CHARACTERIZATION OF WATER IN WOOD BELOW
THE FIBRE SATURATION POINT

by

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Abstract

The purpose of this study was to explore the nature of water in the wood below the fibre saturation point. The approach was two-fold: (1) to experimentally determine the sorption isotherms for sapwood and heartwood of western hemlock (Tsuga heterophylla (Raf.) Sarg.) and sitka spruce (Picea sitchensis (Bong.) Carr.), and use this data to evaluate theoretical concepts; and, (2) to use pulse proton nuclear magnetic resonance (NMR) with matched specimens at moisture contents below the fibre saturation point to determine the interaction of water to the wood structure. Also, water clustering analysis of the sorption data was done using the Zimm-Lundberg water cluster theory.

The initial desorption, adsorption and secondary desorption isotherms were determined and non-linear regression techniques were used to fit four sorption models to the data. The BET model did not fit very well to the data. The Dent and the H-H models were mathematically identical. Since the Le-Ly model had more parameters, it fit the data well. The equilibrium moisture contents were generally lower for the heartwood region compared to the sapwood region for the same species. The adsorption to secondary desorption ratios were found to be: hemlock sapwood: 0.830; hemlock heartwood: 0.823; spruce sapwood: 0.898; and, spruce heartwood: 0.869. Tangential and radial dimensional changes were calculated based on oven dry measurements during the sorption experiments, and it was found that they were independent of the sorption process.

From the NMR experiments, moisture contents and second moments were determined from the free induction decay curve. Average relative spin densities, which were needed to calculate the moisture contents from NMR experiments, were calculated from known moisture
contents and were: hemlock sapwood: 0.616; hemlock heartwood: 0.537; spruce sapwood: 0.679; and, spruce heartwood: 0.421. The second moments were higher at low moisture contents as compared to those near the fibre saturation point. The condition as to how the equilibrium moisture content was attained did not influence the second moments for hemlock; however for spruce the second moments were sorption dependent. The decay curve from the CPMG experiments was decomposed into two components for each species; a long component was determined with a $T_2 > 5$ ms and a short component with $T_2 < 2$ ms. Unfortunately, the heterogeneous and complex chemical composition of wood-water systems produced a mixture of NMR signals that were difficult to interpret relative to verifying specific concepts of cluster theory. An attempt was made to extract as much information as possible and speculate about the nature of the bound water in wood the results.
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Dedication

To Anne and Cliff, my parents,
who are always there when I need them.
"Duj tlvoqtaH"
Always trust your instincts.
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Chapter 1

1.1 Introduction

The moisture content (M) of wood in a freshly cut tree is typically greater than 70%, oven dry basis, and depending on the species or heartwood/sapwood regions, this value may be higher. At high moisture contents, two phases of water can be found: one is free water that is located in the microvoids and the cell-lumen, and, the other is bound water that is located within the cell-wall material. As the wood begins to dry out when exposed to ambient conditions in air, the moisture first leaves the wood from the voids and the lumens while the bound water content remains constant. The moisture content level which corresponds to lumens containing no free water (but will contain water vapour) while no bound water has been desorbed from the cell-wall material, is known as the fibre saturation point (Mp). For most species, the Mp is in the range of 26 - 32%. As the moisture content of the wood decreases below the Mp, the bound water will begin to leave the cell-wall material; this phenomenon is commonly called desorption. At a certain point, an equilibrium will be attained between moisture in the wood and that in the air of the surrounding environment. This is where the wood will not gain or lose with time any moisture and it is known as the equilibrium moisture content (Me) of the wood.

In the hygroscopic range, moisture content between 0% and Mp, the wood is capable of adsorbing and desorbing water molecules in response to its surrounding atmospheric environments. The major factors which affect its moisture content are temperature (T) and relative humidity (H). The graphical representation of the moisture content as a function of
relative humidity at a constant temperature is referred to as a sorption isotherm; an example is shown in Figure 1.

Never dried wood, referred to as green, has a desorption isotherm which is higher compared to the oven-dried wood adsorption and desorption isotherms. Also, the oven dry desorption isotherm is always higher than the adsorption isotherm. This difference is known as sorption hysteresis and it is present for many hygroscopic materials (Skaar, 1988).

The possible mechanisms and mathematical models that describe the sorption isotherm behaviour of water in wood, have been developed by many researchers (Skaar, 1988). Most of the models are based on several assumptions that characterize the wood sorption sites and/or how the water may interact with this surface. Several models have been applied to the wood sorption process, for example, BET theory developed by Brunauer et al. (1938); Dent theory (Dent, 1977); and, H-H theory (Hailwood and Horrobin, 1946). Recently, a sorption model was developed for textile materials by Le and Ly (1992); it is denoted as L-L. The BET, Dent and L-L theories are based on a multilayer concept whereas the H-H theory is based on an ideal solution concept. These models are used to predict sorption isotherms based on their underlying assumptions and statistical regression analysis.

Proton nuclear magnetic resonance (1H-NMR) studies on wood-water systems have provided valuable information at moisture contents above the $M_F$ (Hartley et al., 1992). A NMR study of wood below the $M_F$ could provide more information to describe the sorption isotherm if the responses from the distinct structures can be separated cleanly. NMR is well suited for this work because it can provide insight into structures and dynamics at a molecular level. Recent NMR research by Araujo et al. (1994), using green wood conditioned at moisture contents below $M_F$, had shown that some of the NMR parameters, such as second
Figure 1: A typical isotherm for wood of equilibrium moisture content as a function of relative humidity showing the three different isotherms: (first) desorption 1, adsorption and (secondary) desorption 2.
moments and $T_2$ of the water, were moisture content dependent. However, the research was not extensive and did not consider the conditions at which the moisture contents were attained.

Understanding the wood-water interaction on a molecular level would provide clearer explanations of physical properties that are influenced by the presence of water, for example, mechanical, mechano-sorptive, electrical, creep and mechano-sorptive creep to name a few. The NMR experiments would provide a foundation for non-destructive evaluation of moisture contents in wood products, which could allow for better modelling of wood drying operations.

1.2 Objectives

The research was divided into two main areas: one area was the analysis of the sorption isotherm using the sorption models, and, the other was to utilize NMR experiments to determine the nature of bound water below the $M_p$.

The objectives of the proposed research were:

1. to experimentally determine the three sorption isotherms (initial desorption, adsorption and secondary desorption) for heartwood and sapwood samples of sitka spruce ($Picea sitchensis$ (Bong.) Carr.) and western hemlock ($Tsuga heterophylla$ (Raf.) Sarg.) and to use this data to evaluate theoretical concepts;

2. to perform NMR experiments which would determine, as a function of moisture content below the $M_p$ for each isotherm, (a) the influence of the moisture level on the cell-wall material, and, (b) the behaviour of the bound water.
1.3 Overview of the Thesis

The material presented in the following chapters include a literature review (Chapter 2) introducing a water cluster theory for water sorption in wood. Also, a discussion is presented to bring out the objectives for the research thesis. Chapter 3 outlines the general materials and research plan. Both Chapters 4 and 5 present the results and analysis from the sorption isotherm and NMR experiments, respectively. Chapter 6 contains the conclusions and recommendations for future research.
Chapter 2
Cluster Theory For Water Sorption In Wood

2.1 Literature Review

The sorption of moisture in wood is characterized as "sigmoid"; referring to a plot of equilibrium moisture content versus relative humidity. The sigmoid relationship is not unique to wood, however. Other materials may exhibit different characteristic sorption isotherms (Stamm, 1964). These sigmoidal sorption curves have been studied, both mathematically and physically. From a mathematical viewpoint, several equations have been developed to describe the curve which are based on critical assumptions and conditions. Researchers have discussed various physical mechanisms that could explain the sigmoid shape. These assumptions and mechanism are, by necessity, idealistic, mainly because of the complexity of the polymer structure of wood.

To be able to fully describe the sorption isotherm, detailed information of how water interacts with wood at a molecular level has to be obtained. One method used to obtain this information is nuclear magnetic resonance (NMR) (Riggin et al., 1979). NMR is well suited for probing this hygroscopic material because the technique can provide insight into structure and dynamics at a molecular level. NMR has been used extensively to investigate wood-water systems with the result that different "states" of water within the material are identified. In recent years, modern NMR facilities have been used to study wood and new "states" of water have been found that should be investigated further. In particular, a study of such states as a function of moisture content and temperature should prove informative.
Research during the last decade has brought new insights into the structure and behaviour of water that sorption theories did not consider. For example, water molecules at a hydration (sorption) site may interact with each other so as to form clusters within the pores (Belfort and Sinia, 1980). Also the energies attributed to the hydroxyl sites on cellulose crystals and amorphous cellulose are different because of the proximity of neighbouring sites and/or neighbouring cellulose constituents (Pizzi et al., 1987). It is the purpose of this section to present a brief review of the sorption theories that have been applied to wood and to present a review of these "new insights" into water interaction with wood substances.

2.1.1 Sorption Theory

The basis for a sorption theory is the interaction of the sorbing molecule with the surface. There have been numerous sorption theories presented for different absorbents (e.g. monatomic and diatomic gases) and of the absorbate (e.g. heterogeneous surfaces). Ponec et al. (1974) discuss these different characteristics in greater detail. Venkateswaran (1970) presents an excellent review of mathematical models that were developed for sorption on cellulosic materials and Skaar (1988) details current sorption theories for wood. There are two primary concepts that are used: one is of a multimolecular layer and the other is of a polymer-solution.

The BET and Dent theories are both based on a "layering" concept. Figure 2 shows a schematic view of the formation of layers during sorption. The theories propose a monolayer tightly bound to the hydroxyl groups of the cellulose chains, and secondary layers considered to behave thermodynamically the same, however, different than the monolayer.
Figure 2: Schematic diagram showing multimolecular layering: The vertical lines represent sorption sites, the dark circles represent primary water molecules, and the open circles represent secondary water molecules; (b) is the same as (a) only arranged in ascending order of site occupancy [from Dent (1977) and Skaar (1988)].
Brauner et al. (1938) developed a multimolecular layer theory [here in after referred to as the BET model, named after the authors Brunauer, Emmett and Teller], based on Langmuir’s (1918) treatment of a unimolecular layer, which resulted in the characteristic sigmoidal curve. The BET model considers a multilayer adsorption, assuming a monolayer tightly bonded to the wood substrate, and secondary and higher layers having similar characteristics as liquid water. More recently, Dent (1977) modified the BET theory to consider the secondary and higher layers to be the same thermodynamically, however, different than that of liquid water. The Dent model has been shown to be a more general model with the BET and Langmuir models being limiting cases.

The BET equation states:

\[
\frac{v}{v_m} = \frac{C h}{(1 - h)(1 - h + C h)}, \tag{1}
\]

where \(v\) is volume of gas adsorbed, \(v_m\) is volume of gas adsorbed for a complete unimolecular layer, \(C\) is a constant, and \(h\) is the relative vapour pressure given by the ratio of the partial vapour pressure, \(p\), to the saturated vapour pressure, \(p_o\).

At saturation, \(h\) equals 1 and \(v\) approaches infinity. Substituting \(h\) by \(p / p_o\) into Equation (1) gives the following isotherm equation:

\[
\frac{v}{v_m} = \frac{C p}{(p_o - p) \left(1 + (C - 1) \left(\frac{p}{p_o}\right)\right)}. \tag{2}
\]
This equation does give a sigmoid shape, however, it is for an infinite number of layers.

Brunauer et al. (1938) refined Equation (2) to consider a finite number of layers, n:

\[
\frac{v}{v_m} = \frac{C h}{(1 - h)} \left( \frac{1 - (n + 1) h^n + n h^{n+1}}{1 + (C - 1) h - C h^{n+1}} \right).
\]

(3)

If \( n = 1 \), then Equation (3) reduces to the Langmuir model for unimolecular sorption, and when \( n = \infty \), it becomes Equation (2).

The Dent theory introduces a term to account for a different sorption energy associated with secondary sorbed water molecules. According to this theory,

\[
\frac{v}{v_m} = \frac{b_1 h}{(1 - b_2 h) (1 - b_2 h + b_1 h)},
\]

(4)

where \( b_1 = S_i / (S_0 h) \) and \( b_2 = S_i / (S_{(i+1)} h) \), \( i \neq 1 \). \( S_i \) is the area covered by water in layer \( i \) and \( S_0 \) is the total available sorption area. The term \( b_2 \) is a constant which relates statistical thermodynamic partition function of the secondary sorbed molecules to that of an external condensed liquid in equilibrium with the saturated vapour. In the BET theory, it was assumed that this constant was equal to unity, since the energies of the secondary molecules were the same as liquid water. Also, the term \( b_1 \) is defined as the ratio of the partition function of the primary molecules to the external condensed liquid in the saturated vapour.

The importance of this development is that Dent considered the secondary sorbed water to be different from liquid water as well as different from the primary sorbed water. A
key assumption is that the partition functions of the secondary sorbed water molecules are the same for all layers.

Le and Ly (1992) developed a multilayer theory similar to the BET theory (it is denoted here as L-L model). The development of the L-L model closely follows that of the BET model equation, however, the former has different underlying assumptions. The BET model assumes that the adsorption site area, $S_i$, is covered by $i$ molecular layers, whereas the L-L model assumes that $S_i$ is the area occupied by the $i^{th}$ layer of the adsorbed molecule. Their model presents a possible way to determine the fractions of primary and secondary sites available during the adsorption process. Based on these assumptions, the following model was developed:

$$m = \frac{m_0 \text{Ch}}{1 + \text{Ch}} \left( \alpha \sum_{i=0}^{n-1} h^i + (1 - \alpha) \sum_{i=0}^{p-1} h^i \right).$$  \hspace{1cm} (5)$$

In this equation, $m$ and $m_0$ are the moisture content fraction and the moisture content fraction for the unimolecular layer, respectively. Also, the fraction of the adsorption sites that contain up to $n$ layers is $\alpha$ and the rest of the sites have up to $p > n$ layers. Equation (5) reduces to the following:

$$m = \frac{m_0 \text{Ch}}{1 + \text{Ch}} \left( \frac{1 - \alpha h^n (1 - \alpha) h^p}{1 - h} \right).$$  \hspace{1cm} (6)$$

Hailwood and Horrobin (1946) developed a model for water sorption by assuming
that the process is governed by the formation of a solid solution of water in the polymer and
the formation of hydrates between water and definite units of the polymer molecule. The
mixture of polymer, polymer hydrates and dissolved water forms a single solid phase. The two
component system, water and polymer, exists in two phases, and the dissolved water
molecules in the solid phase are assumed to be mobile. The following equation was developed:

\[
c = \frac{K a}{(1 - K a)} \left( \frac{K a K_1 + 2 (K a)^2 K_1 K_2 + \ldots}{1 + K a K_1 + K_1 K_2 (K a)^2 + \ldots} \right),
\]

where \( c \) is the dry basis mole fraction of water, \( K \) is an appropriate equilibrium constant
between the different phases of water, and \( a \) is the activity of the water (essentially the relative
vapour pressure). The first term on the right-hand side of Equation (7) represents the fraction
of free dissolved water and the other term, the various fractions of water present as
monohydrate, dihydrate, etc.

A one hydrate model gives the simplest form of Equation (7), and still represents
the experimental sorption data quite well. The one hydrate form is:

\[
\frac{M}{18} \frac{m}{\alpha h} = \frac{(\alpha h)}{1 - \alpha h} + \frac{\alpha \beta h}{1 + \alpha \beta h},
\]

where \( \alpha = K a / h \), \( \beta = K_1 \), \( M_p \) is the molecular weight of polymer, \( h \) is the relative vapour
pressure, and \( m \) is the dry basis moisture content fraction.

Using a non-linear regression technique, Simpson (1973, 1979) applied Equations.
(4) and (8), in addition to other sorption theories (Skaar, 1988), to sorption data contained in the USDA Wood Handbook (1955). This was done in order to determine the values of constants contained within the equations. The resulting regression equations have found wide use.

2.1.2 NMR Spectroscopy of Sorbed Water

NMR is an excellent tool to determine the mobility of the polymer as well as the water, as functions of moisture content and temperature. In this section, the discussion will concentrate on water behaviour as determined by NMR spectroscopy.

Much of the NMR research dealing with sorption characteristics of water in cellulosic materials has been done with wideline spectroscopy. More recently, pulse techniques have been used and are considered to be quicker than the wideline technique (Riggin et al., 1979). The research using NMR has concentrated on derivative forms of cellulose, or natural hygroscopic materials such as cotton, wool and wood. Most of the research has been performed on samples that have been equilibrated in a moist environment for a period of time, and only a few experiments have been done while the sample was sorbing water. All of these systems are heterogeneous and interpreting the results can be difficult. However, general trends can be determined readily. For this discussion, the equilibrium condition will be considered and is referred to as a sample being allowed to equilibrate in an environment for a period of time before the start of any experiments. It should be noted that the phrases "bound water" and "free water" for the different states of water as described below are different than the terms used in the wood literature. "Bound water" in the wood literature refers to water
molecules hydrogen bonded to the cell wall substance and "free water" to the water in the lumens beyond fibre saturation. The latter term may be compared to the "bulk water" term in NMR research.

In the 1970's and early 1980's, NMR studies of equilibrated cellulose-water systems revealed that there are at least two states of water: one state consists of water tightly bound to hydroxyl sites and the other state consists of liquid-like bulk water (Childs, 1972; Froix and Nelson, 1975). The spin-spin relaxation times for the bound water increases as the moisture content increases, however, these times are still lower than those of bulk water, in the order of seconds (Figure 3, part a) (Froix and Nelson, 1975). In a more recent NMR study of cellulose- water systems, Peemoeller and Sharp (1985) have defined three different phases of adsorbed water in cellulose. The authors have classified all of the water as bound, influenced by the presence of the cellulose chains: tightly bound, bound, and very loosely bound. The very loosely bound water resembles liquid water.

NMR pulse techniques were used by Hsi et al. (1977) to analyze the proton relaxation time of equilibrated milled white cedar wood. Using the CPMG pulse sequence [named after Carr and Purcell (1954) and Meiboom and Gill (1958)], two T_2 relaxation components were observed. One component was found below the fibre saturation point, determined by NMR to be around 0.38 g/g, and both components were present above that point. Their explanation for the two transverse components was related to the bound water in the wood structure and the water in lumens above the fibre saturation point. Their study also included the effects of temperature as a function of moisture content taken from the amplitude of the free induction decay curve, see Figure 3, part b. They found that in wood with moisture content less than 0.38 g/g, no freezing event occurred; whereas, in wood with moisture
Figure 3: NMR relaxation graphs: a: spin-spin relaxation time of bound water versus moisture content for cellulose (Froix and Nelson, 1975), b: signal intensity for milled wood at M > 38% (solid line) and for M < 38% (dashed line), plotted against temperature (note reverse temperature axis). (Hsi et al, 1977), and c: spin-spin relaxation times of bound water (solid line) and of free water (dashed line) for wood versus moisture content (Riggin et al., 1979).
content greater than 0.38 g/g, a freezing event was noted. This freezing event was characterized by a dramatic drop in signal intensity. Such a decrease in signal was the result of ice protons having a very short $T_2$ of approximately 6 $\mu$s and a very long $T_1$ so that they were not observed in these experiments. As the temperature decreased, the $T_2$ relaxation times of the water in the milled wood decreased.

Riggin et al. (1979) also analyzed $T_2$ relaxation in wood using the CPMG sequence. They identified two different states of water within the wood structure each having its own relaxation relaxation time (Figure 3, part c). The relaxation times followed the same pattern as exhibited by Pittman and Tripp (1970) for cellulose and by Svanson (1978) for cotton and wool. As the moisture content increased, the $T_2$ time constants increased (or the resonance line narrowed as found by Svanson). Samples with low moisture contents showed only one magnetization component with shorter relaxation time. This magnetization had been attributed to protons of water in the bound state.

Menon et al. (1987) and Hartley (1986), using the CPMG pulse sequence, found that the transverse decay curve of water protons in wood could be well described using three $T_2$ components. The additional third component magnetization had a shorter relaxation time than either of the two component magnetizations found by Riggin et al. (1979).

Menon et al. (1987) compared their NMR results to the anatomical structure of the wood samples. The $T_2$ components were described as slow (100's ms), medium (10's ms) and fast (1's ms). The $T_2$ relaxation components were assigned to three physically different structures or compartments within the wood structure: the fast component was associated with water in and on the cell wall fibrils, the medium component with water in the ray and latewood tracheid lumens and the slow component with water in earlywood tracheid lumens. It
is important to note that the authors assumed that there was no exchange among the three compartments.

Hartley (1986) also described the three \( T_2 \) components as fast, medium and slow. The \( T_2 \) of the fast component magnetization increased as the moisture content increased towards the fibre saturation point \( (M_F) \). Above \( M_F \), the \( T_2 \) of this component magnetization appeared to be independent of the moisture content. This was labelled as the bound water within the cell wall. The medium and slow components appeared as the moisture content exceeded the \( M_F \). Hartley’s interpretation of the results were based on the interaction of water in and to the wood matrix.

Work on other hygroscopic materials have relevance to the present discussion. A number of NMR studies that address the macroscopic and the microscopic compartmentation in terms of the transverse decay curve in other materials are considered below.

A NMR study was performed on water adsorbed in porous glass (Belfort and Sinai, 1980). The research concentrated on two different pore sizes, with only a two layer coverage of water. At that coverage the relaxation times \( T_1 \) and \( T_2 \) for both pore sizes were similar (one pore size was about 74 \( \mu \)m and the other 197 \( \mu \)m), indicating the same motional characteristics for water in the two samples. The authors cite the work of Luck (1976), in which he showed, using infrared (IR) spectroscopy, that at low moisture contents, the bond energy between a binding site and the monolayer decreased as adsorption increases. However, NMR results have not clearly shown that the bond weakens as the moisture content increases. In order to explain the differences between the IR and NMR results, Belfort and Sinai (1980) considered that a bulk water cluster is reduced to smaller clusters caused by the influence of the wall (see Figure 4). Also, they determined that at least two layers are necessary to get bulk-like water
Figure 4: Cluster formation at a hydration site on glass surface (from Belfort and Sinai, 1980).
properties. When increasing the relative humidity to 100% and lowering the temperature for both porous glass samples, the smaller pore size sample exhibited no freezing of water, contrary to the observation of the freezing event in the larger pore size sample. It was suggested that the freezing was not observed in the smaller pores because the pore size prevented formation of clusters sufficiently large for water to take on bulk-like properties such as to permit the formation of ice. The authors have used the term fragmented clusters to describe the smaller water clusters made up of dimers, trimers, etc. The above freezing/non-freezing behavior is similar as that noted by Hsi et al. (1977) for milled wood samples.

