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CHAPTER 4.

THEORY AND EXPERIMENTAL RESULTS.

4. 1. *Relaxation time and line width in liquids* (B 10, B 11).

4. 1. 1. *The Fourier Spectrum of a random function.*

In chapter 2 a general theory for the relaxation time was presented. In order to apply it to practical cases we have to evaluate the Fourier spectra of the functions of the position coordinates F_0, F_1 and F_2 of section 2. 5.

In a liquid these functions will vary in a random fashion with time, as the particles containing the magnetic nuclei take part in the Brownian motion. The fluctuating functions $F_0(t)$, $F_1(t)$ and $F_2(t)$ satisfy the condition

$$\overline{\mathrm{Re}\ F(t)} = \overline{\mathrm{Im}\ F(t)} = 0 \tag{4. 1}$$

The statistical character of the motion justifies an assumption, customary in the theory of fluctuation phenomena, that

$$F(t)\,F^*(t+\tau) = k(|\tau|) \tag{4. 2}$$

The left hand side is called the correlation function of $F(t)$.

The correlation function of the random function $F(t)$ is independent of t and an even function of τ. From these assumptions it follows immediately that $k(\tau)$ is real. We shall now derive briefly the relation between this correlation function and the intensity of the Fourier spectrum of $F(t)$. A very general theory of random processes has been given by W a n g and U h l e n b e c k (W 2, R 4), where the reader may find further references. Many other investigators have pointed out the connection between the spectrum and the correlation function. We shall here follow closely K e l l e r 's (K 1) argument, although there are some slight modifications, as we want to distinguish between positive and negative

frequencies and our function $F(t)$ is complex. Expand $F(t)$ in a Fourier integral

$$F(t) = \int_{-\infty}^{+\infty} A(\nu)\, e^{2\pi i \nu t} d\nu$$
$$A(\nu) = \int_{-\infty}^{+\infty} F^*(t)\, e^{-2\pi i \nu t}\, dt \tag{4.3}$$

We assume that $F(t) = 0$ for $|t| > T$, where T is a time large compared to all times in which we ever have made or shall make observations. This assumption therefore will not alter the physical results, and in the end we can get rid of it by taking the limit $T \to \infty$. Between the functions connected by the transformation of Fourier (4.3) exists the Parseval relation

$$\int_{-\infty}^{+\infty} F(t)\, F^*(t)\, dt = \int_{-\infty}^{+\infty} A(\nu)\, A^*(\nu)\, d\nu \tag{4.4}$$

With (4.3) and our assumption we can write this in the form

$$F(t)\, F^*(t) = \frac{1}{2T} \int_{-\infty}^{+\infty} d\nu \int_{-T}^{+T}\int_{-T}^{+T} F(t)\, F^*(t')\, e^{2\pi i \nu (t-t')}\, dt\, dt' \tag{4.5}$$

We next make the substitutions $\sigma = t$ and $\tau = t - t'$. Using the fact that $\overline{F(\sigma)\, F^*(\sigma - \tau)}$ is only different from zero for small values of $|\tau|$ at any rate much smaller than T, we obtain after some calculation

$$\overline{F(t)\, F^*(t)} = \int_{-\infty}^{+\infty} d\nu \int_{-2T}^{+2T} e^{2\pi i \nu \tau}\, F(\sigma)\, F^*(\sigma - \tau)\, d\tau$$
$$= \int_{-\infty}^{+\infty} J(\nu)\, d\nu \tag{4.6}$$

with the expression for the spectral intensity

$$J(\nu) = \int_{-\infty}^{+\infty} k(\tau)\, e^{2\pi i \nu \tau}\, d\tau \tag{4.7}$$

Since $k(\tau)$ is real and even, $J(\nu)$ is real and even. Because we made a distinction between positive and negative frequencies, the intensity in (4.7) is half the value usually found in the literature. In the following discussion we shall see that $k(\tau)$ often has the form:

$$k(\tau) = \overline{F(t)\,F^*(t)} \exp\{-|\tau|/\tau_c\} \tag{4.8}$$

The combination of (4.7) and (4.8) yields

$$J(\nu) = 2\,\overline{F(t)\,F^*(t)}\,\frac{\tau_c}{1 + 4\pi^2\,\nu^2\,\tau_c^2} \tag{4.9}$$

In general we can say that $k(\tau)$ is a function which goes rapidly to zero, if $|\tau|$ exceeds a value τ_c which is characteristic for the mechanism of the Brownian motion and is called the correlation time. The general behaviour of the Fourier spectrum is therefore such that the intensity $J(\nu)$ is practically constant for low frequencies and falls off rapidly, when $2\pi\nu\tau_c > 1$. The time average $\overline{F(t)\,F^*(t)}$ can be replaced by the statistical average according to a general theorem from statistical mechanics.

4.1.2. *Evaluation of the relaxation time in water.*

We start out with one water molecule, surrounded, say, by carbondisulfide, which contains no nuclear magnetic moments. We assume that the rotational magnetic moments of the molecules are also zero. We want to calculate the relaxation time of one proton due to the presence of the other. The functions F consist each of a single term:

$$F_1 = \sin\vartheta\cos\vartheta\,e^{i\varphi}/b^3 \qquad F_2 = \sin^2\vartheta\,e^{2i\varphi}/b^3$$

where b is the constant distance between the two protons. The rotation of the molecule in the liquid will change the angle between the magnetic field H_o and the radius vector connecting the two protons in a random fashion.

The correlation function of the expressions F can be calculated if we adopt the same simple picture as Debye (D 2) did in his famous theory of dielectric absorption and dispersion, namely a rigid sphere of radius a in a medium of viscosity η and absolute temperature T. Debye applies to this model Einsteins theory (E 1) of the Brownian motion. In the case that no external forces besides the thermal collisions are present, the probability to find a fixed axis of the sphere in the solid angle $\sin\vartheta\,d\vartheta\,d\varphi$ is described by the ordinary diffusion equation

$$-\frac{\partial f(\vartheta,\varphi)}{\partial t} = D\,\Delta f(\vartheta,\varphi) \tag{4.11}$$

The diffusion constant D is given by the general expression

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$$D = k\,T/\beta$$

The damping constant β for the rotation of a sphere in a viscous medium was calculated by Stokes: $\beta = 8\,\pi\,\eta\,a$.

The Laplacian Δ acts only on the angle variables ϑ and φ.

A solution of (4. 11) may be written in a series of spherical harmonics $Y_{l,m}$:

$$f = \sum_{l,m} c_{l,m}\, Y_{l,m}(\vartheta, \varphi)\; e^{-t\,D\,l\,(l+1)/a^2}$$

At $t = 0$ the sphere is in the position ϑ_0, φ_0 and $f = \delta(\vartheta - \vartheta_0).\delta(\varphi - \varphi_0)$.

From this condition we find the coefficients

$$c_{l,m} = Y^*_{l,m}(\vartheta_0, \varphi_0) \Big/ \int_0^{\pi}\int_0^{2\pi} |\, Y_{l,m}(\vartheta, \varphi)\,|^2 \sin\vartheta\, d\vartheta\, d\varphi$$

In order to find the correlation function $\overline{F(0)\,F^*(t)}$ note that $F_1 = b^{-3}\, Y_{2,1}(\vartheta, \varphi)$ and $F_2 = b^{-3}\, Y_{2,2}(\vartheta, \varphi)$.

We have $b^3\, F_1^*(t) = \int_0^{\pi}\int_0^{2\pi} f\, Y^*_{2,1} \sin\vartheta\, d\vartheta\, d\varphi = c^*_{2,1}\, e^{-6\,D\,t/a^2}$

The average has to be taken over all possible initial positions, i.e. over ϑ_0 and φ_0.

The final result is

$$\overline{F_1(0)\,F_1^*(t)} = b^{-6}\,\overline{Y^*_{2,1}(\vartheta_0, \varphi_0)\;\; Y_{2,1}(\vartheta_0, \varphi_0)}\; e^{-\frac{6\,D\,t}{a^2}} = \frac{2}{15}\, b^{-6}\, e^{-t/\tau_c}$$

$$\overline{F_2(0)\,F_2^*(t)} = \frac{8}{15}\, b^{-6}\, e^{-t/\tau_c} \qquad (4.\,12)$$

$$\text{with } \tau_c = 4\,\pi\,\eta\,a^3/3\,k\,T \qquad (4.\,13)$$

The characteristic time of Debye τ we obtain by carrying out the same procedure for the function $\cos\vartheta = Y_{1,0}$

The result is

$$\tau = 4\,\pi\,\eta\,a^3/k\,T = 3\,\tau_c \qquad (4.\,14)$$

In Debye's theory τ is the time in which an assembly of water molecules, originally oriented by an electric field, loses its distribution around a preferred direction by the Brownian motion, after the electric field has been switched off. In our case τ_c is the time, in which a molecule is

rotated by the Brownian motion over such an angle that the relative position of the nuclei with respect to the external field and thus the functions F have changed appreciably.

Using (4. 9), (4. 12) and the general formula (2. 53) we find for the relaxation time of a proton in a watermolecule

$$(1/T_1)_{\text{rot}} = 0{,}4\left\{\frac{\tau_c}{1+4\pi^2\nu_0{}^2\tau_c{}^2}+\frac{2\tau_c}{1+16\pi^2\nu_0{}^2\tau_c{}^2}\right\}\gamma^4\hbar^2 I_p(I_p+1)\,b^{-6} \tag{4. 15}$$

Substituting numerical values $T = 300$, $\eta = 10^{-2}$, $a = 1.5 \times 10^{-8}$, $I_p = \frac{1}{2}$ we find that $\tau_c = 0.35 \times 10^{-11}$ sec, and since $\nu_0 = 3 \times 10^7$ cycles/sec we have $2\pi\tau_c\nu_0 << 1$. We see from (4. 15) that in this case $1/T_1$ is proportional to τ_c and we can write with (4. 15)

$$(1/T_1)_{\text{rot}} = 0{,}9\,\gamma^4\hbar^2 b^{-6}\tau_c \tag{4. 16}$$

The value of $\tau = 3\tau_c \approx 10^{-11}$ sec is in excellent agreement with experimental data on the dielectric absorption and dispersion in water at microwave frequencies (C 5)

Next we consider the practical case that the neighbours are not CS_2 molecules, but other H_2O molecules. We can estimate the influence of the other protons on the relaxation time in the following way.

Again the Brownian motion is responsible for the Fourier spectrum, but the cause is now rather the relative translational motion of the molecules than a rotation. Let us consider the protons in the other molecules as independent of one another [1]). We ask for $\overline{F(t)F(t+\tau)}$ and τ_c for the protons in a spherical shell between r and $r + dr$ around the proton of which we wish to determine the relaxation process. A reasonable value for τ_c is apparently the time it takes for a molecule to travel over a distance r. For in that time the relative position and with it the spin spin interaction has changed appreciably. From the theory of Brownian motion we have the expression for the mean square displacement of a particle

$$\overline{x^2} = 2kT\tau_c/\beta \tag{4. 17}$$

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[1]) It would be better to consider the molecules as independent and attribute to them a moment $2\mu_p$ if the spins are parallel, or zero if they are antiparallel, and then apply tc these moments the statistical weight of the parallel and antiparallel state. The same answer would be obtained. In the preceding problem of the rotating molecule also ortho- and para- states should have been distinguished. We shall come back to this question at the end of chapter 5.

where β is a damping constant. For a sphere in a viscous medium Stokes derived $\beta = 6\pi\eta a$

If one prefers to use the diffusion constant $D = kT/\beta$, we find for the correlation time

$$(\tau_c)_{\text{transl.}} = \overline{x^2}/2D = r^2/12D \tag{4.18}$$

since r is the relative displacement of two particles in any direction.

