

CHAPTER 1

INTRODUCTION TO NUCLEAR MAGNETIC RESONANCE OF SUPERCRITICAL FLUIDS

1.1 Introduction

While the existence of the supercritical “phase” has been known for over 150 years it has been only in the last 20 years that the value of supercritical fluids (SCFs) as a medium for extraction, cleaning and synthesis has been recognized. It is now clear that SCF processes are often constrained to very narrow regions of economic feasibility due to the phase behavior of the solute-solvent system. As a result, there need to be very tight controls over any industrial process employing SCFs. If the process parameters must be more exact, then so does the information required to generate the design parameters, which includes experimental measurements, theories, and the correlations that result in predictability in a given system. In an effort to expand the current understanding of SCFs and their applications, an intensive study is ongoing using Nuclear Magnetic Resonance (NMR). A portion of this study makes up the body of this dissertation. In an effort to further explain the physical chemistry inherent to possible applications of SCFs, a brief introduction is given to this odd and often ignored “phase” of substances. Following that is a brief introduction to NMR as it pertains to the study of SCF applications.

1.2. Supercritical Fluids

1.2.1. General Properties

The supercritical state is defined by the supercritical pressure (P_c) and supercritical temperature (T_c), shown in Figure 1.1. One of the most common phenomenological definitions describes critical pressure as the pressure above which, regardless of the applied temperature, a liquid cannot be made to boil. In a similar way, the critical temperature can be thought of as the temperature above which, regardless of the applied pressure, a gas cannot be converted into a liquid. Hence, above the critical point there is no longer a phase boundary between the liquid and the vapor. A liquid/vapor phase boundary represents a coexistence line so that material crossing it requires the expenditure of the latent heat of vaporization.

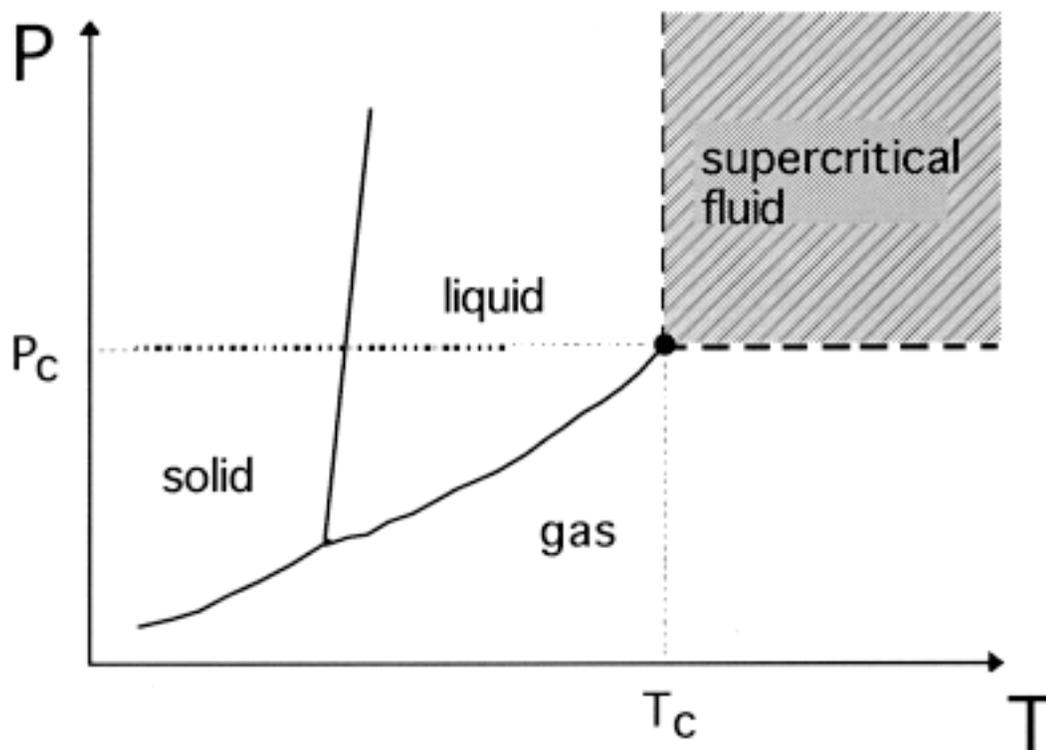


Figure 1.1. Schematic pressure-temperature phase diagram for a pure, one-component system.

The concept of the supercritical state can be illustrated by a physical example. Consider a closed container of constant volume. Inside the container we start with some amount of pure liquid. The space above this pure liquid will be filled with pure vapor at the liquid's equilibrium vapor pressure. Now assume that we begin to heat up this container slowly and uniformly. The density of the liquid will begin to decrease through normal thermal expansion. Meanwhile, the density of the vapor phase begins to increase since more molecules are leaving the liquid to enter the vapor phase. Continued heating results in a further decrease of the liquid density and an increase in the vapor density. Eventually, at some temperature, T_c (and overall, uniform pressure, P_c), the density of the liquid and vapor phases reach the same value, and the vapor and liquid "phases" have identical compositions and identical densities.

The Gibbs phase rule states that

$$P + F = C + 2 \quad (1.1)$$

where P is the number of (homogeneous) phases, F is the number of degrees of freedom (in thermodynamic space), and C is the number of components. In our hypothetical constant-volume system, we have $F = 2$ (we must specify both the temperature and pressure to thermodynamically define the state of the system) and $C = 1$. We see immediately that $P = 1$, meaning that there is really only one phase present in the system: The supercritical fluid phase.

Is this supercritical fluid phase to be considered a liquid or a gas? The answer is that a supercritical fluid reflects properties of both. Table 1.1 shows relative values of the density, diffusion coefficient, and viscosity for a typical liquid, gas, and supercritical fluid. These values indicate the mass transport properties (i.e., diffusivity) are similar to a gas, while the mechanical properties (viscosity and density) are similar to those of a liquid. This unique combination of properties make supercritical fluids attractive for use

Table 1.1
Comparison of Physical Properties for Fluid States

Phase	Density $\left(\frac{\text{g}}{\text{cm}^3}\right)$	Diffusion Coefficient, D_{12} $\left(\frac{\text{cm}^2}{\text{s}}\right)$	Viscosity $\left(\frac{\text{g}}{\text{cm} \cdot \text{s}}\right)$
liquid	1	10^{-6}	10^{-2}
supercritical fluid	0.2 - 0.8	10^{-3}	10^{-4}
gas	10^{-3}	10^{-1}	10^{-4}

as extraction solvents. The high diffusivity and low viscosity allows the fluid to penetrate easily into matrices which are in the form of loose powders, compacted powders, or even fully cemented pre-forms. Further, the ability of a solvent to dissolve other liquids is, to a first approximation, related to the density of the solvent. The relatively high density of supercritical fluids, relative to gases, increases the useful levels of solubility that may be attained.

