NMR Study of
$^3$He Adsorbed on Exfoliated Graphite

By

Laila Ibrahim Abou-El-Nasr
Royal Holloway and Bedford New College

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To My Dearest Family

My thanks to A. Roe who and to me around the crystal and helped me to understand the crystallographic principles.

The Memory of My Father and Sister

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ABSTRACT

The present work has been carried out to investigate the dynamic properties of $^3$He film adsorbed on an exfoliated graphite substrate, using pulsed NMR techniques. It has been found that the dipolar interaction is the dominant mechanism for the spin relaxation, although the effect of the grafoil local fields can not be ignored. The spin-lattice relaxation time $T_1$ and the spin-spin relaxation time $T_2$ which characterize the spin system were determined.

The study has been concentrated on two phases. The registered phase and the solid phase. Some data were taken at the mixed phase which lies between them. Both relaxation times were determined as functions of monolayer capacity, frequency, temperature and spin orientations. For temperatures less than 2 K, the spins exhibit quantum motion behaviour. The frequency of this motion was determined and was found to be inversely proportional to the spin density.

At the registered phase, the activation temperature was determined, where it was a maximum corresponding to perfect registry. Special attention was given to the $T_1$ data at the minima in the solid phase since there the frequency of the motion is comparable to the Larmor frequency.
## CONTENTS

### Chapter 1: Introduction

1.1 The Physisorption Phenomenon ............................................................. 1
1.2 The Choice of $^3$He ................................................................. 2
1.3 Grafoil as a Convenient Substrate ......................................................... 2
1.4 The Phase Diagram ................................................................................... 4
  1.4.1 The Gas Phase ................................................................................. 6
  1.4.2 The Registered Phase ................................................................. 6
  1.4.3 The Mixed Phase ............................................................................ 8
  1.4.4 The Solid Phase ............................................................................. 11
1.5 Why Use NMR? ....................................................................................... 11
1.6 Previous Work ........................................................................................... 12
1.7 Outline of this Work ................................................................................ 13

### Chapter 2: Aspects of the NMR Theory

2.1 Introduction ............................................................................................... 15
2.2 Quantum Mechanical Approach ............................................................ 16
2.3 Evaluation of the Relaxation Functions .............................................. 19
2.4 The Cumulant Approach ........................................................................ 22
2.5 Transformation into Two Dimensions .................................................. 25
2.6 Different Models for the Motion ........................................................... 26
  2.6.1 Diffusion .......................................................................................... 26
    2.6.1a Long-Time Behaviour ...................................................... 27
## Contents

2.6.1b Short-Time Behaviour .................................................... 27  
2.6.1c Longitudinal Relaxation ................................................. 28  
2.6.1d Transverse Relaxation .................................................... 28  
2.6.2 Exchange ........................................................................................ 30  
2.6.2a Short-Time Behaviour .................................................... 31  
2.6.2b Long-Time Behaviour .................................................... 32  
2.6.2c The Interpolation Procedure ......................................... 33  
2.6.2d Longitudinal Relaxation ................................................. 34  
2.6.2e Transverse Relaxation .................................................... 36  
2.7 Relaxation due to Grafoil Platelets ...................................................... 36  

### Chapter 3: Apparatus and Experimental Techniques

(i) The Apparatus ............................................................................................. 39  
3.1 The Cryostat ............................................................................................. 39  
3.2 Sample Chamber ..................................................................................... 41  
3.3 The Rotating Mechanism ........................................................................ 41  
3.4 The Temperature Regulation System ................................................... 43  
3.5 The Gas Handling System ...................................................................... 46  
3.6 The NMR Magnet ..................................................................................... 46  
3.7 The NMR Probe ......................................................................................... 48  
3.8 The NMR Spectrometer ........................................................................... 50  
3.8.1 The Pulsed Transmitter ....................................................................... 50  
3.8.2 The Receiver .................................................................................. 50  
3.8.3 The Essential Requirements of a Pulsed NMR Spectrometer 51  
3.9 Details of the Spectrometer Used .......................................................... 52
(ii) Review on the Experimental Techniques ............................... 56

3.10 Introduction ................................................................. 56

3.10.2 Preparation for the Run ............................................... 56

3.10.3 The Adsorption Isotherm ........................................... 58

3.10.4 Admittance of The Sample ....................................... 58

3.11 Data Acquisition ............................................................. 60

3.11.1 $T_1$ and $T_2$ Measurements ..................................... 60

Chapter 4: The Registered Phase

4.1 Introduction ........................................................................... 64

4.2 Concept of the Registered Phase ........................................ 64

4.3 Display of the Data ............................................................. 66

4.4 The Coverage Dependence ................................................ 66

4.5 The Dependence on Larmor Frequency ............................. 72

4.6 The Temperature Dependence .......................................... 88

4.7 Anisotropy ........................................................................... 88

4.8 Evaluation of the Correlation Time .................................... 94

4.8.1 The Calculations from $T_1$ ........................................... 94

4.8.2 Employment of $T_2$ .................................................... 101

4.8.3 Determination of $\tau_c$ from Angle Dependence ........... 104

4.9 The Activation Energy ....................................................... 111

4.10 The Mixed Phase ............................................................. 114

Chapter 5: The Incommensurate Solid Phase

5.1 Introduction ................................................................. 118

5.2 Dependence of Relaxation Times on Coverage ................... 118
5.3 Frequency Dependence ................................................. 127
5.4 The Characteristic Frequency of the Motion .................. 140
  5.4.1 Determination of $J$ from $T_1$ ................................. 148
  5.4.2 Calculation of $J$ Using $T_2$ Data ......................... 151
5.5 Anisotropy of $T_2$ ...................................................... 163

Chapter 6: Summary and Future Work

6.1 Summary of the Experimental Work ............................ 171
  6.1.1 The Registered Phase ........................................... 171
  6.1.1 The Mixed Phase .............................................. 172
  6.1.1 The Solid Phase .............................................. 173
6.2 Suggestions For Future Work ...................................... 174

Appendix A

The Magnetisation System after applying 90° or 180° pulse ... 175

Appendix B

Transformation of $I_e$ into $I_-$ in the Magnetisation expression ... 178

References ................................................................. 180
CHAPTER 1

Introduction

1.1 The Physisorption Phenomenon:

When one speaks about physisorption it implies a two dimensional (2D) system which consists of two substances. One of them; the adsorbate; is held to the surface of the other; the adsorber. So, if an atom or molecule approaches the surface of a solid, it will experience a net attractive potential of Van-der-Waals nature. As a result, there will be an appreciable probability for the adsorbate to be trapped on the surface (Somorjai 1981) and the phenomenon of adsorption will occur. The adsorber serves only as a substrate to confine the adsorbate to a plane to obtain a 2-d system.

The adsorption happens when the equilibrium temperature of the system is comparable or less than the attractive potential between the adsorbate and the adsorber. As a result, if enough adatoms (adsorbate) are available and the temperature is low enough; then the surface can completely covered by a layer of adsorbed atoms (Dash 1978). Different techniques have been used to study the properties of physisorbed systems, such as Heat Capacity, Positron Annihilation, Mössbauer Effect, Low Energy Electron Diffraction (LEED), Neutron Scattering and Nuclear Magnetic Resonance (NMR). $^3$He adsorbed on exfoliated graphite is considered as an excellent combination to study such phenomenon.
1.2 The Choice of $^3\text{He}$:

It is well known that noble gases are attracted to other substances more than to each other. When the gas is cooled (Dash 1973) it is adsorbed as a thin film on the wall of the vessel rather than to condense into droplets or crystals so it makes an ideal adsorbate.

Helium is one of these gases, the element has two isotopes namely $^3\text{He}$ and $^4\text{He}$. $^3\text{He}$ is a Fermion which has two electrons, two protons and one neutron. The atomic mass is $\approx 3.016$ and the gyromagnetic ratio is \((-3.244 \times 10^{-7}\) Hz T\(^{-1}\).

1.3 Grafoil as a Convenient Substrate:

The use of graphitized carbon black is very common because the adsorption isotherm data (Thomy and Duval 1969) have shown that the basal planes of graphite offer a uniquely uniform surface to rare gas adatoms. The adsorption isotherm of Kr adsorbed on graphite shows as many as seven steps (Thomy and Duval 1970) corresponding to the clear build-up of distinguishable layers. Building such steps, is the behavior expected from adsorption on a uniform surface.

Another form of graphite is used as a successful substrate, known as grafoil (a trade name). This substrate (Bretz et al, errata 1973); (Dash and Schick 1978) is the graphite which has been exfoliated in a strongly oxidizing medium then rinsed and rapidly heated. The expanded particles are pressed together and rolled into binderless flexible sheets which has more surface area than the prototype graphite.

These sheets are composed of graphite crystallites in the form of platelets as shown in the electron micrograph figure (1.3.1). These crystallites tend
Figure 1.3.1

Electron Micrograph of the Grafoil Specimen with different Magnifications.
to align with their C-axes normal to the foil plane (Kjems et al 1976) i.e.,
their basal planes preferentially oriented parallel to the plane of the foil. The
distribution of the C-axes seems to consist of two parts, a purely random
part and an oriented part. The full width at half maximum of the C-axes
distribution was observed to be 30° which is considered as the substrate mean
mis-orientation. The basal plane consists of hexagonal arrays of carbon atoms
(Novaco 1973), with a point of minimum potential energy to trap the helium
atom through the center of the hexagon (the adsorption site). However the
actual length of the exposed basal planes (Kjems et al 1976) is of the order of
100 Å, while the specific area of grafoil is \( \approx 20 \text{ m}^2/\text{g} \) and the area per \(^3\text{He}\) atom
is about 9.95 Å\(^2\) (Grimmer and Luszczynski 1973).

Grafoil is diamagnetic material and its magnetic susceptibility is
anisotropic. Although the substrate is quite uniform, it is not ideal and it has
varying densities and different types of imperfections and impurities. Before
using grafoil in experiments it should be heated in vacuum for several hours
to eliminate water vapour and the impurities adsorbed on the surface. It was
found that even with the heat treatment, grafoil still has traces of impurities
mainly silicon and iron. The analysis of the grafoil used in this work has been
done before and after the heat treatment (Hilger & Watts) and the result is
shown in table (1.3.1).

1.4 The Phase Diagram:

The monolayer of \(^3\text{He}\) film adsorbed on grafoil exhibits several distinct
phases. These phases have been investigated by different methods. One of the
most effective methods is heat capacity measurements. The first experimental
studies have been made by Bretz and Dash (1971). Later on, a phase
<table>
<thead>
<tr>
<th>Element</th>
<th>Before Heating</th>
<th>After Heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Gold</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Aluminium</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>Boron</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>Bismuth</td>
<td>1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Calcium</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Cobalt</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Chromium</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>Copper</td>
<td>1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Iron</td>
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</tr>
<tr>
<td>Manganese</td>
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<tr>
<td>Molybdenum</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Nickel</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
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<td>Antimony</td>
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</tr>
<tr>
<td>Silicon</td>
<td>&gt;500</td>
<td>≈200</td>
</tr>
<tr>
<td>Zinc</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Table 1.3.1

The chemical analysis of impurities (ppm) contained in the grafoil specimen. Before and after heat treatment.
diagram of this system was constructed (Bretz et al 1973), a reproduction of which is displayed in figure (1.4.1). Bearing in mind that the monolayer is completed at \( n = 0.108 \, \text{Å}^{-2} \), where \( n \) is the number of atoms per unit area; the different phases could be mainly classified according to coverage and temperature dependence as follows:

### 1.4.1 The Gas Phase; \( x < 0.5 \) monolayer:

In this region the \(^3\text{He}\) atoms exhibit 2D gas behaviour. The heat capacity measurements (Bretz et al 1973) showed that the specific heat is of the order of Boltzmann’s constant. Except for very low and high coverage, the film displays 2D gas signature for some range of temperature and the atoms are highly mobile. This behaviour was not seen for any other physisorbed system and it has been considered as a proof of the substrate uniformity.

### 1.4.2 The Registered Phase; \( 0.5 < x < 0.66 \) monolayer:

This phase is characterised by its regular adatom arrangement with respect to the substrate lattice. Hence the substrate structure affects the behavior of the film as shown in §4.2.

A series of strong heat capacity peaks around 3 K have been observed by Hickernell et al (1972) and Bretz et al (1973) at this region. These peaks are very sensitive to coverage, but the sensitivity is less with the change of temperature. The peak region of this critical coverage was described by a logarithmic temperature dependence of the specific heat (Bretz et al 1973).

\[
\frac{C}{Nk_B} = -A \ln |t| + B
\]

where \( t = (T - T_c)/T_c \), \( T_c \) is the temperature at the critical density and \( A, B \) are critical parameters, their values were given by (Bretz et al 1973) for different
Figure 1.4.1

Phase Diagram of $^3$He adsorbed on Grafoil as obtained from Heat Capacity Measurements (Bretz et al. 1973)
temperature regions.

These sharp peaks are interpreted (Bretz et al 1973) and (Dash and Schick 1978) as a second-order phase transition from the disordered two dimensional gas phase to an ordered regular lattice in registry with the substrate structure. As the density of atoms is increased above the critical density $N_c$, the specific heat maximum is reduced and occurred at lower temperature as given by Bretz et al (1973) and displayed in figure (1.4.2). These changes were found (Dash and Schick 1978) approximately quadratic functions of the density deviation and obey the following equation:

$$T_{max}(N_c) - T_{max}(N) \propto (N_c - N)^2$$

This transition is dominated by a few parameters (Dash 1975). In order of decreasing importance, the adatom-adatom and adatom-substrate interactions, the number of atoms and the change of temperature.

1.4.3 The Mixed Phase; $0.66 < x < 0.72$ monolayer:

This phase has been predicted as an apparent new phase by Hering, Van Sciver and Vilches (1976). The phase diagram which was investigated by them is shown in figure (1.4.3). They reported that the strongest peak in $^3$He occurs at $n = 0.074 \text{ Å}^{-2}$ with a maximum value of $C/Nk_B = 0.75$ at $T = 1.23$ K. At the lowest temperature, as coverage increases, the specific heat changes from one very similar to the ordered phase to one very similar to a 2D solid and in between there is a range where the specific heat is independent of the number of atoms. This would suggest a form of coexistence of a solid and registered phases. This coexistence was found in the calculations done by Campbell and Schick (1972) as well.
1.4.4. The Solid Phase

For these high densities or coverages, the low-temperature specific heat data were found to be consistent with a solid 3He solid. This result was supported by neutron scattering measurements (Bleckner et al. 1977) which showed a wavevector structure with lattice spacing equal to 3.12 Å. At higher temperatures, specific heat anomalies were observed (Bethe et al. 1974) and (Hering et al. 1976). These anomalies were attributed to solid melting.

Figure 1.4.3

Phase Diagram of $^3$He adsorbed on Grafoil as Constructed by Hering et al. (1976)
1.4.4 **The Solid Phase; 0.72 < \( z \) < 1 monolayer:**

For these high densities coverage, the low temperature specific heat data were found to obey the \( T^2 \) law, which is characteristic of a 2D solid. This result was supported by neutron scattering measurements (Nielsen et al 1977) which showed a triangular lattice structure with lattice spacing equals to 3.32 Å. At higher temperatures specific heat anomalies were observed (Bretz et al 1973) and (Hering et al 1976) These anomalies were attributed to solid melting.

**1.5 Why use NMR?**

NMR is used as a probe to investigate the dynamic properties of the adsorption system. Both continuous wave, *frequency domain NMR*, and pulsed NMR, *time domain NMR*, are widely used. In continuous wave (CW) NMR there are one of two choices; either the external field is kept constant and scanning of the RF is made, or the frequency remains constant while sweeping the external magnetic field. On the other hand, in pulsed NMR, an intense RF pulse at Larmor frequency is applied to the spin system. The frequency of the pulse is kept constant and adjustment of the field strength is made, or the field is kept constant while the frequency is tuned up. However, the resonance condition; \( \Delta E = \hbar \gamma B_0 \) should be satisfied. Where \( \Delta E \) is the energy difference between the energy levels, \( \hbar \) is Plank's constant divided by \( 2\pi \), \( \gamma \) is the gyromagnetic ratio of the adsorbate and \( B_0 \) is the external magnetic field. Hence both frequency and field are kept constant. These two approaches to resonance are Fourier Transform (FT) of each other, and hence, they lead to the same sort of information.

To use any NMR technique; the requirement of an adsorbate which posses a magnetic moment and an adsorber with a large specific area is essential. Hence
$^3$He and grafoil adsorption system is preferably used. Different informations could be gained by using NMR. Knowledge about spin-dependent interactions either adatom-adatom or adatom-substrate interactions are obtained. The activation energy of the atoms may be determined. The correlation time $\tau_c$ of local fields modulation as well as the diffusion coefficient $D$ could give information about the adatoms mobility, so different phases could be distinguished.

$^3$He being a Fermion with a spin half makes NMR studies of its mobility and phase diagram very suitable. The low mass of $^3$He leads to a large zero point energy (Richards 1971) which results in a significant overlapping of the single particle wave function. Hence the quantum effects are very clear and the exchange motion in solid could be studied which is dominant at low temperature.

1.6 Previous Work:

Using NMR as a tool of investigation, experiments on $^3$He film adsorbed on various substrates have been carried out. Zeolite molecular sieve substrates were first used (Careri et al 1965), then followed by porous vycor glass (Brewer et al 1970). Nevertheless, both substrates suffered from inhomogeneity.

With graphitized carbon black as a substrate, Rollefson (1972) has done interesting work at 20.5 MHz using CW technique. He observed broadening in the linewidth at perfect registry, which indicates the slow down of the motion of $^3$He atoms at this region. At $T > 3$ K and $x_{\text{reg.}} > x > x_{\text{reg.}}$, the reduction of the linewidth was interpreted as motional narrowing due to atomic mobility. These results however were not reproduced by any other group.

Several groups have used grafoil as a substrate which has been proved
to be an excellent candidate for NMR experiments. Richards and his group (Cowan 1976), (Owers-Bradley 1978) (Owers-Bradley et al 1978) have made measurements at 1 MHz and 1 K using both CW and pulsed techniques. They observed a small minimum for both $T_1$ and $T_2$ at the density corresponding to registry. While in the solid phase $T_1$ has a minimum and $T_2$ decays as coverage increases to reach a minimum value at complete layer. From the $T_1$ and $T_2$ dependence on temperature they determined the activation energy corresponding to each coverage. On the other hand, pulsed NMR work was done at 10 MHz and 1 K by Sato and Sugawara (1980). In this work, sharp minimum in $T_2$ was observed while there was not a lot of change of $T_1$ with the change of coverage at registry. The activation energy was independent of coverage. Minimum in $T_1$ was observed in the solid phase as well and $T_2$ has its lowest value at one layer completion. The results obtained by both groups were compared with the present work.

1.7 Outline of the work:

This thesis has been divided into six chapters. As it has been shown, chapter (1) is a general introduction for the physisorbed system. A description of the phase diagram of $^3$He adsorbed on grafoil as predicted by heat capacity measurements is done. The reason for the popularity of using NMR to investigate the two dimensional systems is discussed, and why does the $^3$He-grafoil combination is considered as a good example for such study. Then a review of the previous work is given.

Chapter (2) discuss the NMR theory in two dimensional mater; while chapter (3) is devoted to describe the equipment used in the experimental work, the preparation for the run and how the monolayer is determined using
the adsorption isotherm. Different sequences used to determine $T_1$ and $T_2$ are described as well.

Details, analyses and discussion of the experimental data taken at the registered phase and the solid phase are presented in chapter (4) and chapter (5) respectively. Finally, chapter (6) gives a summary for the experimental work discussed previously as well as suggestions for further work.

The NMR phenomenon is caused by the effect of the external magnetic field applied to the experimental samples. The observation of the magnetic field orientation is randomly oriented, while the resonance spin states require solution of the energy levels. If a state resonance line is expected to be in a quantum state with a spin $1/2$, its energy levels are given by the equation: $E = m \cdot g \cdot B / h$, where $g$ is the g-factor, $B$ is the magnetic field, and $h$ is the Planck constant.

If the magnetic field is applied to the sample, the resonance conditions are met. The equation for the magnetic resonance can be written as: $\Delta E = h \cdot \nu$, where $\nu$ is the resonance frequency. The magnetic resonance condition is given by: $\mu_B \cdot H = g \cdot \hbar \cdot \nu / 2 \cdot \mu_B$, where $\mu_B$ is the Bohr magneton, $H$ is the magnetic field, and $\hbar$ is the reduced Planck constant.

