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Neutron Spin Echo Spectroscopy

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Inelastic neutron scattering is potentially the ultimate tool for the investigation of atomic and magnetic dynamics on the microscopic scale in condensed matter. This is because of the unique feature that both the wavelength and the energy of thermal neutron radiation fall within the range relevant to the dynamics of common solids and liquids *viz.* 1-10 Å and 1-100 meV ≅ 0.25 - 25 THz. Neutron scattering is the only microscopic probe able to provide the whole picture in space *and* time although there are a number of other methods, which yield partial information. For example, X-ray scattering is very powerful in the determination of atomic structures, but since X-ray quanta have energies in the 10 keV range, it is not practical (at least so far) to observe changes on the meV or μeV scale associated with atomic motions. To a very rough approximation, the energy changes of the scattered radiation can be looked upon as Doppler shifts caused by the motions of the scattering atoms. In contrast, with light scattering one can observe easily any energy change that might occur, but the basic wavelength of several 1000 Å restricts the space domain studied to one of similar size, *i.e.* to practically macroscopic regions. Or, to take an example at the other extreme, nuclear magnetic resonance (NMR) allows us to study local fluctuations at nuclear sites at an adequate rate, but does not allow us to make direct observation of correlations between neighbouring atomic sites.

Further very useful features of neutron radiation are its interaction with the magnetic moments in the sample via the neutron spin and its large penetration into many materials. This latter is made use of in industrial applications like neutron radiography and testing for phase homogeneity in welds by neutron diffraction.

Inevitably, such outstanding advantages cannot occur in real life without drawbacks! For neutrons there are two: neutron sources are expensive and even the best available beam fluxes are small in absolute terms (*i.e.* compared with the number of atoms in a sample). Thus, while in an NMR experiment we typically have 10^{20} nuclear spins to act on, or a laser can provide 10^{20} light quanta within reasonable time, the highest flux neutron scattering instruments barely provide 10^{13} neutrons over a day. Consequently only relatively big samples and/or strong scattering effects can be studied with neutron scattering and the statistical accuracy of the results is always limited. As a rule of thumb, neutron scattering investigation, giving a detailed, model-independent space-time picture, is indispensable if we are not absolutely sure of the nature of a particular phenomenon, whereas systematic studies on a large number of similar systems, including small samples, is better done by methods mobilizing a larger number of quanta.

For a (neutron) experiment to be productive it is not sufficient to have the right kind of probe, one has also to be able to extract enough information. This is the problem of experimental resolution (which is, *e.g.* the essential reason why we cannot use X-ray scattering for the study of, say, phonons). Conventional neutron scattering methods allow us to determine the energy changes of the neutron radiation in the scattering process with a typical best resolution of 1%. This limits the range of frequencies which can be studied to about 10 GHz - 20 THz. (Epithermal neutron beams which are becoming available with proper intensities at the so-called "spallation sources", extend this range to maybe 500 THz.)

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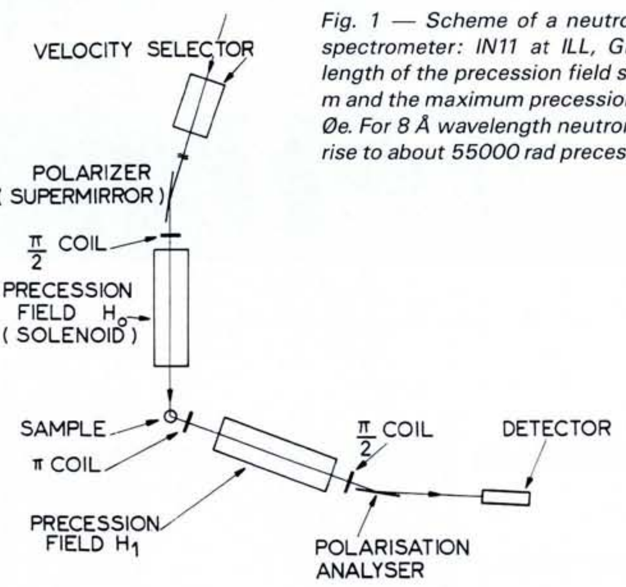

Fig. 1 — Scheme of a neutron spin echo spectrometer: IN11 at ILL, Grenoble. The length of the precession field solenoids is 2 m and the maximum precession field is 750 Øe. For 8 Å wavelength neutrons, this gives rise to about 55000 rad precession.