To find $\overline{F(t)\,F(t)}$ we have to average the angular functions over the spherical shell and multiply with the number of protons in the shell as we treat them independently. Then we have to integrate over r to include all other molecules, so approximately from $2a$, the distance of closest approach, to infinity. Using again (4.9) and (2.53) we find

$$(1/T_1)_{\text{transl.}} = 1.6\pi N\gamma^4\hbar^2 I_p(I_p+1)\int_{2a}^{\infty}\frac{r^2}{r^6}\left\{\frac{\tau_c}{1+4\pi^2\nu_0^2\tau_c^2}+\frac{2\tau_c}{1+16\pi^2\nu_0^2\tau_c^2}\right\}dr \tag{4.19}$$

In the integral we can neglect the term with $\nu_0^2\tau_c^2$ in the denominators, since $2\pi\tau_c\nu_0 \ll 1$ for $r < 10^{-7}$, and the most important contribution to the integral comes from the nearest neighbours. Integration of (4.19) then simply leads to

$$(1/T_1)_{\text{transl.}} = 0.9\pi^2\gamma^4\hbar^2\eta N/kT \tag{4.20}$$

Substituting numerical values in (4.16) and (4.20), $a = 2\times10^{-8}$ $b = 1.5\times10^{-8}$, $\eta = 10^{-2}$, $N = 7\times10^{22}$, $\gamma = 2.7\times10^4$ we find

$$(T_1)_{\text{rot}} = 5.2 \text{ sec.} \qquad (T_1)_{\text{transl}} = 10 \text{ sec.} \qquad T_1 = 3.4 \text{ sec.}$$

This value is in good agreement with the experimental value of 2.3 sec. In the case of a rotating sphere it was possible to calculate the correlation function explicitly. For the translational effect and the rotation of more complicated molecules in liquids this would be very difficult. In these cases one might assume formula (4.8) or a linear combination of them with various τ_c. The correlation time τ_c should be larger in more viscous media as the molecular motion becomes slower. In the next section we shall discuss the general relation between the relaxation and correlation times and the viscosity.

4.1.3. *The relation between the relaxation time, the viscosity, the correlation time and the Debye time.*

There may be some doubt whether is is permissible to extend the macroscopic notions of viscosity and diffusion to regions which contain only a few atoms. The same objection can be raised against Debye's theory. There, as in our case, the procedure is justified by its success. Since we obtain the right order of magnitude for the relaxation time, we might even inversely use the latter to extend our information regarding the motion of the molecules. From our general considerations we would expect that the relaxation time would decrease with increasing viscosity, as long as the condition $2\pi\nu_0\tau_c \ll 1$ is satisfied. This is confirmed by the experimental evidence in Table I and Table II.

Table I

Relaxation time of protons at 29 Mc/sec in hydrocarbons at 20° C

	Viscosity in centipoises	Relaxation time in seconds
Petroleumether	0.48	3.5
Ligroin	0.79	1.7
Kerosin	1.55	0.7
Light machine oil	42	0.075
Heavy machine oil	260	0.013
Mineral oil	240	0.007

Table II

Relaxation time of protons at 29 Mc/sec in polar liquids at 20° C

	Viscosity in centipoises	Relaxation time in seconds
Diethylether	0.25	3.8
Water	1.02	2.3
Ethylalcohol	1.2	2.2
Acetic acid	1.2	2.4
Sulfuric acid	25	0.7[5]
Glycerin	1000	0.02[3]

The viscosities in table I were measured with a viscosimeter, (time of flow measurement), those of table II were taken from the Physikalisch Chemische Tabelle.

We also measured the relaxation time in mixtures of water and glycerin, of which the result is shown in fig. 4.1.

The dependence of the relaxation time on the viscosity is not quite the

inverse proportionality, which one might infer from (4. 16) and (4. 20). The relaxation time in glycerin is only 10^2 times smaller than in water, while the viscosity is 10^3 times larger. In the first place one can remark that in going from one substance to another the quantities a b and N change too. The deviation in sulfuric acid can so partly be understood because the proton density in it is much smaller than in the other substances. But for the latter the density of nuclei nor the internuclear distances b change very much from molecule to molecule. The molecular

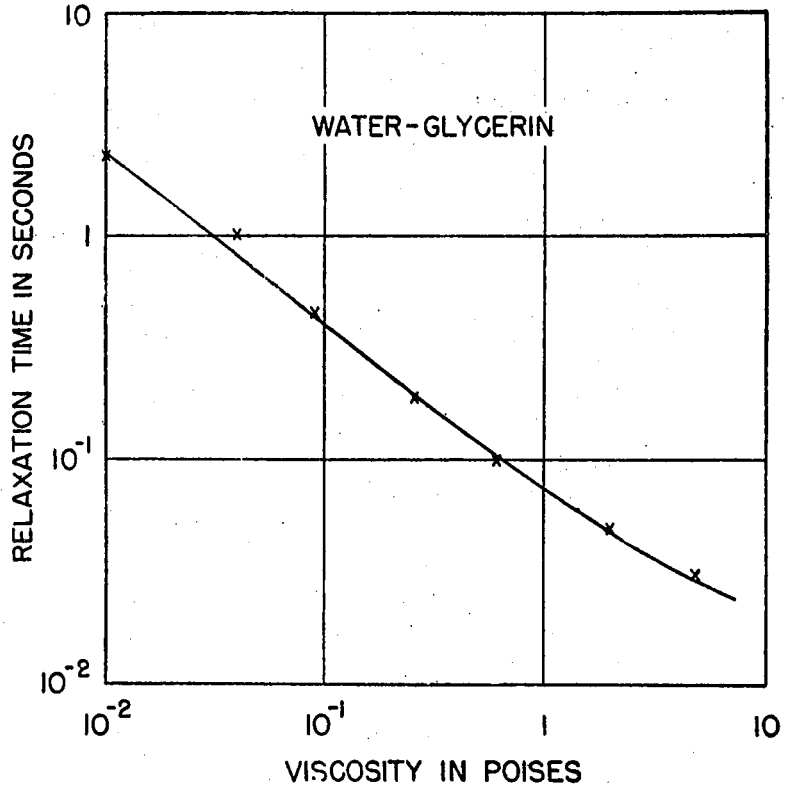

Figure 4. 1.

The relaxation time of the proton resonance at 29 Mc/sec in mixtures of water and glycerin.

diameter a changes of course, but this would cause a deviation from the inverse proportionality with η in the direction opposite to that observed. We can only say that our treatment of a molecule as a sphere with a magnetic moment in the centre becomes very crude for large molecules, each containing several protons. In the modern theory of the viscosity a concept exists, that continually transitions are made between configurations around a given molecule, which are more or less stable. The rate at

which these changes in configurations take place determines our correlation time τ_c which will depend therefore in a complicated manner on the shape and size of the molecule. For the large chain-like molecules in the hydrocarbons one has furthermore the possibility of bending and twisting of a molecule, which changes the relative position of the protons in that molecule.

The reader may be reminded that similar difficulties arise in Debye's theory of dielectric dispersion. His time τ determined experimentally, does not always correspond to the one calculated from (4.14). Attempts have been made to explain this deviation by taking into account the electric dipole interaction between the polar molecules and introducing different models for the electric local field. Note that glycerin which shows the largest deviation in our case, also violates Debye's formula (4.14) most severely. We want to stress, however, that the Debye time τ and our correlation time τ_c characterize different physical processes. Debye's τ refers only to the orientation of the polar group in space, while for τ_c any relative reorientation between the magnetic nuclei must be considered. The following formulation then seems appropriate. The characteristic time τ of Debye and the correlation time τ_c in the magnetic local field spectrum are proportional in one sample. They both vary in proportion to η/T, if the temperature of the sample is changed.

The proportionality constant between τ and τ_c varies from substance to substance, depending on the detailed picture of the molecular motion in each substance, but the ratio will always be of the order of unity. For the model of a sphere in a viscous medium we have $3\,\tau_c = \tau$. Experimental values for the proportionality factor are given in section 4.3.1.

We can obtain a better test of the theory if we carry out measurements of the relaxation time and line width in one substance at various temperatures. We shall first describe in some detail the behaviour of T_1 and T_2, that must be expected from theory. Substitution of (4.9) and (4.12) into (2.54) and (2.53) leads to

$$1/T_1 = K_1\left[\frac{\tau_c}{1+4\pi^2\nu^2\tau_c^2}+\frac{2\tau_c}{1+16\pi^2\nu^2\tau_c^2}\right] \tag{4.21}$$

$$1/T_2' = \sqrt{K_0\int_{-1/\pi T_2'}^{1/\pi T_2'}\frac{\tau_c}{1+4\pi^2\nu^2\tau_c^2}\,d\nu} = \sqrt{\frac{K_0}{\pi}\operatorname{arc\,tg}\frac{2\tau_c}{T_2'}} \tag{4.22}$$

with
$$K_1 = {}^2/_5\,\gamma^4\hbar^2 I(I+1)\,b^{-6} \tag{4.23}$$

and
$$K_0 = 3\,K_1 \tag{4.24}$$

It has been assumed that the averaging over ϑ could be carried out independently. Use has been made of the relations (4.12). Furthermore the formulae are written for a single relaxation time $\tau \sim c\eta/T$. Actually we have a distribution of relaxation times as we have seen for the translational effect in water. We should write instead of the constant c the function $c(\lambda)$ and integrate over the parameter λ. In most cases the distribution will be narrow, since only the nearest neighbours contribute strongly. Strictly speaking the constants K are functions of the temperature, as they vary with the density of the sample, but this effect

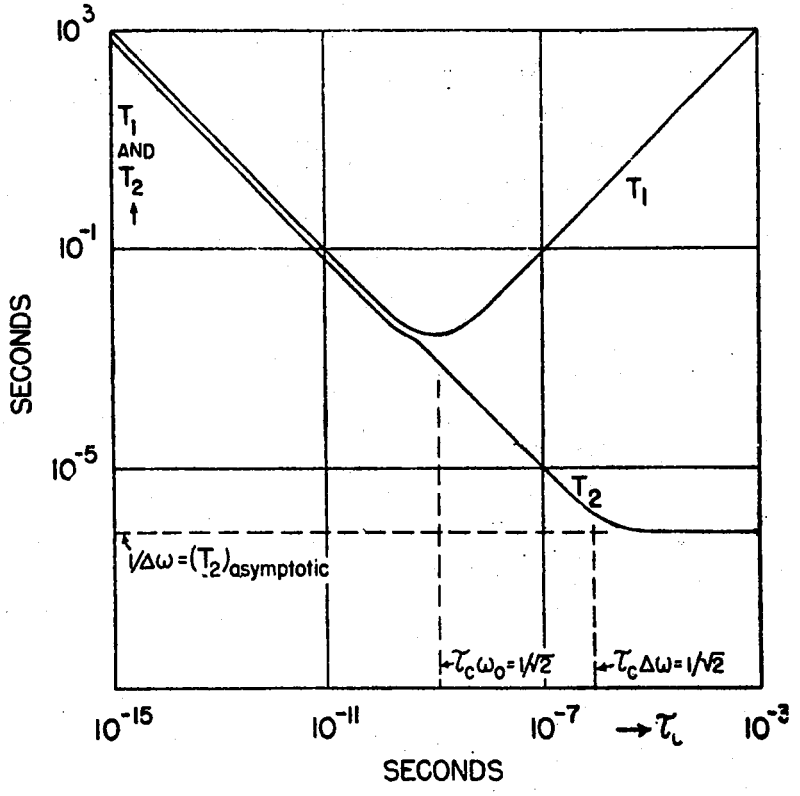

Figure 4.2.

The theoretical behaviour of the relaxation time T_1 and T_2, which is a measure for the inverse line width.

is completely negligible. The simplifying assumptions now permit to point out clearly the general behaviour of T_1 and T_2, which are plotted as a function of τ_c in fig. 4.2. Here T_2 is defined by (2.58).

For $4\pi^2\nu^2\tau_c^2 \ll 1$, T_1 is inversely proportional to τ_c and thus to η/T, and for $4\pi^2\nu^2\tau_c^2 \gg 1$ directly proportional. The plot on a double

logarithmic scale therefore shows two straight lines making angles of 45 and 135° degrees with the x-axis.

