NEUTRON SPIN ECHO

Ferenc Mezei and spin echo

Neutron Spin echo was invented by Ferenc Mezei in 1972

Mezei also invented the Mezei spin flipper and polarising supermirrors

For these and many other contributions to neutron scattering, Mezei was awarded the first

Walter Hälg Prize
for
European Neutron Scattering

by *ENSA,* the European Neutron Scattering Association in 1999

Mezei, Z Phys 255, 146 (1972); Lecture Notes in Physics 128, Springer-Verlag (1980)

Quasi-elastic scattering

Quasi-elastic neutron scattering generally arises from processes such as *e.g. tunneling, diffusion, relaxation and random fluctuations*:

The energy transfers at which such phenomena are observed are very small, often in the range of μeV to neV, corresponding to characteristic time scales of 10^{-11}s to 10^{-7}s

The best conventional (backscattering) quasi-elastic spectrometers offer a resolution of approximately $\Delta E = 0.3\mu eV$ at an incident energy of E=2meV corresponding to a resolution of $\Delta E/E = 1.5\times10^{-4}$

However, it can be shown that for optimally designed spectrometers $I \propto \Delta E^2$, so this resolution can be bettered only at the cost of intensity

Neutron Spin Echo elegantly circumvents this problem by effectively decoupling the instrumental energy resolution from beam monochromatisation

Neutron Spin Echo also provides access to the lowest currently attainable energy transfers, (0.1neV) with a resolution of $\Delta E/E = 10^{-10}$, enabling stochastic processes to be measured on to time scales of tens of microseconds

….with polarization….

Polarization precession

The classical equation of motion of a spin vector (or polarization P) in a magnetic flux density B is simply

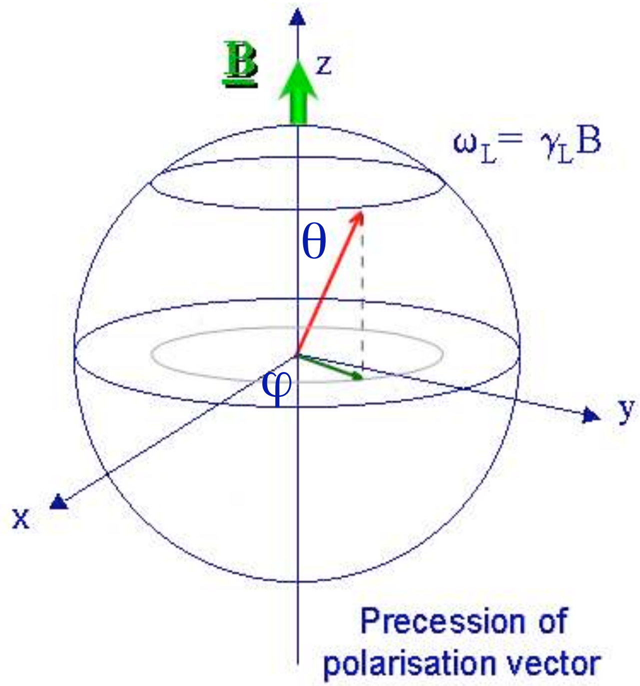
$$\frac{d\mathbf{P}}{dt} = -\gamma_n(\mathbf{P}\times\mathbf{B}) \quad \text{where} \quad \gamma_n = \frac{\omega_L}{|\mathbf{B}|}$$

so, with B aligned with the z-axis we have

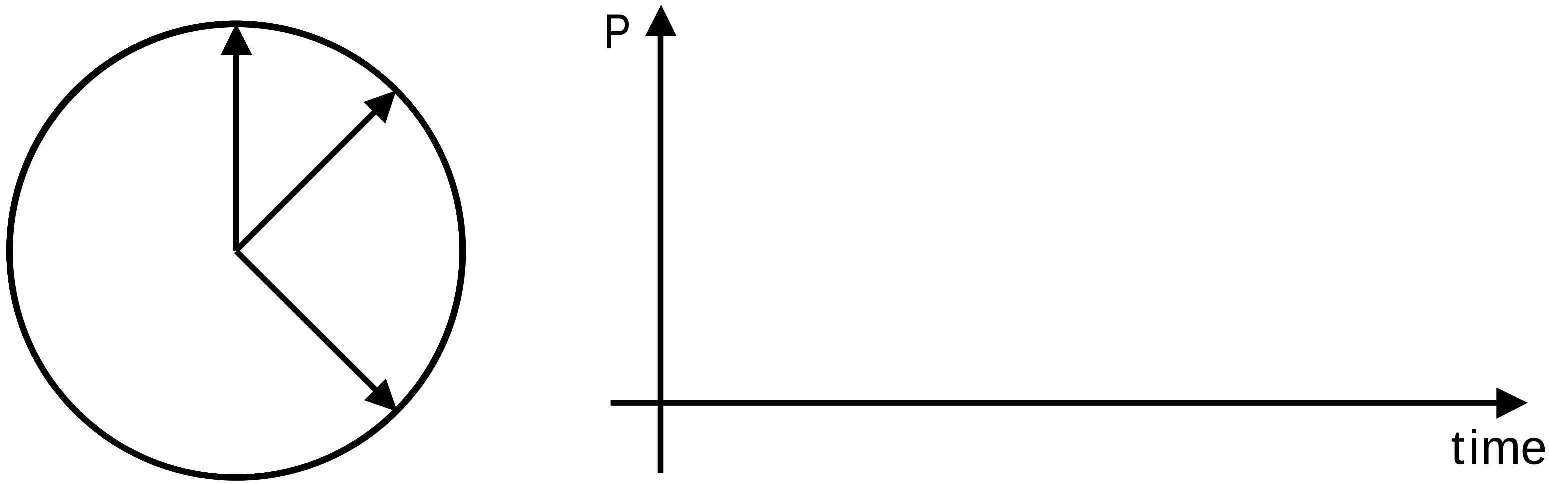
$$\frac{dP_x}{dt} = -\omega_L P_y, \quad \frac{dP_y}{dt} = -\omega_L P_x, \quad \frac{dP_z}{dt} = 0$$

the solutions to which are

$$P_x(t) = P_x\cos(\omega_L t) - P_y\sin(\omega_L t)$$
$$P_y(t) = P_x\sin(\omega_L t) + P_y\cos(\omega_L t)$$
$$P_z(t) = P_z$$

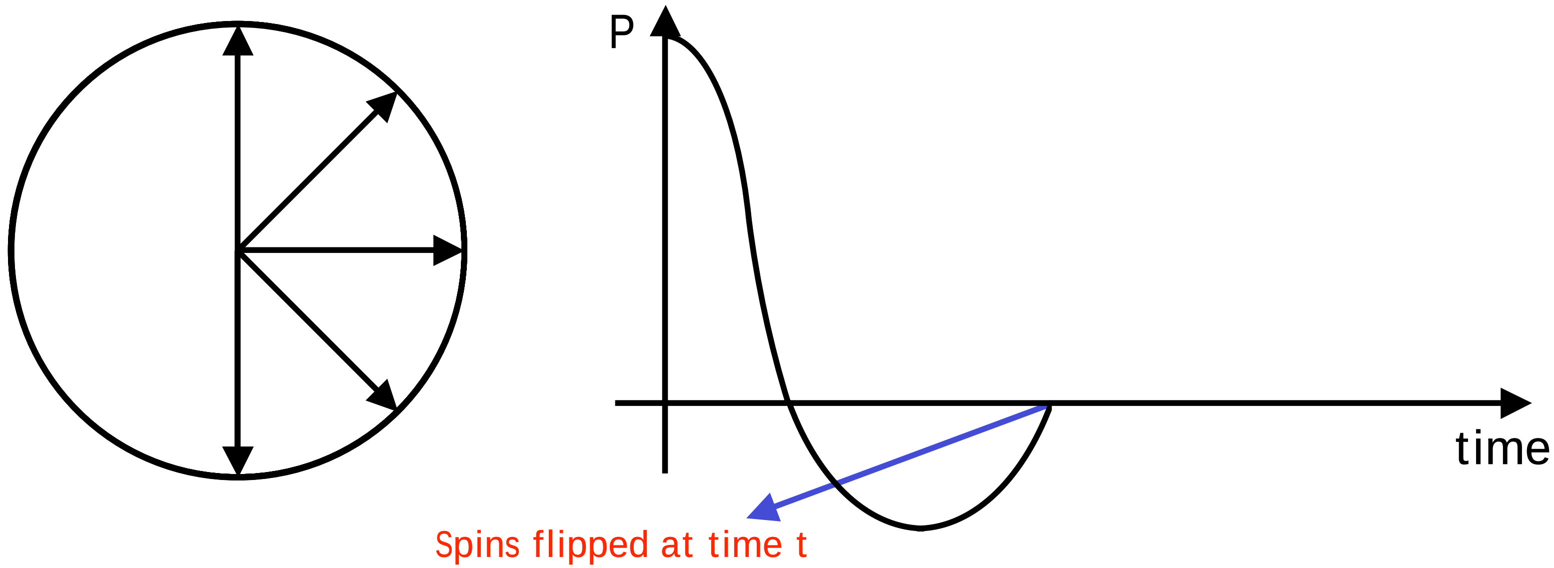


The principles of neutron spin echo



If each spin experiences a different field then the spins will Larmor precess at different rates and “fan out”