1.2.2. Supercritical CO₂

The critical values of temperature and pressure are unique for each gas and are determined by the type of intermolecular interactions occurring between the individual molecules. For example, the critical temperature and pressure required to transform water (H₂O) into a supercritical fluid are 374 C and 218 atmospheres. These values are much higher than those for CO₂ because the water molecules exert an attractive force on each other, making the solid and liquid phases particularly stable. CO₂ molecules, on the other hand, have much weaker intermolecular attractive forces.

The values of temperature and pressure, where the supercritical fluid state of pure CO₂ exists, are represented by the grey region in the pressure-temperature diagram in Figure 1.2. In this figure, we have included relative values of density and viscosity for each of the regions of the diagram (solid, liquid, gas, and supercritical fluid). As might be expected, the solid form of CO₂ has a high density and a very high viscosity. Similarly, the liquid has a high density and a reasonably high viscosity, and the gas has a low density and low viscosity. Conversely, the supercritical fluid phase has a high density but a relatively low viscosity. The density of supercritical CO₂ can vary over a wide range from gas values, around 0.1 g per cubic centimeter, to liquid values of about 2.0 g per cubic centimeter (see Figure 1.3). In other words, the density of supercritical CO₂ can be changed by over 2000% simply by varying the temperature and pressure within

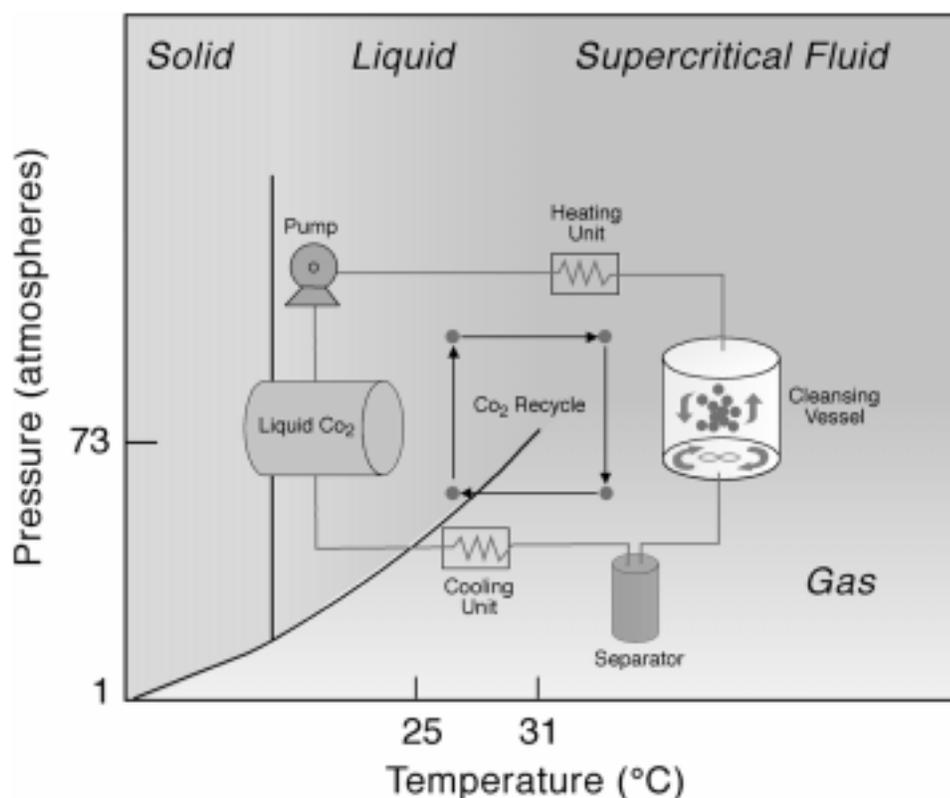


Figure 1.2. Schematic pressure-temperature diagram of carbon dioxide showing the stages of the continuous cycle used in supercritical cleaning: compress --> heat --> clean --> separate --> cool --> uncompress. Relative values of density (ρ) and viscosity (η) are also indicated for each of the four phases (solid, liquid, gas, supercritical fluid).

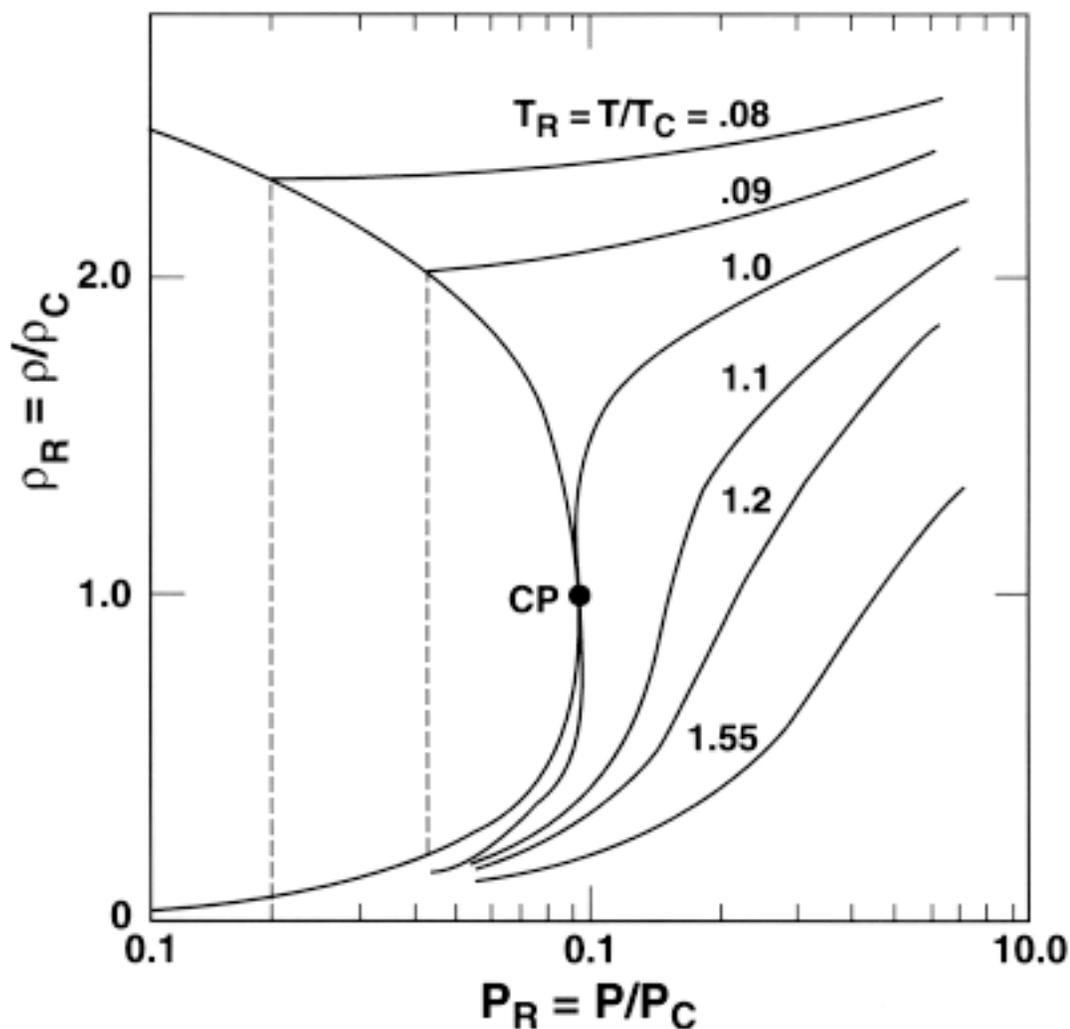


Figure 1.3. Variation of the reduced density (ρ_r) of a pure component in the vicinity of its critical point.

