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

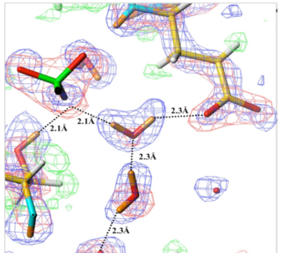
Literature

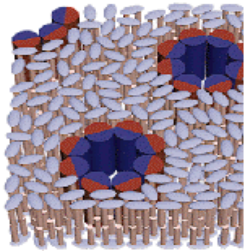
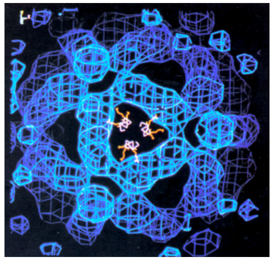
- Slides from this lecture
- Slides Johan Bergenholtz seminar on rheology

Time and length scales

Length scale in nm

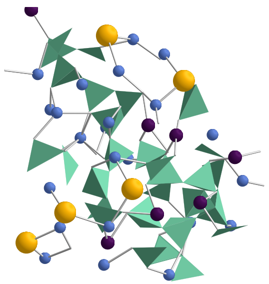
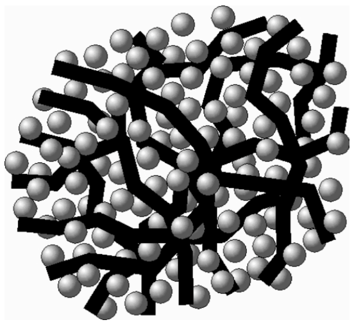
0.01 0.1 0.3 1.0 3.0 10 30 100



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

10^{-13} Time scale (seconds) **10^{-7}-10^{3}**

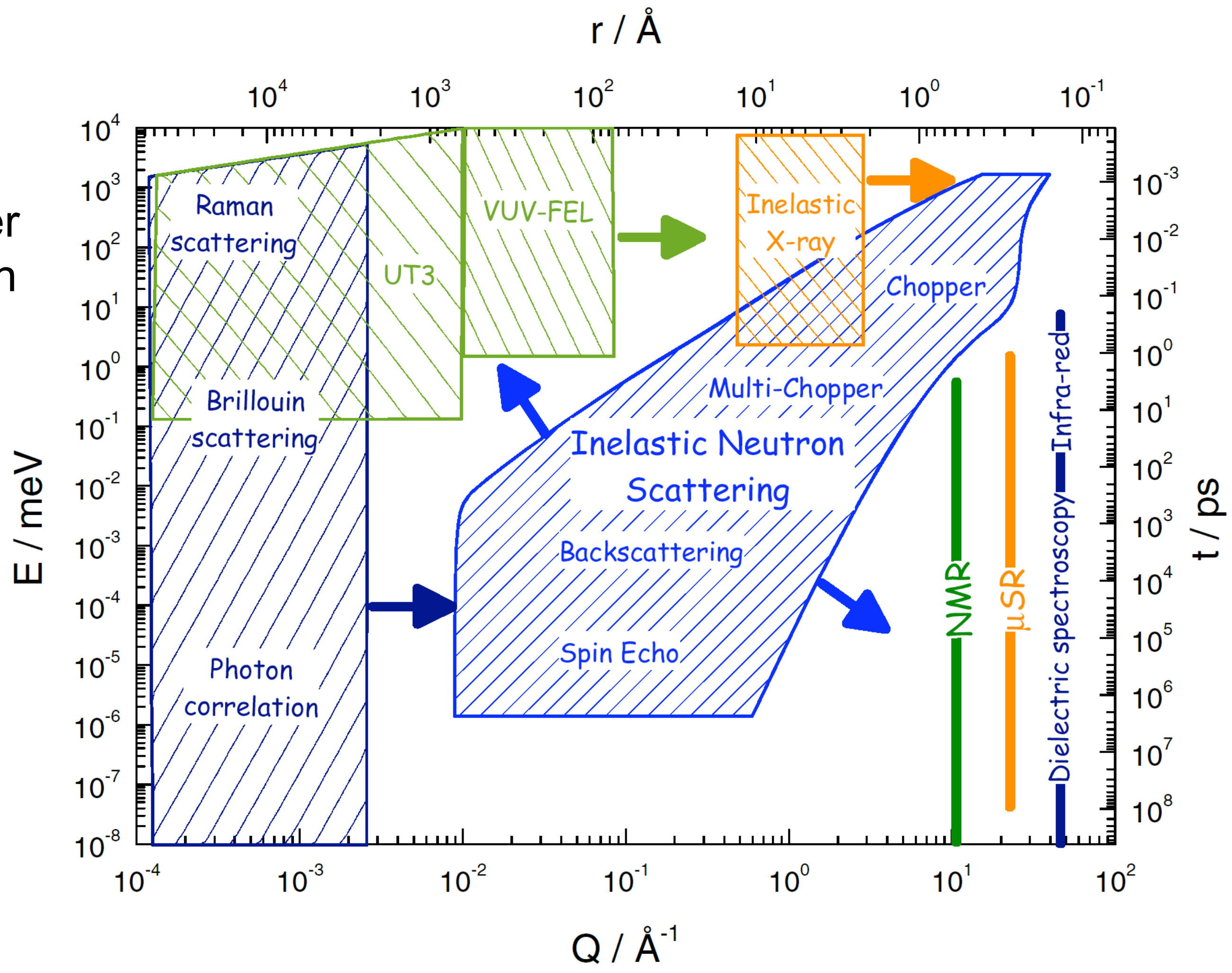




Combining techniques

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

Length scale:
Q (Å⁻¹) or r (Å)

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



Selection of techniques

<u>Technique</u>

Rheology

Nuclear Magnetic Resonance

Optical microscopy

Confocal microscopy

Vibrational spectroscopy

Dynamic light scattering

Dielectric spectrosocpy

Calorimetry

x-ray & neutron scattering

AFM

Electron microscopy

Selection of techniques

Technique

Rheology → Mechanical properties, shear deformation

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

Nuclear Magnetic Resonance

Optical microscopy

Confocal microscopy

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Selection of techniques

Technique

Rheology

Nuclear Magnetic Resonance →

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

Optical microscopy

Confocal microscopy

Vibrational spectroscopy

Dynamic light scattering

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Selection of techniques

Technique

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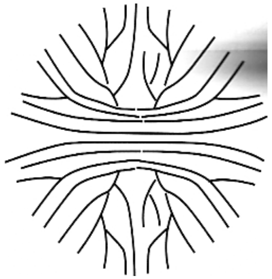
Morphology, optical anisotropy

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

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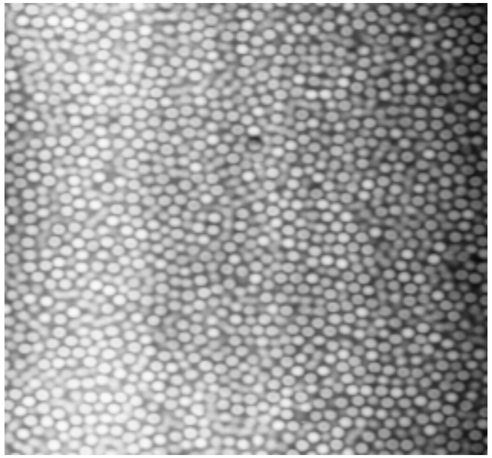
Electron microscopy

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

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Differential scanning calorimetry (DSC)

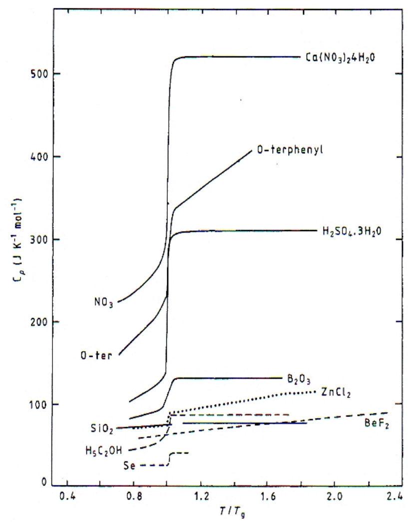


Figure 10. Specific heat C_p against reduced temperature T/T_g in the vicinity of the glass transition temperature T_g for different glass forming liquids. Note that for SiO_2 and BeF_2 a jump in C_p at T_g is not discernible (from Brawer 1983).

follow phase transitions, e.g. glass trans.

Experimental techniques

- General
- **Fluctuations - correlation functions**
- Scattering techniques - general aspects/theory

  $\Rightarrow$ Neutron scattering

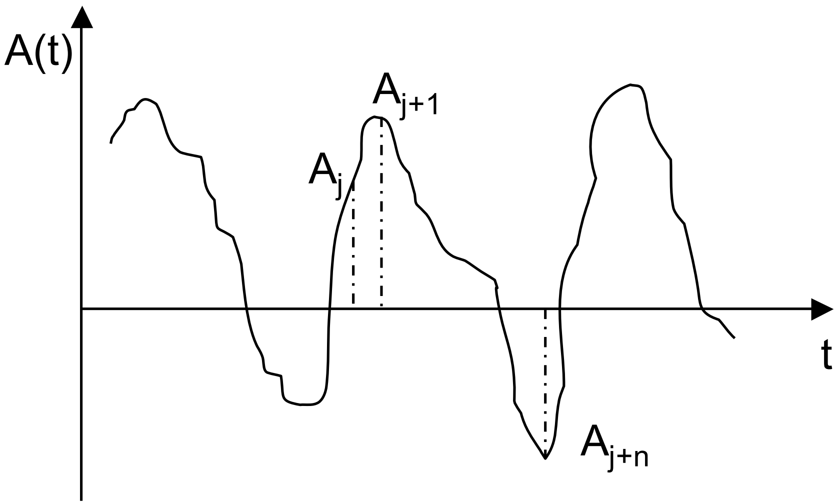
  $\Rightarrow$ Light scattering
  - Raman/IR spectroscopy
  - Photon correlation spectroscopy

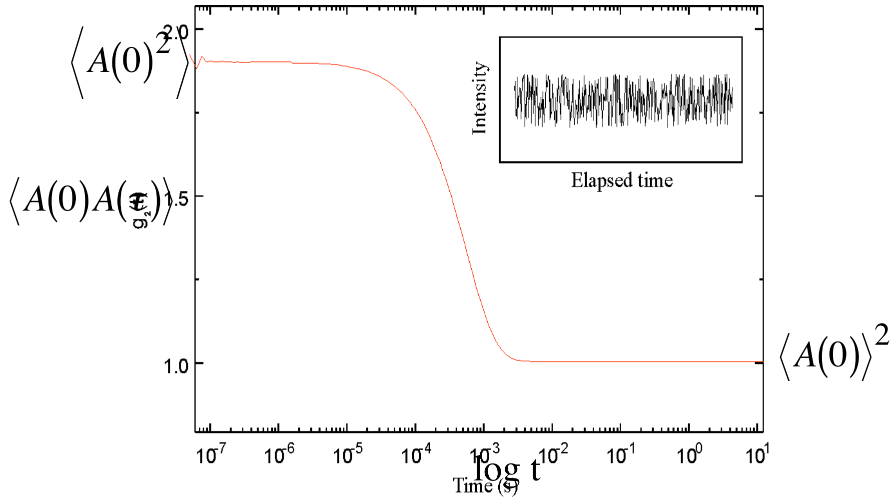
Fluctuations - Correlation functions

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

Autocorrelation function

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





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

g(r,t) - van Hove correlation function

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

$$\rho(r,t) = \sum_i \delta\left\{r - R_i(t)\right\}$$

- particle density operator

- $R_i(t)$ - position of particle i at time t

Self correlation function

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

Distinct correlation function

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

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

g(r,t) - van Hove correlation function

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

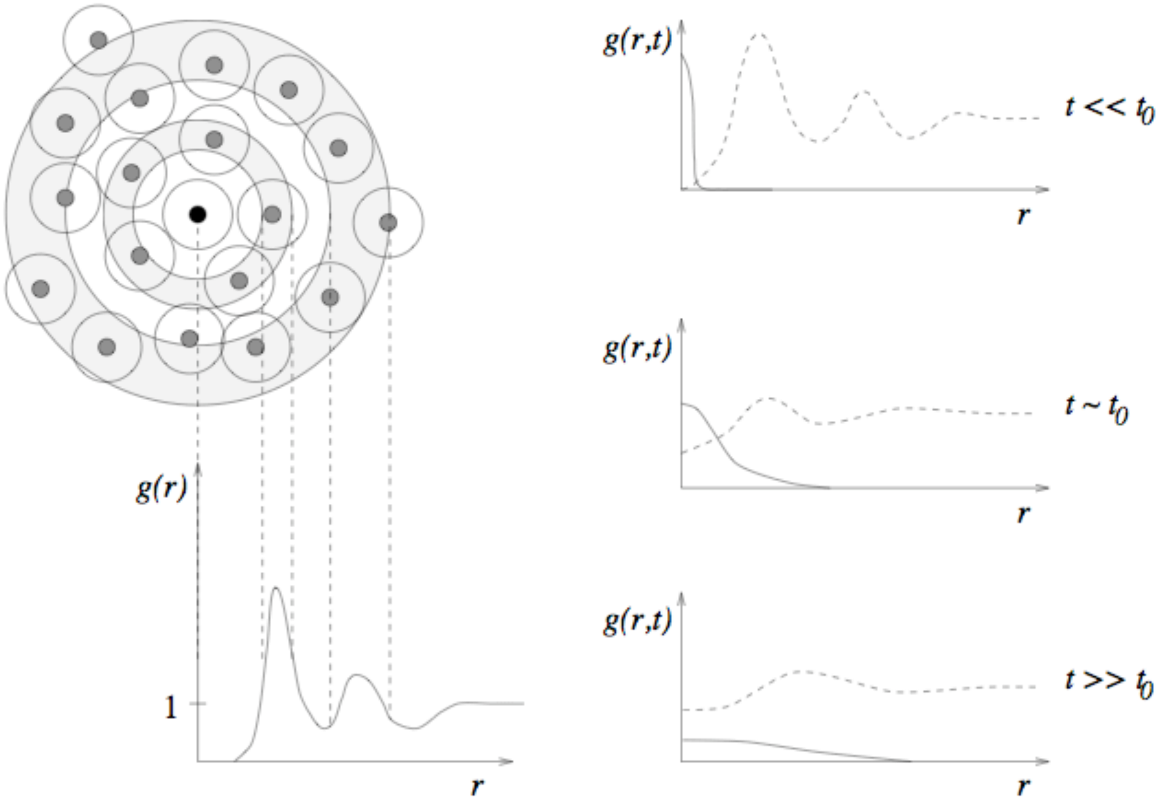
$$g_d(r,t) = \frac{1}{N}\sum_{i\neq j} \int \left\langle \delta\left\{r' - R_j(0)\right\}\delta\left\{r' + r - R_i(t)\right\}\right\rangle dr'$$

In the limit t→0

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

g(r) - static pair distribution ⇒ *the structure of the material*

g(r,t) - van Hove correlation function



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

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

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

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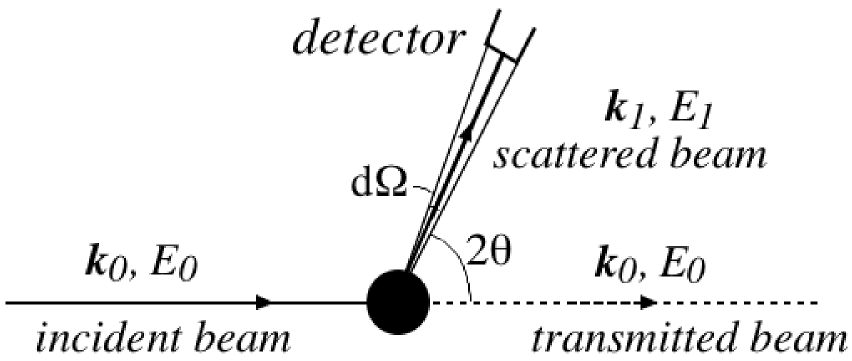
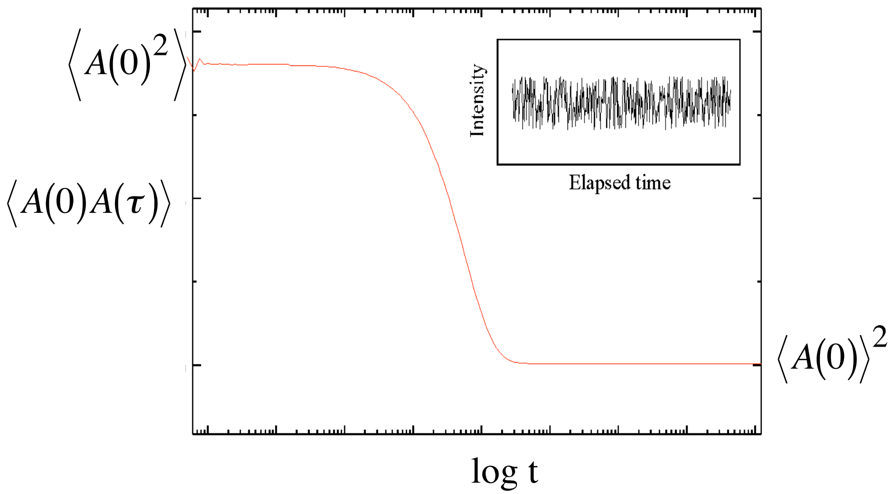
Scattering experiment

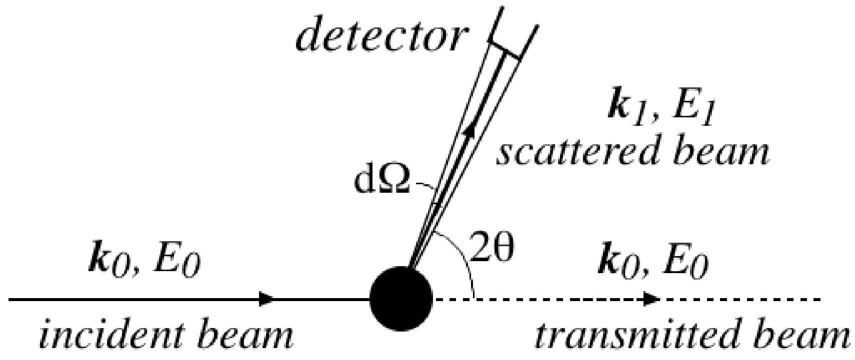


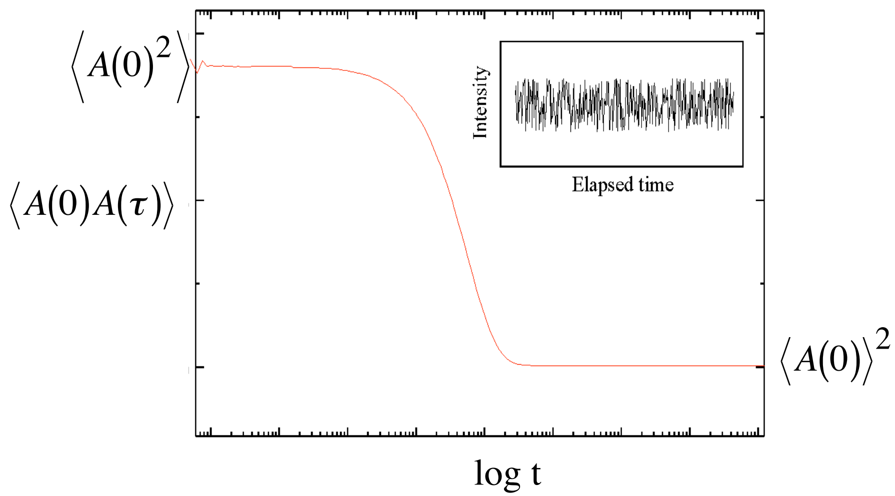


Scattering of particles:
- *Neutrons*
- *electrons*
- *photons*
- *…*

Differ in:
- *wavelength*
- *interaction mechanism*
- *cross section*
- *detection*
- *resolutions*
- *…*

Scattering experiment





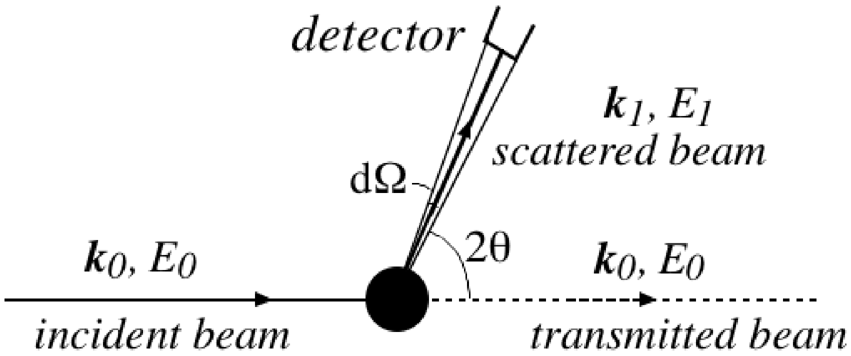
Scattering of particles:

- *Neutrons* - *1 - 30 Å*
- *electrons* - *0.1 - 1 Å*
- *photons* - *1 - 5000 Å*
- *…*

Differ in:

- *wavelength*
- *interaction mechanism*
- *cross section*
- *detection*
- *resolutions*
- *…*

