THE DIFFUSION OF ACETONE INTO POLYVINYL CHLORIDE

By

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A thesis submitted to the Faculty of Science at the University of Surrey for the degree of Doctor of Philosophy

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August 1994
ABSTRACT

The diffusion of small molecules into glassy polymers is often observed to be of the anomalous Case II type. This thesis describes the first comprehensive study of acetone vapour penetrating into PVC. It has been shown that this diffusion process is of the Case II type. The initial stages of the diffusion process have been studied using ion beam nuclear reaction analysis (NRA) whilst long range diffusion has been studied using broadline nuclear magnetic resonance (NMR) imaging techniques. This is the first time that short and long term behaviour has been studied in the same system and has permitted a test of the Thomas and Windle theory covering both regimes. It is also the first time that broadline NMR imaging has been used to study Case II diffusion and this has permitted a study of the polymer as well as the penetrant. A new NMR technique has been developed for this.

Characteristic parameters of the diffusion process have been determined. The velocity of the diffusion front advance is typically 0.042 mm hr\(^{-1}\) and the diffusion coefficient is 7 \times 10^{11} \text{ cm}^2 \text{s}^{-1} at room temperature. The effects of variation of exposure temperature and the activity of the vapour on the diffusion dynamics have been investigated. The NMR profiles have shown an unexpectedly long Fickian precursor extending into the inner glassy core of the samples. To complement the NMR imaging results, the NMR spin spin relaxation times of samples have been measured, and high resolution \(^{13}\text{C}\) NMR spectroscopy has been performed on the samples.

Evidence has been found for continued disentanglement of the polymer chains long after mass equilibration of the region of the PVC swollen by acetone vapour. This disentanglement has been shown to be strongly dependent on the exposure temperature.
ACKNOWLEDGEMENTS

I would like to gratefully acknowledge the help and guidance of my supervisors, Peter McDonald and Tony Clough. I am grateful for the collaboration with Ed Randall of Queen Mary College, London and Klaus Zick of Bruker Analytische Messtechnik GmbH, Rheinstetten; Richard Jones of the Polymer and Colloids group at Cambridge and the ULIRS solid state NMR service at University College, London. I acknowledge the Science and Engineering Research Council for a studentship.

Many thanks go to Willy and Roger in the mechanical workshop, the electronics workshop and all the secretaries who have put up with me for a long time now. I would like to acknowledge the Microstructural Studies Unit for their help with samples and Simon at Cambridge for the use of the DSC machine. Thanks also to John Strange and Morley Halse for useful discussions, to my sister Charlie for typing this thesis and to Mary Gunney for proof reading it.

Now, thanks to all my friends in the Physics department. Firstly to all in the lab, Steve, Tim, Martin and Pete; to everyone in the office, especially Dave for the use of his computer; to Warren, Jo, Gareth and Lawrence, who have survived the department as long as I have; and lastly to Kay.

A big thank you must go to John and James for putting up with me and my computer at home while I've been writing up, it can't have been easy. Now, the most important thank you to my family, especially Mum, and especially to Lewis, whose NMR expertise has been invaluable. Without all your unfailing love, support and guidance throughout this, I don't think I would have completed it.
# TABLE OF CONTENTS

## CHAPTER 1 NUCLEAR MAGNETIC RESONANCE AND CHARGED PARTICLE BEAM ANALYSIS THEORY

1.1 Introduction .......................... 1  
1.2 NMR theory .......................... 2  
  1.2.1 Nuclear excitation and relaxation 2  
    1.2.1.1 Classical approach 2  
    1.2.1.3 Spin locking and $T_1p$ 7  
    1.2.1.4 $T_2^*$ relaxation 9  
    1.2.1.5 Quantum mechanical approach 9  
    1.2.1.6 The complete Hamiltonian 14  
    1.2.1.7 Dipole dipole interaction 15  
    1.2.1.8 BPP theory 18  
  1.2.2 Signal detection ............ 21  
    1.2.2.1 Free induction decay 21  
    1.2.2.2 The Hahn echo 23  
    1.2.2.3 The solid echo 23  
    1.2.2.4 Measurement of relaxation times 23  
  1.2.3 Imaging .................. 26  
    1.2.3.1 Two dimensional Fourier Transform Imaging 29  
    1.2.3.2 Projection reconstruction 30  
    1.2.3.2 The gradient echo 32  
    1.2.3.3 Introduction to the difficulties of broadline imaging 32  
    1.2.3.4 The broadline gradient echo imaging technique 34  
    1.2.3.5 The stray field imaging technique 37  
1.3 Ion Beam Nuclear Reaction Analysis 39  
  1.3.1 Introduction ............... 39  
  1.3.2 The $d(^3\text{He},p)^4\text{He}$ nuclear reaction 39  
  1.3.3 Advantages of using the $d(^3\text{He},p)^4\text{He}$ reaction to measure diffusion profiles 41  
  1.3.4 Experimental geometry 43  
    1.3.4.1 Detection of reaction products 45

## CHAPTER 2 OVERVIEW OF POLYMER SYSTEMS AND DIFFUSION PROCESSES IN POLYMERS

2.1 Introduction ..................... 47  
2.2 Polymers .......................... 48  
  2.2.1 Molecular structure 49  
  2.2.2 Morphology 49  
  2.2.3 Molecular motion 50  
  2.2.4 Differential scanning calorimetry 52
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2.5</td>
<td>Mechanical and thermal properties</td>
<td>54</td>
</tr>
<tr>
<td>2.3</td>
<td>Diffusion processes</td>
<td>54</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Introduction</td>
<td>54</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Fickian diffusion</td>
<td>55</td>
</tr>
<tr>
<td>2.3.3</td>
<td>Case II diffusion</td>
<td>57</td>
</tr>
<tr>
<td>2.3.3.1</td>
<td>Thomas and Windle model</td>
<td>59</td>
</tr>
<tr>
<td>2.3.3.2</td>
<td>Computer simulation of diffusion profiles using Thomas and Windle theory</td>
<td>64</td>
</tr>
<tr>
<td>2.3.3.3</td>
<td>Effects of temperature and activity on Case II diffusion</td>
<td>65</td>
</tr>
<tr>
<td>2.3.3.4</td>
<td>Recent studies of Case II diffusion</td>
<td>66</td>
</tr>
<tr>
<td>2.3.3.5</td>
<td>Review of experimental techniques used to study Case II diffusion</td>
<td>67</td>
</tr>
<tr>
<td>2.4</td>
<td>Application of NMR to the study of diffusion</td>
<td>68</td>
</tr>
<tr>
<td>2.5</td>
<td>Application of ion beam techniques to the study of diffusion</td>
<td>70</td>
</tr>
</tbody>
</table>

CHAPTER 3 DEVELOPMENT OF A REPETITIVE PULSE VARIANT OF BROADLINE GRADIENT ECHO MAGNETIC RESONANCE IMAGING

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>72</td>
</tr>
<tr>
<td>3.2</td>
<td>Degredation of pulse by gradients in the gradient echo imaging technique</td>
<td>72</td>
</tr>
<tr>
<td>3.3</td>
<td>Application of steady state free precession and rapid acquisition techniques to imaging sequences</td>
<td>74</td>
</tr>
<tr>
<td>3.4</td>
<td>Longitudinal interference in repetitive pulse experiments</td>
<td>77</td>
</tr>
<tr>
<td>3.5</td>
<td>Experimental procedure</td>
<td>79</td>
</tr>
<tr>
<td>3.5.1</td>
<td>NMR imaging spectrometer</td>
<td>81</td>
</tr>
<tr>
<td>3.5.2</td>
<td>Gradients</td>
<td>83</td>
</tr>
<tr>
<td>3.5.3</td>
<td>NMR probes</td>
<td>83</td>
</tr>
<tr>
<td>3.6</td>
<td>Results and Discussion</td>
<td>84</td>
</tr>
<tr>
<td>3.6.1</td>
<td>Testing on a rubber phantom</td>
<td>84</td>
</tr>
<tr>
<td>3.7</td>
<td>Conclusion</td>
<td>88</td>
</tr>
</tbody>
</table>

CHAPTER 4 CHARACTERISATION EXPERIMENTS ON THE PVC AND ACETONE SYSTEM

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>89</td>
</tr>
<tr>
<td>4.2</td>
<td>Experimental details</td>
<td>90</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Exposure to solvents</td>
<td>92</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Exposure to reduced vapour activities</td>
<td>93</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Sample preparation</td>
<td>94</td>
</tr>
<tr>
<td>4.3</td>
<td>Relaxation time experiments</td>
<td>94</td>
</tr>
<tr>
<td>4.4</td>
<td>Initial two dimensional imaging experiments using gradient echo and samples with cylindrical geometry</td>
<td>95</td>
</tr>
<tr>
<td>4.5</td>
<td>Tests on different coloured PVC</td>
<td>100</td>
</tr>
<tr>
<td>4.6</td>
<td>Gravimetric analysis</td>
<td>101</td>
</tr>
</tbody>
</table>
### CHAPTER 5 CASE II DIFFUSION PROFILES IN THE PVC AND ACETONE SYSTEM

5.1 One dimensional NMR imaging experiments using the repetitive pulse variant of broadline gradient echo

5.2 Experimental details

5.3 Time variation

5.4 Temperature variation
   5.4.1 Spin spin relaxation time measurements

5.5 Time course experiment

5.6 Discussion

5.7 Ion beam nuclear reaction analysis to measure Case II diffusion profiles

5.8 Sample preparation
   5.8.1 Scanning microbeam method
   5.8.2 Depth profiling technique

5.9 Measurement of diffusion profiles
   5.9.1 Scanning microbeam method
   5.9.2 Depth profiling of surface layers
      5.9.2.1 Experimental details
      5.9.2.2 Detection of reaction products
      5.9.2.3 Interpretation of the channel axis scale
      5.9.2.4 Calibration of energy per channel
      5.9.2.5 Normalisation and determination of depth profiles

5.10 Experimental results
   5.10.1 Room temperature experiments
   5.10.2 Low temperature experiments

5.11 Discussion

5.12 Conclusions

### CHAPTER 6 QUANTITATIVE ANALYSIS OF CASE II DIFFUSION PROFILES

6.1 Introduction

6.2 Stray field magnetic resonance imaging to study Case II diffusion

6.3 Experimental details
   6.3.1 Sample preparation

6.4 Spin spin relaxation time measurements

6.5 Basic Case II profiles
   6.5.1 Unpenetrated rigid PVC
   6.5.2 PVC and acetone vapour
   6.5.3 PVC and deuterated acetone vapour

6.6 Thomas and Windle theory simulation program

6.7 Desorption of acetone from PVC
6.8 The effects of variation of the activity of the acetone vapour
6.9 The effects of the variation of exposure temperature
6.10 Relaxation time contrast
6.11 Analysis of profile shape
6.12 High resolution $^{13}$C NMR spectroscopy
   6.12.1 Experimental details
   6.12.2 Results
6.13 Conclusion

CHAPTER 7 CONCLUSIONS

APPENDIX 1

APPENDIX 2

REFERENCES
CHAPTER 1

NUCLEAR MAGNETIC RESONANCE AND
CHARGED PARTICLE BEAM ANALYSIS THEORY

1.1 INTRODUCTION

This chapter covers the aspects of the theory of Nuclear Magnetic Resonance and charged particle beam analysis relevant to this study. NMR imaging is a branch of science which continues to grow with advancements in both technology and realisation of potential and uses. NMR is a process in which nuclei with a non-integer spin, such as $^1$H, are placed in a static magnetic field. The application of an additional time varying orthogonal magnetic field causes excitation, leading to relaxation processes, resulting in a signal which is subsequently detected. With the use of additional magnetic field gradients the spatially encoded signals produced may be manipulated to form images.

The first two sections of this chapter cover nuclear excitation and relaxation. These may be considered, as with many branches of physics both classically and quantum mechanically. The classical description is introduced first as it provides a more easily understood explanation of the overall process. The quantum mechanical treatment which follows affords more insight and is essential for the progression to more advanced aspects of the subject such as a consideration of the dipolar interaction in solid materials. The next section covers the observed signal in its various forms, such as echoes, and its detection and measurements of relaxation times. Finally all relevant aspects of imaging are discussed along with the imaging sequences used. The theory of the ion beam nuclear reaction analysis technique is then covered, starting with the particular reaction used. All the central and relevant aspects are
discussed following which are sections on the two techniques used to obtain concentration profiles of very different spatial range and resolution.

1.2 NMR THEORY

1.2.1 NUCLEAR EXCITATION AND RELAXATION

1.2.1.1 CLASSICAL APPROACH

NMR is a phenomenon which may be observed if nuclei possessing a magnetic moment are placed in static magnetic field and allowed to interact with an applied time varying orthogonal magnetic field.

If a nucleus of an atom has magnetic moment $\mu$ and angular moment $P$, then $P$ and $\mu$ are related by the magnetogyric ratio $\gamma$

$$\mu = \gamma P$$  \hspace{1cm} 1.1

A magnetic nucleus placed in a magnetic field experiences a torque, equal to the rate of change of angular momentum

$$\frac{dP}{dt} = -\mu \wedge B$$  \hspace{1cm} 1.2

Combining 1.1 and 1.2 gives an expression for the rate of change of the magnetic moment

$$\frac{d\mu}{dt} = \mu \wedge \gamma B$$  \hspace{1cm} 1.3

2
This may be solved by expanding the cross product and integrating with respect to time. Adopting the conventional magnetic field direction of \( z \), gives the solutions

\[
\begin{align*}
\mu_x &= A_1 \cos(-\gamma B_z t + \alpha) \\
\mu_y &= A_1 \sin(-\gamma B_z t + \alpha) \\
\mu_z &= A_2
\end{align*}
\]

Where \( A_1, A_2 \) and angle \( \alpha \) are constants determined by the initial position of \( \mu \) when \( B \) was applied along the \( z \) axis. The equations show that \( \mu_z \) is time independent and therefore the angle \( \mu \) makes with \( z \) axis does not change. It can be arbitrarily set to a value \( \beta \) such as in fig 1.1. So \( \mu_z \) can be rewritten

\[
\mu_z = A_2 = |\mu| \cos \beta
\]

and hence

\[
A_1 = |\mu| \sin \beta
\]

If the magnetic moment is off axis as in fig 1.1 it precesses around \( z \) in accordance with equation 1.4 at a rate \( \omega_0 \), given by

\[
\omega_0 = \gamma B_z
\]

To simplify further analysis the present reference frame, known as the laboratory frame may be transformed by rotating at the precession frequency, \( \omega_0 \). Equation 1.3 in the laboratory frame now becomes

\[
\frac{d\mu}{dt} = \mu \wedge (\gamma B - \omega_0)
\]

In the rotating frame, the magnetic field becomes an effective field given by
Since the frequency of $\omega_0 = -\gamma B$, $B_{\text{eff}} = 0$ leaving the magnetic moment stationary. $\omega_0$ is known as the Larmour frequency and is dependent on the applied magnetic field and through $\gamma$ on the nucleus being studied.

A measurement may be effected by a pulse of oscillating magnetic field orthogonal to $z$. The oscillating field consists of two circularly polarised counter rotating fields of amplitude $B_1$. If the frequency is equal to the Larmour frequency then one will be rotating at $\omega_0$ and will appear stationary while the other will be rotating effectively $2\omega_0$ off resonance and may be ignored. Assuming $B_1$ to be in the $x'$ direction as shown in fig 1.2, where $x'$, $y'$ and $z'$ denote the axes of the rotating reference frame, the effect of $B_1$ is to rotate $\mu$ from $z'$ towards $y'$ through an angle $\phi$. The angle is determined by the duration of the pulse

$$\phi = \gamma B_1 t_p$$  \hspace{1cm} (1.10)

Since the frequency of rotation of the component of the field required for transitions is in the radio frequency region, it is known as the rf pulse. So $\mu$ may be rotated through a desired angle by an rf pulse of the appropriate length. For $\phi = \pi/2 = 90^\circ$ pulse.

A system will consist of a number of such magnetic moments $\mu_i$ and the bulk magnetisation of a sample is simply the vector sum of the components,

$$M = \sum \mu_i$$  \hspace{1cm} (1.11)
FIGURE 1.1  NUCLEAR MAGNETIC MOMENT IN THE LABORATORY FRAME

FIGURE 1.2  NUCLEAR MAGNETIC MOMENT IN THE ROTATING FRAME
When a spin system such as that described in the previous section is placed in a static magnetic field \( B_0 \) the magnetisation in the direction of the field will increase slowly to a maximum value, \( M_0 \). This value is approached exponentially with characteristic time constant, known as \( T_1 \), as noted by Bloch in 1964. Bloch also made postulations regarding the relaxation processes experienced by the components of the magnetisation following the application of an rf pulse. He stated that the \( M_x \) and \( M_y \) components could be described by exponentially decaying functions with the time constant \( T_2 \), known as the transverse relaxation time. The processes that cause the decay of \( M_x \) and \( M_y \) do not alter the total energy of the spin system. Bloch also stated that the motion of the magnetisation around \( B \) and the relaxation processes could be combined and so produced the following equations

\[
\frac{dM_x}{dt} = (M \wedge \gamma B)_x - \frac{M_x}{T_2} \tag{1.12}
\]

\[
\frac{dM_y}{dt} = (M \wedge \gamma B)_y - \frac{M_y}{T_2} \tag{1.13}
\]

\[
\frac{dM_z}{dt} = (M \wedge \gamma B)_z - \frac{(M_z - M_0)}{T_1} \tag{1.14}
\]

In the presence of pulses and in the laboratory reference frame these equations become

\[
\frac{dM_x}{dt} = \gamma (M_y B_0 - M_z B_1 \sin \omega t) - \frac{M_x}{T_2} \tag{1.15}
\]
\[
\frac{dM_y}{dt} = \gamma (-M_x B_0 + M_z B_1 \cos \omega t) - \frac{M_y}{T_2} \tag{1.16}
\]

\[
\frac{dM_z}{dt} = \gamma (M_x B_0 - M_y B_1 \cos \omega t) - \frac{M_z - M_0}{T_1} \tag{1.17}
\]

So there are two main relaxation times following a 90° pulse, the spin lattice relaxation time $T_1$ and the spin spin relaxation time $T_2$. $T_1$ is the time taken for the magnetisation to regain its equilibrium value $M_0$ along the z axis, as indicated in figure 1.3. $T_2$ is the time for the spins to fully dephase in the x-y plane due to the interactions between the spins themselves, as indicated in figure 1.4. In addition to $T_1$ and $T_2$ there are two other relaxation processes which affect the NMR signal, denoted by the characteristic times $T_2^*$ and $T_{1p}$.

### 1.2.1.3 SPIN LOCKING AND $T_{1p}$

Following a 90° rf pulse the magnetisation is in the x-y plane and experiences transverse relaxation. If the phase of the rf is altered by 90° following the pulse and its application continued, it becomes aligned with the magnetisation. In the rotating reference frame it is the only field that affects the magnetisation. The magnetisation is said to be 'spin locked' by the rf field, $B_1$. Its magnitude, however, is larger than $B_1$ can maintain as it was generated by $B_0$ and not allowed to relax as normal by the immediate phase change of the rf. The magnetisation will therefore decay to a value sustainable by $B_1$, and this value is \((B/B_0)M_0\). This relaxation is known as spin lattice relaxation in the rotating frame, or $T_{1p}$, and is commonly exponential in nature. Usually for mobile liquids $T_{1p} = T_1 \approx T_2$, and for solids it may vary substantially from both $T_1$ and $T_2$. $T_{1p}$ is encountered in solid echo sequences.
FIGURE 1.3  SCHEMATIC OF SPIN LATTICE RELAXATION

FIGURE 1.4  SCHEMATIC OF SPIN SPIN RELAXATION
1.2.1.4 \( T_2^* \) RELAXATION

In practice the magnetic field \( B_0 \) is not perfectly homogeneous. Following a 90° pulse the transverse relaxation of the spins is affected by the inhomogeneities of \( B_0 \) in addition to the spin spin interactions. This causes the magnetisation to dephase at a faster rate than for transverse relaxation in a perfectly homogeneous field. This relaxation time is known as \( T_2^* \). Since the broadening effect on the linewidth due to field homogeneity is ordered it may be 'undone'. This means that the extra dephasing can be rephased with the use of an appropriate pulse sequence as will be shown later in the chapter. This is in contrast to true \( T_2 \) relaxation which is a random and irreversible process.

1.2.1.5 QUANTUM MECHANICAL DESCRIPTION

In order to describe NMR theory Quantum Mechanically it is useful to first recall some basic results. The total angular momentum of a nucleus is made up of intrinsic spin angular momentum and orbital angular momentum and is usually known as 'spin'. The total angular momentum vector \( \mathbf{P} \) of an isolated particle is quantised and may be described by an operator \( \hat{\mathbf{P}} \). Only the magnitude \( \mathbf{P}^2 \) and one spatial component for example \( \hat{P}_z \) may be specified,

\[
\mathbf{P}^2 = I(I+1) \hbar^2 \quad \quad I = 0, \frac{1}{2}, 1, \ldots \quad 1.18
\]

\[
\hat{P}_z = m_I \hbar \quad \quad \text{for } m_I = I, I-1, \ldots \quad 1.19
\]

where \( I \) and \( m_I \) are quantum numbers and \( \hbar^2 = h/2\pi \), where \( h \) is Plank's constant. \( m_I \) takes on the values -\( I \),-\( I+1 \),...,\( I \). Once again, considering the
interaction between a magnetic moment and an applied magnetic field we may write the interaction energy as

\[-\mu \cdot B\]  \hspace{1cm} 1.20

This allows the construction of the energy operator or Hamiltonian to express the energy and stationary states of the system

\[\mathcal{H} = -\mu \cdot B\]  \hspace{1cm} 1.21

If the applied field is in the z direction, substitution for \(\mu\) gives,

\[\mathcal{H} = -B_z\gamma_\hbar \hat{I}_z\]  \hspace{1cm} 1.22

Where \(I_z\) is the angular momentum operator in the z direction. The nuclei to be considered are hydrogen nuclei, ie protons, so \(I = \frac{1}{2}\) and \(m\) has 2 values, \(\pm \frac{1}{2}\). This gives two stationary states of the system with energies,

\[E_m = -\gamma_\hbar B_0 m \hspace{1cm} m = \frac{1}{2}, \frac{1}{2}\]  \hspace{1cm} 1.23

The effect of the magnetic field, therefore is to lift the nuclear spin degeneracy of the ground state to give two magnetic sub levels, known as Zeeman levels, aligned either parallel and antiparallel to the field, with a separation of \(\gamma_\hbar B_0\). Transitions between Zeeman levels may be induced by the application of an alternating magnetic field orthogonal to \(B_0\),

\[2 B_1 \cos \omega t = B_1 (\cos \omega t - j \sin \omega t) + B_1 (\cos \omega t - j \sin \omega t)\]  \hspace{1cm} 1.24

As in the previous section this consists of two counter rotating fields, one of frequency \(\omega\) and one of \(-\omega\); \(2\omega\) off resonance, which is ignored.
The effect of the applied field is to introduce a perturbation which may be described by the following Hamiltonian,

\[ H_{\text{pert}} = -\gamma \hbar B_0 \hat{I}_z \cos \omega t \quad 1.25 \]

in the laboratory frame. In order for transitions to be induced the spin operator describing the spin perturbation must have finite values between spin states \( m' \) and \( m \). For \( I_x \) the matrix elements are \( \langle m' | \hat{I}_m | m \rangle \), and vanish unless,

\[ \Delta m = m' - m = \pm 1 \quad 1.26 \]

From 1.23

\[ \Delta E = -\gamma \hbar B_0 (m' - m) = -\gamma \hbar B_0 = -\hbar \omega_0 \quad 1.27 \]

giving

\[ \omega_0 = \gamma B_0 \quad 1.28 \]

Nuclear transitions can therefore only be stimulated by rf radiation with frequency proportional to the field strength. Consider a system of \( N \) non-interacting spin \( \frac{1}{2} \) nuclei. Let us denote the population of the upper level \( N_+ \), the lower level \( N_- \), and the population difference between them \( n \), then

\[ N_+ + N_- = N \quad 1.29 \]
\[ N_+ - N_- = n \]

The probability of a spin transition upward in energy from \( m = +\frac{1}{2} \) to \( m = -\frac{1}{2} \) is denoted by \( W^\uparrow \) and a downward transition by \( W^\downarrow \). The rate governing the population in the upper level is given by,
As there is no spontaneous emission for this system, only stimulated absorption and emission, \( W^\uparrow = W^\downarrow = W \) in this case. So substitution for \( N^+ \) and \( N^- \) gives

\[
\frac{dN^+}{dt} = N^+ W^\uparrow + N^- W^\downarrow
\]

where \( n_0 \) is the value at \( t = 0 \), and the rate of energy absorption is given by,

\[
\frac{dE}{dt} = N^+ \omega - N^- \omega
\]

\[
= \hbar \omega n
\]

The solution of which is,

\[
n = n_0 \exp(-2Wt)
\]

where \( n_0 \) is the value at \( t = 0 \), and the rate of energy absorption is given by,

This result shows that there must be a non-zero population difference between the states for net absorption of rf energy. For this population difference to occur it is clear that the spin system must be coupled to another system with which energy can be exchanged. This thermal reservoir is called the lattice and has a temperature \( T \). If thermal equilibrium is established the populations of the levels \( N_+^0 \) and \( N_-^0 \) obey a Boltzmann distribution,

\[
\frac{N_-^0}{N_+^0} = \exp\left(\frac{-\gamma \hbar B_0}{k_B T}\right)
\]

where \( k_B \) is the Boltzmann constant. In order for the exchange process to occur the nuclear levels will have the same relative populations as the corresponding
lattice levels at thermal equilibrium

\[ \frac{dN}{dt} = 0 \quad 1.35 \]

and,

\[ \frac{W^\uparrow}{W^\downarrow} = \frac{N^0}{N^0} \quad 1.36 \]

So that the probabilities of \( W^\uparrow \) and \( W^\downarrow \) are not equal. Substitution in equation 1.31 from 1.30 gives,

\[ \frac{dn}{dt} = N (W^\downarrow - W^\uparrow) - n (W^\downarrow + W^\uparrow) \quad 1.37 \]

or,

\[ \frac{dn}{dt} = \frac{n_0 - n}{T_1} \quad 1.38 \]

where,

\[ n_0 = \left( \frac{W^\downarrow - W^\uparrow}{W^\downarrow + W^\uparrow} \right) N \quad 1.39 \]

and

\[ \frac{1}{T_1} = (W^\downarrow + W^\uparrow) \quad 1.40 \]

The solution of 1.38 for a sample initially unmagnetised \( n(t=0) = 0 \) is,
This result shows that when a sample is placed in a magnetic field the magnetisation of a spin system rises exponentially to equilibrium with a time constant $T_1$, known as spin lattice relaxation time as it describes the interaction between the spins and the lattice.

1.2.1.6 THE COMPLETE HAMILTONIAN

Earlier in this section it was shown that the interaction between the applied field and the spins is described using a Hamiltonian operator. This however does not form a complete picture of the Hamiltonian for an NMR spin system as there are many more interactions to be considered. The following gives a clearer picture of the extent of the terms of the Hamiltonian which describes the NMR phenomenon.

$$\mathcal{H}_{\text{total}} = \mathcal{H}_{\text{applied field}} + \mathcal{H}_{\text{rf pulses}} + \mathcal{H}_{\text{gradients}} + \mathcal{H}_{\text{dipole dipole}} + \mathcal{H}_{\text{electric field gradients}} + \mathcal{H}_{\text{chemical shielding}} + \mathcal{H}_{\text{spin spin coupling}} + \mathcal{H}_{\text{susceptibility}} + \ldots$$

This more fully reflects the number of interactions to which the nuclei are susceptible with an indication of the relative strengths of the interactions. The
merit of removing the large influence of the applied field by use of the rotating frame is now obvious, as it swamps all other terms. Not all spin systems are affected by all interactions, indeed, one may dominate in certain circumstances. From the discussions in previous sections the first four terms need no further elaboration. However, the electric field gradient interactions are due to electric quadropole interactions present when the nuclei under observation have a spin > $\frac{1}{2}$. The chemical shielding interaction arises because of the screening of the nuclei from the magnetic field by the electrons. The energies of spins in a system may be modified by a small indirect interaction between the spins known as spin-spin coupling. Different materials have different magnetic susceptibilities, leading to changes in the magnetic field which may be severe in the case of liquids in porous solids.