Hills et al. (1989) studied water transverse relaxation decay curves for dextran (Sephadex) beads with various cross-linked densities, using the CPMG sequence. These beads swell to form a porous spherical structure in water, with radii in the range 20 μm to 200 μm. Water within the structure diffuses between the inside and outside of the beads. The samples were allowed to equilibrate in water before use. Their results showed that the beads with a mean radius of 25 μm needed only one exponential curve to describe the transverse relaxation, while beads with larger mean radii required multiple exponential curves. The authors suggested that an infinite number of exponential curves would be required to completely describe the relaxation behaviour mathematically. However, a maximum of three exponential curves was used.

2.1.3 Water Structure

From the discussion presented above, it appears that water can exist in different states. These
states may be described in two manners: one is by water cluster formation and the other is byformation of molecular water layers. The following description is based on two review papers:the first is by Goring (1978) and the second is by Caulfield (1978). Both of these reviews dealwith how a glucose chain affects the structure of bulk (liquid) water, in particular, the mutualinteractions of water molecules with each other.

The basis of Goring's discussion is the "flickering cluster" concept for waterdeveloped by Frank and Wen (1957) and extensively used by Nemethy and Scheraga (1962).Nemethy and Scheraga (1962) have used statistical thermodynamics to obtain a partitionfunction for the different cluster sizes. They developed a theory that indicated that it waspossible to have clusters with as many as 97 molecules. However, x-ray analysis showed therewere no clusters larger than a few molecular diameters present in liquid water (Narten andLevy, 1969). A re-evaluation of the Nemethy and Scheraga theory by Lentz et al. (1974)showed that the cluster sizes were not large, in fact containing only six water molecules orless. Clusters were classified as a solid-like cluster (tetramer, pentamer, and hexamer) and afluid-like cluster (dimer, trimer, and star-pentamer) (Goring, 1978). Therefore, within liquidwater, there is a mixture of fluid-like and solid-like clusters. The clustering of water moleculeswas a result of their mutual interactions in a liquid state. A cluster can contain up to sixhydrogen bonded molecules (Goring 1978), as mentioned above.

When water comes in contact with a surface, the structure of water near that surfacewill be perturbed, changing the equilibrium between the fluid-like and solid-like clusters.Goring presents a molecular arrangement, based on Lentz et al. (1974) for this perturbation.At the surface, the water is envisaged as clusters of dimers, trimers, and star-pentamers, andthe clusters are bonded to hydroxyl sites. Goring points out that the larger clusters would form
away from the surface. Caulfield (1978) suggests that water near a cellulose surface is
structured by the cellulose rather than destructured by it as proposed by Goring (1978). As
cited in Caulfield, there has been some NMR work (Tait et al., 1972) suggesting that glucose
is surrounded by lattice water. This implies that the "concentration of bound water is increased
by the presence of a glucose molecule" (Tait et al., 1972). This argument suggests glucose is a
structure-maker for water, whereas Goring presented glucose as a structure-breaker. Caulfield
uses a theory of multilayer adsorption proposed by Polanyi (1924) which is based on the
polarization of the water molecules. The Polanyi theory is a multilayer adsorption theory,
similar to the BET and the Dent models. However, Polanyi considers the attraction between
successive layers becoming weaker. In fact, the bonding is considered to decrease almost
exponentially. The equation that Bradley (1936) developed using Polanyi's theory is very
similar to the behaviour of the tensile modulus of cellulose as a function of moisture content
(Caulfield, 1978). The argument follows that since the decrease of modulus of elasticity can be
related to the hydrogen-bonded network of the adsorbed layers, "something" can be deduced
about water near cellulosic surfaces. Caulfield contended that if the outer clusters envisaged by
Goring are not in contact with the tightly bonded clusters, then Goring's representation does
not explain a decrease in tensile modulus with an increase in moisture content. Basically, there
is a "participation" of all water molecules when the sample is under stress (Caulfield, 1978).
According to Caulfield's viewpoint a load bearing element for a piece of paper is the hydrogen
bond rather than the fibres as considered by Goring.

It should be pointed out that these two views are different because the authors have
considered interaction of water with glucose for two different environments. Goring (1978)
considered a glucose molecule with water around it, neglecting influence from neighboring
glucose molecules. Caulfield (1978) examined how the water interacts with the cellulose as a solid substrate. By giving water a label A and glucose (cellulose, wood, or paper) a label B, then Goring's view is B in A, while Caulfield presents his view as A in B. These are two different environments for water and the large molecule. It is expected that water will be structurally and dynamically different in the two cases.

2.1.4 Conformational Analysis of Cellulose

It has been discussed previously that water molecules will attach to available hydroxyl sites upon adsorption. Also wood is not homogeneous in terms of morphology or site energies. Therefore, not all sorption sites have the same ability to adsorb molecules. Pizzi et al. (1987a, b) performed a conformational analysis of cellulose crystal I and amorphous cellulose. Their research concentrated on determining the binding energy of the available sites, with respect to that site's surrounding area.

The analysis considered the van der Waals forces, the hydrogen bond energy (Leonard-Jones potential), and the electrostatic potential [details are presented in Pizzi and Eaton (1984) and Pizzi et al. (1987a)]. The cellulose crystals considered were of the five chain elementry I crystal types (Pizzi et al., 1987a). Using the terminology of Pizzi et al., the top and bottom, as well as the sides of the crystals were the best places for adsorption because of the steric hinderence and repulsive forces found for possible sites on the centre chains.

It is interesting to note that a given sorption site may not be able to adsorb water because of the strong influence of a near neighbour, a hydroxyl group. Their work indicates that it is possible for a water molecule to adsorb onto a site which already has a water
molecule sorbed rather than attach to an empty site. However, there is less total energy available to sorb water molecules to a particular site if it has water molecules interacting with it already. A weaker site may not adsorb water until the stronger site with water already adsorbed to it, presents a weaker interaction with adsorbing water than the weaker site. For liquid adsorption, the sites must have greater energy of interaction with water than that of water with itself. For wood, however, most of the water-wood interaction is in the vapour phase.

There are limiting cases where one has to consider the localized temperature effects and Brownian movement of the water molecules. Throughout this discussion, it should be realized that there could be bridging of water molecules between sites and interaction between more than one site and the same water molecules.

Conformation analysis was also considered for amorphous cellulose by Pizzi et al. (1987b). The authors considered the helicoidal representation for this amorphous cellulose similar to and representative of hemicellulose. There are sites in this cellulose with affinity for water larger than such affinity of the cellulose I sites, as a result of the accessibility of the chains. The analysis supports the claim that if one water molecule is sorbed per available site, then the percentage moisture content calculated is very near to the fibre saturation value reported for holocellulose by Skaar (1988).

The research by Pizzi et al. (1987b) included work on cellulose chain networks containing different numbers of cellulose chains. They considered five chains (four glucose each) - elementary crystal; 17 chains - elementary fibril; 86 chains - crystal; and 176 chains - microfibril. The distribution of the frequency of occurrence of sites with particular attractive energies, showed peaks for the attractive energy of 6 kcal/mol for the cellulose I and about 7
kcal/mol for the amorphous chains. The latter has a frequency distribution much narrower than that of cellulose I, attributed to the lower steric hindrance of the sorption site.

The purpose of the above presentation is to indicate that the adsorption of water into wood can only be treated if consideration is given to its heterogeneous nature.

2.2 Discussion of Literature

The sorption theories presented above attempt to describe the nature of water sorption on a hygroscopic surface. These theories were found not to describe exactly the behaviour of moisture adsorption, and some empirical constants are needed. The Dent theory closely matches the observed isotherms because it advances the BET theory to include the realization that the water in secondary layers is not the same as liquid water. However, Dent based his theory on the layering concept. The Hailwood and Horrobin model is a solution-based theory and is used more extensively than the multilayering theory. The success of the Hailwood and Horrobin theory is based on the constants derived by Simpson (1973). It appears that a combination of these concepts would more adequately explain the behaviour of water in wood.

The cluster theory has been used successfully to understand NMR results in hydrated porous glass (Belfort and Sinai, 1980). In the following, the cluster theory is used to describe the sorption of moisture in wood and the discussion is related to NMR.

Frank and Wen (1957), as discussed by Goring (1978), used the "flickering cluster" concept for liquid water. In this concept, the clusters are constantly flickering in size, i.e., from a cluster of three water molecules to a cluster of four or five molecules. The correlation time for the cluster flickering is of the order $10^{12}$ s. From this, it is said liquid water is in a
dynamic state and it follows that the adsorption of water on a surface would also be dynamic.

Eisenberg and Kauzmann (1969) discussed the plausibility of dimers forming in the vapour state. From their presentation, it appears that if the dimers were formed by short range forces, hydrogen bonding, less than one percent would be in a saturated steam condition (one atmosphere). However, they do not rule out the fact that there could be dimers present if forces other than those involved in hydrogen-bonding are involved. Frank (1984) has suggested, however, that larger clusters of water molecules are more stable than the dimer. He further stresses that it is more probable for a single water molecule to bond to a cluster of molecules than to another single water molecule, forming a dimer.

To illustrate how the cluster formation would take place, consider the sorption isotherm. Presented in Figure 5 is a plot of sorption data (USDA Forest Products Laboratory, 1955), equilibrium moisture content versus relative humidity. The three curves shown are isotherms at temperatures of 60 F (16°C), 120 F (49°C) and 180 F (81°C). It is evident from Figure 5 that at higher temperatures, the hygroscopicity of wood is less. The derivative of these curves can provide information on how the moisture content changes as a function of relative humidity (Figure 6). Each curve is divided into three relative humidity regions: region I from 0% to 30%, region II from 30% to 55%, and region III from 55% to 100%. Each of these regions have different characteristics that may help to define the behaviour of water in wood during sorption (keeping in mind the previous discussions).

In region I, there is a decrease of the slope of moisture content change as a function of relative humidity from the initial value. Also, the higher the temperature, the lower the initial moisture content. For example, at 60 F (16°C) the slope is about 0.26, whereas it is approximately 0.15 at 180 F (81°C). This temperature dependence can be explained by the
Figure 5: Average equilibrium moisture contents versus relative humidity: adsorption and desorption isotherm for spruce (from USDA Forest Products Laboratory 1955).
Figure 6: Derivative of sorption curves from Figure 5.
fact that the water molecules at higher temperature have more thermal energy than at lower temperature and are less likely attracted to sorption sites. Chemical attraction is the dominant mechanism for sorption in region I.

Region II is the area of the curve where a change is not noticeable. This region might be considered an organizational region. After the initial sorption of water, and the subsequent decrease in the sorption process, it would appear that the attractiveness of the sites will become the same. At this point, the molecules will re-organize to have all sites with the same energy. Of course, during this phase, more vapour molecules are being adsorbed, and will increase the moisture content slightly. To illustrate this point, consider Figure 7, part a and b, which is a schematic diagram of how water vapour molecules might sorb in wood. In part a, there is an empty site with a water vapour molecule nearby, and in part b, there are two sorption sites, one molecule on both sites and a nearby water vapour molecule. If site 2 has a larger attractiveness than site 3, then the free molecules will be attracted to site 2. If the attractiveness of the sites were reversed, the free molecule would be attracted to site 3. However, if both sites appear equally attractive, the water molecule may be attracted to site 2, gain thermal energy and move to site 3. It may stay at site 3 or move to site 2 or some other site. This particular situation is a dynamic state where the energies of all the sites become uniform, at 55% relative humidity.

In region III physisorption is the dominant mechanism. In Figure 7, part c, site 4 has three water molecules and site 5 has four molecules. In this region molecules may be attracted to different sites, making the water clusters larger. However, at a particular point the hydrogen bond between the first molecule and the hydroxyl site will become weakened
Figure 7: Water cluster formation during sorption process in wood.
(Caulfield, 1978) because of the presence of the cluster. Therefore, the cluster moves as a unit from site to site (Hoever, 1980).

The cellulose is initially bonded together, with intermolecular hydrogen bonded chains in crystalline and amorphous areas. As the wood swells, it will open more sites. Froix and Nelson (1975) described the adsorption and swelling in cellulose in the following manner: as water enters into the cellulose system, it will cause breakage of the cellulose-cellulose hydrogen bonding and result in more mobile molecular chains. Once the cellulose begins to swell and break bonds, there will be more area (free volume) available for more water molecules to adsorb; either on existing sites or on new accessible sites. The adsorption of water will initially occur on sites that are weakly bonded to the neighbouring cellulose chains or on sites that are free. Additional moisture will penetrate fibre bundles and internal surface hydroxyl groups, swelling the cellulose and creating void spaces (free volume). The large rate increase in region III shown in Figure 6 can be attributed to more such free volume caused by swelling of the polymer matrix (wood) allowing more water cluster formation. The increase in region III may also be caused by condensation of water in the larger volumes in the wood, i.e., the microvoids.

Past researchers have studied sorption of water in polymers and have called the point where cluster formation begins, the relative humidity critical point, $H_c$. Considering Figure 6, it appears that the $H_c$ for wood is about 55%. However, the wood isotherm may have two critical points, one each at 30% and 55% relative humidity. The first critical point is that of complete unimolecular adsorption, at which an organization of the site energies begins. $H_c$ at 55% relative humidity is the point of water cluster formation.

It was pointed out earlier that effects due to exchange of water molecules (or
protons) among different sites in the wood on the observed evolution of the NMR transverse decay were assumed unimportant. Unfortunately, few details are known about such exchange in wood. However, in order to derive quantitative information from the NMR results, it is necessary to analyse such results for exchange so as to obtain the intrinsic relaxation parameters, rather than the observed, apparent relaxation parameters.

Information about exchange in other heterogeneous systems may be used as a guide. The exchange rate between bulk and bound water was shown to be 30 s⁻¹ in muscle tissue (Sobol et al., 1986) and in a protein solution (Zhong et al., 1989). However, if a multilayer concept or a cluster concept applies to the bound water, then such information does not tell us much about the exchange between layers or between clusters, except that it is presumably faster than 30 s⁻¹. In wood, hydrated below the fibre saturation point, the water proton T₂ relaxation decay curve can be decomposed into two components; just below the fibre saturation point, one component magnetization has a T₂ of approximately 14 ms and the other has a T₂ of approximately 120 ms. As the moisture content decreases the long T₂ becomes faster, about 100 ms at M = 21%, and the short T₂ becomes somewhat shorter, about 1.5 ms at M = 9% (Menon et al., 1987). Although it might appear reasonable to assign the magnetization with short T₂ to protons in the primary layer or in clusters within which water molecules experience relatively restricted mobility and to assign the magnetization with longer T₂ to protons in secondary layers (and higher layers) or in clusters with larger degree of mobility, such assignment cannot be made without knowing the importance of exchange. Such exchange can be studied using established NMR techniques (Peemoeller, 1989; Zhong et al., 1989).

It has been shown (Peemoeller et al., 1986; Schreiner et al., 1991) that the water
molecule residence time at hydration sites in polymer powders is expected to be less than a microsecond. It is not unreasonable to expect a similar result for water in wood. This would suggest that the two component magnetizations observed below the fibre saturation point are due to water molecules residing in anatomically different wood compartments. This is described in terms of the cluster theory which also allows us to understand why the long $T_2$ becomes longer and the short $T_2$ becomes shorter with decreasing moisture content.

The earlier discussion connects the observed sorption isotherm in wood and the cluster theory, considering that water sorption occurs at surface sites. Although this would be reasonable for the surfaces of the lumen or ray components, some of the hydration sites inside a cell wall would be expected to be more complicated due to neighbouring cellulose chains in a three-dimensional structure. Although the detailed behaviour of the $T_2$ and size of the two component magnetizations with moisture content is not known, the following tentative model is proposed for hydration which qualitatively explains the very different behaviour with moisture content of the $T_2$ of the two component magnetizations.

As water first adsorbs to the wood, hydration sites are occupied by single water molecules (Figure 7, part a). With more water added to the wood, the unimolecular hydration continues, but some of the water molecules will be attracted to sites already occupied, forming water dimers and perhaps trimers (Figure 7, part b and c). Upon such cluster formation the bond to the cellulose substrate is generally expected to be weakened with the cluster experiencing increased mobility. As the clusters grow in size the water molecules experience an environment that more and more resembles that of bulk water. As a consequence the mobility of the water molecules increases with the result that the water proton $T_2$ becomes longer. This is observed for most of the water protons below the fibre saturation point (Menon
The water molecules at the unimolecular sorption sites are expected to be translationally immobile and relatively mobile rotationally. As indicated above, addition of a second water molecule is expected to increase water molecule mobility. However, it is not unreasonable to expect the existence of some sites that allow bond formation not just between the first water molecule and the cellulose but also between the second water molecule and the cellulose (Figure 4, for example). As a consequence both water molecules would be less mobile rotationally than the monomer. This would have the result that the T₂ of these water protons would become shorter. Similarly, as the moisture content is increased certain sites occupied by trimers may form two or three bonds to the wood substrate, restricting the mobility of any particular water molecule in the cluster even more. Thus, the T₂ of the protons at these special sites would become shorter and shorter with increasing moisture content until a point is reached, as the cluster size increases, where a water molecule inside a cluster experiences less and less of the effects due to the hydration site. At this point, the T₂ of the protons involved would increase with increasing moisture content.

Another approach of supporting the clustering of water molecules during adsorption is by using statistical thermodynamics to formally treat this concept. The development of the mathematics for treating clustering of water has been based on research by Mayer (1937), Mayer and Ackermann (1937) and McMillan and Mayer (1945). Zimm (1953) and Zimm and Lundberg (1956) used cluster integrals from McMillan and Mayer (1945) and applied a simplified approach for studying sorption characteristics of vapours by various polymers. This approach is known as the Zimm-Lundberg cluster analysis and it provides insight into the sorption process without predicting the isotherm. Details of the analysis are presented in
Appendix A.

Hartley and Avramidis (1993) used this analysis and they showed that the clustering of water molecules began to form at moisture contents of approximately 20% for the adsorption process and began to break up at 25% during desorption.

Although the models have been classified as being based on either multilayering or solution concepts, they are related in the sense that the water may be bound to primary and/or secondary sites. The presentation above also showed that water molecules form clusters on sorption sites. Therefore, if the BET, Dent, and L-L models can have water molecules form "layers", but be presented from a water clustering point of view and if the H-H model can have the different waters (dissolved and hydrate) being made up of clusters, then the four models may be essentially the same.

The approach of this research was to use the proposed sorption model of water clustering and use NMR techniques to obtain information about the wood-water system. As with any new model, the cluster theory must be consistent with experimental results for wood. For example, the adsorption/desorption hysteresis and the adsorption/desorption ratio, must be explicable with this water cluster theory.

2.3 Research Objectives

In order to investigate the wood-water system, a series of sorption isotherm data analyses and NMR experiments were designed. These experiments would also provide more knowledge of the wood's behaviour below the fibre saturation point. The research was divided into two main areas: one area was the analysis of the sorption isotherm using the sorption models, and, the
other was to utilize NMR experiments to determine the nature of bound water below the \( M_f \).

The objectives of the proposed research were:

1. to experimentally determine the three sorption isotherms (initial desorption, adsorption and secondary desorption) for heartwood and sapwood samples of sitka spruce (\textit{Picea sitchensis} (Bong.) Carr.) and western hemlock (\textit{Tsuga heterophylla} (Raf.) Sarg.) and to use this data to evaluate theoretical concepts;

2. to perform NMR experiments which would determine, as a function of moisture content below the \( M_f \) for each isotherm, (a) the influence of the moisture level on the cell-wall material, and, (b) the sorptive behaviour of the bound water.
Chapter 3

General Methods and Materials

The research was divided into two main approaches: one was a theoretical analysis of the sorption isotherm using the theories discussed in Chapter 2, and, the other was using NMR experiments.

3.1 Materials

The species studied for this research were sitka spruce (*Picea sitchensis* (Bong.) Carr.) and western hemlock (*Tsuga heterophylla* (Raf.) Sarg.). These species were chosen because of their importance to the British Columbia forest products industry. Both species are grown in moist sites on the B.C. coast. The principal uses of these species are for structural lumber, pulp and plywood construction. Table 1 presents some physical properties of the hemlock and spruce. The age of the tree from which the wood was taken for this study was about 70 years.

Throughout the thesis, the abbreviations for the wood species and regions are denoted as follows: HH for hemlock heartwood, HS for hemlock sapwood, SH for spruce heartwood and SS for spruce sapwood.

3.2 Sorption Isotherm: Sample Preparation and Experiments

A sorption experiment was carried out for sapwood and heartwood samples of sitka spruce and western hemlock, determining the initial desorption, adsorption and secondary desorption
Table 1: Relative density and shrinkage values for western hemlock and sitka spruce
(Canadian Woods, 1981)

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<th></th>
<th>Relative density</th>
<th>Shrinkage (%)</th>
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<tr>
<td></td>
<td>$G_{\text{green}}$</td>
<td>$G_{\text{o.d.}}$</td>
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<tr>
<td>western hemlock</td>
<td>0.41</td>
<td>0.47</td>
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<tr>
<td>sitka spruce</td>
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<td>0.39</td>
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Isotherms. Throughout the thesis, initial desorption is denoted as desorption 1 or DS1, adsorption is adsorption or ADS, and secondary desorption is desorption 2 or DS2.

Thirty (30) sapwood and thirty (30) heartwood specimens were cut from green blocks of spruce and hemlock wood, to a size of about 40 mm square (radial by tangential) and 5 mm in thickness (longitudinal). The specimens were carefully taken from the mature region of the wood block, therefore, there was no juvenile wood present. The specimens were carefully examined for visual defects and the best twenty five (25) of each group were used in the sorption experiments, thus resulting in a total of one hundred (100) specimens. The remaining wood blocks were maintained in green condition in a cold room at 5°C until further use.

The order of obtaining the three isotherm curves was as follows: desorption 1, adsorption and desorption 2. After the initial desorption was completed, the specimens were oven dried at 103 ± 2°C to constant weight in order to determine their oven dry weights. These weights were used to calculate their equilibrium moisture contents. The temperature throughout the sorption isotherm experiment was maintained at 26°C.

The specimens were equally spaced using test-tube drying racks and they were
placed into a conditioning chamber. There were two chambers used throughout the study and the specimens were transferred from one to the other when needed. The chambers used were models PGC 4-PC and PGC 9-PC (both from Parameter Generation and Control, Inc.), and controlled the ambient temperature and relative humidity to ± 0.2°C and ± 0.5 %, respectively. The relative humidity was monitored with a pair of wet and dry bulb thermocouples (Type T) inside the chamber. The specimen weights were measured on an electronic balance (Sartorius, type A200s) to 0.01 mg and the radial and the tangential dimensions were measured using a digital caliper (Mitutoyo) to 0.01 mm. Attainment of equilibrium was determined by obtaining daily weight measurements for the specimens individually until constant weight was achieved. The equilibrium period ranged from 14 to 30 days. The weights were measured before taking the dimensional measurements.