In the transition region $(4\pi^2 \tau_c^2 \nu^2 \approx 1)$ T has a minimum value

$$(T_1)_{\text{min}} = {}^4/_8 K_1 \tau_c \tag{4.25}$$

for $$\tau_c = {}^1/_2 \sqrt{2}\, \pi \nu_0$$

The quantity T_2' is a monotonic decreasing function of τ_c and reaches an asymptotic value

$$(1/T_2')_{\text{asymptotic}} = \sqrt{{}^1/_2 K_0} \tag{4.26}$$

for very long correlation times. This value is of course exactly the same as the one we calculated for the static case (2.36) where the nuclei are at rest. For $\tau_c << (T_2')_{\text{asymptotic}}$, T_2' is inversely proportional to τ_c. The horizontal distance between the points, where T_1 and T_2 bend over respectively, is given by the ratio $2\pi\nu_0 (T_2')_{\text{asymptotic}} \approx H_0/H_{\text{loc}}$. For $4\pi^2\nu^2\tau_c^2 << 1$, T_1 and T_2' are proportional and from (4.21) and (4.22) we find for the proportionality constant

$$T_2' = {}^1/_2 \pi T_1 \tag{4.27}$$

The line width is given by (2.58) with one of the relations (3.22) or (3.23). For $4\pi^2\nu_0^2\tau_c^2 >> 1$ we have

$$T_2 \approx T_2' \tag{4.28}$$

for $4\pi^2\nu_0^2\tau_c^2 << 1$ we have with (4.27)

$$T_2 = 0.85\, T_1 \tag{4.29}$$

We must not attach too much weight to this particular ratio, for about the limits in the integral in (4.22) we only know that they must be of the order of magnitude of the line width expressed in cycles/sec. It might be better to take the limits as $\pm\, 1/\pi T_2$ instead of $\pm\, 1/\pi T_2'$. This would not make any difference for long τ_c's, and does not affect the order of magnitude for the region where T_1 and T_2 are proportional. We shall see in the next paragraphs that the experimental ratio between T_1 and T_2 is close to the value predicted by (4.28) and (4.29). On this basis the resonance line in water e.g. with $T_1 = 2.3$ sec. should be very narrow indeed. The width should be of the order of one cycle or about 10^{-7} oersted. The experimental width is then, of course, determined by the inhomogeneity in H_0 as we have already pointed out several times.

4.1.4. *Experimental results in ethyl alcohol and glycerin between + 60° C and —35° C.*

In order to vary the temperature of the sample in the radiofrequency coil, copper tubing (3mm inside diameter) was soldered around the grounded shield of the radiofrequency coil (see fig. 3.8). To obtain low temperatures acetone, cooled by dry ice, could flow through the tubing from a container, which was placed above the magnet, under the influence of the gravitational force. This acetone was not in direct contact with the dry ice. For dissolved CO_2 would be set free, when the acetone was warmed up in passing through the narrow tubing. This would prevent a regular flow. The apparatus in the magnet gap and all other cold parts were thermally insulated with glass wool and asbestos paper. The temperature was measured by a copper-constantan thermo-element. One contact point was brought in the liquid through the small cork stop closing the thin walled glass tube which contained the sample. There was no trouble of pick-up of radio frequencies, since the coupling between the leads of the thermo-element and the coil was very small indeed, as the contact point was kept well outside the volume of the coil. The other contact of the element was put in melting ice. The thermo — E.M.F. was measured with a Leeds & Northrup type K potentiometer. The element was calibrated at + 100° C, 0° C and —78° C, which checked with the calibration data given in the Handbook of Chemistry and Physics, so that this table was used. The temperature of the sample could be varied by changing the flow of the cooling liquid. The temperature remained constant to within 0.5° C during the determination of each saturation curve. The balance of the bridge was also stable, once thermal equilibrium had been established To cover the range of higher temperature, the container was filled with iced water or hot water.

The variation of the viscosity with temperature was taken from the Physikalisch-Chemische Tabelle. The data obtained with ethylalcohol at two frequencies are shown in fig. 4.3. The variation of the relaxation time with viscosity is inversely proportional. The line drawn through the points makes an angle of 135° with the x-axis. Although the variation in the viscosity is not large, the points clearly indicate the theoretical behaviour, to be expected for short τ_c. The real line width could not be measured. The limit set by the inhomogeneity of the field is 0.015 oersted at 4.8 Mc/sec. According to theory the line width should be much narrower than this. As was pointed out in chapter 3, any systematic errors in the relative determination of T_1 cancel out in this case. More interesting are the results for glycerin shown in fig. 4.4. The freezing point of this sub-

stance is 18° C, but it usually gets supercooled and very high viscosities are obtained at low temperature, where the substance becomes almost glasslike. The experimental points show that we have reached the region where $2\pi\nu_0\tau_c > 1$. The drawn lines are theoretical curves. The observed minima are somewhat flatter and on the low temperature side the points do not quite fit a 45° line. This can, at least in part, be explained by a distribution of correlation times τ_c, rather than the single value to which

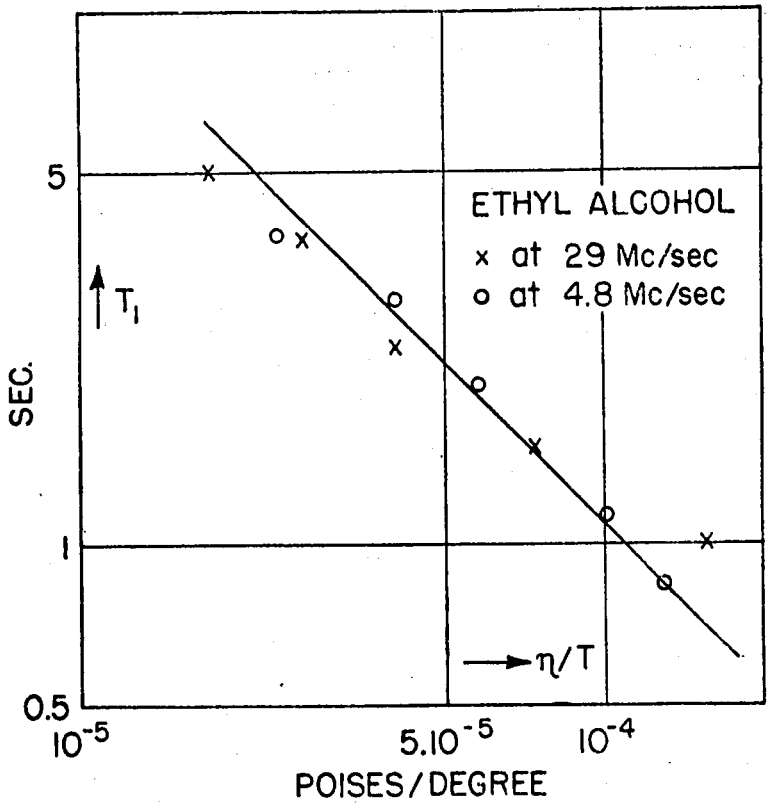

Figure 4. 3.

The relaxation time of the proton resonance in ethyl alcohol between 60° C and — 35° C. The straight line makes an angle of 45° degrees with the negative x-axis.

the theoretical curves pertain. It would be interesting to extend the measurements to lower temperatures to get more information about this distribution. The shift of the minimum with frequency is somewhat less than predicted by (4. 25). We find a factor 4 instead of 6. On the low temperature side the relaxation time should be proportional to ν_0^2. Instead of a factor 36 we find a factor 14. Again this deviation can, at

least partly, be understood by remarking that (4. 25) holds only in case of a single correlation time, or if one wishes, of a single correlation function. The data on the line width are plotted in the same diagram with the aid of formula (3. 22) for a Gaussian curve.

At room temperature the line is narrower than the inhomogeneity of the external field. Extrapolation of the dotted line towards higher temperatures gives the ratio $T_1/T_2' = 1$. In the region where T_1 is proportional to the viscosity and T_2 inversely proportional, the saturation of the line

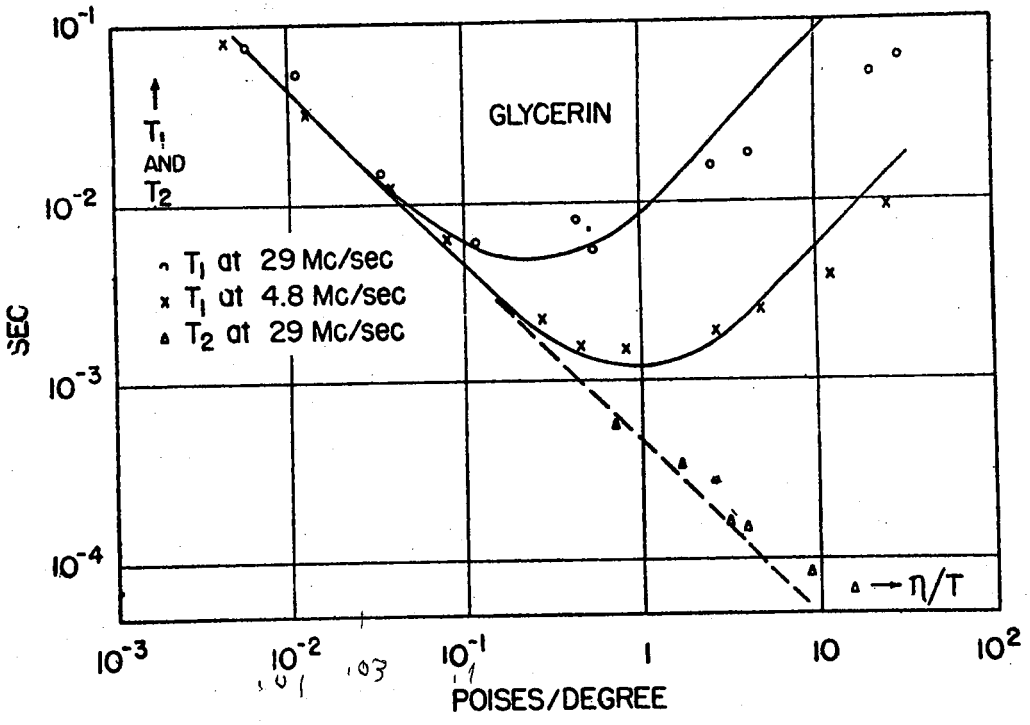

Figure 4. 4.

The relaxation time and the line width of the proton resonance in glycerin between 60° C and −35° C. The lines, drawn through the experimental points, have the theoretical form of fig. 4. 2.

always occurs at the same output power of the generator, that is at the same density of the applied radio frequency field, as the product $T_1 T_2$ is constant. From the viscosity, measured at 20° C, it followed that the glycerin used in the experiment was not pure and probably contaminated with 2 % water. Experiments carried out with mineral oil gave similar results both for the relaxation time and line width.

4.1.5. *The influence of paramagnetic ions.*

So far we have considered the dependence of the relaxation time on τ_c. It is also possible, however, to bring about changes in the quantities K_1 and K_0 in (4.21) and (4.22) by mixing the substance with paramagnetic ions. From (4.23) and (4.24) we see that the large γ-values of the electronic moments will enhance the values of K_1 and K_2. The larger interaction of the nuclear moment with the electronic moment will shorten the relaxation time and enhance the line width, τ_c remaining constant. Let us consider an aqueous solution of ferric nitrate. We can calculate the influence of the Fe^{+++} ions in the same way as we did, when we estimated the contribution of the protons in other molecules to the relaxation time in pure water. An adapted formula (4.20) would read

$$1/T_1 = 12\,\pi^2\,\gamma_p{}^2\,\gamma_{ion}^2\,\hbar^2\,S_{ion}\,(S_{ion}+1)\,N_{ion}\,\eta/5\,k\,T \qquad (4.30)$$

This applies for ions of the iron-group, which are of the "spin-only" type. For others we should replace $\gamma_{ion}^2\,\hbar^2\,S_{ion}\,(S_{ion}+1)$ by μ_{eff}^2.

