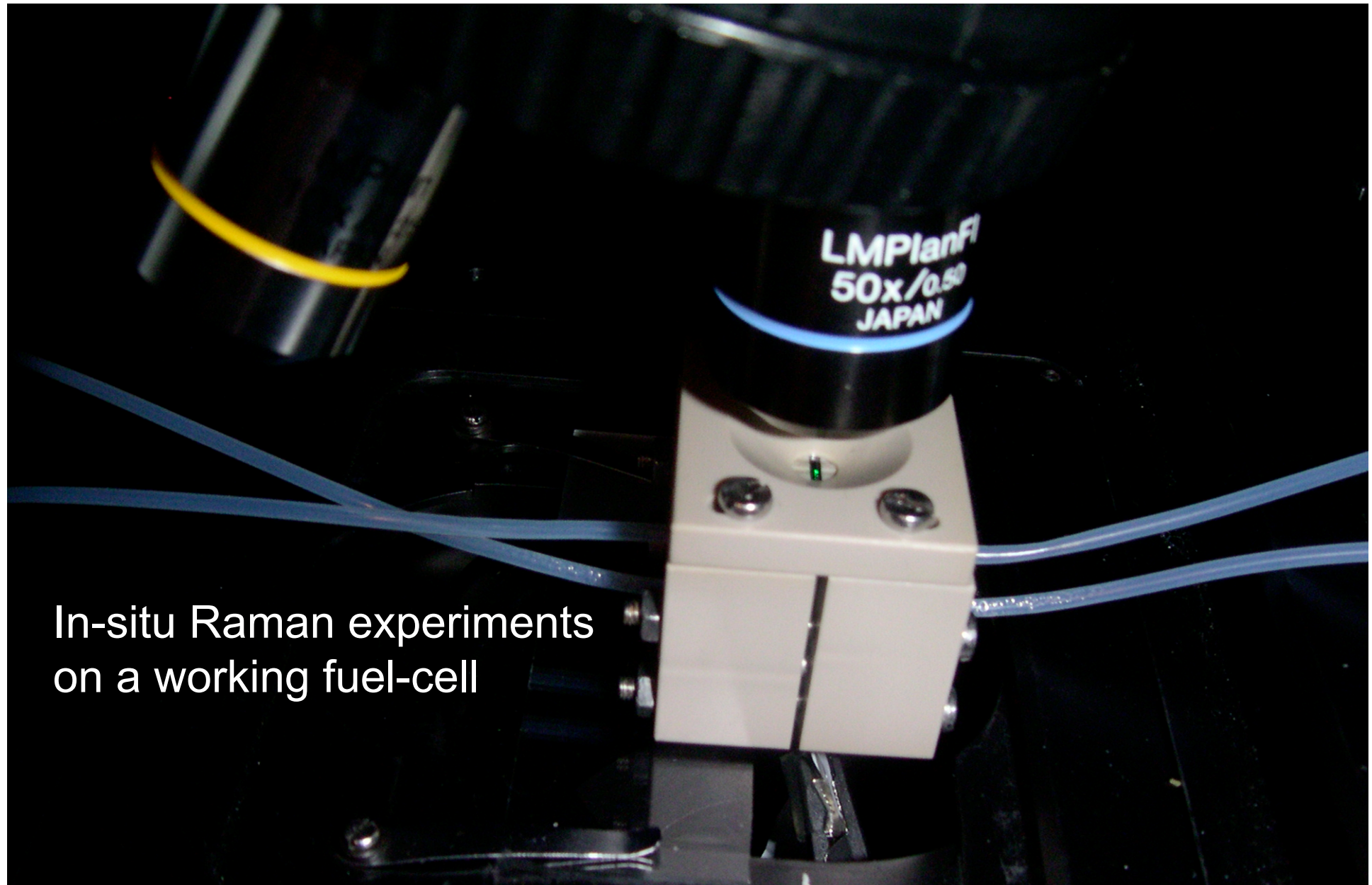
Depth: $\approx 2 \mu\text{m}$

Compositional mapping

Mapping the concentration of active component (PSSA) in a fuel cell membrane.