It is well known that the condition for the magnetic resonance to occur is the existence of a population difference between the energy levels. Therefore...
CHAPTER 2

ASPECTS OF THE NMR THEORY

2.1 Introduction:

The NMR phenomenon is based on the effect of the external magnetic field applied to the spins system. In the absence of the magnetic field, the spins are randomly oriented, while the application of the field causes splitting of the energy levels. If a static magnetic field $B_0$ is applied to a nucleus with a spin $1/2$, its energy levels split into two sub levels with distribution of the spins governed by Boltzmann law:

$$\frac{N_1}{N_2} = \exp\left(\frac{-\Delta E}{k_B T}\right)$$

where $N_1$ and $N_2$ are the population of each level, and the energy difference between these levels is $\Delta E = \gamma h B_0$. This implies that each spin should adopt one of the two orientations.

If the nucleus has an angular momentum $I$ and magnetic moment $\mu$, it will precess around the field at Larmor frequency $\omega_0 = -\gamma B_0$ where $\gamma = \mu / h I$ is the gyromagnetic ratio which is a characteristic parameter for the nucleus.

If the field is chosen to be in the $z$-direction, in bulk matter the equilibrium magnetization $M_z$ parallel to the field will be given by:

$$M_z = M_0 = \frac{\chi_0}{\mu_0} B_0$$

where $\chi_0$ is the equilibrium magnetic susceptibility.

It is well known that the condition for the magnetic absorption to occur, is the existence of a population difference between the energy levels. Therefore,
to introduce this transition, an oscillating field should be applied to the system. Hence an RF field $B_1$ is applied perpendicular to the steady field $B_0$.

It is helpful if the motion of the magnetization is viewed in a coordinate system $(x', y', z')$ which rotates about $B_0$ in the same direction as the nuclear moments precess and with the same angular frequency $\omega_0$. This rotating frame has its $z'$ axis parallel to the steady field $B_0$ and its $x'$ axis in the same direction as $B_1$. Hence, the field $B_1$ could be thought of as rotating in $x$-$y$ plane with an angular frequency $\omega_0$. As a result, the effect of $B_0$ could be cancelled and after a time $t$ the net magnetization would precess about $B_1$ with an angle $\beta = \gamma B_1 t$.

If this angle is chosen to be $90^\circ$, the magnetization $M_z$ will be tipped to the $x$-$y$ plane. The transverse magnetisation will shrink to zero because of the effect of the inhomogeneity of the magnet. The time constant for this shrinking is $T_2$ and the observed time varying signal is the FID. On the other hand, if the angle $\beta$ is chosen as $180^\circ$, the longitudinal magnetisation will rotate to the $-z$-direction. In this case the magnetisation will relax back to its equilibrium value in time $T_1$.

The theoretical approach to the NMR problems has been done quantum mechanically by different groups such as Bloembergen, Purcell and Pound (1948); Van vleck (1948); Kubo and Tomita (1954) and Cowan (1980).

### 2.2 Quantum Mechanical Approach:

In quantum theory, a system is specified by its Hamiltonian operator. Hence, for an assembly of nuclear spins the general form of the Hamiltonian is given by:

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_d + \mathcal{H}_m$$  \hspace{1cm} (2.2.1)

where $\mathcal{H}_z$ is the Zeeman part which represents the interactions between the
individual magnetic moments and the applied static magnetic field. Since the magnetic energy is given as \((-B_0 \cdot M\)), the Zeeman Hamiltonian can be written in the following form:

\[ \mathcal{H}_z = -B_0 \gamma I_z = \hbar \omega_0 I_z \]

where \(I_z\) is the operator of \(z\)-component of the spin angular momentum of the system.

The Hamiltonian \(\mathcal{H}_d\) represents all the inter-spin interactions, mainly the dipole-dipole interaction which is given as:

\[ \mathcal{H}_d = \hbar^2 \gamma^2 \left( \frac{\mu_0}{4\pi} \right) \sum_{i<j} \left\{ I_i \cdot I_j - 3 \frac{(I_i \cdot r_{ij})(I_j \cdot r_{ij})}{r_{ij}^3} \right\} / r_{ij}^3 \]

where \(I_i\) is the angular momentum operator of the \(i^{th}\) spin and \(r_{ij}\) is the distance between the \(i^{th}\) and the \(j^{th}\) spins. It is convenient for the sake of simplicity; to expand \(\mathcal{H}_d\) into its various spin-flip components (Landesman 1973),

\[ \mathcal{H}_d = \sum_{m=-2}^{2} D_m \]

\[ D_m = \hbar^2 \gamma^2 \left( \frac{\mu_0}{4\pi} \right) \frac{4\pi}{5} \frac{1}{r_{ij}^3} \sum_{i<j} Y_2^{-m}(\Omega_{ij})T_{ij}^m(-1)^m / r_{ij}^3 \]

where \(\Omega_{ij}\) is the direction of \(r_{ij}\), \(Y_2^{-m}\) is a spherical harmonic of the second order and \(T_{ij}^m\) is a tensor spin operator. \(T_{ij}\) is given by:

\[ T_{ij}^0 = I^+_i I^-_j - 3I^+_i I^-_j \]

\[ T_{ij}^1 = (3/2)^{1/2}(I^+_i I^+_j + I^-_i I^-_j) = -(T_{ij}^{-1})^+ \]

\[ T_{ij}^2 = -(3/2)^{1/2} I^+_i I^-_j = (T_{ij}^{-2})^+ \]

The significance of these terms is that, due to the properties of the operators \(I_+\) and \(I_-\), they couple together different eigenstates of \(\mathcal{H}_z\) separated in energy by \(m\hbar \omega_0\). So \(T_{ij}^2\) flips two spins and \(T_{ij}^1\) flips only one spin while the adiabatic
term $T_{ij}^m$ implies that there is no net spin flip and hence the Zeeman energy is conserved.

The use of such spin operator is particularly convenient since they satisfy the following angular momentum commutation relations:

$$[I_z, T_{ij}^m] = m T_{ij}^m$$

$$[I^\pm, T_{ij}^m] = [6 - m(m \pm 1)]^{1/2} T_{ij}^\pm.$$  

Finally, the motion Hamiltonian $\mathcal{H}_m$ generates various motions of the spins and most generally contains their potential and kinetic energies. As a special case, in solid helium-3 the small mass of the atoms results in a large zero point motion and a consequent overlap of the wave functions of nearest neighbour particles (Richards 1971). This results in quantum mechanical tunneling whereby the atoms of the solid are able to exchange places and thus possess a degree of mobility. Pairwise exchange motion is described by the Heisenberg Hamiltonian (Landesman 1973),

$$\mathcal{H}_z = -2 \sum_{i<j} J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j$$

Where $J_{ij}$ is the exchange parameter which is constant for nearest neighbour exchange known as the exchange frequency $J$ and zero otherwise. Such a Hamiltonian generates the exchange of two particles $i$ and $j$ at an (angular) frequency $J_{ij}$. Early treatments of exchange in solid $^3$He was based on such a two particle description of motion. However, particularly as a result of the new ordered phases (Roger et al 1980) it seems that this description is inadequate. Therefore, the hierarchy of multiple exchange motion must be introduced. From energetic considerations (Roger 1984), it appears that three particle exchange is dominant in two dimensional triangular lattice. The Hamiltonian for this
process may be written as,

$$\mathcal{H}_3 = -2 \sum_{i<j<k} J_{ijk} (\mathbf{I}_i \cdot \mathbf{I}_j + \mathbf{I}_j \cdot \mathbf{I}_k + \mathbf{I}_k \cdot \mathbf{I}_i)$$

and thus the three particle exchange Hamiltonian could be written as an effective two particle exchange Hamiltonian (Roger 1984) with different frequency,

$$\mathcal{H}_3 = \mathcal{H}_e$$

$$= -2J \sum_{i<j} \mathbf{I}_i \cdot \mathbf{I}_j$$

where,

$$J = 3J_3$$

for this reason, the simple two particle exchange Hamiltonian will be used in all the following.

2.3 Evaluation of the Relaxation Functions:

If the spin system described by the previous Hamiltonian $\mathcal{H}$ is disturbed; then the evolution of the system is governed by the transverse relaxation function $F(t)$ and the longitudinal relaxation function $L(t)$. To evaluate these functions, the following procedures (Cowan 1987) have been followed.

The magnetization of the spins $M(t)$ is a result of the disturbance of the spins equilibrium state. Appendix A is devoted for the mathematical derivation of such state. The resultant magnetization is given by equations (A3) and (A4) for the transverse magnetization and by equation (A5) for the longitudinal magnetization. The Larmor precession is included in a term such as $\exp i\omega t$ in the transverse magnetization. Therefore to extract this term, it is required to introduce the complex magnetization.

$$m_+ = m_x + im_y$$
and the spin raising and lowering operators

\[ I_+ = I_x + iI_y \]
\[ I_- = I_x - iI_y \]

From equations (A3) and (A4), the transverse magnetization can be written as:

\[ m(t) = \frac{\gamma \beta h^2 \omega_0}{V} \left( \frac{\mu_0}{4\pi} \right) Tr \{ I_+ (t) I_y (0) \} / Tr \{ 1 \} \]

which can be proved (Appendix B) to be as follows:

\[ m(t) = \frac{\gamma \beta h^2 \omega_0}{2V} \left( \frac{\mu_0}{4\pi} \right) Tr \{ I_+ (t) I_- (0) \} / Tr \{ 1 \} \]  \hspace{1cm} (2.3.1)

where \( \beta = 1/K_BT \) and \( V \) is a unit volume of the sample.

The major part of the motion of the transverse magnetization is the Larmor precession. Superimposed on this is the actual relaxation. The following procedures were made to distinguish both terms.

Recall that the total Hamiltonian for the spin system is given by equation (2.2.1),

\[ \mathcal{H} = \mathcal{H}_x + \mathcal{H}_d + \mathcal{H}_m \]

If \( \mathcal{H}_d = 0 \), we are left with the Larmor precession part only as will be shown.

The Heisenberg equation of motion of \( I_+ \) is given by

\[ \frac{d}{dt} I_+ (t) = \frac{i}{\hbar} [\mathcal{H}_x + \mathcal{H}_m , I_+ (t)] \]

Since \( \mathcal{H}_m \) operates in the real space and \( I_+ \) operates in spin space then,

\[ [I_+, \mathcal{H}_m] = 0 \] and the equation of motion becomes,

\[ \frac{d}{dt} I_+ (t) = i\omega[I_x, I_+ (t)] \]

\[ = i\omega I_+ \]

integrating this equation we obtain:
$$I_+(t) = \exp(i\omega_0 t)I_+(0)$$

substituting in equation (2.3.1),

$$m_+(t) = \frac{\gamma \beta \hbar^2 \omega_0}{2V} \left( \frac{\mu_0}{4\pi} \right) \exp(-i\omega_0 t) \text{Tr} \{I_+(0)I_-(0)\} / \text{Tr} \{1\}$$

(2.3.2)

It is clear that the time dependence is contained in the oscillatory factor ($\exp - i\omega_0 t$) only; no relaxation term is included yet.

To introduce the relaxation term we should transfer to the interaction representation where the time evolution is contained in both the operator and the wave function. The operator $U(t) = \exp \frac{i}{\hbar} \mathcal{H} t$, is defined such that the time dependence of $I_+(t)$ could be expressed as:

$$I_+(t) = U(t)I_+(0)U^{-1}(t)$$

Now, $\mathcal{H}_a$ is included to the Hamiltonian, which effect is to give the relaxation part; while $\mathcal{H}_m$ is excluded because there is no lattice motion.

$U(t)$ is factorized such that:

$$U(t) = S(t) \exp - \frac{i}{\hbar} \mathcal{H}_a t$$

and

$$U^+(t) = \exp \frac{i}{\hbar} \mathcal{H}_a tS^+(t)$$

It was found that $(\exp \frac{i}{\hbar} \mathcal{H}_a t)$ represents Larmor precession, hence $S(t)$ represents the decay of the magnetization vector. Therefore equation (2.3.2) could be written as:

$$m_+(t) = \frac{\gamma \beta \hbar^2 \omega_0}{2V} \left( \frac{\mu_0}{4\pi} \right) \exp(-i\omega_0 t) \text{Tr} \{S(t)I_+(0)S^+(t)I_-(0)\} / \text{Tr} \{1\}$$

or

$$m_+(t) = \frac{\gamma \beta \hbar^2 \omega_0}{2V} \left( \frac{\mu_0}{4\pi} \right) \exp(-i\omega_0 t) \text{Tr} \{I_+(t)I_-(0)\} / \text{Tr} \{1\}$$
This relaxation term \([\text{Tr} \{I_+(t)I_-(t)\}]\) represents the decay of the envelope which is observed experimentally. This relaxation term is normalized to unity at zero time. Hence the fundamental transverse relaxation function is obtained as:

\[ F(t) = \text{Tr} \{I_+(t)I_-(0)\} / \{I_+I_-\} \]

Following the same fashion, the fundamental longitudinal relaxation function is given by:

\[ L(t) = \text{Tr} \{I_z(t)I_z(0)\} / \{I_z^2\} \]

Finally the actual transverse and longitudinal magnetization were given as follows:

\[
\begin{align*}
    m_+(t) &= \frac{\gamma \beta \hbar^2 \omega_0}{2V} \frac{\text{Tr} \{I_+(0)I_-(0)\}}{\text{Tr} \{1\}} \exp(-i\omega_0 t) F(t) \\
    m_z(t) &= \frac{\gamma \beta \hbar^2 \omega_0}{2V} \frac{\text{Tr} \{I_z^2(0)\}}{\text{Tr} \{1\}} L(t)
\end{align*}
\]

(2.3.3)

2.4 The Cumulant Approximation:

The normalized FID function in x-direction is given (Abragam 1961) by the spin torque correlation function \(G(t)\). Instead of evaluating \(G(t)\) by using the method of moments or by applying the perturbation theory, the cumulant method (Kubo and Tomita 1954) has been employed. The reason was that; for long-time the expansion diverges unless an infinite number of terms is included, while in cumulant method the high-order terms are approximated in terms of the lower-order ones.

Assuming high temperature limit:

\[ G(t) = \text{Tr}\{I_z(t)I_z(0)\}/\text{Tr} \{I_z^2\} \]

where the time development of \(I_z\) is generated by the coupling Hamiltonian
$\mathcal{H}_1$ which includes both $\mathcal{H}_d$ and $\mathcal{H}_z$,

$$i\dot{I}(t) = [I_z(t), \mathcal{H}_1(t)]$$

hence,

$$G(t) = \text{Tr} \left\{ I_z \exp\left( i \varepsilon \int_0^t \mathcal{H}_1(t) \, dt \right) I_z \left[ \exp\left( i \varepsilon \int_0^t \mathcal{H}_1 \, dt \right) \right]^+ \right\} / \text{Tr} I_z^2$$

(2.4.1)

the expansion parameter $\varepsilon$ has been introduced to keep track of the powers of $\mathcal{H}_1$ in a perturbation expansion.

The function $\Psi(t)$ defined by

$$G(t) = \exp \Psi(t)$$

(2.4.2)

is evaluated in different order of $\varepsilon$. From equations (2.4.1) and (2.4.2) the expression for $\Psi(t)$ (Cowan 1977) is given as follows:

$$\Psi(t, \varepsilon) = \ln \text{Tr} \left\{ I_z \exp\left( i \varepsilon \int_0^t \mathcal{H}_1(\tau) \, d\tau \right) I_z \left[ \exp\left( i \varepsilon \int_0^t \mathcal{H}_1 \, d\tau \right) \right]^+ \right\} / \text{Tr} I_z^2$$

expanding $\Psi(t, \varepsilon)$ in a power series in $\varepsilon$ gives,

$$\Psi(t, \varepsilon) = \Psi(t, 0) + \varepsilon \frac{d}{d\varepsilon} \Psi(t, 0) + \frac{\varepsilon^2}{2} \frac{d^2}{d\varepsilon^2} \Psi(t, 0) + \cdots$$

It has been found (Kubo and Tomita 1954) that expanding to the lowest-order non-vanishing term which is the second order of $\varepsilon$ is sufficient. After ignoring the small imaginary terms (Cowan 1977), the transverse relaxation function took the form,

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

(2.4.3)

and similarly, the longitudinal relaxation function could be written as,
\[ L(t) = \exp \left[ - \int_0^t (t - \tau) \sum_{m=-2}^2 m^2 G_m(\tau) \exp(i m \omega_0 \tau) \, d\tau \right] \quad (2.4.4) \]

One should bear in mind that the spin-torque correlation functions \( G_m(t) \) are the autocorrelation functions of the dipolar Hamiltonian components (Cowan 1980),

\[ G_m(t) = \frac{\text{Tr}(D_m(0) D_{-m}(\tau))}{\text{Tr} I_z^2} \quad (2.4.5) \]

and that the time dependence of the \( D_m \) being generated only by the motion Hamiltonian. In general, in both direct space where \( r_{ij} \) varies and spin space where the spin operator varies, one could write:

\[ G_m(t) = \frac{4 \pi h^2 \gamma^4}{5 N} \left( \frac{\mu_0}{4 \pi} \right)^2 \sum_{i < j \atop k < l} Y_2^{-m}(\Omega_{ij}(0)) Y_2^m(\Omega_{kl}(t)) \frac{r_{ij}^3(0) r_{kl}^3(t)}{r_{ij}(0) r_{kl}(t)} \Gamma_{ijkl}(t) \]

where \( \Gamma_{ijkl}(t) \) is a symmetric four spin correlation function which describes the motion in the spin space and defined as:

\[ \Gamma_{ijkl}(t) = N \frac{\text{Tr}(T_{ij}^{m*}(0) T_{kl}^{-m}(t))}{\text{Tr} I_z^2} \]

Assuming that \( G_m(\tau) \) decays to zero sufficiently fast; the upper limit of the integrals in equations (2.4.3) and (2.4.4) would be extended to infinity (Cowan 1980) leading to exponential relaxation,

\[ L(t) \sim \exp(-t/T_1) \]
\[ F(t) \sim \exp(-t/T_2) \]

where \( T_1 \) and \( T_2 \), the spin-lattice and spin-spin relaxation times are given by,

\[ \frac{1}{T_1} = J_1(\omega_0) + 4 J_2(2\omega_0) \]
\[ \frac{1}{T_2} = \frac{3}{2} J_0(0) + \frac{5}{2} J_1(\omega_0) + J_2(2\omega_0) \quad (2.4.6) \]
where the spectral density functions $J_m(\omega)$ are the Fourier Transform of the correlation functions and given by:

$$J_m(\omega) = \int_{-\infty}^{\infty} G_m(t) \exp(i\omega t) \, dt$$

2.5 Transformation into Two Dimensions:

The long time behaviour of the correlation function depends crucially on the dimensionality ($\sim t^{-d/2}$). In three dimensions, the decay of $G_m(t)$ is sufficiently fast and the previous condition is verified. In case of 2D, this dependence causes some functions to diverge. The non-adiabatic part ($m \neq 0$) will ensure convergence through the oscillating factor $\exp(im\omega_0 t)$. The problem is created from the adiabatic term ($m = 0$) in the transverse relaxation function. Hence there is a need of special treatment for 2D.

Transformation into 2D system and using a reference frame based on the substrate surface, the orientation of the spins is then given by the azimuthal angle in this plane and the $G_m(t)$ functions will take the following form:

$$
G_0(t) = \frac{27}{64} \hbar^2 \gamma^4 \left( \frac{\mu_0}{4\pi} \right)^2 \left\{ \sin^2 \beta \left( \frac{2}{3} \right)^2 g_0(t) + \frac{\sin^4 \beta}{2} g_2(t) \right\}
$$

$$
G_1(t) = \frac{9}{32} \hbar^2 \gamma^4 \left( \frac{\mu_0}{4\pi} \right)^2 \left\{ \cos^2 \beta \sin^2 \beta g_0(t) + \frac{\sin^2 \beta(1 + \cos^2 \beta)}{2} g_2(t) \right\}
$$

$$
G_2(t) = \frac{9}{128} \hbar^2 \gamma^4 \left( \frac{\mu_0}{4\pi} \right)^2 \left\{ \sin^4 \beta g_0(t) + \frac{\cos^4 \beta + 6 \cos^2 \beta + 1}{2} g_2(t) \right\}
$$

(2.5.1)

where the positional correlation functions $g_n(t)$ are given as follows:

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

(2.5.2)
As it has been shown from the previous treatment, the problem of determining the relaxation functions has been reduced to evaluate the functions \( g_0(t) \) and \( g_2(t) \) for specific models for the motion.