3.3 NMR: Sample Preparation and Experiments

The NMR experiments were designed to obtain the T₂ relaxation times for the water. The specimens were prepared to represent the three sorption isotherms, namely, initial desorption, adsorption and secondary desorption. Therefore, the moisture contents of the wood for the NMR experiments were in the hygroscopic range.

Approximately two hundred and seventy (270) cylindrical specimens, in total, of sapwood and heartwood were cut from blocks of green spruce and hemlock. Each specimen was approximately 5 mm in diameter and 15 mm in length (longitudinal). The blocks of green wood used for the NMR study were from parts of the original blocks from which the sorption specimens were cut. Each cylindrical specimen was examined for visual defects and to ensure
that there were at least three growth rings present. The specimens were further trimmed with a razor blade to ensure a fresh and clean surface.

The NMR specimens were divided into four sets. One set (denoted as Set 1) was used to determine if there was variability in the wood based on NMR results. The remaining three sets were to consider the three types of sorption of water in wood: Set 2, desorption 1; Set 3, adsorption from an oven dry condition; and, Set 4, desorption 2 from near $M_p$.

Set 1 samples were obtained from green blocks of spruce and hemlock, shown in Fig. 8. This configuration represented sample cuts from the same annual growth ring area (tangentially, circumference of a ring) and cuts from different annual growth ring areas (radially, towards the pith). The cut samples were divided by species and placed into two dessicators with a saturated salt solution of sodium thiosulphate. This salt solution provided a humid environment of approximately 78% at 20°C (Chemical Rubber Company Handbook). This environment ensured that the specimens were conditioned to approximately the same equilibrium moisture content of 20%. There were four control specimens of the same size also placed into the dessicators with the NMR specimens and they were used to determine the average moisture content after equilibration for the remaining specimens. The dessicators were placed into the PGC 4-PC conditioning chamber to maintain a constant ambient temperature of 26°C. After a month, the specimens were weighed on an electronic analytical balance to determine equilibrium. If there was no weight change over a 24-hour period, they were flame sealed in individually labelled glass test tubes. In all cases, the time from weighing the specimen to flame sealing the test tubes, was less than 10 seconds.

Set 2 samples were allowed to dry in a series of seven dessicators containing
Figure 8: Configuration of NMR specimens (Set 1) used to determine variability.
Table 2: Approximate relative humidities and equilibrium moisture contents for saturated salt solutions (Chemical Rubber Company Handbook)

<table>
<thead>
<tr>
<th>Salt</th>
<th>Formula</th>
<th>H (%)</th>
<th>M_E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>copper sulphate</td>
<td>CuSO₄ • 5H₂O</td>
<td>98</td>
<td>M₇</td>
</tr>
<tr>
<td>sodium sulphate</td>
<td>Na₂SO₄ • 10H₂O</td>
<td>93</td>
<td>25</td>
</tr>
<tr>
<td>sodium thiosulphate</td>
<td>Na₂S₂O₃ • 5H₂O</td>
<td>78</td>
<td>16</td>
</tr>
<tr>
<td>sodium bromide</td>
<td>NaBr • 2H₂O</td>
<td>58</td>
<td>10</td>
</tr>
<tr>
<td>chromium trioxide</td>
<td>CrO₃</td>
<td>35</td>
<td>7</td>
</tr>
<tr>
<td>potassium acetate</td>
<td>KC₂H₃O₂</td>
<td>20</td>
<td>4.5</td>
</tr>
</tbody>
</table>

different saturated salt solutions. The conditions inside the dessicators provided the samples with a humid environment, giving a M_E based on the solution. The seven salt solutions used are summarized in Table 2. A final step in the isotherm was an oven dry condition. The sample weights were monitored as they began to equilibrate inside the dessicators. During the equilibrium period, a specimen was chosen, weighed to determine its moisture content, placed into an individual glass tube and then flame sealed. After complete equilibrium, the remaining specimens were transferred into another desiccator with a lower humidity. This procedure continued until the specimens were prepared with moisture contents in the entire hygroscopic range. The actual moisture contents for Sets 1 and 2 were determined by NMR experiments (outlined below).

Set 3 specimens were first dried to obtain their oven dry weights and then they were placed into the same dessicators as above, in order of increasing humidity. A specimen was chosen from the dessicator, weighed to determine its moisture gain, and, if it was at the desired moisture content, it was flame sealed in a glass test tube. The remaining specimens were transferred into another desiccator with a higher humidity.
Set 4 specimens were prepared for desorption conditions. Once the oven dry weights were known, the specimens were placed into an environment near 100% relative humidity over distilled water. They were allowed to remain there until the moisture content was about the $M_F$. Although the time to reach the $M_F$ was approximately fifteen days, the specimens remained in the dessicator for three weeks. The specimens were then dried in the same manner as done for Set 2. During this procedure, some specimens had some mould growth on them; these specimens were not used.

The prepared sets were used at one session in order to reduce possible variability from the day to day operation of the NMR spectrometer. Also, the time between the final completion of the preparation for each set and use in the NMR spectrometer was at least two weeks. This assured that there was little or no moisture gradient present in the specimens during the experiments.

The $^1$H-NMR experiments were conducted on a modified Bruker SXP 4-100 NMR spectrometer, operating at 90 MHz and a field strength of 2.12 T. The pulse sequences used were the free induction decay (FID) and the CPMG sequence. For the FID experiment, spacing between the 180° pulses were 100 $\mu s$ and the number of scans was typically 125 with a repetition time of 8 s between each scan. The spacing between the 180° degree pulses in the CPMG experiment was 200 $\mu s$. The number of echos used to obtain the curve was 75, giving a decay to less than 1% for the last echo height compared to the first echo height. The repetition time was 8 s and the number of scans was typically 125. The details of NMR and the description of the pulse sequences are presented in Appendix B. The prepared sets were used at one time in order to reduce possible variability of the NMR equipment.
4.1 Data Collection

The weight and dimension measurements were collected over a period of 16 months, from April 1992 to August 1993. The weights were continuously monitored for equilibrium and once this was achieved, they were weighed first, and then, the radial and tangential dimensions were obtained. All measurements were recorded in a spreadsheet (Quattro Pro Version 1 for Windows, Borland International, Inc.) where averages and sample standard deviations were calculated. The results are presented in Table 3.

4.2 Sorption Isotherm Model Analysis

The analysis of each sorption isotherm was done by fitting the average data to the four sorption isotherm models: BET, Dent, H-H and L-L. The data in Table 3 were used for the analysis. The parameters for each of the sorption isotherm models were determined by using a nonlinear regression technique, PROC NLIN, in SAS Version 6.07 on the U.B.C.’s UNIXG mainframe computer system. An example of the source code for the H-H model executed in SAS is presented in Appendix C. In the following sorption isotherm model equations, \( m_o \) refers to the moisture content fraction corresponding to the unimolecular layer of water adsorbed and the known variables (data) are \( m \) and \( h \), the moisture content fraction (\( M/100 \)) and humidity fraction (\( H/100 \)), respectively:
Table 3: Sorption data for western hemlock and sitka spruce; temperature was 26°C.

<table>
<thead>
<tr>
<th></th>
<th>western hemlock</th>
<th>sitka spruce</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sapwood (n=26)</td>
<td>heartwood</td>
</tr>
<tr>
<td></td>
<td>ME (%) St Dev</td>
<td>ME (%) St Dev</td>
</tr>
<tr>
<td><strong>Desorption 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(%)</td>
<td>ME (%) St Dev</td>
<td>ME (%) St Dev</td>
</tr>
<tr>
<td>10.0</td>
<td>4.04 0.17</td>
<td>4.64 0.17</td>
</tr>
<tr>
<td>22.0</td>
<td>6.40 0.15</td>
<td>6.54 0.12</td>
</tr>
<tr>
<td>32.5</td>
<td>7.24 0.17</td>
<td>6.96 0.16</td>
</tr>
<tr>
<td>49.2</td>
<td>9.44 0.17</td>
<td>9.00 0.16</td>
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<td>72.1</td>
<td>14.92 0.18</td>
<td>14.02 0.18</td>
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<td>81.1</td>
<td>19.48 0.20</td>
<td>18.17 0.20</td>
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<tr>
<td>89.7</td>
<td>23.99 0.20</td>
<td>21.16 0.23</td>
</tr>
<tr>
<td>93.2</td>
<td>25.65 0.20</td>
<td>23.81 0.24</td>
</tr>
<tr>
<td><strong>Adsorption</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(%)</td>
<td>ME (%) St Dev</td>
<td>ME (%) St Dev</td>
</tr>
<tr>
<td>10.0</td>
<td>1.40 0.16</td>
<td>1.94 0.14</td>
</tr>
<tr>
<td>32.5</td>
<td>5.54 0.17</td>
<td>5.25 0.15</td>
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<tr>
<td>46.1</td>
<td>7.42 0.17</td>
<td>7.01 0.17</td>
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<tr>
<td>64.6</td>
<td>10.23 0.17</td>
<td>9.51 0.17</td>
</tr>
<tr>
<td>77.9</td>
<td>13.53 0.18</td>
<td>12.79 0.22</td>
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<tr>
<td>88.7</td>
<td>17.29 0.18</td>
<td>16.34 0.20</td>
</tr>
<tr>
<td>96.2</td>
<td>22.96 0.20</td>
<td>21.55 0.18</td>
</tr>
<tr>
<td><strong>Desorption 2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(%)</td>
<td>ME (%) St Dev</td>
<td>ME (%) St Dev</td>
</tr>
<tr>
<td>10.0</td>
<td>4.04 0.17</td>
<td>4.64 0.18</td>
</tr>
<tr>
<td>22.0</td>
<td>6.40 0.15</td>
<td>6.54 0.19</td>
</tr>
<tr>
<td>32.5</td>
<td>7.24 0.17</td>
<td>6.96 0.18</td>
</tr>
<tr>
<td>51.1</td>
<td>9.54 0.18</td>
<td>9.10 0.19</td>
</tr>
<tr>
<td>64.2</td>
<td>11.71 0.18</td>
<td>11.15 0.18</td>
</tr>
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<td>77.0</td>
<td>13.92 0.17</td>
<td>13.17 0.16</td>
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<td>85.0</td>
<td>17.86 0.19</td>
<td>16.88 0.17</td>
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<tr>
<td>90.9</td>
<td>21.10 0.19</td>
<td>19.64 0.12</td>
</tr>
</tbody>
</table>
**BET theory:**

\[
m = \frac{m_o C h}{(1 - h)} \frac{1 - (n + 1)h^n - nh^{n-1}}{1 + (C - 1)h - C h^{n-1}}.
\]

(9)

C is a parameter related to the binding energy of water vapour molecules to the surface and n is the number of layers.

**Dent theory:**

\[
m = \frac{m_o b_1 h}{(1 - b_2 h)(1 - b_2 h + b_1 h)}.
\]

(10)

The parameters in this equation are \( b_1 \) and \( b_2 \).

**Hailwood and Horrobin theory:**

\[
m = m_o k_d \left( \frac{h}{1 - k_d h} + \frac{k_h h}{1 + k_h k_d h} \right).
\]

(11)

where \( k_d \) and \( k_h \) are equilibrium constants describing an equilibrium between the dissolved water and the hydrate water, and, between the dissolved water and the external vapour pressure, respectively.

**Le and Ly theory:**

\[
m = \frac{m_o C h}{1 + C h} \left( \frac{1 - \alpha h^n - (1 - \alpha) h^p}{1 - h} \right),
\]

(12)

where \( \alpha \) represents the fraction of sorption sites which correspond to the maximum of \( n \) adsorption layers, called primary sites. The fraction of secondary sites \( (1 - \alpha) \) have \( p \) layers of water molecules.
The results from the regression are presented in Tables 4 to 7, for the BET, Dent, H-H and L-L models, respectively. PROC NLIN in SAS does not provide a F statistic or r² therefore, mean square residual (MSR) errors are presented with the model coefficients.

Figure 9 presents the data graphically with two regression curves (Dent and L-L models) through each set of data. The standard deviations were too small to be plotted with the data. The solid curve is the L-L theory and the dashed curve is the Dent theory.

Table 4: Brauner, Emmett and Teller isotherm model regression coefficients. NC means that the model did not converge.

<table>
<thead>
<tr>
<th></th>
<th>M₀</th>
<th>C</th>
<th>n</th>
<th>MSR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Desorption 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS</td>
<td>4.77</td>
<td>54.07</td>
<td>11.24</td>
<td>2.84 x 10¹</td>
</tr>
<tr>
<td>HH</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
</tr>
<tr>
<td>SS</td>
<td>4.76</td>
<td>65.59</td>
<td>11.43</td>
<td>1.71 x 10⁵</td>
</tr>
<tr>
<td>SH</td>
<td>4.61</td>
<td>31.307</td>
<td>10.77</td>
<td>2.39 x 10⁵</td>
</tr>
<tr>
<td><strong>Adsorption</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS</td>
<td>-0.145</td>
<td>-0.71</td>
<td>0.89</td>
<td>1.63 x 10⁴</td>
</tr>
<tr>
<td>HH</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
</tr>
<tr>
<td>SS</td>
<td>3.83</td>
<td>18.541</td>
<td>11.76</td>
<td>2.87 x 10⁴</td>
</tr>
<tr>
<td>SH</td>
<td>3.63</td>
<td>22.171</td>
<td>11.04</td>
<td>2.25 x 10⁴</td>
</tr>
<tr>
<td><strong>Desorption 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS</td>
<td>4.45</td>
<td>146.92</td>
<td>9.49</td>
<td>1.05</td>
</tr>
<tr>
<td>HH</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
</tr>
<tr>
<td>SS</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
</tr>
<tr>
<td>SH</td>
<td>4.32</td>
<td>51.243</td>
<td>9.01</td>
<td>8.95 x 10⁵</td>
</tr>
</tbody>
</table>
Figure 9: Equilibrium moisture content (%) plotted against relative humidity (%) for desorption 1, adsorption and desorption 2 isotherms for (a) hemlock sapwood, (b) hemlock heartwood, (c) spruce sapwood and (d) spruce heartwood. Symbols (•) is for desorption 1 isotherm, (○) is for adsorption isotherm and (△) is for desorption 2 isotherm. The dashed curve is the fit with the Dent model and the solid curve is the fit with the L-L model.
As shown in Table 4, the BET theory did not provide a very good fit to all of the data and, in some cases, the model did not converge. It is known (Skaar, 1988) that the BET model is best used with sorption data at relative humidities below 50%, and therefore use of the model with some of the current sorption data is not prudent. The coefficients for the adsorption fit of hemlock-sapwood (HS) were negative. Since the development and presentation of the BET model was based on a physical nature of the water and of the adsorbing surface, it is assumed that all coefficients have to be positive. Therefore, the HS (adsorption) regression was rejected.

The results of the nonlinear regression for the Dent and the H-H models are presented in Tables 5 and 6, respectively. Some of the regression parameter estimates for the models as well as the unimolecular layer for both models were identical. Also, the $b_2$ (Dent) and the $k_a$ (H-H) parameters were equal. It was found that any moisture content values calculated using the respective models were the same for the same relative humidities. Therefore, the plotting of both Dent and H-H models coincide when drawn through the experimental data. The Dent model is shown in Figure 9, along with L-L model.

Table 7 summarizes the results of the nonlinear regression for L-L theory. This sorption model developed by Le and Ly (1992) has not appeared in the wood science literature to date. Convergence of the model to the experimental data took over 400 iterations, however, the model fits the data quite well. This is evident from the fit of the model to the data in Figure 9, solid curve.
Table 5: Dent sorption isotherm model regression coefficients.

<table>
<thead>
<tr>
<th></th>
<th>$M_0$</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>MSR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Desorption 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS</td>
<td>6.81</td>
<td>10.29</td>
<td>0.802</td>
<td>3.84 x 10^{-5}</td>
</tr>
<tr>
<td>HH</td>
<td>6.15</td>
<td>19.19</td>
<td>0.801</td>
<td>3.43 x 10^{-5}</td>
</tr>
<tr>
<td>SS</td>
<td>6.79</td>
<td>10.64</td>
<td>0.805</td>
<td>4.14 x 10^{-5}</td>
</tr>
<tr>
<td>SH</td>
<td>6.80</td>
<td>7.68</td>
<td>0.785</td>
<td>2.93 x 10^{-5}</td>
</tr>
<tr>
<td><strong>Adsorption</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS</td>
<td>5.83</td>
<td>4.53</td>
<td>0.786</td>
<td>3.09 x 10^{-5}</td>
</tr>
<tr>
<td>HH</td>
<td>5.21</td>
<td>6.04</td>
<td>0.796</td>
<td>1.12 x 10^{-5}</td>
</tr>
<tr>
<td>SS</td>
<td>5.53</td>
<td>7.56</td>
<td>0.802</td>
<td>8.15 x 10^{-5}</td>
</tr>
<tr>
<td>SH</td>
<td>5.19</td>
<td>8.61</td>
<td>0.792</td>
<td>6.04 x 10^{-5}</td>
</tr>
<tr>
<td><strong>Desorption 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS</td>
<td>5.83</td>
<td>20.83</td>
<td>0.798</td>
<td>2.34 x 10^{-5}</td>
</tr>
<tr>
<td>HH</td>
<td>5.47</td>
<td>25.96</td>
<td>0.794</td>
<td>1.89 x 10^{-5}</td>
</tr>
<tr>
<td>SS</td>
<td>5.63</td>
<td>30.91</td>
<td>0.814</td>
<td>1.99 x 10^{-5}</td>
</tr>
<tr>
<td>SH</td>
<td>5.78</td>
<td>14.34</td>
<td>0.781</td>
<td>2.32 x 10^{-5}</td>
</tr>
</tbody>
</table>

4.3 Zimm-Lundberg Cluster Analysis

The analysis of the sorption data from the Zimm-Lundberg cluster theory was performed by using the following equation:

$$e_i G_{ii} + 1 = (1 - \phi_i) \left( \frac{\partial \ln \phi_i}{\partial \ln h_i} \right)$$  \hspace{1cm} (13)
where $c_1 G_{11} + 1$ is the number of water molecules in the cluster. The term $\phi$ is related to the volume fraction of the wood and $h$ is the humidity fraction. The development of the theory is detailed in Hartley and Avramidis (1993) and it is included in Appendix A for reference. The results are plotted in Figure 10. The desorption 1 curve decreases rapidly at high moisture content. The desorption 2 and the adsorption cluster isotherm are similar, however the DS2 curve is lower than the ADS curve. The results from this study are similar to the results found by Hartley and Avramidis (1993).

Table 6: Hailwood-Horrobin sorption isotherm model regression coefficients

<table>
<thead>
<tr>
<th></th>
<th>$M_o$</th>
<th>$k_h$</th>
<th>$k_d$</th>
<th>MSR</th>
</tr>
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<tbody>
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<td><strong>Desorption 1</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS</td>
<td>6.81</td>
<td>11.84</td>
<td>0.802</td>
<td>3.84 x 10^5</td>
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<td>HH</td>
<td>6.15</td>
<td>22.96</td>
<td>0.801</td>
<td>3.43 x 10^5</td>
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<tr>
<td>SS</td>
<td>6.79</td>
<td>12.21</td>
<td>0.805</td>
<td>4.14 x 10^5</td>
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<tr>
<td>SH</td>
<td>6.80</td>
<td>8.78</td>
<td>0.785</td>
<td>2.93 x 10^5</td>
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<td><strong>Adsorption</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS</td>
<td>5.83</td>
<td>4.76</td>
<td>0.786</td>
<td>3.09 x 10^5</td>
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<tr>
<td>HH</td>
<td>5.21</td>
<td>6.58</td>
<td>0.796</td>
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<tr>
<td>SS</td>
<td>5.53</td>
<td>8.43</td>
<td>0.802</td>
<td>8.51 x 10^5</td>
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<tr>
<td>SH</td>
<td>5.19</td>
<td>9.88</td>
<td>0.792</td>
<td>6.04 x 10^5</td>
</tr>
<tr>
<td><strong>Desorption 2</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS</td>
<td>5.83</td>
<td>25.12</td>
<td>0.798</td>
<td>2.34 x 10^5</td>
</tr>
<tr>
<td>HH</td>
<td>5.47</td>
<td>52.47</td>
<td>0.794</td>
<td>1.89 x 10^5</td>
</tr>
<tr>
<td>SS</td>
<td>5.63</td>
<td>30.91</td>
<td>0.814</td>
<td>1.99 x 10^5</td>
</tr>
<tr>
<td>SH</td>
<td>5.78</td>
<td>17.36</td>
<td>0.781</td>
<td>2.32 x 10^5</td>
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</table>
Table 7: Le-Ly sorption isotherm regression coefficients.

<table>
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<tr>
<th></th>
<th>$M_o$</th>
<th>$C$</th>
<th>$n$</th>
<th>$p$</th>
<th>$\alpha$</th>
<th>MSR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Desorption 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS</td>
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<td>8.601</td>
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<td>2.82 x 10^5</td>
</tr>
<tr>
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<td>6.32</td>
<td>0.166</td>
<td>3.38 x 10^5</td>
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<tr>
<td>SS</td>
<td>7.99</td>
<td>18.067</td>
<td>0.19</td>
<td>6.40</td>
<td>0.362</td>
<td>2.11 x 10^5</td>
</tr>
<tr>
<td>SH</td>
<td>5.99</td>
<td>10.959</td>
<td>4.17</td>
<td>16.47</td>
<td>0.888</td>
<td>4.45 x 10^5</td>
</tr>
<tr>
<td><strong>Adsorption</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS</td>
<td>3.04</td>
<td>0.557</td>
<td>1.22</td>
<td>18.29</td>
<td>0.922</td>
<td>7.75 x 10^5</td>
</tr>
<tr>
<td>HH</td>
<td>6.79</td>
<td>3.597</td>
<td>2.58</td>
<td>17.26</td>
<td>0.846</td>
<td>6.29 x 10^5</td>
</tr>
<tr>
<td>SS</td>
<td>11.59</td>
<td>2.738</td>
<td>1.31</td>
<td>17.83</td>
<td>0.869</td>
<td>5.45 x 10^5</td>
</tr>
<tr>
<td>SH</td>
<td>9.89</td>
<td>2.942</td>
<td>1.44</td>
<td>18.46</td>
<td>0.869</td>
<td>1.25 x 10^5</td>
</tr>
<tr>
<td><strong>Desorption 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS</td>
<td>7.71</td>
<td>9.526</td>
<td>1.54</td>
<td>13.39</td>
<td>0.756</td>
<td>1.66 x 10^5</td>
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<tr>
<td>HH</td>
<td>6.21</td>
<td>22.156</td>
<td>1.76</td>
<td>12.10</td>
<td>0.718</td>
<td>2.04 x 10^5</td>
</tr>
<tr>
<td>SS</td>
<td>6.29</td>
<td>16.509</td>
<td>2.11</td>
<td>14.59</td>
<td>0.733</td>
<td>1.92 x 10^5</td>
</tr>
<tr>
<td>SH</td>
<td>7.81</td>
<td>6.717</td>
<td>1.73</td>
<td>16.12</td>
<td>0.816</td>
<td>1.94 x 10^5</td>
</tr>
</tbody>
</table>

4.4 Dimensional Changes

The dimensional change, DC, was calculated based on the oven-dry dimension using the following equation:

\[
DC_r = \left( \frac{t_M - t_{od}}{t_{od}} \right) \times 100\% \\
DC_r = \left( \frac{r_M - r_{od}}{r_{od}} \right) \times 100\% \tag{14}
\]
Figure 10: Average cluster size as a function of moisture content for (a) hemlock sapwood, (b) hemlock heartwood, (c) spruce sapwood and (d) spruce heartwood. Symbols (•) is for desorption 1 isotherm, (•) is for adsorption isotherm and (°) is for desorption 2 isotherm.
where \( t_M \) and \( r_M \) are the tangential and radial dimensions at moisture content \( M \), and \( t_{od} \) and \( r_{od} \) are the oven-dry tangential and radial dimensions. The dimension changes calculations are expressed in percent.

