Neutron Spin Echo Spectroscopy

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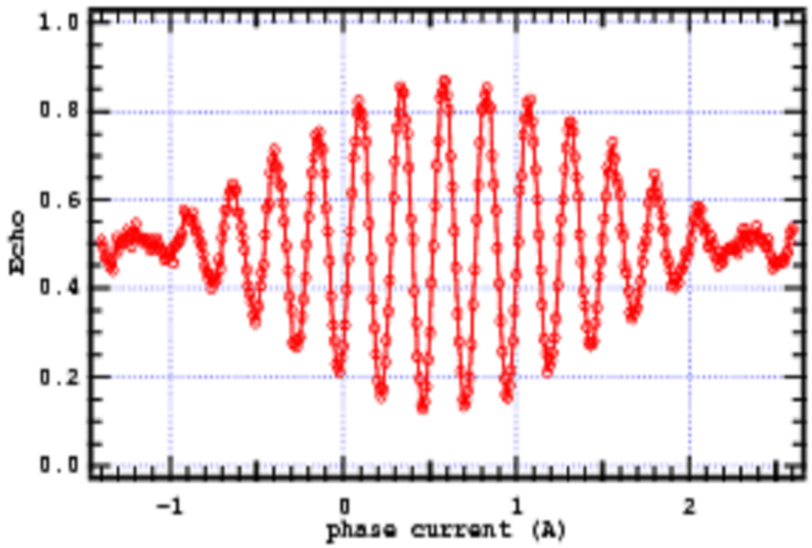
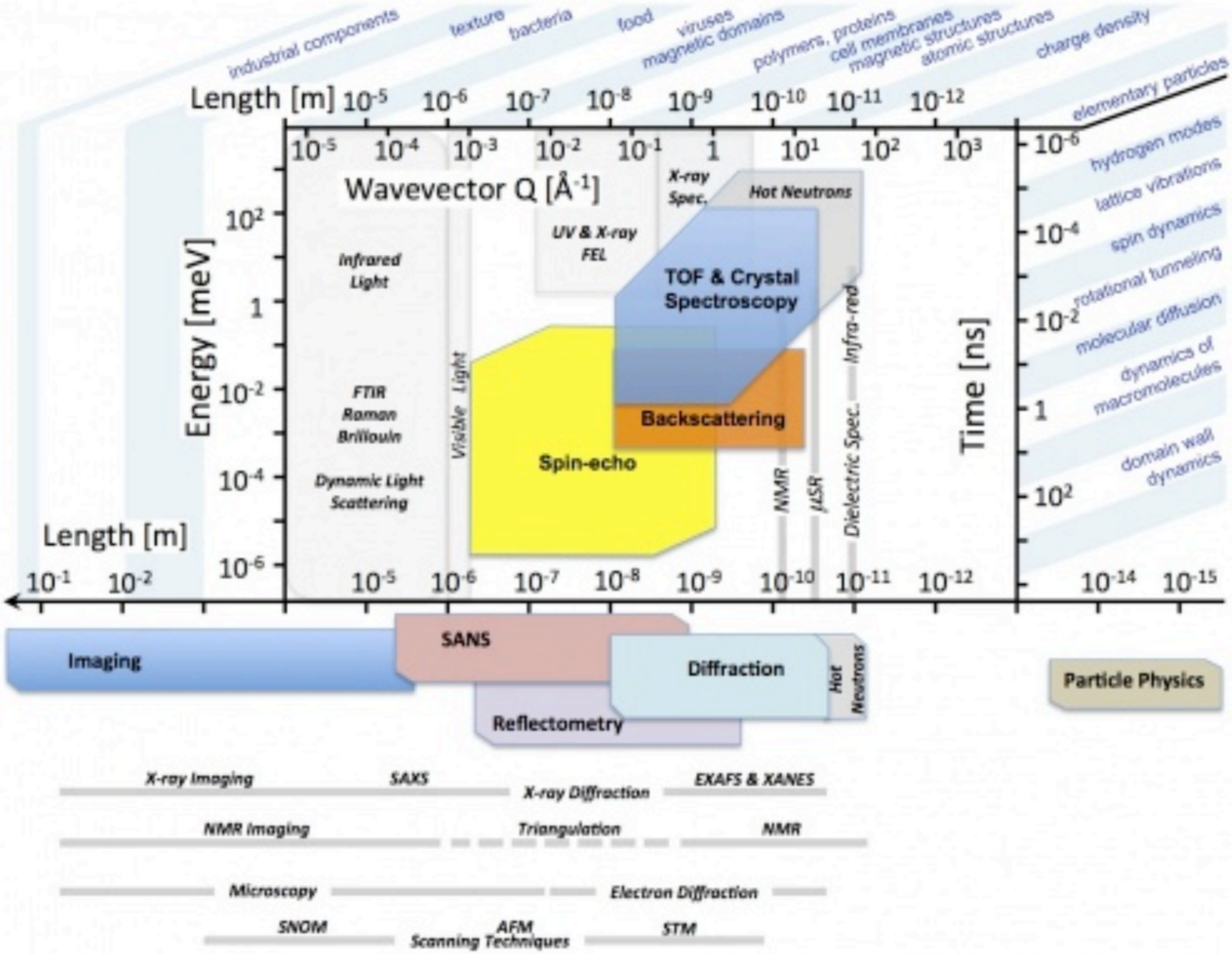


Exploring the structural and dynamic phase space: with neutrons



http://europeanspallationsource.se/what-do-neutrons-tell-us

Detection of slow motions by Neutron Spin echo (NSE)

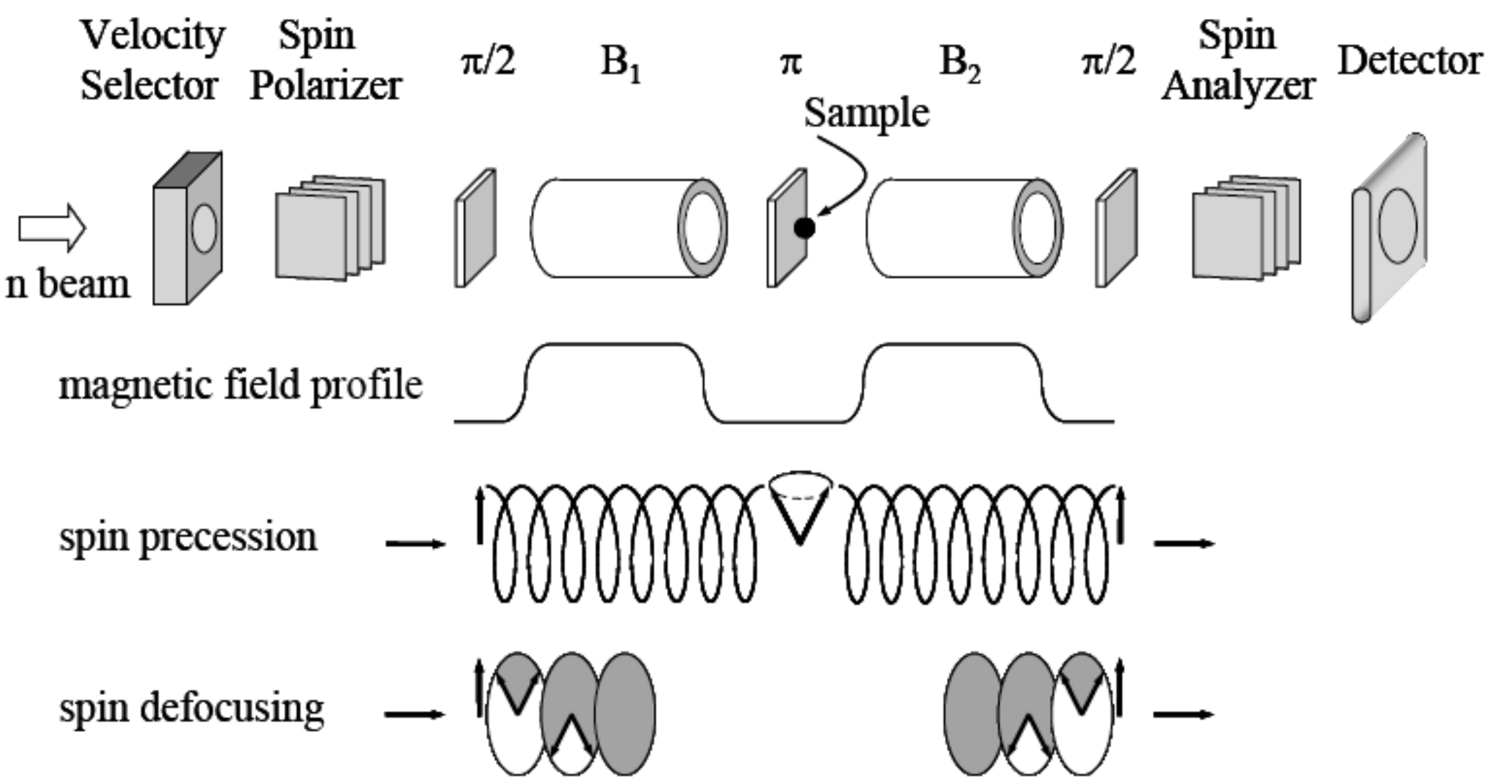
NSE uses the neutron's spin polarisation to encode the difference in energies between incident and scattered beams. Very high energy resolution.

NSE measures the intermediate correlation function in reciprocal space and time S(q,t).

