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Motional Effects in Nuclear Magnetic Resonance

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Résumé.

On donne un résumé des effets de mouvements quelconques en résonance magnétique nucléaire en introduction aux exposés sur la résonance magnétique nucléaire présentés à ce colloque.

I should like to try to give in this lecture an introduction to some of the papers which are to follow, to mention a few effects in this area about which there are no papers offered at this conference to try to give a balanced picture of the present situation, and finally to present a few results which have been obtained recently in my laboratory.

The effects of the motions of the magnetic nuclei in materials on the magnetic resonance signals are very simple to understand in their general effect, but the ramifications are various and important. The effects may be illustrated by considering the interaction of two magnetic nuclei of moment μ separated by a distance r where r makes an angle θ with the main field H_0 . The static field at one nucleus due to the other, in the direction of H_0 is $\pm \mu r^{-3} (3 \cos^2 \theta - 1)$ for a nucleus of spin $\frac{1}{2}$ (Fig. 1) and hence the line width (δH) is $2\mu r^{-3} (3 \cos^2 \theta - 1)$. This is the origin of the ubiquitous function $(3 \cos^2 \theta - 1)$. Allowing for the fluctuating field the effective field is $\pm (3/2) \mu r^{-3} (3 \cos^2 \theta - 1)$. If, however, the nuclei move, r and θ are time dependent and it may be necessary to take some sort of time average of this local field. For example, if the θ variation is isotropic $\cos^2 \theta = \frac{1}{3}$, the local field is zero and we have complete motional line narrowing in the limiting case. However, in many cases the motion is restricted. For example, if θ varies but r is held constant $\cos^2 \theta = \frac{1}{2}$ and the line width is $\frac{3}{2} \mu r^{-3}$. Generally speaking, more and more motion gives more and more narrowing and since the rate of motion and the extent

of motion generally increase with temperature, we expect to find successive falls in line width with increasing temperature (Fig. 2). However these falls are not always well resolved since this requires a difference in rate of motion by a factor of at least twenty at a given temperature. In many cases there are several distinct groups of nuclei which are roughly independent magnetically but which may for instance be in the same molecule. In this case a line narrowing may be due to motion of a part of a molecule and then due to motion of a molecule as a whole. Thus the causes of line narrowing may be complex, but in the cases where they can be interpreted they give a rather detailed account of the movement of the molecule. In the most favourable case one may expect to be able to say what is moving, how it is moving and the rate at which it moves. The nuclei in a given part of a molecule indicate the motion of that part. However, the separation of the nuclei into groups is at best an approximation and if the interaction within a group is motionally reduced then the interaction between groups may increase in importance. For example, if we consider the pair of nuclei above in which the interaction within the pairs is substantially motionally narrowed by isotropic variation of θ there is still a magnetic field in the vicinity due to these nuclei because, in spite of the motion, the nuclei are still aligned by H_0 and at a point (R, ψ) outside the pair the field is still of order $\mu R^{-3} (3 \cos^2 \psi - 1)$. Thus nuclei at this point will show a line broadening of this order, which however is smaller than that of the pair on each other when static, in the ratio $(r/R)^3$ which may be 1/10 or less. Thus the line is not entirely narrowed by motion "sur place" and further narrowing requires variation of R and/or ψ , i.e. self diffusion either of molecules or atoms.