1.2.1.7 DIPOLE DIPOLE INTERACTION

In solids there is not enough molecular motion to average the dipolar interaction between neighbouring nuclei to zero and it becomes the largest influence on the relaxation process. A system of spin $\frac{1}{2}$ nuclei behave as an assembly of nuclear dipoles. The magnetic field of one dipole, $\mu_1$, couples with that of another, $\mu_2$, to give an interaction whose energy is given by

$$E = \frac{\mu_1 \cdot \mu_2}{r^3} - \frac{3 (\mu_1 \cdot r)(\mu_2 \cdot r)}{r^3}$$

or in terms of the angular momentum operators

$$\mathcal{H}_{dd} = \gamma_1 \gamma_2 \hbar^2 \left[ \frac{\mathbf{l}_1 \cdot \mathbf{l}_2}{r^3} - \frac{3 (\mathbf{l}_1 \cdot r)(\mathbf{l}_2 \cdot r)}{r^5} \right] \frac{\mu_2}{4\pi}$$

where $r$ is the vector between $\mu_1$ and $\mu_2$, identical spin $\frac{1}{2}$ nuclei 1 and 2. By expressing the $x$ and $y$ terms of the hamiltonian using the raising and lowering
operators $\hat{I}^+$ and $\hat{I}$ and transforming to spherical coordinates $(r, \theta, \phi)$, as shown in fig 1.5 Van Vleck (1948) showed that the Hamiltonian may be written

$$H_{bo} = \gamma_1 \gamma_2 \hbar^2 \left( \frac{A+B+C+D+E+F}{r^3} \right)$$

where

$$A = \hat{I}_{1z} \hat{I}_{2z} (1-3\cos^2\theta)$$
$$B = -1/4 [\hat{I}_{1z}^2 + \hat{I}_{2z}^2] (1-3\cos^2\theta)$$
$$C = -3/2 [\hat{I}_{1z} \hat{I}_{2z} + \hat{I}_{1z} \hat{I}_{2z}^*] (\sin\theta \cos\theta e^{i\phi})$$
$$D = -3/2 [\hat{I}_{1z} \hat{I}_{2z} + \hat{I}_{1z} \hat{I}_{2z}^*] (\sin\theta \cos\theta e^{-i\phi})$$
$$E = -3/4 \hat{I}_{1z} \hat{I}_{2z}^* \sin^2\theta e^{2i\phi}$$
$$F = -3/4 \hat{I}_{1z} \hat{I}_{2z}^* \sin^2\theta e^{2i\phi}$$

Each of the terms A-F is the product of a spin and spatial operator. Using a set of spin $1/2$ basis states $|m_I, m_s\rangle$ written as $|\alpha\rangle$ etc, the states coupled by each of the terms may be shown diagrammatically, as in figure 1.6.

Term A is diagonal in this basis and does not give rise to any $\Delta m=\pm 1$ or $\pm 2$ transitions. It only slightly affects the energy as it is a function of $\hat{I}_{1z}^1$ and $\hat{I}_{2z}^2$. Term B is a function of $\hat{I}_{1z}^1 \hat{I}_{2z}^2 + \hat{I}_{1z} \hat{I}_{2z}^2$ and couples two otherwise degenerate states. It causes no $\Delta m=\pm 1$ or $\pm 2$ transitions, but causes transitions between states of similar energy by flipping one spin up and the other down. It is known as the flip flop term and links states $|\alpha\beta\rangle$ with $|\beta\alpha\rangle$. Terms C and D are similar and cause transitions with $\Delta m=\pm 1$ at a rate dependent on $\theta, \phi$ as they are functions of $\hat{I}_{1z} \hat{I}_{1z}$ and $\hat{I}_{1z} \hat{I}_{2z}$, i.e. one raising or lowering operator. Terms E and F are functions of two raising or lowering operators and therefore cause $\Delta m=\pm 2$ transitions and flip both spins up or down.

Terms A and B do not result in any net change in the magnetisation of the system being only $\Delta m=0$ transitions and therefore do not contribute to spin lattice relaxation. However they do contribute to spin spin relaxation. Terms
FIGURE 1.5  THE DIPOLE DIPOLE INTERACTION

FIGURE 1.6  DIAGRAMMATIC REPRESENTATION OF THE VAN Vleck TERMS
C, D, E and F represent \( \Delta m = \pm 1 \) and \( \Delta m = \pm 2 \) transitions, altering the net populations of the states and so contribute primarily to spin lattice relaxation mechanisms.

### 1.2.1.8 BPP THEORY

An early successful description of relaxation which is still widely applicable was given by Bloembergen, Purcell and Pound (1948) and has since been known as the BPP theory. The prerequisite for relaxation processes in NMR is a fluctuating field as there is no spontaneous relaxation of the nuclei. This field may be described using an autocorrelation function

\[
G(\tau) = \mathbb{E}_1(\tau) \cdot \mathbb{E}_1(\tau + \tau)
\]

where the bar indicates the time average. For a random, uncorrelated field

\[
\text{As } \tau \to 0 \quad G(\tau) \to \mathbb{E}_1^2(\tau) = \mathbb{B}^2
\]

\[
\text{As } \tau \to \infty \quad G(\tau) \to 0
\]

The exact form of \( G(\tau) \) depends on the type of motion and source of the fluctuation, however in most cases it proves sufficiently accurate to assume that an exponential describes the autocorrelation function

\[
G(\tau) = \mathbb{E}_1^2(\tau) \exp \left( -\frac{\tau}{\tau_c} \right)
\]

where \( \tau_c \) is the correlation time, that is the average time between 'spin moves' or the average fluctuation time. For solids \( \tau_c \) is long and for liquids it is short. From \( G(\tau) \) it is straightforward to find the power spectrum in terms of it's frequency distribution, as \( G(\tau) \) is in the time domain and has a function in the frequency domain, related by Fourier transformation. This is the spectral
density function, $J(\omega)$

$$J(\omega) = \int_0^\infty J_T(\tau) \exp\left(-\frac{\tau}{\tau_c}\right) \exp(-i\omega \tau) \, d\tau$$  \hspace{1cm} 1.48$$

Hence for $G(\tau)$ exponential, the spectral density function always takes the form

$$J(\omega) = \frac{2\tau_c}{1+\omega^2\tau_c^2}$$  \hspace{1cm} 1.49$$

A plot of $J(\omega)$ against frequency, figure 1.7, shows the differences for liquids, a) and solids, b). To proceed further the effects of the different spatial components must be considered. The rotating frame approach is adopted and for any magnetic field to affect a particular component of the magnetisation it cannot be parallel to it and must be static in the rotating frame. It can be seen then, that for the x and y directions the spectral density at the Larmour frequency is appropriate, while for the z axis it will be static, giving

- z relaxation rate \( \propto [J_{xx}(\omega) + J_{yy}(\omega)] \)
- x relaxation rate \( \propto [J_{yy}(\omega) + J_{zz}(0)] \)
- y relaxation rate \( \propto [J_{xx}(\omega) + J_{zz}(0)] \)

$J$ in the above expressions may be replaced by that in equation 1.49 to give the longitudinal relaxation rate, $T_1$ and the transverse relaxation rate, $T_2$

$$\frac{1}{T_1} = 2\gamma^2B^2 \left[ \frac{\tau_c}{1+\omega^2\tau_c^2} \right]$$  \hspace{1cm} 1.51$$

$$\frac{1}{T_2} = \gamma^2B^2 \left[ \tau_c + \frac{\tau_c}{(1+\omega^2\tau_c^2)} \right]$$  \hspace{1cm} 1.52$$

These relaxation rates may be sketched as a function of correlation time as
FIGURE 1.7  SPECTRAL DENSITY AS A FUNCTION OF FREQUENCY

FIGURE 1.8  RELAXATION TIMES AS A FUNCTION OF CORRELATION TIME
shown in figure 1.8. For short $\tau_c J(0) \sim J(\omega)$ which means that $T_2 \sim T_1$. For long $\tau_c J(0) \to \infty$ and $T_2 \to 0$ and so for solids $T_2 < T_1$.

### 1.2.2 SIGNAL DETECTION

#### 1.2.2.1 FREE INDUCTION DECAY

The rf pulse used to manipulate the magnetisation is supplied via a coil, which is placed around the sample. It is this coil which is then used to detect the resulting NMR signal. RF receivers work by mixing the signal emf induced in the coil by the magnetisation with the output from a reference oscillator. By separately mixing the emf with two heterodyne references $90^{\circ}$ out of phase with each other two signals are produced that are in effect the components of the magnetisation in the x and y directions. The mathematics of such signals is conveniently handled using complex numbers, with the real part corresponding to the x direction and the imaginary part to the y direction.

The NMR signal is measured in the time domain as an oscillating, decaying emf induced by the magnetisation in free precession and is therefore known as a free induction decay (FID). If the FID is Fourier transformed it gives the spectrum in the frequency domain, as shown in fig 1.9 (reproduced from Callaghan 1993). The real spectrum is known as the absorption spectrum and the imaginary is known as the dispersion spectrum. In practice the signal is sampled digitally using a finite number of sampling points with sampling interval $T$. 
Figure 1.9

Signal and Fourier transformed signal following a 90° pulse.

- Real signal
- Imaginary signal
- Real spectrum
- Imaginary spectrum

**NOTE:** The diagram illustrates the transformation of a signal from the time domain to the frequency domain after a 90° pulse. The real and imaginary components of the signal are shown, along with their corresponding spectra.
1.2.2.2 THE HAHN SPIN ECHO

The FID is the most basic NMR signal obtainable in a pulsed experiment. However the spins may be manipulated using certain pulses and timings known as sequences to produce a signal in another form, such as an echo. The spin echo was discovered in 1950 by E Hahn and is usually known simply as the Hahn echo. The effect of inhomogeneities in $B_0$ is to add an extra phase to the precessing spins in the x-y plane. By applying a 180° pulse at a time $\tau$ after the 90° pulse the extra phase is reversed, causing a refocussing of the magnetisation into an echo at a time $2\tau$ after the 90° pulse. The process is shown schematically in figure 1.10.

1.2.2.3 THE SOLID ECHO

In the liquid state a spin echo can be formed by simply inverting the spin population with a 180° pulse. However, in solids the dipolar coupling between adjacent spins causes rapid dephasing of the signal. This coherence transfer can be refocussed with an appropriate 90° pulse. In contrast to the spin echo the solid echo is a transient response to a coherent radio frequency pulse sequence and is a purely quantum mechanical phenomenon. It was first described by Powles and Mansfield (1962) and a typical pulse sequence is $90°_x-\tau-(90°_y-\tau$-echo$)_n$. Full explanation of the solid echo requires detailed quantum mechanical treatment (Slichter 1963).

1.2.2.4 MEASUREMENT OF RELAXATION TIMES

The spin lattice relaxation time may be measured using an inversion recovery sequence, shown in figure 1.11. A 180° pulse is applied causing the magnetisation to be tipped down to the negative z axis, from where it will
**FIGURE 1.10**  FORMATION OF A HAHN ECHO IN THE ROTATING FRAME

**FIGURE 1.11**  INVERSION RECOVERY SEQUENCE

**FIGURE 1.12**  CPMG SEQUENCE
relax back to the positive z axis exponentially according to

\[ M_z(t) = M_0 \left[ 1 - 2 \exp\left(\frac{-t}{t_1}\right) \right] \tag{1.53} \]

where \( t \) is the time from the initial 180° pulse. Since only the \( x \) and \( y \) components generate a signal, a 90° pulse is applied to bring the magnetisation into the \( x-y \) plane a time \( t_i \) after the 180° pulse. The signal will be proportional to the value of \( M_z(t_i) \). The sequence is repeated after a time \( T_r \), known as the repetition time, for various values of \( t_i \) and the amplitude of the signal recorded. The magnetisation must relax fully to equilibrium between repetitions, so \( T_r \) is usually chosen to be greater than 5\( T_1 \). The value of \( T_1 \) is calculated by fitting values of \( M_z(t_i) \) to equation 1.53.

The spin spin relaxation rate \( T_2 \) is affected by the presence of inhomogeneities giving rise to \( T_2^* \) relaxation which for many systems is shorter than \( T_2 \). In general

\[ \frac{1}{T_2 \text{obs}} = \frac{1}{T_2} + \frac{1}{T_2^*} \tag{1.54} \]

for solids \( T_2 < T_2^* \) giving

\[ \frac{1}{T_2 \text{obs}} = \frac{1}{T_2} \tag{1.55} \]

but for liquids \( T_2^* < T_2 \) and so

\[ \frac{1}{T_2 \text{obs}} = \frac{1}{T_2^*} \tag{1.56} \]

It follows than that for solid materials the time constant of the FID is a good
approximation to the value of $T_2$. For a more accurate determination of $T_2$ in solids and to measure $T_2$ in liquid systems, spin echoes must be used. Considering the formation of the Hahn echo using a 180° pulse, if a train of such pulses is used in a sequence, a corresponding train of echoes will be detected. The train of echoes is formed from the continual dephasing and rephasing of the magnetisation under the effects of the inhomogeneities which are constant. The transverse magnetisation is not constant, however, and will be decaying according to $T_2$ during the sequence. If the echo amplitude is recorded for each echo, a plot of amplitude against time will yield a value of the true spin spin relaxation time $T_2$ according to

$$M_{xy} = M_0 \exp\left(-\frac{t}{T_2}\right)$$

Trains of echoes were first used in this way by Carr and Purcell (1954) with further changes in the phasing of pulses introduced by Meiboom and Gill (1959). The sequence is now known universally as CPMG (Carr, Purcell, Meiboom, Gill). Alternating phases of the 180° pulses may be implemented to remove pulse timing errors. A typical sequence is shown in figure 1.12.

1.2.3 IMAGING

In 1973 Lauterber, and Mansfield and Grannell separately published the first papers on NMR imaging within months of each other. We have discussed how field inhomogeneities cause differences in precessional frequencies so that after a period of time the spins dephase to different positions. This concept was inverted by Lauterber and Mansfield and Grannell, who added a known inhomogeneity, a magnetic field gradient, to encode the positions of spins within a sample on the NMR signal. This signal is then processed to form an image of the sample.
A simple explanation of imaging is given by considering three test samples with spin densities in the ratio $1/3 : 2/3 : 3/3$ placed in a static magnetic field $B_0$, with an additional field gradient, $g$, in the direction of $B_0$. The resulting field will be

$$B(x) = B_0 + gx$$  \hspace{1cm} (1.58)

The test samples are placed at positions $x_1$, $x_2$, and $x_3$. The measured NMR signal is given by the local spin density and signal frequency $(\gamma g x)$ is given by position, figure 1.13. The measured NMR signal is

$$M(t) = M_0 \int p(x) \exp(i \gamma g x t) \, dx$$  \hspace{1cm} (1.59)

where $M_0$ is the intensity for unit sample density and $p(x)$ is the local spin density as a function of $x$. If this signal is Fourier transformed it is equivalent to changing domains between the time $t$ and the frequency $(\gamma g x)$. The frequency separations are proportional to the actual spatial separations and so the Fourier transform of the signal variation with time gives spatial information. This forms the basis of all imaging techniques. Since 1973 imaging has expanded rapidly and the large differences between liquids and solids have become evident. The constraints imposed on the imaging of solids come from the dipolar interactions which give the very short $T_2$ values which may be of the order of $10 \, \mu$s or less in the lower limit. For this reason imaging of solids has not advanced as quickly as liquids, free from such constraints, with $T_2$ values of the order of seconds. Medical imaging is encompassed under the heading of ‘liquids’ as the human body comprises a large amount of fluid and soft tissue, and is the area that has advanced most rapidly. A brief introduction into the most common imaging methods used in liquids will be followed by a more detailed treatment of broadline imaging and the sequences used in this thesis.
FIGURE 1.13  BASIC REPRESENTATION OF IMAGING

1. slice select
2. phase encode
3. frequency encode

FIGURE 1.14  2DFT SEQUENCE
To fully appreciate the relative merits and differences of two dimensional Fourier transform (2DFT) and projection reconstruction (PR) imaging it is useful to use the k space notation introduced by Mansfield (1973). The k vector has a magnitude expressed in units of reciprocal space, m⁻¹ and k space may be traversed by moving either in time or in gradient magnitude

\[ k = (2\pi)^{-1} \gamma g t \]  

The most common technique in liquids imaging is slice selective 2DFT. It is a three stage experiment, as shown in figure 1.14, where

1) selects a slice
2) phase encodes the slice in one direction within the slice
3) frequency encodes the slice in the orthogonal direction

In more detail, the sequence involves firstly selecting a slice through the sample by means of a shaped pulse and a gradient designed to excite only a certain band of frequencies. The orientation of the slice is controlled by the slice selection gradient. The conventional use of the three cartesian coordinates is now adopted, so the slice select gradient and the static magnetic field are both in the z direction.

Following the slice selection procedure the phase gradient (g_y) causes the spins to precess at a different rate than normal so after a time T_y they have acquired a new phase, which is dependent on their position in the y direction. In order to obtain an image in two dimensions the sequence must be repeated with different values of the phase gradient. This may be done in either of two ways, with a constant amplitude and variable time or a constant time and variable amplitude. The latter is known as spin warp imaging (Edelstein 1980), and is most commonly used as it removes the problem of artifacts that
are present when $T_2$ is of the order of $T_1$ or when magnet inhomogeneities cause phase errors. Considering now only the spin warp variant, as the magnitude of $g_y$ is varied the phase of the spins prior to frequency encoding will change. In phase encoding $k$ space is traversed by changing the gradient magnitude.

Following the phase encoding, the frequency encoding gradient, $g_x$, known as the read gradient, causes the spins to precess at different frequencies. The separation in frequencies is directly proportional to the actual spatial separation. The FID is sampled while the gradient is on so in frequency encoding $k$ space is traversed by moving in time. So the application of successive phase encoding and read gradients gives a two dimensional image of the selected slice for which, in one direction the position is dependent on the phase of the spins and in the other it is dependent on the frequency of the spins.

1.2.3.2 PROJECTION RECONSTRUCTION

Lauterber’s original experiment took the form of projection reconstruction. In this technique a projection is acquired for a particular value of the gradients $g_x$ and $g_y$. The values of $g_x$ and $g_y$ are incremented and another projection acquired until 180° degrees have been covered with as many projections as required. This is particularly simple to implement in practice since it may be performed with a fixed gradient magnitude while the sample is successfully rotated. Standard back projection reconstruction techniques such as those used for x-ray and CT scanning may then be used to form an image.

One can see how 2DFT and PR differ in the way that $k$ space is traversed, with figure 1.15 a) showing the polar raster of PR and b) showing the cartesian traversal of $k$ space associated with 2DFT. PR offers a slight
FIGURE 1.15  K SPACE POLAR AND CARTESIAN RASTERS

FIGURE 1.16  GRADIENT ECHO SEQUENCE
sensitivity advantage over 2DFT especially for short $T_2$ materials as there is the phase encoding delay before sampling in 2DFT. It is also useful to view the profiling of the image as the raster is rotated and this can be a useful indication of problems in the experiment. Despite these advantages, 2DFT offers improvements in image quality and fine details due to the more even sampling of $k$ space.

1.2.3.2 THE GRADIENT ECHO

The gradient echo is analogous to the Hahn spin echo, except that it is the deliberate application of a magnetic field gradient that causes the dephasing and rephasing of the spins, rather than the random inhomogeneities which are responsible for the Hahn echo. If after a $90^\circ$ pulse a positive gradient is applied for a time $\tau$, followed by a negative gradient of the same magnitude for an equal time, then the echo is formed at a time $2\tau$ after the pulse. The gradient echo will however be susceptible to errors from static inhomogeneities. The use of a $180^\circ$ pulse in addition to the gradients will refocus these errors at the echo centre and help to alleviate the problem. It is however, not a total cure if frequency encoding is used. The pulse sequence for a gradient echo is shown in figure 1.16

1.2.3.3 INTRODUCTION TO THE DIFFICULTIES OF BROADLINE IMAGING

The dipolar interactions in solids introduce constraints due to the broadening of the NMR lines and corresponding shortening of the $T_2$ relaxation times. The requirement for imaging is to record the signal in the presence of a magnetic field gradient. The gradient must satisfy the following
where $\Delta r$ is the desired resolution and $\Delta B$ is the linewidth. To obtain images with sensible resolution is simple for liquids, but for solids the large gradient strength required due to the increased linewidth leads to problems.

There are three main problems associated with a very short transverse relaxation time. Firstly, most of the signal is within the receiver deadtime and is useless. Due to the poor signal to noise ratio much signal averaging must be performed to obtain adequate image quality, and experiment times are further increased by the long $T_1$ relaxation times of solids which necessitate long repetition times. For two dimensional imaging especially, the experimental timescales needed for good image quality may be unacceptably long. The field gradient must be allowed to stabilise before sampling and the time for this may be longer than $T_2^*$, so the gradient must be switched on before the rf pulse. This means that the pulse must be very short in order to have the bandwidth needed to cover the frequency range imposed by the gradient, giving the need for large rf power.

There are, therefore, technical difficulties involved in overcoming the broadening found in solids and many successful imaging methods have instead effectively removed it. The dipolar Hamiltonian consists of a spin and a space part and if either of these is put to zero, the broadening effects are removed. There are basically three techniques then which may be used to image solids,

1) The so called 'brute force' methods which simply use a gradient strength large enough to overcome the broadening.

2) Spin manipulation methods whereby the time average of the spin part is made equal to zero with the use of multiple pulse sequences, giving effective line narrowing.
3) Special systems such as the use of high resolution $^{13}$C NMR, and the effective time averaging to zero of the spatial part by spinning the sample.

Included in the first category is the gradient echo imaging method, Cottrell (1990) which uses large oscillatory driven gradients, and the Stray Field Imaging technique (STRAFI), Samoilenko et al (1988), Samoilenko and Zick (1990), both of which will be considered in more detail presently. Multiple pulse sequences, McDonald and Tokarczuk (1990), McDonald and Lonergan (1992) have been used very successfully in obtaining images of short $T_2$ materials, as has the magic angle spinning method, Cory et al (1988), in which the whole sample is rotated at an angle such that the spatial part is time averaged to zero, and the similar magic angle rotating frame method, De Luca et al (1986). Other techniques to image solids include the use of solid echoes, McDonald et al (1987) and NMR microscopy, such as chemical shift selective microimaging, Chudek and Hunter (1992).

1.2.3.4 THE BROADLINE GRADIENT ECHO IMAGING TECHNIQUE

This technique was first developed by Cottrell et al (1990) and successfully uses the large gradient approach to solids imaging, eliminating two of the problems associated with short $T_2$ relaxation times discussed in the previous section. As part of the work in this thesis, this technique has been further developed to give a new sequence which overcomes the third problem as well. The new sequence is discussed fully in chapter 3.

The gradient echo imaging technique uses a field gradient of sufficient strength to overcome the homogeneous broadening, and is driven sinusoidally according to
where \( G_0 \) is the peak amplitude and \( 2\tau \) is the period of the oscillation. The sequence is shown in figure 1.17. The 90° pulse is synchronised to the zero crossing of the gradient, thereby removing the need for large rf power. After one period of oscillation a gradient echo is formed, and as they continue to oscillate an echo is formed after every complete cycle. An image may be made up of one, or a number of the subsequent echoes, whose amplitudes decay with \( T_2 \). The resolution is now given by

\[
G = G_0 \sin\left(\frac{2\pi t}{2\tau}\right)
\]

where \( \langle G(t) \rangle \) is the average value of the sinusoidal gradient over half a period. Choice of the appropriate value of the period will ensure that the first echo is not within the receiver dead time, subsequent echoes are well separated and that enough signal remains to form the echo train. It was found that the echo time, \( 2\tau = T_2 \), was the optimum value. The variation of the field gradient during the data collection from the echo is accounted for by using a non linear sampling method, such as that of Ordidge and Mansfield (1985).

Although the gradient echo method as implemented by Cottrell et al works well, some error may be introduced by magnet inhomogeneities. The effects of these are not refocussed when using gradients to form an echo. However, if a 180° pulse is added to the sequence after one gradient cycle then the resulting echo after two cycles is significantly improved due to the refocussing of the errors at the echo centre. The only drawback to the refocussed gradient echo is that it is now formed at \( 4\tau \) instead of \( 2\tau \), so raising the lower limit of \( T_2 \) relaxation times observable with this technique.
FIGURE 1.17  GRADIENT ECHO SEQUENCE WITH OSCILLATING GRADIENTS
Stray field imaging is a relatively new technique which was first developed by Samoilenko et al (1988) and Samoilenko and Zick (1990). It overcomes the line broadening problems associated with solids by taking the large gradient approach to the extreme, and has the additional advantage of high spatial resolution.

From 1.63 it follows that the resolution of an imaging experiment is given by

$$\Delta x = \frac{2\pi \Delta v_s}{\gamma G}$$  

where $G$ is the applied gradient, $\Delta v_s$ is the linewidth of the sample when $G=0$ and $\gamma$ is the magnetogyric ratio. The STRAFI technique uses the linear region of the stray field gradient, naturally available outside the homogeneous region of the field of superconducting magnets. Numerical calculations on the field profile reveal that for certain magnets there is a planar surface with constant gradient near the edge of the bore. A magnet with a central field of 9.4 T may produce a gradient of the order of 50 T/m. With such large values it is not possible to excite all the spins in a sample with one rf pulse, giving rise to slice selective excitation. The resolution using pulsed selective excitation is described by modifying equation 1.64, giving

$$\Delta x = \frac{2\pi (\Delta v_s + \Delta v_p)}{\gamma G}$$  

where $\Delta v_p$ is the bandwidth of the pulse. Since the gradient is neither dynamic nor controllable, in order to obtain a complete projection across a sample it must be moved stepwise along the bore, with the signal intensity being recorded from each slice as it passes through the sensitive position. No Fourier transformation of the signal is required and thus the method is more
analogous to continuous wave NMR techniques.

In practice, the signal intensity of a solid echo is recorded. Indeed, usually the intensity of each echo in an echo train is recorded, the train being generated by the rf pulse sequence

\[ 90^\circ_x - \tau - (90^\circ_y - \tau - \text{echo} - \tau) \_n \]

where \( \tau \) is a short time interval. This particular sequence is used for two reasons. Firstly, it uses pulses all of the same length, so that the width of the selected slice is constant for all pulses. Secondly, the solid echo partially refocusses the dipolar broadening and the sequence as a whole preserves magnetisation from short \( T_2 \) components in the short \( \tau \) limit. In this limit, the experiment approximates to spin locking and the echo intensities, after the first few echoes during which a pseudo equilibrium is established, decay away according to \( T_{ip} \). Since the sample is moving through the gradient during the measurements the pulses experienced by the nuclei only approximate to true 90° rotations. The recorded signal intensity is thus a complex function of \( T_2 \) and \( T_{ip} \) and other experimental parameters, such as the gradient strength, the pulse length, \( \tau \) and the sample velocity. The complete functional dependence of the echo intensity on these parameters, as well as on the dipolar interaction strengths in the sample has not yet been fully evaluated. Generally, however, only long \( T_2 \) and \( T_{ip} \) components are observed at longer echo times. This gives the potential for substantial relaxation time contrast in profiles constructed from different echoes.

In addition to the obvious benefits for the imaging of solids, STRAFI may be used in the imaging of samples affected by susceptibility distortions, such as liquids in solids, Kinchesh et al (1992). Another example of the implementation of STRAFI is the imaging of teeth, Baumann et al (1993).

38
1.3 ION BEAM NUCLEAR REACTION ANALYSIS.

1.3.1 INTRODUCTION.

This experimental technique was developed to study polymer diffusion in polymer melts, Payne et al (1989). It uses the nuclear reaction between a $^3$He beam ion bombarding a sample normal to its surface and a deuterium nucleus within the sample. Detection of either of the energetic backscattered reaction products, protons and alpha particles leads to a one dimensional profile of deuterium concentration with depth. It is possible to study the concentration profile of a penetrant in a surface layer of up to approximately 8 μm in depth with a resolution of 400 nm. The depth scale is determined from the energy spectrum of the detected product. The technique has been extended to the study of small molecule diffusion into polymers by the use of deuterated penetrants. Alternatively, the beam spot may be focused down to 50 μm in diameter and then scanned across a cross section of a sample (typically 20 mm wide). The concentration profile is determined from the relative yield of backscattered alpha particles at each point. The limiting spatial resolution of the technique depends on the beam spot size.

1.3.2 THE $d(^3$He,$p$)$^4$He NUCLEAR REACTION.

The following reaction provides the basis for this technique

\[ {^3}\text{He} + d \rightarrow p + \alpha \]

It was first identified in 1953 by Yarnell who bombarded gaseous $^3$He with energetic deuterons. It has a strong resonance of 0.9 ± 0.1 barns, the cross
FIGURE 1.18  REACTION CROSS SECTION FOR THE d(He,p)4He REACTION

FIGURE 1.19  SCHEMATIC OF THE D(He,p)4He REACTION SHOWING THE FORMATION OF A 5Li COMPOUND NUCLEUS
section maximum being at a deuterium energy of 430 ± 30 keV, figure 1.18 (reproduced from Yarnell 1953). The reaction proceeds with the formation of a $^6$Li compound nucleus and is extremely exothermic in nature, figure 1.19. The Q value of the reaction is 18.352 MeV, with the result that both emitted particles have energies greater than the incident particles. The reaction may be used in reverse by bombarding a target with $^3$He ions to study deuterium concentrations in various materials, Moeller (1978), Boergesen et al (1978).