A plot of the dimensional changes versus moisture content is shown in Figure 11. The upper and lower data points represent the tangential and radial dimensional changes, respectively, and they include the three sorption isotherms: initial desorption, adsorption and secondary desorption. The error bars are one sample standard deviation of the average.

The radial change is less than the tangential change. In all cases, the desorption 1 dimensional changes are generally higher than the other sorption conditions. A regression curve was generated for all data by fitting them to a five-degree polynomial curve with zero-intercept using PROC REG in SAS. The solid curve in Figure 11 represents the fit from the regression. The \( r^2 \) values for all of the regressions were above 0.999.

The general trend found is that the desorption dimensional changes are higher compared to the adsorption one. However, the regression curves, developed for all data, fall within all of the error bars. The full dimensional changes were calculated, oven-dry basis, from green and oven-dry measurements for each species, these are presented in Table 8.

### Table 8: Dimensional changes from green to oven-dry conditions for radial and tangential directions.

<table>
<thead>
<tr>
<th></th>
<th>Tangential</th>
<th>St Dev</th>
<th>Radial</th>
<th>St Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS</td>
<td>9.63</td>
<td>0.18</td>
<td>6.05</td>
<td>0.21</td>
</tr>
<tr>
<td>HH</td>
<td>8.80</td>
<td>0.21</td>
<td>5.46</td>
<td>0.37</td>
</tr>
<tr>
<td>SS</td>
<td>9.21</td>
<td>0.46</td>
<td>6.04</td>
<td>0.41</td>
</tr>
<tr>
<td>SH</td>
<td>9.62</td>
<td>0.35</td>
<td>5.80</td>
<td>0.34</td>
</tr>
</tbody>
</table>
Figure 11: Tangential (T) and radial (R) dimensional changes as a function of moisture content for (a) hemlock sapwood, (b) hemlock heartwood, (c) spruce sapwood and (d) spruce heartwood. Symbols (★★) is for desorption isotherm, (★) is for adsorption isotherm and (∗) is for desorption 2 isotherm.
4.5 Discussion

In this section, a discussion about the results is presented. It is important to keep in mind the sorption isotherm process. During the desorption process, the water molecules are leaving the wood-water system and during the adsorption process, the reverse is the case. Although the data contained in the thesis are based on equilibrium conditions, the point at which the equilibrium is obtained is based on either the desorption or the adsorption processes. It should also be noted that the sorption process for this study is based on water vapour, i.e., the wood was not soaked in liquid water to attain the moisture content.

4.5.1 Sorption Models

The four sorption models in the analysis were all developed with certain assumptions. The BET, Dent and L-L theories were based on the multilayer concept whereas the H-H model was based on the solution concept. Moreover, each model have different parameters that were characteristic to its theory. For instance, the L-L theory gives water "layering" for both primary and secondary sorption sites. However, generally each model was based on a "picture" or description of the sorption process.

H-H and Dent model

As mentioned above, the H-H and Dent models give the same predicted $M_E$ for the same relative humidity. Also, the unimolecular moisture contents, and both $b_d$ and $k_d$ coefficients
are the same. In the Dent model, the term $b_2$ describes a relationship between the secondary sorbed molecules to that of the external condensed liquid, and the $k_d$ term in the H-H model describes an equilibrium between the dissolved water and the hydrate. If it can be assumed that the external condensed liquid (Dent model) is the same as the hydrate water (H-H model), as well as the dissolved water be the secondary sorbed molecules, then the two terms would be the same.

The term $k_h$ is related to the dissolved water and the external vapour pressure and the $b_1$ term is related to the primary molecules compared to the external condensed liquid in saturated vapour. Therefore, the two terms should be related to each other. In fact, the ratio of the terms $b_1 / k_h$ is between 0.87 to 0.95.

*Le-Ly model*

The uniqueness of this theory is that it is based on a multilayering concept as assumed by the BET model, but considers different proportions of the sorption area to be the primary or the secondary sites. The basic difference between this model and the BET model is the assumption about the area occupied by the adsorbed molecules. The BET model assumes that the area $S_i$ is covered by unimolecular layers, whereas the L-L model assumes that $S_i$ is the area occupied by the $i$th layer of adsorbed molecule. This gives the indication that the adsorption in a substance may occur at various sites with each site having different number of adsorbed molecules. Le (personal communication, 1993) indicates that the substance consists of only two types of adsorption sites and also the uncertainties involved in the determination of $\alpha$ and $p$, the physical interpretation derived from the fitting the equation may only be used as
complementary to other methods of studying the adsorption behaviour.

As can be seen in Table 7, the adsorption isotherm has a relatively lower proportion of sites designated as secondary, \(1-\alpha\), compared to the desorption isotherm. Also, the number of water molecules on the secondary sites is larger than the desorption isotherm. There is a considerable difference between the desorption 1 and desorption 2 isotherms.

There is a difference between the adsorption and desorption 2 isotherms. The fraction of primary sites is higher for the adsorption isotherm and the number of "layers" is generally the same. However, the number of layers on the secondary sites is higher for the adsorption isotherm.

4.5.2 Adsorption to Desorption Ratio

The adsorption to desorption ratio (A/D) is used to determine the amount of hysteresis that is present in hygroscopic materials. It is obtained by dividing the \(M_E\) for the adsorption isotherm by \(M_E\) for desorption 2 isotherm at the same relative humidities. Figure 12 contains the A/D ratios for hemlock (lower pair of curves) and for spruce (upper pair of curves). The curves were calculated from the Dent model. The A/D ratio changes quickly from the low relative humidities and appears to be asymptotic to about 0.9 at higher relative humidities. This value is the upper limit for wood, which ranges between 0.8 to 0.9 (Skaar, 1972). The average value for hemlock and spruce species, and both sapwood and heartwood regions are presented in Table 9. There is not very much difference between the A/D ratios of heartwood and sapwood regions of the hemlock.
Figure 12: Adsorption to desorption 2 ratio for hemlock (lower set of curves) and spruce (upper set of curves) as a function of relative humidity, calculated from the Dent model. The solid curve represents heartwood and the dashed curve represents sapwood.
Table 9: Average adsorption to desorption ratios for hemlock sapwood (HS), hemlock heartwood (HH), spruce sapwood (SS) and spruce heartwood (SH).

<table>
<thead>
<tr>
<th></th>
<th>0% &lt; H &lt; 90%</th>
<th>20% &lt; H &lt; 90%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A/D</td>
<td>St Dev</td>
</tr>
<tr>
<td>HS</td>
<td>0.799</td>
<td>0.172</td>
</tr>
<tr>
<td>HH</td>
<td>0.742</td>
<td>0.191</td>
</tr>
<tr>
<td>SS</td>
<td>0.840</td>
<td>0.136</td>
</tr>
<tr>
<td>SH</td>
<td>0.836</td>
<td>0.078</td>
</tr>
</tbody>
</table>

Based on the ranges from the average values and the standard deviations, there are no significant differences between spruce and hemlock, and between sapwood and heartwood regions.

4.5.3 Fibre Saturation Point

The fibre saturation point has been defined as the moisture content at which the cell-wall material is fully saturated but the lumen is empty of liquid water (Tiemann, 1906). Siau (1984) presents an argument that the fibre saturation point should be redefined as the moisture content which corresponds to abrupt changes in physical properties, such as electrical, mechanical strength and shrinkage properties. This implies that the fibre saturation point is based on the physical nature of wood rather than the adsorption process. However, it should be pointed out that the influence of the physical properties is based on the water interaction with the cell-wall material. The response of the wood with the water can be tested from a macroscopic experiment, but that experiment can only infer what is happening at the molecular level, such as determining the point of full saturation for the cell-wall material. The sorption
isotherm is a direct measure of the wood's response to the environment and the models used to describe it should be used to calculate the full saturation of the cell-wall material.

Based on Tiemann's definition, the wood cell wall is fully saturated at 100% relative humidity. Therefore, $M_F$ can be theoretically calculated with a sorption model. The $M_F$ for hemlock and spruce have been calculated using the Dent isotherm model and are presented in Table 10. The Dent model was used because setting $h$ equal to 1 in either the L-L or BET models causes a division by zero. The $M_F$ for the desorption 1 isotherm is not valid because the green samples were desorbing water and therefore the definition of the fibre saturation point may not hold. However, the oven-dried samples have been prepared in environments of high humidity and with diffusion of water vapour into the cell wall only; there was no liquid water present.

As shown in Table 10, the heartwood regions of both hemlock and spruce have a lower $M_F$ compared to the sapwood regions. Since the extractives in hemlock are not hygroscopic (Stamm, 1964), the difference in the $M_F$ cannot be attributed to the extractives. It is not known if the extractives in the spruce are hygroscopic, this difference between them may or may not be caused by the presence of extractives.

Table 10: Calculated fibre saturation points from the Dent sorption isotherm model.

<table>
<thead>
<tr>
<th></th>
<th>Desorption 1</th>
<th>Adsorption</th>
<th>Desorption 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS</td>
<td>33.7</td>
<td>26.0</td>
<td>28.6</td>
</tr>
<tr>
<td>HH</td>
<td>30.6</td>
<td>24.7</td>
<td>26.3</td>
</tr>
<tr>
<td>SS</td>
<td>34.2</td>
<td>27.2</td>
<td>30.1</td>
</tr>
<tr>
<td>SH</td>
<td>30.8</td>
<td>24.4</td>
<td>26.0</td>
</tr>
</tbody>
</table>
4.5.4 Critical Moisture Contents

In Chapter 2, it was discussed that the isotherm can be divided into three regions. Region I corresponded to the relative humidity range from 0% to 30%, Region II ranged from 30% to 55% and Region III were the higher humidities. Hartley and Avramidis (1993) presented a discussion about these regions in more detail and based it on the Zimm-Lundberg water cluster analysis. They refined the regions' transition points, for a temperature of 25°C, to be 47% relative humidity (Region I to Region II) and 94% relative humidity (Region II to Region III). These critical points correspond to moisture contents of 8% and 21%, respectively. Although Hartley and Avramidis based their analysis on published data (Kelsey, 1957) of sorption isotherms of klinki pine, these two points have also occurred throughout this research for spruce and hemlock. The critical points may have occurred at different points on the sorption isotherm, however, they were present in the sorption data.

There are three important or critical moisture contents on the adsorption isotherm and two critical moisture contents on the desorption isotherm. The common moisture contents on both isotherms are the water cluster and fibre saturation points. On the adsorption isotherm, a third point is the unimolecular point.

*Unimolecular moisture content*

The concept of the unimolecular layer forming has been used for understanding of the adsorption process, whereas its meaning is unclear for the desorption process. This moisture content is the point at which the sorption sites have the first layer of water molecules during
the sorption process. From the analysis of the adsorption isotherm data with the models, the unimolecular moisture content varied, however, this layer occurs at a moisture content of 5 to 6%.

*Water cluster moisture content*

The second critical point described above is the point where clustering of water molecules begin and is denoted as the water cluster moisture content (Hartley and Avramidis, 1993). None of the sorption theories explicitly determines this moisture content, however, the Zimm-Lundberg can give this point directly. This point does vary depending on the sorption process. It is approximately 15% M for adsorption and approximately 20% and 25% for the desorption 2 and desorption 1 isotherms, respectively.

Considering Figure 10, according to Hartley and Avramidis (1993), up to water cluster moisture content, the water molecules were attracted to the sorption sites at random. Near 20% moisture content, the newly adsorbed molecules have a tendency to randomly attach to existing bridges of water molecules. Beyond 20%, the clusters become larger and may have an average cluster size greater than 10.

*Fibre saturation point*

The third critical point in the isotherm is the fibre saturation point. All of the models can provide the theoretical $M_F$, however, the true point is not known. For example, the Dent model gives the $M_F$ of hemlock heartwood between 24.7% and 26.3%. However, during the
preparation of the NMR samples, the highest moisture content for a desorption specimen was 28.2%, see Chapter 5. This is higher than the predicted $M_F$. Therefore, the true fibre saturation point can be only described as a transition.

4.6 Concluding Remarks

The data from the sorption experiments were fitted to four models: BET, Dent, Hailwood-Horrobin, and Le-Ly. It was found that the BET model did not converge, while both Dent and H-H models resulted in the same predicted equilibrium moisture contents. The L-L theory fit the data well. As expected, the hysteresis was present for both hemlock and spruce species and for both regions of the wood, sapwood and heartwood. The adsorption to desorption ratio was not found to be significantly different between spruce and hemlock and between the regions of heartwood and sapwood.

From the analysis of the adsorption data, three moisture levels were discussed in terms of their significance to the sorption process: unimolecular, water cluster and the fibre saturation point. Although the unimolecular moisture content was present in the models, it is not clear if it should be present for the desorption process, as shown in the Zimm-Lundberg water cluster analysis.
Chapter 5

NMR: Analysis and Discussion

The NMR data collected for analysis were from two experiments, namely, the free induction decay (FID) and the Carr-Purcell-Meiboom-Gill. Each set of data was analysed differently. The details of the pulse sequences used are outlined in Appendix B.

5.1 Variability of Wood in NMR Experiments

There were two preliminary experiments designed to determine if the variability of the wood has an influence on the results from the NMR experiments. During an experiment, the specimens that are inside the glass tubes are typically placed inside the probe, which is between the magnetic poles, in the longitudinal direction. However, the orientation of the growth rings is usually random. Since there has been no published work on whether there are differences between specimens taken from one growth ring (tangentially) or through several growth rings (radially) for $^1$H-NMR, one FID experiment was done with one specimen, orienting the growth rings either in the radial or tangential directions to the magnetic field. Another experiment used the Set 1 specimens to determine the heartwood and sapwood variability.

A spruce sapwood specimen was chosen from Set 1 to determine the variability between radial and tangential orientations and the FID experiment, which is outlined below, was used. In the first case, the specimen was placed with the growth rings parallel with the field whereas in the second case, the same specimen was used with the growth rings orientated
perpendicular to the field. It was found that the calculated NMR moisture contents (calculations are detailed below) were different by 1%, namely, the radial was 13.15% whereas the tangential was 14.10%. The second moment was $4.85 \times 10^9 \, s^{-2}$ for radial and $4.82 \times 10^9 \, s^{-2}$ for tangential orientations. The difference between the second moments is within the experimental error of the NMR equipment, which was about 5%.

The specimens from Set 1 were used in a FID experiment to determine the radial and tangential variation within several growth rings. The second moments from these experiments are presented in Figure 13, (a) for hemlock and (b) for spruce as a function of moisture content, determined by NMR. As can be seen, there is a lot of scatter within the heartwood and the sapwood group for both the hemlock and the spruce species. However, this is within the experimental error for the NMR spectrometer.

Therefore, based on these two preliminary experiments, it was concluded that there was no large influence from directional orientation of the sample within the magnetic field and from the wood variation among several growth rings.

5.2 Free Induction Decay Analysis

It is known that the FID curve consists of two components, namely, the wood and the water (Riggin et al., 1978; Hartley et al., 1993). Figure 14 shows a typical decay curve from a FID experiment. The fast decaying portion of the curve is the wood relaxation superimposed on the slower decaying portion of the water component. The solid lines in Figure 14 represent the fitting of the wood component using a moment expansion equation and of the water component using a single exponential equation.
Figure 13: Second moments for (a) hemlock and (b) spruce, heartwood and sapwood regions from Set 1 as a function of $M_{\text{NMR}}$. Symbols (•) is for heartwood, (○) is for sapwood and (△) is for cross-growth rings.
Figure 14: Decomposition of the free induction decay curve for hemlock sapwood, desorption 2 isotherm, moisture content $M_{SNR} = 14.3\%$. Insert is the wood component with the solid line representing the fit to the moment expansion equation.
The FID experiment was mainly used to obtain information about the wood component and to determine the sample's moisture content. Second moments were determined in order to provide an indication about the "rigidity" of the material. This NMR parameter was determined from the wood component of the FID curve.

5.2.1 Moisture Content Determination

The moisture content of the sample was calculated by knowing the signal intensity of the wood and the water at time, $t = 0$. Since the spectrometer had a dead time of approximately 10 $\mu$s and that no data could be collected until after this time, it was necessary to determine the zero-time intercept from the decay curve. This was done by using a moment expansion equation for the wood component and a one-exponential model for the water component.

The regression of the wood component of the FID curve was fitted to a moment expansion equation (Abragam, 1961):

$$S(t) = (S_{\text{total}}(0) - S_{\text{water}}(0)) \left( 1 - \frac{M_2}{2!} t^2 + \frac{M_4}{4!} t^4 - \frac{M_6}{6!} t^6 + \ldots \right) + S_{\text{water}}(0)$$

(15)

where, $M_2$, $M_4$ and $M_6$ are the second, fourth and sixth moments of the lineshape. $S(t)$ is the signal intensity at time $= t$, $S_{\text{total}}(0)$ and $S_{\text{water}}(0)$ are the total and water signal intensity at $t = 0$, respectively. $(S_{\text{total}}(0) - S_{\text{water}}(0))$ is the total wood signal at $t = 0$. The water component was fitted to the following one-exponential equation:
\[ S(t) = S_{\text{water}}(0) e^{-\frac{t}{T_D}}. \] (16)

The moisture content, which is determined by the FID experiment, is denoted as \( \text{M}_{\text{NMR}} \). It was calculated by using the following equation (Hartley, 1986; Menon et al., 1987; Araujo, 1993):

\[ \text{M}_{\text{NMR}} = \left( \frac{S_{\text{water}}(0)}{S_{\text{water}}(0) - S_{\text{wood}}(0)} \right) \times 100 \%, \] (17)

where \( S_{\text{water}}(0) \) and \( S_{\text{wood}}(0) \) are the zero-time intercept signal intensities for the water and for the wood components, respectively. RSD is the relative spin density and it is the ratio of the wood proton spin density to the water proton spin density. The proton spin density of the water (or the wood) is proportional to the signal intensity of the water (or the wood) divided by its mass. The RSD value is necessary to calculate the \( \text{M}_{\text{NMR}} \). Since the RSD may be species dependent, the RSD value had to be determined before the moisture content could be calculated. Since the oven dry weights of the samples are known in this research, a comparison between the moisture content, oven dry basis, \( M_{\text{od}} \), and signal intensities can be used to determine the RSD, and then used to calculate \( \text{M}_{\text{NMR}} \).

To illustrate how the RSD was determined, consider the FID experiment of hemlock sapwood set, prepared for the desorption 2 isotherm. Once the zero-time intercepts were determined from the computer program, the ratio \( S_{\text{water}}(0) / (S_{\text{water}}(0) - S_{\text{wood}}(0)) \) was plotted as a function of \( M_{\text{od}} \) in Figure 15. The solid line in Figure 15 represents a 1:1 relationship between \( \text{M}_{\text{NMR}} \) and \( M_{\text{od}} \). The ratio calculated above is higher than the 1:1 relationship. A
Figure 15: Plot of moisture contents determined by NMR and by oven dry basis for hemlock sapwood, desorption 2 set. The crosses represent the ratio of the signal intensities of water to wood and the solid circles represent the calculations from Equation (17).
simple linear regression between this ratio and \( M_{od} \) was done. A zero intercept was used since it was expected that \( M_{NMR} \) would be zero when \( M_{od} \) was zero. For this example, the regression equation was:

\[
M_{od} = 0.620 \left( \frac{S_{water}(0)}{S_{water}(0) - S_{wood}(0)} \right) \cdot 100\%.
\]  

(18)

The standard error for 0.620 was 0.007. Once this value was determined, it was used for the RSD value in Equation (17). As shown in Figure 15, \( M_{NMR} \) values are quite close to the 1:1 relationship. The procedure described above was used to determine the \( M_{NMR} \) for the rest of the specimens.

Table 11 summarizes the RSD values calculated for most of the set of samples. Since all of the desorption 1 sets were prepared from green wood, and the oven dry weights were not known, the RSD values could not be calculated. The average RSD values were used to determine the \( M_{NMR} \) for the desorption 1 samples.

The values in Table 11 are reasonable compared to published RSD values for other wood species. For example, Araujo et al. (1994) used 0.56 for white spruce which was obtained from Fengel and Wegener (1984). Hartley et al. (1994) determined the RSD for aspen to be 0.53 from NMR measurements of known masses of dry wood and water. Hartley et al. (1994) also determined the RSD to be 0.58 from stoichiometric calculations. From knowing the RSD value, \( M_{NMR} \) can be calculated from a FID experiment.
Table 11: Relative spin densities for hemlock and spruce, sapwood and heartwood species.

<table>
<thead>
<tr>
<th></th>
<th>Adsorption</th>
<th>St Dev</th>
<th>Desorption 2</th>
<th>St Dev</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS</td>
<td>0.611</td>
<td>0.012</td>
<td>0.620</td>
<td>0.007</td>
<td>0.616</td>
</tr>
<tr>
<td>HH</td>
<td>0.531</td>
<td>0.007</td>
<td>0.542</td>
<td>0.008</td>
<td>0.537</td>
</tr>
<tr>
<td>SS</td>
<td>0.691</td>
<td>0.018</td>
<td>0.666</td>
<td>0.017</td>
<td>0.679</td>
</tr>
<tr>
<td>SH</td>
<td>0.405</td>
<td>0.010</td>
<td>0.436</td>
<td>0.009</td>
<td>0.421</td>
</tr>
</tbody>
</table>

5.2.2 Second Moments

The second moments were calculated from the computer program MOMEXP written by the author. The source codes for this program and for another program RAW2FILE are included in Appendix D. The program used the data files created from RAW2FILE and then fitted the wood portion to the moment expansion equation. The number of points used from the wood component decay curve was between 22 and 25. The $M_2$ values are plotted in Figure 16 for hemlock (a) sapwood and (b) heartwood, and for spruce (c) sapwood and (d) heartwood regions. The sorption processes are also included in the graphs.

