Australian Government

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Nuclear-based science benefiting all Australians

Quasi-elastic neutron scattering in soft matter

Nicolas de Souza, ACNS

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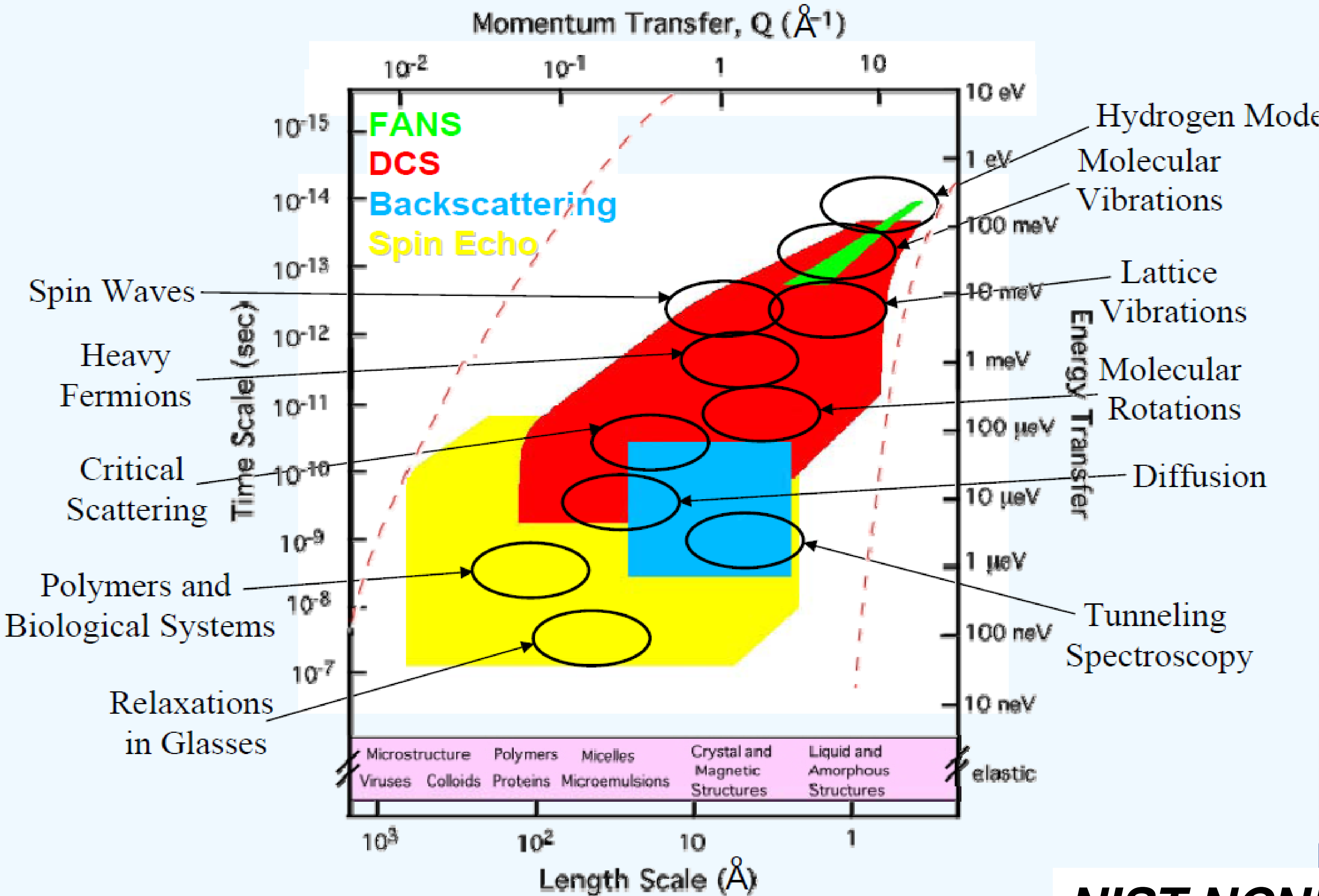
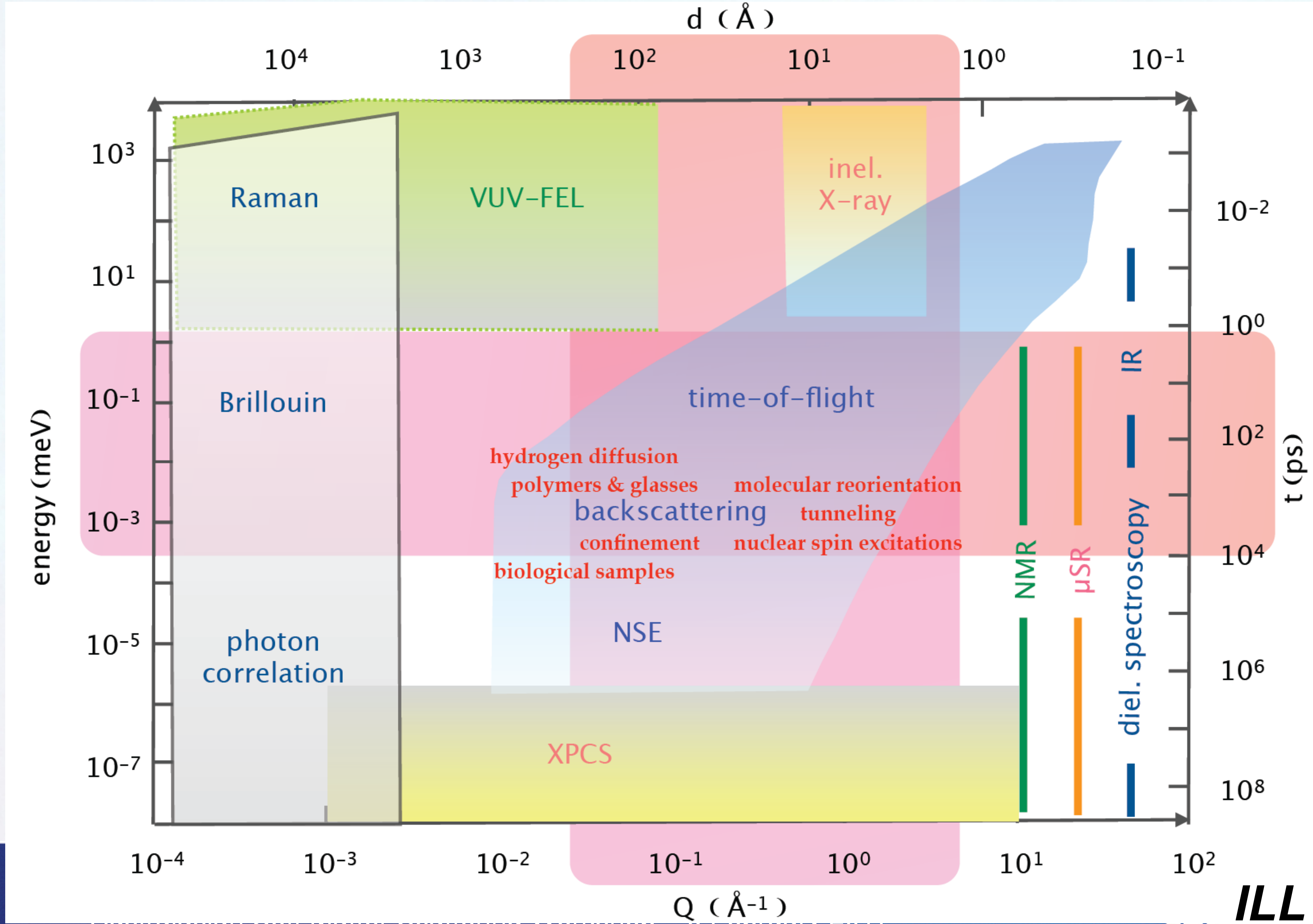
Spectroscopy of condensed matter - neutron instr.