the supercritical region. This unique aspect of the supercritical phase can be illustrated by comparing the change in density associated with changes in the temperature and pressure of a common liquid such as water. Water at 25 C and 1 atmosphere has a density of about 1 g per cubic centimeter, while at 31 C and 73 atmospheres the density increases by less than 1%. The reason that the density of most other liquids changes so little with temperature and pressure is the incompressibility of most liquid materials. A supercritical fluid is by definition both liquid and gas-like, and hence it is compressible. Thus, relatively small changes in temperature and/or pressure can significantly affect the density.

As the density of the CO₂ becomes more liquid-like, so do the solvent properties of the fluid. To a first approximation, the ability of a supercritical fluid to dissolve other fluids can be related to its density in the supercritical region. When operating in the supercritical region, therefore, both temperature and pressure can be used to vary the density, and therefore, the dissolving power of the fluid. It is this ability to alter the solvent power which makes supercritical CO₂ such an attractive solvent. To make the potential for SCFs even more promising, small additions of other components, called co-solvents or entrainers, often modify the observed phase equilibria dramatically. Again this special property affords the chemist the opportunity to *tailor* solvents to achieve a variety of goals, either in separations or reactions.

The viscosity of carbon dioxide has the pressure dependencies given in Figure 1.4. Although the viscosity is observed to change rapidly in the critical region (as is the case also for diffusivity) even at high pressures of 300-400 atmospheres it is still only about 0.09 centipoise, an order of magnitude below typical organic solvents. Because of these density and viscosity properties, supercritical CO₂ possesses certain other characteristics which enhance its attractiveness as a solvent. In addition to possessing liquid-like densities over much of the temperature and pressure range of interest to industry and exhibits the gas-like property of diffusivity with a zero value for the surface tension. These features alter the transport to allow for easy penetration of SCFs into microporous media. Figure 1.5 shows the self-diffusivity of carbon dioxide over a wide range of pressure and temperature. For comparison, the range of diffusivities of solutes in typical organic liquids is also given. The self-diffusion coefficient for carbon dioxide (which is approximately the same for similar sized molecules diffusing through carbon dioxide) is about one to two orders of magnitude higher than the diffusivities of comparable solutes in typical organic liquids. Table 1.2 gives typical values of diffusivity, viscosity, surface tension and density for a gas, supercritical fluid and an organic liquid. The importance of these properties will become clear when the applications of supercritical CO₂ are discussed.

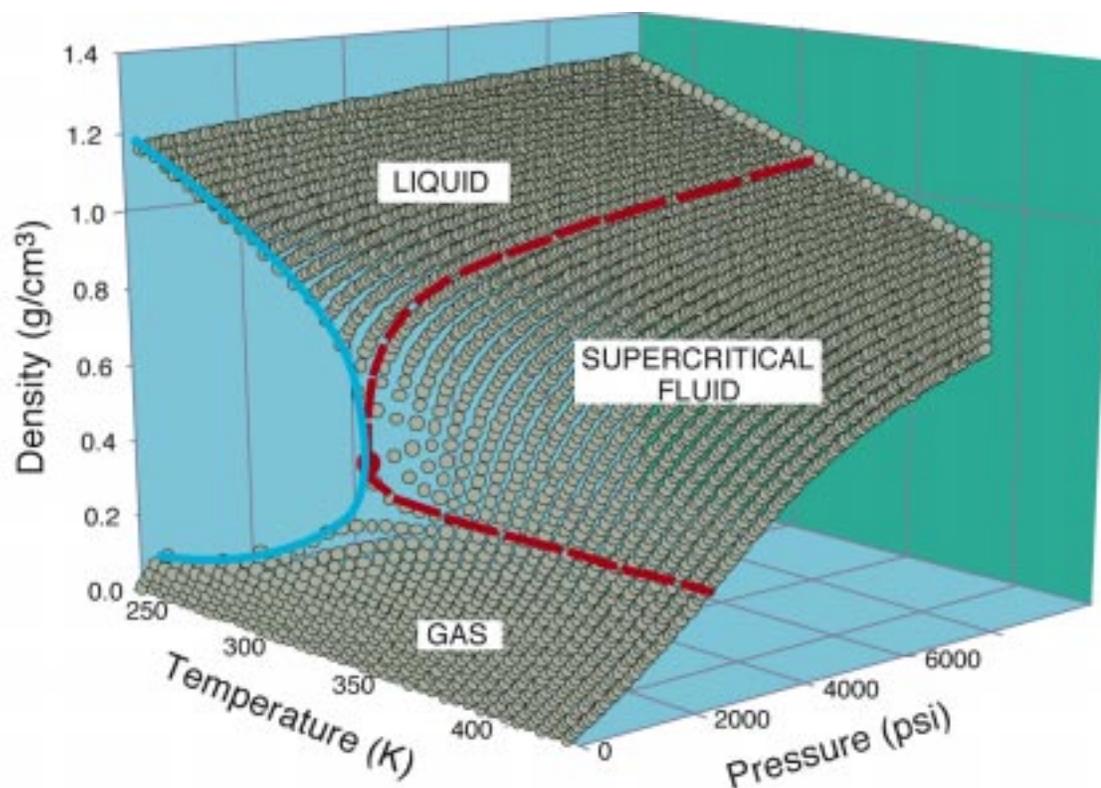


Figure 1.4. Viscosity behavior of carbon dioxide.