The wood cell-wall material is known to be a rigid polymeric structure and the resulting NMR spectra is dominated by dipolar interactions between neighbouring protons. This broad spectra is typically characterized by the the second moment. The second moment is proportional to $r_{ij}^{-6}$, given by the following expression:

$$M_2 = \frac{3}{4} \gamma^4 h^2 I (I + 1) \sum_j \frac{(1 - 3 \cos^2 \theta_j)}{r_{ij}^6}$$

(19)
Figure 16: Second moments for hemlock ((a), sapwood and (b) heartwood) and spruce ((c) sapwood and (d) heartwood) as a function of moisture content (NMR) for the isotherms: (•) is for desorption 1 isotherm, (*) is for adsorption isotherm and (°) is for desorption 2 isotherm.
where $r_{ij}$ is the distance between two neighbouring proton-proton pairs in a rigid structure, $\theta_{ij}$ is the angle between these proton pairs (i and j) and the applied magnetic field, $I$ is the nuclear spin quantum number, $h$ is Planck’s constant divided by $2\pi$, and $\gamma$ is the scalar quantity called a gyromagnetic ratio. As the wood gains molecular motion, the spectra changes, and this change is indicated by the change in second moments. Also, it is assumed that the water molecules undergo isotropic motion, consequently, the second moment is zero. Therefore, considering the cell-wall material, the lower $M_2$ at higher moisture contents indicate that the wood structure is "looser" at these higher moisture contents compared to lower moisture contents.

**Hemlock**

Generally, the $M_2$ values for hemlock decrease at higher moisture contents. Also, there is no clear difference among the two desorptions and adsorption processes. The second moment decreases from about $5.1 \times 10^9$ s$^{-2}$ at low $M_{\text{NMR}}$ to $4.5 \times 10^9$ s$^{-2}$ for heartwood and to $4.35 \times 10^9$ s$^{-2}$ for sapwood at higher $M_{\text{NMR}}$.

**Spruce**

Generally, the second moment for spruce varies inversely proportion to NMR moisture contents. Also, there is a lot of variation of the second moment depending on the sorption process. The desorption 1 data (•) appear not to be as moisture content dependent as the other sorption conditions. A comparison of the range of second moments from 0% to the fibre
saturation point between the spruce and hemlock, shows that the range is higher for spruce than for hemlock.

The adsorption and desorption 2 isotherms for the spruce sapwood region decreases from about $5.0 \times 10^9$ s$^{-2}$ at low $M_{\text{NMR}}$ to about $4.1 \times 10^9$ s$^{-2}$ near the $M_p$. The second moment for the spruce heartwood decreases from about $4.3 \times 10^9$ s$^{-2}$ at low $M_{\text{NMR}}$ to about $3.5 \times 10^9$ s$^{-2}$ near $M_p$. The desorption 1 isotherm is considerably lower than the other isotherms in the sapwood, but covers the same range in both sapwood and heartwood regions: approximately $4 \times 10^9$ s$^{-2}$ at low moisture contents to approximately $3.4 \times 10^9$ s$^{-2}$ near the $M_p$.

5.3 CPMG Analysis

The decay curve from the CPMG experiment was analysed by non-linear regression using SAS on the University's mainframe computer. An example of the source code is included in Appendix E. The data were fitted to one-exponential, two-exponential and three-exponential models. It was found that the two-exponential model followed the data much better than the one-exponential and, in most of cases, the three-exponential failed to converge. An illustration is presented in Figure 17, where the solid curve is the one-exponential model and the dashed curve through the data points is the two-exponential model. Based on this result, the following two-exponential model was used:

$$S(t) = S_1(0) e^{-t/T_1} + S_2(0) e^{-t/T_2},$$

(20)
where $S_1(0)$ and $S_2(0)$ are the zero-time intercepts for the components. The two components from the two-exponential model are referred to as short ($T_{2(1)} \sim 0.5$ ms) and long ($T_{2(2)} > 5$ ms). The $T_2$'s are presented in Figures 18 and 19 for hemlock and spruce, respectively. Also, all data from the samples prepared for the three different sorption isotherms are presented in the same figures.

The long component (a, i and b, i) decreases at higher moisture contents for all sample sets. There is considerable amount of scatter in all of the graphs, but it is most noticeable with the hemlock. For hemlock, this component is approximately 25 ms at low moisture contents and decreases to about 10 ms for sapwood and 15 ms for heartwood near $M_F$. The trend is clearer in the spruce, where the long component decreases from 25 ms at low moisture content to about 16 ms near the fibre saturation point. Above 5% moisture content, the short component (a, ii and b, ii) is higher at higher moisture contents for all species. Also, in all cases, the $T_2$ values appear to be the same above 20% moisture content at 0.5 - 0.7 ms.

5.4 Discussion

5.4.1 Second Moments and Dimensional Changes

Araujo et al. (1994) found that the second moment decreased as a function of moisture content for lodgepole pine ($Pinus contorta$ Dougl. var. latifolia Engelm.) heartwood. In that work, they found a pronounced transition between 8% to 13% moisture content, where there was a decrease in $M_2$ of approximately 15% through the transition, from about 5.6 to $4.9 \times 10^9$ s$^{-2}$. As shown in Figure 16, the majority of the second moments decreased as the moisture content
Figure 17: CPMG decay curve for hemlock sapwood, desorption 2 isotherm, $M = 14.3\%$. The solid curve is the one-exponential model and the dashed curve is the two-exponential model.
Figure 18: Hemlock CPMG decomposition for (a) sapwood and (b) heartwood, (i) long and (ii) short components: (•) is for desorption 1 isotherm, (◦) is for adsorption isotherm and (♦) is for desorption 2 isotherm.
Figure 19: Spruce CPMG decomposition for (a) sapwood and (b) heartwood, (i) long and (ii) short components: (•) is for desorption 1 isotherm, (♦) is for adsorption isotherm and (○) is for desorption 2 isotherm.
increased with no transition present for either hemlock or spruce.

The second moments are consistent in that there is no difference based on the sorption process for the hemlock. However, this consistency is not present for the spruce. The desorption 1 (•) is the same for both sapwood and heartwood regions of spruce. A probable explanation for this difference between the sapwood and heartwood regions, could be based on the extractives and/or on the sorption condition which was achieved. Since no conclusive explanation can be developed without chemical analysis and extractive content determination on the wood specimens, a plausible discussion as to the difference in spruce is presented below.

During the sorption experiments, all of the specimens were prepared in the same manner. All specimens were green for the desorption 1 isotherm and then oven dried. It may be speculated that during the desorption process, and subsequent drying, some extractive material may have been removed and influence the second moment of the cell-wall material. Stamm (1964) reports that western hemlock does not have a high content in either water-insoluble or water-soluble extractives, and that the extracted wood has slightly lower adsorption equilibrium moisture contents as compared to unextracted wood. According to Mantanis et al. (1994), the removal of extractives in sitka spruce does change the swelling properties. In both of the work cited above, Stamm (1964) and Mantanis et al. (1994), it is not known whether the specimens were only sapwood, heartwood or a mixture of both wood regions. However, since the dimensional changes of sitka spruce in this study did not change based on the sorption process (Figure 11, Chapter 4), it may be concluded that the oven drying of the wood did not remove any appreciable amount of extractives that would influence the cell-wall property.
Consider the following explanation for the differences in second moments in the spruce that may occur based on drying. When the wood is losing water from a green condition, the wood begins to shrink. This indicates the sorption sites which are losing water begin to bind with other unoccupied sites. Since the second moments in this study were found to increase as the moisture was removed, it lends support to this notion. The remaining water is removed in the oven drying process and the binding of unoccupied sites continues. Therefore, after drying, the second moment would be higher for low moisture contents on the adsorption isotherm. As the wood adsorbs moisture, the structure "loosens", indicated by the decreasing second moments (Araujo et al., 1994). During the adsorption process, the sorption sites attract water molecules, swelling the cell-wall material, opening more sites. All of the sorption sites that were present during the desorption 1 process may not be present during the adsorption process (Skaar, 1988). At the $M_F$, most, if not all of the sorptions will have clusters of water molecules and the swelling would be at a maximum. During the desorption process, water molecules will leave the wood and the wood will begin to shrink. It is expected that the same sites that were opened up during adsorption will be involved in the desorption process. As well, it is expected that the cell-wall material should behave the same in reverse process as in the adsorption process.

The scenario outlined above may be true for the hemlock and for the spruce sapwood specimens, however, the second moments for the desorption 2 process for the spruce heartwood were found to be lower than the second moments for the desorption 1 process. This indicates that upon reaching the $M_F$, the cell-wall material "loosens" to a condition which was more flexible than the same species in the green condition.

It was shown in Figure 11, Chapter 4, that the changes in the tangential and the
radial dimensions were proportionally related to the moisture content, and that there was no apparent sorption-condition dependence on the amount of dimensional change. This appears to be characteristic with most of the second moment data as well, except for spruce. Since the second moment provides an indication of the "loosening" of the wood structure which in turn provides an indication of the swelling/shrinkage of the wood, a comparison between these experimental results may be made.

Consider the second moment data for the hemlock heartwood set in Figure 16 (b). The upper limit of the second moment at a low moisture contents, after oven drying, is approximately $5.1 \times 10^9 \text{s}^2$. Near the $M_p$, the $M_2$ is about $4.45 \times 10^9 \text{s}^2$. The percentage difference between these values is 12.7%, based on oven dry. Furthermore, the total dimensional change for the same hemlock heartwood set from the sorption isotherm experiments can be approximated by adding the tangential and the radial percentage changes from Table 8. The calculated value is then 14.3%. This number compares well with the 12.7% difference in second moments over the same moisture contents, keeping in mind that the numbers in Table 8 are from green to oven dry conditions.

This comparison holds for the other sets of wood species as well. From Table 8, the total dimensional change for hemlock sapwood set is 15.7% and from the second moments, it is about 16.5%. The spruce sapwood and heartwood sets have dimensional changes from Table 8 of 15.25% and 15.42%, respectively. The second moment change for the same sets are approximately 16.3% and 21%, respectively, based on the adsorption process.
5.4.2 Critical Moisture Contents

In Chapter 4, it was discussed that the adsorption isotherm contains three critical moisture content levels corresponding to the unimolecular layer, the water cluster and fibre saturation points. From the analysis of the NMR data, there appears to be changes in the $T_2$ at these same points as well. Consider the short $T_2$ component, Figures 18 and 19. As the moisture content increases, the $T_2$ decreases rapidly until about 5% and increases slowly until $M_{\text{NMR}}$ is approximately 20%, and then asymptotes until the $M_F$ is reached. It is interesting to note that the sorption condition which is used to attain the equilibrium moisture content does not show any general trends, for example, desorption $T_2$ are not larger than the adsorption $T_2$.

The calculated fibre saturation points in Table 10, Chapter 4, are generally lower than the actual NMR specimens prepared in near 100% relative humidity conditions. This can be explained by the extrapolation of the Dent sorption model to 100% relative humidity.

5.4.3 Water Components Below the Fibre Saturation Point

The decomposition of the CPMG curve was been done with a two-exponential model. As mentioned in the Discussion of the Literature section of Chapter 2, this may imply that the $T_2$'s were from the different types of bound water in the wood, for example, primary and secondary, or were a result of the water molecules residing in different wood compartments. The discussion was based on few published data points and this current research details the water below the fibre saturation point more thoroughly.

There has been no published data on the exchange in the wood-water system to date
and, therefore, one cannot assume that the $T_2$'s in this study were of two types of bound water. The component fractions were multiplied with the moisture content to determine which component was most influenced by the moisture content; this is presented in Figure 20 for both hemlock and spruce, with no differentiation between sorption conditions. From Figure 20, it is clear that the component most affected by the moisture content is the short component. This suggests that the decay curve may come from two distinct compartments. If this is the case, then there may be no exchange present.

However, there has not been any experiments which has detailed possible exchange between two types of water, as may be suggested by decomposition of the curve into two components. As mentioned in Chapter 2, the exchange rate between the bulk and the bound water was about 30 s$^{-1}$ in muscle tissue (Sobel et al., 1986). Therefore, it is difficult to determine if the two-component decay curve was from water residing in two different areas of the wood or if the cluster concept can be applied. Since it is not clear whether the two $T_2$ components were based on compartments, a weighted average of the $T_2$'s was calculated. These results are presented in Figure 21.

Considering Figure 21, a general trend is present for both spruce and hemlock, however, the average $T_2$ for the hemlock appears to sorption dependent. Generally, the initial average $T_2$ at low moisture contents, less than about 7%, decreases rapidly from about 18 ms to about 3.5 ms. At moisture contents greater than 7%, the average $T_2$ becomes asymptotic to a value of about 1.5 ms near the fibre saturation point. This trend does not appear to be sorption dependent for spruce, however, it is sorption dependent for the sapwood and
Figure 20: Component fractions from CPMG decay curve for hemlock ((a), sapwood and (b), heartwood) and spruce ((c), sapwood and (d), heartwood) in terms of moisture content plotted as a function of NMR moisture content. Solid and hollow circles represent the long and short components, respectively.
Figure 21: Weighted average $T_2$'s from the two-component decomposition of the decay curve plotted as function of NMR moisture content for hemlock ((a), sapwood and (b) heartwood) and spruce ((c), sapwood and (d), heartwood): (•) is for desorption 1 isotherm, (●) is for adsorption isotherm and (○) is for desorption 2 isotherm.
heartwood of the hemlock. For the hemlock sapwood specimens, the average $T_2$ for the two desorption are the same, where it decreases from about 3 ms near 5% moisture content to about 1 ms near the fibre saturation point. The adsorption data is lower than the two desorption data sets and the average $T_2$ increases slightly as the moisture content increases. For the hemlock heartwood specimens, the desorption 1 data is about the same as the adsorption data set and the desorption 2 data set is higher than the desorption 2 data.

From the NMR results presented here, and until a thorough investigation is conducted to answer the question of compartments and/or exchange, no conclusions can be made with respect to any difference of desorption or adsorption waters.

Preliminary experiments with the hemlock sapwood, desorption 2, set have shown that the exchange rate between the wood and the water components was about 3 ms which is of the order of the $T_2$ for the water component. It also has been shown that it was constant above a moisture content of 15%.

5.4.4 NMR Parameters and Sorption Process

It is apparent from the NMR experiments that there cannot be any conclusive correlation between the results and the parameters in the sorption isotherm models. However, the critical moisture contents found in the sorption isotherm analysis are consistent with general trends in the NMR results, for example, the unimolecular layer.
5.5 Concluding Remarks

In the hygroscopic range, the second moments for hemlock and for spruce decrease as a function of increasing moisture content. There was no sorption-dependent difference of the second moment for the hemlock, whereas, the spruce's second moment did differ with sorption conditions. The relative spin densities were determined for the hemlock and the spruce, for the sapwood and heartwood regions of the wood. There were two T$_2$'s obtained for the water in the cell-wall material and they were determined on a two-exponential decay model. However, without further experiments to determine any exchange or compartmentation of the water, it was not conducive to make any strong conclusions about the water below the fibre saturation point, based on the NMR results.
Chapter 6
Summary and Recommendations

Throughout the thesis, the research design and results were presented in such a manner as to consider the sorption process. Therefore, when one is discussing the nature of water in wood, it is necessary to mention if the equilibrium condition was achieved by adsorption or desorption, and if the wood was dried before conditioning. From the macroscopic experiments, such as the sorption isotherm, the equilibrium moisture contents are higher for the desorption conditions compared to the moisture contents for the adsorption conditions, at the same relative humidity. The NMR FID experiments for the second moments of the hemlock showed that there was not any noticeable difference between the sorption conditions, however, spruce did have sorption-dependent second moment.

6.1 Sorption Isotherm Experiments

One of the major goals of this research was to introduce the water cluster theory for understanding the nature of water in the wood in the hygroscopic range. If the cluster theory, as presented in Chapter 2, is used to compare the sorption isotherm models, then it can be concluded that they are equivalent. The analysis of the sorption isotherm data with the H-H and Dent models revealed that they are similar, noting that they were developed with different assumptions, namely, multilayering (Dent) and solution (H-H) concepts. However, the L-L model is a combination of both multilayering and solution concepts. The L-L model was based on two-site sorption surface and included a possible description of number of water molecules.
on the primary and secondary sites. One drawback of the L-L model was the lack of consideration of the different binding energies that may be involved for each sorption site. If there was a two-site sorption surface, then the binding term in the model, C, should reflect the fact that the binding energy sites may be different.

Other general conclusion from the thesis research are summarized below:

1. The equilibrium moisture contents were generally lower for the heartwood regions compared to the sapwood regions for the same species. However, the equilibrium moisture contents of both species were found to be the same.

2. There are indications that the adsorption isotherm have three critical moisture content points: the unimolecular layer, the water cluster and the fibre saturation point. Also, that there may be only the latter two points existed for both the desorption 1 and desorption 2 isotherms.

3. The characteristic adsorption to desorption hysteresis was present for both species (hemlock and spruce) and for both regions (heartwood and sapwood). The spruce had a higher A/D ratio compared to the hemlock: hemlock sapwood: 0.830; hemlock heartwood: 0.823; spruce sapwood: 0.898; and, spruce heartwood: 0.869.

4. Tangential and radial changes were calculated based on oven dry measurements during the sorption experiments, and it was found that they were independent of the sorption process.
6.2 NMR Experiments

There were two NMR experiments performed for the same wood specimens, using the FID and CPMG pulse sequences. From the FID curve, the moisture contents of the specimens were determined, after calculating the relative spin densities.

General conclusions for the research are:

1. Average relative spin densities, which were needed to calculate the moisture contents from NMR experiments, were calculated from known moisture contents and were:
   - hemlock sapwood: 0.616; hemlock heartwood: 0.537; spruce sapwood: 0.679; and spruce heartwood: 0.421.

2. The second moments were higher at low equilibrium moisture contents as compared to those near the fibre saturation point. The condition as to how the equilibrium moisture content was attained did not influence the second moments for hemlock. The second moments for spruce were different based on the sorption condition.

3. The water decay curve from the CPMG experiments were decomposed into two components using a two-exponential equation. The long component, \( T_2 > 5 \) ms, was higher at low \( M_{\text{NMR}} \) than compared to those near the \( M_F \), whereas the short component, \( T_2 < 2 \) ms, was lower at low \( M_{\text{NMR}} \) than compared those near the \( M_F \).

6.3 Recommendations

The following list contains some general recommendations for further theoretical and experimental study which resulted from this thesis research:
1. To further develop the L-L sorption isotherm model considering a two-site sorption surface concept, with two binding energies. The refinement of the model would begin with using the same assumptions as used by Le and Ly (1992) to develop their model and would include two energy terms which would represent two sorption sites.

2. To develop a desorption model based on the cluster theory. It has been suggested in Chapter 2 that during the desorption process, the water leaves the cell-wall material in small clusters units instead of individual molecules. Therefore, the use of the current adsorption isotherms to describe the desorption process is questionable. The development of the model would have to consider assumptions of the sorption surface and of the water behaviour, for example, the small cluster units.

3. To investigate the exchange mechanism in the wood-water system. As mentioned in Chapter 5, there have been experiments done using the same hemlock sapwood, desorption 2, set as used with this research. The experiments involved a pulse sequence which isolated the wood and the water and determined if there is any exchange between them. For a complete picture of the wood-water system, this experiment should include all of the wood sets; this study is currently underway.

4. To determine the nature of the decomposition of the CPMG decay curve for the water in wood-water systems. This work would need to consider either discrete or continuous exponential decomposition of the decay. The study could be based on more theoretical analysis of the current data from this research or from new experiments, including isolating compartment that may or may not contribute to the two-component decay.
Literature Cited


Hartley, I.D.; Kamke,F.A.; Peemoeller, H. 1994: Absolute moisture content determination of aspen wood below the fiber saturation point using pulsed NMR. (Submitted to Holzforschung).


### Symbols and Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>ADS</td>
<td>adsorption</td>
</tr>
<tr>
<td>B</td>
<td>magnetic induction, Ampere meter$^{-1}$</td>
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<td>BET</td>
<td>Brunauer, Emmett and Teller isotherm sorption model</td>
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<td>$b_1$</td>
<td>parameter in Dent isotherm sorption model</td>
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<tr>
<td>$b_2$</td>
<td>parameter in Dent isotherm sorption model</td>
</tr>
<tr>
<td>c</td>
<td>molar concentration</td>
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<td>C</td>
<td>parameter in BET, H-H and L-L isotherm sorption models</td>
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<td>H-H</td>
<td>Hailwood and Horrobin isotherm sorption model</td>
</tr>
<tr>
<td>HH</td>
<td>hemlock heartwood</td>
</tr>
<tr>
<td>HS</td>
<td>hemlock sapwood</td>
</tr>
<tr>
<td>i</td>
<td>unit vector, cartesian coordinate system, x-direction</td>
</tr>
<tr>
<td>j</td>
<td>unit vector, cartesian coordinate system, y-direction</td>
</tr>
<tr>
<td>k</td>
<td>unit vector, cartesian coordinate system, z-direction</td>
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\( k_d \) parameter in H-H sorption isotherm model

\( k_h \) parameter in H-H sorption isotherm model

L-L Le and Ly isotherm sorption model

\( M \) moisture content (%)

\( M \) macroscopic magnetization (Ampere meter\(^{-1}\))

\( M_E \) equilibrium moisture content (%)

\( M_F \) fibre saturation point (%)

\( M_o \) moisture content corresponding to the unimolecular layer (%)

MSR mean square residual error

\( m \) moisture content fraction, \( m = M/100 \)

\( m_o \) moisture content fraction corresponding to unimolecular layer, \( m_o = M_o/100 \)

NMR nuclear magnetic resonance

\( n \) parameter in BET and L-L isotherm sorption model, number

\( p \) partial vapour pressure (pascal), parameter in L-L isotherm sorption model

\( p_o \) saturated vapor pressure (pascal)

\( r \) radial

\( r_0 \) distance vector (meter)

\( S \) area (meter\(^2\)), signal intensity (arbitrary units)

SH spruce heartwood

SS spruce sapwood

\( T \) temperature (degrees Kelvin)

\( T_1 \) spin-lattice relaxation time (second)

\( T_2 \) spin-spin relaxation time (second)
t  \( \text{tangential} \)

\( v \)  \( \text{volume (meter}^3\) \)

\( v_m \)  \( \text{volume corresponding to the unimolecular layer (meter}^3\) \)

**Greek Letters**

\( \alpha \)  \( \text{parameter in H-H and L-L isotherm sorption model} \)

\( \beta \)  \( \text{parameter in H-H isotherm sorption model} \)

\( \gamma \)  \( \text{gyromagnetic ratio (meter second}^{-1}\text{Ampere}^1) \)

\( \lambda \)  \( \text{thermal wavelength (meter)} \)

\( \mu \)  \( \text{chemical potential} \)

\( \rho \)  \( \text{density (kilogram meter}^3) \)

\( \phi \)  \( \text{volume fraction} \)

\( \theta \)  \( \text{angle (radians)} \)

\( \omega \)  \( \text{frequency (radians)} \)

**Subscripts**

bw  \( \text{bound water} \)

E  \( \text{at equilibrium} \)

F  \( \text{at fibre saturation point} \)

M  \( \text{at moisture content} \)

NMR  \( \text{nmr basis} \)

o.d.  \( \text{oven dry basis} \)

wet  \( \text{wet basis} \)
Appendix A

Development of the Cluster Theory

The basis for the cluster theory is the use of statistical thermodynamics which is a "tool for studying physical properties of matter in bulk on the basis of dynamical behaviour of its microscopic constituents" (Pathria, 1988). It is not based on the physical nature of the system, such as for the case of wood, ray volumes or lumen sizes. This mathematical approach studies the connection between microscopic and macroscopic systems in thermodynamic contact (Patheria, 1988). As outlined in Chapter 2 and Skaar (1988), most of the currently-used wood sorption isotherm models are based on non-interacting ideal systems between the water molecules. Statistical thermodynamics provides a method to consider interacting systems, as in the case of water molecules interacting with each other to form clusters.