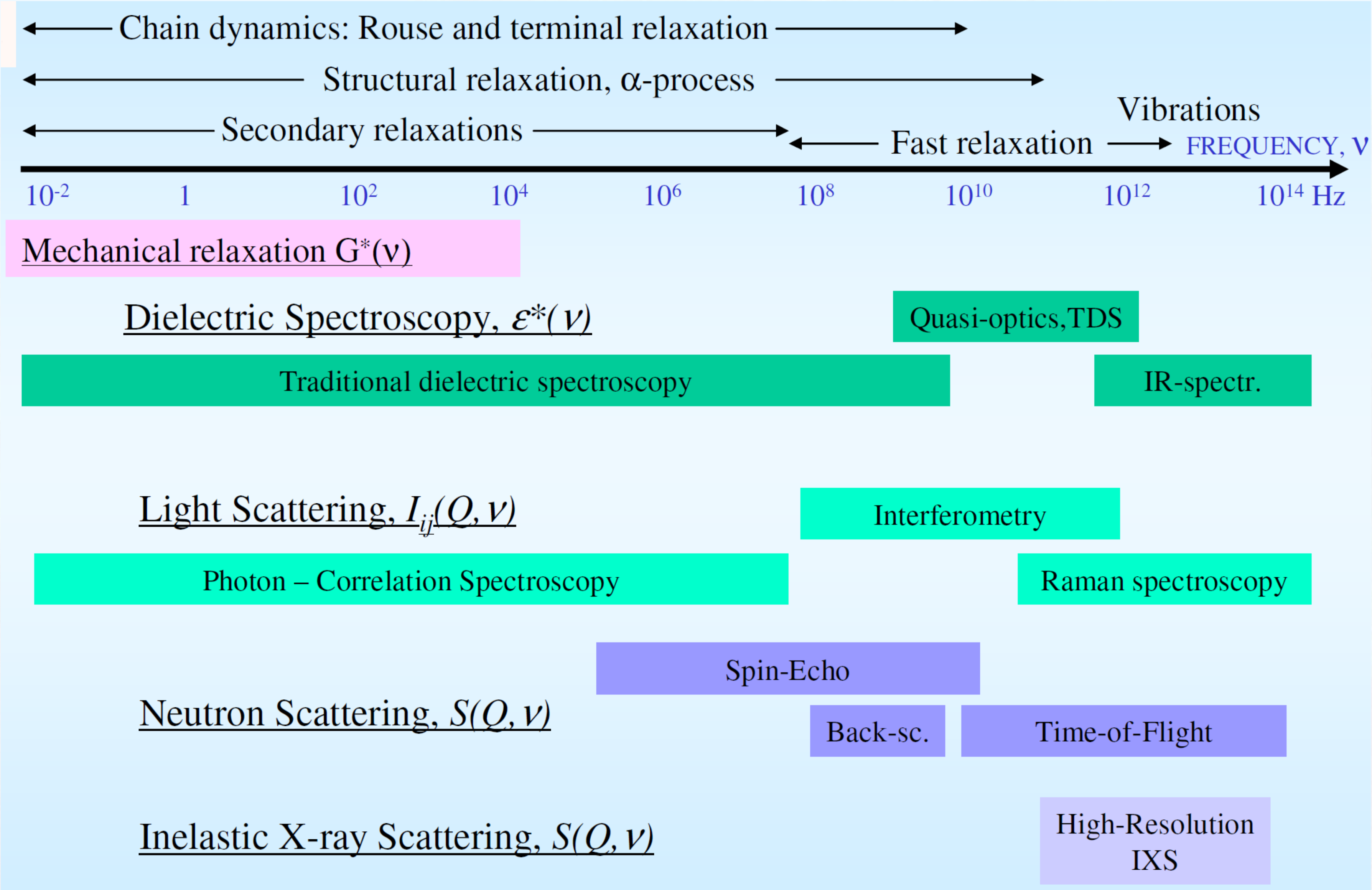


NIST-NCNR

Spectroscopy of condensed matter – exp. techniques



Spectroscopy of condensed matter – polymers



Sokolov

Quasi-elastic neutron scattering

Quasi-elastic neutron scattering is a special inelastic neutron scattering

- specifically broadening of the elastic line
  owing to non-oscillatory motions

- inelastic neutron scattering and QENS resolve

  dynamics, in space and time, *of atoms and molecules* in the sample

- in the first instance QENS resolves an apparent diffusion constant

Quasi-elastic neutron scattering

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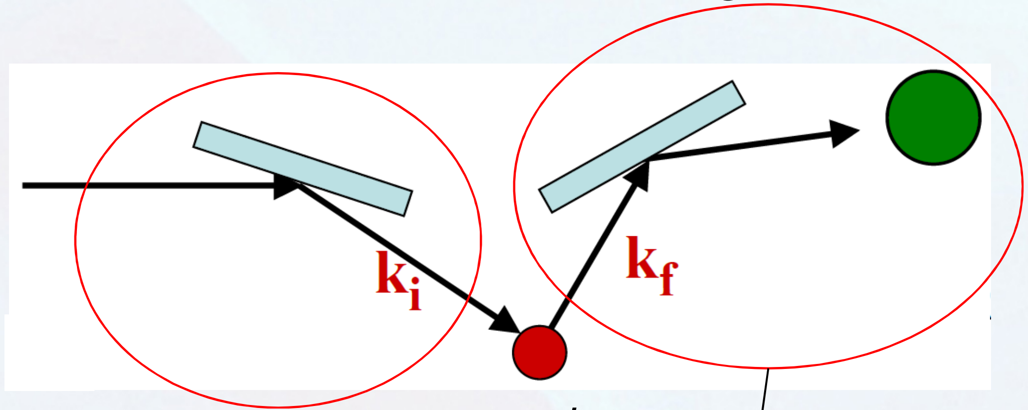
schematic experiment / geometry



sample

incident beam side

wave vector $\mathbf{k_i}$

scattered beam side

wave vector $\mathbf{k_f}$

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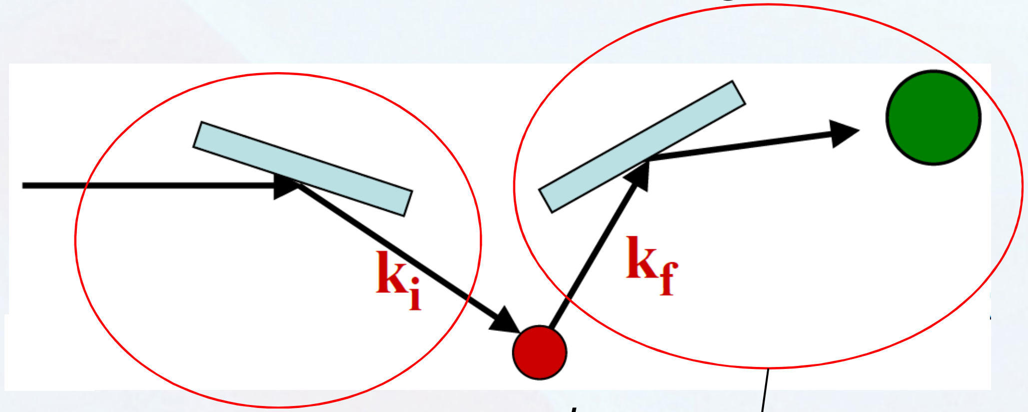

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Scattering measured at:

momentum transfer

$$\mathbf{Q} = \mathbf{k_i} - \mathbf{k_f}$$

energy transfer

$$E = \hbar\omega = \hbar^2 / 2m_n \cdot (k_i^2 - k_f^2)$$

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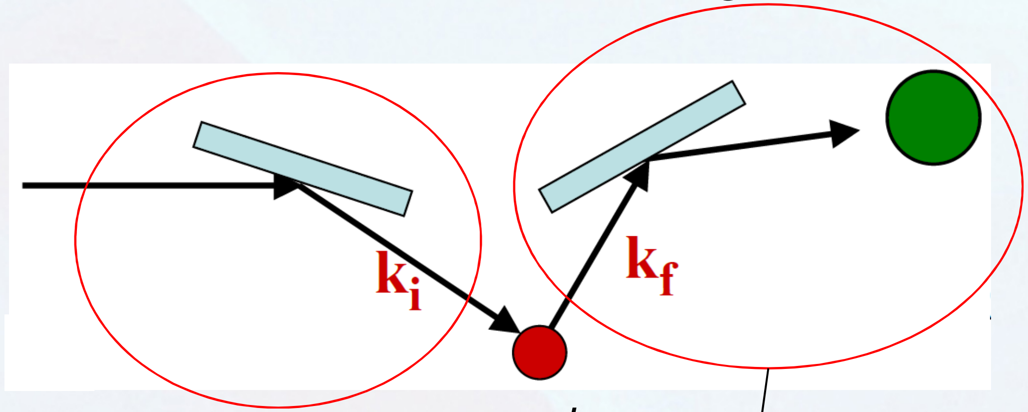

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$$\boldsymbol{E \neq 0}$$

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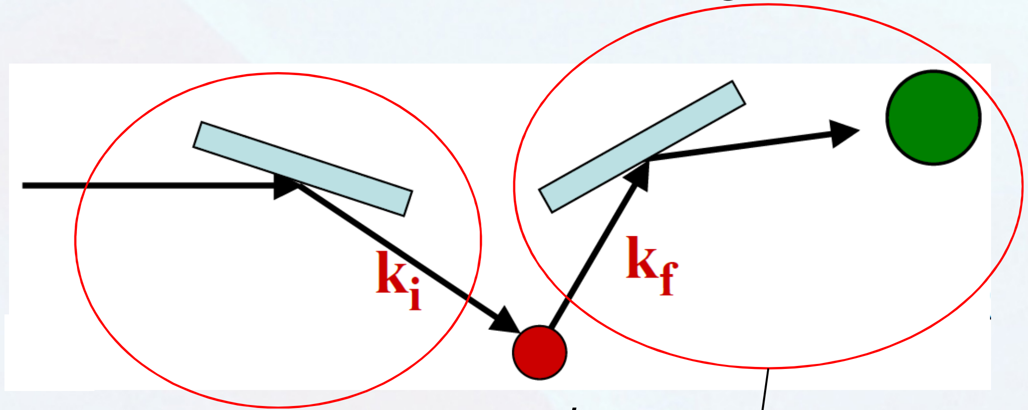

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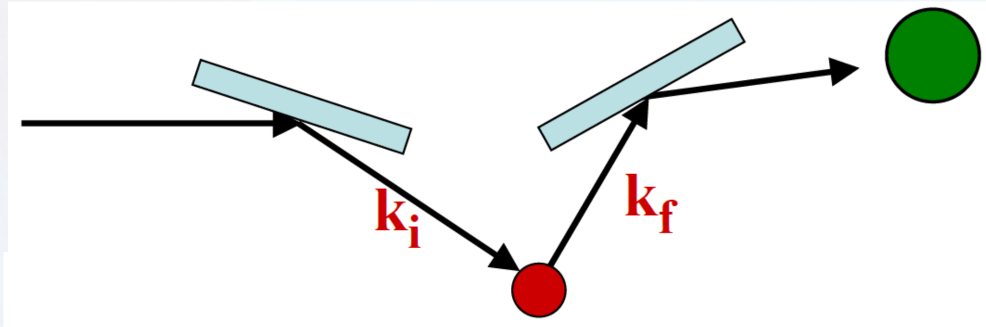
Key techniques :

- backscattering spectroscopy
- time-of-flight spectroscopy

Quasi-elastic neutron scattering



Intensity vs. **Q** and ω represented as:

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{\hbar}\frac{k_f}{k_i} \times \left[\sum_{\alpha,\beta} b_{\alpha,coh} b_{\beta,coh} S_{\alpha\beta,coh}(\mathbf{Q},\omega) + \sum_{\alpha} b^2_{\alpha,inc} S_{\alpha,inc}(\mathbf{Q},\omega) \right]$$