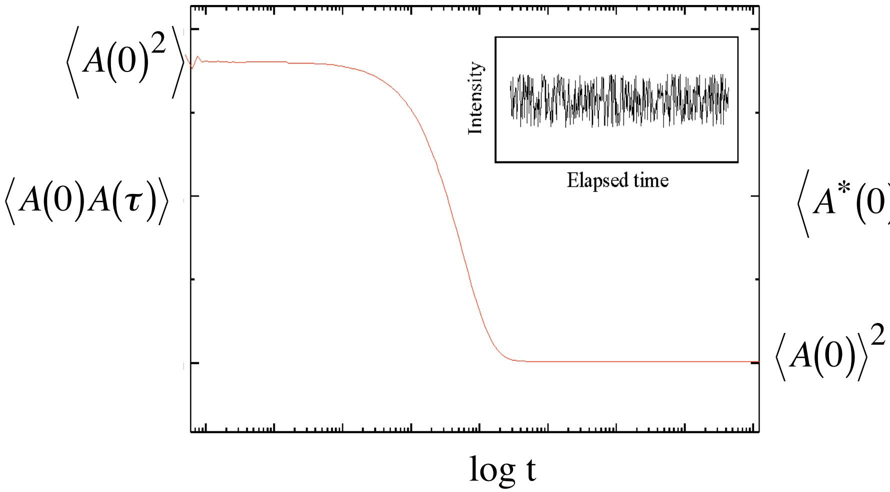
Scattering experiment



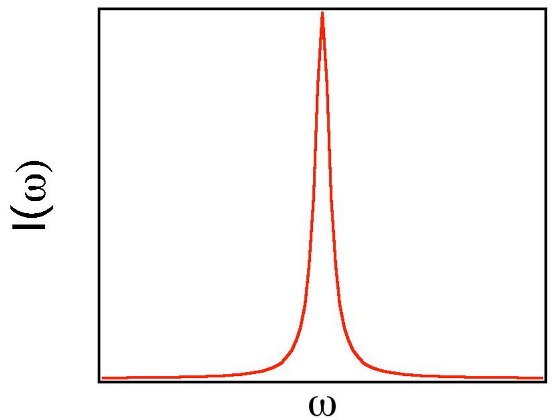
Obtaining the correlations function:

- Directly in time domain
  (PCS, transient grating …)

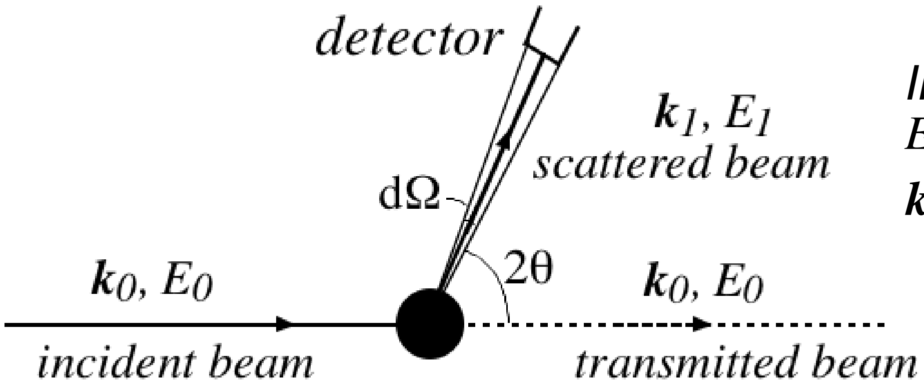
- In frequency domain
  (Brillouin, Raman, neutron,…)
  ⇒ *spectral density I(ω)*



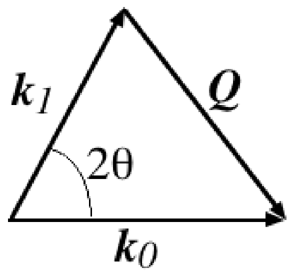
$$\langle A^*(0)A(\tau) \rangle = \int_{-\infty}^{\infty} d\omega e^{i\omega t} I(\omega)$$



Scattering experiment



In the scattering process we can exchange
E_0-E_1=± $\hbar\omega$ *- energy transfer*
$\mathbf{k}_0$-$\mathbf{k}_1$=$\mathbf{G}$±$\mathbf{Q}$ *- momentum transfer*



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

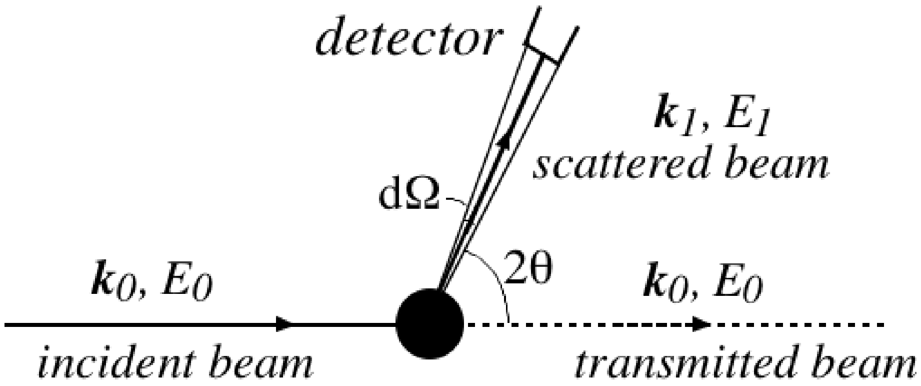
$$Q^2 = \left|\bar{k}_1 - \bar{k}_0\right|^2$$

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

$$Q = 2k_0 \sin\frac{\theta}{2} = \frac{4\pi n}{\lambda_0}\sin\frac{\theta}{2} \qquad \lambda = 2\pi n/k$$

light scattering
n - refractive index

Scattering experiment



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

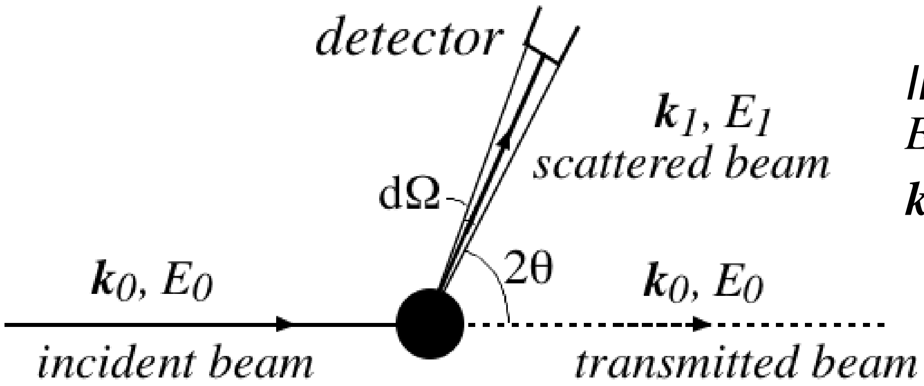
In the experiment we measure the double differential scattering cross section

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

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

$g(r,t) \Leftrightarrow S(Q,\omega)$ *(Fourier transforms)*

Scattering experiment



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$\mathbf{k}_0$-$\mathbf{k}_1$=$\mathbf{G}$±$\mathbf{Q}$ *- momentum transfer*

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

express in fourier components

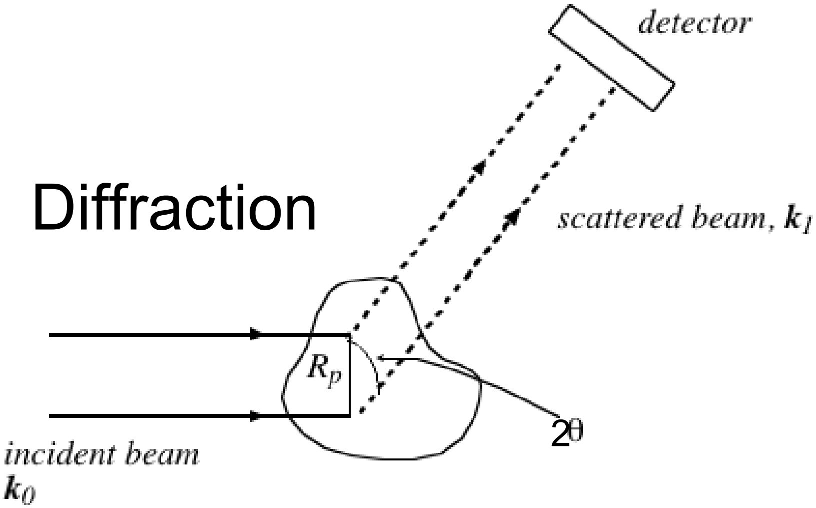
$$\rho(r,t) = \sum_i \delta\left\{r - R_i(t)\right\} = \frac{1}{(2\pi)^3}\int \rho_Q(t)\exp(iQr)dQ$$

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

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

Scattering experiments - structure

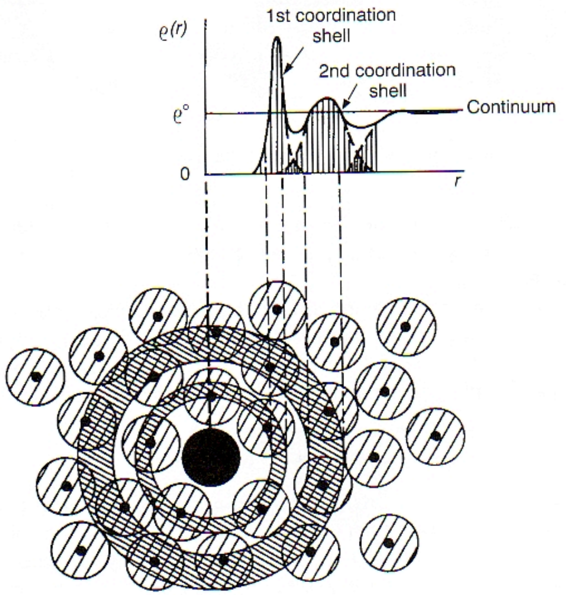
Diffraction



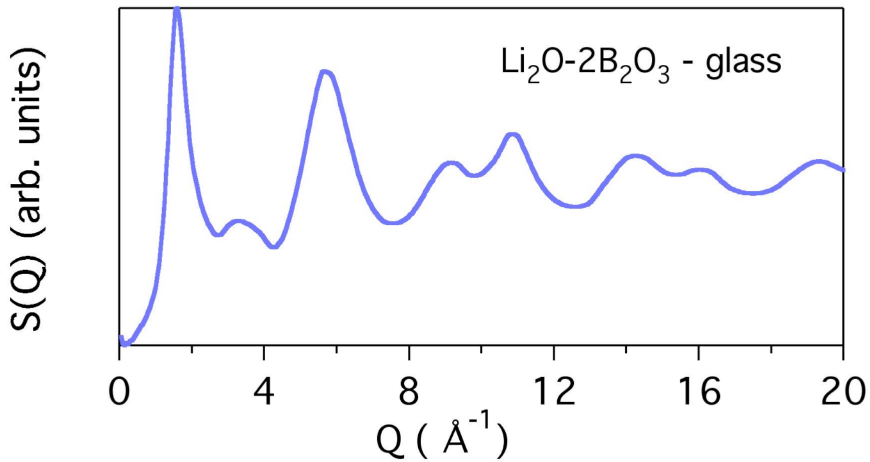
$$g(r,0) = \delta(r) + \sum_i \langle \delta(r - R_i + R_0) \rangle = \delta(r) + g(r)$$

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

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



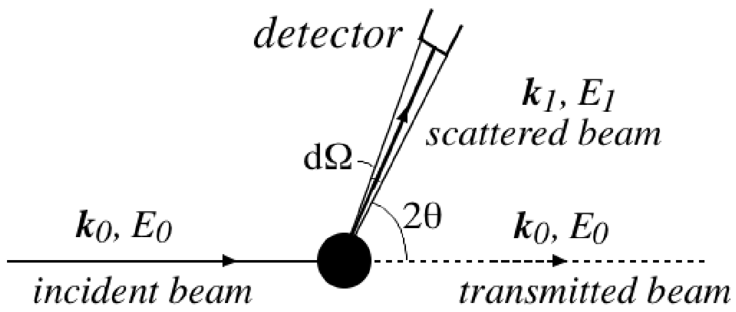
F.T

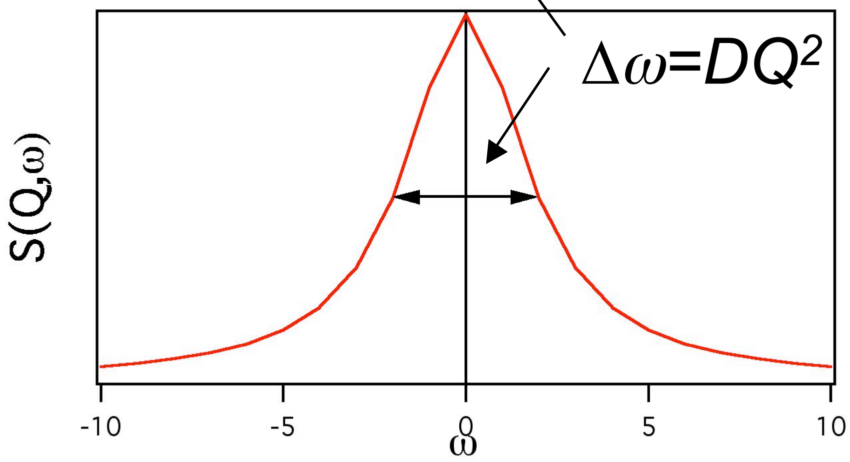


Scattering experiments - dynamics

Liquid like diffusion / Brownian motion

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





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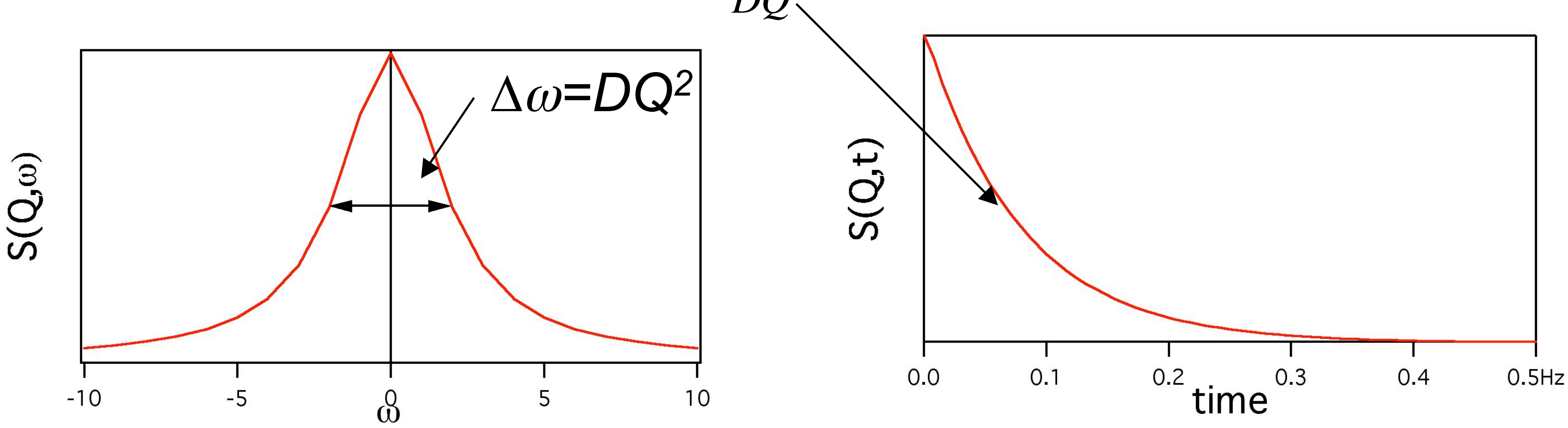
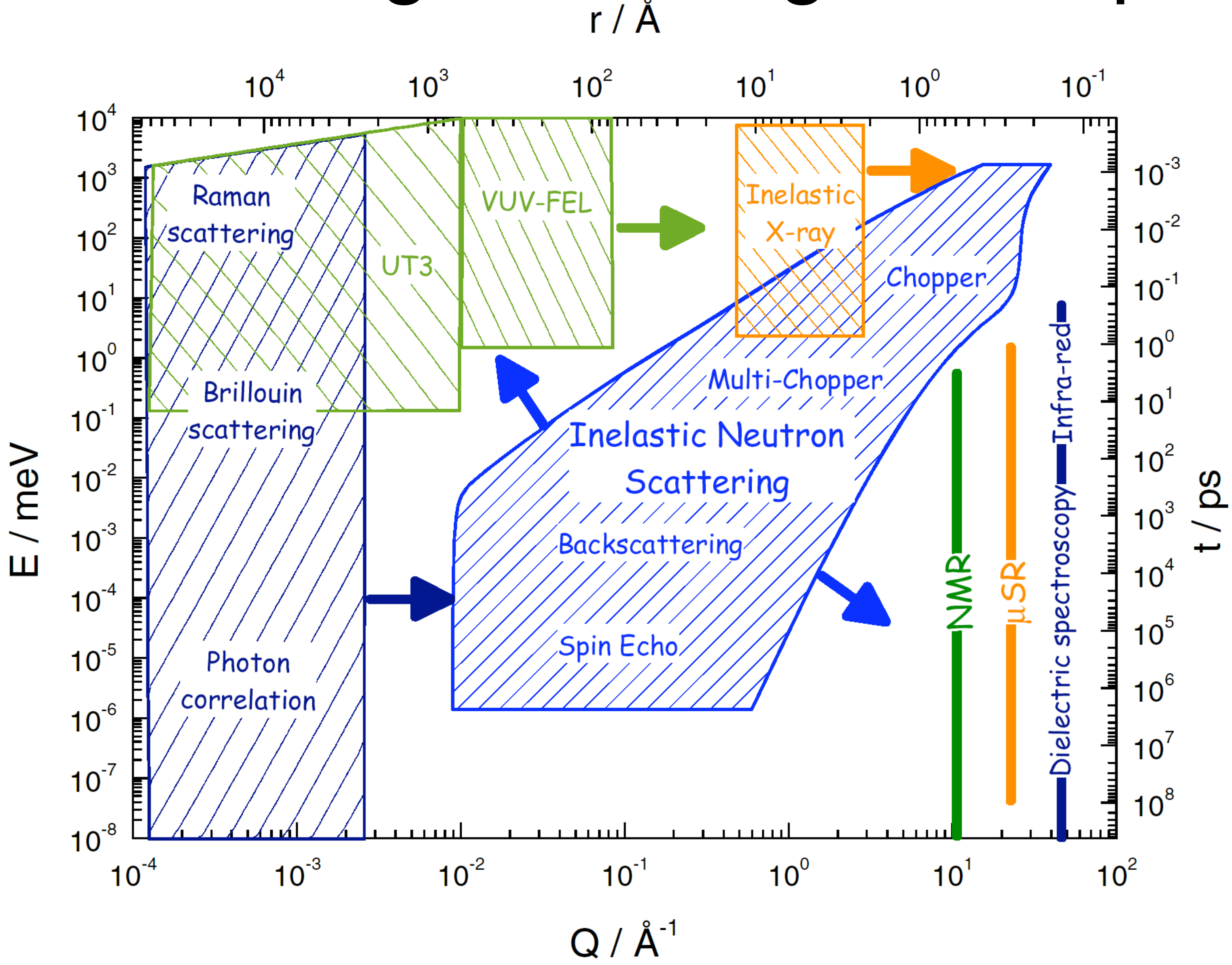
$$S(Q,\omega) \Rightarrow S(Q,t) \propto \exp\{-t/\tau\} \qquad \tau = \frac{1}{DQ^2}$$



Combining scattering techniques



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  ⇒ **Neutron scattering**

  ⇒ Light scattering
    - Raman/IR spectroscopy
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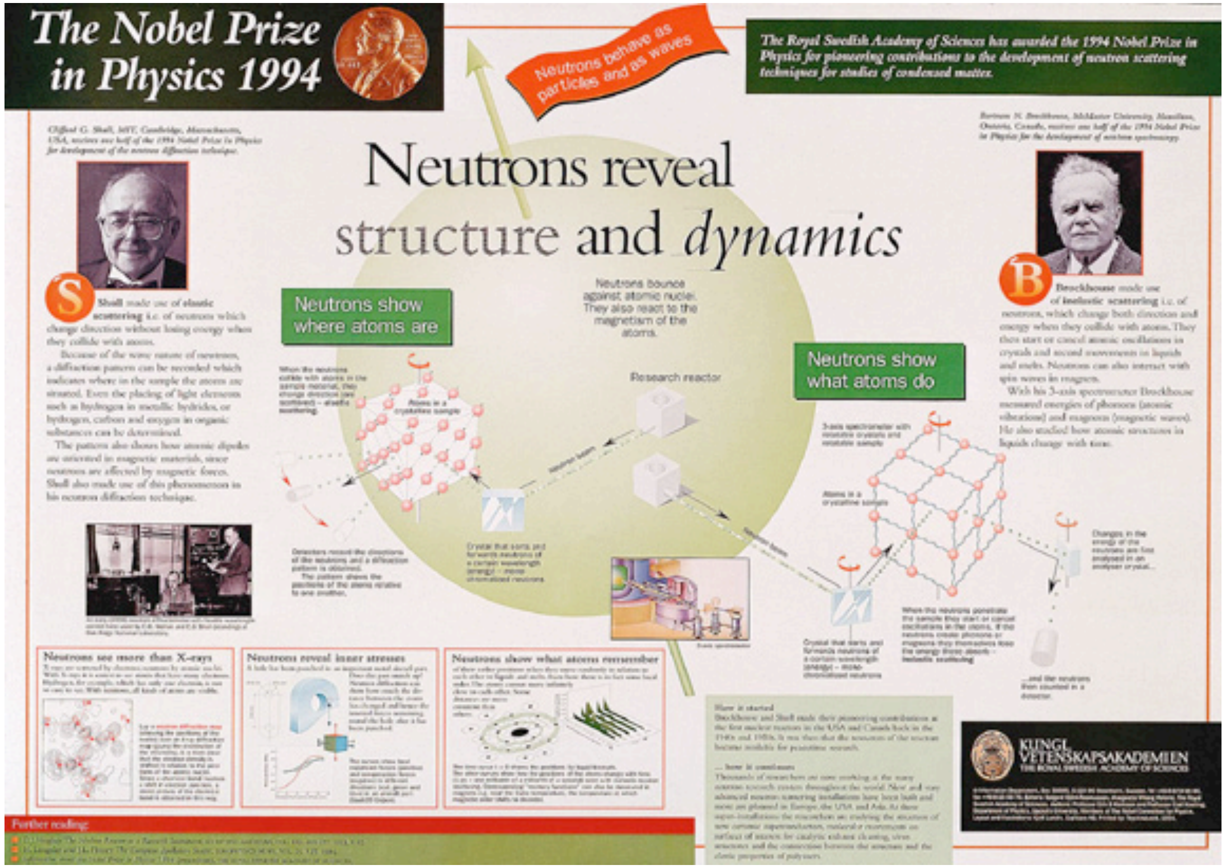
Neutron scattering