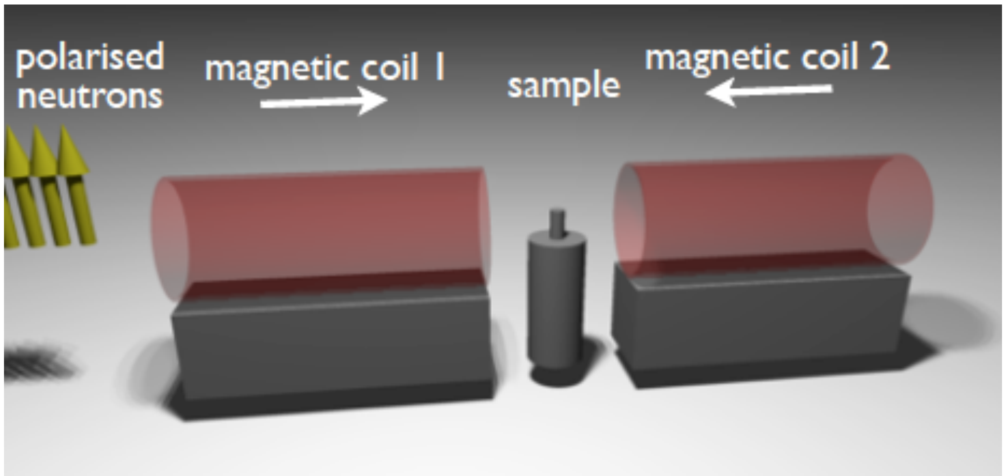
NSE spans a time window from 10^{-12} to 10^{-6} s.

Layout of generic Spin echo Spectrometer

F. Mezei
1978



The measurement principle of neutron spin echo spectroscopy- Classical Description



No strong monochromatisation needed

Neutrons are polarised perpendicular to magnetic fields

Elastic Case: Neutrons Perform the same number of spin rotations in both coils and exit with the original polarisation (spin echo condition)

Quasielastic Case: Time spent in the second coil will be slightly different, i.e., the original polarisation angle is not recovered (loss in polarisation)

The measurement principle of neutron spin echo spectroscopy- Classical Description

Now we will consider how to link the precession to the dynamics in the sample.

Performing a **spin echo experiment** we measure the **polarisation P** with respect to an arbitrarily chosen coordinate x. Px is the projection on this axis and we have to take the average over all precession angles:

$$P_x = \langle \cos\varphi \rangle = \langle \cos(\varphi_{in} - \varphi_{out}) \rangle$$

$$P_x = \langle \cos[\gamma_L (\frac{\int \vec{B}_{in} \cdot d\vec{l}}{v_{in}} - \frac{\int \vec{B}_{out} \cdot d\vec{l}}{v_{out}})] \rangle$$

To first order ϕ is proportional to the energy transfer at the sample ω with the proportionality constant t (spin echo time).

$$\varphi = t\omega$$

This is the "**fundamental equation**" of classical neutron spin echo.

The measurement principle of neutron spin echo spectroscopy – Classical description

We consider the "fundamental equation" φ=tω and we will **calculate t** to first order by Taylor expansion.

Starting point is the energy transfer ω:

$$\hbar\omega = \frac{m}{2}\left[(\bar{v}+\Delta v_{out})^2 - (\bar{v}+\Delta v_{in})^2\right]$$

Taylor expansion to first order gives:

$$\omega = \frac{m}{\hbar}\left[\bar{v}\Delta v_{out} - \bar{v}\Delta v_{in}\right]$$

Now we turn to the phase φ:

$$\varphi = \gamma_L \left[\frac{\int \vec{B}\cdot d\vec{l}}{\bar{v}+\Delta v_{in}} - \frac{\int \vec{B}\cdot d\vec{l}}{\bar{v}+\Delta v_{out}}\right]$$

Here, Taylor expansion to first order gives:

$$\varphi = \gamma_L \left[\frac{\int \vec{B}\cdot d\vec{l}}{\bar{v}^2}\Delta v_{out} - \frac{\int \vec{B}\cdot d\vec{l}}{\bar{v}^2}\Delta v_{in}\right]$$

Combining the equations for ω and φ, we get:

$$t = \frac{\varphi}{\omega} = \frac{\hbar}{m}\frac{\gamma_L \int \vec{B}\cdot d\vec{l}}{\bar{v}^3} = \frac{m^2\gamma_L \int \vec{B}\cdot d\vec{l}}{2\pi h^2}\lambda^3$$

using de Broglie $p = mv = \frac{h}{\lambda}$

The measurement principle of neutron spin echo spectroscopy Classical Description

We return to the equation for the **polarization P_x**

$$P_x = \langle \cos\varphi \rangle = \langle \cos(\omega t) \rangle$$

and use it to prove that we measure the intermediate scattering function.
In a first step we **write down the average as an integral**

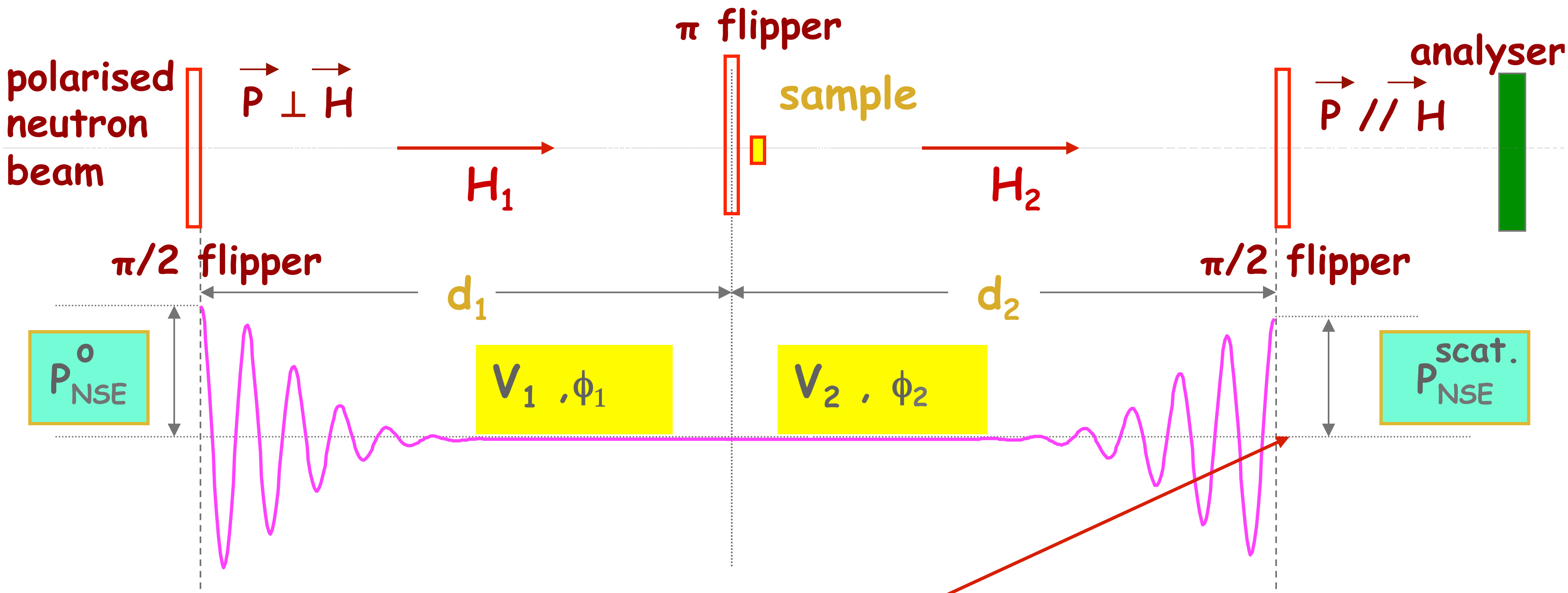
$$P_x(Q,t) = \frac{\int S(Q,\omega)\cos(\omega t)d\omega}{\int S(Q,\omega)d\omega}$$

Here, we exploit that the scattering function $S(Q,\omega)$ *is the probability for scattering a neutron with a given momentum and energy transfer.*

It turns out that **P_x is the cosine transform of the $S(Q,\omega)$**. Thus, P_x is not strictly equal to the intermediate scattering function, but to the real part only.

$$P_x(Q,t) = \frac{\Re(I(Q,t)}{I(Q,0)}$$

For most cases this different is negligible, but this has to be kept in mind.



Total precession angle ∝ energy change of neutrons

$$\Delta\phi = \phi_1 - \phi_2 = \gamma \left[d_1 H_1 / v_1 - d_2 H_2 / v_2 \right] \propto t\, \Delta\omega$$

Intermediate scattering function

$$\frac{P_{NSE}^{sample}(q,t)}{P_{NSE}^{reference}(q,t)} = S(q,t)$$

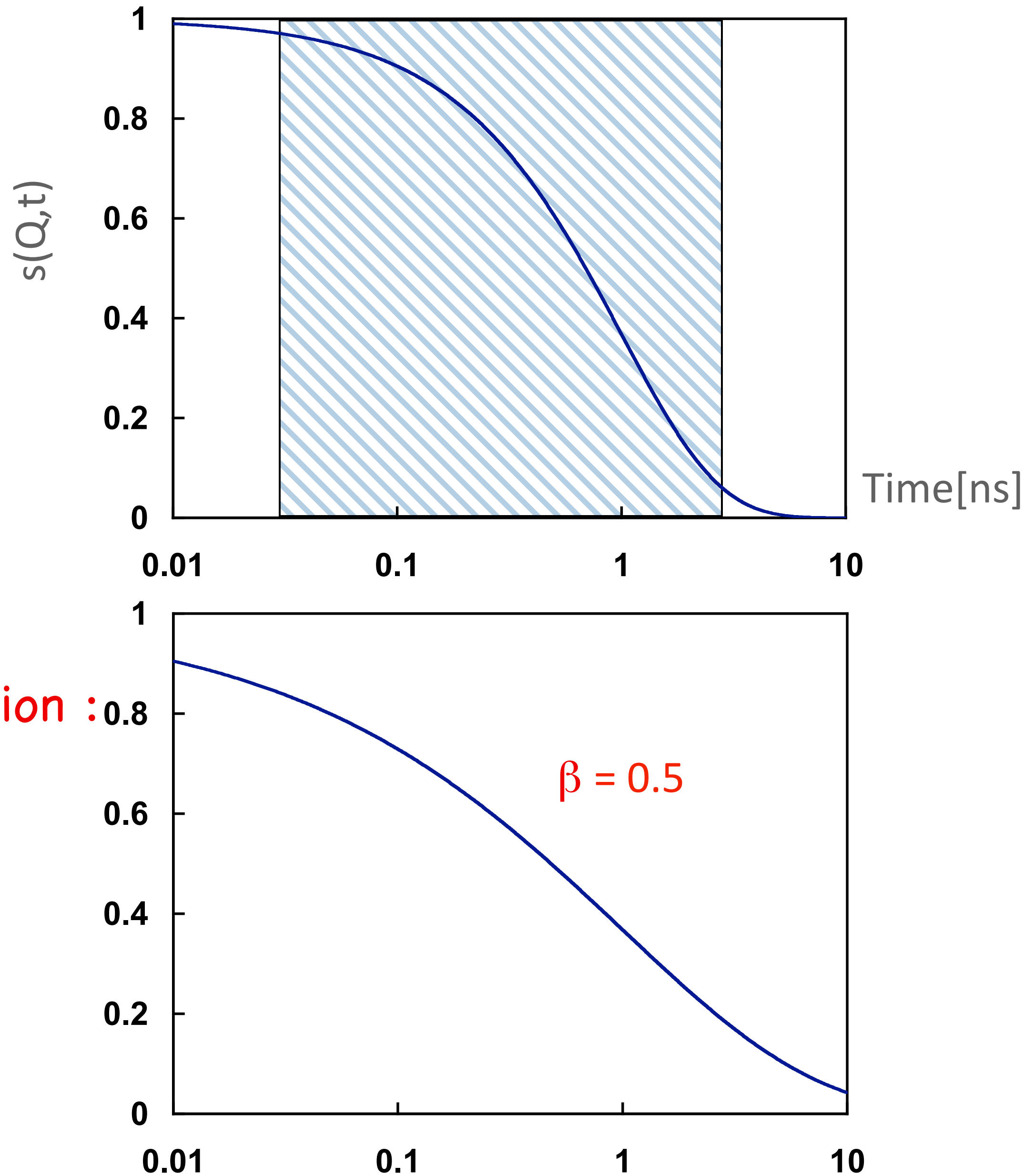
exponential relaxation :