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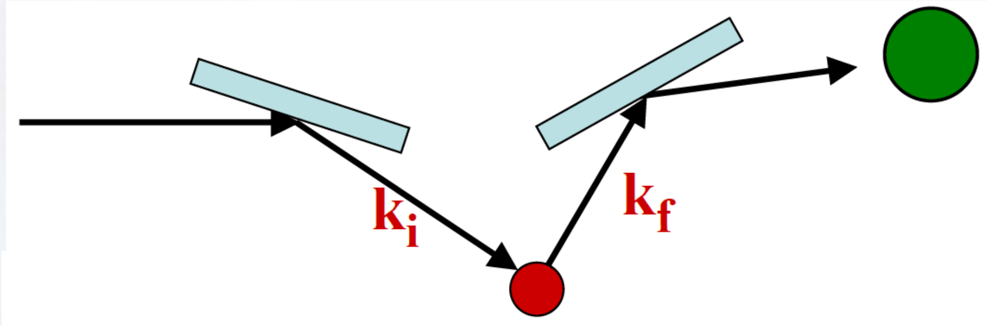

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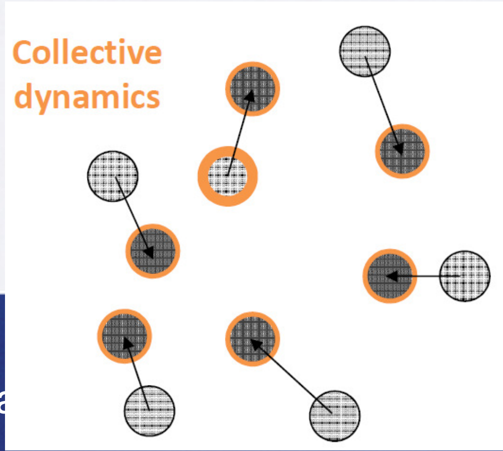
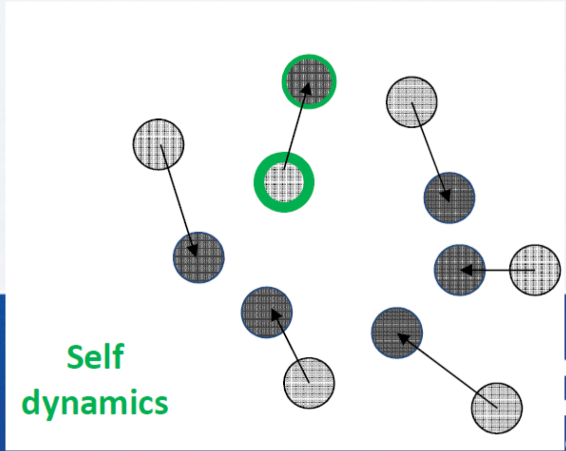
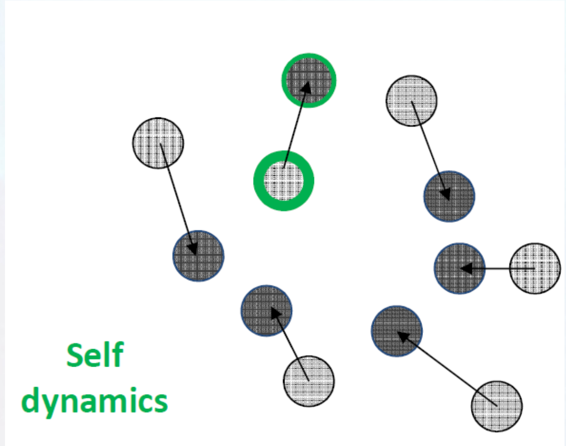




Quasi-elastic neutron scattering

*in the **presence** of H, often (*) :*



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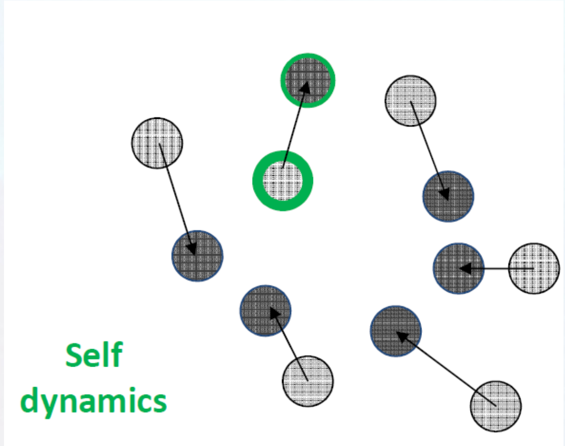

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incoherent scattering

	σ_{coh} (b)	σ_{incoh} (b)	σ_{abs} (b)
Hydrogen	1.76	**80.2**	0.33
Deuterium	5.59	2.05	0.00
Carbon	5.56	0.00	0.00
Nitrogen	11.0	0.50	1.90
Oxygen	4.23	0.00	0.00
Phosphorus	3.31	0.01	0.17
Aluminium	1.50	0.01	0.23
Silicon	2.17	0.00	0.17

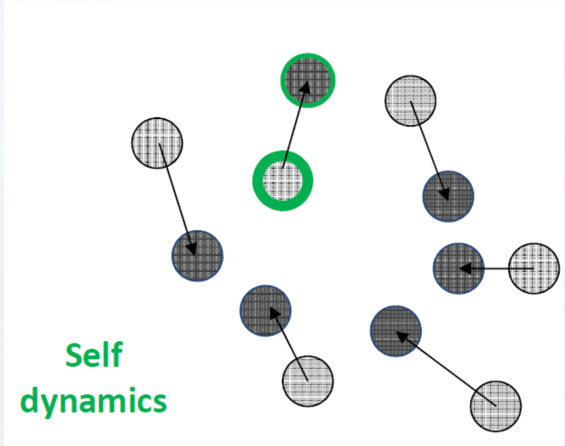
Quasi-elastic neutron scattering

Similarly to neutron small-angle scattering:

- the signal in QENS is *by default* dominated by incoherent scattering from H –

  but it is good for QENS!
- H/D contrast variation enables species or site sensitive probing of the dynamics
- the apparent diffusion constant $D_{app}/r^2 \cdot t = 1$

  $10^{-8} \lesssim D_{app} = r^2/t \lesssim 10^{-4}$ cm²/s



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Quasi-elastic neutron scattering

- Scattering functions (incoherent scattering case):

$$I_{inc}(\mathbf{Q},t) = \frac{1}{\hbar}\int d\omega\, S_{inc}(\mathbf{Q},\omega)\exp(i\omega t)$$

$$G_{self}(\mathbf{r},t) = \frac{1}{(2\pi)^3}\int d\mathbf{Q}\, I_{inc}(\mathbf{Q},t)\exp(-i\mathbf{Q}\cdot\mathbf{r})$$

$$G_{self}(\mathbf{r},t) = \frac{1}{N}\left\langle \sum_N \int d\mathbf{r}'\, \delta(\mathbf{r}+\mathbf{r}_i(0)-\mathbf{r}')\delta(\mathbf{r}'-\mathbf{r}_i(t)) \right\rangle$$

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time *measured*

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real space

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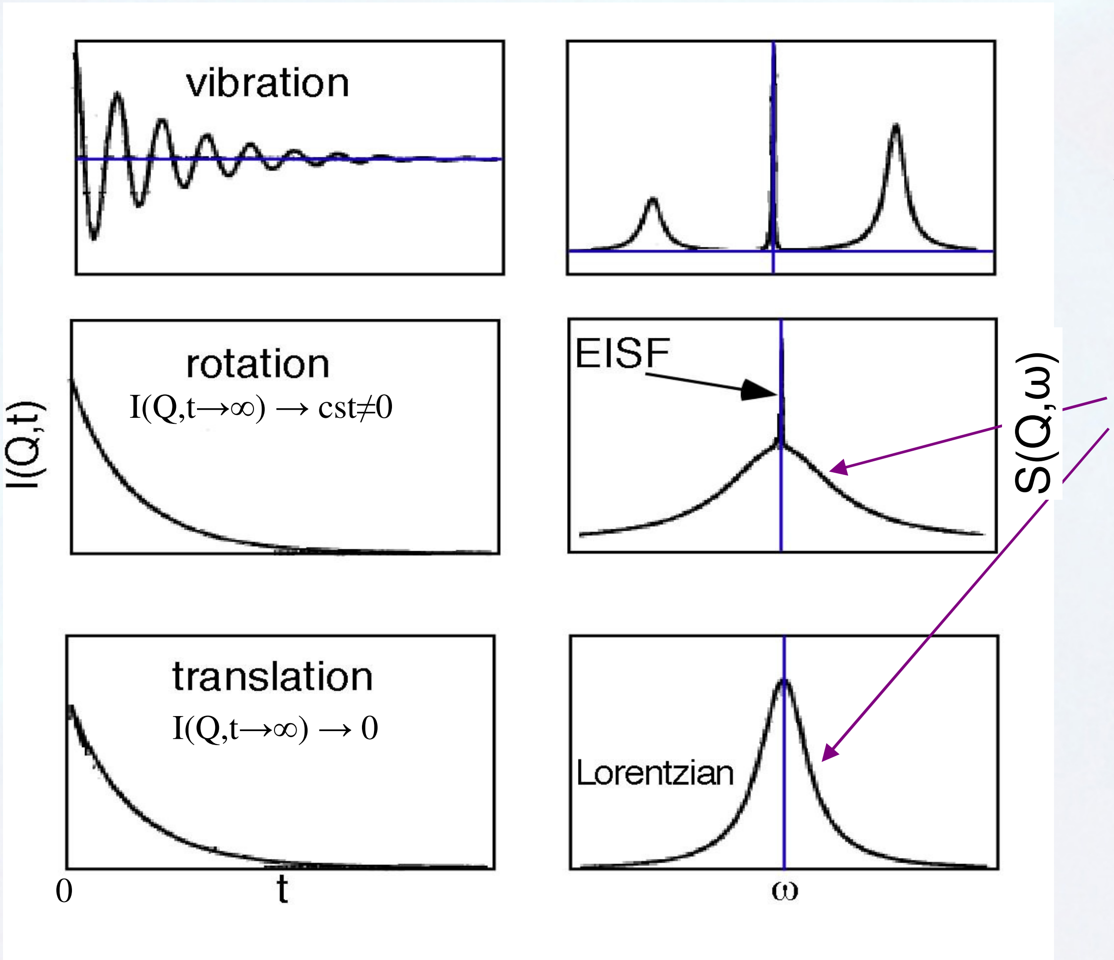
ensemble statistical / fluctuation representation,
connects to computer simulations such as molecular dynamics, …