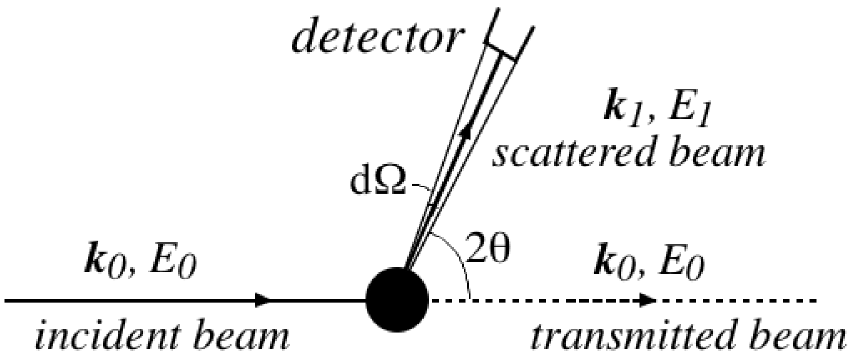


Neutrons tell you where the atoms are and what the atoms do'
(Nobel Prize citation from Brockhouse and Shull 1994)

Neutron scattering

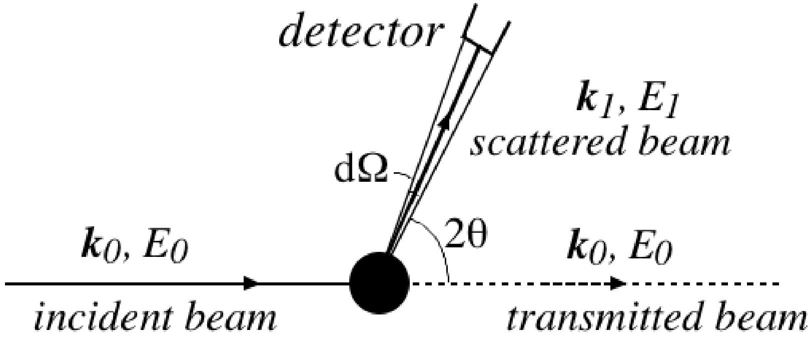
The neutron has a wavelength (*Å*) and an energy (*meV*) comparable to typical atomic spacings and vibrational energies -

⇒ study <u>both</u> atomic structure and dynamics (simultaneously if required)



Typical neutron energy:	0.1-100 meV
Typical wavelength:	30-1 Å

Neutron scattering - dynamics



Incident neutron (E_o,k_o) 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)

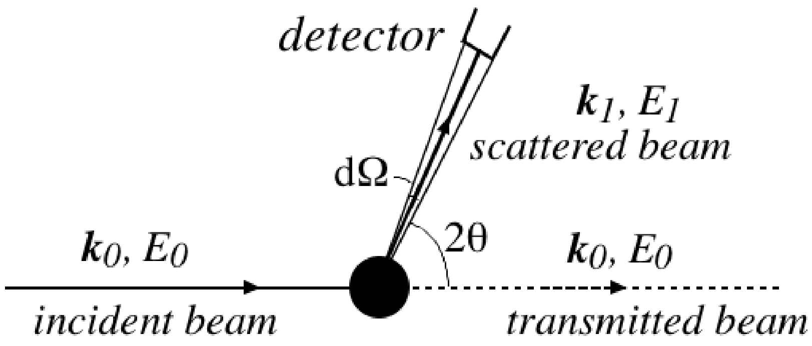
$$S_{inc}(q,\omega) = \int_{-\infty}^{\infty} \exp^{-i\omega t} \sum_{i=1}^{N} \left\langle \exp^{-iq\cdot r_i(0)} \exp^{iq\cdot r_i(t)} \right\rangle dt$$

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

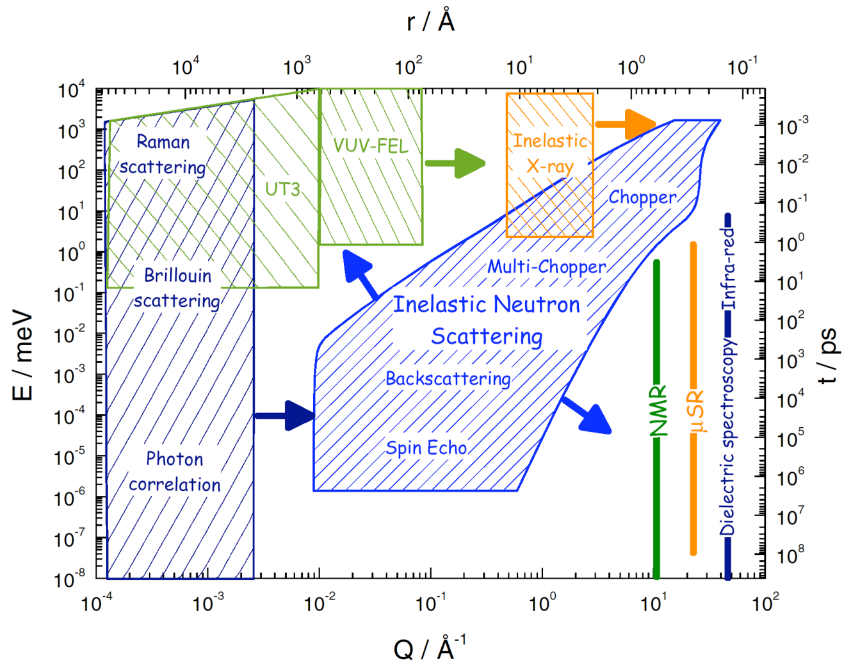


Incident neutron (E_o,k_o) can exchange energy and momentum in the scattering process to (E_1, k_1), $\omega=E_1-E_0$, $q=k_1-k_0$ due to interaction with the material

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:

1. ***i) time and length scales*** — *Probe both structure and dynamics – $\lambda \approx$ Å, $E \approx$ meV*
2. *ii) cross sections*
3. *iii) weak probe*
4. *iv) high penetration*
5. *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

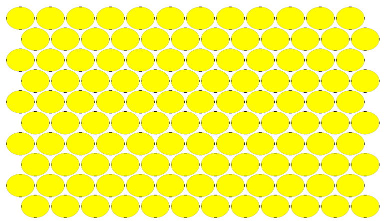
Scattering cross section

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

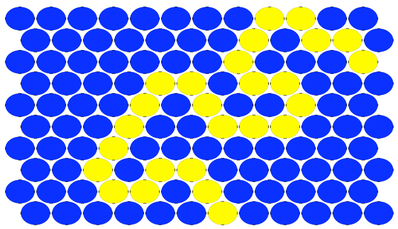
⇒ distinguish light atoms in a matrix of heavy or atoms of similar Z
⇒ contrast variation through isotopic substitution (keeping the chemistry)

Especially valuable:
H and D have very different scattering cross sections

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



H-polymer in H_2O



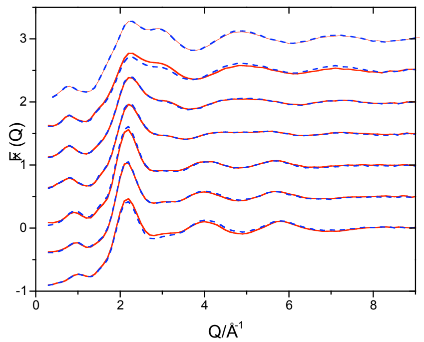
D-polymer in H_2O

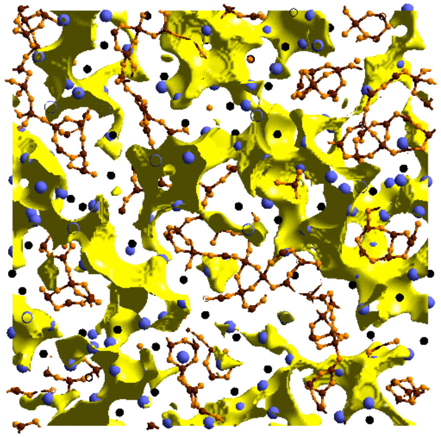
Why neutrons?

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 modell the scattering from computer simulation or theoretical calculations



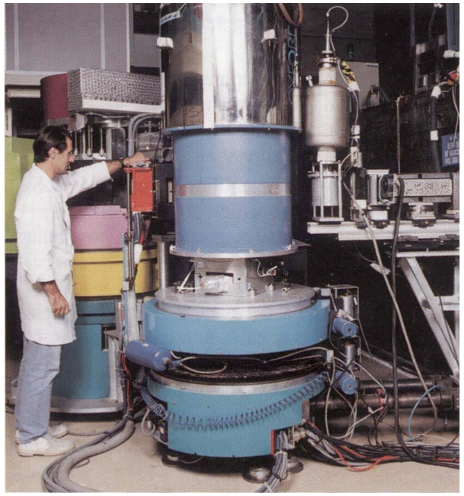


reverse Monte Carlo model of glass structure from diffraction data

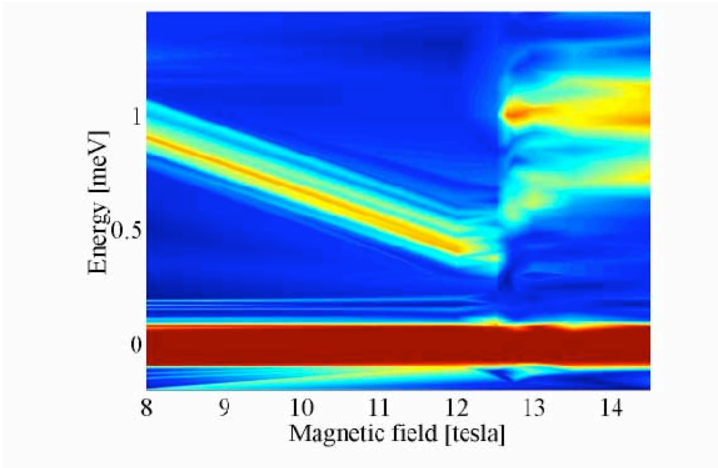
Why neutrons?

Five good reasons:

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



Complex sample environement/
Extreme conditions
M: 0-15 T, T: mK-kK, P: …..



Why neutrons?

Five good reasons:

- *i) time and length scales*
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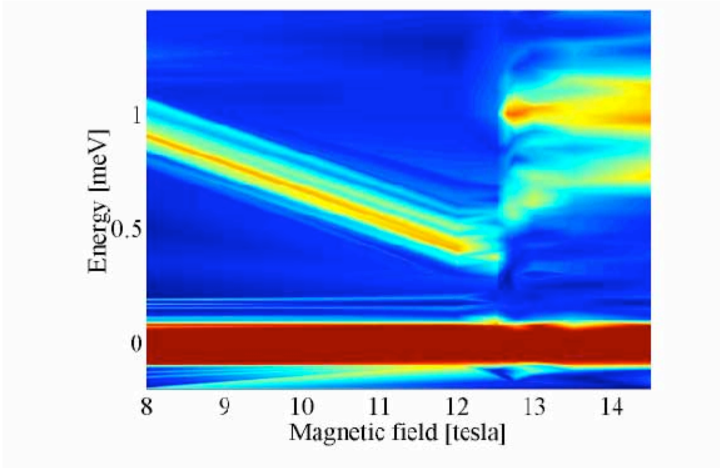
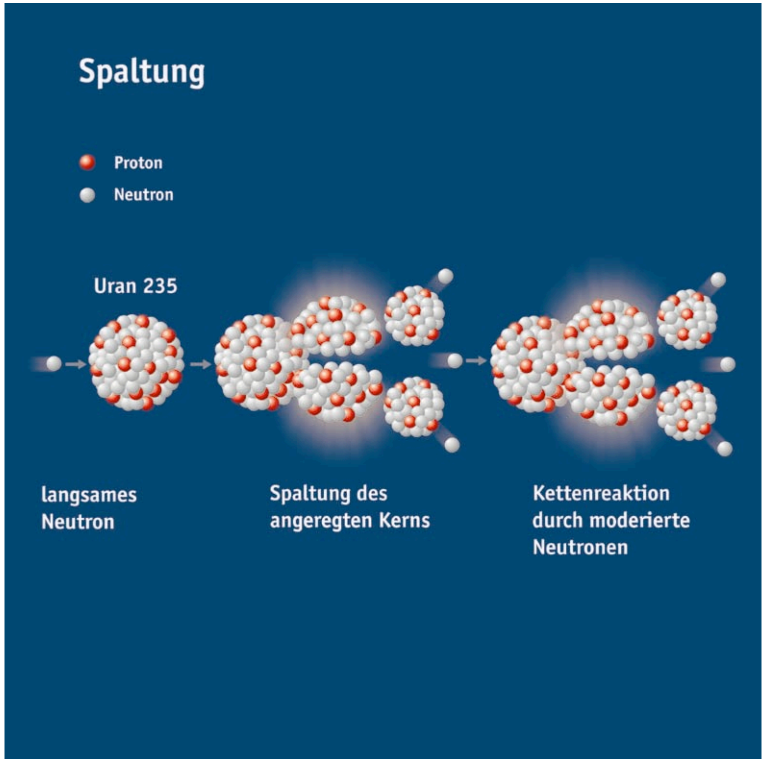
- ***v) magnetic moment***



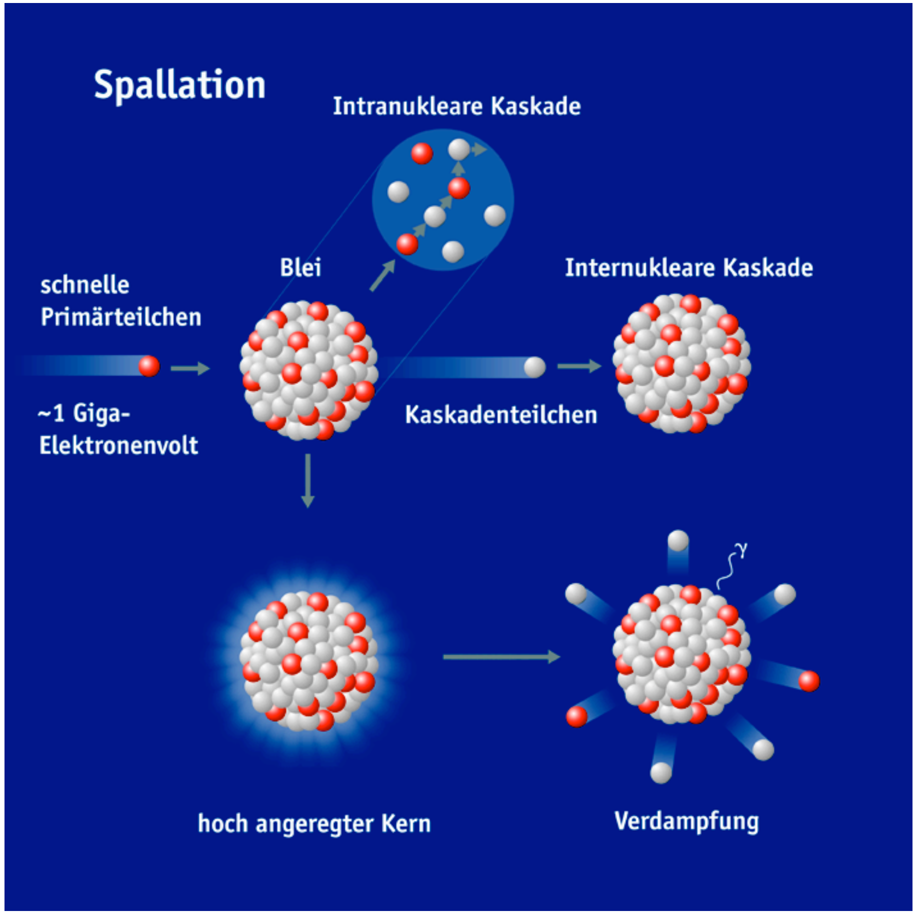
The neutrons have a magnetic moment

⇒ Studies of magnetic structure and dynamics

Where do we get neutrons?

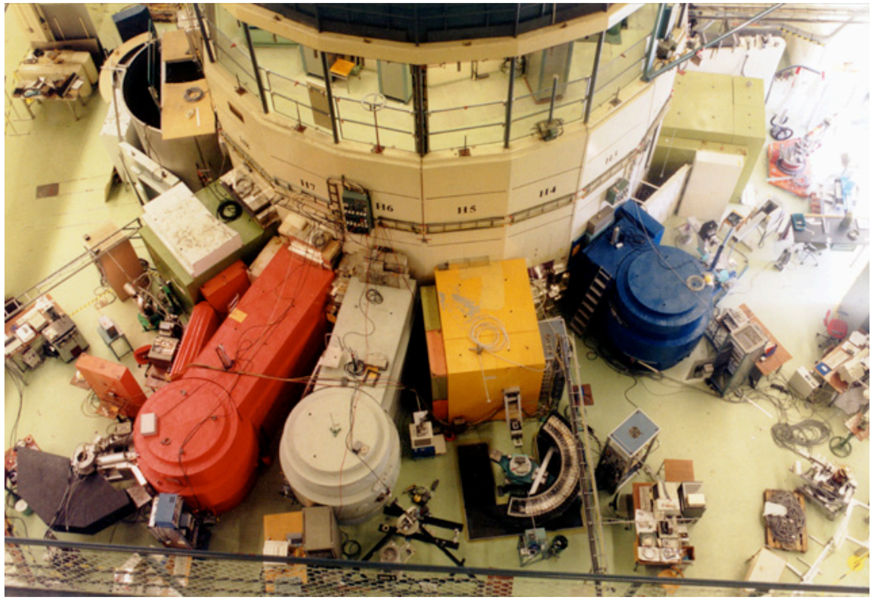


Fission in a nuclear reactor



Bombard heavy nucleus with high energy protons from an accelerator

Where do we get neutrons?



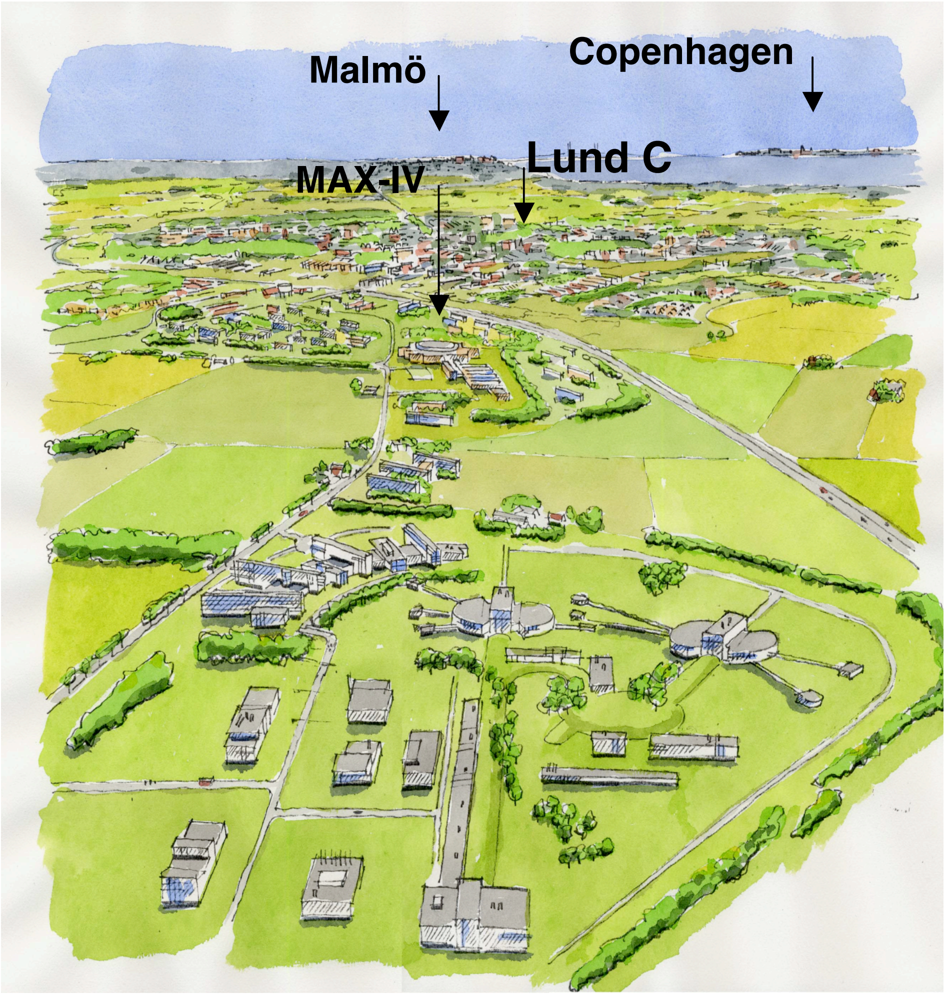
Instruments at the Studsvik reactor (now shut down)

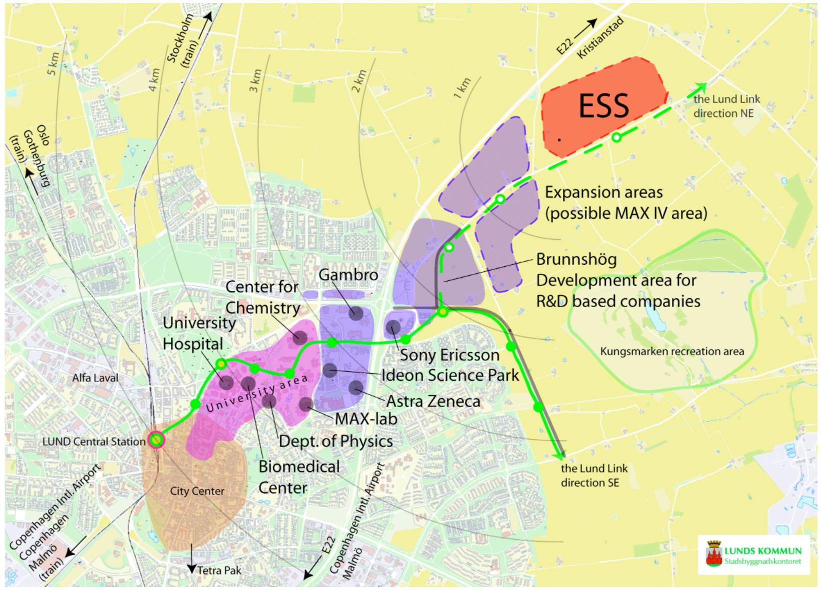
ILL, Grenoble France

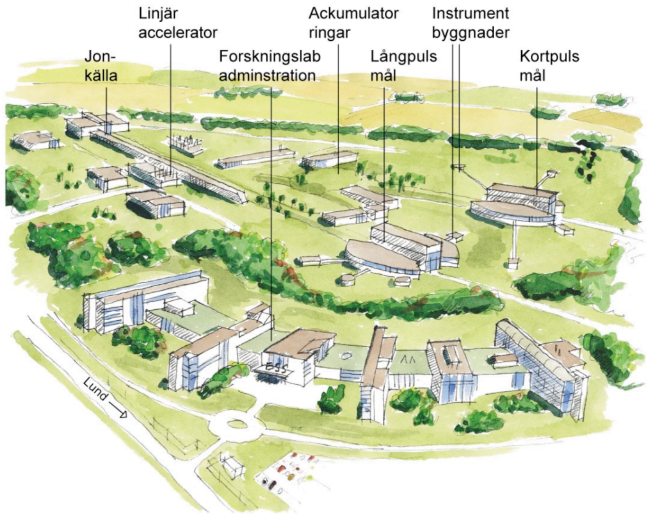
Sketch of spallation neutron source (SNS)

Also sources in UK and Japan

European Spallation Source in Lund?