The principles of neutron spin echo

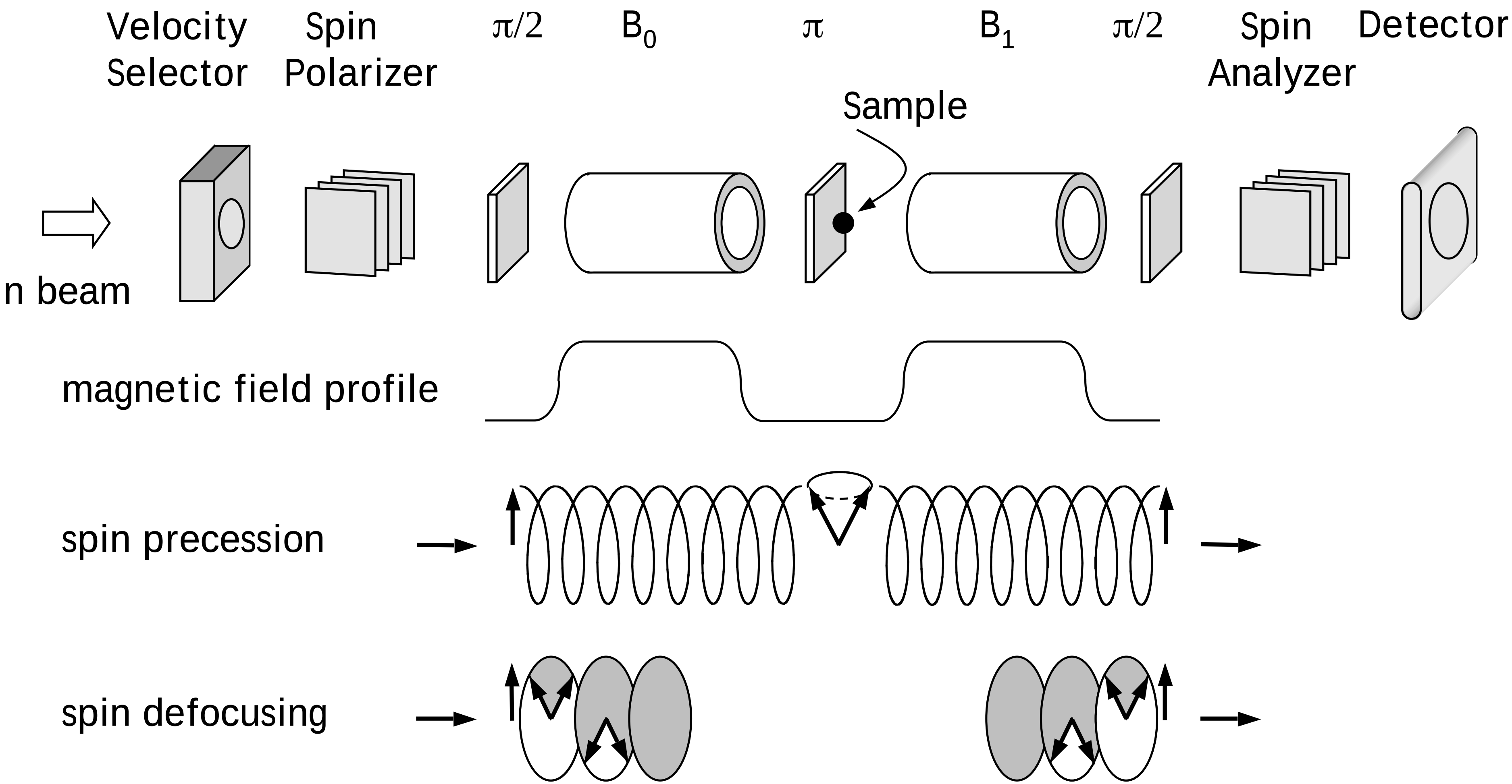


If each spin experiences a different field then the spins will Larmor precess at different rates and "fan out"

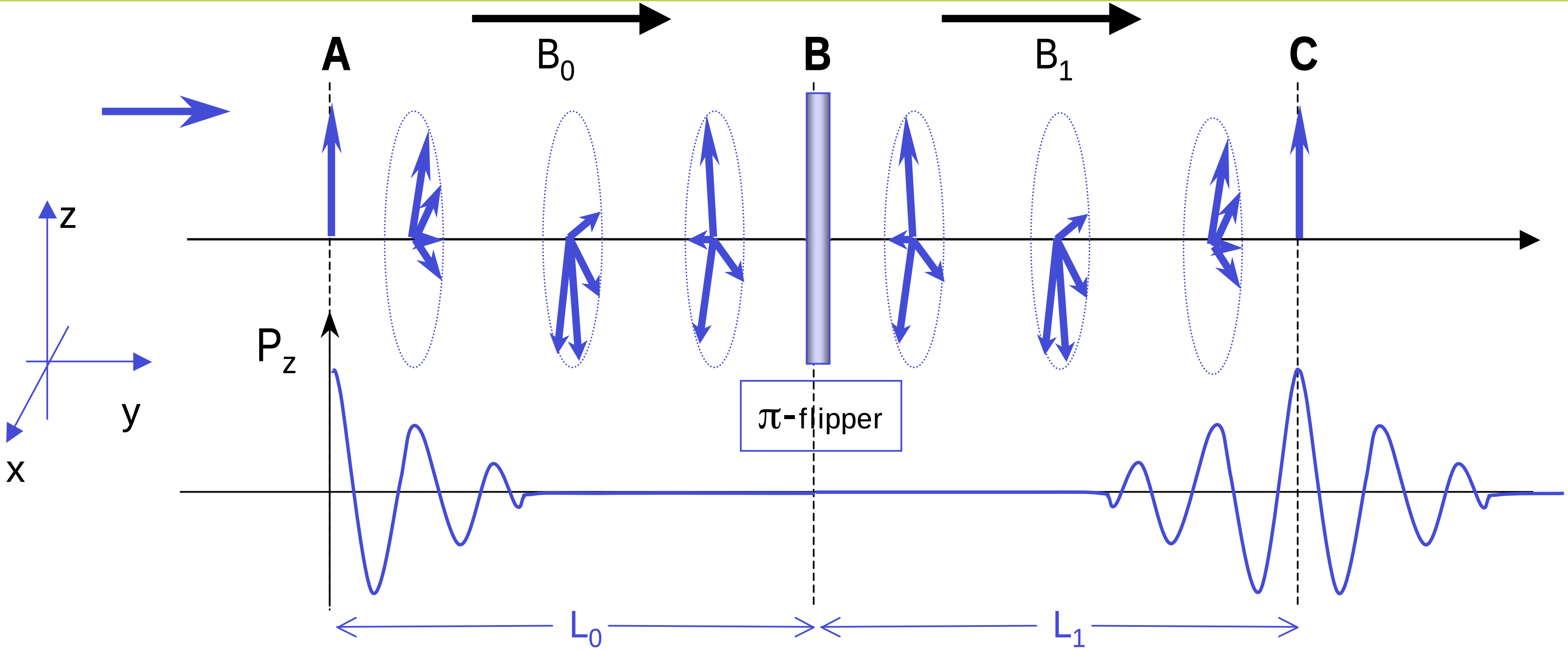
If, after a time t, the fields are suddenly reversed, or the spins "flipped" by π with respect to the fields then the Larmor precession is reversed - ie time is effectively reversed