Processes in the QENS spectral region



• rotational tunneling;

• at higher energy transfers: phonon dispersion curves, molecular vibrations, vibrational DOS, bonding force fields, anharmonicity, …

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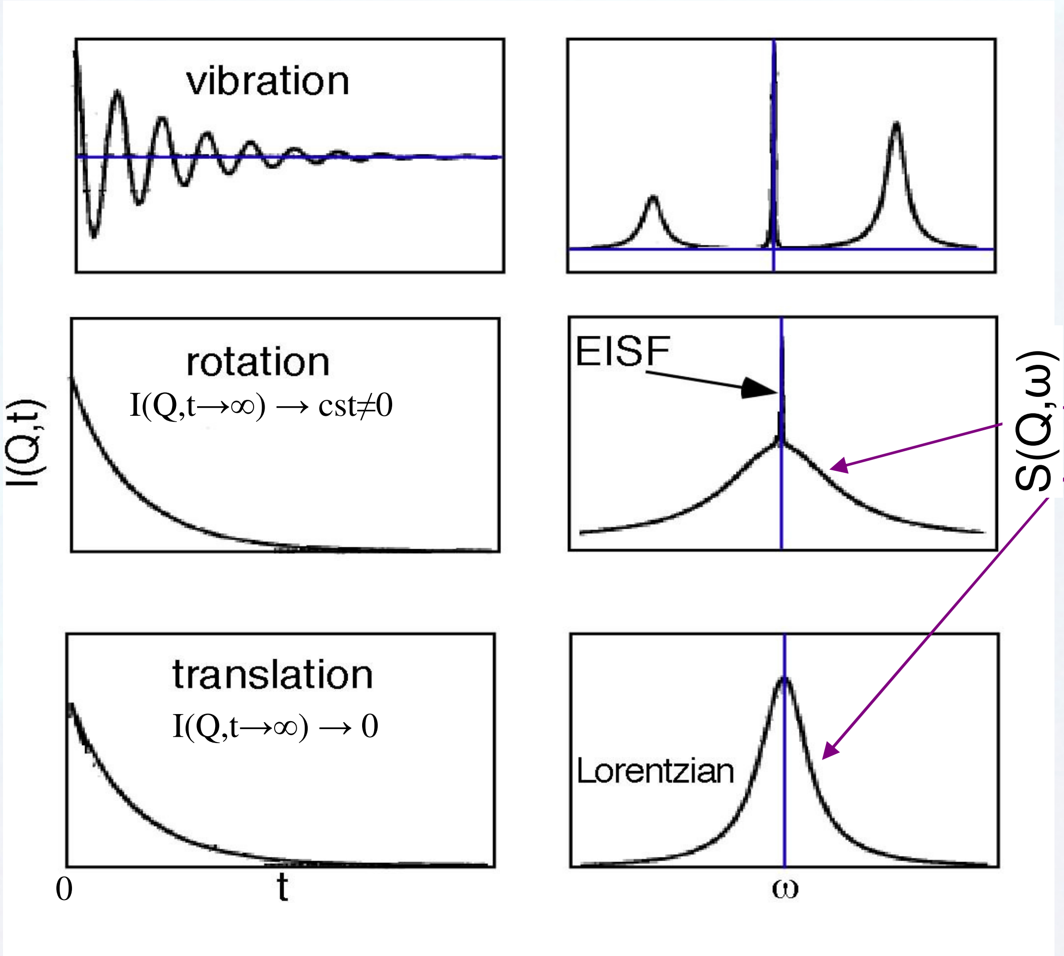

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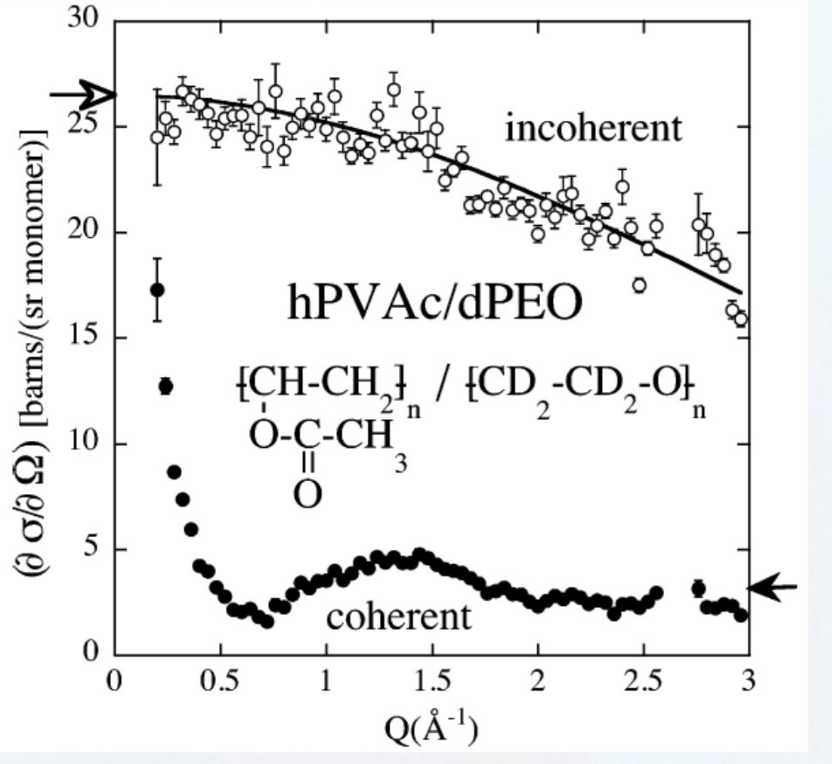
Poly(vinyl acetate) **segmental dynamics** in blends with poly(ethylene oxide)



Tyagi et al., Macromol. 2007

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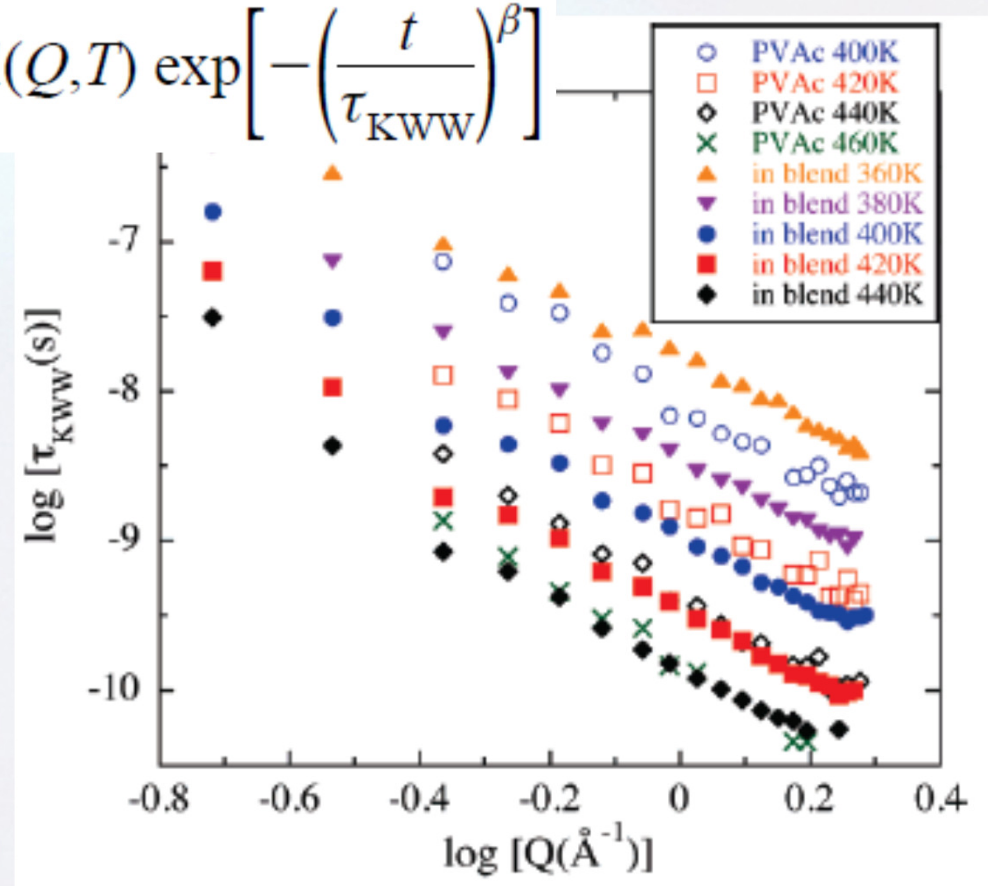