A molecule in close proximity with others will have a form of interaction, either attractive or repulsive. The force is described as a potential energy, may be of the Lennard-Jones type, and is denoted as $u(r_{ij})$, where $r_{ij}$ is the distance vector between two molecules. In terms of water molecules, the interaction may cause them to form clusters; a three dimensional structure of one, two, three, ..., $n$ molecules in a unit. Clusters containing $n$ molecules will have a different mathematical description (integral), compared to clusters of size $n + 1$. For simpler clusters of size $n = 1$ and $n = 2$ the integrals over volume element ($d\tau$) are (Patheria, 1988):

102
\[ b_1 = \frac{1}{V} \left[ 1 \right] \]
\[ = \frac{1}{V} \int d\tau_1 \]
\[ = 1 \]  

(A-1)

\[ b_2 = \frac{1}{2\lambda^3 V} \left[ 1 - 2 \right] = \frac{1}{2\lambda^3 V} \int \int \left[ \exp(-\beta u(r_{12}) - 1) \right] d\tau_1 d\tau_2 \]
\[ = \frac{2\pi}{\lambda^3} \int_0^\infty \left[ \exp(-\beta u(r_{12})) - 1 \right] r^2 dr. \]  

(A-2)

In Eqs. (A-1) and (A-2), \( \lambda \) is the mean thermal wavelength (m) of the molecule and is given by:

\[ \lambda = \frac{h}{2\pi} \left( \frac{2\pi \beta}{m} \right). \]  

(A-3)

where \( h \) is Planck’s constant \((6.626 \times 10^{-23} \text{ J K}^{-1})\), \( m \) is the mass of the molecule (kg) and \( \beta = 1/(kT) \), \( k \) is Boltzmann’s constant \((1.39 \times 10^{-24} \text{ J s})\) and \( T \) is absolute temperature (K).

The integral, \( b_n \), is known as the cluster integral and is dimensionless. As the size of the cluster increases, there are various ways the molecules can interact and the cluster integral must account for these possibilities. As an example, for \( n = 3 \), there are four ways for the three molecules to interact.

The fact that a value or a result could be achieved for the cluster integral \( b_2 \) implies there is clustering of molecules. Zimm (1953) has related \( b_2 \) to volume fractions and relative humidities of a system. Zimm based the discussion on McMillan and Mayer (1945) and
McMillan and Mayer (1945) relate the pressure change to the cluster integral through pressure differences between two states fugacity (essentially the activity of water vapour molecules), $z$ and $z + y$:

$$ P_{z+y} - P_z = \frac{1}{\beta} \sum_{a>0} b_a(z) \prod_s \left[ \frac{Y_s}{Y_s(z)} \right]^{n_s}, \quad (A-4) $$

where $Y_s = z_s/\rho_s(z)$, $s$ is the species type, $z_s$ is the fugacity of the species (water vapour), $\rho_s$ is the density of the species, $y_s$ is the difference in the fugacities between $z$ and $z + y$.

According to Zimm (1953), the cluster integral is:

$$ b_z = 2G_{11} = \beta \frac{z_1^2}{c_1^2} \frac{\partial^2 P}{\partial z_1^2}, \quad (A-5) $$

where $c_1$ is the molar concentration of component 1 and is equal to the ratio of the volume fraction ($\phi_1$) to the partial molar fraction ($v_1$), and $z_1$ is the fugacity of component 1. $G_{11}$ is the notation used by Starkweather (1963, 1975) and others. The fugacity is the activity of the particular component and is related to the chemical potential. From Kirkwood and Buff (1951), an equivalent expression was derived:

$$ c_1 G_{11} = \frac{1}{\beta} \left( \frac{\partial c_1}{\partial P} \right)_{T, \mu_2} - 1. \quad (A-6) $$
Expanding the partial differential term in Eq. (A-6) as a function of pressure and chemical potential ($\mu$) using the Gibbs-Duhem equation and also assuming the compressibility is negligible for the system, the cluster integral becomes (Zimm, 1953):

\[
\mathbf{cG}_{11} = \frac{\phi^2}{\beta} \left( \frac{\partial \ln \phi_1}{\partial \mu_1} \right)_{P,T} + 1.
\]

(A-7)

Given $\mu_1 = (1/\beta) \ln (h_1)$, where $h_1$ is the relative vapour pressure and $\phi_1 = (1 - \phi_2)$, Equation (A-7) becomes:

\[
\mathbf{c}_i \mathbf{G}_{11} = (1 - \phi_1) \left( \frac{\partial \ln \phi_1}{\partial \ln h_1} \right) - 1.
\]

(A-8)

This equation gives the average number of water molecules in the neighbourhood of given water molecules which is in excess of the mean concentration of water. Therefore, the number of water molecules in a cluster (the average cluster size) is given by:

\[
\mathbf{c}_i \mathbf{G}_{11} + 1 = (1 - \phi_1) \left( \frac{\partial \ln \phi_1}{\partial \ln h_1} \right).
\]

(A-9)

If the term $\mathbf{c}_i \mathbf{G}_{11} + 1 < 0$ or $\mathbf{c}_i \mathbf{G}_{11} < -1$, the molecules are adsorbed randomly and exclude their own volume to other molecules. If the term is greater than -1 but less than 1, this
indicates that the number of clusters in the system does not change, and newly adsorbed water molecules attach to existing sorption sites which have water molecules present. Therefore, bridging between two uncorrelated water molecules occurs. If the term is greater than 1, this gives the average size of the cluster in the system.

In order to use Equation (A-9), the volume fraction of water (component 1), the volume fraction of water in the swollen cell-wall was calculated using the following equation (Spalt, 1957):

\[
\phi_1 = \frac{m_{\text{wet}} \rho_o}{\rho_{\text{bw}}} \left( \frac{1}{1 + \frac{m_{\text{wet}} \rho_o}{\rho_{\text{bw}}}} \right),
\]

(A-10)

where \(m_{\text{wet}}\) is the wet basis moisture content fraction (M/100), \(\rho_o\) is the density of the cell wall substance taken as 1.46 g cm\(^{-3}\) (Siau, 1984) and \(\rho_{\text{bw}}\) is the density of adsorbed water (g cm\(^{-3}\)) at the corresponding dry basis moisture content and was obtained graphically from Siau (1984). In this analysis, it was assumed that the bound water density was equal for both adsorption and desorption conditions. In order to use Equation (A-10), sorption data must first be transformed from a dry basis moisture content fraction to a wet basis moisture content fraction. Once the volume fraction was calculated, it was necessary to determine the derivative term for Equation (A-9). This was done by plotting \(\ln \phi_1\) versus \(\ln h_i\) and taking the derivative of the curve.

The above procedure was used to determine the average cluster size from the hemlock and spruce sorption isotherm data.
"Magnetic resonance is a phenomenon found in magnetic systems that possess both magnetic moments and angular momentum." (Slichter, 1989). The spectrum is obtained when the measurement is in tune with the natural frequency of the magnetic system, i.e., is in resonance. The natural frequency that is being tuned is the frequency of the gyroscopic precession of the magnetic moment when an external magnetic field is applied. A typical magnetic system to observe is that of the hydrogen nuclei or protons.

B.1 Nuclear Phenomenon

Protons have a nuclear magnetic moment, \( \mu \) (A m), and an angular momentum, \( J \), which are related by the following equation:

\[
\mu = \gamma J = \gamma I \hbar, \tag{B-1}
\]

where \( \gamma \) (m s\(^{-1}\) A\(^{-1}\)) is a scalar quantity called a gyromagnetic ratio unique to different nuclei, \( \hbar \) (1.0545 x 10\(^{-34}\) J s) is Planck’s constant \( (\hbar = 6.626 \times 10^{-34} \text{ J s}) \) divided by \( 2\pi \) and \( I \) is the nuclear spin quantum number. Applying a magnetic field in the z-direction, \( B = \text{B}_0 k \) (Wb m\(^2\)), to such a nucleus, the Hamiltonian, \( \kappa \), which describes the interaction energy, becomes:
The allowed energies of this Hamiltonian are $2I + 1$ and are multiples of $\gamma h B_0$ given by:

$$E_m = -\gamma h B_0 m$$  \hspace{1cm} (B-3)

where $m = I, I - 1, I - 2, \ldots, -I$ and $E_m$ are in units of $J$. In the case of protons, $I = 1/2$, and, therefore, the number of energy levels is 2. These levels are equally spaced, having an energy separation between adjacent levels equal to $\gamma h B_0$, see Figure B-1.

In NMR the transitions between adjacent levels are produced by a radio frequency alternating magnetic field $B_1 \cos(\omega_0 t)$ applied perpendicular to $B_0$. From the conservation of energy, the allowed transitions between the adjacent levels are:

$$\Delta E = h \omega_0 = \gamma h B_0.$$  \hspace{1cm} (B-4)

giving $\omega_0 = \gamma B_0$ (rad $s^{-1}$). This is the frequency at which the magnetic moment precesses about $B_0$ and it is known as the Larmor frequency.
Figure B-1: Energy levels of spin 1/2 nuclei.
In a magnetic field, nuclear moments will be preferentially aligned parallel to the field, which corresponds to the number of nuclei in \(+1/2\) state \((N+)\) being larger than those in \(-1/2\) state \((N-)\). There is energy given up from the spins to the lattice caused by the induced transitions. Therefore, a net energy (heat) flow will continue until thermal equilibrium is reached, corresponding to the temperature of the lattice, namely:

\[
\frac{N^+}{N^-} = \exp \left( -\frac{\Delta E}{k T} \right) = \exp \left( -\frac{\gamma h B_0}{k T} \right). \tag{B-5}
\]

Since there is a thermal equilibrium condition, there will be a net macroscopic magnetization, \(M\) (\(A\ m^{-1}\)), which is parallel to \(B_0\).

In NMR, it is interesting to study the motion of \(M\), however, this vector is subjected to a torque in an applied field and will precess about the \(z\)-axis, much like a top spinning on its tip. Since it is precessing, this motion can be described with its own coordinate system, \(x', y',\) and \(z'\), which is called a rotating frame. In the rotating frame, \(M\) would appear stationary.

These two frames of reference, namely the laboratory frame and the rotating frame are related mathematically. In a laboratory frame of reference, the equation of motion of the macroscopic magnetization \(M\) is given by the cross product with \(B\) as:

\[
\frac{d M}{d t} = \gamma (M \times B). \tag{B-6}
\]
To transform to a rotating frame, one introduces the following equation which relates the laboratory frame to the rotating frame:

\[
\frac{dM}{dt}_{(lab)} = \frac{\partial M}{\partial t}_{(rot)} + (\omega \times M). \tag{B-7}
\]

Thus Equation (B-6) becomes,

\[
\frac{dM}{dt}_{(rot)} = \gamma (M \times B - \omega \times M). \tag{B-8}
\]

Rearranging,

\[
\frac{dM}{dt}_{(rot)} = \gamma M \times (B + \frac{\omega}{\gamma}), \tag{B-9}
\]

or

\[
\frac{dM}{dt}_{(rot)} = \gamma M \times B_{\text{eff}}. \tag{B-10}
\]

where the effective field, \(B_{\text{eff}} = B + \omega/\gamma\) and \(\omega = \omega_0\) is the Larmor frequency. This equation
is similar to the equation of motion in the laboratory frame of reference except $B$ is replaced by $B_{\text{eff}}$. Consequently, the magnetization, $M$, precesses about $B_{\text{eff}}$ in a rotating frame. For the case $B = B_{0}k$, such that $-\gamma B_{0}k = \omega$, the effective field is zero. In other words, $M$ is invariant with time in this rotating frame.

In the presence of an alternating magnetic field of amplitude $B_{1}$ and frequency $\omega$, the following perturbing term must be added to the Hamiltonian,

$$\mathcal{H}_{p} = -\gamma \hbar B_{1} I_{x} \cos(\omega t) \quad \text{(B-11)}$$

If the frequency of $B_{1}$ is near the Larmor frequency, transitions from lower energy levels to higher levels occur. This means that $M$ is tipped away from $B_{0}$ and will have components $M_{x'i}$, $M_{y'j}$ and $M_{z'k}$. At the Larmor frequency, the effective field is $B_{1}$, say along the $x'$-direction. Viewed in a rotating frame, the magnetic moment will precess about the $y'$-axis. If this field was applied for a short pulse duration, $t_{p}$, $M$ would precess through an angle $\theta = \gamma B_{1} t_{p}$. If $\theta = \pi$ by choosing $t_{p}$ and $B_{1}$ appropriately, the moment would be inverted; this is referred to as a "180 degree pulse." A "90 degree pulse" is attained if $\theta = \pi/2$ and then the magnetization immediately following the pulse would be along the $y'$-axis.
B.2 Relaxation Processes

The torque felt by $M$ causes it to precess about $B_o$. However, such precession does not continue indefinitely because of the relaxation effects. Taking the relaxation process into account, Bloch (1946) developed the following equations of motion, known as the Bloch equations, for $M_x$, $M_y$ and $M_z$:

$$\frac{dM_x}{dt} = \gamma (M_y B_o - M_z B_1 \sin(\omega t)) - \frac{M_x}{T_2}, \quad (B-12)$$

$$\frac{dM_y}{dt} = \gamma (M_z B_1 \cos(\omega t) - M_x B_o) - \frac{M_y}{T_2}, \quad (B-13)$$

and

$$\frac{dM_z}{dt} = \gamma (M_x B_1 \sin(\omega t) + M_y B_1 \cos(\omega t)) - \frac{(M_x - M_o)}{T_1}. \quad (B-14)$$

These equations demonstrate that the $M_x$ and $M_y$ components will decay to an equilibrium value of zero in a relaxation time $T_2$, called the spin-spin or transverse relaxation time. Similarly, the relaxation time $T_1$ describes the spin-lattice relaxation time, or the time for $M_z$ to return to an equilibrium value of $M_o$. 
B.3 Dipole - Dipole Interaction

The Hamiltonian for two weakly interacting dipoles in a magnetic field is:

\[ H = H_Z + H_D, \]  

where \( H_Z \) is the unperturbed Hamiltonian and \( H_D \) is the dipolar Hamiltonian. Consider two spins \( \mu_i = \gamma_i \hbar I_i \) and \( \mu_j = \gamma_j \hbar I_j \), joined by the distance vector \( \mathbf{r}_{ij} \). The dipolar Hamiltonian expressed in polar spherical coordinates and in terms of raising operator \( (I^+ = I_{xi} - iI_{yi}) \) and lowering operator \( (I^- = I_{xi} + iI_{yi}) \), is:

\[ H_D = \sum_{ijk} \gamma_i \gamma_j \hbar^2 (A + B + C + D + E + F), \]  

where

\[ A = I_{xi} I_{yi} F_{ij}^0, \]
\[ B = (-1/4)(I^+_i I^-_j + I^-_i I^+_j) F_{ij}^{00}, \]
\[ C = (-3/2)(I^+_i I^-_j + I^-_i I^+_j) F_{ij}^1, \]
\[ D = (-3/2)(I^+_i I^-_j + I^-_i I^+_j) F_{ij}^{11}, \]
\[ E = (-3/4)(I^+_i I^-_j) F_{ij}^2, \]
\[ F = (-3/4)(I^+_i I^-_j) F_{ij}^{22}. \]
and

\[ F_\theta^2 = 1 - 3 \cos^2(\theta_i t) \ r_i^{-3}, \]

\[ F_\theta^1 = \sin(\theta_i t) \ \cos(\theta_i t) \ \exp(-i\phi_i t) \ r_i^{-3}. \]

(B-18)

\[ F_\theta^0 = \sin(\theta_i t) \ \exp(-2i\phi_i t) \ r_i^{-3}. \]

The asterisk (*) denotes complex conjugate and \( \theta_i \) and \( \phi_i \) are the polar and azimuthal angles of \( r_i \), respectively.

Equation (B-16) is arranged in such a manner to describe \( \Delta m \). Terms A and B produce energy conserving transitions, \( \Delta m = 0 \). Term A corresponds to the change in z-component of the magnetic field by z-components of the neighboring magnetic moments. Terms C and D (\( \Delta m = \pm 1 \)) and E and F (\( \Delta m = \pm 2 \)) involve the transition between the energy levels of the spin system and transitions within the lattice. Dipolar interaction is the primary interaction among the spins in the wood water systems.

**B.4 Transverse Relaxations: Measurement Techniques**

The major work for this research was to obtain the transverse relaxation time, \( T_2 \), as a function of moisture content. This section will concentrate on the techniques and pulse sequences used to obtain the \( T_2 \) values.

In pulsed NMR, \( M \) is rotated to the \( x'-y' \) axis by means of a r.f. pulse. Once \( M \) is aligned on the \( y' \) axis, for example, the nuclear spins making up \( M \) will begin to dephase in
the x'-y' plane. By dephasing, the spins will "fan out" symmetrically about the y' axis in the x'-y' plane because of local magnetic interactions (dipole-dipole). As this "fanning out" continues, the magnitude of $M$ will tend to zero at a rate corresponding to a particular time constant, $T_2$.

Described below are pulsed NMR experimental techniques used to obtain the transverse relaxation time, $T_2$. Each pulse experiment provides different information of the wood-water system: the free induction decay (FID) experiment provided the moisture content and second moment for the wood and the CPMG experiment gives the $T_2$'s for the water.

**B.4.1 Free Induction Decay Pulse Sequence**

After an application of a 90 degree pulse along the x' axis (denoted at $90^\circ_x$) to a group of spins, the magnetization is rotated to the y' axis and, over a period of time, the spins will become out of phase with each other resulting in a free induction decay (FID). Since the field homogeneity of the magnetic is not very good, a series of 180 pulses are applied to complete the decay.

**B.4.2 Carr-Purcell-Meiboom-Gill (CPMG) Sequence**

If the field $B_o$ is entirely homogeneous, the signal would decay with the time constant $T_2$. However, since there are inhomogeneities in the magnetic field, often $T_2^*$ is measured which is defined as:
\[
\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma \Delta \frac{B_0}{2},
\]

(B-19)

where \(\gamma B_0/2\) is the contribution to the dephasing from the inhomogeneity of the magnetic field.

To overcome this problem, a spin-echo method has been introduced: \(90^\circ - \tau - 180^\circ\) pulse sequence. The \(90^\circ\) pulse causes \(M\) to rotate to the \(y'\) axis and the nuclei begin to precess (fan out) at a different frequency because of the inhomogeneity of the field; some faster and some slower than \(\omega_0\). After a time \(\tau\), a \(180^\circ\) pulse is applied causing the partially dephased magnetization components in the \(x' - y'\) plane to rotate about the \(x'\) axis by \(180^\circ\). After \(2\tau\), the spins rephase along the negative \(y'\) axis, producing a spin-echo. The change in echo amplitude with \(\tau\), contains the \(T_2\) information. In systems where the diffusion rate of the nuclei is sufficiently great to carry a nucleus into a different part of the inhomogeneous magnetic field during the time of the measurement, the above spin-echo approach yields \(T_2\) values that are shorter than the true system \(T_2\). This difficulty can be overcome by using the Carr-Purcell technique.

The Carr-Purcell pulse sequence is described as \(90^\circ_x - \tau - 180^\circ_x - 2\tau - (180^\circ_x - 2\tau)_n\), where \(n\) is the number of repetitions of the \(180^\circ\) pulses to complete the pulse sequence. The series of events is essentially the same as the spin-echo method, except that the complete \(T_2\) envelop (obtained from the echo maxima) is acquired by means of the application of a single pulse sequence.

A difficulty that commonly arises when the Carr-Purcell sequence is used, is that if the
lengths of the 180° pulses are not precisely 180°, cumulative error results. As a consequence of this, the measured $T_2$ is too short. This is effectively eliminated through the use of the Meiboom-Gill modified Carr-Purcell (CPMG) sequence. Here, the 180° pulses are 90° phase shifted relative to the initial 90° pulse.
Appendix C

SAS Source Code for Sorption Isotherm Analysis

The program source for performing non-linear regression with SAS for hemlock heartwood sorption isotherm data.

*---------------------------------------------------------------;
* SAS SOURCE CODE
* PROJECT ASSIGNMENT: Sorption Study
* INPUT FILE: as below
* RUN IN UNIXG BY: sas sorphh.sas
*---------------------------------------------------------------;
FILENAME file1 'hemheartdes1.dat';
FILENAME file2 'hemheartads.dat';
FILENAME file3 'hemheartdes2.dat';
DATA data1;
  infile file1;
  input h mfrac;
DATA data2;
  infile file2;
  input h mfrac;
DATA data3;
  infile file3;
  input h mfrac;
*---------------------------------------------------------------;
TITLE1 ' ********** SORPTION STUDY - NONLINEAR EQUATIONS ********** '; SKIP 5;
OPTIONS ls=75 ps=60 center nodate;
*---------------------------------------------------------------;
* MODELLING HH THEORY
*---------------------------------------------------------------;
PROC NLIN DATA=data1 BEST=5;
  title2 'Hailwood-Horrobin Model (Desorption I Isotherm)';
  parms mo=0.05 to 0.10 by 0.005
      kh=3 to 15 by 1
      kd=0.3 to 1 by 0.1;
  model mfrac=((mo*kh*kd*h)/(1+kh*kd*h)+(mo*kd*h)/(1-kd*h));
  output out=hhout1 p=yhat1 r=resh1;
PROC PRINT DATA=hhout1;
*---------------------------------------------------------------;
PROC NLIN DATA=data2 BEST=5;
title2 'Hailwood-Horrobin Model (Adsorption Isotherm)';
  parm mo=0.05 to 0.10 by 0.005
    kh=3 to 15 by 1
    kd=0.3 to 1 by 0.1;
  model mfrac=({mo*kh*kd*h}/(1+kh*kd*h)+({mo*kd*h}/(1-kd*h)));
  output out=hhout2 p=hyathh2 r=reshh2;
PROC PRINT DATA=hhout2;
*----------------------------------------------------------;
PROC NLIN DATA=data3 BEST=5;
  title2 'Hailwood-Horrobin Model (Desorption II Isotherm)';
  parm mo=0.05 to 0.1 by 0.005
    kh=3 to 15 by 1
    kd=0.3 to 1 by 0.1;
  model mfrac=({mo*kh*kd*h}/(1+kh*kd*h)+({mo*kd*h}/(1-kd*h)));
  output out=hhout3 p=hyathh3 r=reshh3;
PROC PRINT DATA=hhout3;
*----------------------------------------------------------END--------;
Appendix D

Fortran Program Source Code for RAW2FILE and MOMEXP

In this section, the source codes for two FORTRAN computer programs, which were used to analyze the FID data, are presented. The first program RAW2FILE was used to decompose the raw FID data from the spectrometer into two files, representing the wood and the water components. The second program, MOMEXP, used both of the files created by RAW2FILE and calculated the second moment for the wood component.