### 2.6 Different Models for the Motion:

#### 2.6.1 Diffusion:

In the case of random motion of the spins, the correlation functions \( g_n(t) \) are completely classical. It is extremely difficult to solve equation (2.5.2), so replacing the summation with an integral over a probability function (Cowan 1980) gives:

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

where the probability function is given by,

\[
p(r,t) = \left( \frac{1}{8\pi Dt} \right) \exp\left( -\frac{r^2}{8Dt} \right)
\]

If the motion of the spins could be described by a two dimensional diffusion equation, \( g_n(t) \) are given by (Cowan 1980),

\[
g_n(t) = \frac{2\pi \alpha}{a^4} \int_0^\infty dx \, x^3 \exp\left( -\frac{tx^2}{\tau_c} \right) \frac{J_n(y) \, dy}{y^2} \left[ \int_x^\infty \frac{J_n(y) \, dy}{y^2} \right]^2 \tag{2.6.1}
\]

Bearing in mind that \( p(x/a, t) \) is the spatial Fourier Transform of \( p(r,t) \) and \( \alpha \) is the assumed uniform spin density within a hard core sphere of radius \( a \) while \( \tau_c \) is the time which is taken by the spin to diffuse a distance \( a \) and given as \( \tau_c = \frac{a^2}{2D} \) where \( D \) is the two dimensional diffusion coefficient and \( J_n(y) \) is the \( n^{th} \) order Bessel function.

The above integrals cannot be evaluated analytically as in the case of three dimensions. However, numerical evaluation was performed by Avogadro and Villa (1977) and the reference in their paper. These calculations showed that the decay of \( g_0(t) \) is much slower than that of \( g_2(t) \).
2.6.1a Long-Time Behaviour:

To find the long-time behaviour of the correlation functions; integrating equation (2.6.1) by parts series expansion for $J_n(y)$, then integrate over $x$ term by term. Therefore, the long time decay of $g_n(t)$ is given as,

$$g_0(t) = g(0) \left\{ 2 \frac{\tau_c}{t} - 2\sqrt{\pi} \left( \frac{\tau_c}{t} \right)^{3/2} + 3 \left( \frac{\tau_c}{t} \right)^2 + \cdots \right\}$$

$$g_2(t) = g(0) \left\{ 2 \frac{\tau_c^2}{9 t} - \frac{\sqrt{\pi}}{8} \left( \frac{\tau_c}{t} \right)^{5/2} + \frac{1}{16} \left( \frac{\tau_c}{t} \right)^3 + \cdots \right\}$$

if $t \gg \tau_c$, the leading term will be dominant and hence

$$g_0(t) \sim g(0) \frac{2 \tau_c}{t}$$

$$g_2(t) \sim g(0) \frac{2}{9} \left( \frac{\tau_c}{t} \right)^2$$

(2.6.2)

2.6.1b Short-Time Behaviour:

It is a great difficulty to examine the short-time behaviour of the correlation functions since the diffusion is a hydrodynamic concept which is valid only for long time.

However, with suitable approximations the short-time spatial correlation functions were found (Cowan 1980) as:

$$g_n(t) = g(0) \times 4 \int_0^\infty dx x^3 exp \left[ - \frac{t^2 x^2}{\tau_c \tau_0} \right] \left[ \int_0^\infty \frac{J_n(y) dy}{y^2} \right]^2$$

where $g(0) = \pi \alpha \nu a^4$ and $\tau_0$ is the mean time between atomic collisions.

The transverse relaxation is dominant by the long tail of $g_0(t)$ while the short-time behaviour affects the longitudinal relaxation time in the high frequency/slow motion limit.
2.6.1c Longitudinal Relaxation:

From equation (2.4.6) $T_1$ is given by the following expression:

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

the spectral densities $J_n(\omega_0)$ are the Fourier Transform of the autocorrelation functions $G_n(t)$,

$$J_0(\omega) = \frac{27}{64} \hbar^2 \gamma^4 \left(\frac{\mu_0}{4\pi}\right)^2 \left\{ (\sin^4 \beta - \frac{2}{3})^2 j_0(\omega) + \frac{1}{2} \sin^4 \beta j_2(\omega) \right\}$$

$$J_1(\omega) = \frac{9}{32} \hbar^2 \gamma^4 \left(\frac{\mu_0}{4\pi}\right)^2 \left\{ \cos^2 \beta \sin^2 \beta j_0(\omega) + \frac{1}{2} \sin^4 \beta (1 + \cos^2 \beta) j_2(\omega) \right\}$$

$$J_2(\omega) = \frac{9}{128} \hbar^2 \gamma^4 \left(\frac{\mu_0}{4\pi}\right)^2 \left\{ \sin^4 \beta j_0(\omega) + \frac{1}{2} (\cos^4 \beta + 6 \cos^2 \beta + 1) j_2(\omega) \right\}$$

where the spectral functions $j_n(\omega)$ are the Fourier Transform of the spatial correlation functions $g_n(t)$.

It was found (Cowan 1980) that the $n = 2$ term exhibits normally of being flat for $\omega_0 \tau_c < 1$. While there is the logarithmic divergence of $n = 0$ term which reduces the value of $T_1$ in the low frequency/fast motion limit.

2.6.1d Transverse Relaxation:

It is clear that equation (2.4.3) splits into two parts; the adiabatic part where $m = 0$ and the non-adiabatic part where $m \neq 0$, therefore we can write:

$$F(t) = \exp\left(-t/T_2^{na}\right) \exp\left(-3 \int_0^t (t - \tau) G_0(\tau) \, d\tau\right)$$  \hspace{1cm} (2.6.3)

where the non-adiabatic part is given by,

$$\frac{1}{T_2^{na}} = \frac{5}{2} J_1(\omega_0) + J_2(2\omega_0)$$

This equation looks similar to that of $\frac{1}{T_1}$, so it was treated in a similar fashion to give a relaxation rate,

$$\frac{1}{T} = \frac{81}{256} \hbar^2 \gamma^4 \left(\frac{\mu_0}{4\pi}\right)^2 \sin^4 \beta j_2(0)$$

or by substituting the value of $j_2(0)$
Now the adiabatic part has contributions from both $g_0(t)$ and $g_2(t)$ functions. Since there is no divergence in the integral of $1/t^2$ in $g_2(t)$, the limit of the integral could be extended to infinity and the result is an exponential contribution to the relaxation.

On the other hand, the $g_0(t)$ correlation function gives a non-exponential contribution to the relaxation because it does not decay to zero fast enough. This component of the relaxation function is,

$$f(t) = \exp \left\{ \frac{81}{64} \frac{\hbar^2 \gamma^4}{4\pi} \left( \frac{\mu_0}{4\pi} \right)^2 \left( \sin^2 \beta - \frac{2}{3} \right)^2 \int_0^t (t - \tau) g_0(\tau) d\tau \right\}$$

this function $f(t)$ is the dominant part of the relaxation. Since it is not exponential it can’t be characterised by a relaxation time. Instead, the instantaneous relaxation rate $1/T(t)$ is introduced;

$$\frac{1}{T(t)} = \frac{81}{64} \frac{\hbar^2 \gamma^4}{4\pi} \left( \frac{\mu_0}{4\pi} \right)^2 \left( \sin^2 \beta - \frac{2}{3} \right)^2 \int_0^t g_0(\tau) d\tau$$

Hence, \[
\frac{1}{T_2} = \frac{1}{T(T_2)}
\]

and

$$\frac{1}{T_2} = \frac{81}{64} \frac{\hbar^2 \gamma^4}{4\pi} \left( \frac{\mu_0}{4\pi} \right)^2 \left( \sin^2 \beta - \frac{2}{3} \right)^2 \int_0^{T_2} g_0(\tau) d\tau$$

Now from equations (2.6.4) and (2.6.5), the following definition were made (Cowan 1980),

$$M'_2 = \frac{81}{128} \frac{\pi \alpha \hbar^2 \gamma^4}{a^4} \left( \frac{\mu_0}{4\pi} \right)^2 \left( \sin^2 \beta - \frac{2}{3} \right)^2$$

$$M''_2 = \frac{81}{256} \frac{\pi \alpha \hbar^2 \gamma^4}{a^4} \left( \frac{\mu_0}{4\pi} \right)^2 \sin^4 \beta$$

where the second moment is defined as,
$M_2 = M'_2 + M''_2$

So equation (2.6.4) tends to be

$$\frac{1}{T} = 0.329 M''_2 \tau_c$$

which takes the form of the NMR rule of thumb,

$$\frac{1}{T_2} = M_2 \tau$$

(2.6.6)

where $M_2$ is the second moment which is the mean square value of the local fields multiplied by $\gamma^2$. While $\tau$ is the characteristic time associated with the motion.

To study the general feature of the relaxation (Cowan 1980), $g_0(t)$ could be approximated to:

$$g_0(t) \sim \frac{g(0)}{1 + t/2\tau_c}$$

this analytical expression has the correct value at $t = 0$ and is asymptotically correct at long times. Therefore integrating equation (2.6.5) for the adiabatic part and add the non-adiabatic contribution of equation (2.6.4) to it,

$$\frac{1}{T_2} = 2 \ln(T_2/2\tau_c e) M'_2 \tau_c + 0.329 M''_2 \tau_c$$

the logarithmic dependence in the $n = 0$ part implies the insensitivity to the motion, specially that it is affected only by the internuclear separation and not the orientation.

2.6.2 Exchange:

As mentioned previously §2.2, the Heisenberg exchange Hamiltonian for two particle exchange could be introduced for three particle exchange but with different frequency,

$$\mathcal{H}_x = -2 \sum_{i<j} J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j$$
it is known that this exchange Hamiltonian leads to the same result as the spin diffusion (Cowan 1977) for long time.

The exchange frequency $J_{ij}$ is a constant equals to $J$ for nearest neighbour and zero otherwise. The diffusion coefficient $D$ is related to $J$ through the following equation,

$$D = cJd^2 \quad (2.6.7)$$

where $d$ is the nearest neighbour separation and $c$ is a numerical factor which depends on the lattice structure and the method of calculations. For triangular lattice its value has been estimated to be of the order of unity (Cowan 1980) and calculated exactly (Mullin and Cowan 1989) and was found to be 1.005.

### 2.6.2a Short-time Behaviour:

The general expression of the $g_n(t)$ for motion in spin space, equation (2.5.2) is reduced to the form,

$$g_n(t) = \frac{4}{3N} \sum_{i<j, k<l} \exp \left[ -in(\phi_{ij} - \phi_{kl}) \right] \frac{1}{r_{ij}^3 r_{kl}^3} \Gamma_{ijkl}(t)$$

where the time dependence is included in the symmetric four-spin correlation functions $\Gamma_{ijkl}(t)$ only.

For short-time the behaviour of $g_n(t)$ could be described by an expansion of $g_n(t)$ in powers of $t$. Bearing in mind that the odd powers vanish and excluding the term $i = j$, the derivatives of $g_n(t)$ for $t = 0$ are given as:

$$g_n^{(m)}(0) = \frac{4}{3N} \sum_{i<j, k<l} \exp \left[ -in(\phi_{ij} - \phi_{kl}) \right] \frac{1}{r_{ij}^3 r_{kl}^3} \Gamma_{ijkl}(0) \quad (2.6.8)$$

First term gives,

$$g(0) = \sum_{i \neq j} r_{ij}^{-6} \quad (2.6.9a)$$
which is for triangular lattice with spacing $d$ (Cowan 1980) equals to

$$g(0) = 6.36 \, d^{-6} \quad (2.6.9b)$$

Evaluating the second coefficient of $g_n(t)$ from equation (2.6.8); the lattice sums may be evaluated for nearest-neighbour exchange and the expression for short-time is given as,

$$\frac{g_0(t)}{g(0)} = 1 - 6 \, J^2 \, t^2 \cdots \quad (2.6.2a)$$

$$\frac{g_2(t)}{g(0)} = 1 - 12.5 \, J^2 \, t^2 \cdots \quad (2.6.2b)$$

2.6.2b Long-time Behaviour:

Long-time spin diffusion leads to equation (2.6.2). The diffusion time $\tau_c$ is of the same order as the exchange time $1/J$. From the relation $\tau_c = a^2 / 2D$ and equation (2.6.7) we find,

$$\tau_c = \frac{1}{J} \times \frac{a^2}{2cd^2} \quad (2.6.10)$$

equating equation (2.6.9a) and equation (2.6.9b) and changing the summation into integral

$$6.36 \, d^{-6} = \alpha \int_a^\infty \frac{2\pi r \, dr}{r^6}$$

substituting the value of $\alpha$ for triangular lattice $\alpha = 2/\sqrt{3} \, d^2$. The hard core $a$ (the smallest distance the spin can diffuse) is related to the nearest neighbour distance $d$ (the distance between two exchange spins) by the expression,

$$a = 0.7308 \, d$$

Hence by substituting in equation (2.6.10), we concluded that:

$$\tau_c = \frac{0.267}{J} \quad (2.6.11)$$
Therefore for Heisenberg exchange, the long-time behaviour of the correlation functions is given by:

\[
\frac{g_0(t)}{g(0)} \sim \frac{1}{1.87 J t} \\
\frac{g_2(t)}{g(0)} \sim \frac{1}{63 J^2 t^2}
\]

2.6.2c The Interpolation Procedure:

In case of two dimensions; since the tail of the correlation function goes as \(1/t\), any approximation procedures for \(G(t)\) should respect both short-time and long-time behaviour. Hence, to join these two behaviours, interpolation was made and different formulae were used. The following form of correlation functions were established by Cowan (1980),

\[
\begin{align*}
\frac{g_0(t)}{g(0)} &= \frac{P(1 + 2aJt)}{(1 + aJt)^2} + Q \exp(-bJ^2 t^2) \\
\frac{g_2(t)}{g(0)} &= \frac{P}{(1 + J^2 t^2)} + Q \exp(-bJ^2 t^2)
\end{align*}
\]

(2.6.12)

where the values of the constants for both \(n = 0\) and \(n = 2\) are,

\[
P = 0.3338 \\
Q = 0.6662 \\
b = 8.2255
\]

and \(a = 1.2485\) for \(n = 0\), while \(a = 21.03\) for \(n = 2\).

A better choice was made (Cowan et al 1987a) and the correlation functions are expressed as:

\[
\begin{align*}
\frac{g_0(t)}{g(0)} &= \frac{P_0}{[1 + a_0^2 t^2/\tau^2]^{1/2}} + \frac{Q_0}{[1 + b_0^2 t^2/\tau^2]} \\
\frac{g_2(t)}{g(0)} &= \frac{P_2}{[1 + a_2^2 t^2/\tau^2]} 
\end{align*}
\]

(2.6.13)
where the constants have the following values:

\[\begin{align*}
P_0 &= 0.524 & P_2 &= 1.0 \\
a_0 &= 0.262 & a_2 &= 0.944 \\
b_0 &= 0.928 & Q_0 &= 0.476
\end{align*}\]

where \(\tau\) is the correlation time which measure the speed of the motion.

When the correlation functions of both choice are expanded, they contain the term \((J^2 t^2)\) which is of the same order as in the calculated short time expansion. On the other hand, the linear term does not exist in the short time expansion; so the correlation functions (Cowan et al 1987) which do not contain the linear term as well, give powerful results when they are used in the analyses.

To evaluate \(T_1\) and \(T_2\), the Fourier Transform of \(g_0(t)\) and \(g_2(t)\) namely \(j_0(\omega)\) and \(j_2(\omega)\) should be determined. Similar to diffusion, the \(n = 2\) term exhibits normal behaviour while the \(n = 0\) function diverges at low frequency.

### 2.6.2d Longitudinal Relaxation:

Except of using the expressions of \(j_n(\omega)\) for exchange; the treatment of the longitudinal relaxation followed the same procedures as diffusion. Since the short-time behaviour of the correlation functions is considered, \(T_1\) at the minimum and above the minimum (high frequency) could be determined, so the whole frequency range could be covered.

Using the correlation functions equation (2.6.12), \(T_1\) was inspected at different angles and a plot of \(1/T_1\) as a function of exchange frequency \(J\) at constant Larmor frequency is demonstrated in figure (2.6.1). The behaviour at angle of orientation \(\beta = 0\) was seen to be normal because the contribution comes from \(j_2(2\omega)\) only (the non-zero term). By increasing \(\beta\) to 45 and 90 degrees, the \(j_2(\omega)\) term will also takes part and \(T_1\) is no longer flat at low frequency.
Theoretical Plot of the Spin-Lattice Relaxation Time as a Function of Exchange Frequency for Different Orientations (Cowan 1980).
It is great advantage to be able to observe $T_1$ at the minimum. The reason is that; at minimum the value of $J$ is approximately equals to the Larmor frequency, so $J$ could be determined. Another reason is that, since the value of $T_1$ at minima is nearly equals to the second moment $M_2$ divided by Larmor frequency (Cowan 1980) and the calculations of $M_2$ is straightforward ($M_2 \propto \frac{1}{\delta}$), it is possible to check whether the dipolar interaction is responsible for the relaxation. For the above reasons, the value of $T_1$ at minimum has been used to analyze some of the experimental data.

2.6.2e Transverse Relaxation:

Following the same fashion as diffusion and using the exchange formula of $g_n(t)$ equation (2.6.12),

$$\int_0^T \frac{g_0(t)}{g(0)} dt \simeq \frac{0.535}{J} \ln[1.11 JT]$$

$$\int_0^\infty \frac{g_2(t)}{g(0)} dt \simeq \frac{0.320}{J}$$

and by applying suitable approximations (Cowan 1980), the complete expression for $T_2$ is given as:

$$\frac{1}{T_2} = 0.535 \frac{M_2'}{M} \ln \frac{J^2}{4M_2'} + 0.93 \frac{M_2''}{J} + \frac{5}{2} J_1(\omega_0) + J_2(2\omega_0)$$

The first two terms can be calculated from the experimental details while the last two terms (the non-adiabatic part) are calculated in a similar way to the calculation of $T_1$ but with different coefficients.

2.7 Relaxation due to Grafoil platelets:

Besides the dipolar interactions, there is another mechanism for spin relaxation in the $^3$He adsorbed on grafoil system which results from the
anisotropic diamagnetism of the graphite surface. Because of the application of the steady magnetic field $B_0$, each graphite platelet will have a certain induced magnetisation. This magnetisation, in turn, produces a small magnetic field normal to the platelet surface. Motion of the helium spins in this spatially varying field is another mechanism for the relaxation.

Robertson (1966) has considered a model for relaxation through bounded diffusion. In this model, the field gradient is assumed to be constant but alternating in sign with a period $a$. In this case the transverse relaxation time is given by:

$$ \frac{1}{T_{2}^{\exp.}} = \frac{1}{T_{2}^{\text{dip.}}} + \frac{a^4 \gamma^2 G^2}{120 D} $$

where $T_{2}^{\exp.}$ is the observed transverse relaxation time and $T_{2}^{\text{dip.}}$ is the relaxation due to the dipolar motion. The last term is the relaxation due to the grafoil local fields gradient, where $D$ is the diffusion coefficient and $a$ would be the typical platelet length.

A more realistic model of the local field spatial variation is a sinusoidal curve, which has been treated by Cowan (1976). The relaxation due to this mechanism is similar to that found by Robertson, but with a different numerical coefficient. This similarity is an evidence that any model for relaxation through motion in spatially varying fields will yield a transverse relaxation rate of the form:

$$ \frac{1}{T_2} \sim \langle \omega_{loc}^2 \rangle \sim T_c $$

where $T_c$ is the time for a spin to diffuse across a platelet and $\gamma^2 \langle \omega_{loc}^2 \rangle$ is a measure of the mean square of the associated fields.

It is clear that these two models imply a transverse relaxation rate proportional to square of the applied magnetic field (or the Larmor frequency). However, all experimental data clearly indicate a linear variation of $1/T_2$ with
ω₀. This is still a major unsolved problem in interpreting the relaxation data in the fluid phase of ³He adsorbed on grafoil.

APPARATUS AND EXPERIMENTAL TECHNIQUES

(i) THE APPARATUS

3.1 The Cryostat

The cryostat used in this work was built in the college’s physics workshops. It was designed to support an Oxford Instruments 7 mK dilution refrigerator. A schematic diagram of the cryostat is displayed in figure (3.1.1).

It has a copper 0.5 litre ⁴He pot. A large vacuum can inner vacuum can (IVC) is bolted directly to the pot and sealed with an o-rubber O-ring. This can contains the sample chamber and the exchange gas. Surrounding the ⁴He pot and the IVC there is another large can which is the outer vacuum can (OVC).

The OVC was evacuated to rather low pressure (~ 10⁻² Torr) to maintain thermal isolation between the pot and ⁴He bath. The IVC was filled with low pressure (~ 1 Torr) exchange ⁴He gas to thermally anchor the ⁴He pot with the sample chamber. To achieve the required temperature, the pot was filled with ⁴He from the bath through a needle valve to reach 4.2 K, then pumped with a large rotary pump (Edward Lee 4810B) to reduce the temperature.

