NUCLEAR MAGNETIC RELAXATION

By N. BLOEMBERGEN, E. M. PURCELL
AND
R. V. POUND*
Harvard University, Cambridge, Massachusetts

THE method of nuclear paramagnetic resonance absorption[1] has been used to study the interaction of nuclei in solids, liquids, and gases with their environment. The two important quantities are the relaxation time T_1, describing the energy transfer from the nuclear spin system to the whole of the sample, representing the heat reservoir, and the interaction among the nuclei alone, which can be described by a spin-spin relaxation time T_2. From the theory of Waller[2] one can predict the relaxation time T_1 caused by interaction of the nuclei with the lattice vibrations. The time obtained is at least 10^4 times larger than the experimental values[3,4,5].

We shall show that another process, occurring in many substances, provides a 'local field spectrum'[5] intense enough to account for the observed relaxation times. Every nucleus experiences not only the constant field H_0, and the applied radio-frequency signal H_1 perpendicular to H_0, but also the local field produced by neighbouring nuclear moments and sometimes by small moments caused by molecular rotation, or in paramagnetic substances by large electronic moments. In liquids and gases, at least, the carriers of these neighbouring moments are not stationary but execute Brownian motion, changing position relative to the nucleus under consideration in a random fashion. Consequently, the local field $H(t)$ will be a random function with a correlation time τ_c, in which the relative position of the neighbours changes significantly. The intensity in the Fourier spectrum of a random function[6] is nearly constant for frequencies $\nu \ll 1/\tau_c$, and falls off rapidly for $\nu \gg 1/\tau_c$. If we assume the correlation function to be of the form,

$$\overline{H(t)H(t+\tau)} = \overline{H^2(t)}\; e^{-t/\tau_c},$$

we obtain for the intensity,

$$H^2(\nu)\Delta\nu = 4\overline{H^2(t)}\;\frac{\tau_c}{1 + 4\pi^2\nu^2\tau_c^2}\;\Delta\nu.$$

Now components of this spectrum perpendicular to H_0 at the Larmor frequency ($\nu_0 = 2\mu H_0/h$) of the nuclei will induce transitions just as does the applied radio-frequency signal. The transition probability for this process is (for spin $I = \frac{1}{2}$)

$$W = \frac{\mu^2}{4\hbar^2}\; H^2(\nu_0).$$

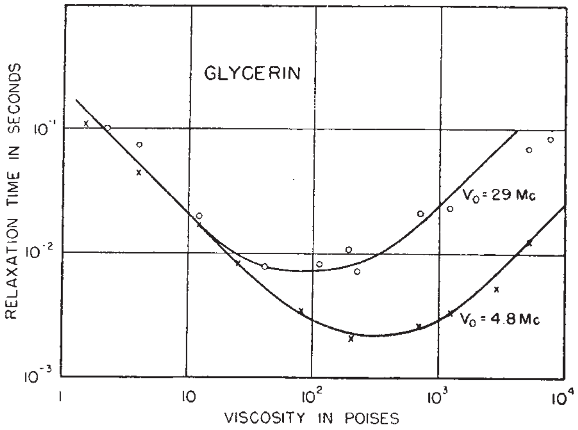
This process provides an interaction between nuclear spins and thermal motion with a relaxation time

$$T_1 = \frac{1}{2W} = \frac{\hbar^2}{\mu^2}\;\frac{1 + 4\pi^2\nu^2\tau_c^2}{\tau_c}\;\frac{1}{\overline{H^2(t)}}. \qquad (1)$$