In order to study slower phenomena, the energy resolution had to be improved well beyond the 1% level. The main difficulty in doing this was not really technical but fundamental: the problem of low beam intensity. The production of a highly monochromatic beam means selecting out a tiny portion from the originally Maxwellian neutron energy distribution. Since low beam intensities are the main limitation in neutron scattering from the outset, the direct path to higher resolution is basically limited by the flux alone. The so-called "backscattering" method, in which 0.01 - 0.1% monochromatic beams are used, follows this conventional path. The price one has to pay for the gain in energy (time) resolution (30-100 MHz lower limit) is that in order to recover some of the lost intensity, the momentum (space) resolution has to be relaxed. Logically, the method has proved to be extremely successful, primarily in the study of non-dispersive (wavenumber independent) phenomena, such as the tunnelling motion of protons and other radicals between various local equilibrium positions within the elementary cell of a crystal.

To overcome the fundamental intensity barrier to higher resolution a radically new approach was needed: the resolution had to be decoupled from the monochromatisation. This apparent contradiction is solved in the neutron spin echo (NSE) method [1]. The basic idea is that instead of monochromatizing the beam impinging on the sample, we make each neutron remember its initial velocity. In order to do this, we use the natural individual clock each neutron possesses: its spin. In effect, the Larmor spin precession frequency ω_L in an external magnetic field H conveniently lends itself to its use as a time base:

$$\omega_L = \gamma_L H \tag{1}$$

where the constant γ_L = 2.916 kHz/Oe.

If a neutron with a velocity v crosses a magnetic field of strength H and length ℓ, the total Larmor precession angle φ will be a measure of its velocity:

$$\varphi = \gamma_L H\ell/v \tag{2}$$

In writing down this equation we implicitly assume that the neutron can be considered as a classical particle, *i.e.* it is pointlike and thus has a well defined trajectory and velocity, while its spin corresponds to a classical vector and performs precessions in a field in the classical mechanical sense, like a top. This is certainly at variance with the "popular" picture, of the spin of a spin 1/2 particle being able to occupy only discrete "up" and "down" states. Such a picture is, of course, an incorrect over-simplification, but it was the reason nevertheless why for a long time, little effort was made to explore the full vectorial character of spin polarization in particle beam experiments. Rigorous quantum mechanical analysis shows [3], that in magnetic fields where the gradients are not too strong (in the absence of the Stern-Gerlach quantum effect) the neutron spin motion can be treated classically, *i.e.* by considering the Larmor precessions governed by the classical equation:

$$d\mathbf{S}/dt = \gamma_L\,[\mathbf{S} \times \mathbf{H}]$$

where **S** is the spin vector.

In a neutron spin echo spectrometer (Fig. 1) a first "precession" field is used to allow each neutron to label its own initial velocity v_o by performing a precession of Φ_o, and after scattering on the sample a second precession field is used to measure the final velocity v_1 via the precession angle Φ_1. The comparison between φ_o and φ_1 is made by making the two precessions to occur (effectively) in the opposite sense, resulting in a total precession angle (if $H_o = H_1 = H$, *cf.* Fig. 1) of:

$$\begin{aligned}\varphi &= \varphi_o - \varphi_1 \\ &= \gamma_L H\ell(1/v_o - 1/v_1) \cong \gamma_L H\ell v_o^{-2}\delta v\end{aligned}$$

where $\delta v = v_1 - v_o$ and we assume $\delta v << v_o$. Remembering that the neutron energy is ½ mv^2, we see that φ is just a measure of the neutron energy change in the scattering process, $\hbar\omega$, which is what interests us:

$$\Phi = (\gamma_L H\ell/mv_o^3)\,\hbar\omega = t\omega \tag{3}$$

if v_o is rather well defined (in practice beams with about ± 10% variation of v_o are used) the proportionality constant $t = \gamma_L H\ell/mv_o^3$ is also.