1.3.3 ADVANTAGES OF USING THE $d(^3\text{He},p)^4\text{He}$ REACTION TO MEASURE DIFFUSION PROFILES.

The use of charged particle induced nuclear reactions offers certain advantages over other methods as a means of measuring diffusion profiles. $d(^3\text{He},p)^4\text{He}$ is a high Q reaction which may be initiated by a low energy beam of helium ions, available at many accelerator laboratories. The reaction has a high cross section and hence low beam currents (a few nanoamperes) can be used which do not overheat the sample appreciably. The reaction yields highly energetic protons and alphas which can escape from relatively large depths within the sample and may be detected at backward angles. Hence at a 2 MeV accelerator depths of up to 8 μm can be probed in polymers if the protons are detected. It allows the use of a light element (deuterium) as a labelling element for a penetrant in heavy element substrates. The results of a measurement using this technique do not depend on chemical state of the nuclei as the reaction yield is determined only by the nuclear cross section.

There are two ways of applying nuclear reactions to measure a profile depending on the width of the resonance. If the resonance is narrow then the incident beam energy must be incremented and a total yield measurement made at each increment, which corresponds to a value of depth within the sample. The resonance of the $d(^3\text{He},p)^4\text{He}$ reaction is wide, as seen in figure
1.20 and for this case a measurement at a single value of incident beam energy is all that is required to give a depth profile. If a sample containing deuterium is bombarded by a beam of helium ions the protons and alpha particles emitted will have a range of energies. The energy of the reaction product varies with the depth at which the reaction occurred. If the experimental geometry is taken into account a measurement of the energy of an emitted particle leads to a determination of the depth at which the reaction occurred.

\[
\text{Excitation curve at } 165^\circ \text{ (lab)}
\]

Therefore the use of the \( d(3\text{He},p)^4\text{He} \) reaction provides a very quick and efficient method of determining concentration depth profiles for use in diffusion studies. The samples are not overheated or destroyed and may be retained for future analysis using this or a complementary technique. The technique may be used to study the initial stages of a diffusion process in detail. In addition the shape of the profile after some considerable time may be studied by using the scanning microbeam method with a large sample.
1.3.4 EXPERIMENTAL GEOMETRY.

The detection of protons at backward angles is thought to give improved results compared to the detection of alpha particles at forward angles. The argument put forward for this is well presented by Murphy (1990), however a summary of the considerations involved is now given.

The energies of the emitted protons and alpha particles are 14.661 MeV and 3.691 MeV respectively, using a value of 18.352 for Q. Dieumegard (1979). Protons are therefore far more penetrating than alpha particles and will have a greater range in matter making them far more suitable for a backscattering arrangement. When detecting protons, their kinetic energy values are high enough to ensure that they lose virtually no energy in traversing the few microns of sample to the surface. Their final energy at the point of detection is therefore only a function of the beam energy at the point of reaction and the angle of detection with respect to the beam direction. It is the energy loss characteristics of the beam ion which yield most of the depth information.

A study of the reaction cross sections shows very little difference in that measured at an angle of 86° and a backward angle of 165°. The difference would have to be significantly larger to favour a forward scattering rather than a backscattering arrangement, so on the basis of cross section neither geometry is particularly preferred.

A further consideration to experimental geometry is the angular dependence of the emitted particle's energy. Figure 1.21 gives an indication of the values of dE/dθ for protons detected at a range of angles. From this it can be seen that at backscatter angles there is much smaller variation of energy with angle leading to a reduced energy spread at the detector, for the same detector collimator slit width.
Another consideration is that of noise due to counts produced by reactions other than \( d(\text{He}_3,p)\text{He} \). The interactions between \( \text{He}_3 \) and other light elements which may be present within a sample may give rise to alphas of a similar energy to those from the deuterium reaction and therefore be detected. However the protons arising from other reactions do not have comparable energies to those from the deuterium reaction, thus ensuring that proton detection is free from spurious counts.

If a forward scatter arrangement is adopted the samples are confined to either being very thin or inclined at a small angle to the beam to ensure that the reaction products reach the detector. In the first case samples are very fragile and in the second only depths \( \leq 1 \) \( \mu \text{m} \) can be probed. If the backscatter arrangement is used there are no restrictions on the sample thickness or orientation to the beam, facilitating ease of preparation and the possibility of re-using the sample for further analysis or testing.
1.3.4.1 DETECTION OF REACTION PRODUCTS.

A typical detector for this type of experiment is a silicon surface barrier detector. It is made of a p-type and n-type bilayer of silicon. A reverse bias across this causes a depletion region around the junction. All the bias voltage is dropped across the depletion region leading to very high localised fields. The effect of these is to separate charge carriers quickly and prevent recombination and subsequent loss of signal as much as possible.

The depletion region forms the sensitive volume of the detector into which an incoming particle should deposit all its energy. To facilitate this the reverse bias is made large which maximises the sensitive volume. On entering the detector the reaction products are ionised, forming ion-hole pairs, which, under the influence of the large localised fields, are swept rapidly to their respective ends of the bilayer. The signal from the detector is therefore a voltage pulse whose amplitude depends on the number of carriers created by the passage of the reaction products.

FIGURE 1.22 TYPICAL DEPTH REQUIRED FOR THE SILICON SURFACE BARRIER DETECTOR USED IN THIS EXPERIMENT
In order to measure the reaction products full energy it must be stopped completely within the depletion region. In the case of the \(d(^{3}\text{He},p)^{4}\text{He}\) reaction the protons and alpha particles have a large range of energies, and whereas a depletion region of 100 \(\mu m\) would be sufficient to stop the alpha particles, it would only slow the protons. Therefore for proton detection, such as we are dealing with, a depletion region of typically 1500 \(\mu m\) is required, figure 1.22.
CHAPTER 2

OVERVIEW OF POLYMER SYSTEMS AND
DIFFUSION PROCESSES IN POLYMERS

2.1 INTRODUCTION

Polymers are one of the most versatile and widely used group of materials in the late twentieth century. Although the concept of polymers emerged in the 1920's it was not until the 1950's that the influence of polymers spread rapidly across all areas of modern science.

The realisation of their huge potential as engineering materials has established a new sector of the chemical industry devoted to the production and application of synthetic polymeric materials such as plastics, rubbers, coatings and adhesives. Fundamental to the production of a new polymer for a specific application must lie a knowledge of how the microscopic structure affects its macroscopic properties. If polymers are to be successfully used as engineering materials or in any number of other applications, their interaction with other materials as well must be fully understood. A good example of the surprises that may result from inadequate understanding is that of polyethylene and its chemical inertness. Polyethylene is unaffected by prolonged exposure to strong acids which attack metals and highly caustic alkalis which damage glass and most organic substances. Yet the pure polymer weathers rapidly when exposed outdoors to the atmosphere, burns easily and is affected by common detergents. This example proves that the chemical properties of polymers and their interaction with other materials is by no means obvious and gives credence to the wealth of study into polymeric systems.
One important area of study is diffusion processes in polymers, and in particular solvent diffusion into polymers. The action of solvents stands apart from other materials as it does not produce permanent chemical change in the polymer (Hall 1989). It does however produce profound physical changes which occur as a result of the interaction between chemical properties of both the solvent and polymer.

This chapter will discuss polymers and solvents, the theory of the diffusion process found in polymers and will review the experimental methods used to date to study them. The applicability of the experimental techniques described in the previous chapter to the study of polymers and their diffusion processes will be highlighted.

2.2 POLYMERS

Polymers are both naturally occurring and synthesised. They are long chain like molecules formed by chemically linking small molecules known as monomers in a process known as polymerisation. Synthetic polymers can be subdivided into thermoplastics and thermosets. Thermoplastics are materials which melt on heating and can be re-cast. They may be processed by a variety of moulding and extrusion techniques. Thermosets cannot be melted and remelted, but set irreversibly. This distinction means that production, processing and fabrication techniques for these two types of polymer differ. In addition to the synthetic polymers the naturally occurring polymers of importance are rubbers, resins, oils and biopolymers, such as found in the human body and wood.

Hydrocarbons, composed of only carbon and hydrogen are usually the most simple in structure. Atoms of other elements may be incorporated into
polymer structures by substitution of the hydrogen atoms. Common elements are chlorine, as in Polyvinylchloride (PVC), fluorine, oxygen, as well as groups such as CN and more complicated substituents composed of groupings of H, C and O as in Polymethylmethacrylate (PMMA).

2.2.1 MOLECULAR STRUCTURE

Polymers may be classified according to their general molecular structure. The chains may be linear or branched, the complexity increasing with chain length. In addition to linear chains two and three dimensional networks of chemical bonds are possible. The two main types of network materials are those formed via the linking of linear chains by small molecules and those formed by the direct reaction of small molecules which gives rise to chain branching. The former are more commonly known as crosslinked polymers. Further types of polymer structure arise when two types of monomer unit are mixed in single chain and these are known as copolymers. The three basic structures are alternating, random and block copolymers.

2.2.2 MORPHOLOGY

Polymers may be further classified according to morphology. This defines how the chains are arranged to form the bulk material. It may be a regular, ordered crystalline structure, a random amorphous structure, or a more complex combination of both. During solidification of a molten polymer as the temperature falls below the melting point the polymer molecules try to form the ordered crystalline state from the molecular disorder of the liquid. Crystalline regions grow round nucleating centres with the gradual addition of further molecules, the rate being determined by the ease of movement of the molecules in the liquid. This mobility is controlled by the viscosity and a
high viscosity at the melting point indicates a reluctance to crystallise. If a liquid is cooled quickly below the melting point the viscosity can rise high enough to prevent crystallisation. The resulting substances at even lower temperatures have the properties of solids but without the crystallinity. They are amorphous and have the characteristics of glasses.

Glassy polymers do not show a sharp phase transition like crystalline polymers, rather they exhibit a gradual change from one recognisable state (liquid) to another (solid). The transitions of polymers may be conveniently monitored by the temperature dependent changes that occur in physical properties such as density, as shown in figure 2.1 (reproduced from Hall 1989). The lower limit of the transition range for a glassy polymer is marked by a change in the coefficient of expansion and defines a characteristic glass transition temperature $T_g$. This is seen on figure 2.1 as a change in the gradient $dp/dT$, but not a discontinuity, as for crystalline polymers at the melting point. Above the glass transition temperature the amorphous polymers exhibit rubbery behaviour, while below it they are glassy. For this reason it is commonly called the glass rubber transition.

To differentiate between a crystalline or amorphous microstructure x-ray diffraction may be used. This technique is also able to identify the presence, and amount of both types of microstructure in a polymer. Crystalline structures are characterised by sharp x-ray diffraction peaks whilst amorphous structures exhibit broad featureless peaks indicating the lack of long range atomic regularity. The degree of crystallinity in a semicrystalline polymer can thus be determined.

2.2.3 MOLECULAR MOTION

The dynamics of polymer chains depend on temperature. Close to absolute
**FIGURE 2.1**  DENSITY VARIATION WITH TEMPERATURE SHOWING THE MELTING TEMPERATURE AND GLASS TRANSITION TEMPERATURE

**FIGURE 2.2**  VARIATION OF PROPERTIES OF TYPE P AND Q WITH TEMPERATURE SHOWING TRANSITION ZONES AND TRANSITION MAXIMA
zero there is very little motion of any kind. However as the temperature rises the thermal energy is distributed amongst all the various modes of motion. These will require different amounts of energy to activate them giving each a threshold temperature before the motion can occur. These temperatures can be detected as transitions in a wide variety of physical properties. In amorphous polymers there is one dominant transition, the glass transition, and the measurement of $T_g$ from changes in the density has just been discussed. In crystalline polymers there exist more transitions although the most prominent one is associated with melting. Properties of type P in figure 2.2, (reproduced from Hall 1989) such as refractive index, heat capacity or electrical permittivity show one or more transition zones, $\alpha, \beta, \gamma, \ldots$ which roughly define transition temperatures $T_\alpha, T_\beta, T_\gamma, \ldots$, whereas properties of type Q in figure 2.2 such as mechanical and dielectric loss show one or more maxima which correspond to the same transitions.

The details of the glass transition are still unclear although the free volume theory provides a good explanation. There is a discontinuity in the expansivity at $T_g$ which indicates a change in the availability of space between molecules. Such space, known as free volume, must be present for large scale motions of polymer chains to occur. Above $T_g$ these motions take the form of movements of the backbone of neighbouring chains, each segment possibly 10-20 monomer units. It is these motions which permit the large deformations characteristic of the rubbery or viscoelastic state. If the polymer is cooled to $T_g$ the free volume diminishes to a critical value below which such segmental motion is impossible or very slow. Below $T_g$ therefore modes of motion are limited to crankshaft rotations of main chains and rotations of side groups.

2.2.4 DIFFERENTIAL SCANNING CALORIMETRY

Differential Scanning Calorimetry (DSC) is an experimental method for the
measurement of \( T_g \). A DSC cell relies on having a sample and reference pan which are heated independently. Sample and reference pans are heated at a specific rate with the temperatures of each being kept equal. If during the heating the sample undergoes an endothermic transition, such as the glass transition, in order to keep both pans at the same temperature, more heat will have to be applied to the sample pan in order to keep the temperatures equal.

A plot of heat flow against temperature is called a DSC thermogram which will show an endothermic peak if the sample has passed through a transition. When used to measure \( T_g \), there is an abrupt change in the DSC thermogram of the heat capacity at \( T_g \), as shown schematically in figure 2.3.

![Schematic of a DSC thermogram of heat capacity around the glass transition temperature](image)

**FIGURE 2.3** SCHEMATIC OF A DSC THERMOGRAM OF HEAT CAPACITY AROUND THE GLASS TRANSITION TEMPERATURE
The scanning rate is quoted with the measured value of $T_g$. A typical value is ten degrees per minute. The effect of dilutents, such as solvents, is to depress the value of $T_g$ by increasing the free volume. This method was used to measure the $T_g$ of the PVC used in the experiments covered in this thesis, and to determine the effect of various concentrations of acetone in the PVC on the value of $T_g$. The results are discussed in chapter 4.

2.2.5 MECHANICAL AND THERMAL PROPERTIES

Amorphous polymers exhibit the behaviour of both the glassy and rubbery state, but between the regions is the zone associated with the glass transition. In this transition zone the mechanical behaviour shows features of both elastic solid and viscous liquid. This gives rise to the consideration and classification of polymer solids as viscoelastic bodies. The concept of polymer viscoelasticity has been shown to be of importance when considering relaxation controlled diffusion behaviour commonly found in glassy polymers, such as Case II diffusion.

2.3 DIFFUSION PROCESSES

2.3.1 INTRODUCTION

A great majority of problems encountered in diffusion studies may be adequately modelled using Fick's laws. However diffusion dynamics are frequently composite in character as is true of the particular area of interest in this study, that is diffusion in and through solids.

The majority of this thesis is concerned with the penetration of the solvent
acetone into the glassy polymer PVC, which exhibits Case II diffusion. Two of the characteristics of Case II diffusion are an induction period and front precursor that are Fickian in nature. Therefore a brief summary of Fick's laws and the appropriate solutions to the diffusion equation will be considered, followed by a more detailed study of Case II diffusion.

2.3.2 FICKIAN DIFFUSION

Two familiar differential forms of Fick's laws of diffusion for movement in the $x$ direction and a constant diffusion coefficient are

$$P = -D \frac{\partial C}{\partial x} \quad 2.1$$

and

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad 2.2$$

The first gives the rate of permeation, in the steady state of flow through unit area of any medium, in terms of the concentration gradient across it, and a constant called the diffusion coefficient (Barrer 1951).

The second refers to the accumulation of matter at a given point in a medium as a function of time, and so refers to a non stationary state of flow and is a statement of Fick's second law of diffusion. The second equation is easily derived from the first by considering diffusion in the $+x$ direction of a cylinder of unit cross section. Assuming an element of volume $dx$ bounded by two planes 1 and 2, the rate of accumulation of matter may be stated as
The above equations represent the most basic forms of Fick's laws. Most systems would be in two or three dimensions and many have concentration dependent diffusion coefficients which introduces more complexity into the diffusion equation. However, the ion beam experiments are used to study one dimensional diffusion and it will be assumed that the diffusion coefficient may be treated as constant. The solution of the diffusion equation for the induction period profiles is that of a species into a thick layer from a source which holds the surface at constant concentration

\[ \phi(x) = \phi_0 \text{erfc} \left( \frac{x}{\sqrt{4DT}} \right) \]

where \( \phi \) is the concentration of the penetrant, \( \phi_0 \) is the equilibrium concentration of the penetrant at the surface, \( T \) is the exposure time, \( x \) is the direction of diffusion and \( D \) is the diffusion coefficient. The problem of the Fickian precursor is that of diffusion ahead of a moving boundary that is at constant concentration. The solution may be stated as

\[ \phi(x) = \phi_0 \exp \left( -\frac{Vx}{D} \right) \]

where \( V \) is the velocity of the front moving in the positive \( x \) direction, Hui et al (1987) and Mills et al (1986).
In recent years research has shown an increasing number of systems which fail to be explained by Fick’s laws. The anomalous phenomenon which seems to have received the most attention and study is Case II diffusion. It is most commonly associated with the penetration of organic solvents into glassy polymers. Case II diffusion was discovered experimentally long before the theories which govern its behaviour were postulated. It was first named as such by Alfrey in 1965, but it was not until 1982 that the most thorough and widely accepted theory to explain Case II diffusion was published by Thomas and Windle (TW). Before introducing the TW theory the general characteristics of Case II diffusion, and how it differs from Fickian behaviour, are briefly discussed.

When a rigid glassy polymer is penetrated by a solvent it becomes softer and rubbery with a sharp boundary between the penetrated rubbery region and the rigid unpenetrated region. The sharp front between the regions moves at a constant velocity through the polymer. Current theories indicate that there should be negligible concentration gradient of the penetrant in the penetrated region. In the unpenetrated region a Fickian precursor, first proposed by Peterlin in 1965, precedes the front. There is an induction period to front formation that is also Fickian in nature. These physical characteristics lead to an idealised concentration profile as in fig 2.4 (Mills et al 1986).

Many people have attempted to model the characteristics of sorption behaviour in glassy polymers. In 1972 Kwei et al studied the diffusion of acetone into PVC by the measurement of weight gain and distance of penetration as a function of time. Using a generalised diffusion equation which accounted for both Case II and Fickian behaviour, they obtained good agreement to experimental results. However this was a one off experiment with no further investigation into the diffusion mechanisms of the
acetone/PVC system. It is typical of the batch of theories proposed prior to the TW theory. Although initially the theories seem to fit isolated sets of sorption data, many are lacking in any real physical basis, as in the case of Kwei et al, or do indeed describe an anomalous phenomenon that is not strictly Case II diffusion. An excellent summary of such theories is given by Thomas and Windle as an introduction to their own deformation model of Case II diffusion (1980).

![Idealised Concentration Profile for Case II Diffusion](image)

**FIGURE 2.4** IDEALISED CONCENTRATION PROFILE FOR CASE II DIFFUSION

The viscosity and diffusivity of glassy polymers are very sensitive to the concentration of the penetrant during Case II diffusion. This leads to a very large decrease in the viscosity and a corresponding increase in the diffusivity within a narrow range of concentration. Once the critical concentration is reached therefore, the polymer becomes plasticised very quickly producing a
dramatic decrease in the polymer segmental relaxation times. The glassy polymer has a very long relaxation time and the rubbery plasticised polymer has a very short relaxation time. Once the relaxation time has shortened the rate of swelling increases rapidly resulting in a sharp front. The induction period is therefore the time taken for the penetrant concentration to reach its critical value.

Thomas and Windle postulate that as the Case II front’s movement is independent of its position it implies that the diffusion of molecules through the swollen layer up to the front is not the rate controlling process. This must occur at the front itself and can be regarded as the movement and relaxation of polymer segments in response to an osmotic swelling stress. This type of sorption is therefore often described as ‘relaxation controlled’ but with no further indication as to the physical nature of the process. Thomas and Windle’s theory is based on the time dependent deformation of the polymer as the rate controlling mechanism.

2.3.3.1 THOMAS AND WINDLE MODEL

Thomas and Windle first established a relationship between concentration of penetrant, its activity and pressure using thermodynamics. The chemical potential per mole of penetrant sorbed into a swollen polymer, with reference to a standard state, is given by

$$\mu_1 - \mu_1^0 = RT \left( \frac{G\bar{V}_1}{V_1} \left[ (1-v_1)^w - (1-v_1) \right] + \ln v_1 \right) + \ln (1-v_1) + \chi (1-v_1)^2$$

where $G$ is the number of network elements in the polymer, $\bar{V}_1$ volume of the penetrant, $v_1$ is the volume of the unswollen polymer, $v_1$ is the volume fraction

59
of the penetrant in the unswollen polymer, \( \chi \) is the polymer solvent interaction parameter, \( T \) is the temperature and \( R \) is the gas constant. The term in the square brackets accounts for entropic constraints caused by the molecular network and the last three terms are derived from considerations arising from one component being macromolecular.

As the penetrant is sorbed into the polymer network there is a force of opposition to the swelling which comes from the kinetic immobility of the network. In quantitative terms Thomas and Windle state that this force may be considered equal to an external hydrostatic pressure \( P \) which acts on the polymer but not on the liquid. Then the sorption of one mole of penetrant of volume \( \bar{V}_iN_A \) will cause work \( PV_iN_A \) to be done, giving

\[
\mu_i - \mu_i^0 = PV_iN_A + RT \left( \frac{GV_i}{V_1} \left[ (1-V_i)^\chi - (1-V_i) \right] + \ln V_1 + (1-V_i) + \chi (1-V_i)^2 \right) + \ln V_1 + (1-V_i) + \chi (1-V_i)^2
\]

This equation may be applied to the swelling of a glassy polymer. Activity is now introduced as a measure of thermodynamic potential in conditions of varying concentration and pressure. The traditional definition of activity, \( a_i \) is

\[
\mu_i - \mu_i^0 = RT \ln a_i
\]

Equating 2.8 and 2.9 gives

\[
\ln a_i = \frac{PV_iN_A}{RT} + \frac{GV_i}{V_1} \left[ (1-V_i)^\chi - (1-V_i) \right] + \ln V_1 + (1-V_i) + \chi (1-V_i)^2
\]

This gives the relationship between activity of the penetrant, it's volume fraction and the additional pressure. To simplify this relationship the volume
ratio $\bar{v}$ is introduced. This is the ratio of the volume fraction $v_i$ to the equilibrium volume fraction under conditions of zero extra pressure and unit activity. If the chemical behaviour is now assumed to be 'ideal' then the following assumption may be made

$$\bar{v} = (a_1)_{p=0}$$  \hspace{1cm} (2.11)

the above relation used in equation 2.10 gives

$$\ln \bar{v} = \frac{GV_i}{v_i} [(1-v_i)^W - (1-v_i)] + \ln v_i + \frac{(1-v_i)}{(1-v_i) + \chi (1-v_i)^2}$$ \hspace{1cm} (2.12)

then

$$\ln a_1 = \frac{Pv_iN_A}{RT} + \ln \bar{v}$$ \hspace{1cm} (2.13)

rearranging equation 2.13 gives

$$P = \frac{RT}{V_iN_A} \ln \left( \frac{a_1}{\bar{v}} \right)$$ \hspace{1cm} (2.14)

which is the simplified form of the pressure equation when ideal chemical conditions are assumed. The theory continues by considering the swelling of a very thin element only, followed by the extension to a bulk system made up of a finite number of very such very thin elements. When considering a very thin element diffusional resistance is assumed negligible and so the instant it is immersed in fluid the sorbed penetrant achieves unit activity throughout the element. To model bulk transport as closely as possible the thin element is theoretically bonded to an inert substrate, so that no change in area may take place on swelling. The following assumptions must now be made in order to
I) The volume increase on swelling is proportional to the volume of absorbed penetrant.

II) The viscosity, \( \eta \) of the polymer decreases exponentially with increasing concentration, according to \( \eta = \eta_0 \exp[-m\bar{V}] \) where \( m \) is a constant and \( \eta_0 \) is the viscosity of the unswollen polymer.

The swelling pressure now becomes

\[
P = \frac{RT}{V_i N_A} \ln \left( \frac{1}{\bar{V}} \right)
\]

The response of the element to this pressure is a strain rate, which may be assumed to be related to the viscosity by

\[
\frac{d\varepsilon}{dt} = \frac{P}{\eta}
\]

The strain experienced by the element may be directly related to the change in volume, especially since the presence of the substrate makes the swelling unidirectional. A parameter \( k \) may be defined as \( \varepsilon/\bar{V} \) leading to

\[
\frac{d\bar{V}}{dt} = \frac{P}{k\eta}
\]

If substitutions for \( P \) and \( \eta \) are made, then one obtains

\[
\frac{d\bar{V}}{dt} = \frac{-RT}{V_i N_A k\eta_0} \ln (\bar{V}) \exp[m\bar{V}]
\]

This equation describes the swelling of a very thin element as a function of
time. The next stage is to apply equation 2.18 to a bulk material made up of many such elements. The elements parallel to, but remote from the surface will swell under conditions of reduced activity. The activity will increase with time, controlled by the diffusional resistance of the material between the element and the surface. The modified version of equation 2.18 for an element i, in the bulk material experiencing a reduced activity a is

\[
\frac{d\bar{V}}{d\tau} = -\frac{RT}{V_1 N_b k \eta_0} \ln \left( \frac{\bar{V}}{a} \right) \exp \left[ m \bar{V} \right]
\]

Since the rate of change of activity is controlled by the diffusional resistance, Fick's first law, stated in terms of chemical potentials is used

\[
J = -D \frac{\bar{V}}{a} \frac{da}{dx}
\]

where D is the diffusion coefficient of the penetrant in the glass and J is the flux. The change in concentration in a thin element of width 5x is given by the difference in fluxes in and out of it's boundaries,

\[
\frac{d\bar{V}}{d\tau} = \frac{J_1 - J_2}{\delta x} = \frac{D_2}{\delta x} \left( \frac{\bar{V}}{a} \right) \frac{da}{dx} - \frac{D_1}{\delta x} \left( \frac{\bar{V}}{a} \right) \frac{da}{dx}
\]

Now using

\[
\frac{\Delta a}{\Delta \bar{V}} = \frac{\Delta a}{\Delta \bar{V}} \frac{\Delta \bar{V}}{\Delta \bar{V}}
\]

For ease of computation finite element form is used, leading to
\[
\left[ \frac{\Delta a}{\Delta t} \right]_i = \left[ \frac{\Delta a}{\Delta V} \right]_i \left[ \frac{D_{i+1} + D_i}{2 \delta x^2} \left( \frac{V_{i+1} + V_i}{a_{i+1} + a_i} \right) (a_{i+1} - a_i) - \right.
\]
\[
\left. \left( \frac{D_{i-1} + D_i}{2 \delta x^2} \left( \frac{V_{i-1} + V_i}{a_{i-1} + a_i} \right) (a_i - a_{i-1}) \right) \right]
\]

For each time increment the change
\[
\left( \frac{\Delta V}{\Delta t} \right)_i
\]

is calculated by equation 2.19 at constant activity and is related to
\[
\left( \frac{\Delta V}{a} \right) \frac{1}{\Delta t}
\]

and
\[
\left( \frac{\Delta a}{\Delta t} \right)_i
\]

is then calculated at constant \((\overline{V}/a)\) ratios. The fact that \((\overline{V}/a)\)is constant for a given time increment means that the term \((\Delta a/\Delta v)_i\) in equation 2.11 is just simply \((a/\overline{V})_i\).

2.3.3.2 COMPUTER SIMULATION OF DIFFUSION PROFILES USING THOMAS AND WINDLE THEORY

A computer simulation of the diffusion profiles using these equations has been developed. The equations 2.19 and 2.23 form the basis of the theory and have
been used in a Fortran program to simulate concentration profiles depicting Case II diffusion behaviour. The calculation proceeds by first determining the change in the activity profile for a fixed profile of $(\bar{\nabla}a)$ using equation 2.23. Then, using the modified activity profile the change in the $(\bar{\nabla}a)$ profile is determined using equation 2.19. The new $(\bar{\nabla}a)$ profile is used to calculate another activity profile, and so on. The program incorporates a timestepping loop within which each of the following are calculated:

I) The diffusion coefficient for each element.
II) The activity gradient at each element.
III) The volume activity ratio in each element.
IV) The volume ratio gradient at each element.