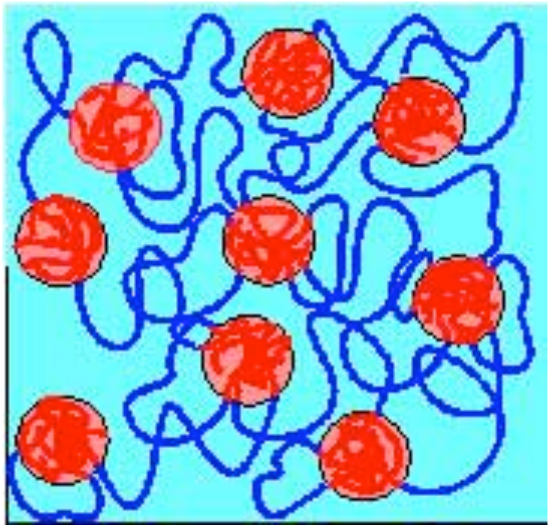




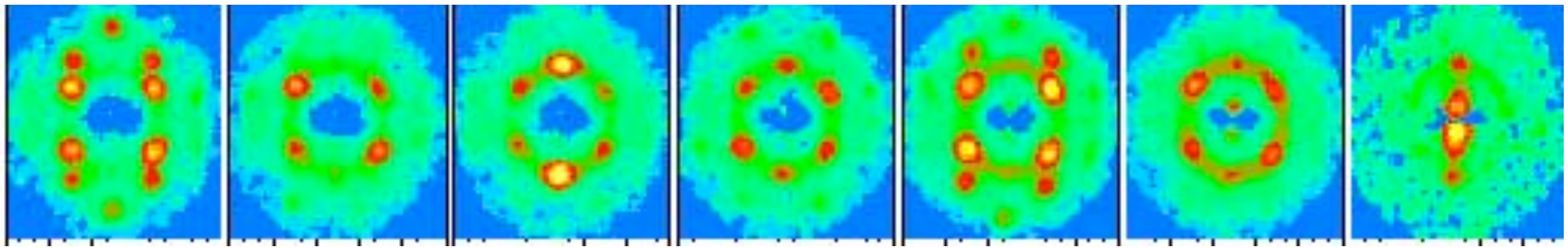
Example: Structure under shear

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

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



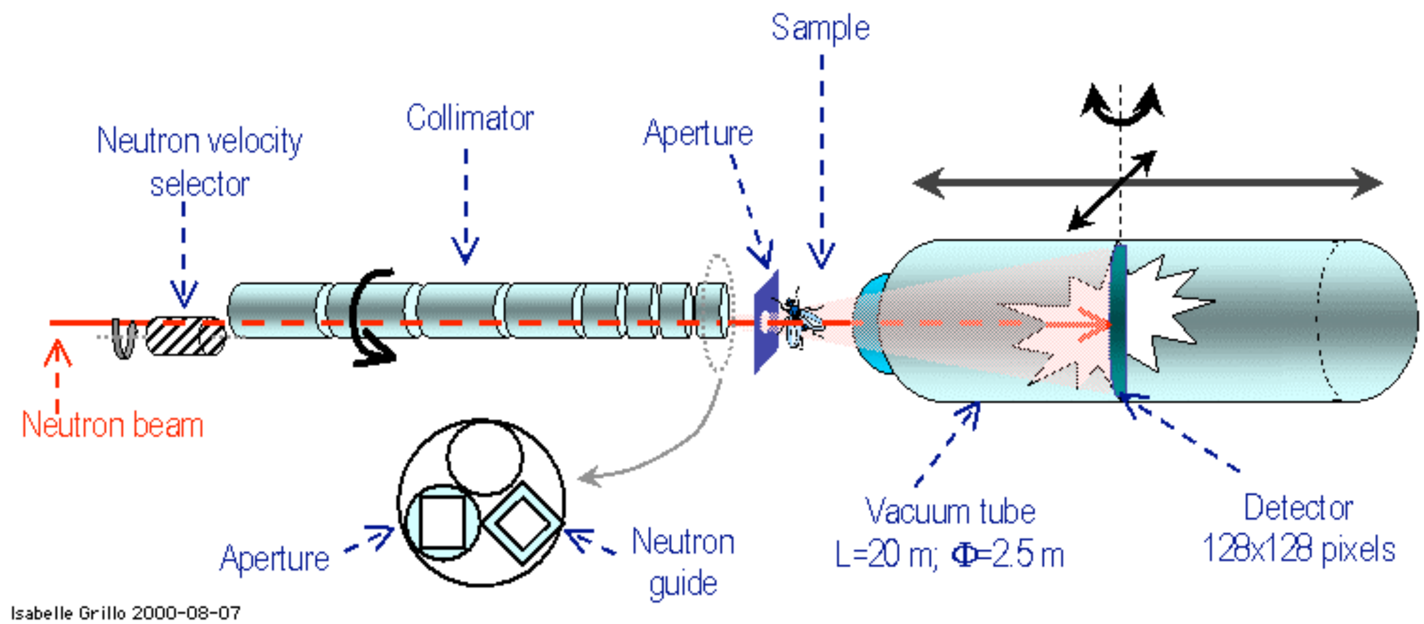
Example (from Risø):
Neutron experiments in a shear cell to simulate processing conditions



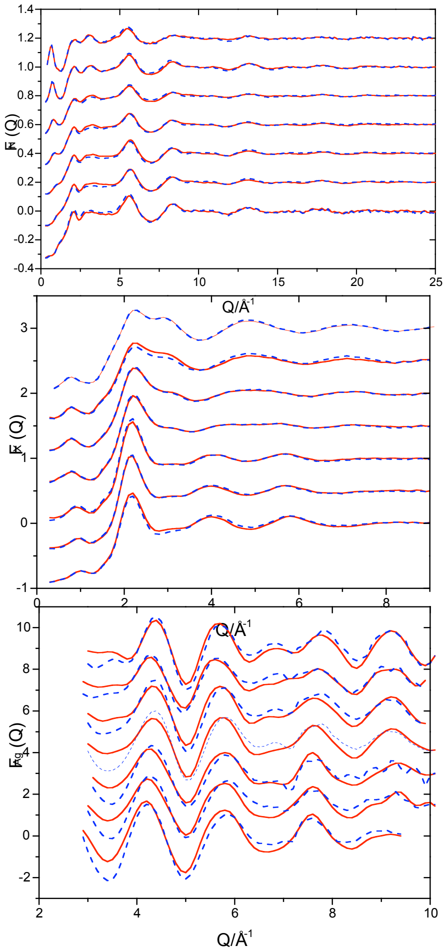
Small angle scattering

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

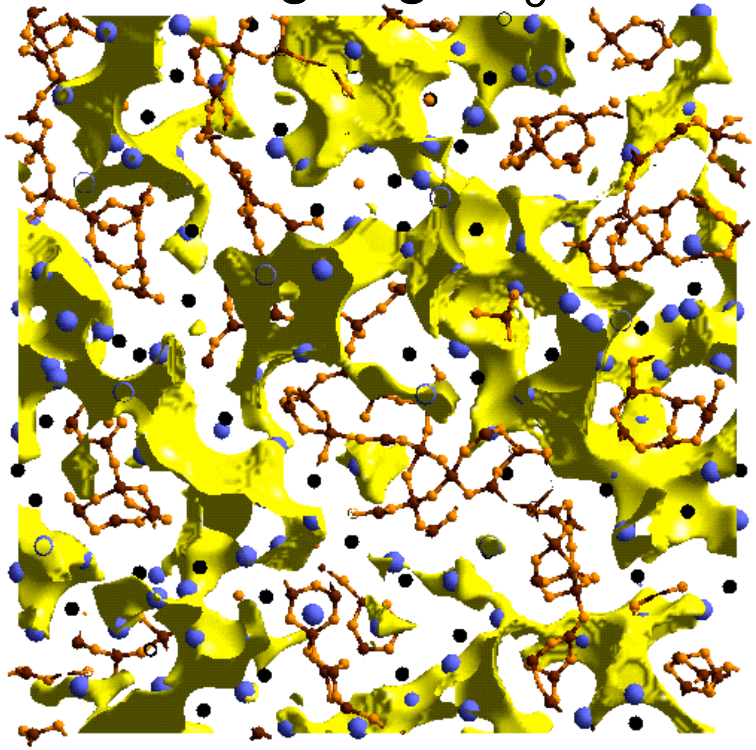
- radius of gyration
- size of phase separated regions
- size and shapes of pores in porous structures



Example: Glass structure



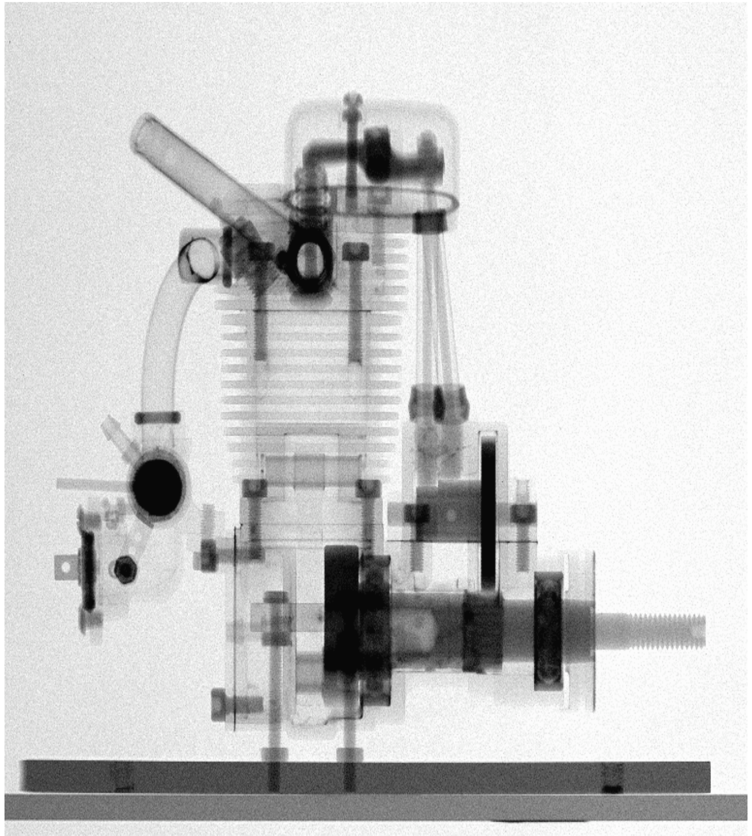
AgI-$AgPO_3$



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

Example: Tomography

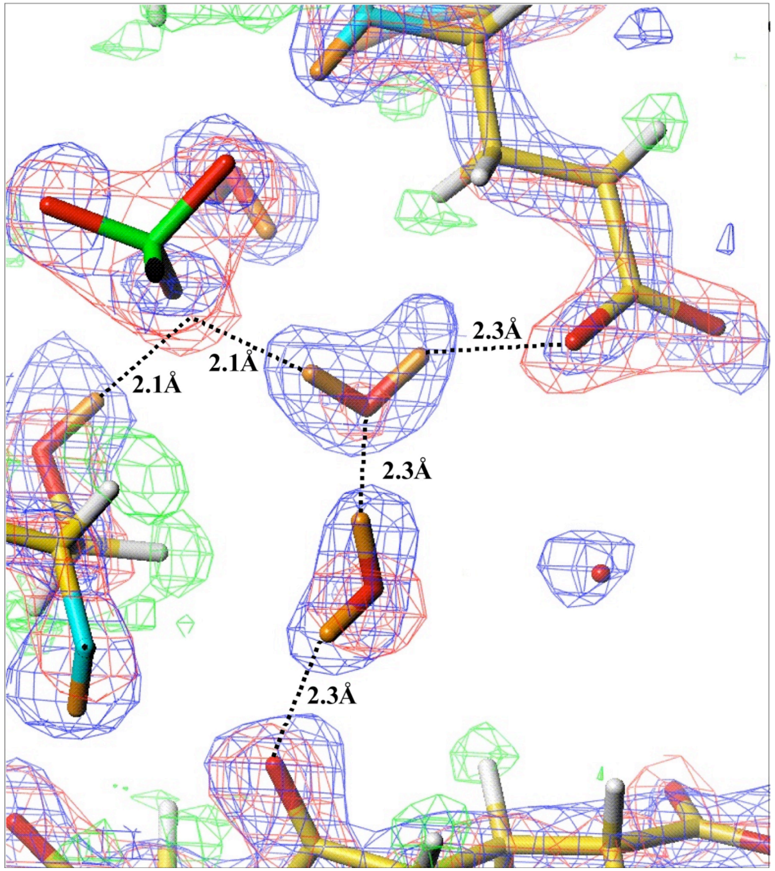
Real materials-Real Conditions-Real Time

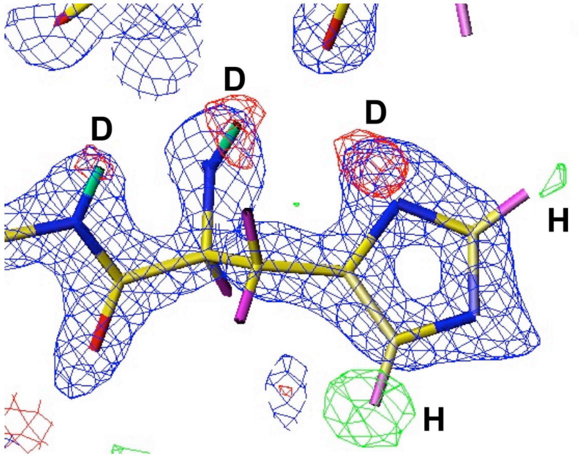


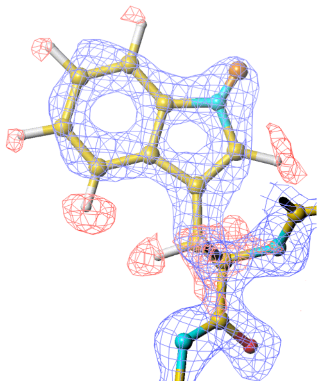
Tomography

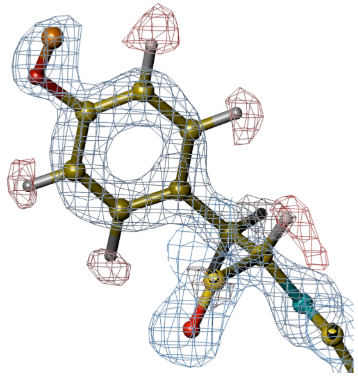
- *large field*
- *submillimeter resolution*
- *TOF structural mapping*

Example: Locating hydrogens







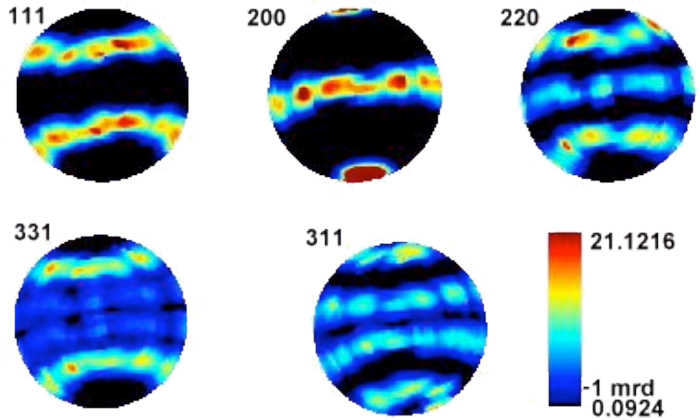


H: σ_{coh}=1.8 σ_{inc}=80.2(10^{-28} m^2)

D: σ_{coh}=5.6 σ_{inc}=2.0

Example: Old stuff

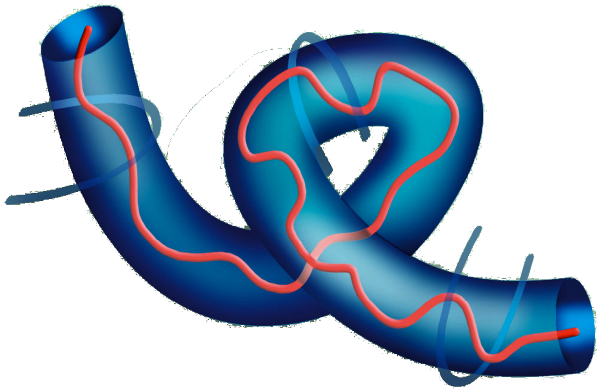
Copper axe (3.200 bc), iceman (Ötztal)

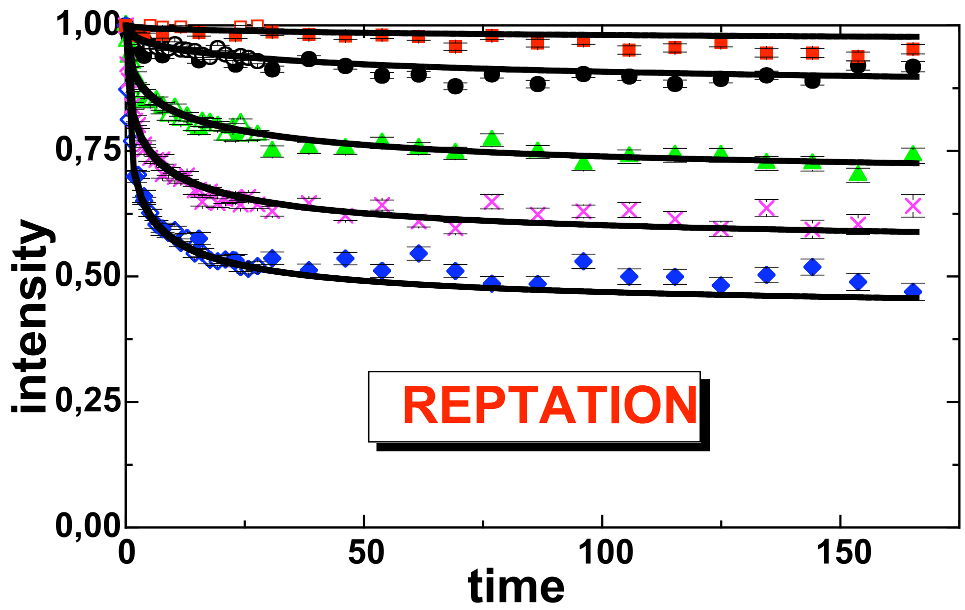


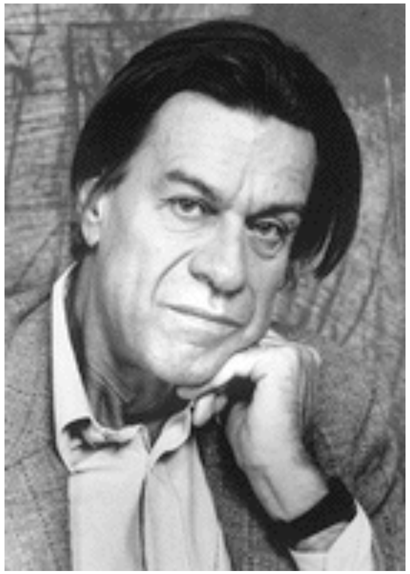
Ancient manufacturing history

- **Heat treatment**
- **Mechanical treatment**

Dynamics - reptation model







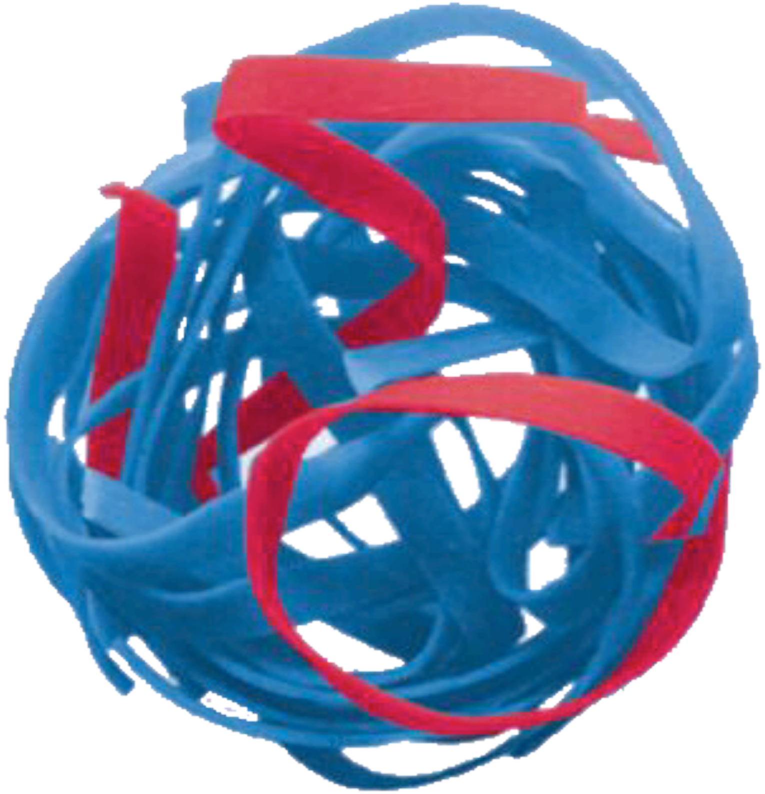
P.G. De Gennes
ESPCI Paris
France

Nobel prize 1991

Confirmation by Neutron Scattering (NSE)

