450

MAGNETIC RELAXATION IN CONDENSED MATTER

A thesis submitted in partial fulfillment of the requirements for the degree of M. Phil. in the Faculty of Science
Bedford College
(The University of London)

by

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October 1982

CONTENTS: PAGE NO.

PAGE NO.

CHAPTER IV- Reduced Density Matrix

CHAPTER V Nuclear Magnetic Relaxation in Two-Dimensional Systems

PAGE NO.

CHAPTER VI Experimental Technique and the Comparison of the Experimental Results

APPENDIX

REFERNCES

ACKNOWLEDGEMENTS

I wish to thank all the people without whose support this thesis would not have been completed.

First of all, I am indebted to my supervisor Dr. Brian P. Cowan for his guidance and understanding and the staff of the department of Physics at Bedford College for bearing with me throughout.

My very special thanks go to my brother Professor Erkan Õngel, the University of Ankara, Turkey for his constant encouragement and financial support.

ABSTRACT

The study of the Nuclear Magnetic Resonance enables people to enhance their knowlwdge on scientific phenomena. For its use, many examples can be given such as in Solid State Physics, it may be used to have more information about the bulk system, in Organic Chemistry, one uses NMR for the analysis of complex molecules and so on ....

This work is a reformulation and unification of the various theories of magnetic relaxation and magnetic resonance.

We start off our discussion on the magnetic relaxation theory with an introductory explanation of the Bloch Equations and the relaxation processes. It is preceeded with a quantum-mechanical treatment introducing the density matrix.

A quantum mechanical theory of frequency dependent susceptibilities of magnetic systems is examined with the case of linear theory which assumes that the external disturbance is always small and the response of the system to it is linear. The method used to calculate the relaxation function is quantum-statistical. We computed the line contour of resonance absorption by using the Fourier integral method. (Chapter III)

In the following chapter, the physical meaning of the reduced density matrix is discussed. Its usefulness is to obtain all the information necessary to evaluate the expectation value.

We continue our discussion with the theory of NMR in homo-

genous adsorbed systems for two dimensional systems. It is shown that the reduced dimensionality has the effect of decreasing the relaxation times.

With the Pulse NMR technique, we measured the relaxation times around 0°C and presented our results in the last chapter. The comparison of the result was made with the PPP people's result.

CHAPTER I

BASIC NMR THEORY

I - 1 - INTRODUCTION

Magnetic resonance was first observed just after the Second World War and the methods on it have been developed very rapidly. Historically, the first good works were done by a group led by Bloch (1946) and another group under Purcell's leadership in the same year. They both used continuous wave (CW) technique in their initial experiments. Shortly after the first CW experiments pulse methods were developed (Hahn 1950).

Nuclear magnetic resonance (NMR) can basically be studied by either nuclear magnetic resonance absorption methods (developed by Purcell) or the magnetic nuclear induction methods (developed by Bloch).

In order to detect NMR signal one either uses the pulse NMR spectrometer by which the free precession or Larmor precession is detected after the removal of the pulse or the limited oscillator which detects the power absorption signal at resonance.

The technique used is to apply a strong magnetic field ($\sim$2 tesla) to the sample which is usually a liquid or solid. A radio-frequency field (1-100 MHz) is imposed at right angles and a small detector coil is wound around the sample. As the magnetic field is varied the spacing of the energy levels changes and at a certain value of the magnetic field, this spacing is such that radio-frequency radiation is strongly absorbed. This resonance produces a signal in the detector coil. A plot of detected signal against the magnetic field gives an NMR spectrum which can be used for determining nuclear magnetic moments.

NMR techniques are being used in many branches of Physics plus other fields of Science. In Physics, it is useful to study liquids and solids, particularly in solid state Physics one uses NMR technique to have information about the bulk. It is also useful in Medicine, Geology, Archaeology especially in organic Chemistry for the analysis of complex molecules.

I - 2 - THE NMR THEORY

Magnetic resonance is an effect seen in a system which has an angular momentum and a magnetic moment. It is in fact a large branch of spectroscopy which deals with the interaction between an applied magnetic field (to the magnetic system) and non-zero magnetic moments of this system.

Where the word "resonance" comes from is that; the natural frequency of the system (Larmor) is just around the frequency of the radio-frequency wave which is applied to the system. Energy is transferred from this radio-frequency (r.f.) circuit to the magnetic system of nuclear spins immersed in a static magnetic field (H_o) due to the transitions among the energy levels of the spin system. Each of N non-interacting spins is characterized by "$I\hbar$" and "m". "I" indicates the nuclear spin quantum number which is ½ for proton and electron. "$\hbar$" is Planck constant divided by 2π and "m" is the magnetic moment. In quantum mechanics, for each I there are 2I + 1 "μ"s (magnetic moment quantum number or eigen values of I_z operator). The relation is:

$$\mu = +I, \ I-1, \text{---------}, -I$$

i.e. $$I \lesssim \mu \lesssim -I$$

Energy transitions obey the selection rule which requires $\Delta\mu = \mp 1$. $\Delta\mu = -1$ case corresponds to absorption and $\Delta\mu = +1$ corresponds to emmission.

I - 3 - THE BLOCH EQUATIONS

We first start off with the proportionality between the magnetic moment of a charged particle and the angular momentum. (see Appendix I - 1 for the proof).

$$\underline{m} = \gamma \underline{J} \qquad \text{(I-1)}$$

where $\underline{m}$ is magnetic moment

$\underline{J}$ is angular momentum

γ is gyromagnetic ratio

Applying a magnetic field (H_o) to $\underline{m}$ we get a torque.

$$\text{Torque} = \underline{m} \times \underline{H} \qquad \text{(I-2)}$$

Torque is also given by the rate of angular momentum.

$$\text{Torque} = d\underline{J}/dt = \dot{\underline{J}} \qquad \text{(I-3)}$$

Combining Equations (I - 1), (I - 2) and (I - 3) we have,

$$\dot{\underline{m}} = \gamma \; \underline{m} \times \underline{H} \qquad \text{(I-4)}$$

Equation (I - 4) is called the gyroscope equation when H is in the Z direction (i.e. $\underline{H} = H_o \hat{\underline{k}}$).

The equations (solutions) of the components of the magnetic moment describe a circular motion in the x-y plane. (see Appendix I-2 for the proof).

The magnetic moment vector precesses about the Z axis with its natural frequency called the Larmor frequency and it is given by,

$$\omega_0 = \gamma H_0 \qquad \text{(I-5)}$$

Bloch combined the components of the gyroscope equation and the relaxation times in the following way.

$$\left.\begin{aligned} \dot{M}_x &= \gamma(\underline{M}\times\underline{H})_x - \frac{M_x}{T_2}\\ \dot{M}_y &= \gamma(\underline{M}\times\underline{H})_y - \frac{M_y}{T_2}\\ \dot{M}_z &= \gamma(\underline{M}\times\underline{H})_z + \frac{M_0-M_z}{T_1}\end{aligned}\right\} \qquad \text{(I-6)}$$

Equation (I-6) is called the Bloch equation.

Where **M** is the magnetization ($\sum_i m_i$ /volume) T_1 and T_2 are respectively the spin-lattice and spin-spin relaxation times.

Introducing,

$$\left.\begin{aligned} M_\mp &= M_x \mp i M_y\\ H_\mp &= H_x \mp i H_y\end{aligned}\right\} \qquad \text{(I-7)}$$

we have,

$$\left.\begin{aligned} \dot{M}_+ &= -i\gamma(H_z M_+ - M_z H_+) - \frac{M_+}{T_2}\\ \dot{M}_z &= -\frac{i\gamma}{2}(M_- H_+ - M_+ H_-) + \frac{M_0-M_z}{T_1}\end{aligned}\right\} \qquad \text{(I-8)}$$

Equation (I-8) is the Bloch Equations of new notations. The solutions of this equation are the following (when $\underline{H} = H_0\,\hat{\underline{k}}$)

$$M_+(t) = M_+(0)\exp - i\gamma H_0 t \exp - it/T_2 \qquad \text{(I-9)}$$

$M_+(0)\exp - i\gamma H_0 t$ part indicates the Larmor precession and $\exp - it/T_2$ part indicates the free induction decay

$$M_z(t) - M_z^{eq.} = \left[M_z(0) - M_z^{eq.}\right]\exp - t/T_1 \qquad \text{(I-10)}$$

Equations (I-9) and (I-10) are related to the spin-spin relaxation and spin-lattice processes respectively.

I - 4 - HOW THE SPIN SYSTEM ABSORBS ENERGY

Let us consider an isolated system where the spin quantum number is $\frac{1}{2}$. The meaning of isolated system is that; spins have no interaction with the lattice. When we apply a magnetic field H_o to this system, the spin system is split into two levels as shown in figure (I-1)

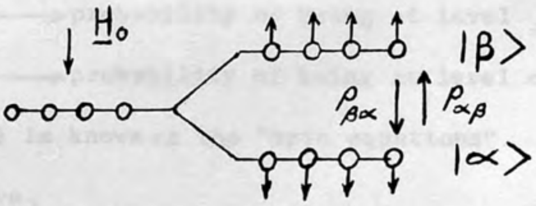


Figure I - 1: H_o splits the spin system into two energy levels.

Now let $|\alpha>$ and $|\beta>$ be respectively the level where the spins show the same direction as H_o and the level where the spins have opposite direction to H_o. And let N_α and N_β be the number of the spins at these levels respectively. The Boltzmann-Maxwell distribution gives us the relation between N_α and N_β

$$\frac{N_\alpha}{N_\beta} = \frac{exp(E_\alpha/kT)}{exp(E_\beta/kT)} \qquad \text{(I-11)}$$

where E_α is the energy of level α

E_β is the energy of level β

k is Boltzmann factor

T is absolute temperature

At equilibrium it is obvious that $N_\alpha > N_\beta$

In the presence of an external magnetic field whose frequency is equal to the natural Larmor frequency, the spin populations among the levels change through a probability.

It follows that,

$$\begin{aligned} \frac{dN_\alpha}{dt} &= N_\beta P_{\beta\alpha} - N_\alpha P_{\alpha\beta} \\ \frac{dN_\beta}{dt} &= N_\alpha P_{\alpha\beta} - N_\beta P_{\beta\alpha} \end{aligned} \qquad \text{(I-12)}$$

where $P_{\alpha\beta} \longrightarrow$ probability of being at level β

$P_{\beta\alpha} \longrightarrow$ probability of being at level α

Equation (I-12) is known as the "spin equations". From this equation we have,

$$\frac{dn}{dt} = -2Pn \qquad \text{(I-13)}$$

with $N = N_\alpha + N_\beta$ and $P_{\alpha\beta} = P_{\beta\alpha} = P$ and $n = N_\alpha - N_\beta$

The solution of equation (I-13) is:

$$n = n_o e^{-2Pt} \qquad \text{(I-14)}$$

where $n_o = N_\alpha - N_\beta$ when $t = o$

During the transitions from one level to the other, each spin absorbs energy from the applied r.f wave. Let ε be the energy absorbed by only one spin. We have,

$$\varepsilon = \Delta E . P \qquad \text{(I-15)}$$

where $\Delta E = E_\alpha - E_\beta$ (energy difference between two levels).

For all the spins at level α, Equation (I-15) becomes

$$E = N_\alpha P \Delta E \qquad \text{(I-16)}$$

The energy rate absorbed from the external effect is given by:

$$\frac{dE}{dt} = \Delta E N_{\alpha} P_{\alpha\beta} - \Delta E N_{\beta} P_{\beta\alpha} \qquad \text{(I-17)}$$

This equation states that the net energy absorbed from the r.f wave is equal to the energy difference between the absorbed energy under $P_{\alpha\beta}$ and emitted energy under $P_{\beta\alpha}$ transition.

Substituting Equation (I-14) into (I-17) we have,

$$\frac{dE}{dt} = \Delta E P n_0 e^{-2Pt} \qquad \text{(I-18)}$$

Now, this equation shows us that the time derivative of absorbed energy from r.f. wave depends on the difference in spin population among the levels and it has an exponential term. In other words, the external effect (r.f.) makes the spin population zero with time. At t = o, this difference is equal to n_o. Then the energy is saturated (i.e. the magnetic resonance stops).

I - 5 - THE SPIN-LATTICE RELAXATION TIME

As already stated at Chapter (I-3), the Bloch Equations include the relaxation terms. Due to the interaction between spins and the lattice, spins pass energy to the lattice until they reach the equilibrium state. The concerned relaxation time because of this intractive process is called T_1 the spin-lattice or longitudinal relaxation time. There are ways of explaining T_1.

a) The Spin-lattice Relaxation Time in Terms of Energy Flux:

When spin system absorbs energy from an r.f. wave, its temperature increases. (At t=o i.e. before the r.f. is applied $T_{spin} = T_{lattice}$). When the magnetic resonance remains saturated ($T_{spin} \gg T_{lattice}$) energy is conveyed to the lattice system from the spin system, in other words, the spin system loses heat, as the lattice gains it. Figure (I-2) represents a block diagram of the heat transfer.

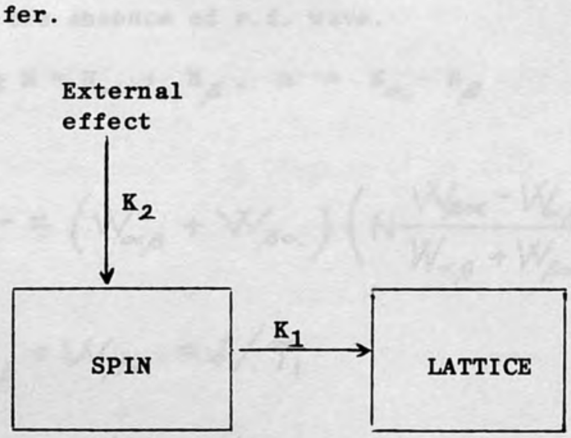


Figure I-2: Energy is conveyed from system to lattice.

The spin system gives away the energy below

$$\frac{dE}{dt} = K_1 k \left(T_{spin} - T_{lattice}\right) \qquad \text{(I-19)}$$

where $K_1 \longrightarrow$ energy flow constant

$T_{spin} \longrightarrow$ temperature of spin-system

$T_{lattice} \longrightarrow$ temperature of lattice system

Now here, K_1 can be written in the form of $1/T_1$. T_1 is the measure of the energy change between two systems. The heat transfer continues until the equilibrium is reached (i.e. $T_{spin} = T_{lattice}$). Therefore, in the absence of an external effect, new transitions occur between the levels of the spin system. The spin equations become in a similar way:

$$\frac{dN_\alpha}{dt} = N_\beta W_{\beta\alpha} - N_\alpha W_{\alpha\beta}$$

$$\frac{dN_\beta}{dt} = N_\alpha W_{\alpha\beta} - N_\beta W_{\beta\alpha} \qquad \text{(I-20)}$$

where $W_{\beta\alpha}$ and $W_{\alpha\beta}$ correspond to respectively $P_{\beta\alpha}$ and $P_{\alpha\beta}$ in the absence of r.f. wave.

Rewriting $N = N_\alpha + N_\beta$, $n = N_\alpha - N_\beta$

we have,

$$\frac{dn}{dt} = \left(W_{\alpha\beta} + W_{\beta\alpha}\right)\left(N\frac{W_{\beta\alpha} - W_{\alpha\beta}}{W_{\alpha\beta} + W_{\beta\alpha}} - n\right) \qquad \text{(I-21)}$$

$$W_{\alpha\beta} + W_{\beta\alpha} = 1/T_1 \qquad \text{(I-22)}$$

$$n_0 = N\frac{W_{\beta\alpha} - W_{\alpha\beta}}{W_{\alpha\beta} + W_{\beta\alpha}} \qquad \text{(I-23)}$$

Substituting Equation (I-22) and Equation (I-23) into Equation (I-21), it becomes,

$$\frac{dn}{dt} = \frac{n_0 - n}{T_1} \tag{I-24}$$

and the solution of this differential equation is:

$$n = n_0 \left(1 - e^{-t/T_1}\right) \tag{I-25}$$

The general expression for dn/dt must be the sum of Equation (I-13) and Equation (I-25)

$$\frac{dn}{dt} = -2Pn + \frac{n_0 - n}{T_1} \tag{I-26}$$

At equilibrium dn/dt = o and it follows that;

$$n = \frac{n_0}{1 + 2PT_1} \tag{I-27}$$

$$\frac{dE}{dt} = \Delta E \, n_0 \frac{P}{1 + 2PT_1} \tag{I-28}$$

We derived a very important equation, because Equation (I-28) tells us that dE/dt is inversely proportional to T_1 i.e. when T_1 is short dE/dt is big and the equilibrium is reached in a short time.

b) The Spin-Lattice Relaxation Time in Terms of Magnetization.

Although it was stated in Chapter (I-2) that magnetization in terms of T_1 appears in the solution of the Bloch Equations, we did not discuss this fact in detail. The Z component of the magnetization is related to T_1 with an exponential expression.

In the NMR theory, the spin system is under two magnetic fields $1 - \underline{H}_0 = H_0 \hat{\underline{k}}$ $\quad 2 - \underline{H}_1 = H_1 \cos \omega t \, \hat{\underline{i}}$

which is perpendicular to $\underline{H}_o$ ($\underline{H}_o \gg \underline{H}_1$). And it is known that resonance is seen when $\omega = \omega_o$. The magnetization vector precesses about the Z axis, as soon as we cut off $\underline{H}_1$, the magnetization vector gets bigger exponentially and precession angle (θ) gets smaller. After a certain time, at equilibrium, the magnetization reaches its biggest value and θ becomes zero and because there transverse components precession stops. T_1 is the measure of this process. Figure (I-3) explains the exponential growth of the magnetization.

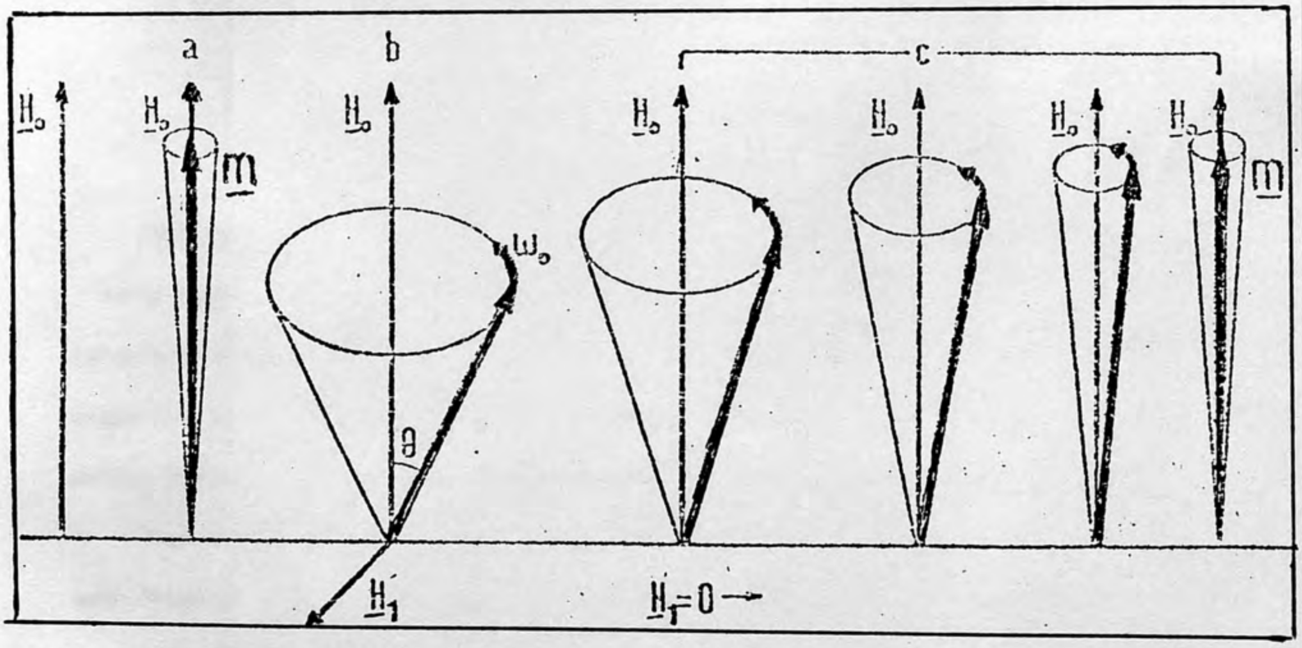


Figure I-3: The Exponential growth of M_z

We can also observe the magnetization growth without introducing $\underline{H}_1$ (because of $t = o$ i.e. before we apply $\underline{H}_o$) the magnetization vector has also transverse components. Furthermore the spin-spin interaction (dipole) works against the magnetization growth, in other words it works in favour of precessive motion. In NMR theory, one thing must always be kept in mind, it is the biggest mistake to treat relaxation times alone. These two processes occur at the same time.

The magnetic energy density $(-\underline{H}.\underline{M})$ decreases as M_z approaches its new equilibrium value because the spin population moves into lower level.

I - 6 - SPIN-SPIN RELAXATION TIME

Because every spin has a magnetic moment there is an interaction among the spins. The most dominant term is the dipole interaction term. Magnetic moment of a spin interacts with the magnetic field produced by the neighbouring spins. This magnetic field is called the local magnetic field.

Let us consider two spins A and B whose magnetic moments are respectively m_A and m_B . The magnetic field at A (produced by B) is given by:

$$\underline{H}_{LA} = \frac{m_B}{r_{AB}^3}\underline{n} \qquad \text{(I-29)}$$

where $r_{AB} \longrightarrow$ separation distance

$\underline{n} \longrightarrow$ normal vector

Therefore, spin A sees two magnetic fields: 1 - static magnetic field $\underline{H}_o$, 2 - Local magnetic field $\underline{H}_{LA}$.

$$\underline{H}_A = \underline{H}_{LA} + \underline{H}_o \qquad \text{(I-30)}$$

(These two spins individually precess about the Z axis under static field $\underline{H}_o$).

Now, in order to study the spin-spin interaction better, it is useful to split $\underline{H}_{LA}$ into two components; one which is parallel (or anti-parallel) to the static field ($\underline{H}_{LAZ}$) and the other being perpendicular to $\underline{H}_o$ ($\underline{H}_{LAP}$). Figure (I-4) shows this representation.

Let us first consider what the parallel component of the local field does:

$\underline{H}_{LAZ}$ vector changes only on the Z direction from one spin to another depending on r and θ . Therefore, all "$\underline{H}_{LAZ}$ s" cause the spin system inhomogenity. At resonance, the line shape gets broadened. (When $\underline{H}_L$ = o line shape is sharpest).

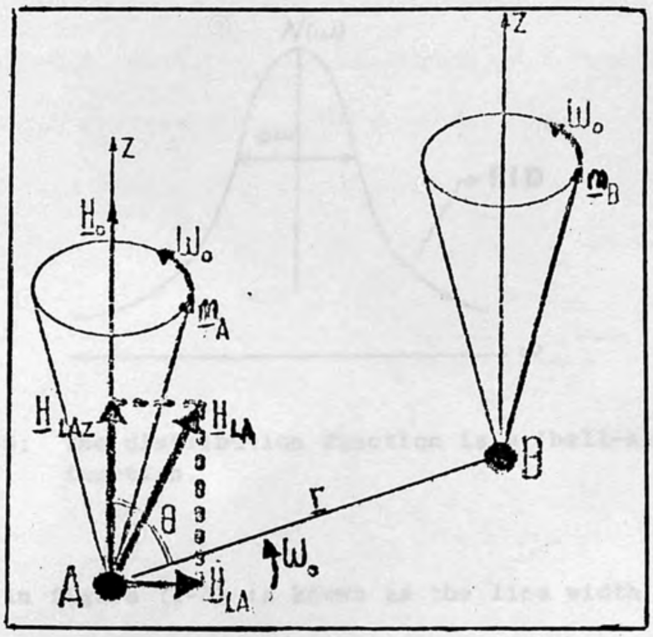


Figure I-4: Local field with its two components $\underline{H}_{LAZ}$ and $\underline{H}_{LAP}$

We now introduce a distribution function $N(\omega)$ to describe the free induction decay (Figure I-5). $N(\omega)$ is a function of spins with different frequencies. Free induction decay (FID) can be expressed in terms of distribution function through a transform called Fourier transform. We have,

$$F(t) = \int_{-\infty}^{\infty} N(\omega) exp -i\omega t \, d\omega \qquad \text{(I-31)}$$

F(t) is the Fourier transfrom of $N(\omega)$ and indicates the free induction decay.

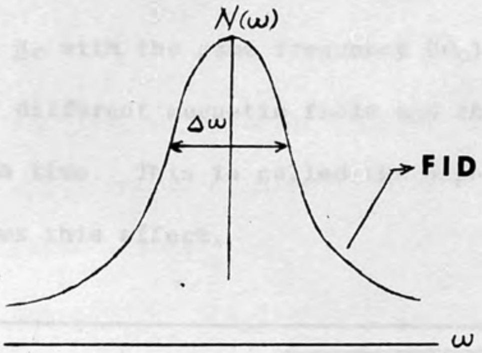


Figure I-5: The distribution function is a 'bell-shape' function.

" $\Delta\omega$ " in figure (I-5) is known as the line width and it is this phenomenon which describes the lineshape.

For this model, for T_2, we can write,

$$T_2 \simeq \frac{1}{\Delta\omega} \qquad \text{(I-32)}$$

Secondly, let us consider the effect of the perpendicular component of the local field:

$\underline{H}_{LAP}$ vector does a precession motion in the plane(x-y) which is perpendicular to $\underline{H}_O$. Because the precession frequency of $\underline{H}_{LAP}$ is equal to the precession frequency of spin A (Larmor), $\underline{H}_{LAP}$ creates such a torque which tends to change the direction of spin A. In this connection, it shortens the life time of spin A at its present state.

What actually happens is that; at t = o, every spin precesses about $\underline{H}_o$ with the same frequency (ω_o) then due to $\underline{H}_{LAP}$, each spin has different magnetic field and changes its first frequency with time. This is called the dephasing effect. Figure (I-6) shows this effect.

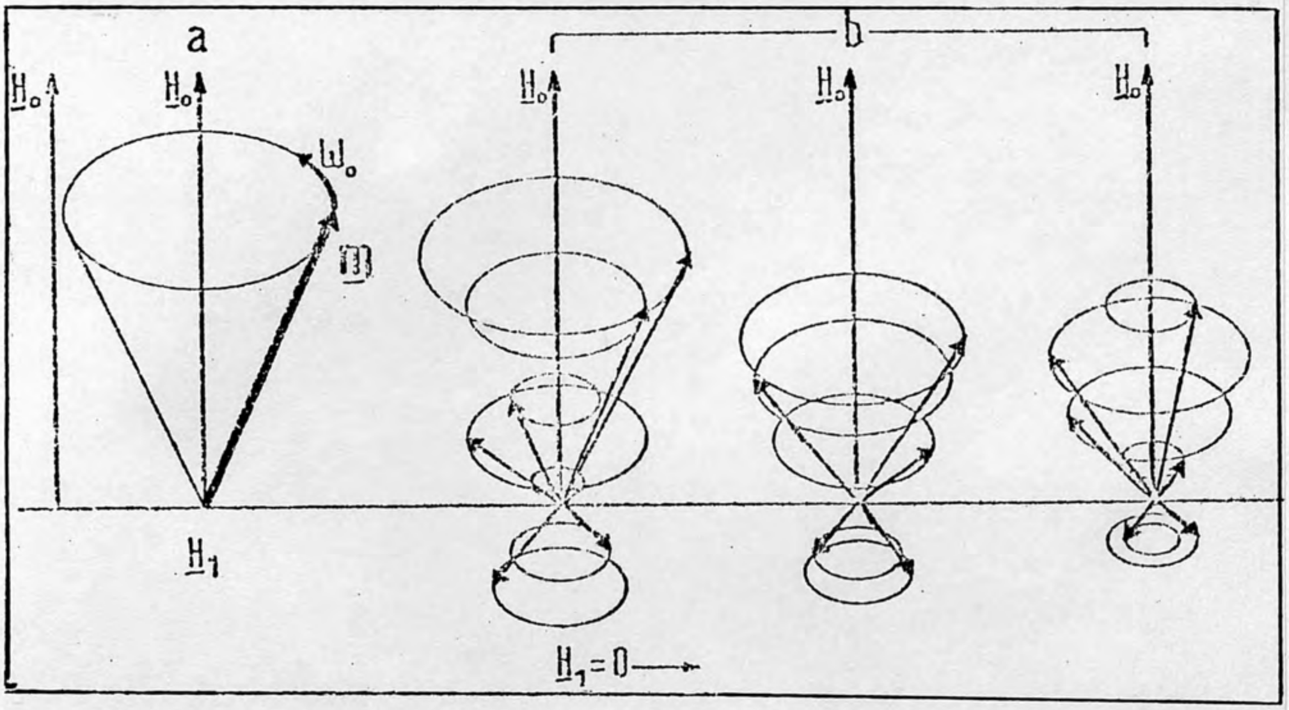


Figure I-6: The dephasing effect.