The program then calculates the volume ratio and activity in each element at the next timestep. The profiles may be printed out at any stage. The program is in appendix 1. A test of the program with the parameters used by Thomas and Windle for diffusion of methanol into PMMA as well as the application of the program to the diffusion of acetone into PVC is in chapter 6.

2.3.3.3 EFFECTS OF TEMPERATURE AND ACTIVITY ON CASE II DIFFUSION

Thomas and Windle's studies of Case II diffusion for a range of exposure temperatures of polymer samples to solvents show that as the temperature rises changes in the fundamental nature of the diffusion occur (1978). They state that at high temperatures the diffusion may become completely Fickian, while intermediate temperatures show a mixture of Fickian and Case II behaviour. As the temperature rises the velocity of the Case II diffusion front increases, although the final equilibrium concentration of solvent within the polymer appears constant. As yet however, there do not appear to have been any studies which have attempted to determine the effect of temperature on
the polymer itself during diffusion.

Another factor which affects the diffusion behaviour is the activity of the penetrant surrounding the polymer. A study by Laskey et al (1988b) has shown that there is a threshold activity below which no Case II diffusion is seen. Below this threshold no front is formed and the diffusion remains Fickian. Above the threshold normal Case II behaviour is seen, however the front velocity is reduced for reduced activities.

2.3.3.4 RECENT STUDIES OF CASE II DIFFUSION

Case II behaviour has been observed in a number of glassy polymer/solvent systems such as polystyrene in acetone, Alfrey et al (1966), and in n-alkanes, Hopfenburg et al (1969), Laskey et al (1988a, 1988b), crosslinked epoxies in benzene, Kwei and Zupko (1969), PMMA in alcohols, Thomas and Windle (1978, 1981) and PMMA in trichloroethane, Mills et al (1986). However, most of the work to date on Case II diffusion can be split into two parts. The first using exposure times in the range 2 to 300 hours and thin films of typically 4 µm to 20 µm to study the induction period and front formation with submicron resolution. The second using exposure times in the range 10 to 200 hours and larger samples of typically 1 mm to 3 mm thick to visualise and study the characteristics of the diffusion until mass equilibration is reached, which may be a number of days.

The extremes which the study of such diffusion process cover, namely submicron to a few of mm, have prohibited detailed study of all aspects of Case II diffusion by one group. The limiting factor has in most cases been the constraints of the experimental techniques used. One of the aims of this work is to link the two extreme areas of study by using two experimental techniques which are complementary to study all aspects of Case II diffusion of acetone.
2.3.3.5 REVIEW OF EXPERIMENTAL TECHNIQUES USED TO STUDY CASE II DIFFUSION

The simplest method used to study Case II diffusion is gravimetric analysis. Two groups who used this technique are Thomas and Windle (1977, 1978, 1981) and Hopfenburg et al (1969). Results can yield quantitative analysis of the Case II front velocity and its dependence on temperature and activity as well as the range over which Case II is seen. While gravimetric measurements can be analysed to obtain the front velocity and equilibrium sorption, they cannot yield detail of the shape of the concentration profile in the polymer. This may be obtained using optical microscopic analysis, Thomas and Windle (1978) radiotracer and x-ray methods, Crank and Park (1968) and Crank (1975), however resolution is not good enough to observe certain features of Case II diffusion, such as the Fickian precursor. Other disadvantages to these techniques are the problems encountered when the x-ray scattering cross section of solid and penetrant are similar as for organic solvents in plastics and destruction of the sample by slicing.

To overcome the problem of poor resolution Rutherford backscattering was applied to the measurement of Case II diffusion profiles, Mills et al (1986). Some advantages of this technique are the sub micron resolution possible, the short exposure times required and ability to study the induction period. A disadvantage however is the limitation in the sample size, as only thin films can be studied in this way. Another successful experimental technique used to study Case II profiles is NMR imaging, Weisenberger and Koenig (1989a, 1989b) and this has provided both 1-d and 2-d images of the solvent concentration. Marechi et al (1988) used NMR imaging and relaxation time analysis to study the swelling of PMMA in chloroform and chain dynamics,
although no mention of Case II diffusion was made. The use of NMR to study diffusion will be further discussed in the next section. All the techniques used to obtain concentration profiles have one common disadvantage. They are only able to provide solvent concentration profiles. None of the techniques used to study Case II diffusion to date have given any quantitative information about the rigid solid, or rubbery polymer and any changes that occur during the diffusion process.

The following section will show how profiles of both solvent and polymer concentration may be obtained using broadline NMR imaging techniques. The use of relaxation time measurements is discussed. These are useful to help analyse changes occurring in the polymer during diffusion.

2.4 APPLICATION OF NMR TO THE STUDY OF DIFFUSION

In systems which exhibit Fickian diffusion the most important parameter is the diffusion coefficient. With a knowledge of this, the concentration profiles of the penetrant may be modelled. Many previous studies of diffusion have been concerned with the measurement of the diffusion coefficient and have used the pulsed field gradient method, first demonstrated by Stejskal and Tanner in 1965. In this technique a magnetic field gradient is used to dephase the magnetisation following a 90° pulse, then after a 180° inverting pulse, a second burst of magnetic field gradient refocusses the magnetisation to form an echo. If diffusion has occurred the spins will be partially refocussed and the diffusion coefficient may be determined from the echo amplitude attenuation.

In addition to the PFG methods imaging techniques have been used to determine values of different coefficient's by modelling 1-d concentration profiles of mobile protons in liquids as they diffuse through a solid material,
such as water into nylon, Blackband and Mansfield (1986) and Mansfield (1991).

Unlike Fickian diffusion, Case II diffusion and other anomalous diffusion phenomena cannot be characterised by the measurement of one coefficient. For studies of these more complex types of diffusion researchers have turned increasingly to imaging methods. Using these, analysis of the profile shape is used to characterise the diffusion. Weisenberger and Koenig have used the FLASH imaging sequence, developed by Haase et al (1986) to study Case II diffusion of methanol and acetone in PMMA, producing both 1-d and 2-d images, (1989a, 1889b).

Most recent studies of diffusion by NMR have been concerned with liquid penetration, using standard liquid imaging sequences. Weisenberger and Koenig took a PMMA sample and immersed it in a container of liquid methanol. This container was then imaged giving profiles whose intensity was made up of a component from the absorbed solvent and the surrounding solvent. The method initially seems advantageous, with the need to use only one sample and leave it in the magnet for the duration of the diffusion time. However the signal from the surrounding free liquid is many orders of magnitude greater than the bound liquid and has a very much longer $T_2$ relaxation time. The makes the accurate study of the exact profile shape of the short $T_2$ component very difficult.

This technique is not able to provide any information regarding actual polymer as FLASH is a liquids imaging sequence designed for long $T_2$ materials. Images of good quality are needed for the determination of exact profile shapes and quantitative analysis from profile. Improvements in the quality may be obtained by restricting the components studied to the bound fluid and penetrated polymer. The $T_2$'s of these components are closer in magnitude that those of the bound and free fluid and have more detailed
profiles are obtainable.

A further advance in the imaging of diffusion is to study the unpenetrated polymer, as well as the penetrated polymer and bound fluid. The $T_2$ values of such components necessitate the use of broadline imaging methods such as gradient echo, Cottrell (1990) and variants, McDonald et al (1993). With the use of these techniques visualisation of the bound fluid and penetrated polymer to submillimetre resolution is possible, Perry et al (1994a). However with the STRAFI technique, Perry et al (1994b) the rigid unpenetrated polymer as well as the other components is visualised.

To make any quantitative analysis concerning possible changes in molecular dynamics of the polymer it is essential to be able to separate the polymer signals from the fluid signals. Isotope labelling of the penetrant with deuterium allows the polymer component to be visualised independently as deuterium is invisible to proton NMR. Subtraction of such profiles from those obtained using normal acetone yields profiles of only the penetrant.

2.5 APPLICATION OF ION BEAM TECHNIQUES TO THE STUDY OF DIFFUSION

Ion beam techniques, like NMR imaging, are particularly suitable for obtaining one dimensional concentration profiles for use in diffusion studies. Rutherford backscattering (RBS) is the ion beam technique that has been used in the study of Case II diffusion. Areas of interest have been the effects of solvent molecular size, Gall (1990), transient swelling, Hui et al (1987a), temperature dependence, Laskey et al (1988b), determination of concentration profiles, Mills et al (1989) and exposure of samples to low vapour activities, Laskey et al (1988a). The debonding of a photoresist caused by Case II diffusion has also
been studied, Mills et al (1989). The RBS work has required the use of thin films, and whilst giving excellent resolution over a very short distance, the potential of the technique for a thorough study of Case II dynamics is somewhat limited.

With the excellent resolution at short exposure times and over thin surface layers ion beam methods seem particularly suited to being supplementary to other experimental techniques in a study of Case II behaviour. The NRA technique offers the possibility to study concentration profiles of either the penetrant or the polymer as the basis of the technique is the nuclear reaction between a deuterium atom and a helium ion. The penetrant or the polymer may be deuterated, so giving the choice of concentration profile. This gives an immediate advantage over other techniques where it is only possible to study the penetrant profile.

In addition to the use of the NRA technique to study surface layers of a few microns thickness it may be used to scan a cross section of a sample of up to approximately 20 mm. These profiles are directly comparable with the NMR profiles obtained. Profiles obtained using both techniques may be compared in order to prove that what is seen is due to a definite physical process and not a consequence of a particular experimental technique.
CHAPTER 3

DEVELOPMENT OF A REPETITIVE PULSE VARIANT
OF BROADLINE GRADIENT ECHO MAGNETIC
RESONANCE IMAGING

3.1 INTRODUCTION

Although the largest area of Nuclear Magnetic Resonance Imaging continues
to be that of medical diagnosis (and clinical research), much recognition is now
being gained for non medical applications. The imaging of solids is an area
that is growing rapidly, despite the problems associated with it discussed in
chapter 1, with the desire to improve both image quality and resolution.

A technique has been developed which is a broadline variation of the FLASH
liquids imaging sequence. However it has been developed to improve image
quality rather than simply increase imaging speed. The sequence uses the
broadline gradient echo technique with repetitive small flip angle pulses to
overcome bandwidth limitations. The improvements in image quality which
can be obtained are demonstrated by one-dimensional profiles of a rubber
phantom obtained with an echo time of only 80 μs.

3.2 DEGRADATION OF PULSE BY GRADIENTS IN THE
GRADIENT ECHO IMAGING TECHNIQUE

The gradient echo method developed by Cottrell et al (1990) has proved to be
very successful for the imaging of larger (10-20 cc) solid samples with spin
spin relaxation times of the order of a few hundred microseconds. In this method large oscillating magnetic field gradients of frequency $\tau^{-1}$ are used to refocus the magnetisation at a time $\tau$ following a 90° RF pulse applied at a zero crossing. The schematic of the pulse sequence used is in figure 1.17. The full echo is recorded and, following a linearisation procedure to account for the time dependence of the gradient, it is Fourier transformed to give a one-dimensional profile. The resolution which can be obtained is determined by the amplitude and frequency of the oscillating gradient. The pixel resolution is

$$\delta r = \frac{\pi}{2\gamma g_0 \tau}$$  \hspace{1cm} (3.1)

Where $g_0$ is the gradient amplitude and $\gamma$ is the magnetogyric ratio.

In practice there is a further consideration which must be borne in mind when considering the achievable resolution and associated field of view. It is assumed that a delta function 90° pulse is applied at the instant the gradient is zero, so that the pulse is not degraded by the gradient. However only an approximation to this is possible. For long $T_2$ systems, where values of $\tau$ may be a few ms and the gradients are relatively weak the problem is small enough to be neglected as the effects on image quality are negligible. As $\tau$ is reduced and the gradient strength is increased however, the problem becomes more significant until at values of 80 µs images become significantly affected.

The finite width of the pulse means that it is necessarily applied while the gradient is on. For a 90° pulse of length $t_{90}$, the edges of the sample at positions $\pm L/2$, where $L$ is the sample length, experience a gradient field of maximum magnitude

$$B_g = \frac{Lg_0}{2} \sin \left( \frac{\pi t_{90}}{\tau} \right)$$  \hspace{1cm} (3.2)
where it is assumed that the centre of the pulse coincides with the gradient zero crossing. The magnitude of the radiofrequency field, for a 90° pulse, is

\[ B_p = \frac{\pi}{2\gamma T_{90}} \]  \hspace{1cm} 3.3

The assumption is that \( B_p \gg B_g \). This places a restriction on the number of pixels \( N_{\text{max}} \) in the field of view. Rearranging equations 3.1 to 3.3 gives

\[ N_{\text{max}} = \frac{L}{\delta t} \left\{ \frac{2\tau}{t_{90} \sin \left( \frac{\pi T_{90}}{\tau} \right)} \right\} \]  \hspace{1cm} 3.4

For a pulse length of 10 μs and a gradient period of 200 μs, \( N_{\text{max}} \ll 256 \), say 64. Reducing the gradient period to 80 μs reduces \( N_{\text{max}} \) to < 42 and sensible spatial resolution is no longer possible.

### 3.3 APPLICATION OF STEADY STATE FREE PRECESSION AND RAPID ACQUISITION TECHNIQUES TO IMAGING SEQUENCES

There is no requirement that a full 90° pulse should be used in a gradient echo sequence. The shortening of the pulse length would go a long way to removing the problem described above. The number of pixels in the field of view can be increased substantially by increasing the pulse bandwidth. For a fixed \( \tau \), and small pulse length \( t_p \) to \( \tau \) ratios, the increase goes approximately as the square of the pulse width reduction since
Equation 3.5 can be understood when it is realised that, for instance, halving the pulse length increases the pulse bandwidth by a factor of two whilst simultaneously decreasing the required bandwidth of the pulse by a further factor of two since the gradients are only on for half the time. The price which is paid for the improved possible resolution is a substantial loss in signal-to-noise ratio since the signal amplitude is proportional to

$$N_{\text{max}} = \frac{2\tau^2}{\pi t_p^2}$$

The signal-to-noise can be recovered by using a train of rapidly repeated pulses. This introduces the concept of steady state free precession (SSFP). Carr (1958) was the first to notice that the steady state magnetisation is retained in a repetitive pulse experiment where the interpulse spacing, \(n\tau\) is less than the \(T_1\) and \(T_2\) relaxation times. For SSFP where \(n\tau < T_1, T_2\) calculation of the equilibrium values of \(M_y\) following each rf pulse must account for both \(T_1\) and \(T_2\) relaxation as well as the precession of the magnetisation due to the RF pulses. The pulses and the interpulse spacing are usually identical, as, although not strictly necessary, it is mathematically much easier.

In liquid systems the main reason for the implementation of sequences which use SSFP is to increase acquisition speed. Aside from the obvious advantages such as increased patient throughput such sequences are extremely good for measuring flow and relaxation time contrasted images. In a repetitive pulse experiment signal arises from both an rf refocussed echo and an SSFP refocussed FID. Sequences have been developed which use either of these signals, or a combination of both. The FAST sequence, Gyngell (1988) uses slice selection rephasing which acts only on the FID generated by the current
RF pulse, and the SSPF echo is therefore suppressed. CE-FAST, Gyngell (1988) uses a rephasing pulse placed at the end of the preceding cycle so that the SSPF echo will be focused but the current FID suppressed. The FISP sequence, Oppett et al (1986) defects both RF and SSPF echo signals simultaneously. Finally the FADE sequence, Redpath et al (1988) also acquires both echoes, but independently so giving the advantage of contrast enhancement as in CE FAST, where there is a degree of $T_2$ weighting in the signal amplitude of the RF and SSPF echoes.

The FLASH sequence was first suggested by Haase et al, (1986) and is a rapid acquisition 2DFT imaging sequences which uses a rapidly repeating train of low angle pulses. The reduction of the tip angle to about 5% shortens the acquisition time, but at the expense of signal for liquid systems, with long $T_2$'s this trade-off between imaging speed and signal-to-noise ratios is possible. FLASH differs from the other steady state sequences described by the loss of transverse coherence of the magnetisation. Snapshot FLASH, Haase et al (1990) is a high gradient rapid acquisition variant and in spoiled FLASH, Frahm et al (1987) spoiler gradients are used to ensure complete loss of transverse magnetisation.

The common feature of all the methods described is to image long $T_2$ systems quickly. This contrasts with short $T_2$ applications of magnetic resonance imaging. Here the need is to improve both image resolution and signal to noise by whatever means possible. This is usually difficult due to the longer $T_1$'s commonly found in solids which do not make signal averaging easy and the shorter $T_2$'s which impair resolution.
3.4 LONGITUDINAL INTERFERENCE IN REPETITIVE PULSE EXPERIMENTS

A limiting case of SSFP is when $T_2 < n\tau < T_1$. In this situation there will be a loss of transverse coherence of the magnetisation between pulses, while preserving the longitudinal coherence of the magnetisation in a steady state equilibrium. Given the short $T_1$'s occurring in solid materials, this limiting case will govern the magnetisation in the majority of cases for a repetitive pulse experiment on a solid sample.

To maximise the accumulated signal, it is necessary to use a fast repetition rate. It is assumed that during the interpulse spacing all the transverse magnetisation has decayed irreversibly. However the recovery of the longitudinal magnetisation towards the equilibrium value $M_0$ is not completed during the interpulse spacing. After a small number of pulses a dynamic equilibrium value of the magnetisation is established. Consider the value of the Z magnetisation just before a pulse to be $M_z(0\_)$.

Now the values of the Z magnetisation at the end of $n\tau$ will be $M_z(n\tau)$, Ernst, Bodenhausen and Wokaun (1987). These are equal so $M_z(0\_) = M_z(n\tau)$. The magnetisation just after a pulse is

$$M_z(0\_\tau) = M_z(0\_) \cos \beta$$  \hspace{1cm} 3.7

Where $\beta$ is the tip angle of the pulse as seen in fig 3.1. At the end of an interpulse spacing the z magnetisation is

$$M_z(n\tau) = M_z(0\_) \exp\left(-n\tau \frac{T_1}{T_1}\right) + M_0\left(1 - \exp\left(-n\tau \frac{T_1}{T_1}\right)\right)$$  \hspace{1cm} 3.8

But in equilibrium we have that $M_z(n\tau) = M_z(0\_)$ giving
FIGURE 3.1  LONGITUDINAL INTERFERENCE IN A REPETITIVE PULSE EXPERIMENT

FIGURE 3.2  SIGNAL AMPLITUDE AS A FUNCTION OF PULSE ROTATION ANGLE
\[ M_x(0+) = M_0 \left( \frac{1 - \exp\left(-\frac{\pi t}{T_1}\right)}{1 - \cos\beta \exp\left(-\frac{\pi t}{T_1}\right)} \right) \]

The initial amplitude of the FID, \( M_x(0+) \) will be

\[ M_x(0+) = M_0 \left( \frac{1 - \exp\left(-\frac{\pi t_p}{2T_{90}}\right)}{1 - \cos\left(\frac{\pi t_p}{2T_{90}}\right) \exp\left(-\frac{\pi t}{T_1}\right)} \right) \sin\left(\frac{\pi t_p}{2T_{90}}\right) \]

where \( \beta = \left(\frac{\pi t_p}{2T_{90}}\right) \). Maximum signal amplitude is now no longer obtained for a 90° pulse, but for \( \beta_{opt} \) determined by the relation

\[ \cos\beta_{opt} = \exp\left(-\frac{\pi t}{T_1}\right) \]

The signal amplitude as a function of pulse rotation angle is shown for various ratios of \( \pi t/T_1 \) in figure 3.2 (reproduced from Ernst, Bodenhausen and Wokaun 1987). It is easily seen that for shorter interpulse spacings, the optimum pulse tip angle decreases.

### 3.5 EXPERIMENTAL PROCEDURE

The new sequence developed is illustrated in figure 3.3. A large amplitude oscillating magnetic field gradient is first established and then a short pulse applied at a gradient node. The subsequent gradient echo is recorded. Further echoes can be recorded as the gradient continues to oscillate if the
FIGURE 3.3  REPETITIVE PULSE VARIANT OF GRADIENT ECHO IMAGING SEQUENCE
signal to noise and $T_2$ warrant it, as originally suggested by Cottrell et al, either to increase signal to noise or to collect a series of $T_2^*$ weighted profiles. After $n$ gradient cycles a second pulse is applied and the subsequent echo(es) added to the first. Pulses continue to be applied and echoes accumulated at intervals of $nt$ until sufficient echoes have been recorded for adequate signal to noise or until the gradient duty cycle dictates that the gradients must be switched off. If the condition $T_2 < nt < T_1$ is met then, as shown in the previous section the echo and hence profile intensity is naturally $T_1$ weighted, since the signal intensity is proportional to

$$\frac{1 - \exp\left(\frac{-nt}{T_1}\right)}{1 - \cos\left(\frac{\pi t_p}{2 T_{90}}\right) \exp\left(\frac{-nt}{T_1}\right)} \sin\left(\frac{\pi t_p}{2 t_{90}}\right)$$

3.12

3.5.1 NMR IMAGING SPECTROMETER

The NMR imaging spectrometer is based on a Magnex superconducting magnet with actively shielded gradient coils and an SMIS solids imaging console. Special features have been custom built to optimise the solids capability. A schematic of the system is shown in fig 3.4. The magnet is a superconducting 1.5T 200 mm horizontal, with shimmed homogeneity of 20 ppm over 100 mm and a field stability of less than 0.05 ppm/hr. The actual running field is currently 0.705 T which corresponds to a proton resonant frequency of 30 MHz.

The SMIS computer generates the gradient waveforms, controls the sequence timing with 100 ns resolution and controls data capture. A PTS synthesizer is used as a reference frequency for both transmit and receive. The RF pulses generated by the transmitter are amplified by a Heatherlite 400 W amplifier.
FIGURE 3.4  SCHEMATIC OF THE NMR SYSTEM
and excite the sample in the coil. The received NMR is amplified by the pre-amp, which is protected from the transmitter by a set of crossed diodes. The pre-amp was designed by members of the physics department for extra fast response. The signal is then demodulated and quadrature, real and imaginary signals are filtered and digested by the ADC’s in the computer. These are special high speed 10 MHz Loughborough boards with 8 bit resolution. The data collection and Fourier transforms are performed by the SMIS computer with software written by S.Roberts and other members of the NMR group.

3.5.2 GRADIENTS

The high speed and technical requirements of solid imaging sequences make it necessary to have high power, fast switching gradient coils. These are Magnex actively shielded gradient coils which have an 80 mm bore. The gradients are powered by Techron amplifiers, themselves powered by a 240 V AC 3 phase transformer. They have a 180 amp peak DC output and amplify from DC to 50 kHz with output of 20 amps/volt control voltage. For standard experiments one Techron for each of the x, y, and z gradient coils is used, but if high resolution 1-d experiment is required, two techrons in a master and slave arrangement may be used to increase the gradient capability. The gradients are sinusoidally driven and must be tuned to reduce inductance. Currently they may be tuned to either 80 µs or 216 µs. The maximum achievable gradient strength is 121 Gcm⁻¹ when tuned to 216 µs and the linear region is 3 cm in diameter.

3.5.3 NMR PROBES

The probes form a resonant circuit tuned to 30 MHZ and transmit and receive the NMR signal. It consists of a coil which surrounds the sample and trimmer
capacitors which allow tuning of the probe. Two types of coil are used for the NMR experiments. A 25 mm internal diameter birdcage coil is used for repetitive pulse imaging experiments. For bulk measurements and imaging sequences which require very short 90° pulses, such as multipulse sequences, a solenoid coil is used. The two solenoid coils are made of teflon to ensure that there is no contribution to the signal and have internal diameters of 8 mm and 30 mm. The 90° pulse length of the 8 mm diameter solenoid coil is typically 2-3 μs.

3.6 RESULTS AND DISCUSSION

3.6.1 TESTING ON RUBBER PHANTOM

To test the new sequence a phantom was made up which consisted of alternating rubber and teflon slices as shown in fig 3.5. Figure 3.6 a) shows a one-dimensional profile of this phantom recorded using the birdcage coil with τ=80 μs and g₀=27 Gcm⁻¹ obtained using the standard gradient echo technique. The 90° pulse length is 15 μs and the profile is a result of two averages. Failure to meet the pulse bandwidth requirement stated in equation 3.4 across the entire phantom results in serious rounding artifacts and a loss of resolution at the ends of the phantom.

Figure 3.6 b) is a one-dimensional profile of the same phantom using a low flip angle pulse. The gradient amplitude and frequency are the same but the pulse length is only 2 μs, equivalent to 12°. Again only 2 averages are recorded and the improvement to the profile is appreciable. Figure 3.6 c) is a one dimensional profile identical to 3.6 b) except that it is the result of averaging 400 echoes in 1.6 seconds. The pulse gap used for figure 3.6 c) is 4ms or 50 gradient cycles, which is of the order of 3T₂* for a sample this large
in our magnet. In both b) and c) the substantially improved resolution towards the ends of the sample is clearly evident. The additional advantage of the profile in c) is the theoretical signal to noise improvement. For small ratios of $\tau$ to $T_I$, this is $\frac{200^h \sin (12^\circ)}{1}$ which is approximately 3:1. This improvement is possible using the repetitive pulse sequence in the same experimental time taken for the standard gradient echo sequence to record the profile shown in a).

FIGURE 3.5 RUBBER SLICE AND TEFлон PHANTOM
FIGURE 3.6  
PROFILES OF SIX RUBBER SLICES WITH a) 90° PULSE AND 2 AVERAGES, b) 12° PULSE AND 2 AVERAGES AND c) 12° PULSE AND 400 AVERAGES USING NEW SEQUENCE
Two dimensional images can be obtained by back projection reconstruction of profiles, and figure 3.7 shows a 120x120 non slice selected image of the same phantom using the repetitive pulse sequence with the same parameters as above. The image was acquired in less than 3 minutes, but most of this time was delays between profiles due to the low gradient duty cycle.
3.7 CONCLUSION

The need for a low flip angle, repetitive pulse variant of broadline gradient echo, analogous to FLASH has been established and a method of achieving it has been demonstrated. The implementation of this sequence has a twofold advantage for broadline imaging. The loss of resolution and rounding of the image edges has been alleviated and the imaging speed has been significantly improved. This allows a 3:1 improvement in the signal to noise ratio in a fraction of the time it would normally take to obtain such data. The method seems particularly suitable to the study of short $T_2$ bound fluid components in porous media, especially where the sample is relatively large. The latter condition relates to the difficulty of obtaining hard 90° pulses in large RF coils without excessive RF power. In addition to the use of this technique in the study of Case II diffusion in the acetone and PVC system it is being applied to the study of connate water in rock cores, Attard et al (1994).
CHAPTER 4

CHARACTERISATION EXPERIMENTS ON THE PVC AND ACETONE SYSTEM

4.1 INTRODUCTION

In chapter 2 Case II diffusion was introduced as an anomalous diffusion phenomenon generally associated with the penetration of organic solvents into amorphous glassy polymers. Poly(vinylchloride) PVC is recognised as being on the borderline between amorphous and crystalline behaviour, yet also shows anomalous diffusion behaviour with organic solvents, such as acetone, Kwei et al (1972).

This chapter describes the preliminary characterisation experiments into the diffusion behaviour exhibited when acetone penetrates PVC. Concentration profiles recorded using NMR imaging have been studied for both cylindrical and rectangular geometries.

Other background experiments were performed to aid in the characterisation of the system prior to a more detailed study. These included Differential Scanning Calorimetry (DSC) to determine the glass transition temperature of the PVC and solubility tests. Bulk T₂ relaxation time analysis of the samples was particularly important for the optimisation of the imaging sequences and to give information about the mobility of the polymer once penetrated by the acetone. Finally gravimetric analysis was used as an additional experimental technique to determine the diffusion behaviour present in the system.
4.2 EXPERIMENTAL DETAILS

The PVC used is manufactured by Simona UK Ltd and distributed by Aquarius Plastics Ltd. It is available in rigid solid form as cylindrical or rectangular rods typically 2 m in length. Cylindrical rods with diameters from 6 mm to 20 mm were used and for the rectangular geometry experiments rods of 25 mm square were used. The PVC is available in a range of colours so the presence of dyes and other additives is inevitable, however the grey rod is the purest commercially available rigid form.

PVC is a borderline polymer between amorphous and crystalline with crystallinity values ranging between 5% and 30% depending on manufacture. The PVC used is not crosslinked, has a glass transition temperature of approximately 73°C and a density of 1.42 gcm$^3$. Exact details of manufacture are unavailable, but the PVC appears to have a homogeneous structure, although due to extrusion processes used in manufacture, has some degree of anisotropy.