As a result of the law of corresponding states the physical properties of supercritical CO_2 applies to all fluids in the supercritical state. The following discussion addresses the question as to why one might be interested specifically in carbon dioxide. As mentioned in the introduction, CO_2 has been implicated in the growing problem of global warming or the *greenhouse effect*. Thus recycling this gas is preferable to letting it escape into the atmosphere where it can be detrimental to the environment. From an industrial perspective, carbon dioxide may be purchased fairly inexpensively, in a highly pure form, and in large quantities. In some cases it may be recycled from other industries. Furthermore, it is nonflammable and is not hazardous to workers. Many of the chemicals currently used in manufacturing processes, on the other hand, are expensive and difficult to dispose of, and dangerous to work with. Having summarized some of the interesting properties of supercritical CO_2 attention is now directed to some of the exciting future

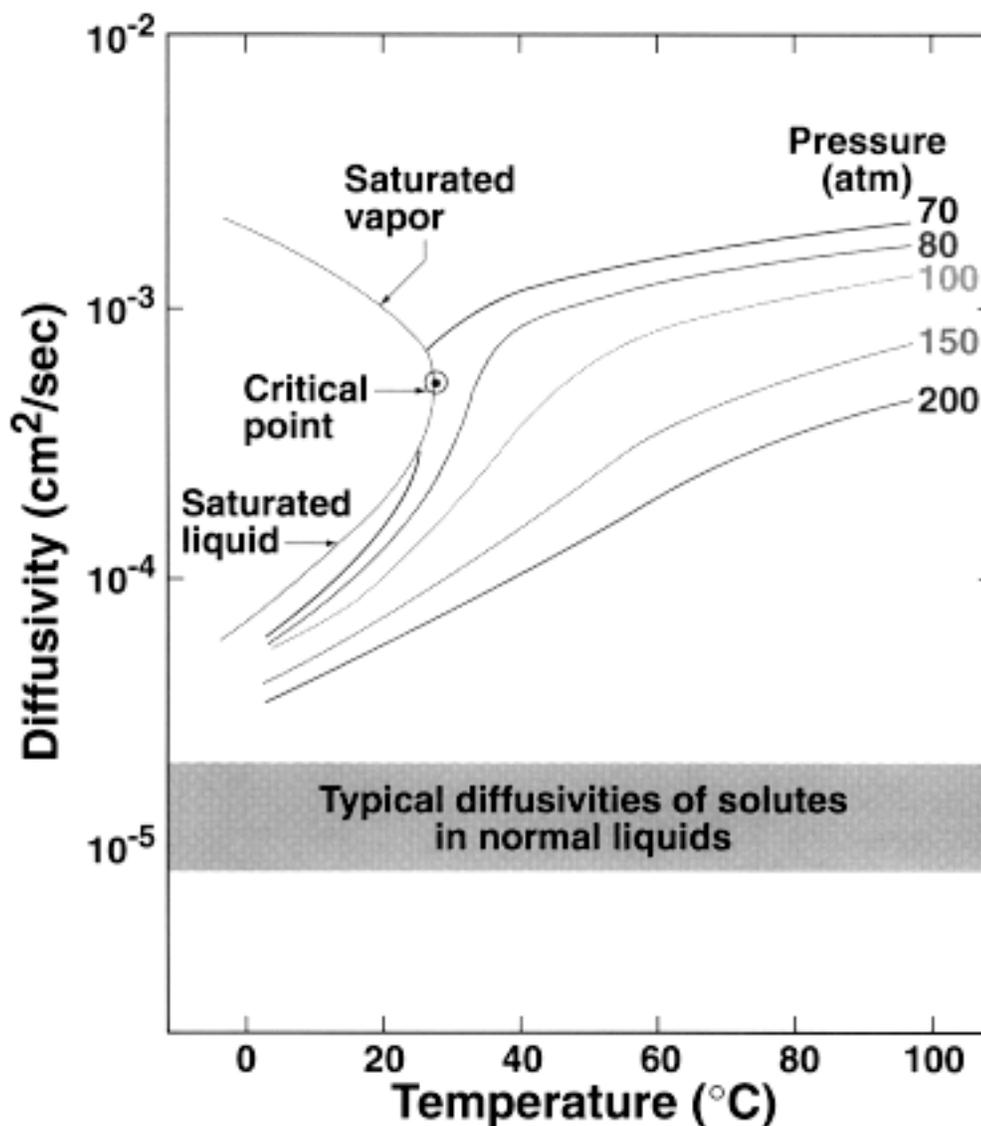


Figure 1.5. Diffusivity behavior of carbon dioxide.

applications such as cleaning and extraction, materials modifications, sterilization, and solvent replacement.

1.2.3. Applications of Supercritical CO₂

1.2.3.1. Cleaning and extraction. The general consideration process of supercritical-fluid cleaning and extraction is conceptually simple. A source of liquid CO₂ in a high-pressure cylinder provides the pump liquid which pressurizes the CO₂ to

Table 1.2
Comparison of the General Physical Properties
of Liquid, Gas and Supercritical Fluid

Phase	Density $\left(\frac{\text{g}}{\text{cm}^3}\right)$	Diffusion Coefficient, D_{12} $\left(\frac{\text{cm}^2}{\text{s}}\right)$	Viscosity $\left(\frac{\text{g}}{\text{cm} \cdot \text{s}}\right)$	Surface Tension $\left(\frac{\text{dynes}}{\text{cm}}\right)$
liquid	1	10^{-6}	10^{-2}	45 - 60
supercritical fluid	0.2 - 0.8	10^{-3}	10^{-4}	0
gas	10^{-3}	10^{-1}	10^{-4}	n/a

above the critical pressure. The temperature is then raised above the critical temperature. The CO_2 is now in a supercritical state where cleaning or extraction process may begin. These processes require that the supercritical CO_2 flows into the chamber containing the parts to be treated. The supercritical fluid then exits through a pressure-reducing valve and is allowed to expand into a separating vessel, where with the decrease in pressure, allows the CO_2 to change back into a gas. In the (low density) gaseous state, the compounds that were soluble in the (high density) supercritical fluid state are now much less soluble and are collected after dropping out of solution. The gaseous CO_2 is then cycled by cooling back to its liquid state and reintroduced back into the flow stream where it may be used again in the cleaning process. It is important to note that this cleaning cycle is self-contained with all of the CO_2 is continuously being reused; the CO_2 is therefore self-cleaning. Included in Figure 1.2 is a simplified process flow diagram for the cleaning cycle.

The first commercial applications for supercritical fluids were in the areas of cleaning and extraction, and these continue to be of primary importance. It has been known for more than one hundred years that many gases exhibit an enhanced ability to dissolve other materials when in a supercritical state, but it is only recently that SCFs have been the focus of active research and development. The motivation for the recent development work on SCF in cleaning and extraction technologies is a result of increased governmental regulation on the use and disposal of chemicals presently used as industrial solvents. An example receiving a great deal of recent attention is a class of solvents called chlorofluorocarbons (CFCs), such as Freon, which is blamed for the destruction of the ozone layer. This has made nontoxic, environmentally-friendly solvents, like supercritical CO₂, very attractive as a possible replacement.

An SCF can be used to extract a particular solute from a multicomponent mixture by capitalizing on the differences in the solubility of the various components in the SCF. Potential applications range from the extraction of oils from plants for use as flavorings in foods and as scents in perfumes, to the removal of specific wastes from large-volume process streams (like those encountered in oil refineries).