RAW2FILE was based on a program written in FORTRAN on the U.B.C. Department of Physics NMR group's microVAX II minicomputer from Digital Equipment Corporation, running VMS operating system, Version 5.4. MOMEXP was completely written by the author based on non-linear algorithms in Numerical Recipes, Second Edition. These programs were written with Watcom's Watfor 77 FORTRAN compiler and executed on a 80486-33MHz IBM Personal Computer running MS-DOS 5.0. RAW2FILE was also compiled on VAX FORTRAN 77 and was executed on the VAX to be used in several batch files.

As discussed in Chapter 5, the moisture content was determined by the zero-time intercepts from the regression analysis of the FID data. The output from MOMEXP gives the estimates for the intercept of the wood and of the water components, as well as the moment expansion equation terms, M₂, M₄ and M₆. However, the intercept of the wood component is sensitive to the zero-time intercept for the water component. Therefore, the programs determines the fit for the water component first using a one-exponential model, and then uses the zero-time intercept while fitting the wood component to the data.
**D.1 RAW2FILE Source Code**

```plaintext
PROGRAM RAW2FILE
C COMPILED ON PC/DOS Watfor77 IBM486/33
C Program is based on FID_MC2 used by NMR physics UBC.
C t=0 is assumed to be midway through the 90 pulse.
C Wood signal is fitted to a+bx**2 using 10 points starting
C from max. amplitude+1. Water signal is fitted to a+bx
C regression. FID sequence contains 180 pulse to refocus
C the water signal at fixed interval. Time of 180 pulses
C is now accounted for.
C All outputs are adjusted for actual time results.
C Written by Huy Le
C Last modified 25 June 1987
C Modified, Liquid.dat output of liquid points, solid.dat for solid
C Cynthia Araujo, 1991
C Sum's are used to extrapolate water signal and are in
double precision to minimize subtraction error
C
C Correction has been edited in the 14 do loop near the end of the
C program. August 1993

IMPLICIT REAL*8(A-H, O-Z)
CHARACTER*35 FileIn,wddout,lqdout
CHARACTER*1 Yes, yorn
REAL*4 MC(4096),a(2048),b(2048),grxpts(2048),CURR
REAL*4 GRXPTB(2048),BADJ(2048)
REAL*8 SumX2, SumY, Var
REAL*8 SumX, SumXY
INTEGER RED,GREEN,YELLOW,BLUE
PARAMETER (RED=2, GREEN=3, YELLOW=4, BLUE=5)

***** CONSTANTS *****
* Default values
* Dwell=time/point; Prtrig=pretrigger; WBegin=time of initial point
* for fitting water; NEnd=points used for water; NFit=points used
* for wood; Search=time used to search for peak; Tau2=time of 1st
* 180 pulse; Tau=180 pulse interval
  Dwell = 1.e-6
  PrTrig = 1e-4
  Tau = 102e-6
  Tau2 = Tau / 2.
  NFit = 40
  Npnts = 2048
* Input formats
110 FORMAT(G20.0)
112 FORMAT(F17.5,F17.5)
```

This text describes the source code for a program named RAW2FILE, which is used for processing NMR data. The program is compiled for PC/DOS and is based on FID_MC2 used by NMR physics at UBC. It is designed to process Wood and water signals, refocusing the water signal at fixed intervals, and adjusting all outputs for actual time results. The program was last modified in 1987 and modified further in 1991. The code includes default values for various parameters and input formats for reading data.
Greetings and data input

FILE SEPARATION PROGRAM

This program converts raw ASCII data from NMR.
The data points are separated into two files: one for wood (*.wdd) and the other for water (*.lqd).
Water signal is fitted by linear regression.

What is the 90 degree pulse duration (in seconds)?
What is the 180 degree pulse duration (in seconds)?
What is the digital point to start (i.e.: 114)?

Current input parameters are:
Dwell time (seconds):
Pretrigger duration (seconds):
Number of points to be used to fit the wood FID:
Interval of 180 degree pulses (seconds):
Number of points (2048, 4096):
Would you like to change this (Y/N)?
124

260  FORMAT('Dwell time (seconds)? ')  
270  FORMAT('Pretrigger duration (seconds)? ')  
271  FORMAT('Number of points to be used to fit the wood FID? ')  
272  FORMAT('Time interval of 180 degree pulses - \( tau \) - (seconds)? ')  
273  FORMAT('Number of points for analysis (2048, 4096)?')

WRITE(6,209)

10  WRITE(6,220)
WRITE(6,209)
WRITE(6,230) Dwell
WRITE(6,240) PrTrig
WRITE(6,245) NFit
WRITE(6,248) Tau
WRITE(6,249) NPNTS
WRITE(6,250)
READ(5,130) Yes
IF (Yes .EQ. 'Y' .OR. Yes .EQ. 'y') THEN

11  WRITE (6,260)
READ (5, 110) Dwell
WRITE (6,270)
READ (5, 110) PrTrig
WRITE (6, 271)
READ (5, 140) NFit
WRITE (6, 272)
READ (5, 110) Tau
WRITE (6, 273)
READ (5,140) NPNTS

* Check for negatives
    ChkNeg=NFit*Dwell*PrTrig*Tau2*Tau*NPNTS
    IF (ChkNeg .LT. 0.0) THEN
        WRITE (6, 9001)
        GOTO 11
    END IF
    GO TO 10
END IF

* Read in data from unformatted file FileIn
*

275  FORMAT('Input filename (include disk drive and extension *.dat):
   *')
280  FORMAT('Reading data .....')
285  FORMAT('There were ',I4,' records read.')
500  FORMAT('Do you want to see the raw data (Y/*)?',A)
505  FORMAT('Do you have to determine the StartPoint (Y/*)?',A)
506  FORMAT('The following plot shows the ring-down of the system.')
507  FORMAT('Determine the StartPoint when the line is near the ')
FORMAT('zero line. Read the point off the x-axis.')
FORMAT('Press <ENTER> twice to get back to main program.')
WRITE(6,275)
READ(5,120) FileIn
OPEN(UNIT=1, FILE=FileIn, STATUS='OLD', ERR=9200)
WRITE(6,280)
READ(1,*)a(i),b(i),I = 1,NPNTS)
CLOSE(UNIT=1)
WRITE(6,209)
WRITE(6,285) NPnts
nend=npnts
DO 16 I = 1, NPnts
MC(I)=a(I)
grxpts(I)=I
16 CONTINUE
WRITE(6,209)
WRITE(6,500)
READ(5,130)YORN
IF (YORN.EQ.'Y'.OR.YORN.EQ.'y') THEN
CALL GRINIT(0)
CALL GRAPH(NPnts,grxpts,A,'Time Interval','Amplitude',FileIn)
CALL GRPLOT(NPnts,grxpts,a,green,yellow)
CALL GRCLEAR
CALL FINISHO
ELSE
WRITE (6,505)
READ (5,130)YORN
IF (YORN .EQ.'Y'.OR.YORN.EQ.'y') THEN
WRITE(6,209)
WRITE(6,507)
WRITE(6,508)
WRITE(6,509)
DO 17 1 = 105, 130
BADJ(I-104)=B(I)
GRXPTB(I-104)=I
17 CONTINUE
CALL GRINIT(0)
CALL GRAPH(25,grxptB,BADJ,'Time Interval','Amplitude',FileIn)
CALL GRPLOT(25,grxptB,BADJ,green,yellow)
CALL GRCLEAR
CALL FINISHO
ENDIF
WRITE(6,221)
READ(5,140)npeak
* Calculate base line average and correct data
  
  \[ \text{BaseAv} = 0. \]
  
  \[ \text{NBase} = \frac{\text{PrTrig}}{\text{Dwell}} \]
  
  DO 20 i = 1, NBase
  
  \[ \text{DO} \quad \text{BaseAv} = \text{BaseAv} + \text{MC}(i) \]
  
  \[ \text{BaseAv} = \frac{\text{BaseAv}}{\text{NBase}} \]
  
* Calculate Variance

\[ \text{Var} = 0. \]

DO 30 i = 1, Nbase

\[ \text{Var} = \text{Var} + (\text{MC}(i) - \text{BaseAv})^2 \]

\[ \text{Var} = \frac{\text{Var}}{\text{Nbase} - 1} \]

* Baseline Correct

DO 21 i = 1, NEnd

\[ \text{MC}(i) = \text{MC}(i) - \text{BaseAv} \]

* Output solid part of FID

* Zero is data point corresponding to \( t=0 \)

C

\[ \text{Zero} = \left( \text{Prtrig} + \frac{T90}{2.} \right) / \text{Dwell} \]

C

C Linear regression for extrapolating water signal

C \[ Y = M_0 + \text{Slope} \times t \]

C \( s = t \) (in seconds)

C \( \text{Pull1} = \) first point to be used in interpolation; middle of 2nd echo

C include 10 points around each echo

C ** COULD MODIFY TO INCLUDE EVERY 2ND ECHO **

C include only every 2nd echo to correct for 180 pulse imperfection

C \( \text{Pull1} = (\tau_2 + \tau_{180} + \tau/2. + \tau + \tau_{180}) / \text{Dwell} \)

C \( \text{PullInc} = 2. * (\tau_2 + \tau_{180}) / \text{Dwell} \)

\[ \text{Pull1} = (\tau_2 + \tau_{180} + \tau/2.) / \text{Dwell} \]

\[ \text{PullInc} = (\tau + \tau_{180}) / \text{Dwell} \]

\[ \text{SumX} = 0.0D0 \]

\[ \text{SumX2} = 0.0D0 \]

\[ \text{SumY} = 0.0D0 \]

\[ \text{SumXY} = 0.0D0 \]

* Do while not past end of data

300 FORMAT('Output filename (include disk drive and extensions)

301 FORMAT('Water (*.lqd):', a)

302 FORMAT('Wood (*.wdd):', a)

304 FORMAT('Saving..... Water filename is: ', a25)

305 FORMAT('Saving..... Wood filename is: ', a25)

9203 WRITE(6,300)

WRITE(6,301)

READ(5,120) lqdout

WRITE(6,302)

READ(5,120) wddout
WRITE(6,209)
WRITE(6,304)lq dout
OPEN(UNIT=12,FILE=lq dout,STATUS='new',IOSTAT=I0S,ERR=9202)
N=0
curr=Zero+Pull
curr=curr-6.
15 do 23 i = 1,10
   curr = curr + 1.
   IF (IFIX(curr) .gt. NEnd) then
      goto 24
   END IF
   s = (curr - Zero)*Dwell
   SumX = SumX + s
   SumX2 = SumX2 + s*s
   SumY = SumY + MC(IFIX(curr))
   SumXY = SumXY + s*MC(IFIX(curr))
   N = N + 1
   WRITE(12,*)s,MC(IFIX(curr))
23 continue
   curr = curr+PullInc-10.
   GO TO 15
24 Factor = 1./(N*SumX2-SumX*SumX)
close(unit=12)
Slope = Factor*(N*SumXY-SumX*SumY)
Int = Factor*(SumX2*SumY-SumX*SumXY)
Water = Int
WRITE(6,305)wddout
OPEN(UNIT=11,FILE=wddout,STATUS='NEW',IOSTAT=I0S,ERR=9202)
WRITE(11,199)nfit, (sqrt(var)), water
DO 14 I = NPEAK+1, NPEAK+NFIT
   WRITE(11 ,*)(I-ZERO-1)*DWELL,MC(I)
14 CONTINUE
CLOSE(UNIT=11)
WRITE(6,*)'For your information: Standard Deviation:',sqrt(Var)
WRITE(6,*)' Water signal MO: ', Water
C
310 FORMAT('Run the program again (Y/*)?',A)
WRITE(6,310)
READ(5,131)yorn
IF(yorn.EQ.'Y'.OR.yorn.EQ.'y')THEN
   GOTO 10
endif
stop
9200 Write(6,*)'ERROR: File may not exist or drive is not ready ....'
pause 'Hit <ENTER> to continue.'
GOTO 9201
9202  Write(6,*)'ERROR: Files already exist or drive is not ready ....'
pause '    Hit <ENTER> to continue.'
GOTO 9203
9999  STOP
C
C Input file error handling
C
9018  CALL IOErr(IOS, FileIn)
      GO TO 9201
   END
C
   SUBROUTINE IOErr(IOS, File)
C
C File error handling
C Routine will handle File Not Found error (29)
C and Invalid File Name error (30, 43)
C (35, 39) Error during read
C Program stops otherwise
C
CHARACTER*(*) File
CHARACTER*1 Yes
105  FORMAT(A1)
IF (IOS .EQ. 29) THEN
   PRINT *, 'Cannot find file: ', File
ELSE IF (IOS .EQ. 43 .OR. IOS .EQ. 30) THEN
   PRINT *, 'Invalid file name/insufficient privilege: ', File
ELSE IF (IOS .EQ. 35 .OR. IOS .EQ. 39) THEN
   PRINT *, 'Error during reading file'
   PRINT *, 'Possibly wrong file type'
   CALL ClosIO
ELSE IF (IOS .EQ. 38) THEN
   PRINT *, 'Error during writing to file'
   PRINT *, 'Possibly out of disk space'
ELSE
   PRINT *, 'Unrecoverable error #', IOS
   CALL ClosIO
   GO TO 9999
END IF
PRINT *, 'Would you like to quit? (Y/N)'
READ (5, 105) Yes
IF (Yes .EQ. 'Y' .OR. Yes .EQ. 'y')GO TO 9999
RETURN
C    Abort
9999  CALL ClosIO
STOP
END
C Close all opened IO units
SUBROUTINE ClosIO
COMMON /LUNITS/IRead, IWrite, IPunch, IData
CLOSE (UNIT=IRead)
CLOSE (UNIT=IWrite)
CLOSE (UNIT=IPunch)
CLOSE (UNIT=IData)
RETURN
END
D.2 MOMEXP Source Code

PROGRAM MOMEXP
C Program  MOMEXP.FOR  April 15, 1993
C Based on  FIDMC.FOR  Updated on May 19, 1993
C Written by Ian D. Hartley
C
IMPLICIT REAL*8 (A-H, O-Z)
DIMENSION  XWOOD(200),XWATER(200),YWATER(200),YWOOD(200)
DIMENSION  COVARA(25,25),ALPHAA(25,25),SIGA(200)
DIMENSION  COVARB(25,25),ALPHAB(25,25),SIGB(200)
DIMENSION  AA(40,4),BB(40,4)
DIMENSION  LISTA(4),LISTB(4),A(4),B(4)
CHARACTER*30  WDFILE,WTFILE,YORN,BIGFIL(40)
REAL*8  LO
C
70  FORMAT(2X,I2,F6.2,4x,E10.2)
71  FORMAT(2X,2E13.4)
80  FORMAT(I6,E12.4)
82  FORMAT(E13.5,E13.5)
84  FORMAT(I6)
86  FORMAT('Wood:  Constant, T2 Time (microsec): ',F6.3,2x,F6.3)
87  FORMAT('Water:  Constant, T2 Time (millisec): ',F6.3,2x,F6.3)
88  FORMAT('Wood (Enter four constants):')
89  FORMAT('Water (Enter two constants):')
90  FORMAT(a)
91  FORMAT('File name: ',A30)
92  FORMAT('Number of points: ',I5)
93  FORMAT('Initial estimates for parameters in equations (Y-intercept * and T2:)
94  FORMAT('Wood: ',F12.0,3x,E9.2,3x,E9.2,3x,E9.2)
95  FORMAT('Water: ',F12.0,3x,E9.2)
97  FORMAT('Note: First and last Y value in data set: ',F8.3,3x,F8.3)
98  FORMAT('First and last X value in data set: ',F8.3,3x,F8.3)
99  FORMAT('Change these values (Y/*)?',A)
C
999  FORMAT ('  MOMEXP.FOR')
1000  FORMAT ('This program uses the wood (*.wdd) and water (*.lqd)')
1001  FORMAT ('files produced by FID_MC2.FOR and determines the water')
1002  FORMAT ('transverse relaxation constants (T2). The MOMENTS are ')
1003  FORMAT ('calculated for the wood data and the water data are ')
1004  FORMAT ('fitted to an EXPONENTIAL model. The results are saved ')
1005  FORMAT ('in one file. Compilation Stardate: 1993.5.19')
1006  FORMAT ('  The Admiral is ready to beam aboard, Captain.')
1007  FORMAT ('  Energize, Mr. O''Brian.')
Welcome aboard!

Greetings and Introductions

Reading in WOOD and WATER data from file on disk

Input file - WOOD - (include disk drive and extension *wdd):

Input file - WATER - (include disk drive and extension *lqd):
OPEN(unit=1, file=WTFile, status='old', err=9200)
NWATER=0
READ(1,'*')XWATER(1), YWATER(1)
 DO 10 I=2,100
    READ(1,'*', END=100)XWATER(I), YWATER(I)
    NWATER=NWATER+1
10 CONTINUE
100 CLOSE(unit=1)
 WRITE(6,1010)
 WRITE(6,91)WTFile
 WRITE(6,92)NWATER
 WRITE(6,97)YWATER(1)/1000., YWATER(NWATER)/1000.
 WRITE(6,98)XWATER(1)*1000., XWATER(NWATER)*1000.
 WRITE(6,1010)
 WRITE(6,*)'Note the number of data points for wood and water to'
 WRITE(6,*)'analyse. Change these values (Y/*)?'
 READ(5,90)YORN
 IF (YORN .EQ. 'Y' .OR. YORN .EQ. 'y') THEN
    WRITE(6,1010)
    WRITE(6,*)'Number of points for wood: '
    READ(5,84)NWOOD
    WRITE(6,*)'Number of points for water: '
    READ(5,84)NWATER
 ENDIF
C
C Initial equation parameters
C
112   CHISQA=0.
   CHISQB=0.
   ALAMDA=-1.0
   ALAMDB=-1.0
   MA=4
   A(1)=YW00D(1)*1.15
   A(2)=1E10
   A(3)=1E15
   A(4)=1E19
   B(1)=YWATER(1)*1.15
   B(2)=.001
   LO=B(1)
   MB=2
 WRITE(6,93)
 DO 11 I=1, MA, 4
    WRITE(6,94)A(I), A(I+1), A(I+2), A(I+3)
7 WRITE(6,95)B(I), B(I+1)
11 CONTINUE
WRITE(6,99)
READ(5,90)YORN
IF (YORN .EQ. 'Y' .OR. YORN .EQ. 'y') THEN
  DO 12 I=1,MA,4
    WRITE(6,88)
    READ(5,*)A(I)
    READ(5,*)A(I+1)
    READ(5,*)A(I+2)
    READ(5,*)A(I+3)
  12 CONTINUE
  DO 13 I=1,MB,2
    WRITE(6,89)
    READ(5,*)B(I)
    READ(5,*)B(I+1)
  13 CONTINUE
ENDIF
DO 15 I=1, NWOOD
  SIGA(I)=SQRVAR
  XWOOD(I)=XWOOD(I)
  YWOOD(I)=YWOOD(I)
  15 CONTINUE
DO 16 I=1, NWATER
  SIGB(I)=SQRVAR
  XWATER(I)=XWATER(I)
  YWATER(I)=YWATER(I)
  16 CONTINUE
DO 20 I=1, 25
  DO 25 J=1, 25
    COVARA(I,J)=1.0
    ALPHAA(I,J)=1.0
    COVARB(I,J)=1.0
    ALPHAB(I,J)=1.0
  25 CONTINUE
  20 CONTINUE
DO 30 I=1, MA
  LISTA(I)=I
  LISTB(I)=I
  30 CONTINUE
C
C Calling subroutines and functions
C
C Water calculations using EXPONENTIAL fitting routine (FEXP)
C
XSQWT=CHISQB
113 FLAG=0
MFIT = MB
NCA = MFIT
ALAMDB = -1.0
CALL MRQMIN(XWATER, YWATER, SIGB, NWATER, B, MB, LISTB, MFIT, COVARB, *ALPHAB, NCA, CHISQB, ALAMDB, FLAG, LO)
C WRITE(6,*)'WATER: ', CHISQB
IF(ABS(CHISQB - XSQWT) GT 0.0000001*CHISQB) THEN
  XSQWT = CHISQB
GOTO 113
ENDIF
ALAMDB = 0
CALL MRQMIN(XWATER, YWATER, SIGB, NWATER, B, MB, LISTB, MFIT, COVARB, *ALPHAB, NCA, CHISQB, ALAMDB, FLAG, LO)
C WRITE(6,*)'WATER: ', CHISQB
C
C Wood calculations using MOMENTS fitting routine (FMOM)
C
XSQWD = CHISQA
114 FLAG = 1
  LO = B(I)
  MFIT = MA
  NCA = MFIT
  ALAMDA = -1.0
  CALL MRQMIN(XWOOD, YWOOD, SIGA, NWOOD, A, MA, LISTA, MFIT, COVARA, *ALPHAA, NCA, CHISQA, ALAMDA, FLAG, LO)
C WRITE(6,*)'WOOD: ', CHISQA
C PAUSE ' THROUGH MRQMIN WITH WOOD DATA..
IF(ABS(CHISQA - XSQWD) GT 0.0000001*CHISQA) THEN
  XSQWD = CHISQA
GOTO 114
ENDIF
ALAMDA = 0
CALL MRQMIN(XWOOD, YWOOD, SIGA, NWOOD, A, MA, LISTA, MFIT, COVARA, *ALPHAA, NCA, CHISQA, ALAMDA, FLAG, LO)
C
C Printing routines
C
302 FORMAT('Parameters (wood): ', 4E13.5, '.')
303 FORMAT('Parameters (water): ', 2E13.5, '.')
306 FORMAT('Run these numbers through again (Y/*) ?', A)
308 FORMAT('Results have negative numbers; ')
309 FORMAT('Please use new initial parameters..... <ENTER > ')
310 FORMAT('Save the results in files (Y/*) ?', A)
The WOOD filename was: ',A)
Run the program again with new files (Y/*)?',A)
ChiSquare Values: WOOD: ',e13.5,' WATER: ',e13.5)

