Magnetic Resonance Microscopy
of
Alkyd Polymers and Emulsions

by

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Abstract

Alkyd emulsions are currently being developed for coating applications. These paints combine the technical advantages of alkyd polymers, which give coatings of a high gloss finish, with the environmental and health benefits of solvent-free systems. Nonetheless, the drying and film formation of these systems involve several steps, none of which is well understood yet. These include creaming or sedimentation, evaporation of the continuous water phase, coalescence of the alkyd droplets, a possible phase-inversion, and the oxidative cross-linking of the alkyd polymer to form a hard coating.

In this thesis, Magnetic Resonance Microscopy is used to investigate the film formation of alkyd emulsion coatings. As the process is complex, studies on a different range of emulsions and related systems are performed to gain further insight into the different steps involved. A combination of Liquid State Microscopy, diffusometry and broad line imaging (Stray Field Magnetic Resonance Imaging) is employed, and it is shown that this combination provides results extremely rich in information.

First, a study of the cream layer and the creaming dynamics of model bulk oil-in-water emulsions containing different concentrations of thickener is presented. The experimental data are compared to the predictions of a numerical model, and evidence is gained that the presence of the thickener induces flocculation according to a depletion mechanism. Then, the water evaporation from alkyd emulsion droplets is investigated and the water concentration across the droplet is modelled according to an original model based on lateral diffusion of water. There is no evidence from spectroscopy and diffusometry for phase-inversion during the drying of alkyd emulsion coatings. Finally the cross-linking of alkyds containing driers is found to be non-uniform across the film thickness.
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Chapter 1

Introduction

Emulsions are widely used in everyday life: milk, butter and margarine, sauces, paints and cosmetic creams are some examples.

An emulsion is a colloidal dispersion of droplets (of sizes of the order of one \( \mu m \), but in food emulsions droplets can be up to several hundred \( \mu m \)) of one liquid in another one with which it is completely immiscible [Dickinson, 1992, page 79]. As oil and water is the most common system, emulsions are broadly classified as oil-in-water (O/W) or water-in-oil (W/O) when the dispersed phase is oil or water, respectively. Under intense agitation, any phase can be broken up into a dispersion of fine droplets in another immiscible phase. However, these systems are thermodynamically unstable and will immediately separate. To enhance the dispersion process and to protect the newly formed droplets against immediate recombination an emulsifying agent is generally added. By far the most important of the emulsifiers are surfactants, which aid in emulsification by reducing the interfacial tension [Dickinson, 1992, pages 11-13]. Surfactants are amphiphilic, low-molecular-weight molecules having two parts of widely different polarity and solubility. They tend to orientate themselves at the interfaces, so that the hydrophilic head-groups, such as carboxyl or hydroxyl groups, are located in the aqueous phase, while the hydrophobic tail groups, usually hydrocarbon chains, are located in the non-aqueous
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Phase. Stabilisers are chemical components, or mixture of components, which can confer long-term stability on an emulsion. High-molecular-weight polysaccharides, such as gum xanthan, act as stabilisers by increasing the viscosity of the aqueous dispersion medium. Proteins are in many cases both emulsifiers and stabilisers [Dickinson and Euston, 1991, page 132]. Generally speaking, there are three primary processes of instability for emulsions. One is creaming (or sedimentation), the gravimetric separation caused by the upward (or downward) motion of emulsion droplets because of the difference in their density and the surrounding medium. A second process is flocculation, the formation of aggregates, or flocs, following the collision of two or more emulsion droplets that are held together by van der Waals forces. Coalescence, the irreversible merging of two or more emulsion droplets to form a larger single droplet leading to the breakdown of the emulsion, is the third process leading to instability.

Even the simplest emulsion, or in general, the simplest colloidal dispersion, is a complex heterogeneous system [Dickinson, 1992, page 14]. For an introduction to the physical chemistry of emulsions, one can refer to the introductory books of Dickinson and Hunter [Dickinson, 1992, Hunter, 1998], while a more in-depth description is reported by Russel et al. and by Hunter [Russel et al., 1991, Hunter, 1995].

The work presented in this thesis has been stimulated by a desire to understand the material properties of alkyd emulsions, which are being developed for coating applications. These emulsions potentially have considerable advantages, as described later in this chapter, but most current formulations have drawbacks in their limited colloidal stability and longer drying times compared to solvent-borne alkyd paints [Bergenstähl et al., 1996].

Alkyds, an example of which is given in figure 1.1, are highly branched polymers (resins), obtained by a condensation reaction of polyfunctional alcohols and acids (or potential acids), from which their name (alc+ids) derives. They are environmentally friendly polymers, as they are synthesised from oils that are derived from renewable raw materials. They represent a technical improvement over oil paints, which are
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Figure 1.1: An example of synthesis of an alkyd polymer from pentaerythritol, phthalic anhydride and fatty acids, but oils can be used as well. The type and amount of oil used identify the alkyd: a "short oil" alkyd contains less than 40% of oil, a "medium oil" alkyd contains 40 to 55% of oil and a "long oil" alkyd contains more than 55% of oil.

Based on natural un-reacted oil from vegetable and marine sources, however oil paints are degraded by water with comparative ease and they yellow rapidly [Brady, 1987]. Alkyd polymers are widely used by the paint industry because of their versatility and low cost [Martens, 1961]. When they are cast from organic solvents, they produce protective coatings with a high gloss finish. However, concern for health and the environment and resulting new regulations, which are becoming stricter especially in the USA [Vito, 1998], have restricted the amount of organic solvents that are allowed to be used in industry and which are believed to be the primary cause of photochemical smog and ozone pollution. Water-borne systems (e.g. alkyd-in-water emulsions) are becoming popular because they offer a healthier, environmentally-friendly option compared to those based on organic solvents. The majority of commercial water-borne paints are colloidal dispersions of polymer particles in water, formed by emulsion polymerisation. Polymers can be acrylcs, polyurethanes, vinyls,
styrenes, etc., however, these paints are inadequate in applications which require a high gloss or penetration into a porous substrate. In such cases, coatings based on alkyd polymers are still often used, hence, there is a continual need for alkyd coatings.

An alkyd emulsion paint is based on a dispersion of alkyd polymer in water, which contains surfactants to stabilise the alkyd droplets and drier additives to catalyse the oxidative cross-linking of the alkyd polymers. In a paint formulation many more ingredients are present such as pigments, dispersing agents (to stabilise the pigments) and thickeners. Alkyd emulsion paints represent an attractive alternative as they combine the technical advantages of alkyd polymers with the environmental and health benefits of systems free from organic solvents. Nevertheless, the drying and film formation of these paints involve several steps, none of which is yet well understood [Bergenstål et al., 1996]. These include evaporation of the water phase, coalescence of the alkyd droplets, creaming or sedimentation, a possible phase-inversion of the emulsion and oxidative cross-linking of the alkyd polymer to form a hard coating.

As alkyd emulsion paints are relatively “new” systems, there is a lack of information about their film formation in the literature. On the other hand, latex systems have been much studied, and an extensive review on film formation of latex dispersions has been recently published [Keddie, 1997]. In short, when a coating dispersion is deposited on a substrate, evaporation occurs and the particles are gradually brought closer as their concentration increases, until they form a close-packed array. The particles deform under the action of capillary forces and/or surface tension to give a densely-packed array of deformed particles, if the temperature is above the minimum film formation temperature (MFT) of the polymer. Below this critical temperature the dry latex is opaque and powdery. Eventually, diffusion across particle boundaries produces a continuous homogeneous coating. This stage cannot occur below the polymer glass transition temperature ($T_g$), which is the temperature below which the polymer ceases to undergo diffusion and flow, and
behaves like a glass. In alkyd emulsions the droplets coalesce within a few seconds, while - in contrast - the mixing of acrylic chains is slow because of their high molecular weight and high viscosity. Hence, alkyds produce coatings with good protective, optical and penetrating properties compared to acrylic dispersions.

In this thesis, for the first time, different Magnetic Resonance Microscopy techniques have been combined with each other in order to gain further insight into the drying and film formation of alkyd emulsions. Magnetic Resonance Imaging (MRI) exploits a linear magnetic field gradient to spread the NMR resonances of the nuclei in a sample, thereby encoding their spatial position. This technique is generally encountered in medical diagnosis, which primarily benefits from its non-invasive nature. However, MRI is being increasingly used for applications in materials science. In fact, different NMR parameters, such as relaxation times, can be exploited for the generation of image contrasts and therefore to visualise material properties with reasonable spatial, temporal and, if required, spectral resolution [Kimmich, 1997, page 317]. In many materials science applications, high spatial resolution is required and short-lived signals (that is, short spin-spin relaxation times) are usually encountered. Magnetic Resonance Microscopy (MRM) relies on the same principles of MRI, but exploits the miniaturisation of coils and gradient sets [McDonald, 1997]. Only modest power is required to generate short pulses, and low currents give rise to relatively large gradients over small distances, so that spatial resolutions up to a few μm can be achieved. These gradients can be rapidly switched on and off without any loss of signal in the meantime. For solids, characterised by spin-spin relaxation times on the μs scale, conventional MRM is not adequate. Different broad-line techniques have been proposed, including Stray Field Magnetic Resonance Imaging (STRAFI) that exploits the intense magnetic field gradient surrounding a conventional NMR spectrometer. Recently, magnets with intentional permanent gradients have been built for specific applications as described in references [Eidmann et al., 1996, Glover et al., 1999]. Finally, NMR diffusometry allows one to study molecular diffusion not only in liquid but even in highly viscous
samples, such as polymer melts. Furthermore, it is useful in the analysis of the microstructure where statistical information is obtained with a resolution on the micrometer scale.

The primary objective of this thesis is to demonstrate that the combination of liquid state microscopy, diffusometry and broad-line imaging is a very powerful technique, as it can provide far richer information on the drying processes than any other single technique. Because of the complexity of the alkyd emulsion drying process, studies on a different range of emulsions and related systems have been performed to gain further insight into the different steps involved.

Chapter 2 provides a basic introduction to the principles of NMR and MRI with particular consideration of the techniques employed in the work described in the following chapters.

In film formation, when an emulsion is cast on a substrate, creaming (or sedimentation) might occur simultaneously as water evaporates. As a result of the creaming process in oil-in-water emulsions, a cream layer, that is a concentrated emulsion, forms above an aqueous layer. In order to slow down the creaming process, which may affect, among other things, the texture and the visual appearance of food emulsions, thickeners are usually used. However, if too much thickener is added, creaming faster than what is expected is observed. “Predicting” the stability of emulsions is of vital importance in industry. The simplest way to determine the creaming rate in dilute emulsions is by visual observation of the movement of the interface between the cream and the aqueous layer. However, no information about the concentration profiles is obtained and the method is inadequate for concentrated, opaque emulsions. In this case, intrusive techniques (such as sampling the emulsion at different heights) may be necessary and are able to provide information on concentration profiles [Dickinson, 1992, page 87]. Over the past ten years, the use of ultrasound has been developed in order to monitor the creaming profiles of concentrated emulsions. Ultrasonic velocity measurements are non-intrusive and achieve a resolution of the order of mm [Gouldby et al., 1991].
Magnetic Resonance Imaging is a suitable alternative and offers greater resolution. The creaming dynamics in thin films of oil-in-water emulsions has already been studied by Newling and co-workers [Newling et al., 1997b] by using Stray Field Magnetic Resonance Imaging, but this work did not investigate in depth the packing of oil droplets in the cream layer. Therefore, the cream layer in oil-in-water emulsions in bulk samples is investigated, and the results are presented in Chapter 3, with particular emphasis on the effect of the concentration of the thickener.

The idea of determining the droplet size in emulsions by using restricted diffusometry is not new. In this thesis, however, NMR diffusometry is combined with MRM in order to obtain the droplet size distribution as a function of the position in the cream layer, and, at the same time, effort is made to ensure that any other signal apart from that of the oil is suppressed. The results obtained are compared to the model of Pinfield et al. [Pinfield et al., 1994], which predicts the concentration profiles in a polydisperse system of oil droplets undergoing creaming under the effects of only buoyancy and diffusion. A limitation of this model is that it does not take into account the formation of flocs. On the other hand, it has been reported [Hunter, 1998, pages 483-488] that the presence of free polymer in solution can either induce flocculation (depletion flocculation) or stabilise (depletion stabilisation) the droplets depending on their size and the concentration of the polymer. Therefore, both mechanisms can in principle be active in highly polydisperse emulsions, like the ones prepared here.

Chapter 4 presents a study of the dynamics of creaming of one of the emulsions studied earlier. Rates of creaming are obtained and the effective size of the flocs is calculated, leaving no doubt about the effect of the thickener.

The evaporation of water from droplets and coatings is not a trivial problem, as one might expect and so there have been numerous publications, both experimental and theoretical, that have appeared on the subject in the last few years and focused on latex dispersions. Chapter 5 concerns the study of water loss from alkyd emulsion droplets by using Magnetic Resonance Microscopy, so that, for the first
time, both the spatial and temporal dependence of the water concentration are obtained. Such rich information allows one to fully test the current theoretical models [Parisse and Allain, 1996, Routh and Russel, 1998]. As these models were originally proposed to describe the evaporation from hard particle dispersions, experiments on a non-deformable latex dispersion are presented for comparison. Unlike hard systems, alkyd droplets are expected to coalesce as soon as they come into contact, thereby filling all available space during drying. As an alternative to the existing models, a new model, based on lateral diffusion of water, is proposed and is found to be more appropriate in describing the water evaporation from alkyd emulsions.

If the volume fraction of the dispersed phase of an emulsion is varied until a critical concentration is reached, the emulsion is expected to phase-invert, that is to change from an oil-in-water emulsion to a water-in-oil emulsion, or vice-versa. Phase-inversion is characterised by a sudden change in viscosity and in visual appearance. In the literature [Beetsma, 1996], it has been suggested that a phase-inversion may occur during the evaporative drying of alkyd coatings, as indicated by the change in appearance of some coatings over time. The phenomenon is investigated in chapter 6, and results contrary to the current beliefs are observed.

The final process that alkyds undergo is a chemical reaction with the oxygen of the atmosphere, leading to a hard cross-linked coating. This process is common to both solvent- and water-borne systems. The effect of cross-linking is to join together molecules thereby creating larger molecules. Eventually, the whole film can be thought of as consisting of one molecule. As this reaction is slow at room temperature, drier additives are usually added in a paint formulation. Driers are metal soaps being present in paints at quantities generally less than 1%. There are two different types of drier additives: primary driers, which are true catalysts, and secondary or “through” driers. Primary driers, such as cobalt, catalyse the uptake of oxygen and the decomposition of peroxides to free radicals. It is suggested in the literature that they lead to a more rapid drying (or cross-linking) at the surface of
the film than in the lower layers. If the surface dries first, the film will wrinkle when the rest of the film contracts as it hardens. For this reason, the so-called “through” driers, such as zirconium and calcium, are usually added. These are claimed to assist the drying of the lower layers of the paint film by mechanisms which are not yet fully understood. When the two types of driers are “balanced”, shrivelling does not occur and the final film will be smooth and flat [Turner, 1988, pages 154-160]. So far investigations on the action of the different driers have been conducted on bulk samples and on coating surfaces, as in reference [Östberg et al., 1992]. Investigations across the thickness of the film would, undoubtedly, provide precious additional information. In chapter 7, the effect of the aforementioned driers is investigated by using a variant of Stray Field Magnetic Resonance Imaging made particularly suitable for the study of planar films and coatings.
Chapter 2

Principles of NMR

2.1 Historical background

In 1945, Purcell, Torrey and Pound at Harvard University [Purcell et al., 1946] and Bloch, Hansen and Packard at Stanford University [Bloch et al., 1946] independently succeeded in observing the phenomena of Nuclear Magnetic Resonance (NMR) in liquids and in solids for the first time. Since then, the importance of Nuclear Magnetic Resonance has steadily increased, and nowadays high-resolution NMR is an essential tool for chemists, thanks to its element and site specific nature. This status was rewarded in 1991 by the award of the Nobel Prize in Chemistry to Richard Ernst.

In 1973 Lauterbur [Lauterbur, 1973] and Mansfield and Grannel [Mansfield and Grannel, 1973], working independently with liquids and solids, respectively, introduced the idea of performing NMR experiments with spatial resolution. This was the beginning of Magnetic Resonance Imaging (MRI). In present times, MRI is routinely performed in hospitals where it is valued for its non-invasive and non-ionising characteristics. The application of MRI to materials science has only recently started to develop. Different methods have been proposed to study solids and confined liquids, among which Stray Field Magnetic Resonance Imaging
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(STRAFI), introduced by Samoilenko in 1987 [Samoilenko et al., 1987], has come to the fore.

The suggestion that NMR can be used to measure molecular motion goes back to 1950 [Hahn, 1950]. In his seminal paper, Hahn reported that self-diffusion influenced the amplitude of spin-echoes. In 1954 Carr and Purcell [Carr and Purcell, 1954] proposed their multiple echo technique to minimise diffusion effects and, at the same time, suggested a method to measure self-diffusion coefficients in the presence of a constant magnetic field gradient. The introduction of the pulsed-field-gradient methods [Stejskal and Tanner, 1965] gave a boost to NMR diffusometry, which is now extensively used in the study of materials. Recently the use of a constant gradient has been “rediscovered” by Kimmich [Kimmich et al., 1991] for use in the fringe field of super-conductive magnets.

2.2 Nuclear Magnetic Resonance

2.2.1 The NMR experiment

According to quantum theory, a nucleus has an intrinsic angular momentum, or spin, \( I \) of magnitude \( \sqrt{I(I + 1)} \hbar \), where the nuclear spin quantum number \( I \) can be 0, 1/2, 1, 3/2, ... . For all nuclei with an odd atomic mass the value of the spin is an odd integral multiple of 1/2. Among these, \(^{13}\text{C}\) and, in particular, \(^{1}\text{H}\), both having \( I=1/2 \), have been extensively studied. Nuclei with even numbers of both protons and neutrons, like \(^{12}\text{C}\), have zero spins and give no NMR absorptions. The other nuclei possess an integral spin \( I \) with value 1, 2, 3, ...

The possession of both spin and charge confers on the nucleus a magnetic dipole moment \( \mu \), which is proportional to the spin angular momentum \( I \). The operator corresponding to the magnetic moment is

\[
\hat{\mu} = \gamma_N \hbar \hat{I},
\]  

(2.1)
where $\gamma_N$ is the magnetogyric ratio and is an intrinsic property of each type of nucleus.

The component of $I$ along the $z$-axis, $I_z$, has the possible eigenvalues $m_I \hbar$, with the magnetic quantum number $m_I = -I$, $-I + 1$, $..., -1, 1, I$. The corresponding $2I + 1$ energy states are degenerate. This degeneracy can be removed by application of an external magnetic field $B_0$ (the Zeeman effect), thereby splitting each level into its component states, each state having a different $m_I$ value [Levine, 1975, page 51] (see figure 2.1). The Hamiltonian which describes the interaction between the magnetic field $B_0$ and the magnetic moment $\mu$ is represented by

$$\hat{H}_z = -\mu \cdot B_0 = -\gamma_N \hbar B_0 \hat{I}_z,$$  \hspace{1cm} (2.2)

where the second identity applies for the case of $B_0$ oriented along the $z$-axis ($B_0 = B_0 \mathbf{k}$). Therefore, the energy of each level is given by:

$$E(m_I) = -\gamma_N \hbar B_0 m_I$$  \hspace{1cm} (2.3)

and the allowed dipole transitions ($\Delta m_I = \pm 1$) all have an energy $\Delta E = \gamma_N \hbar B_0$. In order to induce transitions between two adjacent spin levels, an oscillating electromagnetic field is applied to the system. Absorption of energy occurs provided that the magnetic vector of the oscillating field is perpendicular to $B_0$ [Carrington and MacLachlan, 1967, page 3] and provided that the angular frequency of the electromagnetic field satisfies the resonance condition

$$\omega_L = \gamma_N B_0.$$  \hspace{1cm} (2.4)

Figure 2.1 shows the transition induced by the electromagnetic field in an isolated nucleus with spin $1/2$.

In an ensemble of $N$ spins at thermal equilibrium, the spins are distributed over the different levels according to the Boltzmann distribution. For the specific case $I = 1/2$, at room temperature and normal laboratory field strengths, there is a small
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Figure 2.1: Nuclear spin states for an isolated spin with \( I = \frac{1}{2} \) and positive \( \gamma_N \) (e.g. \(^1\)H or \(^{13}\)C) in a magnetic field. The lower state with \( m_I = +\frac{1}{2} \), labelled \( \alpha \), corresponds to the situation in which \( B_0 \) and the nuclear moment are parallel; in the upper state (\( m_I = -\frac{1}{2} \), spin \( \beta \)) they are antiparallel. The energy separation of the states depends on the magnitude of the applied magnetic field. For ordinary laboratory magnetic fields the resonance frequency has a magnitude in the radio-frequency (RF) region of the electromagnetic spectrum. The arrow corresponds to the spin transition which generates the NMR signal.

Excess (in the order of \( 10^{-6} - 10^{-5} \)) of spins \( \alpha (m_I = +\frac{1}{2}) \) in the lower level with respect to the upper one (spins \( \beta, m_I = -\frac{1}{2} \)). The relative population is given by

\[
\frac{N_\beta}{N_\alpha} = e^{-\gamma_N \hbar B_0/(k_B T)},
\]  

where \( N_\alpha \) and \( N_\beta \) are the number of nuclei in the low and high energy level, respectively \( (N_\alpha + N_\beta = N) \), \( k_B \) is the Boltzmann constant and \( T \) the absolute temperature. The bulk magnetic moment or magnetisation, \( M \), of a macroscopic sample is the resultant of the individual magnetic moments \( \mu \). At thermal equilibrium, \( M \) is along the \( z \) direction and its magnitude \( M_0 \) is (for nuclei with spin \( I \)):

\[
M_0 = \left[ \frac{N \gamma_N^2 \hbar^2 I (I + 1)}{3 k_B T} \right] B_0,
\]  

where the factor in square brackets is the bulk magnetic susceptibility \( \chi_0 \) of the \( N \) spins. By applying an oscillating magnetic field to the spin system, stimulated transitions from one level to another are induced and the levels soon become equally populated (the probability of spontaneous emission is negligible). However, non-radiative transitions tend to restore the thermal equilibrium, as described later on.
2.2.2 Other nuclear interactions

So far, only Zeeman interaction ($\mathcal{H}_Z$) has been discussed. In reality, as the nuclei are not isolated, but interact with each other and with the neighbouring electrons, the spin Hamiltonian may contain several other interactions and can be written as:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_D + \mathcal{H}_{CS} + \mathcal{H}_S + \mathcal{H}_Q. \quad (2.7)$$

In NMR the Zeeman term $\mathcal{H}_Z$ predominates and the other interactions act as a perturbation of the Zeeman energy levels. The dipole-dipole coupling ($\mathcal{H}_D$) is the strongest interaction and is at the origin of broad lines in solid state NMR. However, this interaction is averaged to zero for rotating molecules in the liquid phase, so that liquid phase NMR is dominated by the chemical shift ($\mathcal{H}_{CS}$) and the scalar ($\mathcal{H}_S$) interactions. These interactions generate the line shifts and splittings characteristic of NMR spectra of liquids. Finally, the quadrupolar interaction, $\mathcal{H}_Q$, is characteristic of nuclei with $I \geq 1$. In this section the different terms of eq. 2.7, with the exception of $\mathcal{H}_Z$, are briefly examined.

The dipolar coupling ($\mathcal{H}_D$)

The dipolar coupling interaction results from the direct through space coupling of one magnetic moment with the magnetic fields generated by its near neighbours, in analogy to the classical interaction between magnetic bars. For an ensemble of nuclear spins, the Hamiltonian is given by

$$\mathcal{H}_D = \sum_{i<j} \frac{\mu_0 \gamma_i \gamma_j}{4\pi} \gamma_i \gamma_j \hbar^2 \left( \frac{\vec{I}_i \cdot \vec{r}_{ij}}{r_{ij}^3} - \frac{3(\vec{I}_i \cdot \hat{r}_{ij})(\vec{I}_j \cdot \hat{r}_{ij})}{r_{ij}^5} \right), \quad (2.8)$$

where $i$ and $j$ indicate the $i$-th and $j$-th nucleus, respectively, joined by the vector $\vec{r}_{ij}$. By rearranging equation 2.8, it can be shown that the dominant terms affecting the lineshape have an angular dependence of the form $(3 \cos^2 \Theta - 1)$, where $\Theta$ is the angle between the interproton vector $\vec{r}_{ij}$ and $B_0$. Consequently, in solids where spins are relatively static and there is a spread of $\Theta$ values, the spectrum is usually a broad,
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featureless resonance. In liquids, the total dipolar Hamiltonian is averaged to zero by molecular motion. The averaging of the lineshape terms involving \( 3 \cos^2 \Theta - 1 \) in particular results in narrow lines. In both solids and liquids the dipolar interaction is an important mechanism for spin relaxation. In NMR spectroscopy of solids, Magic Angle Spinning (MAS) is a common technique. By spinning the sample at an angle \( \Theta = 54.4^\circ \) respect to the magnetic field (referred to as magic angle) the dipolar Hamiltonian is time-averaged to zero and the lines narrow.

The chemical shift \( (\mathcal{H}_{CS}) \)

The chemical shift interaction gives rise to the slightly different resonant frequencies of different nuclei in a molecule. In the presence of the magnetic field \( B_0 \), the electrons in an atom are induced to rotate around the nucleus about the direction of \( B_0 \). The resultant currents generate an additional magnetic field at the nucleus, which is proportional and opposite to \( B_0 \). Therefore, the total effective magnetic field acting on a nuclear magnetic moment can be written as \( B_{\text{eff}} = (1 - \sigma) B_0 \), where \( \sigma \) is the so-called shielding constant. Consequently the Zeeman Hamiltonian (eq. 2.2) has to be altered to:

\[
\mathcal{H}_Z = -\gamma_N \hbar (1 - \sigma) B_0 \hat{I}_z. \tag{2.9}
\]

As the induced magnetic field varies depending on the chemical environment of the atoms, different atoms in a molecule will, in principle, originate different lines. Strictly speaking, since the disposition of electrons in a molecule depends on the orientation of the chemical bonds, the shielding depends on the orientation of the molecule with respect to \( B_0 \). However, in a liquid, as molecules rotate rapidly, \( \sigma \) is actually the average over all orientations of an anisotropic chemical shift tensor.