The full initial polarisation is recovered after time 2t

The principle of spin echo

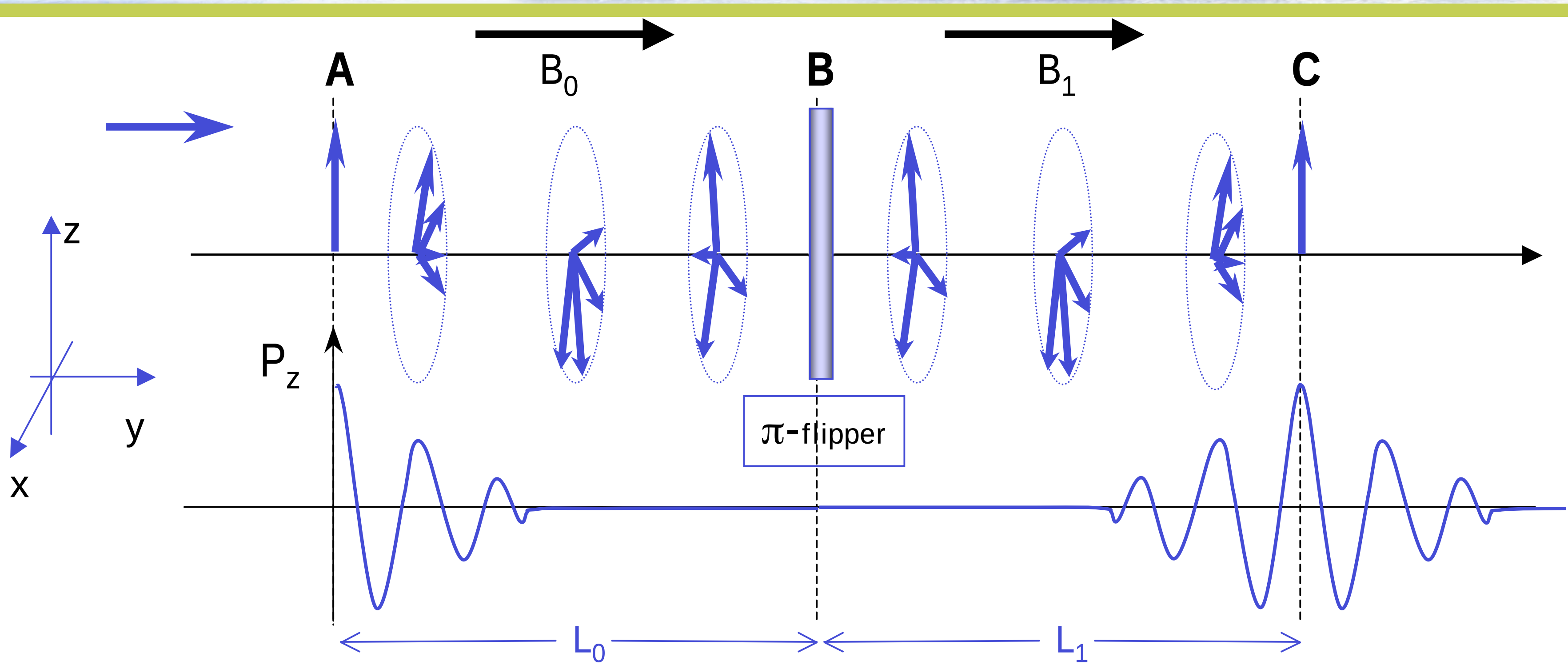


The basis of Neutron Spin Echo



- A broadly monochromatic beam of neutrons is initially polarized in the y-direction. At **A** their spins are flipped through $\pi/2$ to the z-direction
- Between **A** and **B** the spins precess in a uniform field B_o (in the +y direction). Over the distance L_o each neutron precesses by an amount φ depending upon its velocity, v. The beam is effectively depolarized
- At **B** the neutron spins are flipped by π and precess in B_1
- Providing that $B_o L_o = B_1 L_1$ all the neutrons will be in phase again by point **C**

The basis of Neutron Spin Echo



Over a distance L_0 the number of radians each neutron has precessed is

$$\varphi_L = \omega_L t = \gamma_n L B_0 / v \qquad \text{(where } \gamma_n = 1.833\times10^8 \text{ rad.s}^{-1}.\text{T}^{-1}\text{)}$$

At point **C**, after the spin flip, the accumulated precession angle is therefore

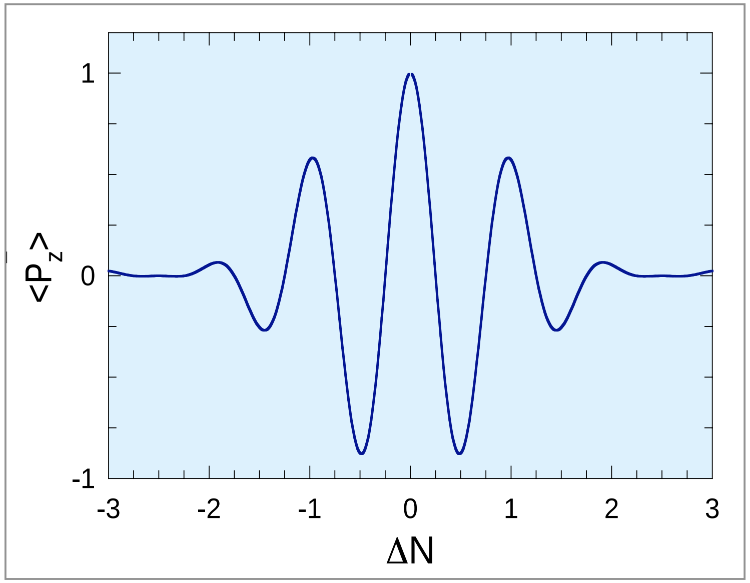
$$\varphi_L = \varphi_{L(AB)} - \varphi_{L(BC)} = \gamma_n (L_o B_o - L_1 B_1)/v$$

where $\varphi_L = 0$ for <u>all neutron velocities</u>, providing that $B_o L_o = B_1 L_1$

Precision of the velocity measurement

The shape of the spin echo envelope or group is

$$P_z = \langle \cos(\varphi) \rangle = \int f(v) \cos\left(\frac{\gamma_n L B_0}{v} \right) dv$$



This is simply the Fourier transform of the distribution function for 1/*v* which is equivalent to the Fourier transform of the wavelength spread of the beam

The wavelength spread is typically $\Delta\lambda/\lambda = 0.15$

Expressing the number of precessions of 2π in terms of mean neutron wavelength λ (in Å), and with *L* in metres and *B* in mT we have

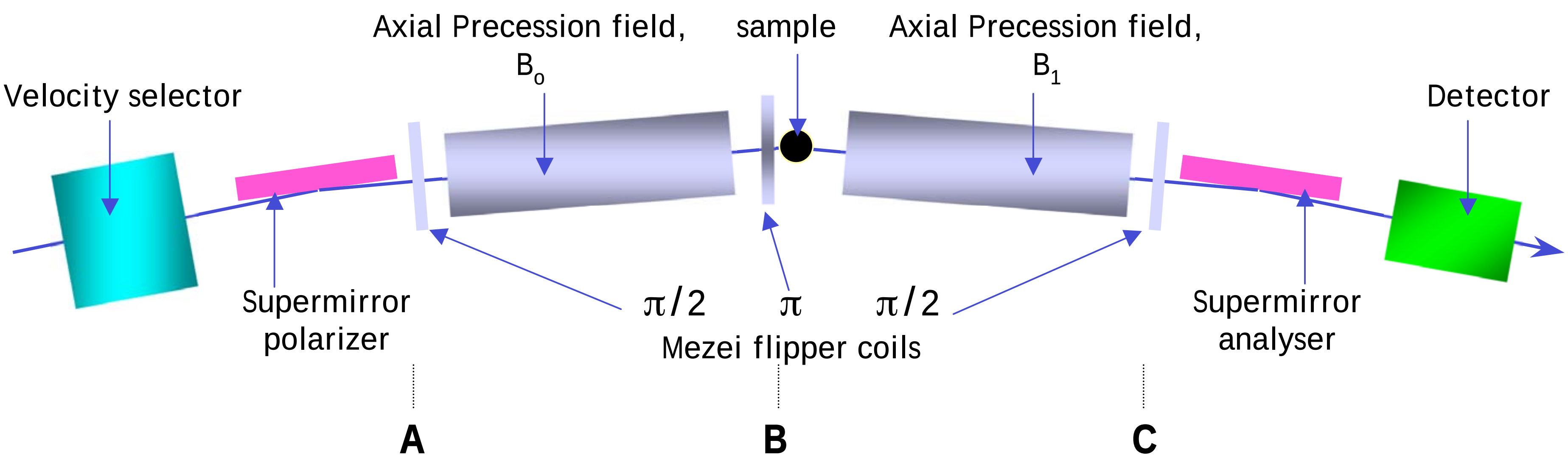
$$N = \varphi_L/2\pi = 7373\, LB_0\lambda$$

A typical spin echo spectrometer (eg IN11 at ILL) has a line integral, $B_o L_o$ or $B_1 L_1$ of 0.3T.m, so with a mean neutron wavelength of say 10 Å we have

$$N = \varphi_L/2\pi = 22200$$

Given that we can measure the polarization, and hence phase to within 1%, this implies an energy resolution $\Delta E/E = 10^{-7}$, despite a wavelength spread of 15%

Beyond Elastic Scattering



So far we have assumed that the neutrons enter and leave the spectrometer with the same distribution of velocities (i.e. any scattering by the sample is elastic)

Quasi-elastic scattering process will change the energy and therefore the velocity of the neutrons. The accumulated precession angle is now

$$\varphi_L = \gamma_n[(L_o B_o)/v_o - (L_1 B_1)/v_1]$$

Thus the accumulated precession angle φ_L can be used as a measure of the energy transfer associated with the scattering process

Measuring the energy transfer

The energy transfer in the scattering process is

$$E_1 - E_0 = \hbar\omega = \frac{m}{2}\left(v_1^2 - v_0^2\right)$$

For small energy transfers (in the quasi-elastic limit) we have

$$\delta E_0 = \hbar\omega = m v_0 \delta v_0 \qquad v_1 = v_0 + \delta v_0 = v_0 + \frac{\hbar\omega}{m v_0}$$

So the accumulated precession angle is now

$$\varphi_L = \frac{\gamma_n B_0 L_0}{v_0} - \frac{\gamma_n B_1 L_1}{v_0 + \hbar\omega / m v_0} = \frac{\gamma_n \left(B_0 L_0 - B_1 L_1\right)}{v_0} + \frac{\gamma_n B_1 L_1 \hbar\omega}{m v_0^3}$$