The important thing is that the observable quantity φ is directly related to the change of the neutron energy, and we do not have to proceed by the determination of the initial and final neutron energies in two separate steps. Therefore $\hbar\omega$ can be determined independently of the scatter of the initial and final neutron energies, and, for the first time, the energy resolution becomes independent of the monochromatization of the beam. This means that we have managed to side-step the normal reciprocal relation between resolution and beam intensity.

The fundamental practical point in NSE is how to produce and analyse Larmor precessions. This can be done surprisingly easily with the help of a simple flat coil (Fig. 2), whose introduction in 1972 at the Central Research Institute for Physics in Budapest was actually the starting point of NSE [1]). If neutrons enter the coil with spin $\vec{S}$ parallel to the external field $\vec{H}$, inside the coil they will start to process around the field $\vec{H}'$ which is the sum of the external field $\vec{H}$ and the field $\vec{H}_c$ produced by the coil. If, as shown, the neutrons leave the coil after half a precession around $\vec{H}'$ which

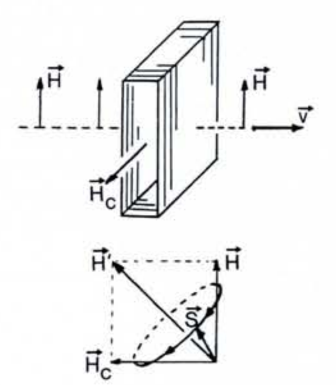

Fig. 2 — The key element of NSE spectroscopy: the spin flip coil (typically activated by 1-3 A DC current) and an example of spin turn by Larmor precession inside the coil.

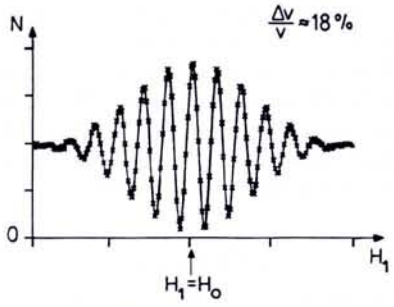

Fig. 3 — NSE signal showing the echo effect as measured with an 18% FWHM velocity-selected beam. The dephasing and decrease of the precessing polarization on both sides of the $H_o = H_1$ echo condition reflect this 18% spread of neutron velocities.

is bisecting the directions of $\vec{H}$ and $\vec{H}_c$, the effect of the coil is to turn $\vec{S}$ from the direction of $\vec{H}$ into that of $\vec{H}_c$. This is how the Larmor precessions can be initiated by turning through 90° the neutron spins, originally parallel to the field (Fig. 2). The inverse procedure, turning a component of the precessing polarisation (i.e. perpendicular to the field) into the field direction and using a conventional spin analyser, allows us to observe Larmor precessions. It turns out that the fields required to achieve such spin turns are rather modest: *e.g.* with 1000 m/s (~ 4 Å wavelength) neutrons and a 1 cm thick coil, H and H_c have to be of 12.1 Øe in order to achieve a 90° spin turn (*cf* eq. (2)). Moreover, neutron radiation will traverse the single layer of Al wire windings that make up the coil without appreciable intensity loss.