A large database for organic and inorganic molecules is available, in which the chemical shift is expressed as [Emsley et al., 1965, page 5]

\[
\delta = \left( \frac{\nu - \nu_r}{\nu_0} \right) \times 10^6. \tag{2.10}
\]
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Here, \( \nu \) is the frequency of a spectral line, \( \nu_r \) the frequency of a reference compound and \( \nu_0 \) is the operating frequency of the spectrometer employed. Hence \( \delta \) is independent of \( \nu_0 \) and is expressed in parts per million (ppm). In proton NMR the reference compound, or standard, is normally tetramethylsilane (TMS), whose absorption peak is set to zero. The \(^1\text{H}\) spectrum of most organic molecules is found within 10 ppm of this. Trends in chemical shifts of \(^{13}\text{C}\) are generally similar to those of \(^1\text{H}\), though the range of shift encountered is about 240 ppm [Steinfeld et al., 1991, page 234].

The scalar coupling (\(H_s\))

The scalar, or spin-spin, coupling produces the fine structure observable in high-resolution NMR spectra. It is an intramolecular interaction which acts through the electrons in the chemical bonds and not through space. The interaction between each pair of spins, I and S, in a molecule is described by the isotropic Hamiltonian

\[
H_s = \hbar J \mathbf{I} \cdot \mathbf{S},
\]

where \( J \) is the coupling constant. In short, the first nucleus perturbs the bonding electrons and the electrons in turn produce a small magnetic field at the other nucleus, and so on, through to the next nucleus, generating a splitting in the absorption lines, as shown in figure 2.2. Unlike the chemical shift, the spin-spin coupling effect is independent of the spectrometer frequency and its value is generally expressed in Hz. Coupling constants between protons rarely exceed 20 Hz [Steinfeld et al., 1991, page 177].

The quadrupolar coupling (\(H_Q\))

Nuclei with a spin number \( I \geq 1 \) have an electric quadrupole moment, \( Q \), which arises from the non-spherical distribution of nuclear charge. These nuclei interact with electric field gradients, such as those generated by the valence electrons.
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Figure 2.2: On the right, energy level diagram for a system of two spin-1/2 nuclei, I and S, under the assumption that the difference in chemical shift expressed in Hz, \( \Delta \nu \), is much larger than the coupling constant \( J \). \( \nu_I \) is assumed bigger than \( \nu_S \). The diagram shows the allowed transitions. The effect of the scalar interaction is to slightly shift the energy levels. On the left, schematic first-order NMR spectrum derived from the energy level diagram. The spectrum consists of two doublets, whose component lines are separated by the \( J \) coupling (\( J > 0 \)), and centred at the I and S chemical shift, respectively.

The quadrupolar interaction for an isolated nucleus is given by [Slichter, 1963, page 172]:

\[
\hat{\mathcal{H}}_Q = \frac{e \mathcal{Q}[3\hat{I}_z^2 - \hat{I}_z]}{[4I(2I-1)]} \frac{\partial^2 V}{\partial \hat{z}^2},
\]

(2.12)

where \( V \) is the electrostatic potential at the nucleus and the electric field is assumed having axial geometry. The quadrupolar interaction gives origin to 2\( I \) lines in anisotropic media, while it is averaged to zero in liquids. For quadrupolar nuclei, the quadrupolar interaction often dominates the relaxation mechanism.

2.2.3 The vector model

An NMR experiment consists of three essential stages. First the sample is inserted in an RF coil, placed in the external magnetic field, \( B_0 \). Then, in the most basic NMR experiment an excitation pulse is applied. Finally, the response of the sample spin system to the perturbation, which produces the signal, is observed as current in the coil. A classical description, known as the vector model, allows one to visualise each part of the NMR experiment. Although the vector model has limitations [Freeman, 1997, page 73], it is a powerful tool to describe most NMR experiments.
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Classically, application of an external magnetic field $B_0$ to a magnetic dipole moment $\mu$ produces a torque $T$ on the dipole, $T = \mu \times B_0$. The torque causes the magnetic moment vector to precess at the Larmor frequency $\omega_L = \gamma B_0$ (identical to the frequency obtained with a quantum mechanical approach, eq. 2.4); that is to revolve about the direction of $B_0$, keeping a fixed angle with respect to it. The macroscopic magnetisation $M$ (sum of all the individual nuclear moments $\mu$) behaves similarly and its time evolution in the presence of a magnetic field $B$ is given by the classical equation:

$$\frac{dM}{dt} = \gamma_N (M \times B). \quad (2.13)$$

When $B = B_0$, the solution of eq. 2.13 corresponds to a precessional motion about $B_0$ at the rate $\omega_L$. At Boltzmann equilibrium the resultant net magnetisation is along the magnetic field direction ($M = M_0 k$). The displacement of the magnetisation $M$ ($M = M_x i + M_y j + M_z k$) from its equilibrium position is obtained by applying a small transverse linearly oscillating RF field, $2B_1 \cos(\omega t)$. This field can be thought of as two components rotating in opposite directions with angular velocity $\pm \omega$ and, normally, the component that rotates in the opposite sense to the nuclear precession is neglected [Freeman, 1997, page 23]. $B_1$ interacts with $M$ to produce a torque which tilts it away from its equilibrium orientation towards the $xy$-plane (according to eq. 2.13) and has an appreciable effect on the system when $\omega = \omega_L$ [Harris, 1986, page 69]. In this case, the bulk magnetisation rotates about the $B_1$ field at an angular frequency $\gamma_N B_1$ (rad·s$^{-1}$) and, at the same time, it precesses about the magnetic field $B_0$ at a frequency $\gamma_N B_0$, as shown in figure 2.3 (a). As a result, the bulk magnetisation spirals down around the $z$ direction. This coordinate system is usually referred to as the laboratory frame. This rather complex problem can be reformulated in a new coordinate system (the so-called rotating frame) that rotates about the $z$-axis at a frequency $\omega_L$ (or, in the more general case at $\omega$). In this new reference system, the motion of the nuclear magnetisation is easier to follow: $B_0$ is transformed to zero when $\omega = \omega_L$, $B_1$ is stationary and $M$ is apparently precessing only about $B_1$ (figure 2.3 (b)). If the $B_1$ field is not on resonance the picture is more
complex and in the rotating frame there is a residual field \( \Delta B = (\omega_L - \omega)/\gamma_N \) along the \( z \) direction. Therefore, the magnetisation precesses along the vector sum of this residual field and \( B_1 \) [Callaghan, 1995a, page 37]. In describing NMR experiments, the transformation into the rotating frame is usually taken for granted. The \( B_1 \) field is applied as a pulse of duration \( t_p \) (a few \( \mu s \) long) giving a rotation through an angle \( \Theta \) of \( \gamma_N B_1 t_p \) radians. The direction, or phase, of \( B_1 \) is specified.

![Figure 2.3: Evolution of the magnetisation \( M \) under the effect of both \( B_0 \) and \( B_1 \) in (a) the laboratory frame and (b) the rotating frame (\( \omega = \omega_L \)). In both cases only the component of \( B_1 \) which interacts constructively with the nuclear spins is shown. The other component, which rotates at \( -\omega \) in the laboratory frame, rotates at twice the Larmor frequency in the rotating frame and can be neglected in both cases.](image)

After excitation, the system returns to thermal equilibrium, that is \( M_z \) increases towards \( M_0 \), while \( M_x \) and \( M_y \) decrease to zero, as shown in figure 2.4. Both processes are assumed to be first order and are characterised by the spin-lattice (or longitudinal) relaxation time \( T_1 \) and the spin-spin (or transverse) relaxation time \( T_2 \), respectively. Changes in \( M_z \) need an exchange of energy with the “surroundings”-the lattice. Changes in \( M_x \) and \( M_y \) do not alter the total energy of the spin system, and correspond to the decay of phase coherence between the individual spins.

The precessing magnetisation in the \( xy \)-plane of the laboratory frame induces an oscillating current in a coil of wire wound around the sample along an axis perpendicular to \( B_0 \). This is the NMR signal. The plot of the signal intensity versus time is referred to as free induction decay (FID). By applying a Fourier transformation to the time-domain data, frequency-domain data, which constitute the NMR spectrum, are obtained. For high-resolution spectra, the lines are
2.2.4 Bloch equations

The effect of relaxation and Larmor precession can be combined in a set of phenomenological equations, known as the Bloch equations [Bloch, 1946]:

\[
\begin{align*}
\frac{dM_x}{dt} &= \omega_L M_y - \frac{M_x}{T_2} \\
\frac{dM_y}{dt} &= -\omega_L M_x - \frac{M_y}{T_2} \\
\frac{dM_z}{dt} &= - \frac{M_z - M_0}{T_1}
\end{align*}
\] (2.14)

In the laboratory frame, the spin system performs a damped precession in which the transverse components of the magnetisation decay to zero with a characteristic time $T_2$, while the $z$ component relaxes towards its equilibrium value $M_0$ (given by eq. 2.6) with a decay time $T_1$.

2.2.5 Spin relaxation theory

For nuclei with spins 1/2, the dominant interaction causing spin relaxation arises from the dipolar Hamiltonian (eq. 2.8). As described in section 2.2.2, in liquids
the dipolar interaction is averaged out by molecular tumbling. However, as molecules randomly rotate and diffuse, any nuclear magnetic moment experiences a rapidly fluctuating magnetic field generated by neighbouring nuclear magnetic moments. The original description of the effect of these fluctuations in the so-called fast-motion regime was given by Bloembergen, Purcell and Pound [Bloembergen et al., 1948], after whom the model is commonly named: BPP theory. Further developments are due to Wangsness and Bloch [Wangsness and Bloch, 1953] and Redfield [Redfield, 1965], hence the BWR theory.

The autocorrelation function of a random force $f(t)$ which fluctuates about a mean value of zero, is given by $G(\tau) = \overline{f^*(t + \tau)f(t)}$ and measures the persistence of the fluctuations [Carrington and MacLachlan, 1967, pages 184-185]. The spectral density of $f(t)$ is the Fourier transform of the autocorrelation function, that is $J(\omega) = \int_{-\infty}^{\infty} G(\tau) e^{-i\omega \tau} d\tau$. Any random perturbation of the local field experienced by a spin can be thought of as containing many fluctuating components oscillating at different frequencies. Relaxation times depend on the spectral densities of this perturbation oscillating at the appropriate transition frequency. A detailed description of the aforementioned theories can be found elsewhere [Abragam, 1961, Slichter, 1963]. In this context, only the results for a dipolar-coupled spin pair system are briefly summarised.

The spin-lattice relaxation time $T_1$ involves transitions between energy levels, which are induced by fluctuating magnetic fields at frequencies of $\omega_L$ and $2\omega_L$ in the $xy$-plane. The spectral density of the fluctuations is denoted $J(\omega)$. The dependence of $T_1$ on $J(\omega_L)$ and $J(2\omega_L)$ is given by:

$$\frac{1}{T_1} = \frac{3}{2} \left( \frac{\mu_0}{4\pi} \right)^2 \gamma_N^2 \hbar^2 I (I + 1) \left[ J^{(1)}(\omega_L) + J^{(2)}(2\omega_L) \right].$$

(2.15)

$T_2$ relaxation is related to linewidth. It can occur under the influence of static magnetic fields. The component of these magnetic fields along the $z$ direction causes transitions between degenerate levels, called flip-flop transitions, so that a term depending on $J(0)$ is included in the expression for $T_2$. Besides this contribution, $T_2$
relaxation also contains a term related to $T_1$ relaxation. The spin-lattice relaxation time leads to a spread in frequency of the energy levels through the uncertainty principle. Hence $T_2$ contains a lifetime broadening term. Combining these two contributions, the expression for $T_2^{-1}$ is:

$$\frac{1}{T_2} = \frac{3}{2} \left( \frac{\mu_0}{4\pi} \right)^2 \gamma^2 \hbar^2 I (I + 1) \left[ \frac{1}{4} J^{(0)}(0) + \frac{5}{2} J^{(1)}(\omega_L) + \frac{1}{4} J^{(2)}(2\omega_L) \right]. \quad (2.16)$$

In order to estimate $T_1$ and $T_2$ (eqs. 2.15 and 2.16), it is necessary to evaluate the spectral density functions for the specific system of interest. The simplest example, which goes back to the origin of BPP theory, is so-called isotropic rotational diffusion. Taking water as an example, the relaxation mechanism arises mainly from the interaction between protons belonging to the same molecule. The molecule is assumed rigid and the motion of one proton relative to the other is a kind of random rotational motion. For this particular case, the autocorrelation function decays exponentially with a time constant $\tau_c$, called the correlation time. $T_1$ and $T_2$ depends on $\tau_c$, which can be loosely associated with the average time between reorientations of the molecule. The dependence of the relaxation times $T_1$ and $T_2$ on $\tau_c$ is shown in fig. 2.5. In liquids, characterised by a short $\tau_c$ ($\omega_L\tau_c \ll 1$), $T_1$ and $T_2$ are equal and long. Lines are narrow: the dipolar Hamiltonian is completely averaged to zero and this situation is usually referred to as "extreme narrowing". At $\omega_L\tau_c \approx 1$, $T_1$ passes through a minimum. For long $\tau_c$, characteristic of less mobile samples, $\omega_L\tau_c > 1$ and $T_1$ and $T_2$ diverge. In rigid systems, $T_2$ is of the order of $\mu s$ and other approaches are necessary for the treatment of the transverse magnetisation, the most elementary of which is the Anderson and Weiss (AW) formalism [Anderson and Weiss, 1953].

Additional interactions, such as the quadrupolar interaction (equation 2.12), the scalar interaction (equation 2.11), the chemical-shift anisotropy, the spin-rotation interaction and the presence of paramagnetic species are additional effective relaxation mechanisms.
Figure 2.5: The relaxation time constants $T_1$ (solid line) and $T_2$ (broken line) according to the BPP theory, as a function of $\omega_L \tau_c$. The Larmor frequency $\omega_L$ is fixed at 400 MHz and the internuclear separation is fixed at 1.5 Å. $T_1$ and $T_2$ are obtained by using $J^0(\omega) = \left(\frac{24}{15\pi^2}_j^2\right) \left(\frac{\gamma}{1+\omega^2\tau_c^2}\right)$, $J^1(\omega) = \left(\frac{4}{15\pi^2}_j^2\right) \left(\frac{\gamma}{1+\omega^2\tau_c^2}\right)$ and $J^{(2)}(\omega) = \left(\frac{16}{15\pi^2}_j^2\right) \left(\frac{\gamma}{1+\omega^2\tau_c^2}\right)$. For $\omega_L \tau_c \gg 1$ the BPP theory fails in describing $T_2$, which tends towards $\frac{8\pi^2 r_0^2}{(\mu_0 \gamma^2 \hbar)}$. The trends of $T_1$ and $T_2$, though strictly valid for the specific case described in the text, are a good “guess” for most liquid systems.

2.2.6 Pulse sequences

In section 2.2.3 the effect of a single pulse on a spin system was described. The Fourier transform of the FID yields an NMR spectrum which already contains precious information about the spin system, such as chemical shift and $J$ couplings in liquid phase. However, a series of pulses can be combined in such a way to provide new information about the spin system. This section presents several pulse sequences that are a useful tool in the measurement of relaxation times. Later on, the same pulse sequences will be combined with the use of magnetic field gradients.

Spin-echo and measurement of $T_2$

The pioneering work of Hahn in 1950 [Hahn, 1950] opened up a whole class of experiments utilising spin-echoes. A detailed theoretical description of spin-echoes is reported in the book by Kimmich [Kimmich, 1997, pages 1-75], while a more
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Figure 2.6: Carr-Purcell spin-echo experiment. The scheme at the top represents the two RF pulses and an envelope of the expected NMR signal. The schematic diagram at the bottom shows the evolution of six representative isochromats (the effect of \( T_2 \) relaxation is not shown). Immediately after the \( (\pi/2)_x \) pulse all isochromats are aligned along the \( y \)-axis. During the time interval \( \tau \), the isochromats precess at their own frequency and, consequently, they fan out. The following \( \pi_x \) pulse rotates the vectors into their mirror positions with respect to the \( xz \)-plane and at time \( 2\tau \) an echo is formed along the \( -y \)-axis. In the Meiboom-Gill modification the \( \pi \) pulse is applied along the \( y \)-axis, generating the echo along the \( +y \)-axis. Spin-echoes refocus chemical shift interactions, but not homonuclear \( J \) couplings.

intuitive approach can be found in Freeman [Freeman, 1997, pages 108-142].

The basic spin-echo experiment is shown in fig. 2.6. In a realistic situation, the macroscopic sample contains many spin isochromats, each of which is an ensemble of spins that experience exactly the same applied magnetic field. Differences in the magnetic field experienced are caused by the inhomogeneity of \( B_0 \) or as a result of magnetic field gradients applied deliberately. Immediately after the \( (\pi/2)_z \) pulse all spin isochromats are aligned, but during the time interval \( \tau \) different spin isochromats precess at different frequencies leading to a phase dispersion, so that the observed FID decays, this occurring in a characteristic time \( T^*_2 \). By applying a \( \pi \) RF pulse it is possible to reverse the isochromat phases. The spin isochromats are refocused at \( 2\tau \) and an echo is observed. The limit to this procedure is given by true spin-spin relaxation, which causes an irreversible attenuation of the echo amplitude, according
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The time constant $T_2$ can be measured by creating echoes with variable $\tau$ and measuring the decay of the amplitude. Since diffusion effects become more pronounced as $\tau$ increases, the CPMG [Carr and Purcell, 1954, Meiboom and Gill, 1958] pulse sequence,

$$(\pi/2)_x - \tau - [\pi_y - \tau - (\text{echo observe})]_n,$$

is a preferable alternative and allows one the measurement of $T_2$ in a single experiment. The $\pi_y$ pulses generate spin-echoes along the $+y$-axis at $2\pi\tau$ and, if $\tau$ is short enough relative to the diffusion time-scale, the amplitude of the maximum of the echo is modulated by the $T_2$ relaxation only. $\pi_y$ pulses and, even better, phase-alternated $\pi_y$ pulses are here preferred to $\pi_x$ pulses in order to minimise errors.

**Hahn-echo and stimulated-echo**

As an alternative to the spin-echo sequence, a three pulse sequence can be used to generate echoes, as shown in fig. 2.7. If the time interval $\tau$ is sufficiently long, the spin isochromats are uniformly distributed in the $xy$-plane and the FID has completely decayed. The second $(\pi/2)_x$ pulse rotates the $y$ component of the spin isochromats along the $z$-axis, while the $x$ components are unaffected by this pulse. The $x$ components form the Hahn- (or primary) echo at time $2\tau$. The $y$ components are stored along $z$ where they are subject only to $T_1$ relaxation. By applying a third $\pi/2$ pulse, the stored magnetisation is recalled in the transverse plane leading to the stimulated-echo formation at time $\tau$ after the last RF pulse. In each case, only one half of the initial magnetisation is refocused.

The stimulated-echo can be sampled when it is necessary to store the magnetisation for a long time, as described in section 2.5.2. As the magnetisation is stored along
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Fig. 2.7: Hahn spin-echo envelopes produced by three RF pulses. Only one primary echo and the stimulated-echo are shown. The primary echo is produced after the first two echoes at time $t=2\tau$, while the stimulated-echo occurs after the third pulse at $t=\tau+T$. At the bottom, a schematic representation of the formation of the stimulated-echo ($T_2$ relaxation is neglected), in the case in which spoiler gradients are applied during the $z$-storage between the second and third RF pulse.

The $z$-axis, the pulse sequence exploits the relatively long $T_1$ time, compared to $T_2$ time, of many materials.

Spin-locking and the relaxation time $T_{1\rho}$

If after a $(\pi/2)_x$ pulse, the $B_1$ field is not switched off but its phase is shifted by $\pi/2$ (spin-lock pulse) so that it is aligned with the magnetisation along $+y$ for a time $\tau$ (see figure 2.8), the magnetisation is said to be spin-locked. In the rotating frame the magnetisation will experience the $B_1$ field only and will undergo no precession. It will, however, decay with a time constant $T_{1\rho}$, the spin-lattice relaxation time in the rotating frame, according to:

$$M(\tau) = M_0 \exp (-\tau/T_{1\rho}).$$  \hspace{1cm} (2.18)

Values of $T_{1\rho}$ are obtained by measurement of the magnetisation at the end of the spin-locking pulse and repetition of the experiment varying $\tau$. 

Figure 2.8: (a) Spin-lock of the magnetisation along the $y$-axis. (b) On the top, RF pulse scheme to spin-lock the magnetisation. The spin-locking pulse (SL) is $\pi/2$ phase-shifted to the $\pi/2$ preparation pulse. In double-resonance experiments of cross-polarisation the spin-locking pulse of the I spins is matched to the contact pulse (CP) of the S spins according to the Hartmann-Hahn condition.

Spin-locking is the mode of preparation used in the Hartmann-Hahn experiment [Hartmann and Hahn, 1962], which allows the transfer of magnetisation from more NMR favourable spins (more abundant and/or with a larger magnitude of $\gamma_N$) to less favourable NMR spins (rare and/or with a smaller magnitude of $\gamma_N$). In a two-spin (I and S) system, the I spins (for example, $^1$H) are locked along an RF field $B_1$ and a second RF field $B_2$ is applied to the S spins (for example, $^{13}$C), as shown in fig. 2.8 (b). If the Hartmann-Hahn condition

$$\gamma_{NI} B_1 = \gamma_{NS} B_2$$

is satisfied in the respective rotating frames (that is, the rotating-frame frequencies "match" each other), then flip-flop transitions take place and coherence can be transferred between the two species. In solid state, the I and S spins interact through dipolar interactions, while in liquids indirect spin-spin or $J$ coupling prevails. In the latter case one speaks of $J$ cross polarisation.

**Methods for measuring $T_1$**

The stimulated-echo allows the determination of the relaxation time $T_1$ from the dependence of the stimulated-echo amplitude on the interval between the second
and third RF pulse (see fig. 2.7).

A popular technique for measuring $T_1$ is inversion recovery [Derome, 1987, pages 86-89]:

\[ \pi_x - \tau - (\pi/2)_x - \text{Acquisition}. \]

The idea is to invert the $z$ magnetisation with a $\pi_x$ pulse, then wait for a variable time $\tau$ during which the magnetisation relaxes back towards the $+z$-axis, and finally apply a $(\pi/2)_x$ pulse and acquire the NMR signal. For $\tau < T_1/\ln 2$ the effect of the two pulses is to leave the magnetisation along the $-y$-axis generating a negative peak if the spectra are phase-correct so that $+y$ is positive. From the intensity of the peaks, $T_1$ is calculated according to

\[ M(\tau) = M_0 [1 - 2 \exp (-\tau/T_1)]. \quad (2.20) \]

An alternative quicker method, referred to as saturation recovery, employs a series of closely spaced $(\pi/2)_x$ pulses to saturate the sample [Markley et al., 1971]:

\[ \pi/2 - \pi/2 - \pi/2... - \tau - \pi/2 - \text{Acquisition}. \]

The system then returns towards equilibrium. At a time $\tau$ a last $\pi/2$ pulse is applied and the resulting FID recorded. The recovery of the magnetisation at $\tau$ is of the form:

\[ M(\tau) = M_0 [1 - \exp (-\tau/T_1)]. \quad (2.21) \]

### 2.3 Magnetic Resonance Imaging

In section 2.2.2 it was described how nuclei in different chemical environments experience slightly different magnetic fields to generate different absorption lines. On the other hand, if a magnetic field gradient is applied to a sample containing
equivalent nuclei, it is possible to encode spatial information along the gradient direction. The case of magnetically non-equivalent nuclei is discussed in section 2.3.1.

In the presence of a magnetic field gradient \( \mathbf{G} = \nabla B_0 = (\partial B_0 / \partial x, \partial B_0 / \partial y, \partial B_0 / \partial z) \), the Larmor frequency becomes a function of the position \( \mathbf{r} \), that is

\[
\omega_L(\mathbf{r}) = \gamma_N B_0 + \gamma_N \mathbf{G} \cdot \mathbf{r}.
\]  

(2.22)

Mansfield and Granell in their original paper in 1973 [Mansfield and Granell, 1973] introduced the formalism of a “reciprocal space”, called \( \mathbf{k} \)-space. The wave vector \( \mathbf{k} \) is defined as the Fourier conjugate to the nuclear spin coordinate \( \mathbf{r} \) and for a constant magnetic field gradient is given by:

\[
\mathbf{k} = \frac{1}{2\pi} \gamma_N \mathbf{G} t.
\]  

(2.23)

Therefore, \( \mathbf{k} \) is determined by the imaging gradients \( G_x, G_y, G_z \), and the encoding time \( t \), during which the magnetic gradients are effective. The time domain signal encoded in all three dimensions is given by the function

\[
S(\mathbf{k}) = \int \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{k} \cdot \mathbf{r}) d\mathbf{r},
\]  

(2.24)

where \( \rho(\mathbf{r}) \) is the spatial distribution of the spin density within the sample, weighted by relaxation, and the integral is over the sample volume. By applying a three-fold Fourier transformation from the reciprocal \( \mathbf{k} \) to real space \( \mathbf{r} \), the spatial distribution of the spins, that is an image, is obtained:

\[
\rho(\mathbf{r}) = \int \int S(\mathbf{k}) \exp(-2\pi i \mathbf{k} \cdot \mathbf{r}) dk.
\]  

(2.25)

Acquisition of the time domain signal is usually visualised as sampling \( \mathbf{k} \)-space. Figure 2.9 shows a typical RF and gradient pulse sequence for two-dimensional \( \mathbf{k} \)-space imaging, which consists of a slice selection, a phase encoding and a frequency encoding step. This structure is common to many schemes for NMR imaging of an object slice.
Figure 2.9: Pulse sequence diagram scheme for a two-dimensional spin-echo imaging experiment. A spin-echo RF pulse sequence generates the signal to be sampled at a time $2\tau$. The time at which the echo occurs is usually called echo time, $T_E$. The first RF pulse is a suitable soft pulse applied in the presence of the slice selection gradient $G_S$. The phase-encoding gradient $G_P$ is incremented in a series of subsequent transients (phase direction). The spin echo is acquired in the presence of a frequency-encoding gradient, $G_R$ (read direction). If only the read-out gradient $G_R$ is applied, a one-dimensional image, generally termed a profile, is obtained.