Since, for an optimised elastic spin-echo $B_1L_1 = B_oL_o$, the first term drops out and we are left with

$$\varphi_L^{'} = \frac{\gamma_n B_1 L_1 \hbar\omega}{m v_0^3} = t_F \omega$$

where t_F is a constant of proportionality which has the units of time - the so-called *Fourier time*

The intermediate scattering function

In the presence of quasi-elastic scattering the final polarization close to the elastic echo condition will therefore be decreased to a value given by $\langle \cos(\varphi'_L) \rangle$, i.e. $\langle \cos(\omega t_F) \rangle$

The probability of scattering with an energy ω at a given scattering vector **Q** is given by the scattering law $S(\mathbf{Q},\omega)$, hence

$$\langle \cos(\omega t_F) \rangle = \frac{\int S(\mathbf{Q},\omega)\cos(\omega t_F)\,d\omega}{\int S(\mathbf{Q},\omega)\,d\omega}$$

This is simply a Fourier transform of $S(\mathbf{Q},\omega)$ with respect to ω. t_F is the <u>Fourier time</u> which, in the quasi-elastic limit, is equivalent to real time

It is also very important to note that the Fourier transform of $S(\mathbf{Q},\omega)$ with respect to ω is the Intermediate Scattering function, $S(\mathbf{Q},t)$

The final polarization, or the NSE polarization, P_{NSE}, is therefore

$$P_{NSE} = P_S \langle \cos(\omega t_F) \rangle = P_S S_N(\mathbf{Q},t)$$

Here P_S has been introduced to account for any polarization dependence in the scattering process, and $S_N(\mathbf{Q},t)$ is the *normalised* intermediate scattering function

Neutron Spin Echo therefore performs the energy Fourier transform for you!!

Lineshape analysis

Many diffusional and relaxation processes are characterised by a Lorentzian dynamical correlation function

$$S(\mathbf{Q},\omega) \propto \frac{\Gamma}{\Gamma^2 + (\omega - \omega_0)^2}$$

On substitution into the equation for the polarization we get:

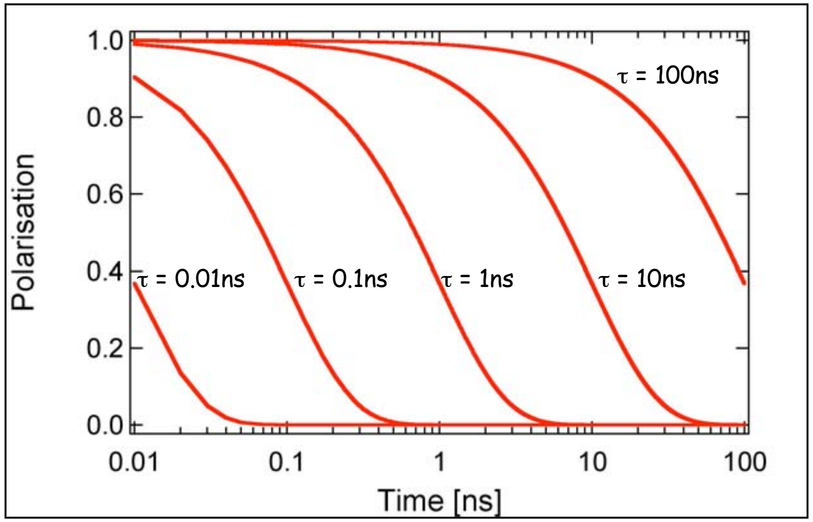
$$P_{NSE} = \frac{\int \left(\Gamma^2 + (\omega - \omega_0)^2\right)^{-1} \cos\left[t(\omega - \omega_0)\right] d\omega}{\int \left(\Gamma^2 + (\omega - \omega_0)^2\right)^{-1} d\omega}$$

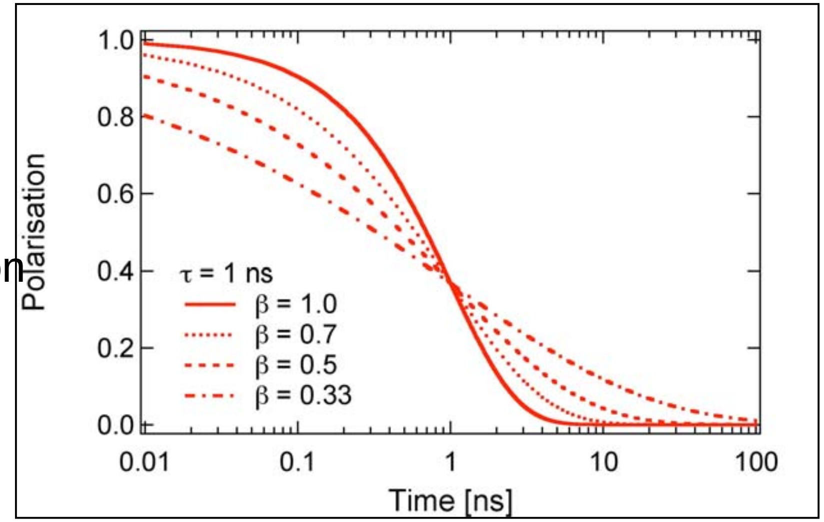
$$= e^{-\Gamma t} = e^{-t/\tau}$$

We expect to see an exponential decay with time

A commonly found form of non-Lorentzian relaxation is the so-called “stretched exponential” or Kohlrausch relaxation:

$$P_{NSE} = \exp\left(-(t/\tau)^{\beta}\right)$$





Polarisation dependent scattering

The measured polarization depends upon the spin dependence of the scattering process under investigation
(*Mezei, Lecture Notes in Physics 128, Springer-Verlag (1980)*)

Also, the configurations of the spin flip coils and magnetic fields at the sample position must be arranged for specific types of scattering sample:

Type of scatterer	Sample (S) region: Spin flip coil(s)	Sample (S) region: Sample field, B_S	Polarisation factor P_s
Coherent nuclear	π	small	1
Nuclear spin-incoherent	π	small	-1/3
Paramagnets	none	small	1/2
Ferromagnets	$\pi/2$ - S - $\pi/2$	High (saturating ||z)	1/2
Antiferromagnets	none	small	$1/2 < P_s < 1$

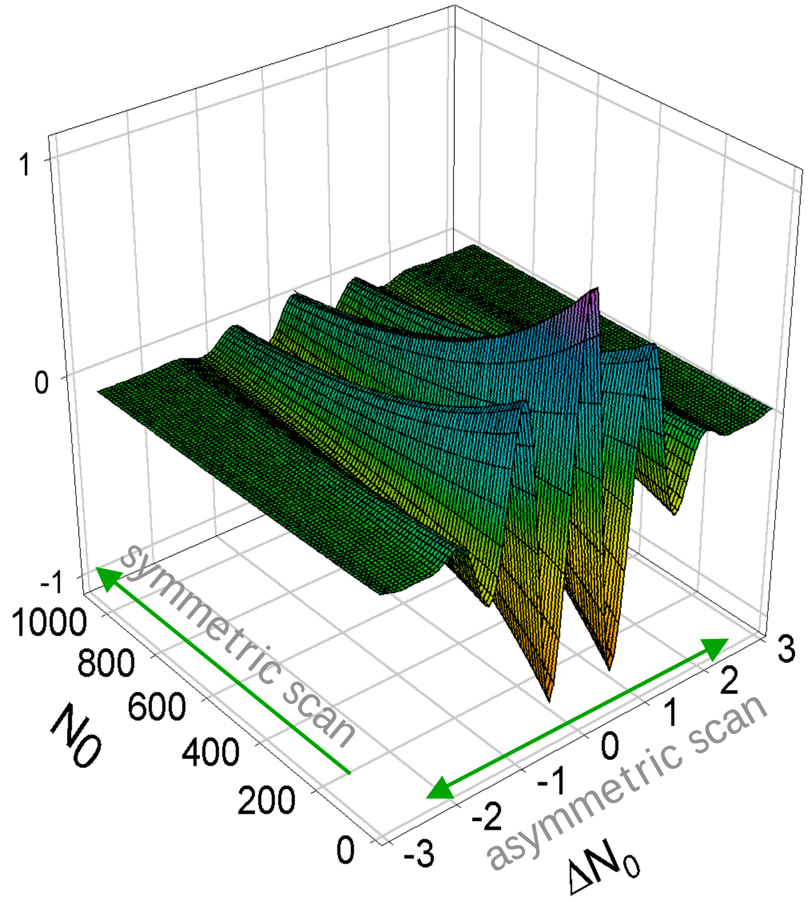
Practicalities

In general P_{NSE} can be defined by

$$P_{NSE}=(I_{max}-I_{min})/2I_o$$

Where I_{max} and I_{min} are the maximum and minimum intensities measured in the spin echo group

In a typical measurement an appropriate value of B_o is chosen and B_1 is scanned (a so-called *asymmetric scan*) to find the centre of the group at ΔN=0