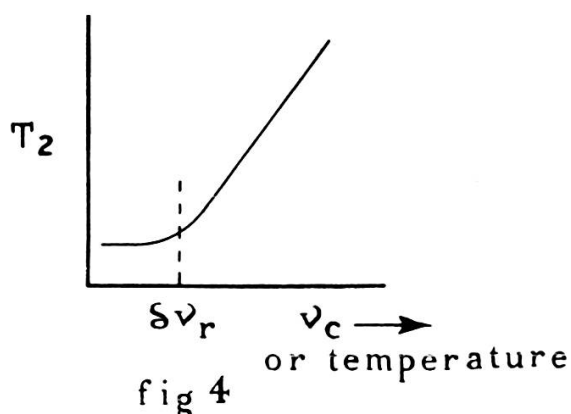
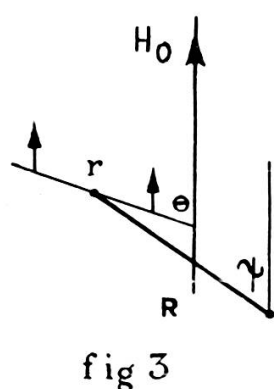
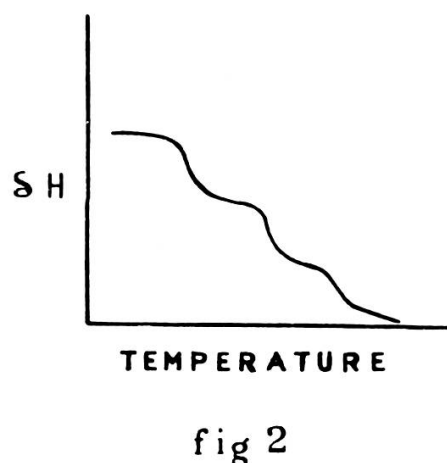
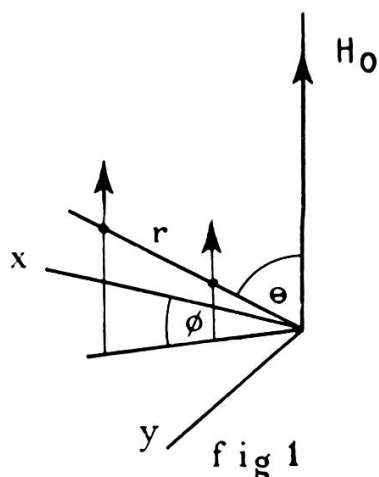
We now ask, how fast must the motion be to cause narrowing? This is readily seen by considering the line breadth as an uncertainty broadening of the energy levels. The line width δH is readily converted to a frequency by use of the resonance relation for the nucleus $2\pi\nu = \gamma H$. Thus the line width in frequency is $\delta\nu = (\gamma/2\pi) \delta H$ and the energy width is $\delta E = h\delta\nu = \gamma\hbar\delta H$ and so since $\delta E\delta t \simeq \hbar$ the lifetime of a state is $\delta t \simeq \hbar/\delta E = 1/\gamma \delta H$ and this lifetime is essentially the quantity called T_2 in magnetic resonance. It controls the decay of transverse magnetisation and the line width. In considering the effect of motion it is therefore important to consider what happens within the time T_2 , since after T_2 the nucleus begins again, so to speak, having made a transition to a new level. Thus if τ_c is a characteristic time for the motion i.e. the time in which "appreciable" motion

occurs, then the averaging effect becomes important when $\tau_c \lesssim T_2$. It is convenient to work in terms of frequency rather than time by writing $2\pi\nu_c \tau_c = 1$ so that for the onset of narrowing $\nu_c \simeq 1/2\pi T_2 = \gamma\delta H/2\pi = \delta\nu$ i.e. the motional frequency must be comparable with the line width expressed in frequency. For a proton line width of 10 gauss this frequency is about 40 kc/s so that nuclear resonance line width "transitions" are produced by comparatively low rates of motion. Further, as the line becomes narrower (T_2 longer) the rate of motion which is effective becomes smaller. Thus a line width is initially narrowed by the fastest motion (if this modifies the nuclear interaction) but once narrowing by this motion has set in the next fastest becomes most effective and so on. We shall see the effect more closely when we come to consider distributions of relaxation frequencies.

Having introduced T_2 it is now convenient to work in terms of it and we see that T_2 increases because of the motion (Fig. 4). It is readily shown on the most general grounds that $T_2 \simeq (2\pi T_{2r})^2 \nu_c$ when the line is well narrowed by one motion characterised by ν_c . Evidently in the general case there are several successive rises in T_2 as various motions become effective corresponding to figure 2 although in practice these may not be well resolved.