**Slice selection**

The slice to be imaged is selected by applying a narrow-band frequency-selective (or "soft") pulse in the presence of a magnetic field gradient $G_S$, so that the pulse becomes spatially-selective. If the gradient is assumed in the $z$ direction ($G_S = G_z$), an orthogonal slice of width depending on the length of the RF pulse and the strength of the gradient applied is selected. The slice position is controlled by adjusting the frequency offset. Ideally, the excitation profile should have sharp edges, in order to obtain a signal from the selected slice with minimum contamination by signals from adjacent regions. It should also be uniform within the slice. A treatment of the slice selection theory by soft pulses can be found elsewhere [Kimmich, 1997, pages 238-246] [Callaghan, 1995a, pages 98-117], and leads to two main conclusions. First, the profile of the excited slice is directly determined by the Fourier transform of the RF pulse envelope function. Truncated sinc-function pulse envelopes are often used because the corresponding profile is approximately rectangular. Second, a
negative gradient of magnitude $G_x$ applied for 1/2 of the duration of the pulse, or of magnitude $1/2 G_x$ applied for a time equal to the duration of the pulse, is necessary to rephase the spin isochromats, after they have experienced the gradient $G_x$. Curiously, \pi soft pulses are found to be self-refoocusing [Callaghan, 1995a, page 109]. More complicated pulses which are self-refoocusing and excite "almost" rectangular slices are reported in literature, such as the BURP pulses [Geen and Freeman, 1991]. In fig. 2.9 the first pulse of the spin echo is made soft and used for the slice selection.

**Phase encoding**

After the slice selection, a phase-encoding gradient $G_P$, assumed in the $y$ direction ($G_P=G_y$), is commonly applied for a fixed length of time ($t_y$). It is stepped through a range of gradient amplitudes in subsequent transients of the experiment. The effect of $G_P$ is to introduce a local phase shift $\phi$, depending on the $y$ coordinate, according to $\phi(t_y, y) = \gamma_N G_y t_y y = 2\pi k_y y$. In the absence of other gradients, the spin isochromats assume a spiral appearance along the $y$ direction of the rotating reference frame [Morris, 1986, pages 164-166], after which this imaging technique has been named the "spin-warp" method [Edelstein et al., 1980].

**Frequency encoding**

Finally, the NMR signal is sampled in the presence of a read-out gradient, $G_R$ assumed along the $x$ direction ($G_R=G_z$). The signal is therefore mapped along the positive $x$-axis in k-space ($k_x = 1/(2\pi) \gamma_N G_z t_x$) at the intercept along the $y$-axis set by the phase evolution. As the read gradient tends to dephase the coherences before the echo is formed, a gradient pulse of length 1/2 of $t_x$ is applied before the inversion RF pulse in order to compensate the first half of the read gradient (see fig. 2.9). Consequently, an echo with maximum at $2\tau$ is obtained and the whole $x$-axis in k-space is sampled. By varying the amplitude of $G_P$ during different transients of the sequence, all k-space can be probed. In fig. 2.9 the compensating gradient
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has a positive magnitude because of the presence of the $\pi$ RF pulse. A popular alternative to the spin-echo imaging sequence is the gradient-echo sequence, in which the refocusing of the magnetisation is achieved by reversing the sense of the first read gradient pulse, so that an echo appears without applying any $\pi$ RF pulse.

**Image resolution, contrasts and artefacts**

The spatial resolution achievable in MRI is limited by two main factors: $T_2$ and diffusion. The former limits the resolution in the read direction to $\Delta x_{\text{best}} = 2\pi/(\gamma_N G_x T_2)$. The latter attenuates the signal according to $\exp(-\gamma_N^2 G_x^2 t_x^2 D/3)$ during the read-out time $t_x$, and yields $\Delta x_{\text{best}} \approx 2.6[D/(\gamma_N G_x)]^{1/3}$ [Goerke et al., 1999]. The presence of internal gradients due to heterogeneity of the sample makes the diffusive broadening worse.

The power of MRI is the large range of image contrasts available using the technique. All NMR parameters, such as relaxation times and chemical shift, can, in principle, be encoded, visualised and mapped. $T_2$ relaxation contrast is, indeed, a natural consequence of the spin-warp imaging sequence.

The quality of the image is affected by numerous parameters. Artefacts can appear, for example, as a consequence of magnetic field and susceptibility inhomogeneity, chemical shift and motion of the spins during the experiment.

### 2.3.1 Chemically resolved imaging

If the NMR spectrum consists of more than one line and their separation is larger than one pixel, image artefacts appear [Callaghan, 1995a, pages 141-143, 278-287]. In the simplest case of two main resonances, as in a system of water and oil, the chemical shift leads to two displaced images, one for each of the two chemical sites. There are several methods available which enable one to obtain separate images from different NMR resonances. The easiest approach to obtain chemically selective images is to make one of the excitation pulses a soft pulse applied in absence of
gradients and to use the other pulse for slice selection. A more sophisticated, but time-consuming approach is obtained by introducing a fourth spectral dimension as in chemical-shift imaging (CSI) [Maudsley et al., 1983]. All spatial dimensions are phase-encoded and the NMR signal is acquired in absence of magnetic field gradients to yield an NMR spectrum for each single point in k-space. Phase-encoded chemical shift imaging is a generalisation of the original method proposed by Dixon [Dixon, 1984], in which the chemical shift is phase-encoded rather than frequency-encoded, as described by Newling et al. [Newling et al., 1997a].

Cyclic $J$ cross polarisation (CYCLCROP) edited imaging represents a reliable, robust and convenient alternative [Heidenreich et al., 1998b] to the previous methods and offers a higher selectivity in chemical shift as it exploits the wider chemical shift range of $^{13}$C with respect to $^1$H (see section 2.2.2). This imaging technique can provide a higher sensitivity compared to the more conventional direct $^{13}$C imaging. The pulse sequence has been implemented by Kimmich and his collaborators [Kunze and Kimmich, 1994] and has already been successfully applied in the study of sugar metabolism [Heidenreich et al., 1998a] and in the selective determination of elastomers in polymer mixtures [Spyros et al., 1998]. It is composed of two modules: an editing part and an imaging part. The latter can be, for example, the spin-echo imaging sequence. The former, which serves to select a single resonance from a specific CH$_n$ group of a molecule while suppressing all other resonances, is now briefly described.

**CYCLCROP editing sequence**

The CYCLCROP editing sequence is shown in fig. 2.10 and consists of a forward transfer of magnetisation from one or more protons (I spins) to the $J$ coupled $^{13}$C (S spins) and in a backward step from the $^{13}$C to the $J$ coupled protons. Each step is composed of a spin-locking pulse (SL) on one side and a contact pulse (CP) on the other. After having transferred the magnetisation from the protons to the carbon spins, the carbon magnetisation is stored along the z direction. All residual proton
spin resonances are saturated by a comb of pulses (at the resonance of the proton spins) in combination with spoiler gradient pulses. The carbon spin magnetisation is then spin-locked again and the polarisation is transferred back to the directly $J$ coupled proton spins, where it can be used for imaging or spectroscopic applications.

**Figure 2.10:** The CYCLCROP editing sequence consisting of a $^1$H $\rightarrow$ $^{13}$C $\rightarrow$ $^1$H polarisation transfer. SL is the spin-lock RF pulse and CP is the contact RF pulse. $^1$H are typical I spins and $^{13}$C S spins. For effective polarisation transfer the contact time $\tau$ (duration of the SL and CP pulses) is optimised according to the chemical shift, coupling constant $J$ and number of protons in the selected molecular group, as described in the text.

The transfer of polarisation is possible if the radiofrequencies applied satisfy the Hartmann-Hahn conditions (see equation 2.19) for the selected $^{13}$CH$_n$ group. Experimentally, the irradiation frequencies for the proton and the carbon channels are set on-resonance with respect to the resonances of the nuclei of the selected group. Moreover, the optimum contact time $\tau$, that is the duration of the spin-locking and cross-polarisation pulses, depends on the spin-spin coupling constant $J$. 

\[
\begin{array}{c}
\text{(RF)}_1 \\
\text{(RF)}_2
\end{array}
\]

\[
\text{G} \quad 
\]

\[
\begin{array}{c}
\text{SL} \quad \cdots \quad \text{CP}
\end{array}
\]

\[
\begin{array}{c}
\text{(RF)}_1 \\
\text{(RF)}_2
\end{array}
\]

\[
\text{G} \\
\]

\[
\text{SL} \quad \cdots \quad \text{CP}
\]
and on the number of protons in the selected molecular group:

\[
\tau = \begin{cases} 
  J^{-1} & \text{for a CH group} \\
  (\sqrt{2}J)^{-1} & \text{for a CH}_2 \text{ group} \\
  \approx 0.61J^{-1} & \text{for a CH}_3 \text{ group} 
\end{cases}
\]

Figure 2.11: Two different cross-polarisation schemes: (a) Mismatch Optimised IS Transfer (MOIST), (b) basic Pulsed Rotating Frame trAnsfer sequence with WiNdows (PRAWN). The total cross-polarisation time for PRAWN is \( \tau = m(\tau_w + \tau_s) \)
and the flip angles \( \Theta \) satisfy the condition \( m\Theta = 2\pi \).

However, the basic transfer of polarisation in figure 2.10 suffers from some limitations as it is susceptible to inaccurate adjustments of the RF amplitudes and to inhomogeneity in the sample. In order to minimise any Hartmann-Hahn mismatch effects, the MOIST modification [Levitt, 1991] of the cross-polarisation transfer can be used. In this variant, shown in fig. 2.11 (a), the SL and CP pulses are divided into consecutive intervals which have \( \pi \)-shifted phases. Figure 2.11(b) presents another cross-polarisation scheme, called PRAWN (Pulsed Rotating Frame trAnsfer sequence with WiNdows), which employs a comb of \( m \) short pulses \( \Theta \) of duration \( \tau_w \) separated one from another by a delay \( \tau_s \). Not only is this scheme characterised by a useful degree of tolerance to the Hartmann-Hahn mismatch but by a very low RF power deposition, but it is adaptable and can be easily implemented for a variety of applications [Chandrakumar and Kimmich, 1999]. For example, in the PRAWN-\( \pi \) version, a \( \pi \) pulse is inserted in the middle of every \( (\Theta - \tau_s) \) segment. This scheme
allows the bandwidth of the Hartmann-Hahn transfer to be substantially increased. PRAWN is the most commonly used variant.

2.4 Broad-line magnetic resonance imaging

"Conventional" MRI cannot cope with the broad lines of solids, which originate from the anisotropy of the quadrupolar, chemical shift and, in particular, dipolar interactions, as described in section 2.2.2. Narrowing the lines using MAS or similar approaches is the most obvious method, but not the optimum one, as the aforementioned interactions are a major source of information. Susceptibility broadening is related to the heterogeneity of the sample and affects confined liquids as well, such as those in porous media. In both cases, one can employ broad-line MRI techniques, which make use of large gradients. Three techniques have been particularly successful: single-point imaging (SPI) and its implementation SPRITE [Balcombe et al., 1996], broad-line gradient-echo imaging [Cottrell et al., 1990, McDonald et al., 1993, Mallett et al., 1996] and Stray Field Magnetic Resonance Imaging [Samoilenko et al., 1987, Samoilenko et al., 1988]. The last offers an improvement in resolution of one or two orders of magnitude and has proved to be suitable in the study of solids, semi-solids, confined liquids and systems containing both liquid and solid components changing with time. An exhaustive description of the technique and its applications can be found in the reviews of McDonald and his collaborators [McDonald, 1995, McDonald, 1997, McDonald and Newling, 1998], while comprehensive reviews on solid state imaging methodologies in general are by Jezzard et al. [Jezzard et al., 1991] and by Blümler and Blümich [Blümler and Blümich, 1994].
2.4.1 Stray Field Magnetic Resonance Imaging (STRAFI)

Stray Field Magnetic Resonance Imaging (STRAFI) exploits the very large magnetic field gradient available in the fringe or stray field of a super-conductive magnet. With gradients of the order of 60 T/m, even extremely short RF pulses are soft and, therefore, slice-selective. As a consequence, it is not possible to frequency encode spatial information along the gradient direction. Rather the NMR signal characteristic of a single slice is acquired. Then, in the basic implementation of the technique, the sample is mechanically moved step by step through the gradient and the process repeated for the next slice so as to build up a magnetisation profile, slice by slice. In this way a data set representing the projection of the object along the gradient direction is obtained (no Fourier transformation is necessary). Because of the presence of such a strong gradient, an FID is usually not observed and the NMR signal is acquired in the form of an echo (or train of echoes). The slice width is inversely proportional to the pulse length $t_p$ and is given by: $\Delta z = (\sqrt{3} \pi)/(t_p \gamma_N G_z)$, where $G_z$ is the gradient strength. This determines the profile resolution.

The major strength and, at the same time, drawback of the technique is the presence of a large constant gradient along one specific direction. First, STRAFI does not offer the same versatility of liquid state MRI and the large frequency bandwidth associated with the large gradient is not ideal to the study of liquids, as the excess bandwidth leads to reduced signal-to-noise [McDonald and Newling, 1998]. However, STRAFI can be the only option to look at solids and liquids at the same time. Second, in order to obtain a 2D or 3D image, the sample needs to be turned along the gradient direction to sample point by point $k$-space and a backprojection procedure [Lauterbur, 1973] is necessary to reconstruct the image. To counter such a long procedure, an appropriate sample preparation, which makes the sample invariant in the $xy$-plane, reduces the problem to one involving a single dimension. Third, attention should be paid in the use of “common” pulse sequences in combination with a constant gradient [Benson and McDonald, 1995b]. The most
used pulse sequence in STRAFI is:

\[(\pi/2)_x - \tau - [(\pi/2)_y - \tau - echo - \tau]_n,\]

which leads to a train of \(n\) echoes. It gives a certain degree of narrowing as it partially refocuses the dipolar Hamiltonian and employs pulses of the same length to excite the same slice width. Spin-echo pulse sequences can be successfully used if the \(\pi\) pulse has twice the amplitude of the \(\pi/2\) pulse rather than twice the length [Benson and McDonald, 1995a].

Up to now, the technique has been used for a variety of applications, including the study of solvent ingress in polymers [Lane and McDonald, 1997, Lane et al., 1998], curing of cement pastes [Nunes et al., 1996], and drying of adhesives [Hughes et al., 1996a] and coatings [Glover et al., 1997]. In particular, Glover et al. introduced the use of a novel surface coil suited to the study of planar films. The coil allows the excitation of only a small central region of a much larger sample, minimising any contribution from the sample edges. The same authors, however, point out that the geometrical configuration of a "conventional" STRAFI system, shown in fig. 2.12 (a), is not the optimum to study planar films and coatings, which need to be kept horizontal with respect to the gradient during the experiment. Ideally, a vertical solenoid surface coil should be employed to improve the sensitivity, requiring the geometrical configuration shown in fig. 2.12 (b). Recently, a permanent magnet with an intentional intense gradient in the vertical direction with respect to the magnetic field, which is specifically designed to study planar films and coatings, has been built [Glover et al., 1999].
Figure 2.12: The two possible geometrical configurations to study planar films and coatings. (a) Geometrical configuration in a conventional super-conductive magnet: the magnetic field $B_0$ is oriented parallel to the gradient in the vertical direction. This necessitates, for a planar horizontal sample, a surface RF coil with the $B_1$ field in the sample plane. (b) Preferable configuration: the gradient is in the vertical direction and $B_0$ in the horizontal plane, so that profiling through the planar sample is possible with a vertically solenoid surface coil.

### 2.5 NMR Diffusometry

If, on one hand, the diffusion of spins limits the resolution in k-space imaging, on the other hand the combined use of gradients and spin-echoes makes for an effective method to study self-diffusion. The translational displacements of molecules due to Brownian motion, or self-diffusion, is characterised by a propagator $P(r; r_1, t)$, which is the probability that a molecule starting at position $r$ will move to position $r_1$ over a time $t$ [Kimmich, 1997, page 175]. For isotropic homogenous media, the propagator obeys the diffusion equation (Fick’s second law):

$$\frac{\partial P}{\partial t} = D \nabla^2 P,$$

where $D$ is the self-diffusion coefficient. In unrestricted Brownian motion, molecules diffuse freely in all directions and the solution to eq. 2.26, with the initial condition
CHAPTER 2. PRINCIPLES OF NMR.

\[ P(\mathbf{r}; r_1, 0) = \delta(\mathbf{r}_1 - \mathbf{r}) \] and the boundary condition \( P \to 0 \) for \( r_1 \to \infty \), is

\[ P(\mathbf{r}; r_1, t) = \frac{1}{(4\pi D t)^{3/2}} \exp \left[ -\frac{(|\mathbf{r}_1 - \mathbf{r}|)^2}{4Dt} \right] \] \hspace{1cm} (2.27)

The mean-squared displacement for diffusion in three dimensions is \( 6D t \).

The measurement of self-diffusion coefficients by NMR diffusometry relies on the following principle: a spatial label is given to each spin at one instant of time and then the labelling is checked at a later time in order to see if the spin has moved. An ensemble average measurement is made.

2.5.1 PGSE Experiment

![Figure 2.13: (a) Pulsed-Gradient Spin-Echo sequence and (b) Stimulated-Echo variant. The magnetic field gradient pulses have magnitude and direction \( g \), duration \( \delta \) and separation \( \Delta \). The vertical arrows indicate the position in which the echo of amplitude \( E(\Delta, \delta, g) \) forms.](image)

The Pulsed-Gradient Spin-Echo (PGSE) NMR experiment in the original form proposed by Stejskal and Tanner [Stejskal and Tanner, 1965] is shown in fig. 2.13 (a) and consists of a spin-echo sequence combined with two magnetic field gradient pulses of magnitude and direction \( g \), applied on each side of the \( \pi \) RF pulse. The first gradient pulse imparts a phase-shift of \( \gamma_N \delta g \cdot \mathbf{r} \) to a spin located at position \( \mathbf{r} \) at the time of the gradient pulse. This phase shift is reversed by the \( \pi \) pulse. Thus, if
the spin does not move during the observation time $\Delta$, the effect of the first gradient pulse is exactly compensated by the second one. However, if the spin moves from $r$ to $r_1$, the dephasing of the first gradient pulse is no longer compensated for and the spin has a net phase shift $\gamma_N \delta g \cdot (r_1 - r)$ at the echo formation time $2\tau$. For an ensemble of spins free to diffuse, the residual phase shifts are distributed and the resultant echo is attenuated by an amount determined by $\delta$, the amplitude $g$ of the gradient and by the average spin displacement, which, in turn, depends on $\Delta$ and the diffusion coefficient $D$. The same technique can be used to measure flow as the coherent motion of the spins imparts a phase rotation to the observed signal.

The attenuation of the echo amplitude $A$ at its centre is defined as $E(\Delta, \delta, g)/E_0$, where $E(\Delta, \delta, g)$ and $E_0$ are the signal intensities at $t = 2\tau$ in the presence and in the absence of gradients, respectively, and is given by [Callaghan, 1995a, page 339]:

$$A(\Delta, \delta, g) = \int_0^\Delta \rho(r) \int_0^{r_1} P(r; r_1; \Delta) \exp [i \gamma_N \delta g \cdot (r_1 - r)] \, dr \, dr_1,$$

(2.28)

where $\rho(r)$ is the starting spin density. Following Callaghan's formalism, eq. 2.28 can be rewritten as:

$$A(\Delta, q) = \int P(R, \Delta) \exp (i2\pi q \cdot R) \, dR,$$

(2.29)

where $P(R, \Delta) = \int P(r; r + R, \Delta) \rho(r) \, dr$ is the average propagator, that is the probability that a molecule at any starting point is displaced by $R = r_1 - r$ in this case over a time $t = \Delta$, and $q = 1/(2\pi) \gamma_N \delta g$ is the reciprocal space vector. Therefore, a Fourier relationship exists between the observed echo attenuation and the averaged propagator, and $q$ is conjugate to the dynamic displacement $R$.

The echo attenuation caused by free Brownian motion with self-diffusion $D$ is obtained by combining eq. 2.28 with eq. 2.27 and is given by:

$$A(\Delta, \delta, g) = \frac{E(\Delta, \delta, g)}{E_0} = \exp \left[ -\gamma_N^2 \delta^2 g^2 D (\Delta - \delta/3) \right],$$

(2.30)

where a correction is already included due to diffusion occurring during the
application of the gradient pulses. Thus, $D$ can be obtained from a semilogarithmic plot of $A(\Delta, \delta, g)$ versus $\gamma_n^2 \delta^2 g^2 (\Delta - \delta/3)$.

NMR diffusometry is successfully used to measure self-diffusion coefficients as low as $10^{-8} \text{ cm}^2 \text{s}^{-1}$ [McDonald, 1997]. In the fringe field, diffusion coefficients as small as $10^{-11} \text{ cm}^2 \text{s}^{-1}$ are reported in a variety of polymer melts [Kimmich et al., 1991] and solutions.

2.5.2 Restricted diffusion and microstructure analysis

If the molecules experience some kind of diffusion barrier during the observation time $\Delta$ [Stejskal, 1965], the propagator will deviate from the gaussian form (eq. 2.27). For the case of spherical barriers, such as a pore or a droplet of radius $a$, diffusion appears unrestricted for short diffusion times, $\Delta \ll a^2/(6D)$. For $\Delta \approx a^2/(6D)$ the maximum distance that the spins can diffuse is limited by the spherical barriers. For longer times, $\Delta \gg a^2/(6D)$, all molecules irrespective of their starting position can be found anywhere within the pore and the mean-squared displacement will appear to be independent of $\Delta$.

In the long time limit $P(r; r_1, \Delta)$ becomes independent of the starting position $r$ and reduces to: $P(r; r_1, \infty) = \rho(r_1) = \rho(r)$. Then

$$A(g, \delta, \infty) = \int \rho(r) e^{i \gamma N \delta \mathbf{g} \cdot \mathbf{r}} \, d\mathbf{r} \right|_2 = |S(q)|^2,$$

(2.31)

where $S(q)$ is a structure factor defined by the above expression with direct analogy to optics and neutron scattering. Therefore, in the long time limit, PGSE is an imaging experiment returning the modulus squared of $q$.

Restricted diffusion or q-space microscopy [Callaghan et al., 1988] is a powerful tool to probe the microstructure of the sample on the micrometer scale [Goerke et al., 1999], significantly smaller than is possible with MRI. However, it yields statistical information on the sample. Measurement of echo attenuation and hence $S(q)$ have been reported for a variety of systems, including porous
media [Callaghan, 1995a, pages 383-399]. In the latter case, NMR diffusometry is complementary to NMR cryoporometry [Strange et al., 1993] and relaxometry [Halperin et al., 1989].

To find an exact description of the propagator over all values of $\Delta$, it is necessary to solve the diffusion equation (eq. 2.26) under the appropriate boundary conditions. The literature contains a number of references to the expression of the echo attenuation for boundaries of different shape. A good starting point is indeed the book written by Callaghan [Callaghan, 1995a, pages 371-419].
Chapter 3

The spatial dependence of the droplet size distribution in the cream layer of oil-in-water emulsions

3.1 Introduction

In oil-in-water emulsions, oil droplets rise to the top of the sample to form a cream layer when the oil is less dense than the water, as is usually the case. More often than not, emulsion droplets are polydispersed in size. By common expectation and predictions of theory, larger oil droplets are to be found predominantly towards the top of the cream. Volume concentrations of oil in the cream above that which is predicted for a random close-packing of identical spheres ($\phi = 0.64$) have been observed [Newling et al., 1997b, Dickinson, 1988, page 53], suggesting a rearrangement of droplets within the cream layer. Either smaller droplets fill up the voids amongst the large ones or the droplets deform from a spherical shape (in the absence of coalescence).
The objectives of this chapter are twofold. First, an investigation of the droplet size distribution as a function of position within the cream layer of simple, fully-creamed oil-in-water emulsions is reported along with analysis of droplet shape. Second, the influence of stabilisers on the distribution is investigated. Polysaccharide stabilisers are frequently used to reduce the rate of creaming by raising the viscosity of the continuous phase. However, if small quantities of polymer are added to the continuous phase of an emulsion, experiments show that creaming may be faster than in the absence of the stabiliser and this effect has been attributed to the flocculation of droplets caused by the presence of the free polymer (i.e. depletion flocculation) [Hibberd et al., 1987].

Emulsions having small and large droplets, that is a bi-modal droplet size distribution, and containing a variable amount of gum xanthan, extensively used in the food industry as a thickener, have been prepared and studied by using a combination of pulsed-field-gradient spin-echo (PGSE) NMR and NMR imaging. The former allows one to measure the droplet size distribution if the conditions of restricted diffusion are satisfied, the latter gives spatial information. In order to selectively observe the oil component, \(^{1}H - ^{13}C\) cyclic \(J\) cross-polarisation (CYCLCROP) PGSE imaging is introduced as a new technique.

In this chapter, a description of the preparation of the emulsions and characterisation by optical microscopy is described first. Relaxation measurements are discussed in section 3.4.1. Section 3.4.2 presents \(^{1}H\) PGSE experiments and section 3.4.3 the corresponding \(^{13}C\)-edited experiments. Finally, the experimental data are compared to a current model of creaming [Pinfield et al., 1994]. The use of a bi-modal droplet size distribution allows for an easier comparison and makes deviations from the model more evident. Evidence for the effects of depletion flocculation is given at the end of the chapter.
3.2 Materials and methods

3.2.1 Emulsion composition and preparation

A series of oil-in-water emulsions was prepared: the emulsions differ in the type of distribution (uni and bi-modal) and in the range of concentration of gum xanthan in the aqueous phase (from 0.0 wt% to 0.1 wt% of water), as indicated in table 3.1.

The emulsions consist of 33.3 wt% oil and 66.6 wt% aqueous solution, the latter containing gum xanthan (commercial grade, Aldrich Chemicals) in various concentrations and 1.0 wt% polyoxyethylene (20) sorbitan monoleate, a non-ionic surfactant sold under the trade name of Tween 80 (Atlas Chemistry Industry). The oil phase was pure decane (Aldrich Chemicals, ρ=0.73004 g/ml) or a mixture of decane and methyl 13C-enriched toluene (Cambridge Isotopes, Cambridge, Mass., USA) in weight ratio 80 to 20 (calculated density of the mixture = 0.75927 g/ml). The latter, barely soluble in the water phase, greatly improved the sensitivity of the 13C-edited NMR imaging.