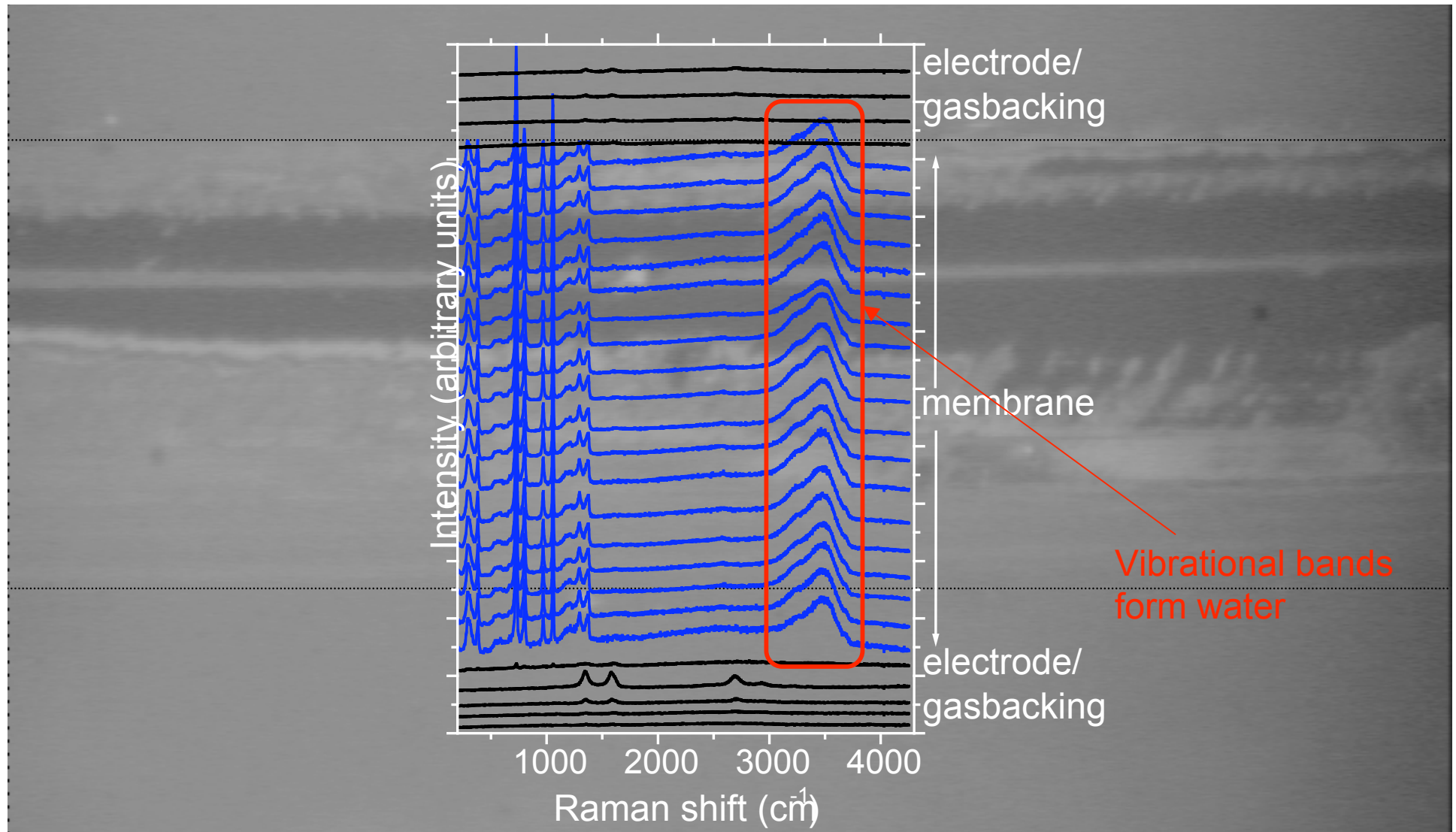


Cell for *in-situ* Raman



In-situ Raman experiments
on a working fuel-cell

Cross section of membrane in the cell

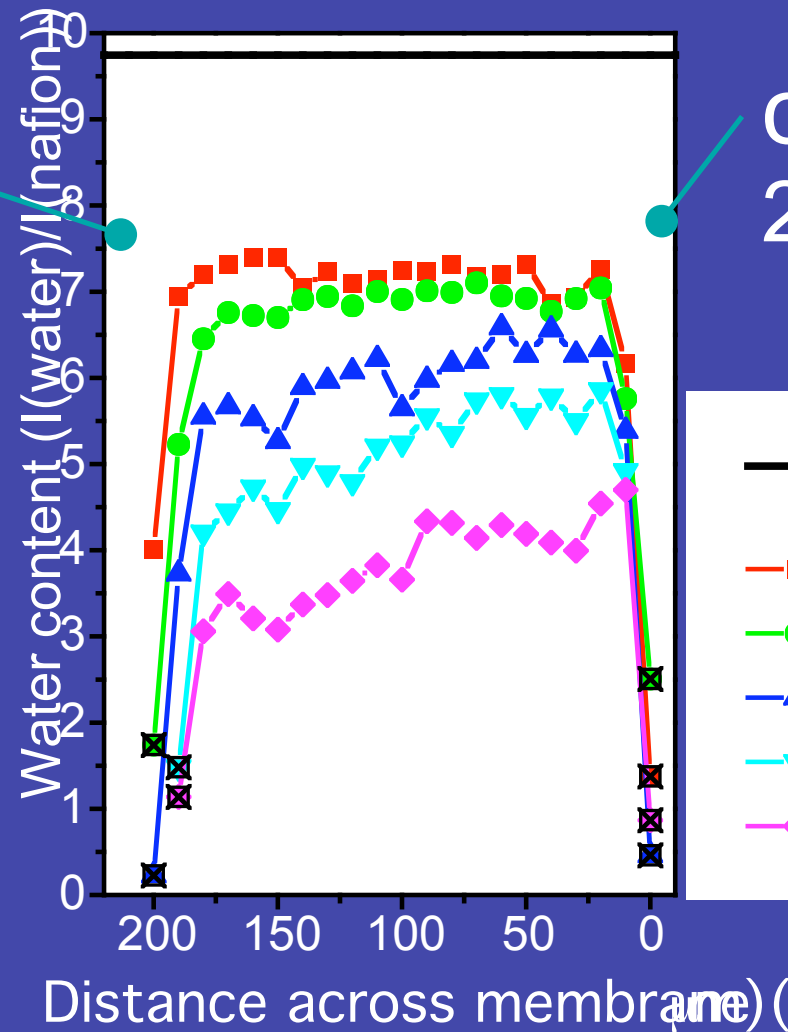


Water profile – potential applied

anode



cathode



Experimental techniques

- **General**
- **Fluctuations - correlation functions**
- **Scattering techniques - general aspects/theory**
 - ⇒ **Neutron scattering**
 - ⇒ **Light scattering**
 - **Raman/IR spectroscopy**
 - **Photon correlation spectroscopy**