We must now look at another observable, the spin-lattice relaxation time, T_1 , which controls the time variation of longitudinal magnetisation. Since this involves an energy exchange of $h\nu_{\text{res}}$ or $2h\nu_{\text{res}}$ with the lattice, the importance of motion for T_1 is the extent to which the lattice can exchange quanta of these magnitudes or, looked at another way, produce alternating magnetic fields at frequencies ν_{res} and $2\nu_{\text{res}}$, with suitable polarisation. Thus the process is most probable, i.e. T_1 is shortest, when the motion has a characteristic frequency of ν_{res} or $2\nu_{\text{res}}$ and is comparatively ineffective outside this range. Thus T_1 has a variation as shown in figure 5. However it is readily shown, again on quite general arguments, that when the motion is effective $T_1 = T_2$ and so finally we have the behaviour shown in figure 6. This behaviour is made more explicit by the theories of Bloembergen Purcell and Pound [1], Kubo and Tomita [2] and others [3, 4, 5, 6, 7]. The early B.P.P. [1] measurements on glycerol are often quoted as showing this behaviour but we do not use them because we believe that they are in error [8]. Many examples of this general behaviour, or at least parts of it in any particular case, are known, but we give one in figure 7, which we have recently obtained for iso-butyl bromide which shows a number of the effects which we have mentioned [9].

It has been found necessary to modify the B.P.P. theory, apart from that due to Kubo and Tomita, in some rather reasonable ways and with these corrections it forms a remarkably good way of interpreting the motional effects in NMR and for the deductions of frequencies of motion.



For liquid iso-butyl bromide a preliminary analysis shows quite a good correlation with dielectric measurements of critical frequency of absorption, a closely related parameter (see figures of reference 9). This sort of comparison was already used in the BPP paper [1]. The discrepancies can be removed by the assumption of a distribution of correlation frequencies of two types, one a discrete two line spectrum and the other a continuous distribution (slides shown at the conference, see ref. 9). The first is required to account for the fact that one methyl group in iso-butyl bromide is freer to reorient than the other and the second to allow for the fact that the molecular motion at low temperatures corresponds to a distribution of correlation frequencies as indicated by the dielectric measurements. The

final result is shown in figure 8, which shows a remarkable correlation of nuclear resonance and dielectric measurements which, it should be emphasised, have been obtained virtually independently. Even the difference between ν_c (NMR) and ν_c (dielectric) by a factor of three predicted by the BPP theory is quite well obeyed. In particular we note that the effect of a distribution of correlation frequencies is to make activation energies deduced from the line width transition curves as a function of temperature quite meaningless in many cases. This is because a distribution of correlation frequencies usually causes a slower variation of the nuclear resonance parameters T_1 and T_2 with temperature. Thus the minimum of T_1 is less sharp than it "should" be (examples shown in lecture from ref. 9). There is one case [10] of a T_1 minimum that is "too sharp" but no doubt some peculiar thermal activation or possibly cooperative process is operative here.