CHKNG1=0
CHKNG2=0
DO 50 I = 1, MA, 4
   WRITE(6,1010)
   WRITE(6,302)A(I),A(I+1),A(I+2),A(I+3)
   WRITE(6,303)B(I),B(I+1)
   CHKNG1=A(I)*B(I)
   CHKNG2=A(I+1)*B(I+1)
50 CONTINUE
WRITE(6,325)CHISQA,CHISQB
WRITE(6,1010)
DO 51 I = 1, NCA
   DO 52 J=1, NCA
      IF (COVARA(I,J).LT.0.0) COVARA(I,J)=25.0
      IF (COVARB(I,J).LT.0.0) COVARB(I,J)=25.0
   WRITE(6,304)I,J,(COVARA(I,J))**0.5,(COVARB(I,J))**0.5
C PAUSE
52 CONTINUE
51 CONTINUE
IF (CHKNG1.LT.0.0 .OR. CHKNG2.LT.0.0) THEN
   WRITE(6,308)
   WRITE(6,309)
   PAUSE
   GOTO 113
ELSE
   WRITE(6,1010)
   WRITE(6,306)
   READ(5,90)YORN
   IF (YORN .EQ.'y' .OR. YORN .EQ. 'Y') THEN
      GOTO 113
   ENDIF
ENDIF
ENDIF
C C Saving Routines C
C WRITE(6,310)
READ(5,90)YORN
IF (YORN .EQ.'y' .OR. YORN .EQ. 'Y') THEN
WRITE(6,312)WDFILE
   CALL DATAOT(XWOOD,YWOOD,XWATER,YWATER,NWOOD,NWATER,
*A,MA,B,MB,CHISQA,CHISQB,K,BIGFIL,AA,BB)
ENDIF
WRITE(6,320)
READ(5,90)YORN
IF (YORN .EQ. 'y' .OR. YORN .EQ. 'Y') THEN
   K = K + 1
   WRITE(6,*) 'The program ran through', k-1, ' files; 40 files max!'
   GOTO 111
ENDIF
350 FORMAT(' HEY! You are about to exit the program. ')
351 FORMAT(' The filenames and parameters are saved. Do you')
352 FORMAT(' want these saved into one file (Y/*)?', A)
WRITE(6,1010)
WRITE(6,350)
WRITE(6,351)
WRITE(6,352)
READ(5,90)YORN
IF (YORN .EQ. 'Y' .OR. YORN .EQ. 'y') THEN
   CALL GLOBAL(BIGFIL, AA, BB, K, MA, MB, NWOOD, NWATER)
ENDIF
CLOSE(UNIT = 3)
WRITE(6,*) 'It has been a pleasure having you on board, Sir'
STOP
C
9200 WRITE(6,*) 'ERROR: File may exist or disk drive in not ready.'
   WRITE(6,*') Hit < ENTER > to continue.......
PAUSE
GOTO 111
END
C
SUBROUTINE
DATA OT(XWOOD, YWOOD, XWATER, YWATER, NWOOD, NWATER,
   * A, NA, B, NB, CHISQA, CHISQB, K, BIGFIL, AA, BB)
IMPLICIT REAL*8(A-H, O-Z)
REAL*4 MCISH
DIMENSION
XWOOD(NWOOD), YWOOD(NWOOD), YFITWD(200), YRSDWD(200)
DIMENSION XWATER(NWATER), YWATER(NWATER), YFITWT(200)
DIMENSION YRSDWT(200), A(NA), B(NB), AA(40,NA), BB(40,NB)
CHARACTER*14 FILEOT, YORN, BIGFIL(40)
INTEGER*2 YEAR, MONTH, DAY
400 FORMAT('Output filename (include disk drive and extension *.RES):
   *')
410 FORMAT(' So far so good (Y/*)?')
420 FORMAT(A, ',', I4, '/', I2.2, '/', I2.2, ',')', I4, I4, E12.4, E12.4, E12.4)
425 FORMAT(A, 1E11.4)
430 FORMAT(E15.4)
CALL GETDAT(YEAR, MONTH, DAY)

DO 10 I = 1, NWATER
   YFITWT(I) = 0.
   ARG = (XWATER(I)) / B(2)
   EX = EXP(-ARG)
   YFITWT(I) = B(1) * EX
   YRSDWT(I) = YWATER(I) - YFITWT(I)
10 CONTINUE

DO 20 I = 1, NWOOD
   YFITWD(I) = 0.
   YFITWD(I) = (A(1) - B(1)) * (1 - (A(2) / 2 * XWOOD(I)**2) + (A(3) / 24 * XWOOD(I)**4) - (A(4) / 720 * XWOOD(I)**6)) + B(1)
   YRSDWD(I) = YWOOD(I) - YFITWD(I)
20 CONTINUE

MCish Calculations: Does not include the relative spin densities!!!

MCish = 100 * b(1) / (a(1) - b(1))

WRITE(6, 400)
READ(5, 450) FILEOT
WRITE(6, 410)
READ(5, 450) YORN
BIGFIL(K) = FILEOT
IF (YORN.EQ.'N'.OR.YORN.EQ.'n') THEN
   WRITE(6, 460)
   GOTO 60
ENDIF
OPEN(UNIT = 2, FILE = FILEOT, STATUS = 'NEW', IOSTAT = IOS, ERR = 9210)

WRITE(2, 420) FILEOT, YEAR, MONTH, DAY, NWOOD, NWATER, CHISQA, CHISQB, MCish
WRITE(2, 430) (A(J), J = 1, NA)
WRITE(2, 430) (B(J), J = 1, NB)
WRITE(2, 440) (XWOOD(J), YWOOD(J), YFITWD(J), YRSDWD(J), J = 1, NWOOD)
WRITE(2, 440) (XWATER(J), YWATER(J), YFITWT(J), YRSDWT(J), J = 1, NWATER)
CLOSE(UNIT = 2)
DO 44 J = 1, NA
   AA(K, J) = A(J)
44 CONTINUE
DO 45 J = 1, NB
   BB(K, J) = B(J)
CONTINUE
RETURN

9210 WRITE(6,*)'ERROR: File may exist or disk drive is not ready.'
   WRITE(6,*)' Hit < ENTER > to continue ....'
PAUSE
GOTO 60
END

C
SUBROUTINE GLOBAL(BIGFIL,AA,BB,K,NA,NB,NWOOD,NWATER)
IMPLICIT REAL*8 (A-H, O-Z)
DIMENSION AA(40,NA),BB(40,NB)
CHARACTER*14 BIGFIL(30),YORN,BGFILE
INTEGER*2 YEAR, MONTH, DAY

400 FORMAT('Output filename (include disk drive and extension *.GLB):
  *')
410 FORMAT('So far so good (Y/*)?')
420 FORMAT(A,'(',I4,'/',I2.2,7',I2.2,')',3I6)
425 FORMAT(A,6E11.4)
426 FORMAT(2E12.4)
450 FORMAT(A)
460 FORMAT(')
CALL GETDAT(YEAR,MONTH,DAY)

60 WRITE(6,400)
READ(5,450)BGFILE
WRITE(6,410)
READ(5,450)YORN
IF (YORN.EQ.'N'.OR.YORN.EQ.'n')THEN
   GOTO 60
ENDIF
OPEN(UNIT=3,FILE=BGFILE,STATUS = 'NEW',IOSTAT=IOS,ERR=9220)
WRITE(3,420)BGFILE,YEAR,MONTH,DAY,K,NWOOD,NWATER
DO 35 I=1,K
   DO 36 J=1,NA-1,4
      WRITE(3,425)BIGFIL(I),AA(I,J),AA(I,J+1),AA(I,J+2),AA(I,J+3),BB(
        &I,J),BB(I,J+1)
   36 CONTINUE
35 CONTINUE
CLOSE(UNIT=3)
RETURN

9220 WRITE(6,*)'ERROR: File may exist or disk drive is not ready.'
   WRITE(6,*)' Hit < ENTER > to continue ....'
PAUSE
GOTO 60
END
SUBROUTINE GETDAT(IYEAR, IMONTH, IDAY)
INTEGER*2 IYEAR, IMONTH, IDAY
INTEGER*2 AX, BX, CX, DX, BP, DI, SI, ES, DS, FLAGS
PARAMETER (AX = 1, BX = 2, CX = 3, DX = 4, BP = 5, DI = 6, SI = 7)
PARAMETER (ES = 8, DS = 9, FLAGS = 10)
INTEGER NUM$REGS
PARAMETER (NUM$REGS = 10)
INTEGER*2 GETDATE, DOSCALL
PARAMETER (DOSCALL = 33, GETDATE = 42)
INTEGER*2 regs(NUM$REGS)
INTEGER*1 mon$day(2), week$(2)
INTEGER*2 year
INTEGER*1 month, day, week
EQUIVALENCE (regs(AX), week$)
EQUIVALENCE (regs(CX), year)
EQUIVALENCE (regs(DX), mon$day)
EQUIVALENCE (month, mon$day(2))
EQUIVALENCE (day, mon$day(1))
EQUIVALENCE (week, week$(1))
REGS(AX) = GETDATE*256
CALL INTR(DOSCALL, REGS)
IYEAR = YEAR
IMONTH = MONTH
IDAY = DAY
END

C
SUBROUTINE FGAUSS(X, A, YFIT, DYDA, NA)
IMPLICIT REAL*8 (A-H, O-Z)
DIMENSION A(NA), DYDA(NA)
YFIT = 0.
DO 11 I = 1, NA-1, 2
   ARG = X/(A(I + 1))
   EX = EXP(-1.*((ARG**2))
   FAC = 2.*A(I)*EX*ARG
   YFIT = YFIT + A(I)*EX
   DYDA(I) = EX
   DYDA(I + 1) = A(I)*EX*((X**2)/(A(I+1)**3))
11 CONTINUE
RETURN
END

C
SUBROUTINE FEXP(X, B, YFIT, DYDA, NB)
IMPLICIT REAL*8 (A-H, O-Z)
DIMENSION B(NB), DYDA(NB)
YFIT = 0.
DO 11 I = 1, NB-1, 2
   ARG = (X)/B(I + 1)
   EX = EXP(-ARG)
   FAC = B(I)*EX*ARG
   YFIT = YFIT + B(I)*EX
   DYDA(I) = EX
   DYDA(I + 1) = FAC*1./B(I + 1)
11 CONTINUE
RETURN
END

C
SUBROUTINE FMOMT(X, A, YFIT, DYDA, NA, LO)
IMPLICIT REAL*8(A-H, O-Z)
REAL*8 LO
DIMENSION A(NA), DYDA(NA)
YFIT = 0
DO 11 I = 1, NA-3, 4
   YFIT = YFIT + ((A(I)-LO)*(1-(A(I+1)/2*X**2)+A(I+2)/24*X**4)-(A(I+3)/
   &720*X**6))+LO)
   DYDA(I) = 1-(A(I+1)/2*X**2)+(A(I+2)/24*X**4)-(A(I+3)/720*X**6)
   DYDA(I + 1) = -(A(I)/2*X**2)+(LO/2*X**2)
   DYDA(I + 2) = (A(I)/24*X**4)-(LO/24*X**4)
   DYDA(I + 3) = -(A(I)/720*X**6)+(LO/720*X**6)
11 CONTINUE
RETURN
END

C
SUBROUTINE MRQMIN(X, Y, SIG, NDATA, A, MA, LISTA, MFIT,
*   COVAR, ALPHA, NCA, CHISQ, ALAMDA, FLAG, LO)
IMPLICIT REAL*8 (A-H, O-Z)
REAL*8 LO
PARAMETER (MMAX = 20)
DIMENSION X(NDATA), Y(NDATA), SIG(NDATA), A(MA), LISTA(MA),
*   COVAR(NCA, NCA), ALPHA(NCA, NCA), ATRY(MMAX), BETA(MMAX), DA(MMAX)
IF(ALAMDA .LT. 0.) THEN
   KK = MFIT + 1
   DO 12 J = 1, MA
      IHIT = 0
      DO 11 K = 1, MFIT
         IF (LISTA(K).EQ.J) IHIT = IHIT + 1
      11 CONTINUE
      IF (IHIT .EQ. 0) THEN
         LISTA(KK) = J
         KK = KK + 1
      END IF
   12 CONTINUE
ELSE IF (IHIT.GT.1) THEN
    PAUSE '1. Improper permutation in LISTA'
ENDIF
12 CONTINUE
IF (KK.NE.(MA + 1)) PAUSE '2. Improper permutation in LISTA'
ALAMDA=0.001
CALL MRQCOF(X,Y,SIG,NDATA,A,MA,LISTA,MFIT,ALPHA,BETA,NCA, *CHISQ,FLAG,LO)
OCHISQ=CHISQ
DO 13 J=1,MA
    ATRY(J)=A(J)
13 CONTINUE
ENDIF
DO 15 J=1,MFIT
    DO 14 K = 1,MFIT
        COVAR(J,K)=ALPHA(J,K)
    CONTINUE
    COVAR(J,J)=ALPHA(J,J)*(1.+ALAMDA)
    DA(J)=BETA(J)
14 CONTINUE
CALL GAUSSJ(COVAR,MFIT,NCA,DA, 1,1)
IF(ALAMDA.EQ.0.)THEN
    CALL COVSRT(COVAR,NCA,MA,LISTA,MFIT)
    DO 21 J=1,MFIT
        A(LISTA(J))=ATRY(LISTA(J))
    CONTINUE
    RETURN
ENDIF
DO 16 J=1,MFIT
    ATRY(LISTA(J))=ATRY(LISTA(J))+DA(J)
16 CONTINUE
CALL MRQCOF(X,Y,SIG,NDATA,ATRY,MA,LISTA,MFIT,COVAR,DA,NCA, *CHISQ,FLAG,LO)
IF(CHISQ.LT.OCHISQ)THEN
    ALAMDA=0.1*ALAMDA
    OCHISQ=CHISQ
    DO 18 J=1,MFIT
        DO 17 K = 1,MFIT
            ALPHA(J,K)=COVAR(J,K)
        CONTINUE
        BETA(J)=DA(J)
        A(LISTA(J))=ATRY(LISTA(J))
    CONTINUE
    ELSE
        ALAMDA = 10. *ALAMDA
SUBROUTINE MRQCOF(X, Y, SIG, NDATA, A, MA, LISTA, MFIT, ALPHA, BETA, NALP, CHISQ, FLAG, LO)

IMPLICIT REAL*8(A-H,O-Z)
REAL*8 LO
PARAMETER (MMAX=20)
DIMENSION X(NDATA), Y(NDATA), SIG(NDATA), ALPHA(NALP), BETA(MA),
* DYDA(MMAX), LISTA(MFIT), A(MA)
DO 12 J = 1, MFIT
  DO 11 K = 1, J
    ALPHA(J,K)=0.
  11 CONTINUE
  BETA(J)=0.
12 CONTINUE
CHISQ=0.
DO 15 I = 1, NDATA
  IF (FLAG.EQ.1) THEN
    CALL FMOMT(X(I), A, YMOD, DYDA, MA, LO)
  ELSE
    CALL FEXP(X(I), A, YMOD, DYDA, MA)
  ENDIF
SIG2I = 1./(SIG(I)*SIG(I))
DY = Y(I) - YMOD
DO 14 J = 1, MFIT
  WT = DYDA(LISTA(J)) * SIG2I
  DO 13 K = 1, J
    ALPHA(J,K) = ALPHA(J,K) + WT*DYDA(LISTA(K))
  13 CONTINUE
  BETA(J) = BETA(J) + DY*WT
14 CONTINUE
CHISQ = CHISQ + DY*DY*SIG2I
15 CONTINUE
DO 17 J = 2, MFIT
  DO 16 K = 1, J-1
    ALPHA(K,J) = ALPHA(J,K)
  16 CONTINUE
17 CONTINUE
RETURN
END
SUBROUTINE COVSRT(COVAR,NCVM,MA,LISTA,MFIT)
IMPLICIT REAL*8(A-H, O-Z)
DIMENSION COVAR(NCVM,NCVM),LISTA(MFIT)
DO 12 J = 1,MA-1
   DO 11 I=J+1,MA
      COVAR(I,J)=0.
   11 CONTINUE
12 CONTINUE
DO 14 I = 1,MFIT-1
   DO 13 J=I + 1,MFIT
      IF(LISTA(J).GT.LISTA(I)) THEN
         COVAR(LISTA(J), LISTA(I))=COVAR(I,J)
      ELSE
         COVAR(LISTA(I), LISTA(J)) = COVAR(I,J)
      ENDIF
   13 CONTINUE
14 CONTINUE
SWAP=COVAR( 1,1)
DO 15 J = 1,MA
   COVAR(1,J)=COVAR(J,J)
   COVAR(J,J)=0.
15 CONTINUE
COVAR(LISTA(1),LISTA(1))=SWAP
DO 16J=2,MA
   DO 17I = 1,J-1
      COVAR(I, J)=COVAR(J, I)
   17 CONTINUE
16 CONTINUE
RETURN
END

SUBROUTINE GAUSSJ(A,N,NP,B,M,MP)
IMPLICIT REAL*8(A-H, O-Z)
PARAMETER (NMAX=50)
DIMENSION A(NP,NP),B(NP,MP),IPIV(NMAX),INDXR(NMAX),INDXC(NMAX)
DO 11 J = 1,N
   IPIV(J)=0
11 CONTINUE
DO 22 I=1,N
   BIG=0.
   DO 13 J=1,N
IF (IPIV(J).NE.1) THEN
  DO 12 K = 1, N
    IF (IPIV(K).EQ.0) THEN
      IF (ABS(A(J,K)).GE.BIG) THEN
        BIG = ABS(A(J,K))
        IROW = J
        ICOL = K
      ENDIF
      ELSE IF (IPIV(K).GT.1) THEN
        PAUSE 'Singular matrix'
      ENDIF
    ENDIF
  12 CONTINUE
ENDIF
13 CONTINUE
IPIV(ICOL) = IPIV(ICOL) + 1
IF (IROW.NE.ICOL) THEN
  DO 14 L = 1, N
    DUM = A(IROW,L)
    A(IROW,L) = A(ICOL,L)
    A(ICOL,L) = DUM
  14 CONTINUE
  DO 15 L = 1, M
    DUM = B(IROW,L)
    B(IROW,L) = B(ICOL,L)
    B(ICOL,L) = DUM
  15 CONTINUE
ENDIF
INDXR(I) = IROW
INDXC(I) = ICOL
IF (A(ICOL,ICOL).EQ.0) PAUSE 'Singular matrix.'
PIVINV = 1./A(ICOL,ICOL)
A(ICOL,ICOL) = 1.
DO 16 L = 1, N
  A(ICOL,L) = A(ICOL,L)*PIVINV
  16 CONTINUE
DO 17 L = 1, M
  B(ICOL,L) = B(ICOL,L)*PIVINV
  17 CONTINUE
DO 21 LL = 1, N
  IF (LL.NE.ICOL) THEN
    DUM = A(LL,ICOL)
    A(LL,ICOL) = 0.
    DO 18 L = 1, N
      A(LL,L) = A(LL,L) - A(ICOL,L)*DUM
    18 CONTINUE
DO 19 L = 1, M
   B(LL,L) = B(LL,L) - B(ICOL,L) * DUM
19  CONTINUE
ENDIF
21  CONTINUE
22  CONTINUE
DO 24 L = N, 1, -1
   IF(INDXR(L) .NE. INDXC(L)) THEN
      DO 23 K = 1, N
         DUM = A(K,INDXR(L))
         A(K,INDXR(L)) = A(K,INDXC(L))
         A(K,INDXC(L)) = DUM
23    CONTINUE
   ENDIF
24  CONTINUE
RETURN
END
Appendix E

SAS Source Code for CPMG Analysis

The program source code used for non-linear regression with SAS on sorption isotherm data is presented below. The data files in this source code below is from the CPMG experiment for hemlock heartwood, adsorption condition. They were transferred via file transfer protocol (FTP) from the VAX computer to the University's UNIXG. The data were fitted to three non-linear routines, PROC NLIN, each being an exponential model of one, two or three terms.

* SAS SOURCE CODE
* PROJECT ASSIGNMENT: NMR fitting
* INPUT FILE: nmr data
* RUN IN UNIXG BY: sas nmr.sas
* DATE OF RUNNING: September 14, 1993

FILENAME file1 'c344cpde.dat';
FILENAME file2 'cnmrtube.dat';
DATA nmrdata;
  infile file1;
  input x1 y;
  if x1 > 50.0 then delete;
  time1=x1*1000;
  y1=y/1000;
DATA tubedata;
  infile file2;
  input x2 y;
  if x2 > 50.0 then delete;
  time2=x2*1000;
  y2=y/1000;
DATA corrdata;
  set nmrdata;
  set tubedata;
  time=x1*1000;
  y3=(y1-y2);
*----------------------------------------;
PROC NLIN BEST=5 DATA=corrdata MAXITER=250 METHOD=MARQUARDT;
title2 'One exponential for decay -- corrected';
parms a=12 to 20 by 2
    b=.1 to 1 by .2;
model y3=a*exp(-time*b);
der.a=exp(-time*b);
der.b=-time*a*exp(-time*b);
output out=outlc p=yhatlc r=reslc;
*PROC PRINT DATA=outlc;
*----------------------------------------;
PROC NLIN BEST=5 DATA=corrdata MAXITER=250 METHOD=MARQUARDT;
title2 'Two exponential for decay -- corrected';
parms a=.5 to 5 by .5
    b=.01 to .1 by .02
    c=10 to 20 by 2
    d=1 to 3 by 1;
model y3=a*exp(-time*b)+c*exp(-time*d);
der.a=exp(-time*b);
der.b=-time*a*exp(-time*b);
der.c=exp(-time*d);
der.d=-time*c*exp(-time*d);
output out=out2c p=yhat2c r=res2c;
*PROC PRINT DATA=out2c;
*----------------------------------------;
PROC NLIN BEST=5 DATA=corrdata MAXITER=250 METHOD=MARQUARDT;
title2 'Three exponential of decay -- corrected';
parms a=.5 to 5 by .5
    b=.01 to .1 by .02
    c=10 to 20 by 2
    d=1 to 3 by 1
    e=1 to 10 by 2
    f=.1 to 1 by .2;
model y3=a*exp(-time*b)+c*exp(-time*d)+e*exp(-time*f);
der.a=exp(-time*b);
der.b=-time*a*exp(-time*b);
der.c=exp(-time*d);
der.d=-time*c*exp(-time*d);
der.e=exp(-time*f);
der.f=-time*e*exp(-time*f);
output out=out3c p=yhat3c r=res3c;
*PROC PRINT DATA=out3c;
*--END---------------------------------------;