Of course we should add to (4.30) the contribution of the protons in the solution, which in pure water are solely responsible for the relaxation time. But as γ_{ion}^2 is about 10^6 times larger than $\gamma_p{}^2$, the influence of the paramagnetic ions is predominating even in a concentration of 10^{-3} N. or 10^{18} ions/cc. According to (4.30) the relaxation time should be inversely proportional to the concentration and to the square of the magnetic moment of the paramagnetic ions. In fig. 4.5 the results for three ions are given. It appears that the curves, also to the absolute magnitude, can be well represented by (4.30). Only for very low frequencies there seems to be a deviation towards longer relaxation times. This is all the more remarkable since the straight lines finally must bend over to the left to the asymptotic value of 2.3 sec. in pure water. We do not know if the effect is real. It certainly seems too big for a systematic error. We would like to point out that (4.30) certainly needs some correction. For while the motion of a watermolecule relative to the ion is still given by (4.17) and (4.18), where a is the radius of the watermolecule, the distance of closest approach is determined by the radius of the ion and its hydratation. We must insert a correction factor a/b. It is very hard to estimate correctly the motion of a watermolecule in the dipole atmosphere around an ion. But if there is an effect from the hydratation, it should become more pronounced at small concentrations.

Furthermore we should take into account that the correlation time in the local field spectrum is not solely determined by the molecular motion in the liquid, but also by changes in quantisation of the electronic spins,

which possibility was already indicated in (2.42). The characteristic time for this latter process is not known experimentally, as the paramagnetic electronic relaxation times $\varrho/2\pi$ in solutions are short, of the order of 10^{-10} sec.[1]). This implies that in the derivation of (4.30) we should have used for τ_c the constant ϱ instead of (4.18) for values of

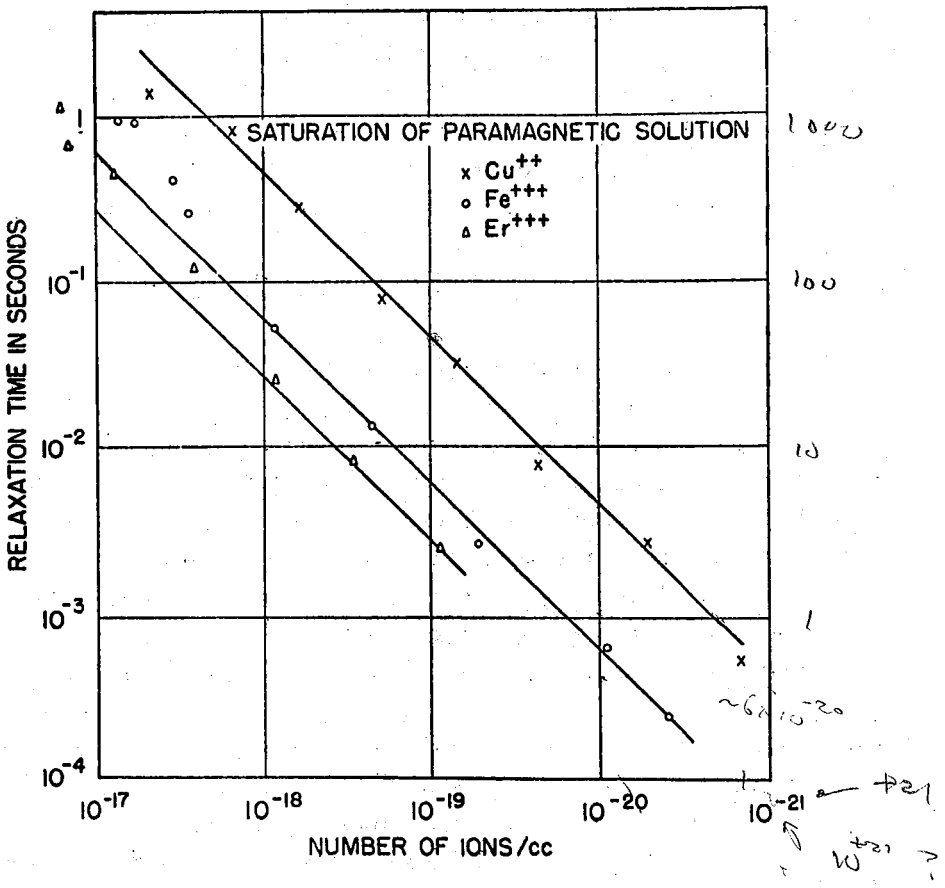

Figure 4.5.

The relaxation time of the proton resonance in aqueous solutions of paramagnetic salts. The lines, drawn through the experimental points, make angles of 45° with the negative X-axis.

r, where τ_c would become larger than ϱ. This reduces only the influence of the ions which are rather far away, so that this correction is not

[1]) One might be tempted to calculate ρ in the same way as we did for the nuclear relaxation time. However, more important than the magnetic interaction between the spins will be the electric interaction in the polar liquid via the spin-orbit coupling. The only experimental information, known to the author, comes from Zavoisky (Z 1).

important. The inverse proportionality with μ_{eff}^2 is rather well realised for some ions, and completely violated for others (Ni^{++}, and especially Co^{++} and $Fe(CN)_6^{---}$), as is shown in Table III.

TABLE III

Ion	μ_{eff} in Bohr magnetons from relaxation experiments	μ_{eff} in Bohr magnetons from susceptibility measurements
Er^{+++}	9.5	9.4
Fe^{+++}	6.3	5.9
Cr^{+++}	4.7	3.8
Cu^{++}	2.3	1.9
Ni^{++}	2.1	3.2
Co^{++}	1.3	4.5—5.3
$Fe(CN)_6^{---}$	0.12	2.4

The second column is computed with (4.30) from measurements of the nuclear relaxation time in solutions of known concentration. The values in the last column were taken from Gorter (G 3).

They were obtained from the measurement of the static susceptibility of solutions (comp. V 1). The value for $Fe(CN_6)^{---}$ was taken from measurements on solid $K_3Fe(CN)_6$ (J 1). The large deviations for the last three ions can be understood, because nondiagonal elements [1]) contribute greatly to the magnetic moment of these ions. With these elements components of the local field spectrum are connected, which have a higner frequency than $\nu_0 + 1/\tau_c$, where $1/\tau_c$ is the limit where the local spectrum caused by the Brownian motion drops off rapidly. Thus these non-diagonal elements do not contribute to the nuclear relaxation mechanism, and the μ_{eff} for this process is correspondingly smaller. The extremely small influence of $Fe(CN)_6^{---}$ is probably partly caused by the six CN groups around the iron atom, so that the b is very large. For variations of b for the various ions have not been taken into account in Table III.

Finally we may ask what the influence can be of oxygen gas dissolved in water. The magnetic moment of O_2 is 2.8. The maximum concentration of dissolved O_2 in water at room temperature under 18 % of the atmospheric pressure is 1.5×10^{17} molecules/cc. The relaxation time, due to O_2 alone, could not be smaller than 2.5 sec. The relaxation time in water is therefore determined by the neighbouring protons and the dissolved

[1]) For Co^{++} and $Fe(CN)_6^{---}$ even important deviations from Curie's law have been found.

oxygen. In the determination of the absolute value of the relaxation time (see chapter 3) distilled water was used. As the distillation was not done in vacuo, we have no guarantee that for pure water the relaxation time is not somewhat longer.

We now consider the line width in the solutions. As the correlation time τ_c in paramagnetic solutions is essentially the same as in water and thus $4\pi_0 \nu_0^2 \tau_c^2 \ll 1$, we expect that T_2 is proportional to T_1. This is confirmed by the experimental result in fig. 4. 6. The line width, measured

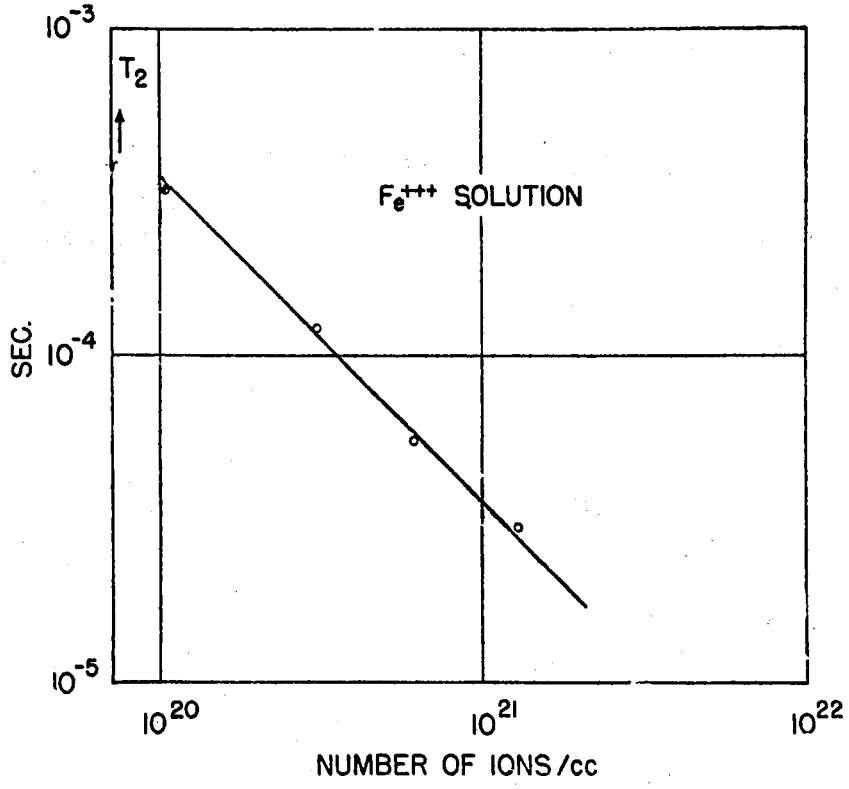

Figure 4. 6.

The line width of the proton resonance in aqueous solutions of $Fe(NO_3)_3$. The quantity T_2 is inversely proportional to the line width, which appears to be proportional to the concentration.

between the points of maximum slope in an assumed Gaussian, is $2/\gamma . T_2$, and is proportional to the concentration. For small concentrations the width is again too narrow to be measured. Comparison of fig. 4. 5 and 4. 6 yields $T_2 = {}^1/_2\ T_1$ or $T_2' = {}^2/_3\, T_1$. The same ratio was found for Cu^{++} solutions and is in good agreement with the value found in glycerin.

It may be well to point out here that the proton resonance in para-

magnetic solutions appears to be shifted, because the field inside the sample is different from the field elsewhere in the gap. The microscopic field inside the sample at the position of the protons always determines the position of the proton resonance. We are interested in the field produced by all paramagnetic ions at the position of a proton and not of all but one at the position of another ion. It is not permissible to put the macroscopic $\vec{H}$ inside the sample into the resonance condition (1.7) One has to take the average microscopic field at the position of the protons. At the same time we might mention another factor which changes slightly the magnetic field experienced by a nucleus, namely the diamagnetism of the surrounding electrons. This effect has been calculated by R a b i and coworkers and is very small for light elements (K 12).

4.1.6. *The resonance of F^{19} and Li^7 in liquids.*

To compare the resonances of F^{19} and H^1 in a liquid compound, a "Freon", $CHFCl_2$, monofluoro-dichloro-methane, was condensed in a glass tube and sealed off. Both the H^1 and F^{19} resonance were narrower than the inhomogeneity in the field. The total intensity of the two lines was the same (within 15 %) so that it was confirmed that F^{19} has the same spin as the proton. The relaxation times were 3.0 sec. for H^1 and 2.6 sec. for F^{19}. The γ_F is 6.5 % smaller than γ_P, but the F^{19} nucleus experiences a somewhat larger local field as its nearest neighbour is the proton in the same molecule, while the proton has in turn the F^{19} nucleus. We should expect on this basis the relaxation times to be the same, as is confirmed within the experimental error.