Table 3.1: Characteristics of the prepared emulsions (dec = decane, tol = methyl-13C-toluene).

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>Composition of the oil phase (wt%)</th>
<th>Gum xanthan (wt% of water)</th>
<th>Droplet distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>100 dec</td>
<td>0.100</td>
<td>Uni-modal</td>
</tr>
<tr>
<td>E2</td>
<td>100 dec</td>
<td>0.100</td>
<td>Bi-modal</td>
</tr>
<tr>
<td>E3</td>
<td>80 dec + 20 tol</td>
<td>0.033</td>
<td>Bi-modal</td>
</tr>
<tr>
<td>E4</td>
<td>80 dec + 20 tol</td>
<td>0.010</td>
<td>Bi-modal</td>
</tr>
<tr>
<td>E5</td>
<td>80 dec + 20 tol</td>
<td>0.003</td>
<td>Bi-modal</td>
</tr>
<tr>
<td>E6</td>
<td>80 dec + 20 tol</td>
<td>0.000</td>
<td>Bi-modal</td>
</tr>
</tbody>
</table>

Emulsion E1 is characterised by a single droplet size distribution. An aqueous solution of the surfactant and 0.1 wt% gum xanthan was prepared by stirring at room temperature until homogenous. Decane was then added dropwise to the aqueous solution while stirring. The resultant crude emulsion was stirred for further 15
minutes and homogenised for 3 hours with an *Ultra Turrax T8* (IKA Labortechnik, Germany) homogeniser at a shear rate of about 210 s\(^{-1}\).

All other emulsions have a bi-modal distribution. In each case, the crude emulsion was prepared as described for E1. The crude emulsion was hand-shaken for 5 minutes in as reproducible a fashion as possible (to produce an emulsion with a large droplet size) and divided into two parts of equal volume. One half was homogenised for 1.25 hours with the *Ultra Turrax T8* homogeniser to produce an emulsion with a smaller average droplet size and this well-homogenised emulsion was re-mixed with the remaining hand-shaken emulsion to give the corresponding bi-modal emulsion in table 3.1.

The emulsions were all stored at room temperature in small sealed pots 20 mm in diameter and typically 13 mm deep. After a variable time (from minutes to a few days) dependent on the concentration of gum xanthan, the rise of a visible meniscus and the formation of two layers were observed. Initially, the cream layer, containing mainly the larger droplets, had a rather indistinct boundary with the rest of the dispersion. With time, a sharp boundary separating the concentrated cream from the continuous clear phase was visible.

### 3.2.2 Characterisation of emulsions

Droplet size distributions in the well-homogenised and hand-shaken emulsions were determined separately using optical microscopy. This approach was preferred because, in the case of very broad distributions, optical microscopy measurements are not reliable [Newling et al., 1997b]. At higher magnifications, where it is possible to count particles that are in the range of a few microns, the observation is focused on small particles and larger ones are neglected. At lower magnifications, smaller particles are underestimated. The emulsions were diluted with water to concentrations of about 5 vol%, so that they were less opaque. The size of several hundred droplets at different depths in the sample was measured in order to obtain
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a reliable droplet size distribution. Creaming during the measurements results in the droplet size distribution varying with the depth of focus of the microscope.

\[(a) \quad 2\,\mu m \quad (b) \quad 10\,\mu m\]

Figure 3.1: Images obtained by optical microscopy of the (a) homogenised and (b) hand-shaken parts of emulsion E2. Note the different scales shown in the two pictures.

Fig. 3.1 presents typical images obtained by optical microscopy of the homogenised and hand-shaken emulsions that, once mixed, formed E2. The length scale shown in the two pictures indicates that the average droplet radius is around 2 and 8 \(\mu m\), respectively, and that in each emulsion the droplets are polydispersed in size.

In common with other work [Packer and Rees, 1972, Newling et al., 1997b, Lönnqvist et al., 1997], it is found that the droplet size number-distribution of all the emulsions prepared is well described by a log-normal size distribution function given by

\[
P(r) = \frac{A}{r\sigma\sqrt{2\pi}} \exp\left(\frac{-(\ln r - \ln r_0)^2}{2\sigma^2}\right),
\]

where \(r\) is the droplet radius, \(r_0\) is the median radius, \(\sigma\) is a dimensionless measurement of the width of the size distribution and \(A\) is a normalisation factor.

Presented in figure 3.2 are the results of the droplet size determination for emulsion E1 as described above. This emulsion is characterised by a narrow distribution of
small droplets. The corresponding volume fraction distribution curve is given by \( \phi(r) = 4/3 \pi r^3 P(r) \), and for emulsion E1 is presented later (see fig. 3.9).

For all the bi-modal emulsions, the prefactor \( A \) in equation 3.1 is chosen so that the normalised volume fraction droplet size distribution of each separate emulsion is 0.5, as follows from the preparation. All emulsions, with the exclusion of E1, possess essentially the same droplet size distribution as E2 (except in emulsion E3 the big droplets are slightly larger than average). Figure 3.3 shows the distribution obtained from optical measurements of emulsion E2. It also shows the volume fraction distribution for the combined emulsion. A clear maximum is present at about 3 \( \mu \text{m} \) and a long tail stretches above 10 \( \mu \text{m} \). It is to this volume distribution rather than to the number distribution that the NMR signal intensity is sensitive.

### 3.2.3 NMR techniques

All NMR measurements were performed on a Bruker DSX400 spectrometer operating with a proton frequency of 400 MHz. The spectrometer was equipped with a 23 mm internal diameter radio frequency excitation/detection coil double tuned to both \(^1\text{H}\)
Figure 3.3: (a) Number fraction droplet size distribution curve obtained with an optical microscope for the homogenised and the hand-shaken emulsions that, once mixed, form E2. Note that the hand-shaken number fraction size distribution curve is multiplied by 100. The solid lines are log-normal size distribution fits to each set of data. For the homogenised emulsion the fit parameters are $A = 1.35 \times 10^{-2}$, $r_0=2.23\ \mu m$ and $\sigma=0.517$, and for the hand-shaken emulsion are $A = 2.93 \times 10^{-4}$, $r_0=7.95\ \mu m$ and $\sigma=0.522$. (b) Volume fraction distribution curve for the combined emulsion E2, calculated using the above fit parameters.

and $^{13}\text{C}$.

$^1\text{H}$ PGSE measurements were performed by using the stimulated version of PGSE to allow for a long observation time $\Delta$. The short $T_2$ of the oil in the cream layer (see section 3.4.1) considerably limits the length of the observation time in a standard PGSE sequence. A long observation time is required in order to observe fully the
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effects of restricted diffusion in the largest droplets. Spatially-resolved diffusion-weighted measurements were obtained by prepending the PGSE pulse sequence to a standard spin-echo profiling sequence with only the read gradient. The profile echo time was 2 ms and the read gradient had a strength of 11.4 G/cm. It was applied along the z-axis, and hence the profile was obtained in the vertical direction, corresponding to the cylindrical axis of the pot and to the direction of the magnetic field. Typical parameters used in the diffusion experiments were $\Delta = 640$ ms and $\delta = 1$ ms (for the definition of $\Delta$ and $\delta$ see fig. 2.13) and the gap between the first and second RF pulse in the stimulated echo was set to 2 ms. The experiments presented in this chapter were recorded as a function of the diffusion gradient strength, which was varied between $G = 0$ and 90 G/cm in steps of about 1 G/cm. The diffusion gradients were applied along the horizontal $x$-axis with the exception of the experiments presented in the discussion of the droplet anisotropy.

Indirectly detected $^{13}$C diffusion-weighted profiles were obtained by using the cyclic-J-cross-polarisation (CYCLCROP) editing pulse sequence, which was prepended to the $^1$H PGSE profiling sequence in place of the initial $\pi/2$ RF pulse. Polarisation transfer was achieved with the PRAWN sequence, with the exception of the data discussed in section 3.4.4 which were recorded with the PRAWN-$\pi$ variant. For the $^{13}$C-enriched emulsions, the proton and carbon channels were centred at the respective frequencies of the methyl group of the toluene, otherwise they were set at the frequencies of the decane methylene group yielding a better signal-to-noise ratio. Saturation pulses were set at the water frequency to suppress the water signal. The contact time was calculated from the corresponding $J$-coupling and the number of protons in the selected CH$_n$ group.

In addition to diffusion experiments, the spatial dependence of the relaxation times was measured across the cream layer of each prepared emulsion. Measurements of $T_1$ were obtained using a saturation recovery pulse sequence prepended to the spin-echo read gradient, varying the recovery times from 0.1 ms to 10 s. $T_2$ measurements were made using spin-echo with variable echo time. The imaging parameters for both $T_1$
and $T_2$ (in the latter case with the exception of $T_E$) were the same as for the diffusion measurements.

The NMR experiments were recorded over a period of one month, during which time the emulsions were stable. Unless stated, the emulsions were left to cream for about three weeks to ensure that creaming was complete before making the measurements. In order to record a simple $^1$H density profile, only a few seconds were necessary. $^1$H PGSE experiments required about 15 minutes on average, while $^{13}$C-edited PGSE experiments required about one hour for the $^{13}$C-enriched emulsions and a few hours for the $^{13}$C natural abundance emulsions, depending on the number of averages and number of gradient steps acquired.

3.3 PGSE theory: restricted diffusion in a sphere

In the PGSE experiments described here, the diffusion time $\Delta$ is sufficiently long that the oil molecules experience the internal surface of the O/W emulsion droplet and their motion is restricted. As a consequence, information about the droplet size can be derived.

The first attempt to derive the echo attenuation function over the whole range of observation times $\Delta$ for spins confined within spherical boundaries goes back to Murday and Cotts [Murday and Cotts, 1968], who proposed an approximate solution based on the assumption of a Gaussian distribution of phase displacements. An exact solution was obtained by Callaghan [Callaghan, 1995b]. However, this expression is complex and not easily applicable in the analysis of the experimental data. A more general expression, but even more complex is given by Codd and Callaghan [Codd and Callaghan, 1998]. In this work, approximate solutions are preferred because they are more tractable.

Tanner and Stejskal [Tanner and Stejskal, 1968] present an analysis, which is exact in the long time-scale limit and otherwise approximate. The echo attenuation is given
by

\[ E(\delta, g, r) = E_0 \frac{9[\gamma_N g \delta r \cos(\gamma_N g \delta r) - \sin(\gamma_N g \delta r)]^2}{(\gamma_N g \delta r)^8}, \]  

(3.2)

where \( r \) is the radius of the sphere. Since the long time limit is assumed, neither \( D \) nor \( \Delta \) appear in eq. 3.2.

A particularly useful extension of eq. 3.2, which allows for a distribution of droplet sizes, is reported by Callaghan and co-workers [Callaghan et al., 1983]. Equation 3.2 approximates to

\[ E(\delta, g, r) \approx E_0 \exp \left( -\frac{\gamma_N^2 \delta^2 g^2 r^2}{5} \right) \]  

(3.3)

for a broad range of attenuation factors. Equation 3.3 can be evaluated with relative ease for a Gaussian volume distribution of spheres of radius \( r \), given by

\[ P(r) = \frac{1}{\sqrt{2\pi} \sigma_v} \exp \left( -\frac{(r - r_v0)^2}{2\sigma_v^2} \right), \]  

(3.4)

where \( r_v0 \) is the mean radius and \( \sigma_v \) is the standard deviation. In this specific case the echo attenuation function becomes:

\[ E(\delta, g, r_v0, \sigma_v) = E_0 \frac{1}{\sqrt{1 + 2 \sigma_v^2 \beta^2}} \exp \left( -\frac{\beta^2 r_v0^2}{1 + 2 \sigma_v^2 \beta^2} \right), \]  

(3.5)

where \( \beta^2 = \gamma_N^2 \delta^2 g^2/5. \)

### 3.4 Results and Analysis

#### 3.4.1 Relaxation time measurements

**Spin-lattice relaxation time (\( T_1 \)) measurements**

Saturation-recovery profiles were recorded for all the creamed emulsions and, as an example, the data obtained for emulsion E6 is presented in fig. 3.4. The horizontal
axis shows the position along the emulsion: the water layer is on the left and the cream layer on the right, separated by a small gap which is the result of different average magnetic susceptibilities and chemical shifts in the two layers. It is evident that $T_1$ is spatially invariant both in the water layer, as expected, and in the cream layer and that, in both cases, it is relatively long. Magnetisation recovery curves for the centre of the water and the cream layer are presented in fig. 3.5 together with the best fit curves to the data according to a single exponential recovery curve function. The water $T_1$ is $2.58 \pm 0.01$ s and the cream $T_1$ is $2.20 \pm 0.01$ s. Although there must be some water in the cream layer, the data only support a single exponential fit. The same results are found in all the other emulsions prepared and similar values of $T_1$ are obtained.

![Figure 3.4](image)

Figure 3.4: Saturation-recovery profiles of emulsion E6 once fully-creamed. The water layer extends from 0.2 to 0.75 cm and the cream layer from 0.75 to 1.35 cm. From the top to the bottom, the saturation-recovery delay is 10, 8, 5, 3.5, 2, 1.5, 1, 0.8, 0.5, 0.35, 0.2 and 0.01 s.

For emulsion E6, containing no gum xanthan, big droplets are expected at the top and small droplets at the bottom of the cream. As $T_1$ is invariant with respect to the position in the cream layer and, therefore, with respect to the droplet size, surface relaxation is not an important relaxation process for the oil molecules [Callaghan, 1995a, page 408].
Figure 3.5: Saturation-recovery curves for the centre of the water layer (circles) and cream layer (squares) of emulsion E6 once fully-creamed. The solid lines are the associated fits according to eq. 2.21 with \( T_1 = 2.58 \) s for the water and \( T_1 = 2.20 \) s for the cream.

It is surprising that the signal of the cream is more intense than that of the water because the proton density of water is about 3.6% greater than that of the oil. Although this discrepancy increases with the concentration of gum xanthan, the presence of the thickener cannot be the only cause, as is evident from fig. 3.10. The effect cannot be attributed either to \( T_2 \) or to diffusive broadening in the imaging gradient. In fact, \( T_2 \) in the water layer is fairly long compared to the echo time, as discussed below (unless there is a very short component undetected). Diffusion broadening, at worst (that is, diffusion of the water only in the aqueous layer), gives an attenuation of the signal of 4% relative to the oil. It was not until late in the experimental programme, after most of the data had been collected, that this contradiction was resolved. It is due to \( B_1 \) inhomogeneity, as experiments with an improved RF coil showed the expected amplitudes; see section 3.4.4.

**Spin-spin relaxation time (\( T_2 \)) measurements**

\( T_2 \) profiles were recorded for all creamed emulsions and typical \( T_2 \) decays for the cream of emulsions E6 and E2 are presented in fig. 3.6 (a) and (b), respectively.
Figure 3.6: Spin-echo $T_2$ decays for the cream layer of emulsion E6 (a) and E2 (b), once fully-creamed. Curves are shown in the order of squares, circles, up-triangles, down-triangles, diamonds, open squares, open circles, open up-triangles, open down-triangles and open diamonds from the bottom of the cream and moving up in steps of 0.41 mm. The $T_2$ values, obtained with single exponential decay fits, are in the order 28.1, 16.4, 12.4, 11.4, 11.4, 11.7, 12.5, 13.3, 14.4, 15.6 and 16.6 ms for E6 and 23.6, 24.5, 25.2, 26.0, 26.9, 27.5, 28.6, 30.3 ms for E2.

The decays are, in all cases, reasonably well fitted by a mono-exponential decay, and the $T_2$ values obtained, similar for all the emulsions, vary only in the detail. The creamed emulsion E6 has the shortest $T_2$ values compared to the other emulsions. The water $T_2$ is $280 \pm 20$ ms, and $T_2$ in the cream goes through a minimum in the centre of the cream (fig. 3.6 (a)). The minimum becomes less marked with increasing concentrations of gum xanthan and it is absent in E2 (fig. 3.6 (b)), containing the
maximum amount of gum xanthan. In the absence of any surface relaxation, the variation of $T_2$ in the cream layer is attributable to a complex average of diffusive broadening in background magnetic field gradients [Callaghan, 1995a, page 209], arising from the difference in magnetic susceptibilities between the water and the oil droplets. For a specific location, droplets of different sizes are found in each of the emulsions. As the field gradient at the surface of a droplet is approximately proportional to the inverse of the droplet radius [Glasel and Lee, 1974], the resultant background magnetic field gradient has a different intensity at each position for each emulsion. The $T_2$ values for the water and the cream layer for all emulsions are larger than typical echo encoding times.

3.4.2 $^1$H PGSE diffusometry

A simple application: the uni-modal emulsion E1

The results for emulsion E1, which contains a uni-modal narrow distribution of small droplets, are presented first to describe the method and validate the general procedure. A thin layer of decane was carefully floated on top of the creamed emulsion E1 to provide a further reference sample.

Figure 3.7 shows representative $^1$H PGSE weighted profiles (every fifth profile is shown) as a function of the gradient strength for emulsion E1 and the decane layer. In the figure, the water layer is on the left, the cream layer in the middle and the bulk decane layer on the right. The topmost profile was recorded with near zero diffusion gradient and reflects the $^1$H distribution as measured in the $T_1$ experiment (not shown for emulsion E1). The lowest profile was recorded with 85.50 G/cm diffusion gradient and is substantially different in shape from the top profile. Both the water and the decane signals are completely attenuated, though at different rates. The cream layer is attenuated much less than the bulk decane, and that can be attributed to restricted diffusion in the oil droplets. As expected from a fairly uniform droplet size distribution, the attenuation in the cream layer does not depend
on the position within the cream layer itself.

Figure 3.8 shows representative echo amplitude data recorded from the water layer, the cream layer and the decane layer, which was used as a reference system. The signal intensity curves for water and decane are taken from the centre of the respective layers. The corresponding fits according to equation 2.30 for unrestricted diffusion for the water and decane are also shown, from which the water self-diffusion coefficient is calculated to be \((2.05 \pm 0.01) \times 10^{-5} \text{ cm}^2\text{s}^{-1}\) and that of decane to be \((1.26 \pm 0.01) \times 10^{-5} \text{ cm}^2\text{s}^{-1}\), both in good agreement with published values [Mills, 1973, Lönnqvist et al., 1997]. Figure 3.8 also shows the signal intensity at the centre of the cream layer as representative of all the positions (there is little spatial variation within the cream layer) and the best fit to the data according to eq. 3.5, obtained with \(r_{\text{m}}=3.06 \mu\text{m}\) and \(\sigma_{\text{v}} = 1.97 \mu\text{m}\). If the mean droplet radius and the distribution width are varied by 10%, noticeably worse fits are obtained, giving an estimation of the errors in the best fit parameters.

It should be noticed that in this experiment and in the following ones the long time limit condition, that is \(\Delta \gg r^2/(6D)\), is well met for the oil droplets. Moreover, the
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Figure 3.8: $^1$H PGSE decays for the centre of the water layer (squares), for the centre of the cream layer (circles) and for the centre of the decane layer (triangles) of emulsion E1. The solid lines are the associated fits according to the unrestricted diffusion equation (eq. 2.30) for the water and decane and to eq. 3.5 for the cream layer.

The restriction on the attenuation factor $q \ll r^{-1}$ [Callaghan, 1995a, page 379], where $q = 1/(2\pi)\gamma_N g \delta$, is satisfied, so that eq. 3.5 can be used.

A Gaussian droplet size distribution function can now be obtained by using eq. 3.4 with the best fit parameters just estimated. Figure 3.9 shows a comparison between the oil droplet distribution of emulsion E1 obtained by optical microscopy analysis and by NMR analysis. Good agreement is observed. As already stated, a log-normal distribution function is used in the optical microscopy analysis, while a Gaussian distribution function is used in the NMR analysis. However, there is no a priori reason to choose one or the other function: the numerical log-normal distribution is normally used in optical microscopy and the Gaussian function makes the calculation tractable in the PGSE NMR analysis.

The bi-modal emulsions

Figure 3.10 presents the $^1$H PGSE weighted profiles as a function of the gradient strength for creamed emulsions E6, E4, E3 and E2 (without any reference decane
Figure 3.9: Volume fraction distribution obtained by optical microscopy for E1. The continuous line is the fit calculated from the corresponding log-normal numerical distribution. Also shown are a Gaussian fit to the optical data ($r_{w0}=2.48 \, \mu m$, $\sigma_v=1.00 \, \mu m$, dotted line) and the Gaussian distribution obtained from NMR experiments (dashed line).

layer), recorded with $\Delta=640$ ms and $\delta=1$ ms. These parameters allow one to use the approximate analysis of Callaghan. The $^1$H PGSE weighted profiles for emulsion E5 are similar to those for emulsion E6, and will be presented later (see fig. 3.13). In each case in fig. 3.10 the water layer is to the left and the cream layer is to the right. The width of the cream layer changes with the concentration of gum xanthan. From the widths of the cream and water layers and the known compositions, it is possible to determine the volume concentration of oil in the cream layer, which goes from 73 % with 0 wt% gum xanthan to 83 % with 0.1 wt%. That is, the cream layer is significantly denser in presence of gum xanthan. The attenuation clearly depends both on the position within the cream layer and the gum xanthan content. At the base of the cream, the signal decays very slowly for emulsion E6 (containing no gum xanthan), while towards the top it decays much more rapidly. By increasing the content of gum xanthan, the attenuation increases at the bottom of the cream layer and decreases at the top, until the decay is almost spatially uniform for emulsion E2. These observations suggest a different distribution of the droplets within the cream
layer: small droplets are expected to be at the bottom and big droplets at the top of the cream layer of emulsion E6, while a more uniform distribution of small and big droplets is expected in emulsion E2, as confirmed by the following analysis.

Figure 3.10: $^1$H PGSE weighted profiles for emulsions (a) E6, (b) E4, (c) E3, and (d) E2. In all cases, $\Delta$=640 ms and $\delta$=1 ms. From the top, profiles are shown for gradient strengths from 0.95 (top profile) to 85.50 G/cm (lower profile) in steps of 4.75 G/cm.

The echo attenuation at each position in the cream layer can be examined and, as an example, the signal intensities at the centre of the cream layer for emulsion E6 and emulsion E2 are shown in figure 3.11. The fit of the data for emulsion E6 according to equation 3.5 is satisfactory, while it is poor for emulsion E2. In the latter case, a better fit is obtained using a bi-modal Gaussian distribution function,
that is, a two component fit. While in the example shown there is no ambiguity in the choice of the fitting function, in some cases the choice between a single Gaussian and a bi-Gaussian is much more difficult. When in doubt, a single Gaussian fit is used in order not to "overinterpret" the data. If a bi-Gaussian fit was considered to be necessary, the best fit parameters for the small droplets were checked against data at $\delta = 4$ ms, where the signal generated by the small droplets is more attenuated. Finally, towards the bottom of the cream layer, the data often show evidence of a mobile component which is taken to be water. Here it is justifiable to fit the data with two components: one according to eq. 3.5 for oil droplets and one according to eq. 2.30 representing the continuous water component.

![Figure 3.11: $^1$H PGSE decay for the centre of the cream layer of emulsion E6 (circles) and E2 (squares). The solid line through the open circles represents the best fit according to eq. 3.5 to the data of emulsion E6, with $r_{v0}=13.1$ $\mu$m, $a_v=5.72$ $\mu$m. The solid line through the open squares is the best fit with a bi-modal Gaussian distribution for emulsion E2. The fit parameters are $r_{v0}^{(1)}=2.87$ $\mu$m, $a_v^{(1)}=2.06$ $\mu$m (36%), $r_{v0}^{(2)}=14.3$ $\mu$m, $a_v^{(2)}=23.0$ $\mu$m (64%). Also shown is the "best" fit obtained with a uni-modal Gaussian distribution (dashed line) for emulsion E2.](image)

By using a Gaussian function and the best fit parameters, the oil droplet distribution at different positions within the cream layer can be obtained. It should be noted that equation 3.5 strictly applies when $r_{v0} \gg \sigma_v$ [Callaghan et al., 1983], or else a significant number of droplets with a "negative radius" are predicted.
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This condition is not always fulfilled in the fitting above. Since all the results depend on \( r^2 \), the droplet distribution with a "negative radius" can be folded back into the corresponding positive radius distribution, giving a resultant non-Gaussian distribution curve. This distribution is assumed to be characteristic of the emulsions studied and the resultant curves obtained are shown in fig. 3.12. Each curve corresponds to the distribution at a particular height in the cream layer. The narrowest curve of fig. 3.12 (a), (b), (c) and (d) and the most intense curve of fig. 3.12 (e) correspond to the base of the cream and the other curves are the oil distributions up through the cream in successive steps of 0.41 mm. With no xanthan (figure 3.12 (a)) the droplet size distribution curves at each position in the cream layer are relatively narrow, indicating that there is a strong separation of small and large droplets according to height. This separation continues with increasing xanthan concentration, but becomes noticeably less marked, as is made evident by the progressive broadening of the curves in fig. 3.12 (b) and (c). Emulsion E3 (see fig. 3.12 (d)) represents the transition from the separation of small and large droplets to a uniform distribution. At the bottom of the cream there are both small droplets and relatively large ones. The amount of small droplets decreases going up the cream and only large droplets are found at the top. Finally, in emulsion E2, containing 0.1 wt% xanthan, the droplet size distribution is more or less constant as a function of height, with both small and large droplets found at each height.

\(^1\)H PGSE profiles have also been recorded with the diffusion gradients along the \( z \)-axis. In this way information about the droplet dimensions along \( z \) and along \( x \) are obtained and any discrepancy between the profiles recorded can be attributed to a departure of the droplet shape from spherical towards ellipsoidal. Figure 3.13 shows a comparison between the profiles recorded with the diffusion gradients along \( z \) and along \( x \) for emulsion E5. An extremely close correspondence is observed between the two sets of data, indicating that the droplets are spherical or, at least, not ellipsoidal. However, the method is not sensitive to near isotropic deformation, like randomly oriented polyhedra.
Figure 3.12: Oil droplet distribution as a function of the height of the cream layer as calculated from NMR data for emulsions (a) E6, (b) E5, (c) E4, (d) E3, (e) E2. See text for explanations.
Figure 3.13: $^1$H PGSE weighted profiles for emulsion E5 recorded with diffusion gradients along the horizontal direction $x$ (continuous line) and along the vertical direction $z$ (dashed line). The gradient strength is 0.95 G/cm for the upper traces and 91.2 G/cm for the lower traces.