I - 7 - THE RESONANCE CASE

We start off with writing the Schroedinger Equation in order to discuss the resononance condition.

$$\mathcal{H}|\psi_i\rangle = E_i|\psi_i\rangle \qquad \text{(I-33)}$$

where $\mathcal{H} \longrightarrow$ Hamiltonian operator (energy operator)

$E_i \longrightarrow$ eigen values of eigen states

$\psi_i \longrightarrow$ eigen states

By finding the solution of the Schroedinger Equation, we can reach the resonance state. Let us do that for proton which has spin ½. Let I_z operator show the z component of this spin. In Quantum Mechanics, there are two possible spin eigen functions (states), namely $|\alpha\rangle$ and $|\beta\rangle$

We have the following:

$$\begin{aligned} I_z|\alpha\rangle &= \frac{1}{2}|\alpha\rangle \\ I_z|\beta\rangle &= -\frac{1}{2}|\beta\rangle \end{aligned} \qquad \text{(I - 34)}$$

Eigen values of operator I_z are ½ and -½. Writing the relation between m̲ and I̲.

$$\underline{m} = \gamma_n \hbar \underline{I} = g_n \frac{e\hbar}{4\pi m_p c}\underline{I} = g_n \mu_n \underline{I} \qquad \text{(I-35)}$$

where $g_n \longrightarrow$ nuclear spectroscopic splitting factor

$\mu_n \longrightarrow$ nuclear magneton

$c \longrightarrow$ light speed

$m_p \longrightarrow$ mass for proton

(In our example $g_n = g_{\text{Proton}} = 5.5855$)

Hamiltonian operator for proton becomes:

$$\mathcal{H} = -\underline{m}\cdot\underline{H}_0 = -m_z H_z = -g_n \mu_n H_z I_z \qquad \text{(I-36)}$$

In this equation $g_n \mu_n H_z$ is a constant and therefore $|\alpha\rangle$ and $|\beta\rangle$ are also eigen states of the Hamiltonian operator. The solution of the Schroedinger equation (I-33) for a proton is:

$$\left.\begin{aligned} \mathcal{H}|\alpha\rangle &= (-g_n \mu_n H_z) I_z |\alpha\rangle = -\tfrac{1}{2} g_n \mu_n H_z \\ \mathcal{H}|\beta\rangle &= (-g_n \mu_n H_z) I_z |\beta\rangle = +\tfrac{1}{2} g_n \mu_n H_z \end{aligned}\right\} \qquad \text{(I-37)}$$

Equation (I-37) indicates that we have two energy levels as shown in figure (I-7).

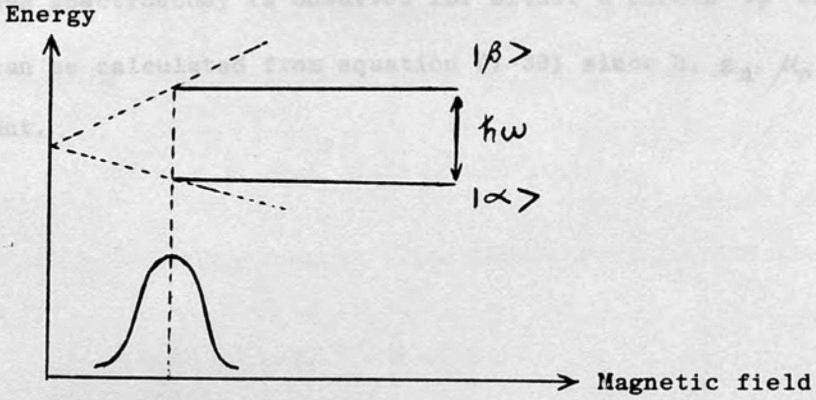


Figure I-7: The NMR Spectrum.

Energies of these two states are given by

$$\boxed{E_{\alpha\beta} = \mp \frac{1}{2} g_n \mu_n H_z} \qquad \text{(I-38)}$$

Equation (I-38) is known as the Zeeman energy term.

The energy needed from the r.f. wave, in order to carry proton from one state to another is given by:

$$E = g_n \mu_n H_z = \hbar \omega \qquad \text{(I-39)}$$

$$E = h\nu_r \quad \text{with} \quad \omega = 2\pi\nu_r , \quad \hbar = h/_{2\pi}$$

Equation (I-39) is the equation for resonance case. ν_r is known as the "resonance frequency" and the corresponding magnetic field is called the "resonance field".

NMR spectroscopy is observed for either a chosen ν_r or $\underline{H}_z$. Each can be calculated from equation (I-39) since h, g_n, μ_n are constant.

CHAPTER II

GENERAL FORMATION OF THE RELAXATION THEORY

II - 1 - INTRODUCTION

In Chapter (I) we have had a historical and elementary look at the NMR theory in which quantum mechanics was not much involved. This chapter is devoted to a more advanced NMR and relaxation theory by introducing the density matrix and related equation of motion.

It is useful to give a brief account of quantum mechanical behaviour of density matrix, the equation of motion and the expectation value of an operator.

II - 2 - DENSITY MATRIX AND THE EQUATION OF MOTION

We deal with all possible products of amplitudes of the wave function with themselves. Let φ_n be a basis set. We have,

$$\psi = a_1\varphi_1 + a_2\varphi_2 + \cdots\cdots + a_n\varphi_n$$

we could use all the products. The matrix presentation for that is:

$$\begin{vmatrix} a_1a_1^* & a_1a_2^* & a_1a_3^* \cdots\cdots & a_1a_n^* \\ a_2a_1^* & a_2a_2^* & \cdots\cdots\cdots\cdots & a_2a_n^* \\ \vdots & & & \vdots \\ a_na_1^* & \cdots\cdots\cdots & \cdots\cdots\cdots & a_na_n^* \end{vmatrix}$$

This matrix contains all the information about the wave function. The diagonal elements of this matrix give the probability of occupation of a particular eigen state without any arbitrary phase factor. In calculating the expectation value of an operator A, it is these products $a_i a_j^*$ which must be multiplied by the matrix elements A_{ij}, so the $a_i a_j^*$ are of more direct use.

The density matrix ρ for a system which has $|\psi>$ states is given by:

$$\rho = |\psi> <\psi| \qquad \text{(II-1)}$$

$|\psi>$ and $<\psi|$ can be expanded in terms of the complete orthogonal set $|\varphi_i>$ and $<\varphi_i|$. Therefore, we can show that ρ is the matrix of all possible products. We have,

$$|\psi> = \sum_i a_i |\varphi_i> \qquad \text{(II-2)}$$

$$<\psi| = \sum_i a_i^* <\varphi_i| \qquad \text{(II-3)}$$

setting ρ we get,

$$\rho = |\psi><\psi| = \sum_{ii'} a_i a_{i'}^* |\varphi_i><\varphi_{i'}| \qquad \text{(II-4)}$$

now taking the mn matrix element:

$$
\begin{aligned}
\langle m|\rho|n\rangle &= \langle \varphi_m|\rho|\varphi_n\rangle \\
&= \langle \varphi_m|\sum_{ii'} a_i a_{i'}^{*}|\varphi_i\rangle\langle\varphi_{i'}|\varphi_n\rangle \\
&= \sum_{ii'} \langle \varphi_m|\varphi_i\rangle a_i a_{i'}^{*}\langle\varphi_{i'}|\varphi_n\rangle \\
&= \sum_{ii'} \delta_{mi}\, a_i\, a_{i'}^{*}\, \delta_{i'n} \qquad \delta_{mi}=1 \quad \delta_{ni'}=1 \\
&\qquad\qquad\qquad\qquad \text{when} \quad m=i \quad n=i'
\end{aligned}
$$

$$\langle m|\rho|n\rangle = a_m a_n^{*} \qquad \text{(II-5)}$$

Density matrix represents a "pure state" of which we know enough information to write a wave function.

In order to derive the equation of motion of the density matrix, we take the time derivative of Equation (II-1); it follows that,

$$\dot{\rho} = |\psi\rangle\left(\frac{\partial}{\partial t}\langle\psi|\right) + \left(\frac{\partial}{\partial t}|\psi\rangle\right)\langle\psi| \qquad \text{(II-6)}$$

since $$\frac{\partial}{\partial t}|\psi\rangle = -\frac{i}{\hbar}\mathcal{H}|\psi\rangle \qquad \text{(II- 7)}$$

(where $\mathcal{H}$ is Hamiltonian operator).

For the Hermitian conjugate equation we have,

$$\frac{\partial}{\partial t}<\psi| = \frac{i}{\hbar}<\psi|\mathcal{H} \qquad \text{(II- 8)}$$

Substituting Equations (II-7) and (II-8) into Equation (II-6), we obtain;

$$\dot{\rho} = \frac{i}{\hbar}\left\{|\psi><\psi|\mathcal{H} - \mathcal{H}|\psi><\psi|\right\}$$

$$\dot{\rho} = -\frac{i}{\hbar}\left[\mathcal{H},\rho\right] \qquad \text{(II-9)}$$

This equation is called the "Von-Neumann" equation. Von-Neumann equation describes the equation of motion in the Heisenberg picture with opposite sign (Appendix 1 covers the equation of motion in both pictures the Schroedinger and Heisenberg).

We now want to obtain the solution of the time dependant Schroedinger equation.

$$i\hbar\frac{\partial}{\partial t}|\psi(t)> = \mathcal{H}|\psi(t)> \qquad \text{(II-10)}$$

(time dependant of the Schroedinger equation)

$|\psi(t)>$ is given by:

$$|\psi(t)> = \exp\left(-\frac{i\mathcal{H}t}{\hbar}\right)|\psi(0)> \qquad \text{(II-11)}$$

This solution is only valid if $\mathcal{H}$ is independent of time. If $\mathcal{H}$ is dependent of time, solution becomes:

$$|\psi(t)\rangle = \left\{ \exp - \frac{i}{\hbar} \int_0^t \mathcal{H}(t')\,dt' \right\} |\psi(0)\rangle \qquad \text{(II-11')}$$

Taking the solution as in Equation (II -11) ,we write for the Hermitian conjugate of $|\psi(t)\rangle$ as:

$$\langle\psi(t)| = \langle\psi(0)| \exp \frac{i\mathcal{H}t}{\hbar} \qquad \text{(II-12)}$$

Establishing the density operator by Equations (II-11) and (II- 12)

$$\rho(t) = |\psi(t)\rangle\langle\psi(t)| = \exp - \frac{i\mathcal{H}t}{\hbar} |\psi(0)\rangle\langle\psi(0)| \exp \frac{i\mathcal{H}t}{\hbar} \qquad \text{(II- 13)}$$

$$\rho(t) = \exp - \frac{i\mathcal{H}t}{\hbar}\, \rho(0) \exp \frac{i\mathcal{H}t}{\hbar} \qquad \text{(II- 14)}$$

with $\rho_0 = |\psi(0)\rangle\langle\psi(0)|$

II - 3 - THE EXPECTATION VALUE OF AN OPERATOR

In Quantum Mechanics, the expectation value of an operator is defined by:

$$\langle G \rangle = \langle \psi | G | \psi \rangle \qquad \text{(II-15)}$$

We can express this in terms of density matrix. To do that we first prove the following identity.

$$\langle A | B \rangle = Tr\big[|B\rangle \langle A| \big] \qquad \text{(II-16)}$$

we have,

$$|A\rangle = \sum_n a_n |n\rangle, \qquad |B\rangle = \sum_n b_n |n\rangle$$

and

$$\langle A| = \sum_n a_n^* \langle n|$$

so, $$\langle A | B \rangle = \sum_n a_n^* b_n \qquad \text{(II-17)}$$

$$\langle A | B \rangle = Tr\big[|B\rangle \langle A| \big] \qquad \text{(II-18)}$$

setting

$$\langle A| = \langle \psi \;, \quad |B\rangle = G|\psi\rangle$$

we obtain,

$$\langle \psi | G | \psi \rangle = Tr\big[G|\psi\rangle \langle \psi| \big] \qquad \text{(II-19)}$$

and we write,

$$<\psi|\Theta|\psi> = T_r\left[\Theta\rho\right] \qquad \text{(II-20)}$$

II - 4 - MAGNETIZATION VECTOR IN TERMS OF DENSITY MATRIX

We are prepared to continue our discussion about magnetization at a more advanced level.

We first write the basic relation (for a single nucleus) between the spin being $\hbar$I and related magnetic dipole moment m.

$$m = \gamma\hbar I \qquad \text{(II- 21)}$$

And we have already mentioned that (in chapter I) when this dipole is placed in a magnetic field H_0 which is directed along the z axis, the Hamiltonian for the nucleus is given by:

$$\mathcal{H}_0 = m\cdot H_0 = \gamma\hbar I_z H_0 \qquad \text{(II- 22)}$$

$\mathcal{H}_0$ is known as the Zeeman Hamiltonian.

The equation of motion for I (in Heisenberg picture) may be written as follows:

$$\frac{\hbar}{i}\frac{dI}{dt} = \left[\mathcal{H}_0, I\right] = \gamma\hbar H_0\left[I_z, I\right] \qquad \text{(II- 23)}$$

Due to this equation, we find I_z, I_+ and I_-

$$I_z(t) = e^{\frac{i}{\hbar}\gamma\hbar H_0 I_z t} I_z \, e^{-\frac{i}{\hbar}\gamma\hbar H_0 I_z t} = I_z \tag{II-24}$$

$$I_+(t) = e^{i\gamma H_0 I_z t} I_+ \, e^{-i\gamma H_0 I_z t} = I_+ e^{+i\omega_0 t} \tag{II-25}$$

$$I_-(t) = e^{i\gamma H_0 I_z t} I_- \, e^{-i\gamma H_0 I_z t} = I_- e^{-i\omega_0 t} \tag{II-26}$$

The expressions we had above are for a single nucleus. We now consider an assembly of like nuclei in thermal equilibrium at temperature T. To do that we recall the magnetization.

$$M = \gamma\hbar \langle I \rangle N \tag{II-27}$$

Where N is the number of spins per unit volume and $\langle I \rangle \hbar$ is the ensemble average of the spin angular momentum.

In the presence of the external magnetic field, the equilibrium density operator for the system is:

$$\rho_{eq} = \frac{\exp -\beta\mathcal{H}}{Tr\{\exp -\beta\mathcal{H}\}} \tag{II-28}$$

Here, Hamiltonian covers two parts. 1. - Zeeman part ($\mathcal{H}_0$) 2. - Interaction part. Ignoring the interaction part, we write,

$$\rho_{eq} = \frac{\exp -\beta\mathcal{H}_0}{Tr\{\exp -\beta\mathcal{H}_0\}} \tag{II-29}$$

Where $\beta = 1/kT$ k ⟶ Boltzmann constant. If $\hbar\omega_0 << kT$, we can expand exp $-\beta\mathcal{H}_0$ and ignore the terms after the first one, we have;

$$\rho_{eq} = \frac{1-\beta\mathcal{H}_0}{Tr\{1\} - Tr\{\beta\mathcal{H}_0\}} \tag{II-30}$$

$$\rho_{eq} = \frac{1-\beta\hbar\omega_0 I_z}{Tr\{1\}} \tag{II-31}$$

with $\mathcal{H}_0 = \hbar\omega_0$ and $Tr\{I_z\} = 0$

Now, M_z can be written in terms of ρ_{eq}

$$M_z = N\gamma\hbar\langle I_z\rangle = N\gamma\hbar\, Tr\{\rho_{eq} I_z\} \tag{II-32}$$

$$M_z = -\frac{N\beta\gamma\hbar^2\omega_0\, Tr\{I_z^2\}}{Tr\{1\}} \tag{II-33}$$

$Tr\{I_z^2\} = \frac{1}{3} I(I+1)(2I+1)$ and since the system has 2I + 1 energy levels, the density operator has 2I + 1 elements. So $Tr\{1\} = 2I + 1$

$$M_z = -(\gamma\hbar)^2 H_0 N I(I+1)/3kT \tag{II-34}$$

Equation (II-34) is known as the Curie Law.

II - 5 - THE RELAXATION FUNCTIONS FOR THE PULSE NMR CASE

It is possible to manipulate the magnetization vector by a 90^o pulse. To do that we need to apply a strong radio-frequency pulse along the axis which is perpendicular to H_θ static field direction. Let H_1 and τ be the magnetic field of r.f. pulse and duration respectively. The spins will start precessing about H_1 direction (say the x axis), during τ time and clearly new precession frequency is given by: $\omega_1 = \gamma H_1$. The new angle is ω_1 times τ .

The 90^o pulse rotates I_z into I_x. But as soon as the pulse disappears, the magnetization continues precessing with its natural Larmor frequency (ω_o) about H_o. Its amplitude decays in time due to the spin-spin relaxation time after a 90^o pulse is applied, equation (II-31) can be written as:

$$\rho = \frac{1 + \beta \omega_o I_x}{Tr\{1\}} \qquad \text{(II-35)}$$

(high temperature approximation)

Expectation value of I_x at time t is:

$$\langle I_x(t) \rangle = Tr\{\rho I_x(t)\}$$

Substituting equation (II-35) into this equation

$$\langle I_x(t)\rangle = \frac{Tr\left\{(1+\beta\omega_0 I_x)\, I_x(t)\right\}}{Tr\left\{1\right\}} \qquad \text{(II-36)}$$

$$I_x(t) = \exp i\mathcal{H}t\, I_x \exp -i\mathcal{H}t$$

then we have,

$$\langle I_x(t)\rangle = \frac{Tr\left\{(1+\beta\omega_0 I_x)\exp i\mathcal{H}t\, I_x \exp -i\mathcal{H}t\right\}}{Tr\left\{1\right\}}$$

$$\langle I_x(t)\rangle = \underbrace{\frac{\beta\omega_0}{Tr\{1\}}}_{constant} Tr\left\{I_x \exp i\mathcal{H}t\, I_x \exp -i\mathcal{H}t\right\} \qquad \text{(II-37)}$$

Here the Hamiltonian consists of two terms. 1 - Zeeman term 2 - Dipolar term. ($\mathcal{H} = \mathcal{H}_z + \mathcal{H}_{dip}$). For the adiabatic case we take the part $\mathcal{H}_{dip}$ which commutes with $\mathcal{H}_z$, namely $\mathcal{H}'$ (Abragam, terms A + B in $\mathcal{H}_{dip}$).

So, we have

$$\left[\mathcal{H}', \mathcal{H}_z\right] = 0$$

consider

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}' \qquad \text{(II-38)}$$

substituting Equation (II-38) into Equation (II-37), we find,

$$\langle I_x(t)\rangle = Tr\left\{I_x(\exp i\mathcal{H}'t)(\exp i\mathcal{H}_z t)I_x(\exp -i\mathcal{H}_z t)\right.$$
$$\left.(\exp -i\mathcal{H}'t)\right\} \qquad \text{(II-39)}$$

We note that since $\mathcal{H}_z$ commutes with $\mathcal{H}'$, exp i $(\mathcal{H}'+\mathcal{H}_z)$ t can be written as exp i $\mathcal{H}'$ t exp i $\mathcal{H}_z$ t $\exp i\mathcal{H}_z t$

$$\exp i\mathcal{H}_z t\, I_x \exp -i\mathcal{H}_z t = I_x \cos\omega_0 t + I_y \sin\omega_0 t$$

with $\mathcal{H}_z = \omega_0 \hbar$ and $\hbar \to 1$

Equation (II-38) becomes

$$\langle I_x(t)\rangle = Tr\left\{I_x e^{i\mathcal{H}'t} I_x e^{-i\mathcal{H}'t}\right\}\cos\omega_0 t +$$
$$\underbrace{Tr\left\{I_x e^{i\mathcal{H}'t} I_y e^{-i\mathcal{H}'t}\right\}\sin\omega_0 t}_{0} \qquad \text{(Abragam)}$$

$$\langle I_x(t)\rangle = Tr\left\{I_x \exp i\mathcal{H}'t\, I_x \exp -i\mathcal{H}'t\right\} \qquad \text{(II-40)}$$

We now write the transverse magnetization

$$M_+(t) = M(0)F(t)\exp i\omega_0 t \qquad \text{(II-41)}$$

(this was zero in the absence of r.f. wave) where F(t) is called the transverse relaxation function. Similar to Equation (I-27) we write,

$$M_+(t) = N\gamma\hbar \langle I_+(t) \rangle = N\gamma\hbar \, Tr\left\{\rho I_+(t)\right\}$$

since $Tr\left\{I_+(t)\right\} = 0$

then $$M_+(t) = \beta\omega_0 N\gamma\hbar \frac{Tr\left\{I_x I_+(t)\right\}}{Tr\left\{1\right\}}$$

This may be written in a more symetric form

$$M_+(t) = 2N\gamma\hbar\omega_0 \, Tr\left\{I_+(t) I_-\right\} / Tr\left\{1\right\} \qquad \text{(II-42)}$$

Combining Equations (II-41) and (II-42)

we find,

$$F(t) = \exp -i\omega_0 t \frac{Tr\left\{I_+(t) I_-\right\}}{Tr\left\{I_+ I_-\right\}} \qquad \text{(II-43)}$$

And the longitudinal relaxation function is given by

$$L(t) = \frac{Tr\left\{I_z(t) I_z\right\}}{Tr\left\{I_z^2\right\}} \qquad \text{(II-44)}$$

In the case of lattice motion (vibration and rotation) the time development of the spin components obeys the Heissenberg equation

$$i\hbar \frac{dI(t)}{dt} = \left[I(t), \mathcal{H} \right] \qquad \text{(II-45)}$$

Now, Hamiltonian $\mathcal{H}$ includes three parts: 1 - Zeeman ($\mathcal{H}_z$) which describes the precession about H_o. 2 - Dipolar ($\mathcal{H}_{dip}$) which gives the dipolar interaction. 3 - Motion part ($\mathcal{H}_m$).

we write,

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_{dip} + \mathcal{H}_m$$

$\mathcal{H}_m$ commutes with $\mathcal{H}_z$ but $\mathcal{H}_m$ and $\mathcal{H}_z$ don't commute with $\mathcal{H}_{dip}$. $\mathcal{H}_{dip}$ is much smaller than $\mathcal{H}_z + \mathcal{H}_m$.

In the frame which the spins move with, we can go through the analysis. We have new operators.

$$\mathcal{H}^*_{dip}(t) = e^{\frac{i}{\hbar}\mathcal{H}_o t}\, \mathcal{H}_{dip}\, e^{-\frac{i}{\hbar}\mathcal{H}_o t} \qquad \text{(II-46)}$$

$$I^*(t) = e^{\frac{i}{\hbar}\mathcal{H}_o t}\, I\, e^{-\frac{i}{\hbar}\mathcal{H}_o t} \qquad \text{(II-47)}$$

where $\mathcal{H}_o = \mathcal{H}_z + \mathcal{H}_m$ since $\left[\mathcal{H}_z, \mathcal{H}_m\right] = 0$

similar to Equations (II-24) and (II-25) we have,

$$I_+^*(t) = I_+ \exp i\omega_0 t \tag{II-48}$$

$$I_z^*(t) = I_z \tag{II-49}$$

Therefore F(t) and L(t) become

$$F(t) = \frac{Tr\{I_+(t)\, I_-\}}{Tr\{I_+\, I_-\}} \tag{II-50}$$

$$L(t) = \frac{Tr\{I_z(t)\, I_z\}}{Tr\{I_z^2\}}$$

CHAPTER III

KUBO'S GENERAL THEORY ON MAGNETIC RESONANCE ABSORPTION AND BROADENING

III - 1 - INTRODUCTION

Shortly after Bloembergen, Purcell and Pound made analysis of their experiments on the nuclear magnetic resonance absorption, Kubo and Tomita published two elegant papers one after another on the same phenomenon (1953-54).

We are first going to give an account of the general theory on magnetic resonance absorption (Part I), then we shall discuss the broadening closely (Part II).

The method used for the general theory of magnetic resonance is quantum-statistical and the expressions are derived in the light of the linear theory of irreversible process. If each of the magnetic moments are independent, the problem is not very complicated. But theoretical analysis becomes more complicated when the magnetic moments are coupled together and the fields on these magnetic moments are correlated. The dipolar and exchange interactions are the typical examples for this case.

We shall first see a quantum-mechanical theory of frequency dependent susceptibilities of magnetic systems. When studying this, we shall confine ourselves to the simple case of the linear theory which assumes that the external disturbance is always small and the response of the system to it is linear. Secondly, we shall calculate the relaxation function in a quantum-mechanical way.

Part II is devoted to develop the Fourier integral method for computing the line contour of resonance absorption and also to apply the method to the theory of magnetic resonance absorption.

PART I

III - 2 - RELAXATION FUNCTION AND SUSCEPTIBILITY

In order to correlate the susceptibility and the relaxation function to the dynamical properties of the system, we first need to derive basic equations. We do this quantum-statistically and use the limitation of the linear theory which means that the response of our system to the external disturbance is given by taking only the first order of perturbation theory.

We apply an oscillating magnetic field (whose wave length is very large compared to the dimension of the sample) to our sample. We write this field as;

$$H_1(t) = H_1 \operatorname{Cos}\omega t \tag{III-1}$$

We can express the induced magnetic moment in the following way:

$$\begin{aligned} M_{ind}(t) &= \operatorname{Re}(\chi' - i\chi'')\, H_1 e^{i\omega t}\, V \\ &= (\chi' \operatorname{Cos}\omega t + \chi'' \operatorname{Sin}\omega t)\, H_1 V \end{aligned} \tag{III-2}$$

and we also have,

$$\chi = \chi' - i\chi'' \tag{III-3}$$

where χ is the complex susceptibility and χ' and χ'' are the real part and imaginary parts of the complex susceptibility respectively.

V is the volume of the sample.

Since we take M_{ind} and H_1 as linear, we can now calculate the magnetic response of the system in the first order of the external field H_1.

The function which describes the time change of the response after the external disturbance is cut down to zero is called the RELAXATION function. Supposing that a constant magnetic field H_1 is applied from $t = -\infty$ to $t = t_o$. Then it is suddenly removed. For $t = -\infty$ to $t = t_o$ we write the density matrix operator as;

$$\rho' = \frac{\exp\left[-\beta(\mathcal{H} - H_1 M)\right]}{Tr\left\{\exp\left[-\beta(\mathcal{H} - H_1 M)\right]\right\}} \qquad \text{(III-4)}$$

where M and $\mathcal{H}$ are respectively the magnetic moment operator and the Hamiltonian of the magnetic system in the absence of H_1.

For $t > t_o$, we write the Von-Nuemann equation

$$i\hbar\dot{\rho} = [\mathcal{H}, \rho] \qquad \text{(III-5)}$$

The time dependent density matrix at t = t is given by,

$$\rho(t) = e^{\left[-\frac{i}{\hbar}(t-t_o)\mathcal{H}\right]} \rho' e^{\left[\frac{i}{\hbar}(t-t_o)\mathcal{H}\right]} \qquad \text{(III-6)}$$

The expectation value of M is,

$$\bar{M}(t) = Tr\left\{\rho(t) M\right\} \qquad \text{(III-7)}$$

Substituting Equation (III-6) into (III-7) we have,

$$\bar{M}(t) = Tr\{\rho' M(t)\} \tag{III-8}$$

with $$M(t) = e^{\left[\frac{i}{\hbar}(t-t_0)\mathcal{H}\right]} M e^{\left[-\frac{i}{\hbar}(t-t_0)\mathcal{H}\right]} \tag{III-9}$$

and with the initial condition $M(t_0) = M$ (III-10)

The equation of motion for the magnetic moment in the Heisenberg representation is:

$$i\hbar \dot{M}(t) = \left[M(t), \mathcal{H}\right] \tag{III-11}$$

By using the expansion method and ignoring the higher order terms (than the first term), ρ' can be rewritten as; (Kubo and Tomita).

$$\rho' = \frac{e^{-\beta\mathcal{H}}}{Tr\{e^{-\beta\mathcal{H}}\}} \times \left[1 + \int_0^{\beta} d\lambda\, e^{\lambda\mathcal{H}} H_1 (M - \bar{M}_0) e^{-\lambda\mathcal{H}}\right] + O(H_1^2) \tag{III-12}$$

with $M(t_0) = M$ initial condition

Substituting Equation (III-12) into Equation (III-8) we obtain;

$$\bar{M}(t) = \bar{M}_0 + \int_0^{\beta} d\lambda\, Tr\{\rho_0\} e^{\lambda\mathcal{H}} H_1 (M - \bar{M}_0) e^{-\lambda\mathcal{H}} M(t-t_0) + O(H_1^2) \tag{III-13}$$

with $\rho_0 = \dfrac{e^{-\beta\mathcal{H}}}{Tr\{e^{-\beta\mathcal{H}}\}}$ (density matrix for unperturbation **(III-14)**

and $\bar{M}_0 = Tr\{\rho_0 M\}$ magnetic moment with unperturbed Hamiltonian) **(III-15)**

we can now define the relaxation function as a tensor,

$$\bar{M}(t) - \bar{M}_0 = H_1 \bar{\Phi}(t-t_0) \qquad \text{(III-16)}$$

and the transposed tensor of $\bar{\Phi}$

$$\bar{M}\,(t) - \bar{M}_0 = \phi\,(t-t_0)\,H_1 \qquad \text{(III-17)}$$

$\bar{\Phi}\,(t-t_0)$ and $\phi_{xy}\,(t-t_0)$ can be respectively expressed from Equation (III-13) as follows

$$\bar{\Phi}(t-t_0) = \int_0^\beta \langle e^{\lambda\mathcal{H}}(M-\bar{M}_0)\,e^{-\lambda\mathcal{H}}M(t-t_0)\rangle d\lambda = \int_0^\beta \langle MM(t-t_0+i\hbar\lambda)\rangle d\lambda - \beta M_0 M_0 \qquad \text{(III-18)}$$

$$\phi_{xy}(t-t_0) = \int_0^\beta d\lambda \langle M_y M_x(t-t_0+i\hbar\lambda)\rangle - \beta\bar{M}_{0y}\bar{M}_{0x} = \int_0^\beta \langle M_x(t-t_0-i\hbar\lambda)M_y\rangle d\lambda - \beta\bar{M}_{0x}\bar{M}_{0y} \qquad \text{(III-19)}$$

In the classical limit ($\hbar \longrightarrow 0$) one can obtain:

$$\bar{\Phi}\,(t-t_0) = \beta\left[\langle MM(t-t_0)\rangle - \bar{M}_0\bar{M}_0\right] \qquad \text{(III-20)}$$

$$\phi\,(t-t_0) = \beta\left[\langle M(t-t_0)M\rangle - \bar{M}_0\bar{M}_0\right] \qquad \text{(III-21)}$$

By assuming $H_1(-\infty) = o$ and $\rho(-\infty) = \rho_0$ we can obtain the quantum-mechanical expression for M(t) for $H_1(t)$. The perturbing field has been switched on at $t=-\infty$ and applied up to t=t'. The expectation value of M at the time t is,

$$\bar{M}(t) = \bar{M}_0 + \int_{-\infty}^{t} \left\{ \frac{d}{dt'} \phi(t-t') \right\} H_1(t')\, dt' \qquad \text{(III-22)}$$

$$= \bar{M}_0 + \phi(0) H_1(t) - \int_{-\infty}^{t} \phi(t-t') \frac{dH_1(t')}{dt'}\, dt' \qquad \text{(III-22')}$$

And the Von-Neumann's equation of motion for the relaxation function is given by

$$i\hbar \dot{\phi}_{xy}(t-t') = \langle [M_x(t-t'), M_y] \rangle \qquad \text{(III-23)}$$

Through the Equations (III-22) and (III-22'), we can obtain the expressions for the susceptibility.

$$\left. \begin{aligned} \chi' &= \chi_0 - \frac{\omega}{V} \int_0^\infty \phi(\tau) \sin \omega\tau \, d\tau \\ \chi'' &= \frac{\omega}{V} \int_0^\infty \phi(\tau) \cos \omega\tau \, d\tau \end{aligned} \right\} \qquad \text{(III-24)}$$

$$\chi^* = \chi' - i\chi'' = \chi_0 - \frac{i\omega}{V}\int_0^\infty \phi(\tau)\, e^{-i\omega\tau}\, d\tau \qquad \text{(III-25)}$$

where χ_0 is the static susceptibility and it is given by:

$$\chi_0 = \frac{\phi(0)}{V} = \frac{1}{V}\left[\int_0^\beta \langle e^{\lambda\mathcal{H}} M e^{-\lambda\mathcal{H}} M \rangle d\lambda - \beta \bar{M}_0 \bar{M}_0\right] \qquad \text{(III-26)}$$

Equation (III-25) can also be written as,

$$\chi^* = -\frac{1}{V}\int_0^\infty \frac{d\phi(\tau)}{d\tau}\, e^{-i\omega\tau}\, d\tau \qquad \text{(III-27)}$$

Equation (III-27) gives the relation between the complex susceptibility and the relaxation time. (The relaxation function is the Fourier transform of the frequency dependent susceptibility).