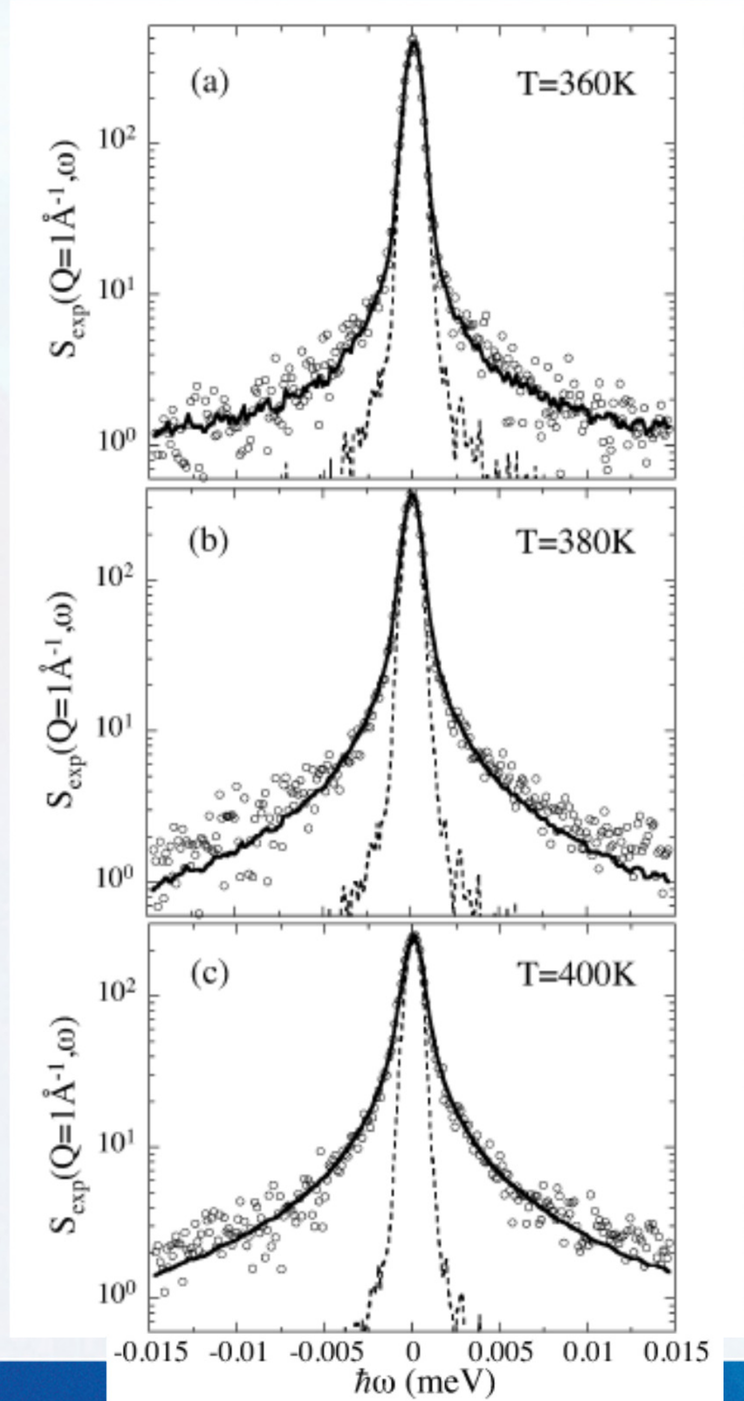

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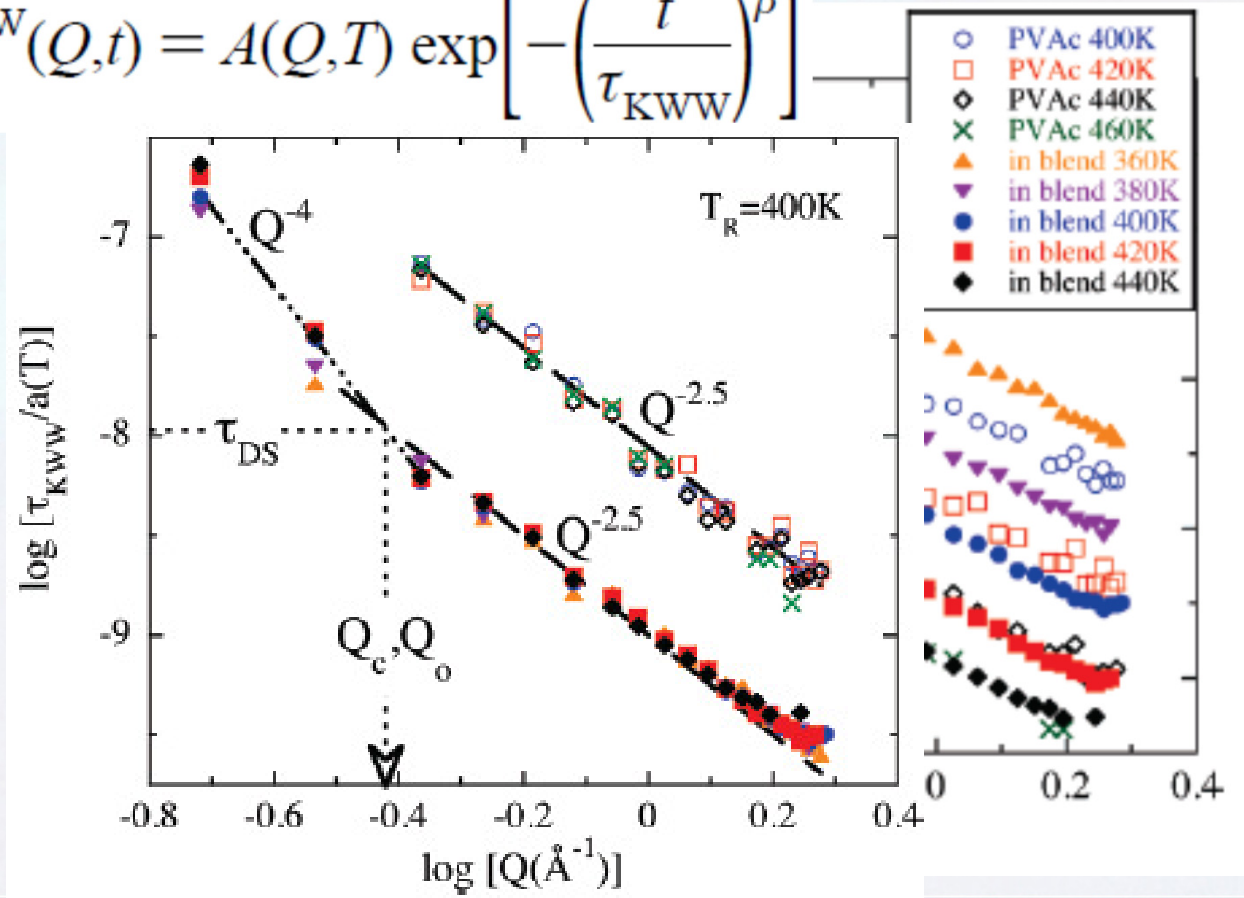