Acetone, both ordinary and in deuterated form was obtained from the Aldrich Chemical Co. The ordinary acetone is 99.5 % pure, has a density of 0.791 and a boiling point of 56°C. The acetone-d$_6$ has a minimum isotopic purity of 99.96%, a density of 0.872 and a boiling point of 55.5°C. Figure 4.1 a) shows the chemical composition of acetone, and b) shows the PVC. In c) a possible structure for the PVC is indicated. The bulky chlorine atoms are above and below the zig zag planar carbon chain, however the exact tacticity of the PVC is not known. It may be syndiotactic, with the chlorine atoms alternately above and below the chain, isotactic, with the chlorines all on one side of the chain or atactic which is a completely random arrangement.
FIGURE 4.1  

a) CHEMICAL COMPOSITION OF ACETONE  
b) CHEMICAL COMPOSITION OF PVC  
c) POSSIBLE STRUCTURE FOR PVC
The samples were exposed to the acetone vapour in conical flasks which formed constant vapour activity chambers, allowing control of both sample preparation temperature and equilibrium solvent concentration. For the majority of experiments the samples were exposed to vapour above a reservoir of liquid acetone. For experiments to determine exposure temperature dependence the flasks were immersed in a temperature controlled water bath, accurate to ± 2.0°C, that was fitted with a stirrer to ensure uniformity of temperature. A schematic of the preparation chamber is shown in figure 4.2.
In order to minimise the time required for re-establishment of equilibrium vapour concentration following removal or insertion of a sample, the volume of the flask was reduced using clean gravel. This was especially important in gravimetric analysis experiments. The flasks stopper was fitted with a one two valve filled with acetone which maintained atmospheric pressure in the chamber. The use of the conical flask ensured that any vapour condensation drips down the sides of the flask to the gravel, hence removing the problem of liquid dripping on to the samples. The use of deuterated acetone in the experiments led to a small alteration to the preparation procedure. The deuterated acetone required the use of a stopper to completely seal the exposure chamber from the atmosphere to minimise exchange processes.

4.2.2 EXPOSURE TO REDUCED VAPOUR ACTIVITIES

The concept of activity was introduced to polymer science as a way of quantifying the 'amount of vapour' surrounding a sample. It is primarily applicable to vapour generated by solvent and polymer mixtures.

Laskey et al (1988a) have used the Flory-Huggins theory for solvent/polymer mixtures and quoted an expression for the activity of the vapour in terms of \( \phi \), the volume ratio of the penetrant, Flory (1953)

\[
a = \phi \exp(1-\phi) \exp(\chi_1 (1-\phi)^2)
\]

Where \( \chi_{1v} \) is the polymer/solvent interaction parameter. It has been assumed that \( \chi_1 \) is of order zero or very small for many polymer/penetrant systems, Guggenheim (1966), thereby reducing equation 4.1 to

\[
a = \phi \exp(1-\phi)
\]
Equation 4.2 is widely accepted and was adopted to quantify the activity of the vapour in all reduced activity exposure experiments undertaken, however it should be noted that for acetone and PVC the assumption that \( \chi_i \) is negligible cannot be validated since no documented values for it can be found.

### 4.2.3 SAMPLE PREPARATION

Although the exposure to solvents takes place in the same type of chamber for all the samples and experiments, the exact sample sizes and other preparation procedures vary depending on the experiment and technique used. For example, NMR imaging experiments and ion beam NRA profiling experiments require specific and different sample sizes and procedures. These will therefore be discussed individually with each experimental section in the next three chapters.

### 4.3 RELAXATION TIME EXPERIMENTS

The spin spin (\( T_2 \)) and spin lattice (\( T_1 \)) relaxation times are key parameters in the study of systems which contains both mobile and rigid components. A knowledge of relaxation times is required for the optimisation of the NMR imaging sequences. Since the repetition times in imaging sequences are usually of the order of several \( T_1 \) to ensure complete re-establishment of the equilibrium of the longitudinal magnetisation, \( T_2 \) becomes the more important parameter when using gradient echo techniques. The \( T_2 \) values present in samples affect the choice of echo time, which must be short enough to ensure that all the required components are present in the signal. Further significance of \( T_2 \) is to give very useful information regarding the mobility of the components within the system, and show changes in mobility from softening.
or breaking of chains over a period of time.

Three $T_2$ components with values ranging over at least three orders of magnitude are estimated to be present in the PVC and acetone system. However, such is the complexity of a polymer and penetrant system that the assignment of only three values of $T_2$ relaxation times may be an underestimation. As the solvent penetrates the polymer, the chains become disentangled, are able to move more freely and hence exhibit a longer $T_2$. It is possible that the polymer chains, or the solvent restricted within them have a range of relaxation times. Indeed, it is most likely that there are continuous distributions centred on three values. This enables the use of three component exponential fitting routines in the analysis of CPMG experimental results of measurements of $T_2$ values. The $T_2$ values of samples used in the imaging experiments were measured and will be discussed in the following two chapters.

4.4 INITIAL TWO DIMENSIONAL IMAGING EXPERIMENTS USING GRADIENT ECHO AND SAMPLES WITH CYLINDRICAL GEOMETRY

Samples cut from 15 mm diameter cylindrical PVC rod were exposed to acetone vapour above a liquid reservoir to allow radial penetration. Immediately prior to imaging the ends of samples that were initially 50 mm in length were cut away to ensure that end effects did not distort the images. This ensured that only radial penetration was observed. Inspection of an FID gave the $T_2^*$ relaxation times present, which for solid or rubbery materials gives a fairly good first approximation to $T_2$. The FID indicated 3 components to be present as shown in the schematic FID representation in figure 4.3.
When acetone penetrates the rigid PVC it becomes soft and rubbery with a clear boundary between the penetrated and unpenetrated regions. The assignment of the 3 components with approximate values of 10-20 µs, approximately 400 µs and several ms was therefore to rigid unpenetrated PVC, rubbery PVC, and absorbed mobile acetone. This approximation of $T_2$ is required in order to optimise the choice of $\tau$ in the imaging sequences. A gradient echo imaging sequence with a 180° refocussing pulse as described in chapter 1 was used with a solenoid coil and oscillating gradients in the x and y directions to give a two dimensional image of the cross section of the sample. Since the refocussing pulse was used the echo time was $2\tau$, where $\tau$ is the period of the gradient sine. For the following experiments $\tau$ was 240 µs, the 90° and 180° pulse lengths were 18 µs and 36 µs, and the gradient strength was 17 Gcm$^{-1}$. The images were the result of 10 averages and all experiments were performed at room temperature. A series of images were recorded from samples exposed for various times at room temperature and typical results are in figure 4.4. The three images shown were exposed for 16, 80 and 96 hours.
FIGURE 4.4  2-D IMAGES OF ACETONE PENETRATION IN CYLINDRICAL PVC SAMPLES USING GRADIENT ECHO SEQUENCE
and are in the form of contour plots. The images were formed from signal from both the acetone and the rubbery PVC. The sharp penetrant front is clearly seen along with the increased penetration with time. Sample swelling of the order of 20% is also visible.

Images formed from only the rubbery PVC signal are obtained if deuterated acetone is used. Deuterium is not detected at the 30MHz proton frequency used, hence conditions within the sample are identical yet the solvent signal is not seen at all. A series of images were recorded using the same NMR parameters as previously for samples exposed to acetone-d₆ for various times. Figure 4.5 shows the results of exposure for 24, 48, 96 and 120 hours, the reduced signal to noise reflecting the reduction in the amount of signal detected. Once again the sharp penetrant front is visible, along with a linear front advance with time, leading to a value of the velocity of 0.046 mmhr⁻¹. These experiments establish the presence of Case II behaviour in the PVC and acetone system.

Quantitative information from imaging experiments is more sensibly obtained from one dimensional profiles. A reconstruction program was developed which averaged all radii round the circumference of the image to give a one-dimensional profile across the diameter. Figure 4.6 shows a one dimensional profile across the image of the sample exposed for 96 hours from figure 4.5. Here again the sharp boundary between the penetrated and unpenetrated regions is seen clearly, however the resolution using this technique is not sufficient to allow any detailed quantitative analysis, except to say that the front velocity is of the order of 0.046 mmhr⁻¹.
FIGURE 4.5 - 2-D IMAGES OF DEUTERATED ACETONE PENETRATION IN CYLINDRICAL PVC SAMPLES USING GRADIENT ECHO SEQUENCE
In addition to the grey PVC used in the experiments to date, Simona UK manufacture red and black PVC. These obviously have different additives and colorants, but all are extruded in the same way. The exact chemical composition was not available from the manufacturers. Truly pure PVC is white. The effects of manufacturing additives on the diffusion characteristics of the PVC was tested by comparison of samples of the three colours available. The imaging experiments described in section 4.4 were performed on the red and black PVC. The results showed that Case II behaviour was present in all three samples when exposed to acetone vapour. A further test was performed to monitor the behaviour of the samples on prolonged exposure to acetone liquid. The effect of liquid acetone on samples of each colour showed that the grey PVC became soft and rubbery, but did not dissolve, whereas the red and black PVC dissolved completely in the liquid after 20 hours, the red dissolving more quickly than the black.
The conclusions drawn from these tests were that manufacturing additives have quite a substantial effect on the behaviour of PVC when in contact with acetone. It was thought that the dissolution of the red and black PVC was due to the presence of more additives, which have a plasticising effect, than were present in the grey PVC. This appears to confirm the manufacturer’s information that the grey PVC is the purest commercially available solid PVC.

4.6 GRAVIMETRIC ANALYSIS

The weight gain characteristics of a solid sample exposed to a vapour or liquid may be used to give an insight into the type of diffusion behaviour present. Such characteristics as a function of time for unidirectional planar diffusion are given by

\[ W(t) \propto t \quad \text{Case II} \]
\[ W(t) \propto t^m \quad \text{Fickian} \]

Where \( W(t) \) is the weight at time \( t \). Such gravimetric analysis has long been used to study diffusion, and was one of the experimental methods used by Thomas and Windle (1978, 1981) and other groups researching relaxation controlled diffusion behaviour, Alfrey (1965) and Hopfenburg et al (1969). With this method the velocity of the front or the equilibrium concentration of penetrant across the swollen region may be monitored. However lack of sensitivity has prevented certain characteristics of Case II behaviour from being studied, such as the Fickian precursor and the induction period. It remains an excellent technique, however, for investigations of large samples which may take several weeks to become fully mass equilibrated. There has been no study of Case II diffusion in samples over 3 mm in thickness or in cylindrical geometry.
The samples used in these experiments were cut from 15 mm diameter rod and were typically 40 mm in length. A series of experiments were performed in the temperature range 5°C to 50°C with samples exposed to vapour as described in section 4.2.1. The objectives of these experiments were to confirm the presence of Case II behaviour over a range of about 7-8 mm in a cylindrical sample, and investigate the temperature dependence of the front velocity and the equilibrium concentration of the penetrant.

Measurements of weight were recorded initially every 12 hours for the first few days, then at varying time intervals until mass equilibration. The results were in the form of percentage weight gain against time curves. For a sample with rectangular geometry sufficiently large that the corners can be ignored, such a graph will yield a straight line for Case II behaviour. The use of cylindrical samples with radii comparable to the diffusion distance introduces curvature into the weight gain characteristics. Figure 4.7 shows typical results for three temperatures, 45°C (circles), 25°C (triangles) and 9°C (squares). These show that Case II behaviour was present at all temperatures and that the diffusion remained Case II over the entire sample until mass equilibration was reached. A typical value for the volume increase was 60 ± 5% and for the mass increase was 35 ± 5%. The time taken for mass equilibration to occur was dependent on sample size and temperature and for the samples in this experiment it took approximately 140 hours at 50°C and approximately 500 hours at 5°C. This reflects the fact that the velocity of the front is strongly exposure temperature dependent, however the equilibrium penetrant concentration was found to be independent of temperature. The length of time required to establish equilibrium vapour pressure and the dependence of this time on the free volume in the flask required careful maintenance of identical conditions in all the chambers used for the preparation of samples.
FIGURE 4.7  PERCENTAGE WEIGHT GAIN AGAINST TIME FOR ACETONE PENETRATION IN PVC SAMPLES FOR 9°C (SQUARES), 25°C (TRIANGLES) AND 45°C (CIRCLES)

FIGURE 4.8  DSC THERMOGRAM OF RIGID PVC SAMPLE
4.7 DIFFERENTIAL SCANNING CALORIMETRY EXPERIMENTS

Differential Scanning Calorimetry (DSC) experiments as described in chapter 2 were performed at the Cavendish Laboratory, University of Cambridge on a Perkin Elmer DSC-7 machine capable of measuring both above and below 0°C. The objectives were to determine the glass transition temperature $T_g$ of the PVC used and the effect of various concentrations of acetone on $T_g$. The thermogram for rigid PVC is shown in figure 4.8, giving a value of $T_g$ of 74°C with a scanning rate of 10°Cmin$^{-1}$.

The $T_g$ values of a set of samples with various acetone concentrations were measured, and the results are shown graphically in figure 4.9. From this it was concluded that all diffusion behaviour to be studied in the exposure temperature range 5°C to 50°C would take place where the exposed PVC was above the glass transition temperature.

The presence of crystalline regions in predominantly amorphous polymers is well known, Hall (1989), the crystallinity generally depending on the manufacturing process. Documented values for PVC, measured using low angle scattering techniques vary from 0% to 20%, Walsh et al (1981). Results from DSC experiments consistently showed the presence of a small amount of crystallinity in the PVC structure by the relaxation peak seen in the thermograms of low acetone concentration samples, figure 4.10.

4.8 DISCUSSION

The initial two dimensional imaging experiments revealed the presence of Case II diffusion in the PVC and acetone system. This was validated by multiple pulse NMR imaging experiments on samples with rectangular geometry and
FIGURE 4.9 VARIATION OF THE GLASS TRANSITION TEMPERATURE OF PVC WITH PERCENTAGE ACETONE CONCENTRATION (BY WEIGHT).

FIGURE 4.10 DSC THERMOGRAM SHOWING A RELAXATION PEAK ATTRIBUTED TO A CRYSTALLINE FRACTION (ACETONE FRACTION = 10%)
gravimetric analysis on samples with cylindrical geometry. The diffusion characteristics were found to be independent of sample geometry. The gravimetric analysis proved that the Case II front velocity is exposure temperature dependent while the equilibrium concentration of the acetone is independent of exposure temperature. It also showed that the diffusion behaviour remains Case II over a range of 7-8 mm.

The effects of different additives in the PVC were tested, and although exposure to vapour produced the same diffusion behaviour in red, black and grey samples, when exposed to liquid acetone the red and black samples dissolved completely while the grey remained solid but rubbery. Differential Scanning Calorimetry was used to determine the glass transition temperature of the PVC and the effects of various acetone concentrations. From these experiments it was concluded that in the temperature range 5°C to 50°C all diffusion experiments were effectively above the glass transition temperature.
CHAPTER 5

CASE II DIFFUSION PROFILES IN THE PVC AND ACETONE SYSTEM

5.1 ONE DIMENSIONAL NMR IMAGING EXPERIMENTS USING THE REPETITIVE PULSE VARIANTS OF BROADLINE GRADIENT ECHO.

Following the confirmation of Case II behaviour in the PVC and acetone system an improvement to the existing gradient echo imaging technique was required to study profile shapes in more detail. The development of the repetitive pulse variant of broadline gradient echo imaging has been covered in chapter 3. In this chapter its use to study diffusion of acetone into PVC is reported.

5.2 EXPERIMENTAL DETAILS

Sample blocks of 25 mm x 25 mm x 50 mm were exposed to acetone vapour above a liquid acetone reservoir as described in chapter 4. After exposure five sides were cut away to leave one penetrated face remaining and samples of approximately 15 mm x 15 mm x 15 mm. The samples were then immersed in liquid nitrogen to freeze the diffusion profiles and allow a complete set of samples to be made up prior to imaging. This ensured all imaging experiments were performed together, hence minimising errors due to changes in equipment gain and drift. It was important in the one dimensional imaging experiments that the edge of the sample was flat and exactly orthogonal to the direction of the gradient. This was achieved by using a cylindrical teflon...
spacer which fitted exactly within the birdcage coil's interior diameter of 25 mm. The sample was attached to one of the spacer's flat ends with PTFE tape. A rubber slice of 0.25 mm thickness was placed at the other end giving a normalisation signal used to correct any significant equipment drift or gain error, figure 5.1. In addition all the profiles were normalised to unit sample cross section to remove variations due to sample cutting.

Unless stated otherwise all imaging experiments discussed in this chapter were performed using the repetitive pulse imaging sequence described in chapter 3 with the following NMR parameters. Profiles were recorded with 1000 averages, using a train of 2 μs pulses, corresponding to a 12° tip angle. The gradients were tuned to 216 μs with 19 gradient cycles between pulses. The gradient was in the Z direction with a strength of 30% of the maximum. Assuming linear behaviour, this corresponds to 36 Gcm\(^{-1}\) peak value. The resolution per pixel for the profiles is given by

\[
\delta r = \frac{\pi}{2\gamma G_0 \tau} \tag{5.1}
\]

Where \(\gamma = 42 \text{ MHz T}^{-1}\) and \(\tau = 216 \mu\text{m}\) and \(G_0 = 36 \text{ Gcm}^{-1}\). Substituting these values gives a value for the resolution of \(4.8 \times 10^{-4} \text{ m per pixel, or 0.48 mm per pixel. However the program uses zero filling and so this value is double the actual value of resolution for this experiment. Consequently the resolution per pixel for all profiles using this technique is 0.24 mm.}

### 5.3 TIME VARIATION

Samples prepared as previously described were used to test the linearity of the Case II front kinetics. Figure 5.2 shows the profiles obtained from samples
FIGURE 5.1 PVC SAMPLE AND TEFILON SPACER

FIGURE 5.2 1-D PROFILES AFTER EXPOSURE TO ACETONE VAPOUR FOR 12 HOURS (OPEN CIRCLES), 24 HOURS (SOLID CIRCLES), 48 HOURS (TRIANGLES) AND 96 HOURS (SQUARES)
exposed for 12 hours (open circles), 24 hours (solid circles), 48 hours (triangles) and 96 hours (squares). The lines connecting data points are added for ease of viewing. The profiles are made up of signal from the absorbed acetone and the swollen PVC only, as the rigid PVC has too short a T2 to contribute any signal using this sequence. The acetone has been penetrating from the left with the edge of the sample at 0 mm on the distance scale. The profiles clearly show a sharp front advancing linearly with time. The shape of the profile in the swollen, penetrated region behind the front did not conform to that expected from Case II diffusion, Thomas and Windle (1978, 1982). The expected shape has a negligible, or at best very small, concentration gradient across the swollen region. These profiles show a large slope behind the front.

The width at half peak height was used as an estimation of the distance the front has travelled during the sample exposure time. However, as the resolution function is expected to be constant across the image, this does not affect a measure of the velocity. The corresponding distance time graph has been plotted to give a value of the characteristic constant velocity for Case II diffusion at 25°C, figure 5.3. The velocity is 0.042 mm hr⁻¹, in good agreement with the value obtained using the standard gradient echo technique described in the previous chapter. The non zero offset in the distance time plot was attributed to profile broadening.

5.4 TEMPERATURE VARIATION

A set of samples was exposed to acetone vapour in conical flasks held in a controlled temperature water bath for 23 hours. The exposure temperatures were in the range 20°C to 50°C. Following exposure and preparation for imaging the samples were immersed in liquid nitrogen to freeze the profiles,
FIGURE 5.3  DISTANCE TIME PLOT FOR THE SAMPLES REPRESENTED IN FIGURE 5.2

FIGURE 5.4  1-D PROFILES AFTER EXPOSURE TO ACETONE VAPOUR AT 20°C (TRIANGLES), 25°C (OPEN CIRCLES), 35°C (SOLID CIRCLES), 40°C (SOLID SQUARES), 45°C (OPEN SQUARES) AND 50°C (CROSSES)
however all experiments were carried out at room temperature. All NMR imaging parameters were as stated in 5.2, and all resulting profiles normalised. A set of profiles for temperatures in the range of 20°C to 50°C is shown in figure 5.4. The profiles shown are for 20°C (triangles), 25°C (open circles), 35°C (solid circles), 40°C (solid squares), 45°C (open squares) and 50°C (crosses). The connecting lines are added for ease of viewing and only every other point is marked. The values of magnetisation of the profile peaks were temperature dependent and possible explanations for this include a temperature dependence in the equilibrium concentration of penetrant. However gravimetric analysis indicates that this is not the case. An alternative explanation is variation in the mobility of the penetrant/rubbery phase resulting from exposure at higher temperatures and therefore changes in relaxation behaviour. A study of the spin spin relaxation times of the samples aids identification of the cause of the temperature dependence of the magnetisation values of the profile peaks.

5.4.1 SPIN-SPIN RELAXATION TIME MEASUREMENTS

The $T_2$ values of each of the samples used in the imaging experiments was measured using a CPMG sequence. The particular sequence used was $90 \tau (180^\circ - \tau - echo - \tau)_n$ with a baseline acquisition after 90 180° pulses. The birdcage coil was used with a 90° pulse length of 11 µs. For each sample 100 averages were recorded for 4 pulse gaps, 120 µs, 240 µs, 400 µs and 800 µs. The use of four pulse gaps is to ensure that both very long and very short components are detected, and to highlight any diffusion effects that might be present. To account for the effects of signal from the cavity a set of data was collected from the empty cavity and subtracted from all the data sets of the samples. Exponential fitting routines were applied to the 120 µs and 800 µs data sets to find the best fits while ensuring both short and long components would be considered. Best fits to the data are obtained using three component
exponential decays. The curves with fits for exposure preparation temperatures of 20 °C, 30 °C, 40 °C and 50 °C are in figures 5.5 to 5.8. The values of $T_2$ for the three components and the relative amplitudes are shown in tabulated form in Table 5.1 for all the exposure temperatures studied.

No evidence of a temperature dependent trend in the values of the relaxation times or their amplitudes is apparent. The only anomalous set of data appears to be that for 50 °C which shows a substantially longer short component than the other data sets. The reason for this is unclear, however if this data set is temporarily disregarded the others may be averaged to give $T_2$ values of 182 μs, 3.1 ms and 12.9 ms (± 20%), with relative amplitudes of 0.52, 0.21 and 0.27.

<table>
<thead>
<tr>
<th>TEMPERATURE (°C)</th>
<th>RELATIVE AMPLITUDE $T_2$ (μs)</th>
<th>RELATIVE AMPLITUDE $T_2$ (μs)</th>
<th>RELATIVE AMPLITUDE $T_2$ (μs)</th>
</tr>
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<tbody>
<tr>
<td>20</td>
<td>0.54</td>
<td>153</td>
<td>0.16</td>
</tr>
<tr>
<td>30</td>
<td>0.52</td>
<td>182</td>
<td>0.31</td>
</tr>
<tr>
<td>40</td>
<td>0.45</td>
<td>164</td>
<td>0.20</td>
</tr>
<tr>
<td>50</td>
<td>--</td>
<td>--</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Table 5.1 Spin spin relaxation time values with relative amplitudes
FIGURE 5.5  CPMG RESULTS FOR A SAMPLE EXPOSED TO ACETONE VAPOUR AT 20°C SHOWING THE DATA FOR PULSE GAPS OF 140 µs (SQUARES) AND 800 µs (CIRCLES)

FIGURE 5.6  CPMG RESULTS FOR A SAMPLE EXPOSED TO ACETONE VAPOUR AT 30°C SHOWING THE DATA FOR PULSE GAPS OF 140 µs (SQUARES) AND 800 µs (CIRCLES)
FIGURE 5.7  CPMG RESULTS FOR A SAMPLE EXPOSED TO ACETONE VAPOUR AT 40°C SHOWING THE DATA FOR PULSE GAPS OF 140 μs (SQUARES) AND 800 μs (CIRCLES)

FIGURE 5.8  CPMG RESULTS FOR A SAMPLE EXPOSED TO ACETONE VAPOUR AT 40°C SHOWING THE DATA FOR PULSE GAPS OF 140 μs (CIRCLES) AND 800 μs (SQUARES)
Although rigid PVC is present in the samples under study the extreme shortness of its T2 (typically less than 20 μs) precludes it from being detected with the sequences used. From a knowledge of the physical processes thought to be present in the samples two longer T2 components were expected from these experiments, and therefore two of the three components may be accounted for relatively easily. The long component is attributed to absorbed mobile acetone and the short component is primarily due to the swollen PVC. The third component is unexpected. Possible explanations including broken and hence more mobile polymer chains or a combination of bound acetone and PVC are discussed in chapter 6.

Returning now to the one dimensional profiles of the samples, it is clear that there is no strong temperature dependent T2 trend which explains the varying values of magnetisation of the profile peaks. It must then be assumed these values are a reflection of the varying amounts of signal remaining at the time of data acquisition arising from the differences in spin spin relaxation times noticed in the results of the bulk CPMG experiments.

The shape of the profiles was not entirely as expected. The concentration gradient behind the sharp front was present in all the profiles, being accentuated in the profiles of samples prepared at elevated exposure temperatures. The shape change with increasing temperature was thought to be suggestive of a trend towards Fickian behaviour and is discussed further in chapter 6.

The profiles in figure 5.4 clearly show that as the samples are exposed at higher temperatures so the front advances more quickly. As before, using the width at half the peak height as the distance travelled by the front, a value of velocity for each temperature was obtained. The front marks the limit of the distance travelled by the acetone molecules within the PVC. This distance may be assumed to be made up of a series of small intermolecular jumps.
Assuming an average time $\tau$ to make a net jump of length $\Delta x$ in the positive $x$ direction,

$$v = \Delta x \ \tau^{-1} \quad 5.2$$

where $v$ is the velocity in terms of the molecular distance to be travelled and the jump rate, $\tau^{-1}$. Let us now introduce the activation energy, $E_a$, which is the energy barrier that must be overcome if any movement of molecules is to take place at all. Arrhenius was the first to propose the concept of activated molecules to explain the influence of temperature on physical processes. He developed an equation relating the rate constant of a chemical reaction and the temperature at which that reaction was taking place,

$$k = A \exp(-E_a/R\theta) \quad 5.3$$

where $A$ is a constant, $k$ is the rate constant, $E_a$ is the activation energy of the reaction, $R$ is the gas constant and $\theta$ is the thermodynamic temperature in Kelvins. Reactions may proceed at different rates at different temperatures. An equation of the Arrhenius type may be used to determine a value for the activation energy of the jump rate $\tau^{-1}$, and if $\Delta x$ is assumed constant, for the velocity, $v$,

$$\Delta x \tau^{-1} = v = A \exp(-E_a/RT) \quad 5.4$$

This may be expressed in logarithmic form as

$$\ln v = \ln A - \frac{E_a}{RT} \quad 5.5$$

The logarithm of the velocity for each temperature was plotted against the
reciprocal of the absolute temperature, figure 5.9. The slope of the line corresponds to an activation energy for the velocity of $18.86 \pm 5.1$ kJmol$^{-1}$, which is of a similar order of magnitude to the value of $103.0 \pm 20.3$ kJmol$^{-1}$ obtained by Laskey et al (1988b) who studied iodohexane penetration into polystyrene, a broadly similar polymer penetrant system.

5.5 TIME COURSE EXPERIMENT

To test the diffusion behaviour after a period of time following removal from acetone vapour a set of samples were reimaged five days after the initial experiment. The samples were left unsealed at room temperature to allow free flow of acetone molecules out of the samples as well as within them. Substantial desorption of acetone from the samples was expected, however the experiment was primarily to check for diffusion of molecules down the concentration gradient from the penetrated region to the unpenetrated region. The sample prepared at 50°C in particular suggested a trend towards Fickian diffusion dynamics, away from Case II dynamics. The results for the 50°C sample are shown in figure 5.10 with the circles representing the profile immediately after removal from the vapour and the triangles representing the profile after five days. The connecting lines are added for ease of viewing. The sample has dried out considerably during the five days as expected, however, it is evident that there was no movement of molecules down the concentration gradient between the penetrated and unpenetrated regions of the polymer following removal from the vapour. From the figure it can be seen that there is a slight movement of the front to the left. This was due to the desorption of molecules causing an overall shrinking of the sample in the five days between experiments. This experiment thus indicates that even at elevated temperatures where it was thought that there may be significant Fickian behaviour, the diffusion kinetics remained predominantly Case II.
FIGURE 5.9  
**ARRHENIUS PLOT TO GIVE THE ACTIVATION ENERGY OF THE FRONT VELOCITY**

FIGURE 5.10  
**1-D PROFILES OF A SAMPLE IMAGED IMMEDIATELY AND AFTER FIVE DAYS AFTER EXPOSURE TO VAPOUR**
5.6 DISCUSSION

The repetitive pulse variant of broadline gradient echo, discussed in chapter 3, has been successfully implemented and used to study Case II diffusion. The improvement in resolution has afforded more insight into the shape of the concentration distance profiles, which have proved to be different to that expected from current Case II theory. The idealised concentration profile shape was discussed in chapter 2, and is thought to be made up of negligible gradient across the swollen region up to a sharp front which separates the penetrated and unpenetrated regions, with a Fickian precursor extending into the glassy region. The profiles obtained in this study have the sharp front as predicted, but show a significant slope behind the front across the swollen penetrated region of the sample. It is not possible to study the Fickian precursor in as much detail as the swollen region with this technique, however the ion beam NRA technique has been used for this purpose and will be discussed later in this chapter.