The ³He bath is contained within a special dewar which has super insulation and a nitrogen jacket. The cryostat service lines are of thin walled stainless steel tubing to minimize thermal conduction.
CHAPTER 3

APPARATUS AND EXPERIMENTAL TECHNIQUES

(i) THE APPARATUS

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It has a copper 0.5 litre $^4$He pot. A large vacuum can inner vacuum can (IVC) is bolted directly to the pot and sealed with an indium "O-ring". This can contains the sample chamber and the exchange gas. Surrounding the $^4$He pot and the IVC there is another large can which is the outer vacuum can (OVC).

The OVC was evacuated to rather low pressure ($\sim 10^{-5}$ Torr) to maintain thermal isolation between the pot and $^4$He bath. The IVC was filled with low pressure ($\sim 1$ Torr) exchange $^4$He gas to thermally anchor the $^4$He pot with the sample chamber. To achieve the required temperature, the pot was filled with $^4$He from the bath through a needle valve to reach $4.2$ K, then pumped with a large rotary pump (Edward 1sc 450B) to reduce the temperature.

The $^4$He bath is contained within a special dewar which has super insulation and a nitrogen jacket. The cryostat service lines are of thin walled stainless steel tubing to minimize thermal conduction.
Figure 3.1.1

Schematic Diagram of the Cryostat
3.2 Sample Chamber:

The sample chamber used is of cylindrical shape, 2.5 cm long and 2.5 cm diameter. It was machined from a block of stycast 1266, and the lid was glued to the chamber with stycast 1266 as well.

For better thermal contact with the sample, a 470 Ω speer resistor was mounted on the inside of the lid to be used for monitoring the temperature.

As mentioned in §1.3, the grafoil should be heated to high temperature in vacuum before use to eliminate water vapor and impurities. Hence, the grafoil used was baked in vacuum at 1000° C for ~ 8 hours before fixing it into the chamber. A single strip of grafoil of 0.4 mm thick and 8.53 gm weight; was folded into concertina to fit in the chamber. Sheets of mylar film were introduced between each layer of the grafoil concertina to reduce the eddy current induced by the NMR coil and RF pulses, which cause heating of the grafoil and reduction of the Q-factor of the coil.

A four turn spiral of $\frac{1}{16}$ inch diameter thin walled stainless steel tube was used for a filling line, it has been sealed into the chamber which was sufficient for the rotation of the chamber between 0° and 90° without damaging the seal.

This was all done in a glove bag with $^4$He atmosphere to avoid recontamination. Leak testing was done and the sample chamber was connected to a high vacuum system for few days before mounting in the cryostat.

3.3 The Rotation Mechanism:

The anisotropy of nuclear magnetic relaxation due to different orientation of the substrate planes with the magnetic field has been studied. It was desirable to rotate the sample chamber without opening the cryostat. For this reason, a home made rotating mechanism which is shown in figure (3.3.1) has been
The Rotating Mechanism shows; a) The Position Sensor, b) The Bevel Driver Gears and the Filling Line.
constructed to support and rotate the sample chamber.

The rotating mechanism consists of bevel gears to change the drive axis from vertical to horizontal direction. To indicate the substrate orientation, a disc of paxolin printed circuit board is fitted to the end of sample chamber. This board is etched to leave a set of radially distributed gold plated copper pads electrically connected. Two metal film resistors were fixed to the board; a 1 kΩ resistor is fixed before the zero angle indicator, while a resistor of 500 Ω was fixed after the location of the 90° angle to simplify the detection. Between zero and 90, angles could be varied in steps of 9 degrees. This was obtained by monitoring the conducting position corresponding to zero ohm and the following non-conducting position with ∞ ohm using an ohm meter. Hence a precise orientation angle could be obtained by starting the rotation from 90° anticlockwise. Guide values for the angles with the corresponding resistors is displayed in table (3.3.1).

3.4 The Temperature Regulation System:

At the start of each run, the calibration of thermometers was performed. Oil manometer, Mercury manometer and Wallace & Tiernan capsule gauge were used to calibrate the Speer (SP) and Allen Bradley (AB) resistors which are attached to different places in the cryostat with thermally anchor leads.

The manometers and the gauge measure the 4He vapor pressure in the pot, then temperature was determined numerically using the T54 temperature scale (Rusby 1985).

A 47 Ω Allen Bradley resistor was used to measure the pot's temperature over the range of 2 to 20 K, where its change with temperature is rapid and the accuracy is ±0.5%. For the same reason a 470 Ω Speer resistor was used for
<table>
<thead>
<tr>
<th>Angle (deg.)</th>
<th>Resistance (Ω)</th>
</tr>
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<tr>
<td>&gt; 99</td>
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<tr>
<td>99</td>
<td>∞</td>
</tr>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>&lt; 0</td>
<td>1000</td>
</tr>
</tbody>
</table>

**Table (3.3.1)**

Angles of the substrate orientation with the corresponding resistances.
temperatures below 2 K.

The following formulae were used for computing temperatures in the range above 2 K (Hoare et al 1961) and below 2 K (Rose-Innes 1973) respectively.

\[
\frac{1}{T} = a_2 (\log_{10} R)^{-1} + b_2 + c_2 (\log_{10} R) \tag{3.4.1}
\]

\[
\log_{10} T = a_1 (\log_{10} R)^{-1} + b_1 + c_1 (\log_{10} R) \tag{3.4.2}
\]

The resistances values as a function of temperatures were fitted to the above equations using the method of least squares. The constants were computed and found to be:

\[
a_1 = 6.3641 \quad a_2 = 0.5029
\]

\[
b_1 = -46.2145 \quad b_2 = -1.4984
\]

\[
c_1 = 83.4158 \quad c_2 = 1.0985
\]

Temperatures between 1.1 K and 4.2 K were controlled by regulating the \(^4\)He pot pumping rate with a needle valve and a solenoid valve. On the other hand, temperatures above 4.2 K were obtained by using a power supply driving a heater resistance attached to the \(^4\)He pot, where a small voltage of about 2 V was enough to raise the temperature of the pot to the required value, provided that the pot is completely empty. A microcomputer unit (RML_380Z) was used to control the temperature during either cooling down or warming up the pot. The computed temperature was written via the interface unit to a digital display mounted in the resistor selector unit adjacent to the SHE conductance bridge/Model PCB.
3.5 The Gas Handling System:

The basic function of the gas handling system is to admit a measured amount of $^3$He gas into the sample chamber. It also enables the vapor pressure of the adsorbed gas to be measured on a Druck gauge for the isotherm measurements.

A block diagram of the gas handling system has been drawn in figure (3.5.1). The $^3$He gas is kept in a special cylinder. The Druck digital pressure indicator was used for measuring the gas pressure through the needle valve with resolution of 0.0001 bar. There are two Druck gauge heads, head 1 is connected to the store of $^3$He gas to enable reading the pressure of the gas inside. While head 2 is attached to the sample line to monitor the pressure in the sample chamber. A charcoal trap in a nitrogen bath (77 K) was connected to the system to clean the sample when it passes through it.

3.6 The NMR Magnet:

The NMR magnet consists of three parts. First, is the main solenoid which provides the static magnetic field $B_0$. The solenoid, a superconducting magnet works in persistent mode, so it is immersed in liquid helium at 4 K. It produces a field up to two Tesla at a current of 50 amp.

Second part is the $Z_1$ shim coil which operates in the persistent mode as well. This coil was provided to improve the inhomogeneity of the main magnet or to narrow the echo when the motion of the spins slow down. The third part of the magnet is a pair of helmholtz coils which are not working in the persistent mode. They are used to provide a field gradient or shift, but they were not used through this work.

A current regulated power supply was used to energise the magnet. It
Figure 3.5.1

The Sample Gas Handling System.
has a heater supply for the main coil and the shim. Using this power supply it was easy to change the current of the main coil according to the chosen Larmor frequency. From the calibration made at the beginning of the run; it has been found that 3.925 amp. was suitable to obtain resonance at 5.0477 MHz.

3.7 The NMR Probe:

The probe comprising the NMR coil and associated tuning and matching components is the central part of the NMR equipments. To maximize the signal to noise ratio of the received signal, the coil must be well designed of high Q and the losses in the probe circuits kept to a minimum.

When a single NMR coil is used, a duplexer is required to protect the input of the pre-amplifier from the high voltage transmitter pulse and to isolate the transmitter during receiving periods. A form of Q switching is also required, so that during and after transmitter periods the Q of the NMR coil is low to reduce ring-down time. Nevertheless, during receiving periods Q must be high for maximum sensitivity.

The probe circuit which is illustrated (Kent 1985) in figure (3.7.1) satisfies these requirements. The circuit includes elements for matching the probe impedance to the transmitter and pre-amplifier. The main advantage of the probe circuit that it is broadband, so changing the resonance frequency was not a great problem.

The NMR coil consists of 14 turns of enamelled copper wire. The wire (in form of 7 strands) were wound onto a tufnol bobbin which was fitted around the sample chamber. Its inductance is 7.8 \( \mu \)H and the Q factor at room temperature is 28 while the natural frequency is \( \sim 5 \) MHz. However, it was possible to obtain higher frequencies by connecting an extra inductance to point A figure
Figure 3.7.1

Circuit of the Matching and Tuning Unit and the Equivalent Circuit of NMR Probe.
(3.7.1), while lower frequencies could be achieved by the connection of a suitable capacitance. Thus the frequency has been changed between 1.3 and 10.2 MHz.

3.8 The NMR Spectrometer:

The NMR spectrometer can be divided into two main parts. First is the pulse transmitter to prepare the magnetisation for measurements. Second is the receiver which amplifies and detects the small voltage induced in the single NMR coil by the precessing magnetization. In general, these two parts work as follows:

3.8.1 The Pulsed Transmitter:

1) The required sequence of pulses of particular width and delay (e.g. 90° or 180° pulse) is set on the pulse generator which gives a series of rectangular TTL sequence d.c. pulses.

2) This sequence together with the RF at Larmor frequency coming from the master oscillator, is fed into the RF gate which produces RF modulated pulses of the same width and separation.

3) The gated RF is amplified by the transmitter from a few volts to hundreds of volts and is fed into the NMR coil through the RF line.

4) This sequence creates the $B_1$ field which interacts with the magnetization to induce a signal in the coil which comes back through the RF line to be amplified and detected by the receiver.

3.8.2 The Receiver:

1) Some time later after the performance of the first stage, the tiny voltage induced in the coil (of the order of $\mu$ V ) is amplified by the pre-amplifier.
2) The resultant RF signal goes to the mixer to be multiplied by the steady reference RF voltage with Larmor frequency produced by the master oscillator. Hence sum and difference frequencies were introduced in the output.

3) The two parts go to the audio frequency amplifier which has variable range of gain and bandwidth. The gain amplifies the "difference" part and the FID is obtained. On the other hand the low pass filter eliminates the "sum" part which is of high frequency (2ω).

4) The last stage is to average this AF signal as many times as required. Then the signal is displayed on the oscilloscope.

3.8.3 The Essential Requirements of a Pulsed NMR Spectrometer:

The minimum requirements of pulsed NMR spectrometer could be summarized (Farrar and Becker 1971) as follows:

1) The transmitter should be able to produce pulses of hundreds of volts to ensure that the $B_1$ field is greater than the inhomogeneity of the static field $B_0$, i.e. $B_1 \gg \Delta B_0$. This condition is important for all the spins to rotate with the same angle.

2) After switching off the RF pulse its power must be quickly dissipated and the receiver must recover as soon as possible. Hence low Q is needed at the end of the pulse.

3) In conflict with condition (3), the tank circuit must have as high Q as possible in the receiving mode for best signal to noise performance.

4) The receiver must be protected from the large RF pulses.

5) The sample must be efficiently coupled to the receiver to obtain maximum $S/N$ from the nuclear induction signal.

6) The receiver and the transmitter should be well isolated from one another,
in order to achieve minimum overload conditions and faster recovery time.
7) The pulse generator must have a very stable time base and allow for precise setting of all time intervals.
8) The master oscillator must have a very stable frequency.
9) The $B_1$ and the $B_0$ fields must be homogeneous as possible over the sample volume to insure that all spins will precess with the same frequency.
10) There should not be any radiation of the RF energy at the resonance frequency in the laboratory.

3.9 Details of the Spectrometer Used:

A block diagram of the pulsed NMR spectrometer used in this work is illustrated in figure (3.9.1). To achieve the essential conditions required of the pulsed spectrometer, our home made spectrometer was built which worked satisfactorily.

To deal with condition (1); the transmitter circuits used the TTL pulses to gate the RF pulses at Larmor frequency. These pulses were then amplified up to power of 1 kW before passing to the NMR coil.

The power amplifier delivers peak pulse amplitude of up to 250 V into 50 $\Omega$ load. The circuit is different of the usual ones by having the output transformer untuned which results in a broad band transmitter. This allows the easy change of Larmor frequency.

The pulsed NMR receiver has a high sensitivity and signal to noise ratio. The dead time, which is the time taken to recover full signal sensitivity following a transmitter pulse, is less than the time taken for the probe voltage to ring down to the noise level which satisfies condition (2).

Conditions (3) and (4) were achieved by special design of the NMR probe
Figure 3.9.1
Schematic Diagram of the Pulsed NMR Spectrometer.
as mentioned before §3.7. On the other hand, to satisfy condition (5) the preamplifier is mounted on the top of the cryostat to avoid using coaxial lines for carrying small signals.

In order to prevent overloading of the synthesizer output and to ensure that the transmit and receive sections are fully isolated, i.e., to verify condition (6), a buffer/isolator providing four independent 50 $\Omega$ outputs from one 50 $\Omega$ input has been constructed. It also includes a detector and voltage comparator stage, which enables the output to be set precisely to the optimum level (1 V pk-pk) for the other circuits.

The phase shifter can be inserted between the RF source and the gate, or between the RF source and the mixer. It enables the RF reference and signal inputs to the mixer to be in phase.

The pulse programmer used was a digitized pulse sequence generator built in the laboratory (Kent 1985). It generates up to four pulses with different length and delay. The pulse width could be varied from 1 $\mu$Sec to 9900 $\mu$Sec in 1 $\mu$Sec steps. The delay could be varied between 10 $\mu$Sec and 9900 mSec in steps of 10 $\mu$Sec. It is possible to vary the repetition time as well in steps of 100 $\mu$Sec starts from minimum value at 100 $\mu$Sec with maximum of 9900 mSec. The pulse sequence could be operated in a cyclic mode or manually controlled by single shot mode, so condition (7) was fulfilled.

The master oscillator used is 5600 Rockland Frequency Synthesizer with excellent stability and low noise which satisfies condition (8). The minimum frequency is 0.1 MHz and the maximum frequency available is 160 MHz. The main magnet homogeneity as claimed from Oxford Instruments is one part per $10^5$ over one inch cube of the solenoid and we did our best to avoid having any radiation of the same RF near by the cryostat, so the last two conditions were
verified.

By using our home made signal averager it was possible to detect the weak signals at very low coverage, high temperature and from both low and high frequencies. The signal was averaged as much as it is needed with maximum of 2048 times.

The last stage of detecting the signal was to display it on the Digital Storage Oscilloscope (Gould 054100) where it becomes ready for measurements.
(ii) REVIEW ON THE EXPERIMENTAL TECHNIQUES

3.10.1 Introduction:

In this part, a short note will be given about the preparation usually made before starting the run, how the monolayer capacity is determined by the adsorption isotherm and then how the sample is admitted to the chamber. Finally, the methods which were used to determine the relaxation times $T_1$ and $T_2$ are explained.

3.10.2 Preparation for the Run:

After closing the cryostat up; the dewar, the IVC and the OVC must be evacuated. Then the sample chamber was pumped out as well. While the needle valve is closed the $^4$He pot was evacuated using its own rotary pump. All these were done at room temperature. $^4$He exchange gas of 1 Torr pressure was admitted to both vacuum cans.

When the system reached suitable vacuum $\approx 10^{-5}$ Torr, pre-cooling to 77 K was begun. This was done by filling the nitrogen jacket and the $^4$He bath by liquid nitrogen. After 24 hours the nitrogen was blown out from the helium bath using a current of $^4$He gas. The first $^4$He transfer then starts using about 25 litres to cool the system to 4.2 K. The temperature of the system was recorded at room temperature, nitrogen temperature and helium temperature to calibrate the thermometers, these values are shown in table (3.10.1) for a specific run. After temperature stabilization, the $^4$He exchange gas was removed from the OVC. During the run, automatic transfer of nitrogen was done every night while nearly 14 litres of $^4$He was transferred every other day to keep the cryostat at 4.2 K.
<table>
<thead>
<tr>
<th>Position of resistors</th>
<th>Cond. at Room Temp.</th>
<th>Cond. at N₂ Temp.</th>
<th>Cond. at ⁴He Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top Baffle</td>
<td>3.549</td>
<td>3.138</td>
<td>2.578</td>
</tr>
<tr>
<td>Middle Baffle</td>
<td>3.677</td>
<td>2.895</td>
<td>1.369</td>
</tr>
<tr>
<td>Bottom Baffle</td>
<td>9.346</td>
<td>7.850</td>
<td>2.849</td>
</tr>
<tr>
<td>Flange</td>
<td>17.766</td>
<td>16.326</td>
<td>2.402</td>
</tr>
<tr>
<td>Pot (SP)</td>
<td>1.934</td>
<td>1.663</td>
<td>1.017</td>
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<tr>
<td>Pot (AB)</td>
<td>17.187</td>
<td>15.918</td>
<td>3.415</td>
</tr>
<tr>
<td>Sample Chamber</td>
<td>1.973</td>
<td>1.752</td>
<td>1.028</td>
</tr>
<tr>
<td>Magnet (Top)</td>
<td>4.092</td>
<td>3.245</td>
<td>0.264</td>
</tr>
<tr>
<td>Magnet (Bottom)</td>
<td>4.055</td>
<td>3.273</td>
<td>0.268</td>
</tr>
</tbody>
</table>

Table 3.10.1

Typical values of Conductance (mho) Sensors at Room Temperature, Nitrogen Temperature and Helium Temperature.
3.10.3 Adsorption Isotherm:

For a uniform surface with a number \( N_s \) of equivalent adsorption sites, the ratio of the number of adsorbed atoms \( N \) to \( N_s \) is defined as coverage, \( x = N/N_s \) (Somorjai 1981). At the same time \( x = V/V_m \) where \( V \) is the volume of the \(^3\text{He}\) admitted gas at STP and \( V_m \) is the volume of monolayer capacity (STP). The monolayer completion \( (x = 1) \) could be determined by calibrating a certain volume of \(^3\text{He}\) gas (which is admitted to the sample chamber) with its vapor pressure at 4.2 K.

According to (Bretz et al 1973), point A or point B criterion is used to determine the volume of \(^3\text{He}\) gas corresponding to a complete monolayer. Point A is the extrapolation of the linear region pressure to zero pressure. While point B is approximately the point where the pressure changes from very low value to the linear region of low pressure points above them. Using point B criterion, it was found experimentally that the volume of \(^3\text{He}\) gas corresponding to monolayer completion equals to 59.5 cc STP as shown in figure (3.10.1).

3.10.4 Admittance of The Sample:

A store of volume 18.83 cm\(^3\) was filled with the sample which is pure \(^3\text{He}\) gas through the needle valves 1 and 2 as illustrated in figure (3.5.1). The initial pressure of the store was read from the Druck gauge through the head (1). The sample volume \( V \) measured in (cc @ STP) is combined with pressure by the following equation (Kay and Laby 1975).

\[
V = \frac{18.83 \Delta P}{1013.25(1 + 0.00367 T)}
\]  

(3.10.1)

Where \( \Delta P = P_{\text{final}} - P_{\text{initial}} \) is the change of the pressure of the store in mbars. \( T \) in degree Celsius is the store temperature which equals to room temperature.
4.2 K isotherm for He-3 adsorbed on grafoil
Bearing in mind that one layer completion is equivalent to 59.5 cc STP of the gas as determined from the adsorption isotherm in the previous section; the volume of gas corresponding to the required coverage could be determined. Hence the final pressure of the store was computed using equation (3.10.1) in a simple computer program.

Admittance of the gas from the store to the sample chamber was done very carefully through the needle valve and valves 3 and 4 figure (3.5.1) in successive steps. The gas was passed into a charcoal trap at 77 K to remove any air contamination from it. The final pressure was then read through the Druck gauge 2 to ensure that the required amount of gas is already admitted. For the same reason the sample chamber was kept at the lowest possible temperature (1 K).

The sample was annealed by heating the sample chamber to 15 K to make sure that the adsorbed gas was spread uniformly on the grafoil surface. The sample was left to cool gradually to 4.2 K; then proceedings for adjustment of the working temperature was started.