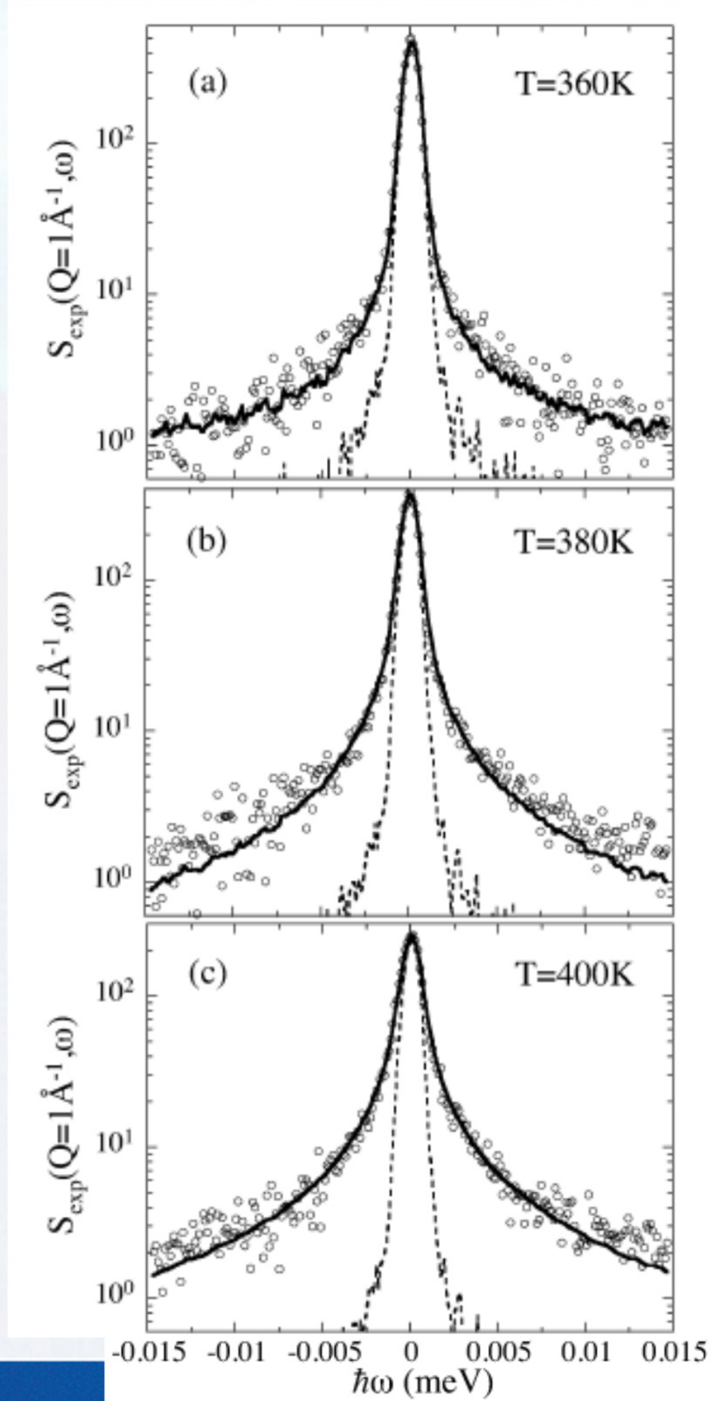

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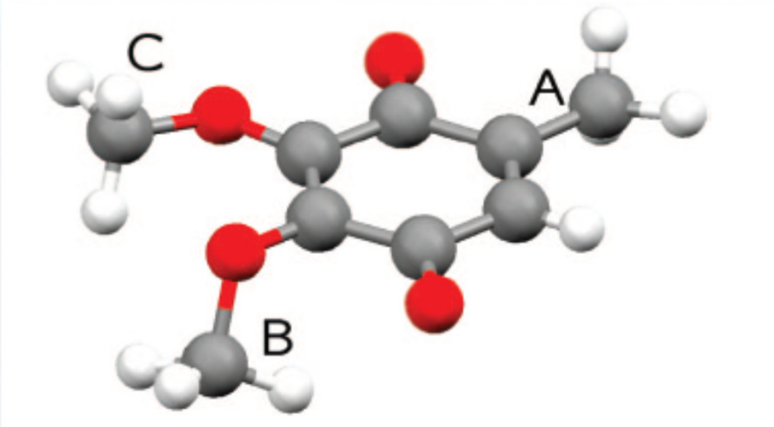
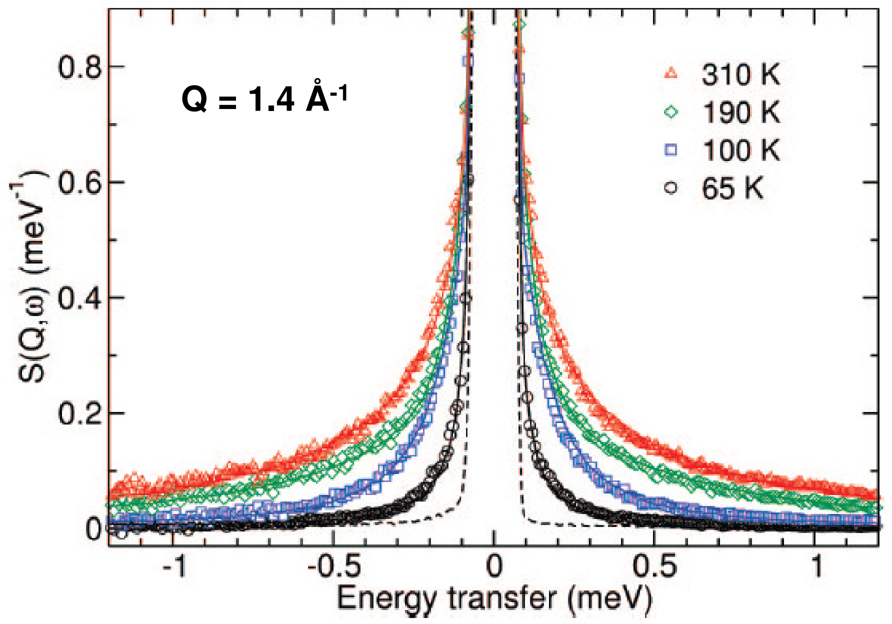
Application – pharmaceutical compound

Methyl group dynamics in coenzyme moiety ubiquinone Q_0 – **dynamical disorder in a crystal**





$$S_{\mathrm{methyl}}(Q,\omega) = A_0(Q)\delta(\omega) + [1 - A_0(Q)]\frac{1}{\pi}\frac{\Gamma}{\omega^2 + \Gamma^2}$$

$$A_0(Q) = \frac{1}{3}[1 + 2j_0(\sqrt{3}Qr)]$$

Smuda et al., JPC B 2010

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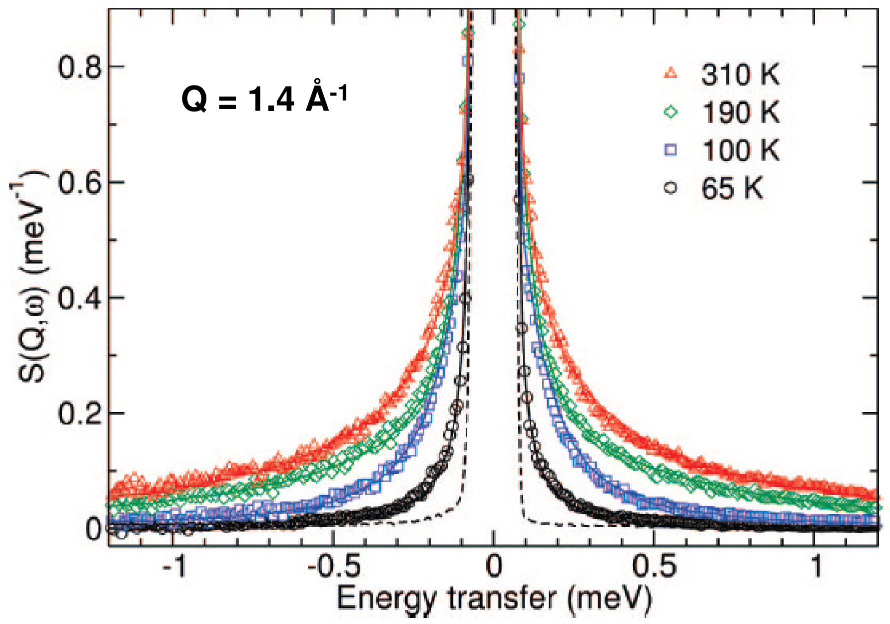

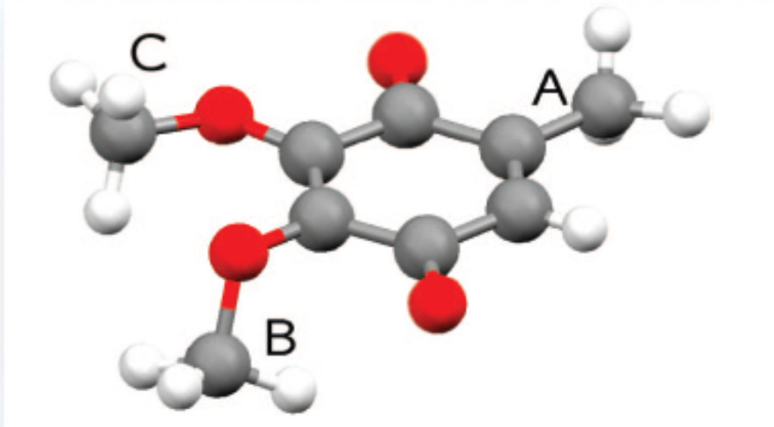

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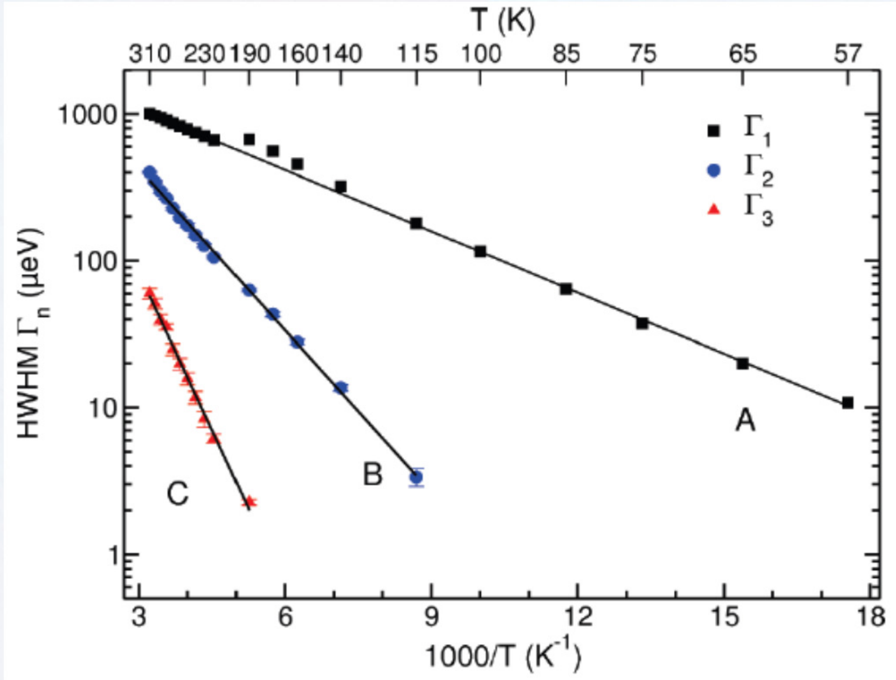