$s(Q,t) \propto \exp(-t/\tau)$

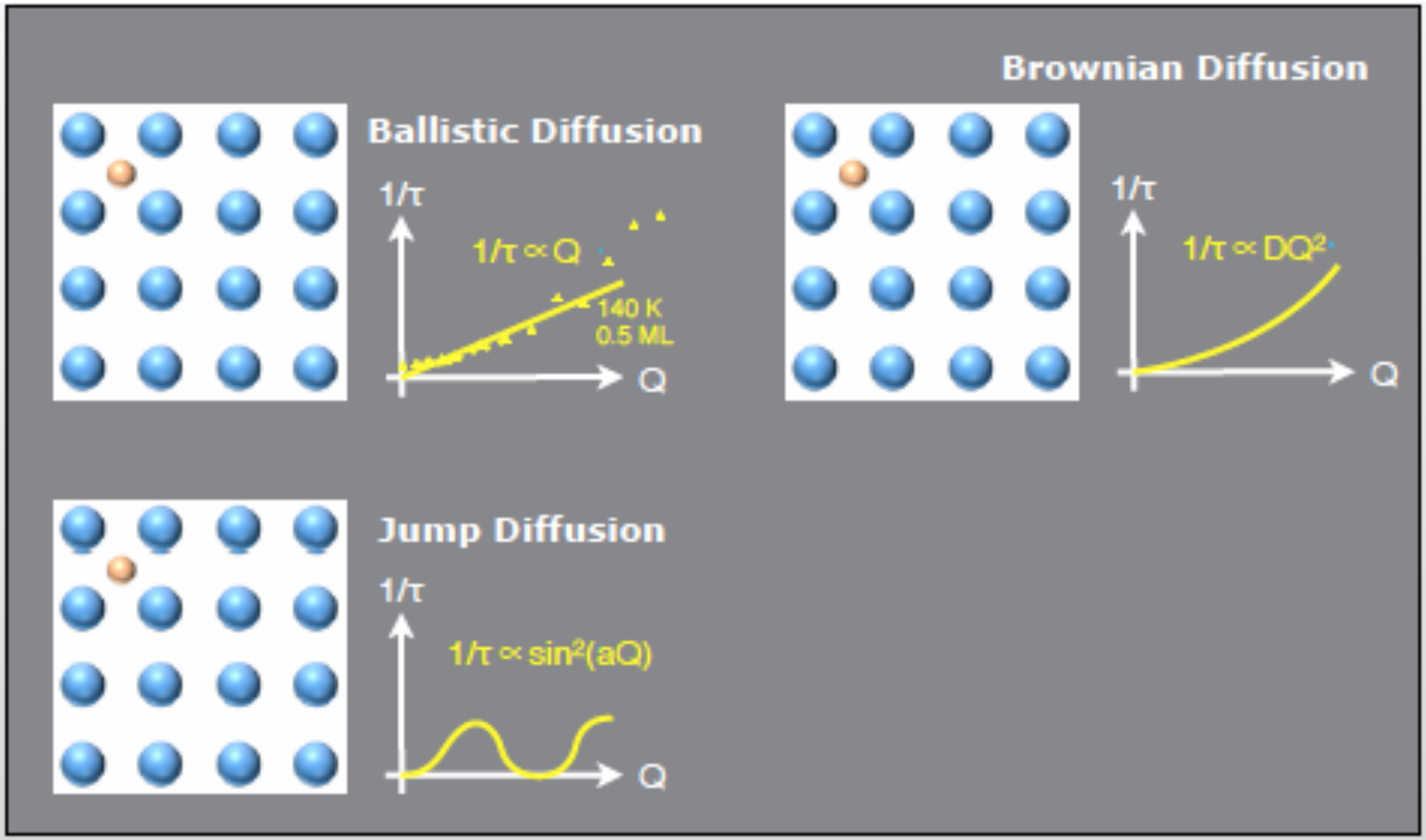
stretched exponential relaxation :

$s(Q,t) \propto \exp(-(t/\tau)^{\beta})$

$\beta < 1$

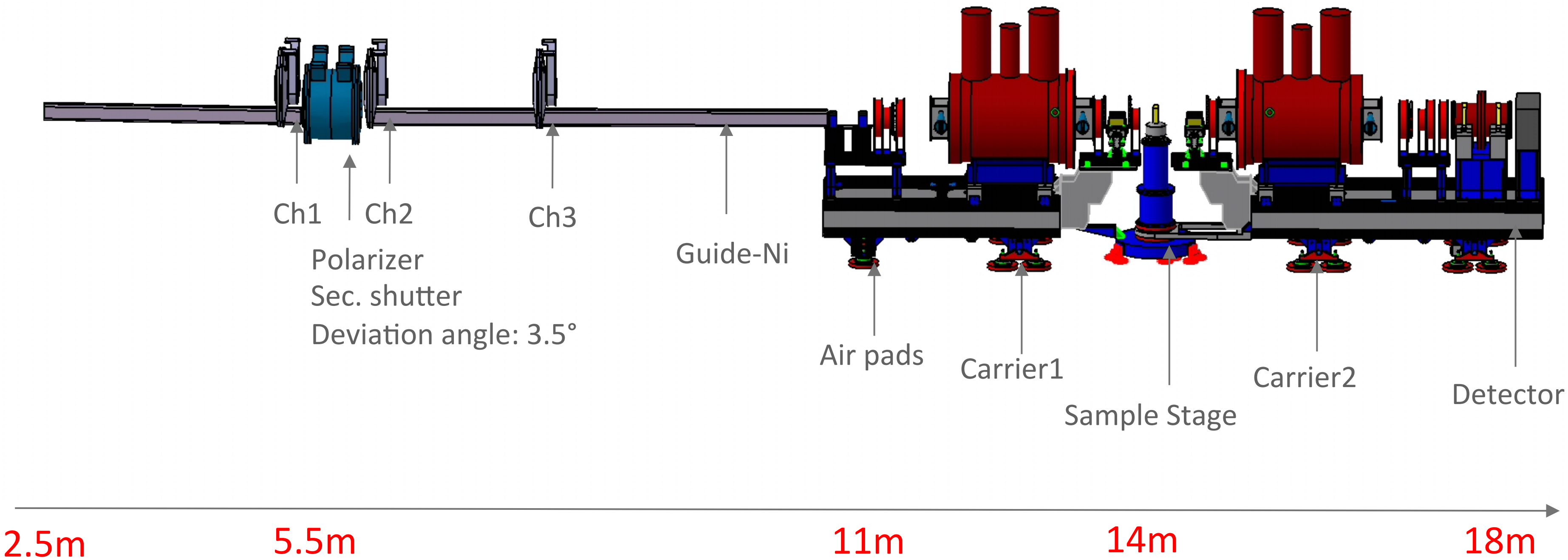


Exploit the Q dependence of tau or Gamma



Neutron spin echo spectrometer
NSE measures S(q,t)