3.11 Data Acquisition:

Any spin system exists in equilibrium state, to take relaxation measurements one should disturb this equilibrium and prepare the magnetization for measurements in the transverse plane. This is because the axis of the NMR coil is lying along the transverse plane and so the longitudinal magnetization has no effect.

3.11.1 $T_1$ and $T_2$ Measurements:

The spin-lattice relaxation time is the time which the spins take to
reach equilibrium with the environment by transferring energy to the lattice. To measure this time, the saturation recovery method (90-90 sequence) was used. The first pulse disturbs the spins while the second pulse measures the magnetization after a waiting period by observing the size $M(t)$ of the FID. Hence the recovery of the nuclear spin population is monitored as a function of time.

The use of the 90-90 pulse sequence is preferable over the use of the usual 180-90 sequence. The reason is that (Fukushima and Roeder 1981) the $z$-component of the magnetisation is reduced to zero after any $\pi/2$ pulse regardless of the state of the magnetisation before the pulse, so no need for long waiting period between the pulse pairs.

Ideally, the magnetization after waiting for a time $t$ is given by:

$$M(t) = M_0 \left[1 - \exp\left(-\frac{t}{T_1}\right)\right]$$

where $M(t)$ is the magnetisation at time $t$ and $M_0$ is the equilibrium magnetisation. Practically, the inaccuracies in the 90° pulse length and the inhomogeneity of the NMR coil result in $M(t)$ does not equal exactly to zero at $t = 0$. Therefore, a small correction is made by using the following equation:

$$M(t) = M_0 [1 - \alpha \exp\left(-\frac{t}{T_1}\right)]$$

where $\alpha$ is the correction parameter which ideally equals to one.

The spin-spin relaxation time $T_2$ is intrinsic relaxation time, i.e. it is the time which the spins take to relax among themselves without any change in their energy. Two methods were employed to determine $T_2$ depending on its value.

At very high coverage it was difficult to observe the echo because $T_2$ was short due to the slowing down of the motion ($\sim 500 \mu S$), which is comparable
to the instrumental dead time. Therefore, the method of FID was applied. But when $T_2$ was long enough, the spin echo technique has been used.

In the first case; data were taken at 4 K, where it was possible to determine $T_2$ by spin echo and $T_2^*$ using the FID method. Thus, if $T_2^*$ is the total spin-spin relaxation time decomposed into two parts; the relaxation time $T_2^{\text{dip}}$ due to dipolar interaction and $T_2^{\text{mag}}$ due to the inhomogeneity of the magnet, then

$$\frac{1}{T_2} = \frac{1}{T_2^{\text{dip}}} + \frac{1}{T_2^{\text{mag}}}. \quad (3.11.1)$$

by substituting with the value of $T_2^{\text{dip}}$ and $T_2^*$; it was possible to calculate $T_2^{\text{mag}}$. Thus by measuring $T_2^*$ and using the value of $T_2^{\text{mag}}$ which is constant for each frequency; $T_2^{\text{dip}}$ could be determined even when the signal is weak.

For long $T_2$, the pulse sequence 90-180 was used and the echo has been observed. The magnetization decay satisfies the following relaxation equation:

$$M(t) = M_0 \exp\left(\frac{-2t}{T_2}\right)$$

where $M(t)$ is the echo height at time $t$.

The advantage of using the spin echo technique which was first introduced by Hahn (1950), was to eliminate the influence of the inhomogeneity of the applied magnetic field. This was made because the effect of the inhomogeneity is reversible, so the decrease of the echo height with time is due to the interaction of the spins which decays exponentially with time constant $T_2$.

The consequence of this method is described (Fukushima Roeder 1981) as follows. Assuming that a 90° pulse has been applied along the x-axis to the spin system at zero time. Shortly after; the spin isochromats will precess with different Larmor frequencies according to the field they see. Some of these
isochromats will get ahead of the average and some will be behined. Hence, the spin isochromats will be dephased in the x'-y' plane and the net magnetisation in this plane will be zero, although the individual isochromats are not dephased. A time $\tau$ later, a 180 ° pulse is applied along the x'-axis as well. As a result, each spin isochromat would be rotated 180° along the x'-axis. Any magnetisation along z-axis would be inverted to the -z direction and be of no consequence of the magnetisation remaining in the x'-y' plane. The spin isochromats which were ahead the average by a certain angle will be behined the average by the same amount, while those who were behind, now will become ahead the average and so the spins catch each other and rephase to form a net magnetisation in the x'-y' plane. As a result, the magnetisation would be rebuilt at -y'-axis at time 2 $\tau$ and form an inverted spin echo. The height of this echo is given by:

$$E(2\tau) = E(0) \exp\left(\frac{-2\tau}{T_2}\right)$$

Hence to determine either relaxation time, the data were collected using the suitable sequence for certain period and the height of magnetisation was plotted as a function of delay time on a semilogarithmic paper. It was considered that the ratio $S/N$ decreases with the increase of time, so cutoff of the data was useful after certain time. The data points were fed to a least square fitting program and the relaxation times were computed.
CHAPTER 4

THE REGISTERED PHASE

4.1 Introduction:

The registered phase is considered as an attractive area for studying NMR properties of the spin system in two dimensions. The reason is that it has a characterized structure where the $^3$He atoms are regularly distributed on the grafoil mesh.

This phase, as observed from heat capacity measurements (Bretz et al 1973) (Hickernell et al 1972) and shown in figure (1.4.1) extends in a narrow range between $x = 0.56$ and $x = 0.625$ monolayer approximately and below temperature of 3 K.

4.2 Concept of the Registered Phase:

The adatoms have a regular arrangement with the substrate lattice. Therefore, the nature of the film and its properties depend crucially on the substrate structure. In the case of $^3$He adsorbed on grafoil, the amount of helium three atoms is just enough for each atom to occupy one out of each three sites of the hexagons of grafoil to form a triangular lattice. The lattice spacing has been found to be equal to 4.26 Å (Nielsen et al 1977). The surface spacing is $\sqrt{3}$ larger than the grafoil mesh and only $1/3$ of the adsorption sites are occupied. This registered structure which is known as $\sqrt{3} \times \sqrt{3}$ structure is illustrated in figure (4.2.1). Therefore, for such a system; the following equation
Figure 4.2.1

Regular Structure of $^3$He Atoms on the Grafoil Lattice.
is verified:

\[ x = \frac{N}{N_\ast} = 1/3 \]  \hspace{1cm} (4.2.1)

According to Bretz et al (1973), perfect registry is centered around \( x \approx 0.6 \) monolayer and temperature \( T < 3 \) K. Nevertheless, over a limited range at lower densities, the phase is still present except it contains a number of vacancies, while at higher densities interstitials exist. In both cases the film is affected by the registered phenomena to various degrees depending on the proximity to the perfect registry.

4.3 Display of the Data:

The spin-lattice relaxation time \( T_1 \) and the spin-spin relaxation time \( T_2 \) were determined as a function of coverage \( x \), frequency \( f_0 \), temperature \( T \) and the angle of orientation \( \beta \) between the external magnetic field and the normal to the substrate surface.

Besides the direct measurements mentioned previously, the dependence of the relaxation times \( T_1 \) and \( T_2 \) on temperature was used to evaluate the activation energy. From the variation of the relaxation times with frequency, the correlation time for the motion of the spins was determined.

Some \( T_1 \) and \( T_2 \) data were taken at the mixed phase, which lies between the registered and the solid phases. These data have been analysed and interpreted.

4.4 The Coverage Dependence:

A display of the variation of \( T_1 \) and \( T_2 \) with coverage was illustrated in figure (4.4.1) and (4.4.2). The NMR frequency was 5.1 MHz and the substrate orientation was 90° while the temperature was 1.2 and 4.2 K respectively. Data
Figure 4.4.1

$T_1$ and $T_2$ as a function of coverage at $f_0=5.1$ MHz, $T=1.2$ K and $\beta=90$ deg.
Figure 4.4.2

$T_1$ and $T_2$ as a function of coverage at $f_o=5.1$ MHz, $T=4.0$ K and $\beta=90$ deg.
for coverage less than 0.5 monolayer were taken from the previous work done on the same cryostat (Kent 1985).

At $T = 1.2$ K, at low coverage, $T_1$ increases monotonically then begins to decrease at $z = 0.4$ monolayer to reach a minimum around registry at 0.6 monolayer. Then the value of $T_1$ varies a little with coverage at the mixed phase, between $z = 0.64$ and $z = 0.7$ monolayer, and starts to decrease at the formation of the solid phase at $z = 0.72$ monolayer. Then $T_1$ has its frequency dependent minimum after which it increases with the increase of coverage.

The display of $T_2$ versus coverage shows that the increase of $T_2$ was gradually at low coverage and it has a shallow maximum around 0.3 monolayer, the exact position of the maximum depends on temperature (Kent 1985). $T_2$ starts to decrease to reach a minimum around perfect registry, then its value slightly increases at the registered boundaries. At the mixed phase $T_2$ becomes approximately coverage independent then decreases sharply to reach its lowest value at complete layer.

On the other hand, at $T = 4$ K, $T_1$ increases monotonically to reach perfect registry while $T_2$ does not change a lot. It was not clear whether there is a minimum or not. However, above this region both of them starts to decrease.

Focusing on the registered phase, it was clear that $T_1$ and $T_2$ exhibit nearly the same behaviour, although $T_1$ is of the order of seconds and $T_2$ is of the order of milliseconds. $T_1$ and $T_2$ obtained at 5.1 MHz, 1.2 K and 90 deg have been displayed in figure (4.4.3). The dip formed at registry is an indication of slowing down of the motion. $T_1$ data showed that the position of this dip is slightly frequency dependent as shown in figure (4.4.4); and it becomes dipper for smaller Larmor frequency. While $T_2$ data indicated that the position of the dip is shifted towards higher coverage for smaller Larmor frequencies; and
Figure 4.4.3

$T_1$ and $T_2$ as a function of coverage at $f_o = 5.1$ MHz, $T = 1.2$ K and $\beta = 90$ deg.
Figure 4.4.4
Spin-lattice relaxation time as a function of coverage at different frequencies.
becomes dipper as well. This dependence was displayed in figure (4.4.5). The same behaviour was seen by Sussex group (Owers-Bradley 1978), (Richards 1980). Figure (4.4.6) shows the dependence of $T_2$ on coverage at 5.1 MHz and 1.2 K for orientation angle equals to 90, 45 and zero degree.

4.5 Dependence on Larmor Frequency:

The spin-lattice relaxation time has been determined over a wide range of frequencies extended from 1.3 to 8.3 MHz and temperature of 1.2 K for different coverage at mainly angle of substrate orientation equals to 90 deg. For coverage $x = 0.58, 0.59, 0.6$ and 0.61 monolayer frequency dependence of $T_1$ was determined at $\beta = 0^\circ, 45^\circ$ and 90 deg.

For $x = 0.61$ monolayer, trial graphs were plotted to compare the different dependence of $T_1$ on frequency. A plot of $1/T_1$ with logarithm frequency was shown in figure (4.5.1) while the change of $T_1$ with frequency was illustrated in figure (4.5.2) and $1/T_1$ dependence on frequency was displayed on figure (4.5.3) for the three angles. Comparing these plots; one can easily notice that for this range of frequencies, $1/T_1$ dependence on frequency obeys a logarithmic law. Hence, for the rest of the data $1/T_1$ was plotted with logarithmic frequency as displayed from figure (4.5.4) to figure (4.5.9) for densities between 0.5 and 0.66 monolayer in steps of 0.005 monolayer.

The slope of these plots has been used to determine the correlation time of the motion $\tau_c$ as it will be seen in §4.8.1. For coverage between 0.52 and 0.62 monolayer this logarithmic law is obeyed while above $x = 0.62$ monolayer the relation deviates away from the logarithmic dependence.

It has been found experimentally that $1/T_2$ has linear dependence on $\omega_0$. The linearity was shown in figures (4.5.10), (4.5.11), (4.5.12) and (4.5.13) for
Spin–spin relaxation time as a function of coverage at $\beta = 0, 45$ and $90$ deg. $T=1.2$ K, $f_0 = 5.1$ MHz.
Figure 4.5.1

Spin-lattice relaxation rate as a function of frequency. \( T=1.2 \) K and \( x=0.61 \) monolayer.
Figure 4.5.2
Spin–lattice relaxation time as a function of frequency. $T=1.2 \text{ K}$ and $x=0.61 \text{ monolayer}$
Figure 4.5.4

The rate of spin-lattice relaxation time as a function of coverage. \( T = 1.2 \) K and \( \beta = 90 \) deg.
The rate of spin-lattice relaxation time as a function of Larmor frequency. $T=1.2$ K and $\beta=90^\circ$
Figure 4.5.6

The rate of spin–lattice relaxation time as a function of coverage.

$T=1.2$ K and $\beta=90$ deg.
The rate of spin-lattice relaxation time as a function of coverage. $T=1.2\ \text{K}$ and $\beta=90\ \text{deg}$. 
Figure 4.5.8

The rate of spin-lattice relaxation time as a function of coverage. \( T = 1.2 \) K and \( \beta = 90 \) deg.
Figure 4.5.9

The rate of spin-lattice relaxation time as a function of coverage. $T=1.2$ K and $\beta = 90$ deg.
Figure 4.5.10

Spin–spin relaxation rate as a function of frequency. $T=1.2$ K and $\beta=90$ deg.
Spin–spin relaxation rate as a function of frequency. $T=1.2$ K and $\beta=90$ deg.
Figure 4.5.12

Spin-spin relaxation rate as a function of frequency. $T=1.2 \text{ K}$ and $\beta=90 \text{ deg.}$
4.9 Temperature dependence

The T$_1$ and T$_2$ were determined at a temperature range between 1 and 5.5 K, frequencies 2.5 MHz and 6 MHz and the substrate orientation of 0°. The variation of T$_1$ and T$_2$ with the temperature rate at 2.6 and 5.1 MHz for coverage 0.59, 0.6, 0.62, 0.64, and 0.66 monolayer was illustrated in figures 4.5.1, 4.5.2, 4.5.3, 4.5.4 and 4.5.5 respectively.

From these plots, it is clear that in the temperature region 1 K < T < 2 K, the values of T$_1$ and T$_2$ are independent of temperature which indicates that the motion of the spins is of quantum nature, in analogy with the bulk $^3$He (Richardson et al). The quantum motion could be either due to exchange between neighboring spins or tunneling to a vacancy. In the range of temperatures 2 < T < 10 K, both relaxation times decrease exponentially with reverse of temperature obeying the Arrhenius relation. Above 3 K, the gradual change of T$_1$ and T$_2$ are possibly due to the existence of spin-glass phase transition or a second-order phase transition.

4.7 Anisotropy

The anisotropy of T$_1$ and T$_2$ with respect to the substrate orientation has been studied, and the values are weaker than the corresponding values of $^{3}$He.

Figure 4.5.13

Spin-spin relaxation rate as a function of frequency. T=1.2 K and $\beta$=90 deg.

T$_1$ was determined with the change of orientation angle at temperature
densities between $x = 0.52$ and $x = 0.66$ monolayer. Nevertheless, theoretical calculations for the model of bounded diffusion in a linear gradient (Robertson 1966) showed that $1/T_2$ depends on $\omega^2$.

### 4.6 Temperature dependence:

For a number of coverage around perfect registry; $T_1$ and $T_2$ were determined at a temperature range between 1 and 4.2 K for frequencies 2.6 MHz and 5.1 MHz and the substrate orientation of 90°. The variation of $T_1$ and $T_2$ with the temperature rate at 2.6 and 5.1 MHz for coverage 0.59, 0.6, 0.605, 0.61 and 0.615 monolayer was illustrated in figures (4.6.1), (4.6.2), (4.6.3), (4.6.4) and (4.6.5) respectively.

From these plots it is clear that; in the temperature region $1 < T < 2$ K, the values of $T_1$ and $T_2$ are independent of temperature which indicates that the motion of the spins is of quantum nature, in analogy with the bulk $^3$He (Richards 1971). This quantum motion could be either due to exchange between neighbouring spins or tunneling to a vacancy. In the range of temperatures $2 < T < 3$ K, both relaxation times decrease exponentially with inverse of temperature obeying the Arrhenius relation. Above 3 K, the gradual change of $T_1$ and $T_2$ support the heat capacity measurements (Bretz et al 1973) of the existence of second-order phase transition to the disordered phase.

### 4.7 Anisotropy:

The anisotropy of $T_1$ and $T_2$ with respect to the substrate orientation has been studied. It was found that the anisotropy of $T_1$ is weaker than the corresponding one for $T_2$.

$T_1$ was determined with the change of orientation angle at temperature
Figure 4.6.1

$T_1$ and $T_2$ as a function of inverse of temperature. $x=0.59$ monolayer and $\beta=90^\circ$
Figure 4.6.2

$T_1$ and $T_2$ as a function of inverse temperature. $x=0.6$ monolayer and $\beta=90$ deg.
Figure 4.6.3

$T_1$ and $T_2$ as a function of inverse of temperature. $x=0.605$ monolayer and $\beta=90^\circ$
Figure 4.6.4
$T_1$ and $T_2$ as a function of inverse of temperature, $x=0.61$ monolayer and $\beta=90$ deg.
From these results we notice that in the solid show a dramatic change when the substrate is coated with the various fields.

On the other hand, it was not unexpected for a monolayer at $T = 300$ K is the same as the 0.6 monolayer at $T = 20$ K. We note that this change does not occur for monolayers with lower dependence on frequency and temperature. This behavior has been observed by direct and by heat treatment (198). Some conclusions are expected from these results in the view of spin-flip relaxation times having been observed in the case of angle of exchange at low frequencies increasing with the angle.

The ratio $T_1(T_2)$ of the exchange rate constant depends on the angle of exchange and frequency. This is not the exact value expected by heat treatment (198).

4.8 Evaluation of exchange constants

Frequency dependent of $T_1$ and $T_2$ is larger as well as the theoretical dependence as seen in Figure 4.5. The change of $T_1$ and $T_2$ is seen as the frequency increases. This is expected to influence the frequency of the quantum motion, or equivalently the exchange rates, which is essentially the time taken by a spin to move from one state to another.

4.8.1 The value of $T_1$ and $T_2$ as a function of inverse of temperature, $x = 0.615$ monolayer and $\beta = 90$ deg.
of 1.2 K and coverage \( x = 0.58, 0.59, 0.6 \) and 0.605 monolayer. This dependence was illustrated in figure (4.7.1) for frequency 2.6 MHz, and figure (4.7.2) for 5.1 MHz. From these graphs we notice that \( T_1 \) did not show a dramatic change when the substrate is rotated with the external field.

On the other hand, figure (4.7.3) demonstrates the appreciable change of \( T_2 \) as a function of orientation angle for coverage \( x = 0.58, 0.59, 0.6 \) and 0.61 monolayer at \( T = 1.2 \) K for frequencies 2.6, 5.1 and 8.3 MHz. One notices that this change does not depend dramatically on coverage while it is frequency dependent. This behaviour has been seen by Sato and Sugawara (1980). Same conclusion was obtained from figure (4.7.4) where the rate of spin-spin relaxation time has been plotted as a function of angle of orientation at the same frequencies for coverage 0.59 and 0.61 monolayer.

The ratio \( T_2(\pi/2)/T_2(0) \) was determined and found to be approximately equal to 2, independent of both coverage and frequency. This is almost the same value as found by Sato and Sugawara (1980).

4.8 Evaluation of the correlation time:

Frequency dependence of \( T_1 \) and \( T_2 \) at \( T = 1.2 \) K and \( \beta = \pi/2 \) as well as the theoretical calculations (Cowan 1980) of the change of \( T_1 \) rate with the tunneling frequency have been employed to evaluate the frequency \( J \) of the quantum motion, or equivalently the correlation time \( \tau_c \), which is essentially the time taken by a spin to move from one site to another.

4.8.1 The calculations from \( T_1 \):

Recalling equation (2.4.6), where \( T_1 \) is given by:

\[
\frac{1}{T_1} = J_1(\omega_0) + 4J_2(2\omega_0)
\]
Figure 4.7.2
Spin-lattice relaxation time as a function of orientation angle. $f_0 = 5.1$ MHz and $T = 1.2$ K
Figure 4.7.4

Spin-spin relaxation rate as a function of orientation angle at T=1.2 K.
The Universal Curve as obtained by Cowan et al. (1987).

\[
1 - \left( \frac{e^{\frac{\frac{Z}{\rho}}}{e^{\frac{Z}{\rho}}}} + \frac{\rho^4}{4} + \frac{Z}{\rho} \right) \times \left( \frac{\rho}{\rho + 1} \right)
\]
substituting for $J_n(\omega_0)$ and $j_n(\omega_0)$ [the F.T of $g_n(t)$, equation (2.6.13)] and for the orientation $\beta$ by the value 90°; a theoretical plot (Cowan et al 1987) for the change of $1/T_1$ with $\omega/J$ was produced as shown in figure (4.8.1).