Whereas extraction involves the removal of substances from the interior of materials, cleaning involves the removal of substances from the surfaces of objects. Appearance, performance, improved service life, and desired product specifications are among the many reasons to include a cleaning operation as part of a manufacturing process. Current cleaning technologies can be divided into two broad categories, water-based and non-water-based. Non-water-based technologies, many of which are based on CFCs, face severe limitations brought on by the Montreal Protocol. The Protocol is a resolution adopted by some 150 industrialized nations in 1987 which calls for the elimination of CFCs as of 1996. The major uses for CFCs are as refrigerants and as industrial cleaning solvents. About 20% of the total, worldwide CFC production is used in cleaning, and the elimination of CFCs has led to a reevaluation of the entire industrial cleaning process and an intense search for alternative solvents. Much of the research that has been done in the

area of SCF cleaning was originally done for the defense industry. This technology for supercritical cleaning of high value precision parts in defense systems is now being transferred for civilian industrial applications.

1.2.3.2. Drycleaning. An interesting application that falls between extraction and cleaning is the use of liquid CO₂ as a replacement solvent for drycleaning. During the development of supercritical cleaning technologies it was discovered that carbon dioxide in its liquid state is an excellent dry cleaning solvent. Dry cleaners currently use a chemical called perchloroethylene (also known as PERC), which is a suspected carcinogen. It is well known that residual amounts of PERC remain in clothing long after treatment. There are concerns as to the effect such a substance worn against the skin might have. After the PERC has been used, it is not cost effective to completely separate it from the grease, oils and other substances removed from clothing. This results in large volumes of dirty PERC which must be discarded. For these reasons, and the possibility of stringent government regulation, the dry cleaning industry is anxious to find alternative solvents. The liquid CO₂ cleaning process works on the same principles as does the supercritical fluid cleaning (see above). LANL has tested liquid carbon dioxide on many common fabrics including cotton, wool, linen, silk, rayon, polyester, diacetate and polyester/cotton blends. The CO₂ was found to clean all of these fabrics as well as, and in some cases better than, existing technology in less time and with little or no waste.² Plans are in progress to begin manufacturing operations for SCF CO₂ dry cleaning machines in Italy and the United States. Prototype SCF CO₂ "washing machines" were unveiled in Las Vegas in June 1997.

1.2.4. Materials Modification

Supercritical carbon dioxide's unusual combination of physical properties can be used to produce desirable modifications to materials. These modifications constitute some of the most exciting potential applications of supercritical fluids. We now describe one such application as it applies to this work.

1.2.4.1. Polymers. The use of SCF CO₂ for the modification and processing of plastics is being explored for specific applications. Initial work on polymer/SCF CO₂ interactions shows that many polymer properties can be varied over wide limits and with a high degree of control. For example, research has shown that we can increase or decrease the crystallinity of a number of polymers under appropriate treatment conditions. This enhances the properties of many plastics by making them either stronger or more flexible. Further, the surface properties of virtually all polymers can be modified to produce better adhesion or to promote specific surface chemistries. For instance, a polymer surface can be made more water repellent, or more water absorbent. Finally, with appropriate treatments, the volume of a polymer fiber can be expanded to produce better insulating properties. We are presently exploiting these discoveries to modify fiber and textiles for specific applications, and to develop novel means of recovering plastic wastes for reuse and recycling.

1.2.4.2. Enhanced oil recovery. Carbon dioxide is commonly found in very pure form as a by-product from oil and gas wells. In fact most of the CO₂ marketed today is “mined” in this way. Oil reservoirs are normally found with an overhead gas “cap” that provides the pressure for the primary recovery from the well. Secondary recovery usually involves flooding the reservoir with an oil immiscible fluid such as brine water to displace the oil thus enhancing the recovery. Typical recoveries are on the order of 20-30% using this technique. Tertiary oil recovery involves flooding the reservoir with an oil miscible fluid. This fluid would need to be inexpensive and readily available at the injection well. This necessitates the use of compressed “cap” gasses such as liquified petroleum gas (LPG), or carbon dioxide (CO₂) normally found co-located with oil reservoirs. The efficiency of enhanced oil recovery by dense CO₂ and LPG is often marred by an unfavorable mobility ratio. This is a result of a viscous fluid being displaced by a non-viscous fluid. This is unfavorable since the frontal instability usually results in the growth of “viscous fingers” and early breakthrough of the displacing fluid. Chapter 6 examines a novel approach to this problem as it looks at the solid-state and solution structure of a

polymeric additive used to increase the viscosity of dense CO₂.

1.2.4.3. Chemical synthesis. The majority of organic synthesis reactions are carried out in a liquid. This is because the collision of reactant molecules to form products is more favorable in the liquid phase. The unusual combination of physical properties of the supercritical state makes it an excellent medium in which to carry out some of these reactions. The high diffusivity of SCF CO₂ suggests that there are many more collisions between molecules, per unit time, than occur within the liquid state. Since the reaction of dissolved molecules is promoted by these collisions, the reaction rate will be much faster in the supercritical fluid. By adjusting the temperature and pressure we can, via the changes in diffusivity, control the collision rates. Thus, we can control the reaction rate over a much broader range than is possible with the simple temperature control available with conventional liquid solvents. We know that temperature and pressure also determine the density of a supercritical fluid, and, since the density largely determines the solubility of a given solute, one can imagine the selective addition and removal of reactants and products from a single synthesis chamber, eliminating the traditional, multiple-stage synthesis techniques. Reactions in SCFs can also be used to promote specific synthetic pathways, producing a higher fraction of a specific molecule.

1.2.5. Summary Statement on Significance of Supercritical CO₂

Thus far, we have described a number of present and future applications of supercritical carbon dioxide. From these descriptions, it may be thought that supercritical CO₂ is a 'free' solution to current industrial manufacturing and environmental problems. There are two obstacles, however, to the conversion from current chemical solvents to "green" carbon dioxide. We mentioned earlier that it is more energy efficient to operate under conditions of high pressure rather than high temperature. However, the equipment required to achieve and maintain high pressures are more expensive than those needed for high temperatures. This one-time expense of high-pressure vessels, pumps, etc. is the first major barrier preventing the more widespread use of supercritical fluids in industry.

The second barrier is our incomplete understanding of the nature of chemical reactions occurring within supercritical fluids. This makes the prediction of the end-result of a given chemical reaction very difficult. However, as the price of energy continues to increase, as our awareness of the fragility of our environment becomes more acute, as our demands for improved materials intensify, as our level of understanding of supercritical-fluid phase reactions improves, and as industry becomes more comfortable with high-pressure operations, the barriers to supercritical fluid processing will fall. Look for supercritical fluids to assume a more important role in the manufacture of the products.

In order to achieve all these lofty goals it is essential to have a good working model of SCF solution behavior, capable of giving good predictability of the interactions of the fluid with solutes.