A *symmetric scan* in Fourier time t_F,

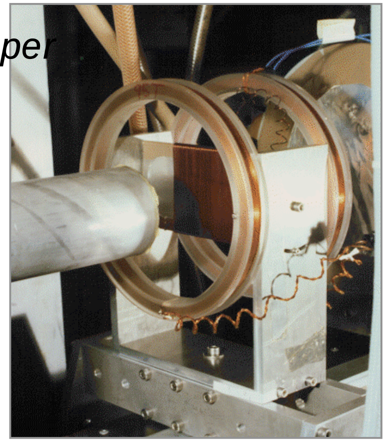
$$t_F = \frac{\gamma_n BL\hbar}{mv_0^3}$$

can then be performed by varying B_o and B_1 but keeping the ratio B_o/B_1 fixed

Instrumental resolution is determined by measuring P_{NSE} for purely elastic scattering, $P^E(t)$. Because the measurement is made in Fourier time, rather than performing a deconvolution, we simply take $P_{NSE}(t)=P^S(t)/P^E(t)$ where $P^S(t)$ is the spin echo polarization measured for the sample

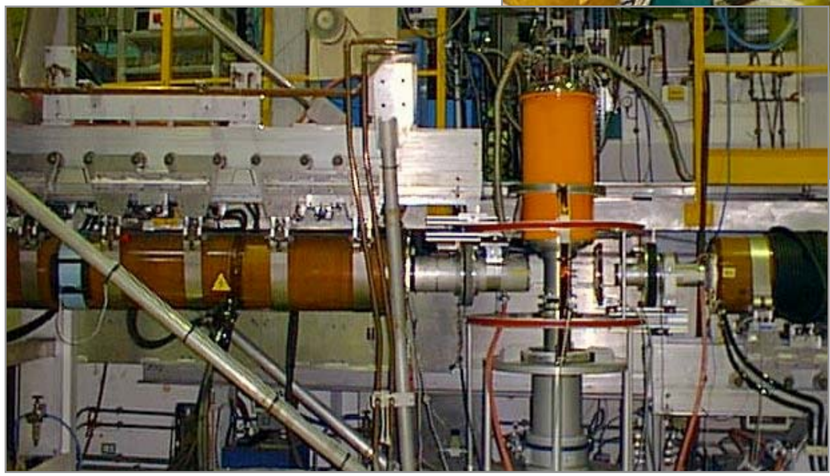
Neutron spin echo spectrometers-IN11

right: π /2 flipper coils



below: IN11

above: Mezei's first spin echo precession coils



right: IN11 multi-detector

left: iN11 sample position

Neutron spin echo spectrometers

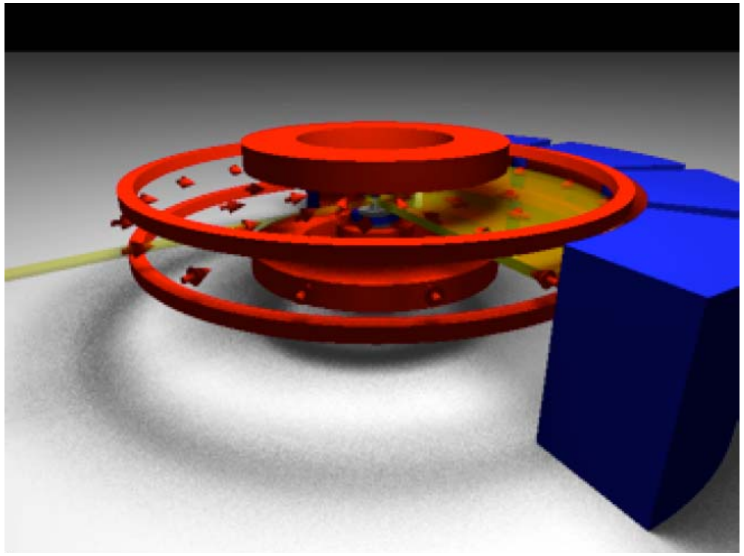
Julich

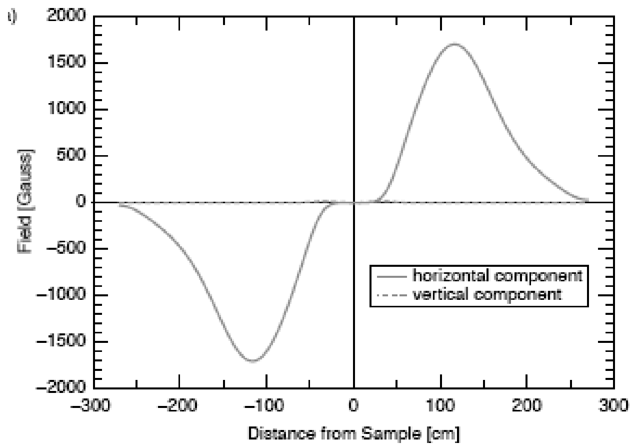
LLB

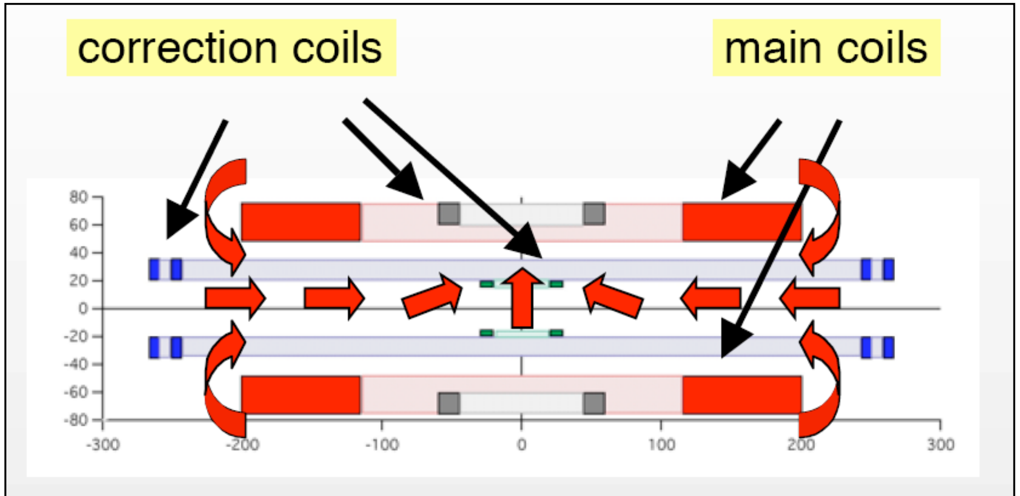
HMI, Berlin

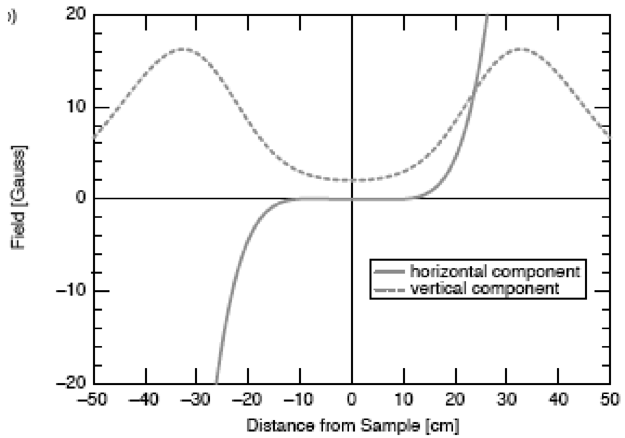
The WASP project

Replacement for IN11 (c. 2011) - multidetector spin-echo



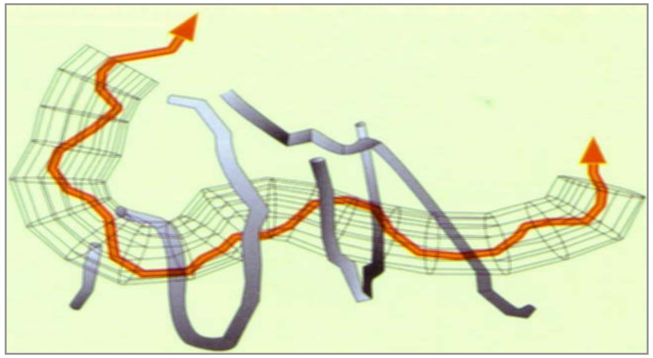






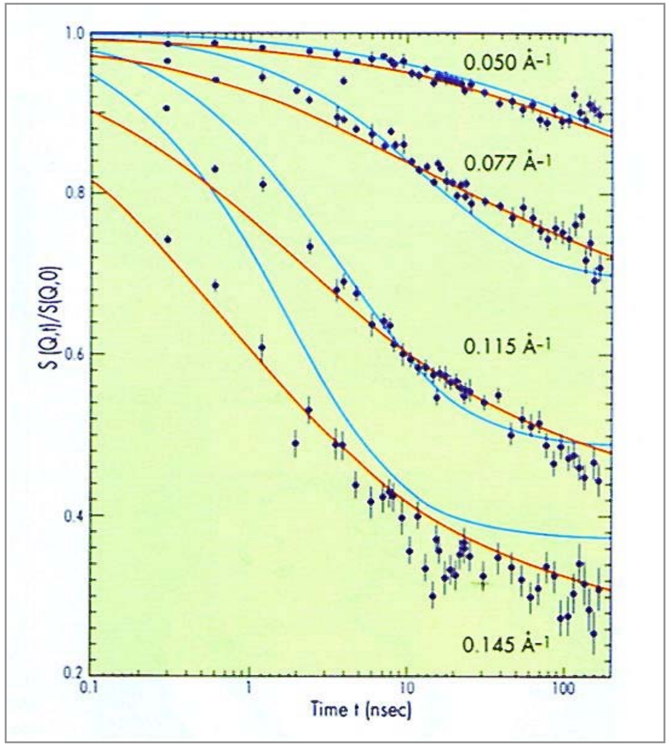
Examples of neutron spin echo studies

Reptation in polyethylene



The dynamics of dense polymeric systems are dominated by entanglement effects which reduce the degrees of freedom of each chain