From experimental data, $1/T_1$ was plotted versus $\ln \omega$ and straight lines were obtained as displayed from figure (4.5.4) to figure (4.5.9). This dependence is satisfied by an equation of the form,

$$\frac{1}{T_1} = C - D \ln \omega_0$$

(4.8.1)

where $C$ and $D$ are constants.

For a narrow range of the calculated frequency dependence, one can approximate the expression of $1/T_1$ as follows:

$$\frac{1}{T_1} \left[ \frac{9}{32} \hbar^2 \gamma^4 \frac{\mu_0^2}{(4\pi)^2} \frac{g(0)}{J} \right]^{-1} = A - B \ln \left( \frac{\omega_0}{J} \right)$$

(4.8.2)

where $A$ and $B$ are constants.

The expression (4.8.1) was fitted to the curve’s tangents of figure (4.8.1) at different values of $\omega/J$ in a self consistent manner. If $B$ is the slope of the tangent, and $D$ is the slope of the experimental line; a simple scaling between equation (4.8.1) and (4.8.2) gives:

$$\tau_c = 8.999 \times 10^{-19} \omega_0^{-3} \frac{D}{B}$$

(4.8.3)

Where $\tau_c$ is given in terms of the frequency of the motion $J$ (Cowan 1980) as $\tau_c = 0.267/J$. For each coverage with certain $D$, different values of $B$ (corresponding to different tangents) were tested, until the obtained value of $\tau_c$ is consistent with the selected tangent. This check has been made by choosing a value of $\omega$ in the middle of the frequency range ($\omega/2\pi = 5$ MHz), then $\omega \tau_c$ was computed and compared with the tangent point of the chosen tangent.
4.8.2 Employment of $T_2$:

It is believed that $T_2$ is affected, not only by the internuclear dipolar interaction, but also by the grafoil local fields which depend on the applied magnetic field. Therefore, it was essential to differentiate between both mechanisms. This has been done by writing the empirical frequency dependence equation for $T_2$ (Cowan et al 1987a),

$$\frac{1}{T_2} = A + B\omega_0$$  \hspace{1cm} (4.8.4)

Where the frequency independent part $A$ is determined by the dipolar relaxation of $^3$He atoms. $B$ is thought to be the relaxation due to the motion in the grafoil local fields.

A plot of the slope $B$ with the change of coverage is shown in figure (4.8.2). From which we notice that the slope increases with the increase of coverage to have its maximum value at registry, then starts to decrease to have approximately constant value. This could be explained by the slowing down of the motion of the spins where the spins are affected more strongly by the substrate local fields. Nevertheless, the substrate diamagnetic contribution is not fully understood yet. On the other hand, figure (4.8.3) demonstrates the variation of the intercept $A$ as a function of coverage $x$. This intercept was found to increase smoothly with coverage at all densities except at registry. It has higher values due to the reduction of the mobility of the spins, where the dipolar interaction increases. Therefore, it seems to be reasonable to suggest that the net dipole-dipole contribution to $T_2$ could be extracted from the smooth baseline in this region corresponding to each coverage.

The analysis was made on the basis of the decomposition of the intercept
The slope of \((1/T_2 \text{ vs. } f_0)\) as a function of coverage, \(T=1.2\text{ K}\) and \(\beta=90\text{ deg.}\)
The intercept of \( \frac{1}{T_2} \) vs. \( f_0 \) as a function of coverage. \( T=1.2 \) K and \( \beta=90 \) deg.
as follows:

\[
\frac{1}{T_2^{\text{freq. indep.}}} = \frac{1}{T_2^{\text{other contr.}}} + \frac{1}{T_2^{\text{dipole-dipole}}}
\]  

(4.8.5)

The FID function (Cowan 1980) was given by equation (2.6.3) as:

\[
F(t) = \exp(-t/T_2^{na}) \exp(-3 \int_0^t (t - \tau)G_0(\tau)d\tau)
\]

Concentrating on the frequency independent part; the adiabatic part; of the above equation and evaluating the integrals of \(g_0(t)\) and \(g_2(t)\) of equation (2.6.13) with a suitable guess value of \(\tau_c\), \(F(t)\) was evaluated.

For a plot of logarithmic \(F(t)\) versus time \(t\), the slope of the straight part at long time was determined for each coverage. This slope represents the theoretical value of \(1/T_2\) dipolar. Hence, comparison with \(1/T_2^{\text{dipole-dipole}}\) at each coverage was done. From the agreement between both values, the correct value for \(\tau_c\) was evaluated.

**4.8.3 Determination of \(\tau_c\) from angle dependence:**

For coverage \(x = 0.58, 0.59, 0.6, 0.61\) and \(0.62\) monolayer and temperature \(T = 1.2\) K, \(T_1\) as a function of frequency was determined at substrate orientation \(\beta = 0^\circ, 45^\circ\) and \(90^\circ\). A logarithmic plot of \(1/T_1\) versus frequency corresponding to each coverage is illustrated from figure (4.8.4) to figure (4.8.8). These plots were compared with the corresponding theoretical plot (Cowan 1980) which has been reproduced in figure (2.6.1), and the value of \(\tau_c\) was extracted for each of the mentioned coverages.

Figure (4.8.9) displays the change of \(\tau_c\) with \(x\), its value increases gradually with the increase of coverage to reach a maximum at perfect registry, then decreases for higher densities. This maximum is expected due to the
Figure 4.8.4

Spin–lattice relaxation rate as a function of Larmor frequency at different angles.

$x = 0.58$ monolayer and $T = 1.2$ K
Figure 4.8.5

Spin-lattice relaxation rate as a function of Larmor frequency at different angles.

$x=0.59$ monolayer and $T=1.2$ K
Figure 4.8.6

Spin–lattice relaxation rate as a function of
Larmor frequency at different angles.

$\beta = 0^\circ$ deg., $\beta = 45^\circ$ deg., $\beta = 90^\circ$ deg.

$x=0.6$ monolayer and $T=1.2$ K
Spin–lattice relaxation rate as a function of Larmor frequency at different angles. $x=0.61$ monolayer and $T=1.2$ K
Figure 4.8.8

Spin-lattice relaxation rate as a function of Larmor frequency at different angles.

\( x = 0.62 \) monolayer and \( T = 1.2 \) K
The correlation time as a function of coverage.

$T = 1.2$ K and $f_0 = 5.1$ MHz.

If the activation energy of the atom is given by $E_a$, then $E_a = E_f + E_m$ (Sullivan et al. 1975), where $E_f$ is the formation energy of vacancies and $E_m$...
slowing down of the motion at this region. The maximum $\tau_c$ was found (Cowan et al 1987a) and (Abou-El-Nasr et al 1988) to be of the order of $10^{-8}$ seconds.

From the change of $\tau_c$ with coverage, it is clear that the values obtained from different methods of analysis, were comparable and they all fall on the same curve. In fact it does not make any difference if we use any of the correlation functions equation (2.6.12) or (2.6.13) because we are comparing the slopes which are the same for both models. The gradual change through a maximum for $\tau_c$ is an indication of the change of the spins mobility with the change of coverage, where the slowest motion occurs at perfect registry.

Several attempts have been made (Secca 1983) to measure the diffusion coefficient $D$ but they were not very successful. Nevertheless, they reported a value for $D$ of the order of $10^{-9} \text{cm}^2 \text{Sec}^{-1}$.

According to Cowan (1980),

$$\tau_c = \frac{a^2}{2D}$$  \hspace{1cm} (4.8.6)

where $a$ is the hard core dimension and can be obtained from the relation $a = 0.7308 \times 10^{-8} \text{ d cm}$, and $d$ is the triangular lattice constant which is given by $3.24 \times 10^{-8}/\sqrt{x} \text{ cm}$. Hence from the calculated $\tau_c$, the diffusion coefficient of the motion at perfect registry has been calculated and was found of the order of $10^{-9} \text{cm}^2 \text{Sec}^{-1}$ which is of the same order of magnitude as obtained by Sussex group (Secca 1983), and one order smaller than that obtained in Tokyo (Sato and Sugawara 1980).

4.9 The Activation Energy:

If the activation energy of the atom is given by $E_a$, then $E_a = E_f + E_m$ (Sullivan et al 1975), where $E_f$ is the formation energy of vacancies and $E_m$
is the migration energy necessary to overcome the potential barrier due to repulsion between the $^3$He atoms.

In solid $^3$He, motion is thought to be quantum tunneling (Sullivan et al 1975), then $E_m = 0$. Assuming the same behaviour is true for two dimensions (Sato and Sugawara 1980), then $E_a$ will be given by $E_f$ only. A direct result of vacancies is the modulation of the internuclear magnetic dipolar interactions (Sullivan et al 1975). Therefore, the mobility of vacancies implies the mobility of adatoms.

At the registered phase, it is assumed that two types of vacancies exist (Sato and Sugawara 1980). First; the ground-state vacancy corresponding to the unoccupied sites naturally present in the triangular lattice. Second; thermally activated vacancy at the lattice site of the triangular lattice. But, at perfect registry there is no ground state vacancies at all. This is because the $^3$He atoms fill all the preferable vacancies. Also, the thermally activated vacancies are expected to be zero at zero K (Sato and Sugawara 1980). This is a result of the equation $x_v = \exp(-E_f/k_BT)$, where $x_v$ is the concentration of vacancies and $k_B$ is the Boltzmann constant. However, at 1.2 K an estimation of the density of vacancies was found to be 4.2% (Sato and Sugawara 1980).

The dependence of $T_1$ and $T_2$ on temperature rate §4.6 was employed to determine the activation temperature corresponding to each coverage. The slope of the line at the middle range where $2 > T < 3$ was determined and was substituted in the Arrhenius law.

A plot of this activation temperature $E_a/k_B$ versus $x$ was illustrated in figure (4.9.1). The values of $E_a/k_B$ obtained from $T_1$ data at $f_0 = 2.6$ and 5.1 MHz have a maximum around 8.8 K which is corresponding to perfect registry. While the lower value is for the data obtained from $T_2$ at the same frequencies.
This difference is attributed to the effect of the substrate local fields on $T_a$. The same behavior was observed in L. L. Dickey [4.12.1] and Richards [4.13.1] who worked at 1 MHz. The London group [4.14.1] and Sugawara et al. [4.15.1] did not see any change of $E_a/E_B$ with coverage. This could be due to different treatment of the substrate and hence different surface nature which affect the mobility of the atoms.

### Figure 4.9.1

The activation temperature as a function of coverage, $f_o = 2.6, 5.1$ MHz and $\beta = 90$ deg.

The experimental data on $T_1$ and $T_2$ dependence on coverage, which were displayed in figures (4.9.1) and (4.9.3), show that both $T_1$ and $T_2$ are nearly independent on coverage in this region. This implies that the dipole-dipole interactions are not the dominant part of relaxation and there are other contributions which affect the relaxation mechanism within this phase.

However, it is thought that this phase is a mixed phase which consists of a contribution from both registered and solid phases. Hence $T_{1\text{exp}}$ is the fraction of atoms which contribute from both phases, and $T_{2\text{exp}}$ is the fraction of atoms which contribute from solid phase. Using probability, $\alpha_1 + \alpha_2 = 1$ and the following equations are satisfied for $T_1$ and $T_2$, respectively:

\[ T_{1\text{exp}} = \frac{\alpha_1}{\alpha_1 + \alpha_2} \]

\[ T_{2\text{exp}} = \frac{\alpha_2}{\alpha_1 + \alpha_2} \]
This difference is attributed to the effect of the substrate local fields on $T_2$. The same behaviour was shown by Sussex group (Owers-Bradley 1978), (Richards 1980) who worked at 1 MHz. They found the maximum activation temperature from $T_1$ at 8 K. On the other hand; working at 10 MHz, Tokyo group (sato and Sugawara 1980) did not see any change of $E_a/k_B$ with coverage. This could be due to different treatment of the substrates and hence different surface nature which affect the mobility of the atoms.

### 4.10 The Mixed Phase:

This phase lies between the registered and solid phases as demonstrated in the phase diagram obtained from heat capacity measurements by Hering et al (1976) figure (1.4.3).

The experimental data of $T_1$ and $T_2$ dependence on coverage, which were displayed in figures (4.4.1) and (4.4.3), show that both $T_1$ and $T_2$ are nearly independent of coverage at this region. This implies that the dipole-dipole interactions are not the dominant part of relaxation and there are other contributions which affect the relaxation mechanism within this phase.

However, it is thought that this phase is a mixed phase which consists of a contribution from both registered and solid phases. Hence if $\alpha_r$ is the fraction of atoms which contribute from registered phase, and $\alpha_s$ is the fraction of atoms which contribute from solid phase; from probability, $\alpha_r + \alpha_s = 1$ and the following equations are satisfied for $T_1$ and $T_2$ respectively:

\[
\frac{1}{T_1^{\text{exper.}}} = \frac{\alpha_r}{T_1} + \frac{\alpha_s}{T_1^*} \quad (4.10.1)
\]

\[
\frac{1}{T_2^{\text{exper.}}} = \frac{\alpha_r}{T_2} + \frac{\alpha_s}{T_2^*} \quad (4.10.2)
\]

Where $T_1^{\text{exper.}}$ and $T_2^{\text{exper.}}$ are the experimental values of $T_1$ and $T_2$. While $T_1^*$ and $T_2^*$
$T_1^*$ are the values of $T_1$ at registry and solid respectively. $T_2^r$ and $T_2^s$ are the corresponding values of $T_2$. From $x = 0.66$ monolayer, where the registered phenomenon is dying away; to $x = 0.72$ monolayer; where the solid phase starts to be formed; the behaviour of the atoms was studied.

It has been found that both $\alpha_r$ and $\alpha_s$ are independent of Larmor frequency for the region of coverage concerned. A plot of these fractions versus coverage as obtained from $T_1$ data was shown in figure (4.10.1). While figure (4.10.2) demonstrates the variation of both fractions with increasing coverage as obtained from $T_2$. Maximum contribution from $\alpha_r$ was found at $x = 0.66$ monolayer, which decreases gradually to reach zero at $x = 0.72$ monolayer. While as expected, $\alpha_s$ has zero value at $x = 0.66$ monolayer and increases gradually to reach one at $x = 0.72$ monolayer.
Figure 4.10.1

Fractions of atoms at registry and solid as obtained from $T_1$, $f_0=5.1$ MHz, $T=1.2$ K and $\beta=90^\circ$
Figure 4.10.2

Fractions of atoms at registry and solid as obtained from $T_2$, $f_0=5.1$ MHz, $T=1.2\,K$ and $\beta=90^\circ$. 

Atoms from registry
Atoms from solid.
CHAPTER 5

THE INCOMMENSURATE SOLID PHASE

5.1 Introduction:

Above $x = 0.72$ of a monolayer and up to a full monolayer completion, the film of $^3$He adsorbed on exfoliated graphite represents a two dimensional solid phase.

The experimental data for spin-lattice relaxation time and spin-spin relaxation time have been determined in this phase. The data were taken over a wide range of Larmor frequencies as well as coverages between 0.7 and 1.02 monolayer. The anisotropy of $T_2$ was studied for a number of coverages. The frequency of the exchange motion was calculated at different coverages from both $T_1$ and $T_2$ data and the motion of atoms has been studied.

The rapid decrease in $T_2$ as the density increases is similar to that observed in bulk solid $^3$He (Cowan et al 1977) and (Richards 1971). This decrease is the result of the quantum tunneling of atoms which averages the dipolar fields, and so the tunneling rate $J$ decreases rapidly as the density increases.

5.2 Dependence of Relaxation Times on Coverage:

For the examined range of coverages, $T_1$ and $T_2$ were determined in a wide range of frequencies extended from 1.3 MHz to 10.2 MHz. The data were taken at temperature of 1.2 and 4.2 K and the angle of orientation was 90°.

As illustrated in figure (5.2.1), for Larmor frequency $f_0 = 5.1$ MHz, $T_1$
Spin–lattice relaxation time as a function of coverage. $f_0=5.1$ MHz and $\beta = 90$ deg.
decreases with coverage to reach a minimum at \( x \approx 0.79 \) monolayer. This parabolic behaviour indicates dipolar dependence of \( T_1 \). At higher coverages, the points start to deviate from the smooth monotonic behaviour. This may imply that at higher densities of the solid, \( T_1 \) is not determined solely by the dipolar interaction and other mechanisms compete to shorten its value.

Figure (5.2.2) displays the variation of \( T_1 \) with coverage for frequencies 1.3, 2.6, 3.9, 5.1, 6.2, 7.5, 8.3 and 10.2 MHz at \( T = 1.2 \) K. We noticed that the behaviour at 5.1 MHz was repeated for all frequencies. The proportionality: \( T_1^{\text{min}} \propto \omega_0 \) is valid and the locus of minima shifts to the left for higher frequencies. This happens because the condition \( \omega_0 \tau_c \approx 1 \) at the minima is fulfilled. The \( T_1^{\text{min}} \) values are given in table (5.2.1) and illustrated in figure (5.2.3) as a function of coverage for all the working frequencies.

At temperature 4.2 K the previous condition is still fulfilled, but the location of the minima are shifted to higher coverage because of the dependence of \( T_1 \) on temperature at this region. From the display of the experimental data in figure (5.2.4) it seems that there are minima around \( x = 0.94 \) monolayer. Unfortunately the data are not enough to confirm their location. The value of \( T_1 \) at minimum is approximately equal to the corresponding value at 1.2 K except that it moves to higher coverage as expected.

The dependence of \( T_2 \) on coverage for the frequency 5.1 MHz is shown in figure (5.2.5) at temperatures 1.2 and 4.2 K. It is clear that \( T_2 \) changes rapidly with the increase of coverage at both temperatures to reach its shortest value of the order of magnitude of \( 10^{-1} \) mSec in the neighbourhood of monolayer completion. Above this coverage \( T_2 \) starts to increase due to the formation of the second layer, where the mobility of the atoms becomes bigger. On display in figure (5.2.6), \( T_2 \) as a function of coverage at frequencies 1.3 and 5.1 MHz. On
<table>
<thead>
<tr>
<th>Coverage</th>
<th>$T_1^{\text{min.}}$ (Sec.)</th>
<th>Frequency (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.818</td>
<td>0.0499</td>
<td>1.3</td>
</tr>
<tr>
<td>0.805</td>
<td>0.0856</td>
<td>2.6</td>
</tr>
<tr>
<td>0.789</td>
<td>0.1503</td>
<td>3.9</td>
</tr>
<tr>
<td>0.785</td>
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<td>0.2711</td>
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<td>0.7676</td>
<td>0.2797</td>
<td>7.5</td>
</tr>
<tr>
<td>0.766</td>
<td>0.3639</td>
<td>8.3</td>
</tr>
<tr>
<td>0.759</td>
<td>0.479</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Table 5.2.1

$T_1$ minima as a function of coverage for different Larmor frequencies.
Spin-lattice relaxation time as a function of coverage. $T=1.2\ K$ and $\beta=90\ deg.$
Figure 5.2.3

Values of $T_1$ (minima) for different frequencies.

$T = 1.2$ K and $\beta = 90^\circ$. 
Figure 5.2.5

Spin-spin relaxation time as a function of coverage at $f_0 = 5.1 \text{ MHz}$ and $\beta = 90 \text{ deg.}$
the same graph, $T_2$ data obtained by Sussex group at 1 MHz and temperature $1.2 \, K$ and angle of orientation $\beta=90$ deg were plotted. Data of Houston and Bradley et al (1978) were plotted using spin echo techniques for lower coverages and the FID for higher coverages when short. The results of Sussex were determined using CW technique. The reproducibility of both methods supports the use of the FID decay in explaining the short $T_2$.

Figure 5.2.6 shows the change of $T_2$ with $\beta$ at temperature $1.2 \, K$ and angle of orientation $\beta=90$ deg. These data were taken at frequencies extended between 1.3 and 5.1 MHz. With reference to figure 5.2.5, we expect that for all frequencies, $T_2$ would have its shortest value close to the maximum coverage. Data shown in figure 5.2.6 for the variation of $T_2$ with $\beta$ at 1.2 K exhibits the same behavior. Hence, $T_2$ decreases monotonically with the increase of coverage towards the complete coverage as shown in figure.