Evidence now exists for the occurrence of rather unusual phenomena in SCF solutions. In addition to extreme entrainer effects of many orders of magnitude,¹ there are the well-known synergistic effects observed for the solubilities of physical mixtures in solids,² the very unusual partial molal volumes,³ and now a plethora of spectral observations.⁴⁻⁹ The burgeoning evidence says ever more strongly that SCF solutions may no longer be treated by classical continuum methods. An attempt must be made to understand from a molecular point of view exactly what is occurring. A majority of the chapters in this dissertation (Chapters 3-5) will be concerned with the use of NMR to measure the effects of co-solvents, or entrainers, as they effect the solubility behavior of liquid and supercritical CO₂ based systems.

1.3. High Pressure NMR

High pressure NMR serves as an effective experimental technique for testing theoretical models of species structure and dynamics in the gas, liquid, and supercritical states. Although the application of high pressure NMR to simple fluids leads to some interesting additional complications, the information gained from the technique more than justifies its use. The pressure axis provides an additional dimension to the experi-

mental matrix. For a liquid it is commonly known that temperature changes at constant pressure will effect the molecular motion via kinetic energy and molecular average volume collisional arguments. One can separate the effects of density and temperature on the molecular motion only if both the temperature and pressure are controlled variables in the NMR experiment. Increased pressure also allows for the experimental range to expand well above the normal boiling point and into the compressible SCF regime. Some examples of the usefulness of high pressure NMR will be given in the text of Chapters 2 through 5. Chapter 2 demonstrates the unique collision properties of supercritical fluids can help elucidate the dynamics of HD in CO₂.

1.3.1. NMR Determination of Structural Dynamics in High-Pressure Fluids

There have been direct spectroscopic probes of the local solvent structure around solutes in supercritical fluids. These include using the solvatochromic scales as in the ultraviolet-visible (UV) absorption of phenol blue in ethylene⁹ and the fluorescence spectroscopy of pyrene in carbon dioxide.⁵ The use of spectroscopic methods to study the local environment surrounding solute molecules in dilute supercritical fluid mixtures has been reviewed.¹⁰ However the use of NMR to determine the local structure within supercritical fluids has thus far been sparse in the literature. Chapters 3 and 4 will address and review this novel application of NMR in high pressure fluids.

1.3.2. NMR Determination of Self-Diffusion Coefficients in High-Pressure Fluids

Many methods exist for measuring the diffusion coefficients of fluids. However, the experimental accuracy of many of these is quite limited.^{11, 12} Furthermore, methods that give reliable results in the low pressure regime are not always suitable at high pressures because the inverse dependence of the diffusion coefficient on pressure makes for experiments that take an inordinately long time. The most widely reported method for the

measurement of diffusion coefficients in the SCF state is a gas chromatographic method based on Taylor dispersion, which has proven unreliable at lower pressures.¹³⁻¹⁵

The only other methods that can be utilized for this measurement in SCF's are photon correlation spectroscopy^{16,17} and NMR.^{18,19} They are not widely used at this time because the equipment is very expensive and their application to industrially important SCF's is still in its infancy. The use of the NMR technique has been confined to the measurement of self diffusion coefficients.^{18,19} Chapter 5 expands upon this work, determining the self diffusion coefficients for alcohol solutes in high pressure systems where the structure of the solute/solvent cluster is based upon Chapters 3 and 4.

1.3.3. The Effects of High Pressure on Polymers.

Chapter 6 focuses on the structure of an associatively bound polymeric additive that can be used with CO₂ to increase the viscosity of the resulting mixture. The solid state and solution structures of this unique polymer system are examined. Chapter 7 utilizes NMR at ambient pressures to elucidate changes in a polymeric material after exposure to supercritical CO₂.

1.3.4. Instrument Requirements for High-Pressure NMR

In order to perform NMR experiments under high pressure, it is necessary to devise a convenient means to control the pressure temperature and sample concentration while it is inside the magnet. Two approaches to the design of high pressure NMR probes have been reported: (1) construction of a probe which is capable of achieving the necessary pressures, or (2) fabrication of a high pressure cell which can be used in a standard commercial NMR probe. We chose to employ the second as it provides a more convenient and cost effective means to carry out experiments up to a few hundred atmospheres covering the region of interest in CO₂.

Pressure control while the cell is in the magnet is a major issue in the cell design. The previously reported designs^{20,21} of the sapphire NMR cells that are employed in these

experiments were unable to control the sample pressure. In our design a movable piston is used to control the sample pressure. With this design it is possible to control temperature and pressure over a wide range of conditions. The sample volume must be restricted to the active coil in order to eliminate errors introduced through molecular diffusion between polarized and nonpolarized volume elements within the cell.

A schematic diagram of the high-pressure NMR cell used in the following experiments is shown in Figure 1.6. The cell consists of three major parts: a) the titanium cap, b) the piston cylinder and c) the sapphire tube. The titanium cap has two connections (d and e) which connect the cell to the pressure pump and the sample source. One of the connections (e) connects the sample source through the movable piston (f), into the sample volume of the sapphire tube with a 100 micron capillary (h) coiled inside the titanium cap to allow for the travel of the piston. A pressure transducer is connected to this line to monitor the sample pressure. The other connection (d) connects to a pressure pump that monitors the pressure across the piston and automatically adjusts to maintain sample pressure at a pre-set level. The other function of the piston is to help isolate the sample under investigation from the pressurizing fluid thus maintaining sample integrity over a wide range of pressures. A press fit Tefzel plug (g) with a micro capillary opening is inserted into the sapphire tube to minimize diffusion of irradiated nuclei from the sample coil.

1.3.5. Introduction to the Basics of High-Pressure NMR

1.3.5.1. Isolated nuclear spins. The NMR signal from the magnetic nuclei in a fluid can be used to obtain information about the nature and rates of molecular motion. If an isolated spin-magnetization of a fluid is perturbed from equilibrium it will return exponentially with the time constant T_1 . The rate $1/T_1$ is the average transition probability for such a nuclear spin responding to molecular reorientations. This depends upon the fluctuating interactions of the spin with the molecule in which the nucleus is a part. The magnitude, manner and rate of these fluctuating interactions depend upon the molecular