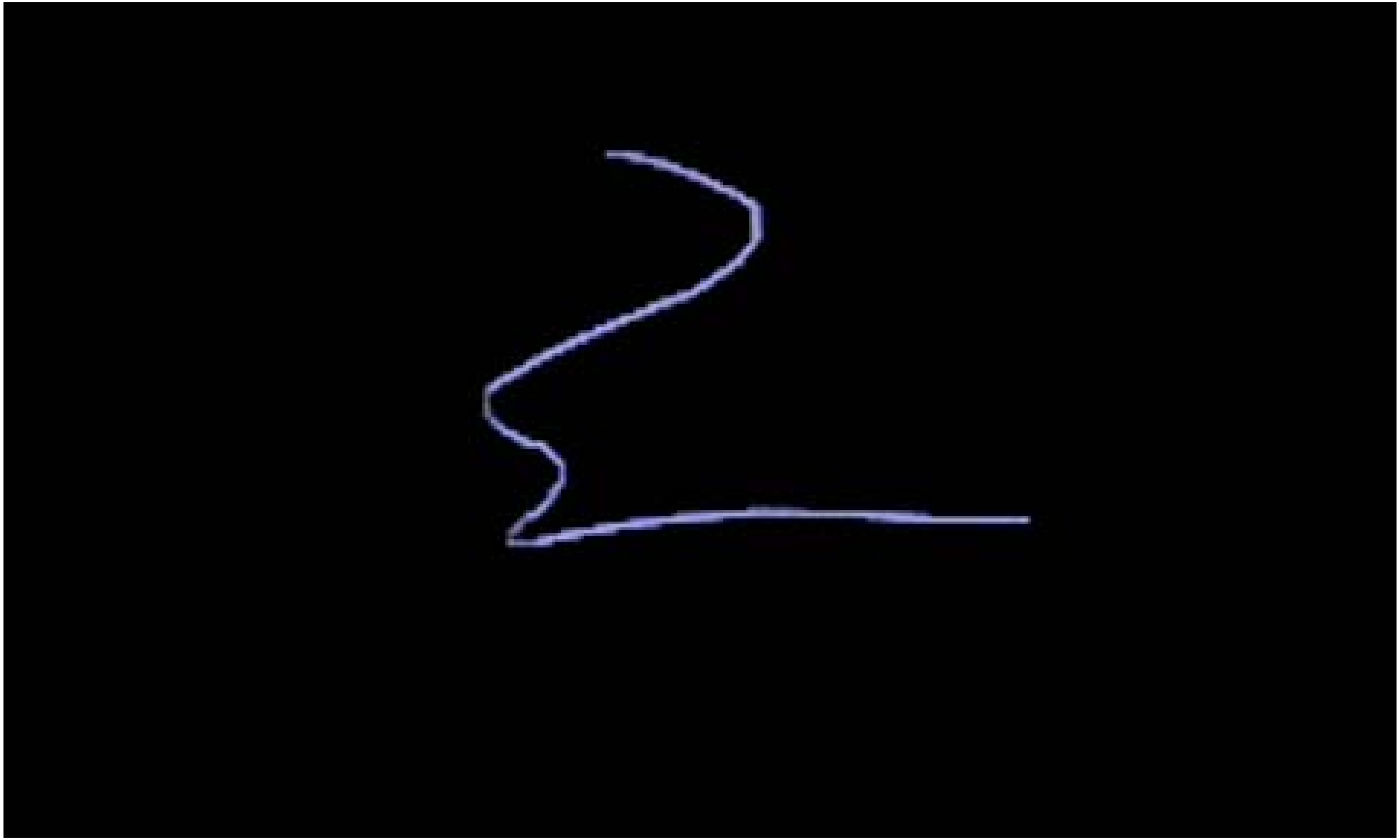
de Gennes formulated the reptation hypothesis in which a chain is confined within a “tube” constraining lateral diffusion - although several other models have also been proposed



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

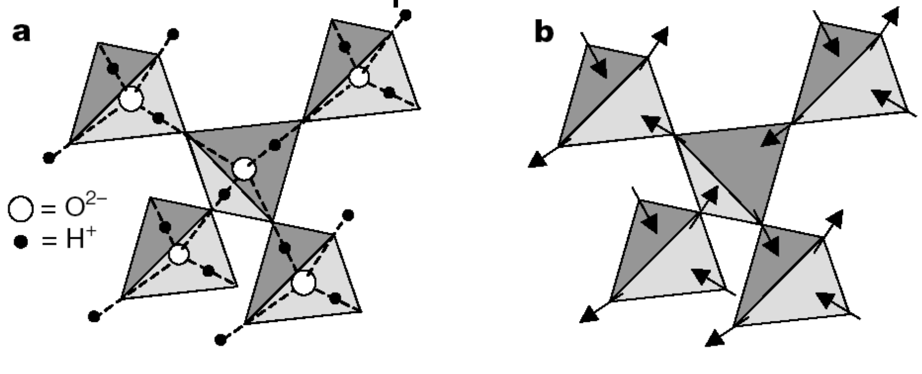
Schleger et al, Phys Rev Lett 81, 124 (1998)

Examples of neutron spin echo studies



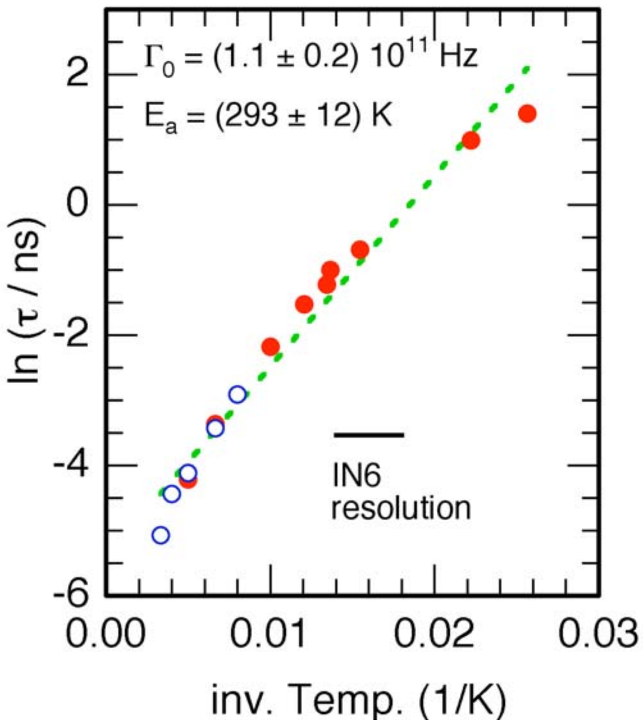
Examples of neutron spin echo studies

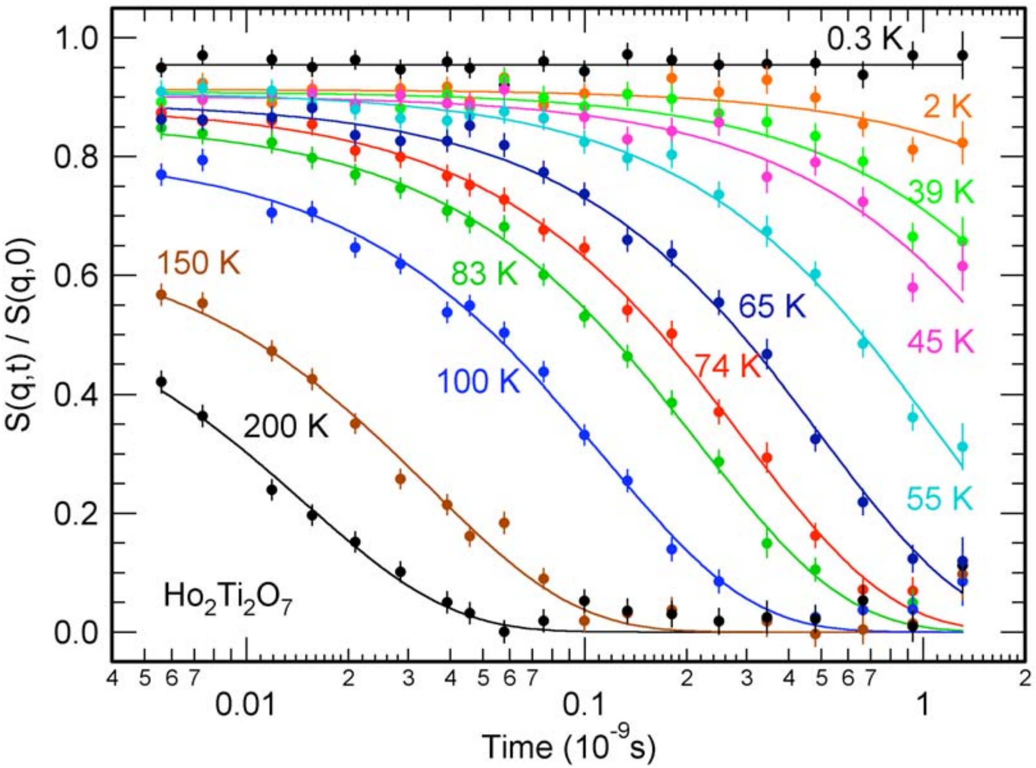
Relaxation in "Spin-Ice"