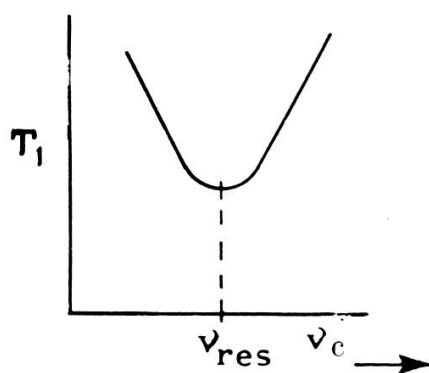


fig 5

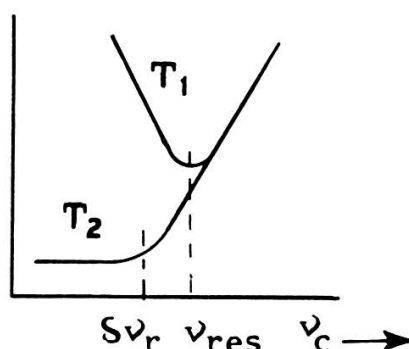


fig 6

Another striking case of multiplicity of motion which will be presented at this conference [11] is that of polyisobutylene where two connected motions are effective, the one which is weakest (in NMR) being this time the slower one (see ref. 11 for figures). This is a case where at a certain temperature (50° C) T_1 is controlled almost entirely by one motion and T_2 almost entirely by the other and so the ratio (T_1/T_2) at the minimum of T_1 is actually 73 instead of 2.25 as for the BPP theory.

NMR has on occasion revealed unexpected molecular motion [12]. A case in which the nuclear resonance measurements reflect the motion of one part of a molecule and dielectric measurements that of another is that of the liquid primary alcohols which will be discussed today [13]. This is a case in which the nuclear magnetic resonance and dielectric measurements give quite different information and so complement each other nicely.

Self diffusion in metals leads to line narrowing [14, 15] and even in some molecular crystals a distinct effect is possible [16]. The diffusion rate (Δ) required is only of order 10^{-11} $\text{cm}^2 \text{sec}^{-1}$ which is very small (Δ for water at 25°C is 2×10^{-5} $\text{cm}^2 \text{sec}^{-1}$).

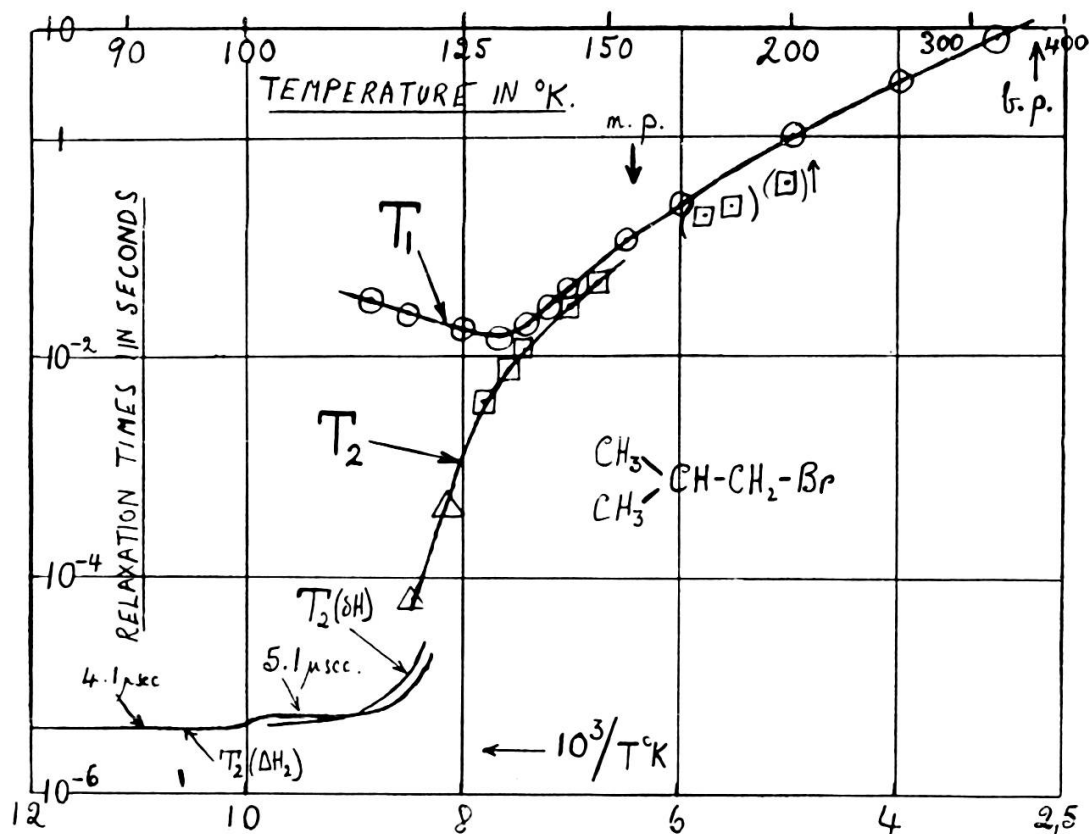


Fig. 7.