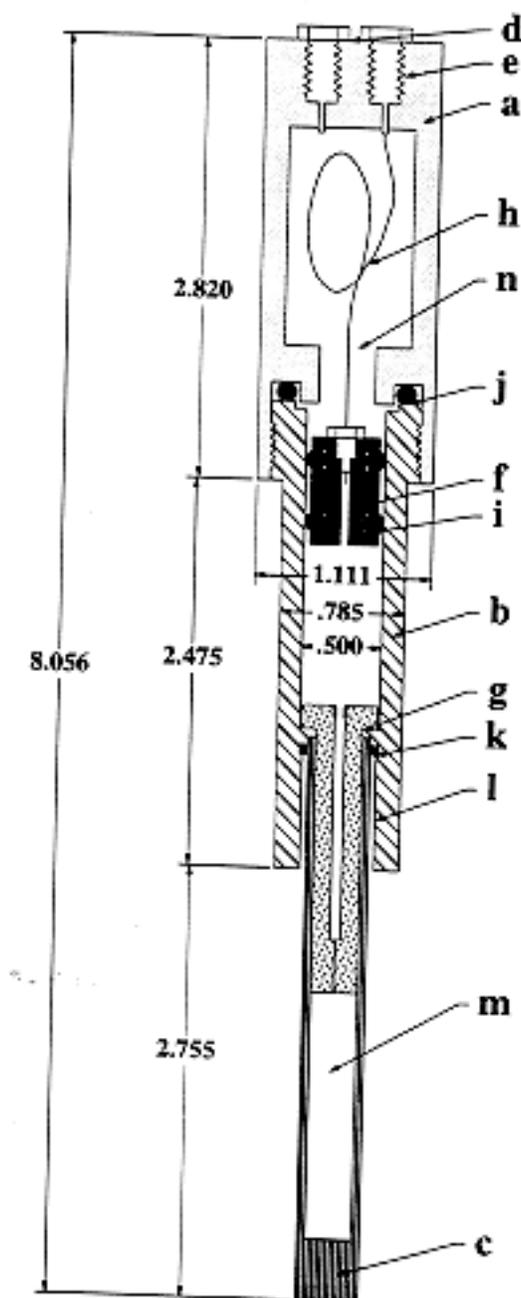


Figure 1.6. Schematic diagram of the NMR high-pressure cell. a.) Titanium cap; b.) Piston cylinder; c.) Sapphire tube; d.) Connector to pressure generator; e.) Connector to sample source; f.) Movable piston; g.) Tefzel plug; h.) Capillary tube; i.) Piston o-ring; j.) O-ring to seal a.) and b.); k.) O-ring to separate glue from fluid under investigation; and l.) glue clearance.

motion in the fluid. Consequently information about molecular motion is available, at least in principle, from the T_1 values.

The motions of molecules in liquids is accessible only through a large number of various models that depend upon phenomenological parameters such as the coefficient of rotational diffusion, the frequency of collisions, the time between jumps, etc. Three such theories: the random walk theory of Torrey,²² the rotational diffusion theory of Abragam,²³ and the rotational Brownian motion of McConnell²⁴ form the basis upon which most NMR relaxation models in liquids are based. Other methods of studying molecular motion (optical, dielectric, neutron scattering, etc.) can in principal give additional detailed information. However, as a consequence of the many-particle effects present in these methods, the interpretation of the experimental results for liquids is often ambiguous. In NMR, the weak coupling of the spin system with the lattice allows one to focus better on isolated molecular motions to describe relaxation in liquids.²⁵ Information on the rotational motion of molecules in liquids of low viscosity, given by NMR, is obtained in the form of the integrals of the time correlation functions, i.e. the correlation times.

Relaxation can be thought of as the thermal contact of the quantum mechanical spin system to a classical “heat bath” with essentially infinite molecular degrees of freedom. As nuclear spin degrees of freedom couple only weakly with their environment or lattice, the spins and the lattice may be treated as independent systems. The lattice will remain essentially unperturbed by the exchange of energy with the spins because the heat capacity of the lattice is many orders of magnitude greater than that of the spins.

1.3.5.2. Coupled nuclear spins and the differential equations governing relaxation. Using irreducible magnetization modes of the system, the density matrix equation is given by

$$dr/dt = Raa'ab'r \quad (1.2)$$

where $Raa'ab'$ is the Redfield²⁶ relaxation matrix for the quantum mechanical density

matrix. Only a finite number of Redfield terms need be considered for longitudinal relaxation in the eigenstate representation. In addition, the indices on the density matrix also may be collapsed to include only the diagonal elements that give the state populations. In this form, the Redfield terms may be considered simple transition probabilities, that is, $R_{aa'ab'} = W_{ab}$, linking the populations of the various eigenstates.²⁷ This new relaxation matrix, G , is a simple transform of the Redfield matrix

$$G = T \cdot R_{aa'ab'} \cdot T^{-1} \quad (1.3)$$

where the unitary matrix T transforms the Redfield matrix, $R_{aa'ab'}$, such that the elements in G become linear combinations of the elements in $R_{aa'ab'}$ to form a new matrix in which all the elements correspond to the observables magnetizations. This is described in more detail in the Appendix.

1.3.5.3. Longitudinal relaxation. From the above treatment, it is clear that rf energies induce a transition between states a and b with equal probability. This would rapidly result in an equalization of Boltzmann populations N_a , and N_b resulting in the ultimate extinction of the NMR signal. This so-called saturation phenomenon is opposed by the relaxation processes that ensure a rapid return to equilibrium of the overall longitudinal magnetization $M_z(t)$

$$M_z(t) = \sum \mu_z \quad (1.4)$$

where the summation is over all the nuclei in the sample in either an a or b state. From a macroscopic point of view, this means that the overall nuclear magnetization M_z , after being rotated by the flip angle from its equilibrium position M_0 along B_0 , spontaneously relaxes to B_0 after the transmitter has been switched off, in accordance with the equation

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} \quad (1.5)$$

where T_1 is the longitudinal relaxation time, typically a few seconds in liquids.

From a microscopic point of view this means that each nucleus spends an average residence time of $2T_1$ in either quantum state a or b, before it suffers a non-radiative transition to the other state b or a. This corresponds to average transition probabilities W_{ba} and W_{ab} in units of per second.

$$W_{\alpha\beta} \approx W_{\beta\alpha} = \frac{1}{2T_1} \quad (1.6)$$

In fact W_{ba} and W_{ab} are slightly different, being in the ratio;

$$\exp\left[-\left(\frac{E_\alpha - E_\beta}{k_b T}\right)\right] \quad (1.7)$$

where the E's are the energies, T is the temperature, and k_b is the Boltzmann constant. This ensures slightly unequal Boltzmann populations N_a and N_b , resulting in an NMR signal.

1.3.5.4 Relaxation rates as a source of dynamical information. Relaxation processes are dependant on the existence of parasitic time dependent magnetic fields $B(t)$ arising from the electronic spins and the magnetic dipoles and quadrupoles of neighboring nuclei. Molecular reorientation and translational diffusion change the relative positions of the interacting centers. The resultant magnetic field, $B(t)$, and the corresponding perturbation Hamiltonian, H_p , are randomly fluctuating and average to zero over time.^{23,26,28,29}

The transverse components of $B(t)$, $B_x(t)$ and $B_y(t)$ corresponding to the off diagonal portion of H_p may introduce transitions between states a and b thus participating in longitudinal relaxation. This is not the case for the longitudinal component $B_z(t)$ which lies colinear with the z projection of the nuclear moment. Transitions are possible because the Fourier transformation, of $B(t)$ contains a component at the Larmor frequency, ω_0 . As the fluctuating field does not decay to zero over time, the FT is not applied to the perturbation Hamiltonian (H_p) itself, but to the effect of the perturbations. This effect is

very limited in time and can be described with the auto-correlation function $g(\tau)$

$$g(\tau) = \overline{H_p(t) \bullet H_p(t - \tau)} \quad (1.8)$$

The bar denotes the ensemble average over all nuclei. The result is independent of the time t at which the observation begins. A simple model is a magnetic field randomly jumping between two opposite values $\pm B_x$. It can then be shown that

$$g(\tau) = B_x^2 e^{\frac{-\tau}{\tau_c}} \quad (1.9)$$

where τ_c is a correlation time characterizing the mean time elapsed between two successive jumps. These jumps are closely related to molecular motions.