$^1$H PGSE profiles recorded 4-5 days after preparation have been compared to the profiles recorded on the fully-creamed emulsions. A slight decrease in the width of the cream layer over time is observed, indicating that the density of the cream was increased. However, the shape of the attenuated profiles do not vary with time, indicating that the droplets do not rearrange themselves within the cream layer over time.

### 3.4.3 $^{13}$C-edited PGSE diffusometry

Until now proton diffusion weighted profiles of the emulsions have been presented and information about the oil droplets obtained. However, one is never sure that the residual water and the surfactant, if present in high enough concentrations, are not contributing to the observed signal. In order to overcome this limitation of $^1$H PGSE diffusometry and confirm the above results, $^{13}$C-edited PGSE diffusometry is introduced. This technique allows the detection of only the oil component in the emulsion.
Figure 3.14: $^{13}$C-edited PGSE weighted profiles of the creamed emulsion E6 (a) and E2 (b). In both cases, $\Delta=640$ ms and $\delta=1$ ms. From the top, profiles are shown for gradient strengths from 1.42 (top profile) to 86.92 G/cm (lower profile) in steps of 4.275 G/cm and from 4.8 (top profile) to 91.2 G/cm (lower profile) in steps of 4.8 G/cm, respectively.

$^{13}$C-edited PGSE weighted profiles for emulsions E6 and E2 are shown in figure 3.14 (a) and (b), respectively. These profiles are the $^{13}$C-edited version of fig. 3.10 (a) and (d) and, in contrast to those, only the oil in the cream layer is visible (data recorded for the other emulsions have similar features). However, the PGSE profiles recorded with small diffusion gradients no longer have the square shape associated with the $^1$H measurements, probably because of a non optimal transfer efficiency in the CYCLCROP editing. Nevertheless, the $^{13}$C-edited profiles show the same trend
observed in the proton measurements: the signal at the top of the cream of emulsion E6 quickly decays, while it is much less attenuated for emulsion E2. Therefore, the $^{13}$C-edited experiments support the results obtained from $^1$H PGSE diffusometry, suggesting that the water in the cream layer is hardly visible in the $^1$H profiles, probably because it is in small quantities and because it is not confined, so that its signal is rapidly attenuated to zero.

Following the same analysis presented for $^1$H measurements, distribution curves at different positions along the cream are obtained, as shown in fig. 3.15. While a good

![Figure 3.15: Oil droplet distribution as a function of the height of the cream layer, as evaluated from $^{13}$C-edited PGSE weighted profiles for emulsions (a) E6 and (b) E2 (the lighter shading corresponds to the base of the cream).](image)
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signal-to-noise ratio is obtained for emulsion E6, which is enriched with methyl-\textsuperscript{13}C-toluene, it has not been possible to fit the echo decays of emulsion E2 (not \textsuperscript{13}C-enriched) with eq. 3.5. In this case, fitting according to the uni and bi-modal versions of the Tanner and Stejskal equation (eq. 3.2) have been performed, but no information about the distribution width is obtained (see fig. 3.15 (b)). However, conclusions similar to those already presented can be drawn.

In summary, the \textsuperscript{13}C-edited results support the conclusions of \textsuperscript{1}H NMR.

3.4.4 Further experiments

Further experiments have been recorded on emulsion E6 at natural \textsuperscript{13}C abundance. The emulsion was stored for a total of three months, during which time the \textsuperscript{13}C-enriched toluene evaporated. The experiments were recorded using a doubly-tuned coil, 7 mm in internal diameter and 10 mm long, which allows better B\textsubscript{1} homogeneity and more uniform cross-coupling than the coil used in the experiments described earlier. The length of the \(\pi/2\) \textsuperscript{1}H pulse was 10 \(\mu s\) and that of the \textsuperscript{13}C was 45 \(\mu s\). Such short pulses allow the use of the PRAWN-\(\pi\) scheme for cross-polarisation [Chandrakumar and Kimmich, 1999], which is suitable for broadband applications, as stated in chapter 2. \textsuperscript{1}H PGSE weighted profiles are presented in fig. 3.16 (a). The water signal is now more intense than the cream signal, as expected. Compared to the earlier measurements, a certain degree of coalescence has occurred during the storage period and, for example, the signal at the base of the cream is about 20\% more attenuated than before. Fig. 3.16 (b) shows the corresponding PGSE weighted, \textsuperscript{13}C-edited profiles, in which the profiles at small diffusion gradients now reflect the shape of the proton measurements. The profile intensity at the top of the cream is higher than at the bottom, indicating that the cream is denser at the top, probably due to the presence of large droplets and some smaller droplets filling the interstices. Finally, figures 3.17 (a) and (b) show the oil distribution curves at different positions in the cream, obtained, according to the analysis presented earlier, from the data in
Figure 3.16: (a) $^1$H PGSE weighted profiles and (b) corresponding $^{13}$C-edited PGSE weighted profiles for emulsion E6 at natural abundance and recorded with the 10 mm probehead. In (a) from the top, profiles are shown for gradient strengths from 0.95 to 90.25 G/cm in steps of 4.75 G/cm. In (b) from the top, profiles are shown for gradient strengths from 4.56 to 86.64 G/cm in steps of 4.56 G/cm. In both cases, $\Delta=640$ ms and $\delta=1$ ms.

fig. 3.16 (a) and (b), respectively.
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Figure 3.17: Oil droplet distribution for E6 at natural abundance as a function of height of the cream layer as calculated from (a) $^1$H PGSE weighted profiles and (b) $^{13}$C-edited profiles, shown in fig. 3.16 (a) and (b), respectively. A single Gaussian distribution fits reasonably well the $^{13}$C-edited data.

3.5 Modelling

3.5.1 Model of creaming: "Pinfield et al."

Several attempts have been made to model the effects of creaming (and sedimentation) in emulsions and an overview of them is given by Dickinson [Dickinson, 1988, pages 48-54]. Recently, Pinfield et al. [Pinfield et al., 1994] have proposed a model that predicts the concentration profiles in a polydisperse system. According to this model, oil droplets rise upwards in the emulsion at their Stokes' velocity. The velocity is measured relative to the water. Since there is conservation of volume, the water is moving downwards and small droplets can go down relative to the container. Droplets continue to rise until a critical oil concentration is reached in the cream layer, after which they can rise no more. The emulsion is divided into horizontal layers and, in order to take into account the oil droplet size distribution, each layer is imagined to be made of bins, each containing droplets of radius $r_i$ at an oil volume fraction $\phi_i$. Droplets of each bin are assumed to move relative to the
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container wall at a velocity $u_i$

$$u_i = \frac{2 \tau_i^2 (\varrho_{\text{water}} - \varrho_{\text{oil}}) g}{9 \eta_0 (1 - \phi \exp(5\phi(1 - \phi)/3))} - u_{\text{water}},$$  \hspace{1cm} (3.6)$$

where $\varrho_{\text{water}} - \varrho_{\text{oil}}$ is the difference in density between the two phases, $\eta_0$ is the zero-shear viscosity of the continuous phase (that is water containing some gum xanthan), $g$ is the acceleration due to gravity and $\phi$ is the total oil volume fraction in the layer containing the bin ($\phi = \sum_i \phi_i$). The first term in eq. 3.6 is the terminal Stokes' velocity modified by a semi-empirical factor and represents the velocity of the droplets relative to the water. The correction introduced is due to Barnea and Mizrahi [Barnea and Mizrahi, 1973] and takes into account the steric hindrance due to the presence of surroundings particles. The second term of eq. 3.6 is the water velocity in the opposite direction, given by

$$u_{\text{water}} = \frac{\sum_i u_i \phi_i}{1 - \sum_i \phi_i}.$$ \hspace{1cm} (3.7)$$

In polydisperse emulsions this term largely influences the motion of small droplets: larger droplets move upwards more quickly than small droplets, causing a large water downflow. Thus, small droplets, while still rising relative to the water, can descend relative to the container.

Droplets also freely diffuse with a diffusion coefficient given by

$$D_i = \frac{k_B T}{6\pi \eta_0 r_i} \left(\frac{1 - \phi}{(1 + \phi)^{1/3} \exp(5\phi(1 - \phi)/3)}\right) (1 + 8\phi + 30\phi^2)(1 - \phi),$$ \hspace{1cm} (3.8)$$

where $T$ is the absolute temperature. The factors are in turn the Stokes-Einstein coefficient, a semi-empirical concentration-dependent coefficient, a thermodynamic particle interaction term, and a term arising from calculating the velocity relative to the container. Diffusion is fastest for the smallest droplets.

The flux of droplets of radius $r_i$, crossing a layer at height $z$ in the emulsion is then given by:

$$F = u_i \phi_i - D_i \frac{\partial \phi_i}{\partial z},$$ \hspace{1cm} (3.9)$$
Hence, the generalised diffusion equation becomes:

\[
\frac{\partial \phi_i}{\partial t} = \frac{\partial}{\partial z} \left( -u_i \phi_i + D_i \frac{\partial \phi_i}{\partial z} \right).
\] (3.10)

By numerical integration of eq. 3.10 with the appropriate boundary conditions, the droplet size distribution as a function of time and space for each droplet size is obtained. The final concentration of oil, the viscosity of the continuous phase, the droplet size distribution and the difference in density between the two media can be adjusted to achieve a better fit to experimental data. However, the viscosity of the continuous phase in practice scales the buoyancy and the diffusion terms in the same way. As a consequence, although the absolute creaming rate varies with the viscosity, the form of the droplet size distribution does not change with the reduced time \( t' = t/\eta_0 \), and the final creaming profiles will be the same if the other three variables are fixed. It is clear that the model does not predict differences in the spatial dependence distribution size between emulsions when only the viscosity varies.

### 3.5.2 Modelling the data

The oil volume fraction was calculated for all layers and bins at each time-step, and numerical simulations were carried out until the emulsion was fully-creamed, that is, until there was no oil left in the aqueous phase and the concentration in the cream layer reached the critical oil volume fraction. The droplets were assumed to be initially uniformly distributed in the emulsion, and the input droplet size distribution was obtained using the optical microscopy data. The initial oil concentration was determined by the emulsion manufacture, as well as the density of the oil phase. The critical oil concentration, that is the final oil volume concentration in the cream, was estimated from the width of the cream and aqueous layers in the NMR profiles. The viscosity of the continuous phase varies with the concentration of gum xanthan, but it was arbitrarily chosen, as it has no effect on the final droplet size distribution, as stated earlier. The only requirement was that the simulation was carried out over a
sufficiently long time to ensure that the emulsion was fully-cream ed. The number of horizontal layers in which the emulsion is divided, the number of bins forming each layer, and the time step were varied to check convergent results.

Fig. 3.18 shows the simulated oil droplet size distribution as a function of position in the cream layer of emulsion E6 (containing no gum xanthan). As the droplet radius distribution is very similar in all emulsions, the only parameter which can affect the simulations is the critical oil volume concentration (besides a slight difference in the density of the oil phase which is negligible). However, the modelled distributions do not change significantly by varying the critical oil volume fraction from 73 wt%, characteristic of E6, to 83 wt%, characteristic of E2. Therefore, fig. 3.18 represents well the simulated data for emulsion E2, with maximum concentration of gum xanthan.

For emulsion E6, with no gum xanthan, figure 3.18 should be compared to the interpreted data shown in figs. 3.12 (a) and 3.15 (a). The proton NMR interpreted data are reproduced in figure 3.19 (a) for easy comparison. Indeed a very good correspondence between simulated and experimental data is seen. By way of contrast, there is poor agreement between theory and experiments for emulsion E2, containing the maximum amount of gum xanthan. Figure 3.19 (b) reproduces the proton NMR interpreted data and the $^{13}$C NMR interpreted data were shown in fig. 3.15 (b).

Though comparison in real space is easy to visualise, it can be affected by potential errors and artefacts in the analysis of the NMR data. In order to minimise these artefacts, comparison between experimental data and predictions of the model can be made in q-space, that is measurement space. In this case, the exact NMR signal expected is calculated from the theoretical droplet size distribution in each layer.

In fig. 3.20 (a), the experimental NMR data are plotted as echo attenuation at different positions in the cream against gradient strengths as obtained by $^1$H PGSE experiments for the creamed emulsion E6. The continuous lines are the
Figure 3.18: Oil droplet size distribution for the creamed emulsion E6 as evaluated according to the Pinfield et al. model. From left to right, the curves range from the bottom to the top of the cream layer in steps comparable with the distribution curves obtained by NMR. The prediction for the other emulsions are very similar.

Figure 3.19: Oil droplet size distribution as a function of the height of the cream layer as calculated from experimental $^1$H NMR data for emulsions E6 (a) and E2 (b), reproduced here for easy comparison.

corresponding echo attenuation predictions of the model, which are obtained by calculating the echo intensity for each radius with the Tanner and Stejskal equation (eq. 3.2) weighted with the theoretical corresponding oil volume fraction and summing over all droplet sizes. Comparison in measurement space for emulsion
Figure 3.20: Comparison between $^1$H PGSE decays at different heights in the cream (symbols) and the predictions of Pinfield et al. model (continuous lines), for emulsion (a) E6, and (b) E2. The top trace corresponds to the bottom of the cream and the peculiar horizontal trace in the centre of (a) corresponds to the water/cream interface, where some water is present and includes its rapid, initial decay in the experimental data.

E2 is shown in fig. 3.20 (b). Again, it is clear that the model reproduces the data for the emulsion with no gum xanthan (E6). This is not the case for the emulsion with 0.1% gum xanthan (E2).

In conclusion, the Pinfield et al. model successfully explains the spatial dependence of the droplet size distribution for emulsion E6 (containing no gum xanthan). In contrast, the model fails to predict the spatial independence of the droplet size
distribution for emulsion E2, which contains 0.1 wt% gum xanthan. As discussed in the introduction, the presence of gum xanthan can induce flocculation, a mechanism that is not included in the model.

3.6 Discussion

3.6.1 Polymeric stabilisation and flocculation

Polymers that are free in solution can influence the stability of a colloidal dispersion by either inducing the aggregation of colloidal particles or by imparting stability. When two spherical particles in a solution containing free polymer approach each other at a distance (surface separation) less than twice the “diameter” of the polymer chains, there is a demixing of polymer chains and solvent, so that the polymer can be excluded from the region between the particles, the “depletion zone”, into the bulk solution (see fig. 3.21 (a)). As a result, the Gibbs free energy of the system increases, as shown in fig. 3.21 (b). Closer approach excludes the essentially pure solvent from between the particles into the bulk solution and lowers the free energy. It follows that there is a potential energy barrier opposing the close approach of the particles. If the barrier is high enough, particles will be stabilised by the presence of the polymer (depletion stabilisation), while if the maximum is lower particles will be held together in flocs, as a result of being in a potential minimum. Flocculation induced by free polymer in solution is called depletion flocculation [Hunter, 1995, pages 483-488].

It has been found for a uni-modal dispersion or emulsion that the height of the barrier is proportional to the particle size and to the square of the polymer concentration and is of the order of $k_B T$ [Feigin and Napper, 1980]. According to Feigin and Napper, the change in free energy $\Delta G^{\text{mix}}$ of close approach of two flat plates (or two spheres) immersed in a polymer solution consists of two terms: $\Delta G^{\text{mix}} = \Delta G_1 + \Delta G_2$. The first term, $\Delta G_1$, describes the mixing of solvent with
Figure 3.21: Schematic representation of (a) the origin of depletion flocculation and (b) the free energy of two colloidal particles immersed in a free polymer solution, as a function of their separation d. D is the “diameter” of the polymer chains. The height of the maximum is comparable to the depth of the minimum and is of the order of a few $k_B T$'s at room temperature.

polymer and is given by:

$$\Delta G_1 = k_B T V \left( \frac{\phi_S}{V_S} \ln \phi_S + \frac{\phi_P}{V_P} \ln \phi_P + \chi \frac{\phi_P \phi_S}{V_S} \right). \quad (3.11)$$

$\phi_S$ and $\phi_P$ are the volume fraction of solvent and polymer respectively, in the depletion zone; $V_S$ and $V_P$ are the volume of a solvent molecule and of a macromolecule respectively; $\chi$ is an interaction parameter and $V$ the volume expelled during the approach. The second term $\Delta G_2$ accompanies the expulsion of the volume $V$ of polymer solution of volume fraction $Q$ ($Q$ approaches the polymer volume fraction in the bulk, $\phi_P^{bulk}$) and is equal to:

$$\Delta G_2 = k_B T \frac{V}{V_S} \left[ \ln \phi_S + \phi_P - Q(1 + \phi_P) + (Q + Q \ln \phi_P - \phi_P) \frac{V_S}{V_P} \right. \\
+ \left. \chi (Q \phi_S^2 - Q \phi_P^2 + \phi_P^2) + \phi_P \phi_S (Q \phi_S + Q \phi_P - \phi_P) \frac{d\chi}{d\phi_P} \right]. \quad (3.12)$$
In addition the two authors introduce a correction to the free energy change $\Delta G$, $\Delta G = \Delta G^\text{mix} - T \Delta S^\text{CONF}$, to take into account that not all macromolecule conformations are allowed. $\Delta S^\text{CONF}$ is given by:

$$
\Delta S^\text{CONF} = -k_B V_{\text{depl}} C_P^{\text{tot}} \left( \frac{C_P}{C_P^{\text{tot}}} \ln \frac{C_P}{C_P^{\text{tot}}} + 1 - \frac{C_P}{C_P^{\text{tot}}} \right),
$$

where $V_{\text{depl}}$ is the volume of the depletion zone, $C_P^{\text{tot}}$ and $C_P$ are the concentration in the whole sample and in the depletion zone, respectively. As a consequence, in a colloidal dispersion of uncharged particles or in an emulsion containing no free polymer, flocs are expected to be held together only by the van der Waals forces. If enough polymer is added, depletion flocculation can occur. By further increasing the polymer concentration, the energy barrier to close approach is increased and depletion stabilisation is induced, although there is not much experimental evidence for this effect.

### 3.6.2 Evidence for the effects of depletion flocculation

The variation of the droplet size distribution with gum xanthan concentration in the emulsions studied can be explained in terms of depletion flocculation and depletion stabilisation. These mechanisms do not occur when there is no free polymer in the emulsion. In this case, large droplets are likely to be found at the top of the cream and small droplets at the bottom, as schematically shown in fig. 3.22 (a) and the gravimetric model due to Pinfield et al. [Pinfield et al., 1994] reasonably describes the dynamic processes taking place during creaming. Low concentrations of free polymer have no effect on the stability, as follows from the study of emulsions E5 and E4. However, increasing the free polymer concentration ultimately results in the onset of flocculation. With 0.1 wt% of gum xanthan in the continuous phase, droplets can randomly aggregate in flocs containing a distribution of droplet sizes. These flocs all have a similar effective size, so that they will rise at a similar creaming rate, yielding a uniform distribution in the cream layer, as schematically shown in fig. 3.22 (b). However, as noted earlier, the energy barrier varies with the droplet radius.
Therefore, it is also possible that large droplets are stabilised by the presence of gum xanthan and that small droplets aggregate into flocs, as indicated in fig. 3.22 (c). Both large droplets and flocs of small droplets can have the same effective size and consequently the same creaming rate, giving, once again, a uniform distribution.

![Figure 3.22: A schematic representation of the oil droplets in the cream layer in absence of free polymer (a) and with 0.1 wt% gum xanthan dissolved in the water. In (b) only depletion flocculation is considered, while in (c) both depletion stabilisation and flocculation are considered.](image)

According to recent calculations [Dickman and Yethiraj, 1994], depletion stabilisation is less likely than depletion flocculation in the emulsions studied, so that the scenario presented in fig. 3.22 (b) is more probable. In order to distinguish between these two situations (that is, depletion flocculation of small and big droplets or depletion stabilisation of big droplets and depletion flocculation of small droplets), it is necessary to gain data on the creaming rates and the time dependence of the spatial distribution of emulsion droplets. That NMR can provide this information is now established, and chapter 4 presents a dynamic creaming study for emulsion E3.
3.7 Conclusions

There are two main conclusions to be drawn from the work presented in this chapter: the former regards the techniques employed and the latter the results obtained.

Firstly, it has been shown that a combination of NMR imaging and pulsed-field-gradient spin-echo restricted diffusometry is a very powerful technique in the study of the spatial dependence of the droplet size distribution in the cream layer of turbid emulsions. CYCLCROP pulsed field gradient diffusometry was introduced as a new technique in order to completely suppress the signal of the water. However, this technique suffers from a low signal-to-noise ratio due to the low natural abundance of $^{13}$C. For this reason $^{13}$C-enriched materials were used in some of the experiments. Moreover, the transfer of magnetisation is a relatively time-consuming process. Here it is on the order of $T_2$ of the oil, so that the $^{13}$C-edited signal is partially attenuated. Finally, care should be taken in assuring an efficient transfer of magnetisation by an appropriate choice of the pulse sequence and cross polarisation scheme. In most of the experiments a highly frequency-selective magnetisation transfer sequence was used and the transfer of magnetisation which resulted was locally reduced because of background field gradients. It has been shown that this limitation can be overcome by using a broadband cross polarisation scheme. This new technique is potentially useful in the study of a wide range of other phenomena, such as coalescence, aggregation and phase separation.

Secondly, the spatial dependence of the droplet size distribution has been obtained for the cream layer of a series of oil-in-water emulsions, and it has been found that the oil droplet size distribution varies with position in a manner dependent on the concentration of gum xanthan. As this dependence can be explained in terms of depletion flocculation and depletion stabilisation, the effect of free polymer should be included in future models of creaming. Incidental to this study, it has been shown that there is no significant deformation of the droplets in the cream layer upon contact and that there is no re-distribution of the droplets within the cream
layer over time.
Chapter 4

Creaming of oil-in-water emulsions

4.1 Introduction

Of the emulsions studied in chapter 3, the emulsion containing 0.033 wt% of gum xanthan (E3), creams at a rate most suitable for study by NMR diffusometry.

$^1$H PGSE spatially resolved experiments of a fresh emulsion containing the same amount of gum xanthan as E3 were recorded while the creaming process was underway. The experiments are analysed using the procedure reported in chapter 3 and the results are, once again, compared to the predictions of the Pinfield et al. model [Pinfield et al., 1994]. Evidence that droplets aggregate in flocs with an effective size considerably larger than the individual droplets is given at the end of the chapter.

4.2 Experimental procedure

An emulsion made up of 33.3 wt% decane and 66.6 wt% aqueous solution (containing 0.033 wt% gum xanthan and 1.0 wt% surfactant Tween 80) was prepared according to the procedure reported in the previous chapter. The emulsion is characterised by a bi-modal droplet size distribution. The droplet size distribution was determined by
optical microscopy and was found to be in good agreement with the results already presented. Rheology measurements of a 0.033 wt% gum xanthan solution were kindly carried out by Mr. P. Hodder of TA Instruments Ltd (Leatherhead, UK) with a CSL\textsuperscript{250} Autogap Set instrument. Controlled stress experiments were performed yielding a zero-shear rate viscosity of the continuous phase, $\eta_0$, of $0.045\pm0.007$ Pa\cdot s at $20\,^\circ\text{C}$. The large error reflects numerous difficulties encountered in the measurements. NMR experiments were performed on the freshly prepared emulsion according to the procedure described in chapter 3. $^1\text{H}$ PGSE profiles were acquired initially at a time interval of 10 minutes. After two hours the acquisition time was increased to 20 minutes and finally to 40 minutes for an overall observation time of 17 hours. At the end of the set of experiments, the aqueous phase of the emulsion was slightly opaque, indicating that some of the smallest droplets were still present within it.

### 4.3 Results

Fig. 4.1 shows typical $^1\text{H}$ diffusion weighted profiles at different times during the creaming of the emulsion. Initially the emulsion is uniform as expected. However, even in the first profile-set the cream layer has started to build up at the very right, fig. 4.1 (a). In figs. 4.1 (b), (c) and (d) three different distinct regions are visible: an aqueous layer on the left, an emulsion layer in the middle and the cream layer on the right. With time, the central region disappears, while the aqueous and cream regions become wider. In fig. 4.1 (f) the emulsion is almost fully-creamed and the oil density is approximately uniform across the cream. The gap between the water phase and the emulsion or cream layer is a magnetic susceptibility and/or chemical shift artefact, as previously discussed.

The water region is quickly attenuated with gradient strength, as observed in the experiments on fully-creamed emulsions, consistent with previous observations that only a small quantity of oil is present. The central region contains two components, one of which is quickly attenuated and therefore is attributed to the water, while
Figure 4.1: $^1$H PGSE weighted profiles of the creaming emulsion at (a) 6, (b) 26, (c) 35, (d) 55, (e) 84 minutes and (f) 17 hours after shaking ($\Delta=640$ ms and $\delta=1$ ms). From the top, profiles are shown for gradient strengths from 1.9 G/cm (top profile) to 87.4 G/cm (bottom profile) in steps of 5.7 G/cm in (a), (b), (c), (d) and (e). In (f) profiles (number of scans four times bigger) are shown for gradient strengths from 0.95 G/cm (top profile) to 86.45 G/cm (bottom profile) in step of 4.75 G/cm.
the other is attributed to the oil droplets. Finally, the cream layer has the same appearance as in the experiments recorded in the previous chapter and, therefore, the water signal is hardly visible.

The shape of the signal as a function of gradient strength in the final cream layer of fig. 4.1 (f) suggests a spatial dependence of the droplet size distribution that is consistent with a partial degree of flocculation, as expected from the results presented in chapter 3.

4.4 Analysis

The analysis of the echo attenuation at each position in the sample was carried out according to the procedure described in the previous chapter. In the central region it was necessary to fit the data to two components: one associated with the mobile water component and the other with the oil droplets. Attempts to distinguish between the two oil droplet size distributions in this region failed because too many constraints needed to be introduced in the fitting procedure. The echo attenuation in the cream layer was fitted according to eq. 3.5, with a single, or, when necessary, a bi-modal Gaussian volume distribution function.