In systems such as hydrogen in metals and alloys the nuclear resonance methods reflect the motion of the hydrogen and the nature of the diffusion process. Results of considerable interest in this field have been obtained by Torrey [17] and more recent results on alloys will be discussed today [18]. In Torrey's measurements of the T_1 of protons in $\text{Ti H}_{1.77}$ there is an example of a distinct double minimum which is not readily explained [17].

When the direct dipole-dipole interaction have been well averaged out, as in many mobile liquids, other effects appear which are well known in high resolution nuclear magnetic resonance mostly substantially motionally independent. However, since most of the effects are molecular, time variation of molecular properties may now become directly measurable. Thus if a molecule can exist in more than one form the shielding of a

magnetic nucleus, σ , may differ for the two forms, by say $\Delta\sigma$ and so the two forms give two lines with separation $\Delta\sigma H_0$ gauss. However, if the interchange between the forms is rapid enough the nucleus sees the average field and so we find only one line. Rapid enough means naturally that the interchange frequency is greater than $(\gamma/2\pi) \Delta\sigma H_0$. Since $\Delta\sigma H_0$ is often

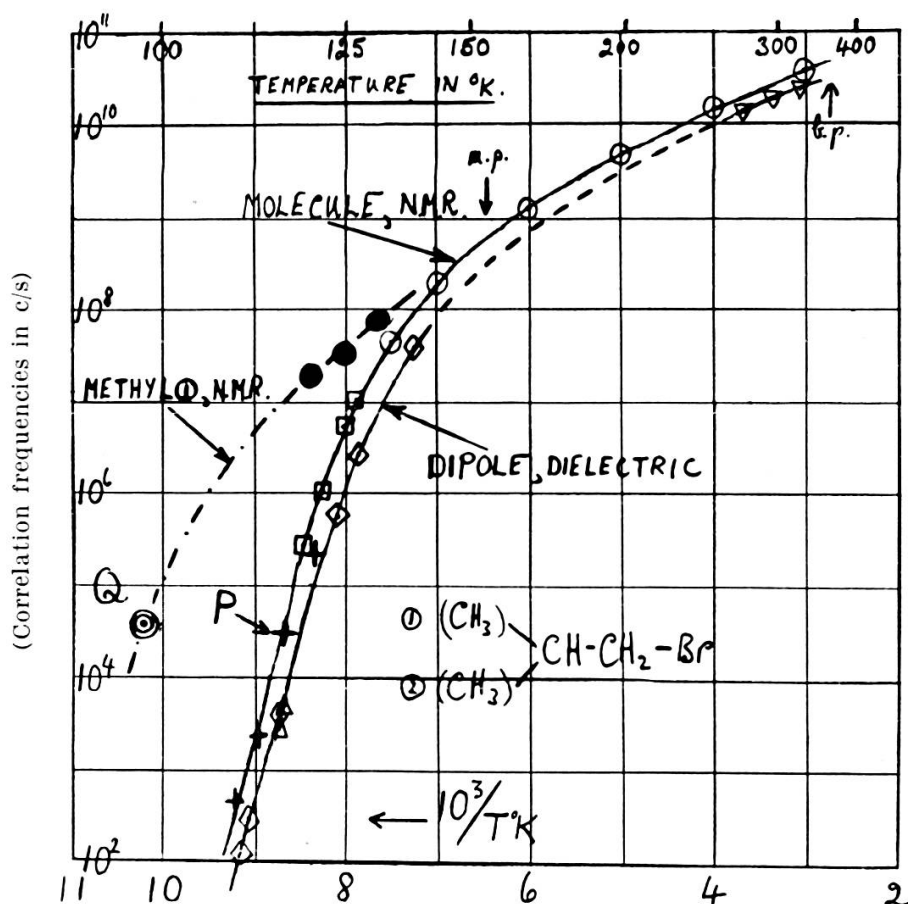


Fig. 8.

rather a small field, say 5 m.gauss the critical frequency is rather low (20 c/s for protons say) and so the value of the method is restricted. However clear examples are known [19]. The fact that the motion occurs, although one cannot measure its rate may follow from the form of the spectrum [20, 21, 22].