Disordered magnetic structure reminiscant of displacement vectors in water ice

- Simple Lorentzian relaxation
- surprisingly large activation energy

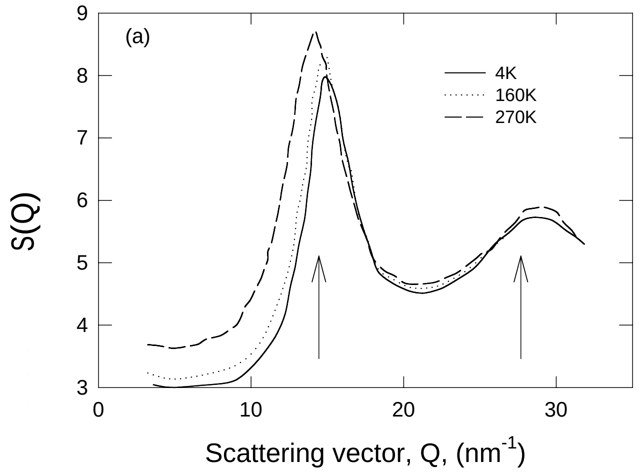




Examples of neutron spin echo studies

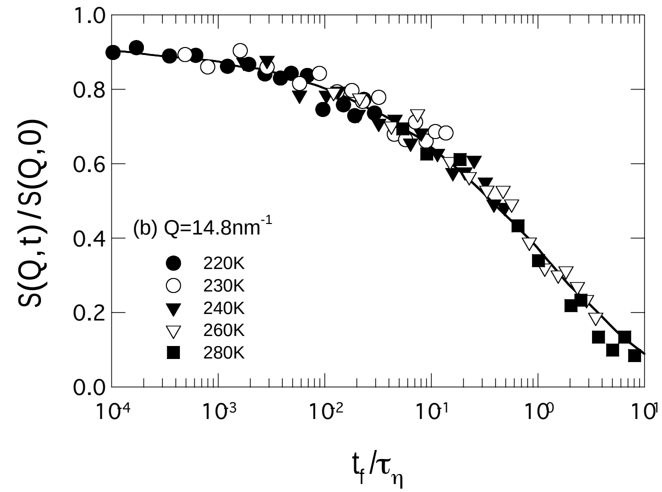
Glassy Dynamics in Polybutadiene

The first peak in the structure factor corresponds to *interchain* correlations (weak Van der Waals forces), the second peak is dominated by *intrachain* correlations (covalent bonding)



Each NSE spectrum was rescaled by the experimentally determined characteristic time, t_h, for bulk viscous relaxation for the corresponding temperature.

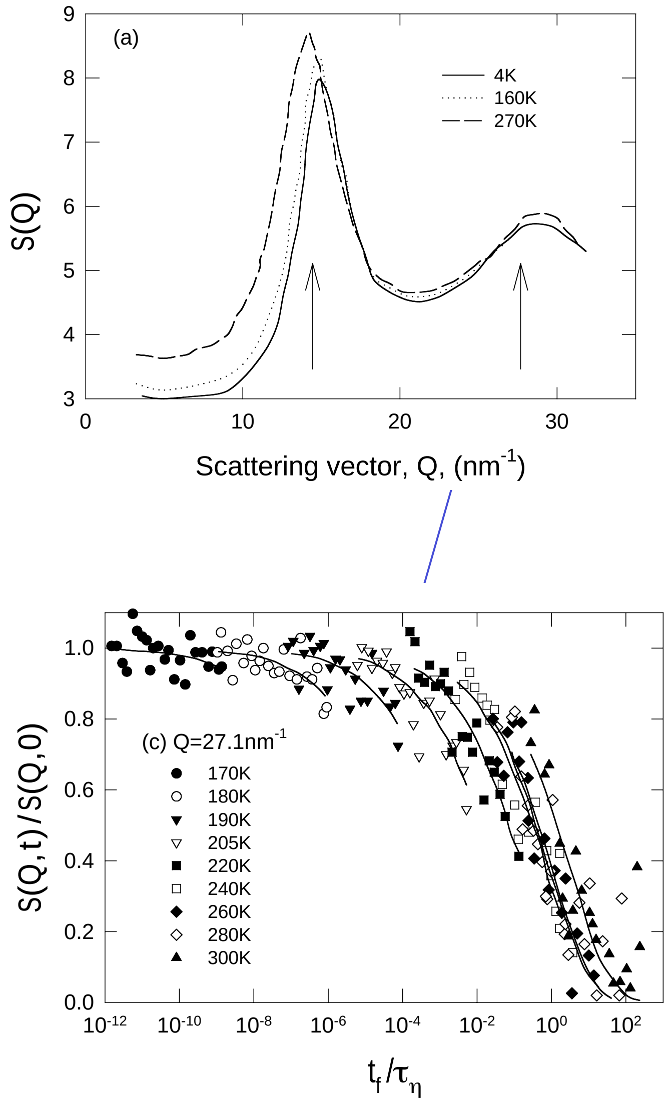
at the first peak the spectra follow a single, stretched exponential (ß=0.4) universal curve, indicating that the interchain dynamics very closely follow the α-relaxational behaviour associated with macroscopic flow of polybutadiene.



Examples of neutron spin echo studies

Glassy Dynamics in Polybutadiene

Those correlation functions measured at the second peak of the structure factor do not rescale. They are characterised by a simple exponential function, with an associated temperature dependent relaxation rate which follows an Arrhenius dependence with the same activation energy as the dielectric β-process in polybutadiene, and which is unaffected by the glass transition.



*A. Arbe et al Phys. Rev. E **54**, 3853 (1996)*

Examples of neutron spin echo studies

Fluctuations in superparamagnetic monodomain Fe nanoparticles

IN11 and IN15 were used to probe the relaxation spectra of fine (20Å) iron particles over the time scale from 0.01ns to 160ns

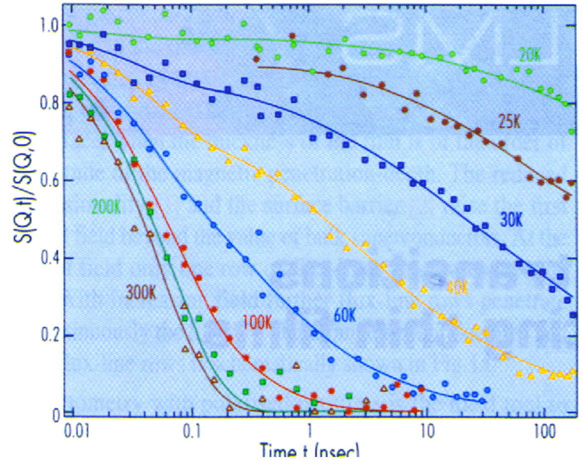
It is found that the particles do not relax according to a simple Arrhenius law with

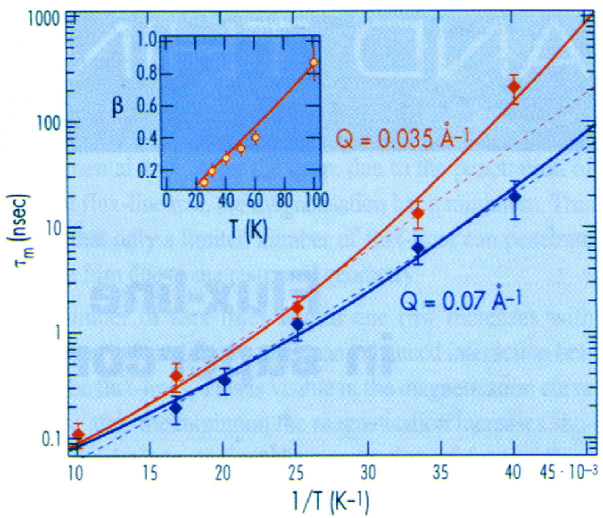
$$\tau_m = \tau_o \exp(-1/\beta) \qquad \beta = k_B T / V_m$$

but instead

$$\beta = T/(k + aT^2)$$

Where the term aT^2 models the effect of a local magnetic interaction
Below 100K two components are evident, related to the transverse and longitudinal fluctuations with respect to the easy axis