The oil droplet distribution at different positions within the sample and at different times is obtained from the aforementioned fits and, as an example, fig. 4.2 shows typical distribution curves for the emulsion, 55 minutes after shaking. The five bottom layers shown in the figure were fitted using a single Gaussian distribution and correspond to the region where some water is observed by NMR, while a bi-modal Gaussian distribution was necessary to fit the top three layers, corresponding to the region where the water is not detected, hence the discontinuity in the trend observed. In spite of this, it is apparent that large droplets cream faster than small droplets, as expected, and that there may be some flocs at the top of the cream. The oil droplet size distribution in the cream at the end of the creaming process was described in chapter 3 and no further comments are reported in this chapter, which
is, instead, focused upon the temporal variation of the oil concentration across the emulsion.

Figure 4.2: Oil volume distribution curves at different positions in the emulsion, as calculated from the NMR data shown in fig. 4.1 (d), recorded 55 minutes after shaking. The curve at the very far left corresponds to a height of 0.68 cm from the base of the sample and the most intense curves moving towards the right are the distributions up through the sample in steps of 0.82 mm. The three layers at the top of the cream were fitted using a bi-modal Gaussian distribution function.

Figure 4.3 shows the oil volume fraction at different times, and a sharp meniscus separating a depleted region from the rest of the emulsion is observable. The curves were obtained by subtracting the water intensity estimated by the aforementioned fits and were calibrated according to the known oil volume fraction at the end of the creaming. As it was impossible to fit the oil component in the small transition region, which separates the aqueous layer from the emulsion, it was arbitrarily assumed to be equal to zero. As a consequence, the water phase width is slightly overestimated and the front of the emulsion, which moves towards the left with time, appears to be very sharp. This assumption is not believed to affect the overall results, as only one or two experimental points per curve are affected by this procedure. Moreover, it should be noted that $^1$H PGSE with the parameters used is not sufficiently sensitive to the small droplets still present in the aqueous layer.

The concentration profiles of figure 4.3 show a distinct gradient in the oil concentration within the cream layer during the creaming process. The top surface
Figure 4.3: Oil concentration profiles at 6 (circles), 26 (squares), 35 (diamonds), 55 (up-triangles), 84 (down-triangles) minutes and 17 hours (stars) after shaking. The first five sets of data were acquired over 10 minutes, while the last data set was acquired over 75 minutes. The x-axis is directly comparable with that in fig. 4.1 and the position of the arrow approximately indicates the base of the sample.

of the cream is the first part of the layer to form and here the oil concentration is highest and soon approaches the critical concentration. The concentration of oil at a specific time decreases lower down into the cream. With time, the oil concentration of the cream layer becomes more uniform as the cream compacts.

4.5 Modelling the data

Data is modelled according to the model due to Pinfield et al. [Pinfield et al., 1994], as described previously. Typical simulations of instantaneous profiles are shown in fig. 4.4 as continuous lines and were obtained using the measured value of zero-shear viscosity of 0.045 Pa-s, the experimental droplet size distribution, the experimental critical oil concentration and the difference in density between water and decane. The simulation curves are affected by a slight instability of the simulation programme
due to a finite time and spatial steps, which cause the small wobbles. The chosen time and space size step is a compromise between the necessity of obtaining good simulations and limiting the required computing time. However, the simulation was run with different step sizes to ensure convergence of the theoretical profiles.

Figure 4.4: Oil volume distribution curves and corresponding simulation curves (solid lines) at (a) 6 minutes (circles), (b) 26 minutes (squares), (c) 55 minutes (up-triangles) and (d) 17 hours (stars) after shaking. The simulated curves were obtained by using the experimental bi-modal droplet size distribution, the experimental value of viscosity (0.045 Pa·s) and real times.

A vast disagreement between simulation curves and experimental data is observed in fig. 4.4. There are two main differences: the rate of creaming and the shape of the curves. The discrepancy in the rate of creaming may be caused by the value of zero-
shear viscosity used (0.045 Pa-s), which has a 15% measured error margin. However, only slightly better fits to the experimental data are obtained if the viscosity is reduced by more than one order of magnitude, a change which is not consistent with the rheology measurements. As an example, fig. 4.5 shows the same experimental data as fig 4.4, compared to simulations with \( \eta_0 \approx 0.0025 \text{ Pa-s} \). The theoretical cream layer is overlapped with the experimental one, at least at the early stages of the creaming. It should be appreciated that changing the value of the viscosity only

![Figure 4.5: Oil volume distribution curves and corresponding simulation curves (solid lines) at (a) 6 minutes (circles), (b) 26 minutes (squares), (c) 55 minutes (up-triangles) and (d) 17 hours (stars) after shaking. The simulated curves were obtained by using the experimental bi-modal droplet size distribution, real times and an arbitrary value of viscosity of \( \approx 0.0025 \text{ Pa-s} \). The effect of changing the viscosity is equivalent to shifting the time-scale.](image-url)
varies the effective time-scale (see section 3.5.1). It does not vary the shape of the cream profile which remains in poor agreement with the theory.

In order to affect the shape of the curves, it is necessary to change the particle size distribution. Discrepancy in the particle size distribution may be due to flocculation of droplets induced by the presence of gum xanthan. Flocs rise at a rate consistent with aggregate or effective size, while the PGSE remains sensitive to the sizes of the constituent droplets. Figure 4.6 shows the same experimental data as figs.

Figure 4.6: Oil volume distribution curves and corresponding simulation curves (solid lines) at (a) 6 minutes (circles), (b) 26 minutes (squares), (c) 55 minutes (up-triangles) and (d) 17 hours (stars) after shaking. The simulated curves were obtained by using a single droplet size distribution with $r_0=36$ μm and $\sigma=0.1$, real times and the experimental value of viscosity.
4.4 and 4.5, but now modelled using a single mode droplet size distribution with $r_0=36 \ \mu m$, $\sigma=0.1$, $\eta_0=0.045 \ Pa\cdot s$ and real times. In order to test the sensitivity of the fits of the droplet size distribution parameters, the mean droplet radius, $r_0$, and the distribution width, $\sigma$, have been systematically varied by 5%. These fits are noticeably worse and therefore yield an estimate of the errors in the best fit parameters. The predictions of the model with $r_0=36 \ \mu m$ better reproduce the experimental data. Both the rate of the creaming and the shape of the concentration profiles fit the experimental data. This result suggests that the droplets of the emulsion are partially aggregated in flocs having an effective Stokes radius of 36 \ \mu m. Such flocs are, for example, made of about 57 droplets with $r=8.05 \ \mu m$, the mean size of the hand-shaken emulsion (containing larger droplets). As the flocs have a radius considerably greater than the radius of the droplets (see fig. 3.3), depletion flocculation rather than depletion stabilisation is considerably the probable mechanism operating in the emulsion.

### 4.6 Conclusions

The creaming of an oil-in-water emulsion containing 0.033 wt% of gum xanthan in the aqueous phase and characterised by a bi-modal droplet size distribution was studied using a combination of $^1$H PGSE diffusometry and profile imaging. The experimental oil volume concentration profiles across the emulsion as a function of time were compared to the predictions of the model due to Pinfield and co-workers. It was found that a single droplet size distribution satisfactorily describes the experimental data. As the flocs have an effective size considerably larger than most of the droplets, it is concluded that depletion flocculation is probably taking place, but there is no depletion stabilisation. There is no evidence for significant amounts of droplet coalescence leading to a larger droplet size, as previous study (chapter 3) has shown that the original droplet size distribution is approximately preserved in the cream layer.
Chapter 5

The evaporative drying of alkyd emulsions

5.1 Introduction

In this chapter, liquid-state magnetic resonance microscopy is used to get a further insight into the evaporative drying of alkyd emulsions. Incidental to the study, further information about the drying of colloidal dispersions is obtained.

While little is known about alkyd emulsions, the evaporative drying of latex dispersions has been intensively studied and different scenarios proposed. Most work deals with the study of drops on solid substrates. Croll [Croll, 1986] concludes that the drying occurs uniformly across the drop surface and that there is a drier layer of latex over a wet one in the interior, while Winnik and Feng [Winnik and Feng, 1996] believe that the drying occurs at the outermost regions and the dry region grows inward towards the centre. These authors assume a lateral flow of matter from the drop to the dry edge. Subsequently Parisse and Allain [Parisse and Allain, 1996, Parisse and Allain, 1997] derived expressions for the lateral flow of water in drying drops and assumed that surface tension considerations dictate the shape of the drop. More complex diffusion models have
been published by Routh and Russel [Routh and Russel, 1998]. In this chapter a new diffusion model based on lateral diffusion of water towards the edges of the droplet is proposed as an alternative to the shape models. Although the derivation is very different in detail, the concept has certain similarities to the Routh and Russel model, which was published during the course of this work. These similarities are explained.

Solid state NMR has already been employed to study latexes [Mellinger et al., 1998, Landfester et al., 1998] and different types of water were distinguished. However, to the best of the author's knowledge, no MRI measurement is reported in literature. MRI can be a better choice than NMR because it can yield the spatial and temporal dependence of the water concentration. MRI results can be used to test the current models of drying, one against another. This chapter is organised as follows. After a description of materials and experimental methods in section 5.2, sections 5.3, 5.4 and 5.5 focus on MRM experiments of alkyd drops under static air and describe how local water concentration across the drop can be obtained. In particular, in section 5.5, after a description of the evaporation-lateral diffusion model and of the shape models of Parisse and Allain, the experimental data are compared with the predictions of these models. In section 5.6 the effect of ambient conditions on the evaporation process is investigated. Finally, in section 5.7 a comparison with a non film-forming latex dispersion is reported.

5.2 Experimental

Experiments were recorded for a number of samples under different ambient conditions and using different drop shapes. However, this chapter deals with the study of convex drops of an alkyd emulsion and a non-deformable latex dispersion, prepared as follows.
5.2.1 Alkyd emulsion composition and preparation

The alkyd emulsion used in the MRM experiments was a model system of a high gloss decorative architectural paint and contained 32.4 wt% alkyd, 1.6 wt% 1-methoxy-2-propanol and 2.4 wt% emulsifier. The long oil alkyd was derived from a tall-oil fatty acid, orthophthalic anhydride and pentaerythritol. The organic solvent (1-methoxy-2-propanol, ICI trade name of Closol) and the non-ionic surfactant (trade name of Atsurf E-3969) used in the preparation were supplied by ICI Paints.

The resin was emulsified using the phase-inversion-method, in which water is gradually added to the alkyd and stirred with an anchor stirrer, producing a viscous water-in-alkyd emulsion. According to this method, adding more water to an alkyd provokes an inversion from a water-in-alkyd emulsion into the desired alkyd-in-water emulsion. The addition of a small amount of organic solvent and an elevated temperature can be used to reduce the viscosity of the alkyd. Phase-inversion emulsification is usually the method of choice for alkyds with high viscosities as it promotes the formation of small alkyd droplets with a narrow particle size distribution [Hofland and Schapp, 1990].

The resin (containing the organic solvent) and the aqueous phase were heated separately to about 40° C. The emulsifier was melted and mixed thoroughly with the resin. The water was gradually added to the resin under magnetic agitation. The resultant crude alkyd-in-water emulsion was cooled to room temperature whilst stirring. More mono-sized droplets were obtained by using an Ultra Turrax T8 homogeniser (IKA Labortechnik, Germany) for two hours at a shear rate of about 210 s\(^{-1}\). The alkyd droplets, observed by optical microscopy, showed an average diameter of 2 \(\mu m\) and a relatively narrow distribution width. The density of the emulsion was 1.02±0.01 g cm\(^{-3}\).
5.2.2 Acrylic latex dispersion composition

The acrylic latex water-based dispersion, obtained from Zeneca Resins, consisted of 39.8 wt% solids and was stabilised by 2 wt% anionic surfactant (Nansa AS40) and 0.5 wt% ammonium persulfate (APS) and was prepared by emulsification polymerisation according to the procedure described by Tzitzinou et al. [Tzitzinou et al., 1999]. The density of the dispersion was 1.03±0.01 g cm$^{-3}$. The acrylic was made of a copolymer of butyl methacrylate (BMA), methyl methacrylate (MMA) and methacrylic acid (MAA) in a weight ratio of 85:10:5 and the mean diameter of the particles was 144 nm. The glass transition ($T_g$) of this copolymer is 73° C and the minimum film formation temperature (MFT) is 59° C. Hence, at room temperature particles do not deform during drying and the resultant dried film is powdery.

5.2.3 MR Microscopy methods

In a typical MRM experiment, a drop of either the alkyd emulsion or the acrylic latex dispersion was placed on the end of a polished glass rod (diameter 0.82 cm) which was inserted into an NMR sample tube, fitting the coil. The distance from the top of the rod to the open end of the tube, $l$, was 3.9 cm. Drop volumes ranging from 7 to 12 µl were used. Experiments were recorded under two different experimental conditions: static air (see fig. 5.1 (a)) and flowing dry air (fig. 5.1 (b)). In the latter case, a small flow of nitrogen was blown into the tube in order to promote convective motions. The flow was small enough not to deform the shape of the drop and was hardly detectable. All drying experiments were performed at room temperature on glass substrates to eliminate absorption.

$^1$H NMR images of a vertical slice of the drop across a diameter were recorded on a 9.4 T Chemagnetics spectrometer. Images of alkyd emulsion drops were obtained using a standard spin-echo imaging sequence, with an echo time of 14.5 ms and a sequence recycle time of 500 ms under static air and 400 ms under flowing air. The image acquisition times were changed depending on the type of experiment.
and, usually, were 17 - 51 minutes under static air and 7 minutes under flowing nitrogen. NMR signal was sampled 512 times during the acquisition interval, and the phase-encoded gradients were typically stepped in 64 repeats of the protocol. A sine-bell apodization was applied in the read direction, corresponding both to the static magnetic field direction and to the vertical direction of the drop, and a zero filling in the phase direction (parallel to the base of the drop) to give magnitude-Fourier-transformed image data of 512×512 pixels. The slice thickness was 0.5 mm under static air and 1 mm under flowing air, while the field of view was 10 mm by 10 mm in both cases. Images of latex dispersion drops were recorded and processed as described for the emulsion experiments: echo time 15 ms, recycle time 400 ms, field of view 10 mm by 10 mm, slice thickness 0.5 mm under static air and 1 mm under flowing air, image time 14 and 7 minutes, respectively.
The MRM measurements yield a signal proportional to the local concentration of water so long as the water signal is monitored independently from that of the dispersed phase and so long as the $T_2$ of the water is spatially uniform and constant with time or $T_2$ is much longer than the echo time. The first condition is fully satisfied for the latex dispersion since the latex particles are invisible to MRM. For the alkyd emulsion the difference in chemical shift between the principal alkyd resonance and the water resonance is sufficient to generate almost fully separated images. Variation in $T_2$ with decreasing water concentration could be due to enhanced surface relaxation at the drop interfaces or to water self-diffusion in stronger background gradients. Both relaxation mechanisms are believed not to be important in the early stages of drying.

The humidity of the room changed from one experiment to the other. During the measurement time of each experiment, varying from one hour to one day, the relative humidity percentage ($RH$) of the room, changing with time, was measured at regular intervals. Its value is expressed as an average of these measurements.

5.3 Results

Successive images of a vertical slice across the diameter of an alkyd emulsion drop were recorded under static air. Typical images obtained are shown in fig. 5.2. Each image exhibits two superimposed images chemically-shifted one from the other by 3.4 ppm, corresponding to 1360 Hz in this experiment. This separation corresponds to the difference in chemical shift between the water resonance and the principal alkyd resonance, generated by the methylene groups bound to $sp^3$ hybridised carbon atoms of the aliphatic chains [Rybicky, 1979]. The upper image is due to water. It shrinks with time as water evaporates, and eventually disappears. The lower image is generated by the alkyd and is still visible at longer time. It is fainter because of the shorter $T_2$ value of the alkyd with respect to that of the water. It should be noted that during the drying process, the water image remains thinner at the
edges than at the centre and that the final deposited alkyd layer is thinner at the edges, as well. These results differ from previous studies on dispersions of solid particles [Deegan et al., 1997, Denkov et al., 1992], in which a deposit of particles at the periphery of the drop was observed.

![Image](image.png)

Figure 5.2: Typical $^1$H images of a drop of alkyd emulsion drying under static air at four different times: (from top to bottom) $t \approx 0, 3, 6$ and 9 hours. The relative humidity of the laboratory was 40%. Each image represents an area of 10 mm x 1.8 mm. The image intensity at drying times of 6 and 9 hours are multiplied by 2 and 6, respectively. The image of the alkyd appears below the water image and is hardly visible at drying times of 0 and 3 hours, while it is more evident at 6 hours. The last image at $t \approx 9$ hours represents the final distribution of the alkyd.

### 5.4 Analysis

#### 5.4.1 Getting quantitative information

The drying behaviour of the whole drop is now considered: analysis of the images, such as those in fig. 5.2, enables one to calculate the total mass of water in the drop
as a function of time and to determine the water mass loss rate, \( W \). The initial shape of the drop is assumed to be a spherical-cap. The first image of each experiment is analysed to confirm this assumption and to determine the geometrical characteristics of the drop (\( r_0 \), the radius at the contact base, and \( h_0 \), the height at the apex) and therefore to calculate \( S \), the surface area of the air/drop interface and \( V \), the volume of the drop. The total initial mass of water is evaluated from \( V \), the density of the dispersion and the initial percentage of water.

The mass of water in the drop at successive times is obtained by reconstructing the droplet in three dimensions from the slice observed by MRI. The total three-dimensional intensity of the drop, \( I_{\text{tot}} \), is evaluated from

\[
I_{\text{tot}} = \sum_{i,k} \frac{2\pi I_{i,k} r_i}{\Delta y},
\]

where \( I_{i,k} \) is the signal intensity of the image pixel at the radius \( r_i \) and height \( h_k \) and \( \Delta y \) is the thickness of the slice (see fig. 5.3). \( I_{\text{tot}} \) is then normalised with respect to the first image to obtain the water mass at a particular time. Where the image of the water is superimposed on that of the alkyd, the alkyd signal contributes to the measured integrals. In this case, the integral of the last image, given only by the alkyd, was subtracted from all the others to obtain a good approximation of the contribution of the water alone.

![Figure 5.3: The MRI image, acquired in the \( zz \)-plane, is a vertical slice of a drying drop of thickness \( \Delta y \). A pixel of coordinates \( r_i, h_k \) and intensity \( I_{i,k} \) is indicated.](image)

Fig. 5.4 shows that the total water mass for the drying drop of fig. 5.2 decreases linearly with time (with the exception of the first few points), until the water has
almost disappeared, as expected [Croll, 1986]. The mass loss due to the evaporation of the organic solvent is negligible because of its low initial concentration. Therefore, NMR is adequate for measuring water concentration. The water mass loss rate $W$ is determined from the value of the slope of this plot divided by $S$. For the alkyd emulsion drop drying under static air, $W$ is found to be $7.9 \times 10^{-7}$ g cm$^{-2}$ s$^{-1}$.

![Water mass vs. Time](image_url)

Figure 5.4: Total mass of water against drying time after casting under static air. The solid line through the circles is the best-fit to the experimental data and yields a water loss rate of $7.9 \times 10^{-7}$ g cm$^{-2}$ s$^{-1}$.

For comparison, values of the free evaporation rate $E_v$ at different relative humidities are reported in table 5.1. They were obtained by using the literature value of $E_v = 3.6 \times 10^{-6}$ g cm$^{-2}$s$^{-1}$ at 22° C, $RH=50\%$, under steady conditions [Croll, 1986] and the assumption that $E_v$ is proportional to $(100 - RH)$ [Hisatake et al., 1993]. This linear relation strictly applies above $RH$ of 40%, but, in the current context, any deviations from linearity are not considered important.

Since the experimentally observed water mass loss rate $W$ is well below the free evaporation rate of water $E_v = 4.3 \times 10^{-6}$ g cm$^{-2}$s$^{-1}$ at the same $RH$ of the laboratory, it follows that, under our experimental conditions and assuming accurate measurements, the evaporation of water is not the rate-determining step of the drying process. This discrepancy in the values leads one to believe that the water
Table 5.1: Free evaporation rate \( E_v \) and water vapour flux \( F_d \) at different values of laboratory \( RH \), obtained as described in the text.

<table>
<thead>
<tr>
<th>( RH ) (%)</th>
<th>( E_v ) (gcm(^{-2})s(^{-1}))</th>
<th>( F_d ) (gcm(^{-2})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>( 4.3 \times 10^{-6} )</td>
<td>( 7.1 \times 10^{-7} )</td>
</tr>
<tr>
<td>50</td>
<td>( 3.6 \times 10^{-6} )</td>
<td>( 5.9 \times 10^{-7} )</td>
</tr>
<tr>
<td>60</td>
<td>( 2.9 \times 10^{-6} )</td>
<td>( 4.7 \times 10^{-7} )</td>
</tr>
</tbody>
</table>

loss is being limited by diffusion of water vapour away from the sample and up the specimen tube to the ambient atmosphere, as suggested by Parisse and Allain [Parisse and Allain, 1997].

The water vapour flux \( F_d \) through the specimen tube and, therefore, the “effective” evaporation rate, can be calculated as follows. Just above the drop, the vapour concentration \( c_1 \) corresponds to that of saturated vapour, while at the top of the sample tube the vapour concentration, \( c_2 \), is determined by the \( RH \) of the laboratory. Under steady state conditions, the concentration \( c \) at all points in the tube remains constant and the monodimensional diffusion equation along the tube \( (z) \) then reduces to \( \partial^2 c / \partial z^2 = 0 \), that is the concentration changes linearly from \( c_1 \) to \( c_2 \). The flux of diffusing vapour is the same across all sections and is given by

\[
F_d = -D_v \frac{\partial c}{\partial z} = D_v \frac{c_1 - c_2}{l} \tag{5.2}
\]

where \( D_v \) is the water vapour diffusion coefficient through air and \( l \) is the length of the tube above the drop. Under the assumption that air is an ideal gas and from the definition of relative humidity

\[
RH = \left( \frac{e}{e_w} \right)_{P,T} \times 100 = \frac{x_v P}{e_w} \times 100 \tag{5.3}
\]

\( e \) is the water vapour partial pressure, \( e_w \) is the saturation vapour pressure over water at the temperature \( T \), \( x_v \) is the water vapour mole fraction in the sample tube and \( P \) is the pressure at \( T \).
quantities to deduce $F_d$ under experimental conditions:

$$F_d = \frac{D_v (100 - RH) e_w M_w}{100 P V_m},$$

(5.4)

where $M_w$ is the molecular weight of water vapour and $V_m$ is the volume of 1 mole of gas at s. t. p. ($22.41 \times 10^3$ cm$^3$). The values of $F_d$ as a function of RH, given in table 5.1, were calculated by using $D_v=0.25$ cm$^2$s$^{-1}$ at 20° C and 1 atm [Wexler, 1965, page 264], $P=101,325$ Pa and $e_w=2337.3$ Pa at 20° C [Wexler, 1965, page 123] (this value refers to pure water vapour in equilibrium with pure water, instead of moist air in equilibrium with pure water, but the difference is negligible). The calculated water loss rate of $F_d = 7.1 \times 10^{-7}$ gcm$^{-2}$s$^{-1}$ (RH=40%) is similar to the experimental value reported above, $7.9 \times 10^{-7}$ gcm$^{-2}$s$^{-1}$, at least within the experimental error. Therefore, it is concluded that the total water loss rate under static air is governed by water vapour diffusion in the specimen tube driven by a gradient in relative humidity within the tube.

5.4.2 Getting spatial information

The previous results could have been obtained much more easily and cheaply using a very sensitive balance. However, MRI provides additional spatial information about the water content, so that a further insight into the mechanism of the evaporative drying process is obtained.

The summation in equation 5.1 on the only index $k$, yields, after the normalisation procedure described above, the intensity as a function of the distance $r_i$ from the centre of the drop and, therefore, the mass of water contained in each concentric vertical partition. Figure 5.5 shows the mass of water in each partition divided by the relative surface area of the partition as a function of time after casting for the alkyd emulsion drop. Two features of this plot should be noted. First, the local water loss rate in the centre of the drop is faster than the average $W$ (dashed line), whereas it is slower at the edge. Second, at later times, when the drop is nearly
Figure 5.5: Water concentration (expressed in mass per unit area of partition) shown as a function of position across the alkyd emulsion drop drying under static air. The correspondent images are in figure 5.2. The dashed line is the average water loss rate, $W$, expressed in g cm$^{-2}$ hour$^{-1}$. Symbols are shown in the order of open down-triangles, down-triangles, open diamonds, diamonds, open up-triangles, up-triangles, open squares, squares, open circles and circles from the edge of the drop and moving inwards in steps of 0.41 mm.

Dried ($t \approx 7$ hours), there is an increase in the water loss rate from the centre, while the average remains constant.

## 5.5 Modelling

An original model, here called the evaporation-lateral diffusion model, and two models due to Parisse and Allain [Parisse and Allain, 1996] are now described and subsequently applied to try to explain the foregoing experimental results.

### 5.5.1 The evaporation-lateral diffusion model

The water loss is assumed to be initially uniform across the drop surface. As the drop has a convex shape, there is less water near the drop edge compared to the centre. As the water evaporates, the alkyd concentration increases faster at the
edges than at the centre and the periphery of the drop dries to pure alkyd first. As a consequence, the surface of the wet region of the drop, from which water evaporation takes place, reduces with time. Lateral diffusion of water from the centre towards the edges of the drop is supposed in order to balance the lateral gradient of water concentration. The radial transport of water causes the water loss to be fastest at the sample centre. Only the initial shape of the drop is assumed. At successive times the shape of the drop is determined both by evaporation and by diffusion. However, the diffusion of water on its own does not alter the shape of the drop because it is compensated by reverse diffusion of alkyd, which, as will be explained below, can be envisaged as a reverse flow of emulsion (fig. 5.6). Water evaporation and diffusion are at first discussed separately and put together afterwards.

Evaporation of water

Figure 5.6: Schematic representation of the evaporation-lateral diffusion model with the directions of the processes occurring.

Evaporation

Under static air the total water loss rate is governed by the diffusion of water vapour in the specimen tube. The flux of water vapour up the tube is constant with time. As the area of the wet region of the drop decreases with time, the water loss from the wet drop per unit area increases according to:

$$E_d(t) = F_d \frac{r_0^2}{r(t)^2},$$

(5.5)
where \( r(t) \) is the radius of the water in the drop at time \( t \), \( r_0 \) is the initial drop radius and the two surface areas of the wet region are approximated to their projection in the \( xy \)-plane. This assumption is reasonable as evaporation is mainly along the \( z \) direction, at least at the beginning. Equation 5.5 cannot hold at later stages of the drying process when the wet area decreases towards zero, as it predicts that \( E_d \) tends to infinity. However, this very late regime is beyond the spatial and temporal sensitivity of MRI.