The relaxation function has the following properties:

a) $\bar{\phi}_{xy}(t) = \phi_{xy}(t)$ they are conjugates

b) $\lim_{t \to \infty} \phi(t) = 0$

c) ϕ is a symmetric tensor

$$\phi(-t) = \bar{\phi}(t)$$

or

$$\phi_{xy}(-t) = \phi_{yx}(t)$$

d) In the case of a constant magnetic field H_c (applied to our system continually). We have the following;

$$\phi(t, H_c) = \phi(-t, -H_c)$$

$$\phi(t, H_c) = \bar{\phi}(t, -H_c)$$

or

$$\phi_{xy}(t, H_c) = \phi_{yx}(t, -H_c)$$

$$\chi(\omega, H_c) = \tilde{\chi}^*(\omega, -H_c)$$

The classical case requires only that the energy differences $E_m - E_n$ of the various levels of the system connected by matrix elements of M should be much smaller than kT.

$$| E_m - E_n | = \hbar\omega_{nm} \ll kT \qquad \text{(III-28)}$$

Using the expansion

$$M_x(t + i\hbar\lambda) = M_x(t) + i\hbar\lambda\dot{M}_x(t) + \tfrac{1}{2}(i\hbar\lambda)^2\ddot{M}_x(t) + \text{--------}$$

and substituting this into Equation (III-19), we obtain,

$$\phi_{xy}(t) + \beta\bar{M}_{ox}\bar{M}_{oy} = \beta\langle M_x(t)\, M_y\rangle + \text{second order of } \beta^2 \qquad \text{(III-29)}$$

Condition (III-28) tells us β is very small ($\beta = \frac{1}{kT}$) so, that is to say we can ignore "β^2" terms in Equation (III-29), we then get;

$$\phi_{xy}(t) = \beta \left[\left< M_x(t)\, M_y \right> - \bar{M}_{ox}\bar{M}_{oy} \right] \qquad \text{(III-30)}$$

This equation satisfies all the properties of the relaxation function. The function $\left< M_x(t+\tau) M_y(\tau) \right> = \left< M_x(t)\, M_y(o) \right>$ is the correlation of $M_x(t+\tau)$ and $M_y(t)$. It is called the x-y component of the correlation tensor of magnetic moment at time interval t. In the low frequency cases, we see that, the relaxation function (Eq. III-30) is proportional to the correlation tensor of the magnetic moment.

III - 3 - SYMMETRIC AND ANTISYMMETRIC TENSORS

The symmetric and antisymmetric parts of the relaxation tensor are respectively defined by,

$$\phi^{s}_{xy}(t) = \frac{1}{2}\left[\phi_{xy}(t) + \phi_{yx}(t)\right] = \frac{1}{2}\left[\phi_{xy}(t) + \bar{\phi}_{xy}(t)\right] \qquad \text{(III-31)}$$

$$\phi^{a}_{xy}(t) = \frac{1}{2}\left[\phi_{xy}(t) - \phi_{yx}(t)\right] = \frac{1}{2}\left[\phi_{xy}(t) - \bar{\phi}_{xy}(t)\right] \qquad \text{(III-32)}$$

substituting Equation (III-19) in these equations, we have, (t_o=o)

$$\phi^{s}_{xy}(t) = \int_{0}^{\beta} \frac{1}{2} \langle M_x(t-i\hbar\lambda)M_y + M_x(-t-i\hbar\lambda)M_y \rangle d\lambda - \beta \bar{M}_{ox} \bar{M}_{oy}$$

$$= \int_{0}^{\beta} \frac{1}{2} \langle M_y(t-i\hbar\lambda)M_x + M_y(-t-i\hbar\lambda)M_x \rangle d\lambda - \beta \bar{M}_{ox} \bar{M}_{oy} \qquad \text{III-33)}$$

$$\left.\begin{aligned} \phi^{a}_{xy}(t) &= \int_{0}^{\beta} \frac{1}{2} \langle M_x(t-i\hbar\lambda)M_y - M_x(-t-i\hbar\lambda)M_y \rangle d\lambda \\ &= \int_{0}^{\beta} \frac{1}{2} \langle -M_y(t-i\hbar\lambda)M_x + M_y(-t-i\hbar\lambda)M_x \rangle d\lambda \end{aligned}\right\} \qquad \text{(III-34)}$$

$\phi^{s}_{xy}(t)$ is real and even in "t", whereas , $\phi^{a}_{xy}(t)$ is odd in "t".

For β = small (low frequency approximation) $i\hbar\beta \cong o$ and our equations become

$$\phi^{s}_{xy}(t) = \tfrac{1}{2}\beta \langle \left[M_x(t)M_y \right] + \left[M_x(-t)M_y \right] \rangle - \beta \bar{M}_{ox} \bar{M}_{oy}$$

$$= \tfrac{1}{2}\beta \langle \left[M_xM_y(t) \right] + \left[M_xM_y(-t) \right] \rangle - \beta \bar{M}_{ox} \bar{M}_{oy} \qquad \text{(III-35)}$$

$$\phi^{a}_{xy}(t) = \tfrac{1}{2}\beta \langle \left[M_x(t)M_y \right] - \left[M_x(-t)M_y \right] \rangle$$

$$= \tfrac{1}{2}\beta \langle -\left[M_xM_y(t) \right] + \left[M_xM_y(-t) \right] \rangle \qquad \text{(III-36)}$$

Now, we write the symmetric and antisymmetric parts of the susceptibility tensor as;

$$\chi_s^* = \chi_0 - \frac{i\omega}{V}\int_0^\infty \phi^s(t)\, e^{-i\omega t}\, dt \qquad \text{(III-37)}$$

$$\chi_a^* = -\frac{i\omega}{V}\int_0^\infty \phi^a(t)\, e^{-i\omega t}\, dt \qquad \text{(III-38)}$$

Neglecting the effect of χ' in energy absorption, we write the rate of energy absorption by the magnetic system for linearly polarized radiation.

$$Q = (\pi\nu H_1 \chi'' H_1)V = (\pi\nu H_1 \chi_s'' H_1)V \qquad \text{(III-39)}$$

we have for χ''_s and χ''_{sxy}

$$\chi_s'' = \frac{\omega}{2V}\int_{-\infty}^{\infty} \phi^s(t)\, e^{-i\omega t}\, dt \qquad \text{(III-40)}$$

and $$\chi_{sxy}'' = \frac{\omega\beta}{4V}\int_{-\infty}^{\infty}\left[\left\langle \{M_x(-t)M_y\} + \{M_x(-t)M_y\}\right\rangle - 2\bar{M}_{0x}\bar{M}_{0y}\right] e^{-i\omega t}\, dt$$

(III-41)

that is because ϕ^s is even in "t". i.e $M_x(t) = M_x(-t)$

Let us consider that the absorption of radiation linearly polarized in the x direction for β = small case. We here define $A(\omega)$ the absorption coefficient as,

$$A(\omega) = \nu \chi''_{xx}(\omega) \tag{III-42}$$

with the help of Equation (III-41),

$$A(\omega) = \frac{\omega^2 \beta}{2\pi \nu} \int_{-\infty}^{\infty} \left[\left\langle \left\{ M_x(t) M_x \right\} \right\rangle - \bar{M}_{0x}^2 \right] e^{-i\omega t} dt \tag{III-43}$$

$$\boxed{A(\omega) = \frac{\omega^2 \beta}{2\pi \nu} \int_{-\infty}^{\infty} G(t) e^{-i\omega t} dt} \tag{III-44}$$

with $G(t) = \left\langle \left\{ M_x(t) M_x \right\} \right\rangle - \bar{M}_{ox}^2 = \left\langle \left\{ M_x(t+\tau) M_x(\tau) \right\} \right\rangle - \bar{M}_{ox}^2$

(III-45)

$$\boxed{G(t) = \frac{\nu}{\beta} \int_{-\infty}^{\infty} \frac{A(\omega)}{\omega^2} e^{i\omega t} d\omega} \tag{III-46}$$

Equations (III-44) and (III-46) tell us a very important statement: $A(\omega)$ is the Fourier transform of the "auto-moment" of M_x and conversely the "auto-moment" of G(t) is Fourier transform of $A(\omega)/\omega^2$

We now define the "spectral density" as,

$$I(\omega) = \lim_{T \to \infty} \frac{T}{2} \left\langle \left[\frac{1}{T} \int_0^T \left\{ M_x(t) - \bar{M}_{0x} \right\} e^{-i\omega t} dt \right]^2 \right\rangle \tag{III-47}$$

it follows that; (Kubo and Tomita)

$$I(\omega) = \int_0^{\infty} G(t)\ \mathrm{Cos}\,\omega t\ dt = \tfrac{1}{2}\int_{-\infty}^{\infty} G(t)e^{-i\omega t}\ dt \qquad \text{(III-48)}$$

G(t) is an even function of t, so we write,

$$G(t) = \frac{2}{\pi}\int_0^{\infty} I(\omega)\,\mathrm{Cos}\,\omega t\,d\omega = \frac{1}{\pi}\int_{-\infty}^{\infty} I(\omega)e^{i\omega t}d\omega \qquad \text{(III-49)}$$

The auto correlation of $M_x(t)$ is $G(t)/G(o)$. The distribution of $A(\omega)/\omega^2$ is the spectral density of the random variation of $M_x(t)$, or the Fourier transform of the auto-correlation function.

PART II

III - 4 - BROADENING

We write the Hamiltonian of the system under consideration as;

$$\mathcal{H} = \mathcal{H}_o + \varepsilon\mathcal{H}' \qquad \text{(III-50)}$$

where the unperturbed Hamiltonian ($\mathcal{H}_o$) is a measure of sharpness of the resonance line and the perturbed Hamiltonian ($\varepsilon\mathcal{H}'$) indicates broadening and shifting at this resonance curve. We call ε the Interaction Constant. We can expand the Fourier transform or the characteristic function of the intensity distribution of the absorption in successive powers of the perturbation (ε). To be precise, we assume that the logarithm of the characteristic function of each of the resonance lines can be expanded in powers of ε. After obtaining the characteristic function, we shall be able to produce the intensity distribution or the shape of the resonance line. Doing that we go up to the second order of ε because the second order of ε gives us most of general feature of the general feature of the shape of resonance line. The resonance lines with $\varepsilon = o$ (i.e. absorptions corresponding to the unperturbed case) are called the Main Lines or the Resonance Lines of Zero-th Order. The perturbation of course gives rise to shifts and the broadening of these lines and causes the appearance of other lines. We call them the satellites or the Resonance Lines of Higher Orders.

We make the following assumptions for our theory:

1) Low frequency approximation is made. The absorption energy is much smaller than the thermal energy. We write

$$\hbar w \ll kT$$

2) We consider only a single main absorption. The satellites are not in our concern and they are far enough from the main line to neglect their effects (contributions).

3) If the main line has more than one peak, it will not be the object of our theory.

4) The absorption curve is smooth and differentiable to any order.

Let us introduce the Hamiltonian of the system under consideration as follows

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_L + \mathcal{H}_p \qquad \text{(III-51)}$$

where $\mathcal{H}_z$ is the Zeeman part

$\mathcal{H}_p$ is the dipolar interaction part

$\mathcal{H}_L$ is the motion part

H_p dipolar interaction depends on the nuclear spins and space coordinates of nuclei.

In Quantum Mechanics, the averages over the nuclear spins are given by (trace operation):

$$\left\langle (\ldots\ldots) \right\rangle_{spin} = \frac{Tr_{spin}(\ldots\ldots)}{Tr\left\{1\right\}} \tag{III-52}$$

and the averages over the motions are,

$$\left\langle (\ldots\ldots) \right\rangle_{\substack{nuclear\\ motion}} = \frac{Tr\left\{e^{-\beta\mathcal{H}}(\ldots\ldots)\right\}}{Tr\left\{e^{-\beta\mathcal{H}}\right\}} \tag{III-53}$$

Therefore, the Fourier transform of the intensity distribution function G(t) can be expressed as follows.

$$G(t) = \frac{Tr\left\{e^{-\beta\mathcal{H}}\frac{1}{2}\left[Me^{i\mathcal{H}t}Me^{-i\mathcal{H}t} + e^{i\mathcal{H}t}Me^{-i\mathcal{H}t}M\right]\right\}}{Tr\left\{e^{-\beta\mathcal{H}}\right\}} \tag{III-54}$$

$$= \left\langle M_tM \right\rangle \quad \text{with} \quad M_t = e^{i\mathcal{H}t}Me^{-i\mathcal{H}t}, \quad M_t = M(t) \tag{III-55}$$

Dipole moment operator M represents the interaction of the system with radiation field. Equation (III-54) is the same as Equation (III-45) and M replaces M_x because as mentioned earlier, the magnetic field of the radiation is linearly polarized in the x direction.

The calculation of the intensity distribution function is reduced to that of the function G(t). This is the basis of the Fourier Integral Method. Calculating G(t) requires the knowledge of the magnetic moments. We first write the equation of motion for M_t. (Equation III-11).

$$i\hbar\dot{M}_t = \left[M_t, \mathcal{H} \right] \tag{III-56}$$

with the initial condition $M_{t=o} = M$

Secondly, we expand the solution of this equation in powers of the perturbation (ε). We have;

$$M_t = \varepsilon^0 M_t^0 + \varepsilon^1 M'_t + \varepsilon^2 M''_t + \text{-------} + \varepsilon^n M_t^{(n)} \tag{III-57}$$

the general term is given by;

$$M_t^{(n)} = (-i\hbar)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots\cdots \int_0^{t_{n-1}} dt_n \tag{III-58}$$

$$\times \left[\text{----} \left[M_t^0, H'(t_1) \right] H'(t_2) \right] \text{-----} \Big] H'(t_n) \Big]$$

The magnetic moment and field corresponding to the unperturbed motion can be respectively expressed as,

$$M_t^o = e^{i\mathcal{H}_o t} \, M \, e^{-i\mathcal{H}_o t} \qquad \text{(III-59)}$$

$$\mathcal{H}'(t) = e^{i\mathcal{H}_o t} \, H' \, e^{-i\mathcal{H}_o t} \qquad \text{(III-60)}$$

We can easily see that, with the expansion of M_t, the function G(t) becomes

$$\boxed{G(t) = \varepsilon^0 \left\langle M_t^0 M \right\rangle + \varepsilon^1 \left\langle M_t' M \right\rangle + \varepsilon^2 \left\langle M_t'' M \right\rangle + \cdots}$$

(III-61)

Now all we need to do is to calculate the terms in G(t). Let us first introduce the decomposition of the dipolar interaction in the following form:

$$\mathcal{H}_p = c \sum_{m=-2}^{2} \sum_{i<j} Y_2^{-m}(\theta_{ij}, \varphi_{ij}) \, T_{ij}^m (-1)^m \Big/ r_{ij}^3 \qquad \text{(III-62)}$$

where $c = \hbar^2 \gamma^2 \sqrt{4\pi/5}$

Y_2^{-m} is a spherical harmonic

$(\theta_{ij}, \varphi_{ij})$ is the direction of r_{ij}

T_{ij}^m is an irreducible tensorial spin operator.

We here introduce some ideas related to irreducible spherical tensor operator T.

T_L^M is defined as a tensor of rank L with (2L + 1) elements. T_L^M has the following communication relation with the angular momentum operator.

$$\left[I_{\pm} , T_L^M \right] = \left[(L \mp M) (L \pm M + 1) \right]^{1/2} T_L^{M \pm 1} \qquad \text{(III-63)}$$

$$\left[I_z , T_L^M \right] = M \, T_L^M \qquad \text{(III-64)}$$

where $I_{\pm} = I_x \pm iI_y$

Also the spherical harmonic has the same commutation relation with angular momentum operator.

$$\left[I_{\pm} , Y_L^M \right] = \left[(L \mp M) (L \pm M + 1) \right]^{1/2} Y_L^{M \pm 1} \qquad \text{(III-65)}$$

$$\left[I_z , Y_L^M \right] = M \, Y_L^M \qquad \text{(III-66)}$$

As an example, let us take rank of 1, (angular momentum by itself).

$$T_1^M = I_1^M$$

claearly I_1^M has three components ($M = -1, 0, 1$)

$M = -L, \ldots\ldots, +L$

These three components are given by:

$$I_1 = -\frac{1}{\sqrt{2}}\left(I_x + iI_y\right) = -\frac{1}{\sqrt{2}} I_+ \qquad \text{(III-67)}$$

$$I_0 = I_z \qquad \text{(III-68)}$$

$$I_{-1} = \frac{1}{\sqrt{2}}\left(I_x - iI_y\right) = \frac{1}{\sqrt{2}} I_- \qquad \text{(III-69)}$$

Now, coming back to the decomposition of the dipolar interaction, as we consider the interaction between two spins, we must take into account the possible combinations of their components. These components would be 1 - Step up I_+ 2 - Step down I_- 3 - Spin of z-direction I_z. And the combinations are:

(a) $I_z I_z$ (b) $I_z I_+$ (c) $I_z I_-$ (d) $I_+ I_+$ (e) $I_+ I_-$ (f) $I_- I_-$

From the last three equations, we can clearly see that items (a) and (e) are zero, (b) is +1, (c) is -1 (d) is +2 and (f) is -2.

Therefore, we have the following:

$$T_{ij}^{0} = I^{i} \cdot I^{j} - 3 I_z^{i} I_z^{j} \qquad \text{(III-70)}$$

$$T_{ij}^{1} = \sqrt{\tfrac{3}{2}}\left(I_z^{i} I_+^{j} + I_z^{j} I_+^{i}\right) = -\left(T_{ij}^{-1}\right)^{\dagger} \qquad \text{(III-71)}$$

$$T_{ij}^{2} = -\sqrt{\tfrac{3}{2}}\, I_+^{i} I_+^{j} = \left(T_{ij}^{-2}\right)^{+} \qquad \text{(III-72)}$$

for L = 2 we write Equation (III-63) as:

$$[I_\pm , T_{ij}^{m}] = [6 - m(m \pm 1)]^{1/2}\, T_{ij}^{m\pm 1} \qquad \text{(III-73)}$$

we obtain, (we took C = 1) for simplicity)

$$\langle M_t^{\circ} M \rangle = -\frac{1}{6} N I(I+1)\left(e^{i\omega_z t} + e^{-i\omega_z t}\right) \qquad \text{(III-74)}$$

$$\langle M_t' M \rangle = 0 \qquad \text{(III-75)}$$

$$\langle M_t'' M \rangle = -\int_0^t dt_1 \int_0^{t_1} dt_2 \sum_m \sum_{m'} \sum_{ij} e^{-i\omega_z (m t_1 + m' t_2)} \qquad \text{(III-76)}$$

$$\langle [M_t^{\circ}, T_{ij}^{m}][T_{ij}^{m'}, M] \rangle F_{ij}^{-m, -m'}(t_1 - t_2)$$

$$\text{Where} \quad F_{ij}^{mm'}(t_1 - t_2) = \langle \{ \Phi_{ij}^{m}(t_1)\, \Phi_{ij}^{m'}(t_2) \} \rangle \qquad \text{(III-77)}$$

$$\Phi_{ij}^{m} = Y_2^{m}(\theta_{ij}, \varphi_{ij}) / r_{ij}^{3} \qquad \text{(III-78)}$$

Functions "F_s" are the correlation functions of the coefficients of the dipolar interaction which are functions of nuclear coordinates.

Neglecting the unimportant terms, we rewrite Equation (III-76)

$$\langle M_t'' M\rangle = -\frac{1}{4}N[I(I+1)]^2 e^{i\omega_z t}\int_0^t dt_1\int_0^{t_1} dt_2$$

$$\times\left\{F^{0,0}(\tau)+\frac{16}{9}e^{i\omega_z\tau}F^{1,-1}(\tau)+\frac{8}{3}e^{-i\omega_z\tau}F^{-1,1}(\tau)+\frac{16}{9}e^{-2i\omega_z\tau}F^{-2,2}(\tau)\right\}+\text{Conj.} \tag{III-79}$$

with $\tau = t_1 - t_2$

The F-Functions in this equation are the correlation functions of the tensor components of the local field due to the dipolar forces. We define them as:

$$F^{mm'}(\tau) = \sum_j F_{ij}^{mm'}(\tau) \tag{III-80}$$

And they have the following properties,

$$\overline{F^{m,-m}(\tau)} = F^{-m,m}(\tau) = F^{m,-m}(-\tau) \tag{III-81}$$

We now collect the terms in the expansion which have the time factor $e^{i\omega_z t}$ and regard them as the expanded form of an exponential function, which is assumed to be a good approximation to the actual characteristic function of the absorption intensity of the main line. And we take the function G(t) as

$$G(t)=\frac{C_1 N}{6kT}I(I+1)e^{i\omega_z t}\exp\left[-\frac{3}{2}I(I+1)\int_0^t dt_1\int_0^{t_1} dt_2 \right. \tag{III-82}$$

$$\left.\left\{F^{0,0}(\tau)+\left[\frac{16}{9}e^{i\omega_z\tau}F^{1,-1}(\tau)+\frac{8}{9}e^{-i\omega_z\tau}F^{-1,1}(\tau)+\frac{16}{9}e^{-2i\omega_z\tau}F^{-2,2}(\tau)\right]\right\}\right]$$

(here C_1 is a constant)

We are now able to show the proper choice of the combinations of the perturbation by looking at the time factors of expanded terms. There is a certain mathematical reason for our procedure. Assumption (4) means mathematically that the characteristic function has to satisfy an integrability condition. It is to say that G(t) is always integrable over $(-\infty,\infty)$ when multiplied by $t^n (n > 0)$.

Equation (III-82) is called the second approximation of the characteristic function. Limiting ourselves to this approximation means that we start from a Gaussian distribution for the ideally rigid lattice and treat the change in the resonance shape caused by the nuclear motion.

As to the effect of nuclear motion, it is a sort of Gaussian process for the random modulation of the resonance frequency of a magnetic unit due to the fluctuation of interactions with other magnetic units.

In the case of a rigid lattice, all of the F-functions are constant. The first term in the exponent of Equation (III-82) becomes $\omega_p^2 t^2/2$. ω_p^2 is the second moment of the rigid lattice due to the dipolar broadening. And all the other terms in the heavy bracket in the integrand give rise to the satellites at $\omega = o$ and $\omega = 2\omega_z$. They also cause a shift and decrease of the height of the main absorption.

But for a non-rigid lattice, these terms contribute to the broadening of the main line. We take the asymptotic limits of Equation (III-82) for $|t| \to \infty$, we have,

$$G(t) = \frac{c_1}{6kT} N I(I+1) e^{i\omega_z t} \exp\Big[-\frac{3}{2} I(I+1) \int_0^t (t-\tau) F^{0,0}(\tau)\, d\tau$$

$$-\frac{3}{2} I(I+1) |t| \, Re\Big\{ \frac{20}{9} \int_{-\infty}^{\infty} e^{-\omega_z t} F^{-1,1}(\tau)\, d\tau + \frac{8}{9} \int_{-\infty}^{\infty} e^{-2i\omega_z \tau} F^{2,2}(\tau)\, d\tau \Big\}$$

$$-\frac{3}{2} I(I+1)\, i t \, I_m \Big\{ \frac{8}{9} \int_0^{\infty} e^{-i\omega_z t} F^{-1,1}(\tau)\, d\tau + \frac{16}{9} \int_0^{\infty} e^{-2i\omega_z \tau} F^{-2,2}(\tau)\, d\tau \Big\} \Big]$$

(III-82')

The first term in the exponent of Equation (III-82') (i.e. $\frac{3}{2} I(I+1) \int_0^t (t-\tau) F^{0,0}(\tau)\, d\tau$) is called the adiabatic term. The integral in the exponent is proportional to $t^2/2$ if t is small enough. And this proportionality constant is exactly the second moment ω_p^2 for the rigid lattice. The second moment of the intensity distribution function remains constant throughout the narrowing process. And the non-adiabatic broadening is not effective. (The rest of the terms in the exponent of Equation (III-82') is called non-adiabatic terms.

We can express the adiabatic effect (spin-spin relaxation effect) as;

$$G_{ad}(t)=\exp\left[-\omega_p^2\int_0^t (t-\tau)\, f(\tau)\, d\tau\right] \qquad \text{(III-83)}$$

where $f(\tau)=F^{0,0}(\tau)/F^{0,0}(0)$ (III-84)

and $f(-\tau)=f(\tau)$

Let us write the integrand in the exponent of Equation above (with $t \longrightarrow \infty$) as,

$$\int_0^\infty (t-\tau)\, f(\tau)\, d\tau = t\underbrace{\int_0^\infty f(\tau)\, d\tau}_{A=\tau_c^0}-\underbrace{\int_0^\infty \tau f(\tau)\, d\tau}_{B} \qquad \text{(III-85)}$$

where τ_c^0 is the correlation time.

If (A) and (B) are convergent, $G_{ad}(t)$ becomes:

$$G_{ad}(t)=\exp\left[-\omega_p^2\, \tau_c^0\, |t| + \omega_p^2\int_0^\infty f(\tau)\, \tau\, d\tau\right] \qquad \text{(III-86)}$$

The adiabatic term gives a resonance curve which is always Lorentzian (or the damped oscillator type) at the centre of the resonance, if the lattice is not rigid. And $\omega_p^2\tau_c^0$ is the half width of this curve.

The most effective narrowing is seen when $\omega_p \tau_c^0 \lesssim 1$.

We here note that for the special case where

$$f(\tau) = \exp(-|\tau|/\tau_c^\circ) \quad \text{(III-87)}$$

BPP's equation can be obtained.

$$\left(\frac{1}{T_2'}\right)^2 = \left(\frac{1}{T_2''}\right)^2 \frac{2}{\pi} \tan^{-1} \frac{2\tau_c^\circ}{T_2'} \quad \text{(III-88)}$$

where T_2' ⟶ spin-spin relax. time with lattice motion

T_2'' ⟶ spin-spin relax. time with rigid lattice case.

Kubo and Tomita made some numerical calculations by using Equations (III-86) and (III-87). They found that the general direction of the change in the half width $\Delta\omega$ is much similar to that described by Equation (III-88), and the exact curve fits well to a modified form of (III-88). We have

$$(\Delta\omega)^2 = \frac{4\log 2}{\pi} \omega_p^2 \tan^{-1}\left(\frac{\pi\tau_c^\circ}{4\log 2}\Delta\omega\right) \quad \text{(III-89)}$$

The figure overleaf shows us the narrowing proceed with the decrease of τ_c°.

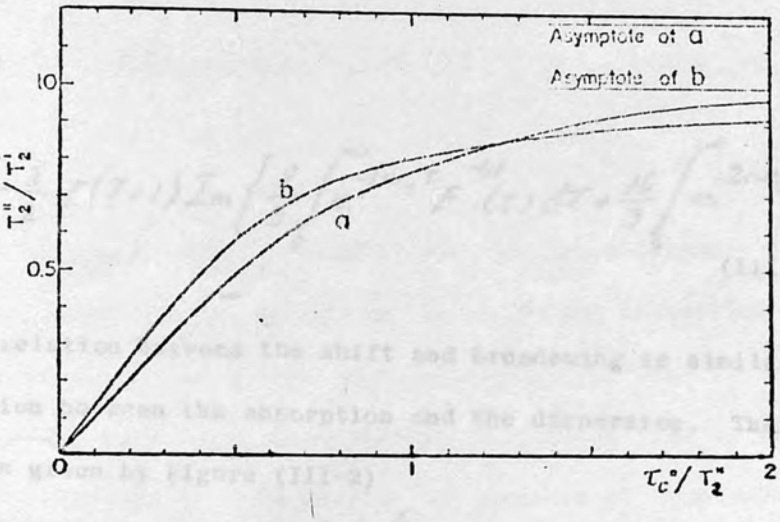


Figure III-1. Half width due to the adiabatic effect from Equation(III-86) and (III-87). The unit of the width $1/T_2'$ is $1/T_2''$. (Kubo and Tomita)

(Curve "a" is by a rigorous numerical calculation (Eq. 86 and 87) Curve "b" is by Equ. 88).

Now we can express the non-adiabatic effect (spin-lattice relaxation) with the characteristic function of the form,

$$G_{non\text{-}ad}(t) = \exp\left(-\frac{|t|}{T_1'} + it\delta\right) \tag{III-90}$$

The importance of the non-adiabatic effect is two.