Detection of slow motions 1 ps < t < 1 μs

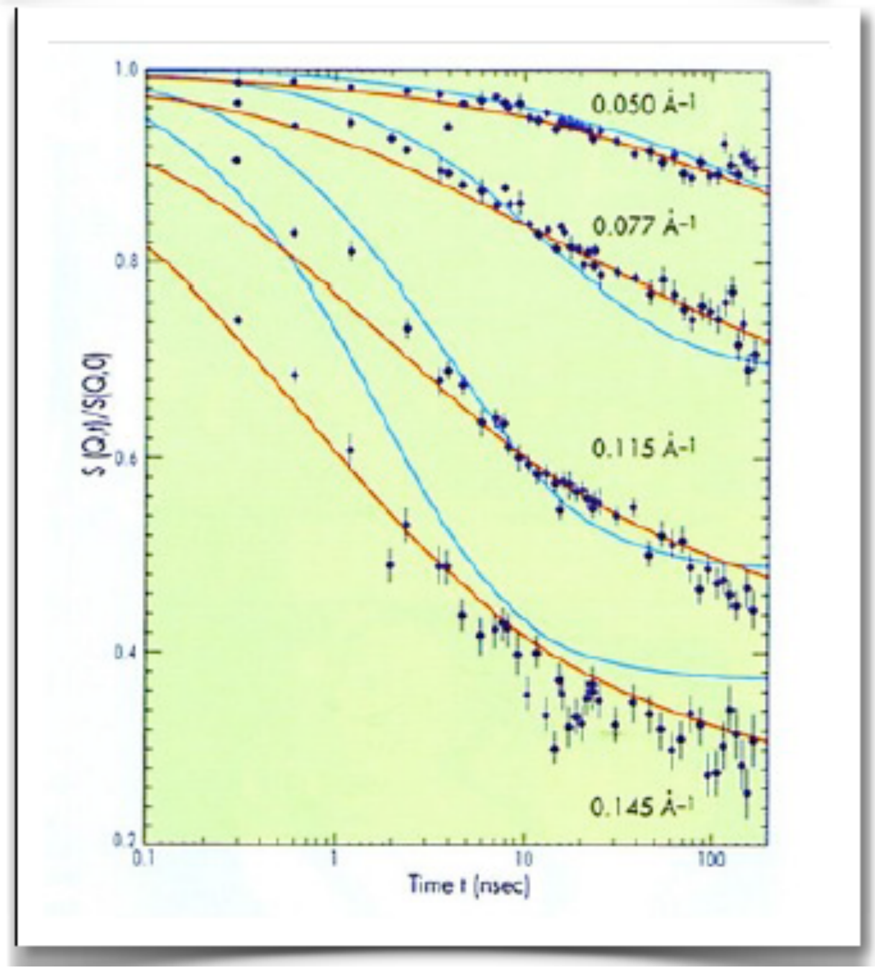


Examples of NSE studies

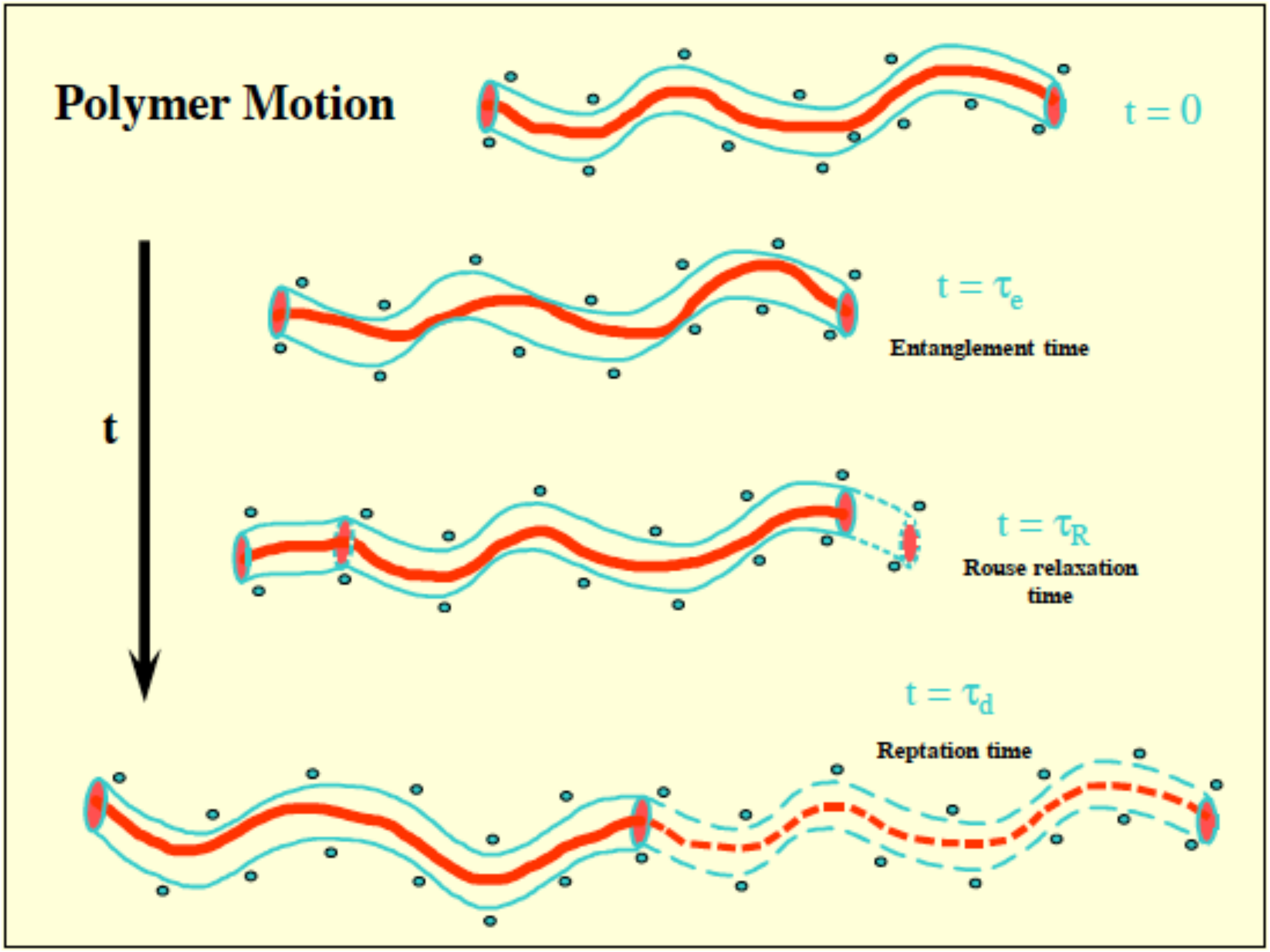
Reptation in polyethelene

de Gennes formulated the reptation hypothesis in which a chain is confined within a “tube” constraining lateral diffusion - although several other models have also been proposed

The measurements on IN15 are in agreement with the reptation model. Fits to the model can be made with one free parameter, the tube diameter, which is estimated to be 45Å



Schleger et al, Phys Rev Lett 81, 124 (1998)



$\Gamma \sim q^4$

At larger distances slow creep or reptation

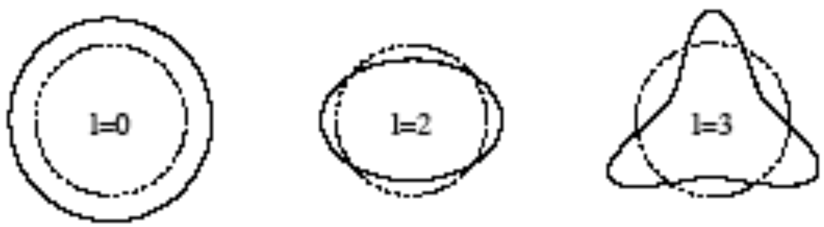
Undulations of a planar membrane

(Papoular & de Gennes 1969)

$$< h_q(t) h_{-q}(t) > = < h_q h_{-q} > e^{-\omega_q t} \quad \begin{cases} < h_q h_{-q} > = \dfrac{k_B T}{\kappa q^4} \\ \omega_q = \dfrac{\kappa}{4\eta} q^3 \end{cases}$$

Undulations of a sphere

(Schneider, Jenkins & Webb, 1984. Milner & Safran 1987)



$$r(\Omega) = R[1 + \Sigma_{l,m} u_{l,m} Y_{l,m}(\Omega)]$$

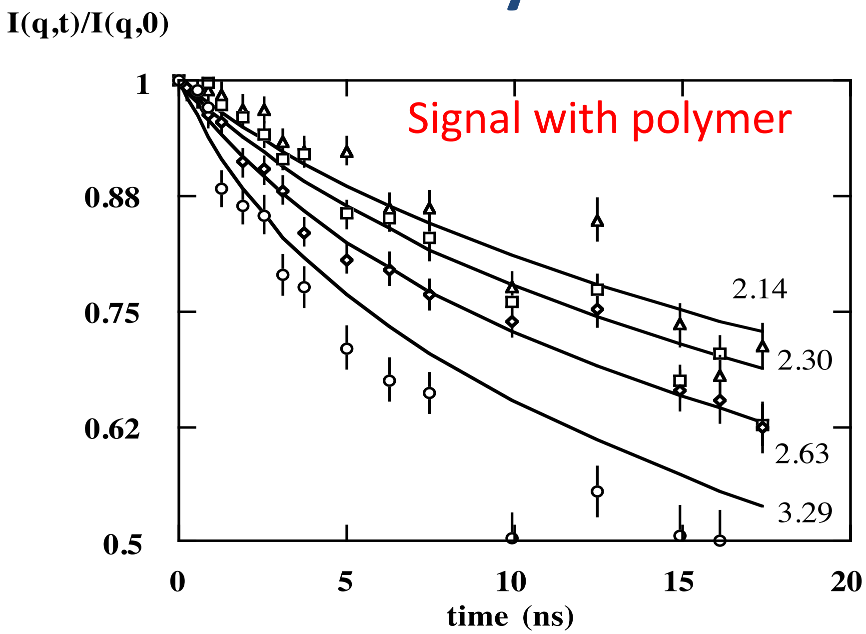
$$< u_{l,m}(t) u_{l,m}(0) > = < | u_{l,m} |^2 > e^{-\omega_{l,m} t} \quad \begin{cases} < u_{l,m} > = \dfrac{k_B T}{\kappa} \dfrac{1}{(l+2)(l-1)[l(l+1)-\gamma]} \\ \omega_{l,m} = \dfrac{\kappa}{\eta R^3} \dfrac{(l+2)(l-1)[l(l+1)-\gamma] l(l+1)}{(2l+1)(2l^2+2l-1)} \end{cases}$$

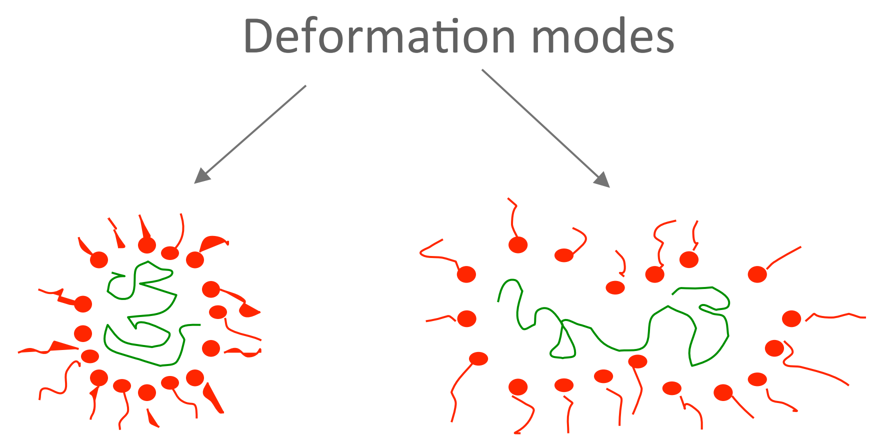
$$q_l^{\ 2} = l(l+1)/R^2 \qquad h_q \leftrightarrow R u_{l,m}$$