*Casalata et al, PRL **82**, 1301 (1999)*

Examples of neutron spin echo studies

Correlations in spin glass systems

Monte Carlo calculations suggest that the spin autocorrelation function in spin glasses should follow the form (*Ogielski, PRB **32,** 7384, (1985)*)

$$\langle s(0)s(t)\rangle \propto t^{-x} \exp(-(t/\tau)^{\beta})$$

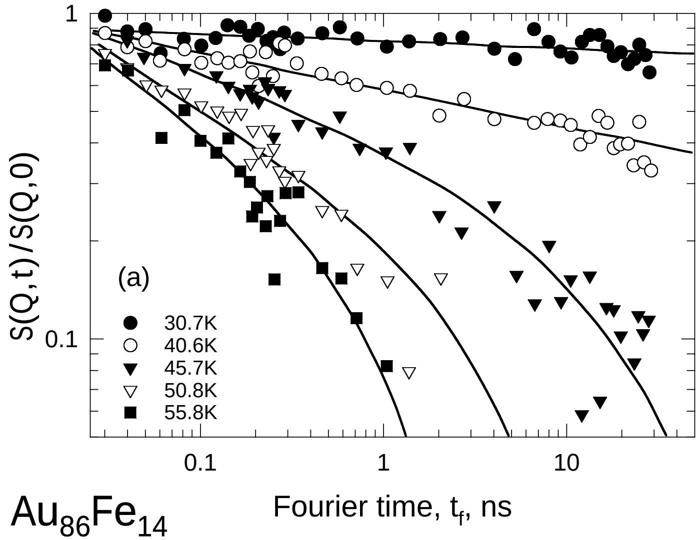
with β approaching 1/3 at the glass transition

Ogielski relates x(T) at the glass temperature to the static and dynamic universal critical exponents,

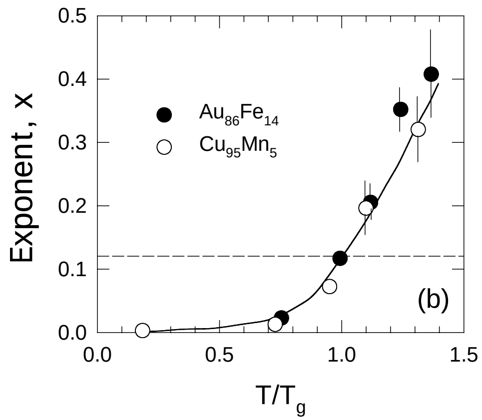
$$x = \frac{(d-2+\eta)}{2z}$$

where d is the dimensionality of the system, h is the static Fisher exponent and z is the dynamic exponent.

NSE experiments support this model
*Pappas et al, Appl. Phys. **A74** , S907 (2002)*



$Au_{86}Fe_{14}$



Examples of neutron spin echo studies

Complex Correlations in spin glasses

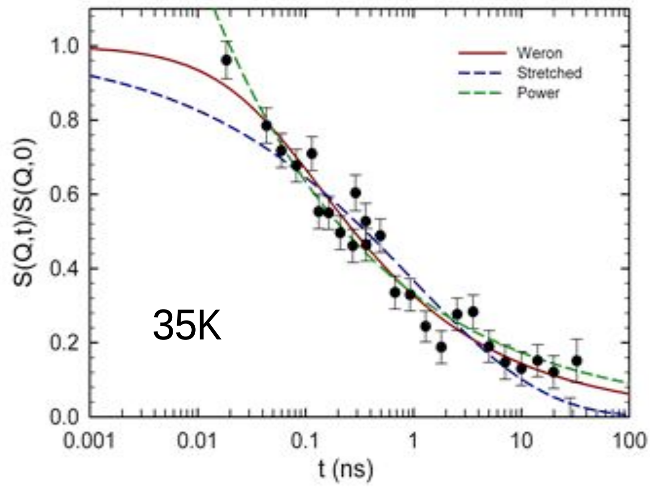
Our recent measurements on the complex spin glass $Co_{50+x}Ga_{50-x}$ show that simple relaxation functions are inadequate

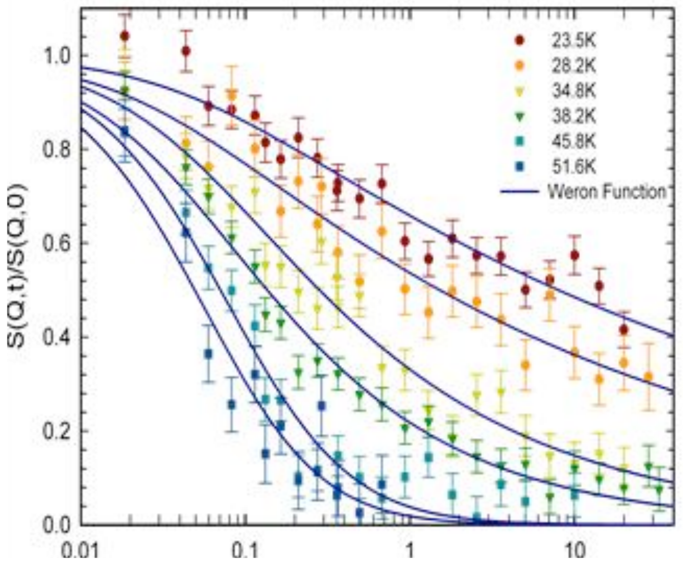
A "universal" relaxation function (*Weron, J Phys C: Condens Matt 3 (1991) 9151)* which embodies both exponential and stretched exponential relaxation as special cases fits the data well:

$$S(t) = S_o[1 + k(t/\tau_0)^{\beta}]^{-1/k}$$

where k is an ''interaction parameter''

For $Co_{50+x}Ga_{50-x}$ β=1, but both τ_o and k are temperature dependent





Examples of neutron spin echo studies

Complex Correlations in spin glasses

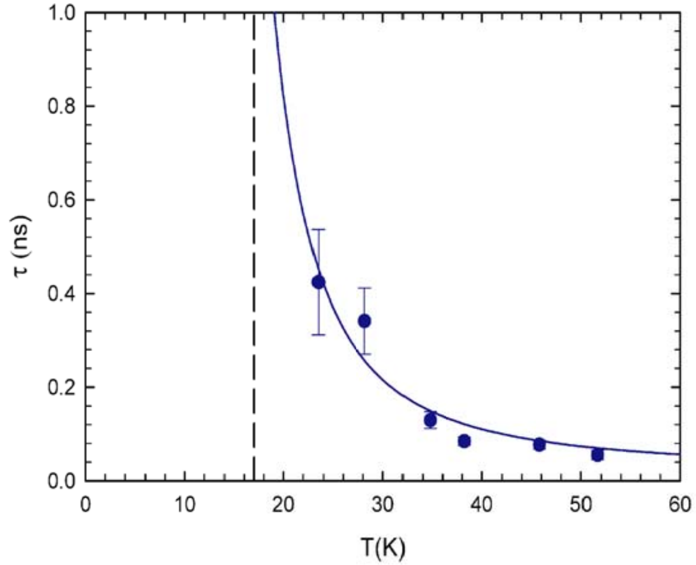
Our recent measurements on the complex spin glass $Co_{50+x}Ga_{50-x}$ show that simple relaxation functions are inadequate

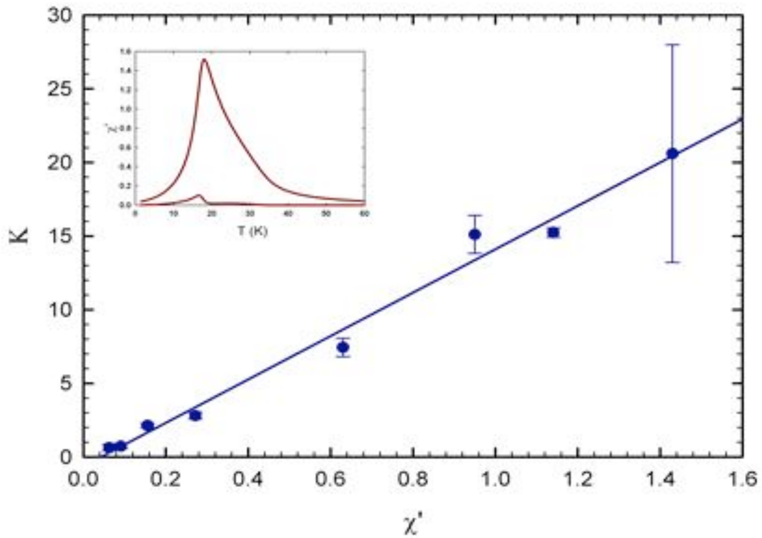
A "universal" relaxation function (*Weron, J Phys C: Condens Matt 3 (1991) 9151)* which embodies both exponential and stretched exponential relaxation as special cases fits the data well:

$$S(t) = S_o[1 + k(t/\tau_0)^\beta]^{-1/k}$$

where k is an ''interaction parameter''

For $Co_{50+x}Ga_{50-x}$ β=1, but both τ_o and k are temperature dependent





Conclusions

Polarised neutron scattering provides fundamental and unique information on the magnetic structures, defects and dynamics of materials

It often allows the unambiguous separation of magnetic and nuclear scattering

The precession of the polarisation of a neutron beam can also be used as an extremely sensitive label of the neutrons' velocity - and therefore provides unequalled precision in quasielastic scattering measurements

The sacrifice of at least half of the neutrons in the process of polarisation is always well justified !!