1-) It gives rise to a broadening with a Lorentzian form. And its half-width is,

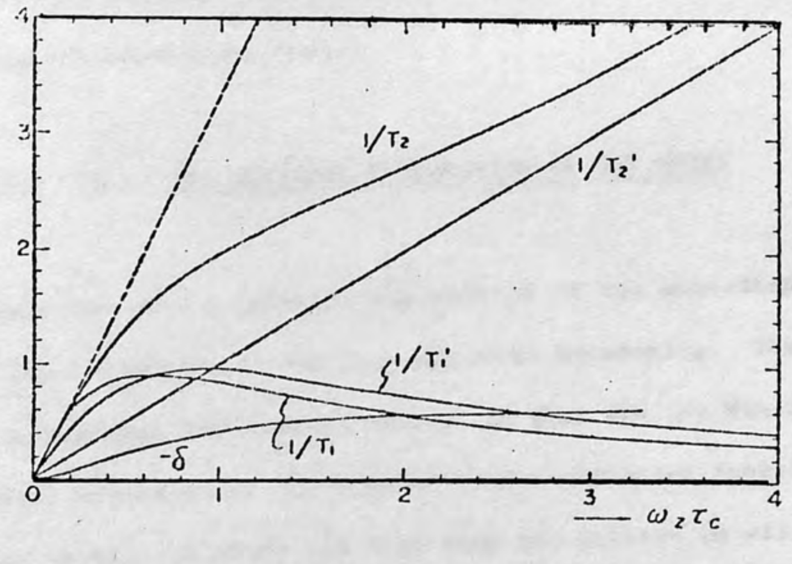
$$\frac{1}{T_1'} = \frac{3}{2} I(I+1)\left\{\frac{20}{9}\int_{-\infty}^{\infty} e^{-i\omega_z\tau} F^{-1,1}(\tau)\,d\tau + \frac{8}{9}\int_{-\infty}^{\infty} e^{-2i\omega_z\tau} F^{-2,2}(\tau)\,d\tau\right\} \tag{III-91}$$

2-) It causes a shift of the resonance peak, δ which is given by;

$$\delta = -\frac{3}{2} I(I+1) I_m \left\{ \frac{8}{9} \int_0^{\infty} e^{-i\omega_z \tau} F^{-1,1}(\tau) d\tau + \frac{16}{9} \int_0^{\infty} e^{-2i\omega_z \tau} F^{-2,2}(\tau) d\tau \right\} \quad \text{(III-92)}$$

The relation between the shift and broadening is similar to the relation between the absorption and the dispersion. Their behaviour is given by Figure (III-2)

If the condition $\omega_z \lesssim 1/\tau_c$ is satisfied, the non-adiabatic effect becomes important.



Figure(III-2) Curves for the adiabatic half-width $1/T_2'$, the nonadiabatic half-width $1/T_1'$, the nonadiabatic shift δ and the spin-lattice relaxation rate $1/T_1$. The assumption for this calculation are: 1) all of the correlation functions are given by Eq.(87), 2) the atomic arrangement is isotropic , and 3)

The unit of all of these rates is ω_p^2 / ω_z . (Kubo and Tomita)

It is also interesting to point out the exact relation between the non-adiabatic broadening and the spin-lattice relaxation time. They are both described by the same characteristic time T_1. But this is not the case. The spin-lattice relaxation time is defined as the time constant characterizing the decrease of temperature difference between the lattice system and the spin system. The spin-lattice relaxation time is the rate of energy transfer. But the non-adiabatic broadening comes from the limitation of the life time of each of quasi-stationary levels.

III - 5 - THE PHYSICAL EXPLANATION OF THE SHIFT

We shall now give a physical explanation of the non-adiabatic shift and its relaxation to the non-adiabatic broadening. The shift and broadening are clearly related as they are the Sin. and Cos. Fourier transform of the dipolar auto-correlation function. And in this section we shall see that they are related to virtual and real transition between the energy levels of the spin. A virtual transition occurs when a spin is at energy level E_m jumps to another energy level E_n (where it remains for a short time before returning to the initial state). This occurs in violation of the conservation of energy, so the time t of the excursion is limited by

$$t \sim \frac{1}{E_m - E_n}$$

The figure below shows the energy levels caused by the virtual transitions.

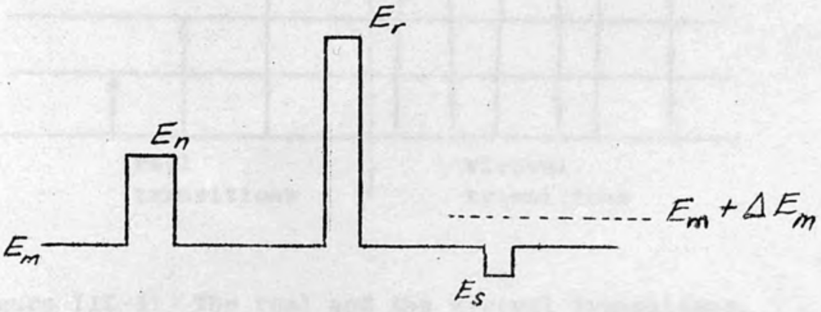


Figure III-3: The mean energy of the state is no longer E_m, but $E_m + \Delta E_m$

Now the lattice or the motion of the spins gives a finite lifetime to the spin levels of duration τ_c

Spins also make their own natural transitions called the real transitions obeying the selection rules. And the real transitions can disappear if only and only the magnetic field is removed. We must consider the distinguish between the virtual and real transitions. Figure (III-4) represents the transitions:

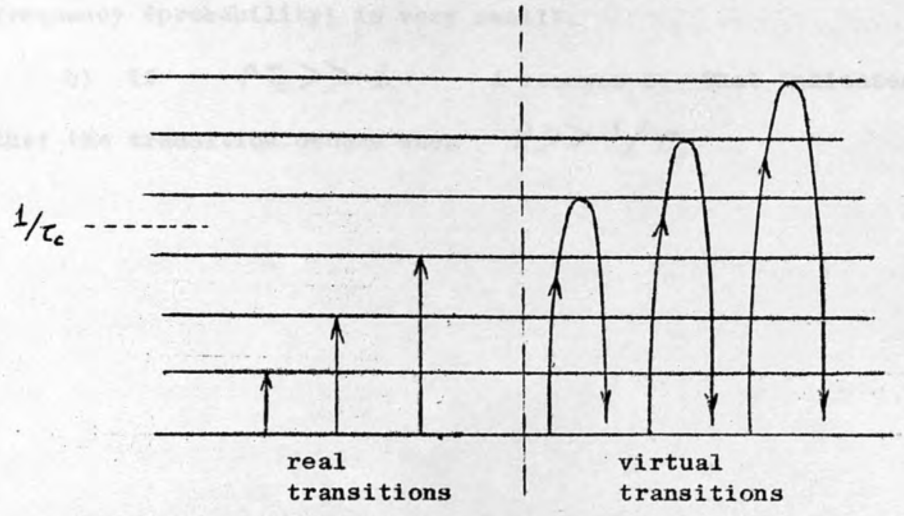


Figure III-4: The real and the virtual transitions.

We here note that virtual transition process occurs suddenly, quickly with high frequency as its life-time is short.

The expression for the shifted energy level ΔE_m is given by;

$$\Delta E_m = \sum_{p \neq 0} \frac{\overline{\langle m|H(t)|m+p\rangle\langle m+p|H(t)|m\rangle}}{p} \cdot \underbrace{\left(1-\frac{1}{1+p^2\tau_c^2}\right)}_{A}$$

In this equation the term (A) in the bracket can be studied closely.

a) If $p\tau_c \ll 1$ A becomes zero. That means no virtual transition for such a case $p \ll 1/\tau_c$ (The transition frequency (probability) is very small).

b) If $\rho\tau_c \gg 1$ A becomes 1. That indicates that the transition occurs when $\rho \gg 1/\tau_c$

CHAPTER IV

REDUCED DENSITY MATRIX

IV - 1 - PHYSICAL MEANING OF REDUCED DENSITY MATRIX.

As mentioned in Chapter II, in order to have full information about a complete system, we introduce the complete density matrix "ρ". And also we showed that the expectation value of an operator is given by this matrix element. Our concern is here to find the expectation value of an operator which is a function of only a few of the variables of ρ.

Let A(p) be an operator for our particular interest with the variable p. We have the following expression:

$$\langle A(\rho)\rangle = \mathrm{Tr}_{pq}\left\{ \rho\ (\rho, q)\ A(\rho) \right\} \qquad \text{(IV-1)}$$

(where "q"s are the other variables which specify ρ). Since A is independent of ρ , Equation (IV-1) can be factorised in the following way,

$$\langle A(\rho)\rangle = \mathrm{Tr}\left[\left[\mathrm{Tr}_q\ \rho(\rho,q)\right]\ A(\rho) \right] \qquad \text{(IV-2)}$$

$\mathrm{Tr}_q\ \rho\,(\rho,q)$ is called the "Reduced Density Matrix" and it contains all the information necessary to evaluate the expectation value. We will use σ to symbolize it. We write,

$$\sigma(\rho) = \mathrm{Tr}_q\ \rho\,(\rho,q) \qquad \text{(IV-3)}$$

$\sigma(\rho)$ can be regarded as a complete density matrix in its own right. We don't have any operators which depend on more variables than p. The expectation value of A(p) in terms of σ(p) is through Equations (IV-2) and (IV-3) given by:

$$\langle A(p)\rangle = \mathrm{Tr}\left\{\sigma(p)\ A(p)\right\} \qquad \text{(IV-4)}$$

The Von-Neumann equation can also be written in terms of $\sigma(p)$

$$i\hbar\dot{\sigma}(\rho) = \left[\mathcal{H}, \sigma(\rho)\right] \qquad \text{(IV-5)}$$

The relation between the reduced density matrix and the density matrix for the complete set is:

$$\sigma = \langle \rho \rangle \qquad \text{(IV-6)}$$

IV - 2 - THE MASTER EQUATION FOR THE DENSITY MATRIX

In the case of NMR, we are only interested in the spin part of the density operator. In fact, our system has the degrees of freedom for spin and lattice (bath). Therefore, as already mentioned, the total Hamiltonian ($\mathcal{H}$) of the system covers 1 - Zeamann. 2 - dipolar 3-motion parts. We can also express the Hamiltonian (Abragam) as a sum of unperturbed and perturbed parts. The equation of motion of the density matrix ρ can be written in the following way:

$$i\hbar\dot{\rho}(t) = \left[\mathcal{H}_0 + \mathcal{H}_1(t), \rho\right] \qquad \text{(IV-7)}$$

where $\mathcal{H}_0$ and $\mathcal{H}_1$ (t) are respectively the unperturbed and perturbed parts of the Hamiltonian. The perturbing Hamiltonian $\mathcal{H}_1(t)$ is a stationary random operator.

We now introduce σ and $\mathcal{H}_1^*(t)$ in the interaction form

$$\sigma = e^{i\mathcal{H}_0 t}\,\rho\,\,e^{-i\mathcal{H}_0 t} \tag{IV-8}$$

$$\mathcal{H}_1^*(t) = e^{i\mathcal{H}_0 t}\,\mathcal{H}_1(t)\,e^{-i\mathcal{H}_0 t} \tag{IV-9}$$

by using these two equations, Equation (IV-7) becomes;

$$i\hbar\dot{\sigma} = \left[\sigma, \mathcal{H}_1^*(t)\right] \tag{IV-10}$$

And the solution of (IV-10) is (up to second order):

$$\sigma(t) = \sigma(0) - i\int_0^t \left[\mathcal{H}_1^*(t'), \sigma(0)\right]dt' - \int_0^t dt' \int_0^{t'} dt'' \left[\mathcal{H}_1^*(t'), \left[\mathcal{H}_1^*(t''), \sigma(0)\right]\right] \tag{IV-11}$$

taking the time derivative of (IV-11)

$$\dot{\sigma}(t) = -i\left[\mathcal{H}_1^*(t), \sigma(0)\right] - \int_0^t d\tau \left[\mathcal{H}_1^*(t), \left[\mathcal{H}_1^*(t-\tau), \sigma(0)\right]\right] \tag{IV-12}$$

with $\tau = t - t'$

Because we are interested in total spin not the spin of individual particle, we take the average of Equation (IV-12) over all the random Hamiltonians ($\mathcal{H}_1$). σ is a random operator like $\mathcal{H}_1(t)$ according to Equation (IV-12). When doing the averaging process, we make the following assumptions (Abragam):

1 - It is permissible to neglect the correlation between $\mathcal{H}_1^*(t)$ and $\sigma(o)$ in the averaging of Equation (IV-12) and average them separately.

2 - It is then permissible to replace $\sigma(o)$ by $\sigma(t)$ on the right-hand side of Equation (IV-12).

3 - It is permissible to extend the upper limit of the integral to $+\infty$

4 - All unwritten higher-order terms on the right-hand side of Equation (IV-12) can be neglected.

Then we have;

$$\dot{\sigma} = -\int_0^\infty d\tau \overline{\left[\mathcal{H}_1^*(t), \left[\mathcal{H}_1^*(t-\tau), \sigma(t)\right]\right]} \tag{IV-13}$$

we can also derive this equation from Kubo's;

$$\rho(t) = e^{i\mathcal{H}t} \rho(o)\, e^{-i\mathcal{H}t} \quad \text{with} \quad |\psi(t)\rangle = e^{i\mathcal{H}t}|\psi(o)\rangle$$

we average this density operator over the bath variables. $\rho(t)$ is given by (time dependent)

$$\rho(t) = \left[\exp i\int_0^t \mathcal{H}^1(\tau)\, d\tau\right] \rho(o) \tag{IV-14}$$

If ρ is a function of spin variables only then we need to look at

$$\left\langle e^{i\int_0^t \mathcal{H}^1(\tau)d\tau} \right\rangle \quad \Big| \quad \text{with } \mathcal{H}^1 = [\mathcal{H}, \ ]$$

$$\left\langle e^{i\int_0^t \mathcal{H}^1(\tau)d\tau} \right\rangle = \exp -\int_0^t (t-\tau) \left\langle \mathcal{H}^1(o)\, \mathcal{H}^1(\tau) \right\rangle d\tau \tag{IV-15}$$

i.e. $$\sigma(t) = \exp - \int_0^t (t-\tau) \langle \mathcal{H}^1(0)\mathcal{H}^1(\tau) \rangle d\tau\, \sigma(0) \qquad \text{(IV-16)}$$

let f(t) and g(t) be two functions, we have,

$$f(t) = \exp - \int_0^t (t-\tau)\, g(\tau)\, d\tau$$

$$\dot{f}(t) = -f(t) \int_0^t g(\tau)\, d\tau$$

similar to this we have,

$$\dot{\sigma}(t) = - \int_0^t \langle \mathcal{H}^1(0)\mathcal{H}^1(\tau) \rangle d\tau\, \sigma(t) \qquad \text{(IV-17)}$$

$$\dot{\sigma}(t) = - \int_0^\infty \left[\mathcal{H}^1, \left[\mathcal{H}(\tau), \sigma(t) \right] \right] d\tau \qquad \text{(IV-18)}$$

V - 3 - THE DYNAMICAL THEORY OF NUCLEAR INDUCTION

Wangness and Bloch developed a theory which starts from the microscopic viewpoint and derives the dynamics of nuclear induction by means of statistical methods. In their paper, it was assumed that each nucleus under consideration reacts independently of the other nuclei in the sample to the external field and the molenuclear surroundings (as a heat reservoir in the thermal equilibrium). Therefore, the magnetic moments of neighbouring nuclei are considered as a part of the heat reservoir.

We shall derive a set of first order linear differential equations for the "distribution matrix" which determines the average value of the nuclear polarization or of any other quantity which depends on the orientation of the nuclear spin. The equations for the distribution matrix express the time derivative of the average value of an arbitrary spin function in terms of the average value of other spin functions.

We write the Hamiltonian of the system in the form of:

$$\mathcal{H} = \hbar E + \hbar F + \hbar G \qquad \text{(IV-19)}$$

The term ($\hbar E$) gives the energy of the nucleus in the external field H_{ext}. We write,

$$E = -\gamma(\underline{H}_{ext} \cdot \underline{I}) \qquad \text{(IV-20)}$$

However, the external field contains two parts. 1 - H_o static part (strong, time independent and in the z direction). 2 - $H_1(t)$ part (relatively weak and time dependent). So, we have

$$\underline{H}_{ext} = \hat{\underline{k}} H_o + \underline{H}_1(t) \qquad \text{(IV-21)}$$

Therefore, E can be split into two parts.

$$E = E_o + E_1 \qquad \text{(IV-22)}$$

where E_o and E_1 respectively state the unperturbed and perturbed parts of the system.

We write;

$$E_o = -\gamma H_o I_z = -\omega I_z \qquad \text{with} \qquad \omega = \gamma H_o$$

$$\text{and} \qquad E_1 = -\gamma(\underline{H}_1 \cdot \underline{I}) \qquad \text{(IV-23)}$$

The second term ($\hbar F$) in Equation (IV-19) represents the energies of the molecular surroundings and the last term ($\hbar G$) gives the interaction of the molecular surroundings with the nucleus. (In a completely general theory, we have to take into account all of the nuclei in interaction with each other, but here we left this point out).

The energy $\hbar F$ of the molecular surroundings is expressed in an orthogonal set and the eigen values of F will be denoted by a frequency "f". Because the molecular surroundings act as a heat reservoir, they must have very many degrees of freedom. Therefore, its energy levels are highly degenerate. We use symbol "s" to specify one of the possibly many states with the same energy $\hbar f$.

The density matrix for the complete system describes the dynamical behaviour of our system as a whole. We have;

$$\langle mfs \mid \rho(t) \mid m'f's' \rangle = a_{mfs}(t)\, a^{*}_{m'f's'}(t) \qquad \text{(IV-24)}$$

where "a" is a probability amplitude and $a_m a^*_{m'}$ indicates the occupation probability of the state m.

With respect to our Hamiltonian, Von-Neumann equation can be written as,

$$i\dot{\rho}(t) = \left[E + F + G, \rho \right] \qquad \text{(IV-25)}$$

The density matrix ρ obeys the normalization condition, we write,

$$Tr\{\rho(t)\} = \sum_{mfs} \langle mfs \mid \rho(t) \mid mfs \rangle = 1 \qquad \text{(IV-26)}$$

As mentioned earlier, the expectation value of any physical quantity is given by ρ. For this set, we write,

$$\langle Q(t) \rangle = \langle mfs \mid Q \mid m'f's' \rangle = Tr\{Q\rho(t)\} \qquad \text{(IV-27)}$$

Now, going back to our symbols in our Hamiltonian, the terms E_0 and F can be treated as large whereas the terms E_1 and G represent a small perturbation.

Introducing;

$$A = e^{-iE_0 t} \qquad B = e^{-iFt}$$

$$A^{-1} = e^{iE_0 t} \qquad B^{-1} = e^{iFt} \tag{IV-28}$$

we write the density matrix ρ in the form of;

$$\rho = A\,B\,\rho^{*}\,B^{-1}\,A^{-1} \tag{IV-29}$$

Von-Neumann equation becomes in terms of asterix representation,

$$i\,\dot{\rho}^{*}(t) = \left[E_1^{*} + G^{*}, \rho^{*} \right] \tag{IV-30}$$

$$\left.\begin{array}{ll} \text{with} & E_1^{*} = A^{-1}\,E\,A \\ \text{and} & G^{*} = B^{-1}A^{-1}G\,A\,B \\ & A^{-1}E\,A = B^{-1}A^{-1}E\,A\,B \end{array}\right\} \tag{IV-31}$$

Through Equ. (IV-29), we can easily see that,

at t=o $\quad \rho^{*}(0) = \rho(0)$ $\quad$ (IV-32)

From this initial value, we can obtain (by forward integration in two successive approximations) the value of $\rho^{*}(t)$ at a late time t in the form of,

$$\rho^{*}(t) = \rho(0) + \Delta^{(1)}\rho^{*} + \Delta^{(2)}\rho^{*} \tag{IV-33}$$

The first-order increment is;

$$\Delta^{(1)}\rho^{*} = -i\int_0^t \left[E_1^{*}(t'), \rho(0) \right] dt' - i\int_0^t \left[G^{*}(t'), \rho(0) \right] dt' \tag{IV-34}$$

and the second-order increment is approximately,

$$\Delta^{(2)}\rho^{*}=-\int_{0}^{t}dt'\left(\int_{0}^{t'}\left[G^{*}(t'),\left[G^{*}(t''),\rho(0)\right]\right]dt''\right) \quad \text{(IV-35)}$$

We are interested only in the expectation value of quantities concerning the nuclear spin alone, such as the components of the angular momentum of the nucleus I. In other words, we can call any quantity concerning the nuclear spin "spin functions". And these functions in our representation are diagonal in the variables f and s, referring to the molecular surroundings. We have,

$$\langle mfs\,|\,Q\,|\,m'f's'\rangle=\langle m\,|\,Q\,|\,m'\rangle\,\delta_{ff'}\,\delta_{ss'} \quad \text{(IV-36)}$$

Now, the crucial point is that; since Q is a spin function, we don't need to use the density matrix of the complete system which has all the information about the whole system. We use the "distribution matrix σ " which is the matrix element of the spin system. Doing that, we cleared the theory from the complicated unnecessary information.

σ is defined by;

$$\langle m|\sigma|m'\rangle=\sum_{fs}\langle mfs\,|\,\rho\,|\,m'fs\rangle \quad \text{(IV-37)}$$

It follows that, the expectation value of a spin function Q is given in terms of σ

$$\langle Q\rangle=Tr\{Q\sigma\}=\sum_{mm'}\langle m'|Q|m\rangle\langle m|\sigma|m'\rangle \quad \text{(IV-38)}$$

In a similar way to the transformation (Equ. (IV-29)), we can write σ^* as;

$$\langle m|\sigma^*|m'\rangle = \sum_{fs} \langle mfs|\rho^*|m'fs\rangle \qquad \text{(IV-39)}$$

with $\sigma = A\,\sigma^*\,A^{-1}$ (IV-40)

Inserting Equ. (IV-33) in Equ. (IV-39) we get,

$$\langle m|\sigma^*(t)|m'\rangle = \langle m|\sigma^*(o)|m'\rangle + \langle m|\overset{(1)}{\Delta}\sigma^*|m'\rangle + \langle m|\overset{(2)}{\Delta}\sigma^*|m'\rangle \qquad \text{(IV-41)}$$

with

$$\left.\begin{aligned} \langle m|\sigma^*(o)|m'\rangle &= \sum_{fs}\langle mfs|\rho(o)|m'fs\rangle \\ \langle m|\overset{(1)}{\Delta}\sigma^*|m'\rangle &= \sum_{fs}\langle mfs|\overset{(1)}{\Delta}\rho^*|m'fs\rangle \\ \langle m|\overset{(2)}{\Delta}\sigma^*|m'\rangle &= \sum_{fs}\langle mfs|\overset{(2)}{\Delta}\rho^*|m'fs\rangle \end{aligned}\right\} \qquad \text{(IV-42)}$$

A knowledge of the density matrix ρ at t=o is required in order to evaluate Equ. (IV-42). In fact, it is not this matrix ρ(o) which is known but its statistical average ($\bar{\rho}$(o)). It indicates the fact that the surroundings are for t=o in statistical equilibrium at the absolute temperature T. The probability of finding the surroundings in a state is given by the Boltzmann factor P(f) which depends only on the energy ħf.

The statistically averaged $\bar{\rho}$(o) is given by;

$$\langle mfs|\bar{\rho}(o)|m'f's'\rangle = \langle m|\sigma(o)|m'\rangle\, P(f)\,\delta_{ff'}\,\delta_{ss'} \qquad \text{(IV-43)}$$

Here, the appearance of the arbitrary matrix $\langle m|\sigma(0)|m'\rangle$ signifies that we maintain complete generality in regard to the initial state of the nucleus.

IV - 4 - THE SPIN-ROTATIONAL INTERACTIONS IN LIQUIDS

The interaction of a nuclear magnetic moment with the magnetic field produced at the position of nucleus by the rotation of the molecule containing the nucleus is called a spin-rotational interaction. Its contribution has been seen to the nuclear magnetic relaxation of some liquids.

Gutowsky, Lawrenson and Shimomura have measured the spin-lattice relaxation time of the fluorine nuclei fasten than that of the protons. And they concluded that the spin rotational interaction for the fluorine nuclei was greater than for proton.

It has also been shown by Johnson, Waugh and Pinkerton that spin-rotational interactions are important for the relaxation mechanism of the fluorine nuclei in liquid CHF_3.

Brown, Gutowsky and Shimomura have pointed out that the statistical properties of the spin-rotation Hamiltonian in a liquid may be quite different from those of the orientation-dependent interactions. They introduced a transient rotation model in which molecules jump from one orientation to another at random times. The spin-rotational interaction is assumed to operate during these jumps when the molecule is actually rotating.

Hubbard calculated the contribution of spin-rotational interaction to the nuclear magnetic relaxation of identical spin ½ nuclei at equivalent positions in spherical molecules in a liquid and he employed the semiclassical form of the density operator theory of relaxation.

The interaction Hamiltonian ($\hbar G$) of the system can then be split into two parts. 1 - the spin-rotational interaction ($\hbar G_1$). 2 - the dipole-dipole interaction ($\hbar G_2$). $\hbar G_1$ term for the ith nucleus can be written

$$\hbar G_1^{(i)} = \hbar \underset{\sim}{I}_i C^{(i)} \underset{\sim}{J}_i \tag{IV-44}$$

where $\hbar \underset{\sim}{J}_i$ is the angular momentum of the molecule containing the ith nucleus and $C^{(i)}$ is a dyadic. Suppose that $S^{(i)}$ is a coordinate system fixed in the molecule, having its Z axis directed from the centre of the molecule to the ith nucleus. Because of the ith nucleus. Because of the assumed symmetry of the molecules, $C^{(i)}$ is diagonal in $S^{(i)}$ with elements

$$C_z^{(i)} \equiv C_{\parallel}, \quad C_x^{(i)} = C_y^{(i)} \equiv C_{\perp}$$

We rewrite G_1 in terms of the components of I_i and J_i in $S^{(i)}$.

$$G_1^{(i)} = C_{\perp}\left(I_{ix}^{(i)} J_{ix}^{(i)} + I_{iy}^{(i)} J_{iy}^{(i)}\right) + C_{\parallel} I_{iz}^{(i)} J_{iz}^{(i)} \tag{IV-45}$$

We now define the spherical components of I_i and J_i

$$V_i^0 \equiv I_{iz}, \quad V_i^{\pm 1} \equiv \mp\left(I_{ix} \pm i I_{iy}\right)/\sqrt{2} = \mp I_i^{\pm 1}/\sqrt{2}$$

$$J_i^0 \equiv J_{iz}, \quad J_i^{\pm 1} \equiv \mp\left(J_{ix} \pm i J_{iy}\right)/\sqrt{2}$$

and we have,

$$G_1^{(i)} = \sum_{k'=1}^{1} C_{k'} (V_i^{k'})^{(i)} (J_i^{-k'})^{(i)} \qquad \text{(IV-46)}$$

where $c_0 \equiv c_{\parallel}, c_{\pm} \equiv -C_{\perp}$

The spherical components of a vector constitute a first rank irruducible tensor, the components $(V_i^{k'})^{(i)}$ in $S^{(i)}$ are related to the components V_i^k in the laboratory coordinate system S by (Hubbard),

$$(V_i^{k'})^{(i)} = \sum_{k=1}^{1} V_i^k \mathcal{D}^{(1)}_{k'k} (\alpha_i \beta_i \gamma_i) \qquad \text{(IV-47)}$$

where $(\alpha_i \beta_i \gamma_i) \equiv \Omega_i$ are the Euler angles of $S^{(i)}$ with respect to S. There is a similar relation between the components $(J_i^{k'})^{(i)}$ in $S^{(i)}$ and the components J_i^k in the laboratory coordiante system.

The sum of all the spin-rotational interactions $G_1 \equiv \sum_i G^{(i)}$ can be written in the laboratory coordinate system as, (Hubbard)

$$G_1 = \sum_{i=1}^{N} \sum_{k=-1}^{1} u_i^k V_i^k \qquad \text{(IV-48)}$$

where

$$u_i^k \equiv \sum_{k',k''=-1}^{1} C_{k'} \mathcal{D}^{(1)}_{k'k} (\Omega_i) \mathcal{D}_{-k'k''} (\Omega_i) J_i^{k''}$$

We write that the spin-rotational interaction in general depends on the orientation of the molecule, since it involves the sets of Euler angles which specify the orientation with respect to the laboratory system of each body coordinate system $S^{(i)}$ in which the spin-rotational interaction of one of the spins is diagonal. If $C_{\perp} = C_{\parallel}$, G_1 doesn't depend on the orientation of the molecule.

CHAPTER V

NUCLEAR MAGNETIC RELAXATION IN TWO-DIMENSIONAL SYSTEMS

V - 1 - THE IMPORTANCE OF THE STUDY OF TWO-DIMENSIONAL SYSTEMS

Throughout the study of the nuclear magnetic relaxation theory for two-dimensional systems, it can be shown that the reduced dimensionality has the effect of decreasing the relaxation times from their expected values by as much as a few orders of magnitude. In addition to that, T_1 and T_2 relaxation times are to be seen unequal even in the presence of fast atomic motion. Cowan (1980) by observing the relaxation times of adsorbed helium-3 showed that the theory is in close agreement with the experimental results.

The NMR properties of adsorbed systems behave differently from those of the corresponding bulk system for a number of reasons. 1 - The anisotrophy of the internuclear dipolar interaction causes the relaxation times to depend on the orientation of the substrate plane with respect to the static field. 2 - The rotational symmetry of the dipolar Hamiltonian can not be completely averaged by fast planar motion, except when the normal of the plane makes an angle of 54.7^{o} ($\mathrm{Cos}^{-1}\sqrt{2/3}$) with the static field. 3 - As far as diffusive motion is concerned, the long time behaviour of the spin correlation function depends on the dimensionality of the system.

We are now going to present a consistent theory of dipolar mediated spin relaxation for two-dimensional systems. Kubo and Tomita's (1954) treatment of NMR lineshape (Chapter III) became a light for our theory. However, it is not certain that the Kubo theory is valid for two-dimensional systems. Reiter and Boucher (1975) checked their result against the Kubo result and found that the validity in three-dimensional case can be extended to two-dimensional case but not to one.