5.3 Frequency Dependence

As mentioned before (4.6, although the theory of Sonoda et al., diffusion (Robertson 1965) suggests a quadratic dependence on spin-spin relaxation rate on frequency, the experimental data showed linearity. For coverages between 0.7 and 0.8, one notices a decrease in $T_2$ which is a result of the strong coupling as well as other mechanisms. The data dependencies of $1/T_2$ and angle of rotation $\beta$ at 1 MHz were investigated in figures 5.3.1, 5.3.2, 5.3.3 and 5.3.4. For higher coverages, the value of $1/T_2$ decreases steeply as the relaxation increases. At lower coverages, the value of $1/T_2$ increases slightly. At higher coverages, the value of $1/T_2$ changes dramatically at $\beta=90$ deg.

**Figure 5.2.6**

Comparison between $T_2$ taken at 1.3 and 5.1 MHz and $T_2$ taken at Sussex at 1 MHz. $T=1.2 \, K$ and $\beta=90$ deg.
the same graph, $T_2$ data obtained by Sussex group at 1 MHz and temperature 1.2 K and angle of orientation of $\pi/2$ (Cowan et al 1977) and (Owers-Bradley et al 1978) were plotted for comparison. Our data were determined by pulsed technique using spin echo for lower coverages and the FID for higher coverages when $T_2$ is short. Those of Sussex were determined using CW technique. The reproducibility of both data supports the use of the FID decay in determining short $T_2$.

Figure (5.2.7) demonstrates the change of $T_2$ with $x$ at temperature of 1.2 K and angle of orientation equals 90 deg. These data were taken at frequencies extended between 1.3 and 10.2 MHz. With reference to figure (5.2.5), one expects that for all frequencies $T_2$ would have its shortest value close to monolayer completion. Data shown in figure (5.2.8) for the variation of $T_2$ with $x$ at 4.2 K exhibits the same behavior. Hence, $T_2$ decreases monotonically with the increase of coverage towards the complete layer as shown before.

5.3 Frequency Dependence:

As mentioned before §4.5, although the theory of bounded diffusion (Robertson 1966) suggests a quadratic dependence of spin-spin relaxation rate on Larmor frequency, the experimental data showed linearity. For coverages between 0.7 and 0.9 monolayer the relaxation is a result of dipolar coupling as well as other mechanisms. The linear dependence of $1/T_2$ and $\omega_0$ at these coverages for temperature 1.2 K and angle of rotation $\pi/2$ is illustrated in figures (5.3.1), (5.3.2), (5.3.3) and (5.3.4). Nevertheless, for higher coverages, the value of $1/T_2$ scattered as shown in figure (5.3.5) for $x = 0.94$ monolayer, so the relaxation is considered to be mainly dipolar. From figures (5.3.1) and (5.3.2), we notice that for lower densities of solid, $T_2$ does not change dramatically at
Figure 5.2.7
Spin-spin relaxation time as a function of coverage. T=1.2 K and $\beta$=90 deg.
Figure 5.3.1

Spin-spin relaxation rate as a function of Larmor frequency. $T=1.2$ K and $\beta=90^\circ$.
Figure 5.3.2

Spin-spin relaxation rate as a function of Larmor frequency. $T=1.2 \text{ K}$ and $\beta=90^\circ$
Figure 5.3.3

Spin-spin relaxation rate as a function of Larmor frequency. $T=1.2$ K and $\beta=90^\circ$. 
Figure 5.3.4

Spin–spin relaxation rate as a function of Larmor frequency. $T=1.2$ K and $\beta=90^\circ$
different coverages for the same frequency. As the density increases the change becomes linear and eigen. Possible isotherms obtained at 1.2 K with the variation of frequency. Figures (5.3.6) and (5.3.7) show the behaviour at different densities, from which we conclude that $T_2$ is frequency dependent at all coverages, hence the dipolar relaxation is not dominant.

Because $T_2$ has short values at high coverages, it was not possible to determine $T_2$ by using the spin echo technique. Hence, its value was extracted from the FID following a 90 degree pulse by using equation (3.11.1).

where $T = 4$ K where it was possible to determine $T_2^{\text{isp}}$ by spin echo. $T_2$ from the FID, the inhomogeneity of the magnet $T_2^{\text{magn}}$ was determined and not been used in the previous equation with $T_2$ to determine $T_2^{\text{isp}}$ at any frequency or orientation.

It was found that the value of $T_2^{\text{isp}}$ is very sensitive to temperature, for example at $x_0 = 0.1$ MHz the value of $T_2^{\text{isp}}$ at $T = 1.2$ K was 0.8174 ms, while its value at 4 K was equal to 0.8459 ms. This sensitivity was less with respect to frequency and it was approximately independent on coverage at this short range examined. Figure (5.3.8) illustrates the change of $T_2$ and $T_2^{\text{isp}}$ with Larmor frequency 3.1 MHz, the variation of $1/T_2$ and $1/T_2^{\text{isp}}$ with the angle $\beta$ is displayed in figure (5.3.9) which shows that all of them have a qualitative angle dependence at 1.2 K.

Experimental data were taken for the various of the spin-lattice relaxation time. Spin-spin relaxation frequencies were 1.3, 2.6, 3.9, 5.2, 6.4, 8.4 MHz and the results have been taken at orientation $\beta = 90^\circ$ and temperature 1.2 and 4.2 K. The range of coverages

**Figure 5.3.5**

Spin-spin relaxation rate as a function of Larmor frequency. $T=1.2$ K and $\beta=90^\circ$
different coverages for the same frequency. As the density increases the change becomes bigger and bigger. Parallel to this data, $T_2$ was obtained at 4.2 K with the variation of frequency. Figures (5.3.6) and (5.3.7) show the behaviour at different densities, from which we conclude that $T_2$ is frequency dependent at all coverages, hence the dipolar relaxation is not dominant.

Because $T_2$ has short value at higher coverages, it was not possible to determine it by using the spin echo technique. Hence, its value was extracted from the FID following a 90 degree pulse by using equation (3.11.1),

$$\frac{1}{T_2} = \frac{1}{T_2^{\text{dip}}} + \frac{1}{T_2^{\text{mag}}}.$$  

At temperature $T = 4$ K where it was possible to determine $T_2^{\text{dip}}$ by spin echoes and $T_2^{\text{mag}}$ from the FID, the inhomogeneity of the magnet $T_2^{\text{mag}}$ was determined and so it has been used in the previous equation with $T_2^{\text{dip}}$ to determine $T_2$ at any frequency or orientation.

It was found that the value of $T_2^{\text{mag}}$ is very sensitive to temperature, for example; at $f_0 = 5.1$ MHz the value of $T_2^{\text{mag}}$ at $T = 1.2$ K was 0.3274 mSec, while its value at 4 K was equal to 0.8459 mSec. This sensitivity was less with respect to frequency and it was approximately independent on coverage at this short range examined. Figure (5.3.8) illustrates the change of $T_2^{\text{mag}}$ with Larmor frequency at 4 K. At Temperature of 1.2 K and frequency 5.1 MHz, the variation of $1/T_2$, $1/T_2^{\text{mag}}$, and $1/T_2^{\text{dip}}$ with the angle $\beta$ is displayed in figure (5.3.9) which shows that all of them have a qualitative angle dependence at 1.2 K.

Experimental data were taken for the variation of the spin-lattice relaxation time $T_1$ with different Larmor frequencies. These working frequencies were 1.3, 2.6, 3.9, 5.1, 6.2, 7.5, 8.3 and 10.2 MHz. The data have been taken at orientation $\beta = 90^\circ$ and temperatures 1.2 and 4.2 K. The range of coverages
Figure 5.3.6

Spin-spin relaxation rate as a function of Larmor frequency. $T=4.2$ K and $\beta=90^\circ$
Figure 5.3.7

Spin–spin relaxation rate as a function of Larmor frequency. $T=4.2$ K and $\beta=90^\circ$
Figure 5.3.8

Variation of $T_2^*$ and $T_2^{\text{mag.}}$ with Larmor frequency.

$x=0.96$ monolayer, $T=4.2$ K and $\beta=90$ deg.
Angle dependence of $1/T_2$, $1/T_{2\text{mag.}}$, and $1/T_{2\text{*}}$ vs. $x=0.96$ monolayer, $f_0=5.1$ MHz and $T=1.2$ K

Figure 5.3.9
extends from $x = 0.7$ to $x = 0.9$ monolayer changed in 0.2 steps. The variation of $1/T_1$ with Larmor frequency at $T = 1.2$ K is displayed from figure (5.3.10) to figure (5.3.13). It is clear that $T_1$ increases with the increase of frequency. As we shall see next section, a theoretical fitting of these data has been carried out. For temperature of 4.2 K, the $T_1$ dependence on frequency is displayed in figures (5.3.14), (5.3.15) and (5.3.16). In the first two graphs the experimental errors were big so the behaviour was not very clear. But for higher coverages which is displayed in figure (5.3.16), it seems that the dependence seen at 1.2 K was followed at 4.2 K.

5.4 The Characteristic Frequency of the Motion:

The overlapping of the wave functions of the particles results in particle exchange. This could be two, three or higher order particles exchange. This overlap depends crucially on the interatomic distance, so it depends upon the amount of $^4$He admitted. As the atoms come closer, the wave function becomes narrower which result in reducing the overlapping. So the exchange frequency decreases and the motion of the atoms slows down (Guyer et al 1971).

It is established that in the solid phase (Cowan et al 1987b), the dipole-dipole interaction is the mechanism which fully affects $T_1$ and is the dominant cause of $T_2$. For densities between 0.76 and 0.86 monolayer the exchange frequency $J$ was extracted from $T_1$ data at the minima and also from data away from minima. On the other hand, straight forward extraction of $J$ from $T_2$ at these densities was not possible. This was because $T_2$ is not purely dipolar in these regions; it is affected by other mechanisms as well. Nevertheless, for densities near the monolayer completion where the dipolar coupling is the only cause of the spin-spin relaxation, direct calculations could be done.
Figure 5.3.10

Spin-lattice relaxation rate as a function of Larmor frequency. T=1.2 K and $\beta=90^\circ$
Figure 5.3.11

Spin–lattice relaxation rate as a function of Larmor frequency. $T=1.2$ K and $\beta=90^\circ$
Figure 5.3.12

Spin-lattice relaxation rate as a function of Larmor frequency. $T=1.2\, \text{K}$ and $\beta=90^\circ$
Figure 5.3.13

Spin-lattice relaxation rate as a function of Larmor frequency. T=1.2 K and $\beta=90^\circ$. 
Figure 5.3.14

Spin-lattice relaxation rate as a function of Larmor frequency. $T=4.2\,\text{K}$ and $\beta=90\,\text{deg}$.
Figure 5.3.15

Spin-lattice relaxation rate as a function of Larmor frequency. $T=4.2$ K and $\beta=90^0$
Figure 5.3.16

Spin-lattice relaxation rate as a function of Larmor frequency. T = 4.2 K and \( \beta = 90^\circ \)
5.4.1 Determination of $J$ from $T_1$:

The analysis of $T_1$ is based on using the correlation functions equation (2.6.13) which have been proposed by Cowan et al (1987a). The spectral densities which are their Fourier Transforms are given as follows:

$$\frac{j_0(\omega)}{g(0)} = \frac{2p_0}{a_0J} K_\theta\left(\frac{\omega}{a_0J}\right) + \frac{q_0\pi}{b_0J} \exp\left(-\frac{\omega}{b_0J}\right)$$

$$\frac{j_2(\omega)}{g(0)} = \frac{p_2\pi}{a_2J} \exp\left(-\frac{\omega}{a_2J}\right)$$

(5.4.1)

where $K_\theta(\omega/a_0J)$ is a reduced Bessel function of zero order. For $\beta = 90^\circ$ the expression for $1/T_1$ could be written on the following form:

$$\frac{1}{T_1} = \frac{9}{32} \hbar^2 \gamma^4 \frac{\mu_0^2}{4\pi^2} \frac{g(0)}{J} \times \left[ \frac{1}{2} \frac{p_2\pi}{a_2} \exp\left(-\frac{\omega}{a_2J}\right) + \frac{2p_0}{a_0} K_\theta\left(\frac{2\omega}{a_0J}\right) \right. $$

$$+ \left. \frac{q_0\pi}{b_0} \exp\left(-\frac{2\omega}{b_0J}\right) + \frac{1}{2} \frac{p_2\pi}{a_2} \exp\left(-\frac{2\omega}{a_2J}\right) \right]$$

(5.4.2)

Substituting by the values of the constants, the previous equation takes the following form:

$$\frac{J}{T_1 a^3} = 2.97 \times 10^8 \left[ \frac{1}{2} \frac{p_2\pi}{a_2} \exp\left(-\frac{\omega}{a_2J}\right) + \frac{2p_0}{a_0} K_\theta\left(\frac{2\omega}{a_0J}\right) \right.$$

$$+ \frac{q_0\pi}{b_0} \exp\left(-\frac{2\omega}{b_0J}\right) + \left. \frac{1}{2} \frac{p_2\pi}{a_2} \exp\left(-\frac{2\omega}{a_2J}\right) \right]$$

(5.4.3)

This equation represents a universal curve which does not depend on any parameters except the ratio $(\omega/J)$. Substituting a guess value for $J$ as well as the experimental data to the above equation, the value of $J$ was extracted from the best fit to the universal curve corresponding to each coverage. As shown in figure (5.4.1) for $x = 0.8$ monolayer, the best value of $J$ was found to be $7.7 \times 10^6$ Sec$^{-1}$. The optimum values of $J$ for densities extended between $x = 0.74$ and $x = 0.86$ monolayer were fitted to the universal curve as illustrated in figure (5.4.2).
Figure 5.4.1

Choice of $J$ from $T_1$ data. $x=0.8$ monolayer, $T=1.2$ K and $\beta=90$ deg.
Universal curve for the determination of $J$ at different coverages. $T=1.2\,K$ and $\beta=90^\circ$. 

Figure 5.4.2
On the other hand, the exchange frequency \( J \) was evaluated from \( T_1 \) at the minima (Cowan et al 1987). These values were excellently agreed with the values of \( J \) evaluated from \( T_1 \) away of minima as will see in figure (5.4.8).

The values of \( J \) were then substituted into equation (5.4.2) and the theoretical curve of the variation of \( 1/T_1 \) with frequency for the corresponding coverage was fitted to the experimental data as shown in figures (5.4.3), (5.4.4) and (5.4.5).

5.4.2 Calculation of \( J \) using \( T_2 \) Data:

As mentioned previously §4.5, the substrate local fields make a significant contribution to \( T_2 \). Experimentally, a linear relation between \( T_2 \) and Larmor frequency \( \omega_0 \) has been observed and the following equation is satisfied (Cowan et al 1987b):

\[
\frac{1}{T_2} = A + B\omega_0
\]  
(5.4.4)

where the frequency dependent part \( B \) is the contribution from the diamagnetism of the grafoil local fields. The intercept \( A \) is the dipolar part of the relaxation.

Figure (5.4.6) shows the variation of the intercept with coverage at the high density region. The values of \( A \) increases monotonically with \( x \). The extrapolation of \( A \) at lower densities of the solid phase gave a base line of value \( \approx 80 \text{Sec}^{-1} \). The contribution from the dipole-dipole interaction is still considered as the main part of relaxation. But the fact that there are other mechanisms (Cowan and Kent 1984) which affect the relaxation cannot be ignored. The relaxation of the particles which are trapped in positions of high adsorption energy such as touching platelet edges, is one of these mechanisms. By increasing the amount of sample, these effects become negligible with respect
Figure 5.4.3

Theoretical fitting of the variation of experimental $1/T_1$ with frequency.  

$T=1.2\, K$ and $\beta=90^\circ$
Figure 5.4.4

Theoretical fitting of the variation of experimental $1/T_1$ with frequency.

$T=1.2$ $K$ and $\beta=90$ deg.
Theoretical fitting of the variation of experimental $1/T_1$ with frequency.

$T=1.2$ K and $\beta=90$ deg.
Figure 5.4.6

The variation of the intercept of \((1/T_2 & f_0)\) with the change of coverage.

\(T=1.2\) K and \(\beta=90\) deg.
Figure 5.4.7

\( J \) obtained from \( T_2 \) data, \( T_1 \) (min.) and \( T_1 \) away from minima, as functions of coverage. \( T=1.2 \) K and \( \beta = 90^\circ \). Values of \( T_2 \) are not corrected for the "solid patches"."
Figure 5.4.8

The variation of $J$ obtained from $T_2$, $T_1$ (min.) and $T_1$ away from minima with coverage.

$T=1.2$ K and $\beta=90^\circ$
to the ordinary dipolar relaxation. To eliminate such contributions, subtraction of the base line was essential especially in the low densities of solid. Based on the following equation the values of $T_2^{\text{dipolar}}$ have been distinguished.

$$
\frac{1}{T_2^{\text{intercept}}} = \frac{1}{T_2^{\text{dipolar}}} + \frac{1}{T_2^{\text{base-line}}}
$$

(5.4.5)

The analysis of $T_2$ has been done by following the same fashion as at registry. Therefore, the same dipolar correlation functions were substituted in equation (2.5.2) for the FID. As before, the small contribution from the non-adiabatic part of the relaxation has been ignored and the attention was paid to the adiabatic part only. Thus the values of the exchange frequency $J$ corresponding to each coverage were evaluated.

The values of $J$ vary from $4.5 \times 10^7$ sec.$^{-1}$ at $x = 0.74$ monolayer to $2 \times 10^6$ Sec.$^{-1}$ at $x = 0.88$ monolayer. At higher densities, from $x = 0.9$ monolayer up to monolayer completion, the values of $T_2$ become very short and dipole-dipole interaction dominates. Hence the linearity of $1/T_2$ with $\omega_0$ is not seen any more, as shown in figure (5.3.5). Then $J$ can be deduced directly from $T_2$ without the need to subtract a base line value. Nevertheless, we subtracted it from the whole region to be sure that we were analyzing solely the dipolar part. Figure (5.4.7) displays the change of $J$ with coverage if we ignored the effect of the other mechanisms and considered that the values of the intercept $A$ present the pure dipolar effect for all densities. However, this is not the case at least for the low density solid since the discrepancy between the values of $J$ obtained from both $T_1$ and $T_2$ is clear. Figure (5.4.8) displays the values of $J$ obtained from $T_1$ away from minima and from $T_1$ at the minima (Cowan et al 1987) as well as from $T_2$ dipolar. The agreement between these values is striking. Table (5.4.1) shows most of the values of $J$ with the corresponding coverage
Table 5.4.1

The Change of Exchange Frequency as a function of Interatomic Distance and Coverage.

<table>
<thead>
<tr>
<th>R(Å)</th>
<th>J × 10⁻⁸ (Sec.)⁻¹</th>
<th>Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.256</td>
<td>0.1</td>
<td>0.984</td>
</tr>
<tr>
<td>3.27</td>
<td>0.1</td>
<td>0.976</td>
</tr>
<tr>
<td>3.289</td>
<td>0.11</td>
<td>0.964</td>
</tr>
<tr>
<td>3.306</td>
<td>0.41</td>
<td>0.955</td>
</tr>
<tr>
<td>3.34</td>
<td>0.64</td>
<td>0.935</td>
</tr>
<tr>
<td>3.42</td>
<td>0.97</td>
<td>0.892</td>
</tr>
<tr>
<td>3.45</td>
<td>2.0</td>
<td>0.877</td>
</tr>
<tr>
<td>3.494</td>
<td>1.8</td>
<td>0.855</td>
</tr>
<tr>
<td>3.54</td>
<td>3.3</td>
<td>0.833</td>
</tr>
<tr>
<td>3.58</td>
<td>3.5</td>
<td>0.814</td>
</tr>
<tr>
<td>3.599</td>
<td>5.53</td>
<td>0.805</td>
</tr>
<tr>
<td>3.612</td>
<td>7.456</td>
<td>0.8</td>
</tr>
<tr>
<td>3.622</td>
<td>7.71</td>
<td>0.795</td>
</tr>
<tr>
<td>3.62</td>
<td>9.6</td>
<td>0.793</td>
</tr>
<tr>
<td>3.645</td>
<td>10.7</td>
<td>0.785</td>
</tr>
<tr>
<td>3.648</td>
<td>11.184</td>
<td>0.784</td>
</tr>
<tr>
<td>3.656</td>
<td>14.6253</td>
<td>0.781</td>
</tr>
<tr>
<td>3.685</td>
<td>17.7797</td>
<td>0.768</td>
</tr>
<tr>
<td>3.692</td>
<td>20.73</td>
<td>0.765</td>
</tr>
<tr>
<td>3.698</td>
<td>21.5078</td>
<td>0.763</td>
</tr>
<tr>
<td>3.703</td>
<td>23.8019</td>
<td>0.761</td>
</tr>
<tr>
<td>3.717</td>
<td>28.82</td>
<td>0.755</td>
</tr>
<tr>
<td>3.72</td>
<td>30.0</td>
<td>0.754</td>
</tr>
<tr>
<td>3.77</td>
<td>45.0</td>
<td>0.734</td>
</tr>
</tbody>
</table>
or equivalently the interatomic distance. As observed; the value of $J$ decreases with the increase of the amount of sample as expected.