$\overline{H^2(t)}$ could, in principle, be calculated for each substance, but will always be of the order $(\mu/r^3)^2$, where μ is the value of the neighbouring moment and r the internuclear distance. The correlation time τ_c can be estimated roughly, as in Debye's theory[7] of polar liquids, from the viscosity and the molecular dimensions. It is perhaps just as accurate in some cases to adopt the experimentally measured Debye time for reorientation of molecules under the influence of Brownian motion, although we must note that in the motion here discussed the neighbours of a molecule as well as the molecule itself are involved. A more refined theory would provide an appropriate distribution of relaxation times. In any event, we expect τ_c to be proportional to the viscosity. We now distinguish two cases: (A) $\tau_c \ll 1/\nu_0$, (B) $\tau_c \gg 1/\nu_0$. We see from (1) that in case (A) T_1 is inversely proportional to the viscosity. In case (B) T_1 is directly proportional to the viscosity. In most liquids we have case (A). The Debye relaxation in water, for example, occurs in 3×10^{-11} sec. at 20° C. Taking this as τ_c, we obtain with $\nu_0 = 29$ Mc./sec. a nuclear relaxation time of 5 sec., whereas the value of T_1 found in our experiments is 1·5 sec.

The relaxation time is measured by a saturation procedure. The power absorbed by the nuclei relative to the incident power is proportional to the surplus number of nuclei in the state of lower energy. This surplus will fall off rather abruptly if the incident power is increased sufficiently to raise the temperature of the system of nuclear spins.

The relaxation time in ethyl alcohol has been measured at 29 Mc./sec. and 4·8 Mc./sec., between + 60° C. and − 30° C. T_1 is found to be inversely proportional to the viscosity and independent of frequency (case A). The accompanying graph shows the relaxation time in glycerin for the same two frequencies and in the same temperature range. It displays all the features predicted by the theory, and shows the transition from case (A) to case (B). The minimum occurs for $\tau_c = 1/2\pi\nu_0$.



NUCLEAR MAGNETIC RELAXATION TIME T_1 FOR PROTONS IN GLYCERINE

Similar considerations seem to hold for some solids, in which the molecules still have, to some extent, a rotational degree of freedom. This is the case in ice, which also shows a dielectric dispersion. The relaxation time in ice has been measured from −2° C. (0·8 sec.) to −40° C. (20 sec.) at 29 Mc./sec., and is proportional to the Debye time τ_c, obtained from electric dispersion data. It is of the same order of magnitude as in water, but for a different reason, as we are on the other side of the minimum. Although Debye's theory is only concerned with polar molecules, it is clear that τ_c can be defined in a similar way for non-polar liquids. Measurements on a series of hydrocarbons from petroleum ether to heavy mineral oil show a decrease of the relaxation time from 2 sec. to 0·005 sec. with increasing viscosity. The local field $H(t)$ can be greatly enhanced by

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* Society of Fellows.

addition of a paramagnetic substance, resulting in a corresponding decrease in relaxation time. Data have been obtained for solutions containing Fe^{+++}, Cu^{++}, Er^{+++} in concentrations from 0·0002 to 0·5 mol. The relaxation time is inversely proportional to the concentration and, roughly, to the square of the magnetic moment of the ion. For F^{19} and Li^{7} resonances in liquids results have been found similar to those for protons. Furthermore, the deuteron resonance has been observed at 4·8 mc. in a water sample containing 50 per cent deuterium. The relaxation time for D in this sample is 0·1 sec. Although the deuteron has a much smaller magnetic moment than the proton, this time is twenty times shorter than that for protons in the same sample, and must be ascribed almost entirely to the action of the quadrupole moment. One can repeat the above calculations for the electric quadrupole transitions by considering the 'local field spectrum' of the tensor grad **E**. With the known value of the quadrupole moment, one obtains the experimental value of the relaxation time for a reasonable value of grad **E** in the polar liquid.