V - 2 - RELAXATION FUNCTIONS AND TIMES

In Chapter II, we have already mentioned the theoretical expressions for the longitudinal and transverse relaxation functions ((Eq. II-43) and (Eq. II-49)). Kubo has introduced a method for the relaxation functions by using the expansion in dipolar Hamiltonian and he accepted the higher-order terms as an approximation of the lower-order ones. His method is known as commulant expansion method. The second term as the first non-vanishing term is generally used for the theory.

Following Kubo's idea, Cowan introduced (neglecting small imaginary terms) the relaxation functions as;

for transverse

$$F(t) = \exp\left[-\int_0^t (t-\tau)\sum_{m=-2}^{2}\left(3-\frac{m^2}{2}\right)G_m(\tau)\exp(im\omega_0\tau)\,d\tau\right] \qquad \text{(V-1)}$$

and for longitudinal

$$L(t) = \exp\left[-\int_0^t (t-\tau)\sum_{m=-2}^{2} m^2 G_m(\tau)\exp(im\omega_0\tau)\,d\tau\right] \tag{V-2}$$

where $G_m(\tau)$ are the spin-torque correlation functions and they are the auto-correlation functions of the dipolar Hamiltonian components. We have,

$$G_m(\tau) = \frac{\mathrm{Tr}\left\{D_m(0)D_{-m}(\tau)\right\}}{\mathrm{Tr}\, I_z^2}\,, \tag{V-3}$$

where

$$D_m = \hbar^2\gamma^2\sqrt{\tfrac{4}{5}\pi}\sum_{i<j} Y_2^{-m}(\theta_{ij},\phi_{ij})\,T_{ij}^{m}(-1)^m/r_{ij}^3$$

(in Equation III-62)

$G_m(\tau)$ is the time dependence of the D_m being generated only by the motion Hamiltonian.

In the general case of motion in spin and direct space with the spin operators varying we obtain $G_m(t)$ as

$$G_m(t) = \frac{4\pi\hbar^2\gamma^4}{5N}\sum_{\substack{i<j\\k<l}} \frac{Y_2^{-m}(\Omega_{ij}(0))\,Y_2^{m}(\Omega_{kl}(t))}{r_{ij}^3(0)\,r_{kl}^3(t)}\,\Gamma_{ijkl}(t) \tag{V-4}$$

where Ω_{ij} indicates the direction r_{ij} (i.e. θ_{ij}, ϕ_{ij}).

We have introduced a symmetric four-spin correlation function $\Gamma_{ijkl}(t)$.

If we develop our theory for a four-spin correlation function, we can then generalize it for N spins. We have,

$$\Gamma_{ijkl}(t) = N\,Tr\left\{T_{ij}^{m}(0)\,T_{kl}^{-m}(t)\right\} \Big/ Tr\,I_z^2 \qquad \text{(V-5)}$$

$T_{ij}(t)$ tensorial operators are generated by the Hamiltonian for motion in spin space. If this Hamiltonian is rotationally invariant then $\Gamma(t)$ doesn't depend on spin-flip index m. Whereas the spherical harmonics and the r_{ij} are generated by the Hamiltonian for bodily motion in direct space.

We write the zero time value for Γ as:

$$\Gamma_{ijkl}(0) = \frac{3}{2}\left(\delta_{ik}\,\delta_{jl} + \delta_{il}\,\delta_{jk}\right). \qquad \text{(V-6)}$$

Taking the spin-torque correlation functions decaying to zero fast enough, the upper limits of the integrals in equations (V-1) and (V-2) can be extended to infinity leading to exponential relaxation. We have,

$$L(t) \sim \exp(-t/T_1) \qquad \text{(V-7)}$$

$$F(t) \sim \exp(-t/T_2) \qquad \text{(V-8)}$$

where T_1 and T_2 relaxation times are:

$$\frac{1}{T_1} = J_1(\omega_0) + 4\,J_2(2\omega_0) \qquad \text{(V-9)}$$

$$\frac{1}{T_2} = \frac{3}{2}\,J_0(0) + \frac{5}{2}\,J_1(\omega_0) + J_2(2\omega_0) \qquad \text{(V-10)}$$

where $J_m(\omega)$ are the spectral density functions and they are the Fourier transform of the spin-torque correlation functions.

$$J_m(m) = \int_{-\infty}^{\infty} G_m(t) \exp i\omega t \, dt \qquad \text{(V-11)}$$

For three-dimensional systems with motion the decay of the $G_m(t)$ is sufficiently fast and above expression can be true. But for two-dimensional systems, it is not always so.

V - 3 - THE CORRELATION FUNCTIONS ON THE SUBSTRATE FRAME

It is convenient to consider the correlation functions (Eq. V-4) on a frame where the polar axis ($\theta = 0$) is parallel to the static field H_o. For simplicity, we take the substrate surface as a reference frame for the spins. The orientation of the spins is given by the azimuthal angles in this plane. Using the Wigner rotation operators $\mathcal{D}(\alpha,\beta,\gamma)$ the argument of the Spherical harmonics can be expressed as:

$$Y_2^q(\Omega) = \sum_{p=-2}^{2} \mathcal{D}^2_{pq}(\alpha\beta\gamma)\, Y_2^p(\Omega') \qquad \text{(V-12)}$$

where (α,β,γ) are the Euler angles of the rotation. We choose the direction $\phi = \frac{\pi}{2}$ in the laboratory frame to lie in the substrate plane. For this simplicity, the Euler angles become $(0\beta0)$.

With the help of the rotation matrix d(β) whose elements are tabulated in Brink and Satcher (1968), we express the correlation functions in the following form:

$$G_m(t) = \frac{4\pi\hbar^2\gamma^2}{5} \sum_{\substack{i<j \\ k<l}} \sum_{p,p'=-2}^{2} d^2_{-p-m}(\beta) d^2_{p'm}(\beta) \frac{Y_2^{-p}(\pi/2, \phi_{ij}(0)) Y_2^{p}(\pi/2, \phi_{kl}(t))}{r_{ij}^3(0)\, r_{kl}^3(t)} \Gamma_{ijkl}(t) \tag{V-13}$$

And on substituting in the values for the matrix elements $d_{pm}(\beta)$ we have,

$$G_0(t) = \frac{27\hbar^2\gamma^4}{64} \left\{ \left(\sin^2\beta - \frac{2}{3}\right)^2 g_0(t) + \frac{\sin^4\beta}{2} g_2(t) \right\}$$

$$G_1(t) = \frac{9\hbar^2\gamma^4}{32} \left\{ \cos^2\beta \sin^2\beta\, g_0(t) + \frac{\sin^2\beta(1+\cos^2\beta)}{2} g_2(t) \right\} \tag{V-13'}$$

$$G_2(t) = \frac{9\hbar^2\gamma^4}{128} \left\{ \sin^4\beta\, g_0(t) + \frac{\cos^4\beta + 6\cos^2\beta + 1}{2} g_2(t) \right\}$$

The positional correlation functions $g_n(t)$ can be expressed as below,

$$g_n(t) = \frac{4}{3N} \sum_{\substack{i<j \\ k<l}} \frac{\exp(-in\phi_{ij}(0)) \exp(in\phi_{kl}(t))}{r_{ij}^3(0)\, r_{kl}^3(t)} \Gamma_{ijkl}(t) \tag{V-14}$$

The $g_n(t)$ functions can be considered as the determination of the spin-torque correlation functions. For our theory as mentioned earlier we go to $g_2(t)$ term and we know that $g_1(t)$ does indeed vanish. The index "n" means the number of the spins flipped and it refers to eigenstates parallel and anti-parallel to the substrate normal.

Equation (V-14) has a very important statement. Because it shows that the "n" factor in the exponent means that $g_o(t)$ does not depend on the orientations $\phi_{ij}, \phi_{k\ell}$ of the spins but only their separations r_{ij}, $r_{k\ell}$. Whereas the $g_2(t)$ depends both on separation and orientation. Because the exponential terms give the destructive interference. Therefore, we expect $g_2(t)$ to decay to zero very much faster than $g_o(t)$.

V - 4 - TWO-DIMENSIONAL FLUIDS

The reasons for considering a fluid are two. 1 - We describe the motion classically, treatment is simpler than quantum-mechanical case. 2 - Since the Heisenberg exchange Hamiltonian takes into account of spin diffusion in the hydrodynamic limit, we use the results of classical diffusive motion.

Then, our next step would be to obtain the correlation functions for classical motion. As far as random bodily motion of the spins is concerned, the positional correlation functions $g_n(t)$ are treated completely classically.

Combining Equations (V-6) and (V-14) we obtain,

$$g_n(t) = \frac{1}{N} \sum_{i \neq j} \frac{\exp[-in(\phi_{ij}(o) - \phi_{ij}(t)]}{r_{ij}^3(o)\, r_{ij}^3(t)}$$

(V-15)

Now we shall be following a probabilistic method in order to make a practical calculation for the time dependence of Θ_{ij} and $\emptyset_{ij}$ (the dynamical behaviour of the spins). We use the probability function which is related to the time dependent pair distribution function introduced by van Hove (1954). The idea of this probability function is in fact in Boltzmann sense to replace the summation over spins. The van Hove correlation function $G(\underline{r},t)$ gives us the average density distribution at a time t + t' as seen from a point where a particle passed at time t'. This function can be split into two parts, self part G_s and distinct part G_d. We write,

$$G(\underline{r},t) = G_s(\underline{r},t) + G_d(\underline{r},t) \qquad \text{(V-16)}$$

$G_s(\underline{r},t)$ indicates the correlation between positions of the same particle whereas $G_d(\underline{r},t)$ states the correlation for different particles.

At t = o we have,

$$G_s(\underline{r},o) = \delta(\underline{r}) \text{ and } G_d(\underline{r},o) = g(\underline{r}) \qquad \text{(V-17)}$$

$g(\underline{r})$ is known as the radial distribution function.

For long times: $G_s(\underline{r},t)$ is a broad bell shape of unit area and $G_d(\underline{r},t)$ is a constant.

Let $\underline{r}_i(o)$ and $\underline{r}_j(o)$ be respectively the coordinate of the ith spin and jth at t = o. Their initial separation is:

$$\underline{r}_o = \underline{r}_i(o) - \underline{r}_j(o)$$

At t = t they will have a separation distance given by,

$$\underline{r} = \underline{r}_i(t) - \underline{r}_j(t)$$

Now, the probability that the pair separation will increase by $\underline{R} = \left[\underline{r}_i(t) - \underline{r}_j(t)\right] - \left[\underline{r}_i(0) - \underline{r}_j(o)\right]$ is expressed as,

$$P(\underline{R},t) = \int G_s(\underline{R}-\underline{r},t)\, G_s(\underline{r},t)\, d\underline{r} \qquad \text{(V-18)}$$

if the motion of the particles is uncorrelated. Here, $P(\underline{R},t)$ is the convolution of the single particle probabilities.

The radial distribution function $g(\underline{r})$ gives the probability of a particular initial separation $\underline{r}$.

Due to the probabilistic method, we should replace the summation over particles (for Equ.((V-17)) by the integral:

$$\sum_{i\neq j} \longrightarrow N\int d\underline{r}_o \int d\underline{r}\; P(\underline{r}-\underline{r}_o,t)\, g(\underline{r}_o) \qquad \text{(V-19)}$$

The precise details of the radial distribution function are not sufficient for the nuclear relaxation properties of a system. We therefore approximate $g(r_o)$ by a step function $\Theta(r_o)$. We have

$$\Theta(r_o) = o \quad \text{for} \quad r_o < a$$

$$\Theta(r_o) = \alpha \quad \text{for} \quad r_o > a$$

$\Theta(r_o)$ then gives a uniform spin density α for $r_o > a$ and zero within a hard core sphere of radius "a". Assuming that the approximation for the second moment is correct, in two-dimensions "a" is given by

$$a^{-4} = \frac{1}{\alpha} \int_0^\infty \frac{2\pi g(r)}{r^5}\, dr \qquad \text{(V-20)}$$

Now in case the separation of the particles is so small, the motion of the particles is then correlated and the convolution expression for $P(\underline{R},t)$ is not valid. Therefore, we exclude a sphere of radius "a" from the final separation. Regarding to this statement Equa. (V-19) becomes:

$$\sum_{i \neq j} \longrightarrow N\alpha \int_{r_o < a} dr_o \int_{r < a} dr\, P(\underline{r} - \underline{r}_o, t) \qquad \text{(V-21)}$$

Introducing the spatial Fourier transform of the probability function, the above integral can be rewritten without the double set. We then have,

$$P(\underline{r},t)=\frac{1}{(2\pi)^2}\int d\underline{Q}\, p(\underline{Q},t)\, e^{i\underline{Q}\cdot\underline{r}} \qquad \text{(V-22)}$$

Because the convolution expression for $P(\underline{r},t)$ is given by the square of the Fourier transform of the van Hove function we write,

$$p(\underline{Q},t) = \left[g_S(\underline{Q},t) \right]^2 \qquad \text{(V-23)}$$

Combining Equations (V-15), (V-21) and (V-22) we can see that

$$g_n(t)=\frac{\alpha}{(2\pi)^2}\int d\underline{Q}\, p(\underline{Q},t)\int d\underline{r}\,\frac{\exp[i(\underline{Q}\cdot\underline{r}+n\phi)]}{r^3}\int d\underline{r}_0\,\frac{\exp[-i(\underline{Q}\cdot\underline{r}_0+n\phi_0)]}{r_0^{\,3}}$$

$$\text{(V-24)}$$

In this equation, it is seen that the last two integrals are mutual complex conjugates and we have,

$$g_n(t)=\frac{\alpha}{(2\pi)^2}\int d\underline{Q}\, p(\underline{Q},t)\left|\int d\underline{r}\,\frac{\exp i(\underline{Q}\cdot\underline{r}+n\phi)}{r^3}\right|^2 \qquad \text{(V-25)}$$

We use the Bessel functions of order n and express this equation as,

$$g_n(t) = \alpha \int d\underline{Q}\, p(\underline{Q},t) \left[\int_0^\infty \frac{J_n(Qr)}{r^2}\, dr \right]^2 \qquad \text{(V-26)}$$

[We note that in the space integral (Equ. (V-25)), $\underline{r}$ and $\underline{Q}$ are respectively given by (r,ϕ) and (Q,ψ). So we write $\underline{Q}.\,\underline{r} = Qr \cos(\phi-\psi)$ and the integral takes the form of;

$$\int d\underline{r} = \int_0^\infty r\,dr \int_0^{2\pi} d\phi \quad]$$

Because the motion is rotationally invariant in the plane, $p(\underline{Q},t)$ depends only the magnitude of Q. Therefore, Equa.(V-26) can be expressed as,

$$g_n(t) = \frac{2\pi\alpha}{a^4} \int_0^\infty dx\, x^3 p(x/a, t) \left[\int_0^\infty \frac{J_n(y)}{y^2}\, dy \right]^2 \qquad \text{(V-27)}$$

Apart from rotational invariance, no other nature of the motion is given by this equation.

V - 5 - DIFFUSION

We assume that two-dimensional diffusion equation is good enough to describe the motion of the spins. The translational probability function $P(\underline{r},t)$ can be expressed in the form of a gaussian distribution as follows:

$$P(\underline{r},t)=\frac{1}{8\pi Dt}\exp\left(-\frac{r^2}{8Dt}\right) \qquad \text{(V-28)}$$

Let $p(\underline{Q},t)$ be the spatial Fourier transform of $P(\underline{r},t)$ we have,

$$p(\underline{Q},t) = \exp(-2Q^2 Dt) \qquad \text{(V-29)}$$

where we shall define "D" as the two-dimensional diffusion constant.

Putting $Q = x/a$ in $p(Q,t)$ we rewrite Equation (V-27) as below,

$$g_n(t)=\frac{2\pi\alpha}{a^4}\int_0^{\infty} dx\, x^3 \exp -\frac{t x^2}{\tau_0}\left[\int_x^{\infty}\frac{J_n(y)dy}{y^2}\right]^2 \qquad \text{(V-30)}$$

with $\tau_0 = a^2/2D$

τ_0 is the time which takes for a spin to diffuse a distance of the hard core dimension "a". The diffusion may not be described by this time scale.

The numerical calculation of Equa.(V-30) has been made by a number of people (Kokin-Izmezter (1965), Chapman and Bloom (1976) and Avogadro and Villa (1977)}. Figure V-1 shows the shape of $g_n(t)$ functions calculated by them.

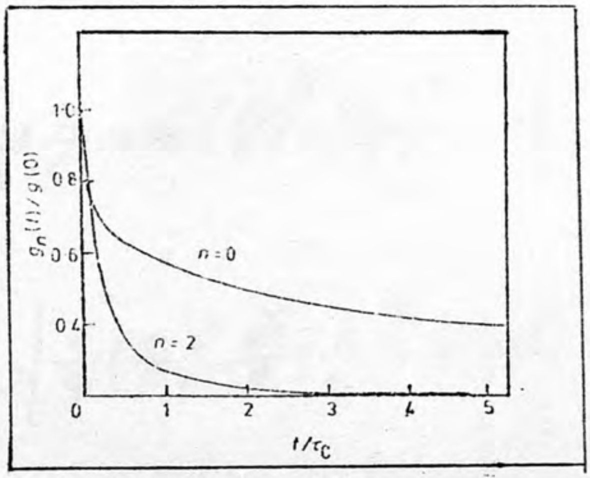


Figure V-1: Correlation functions for a diffusive fluid. (Cowan)

Here we notice that the decay of g_o is much slower than g_2. We can also see that at $t = o$ g_o and g_2 are equal. It is possible to prove that through Equation (V-15). The probability function is a delta function and the integral can be evaluated giving:

$$g(o) = \pi\alpha/2a^4 \qquad \text{(V-31)}$$

Our next step is now to consider the behaviour of the spin-torque correlation functions at long time.

The long-time behaviour:

The convergence of the integrals for the relaxation functions depends on the long-time behaviour of the correlation functions. We use an expansion in inverse powers of "t" in order to examine the long-time behaviour. Doing the calculation for Equa.(V-30) and substituting Equa.(V-31) into the calculation, we have,

$$g_0(t) = g(0)\left\{2\frac{\tau_0}{t} - 2\sqrt{\pi}\left(\frac{\tau_0}{t}\right)^{3/2} + \left(\frac{\tau_0}{t}\right)^{2} + \cdots\right\} \qquad \text{(V-32)}$$

$$g_2(t) = g(0)\left\{\frac{2}{9}\left(\frac{\tau_0}{t}\right)^{2} - \frac{\sqrt{\pi}}{12}\left(\frac{\tau_0}{t}\right)^{5/2} + \frac{1}{6}\left(\frac{\tau_0}{t}\right)^{3} + \cdots\right\} \qquad \text{(V-33)}$$

For $t \gg \tau_0$, the equations above can be approximated by

$$g_0(t) \sim g(0)\, 2\,\frac{\tau_0}{t} \qquad \text{(V-32')}$$

$$g_2(t) \sim g(0)\,\frac{2}{9}\left(\frac{\tau_0}{t}\right)^{2} \qquad \text{(V-33')}$$

where we must notice that $g_2(t)$ is much smaller than $g_0(t)$. Through these expressions we reach the consequence for the spin-torque correlation functions $G_n(t)$. Especially, the long-time behaviour of $G_0(t)$ affects the transverse relaxation as we shall see later.

V - 6 - THE FOURIER TRANSFORM OF $g_n(t)$ FUNCTIONS AND RE-EXAMINING OF THE RELAXATION TIMES

In Equa.(V-13'), we expressed the spin-torque correlation functions in terms of the positional correlation functions $g_n(t)$. Can we also express the Fourier transform of the spin-torque correlation functions $J_m(\omega)$ in terms of the Fourier transform of the positional correlation functions $j_m(\omega)$? The answer is YES. Similar to Equation (V-13'), we have,

$$J_0(\omega) = \frac{27}{64}\hbar^2\gamma^4\left\{\left(\sin^2\beta - \frac{2}{3}\right)^2 j_0(\omega) + \frac{\sin^4\beta}{2} j_2(\omega)\right\}$$

$$J_1(\omega) = \frac{9}{32}\hbar^2\gamma^4\left\{\cos^2\beta\sin^2\beta\, j_0(\omega) + \frac{\sin^2\beta(1+\cos^2\beta)}{2} j_2(\omega)\right\}$$

$$J_2(\omega) = \frac{9}{128}\hbar^2\gamma^4\left\{\sin^4\beta\, j_0(\omega) + \frac{\cos^4\beta + 6\cos^2\beta + 1}{2} j_2(\omega)\right\}$$

(V-34)

The spectral functions $j_n(\omega)$ are (from Equa. V-27):

$$j_n(\omega) = \frac{2\pi\alpha}{a^4}\int_0^\infty dx\, \bar{P}\left(\frac{x}{a}, \omega\right)\left[\int_0^\infty \frac{J_n(y)}{y^2} dy\right]^2 \tag{V-35}$$

where $\tilde{p}(\underline{Q}, \omega)$ is the space and time Fourier transform of the translational probability function and for diffusion, it is given by

$$\bar{P}(\underline{Q},\omega) = \frac{4DQ^2}{\omega^2+4D^2Q^4} \tag{V-36}$$

The figure below shows a computer calculation of resultant $j_n(\omega)$.

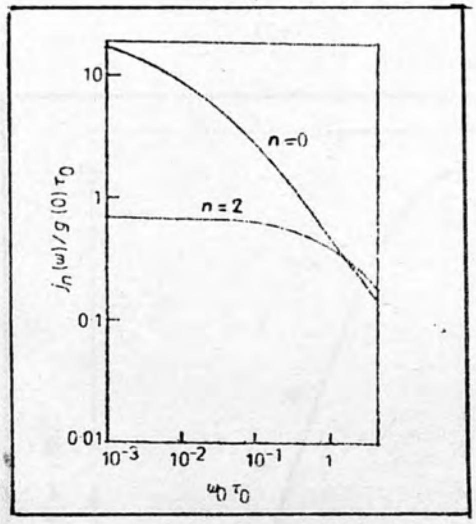


Figure V-2: Spectral functions for a diffusive fluid (Cowan)

We already know that for non-adiabatic case the longitudinal relaxation time is given by Equa.(V-9)

$$\frac{1}{T_1} = J_1(\omega_0) + 4J_2(2\omega_0)$$

In figure (V-2), we can easily see that the n = 2 term gives the normal behaviour of being almost flat for $\omega_0\tau_0 < 1$.

There is however, a logarithmic divergence of the n = o term which causes a reduction in the T_1 values in the low frequency - fast motion case. Figure (V-3) represents calculated values of T_1 as a function of β for various ratios of $\omega_0 \tau_0$. For $\omega_0 \tau_0 = 10^{-3}$ T_1 changes by a factor of 5 between orientation of $\beta = 0^0$ and 90^0. The limitation of $\omega_0 \tau_0 \leqslant 1$ indicates that one cannot go as far as the T_1 minimum which should occur at $\omega_0^2 \tau_0 \tau_c \sim 1$

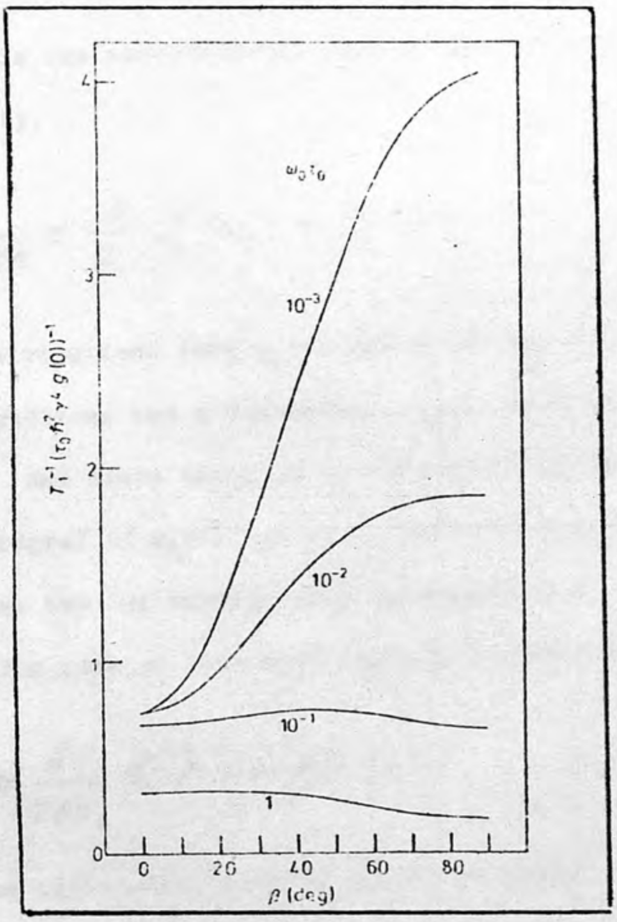


Figure V-3: Spin-lattice relaxation times for a diffusive fluid. (Cowan)

As to the transverse relaxation function as mentioned earlier (Equa. (V-1), it splits into a product of terms for each m value. The non-adiabatic terms give an exponential contribution. We have,

$$F(t) = \exp\left(-t/T_2^{na}\right) \exp\left(-3\int_0^t (t-\tau)\, G_0(\tau)\, d\tau\right. \qquad \text{(V-37)}$$

where T_2^{na} is the non-adiabatic part of the relaxation time and it is given by,

$$\frac{1}{T_2^{na}} = \frac{5}{2} J_1(\omega_0) + J_2(2\omega_0) \qquad \text{(V-38)}$$

T_2^{na} has contributions from $g_0(t)$ and $g_2(t)$ due to the relation between J functions and g functions. $g_2(t)$ term has proportionality to t^{-2}. And since there is no divergence in the integral of t^{-2}, the integral of $g_2(t)$ can be extended to infinity. This part provides the relaxation with an exponential contribution. The relaxation rate of this contribution is given by;

$$\frac{1}{T} = \frac{81}{256} \hbar^2 \gamma^4 \sin^4\beta\, j_2(0) \qquad \text{(V-39)}$$

and with the calculated value of $j_2(o)$, we have,

$$\frac{1}{T} = 0.237 \frac{\hbar^2 \gamma^4 \alpha}{a^4} \tau_0 \sin^4\beta \qquad \text{(V-40)}$$

The $g_o(t)$ function does not decay to zero fast enough, therefore, it gives a non-exponential contribution to the relaxation. This component of the relaxation function is a factor f(t). We write

$$f(t) = \exp -\left\{ \frac{81}{64} \hbar^2 \gamma^4 \left(\sin^2\beta - \frac{2}{3}\right)^2 \int_0^t (t-\tau) g_0(\tau) d\tau \right\}$$

(V-41)

f(t) is the dominant part in most cases. Here we introduce the instantaneous relaxation rate $T^{-1}(t)$ as f(t) cannot be characterized by a relaxation time. We then have,

$$\frac{1}{T(t)} = \frac{81}{64} \hbar^2 \gamma^4 \left(\sin^2\beta - \frac{2}{3}\right)^2 \int_0^t g_0(\tau) d\tau$$

(V-42)

We define a phenomenological relaxation time in the form of

$$T_2^{-1} = T^{-1}(T_2) \qquad \text{(V-43)}$$

combining Equa.(V-43) and (V-42) we obtain,

$$\frac{1}{T_2} = \frac{81}{64} \hbar^2 \gamma^4 \left(\sin^2\beta - \frac{2}{3}\right)^2 \int_0^{T_2} g_0(\tau) d\tau$$

(V-44)

with the NMR rule of thumb for T_2 we have

$$\frac{1}{T_2} = M_2 \tau \qquad \text{(V-45)}$$

The second moment is the mean square value of the local dipolar fields (multiplied by γ^2) which cause the resonance line to have breadth. The correlation time τ is the characteristic time associated with the motion which averages the fields and narrows the line.

For our theory, the local field has two parts. 1-) n=o 2-) n=2 . Combining Equa.(V-13') for $G_o(t)$ andEqua. (V-32') + (V-33') we find,

$$M_2 = M_2' + M_2'' \qquad \text{(V-46)}$$

where $M_2' = \frac{81}{128}\frac{\pi\alpha\hbar^2\gamma^4}{a^4}\left(\sin^2\beta - \frac{2}{3}\right)^2$

$$M_2'' = \frac{81}{256}\frac{\pi\alpha\hbar^2\gamma^4}{a^4}\sin^4\beta \qquad \text{(V-47)}$$

It is easily seen that for n=2 Equa.(V-40) becomes:

$$\frac{1}{T} = 0.329\, M_2''\, \tau_0 \qquad \text{(V-48)}$$

As for the n=o part, we first need to know the form of the function $g_o(t)$. We approximate $g_o(t)$ by an analytic expression which is asymtotically correct at long times and has the correct value at t=o.

$$g_0(t) \sim \frac{g(0)}{1 + t/2\tau_0} \qquad \text{(V-49)}$$

Adding the n=2 part to the result of Equa.(V-44), we get,

$$\frac{1}{T_2} = 2 \ln\left(\frac{T_2}{2\tau_0 e}\right) M_2' \tau_0 + 0.329\, M_2'' \tau_0 \tag{V-50}$$

The n=2 part of the local field is averaged in the conventional way obeying Equa.(V-45), whereas the n=o has not much importance to the motion. It is only affected by the internuclear separation and not the orientation. This degeneracy with respect to rotational motion gives the long t^{-1} tail to the $g_o(t)$ function and it is the effect of this inefficiency in the averaging process (expressed by a logarithm factor) which shortens the relaxation time from its expected value. Since the logarithm is a very slowly varying function of T_2/τ_o, we can obtain a reasonable estimate of the relaxation time by assuming a typical value for this ratio in the logarithm. $T_2 \sim 10^{-3}$sec and $\tau_0 \sim 10^{-7}$sec are the typical values. The figure below represents how T_2 varies for such a case.