Contrast variation

Partial H-D substitution



Isotopic contrasting in a polymer

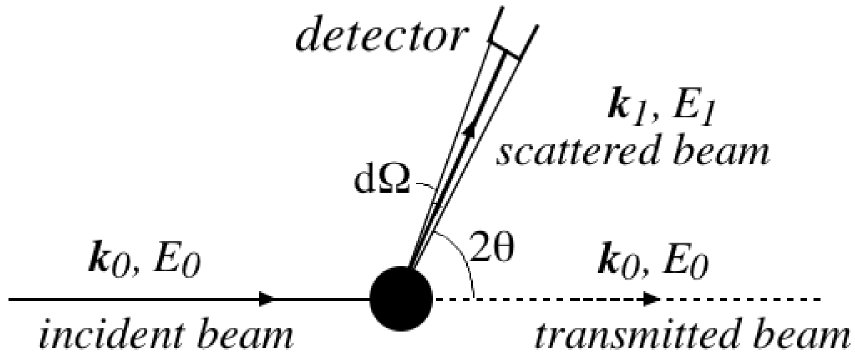
Experimental techniques

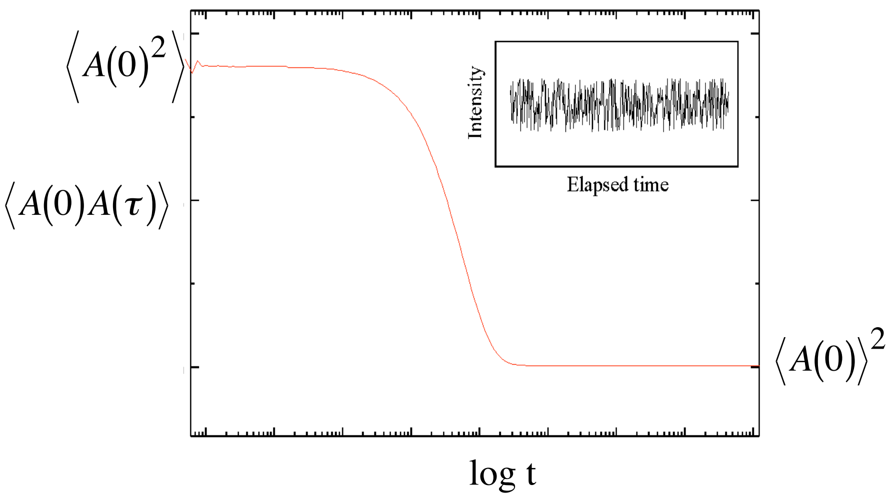
- General
- Fluctuations - correlation functions
- Scattering techniques - general aspects/theory

  ⇒ 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*
- *…*

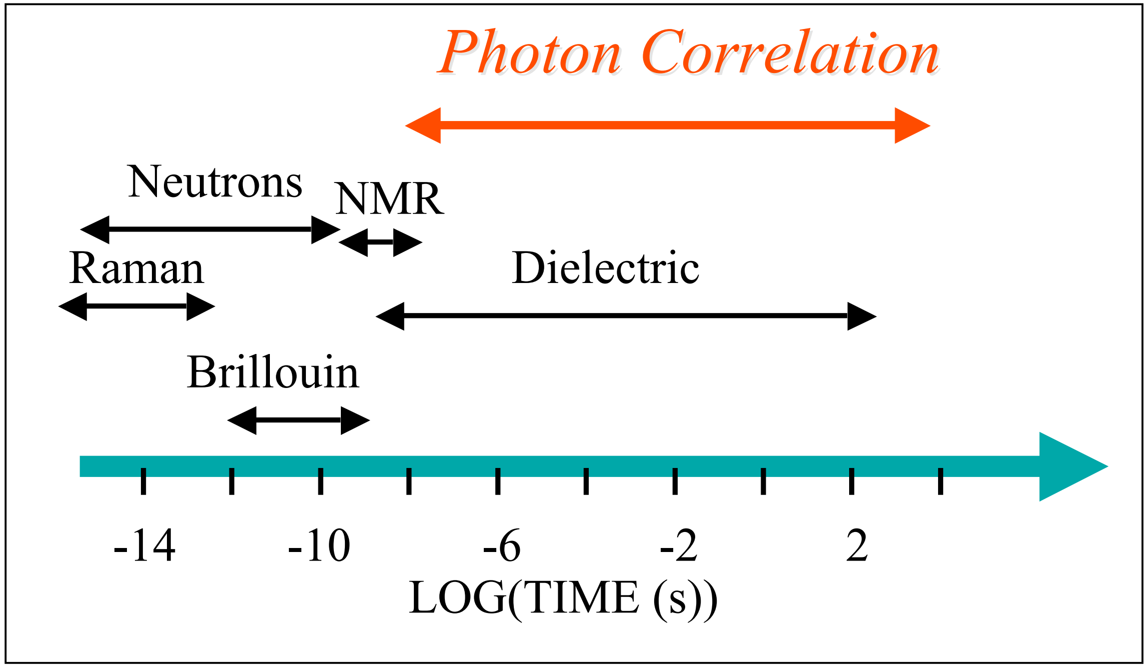
Photon Correlation Spectroscopy or dynamic light scattering

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!

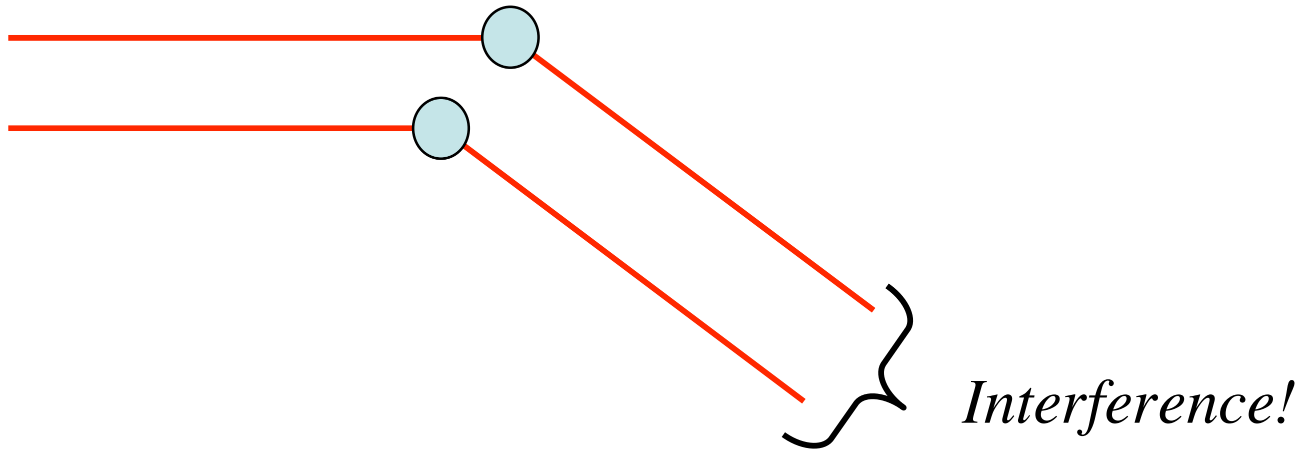
$t \approx 10^{-8} - 10^{3}$ s

Visible light ⇒ Q-range:

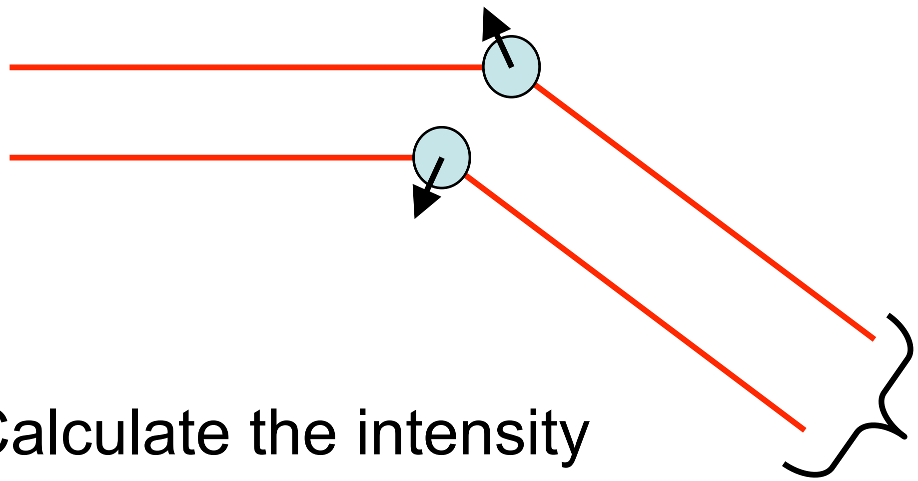
$Q = 4\pi \sin(\theta/2)/\lambda \sim 10^{-3}$ Å^{-1}

⇒ length scales: $r \sim \mu m$

Dynamic light scattering



Dynamic light scattering



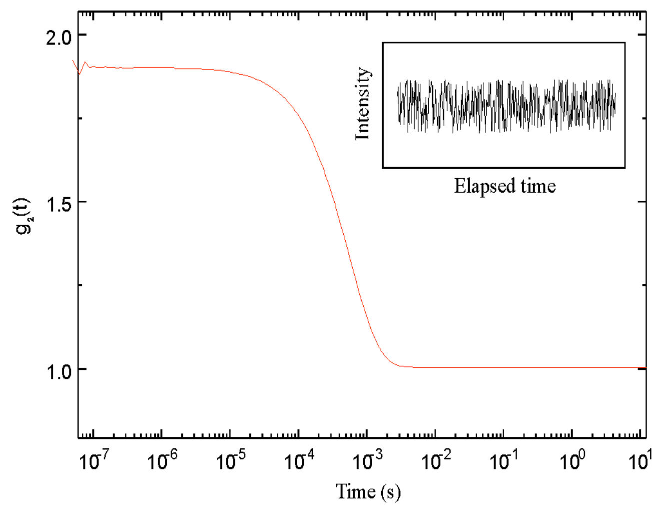
Time-dependent interference!

Calculate the intensity correlation function:

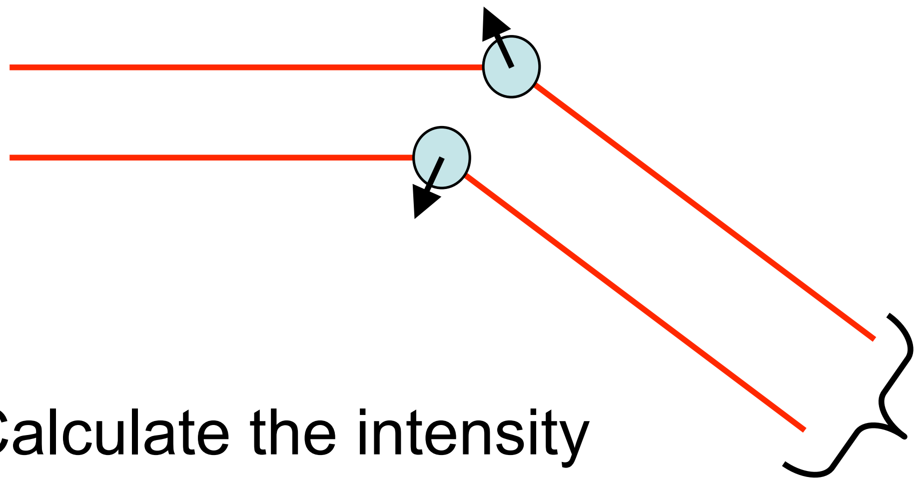
$$\langle I(t)I(t+\tau)\rangle = \frac{1}{N}\sum_{i=1}^{N} I(t_i)I(t_i+\tau)$$

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

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



Dynamic light scattering



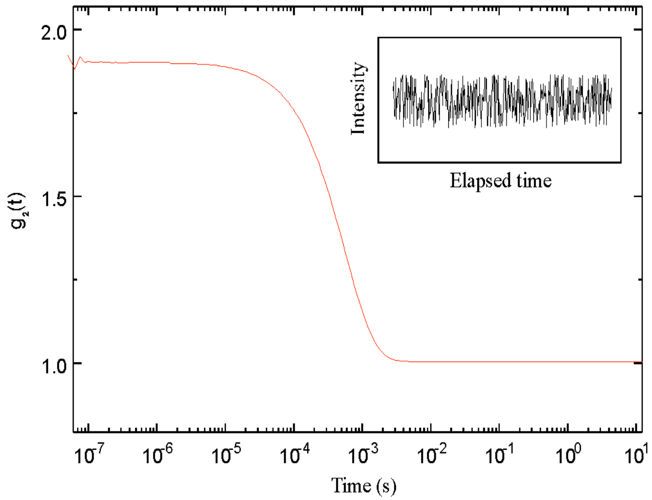
Time-dependent interference!

Calculate the intensity correlation function:

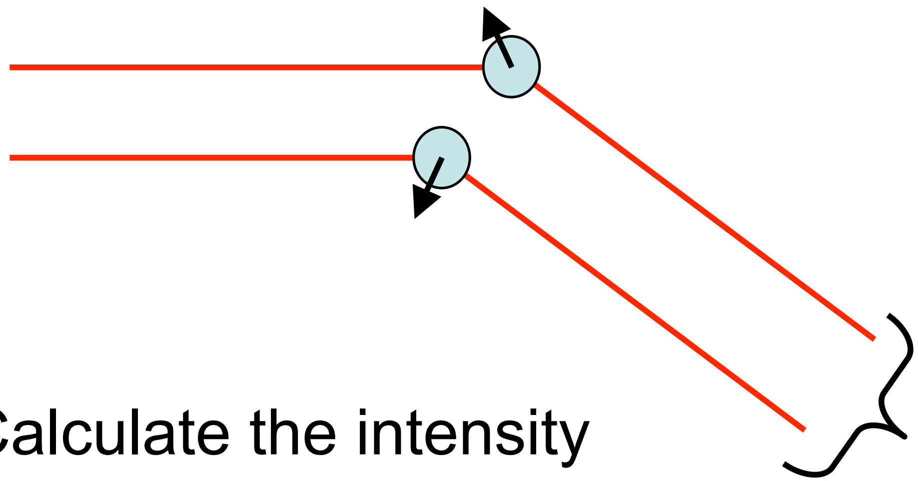
$$\langle I(t)I(t+\tau)\rangle \Rightarrow \langle I(0)I(t)\rangle \text{ start time not important}$$

Normalized intensity auto-correlation funciton

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



Dynamic light scattering



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

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

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

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

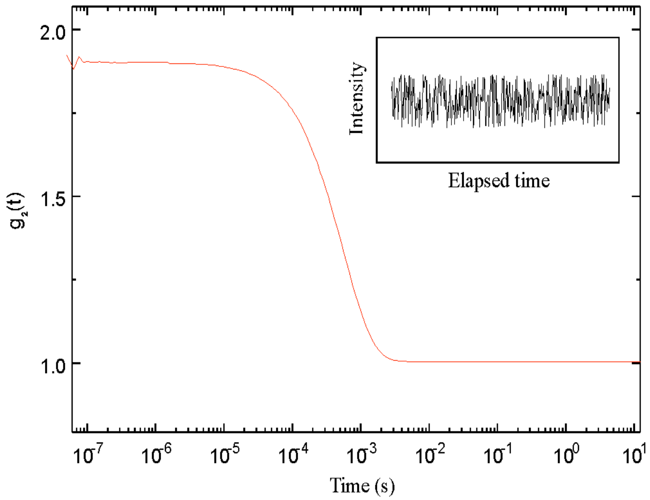
Time-dependent interference!

Calculate the intensity correlation function:

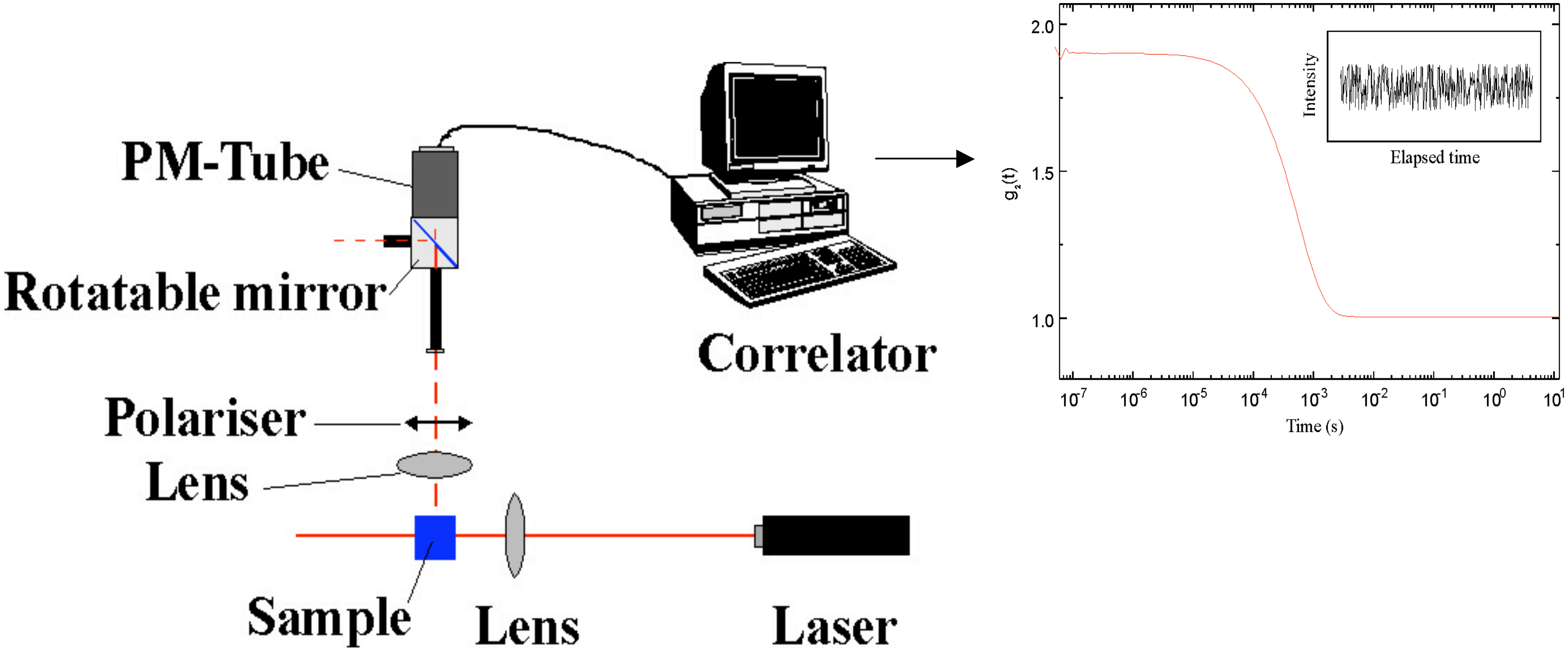
$\langle I(t)I(t+\tau)\rangle \Rightarrow \langle I(0)I(t)\rangle$ start time not important

Normalized intensity auto-correlation funciton

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



Schematic set-up for PCS

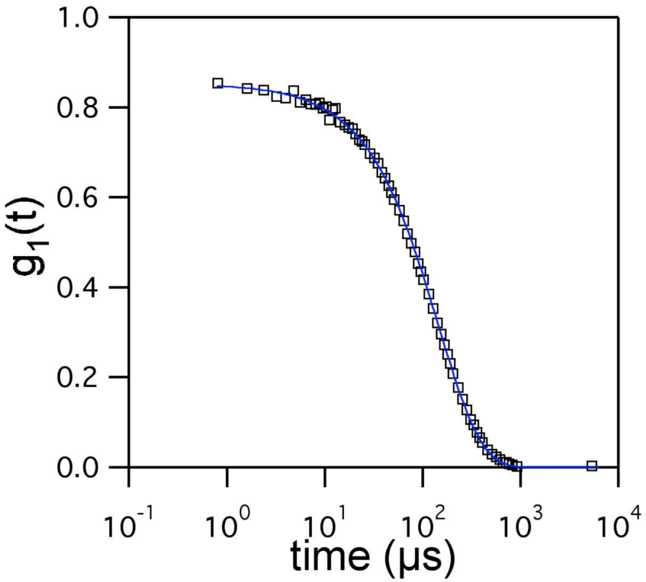


Determining particle size

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:

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

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

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

Determining particle size

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

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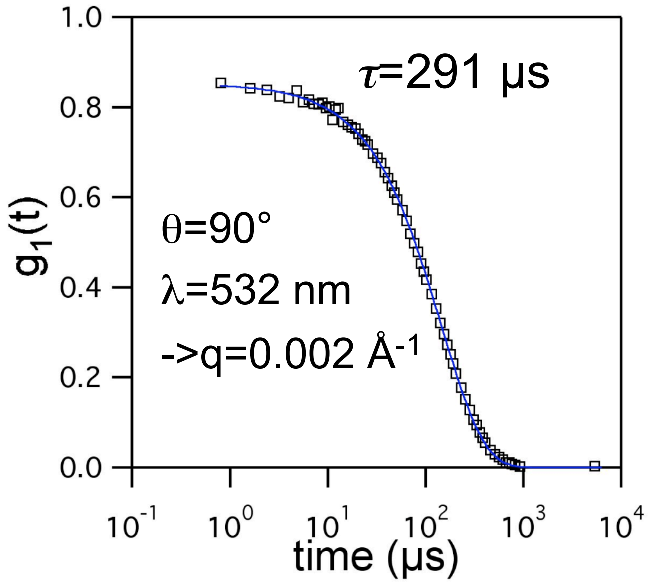

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$$\Rightarrow \tau_q = \frac{6\pi\eta r}{k_B T q^2} \quad \text{or} \quad r = \frac{\tau_q k_B T q^2}{6\pi\eta}$$

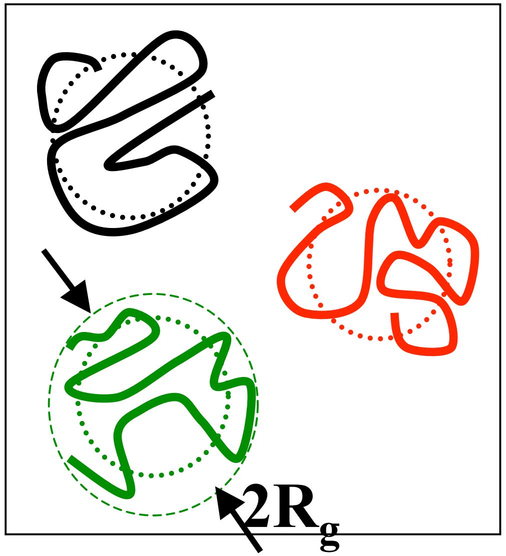
Polystyrene sphere in water:

n=1.33, η=0.89·10^{-3} Pas, T=293 K

-> *r=28 nm*

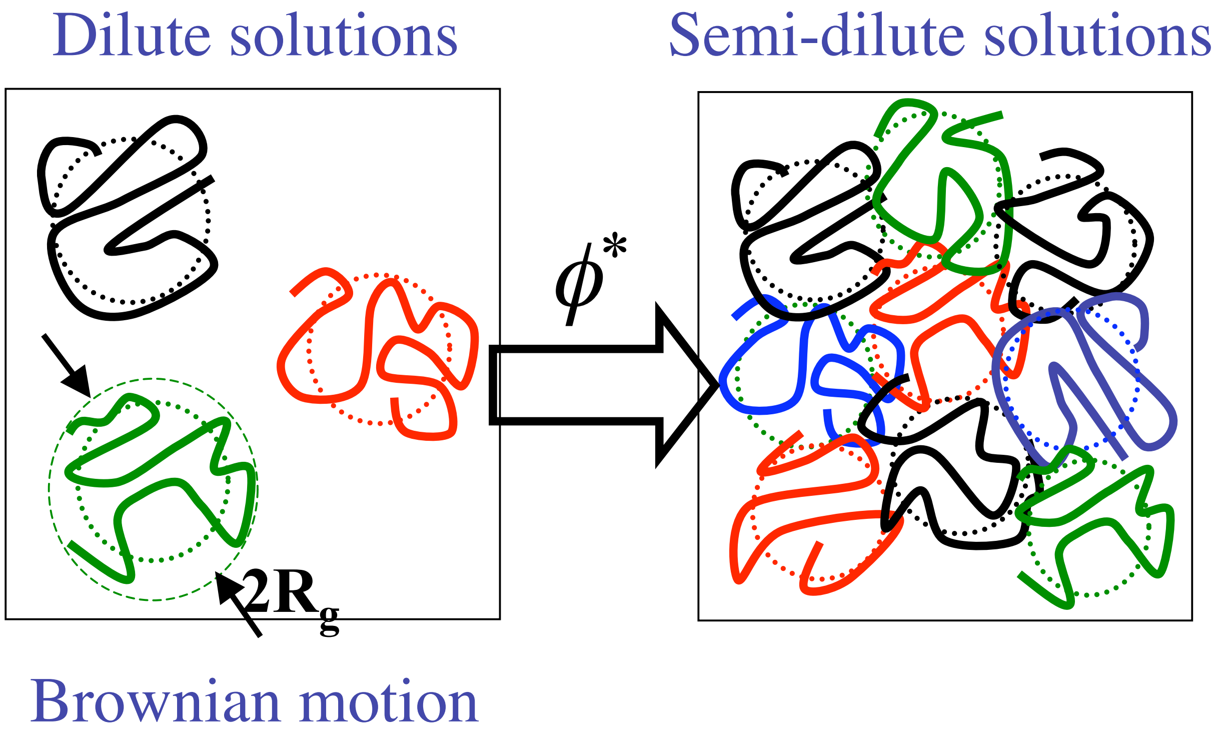
Polymer Dynamics

Dilute solutions

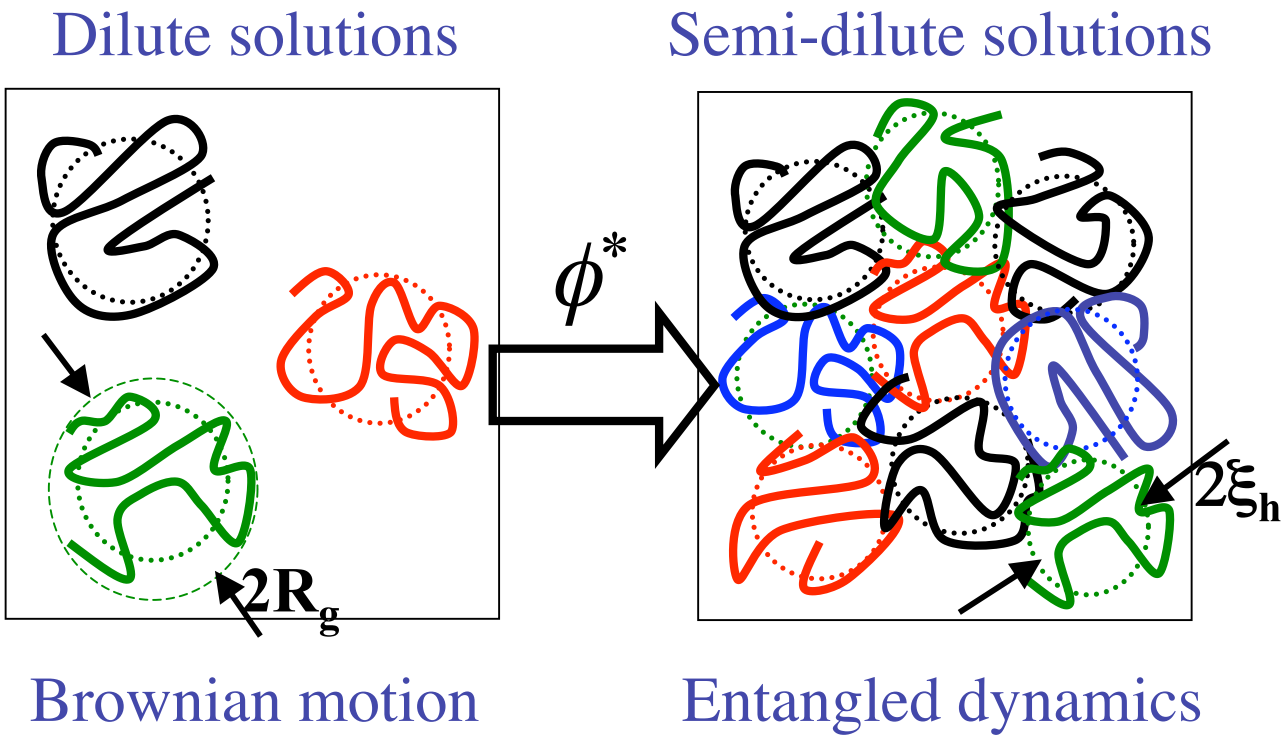


Brownian motion

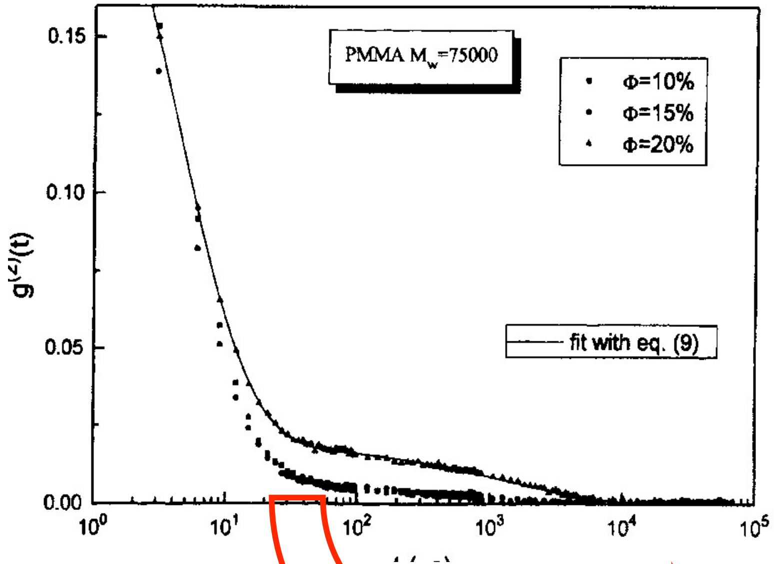
Polymer Dynamics



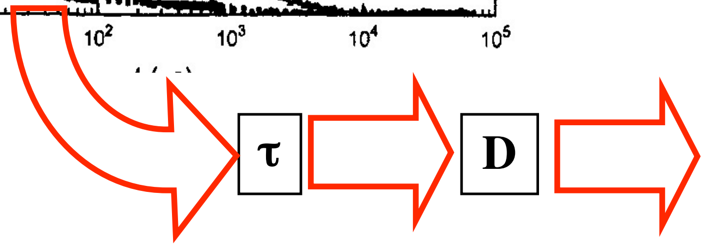
Polymer Dynamics

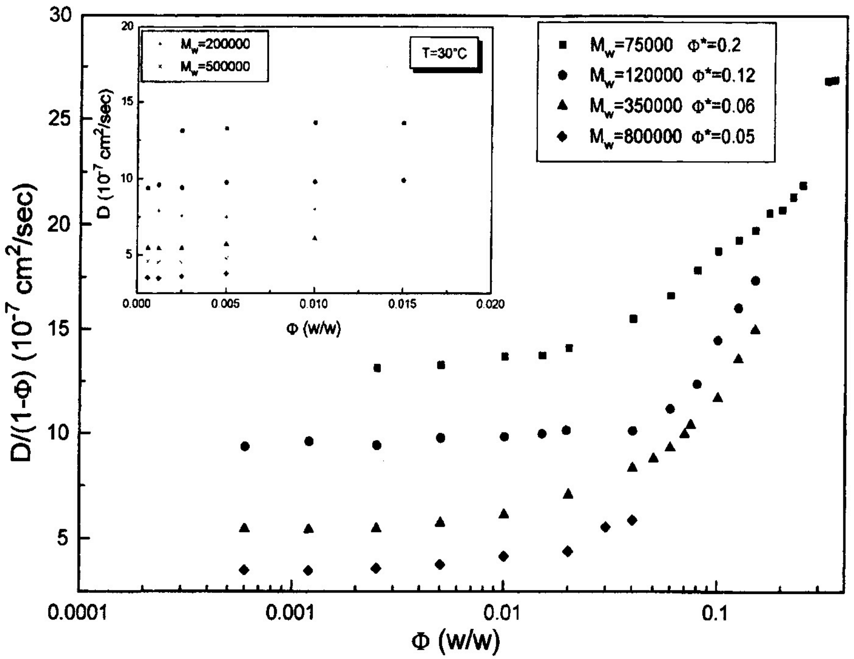


Determining R_g and ϕ_c *from PCS*



PCS experiment on PMMA/acetone solutions



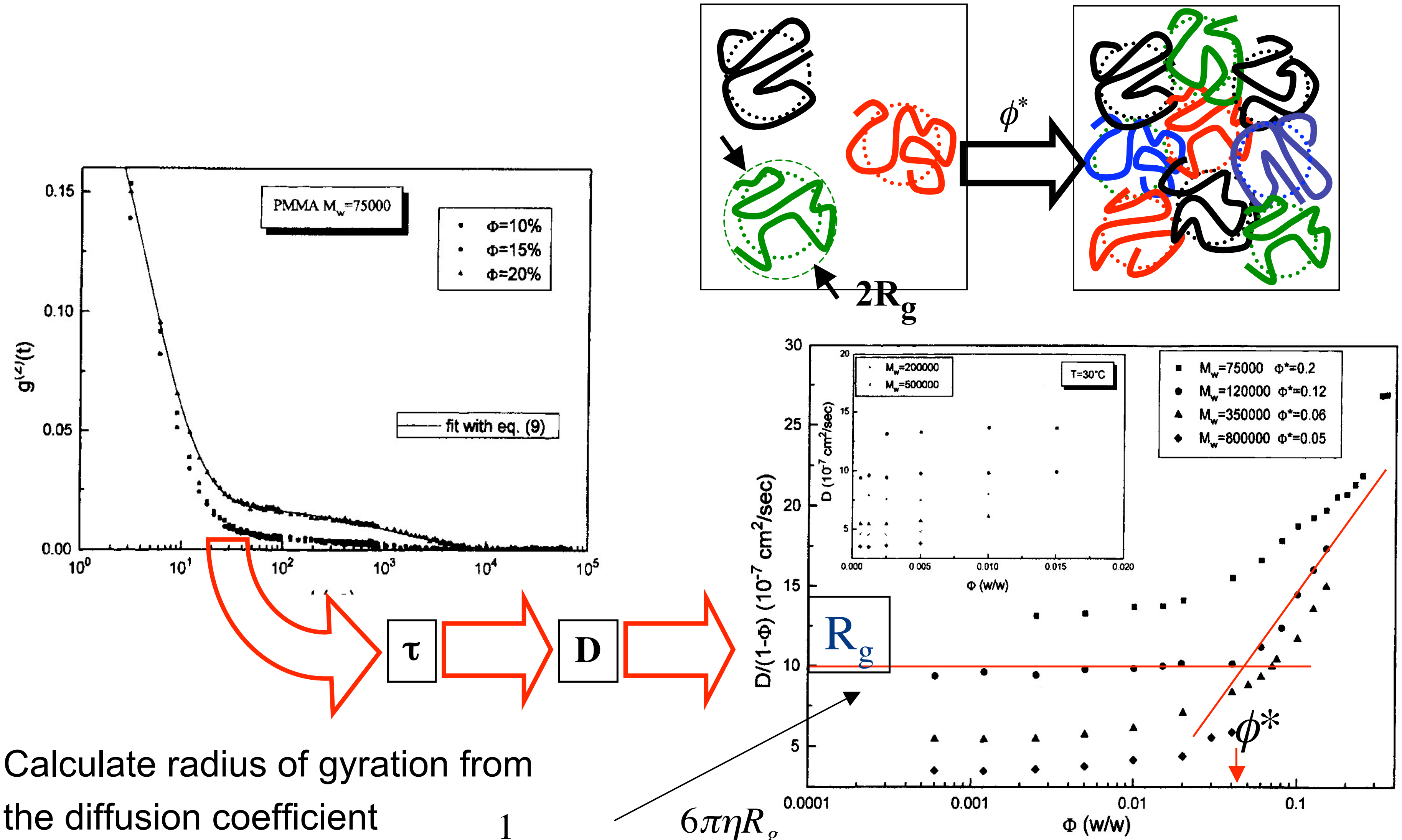


A. Faraone *et al*. Macromolecules **1999**, *32,* 1128

Obtain diffusion coefficient by measuring the relaxation time for several q

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

Determining R_g and ϕ_c *from PCS*

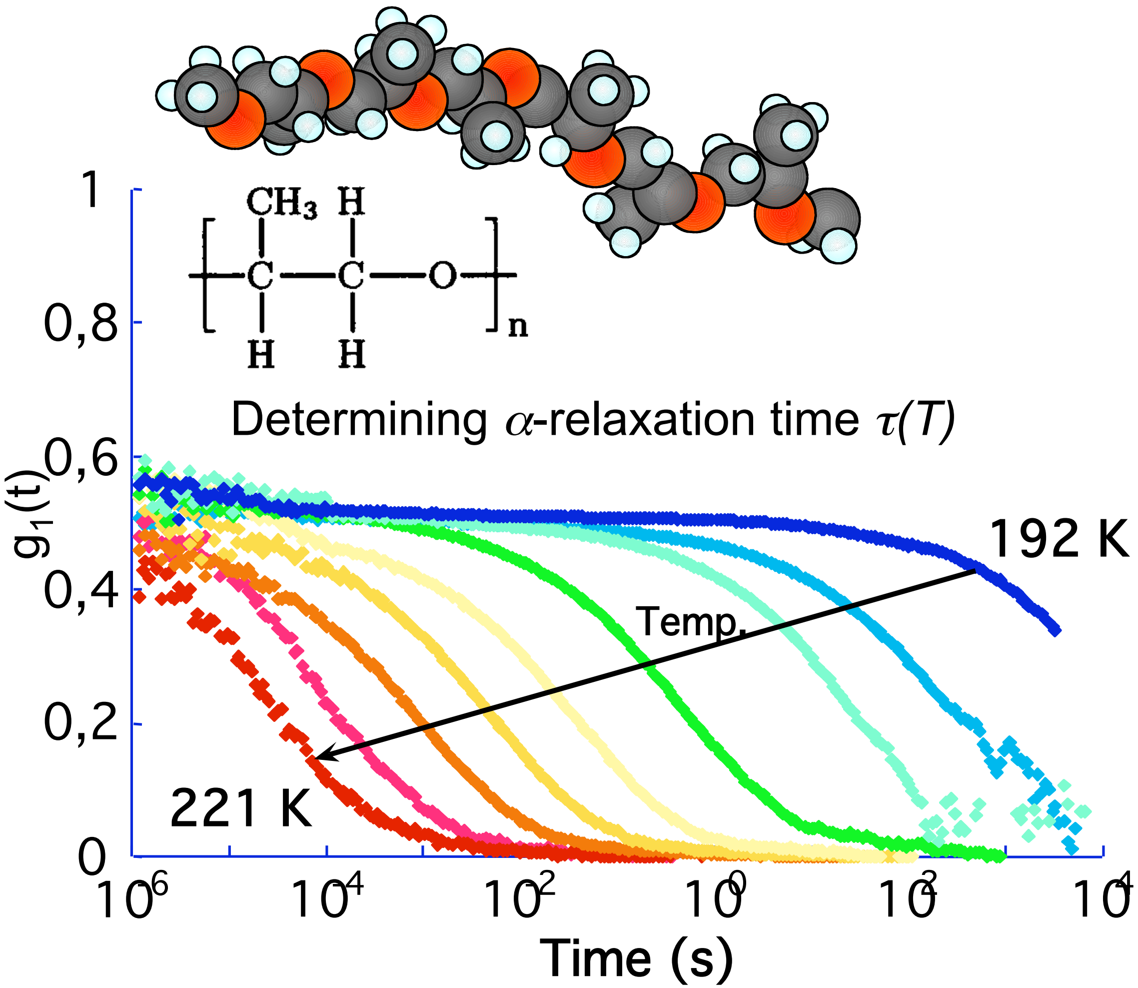


Calculate radius of gyration from the diffusion coefficient

$$\tau_q = \frac{1}{Dq^2} \qquad \tau_q = \frac{6\pi\eta R_g}{k_B T q^2}$$

Glass transition dynamics

a glass forming polymer - poly(propylene glycole)



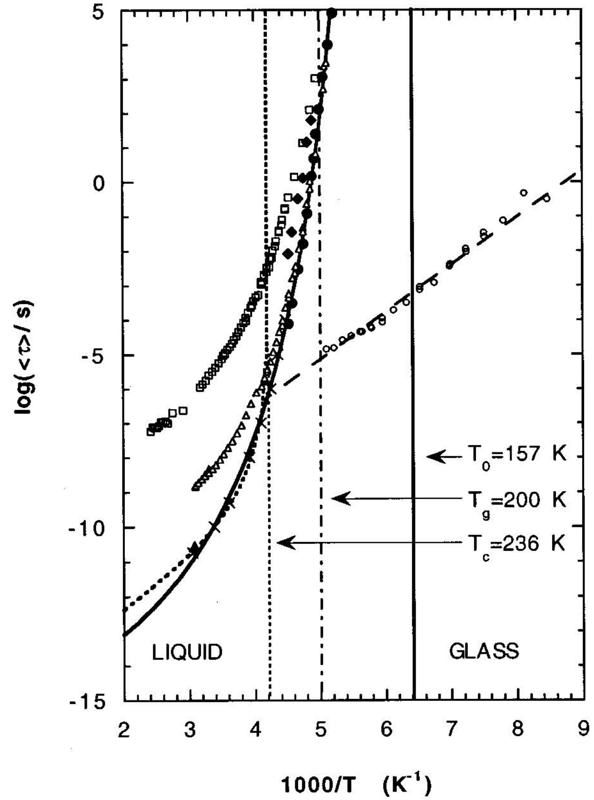


FIG. 4. Arrhenius plot of the mean relaxation times for PPG)00). Photon correlation data for the main α process are marked th filled circles, whereas data for the α' relaxation are marked th filled diamonds. ISS (Ref. 33) and Brillouin data (Ref. 32) are arked with crosses and a filled triangle, respectively. Dielectric ta reported by Schönhals *et al.* (Refs. 30 and 31) for the α', α, d β relaxations are marked with open squares, open triangles and en circles, respectively. Solid curve represents a fit of the VFT uation [Eq. (3)] to the α process observed with the different light-attering techniques, the dotted curve represents a fit of the MCT wer law [Eq. (5)] to the high-temperature data and the dashed rve represents an Arrhenius equation through the dielectric β re-