Experiments were also carried out in solutions of KF. Since the signal to noise ratio drops proportional to the number of nuclei per cc, only very concentrated solutions could be investigated to obtain a sufficiently intense F^{19} resonance. Again the resonance lines are narrow. The result for the relaxation times is shown in fig. 4.7. The decrease in the proton relaxation time can be explained by the increase in viscosity of the concentrated solution. The much more pronounced decrease for fluorine may be an indication that the motion of these ions is more quenched, when one comes very close to the transition point, where the solution changes into the solid hydrate $KF.2H_2O$. A more careful study of the nuclear relaxation might give information about the character of this, and other, transitions. Anticipating the results for solids we can say that in the crystalline $KF.2H_2O$ the lines are wide and that we are in the region where $4\pi^2 \tau_c^2 \nu_0^2 >> 1$.

An interesting substance is also BeF_2, which can be mixed with water

in any proportion. For high concentrations the substance becomes very viscous, and finally goes over into the glasslike, amorphous BeF_2, when no water is present. Preliminary experiments showed that the behaviour of both the proton and the fluorine resonance in $BeF_2 + H_2O$ is similar to that of the proton resonance in glycerin. With increasing viscosity of the mixture the relaxation time first drops to about 10^{-3} sec., then rises

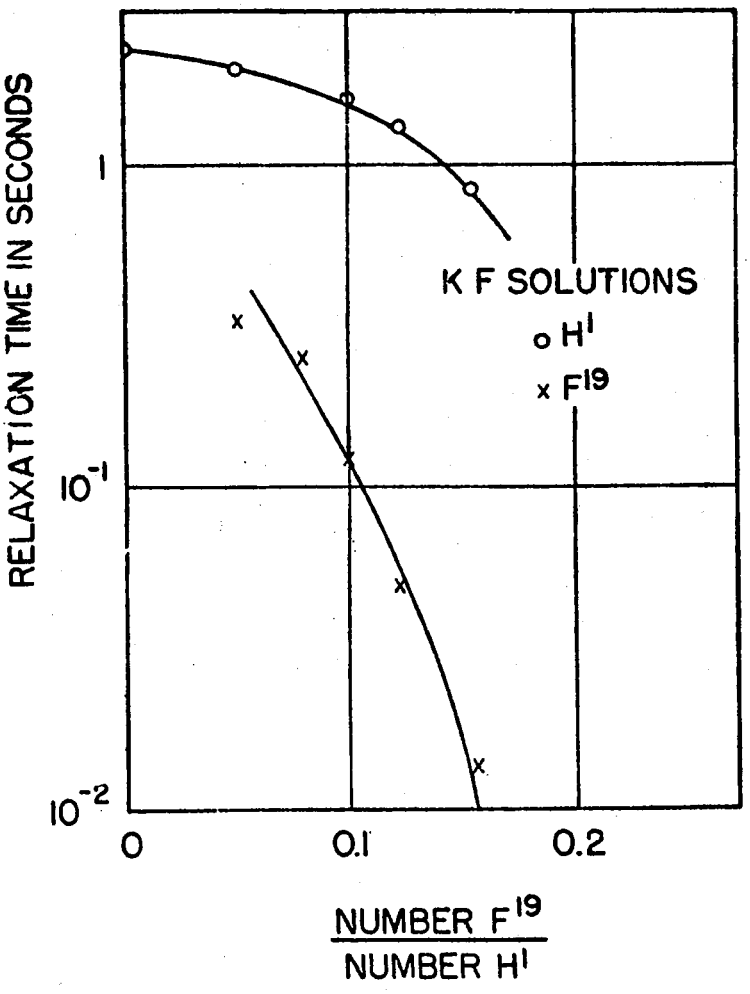

Figure 4.7.

The relaxation time of the proton and fluorine resonance in aqueous solutions of K F of various concentrations.

again to 0.2 sec in pure BeF_2. The line width measured between the points of maximum slope increases from very small values to about 10 oersted in pure BeF_2.

Experiments on the Li^7 resonance were carried out at 14.5 Mc/sec

TABLE IV.

Substance	Number of Li atoms / Number of H atoms	Relaxation time in seconds for Li^7	Relaxation time in seconds for H^1
$LiCl + H_2O$	5.8	1.75	0.4
$LiNO_3 + H_2O$	14	2.7	1.1
$LiNO_3 + H_2O + Fe(NO_3)_3$	8	0.11	0.002[3]
$LiCl + H_2O + CrCl_3$	6.5	0.24	0.009[5]
$LiCl + H_2O + CuSO_4$	6.6	0.18	0.01[3]

in solutions of LiCl and $LiNO_3$. Table IV gives some results. For the solutions without paramagnetic ions the decrease in relaxation time of the proton resonance compared to pure water can be explained by an increase in viscosity of the concentrated solutions. The relaxation time for Li^7 in this case is somewhat longer. The ratio of the local field spectra is given by

$$\frac{\text{Spectral intensity at } Li^7 \text{ nucleus}}{\text{Spectral intensity at proton}} = \frac{(T_1 \gamma^2)_p}{(T_1 \gamma^2)_{Li^7}}$$

Since $\gamma_p^2 / \gamma_{Li}^2 = 6.6$, the local field has a somewhat higher intensity at the Li-nucleus. The cause could be the slower motion of the largely hydrated Li-ion. A more likely explanation however, is, as we shall see later, that the intensity of the magnetic local field is the same, or even smaller but that there is a contribution to the relaxation process from the quadrupole moment of Li^7, which has a spin $I = 3/2$.

The influence of paramagnetic ions is much smaller on Li^7 than on the protons. In the first place the local field spectrum at the Li^7 nucleus will be smaller because the repulsion of two positive ions will make it less likely for them to come close together, and then they have to compete with the quadrupole transitions (cf. chapter 5). At the conclusion of this paragraph we direct the attention of the reader to the results found by other investigators (B 2, B 7, R 5), which seem to be in agreement with the general ideas, here proposed. Especially we might mention the experiment in liquid hydrogen by Rollin (R 6).

4. 2. *The relaxation time and line width in gases*

4. 2. 1. *Hydrogen.*

The only experiment of nuclear magnetic resonance (P 6) in gases which has been reported was performed with hydrogen gas at room temperature between 10 and 30 atmospheres of pressure. The accuracy

was poor, as the density of the nuclei is low. It was found that the line is narrow (< 0.15 oersted) and that the relaxation time at 10 atmospheres $T_1 \approx 0.015$ sec. with an indication that T_1 increases with increasing pressure. We shall now investigate what the theory predicts for this case.

The local field at the position of a proton in an H_2-molecule in a volume of hydrogen gas consists in the first place of the contribution connected with the rotational moment $\vec{J}$ of the molecule and the magnetic moment of the other proton. According to P a u l i's exclusion principle the spins of the two protons can only be parallel, if the electronic wave function is antisymmetric (J odd, orthohydrogen), and only antiparallel, if the electronic wave function is symmetric (J even, parahydrogen) The transitions from the ortho- to the para-state in hydrogen gas are extremely rare. Furthermore, if the system is in thermal equilibrium at room temperature, 13 % of the H_2 molecules have $J = 0$, 66 % have $J = 1$, 12 % have $J = 2$ and 9 % have $J = 3$. We ignore for the sake of the simplicity transitions from $J = 1$ to $J = 3$. We assume that the rotational angular momentum of orthohydrogen is a constant of the motion. The total nuclear spin $I = I_1 + I_2$, $I = 0$ for parahydrogen, $I = 1$ for orthohydrogen. Only orthohydrogen will show nuclear resonance. At room temperature equilibrium the ratio of molecules in ortho- and para-states is as 3 : 1. So the total intensity of the nuclear magnetic absorption line is proportional to $\frac{3}{8} NI(I + 1)$ This is equal to $(\frac{1}{2} \cdot \frac{3}{2})N$. Thus the total intensity of the line of orthohydrogen is the same as if all N protons were uncoupled in hydrogen atoms.

If the molecule is placed in a strong magnetic field, in zero approximation not only I and J, but also m_I and m_J are constants of the motion. We first consider the interaction of the nuclear spin with the rotational moment. The perturbation term in the Hamiltonian is given by

$$H_{op} = \gamma \hbar H' \vec{I} \vec{J}$$

$$= \tfrac{1}{2} \gamma \hbar H' \{(I_x + i I_y)(J_x - i J_y) + (I_x - i I_y)(J_x + i J_y)\} + \gamma \hbar H' I_z J_z \tag{4.31}$$

From R a b i's experiments (K 3) follows the value of H'; the magnetic field at the position of the protons produced by the rotation of the molecule is 27 oersted. With (4.31) we can once more repeat the reasoning explained in sections 2.4 and 2.5 in order to calculate the relaxation time. If the quantisation of J were fixed, that is if m_J did not change during collisions, we would have no transitions in m_I For the

first two terms on the left hand side in (4. 31), which have non-diagonal elements in m_I, involve also a change in m_J. But the collisions in the gas will change m_J and we can assume that after each collison m_J has equal chance for any of its $2J + 1$ values. As the distribution of the collisions in time of a given molecule, measured from the time of the preceding collision, is given by $\frac{1}{\tau_c} \exp - t/\tau_c$, where τ_c is the mean collision time in the gas, we have a Fourier spectrum for m_J and thus for $J_x - i J_y$. The intensity of the spectrum of the latter is with (4. 9)

$$J(\nu) = \frac{4J(J+1)}{3} \frac{\tau_c}{1 + 4\pi^2 \nu^2 \tau_c^2} \tag{4.32}$$

From this and (4. 31) we obtain a relaxation time

$$1/T_1 = \frac{2\tau_c}{1 + 4\pi^2 \nu_0^2 \tau_c^2} H'^2 \gamma_p^2 \frac{J(J+1)}{3} \tag{4.33}$$

with

$$\tau_c = 1{,}4/\, v\, \sigma\, N \tag{4.34}$$

The number of molecules per cc, proportional to the pressure, is denoted by N, σ is the collision cross section, v is the average velocity of the molecules.

To (4. 33) we have to add the contribution of the spin-spin interaction, which is represented by the perturbation term

$$H_{op}'' = \frac{-\gamma_p^2 \hbar^2}{r^3} \left[3 (\vec{I}_1 . \vec{n})(\vec{I}_2 . \vec{n}) - \vec{I}_1 . \vec{I}_2 \right] \tag{4.35}$$

where $\vec{n}$ is the unit vector pointing from one proton to the other, and r is the distance between them. The expression (4. 35) can be transformed to one which only contains constants and the operators $\vec{J}$ and $\vec{I} = \vec{I}_1 + \vec{I}_2$.

$$H_{op}'' = \gamma_p^2 \hbar^2 \frac{1}{r^3} \frac{I(I+1) + 4\, I_1 (I_1 + 1)}{(2I-1)(2I+3)(2J-1)(2J+3)} \left[3\, (\vec{I}.\vec{J})^2 + {}^3/_2 \vec{I}.\vec{J} - \vec{I}^2 . \vec{J}^2 \right] \tag{4.36}$$

In order to find the contribution of this interaction to the relaxation process, we have to write the operator between square brackets in the

m_I, m_J representation. R a b i and collaborators (K 4) found that this operator is equal to

$$
\begin{aligned}
&{}^1/_2\,[3J_z^2 - J(J+1)]\,[3I_z^2 - I(I+1)] + && \Delta m_I = \Delta m_J = 0\\
&+ {}^3/_4\,[J_z(J_x + iJ_y) + (J_x + iJ_y)J_z]\,[I_z(I_x - iI_y) + (I_x - iI_y)I_z] \\
&\qquad - \Delta m_I = + \Delta m_I = 1\\
&+ {}^3/_4\,[J_z(J_x - iJ_y) + (J_x - iJ_y)J_z]\,[I_z(I_x + iI_y) + (I_x + iI_y)I_z] \\
&\qquad \Delta m_I = - \Delta m_J = 1\\
&+ {}^3/_4\,(I_x + iI_y)^2\,(J_x - iJ_y)^2 && \Delta m_I = - \Delta m_J = 2\\
&+ {}^3/_4\,(I_x - iI_y)^2\,(J_x + iJ_y)^2 && - \Delta m_I = \Delta m_J = 2
\end{aligned}
\qquad (4.37)
$$

The matrix elements can be written down immediately with the rules of matrix multiplication and the expressions (1,1), (1,2) and (1,3). The matrix elements of (4. 37) with $\Delta m_J = 1$ and 2, combined with the components at ν_0 and $2\nu_0$ of the frequency spectrum of the corresponding terms in m_J give an expression for $1/T_1$, which must be added to (4. 33).