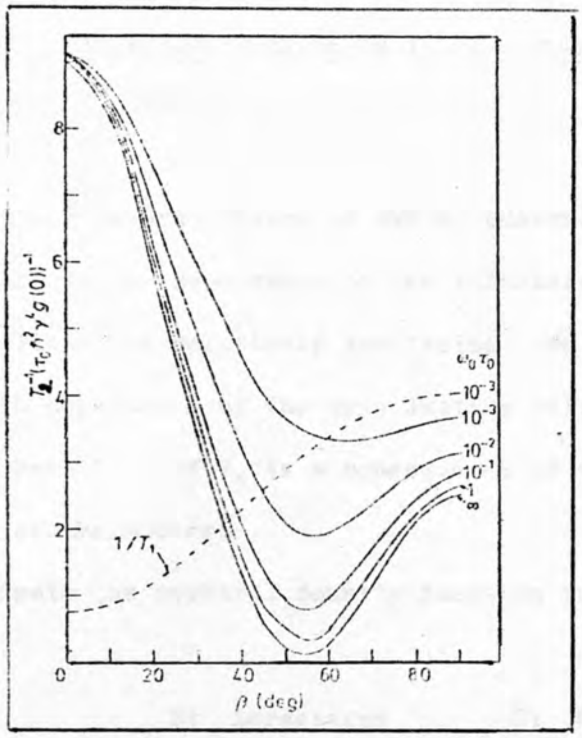


Figure V-5: Spin-spin relaxation times for a diffusive fluid. The correlation time to remaining approximately constant with $\ln(T_2/\tau_0) \sim 9$ (Cowan)

When T_2 gets shorter, it becomes less than T_1 too even in the fast motion-low field case for most orientations β. Ordinarily they would be equal. Figure (V-4) also contains T_1 for this case ($\omega_0 \tau_0 = 10^{-3}$) and we can see that at $\beta = 0$ $T_1 = 10 \times T_2$. But for $\beta \geqslant 60^\circ$ T_2 is greater than T_1. It may be surprising for spins to come to equilibrium with the lattice faster than amongst themselves, but thermodynamic arguments show that in the limit of the spin-spin interaction through the lattice, the limiting requirement is that T_2 should be less than twice T_1.

V - 7 - ANOMALOUS FEATURE OF T_1 OF ADSORBED PHASES OF ^{3}He

After giving a general theory of NMR in adsorbed systems, we shall discuss the linear dependence of the relaxation time on applied magnetic field for relatively low fields. We shall show a weak temperature dependence of the spin lattice relaxation time. This anomalous behaviour of T_1 is a consequence of the reduced dimensionality of the motion.

We approximate the spectral density function in the following three forms:

1) Gaussian 2) Lorentzian 3) Exponential

The spectral density functions can be derived from their autocorrelation function through the relation given by Equa. (V-11). For the above three cases, the correlation functions and their spectral densities can be written as:

$$1)\quad G(t) = G(o)\ \exp - \omega_c^2 t^2/2$$

$$J(\omega) = \left[G(o)\ \sqrt{2\pi}/\omega_c \right] \exp - \omega^2/2\omega_c^2 \qquad \text{(V-51)}$$

$$2)\quad G(t) = G(o)\ \exp - \omega_c |t|$$

$$J(\omega) = \left[2G(o)/\omega_c \right] \left[1 + (\omega/\omega_c)^2 \right]^{-1} \qquad \text{(V-52)}$$

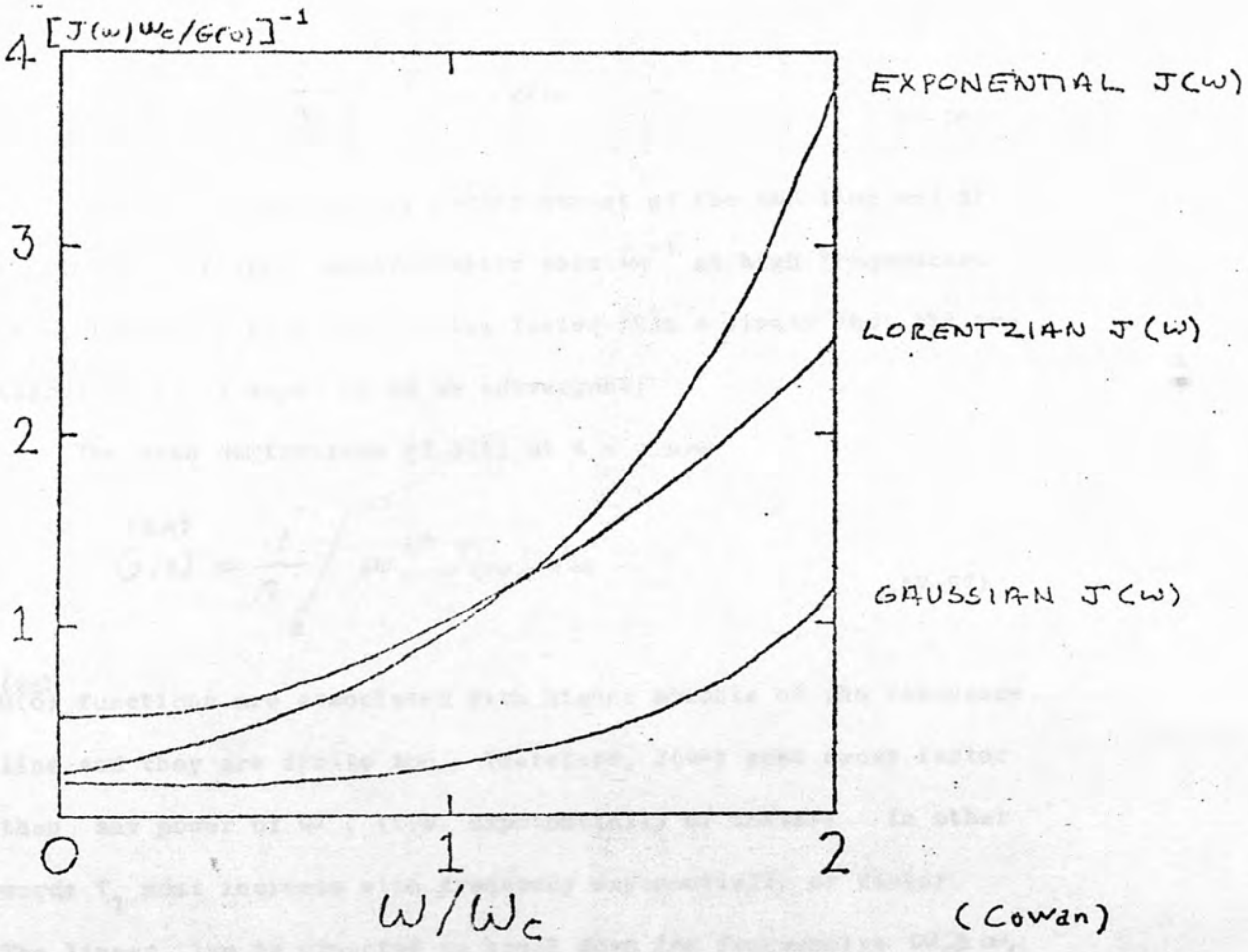
3) $$G(t) = G(o)/\left[1 + \omega_c^2 t^2/2\right]$$

$$J(\omega) = \left[G(o)\,\pi\,\sqrt{2}/\omega_c\right] \exp - \sqrt{2}\,\omega/\omega_c \qquad \text{(V-53)}$$

ω_c is the characteristic frequency of the atomic motion and it is defined by,

$$\omega_c^2 = \frac{\int_{-\infty}^{\infty} \omega^2 J(\omega)\,d\omega}{\int_{-\infty}^{\infty} J(\omega)\,d\omega} \qquad \text{(V-54)}$$

Equa. (V-9) can be simplified by neglecting the double frequency term and therefore T_1 becomes the reciprocal of $J(\omega)$. The figure below shows $J^{-1}(\omega)$ as a function of Larmor frequency for our three cases.



(Cowan)

Figure V-5:

The linearity of T_1 breaks down at high frequencies. From the inverse process of Equa. (V-11) we have,

$$G(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} J(\omega) \exp -i\omega t \, d\omega \qquad \text{(V-55)}$$

for t = o we obtain,

$$G(o) = \frac{1}{\pi} \int_0^\infty J(\omega) d\omega \qquad \text{(V-56)}$$

G(o) is proportional to the second moment of the NMR line and it is finite. If J(ω) decays faster than ω^{-1} at high frequencies or T_1 increases with frequencies faster than a linear law, the integral above is expected to be convergent.

The even derivatives of G(t) at t = o are

$$\overset{(2n)}{G}(o) = \frac{1}{\pi} \int_0^\infty \omega^{2n} J(\omega) d\omega \qquad \text{(V-57)}$$

$\overset{(2n)}{G}(o)$ functions are associated with higher moments of the resonance line and they are finite too. Therefore, J(ω) must decay faster than any power of ω . (i.e. expotentially or faster). In other words T_1 must increase with frequency exponentially or faster. The linear law is expected to break down for frequencies $\omega \gtrsim \omega_c$

However, the linear law works for low frequencies. The low frequency behaviour of J(ω) is determined by the long time part of G(t) function. The low frequency case corresponds to the hydrodynamic region where the precise microscopic nature of the atomic motion is not important. As mentioned at the beginning of this chapter, the long-time behaviour of spin correlation function decays with $t^{-d/2}$ where d is the dimensionality of the system. The correlation function has a t^{-1} tail. Therefore, the spectral density has a logarithmic divergence at low frequencies.

We may approximate the correlation function as

$$G(t) = \frac{G(0)}{1+\sqrt{2}\,\omega_c t} \qquad \text{(V-58)}$$

And the Fourier transform of this expression is:

$$J(\omega) = \frac{\sqrt{2}\,G(0)}{\omega_c}\, g\left(\frac{\omega}{\sqrt{2}\,\omega_c}\right) \qquad \text{(V-59)}$$

where g(x) is the auxiliary function being the sinus and cosinus integrals. We have,

$$g(x) = \int_0^\infty \frac{\cos t}{t+x}\, dt \qquad \text{(V-60)}$$

We plotted the reciprocal of the spectral density function against ω/ω_c in Figure (V-6). It is then seen that the curve can be approximated by a straight line over a range $0 \leqslant \frac{\omega}{\omega_c} \leqslant 2$ to within an error of $\sim$ 5%.

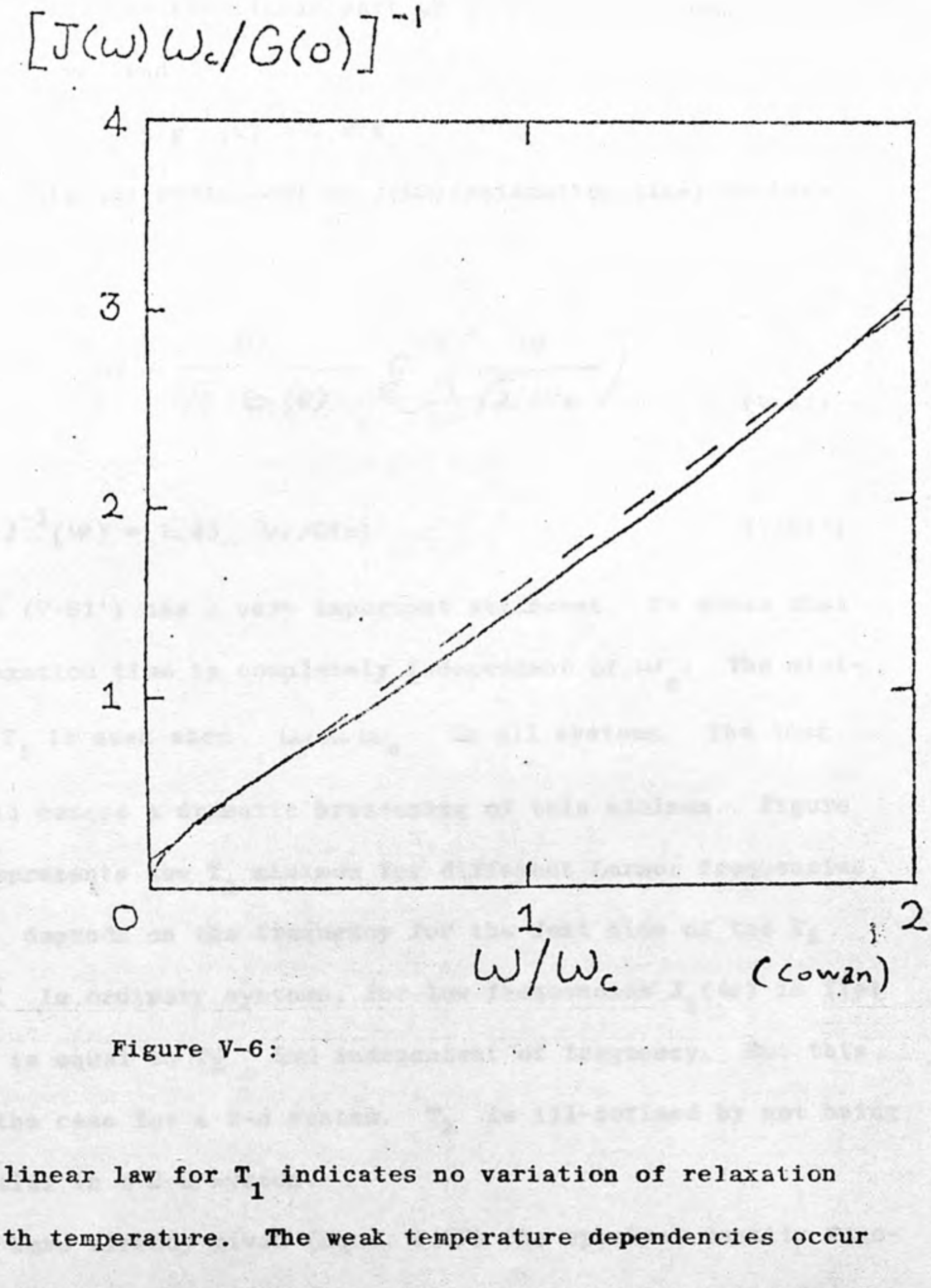


Figure V-6:

A linear law for T_1 indicates no variation of relaxation rate with temperature. The weak temperature dependencies occur when we derivate from this law. The characteristic frequency for the atomic motion is a function of the temperature. We shall now see how the relaxation time varies with ω_c .

Approximating the linear part of $g^{-1}(x)$ by its tangent through the origin, we find

$$g^{-1}(x) = 2.87x$$

and with this the reciprocal of $J(\omega)$(relaxation time) becomes:

$$J^{-1}(\omega) = \frac{\omega_c}{\sqrt{2}\ G(o)}\ g^{-1}\left(\frac{\omega}{\sqrt{2}\ \omega_c}\right) \qquad \text{(V-61)}$$

$$J^{-1}(\omega) = 1.43 \quad \omega/G(o) \qquad \text{(V-61')}$$

Equation (V-61') has a very important statement. It shows that the relaxation time is completely independent of ω_c. The minimum for T_1 is seen when $\omega \sim \omega_c$ in all systems. The long time tail causes a dramatic broadening of this minimum. Figure (V-7) represents the T_1 minimum for different Larmor frequencies.

T_1 depends on the frequency for the fast side of the T_1 minimum. In ordinary systems, for low frequencies $J_1(\omega)$ is flat and T_1 is equal to T_2 and independent of frequency. But this is not the case for a 2-d system. T_2 is ill-defined by not being exponential in a 2-d system.

We have already given (Equa. V-37) the spectral density function for spins confined to a flat surface making an angle β with the external field. We leave the approximations made before for $g_n(t)$ and $j_n(\omega)$ and confine our attention to the approximation of Equa. (V-59). We see that only the $j_o(\omega)$ terms are important and we obtain,

$$j_o(\omega) = \frac{\pi\alpha}{\sqrt{2}\, a^4 \omega_c}\, g\left(\frac{\omega}{\sqrt{2}\, \omega_c}\right) \tag{V-62}$$

where "a" is the radius of the closest approach of the spins and "α " is the number of the spins per unit area.

We have the expression for T_1 ,

$$\frac{1}{T_1} = 0.154\, \frac{\alpha}{a^4}\, \frac{\hbar^2\gamma^4}{\omega}\left[2\sin^2\beta - \sin^4\beta\right] \tag{V-63}$$

This equation vanishes for $\beta = o$. But we have made an approximation by neglecting the $j_2(\omega)$ terms. For $\beta = o$, we get no anomalous contribution to the relaxation.

For an isotropic system, where there is a uniform spread of plane orientations on a porous system where the pore dimension is much greater than the atomic dimension, we average the angular factor in Equation (V-63). We have;

$$T_1 = 12.4\, \frac{a^4}{\alpha\hbar^2\gamma^4}\, \omega \tag{V-64}$$

For a completed monalayer taking d = 3.2 A^o we find the following result for ^3He:

$$T_1 = 7.5 \times 10^{-8}\, \omega \tag{V-65}$$

In calculating T_1 we must consider the following cases:

a) The evaluation of the initial value G(o) related the spin separations depends on the geometry of the surface and differs from that for a plane.

b) The averaging process over orientation β depends on the motion.

We introduce a correlation factor to Equation (V-65) in order to overcome the difficulties.

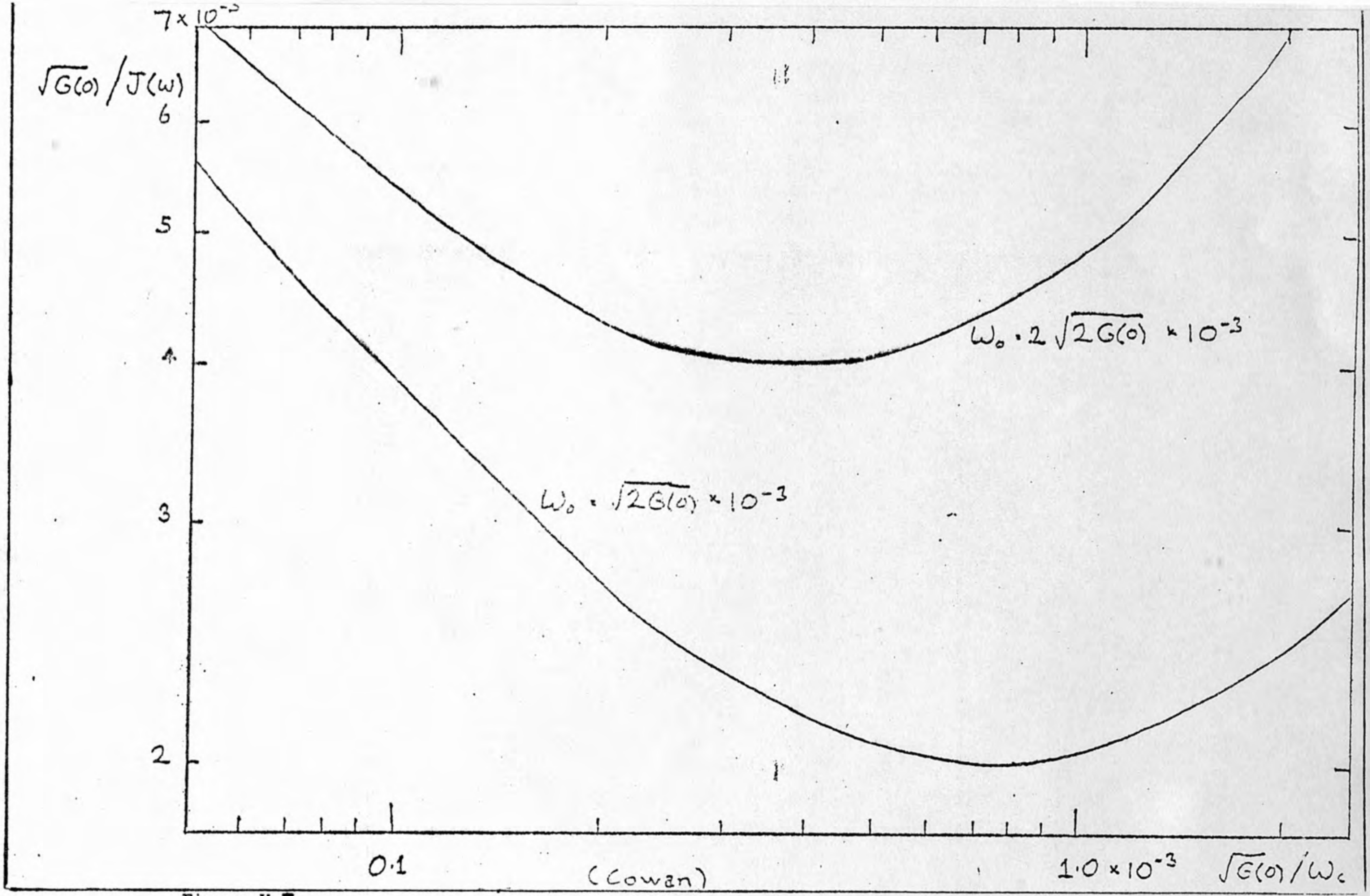


Figure V-7:

CHAPTER VI

EXPERIMENTAL TECHNIQUE AND THE COMPARISON OF THE EXPERIMENTAL RESULTS

VI - 1 - PULSE NMR

NMR experiments can be done with two basic methods.

1. Pulsed NMR technique 2. CW NMR technique.

In addition to dealing with the CW method in our work, we mostly considered the pulse NMR case and took measurements with this method.

It is useful to give a brief account of the pulsed NMR theory. The r.f. magnetic field (around the Larmor frequency) is applied in the form of pulses. We can manipulate the magnetization with either a 90° pulse or a 180° pulse. We put our sample wound with an r.f. coil in the static field H_o. A pulsed r.f. magnetic field of magnitude H_1 makes a right angle with H_o. For a short pulse duration t_p, we have the angle θ ,

$$\theta = \gamma H_1 t_p \tag{VI-1}$$

Therefore, the magnetization due to H_o will be changed by the r.f. pulse and will start precessing about the direction H_1 . But at the end of the pulse, the magnetization will decay back with a time constant T_2. The induced r.f. voltage in the coil gives us a signal and after amplifying, it can be displayed in an oscilloscope.

Let us take H_o in the Z direction. An r.f. magnetic field can then be given by

$$H_x = 2\,H_1 \mathrm{Cos}\,\omega t \qquad (VI-2)$$

And it can be divided into two rotating fields each of amplitude H_1 rotating in opposite directions.

$$H_x\ \mathrm{rot} = H_1\,\mathrm{Cos}\,\omega t$$

$$H_y\ \mathrm{rot} = -H_1\,\mathrm{Sin}\,\omega t$$

In case of resonance, we consider only one field which rotates in the same sense as the precession of the moment.

The width of a pulse t_p must be very much less than the relaxation times. (We calculated it around $10\mu Sec$ see appendix VI-1).

VI - 2 - THE MEASUREMENTS OF THE RELAXATION TIMES WITH SPIN-ECHO METHOD

The spin-echo method has been used since 1950 (Hahn). It was found convenient to measure the relaxation times. If the time interval between the pulses is τ, the echo will be formed at a time $t = 2\tau$.

It was seen that this technique works better for the substances (gases and liquids) whose relaxation times are long.

Let us send a 90^o and a 180^o pulses one after another and study the spin-echo case more closely. The figure below represents this formation.

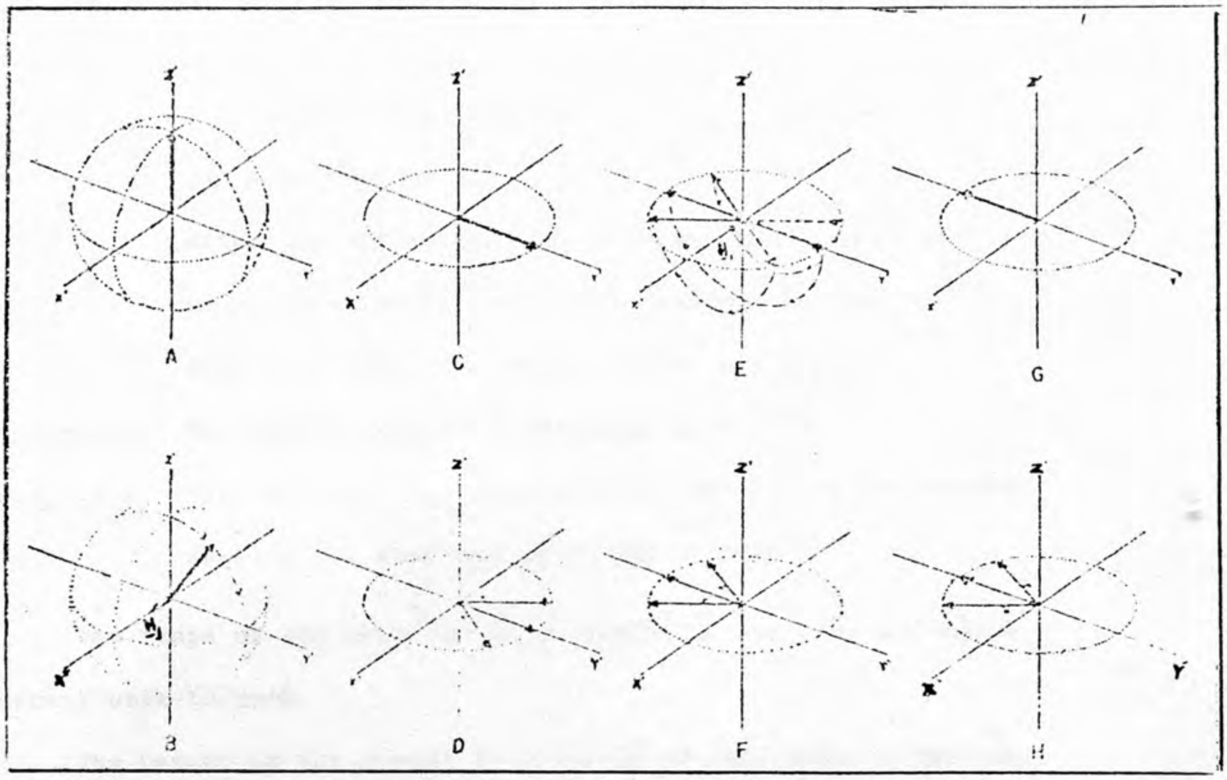


Figure VI-1: The formation of a spin-echo

Diagram A: The static strong field $H_0\hat{k}$ sets the resultant magnetic moment vector at equilibrium along the direction of the field.

Diagram B: The first pulse (90°) is sent in the x' direction of the rotating frame and the resultant magnetic moment rotates about the direction of H_1.

Diagram C: The resultant magnetic moment vector takes its final position in the x'-y' plane at the end of the pulse.

Diagram D: The decay of this vector with a constant time T_2^* (which is given by $1/\gamma\Delta H$) due to the inhomogenity of the external field over the sample.

Diagram E: We now send a 180° pulse after a period of τ. All the incremental vectors flip through an angle 180° about the direction of H_1.

Diagram F: After the second pulse is removed, these vectors start to precess but the effect is opposite to that at "D" such that induction signal is reconstituted.

Diagram G: The maximum signal is obtained at $t = 2\tau$

Diagram H: This maximim signal induced in the coil (echo) decays away in the same way as it was at case "D".

The shape of the echo can be described as two free induction decays back-to-back.

The height of the signal is directly proportional to the magnetization and it decreases exponentially with a time constant T_2 as a function of τ . We used this technique for measuring T_2.

The magnetization expression as a function of τ is given by,

$$M(\tau) = M_o \, e^{-2\tau/T_2}$$

With respect to the statement we made above, $M(\tau)$ can be replaced by the height (h), we then write,

$$h(\tau) = h_o \, e^{-2\tau/T_2}$$

Let us take $h_o = 1$. We have,

$$\ln h(\tau) = -\frac{1}{T_2}(2\tau) \qquad \text{(VI-3)}$$

It is a linear equation when taking a logarithmic graph paper. (We must note that if we use a nature logarithmic graph paper we must express " ln" in terms of "log". That is to say

$\log_{10} h = \ln h / 2.3)$.

We also used the spin-echo technique in order to measure T_1. Three pulses (Figure V-2) instead of two have been employed for this aspect. (Either 180° - 90° - 180° or 90° - 90° - 180° sequence). The initial pulse causes a non-equilibrium orientation of the magnetic moment vectors after the driving pulse has been removed. The magnetization after a period of τ_1 is:

$$M_o(\tau_1) = Meq.\ (1-e^{-\tau_1/T_1})$$

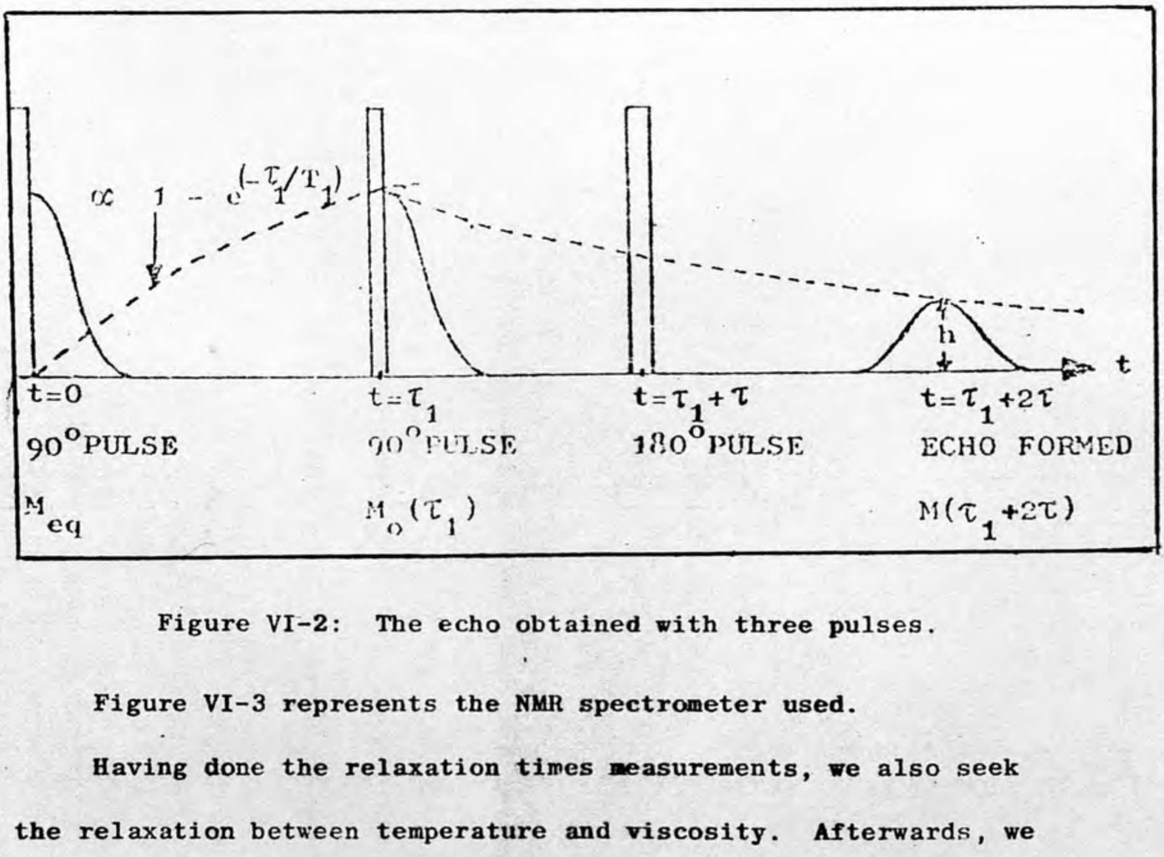


Figure VI-2: The echo obtained with three pulses.