All the above analyses have been done using the Heisenberg exchange Hamiltonian which represents a two particle exchange. On the other hand, based on three-particles exchange, Roger (1984) has deduced an expression for the exchange frequency $J$ with the change of the interatomic distance $a$ given as follows:

$$\frac{J_T}{k_B} \approx 73 \left( \frac{\sigma^*}{a} \right)^{19/2} \exp \left[ -51.7 \left( \frac{\sigma^*}{a} \right)^5 \right]$$

This expression is given in units of the temperature K. Where $\sigma^* = \sigma = 2.65$ Å is the Lenard-Jones parameter. $k_B$ is Boltzmann constant and $J_T = J \hbar$ is in units of energy. Hence the exchange frequency $J$ is given theoretically by the following equation:

$$J \approx 73 \frac{k_B}{\hbar} \left( \frac{\sigma^*}{a} \right)^{19/2} \exp \left[ -51.7 \left( \frac{\sigma^*}{a} \right)^5 \right] \quad (5.4.6)$$

Comparison between the experimental values of $J$ and the theoretical curve is made. As displayed in figure (5.4.9), the agreement between both of them was satisfactory specially at lower densities.

The best fit for the change of $J$ with the interatomic distance was found to be a straight line which satisfies the following equation:

$$J = \exp(c_1 + c_2 a) \quad (5.4.7)$$

Where the parameters $c_1 = -39.6107$ and $c_2 = 11.5222$ were determined from a least square fitting of the values of $J$ determined from both $T_1$ and $T_2$. This fitting is shown in figure (5.4.10). Comparison with $J$ obtained by Sussex group (Cowan et al 1977), (Owers-Bradley 1978) was made. Although the
Comparison between $J$ obtained from both $T_1$ and $T_2$ with $J$ calculated by Roger.
Least square fitting of $J$ obtained from $T_1$ and $T_2$
experimental data are more or less the same, nevertheless using different model for the spectral densities to analyze these data gave an order of magnitude difference between $J$ obtained by them and our $J$.

5.5 Anisotropy of $T_2$:

With grafoil used as a substrate, it was possible to study the anisotropy of $T_1$ and $T_2$ at different coverage. Figure (5.5.1) illustrates the change of $1/T_2$ with the angle $\beta$ at coverages $x = 0.96, 0.98$ monolayer and one complete layer at temperature equals 1.2 K and Larmor frequency of 5.1 MHz. It is clear that $1/T_2$ goes through a minimum around the angle $\beta = 50^\circ$ for coverages $x < 1.0$ complete layer. Sato and Sugawara (1980) observed a peak around $\beta = 45^\circ$ for $T_2$ angle dependence at $T = 1.2$ K and $f_0 = 10$ MHz. According to their report, as well as Cowan (1980), this is a characteristic of the two dimensional system of spins interacting through dipolar interaction. The variation of $1/T_2$ with the angle of orientation at $x = 1.01$ layer is illustrated in figure (5.5.2) where the minimum does not exist anymore.

Figure (5.5.3) shows the change of $1/T_2$ with angle at $f_0 = 5.1$ MHz for temperatures 1.2 K and 4.2 K at $x = 0.96$ monolayer. The dependence at 4.2 K looks similar to that obtained at registry figure (4.7.4). According to Sato and Sugawara (1980) who found the same behaviour, the mechanism of $T_2$ at this temperature is provided by Robertson's mechanism of bounded diffusion. The anisotropy of $1/T_2$ determined at $T = 4.2$ K for coverage $x = 0.99$ monolayer and one layer completion is displayed in figure (5.5.4).

Recall equation (2.5.2) and Compare the experimental $T_2$ at $T = 1.2$ K and $f_0 = 5.1$ MHz with the calculated $T_2$ using different $J$ at various angles. This was made to check the accuracy of the obtained value of $J$ from $T_2$ data. Figure (5.5.5) illustrates the experimental values as well as values obtained using
Figure 5.5.3

The variation of spin-spin relaxation rate & angles. \( x = 0.96 \) monolayer and \( f_0 = 5.1 \) MHz.
Figure 5.5.4

The rate of spin-spin relaxation time as a function of the angle of orientation.

$T=4.2 \text{ K and } f_0=5.1 \text{ MHz.}$
arbitrary $J$ at coverage $\varphi = 0.98$ monolayer. The values $J = 0.5 \times 10^4, 1.5 \times 10^4$ and $3 \times 10^4$ Sec. were used to plot the curves for $T_f$ dipolar. Similar calculations were made for $\varphi = 0.98$ monolayer at $J = 10^4$ and $1 \times 10^5$ Sec. as shown in figure (5.5.6).

**Figure 5.5.6**

Comparison between $1/T_2$ obtained experimentally and by using arbitrary $J = 0.98$.
arbitrary $J$ at coverage $x = 0.96$ monolayer. The values $J = 9.5 \times 10^4$, $1.7 \times 10^5$ and $4.1 \times 10^5$ Sec$^{-1}$ were chosen. The latest was the value of $J$ obtained from $T_2$ dipolar. Similar calculations were made at $x = 0.98$ monolayer at $J = 1 \times 10^5$ and $4 \times 10^5$ Sec$^{-1}$ as shown in figure (5.5.6).

6.1 Summary of the Experimental Work

This work has been done to study the NMR properties of the adsorbed
on exfoliated graphite through the determination of the relaxation times $T_1$ and $T_2$ of the same system. In this final chapter, a picture of the work and
comparison with other groups will be given.

$T_1$ and $T_2$ were determined as functions of coverage, frequency,
temperature and angle of orientation at the registered phase and solid phase.
Some data were taken at similar phase as well. If not stated, then the
frequency is 5.7 MHz, the temperature is 1.3 K and $\theta$ is 30 degree.

6.1.1 The Registered Phase

At this phase, $T_1$ and $T_2$ were determined at coverages of 0.85
and 0.97 monolayers where the change was every 0.2 monolayers. Each for several
between 0.85 and 0.97 monolayer the coverage was in 0.05 steps. The frequencies were
1.3, 2.6, 3.9, 5.1, 6.2, 7.5 and 8.8 MHz. $T_1$ and $T_2$ at 1.3 K and $\theta = 30^\circ$ were
found at perfect registration with $T_1$ and $T_2$ which indicates the flexibility of the
spin mobility. This opinion were studied by present phase.
CHAPTER 6

Summary and Future Work

6.1 Summary of the Experimental Work:

This work has been done to study the NMR properties of $^3$He adsorbed on exfoliated graphite through the determination of the relaxation times $T_1$ and $T_2$ of the spins system. In this final chapter, a summary for the work and comparison with other groups will be given.

$T_1$ and $T_2$ were determined as functions of coverage, frequency, temperature and angle of orientation at the registered phase and solid phase. Some data were taken at mixed phase as well. If did not state; then the working frequency is 5.1 MHz, the temperature is 1.2 K and $\beta$ is 90 degree.

6.1.1 The Registered Phase:

At this phase, $T_1$ and $T_2$ were determined at coverages $x = 0.5$ to 0.57 monolayer where the change was every 0.2 monolayer, while for coverages between 0.57 and 0.625 monolayer the change was in 0.005 steps. For frequencies 1.3, 2.6, 3.9, 5.1, 6.2, 7.5 and 8.3 MHz; $T = 1.2$ K and $\beta = 90^\circ$, a minima were found at perfect registry for both $T_1$ and $T_2$ which indicate the reduction of the spins mobility. This minima were found by Sussex group.

Frequency dependence of $T_1$ and $T_2$ was determined for the mentioned coverages. It was found that $T_1$ obeys a logarithmic law with frequency while $T_2$ is linear. For coverages $x = 0.59$, 0.6, 0.61 and 0.62; frequency dependence of $T_1$ was determined at angles 0 and 45 besides 90°.
For a number of coverages at \( \varphi = 0.59, 0.6, 0.605, 0.61 \) and \( 0.615 \) monolayer, \( T_1 \) and \( T_2 \) were determined as a function of temperature rate for frequencies 5.1 and 2.6 MHz. The activation temperature was evaluated from these graphs and was found to have a maximum of 8.8 K at perfect registry in agreement with Sussex group.

The anisotropy of \( T_1 \) was determined at \( \varphi = 0.58, 0.59, 0.6 \) and 0.605 monolayer for frequencies 2.6 and 5.1 MHz, but it did not show a dramatic change. On the other hand, the anisotropy of \( T_2 \) was determined at \( \varphi = 0.58, 0.59, 0.6 \) and 0.61 at frequencies 2.6, 5.1 and 8.3 MHz. It was found that the change of \( T_2 \) is frequency dependent while it was coverage independent, the same behaviour was found by Sato and Sugawara.

The correlation time of the quantum motion \( \tau_c \) was evaluated using different data. It was obtained from \( T_1 \) by using the dipolar correlation functions model; as well as from \( T_1 \) angle dependence. \( T_2 \) data were used to extract \( \tau_c \) by separating the dipolar relaxation from other mechanisms. The change of \( \tau_c \) with coverage gave a maximum value of the order of \( 10^{-8} \) Sec corresponding to perfect registry. By using this value of \( \tau_c \), it was found that the diffusion coefficient \( D \) in this region is of the order of \( 10^{-9} \) cm\(^2\) Sec\(^{-1}\) which is the same order as obtained by Sussex group.

6.1.2 The Mixed Phase:

On the mixed phase which extends between the registered phase and the solid phase; \( T_1 \) and \( T_2 \) data showed coverage independence. It is thought that this phase is a combination of both registry and solid. The contribution from both phases was determined.
6.1.3 The Solid Phase:

For a wide range of frequencies extended between 1.3 and 10.2 MHz; $T_1$ and $T_2$ were determined at coverages between 0.7 and one layer completion in 0.2 steps. At $T = 1.2$ K, $T_1$ showed a minimum which shifts to lower coverage for higher frequencies, while at $T = 4.2$ K the minima seems to occur at higher coverage. For both temperatures $T_2$ decreases to reach its lowest value near by the complete layer. The same behaviour was observed by Sussex group for both $T_1$ and $T_2$.

$T_1$ and $T_2$ were determined with the change of frequency at both $T = 1.2$ and $T = 4.2$ K. For coverages between 0.7 and 0.94 monolayer $T_2$ was determined using the spin echo technique, while because of the short value of $T_2$ at higher coverages, the FID method was used. At these high coverages, the inhomogeneity of the magnet $T_2^{\text{mag}}$ was determined.

The characteristic frequency of the exchange motion $J$ was determined. Using the same correlation functions which have been used at registry for $T_1$ and fitting guess values for $J$ on a universal curve, the optimum values of $J$ were obtained from $T_1$. Following the same way of analysis as the registered phase and separate $T_2$ dipolar, the values of $J$ were determined. Comparison with $J$ obtained from $T_1$ at the minima (Cowan et al 1987), it was found that $J$ decreases with the increase of density which indicates slowing down of the spins motion. These values of $J$ were found one order of magnitude difference than the corresponding values obtained by Sussex.

Some $T_2$ anisotropy data were taken at 1.2 K for coverages $x = 0.96, 0.98$ and one layer showed minima for $1/T_2$ around $\beta = 50^\circ$ which indicate dipolar relaxation (Cowan 1980), these minima were observed by Sato and Sugawara as well. The anisotropy of $T_2$ at 4.2 K and coverages $x = 0.96, 0.99$ and complete
layer for frequency 5.1 MHz showed the same behaviour as found at registry which concludes that at high temperature, the dipole-dipole relaxation is not dominant.

6.2 Suggestions for Future Work:

In the light of this work and the work of other groups, attention should be paid to several points either theoretically or experimentally and the need of new work to be done such as:

(1) Theoretical study of the effect of the diamagnetic local fields of grafoil which affect the spin-spin relaxation time.

(2) Study of the effect of the edges of grafoil layers and the wall domains on the amount of $^3$He adsorbed on the grafoil surface.

(3) On the same time, a better substrate than grafoil might be used. Provided that it has a bigger surface area and lower diamagnetic effects.

(4) Experiments should be carried on the mixed phase at temperature less than 1.2 K to investigate the nature of the film and determine the actual contribution from both registry and solid phases.

(5) Experiments to determine the diffusion coefficient at different fractions of monolayer should be tried.

(6) New theories to investigate the linear dependence seen between $1/T_2$ and $\omega_0$ in all experiments at the registered phase and the solid phase.
APPENDIX "A"

The Magnetization System After Applying 90° or 180° Pulse:

For a system in thermal equilibrium, the expectation value $a(t)$ of an operator $A(t)$ is given (Cowan 1987) as:

$$a(t) = \frac{\text{Tr} \{ A(t) \exp(-\beta \mathcal{H}) \}}{\text{Tr} \{ \exp(-\beta \mathcal{H}) \}}$$

where $\beta = \frac{1}{k_B T}$.

The time evolution of an operator is described by the Heisenberg equation of motion as follows:

$$\frac{d}{dt} A(t) = \frac{i}{\hbar} [\mathcal{H}, A(t)]$$

by integrating the previous equation we obtain:

$$A(t) = \exp \left( \frac{i}{\hbar} \mathcal{H} t A \exp - \frac{i}{\hbar} \mathcal{H} t \right)$$

where $A = A(0)$ is the Schrödinger representation for the operator. Hence the equation of $a(t)$ takes the form:

$$a(t) = \frac{\text{Tr} \left\{ \exp \left( \frac{i}{\hbar} \mathcal{H} t A \exp - \frac{i}{\hbar} \mathcal{H} t \exp(-\beta \mathcal{H}) \right) \right\}}{\text{Tr} \{ \exp(-\beta \mathcal{H}) \}} \quad (A1)$$

Since in NMR the spin system is disturbed, then, a non-equilibrium system should be introduced. However, the non-equilibrium state could be treated as an equilibrium state of different or fictitious Hamiltonian (Cowan 1987). If the system initially had the fictitious Hamiltonian $\mathcal{H}'$ and the time
evolution is generated by the real Hamiltonian $\mathcal{H}''$; equation (A1) can be written on the form:

$$a(t) = \text{Tr} \left\{ \exp \left[ \frac{i}{\hbar} \mathcal{H}'' t A \exp \left( - \frac{i}{\hbar} \mathcal{H}'' t \exp - \beta \mathcal{H}' \right) \right] \right\} / \text{Tr} \left\{ \exp - \beta \mathcal{H}' \right\}$$

The general Hamiltonian of the NMR system is given by equation (2.2.1).

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_d + \mathcal{H}_m$$

Where $\mathcal{H}_z + \mathcal{H}_m \gg \mathcal{H}_d$; and so $\mathcal{H}_d$ could be ignored. Thus the spin energy states are the equally spaced eigenstates of the Zeeman Hamiltonian. Assuming high temperature limit and bearing in mind that $\text{Tr} A(t) = 0$, the expectation value equation could be reduced (Cowan 1987) to the form:

$$a(t) = \text{Tr} \left\{ -\beta \mathcal{H} A(t) \right\} / \text{Tr} \left\{ 1 \right\}$$

(A2)

In a real NMR system, the non-equilibrium states are created either by applying $90^\circ$ pulse or/and $180^\circ$ pulse to the spin system. The first pulse rotates the equilibrium magnetization which was pointing in $z$-direction to the $x$-$y$ plane; while the second one rotates it to $-z$-direction. Where the Hamiltonian in both cases is given as:

$$\mathcal{H}_{90^\circ} = -B_0 \gamma \hbar I_x$$

$$= -\hbar \omega_0 I_x$$

$$\mathcal{H}_{180^\circ} = -\hbar \omega_0 I_y$$

Following Cowan (1987), and by comparison with equation (A2), the transverse magnetization $m_x(t)$ could take the following form:

$$m_x(t) = \beta \hbar \omega_0 \text{Tr} \left\{ M_z(t) I_x \right\} / \text{Tr} \left\{ 1 \right\}$$
but $M_x(t)$ is the magnetic moment per unit volume in x-direction.

$$M_x(t) = \frac{1}{V} \sum_j \mu_{xj} = \frac{1}{V} \gamma \hbar I_x(t)$$

Hence we can write:

$$m_x(t) = \frac{\gamma \beta \hbar^2 \omega_0}{V} \text{Tr} \{ I_x(t) I_x(0) \} / \text{Tr} \{ 1 \} \quad (A3)$$

$$m_y(t) = \frac{\gamma \beta \hbar^2 \omega_0}{V} \text{Tr} \{ I_y(t) I_y(0) \} / \text{Tr} \{ 1 \} \quad (A4)$$

similarly, after applying 180° the equilibrium magnetization will have the form

$$m_x(t) = -\frac{\gamma \beta \hbar^2 \omega_0}{V} \text{Tr} \{ I_x(t) I_x(0) \} / \text{Tr} \{ 1 \} \quad (A5)$$

to transfer this equation to the following form,

$$m(t) = \frac{\Delta m}{2} \text{Tr} \{ I_x(0) I_x(0) \} / \text{Tr} \{ 1 \}$$

this implies that the following equality should be valid,

$$\Delta \text{Tr} \{ I_x(0) I_x(0) \} = \text{Tr} \{ m_x(t) M_x(0) \}$$

It seems reasonable to try the effect of adding the other part of the operator $I_{xz}$, by which is meant $I_y$. First, this operator is treated as follows:

$$H = \text{Tr} \{ I_x(0) I_y(0) \}$$

$$= \text{Tr} \{ I_x(0) + I_y(0) \}$$

$$= \text{Tr} \{ I_x(0) I_y(0) + I_y(0) I_x(0) \}$$

$$= \text{Tr} \{ I_x(0) I_y(0) \} - \text{Tr} \{ I_y(0) I_x(0) \}$$

since the rotation about z-direction does not affect the operators, we have $I_y = I_z$ and $I_y = I_z$,

$$H = \text{Tr} \{ I_x(0) I_y(0) \} = \text{Tr} \{ I_y(0) I_x(0) \}$$
APPENDIX "B"

Transformation of $I_z$ into $I_-$ in Magnetization expression:

In equation (2.2.6), the expression of the complex magnetization is given by:

$$m(t) = \frac{\gamma \beta h^2 \omega_0}{V} \frac{Tr \{I_+(t)I_z(0)\}}{Tr \{1\}}$$

to transfer this equation to the following form,

$$m(t) = \frac{\gamma \beta h^2 \omega_0}{2V} Tr \{I_+(t)I_-(0)\} / Tr \{1\}$$

this implies that the following equality should be valid,

$$2Tr \{I_+(t)I_z(0)\} = Tr \{I_+(t)I_-(0)\}$$

It seems reasonable to try the effect of adding the other part of the operator $I_-$, by which is meant $I_y$. First; this operator is treated as follows:

$$II = iTr \{I_+(t)I_y(0)\}$$

$$= iTr \{[I_z(t) + iI_y(t)]I_y\}$$

$$= iTr \{I_z(t)I_y + iI_y(t)I_y\}$$

$$= iTr \{I_z(t)I_y(0)\} - Tr \{I_y(t)I_y(0)\}$$

since the rotation about z-direction does not affect the behaviour of the system;

$I_y \rightarrow I_z$ and $I_z \rightarrow -I_y$,

$$II = iTr \{-I_y(t)I_z(0)\} - Tr \{I_z(t)I_z(0)\}$$

$$= -iTr \{I_y(t)I_z(0)\} - Tr \{I_z(t)I_z(0)\}$$
\[ II = -\text{Tr} \{ I_x(t)I_x(0) + iI_y(t)I_z(0) \} \]
\[ = -\text{Tr} \{ [I_x(t) + iI_y(t)]I_x(0) \} \]

Finally this means that,
\[ i\text{Tr} \{ I_z(t)I_y(0) \} = -\text{Tr} \{ I_z(t)I_y(0) \} \]

Therefore if we add and subtract the above equation from the original term \( \text{Tr} \{ I_z(t)I_y(0) \} \) we obtain,
\[ \text{Tr} \{ I_z(t)I_y(0) \} = \text{Tr} \{ I_z(t)I_y(0) \} - i\text{Tr} \{ I_z(t)I_y(0) \} - \text{Tr} \{ I_z(t)I_y(0) \} \]
\[ 2\text{Tr} \{ I_z(t)I_y(0) \} = \text{Tr} \{ I_z(t)I_y(0) - iI_z(t)I_y(0) \} \]
\[ = \text{Tr} \{ I_z(t)[I_z(0) - iI_y(0)] \} \]
\[ = \text{Tr} \{ I_z(t)I_- (0) \} \]

And hence, our target will be reached.
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