It must be taken into account that the profiles obtained and predicted by other researchers such as Thomas and Windle (1978, 1981), Mills et al (1989) and Weisenberger and Koenig (1989a, 1989b) are of the penetrant concentration only. Such profiles may be obtained using NMR if deuterated acetone is used since deuterium is invisible to proton NMR. Subtraction of a profile of a deuterated sample from an ordinary sample yields a penetrant only profile. Unfortunately the signal to noise ratio for the repetitive pulse technique is not good enough to obtain acceptable profiles from a deuterated sample at present. For such an experiment a shorter T2 imaging sequence is currently required. Weisenberger and Koenig, who have studied Case II diffusion using NMR imaging used sufficiently long echo times in their imaging sequences to effectively remove the polymer signal from their profiles completely.
It is then reasonable to assume that the fact that signal is obtained from both the swollen polymer and the absorbed penetrant has much to do with the presence of the slope behind the front. This being the case it remains impossible using this technique to postulate about the presence of Fickian behaviour at high temperatures being the cause of the significant slope in the swollen region as noted by Thomas and Windle (1981). In fact the time course experiment seems to indicate that very little, if any, Fickian behaviour is present, strengthening the argument that the swollen polymer is somehow responsible for the slope. It is clear that in order to fully explain the profile shape and attribute it to physical processes occurring within the sample that further, more detailed experiments must be performed.

The width of the profiles at half peak height is used as a measure of the distance that the sharp front has travelled. Consequently it is possible from the data in figure 5.2 to plot a distance time graph which confirms the linear kinetics and gives a value for the velocity at 25°C of 0.042 mm/hr.

Samples were exposed to acetone vapour at a range of temperatures between 20°C and 50°C to obtain some data regarding the temperature dependence of Case II diffusion. The front velocity is strongly temperature dependent, as seen by the profiles in figure 5.4 which clearly show the increased penetration with higher exposure temperatures. An Arrhenius type analysis has been used to determine the activation energy of the velocity which is $18.86 \pm 5.1$ kJmol$^{-1}$. The spin spin relaxation time analysis of the samples indicates no appreciable temperature dependence, however it does indicate that three longer components are present, which is not as expected. The shortest (182 μs ± 20%) is attributable to the swollen polymer and the longest (12.9 ms ± 20%) to the absorbed mobile acetone. The physical basis for the middle component is as yet not definite, although it appears logical to assume that it has to be connected with the presence of the unexpected slope detected in the swollen region of the samples.
This is the first test of the new repetitive pulse technique and although excellent improvements to the resolution have been obtained there remains a small element of doubt as to whether the extent of the slope of the profile was due to a valid physical process or experimental broadening. To verify the results which appear to be in contradiction with the expectations of current Case II theory requires the use of another technique able to give better resolution and signal to noise ratio for solid materials, such as stray field imaging (STRAFI).

5.7 ION BEAM NUCLEAR REACTION ANALYSIS TO MEASURE CASE II DIFFUSION PROFILES

Nuclear Reaction Analysis (NRA) was used to complement the NMR techniques for the study of Case II diffusion behaviour in PVC. The scanning microbeam method was comparable to NMR imaging in the determination of diffusion profiles over a relatively large distance, such as 20 mm. The use of deuterated acetone in these experiments meant that only profiles of the penetrant concentration were obtained. The use of the technique to measure diffusion profiles of the initial stages of the diffusion offered great potential and gave information not obtainable using NMR. In addition, it offered an advantage over similar experimental techniques used to study thin layers such as forward recoil analysis. This was due to the backscattered angle of detection which removed the requirement for thin and fragile samples or glancing incident angles and facilitated the use of samples cut from the same rod as those used in all other experimental work. For most other thin film techniques samples would have to be dissolved and cast on to substrates, often a difficult and time consuming task.
5.8 SAMPLE PREPARATION

5.8.1 SCANNING MICROBEAM METHOD.

The exposure to solvents for the scanning microbeam method was very similar to that for the NMR imaging experiments. This method was used to give profiles from a cross section and so samples of 40 mm in length were cut from the 15 mm rod as for the NMR experiments. The samples were exposed to vapour in conical flasks as before, however due to the hygroscopic nature of the deuterated acetone, the flasks had to be completely sealed to prevent proton exchange. After variable exposure times a 2 mm slice from the middle of the sample was cut to expose a cross section, which showed an outer ring of penetrated polymer and an inner core of unpenetrated glassy polymer.

The initial experiments revealed a problem with the sample preparation. The method of cutting the sample had the effect of 'smearing' deuterium atoms from the profile into the central unpenetrated region and so contaminating the results. Different cutting methods were tested with no success. The only method found to adequately expose a cross section from which a true profile could be obtained was to freeze the sample in liquid nitrogen for some time and then to break it while brittle. The drawback to this method was the uneven surface obtained which was not ideal for these experiments.

5.8.2 DEPTH PROFILING TECHNIQUE.

For these experiments smaller samples were required, and, due to the reduced exposure times, were cut prior to exposure to deuterated acetone. Samples of 15 mm x 20 mm x 2 mm were cut from the outer edges of the 25 mm square rod. As for the previous method the samples were exposed to deuterated
acetone vapour in the conical flasks which were sealed to prevent exchange processes. For these experiments the exposure times were very much shorter than before, typically of the order of minutes rather than hours. Following exposure the samples were removed from the flasks and immediately placed in liquid nitrogen. This was to freeze the diffusion profile and prevent any diffusion of molecules out of the sample. The samples had to be coated with a very thin gold layer of approximately 200 Å which served a dual purpose. Since polymers are not generally good conductors it acted as a conducting layer to prevent charge building up on the surface of the sample during analysis. In addition to the protons from the nuclear reactions an RBS peak from the gold on the surface of the sample was detected, and this was used in the calibration of the energy per channel. After being coated with a gold layer the samples were replaced in the nitrogen until the experiments commenced.

5.9 MEASUREMENT OF DIFFUSION PROFILES

5.9.1 SCANNING MICROBEAM METHOD

The NRA technique may be implemented in two ways to measure diffusion profiles, dependent on the sample geometry and length of exposure to penetrant. For more established profiles, or diffusion rates too great to give a discernable profile within 8 μm, the scanning microbeam method is implemented. The experimental arrangement is shown in figure 5.11.

This method requires the use of a beam line with the capability to focus the beam spot to a diameter of 50 μm. The depth profile is obtained by total yield measurements at each position as the beam is moved stepwise across the sample. The yield represents the deuterium concentration at that particular
position. The cross sections of samples of up to typically 20 mm may be studied in this way. The resolution is variable and depends on the beam spot size and the distance moved between steps. It is therefore possible to scan a sample quickly with relatively poor resolution to give a first approximation of the profile characteristics. Since using this method samples are not destroyed, this may be followed by a more in depth study of a particular area of interest. Figure 5.12 shows a typical profile obtained from a circular cross section of a sample exposed to acetone vapour as described earlier for 96 hours. The spot size is 100 μm and the resolution is 400 μm per point. The counts were accumulated for approximately 2.5 minutes in each beam position and the total acquisition time was of the order of 2 hours 15 minutes. The central unpenetrated region is clearly seen, however a more detailed study of the front itself would have to be performed before any quantitative analysis could be attempted. It is thought that the uneven surface due to the sample preparation technique required accounted for the noisy signal seen in the penetrated regions.

Although this method enables large distances to be probed with resolution better than or comparable to many other experimental methods it is time consuming when used to study a large distance with the best resolution possible. This reduces the throughput of samples to an extent that does not give optimum usage of beam time which is expensive. With particular reference to this work, the NMR imaging method seems more appropriate to use as the main method of obtaining one dimensional profiles of large distances of up to 20 mm. More samples can be studied as the experimental time required to obtain an image time is substantially shorter than that required for the scanning microbeam method. The allocated beam time is used to best advantage to concentrate on the study of the initial stages of the diffusion process using the depth profiling method on the surface layers of samples.
Beam scanned stepwise across the sample

**FIGURE 5.11** SCANNING MICROBEAM EXPERIMENTAL ARRANGEMENT

**FIGURE 5.12** 1-D PROFILE OF A CROSS SECTION OF A PVC SAMPLE
This method of implementation of the NRA technique relies on the energy spectrum of the reaction products to give depth information of the top surface layers of a sample. It is a very quick and simple way of obtaining a diffusion profile.

5.9.2.1 EXPERIMENTAL DETAILS

The analysis chamber is located at the end of line 2 of the Van de Graaff area of the D.R. Chick Ion Beam Facility at the University of Surrey. It is a stainless steel chamber that can be evacuated to a pressure of $10^{-6}$ torr using an oil diffusion pump. There are openings in the chamber wall which allow the beam to enter, the samples to be inserted and removed, and two windows allow the positioning of the sample and the beam to be observed.

The detector is mounted on an electrically insulated stand that is bolted to a ring on the chamber floor. It has a brass collimator in front of it with an aperture 2mm wide x 10 mm length. It may be positioned at almost any angle to the beam, however for these experiments the angle chosen was 165°. Attached to the chamber lid is a hollow rod which extends down into the chamber and upon which the sample is mounted. Liquid nitrogen is poured down into the rod to cool the sample during analysis. The rod may also be turned through 360°, enabling the sample to be inserted and then the appropriate angle chosen for the incident beam to hit the target. The sample holders are metal blocks which were designed to slide on to a dove tail at the end of the rod. The holders are screwed on to an arm which is used to insert and remove the samples through a load lock. With this arrangement the samples are changed without affecting the vacuum significantly. The pressure in the load lock is typically $10^4$ torr. Figures 5.13 and 5.14 are photographs of
FIGURE 5.13  PHOTOGRAPH OF ANALYSIS CHAMBER

FIGURE 5.14  PHOTOGRAPH OF BEAM LINE
FIGURE 5.15  SCHEMATIC REPRESENTATION OF THE SAMPLE HOLDER FOR THE DEPTH PROFILING EXPERIMENTS

FIGURE 5.16  EXPERIMENTAL ARRANGEMENT FOR THE DEPTH PROFILING EXPERIMENTS
the analysis chamber and beam line, and figure 5.15 is a diagrammatic representation of the sample holder.

The experimental arrangement is shown in fig 5.16. The sample is probed with a beam of $^3$He ions energies typically in the range 0.7 MeV to 2.0 MeV, the upper limit being set by the capabilities of the generator at Surrey. Beam ions enter the sample, and those that react with deuterium atoms initially form compound excited states of $^5$Li which break up to give protons and alpha particles.

5.9.2.2 DETECTION OF REACTION PRODUCTS.

The detector is a 1500 µm thick silicon surface barrier detector (ORTEC CA-17-100-1500) situated 10 cm from the target. The output from the detector is a pulse that is routed through an ORTEC preamplifier 142 AH and ORTEC amplifier 572 into a multichannel analyser (MCA). The MCA consists of an EG&G ACE multichannel buffer (MCB) card in an expansion port of an Amstrad 1512 PC. The buffer reads pulse heights from the amplifier by means of an analogue to digital convertor (ADC) and then displays a pulse height spectrum. Each channel on the MCA represents a narrow range of pulse heights which in turn reflect a range of energies of the emitted particle.

5.9.2.3 INTERPRETATION OF THE CHANNEL AXIS SCALE.

The channel axis of the spectrum is a representation of the energy scale, which is interpreted as follows. When emitted, the proton has an energy significantly larger than the beam ion and is more penetrating. Very little energy is lost in traversing the range of material needed to stop the beam ion. This means that the energy of the proton is only dependent on the angle of emission and the
energy of the beam ion at the point of reaction. Now, these protons are emitted in a backward direction which means that their energy increases as the beam energy decreases. This is due to the influence of the velocity of the centre of mass reference frame. This is always in the forward direction and decreases as the beam energy decreases. This causes the backward component of the resultant in the lab frame to increase. Overall the products emitted in a backward direction from events at the surface have less energy than those produced from events within the sample. The display from the MCA therefore gives an approximation of the concentration against depth profile.

5.9.2.4 CALIBRATION OF ENERGY PER CHANNEL.

The first stage in the conversion of the channel axis to a true depth scale is to obtain an energy per channel calibration figure. This is achieved using the energies of known peaks and their corresponding channel numbers to plot a calibration curve. A triple alpha source was used for these experiments, giving three peaks corresponding to the energies 5.155, 5.486 and 5.805 MeV, which were plotted against channel number and are shown in figure 5.17. The channel number of the gold RBS peak was then used with the best fit line to determine the energy of the peak. Using the relation

\[ E_{\text{RBS}} = E_{\text{He}} \cdot k \]  \hspace{1cm} (5.6)  

where \( k \), the kinematic factor, was

\[ k = \left( \frac{m_2 - m_1}{m_2 + m_1} \right)^2 \]  \hspace{1cm} (5.7)  

an accurate value of the energy of the \(^3\text{He}\) beam was determined to be 1.949 MeV. Using this value of the beam energy a program was used which
FIGURE 5.17 ENERGY AGAINST CHANNEL NUMBER CALIBRATION CURVE

FIGURE 5.18 ENERGY AGAINST CHANNEL NUMBER CALIBRATION CURVE
determined the corresponding value of the proton energy, which was 11.816 MeV. This energy and the channel number corresponding to the surface of the sample gave another point on the calibration curve, figure 5.18. Another best fit line was calculated, the gradient of which was the calibration figure of 7.00 keV per channel.

5.9.2.5 NORMALISATION AND DETERMINATION OF DEPTH PROFILES.

The concentration profiles have to be normalised in order to remove the effects of attenuation and cross section variation. In chapter 1 it was shown how strongly the reaction cross section varied with energy. Consequently, an evenly deuterated sample shows more counts at the energy corresponding to the reaction cross section peak. To counteract this all the spectra are divided by the spectrum of an evenly deuterated sample. This division is performed by the program used to determine the depth scale, a listing of which is in appendix 2. The energy per channel calibration figure is input into the program along with the diffused and the normalisation spectra. The channel numbers of leading edges of both the spectra are input and the program automatically corrects for any slight variation between the two. A separate program is used to find the range of the $^3$He ions in the PVC used, and the result input to the original program for use in determination of the depth scale. The resulting concentration depth profile is written to a file for further analysis.

5.10 EXPERIMENTAL RESULTS.

Although the initial stages of Case II have been studied before, Laskey et al
(1988a), there has been to my knowledge no quantitative analysis of the shape of the profiles in the induction period, and researchers have simply made qualitative observations, stating that it appeared to be a 'smoothly decreasing function of distance'. In order to obtain a value of the diffusion coefficient they have reduced the activity of the penetrant, consequently slowing the whole process enough to allow a front to form within their experimental timescale. The problem then became the solution of Fickian diffusion ahead of a moving front, with the quantitative analysis of the Fickian precursor, Mills et al (1989),

\[ \phi(x) = \phi_0 \exp \left( \frac{-vx}{D} \right) \]

where \( \phi \) is the concentration of the penetrant, \( \phi_0 \) is the equilibrium concentration of the penetrant behind the front, \( v \) is the front velocity and \( D \) is the diffusion coefficient of the acetone in the PVC ahead of the front.

One of the benefits of using the NRA technique in this work is that it complements the NMR results. The value of diffusion coefficient obtained is to be input into a simulation program to fit to a profile obtained from the STRAFI NMR technique. In this experiment the samples were exposed to vapour with unit activity and therefore no reduction of vapour activity was possible, and the diffusion was rapid. The profiles from the induction period had to be quantitatively analysed to determine the diffusion coefficient. The predicted shape was the solution of Fickian diffusion of a species into a thick layer from a source which holds the surface at a constant concentration,

\[ \phi(x) = \phi_0 \text{erfc} \left( \frac{x}{\sqrt{4DT}} \right) \]

where \( T \) is the exposure time.
5.10.1 ROOM TEMPERATURE EXPERIMENTS.

A set of experiments was performed on samples exposed to deuterated acetone vapour at room temperature. The laboratory temperature was maintained by an air conditioning system and was 22°C ± 1°C throughout the course of the sample preparation. Once prepared the samples were immersed in liquid nitrogen and remained at 70°K for the duration of the experiment. Initially samples were prepared for a range of times to determine the approximate timescale and characteristics of the diffusion. At room temperature the diffusion was rapid with the first 6 μm of the sample being penetrated evenly after approximately 2 minutes. This reduced the scope of the experiments possible and increased the difficulty associated with the sample preparation. The time for insertion and removal of the samples from the conical flask became significant when compared to the time of exposure. Extreme care was taken to open and close the flask as quickly as possible, however some margin of error was obviously introduced with such short exposure times.

All the following profiles in this chapter have been analysed and normalised as described in section 5.9.2.5 and are shown as a function of depth. The vertical scale is a measure of the yield of protons detected and is an indication of concentration in arbitrary rather than definite units. For these experiments where the objective was to determine the diffusion coefficient, the shape of the profiles was deemed more important than an accurate value for the concentration of penetrant molecules. It was therefore sufficient to analyse profiles of arbitrary concentration against depth rather than determine the actual concentration.

Figure 5.19 a) and b) show the profile obtained from a sample exposed to deuterated acetone vapour for one minute at 22°C. The profile shows a flat region within approximately the first 2 μm. It was thought to be extremely
FIGURE 5.19

a) 1-D PROFILE AFTER 1 MINUTE EXPOSURE AT ROOM TEMPERATURE

b) 1-D PROFILE AFTER 1 MINUTE EXPOSURE AT ROOM TEMPERATURE
unlikely that this was due to the formation of a Case II front, especially with the very short exposure time. A considerably more likely explanation was the loss of signal caused by surface drying effects resulting from a delay in placing the sample in liquid nitrogen. This highlighted the necessity of 'freezing' the profiles and cooling the sample holder to allow the experiment to be performed at 70°C.

The shape of the profile after 2 μm in figure 5.19 a) was fitted with equation 5.9 and is shown by the solid line. This yielded a value for the diffusion coefficient of 5.385x10⁻¹¹ cm²s⁻¹ (± 20%). It has been noted by some researchers, Mills et al (1989), Laskey et al (1988a) that the shape of the profiles of the induction period and the Fickian precursor look the same qualitatively. Indeed the conditions are almost identical, with a constant concentration at the surface, except in one case the 'surface' is really the sharp front and is moving. To test this hypothesis the profile was fitted with equation 5.8 and is shown in figure 5.19 b) by the solid line, giving a value of 1.625x10⁻¹⁰ cm²s⁻¹ (± 20%). This shows that indeed the shape of the profile was well approximated by this solution even though the boundary conditions were not strictly appropriate.

Further samples were prepared at room temperature, with improvements to sample handling to minimise surface drying effects, with exposure times of 0.5 minutes (triangles), 1 minute (circles) and 2 minutes (diamonds) and the resulting profiles are in figure 5.20. The vertical scale has been normalised to the detection time, allowing comparison of the different samples. The loss of signal from surface drying was again evident on the left hand side of the profiles. From this it was seen that the sample has been evenly penetrated over the first 5 μm after 2 minutes exposure. The profile obtained from the 1 minute exposure time was fitted with equation 5.9 to give another value of the diffusion coefficient and check the reproducibility of the results. The fit is shown in figure 5.21 and gave a value of 8.57x10⁻¹¹ cm²s⁻¹ (± 20%), in good
FIGURE 5.20 1-D PROFILES AFTER EXPOSURE AT ROOM TEMPERATURE FOR 0.5 MINUTES (SQUARES), 1 MINUTE (CIRCLES AND 2 MINUTES (DIAMONDS).
FIGURE 5.21  1-D PROFILE AFTER 1 MINUTE EXPOSURE AT ROOM TEMPERATURE WITH A FIT TO GIVE A VALUE OF DIFFUSION COEFFICIENT
agreement with the previous value obtained from figure 5.19 a). In addition to obtaining a value of the diffusion coefficient for use in the simulation program, NRA was used to show how changes in experimental parameters such as exposure temperature affected the profiles.

5.10.2 LOW TEMPERATURE EXPERIMENTS.

The effect of a reduction in the exposure temperature to vapour was to slow the front velocity as shown in the NMR section of this chapter. Consequently a corresponding lengthening of the induction period was expected before the critical penetrant concentration was reached. This meant that the exposure times required to show a diffusion profile were lengthened. Investigations showed that the samples could be exposed for approximately 30 minutes before the first $6 \mu m$ were evenly penetrated.

Samples were exposed to deuterated acetone vapour above a liquid reservoir for a range of times in a refrigerator at $3^\circ C \pm 2^\circ C$. Figure 5.22 is of profiles obtained from samples exposed for 2 minutes (diamonds), 10 minutes (squares), 15 minutes (triangles) and 20 minutes (circles), clearly showing increased penetration with time. These profiles indicated that the penetration rate had decreased substantially with the reduction in temperature. The vertical scale has been normalised to allow the comparison of profiles obtained from different samples. The profiles from 10 and 15 minutes exposure times were fitted with equation 5.9 to obtain a values of the diffusion coefficient for the reduced temperature diffusion, figure 5.23 a) and b). The values obtained were $5.80 \times 10^{-12} \text{cm}^2\text{s}^{-1}$ (± 20%) and $4.78 \times 10^{-12} \text{cm}^2\text{s}^{-1}$ (± 20%) respectively.
FIGURE 5.22  1-D PROFILES AFTER EXPOSURE AT 3°C FOR 2 MINUTES (DIAMONDS), 10 MINUTES (SQUARES), 15 MINUTES (TRIANGLES) AND 20 MINUTES (CIRCLES)
FIGURE 5.23

a) 1-D PROFILE AFTER 10 MINUTES EXPOSURE AT 3°C
b) 1-D PROFILE AFTER 15 MINUTES EXPOSURE AT 3°C
5.11 DISCUSSION.

One dimensional concentration distance profiles of acetone penetrating PVC in the initial stages of Case II diffusion have been obtained. Although the overall behaviour of this system is Case II, the induction period is Fickian in nature.

A simulation program was been written, based on the Thomas and Windle theory of Case II diffusion (1982), which computes concentration distance profiles. The program may be used to model the profiles obtained using the STRAFI NMR technique to be discussed in the following chapter. The value of the diffusion coefficient of the penetrant in the glassy polymer is required as an input parameter to the simulation program and has been determined using the depth profiling method.

For the first time profiles of the penetrant during the induction period have been quantitatively analysed to yield a value of the diffusion coefficient of acetone in glassy PVC. At room temperature and under conditions of unit activity of acetone vapour the diffusion coefficient values are $5.38 \times 10^{11}$ and $8.57 \times 10^{11}$ cm$^2$s$^{-1}$ ($\pm 20\%$).

Previous studies of the induction period of Case II diffusion have been based on a determination of the swelling kinetics and the variation of the surface penetrant volume fraction with time until the critical concentration for front formation is reached, Laskey et al (1988a). The Thomas and Windle model has been tested as it can be used to predict the surface swelling as a function of exposure time as well as to predict the shape of concentration distance profiles. The group who tested the model found that their results showed qualitatively similar trends to Thomas and Windle but had relatively poor quantitative agreement of experimental data. The testing of the Thomas and Windle model using the value of diffusion coefficient obtained with these experiments will
be covered in the next chapter.

Researchers who have studied the induction period and the Fickian precursor, Laskey et al (1988a) have made qualitative statements that the profiles in each appear to look very similar. Both are known to be Fickian in nature, however, they have different boundary conditions which affects the quantitative analysis. It would appear that the physical processes affecting the diffusion in both cases are similar and therefore a profile was fitted with both solutions. The solution with the correct boundary conditions provided the best fit, however the other solution also provided a good fit to the experimental data. Whilst this test was not of great importance, it has provided quantitative evidence to substantiate the claims that the profiles of the induction period and the Fickian precursor look almost identical.

The effect of a reduction in the exposure temperature has been tested by exposing the samples to vapour at 3°C for a range of times. The rate of diffusion slows substantially yet is still Fickian in nature with a typical value of the diffusion coefficient of 5.40x10⁻¹² cm²s⁻¹ (± 20%).

5.12 CONCLUSIONS

The work covered in this chapter represents the first thorough investigation into the diffusion characteristics of acetone penetration into PVC. The presence of Case II behaviour has been confirmed using two different, yet complementary, experimental techniques which, when used together give unique possibilities for such a study. The initial stages of diffusion have been captured using the Ion Beam NRA technique, providing a value of the
diffusion coefficient for use in a simulation program to model the profiles obtained using NMR imaging. The NMR imaging has allowed an insight into Case II diffusion previously unavailable, by giving profiles of the swollen polymer as well as the penetrant. This has proved to be the most exciting area of study to date as it has shown a slope to be present in the shape of the profile behind the front, which is in contradiction to all previous documented results. It is thought that this slope must be due to physical processes occurring within the polymer itself, a postulation which has been substantiated by NMR relaxation time analysis.

The results of the experimental work to date have firmly laid the foundations for further investigative study into Case II diffusion of acetone into PVC. The requirement is for a technique with improved resolution and the ability to study the solid polymer in greater detail. It is hoped that this will validate both the postulations regarding Case II diffusion and the new repetitive pulse technique.
CHAPTER 6

QUANTITATIVE ANALYSIS OF CASE II DIFFUSION PROFILES

6.1 INTRODUCTION

The majority of recent studies of Case II diffusion have concentrated on testing the theoretical model of Thomas and Windle (1982), this model generally being the most successful in describing the observed behaviour. A limiting factor in these studies, and in the model itself has been the restriction to analysis of penetrant profiles only. NMR imaging has already been added to the wealth of experimental work dedicated to understanding the process of diffusion into glassy polymers (Weisenberger and Koenig, 1989a, 1989b). However, limited by T₂ relaxation times, this work has again only yielded information on the penetrant concentration profiles. The requirement for an experimental technique capable of giving profiles of both penetrant and polymer for quantitative analysis has now been firmly established.

In chapter 5 the first steps in the study of the swollen polymer during Case II diffusion were reported with the use of a new NMR imaging sequence. Although this technique represented a major advance in this area it was concluded that for quantitative analysis improvements to resolution and signal to noise were required. This chapter reports the progress that has been made in this area with the implementation of a short T₂ NMR imaging technique called Stray Field Imaging. For the first time in a ¹H NMR imaging experiment the penetrant, the swollen polymer and the rigid polymer have
been simultaneously visualised. Quantitative dynamical information about the swollen penetrated polymer and the effects of exposure temperature have been obtained. High resolution $^{13}$C NMR spectroscopy has been used to complement the imaging results in obtaining valuable information about the polymer primary chain structure and conformation.

The use of deuterated acetone in a $^1$H NMR imaging experiment has given profiles of the swollen and rigid polymer only. A penetrant only profile has also been used to test a simulation program based on the Thomas and Windle theory which predicts the profile shape. The effects of reduced activity vapour on the diffusion behaviour have been studied for a range of activities, and this has given valuable information about the Fickian precursor and the limits of Case II behaviour.

6.2 STRAY FIELD MAGNETIC RESONANCE IMAGING TO STUDY CASE II DIFFUSION.

Stray Field Magnetic Resonance Imaging (STRAFI) (Samoilenko et al 1988, Samoilenko and Zick 1990) is a relatively new technique which overcomes short $T_2$ limitations of conventional imaging experiments, and has the additional advantage of high spatial resolution. The STRAFI technique has previously been used to image rigid solid materials and remove magnetic susceptibility distortions commonly present when one images bound fluid in restricted geometries (Kinchesh et al 1992). This work represents the first STRAFI measurements of Case II diffusion dynamics in a polymer (Perry et al 1994). The potential of STRAFI for the study of diffusion processes is enormous as it offers images of both solid and liquid components which may be studied together or separately if deuterated penetrants are used. This
proves especially useful for glassy polymers where the diffusion is a relaxation controlled process based on changes occurring in the polymer structure. The theory of the STRAFI technique has been covered in chapter 1, however some salient points may be discussed further in the following sections where relevant.

6.3 EXPERIMENTAL DETAILS

The STRAFI experiments were performed at Bruker Analytische Messtechnik GMBH, Rheinstetten, near Karlsruhe, in Germany. The spectrometer used was a Bruker MSL 400 with an 89 mm bore superconducting magnet with a central field of 9.4 T, which gives a fringe gradient field of 50 Tm⁻¹. Figure 6.1 is a photograph of the magnet used. In this very large gradient even a broadband pulse excites nuclei in only a very thin slice of the sample orthogonal to the gradient. The slice thickness is typically 7-70 µm and is inversely proportional to the pulse length. Obviously the field is neither dynamic nor controllable and therefore the data acquisition and analysis technique is different to that normally employed in the previous imaging sequences described. The sample is moved through the gradient and the signal intensity recorded from each slice as it passes through the sensitive position. No Fourier transformation of the signal is required, making the method more analogous to continuous wave NMR.