If the experimental conditions are changed so that the process is governed by the evaporation of water, the water loss rate is equal to the free evaporation rate \( E_v \).

Under the assumption that water evaporation from the air/wet drop surface is uniform, the variation of the height of the drop due to evaporation is given by:

\[
\frac{dh}{dt} = -\frac{E}{\rho_w},
\]

where \( E \) is equal to \( E_d \) (eq. 5.5) or \( E_v \), depending on the water loss regime and \( \rho_w \) is the water density. The equation holds as long as there is locally some water, then the height is put equal to the final alkyd profile.

In an analogous way, the variation of the water volume fraction \( \phi \) in the emulsion with time due to the only evaporation can be expressed as:

\[
\frac{d\phi}{dt} = \frac{(\phi - 1) E}{h \rho_w}.
\]

**Diffusion**

Changes in the local content of water due to evaporation lead to changes in the water volume fraction \( \phi \). The gradient in \( \phi \) drives Fickian diffusion of water across the drop. Although the problem is strictly three-dimensional, it can be considerably simplified. Cylindrical symmetry reduces it to cylindrical coordinates. Moreover, as the height of the drop is much smaller than the radius, the problem can be reduced to a single radial dimension. As the wet region becomes more concentrated with
time, the apparent water diffusion coefficient depends on $\phi$ and therefore changes with time. The model assumes that water diffusion does not alter the shape of the drop. As a consequence, any volume of water diffusing in one direction should be balanced by an equal volume of alkyd droplets in the other direction. However, as the diffusivity of the alkyd droplets is much smaller than that of water molecules, the lateral diffusion of water is compensated by a bulk-flow of water and alkyd droplets [Crank, 1994, page 209]. In other words, there is a back-flow of emulsion towards the centre (see fig. 5.6). Under this condition, the apparent diffusion coefficient takes the form $(1 - \phi) D_0$, where $D_0$ is the self-diffusion coefficient of water and is a well-known parameter. Another modification can be made to the expression of the apparent diffusion coefficient. As the water fraction decreases, the tortuosity of the water diffusion path around the alkyd droplets increases. In analogy with previous works on water diffusion in porous media [Kärger et al., 1993, Hughes et al., 1996b], an additional term $\phi^{1/2}$ is introduced to give an apparent diffusion coefficient of $(1 - \phi) \phi^{1/2} D_0$. The latter expression predicts that the diffusivity of water tends towards zero for water concentrations approaching both one and zero. Under the above assumptions and taking into account that the cylindrical cross section of the drop around its centre is $2\pi h(r)r$, Fick's second law of diffusion becomes:

$$
\frac{\partial \phi}{\partial t} = \frac{1}{r h(r)} \frac{\partial}{\partial r} \left[ r h(r) (1 - \phi) \phi^{1/2} D_0 \frac{\partial \phi}{\partial r} \right].
$$

Equation 5.8 is not very dissimilar from a corresponding equation given by Routh and Russel [Routh and Russel, 1998]. Routh and Russel derive their diffusion equation from a detailed consideration of chemical potential. These authors keep separated the flux term from the diffusion term, while in the model proposed here the flux term is incorporated into the diffusion expression, leading to a reduction in the apparent diffusion coefficient. The same authors include a term akin to $\phi^{1/2}$, which accounts for hydrodynamic and thermodynamic interactions, that can be evaluated for monodisperse dispersions of hard spheres with solid fractions up to 0.74 (the
hexagonal close-packing limit) [Russel et al., 1991, page 435]:

\[(1 - \rho)^{2.55} (1 + 4\rho + 4\rho^2 - 4\rho^3 + \rho^4), \quad (5.9)\]

where \(\rho = (1 - \phi)\) is the particle fraction. However, in the model proposed here, the less specific expression \(\phi^{1/2}\) is preferred because alkyd droplets are deformable.

By combining equation 5.8 and eq. 5.7, the following master equation is obtained:

\[
\frac{\partial \phi}{\partial t} = \frac{1}{r h(r)} \frac{\partial}{\partial r} \left[ r h(r) (1 - \phi) \phi^{1/2} D_0 \frac{\partial \phi}{\partial r} \right] + \frac{(1 - \phi)}{h(r) \rho_w} E \quad (5.10)
\]

Equations 5.6 and 5.10 fully characterise the drop throughout the drying process and can be numerically evaluated. The only free parameters of this model are the initial shape of the drop, the initial emulsion composition, the diffusivity of the water and the evaporation rate. The initial shape of the drop is defined by \(r_0, h_0\) and the assumption of a spherical-cap shape. The initial water concentration is determined by the emulsion manufacture. The diffusivity of water is a known value [Mills, 1973] and the evaporation rate can be experimentally obtained by using the procedure described above. Therefore, there are no free parameters in the evaporation-lateral diffusion model.

5.5.2 “Parisse and Allain” models

As an alternative to the evaporation-lateral diffusion model, a brief description of the two models proposed by Parisse and Allain [Parisse and Allain, 1996] is now given. Both models are based on the same idea: the drop preserves a specific shape during water evaporation. The drop is supposed to be composed of two concentric regions: an outer region, called the “foot”, in which the particles form a gel of solid volume fraction \(\rho_g\), and a liquid central region of lower solid volume fraction. The foot forms at the edges and remains pinned to the substrate. It builds up inwards with time and, once formed, its height at a specific radius is constant. The solution
becomes more concentrated as an effect of the water evaporation. As evaporation occurs from the whole drop surface including the foot, there is a flow of matter towards the foot. The effect of the flow is indeed to build up the foot. The two models assume a spherical-cap shape of the central region. In the constant angle model the spherical-cap shrinks inwards maintaining a constant contact angle $\alpha$ with the horizontal, as shown in fig. 5.7 (a). In the constant base model (fig. 5.7 (b)) the “extended” spherical-cap (dashed line) has a constant base area. The drying of the drop is described by the inner radius of the foot $r_f$ and its height $h_f$. These two parameters are calculated on the basis of the specific geometrical assumption and on mass balance considerations.

Figure 5.7: Schematic representation of the drop profiles according to (a) constant angle and (b) constant base model after Parisse and Allain. The foot is defined by $r_f$, the position at which it meets the central liquid part, and by its height $h_f$ at $r_f$. The foot has a solid volume fraction $\rho_g$ and the initial solid volume fraction of the central liquid part is $\rho$. The radius of the drop is $r_0$.

**Constant angle model**

For the constant contact angle model Parisse and Allain derive the two following differential equations:

\[
\pi r_f^2 \frac{(1 - \cos \alpha)^2}{\sin^3 \alpha} (2 + \cos \alpha) \, dr_f - \pi r_f^2 \, dh_f = \frac{E}{\rho_w} \left( s_f + 2\pi r_f^2 \frac{(1 - \cos \alpha)}{\sin^2 \alpha} \right) \, dt \quad (5.11)
\]
and
\[
\frac{E s_f}{\rho_w} \frac{dt}{dt} = \frac{\rho_g - \rho}{\rho} 2\pi r_f h_f dr_f,
\]  
(5.12)

where \( s_f \) is the surface area of the foot. Equations 5.11 and 5.12 can be integrated numerically. In their derivation, the two authors, concerned only with the early stages of drying of concentrated colloidal suspensions, assume that the solid fraction \( \rho \) and, therefore, the water fraction in the central region are constant. Even allowing for this approximation, which is not valid in the late stages, the two equations are valid only while the central region remains and do not describe the drying at later stages when the only foot is present.

**Constant base model**

For the constant base model, explicit solutions for the height of the foot and for the time \( t_f \) at which it forms are provided:

\[
h_f = \frac{\rho G(r_f) h_{0f}(r_f)}{\rho G(r_f) + (\rho_g - \rho) F(r_f)}
\]
(5.13)

\[
t_f = \frac{2\pi r_0 r_f}{s E} \frac{(\rho_g - \rho) h_{0f}(r_f)}{\rho G(r_f) + (\rho_g - \rho) F(r_f)},
\]
(5.14)

where \( s \) is the surface of the cap and \( h_{0f} \) the initial height at the radius \( r \). The two functions \( F \) and \( G \) are given by:

\[
F(r) = \frac{6}{r_0} \frac{r}{1 - \cos \alpha} \frac{\sin^2 \alpha}{2 + \cos \alpha} \left[ \left( 1 - \frac{r^2}{r_0^2} \sin^2 \alpha \right)^{1/2} - \cos \alpha \right],
\]
(5.15)

\[
G(r) = \frac{r}{r_0} \frac{\sin^2 \alpha}{1 - \cos \alpha} \left( 1 - \frac{r^2}{r_0^2} \sin^2 \alpha \right)^{-1/2}.
\]
(5.16)

The derivation of the above equations includes a number of approximations, among which is that the contact angle \( \alpha \) is initially smaller than \( \pi/4 \). As in the previous model, \( \rho \) in the wet region is assumed constant and the equations are valid as long as the central region exists.
5.5.3 Modelling the data

Figure 5.8 shows the predictions of the evaporation-lateral diffusion model for the alkyd emulsion drop drying under static air. This model well describes the experimental data and, in particular, predicts both the features pointed out in section 5.4.2: the non uniform drying rate across the drop and the acceleration of drying at the centre with time. Diffusion is a very important feature of the model and, if set to zero, a set of parallel lines, which poorly fit the data, are obtained.

Figure 5.8: The symbols are the experimental data of the alkyd emulsion drop drying under static air, as in fig. 5.5. The solid lines are the predictions of the evaporation-lateral diffusion model using $D_0 = 2.5 \times 10^{-5}$ cm$^2$s$^{-1}$, $F_d = 7.35 \times 10^{-7}$ gcm$^2$s$^{-1}$ (a value between the experimental value and the predicted one), $r_0 = 0.41$ cm, $h_0 = 0.68$ mm and an initial water volume fraction of 0.636.

As a comparison, fig. 5.9 shows the same data of fig. 5.8, but now analysed according to the two models of Parisse and Allain. The top plot presents the simulations according to the constant angle model, which was slightly modified to describe the drying of the drop at longer times. The solid fraction $\rho$ in the central region is still assumed to be spatially uniform, but is allowed to change with time. To do this, the value of $\rho$ in eq. 5.12 was evaluated as a function of time from the volumes of the foot and the central region and from $\rho_f$. The lower figure is for the constant base model. Attempts to modify the constant base model to allow for $\rho(t)$
Figure 5.9: The symbols are the experimental data of the alkyd emulsion drop drying under static air, as in figs. 5.5 and 5.8. The solid lines are the predictions of the constant angle (top) and constant base (bottom) models of Parisse and Allain, using \( \rho_g = 1, \rho = 0.364, \alpha = 19^\circ \) and \( F_d = 7.35 \times 10^{-7} \) and \( 1.0 \times 10^{-6} \text{ g cm}^{-2} \text{ s}^{-1} \), respectively.

in the same way have failed due to intractable integrals involved in the derivation of equations 5.13 and 5.14. The step-like feature present in the theoretical curves of both plots is a consequence of having assumed \( \rho \) spatially uniform and occurs when a partition belonging to the wet region suddenly becomes part of the foot. The foot is assumed to have \( \rho_g = 1 \) because the alkyd droplets coalesce. However, this assumption raises the question of how water can evaporate from the foot as assumed by the model.

The constant angle model generates curves that are very different from those of the experimental data. The water concentration expressed in mass per unit area of partition is proportional to the height of the partition itself. The parallel lines in
the plot are derived from the assumption that the drop maintains at all the times a constant contact angle. For the constant base model, a value of evaporation rate much larger than the experimentally measured value is required to get "reasonable" fits. Although not satisfactory, the base model fits reproduce the experimental data better than the constant angle model, in agreement with the observations of Parisse and Allain for solid particle dispersions, but neither is as good as the lateral diffusion model.

As a further test of the three models, in fig. 5.10 the final experimental distribution of the dry alkyd is compared with the theoretical predictions of the three models. The constant base model produces an alkyd profile much flatter than that measured, while the constant angle predicts a flow of alkyd towards the periphery, not observed experimentally. The diffusion model is in reasonable agreement with the data.

As a further test of the three models, in fig. 5.10 the final experimental distribution of the dry alkyd is compared with the theoretical predictions of the three models. The constant base model produces an alkyd profile much flatter than that measured, while the constant angle predicts a flow of alkyd towards the periphery, not observed experimentally. The diffusion model is in reasonable agreement with the data.

![Figure 5.10: Experimental final distribution of the alkyd (circles). The solid line is the prediction of the evaporation-lateral diffusion model, the dotted line of the constant angle model and the dashed line of the constant base model.](image)

**5.6 Changing experimental conditions**

When a hardly detectable flow of nitrogen is applied above an alkyd emulsion drop, $^1$H images like those shown in fig. 5.11 are obtained. They show similar features to
Figure 5.11: Typical $^1$H images of a drop of alkyd emulsion drying under a slow flow of nitrogen at four different times: $t \approx 0, 0.3, 0.7$ and $1.3$ hours (from top to bottom). Each image depicts an area $10\text{ mm}$ by $1.8\text{ mm}$. Only the signal of the water is visible in the three top images. The last image (intensity multiplied by 8, acquisition matrix $512 \times 32$) shows the deposited alkyd layer, which is thinner at the periphery of the drop as in the static air experiment. The relative humidity of the laboratory was $35\%$.

those recorded under static air (fig. 5.2), although the evaporation is much faster. The acquisition time of each image is shorter and, consequently, the signal-to-noise ratio of the data is lower because the evaporative process is faster, as becomes evident if the total water mass is plotted against time after casting (fig. 5.12). The experimental total loss rate, $W = 6.7 \times 10^{-6} \text{ g cm}^{-2}\text{s}^{-1}$, is now approximately an order of magnitude faster than before and, within the experimental error, is in agreement with the value of the free evaporation rate expected for the RH of the experiment ($4.6 \times 10^{-6} \text{ g cm}^{-2}\text{s}^{-1}$ at $RH=35\%$). The water mass loss rate is now governed by the evaporation of water.

Again, spatial information across the diameter of the drop can be obtained. Fig. 5.13 shows the experimental local concentrations of water at different radial positions
Figure 5.12: Total mass of water decreases linearly as a function of time after casting for the alkyd emulsion drop of fig. 5.11 drying under flowing nitrogen. The solid line through the squares is a least-squares fit to the data yielding an experimental evaporation rate of $6.7 \times 10^{-6}$ g cm$^{-2}$ s$^{-1}$.

in the drop against time. In the upper part of the figure, the experimental data are overlaid on the theoretical fits according to the evaporation-lateral diffusion model, obtained assuming the experimental value of $E = E_v$. Once again, a good agreement between experimental data and simulations is observed suggesting that the model is valid both under diffusion-limited conditions and free evaporation-limited conditions. The lower part of fig. 5.13 shows, for comparison, the best attempt to fit the experimental data according to the constant base model with $p_g=1$, $\rho=0.364$, $\alpha=16^\circ$ and $E_v = 6.7 \times 10^{-6}$ g cm$^2$s$^{-1}$, the latter being equal to the experimental value. The quality of the fits is similar to those under diffusion-limited conditions and the same considerations and criticisms are valid. Finally, in fig. 5.14 the shape of the deposited alkyd layer, obtained from the bottom image of fig. 5.11, is compared to the theoretical profiles of the lateral diffusion and constant base models. The constant base model still predicts a flat final alkyd layer, which is not experimentally observed. Following the previous discussion, it is clear that the constant angle model is inadequate in describing the final alkyd experimental data.
Figure 5.13: Water concentration, expressed in mass per unit area of partition, shown as a function of position across the alkyd emulsion drop of fig. 5.11 drying under flowing air. Symbols are shown in the order of open down-triangles, down-triangles, open diamonds, diamonds, open up-triangles, up-triangles, open squares, squares, open circles and circles from the edge of the drop and moving inwards in steps of 0.38 mm. The dashed line is the average water loss rate. The solid lines are the simulations according to the evaporation-lateral diffusion model (top) and Parisse and Allain constant base model (bottom).

5.7 Changing to incompressible particles

In the previous sections, alkyd emulsions which contain coalescing particles have been studied. Here the behaviour of a non film-forming acrylic latex dispersion containing incompressible particles is investigated. Images of a latex dispersion drop under the two different experimental conditions are presented and the different models are
Figure 5.14: Experimental final distribution of the alkyd (open circles), obtained from the bottom image of fig. 5.11, and relative predictions according to the evaporation-lateral diffusion model (solid line) and the constant base model (dashed line).

compared with each other once again.

Typical $^1$H images of a non film-forming latex dispersion drop under static and flowing nitrogen are shown in fig. 5.15 (a) and (b), respectively. The copolymer proton $T_2$ is sufficiently short that its contribution to the image intensity is negligible and the signal results only from the water. Depending on ambient conditions, very different water profiles are evident. Under static air (fig. 5.15 (a)), the water recedes from the edges leaving behind a region of lower water concentration. Later on, this region at lower water concentration fades away gradually and uniformly. Under flowing nitrogen (fig. 5.15 (b)), the drop is drier near the polymer/air interface, in agreement with the description given by Croll [Croll, 1986]. On the basis of the water concentration determined in the two regions, it is plausible that in the region at lower concentration there is only bound water, that is water adsorbed on the surface of the solid particles, while in the region at higher concentration both bound and mobile water is present. The latter is water free to move in the interstices among the particles.

The images can be analysed by using the same procedure proposed for the alkyd
CHAPTER 5. THE EVAPORATIVE DRYING OF ALKYD EMULSIONS

Figure 5.15: Typical $^1$H images of an acrylic latex dispersion below its minimum film formation temperature, under (a) static air, and (b) flowing nitrogen, recorded after 4 and 1.5 hours, respectively. The images represent an area of 10 mm by 1.5 mm. A threshold is imposed to the images to emphasize the presence of two regions at different concentration of water. The brighter regions have a water concentration above 40 wt%, the grey region of about 10-20 wt%. In the black regions the water concentration is below 10 wt%.

emulsion drops. However, as the images recorded under flowing nitrogen are very noisy (the process was too fast, so that the acquisition time was considerably reduced) any attempt to get reliable quantitative spatial information has failed. While in this case no further consideration is possible, the experiment recorded under static air is worthy of further analysis. Figure 5.16 shows the local water mass loss rate at different partitions across the latex drop drying under static air, with the fits according to the evaporation-lateral diffusion model (top plot) and constant base model (bottom plot). If the experimental data are carefully observed, a small break of gradient is visible, which occurs in all the curves at about half the initial water concentration and corresponds to a water fraction of 30 wt% everywhere in the drop. This break in the gradient is the basis of the threshold imposed in the images.

While the fits obtained with the evaporation-lateral diffusion model with $F_d = 7.25 \times 10^{-7}$ g cm$^2$s$^{-1}$ (top plot of fig. 5.16) approximately reproduce the experimental data, they fail to predict them in detail as they lack the change in gradient. The model, as it stands, is not able to simulate any sudden change in concentration. The bottom half of figure 5.16 shows the fits to the same data according to the constant base model with $p_g=0.7$, $\alpha=19^\circ$ and an evaporation rate of $1.0 \times 10^{-6}$ g cm$^2$s$^{-1}$, about
Figure 5.16: Water concentration (mass per unit area of partition) at different partitions across a non film-forming acrylic latex drop drying under static air, with an experimental average loss rate of $7.25 \times 10^{-7} \text{gcm}^2\text{s}^{-1}$, as a function of drying time. The experiments were recorded at a laboratory RH of 45%. Symbols are shown in the order of open down-triangles, down-triangles, open diamonds, diamonds, open up-triangles, up-triangles, open squares, squares, open circles and circles from the edge of the drop and moving inwards in steps of 0.41 mm. The continuous lines are the predictions according to the evaporation-lateral diffusion model (top) and constant base model (bottom).

40% greater than measured. In spite of this, the model seems to reproduce better the experimental trend in the early stages of drying. In fact, the end points of the theoretical curves, which corresponds to the formation of the foot, equate with the position of the experimental break in gradient. Thus, the foot of Parisse and Allain probably corresponds to the grey region of fig. 5.15 (a).
5.8 Conclusions

The evaporative drying from alkyd emulsion drops has been studied using liquid-state magnetic resonance microscopy. The technique does not achieve the same spatial or temporal resolution as optical methods used in previous studies on dispersions of solid particles [Deegan et al., 1997, Denkov et al., 1992]. In spite of that, MRI yields precious spatially resolved composition information. It was possible to determine the water concentration in drops as a function of time and space with a resolution of 20 μm. The water loss was monitored under diffusion-limited and evaporation-limited conditions. A new simple model for water loss rate, the evaporation-lateral diffusion model, which includes a lateral diffusion of water from the centre towards the edges, has been presented. This model makes no assumption about the shape of the drop and has no free parameters. It was found that it reproduces the experimental data under both water loss regimes and that it is more successful than the models of Parisse and Allain [Parisse and Allain, 1996]. The latter are based on constraints in the drop shape dictated by surface tension, but do not include diffusion.

The drying behaviour of alkyd emulsions has been compared to that of a non film-forming latex dispersion. While alkyd droplets coalesce, the solid particles of the latex are not deformable. It has been shown that ambient conditions have a large influence on the water profiles during drying of latex dispersions. Under static air the drop is "drier" at the edges, while under flowing air the drop forms a sort of "crust". The evaporation-lateral diffusion model coarsely describes the experimental data, but fails to reproduce them in detail. In this case, the constant base model of Parisse and Allain is found to be more appropriate.

The procedure proposed can be applied to study other innovative coatings materials, like polyurethane dispersions, or the effect of different substrates. The model proposed could be improved by combining the idea of water diffusion with shape considerations. However, this modification is not so straightforward.
Chapter 6

A possible phase-inversion in alkyd emulsion coatings?

6.1 Introduction

When an alkyd coating is cast from an alkyd-in-water emulsion, four different phases, each with a different visual appearance, may appear during the film formation. Figure 6.1 shows a snapshot of a drying film on a glass substrate.

The formation of the different phases is not common to all alkyd emulsion coatings (an exception is, for example, the alkyd emulsion studied in chapter 5) and it may be related to the alkyd droplet size and viscosity [Weissenborn, 1999]. It has been suggested in the literature [Beetsma, 1996, Beetsma, 1998, van Hamersveld et al., 1998] that the alkyd-in-water emulsion inverts through a metastable state into a water-in-alkyd emulsion, and that the four different phases of figure 6.1 are, from the centre towards the edges, an alkyd-in-water emulsion, a metastable intermediate phase, a water-in-alkyd emulsion and neat alkyd, as shown schematically in fig. 6.2. To the best of the author's knowledge, there is no direct experimental evidence of this phase-inversion.

If the scenario depicted in figure 6.2 is realistic, NMR diffusometry can be
CHAPTER 6. PHASE-INVERSION IN ALKYD EMULSION COATINGS

Figure 6.1: Apparent phases in an alkyd emulsion cast on a substrate: (1) the opaque (white) initial alkyd-in-water emulsion, (2) a clear, transparent zone, usually called the metastable state, (3) an opaque region, which is believed to be a water-in-alkyd emulsion, and (4) the clear pure alkyd. With time the boundaries of the phases move from outside to inside, leaving behind the pure alkyd. The relative width of the different regions changes with the ageing of the emulsion, and region 2 becomes larger.

Figure 6.2: Film formation of an alkyd emulsion coating according to current beliefs. When the emulsion reaches a critical composition during the evaporation of water, probably related to close-packing of droplets, the alkyd-in-water emulsion is believed to invert, via a metastable state, into a water-in-alkyd emulsion. The metastable state is described as a bicontinuous phase, where there are no inhomogeneities with dimensions comparable to the wavelength of visible light (or larger), to explain its transparency.

used to gain a further insight into the phase-inversion of alkyd emulsion coatings. PGSE measurements performed on the alkyd-in-water emulsion would yield the self-diffusivity of water and information about the alkyd droplet size. While it is relatively easy to obtain these results with conventional optical methods, as the
emulsion can be diluted, water-in-alkyd emulsions are more difficult to study with optical techniques [Balinov et al., 1994]. In this case, NMR diffusometry offers a powerful alternative as it can yield the size of any water droplets.

6.2 Experimental details

6.2.1 Alkyd emulsion characteristics

The alkyd emulsion used in the NMR experiments was kindly donated by Dr. P. Weissenborn of the Institute for Surface Chemistry, Stockholm, Sweden. It consists of 45 wt% of a low-viscosity long oil alkyd, 50 wt% of water, 5% w/w per alkyd of a non-ionic surfactant (C_{12}/C_{14}EO_{30}) and 0.05% w/w per alkyd of a cobalt drier (cobalt (II) neodecanoate). The resin is based on tall oil fatty acids and isophthalic acid and has an oil length of 83%. The Co-drier was added to the alkyd phase prior to emulsification. The average particle diameter is 0.6 \mu m and the distribution is very narrow.

6.2.2 Sample preparation

Thin film samples of the different phases used in the NMR experiments were prepared according to the following procedure. The alkyd-in-water emulsion was cast on a thin glass coverslip (22 mm \times 50 mm). The backside was scored to enable easy breaking later. The film was allowed to dry for a certain time in order to obtain the maximum area of the phase to be monitored. The glass substrate was cut to the correct dimensions in order to fit the NMR coil, and the other phase regions, if present, were scraped away. Then, the sample was lightly sealed between glass coverslips (spacers made from small pieces of coverslips were used to prevent damaging of the sample) to prevent evaporation of water. Finally, the sample was inserted into a slit in a cylindrical PTFE sample holder fitting the NMR coil and the sample holder
was sealed with PTFE tape. Samples prepared in this way were found to be stable over a period of days. On the other hand, samples, sealed with less care, showed a change in their visual appearance within one hour.

When the initial bulk emulsion is cast on the aforementioned coverslips, the boundaries of the different phases, along the long side of the substrate, remain parallel with each other over time, until the later stages of drying, as one may infer from fig. 6.1. Samples containing all four phases were prepared according to the procedure above described (but without scraping out any phase). Samples prepared in such a way were used in MRM experiments as they allow one to reduce the imaging of all four phases to a single dimension (corresponding to the short side of the glass substrate of fig. 6.1) problem.