Figure VI-3 represents the NMR spectrometer used.

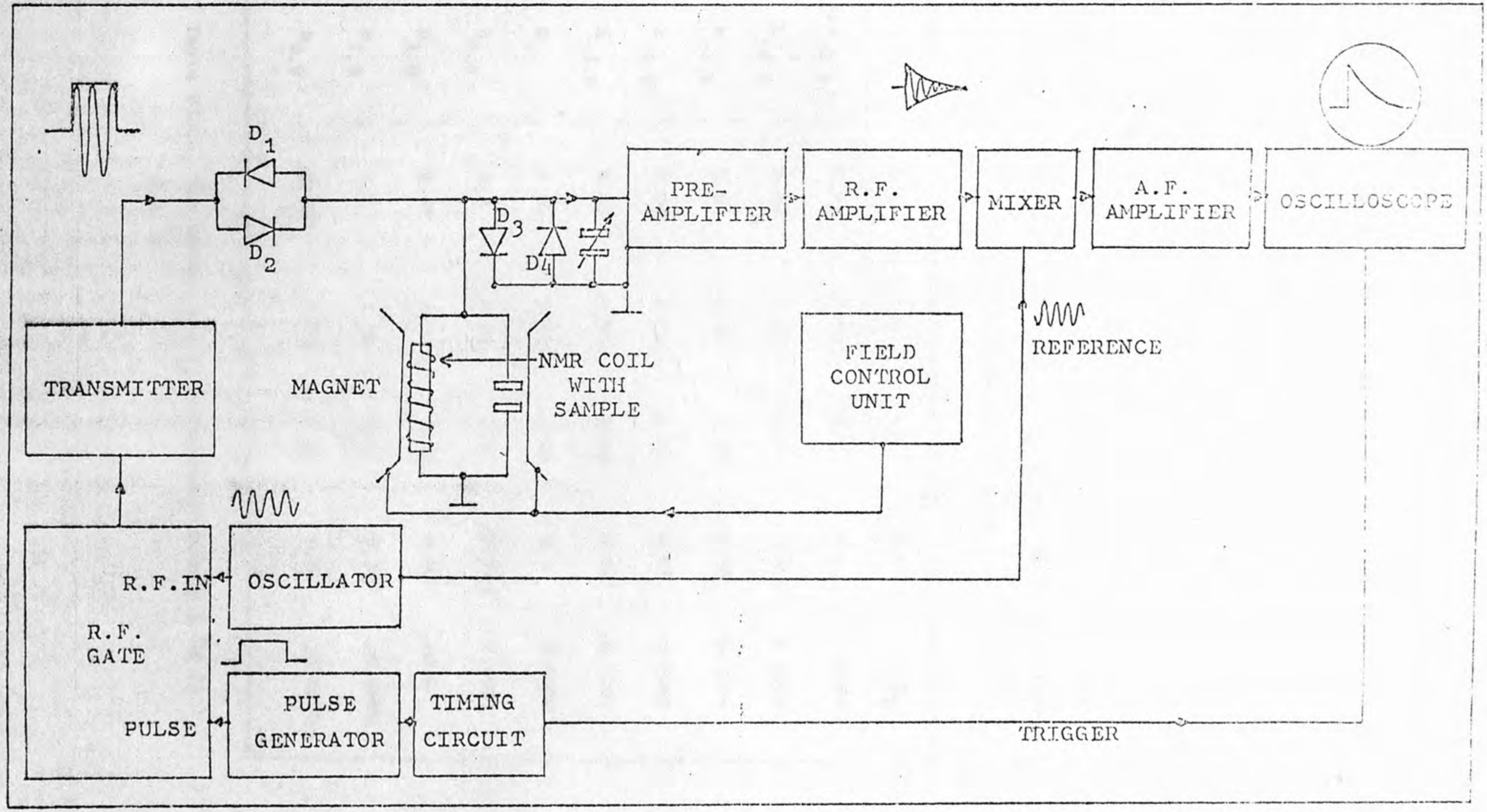
Having done the relaxation times measurements, we also seek the relaxation between temperature and viscosity. Afterwards, we converted the temperatures (for the concerned range) into the viscosities. The information has been obtained ("handbook of Chemist-

ry and Physics" 44the edition, page: 2261) between -4.2°C and 6°C as seen in Graph VI-1.

The relaxation times have been plotted as a function of temperature and temperature/viscosity as they are represented in Graphs VI-2 and VI-3 respectively.

Finally, we summarize our results in Table VI-3.

Figure VI-3: Pulsed NMR Spectrometer.



VI - 3 - EXPERIMENTAL RESULTS AND COMPARISON

On the following pages, we represent some typical experimental results. In Table VI-1, we show the T_2 values for Glycerol in the temperature range between -2.5 °C and 2.0 °C. And similarly, Table VI-2 represents the T_1 values for the same temperature range.

(msec) 2τ	0.4	1.0	1.6	2.0	T_2
(volt) $h_{-2.5}$	2.75	1.475	0.79	0.4	7.9365
$h_{-2.0}$	2.80	1.50	0.9	0.4	8.3334
$h_{-1.5}$	2.80	1.40	0.85	0.56	8.3334
$h_{-1.0}$	2.745	1.52	0.84	0.65	8.6207
$h_{-0.5}$	2.80	1.54	1.02	0.78	8.6207
h_o	2.80	1.65	1.02	0.7	9.0909
$h_{0.5}$	3.2	1.52	1.0	0.715	9.4340
$h_{1.0}$	2.85	1.7	1.05	0.83	10.0
$h_{1.5}$	2.7	1.73	1.1	0.85	10.8696
$h_{2.0}$	2.525	1.72	1.2	0.9	13.1579

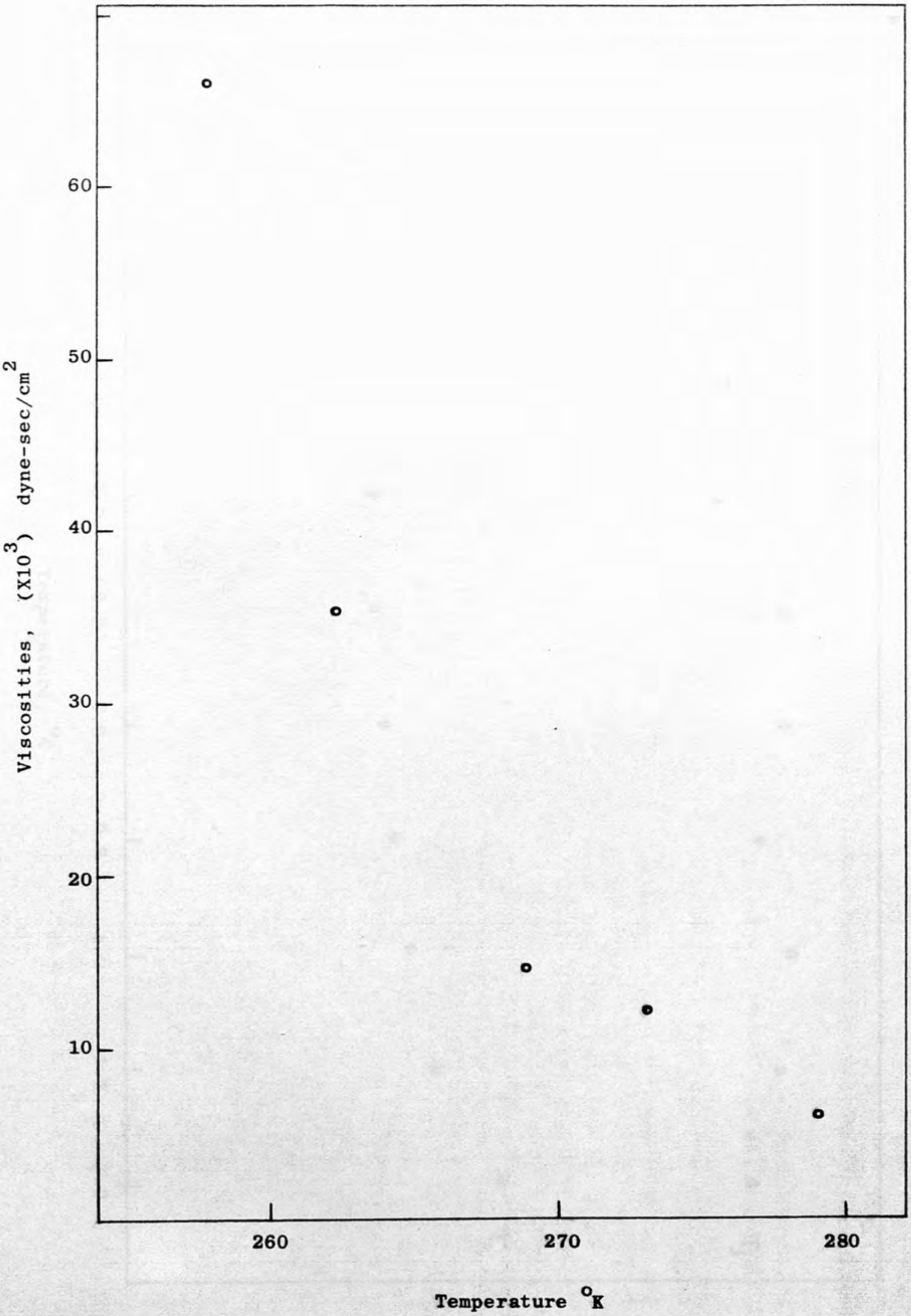
Table VI-1: The values for T_2 measurement from 2.5 °C to 2.0 °C.

(msec.) τ	∞	0.5	1.5	2.5	3.5	∞ -0.5	∞-1.5	∞ -2.5	∞ -3.5	T_1
(volt) $h_{-2.5}$	2.02	0.50	0.99	1.4	1.78	1.52	1.03	0.62	0.44	23.8045
$h_{-2.0}$	2.10	0.55	1.05	1.4	1.72	1.55	1.05	0.7	0.38	22.72
$h_{-1.5}$	2.19	0.57	1.125	1.52	1.725	1.62	1.065	0.67	0.465	20.8333
$h_{-1.0}$	2.20	0.57	1.1	1.5	1.68	1.63	1.1	0.7	0.52	20.6180
$h_{-0.5}$	2.285	0.59	1.11	1.45	1.7	1.685	1.175	0.835	0.585	22.9885
h_o	2.3	0.6	1.12	1.45	1.71	1.7	1.18	0.85	0.59	22.9885
$h_{0.5}$	2.3	0.59	1.115	1.4	1.75	1.71	1.185	0.9	0.55	22.2222
$h_{1.0}$	2.35	0.585	1.01	1.45	1.7	1.765	1.34	0.9	0.65	23.2558
$h_{1.5}$	2.38	0.540	0.98	1.42	1.77	1.87	1.4	0.96	0.61	22.9885
$h_{2.0}$	2.37	0.50	1.0	1.5	1.78	1.87	1.37	0.87	0.58	21.9780

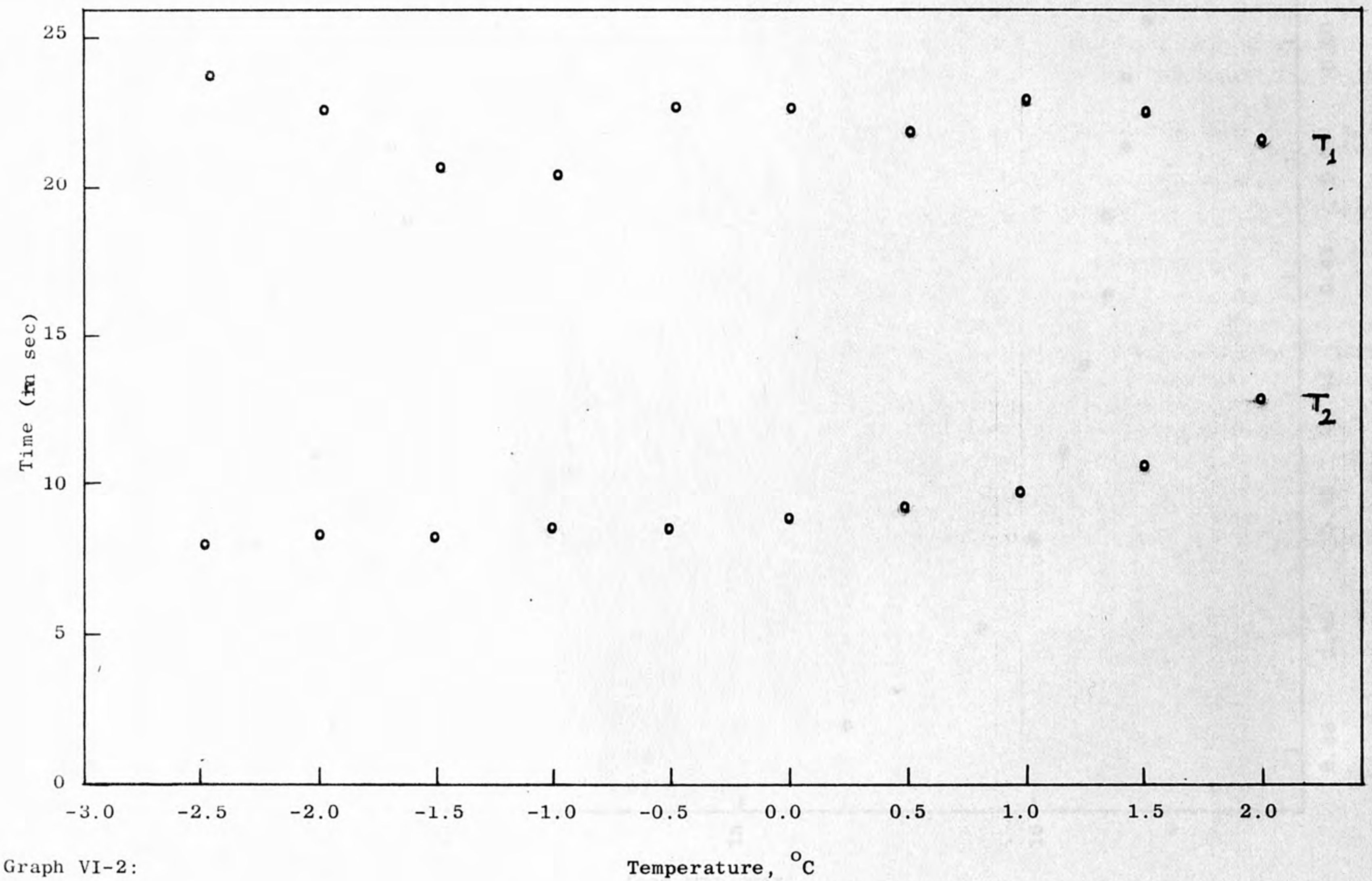
TABLE VI-2: The values for T_1 measurement from -2.5 °C to 2.0 °C

Temperature (Kelvin)	T_2 (m.sec)	T_1 (m.sec)	η (x 10) (cgs)	η/Temp.
270.5	7.9365	23.8045	13.6	0.5028
271	8.3334	22.72	13.34	0.4923
271.5	8.3334	20.8333	13.06	0.4810
272	8.6207	20.6186	12.76	0.4691
272.5	8.6207	22.9885	12.44	0.4565
273	9.0909	22.9885	12.10	0.4432
273.5	9.4340	22.2222	11.74	0.4293
274	10.0	23.2558	11.36	0.4146
274.5	10.8696	22.9885	10.96	0.3993
275	13.1579	21.9780	10.54	0.3813

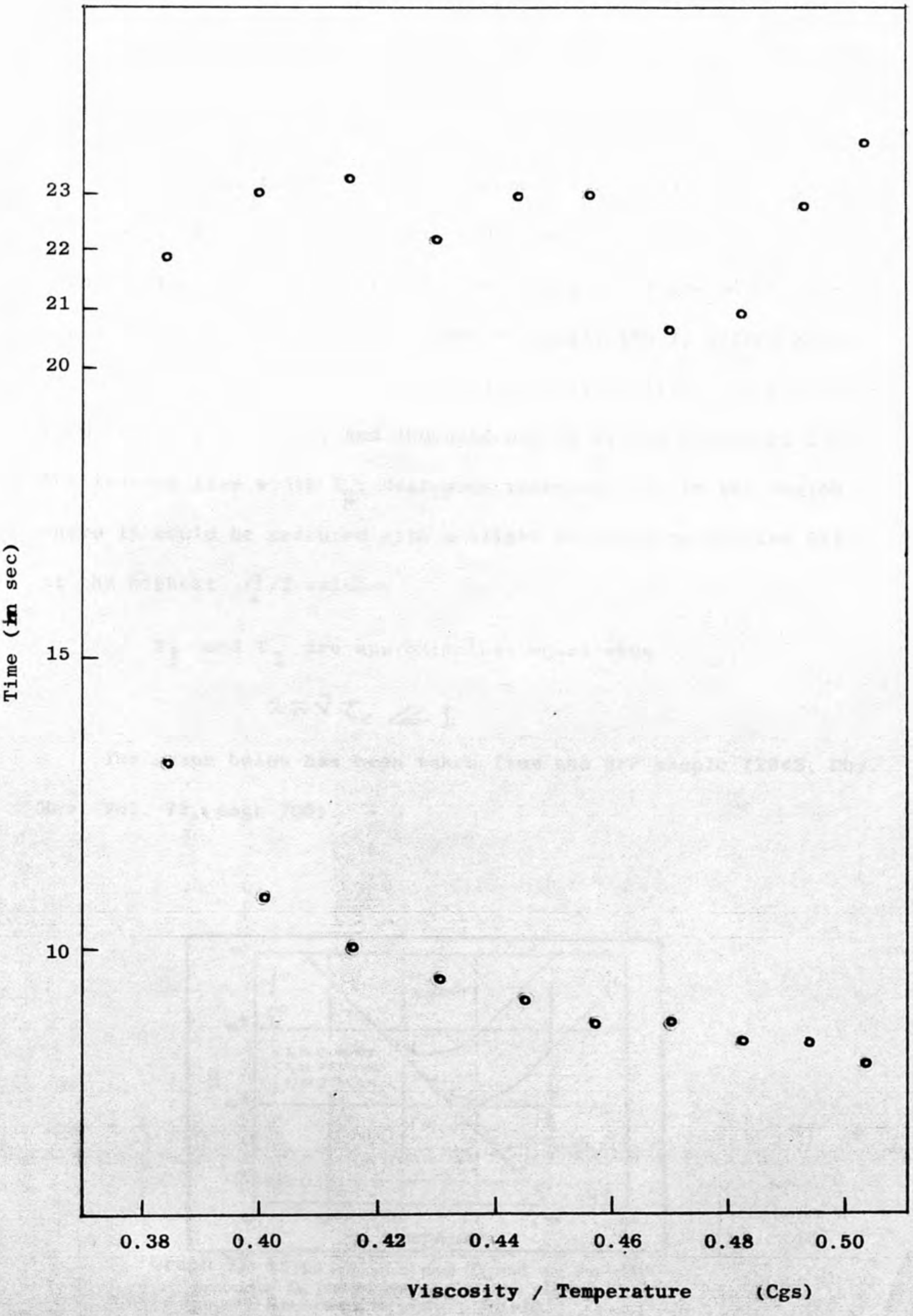
Table VI-3:


Viscosities, (X10^3) dyne-sec/cm^2
60
50
40
30
20
10
260
270
280
Temperature °K

Graph VI-1:


Time (m sec)
0
5
10
15
20
25
-3.0
-2.5
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
Temperature, °C
T_1
T_2

Graph VI-2:


23
22
21
20
15
10
Time (m sec)
0.38
0.40
0.42
0.44
0.46
0.48
0.50
Viscosity / Temperature (Cgs)

Graph VI-3:

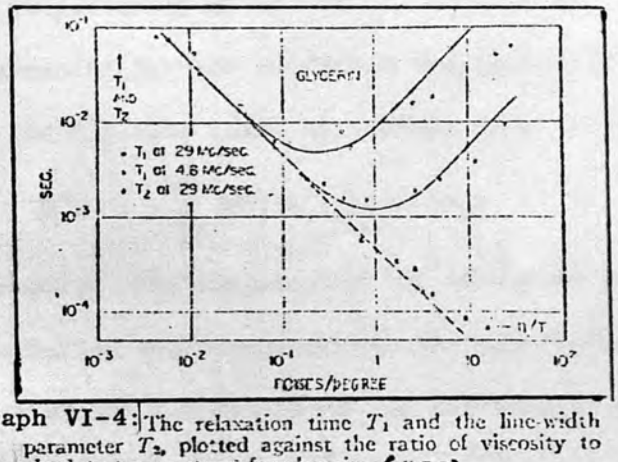
VI - 4 - THE BPP PEOPLE'S RESULTS FOR GLYCEROL

Glycerol at low temperatures becomes glass-like due to its viscosity. Bloembergen, Purcell and Pound (1948) measured T_1 relaxation time and the inverse line width T_2 for glycerol and they concluded that in the region of low viscosity the T_1 values show the behaviour encountered in alcohol, namely inverse proportionality between T_1 and η/T, and independence of T_1 and frequency (ν). The inverse line width T_2, decreases monotonically in the region where it could be measured with a slight tendency to flatten off at the highest η/T values.

T_1 and T_2 are approximately equal when

$$2\pi\nu\tau_c \ll 1$$

The graph below has been taken from the BPP people (1948, Phy. Rev. Vol. 73, page 705).



Graph VI-4: The relaxation time T_1 and the line-width parameter T_2, plotted against the ratio of viscosity to absolute temperature, for glycerin. (BPP)

VI - 5 - THE NON-SECULAR FREQUENCY SHIFT OF THE NMR LINE IN SOLID He^3

It is interesting to consider the work on the frequency shift done by Homer and Richards (1969). They observed the non-secular frequency shift in the NMR line for solid He^3.

Kubo and Tomita explained that frequency shift can occur in the NMR line of a system due to the presence of off-diagonal terms in the perturbing Hamiltonian coupling the spins together. The moment method was used by Van Vleck and Pyrce to discuss the line shapes of the magnetic resonance absorption. The moment expansion is basically an expansion of the auto-moment correlation function G(t) in powers of t. They calculated the moments of the whole spectrum. Kubo was interested in a certain line or a group of lines which are observed experimentally. Therefore, they calculated the moments of the intensity distribution function concerning with this particular absorption. Their expansion method was an expansion in the perturbation not in t.

The expression for the perturbed Hamiltonian $\mathcal{H}'(\omega)$ can be written for the discrete cases as follows (Kubo 1954).

$$\mathcal{H}'(\quad) = \sum_{\alpha} \mathcal{H}'(\omega_{\alpha})\,\delta(\omega - \omega_{\alpha})$$

In this expression, the component $\mathcal{H}'(o)$ is called the secular part of the perturbation and commutes with the unperturbed Hamiltonian $\mathcal{H}_0$. The rest of the components is the non-secular parts of the perturbation. ($\mathcal{H}'(\omega_\alpha)$, $\omega_\alpha \neq 0$). The secular part gives the narrowing to the magnetic absorption line and the non-secular perturbation contributes the additional broadening. The shifts accompany to the secular and non-secular perturbation. (But called usually the non-secular shift).

For the case of dipolar Hamiltonian, the effect can be studied by traversing the region from Larmor frequency $\omega_0 \ll \omega_m$, where ω_m is the frequency with which the local dipole field is modulated, (e.g. by the motion of the spins) to $\omega_0 \ll \omega_m$. In the transversing process, if ω_0 varies we have an extra contribution to the line width, if ω_m varies we get a non-secular shift in the resonance line centre. In the case of complete traversal; the effects are independent of the form of the correlation frunctions $g(\tau)$ which describes the modulation of the dipolar field due to the motion of the spins. If it is not possible to traverse the region completely, we make an assumption about the form of $g(\tau)$ in order to obtain an expression for the shift. The spin motion is due to direct nuclear-spin exchange in solid He^3 below $2^\circ K$ (Homer and Richards). This type of motion can be described by a Gaussian correlation function

$g(\tau) = \exp(-\frac{1}{2}\omega_\ell^2 \tau^2)$. Where $\omega_\ell = \omega_m = J$. The exchange Hamiltonian is given by;

$$\mathcal{H}_{ex} = -\frac{1}{2}\hbar J \sum_{i \neq j} \underset{\sim}{I}_i \cdot \underset{\sim}{I}_j$$

Assuming isotropy of the relaxation rates with respect to the applied field direction, the frequency shift expression is:

$$\delta = -\sum_{\gamma=-1,1,2} \sigma_\gamma^2 \tau''$$

where $\sigma_\gamma^2 \longrightarrow$ the second moments of the satellite lines caused by the off-diagonal terms in the dipolar Hamiltonian

$\tau''_\gamma \longrightarrow$ imaginary part of the Fourier transform of g(τ) at frequency $\gamma\omega_o$

τ''_γ is given by,

$$\tau'' = \frac{1}{\omega_\ell} e^{-\gamma^2\omega_o^2/2\omega_\ell^2} \int_0^{\gamma\omega_\ell/\omega_o} e^{u^2/2}\, du$$

and the frequency shift becomes:

$$\delta = \frac{\sigma_o^2}{3\omega_\ell} \left\{ e^{-\omega_o^2/2\omega_\ell} \int_0^{\omega_\ell/\omega_o} e^{u^2/2}\, du + 2e^{-2\omega_o^2/\omega_\ell^2} \int_0^{2\omega_o/\omega_\ell} e^{u^2/2}\, du \right\}$$

where $\sigma_o^2 = \sigma_1^2 = \frac{3}{2}\sigma_{-1} = \frac{3}{2}\sigma_2^2$ is the second moment of the main NMR line at $\omega = \omega_o$ (when $\omega_o \gg \omega_\ell$)

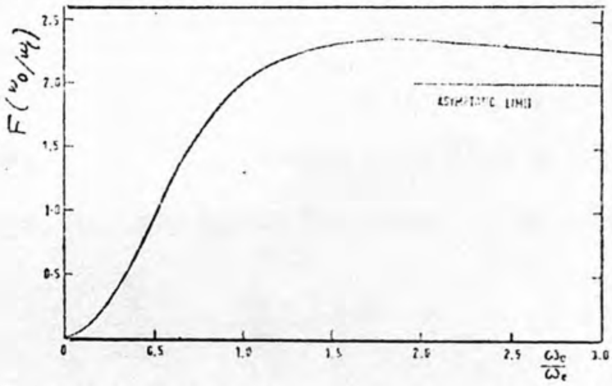
For the calculated value of σ_o , we have,

$$-\frac{\delta}{2\pi} = \frac{1.93\times10^9}{(\omega_\ell/2\pi)V^2} F'(\omega_o/\omega_\ell) \equiv \frac{1.93\times10^9}{(\omega_o/2\pi)V^2} F(\omega_o/\omega_\ell)$$

with $F'(\omega_o/\omega_\ell) = \frac{\omega_\ell}{\omega_o} F(\omega_o/\omega_\ell)$

where $F(\omega_o/\omega_\ell) = e^{-\omega_o^2/2\omega_\ell^2}$ and V is the molar volume of the solid in cm^3.

In the expression for the shift, it is easily seen that δ is directly proportional to $F(\omega_0 / \omega_\ell)$. The figure below has been taken from Homer and Richards shows the variation of $F(\omega_0/\omega_\ell)$ (i.e. the shift) against ω_0 / ω_ℓ.



Graph VI-5: $F(\omega_0/\omega_e)$ as defined in Eqs. (1) and (2) of the text plotted against ω_0/ω_e. For a fixed Larmor frequency ω_0 and molar volume, $F(\omega_0/\omega_e)$ is proportional to δ, the nonsecular frequency shift on the NMR-line of solid He^3. (Homer and Richards).

The calculated shift is found maximum when working $\omega_0 \approx \omega_\ell$. They worked with $\omega_0 = 0.825 \times 2\pi$ MHz and $V = 19.3$ cm^3. The experiment was run by a cw method by using a superconducting magnet and a crystal controlled oscillator. The magnetic field was modulated by a triangular sweep through the central portion of the NMR line (about 0.05 Gauss) with a period of 50sec. The resultant amplitude modulation of the carrier wave was displayed on a chart recorder using r.f. amplification and detection. The change of the shift δ in NMR frequency appears as a change in χ, the separation of adjacent peaks of the NMR signal.

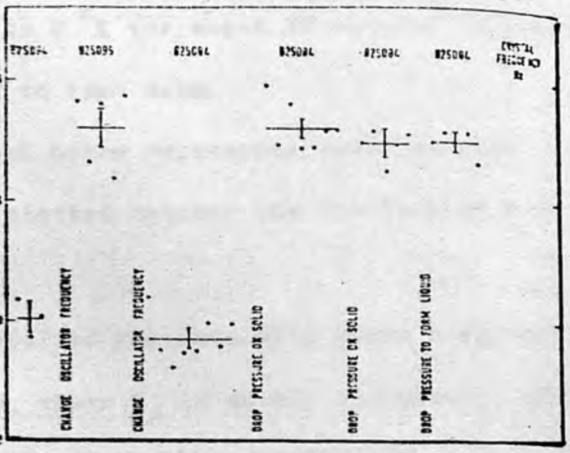
The resonance line is first observed in the region of maximum shift. The peak separation χ is measured (χ_1) and the crystal frequency noted on a counter (ω_c). ω_c is increased by "Δ" and χ_2 is measured. The crystal frequency is returned to ω_c and χ measured (χ_3). Now the pressure on the sample is dropped to a value such that the shift is negligible and χ_4 measured. Finally the pressure is dropped in two more stages ending up with a liquid sample. A check is made that χ doesn't change after these two changes. Due to the linearity of the sweep, we have

$$-\frac{\delta}{\Delta} = \frac{\chi_4 - \chi_3}{\chi_2 - \frac{1}{2}(\chi_1 + \chi_3)}$$

As it is seen in the figure below, we find

$$-\frac{\delta}{2\pi} = \frac{87 \pm 6}{83 \pm 11} \times (11.0 \pm 0.5)\,\mathrm{Hz} = 11.5 \pm 2\ \mathrm{Hz}$$

This experimental result is very close to the theoretical result. And also it is in good agreement with Kubo and Tomita's theory using published data for the spin-exchange rate.