The sample size is set by the dimensions of the Bruker probe and associated sample holder. Samples must be typically 10 mm³ and are stuck on to the holder with superglue. A diagrammatic representation of the probe is given in figure 6.2. The probe is attached to 3 arms connected to motors which move the sample up and down the bore of the magnet through the gradient and also provide rotation for 3-d acquisition and sample alignment. Data is
FIGURE 6.1
PHOTOGRAPH OF MAGNET USED FOR STRAFI EXPERIMENTS

FIGURE 6.2
SCHEMATIC REPRESENTATION OF STRAFI PROBE

149
acquired as the sample is moved upward only, and the speed with which it is moved may be varied.

6.3.1 SAMPLE PREPARATION

Sample blocks 25x25x40 mm³ in size were cut from extruded rods prior to exposure to acetone vapour. The blocks were placed in constant acetone vapour activity chambers which allowed control of both the sample preparation temperature and the equilibrium acetone concentration. The blocks were exposed to either vapour above a liquid acetone reservoir or to granular PVC mixed with acetone equilibrated to a known volume ratio, φ. The latter gave vapour of reduced activities depending on the value of φ, as described in chapter 4.

After exposure the blocks were cut down to 10 mm cubes with only one exposed face remaining, identical to the procedure adopted for the repetitive pulse NMR imaging experiments. This allowed one dimensional profiling experiments to be carried out across one exposed face. One dimensional profiling experiments are orders of magnitude faster to carry out than two and three dimensional analyses, which would not have yielded any additional information. Between preparation and measurement the samples were stored in liquid nitrogen, except for the five hours required to transport them between Guildford and Rheinstetten, during which time they were kept in a vacuum flask containing ice, itself previously cooled with liquid nitrogen. It was strongly believed that no diffusion or dynamical changes took place during this period.
In order to aid characterisation of mass equilibrated samples of PVC exposed to acetone and deuterated acetone vapour, the hydrogen spin spin relaxation times were measured at 30 MHz and at room temperature. The samples were prepared at a range of exposure temperatures using the liquid acetone reservoir. As for the experiments described in chapter 5, the following CPMG sequence was used, $90_x\tau-(180_y-\tau\text{-echo}-\tau)_n$ with a baseline acquisition and a typical value of 90 for $n$. Additionally, the FID was recorded up to the first refocussing pulse in order to accurately record any short components present. The sequence was run for $\tau$ values of 140 µs, 240 µs, 400 µs and 800 µs, recording 100 averages for each sample. The samples were approximately 12 mm in length and 8 mm diameter, the exact size depending on the temperature and length of exposure. All experiments were performed in a solenoid coil with 90° and 180° pulse lengths of approximately 2.5 µs and 5 µs. These values altered by no more than 10% due to coil detuning and equipment variations during the course of the experiments, which took two to three weeks to perform.

Samples were prepared under the same conditions as for the imaging experiments and were fully mass equilibrated prior to the experiments. Samples were prepared for exposure temperatures of 20°, 30°, 40° and 50° as well as for a sample prepared with deuterated acetone at 20°C. Best fits to the data were obtained using three component exponential decays fitted to the curves from the 140 µs and 800 µs pulse gap data. Figure 6.3 shows such a dataset for an exposure temperature of 20 °C with the 140 µs data represented by the solid squares, the 800 µs data represented by the open squares and the fit represented by the solid line.
Such fits gave average $T_2$ values of 90 $\mu$s, 2.0 ms and 25 ms (± 20%), with relative amplitudes of 0.21, 0.17 and 0.62 (± 20%). These results seem to be consistent with those discussed in chapter 5, with similar values of the three components, although the values of the relative amplitudes have changed quite significantly. The amplitude of the shortest component is 0.21 for the fully mass equilibrated sample but was 0.52 for the partially equilibrated sample. The amplitude of the longest component also shows an increase from 0.27 to 0.62. These changes are very interesting, and, as will be seen, could be due to changes to the PVC chains which continue to occur even after they have been swollen by the acetone.

When the experiments were repeated with samples prepared with deuterated acetone vapour, the $T_2$ values obtained were 90 $\mu$s, 1.5 ms and 30 ms (± 20%),
with relative amplitudes of 0.52, 0.32 and 0.16 (± 20%). As noted in chapter 5, the long T2 component is thought to be due primarily to the absorbed mobile acetone and the short component is attributable to the swollen PVC. The long component exhibited by the sample exposed to deuterated acetone is almost certainly the result of chemical exchange occurring during the long preparation period, and is notably much smaller in magnitude than the other components. The middle component is thought to be due to either broken, and hence more mobile polymer chains, or a combination of bound acetone and PVC.

6.5 BASIC CASE II DIFFUSION PROFILES

All the following STRAFI experiments described were performed over two days, and all measurements were made at room temperature. The objectives of the first set of measurements were to become familiar with the capabilities of the technique, to obtain some basic profiles and to optimise the experimental parameters for the remainder of the experiments.

6.5.1 UNPENETRATED RIGID PVC

During the course of all the following experiments certain NMR parameters remained constant and so, to avoid unnecessary repetition they are mentioned now and then assumed to remain constant throughout the following sections. The experiments were all performed at room temperature, the gradient strength was 50 Tm⁻¹ and the NMR frequency was 160 MHz. The velocity of the sample, although not constant for all measurements, was in the range 5 mms⁻¹ to 20 mms⁻¹ with the slower speeds corresponding to the higher resolution measurements.
Figure 6.4 shows a one dimensional profile of a sample of rigid unpenetrated PVC. The profile was the result of 256 averages of signal from the first echo only. The pixel resolution was 39 μm, the echo time used was 2τ=100 μs and the pulse length was 20 μs. The connecting line is added for ease of viewing. The spike on the right hand side of the sample at 10 mm on the distance scale represents the glue used to stick the sample on to the holder. The T₂ of the rigid PVC was too short to be accurately determined using the equipment in the laboratory at Surrey, however estimates indicate that it was certainly less than 20 μs. The advantages of the STRAFI technique for the imaging of short T₂ materials becomes immediately evident when considering figure 6.4. The repetitive pulse technique of chapter 5 gave a significant improvement for short T₂ components of the order of 100 - 400 μs but could not visualise the rigid PVC. Using STRAFI it is now possible to study the rigid polymer in addition to obtaining a further major improvement in the signal to noise of the signal from the swollen polymer.

**FIGURE 6.4** 1-D PROFILE OF A RIGID PVC SAMPLE

154
6.5.2 PVC AND ACETONE VAPOUR

Figure 6.5 shows a typical one dimensional profile of a PVC sample that has been exposed to acetone vapour obtained using STRAFI. The sample was prepared at 20 °C for 48 hours using the liquid acetone reservoir. The pixel resolution was 78 μm, the pulse length was 10 μs and the echo time used was $2\tau=100$ μs. The profile was the result of summing the first four echoes and included 256 averages. Before presenting further results principle features are explained, which will also apply to most of the results discussed later in the chapter.

The acetone has penetrated the sample from the left, the front face of the PVC being at 0 mm on the scale. The main peak was the combined signal coming from the penetrating acetone and the swollen rubbery PVC. It was slightly rounded on the left due to surface drying and on the right due to diffusion dynamics. The downward slope of the main peak, to between one third and one half the maximum intensity, as it goes into the sample was characteristic of all the samples studied, as was the sharp front, seen here at 3 mm. Behind the front the rigid PVC was seen up to 11 mm. The small peak at 11 mm was signal from the super glue used to mount the sample to the probe.

The majority of further profiles will show only the main peak as this is the principle area of interest and this allows it to be observed in more detail than if the profile of a complete sample is shown. Where, in future analysis, profiles are to be compared to each other normalisation to the rigid PVC component was performed. Since the intensity of the rigid PVC component was identical for all the samples this removes any error due to experimental variations. In all further profiles where lines connecting points have been added this is for ease of viewing.
FIGURE 6.5  1-D PROFILE OF A SAMPLE EXPOSED TO ACETONE VAPOUR
The acetone and PVC showed as a considerably more intense peak than the rigid PVC. This, in part, was due to the extra hydrogen present, but the greater part of the increase resulted from the longer spin-spin relaxation times of these components so that more signal was remaining at the time of the echoes. The spin-spin relaxation time of the rigid polymer was significantly less than \( \tau \) whereas the spin-spin relaxation times of the other components were significantly longer. This was the first NMR polymer diffusion experiment in which the complete sample has been seen, instead of just the more mobile components.

6.5.3 PVC AND DEUTERATED ACETONE VAPOUR

To obtain a profile of only acetone concentration using NMR, profiles from two different samples must be used. Acetone-\( \text{d}_6 \) is used in the preparation of one of the samples and ordinary acetone for the other. Acetone-\( \text{d}_6 \) is subsequently not detected at the frequency used for proton NMR. Therefore the physical state of both the samples used in this experiment is identical yet NMR measurements of both give one profile with signal from all components and one profile with signal from only the PVC components. Subtraction of one from the other gives a typical profile of only the acetone concentration. This experiment was performed using two samples identically prepared at \( 20^\circ \text{C} \) and with a vapour activity of 0.82 for 48 hours.

Figure 6.6 a) shows the measured profiles. The acetone has penetrated approximately 2 mm into the sample in the 48 hrs exposure time. Only the main peaks are shown in the figures. The profiles are the result of 256 averages and the sum of the first four echoes of the echo train. The echo time was 100 \( \mu \text{s} \), the pulse length was 10 \( \mu \text{s} \) and the pixel resolution was 78 \( \mu \text{m} \). The profile from the sample exposed to acetone is indicated by the squares and the sample exposed to acetone-\( \text{d}_6 \) is indicated by the circles. The middle
trace, shown by triangles is the result of subtraction of the acetone-d$_6$ profile from the acetone profile and is therefore a profile indicating the penetrant concentration only.

The use of two different samples introduces the problem of reproducibility of profiles due to very slight variations in sample size, mounting and spectrometer drift. The apparent variation in penetration depth between the samples is approximately 0.2 mm. The profiles have been adjusted to ensure that the Case II fronts are in the same position prior to subtraction. Moreover the profiles are normalised to the same rigid PVC intensity. In doing this the implicit assumption is made that in the region 2 mm to 10 mm there is negligible Fickian precursor, and consequently the acetone only profile shows no precursor. It is however evident in the profiles in figures 6.10 and 6.11 which have had no such normalisation.

Figure 6.6 b) shows only the penetrant concentration profile. This profile was comparable to those obtained by other researchers who have only observed penetrant profiles. It shows rounding errors on the left hand side of the profile due to surface drying and on the right due to the finite experimental resolution. Nevertheless, it shows that the concentration gradient is negligible, as predicted by Thomas and Windle (1982). This leads to the conclusion that the considerable slope seen in the main peak of profiles such as that in figure 6.5 is due to the swollen polymer, and the acetone is uniformly absorbed to form a rectangular pedestal part of the profile. The profile in figure 6.6 b) was used to test the Thomas and Windle theory which predicts the shape of the profiles.
FIGURE 6.6
a) 1-D PROFILES OF SAMPLES EXPOSED TO DEUTERATED ACETONE VAPOUR AND ACETONE VAPOUR AND THE DIFFERENCE PROFILE
b) 1-D PROFILE SHOWING ACETONE CONCENTRATION ONLY
As discussed in chapter 2 a program was written which simulates diffusion profiles according to the Thomas and Windle theory of Case II diffusion. The parameters used in the program are:

- \( \eta_0 \) = viscosity of the unswollen polymer
- \( k = \frac{c}{\sqrt{V}} \)
- \( a_i = \) activity at spacestep i
- \( D_i = \) diffusion coefficient at spacestep i
- \( (V_iN_A) = \) molecular volume of penetrant
- \( \delta x = \) width of spacesteps
- \( T = \) temperature
- \( R = \) molar gas constant
- \( M = \) constant
- \( \bar{V}_i = \) volume ratio at spacestep i
- \( \text{TSTEP} = \) timestep length

The logarithmic pre factors in equation 2.18 may be combined to give a single parameter \( B \) for ease of computing,

\[
B = \frac{RT}{(V_iN_A)k\eta_0}
\]

The program was first tested using the original parameters for methanol and PMMA quoted by Thomas and Windle. These are:

- \( (V_iN_A) = 40.5 \times 10^{-6} \text{ m}^3 \)
- \( k = 0.23 \)
- \( \eta_0 = 2 \times 10^{14} \text{ Nm}^{-2} \)
- \( R = 8.31 \text{ JK}^{-1} \text{ mol}^{-1} \)
T = 297 K
So, $B = 1.35 \times 10^{-6}$
$M = 15$
$TSTEP = 15 \text{ s}$
$\delta x = 2 \times 10^{5} \text{ m}$
Number of spacesteps = 25
$D = 1 \times 10^{-14} \text{ m}^{2} \text{s}^{-1}$ for the glassy state, rising exponentially to $5 \times 10^{-12} \text{ m}^{2} \text{s}^{-1}$ for equilibrium sorption.

The initial conditions were set to
$a_{(i=1)} = 1$
$a_{(n=1)} = 1 \times 10^{-5}$
$V_{(n=1)} = 1 \times 10^{-5}$

The effect of changing certain parameters was tested. Figure 6.7 a) shows the profiles obtained equivalent to 48 hours exposure with three different viscosity values, $1 \times 10^{14} \text{ Nsm}^{-2}$ (squares), $2 \times 10^{14} \text{ Nsm}^{-2}$ (circles) and $5 \times 10^{14} \text{ Nsm}^{-2}$ (triangles) and the effect of reducing and increasing the viscosity is clearly seen. The diffusion coefficient was then altered and figure 6.7 b) shows the profiles obtained equivalent to 48 hours exposure with values of $1 \times 10^{14} \text{ m}^{2} \text{s}^{-1}$ (squares), $1 \times 10^{15} \text{ m}^{2} \text{s}^{-1}$ (circles) and $2 \times 10^{14} \text{ m}^{2} \text{s}^{-1}$ (triangles). These profiles reproduced the results obtained by Thomas and Windle. Following the successful test of the simulation program, the following parameters were input, to produce profiles representative of the PVC and acetone system:

$(V,V_{a}) = 73.3 \times 10^{6} \text{ m}^{3}$
$R = 8.31 \text{ JK}^{-1} \text{ mol}^{-1}$
$T = 295 \text{ K}$
$M = 15$
FIGURE 6.7  THEORETICAL PROFILES EQUIVALENT TO 48 HOURS EXPOSURE a) FOR VISCOSITIES OF $1 \times 10^{14}$ Nsm$^{-2}$ (SQUARES), $2 \times 10^{14}$ Nsm$^{-2}$ (CIRCLES) AND $5 \times 10^{14}$ Nsm$^{-2}$ (TRIANGLES) AND b) FOR DIFFUSION COEFFICIENTS OF $1 \times 10^{14}$ m$^2$s$^{-1}$ (SQUARES), $1 \times 10^{15}$ m$^2$s$^{-1}$ (CIRCLES) AND $2 \times 10^{14}$ m$^2$s$^{-1}$ (TRIANGLES)
TSTEP = 15 s
δx = 5 \times 10^{-5} \text{ m}

Number of spacesteps = 100

D = 5 \times 10^{15} \text{ m}^2\text{s}^{-1} \text{ for the glassy state, rising exponentially to } 3.5 \times 10^{12} \text{ m}^2\text{s}^{-1} \text{ for equilibrium sorption. The initial conditions remained the same as before.}

The value of the diffusion coefficient was that measured using the depth profiling NRA technique discussed in chapter 5. A theoretical profile was generated equivalent to 48 hours exposure using a value of B chosen to fit the NMR experimental. The parameter B, as described in equation 6.1 is made up of a number of parameters and for the acetone and PVC system the values of the molecular volume, temperature and the gas constant are fixed, leaving the product \((k\eta_0)\) as the only variable. It was not possible to obtain an exact value for the viscosity of rigid PVC, however it has been shown that under certain conditions it is comparable to that of PMMA (Turner 1973). The value of B required to obtain a good fit to the experimental data was 4.0 \times 10^6. Using equation 6.1 this gives 8.4 \times 10^{12} for \((k\eta_0)\). Assuming that the value of k is approximately equal to that used for methanol and PMMA, then the viscosity would be 3.6 \times 10^{13}, which shows reasonably good agreement with the value for PMMA.

The simulated profile is in figure 6.8. It shows negligible concentration gradient, as predicted, and a very short Fickian precursor. This theoretically generated profile of Case II dynamics, using a value for the diffusion coefficient measured with the NRA technique, shows a good agreement with the experimental NMR profile. The theory has been shown to predict the correct rate of front advance for the PVC and acetone system. However the length of the precursor seen in the experimental NMR profiles is not accounted for theoretically. This is perhaps due to the approximate nature of the test and will be the subject of future study into simulations of Case II behaviour.
Inherent in the Thomas and Windle theory is the assumption that the activity is unity. This was not the case for the experiment in which the acetone only concentration profile was obtained. Tests on the simulation program indicated that reduction of the activity introduced baseline errors which could not easily be accounted for. It is anticipated that the adaption of the simulation of Case II diffusion to account for reduced activities will be part of a future project. Due to this and other necessary assumptions about certain parameters the test described here represents the first approximate use of the simulation program to model diffusion profiles in the acetone and PVC system.

Using two different experimental techniques it has been possible for the first time to use data obtained in the first few minutes of diffusion to determine the diffusion behaviour 48 hours later.

**FIGURE 6.8** THEORETICAL PROFILE FOR THE ACETONE AND PVC SYSTEM
An experiment was performed to observe the rate of desorption of acetone from a sample and to test for any changes in the shape of the profile. The sample was prepared at 20 °C for 24 hours using the liquid acetone reservoir. The sample was placed in the probe and left overnight in a fully automated experiment. A total of 16 consecutive runs were performed with the following parameters. The pulse length was 20 μs, the pixel resolution was 39 μm and the value of echo time was 100 μs. The profiles were the result of 128 averages and used signal from the first echo only.

Figure 6.9 shows profiles from a selection of the runs. The profiles shown are from the first (open circles), second (open squares), third (triangles), fourth (solid circles), tenth (solid squares) and sixteenth (triangles) runs. Only every other point is marked for ease of viewing. The surface drying on the left of the main profile peaks was evident and quite substantial. Also noted was the nonlinearity in the desorption of acetone from the sample, which was initially rapid, but slowed quite considerably after the first 5 runs. There was no change in the shape of the profiles, proving that the Case II front remains stationary after the sample has been removed from the acetone vapour. No further diffusion into the unpenetrated region of the sample occurred.

6.8 THE EFFECTS OF VARIATION OF THE ACTIVITY OF THE ACETONE VAPOUR

STRAFI has been used to study the onset of front formation in Case II diffusion as a function of acetone vapour activity. The sample blocks of 25x25x40 mm were exposed to vapour of reduced activities by using granular
FIGURE 6.9 1-D PROFILES SHOWING DESORPTION FROM A SAMPLE

Position (mm)

Magnetisation (arbitrary units)
PVC mixed with acetone and equilibrated to a known acetone/PVC ratio, \( \phi \). The procedure for obtaining a vapour of reduced activity was covered in chapter 4. After exposure the blocks were cut to 10 mm\(^3\) samples with one exposed face remaining for the one dimensional imaging experiments.

Samples were exposed to vapour of activities of 0.13, 0.35, 0.6, 0.82, and 1.0 for 48 hours at 20\(^\circ\)C. Figure 6.10 a) to e) shows the profiles obtained using 256 averages and the summation of signal from the first four echoes. The pulse length was 10 \( \mu \)s, the resolution was 78 \( \mu \)m and the echo time was 100 \( \mu \)s. In a) where the activity was 0.13 there was no evidence of a Case II front at all, whereas in b), at an activity of 0.35 the front has just formed. In the profiles in c), d) and e) which correspond to the activities 0.6, 0.82 and 1.0 the front was observed to have formed and the penetrant to have advanced a little further in each case. This proved the profound effect that the vapour activity had on the diffusion behaviour. It was noted by Laskey et al (1899a), who studied iodohexane penetrating into polystyrene, that a threshold value of vapour activity exists, below which front formation is inhibited and the diffusion remains Fickian. For PVC and acetone this threshold was between 0.13 and 0.35. In order to determine the exact value further experiments would have been required, however it was thought that the determination of an exact value of the threshold for this system would not have benefited the study significantly.

The experiments using reduced vapour activities revealed interesting and valuable information on the nature of the Fickian precursor in the PVC and acetone system. In figure 6.11 a) to d) profiles are shown which correspond to those in figure 6.10 a) to d). The profiles, however, have been rescaled to show the region of the Fickian precursor in more detail. The extent of the diffusion in a) where no Case II front has formed may now be clearly seen. Acetone has penetrated the sample to a depth of at least 5 mm even though no front has been formed. In the other three profiles where the front has
FIGURE 6.11 1-D PROFILES OF SAMPLES AFTER EXPOSURE TO A RANGE OF VAPOUR ACTIVITIES SHOWING THE FICKIAN PRECURSOR. a) 0.13, b) 0.35, c) 0.6, d) 0.82
FIGURE 6.10 1-D PROFILES OF SAMPLES AFTER EXPOSURE TO A RANGE OF VAPOUR ACTIVITIES. (a) 0.13, (b) 0.35, (c) 0.6, (d) 0.82, (e) 1.0
formed the precursors were seen extending a surprisingly long way into the samples, ranging over 3 mm. This value far exceeds those currently documented in the literature for Case II diffusion (Laskey et al, 1988b) in broadly similar polymer and penetrant systems. It is the first time that the Fickian precursor in Case II diffusion has been observed using NMR.

6.9 THE EFFECTS OF THE VARIATION OF EXPOSURE TEMPERATURE

A set of samples were prepared at a range of exposure temperatures between 20 °C and 50 °C using acetone vapour above the liquid acetone reservoir for 48 hours. Sample blocks of 25 x 25 x 40 mm³ were exposed to the vapour and then cut down in the same way as described previously to give 10 mm³ samples with one exposed face for the one dimensional experiments. The pixel resolution for these experiments was 78 μm, the pulse length was 10 μs and the echo time used was 100 μm. The profiles recorded were the result of accumulating 256 averages and summing the first four echoes.

After exposure the samples were kept at liquid nitrogen temperature and all experiments were performed at room temperature. The resulting profiles from samples exposed at 20°C (open circles), 30°C (squares), 40°C (triangles) and 50°C (solid circles) are in figure 6.12. For ease of viewing only every fourth point is marked. The effects of varying the exposure temperature are now clearly seen, with a marked increase in the front velocity with increasing exposure temperature. The values of velocity for 20°C, 30°C, 40°C and 50°C are 0.01, 0.03, 0.06, and 0.11 mm/hour, in good agreement the values in chapters 4 and 5. The profiles have intensities which show a marked temperature dependence, however the T₂ relaxation time experiments performed have shown an exposure temperature independence. This means
FIGURE 6.12  1-D PROFILES OF SAMPLES AFTER EXPOSURE TO A RANGE OF TEMPERATURES
that the difference in the intensity cannot be attributed to more signal remaining at the time of the echo due to a longer $T_2$ at higher exposure temperatures. Therefore, any physical processes causing structural changes in the PVC during or after penetration with acetone are exposure temperature dependent.

6.10 RELAXATION TIME CONTRAST

In section 6.5.3 it was concluded that the main peak of the profiles was made up of two distinct components. The absorbed mobile acetone constitutes a uniform rectangular pedestal and the sloping part of the peak is due to the swollen polymer. This assumption was further substantiated by the use of a relaxation time contrast experiment.

The samples prepared at different exposure temperatures and described in the previous section were also used in this experiment. The echo time was 250 $\mu$s and the pulse length was 10 $\mu$s, corresponding to a 10 mm field of view and a resolution of 39 $\mu$m per pixel. A train of 16 echoes was recorded, each with 256 averages. As noted in a previous section, the complete functional dependence of the signal intensity on relaxation times is complex and is being fully evaluated theoretically by other members of the research group. However for the purposes of this experiment it is acknowledged that only long $T_2$ and $T_{1p}$ components are observed at longer echo times, leading to substantial relaxation time contrast in this 16 echo experiment.

A one dimensional profile was constructed from each of the echoes in the train recorded for each sample. Figure 6.13 a) to d) shows profiles from the samples prepared at 20 °C, 30 °C, 40 °C and 50 °C. Profiles from the 2nd (diamonds), 7th (triangles), 12th (squares) and the 16th (circles) echoes only are shown for
FIGURE 6.13  1-D PROFILES OF SELECTIVE ECHOES SHOWING RELAXATION TIME CONTRAST FOR a) 20 C, b) 30 C, c) 40 C, d) 50 C
ease of viewing. Only every other point is marked for ease of viewing.

There are two main features of note when considering these results. The first is the confirmation of two components of substantially different relaxation times in the peak of the profile. By the 16th echo in the train the sloping part of the profile which is believed to be due to the polymer has decayed away leaving only the rectangular pedestal. The mobile acetone has a longer relaxation time than the swollen polymer and so it is observed out to considerably later echoes in the series, giving the rectangular part of the profile. The mass analysis described in chapter 4 also indicated approximately uniform acetone concentration across the swollen region, consistent with these results.

The second point of note which may be taken from this experiment is the obvious temperature dependence of the slope in the profile peak. Observation of the profiles in figure 6.13 clearly shows that as the exposure temperature increases the slope becomes more accentuated. This lends weight to the theory that a physical process continues to alter the PVC structure and conformation after being swollen by the acetone, and that the rate of this process is dependent on the exposure temperature.

6.11 ANALYSIS OF PROFILE SHAPE

Substantial experimental data has been given which shows that the profile peak is made up of a rectangular pedestal contribution from acetone and a sloping contribution from the swollen PVC. With this assignment however, the problem of accounting for the slope in the polymer profile is introduced.
Clearly the PVC concentration is uniform across the swollen region so a molecular process must be responsible for the slope. The results of the relaxation time contrast experiment may be used to try and solve the problem.

At this stage two possible explanations for the slope appear to be possible. The first is that whilst the hydrogen density across the peak is constant, the NMR relaxation time of the polymer on the left of the peak is longer than that on the right, perhaps because it has been in contact with acetone for a considerably longer period. A suitable model is based on the concepts of a multi component/relaxation time system with fast exchange between different molecular environments in which

\[
\frac{1}{T_{\text{2 observed}}} = \sum \left( \frac{f_i}{T_{2,1}} \right)
\]

and \(f_i\) is the fraction of the \(i\)th component of the system (Zimmerman and Brittin, 1957). The results from the previous section were used to test this theory in the following way. First the intensity of the peak at various positions along it was recorded for each echo. The rectangular pedestal part of the peaks was subtracted to leave only the PVC part. The intensity was then plotted as a function of echo time for each of the positions. An attempt was made to fit single exponential decays with constant amplitude and variable relaxation time to these curves. This was not possible and proved that this theory was incorrect. Indeed, if anything, and the effect was slight, the relaxation time on the left was shorter.

Previous experiments have tended to indicate that something continues to happen to the PVC after it has initially been penetrated by the acetone, which leads to the alternative explanation for the slope. This is that the PVC is slowly softening for some considerable period after the acetone has penetrated and that the softened polymer exhibits a distinct, longer relaxation time than
the unsoftened polymer. The signal from the softened polymer dominates the profile whilst the signal from the unsoftened polymer does not contribute significantly to the intensity.

The analysis for this theory is again done using the results of the relaxation time contrast experiment. The profiles obtained from the sample prepared at an exposure temperature of 50 °C will be used as an example. Once again the intensity at various points across the peak are noted for each echo number and these intensities plotted as a function of echo number. This in effect gives a plot of NMR signal intensity as a function of time after the first pulse as the echoes were recorded at 250 µs intervals. The polymer part of the peak is then isolated by subtraction of the rectangular pedestal part of the profile due to the acetone. Each of the intensity against echo number curves is then fitted with a single exponential function from which the value of signal amplitude at zero time may be measured. Figure 6.14 is a schematic representation of the profiles. Obviously those curves from positions on the left of the peak will show more intensity than those on the right. Figure 6.15 shows such a curve from one of the positions on the left of the peak (circles), the exponential fit being indicated by the solid line. In this analysis, the relaxation time is allowed to vary as well as the amplitude. However, most of the significant variations with position are in the amplitude. A different value of intensity at zero time was obtained for each position across the peak and these were plotted to give an intensity against distance curve, figure 6.16.

Each peak is, in effect, an exposure time course experiment with the time axis running from right to left and with the origin at the penetrant front edge. The above curve must therefore be transformed so the distance and time axes conform to these conditions. One of the features of Case II diffusion is a constant front velocity, consequently the distance axis of figure 6.16 may be converted to a time axis. The resulting curve is a measure of the fraction of softened swollen polymer as a function of the time for which the polymer has
Intensity against echo number for a constant value of distance across swollen region.