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Water-in-oil microemulsion droplet dynamics
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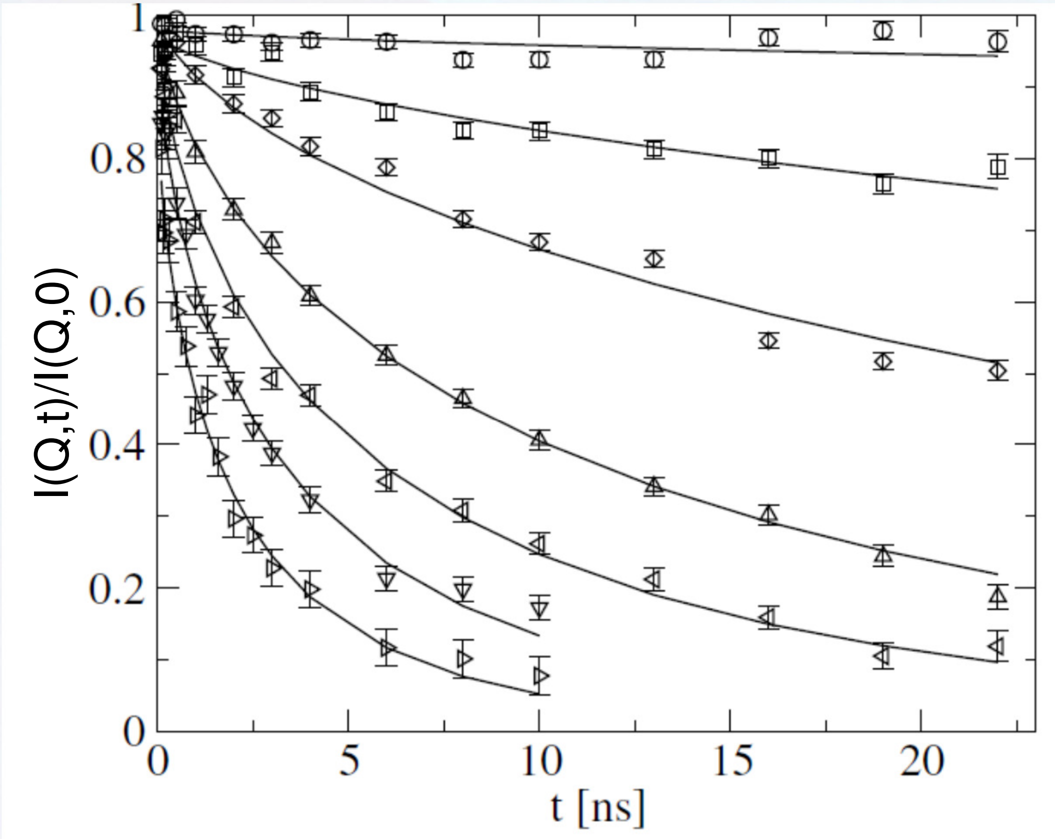
surface (shape) fluctuations

$$\frac{I(Q,t)}{I(Q,0)} = \exp\left[-D_{\mathrm{eff}}(Q)Q^2t\right].$$



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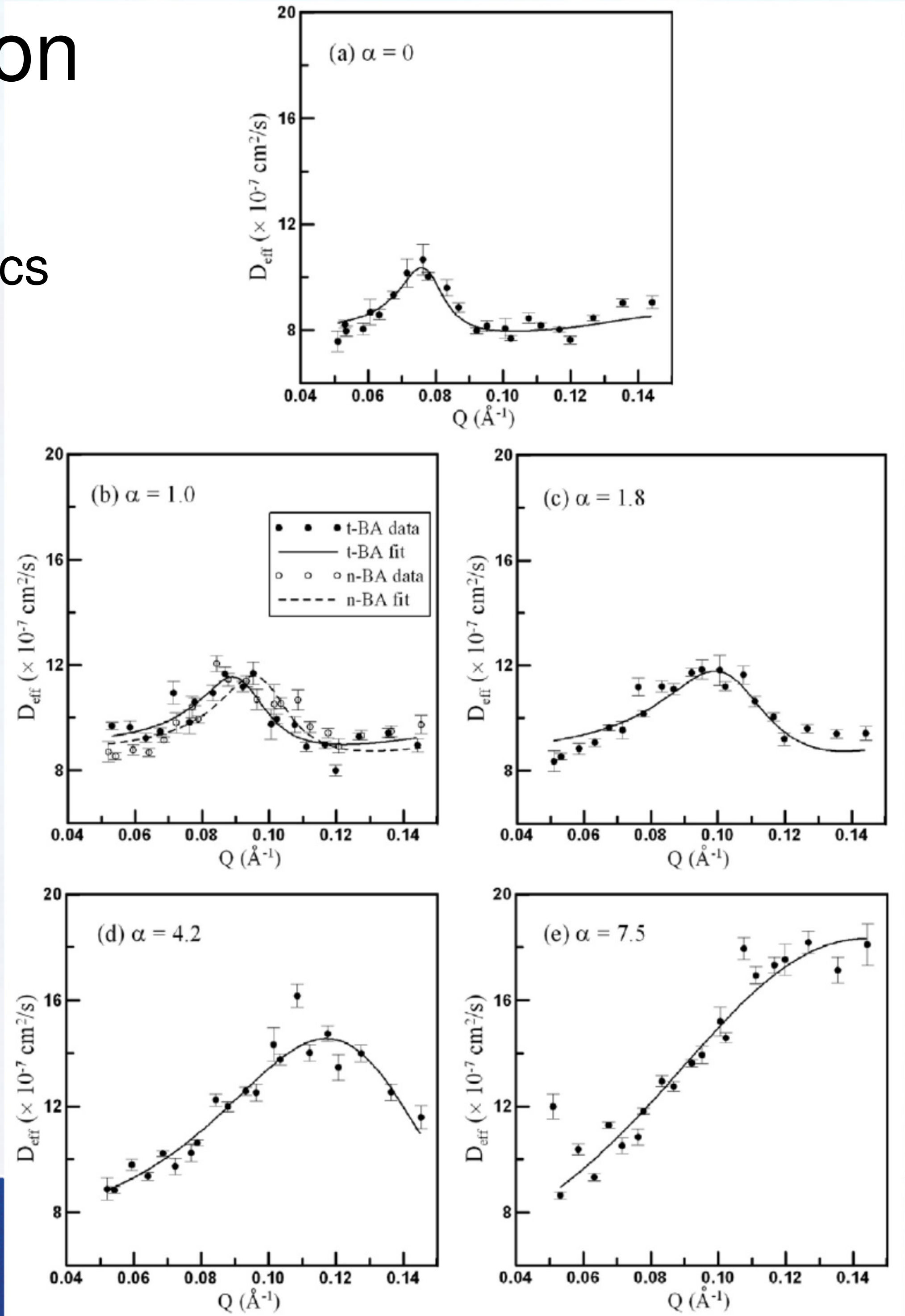

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$$D_{\mathrm{eff}}(Q) = D_{\mathrm{tr}} + D_{\mathrm{def}}(Q),$$

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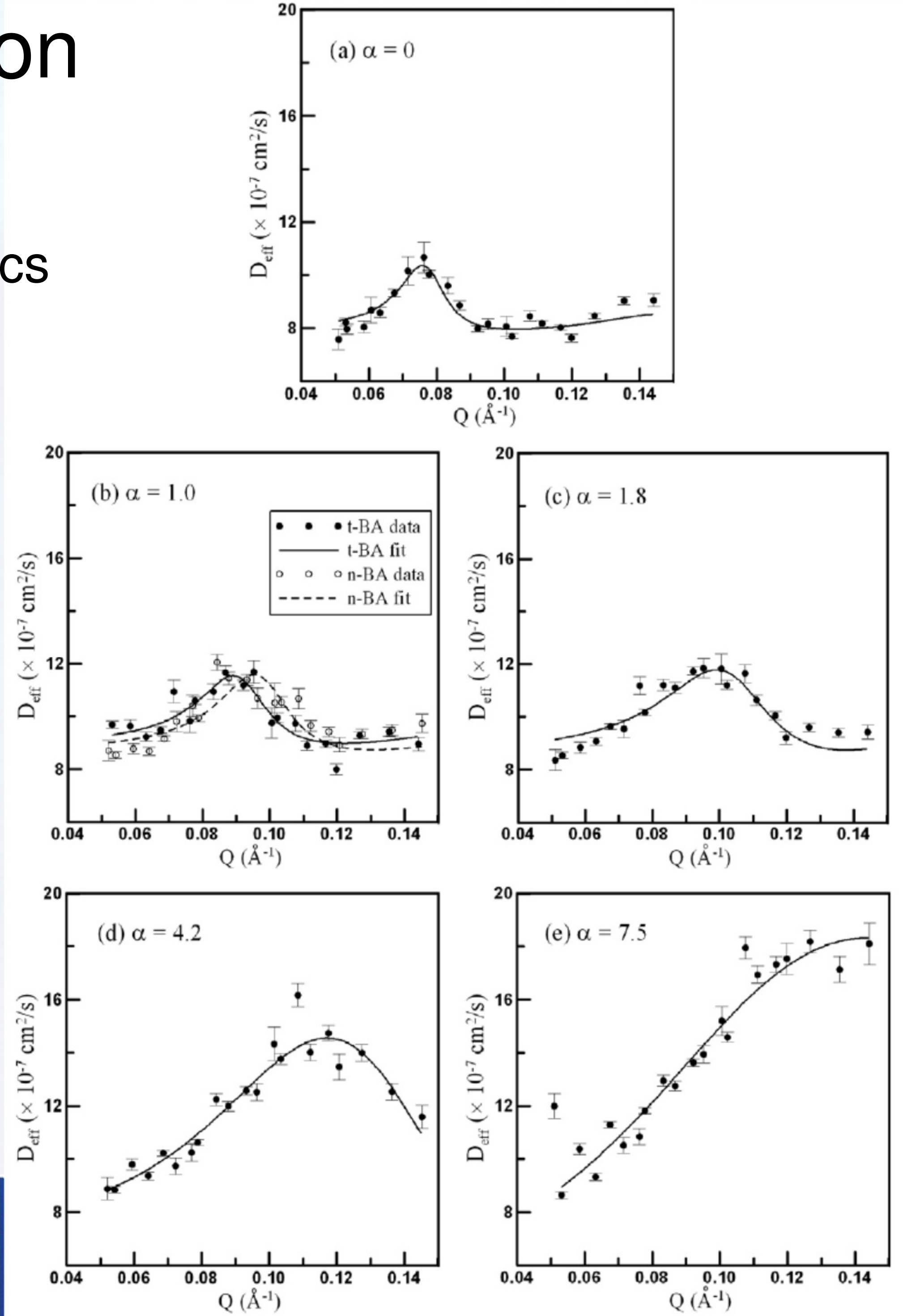

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- Generally: know in advance as much of the structure as possible – e.g. wide- or small- angle scattering, optical spectroscopy

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- Generally: know in the advance the thermodynamics

  Why: except for special measurements, material must be at equilibrium during the QENS experiment

- Relaxation processes may be determined by NMR, dielectric spectroscopy, etc.