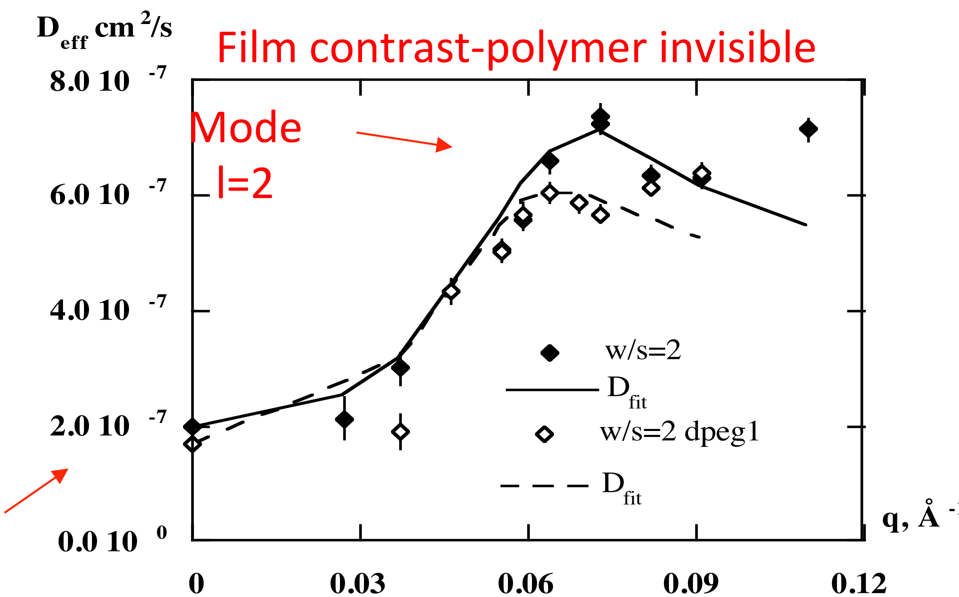
$$\omega_{l,m} \leftrightarrow \omega$$

$$I(Q,t) = e^{-DQ^2 t} V_s^2 (\Delta\rho)^2 \left[f_0(Qr_0) + \sum_{l>1} \frac{2l+1}{4\pi r_0^2} f_l(Qr_0) \langle a_l(0) a_l(t) \rangle \right]$$

Dynamics-Droplet Microemulsions







Rough analysis
1)Safran -Milner
2) Polydispersity

Dynamics of the mode l=2
is slowed down with polymer inside τ_2

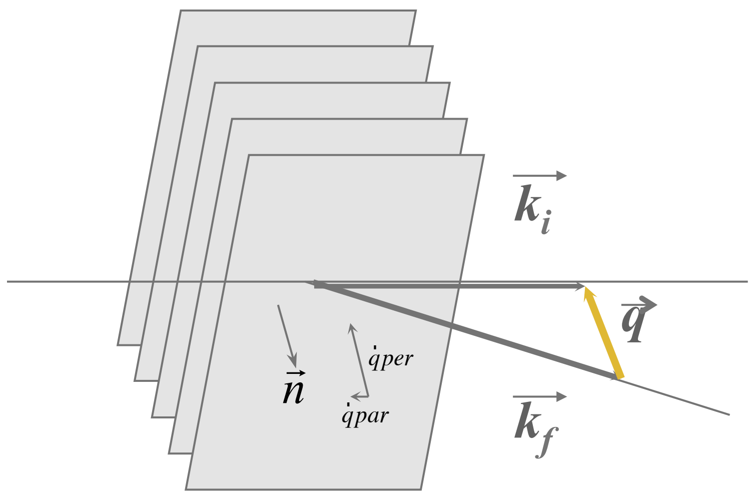
Dissipation is mainly viscous η

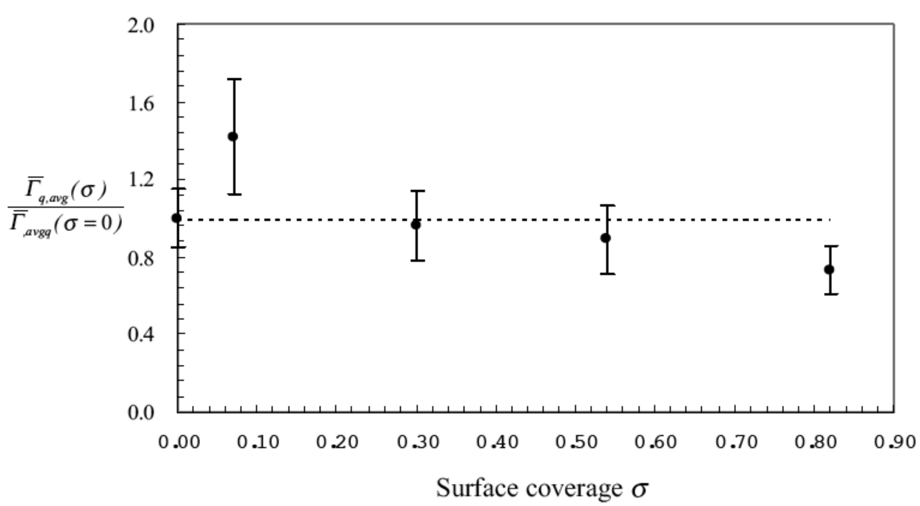
K, U_2 constant

J. Lal, B. Farago and L. Auvray, 1994 MRS Fall Meeting Symposium
Proceedings-Dynamics in Small Confining Systems II vol. 366, pgs. 427-438

Hydrophobically Modified Polymer Confined in Surfactant Bilayers

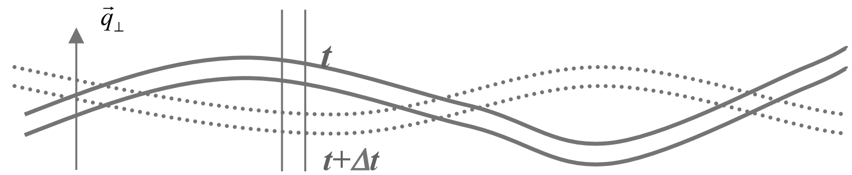
Yang, Lal, Mihailescu, Monkenbusch, Richter, Huang, Kohn, Russel, and Prud'homme



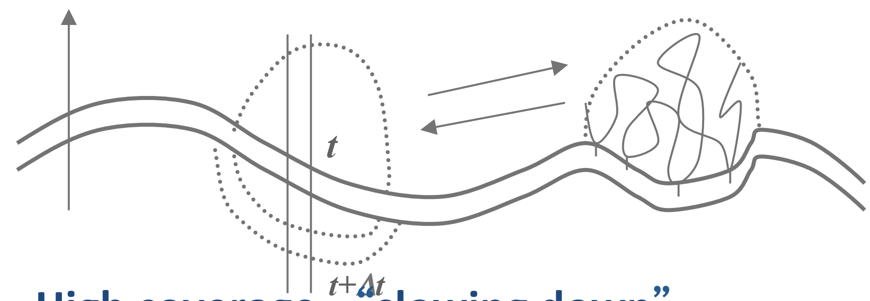


Low coverage "speeding up"

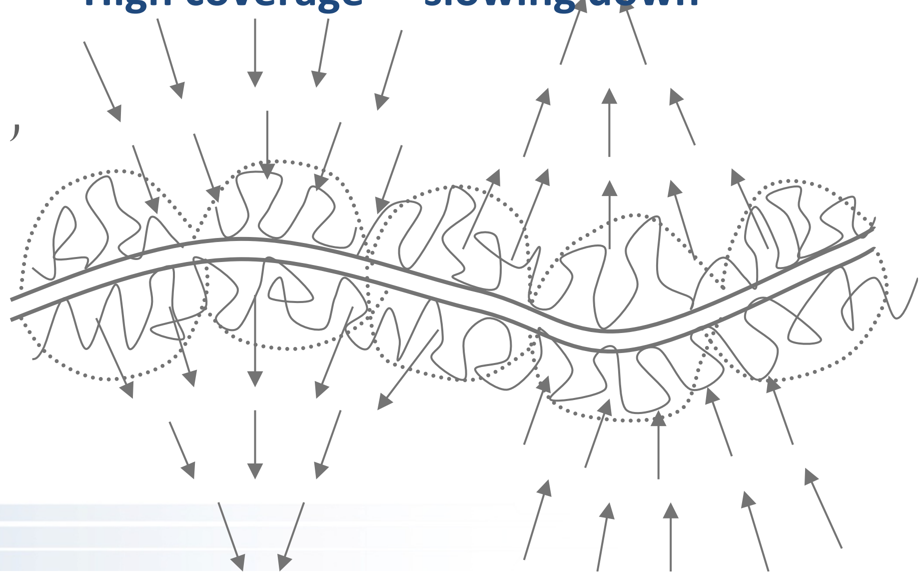
(a) due to membrane being stiffer



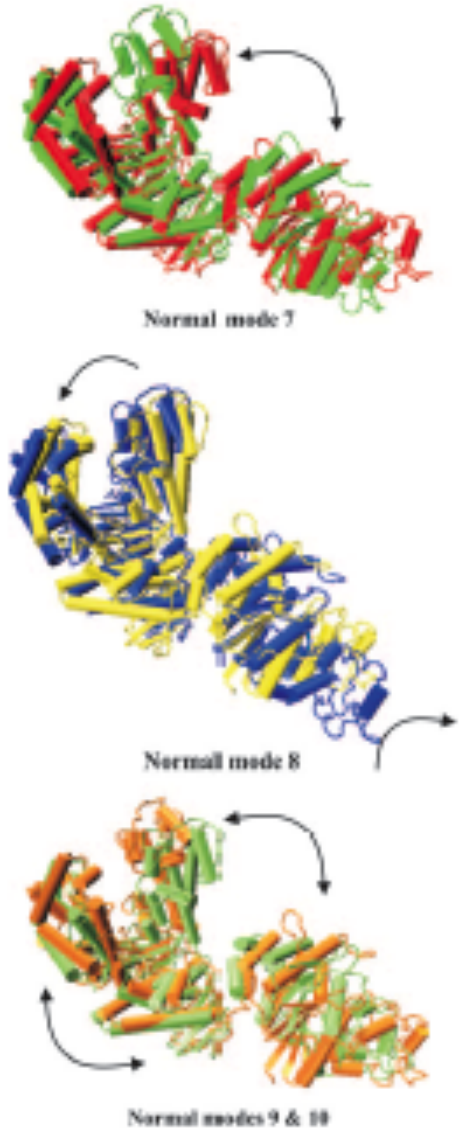
(b) coupling between lateral polymer diffusion and relaxation of undulations