FIGURE 6.14 THREE DIMENSIONAL REPRESENTATION OF THE RELAXATION TIME CONTRAST EXPERIMENTAL PROFILES
FIGURE 6.15 PLOT OF INTENSITY AGAINST ECHO NUMBER FOR THE POLYMER PART OF A PROFILE (50°C, ECHO SEPARATION IS 250 µs)

FIGURE 6.16 PLOT OF INTENSITY AGAINST DISTANCE ACROSS A PROFILE PEAK (50°C)
FIGURE 6.17  
PLOT OF INTENSITY AGAINST TIME SHOWING THE FRACTION OF SOFTENED SWOLLEN POLYMER AS A FUNCTION OF TIME (50°C)

FIGURE 6.18  
PLOT OF INTENSITY AGAINST TIME SHOWING THE FRACTION OF SOFTENED SWOLLEN POLYMER FOR 20°C (DIAMONDS), 30°C (TRIANGLES), 40°C (SQUARES) AND 50°C (CIRCLES)
been in contact with acetone, figure 6.17. The data is fitted with the exponential function $A(1-\exp(-t/\tau_c))$ where $\tau_c^{-1}$ is the 'softening rate', the fit being shown by the solid line.

This analysis has been applied to the results for all four exposure temperatures. To correct for any slight variations in intensity due to experimental drift all profiles were normalised to the same rigid PVC intensity. The softening rate increases dramatically with exposure temperature as can be seen in figure 6.18 where the softened swollen polymer fraction as a function of time is shown for all four temperatures. The diamonds represent 20°C, the triangles represent 30°C, the squares represent 40°C and the circles represent 50°C. Since the PVC / acetone density of fully mass equilibrated samples is known to be independent of sample exposure temperature, the pre-exponential factor, $A$, is constant and normalised to 1 in each case. The measured values of $\tau_c$ are 86, 26, 15 and 11 (± 10%) hours for the samples exposed at 20°C, 30°C, 40°C and 50°C respectively.

This theory appears to explain the results well, however further evidence to support such suggestions would obviously be desirable. An increase in chain mobility with acetone contact time is plausible on the grounds of chemical breakdown of the chains or more likely changes in the chain conformation/tertiary structure. An excellent technique for studying changes in the primary chain structure or conformation and giving the evidence to support the softening theory is available within the bounds of NMR. It is high resolution $^{13}$C cross polarisation/magic angle spinning (CP/MAS) NMR and the use of this technique was available with the kind cooperation of the ULIRS solid state NMR service at University College London.
NMR spectroscopy suffers from the same problems as imaging where the study of solid materials is concerned. However, the angular dependence of the dipolar Hamiltonian may be effectively eliminated by the fast rotation of samples at an angle of 54.7° to the static field, the ‘magic angle’. Another significant problem encountered in NMR is that of sensitivity, particularly for nuclei of low natural abundance, such as $^{13}$C. To overcome this, signal enhancement techniques such as cross polarisation (CP) are particularly useful. In addition CP overcomes a problem encountered frequently in solids, that is the tendency for T$_1$ relaxation times to be very long leading to unacceptably long delays between scans in order to obtain reasonable spectra. CP may be used when there are protons in the vicinity of the nucleus under investigation. The dipole-dipole interaction is used to transfer magnetisation from the protons to the nucleus under investigation. The pulse sequence first excites the protons and then spin locks them for a certain time, known as the contact time, during which the nucleus under investigation is also pulsed. The signal is then recorded and the cycle repeated after a delay time.

Another technique which uses the dipole-dipole interaction to advantage is non-quaternary suppression (NQS) which is commonly applied to $^{13}$C. It allows the system to evolve for a short time without any proton decoupling, which has the effect of removing those signals from the spectrum which have directly bonded protons.

6.12.1 EXPERIMENTAL DETAILS

The sample preparation was identical to that described for the imaging experiments. Samples were cylindrical and of no more than 7 mm diameter
and 20 mm in length when swollen. All the samples were cut from 6 mm diameter rod and swelled different amounts depending on the exposure time and conditions. Any samples that were not quite 7 mm in diameter were wrapped in PTFE tape to ensure a snug fit within the rotor, which is essential if the sample is to be spun.

The experiments were carried out on a dedicated Bruker MSL-300 multinuclear spectrometer equipped with a variety of hardware. Associated with the spectrometer is a 7.05 Tesla superconducting magnet, which is equivalent to a resonant frequency of 75 MHz for $^{13}$C or 300 MHz for protons. The spectrometer features high power amplifiers for both broadband and proton channels, enabling short 90° pulses to be achieved. Typical values are 3.85 µs for a 90° pulse and 7.7 µs for a 180° pulse. The probe is a Bruker 7 mm rotor capable of MAS, with or without CP, at spinning speeds up to 5 kHz. Sample spinning is driven by a filtered and dried compressed air supply. All the following experiments were carried out at room temperature.

6.12.2 RESULTS

The first experiment was a CP/MAS scan of rigid PVC to characterise it. The spinning speed was 4.5 kHz, the contact time 1 ms and the recycle time 5 s. The resulting spectrum is in figure 6.19 a) with the CHCl PVC peak at approximately 57 ppm and the CH$_2$ PVC peak at approximately 47 ppm. The other peaks represent additives or impurities which are present in the PVC. The next experiment was an NQS scan of the same sample, with the same basic NMR parameters. This effectively removed the signal from any carbon with directly bonded protons and as such was a method of determining the amount of branching, if any, within the polymer structure. The spectrum is shown in figure 6.19 b) and from this it is concluded that the PVC used has very little structural branching.
FIGURE 6.19

a) CP/MAS SPECTRUM OF RIGID PVC
b) CP/MAS NOS SPECTRUM OF RIGID PVC
The next spectrum is of a sample that has been exposed at room temperature to acetone vapour above the liquid reservoir for 48 hours. The experiment was a CP/MAS scan with a contact time of 1 ms, a recycle time of 5 s and a spinning rate of 4.5 kHz. Figure 6.20 shows the spectrum and the two PVC peaks are seen clearly, along with a methyl group from the acetone at 33.07 ppm. The carbonyl group of the acetone, however is not present in the spectrum. The reason for this was thought to be due to the rapid motion of the carbonyl group within the acetone molecule. Unlike other enhancement techniques, with the phase cycling employed in this experiment no signal is seen if there is no magnetisation transfer. It was therefore decided that a single pulse $^{13}$C experiment with no CP should be used for the remainder of the experiments and would be sufficient in view of the large amount of signal detected from the samples.

FIGURE 6.20  CP/MAS SPECTRUM OF A SAMPLE EXPOSED TO ACETONE VAPOUR FOR 48 HOURS
Some difficulty was experienced in sustaining a spinning rate of 4.5 kHz with some of the samples. This was thought to be due to the fact that solid samples were used instead of the customary powdered ones. Consequently if the samples did not exactly fit in the rotor and had to be wrapped in tape it was sometimes difficult to ensure the totally even weight distribution required to make a sample spin. However, all the samples except the rigid PVC has $T_2$'s that were long enough to obtain a spectrum with a static experiment and so the remainder of the experiments were a mixture of MAS and static ones.

Figure 6.21 a) and b) shows spectra of a sample which has been fully mass equilibrated with acetone vapour above the liquid acetone reservoir. The experiment is a static decoupling one and on both spectra the missing carbonyl group is now clearly seen at 206 ppm. In a) the recycle time is 10 s whereas in b) it is 3 s and the effect on the signal intensity is obvious. The shorter recycle time enhances the more solid PVC components present.

Although both the static and MAS experiments yield a spectrum of the samples there will obviously be a great deal more narrowing of spectral lines in the MAS experiment, giving the opportunity to see in more detail the structure present. Figure 6.22 a) and b) shows this very well, as both are of the same sample but a) shows the static experiment while b) shows the MAS results. The recycle time was 10 s for both experiments. The sample has had prolonged exposure to liquid acetone after becoming fully mass equilibrated at room temperature. In a) the spectrum is shown on an enlarged scale to previous spectra to show the PVC peaks in more detail. There is some structure in the peaks which is clearly seen but is not enough to be able to deduce anything of interest. The MAS experiment, shown by the spectrum in b) however, has been able to resolve the structure into a 1:2:1 triplet. The improvement in using the MAS experiment now becomes obvious.
FIGURE 6.21  STATIC DECOUPLING SPECTRA OF A SAMPLE AFTER PROLONGED EXPOSURE TO ACETONE VAPOUR. a) 10s RECYCLE TIME. b) 3s RECYCLE TIME.
FIGURE 6.22 SPECTRA OF A SAMPLE FOLLOWING PROLONGED EXPOSURE TO ACETONE VAPOUR. a) STATIC DECOUPLING EXPERIMENT, b) MAS EXPERIMENT
6.12.3 DISCUSSION

The purpose of these experiments was to check for changes in the structure of the PVC, and more specifically any breaking of chains which may be the cause of the softening of the PVC. Throughout the experiments the only change observed in the PVC was an increase in mobility with increased exposure to acetone, reflected by a decrease in the spectral linewidths and the introduction of some structure. The structure seen in the CHCl peak at approximately 57 ppm was eventually resolved into a triplet for a sample that had prolonged exposure instead of the broad spectral line seen with samples that had been exposed to acetone for a shorter time. There has been no evidence of any breaking of the chains. It must therefore be concluded that on prolonged exposure to acetone the mobility of the samples increases slowly but substantially and the chains simply become more disentangled leading to the gradual softening of the swollen PVC as detected using STRAFI.

It has been shown that little, or no branching is present in the primary chain structure. The presence of the 1:2:1 triplet of the CHCl peak leads to a conclusion regarding the tacticity of the PVC, that is the arrangement of the chlorine atoms on the chain, mentioned in chapter 4. The fact that the triplet is a 1:2:1 indicates that the PVC is atactic in structure. This may be explained by the fact that the spectrum of the carbon with attached chlorine being observed is influenced by the relative stereochemistry on the neighbouring carbons. They may have attached atoms with spins that are "up up", "down down", "up down" or "down up" relative to the chlorine on the observed carbon. The "up down" and "down up" are effectively the same, giving four possibilities for the neighbouring stereochemistry, two of which are the same, hence a 1:2:1 triplet.
6.13 CONCLUSION

The work in this chapter covers the implementation of the NMR imaging technique STRAFI to study Case II diffusion of acetone into PVC and high resolution $^{13}$C spectroscopy experiments. STRAFI has successfully met the requirements outlined in the conclusions of chapter 5 by it's capability to simultaneously visualise the rigid PVC, swollen PVC and the acetone, with enough sensitivity and resolution to allow quantitative analysis. A complete discussion of these results is in the following chapter.
CHAPTER 7

CONCLUSIONS

The bulk of the experimental work in this thesis is concerned with the study of Case II diffusion through analysis of one dimensional concentration profiles obtained experimentally. The ion beam NRA technique gives profiles of acetone concentration only, whilst the short T$_2$ NMR imaging techniques gave profiles composed of signal from both acetone and PVC. This is the first time that combined polymer and penetrant concentration profiles have been used to analyse Case II diffusion.

The characterisation experiments of the diffusion of acetone into PVC detailed in chapter 4 provided essential information for the optimisation of further experiments and techniques. Once Case II diffusion behaviour had been established, a detailed study combined, for the first time, two very different experimental techniques. This gave the ability to study both the initial stages of diffusion resulting from exposure for a few minutes, and established diffusion resulting from exposure for many hours. Although both of these regimes have been the subject of much previous study (Thomas and Windle 1978, 1981; Weisenberger and Koenig 1989a, 1989b; Mills et al 1986; Laskey et al 1988a, 1988b), no experimental link has been made between short and long term behaviour.

The induction period was studied using the depth profiling NRA technique, giving profiles with Fickian characteristics from which diffusion coefficient values were obtained. A typical value is $7.0 \times 10^{-11} \text{ cm}^2\text{s}^{-1} (\pm 20\%)$ for room temperature exposure. For long range diffusion and studies of the swollen PVC, a repetitive pulse variant of broadline gradient echo magnetic resonance imaging was developed. This new technique very successfully showed the sharp front between the penetrated and unpenetrated regions. The penetrant
front advances at a constant velocity of typically 0.042 mm/hr$^1$ ($\pm$ 10%) at room temperature. The temperature dependence of the front velocity was found to be of the Arrhenius type leading to an activation energy of 18.9 ± 5.1 kJ/mol$^1$.

For a more detailed quantitative analysis of one dimensional concentration profiles the relatively new short T$_2$ NMR imaging technique STRAFI was adopted. This allowed, for the first time visualisation of the rigid PVC as well as the swollen PVC and the acetone. Through a study of the variation of the activity of the acetone vapour surrounding the PVC samples the presence of the threshold value for front formation was found to be 0.24 ± 0.11.

Replacing acetone with deuterated acetone has been shown to be an effective method for selectively observing the signal from the PVC when using $^1$H NMR. Using two samples prepared independently yet identically with ordinary and deuterated acetone and subtracting the profiles obtained gave a typical acetone only profile. This was comparable to those obtained by other researchers for other systems (Thomas and Windle 1978, 1981; Mills et al 1986; Weisenberger and Koenig 1989a, 1989b) and permitted a quantitative test of the Thomas and Windle theory of Case II diffusion. Using the value of the diffusion coefficient measured with the depth profiling NRA technique and realistic values for other parameters describing the system, the model simulated a profile which was compared to that obtained experimentally using NMR. The theory showed good agreement with the rate of front advance. However it failed to predict the increased length of the Fickian precursor observed in the acetone and PVC system. Both theoretical and experimental profiles showed the predicted negligible concentration gradient across the penetrated region.

The profiles obtained using the short T$_2$ NMR imaging techniques showed quite a considerable slope in the swollen region of the PVC. Previous studies on methanol and PMMA have shown a similar slope in penetrant profile shape
at elevated temperatures (Thomas and Windle, 1978). This was explained by the introduction of Fickian behaviour into the diffusion dynamics. However a time course experiment on a PVC and acetone sample prepared at an exposure temperature of 50°C has indicated that this is not the case for acetone and PVC. The profile peaks have been shown to be made up of a rectangular pedestal due to the acetone and a sloping peak due to the swollen PVC. Analysis of the results of a relaxation time contrast experiment have provided evidence to support a new model concerning the physical process responsible for the slope in the NMR profile of the swollen polymer. According to this model the observed slope in the polymer part of the profiles is due to the gradual softening of the polymer for some time after the acetone has penetrated. This evidence has been further corroborated with $^{13}$C spectroscopy including CP/MAS, single pulse static and MAS experiments. Through these experiments it is also now known that the PVC used has no branching and is atactic in structure.

Experiments to study the dependence of the diffusion characteristics on the exposure temperature have found that the rate of softening is strongly exposure temperature dependent. The softening times for 20°C, 30°C, 40°C and 50°C are 86, 26, 15 and 11 (± 10%) hours respectively. The softening is presumably due to the further disentanglement of the PVC chains after they have been initially swollen as the $^{13}$C spectroscopy experiments have proved that negligible breaking of chains occurs even after prolonged exposure.

The existence of swollen but unsoftened PVC alongside swollen and softened PVC across the penetrated region of the sample makes it possible to explain the existence of multiple $T_2$ values. The shortest component (90 µs) is the swollen but unsoftened PVC, the middle component (2 ms) is the swollen softened PVC and the longest component (25 ms) is the absorbed mobile acetone. The fitting of multiple $T_2$ components is an extremely difficult procedure. It is entirely probable that a continuous distribution of relaxation
times including the shorter two values exists, reflecting the continuous
distribution in the degree of softening across the sample.

Recalling the results of chapter 5, the amplitude of the shortest component was
0.52. This was for a sample which was not fully mass equilibrated and
certainly not fully softened, even though swollen by acetone. The
corresponding amplitude for the fully mass equilibrated samples, which would
have softened far more but not completely, was 0.21. This reduction in the
amplitude of the unsoftened polymer component is again further evidence to
support the theory that on prolonged exposure to acetone the PVC continues
to soften after initial swelling.

A particularly interesting result of the STRAFI experiments was the
observation of a long Fickian precursor extending into the inner glassy core of
the samples. It was found to extend over 3 mm in some cases, far in excess
of published values for broadly similar polymer/penetrant systems. For
example, it is typically 1.6 μm for iodohexane in polystyrene (Laskey et al,
1988b). This highlights the enormous potential for new discoveries possible
with broadline NMR imaging.
APPENDIX 1

C THIS PROGRAM SIMULATES CONCENTRATION PROFILES USING THE
C THOMAS AND WINDLE MODEL.
C
C
C SET UP THE VARIABLE TYPES
C
IMPLICIT NONE
INTEGER NS,NT,K,J,P,S
PARAMETER(NS=100)
PARAMETER(NT=20000)
DOUBLE PRECISION DELTAX,ACTIV(NS),DIFFN(NS),
$VACT(NS),VRAT(NS),DACT(NS),TSTEP,DVRAT(NS)
PARAMETER(DELTAX= 5.0D-5)
CHARACTER*10 FILENAME

open(unit=16, file ='diffvrat.out')
open(unit=18, file ='/diffp.out/)
open(unit=17, file ='/diff1.par')

read(17,*),s
print *,s

C
C SET UP THE INITIAL CONDITIONS
C
DO 60 J=1,NS
VRAT(J)=1.0D-5
ACTIV(J)=1.0D-5
VACT(J)=VRAT(J)/ACTIV(J)
60 CONTINUE
C
C SET THE TIMESTEP LENGTH
C
TSTEP = 15
C
C BEGINNING THE STEPPING LOOP
C
DO 61 P=1,NT
ACTIV(1)=1.0D0
C
C CALCULATION OF THE DIFFUSION COEFFICIENT IN EACH ELEMENT
C
CALL DEVAL(VRAT,DIFFN,P,NS,NT)
C CALCULATION OF THE ACTIVITY GRADIENT
C
CALL DAEVAL(DIFFN,VRAT,ACTIV,DACT,P,NS,NT,DELTAX,VACT)
DO 63 K=2,NS
   ACTIV(K)=ACTIV(K)+DACT(K)*TSTEP
   IF(ACTIV(K).GT.1.0D0) THEN
      ACTIV(K)=1.0D0
   ENDIF
63 CONTINUE
C CALCULATION OF THE VOLUME-ACTIVITY RATIO
C
CALL VAEEVAL(VRAT,ACTIV,VACT,P,NS,NT)
C CALCULATION OF THE VOLUME RATIO GRADIENT
C
CALL DVEEVAL(VACT,VRAT,DVRAT,P,NS,NT)
C CALCULATION OF THE VALUES OF THE VOLUME RATIO AND ACTIVITY AT THE NEXT STEP.
C
DO 64 K=1,NS
   VRAT(K) = VRAT(K)+DVRAT(K)*TSTEP
   IF(VRAT(K).GT.1.0D0) THEN
      VRAT(K)=1.0D0
   ENDIF
   IF(P.EQ.S) THEN
      WRITE(16,*) K,VRAT(K)
   ENDIF
64 CONTINUE
C PRINTING OUT THE PROFILES
C
IF(P.GT.S) THEN
   WRITE(18,*) P
   STOP
ENDIF
C
61 CONTINUE
END
C
SUBROUTINE TO CALCULATE THE DIFFUSION COEFFICIENT

SUBROUTINE DEVAL(VRAT, DIFFN, P, NS, NT)
INTEGER NS, NT, J, P
DOUBLE PRECISION D0, A, VRAT(NS), DIFFN(NS)
D0 = 6.98D-15
A = 6.214608098D0
DO 10 J = 1, NS
DIFFN(J) = D0*DEXP(A*VRAT(J))
PRINT *, DIFFN(J)
10 CONTINUE
END

SUBROUTINE TO CALCULATE THE VOLUME ACTIVITY RATIO

SUBROUTINE VAEVAL(VRAT, ACTIV, VACT, P, NS, NT)
INTEGER NS, NT, J, P
DOUBLE PRECISION ACTIV(NS), VACT(NS), VRAT(NS)
DO 20 J = 1, NS
VACT(J) = VRAT(J) / ACTIV(J)
IF(VACT(J) .GT. 1.0D0) THEN
VACT(J) = 1.0D0
ENDIF
PRINT *, VACT(J)
20 CONTINUE
END

SUBROUTINE TO CALCULATE THE ACTIVITY GRADIENT

SUBROUTINE DAEVAL(DIFFN, VRAT, ACTIV, DACT, P, NS, NT, DELTAX, VACT)
INTEGER NS, NT, J, P
DOUBLE PRECISION DELTAX, FIRST, SECOND, DIFFN(NS), VRAT(NS), ACTIV(NS), DACT(NS), VACT(NS)
DACT(1) = 0.0D0
FIRST = (0.5D0*(DIFFN(2)+DIFFN(1))/(DELTAX)**2)*
$((VRAT(2)+VRAT(1))/(ACTIV(2)+ACTIV(1)))*$
$(ACTIV(2)-ACTIV(1))$
DO 30 J = 2, NS
SECOND = FIRST
IF(J .EQ. NS) THEN
FIRST = 0.0D0
ELSEIF(ABS((ACTIV(J+1)-ACTIV(J)))/LT.1.0D-40) THEN

196
FIRST = 0.0D0
ELSE
FIRST=(0.5D0*(DIFFN(J+1)+DIFFN(J))/(DELTAX)**2)*
$((VRAT(J+1)+VRAT(J))/(ACTIV(J+1)+ACTIV(J)))*$
$((ACTIV(J+1)-ACTIV(J))$
ENDIF
DACT(J)=(FIRST-SECOND)/(VACT(J))
C PRINT *,DACT(J)
30 CONTINUE
END
C
SUBROUTINE TO CALCULATE THE VOLUME RATIO GRADIENT
C
SUBROUTINE DVEVAL(VACT,VRAT,DVRAT,P,NS,NT,S)
INTEGER NS,NT,J,P,S
DOUBLE PRECISION M,B,VACT(NS),VRAT(NS),DVRAT(NS)
M=15D0
B=4.0D-6
DO 40 J=1,NS
DVRAT(J)= -B*DLOG(VACT(J))*DEXP(M*VRAT(J))
C PRINT *,DVRAT(J)
40 CONTINUE
END
APPENDIX 2

dim kk(2500),l(2500)
dim da(1100:2000),de(1100:2000)
rem MASSES OF PROTON,HE3,DEUTERON,HE4 IN MEV/C^2
mp=938.28
m3=2808.413
md=1875.63
m4=3727.41
rem READ IN HE3 BEAM ENERGY(E3B),ANGLE OF DETECTOR(ANG),ANGLE OF SAMPLE(ALPH)
171
gosub 124
gosub 125
gosub 126
rem READ IN NORMALISATION FILE
gosub 127
rem CONVERT ALPH, ANG TO RADIANS
129 alpha=alph*3.14159/180
phi= ang*3.14159/180
rem DO CALCULATION OF PROTON ENERGY AT HALF-HEIGHT OF
rem DIFFUSED SPECTRUM LEADING EDGE
q=m3+md-mp-m4
bb=-2*(m3*mp*e3b)^.5*cos(phi)
bbb=-25*(m3*m4*e3b)^.5*cos(phi)
aa=mp+m4
cc=m3*e3b-m4*e3b-m4*q
ccc=m3*e3b-mp*e3b-mp*q
rem PROTON ENERGY AT HALF-HEIGHT OF DIFFUSED SPECTRUM LEADING EDGE
ep0=(-bb+(bb^2-4*aa*cc)^.5)/(2*aa)^
rem INPUT DIFFUSED FILE
? " Input Diffused Filename: ": line input namein1$
OPEN namein1$ AS #4 LEN=8605
FIELD #4,2 AS F$,2 AS M$,2 AS S$,2 AS E$,2 AS R1$,2
                AS R2$,2 AS L1$,2 AS L2$,8 AS D$,4 AS T$,2
                AS C$,2 AS N$,8192 AS I$,321 AS FF$,60 AS P$
GET #4
PRINT namein1$; " INFO.: ":PRINT P$
CLOSE #4
INPUT "ENTER 1st CHN.(PRECISELY 5 CHNS BELOW HALF-HIGHT OF LEADING EDGE) ",J1
INPUT "ENTER THE LAST CHANNEL NO. TO BE ANALYSED ":J2
open namein1$ as #4 len=16
field #4, 4 as a$, 4 as b$, 4 as c$, 4 as d$
tempsize= lof(4)/16
for i=3 to tempsize
get 4,i
m=(i-2)*4
kk(m-3) = cvl(a$)
kk(m-2) = cvl(b$)
kk(m-1) = cvl(c$)
kk(m) = cvl(d$)
next i
close #4

j0=j1+5
jdif=j1-j1n
for j = j1 to j2
jj=j-jdif
if l(jj)=0. THEN GOTO 20
da(j)=kk(j)/l(jj)
if kk(j)=0 then da(j)=1/l(jj);kk(j)=1
GOTO 22
20 PRINT "THE NORMALISATION CHANNEL " jj "WAS ZERO."
22 print j,da(j)
next j

rem TO CALCULATE DEPTH ASSOCIATED WITH EACH CHANNEL
111 for j=j0 to (j2 -j1+j0)
rem FIRST DO CALCULATION OF MEASURED PROTON ENERGY OF CHANNEL J
ep = ep0 +(j-j0)*ke/1000
z=0
rem THEN DO CALCULATION OF ESTIMATED HE3-ENERGY ASSOCIATED WITH CHANNEL J
30 b=-(2*sqr(m3*mp*ep)*cos(phi))
a=m3-m4
c=(mp+m4)*ep-m4*q
ans1=(-b+sqr(b^2-4*a*c))/(2*a)
e3=ans1^2
e=e3
gosub 130
rem RANGE OF HE3 IN POLYSTYRENE ASSOCIATED WITH CHANNEL J IN MICRONS
Re3=range
if z=1 goto 31
e=e3b
gosub 130
rem RANGE OF INCIDENT HE3 IN POLYSTYRENE IN MICRONS
Re3b=range
rem DE(j)-INITIAL ESTIMATION OF DEPTH ALONG THE BEAM
DIRECTION IN MICRONS
rem IS DIFFERENCE IN RANGES OF Re3b AND Re3
de(j)=Re3b-Re3
rem NOW ESTIMATE TRUE PROTON ENERGY AT THIS DEPTH
rem DEPDX IS IN MEV/MICRON - FOR 12 MEV PROTONS in polystyrene
depdx=0.0043
ep=ep+depdx*de(j)*sin(alpha)/sin(phi-alpha)
rem NOW WORK OUT REVISED HE3 ENERGY AT THIS DEPTH, REVISED
RANGE AND DEPTH
z=1
goto 30
31 de(j)=Re3b-Re3
rem DEPTH PERPENDICULAR TO SURFACE IN MICRONS
xxx=de(j)*sin(alpha)
PRINT j,xxx
40 NEXT j
input"Have you finished ? (Type YES or NO ) :"",A$
aa$=lcase$(a$)
aaa$=left$(aa$,l)
if(aaa$="y") then goto 119
goto 171

124 input "he3 beam energy in MEV (e.g. 1.1) : " ,e3b
rem convert ion energy to he3-nucleus energy
e3b=e3b*m3/(m3+.511)
RETURN
125 input "angle of detector in degrees (e.g.160) :"",ang
RETURN
126 input "angle of sample to beam (normally 90 deg) in deg. :"",alph
RETURN
127 ?"Input SMOOTHED Normalisation Filename: "; line input namein2$
OPEN namein2$ AS #4 LEN=8605
FIELD #4,2 AS F$,2 AS M$,2 AS S$,2 AS E$,2 AS R1$,2
2 AS R2$,2 AS L1$,2 AS L2$,2 AS D$,4 AS T$_,
2 AS C$,2 AS N$,8192 AS I$,321 AS FF$,60 AS P$
GET #4
PRINT namein2$; " INFO.: ":PRINT P$
CLOSE #4
input " enter 1st channel -5 channels below half-height of leading edge:" ,jln
INPUT "ENTER PROTON ENERGY PER CHN. IN keV/CHN.(7.88 for
Durham) :" ,ke
open namein2$ as #4 len=16

200
field #4, 4 as a$, 4 as b$, 4 as c$, 4 as d$

tempsize= lof(4)/16
for i= 3 to tempsize
get 4,i
m=(i-2)*4
l(m-3) = cvl(a$)
l(m-2) = cvl(b$)
l(m-1) = cvl(c$)
l(m) = cvl(d$)
next i
CLOSE #4

RETURN
rem Range calculated for HE3 in polystyrene
rem 130 range = .351295*e +.978538*e^2 +.837949*e^3 + .221045*e^4
rem Range calculated for HE3 in rigid PVC
130 range = 0.567 +0.00356*e - 7.43e-7*e^2 +9.29e-10*e^3 -1.72e-13*e^4
return
119 stop
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206