Finally, we must consider the spin-spin relaxation time and the closely related problem of the line width. In the limiting case of a solid in which the motion of molecules is very small, the line width can be calculated on the basis that the nuclei are at rest[8], and spin-spin relaxation is produced by the fact that neighbouring nuclei precessing with the Larmor frequency can exchange their energy. On the other hand, in a liquid like water, this exchange will be much smaller, since the rapid Brownian motion smears out the spectrum and averages out the local field. We conclude that in liquids $(\tau_c \ll 1/\nu_0)$, T_1 and T_2 are proportional and of the same order of magnitude. But while T_1 passes through a minimum at $\tau_c = 1/2\pi\nu_0$, T_2 continues to decrease. The line width is a monotonic function of viscosity, at first linear, and asymptotically reaching a limiting value in the solid. Confirming this view, we find experimentally that the resonance line in water, glycerin, and other liquids at room temperature is extremely narrow. At 4·8 Mc./sec., an upper limit of 0·015 gauss has been established. The theoretical value according to the above considerations would be 0·007 gauss for glycerin and about 10^{-4} gauss for water. The broadening of the line in glycerin, mineral oil and ice, which can be observed at sufficiently low temperatures, is such that the line width is initially proportional to τ_c. In glycerin at $-30°$ C. the width is 1·5 gauss, in ice at $-5°$ C., 5 gauss, at $-30°$ C., 15 gauss. The line width in solutions of ferric nitrate is proportional to the concentration of the paramagnetic ion, and is 0·6 gauss in a 0·5 mol. solution with a relaxation time $T_1 = 3 \times 10^{-4}$ sec.

A detailed account of this investigation will be sent to the *Physical Review* and will appear in a thesis to be submitted by one of us (N. B.) at the University of Leyden.

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STATE LABORATORY FOR EXPERIMENTAL BIOLOGY AND MEDICINE, NOVI SAD, YUGOSLAVIA

By Dr. PETAR N. MARTINOVITCH
Director

WHILE fighting was still going on in the Pannonian plains north-west of Beograd in 1944, a small group of young medical men and medical students (most of them in uniform) was busy collecting material left behind by the Germans, destined to become the nucleus of the present Laboratory for Experimental Biology and Medicine at Novi Sad, Yugoslavia. In due course they called on me to tell me that they wanted a laboratory for biomedical research. A site for the laboratory was yet to be found. Eventually, a deserted villa on the outskirts of the town was selected; but it was in an appalling condition, and many months of work were necessary to make it suitable for our purpose.

The United Nations Relief and Rehabilitation Administration sent a large amount of laboratory material to Yugoslavia; but it had to be shared by many laboratories and much of it was assigned to field work. Some valuable items, however, were allotted to our institute. Finally, due credit should be given to the progressive citizens of Novi Sad, who spared no effort to help the new laboratory. To-day the Laboratory is a State institution, and the authorities are giving ample credits for its support.

The available space in the Laboratory consists of four large rooms and six smaller ones. One room has been fitted for tissue culture work, and in the cellar there are a workshop, a washing room and a room where experimental animals can be kept. The building stands in a small park, and at the back is a garden with an enclosed space for poultry. The Laboratory is equipped with essential apparatus, instruments and a fair amount of glassware and necessary chemicals; all the equipment of my tissue-culture laboratory at Beograd was transferred to Novi Sad. The Laboratory owns eight hectares of arable land, where the animals are kept and the animal food grown.

Although the official status of the Laboratory was established in May 1946, experimental work did not begin until several months later.

The new Laboratory is being organised on a modest scale along the lines of the Strangeways Research Laboratory at Cambridge. No separate departments are planned and no programme of 'division of labour' on the research level will be attempted. Each laboratory unit will be developed around the man and the field in which he is most interested. Collaboration will be encouraged whenever necessary. No attempt will be made to encourage the Laboratory to grow beyond a certain definite size.

The Laboratory has four objectives, as follows: to bring under the same roof workers engaged in various fields of experimental biology and medical research; to establish the closest possible contacts with laboratories in other lands engaged in the same kind of work; to give an opportunity to promising young people interested in biomedical research to obtain elementary instruction in research methods, in order that they may be sent abroad sufficiently trained for advanced work; to 'popularize' bio-