We write down the final result, first derived by S c h w i n g e r for the case realized in practice that τ_c is short compared to the Larmor period $1/\nu_0$.

$$
(1/T_1)_{H_2\,-\,\text{gas}} = 2\,\tau_c\,\gamma_p^2\left[\frac{1}{3}H'^2\,J(J+1) + 3\,H''^2\,\frac{J(J+1)}{(2J-1)(2J+3)}\right] \qquad (4.38)
$$

where $H'' = \dfrac{1}{r^3}\,{}^1/_2\gamma\hbar$ is the effective field from one proton at the position of the other. From R a b i's experiments (K 3) follows $H'' = 34$ oersted. In (4. 38) we have already asumed $4\pi^2\nu_0^2\tau_c^2 \ll 1$. This is always fulfilled under practical conditions. The opposite case $4\pi^2\nu_0^2\tau_c^2 \gg 1$ would occur at pressures of 1 mm Hg or less, where the signal is much too small to be detected. From (4. 38) and (4. 34) it follows that the relaxation time T_1 is proportional to the pressure. Substituting numerical values $\gamma_p = 2.7 \times 10^4$, $J = 1$, $\tau_c = 10^{-11}$ sec. (Handbook of Chemistry and Physics) for a pressure of 10 atmospheres, we find $T_1 = 0.03$ sec, which is in agreement with the experimental value.

The line width can be calculated on similar lines as we did in chapter 2 from (4.31) and (4.32). As in liquids we find again that T_2 is of the same order as T_1, so that the resonance line should be very narrow. As T_2 is proportional to T_1, the line width should be inversely proportional to the pressure. We can speak of "pressure-narrowing" of the nuclear resonance line in H_2-gas.

The conclusion is: The magnetic interactions in the H_2-molecule give rise to a fine structure of the radiofrequency spectrum in Rabi's molecular beam method (K 3). Combined with the collisions in the gas sample for pressures > 10 mm Hg, as used in Purcell's method, they give rise to a relaxation mechanism and the local fields average out to a single very narrow line.

We have not considered the influence of the other molecules during a collision on the relaxation time. In the next paragraph we shall see, that this effect can usually be neglected in H_2-gas.

4.2.2. *Helium.*

An entirely different state of affairs occurs in the interesting case of He^3 gas. The atoms are in an S-state. The only perturbation is brought about during the collisions by the nuclear magnetic moment of the colliding atom. Unlike in hydrogen, here the influence of the other molecules is the only effect. Suppose that the He^3 nucleus has the set of eigenfunctions ψ_n in the constant field H_o. We ask for the chance that the perturbation by a collision brings the system from the initial state i with energy E_i to the final state f with energy E_f. The perturbation method, which may be applied, if the chance in one collision is small compared to unity, gives for the probability to find the system in state f after the collision

$$w_f = \frac{\sin^2 \frac{E_f - E_i}{\hbar} t}{(E_f - E_i)^2} \left| (f \mid H_{op} \mid i) \right|^2 \qquad (4.39)$$

We cannot say precisely, what is going on during the collision. But the order of magnitude of the matrix element of the perturbation operator between the initial and final state will be the same as that of the interaction energy $\approx \gamma_1 \gamma_2 \hbar^2 d^{-3}$. The colliding particles have magnetogyric ratio's γ_1 and γ_2 and d is the distance of closest approach between the moments during the collision. The time t, during which a strong inter-

action takes place. is probably $\approx 10^{-16}$ sec, at any rate $t << \hbar/E_f - E_i \approx 10^{-8}$ sec. We can therefore write instead of (4.39)

$$w_f = \gamma_1^2 \gamma_2^2 \hbar^2 t^2 d^{-6} \tag{4.40}$$

If v is the relative velocity of the colliding particles, we have $t \approx d/v$. We then multiply by the number of collisions per second $1/\tau_c$ and find for the relaxation time

$$1/T_1 = 2 \gamma_1^2 \gamma_2^2 \hbar^2 d^{-4} v^{-2} \tau_c^{-1} \tag{4.41}$$

Substituting numerical values for He^3 at room temperature and atmospheric pressure, $v = 1.4 \times 10^5$ cm/sec., $\tau_c = 2 \times 10^{-10}$ sec, $d = 2 \times 10^{-8}$ cm, $\gamma_1 = \gamma_2 = 2.4 \times 10^4$, we find $T_1 = 10^6$ sec. In order to avoid saturation during the resonance measurements it is therefore necessary to admit oxygen gas. The magnetic moment of an O_2 molecule is about 10^3 times as large as of a He^3 atom.

Taking $\gamma_1 = 2.4 \times 10^4$, $\gamma_2 = 2.8 \times 10^7$, $d = 2.5 \times 10^{-8}$ cm, $\tau_c = 10^{-10}$ sec we find for the relaxation time of He^3 resonance, if the partial pressure of the oxygen is one atmosphere, $T_1 \approx 1$ sec. From (4.41) and (4.35) it follows that in this case the relaxation time is inversely proportional to the pressure. Strictly speaking we ought to add a term which is similar to (4.41) to (4.38) in the case of H_2. From the order of magnitudes, resulting from (4.38) and (4.41), we see that such a term in pure H_2 gas is completely negligible for pressures below 10^3 atmospheres. For O_2 pressures of 10^2 atmospheres, however, it is an important contribution. In general we can say that most gases, consisting of molecules, will behave like hydrogen and show the "anomalous" pressure-narrowing. The noble gases, consisting of atoms in an S-state, will behave like He^3 and have pressure broadening.

We shall now derive the relation between T_1 and T_2 for the case of He^3. At the same time we obtain an independent derivation of the saturation formula (2.64). The He-nuclei can be considered as completely free most of the time, but during each collision there is a small chance for the nucleus to change its orientation. The probability $w = \frac{1}{2}T_1$ for such a transition is given by (4.40). If a radio frequency field H_1 is switched on at $t = 0$, the free nuclei will oscillate between the upper and lower state according to Rabi's formula (2.11), until the situation is interrupted by a thermal transition. We start out with the system of nuclei in thermal equilibrium. The situation can be described by the number of surplus nuclei, originally $+ n_o$ in the lower state, oscillating

between $+ n_o$ and $-n_o$, while the collisions tend to restore the equilibrium value $+ n_o$. The probability that this is achieved in the time interval between t and $t + dt$ is given by $1/T_1 \exp(-t/T_1)\, dt$, as T_1 is the average time and the distribution of gas kinetic collisions in time is given by an exponential. The average energy dissipated from the spin system and absorbed during the collisions is

$$n_0 h \nu_0 \int_0^\infty w_{1/2,-1/2} \frac{1}{T_1} e^{-t/T_1} dt \tag{4.42}$$

where $w_{1/2,-1/2}$ is the probability that the surplus nuclei are in the upper state at time t (2.11).

After the equilibrium has been restored, the process repeats itself. In our description we have artificially broken up the natural process into self repeating steps. In reality the individual nuclei each have a chance to make transitions both up and down, with a preference for the latter. The energy absorbed per second, which must be supplied by the radio frequency field, is obtained if we multiply (4.42) by $1/T_1$ the number of times that the process is repeated per second. The integration over t can be evaluated by partial integrations. The absorbed power P is given by

$$P = n_0 h \nu_0^3 \sin^2 \vartheta \frac{2\pi^2 T_1}{1 + 4\pi^2 T_1^2 (\nu^2 + \nu_0^2 - 2\nu\nu_0 \cos\vartheta)} \tag{4.43}$$

Since always $H_1/H_o << 1$, we can put $\sin\vartheta \approx H_1/H_o$ and $\cos\vartheta \approx 1 - H_1^2/H_0^2$, $\gamma = 2\pi\nu_0/H_0$. Near resonance $\nu \approx \nu_0$ we then have

$$P = \tfrac{1}{4} n_0 h \nu_0 \gamma^2 H_1^2 \frac{2T_1}{1 + T_1^2(\omega - \omega_0)^2 + \gamma^2 H_1^2 T_1^2} \tag{4.44}$$

which on comparison with (2.71) and (2.66) appears to be the Bloch formula with $T_1 = T_2$.

It is interesting to apply the noise formula (3.21) to the case of He^3 and see what the minimum detectable amount is. It is not justified, however, to put in that formula $T_1 = T_2$, since the line width will always be determined by the inhomogeneity in the field. Using 10 atmospheres of O_2 we have $T_1 = 10^{-1}$ sec and we can take $T_2/T_1 \sim 10^{-2}$.

Substituting for q, λ and F each $\frac{1}{2}$ of their ideal values of unity and taking $Q = 10^2$, $\gamma = 2.4 \times 10^4$, $H_o = 10^4$, we find that 1 cc of He^3 gas at room temperature and atmospheric pressure would give a signal to noise ratio about 5, if the indication time of the meter is one second. In practice it would be very hard to find such a signal of such an extre-

mely narrow line. One would have a better chance by searching for the moment in liquid He^3 at 1° K.

Added in the proof:

Very recently A n d e r s o n (A 5) succeeded in measuring γ_{He^3} in a mixture of He^3 and O_2, each at a partial pressure of 10 atmospheres.

4. 3. *The relaxation time and line width in solids.*

4. 3. 1. *Solids, to which the theory for liquids is applicable.*

In some solids there seems to be sufficient freedom of motion (S 5)

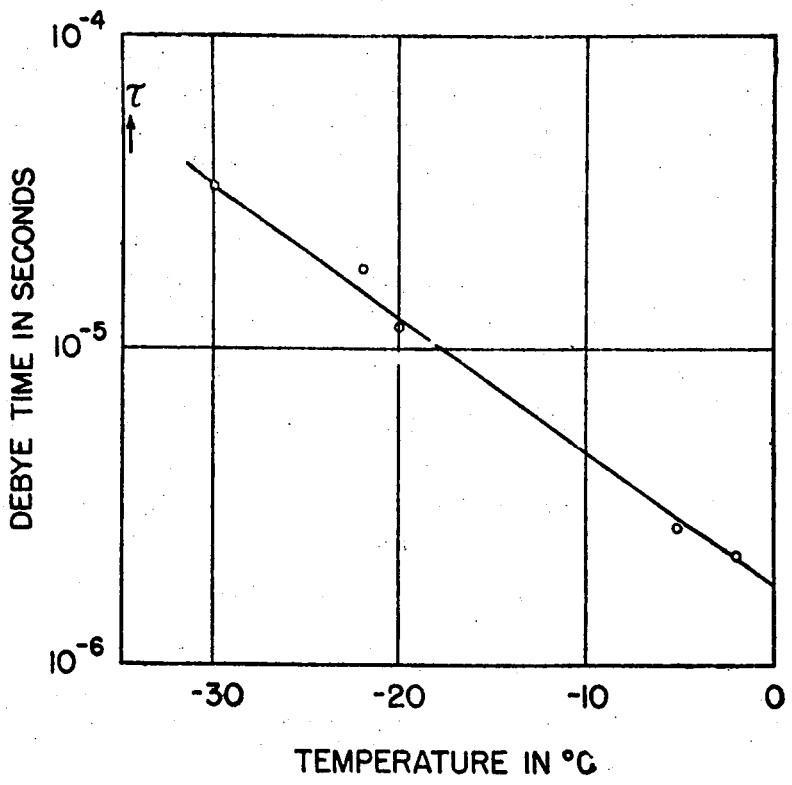

Figure 4. 8.

Values of the dielectric relaxation time τ defined by Debye, in ice at various temperatures. The points, indicated in the graph, are obtained from measurements of the anomalous dielectric dispersion in ice by Wintsch.

for the particles, that we can apply the same theory as in liquids. This state of affairs was already evident from the dielectric dispersion of the D e b y e type occurring in solids (D 2). The typical example is ice, of which we show the D e b y e time τ as a function of temperature in fig. 4.8.