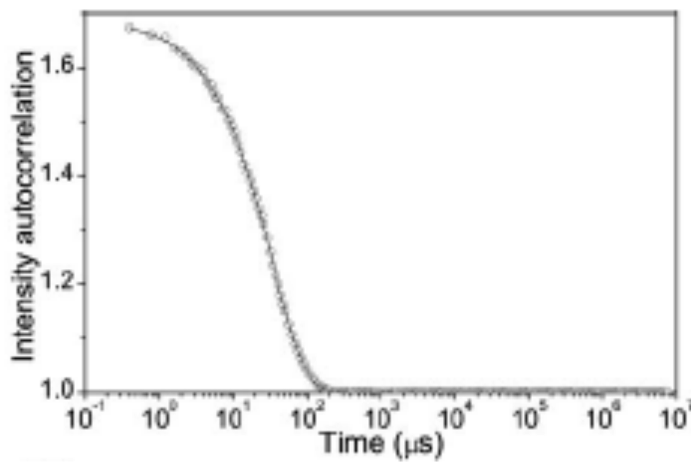


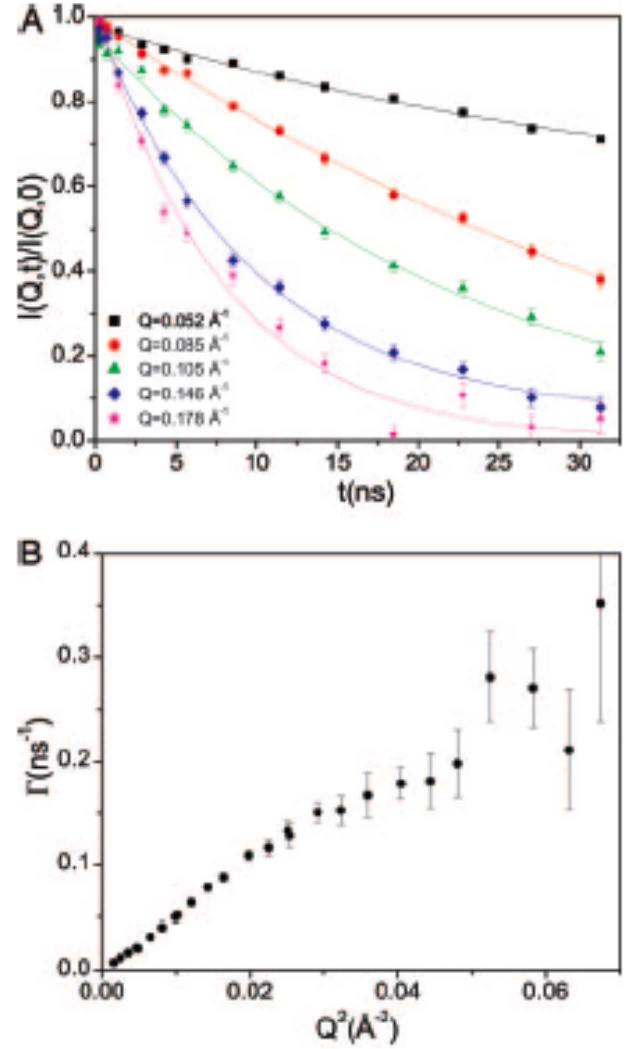
High coverage "slowing down"



Scattering techniques for dynamics - NSE & DLS



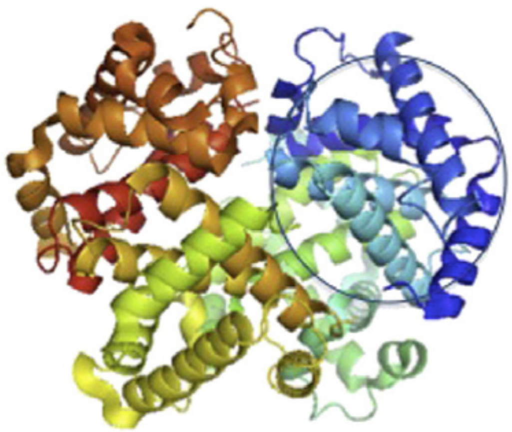


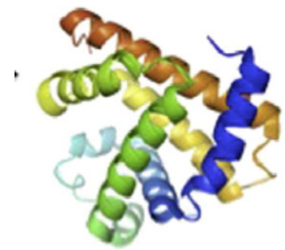


Coupled protein domain motion Taq polymerase-D. Callaway

NSE study of homologous proteins

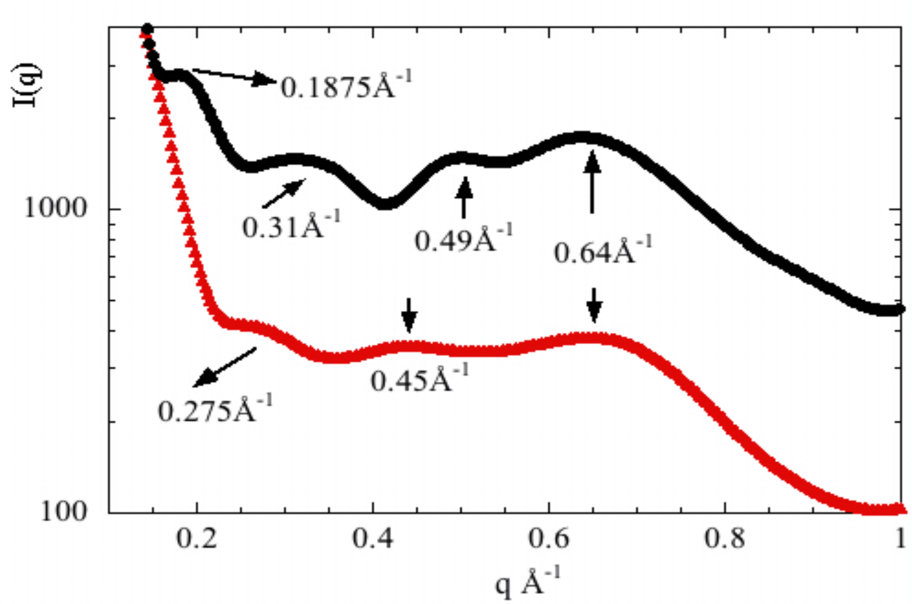
Hemoglobin tetramer





Myoglobin monomer

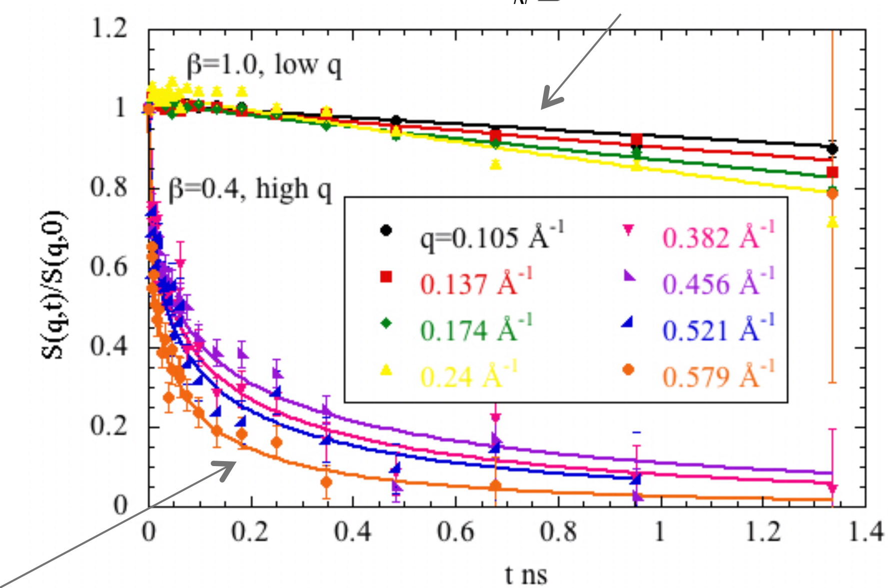
$R_{Hb} \sim 4^{1/3} R_{Mb}$



WAXS

APS

$$S_{ij}(q,t) = \frac{1}{N} \sum < \exp[-i\mathbf{q}.(\mathbf{r}_i(t=0) - \mathbf{r}_j(t))] >$$