Again, a nucleus may exchange from one molecule to another and hence see a different local field. Thus if the local fields differ by δH and if the rate of exchange is greater than $(\gamma/2\pi) \cdot \delta H$ we shall see a single line rather than a double one. Indeed, if the proportion of time spent at the second

site is α , we shall see a single line at $(1 - \alpha) \delta H$ from the first of the original ones. Thus water shows a single line whereas the forms OH_3^+ , OH^- and H_2O exist which must have very different proton shielding. Indirect spin-spin coupling is averaged out in a rather similar way since the phases of processional nuclear motion in different molecules is not related. This occurs in the well known example of the hydroxyl proton in ethyl alcohol [23] where the hyperfine structure is averaged out unless the exchange is suppressed to a rate lower than the splitting frequency. Proton exchange is of course rather common and the nuclear resonance measurements are in accord with the commonly accepted understanding of these exchange processes. Another example is that of ammonia containing a trace of moisture [24], presumably due to exchange via ammonium ions.

Another motional effect is the relaxation caused by anisotropy of the magnetic shielding in a molecule which owing to the thermal agitation in a liquid produces fluctuating fields at the nuclei. Thus in 1, 3, 5-trifluorobenzene T_1 for the protons is 26 sec but for ^{19}F is only 17 sec. at room temperature. The difference is thought to be due to the larger shielding anisotropy of the fluorine nuclei [25]. One deduces a correlation frequency for the motion of order 10^{11} c/s which is reasonable.

The moving entities need not be nuclei, although that is the common case. Moving conduction electrons, which have free spins and so produce fluctuating magnetic fields, produce nuclear magnetic relaxation from which information concerning their motion can be obtained [26]. The effect of paramagnetic ions or molecules is similar and forms a large field in itself.

Motion may be restricted in various ways and one common restriction in suitable liquids is due to association. The effects, as for instance, in the alcohols give anomalous behaviour in other properties and these effects are reflected in nuclear magnetic resonance as shown by Giulotto [27].

A remarkable restriction in a liquid occurs in so called liquid crystals and in these nuclear magnetic resonance has been most helpful in exposing the nature of the restriction. It appears that the molecules may only rotate about their long axes and one gets, for example, proton resonance lines even several gauss wide which are only normally found in solids [28, 29, 30]. A liquid crystal effect in high resolution spectra is reported at this conference [31].

The motion in molecular compounds can be restricted by well known chemical methods, thus a rubber can be cross-linked making it mechan-

ically harder. This is accompanied by a corresponding change in the nuclear magnetic resonance measurements [32]. Similarly a stretched rubber gives a different signal from an unstretched one partly because of the changed molecular mobility [33, 34].

Again an interesting change in the extent and effectiveness of motion is found in materials which can exist in both a crystalline and an amorphous form. An example of this is iso-butyl bromide which will be discussed at this conference [35]. Again, in many polymers part of the material is crystalline and part is amorphous and there are striking differences in the NMR results as a result of the difference in molecular mobility [36]. Indeed this has some possibility of being used as a method of measuring crystallinity [37].

The effect of hydrostatic pressure on certain motions is quite marked and interesting results in nuclear resonance have been obtained, in particular on organic liquids [38, 39] and rubbers [40].