Fourier transformation of the auto-correlation function will result in a distribution of frequencies termed the spectral density $J(\omega)$, a Lorentzian function of ω

$$J(\omega) = B_x^2 \frac{\tau_c}{1 + \omega^2 \tau_c^2} \quad (1.10)$$

The contribution of the perturbation to the longitudinal relaxation, that is, the transition probability W_{ab} , reaches a maximum when $1/\tau_c$ approaches the resonance frequencies of the perturbing Hamiltonian H_p . This falls into the range of 10^{-8} to 10^{-12} seconds. This is the quintessential piece of information for all the dynamical information obtained by NMR in the following chapters.

1.3.6. The Origin of Nuclear Spin Relaxation

Direct time dependant interactions have been shown to cause spin relaxation. However any static interaction can simply be treated as part of the normal spin Hamiltonian, altering the positions and intensities of the spectral lines. For example, a nuclear spin may experience a local magnetic field from the spins of other nuclei moving in its vicinity, from an unpaired electron, or from a variety of other mechanisms, such as the spin-rotation interaction in which the rotation of the molecular electrons generates a

magnetic field at the nucleus. In general, rotational and diffusional motions are important sources of relaxation in liquids. Some mechanisms that make contributions to spin-lattice relaxation will be discussed in the following section.

1.3.6.1. Nuclear spin relaxation mechanisms. There are a number of processes that provide the basis for nuclear spin relaxation. These include the nuclear magnetic dipole-dipole interactions (DD), the spin-rotation interactions (SR), the quadrupolar interactions (Q), and the chemical shift interactions, (CSA). The overall relaxation rate can be expressed as a sum of contributions from each mechanism.

1.3.6.2. Dipole-dipole interaction. The magnetic nuclei in molecules provide magnetic dipole fields that are proportional to the magnetic moments of the nuclei. These fields fluctuate in magnitude and direction as the molecule tumbles through space. When these random oscillating fields have magnetic field components at the Larmour frequency, the nuclear spin relaxes. This interaction depends upon the correlation time of the tumbling molecule as well as the distance between the interacting nuclei. The dipole interactions can be divided into intramolecular and intermolecular interactions. For both of these types of interactions there is a homo, and hetero-nuclear subinteraction. These are reflected in the following equations

$$\begin{aligned}
 \text{For intra-homo: } \frac{1}{T_1^{DD}} &= \frac{3\gamma_A^4 \hbar^2 \tau_c}{2r^6} \\
 \text{For intra-hetero: } \frac{1}{T_1^{DD}} &= \frac{\gamma_A^2 \gamma_X^2 \hbar^2 \tau_c}{r^6} \\
 \text{For inter-hetero: } \frac{1}{T_1^{DD}} &= \frac{2N_X \gamma_A^2 \gamma_X^2 \hbar^2}{Da}
 \end{aligned} \tag{1.11}$$

where r is the distance between the interacting nuclei, D is a mutual translational self-diffusion coefficient for the molecules containing A and X , and a is the distance of closest approach between A and X . τ_c is a rotational diffusion correlation time for molecular tumbling. This corresponds to the average time it takes for a molecule to rotate through one radian.

1.3.6.3. The spin-rotation (SR) interaction. Spin-rotation relaxation of the nuclear

magnetization in molecules is due to the intramolecular coupling of the individual nuclear spins to the molecular angular momentum. A fluctuating local magnetic field, which relaxes the nuclear spins, is the result of the collisional reorientation of the molecular rotational angular momentum. For linear molecules, the spin-rotation contribution to the total spin-lattice relaxation can be expressed as

$$\frac{1}{T_1^{SR}} = \frac{4C_{\perp}^2 I k T \tau_j}{3\hbar^2} \quad (1.12)$$

C_{\perp} is the spin-rotation constant and I is the moment of inertia. For a spherical top molecule, the relaxation rate has the form

$$\frac{1}{T_1^{SR}} = \frac{2C_{\text{eff}}^2 I k T \tau_j}{\hbar^2} \quad (1.13)$$

C_{eff} is the effective spin-rotation tensor, which will be discussed more in Chapter 4. The τ_j is the correlation time for angular momentum transfer and therefore is closely related to the average time between collisions. The higher the temperature the faster the molecule reorients in accordance with the kT term. The result is that the spin-rotation contribution to the total spin-lattice relaxation increases with temperature. This is quite the opposite in all other mechanisms examined in this work.

1.3.6.4. Quadrupolar relaxation. Quadrupolar occurs when the nuclear electric quadrupole moment, eQ , interacts with electric field gradients to provide a very efficient nuclear relaxation process. The equation for these interactions is similar in form to that of the dipole interaction. For the hydrogen deuteride (HD) molecule in Chapter 2 for example the quadrupolar interaction is stronger than the dipole interaction. The electric quadrupolar interaction between spin I and an electric field gradient can be written in the form given in equation 1.14.

$$\frac{1}{T_1^Q} = \frac{3\pi^2(2I+3)\chi^2\tau_c}{10[I^2(2I-1)]} \quad (1.14)$$

where

$$\chi = \frac{e^2 Q q_{zz}}{h} \quad (1.15)$$

is known as the nuclear quadrupolar coupling constant and is in units of frequency. The τ_c here is the rotational diffusion correlation time as it appeared in the dipolar equation.

1.3.6.5. Chemical Shift Anisotropy. Anisotropic shielding at the nucleus changes with the orientation of the molecule in a static field. Therefore the molecular tumbling modulates the local magnetic field resulting in relaxation. The spin-lattice relaxation rate due to this interaction is proportional to the square of the magnetic field:

$$\frac{1}{T_1^{CSA}} = \frac{2}{15} \gamma_A^2 B^2 \Delta\sigma^2 \tau_c \quad (1.16)$$

where $\Delta\sigma = (\sigma_{\parallel} - \sigma_{\perp})$ is the chemical shielding anisotropy of the nucleus and τ_c has the same meaning as before.

The spin-lattice relaxation can be measured and contributions from each of the mechanisms decoupled to yield dynamic and structural information pertaining to the species of interest. As an example, analysis of relaxation effects in double resonance spectra of hydrogen deuteride (HD, Chapter 2) provides information on the relative contributions of these relaxation mechanisms in this spin system. Each of the following chapters will contain its own introduction to the specific observation techniques and theoretical treatments used to provide insight into the often strange and unpredictable world of supercritical fluids.

1.4. References and Notes

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