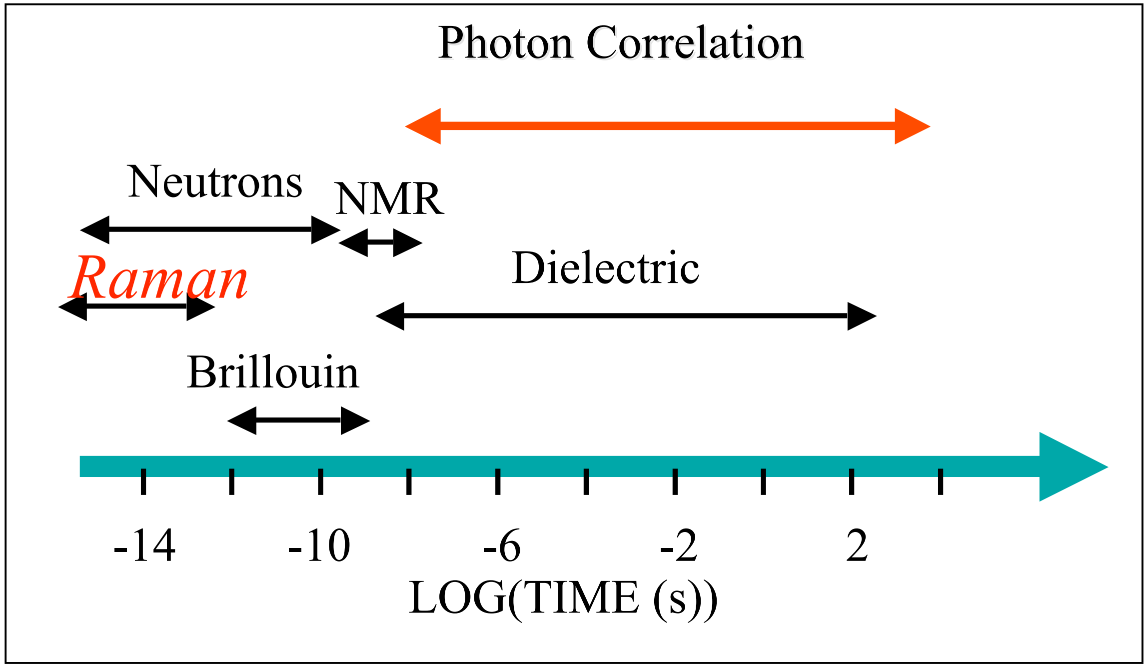
Experimental techniques

- General
- Fluctuations - correlation functions
- Scattering techniques - general aspects/theory

  $\Rightarrow$ Neutron scattering

  $\Rightarrow$ **Light scattering**
  - **Raman/IR spectroscopy**
  - Photon correlation spectroscopy

Vibrational spectroscopy



Probing molecular vibrations

Time scale:

$\Rightarrow$ fs-ps processes

Length scale:

$q \approx 10^{-3}$ Å^{-1}

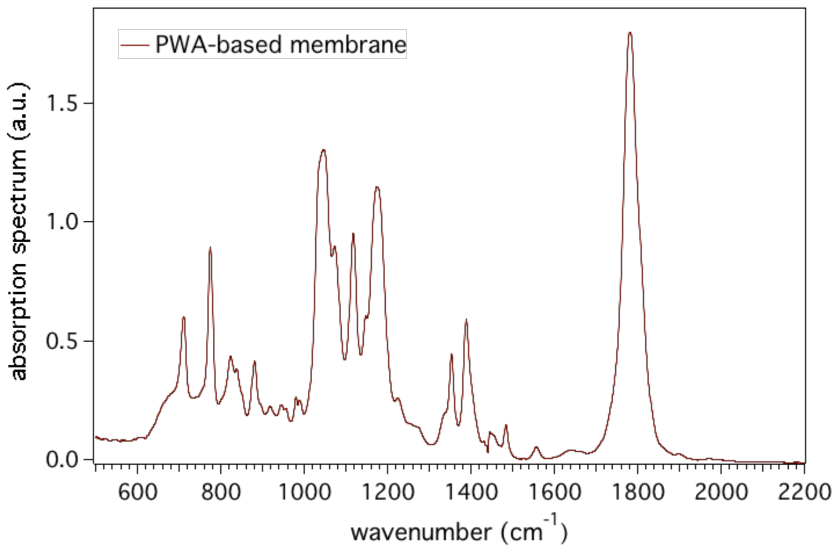
but probing local vibrations

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

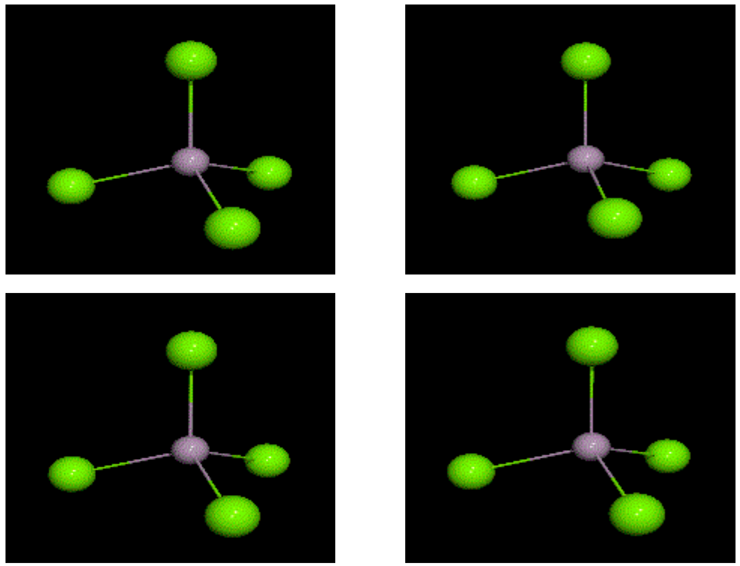
Vibrational spectroscopy

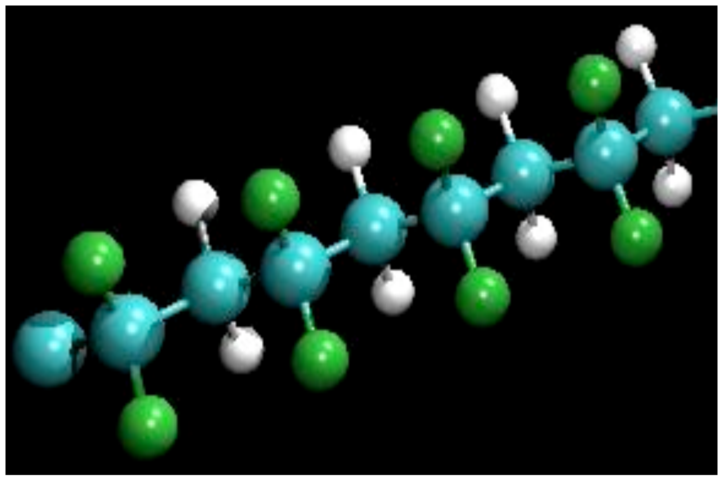
- potential energy, *V(r)*
- chemical bonds/forces, F_i

$\Rightarrow$ frequency of vibration, ν_k

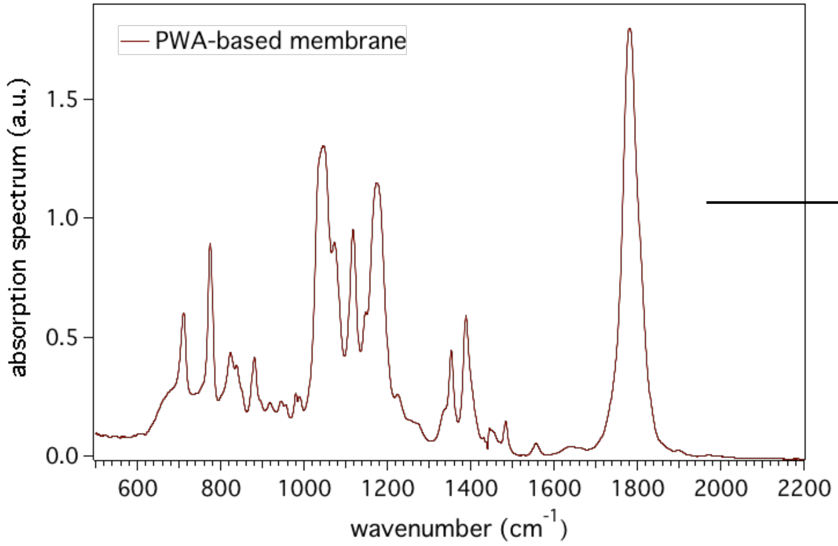


3N-6 vibrational modes

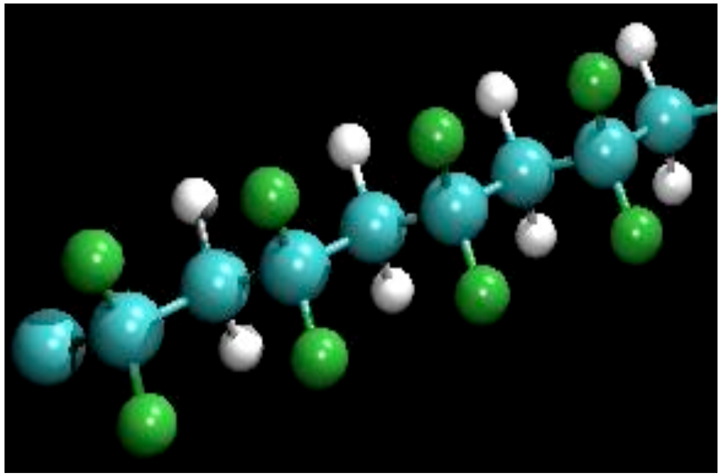




Vibrational spectroscopy



- composition
- coordination
- conformations
- interactions



Vibrational levels

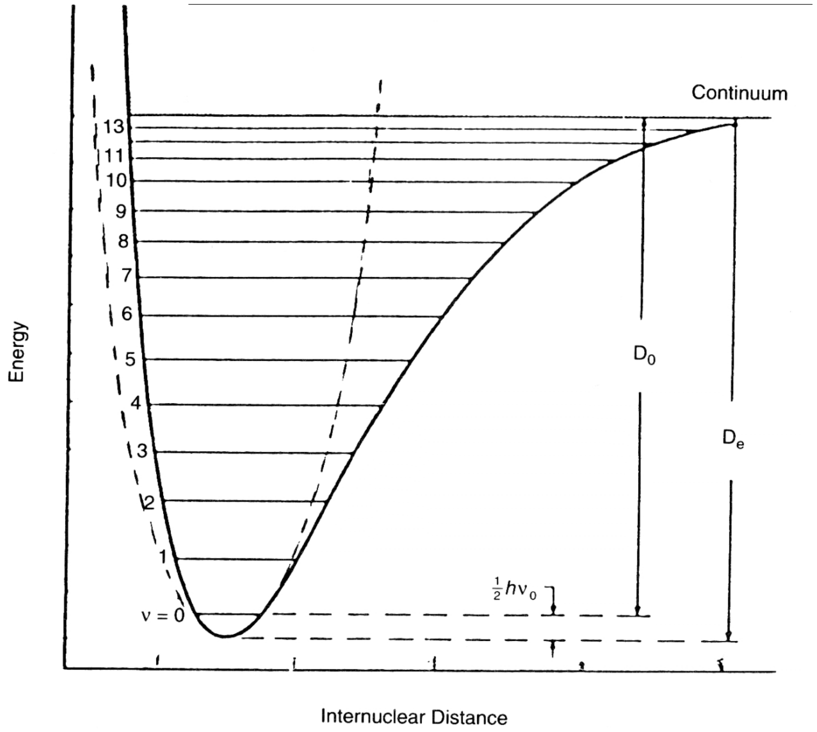
• molecular motion is quantized; vibrational quantum levels (quantum number “v”)

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

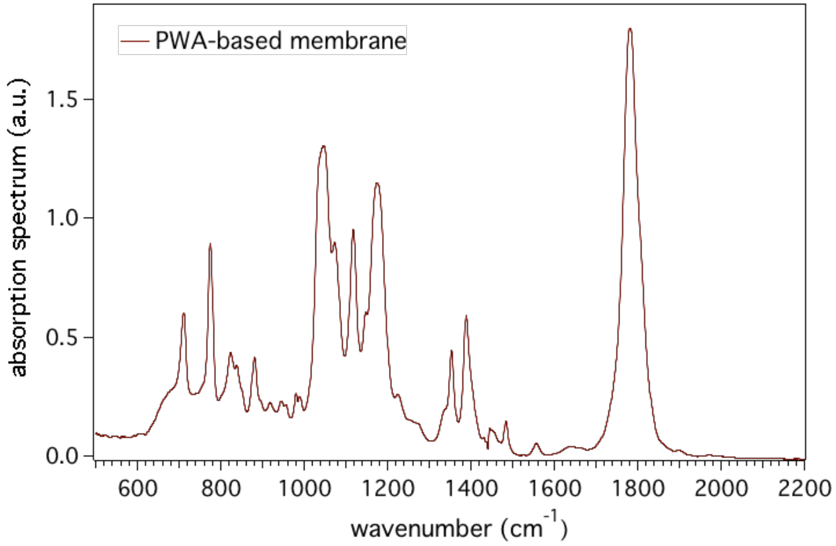
$$\hbar = \frac{h}{2\pi} \qquad \omega = 2\pi\nu \qquad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

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

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



Vibrational spectroscopy

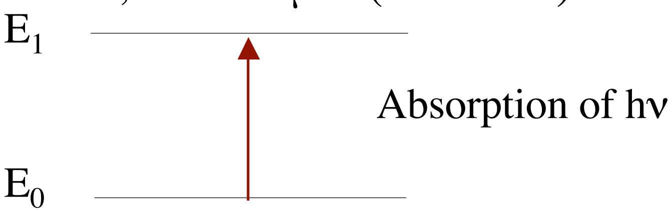


IR-spectrosocopy

Polychromatic incident light

$\lambda = h\nu$

$\lambda \sim 0{,}7$- 1000 μm (NIR-FIR)

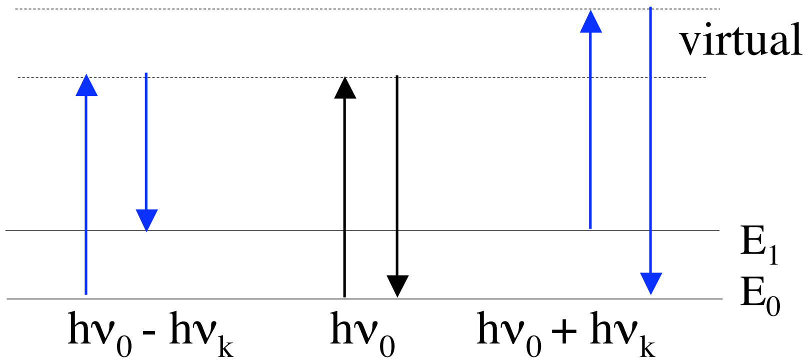


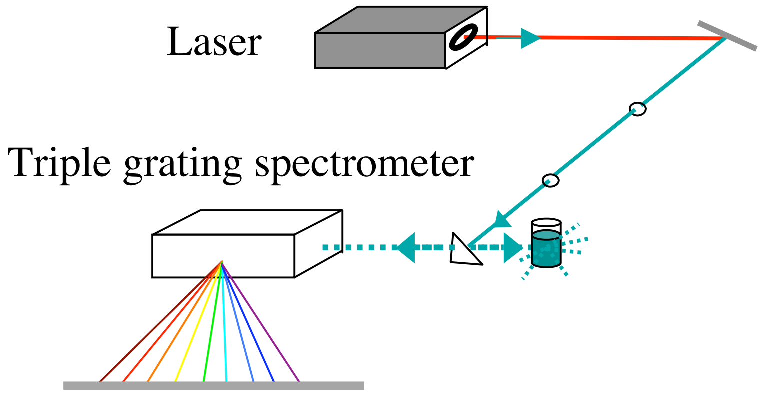
Raman spectroscopy

Monochromatic incident light

$\lambda = h\nu_0$

$\lambda \sim 400$-700 nm

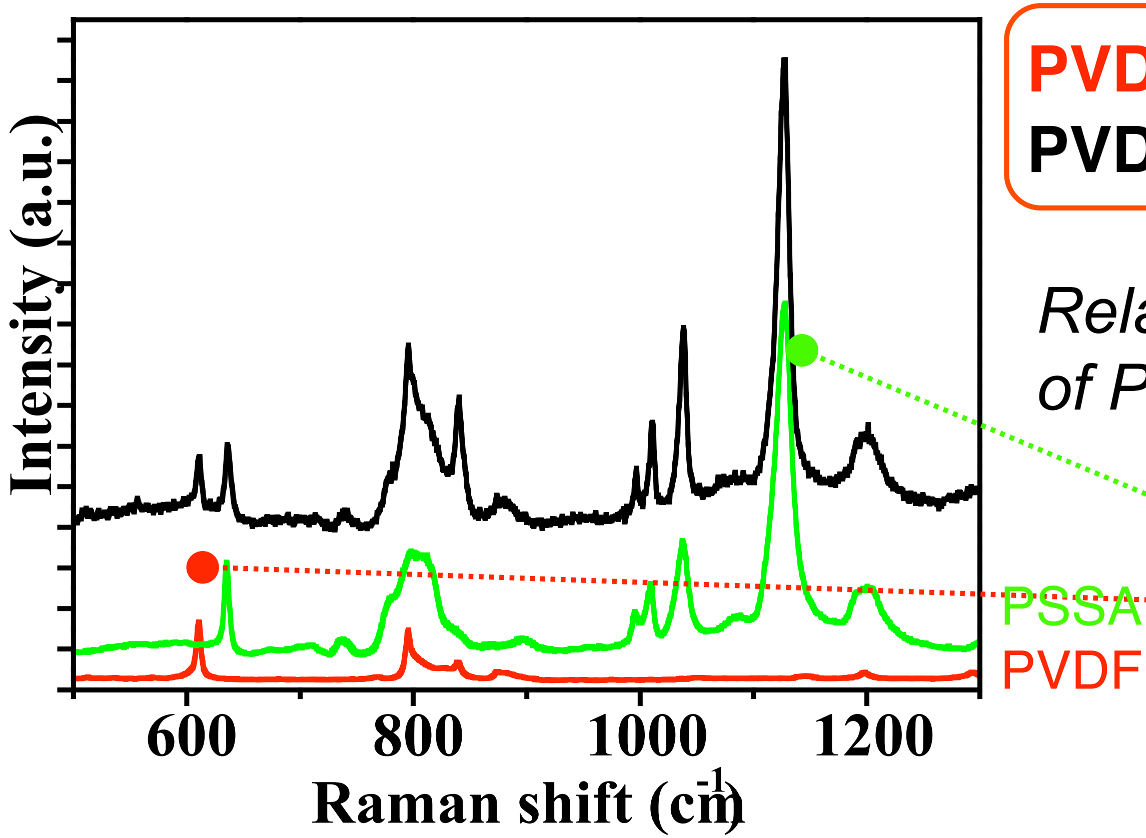




Raman vs. IR

	Infrared Spectroscopy	Raman Spectroscopy
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