In materials containing an impurity, or in mixtures, the different motions or mobilities of the several components may allow their signals to be distinguished. The determination of water in various materials is of vast commercial importance. A typical example is the water in nylon which is readily measured and which evidently has a much higher mobility than the nylon molecules themselves [41]. A case of adsorbed water is discussed at this conference [42].

Polymers may be "swelled" by the addition of organic solvents and this may very materially change the mobility of the polymer molecules [43, 44].

Again mobility may be affected by irradiation and hence so are the nuclear resonance parameters. Such effects have been most extensively investigated in polymers [45, 46, 47, 48].

In solid hydrogen we have an example of the effect of "quantum mechanical" motion. The "magnetic" molecules, in the ortho state, have a lowest energy state with $J = 1$ even at absolute zero and so it is still "rotating" even at very low temperatures and so the interaction between the pair of protons is motionally reduced. The actual situation is rather complex and will not be discussed here [49]. Another case of possible quantum mechanical motional narrowing of a rather different kind is found for the reorientation of methyl groups when the energy barriers are low enough [50, 51]. In some cases the "rigid lattice" line width should never be observed [50]. An example approaching this situation, persistence of

reorientation of methyl groups at 20° K, is given at this conference [52]. The same is true of course of zero point vibrational motion but the effect of this is less apparent in nuclear resonance.

We have so far ignored lattice vibrations as a motional effect in a crystal and the reason is that these vibrations, although they carry the magnetic nuclei, are not usually very effective in causing relaxation, as compared with other motions. (They do tend however to be more important for nuclei with electric quadrupole moments). The reason is that the vibrations are not strongly excited in the radio frequency region which is suitable for causing relaxation and so the effects are weak. Even the indirect effect, "Raman" scattering of phonons, is quite weak. Again the motions to which nuclear resonance parameters are sensitive are ones where r and θ vary by large amounts and so amplitudes of vibration of order 10° or more are required and changes in r comparable with the lattice spacing. Such large vibrations do occur more readily in molecular crystals and indeed nuclear magnetic resonance has led to some reconsideration of X-ray measurements where perhaps the magnitude and importance of certain vibrational motions has been underestimated. Such large amplitude vibrations may also occur in crystals of long chain compounds.

The effect of crystal size on the phonon distribution at low temperatures has been studied via nuclear spin lattice relaxation times [53].

The motions we have considered so far are thermal motions but similar considerations apply to macroscopic or directed motions of the nuclei. This is of importance in high resolution work in averaging out residual inhomogeneity of H_0 and is practicable if the inhomogeneity is small. More recently the use of macroscopic motion to produce line narrowing has thrown a great deal of light on some of the more subtle aspects of motional narrowing of dipolar broadened lines [54].

A semi-macroscopic effect is the measurement of self diffusion constants by the attenuation of an echo [55]. In this case macroscopic diffusional motion in an externally applied inhomogeneous field is detected by the resulting incoherent dephasing of the nuclear precession. Some results obtained by this method are reported at this conference [13]. This method is at present suitable for diffusion constants in the range of about 10^{-6} to 10^{-4} $\text{cm}^2 \text{sec}^{-1}$ and a flood of results may be expected shortly where there has in the past been a very great dearth, since this range embraces the magnitude of the diffusion constants of many liquids near room tempera-

ture [56]. It is also possible to observe the effect of macroscopic flow in this way although the method is hardly practicable [57]. (Rates of flow of liquids can be measured by measuring the rate of nuclear polarisation.) Interesting effects of macroscopic motion may occur when the magnetic nucleus interacts with the lattice via another nucleus having an electric quadrupole moment rather than directly [58].

I have not discussed quadrupole effects because rather less work has been done on these as far as motional effects are concerned. This is unfortunate because the effect of motion in these cases might in favourable cases be rather simpler on the whole than the ones we have been discussing and the interpretation should be rather more direct. We know that quadrupole effects are rather sensitive to vibrational motion, for instance.

I regret not having had the space or time to give many more examples of motional effects in nuclear magnetic resonance but I hope that this brief review gives some impression of the range and possibilities of the method.

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