The data are calculated from measurements by Wintsch (W 5) Of course, the molecules are not as free as in water; τ is about 10^6 times larger than in water. We expect then that the correlation time τ_c in the local field spectrum has increased by about the same factor, so that the relaxation time in ice will behave in the same way as in glycerin at low temperatures where $4\pi^2\nu_0^2\tau_c^2 >> 1$. In fig. 4. 9 T_1 in ice between —2° C and —40° C is shown as a function of the Debye

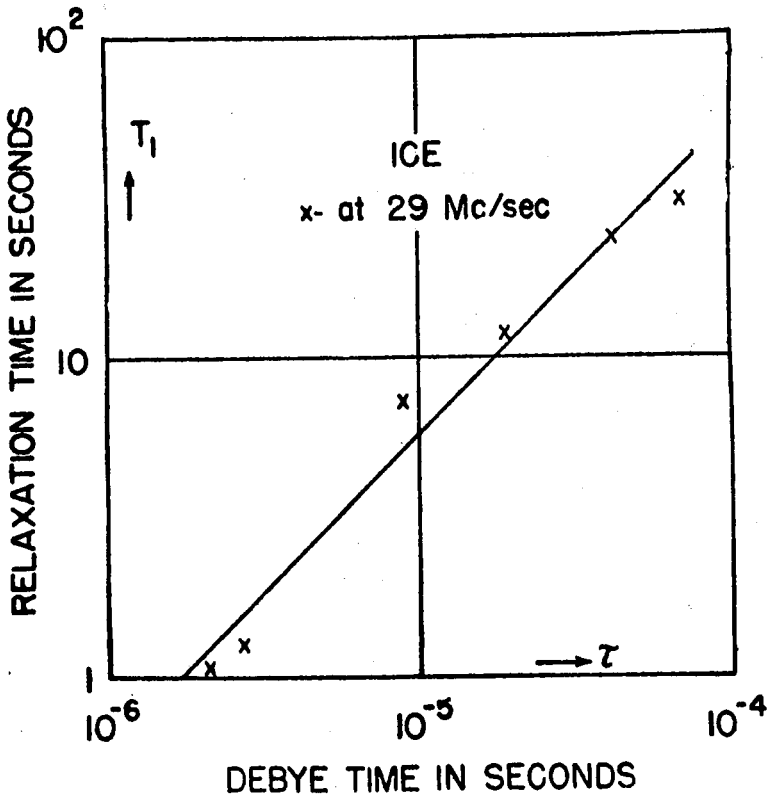

Figure 4. 9.

The relaxation time of the proton resonance in ice between — 2° C and — 40° C, plotted against the Debye time τ. The line drawn through the experimental points, makes an angle of 45° with the positive X-axis.

time, to which τ_c is proportional. The graph apparently confirms the ideas set forth in the beginning of this chapter. The straight line drawn through the points makes an angle of 45° with the x-axis. Unfortunately we were not able to investigate the resonance in ice at 4.8 Mc/sec, because the signal to noise ratio became too low in that case. We would

expect, of course, the relaxation time to be shorter, but having the same dependence on τ

Measurements of the line width yield values of T_2, which are shown in fig. 4.10. The drawn line is the theoretical curve computed from (4.22). So here τ_c becomes so large that we approach the asymptotic value of the line width which should be, according to the graph, about 16 oersted for a Gaussian. This is in good agreement with the value calculated from the crystal structure of ice (B 15), assuming that the

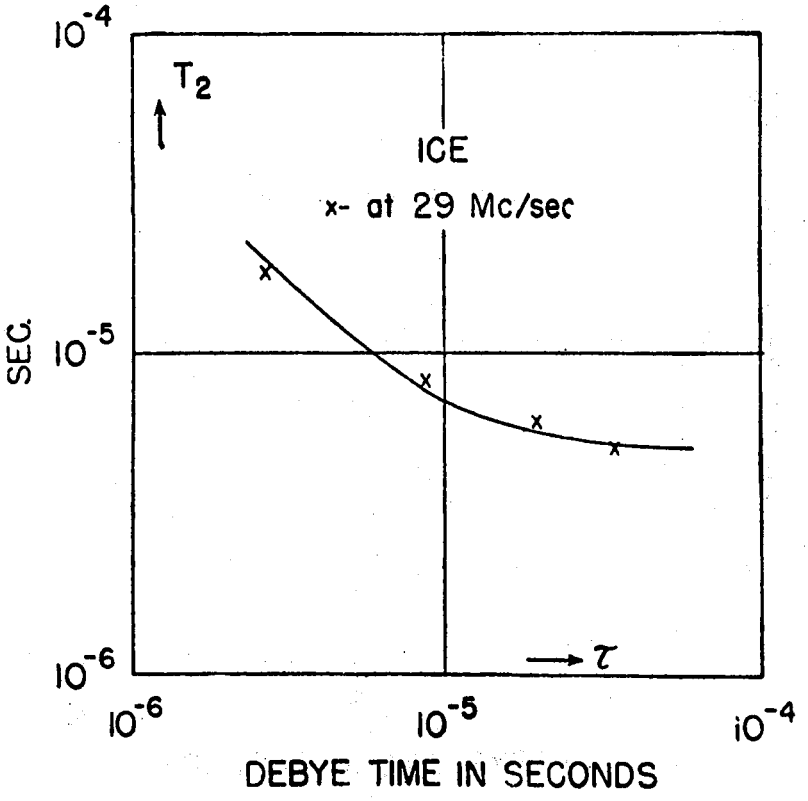

Figure 4.10.

The line width of the proton resonance in ice between — 2° C and — 40° C. The theoretical curve (4.22) for the quantity T_2, which is inversely proportional to the line width, is drawn through the experimental points.

nuclei are at rest. In ice a translational motion of the molecules in a viscous surrounding is apparently excluded. One might assume with Debye a hindered rotation of the H_2O molecules in the crystalline structure, although a more recent picture by Onsager suggests, that chains of lined up dipoles will reorient themselves at the positions, where

there are misfits with other chains. Either picture will produce the required fluctuations in the local magnetic field and will only affect the proportionality constant between τ and τ_c. The best explanation for the fluctuations in the local field are perhaps the transitions between the two available positions for the proton in the O-H-O bond, as proposed by Pauling (P 8). For comparison the results for alcohol, glycerin and ice at 29 Mc are shown together in fig. 4.11. For glycerin we can

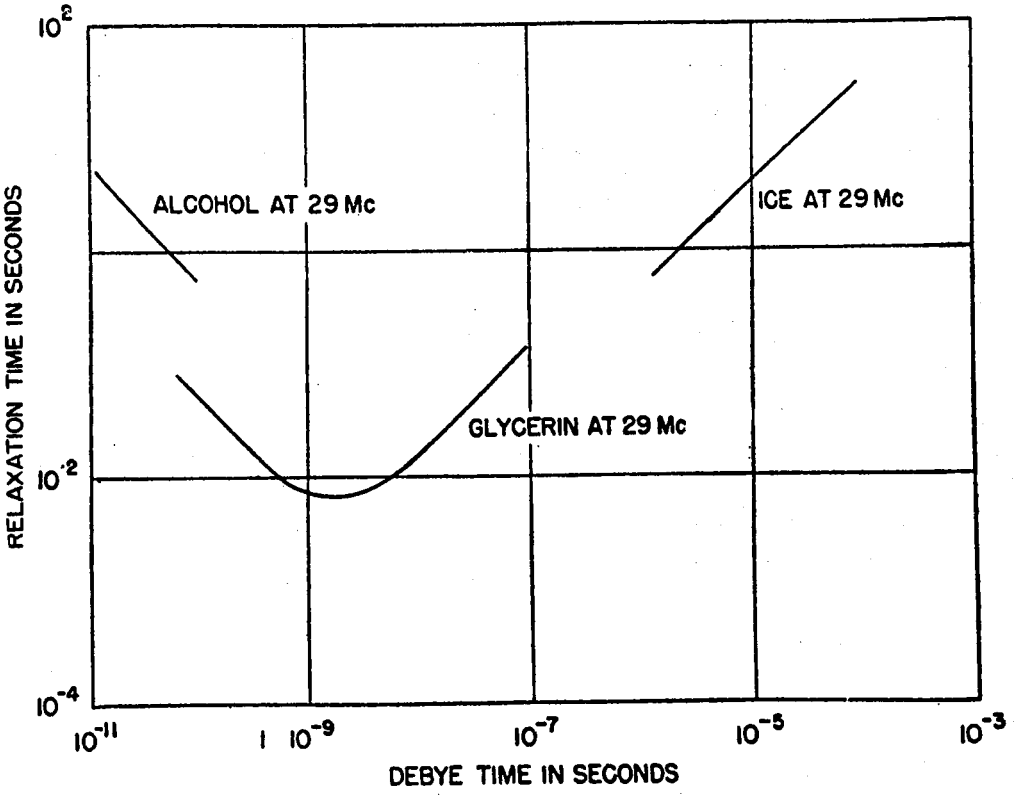

Figure 4.11.

The relaxation time T_1 of the proton resonance in ethyl alcohol, glycerin and ice at 29 Mc/sec between $-40°$ C and $+60°$ C.

determine the ratio τ/τ_c from comparison of the experimental result of the minimum in the curve with formula (4.25). We find $\tau_c = 2\,\tau$. Then we must have for alcohol $\tau_c = 0.2\,\tau$ and for ice $\tau_c = 0.8\,\tau$. These results are very satisfactory and must be considered as additional proof for our theory.

We now give a very brief account of what can be expected in other solids with some preliminary experimental results to confirm our view. Much more detailed investigations have to be carried out to refine the

following global exposition. In hydrated paramagnetic salts like $CuSO_4 . 5\ H_2O$ the field at the position of a proton will fluctuate, because the electron spins of the Cu^{++} ion change their quantisation with respect to H_o at the rate of the short electronic relaxation times ρ, to which we must put equal the correlation time τ_c. The proton resonance in $CuSO_4 . 5\ H_2O$ and $CoSO_4 . 7\ H_2O$ show line widths of only 12—14 oersted, while the instantaneous value of the internal fields in these paramagnetic salts is several hundred oersted. This can be explained by the short τ_c. The high intensity of local field, arising from the electronic moments, makes the relaxation time so short ($< 3 \times 10^{-4}$ sec), that we could not saturate the proton line.

In paraffin the relaxation time was found to be 0.01 sec. and the line width 4.5 oersted. These data are in agreement with the estimates of other investigators. In molten paraffin the line is narrow. Paraffin behaves again in a similar way as glycerin. In the solid state there still must be an appreciable opportunity for motion, either rotation or twisting or realignment, of the molecules. About the same as for solid paraffin holds for the F^{19} resonance in teflon. This carbon fluoride compound can be considered for our purpose as paraffin, in which the protons are replaced by F^{19} nuclei.

For the proton resonance in NH_4Cl a relaxation time of 0.12 sec. at + 20° C and 0.015 sec at — 20° C was found. The line width at both temperatures was 4 oersted. These results can probably be explained by a hindered rotation of the NH_4 tetrahedron (S 5).

Very interesting experiments have been carried out by Bitter (B 2, A 1), who observed a sharp transition point in the line width of the proton resonance in solid CH_4, at the same temperature where there is known to be a transition point in the rotational degree of freedom of the molecule. The attention of the reader is also called to the measurements at very low temperatures by Rollin and collaborators (R 7). Possibly the rotation of the hydrogen molecule can be helpful in explaining the experimental results in solid ortho-hydrogen.

4. 3. 2. *Ionic crystals; the influence of the lattice vibrations.*

4. 3. 2. 1. *The relaxation time.*

We now take up the question of the relaxation time in those crystals, in which lattice vibrations are the only motion. For this case the theory of the relaxation time had been worked out by Waller (W 1, H 2), who considered the interaction of the magnetic moments with the lattice vibrations. We shall show that our procedure, which gave

the new results for liquids and gases, is essentially aequivalent to W a l l e r 's considerations, when it is applied to crystals.