$$S_i(q,t) \cong < \exp[-i\mathbf{q}.(\mathbf{r}_i(0) - \mathbf{r}_i(t))] >$$

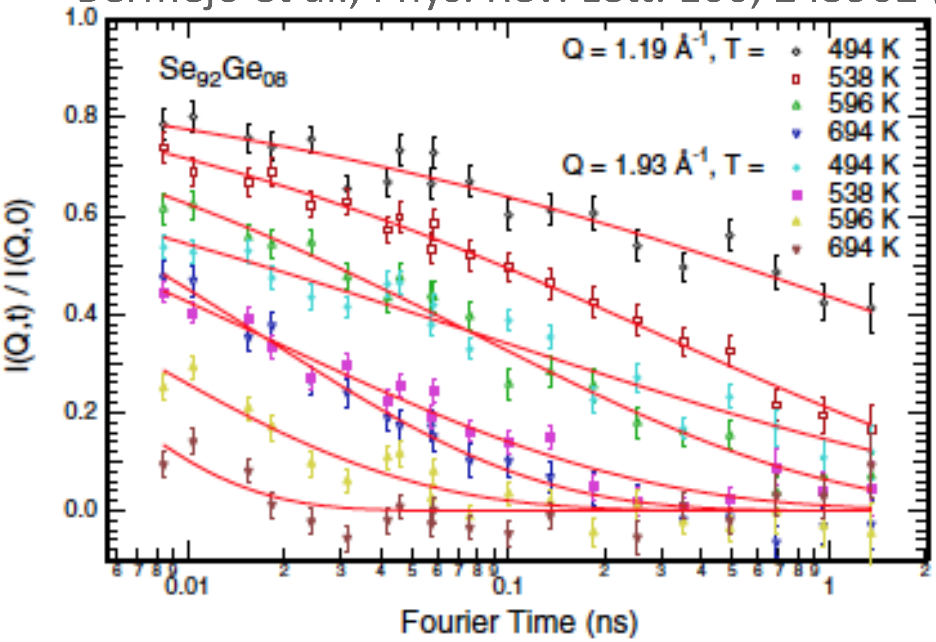
NSE

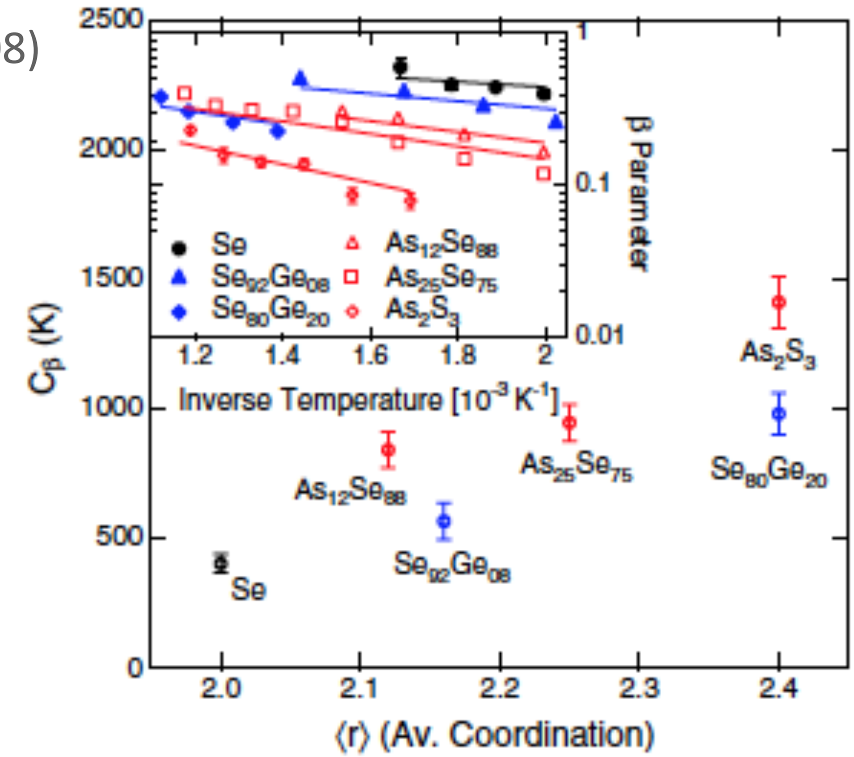
ILL

J. Lal et al J. Mol. Bio. 2008

Dynamics of Glasses

Bermejo et al., Phys. Rev. Lett. 100, 245902 (2008)





$Ge_xAs_ySe_{1-x-y}$ is a prime example of a network glass

Normal liquids dynamics show a thermal activation according to exp[-kT/E_a]

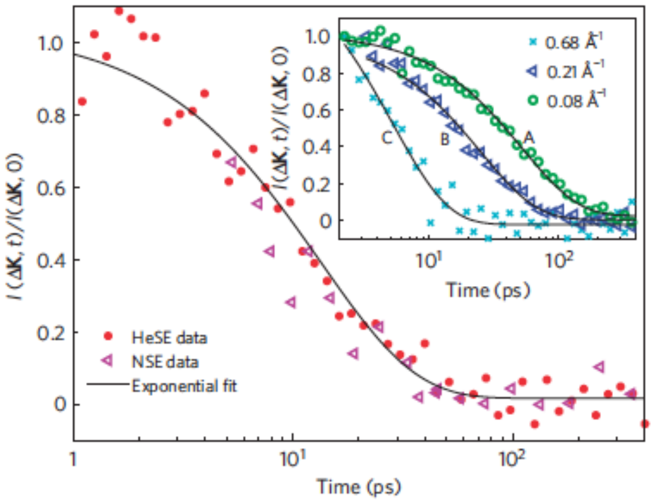
Dynamics of glasses close to the transition temperature, however, show sometimes strong deviations from exponential behaviour

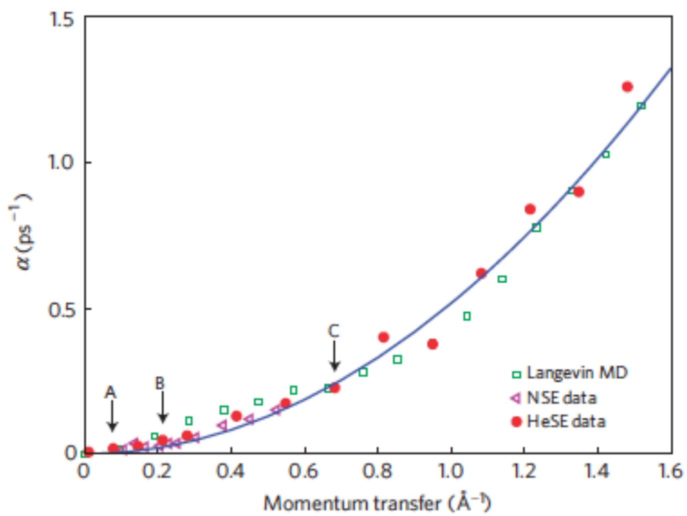
With measurements on IN11 it was possible to see this effect even far away from the glass transition and the dynamics were linked to the average co-ordination number <r>

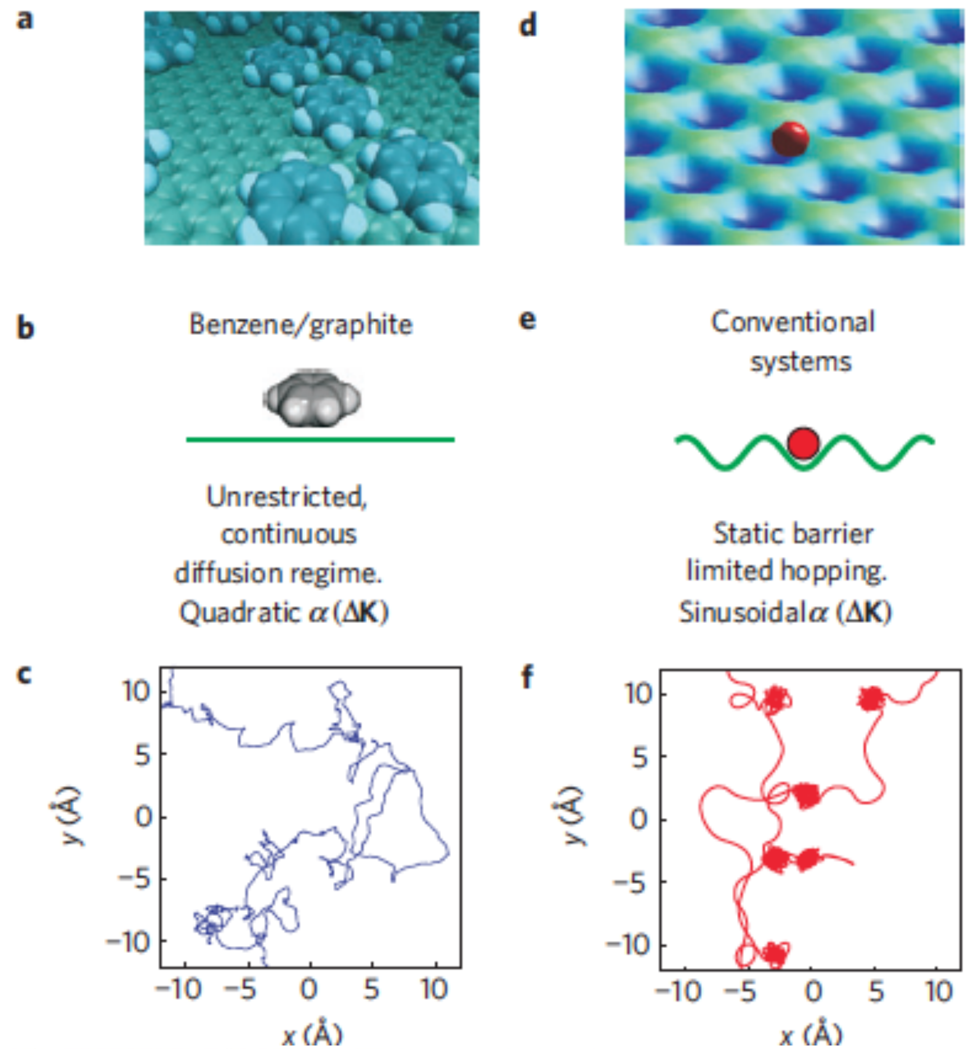
$$\langle r\rangle = 4x + 3y + 2(1-x-y)$$

Measurement of single-molecule frictional dissipation benzene on a graphite surface

NSE - and its surface equivalent helium spin-echo – see "perfect" molecular Brownian diffusion.