The analysis of the precessing polarisation in the beam does not mean in practice the direct measurement of the angle φ, but the observation of one component (say x) of the polarization P. If φ is measured with respect to the x axis, we have

$$P_x = \langle \cos \varphi \rangle$$

where the bracket stands for the average over all neutrons in the beam. Thus, in view of eq. (3), in a NSE experiment we determine

$$P_{NSE} = \langle \cos \varphi \rangle \cong \int S(\omega) \cos (t\omega) d\omega \quad (4)$$

where $S(\omega)$ is the probability distribution of $\hbar\omega$ neutron energy changes in the scattering. It is known from the fundamentals of neutron scattering that $S(\omega)$ is just the Fourier transform of the correlation function $S(t)$ describing the atomic motions in real time. Since eq. (4) implies a backward Fourier transformation, it is $S(t)$ that we measure directly. Thus *e.g.* in a simple relaxation decay process we have

$$P_{NSE} = S(t) = \exp(-\Gamma t)$$

where Γ is the relaxation rate. The direct exploration of the time domain is sometimes a very useful additional feature of NSE. Note that in an NSE experiment P_{NSE} is determined as a function of t, the latter being varied most simply by changing the precession field H_1 (*cf* eq. (3)).

Evidently the name given to the method has little to do with the above considerations, rather is it justified technically. Fig. 3 shows what we actually observe measuring the x component of the precessing polarization after the second precession field H_1 as a function of that field [1]. As we have seen, at $H_o = H_1$, φ will be the same, *i.e.* zero, for all neutrons with $v_1 = v_o$. This is not the case when $H_o \neq H_1$, and the distribution of v_o (or v_1) introduces a distribution of precession angles φ which ultimately makes P_x average to zero. Therefore the "echo signal" in Fig. 3 can only be observed around $H_o = H_1$ (if $v_o \cong v_1$). It is interesting to note that this echo signal is just the image of how the neutron waves in the beam would look if we described them by quantum mechanical (coherent) wave-packets as opposed to a distribution of classical velocities v. The two approaches lead to exactly the same results, of course [3].

Since the IN11 NSE spectrometer (built by the author in collaboration with Paul Dagleish and John Hayter) went into operation in 1978 at the ILL, many successful and significant experiments have been performed on the dynamics of polymers and biopolymers in solutions, on atomic and molecular diffusion in liquids and solids, on critical fluctuations in structural and magnetic phase transitions, on the nature of the spin glass transition, on the decay of elementary excitations in superfluid helium, on soliton dynamics, etc. It is not our purpose here to consider in depth any of these results (an early summary can be found in Ref. 2). To illustrate the performance of the method only we shall look at just two examples instead.

Fig. 4 shows the relaxation rate Γ of correlations in a solution of pig immunoglobulin G (IgG) molecules as a function of the wavenumber q [4]. We expect Γ to reflect diffusive motion: in time t the molecules diffuse away on the average by a distance $r = \sqrt{(Dt)}$ (where D is the diffusion constant) and thus the lifetime of $r = 1/q$ wavelength correlations is

$$\Gamma^{-1} = r^2/D \text{ or } \Gamma = Dq^2,$$

which is the well known diffusion equation. The results in the figure show this relation in a q and Γ domain, in practice only accessible by NSE. The diffusion constant D corresponding to the straight line in the figure was found to be 40% higher than that relevant to $q = 0$ as

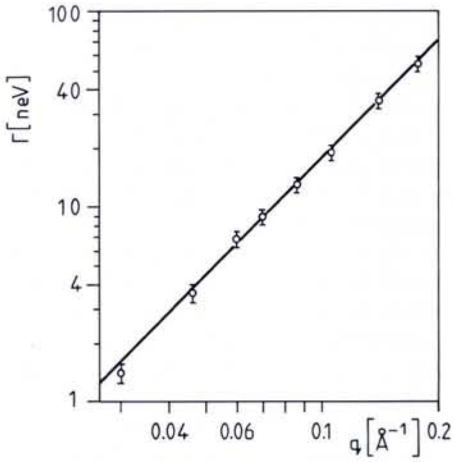

Fig. 4 — The relaxation rate measured in pig immunoglobulin G-D_2O solution of 7.33 wt.% concentration [4]. The line corresponds to the Dq^2 law with a diffusion constant $D = 2.74 \times 10^{-7}$ cm^{2}s^{-1}.