Graph VI-5: The peak separation χ of adjacent NMR lines under various conditions of sample pressure and crystal oscillator frequency described on the figure. The NMR lines are generated by a triangular sweep of the dc magnetic field. (Homer and Richards).

IV - 6 - MEASUREMENTS OF LINEWIDTH FOR ^{3}He ADSORBED ON GRAFOIL

Cowan, Richards, Thomson and Mullin (1976) measured the NMR linewidth as a function of the amount of ^{3}He gas adsorbed at 1 °K. The substate was made up of a multiple sandwich of layers of 0.015 inch. and grafoil was used (by insulating) in order to separate sheets of Mylar. They heated the grafoil to 1000 °C for 24 hours in vacuo and transferred it to a helium atmosphere where the Mylar sheets were inserted. The sandwich was sealed into an epoxy chamber with a sealed filling capillary. The chamber was then transferred to the main apparatus and fixed inside an r.f. coil whose axis was the plane of the grafoil sheets. The superconducting magnet also had its axis in the same plane.

Using the pulsed NMR at frequencies between 0.3 and 2.0 MHz, no significant heating by the r.f. pulses was observed. The data were taken by progressively adding gas at 1 °K and the warming of the samples to 8 °K for about 20 minutes followed by slow cooling back to 1 °K to take data.

The graph below represents their results. T_2 relaxation time at 1 MHz is plotted against the fraction of a saturated monolayer (x).

They obtained the data with three clear-cut regions.

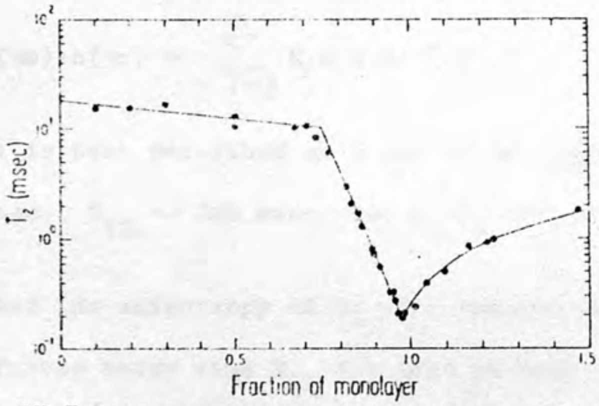
a) $x < 0.75$, where T_2 is nearly independent of x but shows a dependence on the applied magnetic field.

b) $0.75 < \chi < 0.98$, where T_2 is independent of the magnetic field but is strongly dependent on χ so that,

$$T_2 = 0.18 \ \mathrm{e\,x\,p} \left[(0.98-\chi)/0.06 \right] \quad \mathrm{msec.}$$

c) $0.98 < \chi < 1.5$, where T_2 now increases as χ increases so that;

$$T_2 - 0.18 = 3.0 \ (\chi - 0.98)$$



Graph IV-7: Measurements of T_2, the NMR transverse relaxation time, for ^{3}He adsorbed on Grafoil at 1 K as a function of the fractional coverage x. The measuring frequency is 1 MHz, and $\chi = 1$ corresponds to a complete monolayer as defined by a 4.2-K isotherm.

(Cowan, Richards, Thomson and Mullin).

IV - 7 - THE ANISOTROPY OF T_1 AND T_2 OF ^{3}He ADSORBED ON MYLAR FILM

Kent's recent work (1982) was the study of ^{3}He adsorbed on Mylar film between 1 °K and 4.2 °K. He measured the relaxation times T_1 and T_2 at 4.2 °K using 180°-90°-180° and 90°-180° pulse

sequences respectively.

The recovery of longitudinal magnetization at $\beta = 0^{\circ}$ at $T = 4.2\ ^{\circ}K$ is represented in Graph (VI-8). It is non-exponential as is found with multilayer films on grafoil. It has been shown that if the system consists of n separate phases each of which relaxes exponentially at the rate T_{1n}, if the rate of exchange of particles between these phases is slow when compared with the T_{1n}, the total relaxation is the sum of each of the exponential decays weighted with the number of particles, in each phase, N_i,

$$h(\infty)-h(\tau) = \sum_{i=1}^{n} N_i \, \mathrm{exp}(\tau/T_{1i})$$

Figure (VI-8) is best described as a sum of two exponentials with $T_{11} \sim 100$ msec., $T_{12} \sim 350$ msec. and $N_1/N_2 \sim 1.6$

We plotted the anisotropy of $T_{\perp}$ with respect to β (Figure VI-9). The faster decay time T_{11} was used in each case since it could be determined with much greater accuracy than T_{12}. The shape of the anisotropy curve and the relative values of $1/T_1$ at 0° and 90° are in good agreement with the theory for a diffusive fluid with $\omega_0 \tau_d \sim 10^{-2}$.

The decay of transverse magnetization following a 90° pulse was observed to be a single exponential. This seems unexpected since if the interlayer particle exchange rate is slow compared to T_1, it is even slower when compared to the shorter T_2. It may be that the early part of a non-exponential decay was hidden by the receive dead time or the later part lost in the noise as the echo became small. There are two decays visible but the relaxation times are very similar making it hard to discern between them on a semilogarithmic plot.

The anisotropy in T_2 is represented in Graph VI-10. It shows a definite minimum in the region of 32° and the overall anisotropy is about 25%. It is not clear from the relaxation times, whether we are looking at a solid or a fluid phase, however, the position of the minimum seems to agree with the theory for a 2-D solid with $\omega_0/J \gtrsim 10$, but the overall anisotropy is less than the theory predicts.

Neither of the theoretical curves on Graph VI-10 fit the data above 55° while below this angle the agreement is good.

The conclusion is that: As far as the anisotropy study of Helium - 3 on Mylar is concerned, the results appear somewhat confusing. T_1 measurements suggest that we are observing a 2-D fluid phase while T_2 data points to a 2-D solid. Both of these phases are present and the experimental conditions for T_1 and T_2 measurement were such that one of these phases was obscured. Alternatively, we do not understand the behaviour of multilayer films well enough to explain the results.

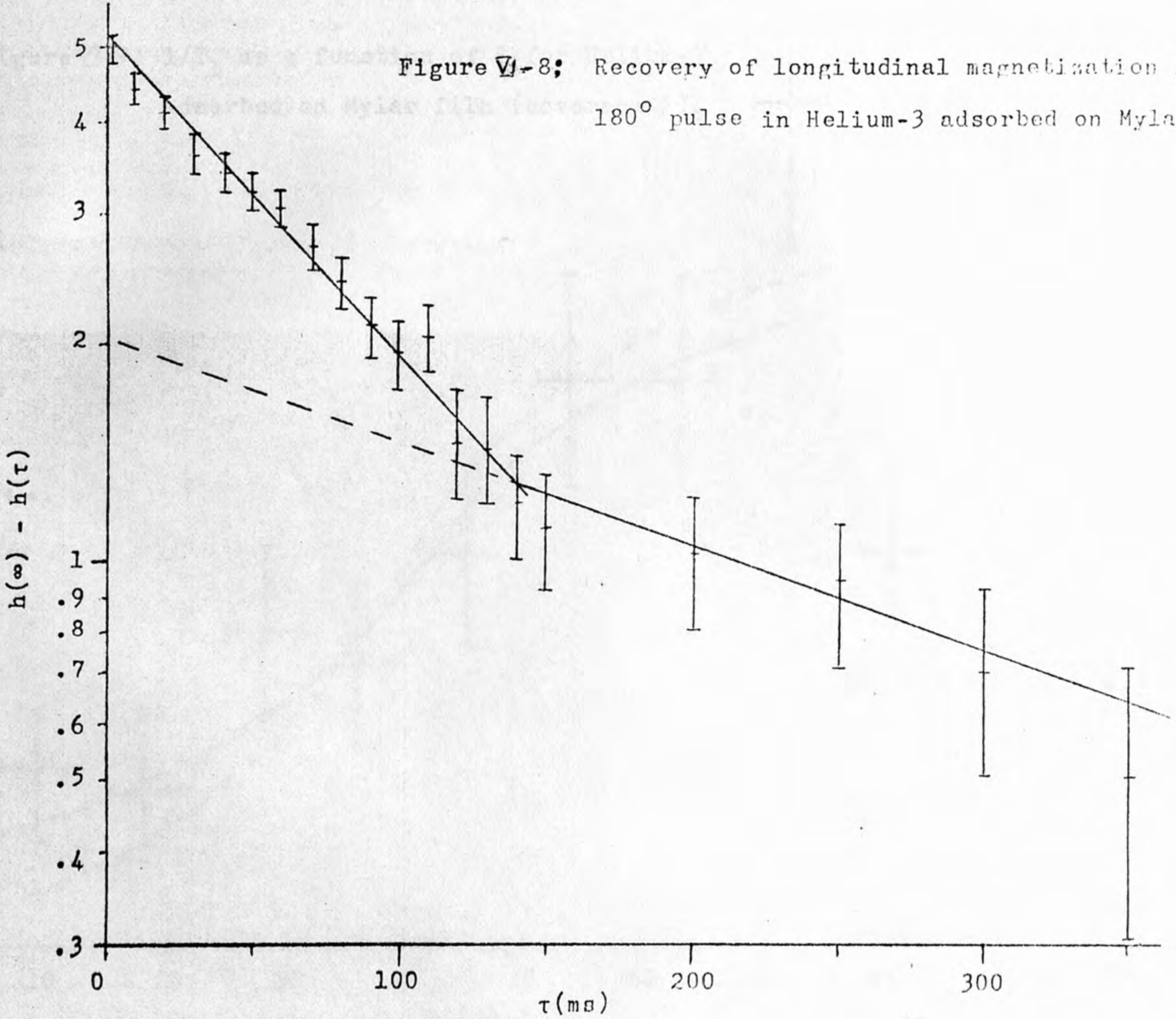


Figure VI-8; Recovery of longitudinal magnetization following a 180° pulse in Helium-3 adsorbed on Mylar, coverage 5.

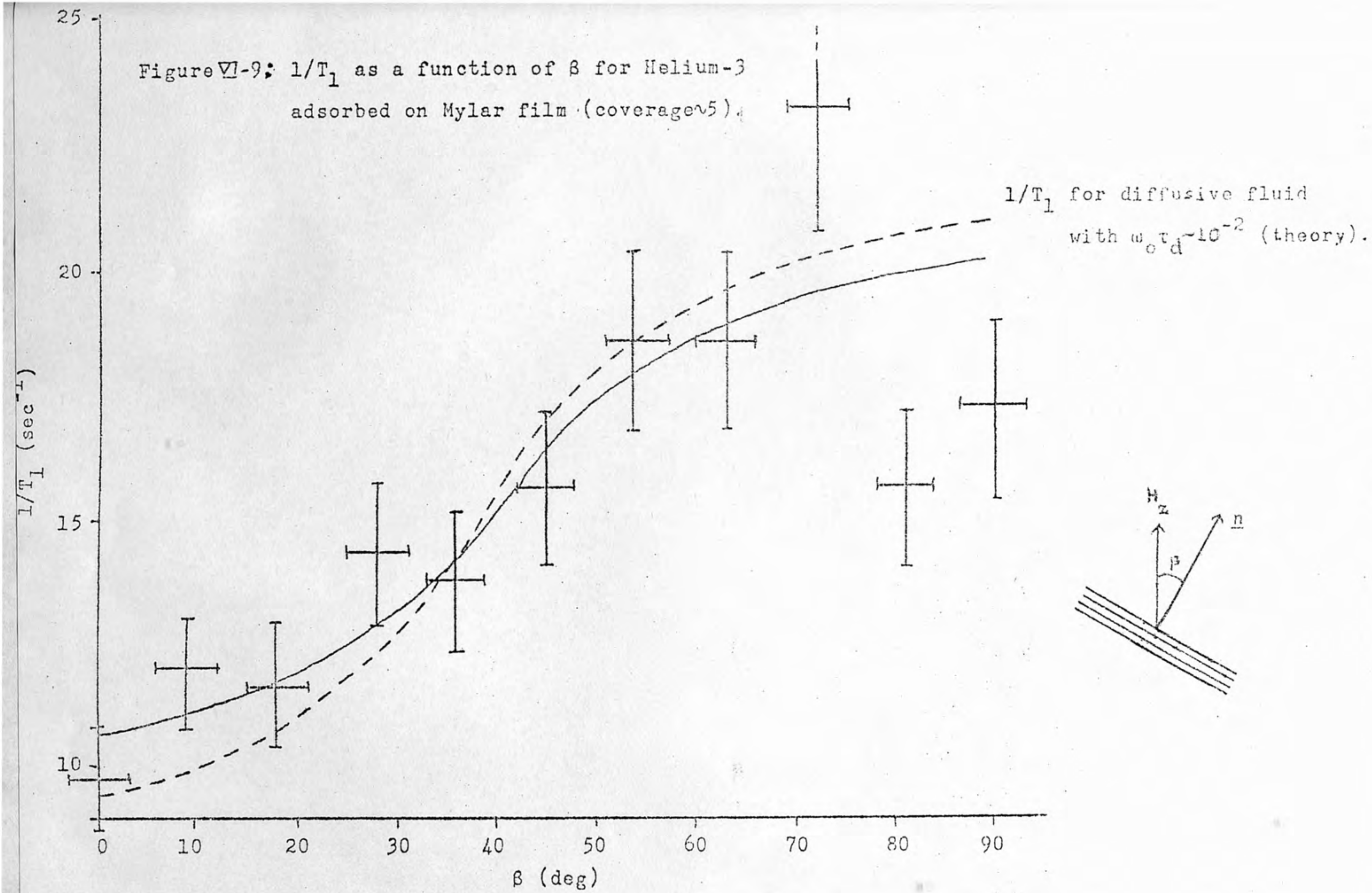
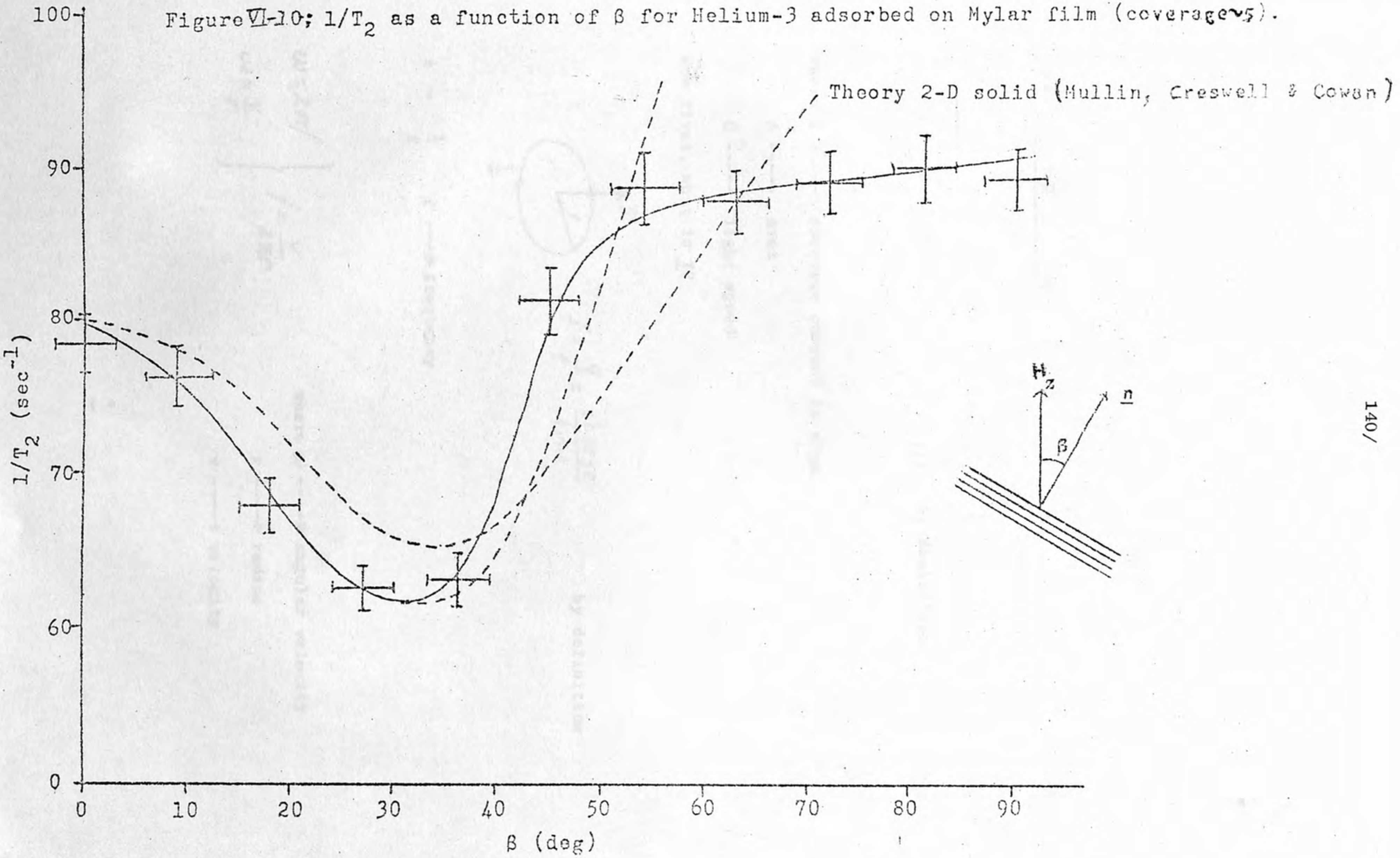


Figure VI-9: $1/T_1$ as a function of β for Helium-3 adsorbed on Mylar film (coverage~5).

Figure VI-10; $1/T_2$ as a function of β for Helium-3 adsorbed on Mylar film (coverage~5).



APPENDIX (I - 1)

PROOF THAT $\underline{m} = \gamma\ \underline{J}$

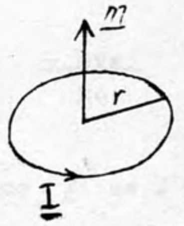
$$\boxed{\underline{m} = \underline{I}\cdot\underline{A}/c}$$ (I) by definition

where I ----- electric current in atom

A ----- area

C ----- light speed

Now first, what is $\underline{I}$?



$$I = \frac{q}{t} = \frac{\text{charge}}{\text{time}}$$ by definition

$t = \frac{1}{f}$ f ---> frequency

$$\left.\begin{array}{l} \omega = 2\pi f \\ \omega = \frac{v}{r} \end{array}\right\} f = \frac{v}{2\pi r}$$

where ω ----> angular velocity

r ----> radius

v ----> velocity

substituting "f" into "I", we have

$$I = \frac{-ev}{2\pi r}$$ (II) with $q = -e$ for electron

what is A?

$$A = \pi r^2$$ (III)

substituting Equations (III) and (II) into Equation (I), we have,

$$m = \frac{-evr}{2c}$$

define $\underline{J}$ as $J = m_e v r$

J ---> angular momentum

m_e --> mass for electron

"m" becomes

$$\underline{m} = -\frac{e}{2m_e c}\underline{J} \quad \text{and} \quad \boxed{m = \gamma J} \quad \text{with } \gamma = -\frac{e}{2m_e c}$$

(gyromagnetic ratio)

APPENDIX (I - 2)

WHEN $\underline{H} = H_0 \hat{\underline{k}}$, MAGNETIC MOMENT DOES A CIRCULAR MOTION IN THE x-y PLANE AND PRECESSES ABOUT THE Z AXIS WITH THE LARMOR FREQUENCY $\omega_0 = H_0 \gamma$.

The Gyroscope equation:

$$\dot{\underline{m}} = \gamma \, \underline{m} \times \underline{H} \qquad \text{(I)}$$

Solution for constant $\underline{H}$: $(\underline{H} = H_0 \hat{\underline{k}})$

Equation (I) can be written as

$$\dot m_x \hat{\underline{i}} + \dot m_y \hat{\underline{j}} + \dot m_z \hat{\underline{k}} = \gamma \begin{vmatrix} \hat{\underline{i}} & \hat{\underline{j}} & \hat{\underline{k}} \\ m_x & m_y & m_z \\ \cancel{H_x} & \cancel{H_y} & \cancel{H_z} \\ 0 & 0 & H_0 \end{vmatrix}$$

we have,

$$\left. \begin{aligned} \dot m_x &= \gamma m_y H_0 \\ \dot m_y &= \gamma m_x H_0 \\ \dot m_z &= 0 \end{aligned} \right\} \qquad \text{(II)}$$

therefore, m_z = constant

The second time derivatives of m_x and m_y are

$$\left.\begin{aligned} \ddot{m}_x &= -\gamma^2 H_o^2 m_x \\ \ddot{m}_y &= -\gamma^2 H_o^2 m_y \end{aligned}\right\} \qquad \text{(III)}$$

and the solution of these equations are respectively the following:

$$\begin{aligned} m_x(t) &= m_x(o)\ \mathrm{Cos}\left[(\gamma H_o)\ t\right] + m_y(o)\ \mathrm{Sin}\left[(\gamma H_o)\ t\right] \\ m_y(t) &= -m_x(o)\ \mathrm{Sin}\left[(\gamma H_o)\ t\right] + m_y(o)\ \mathrm{Cos}\left[(\gamma H_o)\ t\right] \end{aligned} \qquad \text{(IV)}$$

If we square equation (IV) and add them side by side, it follows that;

$$m_x^2(t) + m_y^2(t) = \underbrace{m_x^2(o) + m_y^2(o)}_{R^2} \qquad \text{(V)}$$

Equation (V) describes a circle

General equation of a circle is given by:

$$(x-\alpha)^2 + (y-\beta)^2 = R^2$$

if $\alpha = \beta = 0$

circle equation becomes:

$x^2 + y^2 = R^2$ (i.e. centre is on the origin)

APPENDIX II-1

QUANTUM MECHANICAL EQUATION OF MOTION IN THE SCHRÖDINGER AND HEISENBERG PICTURES

We postulate that all the information about the state is contained in a multidimensional complex vector - KET.

Let us have the following:

a) We wish to be able to infer a state at time "t" from the knowledge of the state at time "to". ($t > t_0$). Equation will be the first order in t.

b) Principle of superposition is to hold throughout the undisturbed motion. We introduce operator "T" which is: 1 - linear 2 - independent of state 3 - dependent of t and t_0 such that

$$|Pt\rangle = \underline{T}\,|Pt_0\rangle \qquad (1)$$

c) $\underline{T}\,T^{+} = 1$ unitary operator

Lengths of vectors are unchanged

$$\langle Pt\,|\,Pt\rangle = \langle Pt_0\,|\,Pt_0\rangle$$

Now, from equation (1), we can write

$$\begin{aligned} |Pt\rangle - |Pt_0\rangle &= \underline{T}\,|Pt_0\rangle - |Pt_0\rangle \\ |Pt\rangle - |Pt_0\rangle &= (\underline{T} - 1)\,|Pt_0\rangle \end{aligned} \qquad (2)$$

Dividing both sides of equation (2) by $(t-t_o)$ we get,

$$\frac{|Pt\rangle - |Pt_o\rangle}{t-t_o} = \frac{\underline{T}-1}{t-t_o}\,|Pt_o\rangle \qquad (3)$$

The left-hand side of Equation (3) is $\frac{d}{dt}|Pt\rangle$

We can expand $\underline{T}$ for small $t-t_o$

i.e. $\underline{T} = 1 + (t-to)\,\underline{u} + \text{------}$

$\underline{T}\underline{T}^+ = 1$ becomes:

$$\left[1+(t-t_o)\,\underline{u}^+ + \text{----}\right]\left[1+(t-t_o)\,\underline{u} + \text{----}\right] \qquad (4)$$

Retaining only terms to first order in $t-t_o$, we have,

$(t-t_o)\quad(\underline{u}^+ + \underline{u}) = o$

$\underline{u}^+ + \underline{u} = o$ (5) **Antihermitean**

Introducing a Hermitean operator $\underset{\sim}{H}$, we write $\underline{u}$ in terms of $\underline{\mathcal{H}}$

$$\underline{u} = \underline{\mathcal{H}}/i\hbar$$
$$\underline{u}^+ = -\underline{\mathcal{H}}/i\hbar \qquad (6)$$

With Equation (6), Equation (3) becomes:

$$i\hbar\frac{d}{dt}|Pt\rangle = \mathcal{H}|Pt\rangle \qquad (7)$$

This "equation of motion" in SCHRÖDINGER picture (evolution in terms of <u>kets</u>).

Equation of motions can be expressed in terms of the evolution of <u>operators</u> rather than <u>kets</u>. This is to refer to the HEISENBERG picture.

Let $\underline{\alpha}_S$ and α_H be two operators used in the Schrodinger and Heisenberg pictures respectively.

We have the following:

$$\underline{\alpha}_S \,|Pt\rangle = |Qt\rangle \qquad (8)$$

$$|Pt\rangle = T\,|Pt_0\rangle \;;\; |Qt\rangle = \underline{T}\,|Qt_0\rangle \qquad (9)$$

from Equations (8) and (9) we write

$$\underline{\alpha}_S \,\underline{T}\,|Pt_0\rangle = \underline{T}\,|Qt_0\rangle \qquad (10)$$

$$\underline{\alpha}_H \,|Pt_0\rangle = |Qt_0\rangle \qquad (11)$$

$$\underline{\alpha}_H = \underline{T}^{-1}\,\underline{\alpha}_S\,\underline{T} \qquad (12)$$

We are seeking

$$\frac{d}{dt}\underline{\alpha}_H$$

Substituting Equation (8) into Equation (7), we get,

$$i\hbar\,\frac{d\underline{T}}{dt}\,|Pt_0\rangle = \underline{H}\,\underline{T}\,|Pt_0\rangle \qquad (13)$$

and it follows that;

$$\left.\begin{aligned} i\hbar\frac{d\underline{T}}{dt} &= \underline{\mathcal{H}}\,\underline{T} \\ -i\hbar\frac{d\underline{T}^+}{dt} &= \underline{T}^+\underline{\mathcal{H}}^+ = \underline{T}^+\underline{\mathcal{H}} \end{aligned}\right\} \quad (14) \text{ with } \mathcal{H}^+ = \mathcal{H}$$

using Equation (12) in $d\underline{\alpha}_H/dt$, we write

$$\frac{d}{dt}\underline{\alpha}_H = \underline{T}^+\underline{\alpha}_s\frac{d}{dt}\underline{T} + \frac{d}{dt}\underline{T}^+\underline{\alpha}_s\underline{T} \qquad (15)$$

now we use Equation (14) in Equation (15), so,

$$i\hbar\frac{d}{dt}\underline{\alpha}_H = \underline{T}^+\underline{\alpha}_s\underline{\mathcal{H}}\,\underline{T} - \underline{T}^+\underline{\mathcal{H}}\,\underline{\alpha}_s\underline{T} \qquad (16)$$

$$= \underline{T}^+\left[\underline{\alpha}_s, \underline{\mathcal{H}}\right]\underline{T}$$

$$= \underbrace{\underline{T}^+\underline{\alpha}_s\underline{T}}_{\underline{\alpha}_H}\,\underbrace{\underline{T}^+}_{1}\underbrace{\underline{\mathcal{H}}\,\underline{T}}_{\underline{\mathcal{H}}_H} - \underline{T}^+\underline{\mathcal{H}}\,\underline{T}\,\underline{T}^+\underline{\alpha}_s\underline{T}$$

$$= \underline{\alpha}_H\underline{\mathcal{H}}_H - \underline{\mathcal{H}}_H\underline{\alpha}_H$$

$$i\hbar\frac{d}{dt}\underline{\alpha}_H = \left[\underline{\alpha}_H, \underline{\mathcal{H}}_H\right] \qquad (17)$$

Equation of motion in the new operator $\mathcal{H}_H$.

APPENDIX VI - 1:

THE CALCULATION OF THE PULSE LENGTH

For a 90° pulse ($\Theta = \frac{\pi}{2}$), from Equation VI-1, we write;

$$\frac{\pi}{2} = \omega_1 t_p \qquad \text{(I)} \qquad \text{with} \quad \omega_1 = \gamma H_1$$

The magnetic flux Φ across a coil of inductance L is:

$$\Phi = 2H_1 n A = L i \qquad \text{(II)}$$

where the field "$2H_1$" is the amplitude of the linearly polarized magnetic field produced by current i circulating in the coil. "A" is the area of cross-section with diameter "d". "n" is the number of the turns of the coil.

From (I) and (II), we have,

$$t_p = \frac{\pi^2 n d^2}{4 \gamma L i} \qquad \text{(III) with} \quad A = \tfrac{1}{4} \pi d^2$$

For a coil system the voltage across it is given by

$$V = i \omega L \qquad \text{(IV)}$$

And with this, Equation III becomes:

$$V \cdot t_p = \frac{n \pi^2 d^2 \omega}{4 \gamma} = \frac{n \pi^3 d^2}{2 \gamma} f_0 \qquad \text{(V) with} \quad \omega = 2 \pi f_0$$

If we eliminate n, we have,

$$L = \frac{\mu_0 n^2 A}{l} \times 0.7 \Longrightarrow n = \sqrt{\frac{L . l}{0.7 \mu_0 A}}$$

(VI)

From V and VI, we obtain,

$$V t_p = \frac{\pi}{\gamma} \sqrt{\frac{v}{0.7 \mu_0 C}}$$

(VII) with $l . A = v$

$L = 1/\omega^2 C$

l ⟶ length

v ⟶ volume

C ⟶ capacitance

μ_0 ⟶ permebility

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