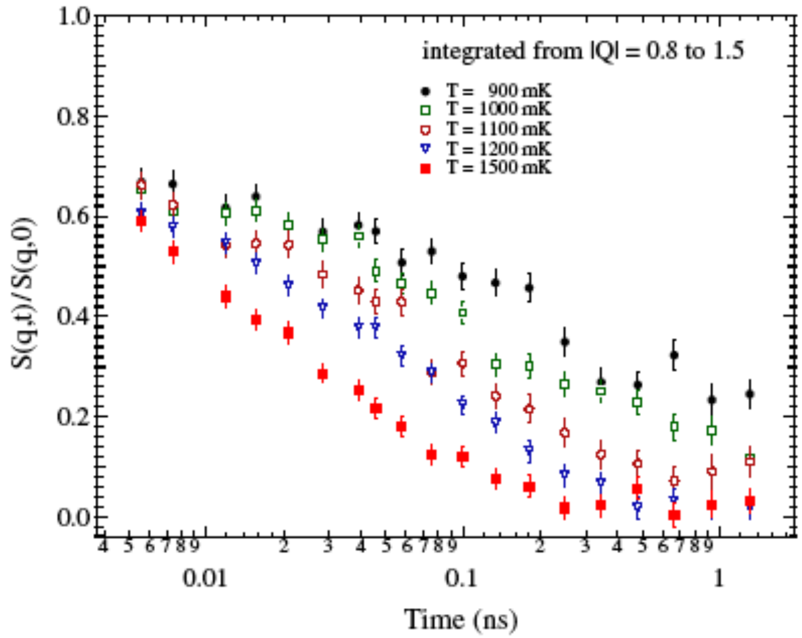




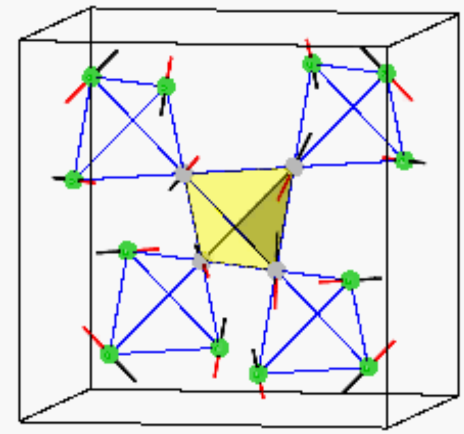
Dynamic friction can be determined.

Hedgeland et al., Nature Physics 5, 561 (2009)

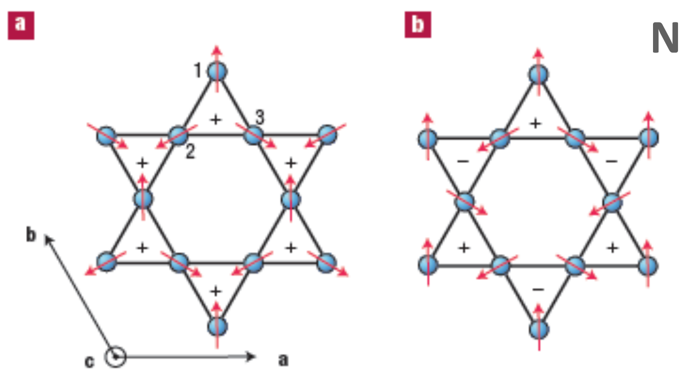
Dynamics of Frustrated Magnets



J. of Phys.-Cond. Matter 16 (11) 2004.



$Gd_2Ti_2O_7$: The normalized intermediate scattering function at several different temperatures around the 1 K transition.



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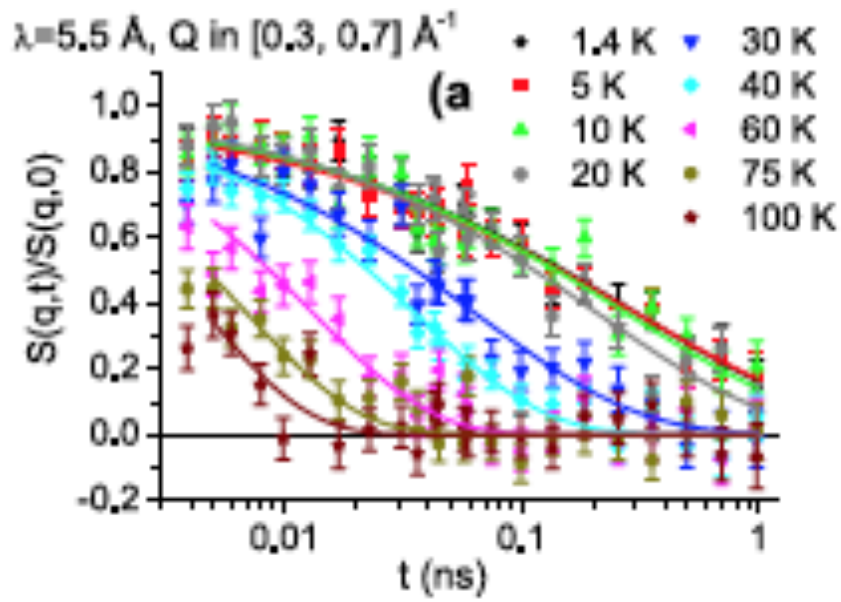
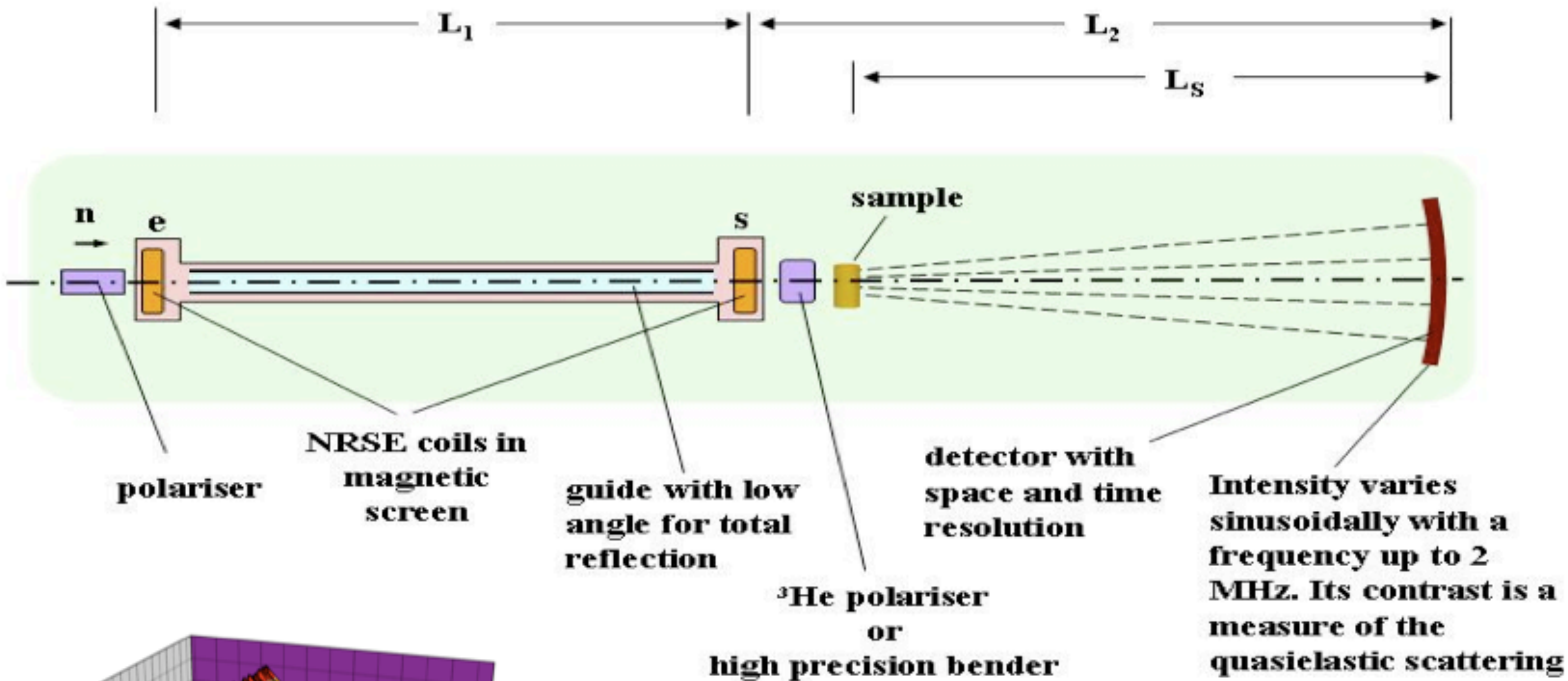
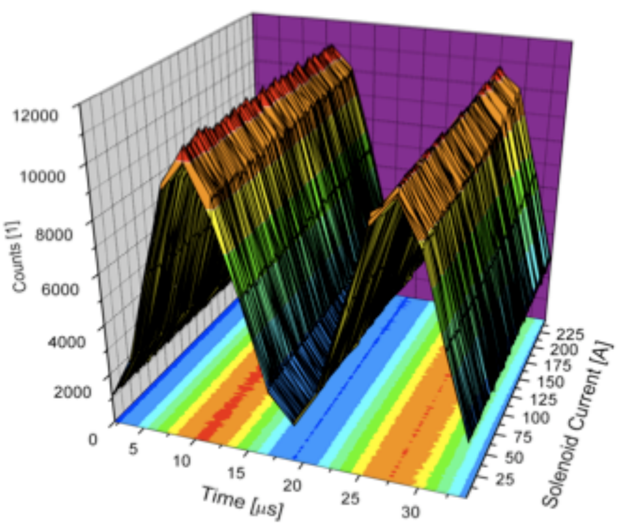
D. Grohol et al., Nature Materials 4, 323 (2005)



V. Simonet et al., PRL 100, 237204 (2008)

MISANS (Modulated Intensity Small Angle Scattering)





R. Gähler et al., Physica B 180-181 (1992) 899

$$I(t_D) = \frac{I_0}{2}\left(1 + \cos[2\left(\omega_B - \omega_A\right)t_D]\right)$$

M. Bleuel , JL et al , First tests of a MIEZE, 2006.
http://www.sns.gov/research/highlights/MISANS/
R. Georgii, JL et al *Applied Physics Letters* 2011.