determined by sedimentation. Observing that the q range of the NSE experiment corresponds to the size of the constituant subunits of the IgG molecule, this difference can be interpreted as evidence for intramolecular motion: on a length scale smaller than the size of the molecule, the subunits move faster than the molecule as a whole. On the purely technical side, on the other hand, note that the neutron energy changes (corresponding to the Γ values in the figure) are on the neV (10^{-9} eV) scale compared with the incoming neutron energies that

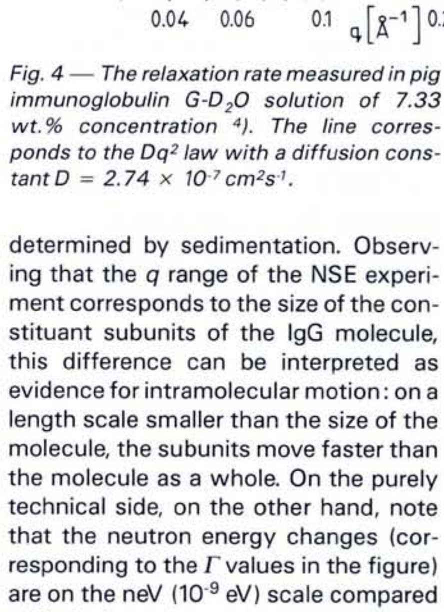

Fig. 5 — Decay rate of the roton excitation in superfluid ^4He at various temperatures [5]. The NSE results (open circles) are compared with indirect light scattering data (dots) and conventional neutron scattering results (other symbols) resolution limited to line widths above 0.5 K. The line represents the theoretical prediction for temperature well below the λ point (2.17 K).

are around 1.2 × 10^{-3} eV with a scatter of ± 10%. This is a fine illustration of the independence of energy resolution and beam monochromatization, which is the essence of NSE. These results represent the present absolute resolution limits in inelastic neutron scattering (10^{-9} eV corresponds to 0.25 MHz).

The other example (Fig. 5) shows a rather more elaborate use of NSE: the measurement of the lifetime of roton excitation in superfluid ^{4}He [5]. In this case the deviation of the neutron energy change from a well defined value,

$\hbar\omega_o$ = 8.61 K = 0.742 meV

(the minimum roton energy) is observed by the NSE difference method. This is done by using a special H_o/H_1 precession field ratio. NSE in this case provides a resolution nearly two orders of magnitude better than classical neutron scattering methods. The existence of light scattering results for comparison (full circles) is also quite exceptional: it is the appearance of two-roton bound states with total $q \cong 0$ that makes the high wave number (q = 1.92 Å^{-1}) roton excitation accessible to investigation.

These examples taken from amongst many demonstrate that by the application of a new approach, the domain of applicability of inelastic neutron scattering, a fundamental tool in condensed matter research, could be substantially extended. It is worth noting that the new method is based on ideas and techniques which were originally developed at one of the smallest neutron research facilities in Europe, namely that in Budapest, and which were then completed and fully exploited at the most powerful facility in Grenoble. This is certainly a rather fortunate, but nevertheless significant example of fruitful collaboration in Europe.

REFERENCES

1. Mezei F., *Z. Physik* **255** (1972) 146.
2. *Neutron Spin Echo*, ed. F. Mezei (Springer Verlag, Heidelberg) 1980.
3. See Mezei F., *J. de Physique* **45** (1984) C3-223, and references therein.
4. Alpert Y., Cser L., Farago B., Franek F., Mezei F. and Ostanevich Y.M., *Symposium on Neutron Scattering*, Berlin (West), 6-8 August 1984.
5. Mezei F., *Phys. Rev. Lett.* **44** (1980) 1602.

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