PVDF + PSSA ⇒ PVDF-g-PSSA

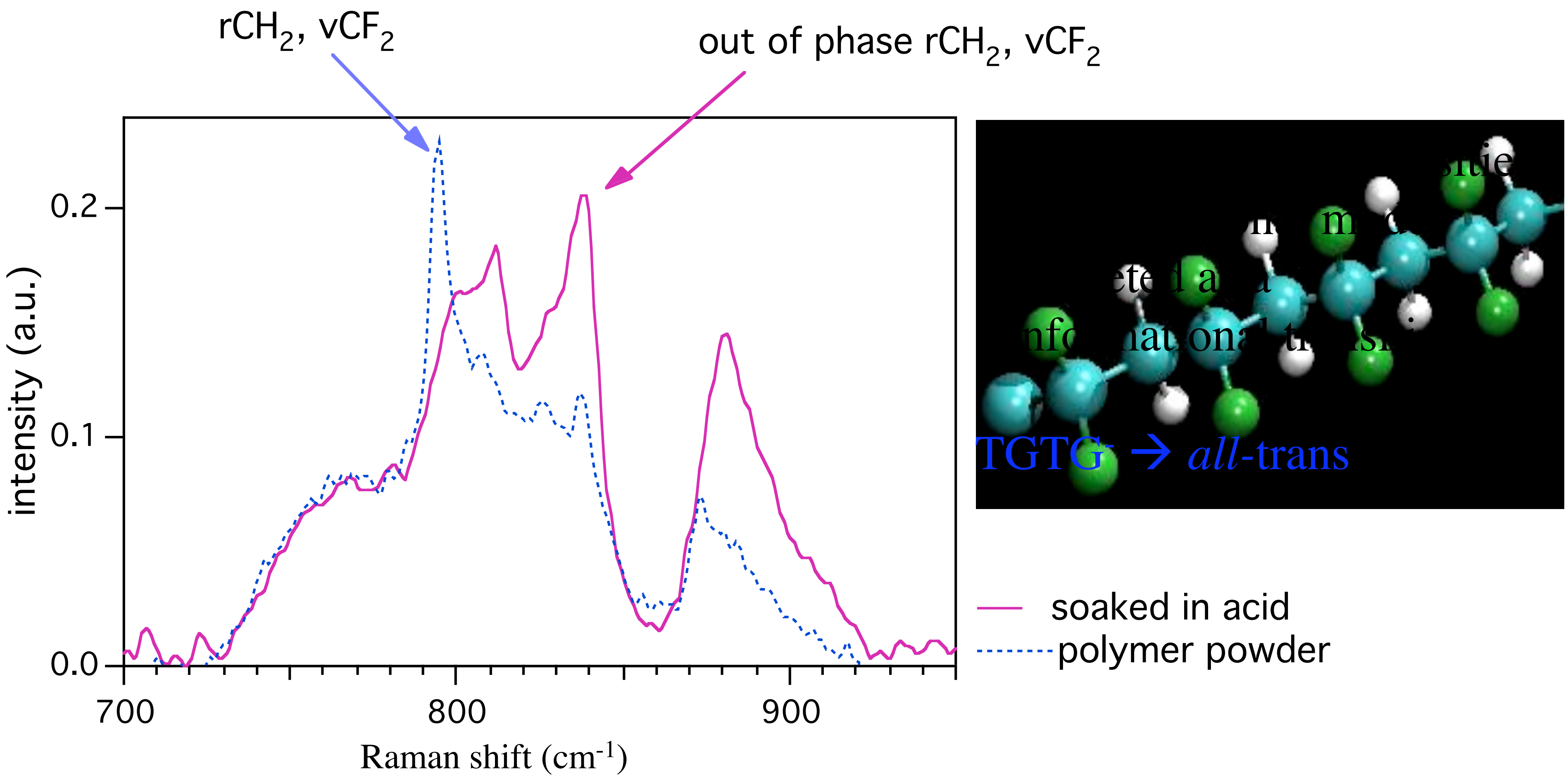
Relative concentration of PSSA:

$$\frac{I(1127)\ (PSSA)}{I(610)\ (PVDF)}$$

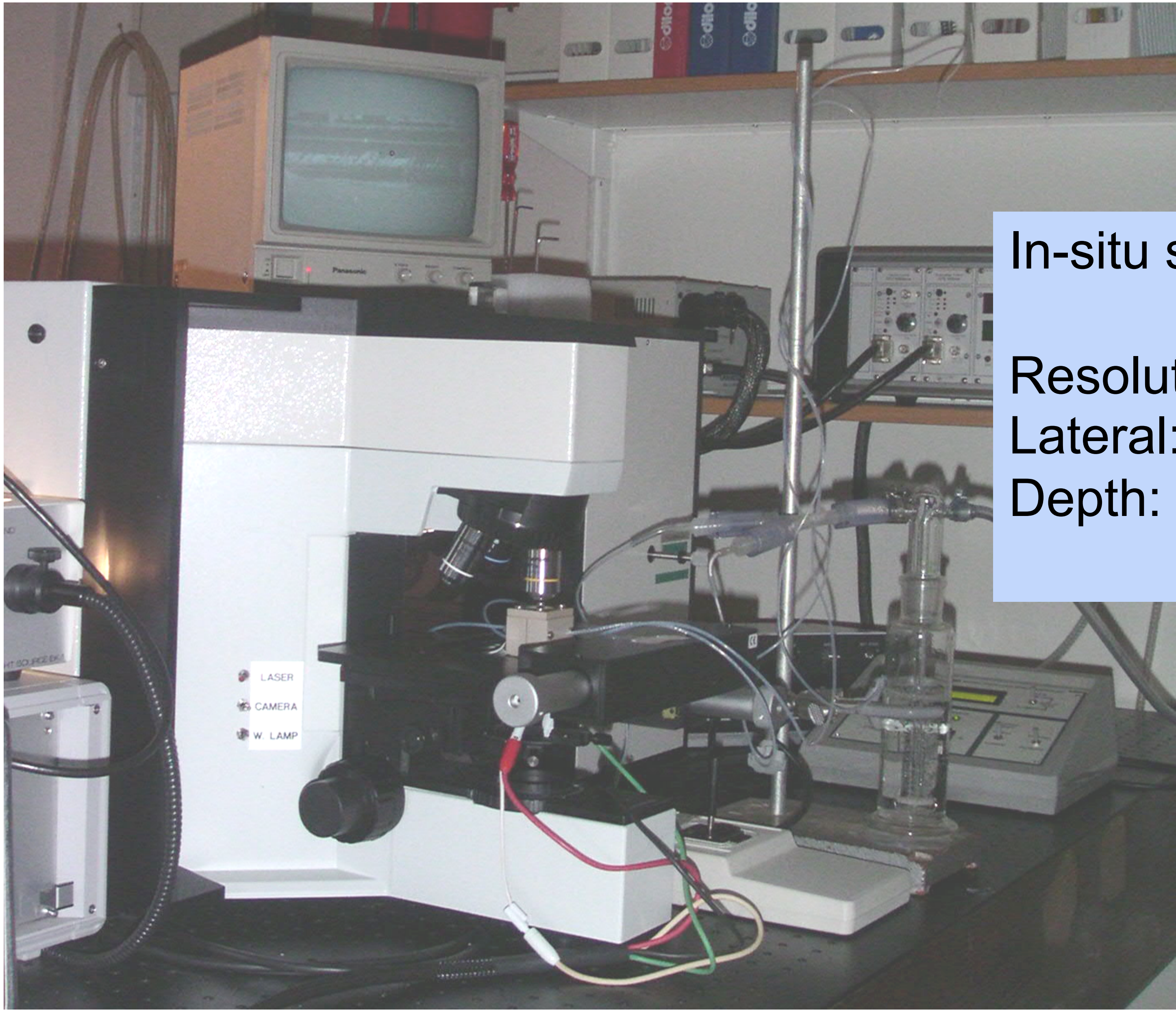
The vibrational spectrum is a ”fingerprint” of a substance

Conformation

Raman spectra of PVDF in pure powder or in an membrane



Raman microscope

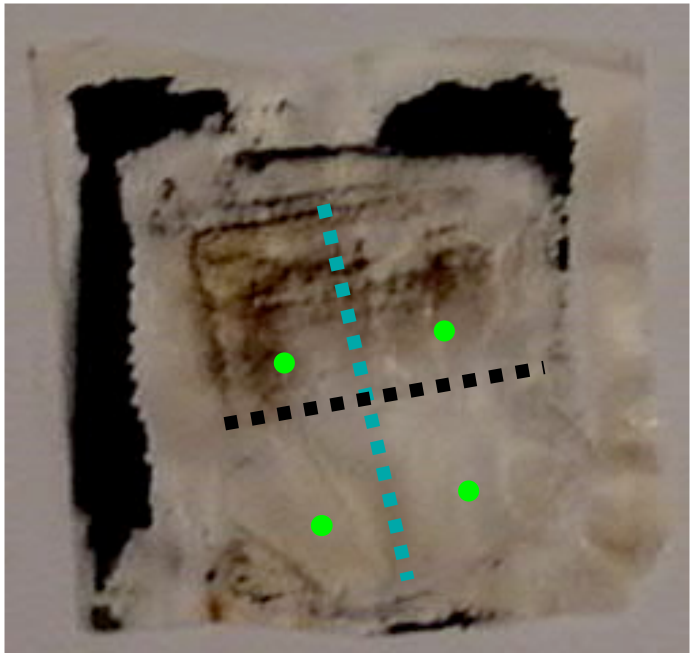


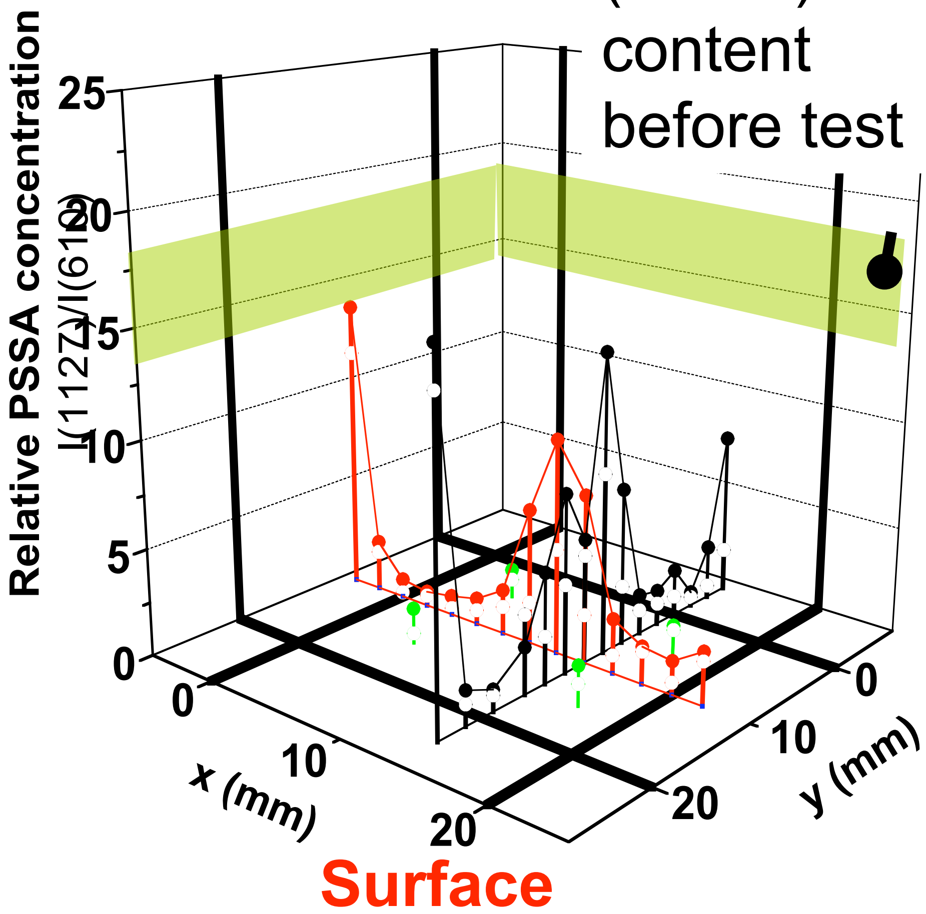
In-situ studies

Resolution:
Lateral: ≈ 1 μm
Depth: ≈ 2 μm

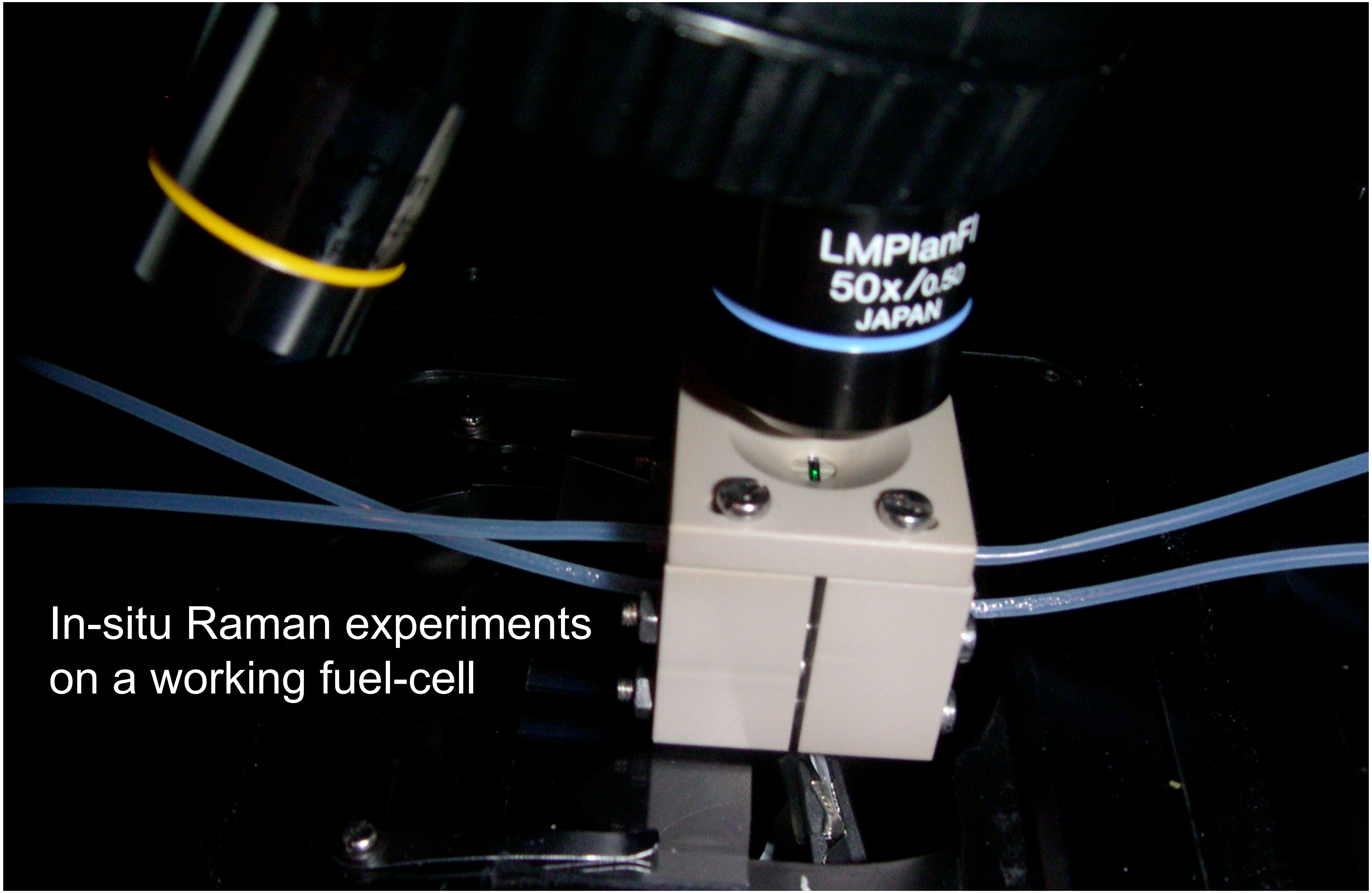
Compositional mapping

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

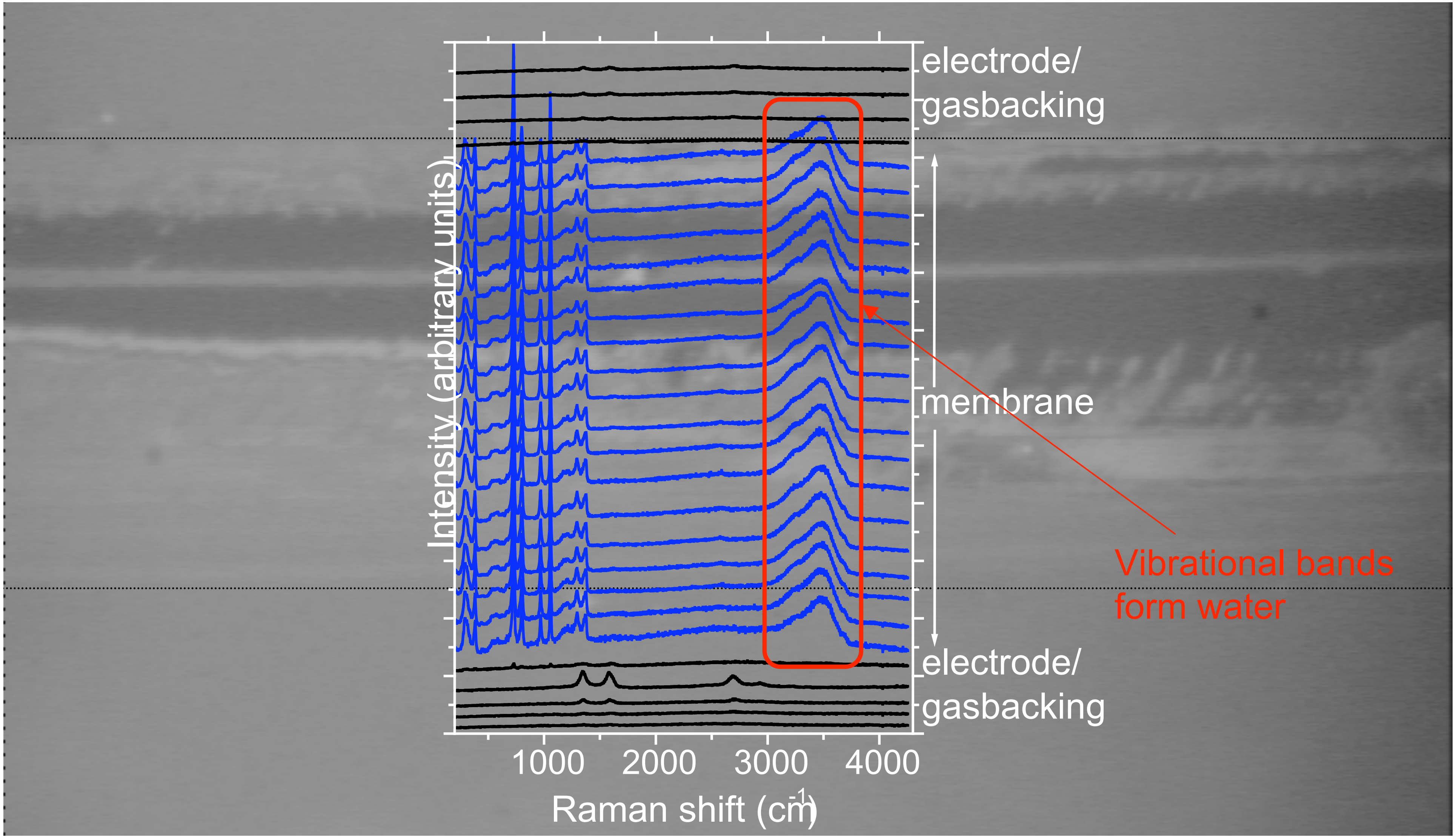




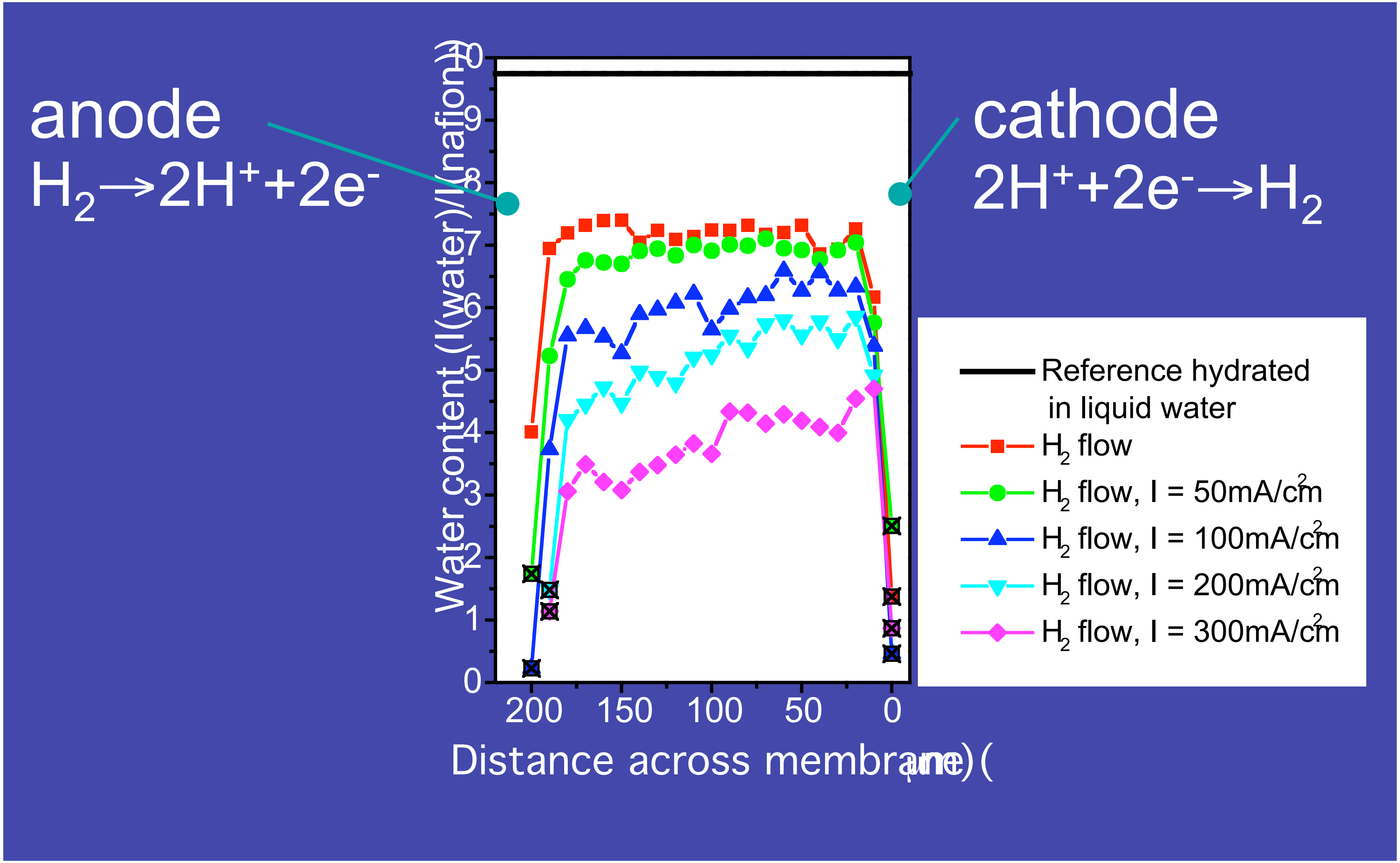
Cell for *in-situ* Raman



Cross section of membrane in the cell



Water profile – potential applied



Experimental techniques

- **General**
- **Fluctuations - correlation functions**
- **Scattering techniques - general aspects/theory**

  ⇒ Neutron scattering

  ⇒ Light scattering
  - **Raman/IR spectroscopy**
  - **Photon correlation spectroscopy**