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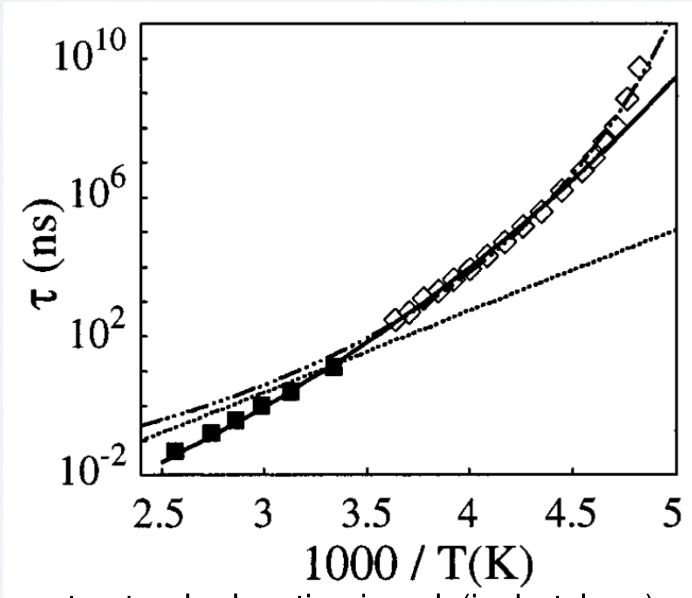
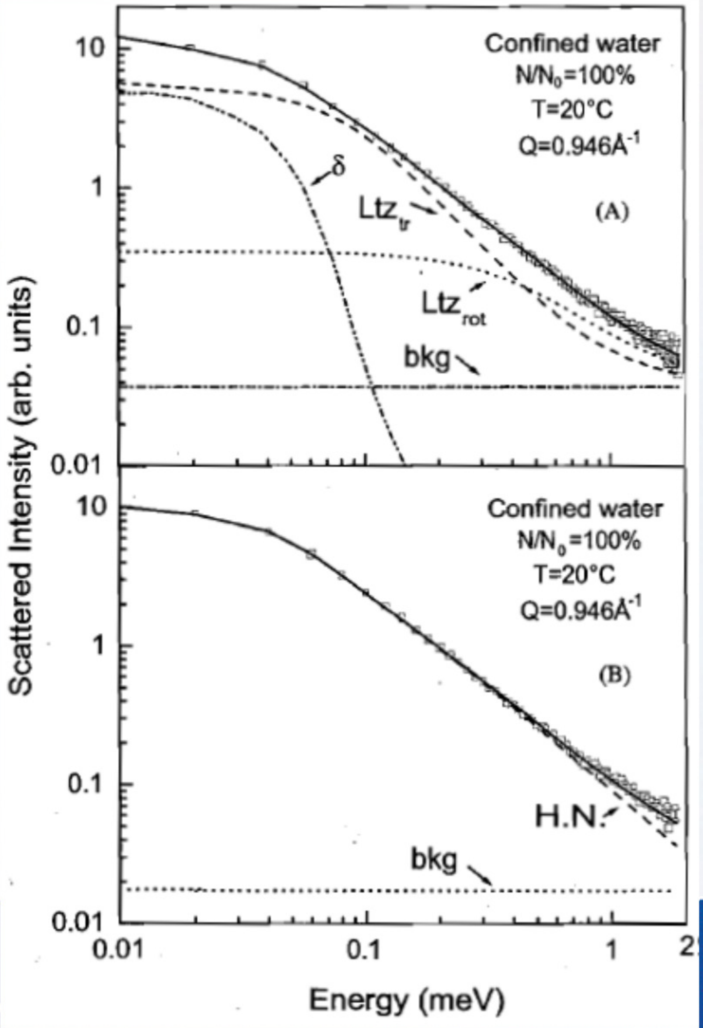
QENS determines their geometry!



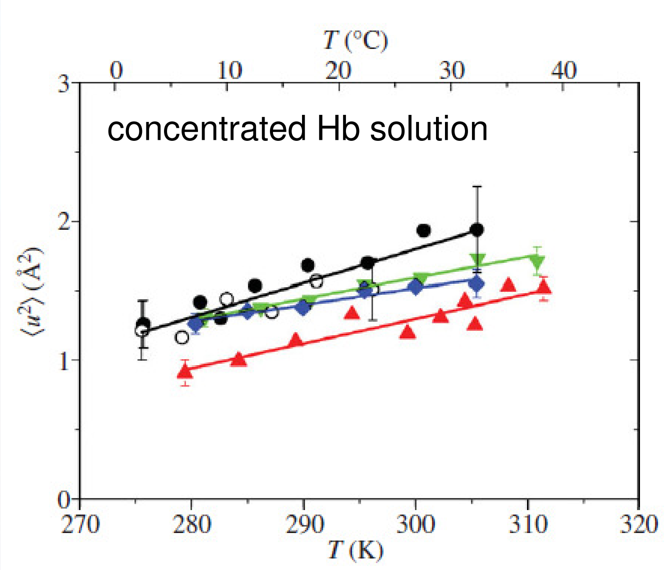
structural relaxation in poly(isobutylene), *Richter et al. 1998*

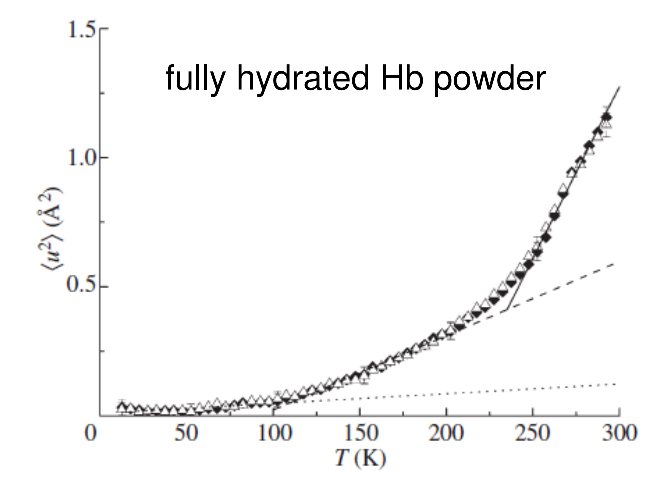
Complementary methods

- Computer simulations are essential to analyse QENS from complex systems



Crupi et al., Physica A 2002





Stadler et al., J R Soc Interface 2012

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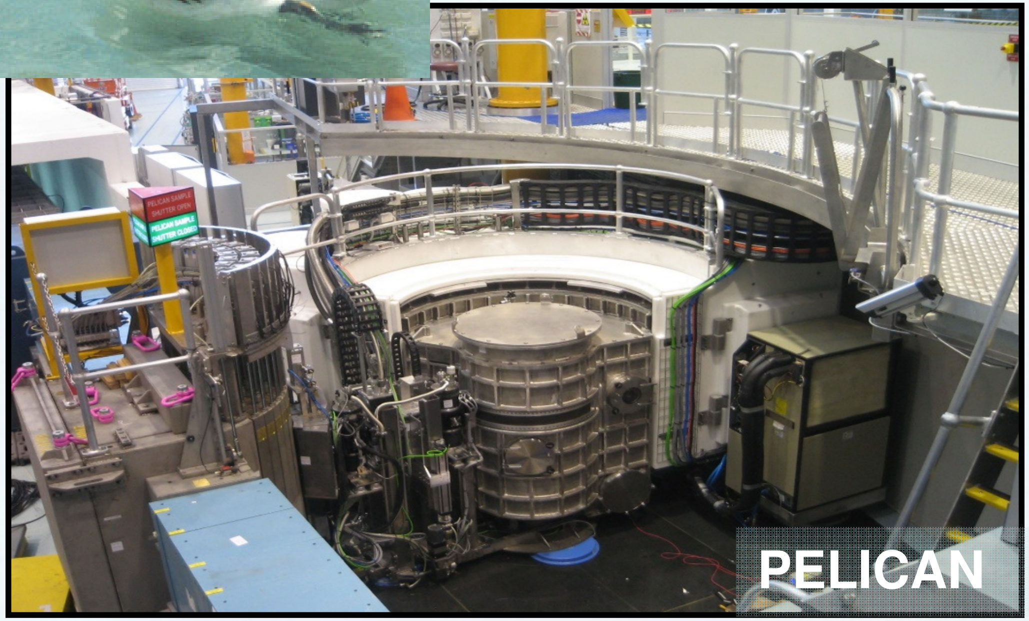
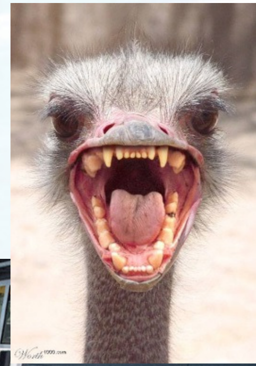
The ACNS landscape





- Berrod et al., Nanoscale 8 (2016) 7845
  ionic liquids in carbon nanotube confinement
- Shi et al., Phys Rev Lett 117 (2016) 238102
  amino acids and peptides in aqueous solutions

- User operation from Sep 2016
- first soft-matter experiments on liquid-crystalline mesophases

- T. Imae et al. eds., *Neutrons in Soft Matter*, 2011 (Wiley)
- García Sakai and Arbe, "Quasielastic neutron scattering in soft matter", Curr. Op. Coll. Int. Sci. 14 (2009) 381
- M. Bée, *Quasielastic neutron scattering – Principles and applications in solid state chemistry, biology and materials science*, 1988 (A. Hilger / IoP)
- G.L. Squires, *Introduction to the theory of the thermal neutron scattering,* 1978 (Dover reprint)

Thank you for your attention

Questions : now or nds@ansto.gov.au

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