### 6.2.3 NMR methods

$^1$H NMR experiments were recorded on a 400 MHz Chemagnetics spectrometer. In diffusometry experiments the stimulated variant of PGSE was employed to allow for long observation times, $\Delta$. Typical diffusion experiments were recorded as a function of the gradient strength, which was varied between 0 and 160 G/cm, and for different $\Delta$s ($\Delta = 10, 200, 450$ ms). The length of the PGSE diffusion gradients, $\delta$, was set to 2 ms and the gap between the first and the second RF pulse in the stimulated-echo to 3 ms. Diffusion measurements on the bulk alkyd-in-water emulsion required less than one hour for a complete set. Experiments recorded on thin film samples required much longer (several hours), especially when a long $\Delta$ was used. Long observation times were chosen in order to fulfil the long time condition ($\Delta \gg \tau^2/(6D)$) for the alkyd droplets and the water droplets, if present. However, this requirement contrasts with the relative short spin-lattice relaxation times for the alkyd and the water, which in the bulk emulsion were measured to be $0.42 \pm 0.02$ s both for the alkyd and the water. Finally, $^1$H diffusion weighted profiles were acquired by prepending the PGSE experiment to a standard spin-echo profiling experiment with a single read
gradient. The profile spin-echo time was 3 ms and the read gradient was applied in the direction perpendicular to the phase boundaries.

6.3 Results and Analysis

6.3.1 $^1$H NMR spectroscopy

$^1$H NMR spectra of the bulk alkyd-in-water emulsion and of the different phase regions appearing during the drying of alkyd-in-water emulsion coatings were recorded. The different phases are referred to according to the numeration in figure 6.1, these being phase 1 - the alkyd-in-water emulsion, phase 2 - the supposed metastable transition state, phase 3 - the supposed water-in-alkyd emulsion, and phase 4 - the neat alkyd.

Bulk alkyd-in-water emulsion

$^1$H NMR spectra (not shown, but similar in appearance to that in fig. 6.3 (a) but with a much more intense water peak) of the bulk alkyd-in-water emulsion show an intense peak, attributable to the protons in the methylene groups of the alkyd, chemically shifted from the water peak by 3.4 ppm, in agreement with the results reported in chapter 5. The other peaks are attributable to other proton resonances of the alkyd [Rybicky, 1979].

Phase 1: the alkyd-in-water emulsion

Figure 6.3 (a) shows a $^1$H NMR spectrum of the fresh alkyd-in-water emulsion prepared as described above and has the same features of the bulk alkyd-in-water emulsion spectra. On the shoulder of the water peak (the intense peak to the left) there is a probable contribution from the alkyd protons on double-bonded carbons [Rybicky, 1979]. Spectra of alkyd-in-water emulsion thin films, purposely sealed
Figure 6.3: $^1$H NMR spectra of thin films of: (a) alkyd-in-water emulsion, (b) supposed metastable transition phase, (c) supposed water-in-alkyd emulsion, and (d) neat alkyd. All spectra are displayed on the same horizontal scale of (d) but the intensity of (a) is divided by 2.

less tightly, show a reduction of intensity of the water peak, confirming the above attribution.

**Phase 2: the metastable phase**

Figure 6.3 (b) shows a $^1$H NMR spectrum of the supposed metastable phase and, contrary to expectations, no water signal is visible. The peak still present on the left of the spectrum is attributable to the alkyd, as proved by the spectrum recorded on the neat alkyd discussed below (fig. 6.3 (d)).
Phase 3: the water-in-alkyd emulsion

A $^1$H NMR spectrum of phase 3, the supposed water-in-alkyd emulsion, is shown in fig. 6.3 (c). The spectrum highly resembles that of phase 2, with no visible water signal.

Phase 4: the pure alkyd

Figure 6.3 (d) shows the $^1$H NMR spectrum of phase 4, the neat alkyd and, as expected, substantially differs from fig. 6.3 (a), whilst displaying the same features of figs. 6.3 (b) and (c).

The result that no water signal is present in phases 2 and 3 is surprising, because water is very easy to monitor with NMR [Freeman, 1997, pages 335-336] and indeed a lot of effort is usually made to suppress the water peak. NMR, at its best performance, can detect concentrations as low as $10^{-5}$ M [Günther, 1995, page 65]. In this specific case, its sensitivity is reduced because the water resonance is superimposed over an alkyd peak. However, the integral ratio of the main resonance of the alkyd and the water region does not change moving from figure 6.3 (b) to (c) and to (d), which is the pure alkyd. If some water is present, it is indeed in trace amounts, unless the water peak is so broad that it is not visible in spectra recorded even with large bandwidths. Such a broad peak can arise from water self-diffusion through strong magnetic field gradients, due to discontinuities in the magnetic susceptibility at highly curved alkyd-water interfaces.

6.3.2 $^1$H PGSE measurements

In order to confirm that the water is never confined within droplets during the drying of an alkyd emulsion coating, $^1$H PGSE experiments were performed on thin films of the alkyd-in-water and the supposed water-in-alkyd emulsions. The experimental procedure was optimised on the bulk alkyd-in-water emulsion and these experiments
are described first.

**Bulk alkyd-in-water emulsion**

As an example, figure 6.4 shows typical PGSE spectra of the bulk alkyd-in-water emulsion recorded with $\Delta=10$ ms and $\delta=2$ ms. By analysing the attenuation of the water signal (figure 6.5), the water self-diffusion is calculated to be $1.9 \times 10^{-5}$ cm$^2$s$^{-1}$, in good agreement with published data [Mills, 1973]. The results of the analysis of the alkyd peak are reported in table 6.1. The diffusivity decreases with increasing “diffusion time” $\Delta$, the PGSE observation time. This is suggestive of restricted diffusion of the alkyd polymer, as might be expected for alkyd confined within droplets. However, the alkyd droplet size estimated by NMR diffusometry is almost one order of magnitude larger than the one estimated by optical microscopy.

![Figure 6.4: Typical $^1$H PGSE (base-corrected) spectra of the bulk alkyd-in-water emulsion, recorded as a function of gradient strength. From the top to the bottom, $g$ is 5, 70 and 100 G/cm. $\Delta=10$ ms and $\delta=2$ ms. The intense signal on the left, quickly attenuated with the increase of gradient strength, is due to the water, free to diffuse. The other smaller peaks are attributed to different resonances of the alkyd and are much less attenuated with increasing gradient strength.](image-url)
Figure 6.5: $^1$H PGSE decay for the water signal (circles) in the bulk alkyd-in-water emulsion as obtained from the experimental data of fig. 6.4 and associated fit (solid line) according to unrestricted diffusion decay.

Table 6.1: Diffusion coefficients of the alkyd in the bulk alkyd-in-water emulsion, calculated from $^1$H NMR diffusion weighted spectra at different $\Delta$ and $\delta=2$ ms. The error on $D$ is estimated to be within 10%.

<table>
<thead>
<tr>
<th>$\Delta$ (ms)</th>
<th>$D$ (cm$^2$s$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>$4.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>200</td>
<td>$3.7 \times 10^{-7}$</td>
</tr>
<tr>
<td>450</td>
<td>$2.7 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

**Thin film samples**

Experiments recorded on thin films of the alkyd-in-water emulsion show that the water peak quickly decays with gradient strength and suggest that the water is free to diffuse as in the bulk alkyd-in-water emulsion. However, the quality of the diffusion weighted spectra in thin film samples is considerably inferior to the bulk sample spectra.

A similar procedure was attempted at later stages of the drying of thin films to determine if the alkyd polymer is now free to diffuse. While no water signal is observed, any conclusions about the alkyd signal are difficult to make due to the low signal-to-noise ratio of the spectra recorded. The bulk neat alkyd was studied with
the aid of fringe field NMR diffusometry using a three-pulse relaxation compensated pulse sequence [Kimmich and Fischer, 1994]. The sequence is a standard stimulated-echo made relaxation independent by obtaining the quotient of the stimulated and primary echo signals. Experiments were recorded as a function of $\delta$ and for a range of $\Delta s$. These experiments are not straightforward to interpret because of the complex chemical structure of the alkyd, but they suggest that the alkyd diffusion coefficient is of the order of $10^{-9}$ cm$^2$s$^{-1}$. PGSE is inadequate in the study of such small diffusivity values.

$^1$H PGSE profiles were recorded on thin film samples containing all different phases in order to directly compare the different phases. Although the echo time (3 ms) and the gap between the first and second RF pulse (3 ms) were kept as short as possible, the transverse magnetisation quickly decays (the $T_2$ of the alkyd-in-water phase and the alkyd were estimated to be on the order of 14 and 10 ms, respectively). These experiments required a very long experimental time, during which the water was believed to evaporate, maybe due to a non-optimum preparation of the sample.

### 6.4 Conclusions

The "supposed" phase-inversion of alkyd-in-water emulsion coatings has been studied by NMR spectroscopy and PGSE diffusometry.

During the optimisation of the sample preparation, it was observed that the different phases which appear during the film formation of the coatings were not stable unless well sealed. This observation suggests that evaporation of trace amounts of water (or other solvents, if present) leads to changing optical properties and morphologies.

It has been found by NMR that water is continuous and free to diffuse in the first stage of drying, as expected. However, no water, or at least a very small amount of it, has been observed in the second (the supposed metastable phase) and in the
third (the supposed water-in-alkyd emulsion) stage of drying (the only limitation to the experiments performed is water diffusion through the local field gradients, which can extremely broaden the water peak). This result suggests that alkyd-in-water emulsion coatings do not undergo a phase-inversion during their film formation.

In general, visual opacity results when there are two phases with different refractive index values and when the size of the phases approaches the wavelength of light. If indeed there is no water in the supposed water-in-alkyd emulsion, then its cloudiness must be due to the presence of another phase. The alkyd samples containing only driers, investigated in chapter 7, do not display any change in their visual appearance during the oxidative drying process, and in any case driers are used in small percentages. On the other hand, it has been reported in the literature [Keddie, 1997], that, in latex, surfactant molecules can form membranes at particle/particle boundaries, prior to polymer diffusion. This observation and the above results suggest that the opacity of the supposed water-in-alkyd emulsion may be related to the presence of surfactant, which is non-uniformly distributed within it. With time, the surfactant may diffuse to give a final transparent film. Without taking into account the presence of water, it is more difficult to speculate on the reason why the supposed metastable phase is transparent.
Chapter 7

The oxidative cross-linking of alkyd polymers

7.1 Introduction

Alkyd polymer coatings dry (i.e. cross-link) as a result of a chemical reaction with the oxygen of the atmosphere. Experimentally, it has been found that alkyds uptake large quantities of oxygen [Turner, 1988, page 154] to give polyperoxides, which are exceptionally stable peroxides. However, the mechanism through which the peroxides are formed from alkyds [Hubert et al., 1997, Muizebelt et al., 1998] or fatty acids [Muizebelt and Nielen, 1996] is still under study. Moreover, it is still not known how the different drier additives affect the drying of the film. In chapter 1 a brief description of the different types of driers was given.

The aim of this chapter is twofold. First, it aims to prove that the magnet designed by Glover and described in reference [Glover et al., 1999] is highly suitable to study thin films and, in particular, paint coatings because it provides spatial information across the thickness of the film. As the technique is not destructive the same film can be monitored over time. Second, the effects of different combinations of drier additives on the cross-linking profiles are explored.
7.2 Experimental

7.2.1 Sample composition and preparation

The alkyd polymer and the drier additives used in the NMR experiments were provided by ICI. Samples containing 80 wt% of a long low-molecular-weight alkyd polymer and 20 wt% of 1-methoxy-2-propanol (Aldrich) and a combination of driers were prepared to give the concentrations reported in table 7.1. A cobalt drier (ICI trade name of Nuodex Co), a calcium drier (Nuodex Ca) and a zirconium drier (Nuodex Zr) were used. The drier additives were added to the mixture of alkyd polymer and organic solvent and stirred for several hours under nitrogen. The organic solvent was added to lower the alkyd viscosity in order to spin-cast the alkyd polymer, otherwise too viscous, on 18 mm × 18 mm 110-μm-thick glass coverslips. The as-cast films were 40-100 μm thick. Experiments were repeated for numerous coatings to check the reproducibility of the technique. In this chapter, the drying of the coatings reported in table 7.1 is described in detail.

Table 7.1: Content of metals (expressed in wt% of alkyd) present in the drier additives, which were used in the preparation of the alkyd coatings employed in the MRI experiments.

<table>
<thead>
<tr>
<th>Coating name</th>
<th>Co</th>
<th>Ca</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1, C2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C3</td>
<td>0.05</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C4, C5</td>
<td>0.05</td>
<td>0.35</td>
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</tr>
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</table>

7.2.2 MRI measurements

MRI experiments were performed on the magnet described by Glover and co-workers [Glover et al., 1999], having an intense intentional magnetic field gradient orthogonal to the modulus of the magnetic field. $^1$H measurements were performed at 0.7 T (30 MHz) and with a gradient of 17.5 Tm$^{-1}$. A surface coil was used to monitor
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a sample area approximately 3 mm in diameter. Profiles were acquired across the thickness of the samples using a multiple quadrature echo sequence (see sect. 2.4.1), with \( \pi/2 \) pulse widths of 1 \( \mu \)s, echo times varying from \( 2\tau=150 \) to \( 600 \) \( \mu \)s and 8 or 32 echoes. Each profile is the Fourier transform of a separate echo. For each echo 512 or 256 data points were acquired at a sampling interval of 0.4 \( \mu \)s and the resulting profiles have a nominal pixel resolution of 6.5 and 13 \( \mu \)m, respectively. Profiles were generally acquired using 5000 averages and a repetition time of 200 ms, giving a total image time of 17 minutes. For the sequence used, applied in the presence of a high gradient, the first echo has an amplitude 2/3 smaller than the second [Benson and McDonald, 1995b], therefore its intensity has been multiplied by 1.5 according to the standard procedure. When no signal was visible at an echo time of 150 \( \mu \)s, a half-k space technique [Callaghan, 1995a, page 133] was used and a single asymmetric echo was acquired for each experiment, so that it was possible to obtain echo times as small as 50 \( \mu \)s.

NMR measurements were started just after casting and taken at half-hour intervals throughout the initial 3-hour period and then at hourly intervals for a further 9 hours. After 12 hours measurements were repeated daily and weekly thereafter.

7.3 A model sample

A glycerol film sandwiched between two glass coverslips, with spacers made from small pieces of 110 \( \mu \)m thick coverslips, was prepared. A uniform profile across the thickness of the sample is expected. In fig. 7.1 typical profiles recorded at variable echo times are shown: the bottom of the sample, close to the NMR coil, is on the right and the top of the sample is on the left. The profiles are indeed squared, at least, for the first 60-70 \( \mu \)m. This preliminary experiment proves that the probe is levelled to better than 10 \( \mu \)m over the planar central region of interest and that there is no reduction in sensitivity across the thickness of the film (for thicknesses less than 100 \( \mu \)m). Non-squared profiles will, therefore, reflect a non-uniformity within the
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Figure 7.1: One-dimensional profiles of a glycerol film recorded with variable pulse gap. 500 averages and 512 points were acquired for each echo and the pixel resolution is 6.5 μm. From the top, profiles are shown for an echo time of 300 μs (circles), 2 ms (squares), 4 ms (diamonds), 6 ms (up-triangles), 10 ms (down-triangles). The coil is on the far right (not shown).

7.4 Results

Figure 7.2 shows typical profiles recorded with a pulse gap of 150 μs across the alkyd polymer coating C1, containing no drier additives. The glass coverslip is on the right, while the left side of the film is exposed to air. The reduced signal intensity during the first hour reflects the evaporation of the organic solvent and, after that, no change in the profiles is observed for several days.

Figure 7.3 shows profiles recorded across the coating C4, containing a mixture of all drier additives. After the evaporation of the solvent (which takes about an hour), the shape of the profiles continues to change and the difference in the shape between the alkyd polymer coatings with and without drier additives is evident, especially after two days. The gradient on the top side in the profiles shown in fig. 7.3 reflects a change in $T_2$ across the thickness of the film. The decrease in $T_2$ moving from the
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Figure 7.2: One-dimensional profiles of C1 (no driers), obtained from the Fourier transform of the first echo only. Symbols indicate the profile of the film 0.25 hour after spin-casting (circles), 1 hour (squares) and 2 days (up-triangles). The lines connecting the points are added for ease of viewing only. The nominal resolution is 6.5 μm and the echo time 300 μs.

Figure 7.3: One-dimensional profiles of C4 (with driers) recorded with the same parameters of fig. 7.2. Symbols indicate the profile of the film 0.25 hour after spin-casting (circles), 1 hour (squares), 3 hours (diamonds), 2 days (up-triangles) and 5 days (down-triangles).

Bottom towards the top of the film is directly attributable to the cross-linking of the alkyd and consequent reduction in the polymer mobility.
Figure 7.4: One-dimensional profiles of the coating C2 (no drier additives), obtained from the Fourier transform of the first echo. Symbols indicate the profile of the film 0.5 hour after spin-casting (circles), 1 day (squares), 4 days (diamonds), 6 days (up-triangles), 7 days (down-triangles) and 13 days (stars). The lines connecting the points are added for ease of viewing only. 256 points were acquired at a sample interval of 0.4 μs, giving a nominal resolution of 13 μm. The echo time is 150 μs.

Figure 7.5: One-dimensional profiles of the coating C5 (with combination of drier additives), recorded with the same experimental parameters of fig. 7.4. Symbols indicate the profile of the film 0.5 hour after spin-casting (circles), 1 hour (squares), 3.5 hours (diamonds), 19 hours (up-triangles), 3 days (down-triangles) and 10 days (stars).
The reduction in width observed in figure 7.3 suggests that the top of the film is much “drier” than the bulk, that is it has a much shorter $T_2$. Experiments were repeated at an echo time of 150 $\mu$s in order to obtain data less weighted in $T_2$. Profiles for the coatings C2 (containing no driers) and C5 (with all driers) are shown in figs. 7.4 and 7.5, respectively. The increase in width with time observed in fig. 7.4 is probably caused by a non-optimum preparation of the sample C2: the coating was initially thicker at the edges and the alkyd, still mobile, flowed back towards the centre. The profiles for the coating C5 still have the same shape as the ones recorded at a longer echo time (fig. 7.3), suggesting that the top of the coating is characterised by a very short $T_2$. In order to visualise the cross-linked alkyd, a single asymmetric echo acquisition was used so that the effective echo time was considerably reduced. As an example, fig. 7.6 shows profiles of the same sample as in fig. 7.5 recorded 10 days after casting. While no signal from the polymer is seen at all using the 150 $\mu$s echo time, the alkyd is visible at shorter echo times. The apparent decrease in coating thickness in figures 7.3 and 7.5, therefore, reflects a decrease in $T_2$ at the surface and not film shrinkage.

Figure 7.6: One-dimensional profiles of the coating C5 after 10 days after casting, recorded with a half-$k$ space technique. The “effective” echo times are, from the top to the bottom, 50, 80, 100, 110, 120, 130, 140 $\mu$s. At an echo time of 50 $\mu$s the glass coverslip and the polyamide tape layer (not shown) just below the coverslip, which protects the RF coil, are visible.
Experiments on a coating containing only the catalyst Co were also recorded at an echo time of 300 $\mu$s and, for completeness, a set of them is shown in fig. 7.7. There is a visible reduction in width with time, analogous to that observed in coatings containing all driers (fig. 7.7 is directly comparable to fig. 7.3), indicating that the cross-linking starts from the top of the film and extends inwards with time. However, a further quantitative analysis of these results is difficult because the film becomes wrinkled as it dries, and the following analysis focuses on the coatings with all and without driers only.

Figure 7.7: One-dimensional profiles of the coating C3 (containing only Co), recorded with the same experimental parameters of figs. 7.2 and 7.3, at 6.5 $\mu$m nominal resolution. Symbols indicate the profile of the film 0.25 hour after spin-casting (circles), 0.5 hour (squares), 3.5 hours (diamonds) and 4 days (up-triangles). Note that this coating is slightly thicker than the ones earlier presented and that the initial profile does not have a square form.

7.5 $T_2$ analysis and discussion

Quantitative $T_2$ values can be calculated from single exponential fits to the multi-echo profiles. Figure 7.8 shows the $T_2$ profiles for a coating without driers (top) and with driers (bottom), as obtained from figures 7.4 and 7.5, respectively. The
evaporation of the organic solvent induces a noticeable drop in $T_2$, not so evident in the figure because part of the solvent has already evaporated during the first half an hour. Then, the $T_2$ value of the alkyd coating without driers steadily decreases over a period of weeks, indicating that the alkyd slowly reacts with the oxygen of the atmosphere and that the cross-linking is spatially uniform across the film. On the other hand, there is evidence (especially after 3.5 hours) that the cross-linking of the coating containing all driers is spatially non-uniform across the thickness of the film.

$T_2$ of the coatings at longer times can be measured from a series of profiles like the ones shown in fig. 7.6, each recorded with a single asymmetric echo acquisition. $T_2$ of the sample C5 ten days after casting was found to be uniform across the film and equal to $88 \pm 3 \mu s$. It dropped to $68 \pm 4 \mu s$ after 17 days and to about $44 \pm 6 \mu s$ after about three months, indicating that the process of hardening of the coating continues over very long times.

### 7.6 Modelling oxygen diffusion

Oxygen diffuses with time through the coating to react with the alkyd. The coating can be thought of as a plane sheet of thickness $l$ maintained at a constant oxygen concentration $C_0$ at one surface and with no oxygen diffusion across the other surface. Under the assumption that the diffusion coefficient $D$ is independent on the concentration of diffusing substance, the solution to the Fick's second law of diffusion, with the boundary conditions

$$C = C_0, \ x = l \ \text{and} \ t \geq 0$$

and

$$\frac{\partial C}{\partial x} = 0, \ x = 0 \ \text{and} \ t \geq 0$$
Figure 7.8: $T_2$ profiles of the coatings C2 (top) and C5 (bottom), obtained from single exponential fits to 32 profiles at an echo time of 150 μs. The corresponding profiles obtained from the Fourier transform of the first echo are shown in fig. 7.4 and fig. 7.5, respectively. In those cases in which the fits were considered unacceptable (in the fitting procedure it was required that the intensity of the first point was approximately larger than 0.15, see figs. 7.4 and 7.5) $T_2$ is plotted with a value of zero. For C2, symbols indicate data 0.5 hour after spin-casting (circles), 1 day (squares), 4 days (diamonds), 6 days (up-triangles) and 7 days (down-triangles). After the evaporation of the solvent, no visible change was observed for the first few hours. For C5, symbols indicate data 0.5 hour after spin-casting (circles), 1 hour (squares), 3.5 hours (diamonds), 19 hours (up-triangles) and 3 days (down-triangles).

and the initial condition

$$C(x) = 0, \ 0 \leq x < l \ \text{and} \ t = 0,$$
The assumption that the diffusion coefficient of oxygen is independent of its concentration and therefore is constant through the coating is valid when there are relatively small quantities of oxygen involved [Hepworth et al., 1999]. However, it is known that the diffusion of vapours in high-polymers depends on the concentration of diffusing substances [Crank, 1994, page 105] and indeed, in the case under study, the reaction of oxygen with the polymer leads to an increment in its molecular weight.

The profiles recorded reflect the progress of diffusing oxygen through the coating. For example, the profile of C4 in fig. 7.3 three hours after casting suggests that the film is partially cross-linked. Unfortunately, the $T_2$ values measured cannot be easily correlated to the degree of cross-linking of the alkyd [Charlesby, 1979]. In order to get an estimation of the order of magnitude of the diffusion coefficient of oxygen into the coating, it is assumed that the film C4 three hours after casting is cross-linked to a depth of half of its thickness and that the concentration of oxygen there is 50% of the surface concentration. By using eq. (7.1) with $x = 0.5l$ where $x$ is assumed to correspond to where $C = 0.5C_0$, and the measured time, $D$ is estimated to be in the order of $10^{-9}$ cm$^2$s$^{-1}$. Equation 7.1 converges quickly [Crank, 1994, page 22] and $n$ was set to 3.

To the best of the author’s knowledge, the diffusion coefficient of oxygen through alkyd polymers has not been measured yet. A comparison with known oxygen diffusion coefficients through other polymers is not straightforward, as $D$ strongly depends on the type of polymer and its state. For natural rubber, $D$ is on the order of $10^{-6}$ cm$^2$s$^{-1}$ [Sperling, 1992], while in rigid polymers it is lower, about $10^{-8}$ cm$^2$s$^{-1}$ for rigid poly(vinyl chloride) [Sperling, 1992] and $3 \times 10^{-9}$ cm$^2$s$^{-1}$ for poly(ethylene terephthalate) at 25° C [Mark et al., 1989]. Initially the alkyd coating is soft and resembles natural rubber. However, with time, it becomes rigid and $D$ will soon
approach lower values, as in glassy and crystalline polymers.

7.7 Conclusions

The experiments reported in this chapter represent the first application of the magnet described by Glover et al. [Glover et al., 1999] and illustrate its enormous utility in the study of thin films and coatings.

Cross-linking profiles of alkyd coatings with and without drying additives at 6.5 μm nominal resolution have been obtained and the spatial resolution of $T_2$ relaxation rate through the coatings has been monitored and followed with time. It has been found that alkyd coatings containing no driers cross-link uniformly and slowly harden (in coatings ≈65 μm thick, it takes 7 days for $T_2$ to decrease to about 2 ms). $T_2$ does not vary significantly with depth. The hardening of coatings with the cobalt drier is considerably quicker. It starts from the air-surface and extends progressively inwards, leaving behind the cross-linked alkyd with a very short $T_2$. In this specific case, the presence of cobalt caused wrinkling of the coatings prepared, which prevented the gain of further reliable quantitative information. The cross-linking of alkyd coatings containing cobalt, calcium and zirconium is quicker than in coatings without driers. In coatings ≈65 μm thick a substantial decrease in $T_2$ (to less than 2 ms at the top of the coating) is observed within the very first few hours. Cross-linking profiles are non-uniform with depth, even when the so-called “through” driers (i.e. calcium and zirconium) are used. There is no evidence that calcium and zirconium driers encourage uniform cross-linking.

It was possible to measure $T_2$ values of the order of μs several months after casting, indicating that the cross-linking of the alkyd carries on for months. Finally, the diffusion coefficient of the oxygen through the coating has been estimated to be on the order of $10^{-9}$ cm$^2$s$^{-1}$. 
Bibliography


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