For the lattice vibrations we shall adopt the same simplified picture, which D e b y e introduced in his theory of the specific heat of solids (S 5). According to this picture there is an isotropic distribution of lattice oscillators. In the volume V_c of the crystal there are $4\pi\nu^2 V_c/c^3$ oscillators for one direction of polarisation in the frequency range ν, $\nu + d\nu$.

Here c denotes the velocity of propagation of elastic waves in the crystal, which is taken to be the same for longitudinal and transverse modes.

This formula is valid up to the frequency ν_m determined by the equation

$$\int_0^{\nu_m} 12\pi\nu^2 V_c c^{-3} d\nu = 3N \tag{4.45}$$

For $\nu > \nu_m$ there are no lattice oscillators; (4.45) expresses that the total number of oscillators is equal to the degrees of freedom of the system of N atoms.

We first consider the contribution of one neighbour j to the Fourier spectrum of $\sum_j \sin\vartheta_{ij}\cos\vartheta_{ij}\, e^{i\varphi_{ij}}/r^3_{ij}$.

We take the z-axis in the direction of H_o. The radius vector $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ connecting the equilibrium positions of the two nuclei makes an angle ϑ with the z-axis. The displacement $\vec{u}_i$ of the i^{th} nucleus from its equilibrium position by the lattice vibrations is

$$\vec{u}_i = \sum_{\nu_k} \vec{A}_k \sin 2\pi\nu_k (t - r_i/c + \varphi_k) \tag{4.46}$$

The relative displacement of the i^{th} and j^{th} nucleus for waves propagating in the direction of $\vec{r}_{ij}$

$$\triangle \vec{u}_{ij} = r_{ij} \sum_{\nu_k} \frac{2\pi\nu_k}{c} \vec{A}_k \cos 2\pi\nu_k (t - r_i/c + \varphi_k) \tag{4.47}$$

since $\lambda_k = c/\nu_k >> r_{ij}$. The variation in

$$F_1 = \sin\vartheta_{ij}\cos\vartheta_{ij}\, e^{i\varphi_{ij}}/r^3_{ij}$$

can be expressed by a Taylor series

$$\Delta F_1 = \frac{\partial F_1}{\partial r}\,\Delta r + \frac{\partial F_1}{\partial \vartheta}\,\Delta \vartheta + \frac{\partial F_1}{\partial \varphi}\,\Delta \varphi + {}^1/_2\,\frac{\partial^2 F_1}{\partial r^2}\,(\Delta r)^2 + \ldots . \quad (4.48)$$

We dropped the subscripts i and j. For longitudinally polarised waves we have only changes in r; for these $\Delta r = (\Delta u)$ long

The direction of polarisation of one of the transverse modes is taken in the plane through $\vec{r}_{ij}$ and the z-direction. For this mode we have $r_{ij}\,\Delta\vartheta = (\Delta u)$ tr. I. For the second transverse mode we have $\mathrm{tg}\,\Delta\varphi = (\Delta u)$ tr. II$/r \sin\vartheta$. If $\Delta u \ll r \sin\vartheta$, we may write $r \sin\vartheta\,\Delta\varphi = (\Delta u)$ tr. II. Only for very small ϑ this relation is not satisfied. For this last mode and very small values of ϑ the expansion (4.48) of F is not suitable.

To find the intensity $J_1(\nu)$ of the spectrum of F_1, we have to determine the sum of the mean square deviations $(\Delta F_1)^2$ in each of the independent waves in the frequency interval ν, $\nu + d\nu$.

We can find an expression for the amplitude A_k of each wave by means of the aequipartition theorem. Each lattice vibrator has an energy $h\nu \Big/ \left(e^{\frac{h\nu}{kT}} - 1\right)$ For small ν or large T this is equal to kT. Let M be the mass of the crystal, $\varrho = M/V_c$ the density. The æquipartition theorem can be written with (4.46) as

$$|A|^2 = \frac{h\nu}{2\pi^2\nu^2 M\left(e^{\frac{h\nu}{kT}} - 1\right)} \approx \frac{kT}{2\pi^2\nu^2 M} \quad (4.49)$$

We use the last approximation for the three first order terms in (4.48). These terms can be treated independently, as they belong to different directions of polarisation. By squaring each of them and multiplying with the number of oscillators, we find with (4.47, 4.48, 4.49) for the intensity of the spectrum of the first orders terms

$$J_1(\nu) = \frac{4\pi\nu^2 V_c}{3c^3}\,\frac{kT}{M}\,\frac{1}{r^6_{ij}}\left[9\sin^2\vartheta_{ij}\,\cos^2\vartheta_{ij} + \cos^2 2\vartheta_{ij} + \cos^2\vartheta_{ij}\right] \quad (4.50)$$

J_1''

A factor ${}^1/_3$ is inserted, because the two directions of wave propagation perpendicular to $\vec{r}_{ij}$ do not contribute, as in those waves the two nuclei have the same phase.

Now we can sum (4.50) over all nuclei $j \neq i$. This is legitimate,

although there are fixed phase relations between the deviations of the nuclei in one wave. For the quantisation of the various nuclei is independent, so that their fields aid or counteract at random. If we do not have a single crystal we can average over the angle ϑ, which yields a factor 2 for the expression between brackets in (4.50). The contribution of the Z nearest neighbours at a distance a will be the most important. Applying (2.53) we find for the relaxation time

$$1/T_1 = 4\pi\gamma^4\hbar^2 I(I+1) Z k T \nu_0^2/\varrho c^5 a^6 \qquad (4.51)$$

This result is essentially the same as Waller's formula 51 (W 1, p. 386), derived for the transition probability of electronic spins with $I = \frac{1}{2}$. If we take $h\nu_0/kT << 1$, $\gamma = 2\mu/\hbar$ and multiply Waller's result by 2 to get $1/T_1$, we find that our numerical factor is $12\pi/5$ times larger. This difference could probably be explained by noting that Waller used a more detailed picture for the lattice vibrations in a simple cubic lattice. He followed Born's representation of coupled harmonic oscillators. Furthermore Waller quantised the lattice oscillators. To Waller's result and our formula (4.51) a contribution of the processes in which two spins flop simultaneously should be added. It will appear to be much more important, however, to consider the influence of the second order terms in (4.48). On substitution of (4.47) into these terms we see that products of two harmonic functions are present and terms with frequency ν_0 in the expression of ΔF_1 occur as the sum or the difference of two frequencies ν_1 and ν_2. The whole spectrum of the lattice vibrations is important for the second order spectral intensity of F. Since the density of oscillators near the upper limit ν_m is so much higher than at the frequency ν_0, it will turn out that the second order contributions are larger than the first order effects. We find by the same argument which led to (4.50) for the contribution of the first second order term in (4.48) to the spectral intensity

$$J_1''(\nu) = \frac{1}{18}\sin^2\vartheta_{ij}\cos^2\vartheta_{ij}\frac{3^2\cdot 4^2}{4 r_{ij}^6 c^4}\int_{\substack{0 \\ \nu_1 \pm \nu_2 = \nu_0}}^{\nu_m}\int_0^{\nu_m}\frac{4\pi^2\nu_1^2 V_c\, h\nu_1}{Mc^3\left(e^{\frac{h\nu_1}{kT}}-1\right)}\cdot\frac{4\pi^2\nu_2^2 V_c\, h\nu_2}{Mc^3\left(e^{\frac{h\nu_1}{kT}}-1\right)}\,d\nu_1\,d\nu_2$$

and, since $\nu_0 << \nu_m$,

$$J_1''(\nu) \approx \frac{32\pi^2 h^2}{\varrho^2 c^{10}}\frac{\sin^2\vartheta_{ij}\cos^2\vartheta_{ij}}{r_{ij}^6}\int_0^{\nu_m}\frac{\nu'^6}{\left(e^{\frac{h\nu'}{kT}}-1\right)^2}\,d\nu' \qquad (4.52)$$

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Since all frequencies up to ν_m are involved, we cannot make use of of the condition $x = h\nu'/kT << 1$, unless the temperature T is large compared to the Debye temperature $\Theta = h\nu_m/k$ of the crystal. The relaxation time, determined by this second order process, is by the same arguments which led to (4.51),

$$1/T_1 = \frac{8}{5}\gamma^4 Z I(I+1)\frac{(kT)^7}{\varrho^2 c^{10} a^6 h^3}\int_0^{\Theta/T}\frac{x^6}{(e^x-1)^2}\,dx \qquad (4.53)$$

To (4.53) should be added the result of the other second order terms and the contribution of the double processes, in which two spins make a simultaneous transition. The numerical factor in (4.53) would become somewhat larger. But as it is, it is already $18\pi^2 \times 192/245$ larger than in Waller's formula 56 (p. 388) for the quantised lattice oscillators. In the language of quantummechanics we can say that to (4.53) correspond transitions of the nuclear spin accompanied by the emission of a phonon and the absorption of another in the lattice. One could develop (4.48) to the third order terms, etc. It turns out that the contribution of the successive higher terms decreases as $kT\nu_m^3/\varrho c^5 \approx 10^{-2}$; so they can be neglected.

We see from (4.51) and (4.53) that the first order transition probability goes as T, the second order one as T^2 for $\Theta/T \approx 1$ but as T^7 for $\Theta/T >> 1$. At room temperature the second order terms are more important. Substituting numerical values $\varrho = 2$, $c = 2\times 10^5$, $\nu_0 = 3\times 10^7$, $a = 2\times 10^{-8}$, $Z = 6$, $\gamma = 3\times 10^4$, $T = 300°$, $\Theta << T$ we find that (T_1) first order $\approx 10^{14}$ sec and (T_1) second order $\approx 10^3$ sec.

It was a surprise that, while Waller's theory predicted such long relaxation times for the nuclear magnetic resonance, the first experimental results gave much shorter times (10^{-2} sec in paraffin). We have shown that in many solids the spectral intensity of the local field is caused by other motions than the lattice vibrations and that so many observed relaxation times could be explained. In ionic crystals like CaF_2, however, one would expect Waller s theory to be applicable. Nevertheless the relaxation time for the F^{19} resonance in a single crystal of CaF_2 appeared to be 8 sec. Relaxation times of the order of one second were also found in powdered AlF_3 and NaF, and by other authors in Li F. There are some indications that impurities and lattice defects play an important role in the relaxation process of these crystals (Compare the note at the end of this chapter).

4. 3. 2. 2. *The line width.*

The line width must be calculated from the components near zero frequency in the spectrum of $F_0 = \sum_{ij} (1 - 3\cos^2 \vartheta_{ij})/r^3_{ij}$. In the evaluation we can safely neglect the small and rapid lattice vibrations and assume that the nuclei are at rest. For this static problem the line width is given by (2. 36). It should be independent of the temperature, but vary with the orientation of the axes of a single crystal with respect to the direction of $\vec{H}_o$. Experiments (P 5) with a single crystal of Ca F_2 gave results for the line width in accordance with (2. 36) applied to the simple cubic lattice of F^{19} nuclei, the Ca ions having no magnetic moment. A detailed investigation of the line width in solids with special attention to the line shape was made by P a k e (P 1). In many compounds the same element can occur in more than one position in the unit cell of the crystal. When these positions are not aequivalent with respect to the internal magnetic field, one should distinguish more than one relaxation time and line width at the resonance of those nuclei. It is of no use, however, to discuss the situation in crystalline solids in detail, before more experimental material has become available.

Note added in the proof:

Recents experiments carried out in the Kamerlingh Onnes Laboratory of the University of Leiden confirm the hypothesis that the relaxation mechanism in ionic crystals is determined by paramagnetic impurities.

A theory, taking these into account, gives for T_1 a value of the order of a few seconds, if the crystal is contaminated with 0.0001 % iron. Furthermore this theory predicts that T_1 should be largely independent of the temperature of the lattice. These features are in striking contrast with W a l l e r's results for an ideal lattice and agree much better with the experimental data (comp. R 7).

A full account of these researches will be given elsewhere.